Supporting Information

Rapid one pot sequential cyclization, ~~Copper and Ligand free~~ Palladium Precatalyst mediated Coupling reactions of 6-Bromo-2-chloroquinoline-3-carboxaldehyde in aqueous medium

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Table of Contents

General Information

General Reagent Information

All reactions were carried out under argon atmosphere. The THF, Toluene and Acetone were purchased from Rankem Laboratories in 500 mL bottles. 6-Bromo 2-chloro-3-formylquinoline was purchased from Sigma-Aldrich Chemicals, 1, 3-cyclohexanedione and Potassium Phosphate tribasic was purchased from Aldrich Chemical Co. Both THF and deionized water were degassed by performing evacuation / Argon refill cycles and stored under Argon prior to use. All the aryl boronic acids (Table 2) were purchased from Frontier Scientific, Aldrich Chemical Co., Alfa-Aesar, Combi-Blocks and used as received without further purification. All the halides (Table 3) was purchased from Aldrich Chemical Co., Alfa-Aesar and used as received without further purification. The ligand XPhos and the catalyst $Pd(OAc)_2$ was purchase from Johnson Matthey Chemicals. Flash Chromatography was performed using a Biotage SP4 instrument with prepacked silica cartridges.

General Analytical Information

All compounds were characterized by ^{1}H NMR, ^{13}C NMR and LC-MS spectroscopy, copies of the ^{1}H and ^{13}C NMR spectra can be found at the end of the Supporting Information. The proton (^{1}H) and carbon (^{13}C) NMR spectra were recorded on a Bruker 400 MHz instrument using TMS as an internal standard. All the 1H NMR experiments are reported in δ units, parts per million (ppm), and were measured relative to the signals for residual DMSO (2.50) in the deutrated solvent. All the ^{13}C NMR spectra were reported in ppm relative to DMSO-d6 (40.01 ppm), and all were obtained with ^{1}H decoupling. All the LC-MS spectra were obtained using Atlantis dC_{18} and Zorbax $XDBC_{18}$ Columns

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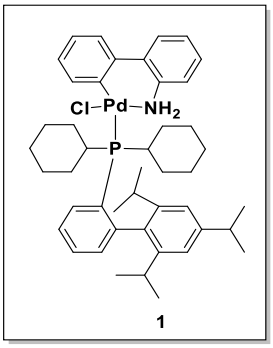
Experimental Sections



1

Synthesis of Precatalyst 1

A mixture of $Pd(OAc)_2$ (1.69 g, 7.5 mmol) and 2-amino-biphenyl (1.32 g, 7.8 mmol) in anhydrous toluene (45 mL) was heated at 60 °C under argon for 30 min, at which point the initial red color of the solution became grey precipitate had formed. After the reaction cooled at room temperature, the toluene was removed via canula. The remaining solid was washed with anhydrous toluene (2 X 20mL) and then suspended in anhydrous acetone (45 mL). After addition of lithium chloride (0.96 g, 22.5 mmol), the resulting slurry was stirred at room temperature under argon for 1 h to give a homogenous green solution. XPhos (3.38 g, 7.12 mmol) was then added portion wise over 5 min. The mixture was stirred at room temperature for 2.5 h, at which point a significant amount of precipitate had formed. Removal of about 90% of the solvent under vacuum afforded yellow slurry, which was treated with MTBE (10 mL) and pentane (25 mL). The mixture was then placed in a refrigerator for 1 h. At this point, the product was collected by suction filtration, washed with water (3 X 10 mL), and dried under vacuum to afford off white solid. Yield: 5 g (85%). Melting Point : 205.4 °C – 211.7 °C ; ^{1}H NMR (400 MHz, $CDCl_3$)): δ 7.55-7.46 (m, 1H), 7.31-7.29 (m, 2H), 7.28-6.90 (m, 2H), 6.79-6.52 (m, 1H), 4.88-4.67 (m, 1H), 2.37-1.85 (m, 3H), 1.54-1.20 (m, 10H), 0.96-0.78 (m, 6H), 0.49-0.25 (m, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.7, 146.5, 143.2, 140.3, 135.6, 128.6, 127.4, 125.8, 121.3, 120.0, 34.3, 30.3, 27.4, 25.4, 24.1.

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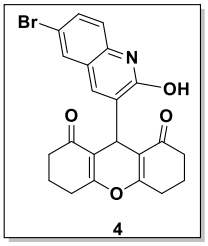
Synthesis of 9-(6-bromo-2-hydroxyquinolin-3-yl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (4).



4

A mixture of 6-bromo-2-chloro quinoline-3-carbaldehde (5 g, 18.52 mmol) and 1, 3-cyclohexadienone (4.15 g, 37.04 mmol) in deionized water (100 mL) was heated at 90 °C for 4 h. After completion of the reaction, diluted with water (100 mL), extracted with dichloromethane (3x150 mL). The organic layers were combined, dried over Na_2SO_4, concentrated under reduced pressure, and purified via Biotage SP4 (Silica packed 50 g snap cartridge column; 3-6% methanol/DCM) to provide the title

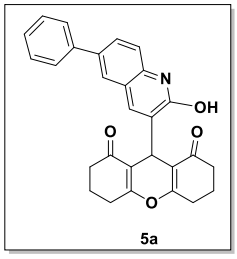
compound as pale yellow solid (6.85 g, 84%). Melting Point : 292.1 °C – 298.4 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.49 (s, 1H), 7.97 (d, J = 2.0 Hz, 1H), 7.89 (s, 1H), 77.55 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 7.17 (d, J = 8.8 Hz, 1H), 4.59 (s, 1H), 2.59- 2.49 (m, 4H), 2.27- 2.19 (m, 4H), 1.96- 1.952 (m, 2H), 1.93-1.92 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.8, 166.3, 160.5, 137.7, 137.5, 134.7, 132.4, 130.1, 121.3, 117.0, 113.4, 112.8, 36.9, 30.1, 27.0, 20.4; LC-MS m/z calcd for $C_{22}H_{18}BrNO_4$ $[M+H]^+$ 440.29, found 440.02.

Suzuki-Miyaura cross-coupling reactions

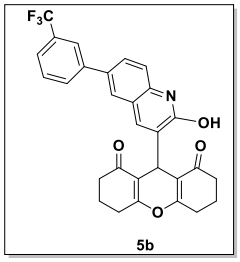
General Procedure for Table 2 and Table 3

A solution of 9-(6-bromo-2-hydroxyquinolin-3-yl) -3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione **4**, (1 mmol) in degassed THF (2 mL) was sealed with a screw-cap septum, and then evacuated and backfilled with argon (this process was repeated a total of 2 times). Then, the boronic acid (1.2 mmol) (Table 2) or halides (1.1 mmol) (Table 3) were added at room temperature. Then, degassed aqueous K_3PO_4 (2 mmol) solution (2 mL) was added via syringe, followed by the addition of Precatalyst, **1** (2 mol %) and then evacuated and backfilled with argon (this process was repeated a total of 2 times) and the reaction was stirred at room temperature for 30 min or 2 h. After completion of the reaction monitored by TLC, ethyl acetate (10 mL) and water (10 mL) were added to the reaction mixture, and the aqueous phase was extracted with ethyl acetate (3 x 10 mL). The organic layers were combined, dried over Na_2SO_4, concentrated in vacuo, and purified via the Biotage SP4 (silica – packed 12 g snap cartridge).

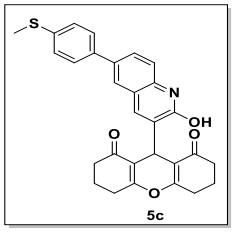
Experimental Procedure for Examples Described in Table 2



9-(2-hydroxy-6-phenylquinolin-3-yl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (5a) : Following the general procedure, a mixture of **4** (100 mg, 0.227 mmol), phenyl boronic acid (33 mg, 0.272 mmol), precatalyst, **1** (3.5 mg, 2 mol%), degassed THF (2 mL) and K_3PO_4 (96 mg, 0.454 mmol) dissolved in degassed water (2 mL) were stirred at room temperature for 1 h. The crude product was purified via the Biotage SP4 (silica – packed 12 g snap cartridge column; 3-5% methanol/DCM) to provide the title compound **(5a)** as a white solid (89 mg, 90%). Melting Point : 287.5 °C-294.6 °C ; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.45 (s, 1H), 8.04 (s, 1H), 7.88 (s, 1H), 7.77 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 7.72 (d, J = 7.2 Hz, 2H), 7.49-7.45 (m, 2H), 7.37-7.30 (m, 2H), 4.62 (s, 1H), 2.60-2.51 (m, 4H), 2.33-2.26 (m, 4H), 1.99-1.94 (m, 2H), 1.87-1.78 (m, 2H) ; ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.8, 166.2, 160.7, 139.8, 139.1, 138.0, 133.8, 129.3, 128.5, 126.8, 125.8, 119.9, 115.5, 112.9, 37.0, 31.4, 30.3, 27.0, 22.5, 20.4, 14.4 ; LC-MS m/z calcd for $C_{28}H_{23}NO_4$ $[M+H]^+$ 437.49, found 438.21.



9-(2-hydroxy-6-(3-(trifluoromethyl)phenyl)quinolin-3-yl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (5b) : White solid (105 mg, 92%). Melting Point : 293.7 °C – 298.9 °C ; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.48 (s, 1H), 8.18 (s, 1H), 8.04-8.02 (m, 2H), 7.89 (s, 1H), 7.84 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 7.69 (d, J = 4.0 Hz, 2H), 7.33 (d, J = 8.4 Hz, 1H), 4.63 (s, 1H), 2.59-2.56 (m, 4H), 2.31-2.19 (m, 4H), 1.96-1.79 (m, 4H) ; ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.8, 166.2, 160.7, 140.8, 139.0, 138.5, 138.1, 134.1, 131.9, 130.7, 130.4, 130.1, 128.6, 126.3, 124.1, 123.4, 120.0, 115.6, 113.0, 37.1, 30.1, 27.0, 20.4 ; ^{19}F NMR (376.7 MHz, DMSO-d_6): δ -60.54 ;LC-MS m/z calcd for $C_{29}H_{22}F_3NO_4$ $[M+H]^+$ 505.48, found 506.20



9-(2-hydroxy-6-(4-(methylthio)phenyl)quinolin-3-yl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (5c) : Pale Yellow solid (106 mg, 96%). Melting Point : 310.5 °C – 322.5 °C ; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.44 (s,1H), 8.03 (d, J = 2.0 Hz, 1H), 7.87 (s, 1H), 7.75 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 7.68 (d, J = 8.4 Hz, 1H), 7.36-7.29 (m, 3H), 5.76 (s, 1H), 2.60-2.50 (m, 8H), 2.33-2.20 (m, 4H), 1.97-1.80 (m, 4H) ; ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.8, 166.2, 160.7, 139.1,

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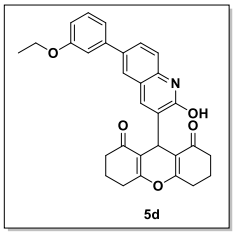
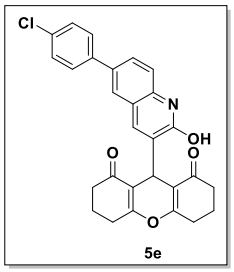
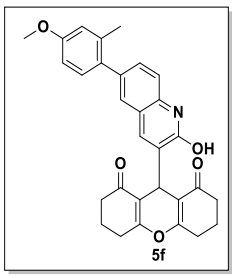
137.9, 137.5, 136.3, 133.6, 133.1, 128.2, 127.2, 126.9, 125.4, 120.0, 115.5, 112.9, 37.0, 30.3, 27.0, 20.4, 15.2 ; LC-MS m/z calcd for $C_{29}H_{25}NO_4S$ $[M+H]^+$ 483.58, found 484.20.



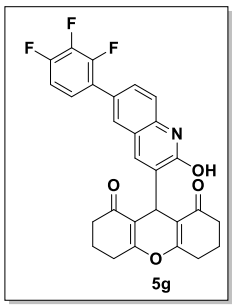
9-(6-(3-ethoxyphenyl)-2-hydroxyquinolin-3-yl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (5d) : Pale yellow solid (80 mg, 73%). Melting Point : 290.7 °C-297.3 °C ; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.44 (s, 1H), 8.06 (s, 1H), 7.87 (s, 1H), 7.77 (d, J = 8.8 Hz, 1H), 7.38-7.24 (m, 4H), 6.90 (d, J = 8.0 Hz, 1H), 4.62 (s, 1H), 4.14-4.09 (m, 2H), 2.67-2.50 (m, 4H), 2.30-2.20 (m, 4H), 1.97-1.82 (m, 4H), 1.36 (t, J = 6.8 Hz, 3H) ; ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.9, 166.3, 160.7, 159.5, 141.3, 139.2, 138.0, 133.6, 130.4, 128.6, 125.9, 119.9, 118.9, 115.4, 113.7, 112.9, 112.7, 63.5, 37.0, 31.4, 30.3, 27.0, 20.4, 15.1 ; LC-MS m/z calcd for $C_{30}H_{27}NO_5$ $[M+H]^+$ 481.54, found 482.20.



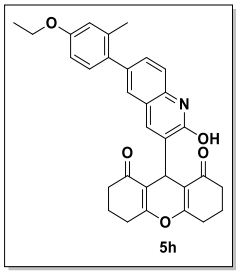
9-(6-(4-chlorophenyl)-2-hydroxyquinolin-3-yl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (5e) : White solid (88 mg, 82%). Melting Point : 288.8 °C-293.2 °C ; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.46 (s, 1H), 8.05 (s, 1H), 7.86 (s, 1H), 7.77 - 7.73 (m, 3H), 7.51 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.4 Hz, 1H), 4,61 (s, 1H), 2.58-2.49 (m, 4H), 2.32-2.19 (m, 4H), 1.95-1.92 (m, 2H), 1.83-1.82 (m, 2H) ; ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.8, 166.2, 138.7, 133.8, 132.3, 129.3, 128.5, 125.9, 112.9, 37.0, 27.0, 20.4 ; LC-MS m/z calcd for $C_{28}H_{22}ClNO_4$ $[M+0]^+$ 471.93, found 471.90.



9-(2-hydroxy-6-(4-methoxy-2-methylphenyl)quinolin-3-yl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (5f) : Off white solid (92 mg, 84%). Melting Point : 286.2 °C – 290.9 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.39 (s, 1H), 7.81 (s, 1H), 7.58 (s, 1H), 7.33 (d, J = 7.6 Hz, 1H), 7.24 (d, J = 7.6 Hz, 1H), 7.11 (d, J = 8.0 Hz, 1H), 6.85-6.79 (m, 2H), 5.73 (s, ~~2~~1H), 4.57 (s, 1H), 3.75 (s, 3H), 2.48 (s, 6H), 2.19 (s, ~~6~~4H), 1.90-1.79 (m, 4H), ~~1.24-1.22 (m, 2H), 0.83 (s, 1H)~~ ; ^{13}C NMR (100 MHz, DMSO-d_6): δ 201.6, 171.0, 165.5, 163.6, 143.9, 142.0, 141.5, 139.6, 138.4, 136.0, 135.9, 132.9, 124.2, 120.8, 119.4, 117.5, 116.6, 60.2, 41.7, 38.7, 35.2, 31.8, 26.9, 25.7, 19.1 ; LC-MS m/z calcd for $C_{30}H_{27}NO_5$ $[M+H]^+$ 481.54, found 482.00.



9-(2-hydroxy-6-(2,3,4-trifluorophenyl)quinolin-3-yl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (5g) : Off white solid (100 mg, 90%). Melting Point : 307.1 °C – 315.5 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.53 (s, 1H), 7.91 (s, 1H), 7.86 (s, 1H), 7.61 (d, J = 8.8 Hz, 1H), 7.45-7.42 (m, 2H), 7.34 (d, J = 8.4 Hz, 1H), 4.62 (s, 1H), 2.60-2.57 (m, 4H), 2.33-2.28 (m, 4H), 1.99-1.93 (m, 2H), 1.91-1.80 (m, 2H) ; ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.8, 166.3, 160.7, 138.8, 134.0, 130.4, 128.3, 126.8, 125.2, 119.7, 115.3, 113.4, 112.8, 36.9, 30.2, 27.0, 20.4 ; LC-MS m/z calcd for $C_{28}H_{20}F_3NO_4$ $[M+H]^+$ 491.46, found 491.90.



9-(6-(4-ethoxy-2-methylphenyl)-2-hydroxyquinolin-3-yl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (5h) : Off white solid (98 mg, 87%). Melting Point : 291.3 °C – 297.1 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.41 (s, 1H), 7.83 (s, 1H), 7.61 (s, 1H), 7.37 - 7.35 (m, 1H), 7.26 (d, J = 8.4 Hz, 1H), 7.12 (d, J = 8.4 Hz, 1H), 6.86 (s, 1H), 6.81 (d, J = 8.0 Hz, 1H), 4.60 (s, 1H), 4.07-4.02 (m, 2H), 3.57 (s, 1H) 2.58-2.49 (m, ~~5~~4H), 2.28-2.21 (m, ~~9~~6H), 1.95-1.92 (m, ~~3~~2H), 1.83-1.82 (m, ~~3~~2H), 1.36-1.32 (m, 3H) ; ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.9, 166.3, 160.7, 158.1, 139.1, 136.7, 134.8, 133.5, 133.2, 131.2, 128.1, 119.4, 116.6, 114.6, 112.8, 112.3, 66.8, 63.3, 55.3, 37.0, 30.4, 27.0, 20.9, 20.5, 15.2 ; LC-MS m/z calcd for $C_{31}H_{29}NO_5$ $[M+H]^+$ 495.57, found 496.20.

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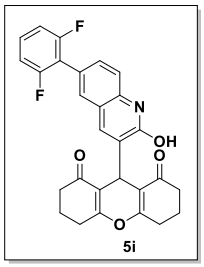
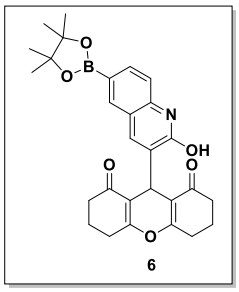


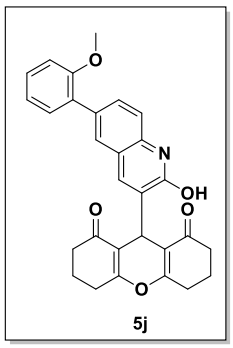
9-(6-(2,6-difluorophenyl)-2-hydroxyquinolin-3-yl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (5i) : White solid (100 mg, 90%). Melting Point : 298.6 °C – 304.2 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ11.53 (s, 1H), 7.85 (s, 1H), 7.81 (s, 1H), 7.49-7.47 (m, 2H), 7.34 (d, J = 8.4 Hz, 1H), 7.25-7.21 (m, 2H), 4.61 (s, 1H), 2.58-2.50 (m, 4H), 2.28-2.24 (m, 4H), 1.99-1.92 (m, 2H), 1.84-1.82 (m, 2H) ; ^{13}C NMR (100 MHz, DMSO-d_6): δ196.8, 166.3, 161.1, 160.8, 158.7, 138.8, 138.4, 133.8, 131.6, 130.39, 129.7, 121.0, 119.5, 117.7, 117.5, 115.0, 112.8, 112.5, 112.3, 37.0, 30.3, 27.0, 20.4 -; ^{19}F NMR (376.7 MHz, DMSO-d_6): δ -137.13, -115.28 ; LC-MS m/z calcd for $C_{28}H_{22}F_2NO_4$ $[M+H]^+$ 473.47, found 474.0.

Synthesis of -(2-hydroxy-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)quinolin-3-yl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (6) :

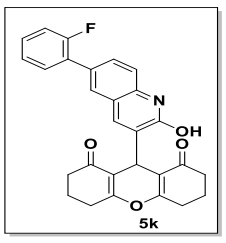


A solution of 9-(6-bromo-2-hydroxyquinolin-3-yl) -3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione, **4** (1g, 2.27 mmol) in degassed THF (10 mL) was sealed with a screw-cap septum, and then evacuated and backfilled with argon (this process was repeated a total of 2 times). Then, the Bis(pinacolato)diboron (0.57g, 2.27 mmol), K_3PO_4 (0.96g, 4.54 mmol) were added at room temperature, followed by the addition of Pd precatalyst, **1** (0.036g, 2 mol %) and then evacuated and backfilled with argon (this process was repeated a total of 2 times) and the reaction was stirred at room temperature for 1 h. After completion of the reaction monitored by TLC, ethyl acetate (50 mL) and water (50 mL) were added to the reaction mixture, and the aqueous phase was extracted with ethyl acetate (3 x 50 mL). The organic layers were combined, dried over Na_2SO_4, concentrated in vacuo, and purified via the Biotage SP4 (Silica – packed 12 g snap cartridge column; 1-3% DCM / Methanol) to provide the title compound (**6**) as pale yellow solid (0.8g, 72%). Melting Point : 289.2 °C – 295.7 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.53 (s, 1H), 7.95 (s, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.21 (d, J = 8.4 Hz, 1H), 4.61 (s, 1H), 2.59-2.57 (m, 4H), 2.30-2.17 (m, 4H), 1.98-1.81 (m, 4H), 1.34-1.25 (m, 118H), 1.18 (s, 4H) ; ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.7, 166.0, 160.8, 140.7, 138.8, 135.3, 134.6, 119.1, 114.4, 113.5, 119.1, 114.4, 113.5, 84.0, 83.3, 66.8, 60.2, 37.0, 29.3, 27.0, 25.2, 24.9, 21.2, 20.4-, 14.5 ; LC-MS m/z calcd for $C_{28}H_{30}BNO_6$ $[M+H]^+$ 487.35, found 488.0.

Experimental Procedure for Examples Described in Table 3



9-(2-hydroxy-6-(2-methoxyphenyl)quinolin-3-yl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (5j) : Following the general procedure, a mixture of **6** (100 mg, 0.205 mmol), 2-bromo anisole (42 mg, 0.225 mmol), precatalyst **1** (3.0 mg, 2 mol%), degassed THF (2 mL) and K_3PO_4 (87 mg, 0.410 mmol) dissolved in degassed water (2 mL) were stirred at room temperature for 2 h. The crude product was purified via the Biotage SP4 (silica – packed 12 g snap cartridge column; 2-5% methanol/DCM) to provide the title compound **(5j)** as white solid (78 mg, 82%). Melting Point : 282.3 °C – 288.9 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.40 (s, 1H), 7.80 (s, 1H), 7.74 (s, 1H), 7.52 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 7.35-7.24 (m, 3H), 7.11 (d, J = 8.0 Hz, 1H), 7.04-7.00 (m, 1H), 4.59 (s, 1H), 3.76 (s, 3H), 2.58-2.50 (m, 4H), 2.30-2.19 (m, 4H), 1.96-1.91 (m, 2H), 1.90-1.81 (m, 2H) ; ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.8, 166.2, 160.7, 156.6, 139.1, 137.5, 133.2, 131.9, 131.3, 130.8, 129.7, 129.1, 128.3, 121.2, 119.3, 114.5, 112.9, 112.2, 56.0, 37.0, 30.3, 27.0, 20.4 ; LC-MS m/z calcd for $C_{29}H_{25}NO_5$ $[M+H]^+$ 467.51, found 468.40.



9-(6-(2-fluorophenyl)-2-hydroxyquinolin-3-yl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (5k) : Off white solid (82 mg, 87%). Melting Point : 283.5 °C – 288.2 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.49 (s, 1H), 7.89-7.86 (m, 2H), 7.62-7.54 (m, 2H), 7.43-7.39 (m, 1H), 7.34-7.29 (m, 3H), 4.62 (s, 1H), 2.60-2.50

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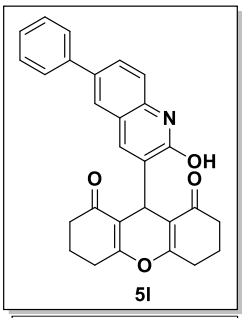
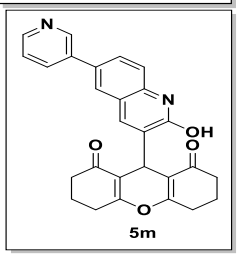
(m, 4H), 2.30-2.22 (m, 4H), 1.97-1.96 (m, 2H), 1.94-1.92 (m, 2H) ; ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.8, 166.2, 160.7, 138.9, 138.1, 133.8, 131.1, 130.6, 129.7, 129.1, 128.7, 128.2, 125.4, 119.6, 116.6, 116.4, 115.1, 112.9, 37.0, 30.2, 27.0, 20.4 ; ^{19}F NMR (376.7 MHz, DMSO-d_6): δ -117.89 ; LC-MS m/z calcd for $C_{28}H_{22}FNO_4$ $[M+H]^+$ 455.48, found 456.20.



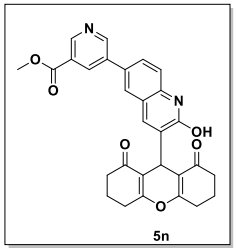
5l

9-(2-hydroxy-6-phenylquinolin-3-yl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (5l) : White solid (72 mg, 80%). Melting Point : 287.5 °C-294.6 °C ; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.45 (s, 1H), 8.04 (s, 1H), 7.88 (s, 1H), 7.77 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 7.72 (d, J = 7.2 Hz, 2H), 7.49-7.45 (m, 2H), 7.37-7.30 (m, 2H), 4.62 (s, 1H), 2.60-2.51 (m, 4H), 2.33-2.26 (m, 4H), 1.99-1.94 (m, 2H), 1.87-1.78 (m, 2H) ; ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.8, 166.2, 160.7, 139.8, 139.1, 138.0, 133.8, 129.3, 128.5, 127.5, 126.8, 125.8, 119.9, 115.5, 112.9, 37.0, 31.4, 30.3, 27.0, ~~22.5,~~ 20.4, 14.4 ; LC-MS m/z calcd for $C_{28}H_{23}NO_4$ $[M+H]^+$ 437.49, found 438.21.



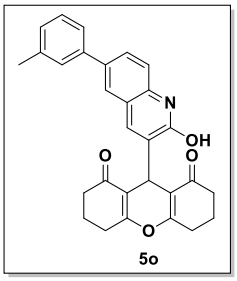
5m

9-(2-hydroxy-6-(pyridin-3-yl)quinolin-3-yl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (5m) : White solid (67 mg, 74%). Melting Point : 292.3 °C – 300.2 °C ; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.50 (s, 1H), 8.96 (s, 1H), 8.56 (s, 1H), 8.14 (s, 1H), 7.88 (s, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.51 (s, 1H), 7.34 (d, J = 8.4 Hz, 1H), 4.62 (s, 1H), 2.59-2.51 (m, 4H), 2.33-2.20 (m, 4H), 1.94-1.83 (m, 4H), ; ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.8, 166.3, 160.7, 148.5, 147.8, 139.0, 138.4, 135.3, 134.1, 133.8, 130.6, 128.5, 126.2, 124.3, 120.0, 115.7, 112.8, 36.9, 30.3, 27.0, 20.4, ; LC-MS m/z calcd for $C_{27}H_{22}N_2O_4$ $[M+H]^+$ 438.47, found 439.20.



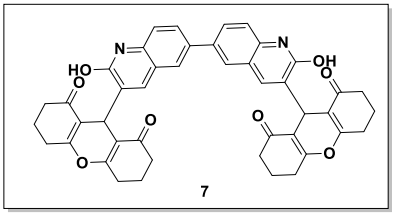
5n

Methyl 5-(3-(1,8-dioxo-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-9-yl)-2-hydroxyquinolin-6-yl)nicotinate (5n) : White solid (72 mg, 70%). Melting Point : 296.7 °C – 304.6 °C ; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.53 (s, 1H), 9.20 (s, 1H), 9.06 (s, 1H), 8.55 (s, 1H), 8.24 (s, 1H), 7.90 (d, J = 6.0 Hz, 2H), 7.36 (d, J = 8.4 Hz, 1H), 4.63 (s, 1H), 3.94 (s, 3H), 3.57 (s, 1H), 2.59-2.57 (m, ~~5~~4H), 2.29-2.20 (m, ~~5~~4H), 1.96-1.94 (m, ~~3~~2H), 1.93-1.83 (m, ~~3~~2H), ; ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.8, 166.2, 165.7, 160.7, 151.8, 148.7, 138.9, 135.4, 134.3, 129.3, 128.6, 126.6, 126.2, 120.1, 115.8, 113.0, 112.8, 66.8, 53.0, 37.0, 30.4, 27.0, 20.4 ; LC-MS m/z calcd for $C_{29}H_{24}N_2O_6$ $[M+H]^+$ 496.51, found 497.20.



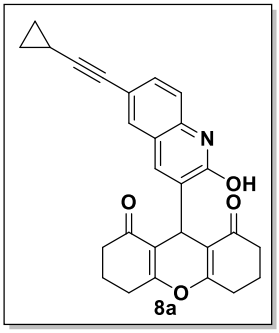
5o

9-(2-hydroxy-6-m-tolylquinolin-3-yl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (5o) : White solid (81 mg, 87%). Melting Point : 291.6 °C-296.1 °C ; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.43 (s, 1H), 8.02 (s, 1H), 7.86 (s, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.55-7.35 (m, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.17 (s, 1H), 4.62 (s, 1H), 3.32 (s, 3H), 2.67-2.58 (m, 4H), 2.39-2.25 (m, 4H), 1.93-1.82 (m, 4H) ; ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.8, 166.2, 160.7, 139.8, 139.1, 138.5, 137.9, 133.8, 129.2, 128.2, 127.5, 125.7, 123.9, 119.9, 115.4, 113.0, 37.0, 30.2, 27.0, 21.6, 20.4 ; LC-MS m/z calcd for $C_{29}H_{25}NO_4$ $[M+H]^+$ 451.51, found 452.20.

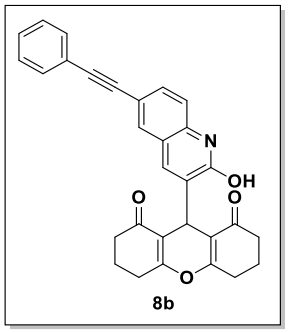


7

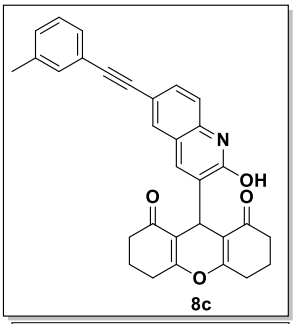
9,9'-(2,2'-dihydroxy-[6,6'-biquinoline]-3,3'-diyl)bis(3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione) (7) : White solid (50 mg, 30%). Melting Point : 342.6 °C-360.1 °C ; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.44 (s, 2H), 8.08 (s, 2H), 7.85- 7.81(m, 4H), 7.31 (d, J = 8.4 Hz, 2H), 4.63 (s, 2H), 3.33 (s, 4H), 2.51-2.50 (m, 4H), 2.34-2.25 (m, 8H), 2.12-2.09 (m, 4H), 1.99-1.85 (m, 4H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.1, 170.7, 140.7, 138.8, 132.7, 129.8, 128.2, 124.4, 121.0, 119.3, 116.8, 53.2, 53.0, 52.8, 52.6, 52.4, 52.2, 51.9, 40.7, 34.7, 31.0, 24.1 ; LC-MS m/z calcd for $C_{44}H_{36}N_2O_8$ $[M+H]^+$ 720. 78, found 721.9.



