Supplementary Information

for

Inhibition of Acrylic Acid and Acrylate Autoxidation

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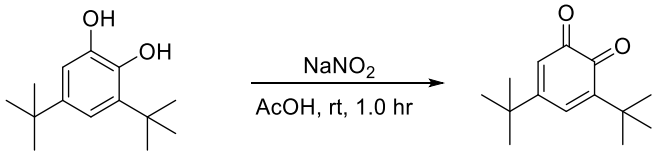
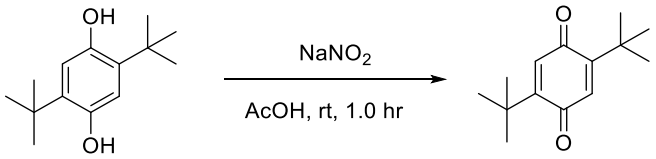
General

All chemicals and solvents were purchased from commercial suppliers (Sigma, Combi-Blocks, Oakwood Chemical and A2B chemicals) and used without further purification unless otherwise indicated except 2-ethylhexanol (EH), *n*-butyl acrylate (BA) and acrylic acid (AA). These three chemicals were directly obtained from BASF SE. BA and AA were each distilled twice at 50 to 60 °C under 10-mbar vacuum. The purified material could be kept at -20 °C for up to 5 days. EH was percolated through a column of basic alumina immediately before use. STY-BODIPY,[1] *N*-alkylated phenoxazines and phenothiazines,[2] phenoxazine *N*-oxy,l[3] 3,5-di-*tert*-butyl-1,2-benzoquinone and 2,5-di-*tert*-1,4-bbenzoquinone[4] were synthesized according to methods reported for either the exact same or very similar compounds and purified by column chromatography using flash silica gel (230-400 mesh). ^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE 300, 400 or 600 spectrometers. High resolution mass spectra were obtained on a Kratos Concept Tandem mass spectrometer.

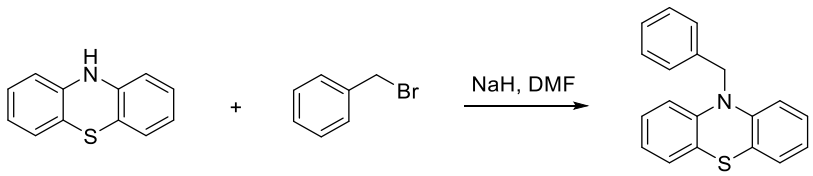
Synthetic procedures



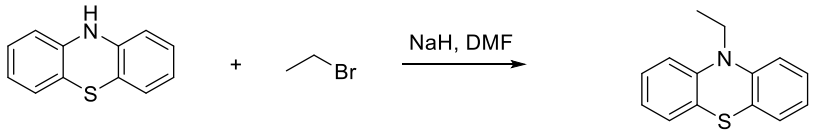
3,5-Di-tert-butyl-1,2-benzoquinone. A solution of sodium nitrite (1.4 g, 20 mmol) in water (5 mL) was added dropwise (foaming) to a stirred solution of 3,5-di-tert-butylcatechol (2.2 g, 10 mmol) in acetic acid (10 mL). After stirring for 1 hour at room temperature, water (20 mL) was added, which lead to precipitation of the benzoquinone. The product was isolated by filtration, washed and dried to give a dark brown solid (2.1 g, 95%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.94 (d, J = 2.3 Hz, 1H), 6.22 (d, J = 2.3 Hz, 1H), 1.28 (s, 9H), 1.23 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 181.1, 180.1, 163.3, 150.0, 133.5, 122.1, 36.0, 35.5, 29.2, 27.9. HRMS (EI): Calc'd for $C_{14}H_{20}O_2$: 220.1463, Found: 220.1440.



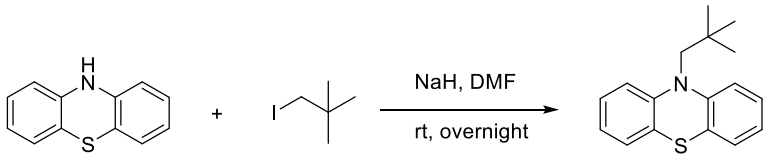
2,5-Di-tert-butyl-1,4-benzoquinone. A solution of sodium nitrite (1.4 g, 20 mmol) in water (5 mL) was added dropwise (foaming) to a stirred solution of 2,5-di-tert-butylhydroquinone (2.2 g, 10 mmol) in acetic acid (10 mL). After stirring for 1 hour at room temperature, water (20 mL) was added, which lead to the precipitation of the benzoquinone. The product was isolated by filtration, washed and dried to give a yellow solid (2.15 g, 97%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.49 (s, 2H), 1.28 (s, 18H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 188.6, 154.3, 133.6, 34.6, 29.1. HRMS (EI): Calc'd for $C_{14}H_{20}O_2$: 220.1463, Found: 220.1439.



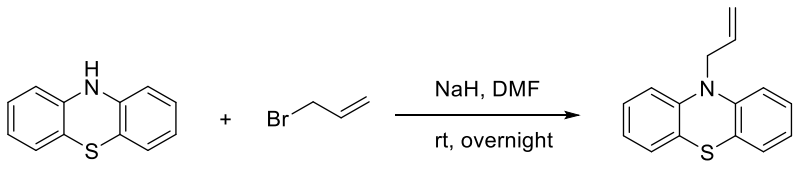
10-Benzyl-10H-phenothiazine. To a solution of phenothiazine in DMF (10-50 mmol, 1.0 equiv. Conc. ≈ 0.5 M) at room temperature, sodium hydride (1.05 equiv.) was slowly added, and the mixture was stirred for 10 minutes under nitrogen atmosphere. Benzyl bromide (1.2 equiv.) was added dropwise, and the reaction was monitored by TLC until the full conversion of phenothiazine. The reaction mixture was diluted with water and extracted with diethyl ether. The organic phases were combined, washed with brine and concentrated under reduced pressure to afford the desired product as a white solid in 87% yield. ^{1}H NMR (600 MHz, d_6-acetone) δ 7.43 (d, J = 8.0 Hz, 2H), 7.38 (t, J = 7.7 Hz, 2H), 7.29 (t, J = 7.3 Hz, 1H), 7.17 (dd, J = 7.6, 1.7 Hz, 2H), 7.09 (ddd, J = 8.2, 7.3, 1.6 Hz, 2H), 6.95 (td, J = 7.5, 1.3 Hz, 2H), 6.85 (dd, J = 8.3, 1.3 Hz, 2H), 5.23 (s, 2H). ^{13}C NMR (151 MHz, d_6-acetone) δ 144.8, 137.2, 128.6, 127.4, 126.9, 126.8, 126.8, 123.4, 122.6, 115.9, 51.7. HRMS (EI): Calc'd for $C_{19}H_{15}NS$: 289.0925, Found: 289.0942.



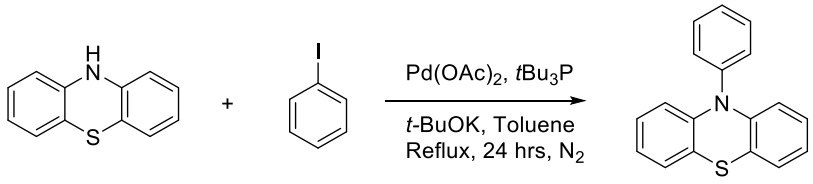
10-Ethyl-10H-phenothiazine. To a solution of phenothiazine in DMF (10-50 mmol, 1.0 equiv. Conc. ≈ 0.5 M) at room temperature, sodium hydride (1.05 equiv.) was slowly added, and the mixture was stirred for 10 minutes under nitrogen atmosphere. Ethyl bromide (1.2 equiv.) was added dropwise, and the reaction was monitored by TLC until the full conversion of phenothiazine. The reaction mixture was diluted with water and extracted with diethyl ether. The organic phases were combined, washed with brine, passed through anhydrous sodium sulfate and concentrated under reduced pressure to afford the desired product as a white solid in 90% yield. ^{1}H NMR (600 MHz, d_6-DMSO) δ 7.22 –7.16 (m, 2H), 7.13 (dd, J = 7.6, 1.5 Hz, 2H), 7.00 (d, J = 7.6 Hz, 2H), 6.93 (t, J = 7.4 Hz, 2H), 3.90 (q, J = 6.9 Hz, 2H), 1.29 (t, J = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 143.8, 127.0, 126.4, 122.4, 121.8, 114.9, 40.4, 12.1. HRMS (EI): Calc'd for $C_{14}H_{13}NS$: 227.0769, Found: 227.0763.



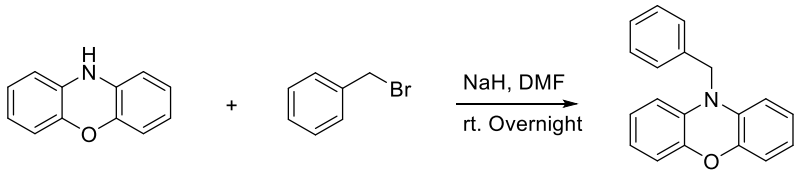
10-Neopentyl-10H-phenothiazine. To a solution of phenothiazine in DMF (1.0 mmol, 1.0 equiv. Conc. ≈ 0.5 M) at room temperature, sodium hydride (2.0 equiv., 2.0 mmol) was slowly added, and the mixture was stirred for 10 minutes under nitrogen atmosphere. Neopentyl iodide (1.5 mmol, 1.5 equiv.) was added dropwise and the reaction was stirred for 24 hours. The reaction mixture was diluted with water and extracted with petroleum ether. The organic phases were combined, passed through anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography with hexane and ethyl acetate (98:2) to afford the desired product as a white solid in 30% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 – 7.06 (m, 4H), 7.04 (dd, J = 8.3, 1.5 Hz, 2H), 6.87 (td, J = 7.4, 1.4 Hz, 2H), 3.93 (s, 2H), 0.88 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.2, 127.9, 127.1, 126.7, 122.4, 117.5, 58.1, 35.7, 28.0. HRMS (EI): Calc'd for $C_{17}H_{19}NS$: 269.1238, Found: 269.1276.



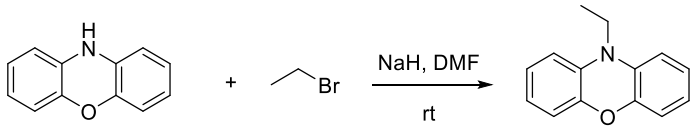
10-Allyl-10H-phenothiazine. To a solution of phenothiazine in DMF (1.0 mmol, 1.0 equiv.) at room temperature, sodium hydride (2.0 equiv.) was slowly added, and the mixture was stirred for 10 minutes under nitrogen atmosphere. Allyl bromide (1.5 mmol, 1.0 equiv.) was then added dropwise, and the reaction was stirred overnight. The reaction mixture was diluted with water and extracted with petroleum ether. The organic phases were combined, passed through anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography with hexane and ethyl acetate (98:2) to afford the desired product as a white solid in 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, *J* = 6.8 Hz, 4H), 6.90 – 6.79 (m, 4H), 6.04 – 5.93 (m, 1H), 5.35 – 5.22 (m, 2H), 4.46 (dt, *J* = 4.2, 2.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 133.2, 127.2, 126.8, 123.0, 122.4, 117.5, 115.3, 51.3. HRMS (EI): Calc'd for $C_{15}H_{13}NS$: 239.0769, Found: 239.0724.



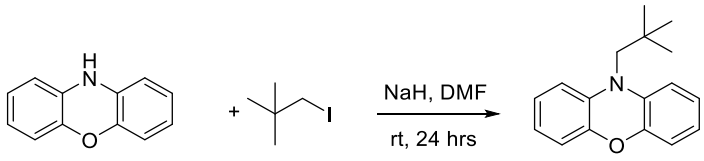
10-Phenyl-10H-phenothiazine. Under a nitrogen atmosphere, phenothiazine (1.99 g, 10.0 mmol), iodobenzene (2.04 g, 10.0 mmol), potassium tert-butoxide (1.68 g, 15.0 mmol), $Pd(OAc)_2$ (0.11g, 0.5 mmol) and tri-*tert*-butylphosphine (250 μL, 1.0 mmol) were dissolved in 90 mL of toluene and heated to reflux for 24 hours. The reaction was then cooled to room temperature, water was added and the mixture extracted with dichloromethane three times. The organic phases were combined, dried with anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography to obtain the desired product as a white solid in 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (t, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.41 – 7.35 (m, 2H), 7.01 (dd, *J* = 7.3, 1.8 Hz, 2H), 6.87 – 6.75 (m, 4H), 6.19 (d, *J* = 7.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 141.0, 130.9, 130.8, 128.2, 126.9, 126.7, 122.5, 120.2, 116.1. HRMS (EI): Calc'd for $C_{18}H_{13}NS$: 275.0769, Found: 275.0746.



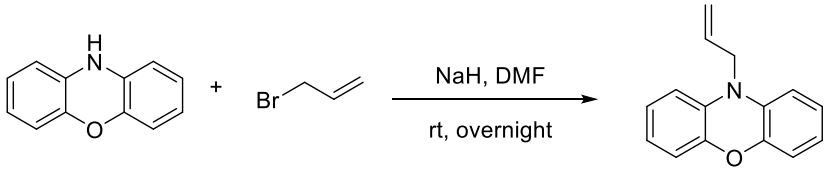
10-Benzyl-10H-phenoxazine. To a solution of phenoxazine in DMF (1.0 mmol, 1.0 equiv. Conc. ≈ 0.5 M) at room temperature, sodium hydride (1.05 equiv.) was slowly added, and the mixture was stirred for 10 minutes under nitrogen atmosphere. Benzyl bromide (1.0 mmol, 1.2 equiv.) was added dropwise, and the reaction was monitored by TLC until the full conversion of phenoxazine. The reaction mixture was diluted with water and extracted with diethyl ether. The organic phases were combined, washed with brine and concentrated under reduced pressure to afford the desired product as a white solid in 87% yield. ^{1}H NMR (600 MHz, d_6-acetone) δ 7.43 – 7.38 (m, 4H), 7.34 – 7.30 (m, 1H), 6.80 – 6.76 (m, 2H), 6.75 – 6.71 (m, 4H), 6.51 (d, J = 7.4 Hz, 2H), 4.94 (s, 2H). ^{13}C NMR (151 MHz, d_6-acetone) δ 144.9, 136.7, 133.8, 128.8, 127.0, 126.2, 123.9, 121.2, 115.1, 112.5, 48.0. HRMS (EI): Calc'd for $C_{19}H_{15}NO$: 273.1154, Found: 273.1133.



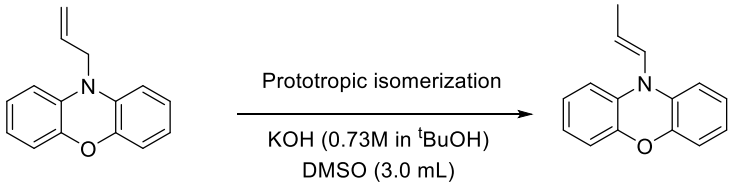
10-Ethyl-10H-phenoxazine. To a solution of phenoxazine in DMF (1.0 mmol, 1.0 equiv. Conc. ≈ 0.5 M) at room temperature, sodium hydride (1.05 equiv.) was slowly added, and the mixture was stirred for 10 minutes under nitrogen atmosphere. Ethyl bromide (1.2 equiv.) was added dropwise, and the reaction was monitored by TLC until the full conversion of phenoxazine. The reaction mixture was washed diluted with water and extracted with diethyl ether. The organic phases were combined, washed with brine and concentrated under reduced pressure to afford the desired product as white solid in 93% yield. ^{1}H NMR (600 MHz, d_6-DMSO) δ 6.87 – 6.81 (m, 2H), 6.69 (d, J = 7.4 Hz, 2H), 6.65 (q, J = 2.7 Hz, 4H), 3.64 (q, J = 7.0 Hz, 2H), 1.13 (t, J = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 143.6, 132.0, 123.5, 120.1, 114.4, 111.2, 36.8, 9.2. (EI): Calc'd for $C_{14}H_{13}NO$: 211.0997, Found: 211.1005.



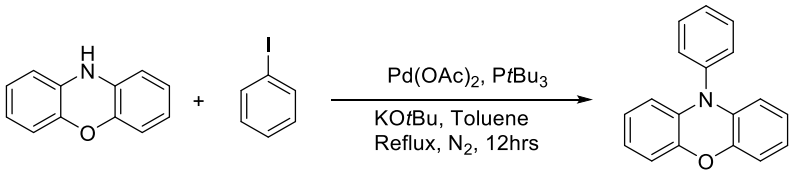
10-Neopentyl-10H-phenoxazine. To a solution of phenoxazine in DMF (1.0 mmol, 1.0 equiv. Conc. ≈ 0.5 M) at room temperature, sodium hydride (2.0 mmol, 2.0 equiv.) was slowly added, and the mixture was stirred for 10 minutes under nitrogen atmosphere. Neopentyl iodide (1.5 mmol, 1.5 equiv.) was added dropwise, and the reaction was stirred for 24 hours. The reaction mixture was diluted with water and extracted with petroleum ether. The organic phases were combined, passed through anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography with hexane and ethyl acetate (98:2) to afford the desired product as a dirt white solid in 32%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.79 (ddd, J = 8.2, 6.8, 2.2 Hz, 2H), 6.71 – 6.65 (m, 6H), 3.49 (s, 2H), 1.00 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.7, 135.7, 123.2, 120.9, 115.8, 113.0, 77.2, 77.0, 76.8, 51.8, 35.2, 28.7. HRMS (EI): Calc'd for $C_{17}H_{19}NO$: 253.1467, Found: 253.1493.



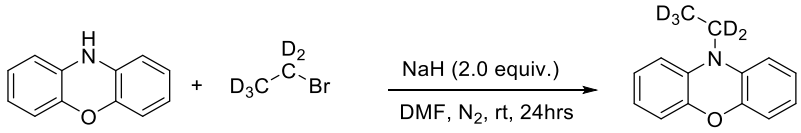
10-Allyl-10H-phenoxazine. To a solution of phenoxazine in DMF (1.0.0 mmol, 1,0 equiv.) at room temperature, sodium hydride (1.0 equiv.) was slowly added, and the mixture was stirred for 10 minutes under nitrogen atmosphere. Allyl bromide (1.5 mmol, 1.5 equiv.) was added dropwise, and the reaction was stirred overnight. The reaction mixture was diluted with water and extracted with petroleum ether. The organic phases were combined, passed through anhydrous sodium sulfate and concentrated under reduced pressure and dried. The residue was purified by column chromatography with hexane and ethyl acetate (98:2) to afford the desired product as a white solid in 90%. ^{1}H NMR (400 MHz, d_6-DMSO) δ 6.77 (ddd, J = 7.9, 5.4, 3.6 Hz, 2H), 6.63 (d, J = 0.8 Hz, 2H), 6.63 – 6.61 (m, 2H), 6.52 (d, J = 7.2 Hz, 2H), 5.83 (ddt, J = 17.1, 10.6, 4.1 Hz, 1H), 5.18 – 5.10 (m, 2H), 4.18 (dt, J = 4.1, 2.0 Hz, 2H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 144.6, 133.6, 131.8, 124.4, 121.4, 116.8, 115.4, 112.9, 46.4. HRMS (EI): Calc'd for $C_{15}H_{13}NO$: 223.0997, Found: 223.0998.



(E)-10-(Propenyl)-10H-phenoxazine. A mixture of 223 mg (1.0 mmol) of *N*-allylphenoxazine, 3.0 ml of DMSO, and 0.5 ml of an 0.73 N solution of potassium *tert*-butoxide in *tert*-butanol was kept at room temperature overnight (or followed by TLC). The mixture was poured into 10 mL of water, extracted with DCM (10 mL), and the combined extracts washed with water (3 x 5 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was further dried under high vacuum to afford 212 mg (95%) of desired product as a yellow-brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79 – 6.72 (m, 2H), 6.67 (d, *J* = 3.9 Hz, 4H), 6.47 (d, *J* = 7.9 Hz, 2H), 5.91 (p, *J* = 6.8 Hz, 1H), 5.76 – 5.71 (m, 1H), 1.64 (dd, *J* = 6.9, 1.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1, 132.4, 130.1, 124.2, 123.5, 121.5, 115.5, 113.1, 12.7. Calc'd for $C_{15}H_{13}NO$: 223.0997, Found: 223.1026.



10-Phenyl-10H-phenoxazine. Under a nitrogen atmosphere, phenoxazine (183 mg, 1.0 mmol), iodobenzene (204 mg, 1.0 mmol), potassium *tert*-butoxide (168 mg, 1.5 mmol), $Pd(OAc)_2$ (11 mg, 0.05 mmol) and tri-tert-butylphosphine (25.0 µL, 0.1 mmol) were dissolved in 9.0 mL of toluene and heated to reflux for 24 hours. The reaction was then cooled to room temperature, water was added, and the mixture was extracted with dichloromethane three times. The organic phase was combined, dried with anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography to obtain the desired product as a tan-white solid in 90% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 2H), 7.50 (ddt, *J* = 8.9, 7.1, 1.4 Hz, 1H), 7.38 (s, 2H), 6.72 (dd, *J* = 7.8, 1.6 Hz, 2H), 6.67 (td, *J* = 7.5, 1.4 Hz, 2H), 6.61 (td, *J* = 7.7, 1.6 Hz, 2H), 5.94 (dd, *J* = 7.9, 1.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.9, 139.0, 134.5, 131.1, 130.9, 128.5, 123.2, 121.3, 115.4, 113.3. HRMS (EI): Calc'd for $C_{18}H_{13}NO$: 259.0997, Found: 275.1019.



d_5-10-Ethyl-10H-phenoxazine. To a solution of phenoxazine in DMF (1.0 mmol, 1.0 equiv. Conc. ≈ 0.5 M) at room temperature, sodium hydride (1.05 equiv.) was slowly added, and the mixture was stirred for 10 minutes under nitrogen atmosphere. Perdeuterated ethyl bromide (1.2 equiv.) was added dropwise, and the reaction was monitored by TLC until the full conversion of phenoxazine. The reaction mixture was diluted with water and extracted with diethyl ether. The organic phases were combined, washed with brine and concentrated under reduced pressure to afford the desired product as a white solid in 93% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.81 – 6.75 (m, 2H), 6.65 – 6.61 (m, 4H), 6.48 (d, J = 8.3 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.1, 133.2, 123.7, 120.7, 115.4, 111.1, 37.6 (p, J = 20.7 Hz), 9.3 (dt, J = 38.7 Hz, 19.5 Hz. (EI): Calc'd for $C_{14}H_8D_5NO$: 216.1311, Found: 216.1283.

