Supporting Information for

Quinine-Catalyzed Highly Enantioselective Cycloannulation of *o*-Quinone Methides with Malononitrile

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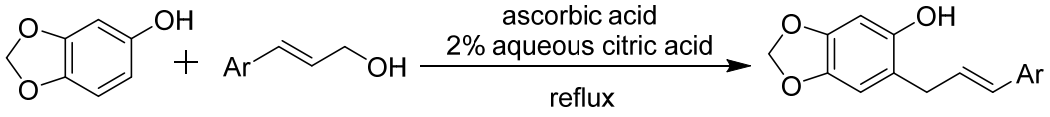
Table of Contents

I. General data: NMR spectra were recorded on a Brucker-400 MHz spectrometer. ESIMS spectra were recorded on BioTOF Q. Infrared spectra were recorded on a Nicolet MX-1E FT-IR spectrometer. Optical rotations were determined at 589 nm (sodium D line) by using a Perkin-Elmer-343 polarimeter. HPLC analysis was performed on Waters-Breeze (2487 Dual λ Absorbance Detector and 1525 Binary HPLC Pump, UV detection monitored at 254 nm) and Angilent 1200 (2487 Dual λ Absorbance Detector and 1525 Binary HPLC Pump, UV detection monitored at 254 nm). All chiral columns were purchased from Daicel Chemical Industries, LTD. Toluene, diethyl etherand tetrahydrofuran were dried over Na and distilled prior to use. Dichloromethane and dichloroethane were dried over CaH_2 and distilled prior to use.

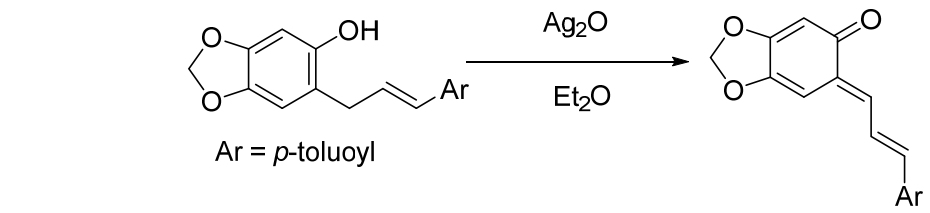
II.Materials: Analytical grade solvents for the column chromatography were used as received. All starting materials were purchased from Aldrich, Alfa and Acros and used directly. Toluene and THF were dried over Na and distilled prior to use.

III. General Procedures and Characterization Data

Procedure for vinyl *ortho*-quinone methide



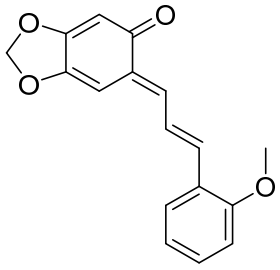
According to Jurd`s method[1]:A suspension of sesamol (2.68g, 20.0 mmol) and alcohol(1eq. 20 mmol) in 2% aqueous citric acid (100 ml) containing ascorbic acid(1.0 g, 5.6 mmol) was heated under reflux for over 15 hrs. On cooling, the oily product crystallized. After a crude recrystallization from benzene, yellowish solid directly used in the next step.



Modified Jurd synthesis of ortho-quinone methide.[2] A solution of (*E*)-6-(3-(*p*-tolyl) allyl) benzo [*d*][1,3]dioxol-5-ol (1.0 g, 3.73 mmol) in ether (50 mL) was added silver oxide (1.5 g, 6.47 mmol) then stirred overnight. The solution was filtered, then concentrated to 20 mL, cooled the recrystaled with DCM from Et_2O and orange-red crystals were collected (0.35g, 1.31 mmol), yield = 35%. The product is acid and heat sensitive.

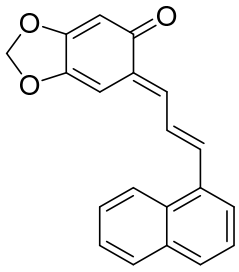
Characterization of the ortho-quinone methides

(*E*)-6-((*E*)-3-(2-methoxyphenyl)allylidene)benzo[*d*][1,3]dioxol-5(6*H*)-one (1c)



(Red solid):^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.35 (ddd, *J* = 7.9, 1.4, 0.4 Hz, 1H), 7.24 – 7.10 (m, 1H), 6.83 (dd, *J* = 11.7, 4.1 Hz, 2H), 6.42 (s, 1H), 6.35 – 6.19 (m, 2H), 6.11 (dd, *J* = 3.6, 1.7 Hz, 1H), 5.78 (ddd, *J* = 4.7, 1.2, 0.5 Hz, 2H), 5.61 (d, *J* = 3.7 Hz, 1H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, CD2Cl2) δ 155.36, 148.10, 147.06, 140.94, 128.47, 128.04, 126.83, 122.73, 121.59, 119.69, 113.67, 109.96, 105.00, 100.43, 97.70, 70.61, 54.71. ESI HRMS exact mass calcd for $(C17H14O4)^+$ requires m/z 282.0892, found m/z 282.0889. IR: 1623, 1573, 1516, 1425, 1367, 1309, 945, 838, 747, 656. Mp = 139 - 140℃.

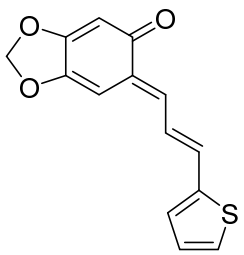
(*E*)-6-((*E*)-3-(naphthalen-1-yl)allylidene)benzo[*d*][1,3]dioxol-5(6*H*)-one(1i)



(Red solid)$^{-1}$H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.3 Hz, 1H), 7.99 (d, *J* = 14.9 Hz, 1H), 7.87 (t, *J* = 6.7 Hz, 3H), 7.75 (d, *J* = 12.2 Hz, 1H), 7.55 (ddd, *J* = 20.5, 14.7, 7.3 Hz, 3H), 7.38 (dd, *J* = 14.9, 12.3 Hz, 1H), 6.65 (s, 1H), 5.98 (s, 1H), 5.93 (d, *J* = 6.7 Hz, 2H). ^{13}C NMR (101 MHz, CDCl3) δ 148.95, 147.89, 141.94, 135.13, 134.17, 131.04, 129.16, 128.81, 126.32, 125.78, 125.75, 125.23, 125.04,

124.11, 122.20, 114.80, 105.95, 101.47, 101.04, 99.00, 74.73. ESI HRMS exact mass calcd for $(C_{20}H_{14}O_3N_2Na)^+$ requires m/z 325.0835, found m/z 352.0829. IR: 1607, 1524, 1425, 1218, 1207, 946, 846, 804, 755. Mp = 133 - 135℃.

(*E*)-6-((*E*)-3-(thiophen-2-yl)allylidene)benzo[*d*][1,3]dioxol-5(6*H*)-one(1h)



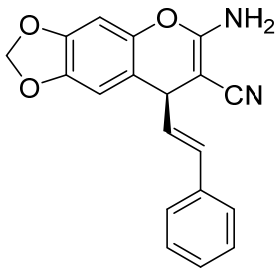
(Red solid) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 12.3 Hz, 1H), 7.36 (d, *J* = 5.0 Hz, 1H), 7.29 – 7.19 (m, 2H), 7.09 – 6.98 (m, 2H), 6.57 (s, 1H), 5.94 (s, 1H), 5.90 (s, 2H). ^{13}C NMR (101 MHz, CDCl3) δ 148.04, 147.88, 143.49, 142.03, 126.71, 126.26, 126.19, 124.80, 121.23, 114.58, 105.87, 101.07, 99.25, 71.59, 65.86, 15.29. ESI HRMS exact mass calcd for $(C_{14}H_{10}O_3S)^+$ requires m/z 258.0351, m/z, found m/z 258.0349. IR: 1615, 1532, 1416, 1376, 1227, 946, 830, 780, 702. Mp = 104 - 106℃.

Procedure for cycloannulation of ortho-quinone methides and malononitrile

A mixture of ortho-quinone methide (0.1 mmol) and **3** (0.01 mmol) was solved in toluene (1.0 mL) at corresponding temperature. After stirring at this temperature for ten minutes, malononitrile (7.9 mg, 0.12 mmol) dissolved in 1.0 mL of toluene was added dropwise to the mixture in 5 minutes. After 12 - 24hours, the solution was directly subjected to a column chromatography on silica gel (ethyl acetate/petroleum ether = 1:3) to afford the product **4**.

Characterization of the cycloannulation products

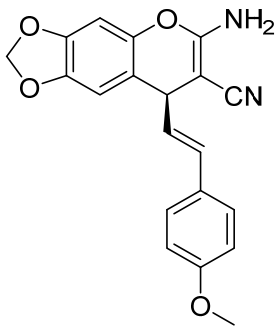
(*S*,*E*)-6-amino-8-styryl-8*H*-[1,3]dioxolo[4,5-*g*]chromene-7-carbonitrile (4a)



(White solid. Yield: 99%) ^{1}H NMR (400 MHz, acetone-d^6) δ 7.49 – 7.42 (m, 2H), 7.36 – 7.27 (m, 2H), 7.26 – 7.18 (m, 1H), 6.71 (s, 1H), 6.64 – 6.51 (m, 2H), 6.24 – 6.17 (m, 1H), 6.11 (s, 2H), 6.00 (dd, *J* = 6.5, 0.9 Hz, 2H), 4.22 (d, *J* = 8.5 Hz, 1H).

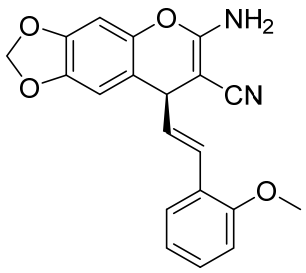
^{13}C NMR (101 MHz, acetone-d^6) δ 161.27, 161.24, 148.37, 145.59, 144.13, 137.80, 133.29, 130.64, 129.41, 128.36, 127.39, 120.30, 115.06, 108.35, 102.78, 98.69, 56.82, 40.15. ESI HRMS exact mass calcd for $(C_{19}H_{14}O_3N_2Na)^+$ requires m/z 341.0896, found m/z 341.0891. IR: 3350, 2920，2846, 2201, 1673, 1606, 1482, 1408, 1243, 1160, 1027, 739, 697. $[\alpha]_D^{20}$ = 94.4 (c 0.566, CH_2Cl_2). Enantiomeric excess was determined by HPLC (Chiracel-OD-H, hexane /isopropanol = 80/20, flow rate 1.0 mL/min, T = 30 ºC, 254 nm): t_R = 12.39min (major), t_R = 11.327min, 92% ee. Mp = 175 - 177℃.

(*S*,*E*)-6-amino-8-(4-methoxystyryl)-8*H*-[1,3]dioxolo[4,5-*g*]chromene-7-carbonitrile (4b)



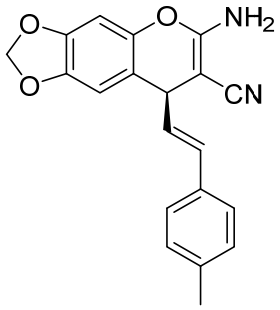
(White solid. Yield: 98%) ^{1}H NMR (400 MHz, acetone-d^6) δ 7.41 – 7.36 (m, 2H), 6.90 – 6.85 (m, 2H), 6.69 (t, *J* = 2.2 Hz, 1H), 6.53 (t, *J* = 7.8 Hz, 2H), 6.07 (s, 2H), 6.02 (dd, *J* = 12.9, 4.4 Hz, 1H), 5.99 (dd, *J* = 6.5, 1.0 Hz, 2H), 4.17 (d, *J* = 8.5 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (101 MHz, acetone-d^6) δ 161.16, 161.14, 160.35, 148.29, 145.55, 144.11, 131.07, 130.39, 130.19, 128.59, 120.35, 115.34, 114.82, 108.36, 102.75, 98.64, 57.15, 55.57, 40.19 ESI HRMS exact mass calcd for $(C_{20}H_{17}O_4N_2)^+$ requires m/z 349.1182, found m/z 349.1180. IR: 3350, 2920, 2854, 2185 , 1664, 1590, 1507, 1474, 1400, 1251, 1143, 1036, 821, 739. $[\alpha]_D^{20}$ = -135.4 (c 0.70, CH_2Cl_2). Enantiomeric excess was determined by HPLC (Chiracel-OD-H, hexane /isopropanol = 80/20, flow rate 1.0 mL/min, T = 30 ºC, 254 nm): t_R = 13.20min (major), t_R =16.18min, 92% ee; Mp = 176 - 177℃.

(*S*,*E*)-6-amino-8-(2-methoxystyryl)-8*H*-[1,3]dioxolo[4,5-*g*]chromene-7-carbonitrile (4c)



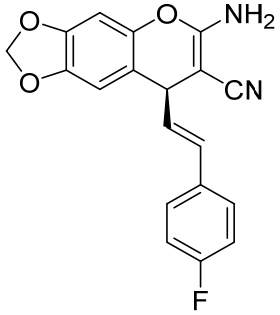
(White solid. Yield: 97%) ^{1}H NMR (400 MHz, acetone-d^{6}) δ 7.48 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.22 (ddd, *J* = 8.4, 7.4, 1.7 Hz, 1H), 6.97 (dd, *J* = 8.3, 0.8 Hz, 1H), 6.91 – 6.85 (m, 2H), 6.70 (d, *J* = 0.4 Hz, 1H), 6.55 (s, 1H), 6.19 (dd, *J* = 15.8, 8.6 Hz, 1H), 6.09 (s, 2H), 6.00 (dd, *J* = 6.1, 1.0 Hz, 2H), 4.21 (d, *J* = 8.6 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, acetone-d^{6}) δ 161.15, 157.87, 148.31, 145.55, 144.11, 133.60, 129.56, 127.64, 126.35, 125.42, 121.38, 120.34, 115.28, 112.01, 108.40, 102.76, 98.65, 57.13, 55.87, 40.65. ESI HRMS exact mass calcd for $(C_{20}H_{17}O_4N_2)^+$ requires m/z 349.1183, found m/z. 349.1178. IR:3433, 2920, 2185, 1648, 1606, 1482, 1400, 1234, 1152, 1036, 937, 763. $[\alpha]_D^{20}$ = -88.2 (c 0.552, CH_2Cl_2). Enantiomeric excess was determined by HPLC (Chiracel-OD-H, hexane /isopropanol = 80/20, flow rate 1.0 mL/min, T = 30 ºC, 254 nm): t_R = 17.58min (major), t_R =12.75min, 91% ee; Mp = 174 - 175℃.

(*S*,*E*)-6-amino-8-(4-methylstyryl)-8*H*-[1,3]dioxolo[4,5-*g*]chromene-7-carbonitrile (4d)



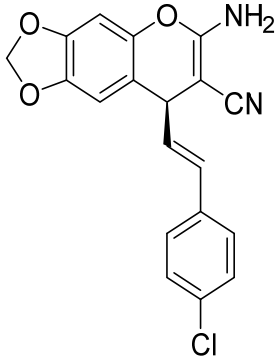
(White solid. Yield: 98%)^{1}H NMR (400 MHz, acetone-d^{6}) δ 7.33 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.75 – 6.66 (m, 1H), 6.55 (dd, *J* = 12.6, 3.0 Hz, 2H), 6.13 (dd, *J* = 15.6, 8.5 Hz, 1H), 6.03 – 5.94 (m, 2H), 4.19 (d, *J* = 8.5 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, acetone-d^{6}) δ 161.20, 148.32, 145.57, 144.10, 138.04, 135.01, 132.28, 130.55, 130.04, 127.33, 127.19, 120.36, 115.19, 108.35, 102.77, 98.68, 56.93, 40.14, 21.18. ESI HRMS exact mass calcd for （$C_{20}H_{17}O_3N_2$）$^+$requires m/z 333.1234, found m/z 333.1228. IR: 3450, 2920, 2139, 1673, 1599, 1482, 1400, 1243, 1160, 1027, 813. $[\alpha]_D^{20}$ = -101.93 (c 0.654, CH_2Cl_2). Enantiomeric excess was determined by HPLC (Chiracel-OD-H, hexane /isopropanol = 80/20, flow rate 1.0 mL/min, T = 30 ºC, 254 nm): t_R = 9.60min (major), t_R =11.225min, 90% ee; Mp = 177 - 188℃.

(*S*,*E*)-6-amino-8-(4-fluorostyryl)-8*H*-[1,3]dioxolo[4,5-*g*]chromene-7-carbonitrile (4e)



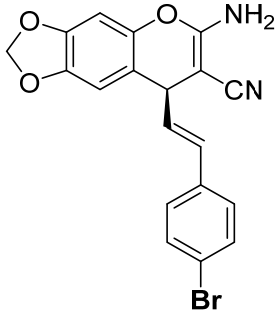
(White solid. Yield: 98%) ^{1}H NMR (400 MHz, acetone-d^6) δ 7.56 – 7.45 (m, 2H), 7.14 – 7.02 (m, 2H), 6.70 (t, *J* = 2.2 Hz, 1H), 6.64 – 6.52 (m, 2H), 6.15 (dd, *J* = 15.6, 8.5 Hz, 1H), 6.00 (dd, *J* = 6.2, 1.0 Hz, 2H), 4.21 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (101 MHz, acetone-d^6) δ163.12, 161.22, 148.38, 145.59, 144.11, 134.27, 133.26, 129.41, 129.23, 129.15, 120.27, 116.13, 108.34, 102.79, 98.68, 56.74, 40.10. ESI HRMS exact mass calcd for $(C_{19}H_{13}O_3N_2FNa)^+$ requires m/z 359.0802, found m/z 359.0798. IR: 3491, 2920, 2854, 2185, 1655, 1490, 1399, 1243, 1152, 1027, 953, 821. $[\alpha]_D^{20}$ = -54.1 (c 0.618, CH_2Cl. Enantiomeric excess was determined by HPLC (Chiracel-OD-H, hexane /isopropanol = 80/20, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 10.51min (major), t_R = 12.05min, 92% ee; Mp = 182 - 183℃.

