

Supporting Information

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General methods

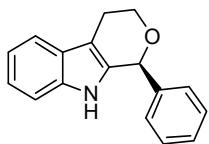
Proton (^1H NMR) and carbon (^{13}C NMR) nuclear magnetic resonance spectra were recorded at 500 MHz and 126 MHz, respectively. The chemical shifts are given in parts per million (ppm) on the delta (δ) scale. The solvent peak was used as a reference value, for ^1H NMR: $\text{CDCl}_3 = 7.27$ ppm; for ^{13}C NMR: $\text{CDCl}_3 = 77.23$ ppm. Analytical TLC was performed on precoated silica gel GF254 plates. Column chromatography was carried out on silica gel (200–300 mesh). HRMS were carried out on an Orbitrap analyzer. Optical rotations were measured using a 2.5 mL cell with a 10 cm path length on Hanon P850 Automatic Polarimeter and concentrations (c) were reported in $\text{g} \times (100 \text{ mL})^{-1}$. Enantiomeric excesses were determined by HPLC using a Daicel Chiralpak AD-H, AS-H, OD-H or IB column with hexane/*i*-PrOH as the eluent.

General procedure

Procedure for 1,3,4,9-tetrahydropyrano[3,4-*b*]indole substrates¹

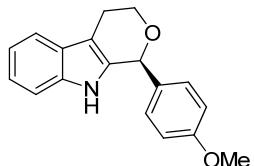
To a solution of rac-**1** (0.05 mmol, 1.0 eq) in CH₂Cl₂ (0.5 mL) was added EtOH (0.15 mmol, 3.0 eq) and DDQ (0.055 mmol, 1.1 eq) at room temperature. Upon starting material consumption, Hantzsch ester **2** (0.07 mmol, 1.4 eq), 4 Å molecular sieves (20 mg), and chiral SPINOL-derived **4b** (0.0025 mmol, 5 mol %) in Et₂O (5.0 mL) was added at 0 °C. The mixture was stirred at that temperature for 24 h. The reaction was quenched by saturated aqueous Et₃N, extracted with EtOAc (10 mL × 3), and the combined organic layer was dried over MgSO₄, filtered and evaporated under vacuum. The residue was purified by flash column chromatography to give the desired product.

Analytical data for products



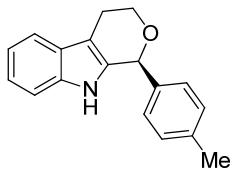
(S)-1-Phenyl-1,3,4,9-tetrahydropyrano[3,4-b]indole (1a)

It was prepared following the general procedure by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **1a** (11.2 mg, 90%). ¹H NMR (500 MHz, CDCl₃) δ 7.57 (d, *J* = 7.2 Hz, 1H), 7.44 (s, 1H), 7.39 (s, 5H), 7.24 (d, *J* = 7.3 Hz, 1H), 7.19–7.10 (m, 2H), 5.81 (s, 1H), 4.34 (ddd, *J* = 11.2, 5.4, 2.9 Hz, 1H), 4.04–3.96 (m, 1H), 3.15–3.07 (m, 1H), 2.87–2.79 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 139.6, 136.18, 133.8, 129.1, 129.0, 128.6, 127.2, 122.1, 119.8, 118.5, 111.1, 108.9, 76.3, 65.1, 22.5. These data are consistent with reported literature values.² HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 215 nm), retention time: t_{major} = 12.894 min, t_{minor} = 16.954 min, ee = 95%; [α]_D²⁰ = + 15.5 (c = 0.28, CHCl₃) CHCl₃.



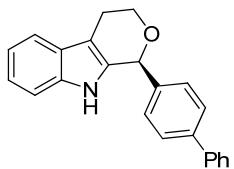
(S)-1-(4-Methoxyphenyl)-1,3,4,9-tetrahydropyrano[3,4-b]indole (1b)

It was prepared following the general procedure by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **1b** (11.9 mg, 85%). ¹H NMR (500 MHz, CDCl₃) δ 7.56 (d, *J* = 7.5 Hz, 1H), 7.45 (s, 1H), 7.31–7.27 (m, 2H), 7.24 (d, *J* = 7.9 Hz, 1H), 7.19–7.09 (m, 2H), 6.94–6.85 (m, 2H), 5.76 (s, 1H), 4.31 (ddd, *J* = 11.2, 5.4, 2.9 Hz, 1H), 4.02–3.94 (m, 1H), 3.81 (s, 3H), 3.13–3.05 (m, 1H), 2.86–2.78 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 160.2, 136.1, 134.1, 131.8, 130.0, 127.2, 122.1, 119.8, 118.5, 114.3, 111.1, 109.0, 75.8, 65.0, 55.5, 22.5. These data are consistent with reported literature values.² HPLC: the ee value was determined by HPLC analysis (Chiralcel OD-H, *i*-PrOH/Hexane = 20/80, 1.0 mL/min, 215 nm), retention time: t_{major} = 8.320 min, t_{minor} = 12.283 min, ee = 95%; [α]_D²⁰ = + 16.1 (c = 0.34, CHCl₃).



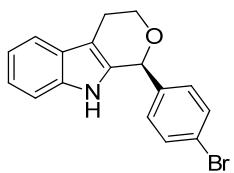
(S)-1-(*p*-Tolyl)-1,3,4,9-tetrahydropyrano[3,4-*b*]indole (1c)

It was prepared following the general procedure by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **1c** (12.0 mg, 91%). ¹H NMR (500 MHz, CDCl₃) δ 7.56 (d, *J* = 7.2 Hz, 1H), 7.44 (s, 1H), 7.28–7.26 (m, 1H), 7.26–7.25 (m, 1H), 7.25–7.22 (m, 1H), 7.19 (d, *J* = 7.9 Hz, 2H), 7.18–7.11 (m, 2H), 5.77 (s, 1H), 4.33 (ddd, *J* = 11.2, 5.4, 2.9 Hz, 1H), 4.03–3.95 (m, 1H), 3.14–3.05 (m, 1H), 2.86–2.79 (m, 1H), 2.37 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 156.7, 135.9, 134.4, 129.5, 128.8, 128.5, 127.1, 121.8, 121.4, 119.5, 118.3, 111.1, 111.0, 108.3, 69.5, 65.1, 56.1, 22.5. These data are consistent with reported literature values.² HPLC: the ee value was determined by HPLC analysis (Chiralcel OD-H, *i*-PrOH/Hexane = 30/70, 1.0 mL/min, 220 nm), retention time: t_{major} = 5.900 min, t_{minor} = 8.760 min, ee = 92%; [α]_D²⁰ = + 3.7 (c = 0.32, CHCl₃).



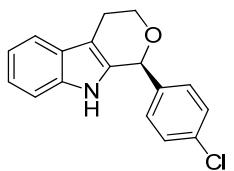
(S)-1-([1,1'-Biphenyl]-4-yl)-1,3,4,9-tetrahydropyrano[3,4-*b*]indole (1d)

It was prepared following the general procedure by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **1d** (14.6 mg, 90%). ¹H NMR (500 MHz, CDCl₃) δ 7.66–7.60 (m, 5H), 7.56 (s, 1H), 7.51–7.45 (m, 4H), 7.42–7.38 (m, 1H), 7.26–7.23 (m, 1H), 7.22–7.16 (m, 2H), 5.85 (s, 1H), 4.37 (ddd, *J* = 11.2, 5.3, 3.1 Hz, 1H), 4.07–3.99 (m, 1H), 3.20–3.10 (m, 1H), 2.92–2.83 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 142.0, 140.7, 138.5, 136.2, 133.6, 129.1, 128.9, 127.6, 127.3, 127.1, 122.1, 119.8, 118.5, 111.2, 109.0, 75.9, 64.9, 22.4; HRMS (EI) *m/z* [M + H]⁺ calculated for C₂₃H₂₀NO: 326.1539, found 326.1526; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 30/70, 1.0 mL/min, 222 nm), retention time: t_{major} = 8.327 min, t_{minor} = 9.231 min, ee = 96%; [α]_D²⁰ = + 17.6 (c = 0.84, CHCl₃).



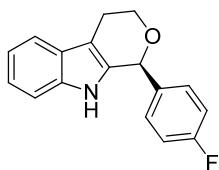
(S)-1-(4-Bromophenyl)-1,3,4,9-tetrahydropyrano[3,4-b]indole (1e)

It was prepared following the general procedure by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **1e** (14.4 mg, 88%). ¹H NMR (500 MHz, CDCl₃) δ 7.56 (d, *J* = 7.5 Hz, 1H), 7.54–7.49 (m, 2H), 7.41 (s, 1H), 7.27–7.26 (m, 1H), 7.25 (s, 2H), 7.20–7.11 (m, 2H), 5.77 (s, 1H), 4.31 (ddd, *J* = 11.3, 5.4, 3.0 Hz, 1H), 4.02–3.94 (m, 1H), 3.13–3.04 (m, 1H), 2.87–2.80 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 138.7, 136.2, 133.1, 132.1, 130.2, 127.1, 123.1, 122.3, 120.0, 118.6, 111.2, 109.2, 75.6, 65.0, 22.4; these data are consistent with reported literature values.² HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 20/80, 1.0 mL/min, 215 nm), retention time: t_{major} = 9.100 min, t_{minor} = 10.807 min, ee = 91%; [α]_D²⁰ = + 8.5 (c = 0.36, CHCl₃).



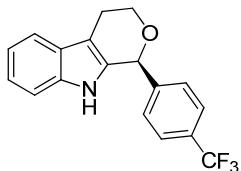
(S)-1-(4-Chlorophenyl)-1,3,4,9-tetrahydropyrano[3,4-b]indole (1f)

It was prepared following the general procedure by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **1f** (12.7 mg, 90%). ¹H NMR (500 MHz, CDCl₃) δ 7.56 (d, *J* = 7.5 Hz, 1H), 7.42 (s, 1H), 7.38–7.30 (m, 4H), 7.26–7.23 (m, 1H), 7.21–7.11 (m, 2H), 5.78 (s, 1H), 4.31 (ddd, *J* = 11.3, 5.4, 3.0 Hz, 1H), 4.03–3.93 (m, 1H), 3.15–3.04 (m, 1H), 2.88–2.80 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 138.2, 136.2, 135.0, 133.2, 129.9, 129.1, 127.1, 122.3, 119.9, 118.6, 111.2, 109.2, 75.5, 65.0, 22.4; these data are consistent with reported literature values.² HPLC: the ee value was determined by HPLC analysis (Chiralcel OD-H, *i*-PrOH/Hexane = 20/80, 1.0 mL/min, 215 nm), retention time: t_{major} = 13.563 min, t_{minor} = 16.493 min, ee = 95%; [α]_D²⁰ = + 10.9 (c = 0.24, CHCl₃).



(S)-1-(4-Fluorophenyl)-1,3,4,9-tetrahydropyrano[3,4-b]indole (1g)

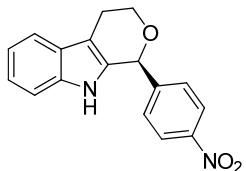
It was prepared following the general procedure by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **1g** (12.0 mg, 90%). ¹H NMR (500 MHz, CDCl₃) δ 7.58 (d, *J* = 7.4 Hz, 1H), 7.45 (s, 1H), 7.38–7.32 (m, 2H), 7.25 (d, *J* = 1.2 Hz, 1H), 7.21–7.13 (m, 2H), 7.11–7.04 (m, 2H), 5.79 (s, 1H), 4.31 (ddd, *J* = 11.2, 5.4, 3.0 Hz, 1H), 4.03–3.95 (m, 1H), 3.14–3.07 (m, 1H), 2.87–2.81 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 164.2, 162.2, 136.2, 135.5, 135.5, 133.4, 130.5, 130.4, 127.1, 122.3, 119.9, 118.5, 115.9, 115.8, 111.2, 109.1, 75.5, 65.0, 22.4; these data are consistent with reported literature values.² HPLC: the ee value was determined by HPLC analysis (Chiralcel AS-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 222 nm), retention time: t_{major} = 12.267 min, t_{minor} = 14.843 min, ee = 96%; [α]_D²⁰ = +10.4 (c = 1.02, CHCl₃).



(S)-1-(4-(Trifluoromethyl)phenyl)-1,3,4,9-tetrahydropyrano[3,4-b]indole (1h)

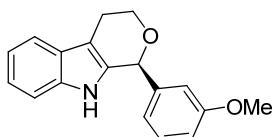
It was prepared following the general procedure A by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **1h** (14.4 mg, 91%). ¹H NMR (500 MHz, CDCl₃) δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.60 (d, *J* = 7.4 Hz, 1H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.47 (s, 1H), 7.27–7.24 (m, 1H), 7.23–7.14 (m, 2H), 5.85 (s, 1H), 4.33 (ddd, *J* = 11.2, 5.3, 3.1 Hz, 1H), 4.07–3.97 (m, 1H), 3.18–3.07 (m, 1H), 2.93–2.83 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 143.6, 136.3, 132.7, 131.2 (q, *J* = 32.5 Hz), 128.8, 127.0, 125.9 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 272.2 Hz), 122.4, 120.0, 118.6, 111.2, 109.2, 75.5, 64.9, 22.3; HRMS (EI) *m/z* [M + H]⁺ calculated for C₁₈H₁₅F₃NO: 318.1100, found 318.1109; HPLC: the ee value was determined by HPLC analysis

(Chiralcel OD-H, *i*-PrOH/Hexane = 10/90, 1.0 mL/min, 215 nm), retention time: $t_{\text{major}} = 15.555$ min, $t_{\text{minor}} = 18.076$ min, ee = 90%; $[\alpha]_D^{20} = + 13.9$ ($c = 0.48$, CHCl₃).



(S)-1-(4-Nitrophenyl)-1,3,4,9-tetrahydropyrano[3,4-*b*]indole (1i)

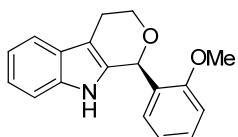
It was prepared following the general procedure by flash chromatography on silica gel using ethyl acetate/petroleum ether (20:80) as eluent to afford **1i** (13.5 mg, 92%). ¹H NMR (500 MHz, CDCl₃) δ 8.22 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 3H), 7.42 (s, 1H), 7.27 (d, *J* = 7.8 Hz, 1H), 7.24–7.12 (m, 2H), 5.91 (s, 1H), 4.32 (ddd, *J* = 11.3, 5.3, 3.0 Hz, 1H), 4.07–3.96 (m, 1H), 3.18–3.06 (m, 1H), 2.93–2.82 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 148.3, 146.8, 136.3, 132.1, 129.3, 127.0, 124.1, 122.6, 120.1, 118.7, 111.3, 109.4, 75.1, 65.0, 22.3; HRMS (EI) *m/z* [M + H]⁺ calculated for C₁₇H₁₅N₂O₃: 295.1077, found 295.1061; HPLC: the ee value was determined by HPLC analysis (Chiralcel OD-H, *i*-PrOH/Hexane = 40/60, 1.0 mL/min, 275 nm), retention time: $t_{\text{major}} = 8.600$ min, $t_{\text{minor}} = 11.837$ min, ee = 91%; $[\alpha]_D^{20} = + 3.2$ ($c = 0.32$, CHCl₃).



(S)-1-(3-Methoxyphenyl)-1,3,4,9-tetrahydropyrano[3,4-*b*]indole (1j)

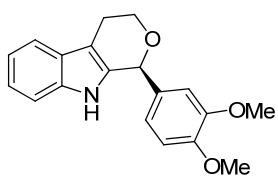
It was prepared following the general procedure by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **1j** (11.2 mg, 80%). ¹H NMR (500 MHz, CDCl₃) δ 7.57 (d, *J* = 7.1 Hz, 1H), 7.52 (s, 1H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.23 (d, *J* = 7.0 Hz, 1H), 7.20–7.12 (m, 2H), 6.98 (d, *J* = 7.5 Hz, 1H), 6.96–6.89 (m, 2H), 5.77 (s, 1H), 4.36 (ddd, *J* = 11.2, 5.4, 2.8 Hz, 1H), 4.05–3.95 (m, 1H), 3.78 (s, 3H), 3.17–3.07 (m, 1H), 2.88–2.79 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 160.1, 141.2, 136.2, 133.7, 129.9, 127.2, 122.1, 120.7, 119.7, 118.4, 114.8, 113.6, 111.2, 108.7, 76.2, 65.1, 55.4, 22.4; these data are consistent with reported literature values.²

HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 30/70, 1.0 mL/min, 222 nm), retention time: $t_{\text{major}} = 9.900$ min, $t_{\text{minor}} = 13.820$ min, ee = 90%; $[\alpha]_D^{20} = + 17.0$ ($c = 0.32$, CHCl₃).



(S)-1-(2-Methoxyphenyl)-1,3,4,9-tetrahydropyrano[3,4-*b*]indole (1k)

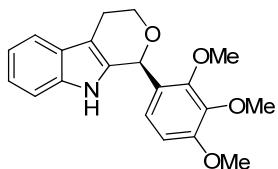
It was prepared following the general procedure by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **1k** (10.0 mg, 72%). ¹H NMR (500 MHz, CDCl₃) δ 7.88 (s, 1H), 7.56–7.50 (m, 1H), 7.37–7.28 (m, 2H), 7.26–7.24 (m, 1H), 7.18–7.08 (m, 2H), 7.03–6.99 (m, 1H), 6.95 (td, $J = 7.5, 0.8$ Hz, 1H), 6.31 (s, 1H), 4.38 (ddd, $J = 11.2, 5.2, 3.0$ Hz, 1H), 4.06–4.00 (m, 1H), 3.99 (s, 3H), 3.12–3.04 (m, 1H), 2.85–2.79 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 138.9, 136.6, 136.2, 134.0, 129.6, 128.5, 127.2, 122.0, 119.8, 118.5, 111.1, 108.9, 76.1, 65.0, 22.5, 21.4; HRMS (EI) m/z [M + H]⁺ calculated for C₁₈H₁₈NO₂: 280.1332, found 280.1341; HPLC: the ee value was determined by HPLC analysis (Chiralcel OD-H, *i*-PrOH/Hexane = 30/70, 1.0 mL/min, 215 nm), retention time: $t_{\text{major}} = 6.903$ min, $t_{\text{minor}} = 10.128$ min, ee = 90%; $[\alpha]_D^{20} = + 60.0$ ($c = 0.16$, CHCl₃).



(S)-1-(3,4-Dimethoxyphenyl)-1,3,4,9-tetrahydropyrano[3,4-*b*]indole (1l)

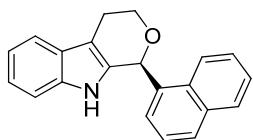
It was prepared following the general procedure by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **1l** (14.4 mg, 93%). ¹H NMR (500 MHz, CDCl₃) δ 7.63 (s, 1H), 7.56 (d, $J = 7.7$ Hz, 1H), 7.36 (dd, $J = 5.0, 1.0$ Hz, 1H), 7.29 (d, $J = 7.9$ Hz, 1H), 7.21–7.10 (m, 3H), 7.02 (dd, $J = 5.0, 3.5$ Hz, 1H), 6.11 (s, 1H), 4.33–4.25 (m, 1H), 4.05–3.97 (m, 1H), 3.87 (s, 3H), 3.80 (s, 3H), 3.07–2.98 (m, 1H), 2.90–2.82 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 149.6, 149.5, 136.1, 133.9, 132.1, 127.2, 122.0, 121.1, 119.7, 118.4, 111.3, 111.2, 111.0, 108.8, 76.3,

65.1, 56.0, 56.0, 22.4; HRMS (EI) m/z [M + H]⁺ calculated for C₁₉H₂₀NO₃: 310.1438, found 310.1451; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 30/70, 1.0 mL/min, 222 nm), retention time: t_{major} = 9.691 min, t_{minor} = 11.534 min, ee = 96%; $[\alpha]_D^{20} = + 30.6$ (c = 0.23, CHCl₃).



(S)-1-(2,3,4-Trimethoxyphenyl)-1,3,4,9-tetrahydropyrano[3,4-*b*]indole (1m)

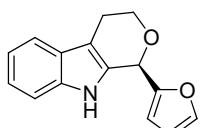
It was prepared following the general procedure by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **1m** (14.9 mg, 88%). ¹H NMR (500 MHz, CDCl₃) δ 8.03 (s, 1H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.27 (d, *J* = 7.0 Hz, 1H), 7.19–7.08 (m, 2H), 6.99 (d, *J* = 8.7 Hz, 1H), 6.63 (d, *J* = 8.7 Hz, 1H), 6.16 (s, 1H), 4.35 (ddd, *J* = 11.1, 5.1, 3.2 Hz, 1H), 4.03 (s, 3H), 4.02–3.98 (m, 1H), 3.96 (s, 3H), 3.85 (s, 3H), 3.10–3.02 (m, 1H), 2.85–2.79 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 153.9, 151.5, 142.2, 135.9, 134.2, 127.1, 126.2, 123.0, 121.8, 119.5, 118.3, 111.1, 108.5, 107.7, 70.0, 64.9, 61.9, 61.1, 56.1, 22.5; HRMS (EI) m/z [M + H]⁺ calculated for C₂₀H₂₂NO₄: 340.1543, found 340.1536; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 25/75, 1.0 mL/min, 215 nm), retention time: t_{major} = 8.033 min, t_{minor} = 14.083 min, ee = 90%; $[\alpha]_D^{20} = + 15.5$ (c = 0.60, CHCl₃).



