Supplementary Information for

Simple Efficient Syntheses of 2-Hydroxy-3*H*-phenoxazin-3-ones in Water by Aerobic Oxidative Cross-Cyclocondensations

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Contents

(A) General Remarks

All starting materials and catalysts were purchased from commercial sources and used without further treatment unless noted.

High Performance Liquid Chromatography was conducted using a WATERS 1525 LC system with UV detector and a Symmetry C18 5μm column (4.8×250 mm).

^{1}H NMR and ^{13}C NMR spectra were recorded on 600 MHz or 400 MHz BRUKER spectrometers. The used abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad).

High resolution mass spectra (HRMS) data were measured on a AB SCIEX TripleTOF 6600 or a Thermo Fisher Scientific Q Exactive Focus Mass spectrometer by means of the positive or negative ESI modes.

The single crystal diffraction was performed on the RIGAKU Gemini E X-ray single crystal diffractometor.

The melting points were determined by an X-4 micro-melting point apparatus (Beijing, China).

The pH values were determined by a REX PHS-3C pH meter of Shanghai Rex Instrument Factory.

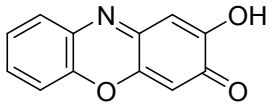
A KQ3200E ultrasonic cleaner of Kunshan Ultrasonic Instrument Co., Ltd. was used in all ultrasonication.

(B) Typical experimental procedure

General Typical Procedure for the Aerobic Oxidative Corss-Cyclocondensation

The catalytic reactions were performed in a 150-mL autoclave and the general procedure is described typically with corss-cyclocondensation of **1a** and **2a** as follows: 2-aminophenol (1.0 mmol), 2-hydroxylphenol (1.0 mmol) and H_2O (50 mL) are added into 250-mL beaker, and treated by ultrasound sonication in an ultrasonic cleaner. After sonication, the resulted clear solution and 0.5 mL solution of **GA** (0.25 mol%) and $Mn(OAc)_2$ (0.25 mol%) are transferred into the autoclave, and then is adjusted pH to 10 by NaOH solution under stirring. After the reactor closed, the atmosphere over the mixture is changed with O_2 for three times. The reactor was heated to 25 °C under stirring under 0.3 MPa for the desired reaction time. When the pressure dropped down below 0.2 MPa, O_2 was recharged up to 0.3 MPa. As soon as the pressure stops falling stirring is stoped. The ending reaction mixture was acidized with HCl solution to pH 1-2, and centrifugated. The solid cake was washed with water for three times. The pure product **3a** was obtained by recrystallization of the dried solid cake with ethanol-H_2O (v:v = 1:1).

(C) Characterization Data of the Products 3a-z



2-hydroxy-3*H*-phenoxazin-3-one (3a)

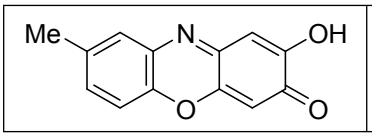
Color and State: orange solid; mp: 262 °C (decomp.) (lit[1] 264 °C (decomp.); lit[2] 264 °C; lit[3] ＞240 °C).

^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.84 (s, 1H), 7.80 (d, J = 7.6 Hz, 1H), 7.61-7.53 (m, 2H), 7.47-7.43 (m, 1H), 6.69 (s, 1H), 6.43 (s, 1H).

^{13}C NMR (100 MHz, DMSO-d_6) δ: 180.7, 156.2, 149.5, 149.1, 143.0, 133.6, 131.5, 129.4, 126.0, 116.6, 107.2, 104.7.

HRMS (ESI, $[M+H]^+$) calcd for $C_{12}H_8NO_3$ 214.0499, found 214.0498.

HRMS (ESI, $[M-H]^-$) calcd for $C_{12}H_6NO_3$ 212.0353, found 212.0347.



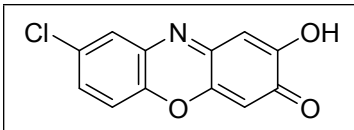
2-hydroxy-8-methyl-3*H*-phenoxazin-3-one (3b)

Color and State: brownish red solid; mp: 264 °C (decomp.)

^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.78 (s, 1H), 7.62 (s, 1H), 7.46-7.40 (m, 2H), 6.69 (s,1H), 6.42(s, 1H), 2.41(s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ: 180.6, 156.1, 149.4, 149.2, 141.1, 135.5, 133.4, 132.5, 129.0, 116.3, 107.2, 104.4, 20.8.

HRMS (ESI, $[M+H]^+$) calcd for $C_{13}H_{10}NO_3$ 228.0655, found 228.0655.



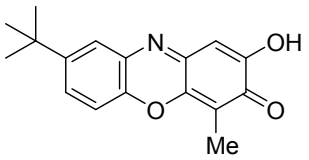
8-chloro-2-hydroxy-3*H*-phenoxazin-3-one (3c)

Color and State: brownish yellow solid; mp: 264 °C (decomp.)

^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.03 (s, 1H), 7.87 (s, 1H), 7.63-7.57 (m, 2H), 6.69 (s, 1H), 6.45 (s, 1H).

^{13}C NMR (100 MHz, DMSO-d_6) δ: No useful spectrum was obtained due to the poor solubility of **4c** in DMSO or CD_3OD.

HRMS (ESI, $[M+H]^+$) calcd for $C_{12}H_7ClNO_3$ 248.0109, found 248.0109.



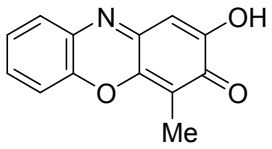
8-(*tert*-butyl)-2-hydroxy-4-methyl-3*H*-phenoxazin-3-one (3d)

Color and State: orange solid; mp: 183-184 °C

^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.70 (s, 1H), 7.72 (s, 1H), 7.60 (s, J = 8.3 Hz, 1H), 7.49 (d, J = 8.4 Hz, 1H), 6.55 (s, 1H), 2.08 (s, 3H), 1.35 (s, 9H).

^{13}C NMR (125 MHz, DMSO-d_6) δ: 180.4, 155.4, 149.2, 148.4, 145.1, 141.4, 133.0, 128.7, 125.5. 116.1, 112.6, 106.3, 34.8, 31.5, 8.1.

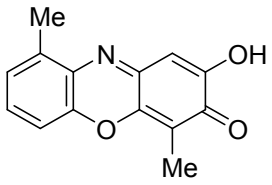
HRMS (ESI, $[M+H]^+$) calcd for $C_{17}H_{18}NO_3$ 284.1281, found 284.1278.

	**2-hydroxy-4-methyl-3*H*-phenoxazin-3-one (3e)** *Color and State*: orange solid; mp: 243-244 °C (lit[2] 244-246 °C)

^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.69 (s, 1H), 7.77 (d, J = 7.2 Hz, 1H), 7.56-7.54 (m, 2H), 7.42 (d, J = 7.2, 1H), 6.62 (s, 1H), 2.07 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ: 180.5, 155.5, 149.3, 144.9, 143.4, 133.4, 131.2, 129.2, 125.7, 116.6, 112.8, 106.3, 8.1.

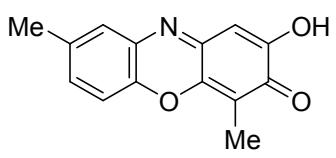
HRMS (ESI, $[M+H]^+$) calcd for $C_{13}H_{10}NO_3$ 228.0655, found 228.0656.

	**2-hydroxy-4,9-dimethyl-3*H*-phenoxazin-3-one (3f)** *Color and State*: orange solid; mp: 222 °C (decomp.)

^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.63 (s, 1H), 7.47-7.44 (m, 1H), 7.37 (d, J = 8.4 Hz, 1H), 7.29 (d, J = 7.2 Hz, 1H), 6.64 (s, 1H), 2.60 (s, 3H), 2.08 (s, 3H).

^{13}C NMR (125 MHz, DMSO-d_6) δ: 180.4, 155.4, 148.0, 144.8, 143.5, 137.9, 132.0, 130.7, 126.5, 114.2, 112.4, 106.5, 17.0, 8.0.

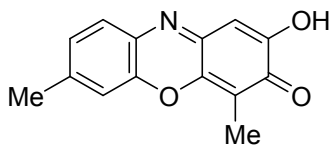
HRMS (ESI, $[M+H]^+$) calcd for $C_{14}H_{12}NO_3$ 242.0812, found 242.0814.

	**2-hydroxy-4,8-dimethyl-3*H*-phenoxazin-3-one (3g)** *Color and State*: orange solid; mp: 272 °C (decomp.)

^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.66 (s, 1H), 7.60 (s, 1H), 7.47 (d, J = 8.3 Hz, 1H), 7.40-7.38 (m, 1H), 6.63 (s, 1H), 2.41 (s, 3H), 2.08 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ: No useful spectrum was obtained due to the poor solubility of **4g** in DMSO or CD_3OD.

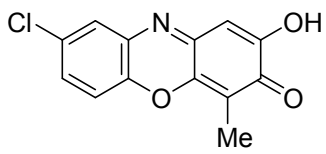
HRMS (ESI, $[M+H]^+$) calcd for $C_{14}H_{12}NO_3$ 242.0812, found 241.0812.

	**2-hydroxy-4,7-dimethyl-3*H*-phenoxazin-3-one (3h)** *Color and State*: orange solid; mp: 243 °C (decomp.)

^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.56 (s, 1H), 7.64 (d, J = 7.8 Hz, 1H), 7.37 (s, 1H) 7.23 (d, J = 7.8 Hz, 1H), 6.59 (s, 1H), 2.44 (s, 3H), 2.06 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ: No useful spectrum was obtained due to the poor solubility of **4h** in DMSO or CD_3OD.

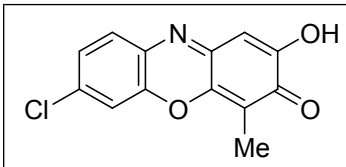
HRMS (ESI, $[M+H]^+$) calcd for $C_{14}H_{12}NO_3$ 242.0812, found 242.0812.

	**8-chloro-2-hydroxy-4-methyl-3*H*-phenoxazin-3-one (3i)** *Color and State*: orange red solid; mp: 260 °C (decomp.)

^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.90 (s, 1H), 7.80 (s, 1H), 7.57 (s, 2H), 6.60 (s, 1H), 2.06 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ: No useful spectrum was obtained due to the poor solubility of **4i** in DMSO or CD_3OD.

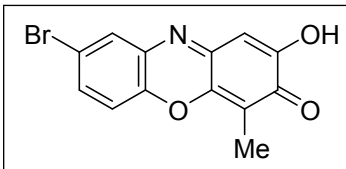
HRMS (ESI, $[M+H]^+$) calcd for $C_{13}H_9ClNO_3$ 262.0265, found 262.0264.

	**7-chloro-2-hydroxy-4-methyl-3*H*-phenoxazin-3-one (3j)** *Color and State*: orange yellow solid; mp: 224 °C (decomp.)

^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.80 (s, 1H), 7.75 (d, J = 8.5, 1H), 7.72 (s, 1H), 7.45 (d, J = 8.4, 1H), 6.60 (s, 1H), 2.06 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ: 180.7, 156.1, 149.4, 144.5, 143.7, 134.4, 132.3, 130.1, 125.9, 116.7, 113.3, 106.2, 8.1.

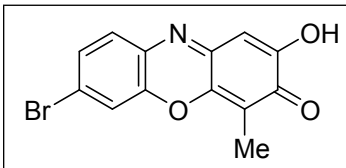
HRMS (ESI, $[M+H]^+$) calcd for $C_{13}H_9ClNO_3$ 262.0265, found 262.0264.

	**8-bromo-2-hydroxy-4-methyl-3*H*-phenoxazin-3-one (3k)** *Color and State*: orange red solid; mp: 237 °C (decomp.)

^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.90 (s, 1H), 7.93 (s, 1H), 7.69 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 7.52 (d, J = 8.8 Hz, 1H), 6.59(s, 1H), 2.07 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ: No useful spectrum was obtained due to the poor solubility of **4k** in DMSO or CD_3OD.

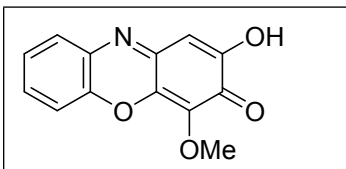
HRMS (ESI, $[M+H]^+$) calcd for $C_{13}H_9BrNO_3$ 305.9760, found 305.9754.

	**7-bromo-2-hydroxy-4-methyl-3*H*-phenoxazin-3-one (3l)** *Color and State*: orange-yellow solid; mp: 249 °C (decomp.)

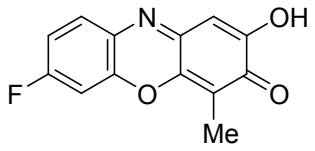
^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.83 (s, 1H), 7.85-7.66 (m, 2H), 7.58-7.43 (m, 1H), 6.60 (s, 1H), 2.06 (s, 3H).

^{13}C NMR (100 MHz, *DMSO-d*$_6$) δ: No useful spectrum was obtained due to the poor solubility of **4l** in DMSO or CD_3OD.

HRMS (ESI, $[M+H]^+$) calcd for $C_{13}H_9BrNO_3$ 305.9760, found 305.9754.

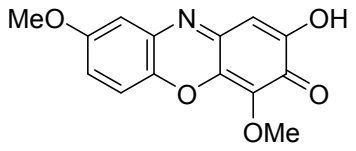
	**2-hydroxy-4-methoxy-3*H*-phenoxazin-3-one (3m)** *Color and State*: red solid; mp: 207 °C (decomp.)

^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.89 (s, 1H), 7.78 (d, J = 6.3 Hz, 1H), 7.60-7.57 (m, 2H), 7.43 (t, 1H), 6.62 (s, 1H), 3.91 (s, 3H).
^{13}C NMR (125 MHz, DMSO-d_6) δ: 176.8, 156.0, 148.8, 142.9, 138.0, 135.4, 133.4, 131.2, 129.0, 125.8, 116.6, 105.4, 60.5.
HRMS (ESI, $[M+H]^+$) calcd for $C_{13}H_{10}NO_4$ 244.0604, found 244.0604.



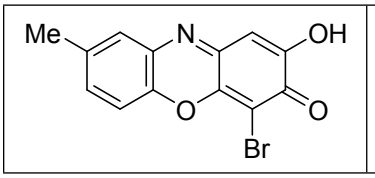
7-fluoro-2-hydroxy-4-methyl-3*H*-phenoxazin-3-one (3n)
Color and State: brown solid; mp: 222 °C (decomp.)

^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.71 (s, 1H), 7.79-7.76 (m, 1H), 7.49 (dd, J_1 = 9.2 Hz, J_2 = 2.4 Hz, 1H), 7.26 (m, 1H), 6.56 (s, 1H), 2.03 (s, 3H)
^{13}C NMR (100 MHz, DMSO-d_6) δ: No useful spectrum was obtained due to the poor solubility of **4n** in DMSO or CD_3OD.
HRMS (ESI, $[M+H]^+$) calcd for $C_{13}H_9FNO_3$ 246.0561, found 246.0562.



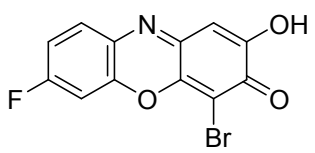
2-hydroxy-4,8-dimethoxy-3*H*-phenoxazin-3-one (3o)
Color and State: red solid; mp: 183 °C (decomp.)

^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.89 (s, 1H), 7.55 (d, J = 9.0 Hz, 1H), 7.32 (s, 1H), 7.18 (d, J = 7.7, 1H), 6.60 (s, 1H), 3.89 (s, 3H), 3.85 (s, 3H).
^{13}C NMR (125 MHz, DMSO-d_6) δ: 176.3, 156.8, 156.0, 148.8, 138.2, 137.2, 135.2, 133.9, 118.9, 117.2, 111.1, 105.1, 60.4, 56.2.
HRMS (ESI, $[M+H]^+$) calcd for $C_{14}H_{12}NO_5$ 274.0710, found 274.0714.



4-bromo-2-hydroxy-8-methyl-3*H*-phenoxazin-3-one (3p)
Color and State: orange-yellow solid; mp: 265°C (decomp.)

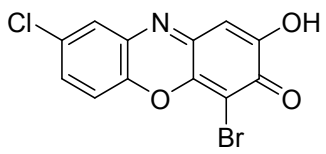
^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.55 (s, 1H), 7.74 (s, 1H), 7.52-7.46 (m, 2H), 6.46 (s, 1H), 2.43 (s, 3H)
^{13}C NMR (100 MHz, DMSO-d_6) δ: No useful spectrum was obtained due to the poor solubility of **4p** in DMSO or CD_3OD.
HRMS (ESI, $[M+H]^+$) calcd for $C_{13}H_9BrNO_3$ 305.9760, found 305.9763.



4-bromo-7-fluoro-2-hydroxy-3*H*-phenoxazin-3-one (3q)
Color and State: brown solid; mp: 253 °C (decomp.)