(*S*,*E*)-6-amino-8-(4-chlorostyryl)-8*H*-[1,3]dioxolo[4,5-*g*]chromene-7-carbonitrile (4f)



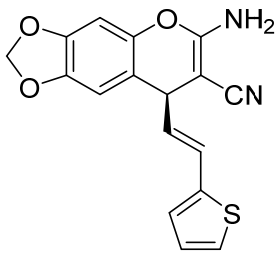
(White solid. Yield: 97%) ^{1}H NMR (400 MHz, acetone-d^6) δ 7.48 (d, *J* = 8.5 Hz, 2H), 7.34 (dd, *J* = 6.3, 4.5 Hz, 2H), 6.70 (s, 1H), 6.63 – 6.53 (m, 2H), 6.23 (dd, *J* = 15.6, 8.5 Hz, 1H), 6.13 (s, 1H), 6.00 (d, *J* = 5.6 Hz, 2H), 4.22 (d, *J* = 8.4 Hz, 1H).^{13}C NMR (101 MHz, acetone-d^6) 161.28, 148.41, 145.61, 144.13, 136.70, 134.27, 133.44, 129.46, 129.29, 128.95, 120.26, 114.83, 108.33, 102.80, 98.71, 56.54, 40.10. ESI HRMS exact mass calcd for $(C_{19}H_{14}O_3N_2NClNa)^+$ requires m/z 375.0507, found m/z 375.0501. IR: 3449, 2904, 2185, 1673, 1599, 1482, 1399, 1243, 1152, 1036, 929, 871, 830. $[\alpha]_D^{20}$ = -127.8 (c 0.77, CH_2Cl_2). Enantiomeric excess was determined by HPLC (Chiracel-OD-H, hexane /isopropanol = 80/20, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 11.47min (major), t_R = 14.06min, 93% ee; Mp = 184 - 186℃.

(*S*,*E*)-6-amino-8-(4-bromostyryl)-8*H*-[1,3]dioxolo[4,5-*g*]chromene-7-carbonitrile (4g)



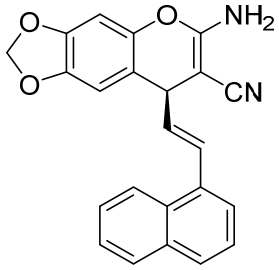
(White solid. Yield: 97%) ^{1}H NMR (400 MHz, acetone-d^{6}) δ 7.49 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 6.76 – 6.68 (m, 1H), 6.63 – 6.50 (m, 2H), 6.25 (dd, *J* = 15.6, 8.4 Hz, 1H), 6.16 (d, *J* = 16.3 Hz, 2H), 6.02 – 5.97 (m, 2H), 4.22 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (101 MHz, acetone-d^{6}) δ 161.32, 148.42, 145.61, 144.16, 137.11, 134.39, 132.45, 129.33, 129.27, 121.56, 120.25, 114.80, 108.32, 102.80, 98.70, 56.55, 40.14. ESI HRMS exact mass calcd for $(C_{19}H_{14}O_3N_2NBr)^+$ requires m/z 397.0182, found m/z 397.0176. IR: 3457, 2920, 2846, 2193, 1673, 1599, 1482, 1399, 1234, 1152, 1027, 937, 821. $[\alpha]_D^{20}$ = -122.3 (c 0.74, CH_2Cl_2). Enantiomeric excess was determined by HPLC (Chiracel-OD-H, hexane /isopropanol = 80/20, flow rate 1.0 mL/min, T = 30 ºC, 254 nm): t_R = 12.28min (major), t_R = 14.97min, 91% ee; Mp = 192 - 193℃.

(*R*,*E*)-6-amino-8-(2-(thiophen-2-yl)vinyl)-8*H*-[1,3]dioxolo[4,5-*g*]chromene-7-carbonitrile (4h)



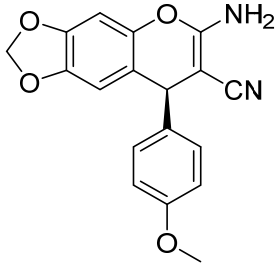
(White solid. Yield: 97%) ^{1}H NMR (400 MHz, DMSO-d^{6}) δ 7.39 (d, J = 5.1 Hz, 1H), 7.11 (d, *J* = 3.4 Hz, 1H), 7.01 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.90 (s, 2H), 6.74 (s, 1H), 6.72 – 6.61 (m, 2H), 6.02 (dd, J = 11.7, 0.9 Hz, 2H), 5.90 (dd, *J* = 15.4, 8.2 Hz, 1H), 4.16 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d^{6}) δ 160.49, 146.96, 144.07, 142.72, 141.13, 132.17, 127.70, 126.22, 124.82, 122.32, 120.53, 113.79, 107.28, 101.66, 97.85, 53.22, 38.28. ESI HRMS exact mass calcd for $(C_{17}H_{12}N_2O_3S)^+$ requires m/z324.0596, found m/z 324.0570. IR: 3457, 2920, 2193, 1673, 1599, 1483, 1408, 1243, 1143, 1027, 937, 706. $[\alpha]_D^{20}$ = 77.0 (c 0.574, CH_2Cl_2). Enantiomeric excess was determined by HPLC (Chiracel-OD-H, hexane /isopropanol = 80/20, flow rate 1.0 mL/min, T = 30 ºC, 254 nm): t_R = 12.10 min (major), t_R = 14.35 min, 88% ee; Mp = 160 - 163℃.

(*S*,*E*)-6-amino-8-(2-(naphthalen-1-yl)vinyl)-8*H*-[1,3]dioxolo[4,5-*g*]chromene-7-carbonitrile (4i)



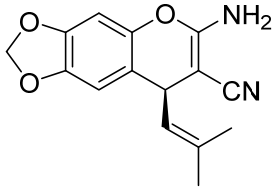
(White solid. Yield: 95%) ^{1}H NMR (400 MHz, acetone-d^{6}) δ 8.29 (d, *J* = 8.4 Hz, 1H), 7.91 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.60 – 7.50 (m, 2H), 7.45 (dd, *J* = 19.1, 11.5 Hz, 2H), 6.85 (d, *J* = 0.4 Hz, 1H), 6.58 (s, 1H), 6.24 – 6.18 (m, 1H), 6.16 (s, 2H), 6.01 (dd, *J* = 7.6, 1.0 Hz, 2H), 4.41 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (101 MHz, acetone-d^{6}) δ 161.29, 148.41, 145.65, 144.18, 136.45, 135.38, 134.73, 132.20, 129.35, 128.73, 127.89, 126.98, 126.69, 126.53, 124.72, 120.37, 115.03, 108.43, 102.80, 98.73, 56.86, 40.36. ESI HRMS exact mass calcd for $(C_{23}H_{17}O_3N_2)^+$ requires m/z 369.1234, found m/z 369.1229. IR: 3317, 2920, 2854, 2185, 1648, 1599, 1474, 1408, 1160, 1028, 937, 763. $[\alpha]_D^{20}$ = -70.1 (c 0.64, CH_2Cl_2). Enantiomeric excess was determined by HPLC (Chiracel-OD-H, hexane /isopropanol = 80/20, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 26.925 min (major), t_R = 20.04 min, 90% ee; Mp = 194 - 195℃.

(*S*)-6-amino-8-(4-methoxyphenyl)-8*H*-[1,3]dioxolo[4,5-*g*]chromene-7-carbonitrile (4j)



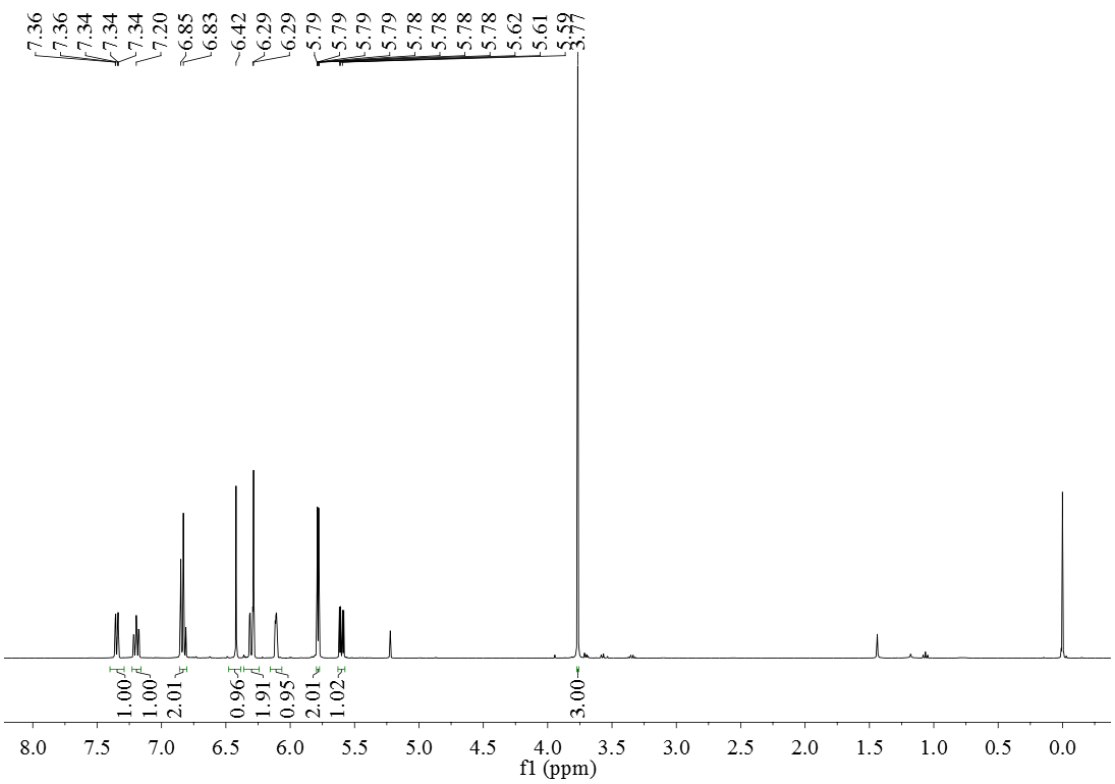
(White-yellow solid. Yield: 98%) ^{1}H NMR (400 MHz, acetone-d^{6}) δ 7.19 – 7.14 (m, 2H), 6.90 – 6.85 (m, 2H), 6.57 (s, 1H), 6.46 (d, *J* = 0.4 Hz, 1H), 6.05 (s, 1H), 5.96 (dd, *J* = 14.9, 1.0 Hz, 2H), 4.61 (s, 1H), 3.76 (s, 3H) . ^{13}C NMR (101 MHz, acetone-d^{6}) δ 160.89, 159.75, 148.08, 145.53, 144.03, 138.92, 129.53, 120.26, 116.91, 114.87, 108.36, 102.72, 98.46, 59.45, 55.52, 41.55. ESI HRMS exact mass calcd for $(C_{18}H_{14}O_4N_2Na)^+$ requires m/z 345.08458, found m/z 345.08395. IR: 3342, 2929, 2185, 1664, 1598, 1524, 1474, 1408, 1243, 1152, 1027, 929, 739. $[\alpha]_D^{20}$ = -43.2 (c 0.66, CH_2Cl_2). Enantiomeric excess was determined by HPLC (Chiracel-OD-H, hexane /isopropanol = 80/20, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 11.55 min (major), t_R = 16.78 min, 90% ee; Mp = 186 - 188℃.

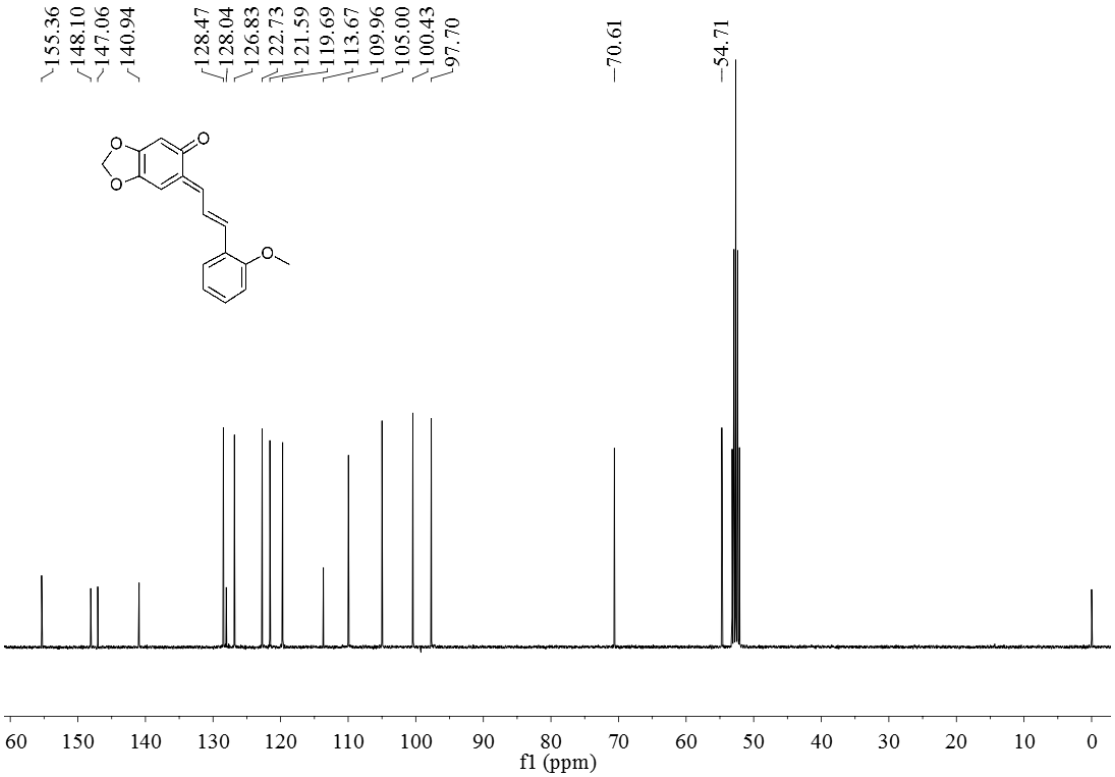
(*S*)-6-amino-8-(2-methylprop-1-en-1-yl)-8*H*-[1,3]dioxolo[4,5-*g*]chromene-7-carbo nitrile (4k)

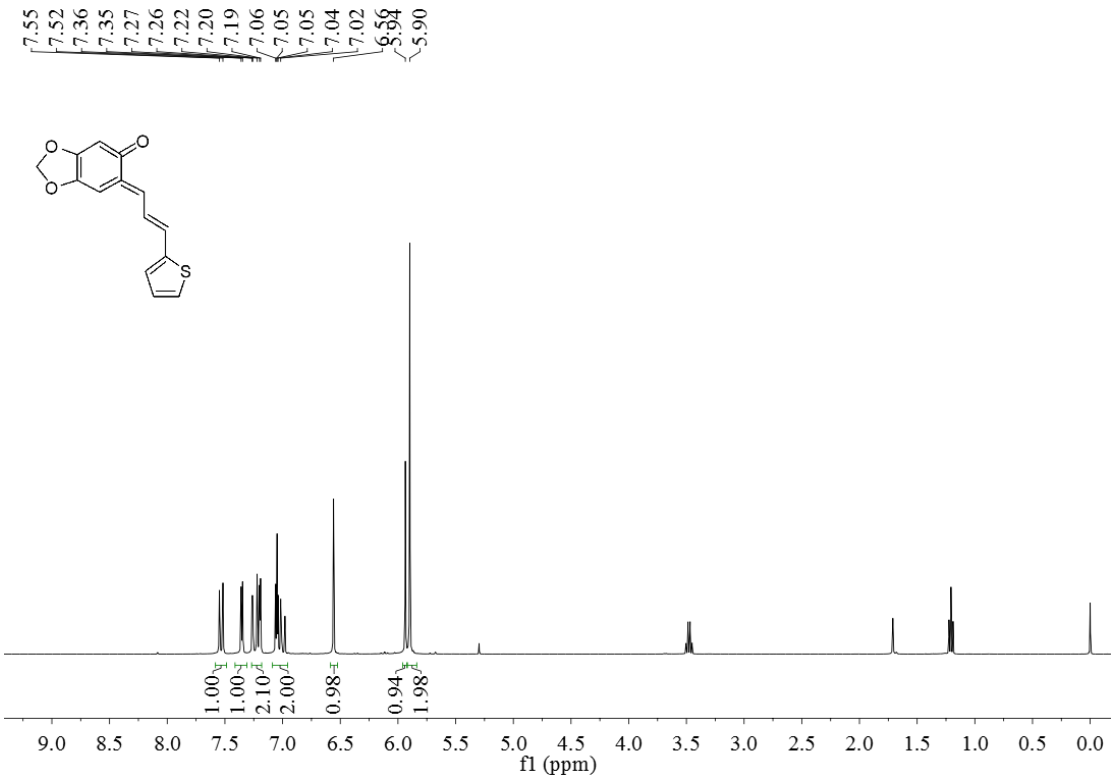


(Green-yellow oil. Yield: 98%) ^{1}H NMR (400 MHz, acetone-d^{6}) δ 6.49 (d, *J* = 2.9 Hz, 2H), 5.98 (dd, *J* = 3.4, 1.0 Hz, 2H), 5.08 – 5.03 (m, 1H), 4.35 (d, *J* = 9.9 Hz, 1H), 1.85 (d, *J* = 1.3 Hz, 3H), 1.75 (d, *J* = 1.3 Hz, 3H). ^{13}C NMR (101 MHz, acetone-d^{6}) δ 160.77, 148.02, 145.45, 144.05, 132.89, 129.10, 120.39, 116.24, 108.07, 102.66, 98.49, 57.75, 34.67, 25.82, 17.99. ESI HRMS exact mass calcd for $(C_{15}H_{14}O_3N_2Na)^+$ requires m/z 293.0897, found m/z 293.0891. IR: 3560, 2978, 2936, 2276, 1623, 1482, 1399, 1267, 1185, 978, 937, 887. $[\alpha]_D^{20}$ = -39.5 (c 0.538, CH_2Cl_2). Enantiomeric excess was determined by HPLC (Chiracel-OD-H, hexane /isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ºC, 254 nm): t_R = 12.79 min (major), t_R = 13.80 min, 91% ee.