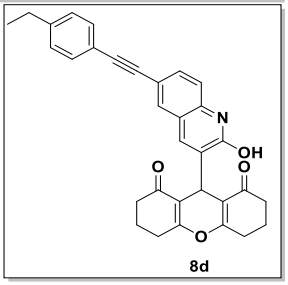
9-(6-(cyclopropylethynyl)-2-hydroxyquinolin-3-yl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (8a) : Off-White solid (80 mg, 82%). Melting Point : 268.3 °C – 274 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.44 (s, 1H), 7.75-7.72 (m, 2H), 7.37 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 7.17 (d, J = 8.8 Hz, 1H), 4.58 (s, 1H), 2.59-2.51 (m, 4H), 2.30-2.22 (m, 4H), 1.96-1.90 (m, 2H), 1.84-1.79 (m, 2H), 1.54 (s, 1H), 0.91-0.86 (m, 2H), 0.74-0.71 (m, 2H). ; ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.8, 166.3, 160.7, 159.8, 159.1, 157.4, 132.7, 129.8, 119.5, 116.8, 115.0, 112.8, 39.3, 36.9, 27.0, 20.4, 8.8; LC-MS m/z calcd for $C_{27}H_{23}NO_4$ $[M+H]^+$ 425.48, found 426.1



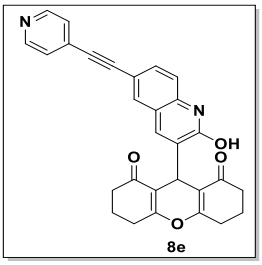
Synthesis of 9-(2-hydroxy-6-(phenylethynyl)quinolin-3-yl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (8b) : A solution of 9-(6-bromo-2-hydroxyquinolin-3-yl) -3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione, **4** (0.1g, 0.227 mmol) in degassed N,N-dimethylformamide (2 mL) was sealed with a screw-cap septum, and then evacuated and backfilled with argon (this process was repeated a total of 2 times). Then, phenyl acetylene (28 mg, 0.273 mmol), triethylamine (0.16 mL, 1.14 mmol) were added at room temperature, followed by the addition of Precatalyst, **1** (8.9 mg, 5 mol %) and the reaction was stirred at room temperature for 3 h. After completion of the reaction monitored by TLC, ethyl acetate (10 mL) and water (10 mL) were added to the reaction mixture, and the aqueous phase was extracted with ethyl acetate (3 x 10 mL). The organic layers were combined, dried over Na_2SO_4, concentrated in *vacuo*, and purified via the Biotage SP4 (silica – packed 12 g snap cartridge column; 1-3% DCM / Methanol) to provide the title compound **(8b)** as White solid (92 mg, 88%). Melting Point : 299.6 °C – 316.4 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.58 (s, 1H), 7.94 (s, 1H), 7.82 (s, 1H), 7.57 (d, J = 8.4 Hz, 3H), 7.43 (d, J = 2.4 Hz, 3H), 7.26-7.24 (m, 1H), 4.60 (s, 1H), 2.73-2.57 (m, 4H), 2.32-2.24 (m, 4H), 1.93-1.82 (m, 4H) ; ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.8, 166.3, 160.6, 159.8, 159.1, 157.4, 138.5, 134.4, 132.7, 131.1, 129.2, 122.9, 119.6, 115.5, 112.8, 89.7, 88.5, 36.9, 30.1, 27.0, 20.4 ; LC-MS m/z calcd for $C_{30}H_{23}NO_4$ $[M+H]^+$ 461.51, found 462.0.



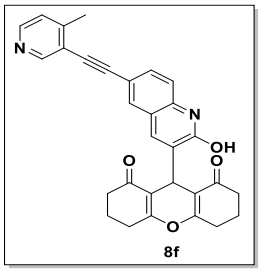
9-(2-hydroxy-6-(m-tolylethynyl)quinolin-3-yl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dionedione (8c) : White solid (87 mg, 80%). Melting Point: 302.1 °C – 312. 7 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.57 (s, 1H), 7.93 (s, 1H), 7.82 (s, 1H), 7.56 (dd, J = 8.4 Hz, 1.2 Hz, 1H), 7.37-7.31 (m, 3H), 7.29-7.22 (m, 2H), 4.61 (s, 1H), 2.59-2.56 (m, 4H), 2.40-2.30 (m, 7H), 1.96-1.91 (m, 2H), 1.85-1.82 (m, 2H). ; ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.8, 166.3, 160.6, 138.5, 138.3, 134.3, 132.7, 132.1, 131.2, 129.8, 129.1, 128.8, 122.7, 119.6, 115.6, 115.4, 112.8, 89.4, 89.0, 37.0, 30.2, 27.0, 21.2, 20.4 ; LC-MS m/z calcd for $C_{31}H_{25}NO_4$ $[M-H]^{+-}$ 475.54, found 474.0.



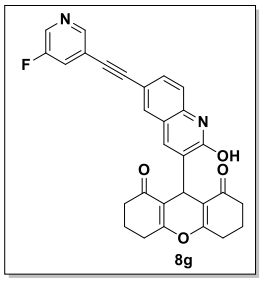
9-(6-((4-ethylphenyl)ethynyl)-2-hydroxyquinolin-3-yl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (8d): Off-White solid (93 mg, 83%). Melting Point : 288.6 °C – 294.1 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.56 (s, 1H), 7.93 (s, 1H), 7.92 (s, 1H), 7.56 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 7.46 (d, J = 8.0 Hz, 2H), 7.28-7.23 (m, 3H), 4.61 (s, 1H), 2.67-2.51 (m, 6H), 2.33-2.29 (m, 4H), 1.99-1.91 (m, 2H), 1.9987-1.82 (m, 4H), 1.21 (t, 3H). ; ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.8, 166.3, 160.6, 145.0, 138.4, 138.3, 134.3, 132.7, 132.7, 131.7, 131.1, 128.6, 120,1, 119.6, 115.7, 115.4, 112.9, 89.0, 37.0, 30.1, 28.5, 27.0, 20.4, 15.7 ; LC-MS m/z calcd for $C_{32}H_{27}NO_4$ $[M+H]^+$ 489.57, found 490.2



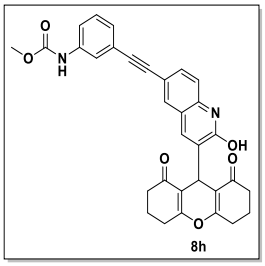
9-(2-hydroxy-6-(pyridin-4-ylethynyl)quinolin-3-yl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (8e) : White solid (90 mg, 80%). Melting Point : 268.3 °C – 276 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.54 (s, 1H), 8.02-7.91 (m, 2H), 7.84-7.80 (m, 2H), 7.79-7.71 (m, 1H), 7.66-7.61 (m, 2H), 7.28 (d, J = 8.4 Hz, 1H), 4.61 (s, 1H), 2.59-2.51 (m, 4H), 2.31-2.26 (m, 4H), 1.96-1.90 (m, 2H), 1.85-1.79 (m, 2H). ; ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.8, 166.3, 160.6, 139.1, 138.2, 135.0, 134.9, 132.9, 131.8, 130.9, 130.8, 119.7, 115.5, 114.4, 112.8, 94.0, 36.9, 30.1, 27.0, 20.4; LC-MS m/z calcd for $C_{29}H_{22}N_2O_4$ $[M+H]^+$ 462.51, found 463.1



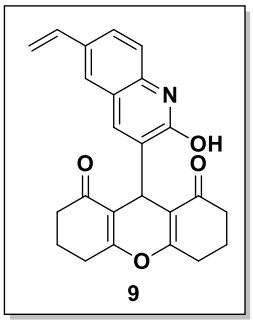
9-(2-hydroxy-6-((4-methylpyridin-3-yl)ethynyl)quinolin-3-yl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dionedione (8f) : Off-White solid (96 mg, 88%). Melting Point : 272.8 °C – 289.3 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.60 (s, 1H), 7.99-7.97 (m, 2H), 7.83-7.74 (m, 2H), 7.60 (d, J = 7.6 Hz, 1H), 7.27 (d, J = 8.0 Hz, 1H), 4.62 (s, 1H), 2.75-2.67 (m, 4H), 2.41-2.20 (m, 7H), 1.95-1.92 (m, 2H), 1.84-1.83 (m, 2H). ; ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.8, 166.2, 160.6, 138.8, 138.2, 134.7, 132.8, 131.6, 119.6, 115.4, 114.9, 113.0, 37.0, 30.0, 27.0, 20.4; LC-MS m/z calcd for $C_{30}H_{24}N_2O_4$ $[M+H]^+$ 476.53, found 477.1



9-(6-((5-fluoropyridin-3-yl)ethynyl)-2-hydroxyquinolin-3-yl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (8g) : Off-White solid (94 mg, 86%). Melting Point : 280.1 °C – 294 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.62 (s, 1H), 8.63 (s, 2H), 7.99-7.97 (m, 2H), 7.83 (s, 1H), 7.60 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 7.27 (d, J = 8.8 Hz, 1H), 4.61 (s, 1H), 2.59-2.50 (m, 4H), 2.33-2.28 (m, 4H), 1.96-1.90 (m, 2H), 1.87-1.79 (m, 2H). ; ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.8, 166.3, 160.6, 157.7, 148.4, 139.0, 138.2, 138.0, 137.7, 134.6, 132.8, 131.6, 125.6, 121.3, 119.6, 115.5, 114.4, 112.8, 93.7, 84.4, 36.9, 30.1, 27.0, 20.4 ; ^{19}F NMR (376.7 MHz, DMSO-d_6): δ -100.09 ; LC-MS m/z calcd for $C_{29}H_{21}FN_2O_4$ $[M+H]^+$ 480.50, found 480.9



methyl (3-((3-(1,8-dioxo-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-9-yl)-2-hydroxyquinolin-6-yl)ethynyl)phenyl) carbamate (8h) : Pale yellow solid (89 mg, 73%). Melting Point : 272.6 °C – 284.3 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.56 (s, 1H), 9.82 (s, 1H), 7.98 (s, 1H), 7.82 (s, 1H), 7.67 (s, 1H), 7.58 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 7.54-7.49 (m, 1H), 7.36-7.32 (m, 1H), 7.25 (d, J = 7.6 Hz, 1H), 7.17 (d, J = 6.4 Hz, 1H), 4.61 (s, 1H), 3.69 (s, 3H), 2.59-2.51 (m, 4H), 2.29-2.22 (m, 4H), 1.99-1.92 (m, 2H), 1.91-1.82 (m, 2H). ; ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.8, 166.3, 160.6, 154.4, 139.9, 138.6, 134.4, 132.8, 131.3, 129.7, 125.7, 123.2, 120.8, 119.7, 118.9, 115.4, 112.8, 52.2, 49.0, 36.9, 30.1, 27.0, 20.4 ; LC-MS m/z calcd for $C_{32}H_{26}N_2O_6$ $[M+H]^+$ 534.57, found 535.1



Synthesis of 9-(2-hydroxy-6-vinylquinolin-3-yl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (9) : A solution of 9-(6-bromo-2-hydroxyquinolin-3-yl) -3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione, **4** (0.1g, 0.227 mmol) in degassed N,N-dimethylformamide (5 mL) was sealed with a screw-cap septum, and then evacuated and backfilled with argon (this process was repeated a total of 2 times). Then, Tributyl vinyl tin (87 mg, 0.273 mmol) were added at room temperature, followed by the addition of Precatalyst, **1** (8.9 mg, 5 mol %) and the reaction was stirred at 60 °C for 3 h. After completion of the reaction monitored by TLC, ethyl acetate (10 mL) and water (10 mL) were added to the reaction mixture, and the aqueous phase was extracted with ethyl acetate (3 x 10 mL). The organic layers were combined, dried over Na_2SO_4, concentrated in

vacuo, and purified via the Biotage SP4 (Silica – packed 12 g snap cartridge column; 2-4% methanol/DCM) to provide the title compound (**9)** as Pale yellow solid (76 mg, 86%). Melting Point : 273.5 °C – 286.9 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.42 (s, 1H), 7.77 (s, 2H), 7.57 (d, J = 8.4 Hz, 1H), 7.20 (d, J = 8.4 Hz, 1H), 6.77-6.70 (m, 1H), 5.81 (d, J = 18.0 Hz, 1H), 5.21 (d, J = 10.8 Hz, 1H), 4.59 (s, 1H), 2.57-2.50 (m, 4H), 2.27-2.19 (m, 4H), 1.94-1.91 (m, 2H), 1.82-1.81 (m, 2H) ; ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.8, 166.2, 160.6, 138.9, 138.2, 136.4, 133.6, 131.1, 127.7, 125.8, 119.5, 115.1, 113.4, 112.9, 36.9, 30.2, 27.0, 20.4 , ; LC-MS m/z calcd for $C_{24}H_{21}NO_4$ $[M+H]^+$ 387.43, found 388.20.

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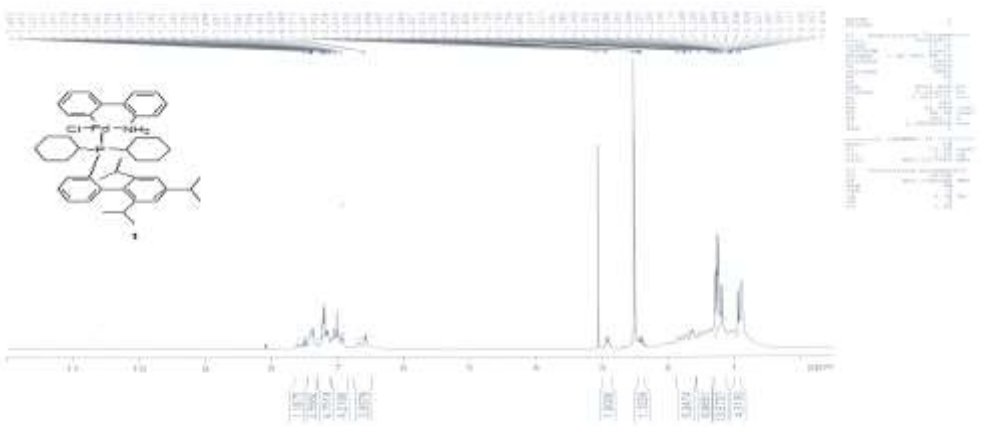
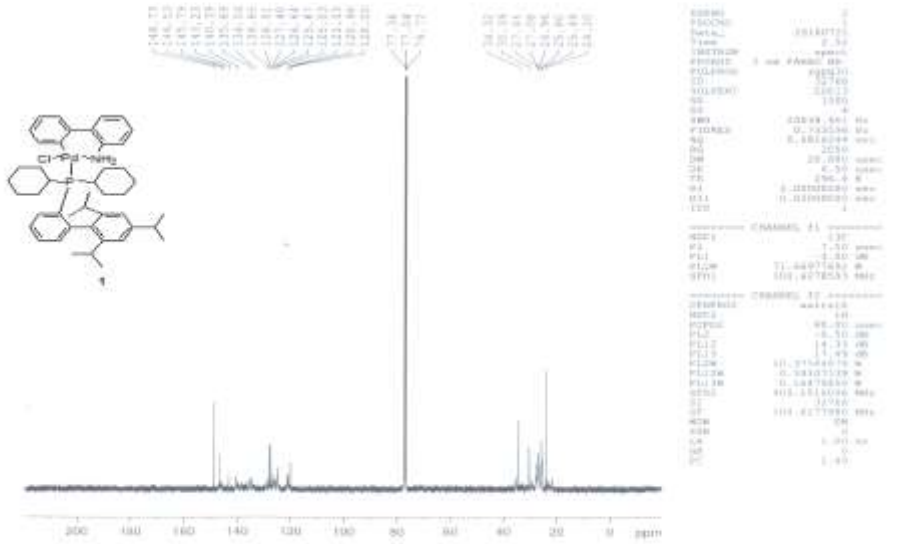
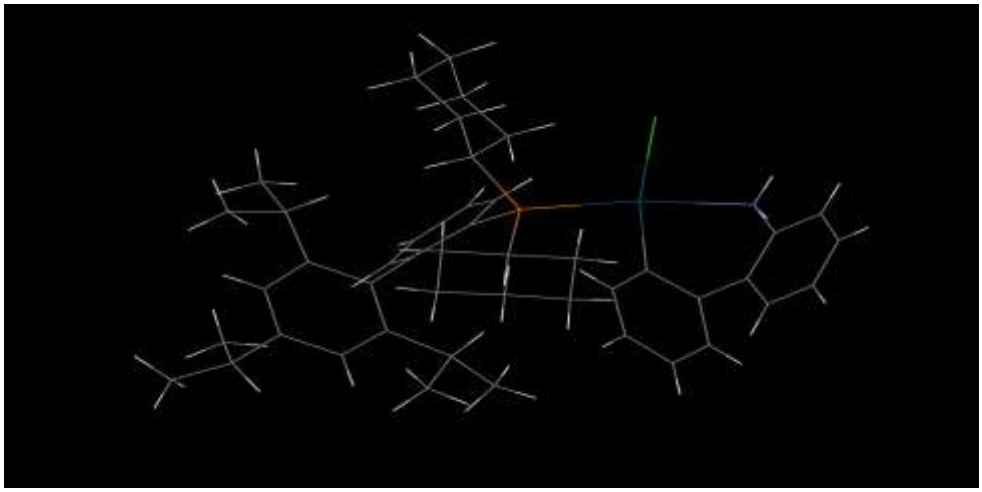
Copies of Analytical Data's:





XRD Analysis of Precatalyst **1**



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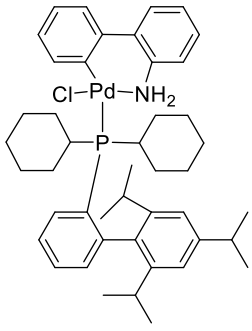
XRD Analysis of Precatalyst **1**



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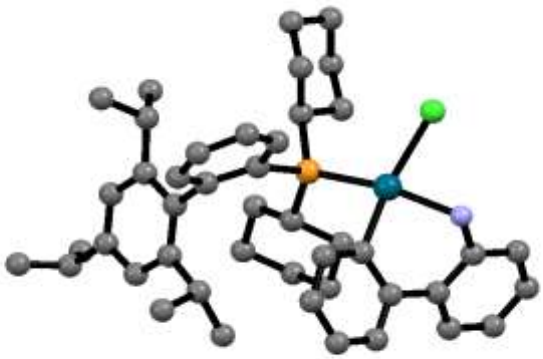


Table 1 Crystal data and structure refinement for red.

Identification code	red
Empirical formula	$C_{45}H_{59}ClNPPd$
Formula weight	786.75

Temperature/K	298(2)
Crystal system	triclinic
Space group	P-1
a/Å	10.2586(5)
b/Å	13.4187(12)
c/Å	15.8317(13)
α/°	96.297(7)
β/°	100.674(5)
γ/°	102.253(6)
Volume/$Å^3$	2067.5(3)
Z	2
$\rho_{calc}g/cm^3$	1.264
μ/mm^{-1}	0.583
F(000)	828.0
Crystal size/mm^3	0.21 × 0.23 × 0.22
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.084 to 50
Index ranges	-12 ≤ h ≤ 12, -15 ≤ k ≤ 15, -18 ≤ l ≤ 18
Reflections collected	14132
Independent reflections	7252 [R_{int} = 0.0535, R_{sigma} = 0.0793]
Data/restraints/parameters	7252/0/448
Goodness-of-fit on F^2	1.020
Final R indexes [I>=2σ (I)]	R_1 = 0.0517, wR_2 = 0.1117
Final R indexes [all data]	R_1 = 0.0688, wR_2 = 0.1229
Largest diff. peak/hole / e $Å^{-3}$	0.55/-0.50

Table 2 Fractional Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2\times10^3$) for red. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Pd01	7569.5(3)	4375.5(2)	6150.2(2)	37.33(12)
P1P	6468.3(9)	3058.3(8)	6760.7(6)	32.9(2)
Cl1C	8950.1(11)	3524.9(9)	5383.9(7)	56.1(3)
N1N	8741(3)	5782(3)	5895(2)	47.5(9)
C25C	4638(4)	2672(3)	6225(2)	32.3(8)
C19C	7022(3)	1832(3)	6666(2)	37.4(9)
C31C	3404(4)	2197(3)	7479(2)	36.7(9)
C26C	4457(4)	2682(3)	5323(2)	39.1(9)
C12C	6452(4)	5318(3)	6577(3)	43.1(10)
C17C	6637(4)	2608(3)	8532(2)	44.8(10)
C28C	2035(4)	2233(3)	5120(3)	44.1(10)
C18C	6713(4)	3460(3)	7956(2)	35.9(9)
C32C	3313(4)	1183(3)	7662(3)	44.4(10)

C30C	3463(3)	2387(3)	6565(2)	32.8(8)
C24C	8555(4)	1982(3)	7045(3)	43.9(10)
C29C	2191(4)	2204(3)	6004(3)	43.4(10)
C11C	5055(4)	5159(3)	6254(3)	52.8(12)
C1C	9441(4)	6366(3)	6730(3)	45.5(10)
C20C	6633(4)	1213(3)	5745(3)	45.4(10)
C13C	8049(4)	4290(3)	8311(2)	45.5(10)
C27C	3183(4)	2444(3)	4785(3)	46.6(11)
C21C	7049(4)	184(3)	5747(3)	54.0(12)
C37C	3396(4)	306(3)	6993(3)	53.5(12)
C7C	7160(5)	6275(4)	7099(3)	51.5(11)
C38C	3240(4)	4061(3)	7914(3)	48.2(11)
C36C	3237(4)	2964(3)	8098(3)	43.7(10)
C23C	8943(4)	951(4)	7048(3)	58.4(13)
C6C	8672(5)	6597(3)	7339(3)	49.7(11)
C2C	10850(5)	6668(4)	6938(3)	60.3(12)
C33C	3078(5)	984(4)	8478(3)	63.8(14)
C22C	8560(4)	335(4)	6144(3)	64.1(14)
C42C	4064(5)	4921(4)	8645(3)	68.3(14)
C14C	8181(5)	4717(4)	9270(3)	61.3(13)
C35C	3033(5)	2723(4)	8904(3)	60.2(13)
C16C	6776(5)	3047(4)	9487(3)	63.8(14)
C8C	6401(6)	6980(4)	7325(3)	69.2(15)
C41C	2007(5)	-369(4)	6549(3)	69.5(14)
C9C	5020(6)	6788(5)	7026(4)	77.4(17)
C40C	4331(5)	-365(4)	7380(3)	70.2(14)
C5C	9373(6)	7145(4)	8148(3)	66.9(14)
C34C	2940(5)	1731(5)	9095(3)	69.3(15)
C10C	4334(5)	5887(4)	6468(4)	73.2(16)
C43C	1773(5)	4183(4)	7677(4)	83.9(18)
C15C	8110(5)	3871(4)	9822(3)	67.2(14)
C3C	11508(6)	7193(4)	7759(4)	76.7(16)
C4C	10769(7)	7436(4)	8359(4)	82.3(17)
C45C	1350(13)	994(10)	9935(6)	303(10)
C39C	2720(8)	1497(6)	9996(4)	112(2)
C44C	3786(14)	1130(11)	10489(6)	300(10)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for red. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Pd01	38.25(19)	37.2(2)	44.6(2)	13.30(15)	20.19(14)	13.01(15)

P1P	29.1(5)	36.0(6)	36.1(5)	9.4(4)	10.6(4)	8.0(5)
Cl1C	64.8(7)	48.4(7)	72.1(7)	16.9(6)	43.9(6)	21.3(6)
N1N	55(2)	37(2)	62(2)	15.9(18)	30.7(18)	16.0(18)
C25C	36(2)	33(2)	31.4(19)	6.2(16)	8.1(16)	14.0(18)
C19C	32(2)	35(2)	47(2)	8.9(19)	11.2(17)	9.6(18)
C31C	32(2)	40(3)	41(2)	11.1(19)	13.1(17)	7.8(18)
C26C	37(2)	45(3)	40(2)	14.6(19)	10.8(18)	14(2)
C12C	55(3)	35(3)	52(2)	15(2)	31(2)	17(2)
C17C	37(2)	53(3)	41(2)	15(2)	4.6(18)	2(2)
C28C	40(2)	41(3)	46(2)	7(2)	-5.8(19)	11(2)
C18C	34(2)	44(3)	32.3(19)	8.0(18)	9.0(16)	11.1(19)
C32C	38(2)	50(3)	49(2)	15(2)	14.5(19)	11(2)
C30C	31(2)	30(2)	40(2)	9.1(17)	8.1(16)	11.5(17)
C24C	34(2)	43(3)	54(2)	5(2)	8.2(18)	11(2)
C29C	30(2)	42(3)	59(3)	12(2)	9.0(19)	6.0(19)
C11C	51(3)	44(3)	76(3)	25(2)	28(2)	20(2)
C1C	57(3)	29(2)	56(3)	14(2)	20(2)	11(2)
C20C	36(2)	46(3)	52(2)	3(2)	7.4(19)	10(2)
C13C	38(2)	47(3)	45(2)	6(2)	3.0(18)	3(2)
C27C	63(3)	45(3)	35(2)	9.9(19)	8(2)	19(2)
C21C	44(3)	42(3)	71(3)	-4(2)	6(2)	10(2)
C37C	51(3)	49(3)	68(3)	25(2)	22(2)	14(2)
C7C	68(3)	49(3)	55(3)	22(2)	38(2)	25(3)
C38C	45(2)	51(3)	52(3)	6(2)	17(2)	14(2)
C36C	33(2)	50(3)	47(2)	11(2)	10.1(18)	4(2)
C23C	41(3)	55(3)	80(3)	17(3)	4(2)	19(2)
C6C	66(3)	36(3)	58(3)	17(2)	29(2)	17(2)
C2C	60(3)	49(3)	76(3)	21(3)	24(3)	10(3)
C33C	65(3)	70(4)	68(3)	40(3)	27(3)	15(3)
C22C	48(3)	47(3)	91(4)	-10(3)	3(2)	20(2)
C42C	61(3)	67(4)	70(3)	-14(3)	9(3)	16(3)
C14C	48(3)	62(3)	59(3)	-4(2)	-6(2)	6(2)
C35C	65(3)	63(4)	56(3)	5(3)	30(2)	11(3)
C16C	58(3)	89(4)	46(3)	20(3)	12(2)	14(3)
C8C	92(4)	57(4)	81(4)	16(3)	51(3)	34(3)
C41C	59(3)	60(4)	87(4)	8(3)	14(3)	11(3)
C9C	88(4)	68(4)	115(5)	37(4)	69(4)	50(4)
C40C	69(3)	52(3)	101(4)	29(3)	28(3)	23(3)
C5C	90(4)	56(3)	57(3)	6(3)	26(3)	12(3)
C34C	72(3)	92(5)	53(3)	23(3)	32(3)	17(3)
C10C	66(3)	63(4)	117(5)	42(4)	48(3)	34(3)
C43C	61(3)	67(4)	123(5)	10(4)	9(3)	25(3)
C15C	60(3)	89(4)	44(3)	5(3)	-1(2)	12(3)

C3C	60(3)	66(4)	101(4)	34(3)	10(3)	2(3)
C4C	110(5)	67(4)	63(3)	12(3)	19(3)	5(4)
C45C	315(16)	354(18)	128(8)	-43(10)	145(10)	-208(14)
C39C	158(7)	119(6)	84(4)	46(4)	77(5)	30(5)
C44C	390(18)	550(30)	147(8)	231(13)	171(10)	320(20)

Table 4 Bond Lengths for red.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd01	P1P	2.2949(10)	C1C	C6C	1.402(5)
Pd01	Cl1C	2.4082(10)	C1C	C2C	1.381(6)
Pd01	N1N	2.134(3)	C20C	C21C	1.530(5)
Pd01	C12C	2.021(4)	C13C	C14C	1.533(5)
P1P	C25C	1.848(4)	C21C	C22C	1.522(5)
P1P	C19C	1.852(4)	C37C	C41C	1.512(6)
P1P	C18C	1.865(4)	C37C	C40C	1.542(5)
N1N	C1C	1.436(5)	C7C	C6C	1.482(6)
C25C	C26C	1.408(5)	C7C	C8C	1.405(6)
C25C	C30C	1.406(5)	C38C	C36C	1.532(6)
C19C	C24C	1.537(5)	C38C	C42C	1.522(6)
C19C	C20C	1.535(5)	C38C	C43C	1.529(5)
C31C	C32C	1.410(5)	C36C	C35C	1.391(6)
C31C	C30C	1.508(5)	C23C	C22C	1.510(6)
C31C	C36C	1.401(5)	C6C	C5C	1.389(6)
C26C	C27C	1.373(5)	C2C	C3C	1.384(7)
C12C	C11C	1.391(5)	C33C	C34C	1.370(7)
C12C	C7C	1.417(6)	C14C	C15C	1.506(6)
C17C	C18C	1.536(5)	C35C	C34C	1.384(7)
C17C	C16C	1.530(5)	C16C	C15C	1.528(6)
C28C	C29C	1.385(5)	C8C	C9C	1.366(7)
C28C	C27C	1.367(5)	C9C	C10C	1.382(7)
C18C	C13C	1.538(5)	C5C	C4C	1.368(7)
C32C	C37C	1.521(6)	C34C	C39C	1.540(7)
C32C	C33C	1.402(6)	C3C	C4C	1.373(7)
C30C	C29C	1.392(5)	C45C	C39C	1.404(11)
C24C	C23C	1.518(5)	C39C	C44C	1.430(10)
C11C	C10C	1.394(6)			

Table 5 Bond Angles for red.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°

P1P	Pd01	Cl1C	101.68(4)	C2C	C1C	N1N	120.4(4)
N1N	Pd01	P1P	166.36(10)	C2C	C1C	C6C	120.7(4)
N1N	Pd01	Cl1C	86.21(9)	C21C	C20C	C19C	110.5(3)
C12C	Pd01	P1P	90.89(12)	C14C	C13C	C18C	111.4(3)
C12C	Pd01	Cl1C	166.18(11)	C28C	C27C	C26C	120.6(4)
C12C	Pd01	N1N	82.64(15)	C22C	C21C	C20C	111.8(4)
C25C	P1P	Pd01	109.84(11)	C32C	C37C	C40C	112.6(4)
C25C	P1P	C19C	103.59(16)	C41C	C37C	C32C	112.6(3)
C25C	P1P	C18C	111.43(16)	C41C	C37C	C40C	109.8(4)
C19C	P1P	Pd01	117.38(13)	C12C	C7C	C6C	122.4(4)
C19C	P1P	C18C	104.17(16)	C8C	C7C	C12C	118.4(4)
C18C	P1P	Pd01	110.20(13)	C8C	C7C	C6C	119.0(5)
C1C	N1N	Pd01	105.9(2)	C42C	C38C	C36C	115.2(4)
C26C	C25C	P1P	111.0(3)	C42C	C38C	C43C	109.4(4)
C30C	C25C	P1P	131.2(3)	C43C	C38C	C36C	110.0(4)
C30C	C25C	C26C	117.8(3)	C31C	C36C	C38C	122.3(3)
C24C	C19C	P1P	112.5(3)	C35C	C36C	C31C	119.3(4)
C20C	C19C	P1P	114.6(2)	C35C	C36C	C38C	118.4(4)
C20C	C19C	C24C	110.3(3)	C22C	C23C	C24C	111.0(4)
C32C	C31C	C30C	118.1(3)	C1C	C6C	C7C	119.8(4)
C36C	C31C	C32C	120.1(3)	C5C	C6C	C1C	117.8(4)
C36C	C31C	C30C	121.1(3)	C5C	C6C	C7C	122.4(4)
C27C	C26C	C25C	121.9(4)	C1C	C2C	C3C	119.5(5)
C11C	C12C	Pd01	122.7(3)	C34C	C33C	C32C	122.7(5)
C11C	C12C	C7C	118.3(4)	C23C	C22C	C21C	111.5(4)
C7C	C12C	Pd01	117.9(3)	C15C	C14C	C13C	111.4(4)
C16C	C17C	C18C	111.7(4)	C34C	C35C	C36C	121.4(4)
C27C	C28C	C29C	118.4(3)	C15C	C16C	C17C	110.8(4)
C17C	C18C	P1P	117.7(3)	C9C	C8C	C7C	122.0(5)
C17C	C18C	C13C	109.3(3)	C8C	C9C	C10C	120.0(4)
C13C	C18C	P1P	110.9(3)	C4C	C5C	C6C	121.6(5)
C31C	C32C	C37C	122.3(4)	C33C	C34C	C35C	118.6(4)
C33C	C32C	C31C	117.8(4)	C33C	C34C	C39C	121.6(5)
C33C	C32C	C37C	119.9(4)	C35C	C34C	C39C	119.8(5)
C25C	C30C	C31C	127.3(3)	C9C	C10C	C11C	119.2(5)
C29C	C30C	C25C	118.4(3)	C14C	C15C	C16C	110.3(4)
C29C	C30C	C31C	114.2(3)	C4C	C3C	C2C	120.5(5)
C23C	C24C	C19C	111.1(3)	C5C	C4C	C3C	119.8(5)
C28C	C29C	C30C	122.8(4)	C45C	C39C	C34C	109.9(7)
C12C	C11C	C10C	121.9(5)	C45C	C39C	C44C	119.7(9)
C6C	C1C	N1N	118.9(4)	C44C	C39C	C34C	114.6(6)

Table 6 Torsion Angles for red.