(S)-1-(Naphthalen-1-yl)-1,3,4,9-tetrahydropyrano[3,4-*b*]indole (1n)

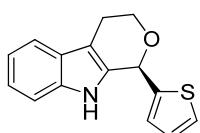
It was prepared following the general procedure by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **1n** (13.6 mg, 91%). ¹H NMR (500 MHz, CDCl₃) δ 8.33–8.24 (m, 1H), 7.96–7.85 (m, 2H), 7.65–7.57 (m, 1H), 7.57–7.39 (m, 5H), 7.22–7.11 (m, 3H), 6.50 (s, 1H), 4.40–4.31 (m, 1H), 4.09 (ddd, *J* = 11.3, 8.6, 4.3 Hz, 1H), 3.22–3.12 (m, 1H), 2.95 (dtd, *J* = 15.5, 4.1, 1.7 Hz, 1H); ¹³C

NMR (126 MHz, DMSO) δ 136.1, 135.23, 133.8, 133.7, 131.5, 129.1, 128.4, 127.6, 126.4, 126.2, 125.8, 125.1, 124.6, 120.9, 118.5, 117.8, 111.3, 107.2, 73.0, 62.7, 22.1; HRMS (EI) m/z [M + H]⁺ calculated for C₂₁H₁₈NO: 300.1383, found 300.1378; HPLC: the ee value was determined by HPLC analysis (Chiralcel IB-H, *i*-PrOH/Hexane = 30/70, 1.0 mL/min, 215 nm), retention time: t_{major} = 6.560 min, t_{minor} = 11.640 min, ee = 82%; $[\alpha]_D^{20} = +46.0$ (c = 0.40, CHCl₃).



(R)-1-(Furan-2-yl)-1,3,4,9-tetrahydropyrano[3,4-*b*]indole (1o)

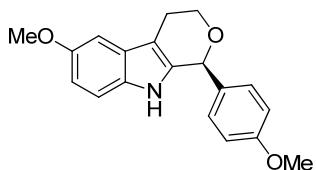
It was prepared following the general procedure by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **1o** (10.3 mg, 86%). ¹H NMR (500 MHz, CDCl₃) δ 7.79 (s, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 1.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.23–7.18 (m, 1H), 7.18–7.11 (m, 1H), 6.41–6.36 (m, 1H), 6.31 (d, *J* = 3.2 Hz, 1H), 5.95 (s, 1H), 4.24–4.16 (m, 1H), 4.06–3.98 (m, 1H), 2.99–2.85 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 152.6, 143.5, 136.1, 130.7, 127.0, 122.3, 119.8, 118.6, 111.2, 110.5, 109.8, 109.5, 68.4, 63.5, 22.2; HRMS (EI) m/z [M + H]⁺ calculated for C₁₅H₁₄NO₂: 240.1019, found 240.1010; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 20/80, 1.0 mL/min, 222 nm), retention time: t_{minor} = 8.243 min, t_{major} = 9.061 min, ee = 92%; $[\alpha]_D^{20} = -18.1$ (c = 0.44, CHCl₃).



(R)-1-(Thiophen-2-yl)-1,3,4,9-tetrahydropyrano[3,4-*b*]indole (1p)

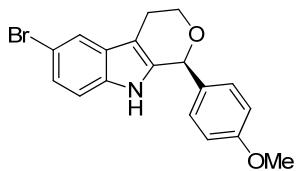
It was prepared following the general procedure by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **1p** (10.3 mg, 81%). ¹H NMR (500 MHz, CDCl₃) δ 7.63 (s, 1H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.36 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 1H), 7.21–7.10 (m, 3H), 7.02 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.11 (s, 1H), 4.33–4.25 (m, 1H), 4.05–3.97 (m, 1H), 3.07–2.98 (m, 1H), 2.90–

2.82 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 143.0, 136.1, 132.9, 127.3, 127.1, 126.8, 122.3, 119.9, 118.6, 111.2, 109.0, 70.7, 64.2, 22.3; HRMS (EI) m/z [M + H] $^+$ calculated for $\text{C}_{15}\text{H}_{14}\text{NOS}$: 256.0791, found 256.0776; HPLC: the ee value was determined by HPLC analysis (Chiralcel OD-H, *i*-PrOH/Hexane = 20/80, 1.0 mL/min, 215 nm), retention time: $t_{\text{major}} = 10.070$ min, $t_{\text{minor}} = 13.543$ min, ee = 80%; $[\alpha]_D^{20} = -5.4$ ($c = 0.36$, CHCl_3).



(S)-6-Methoxy-1-(4-methoxyphenyl)-1,3,4,9-tetrahydropyrano[3,4-*b*]indole (1q)

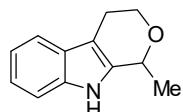
It was prepared following the general procedure by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **1q** (14.5 mg, 94%). ^1H NMR (500 MHz, CDCl_3) δ 7.28–7.24 (m, 2H), 7.19 (d, $J = 2.3$ Hz, 1H), 7.14 (dd, $J = 8.7, 2.4$ Hz, 1H), 6.92 (d, $J = 8.7$ Hz, 1H), 6.88–6.80 (m, 2H), 6.52 (s, 1H), 5.64 (s, 1H), 4.19–4.13 (m, 1H), 3.86–3.79 (m, 1H), 3.65 (s, 3H), 3.35 (s, 3H), 2.98–2.91 (m, 1H), 2.71–2.64 (m, 1H); ^{13}C NMR (126 MHz, C_6D_6) δ 160.5, 155.0, 134.9, 132.8, 131.6, 130.5, 114.2, 112.2, 112.0, 108.9, 100.8, 75.7, 64.0, 55.5, 54.9, 22; HRMS (EI) m/z [M + H] $^+$ calculated for $\text{C}_{19}\text{H}_{20}\text{NO}_3$: 310.1438, found 310.1453; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 20/80, 1.0 mL/min, 215 nm), retention time: $t_{\text{major}} = 11.243$ min, $t_{\text{minor}} = 15.150$ min, ee = 95%; $[\alpha]_D^{20} = +23.8$ ($c = 0.48$, CHCl_3).



(S)-6-Bromo-1-(4-methoxyphenyl)-1,3,4,9-tetrahydropyrano[3,4-*b*]indole (1r)

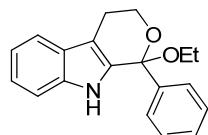
It was prepared following the general procedure by flash chromatography on silica gel using ethyl acetate/petroleum ether (10:90) as eluent to afford **1r** (16.1 mg, 90%). ^1H NMR (500 MHz, CDCl_3) δ 7.67 (d, $J = 1.5$ Hz, 1H), 7.50 (s, 1H), 7.28 (d, 2H), 7.23

(dd, $J = 8.6$, 1.8 Hz, 1H), 7.10 (d, $J = 8.5$ Hz, 1H), 6.90 (d, $J = 8.6$ Hz, 2H), 5.73 (s, 1H), 4.30 (ddd, $J = 11.3$, 5.4, 2.8 Hz, 1H), 4.00–3.92 (m, 1H), 3.81 (s, 3H), 3.08–2.99 (m, 1H), 2.79–2.71 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 160.4, 135.5, 134.8, 131.4, 129.9, 129.0, 124.8, 121.2, 114.4, 113.0, 112.5, 108.7, 75.7, 64.9, 55.5, 22.3; HRMS (EI) m/z [M + H] $^+$ calculated for $\text{C}_{18}\text{H}_{17}\text{BrNO}_2$: 358.0437, found 358.0423; HPLC: the ee value was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/Hexane = 20/80, 1.0 mL/min, 222 nm), retention time: $t_{\text{major}} = 12.620$ min, $t_{\text{minor}} = 19.572$ min, ee = 92%; $[\alpha]_D^{20} = +95.0$ ($c = 0.26$, CHCl_3).



1-Methyl-1,3,4,9-tetrahydropyrano[3,4-b]indole (1s)

It was prepared following the general procedure, which did not work.. ^1H NMR (500 MHz, CDCl_3) δ 7.78 (s, 1H), 7.54 (d, $J = 7.7$ Hz, 1H), 7.34 (d, $J = 7.9$ Hz, 1H), 7.23–13 (m, 2H), 4.97 (q, $J = 6.5$ Hz, 1H), 4.39–4.24 (m, 1H), 3.93–3.84 (m, 1H), 3.09–2.94 (m, 1H), 2.74 (dd, $J = 15.3$, 1.7 Hz, 1H), 1.56 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 136.0, 135.9, 127.4, 122.0, 120.0, 118.4, 111.1, 107.7, 69.3, 64.9, 22.6, 20.5. HRMS (EI) m/z [M + H] $^+$ calculated for $\text{C}_{12}\text{H}_{14}\text{NO}$: 188.1070, found 188.1041.



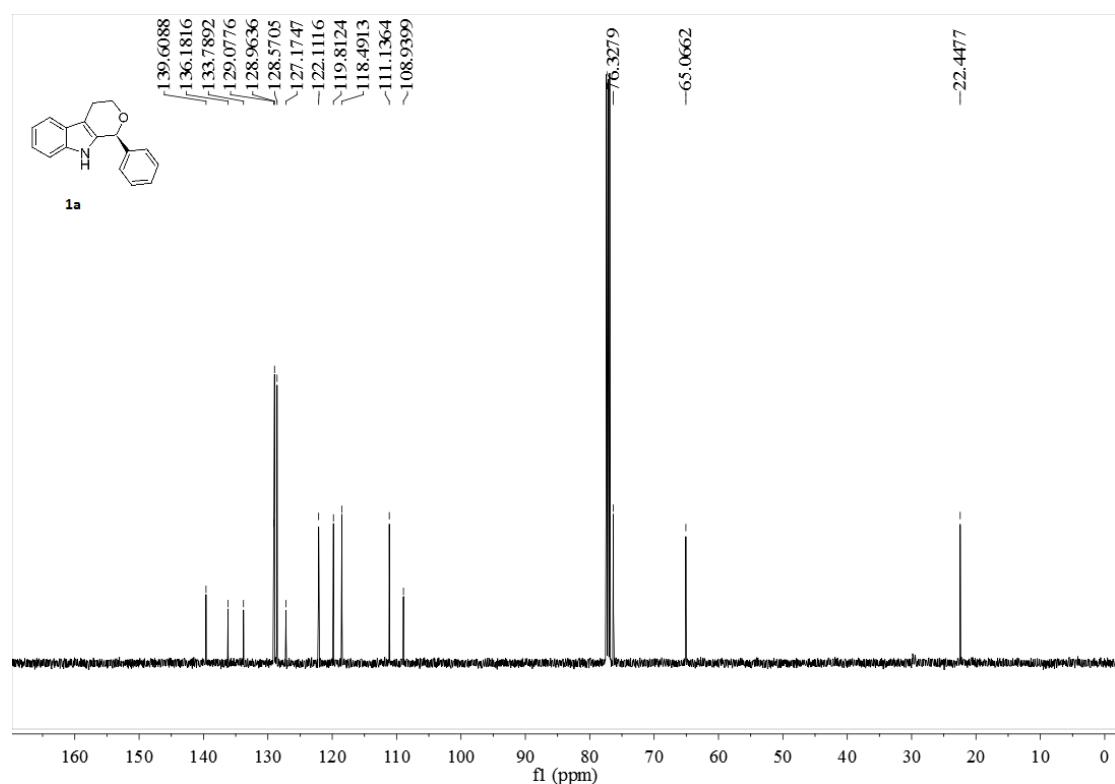
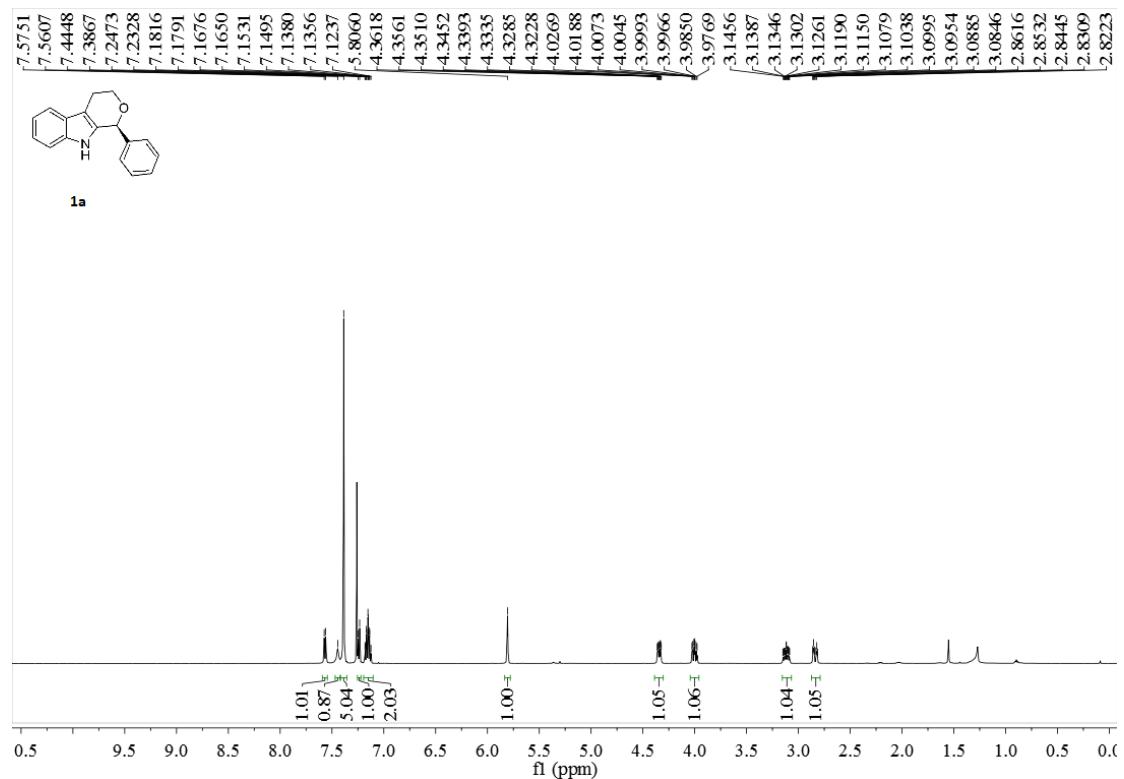
1-Ethoxy-1-phenyl-1,3,4,9-tetrahydropyrano[3,4-b]indole (5)

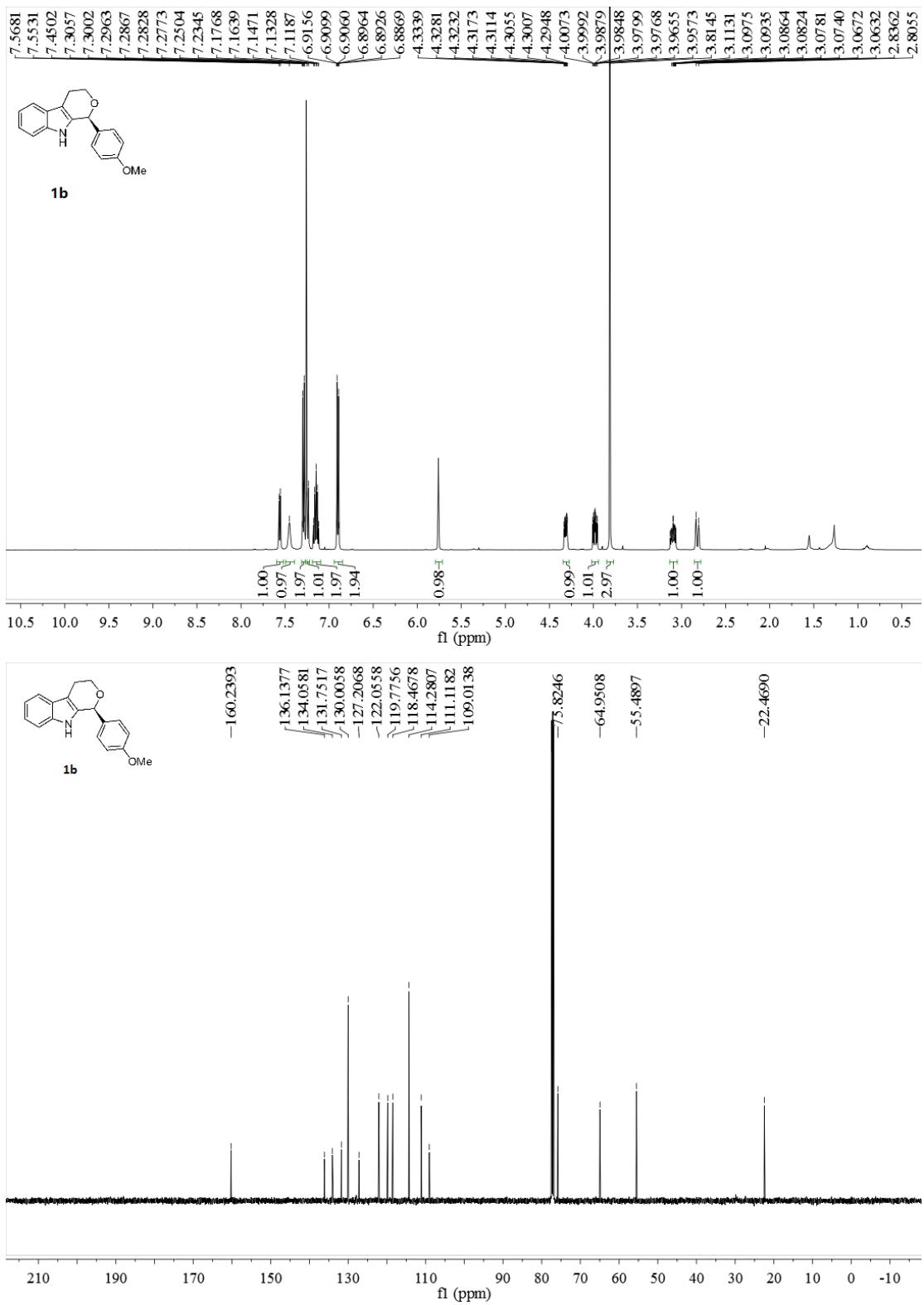
^1H NMR (500 MHz, CDCl_3) δ 7.73 (s, 1H), 7.68–7.62 (m, 2H), 7.54 (d, $J = 7.8$ Hz, 1H), 7.41 (t, $J = 7.5$ Hz, 2H), 7.35 (t, $J = 7.3$ Hz, 1H), 7.24 (d, 1H), 7.20–7.14 (m, 1H), 7.10 (t, $J = 7.4$ Hz, 1H), 4.41–4.32 (m, 1H), 4.27–4.19 (m, 1H), 3.63–3.54 (m, 2H), 3.12–3.02 (m, 1H), 2.90–2.81 (m, 1H), 1.29 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 141.1, 136.3, 133.8, 128.8, 128.6, 126.5, 122.7, 119.76, 119.1, 111.5, 109.6, 98.5, 61.0, 58.7, 22.2, 15.7; HRMS (EI) m/z [M + H] $^+$ calculated for $\text{C}_{19}\text{H}_{20}\text{NO}_2$: 294.1489, found 294.1496.