IV. NMR Spectra



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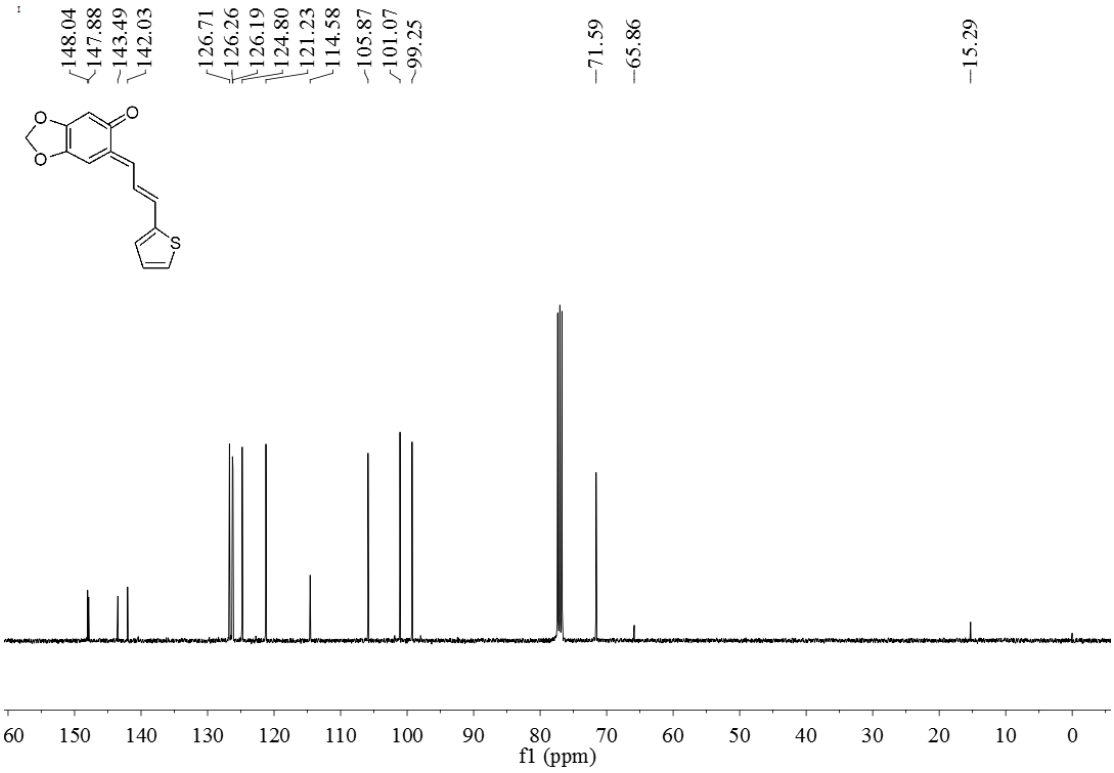
7.52
7.36
7.35
7.27
7.26
7.22
7.20
7.19
7.06
7.05
7.05
7.04
7.02
6.56
6.54
5.90
O
O
O
S
1.00
1.00
2.10
2.00
0.98
0.94
1.98
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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147.88
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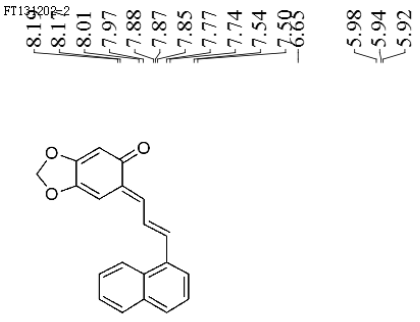
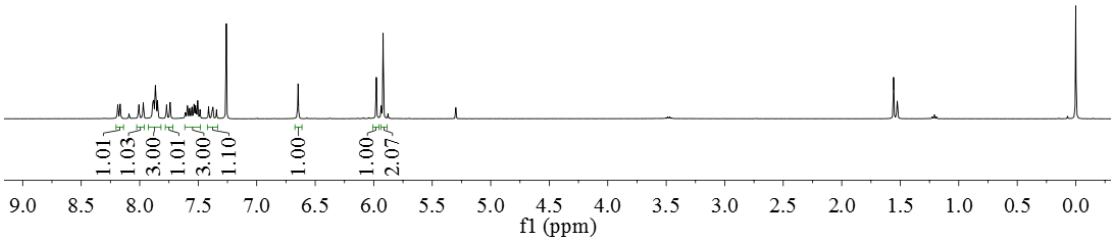
142.03
126.71
126.26
126.19
124.80
121.23
114.58
105.87
101.07
99.25
71.59
65.86
15.29
O
O
O
S
60 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.19
8.17
8.01
7.97
7.88
7.87
7.85
7.77
7.74
7.54
7.50
6.65
5.98
5.94
5.92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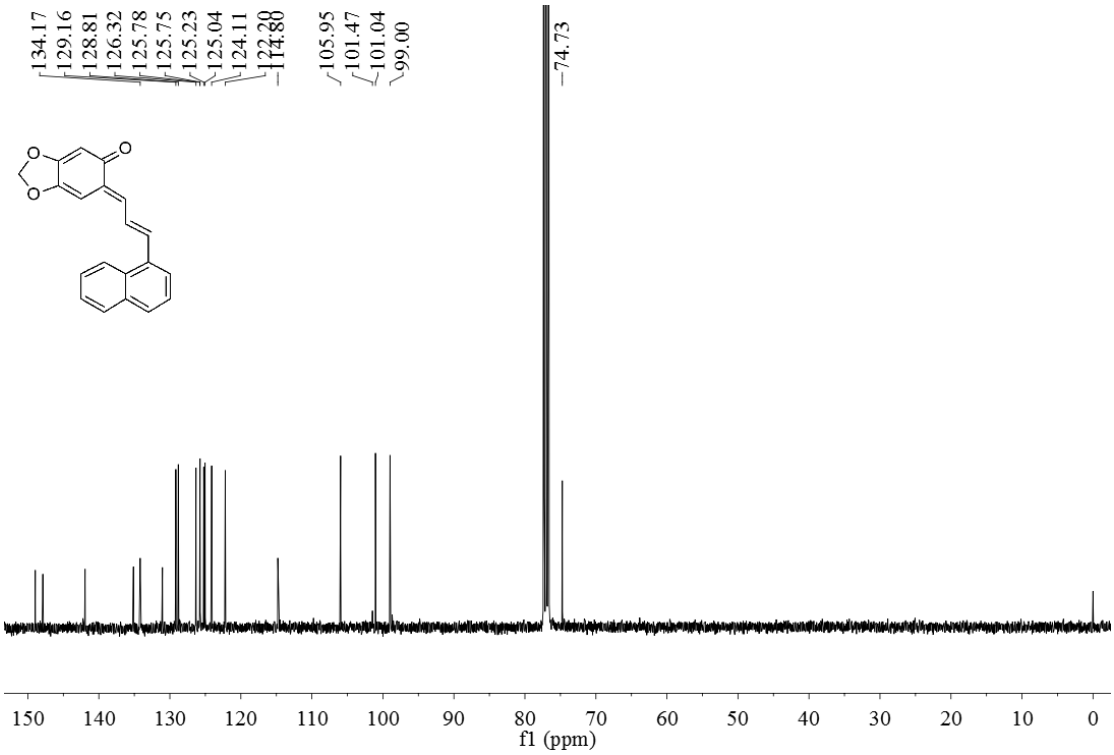
1.03
3.00
1.01
3.00
1.10
1.00
1.00
2.07
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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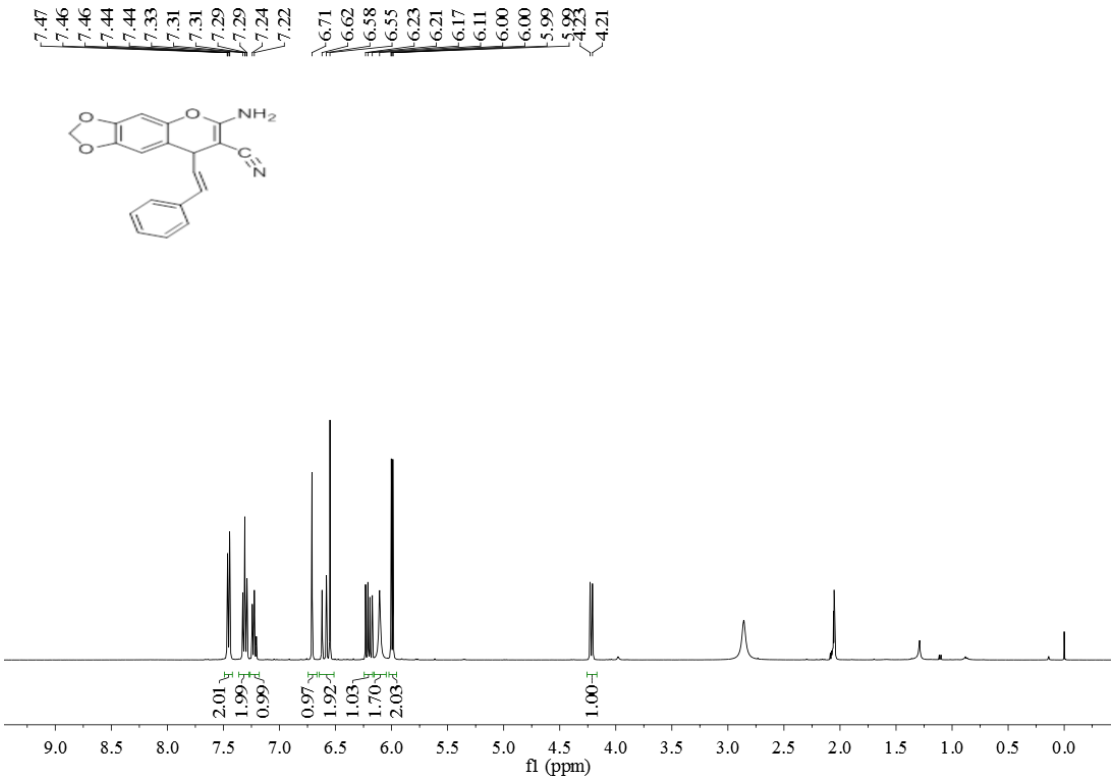
129.16
128.81
126.32
125.78
125.75
125.23
125.04
124.11
105.95
101.47
101.04
99.00
74.73
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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6.62
6.58
6.55
6.23
6.21
6.17
6.11
6.00
6.00
5.99
5.98
4.23
4.21
NH2
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O
O
N
2.01
1.99
0.99
0.97
1.92
1.03
1.70
2.03
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
3.0
2.5
2.0
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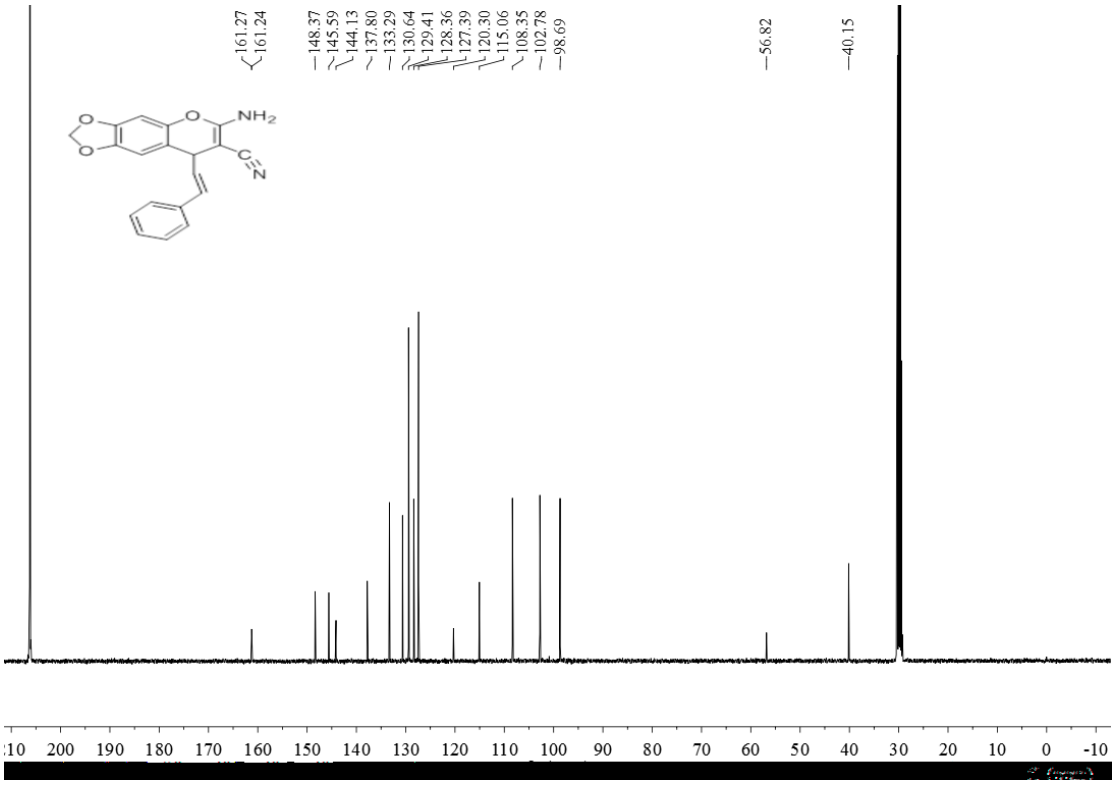
1.0
0.5
0.0
f1 (ppm)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130.64
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128.36
127.39
120.30
115.06
108.35
102.78
98.69
56.82
40.15
NH2
O
O
O
N
210
200
190
180
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140
130
120
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100
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60
50
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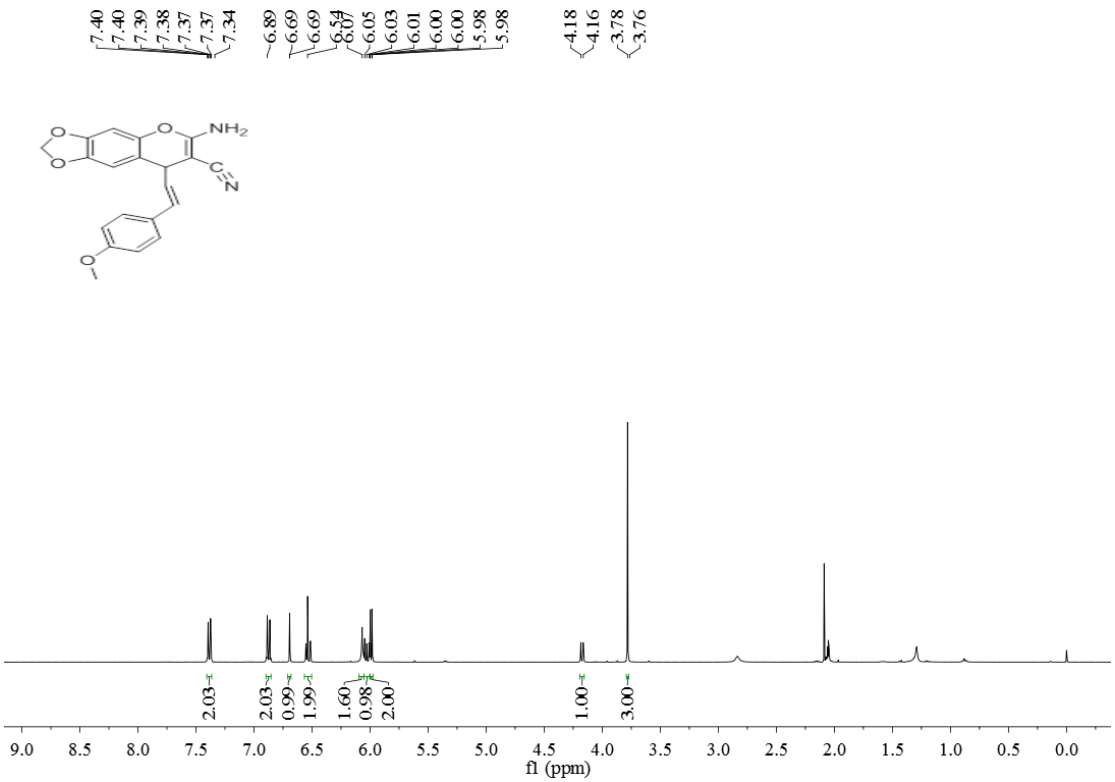
20
10
0
-10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6.00
5.98
5.98
4.18
4.16
3.78
3.76
NH2
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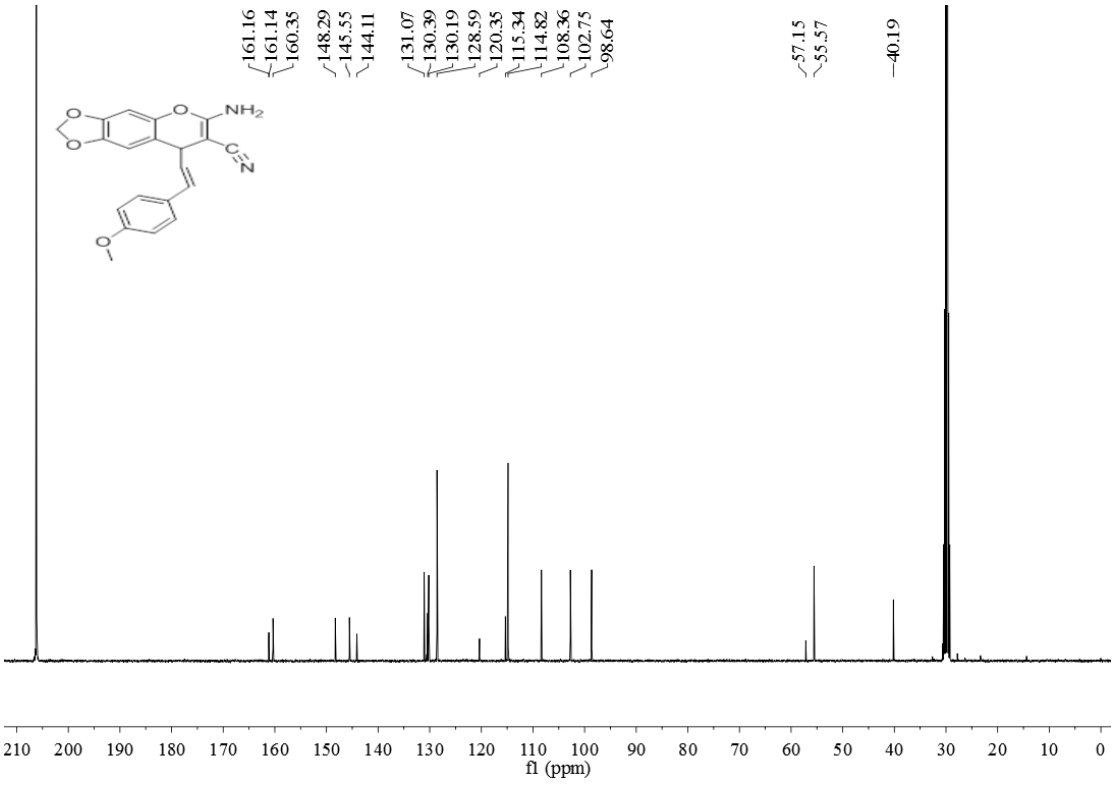
O
O
N
O
2.03
2.03
0.99
1.99
1.60
0.98
2.00
1.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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115.34
114.82
108.36
102.75
98.64
57.15
55.57
40.19
NH2
O
O
O
N
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.49
7.49
7.47
7.47
7.22
6.99
6.98
6.96
6.96