A	**B**	**C**	**D**	**Angle/**°	**A**	**B**	**C**	**D**	**Angle/**°

Pd01	P1P	C25C	C26C	39.2(3)	C32C	C31C	C36C	C38C	-176.2(4)
Pd01	P1P	C25C	C30C	-140.6(3)	C32C	C31C	C36C	C35C	2.5(6)
Pd01	P1P	C19C	C24C	56.5(3)	C32C	C33C	C34C	C35C	0.1(7)
Pd01	P1P	C19C	C20C	-70.6(3)	C32C	C33C	C34C	C39C	-178.4(5)
Pd01	P1P	C18C	C17C	-153.5(2)	C30C	C25C	C26C	C27C	1.3(5)
Pd01	P1P	C18C	C13C	-26.7(3)	C30C	C31C	C32C	C37C	5.4(5)
Pd01	N1N	C1C	C6C	-57.0(4)	C30C	C31C	C32C	C33C	-171.8(3)
Pd01	N1N	C1C	C2C	121.1(3)	C30C	C31C	C36C	C38C	-5.9(5)
Pd01	C12C	C11C	C10C	-171.3(3)	C30C	C31C	C36C	C35C	172.8(4)
Pd01	C12C	C7C	C6C	-0.1(5)	C24C	C19C	C20C	C21C	55.6(4)
Pd01	C12C	C7C	C8C	173.6(3)	C24C	C23C	C22C	C21C	-55.8(5)
P1P	C25C	C26C	C27C	-178.6(3)	C29C	C28C	C27C	C26C	-3.9(6)
P1P	C25C	C30C	C31C	-8.1(6)	C11C	C12C	C7C	C6C	-168.5(4)
P1P	C25C	C30C	C29C	175.3(3)	C11C	C12C	C7C	C8C	5.2(6)
P1P	C19C	C24C	C23C	173.7(3)	C1C	C6C	C5C	C4C	-1.3(7)
P1P	C19C	C20C	C21C	-176.2(3)	C1C	C2C	C3C	C4C	-1.6(7)
P1P	C18C	C13C	C14C	173.4(3)	C20C	C19C	C24C	C23C	-56.9(4)
N1N	C1C	C6C	C7C	-2.6(6)	C20C	C21C	C22C	C23C	55.2(5)
N1N	C1C	C6C	C5C	178.7(4)	C13C	C14C	C15C	C16C	-57.2(5)
N1N	C1C	C2C	C3C	-177.2(4)	C27C	C28C	C29C	C30C	0.5(6)
C25C	P1P	C19C	C24C	177.7(3)	C37C	C32C	C33C	C34C	-177.4(4)
C25C	P1P	C19C	C20C	50.6(3)	C7C	C12C	C11C	C10C	-3.5(6)
C25C	P1P	C18C	C17C	84.3(3)	C7C	C6C	C5C	C4C	-180.0(4)
C25C	P1P	C18C	C13C	-148.9(2)	C7C	C8C	C9C	C10C	-1.4(8)
C25C	C26C	C27C	C28C	3.0(6)	C38C	C36C	C35C	C34C	176.2(4)
C25C	C30C	C29C	C28C	3.7(6)	C36C	C31C	C32C	C37C	176.0(3)
C19C	P1P	C25C	C26C	-86.9(3)	C36C	C31C	C32C	C33C	-1.2(6)
C19C	P1P	C25C	C30C	93.2(4)	C36C	C31C	C30C	C25C	98.1(4)
C19C	P1P	C18C	C17C	-26.8(3)	C36C	C31C	C30C	C29C	-85.2(4)
C19C	P1P	C18C	C13C	100.0(3)	C36C	C35C	C34C	C33C	1.2(7)
C19C	C24C	C23C	C22C	56.9(5)	C36C	C35C	C34C	C39C	179.8(5)
C19C	C20C	C21C	C22C	-55.0(5)	C6C	C1C	C2C	C3C	0.8(6)
C31C	C32C	C37C	C41C	-99.8(5)	C6C	C7C	C8C	C9C	171.0(4)
C31C	C32C	C37C	C40C	135.3(4)	C6C	C5C	C4C	C3C	0.5(8)
C31C	C32C	C33C	C34C	-0.1(6)	C2C	C1C	C6C	C7C	179.4(4)
C31C	C30C	C29C	C28C	-173.3(4)	C2C	C1C	C6C	C5C	0.6(6)
C31C	C36C	C35C	C34C	-2.5(7)	C2C	C3C	C4C	C5C	1.0(8)
C26C	C25C	C30C	C31C	172.1(4)	C33C	C32C	C37C	C41C	77.3(5)
C26C	C25C	C30C	C29C	-4.5(5)	C33C	C32C	C37C	C40C	-47.6(5)
C12C	C11C	C10C	C9C	-0.8(7)	C33C	C34C	C39C	C45C	-78.7(9)
C12C	C7C	C6C	C1C	38.2(6)	C33C	C34C	C39C	C44C	59.4(11)
C12C	C7C	C6C	C5C	-143.2(4)	C42C	C38C	C36C	C31C	-136.2(4)
C12C	C7C	C8C	C9C	-2.9(7)	C42C	C38C	C36C	C35C	45.1(5)

C17C	C18C	C13C	C14C	-55.3(4)	C35C	C34C	C39C	C45C	102.8(9)
C17C	C16C	C15C	C14C	57.0(5)	C35C	C34C	C39C	C44C	-119.1(9)
C18C	P1P	C25C	C26C	161.6(3)	C16C	C17C	C18C	P1P	-176.8(3)
C18C	P1P	C25C	C30C	-18.2(4)	C16C	C17C	C18C	C13C	55.6(4)
C18C	P1P	C19C	C24C	-65.6(3)	C8C	C7C	C6C	C1C	-135.5(4)
C18C	P1P	C19C	C20C	167.3(3)	C8C	C7C	C6C	C5C	43.2(6)
C18C	C17C	C16C	C15C	-57.0(5)	C8C	C9C	C10C	C11C	3.3(8)
C18C	C13C	C14C	C15C	57.3(5)	C43C	C38C	C36C	C31C	99.7(5)
C32C	C31C	C30C	C25C	-91.3(5)	C43C	C38C	C36C	C35C	-79.0(5)
C32C	C31C	C30C	C29C	85.3(4)					

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for red.

Atom	***x***	***y***	***z***	**U(eq)**
H1NA	9337	5655	5579	57
H1NB	8199	6126	5607	57
H19C	6542	1399	7027	45
H26C	5223	2854	5084	47
H17A	5771	2105	8328	54
H17B	7361	2257	8483	54
H28C	1171	2112	4763	53
H18C	5973	3794	8034	43
H24A	9078	2395	6700	53
H24B	8779	2351	7634	53
H29C	1412	2056	6233	52
H11C	4589	4550	5884	63
H20A	5655	1085	5528	54
H20B	7085	1610	5360	54
H13A	8819	3995	8253	55
H13B	8070	4850	7971	55
H27C	3100	2426	4189	56
H21A	6513	-244	6076	65
H21B	6852	-174	5155	65
H37C	3800	621	6543	64
H38C	3640	4153	7403	58
H23A	9919	1068	7269	70
H23B	8480	562	7433	70
H2C	11353	6520	6529	72
H33C	3014	318	8607	77
H22A	8771	-334	6170	77
H22B	9099	691	5776	77
H42A	3654	4887	9142	102
H42B	4077	5577	8454	102
H42C	4982	4841	8799	102
H14A	9045	5222	9479	74

H14B	7453	5063	9322	74
H35C	2959	3239	9322	72
H16A	6010	3346	9545	77
H16B	6759	2494	9834	77
H8C	6851	7597	7690	83
H41A	1528	-615	6980	104
H41B	2117	-946	6177	104
H41C	1495	25	6209	104
H9C	4542	7264	7197	93
H40A	5190	71	7695	105
H40B	4481	-825	6919	105
H40C	3904	-759	7768	105
H5C	8882	7318	8557	80
H10C	3403	5768	6239	88
H43A	1286	3701	7165	126
H43B	1784	4873	7565	126
H43C	1330	4051	8150	126
H15A	8162	4159	10421	81
H15B	8879	3560	9809	81
H3C	12457	7382	7906	92
H4C	11216	7799	8907	99
H45A	774	1241	9498	455
H45B	1107	1133	10486	455
H45C	1234	264	9781	455
H39C	2804	2181	10322	134
H44A	4006	595	10127	451
H44B	3488	860	10976	451
H44C	4581	1689	10695	451

Experimental

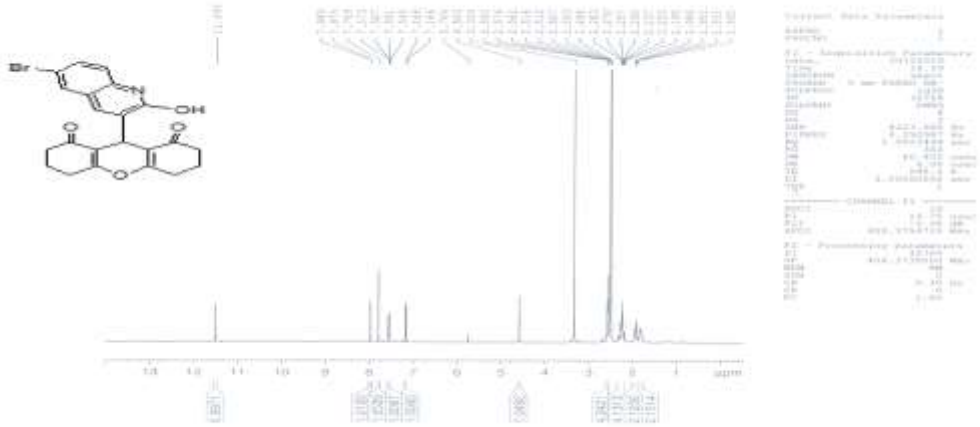
Single crystals of $C_{45}H_{59}ClNPPd$ [red] were []. A suitable crystal was selected and [] on an Xcalibur, Eos, Nova diffractometer. The crystal was kept at 298(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

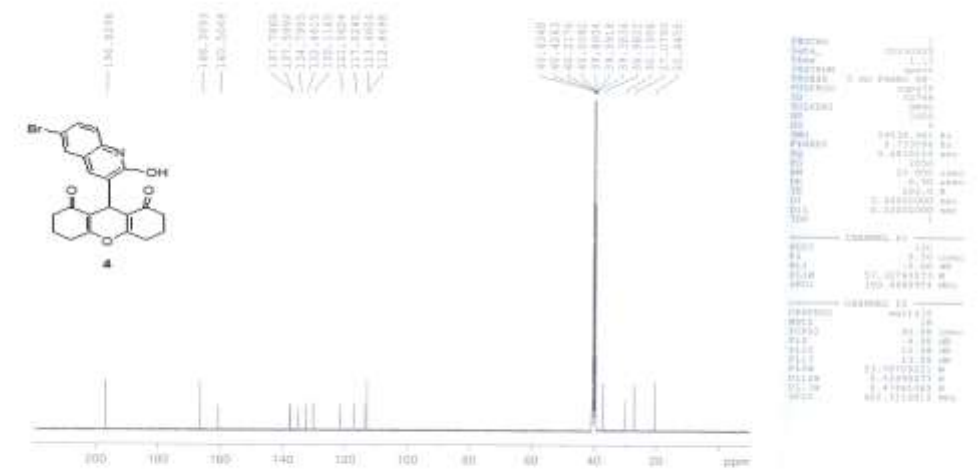
1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

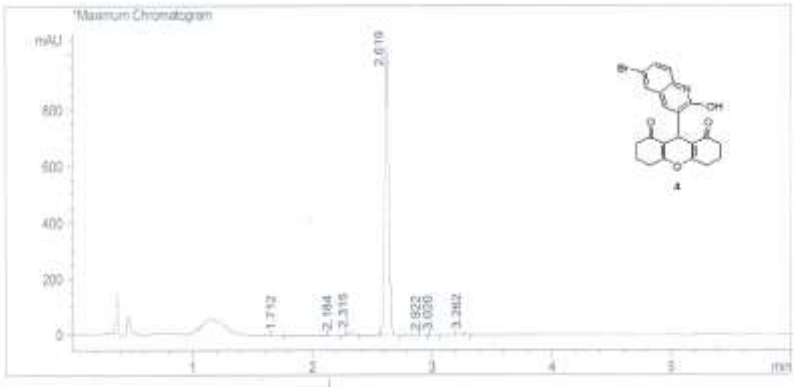
Crystal structure determination of [red]

Crystal Data for $C_{45}H_{59}ClNPPd$ (M =786.75 g/mol): triclinic, space group P-1 (no. 2), a = 10.2586(5) Å, b = 13.4187(12) Å, c = 15.8317(13) Å, α = 96.297(7)°, β = 100.674(5)°, γ = 102.253(6)°, V = 2067.5(3) $Å^3$, Z = 2, T = 298(2) K, μ(MoKα) = 0.583 mm^{-1}, $Dcalc$ = 1.264 g/cm^3, 14132 reflections measured (5.084° ≤ 2Θ ≤ 50°),

7252 unique (R_{int} = 0.0535, R_{sigma} = 0.0793) which were used in all calculations. The final R_1 was 0.0517 (I > 2σ(I)) and wR_2 was 0.1229 (all data).



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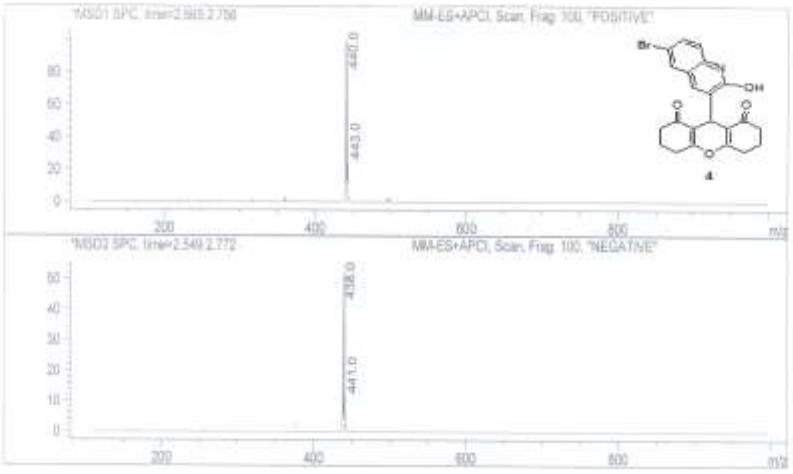
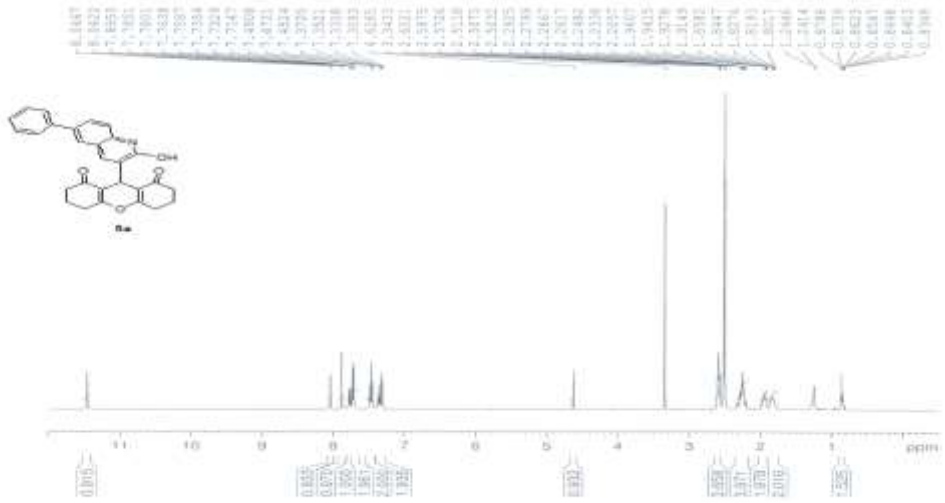
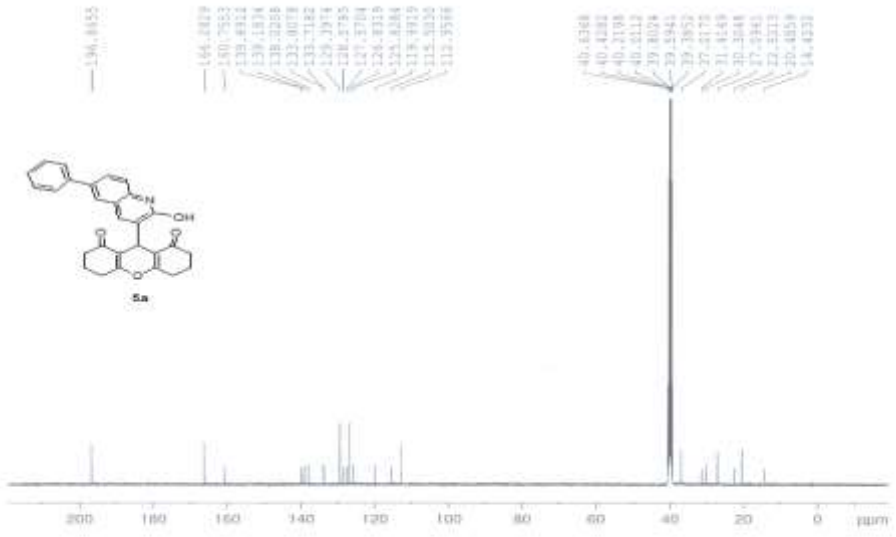
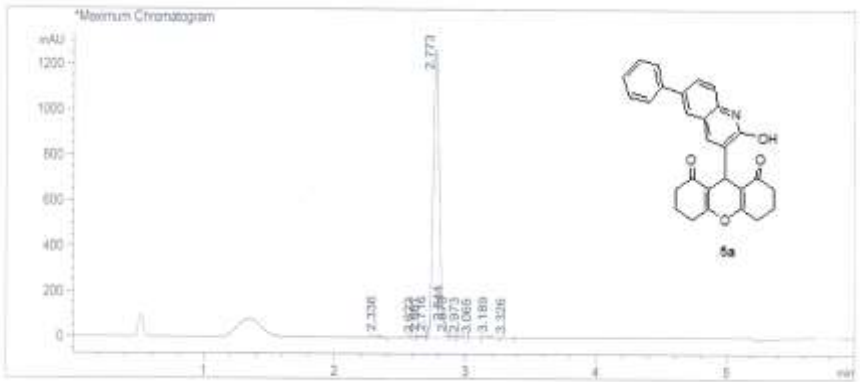
mAU
800
600
400
200
0
2.619
1.712
2.164
2.315
2.822
3.026
3.262
1
2
3
4
5
min
Br
OH
O
O
O
4

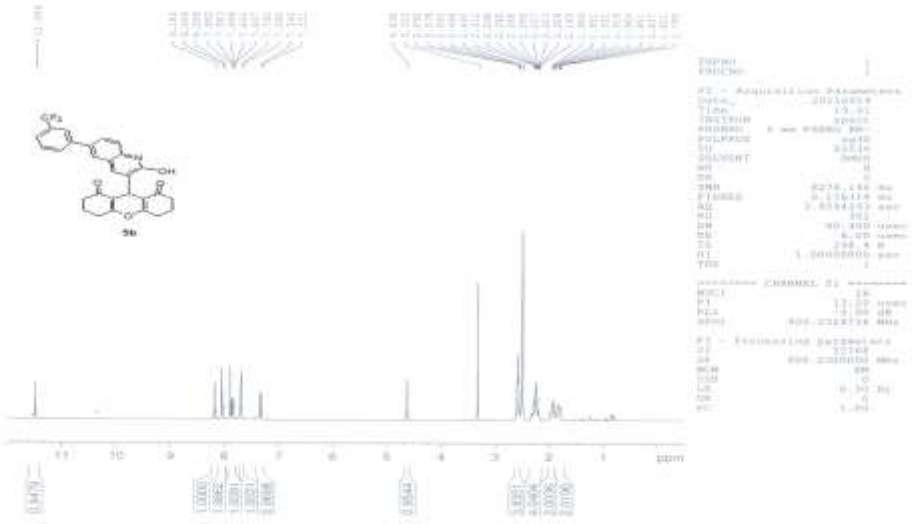

*MSD1 SPC, time=2.663:2.756
MM-ES+APCI, Scan, Frag: 100, "POSITIVE"
440.0
443.0
80
60
40
20
0
200
400
600
800
m/z
Br
OH
O
O
O
4
*MSD2 SPC, time=2.549:2.772
MM-ES+APCI, Scan, Frag: 100, "NEGATIVE"
438.0
441.0
50
40
30
20
10
0
200
400
600
800
m/z

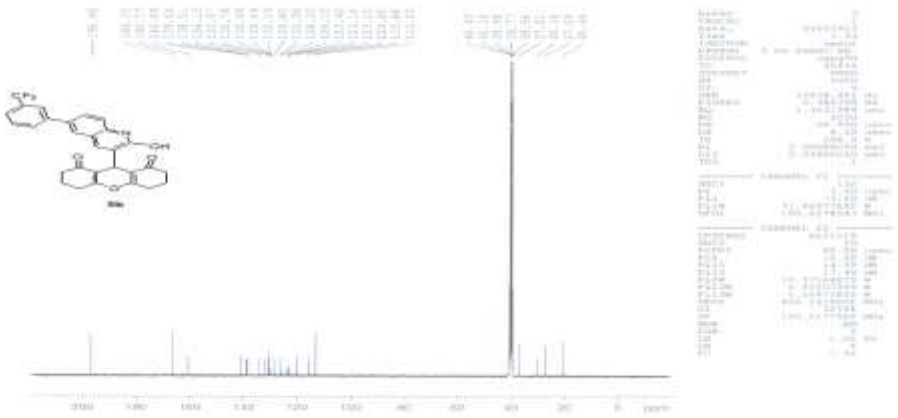


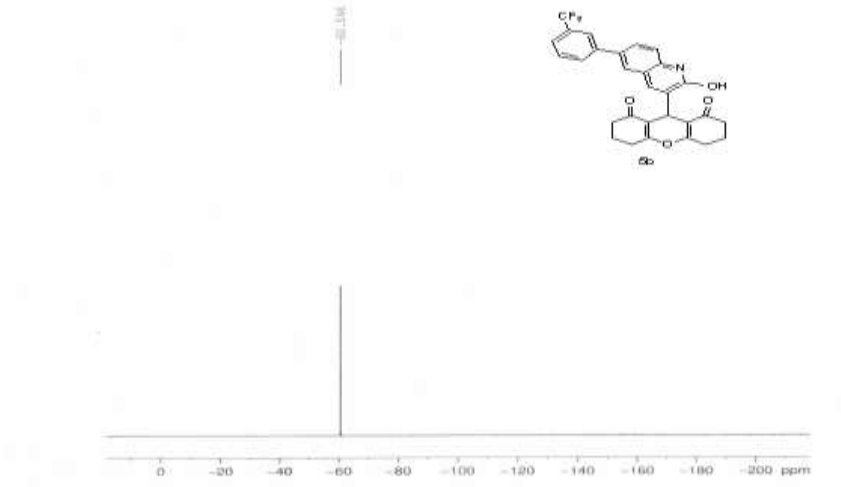


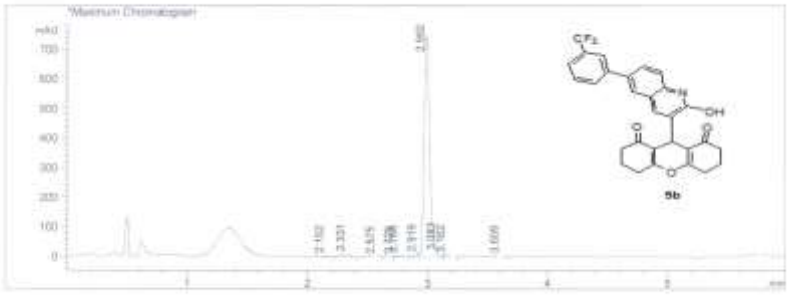

*Maximum Chromatogram
mAU
2.777
2.336
5a

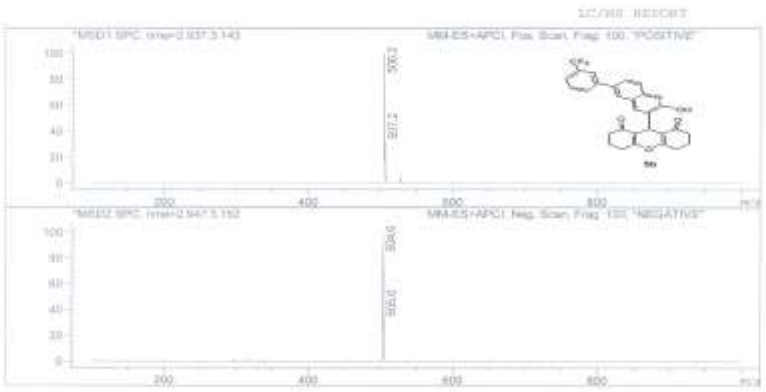

*MSD1 SPC, time=2.769:2.975
MM-ES+APCI, Pos, Scan, Frag: 100, "POSITIVE"
436.2
439.2
897.2
5a
*MSD2 SPC, time=2.778:2.947
MM-ES+APCI, Neg, Scan, Frag: 100, "NEGATIVE"
436.2
437.2

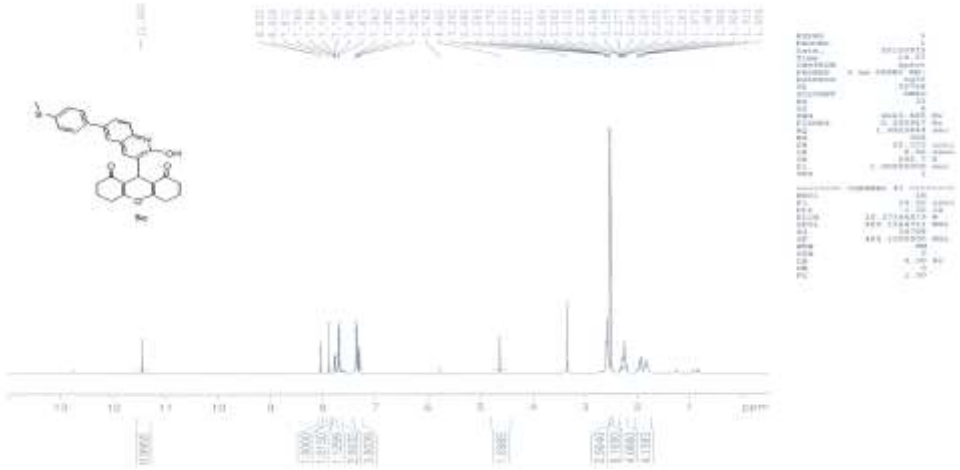


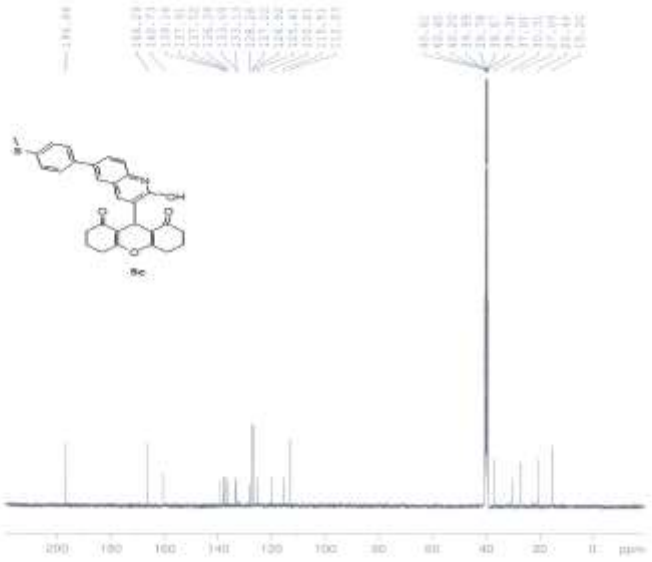



CF3
N
OH
O
O
O
5b
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200 ppm

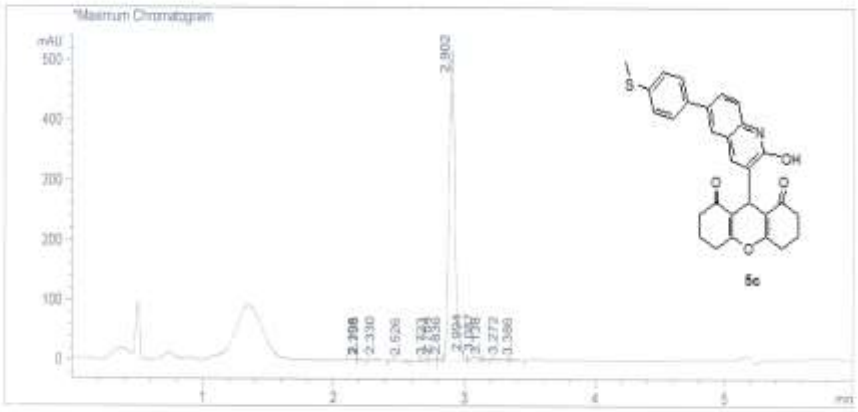

Maximum Chromatogram
CF3
N
OH
O
O
O
5b


MM-ES+APCI, Pos, Scan, Frag: 100, "POSITIVE"
CF3
N
OH
O
O
O
5b
MM-ES+APCI, Neg, Scan, Frag: 100, "NEGATIVE"