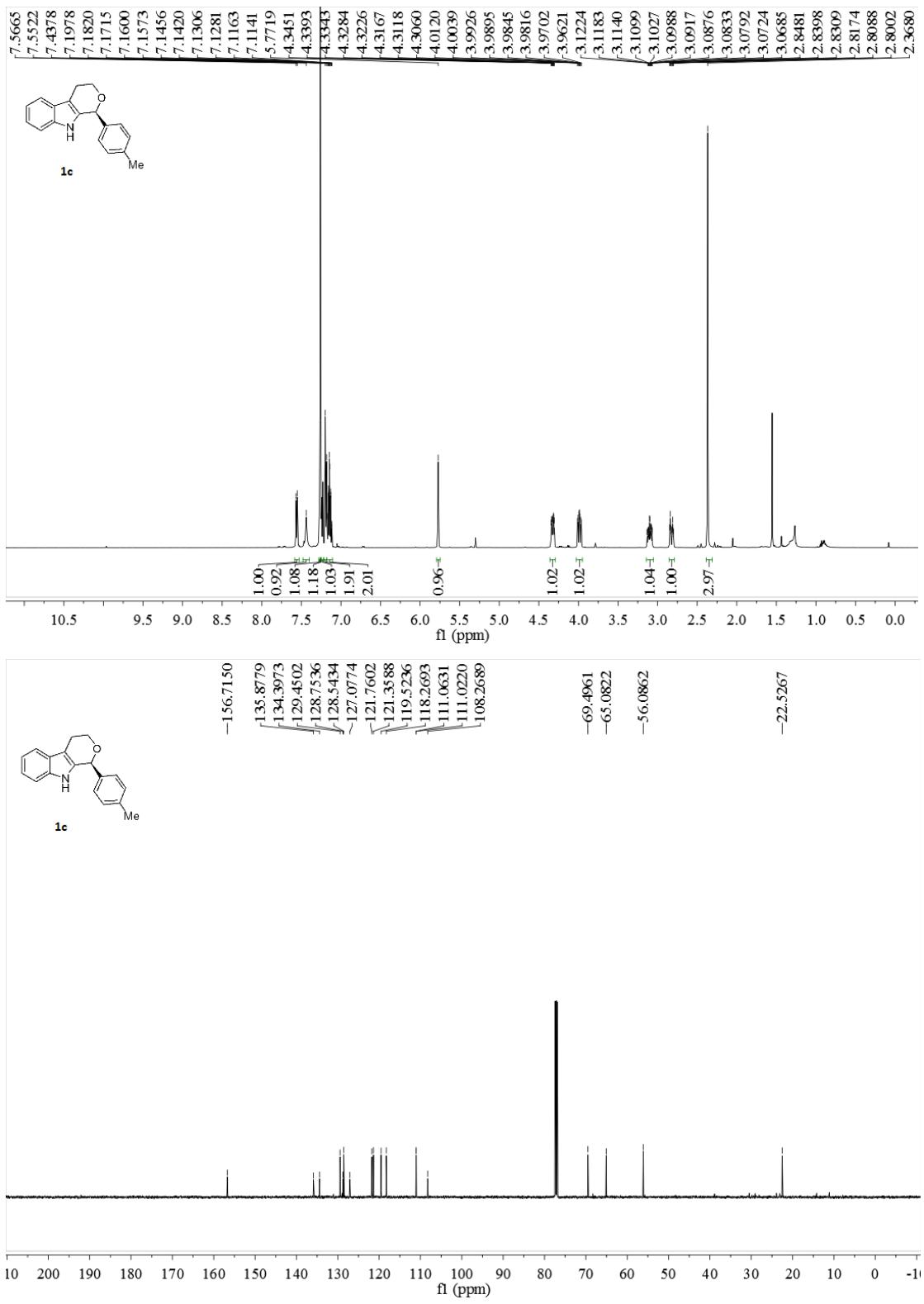
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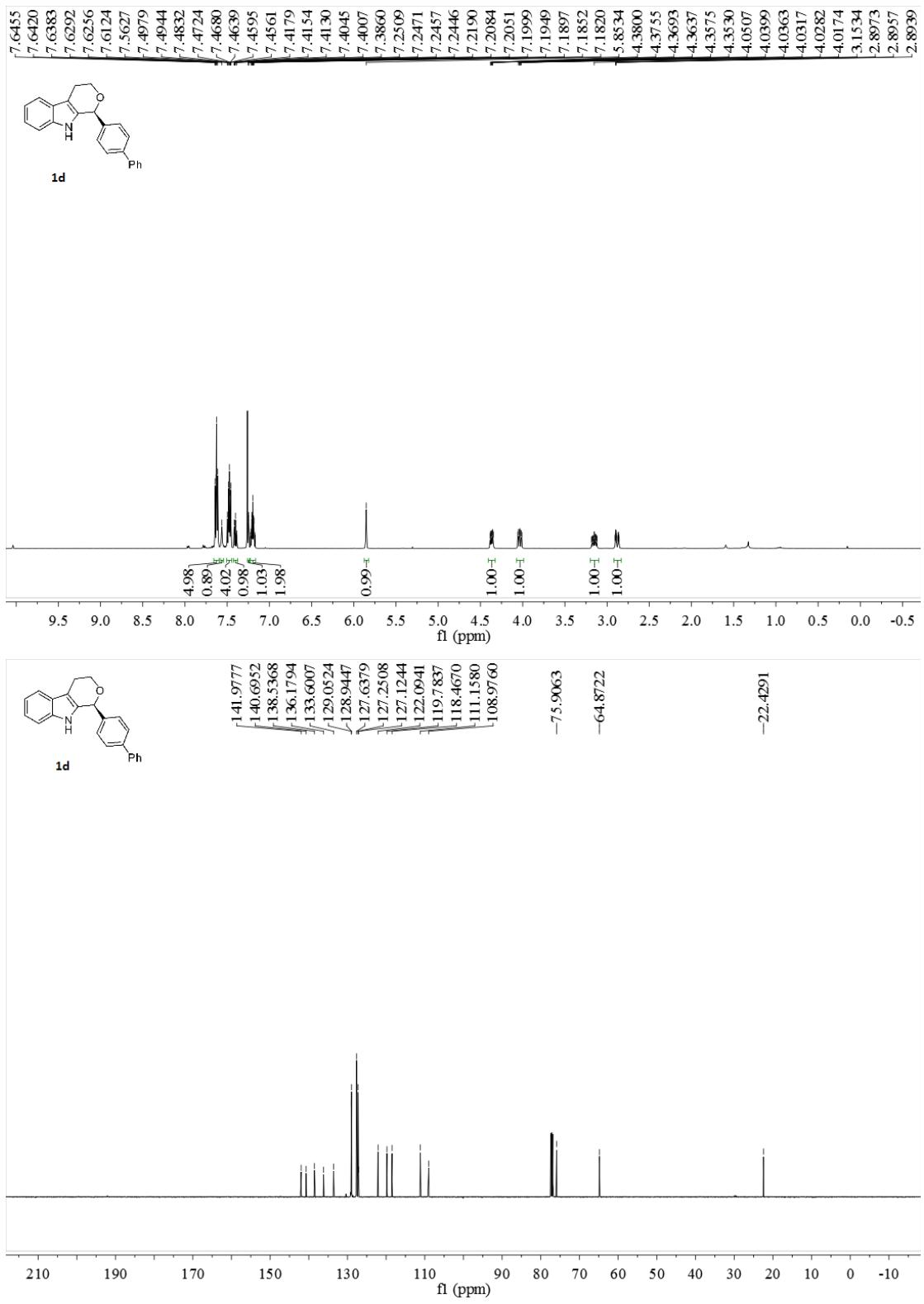
1. B. Bouguerne1, C. Lherbet, M. Baltas. *Letters in Organic Chemistry*, **2010**, 7, 420.
2. C. Zhao, S. B. Chen, D. Seidel. *J. Am. Chem. Soc.* **2016**, 138, 9053.