6.90
6.89
6.89
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6.70
6.70
6.55
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6.00
5.99
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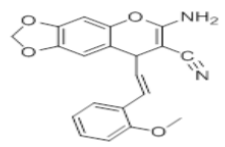
4.20
3.85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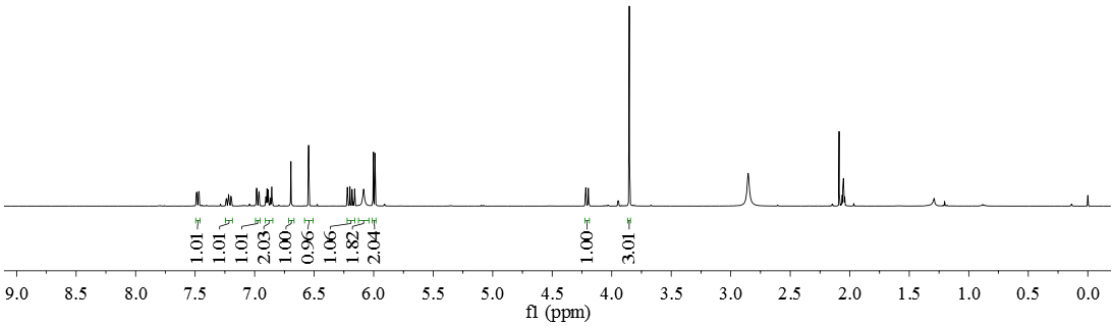
O
O
O
N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1.01
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1.00
0.96
1.06
1.82
2.04
1.00
3.01
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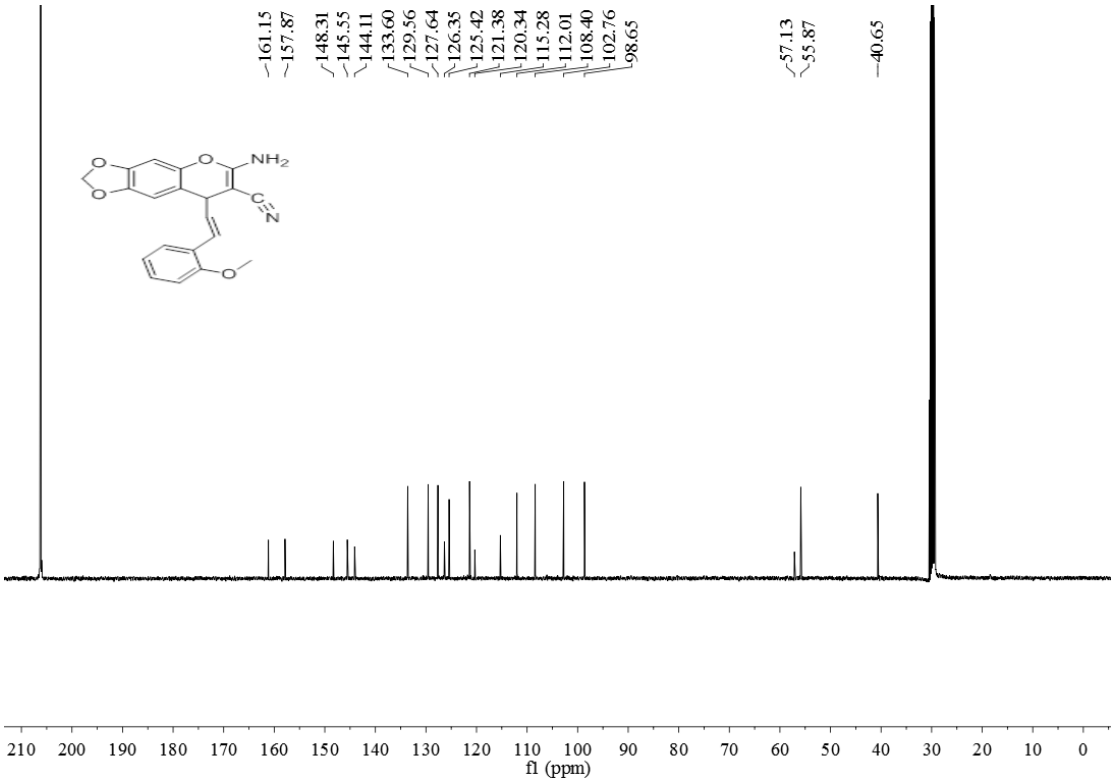
f1 (ppm)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121.38
120.34
115.28
112.01
108.40
102.76
98.65
57.13
55.87
40.65
NH2
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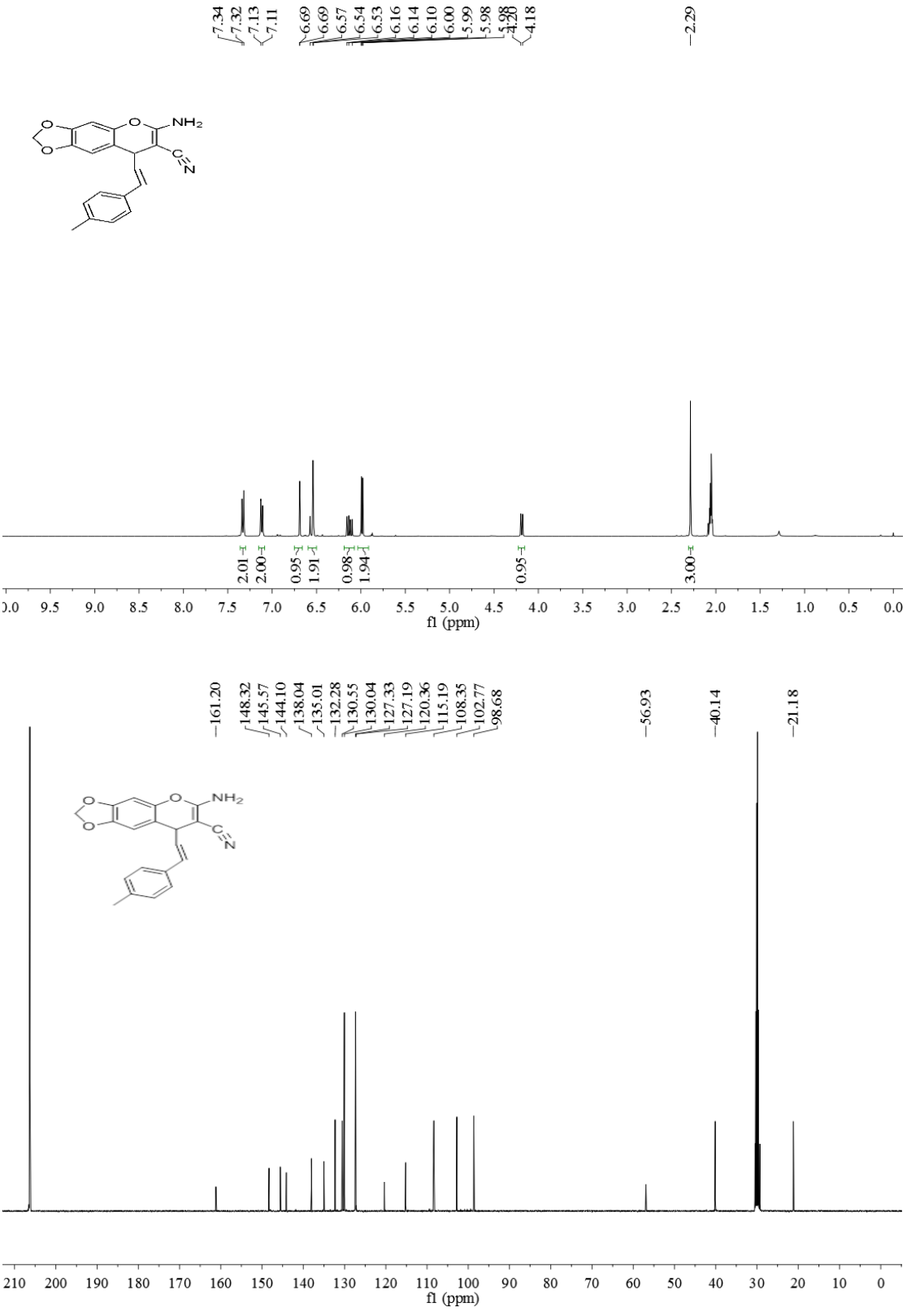
O
O
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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6.69
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6.16
6.14
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6.00
5.99
5.98
5.98
4.20
4.18
2.29
NH2
2.01
2.00
0.95
1.91
0.98
1.94
0.95
3.00
fl (ppm)
161.20
148.32
145.57
144.10
138.04
135.01
132.28
130.55
130.04
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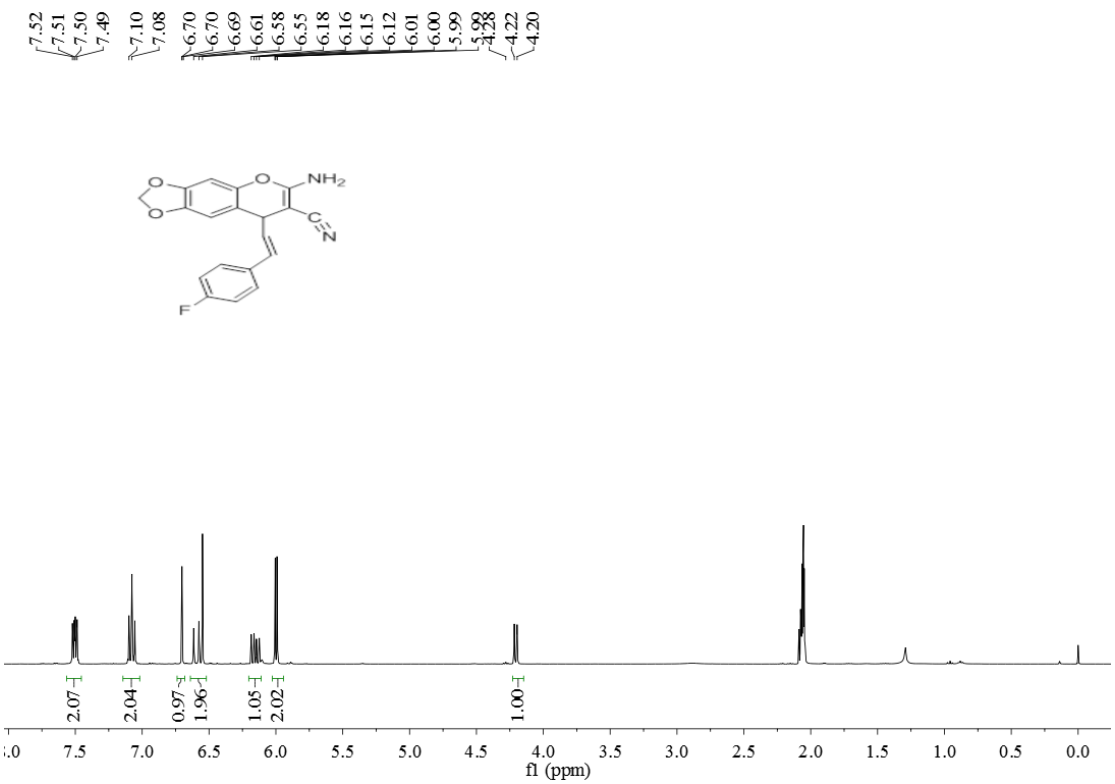
NH2
fl (ppm)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6.70
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6.15
6.12
6.01
6.00
5.99
5.98
4.28
4.22
4.20
NH2
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C
N
F
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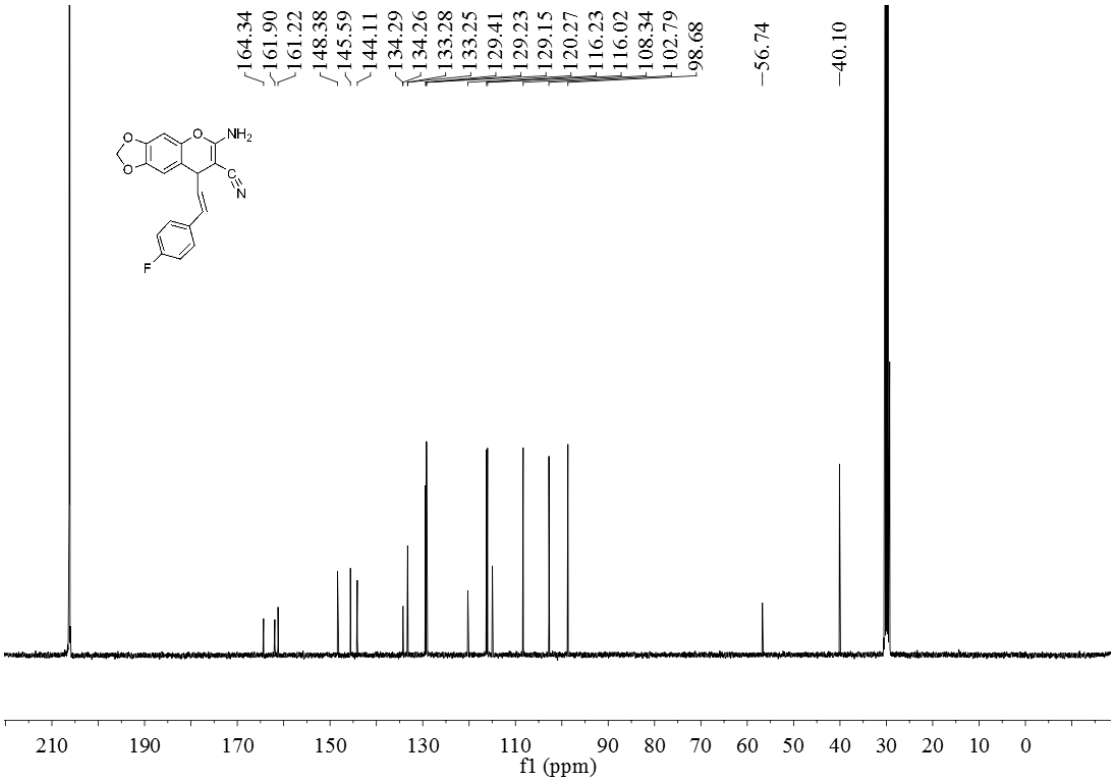
2.04
0.97
1.96
1.05
2.02
1.00
fl (ppm)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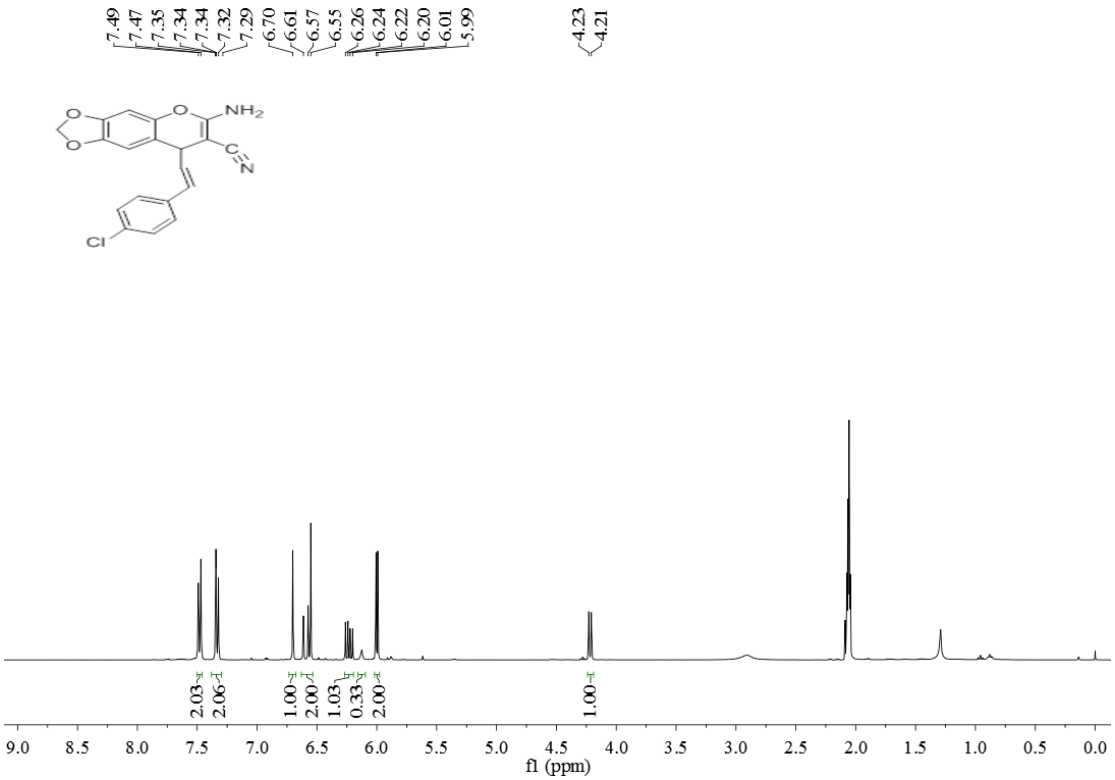
O
O
O
C
N
F
fl (ppm)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6.57
6.55
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6.24
6.22
6.20
6.01
5.99
4.23
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Cl
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2.06
1.00
2.00
1.03
0.33
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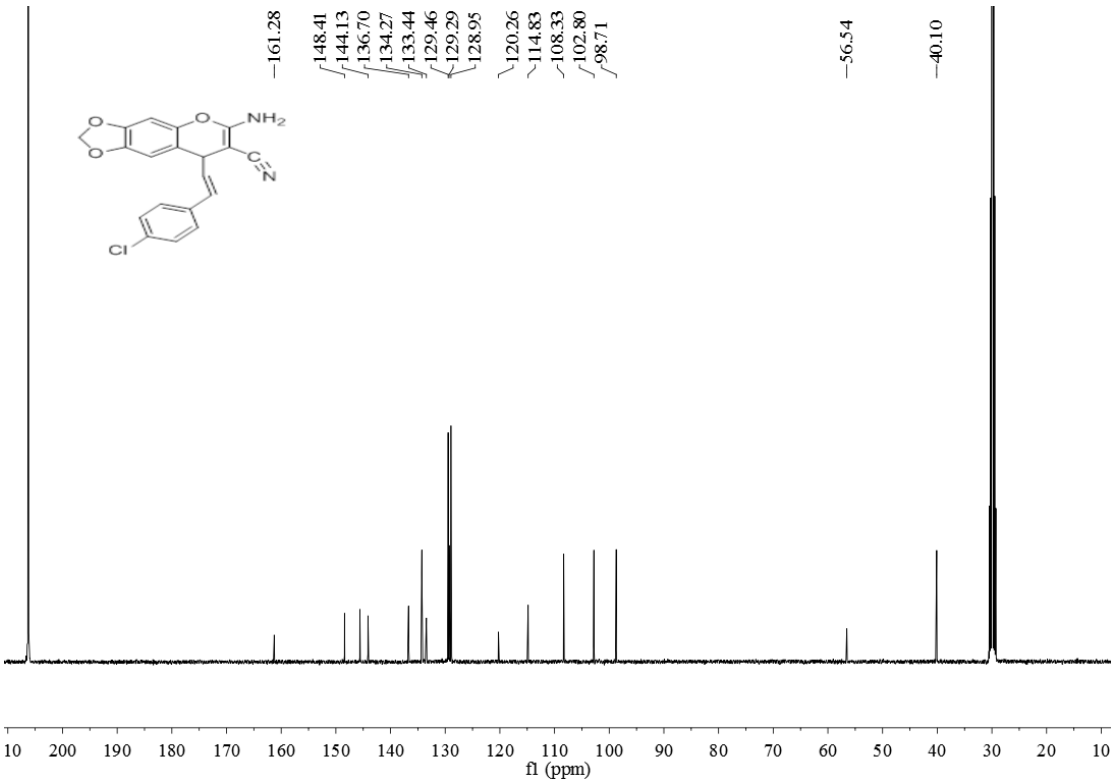
1.00
f1 (ppm)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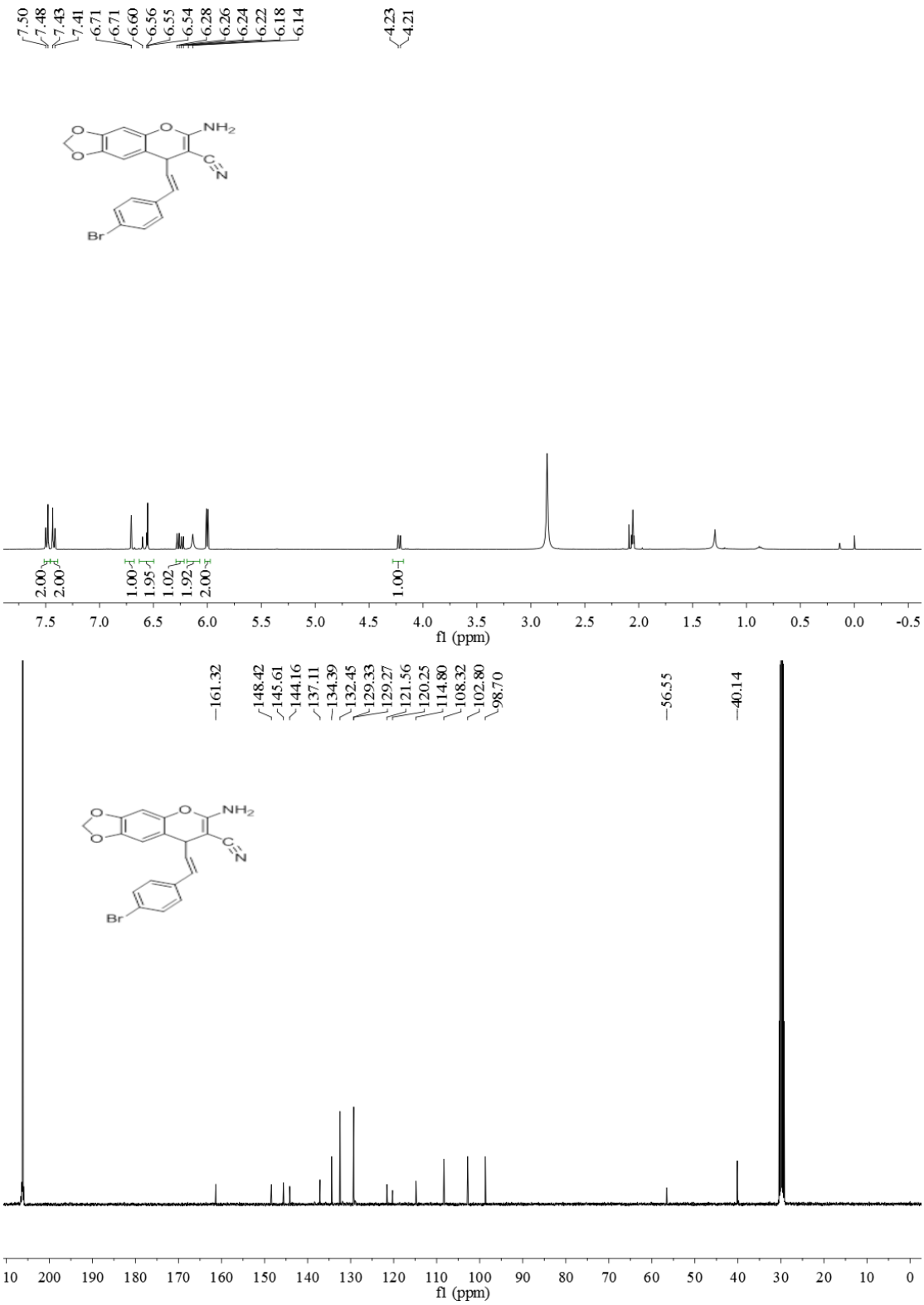
98.71
56.54
40.10
NH2
CN
Cl
f1 (ppm)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6.24
6.22
6.18
6.14
4.23
4.21
NH2
O
O
O
C
N
Br
2.00
2.00
1.00
1.95
1.02
1.92
2.00
1.00
fl (ppm)
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148.42
145.61
144.16
137.11