Inhibited co-autoxidations of STY-BODIPY and EH

To a 3 mL cuvette were added EH (1.14 mL) and chlorobenzene (1.16 mL). After equilibration for 5 minutes at 70 °C, the cuvette was blanked, and to the cuvette were added STY-BODIPY (15 μL of 1.74 mM solution in DMSO) and DTBP (235 μL) followed by thorough mixing. The absorbance at 568 nm was monitored for 20-25 minutes to ensure linear reaction progress, after which antioxidant (50 μL of 0.3 mM solution in TCB) was added. The solution was thoroughly mixed and the readings were resumed. The inhibition rate constant (k_{inh}) and radical-trapping stoichiometry (n) were determined according to eq. (2) and (3) in Fig. 3 and are reported in ±SD from two independent experiments.

Inhibited co-autoxidation of STY-BODIPY and BA

To a 3 mL cuvette were added BA (1.0 mL) and 1,2,4-trichlorobenzene (1.15 mL). After equilibration for 5 minutes at 70 °C, the cuvette was blanked, and to the cuvette were added STY-BODIPY (14 μL of 1.74 mM solution in DMSO) and DTBP (235 μL) followed by thorough mixing. The absorbance at 569 nm was monitored for 5-10 minutes to ensure linear reaction progress, after which antioxidant (100 μL of 0.3 mM solution in TCB) was added. The solution

was thoroughly mixed, and the readings were resumed. The inhibition rate constant (k_{inh}) and radical-trapping stoichiometry (n) were determined according to eq. (2) and (3) in Fig. 3 and are reported in ±SD from two independent experiments.

Inhibited co-autoxidation of STY-BODIPY and AA

To a 3 mL cuvette were added 2-AA (0.5 mL) and 1,2,4-trichlorobenzene (1.85 mL). After equilibration for 5 minutes at 70 °C, the cuvette was blanked, and to the cuvette were added STY-BODIPY (15 μL of 1.74 mM solution in DMSO) and DTBP (235 μL) followed by thorough mixing. The absorbance at 572 nm was monitored for 5 minutes to ensure linear reaction progress, after which antioxidant (200 μL of 0. 3 mM solution in TCB) was added. The solution was thoroughly mixed, and the readings were resumed. The inhibition rate constant (k_{inh}) and radical-trapping stoichiometry (n) were determined according to eq. (2) and (3) in Fig. 3 and are reported in ±SD from two independent experiments.

Cyclic voltammetry

Cyclic voltammetry was performed in a three-electrode cell (SVC-3, from BioLogic Science Instruments), using a glassy carbon working electrode (from CH Instruments), a graphite rod counter electrode (from McMaster Carr) and a hand-made silver nitrate/silver ($AgNO_3$/Ag) reference electrode (0.005 M). CH Instruments model 620E potentiostat was used throughout. The glassy carbon electrode was polished with 5, 1, and 0.05 μm alumina slurries and dried with a flow of nitrogen after each experiment. Voltammagrams were obtained at 25 °C for the given analyte at 3 mM in dry acetonitrile containing Bu_4NPF_6 (0.1 M) as electrolyte. The given E^o were determined relative to the ferrocene/ferrocenium couple measured under the same conditions (Fc/Fc+ vs NHE +0.64 V).

UV-Vis spectra and determination of extinction coefficients of STY-BODIPY in different substrates

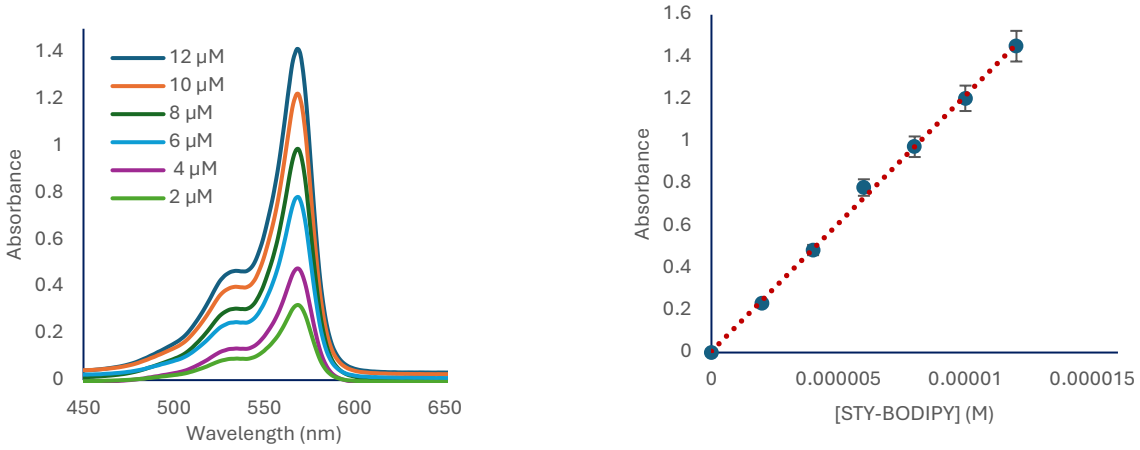


Figure S1. UV-Vis spectra of STY-BODIPY in 2.91 M 2-EH and PhCl (left) and corresponding extinction coefficient determination (right) at λ_{max} = 568 nm, ε = 117736 M^{-1} cm^{-1}.

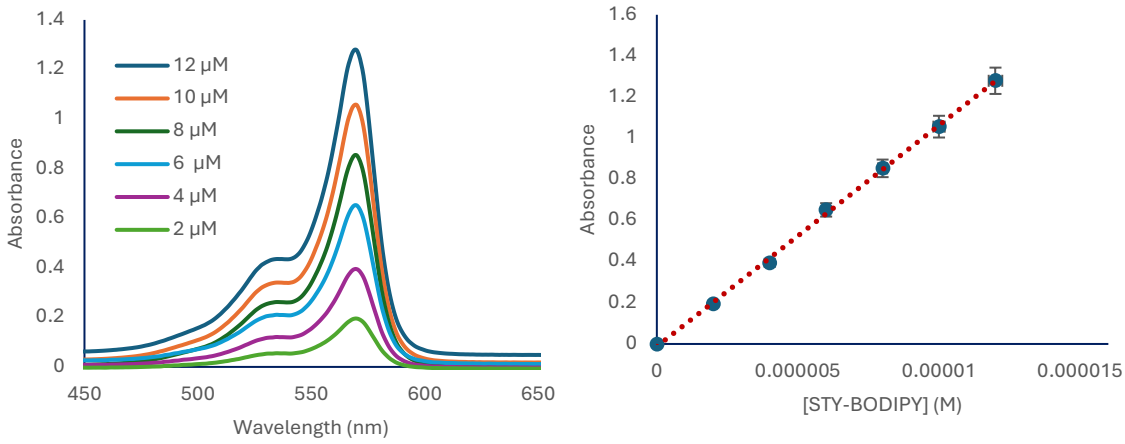


Figure S2. UV-Vis spectra of STY-BODIPY in 2.91 M BA and 1,2,4-trichlorobenzene (left) and corresponding extinction coefficient determination (right) at λ_{max} = 569 nm, ε = 107571 M^{-1} cm^{-1}.

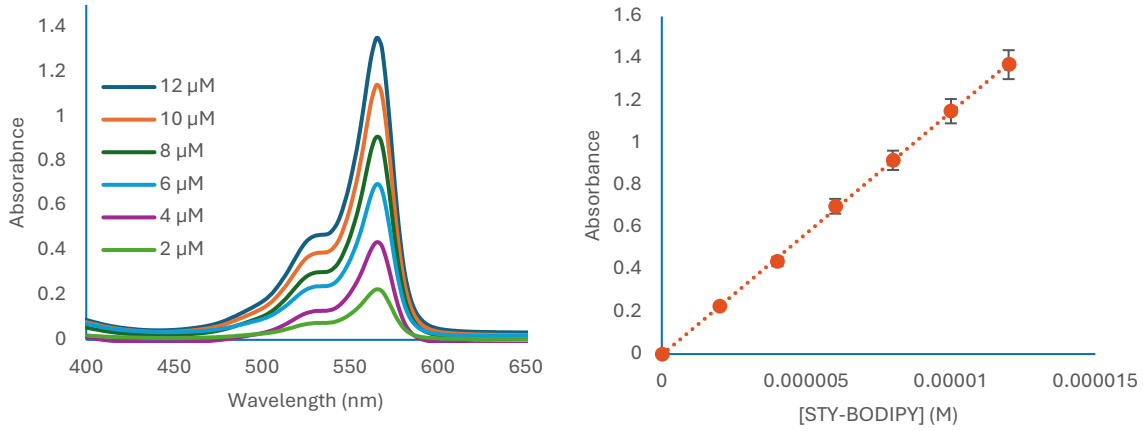


Figure S3. UV-Vis spectra of STY-BODIPY in 2.91 M BA and 1,2,4-trichlorobenzene containing 5 M acetic acid (left) and corresponding extinction coefficient (right) at λ_{max} = 566 nm, ε = 115395 M^{-1} cm^{-1}.

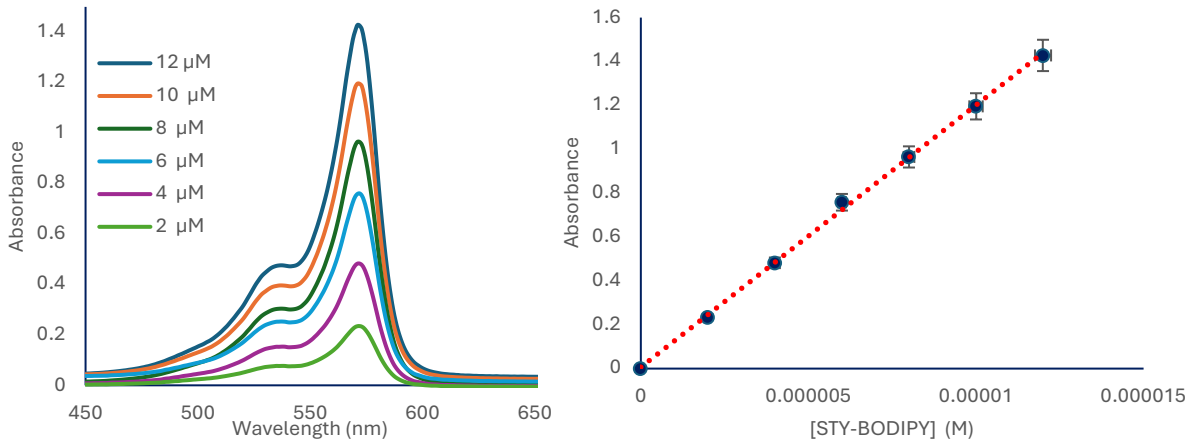


Figure S4. UV-Vis spectra of STY-BODIPY in 2.91 M AA and 1,2,4-trichlorobenzene (left) and corresponding extinction coefficient determination (right) at λ_{max} = 572 nm, ε = 117736 M^{-1} cm^{-1}.

Determination of the inhibition rate constant (k_{inh}) and radical-trapping stoichiometry (n)

The inhibition rate constant (k_{inh}) for each RTA in the various co-autoxidation systems (EH, BA and AA) reported in the manuscript are derived from equation 1.

$$\frac{-\delta[STY-BODIPY]}{\delta t} = \frac{k_{STY-BODIPY}[STY-BODIPY]R_i}{nk_{inh}[\mathrm{RTA}]} \quad (1)$$

This requires knowledge of the apparent propagation rate constant for STY-BODIPY ($k_{\mathrm{STYBODIPY}}$) in the different media, which were derived from plots of the rates of the uninhibited autoxidations as a function of STY-BODIPY concentration using equation 2.

$$\frac{-\delta[\mathrm{STY-BODIPY}]}{\delta t} = \frac{k_{\mathrm{STY-BODIPY}}}{\sqrt{2k_t}} \sqrt{R_i}\,[\mathrm{STY-BODIPY}] \quad (2)$$

These data are shown in Figures **S5 – S7**.

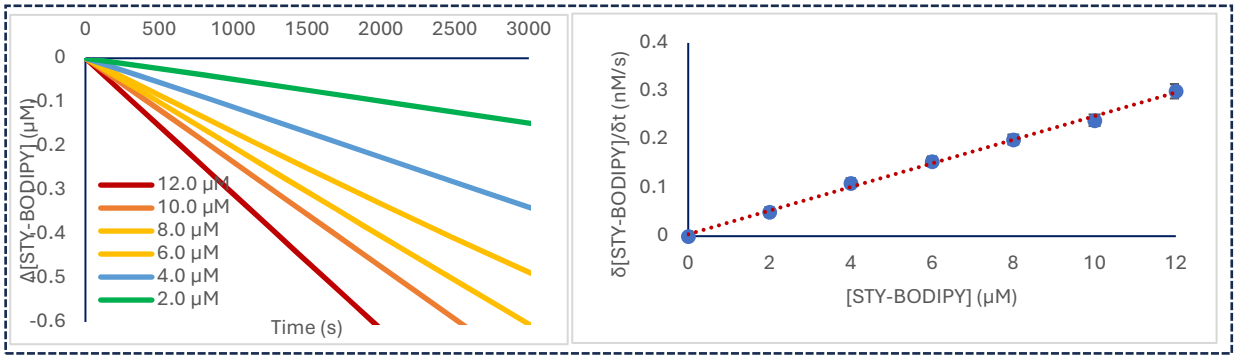


Figure S5. STY-BODIPY consumption as a function of STY-BODIPY concentration in DTBP-initiated (295 mM) co-autoxidation of STY-BODIPY and EH (2.91 M) in PhCl at 70 °C (left) and plot of the corresponding initial rates as a function of STY-BODIPY concentration (right). Reaction progress was monitored by absorbance at 568 nm (ε = 117,736 M^{-1} cm^{-1}).

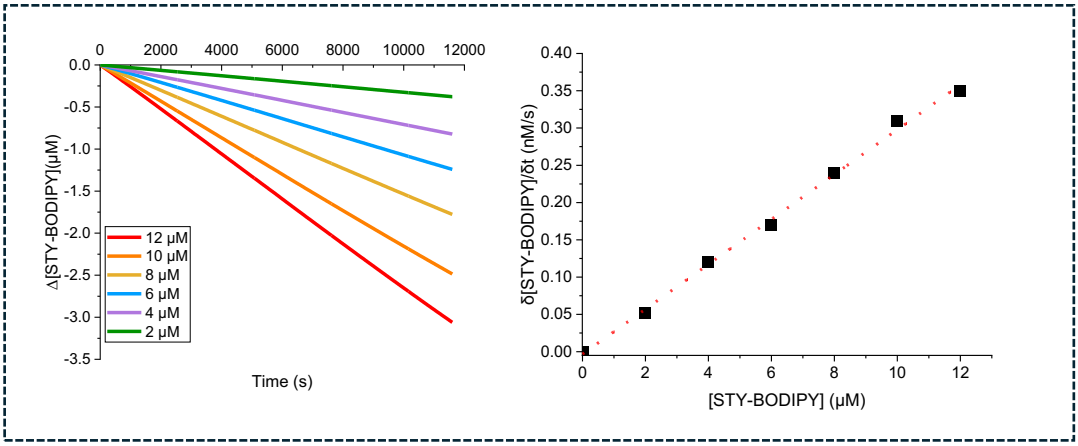


Figure S6. STY-BODIPY consumption as a function of STY-BODIPY concentration in DTBP-initiated (295 mM) co-autoxidation of STY-BODIPY and BA (2.91 M) in TCB at 70 °C (left) and plot of the corresponding initial rates as a function of STY-BODIPY concentration (right). Reaction progress was monitored by absorbance at 569 nm (ε = 107,571 M^{-1} cm^{-1}).

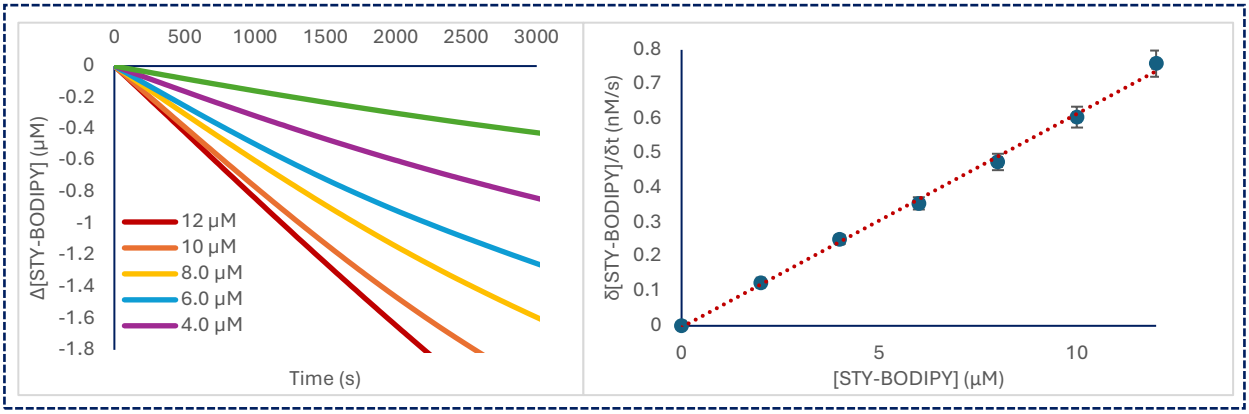


Figure S7. Rate of STY-BODIPY consumption as a function of STY-BODIPY concentration in DTBP-initiated (295 mM) co-autoxidation of STY-BODIPY and AA (2.91 M) in TCB at 70 °C (left), and plot of the corresponding initial rates as a function of STY-BODIPY concentration (right). Reaction progress was monitored by absorbance at 572 nm (ε = 118,469 M^{-1} cm^{-1}).

The $k_{STYBODIPY}$ was derived from the slope of the line of best fit using the rate of initiation (R_i) which was independently determined for each of the various co-autoxidation systems and the value of termination rate constant ($\sqrt{2k_t}$) has been taken from the previously reported literature, as shown below.

Determination of propagation rate constants for STY-BODIPY in different substrates

The value of 2kt for EH, BA, and AA has been taken from previously reported literature.[5,6]

$2k_t = 1.1\ X\ 10^9\ M^{-1}s^{-1}$ (Previously reported for Isopropanol)

$\sqrt{2kt} = 33166.2479$ (2.1)

$R_i = 4.84\ X\ 10^{-9}\ M\ s^{-1}$ (calculated from the raw data)

$\sqrt{R_i} = 6.96\ X\ 10^{-5}$ (2.2)

$$\frac{-\delta[STYBODIPY]/\delta t}{[STY-BODIPY]} = \frac{k_{STY-BODIPY}}{\sqrt{2k_t}} \times \sqrt{R_i} \quad (2.3)$$

$$\frac{-\delta[STYBODIPY]/\delta t}{[STY-BODIPY]} = \text{Slope} \quad (2.4)$$

Slope = 2.099 X 10^{-05} (calculated from the raw data) (2.5)

So, $$\text{Slope} = \frac{k_{STY-BODIPY}}{\sqrt{2k_t}} \times \sqrt{R_i} \quad (2.6)$$

After putting the calculated values from 2.1, 2.2 and 2.5 into the equation 2.6

$k_{STYBODIPY} = 10010.14861\ M^{-1}s^{-1}$.

for BA: $k_{STYBODIPY}$ = 1544 M^{-1} s^{-1} where $2k_t$ = 1.4 x 10^7 M^{-1} s^{-1} ; R_i = 6.85 X 10^{-9} M s^{-1}

for AA: $k_{STYBODIPY}$ = 1785 M^{-1} s^{-1} where $2k_t$ = 1.4 x 10^7 M^{-1} s^{-1} ; R_i = 1.54 X 10^{-8} M s^{-1}

Determination of the rate of initiation by the inhibitor method

The rate of initiation (R_i) can be determined readily under the exact experimental conditions, simply from the length of the inhibited period (t_{inh}) of an inhibited autoxidation for a given concentration of RTA with known radical-trapping stoichiometry (n) using Eq. 3. We selected the phenolic RTA standard 2,2,5,7,8-pentamethyl-6-hydroxychroman (PMC), known to inhibit autoxidation of hydrocarbons with consistent stoichiometry of n = 2.

$$R_i = \frac{n\ [\text{RTA}]}{t_{inh}} \quad (3)$$

See Figure S8 for an example.

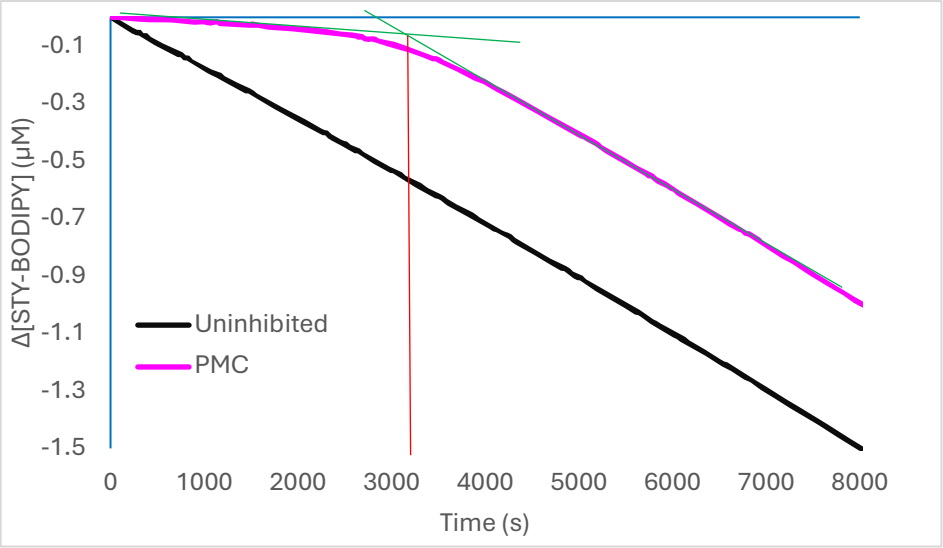


Figure S8. The inhibited period (t_{inh}) is determined in a PMC-inhibited DTBP-initiated co-autoxidation of STY-BODIPY (10 μM) and EH (2.91M) in PhCl at 70°C from the tangential intercept between inhibited and uninhibited phases of the reaction. Reaction was monitored by absorbance at 568 nm (ε = 117736 M^{-1} cm^{-1}).