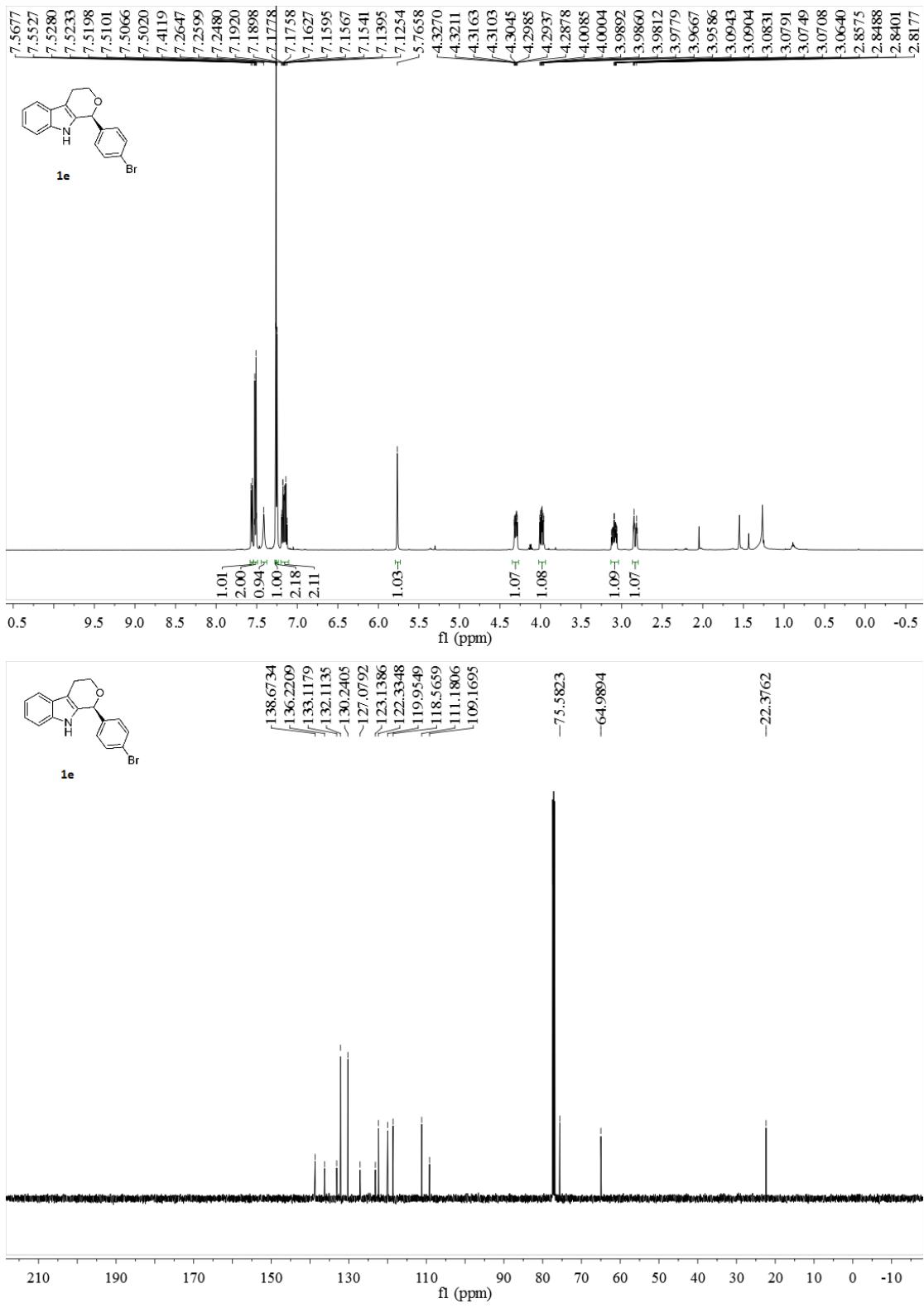
¹H and ¹³C NMR spectra

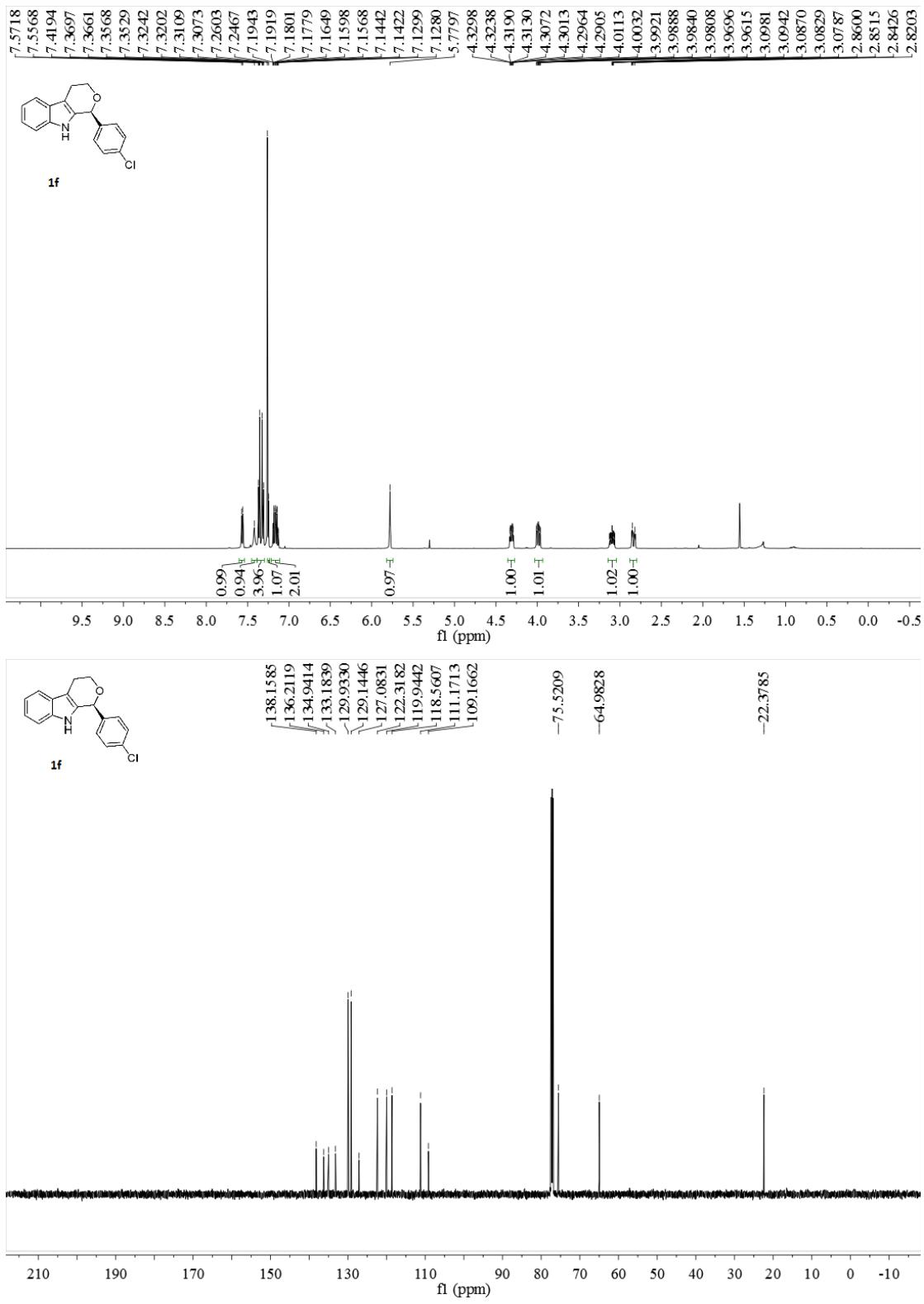


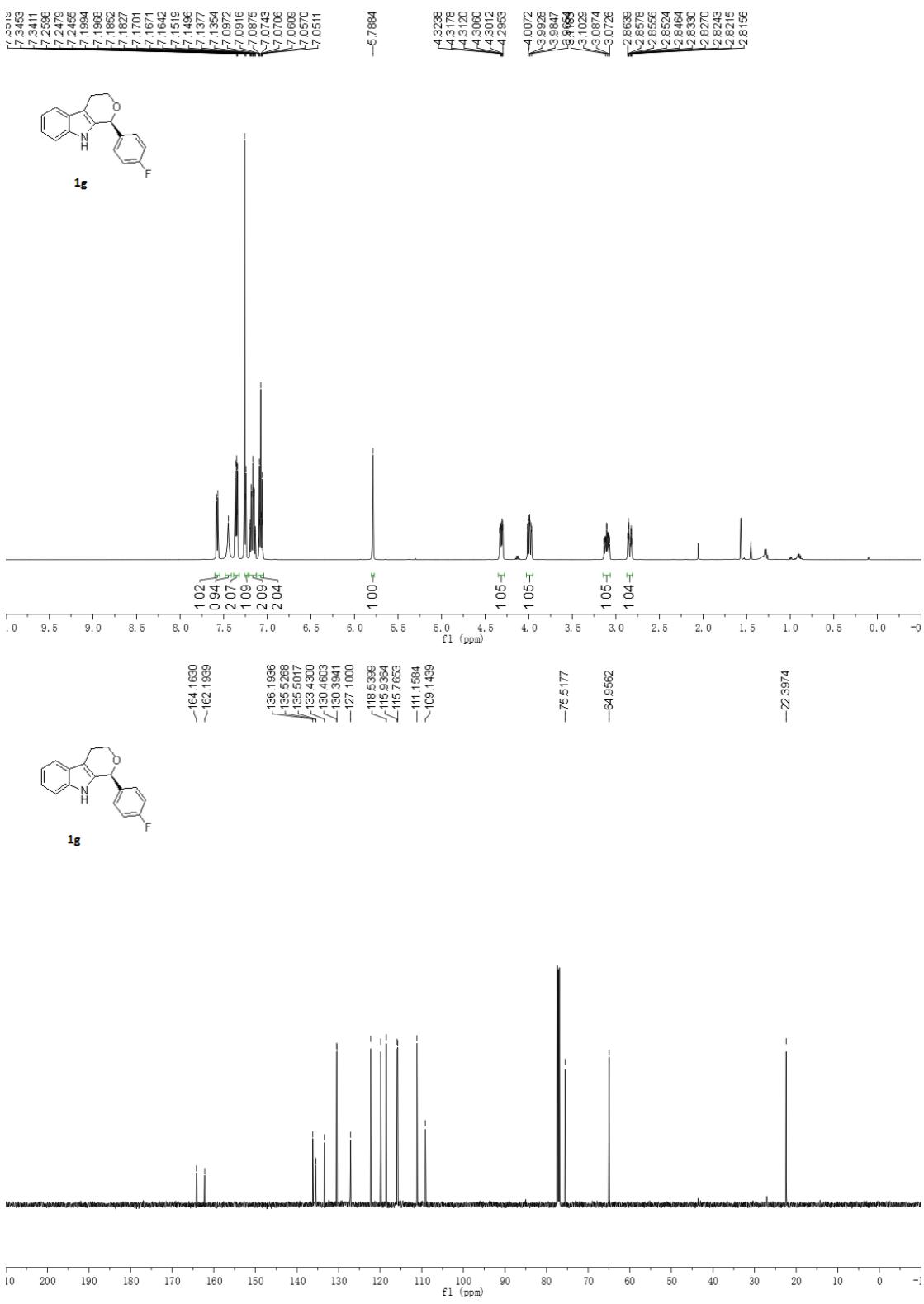


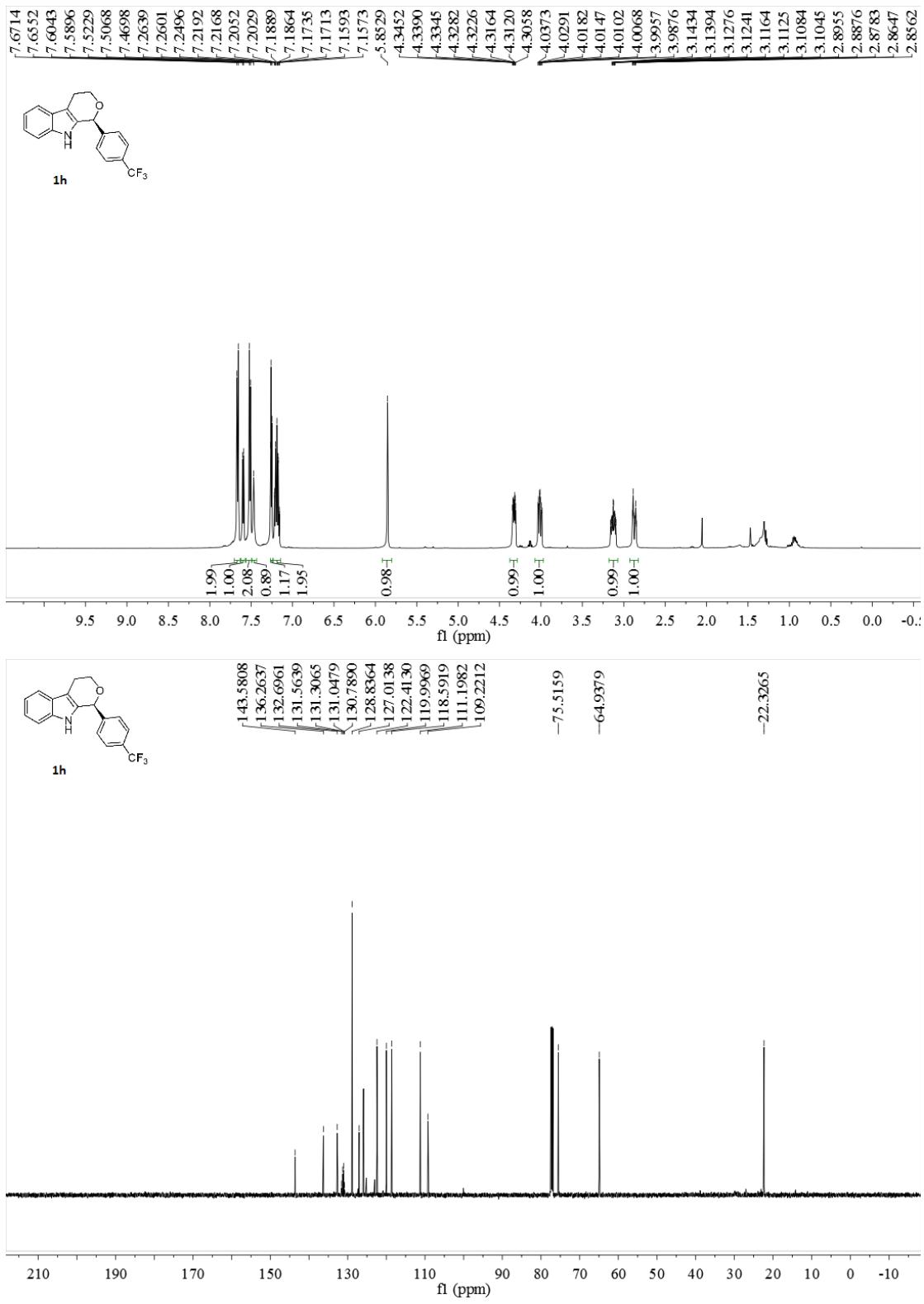


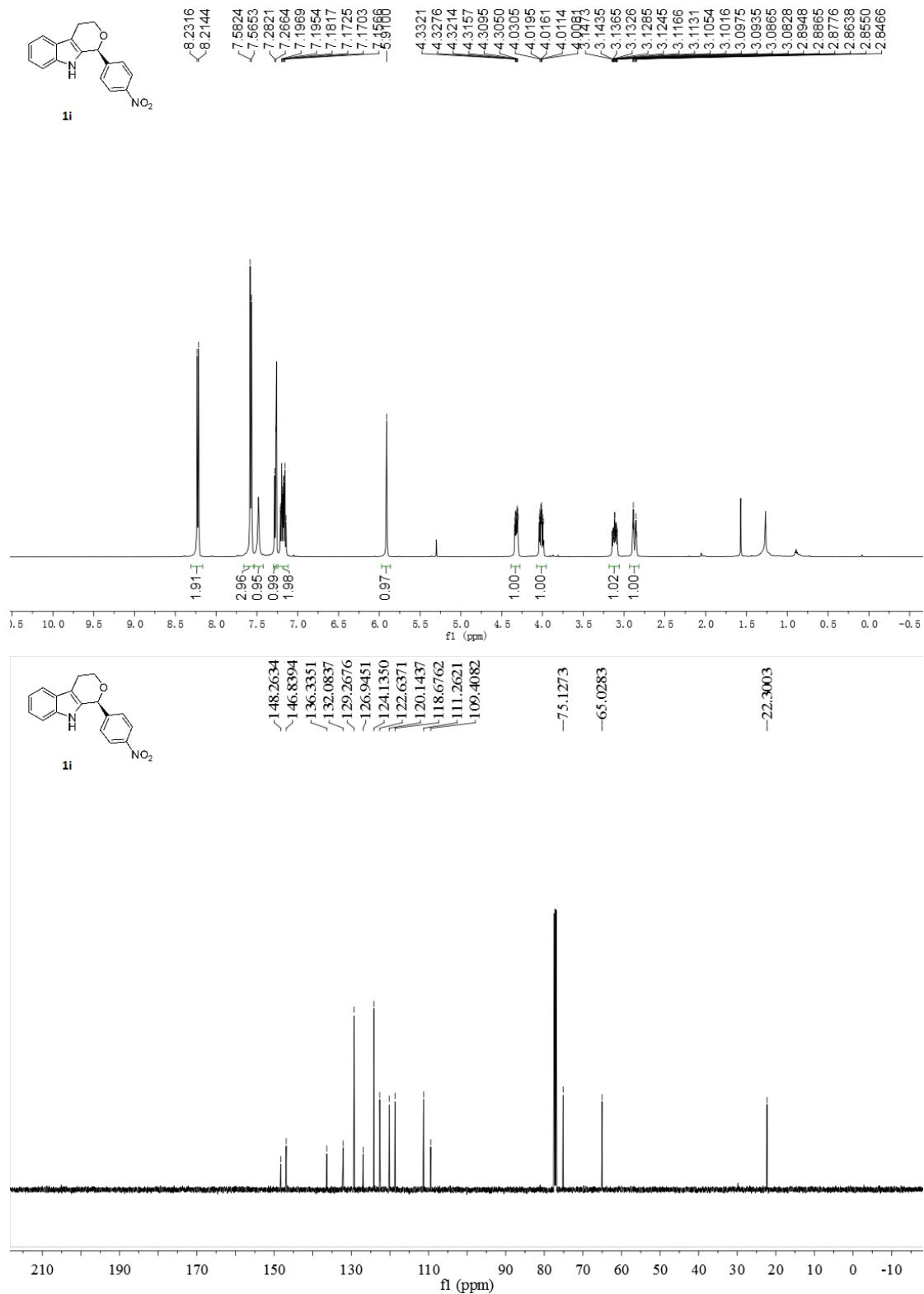


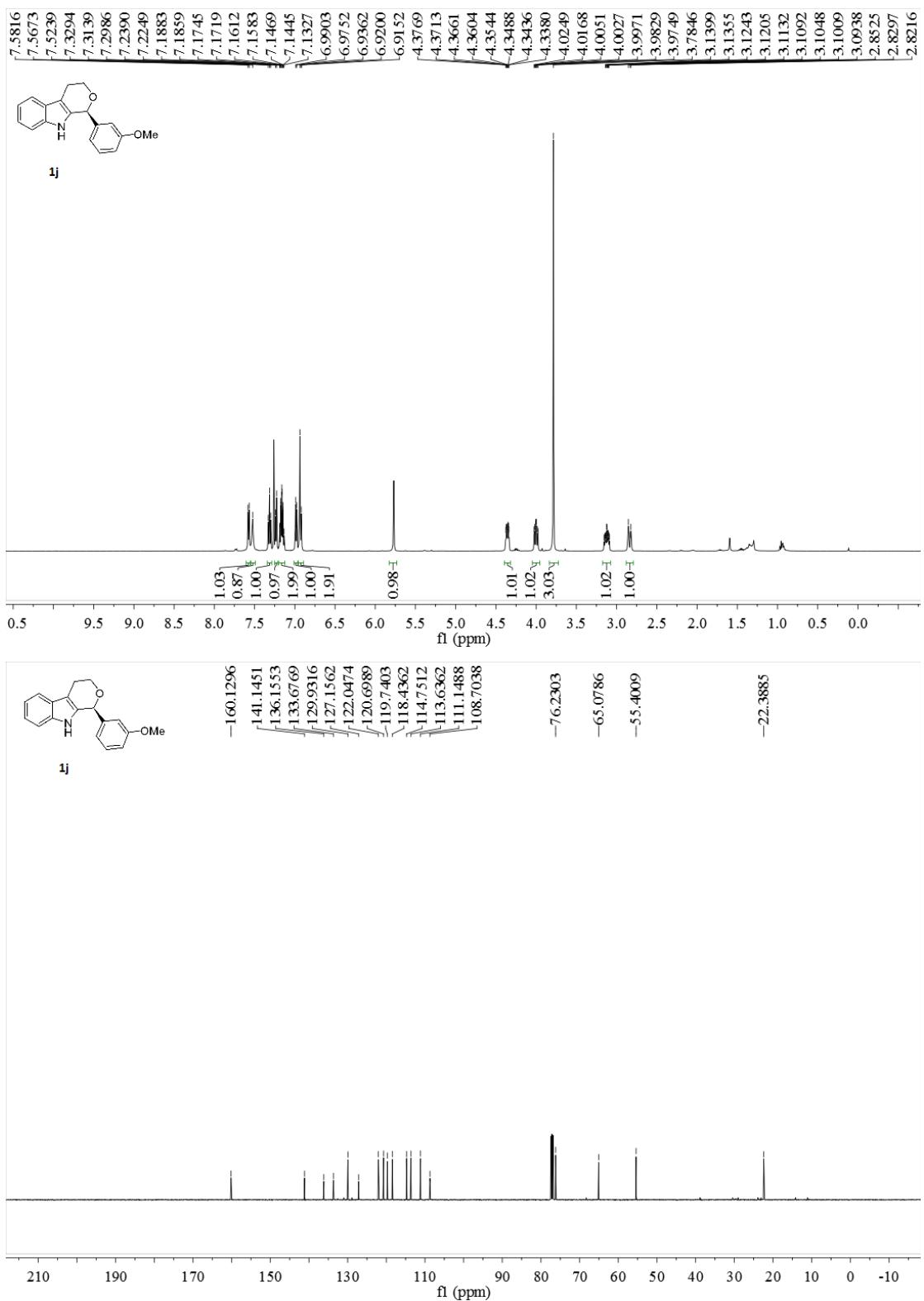


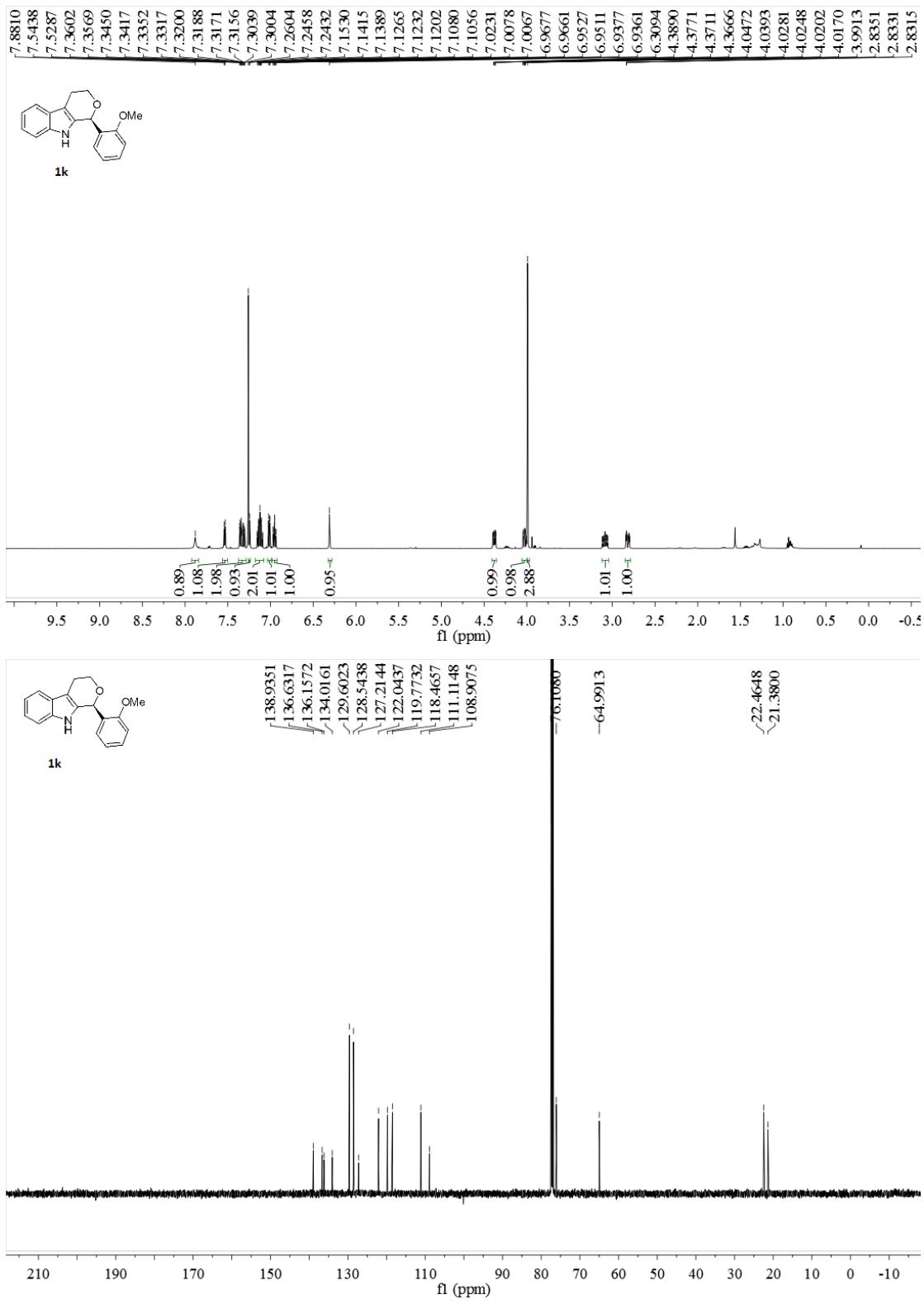


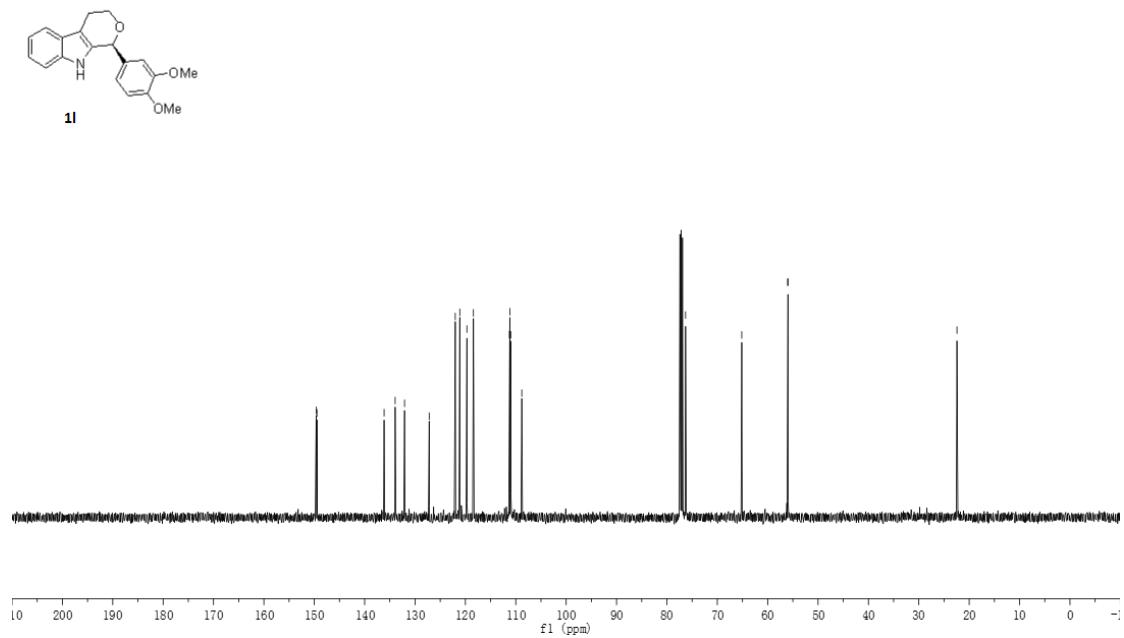
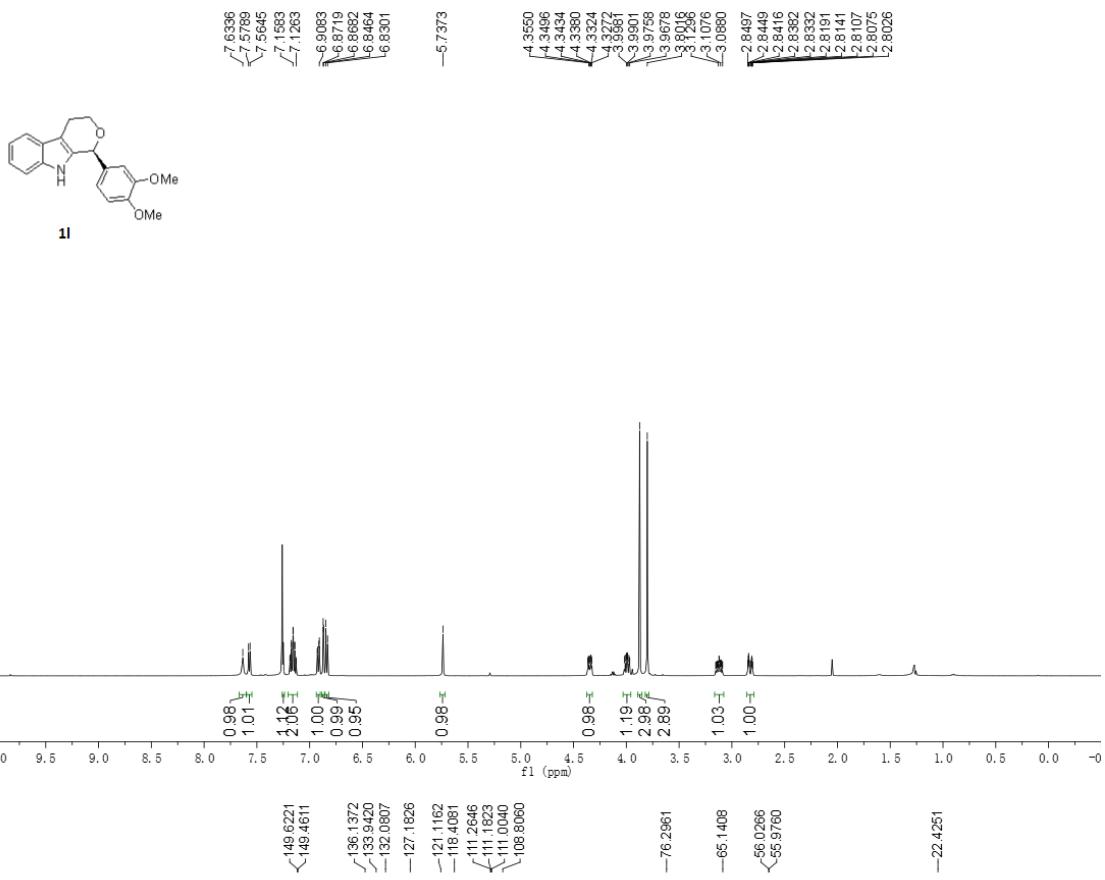