134.39
132.45
129.33
129.27
121.56
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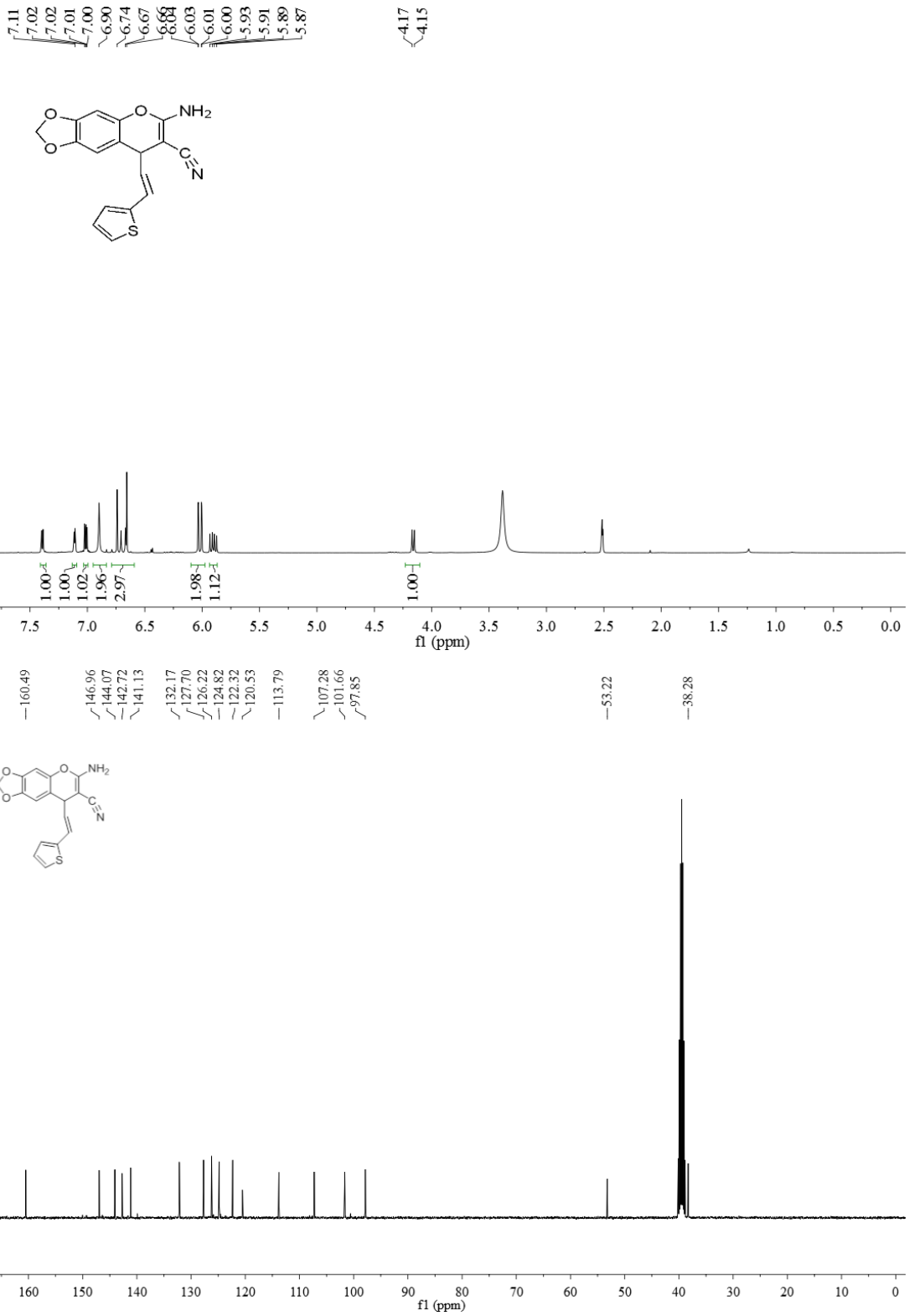
114.80
108.32
102.80
98.70
56.55
40.14
fl (ppm)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6.00
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5.91
5.89
5.87
4.17
4.15
NH2
O
O
O
C
N
S
1.00
1.00
1.02
1.96
2.97
1.98
1.12
1.00
7.5
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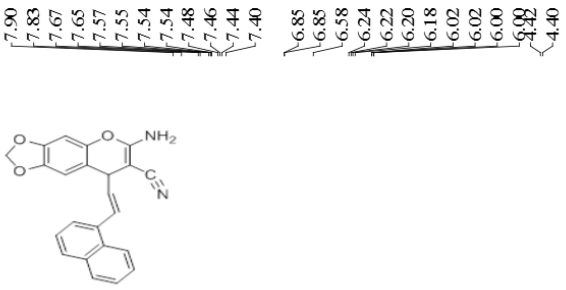
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
160.49
146.96
144.07
142.72
141.13
132.17
127.70
126.22
124.82
122.32
120.53
113.79
107.28
101.66
97.85
53.22
38.28
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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6.85
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6.22
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4.40
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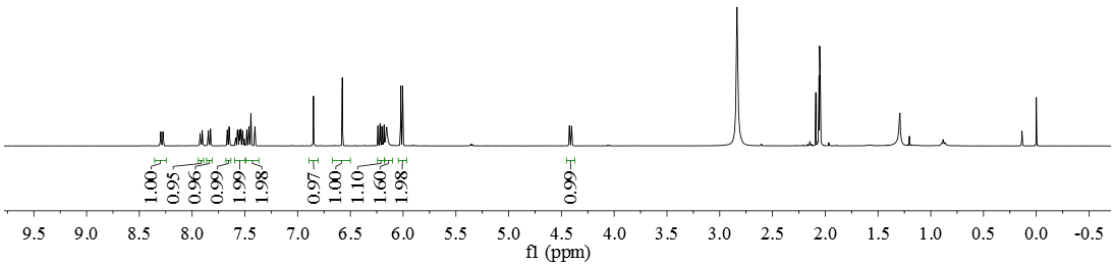
O
O
C
N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1.98
0.99
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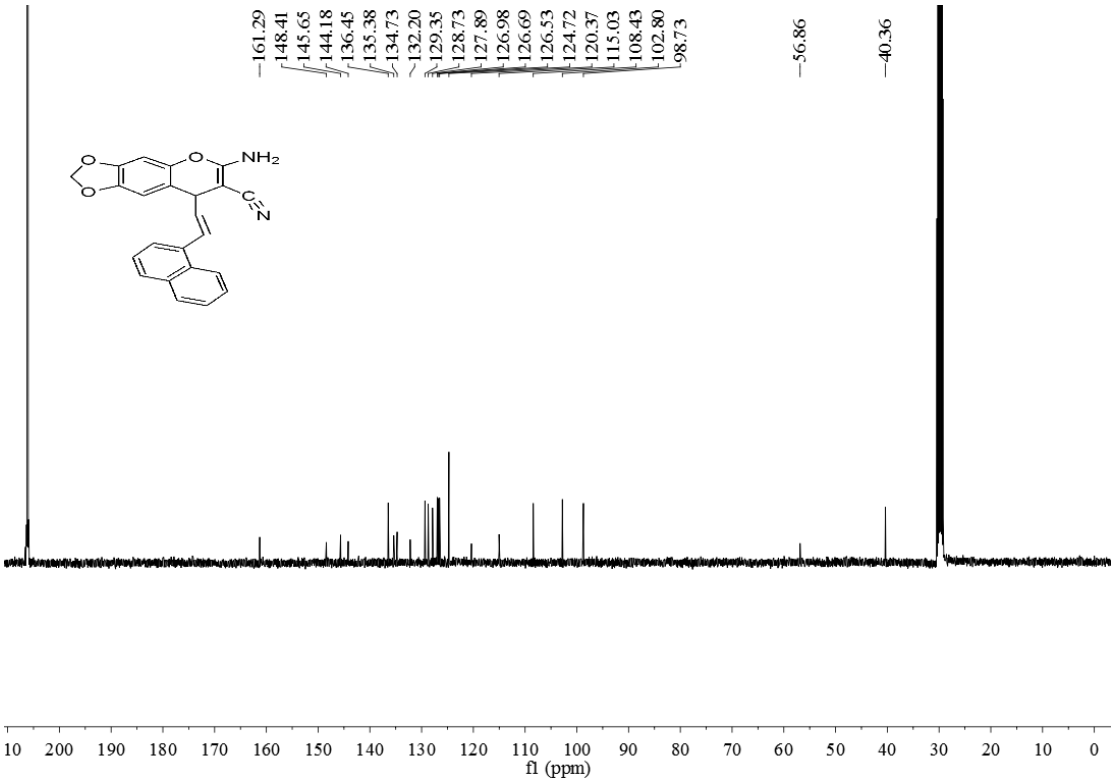
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124.72
120.37
115.03
108.43
102.80
98.73
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40.36
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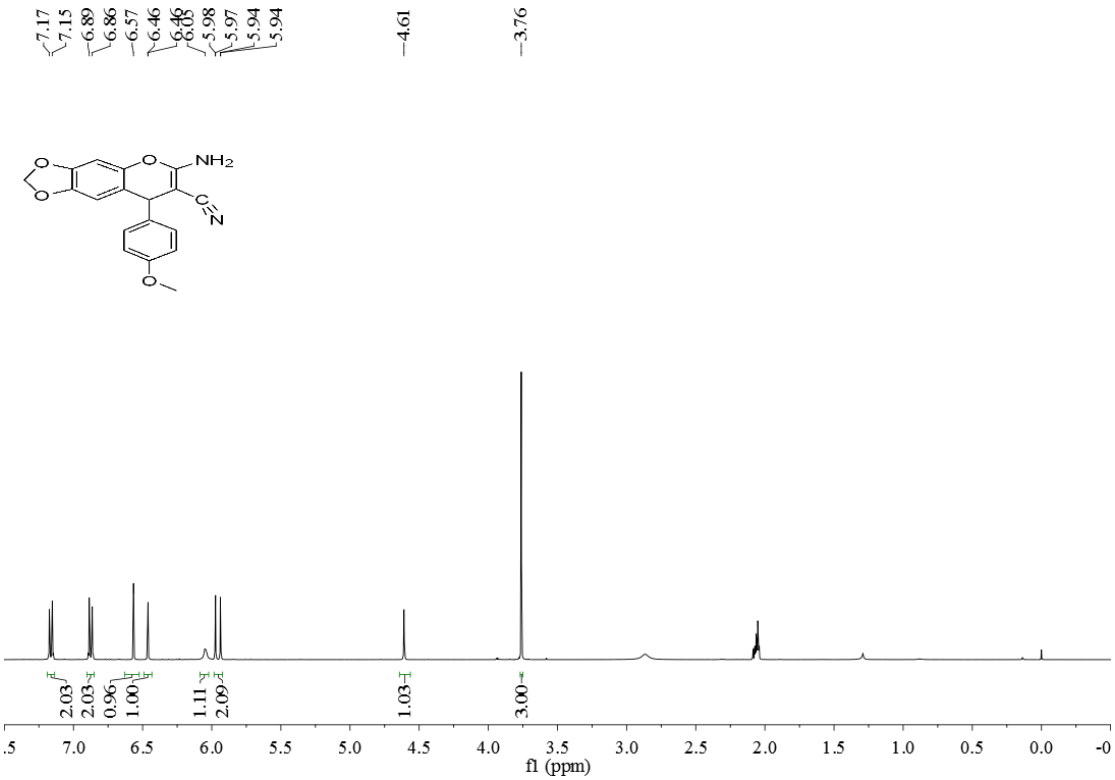
O
O
C
N
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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5.97
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3.76
NH2
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O
O
O
O
2.03
2.03
0.96
1.00
1.11
2.09
1.03
3.00
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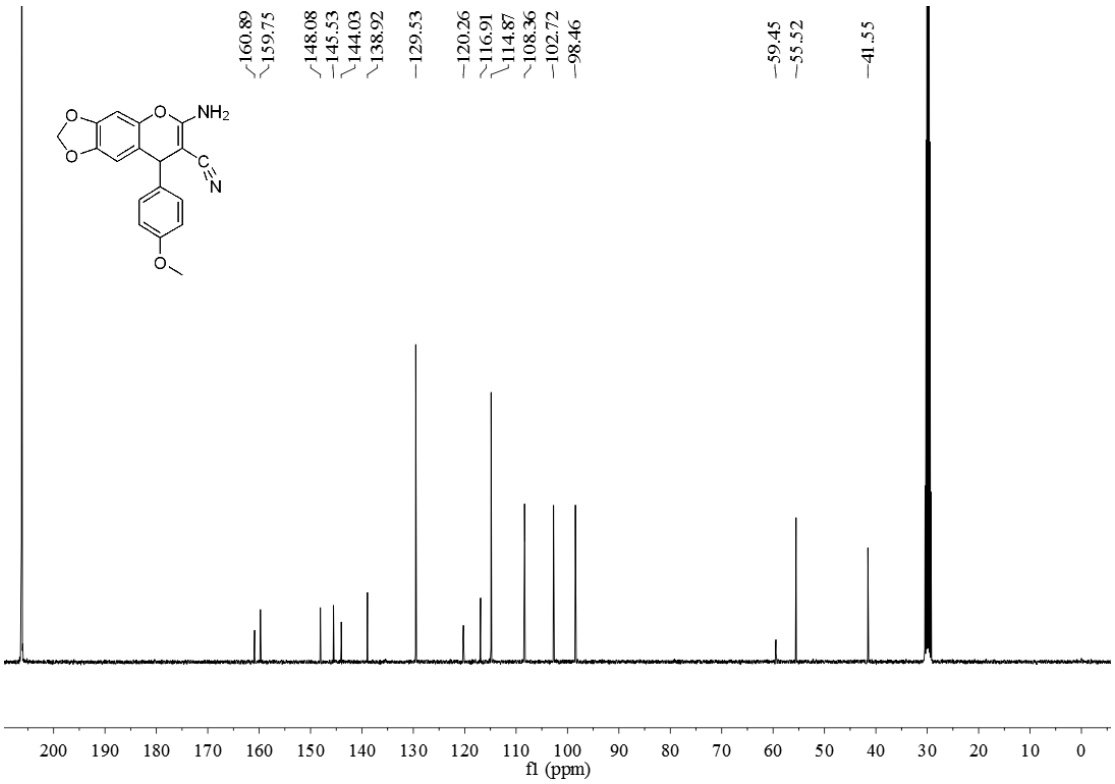
f1 (ppm)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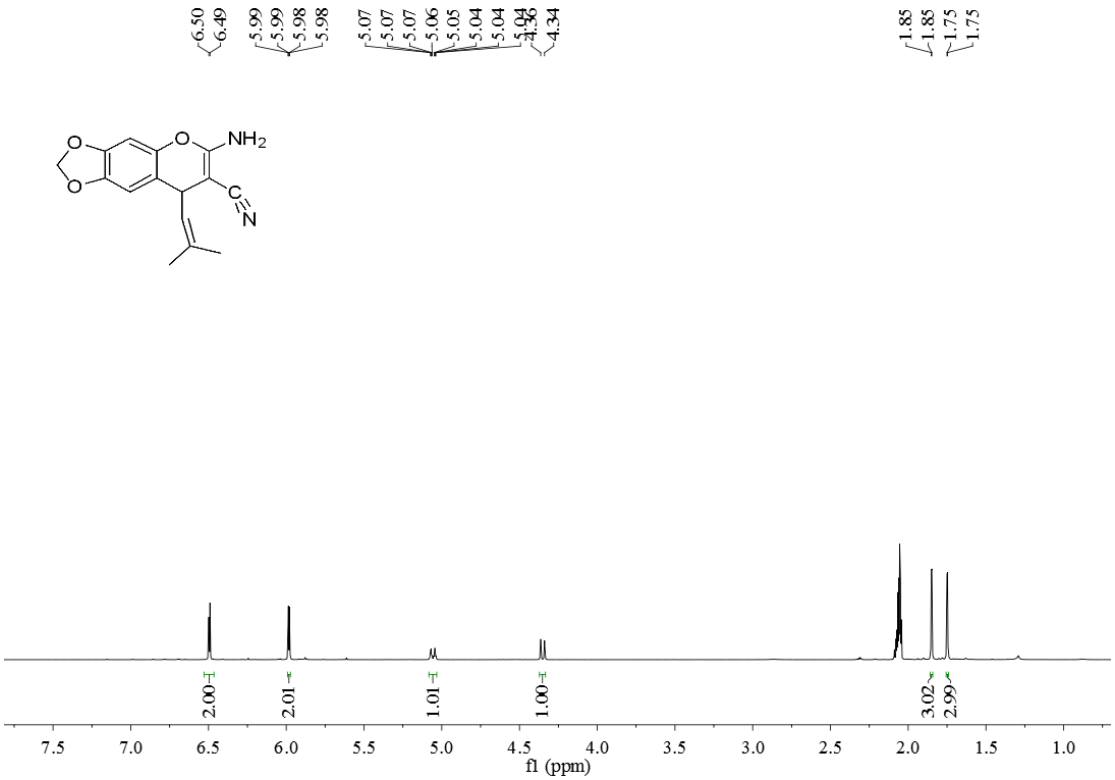
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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O
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C
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1.00
3.02
2.99
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7.0
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3.0
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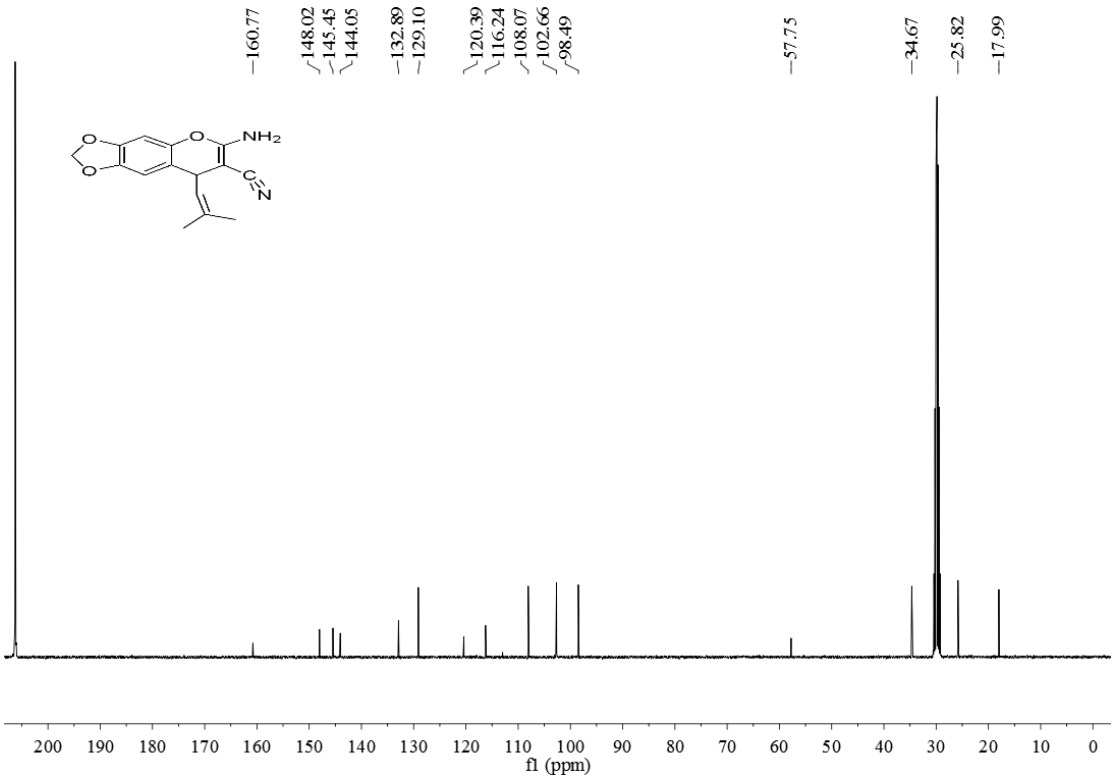
1.5
1.0
f1 (ppm)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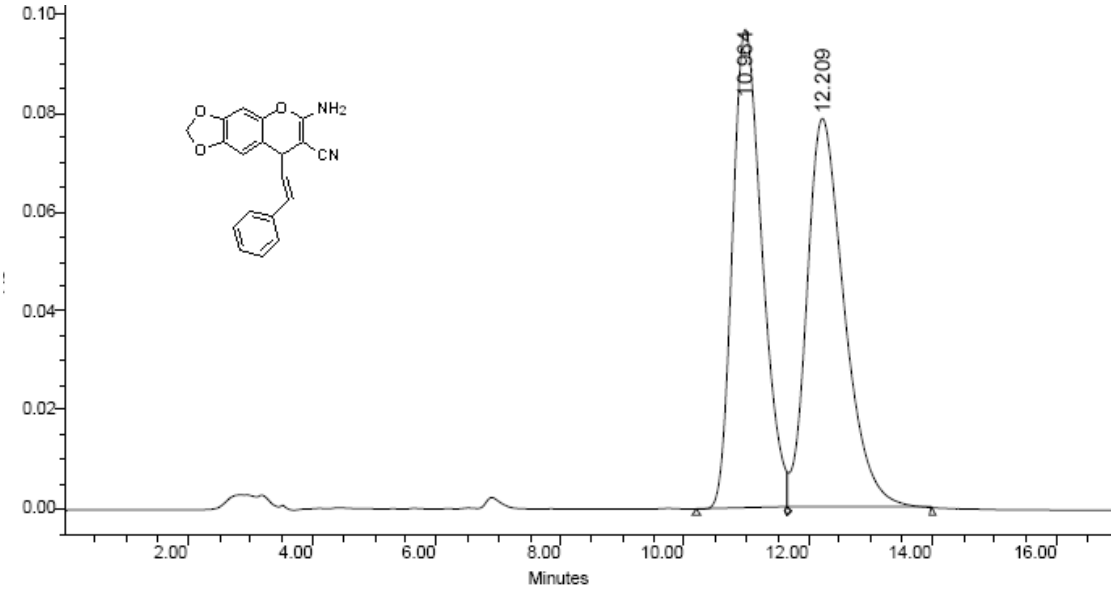
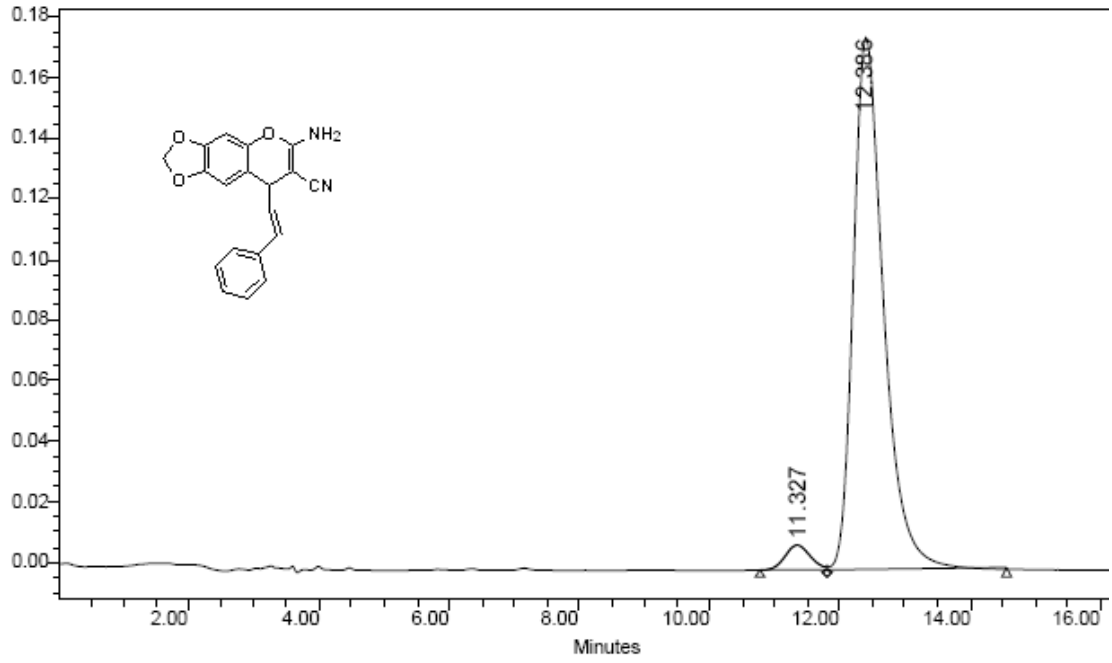
25.82
17.99
NH2
O
O
O
C
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

