Supporting Information

Enantioselective 1,4-addition of kojic acid derivatives to β-nitroolefins catalyzed by a cinchonine derived sugar thiourea.

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Contents

1. General Remarks.

All the solvents were purchased from commercial source and dried prior to use. All the enantioselective Michael reactions were performed in an oven-dried Schlenk flask under an inert atmosphere of argon. All products were purified by column chromatography on silica gel 60-120 mesh using a mixture of ethyl acetate-hexane as eluents. Progress of the reaction was monitored by Thin Layer Chromatography. ^{1}H NMR spectra were recorded in $CDCl_3$ using 300 MHz or 500 MHz spectrometers. ^{13}C NMR spectra were recorded in $CDCl_3$ using 75 MHz and 125 MHz NMR spectrometers. The chemical shifts (δ) were reported in parts per million (ppm) with respect to TMS as an internal standard. The coupling constants (J) are quoted in Hertz (Hz). Mass spectra were recorded on mass spectrometer by Electrospray ionization (ESI) technique. HPLC analysis was carried out in a Shimadzu LC-20 using chiral columns. A mixture of hexane-isopropyl alcohol was used as eluent. Optical rotations of the products were recorded on Digipol-781 M6U Polarimeter.

2. Preparation of starting materials.

Nitro olefins were purchased from Aldrich.

a) General procedure for preparation of 2-(*tert*-butyldimethylsilanyloxymethyl)-5-hydroxypyrane-4-one[(1)] (1)

To a stirred solution of kojic acid (5 mmol) in 25 ml CH_2Cl_2, triethylamine (10 mmol) and dimethylaminopyridine (2 mg) were added. To this mixture, *tert*-butyldimethylsilyl chloride (10 mmol) was added at 0°C, and then the resulting mixture was stirred at the same temperature for 1 h. Up on completion, the mixture was quenched with water, extracted with ethyl acetate and the organic layer was dried over sodium sulfate. After removal of the solvent, the residue was

then stirred for 1h in the presence of 30% formic acid/chloroform solution (25/25 ml). After the completion, the mixture was diluted with water (50 ml), extracted with chloroform and the organic layer was dried over sodium sulfate. The solvent was evaporated under reduced pressure and the residue was purified through column chromatography on silica gel (Hexane/EtOAc = 80/20) to give the 2-(*tert*-butyldimethylsilanyloxymethyl)-5-hydroxypyrane-4-one (white solid, 94%(1204.93 mg) of yield).

b) General procedure for the preparation of 2-methyl-5-hydroxypyran-4-(1*H*)-one[1a] (4a)

A mixture of kojic acid (1 mmol) and thionyl chloride (20 mmol) was stirred at room temperature for 30 min. The resulting precipitate was filtered and washed with hexane to give the product (chlorokojic acid, 98 %(157.33 mg) yield) as a white solid, which was then dissolved in 5 ml of distilled water at 50 °C. To this solution were added zinc dust (3 mmol) followed by conc. hydrochloric acid (56.1 mL) over 1 h in dropewise manner under vigorous stirring maintaining the temperature between 70 and 80 °C. The mixture was stirred for another 3h at 70 °C then the solid was removed by filtration. The filtrate was extracted with CH_2Cl_2 and the organic extracts were dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure and the residue was purified through column chromatography on silica gel (Hexane/EtOAc = 40/60) to give the 2-methyl-5-hydroxypyran-4(1H)-one in 74 %(93.32 mg) yield as a white solid.

c) General procedure for the preparation of 2-((4-chlorophenylthio)-methyl)-5-hydroxy-4*H*-pyran-4-one[2] (4b)

To a stirred solution of chlorokojic acid (3 mmol) and triethylamine (4 mmol) in THF (10 mL) under N_2 was added 4-chlorobenzenethiol (3.3 mmol). The mixture was stirred for 10 h at room temperature, after which THF was evaporated in vacuo. The residue was extracted with ethyl acetate and washed with water. The organic layer was dried over anhydrous sodium sulfate and the solvent was evaporated under reduced pressure. The resulting residue was purified through column chromatography on silica gel (Hexane/EtOAc = 3/7) to give the (2-((4-

chlorophenylthio)methyl)-5-hydroxy-4H-pyran-4-one, 75%(604.59 mg) in yield as a white solid.

3. General procedure for preparing thiourea catalysts.

a) Preparation of thiourea II

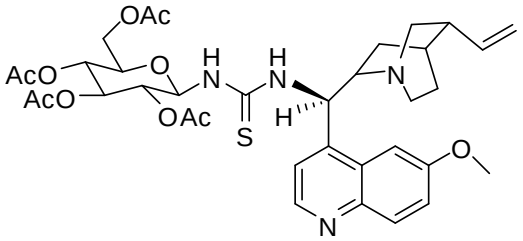
To a stirred solution of the (1*R*)-(6-methoxyquinolin-4-yl)(8-vinylquinuclidin-2-yl)methanamine[3] (4 mmol) in CH_2Cl_2 (10 mL) was added a solution of glycosyl isothiocyanate[4] (4.4 mmol) in CH_2Cl_2 (15 mL) in dropwise manner under N_2 atmosphere. The resulting mixture was stirred at room temperature until total consumption of the isothiocyanate (monitored by TLC). After removal of the solvent, the residue was purified through column chromatography on silica gel (EtOAc/MeOH = 85/15) to give the thiourea catalyst as a white solid.

b) Preparation of thiourea III and VI

To a solution of the corresponding chiral amine (2 mmol) in methylene chloride (8 mL) was added dropwise a solution of dehydroabietic isothiocyanate [5] (2.4 mmol) in methylene chloride (12 mL) under nitrogen atmosphere. The resulting mixture was stirred at room temperature until total consumption of the isothiocyanate (monitored by TLC). After removal of the solvent, the residue was purified through column chromatography on silica gel (Hexane/EtOAc = 5/95).

4. Spectral data of thiourea catalysts.

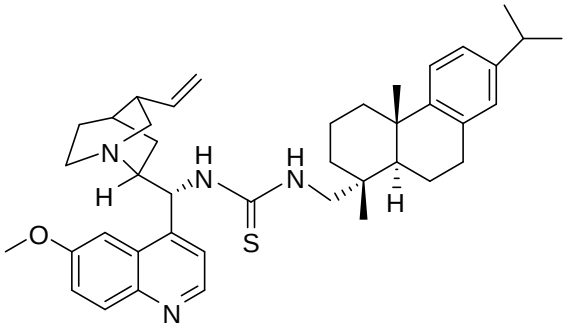
Ligand II



White solid, m.p. = 101-103 °C; Yield: 76% (2168.37 mg); $[\alpha]_D^{28}$ = +116.8 (*c* = 0.5, in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.17-1.32 (m, 1H), 1.40-1.52 (m, 1H), 1.75 (s, 2H), 1.79-1.94 (m, 2H), 1.96-2.14 (m, 14H), 2.65 (brs, 1H), 3.11-3.50 (m, 2H),

3.72-3.86 (m, 1H), 4.03 (s, 3H), 4.08-4.17 (m, 1H), 4.22-4.51 (m, 5H), 4.93-5.13 (m, 2H), 5.21-5.50 (m, 2H), 5.70 (brs, 1H), 5.86-6.02 (m, 1H), 7.32-7.42 (m, 1H), 7.48 (d, *J* = 14.5 Hz, 1H), 7.88 (brs, 1H), 7.93-8.02 (m, 1H), 8.70 (d, *J* = 4.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.4, 20.6, 23.2, 23.9, 24.2, 26.4, 36.9, 46.2, 48.6, 55.7, 60.2, 61.5, 68.0, 70.2, 73.2, 73.3, 82.6, 101.8, 116.7, 120.3, 122.5, 127.7, 129.3, 131.3, 137.3, 142.3, 144.5, 147.3, 158.2, 169.4, 169.8, 169.9, 170.6, 178.9, 184.1. IR (KBr): υ 2935, 1752, 1622, 1545, 1373, 1227, 1035, 912, 759, 601 cm^{-1}; MS (ESI) *m/z* 714 $[M+H]^+$; HRMS (ESI): Exact mass calcd for $C_{35}H_{45}O_{10}N_4S$ 713.28509. Found: 713.28602.

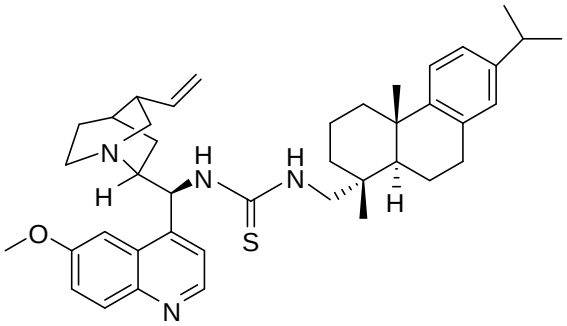
Ligand III



III

White solid, m.p. 129-131°C; Yield: 71% (924.98 mg); $[\alpha]_D^{27}$ = +164.4 (*c* = 0.5, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 0.54 (s, 3H), 0.81-1.10 (m, 7H), 1.17-1.36 (m, 11 H), 1.37-1.93 (m, 6H), 2.04-2.40 (m, 2H), 2.58-3.07 (m, 9H), 3.22 (s, 1H), 3.81 (s, 2H), 5.02-5.16 (m, 2H), 5.79-5.96 (m, 1H), 6.86 (s, 1H), 7.00 (d, *J* = 8.2 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 1H), 7.31-7.67 (m, 4H), 8.00 (d, *J* = 9.1 Hz, 1H), 8.71 (s, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 18.0, 18.2, 18.8, 23.9, 25.1, 26.3, 27.2, 30.1, 33.4, 35.9, 36.9, 37.2, 37.8, 38.6, 45.9, 46.7, 48.9, 55.5, 56.6, 114.8, 122.6, 123.8, 124.1, 126.7, 128.6, 131.9, 134.4, 140.2, 144.8, 145.5, 146.8, 147.6, 158.2, 182.1. IR (KBr): υ 3372, 3067, 2930, 1711, 1620, 1552, 1378, 1235, 1028, 829, 724 cm^{-1}. HRMS (ESI) calcd for $C_{41}H_{55}ON_4S$: 651.4091, found: 651.4092.

Ligand VI



VI

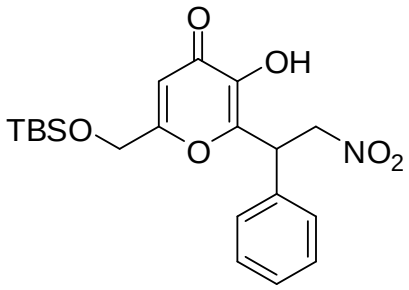
White solid, m.p. 132-134°C; Yield: 70% (911.96 mg); $[\alpha]_D^{27}$ = -69.2 (*c* = 0.5, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.86 (s, 3H), 1.01-1.36 (m, 16H), 1.43-1.77 (m, 3H), 1.79-2.00 (m, 5H), 2.13-2.32 (m, 1H), 2.35-3.00 (m, 6H), 3.14-3.91 (m, 4H), 4.01 (s, 3H), 4.96-5.19 (m, 2H), 5.55-5.74 (m, 1H), 6.18-6.65 (s, 1H), 6.78-6.92 (m, 1H), 6.97 (d, *J* = 8.12 Hz, 1H), 7.14 (d, *J* = 8.1 Hz, 1H), 7.29-7.61 (m, 2H), 7.86-8.08 (m, 2H), 8.66-8.79 (m, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 18.5, 19.1, 23.7, 23.9, 24.8, 25.2, 26.7, 29.8, 33.3, 35.8, 36.8, 37.2, 37.5, 37.8, 40.9, 44.9, 53.5, 55.2, 55.8, 59.8, 102.1, 116.9, 120.7, 122.3, 123.5, 123.9, 126.5, 127.7, 131.5, 134.7, 137.0, 142.7, 144.8, 145.2, 147.1, 147.5, 158.2, 182.7. IR (KBr): υ 3417, 3069, 2929, 1711, 1620, 1548, 1376, 1236, 1029, 826, 738 cm^{-1}; HRMS (ESI) calcd for $C_{41}H_{55}ON_4S$: 651.4091, found: 651.4092.

5. General procedure for Michael reaction.

To a stirred solution of organocatalyst II (5 mol %) and nitro olefin (2) (0.11 mmol) in i-PrOH (1 mL) at 5 °C was added 2-((tert-butyldimethylsilyloxy)-methyl)-5-hydroxy-4H-pyran-4-one (1) (0.1 mmol). The resulting mixture was stirred for 7 h at the same temperature. After completion of the reaction, the mixture was concentrated in vacuo and the resulting residue was purified by column chromatography on silica gel (hexane/EtOAc) to afford the optical pure Michael adduct.

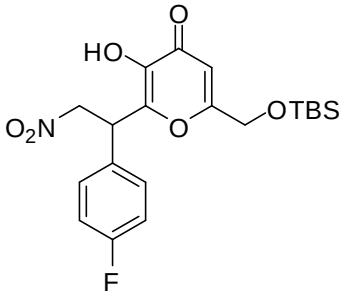
6. Characterization data of all products.

(R)-6-((*tert*-Butyldimethylsilyloxy)methyl)-3-hydroxy-2-(2-nitro-1-phenylethyl)-4*H*-pyran-4-one (3a).[6]



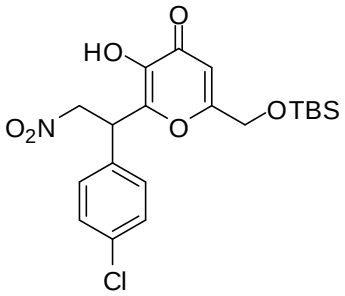
Brown solid; m.p. 158-159 °C (Lit. m.p. 159-160 °C)[6]; Yield 97% (39.33 mg); $[\alpha]_D^{27}$ = +69.2 (*c* = 0.5, $CHCl_3$). The ee was determined by HPLC using a DaicelChiralcel OJ-H column, n-hexane/i-PrOH 90:10, flow rate 1.00 mL/min, 254 nm; t_{major} = 10.9 min, t_{minor} = 17.15 min (99% ee); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.11 (s, 6H), 0.92 (s, 9H), 4.48 (s, 2H), 4.90 (dd, *J* = 6.8, 13.6 Hz, 1H), 5.01-5.11 (m, 1H), 5.20 (dd, *J* = 9.1, 13.6 Hz, 1H), 6.50 (s, 1H), 7.35 (m, 5H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ -5.6, 18.0, 25.6, 29.6, 43.3, 61.4, 75.4, 108.5, 127.7, 128.5, 129.4, 135.3, 142.0, 146.0, 167.5, 173.9. IR (KBr): υ 3251, 2930, 2855, 1652, 1630, 1590, 1551, 1456, 1377, 1252, 1217, 1083, 949, 842, 780, 699 cm^{-1}.

(R)-6-((*tert*-Butyldimethylsilyloxy)methyl)-2-(1-(4-fluorophenyl)-2-nitroethyl)-3-hydroxy-4*H*-pyran-4-one (3b).[6]



Brown solid; m.p. 153-155 °C (Lit. m.p. 154-155 °C)[6]; Yield: 98% (41.50 mg); $[\alpha]_D^{27}$ = +59.2 (*c* = 0.5, $CHCl_3$). The ee was determined by HPLC using a DaicelChiralcel OJ-H column, n-hexane/i-PrOH 90:10, flow rate 1.00 mL/min, 254 nm; t_{major} = 12.8 min, t_{minor} = 20.2 min (96% ee); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.11 (s, 6H), 0.92 (s, 9H), 4.48 (s, 2H), 4.89 (dd, *J* = 6.8, 12.8 Hz, 1H), 5.01-5.10 (m, 1H), 5.16 (dd, *J* = 9.1, 12.8 Hz, 1H), 6.51 (s, 1H), 7.05 (t, *J* = 8.3 Hz, 2H), 7.28-7.40 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ -5.5, 18.2, 25.6, 42.6, 61.3, 75.3, 108.6, 116.1, 116.4, 129.5, 131.1, 142.0, 145.7, 161.0, 164.2, 167.5, 174.0. IR (KBr): υ 3251, 2935, 2859, 1630, 1592, 1553, 1511, 1458, 1373, 1242, 1090, 842, 778 cm^{-1}.

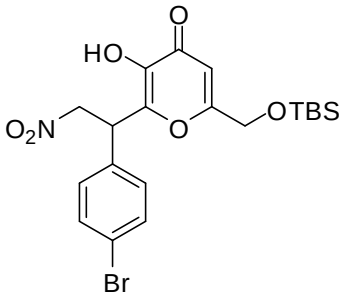
_(R)_-6-((_tert_-Butyldimethylsilyloxy)methyl)-2-(1-(4-chlorophenyl)-2-nitroethyl)-3-hydroxy-4_H_-pyran-4-one (3c).[6]



Brown solid; m.p. 74-76 °C (Lit. m.p. 74-75 °C)[6]; Yield: 97% (42.67 mg); $[\alpha]_D^{27}$ = +68.1 (*c* = 0.5, $CHCl_3$). The ee was determined by HPLC using a DaicelChiralcel OJ-H column, n-hexane/i-PrOH 90:10, flow rate 1.00 mL/min, 254 nm; t_{major} = 16.7 min, t_{minor} = 24.1 min (94% ee); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.11 (s, 6H), 0.92 (s, 9H), 4.47 (s, 2H), 4.90 (dd, *J* = 6.8, 12.8 Hz, 1H), 5.00-5.08 (m, 1H), 5.16 (dd, *J* = 8.3, 12.8 Hz, 1H), 6.51 (s, 1H), 7.25-7.39 (m, 5H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ -5.5, 18.2, 25.6, 42.6, 61.3, 75.1, 108.6, 129.1, 129.5, 133.7, 134.6, 142.0, 145.4, 167.6,

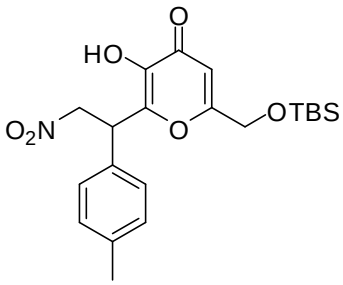
173.9. IR (KBr): υ 3250, 2932, 2857, 1629, 1589, 1553, 1457, 1372, 1252, 1220, 1088, 840, 780 cm^{-1}.

_(R)_-2-(1-(4-Bromophenyl)-2-nitroethyl)-6-((_tert_-butyldimethylsilyloxy)methyl)-3-hydroxy-4_H_-pyran-4-one (3d).[(6)]



Brown solid; m.p. 135-137 °C (Lit. m.p. 137-138 °C)[(6)]; Yield: 95% (46.01 mg); $[\alpha]_D^{27}$ = +68.1 (*c* = 0.5, $CHCl_3$). The ee was determined by HPLC using a DaicelChiralcel OJ-H column, n-hexane/i-PrOH 95:5, flow rate 1.00 mL/min, 254 nm; t_{major} = 40.8 min, t_{minor} = 54.1 min (94% ee); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.11 (s, 6H), 0.92 (s, 9H), 4.48 (s, 2H), 4.90 (dd, *J* = 6.8, 12.8 Hz, 1H), 5.00-5.08 (m, 1H), 5.16 (dd, *J* = 9.1, 12.8 Hz, 1H), 6.58 (s, 1H), 7.20-7.30 (m, 2H), 7.50 (d, 2H, *J* = 8.3 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ -5.5, 18.2, 25.6, 42.7, 61.3, 75.0, 108.6, 108.9, 122.7, 129.4, 132.5, 134.3, 137.3, 142.0, 145.3, 167.6, 173.9. IR (KBr): υ 3237, 2930, 2857, 1653, 1629, 1589, 1552, 1455, 1375, 1253, 1211, 1090, 840, 780 cm^{-1}.

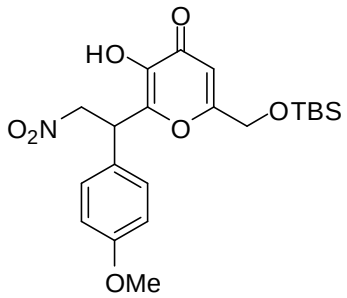
_(R)_-6-((_tert_-Butyldimethylsilyloxy)methyl)-3-hydroxy-2-(2-nitro-1-p-tolylethyl)-4_H_-pyran-4-one (3e).[(6)]



Brown solid; m.p. 124-126 °C (Lit. m.p. 123-124 °C)[(6)]; Yield: 90% (37.75 mg); $[\alpha]_D^{27}$ = +111.6 (*c* = 0.5, $CHCl_3$). The ee was determined by HPLC using a DaicelChiralcel OJ-H column, n-hexane/i-PrOH 95:5, flow rate 1.00 mL/min, 254

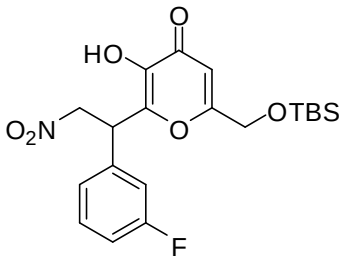
nm; t_{major} = 14.6 min, t_{minor} = 20.1 min (91% ee); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.11 (s, 6H), 0.92 (s, 9H), 2.33 (s, 3H), 4.48 (s, 2H), 4.87 (dd, *J* = 6.6, 13.0 Hz, 1H), 4.98-5.09 (m, 1H), 5.17 (dd, *J* = 9.1, 13.0 Hz, 1H), 6.50 (s, 1H), 7.12-7.34 (m, 4H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ -5.5, 18.2, 21.0, 25.7, 43.0, 61.4, 75.5, 108.4, 108.8, 127.6, 129.9, 132.3, 137.1, 138.4, 141.9, 145.5, 168.5, 174.3. IR (KBr): υ 3251, 2929, 2855, 1652, 1630, 1589, 1553, 1455, 1378, 1253, 1215, 1081, 843, 782 cm^{-1}.

(*R*)-6-((*tert*-Butyldimethylsilyloxy)methyl)-3-hydroxy-2-(1-(4-methoxyphenyl)-2-nitroethyl)-4*H*-pyran-4-one (3f).[(6)]



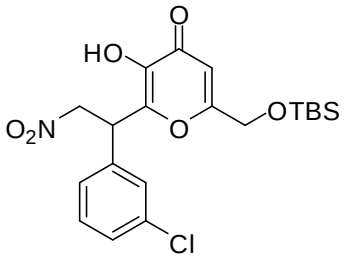
Brown solid; m.p. 143-145 °C (Lit. m.p. 142-143 °C)[(6)] ; Yield: 95% (41.37 mg); $[\alpha]_D^{27}$ = +118.6 (*c* = 0.5, $CHCl_3$). The ee was determined by HPLC using a DaicelChiralcel OJ-H column, n-hexane/i-PrOH 90:10, flow rate 1.00 mL/min, 254 nm; t_{major} = 19.9 min, t_{minor} = 30.8 min (91% ee); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.11 (s, 6H), 0.92 (s, 9H), 3.79 (s, 3H), 4.48 (s, 2H), 4.86 (dd, *J* = 6.6, 12.8 Hz, 1H), 4.97-5.04 (m, 1H), 5.16 (dd, *J* = 8.9, 13.0 Hz, 1H), 6.49 (s, 1H), 6.88 (d, *J* = 8.9 Hz, 2H), 7.26 (d, *J* = 8.9 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ -5.5, 18.1, 25.6, 42.6, 55.2, 61.3, 75.5, 108.5, 108.9, 114.6, 127.2, 128.9, 137.3, 141.8, 145.5, 146.3, 159.6, 167.4, 168.5, 173.9. IR (KBr): υ 3244, 2953, 2931, 2855, 1655, 1630, 1592, 1548, 1513, 1456, 1374, 1253, 1229, 1084, 839, 778 cm^{-1}.

(*R*)-6-((*tert*-Butyldimethylsilyloxy)methyl)-2-(1-(3-fluorophenyl)-2-nitroethyl)-3-hydroxy-4*H*-pyran-4-one (3g).



Brown solid; m.p. 139-141 °C; Yield: 96% (40.65 mg); $[\alpha]_D^{27}$ = +42.6 (*c* = 0.5, $CHCl_3$). The ee was determined by HPLC using a DaicelChiralcel OJ-H column, n-hexane/i- PrOH 90:10, flow rate 1.00 mL/min, 254 nm; t_{major} = 14.2 min, t_{minor} = 22.1 min (85% ee); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.11 (s, 6H), 0.92 (s, 9H), 4.49 (s, 2H), 4.91 (dd, *J* = 6.8, 12.8 Hz, 1H), 5.03-5.11 (m, 1H), 5.17 (dd, *J* = 9.1, 12.8 Hz, 1H), 6.51 (s, 1H), 6.98-7.18 (m, 3H), 7.29-7.39 (m, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ -5.5, 25.6, 42.8, 61.3, 75.0, 108.6, 114.7, 115.5, 123.5, 130.8, 137.5, 142.2, 145.3, 164.6, 167.6, 174.0. IR (KBr): υ 3256, 2955, 2932, 2858, 1653, 1630, 1590, 1552, 1451, 1378, 1251, 1085, 841, 781, 704 cm^{-1}. HRMS (ESI) calcd for $C_{20}H_{27}O_6FNSi$: 424.1586, found: 424.1575.

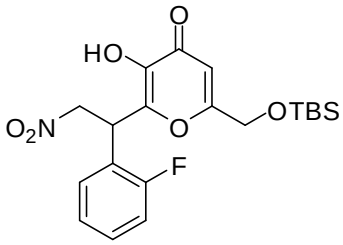
***(R)*-6-((*tert*-Butyldimethylsilyloxy)methyl)-2-(1-(3-chlorophenyl)-2-nitroethyl)-3-hydroxy-4*H*-pyran-4-one (3h).**



Brown solid; m.p. 128-130 °C; Yield: 95% (41.79 mg); $[\alpha]_D^{27}$ = +58.6 (*c* = 0.5, $CHCl_3$). The ee was determined by HPLC using a DaicelChiralcel OJ-H column, n-hexane/i-PrOH 90:10, flow rate 1.00 mL/min, 254 nm; t_{major} = 13.8 min, t_{minor} = 28.1 min (88% ee); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.11 (s, 6H), 0.92 (s, 9H), 4.49 (s, 2H), 4.90 (dd, *J* = 6.8, 12.8 Hz, 1H), 5.00-5.07 (m, 1H), 5.12-5.23 (m, 1H), 6.52 (s, 1H), 7.21-7.37 (m, 5H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ -5.5, 18.1, 25.7, 42.9, 61.4, 75.0, 108.6, 125.9, 127.9, 128.8, 130.5, 135.1, 137.2, 142.0, 145.1, 167.7, 173.9. IR (KBr): υ 3251, 2953, 2930, 2857, 1653, 1629, 1590, 1552, 1456, 1375, 1252, 1213,

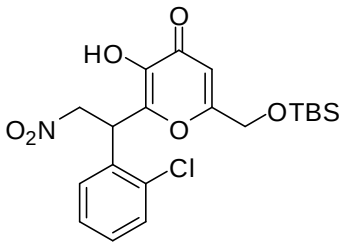
1086, 841, 781, 686 cm^{-1}. HRMS (ESI) calcd for $C_{20}H_{27}O_6ClNSi$: 440.1290, found: 440.1290.

***(R)*-6-((*tert*-Butyldimethylsilyloxy)methyl)-2-(1-(2-fluorophenyl)-2-nitroethyl)-3-hydroxy-4*H*-pyran-4-one (3i).**



Brown solid; m.p. 114-116 °C; Yield: 99% (41.92 mg); $[\alpha]_D^{27}$ = +64.2 (*c* = 0.5, $CHCl_3$). The ee was determined by HPLC using a DaicelChiralcel OJ-H column, n-hexane/i-PrOH 90:10, flow rate 1.00 mL/min, 254 nm; t_{major} = 9.9 min, t_{minor} = 15.1 min (95% ee); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.11 (s, 6H), 0.92 (s, 9H), 4.48 (s, 2H), 4.90 (dd, *J* = 7.5, 13.6 Hz, 1H), 5.18-5.29 (m, 1H), 5.31-5.40 (m, 1H), 6.53 (s, 1H), 7.05-7.19 (m, 2H), 7.28-7.40 (m, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ -5.5, 18.2, 25.6, 37.6, 61.3, 73.9, 108.4, 116.1, 116.3, 122.0, 122.2, 129.5, 130.3, 130.4, 142.4, 144.6, 159.4, 161.3, 167.8, 173.9. IR (KBr): υ 3255, 2928, 2854, 1652, 1631, 1592, 1550, 1456, 1374, 1253, 1228, 1080, 952, 842, 748, 754, 683 cm^{-1}. HRMS (ESI) calcd for $C_{20}H_{27}O_6FNSi$: 424.1586, found: 424.1602.

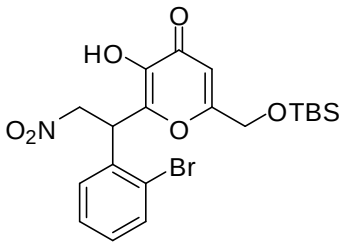
***(R)*-6-((*tert*-Butyldimethylsilyloxy)methyl)-2-(1-(2-chlorophenyl)-2-nitroethyl)-3-hydroxy-4*H*-pyran-4-one (3j).[(6)]**



Brown solid; m.p. 72-74 °C (Lit. m.p. 71-72 °C)[(6)] ; Yield: 98% (43.11 mg); $[\alpha]_D^{27}$ = +78.1 (*c* = 0.5, $CHCl_3$). The ee was determined by HPLC using a DaicelChiralcel OJ-H column, n-hexane/i-PrOH 95:5, flow rate 1.00 mL/min, 254 nm; t_{major} = 13.6 min, t_{minor} = 22.7 min (88% ee); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.11 (s, 6H), 0.92 (s, 9H),

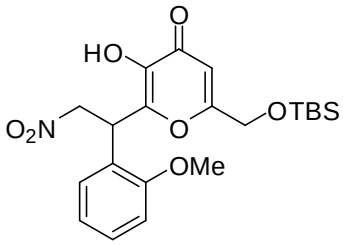
4.41-4.55 (m, 2H), 4.84 (dd, *J* = 5.7, 14.2 Hz, 1H), 5.20 (dd, *J* = 10.2, 14.2 Hz, 1H), 5.55 (dd, *J* = 5.7, 10.2 Hz, 1H), 6.53 (s, 1H), 7.22-7.35 (m, 4H), 7.41-7.49 (m, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ -5.5, 18.2, 25.7, 40.7, 61.4, 73.7, 108.5, 127.6, 128.9, 129.8, 130.4, 132.8, 133.8, 142.7, 144.8, 167.8, 173.9. IR (KBr): υ 3230, 2954, 2931, 2857, 1660, 1632, 1554, 1459, 1317, 1254, 1230, 1139, 843, 778, 685 cm^{-1}.

_(R)_-2-(1-(2-Bromophenyl)-2-nitroethyl)-6-((_tert_-butyldimethylsilyloxy)methyl)-3-hydroxy-4_H_-pyran-4-one (3k).[(6)]



Brown solid; m.p. 60-62 °C (Lit. m.p. 59-60 °C)[(6)] ; Yield: 96% (46.50 mg); $[\alpha]_D^{27}$ = +112.4 (*c* = 0.5, $CHCl_3$). The ee was determined by HPLC using a DaicelChiralcel OJ-H column, n-hexane/i-PrOH 90:10, flow rate 1.00 mL/min, 254 nm; t_{major} = 9.4 min, t_{minor} = 14.8 min (91% ee); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.11 (s, 6H), 0.92 (s, 9H), 4.40-4.56 (m, 2H), 4.83 (dd, *J* = 5.5, 14.2 Hz, 1H), 5.19 (dd, *J* = 10.4, 14.2 Hz, 1H), 5.55 (dd, *J* = 5.5, 10.2 Hz, 1H), 6.53 (s, 1H), 7.16-7.37 (m, 4H), 7.64 (dd, *J* = 8.3 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ -5.5, 18.1, 25.6, 43.2, 61.3, 73.7, 108.4, 124.2, 128.3, 128.9, 130.0, 133.7, 134.4, 142.7, 144.9, 167.9, 173.9. IR (KBr): υ 3239, 2935, 2861, 1659, 1631, 1591, 1552, 1457, 1251, 1217, 1093, 847, 778 cm^{-1}.

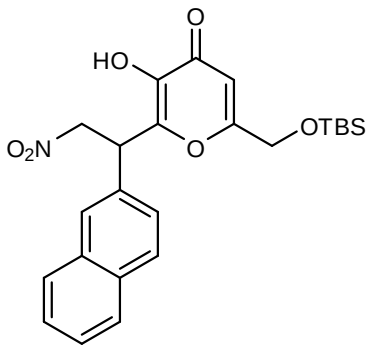
_(R)_-6-((_tert_-Butyldimethylsilyloxy)methyl)-3-hydroxy-2-(1-(2-methoxyphenyl)-2-nitroethyl)-4_H_-pyran-4-one (3l).



Brown solid; m.p. 110-112 °C; Yield: 97% (42.24 mg); $[\alpha]_D^{27}$ = +107.2 (*c* = 0.5, $CHCl_3$). The ee was determined by HPLC using a DaicelChiralcel OJ-H column, n-

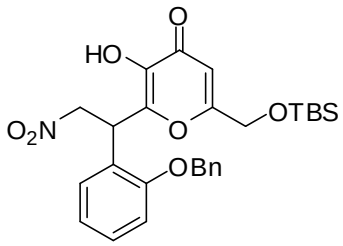
hexane/i-PrOH 90:10, flow rate 1.00 mL/min, 254 nm; t_{major} = 10.1 min, t_{minor} = 16.8 min (88% ee); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.11 (s, 6H), 0.92 (s, 9H), 3.88 (s, 3H), 4.48 (s, 2H), 4.77-4.87 (m, 1H), 5.10-5.21 (m, 1H), 5.44 (dd, *J* = 5.3, 10.6 Hz, 1H), 6.54 (s, 1H), 6.87-7.01 (m, 2H), 7.09-7.17 (m, 1H), 7.25-7.39 (m, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ -5.5, 18.2, 25.7, 38.1, 55.6, 61.4, 74.0, 108.1, 111.0, 121.0, 123.3, 127.0, 128.6, 129.6, 132.1, 134.4, 146.3, 156.6, 167.4, 174.6. IR (KBr): υ 3265, 2953, 2931, 2858, 1650, 1615, 1558, 1462, 1318, 1250, 1204, 1141, 1027, 841, 784, 756 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{30}O_7NSi$: 436.1786, found: 436.1792.

_(R)_-6-((_tert_-Butyldimethylsilyloxy)methyl)-3-hydroxy-2-(1-(naphthalen-2-yl)-2-nitroethyl)-4_H_-pyran-4-one (3m)



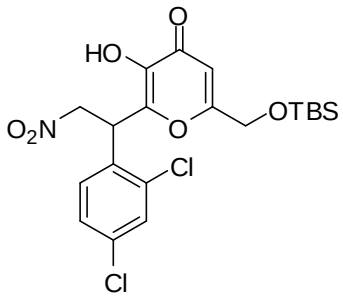
Brown solid; m.p. 116-118 °C; Yield: 93% (42.36 mg); $[\alpha]_D^{27}$ = +57.4 (*c* = 0.5, $CHCl_3$). The ee was determined by HPLC using a DaicelChiralcel OJ-H column, n-hexane/i-PrOH 90:10, flow rate 1.00 mL/min, 254 nm; t_{major} = 28.6 min, t_{minor} = 52.3 min (91% ee); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.11 (s, 6H), 0.92 (s, 9H), 4.48 (s, 2H), 5.02 (dd, *J* = 6.0, 12.1 Hz, 1H), 5.17-5.37 (m, 2H), 6.51 (s, 1H), 7.41-7.56 (m, 3H), 7.74-7.88 (m, 4H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ -5.5, 18.2, 25.7, 43.6, 61.4, 75.3, 108.5, 125.0, 126.7, 127.0, 127.7, 127.9, 129.3, 132.7, 133.0, 133.3, 137.2, 142.1, 145.6, 145.8, 167.6, 173.9. IR (KBr): υ 3237, 2952, 2930, 2856, 1653, 1627, 1589, 1549, 1455, 1374, 1253, 1209, 1086, 948, 841, 780, 743 cm^{-1}. HRMS (ESI) calcd for $C_{24}H_{30}O_6NSi$: 456.1836, found: 456.1841.

_(R)_-2-(1-(2-(Benzyloxy)phenyl)-2-nitroethyl)-6-((_tert_-butyldimethylsilyloxy)methyl)-3-hydroxy-4_H_-pyran-4-one (3n).



Brown solid; m.p. 144-146 °C; Yield: 92% (47.12 mg); $[\alpha]_D^{27}$ = +78.2 (*c* = 0.5, $CHCl_3$). The ee was determined by HPLC using a DaicelChiralcel OJ-H column, n-hexane/i-PrOH 98:2, flow rate 1.00 mL/min, 254 nm; t_{major} = 71.4 min, t_{minor} = 88.4 min (84% ee); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.09 (s, 6H), 0.92 (s, 9H), 4.30 (s, 2H), 4.84 (dd, *J* = 5.3, 13.6 Hz, 1H), 5.01-5.24 (m, 3H), 5.47 (dd, *J* = 5.3, 9.8 Hz, 1H), 6.50 (s, 1H), 6.87-7.05 (m, 2H), 7.17-7.49 (m, 8H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ -5.5, 18.1, 25.6, 38.4, 61.1, 70.3, 73.9, 108.1, 112.3, 121.3, 123.4, 127.3, 128.7, 129.0, 129.7, 136.2, 142.5, 145.9, 145.8, 155.8, 167.6, 173.9. IR (KBr): υ 3274, 2928, 2853, 1650, 1616, 1581, 1554, 1495, 1459, 1326, 1243, 1123, 1013, 843, 782, 752, 693 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{34}O_7NSi$: 512.2099, found: 512.2091.