^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.60 (s, 1H), 7.97 (dd, J_1 = 8.9 Hz, J_2 = 6.1 Hz, 1H), 7.60 (dd, J_1 = 9.1 Hz, J_2 = 2.6 Hz, 1H), 7.37(m, 1H), 6.49 (s, 1H).
^{13}C NMR (125 MHz, DMSO-d_6) δ: 178.1, 164.1, 162.5, 154.5, 149.4, 144.9, 144.0, 143.9, 131.5, 130.4, 114.0, 103.9.

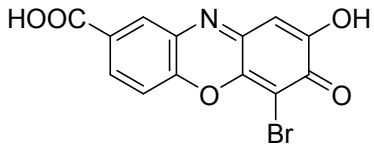
HRMS (ESI, $[M+H]^+$) calcd for $C_{12}H_6BrFNO_3$ 309.9510, found 309.9514.

	**4-bromo-8-chloro-2-hydroxy-3H-phenoxazin-3-one (3r)** *Color and State*: brownish yellow solid; mp: 275 °C (decomp.)

^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.79 (s, 1H), 7.96 (d, J = 2.0 Hz, 1H), 7.65-7.61 (m, 2H), 6.49 (s, 1H).

^{13}C NMR (100 MHz, DMSO-d_6) δ: No useful spectrum was obtained due to the poor solubility of **4r** in DMSO or CD_3OD.

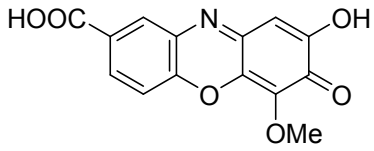
HRMS (ESI, $[M+H]^+$) calcd for $C_{12}H_6BrClNO_3$ 325.9214, found 325.9214.

	**4-bromo-2-hydroxy-3-oxo-3*H*-phenoxazine-8-carboxylic acid (3s)** *Color and State*: yellow solid; mp: ＞300 °C

^{1}H NMR (600 MHz, DMSO-d_6) δ: 13.29 (s, 1H), 11.73 (s, 1H), 8.31 (s, 1H), 8.10 (d, J = 5.8 Hz, 1H), 7.64 (d, J = 8.5 Hz, 1H), 6.52 (s, 1H).

^{13}C NMR (125 MHz, DMSO-d_6) δ: No useful spectrum was obtained due to the poor solubility of **4s** in DMSO or CD_3OD.

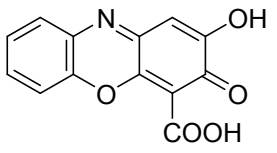
HRMS (ESI, $[M+H]^+$) calcd for $C_{13}H_7BrNO_5$ 335.9502, found 335.9502.

	**2-hydroxy-4-methoxy-3-oxo-3*H*-phenoxazine-8-carboxylic acid (3t)** *Color and State*: orange yellow solid; mp: 251°C (decomp.)

^{1}H NMR (600 MHz, DMSO-d_6) δ: 13.20 (s, 1H), 11.06 (s, 1H), 8.21 (s, 1H), 8.05 (d, J = 7.0 Hz, 1H), 7.65 (d, J = 8.5 Hz, 1H), 6.63 (s, 1H), 3.92 (s, 3H).

^{13}C NMR (125 MHz, DMSO-d_6) δ: 177.0, 166.6, 155.7, 150.0, 145.9, 137.5, 135.6, 133.4, 131.7, 130.2, 128.1, 117.0, 105.7, 60.6.

HRMS (ESI, $[M+H]^+$) calcd for $C_{14}H_{10}NO_6$ 288.0503, found 288.0499.

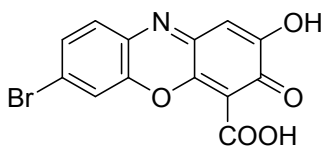
	**2-hydroxy-3-oxo-3*H*-phenoxazine-4-carboxylic acid (3u)** *Color and State*: brown solid; mp: 275 °C (decomp.)

^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.10 (s, 1H), 8.62 (s, 1H), 7.27 (d, J = 7.9 Hz, 1H), 7.02 (t, J_1 = 7.9 Hz, J_2 = 7.5 Hz, 1H), 6.94 (d, J = 7.9 Hz, 1H), 6.85 (t, J_1 = 7.7 Hz, J_2 = 7.6 Hz, 1H), 5.67 (s, 1H).

^{13}C NMR (125 MHz, DMSO-d_6) δ: 181.4, 176.8, 176.1, 150.3, 148.2, 126.4, 125.9, 122.9, 119.9, 119.0, 116.3, 98.2, 87.3.

HRMS (ESI, $[M-H]^-$) calcd for $C_{13}H_6NO_5$ 256.0251, found 256.0439; (ESI, $[M-2H]^{-\bullet}$) calcd

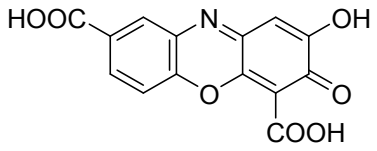
for $C_{13}H_5NO_5$ 255.0179, found 255.0408.

	**7-bromo-2-hydroxy-3-oxo-3*H*-phenoxazine-4-carboxylic acid (3v)** *Color and State*: red solid; mp: 262 °C (decomp.)

^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.67 (s, 1H), 8.64 (s, 1H), 7.23 (d, J = 8.5 Hz, 1H), 7.09 (d, J = 1.9 Hz, 1H), 7.02 (dd, J_1 = 8.4 Hz, J_2 = 1.9 Hz, 1H), 5.62 (s, 1H).

^{13}C NMR (125 MHz, DMSO-d_6) δ: 181.6, 176.7, 176.0, 151.6, 148.1, 125.4, 124.5, 122.4, 118.91, 118.85, 117.8, 98.6, 87.3.

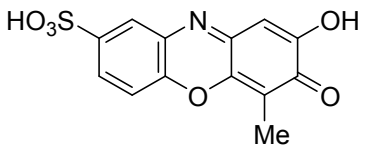
HRMS (ESI, [M－H]$^-$) calcd for $C_{13}H_5BrNO_5$ 333.9357, found 333.9550; (ESI, [M-2H]$^{-\bullet}$) calcd for $C_{13}H_4BrNO_5$ 332.9284, found 332.9516.

	**2-hydroxy-3-oxo-3*H*-phenoxazine-4,8-dicarboxylic acid (3w)** *Color and State*: black solid; mp: ＞300 °C.

^{1}H NMR (600 MHz, DMSO-d_6) δ: 12.67 (s, 1H), 11.19 (s, 1H), 8.71 (s, 1H), 7.79 (d, J = 1.6 Hz, 1H), 7.65 (dd, J_1 = 8.5 Hz, J_2 = 1.7 Hz, 1H), 7.08 (d, J = 8.4 Hz, 1H), 5.64 (s, 1H).

^{13}C NMR (125 MHz, DMSO-d_6) δ: 181.6, 176.6, 176.0, 167.2, 154.7, 148.3, 128.2, 125.7, 124.0, 122.1, 118.9, 116.1, 98.4, 87.3.

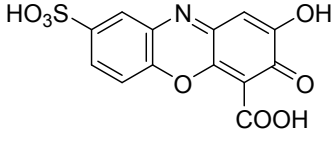
HRMS (ESI, [M－H]$^-$) calcd for $C_{14}H_6NO_7$ 300.0150, found 300.0339; (ESI, [M-2H]$^{-\bullet}$) calcd for $C_{14}H_5NO_7$ 299.0077, found 299.0307.

	**2-hydroxy-4-methyl-3-oxo-3*H*-phenoxazine-8-sulfonic acid (3x)** *Color and State*: yellow solid; mp: ＞300 °C.

^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.80 (s, 1H), 7.91 (s, 1H), 7.76 (d, J = 7.6 Hz, 1H), 7.51 (d, J = 8.3 Hz, 1H), 6.68 (s, 1H), 2.08 (s, 3H).

^{13}C NMR (125 MHz, DMSO-d_6) δ: 180.6, 155.6, 149.7, 145.4, 144.9, 143.4, 132.5, 128.6, 126.0, 116.1, 113.1, 106.4, 8.1.

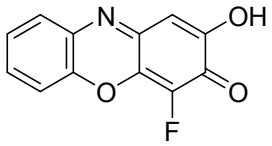
HRMS (ESI, [M+H]$^+$) calcd for $C_{13}H_{10}NO_6S$ 308.0223, found 308.0223.

	**2-hydroxy-3-oxo-8-sulfo-3*H*-phenoxazine-4-carboxylic acid (3y)** *Color and State*: red solid; mp: ＞300 °C.

^{1}H NMR (600 MHz, DMSO-d_6) δ: 10.61 (s, 1H), 8.74 (s, 1H), 7.50 (s, 1H), 7.29 (d, J = 8.4 Hz, 1H), 6.98 (d, J = 8.4 Hz, 1H), 5.68 (s, 1H).

^{13}C NMR (125 MHz, DMSO-d_6) δ: 181.5, 176.9, 176.1, 150.8, 148.4, 139.7, 124.6, 124.1, 120.3, 118.8, 115.3, 98.0, 87.3.

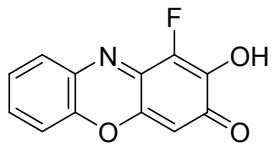
HRMS (ESI, [M－H]$^-$) calcd for $C_{13}H_6NO_8S$ 335.9820, found 336.0015; (ESI, [M-2H]$^{-\bullet}$) calcd for $C_{13}H_5NO_8S$ 334.9747, found 334.9978.

	**4-fluoro-2-hydroxy-3*H*-phenoxazin-3-one (3z-4)** *Color and State*: orange solid; mp: 235 ^{o}C (decomp.)

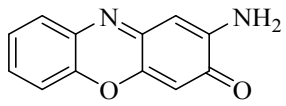
^{1}H NMR (600 MHz, DMSO-d_6) δ: 11.36 (s, 1H), 7.81 (d, J = 7.3 Hz, 1H), 7.66-7.56 (m, 1H), 7.48 (d, J = 5.4 Hz, 1H), 6.67 (s, 1H).

^{13}C NMR (125 MHz, DMSO-d_6) δ: 127.7, 156.1, 147.5, 142.2, 140.2, 138.5, 133.6, 131.8, 129.5, 126.3, 116.7, 105.9.

HRMS (ESI, [M+H]$^+$) calcd for $C_{12}H_7NO_3$ 232.0404, found 232.0400.

	**1-fluoro-2-hydroxy-3*H*-phenoxazin-3-one (3z-1)** *Color and State*: brown solid; mp: 239 ^{o}C (decomp.)

HRMS (ESI, [M+H]$^+$) calcd for $C_{12}H_7NO_3$ 232.0404, found 232.0401.

	**2-amino-3*H*-phenoxazin-3-one (4a)** *Color and State*: Reddish brown solid; mp: 248-250 ^{o}C (lit[4] 249-250 ^{o}C; lit[5] 258 ^{o}C; lit[6] 250-252 ^{o}C; lit[7] 259 ^{o}C; lit[8] 256-258 ^{o}C; lit[9] 256-257 ^{o}C; lit[10] 254-256 ^{o}C)

^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.69 (dd, J = 7.9, 1.3 Hz, 1H), 7.50-7.43 (m, 2H), 7.40-7.36 (m, 1H), 6.82 (s, 2H), 6.35(d, J = 1.5 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d_6) δ: 180.7, 149.3, 148.7, 147.8, 142.4, 134.2, 129.2, 128.4, 125.7, 116.4, 103.9, 98.8.

HRMS (ESI, [M+H]$^+$) calcd for $C_{12}H_8N_2O_2$ 213.0659, found 213.0669.

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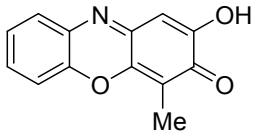
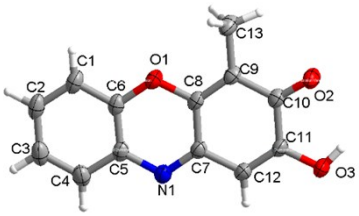
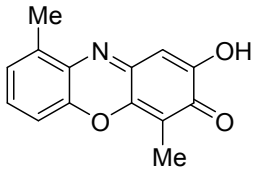
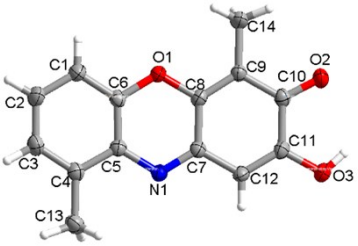
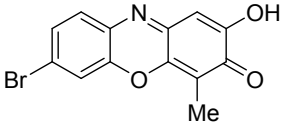
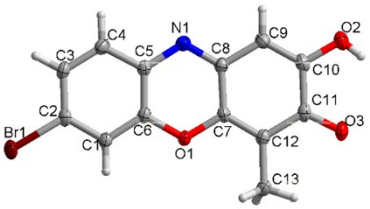
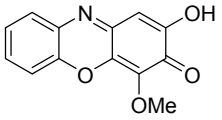
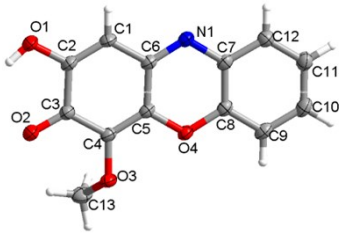
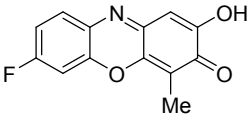
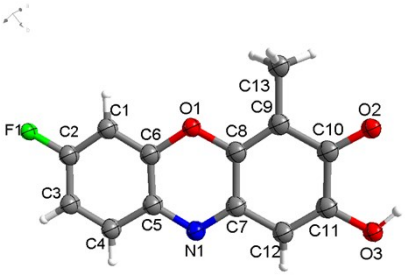
[7] M. Puiu, A. Raducan, D. Oancea, *Rev. Roum. Chim.* **2008**, *52(11)*, 1039-1044.

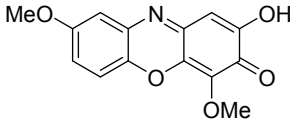
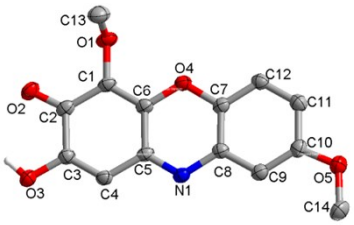
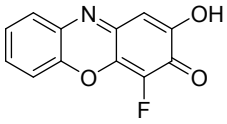
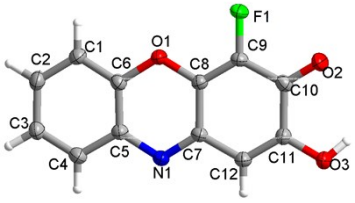
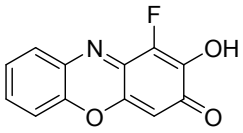
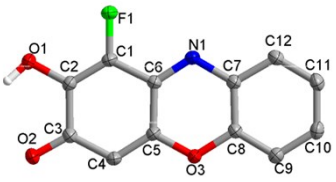
[8] M. B. Gents, S. T. Nielsen, Mortensen, G. Anne, C. Christophersen, I. S. Fomsgaard, *Chemosphere* **2005**, *61(1)*, 74-84

[9] G. W. K. Cavill, P. S. Clezy, F. B. Whitfield, *Tetrahedron* **1961**, *12*, 139-45

[10] M. R. Maurya, S. Sikarwar, T.Joseph, S. B. Halligudi, *J. Mol. Catal. A Chem.* **2005**, *236(1-2)*, 132-138

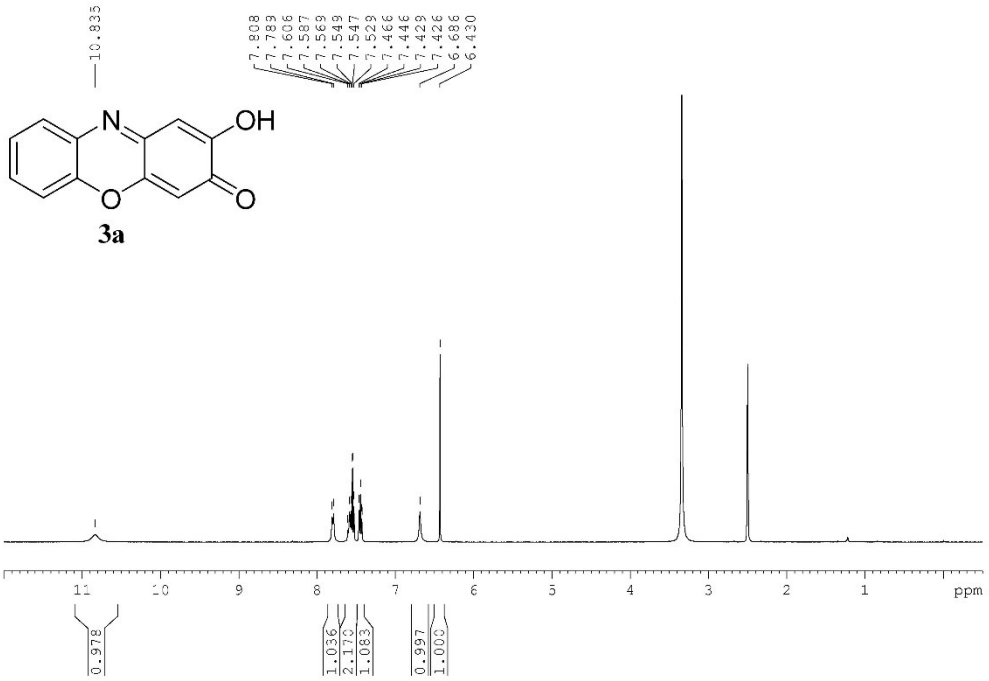
(D) Single crystal diffraction patterns of eight products