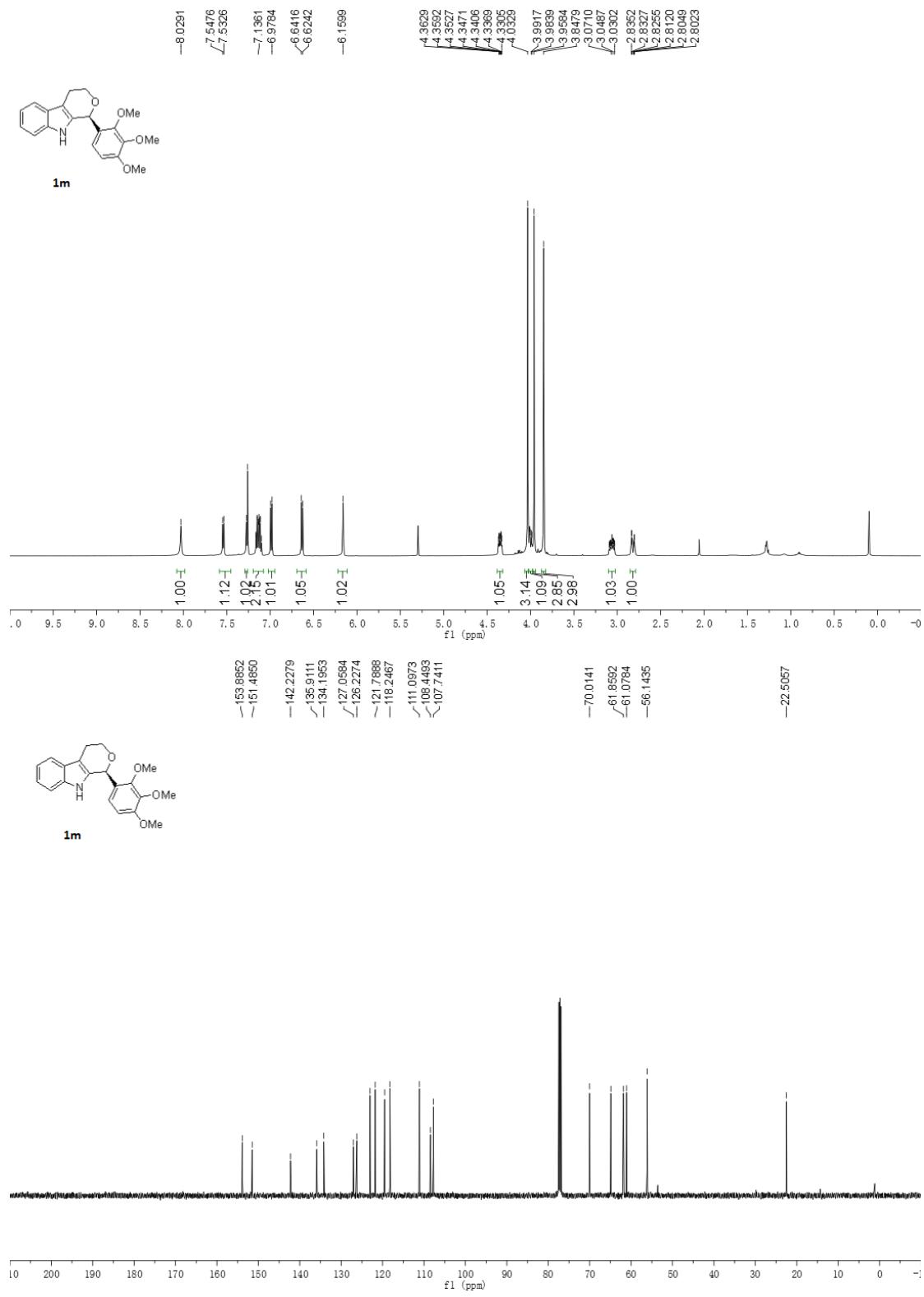


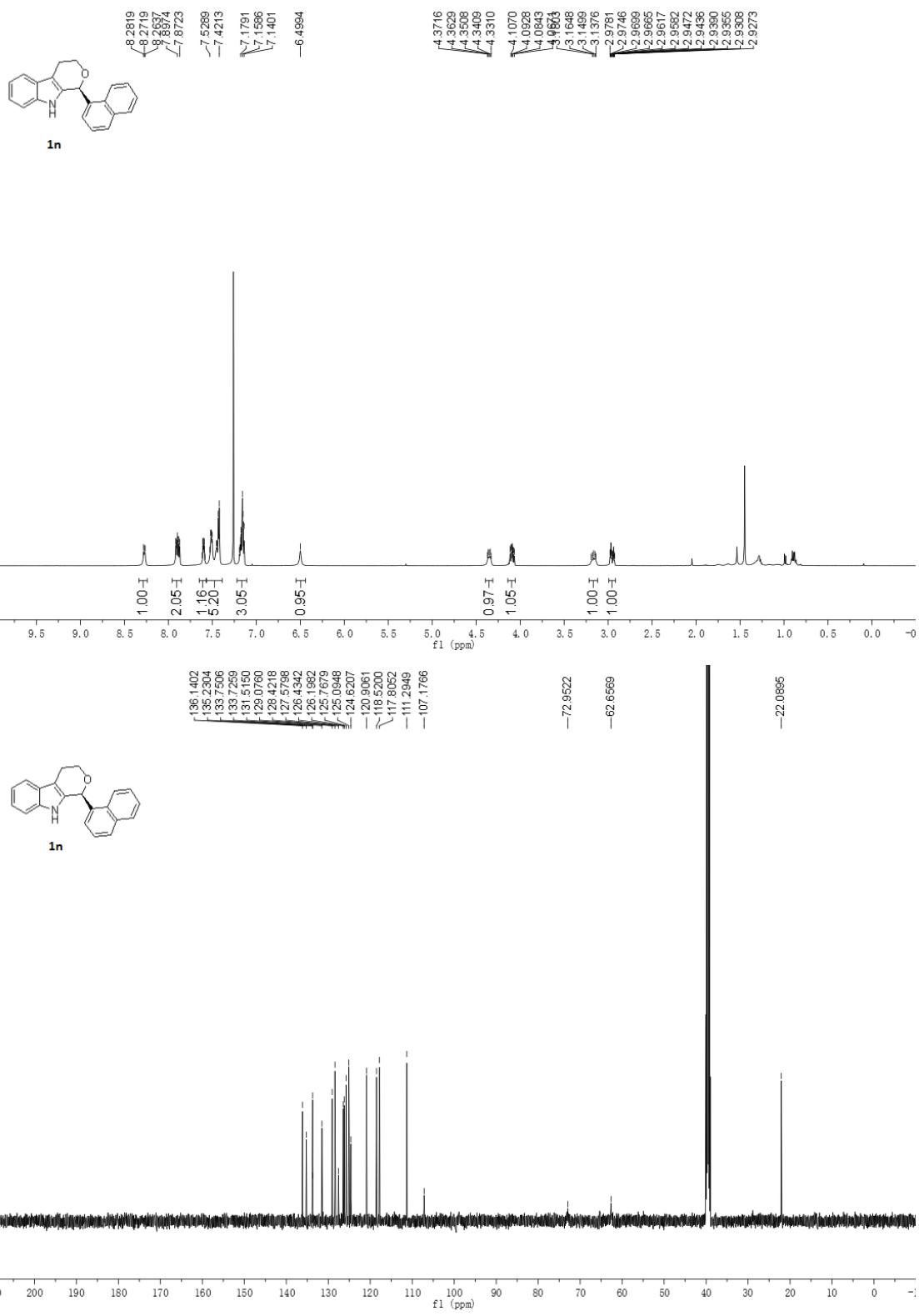


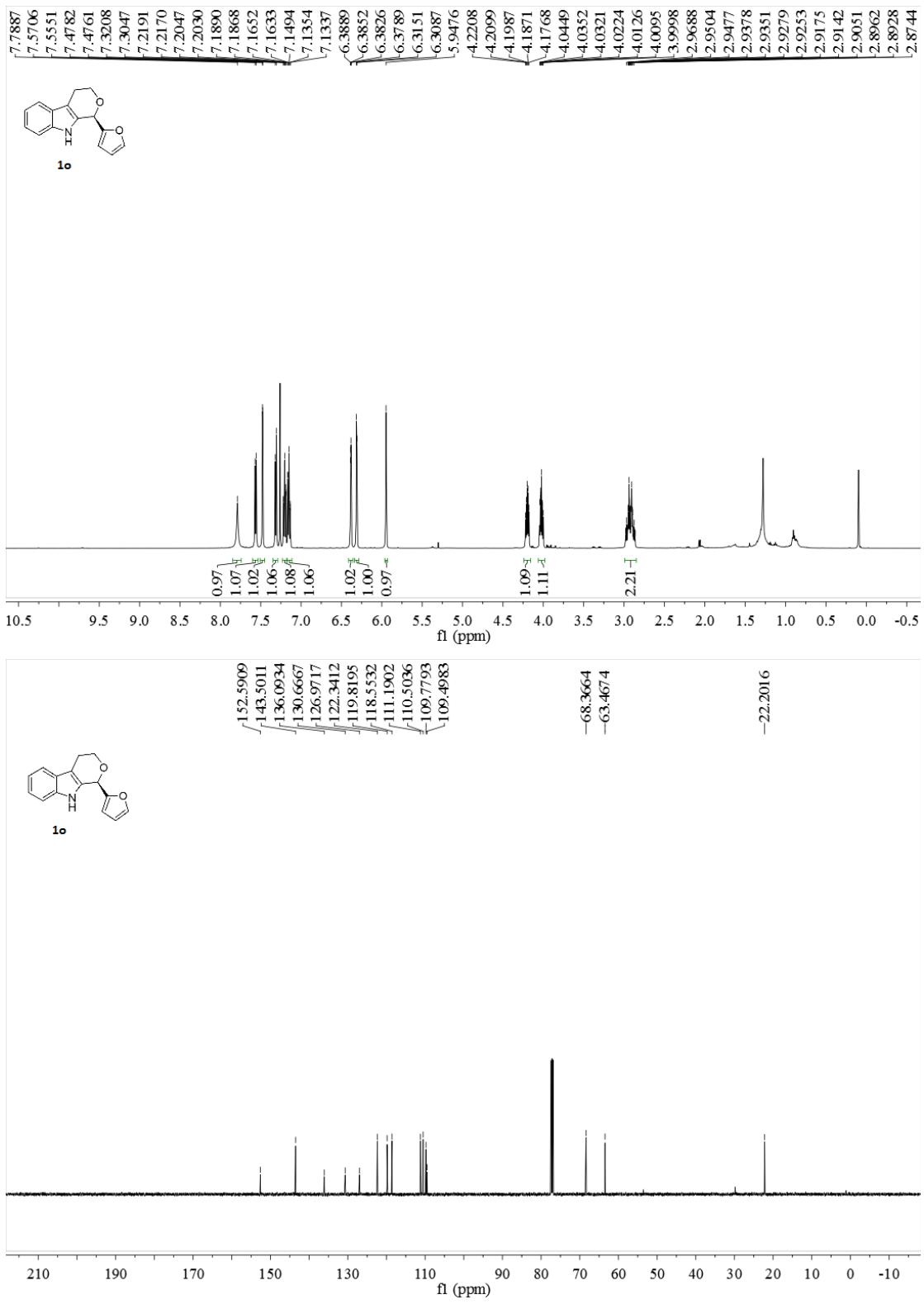


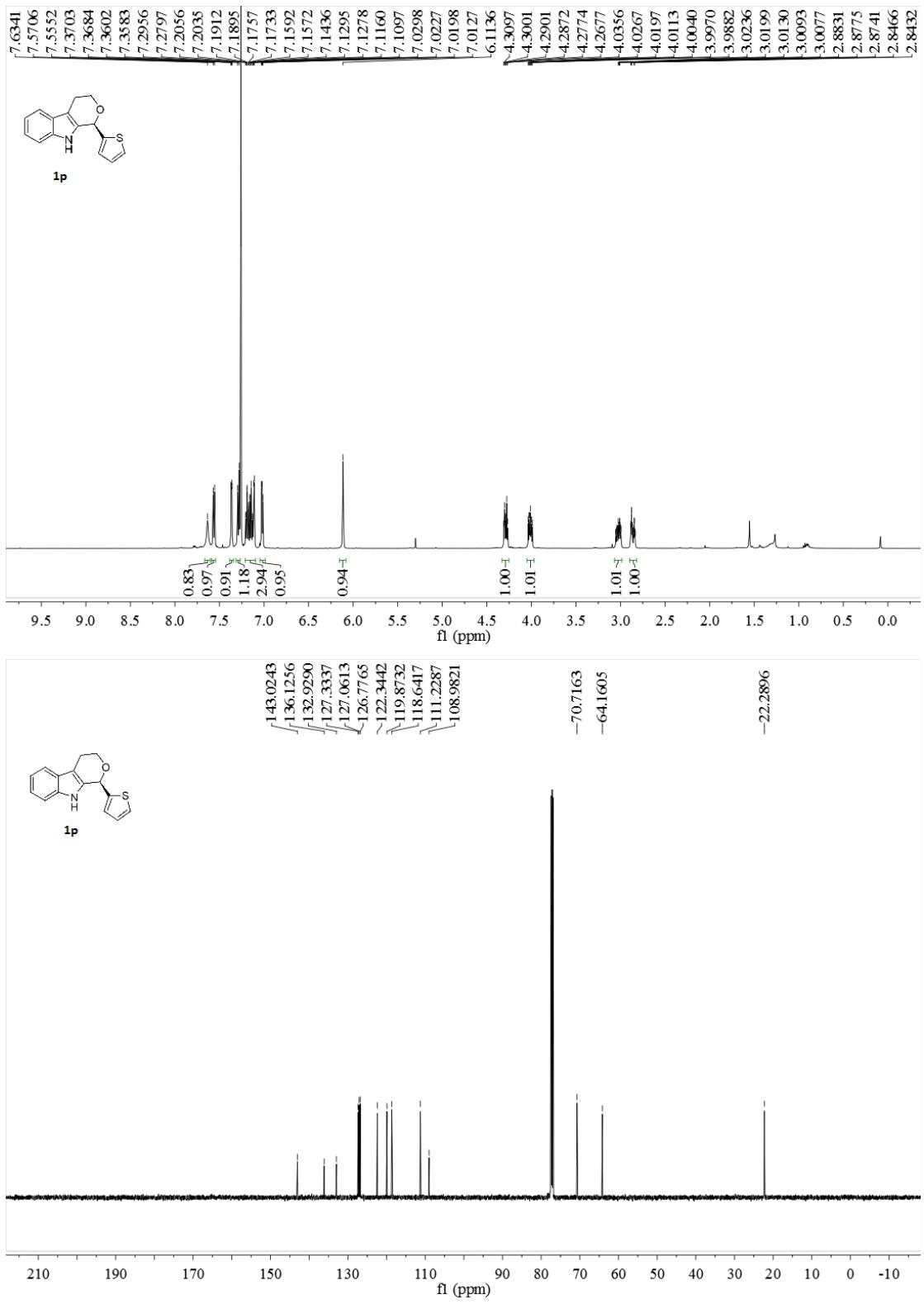


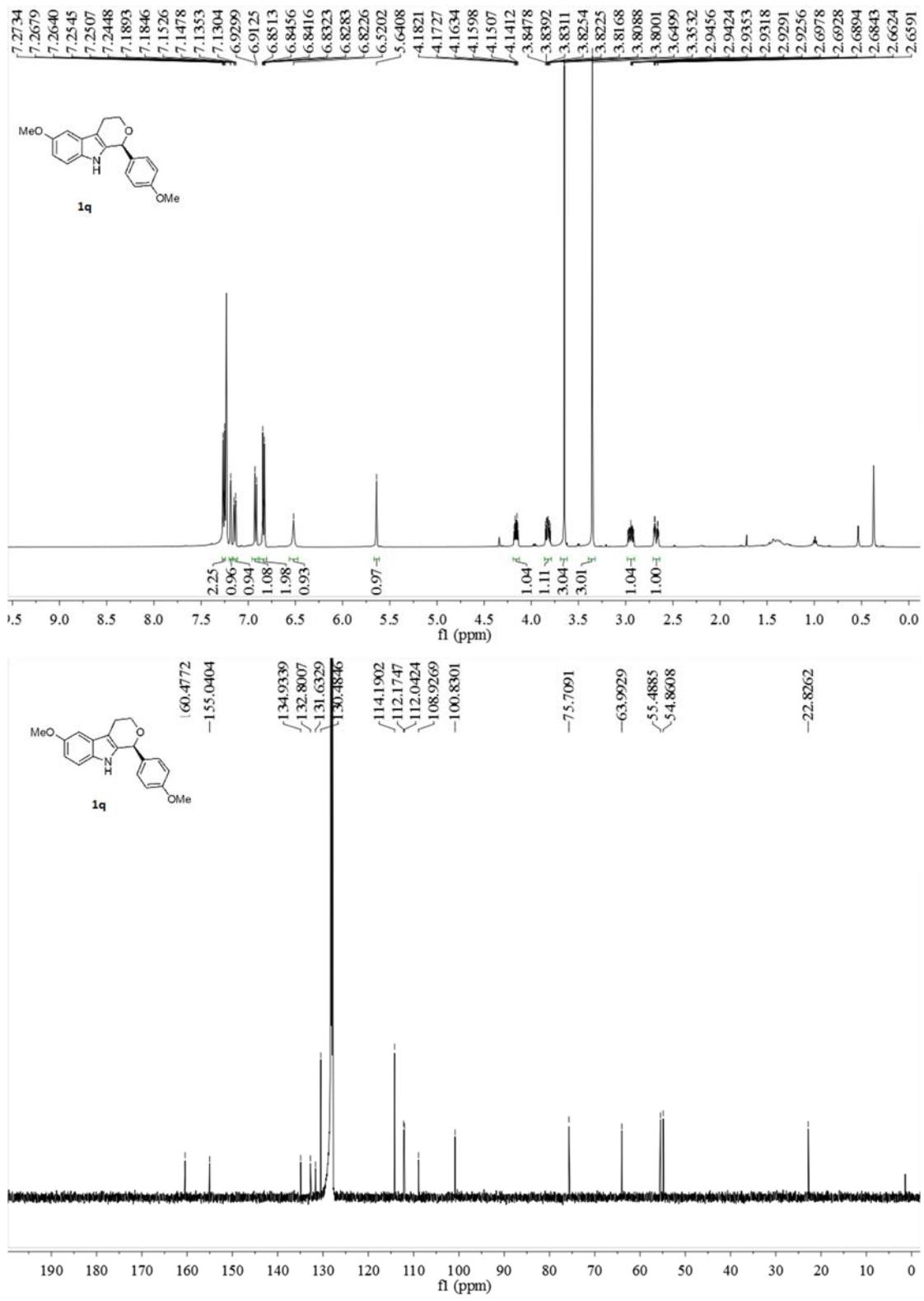


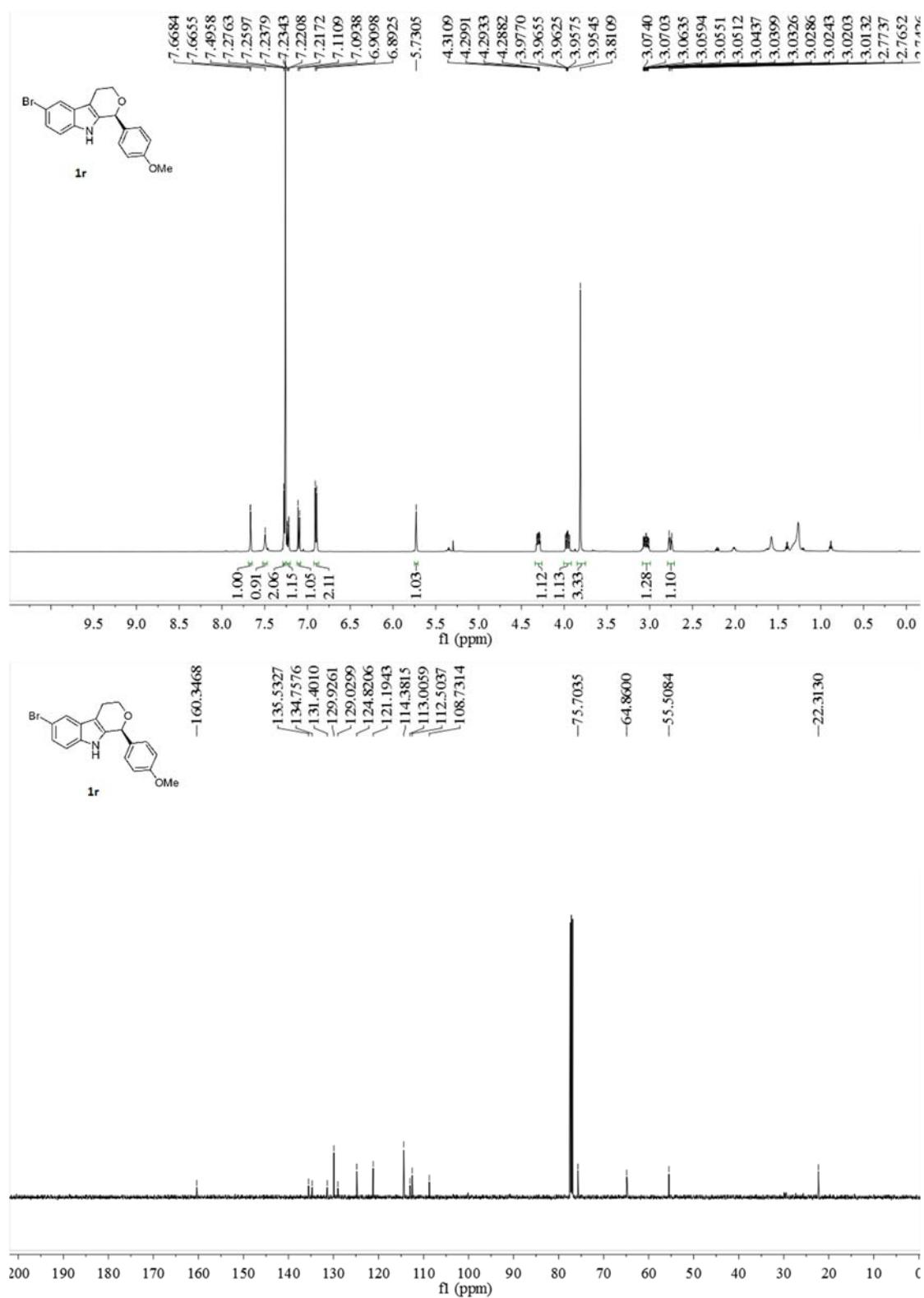


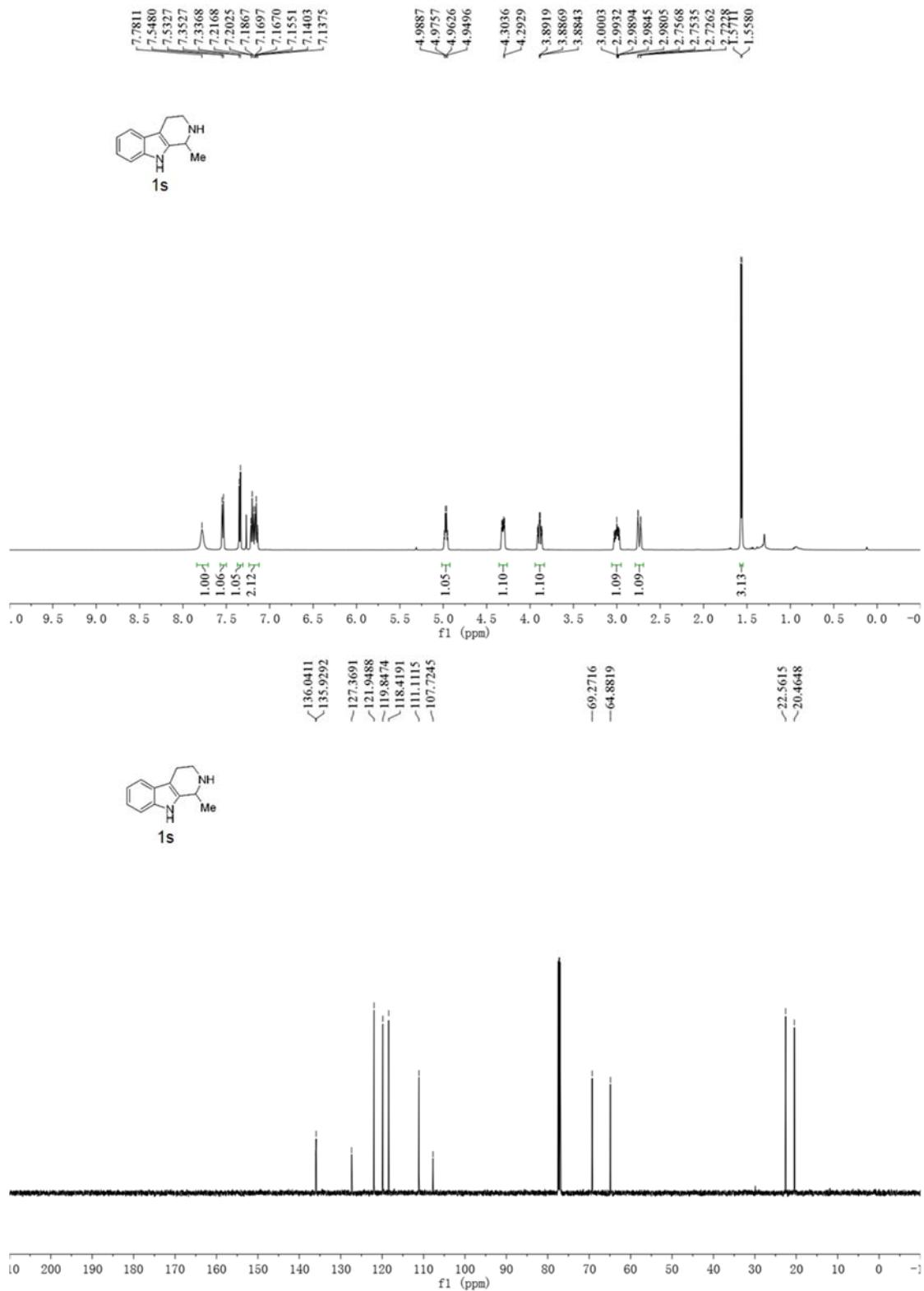


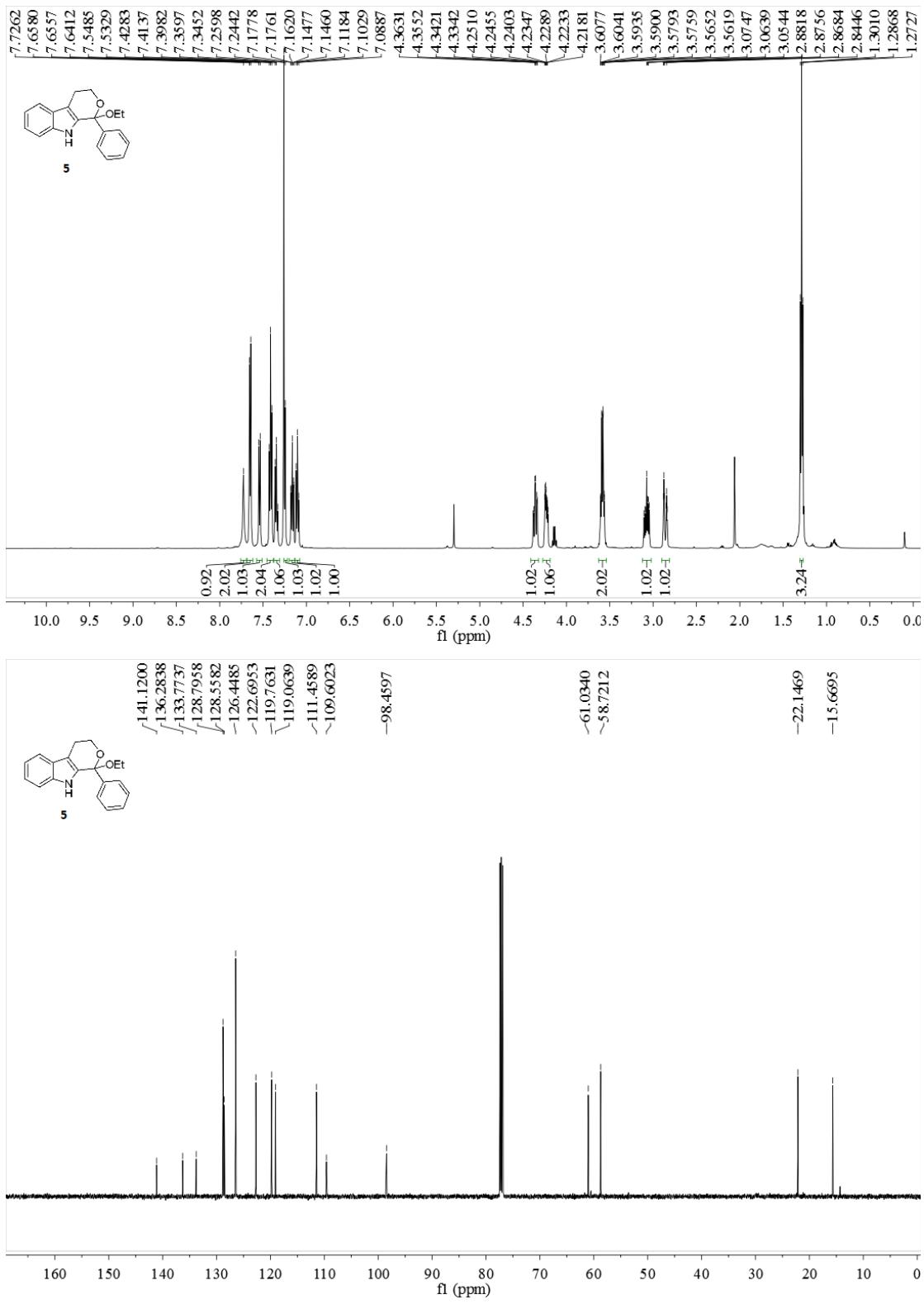




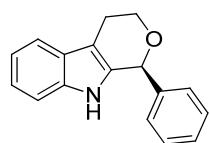






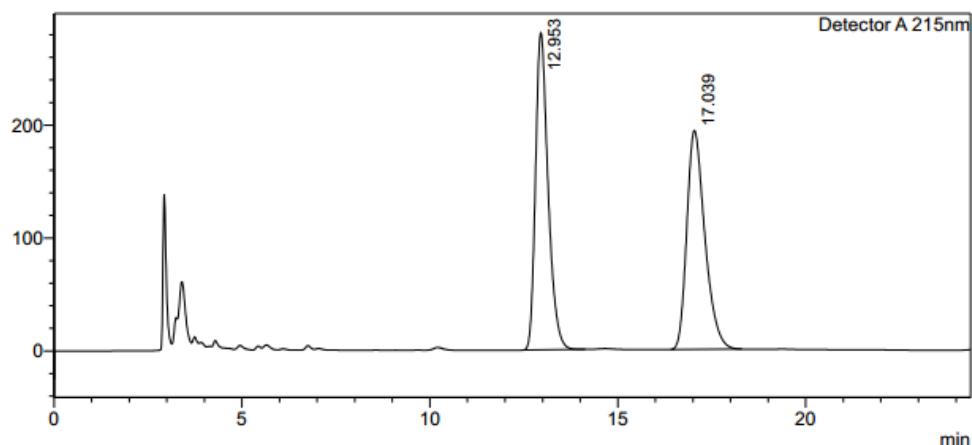


HPLC data



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mV



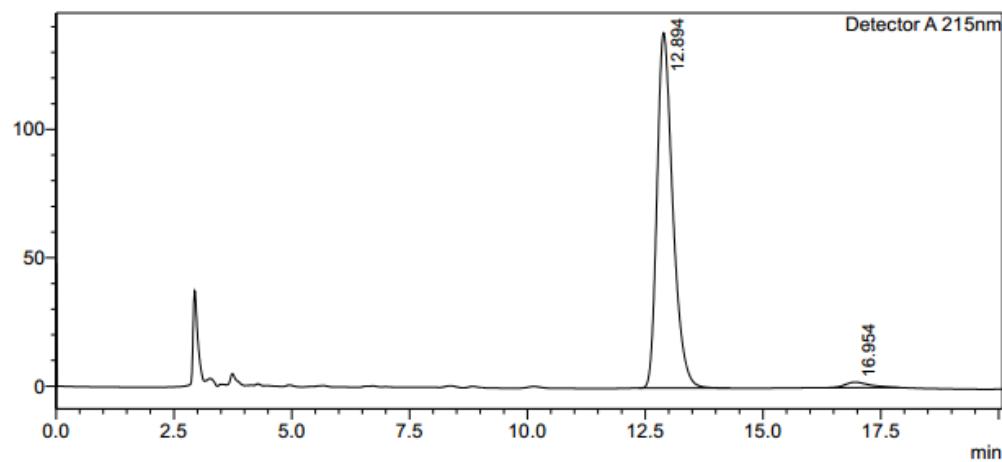
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Detector A 215nm

Peak#	Name	Ret. Time	Area	Area%	Height	Unit	Mark
1		12.953	6543307	50.257	280776		M
2		17.039	6476390	49.743	193781		M
Total			13019696	100.000	474557		

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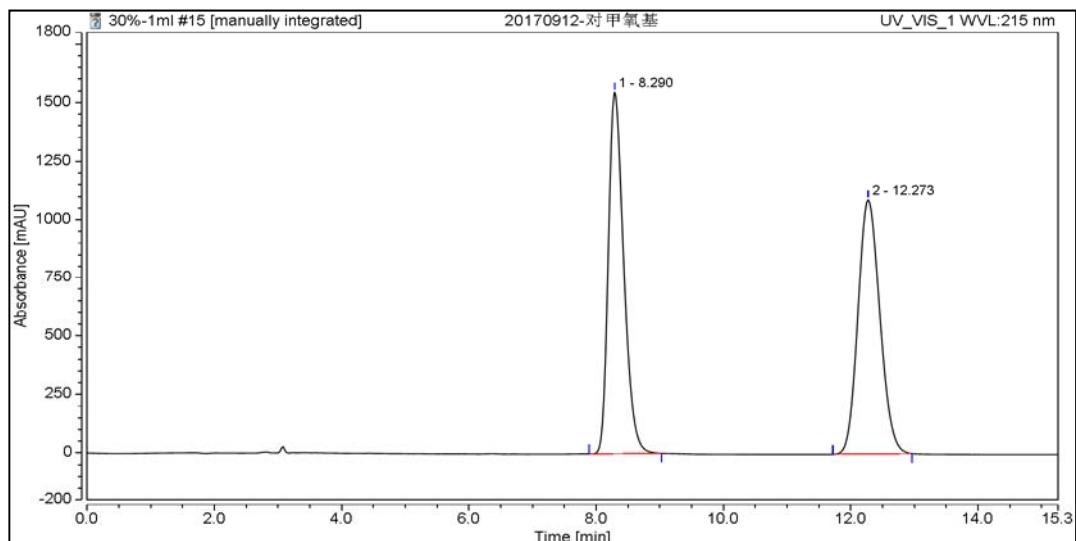
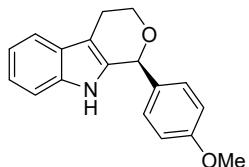
mV



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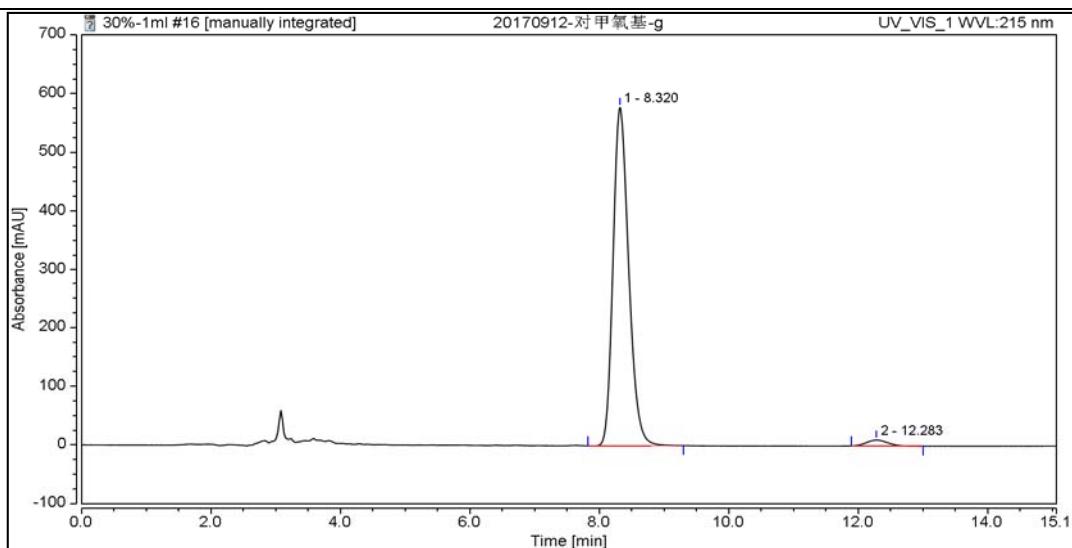
Detector A 215nm

Peak#	Name	Ret. Time	Area	Area%	Height	Unit	Mark
1		12.894	3216533	97.638	138389		M