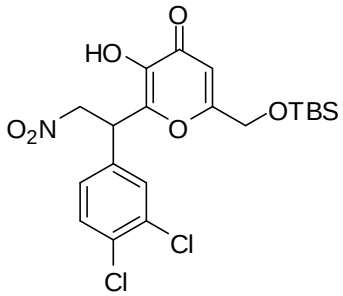
_(R)_-6-((_tert_-Butyldimethylsilyloxy)methyl)-2-(1-(2,4-dichlorophenyl)-2-nitroethyl)-3-hydroxy-4_H_-pyran-4-one (3o).[(6)]



Brown solid; m.p. 52-54 °C (Lit. m.p. 51-52 °C)[(6)] Yield: 95% (45.06 mg); $[\alpha]_D^{27}$ = +56.2 (*c* = 0.5, $CHCl_3$). The ee was determined by HPLC using a DaicelChiralcel OJ-H column, *n*-hexane/i-PrOH 95:5, flow rate 1.00 mL/min, 254 nm; t_{major} = 13.6 min, t_{minor} = 22.8 min (87% ee); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.11 (s, 6H), 0.92 (s, 9H), 4.39- 4.55 (m, 2H), 4.84 (dd, *J* = 5.8, 14.2 Hz, 1H), 5.14-5.26 (m, 1H), 5.55 (dd, *J* = 5.7, 10.2 Hz, 1H), 6.53 (s, 1H), 7.24-7.34 (m, 3H), 7.42-7.49 (s, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ -5.5, 18.2, 25.6, 40.6, 61.3, 73.6, 108.4, 127.6, 128.9, 129.8, 130.3,

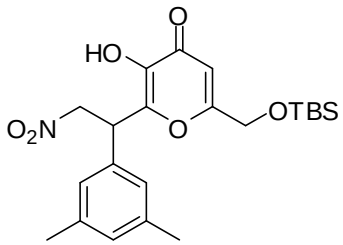
132.7, 133.7, 142.7, 144.8, 167.9, 173.9. IR (KBr): υ 3230, 2931, 2858, 1633, 1555, 1463, 1318, 1229, 1138, 844, 779 cm^{-1}.

_(R)_-6-((_tert_-Butyldimethylsilyloxy)methyl)-2-(1-(3,4-dichlorophenyl)-2-nitroethyl)-3-hydroxy-4_H_-pyran-4-one (3p).



Brown solid; m.p. 116-118°C; Yield: 94% (44.59 mg); $[\alpha]_D^{27}$ = +59.1 (_c_ = 0.5, $CHCl_3$). The ee was determined by HPLC using a DaicelChiralcel OJ-H column, n-hexane/i-PrOH 90:10, flow rate 1.00 mL/min, 254 nm; t_{major} = 16.1 min, t_{minor} = 31.6 min (91% ee); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.11 (s, 6H), 0.92 (s, 9H), 4.44- 4.53 (m, 2H), 4.91 (dd, _J_ = 6.0, 12.8 Hz, 1H), 4.98-5.07 (m, 1H), 5.15 (dd, _J_ = 8.3, 12.8 Hz, 1H), 6.52 (s, 1H), 7.19-7.24 (m, 3H), 7.42-7.48 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ -5.4, 18.2, 25.7, 42.5, 61.4, 74.8, 108.7, 127.1, 129.8, 131.3, 133.1, 133.5, 135.4, 142.1, 144.8, 167.8, 173.8. IR (KBr): υ 3250, 2953, 2857, 1656, 1629, 1548, 1456, 1369, 1252, 1229, 1092, 840, 781 cm^{-1}. HRMS (ESI) calcd for $C_{20}H_{26}O_6NCl_2Si$: 474.0901, found: 474.0919.

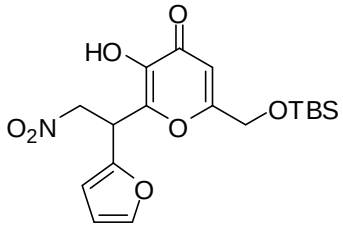
_(R)_-6-((_tert_-Butyldimethylsilyloxy)methyl)-2-(1-(3,5-dimethylphenyl)-2-nitroethyl)-3-hydroxy-4_H_-pyran-4-one (3q).



Brown solid; m.p. 96-98 °C; Yield: 90% (39.07 mg); $[\alpha]_D^{27}$ = +96.4 (_c_ = 0.5, $CHCl_3$). The ee was determined by HPLC using a DaicelChiralcel OJ-H column, _n_-hexane/i-PrOH 95:05, flow rate 1.00 mL/min, 254 nm; t_{major} = 9.9 min, t_{minor} = 12.7 min (95%

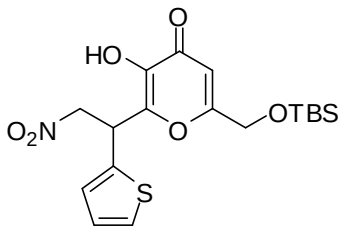
ee); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.11 (s, 6H), 0.92 (s, 9H), 2.29 (s, 6H), 4.48(s, 2H), 4.86 (dd, *J* = 6.8, 12.8 Hz, 1H), 4.94-5.04 (m, 1H), 5.12-5.25 (m, 1H), 6.52 (s, 1H), 6.87-6.99 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ -5.5, 21.3, 25.7, 43.3, 61.4, 75.3, 108.4, 125.4, 130.2, 135.2, 138.9, 141.9, 146.1, 167.5, 173.9. IR (KBr): υ 3273, 2931, 2858, 1626, 1589, 1557, 1460, 1374, 1253, 1127, 841, 781, 712 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{32}O_6NSi$: 434.1993, found: 434.2000.

_(R)_-6-((_tert_-Butyldimethylsilyloxy)methyl)-2-(1-(furan-2-yl)-2-nitroethyl)-3-hydroxy-4_H_-pyran-4-one (3r).



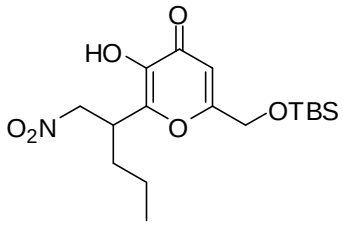
Brown solid; m.p. 102-104 °C; Yield: 94% (37.23 mg); $[\alpha]_D^{27}$ = +86.3 (*c* = 0.5, $CHCl_3$). The ee was determined by HPLC using a DaicelChiralcel OJ-H column, n-hexane/i-PrOH 98:2, flow rate 1.00 mL/min, 254 nm; t_{major} = 37.6 min, t_{minor} = 46.0 min (95% ee); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.12 (s, 6H), 0.92 (s, 9H), 4.47 (s, 2H), 4.92-5.13 (m, 2H), 5.21-5.30 (m, 1H), 6.22-6.30 (m, 1H), 6.31-6.39 (m, 1H), 6.54 (s, 3H), 7.38 (s, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ -5.5, 18.2, 25.7, 29.7, 37.1, 61.3, 73.4, 108.4, 108.6, 110.7, 142.9, 143.7, 147.5, 167.8, 174.1. IR (KBr): υ 3250, 2958, 2931, 2855, 1652, 1630, 1590, 1554, 1458, 1375, 1254, 1220, 1083, 1011, 842, 782, 734, 682 cm^{-1}. HRMS (ESI) calcd for $C_{18}H_{26}O_7NSi$: 396.1473, found: 396.1487.

_(R)_-6-((_tert_-Butyldimethylsilyloxy)methyl)-3-hydroxy-2-(2-nitro-1-(thiophen-2-yl)ethyl)-4_H_-pyran-4-one (3s).[(6)]



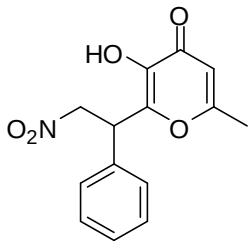
Brown solid; m.p. 128-130 °C (Lit. m.p. 128-129 °C)[6] Yield: 85% (34.97 mg); $[\alpha]_D^{27}$ = +76.7 (*c* = 0.5, $CHCl_3$). The ee was determined by HPLC using a DaicelChiralcel OJ-H column, n-hexane/i-PrOH 90:10, flow rate 1.00 mL/min, 254 nm; t_{major} = 12.9 min, t_{minor} = 17.5 min (92% ee); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.11 (s, 6H), 0.92 (s, 9H), 4.49 (s, 2H), 4.91 (dd, *J* = 6.98, 13.4 Hz, 2H), 5.07-5.20 (m, 1H), 5.37-5.47 (m, 1H), 6.52 (s, 1H), 6.95-7.01 (m, 1H), 7.03-7.08 (m, 1H), 7.16-7.33 (m, 1H) . ^{13}C-NMR (75 MHz, $CDCl_3$): δ -5.5, 25.7, 38.3, 61.3, 75.8, 108.6, 125.9, 126.7, 127.2, 128.5, 128.9, 129.1, 136.3, 137.4, 141.8, 144.8, 167.7, 174.0. IR (KBr): υ 3237, 2930, 2856, 1630, 1589, 1552, 1458, 1373, 1253, 1080, 841, 780, 696 cm^{-1}.

_(S)_-6-((_tert_-Butyldimethylsilyloxy)methyl)-3-hydroxy-2-(1-nitropentan-2-yl)-4_H_-pyran-4-one (3t).



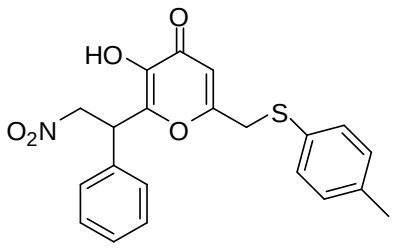
White solid; m.p. 111-113 °C; Yield: 90% (33.49 mg); $[\alpha]_D^{27}$ = -96.7 (*c* = 0.5, $CHCl_3$). The ee was determined by HPLC using a DaicelChiralcel OJ-H column, n-hexane/i-PrOH 99:01, flow rate 1.00 mL/min, 254 nm; t_{minor} = 33.0 min, t_{major} = 36.8 min (89% ee); ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.12 (s, 6H), 0.83-1.01 (m, 12H), 1.21-1.42 (m, 2H), 1.53-1.86 (m, 2H), 3.78-3.92 (m, 1H), 4.48 (s, 2H), 4.58 (dd, *J* = 6.20, 12.8 Hz, 1H), 4.69-4.81 (m, 1H), 6.52 (s, 1H) . ^{13}C-NMR (125 MHz, $CDCl_3$): δ -5.5, 13.6, 18.2, 19.9, 25.6, 31.6, 37.7, 61.3, 75.9, 108.4, 142.9, 146.9, 167.4, 174.0. IR (KBr): υ 3256, 2957, 2933, 2860, 1660, 1628, 1592, 1552, 1464, 1322, 1230, 1135, 844, 781, 678 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{30}O_6NSi$: 372.1836, found: 372.1836.

_(R)_-3-Hydroxy-6-methyl-2-(2-nitro-1-phenylethyl)-4_H_-pyran-4-one (5a).



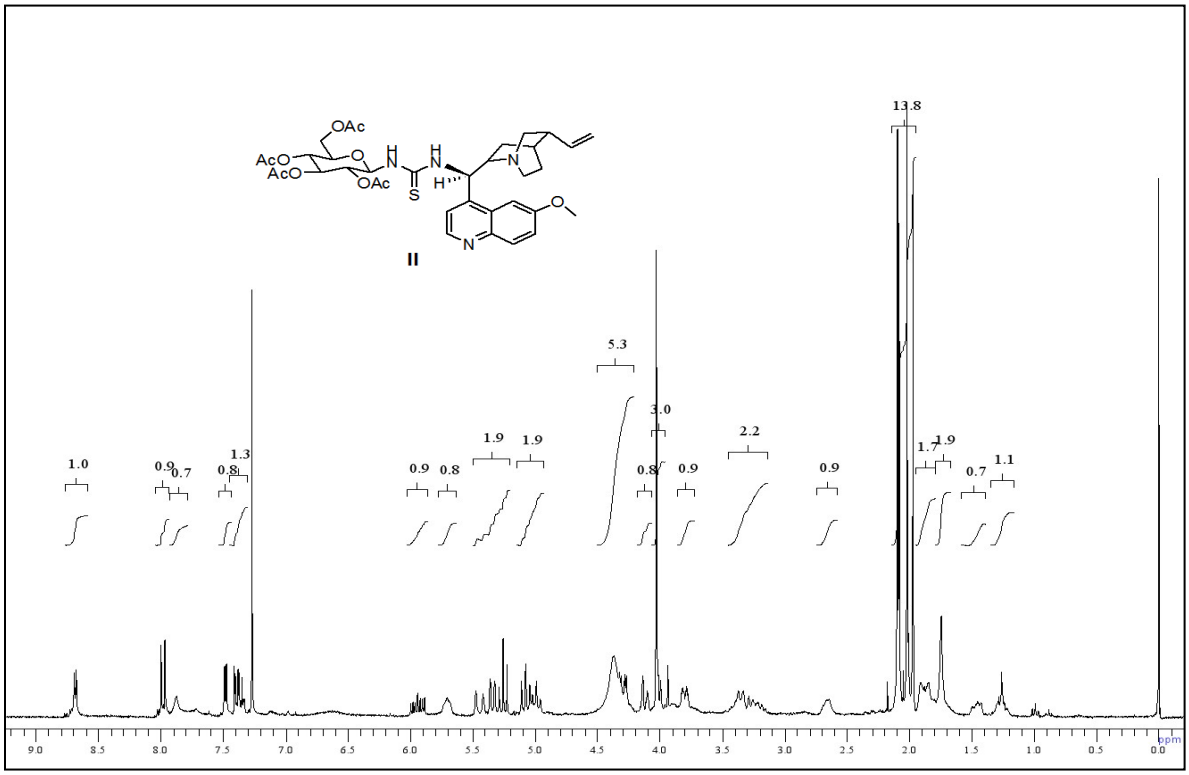
Brown solid; m.p. 120-122°C; Yield: 96% (26.50 mg); $[\alpha]_D^{27}$ = +36.6 (*c* = 0.5, $CHCl_3$). The ee was determined by HPLC using a DaicelChiralcel OJ-H column, n-hexane/i-PrOH 90:10, flow rate 1.00 mL/min, 254 nm; t_{major} = 21.7 min, t_{minor} = 44.5 min (95% ee); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 2.30 (s, 3H), 4.91 (dd, *J* = 6.7, 13.4 Hz, 1H), 5.05-5.27 (m, 2H), 6.24 (s, 1H), 7.28-7.48 (m, 5H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 20.0, 29.2, 43.1, 75.5, 110.6, 127.8, 128.4, 129.2, 135.5, 142.6, 146.7, 160.4, 165.5, 174.6. IR (KBr): υ 3213, 2923, 1650, 1625, 1559, 1451, 1376, 1335, 1207, 952, 863, 769, 703 cm^{-1}. HRMS (ESI) calcd for $C_{14}H_{14}O_5N$: 276.0866, found: 276.0870.

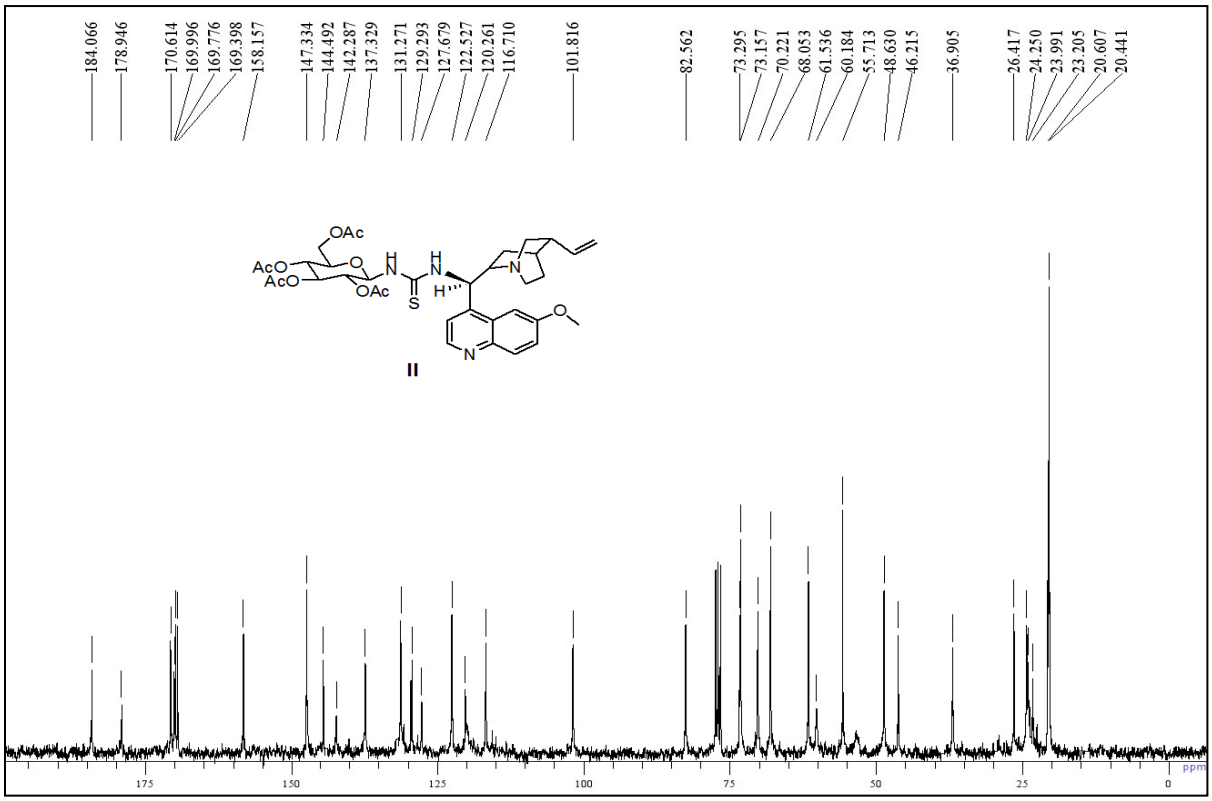
_(R)_-6-((4-Chlorophenylthio)methyl)-3-hydroxy-2-(2-nitro-1-phenylethyl)-4*H*-pyran-4-one (5b).

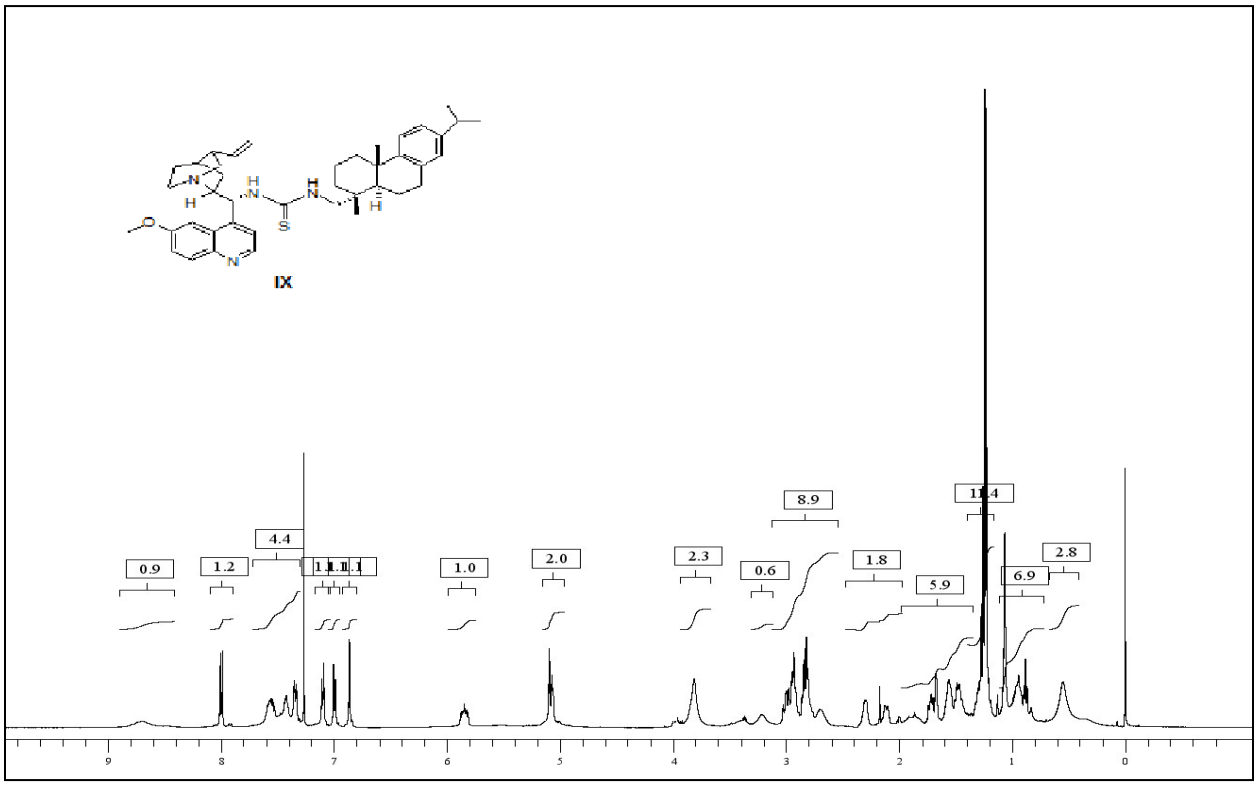


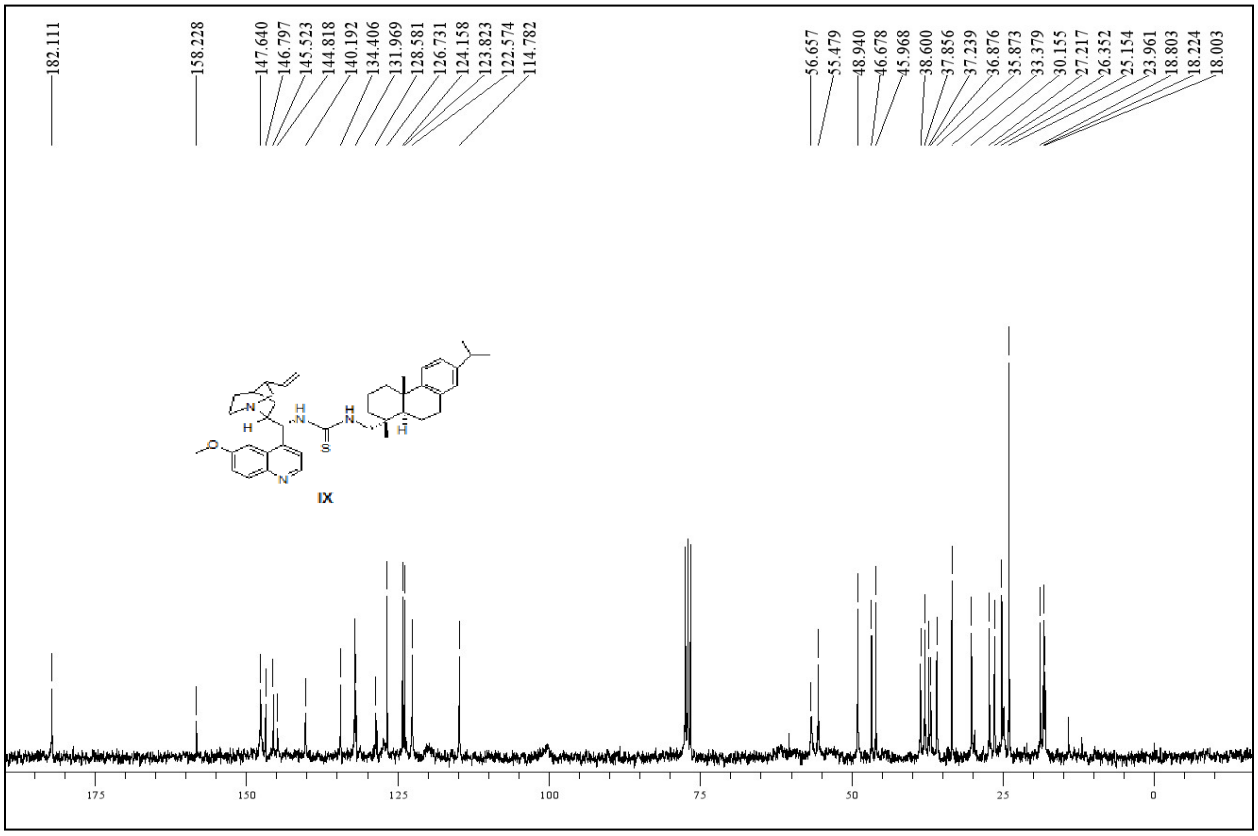
Semi solid; Yield: 95% (39.71 mg); $[\alpha]_D^{27}$ = +22.7 (*c* = 0.5, $CHCl_3$). The ee was determined by HPLC using a DaicelChiralcel OJ-H column, n-hexane/i-PrOH 70:30, flow rate 1.00 mL/min, 254 nm; t_{major} = 36.4 min, t_{minor} = 56.8 min (97% ee); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 3.83 (s, 2H), 4.83 (*J* = 6.1, 13.3 Hz, 1H), 5.01-5.07 (m, 1H), 5.08-5.16 (m, 1H), 6.15 (s, 1H), 7.16-7.40 (m, 10H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 25.3, 29.6, 37.4, 42.9, 75.1, 111.2, 127.7, 128.5, 129.3, 129.5, 131.5, 133.1, 134.4, 135.1, 142.0, 146.8, 163.7, 173.5. IR (KBr): υ 3240, 2924, 2853, 1624, 1554, 1475, 1450, 1375, 1335, 1209, 1094, 1011, 818, 700 cm^{-1}. HRMS (ESI) calcd for $C_{20}H_{17}O_5NClS$: 418.0510, found: 418.0525.

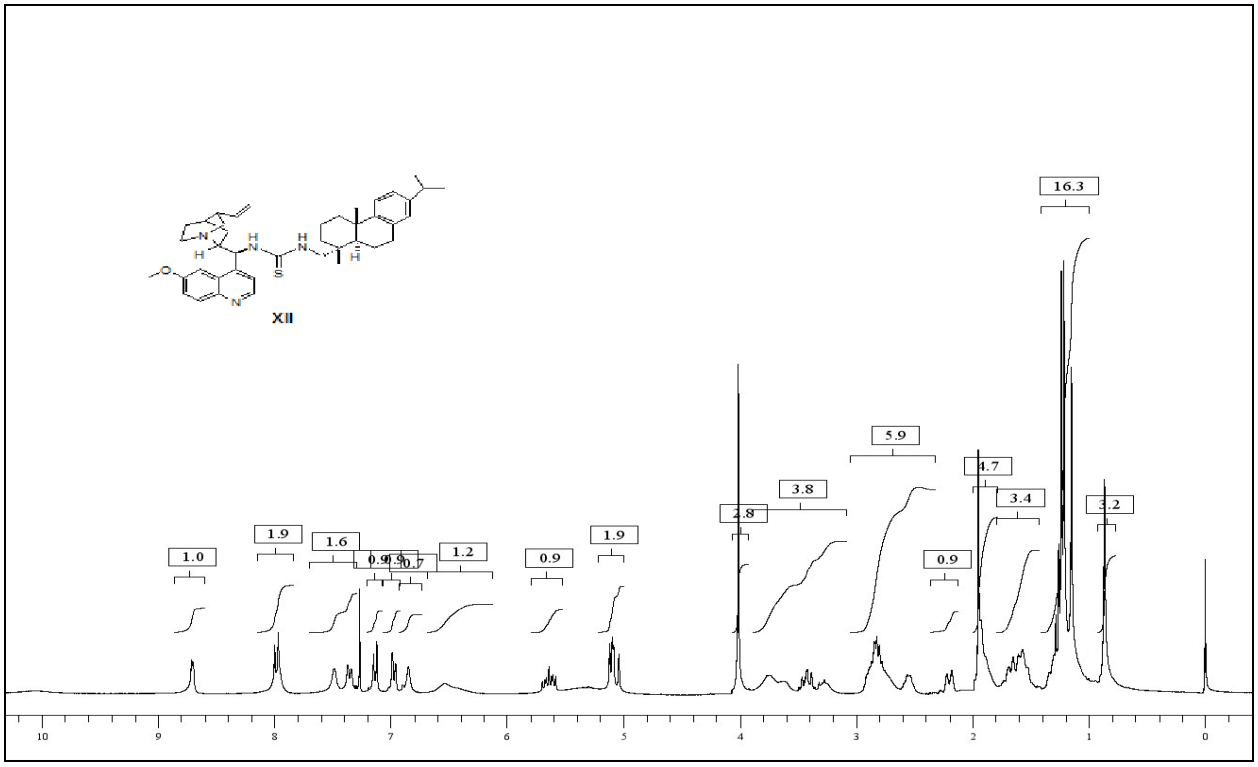
7. Copy of ^{1}HNMR and ^{13}C NMR of ligands.