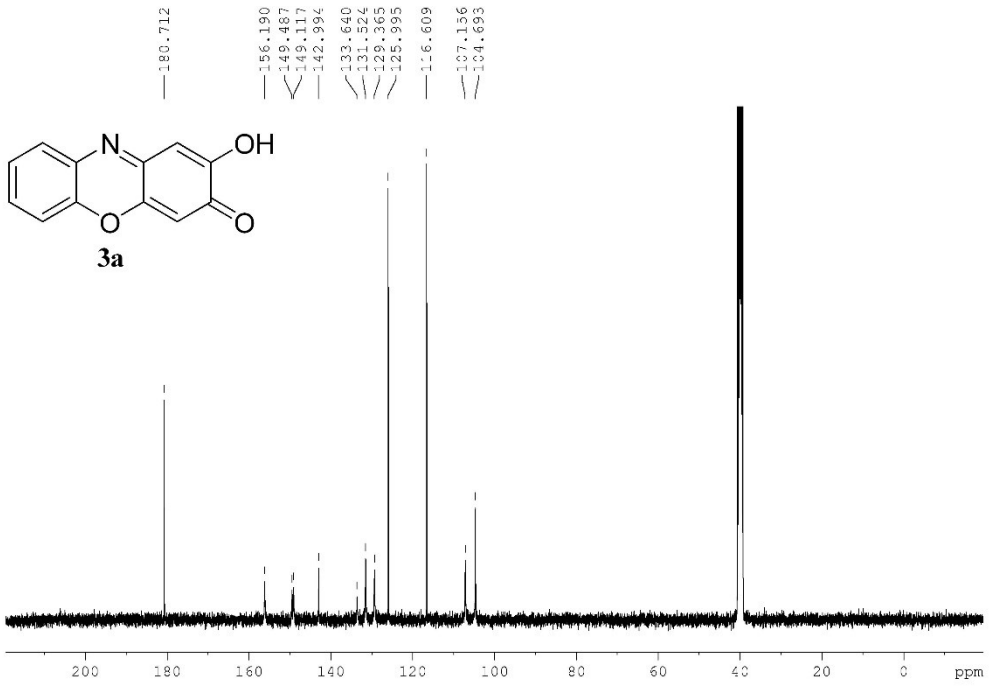
Product Number	Structure	Single crystal diffraction pattern	CCDC Number
3e			2012641
3f			2012642
3l			2012644
3m			2020212
3n			2012643

3o			2023111
3z-4			2012640
3z-1			2020211

(E) Copies of all NMR spectra

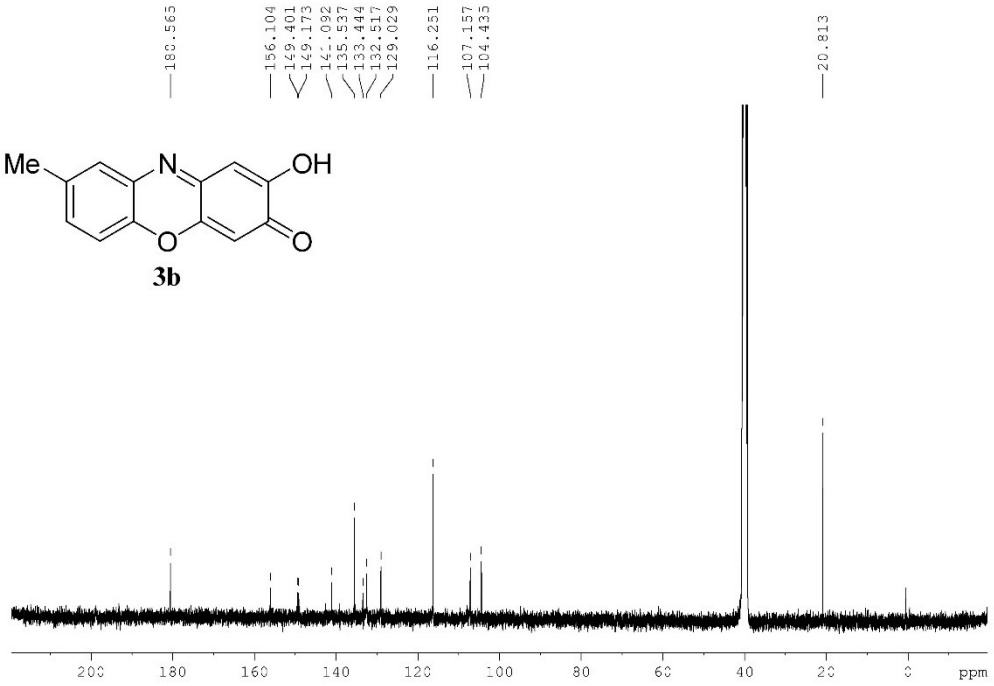
3a



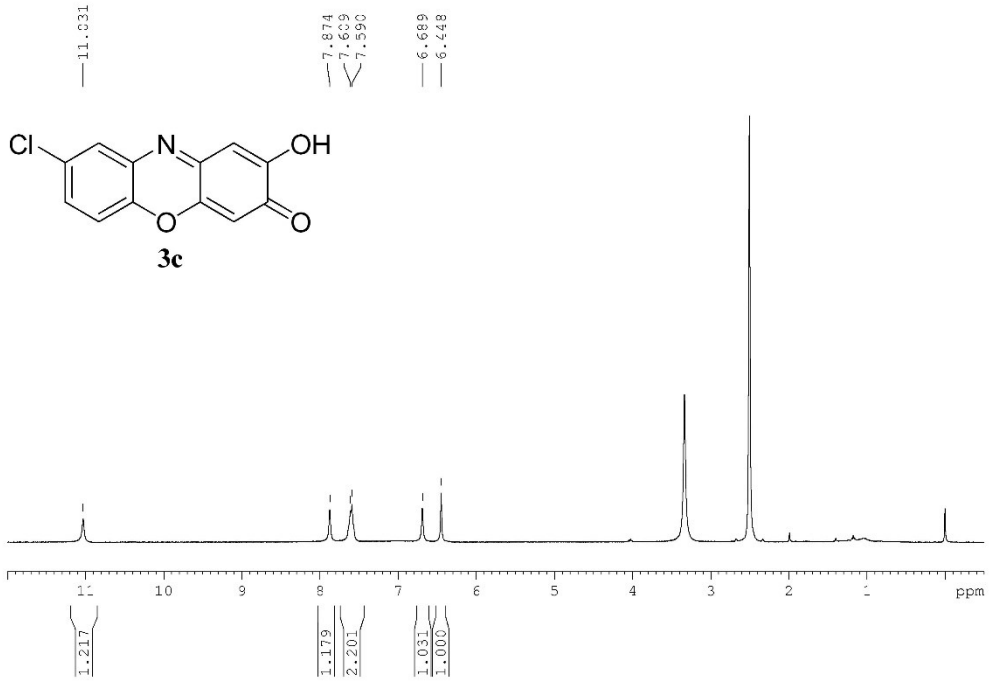


3b

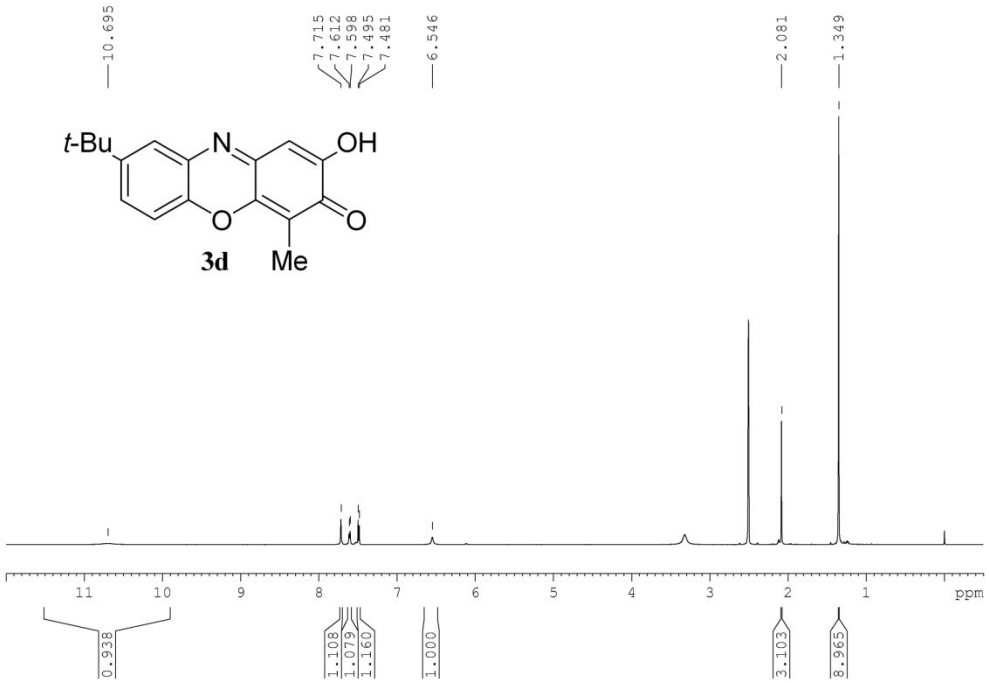

10.781
7.622
7.462
7.441
7.424
7.403
6.690
6.415
2.413
Me
N
OH
O
O
3b
ppm
0.956
0.997
2.164
1.096
1.000
3.268


180.565
156.104
149.401
149.173
140.092
135.537
133.444
132.517
129.029
116.251
107.157
104.435
20.813
Me
N
OH
O
O
3b
ppm

3c


11.931
7.874
7.669
7.590
6.689
6.448
Cl
N
OH
O
O
3c
ppm
1.217
1.179
2.201
1.031
1.000

3d


10.695
7.715
7.612
7.598
7.495
7.481
6.546
2.081
1.349
t-Bu
N
OH
O
O
3d
Me
11
10
9
8
7
6
5
4
3
2
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1.108
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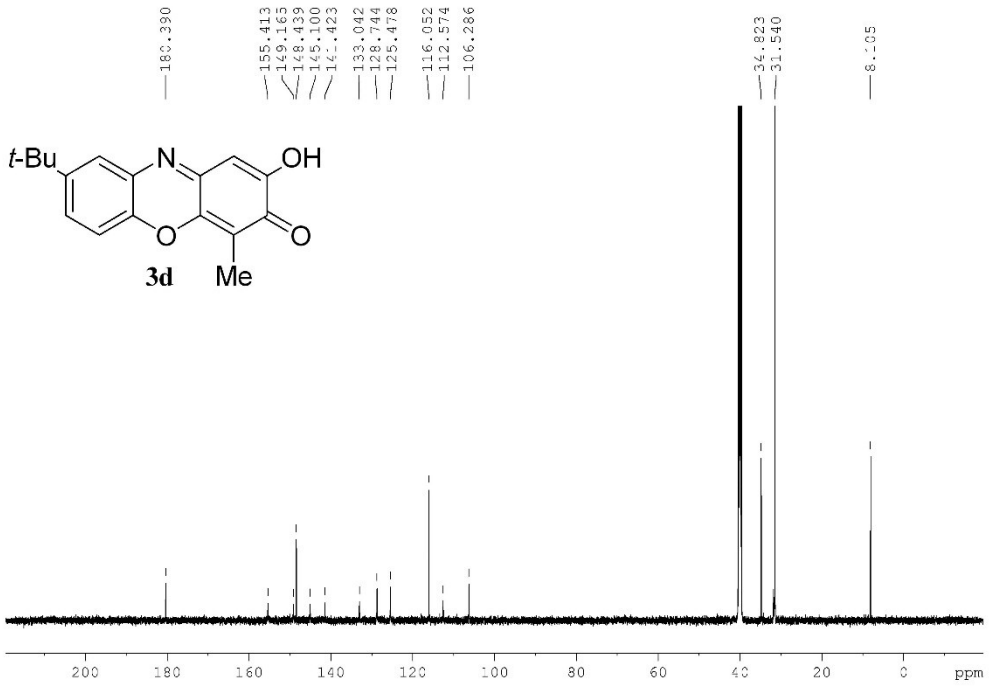
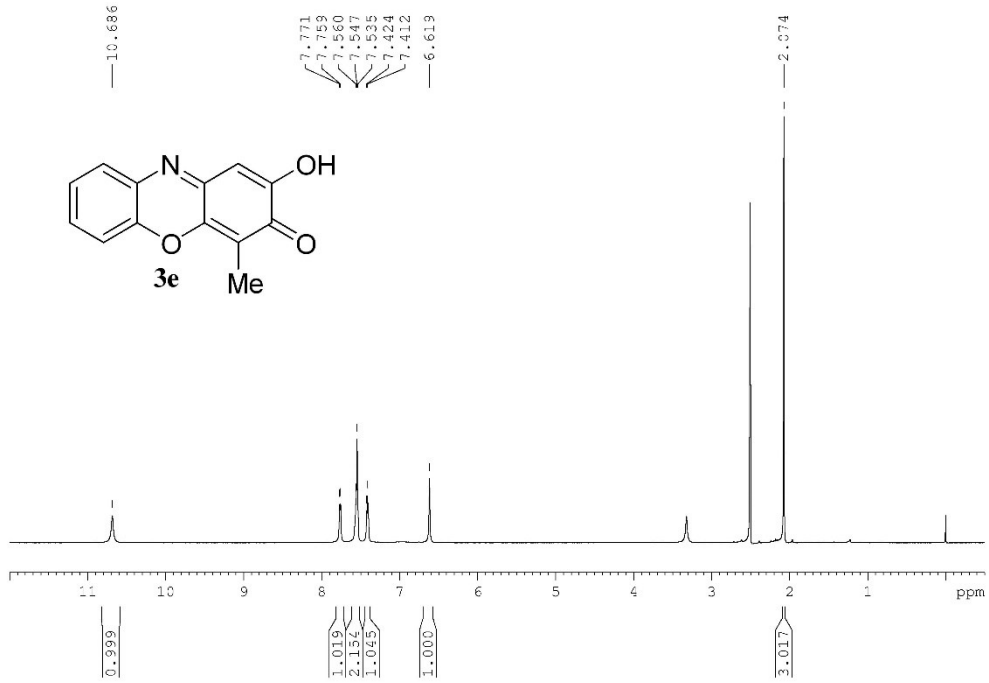
1.160
1.000
3.103
8.965


180.390
155.413
149.165
148.439
146.100
142.423
133.042
128.744
125.478
116.052
112.574
106.286
34.823
31.540
8.205
t-Bu
N
OH
O
O
3d
Me
200
180
160
140
120
100
80
60
40
20
0
ppm

3e


10.686
7.771
7.759
7.560
7.547
7.535
7.424
7.412
6.619
2.674
N
OH
O
O
3e
Me
11
10
9
8
7
6
5
4
3
2
1
ppm
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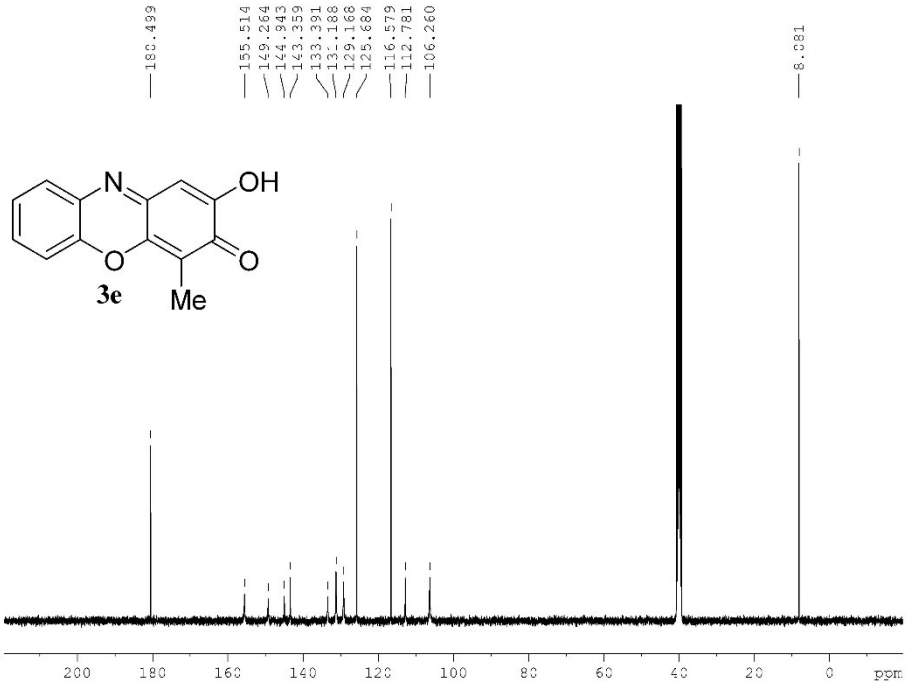
1.019
2.154
1.045
1.000
3.017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155.514
149.264
144.943
143.359
133.391
131.188
129.168
125.684
116.579
112.781
106.260
8.881
N
OH
O
O
3e
Me
200
180
160
140
120
100
80
60
40
20
0
ppm