2		16.954	77810	2.362	2140		M
Total			3294343	100.000	140529		



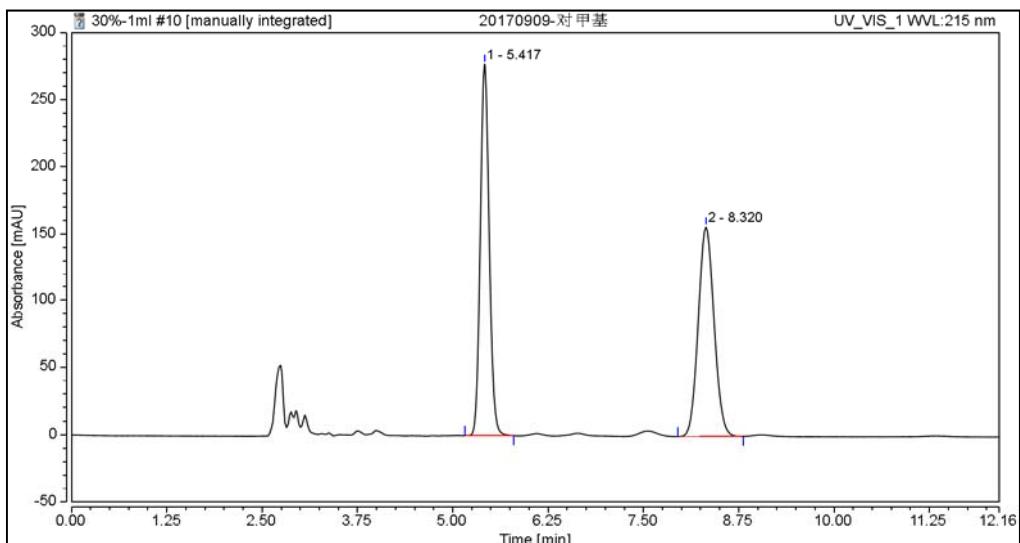
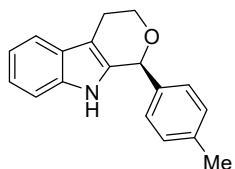
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Relative Area %	Amount n.a.
1		8.290	432.794	49.97	n.a.
2		12.273	433.308	50.03	n.a.
Total:			866.103	100.00	



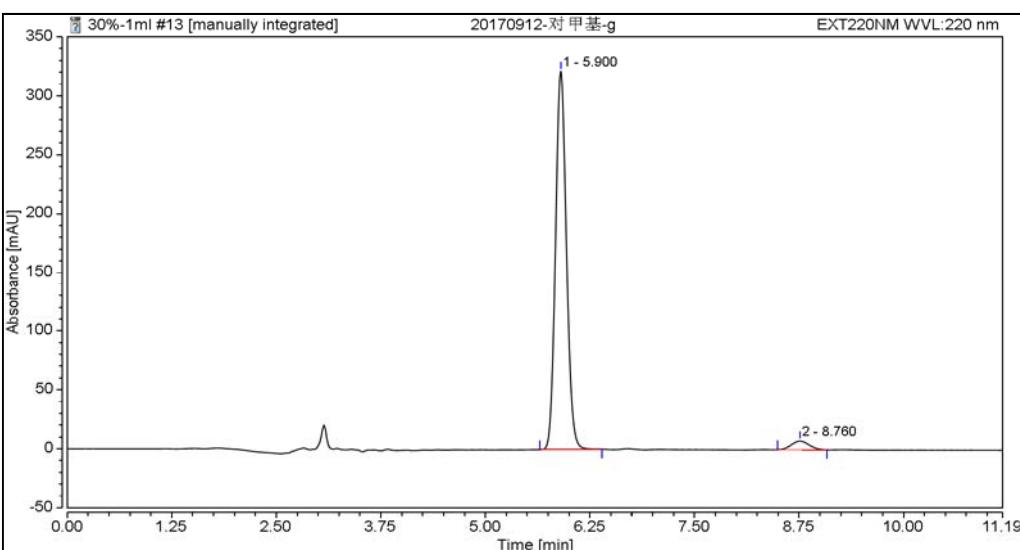
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Relative Area %	Amount n.a.
1		8.320	161.376	97.67	n.a.
2		12.283	3.847	2.33	n.a.
Total:			165.223	100.00	



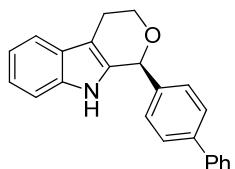
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Relative Area %	Amount n.a.
1		5.417	37.532	50.08	n.a.
2		8.320	37.414	49.92	n.a.
Total:			74.946	100.00	



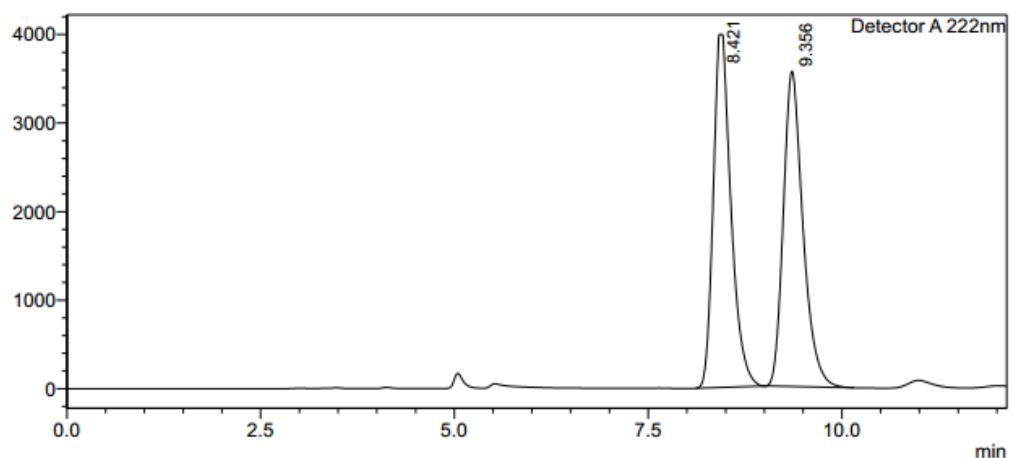
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Relative Area %	Amount n.a.
1		5.900	48.491	96.42	n.a.
2		8.760	1.798	3.58	n.a.
Total:			50.289	100.00	



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mV



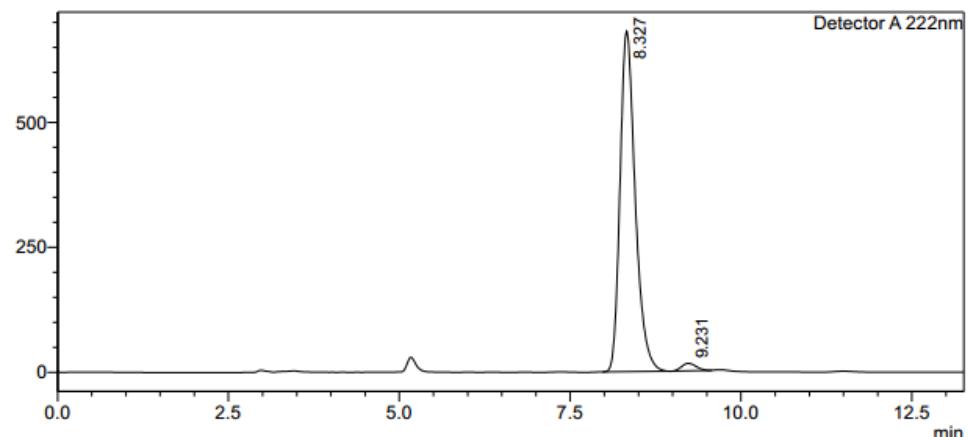
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Detector A 222nm