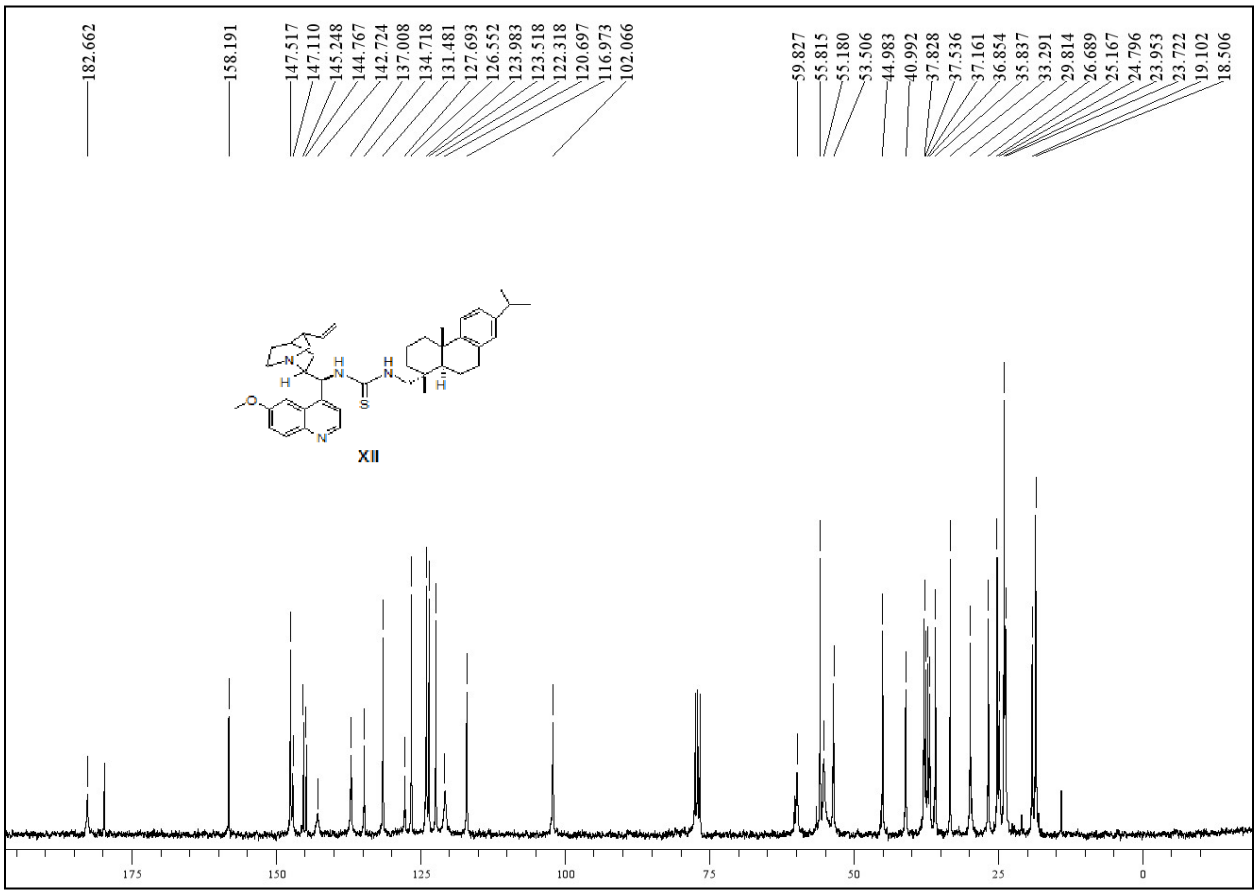




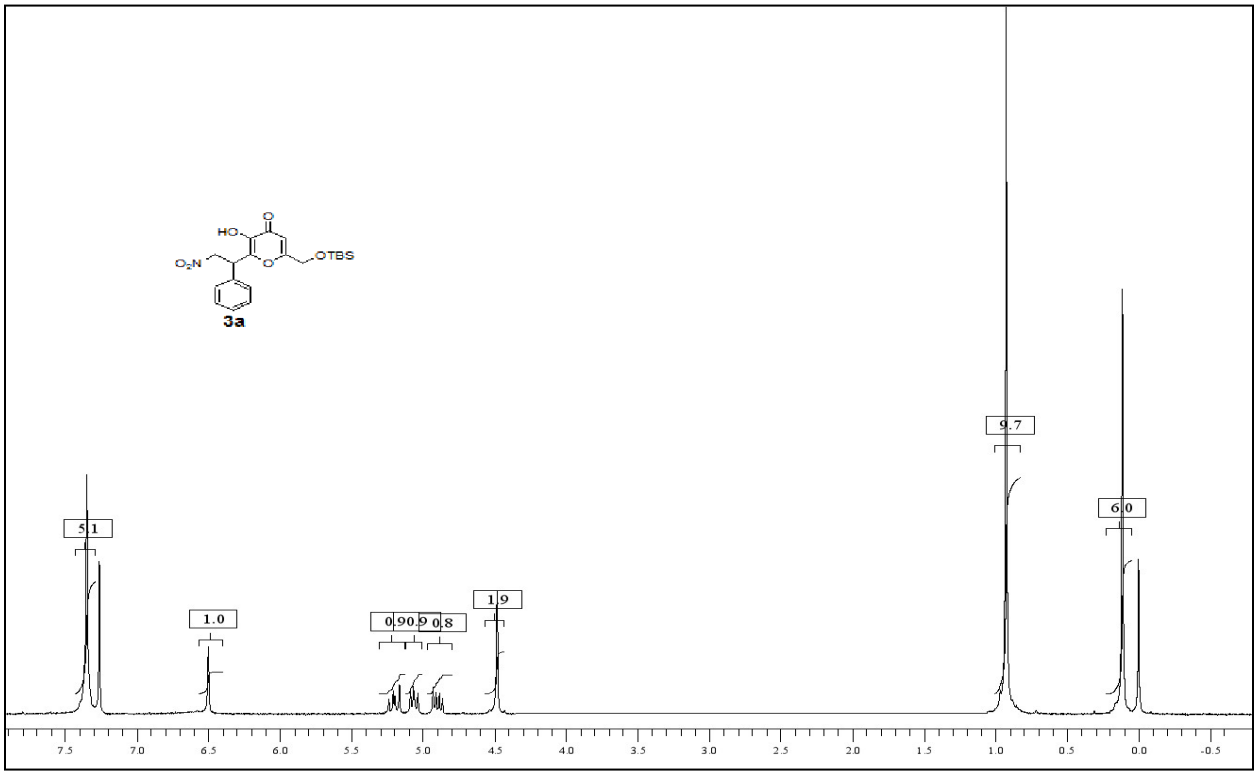


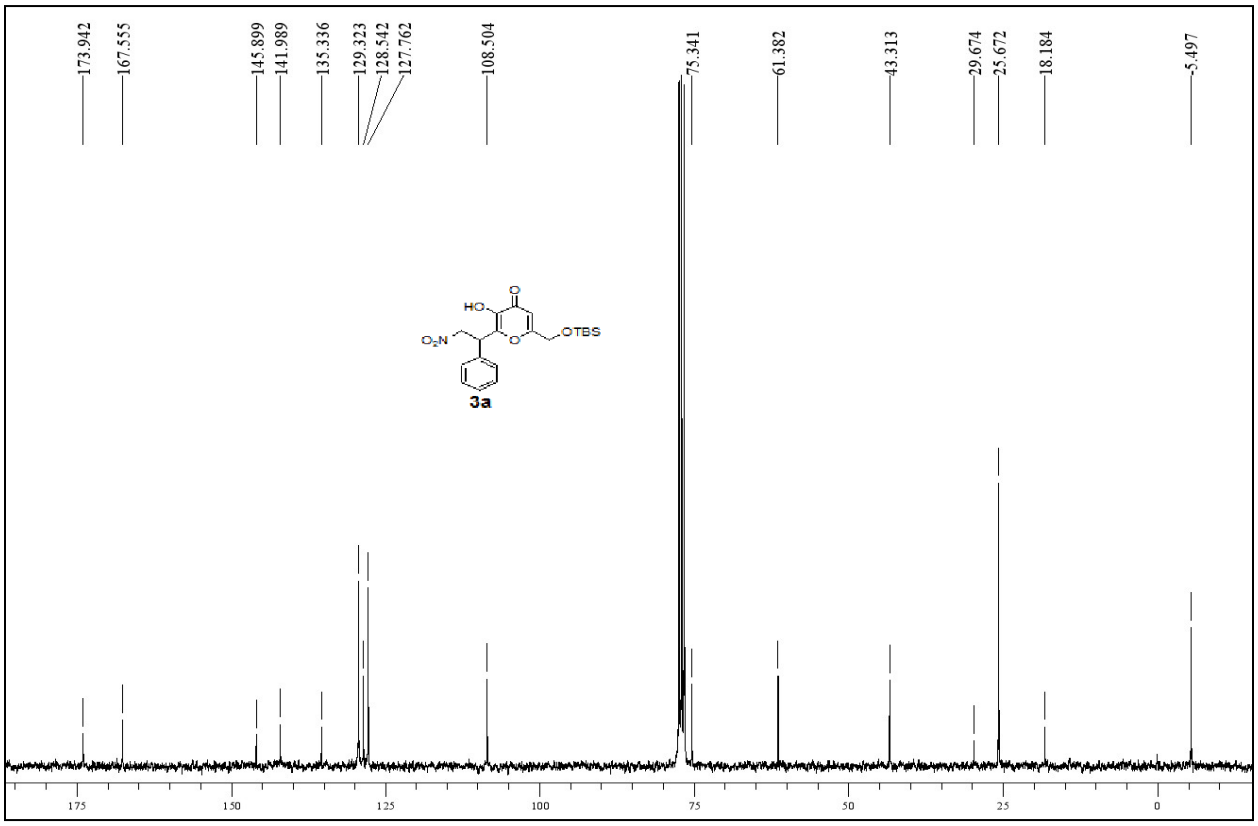


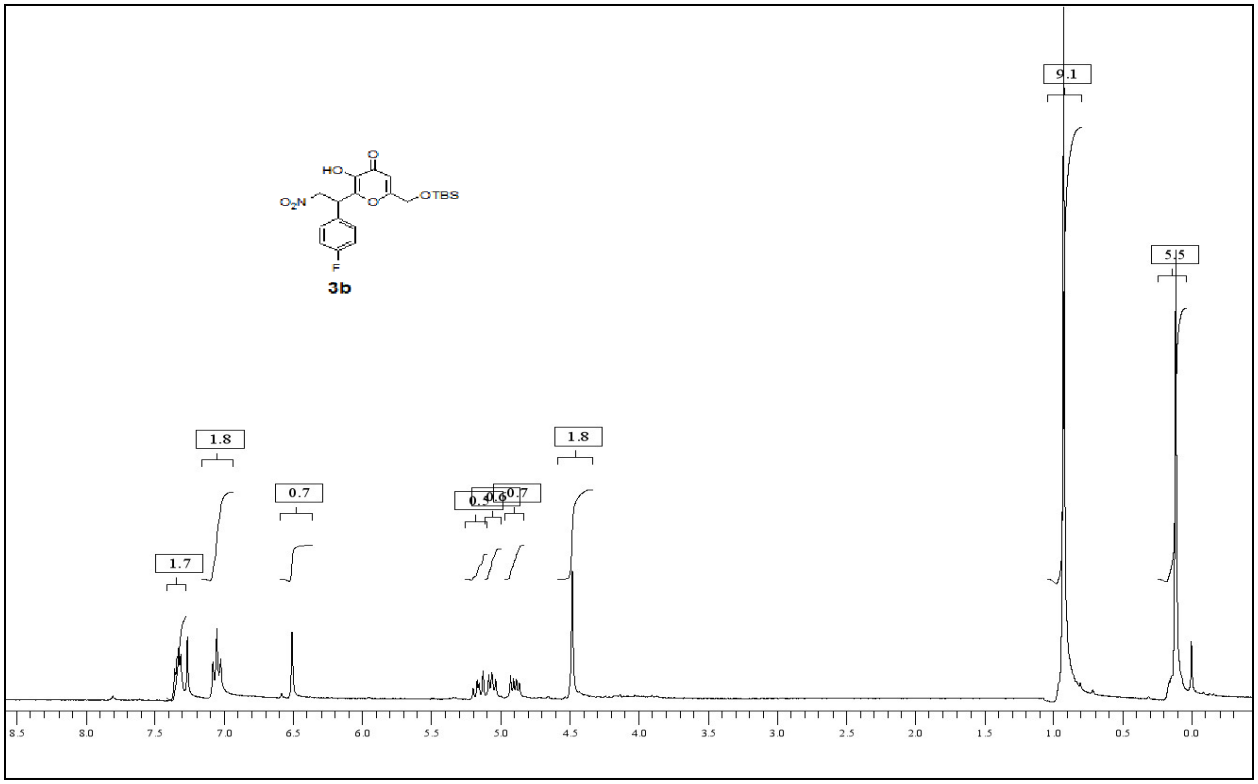




8. Copy of ^{1}HNMR and ^{13}C NMR of all products.



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O
O
O2N
OTBS
F
3b
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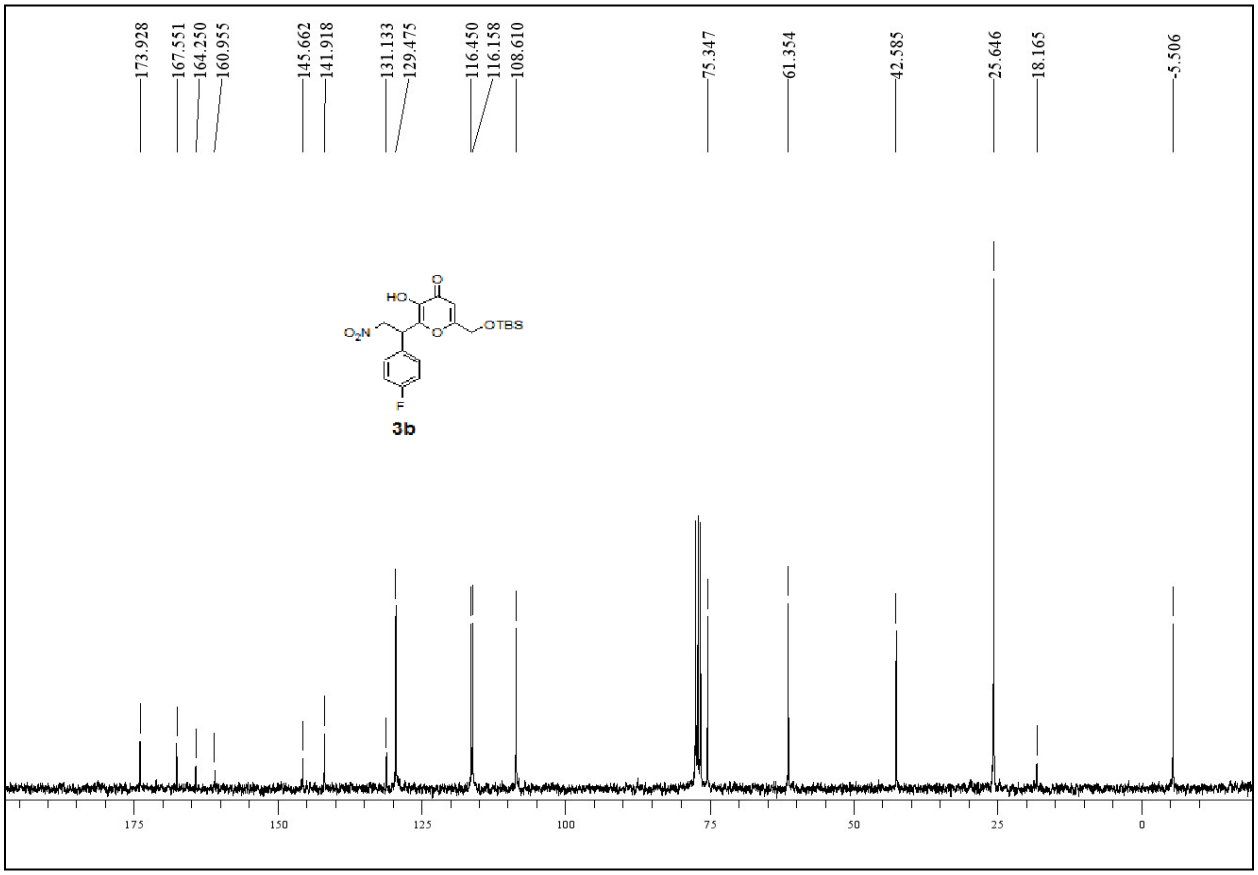
5.5
1.8
0.7
1.8
1.7
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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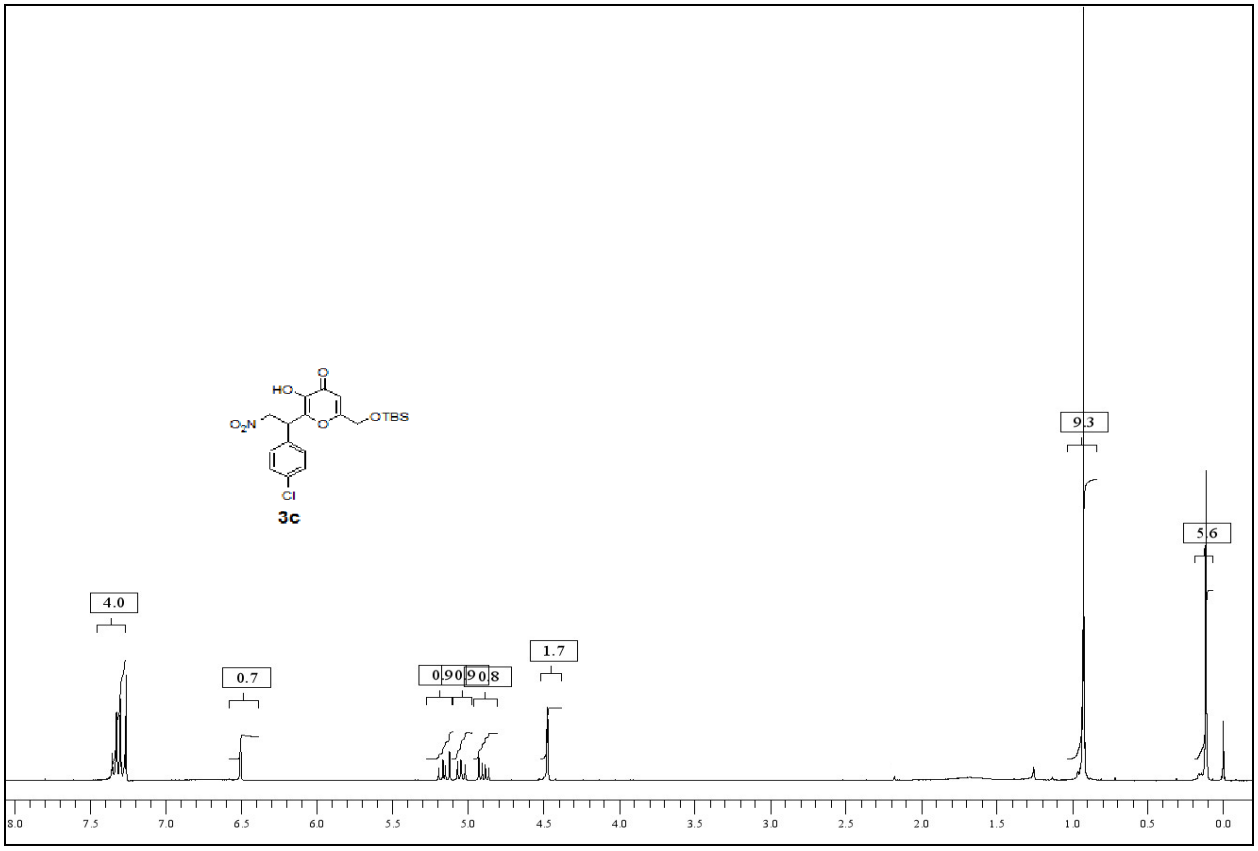
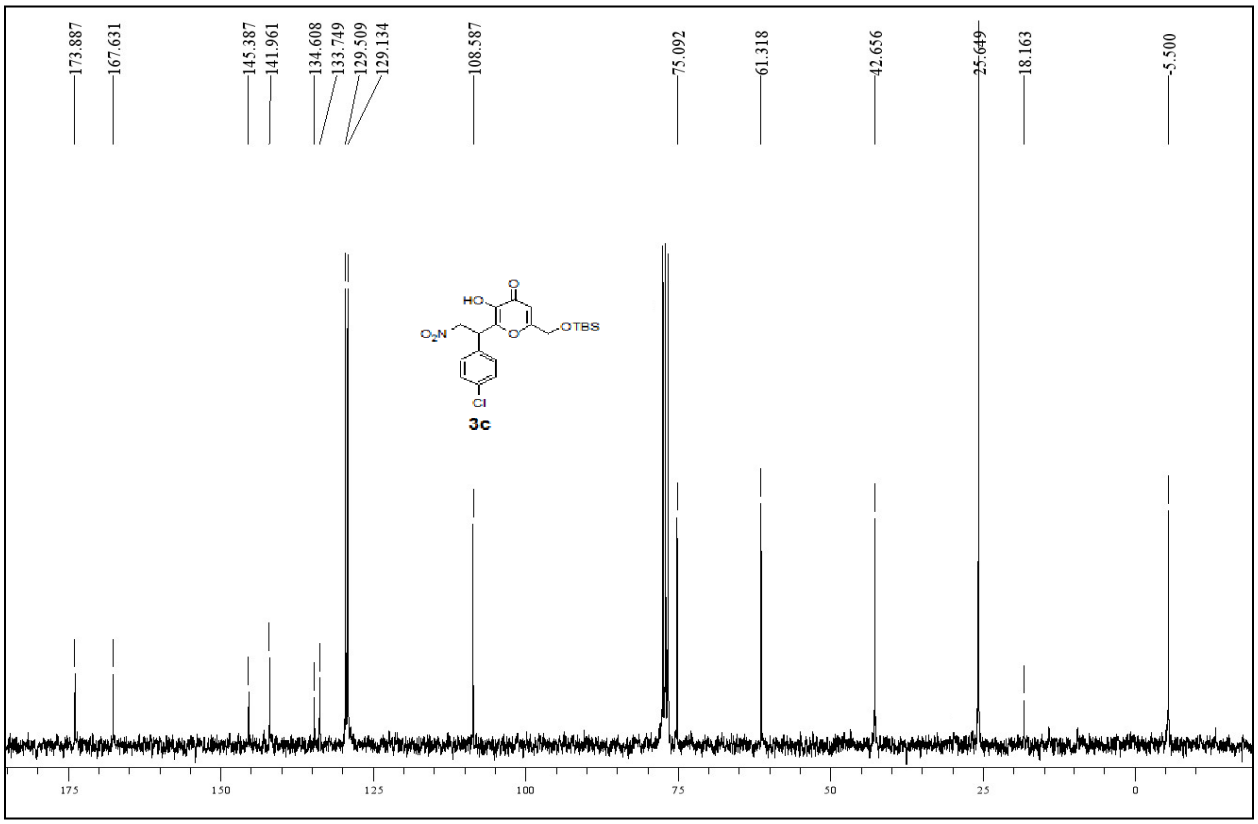
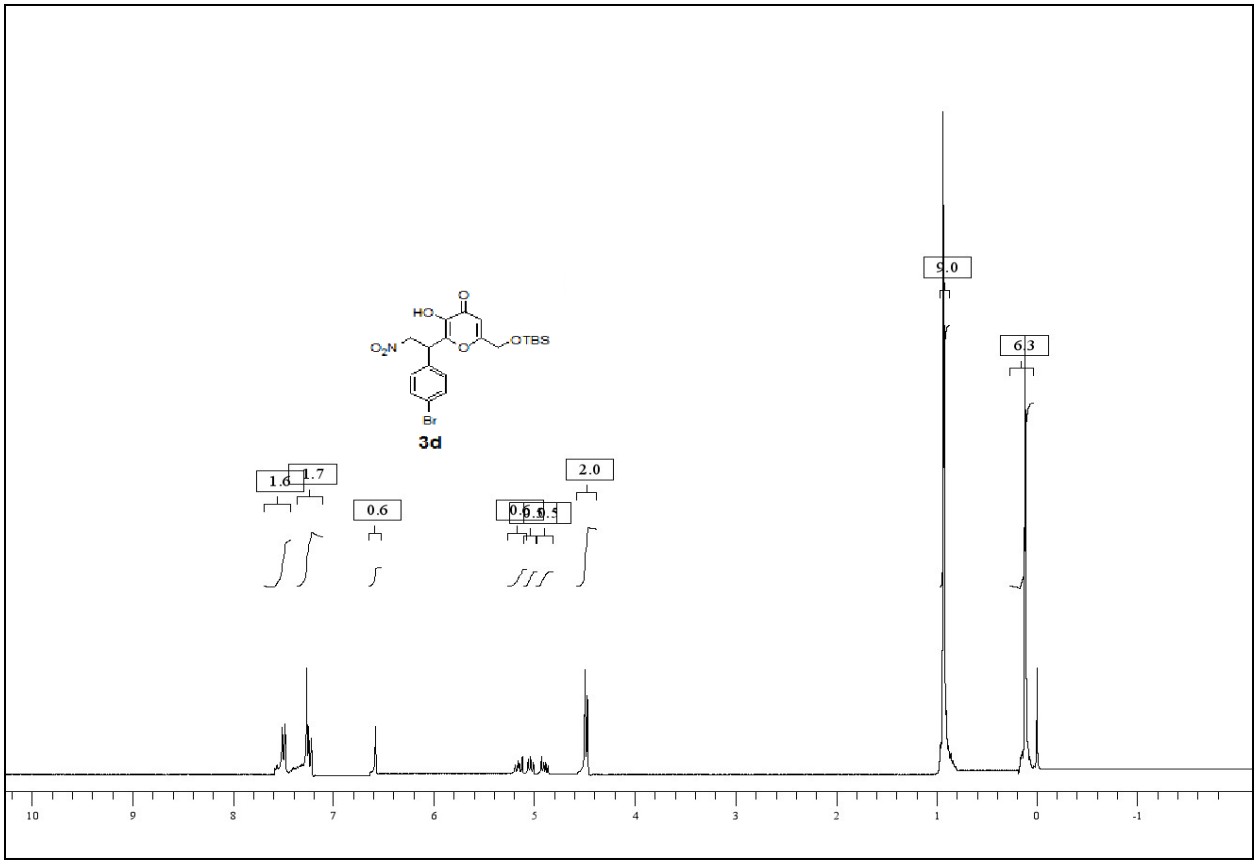
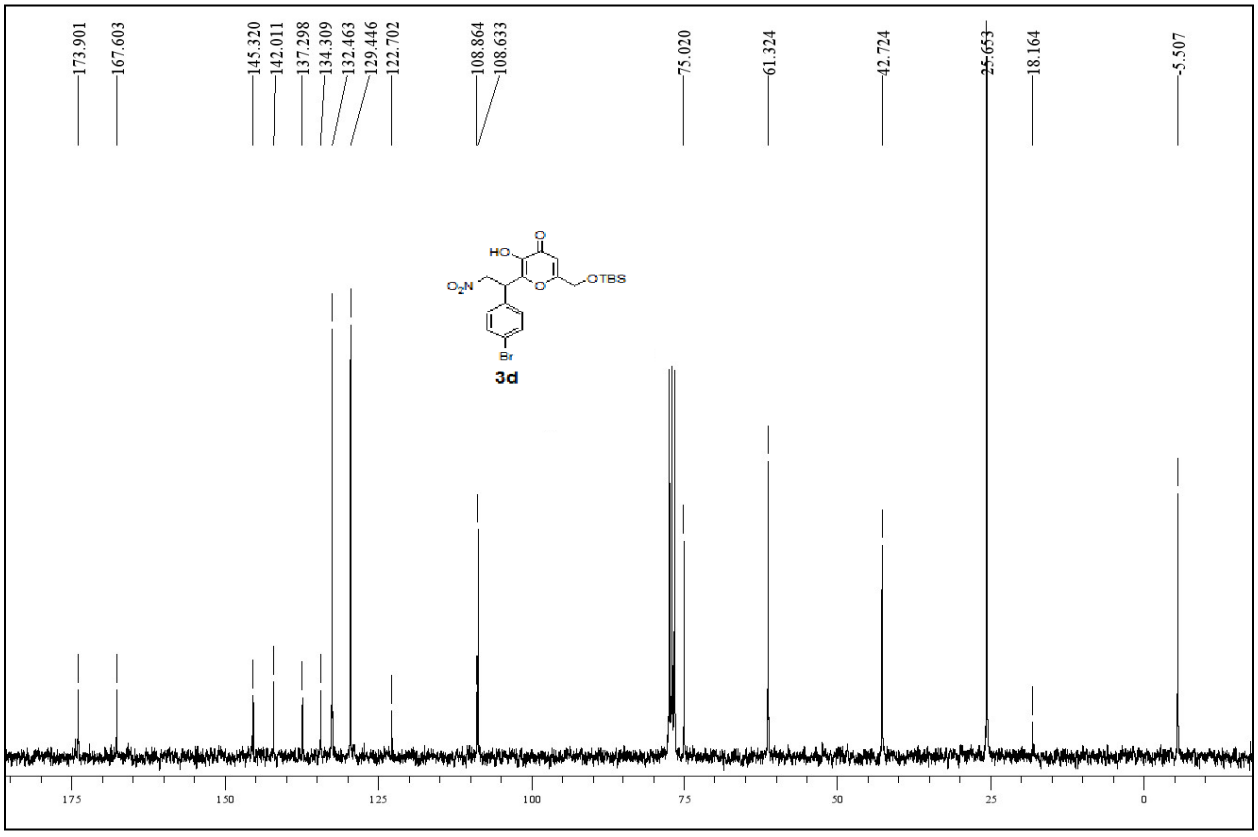
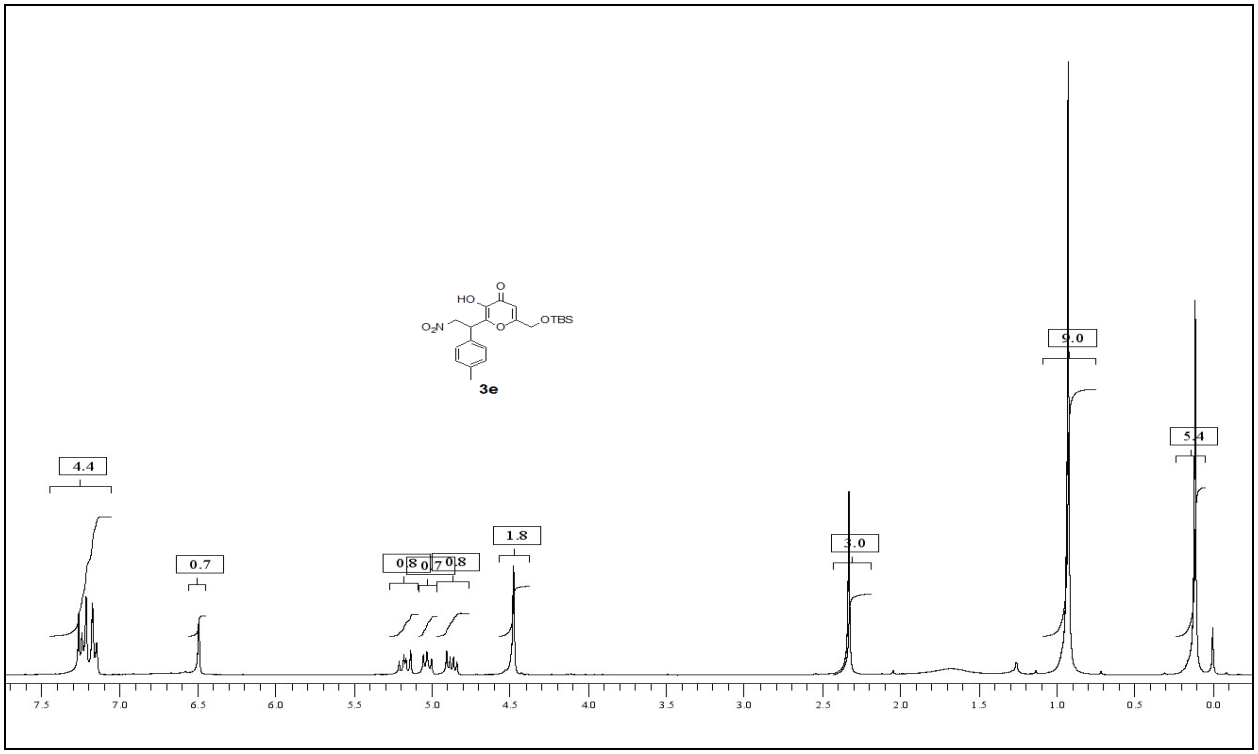
167.551
164.250
160.955
145.662
141.918
131.133
129.475
116.450
116.158
108.610
75.347
61.354
42.585
25.646
18.165
-5.506
HO
O
O
O2N
OTBS
F
3b
175
150
125
100
75
50
25
0