3f


10.634
7.465
7.452
7.439
7.381
7.367
7.297
7.285
6.640
2.595
2.078
Me
N
OH
O
O
3f
Me
11
10
9
8
7
6
5
4
3
2
1
ppm
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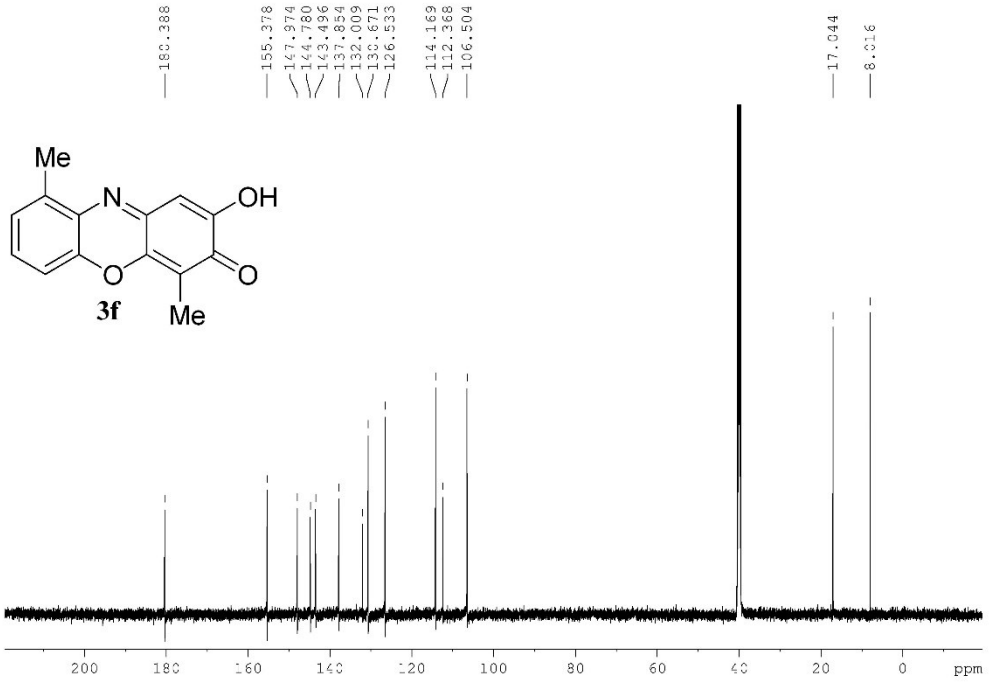
1.042
1.046
1.000
3.047
3.084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132.009
130.671
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114.169
112.368
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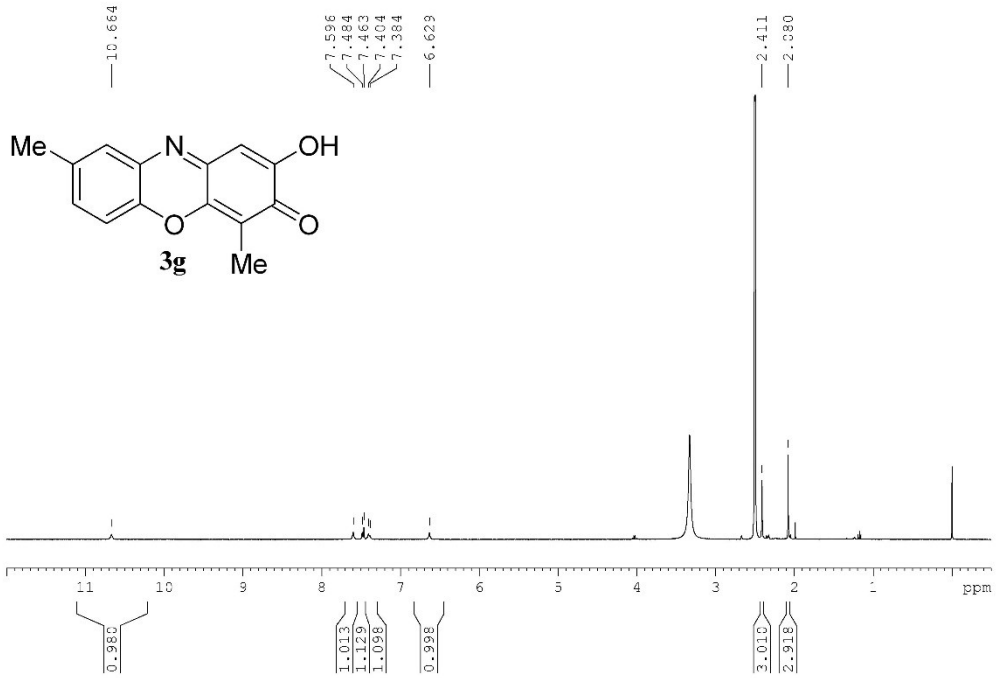
17.044
8.816
Me
N
OH
O
O
3f
Me
200
180
160
140
120
100
80
60
40
20
0
ppm

3g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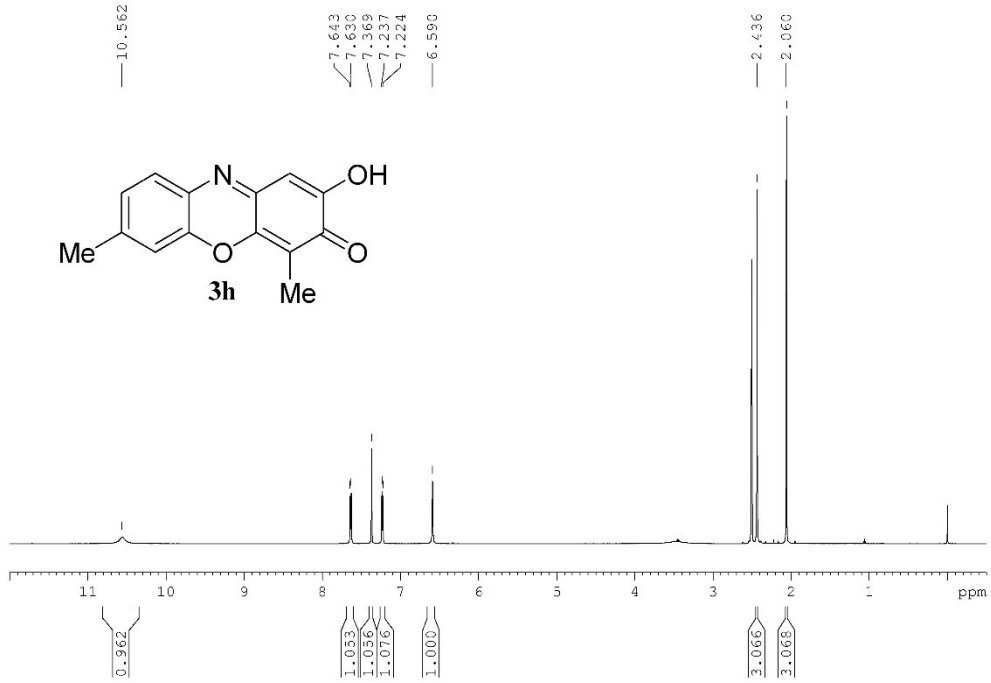
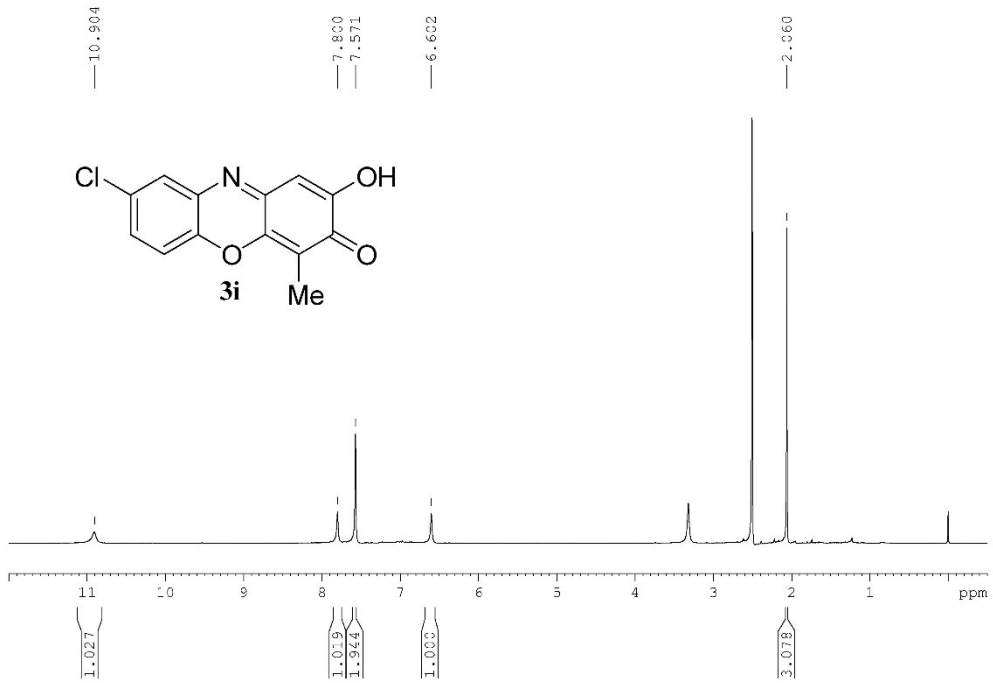
7.596
7.484
7.463
7.404
7.384
6.629
2.411
2.280
Me
N
OH
O
O
3g
Me
11
10
9
8
7
6
5
4
3
2
1
ppm
0.980
1.013
1.129
1.098
0.998
3.010
2.918

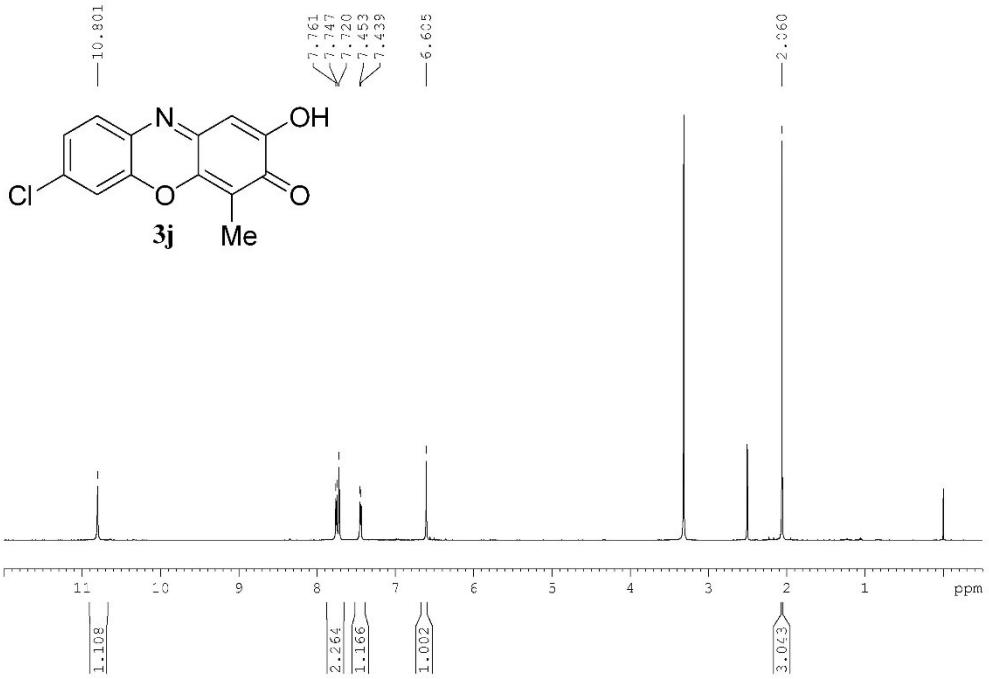
3h

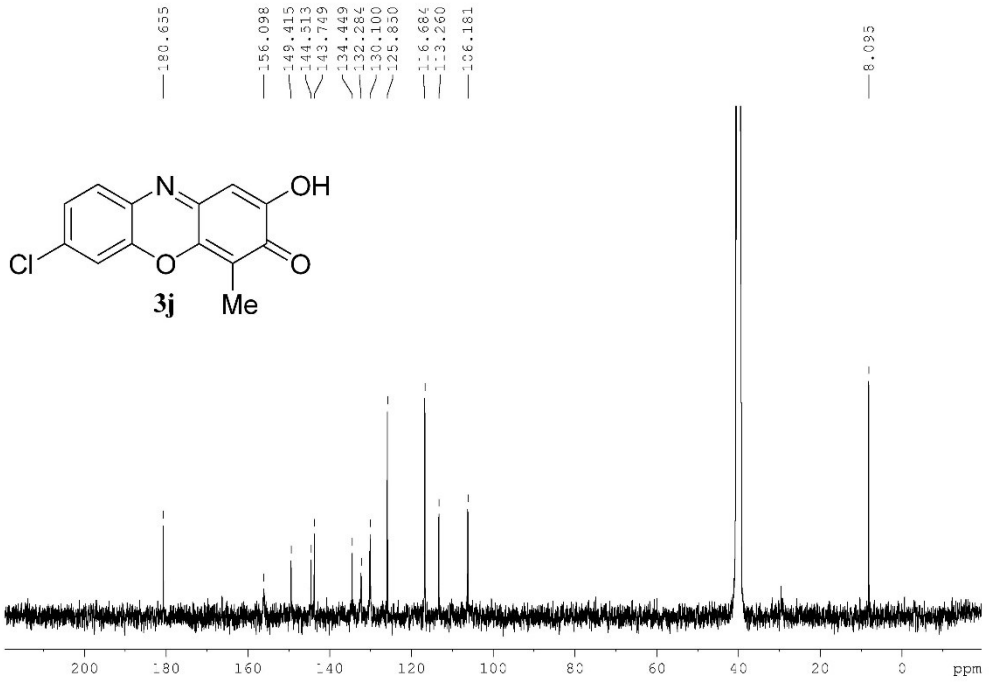

10.562
7.643
7.630
7.369
7.237
7.224
6.590
2.436
2.060
N
OH
Me
O
O
Me
3h
11
10
9
8
7
6
5
4
3
2
ppm
0.962
1.053
1.056
1.076
1.000
3.066
3.068

3i


10.904
7.830
7.571
6.632
2.960
Cl
N
OH
O
O
Me
3i
11
10
9
8
7
6
5
4
3
2
1
ppm
1.027
1.019
1.944
1.003
3.078

3j

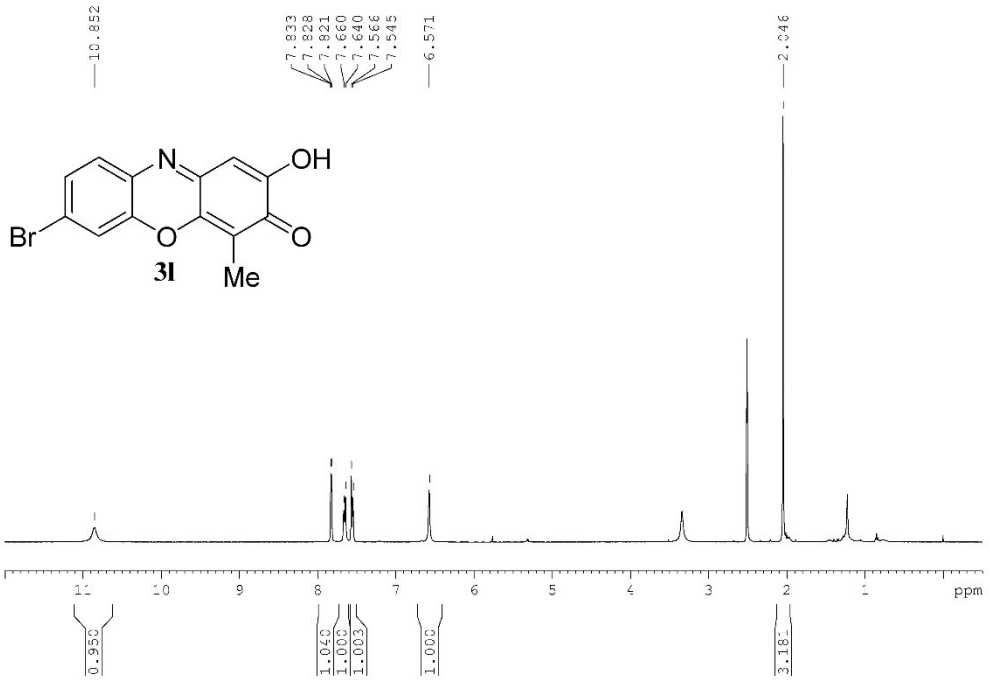

10.801
7.761
7.747
7.720
7.453
7.439
6.605
2.060
N
OH
Cl
O
O
3j
Me
11
10
9
8
7
6
5
4
3
2
1
ppm
1.108
2.264
1.166
1.002
3.043