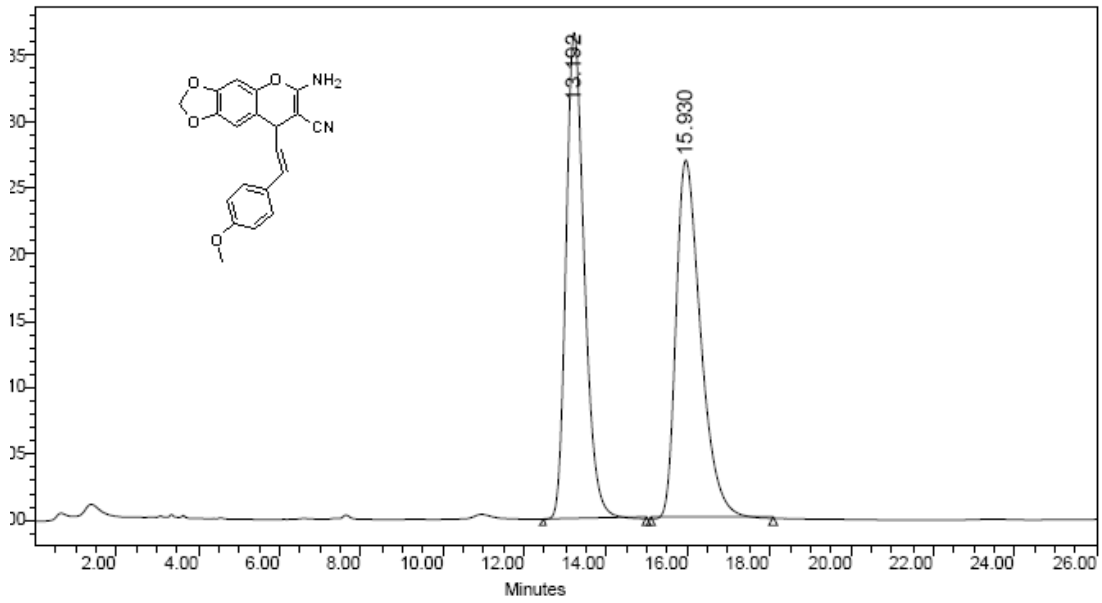
V. HPLC Data



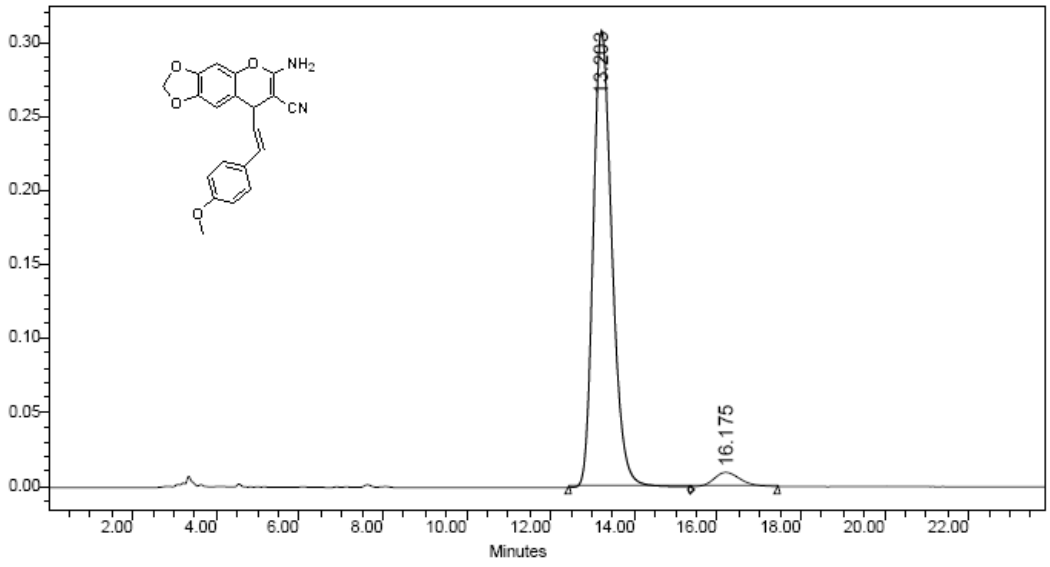
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	10.964	3229202	49.40	96974	55.12
2	12.209	3307135	50.60	78950	44.88



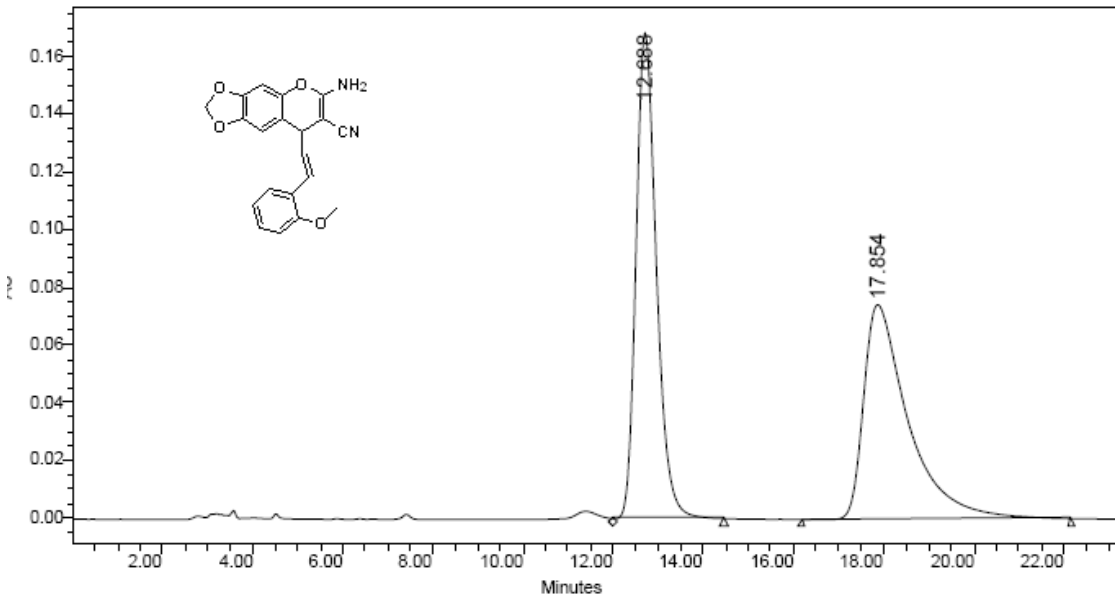
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	11.327	223820	3.79	8242	4.48
2	12.386	5684067	96.21	175579	95.52