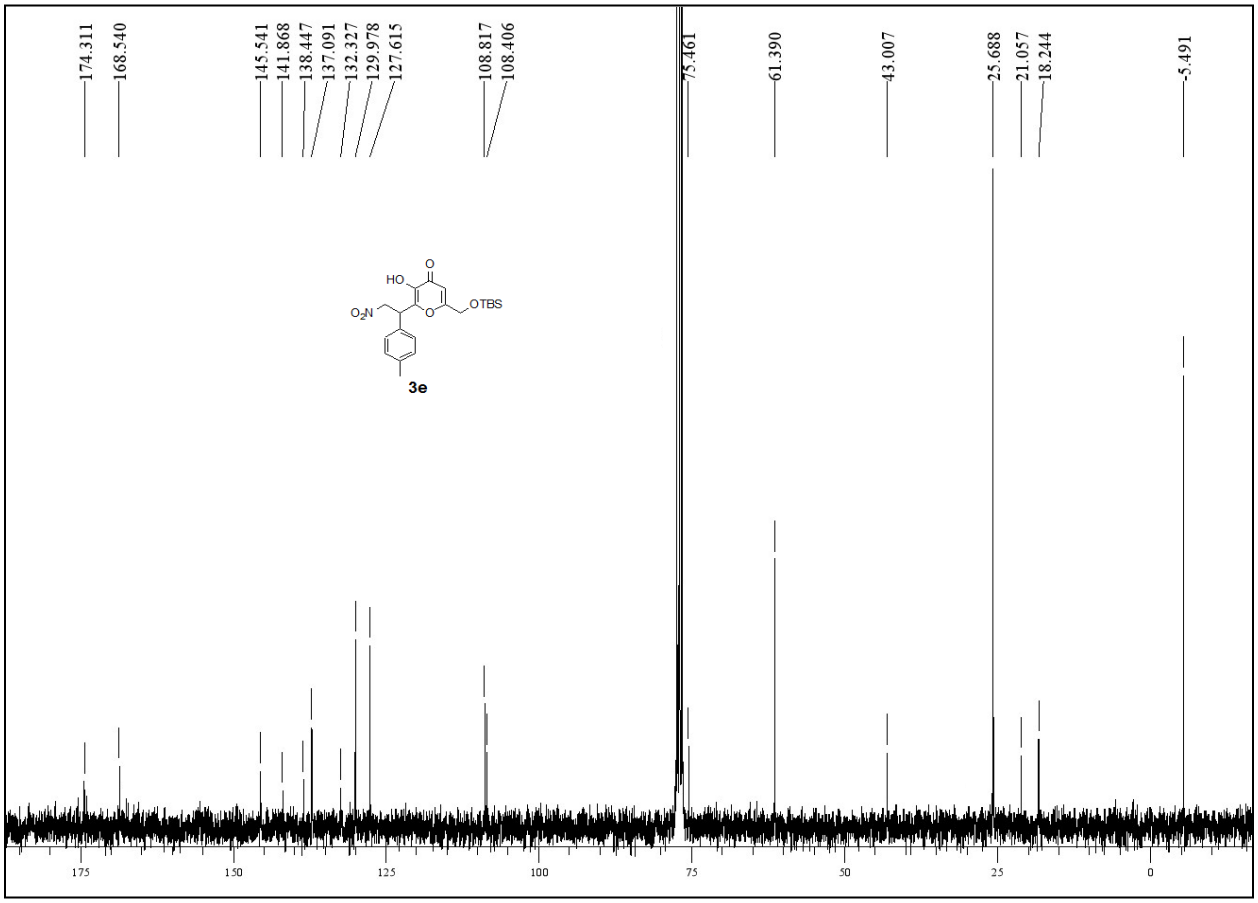


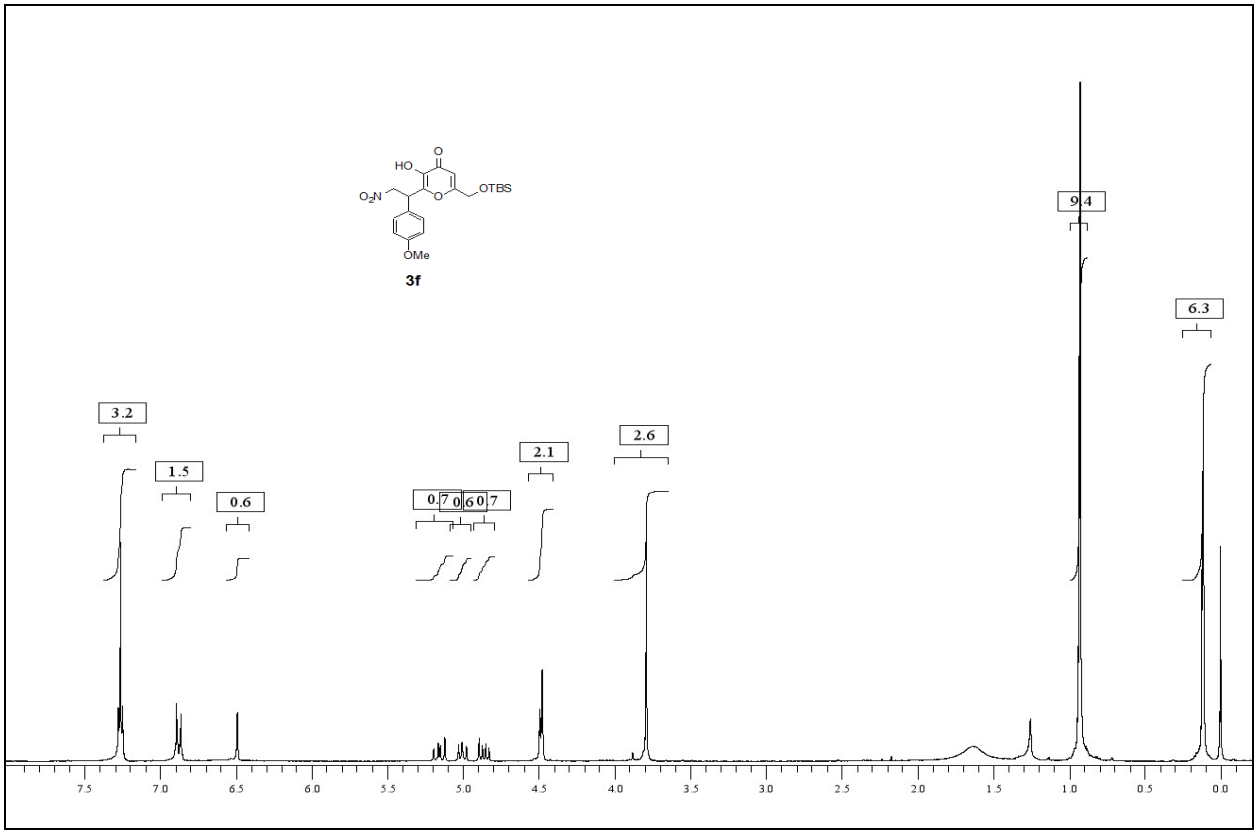


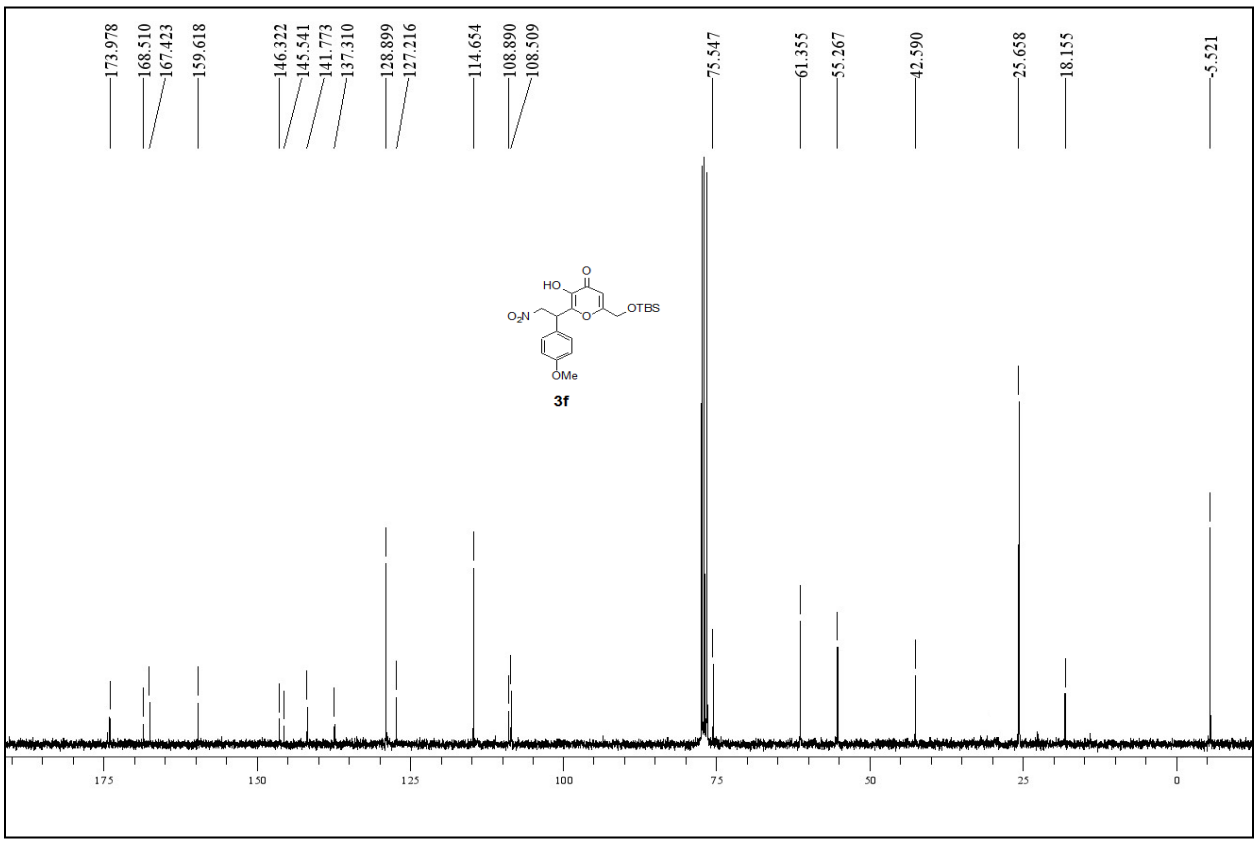


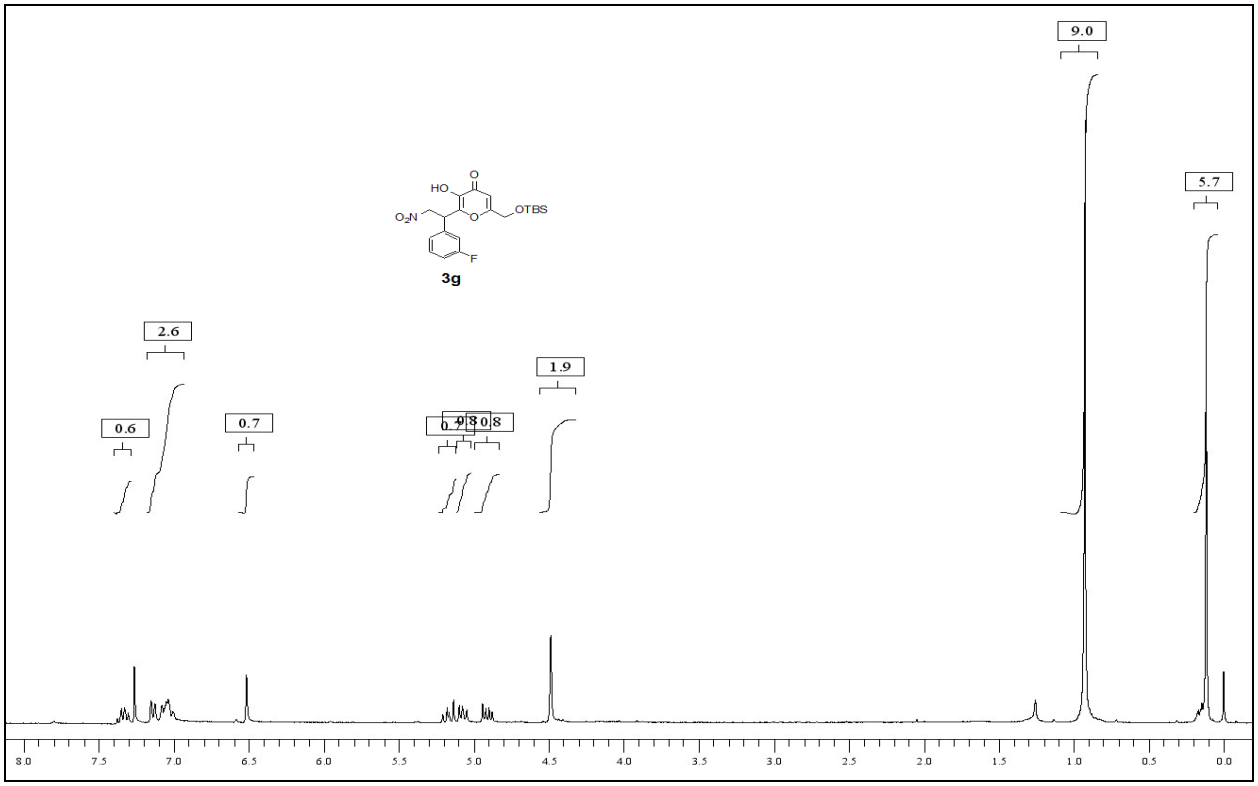


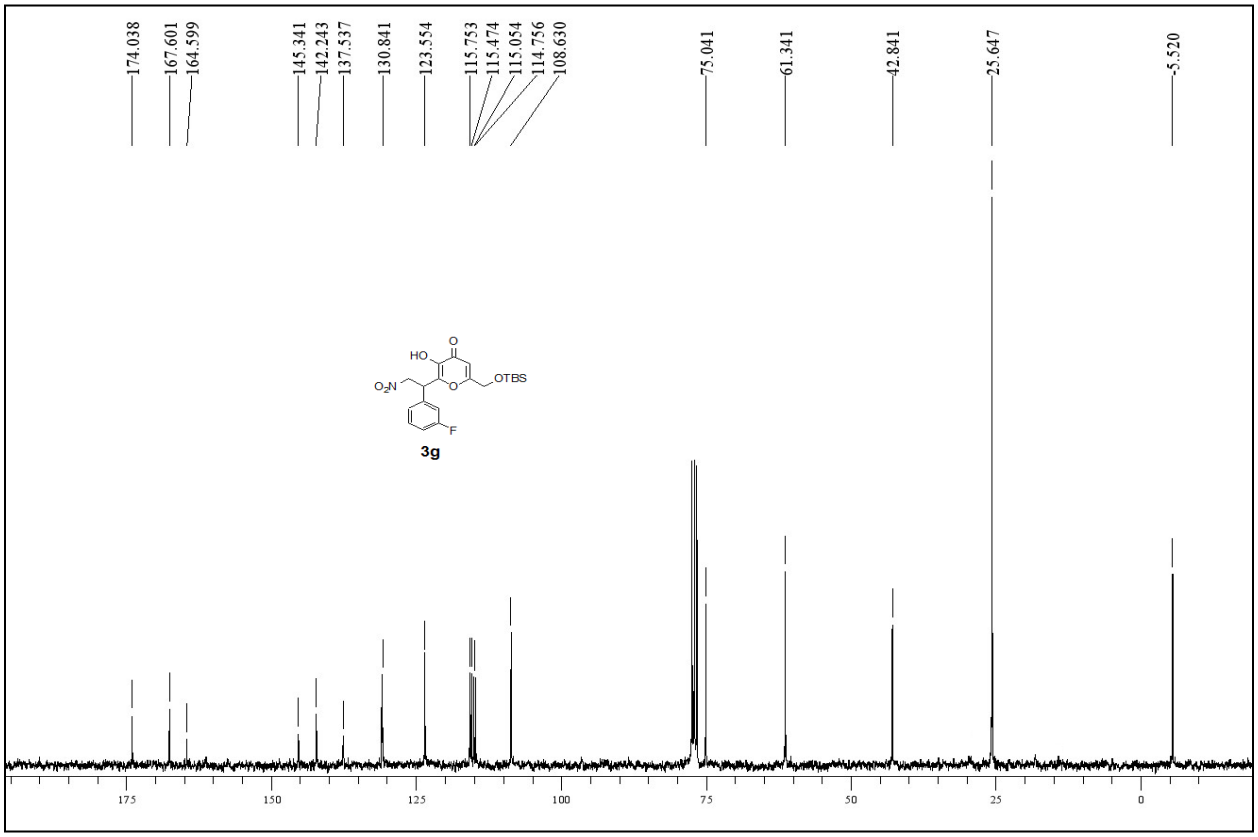


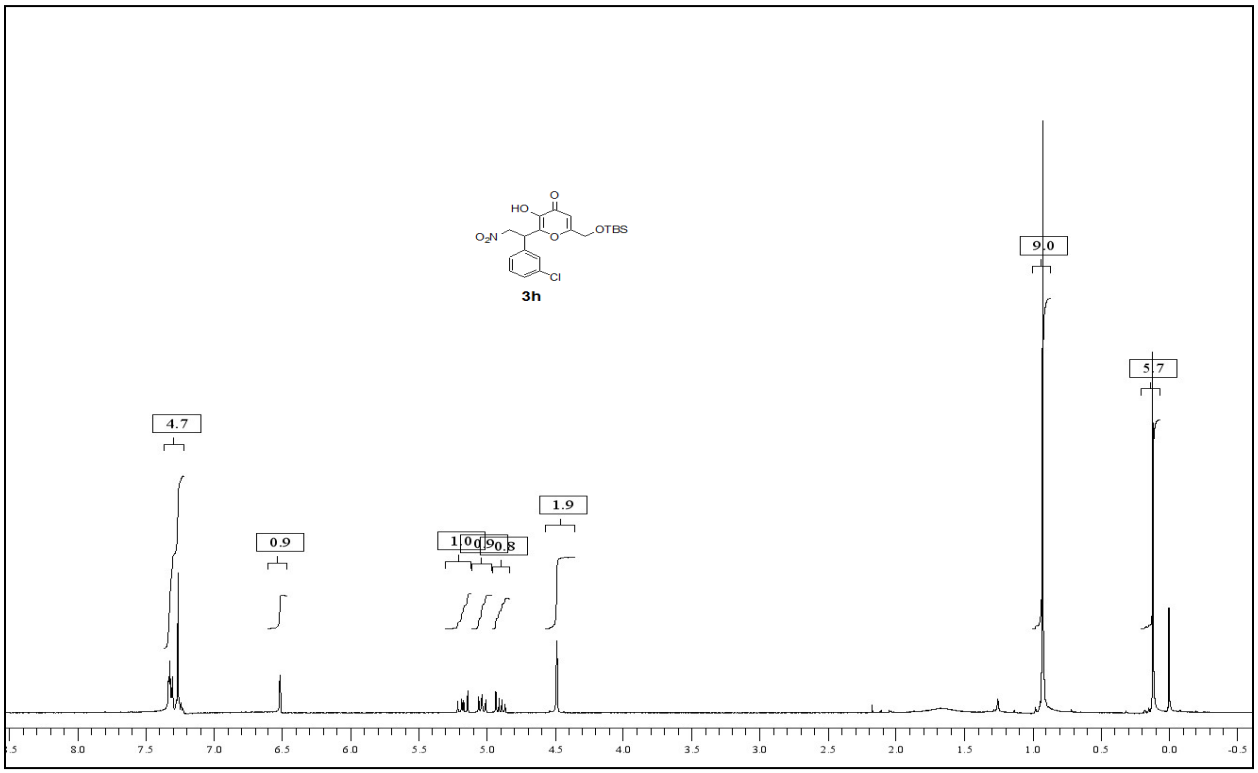


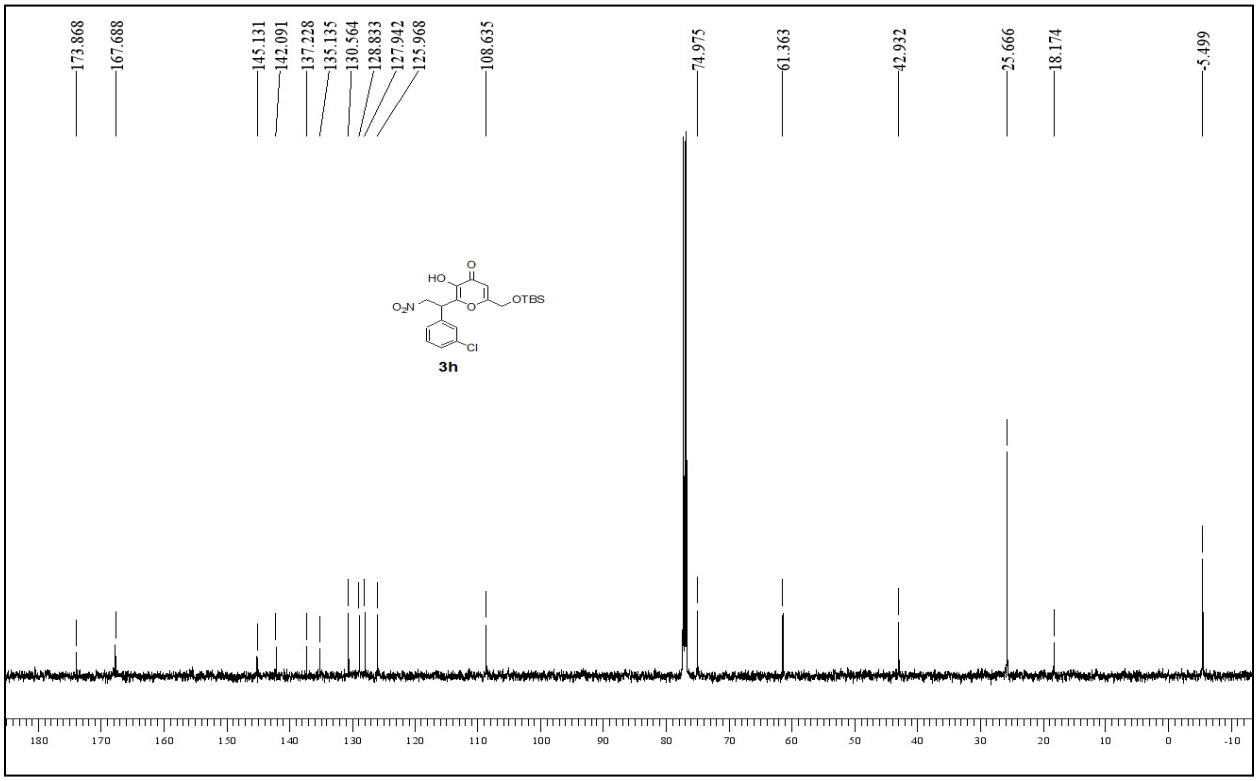


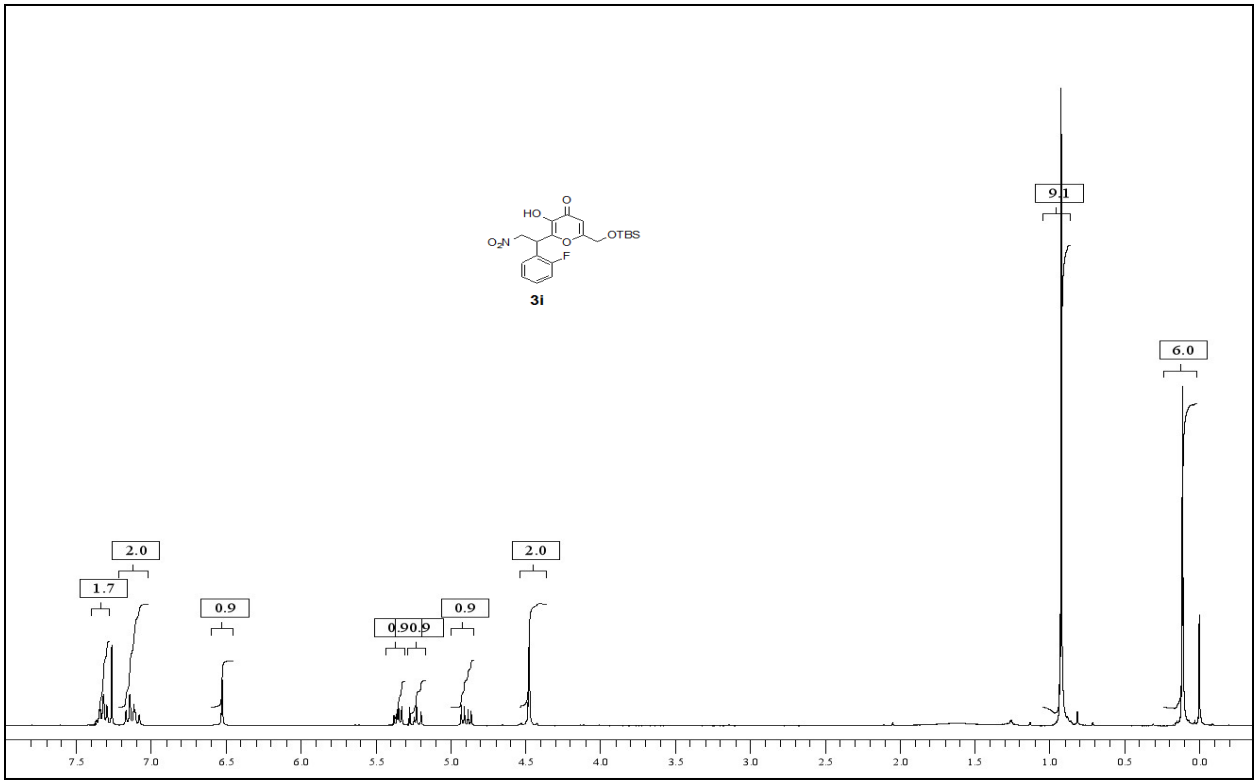


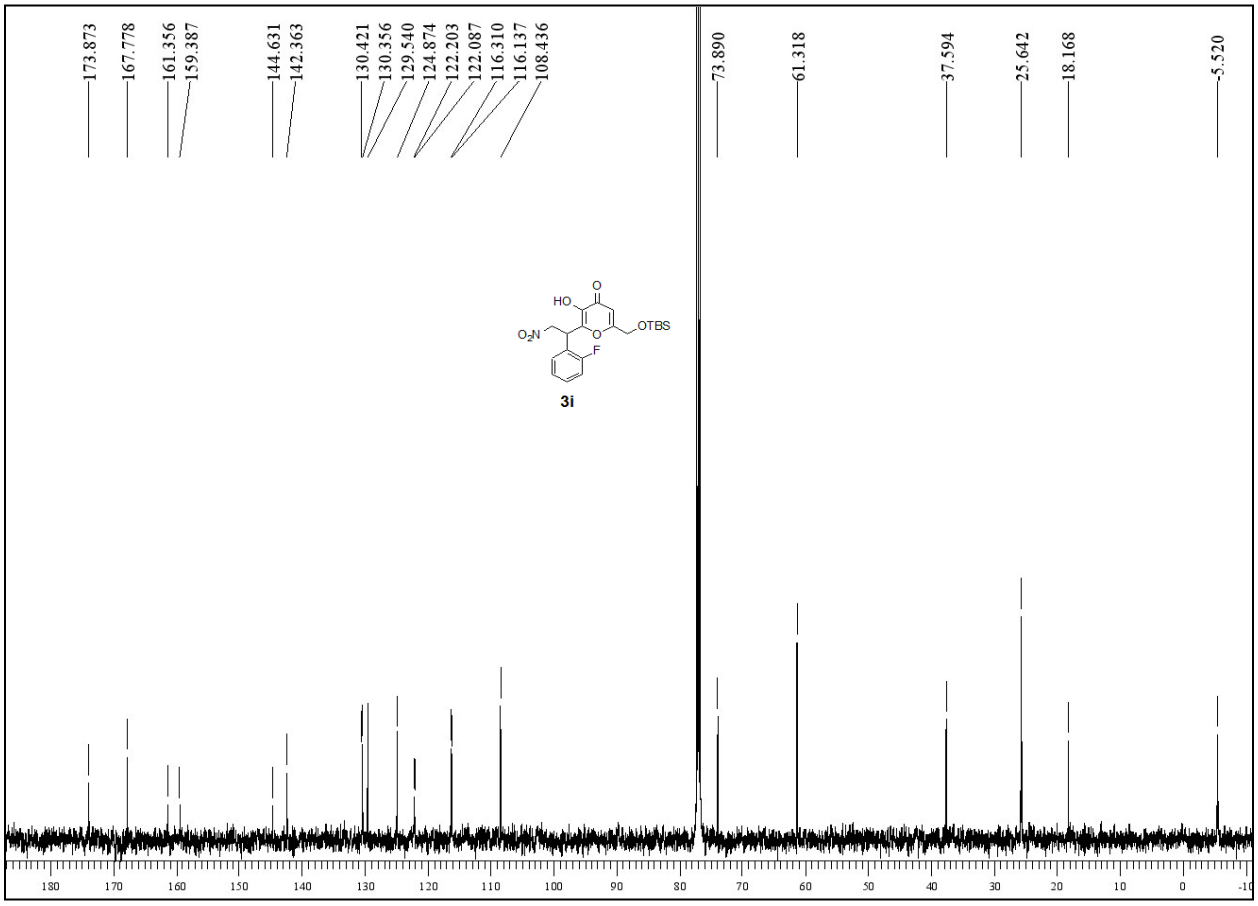


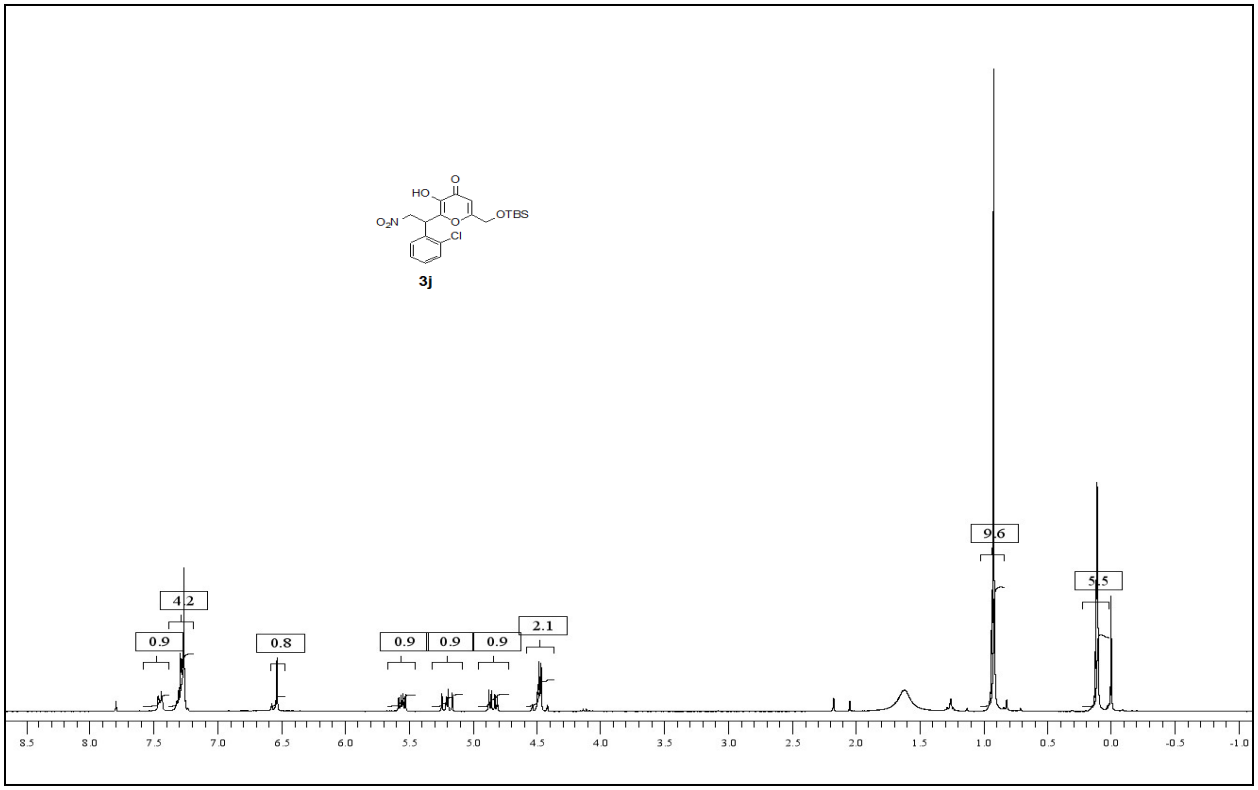


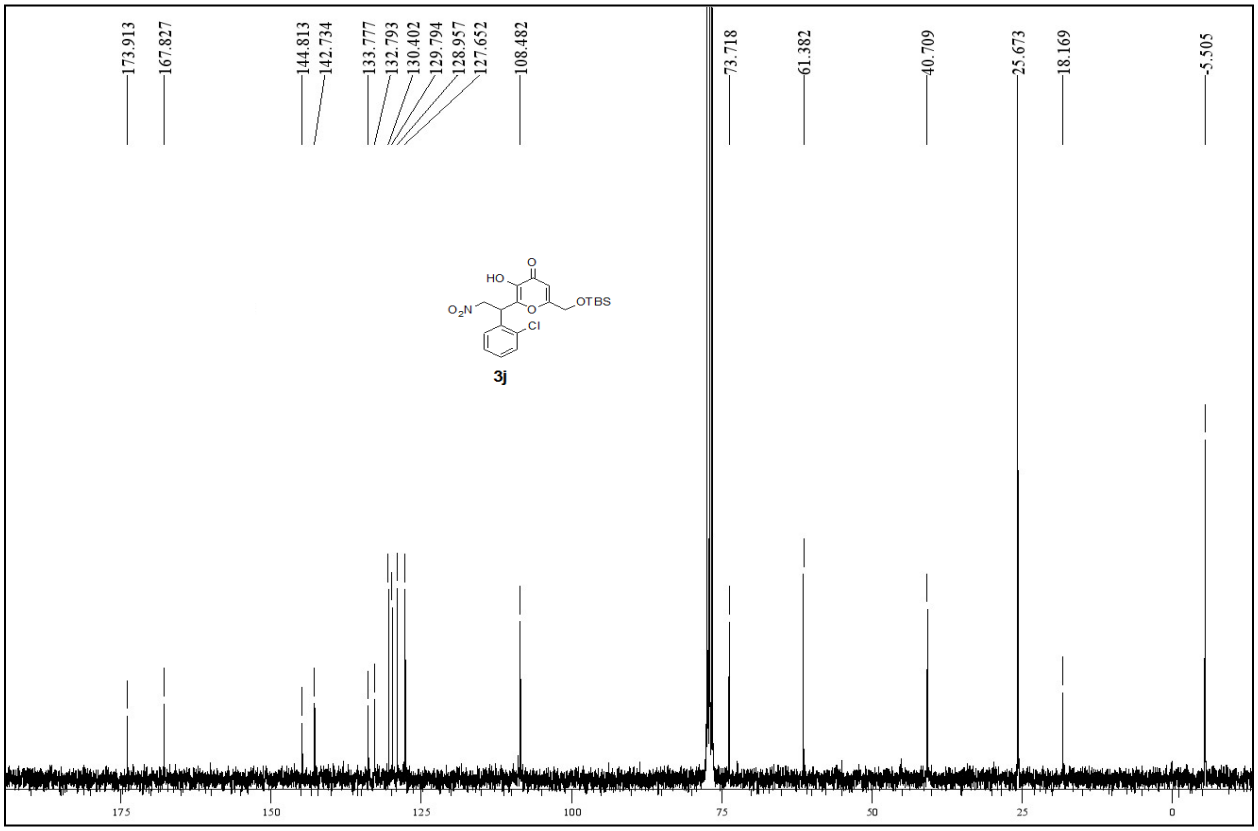


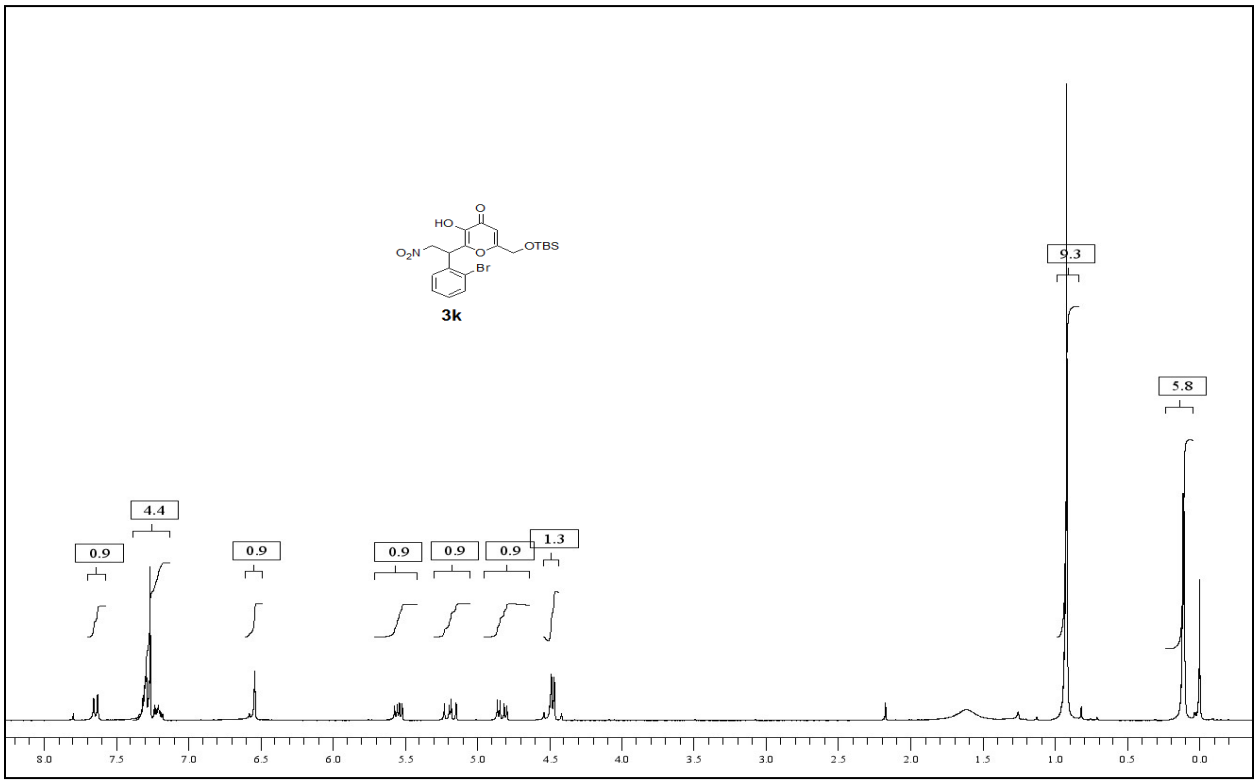


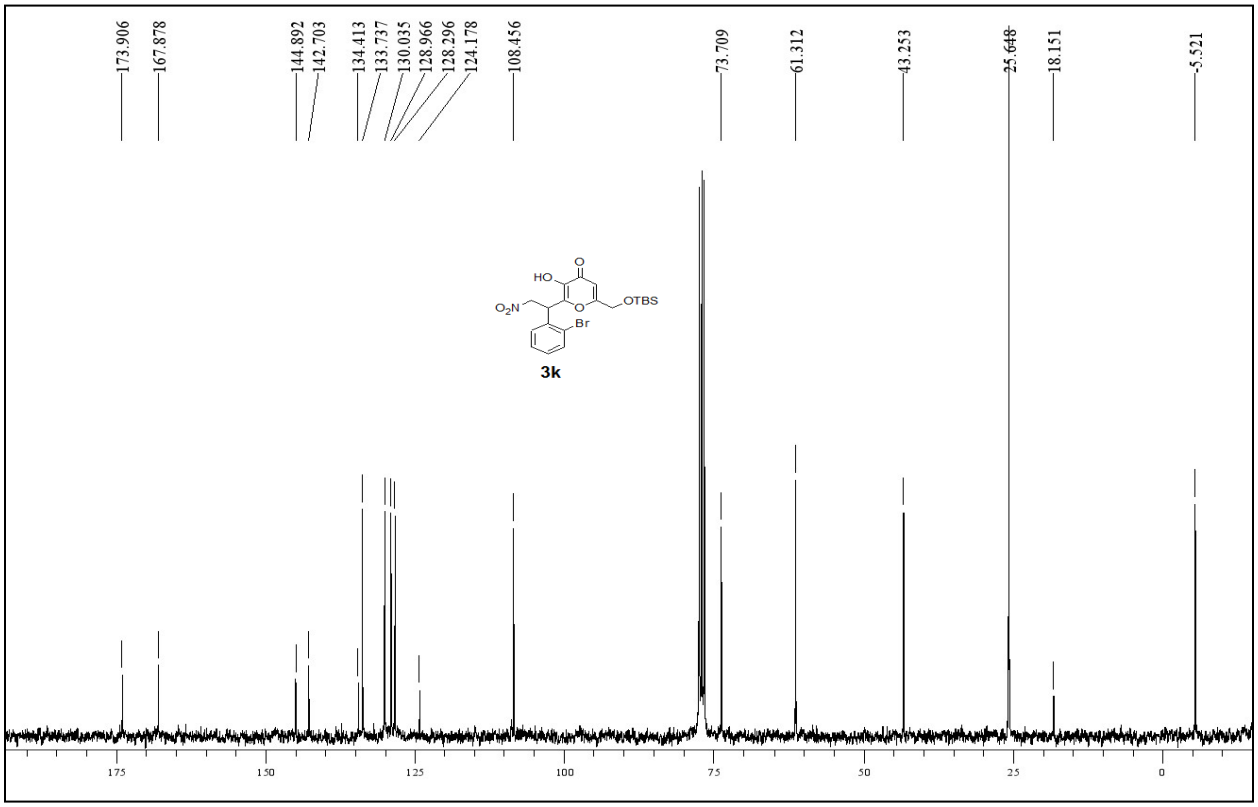


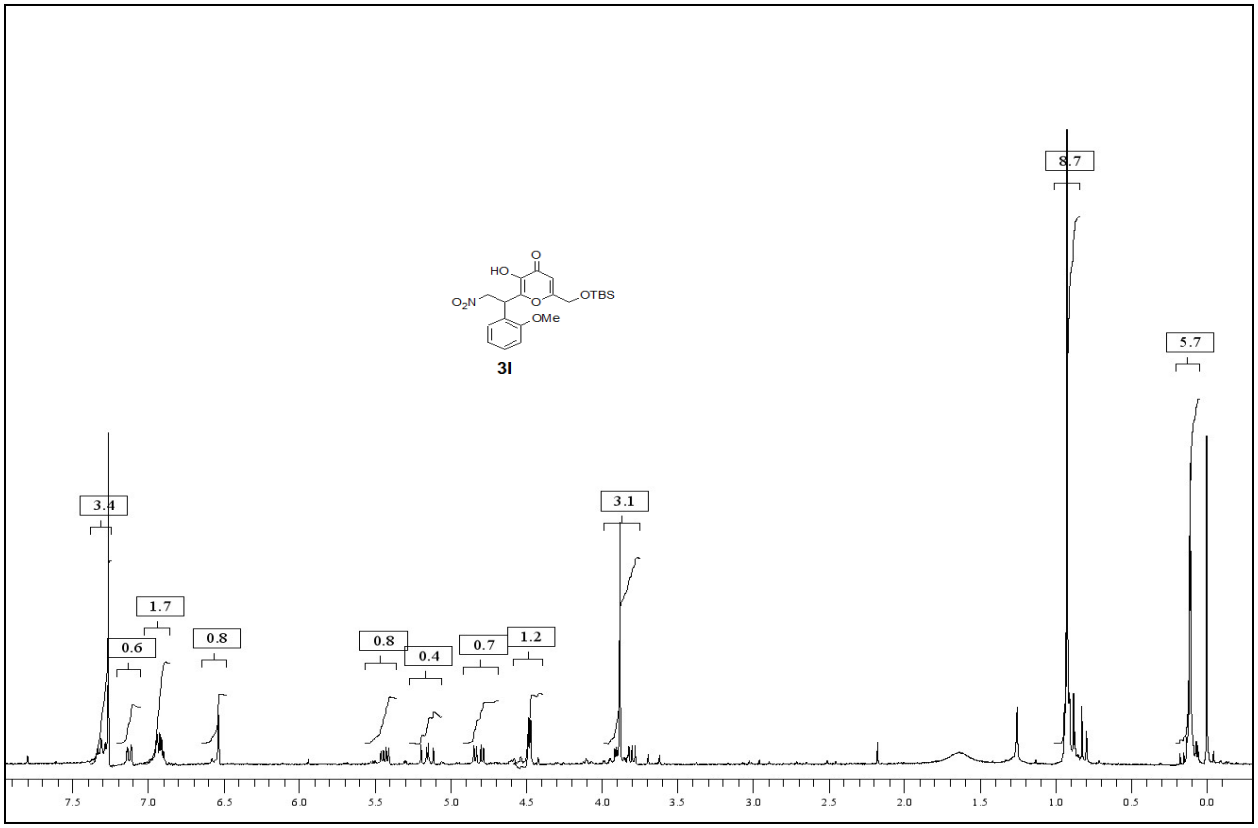


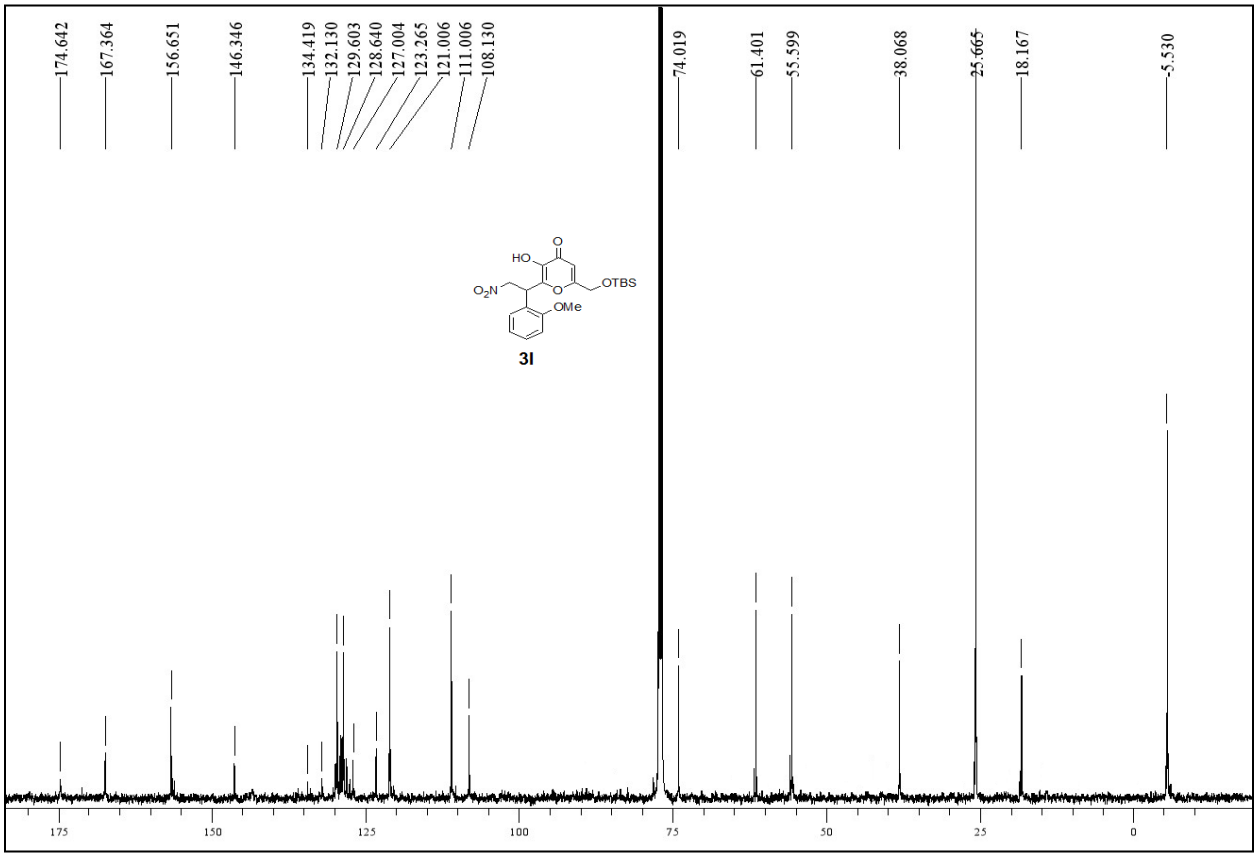


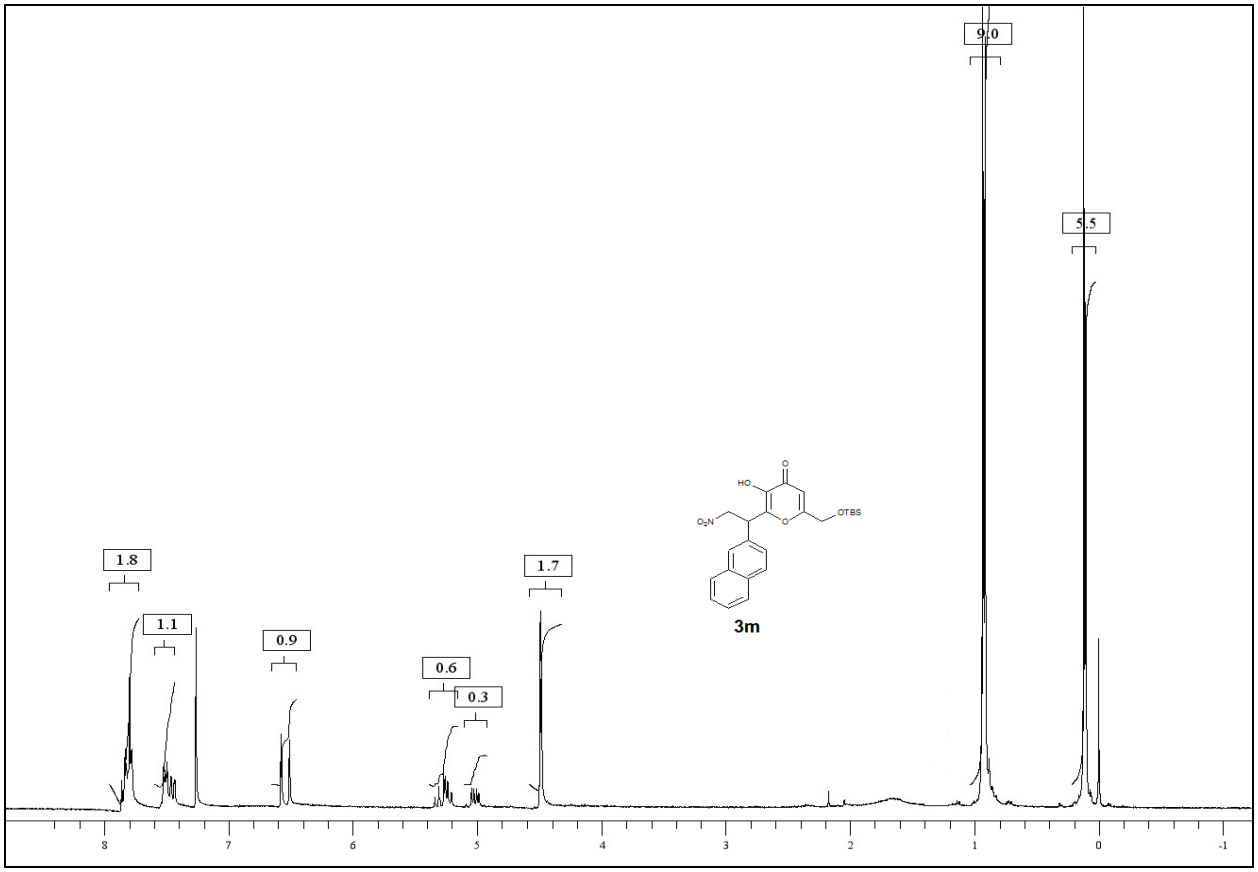


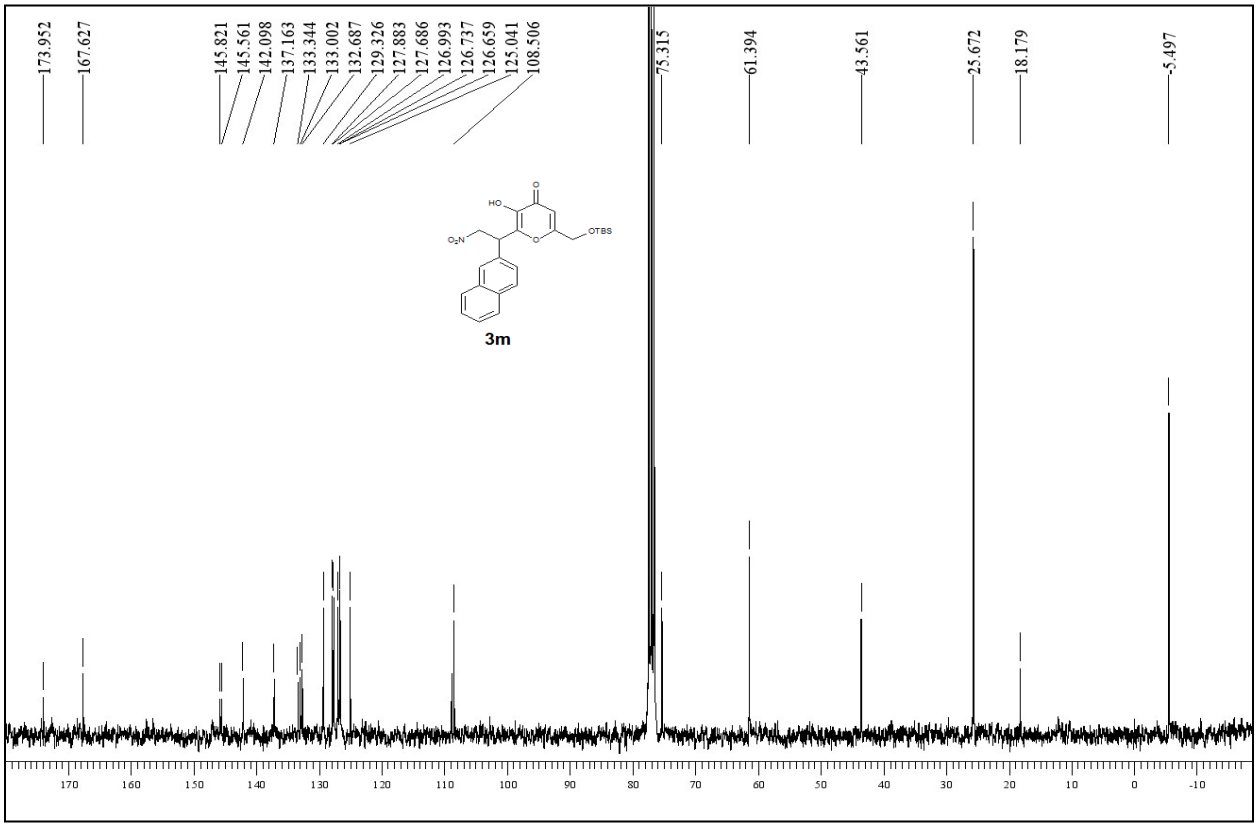


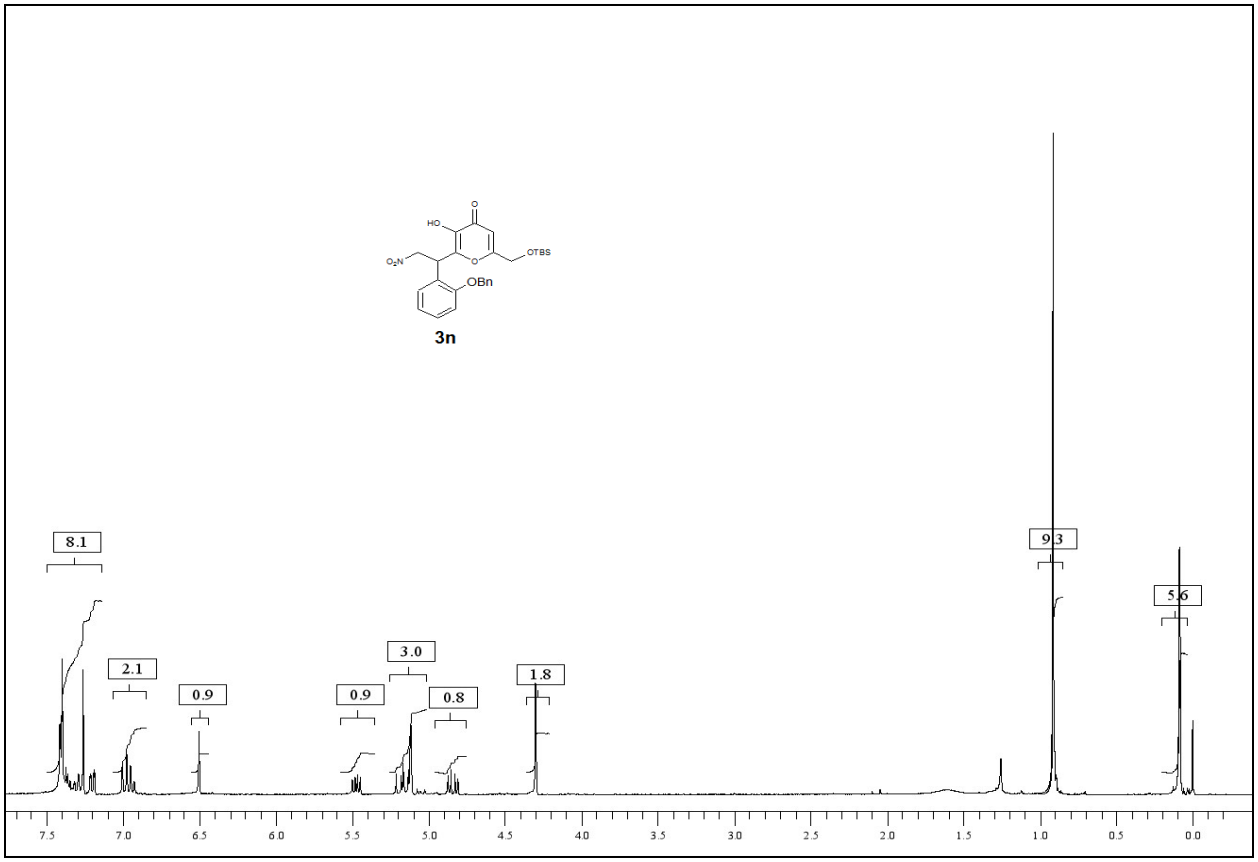


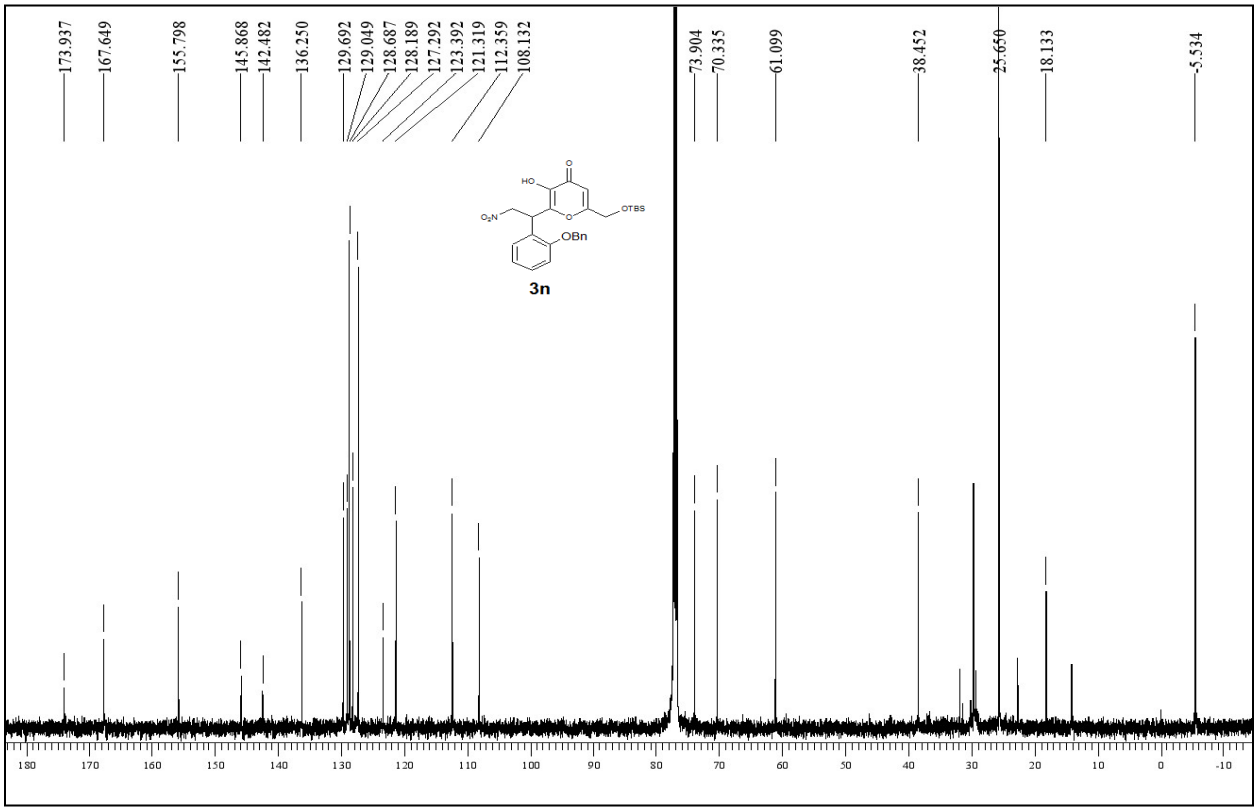


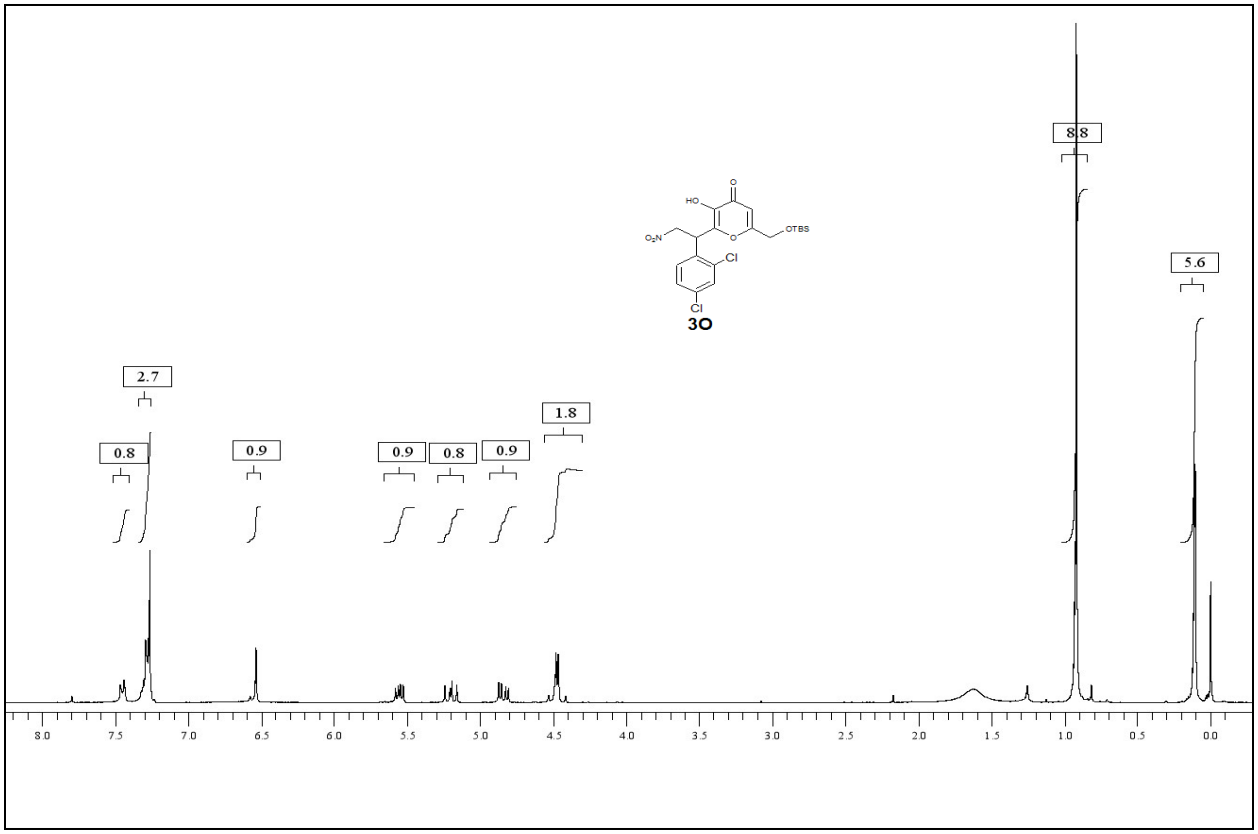


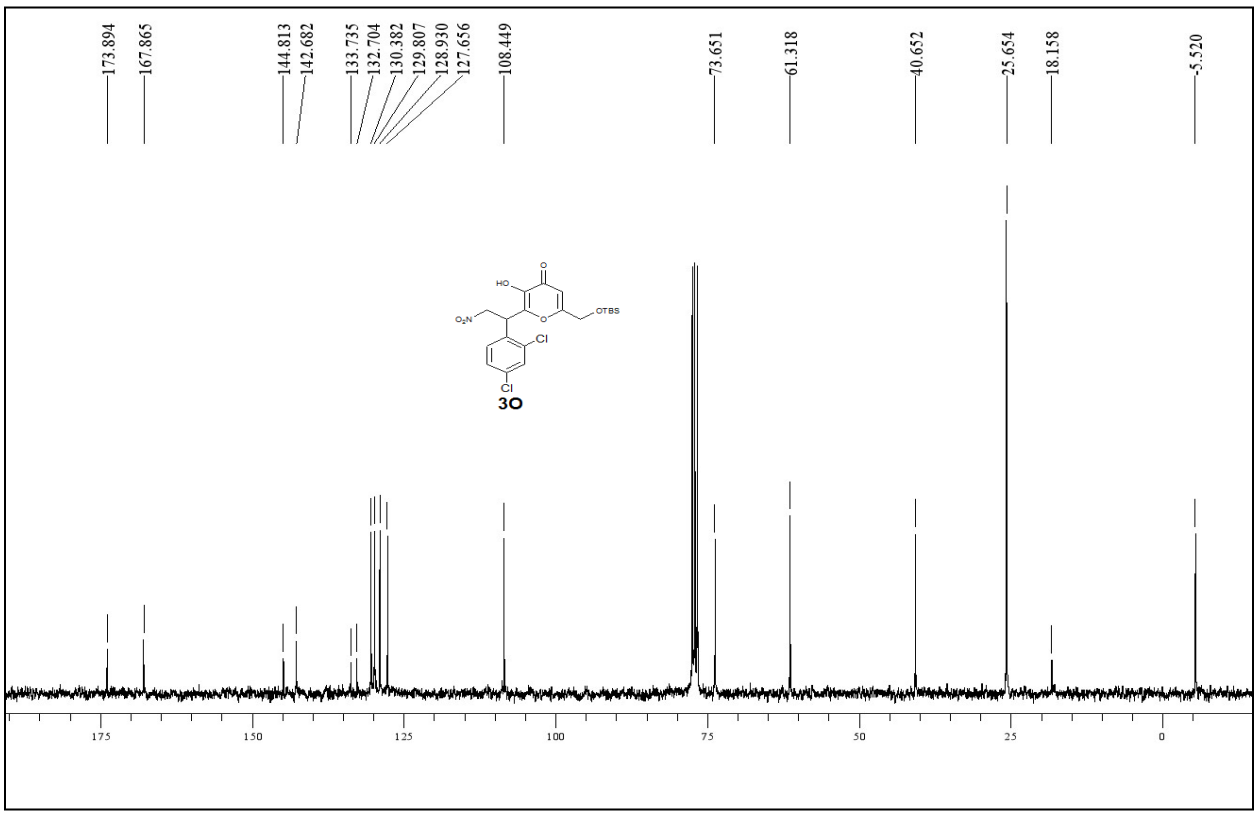