180.655
156.098
149.415
144.513
143.749
134.449
132.284
130.100
125.830
116.684
113.260
106.181
8.095
N
OH
Cl
O
O
3j
Me
200
180
160
140
120
100
80
60
40
20
0
ppm

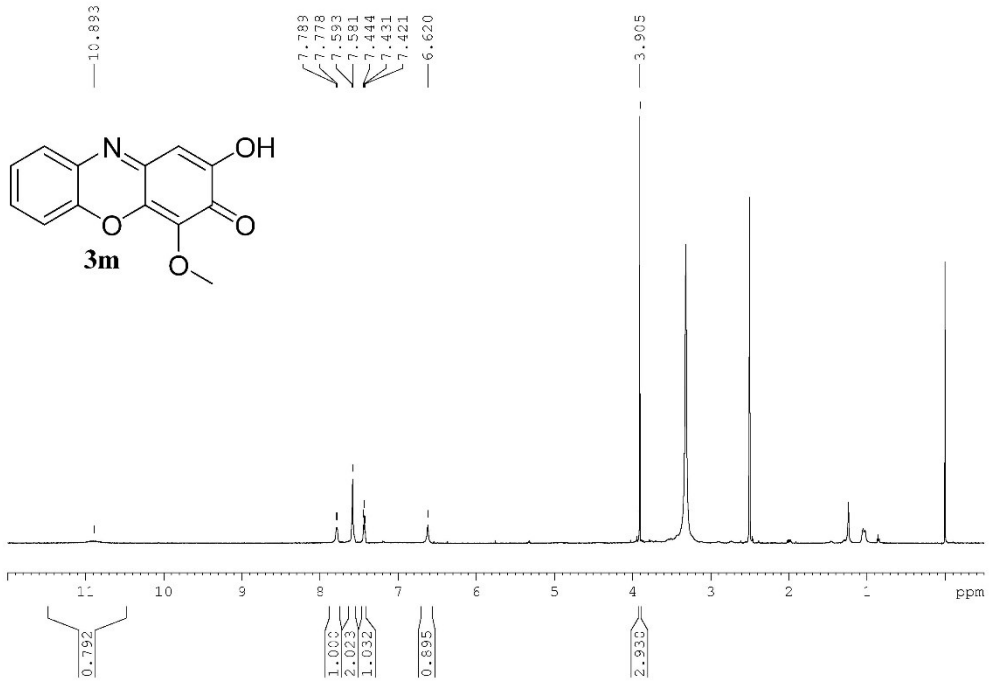
3k

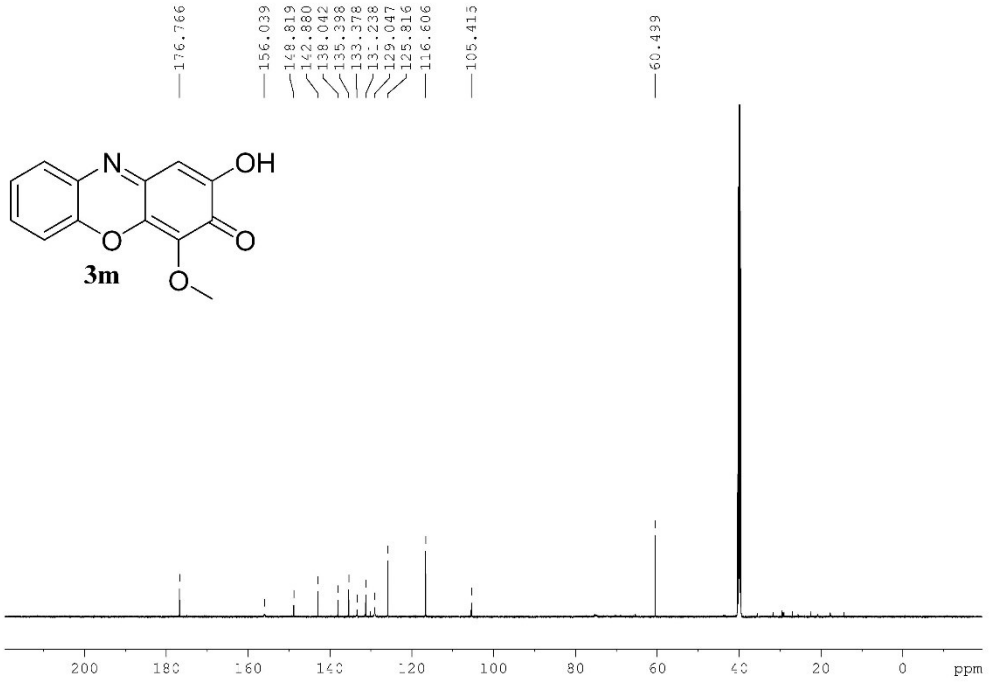

10.903
7.928
7.703
7.698
7.681
7.676
7.535
7.513
6.592
2.666
Br
N
OH
O
O
3k
Me
11
10
9
8
7
6
5
4
3
2
1
ppm
0.932
0.999
1.066
1.053
1.000
3.153

3l

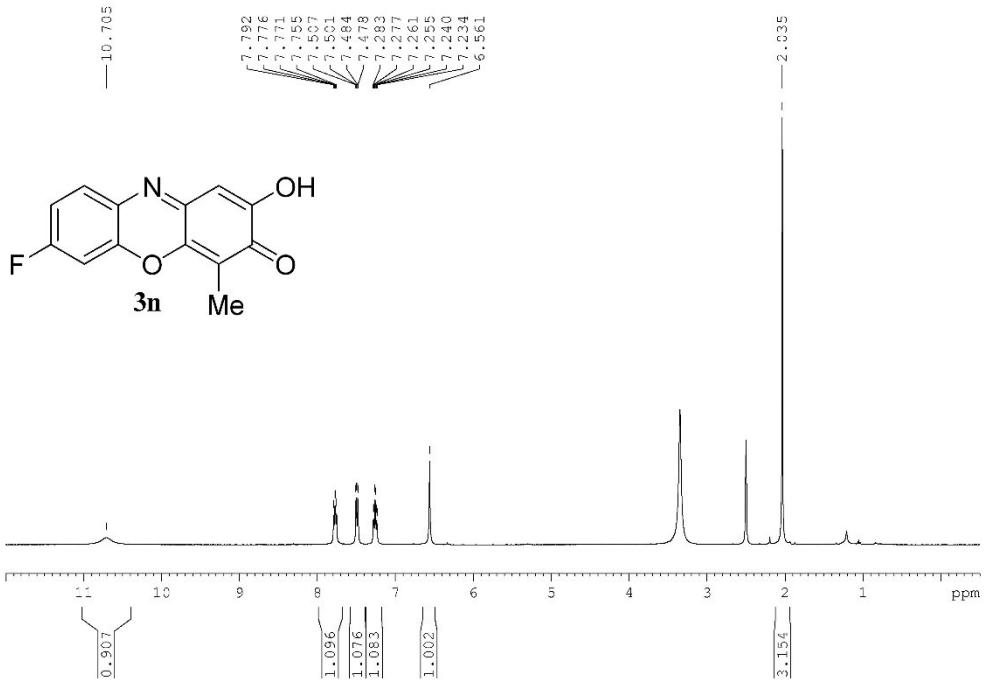

10.852
7.833
7.828
7.821
7.660
7.640
7.566
7.545
6.571
2.646
N
OH
Br
O
O
Me
3l
ppm
0.956
1.040
1.000
1.003
1.000
3.181

3m

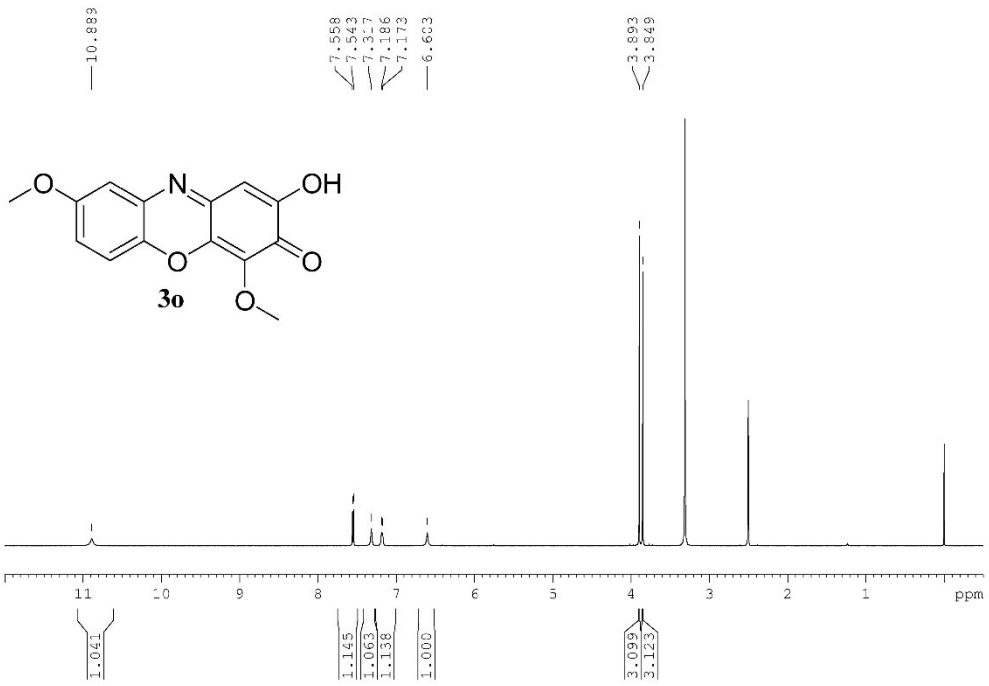

10.893
7.789
7.778
7.593
7.581
7.444
7.431
7.421
6.620
3.905
N
OH
O
O
O
3m
ppm
0.792
1.008
2.023
1.032
0.895
2.933

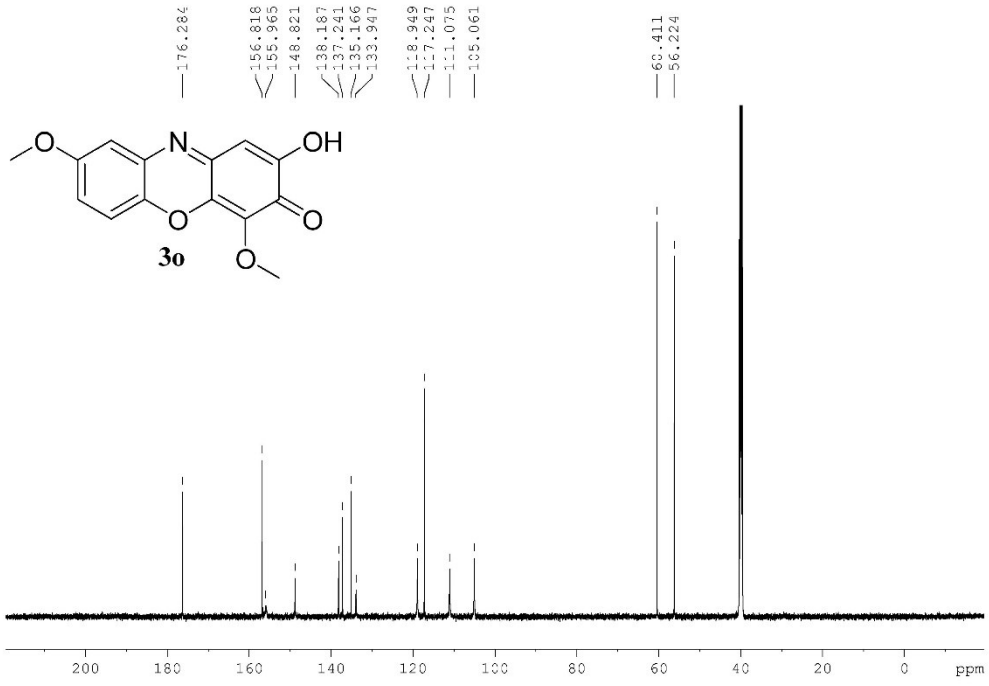

176.766
156.039
148.819
142.880
138.042
135.398
133.378
13..238
129.047
125.816
116.606
105.415
60.499
N
OH
O
O
O
3m
200
180
160
140
120
100
80
60
40
20
0
ppm

3n

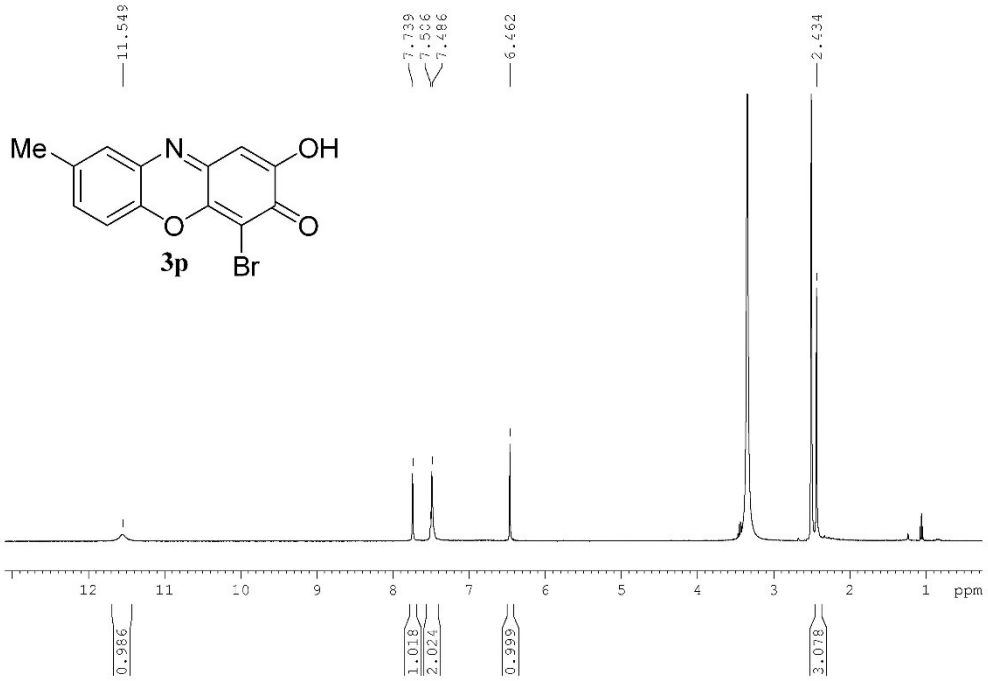

10.705
7.792
7.776
7.771
7.755
7.507
7.501
7.484
7.478
7.283
7.277
7.261
7.255
7.240
7.234
6.561
2.035
N
OH
F
O
O
3n
Me
11
10
9
8
7
6
5
4
3
2
1
ppm
0.907
1.096
1.076
1.083
1.002
3.154

3o

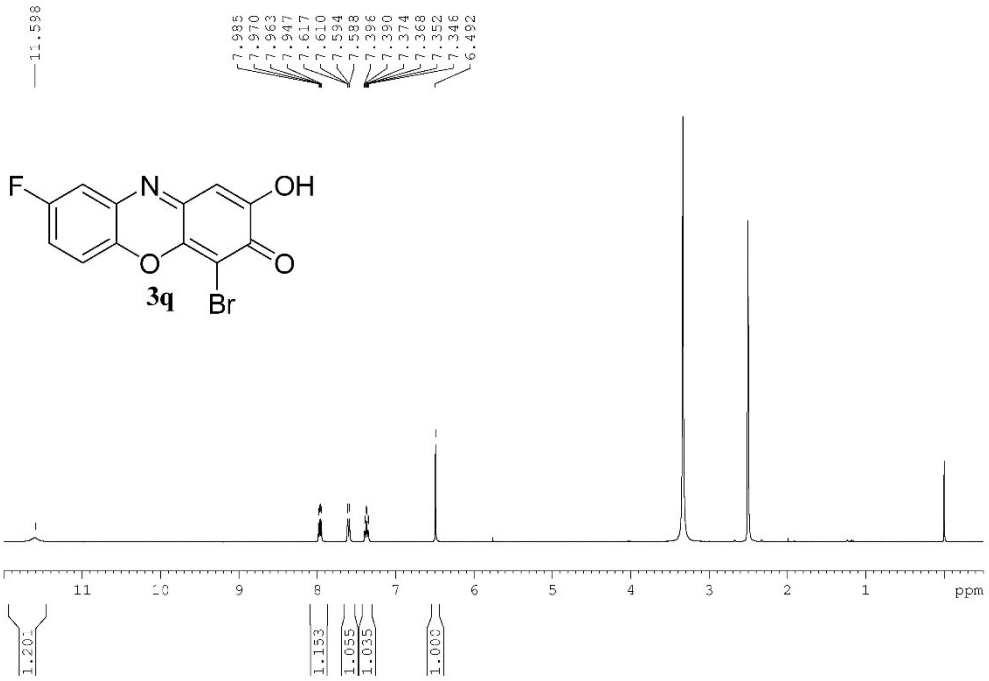

10.883
7.558
7.543
7.327
7.186
7.173
6.603
3.893
3.849
OH
O
N
O
O
O
3o
11
10
9
8
7
6
5
4
3
2
1
ppm
1.041
1.145
1.063
1.138
1.000
3.099
3.123