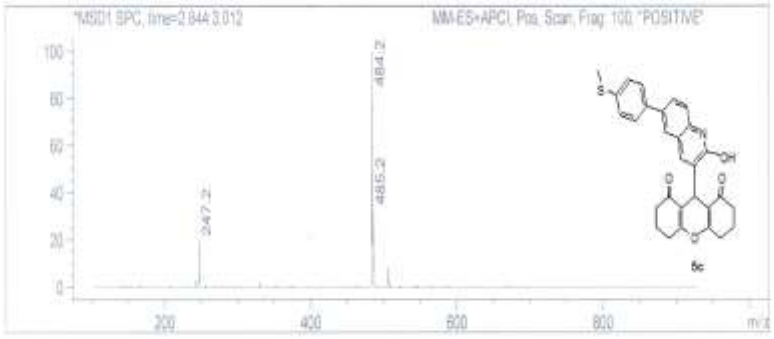


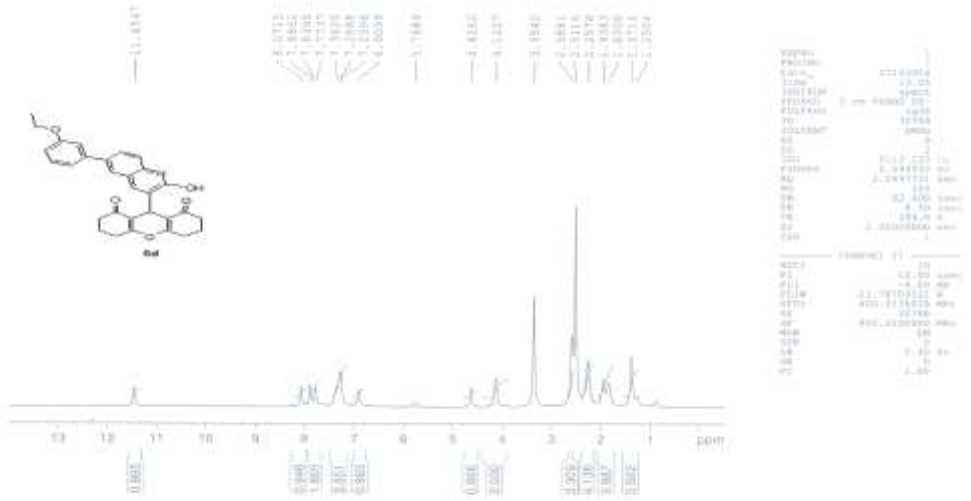


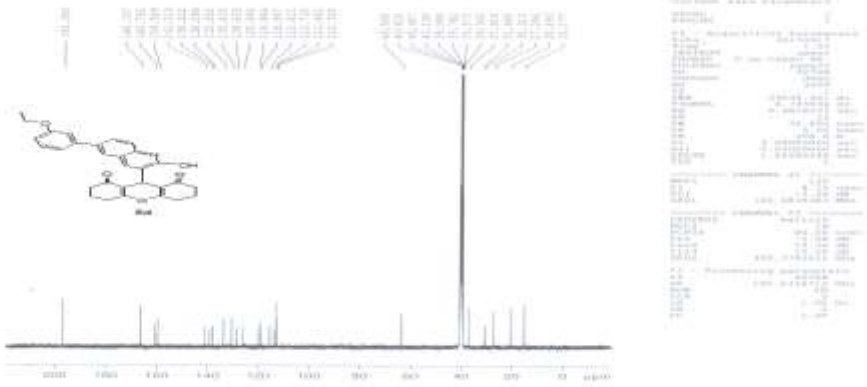
LC/MS REPORT



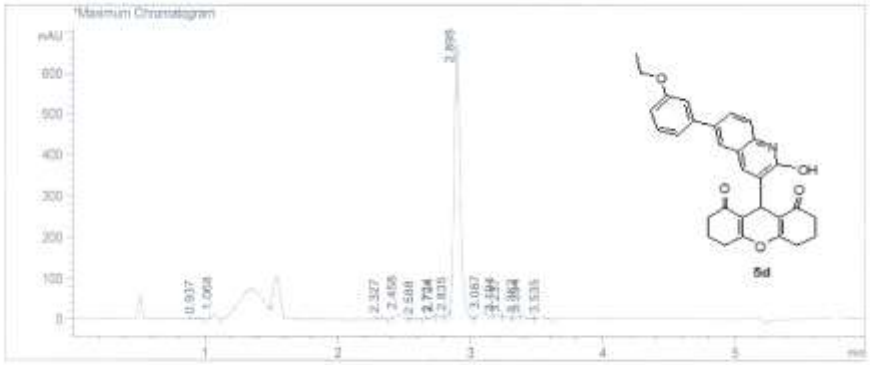
LC/MS REPORT

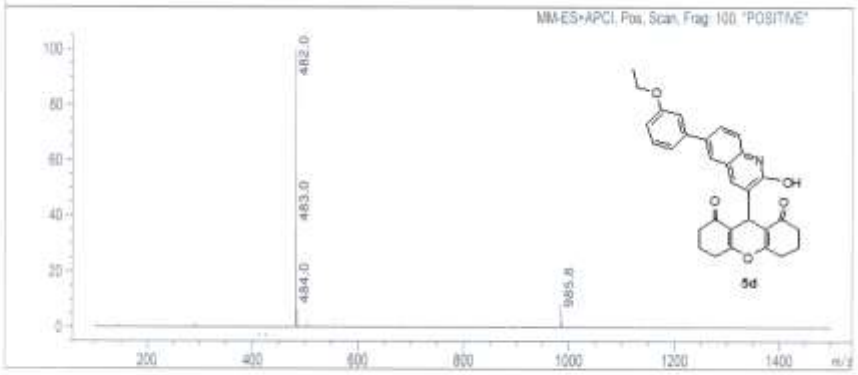


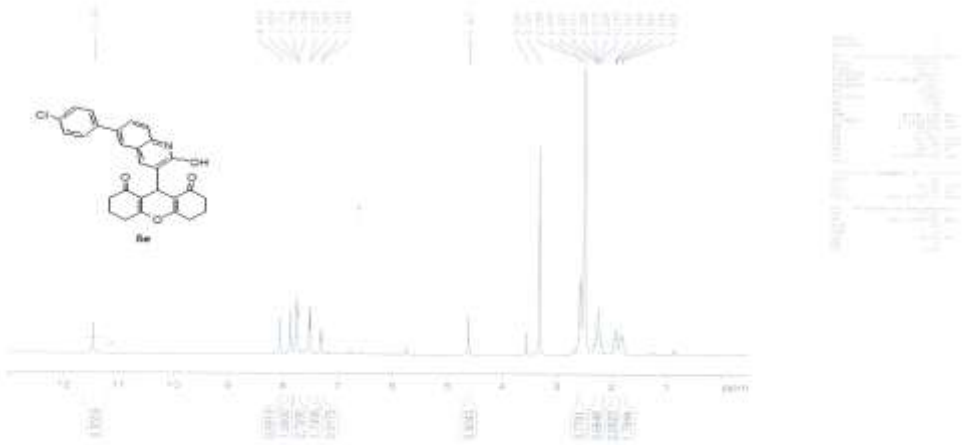


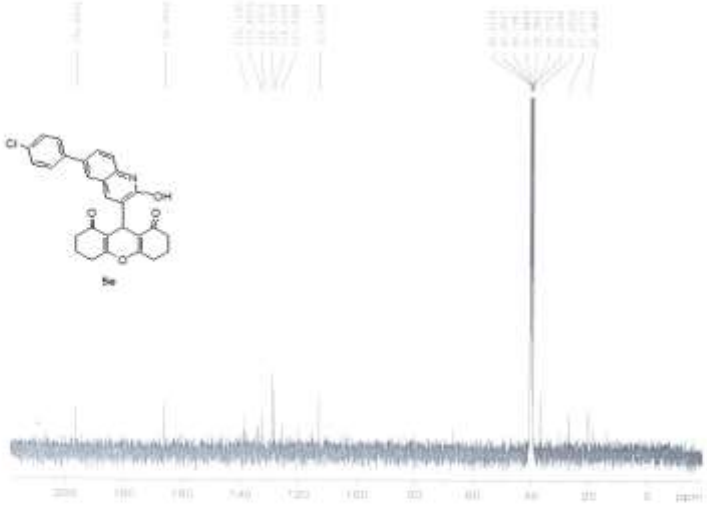


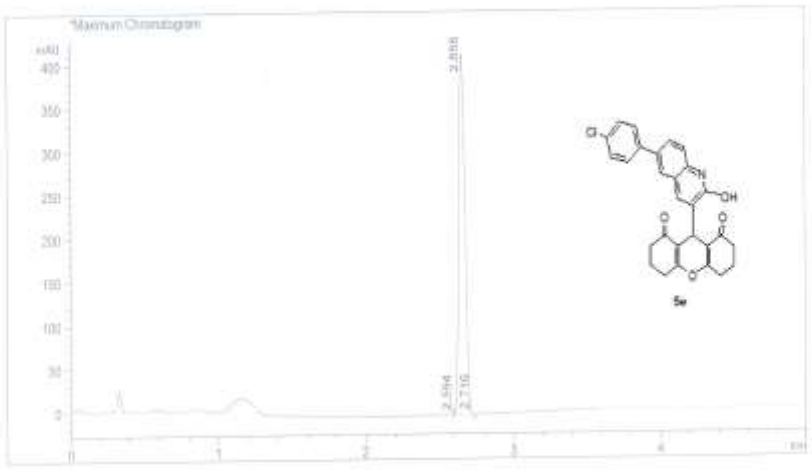
LC/MS REPORT

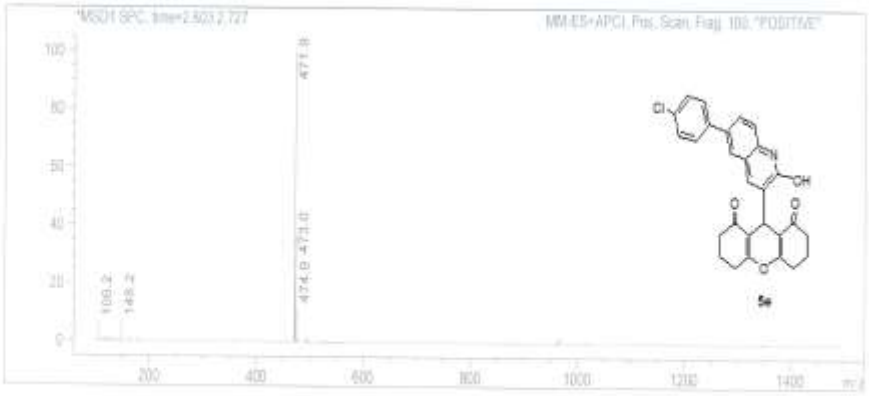

*Maximum Chromatogram
mAU
2.895
0.917
1.058
2.327
2.456
2.588
2.734
2.839
3.067
5.535
5d
min

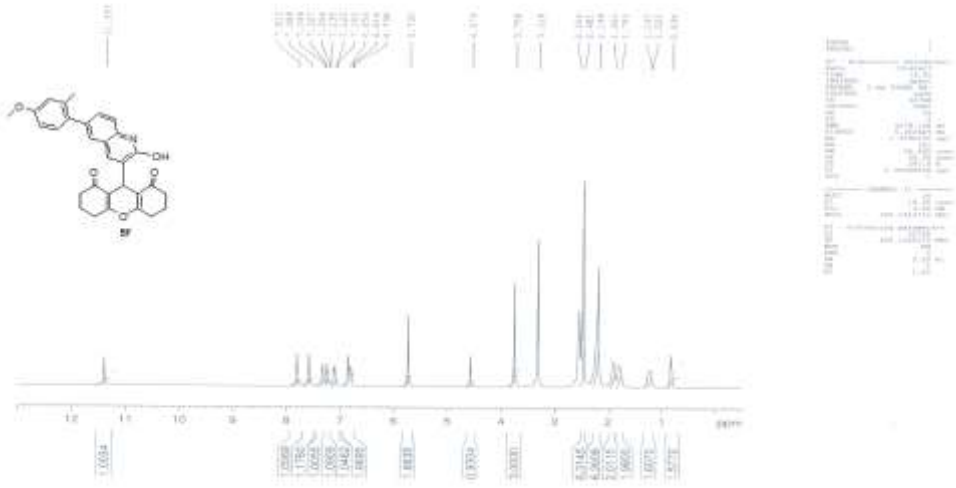

MM-ES+APCI, Pos, Scan, Frag: 100, "POSITIVE"
482.0
483.0
484.0
985.8
5d
m/z

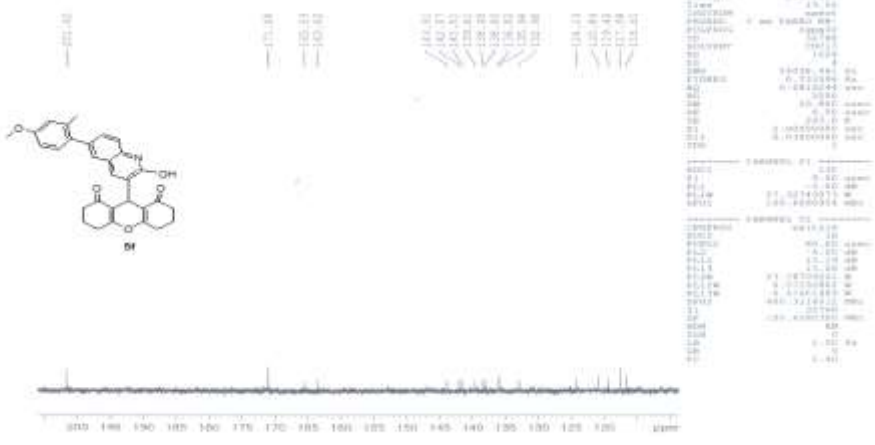


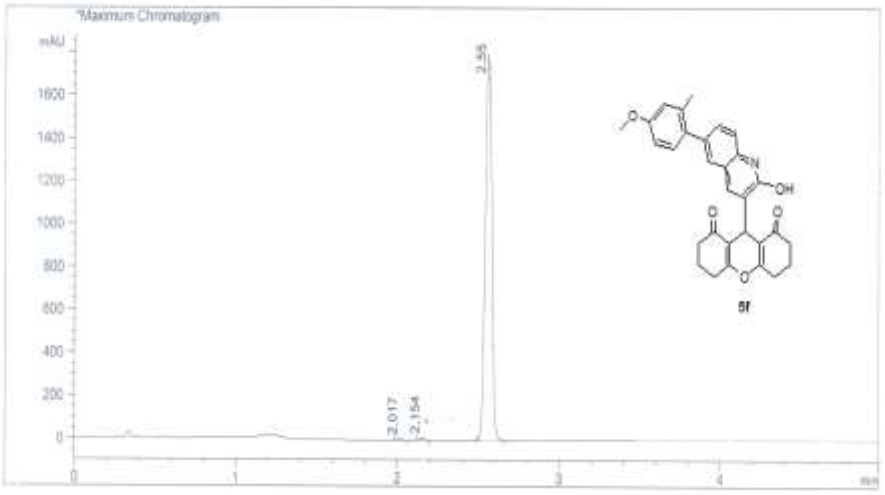


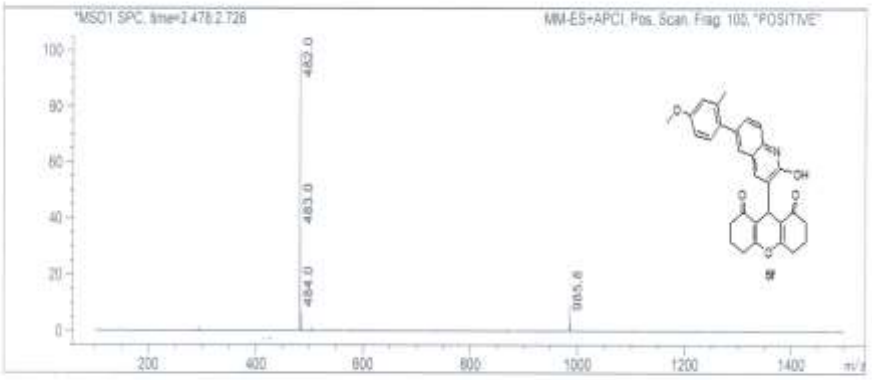

Maximum Chromatogram
mAU
400
350
300
250
200
150
100
50
0
2.866
2.544
2.710
0
1
2
3
4
min
Cl
N
OH
O
O
O
5e

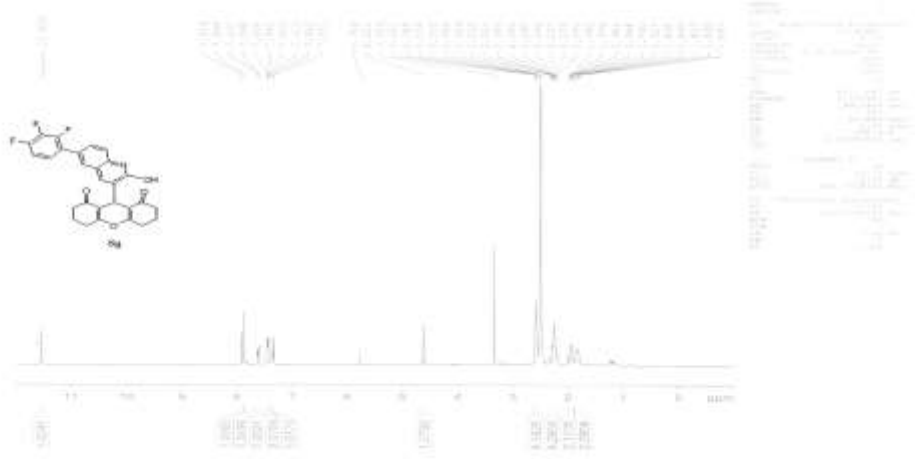

MSD1 SPC, time=2.503:2.727
MM-ES+APCI, Pos, Scan, Frag: 100, "POSITIVE"
100
80
60
40
20
0
471.8
474.0
473.0
109.2
149.2
200
400
600
800
1000
1200
1400
m/z
Cl
N
OH
O
O
O
5e

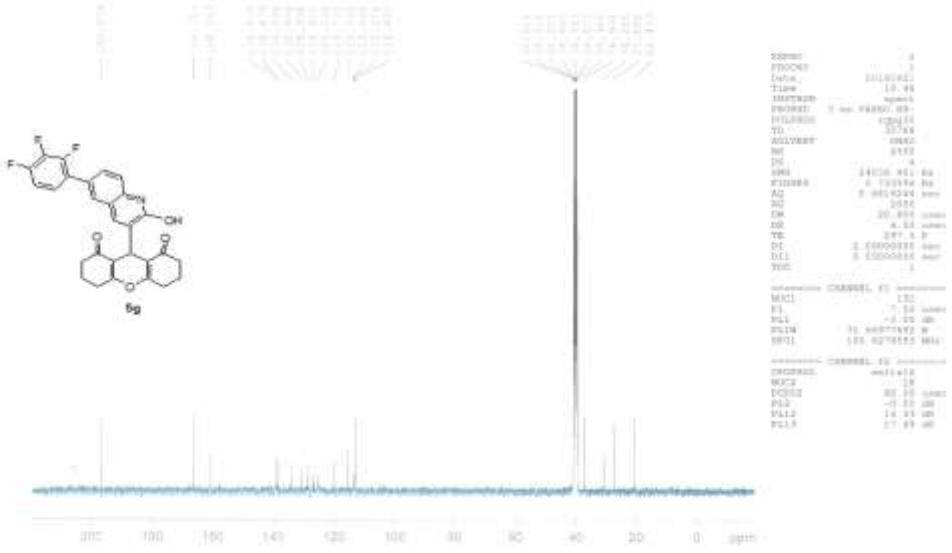


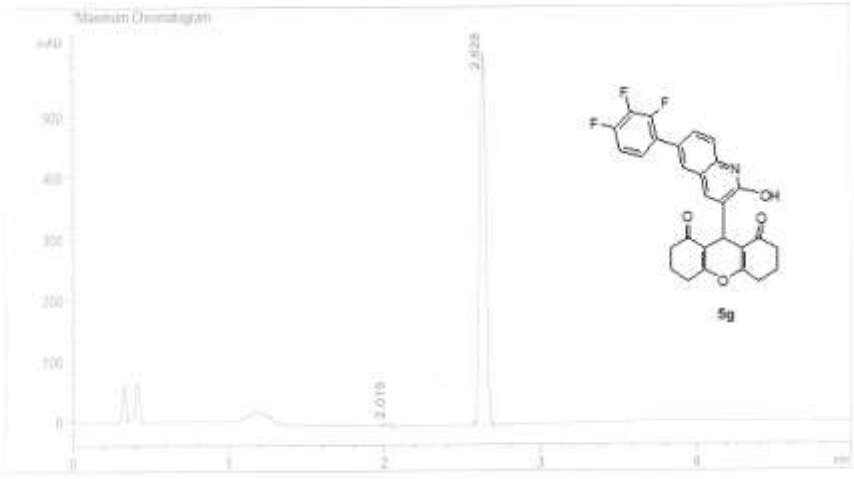


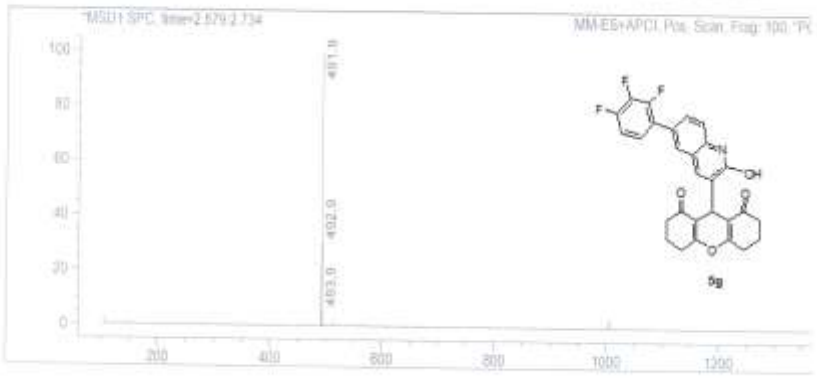

*Maximum Chromatogram
mAU
1800
1600
1400
1200
1000
800
600
400
200
0
2.017
2.154
2.55
0
1
2
3
4
min
OH
O
O
O
O
5f

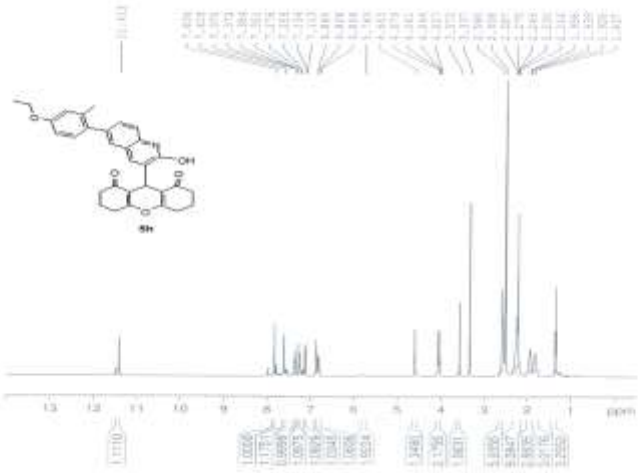

*MSD1 SPC, time=2.478:2.726
MM-ES+APCI, Pos, Scan, Frag: 100, "POSITIVE"
100
90
80
60
40
20
0
482.0
483.0
484.0
965.8
200
400
600
800
1000
1200
1400
m/z
OH
O
O
O
O
5f

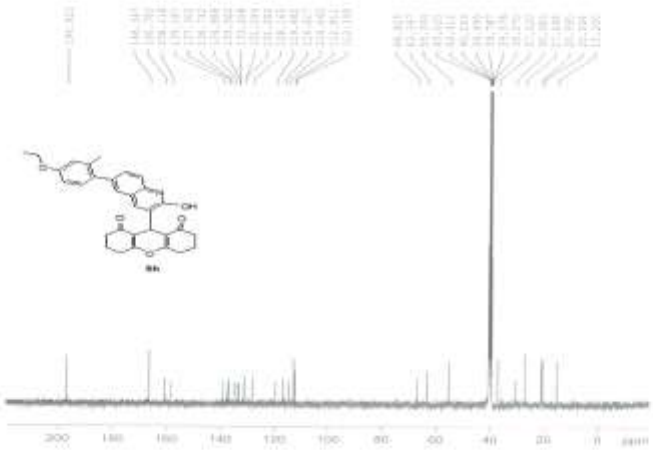


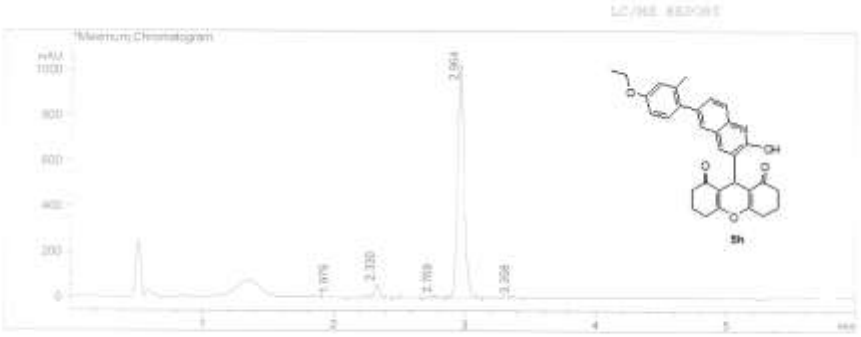


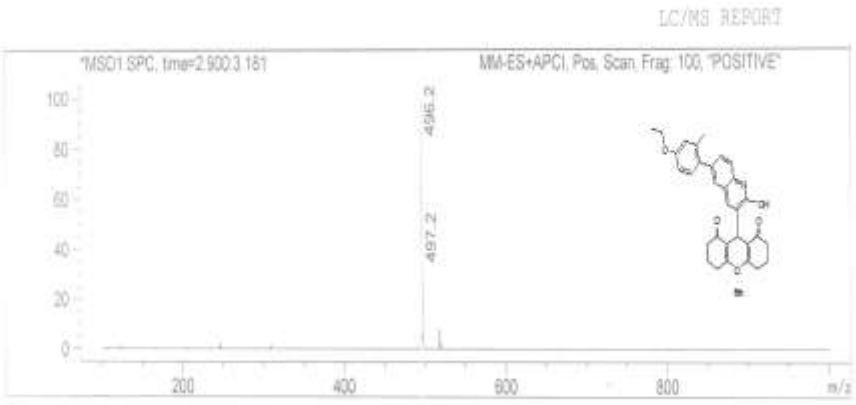

Maximum Chromatogram
2.019
2.628
5g

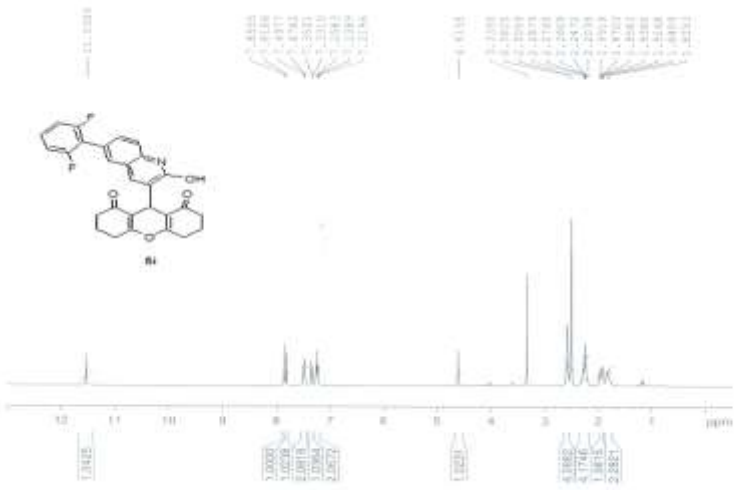

MM-ES+APCI Pos. Scan Frag: 100 "Pi
491.0
402.0
403.0
5g

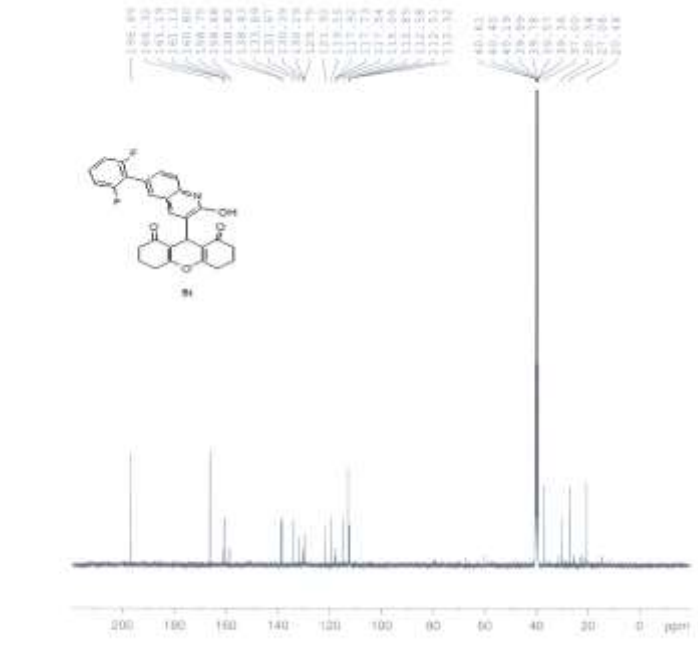


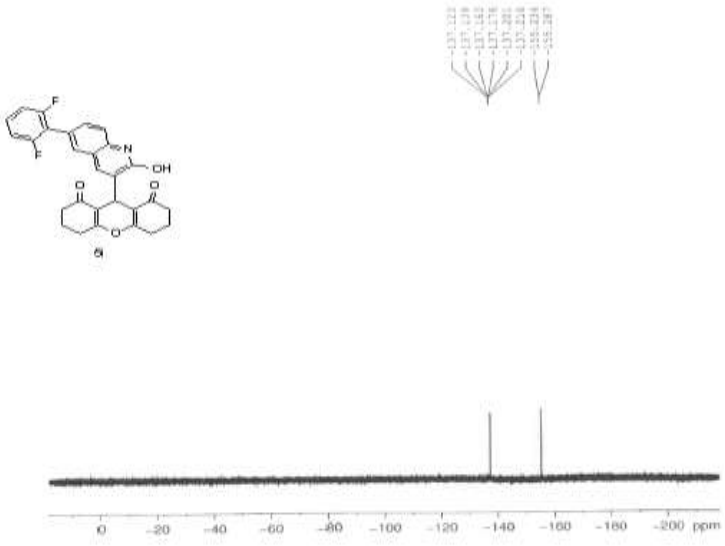


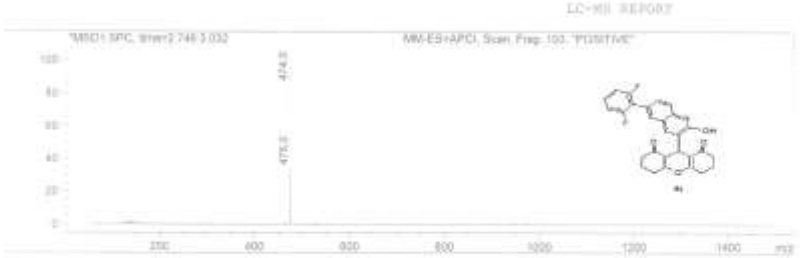

LC/MS REPORT
*Maximum Chromatogram
2.964
1.976
2.330
2.769
3.356
5h


LC/MS REPORT
*MSD1 SPC, time=2.900:3.181
MM-ES+APCI, Pos, Scan, Frag: 100, "POSITIVE"
496.2
497.2
100
80
60
40
20
0
200
400
600
800
m/z
5h





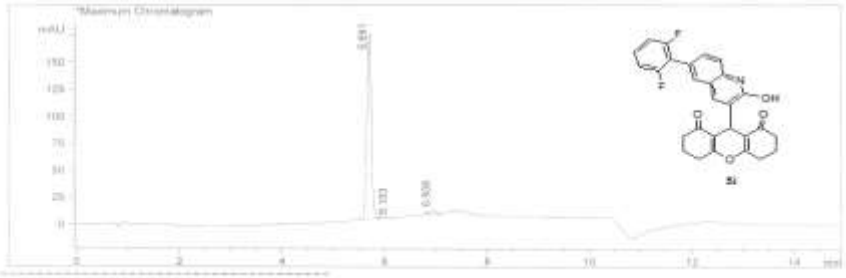

F
F
N
OH
O
O
O
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200 ppm



Formatted: Left, Tab stops: 12.99 cm, Left + Not at 14.38 cm

HPLC REPORT

```
Method info:COLUMN:Atlantis dC18(150X4.6mm)5u
            MOBILE PHASE A:0.1%TFA in water
            MOBILE PHASE B:Methanol
            FLOW:1.0mL/min
            TIME   %B
            00     05
            06     100
            09     100
            11     05
            13     05
```



Peak No.	RT min	Area	Area %
1	5.69	1018.73	97.086
2	6.10	4.81	0.459
3	6.94	25.74	2.455

```
***End of report***
```

This sample was measured on an Autopol V, serial number 80105,
manufactured by Rudolph Research Analytical, Hackettstown, NJ, USA.