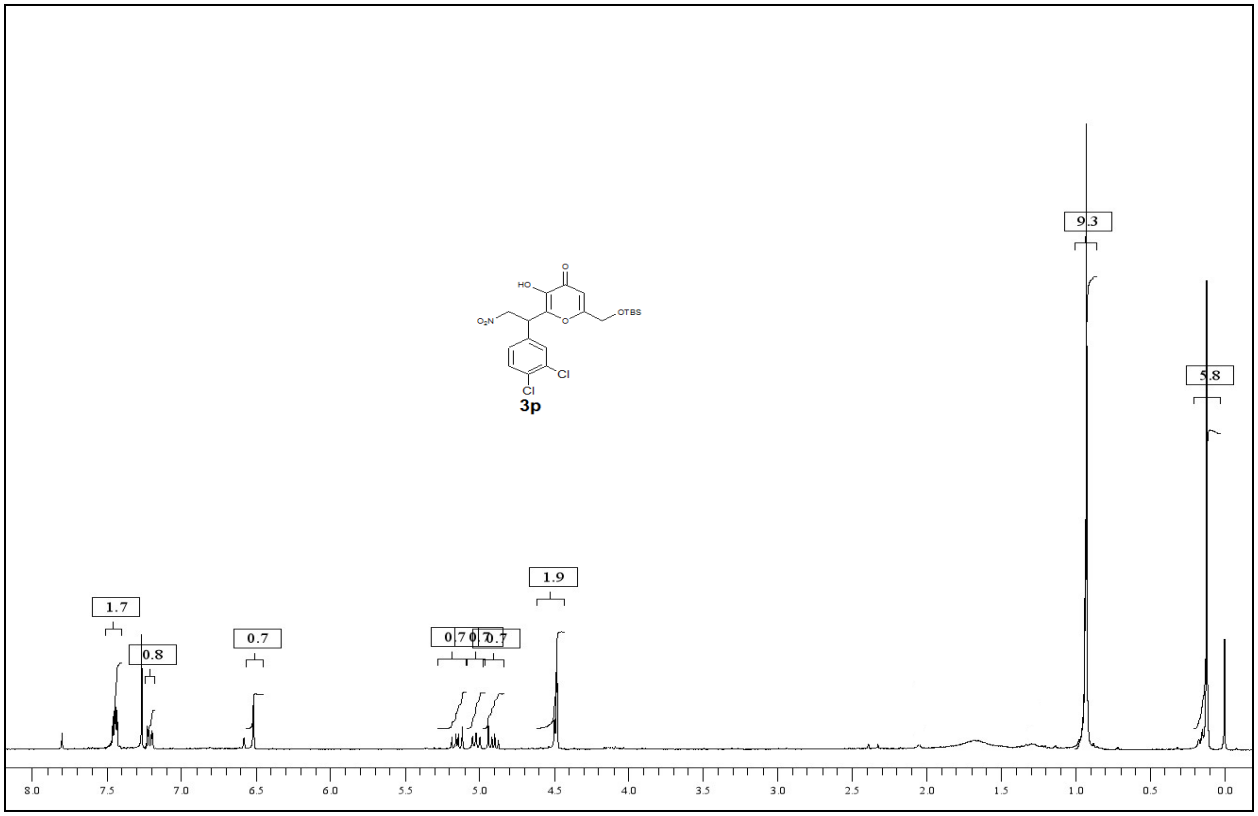


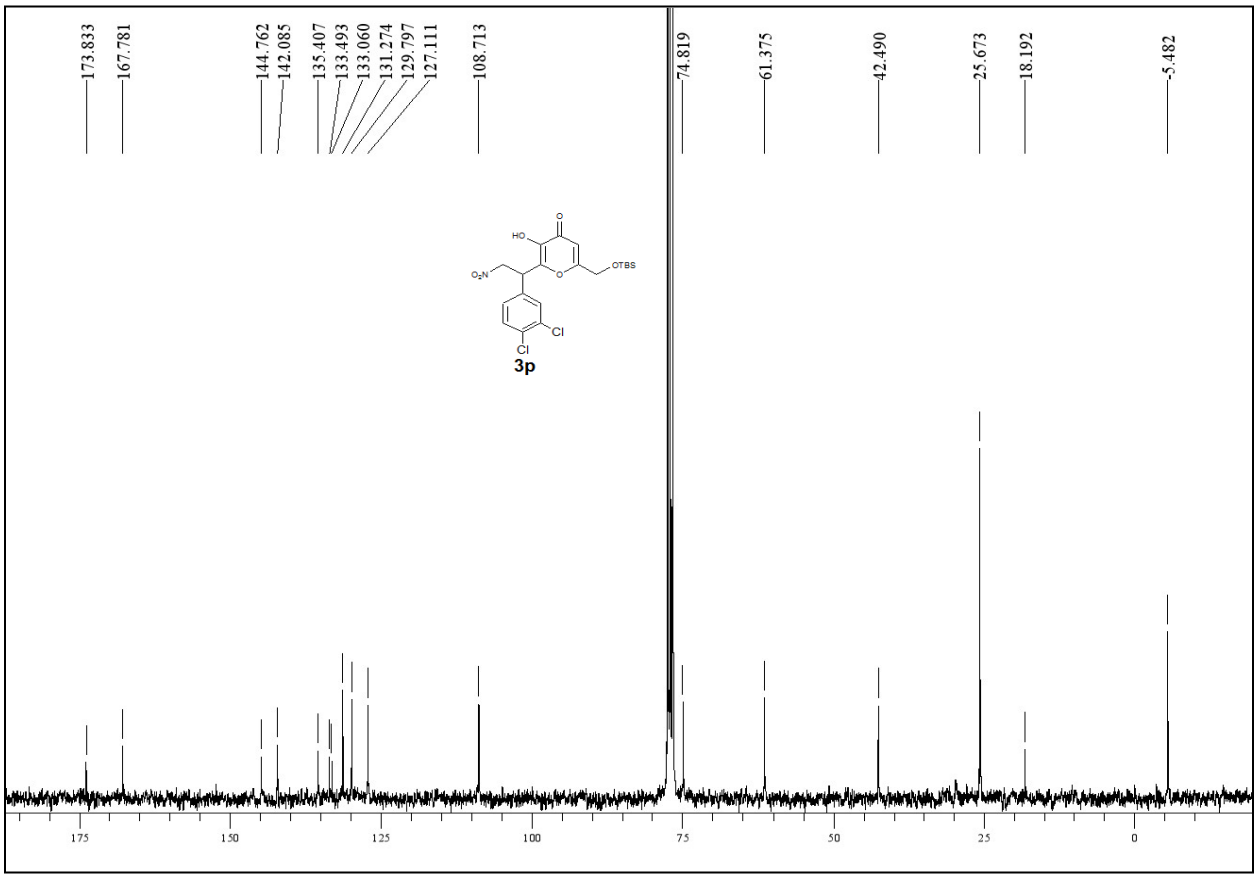


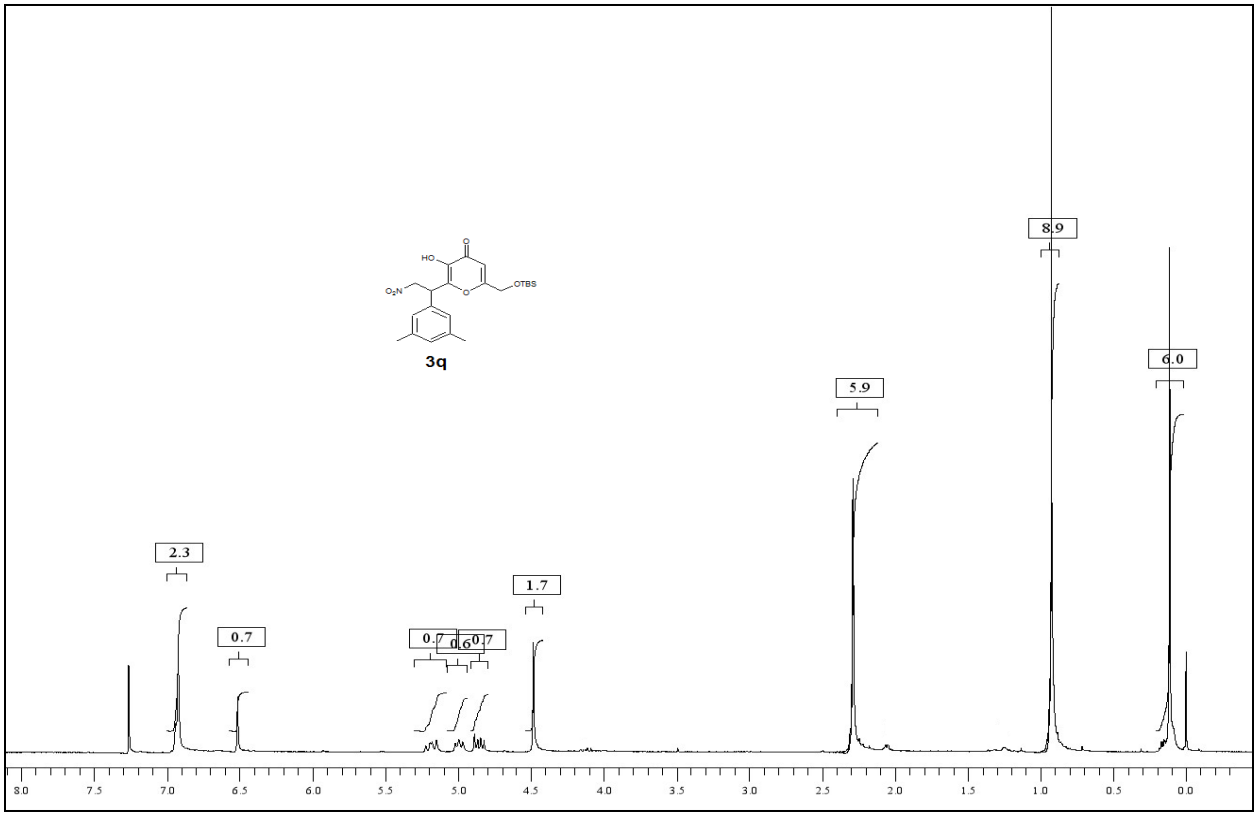


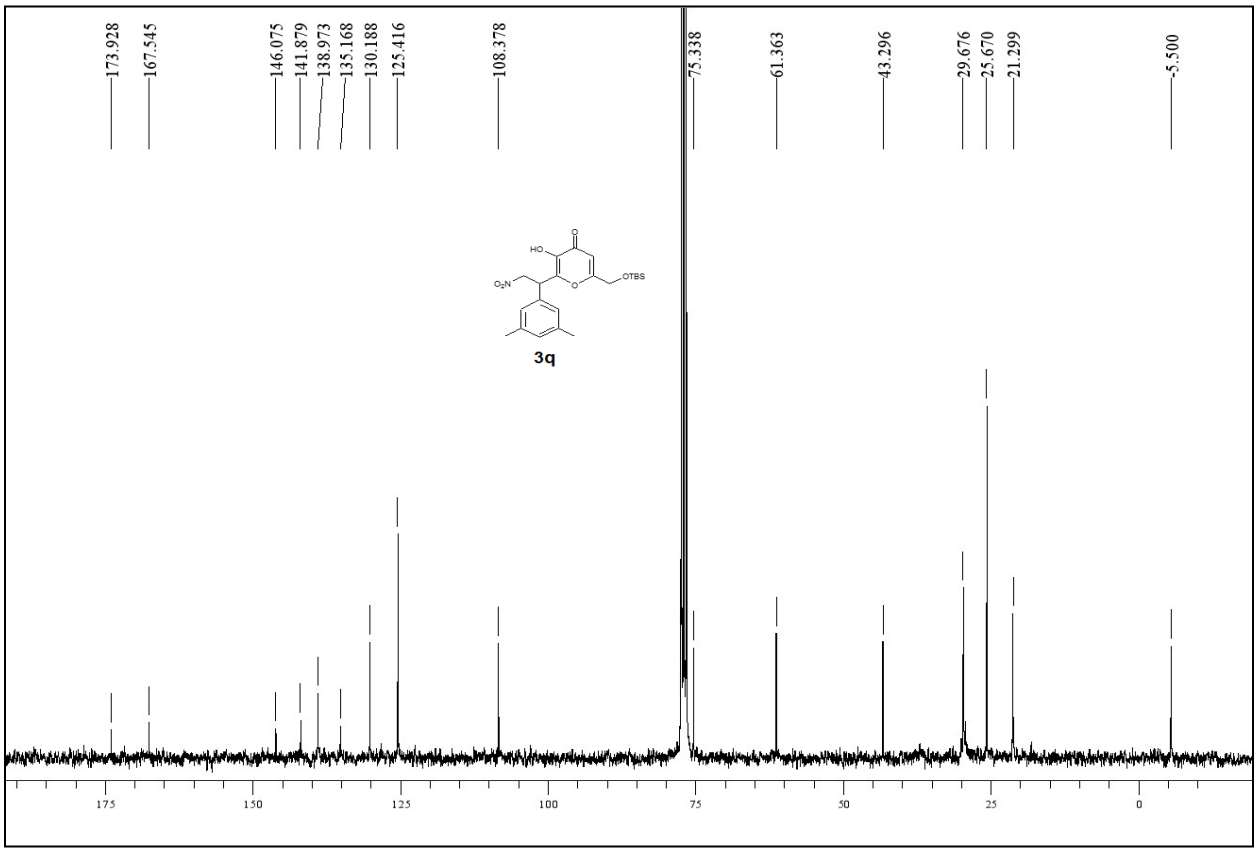


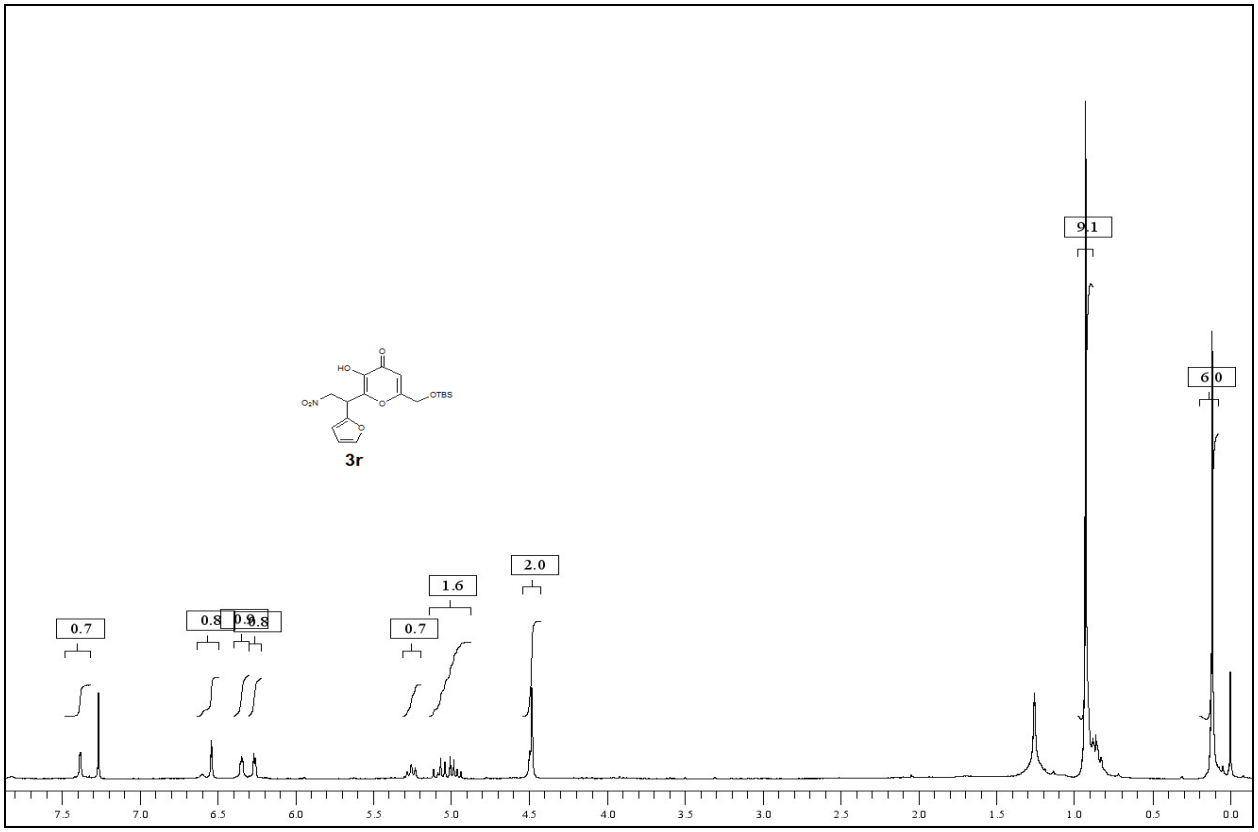


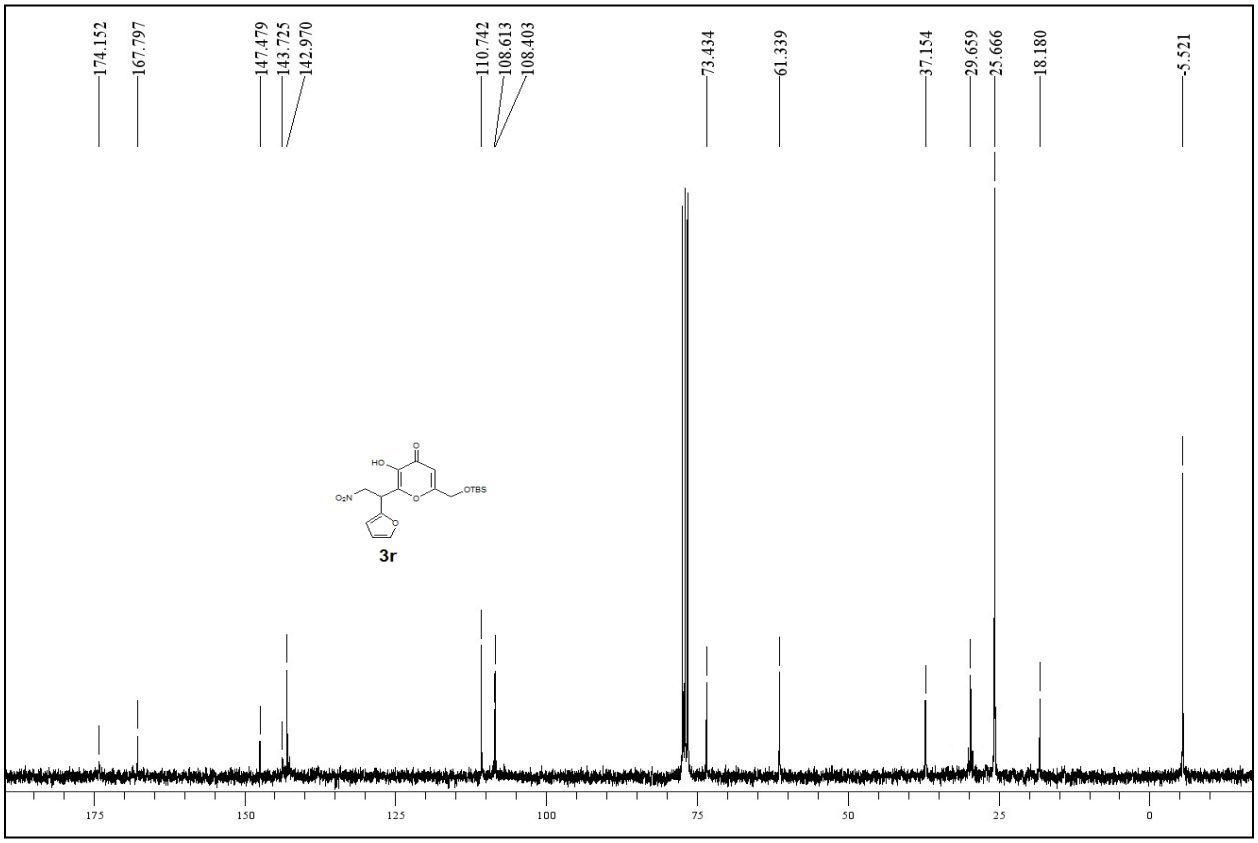


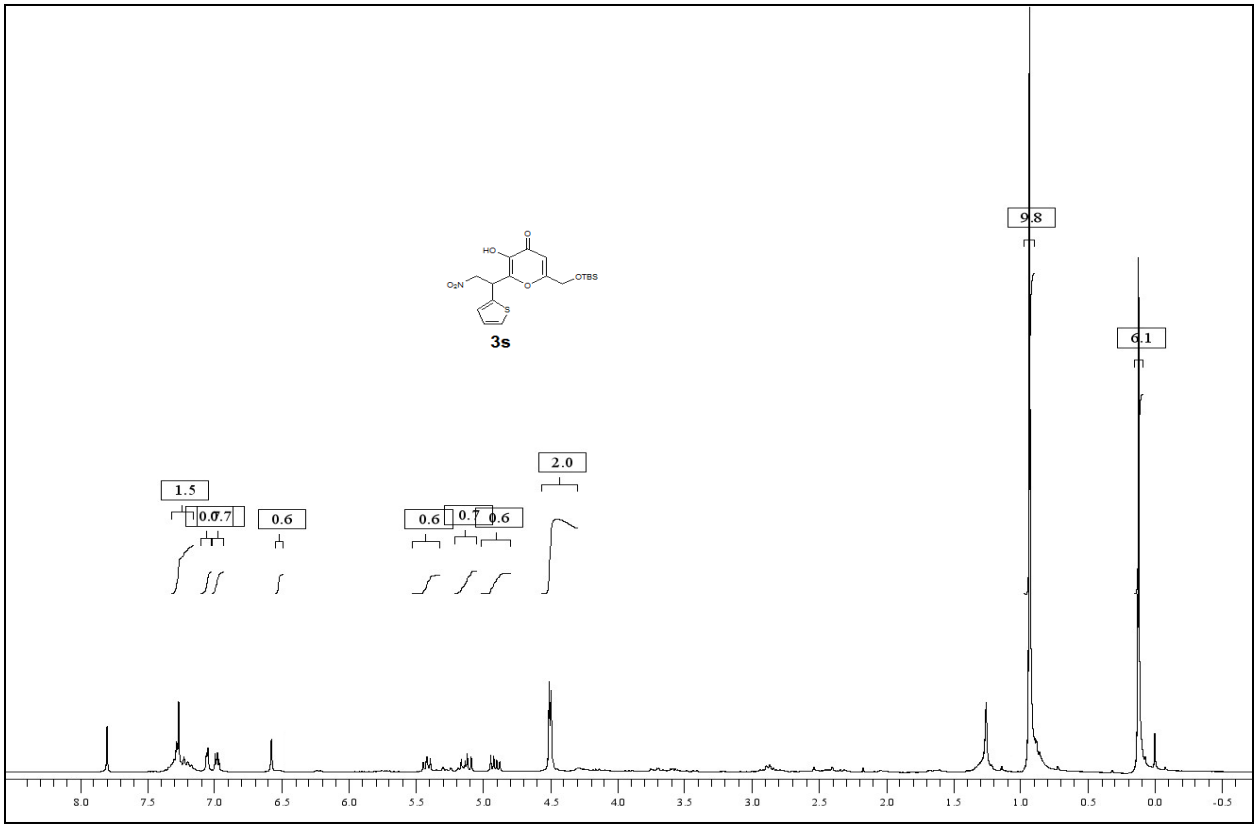


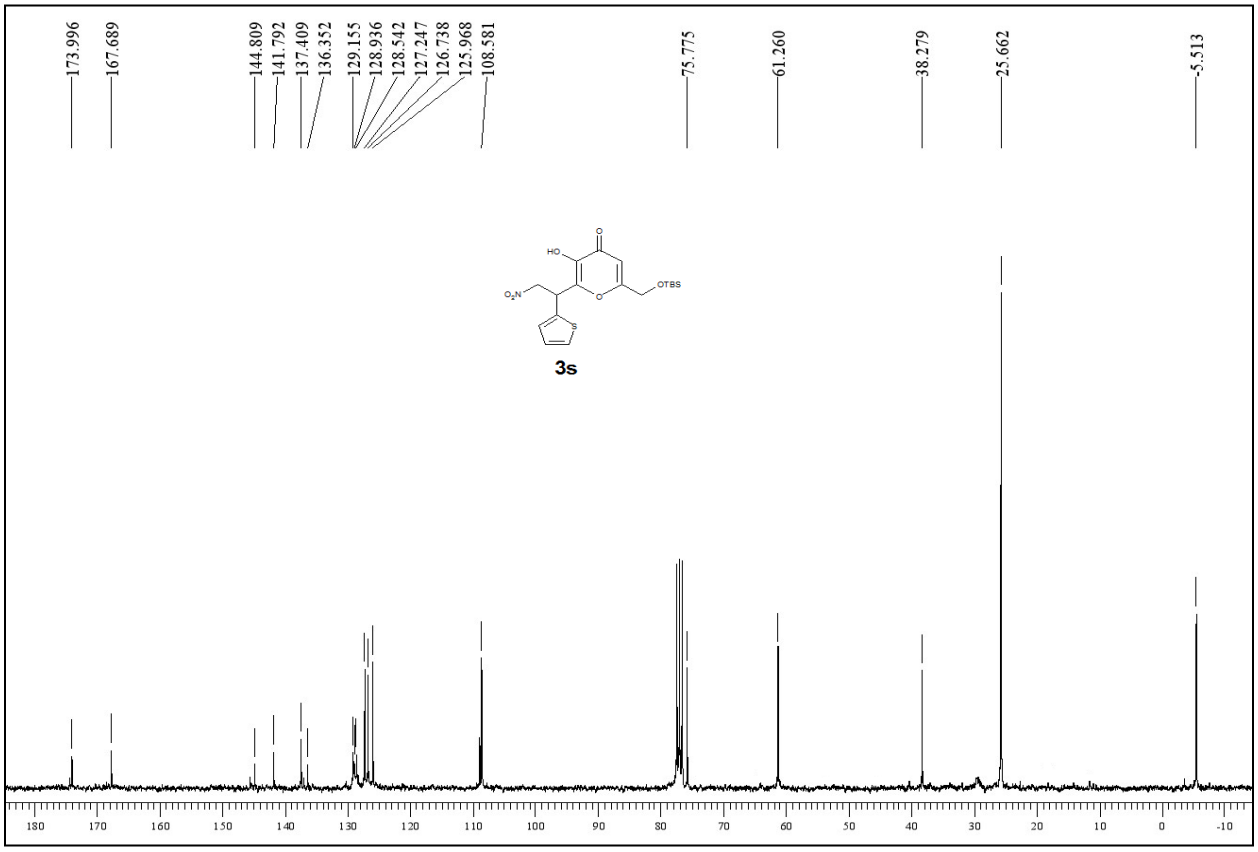


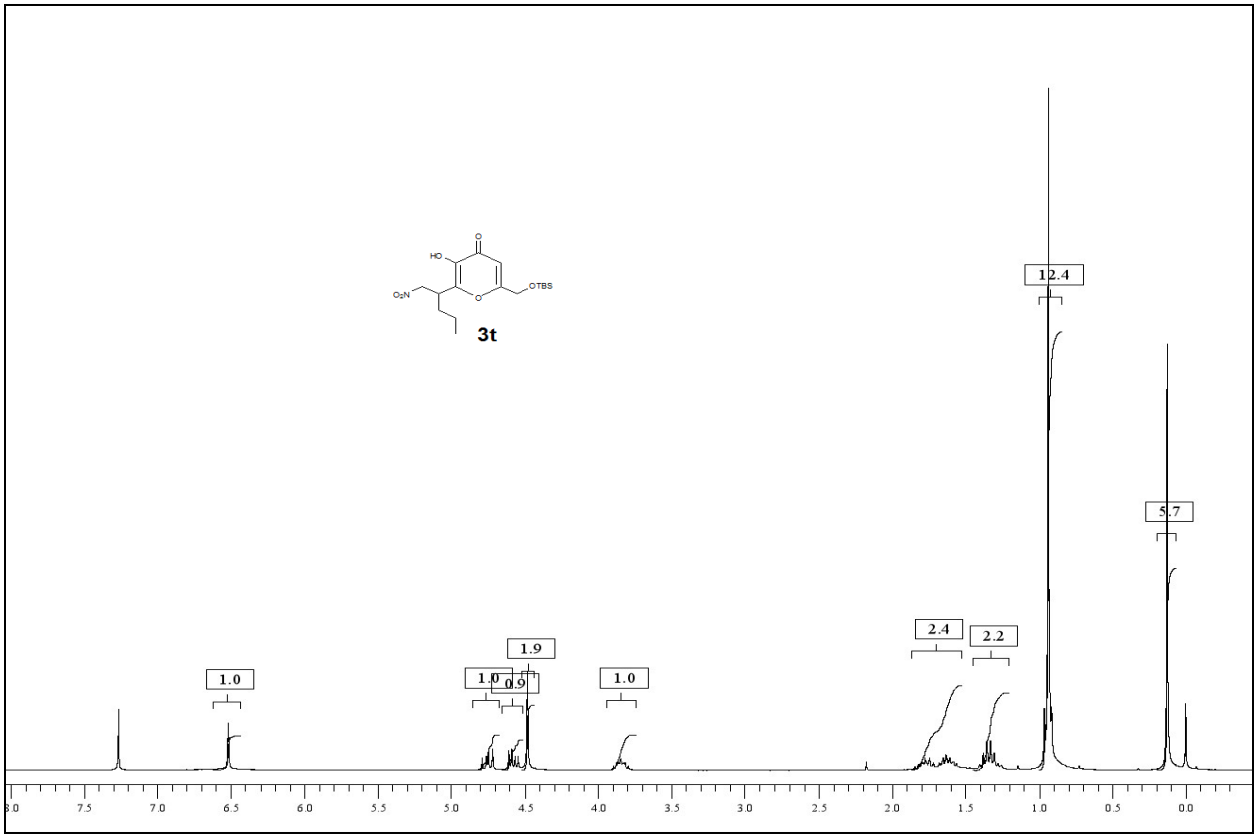


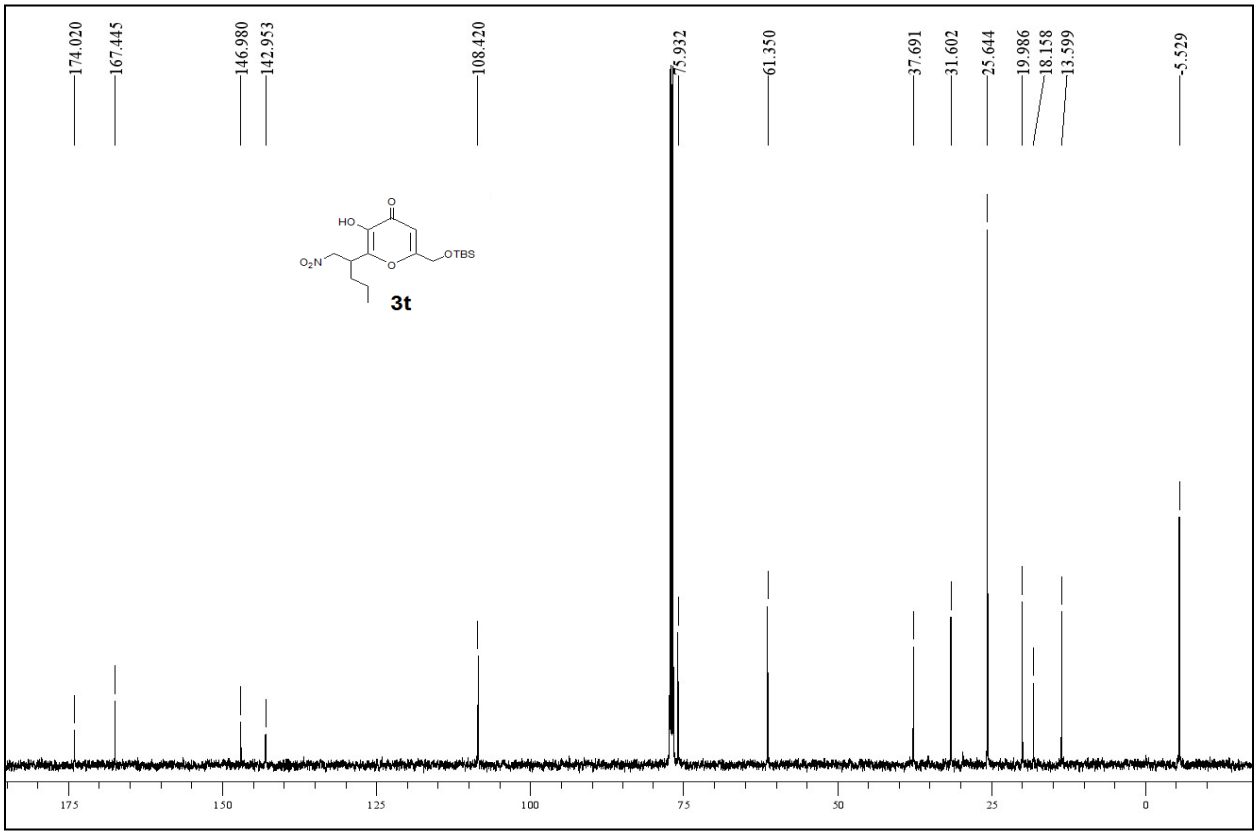


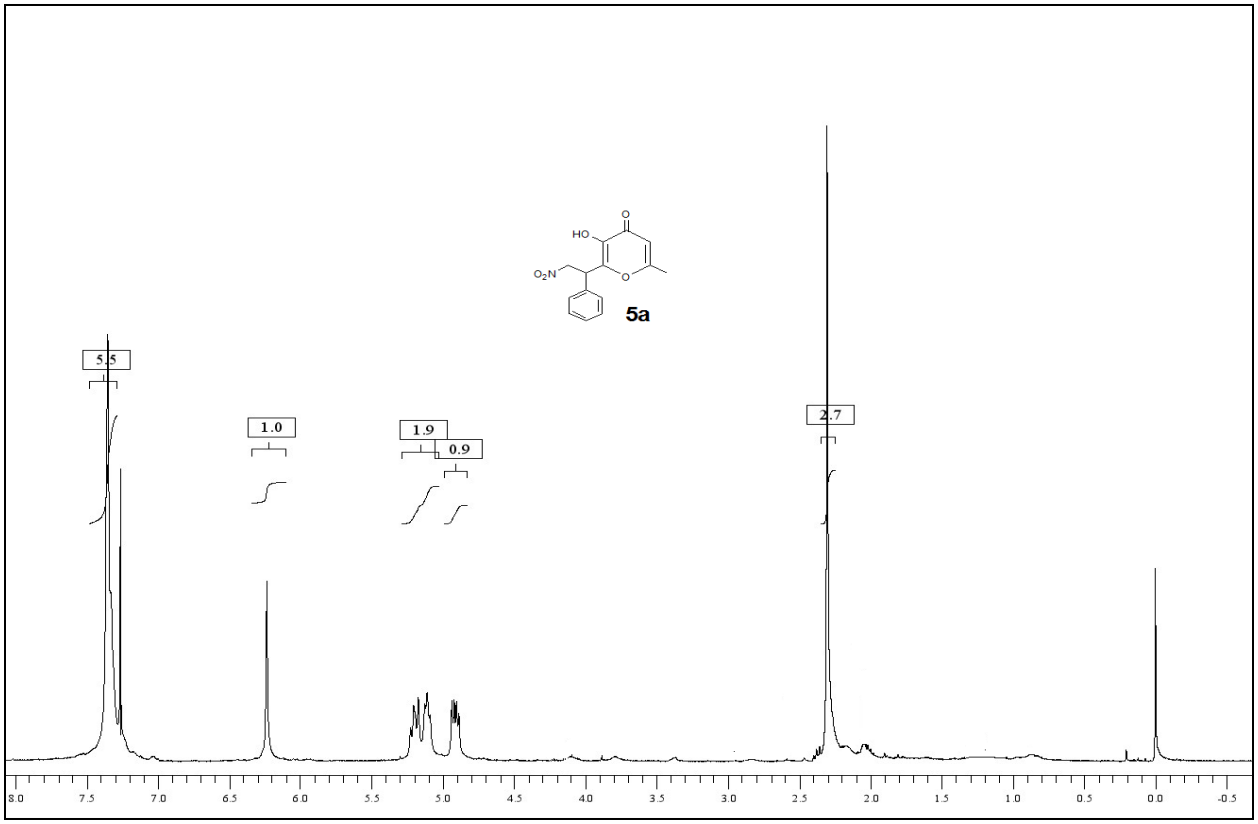


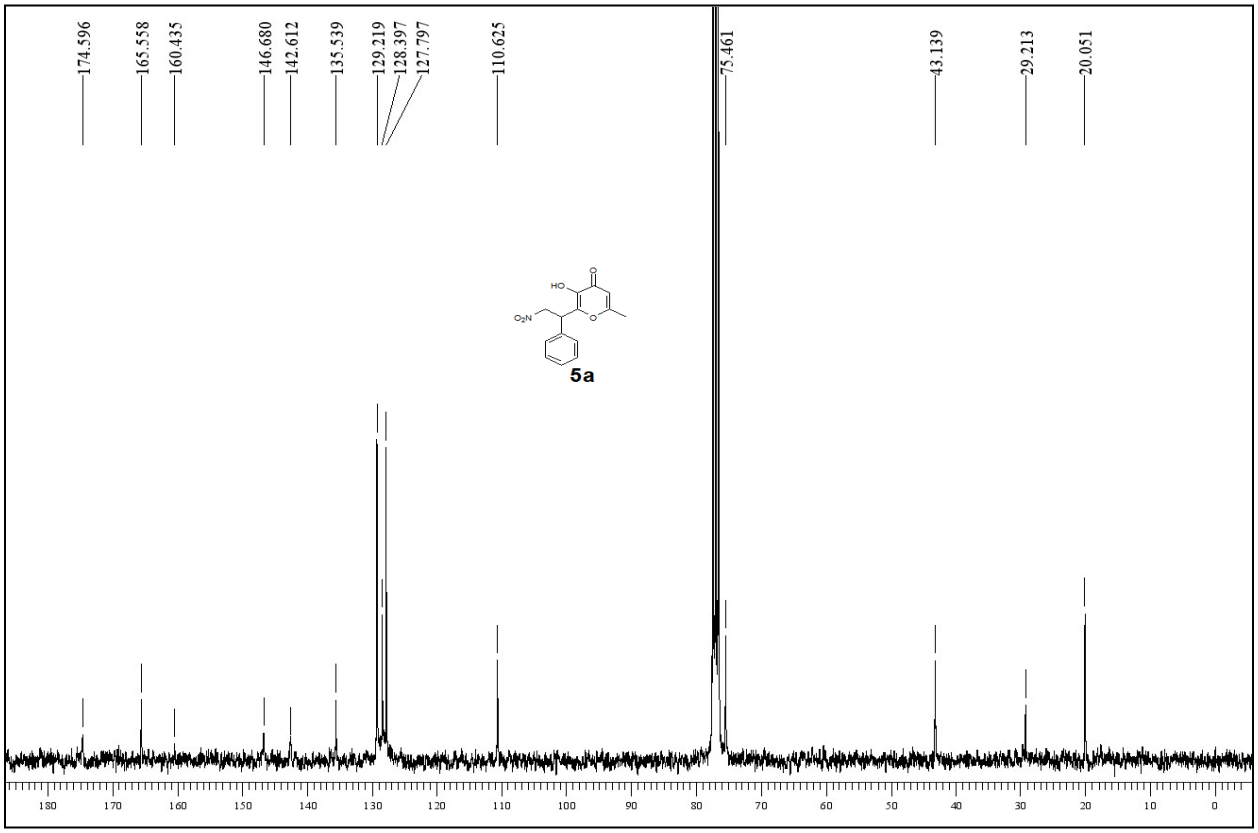


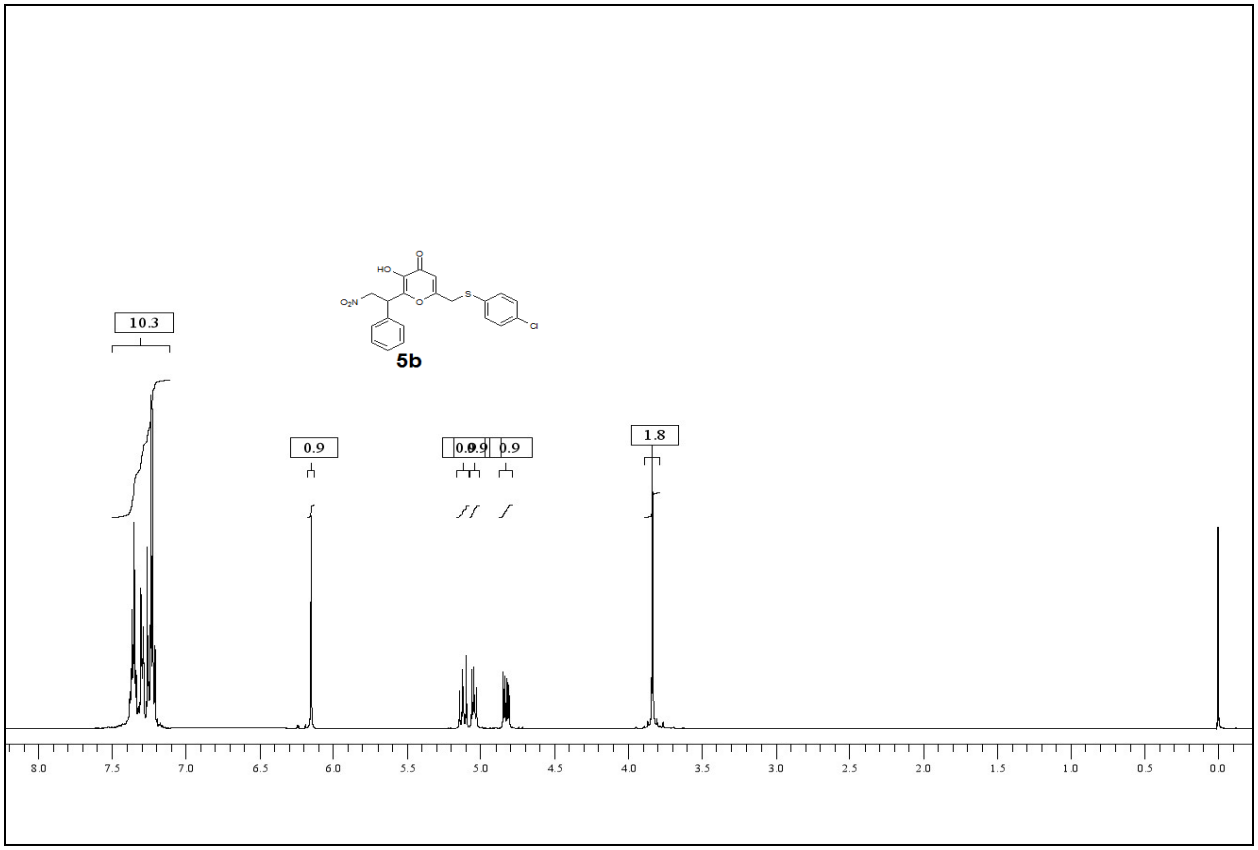


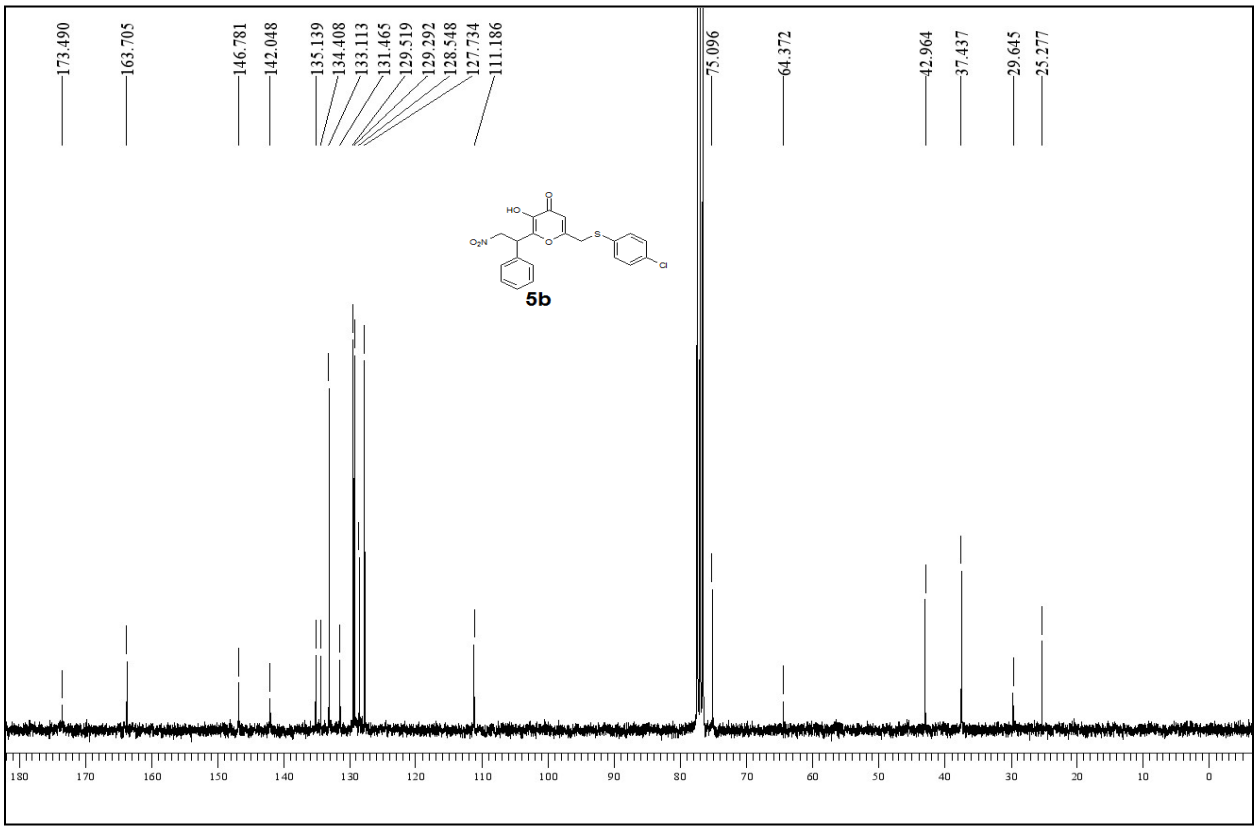




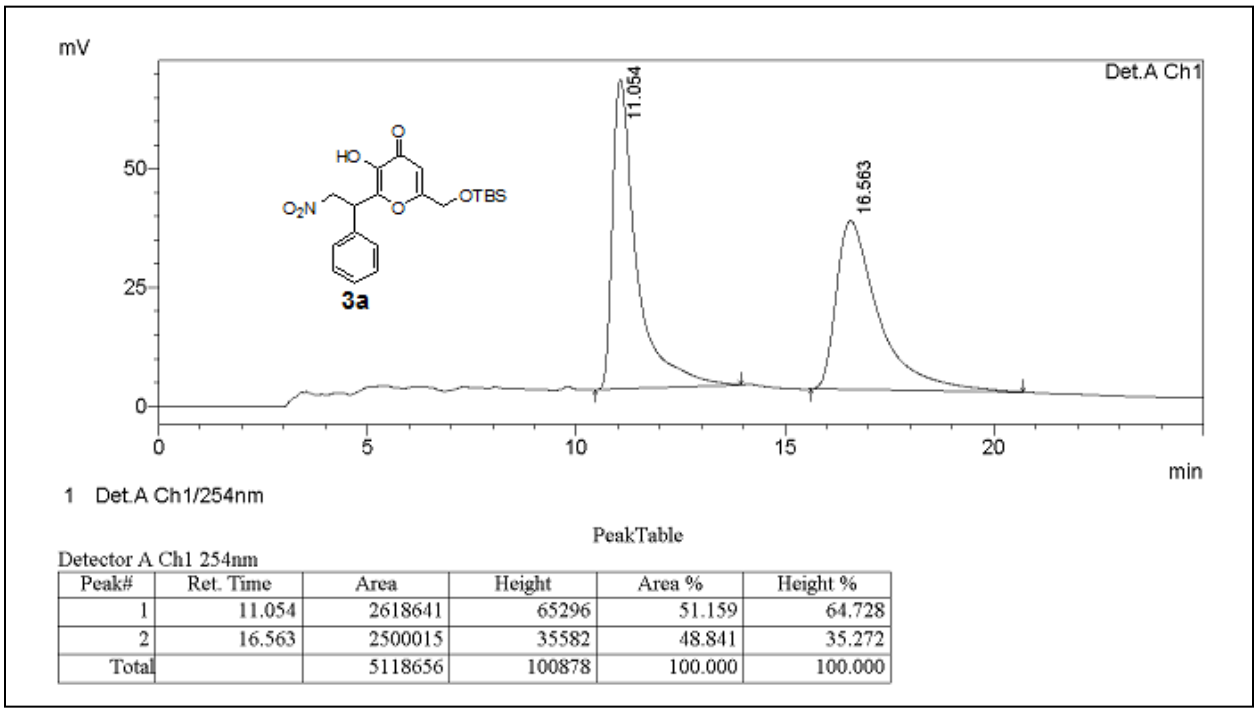








9. HPLC diagram of all compounds.

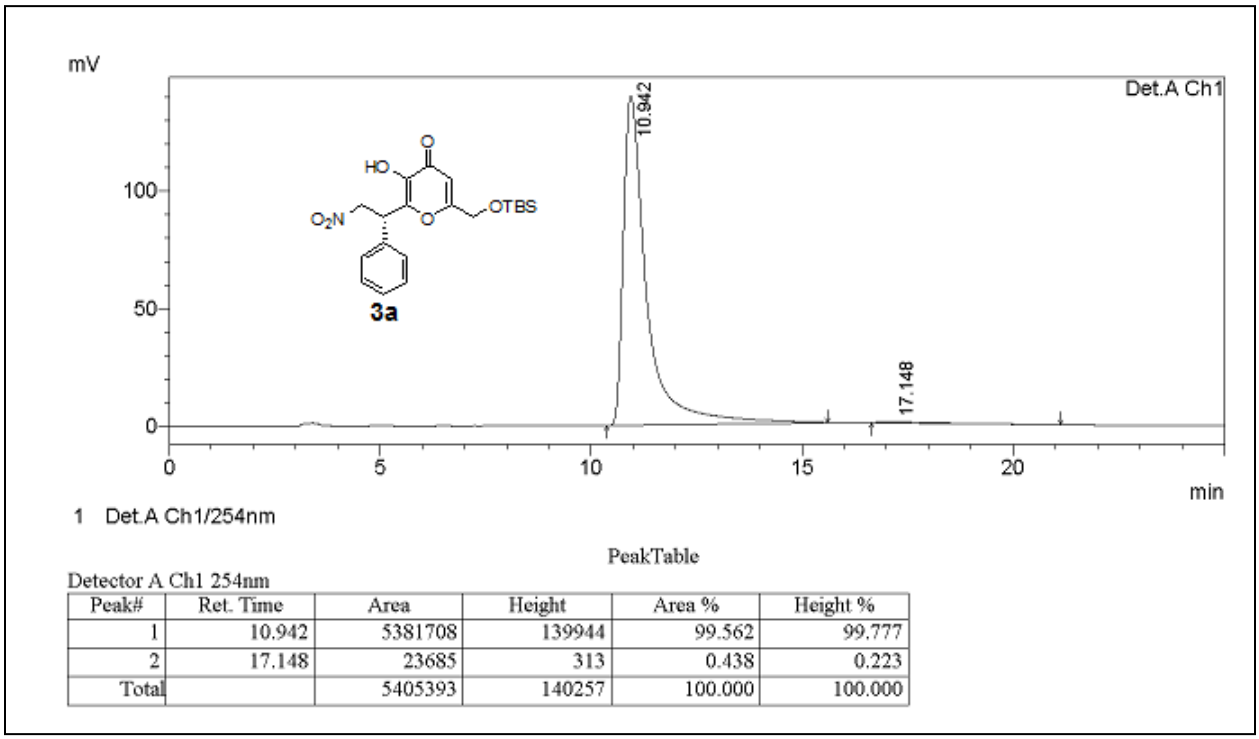


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.054	2618641	65296	51.159	64.728
2	16.563	2500015	35582	48.841	35.272
Total		5118656	100878	100.000	100.000

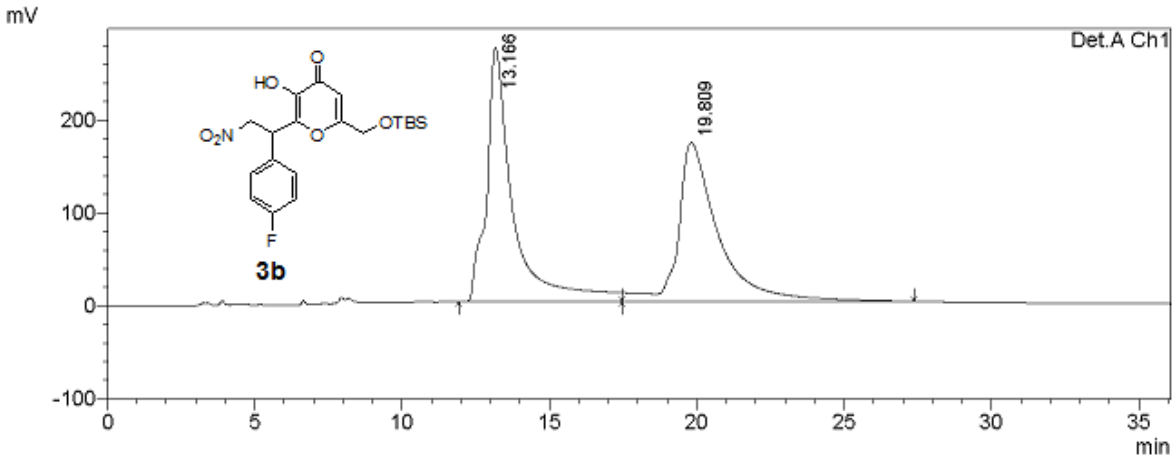