Example of substrate polymerization during STY-BODIPY/AA co-autoxidation

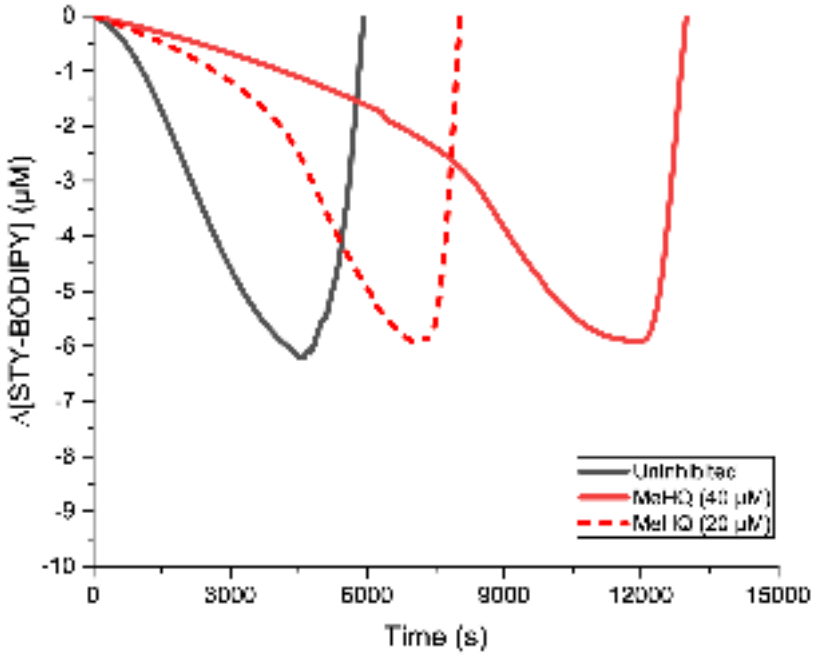
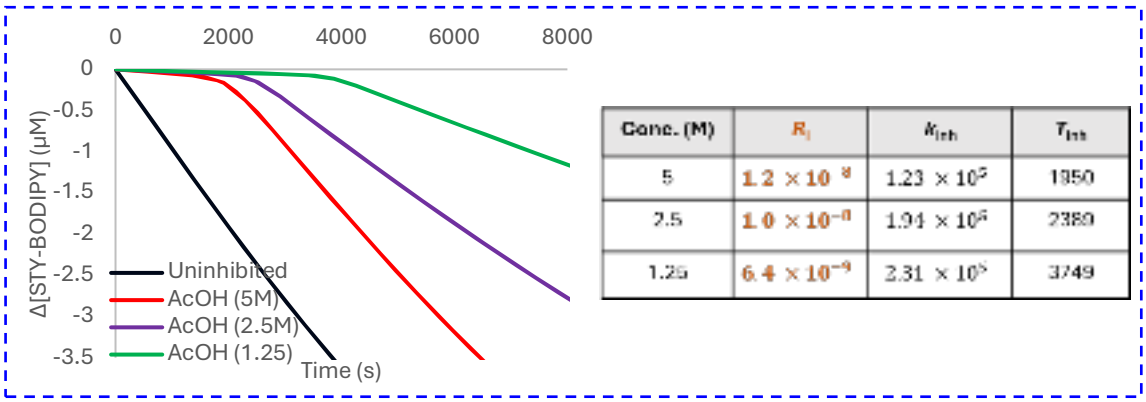


Figure S9. Representative co-autoxidation of AA (2.91 M) and STY-BODIPY (10 μM) initiated by di-*tert*-butylperoxide (100 mM) and 1-octanal (X) in chlorobenzene at 70 °C and inhibited by either 20 μM or 40 μM MeHQ. STY-BODIPY consumption was monitored by absorbance at 572 nm and ε = 118469 M^{-1} cm^{-1}.

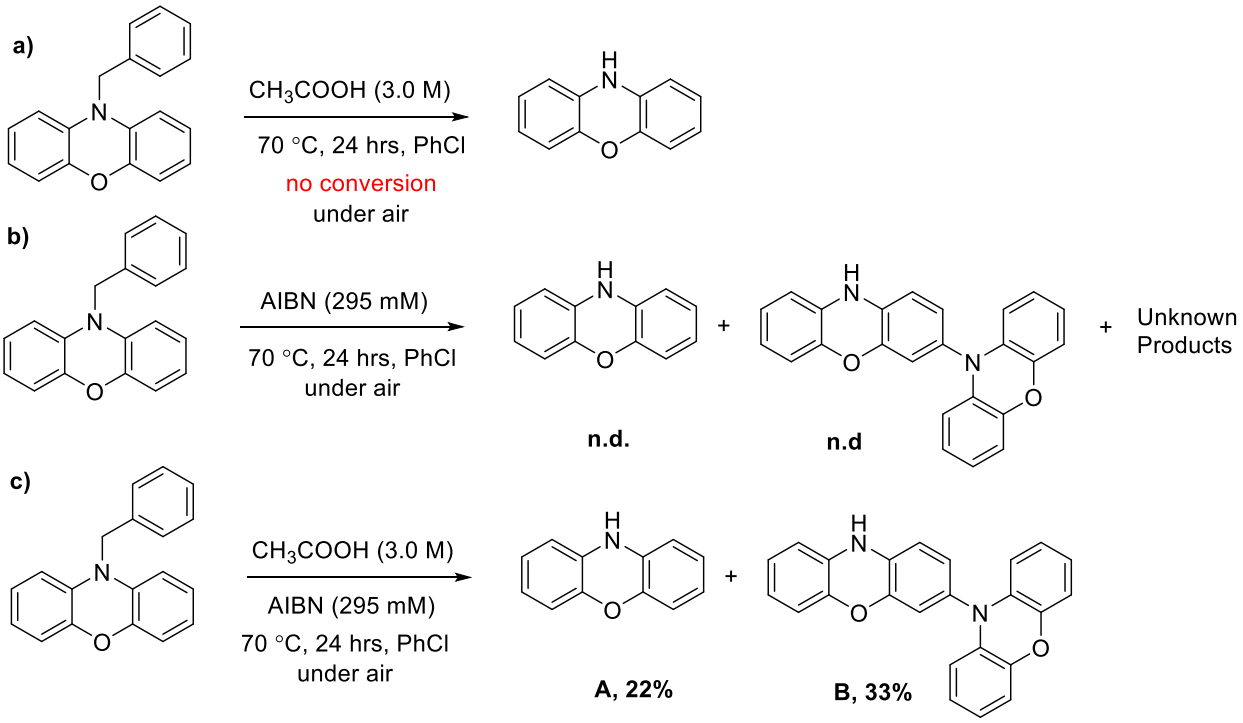
Effect of acetic acid on the rate of initiation



Conc. (M)	R_i	k_{inh}	T_{ind}
5	1.2×10^{-8}	1.23×10^{5}	1950
2.5	1.0×10^{-8}	1.94×10^{5}	2389
1.25	6.4×10^{-9}	2.31×10^{5}	3749

Figure S10. Co-autoxidation of BA (2.91 M) and STY-BODIPY (10 μM) initiated by DTBP (295 mM) in TCB at 70 °C (black line) and inhibited by PMC (12.0 μM) in the presence of 1.25 M to 5.0 M acetic acid.

Dealkylation of *N*-alkylated phenoxazine under acidic conditions

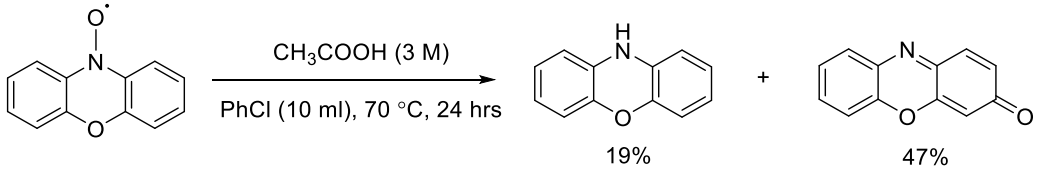


Scheme S1. Dealkylation of *N*-BnPNX requires both acid and peroxyl radicals.

To a solution of 10-benzyl-10H-phenoxazine in PhCl (1.0 mmol, 1.0 equiv. Conc. ≈ 73.23 mM) at room temperature, AIBN (4.0 mmol, 4.0 equiv.) was added, and the mixture was stirred for 1-2 minutes under air. Then acetic acid was added dropwise into the solution to make the 3M acidic

solution, and the reaction was stirred at 70 °C for 24 hours. The reaction mixture was diluted with water and extracted with ethyl acetate. The organic phases were combined, passed through anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography using hexane and ethyl acetate (97:3) to yield phenoxazine as a light-white solid in 22% yield. Upon increasing the polarity of the mobile phase to 95:5 the phenoxazine dimer was isolated in 33% yield. **Phenoxazine**: ^{1}H NMR (600 MHz, d_6-DMSO) δ 8.17 (s, 1H, N**H**), 6.72 (td, J = 7.3, 1.6 Hz, 2H), 6.62 – 6.54 (m, 4H), 6.46 (dd, J = 7.7, 1.5 Hz, 2H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 142.2, 131.8, 123.3, 119.7, 114.5, 112.7. (EI): Calc'd for $C_{12}H_9NO$:183.0684 found 183.0654. **10H-3,10'-biphenoxazine:** ^{1}H NMR (600 MHz, d_6-DMSO) δ 8.50 (s, 1H, N**H**), 6.79 – 6.72 (m, 2H), 6.70 – 6.64 (m, 7H), 6.64 – 6.59 (m, 3H), 6.51 (d, J = 7.7 Hz, 1H), 6.04 (d, J = 7.6 Hz, 2H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 143.8, 142.5, 141.7, 133.4, 132.3, 131.2, 129.5, 127.7, 125.1, 123.7, 123.1, 120.6, 120.2, 116.1, 114.5, 114.2, 112.6. (EI): Calc'd for $C_{24}H_{16}N_2O_2$: 364.1212 found 364.1189.

Decomposition of phenoxazine-*N*-oxyl under acidic conditions



In a 100 mL round-bottom flask, phenoxazine *N*-oxyl (2.0 mmol) was dissolved in 10 mL chlorobenzene containing 3 M acetic acid. The solution was stirred at 70 °C for 24 hours. The reaction mixture was extracted with ethyl acetate/water (1:2) and washed with sodium bicarbonate and brine solution. The organic phase was passed through anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography with hexane and ethyl acetate (97:3) and phenoxazine and phenoxazine-3-one were obtained as white and dark brown solids in 19% and 47 % yield, respectively. **Phenoxazine**: ^{1}H NMR (600 MHz, d_6-DMSO) δ 8.17 (s, 1H, NH), 6.72 (td, J = 7.3, 1.6 Hz, 2H), 6.62 – 6.54 (m, 4H), 6.46 (dd, J = 7.7, 1.5 Hz, 2H). ^{13}C NMR (151 MHz, d_6-DMSO) δ 142.2, 131.8, 123.3, 119.7, 114.5, 112.7. (EI): Calc'd for $C_{12}H_9NO$:183.0684 found 183.0654. **3H-Phenoxazin-3-one:** ^{1}H NMR (600 MHz, d_6-DMSO) δ 7.85 (dd, J = 7.9, 1.6 Hz, 1H), 7.68 – 7.64 (m, 1H), 7.56 (d, J = 9.8 Hz, 1H), 7.50 (dd, J = 8.3, 1.3 Hz, 1H), 7.47 – 7.44 (m, 1H), 6.85 (dd, J = 9.8, 2.0 Hz, 1H), 6.30 (d, J = 2.1 Hz,

1H).^{13}C NMR (151 MHz, d_6-DMSO) δ 185.1, 149.1, 148.0, 142.9, 134.5, 134.2, 132.6, 132.4, 129.5, 125.0, 115.6, 105.3. (EI): Calc'd for $C_{12}H_7NO_2$: 197.0477 found 197.0495.

References:

1. E. A. Haidasz, A. T. M. Van Kessel, and D. A. Pratt, *J. Org. Chem*. 2016, **81**, 737−744.
2. a) J. Mosnáček, R. Nicolaÿ, K. K. Kar, S. O. Fruchey, M. D. Cloeter, R. S. Harner and K. Matyjaszewski, *Ind. Eng. Chem. Res.* 2012, **51**, 3910–3915; b) D.-G. Chen, Y. Chen, C.-H. Wu, Y.-A. Chen, M.-C. Chen, J.-A. Lin, C.-Y. Huang, J. Su, H. Tian, P.-T. Chou, *Angew. Chem. Int. Ed.* 2019, **131**, 13431–13435; c) G. K. Musorin, *Russ. J. Org. Chem*, 2003, **39**, 915−918; d) P. Borowicz, J. Herbich, A. Kapturkiewicz, R. A-Ostrowska, J. Nowacki and G. Grampp, *Phys. Chem. Chem. Phys*., 2000, **2**, 4275-4280; e) P. R.-Castillo and S. L. Buchwald, *Chem. Rev*. 2016, **116**, 12564–12649.
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4. V. A. Timoshchuk and R. I. Hogrefe, *Nucleosides, Nucleotides and Nucleic Acids*, 2009, **28**, 464–472.
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6. N. N. Pozdeeva and E. T. Denisov, *Kinetics and Catalysis*, 2010, **51**, 211–218.

Cyclic voltammograms

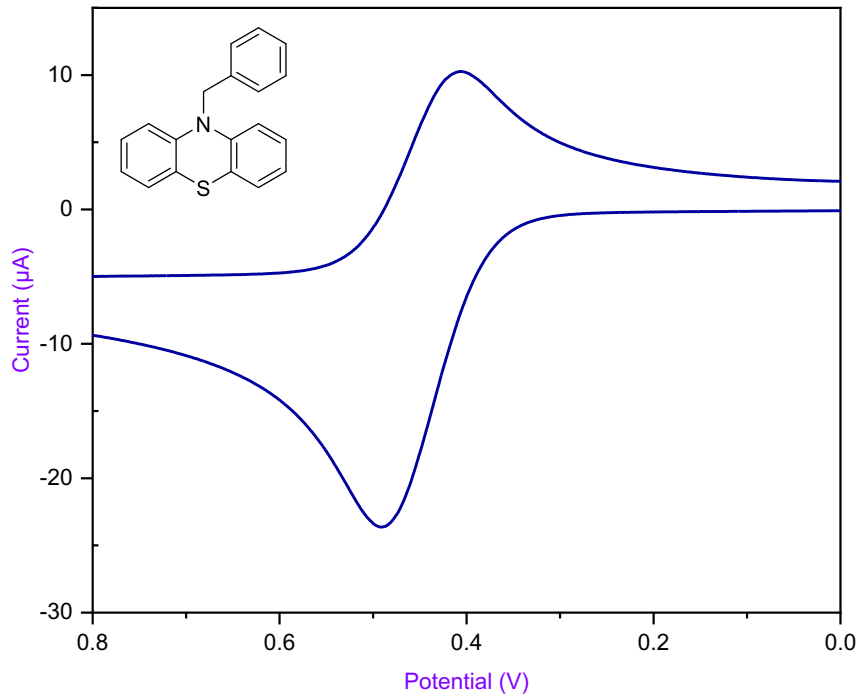


Figure S11. CV of 10-*N*-Benzyl phenoxazine vs. Ag/Ag^{+}. E° = 0.98 V vs. NHE.

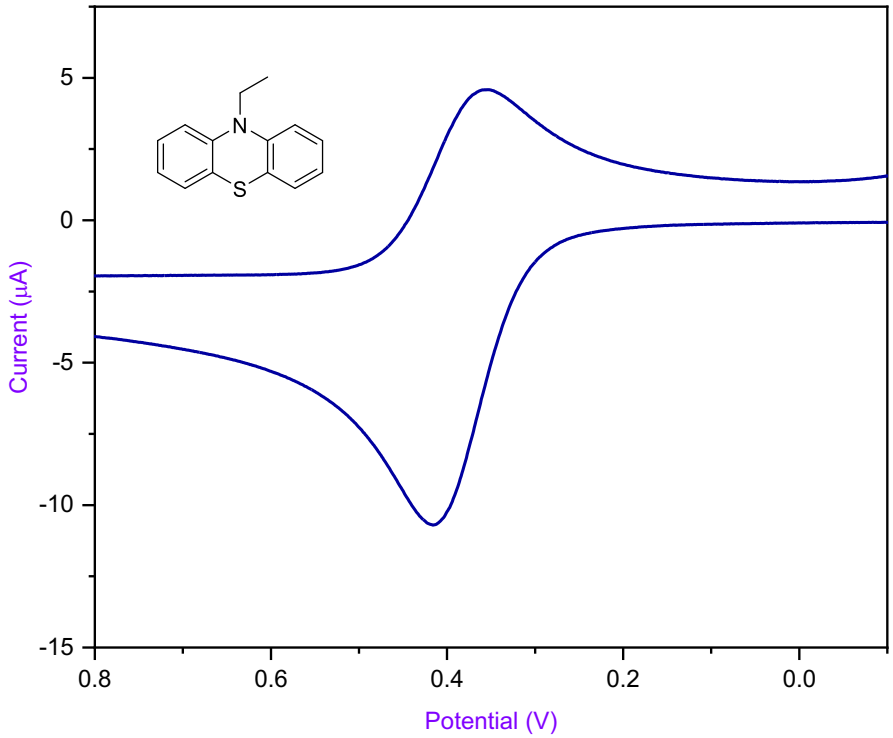


Figure S12. CV of 10-*N*-ethyl phenoxazine vs. Ag/Ag^{+}. E° = 0.92 V vs. NHE.

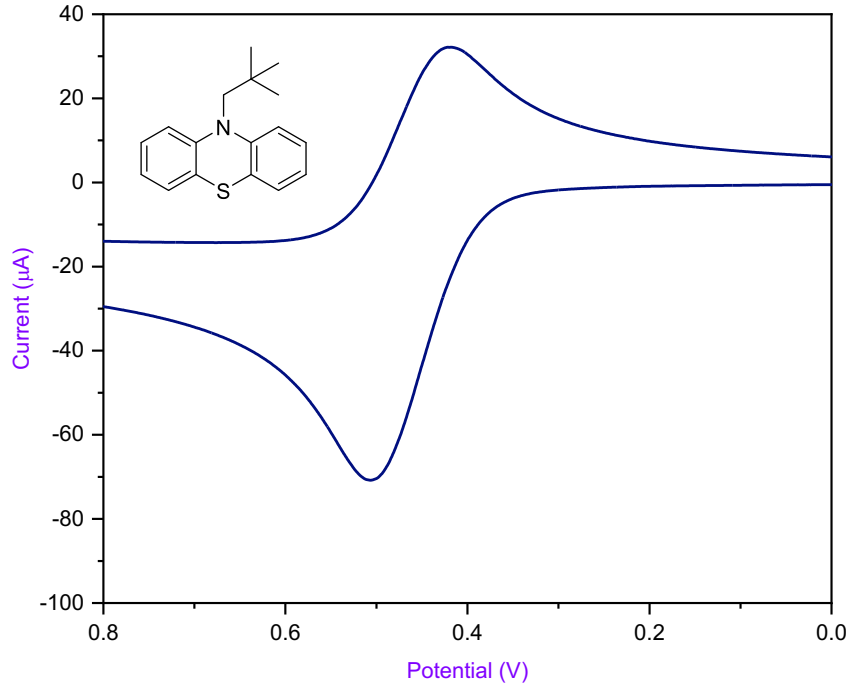


Figure S13. CV of 10-*N*-neopentylphenothiazine vs. Ag/Ag^{+}. E° = 1.0 V vs. NHE.

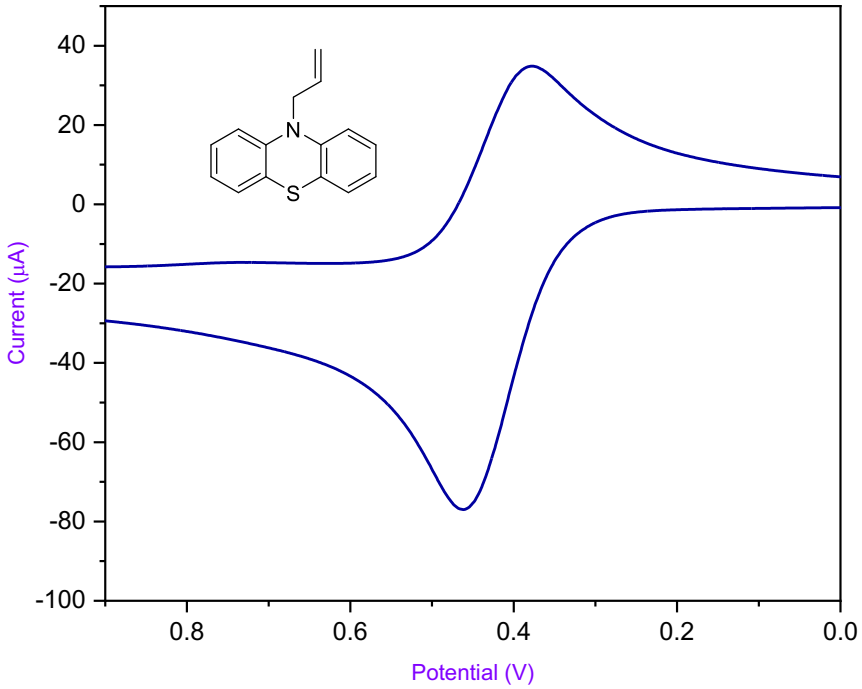


Figure S14. CV of 10-*N*-allylphenothiazine vs. Ag/Ag^{+}. E° = 0.96 V vs. NHE.

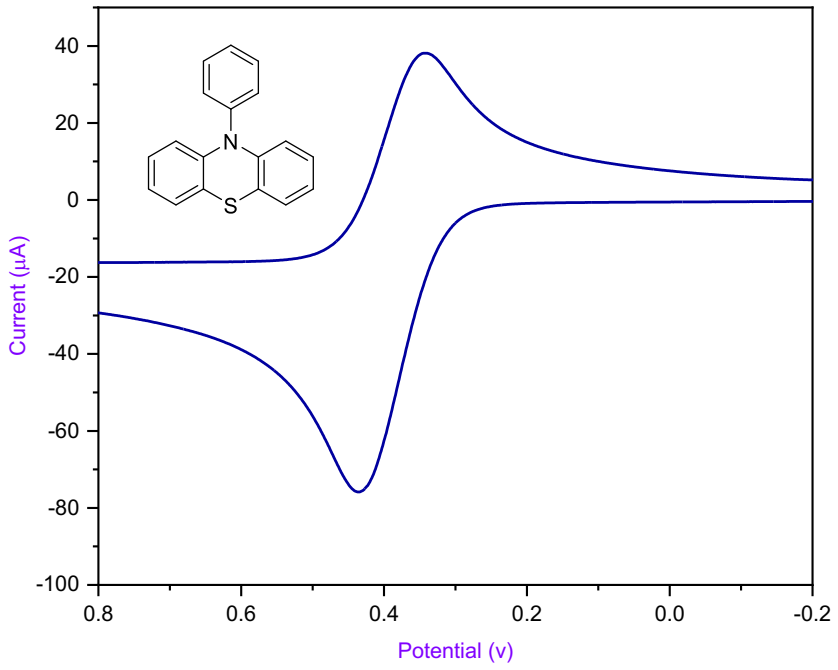


Figure S15. CV of 10-*N*-phenylphenothiazine vs. Ag/Ag+. E° = 0.93 V vs. NHE.