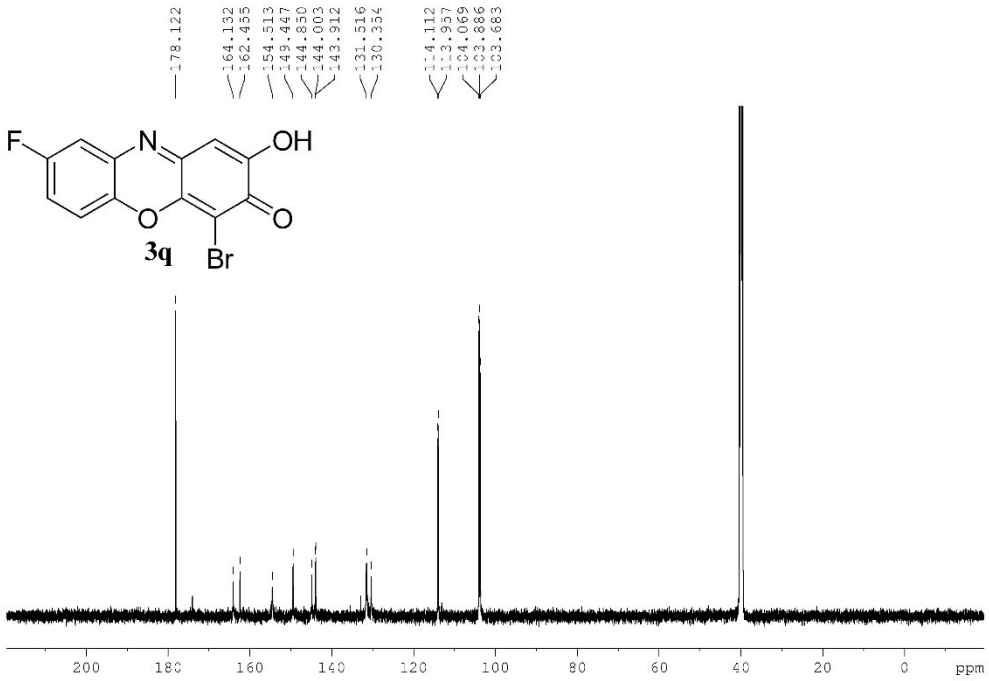

176.284
156.818
155.965
148.821
138.187
137.241
135.166
133.947
118.949
117.247
111.075
105.061
60.411
56.224
OH
O
N
O
O
O
3o
200
180
160
140
120
100
80
60
40
20
0
ppm

3p

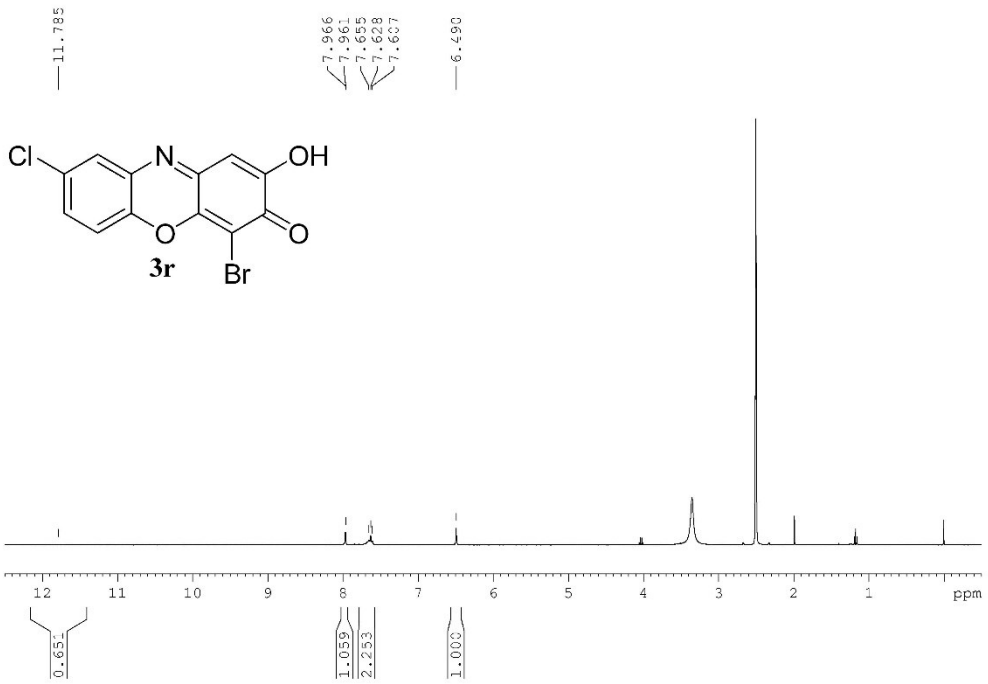

11.549
7.739
7.506
7.486
6.462
2.434
Me
N
OH
O
O
Br
3p
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.986
1.018
2.024
0.999
3.078

3q

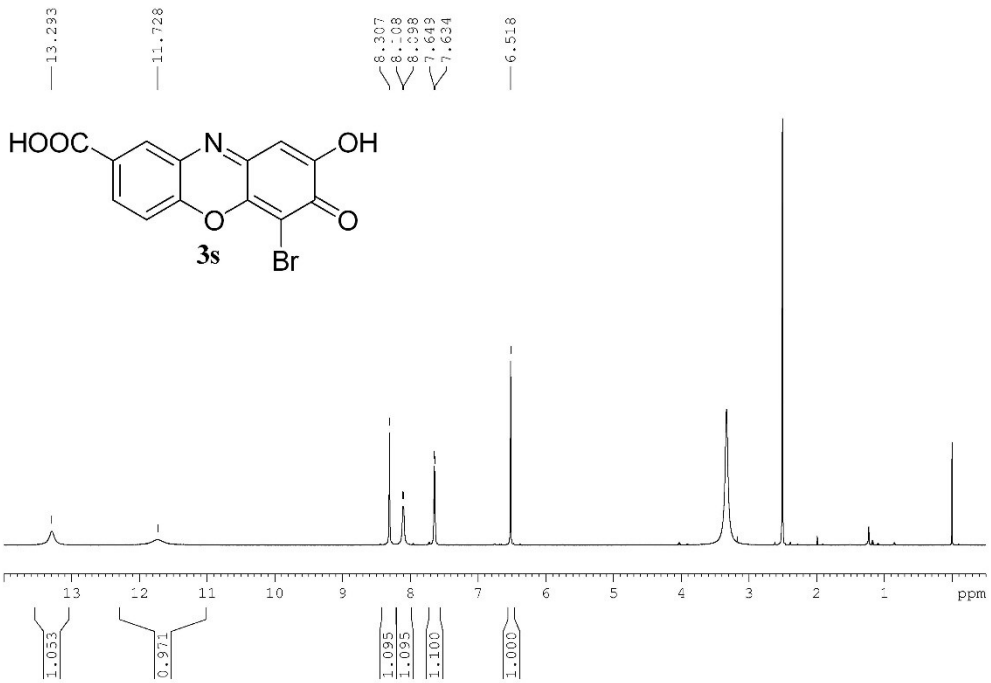

11.598
7.985
7.970
7.963
7.947
7.617
7.610
7.594
7.588
7.396
7.390
7.374
7.368
7.352
7.346
6.492
F
N
OH
O
O
Br
3q
11
10
9
8
7
6
5
4
3
2
1
ppm
1.201
1.153
1.055
1.035
1.000


178.122
164.132
162.455
154.513
149.447
144.830
144.003
143.912
131.516
130.354
114.112
113.957
104.069
103.886
103.683
F
N
OH
O
O
Br
3q
200
180
160
140
120
100
80
60
40
20
0
ppm

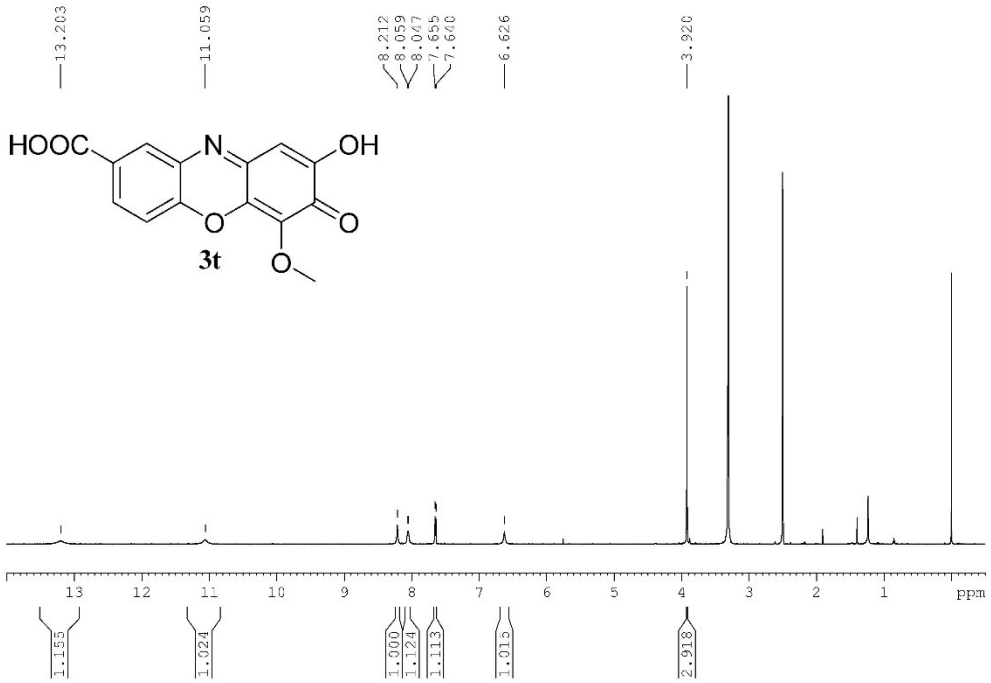
3r

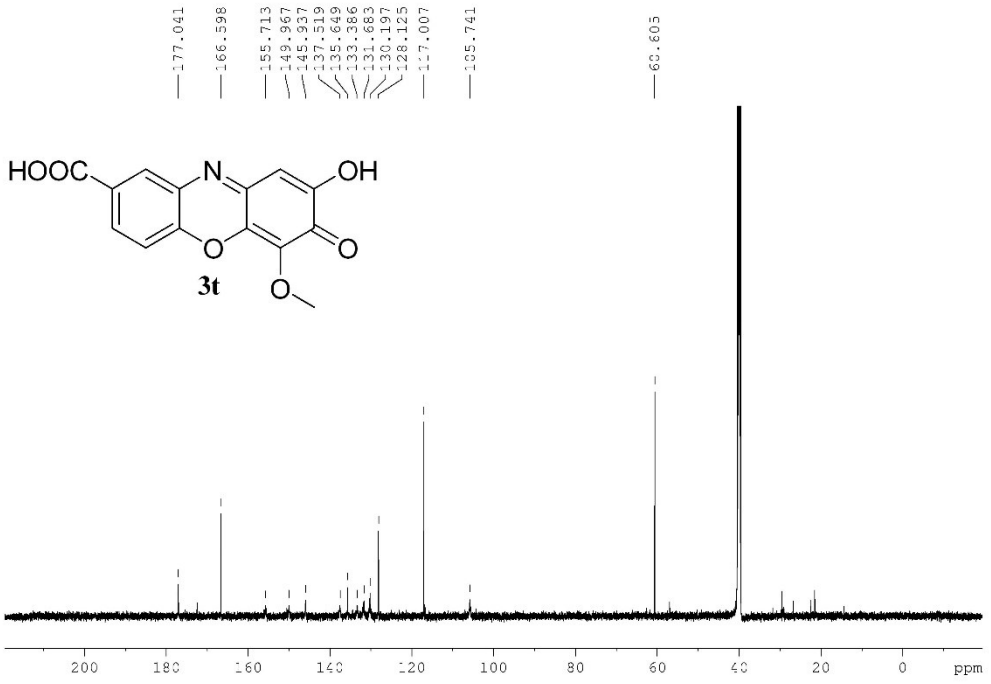

11.785
7.966
7.961
7.655
7.628
7.607
6.490
Cl
N
OH
O
O
Br
3r
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.651
1.059
2.253
1.000

3s

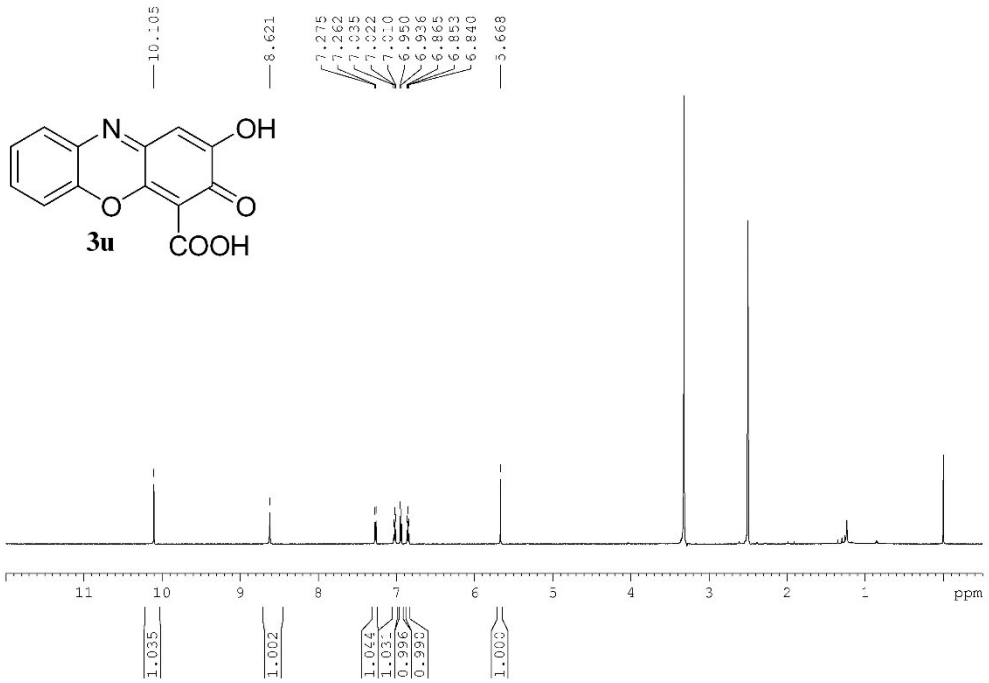

13.293
11.728
8.307
8.108
8.098
7.643
7.634
6.518
HOOC
N
OH
O
O
Br
3s
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.053
0.971
1.095
1.095
1.100
1.000

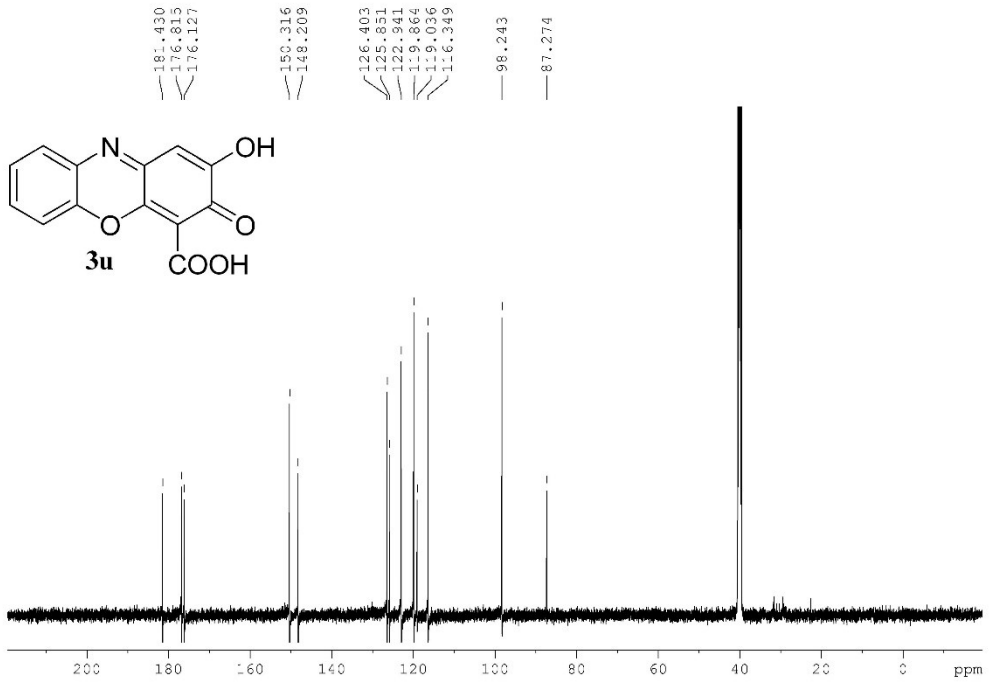
3t


13.203
11.059
8.212
8.059
8.047
7.655
7.640
6.626
3.920
HOOC
N
OH
O
O
3t
O
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.155
1.024
1.000
1.124
1.113
1.015
2.918