Peak#	Name	Ret. Time	Area	Area%	Height	Unit	Mark
1		8.421	63362099	50.255	3986372		M
2		9.356	62718785	49.745	3557627		M
Total			126080885	100.000	7543999		

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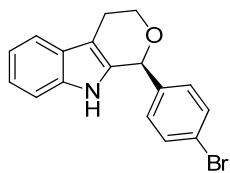
mV



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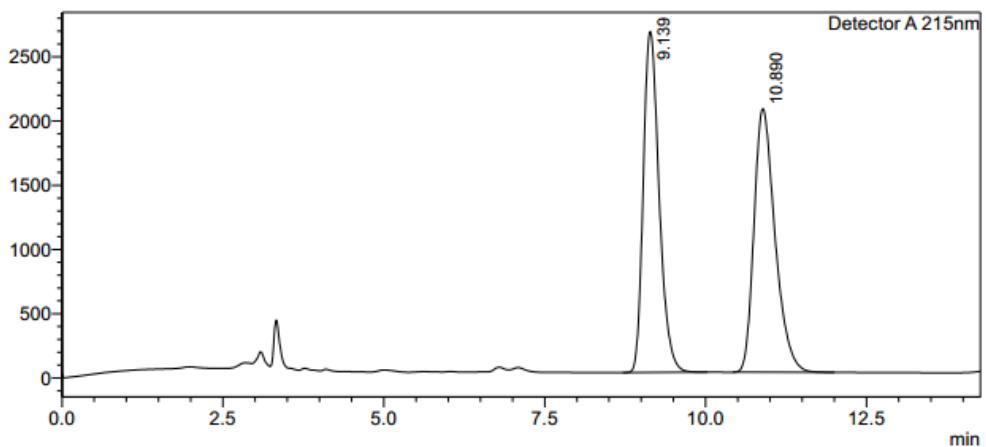
Detector A 222nm

Peak#	Name	Ret. Time	Area	Area%	Height	Unit	Mark
1		8.327	10540500	97.936	680600		M
2		9.231	222186	2.064	14910		M
Total			10762686	100.000	695510		



<Chromatogram>

mV

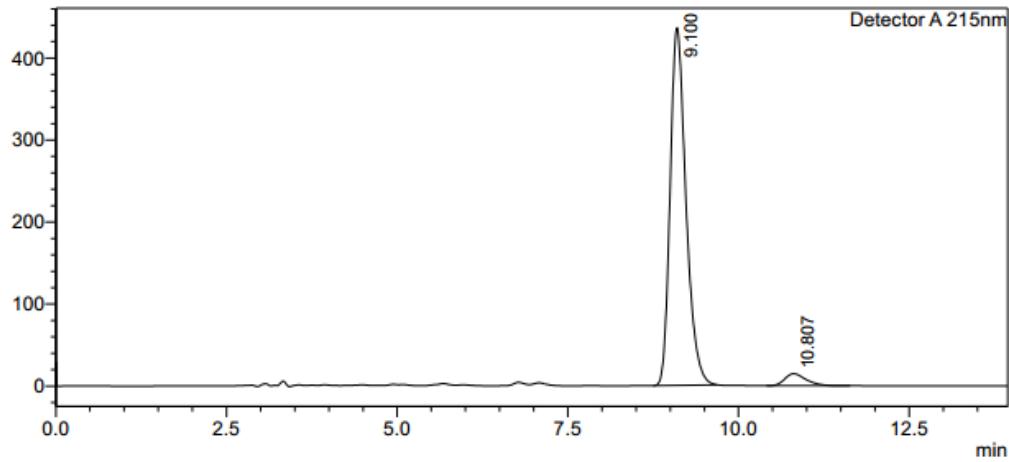

<Peak Table>

Detector A 215nm

Peak#	Name	Ret. Time	Area	Area%	Height	Unit	Mark
1		9.139	45558130	49.372	2652674		M
2		10.890	46717254	50.628	2051583		M
Total			92275384	100.000	4704258		

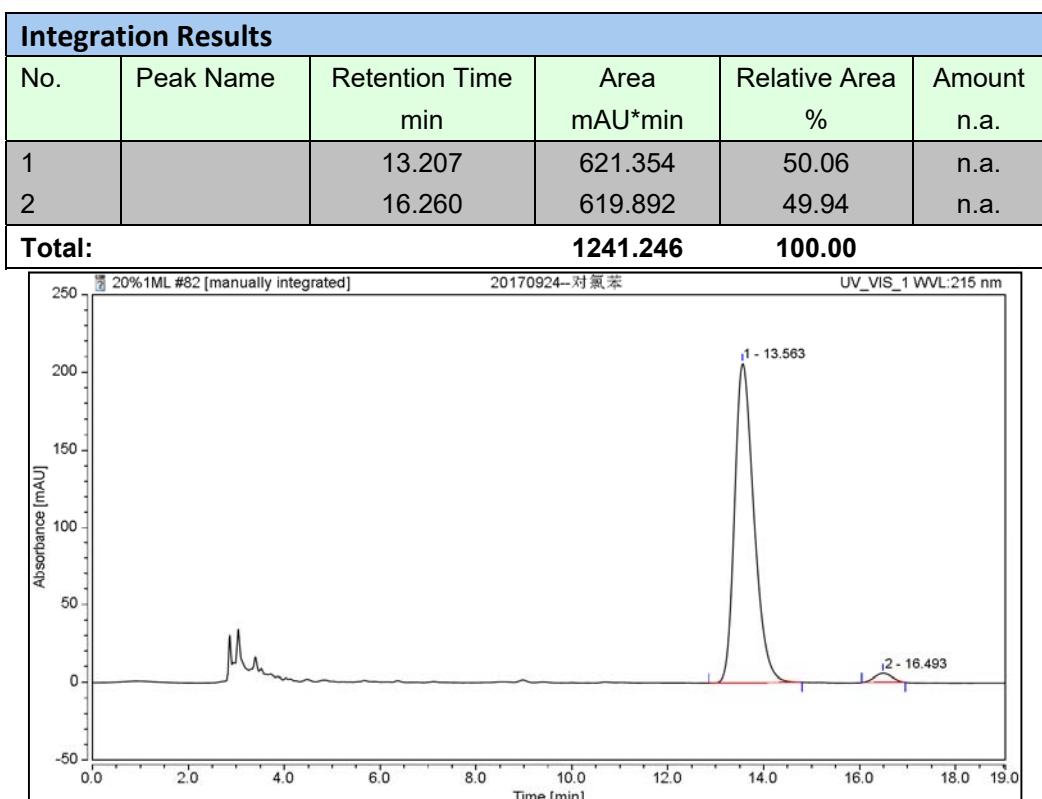
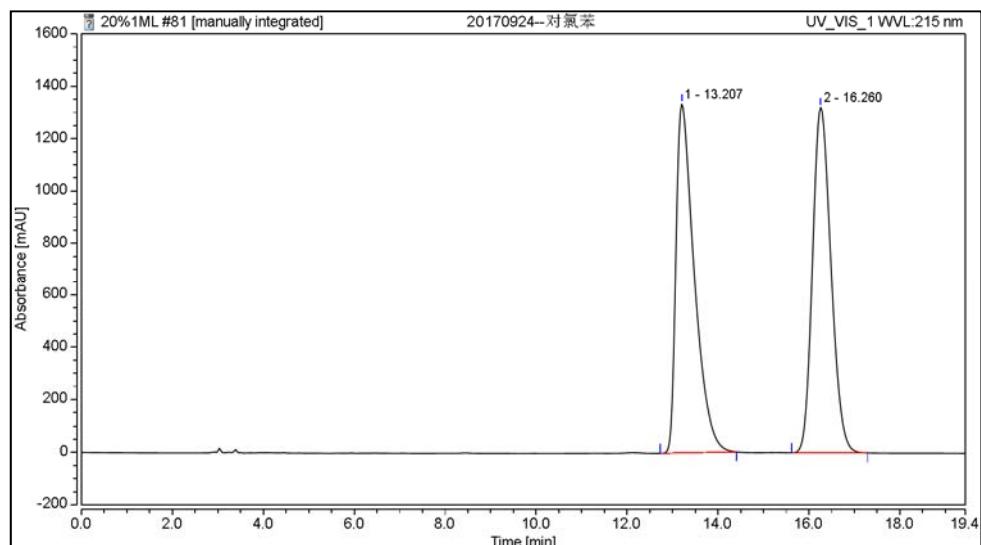
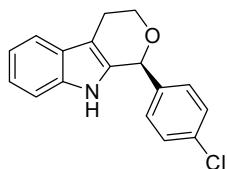
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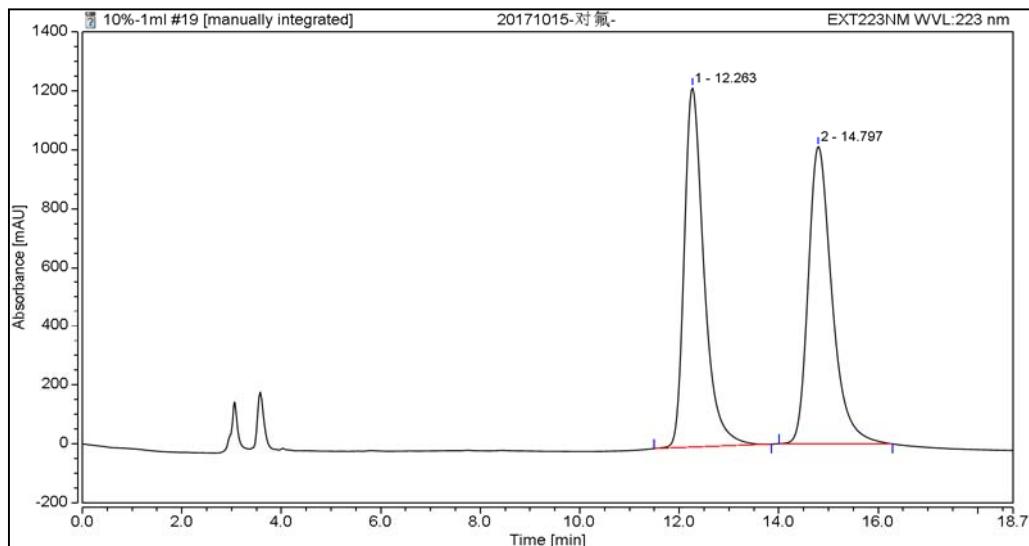
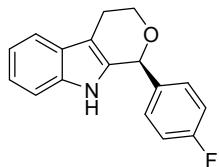
mV


<Peak Table>

Detector A 215nm

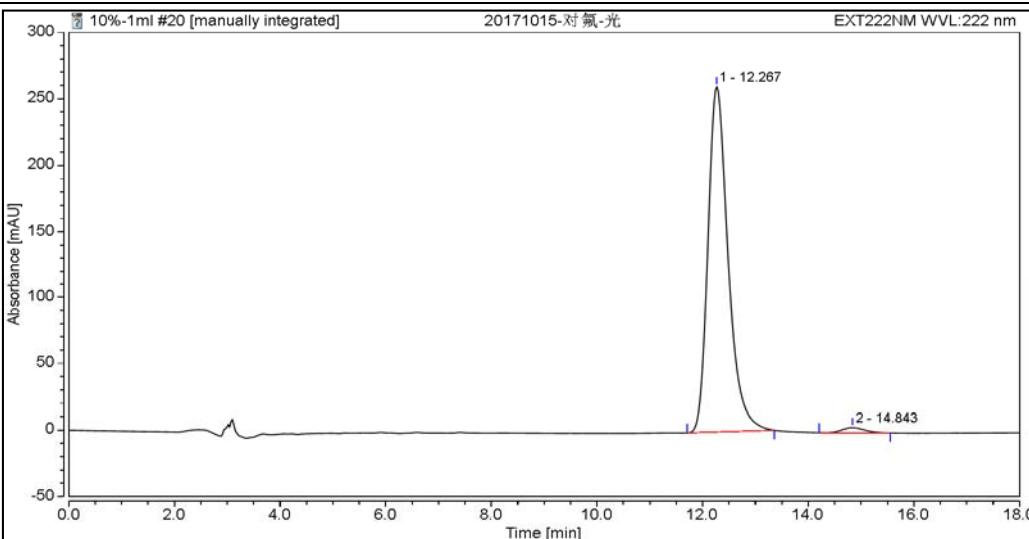
Peak#	Name	Ret. Time	Area	Area%	Height	Unit	Mark
1		9.100	7036217	95.703	435503		M
2		10.807	315908	4.297	14663		M
Total			7352125	100.000	450166		





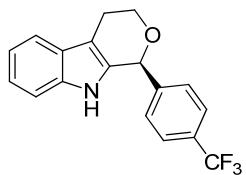
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Relative Area %	Amount
1		12.263	560.505	50.09	n.a.
2		14.797	558.451	49.91	n.a.
Total:			1118.956	100.00	



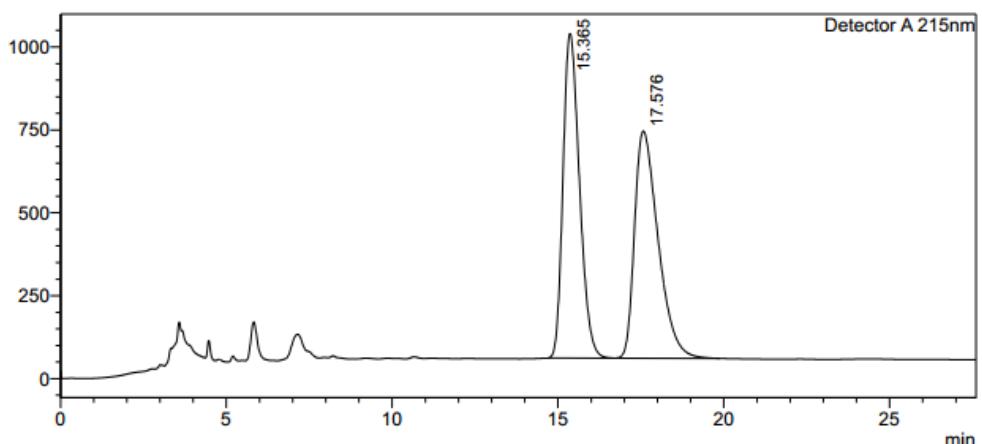
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Relative Area %	Amount
1		12.267	114.959	98.37	n.a.
2		14.843	1.903	1.63	n.a.
Total:			116.863	100.00	



<Chromatogram>

mV



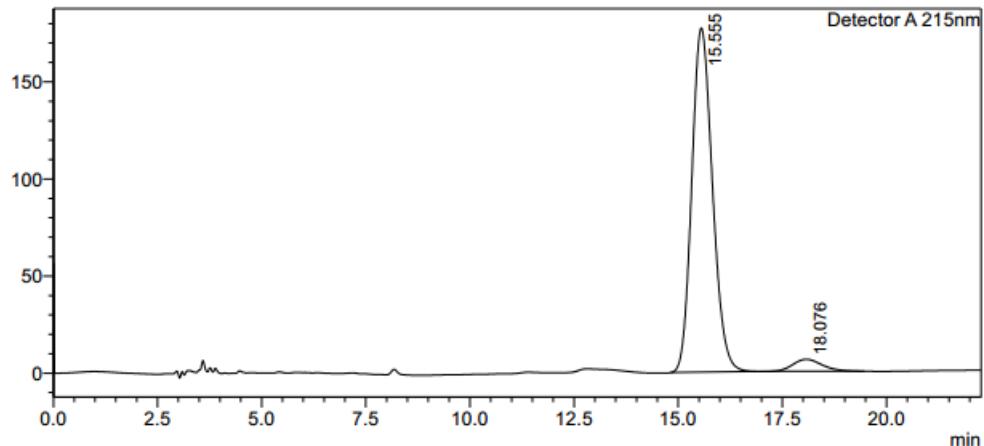
<Peak Table>

Detector A 215nm

Peak#	Name	Ret. Time	Area	Area%	Height	Unit	Mark
1		15.365	33758532	49.930	978664		M
2		17.576	33853855	50.070	684755		M
Total			67612387	100.000	1663419		

<Chromatogram>

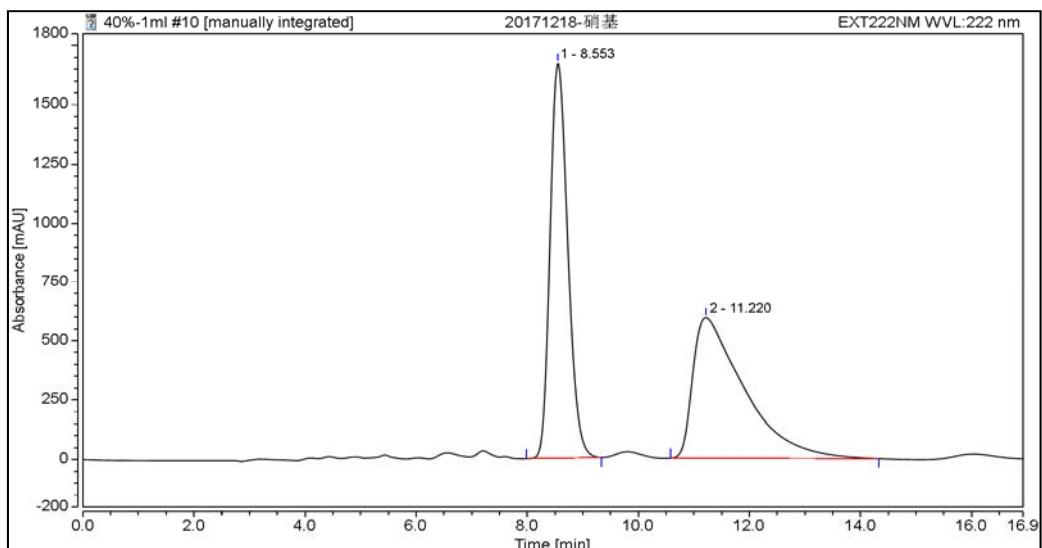
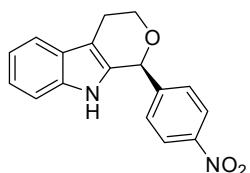
mV



<Peak Table>

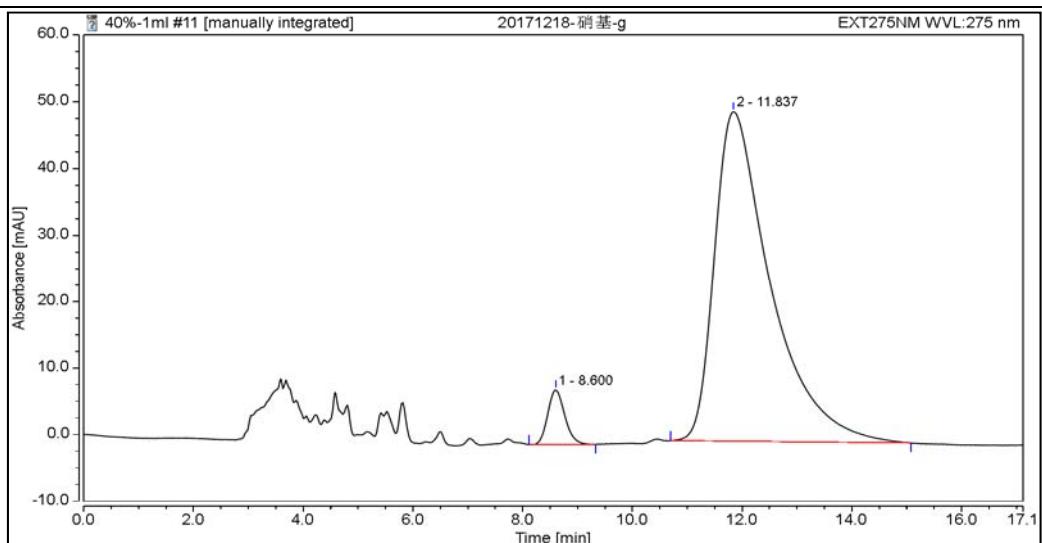
Detector A 215nm

Peak#	Name	Ret. Time	Area	Area%	Height	Unit	Mark
1		15.555	6129126	95.325	177180		M
2		18.076	300590	4.675	6149		M
Total			6429717	100.000	183328		