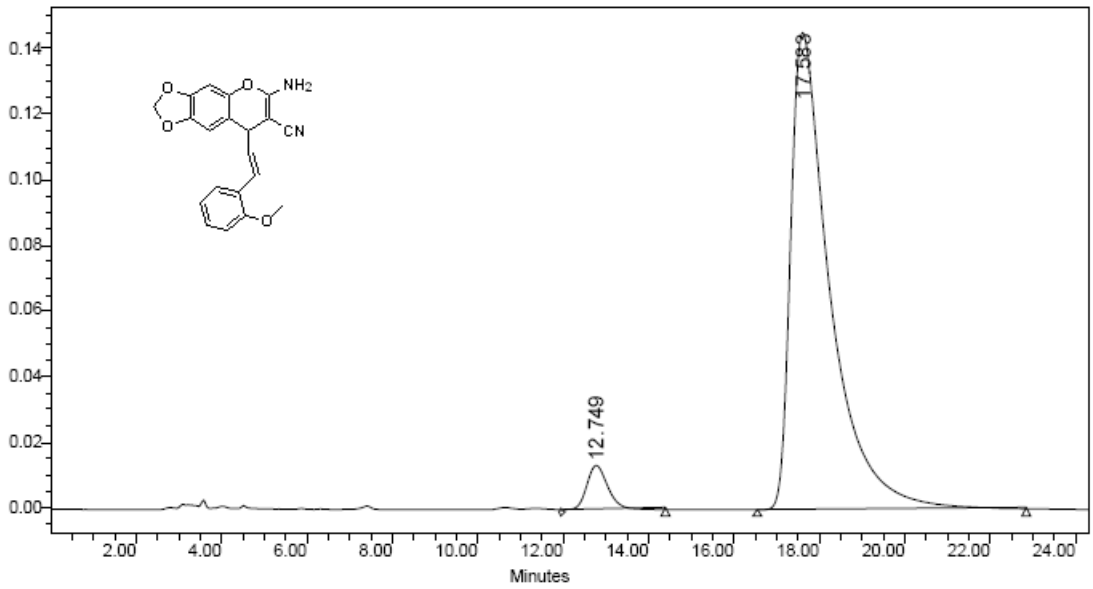
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	13.192	11439151	50.15	366568	57.57
2	15.930	11368973	49.85	270190	42.43



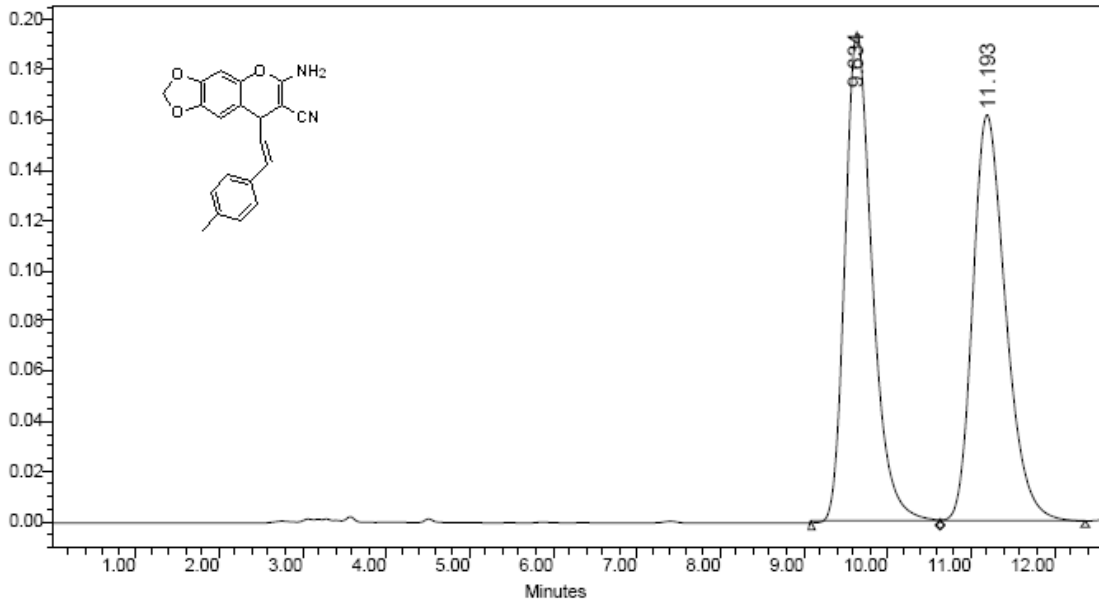
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	13.203	9600958	95.75	308066	96.97
2	16.175	425980	4.25	9613	3.03



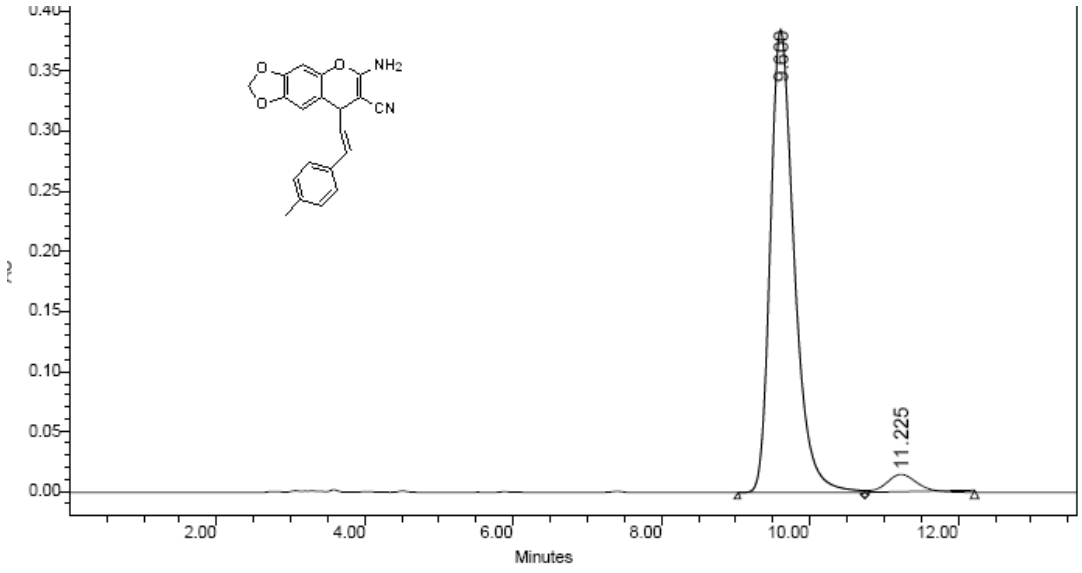
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	12.688	5294948	50.89	168518	69.38
2	17.854	5109142	49.11	74371	30.62



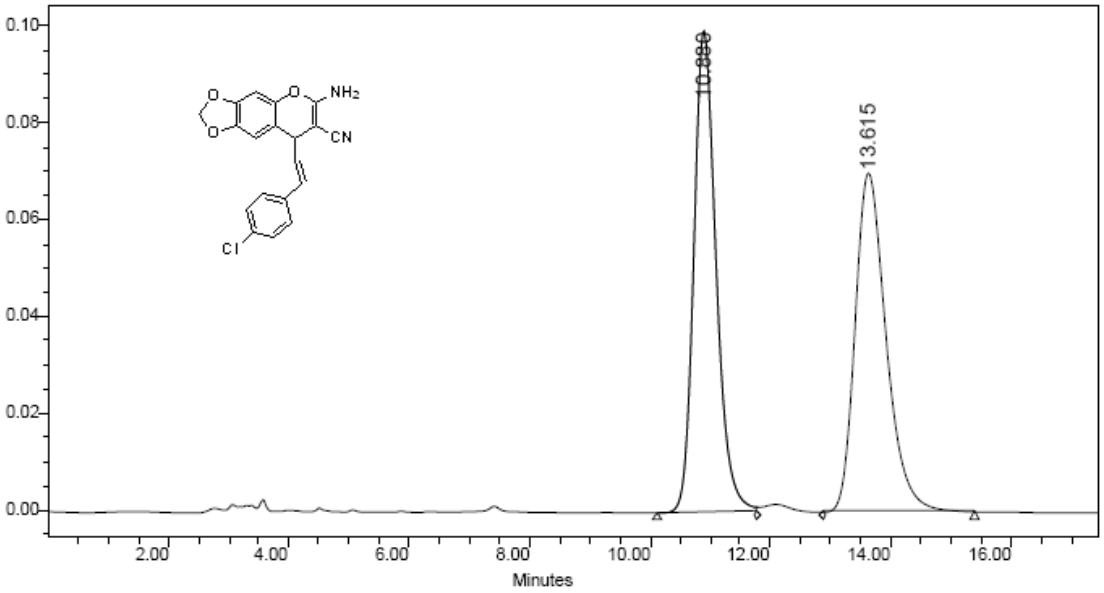
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	12.749	460403	4.71	13432	8.46
2	17.583	9309275	95.29	145272	91.54



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.634	4448408	49.97	195451	54.65
2	11.193	4454394	50.03	162217	45.35



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.600	8650871	95.18	385178	96.24
2	11.225	437901	4.82	15033	3.76



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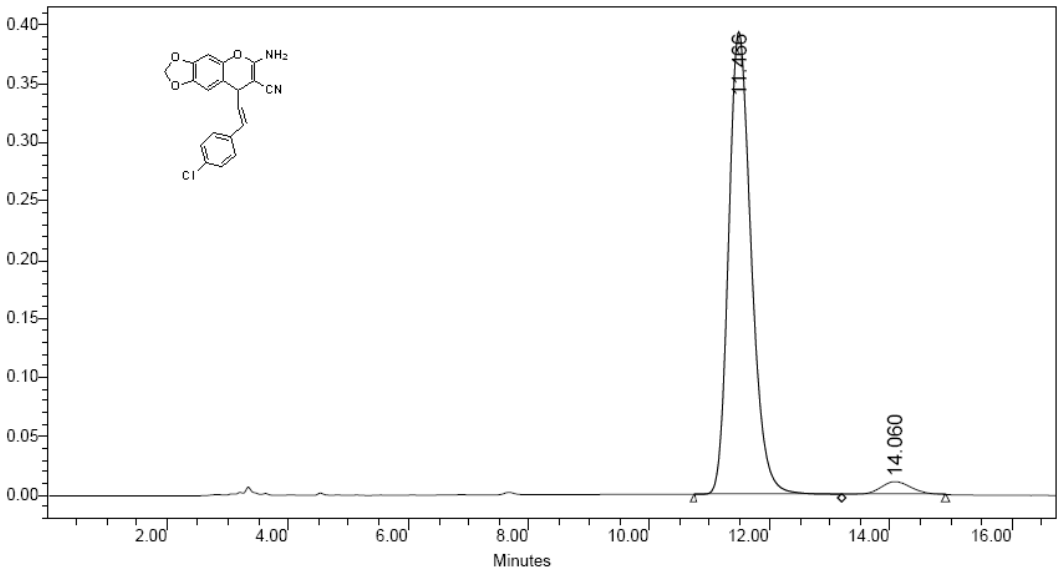
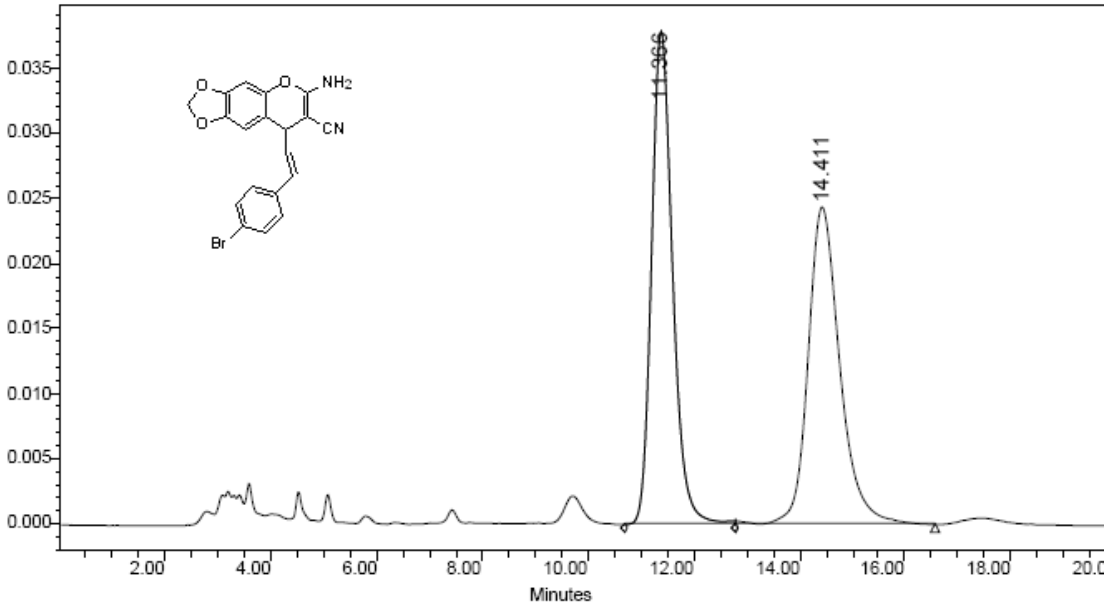
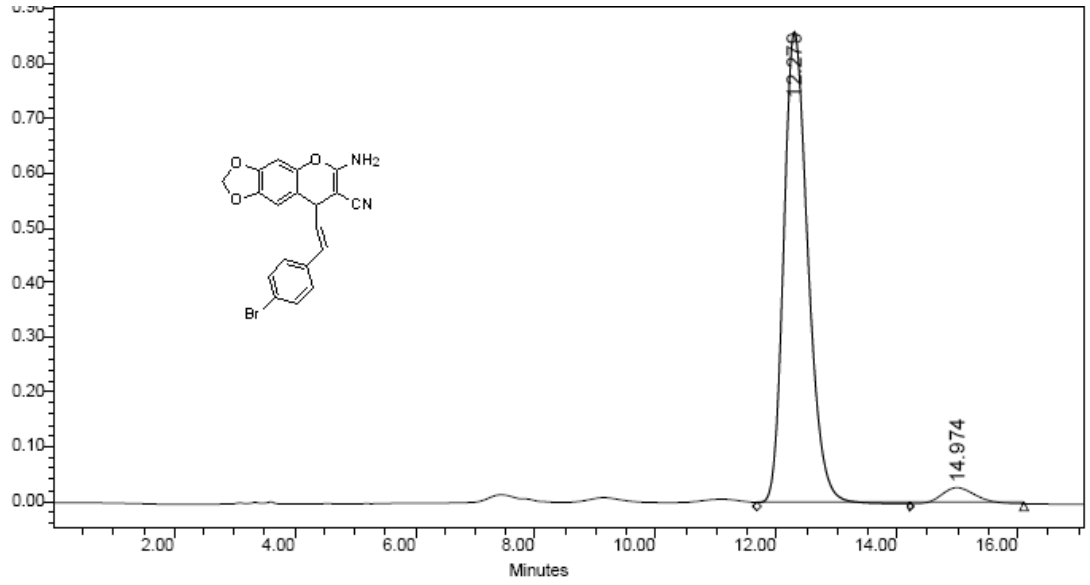
1	10.880	2556382	50.49	99307	58.69
2	13.615	2507055	49.51	69894	41.31



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	11.466	10274776	96.27	393516	97.27
2	14.060	398421	3.73	11037	2.73



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	11.366	1050926	50.63	37926	60.84
2	14.411	1024803	49.37	24416	39.16



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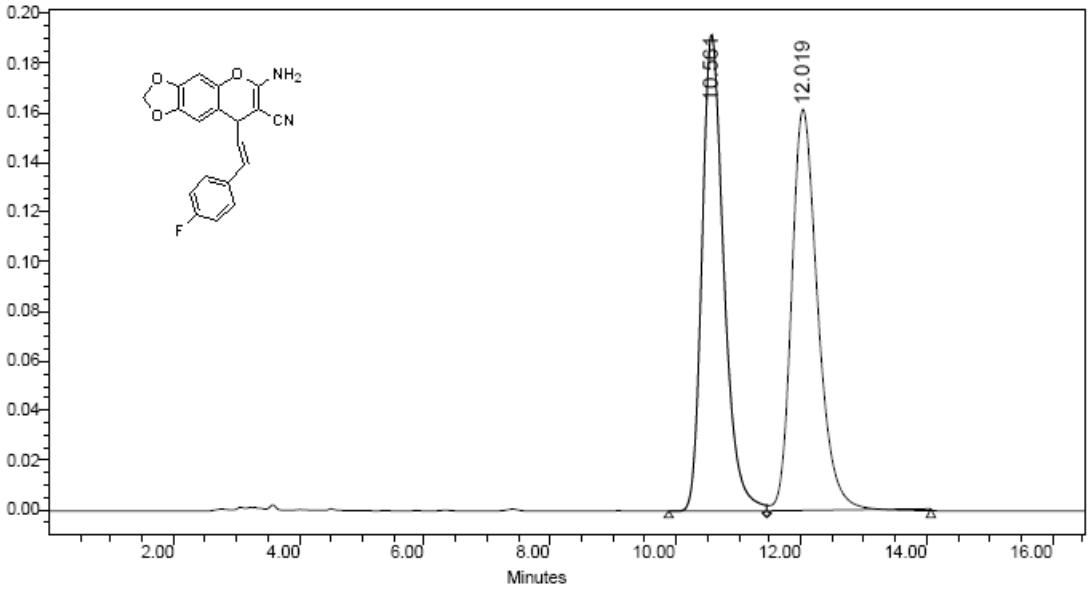
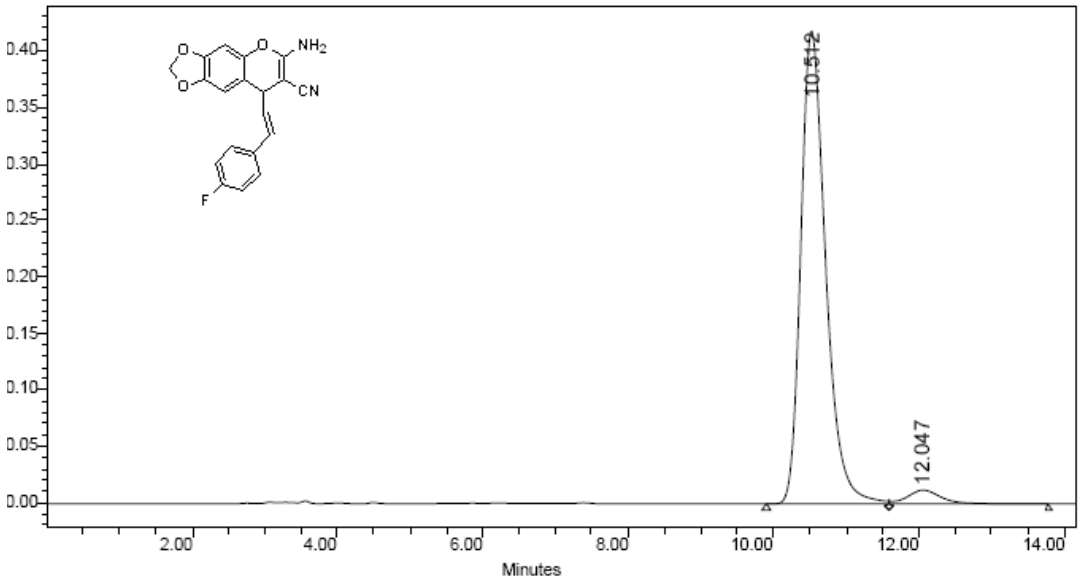
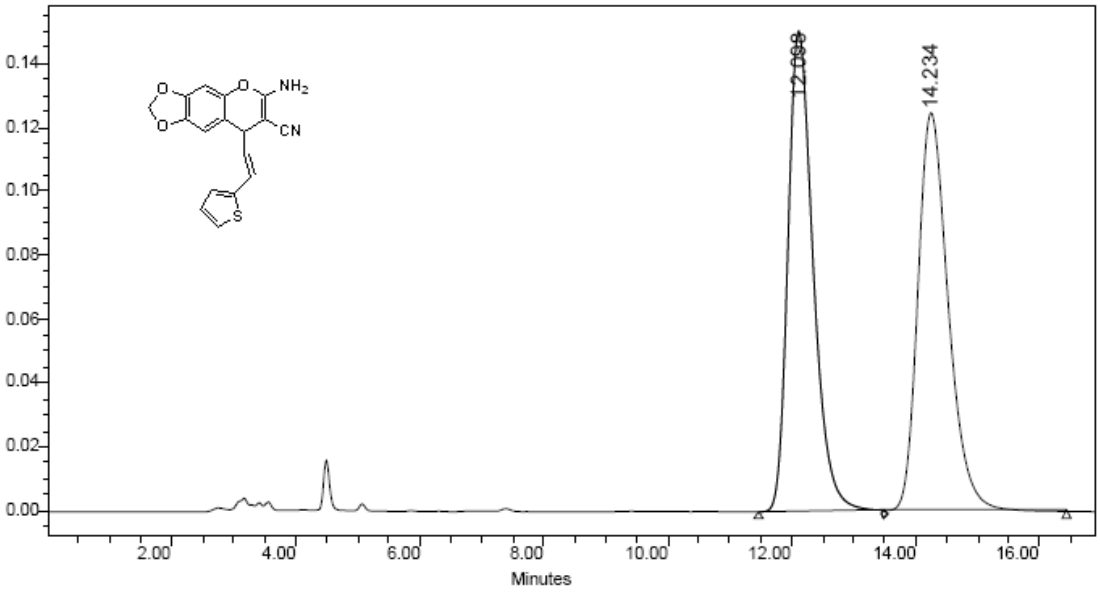
1	12.279	24153844	95.39	862523	96.69
2	14.974	1166254	4.61	29492	3.31