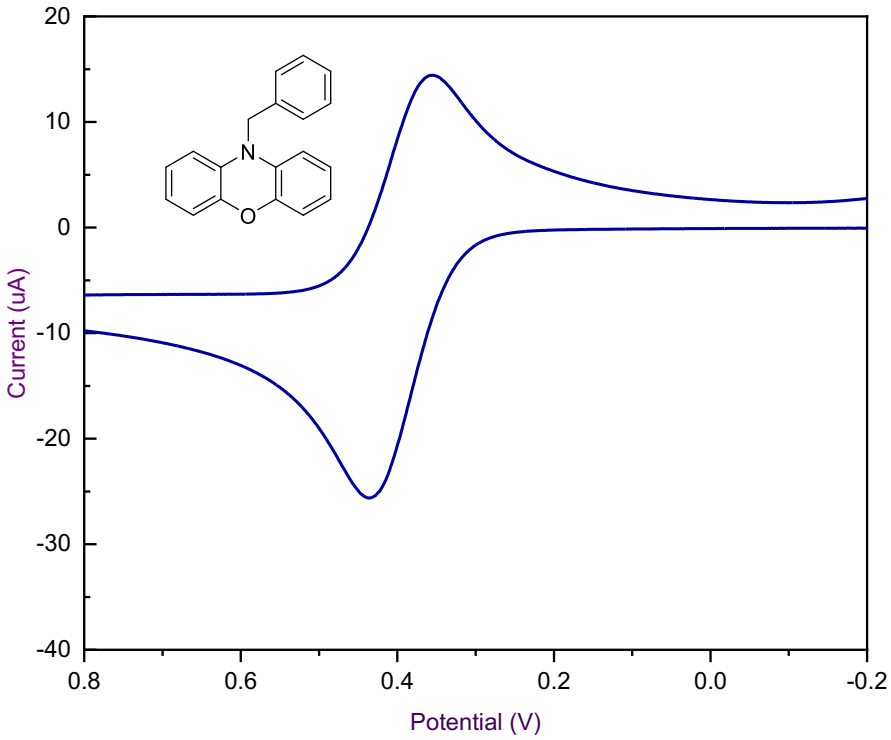


Figure S16. CV of 10-*N*-benzylphenoxazine vs. Ag/Ag^{+}. E° = 0.93 V vs. NHE.

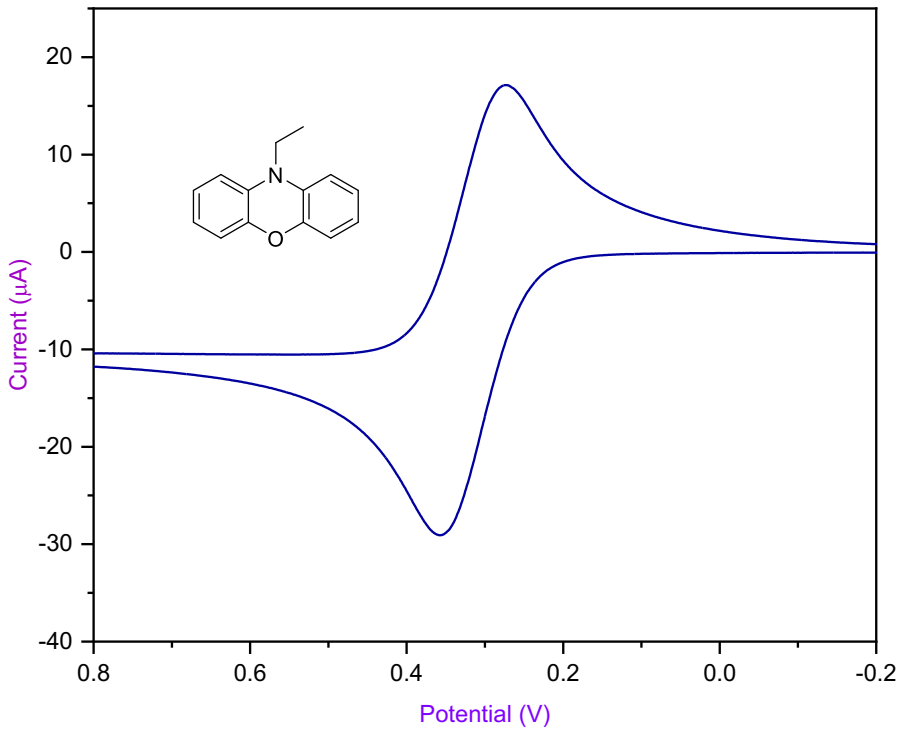


Figure S17. CV of 10-*N*-ethylphenoxazine vs. Ag/Ag^{+}. E° = 0.85 V vs. NHE.

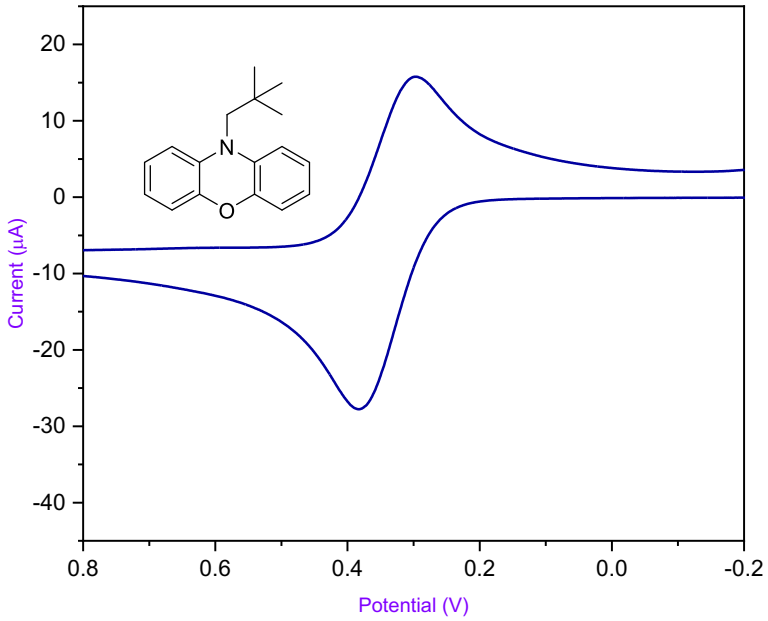


Figure S18. CV of 10-*N*-neopentylphenoxazine vs. Ag/Ag^{+}. E° = 0.87 V vs. NHE.

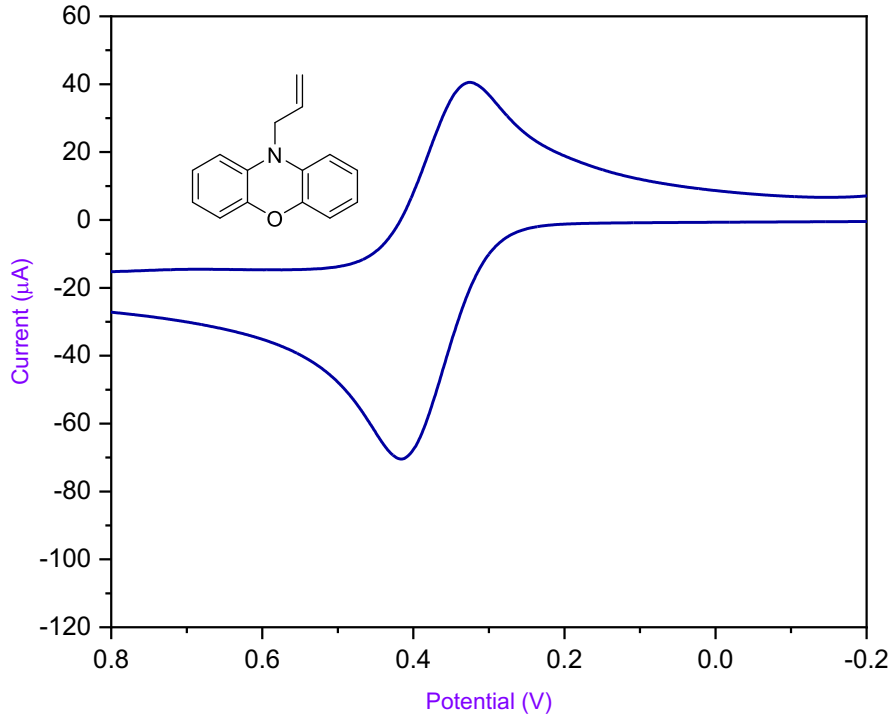


Figure S19. CV of 10-*N*-allylphenoxazine vs. Ag/Ag^{+}. E° = 0.91 V vs. NHE.

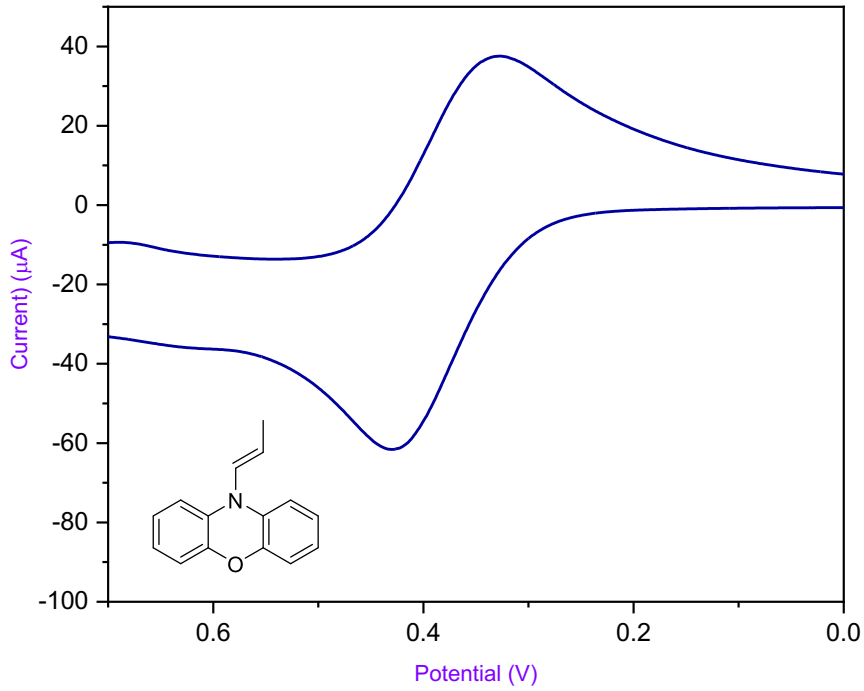


Figure S20. CV of 10-*N*-vinylphenoxazine vs. Ag/Ag^{+}.. E° = 0.91 V vs. NHE.

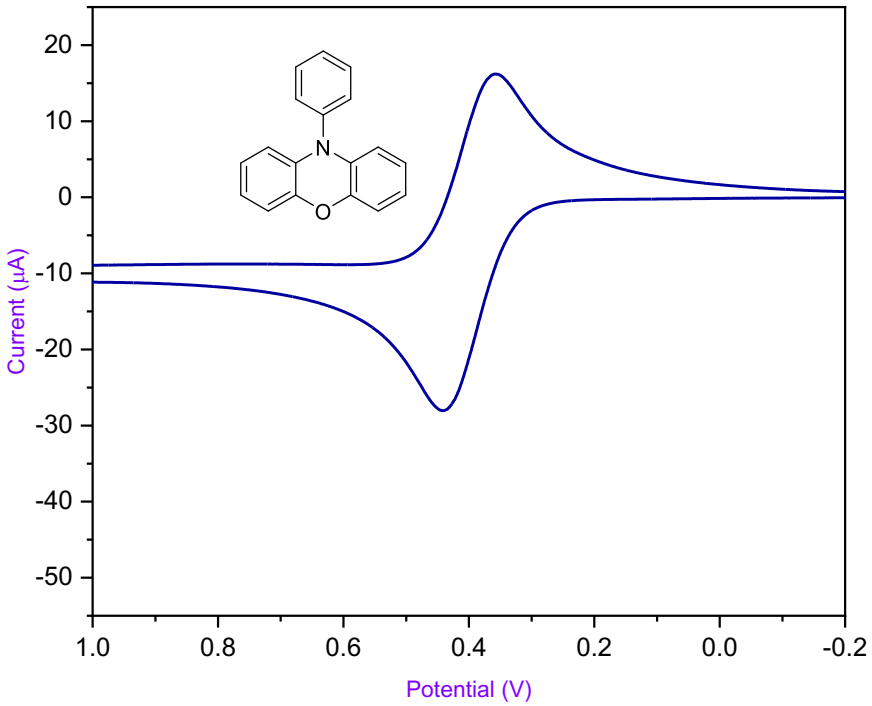


Figure S21. CV of 10-*N*-phenylphenoxazine vs. Ag/Ag+. E° = 0.94 V vs. NHE.

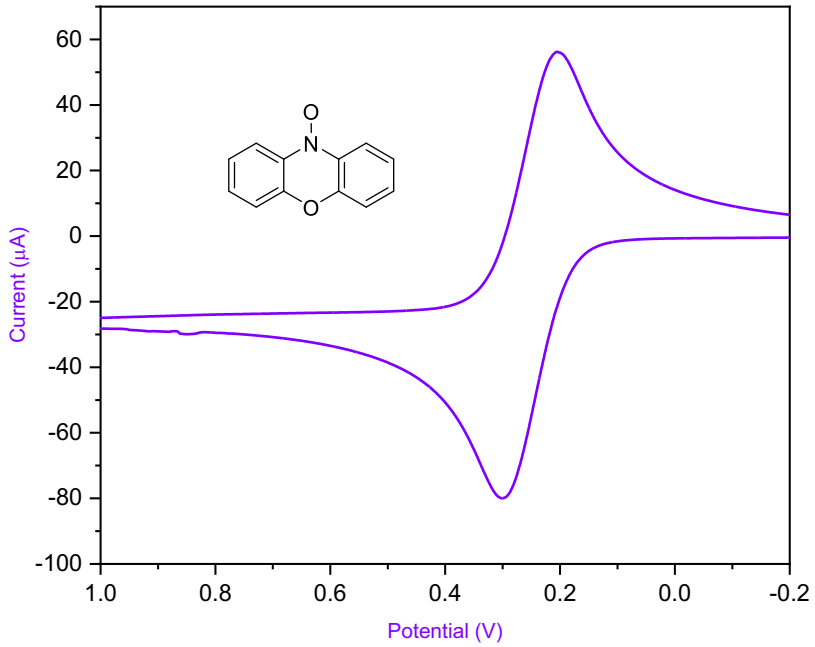


Figure S22. CV of 10-*N*-phenoxazine nitroxide vs. Ag/Ag^{+}. E° = 0.79 V vs. NHE.

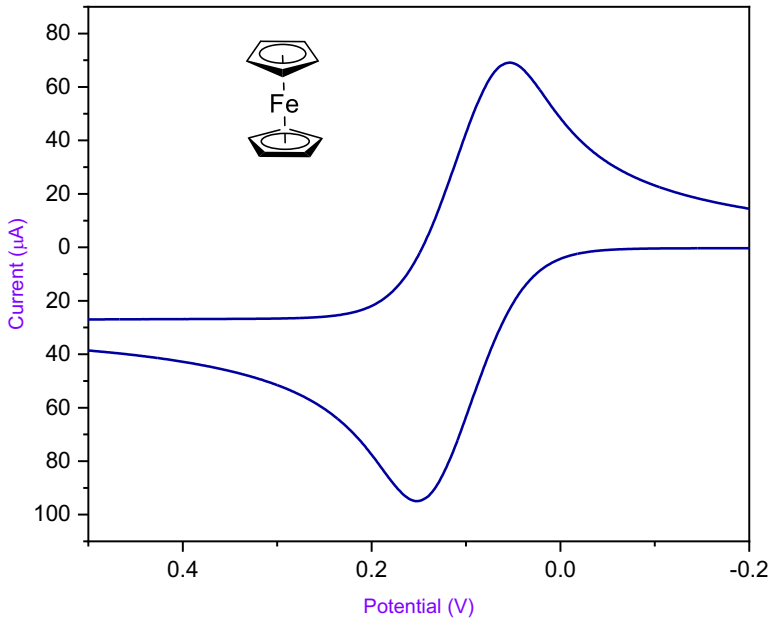
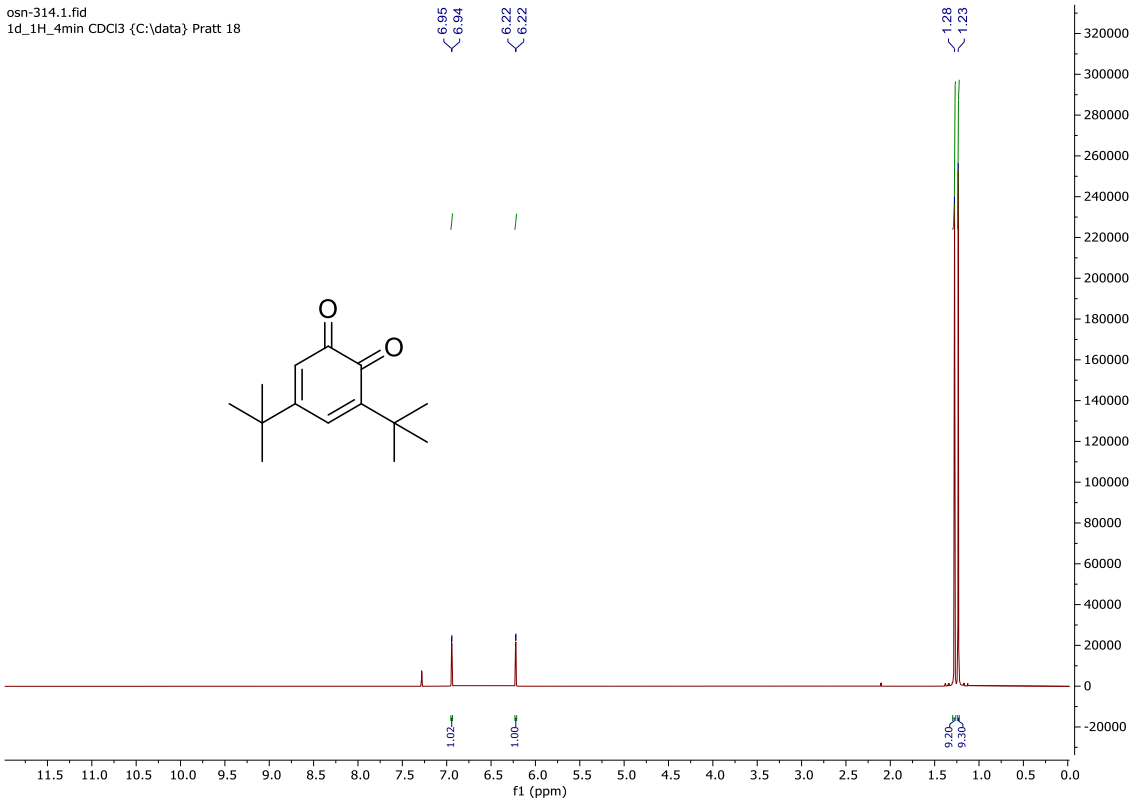
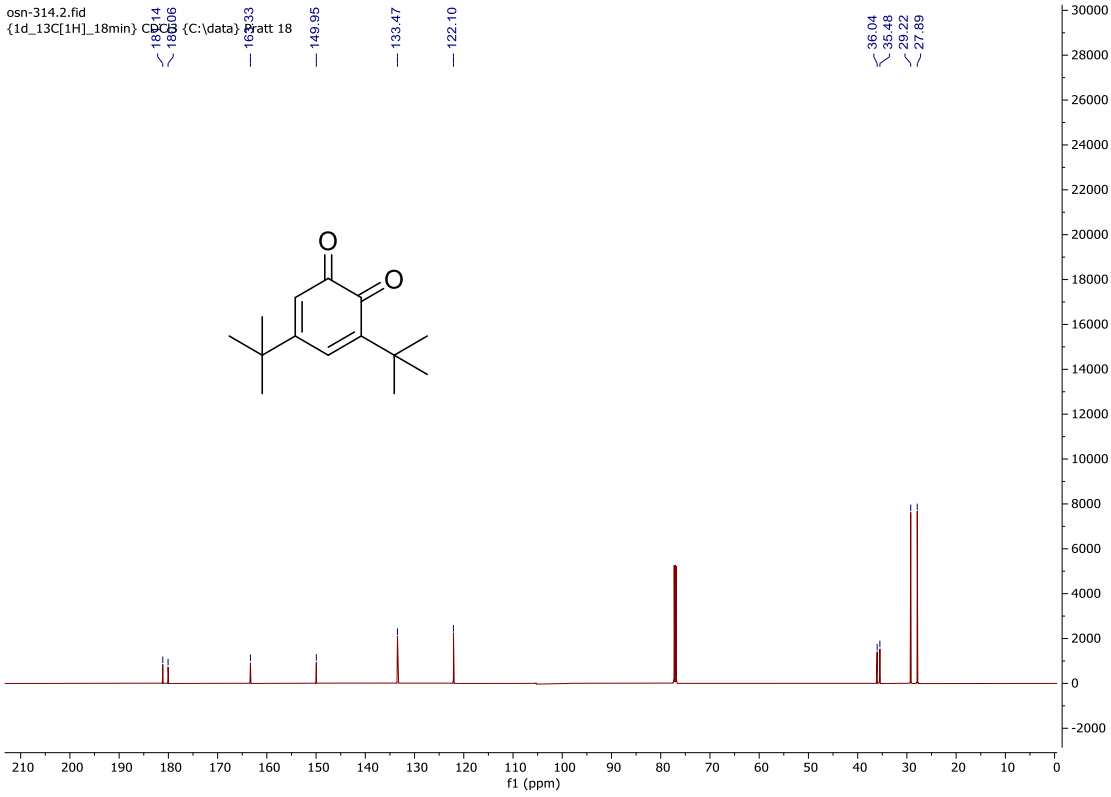