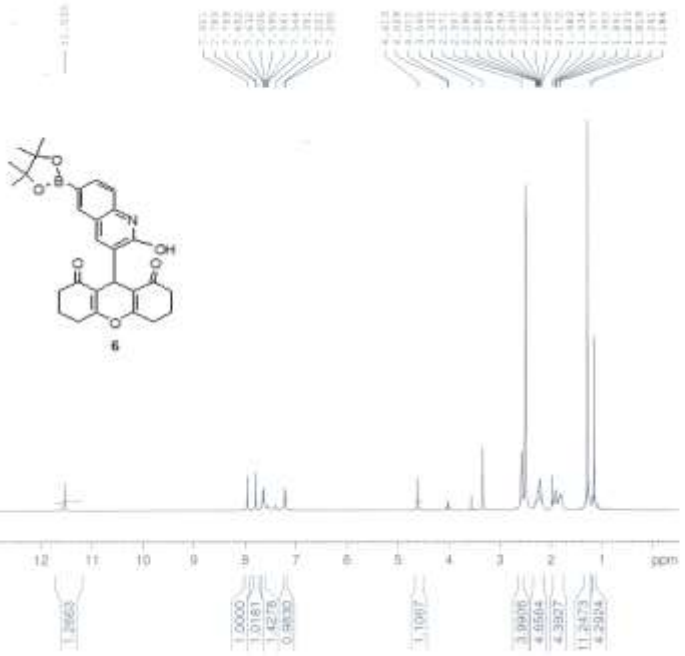
Set Temp : Off
Temp Corr: Off

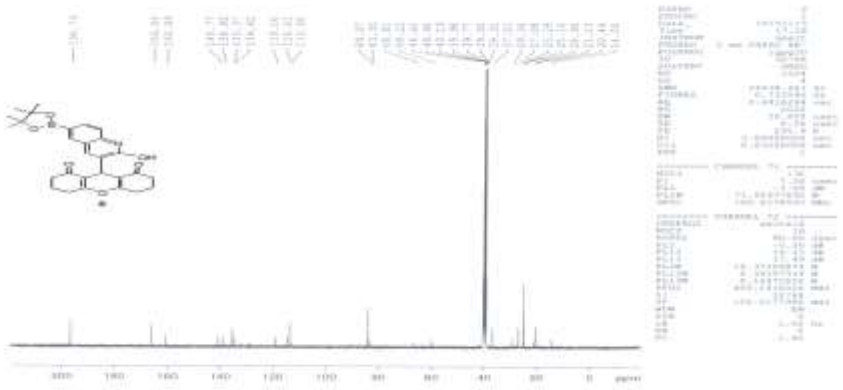
Operator: ANALYTICAL

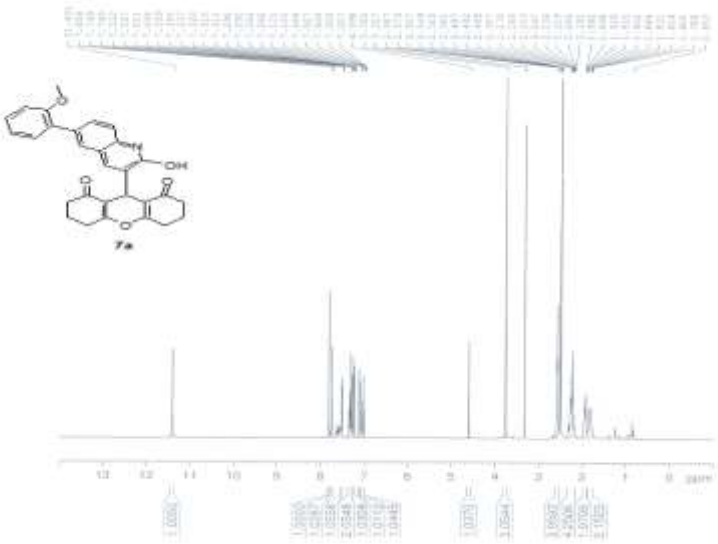
No.	SampleID	OpRot	Measurement		Wlg	Cell[dm]	Concn	Temp	Time
1	A733116	-0.007	-7.000	SR	589	100.00	0.100	27.3	03:50:36 PM
2	A733116	-0.007	-7.000	SR	589	100.00	0.100	27.3	03:50:38 PM
3	A733116	-0.007	-7.000	SR	589	100.00	0.100	27.3	03:50:43 PM
4	A733116	-0.007	-7.000	SR	589	100.00	0.100	27.3	03:50:45 PM
5	A733116	-0.007	-7.000	SR	589	100.00	0.100	27.3	03:50:48 PM

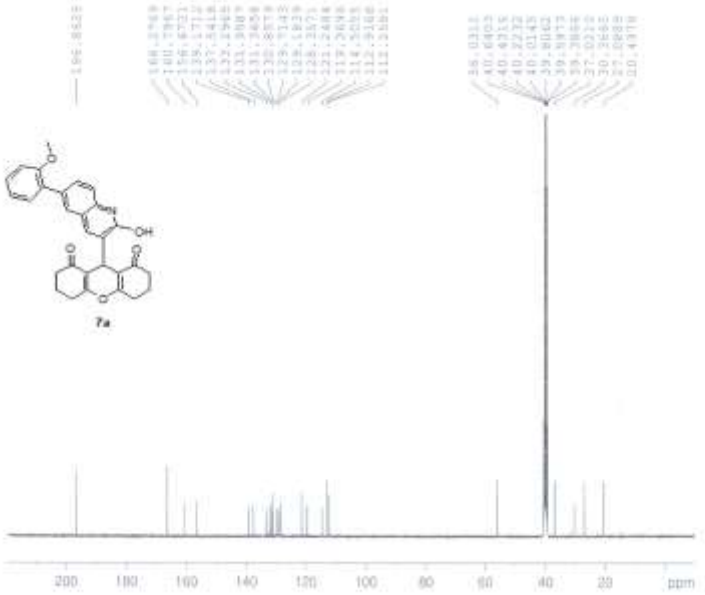
Counts : 5
Average : -7.000
Std.Dev.: 0.0000
Maximum : -7.000
Minimum : -7.000

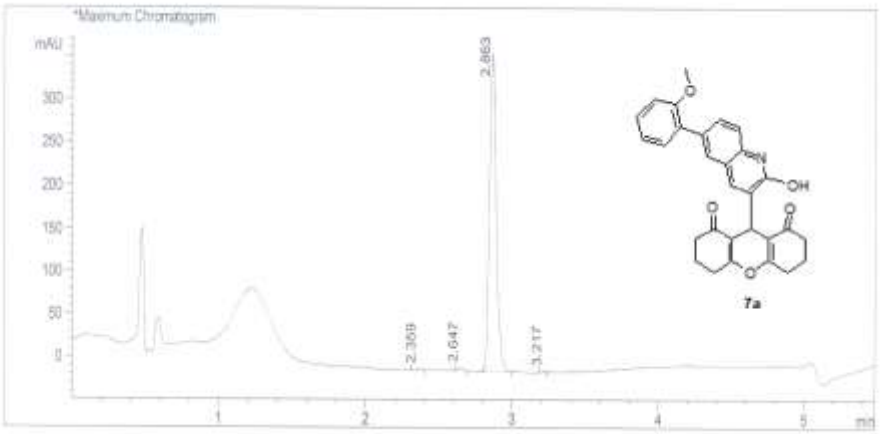
SOR: -7.000/Solvent: MeOH/Conc: 0.100(g/100mL)/Temp: 27.3°C

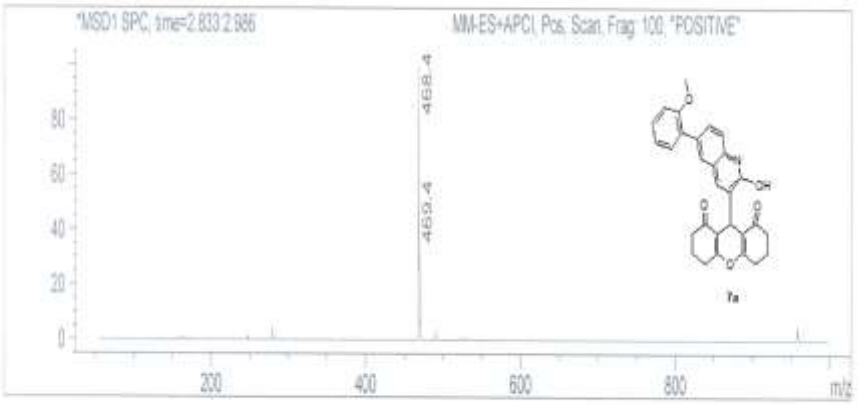


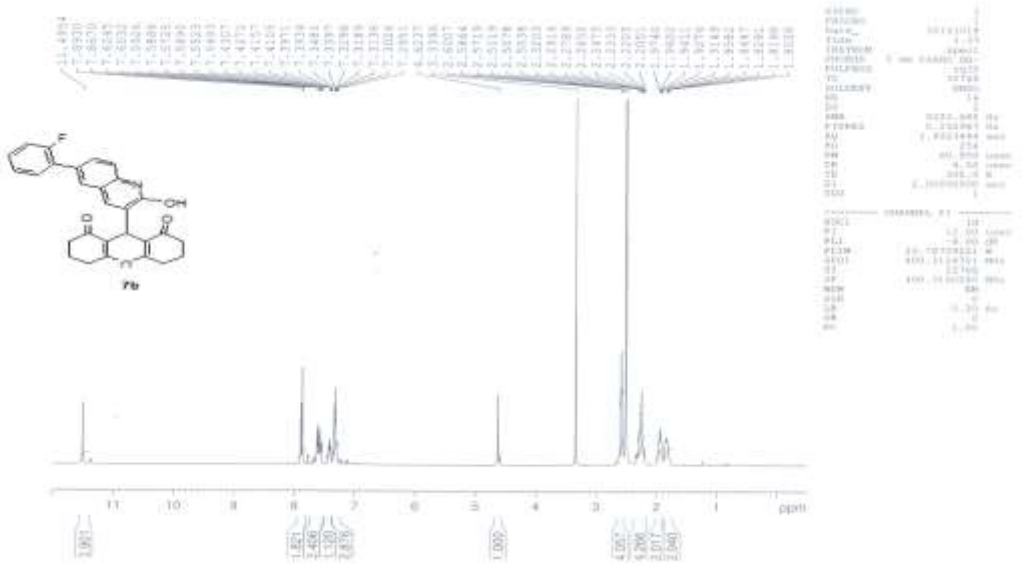


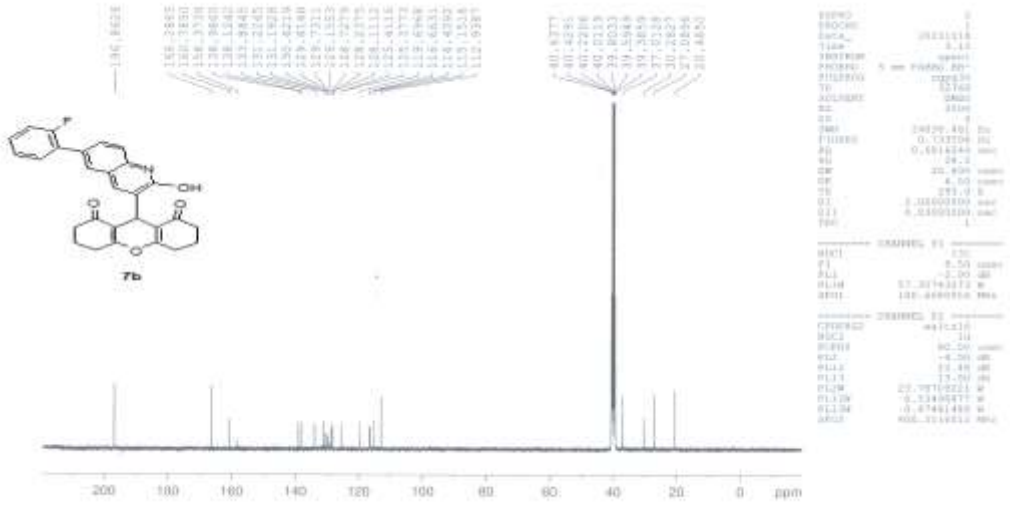

7a
13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm

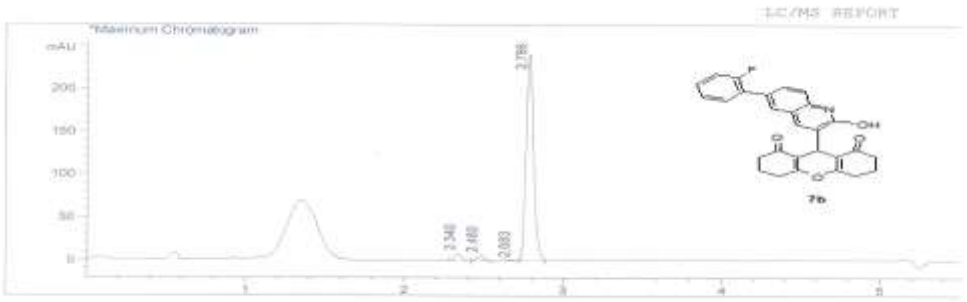

7a
200 180 160 140 120 100 80 60 40 20 ppm

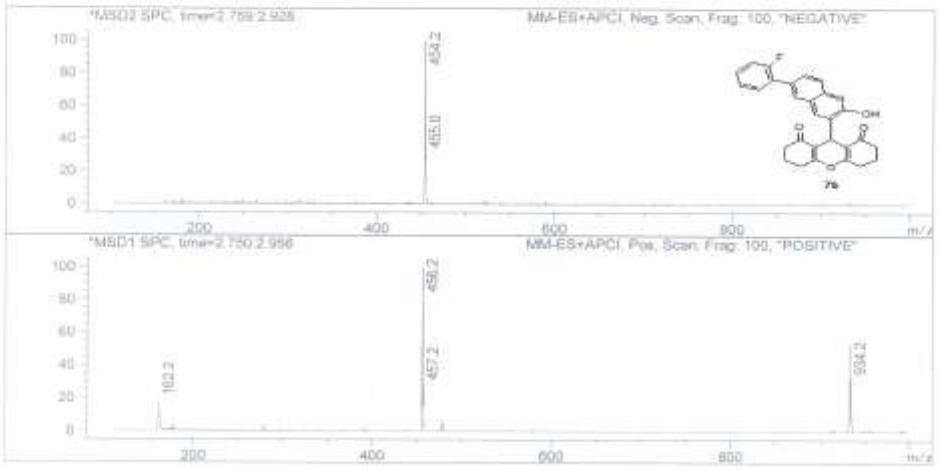

*Maximum Chromatogram
mAU
300
250
200
150
100
50
0
2.359
2.647
2.863
3.217
1
2
3
4
5
min
OH
O
O
O
7a

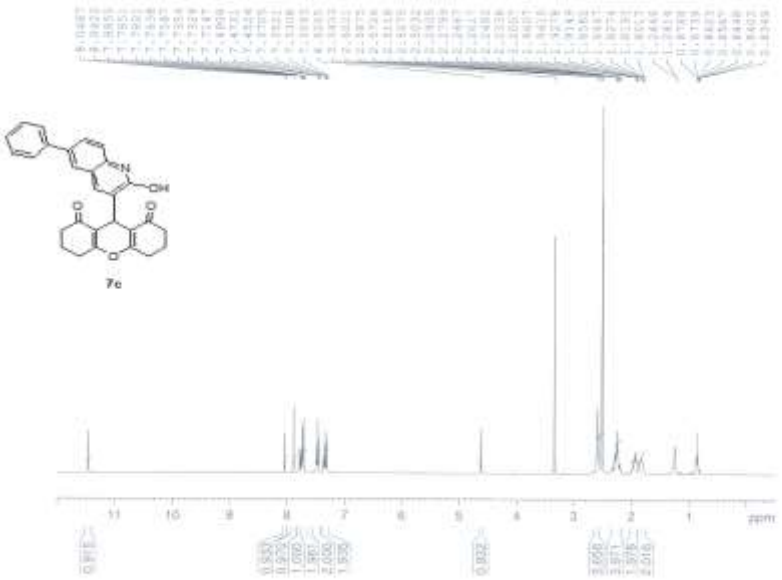

*MSD1 SPC, time=2.833:2.986
MM-ES+APCI, Pos, Scan, Frag: 100, "POSITIVE"
468.4
469.4
80
60
40
20
0
200
400
600
800
m/z
OH
O
O
O
7a

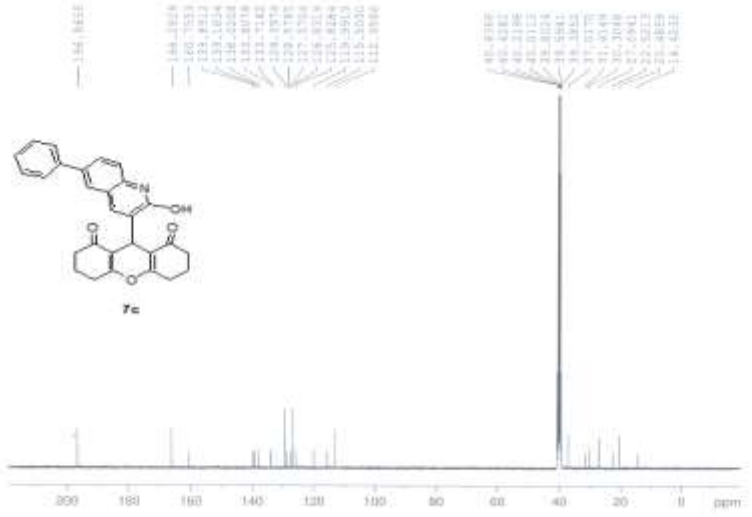

7b
ppm

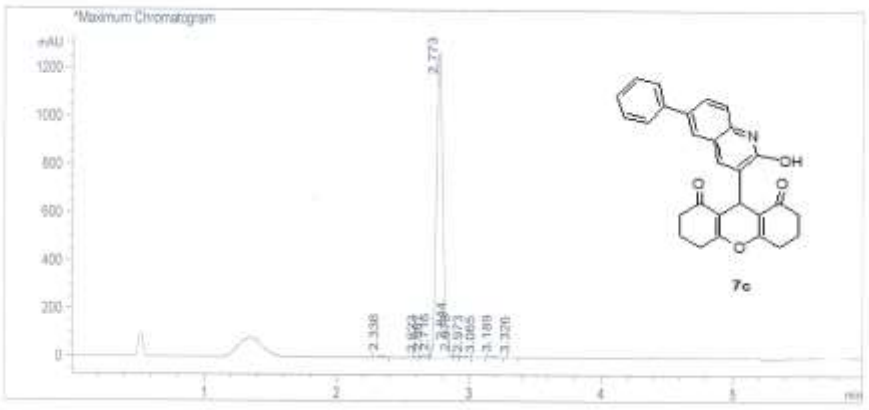

7b
ppm

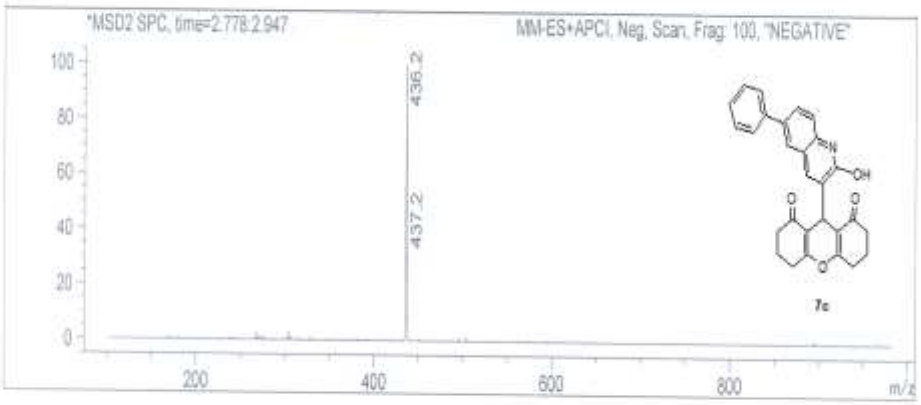

LC/MS REPORT
Maximum Chromatogram
mAU
2.788
3.348
2.468
2.083
7b

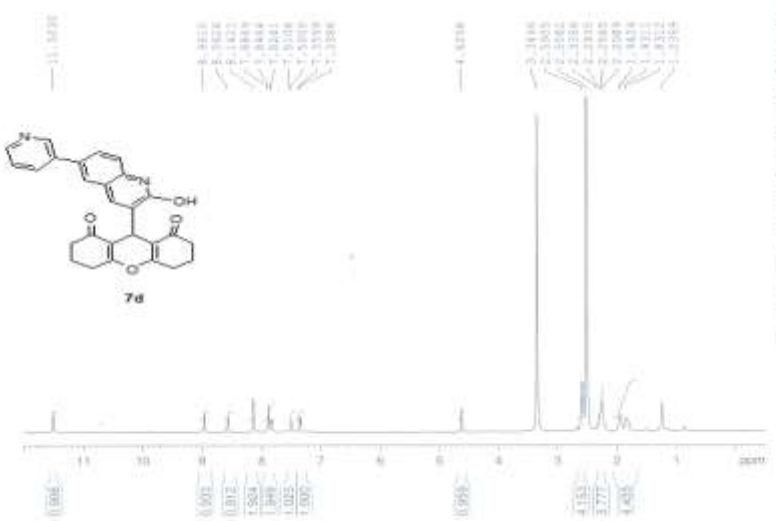

MM-ES+APCI, Neg, Scan, Frag: 100, "NEGATIVE"
454.2
455.0
7b
MM-ES+APCI, Pos, Scan, Frag: 100, "POSITIVE"
456.2
457.2
934.2
162.2

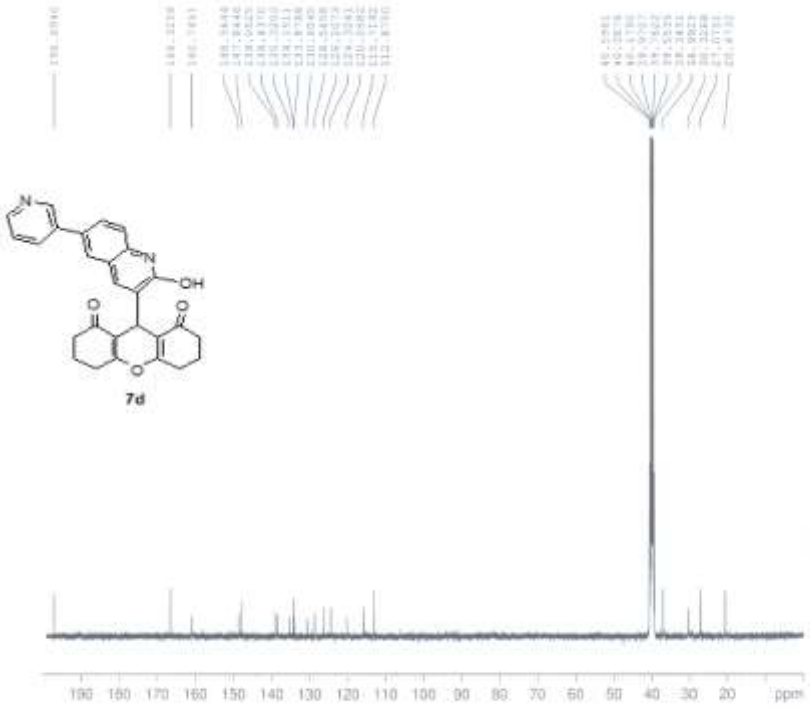

7c
11
10
9
8
7
6
5
4
3
2
1
ppm

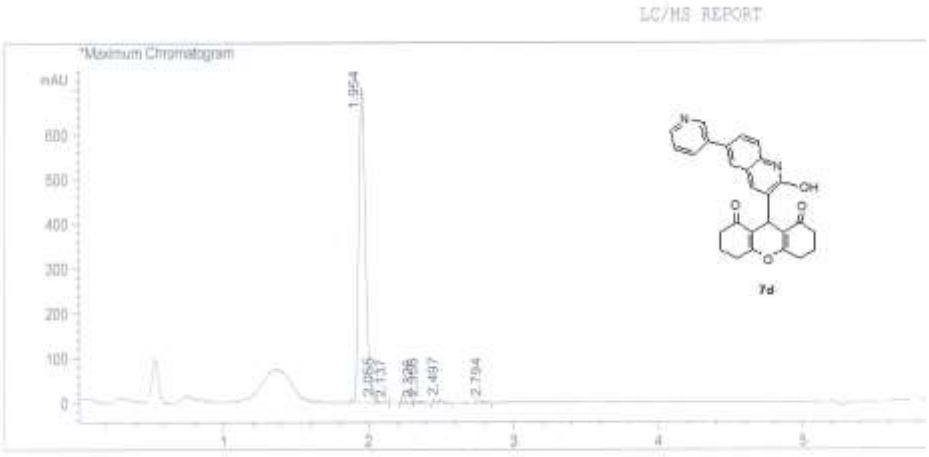

7c
200
180
160
140
120
100
80
60
40
20
0
ppm

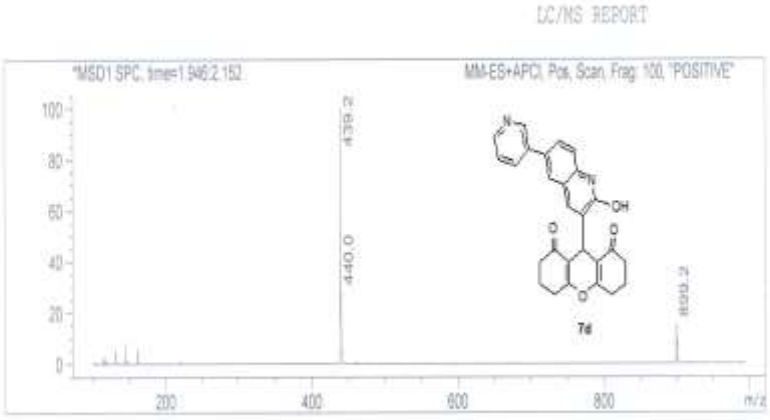

*Maximum Chromatogram
mAU
1200
1000
800
600
400
200
0
2.773
2.338
7c

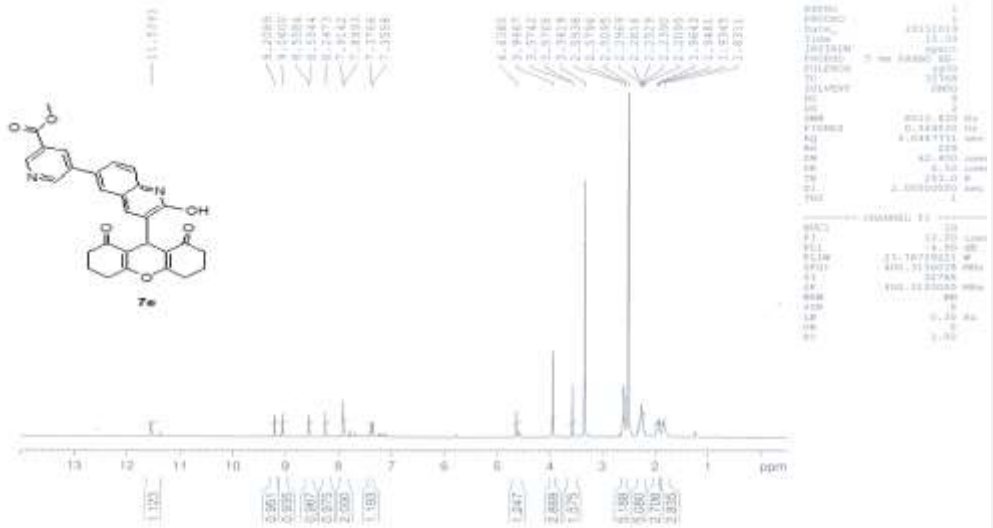

*MSD2 SPC, time=2.778:2.947
MM-ES+APCI, Neg, Scan, Frag: 100, "NEGATIVE"
100
80
60
40
20
0
436.2
437.2
200
400
600
800
m/z
7c