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.942	5381708	139944	99.562	99.777
2	17.148	23685	313	0.438	0.223
Total		5405393	140257	100.000	100.000

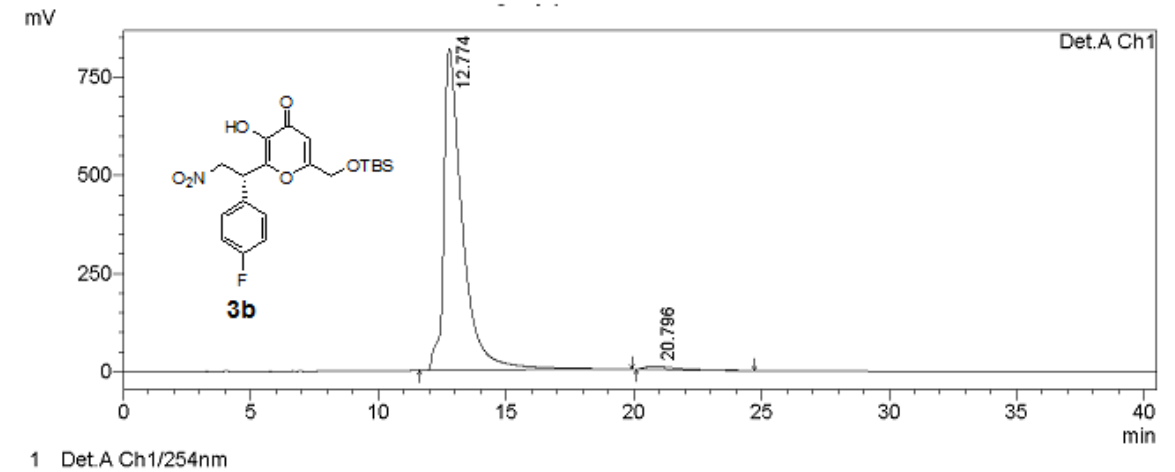


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.166	17079845	273598	51.353	61.528
2	19.809	16180054	171071	48.647	38.472
Total		33259898	444669	100.000	100.000

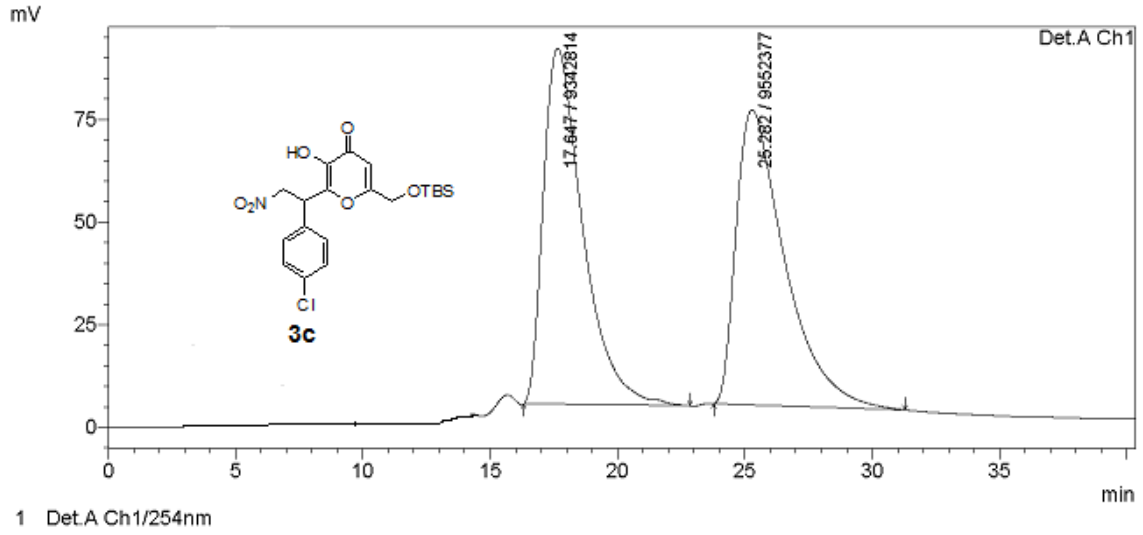


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

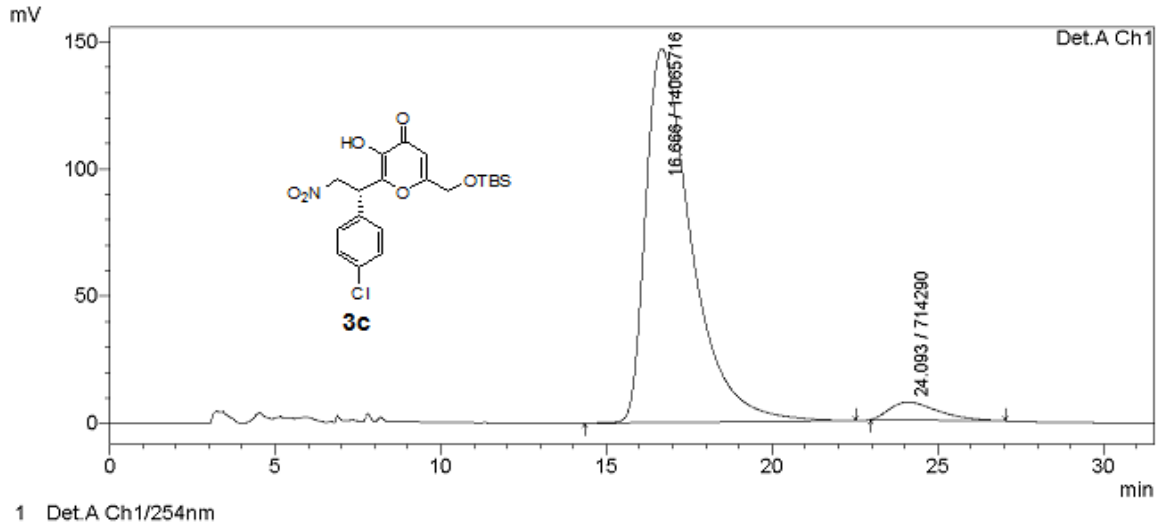
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.774	41701250	817704	98.515	99.028
2	20.796	628697	8025	1.485	0.972
Total		42329947	825729	100.000	100.000



PeakTable

Detector A Ch1 254nm

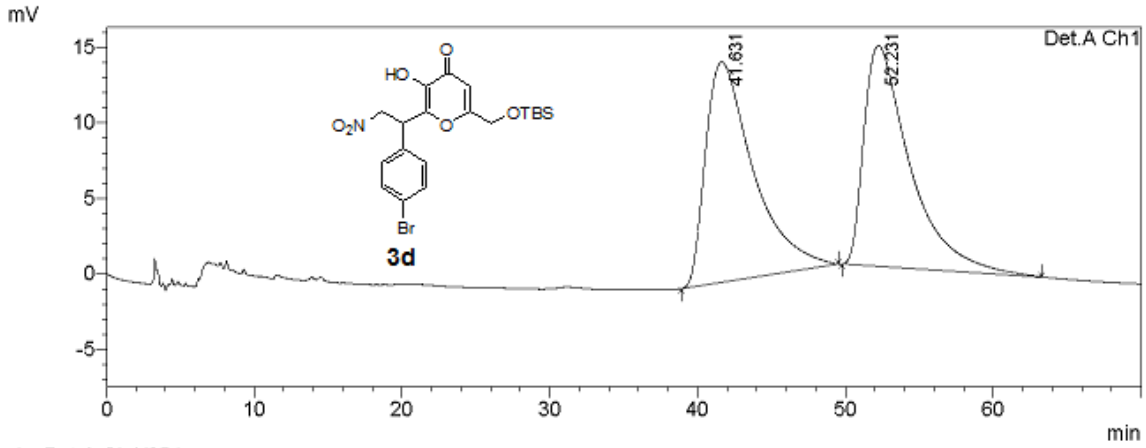
Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.647	9342814	86652	49.445	54.666
2	25.282	9552377	71861	50.555	45.334
Total		18895191	158513	100.000	100.000