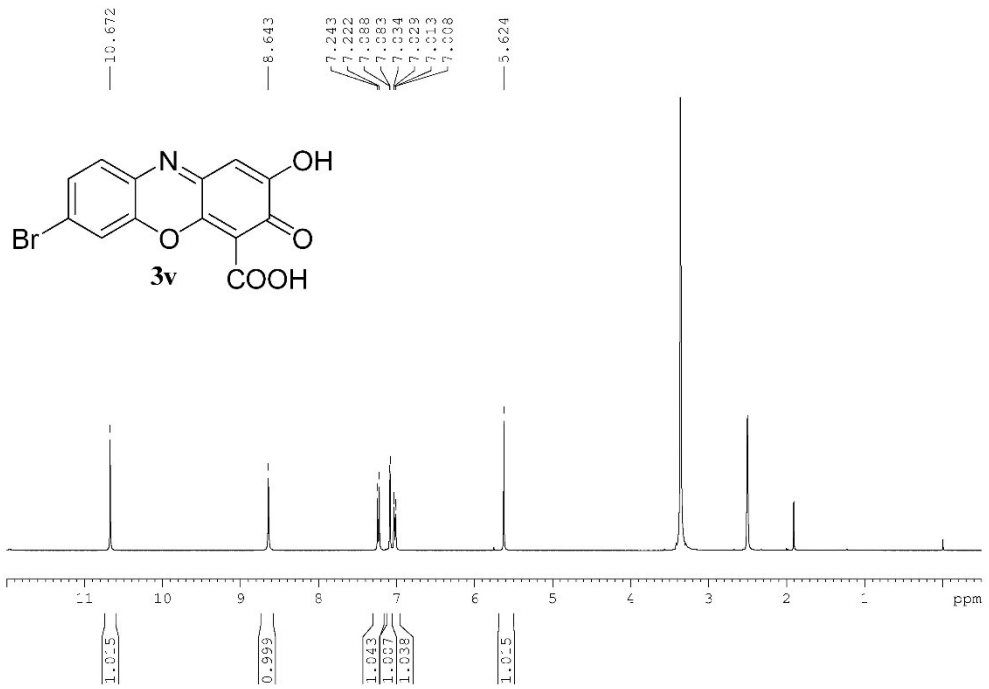

177.041
166.598
155.713
149.967
145.937
137.519
135.649
133.386
131.683
130.197
128.125
127.007
105.741
60.605
HOOC
N
OH
O
O
3t
O
200
180
160
140
120
100
80
60
40
20
0
ppm

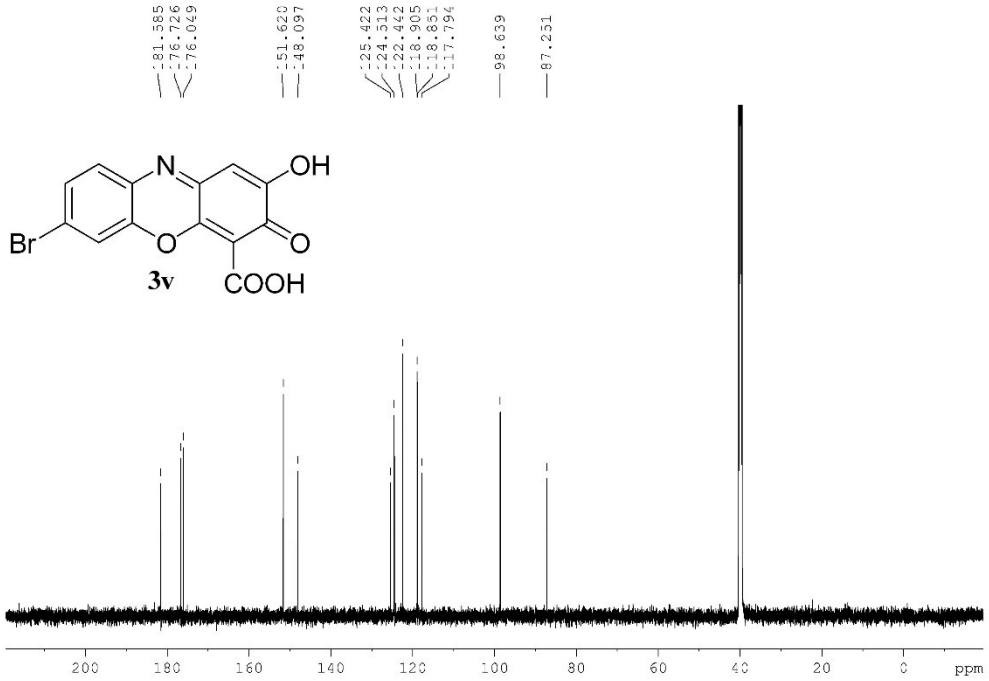
3u


10.105
8.621
7.275
7.262
7.035
7.022
7.010
6.950
6.936
6.865
6.853
6.840
5.668
N
OH
O
O
COOH
3u
11
10
9
8
7
6
5
4
3
2
1
ppm
1.035
1.002
1.044
1.031
0.996
0.990
1.003

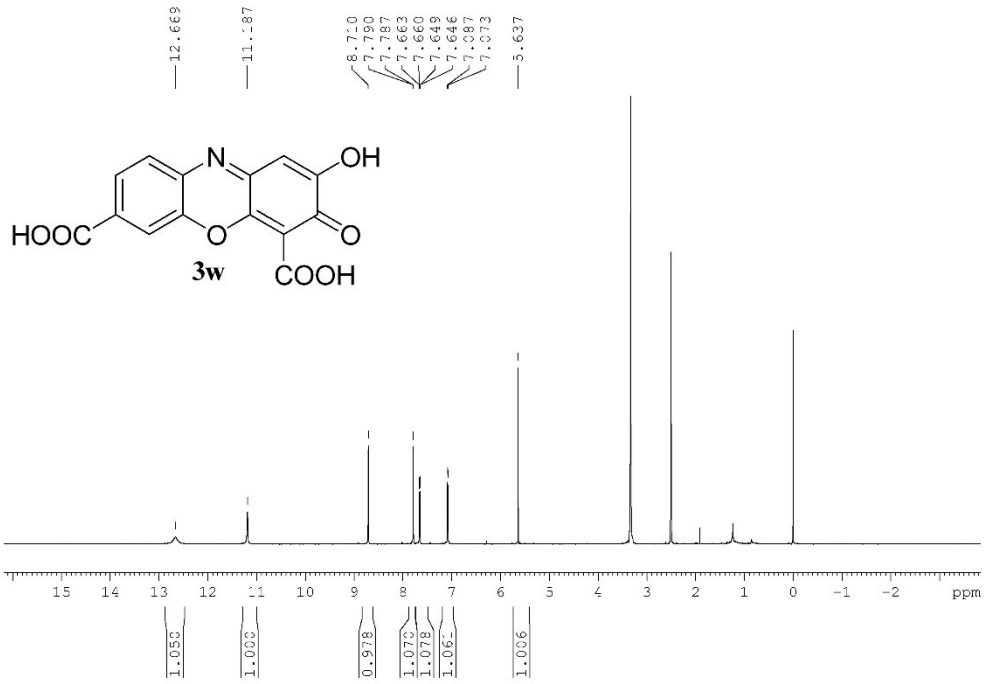

181.430
176.815
176.127
150.316
148.209
126.403
125.851
122.941
119.864
119.036
116.349
98.243
87.274
N
OH
O
O
COOH
3u
200
180
160
140
120
100
80
60
40
20
0
ppm

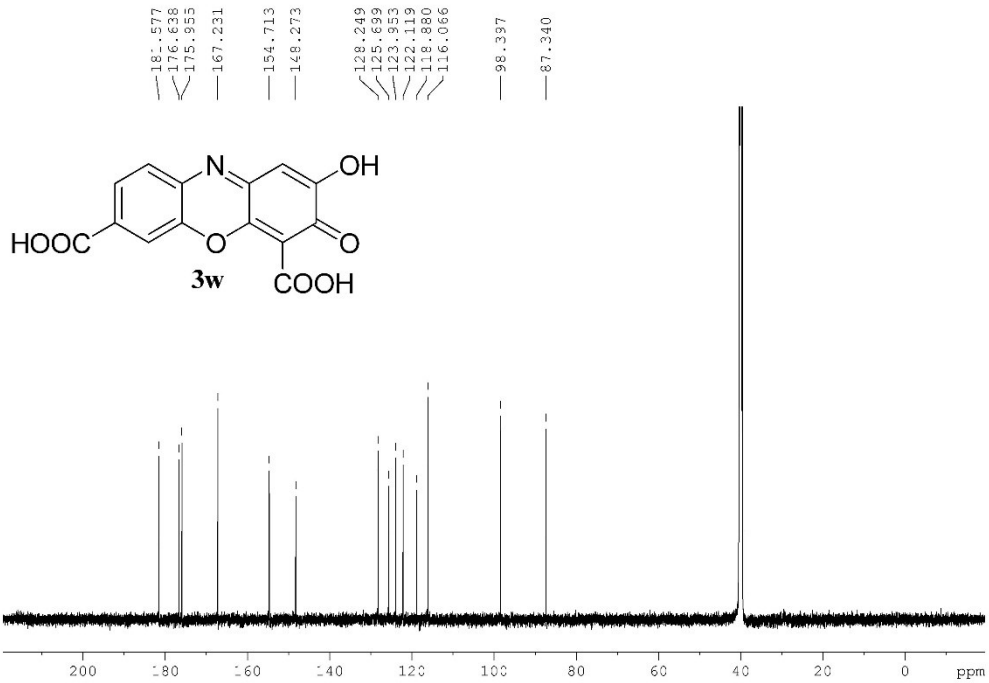
3v


10.672
8.643
7.243
7.222
7.088
7.083
7.034
7.029
7.013
7.008
5.624
N
OH
Br
O
O
3v
COOH
ppm
1.025
0.999
1.043
1.007
1.038
1.015

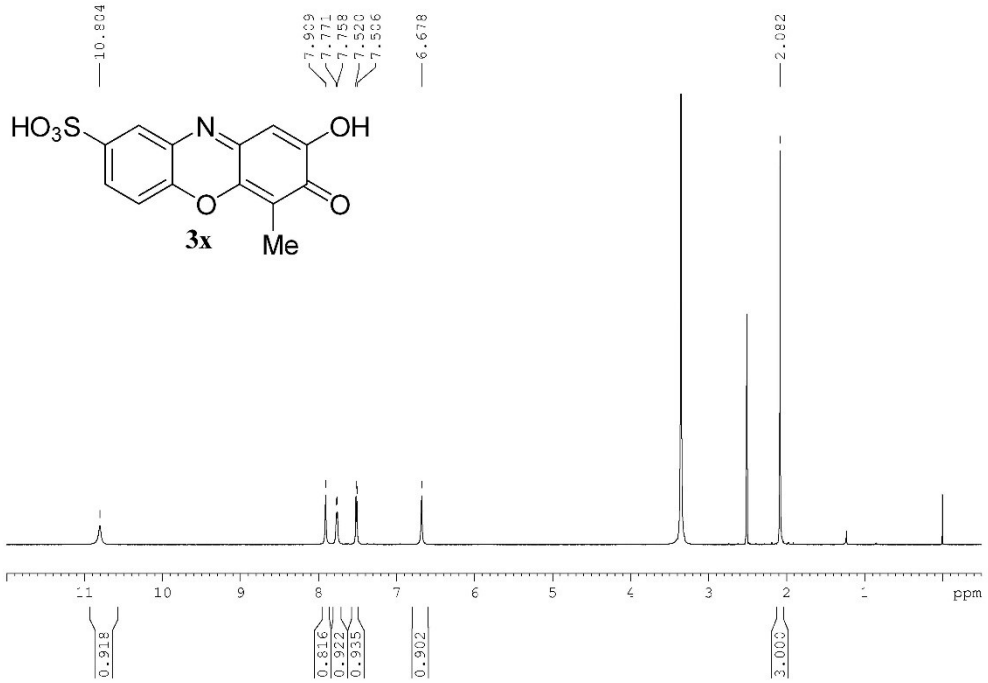

181.585
176.726
176.049
151.620
148.097
125.422
124.513
122.442
118.905
118.851
117.794
98.639
87.251
N
OH
Br
O
O
3v
COOH
ppm

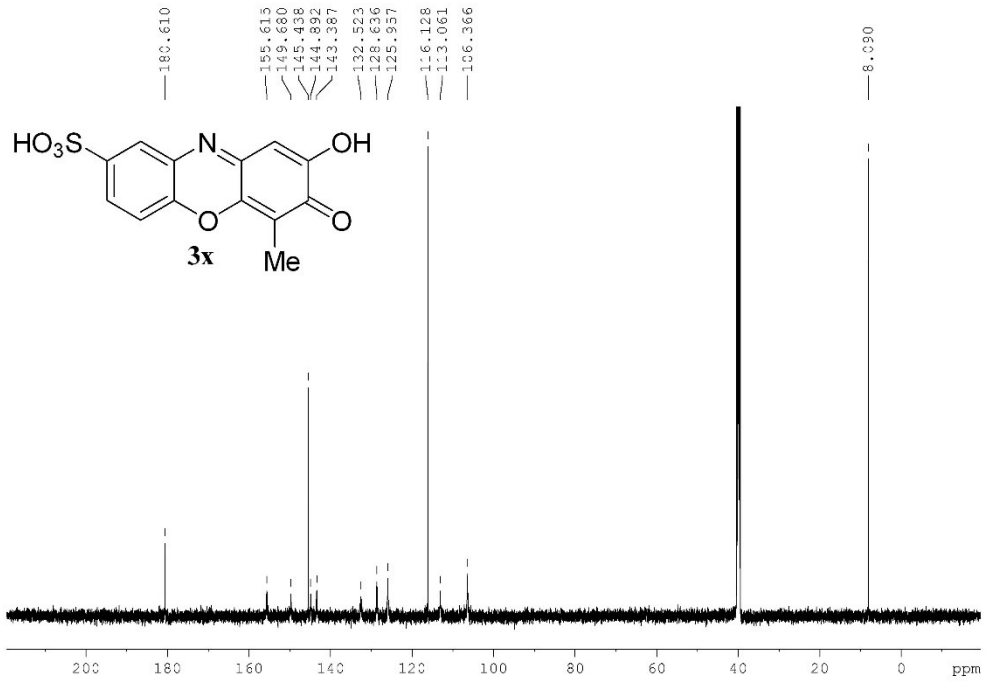
3w


12.669
11.187
8.720
7.790
7.787
7.663
7.660
7.649
7.646
7.587
7.573
5.637
N
OH
HOOC
O
O
3w
COOH
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 ppm
1.058
1.003
0.978
1.078
1.078
1.066
1.006

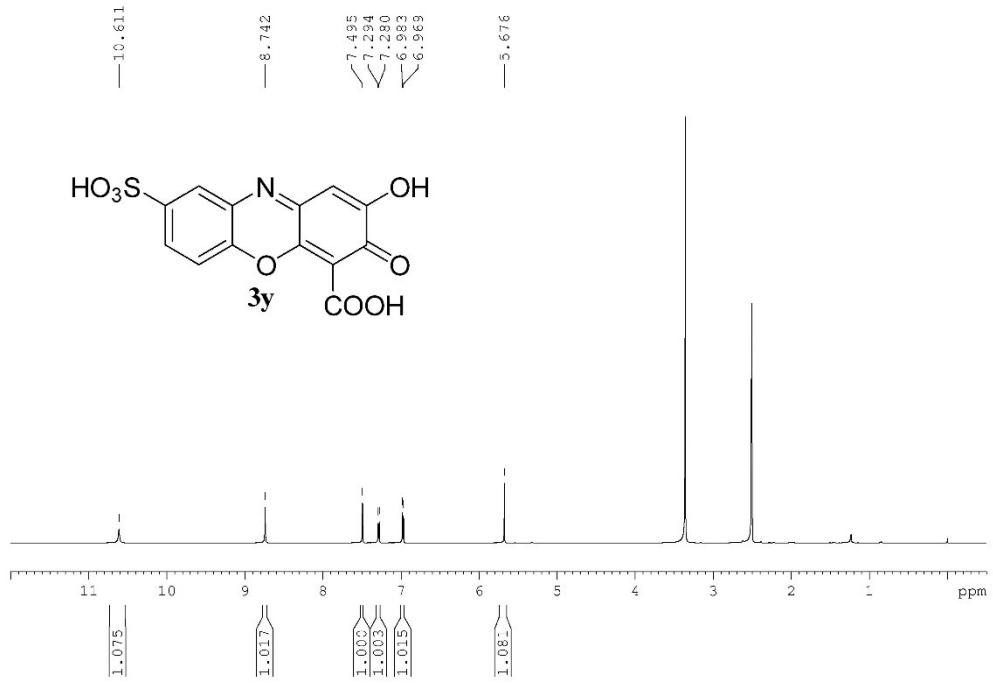

18..577
176.638
175.955
167.231
154.713
148.273
128.249
125.699
123.953
122.119
118.880
116.066
98.397
87.340
N
OH
HOOC
O
O
3w
COOH
200 180 160 140 120 100 80 60 40 20 0 ppm