Figure S23. CV of Ferrocene vs. Ag/Ag+. E° = 0.87 V vs. NHE

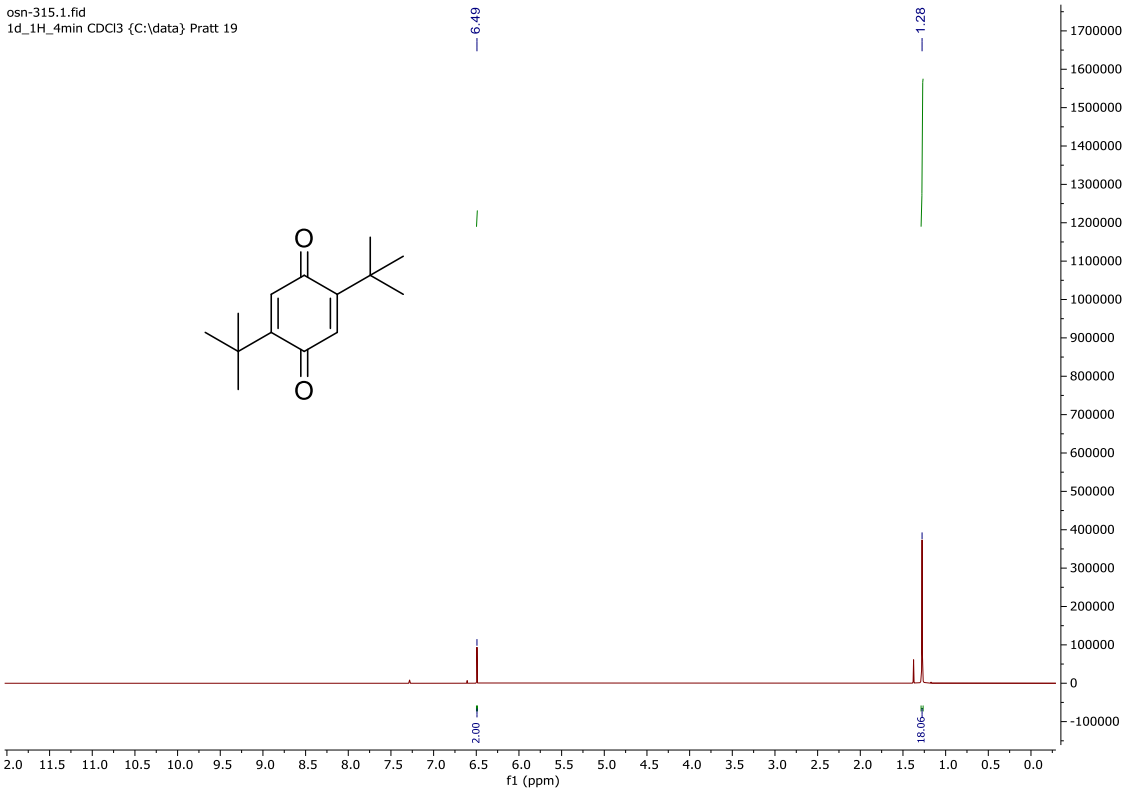
^{1}H NMR spectrum of 3,5-di-*tert*-butyl-1,2-benzoquinone



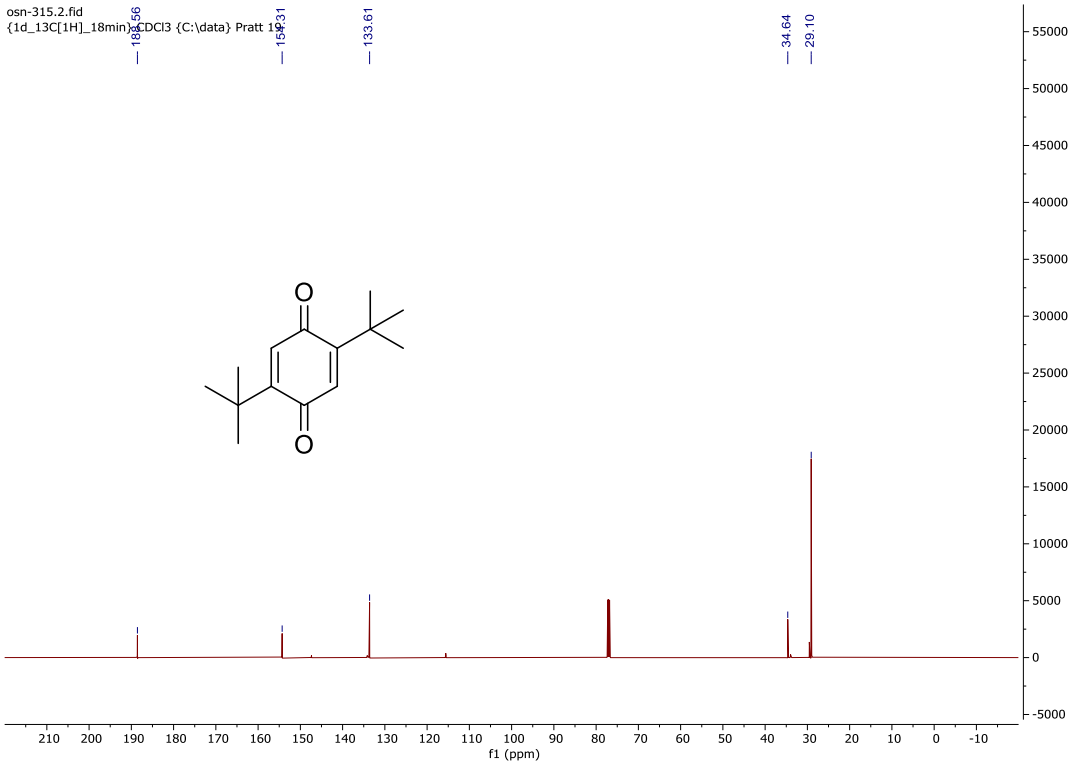
^{13}C NMR spectrum of 3,5-di-*tert*-butyl-1,2-benzoquinone



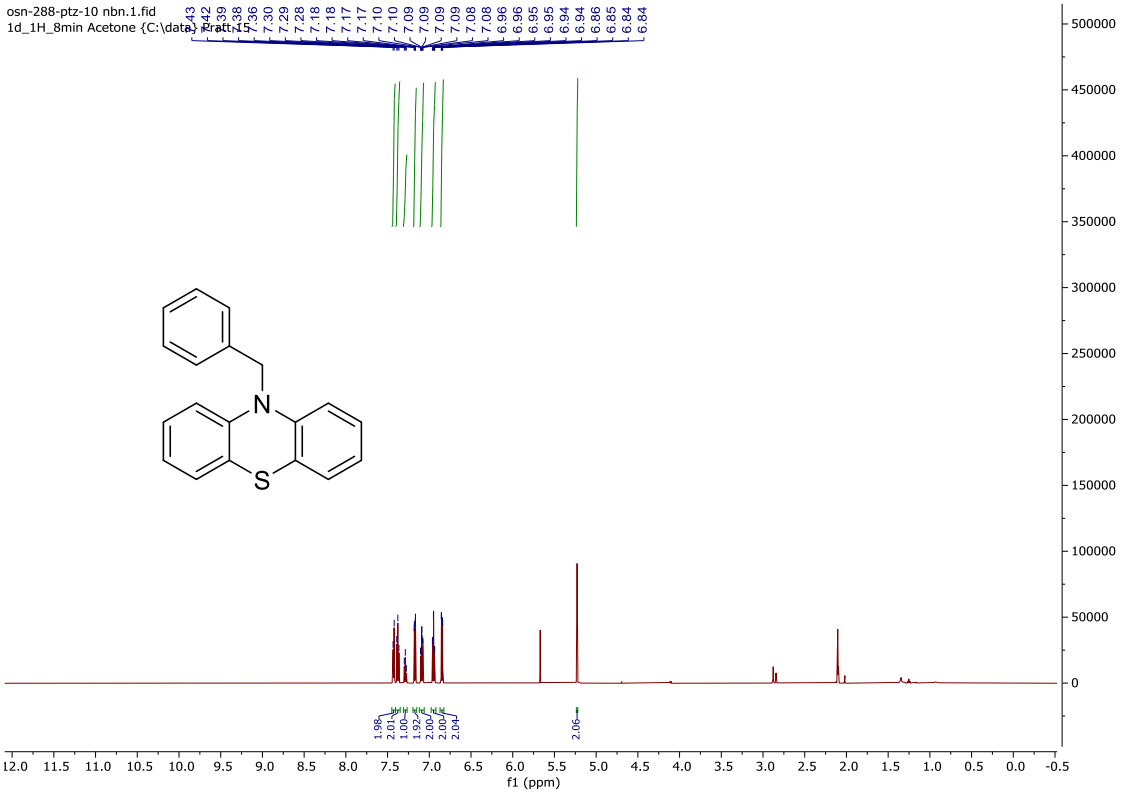
^{1}H NMR spectrum of 2,5-di-*tert*-butyl-1,4-benzoquinone



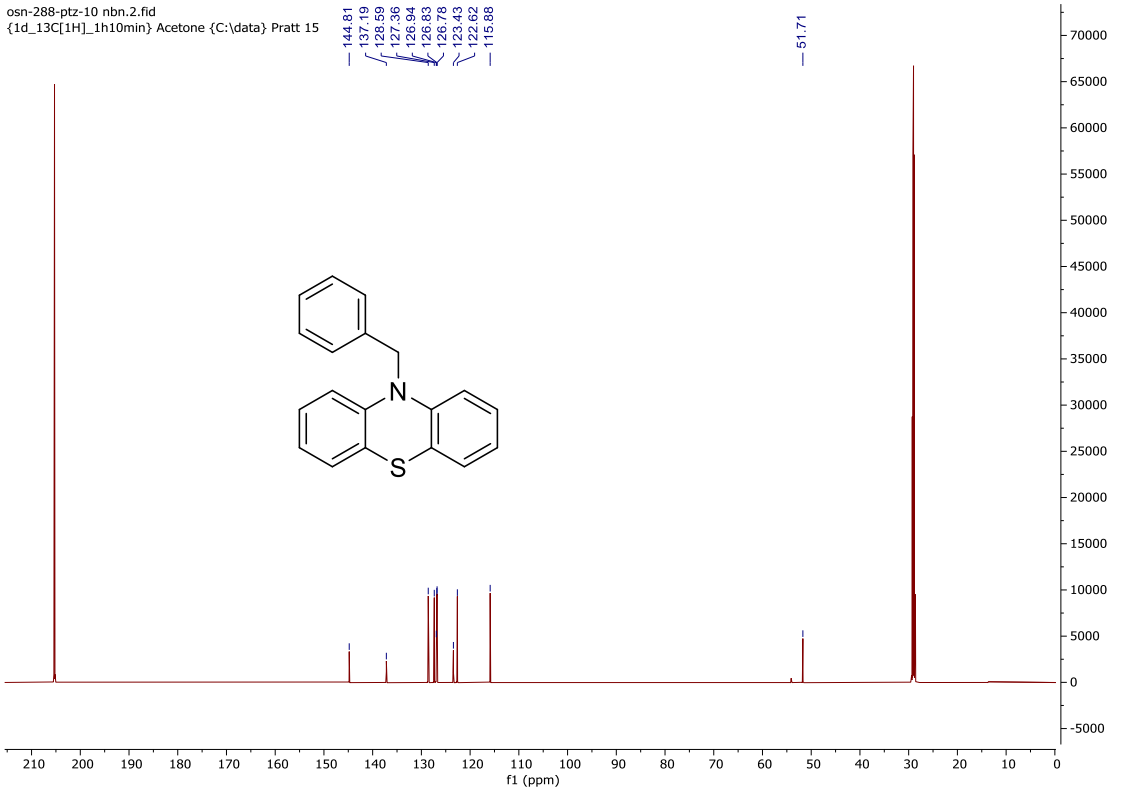
^{13}C NMR spectrum of 2,5-di-*tert*-butyl-1,4-benzoquinone



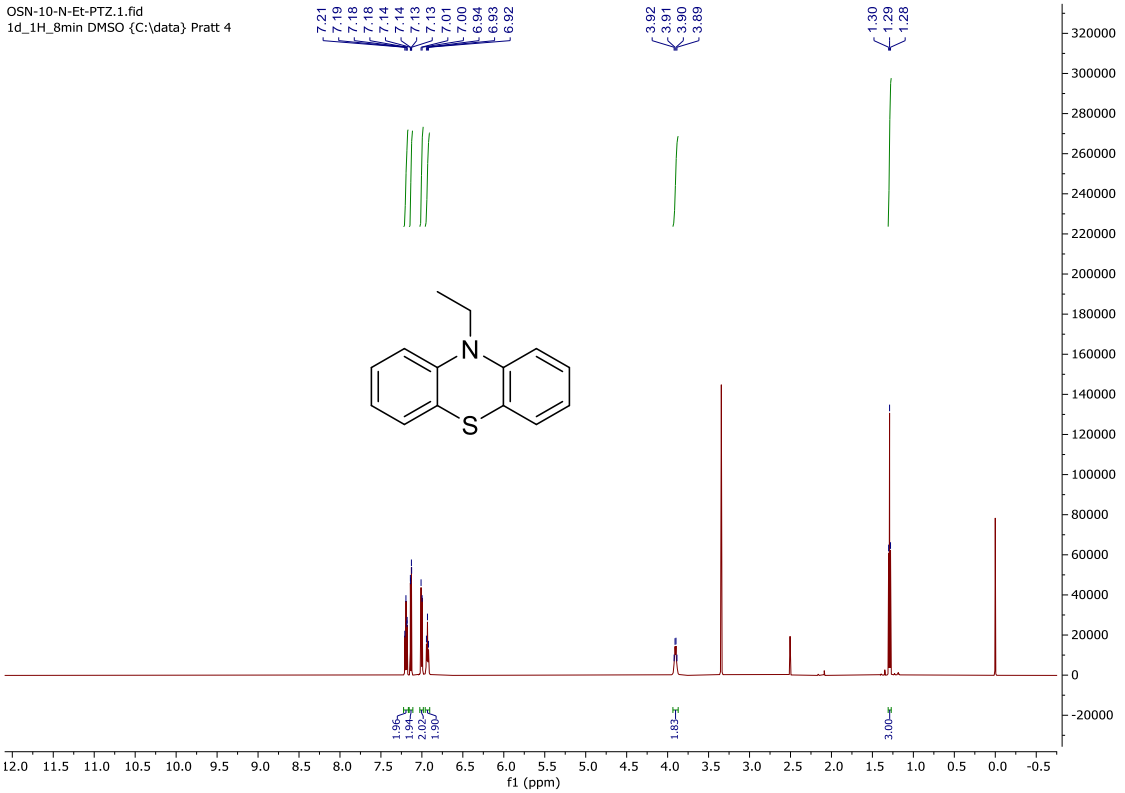
^{1}H NMR spectrum of 10-benzyl-10H-phenothiazine



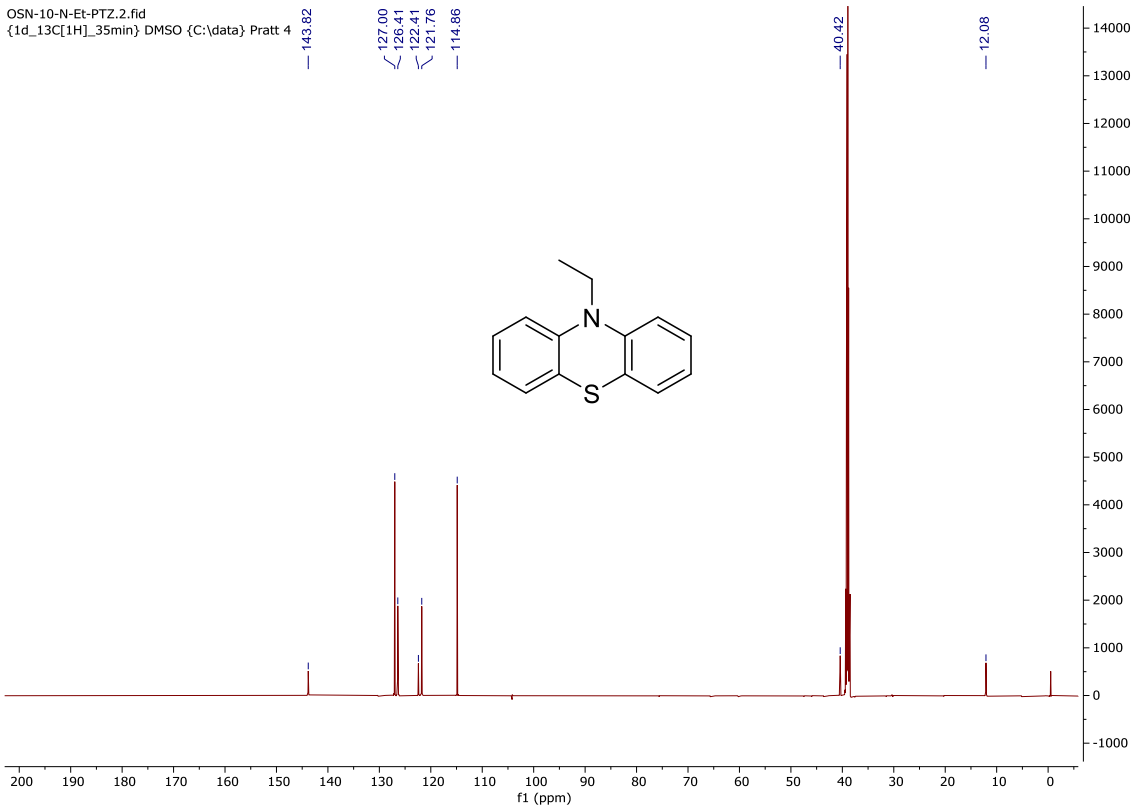
^{13}C NMR spectrum of 10-benzyl-10H-phenothiazine



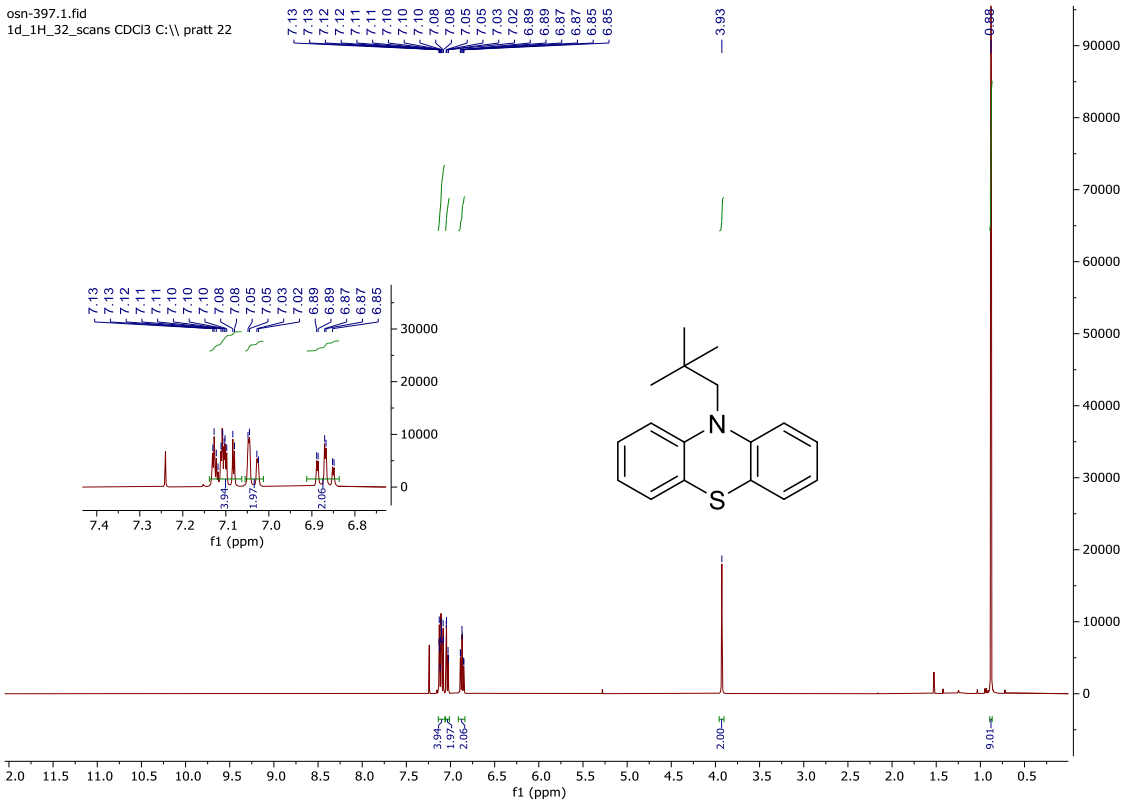
^{1}H NMR spectrum of 10-ethyl-10H-phenothiazine



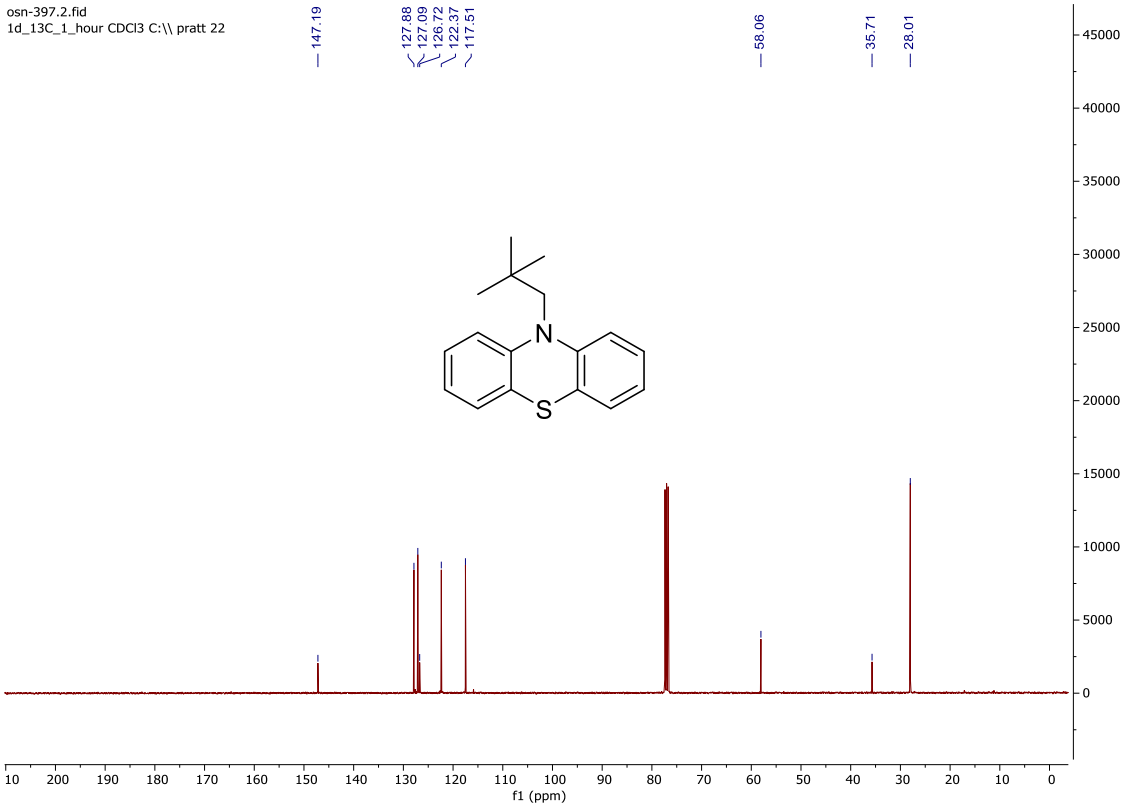
^{13}C NMR spectrum of 10-ethyl-10H-phenothiazine