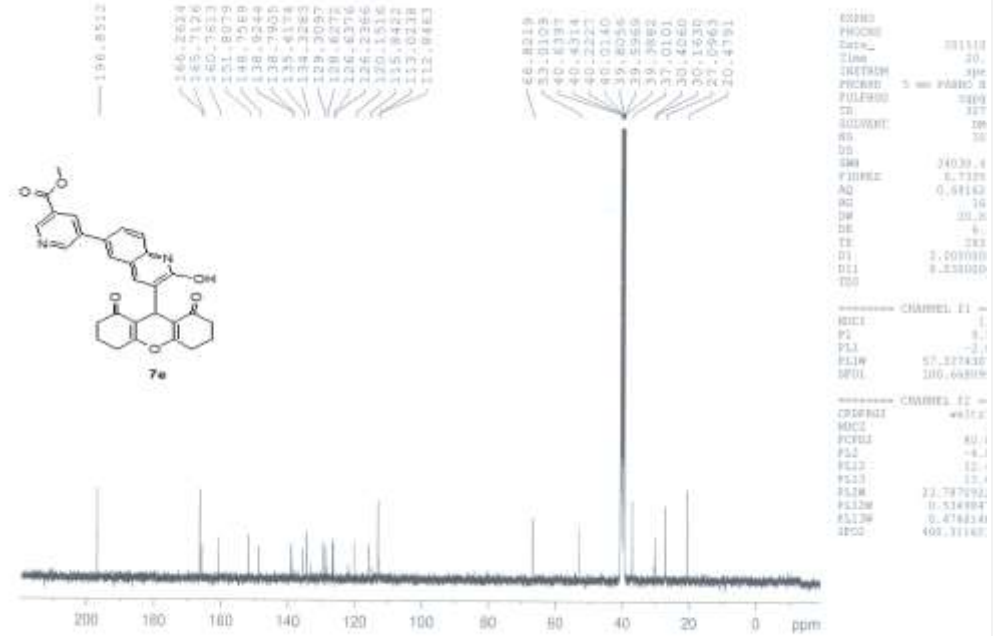

OH
7d
ppm


OH
7d
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

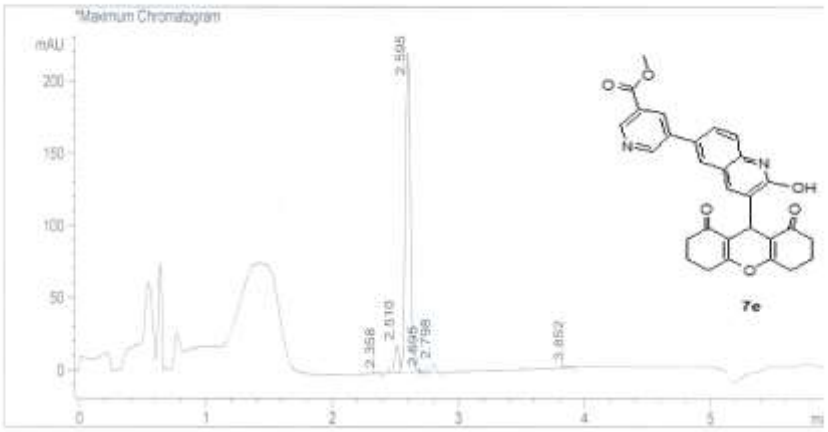

LC/MS REPORT
*Maximum Chromatogram
mAU
1.954
2.137
2.497
2.794
7d


LC/NS REPORT
*MSD1 SPC, time=1.946:2.152
MM-ES+APCI, Pos, Scan, Frag: 100, "POSITIVE"
439.2
440.0
7d

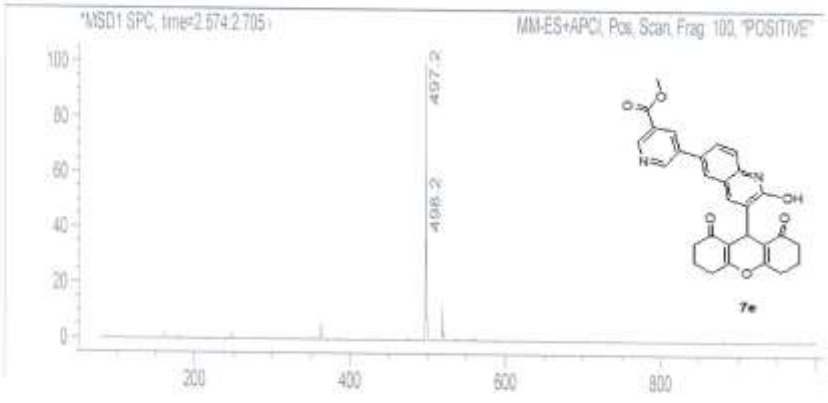

7e
ppm

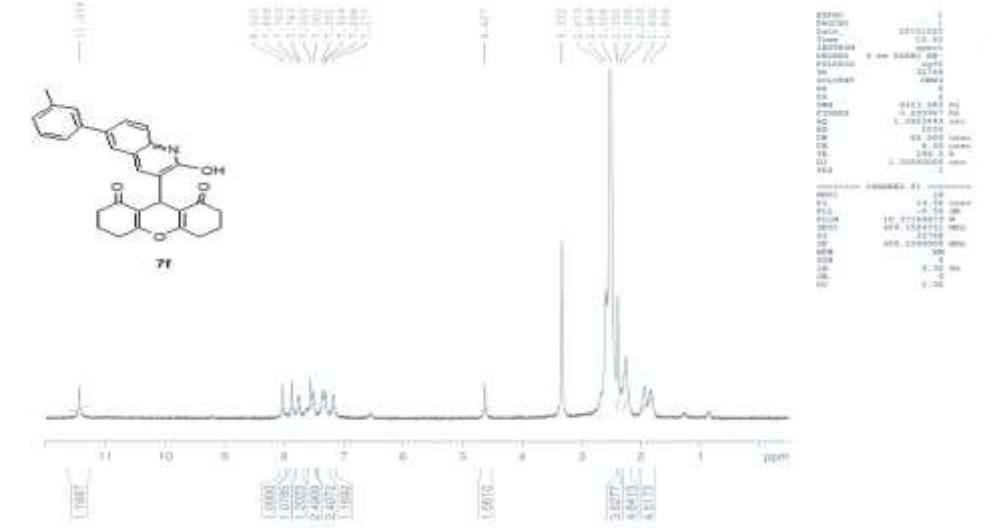

7e
ppm

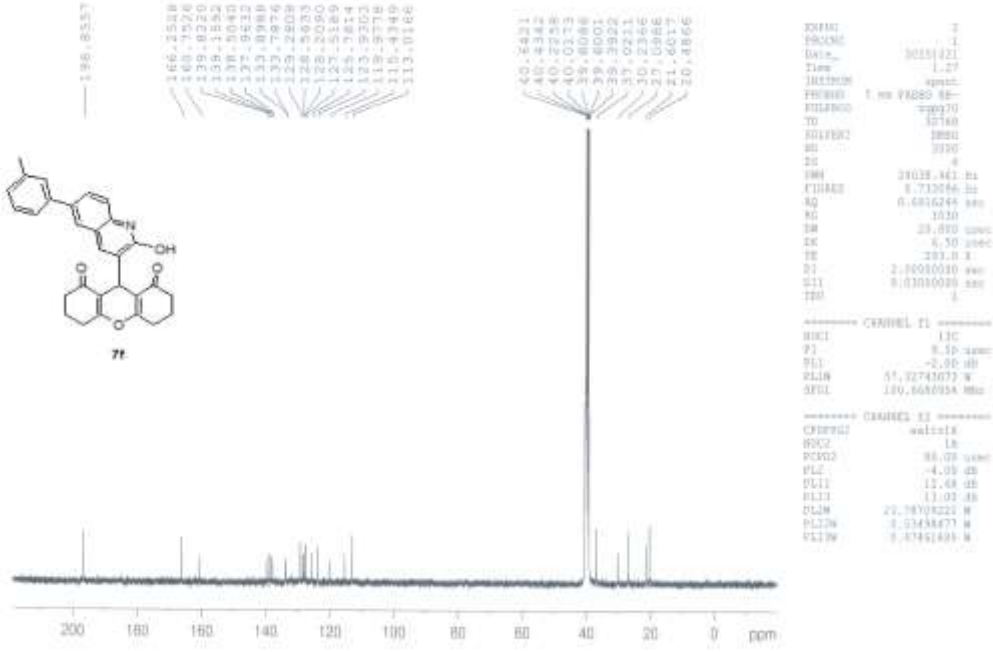
LC/MS REPORT



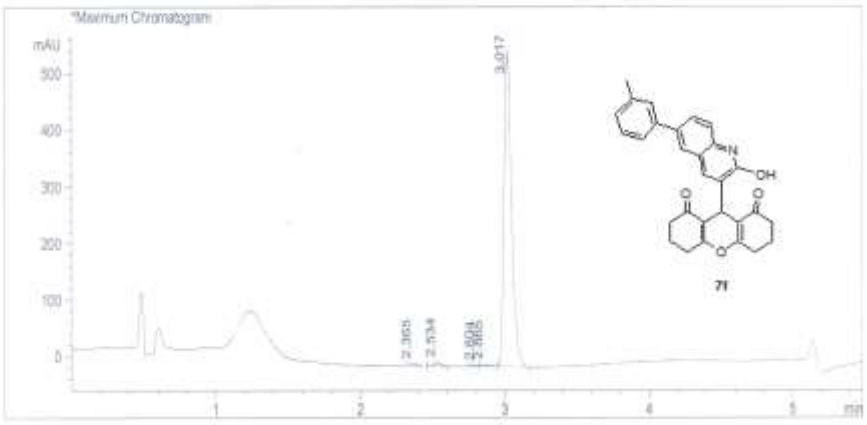
LC/MS REPORT



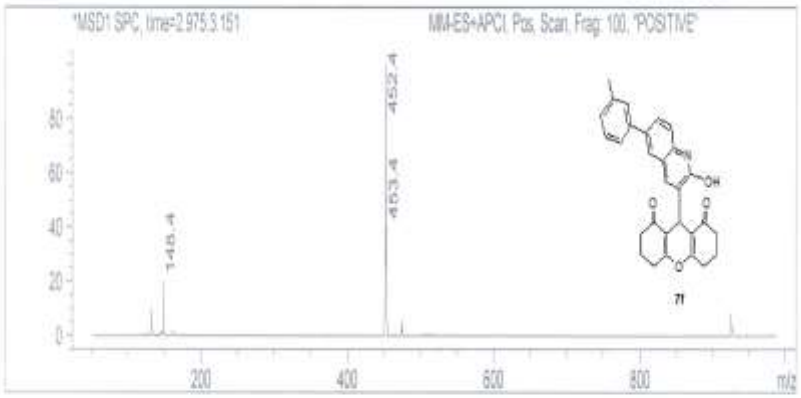

OH
7f
ppm

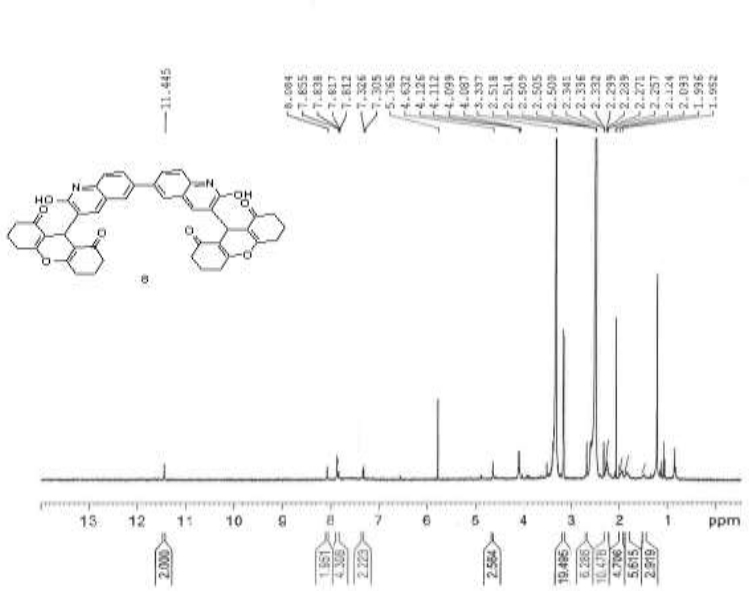

OH
7f
ppm

LC-MS REPORT

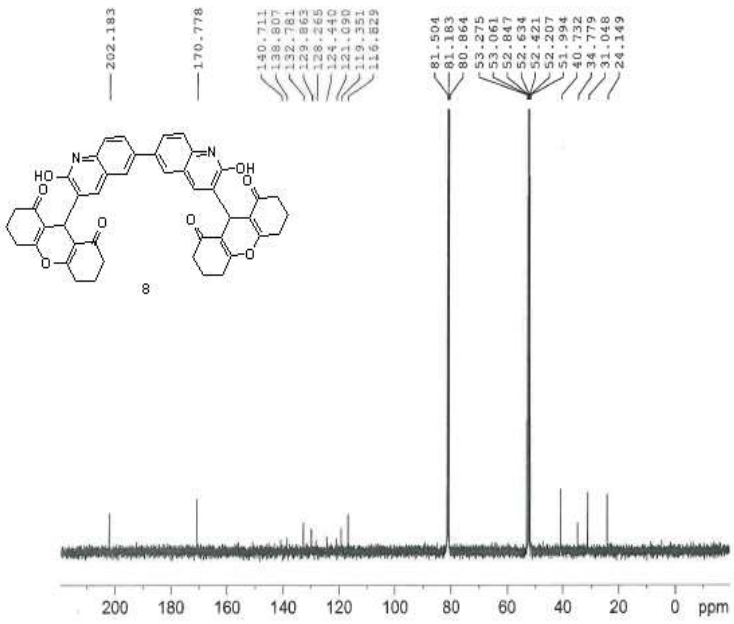


LC-MS REPORT






```
Current Data Parameters
NAME
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_
Time                 2.06
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT             DMSO
NS                     16
DS                      2
SWH              8223.685 Hz
FIDRES           0.250967 Hz
AQ               1.9922964 sec
RG                    406
DW                60.800 usec
DE                 4.50 usec
TE                 300.0 K
D1               1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          400.3124721 MHz
NUC1                    1H
P1                  13.10 usec
PLW1          15.00000000 W

F2 - Processing parameters
SI                  32768
SF            400.3100000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



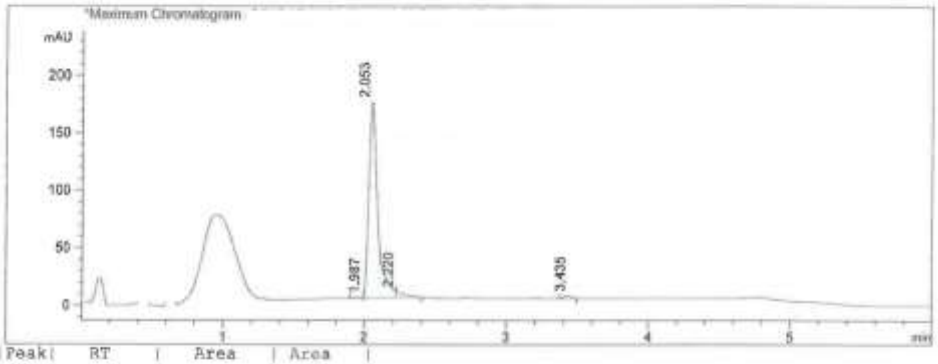

```
Current Data Parameters
NAME
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_
Time                22.07
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG          zgpg30
TD                 32768
SOLVENT             CDCl3
NS                   1024
DS                      4
SWH             24038.461 Hz
FIDRES           0.733596 Hz
AQ               0.6815744 sec
RG                   2050
DW                20.800 usec
DE                 6.50 usec
TE                 293.0 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          100.6680954 MHz
NUC1                    13C
P1                   8.23 usec
PLW1          58.00000000 W

======== CHANNEL f2 ========
SFO2          400.3116012 MHz
NUC2                    1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2          16.00000000 W
PLW12          0.42903000 W
PLW13          0.17050999 W

F2 - Processing parameters
SI                  32768
SF            100.6580300 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

LCMS REPORT

Data file : D:\DATA
Acq Method : C:\CHEM32\1\METHODS\AT_595FA.M
Injection Date : Vial No. : D1F-C3
Injection Time : 12:05:15 Injection vol : 1.000µL
Sample Name :

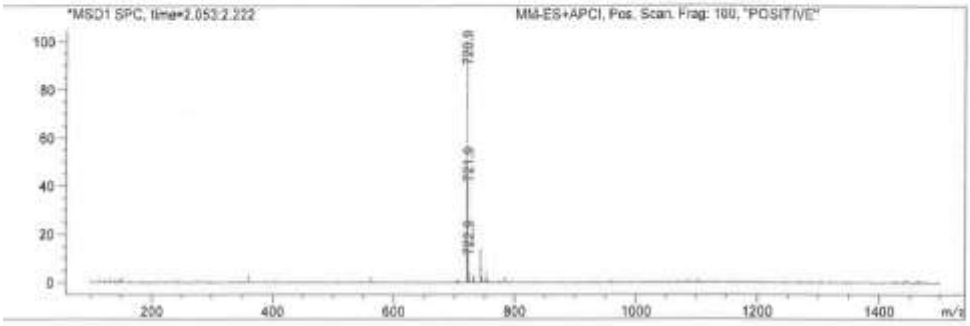
Method info : Column :Atlantis dC18 (50*4.6)5µ
Mobile phase :A :0.1%Formic Acid in H2O B: ACN
Flow Rate :1.5 ml/min

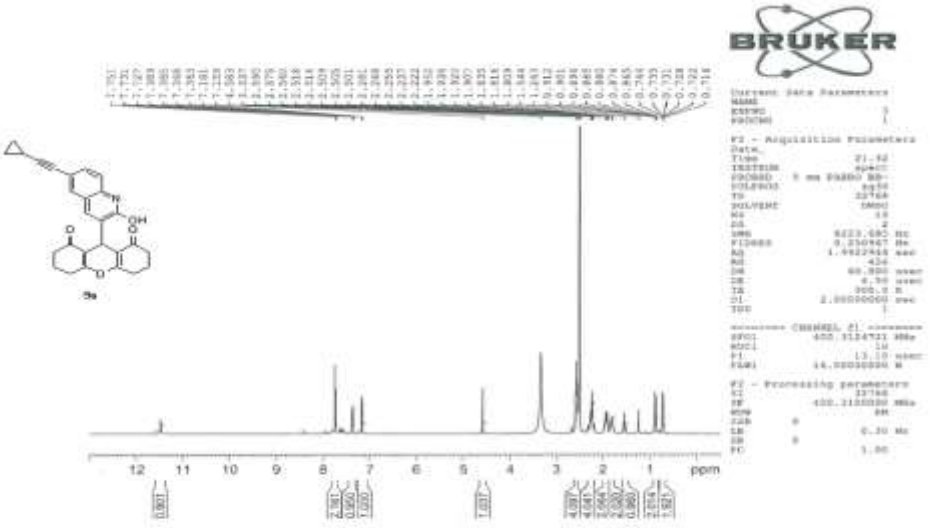
Time (min)	%B
0.0	05
2.5	95
4.0	95
4.5	05
6.0	05

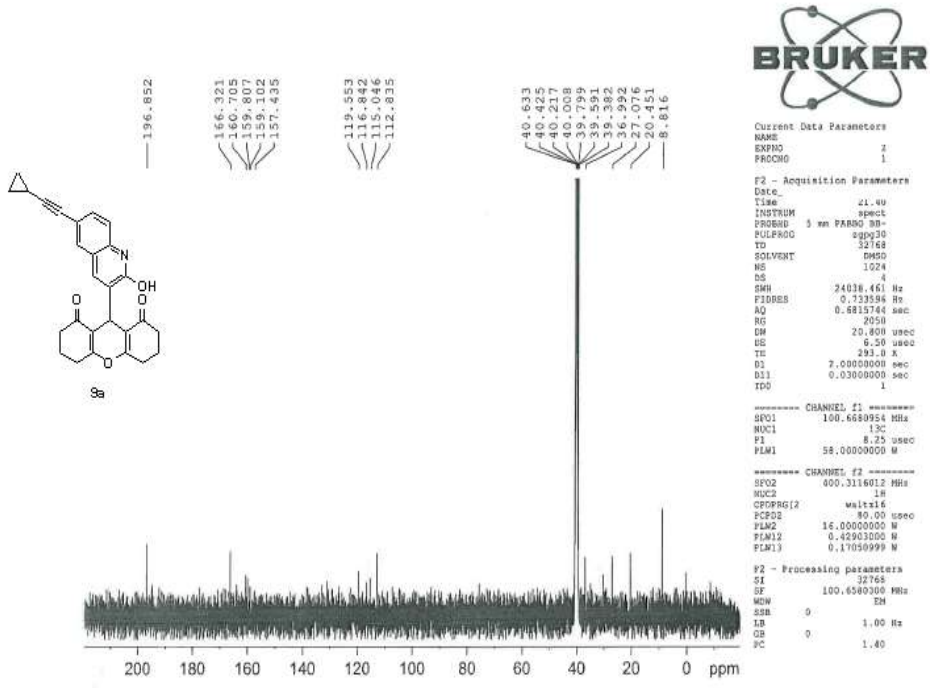


Peak No	RT min	Area	Area %
1	1.987	3.478	0.456
2	2.053	729.893	95.632
3	2.220	21.472	2.813
4	3.435	8.387	1.099

LCMS REPORT




BRUKER
9a
12 11 10 9 8 7 6 5 4 3 2 1 ppm

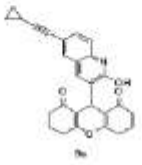

BRUKER
196.852
166.321
160.705
159.807
159.102
157.435
119.553
116.842
115.046
112.835
40.633
40.425
40.217
40.008
39.799
39.591
39.382
36.992
27.076
20.451
8.816
9a
200 180 160 140 120 100 80 60 40 20 0 ppm

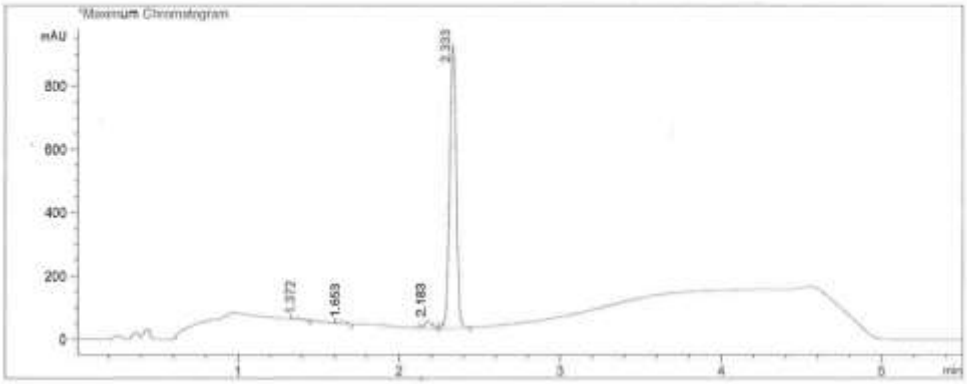
LCMS REPORT

Data file :D:\DATA\
Acq Method :D:\DATA\ XB_595TFA_6MIN.M
Injection Date :
Vial No. : D1F-F7
Injection Time : 5:52:49 PM
Injection vol : 2.0 µL
Sample Name :

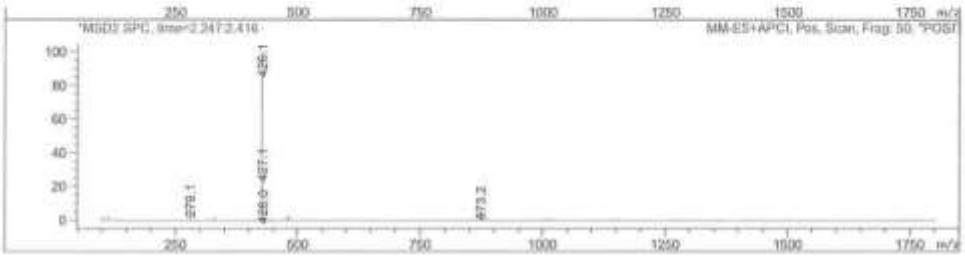
Method info : Column :XBridge C8 (50x4.6mm) 3.5 µm
Mobile phase :A :0.1% TFA in H2O
Mobile phase: B: 0.1% TFA in ACN
Flow Rate :1.5ml/min

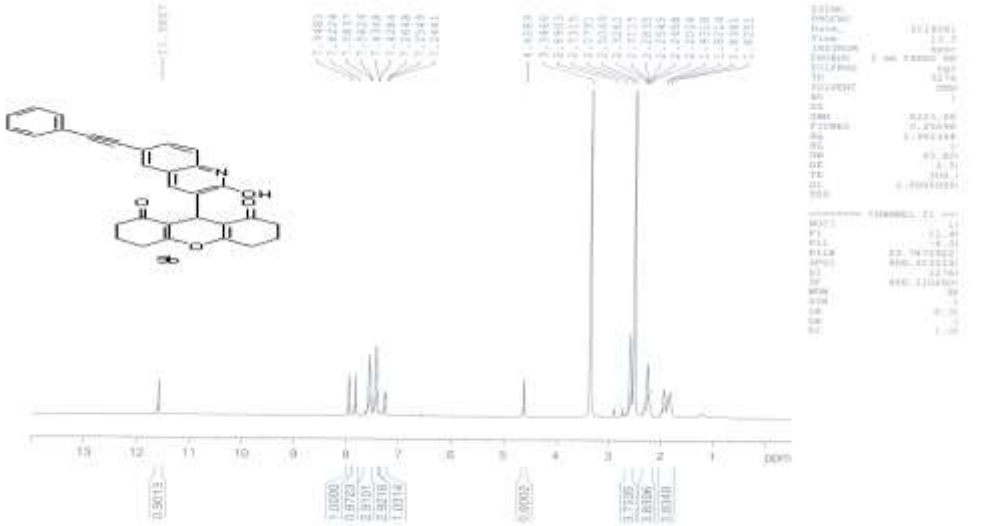
Time (min)	%B
0.0	5
2.5	95
4.0	95
4.5	5
5.5	5

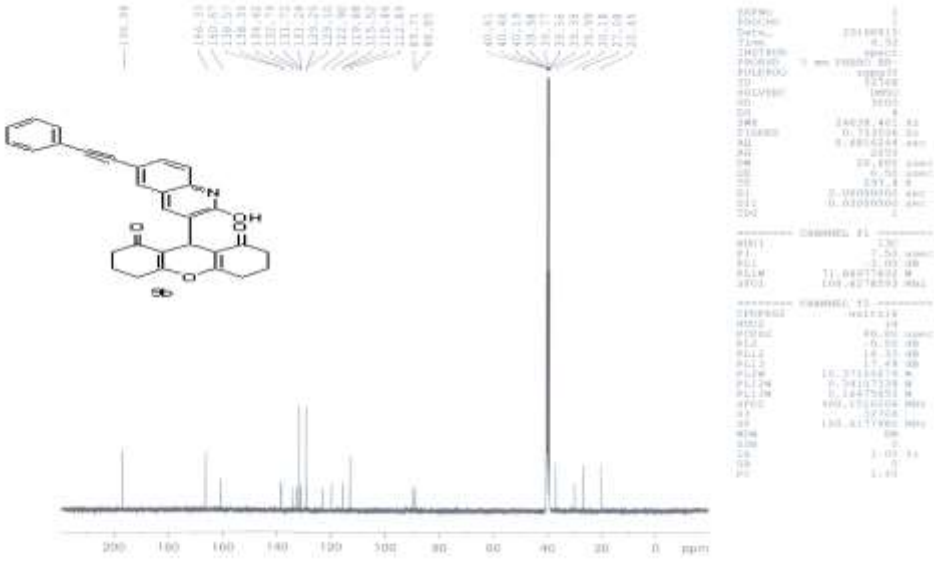


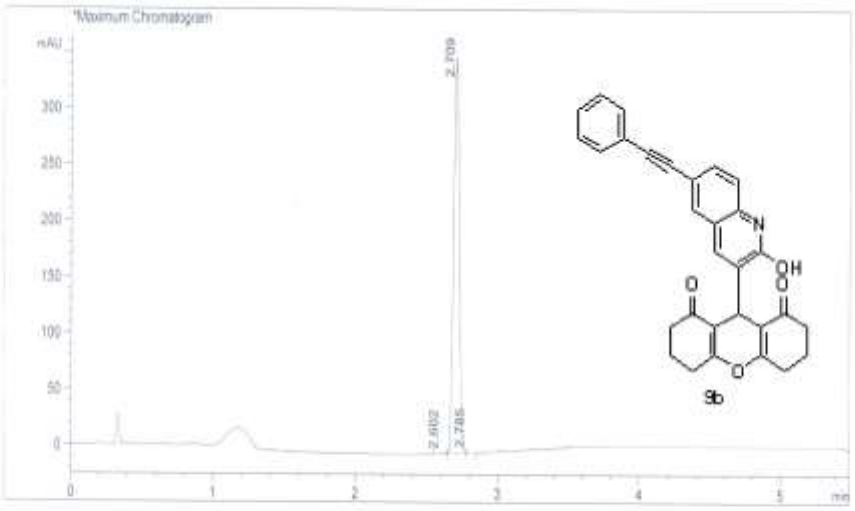


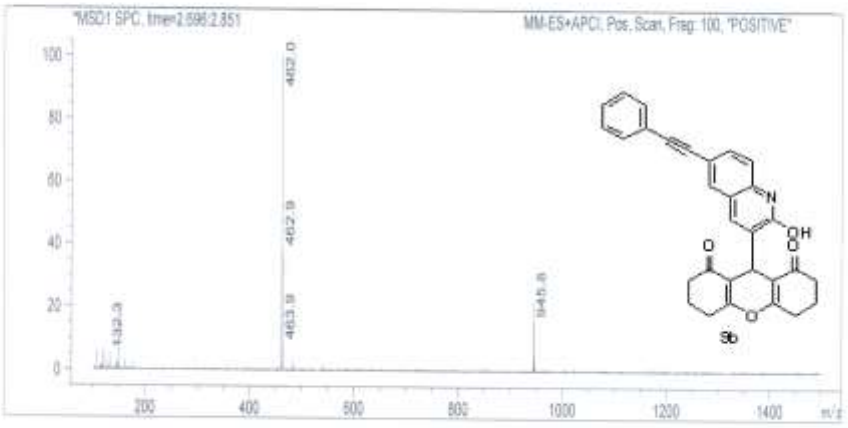
Peak No	RT min	Area	Area %
1	1.372	26.198	0.980
2	1.653	26.991	1.010
3	2.183	69.713	2.571
4	2.333	2551.064	95.439