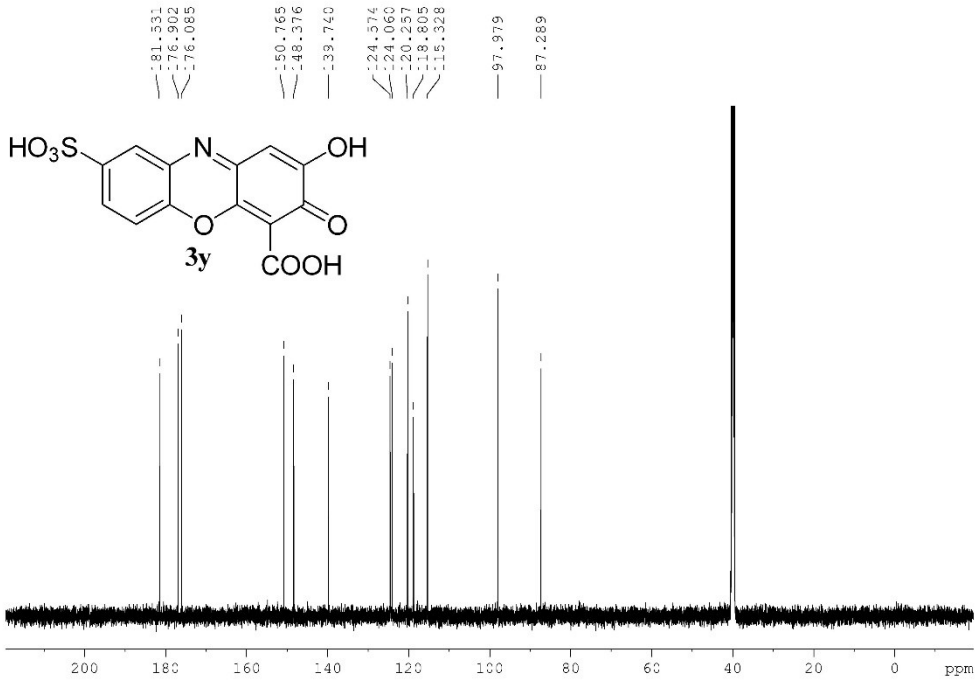
3x


10.804
7.909
7.771
7.758
7.520
7.506
6.678
2.082
HO3S
N
OH
O
O
Me
3x
ppm
0.918
0.816
0.922
0.935
0.902
3.003

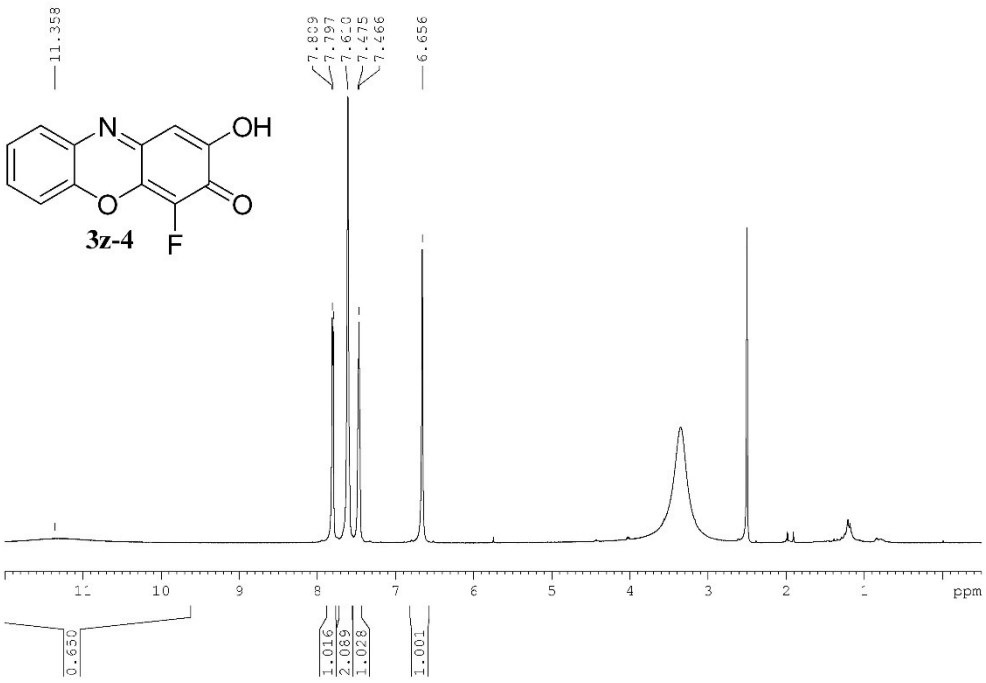

180.610
155.615
149.680
145.438
144.892
143.387
132.523
128.636
125.957
116.128
113.061
106.366
8.090
HO3S
N
OH
O
O
Me
3x
ppm

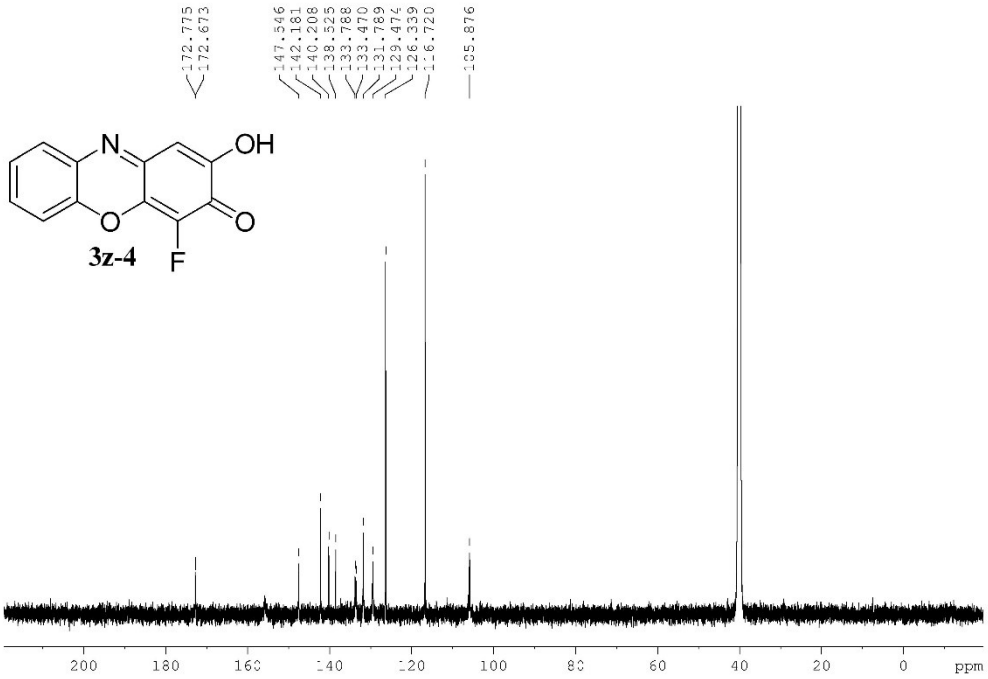
3y


10.611
8.742
7.495
7.294
7.280
6.983
6.969
5.676
HO3S
N
OH
O
O
3y
COOH
11
10
9
8
7
6
5
4
3
2
1
ppm
1.075
1.017
1.000
1.003
1.015
1.081

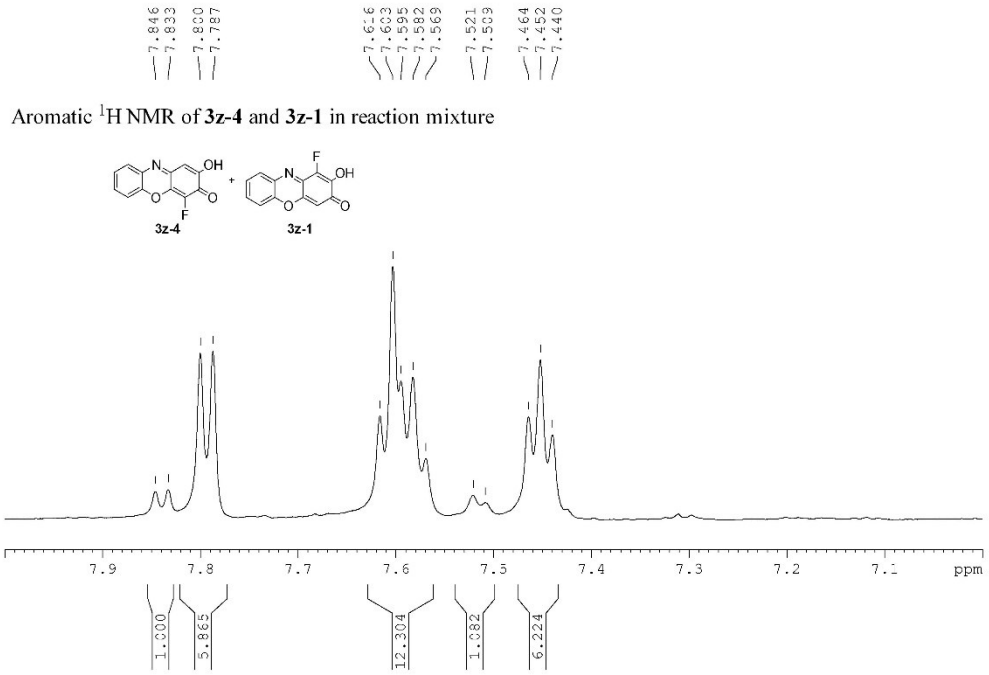

181.531
176.902
176.085
150.765
148.376
139.740
124.574
124.060
120.257
118.805
115.328
97.979
87.289
HO3S
N
OH
O
O
3y
COOH
200
180
160
140
120
100
80
60
40
20
0
ppm

3z-4

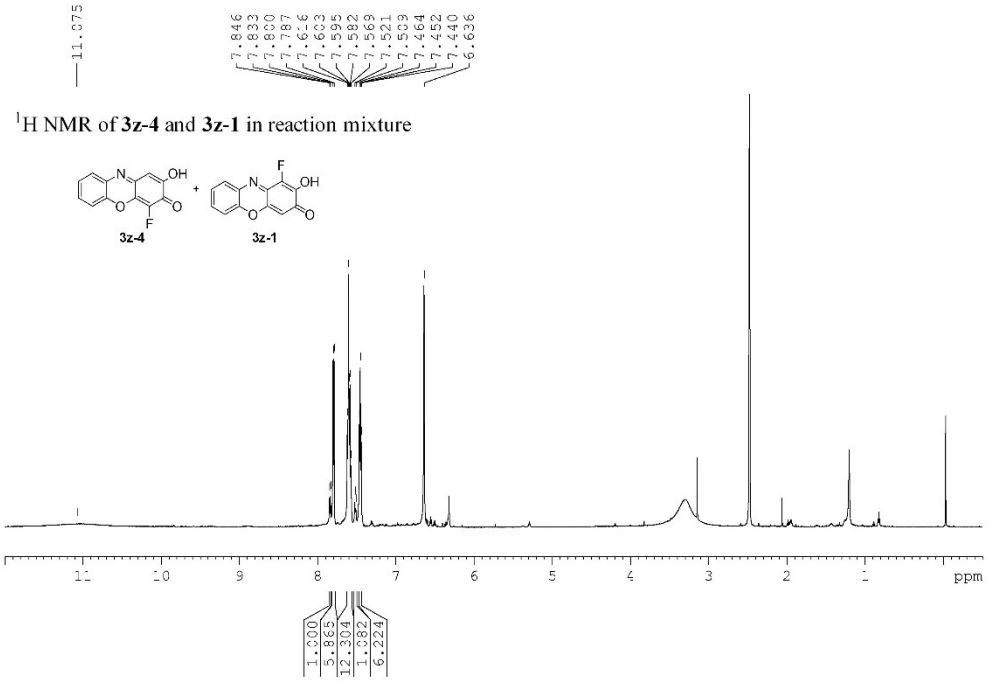

11.358
7.839
7.797
7.610
7.475
7.466
6.656
N
OH
O
O
F
3z-4
ppm
0.650
1.016
2.089
1.028
1.001


172.775
172.673
147.546
142.181
140.208
138.525
133.788
133.470
131.789
129.476
126.339
116.720
105.876
N
OH
O
O
F
3z-4
200
180
160
140
120
100
80
60
40
20
0
ppm

3z-4 and **3z-1**

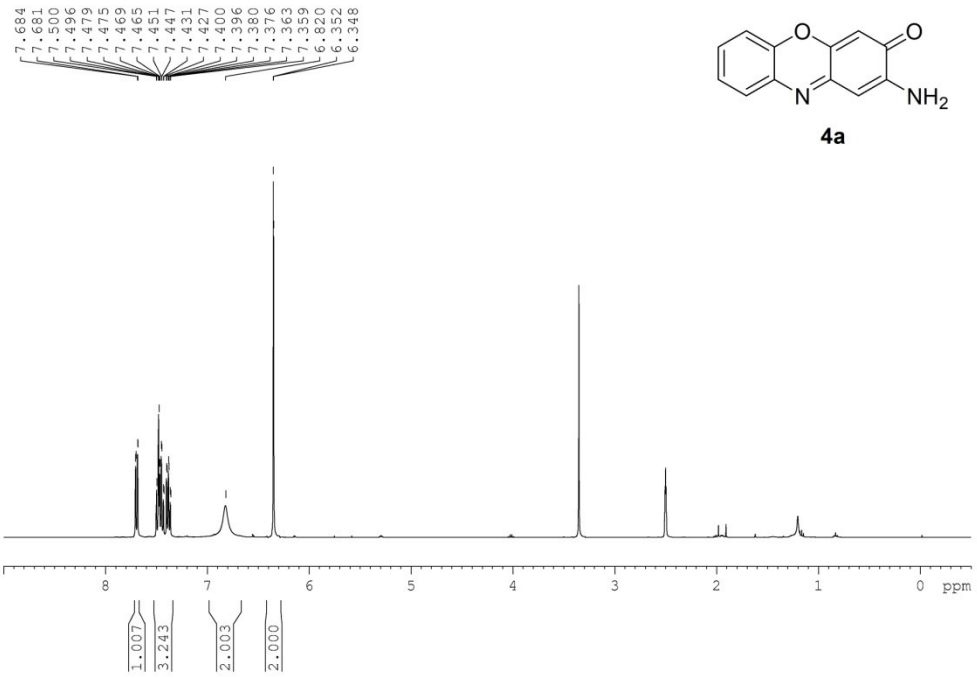


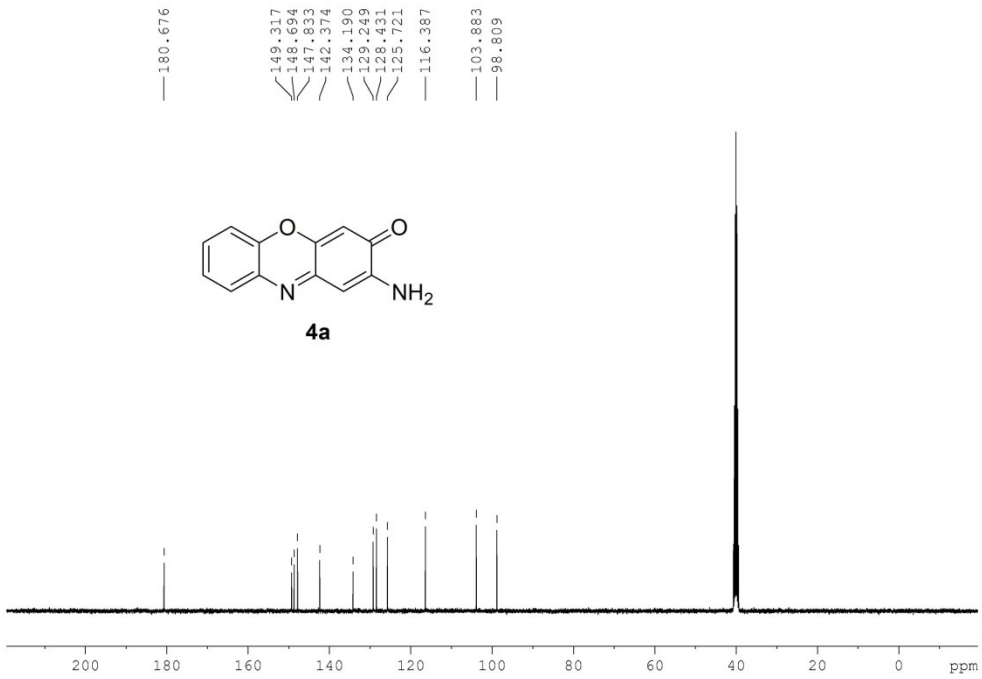
Aromatic ^{1}H NMR of **3z-4** and **3z-1** in reaction mixture



^{1}H NMR of **3z-4** and **3z-1** in reaction mixture

4a


7.684
7.681
7.500
7.496
7.479
7.475
7.469
7.465
7.451
7.447
7.431
7.427
7.400
7.396
7.380
7.376
7.363
7.359
6.820
6.352
6.348
O
O
N
NH2
4a
8
7
6
5
4
3
2
1
0
ppm
1.007
3.243
2.003
2.000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148.694
147.833
142.374
134.190
129.249
128.431
125.721
116.387
103.883
98.809
O
O
N
NH2
4a
200
180
160
140
120
100
80
60
40
20
0
ppm