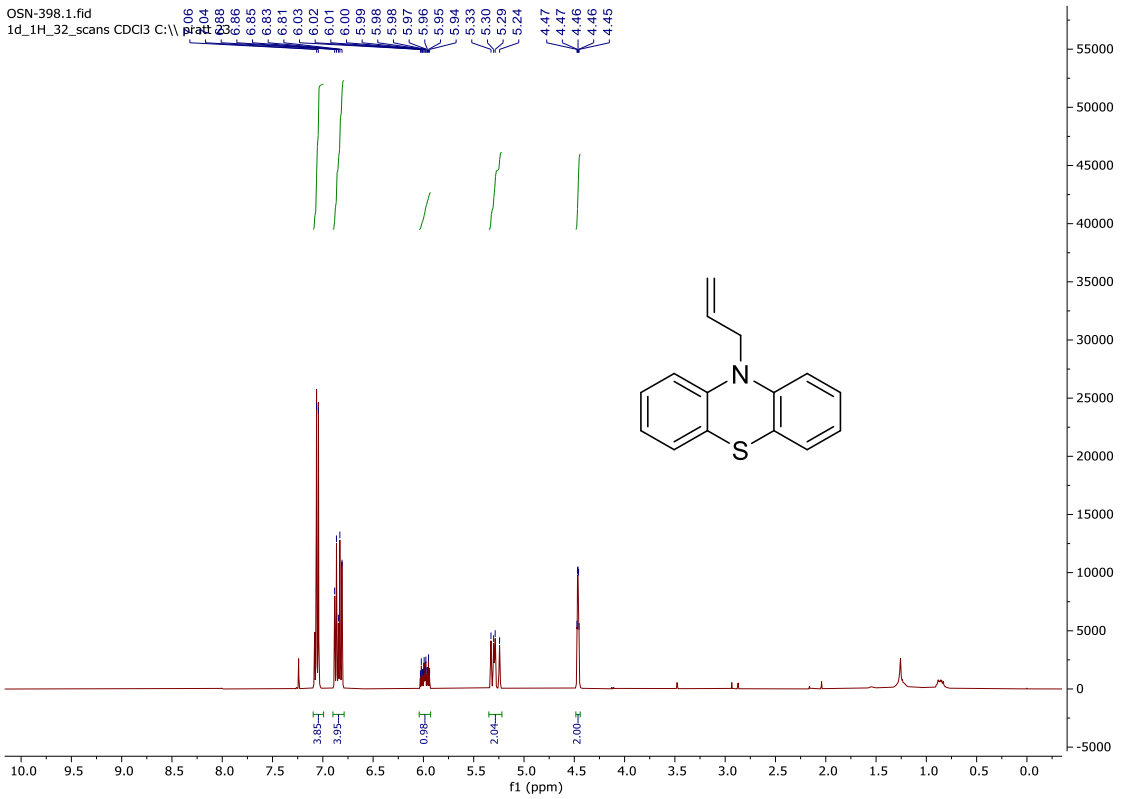
^{1}H NMR spectrum of 10-neopentyl-10H-phenothiazine



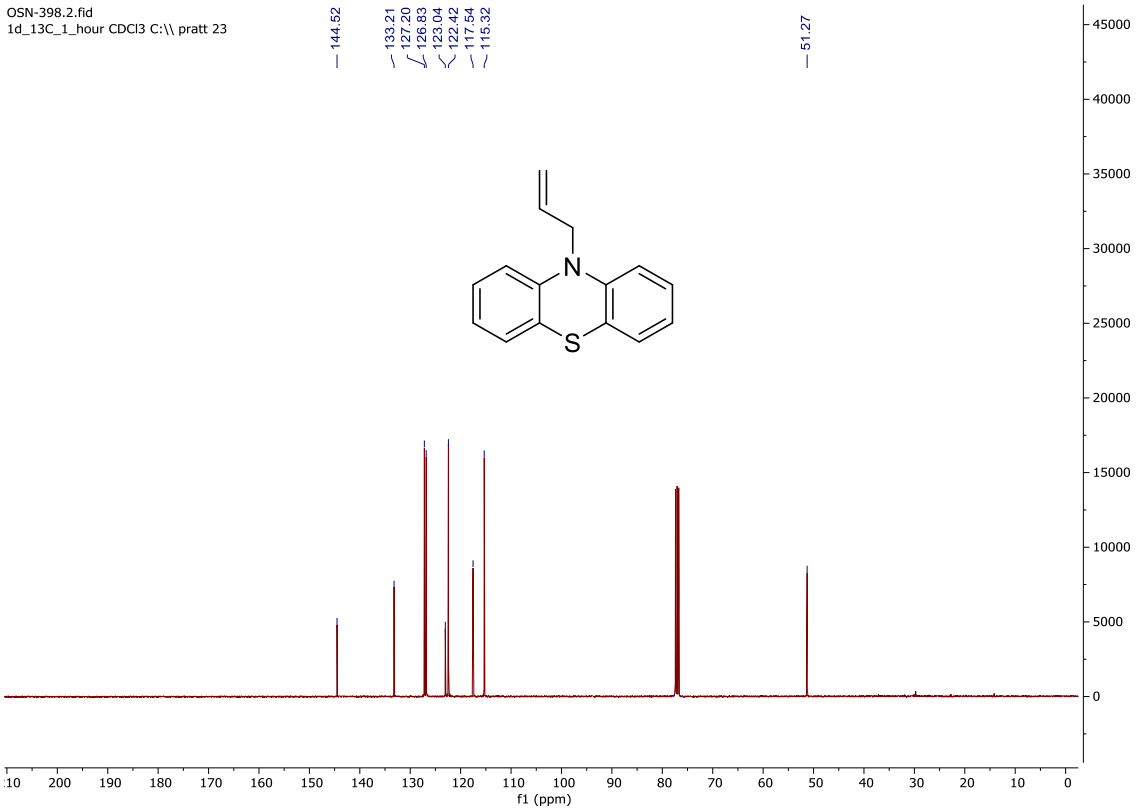
^{13}C NMR spectrum of 10-neopentyl-10H-phenothiazine



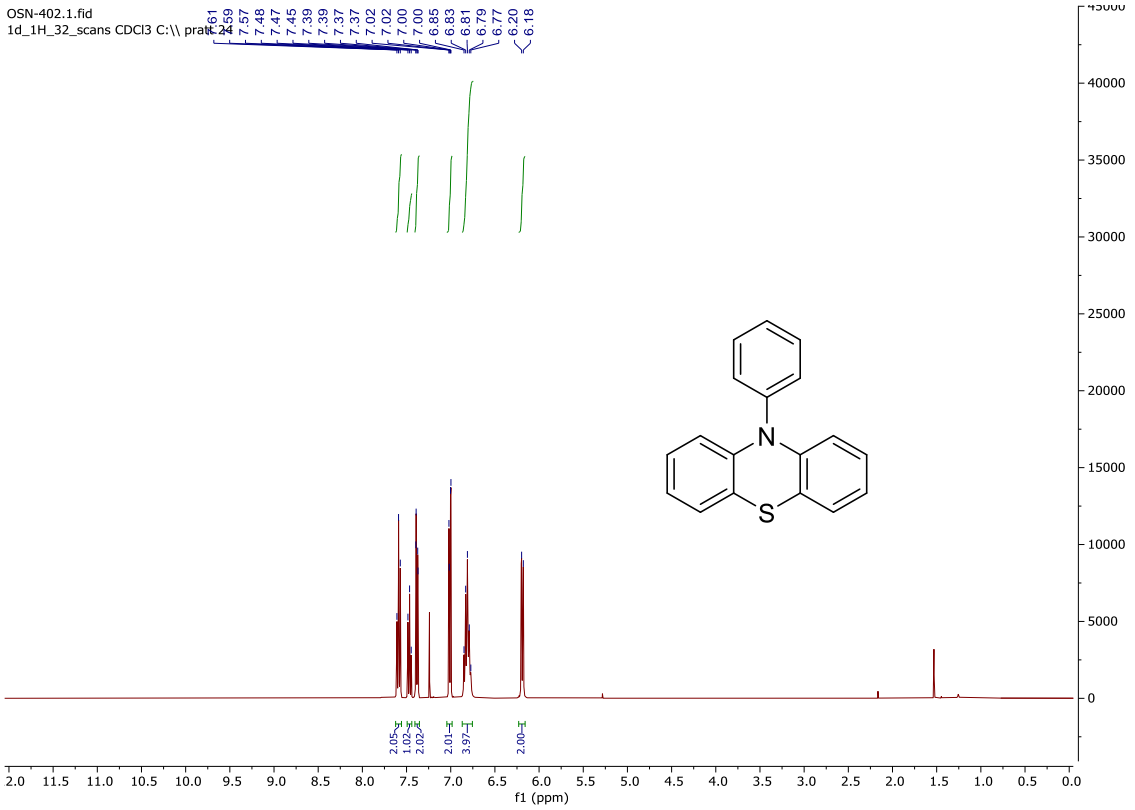
^{1}H NMR spectrum of 10-allyl-10H-phenothiazine



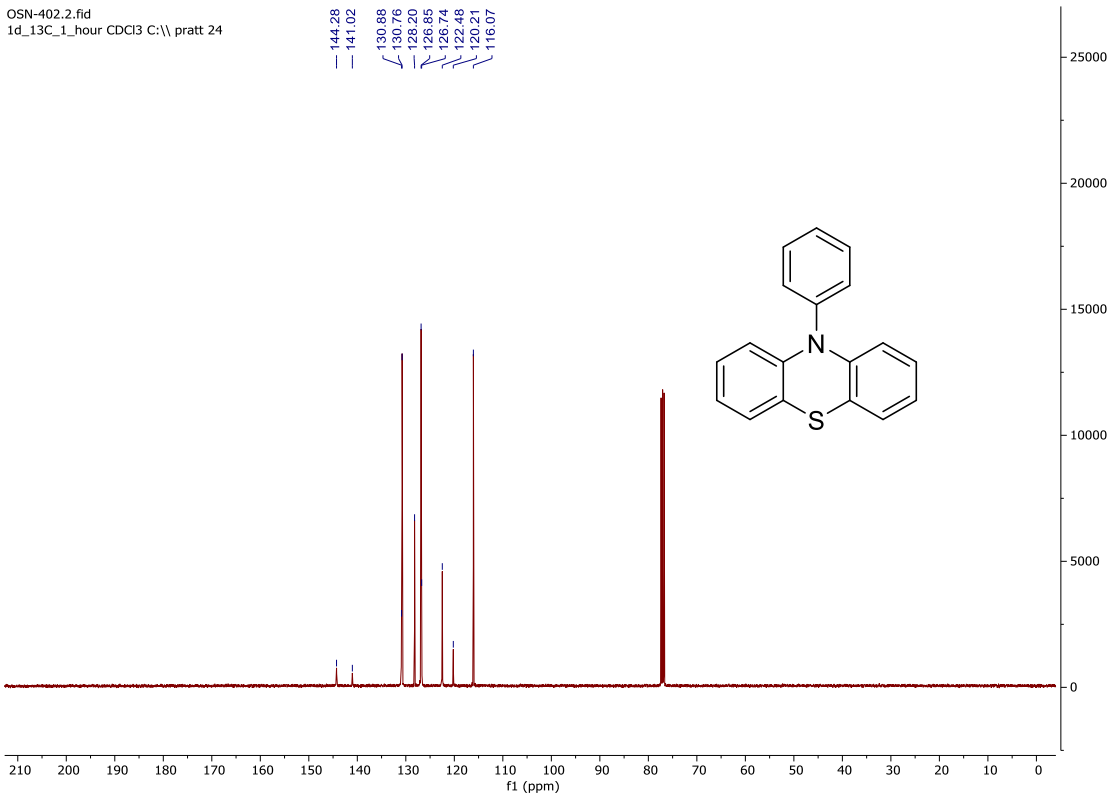
^{13}C NMR spectrum of 10-allyl-10H-phenothiazine



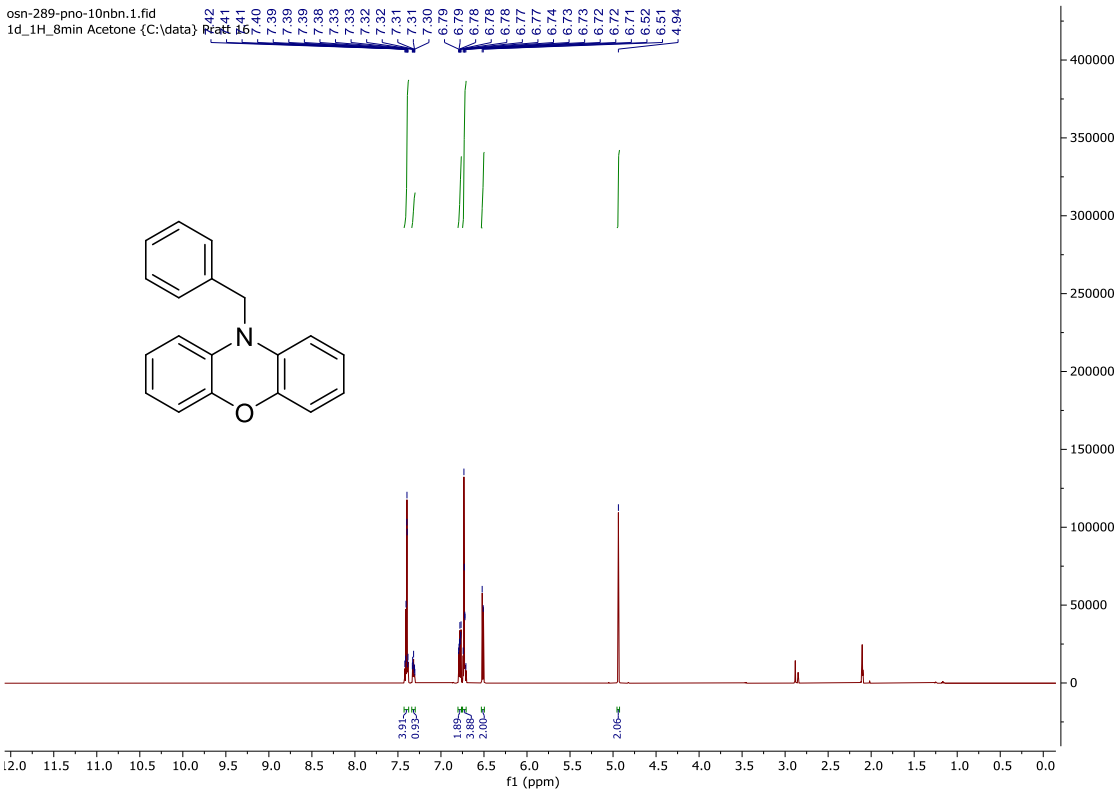
^{1}H NMR spectrum of 10-phenyl-10H-phenothiazine



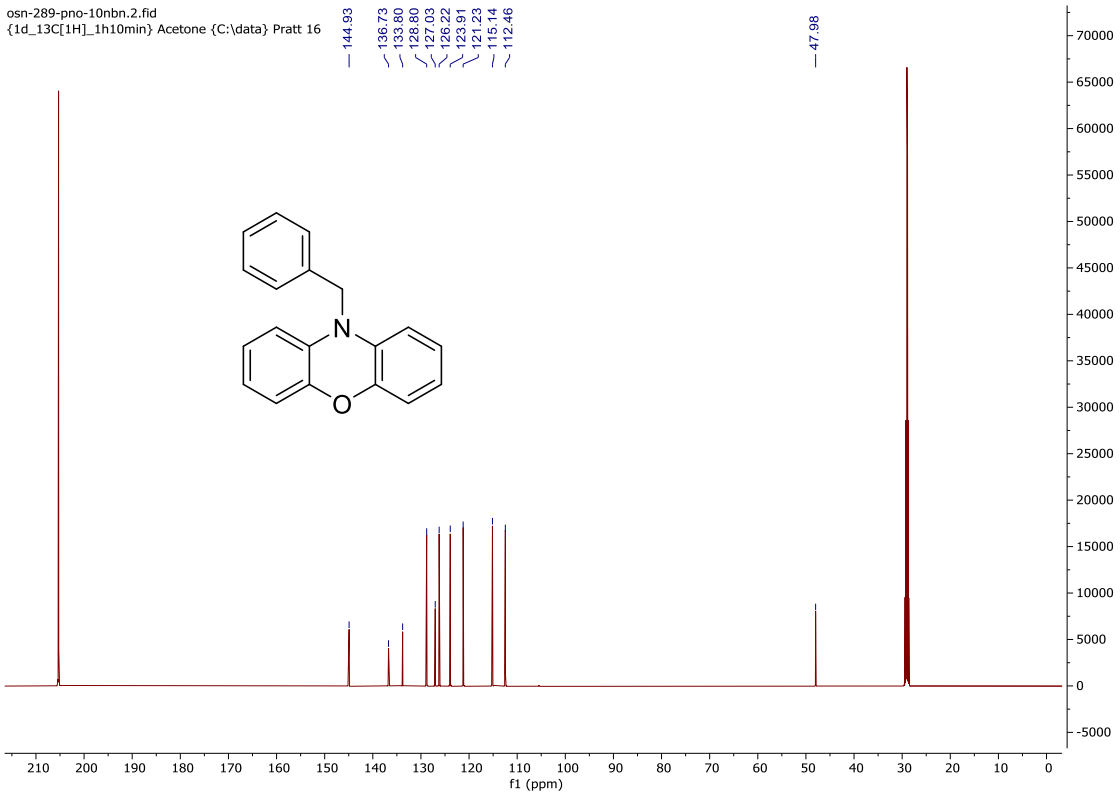
^{13}C NMR spectrum of 10-phenyl-10H-phenothiazine



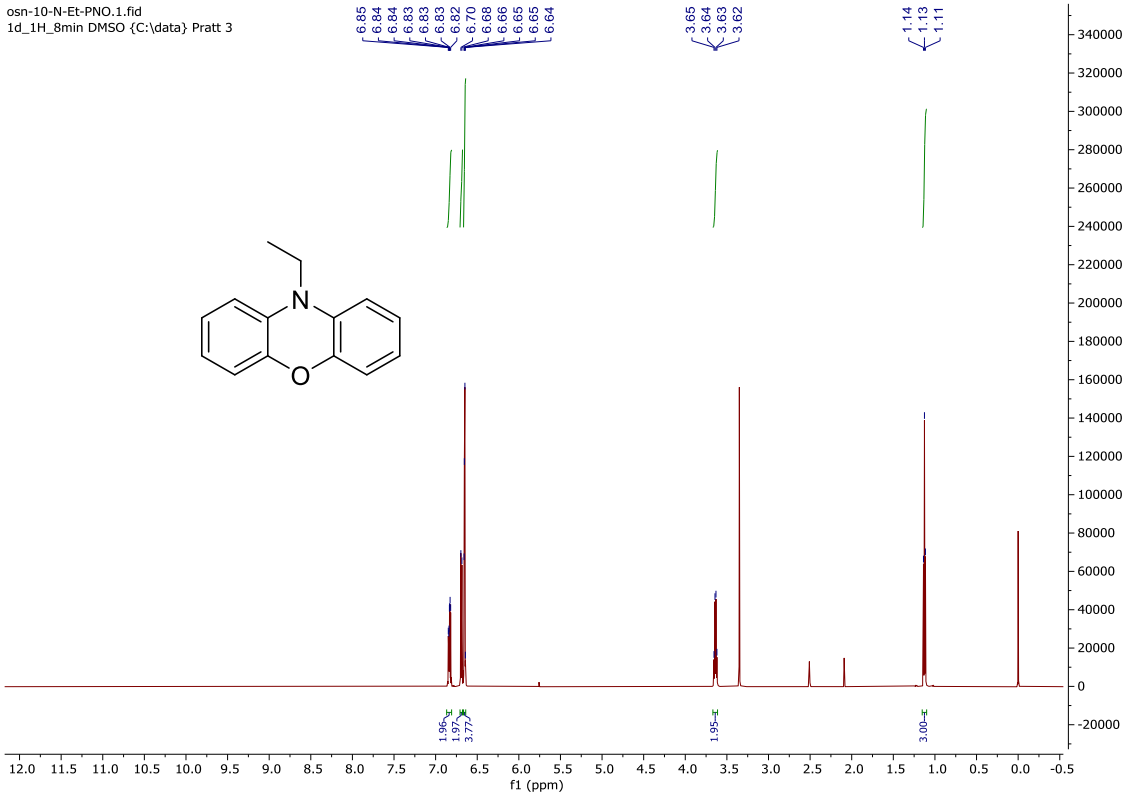
^{1}H NMR spectrum of 10-benzyl-10H-phenoxazine