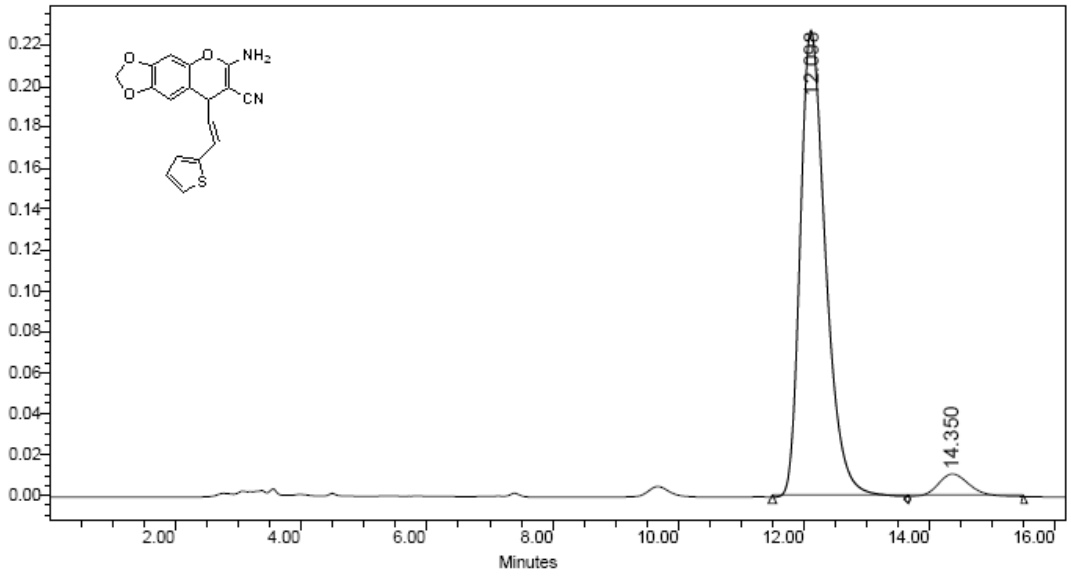
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	10.561	4639488	49.69	192066	54.26
2	12.019	4696785	50.31	161934	45.74



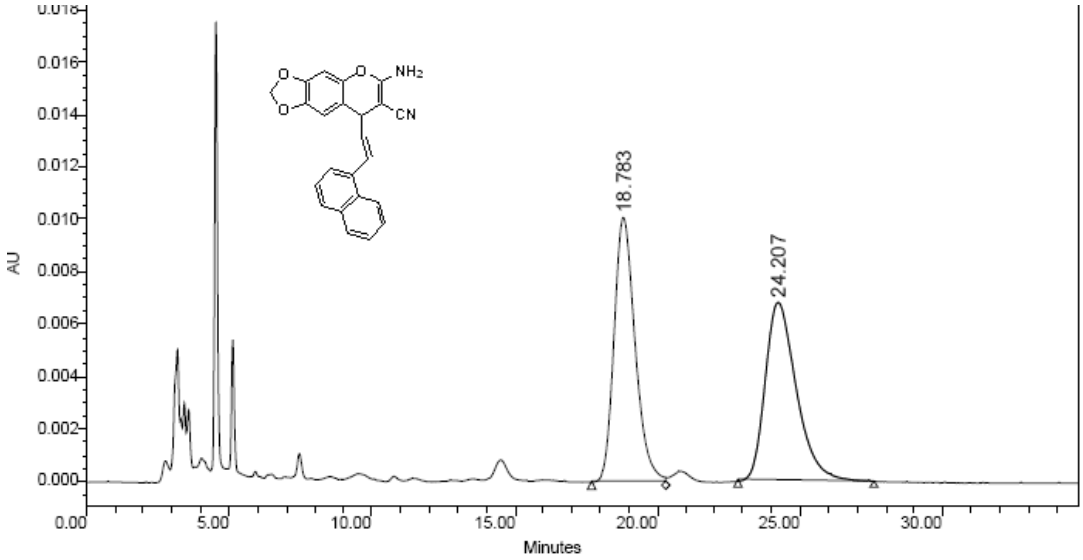
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	10.512	9908792	96.18	418341	97.16
2	12.047	393628	3.82	12209	2.84



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	12.098	4256078	49.91	150321	54.65
2	14.234	4271794	50.09	124756	45.35



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	12.098	6404184	94.21	227809	95.35
2	14.350	393498	5.79	11105	4.65



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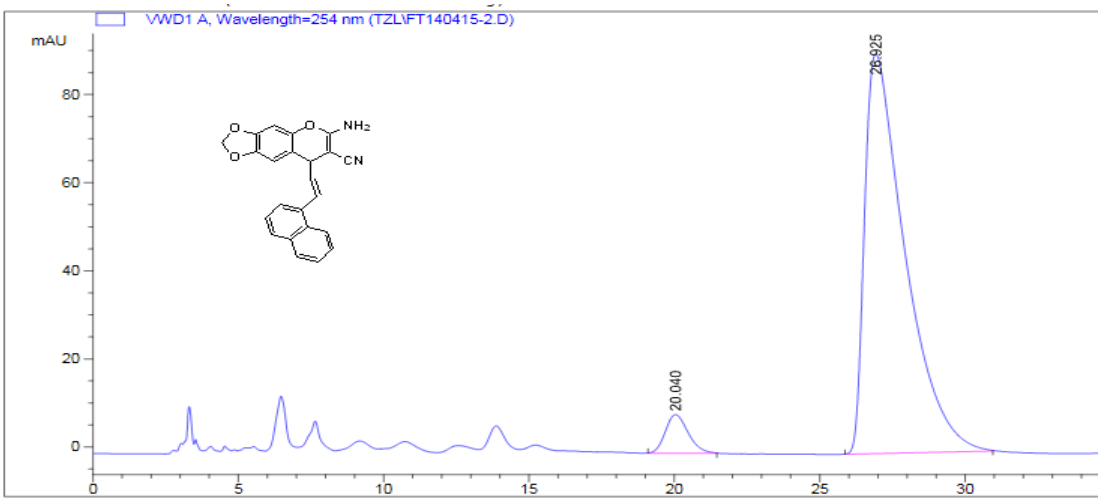
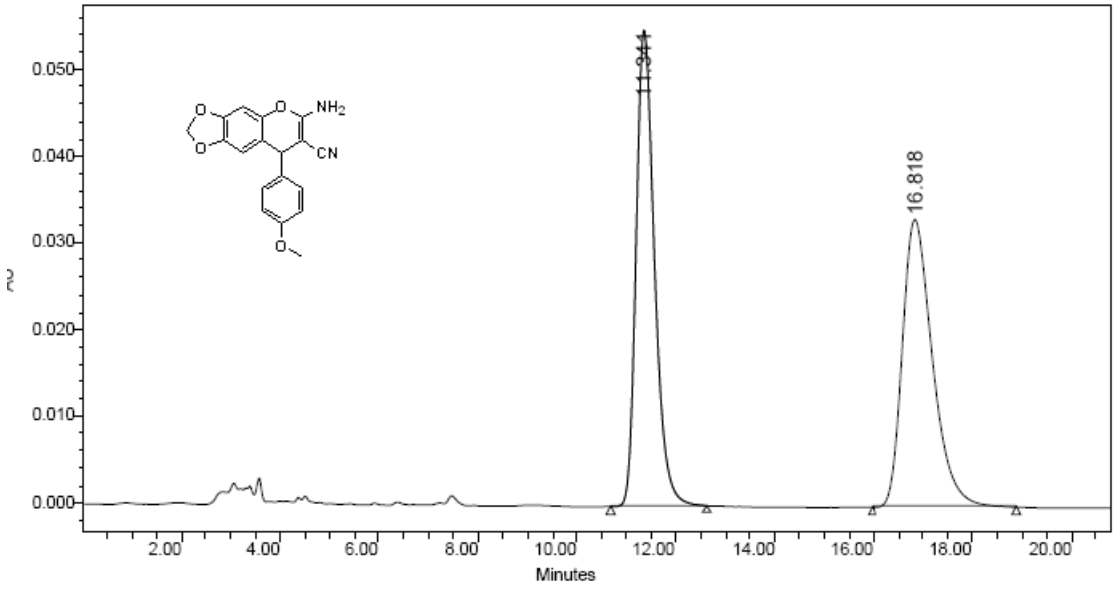
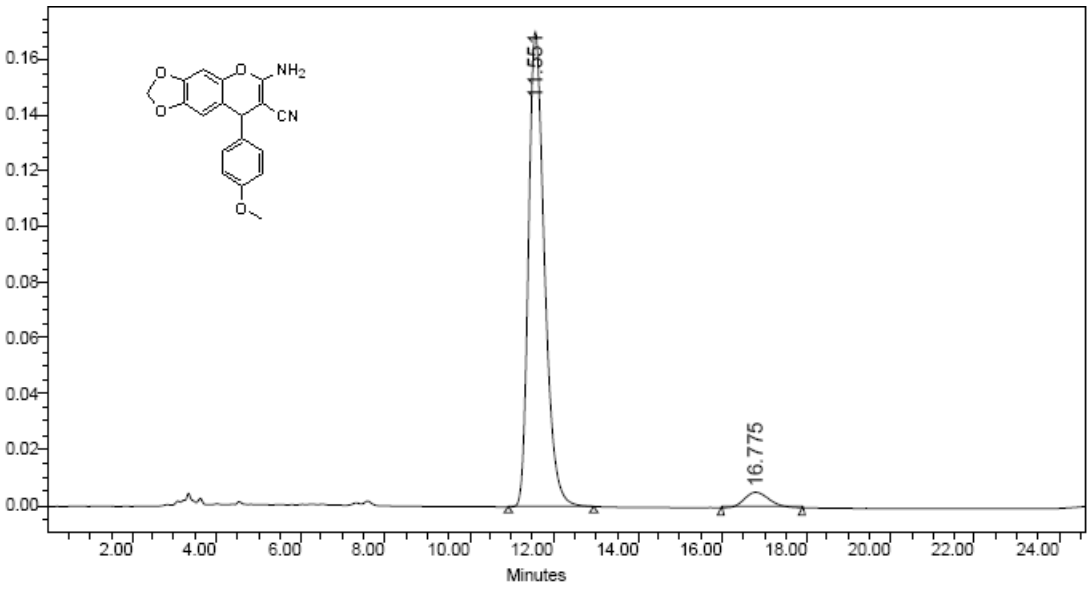
1	18.783	519185	49.93	10107	59.71
2	24.207	520578	50.07	6820	40.29



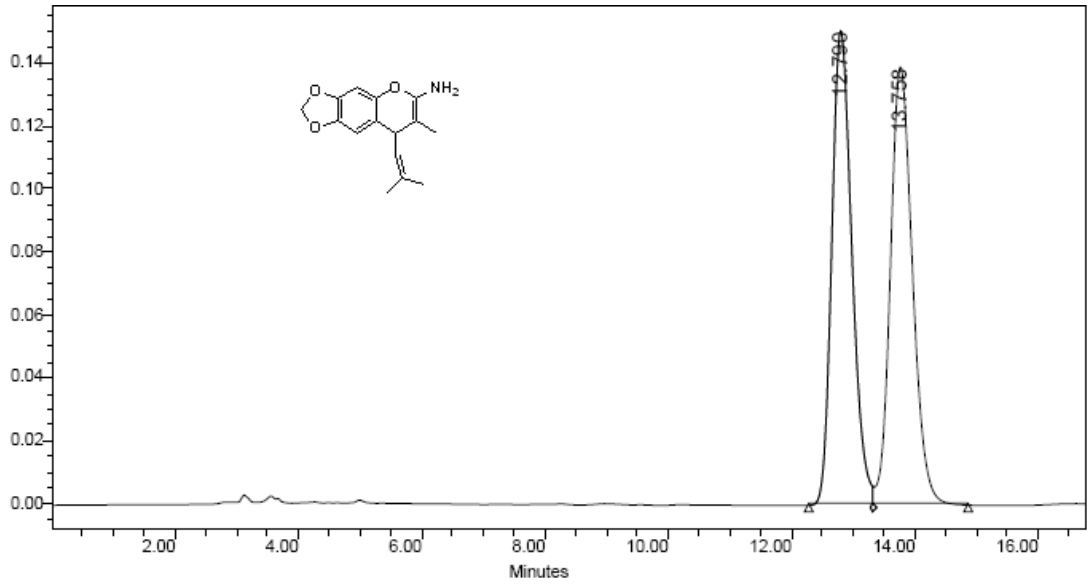
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.040	BB	0.8170	476.37085	8.75285	5.1621
2	26.925	BB	1.3769	8751.80762	90.76170	94.8379



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	11.341	1415825	50.10	55007	62.32
2	16.818	1410041	49.90	33260	37.68



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	11.551	4489403	95.09	170669	96.84
2	16.775	232008	4.91	5578	3.16



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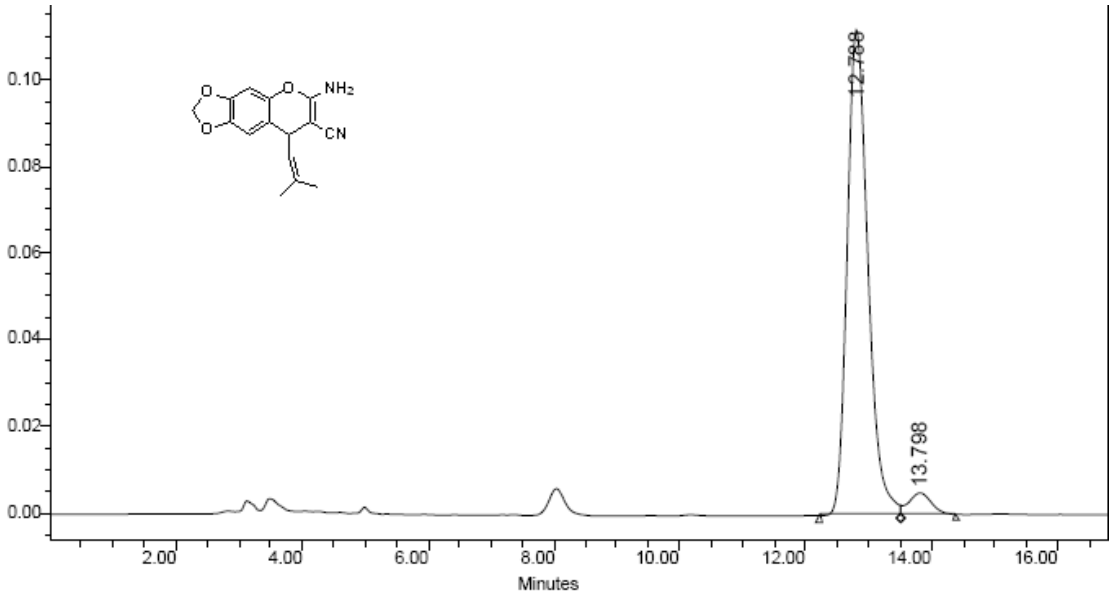
1	12.790	3417097	49.62	150749	51.98
2	13.758	3469469	50.38	139281	48.02



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1	12.788	2567052	95.41	112039	95.70
2	13.798	123536	4.59	5032	4.30

VI. References

(1)（a）L. Jurd, *Tetrahedron* **1977**, *33*, 16. (b) P. N. Moquist, Moquist, T. Moquist, S. E. Schaus, *Angew. Chem. Int. Ed.* **2010**, *49*, 7096.

(2) L. Luan, S. E. Schaus, *J. Am. Chem. Soc.* **2012**, *134, 19965*.