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.666	14065716	147057	95.167	95.470
2	24.093	714290	6978	4.833	4.530
Total		14780007	154035	100.000	100.000

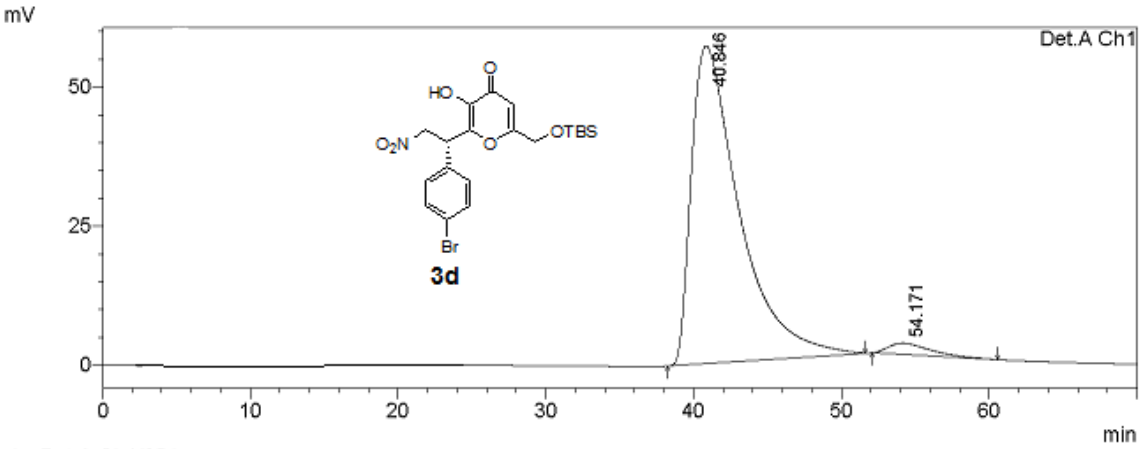


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	41.631	3290558	14583	50.960	49.942
2	52.231	3166533	14617	49.040	50.058
Total		6457091	29199	100.000	100.000

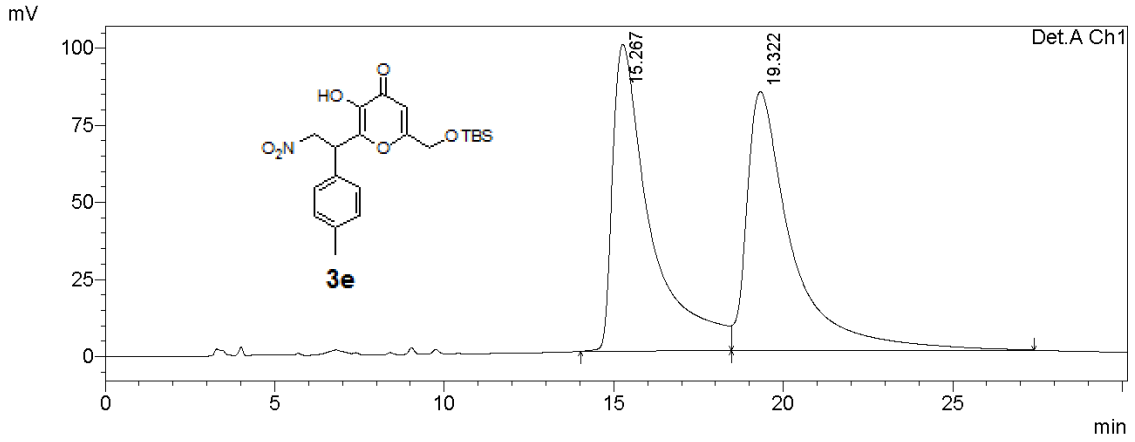


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	40.846	12913522	57130	96.954	96.588
2	54.171	405664	2018	3.046	3.412
Total		13319186	59148	100.000	100.000

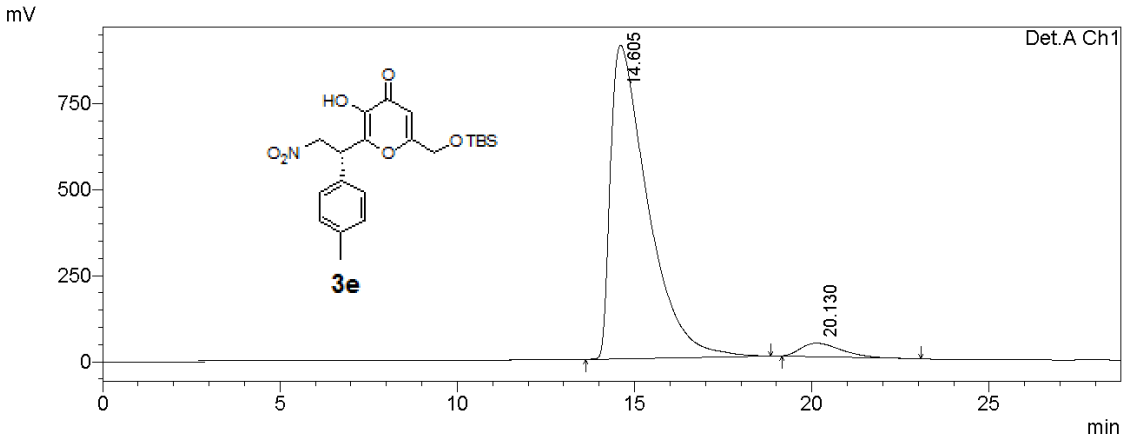


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.267	7717414	99502	49.833	54.202
2	19.322	7769106	84075	50.167	45.798
Total		15486521	183577	100.000	100.000

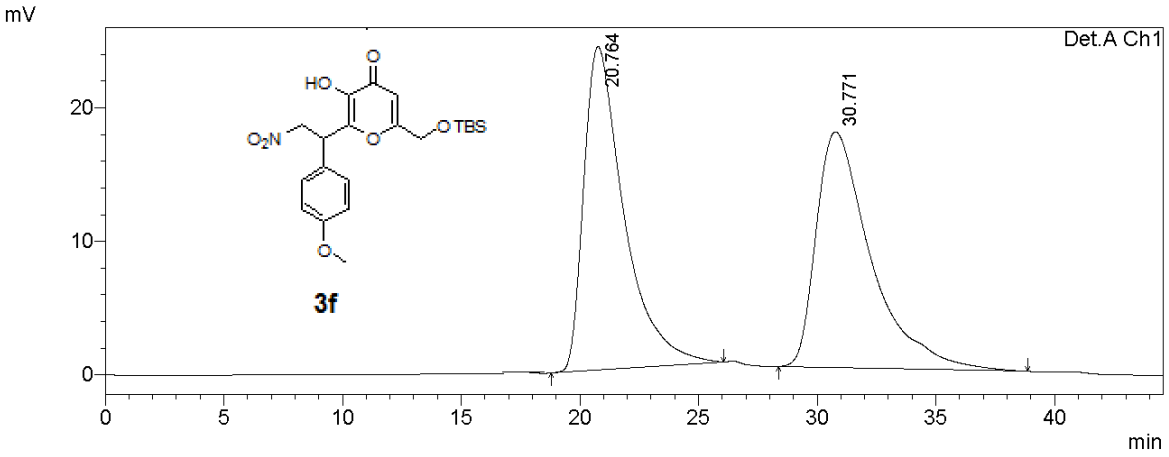


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.605	66566652	911047	95.522	95.904
2	20.130	3120252	38915	4.478	4.096
Total		69686904	949962	100.000	100.000

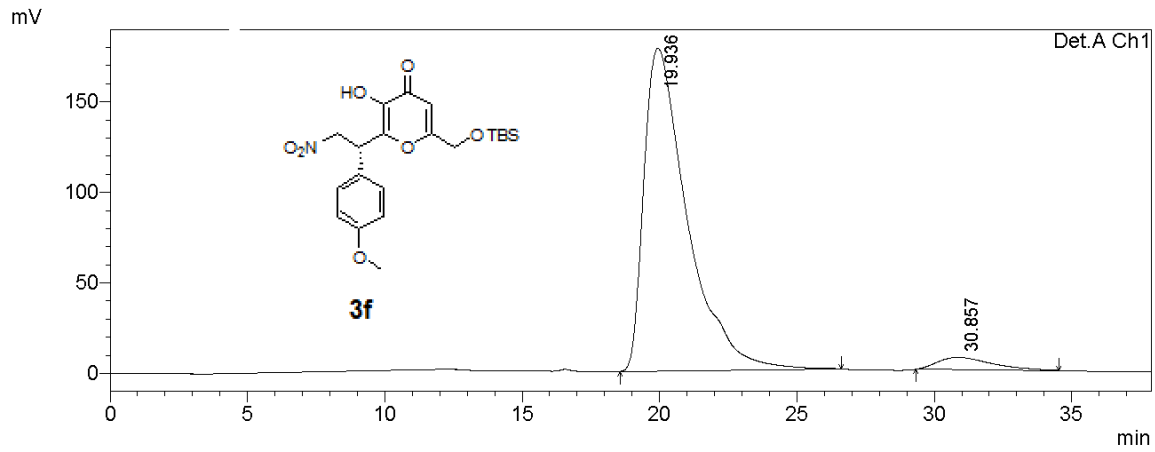


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.764	2858134	24245	50.171	57.853
2	30.771	2838598	17663	49.829	42.147
Total		5696731	41908	100.000	100.000



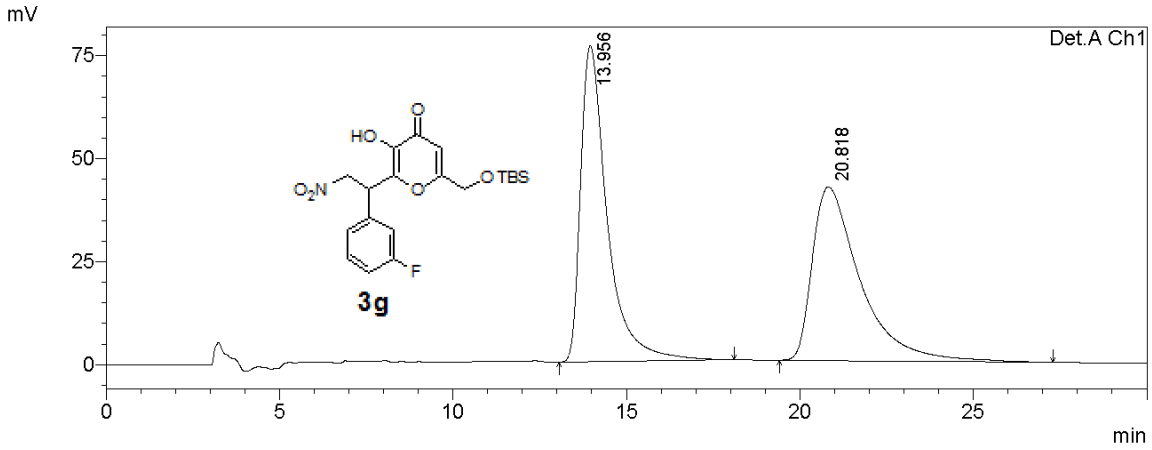
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.936	19562367	178217	95.481	96.344
2	30.857	925940	6762	4.519	3.656
Total		20488307	184980	100.000	100.000

<Chromatogram>

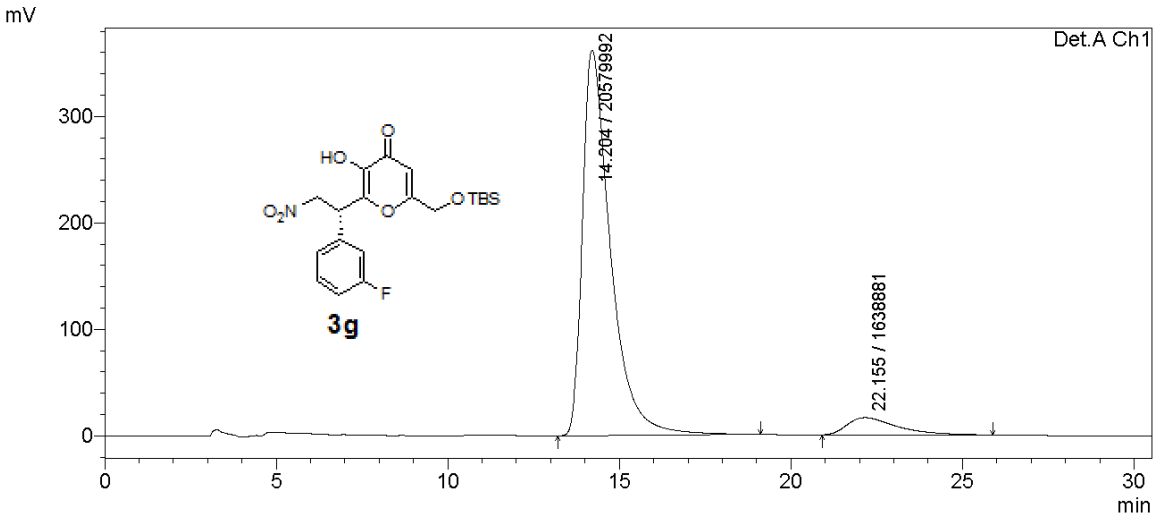


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.956	4087366	76721	50.334	64.574
2	20.818	4033055	42089	49.666	35.426
Total		8120421	118810	100.000	100.000

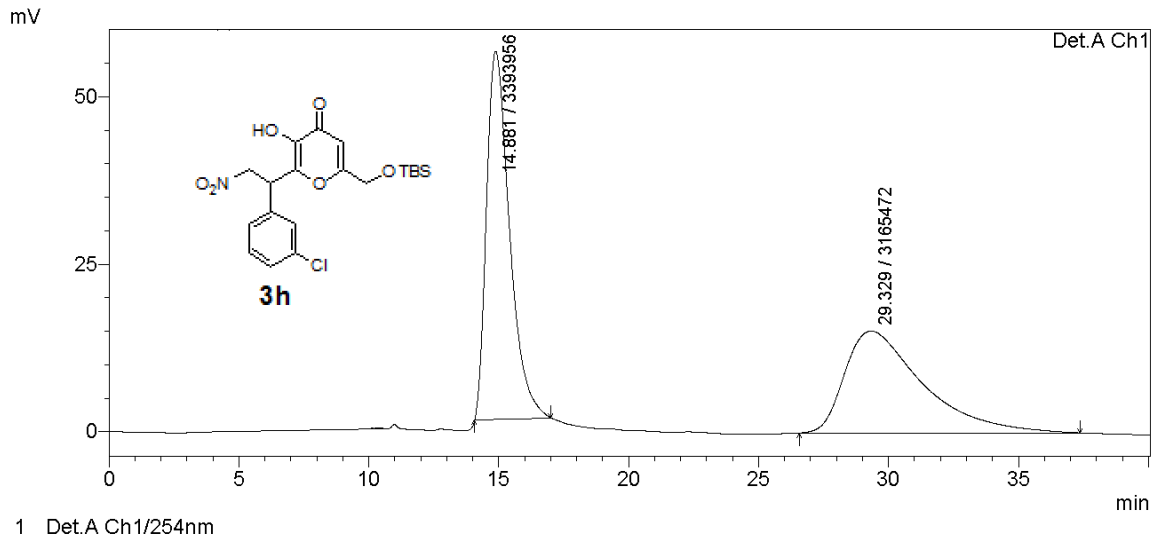


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

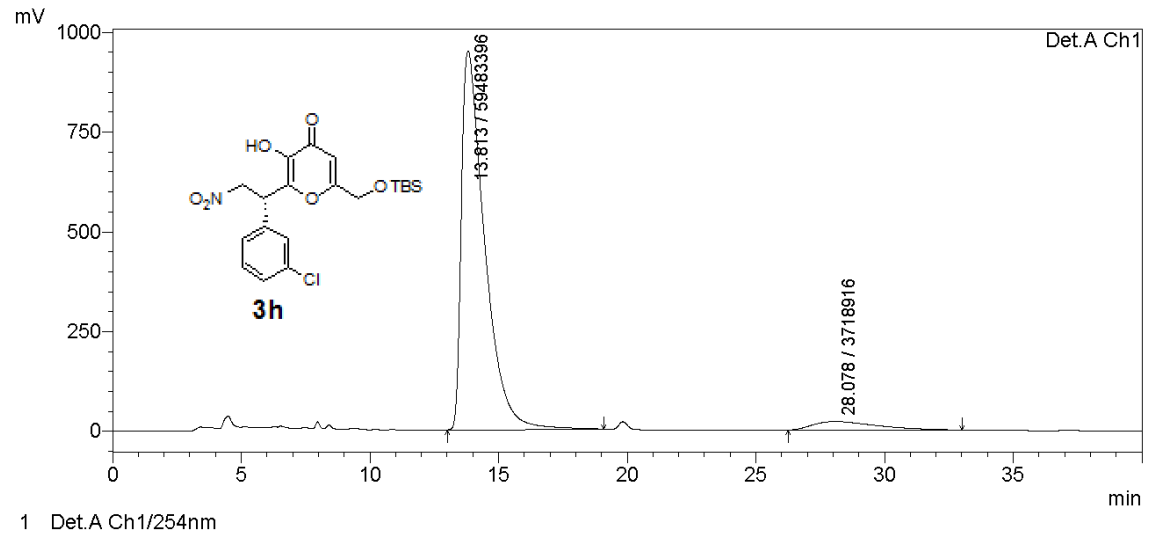
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.204	20579992	362176	92.624	95.723
2	22.155	1638881	16181	7.376	4.277
Total		22218873	378357	100.000	100.000



PeakTable

Detector A Ch1 254nm

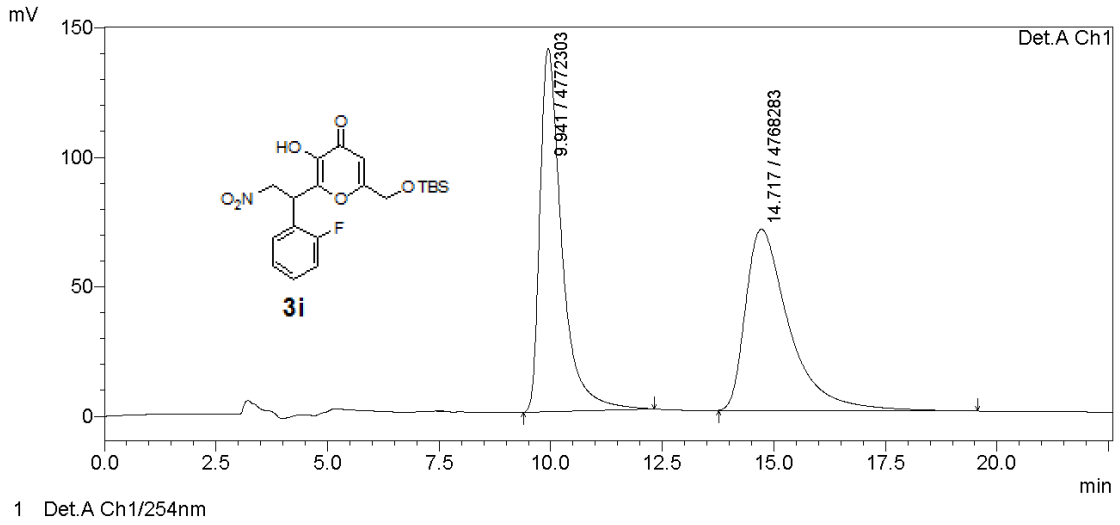
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.881	3393956	54985	51.742	78.326
2	29.329	3165472	15215	48.258	21.674
Total		6559428	70201	100.000	100.000



PeakTable

Detector A Ch1 254nm

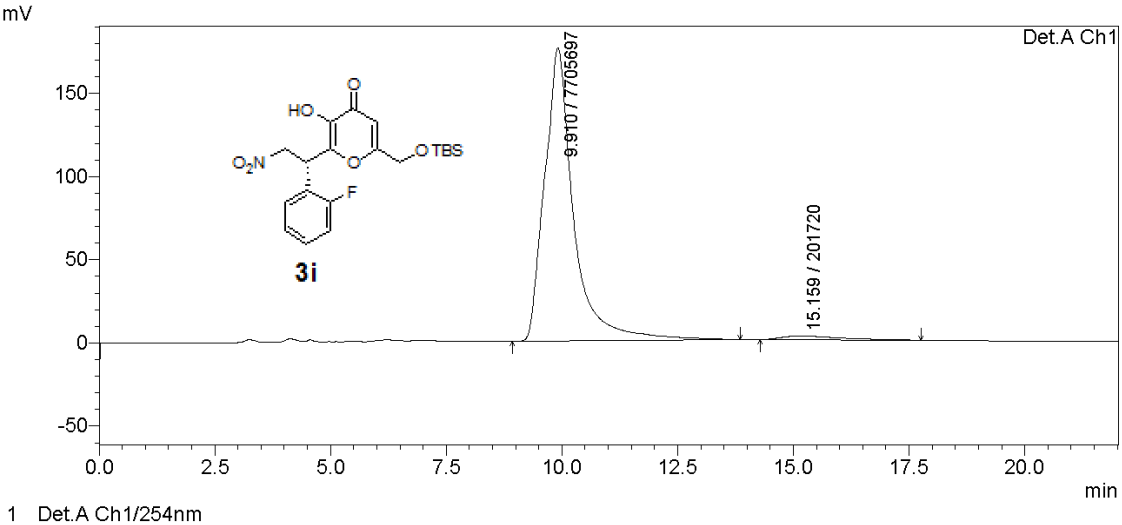
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.813	59483396	949706	94.116	97.788
2	28.078	3718916	21478	5.884	2.212
Total		63202312	971184	100.000	100.000



PeakTable

Detector A Ch1 254nm

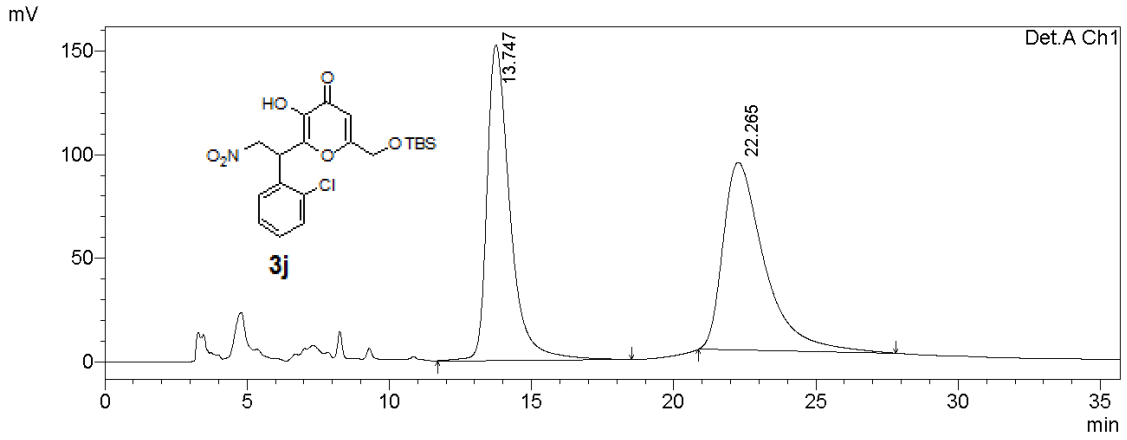
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.941	4772303	140365	50.021	66.716
2	14.717	4768283	70028	49.979	33.284
Total		9540586	210393	100.000	100.000



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.910	7705697	176374	97.449	98.718
2	15.159	201720	2290	2.551	1.282
Total		7907417	178664	100.000	100.000

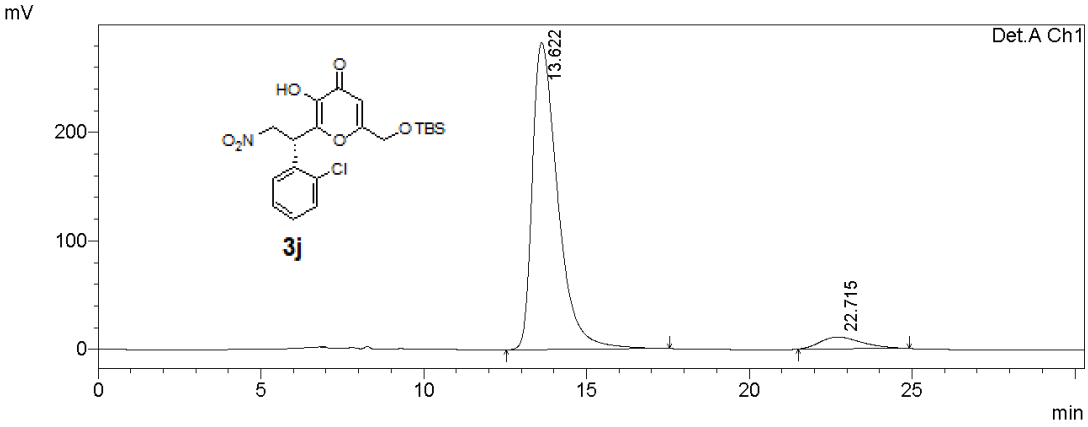


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.747	8546464	152408	48.148	62.683
2	22.265	9204086	90731	51.852	37.317
Total		17750551	243140	100.000	100.000

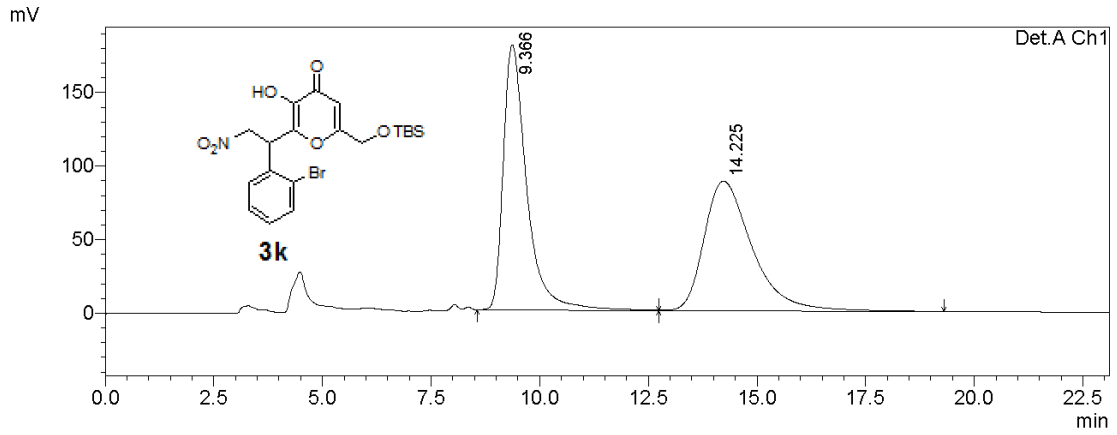


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.622	15376982	283193	93.976	96.286
2	22.715	985601	10924	6.024	3.714
Total		16362583	294117	100.000	100.000

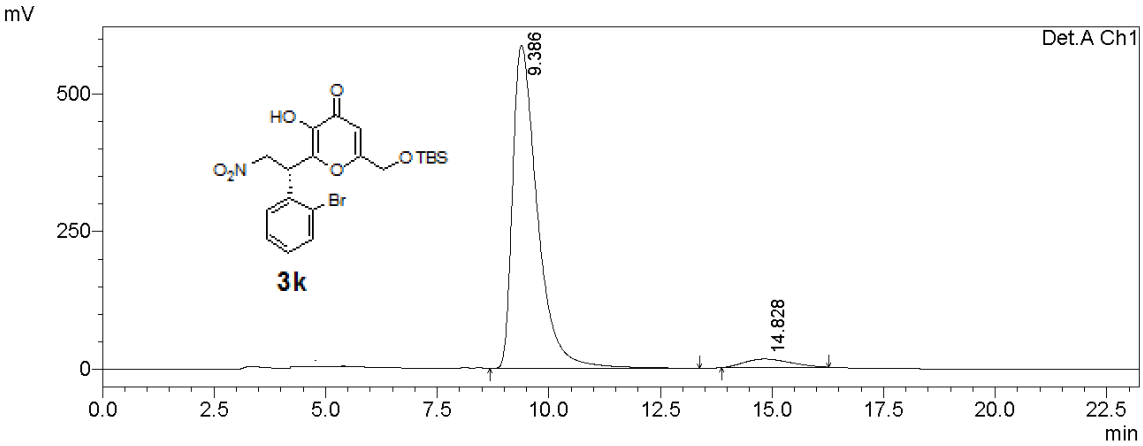


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.366	6765780	180195	50.039	67.161
2	14.225	6755362	88107	49.961	32.839
Total		13521142	268302	100.000	100.000

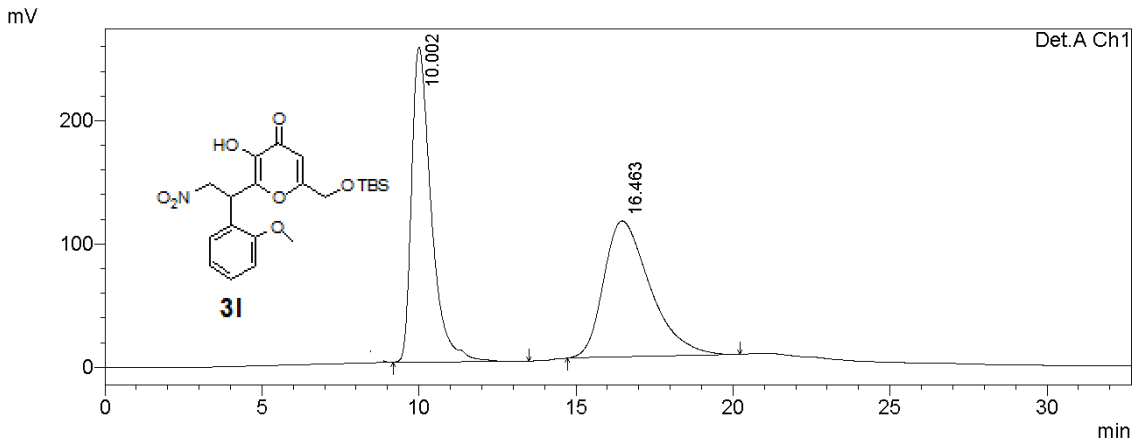


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.386	22679375	586828	95.417	97.476
2	14.828	1089431	15198	4.583	2.524
Total		23768806	602026	100.000	100.000

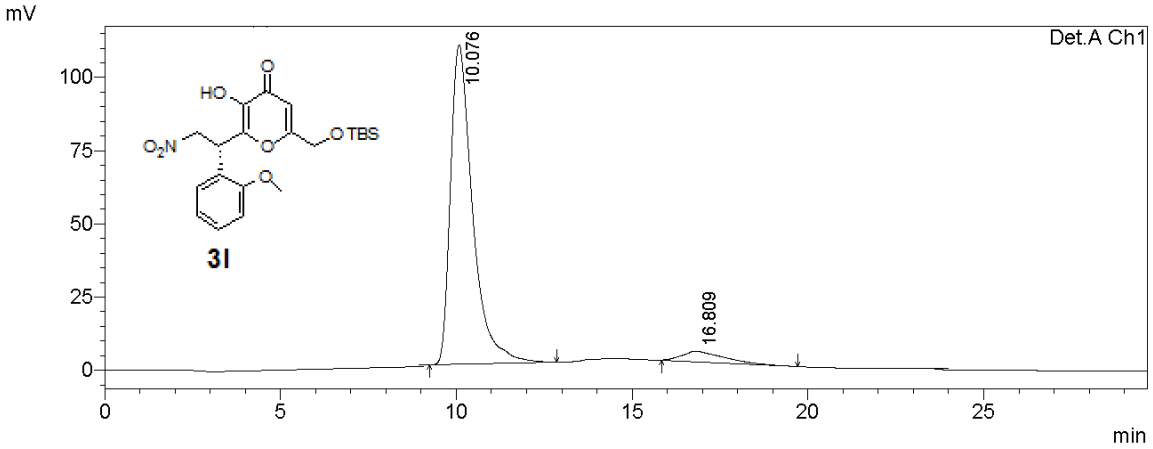


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.002	11101533	255379	49.498	69.843
2	16.463	11326624	110269	50.502	30.157
Total		22428157	365648	100.000	100.000

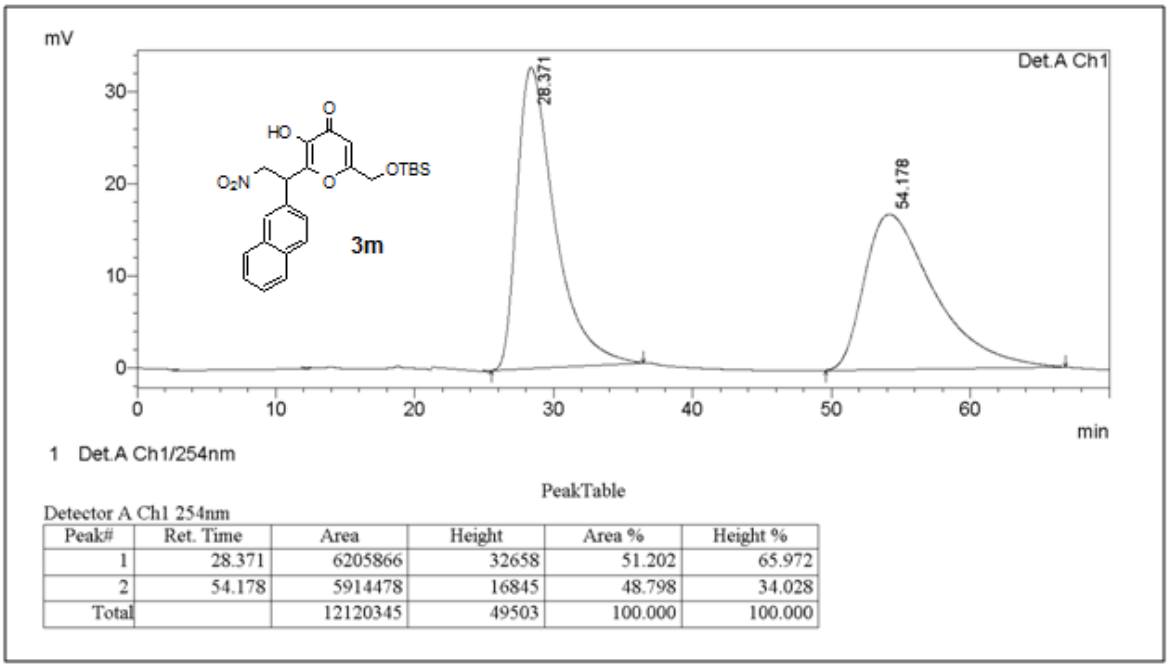


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

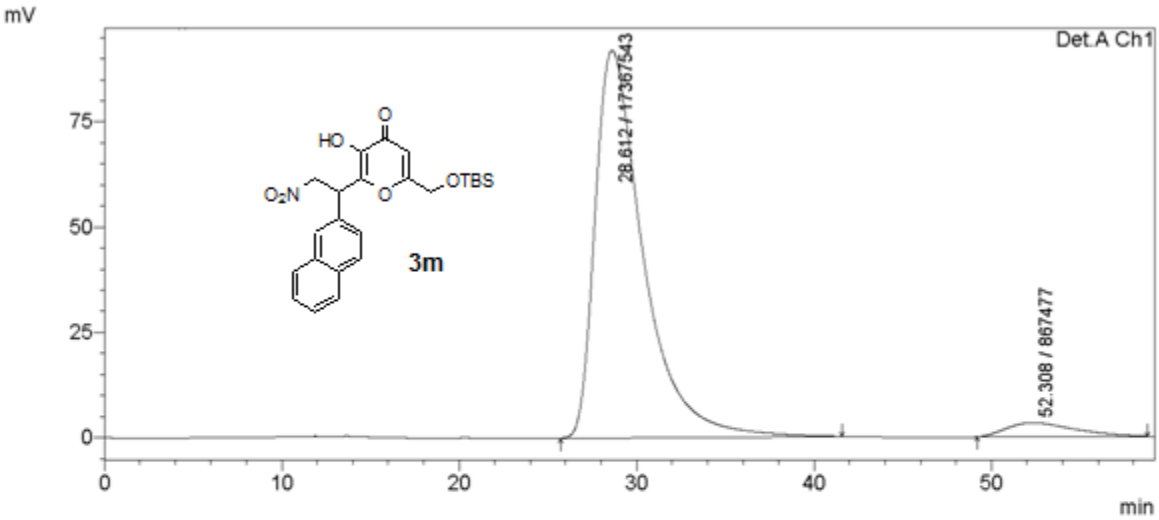
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.076	4791337	109086	94.157	96.770
2	16.809	297308	3641	5.843	3.230
Total		5088645	112727	100.000	100.000