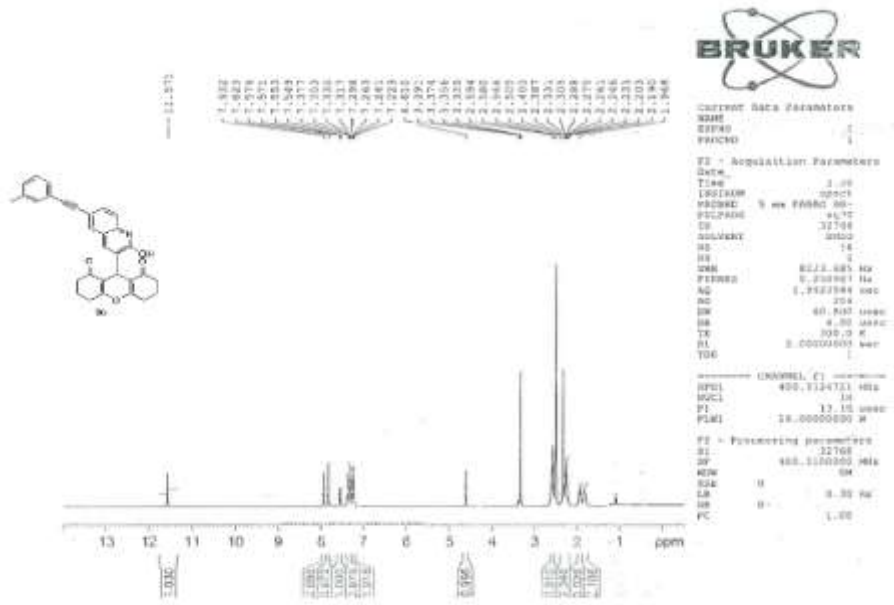


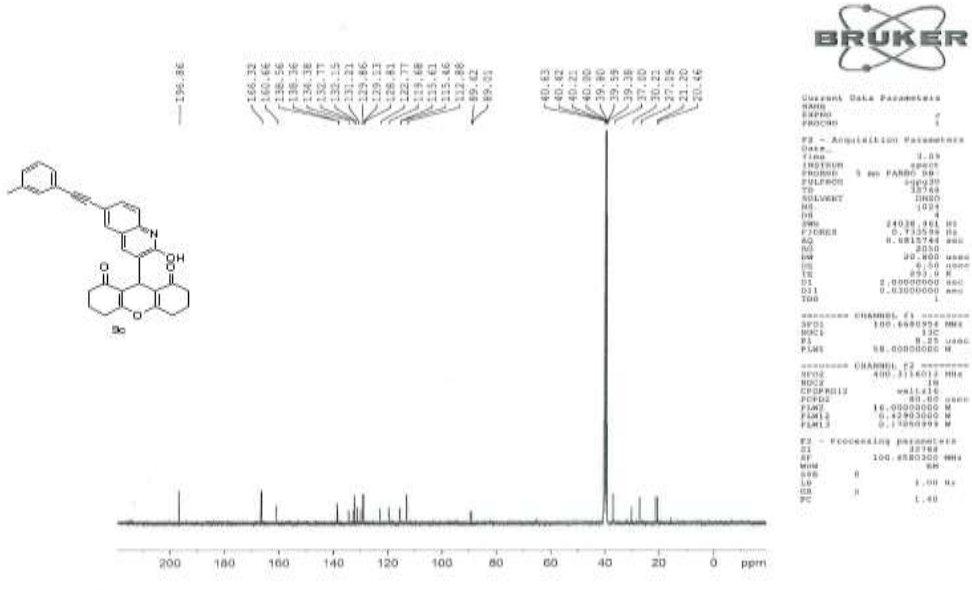





*Maximum Chromatogram
mAU
300
250
200
150
100
50
0
2.709
2.602
2.785
0
1
2
3
4
5
min
N
OH
O
O
O
9b


*MSD1 SPC, time=2.596:2.851
MM-ES+APCI, Pos, Scan, Frag: 100, "POSITIVE"
100
80
60
40
20
0
462.0
462.9
463.9
132.3
945.6
200
400
600
800
1000
1200
1400
m/z
N
OH
O
O
O
9b



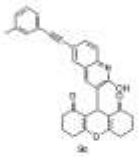


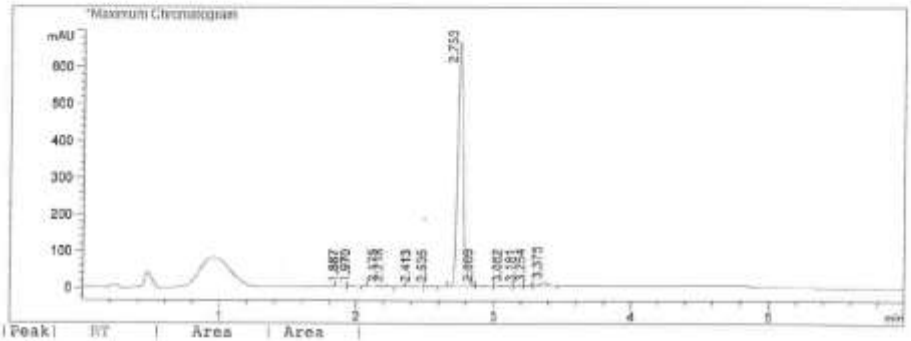
LCMS REPORT

Data file : D:\DATA
Acq Method : C:\CHEM32\1\METHODS\AT_595FA.M
Injection Date : Vial No. : D1F-E6
Injection Time : 17:51:46 Injection vol : 1.000µL
Sample Name :

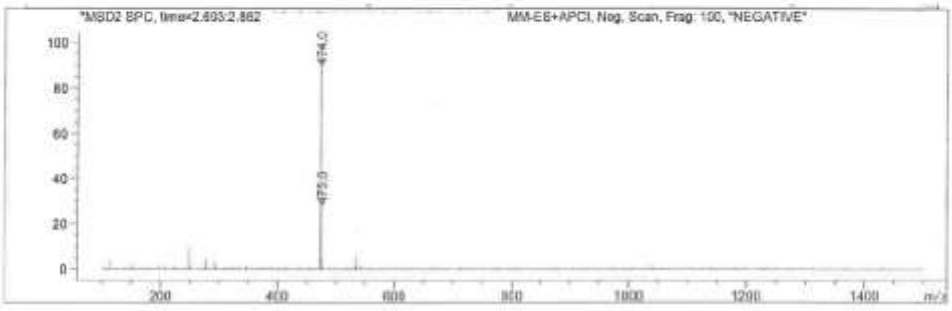
Method info : Column :Atlantis dC18 (50*4.6)5µ
Mobile phase :A :0.1%Formic Acid in H2O B: ACN
Flow Rate :1.5 ml/min

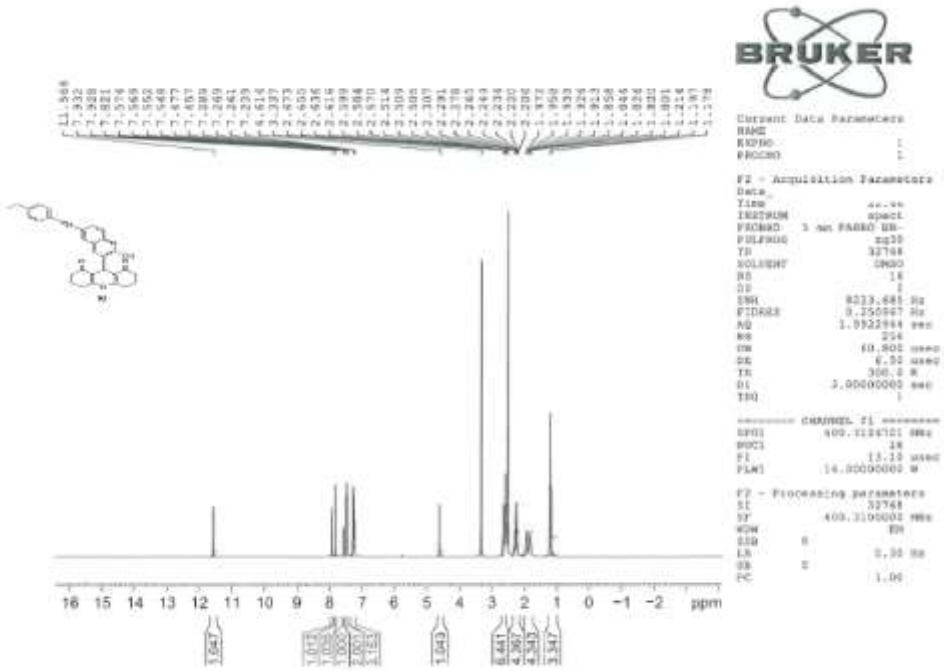
Time (min)	%B
0.0	05
2.5	95
4.0	95
4.5	05
6.0	05

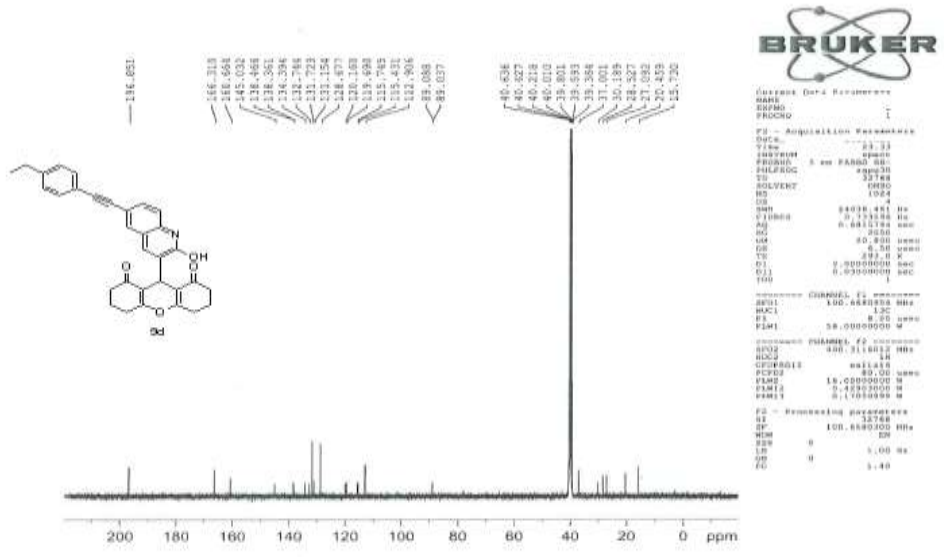




Peak No	RT min	Area	Area %
1	1.887	1.451	0.073
2	1.970	2.692	0.136
3	2.175	3.071	0.155
4	2.218	4.523	0.228
5	2.413	3.227	0.163
6	2.535	2.960	0.149
7	2.759	1913.176	96.542
8	2.866	6.069	0.306
9	3.082	4.759	0.240
10	3.181	3.241	0.164
11	3.254	4.500	0.227
12	3.375	32.027	1.616





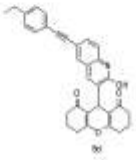


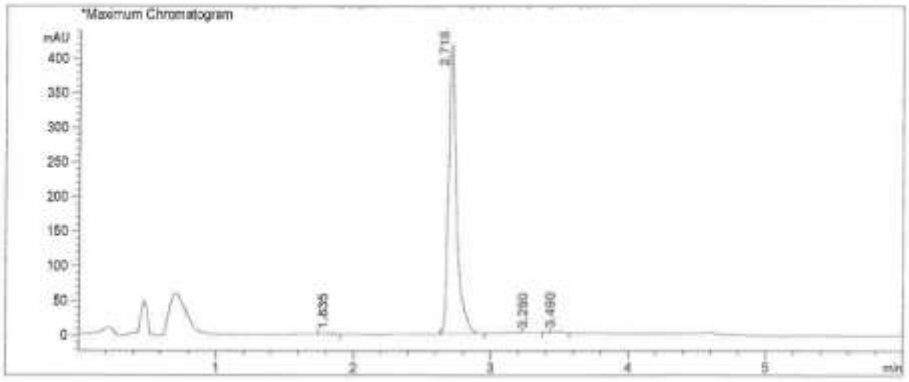
LCMS REPORT

Data file : D:\CHEM32\
Acq Method : D:\CHEM32\1\METHODS\AT_595FA.M
Injection Date : Vial No. : D1P-E4
Injection Time : 3:47:12 PM Injection vol : 2.0 µL
Sample Name :

Method info : Column :Atlantis dC18 (50*4.6)5
Mobile phase :A :0.1%Formic Acid in H2O B: ACN
Flow Rate :1.5 ml/min

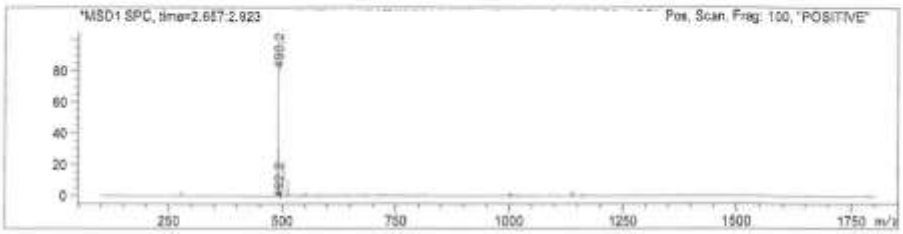
Time (min)	%B
0.0	05
2.5	95
4.0	95
4.5	05
6.0	05

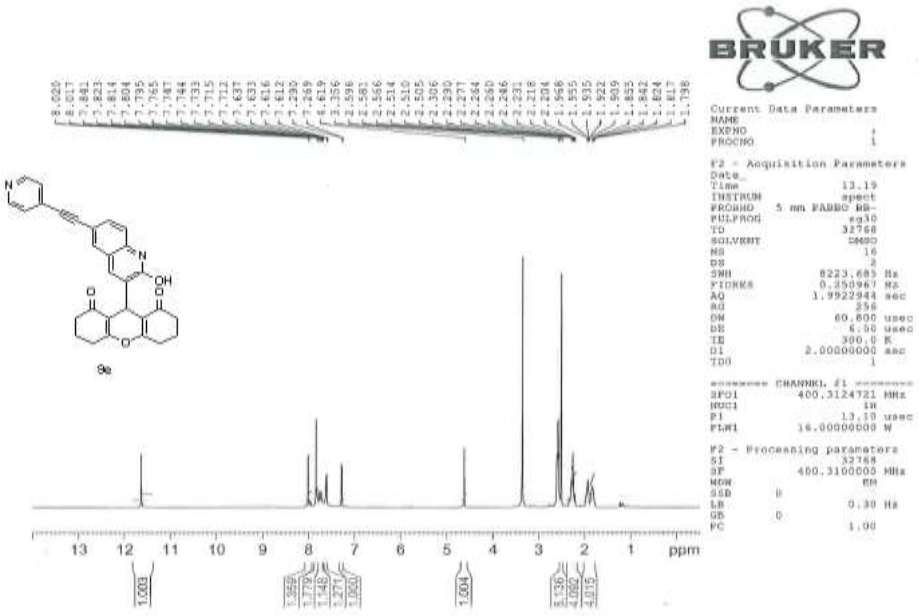




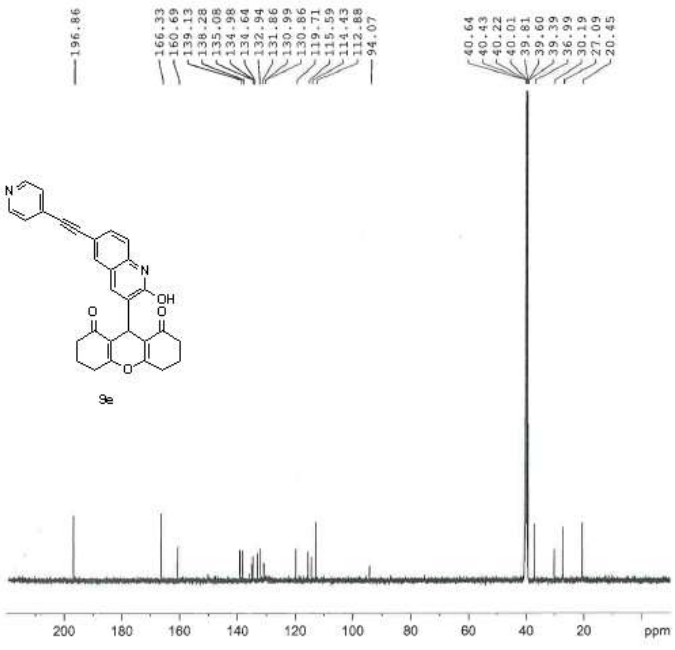
Peak No	RT min	Area	Area %
1	1.835	3.810	0.220
2	2.716	1717.572	99.235
3	3.290	3.443	0.199
4	3.490	5.982	0.346

LCMS REPORT




8.020
8.017
7.841
7.823
7.814
7.804
7.795
7.765
7.747
7.744
7.733
7.715
7.712
7.637
7.633
7.616
7.612
7.290
7.269
6.619
3.356
2.596
2.581
2.566
2.514
2.510
2.505
2.306
2.290
2.277
2.264
2.260
2.246
2.231
2.218
2.204
1.966
1.955
1.535
1.522
1.509
1.835
1.842
1.824
1.817
1.798
N
OH
O
O
O
9e
13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.003
3.889
1.779
1.148
1.271
1.000
1.004
5.136
4.062
4.015

BRUKER
Current Data Parameters
NAME
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_
Time 13.19
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT DMSO
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9922944 sec
RG 256
DW 60.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.3124721 MHz
NUC1 1H
P1 13.10 usec
PLW1 16.00000000 W
F2 - Processing parameters
SI 32768
SF 400.3100000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


196.86
166.33
160.69
139.13
138.28
135.08
134.98
134.64
132.94
131.86
130.99
130.86
119.71
115.59
114.43
112.88
94.07
40.64
40.43
40.22
40.01
39.81
39.60
39.39
39.19
36.99
30.19
27.09
20.45
N
OH
O
O
O
9e
200 180 160 140 120 100 80 60 40 20 ppm

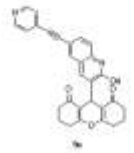

BRUKER
Current Data Parameters
NAME
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_
Time 14.06
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT DMSO
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6815744 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 293.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6680954 MHz
NUC1 13C
P1 8.25 usec
PLW1 58.00000000 W
======== CHANNEL f2 ========
SFO2 400.3116012 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 16.00000000 W
PLW12 0.42903000 W
PLW13 0.17050999 W
F2 - Processing parameters
SI 32768
SF 100.6580300 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

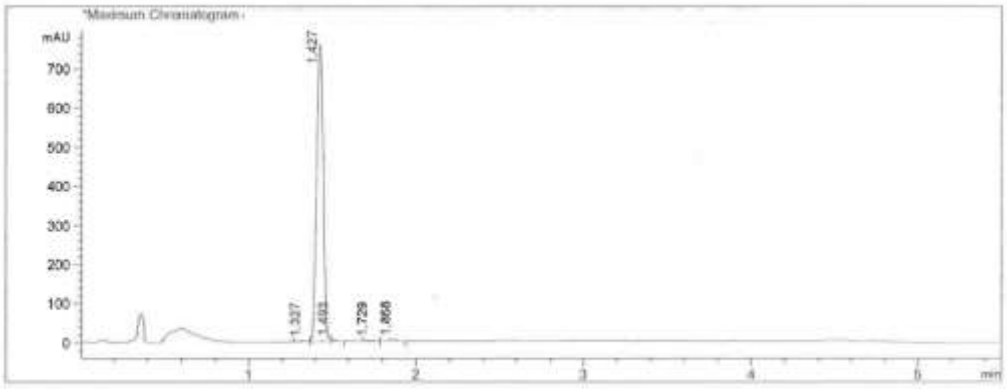
LCMS REPORT

Data file :D:\DATA'
Acq Method :D:\DATA' ,ZX_595FA.M
Injection Date :
Vial No. : D1B-A4
Injection Time : 6:17:23 PM
Injection vol : 2.0 µL
Sample Name :

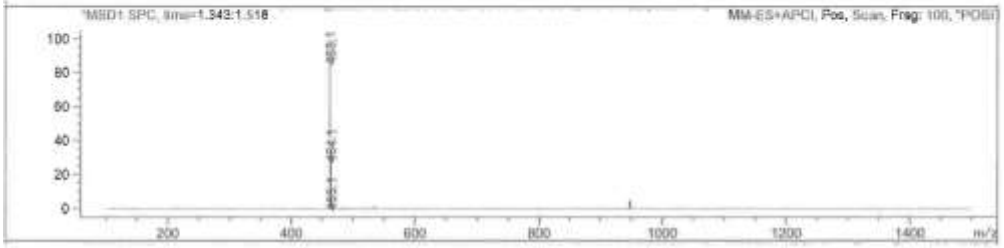
Method info : Column :ZORBAX XDB C-18 (50x4.6mm) 3.5 µm
Mobile Phase :A :0.1% HCOOH in H2O:ACN(95:5)
Mobile phase :B:ACN
Flow Rate :1.5ml/min

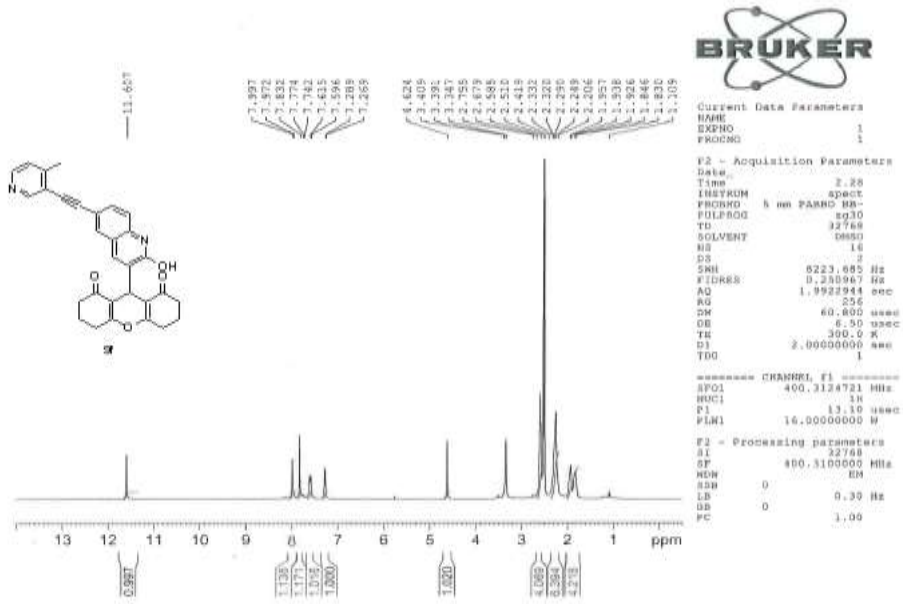
Time (min)	%B
0.0	5
2.5	95
4.0	95
4.5	5
5.5	5



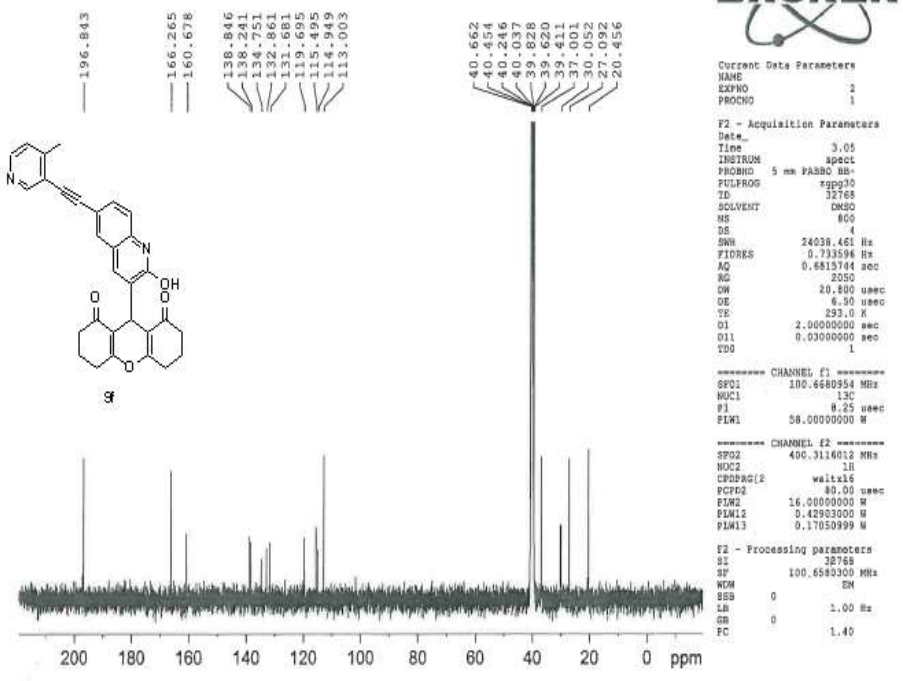


Peak No	RT min	Area	Area %
1	1.327	11.266	0.535
2	1.427	2061.119	97.798
3	1.493	7.344	0.348
4	1.729	9.586	0.455
5	1.868	18.222	0.865




11.657
7.997
7.972
7.832
7.774
7.742
7.615
7.596
7.288
7.269
4.624
3.405
3.391
3.347
2.755
2.679
2.588
2.510
2.418
2.332
2.320
2.299
2.289
2.206
1.957
1.938
1.926
1.846
1.830
1.309
OH
O
O
O
9f
13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
0.987
1.138
1.171
1.076
1.000
1.620
4.069
0.994
4.218

BRUKER
Current Data Parameters
NAME
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_
Time 2.28
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT DMSO
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9922944 sec
RG 256
DW 60.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.3134721 MHz
NUC1 1H
P1 13.10 usec
PLW1 16.00000000 W
F2 - Processing parameters
SI 32768
SF 400.3100000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


196.843
166.265
160.678
138.846
138.241
134.751
132.861
131.681
119.695
115.495
114.949
113.003
40.662
40.454
40.246
40.037
39.828
39.620
39.411
37.001
30.052
27.092
20.456
OH
O
O
O
9f
200 180 160 140 120 100 80 60 40 20 0 ppm

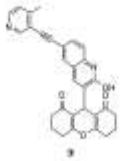
BRUKER
Current Data Parameters
NAME
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_
Time 3.05
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT DMSO
NS 800
DS 4
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6815744 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 293.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6680954 MHz
NUC1 13C
P1 8.25 usec
PLW1 58.00000000 W
======== CHANNEL f2 ========
SFO2 400.3116012 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 16.00000000 W
PLW12 0.42903000 W
PLW13 0.17050999 W
F2 - Processing parameters
SI 32768
SF 100.6580300 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

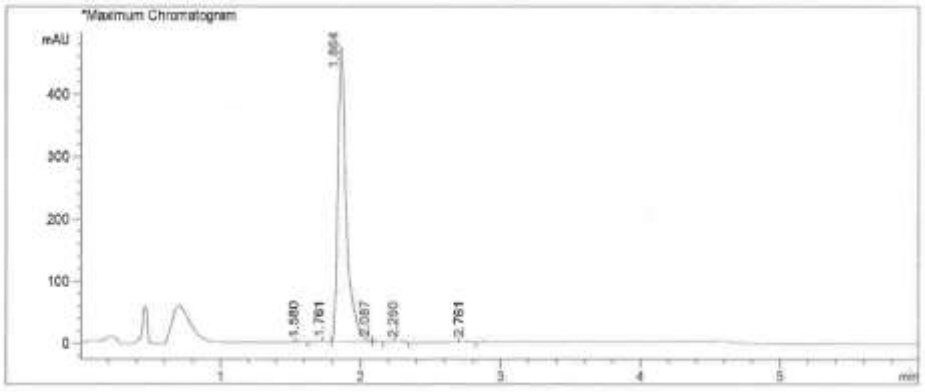
LCMS REPORT

Data file : D:
Acq Method : D: \METHODS\AT_595FA.M
Injection Date :
Vial No. : D1F-E5
Injection Time : 3:54:30 PM
Injection vol : 2.0 µL
Sample Name :

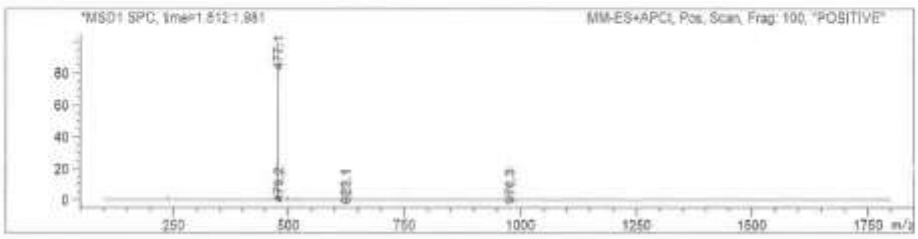
Method info : Column :Atlantis dC18 (50*4.6)5
Mobile phase :A :0.1%Formic Acid in H2O B: ACN
Flow Rate :1.5 ml/min

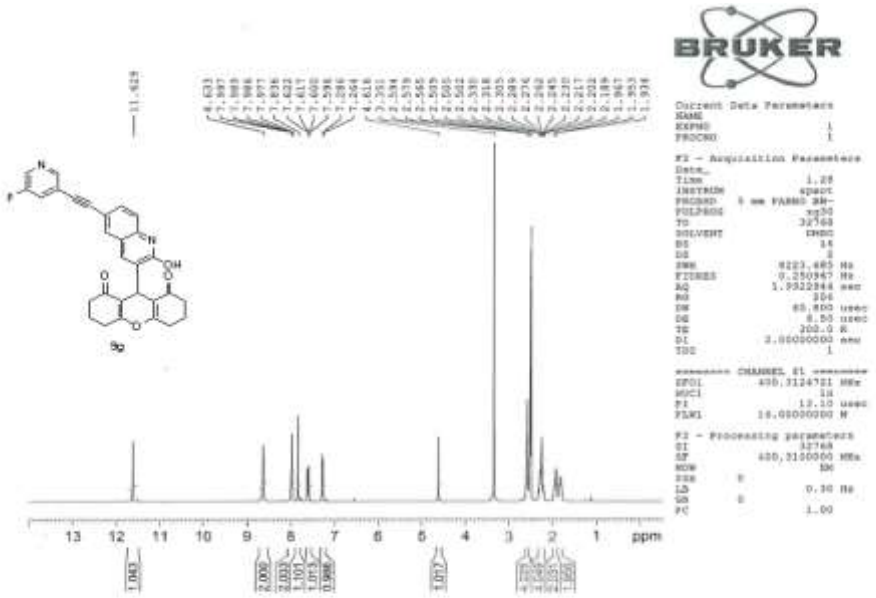
Time(min)	%B
0.0	05
2.5	95
4.0	95
4.5	05
6.0	05





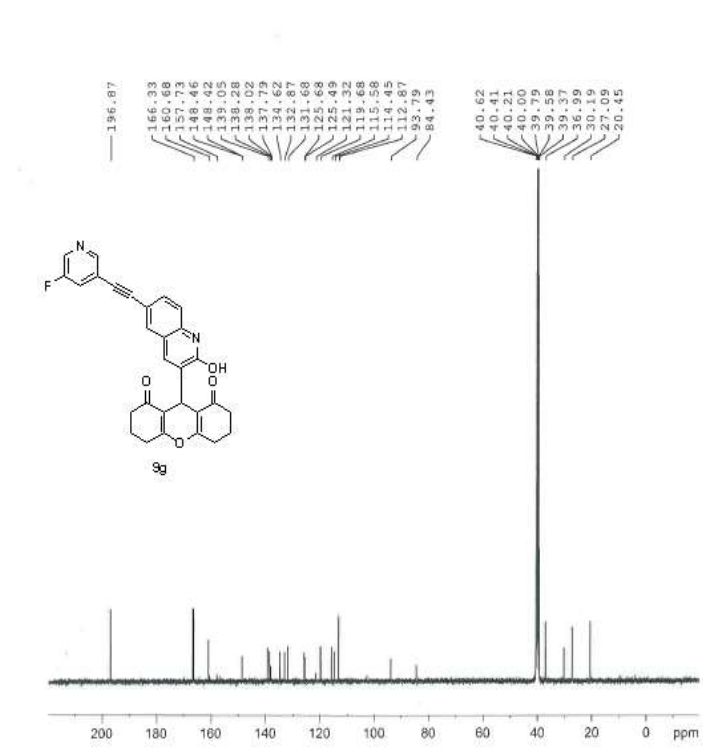
Peak No	RT min	Area	Area %
1	1.580	0.694	0.034
2	1.761	2.093	0.104
3	1.864	2012.435	99.570
4	2.087	3.003	0.149
5	2.290	0.774	0.038
6	2.761	2.123	0.105