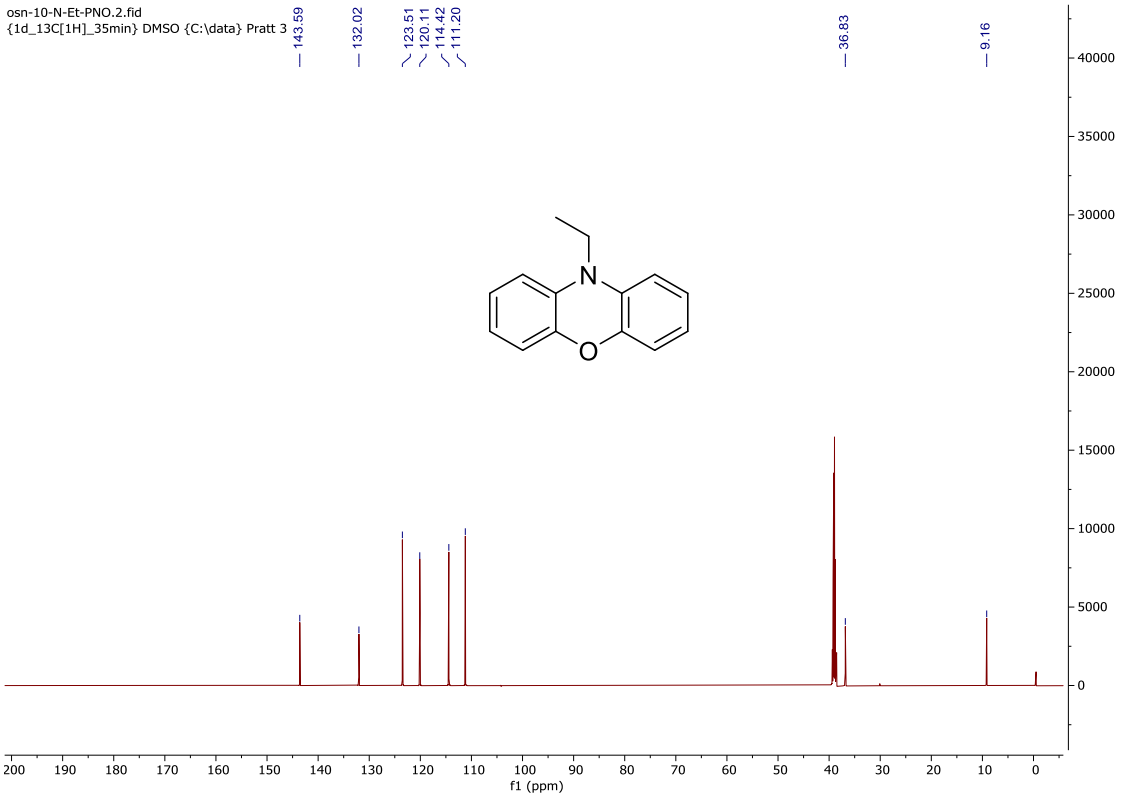
^{13}C NMR spectrum of 10-benzyl-10H-phenoxazine



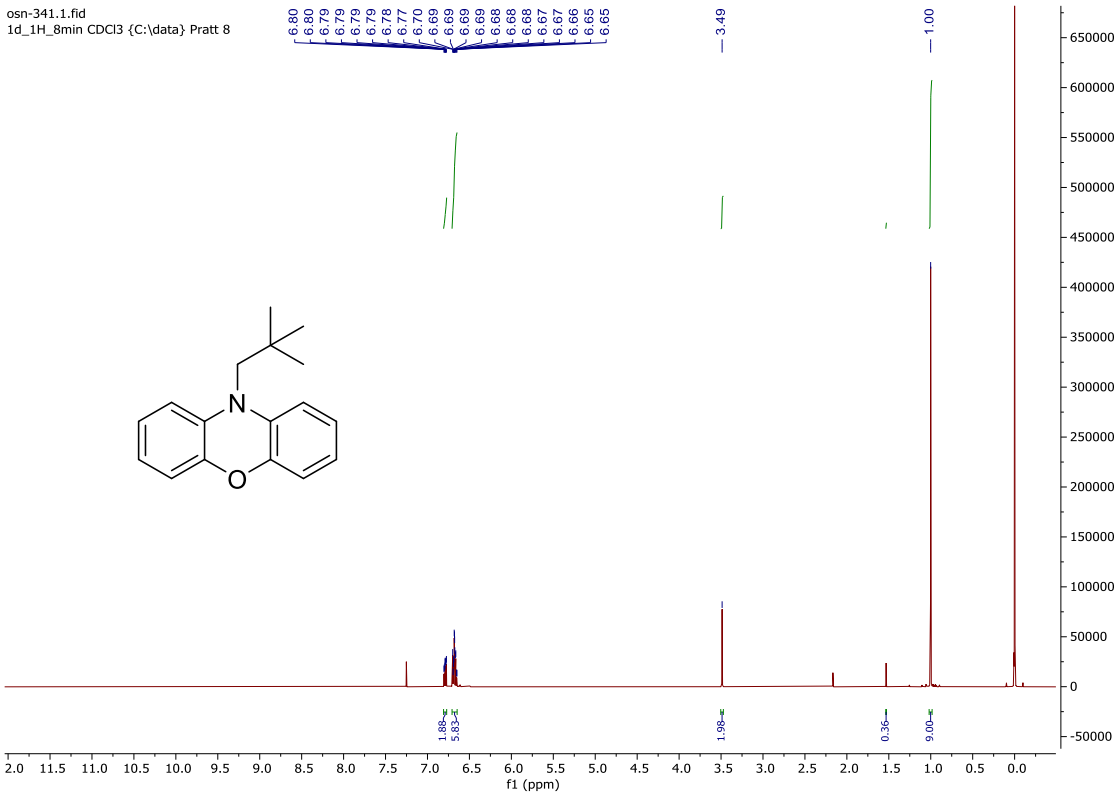
^{1}H NMR spectrum of 10-ethyl-10H-phenoxazine



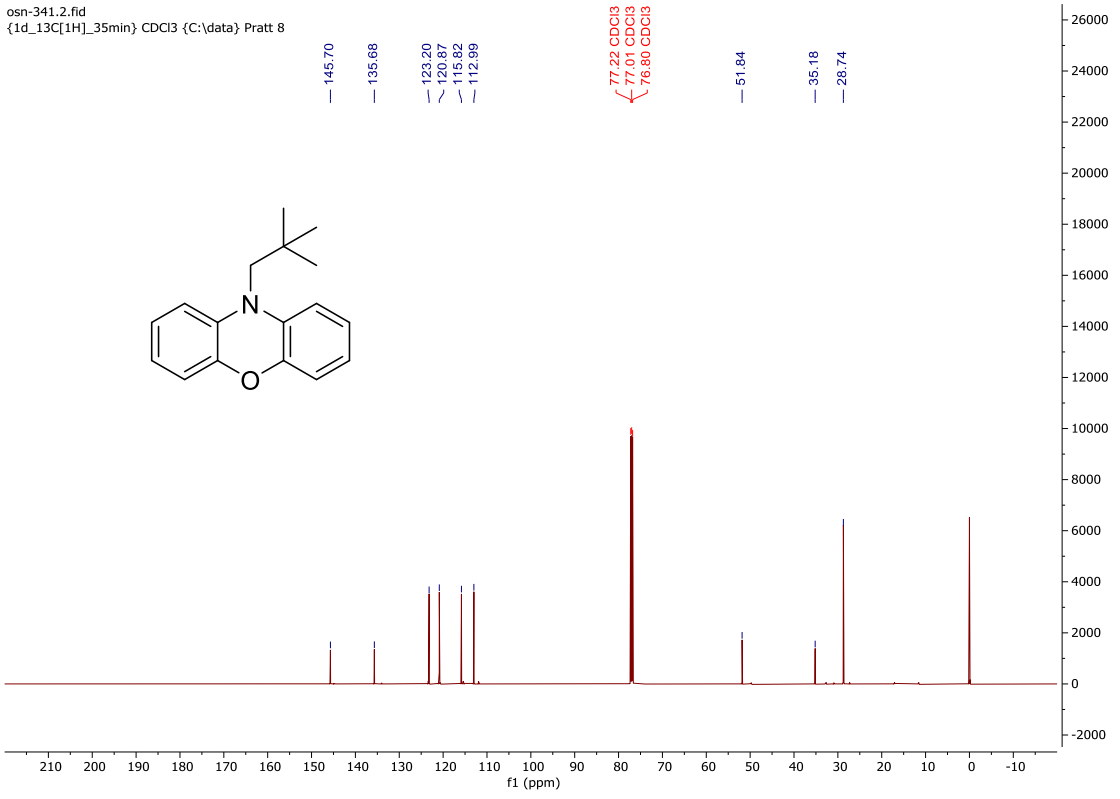
^{13}C NMR spectrum of 10-ethyl-10H-phenoxazine



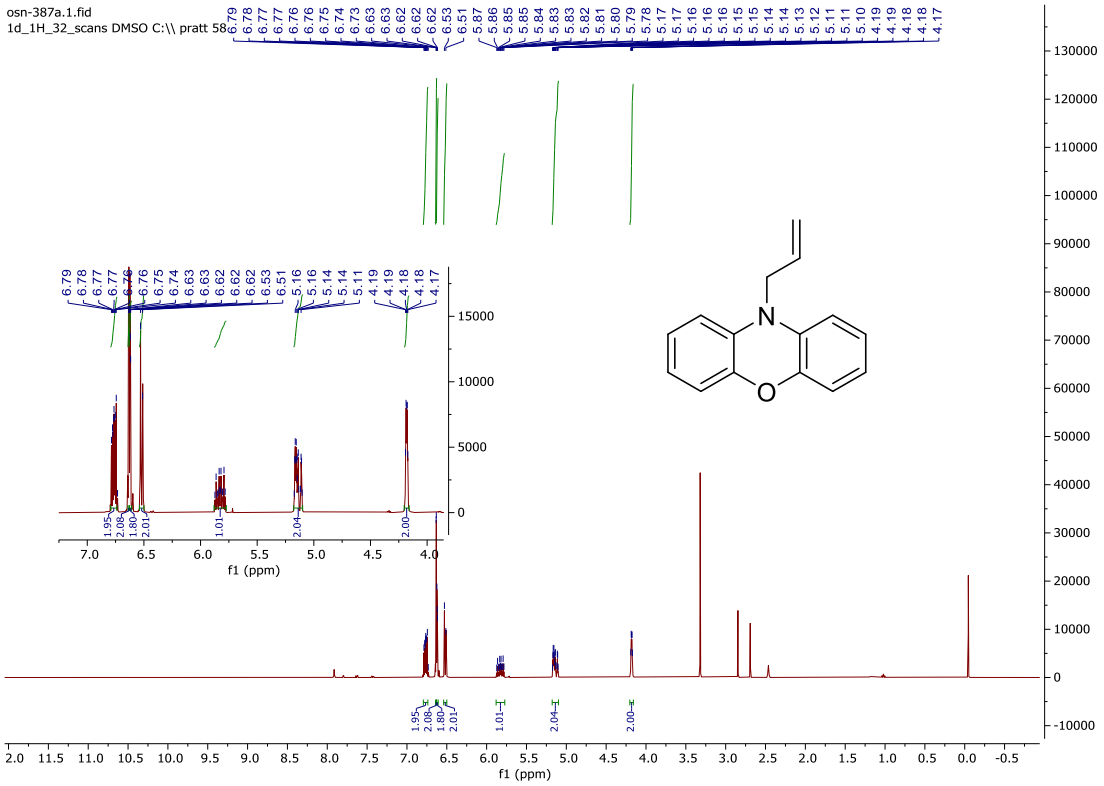
^{1}H NMR spectrum 10-neopentyl-10H-phenoxazine



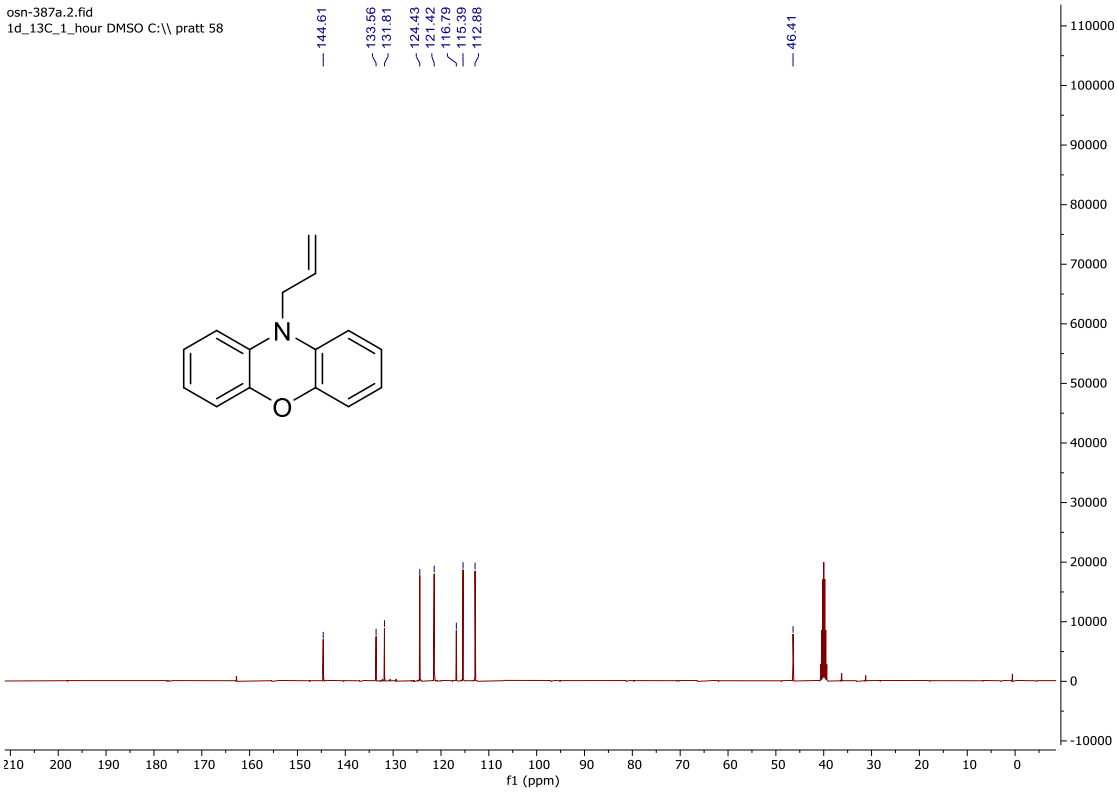
^{13}C NMR spectrum of 10-neopentyl-10H-phenoxazine



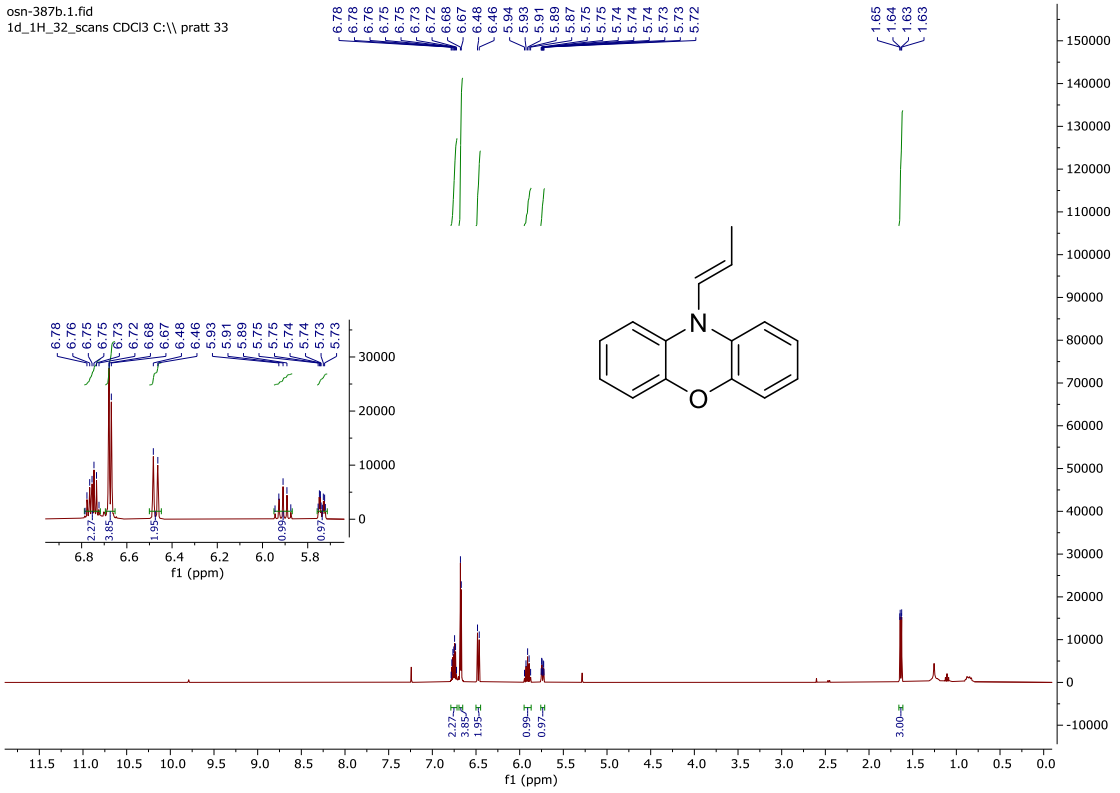
^{1}H NMR spectrum of 10-allyl-10H-phenoxazine



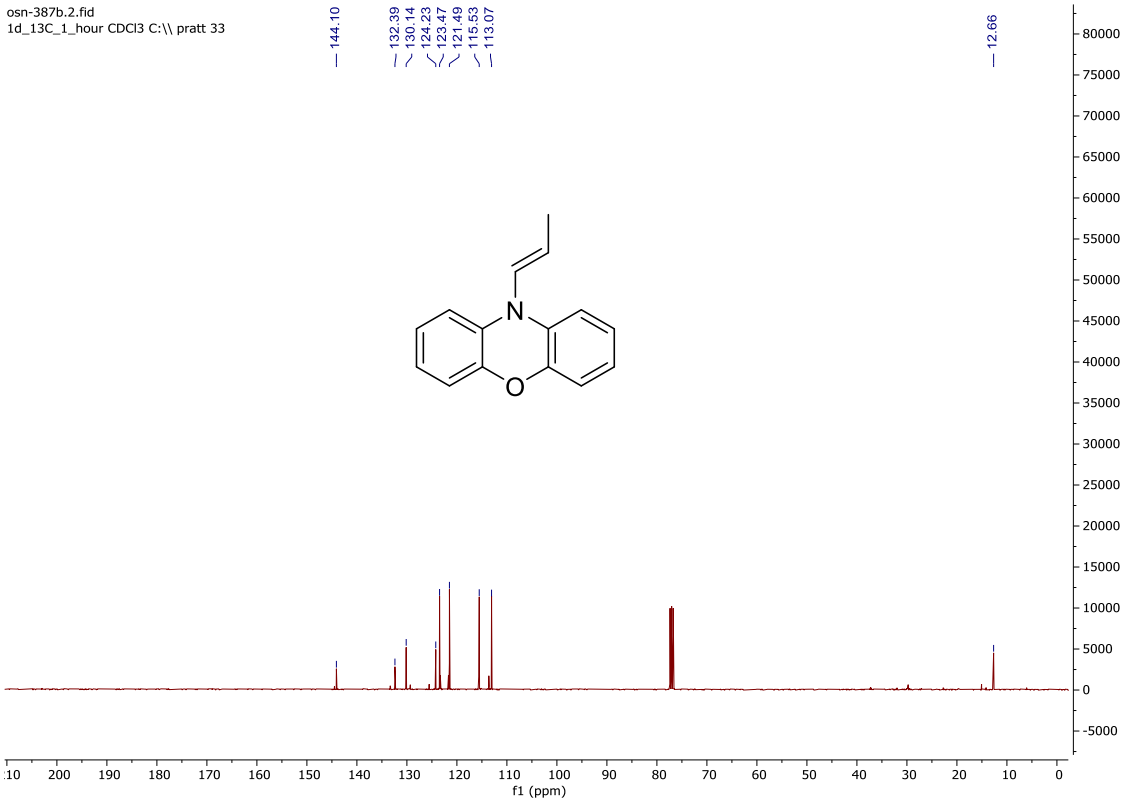
^{13}C NMR spectrum of 10-allyl-10H-phenoxazine



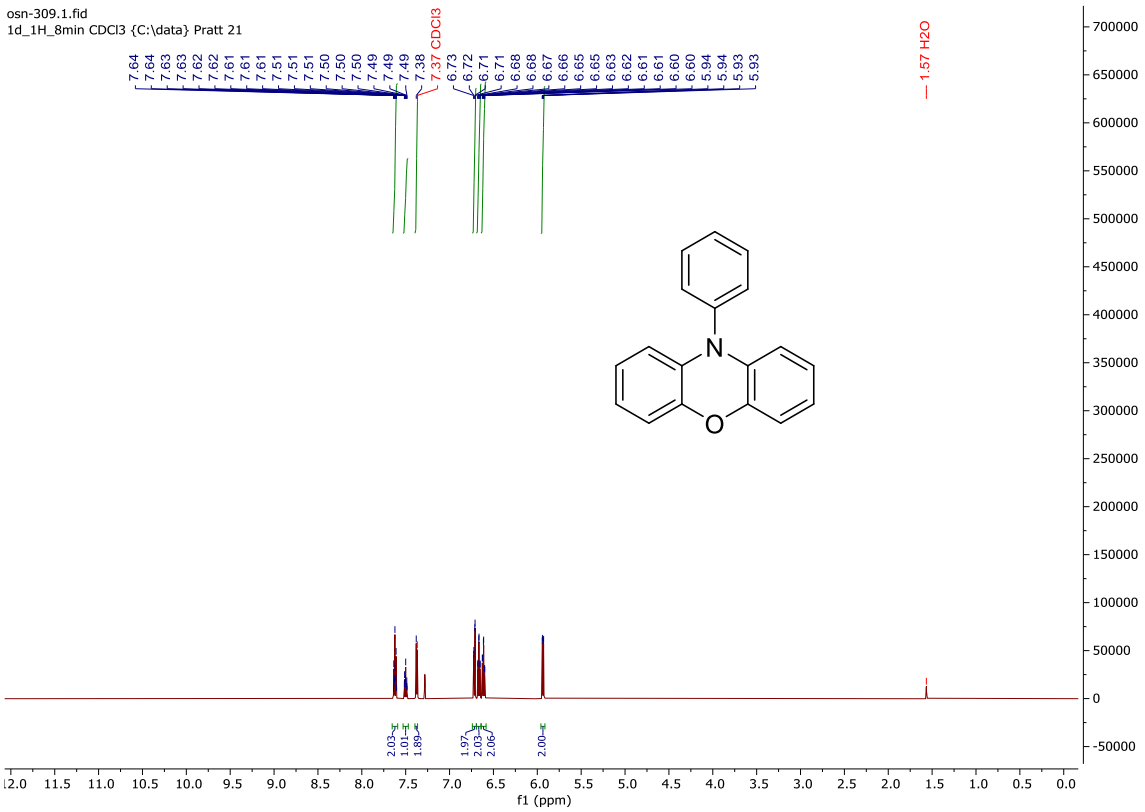
^{1}H NMR spectrum of 10-propenyl-10H-phenoxazine