PeakTable

Detector A Ch1 254nm

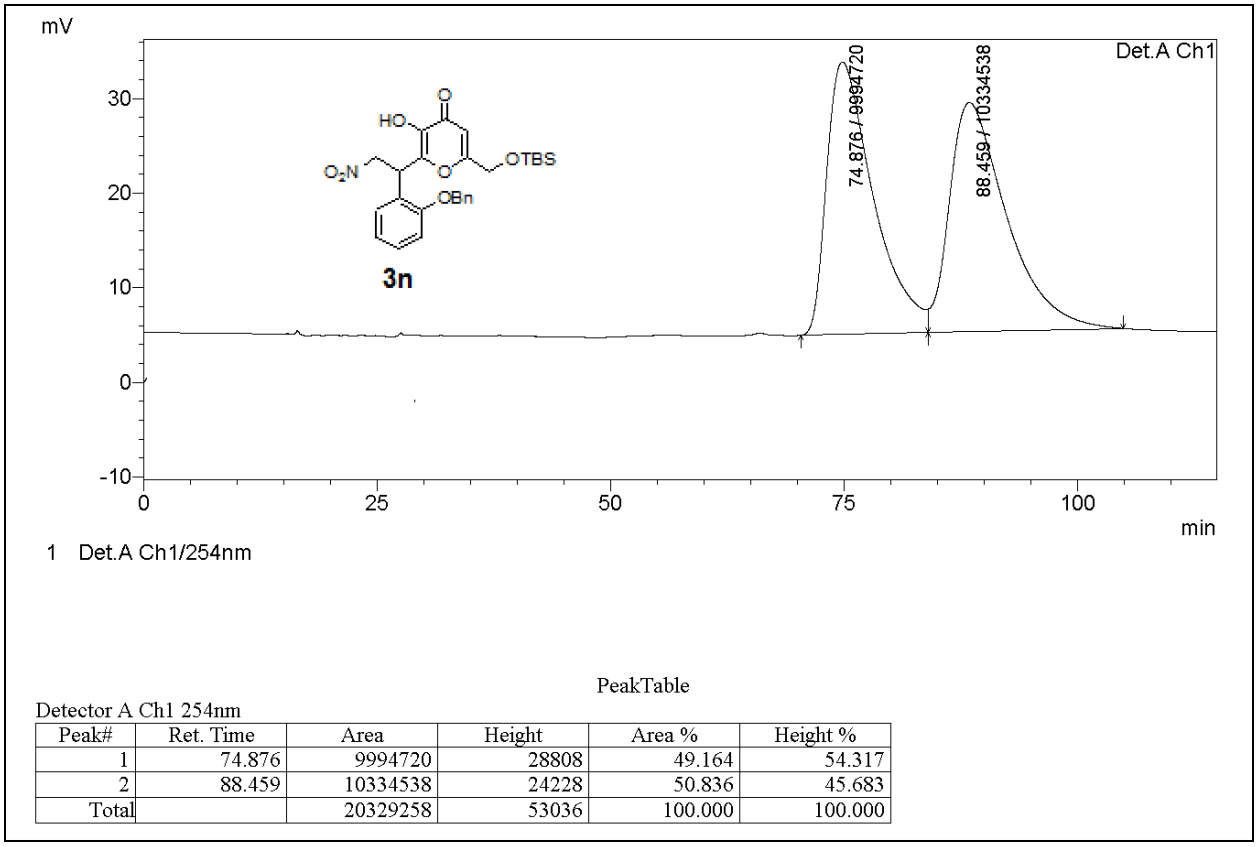
Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.371	6205866	32658	51.202	65.972
2	54.178	5914478	16845	48.798	34.028
Total		12120345	49503	100.000	100.000



PeakTable

Detector A Ch1 254nm

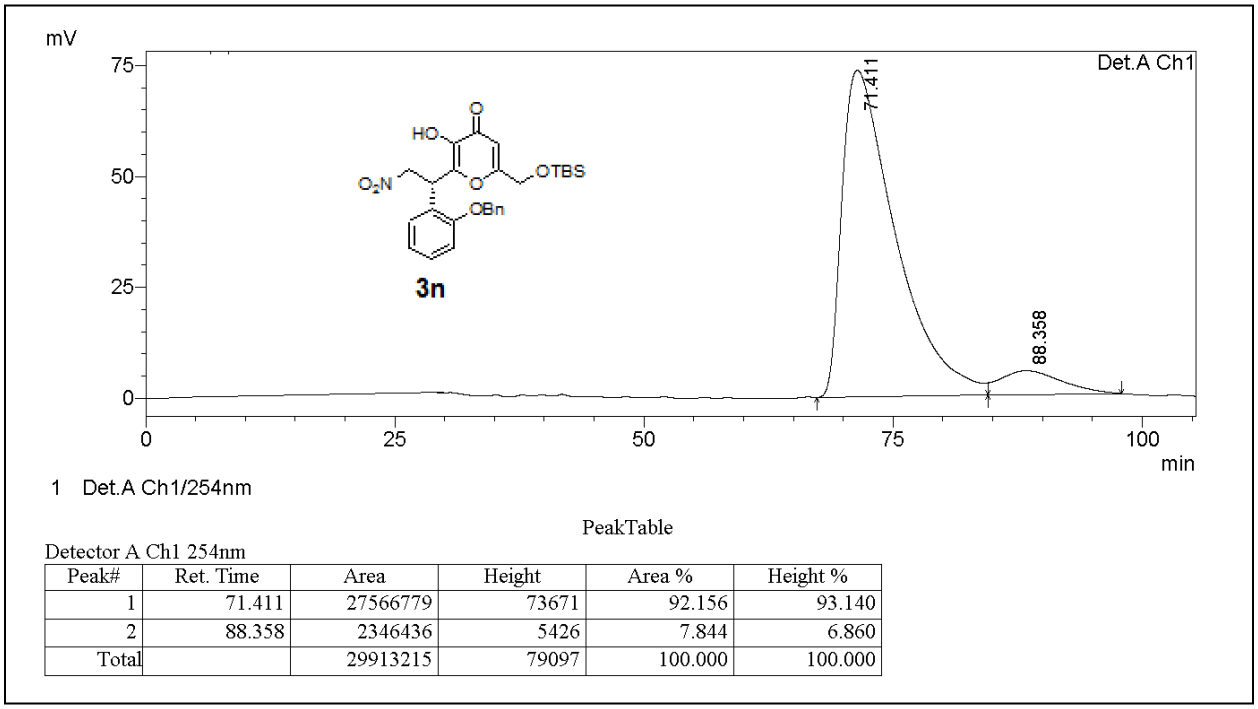
Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.612	17367543	92081	95.343	96.573
2	52.308	867477	3267	4.657	3.427
Total		18235020	95348	100.000	100.000



PeakTable

Detector A Ch1 254nm

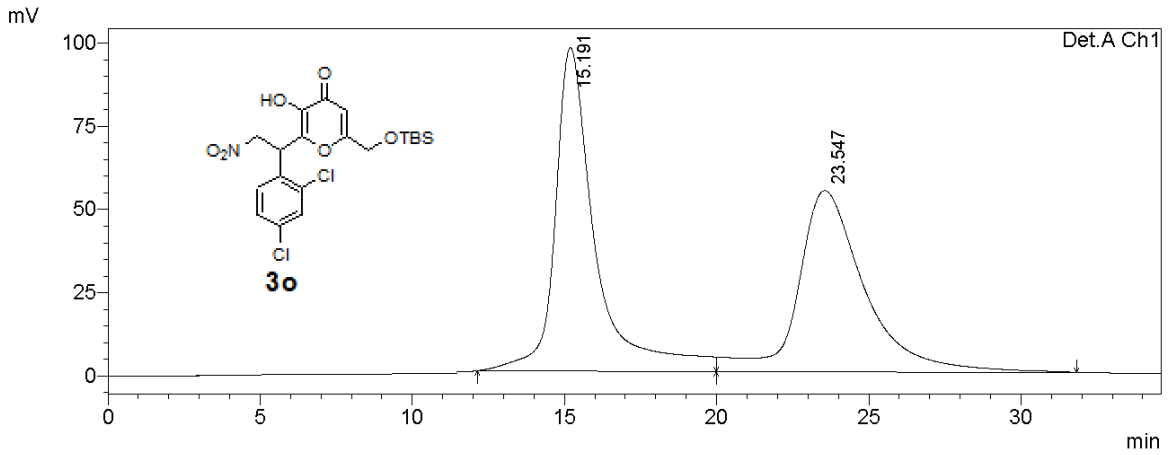
Peak#	Ret. Time	Area	Height	Area %	Height %
1	74.876	9994720	28808	49.164	54.317
2	88.459	10334538	24228	50.836	45.683
Total		20329258	53036	100.000	100.000



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	71.411	27566779	73671	92.156	93.140
2	88.358	2346436	5426	7.844	6.860
Total		29913215	79097	100.000	100.000

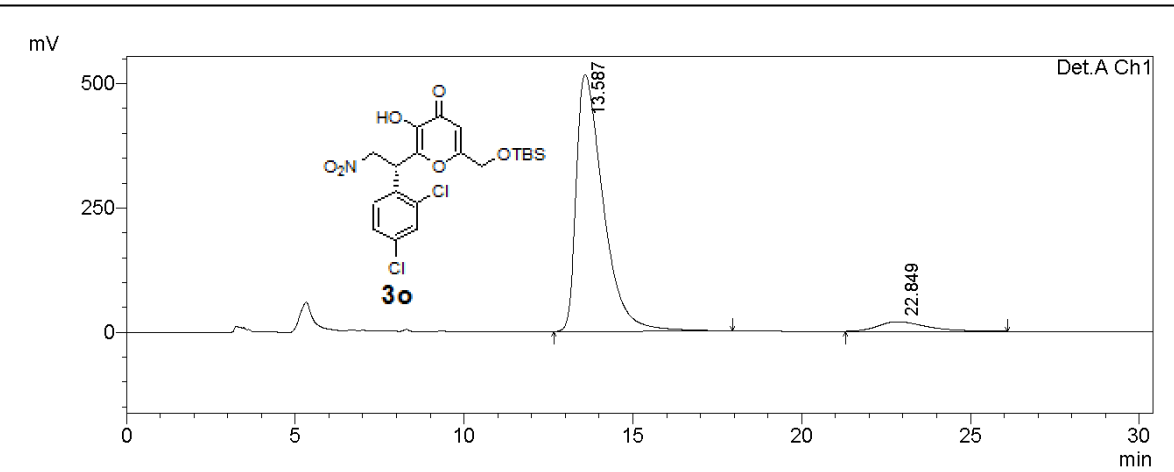


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.191	8924532	97265	51.869	64.130
2	23.547	8281232	54405	48.131	35.870
Total		17205764	151670	100.000	100.000

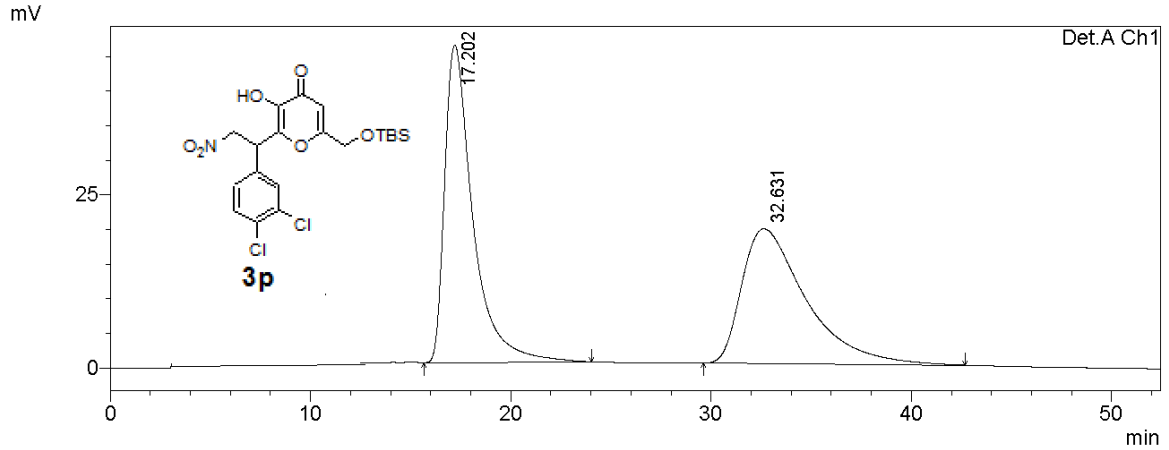


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.587	28696217	516328	93.694	96.383
2	22.849	1931408	19378	6.306	3.617
Total		30627625	535707	100.000	100.000

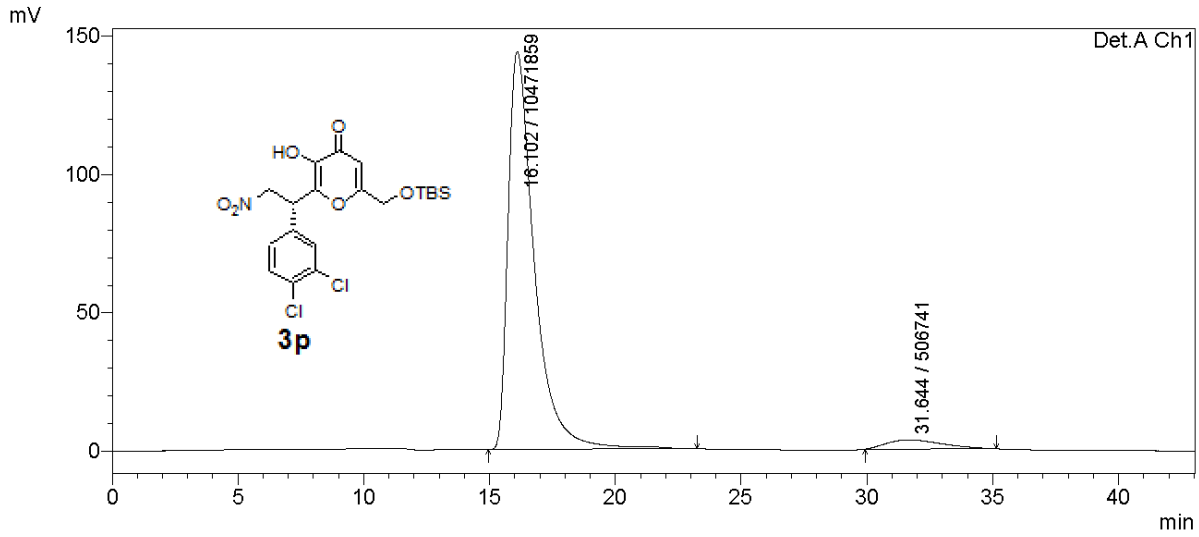


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.202	4491214	45853	50.890	70.195
2	32.631	4334138	19469	49.110	29.805
Total		8825352	65321	100.000	100.000

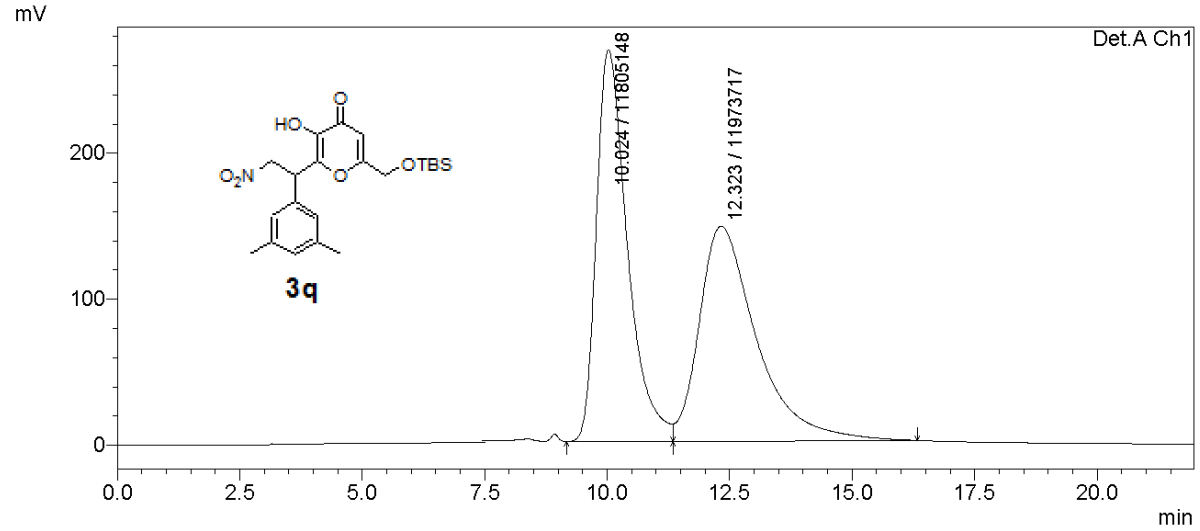


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

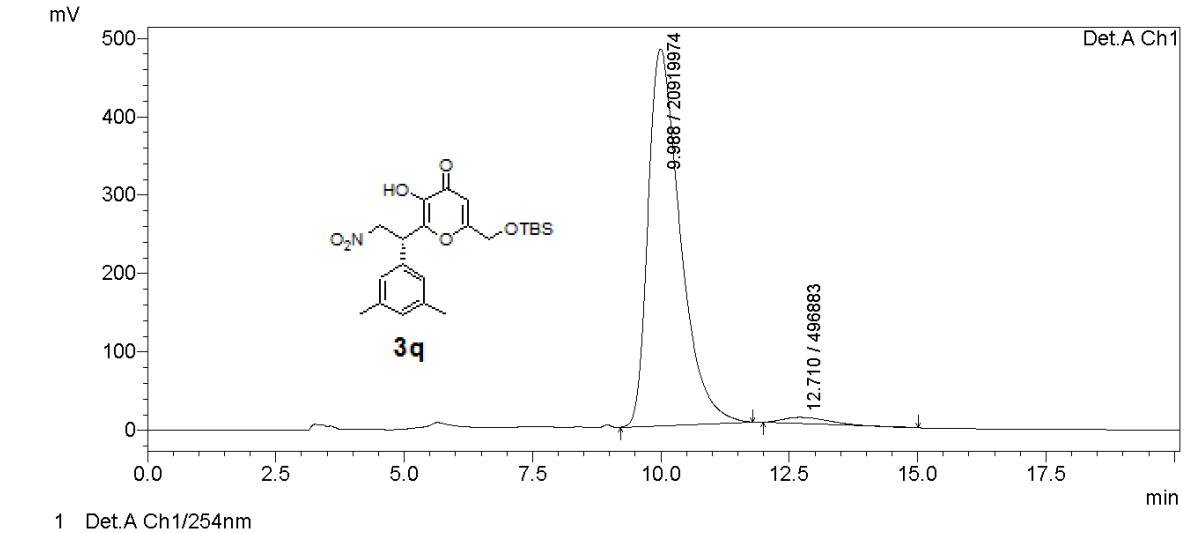
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.102	10471859	143935	95.384	97.767
2	31.644	506741	3287	4.616	2.233
Total		10978599	147222	100.000	100.000



PeakTable

Detector A Ch1 254nm

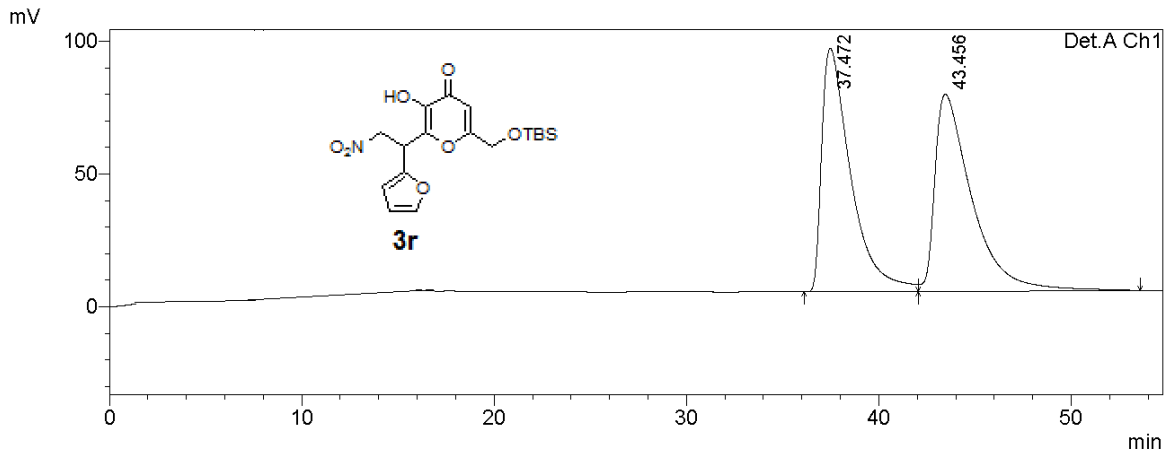
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.024	11805148	268282	49.646	64.574
2	12.323	11973717	147180	50.354	35.426
Total		23778865	415462	100.000	100.000



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.988	20919974	480382	97.680	98.385
2	12.710	496883	7888	2.320	1.615
Total		21416857	488270	100.000	100.000

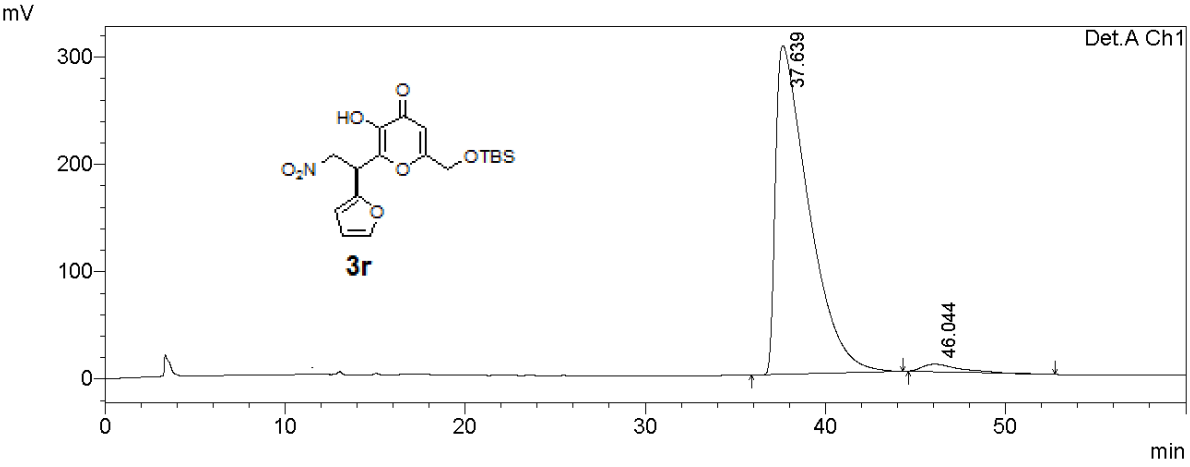


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	37.472	9635043	91676	49.296	55.254
2	43.456	9910257	74242	50.704	44.746
Total		19545300	165919	100.000	100.000

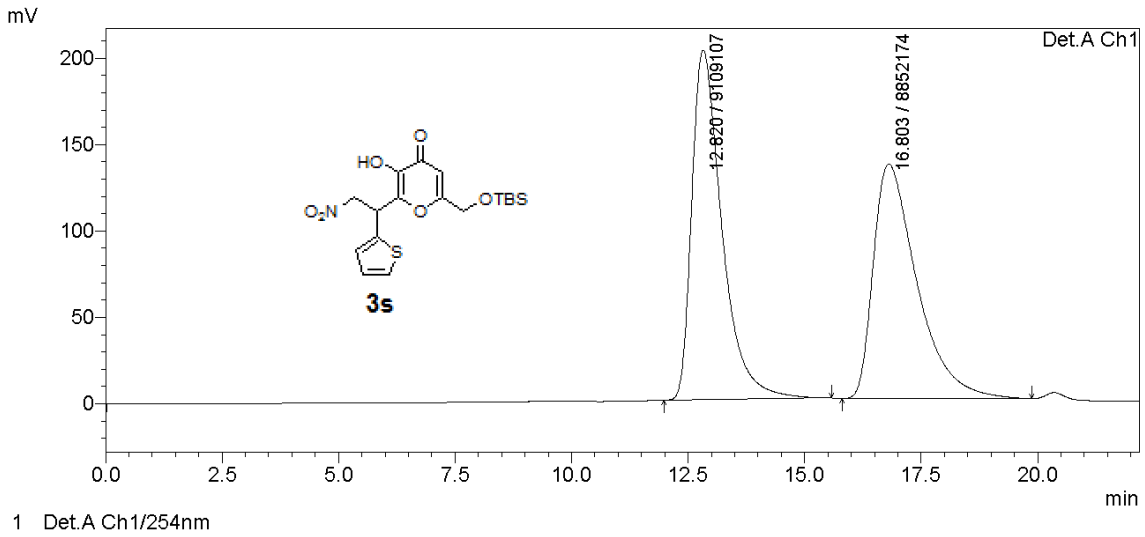


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

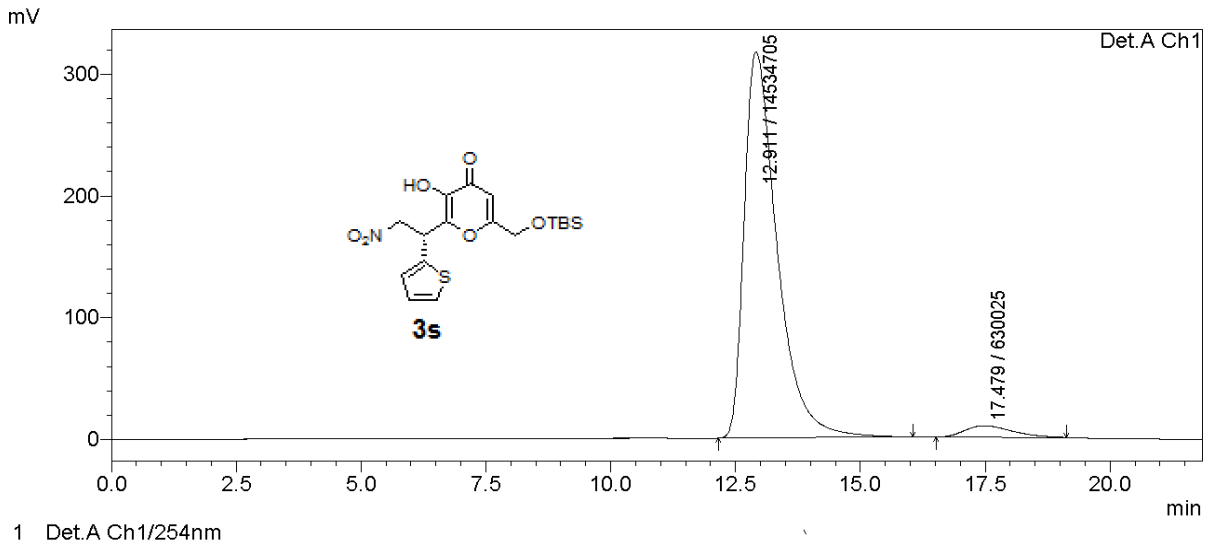
Peak#	Ret. Time	Area	Height	Area %	Height %
1	37.639	39138285	306313	97.440	97.748
2	46.044	1028451	7057	2.560	2.252
Total		40166736	313370	100.000	100.000



PeakTable

Detector A Ch1 254nm

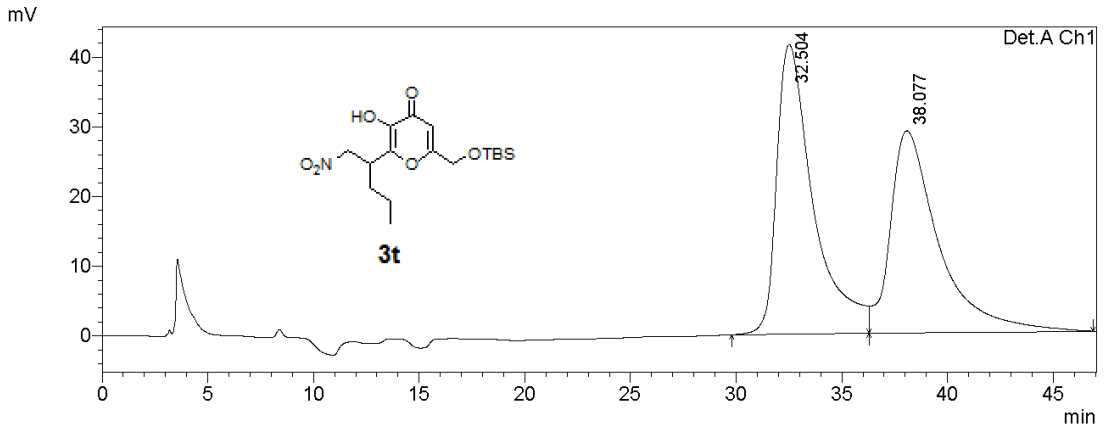
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.820	9109107	202352	50.715	59.845
2	16.803	8852174	135773	49.285	40.155
Total		17961281	338124	100.000	100.000



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.911	14534705	317312	95.845	97.087
2	17.479	630025	9520	4.155	2.913
Total		15164730	326831	100.000	100.000

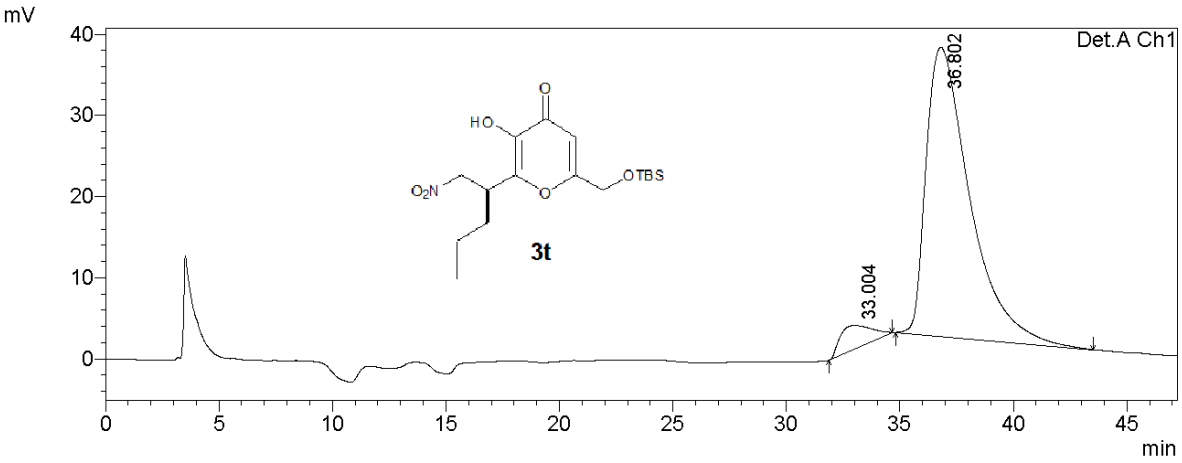


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.504	5012038	41584	52.046	58.877
2	38.077	4618052	29045	47.954	41.123
Total		9630090	70630	100.000	100.000

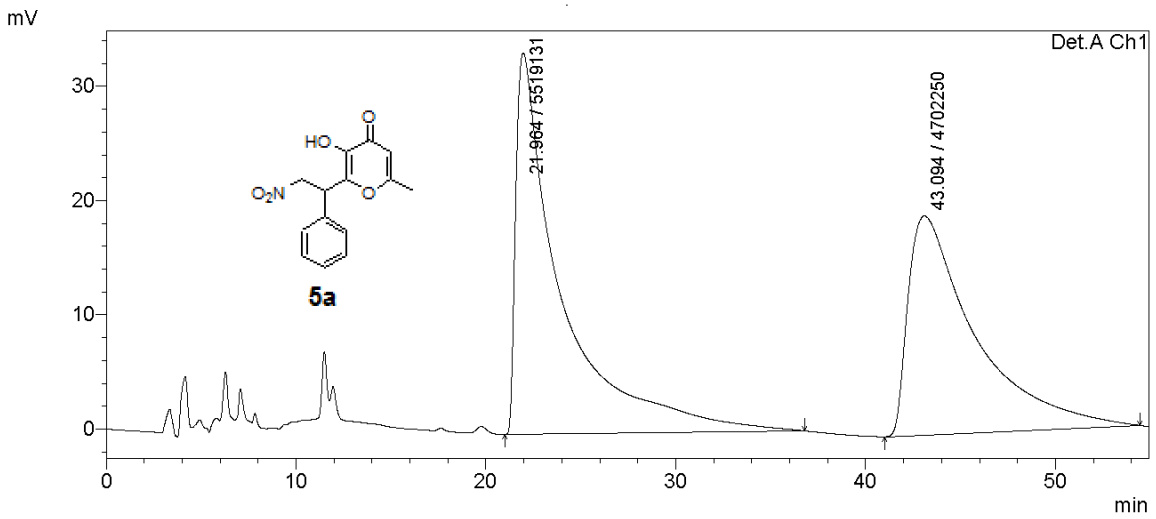


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

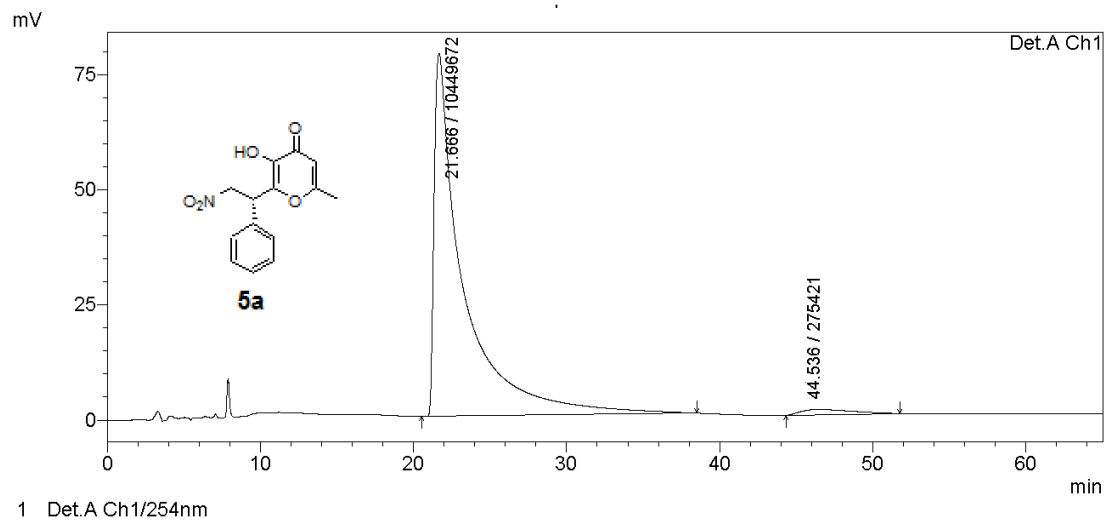
Peak#	Ret. Time	Area	Height	Area %	Height %
1	33.004	281195	2901	5.581	7.532
2	36.802	4757648	35613	94.419	92.468
Total		5038843	38514	100.000	100.000



PeakTable

Detector A Ch1 254nm

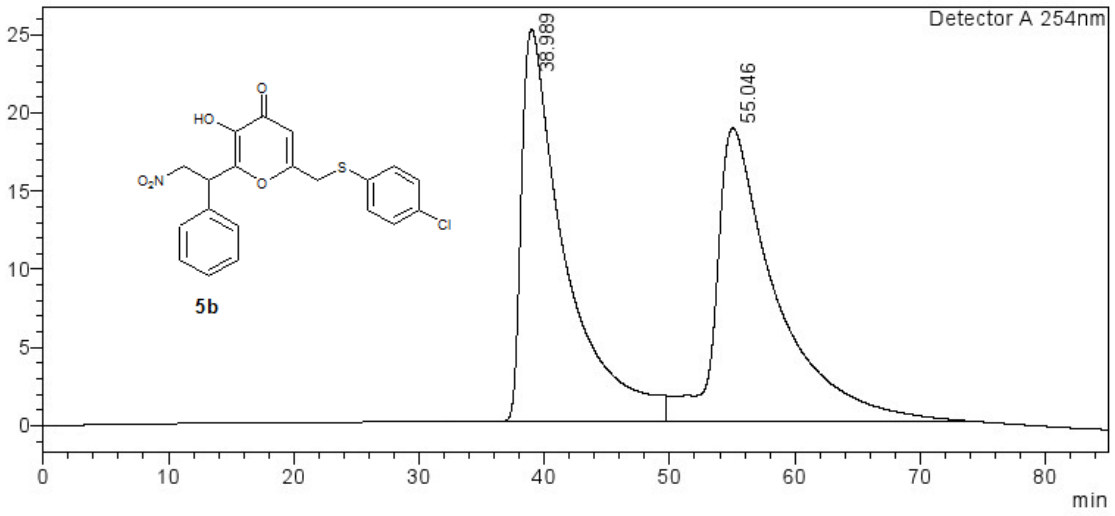
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.964	5519131	33412	53.996	63.539
2	43.094	4702250	19174	46.004	36.461
Total		10221382	52586	100.000	100.000



PeakTable

Detector A Ch1 254nm

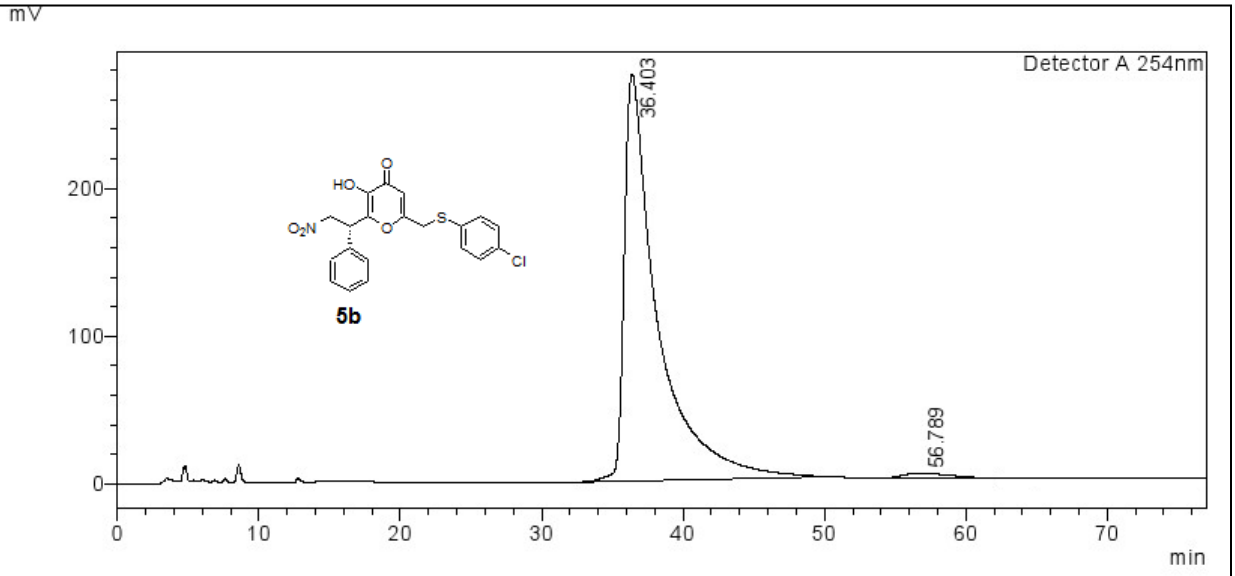
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.666	10449672	78898	97.432	98.552
2	44.536	275421	1159	2.568	1.448
Total		10725093	80058	100.000	100.000



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	38.989	6022358	25088	49.093
2	55.046	6244813	18761	50.907
Total		12267170	43848	



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	36.403	44619211	275034	98.478
2	56.789	689721	2894	1.522
Total		45308932	277928	

10. References.

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(5) X. Jiang, Y. Zhang, L. Wu, G. Zhang, X. Liu, H. Zhang, D. Fu, R. Wanga, *Adv. Synth. Catal.* 2009, **351**, 2096.

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