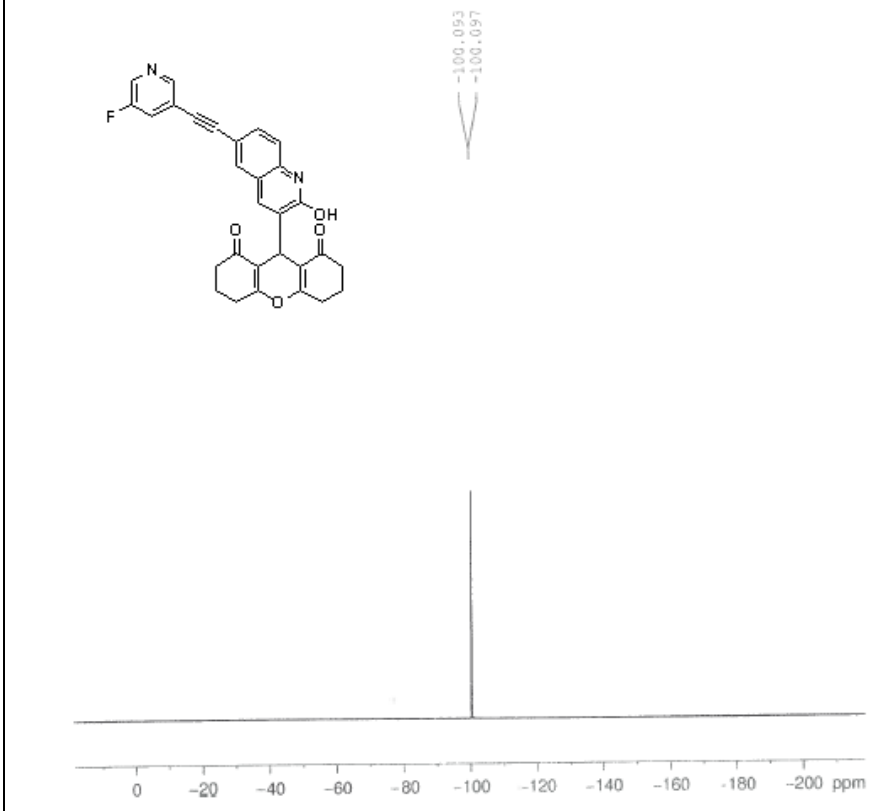
BRUKER

```
Current Data Parameters
NAME
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_
Time                 1.28
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT             DMSO
NS                     16
DS                      2
SWH              8223.685 Hz
FIDRES           0.250947 Hz
AQ               1.9922944 sec
RG                    304
DW                 60.800 usec
DE                  6.50 usec
TE                 300.0 K
D1              2.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         400.3124731 MHz
NUC1                1H
P1                12.10 usec
PLW1        16.68000000 W

F2 - Processing parameters
SI                 32768
SF          400.3100000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



BRUKER

```
Current Data Parameters
NAME
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_
Time                 2.15
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 32768
SOLVENT             DMSO
NS                   1024
DS                      4
SWH              24038.461 Hz
FIDRES           0.733596 Hz
AQ               0.6815744 sec
RG                   2050
DW                 20.800 usec
DE                  6.50 usec
TE                 293.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         100.6680954 MHz
NUC1                13C
P1                 8.25 usec
PLW1        58.00000000 W

======== CHANNEL f2 ========
SFO2         400.3116012 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2        16.00000000 W
PLW12        0.42903000 W
PLW13        0.17050999 W

F2 - Processing parameters
SI                 32768
SF          100.6580300 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

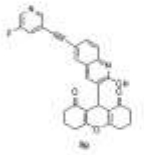

-100.093
-100.097
N
F
N
OH
O
O
O
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200 ppm

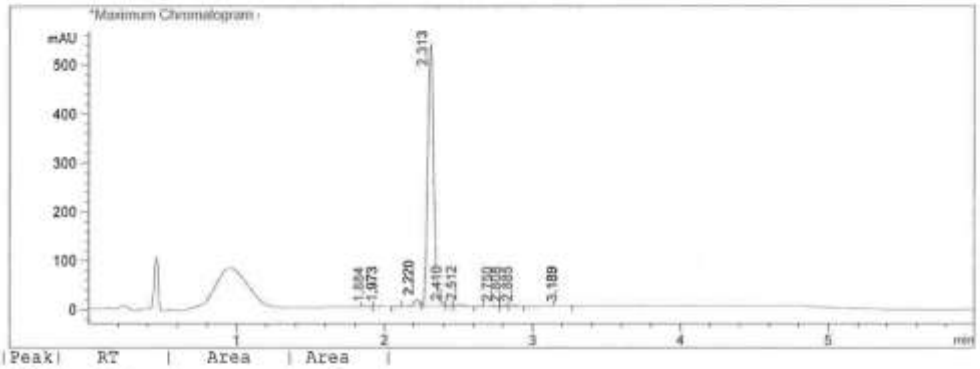
LCMS REPORT

Data file : D:
Acq Method : C: METHODS\AT_595FA.M
Injection Date :
Injection Time : 17:44:44
Sample Name :
Vial No. : D1F-E5
Injection vol : 1.000µL

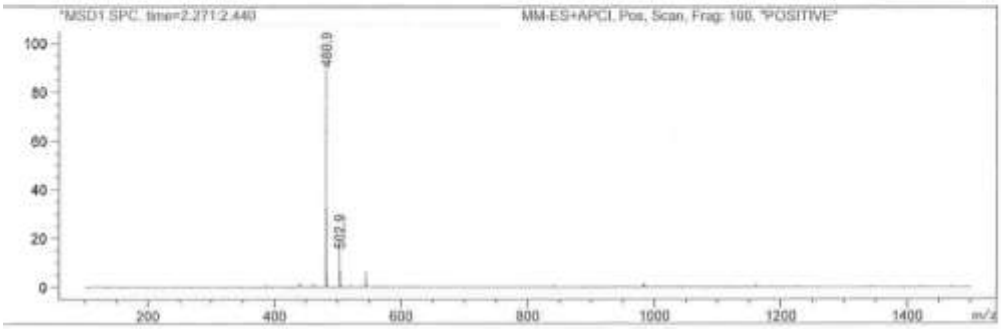
Method info : Column :Atlantis dC18 (50*4.6)5µ
Mobile phase :A :0.1%Formic Acid in H2O B: ACN
Flow Rate :1.5 ml/min

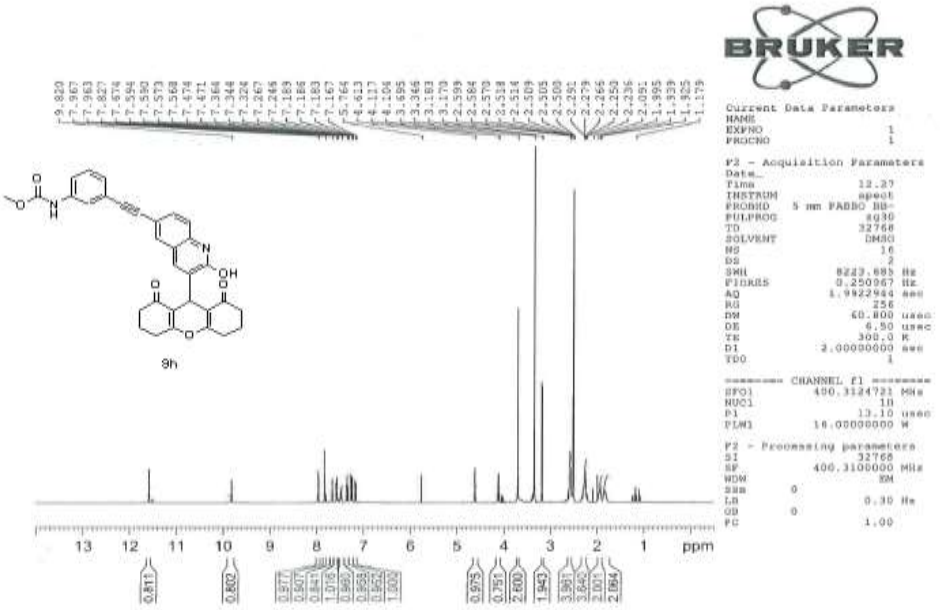
Time (min)	%B
0.0	05
2.5	95
4.0	95
4.5	05
6.0	05

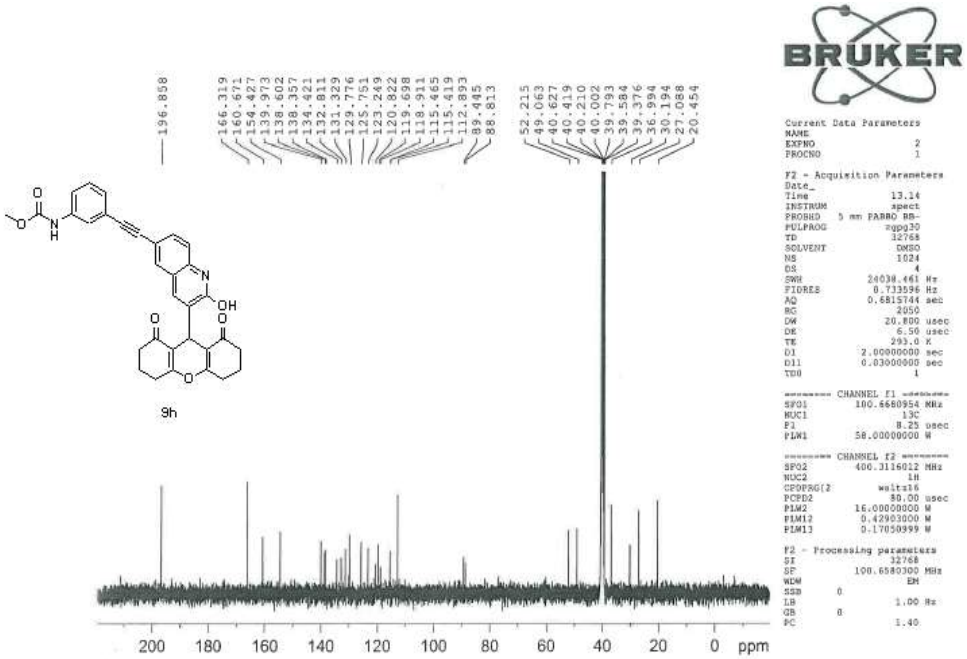




Peak No	RT min	Area	Area %
1	1.884	1.171	0.075
2	1.973	3.415	0.219
3	2.220	39.482	2.535
4	2.313	1487.109	95.489
5	2.410	3.615	0.232
6	2.512	12.531	0.805
7	2.750	2.386	0.153
8	2.808	1.546	0.099
9	2.885	4.301	0.276
10	3.189	1.800	0.116




9h
Current Data Parameters
NAME
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_
Time 12.27
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT DMSO
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9922944 sec
RG 256
DW 60.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.3124721 MHz
NUC1 1H
P1 13.10 usec
PLW1 16.00000000 W
F2 - Processing parameters
SI 32768
SF 400.3100000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
0.811
0.802
0.977
0.947
0.841
1.076
0.960
0.959
0.922
1.000
0.975
0.751
2.600
1.943
3.961
3.840
2.001
2.064

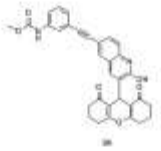

9h
196.858
166.319
160.671
154.427
139.373
138.602
138.357
134.421
132.821
131.729
131.176
123.761
120.249
120.022
119.698
118.911
115.465
115.419
112.893
89.445
88.813
52.215
49.063
40.627
40.419
40.210
40.002
39.793
39.584
39.376
36.994
30.194
27.088
20.454
Current Data Parameters
NAME
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_
Time 13.14
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT DMSO
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6815744 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 293.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6680954 MHz
NUC1 13C
P1 8.25 usec
PLW1 58.00000000 W
======== CHANNEL f2 ========
SFO2 400.3116012 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 16.00000000 W
PLW12 0.42903000 W
PLW13 0.17050999 W
F2 - Processing parameters
SI 32768
SF 100.6580300 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 180 160 140 120 100 80 60 40 20 0 ppm

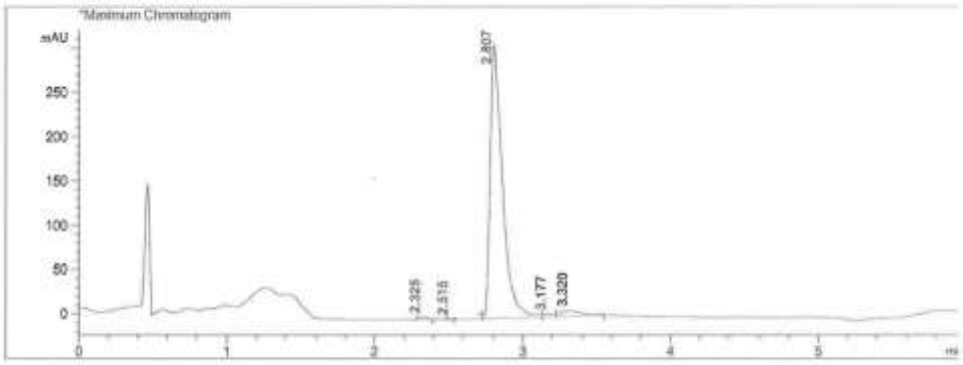
LC/MS REPORT

Data file	: C:\		
Acq Method	: C:\METHODS\AT 595FA.M		
Injection Date	: 6/28/2019	Vial No.	: Vial 52
Injection Time	: 6:13:14 PM	Injection vol	: 12.0µL
Sample Name	: IS00412672_B856381		

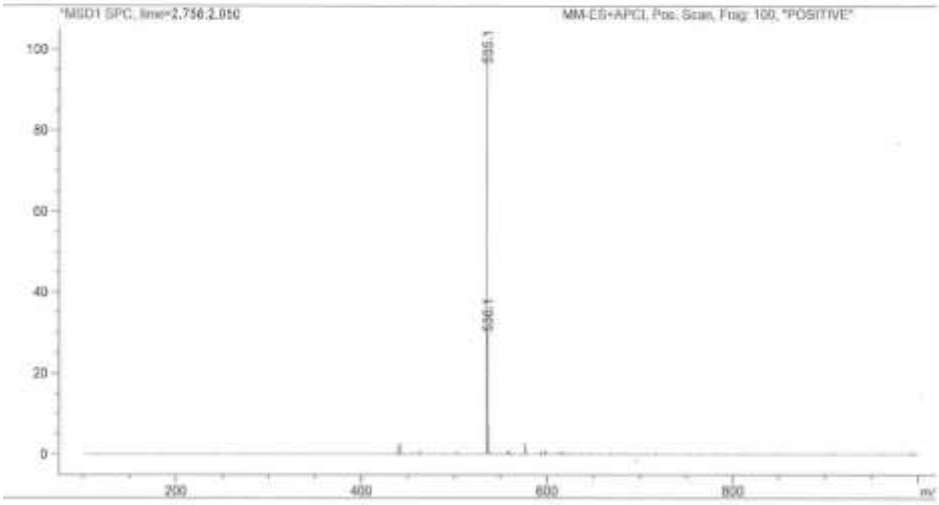
Method info : Column :Atlantis dC18 (50*4.6)5µ
Mobile phase :A :0.1%Formic Acid in H2O B: ACN
Flow Rate :1.5 ml/min

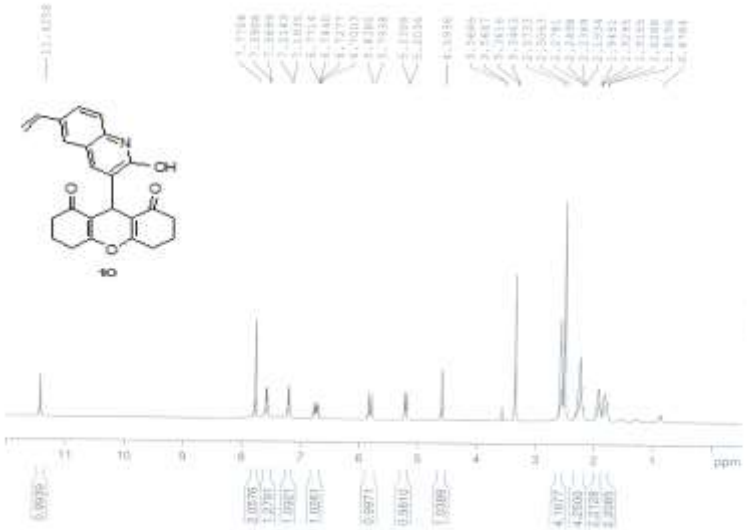
Time(min)	%B
0.0	05
2.5	95
4.0	95
4.5	05
6.0	05

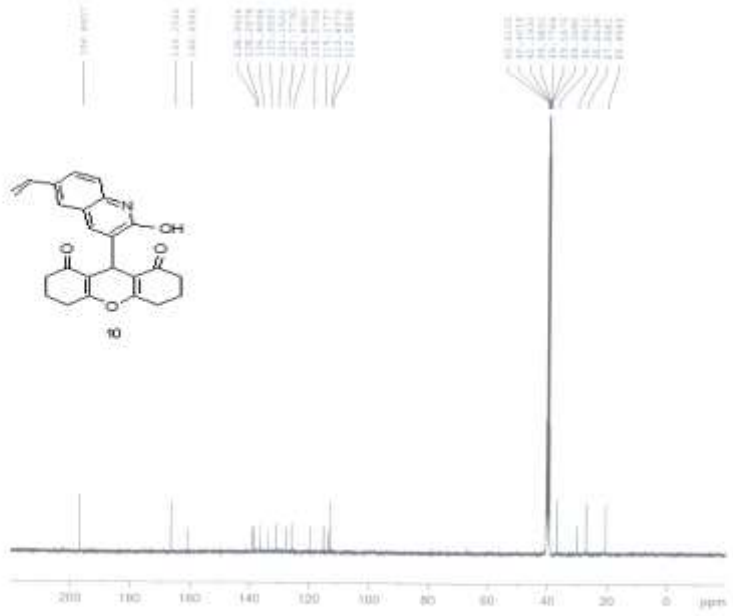


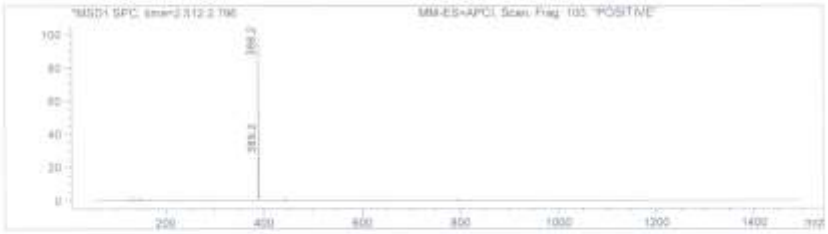


LC/MS REPORT



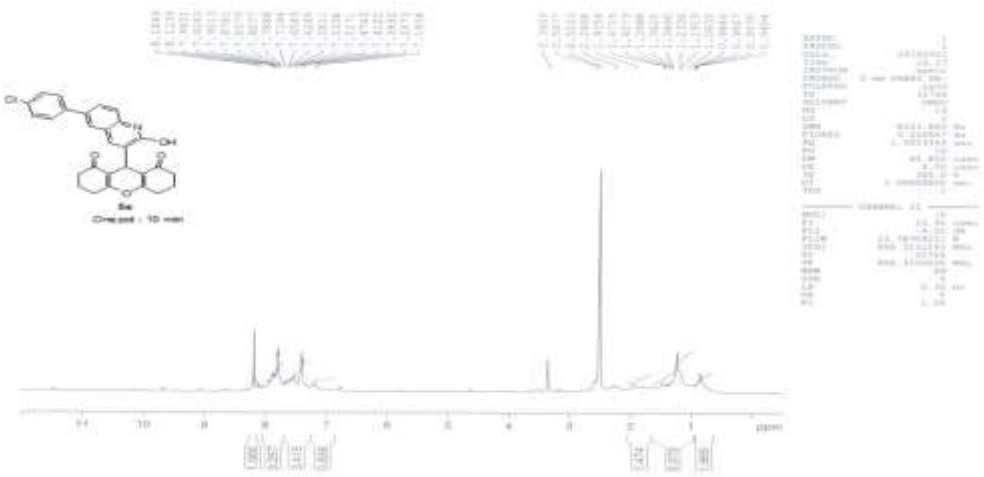

OH
O
O
O
10
11
10
9
8
7
6
5
4
3
2
1
ppm

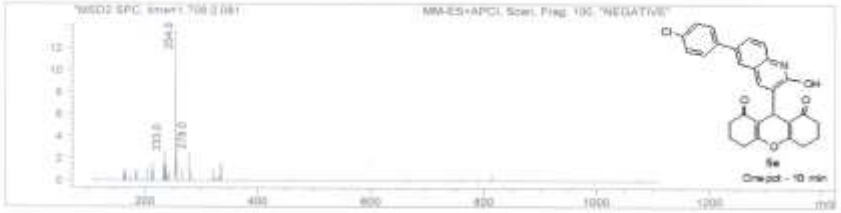

OH
O
O
O
10
200
180
160
140
120
100
80
60
40
20
0
ppm

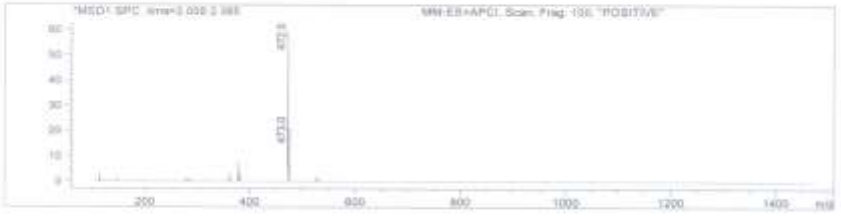


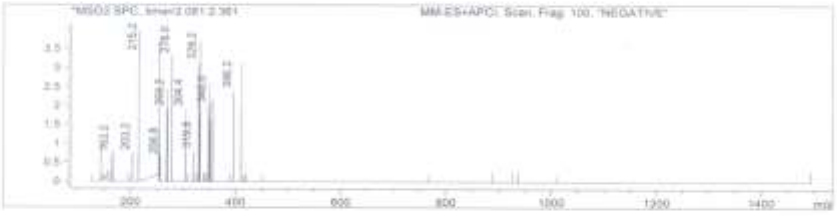
<u>One pot Suzuki-Miyaura Coupling Reactions with 4-Chloro phenyl boronic acid:</u>

Conditions tried with 10 min, 10% Product.

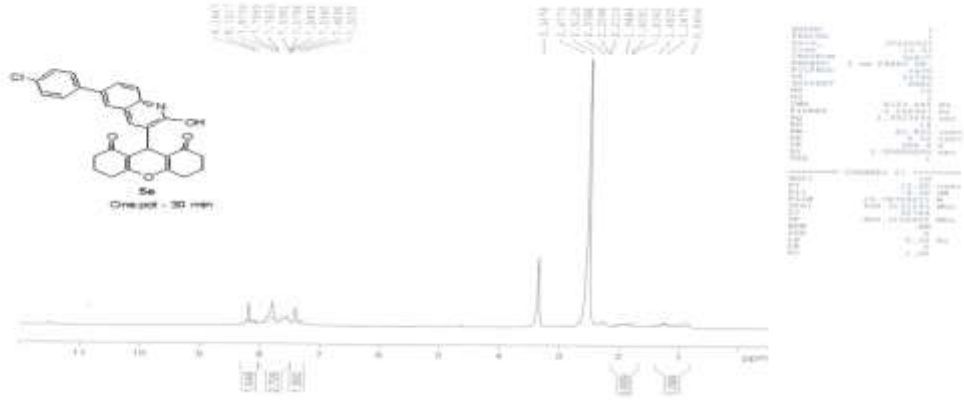








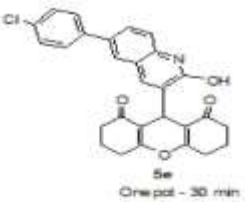
Conditions tried with 30 min, 21% of Product.

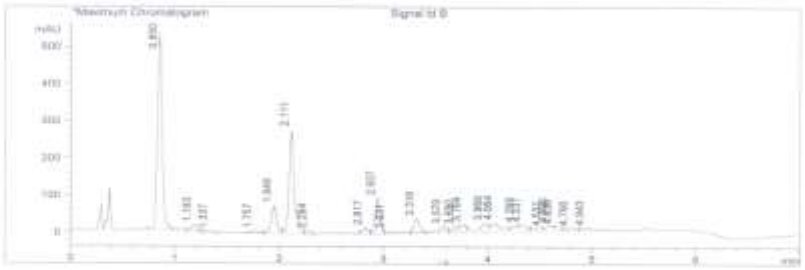


LC-MS REPORT

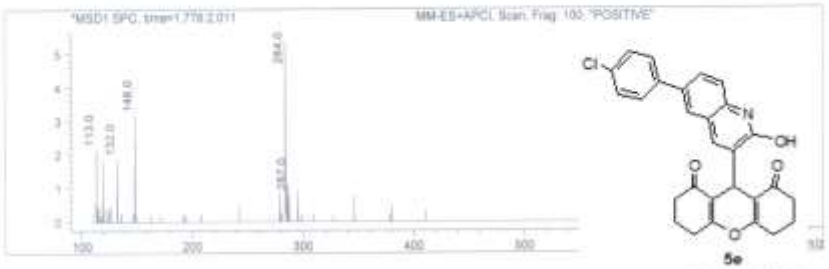
Method info :

A=0.1%FORMIC ACID IN WATER :B=ACN Flow = 1.5ML/MIN
Column=xbridge XDBC18 (50X4.6mm-5µm)
Time (min.) : 0--3.0 3.0--5.0 5.0--6.0 6.0--7.0
% B : 40-95 95 95-40 40



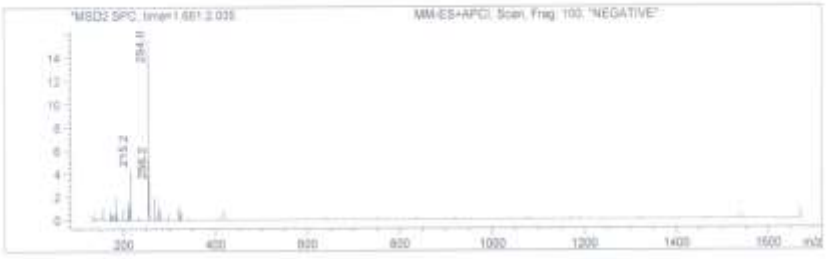


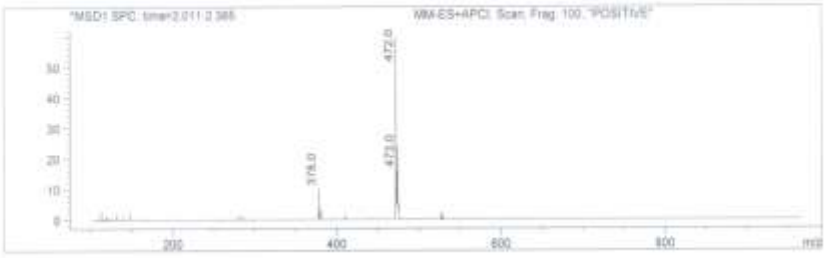
Peak No	RT Min	Area	Area %
1	0.850	1634.305	35.781
2	1.183	64.084	1.402
3	1.337	13.272	0.290
4	1.757	32.574	0.713
5	1.948	276.329	6.047
6	2.111	975.653	21.352
7	2.284	27.239	0.596
8	2.817	56.551	1.238
9	2.937	306.840	6.715
10	3.031	34.702	0.759
11	3.316	139.083	3.044
12	3.570	89.543	1.960



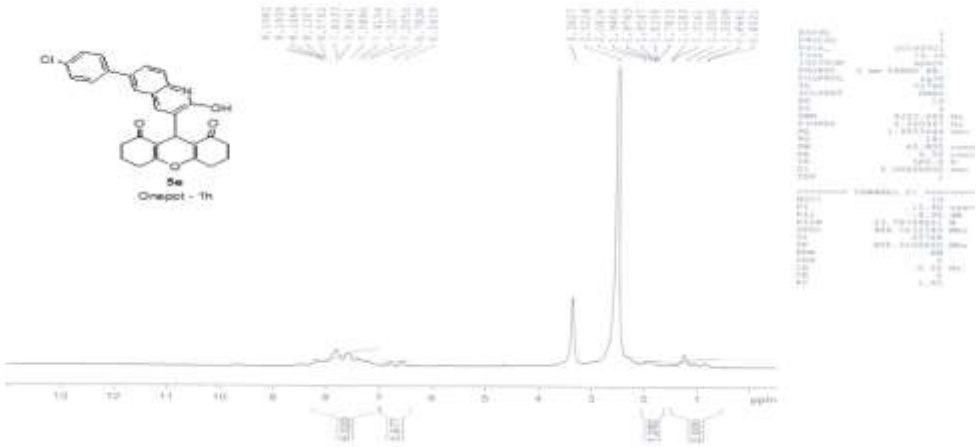
5e

One pot - 30 min

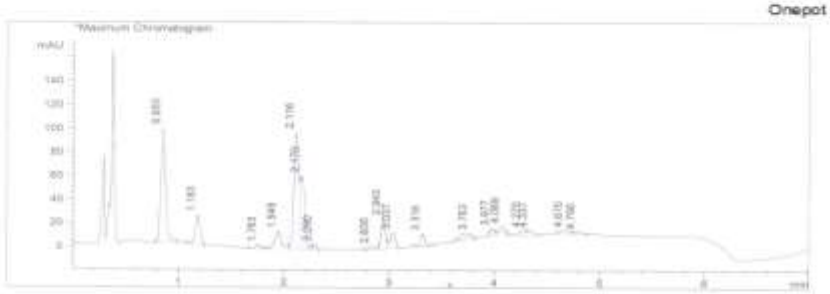




Conditions tried with 1h, 38% of Product.



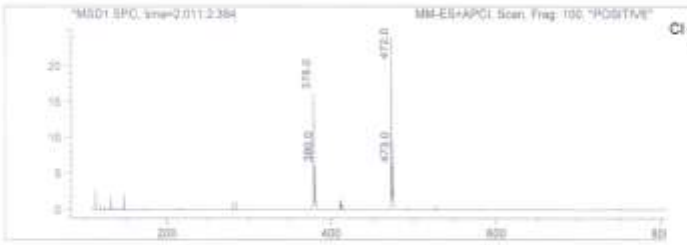
5e
Onepot - 1h

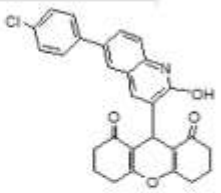


Peak No	RT min	Area	Area %
1	0.850	304.082	23.322
2	1.183	78.245	6.001
3	1.763	10.942	0.839
4	1.948	68.851	5.281
5	2.116	328.562	25.199
6	2.170	172.456	13.227
7	2.290	10.249	0.786
8	2.838	11.345	0.870
9	2.943	77.677	5.957
10	3.027	44.463	3.410
11	3.316	31.030	2.380
12	3.743	39.853	2.596

Analysed by :

LC-MS REPORT





5e
Onepot - 1h