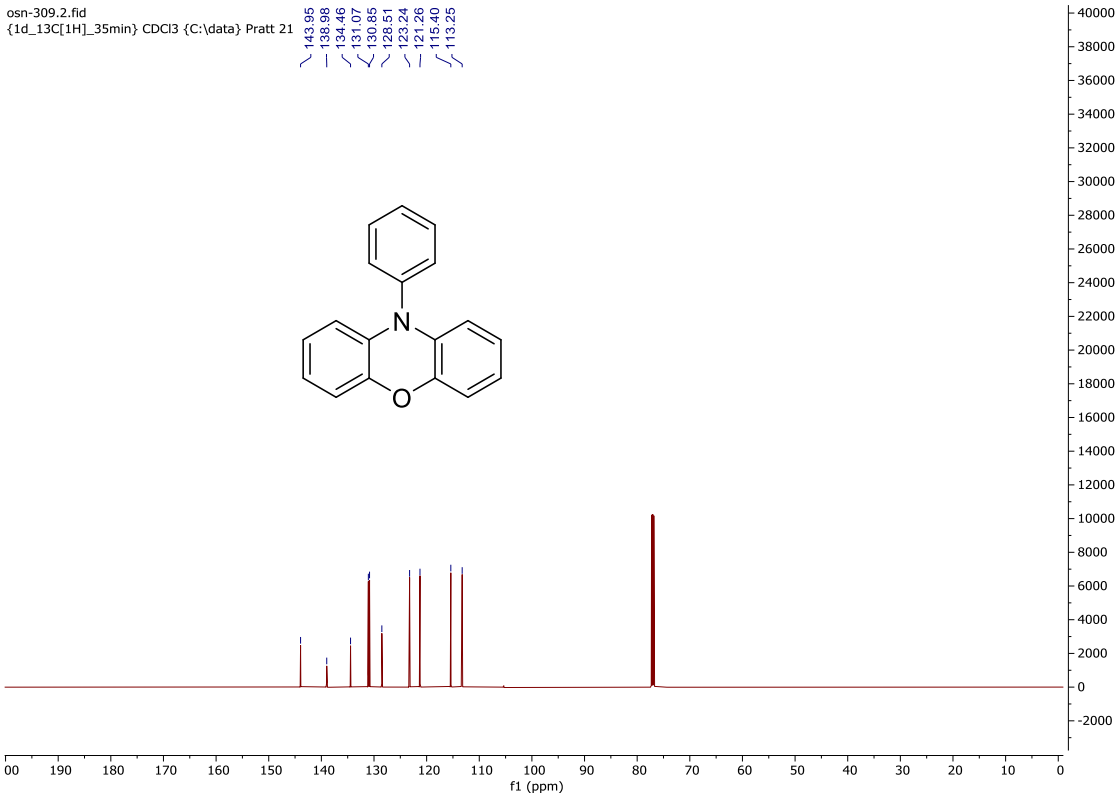
^{13}C NMR spectrum of 10-propenyl-10H-phenoxazine



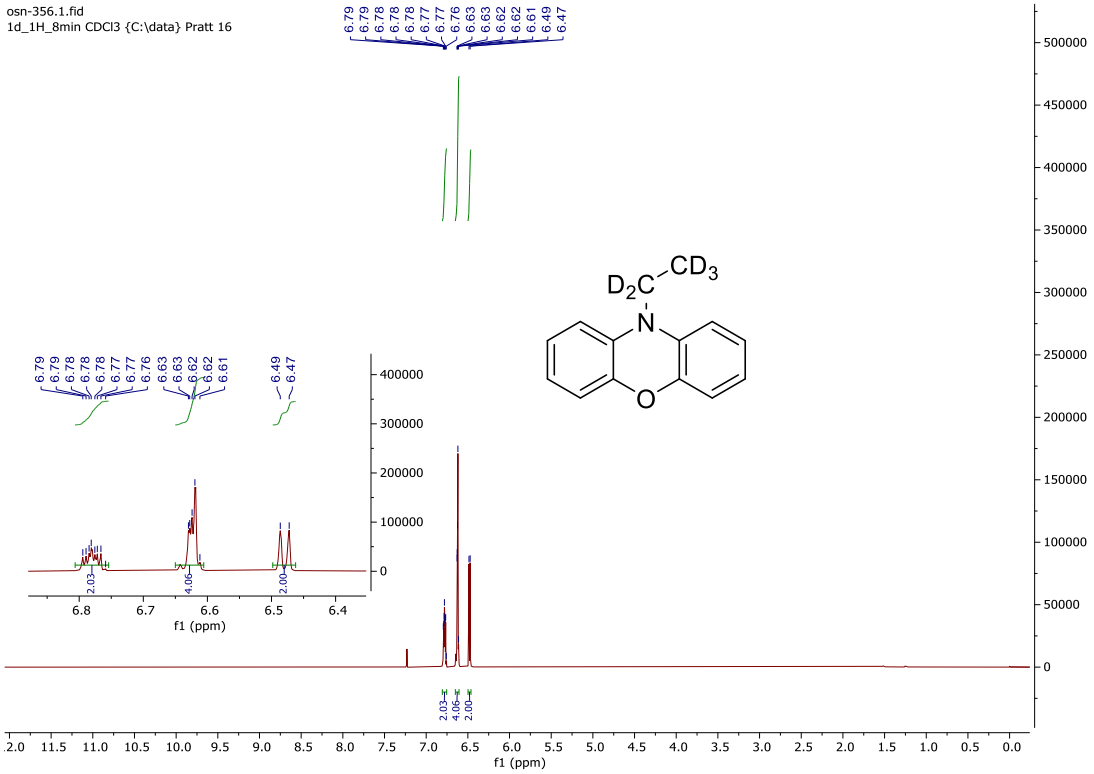
^{1}H NMR spectrum of 10-phenyl-10H-phenoxazine



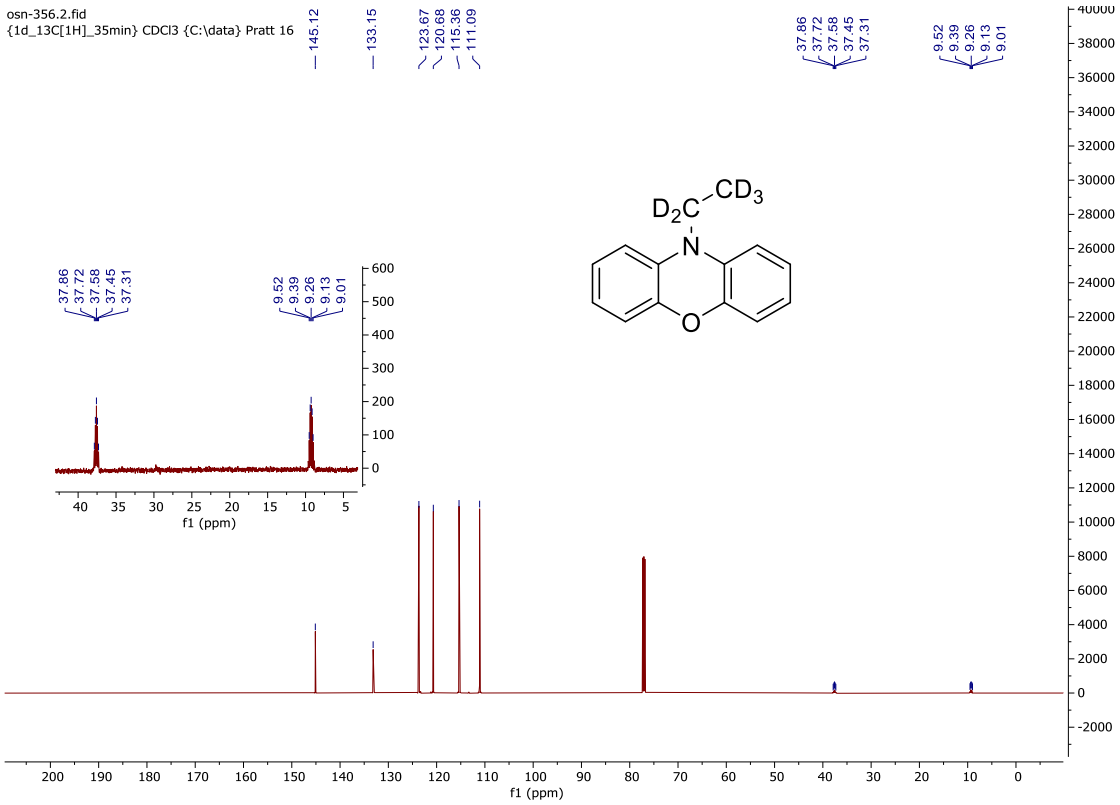
^{13}C NMR spectrum of 10-phenyl-10H-phenoxazine



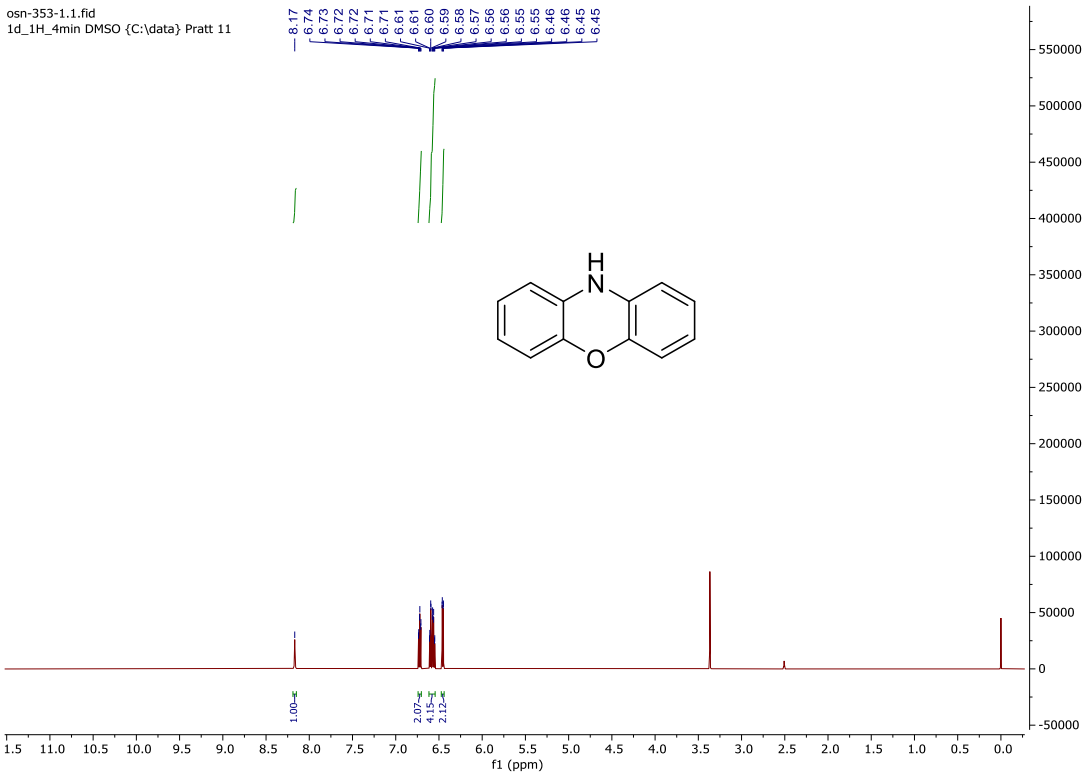
^{1}H NMR spectrum of deuterated 10-ethyl-10H-phenoxazine



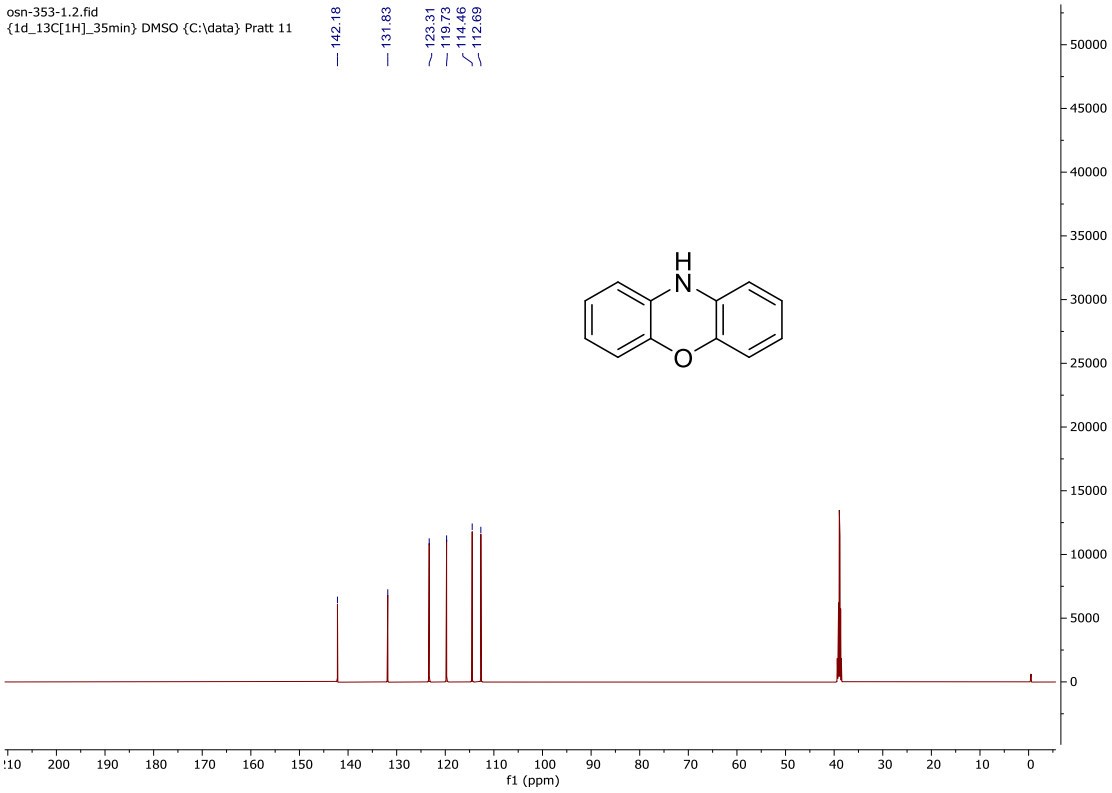
^{13}C NMR spectrum of deuterated 10-ethyl-10H-phenoxazine



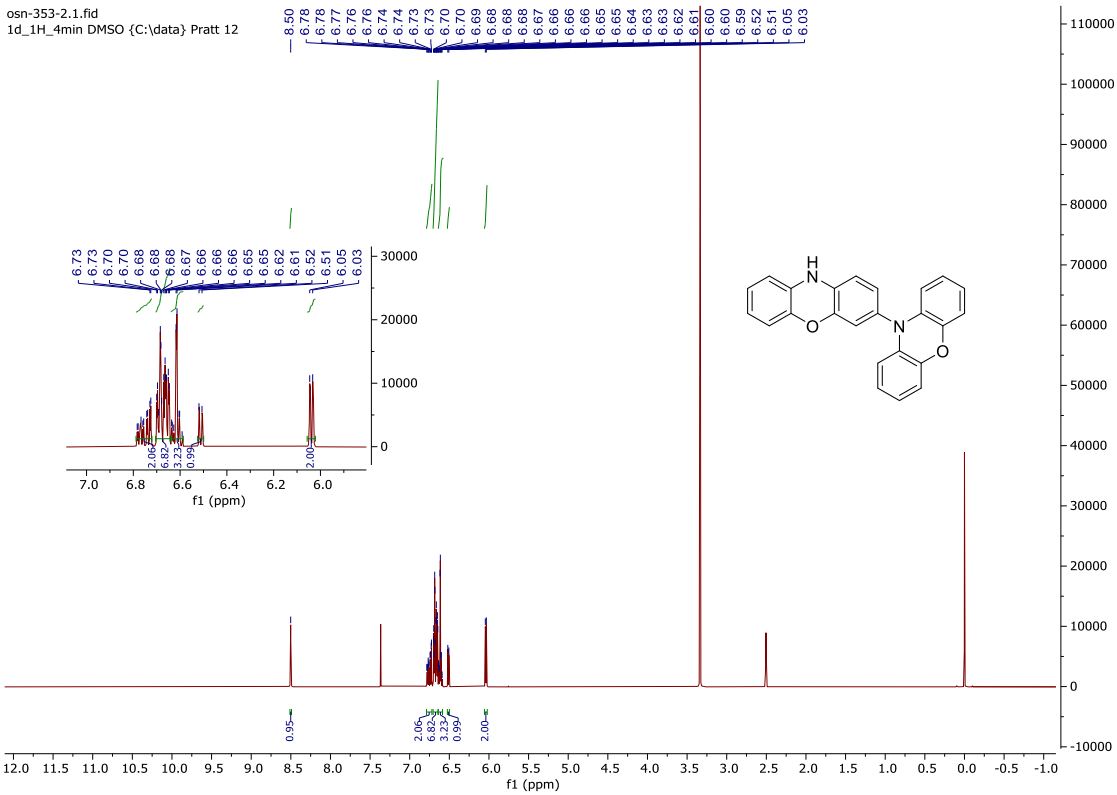
^{1}H NMR spectrum of phenoxazine



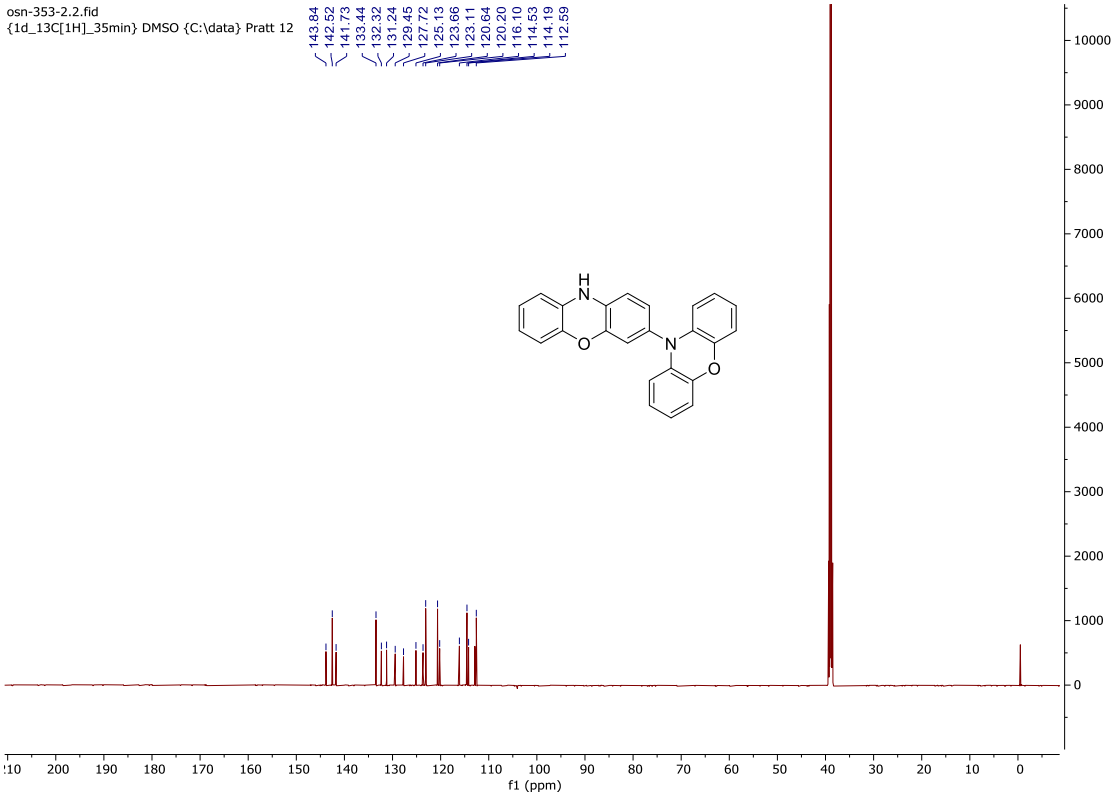
^{13}C NMR spectrum of phenoxazine



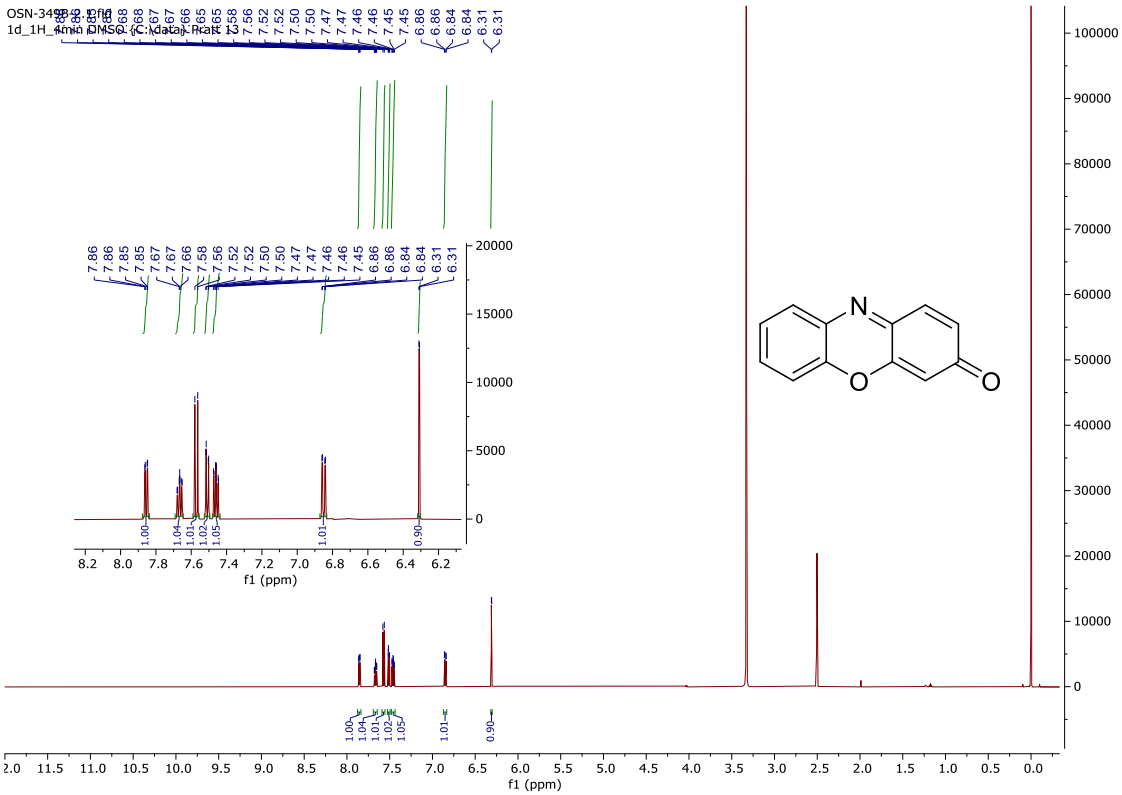
^{1}H NMR spectrum of phenoxazine dimer



^{13}C NMR spectrum of phenoxazine dimer



^{1}H NMR spectrum of 3H-phenoxazin-3-one



^{13}C NMR spectrum of 3H-phenoxazin-3-one