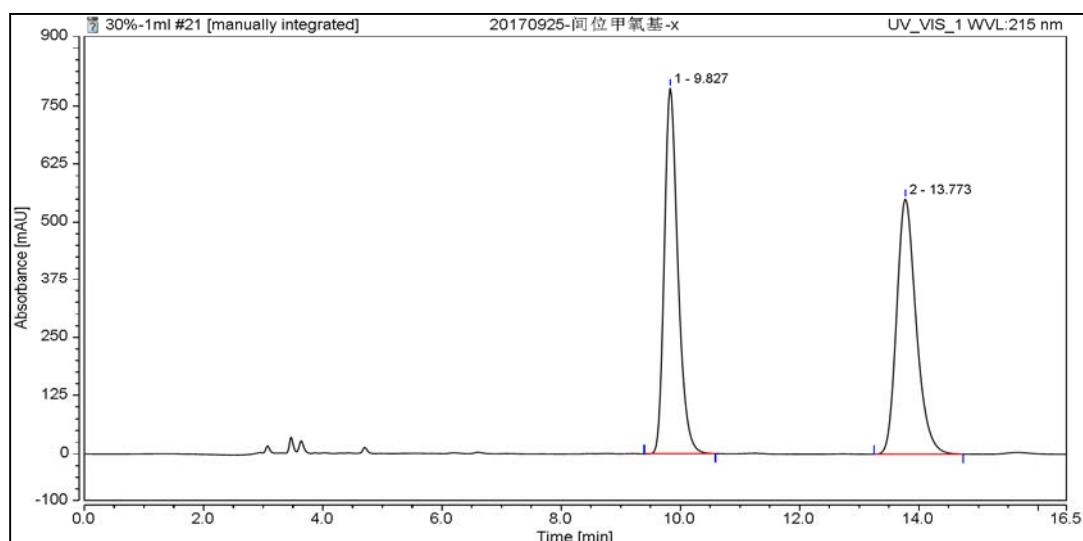
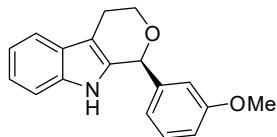
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Relative Area %	Amount
1		8.553	616.234	49.34	n.a.
2		11.220	632.792	50.66	n.a.
Total:			1249.026	100.00	



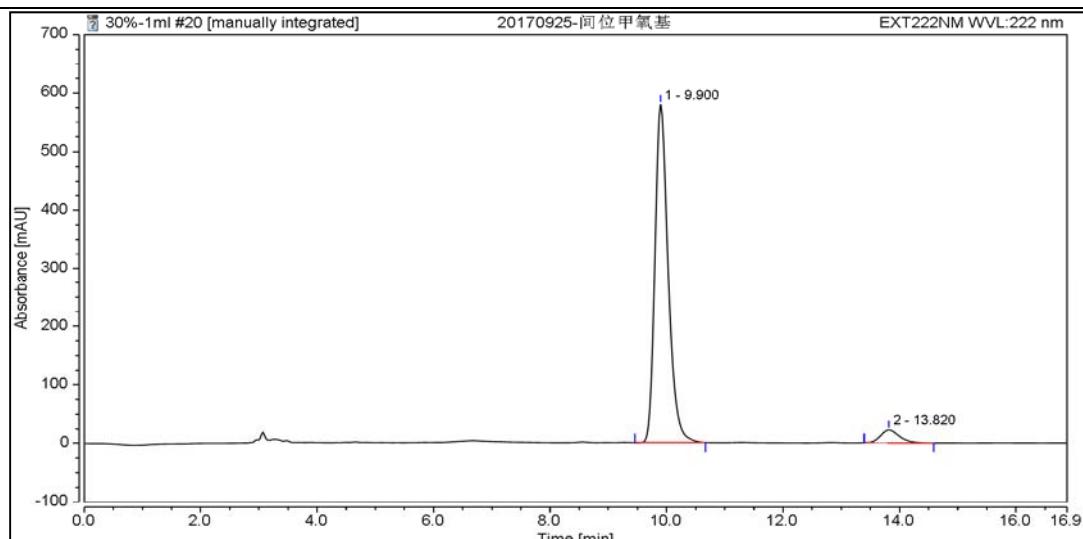
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Relative Area %	Amount
1		8.600	2.925	4.76	n.a.
2		11.837	58.540	95.24	n.a.
Total:			61.465	100.00	



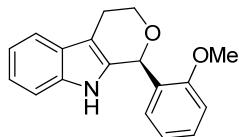
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Relative Area %	Amount n.a.
1		9.827	207.708	49.97	n.a.
2		13.773	207.920	50.03	n.a.
Total:			415.628	100.00	



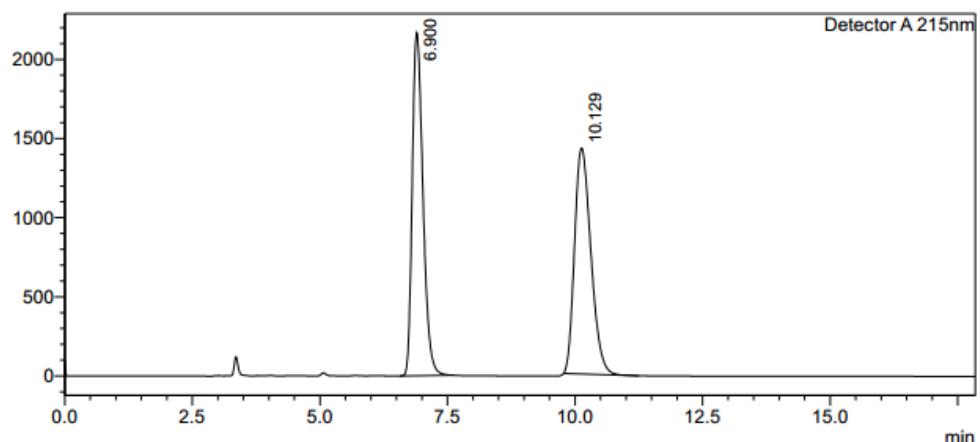
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Relative Area %	Amount n.a.
1		9.900	152.269	94.83	n.a.
2		13.820	8.294	5.17	n.a.
Total:			160.563	100.00	



<Chromatogram>

mV



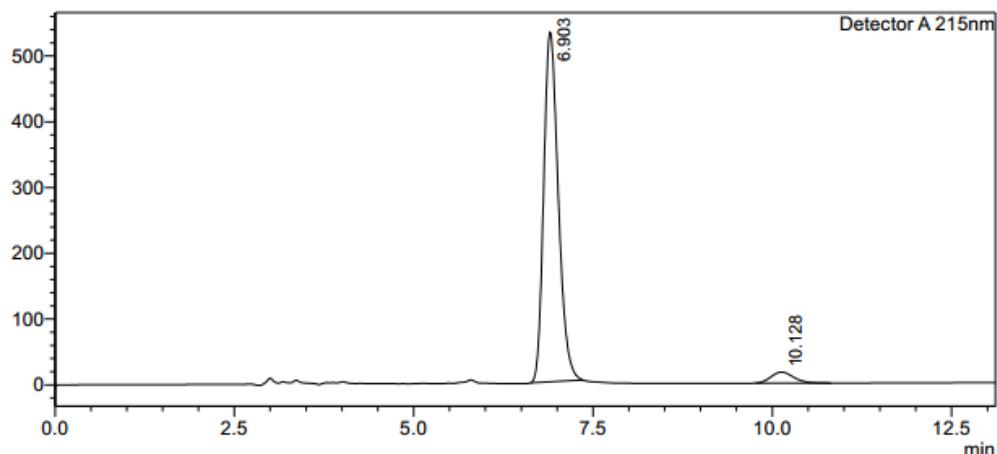
<Peak Table>

Detector A 215nm

Peak#	Name	Ret. Time	Area	Area%	Height	Unit	Mark
1		6.900	31676338	49.874	2165593		M
2		10.129	31836849	50.126	1426718		M
Total			63513187	100.000	3592311		

<Chromatogram>

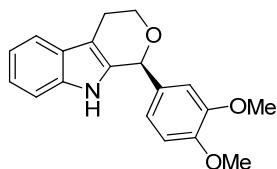
mV



<Peak Table>

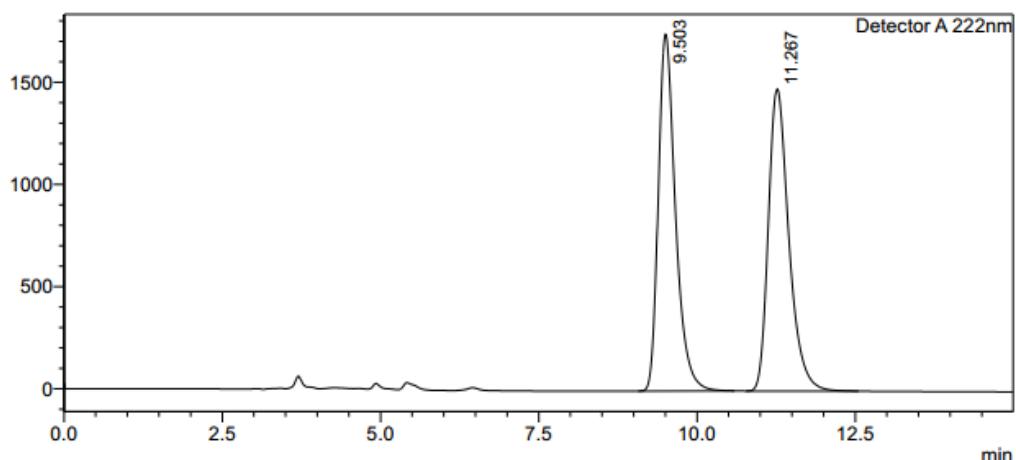
Detector A 215nm

Peak#	Name	Ret. Time	Area	Area%	Height	Unit	Mark
1		6.903	7521699	95.375	531451		M
2		10.128	364782	4.625	16619		M
Total			7886481	100.000	548070		



<Chromatogram>

mV

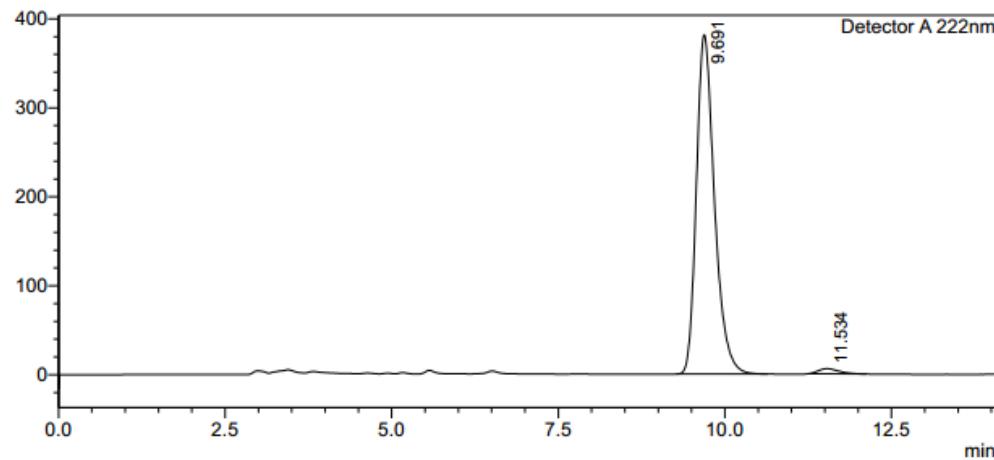

<Peak Table>

Detector A 222nm

Peak#	Name	Ret. Time	Area	Area%	Height	Unit	Mark
1		9.503	32983524	49.853	1745112		M
2		11.267	33178644	50.147	1477386		M
Total			66162169	100.000	3222498		

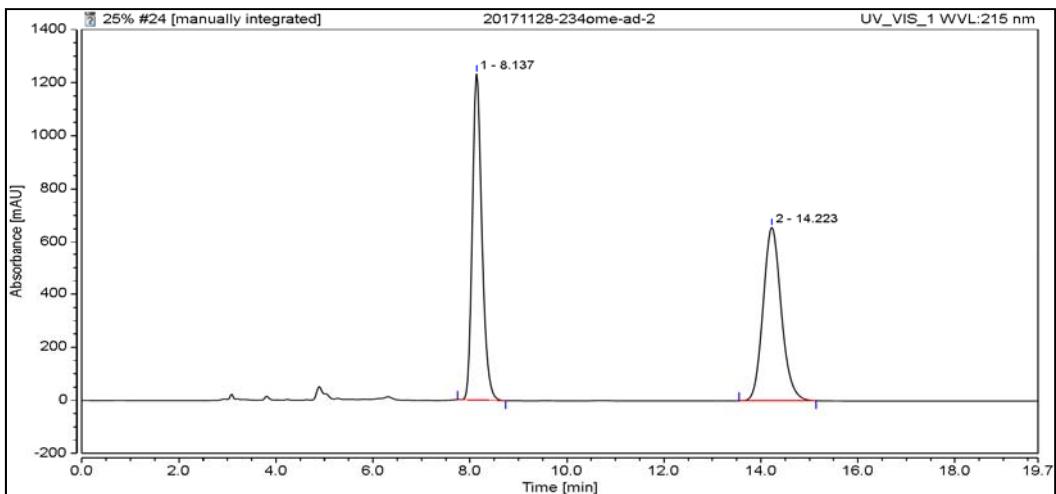
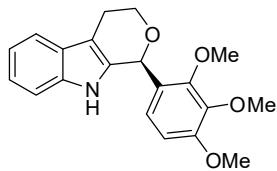
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mV


<Peak Table>

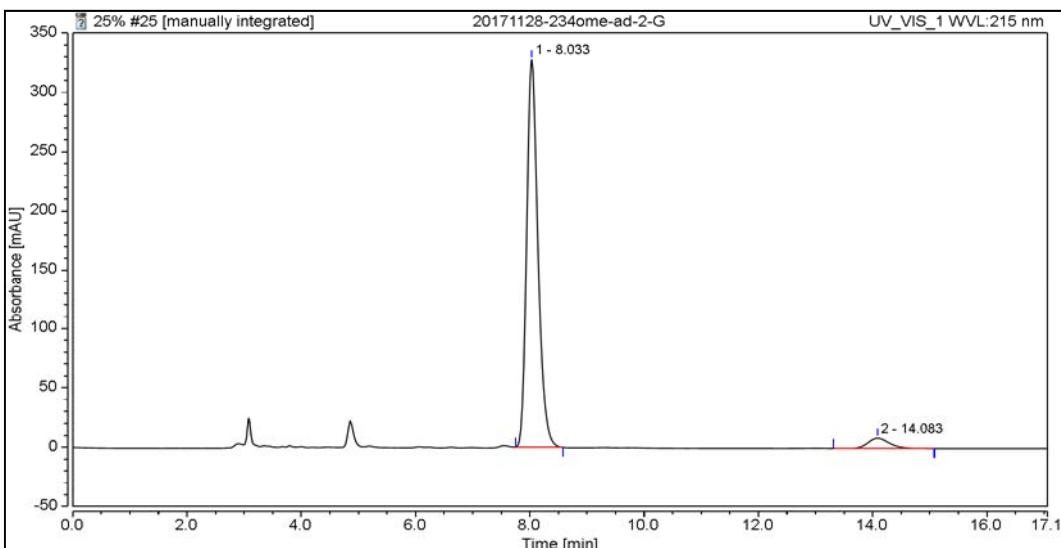
Detector A 222nm

Peak#	Name	Ret. Time	Area	Area%	Height	Unit	Mark
1		9.691	7205524	98.272	381076		M
2		11.534	126709	1.728	5857		M
Total			7332234	100.000	386933		



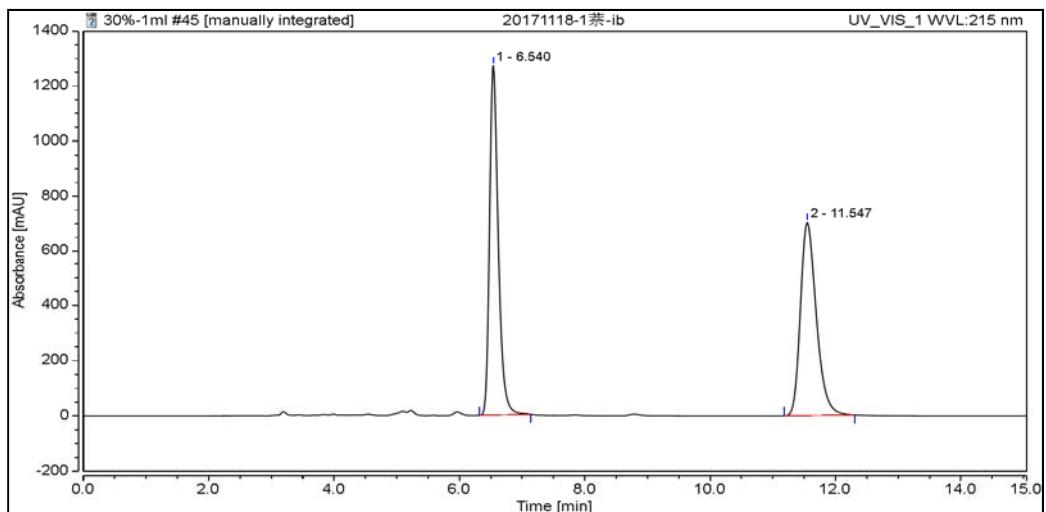
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Relative Area %	Amount n.a.
1		8.137	281.487	49.76	n.a.
2		14.223	284.257	50.24	n.a.
Total:			565.744	100.00	



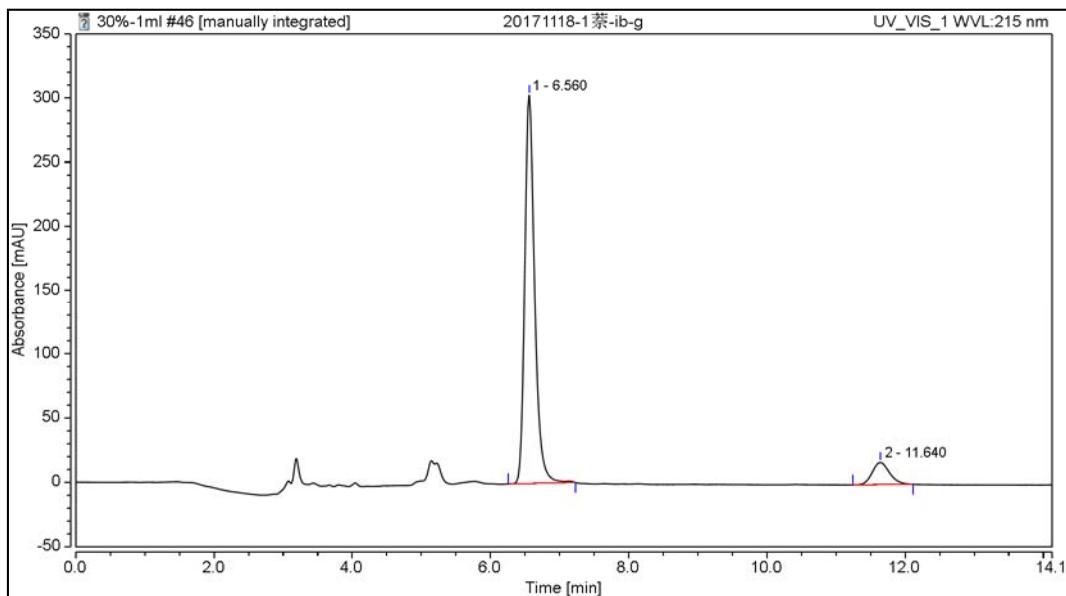
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Relative Area %	Amount n.a.
1		8.033	74.576	95.12	n.a.
2		14.083	3.822	4.88	n.a.
Total:			78.398	100.00	



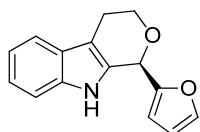
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Relative Area %	Amount n.a.
1		6.540	204.725	49.87	n.a.
2		11.547	205.781	50.13	n.a.
Total:			410.506	100.00	



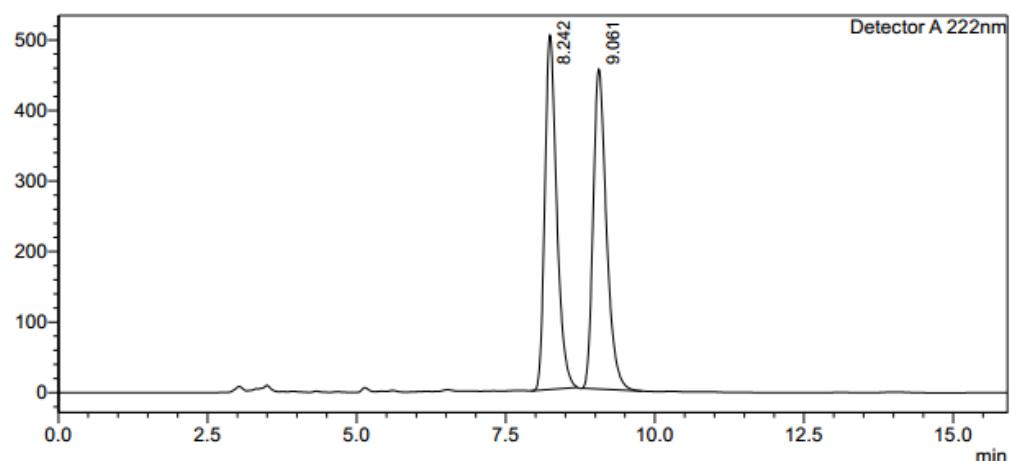
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Relative Area %	Amount n.a.
1		6.560	50.344	90.94	n.a.
2		11.640	5.017	9.06	n.a.
Total:			55.361	100.00	



<Chromatogram>

mV



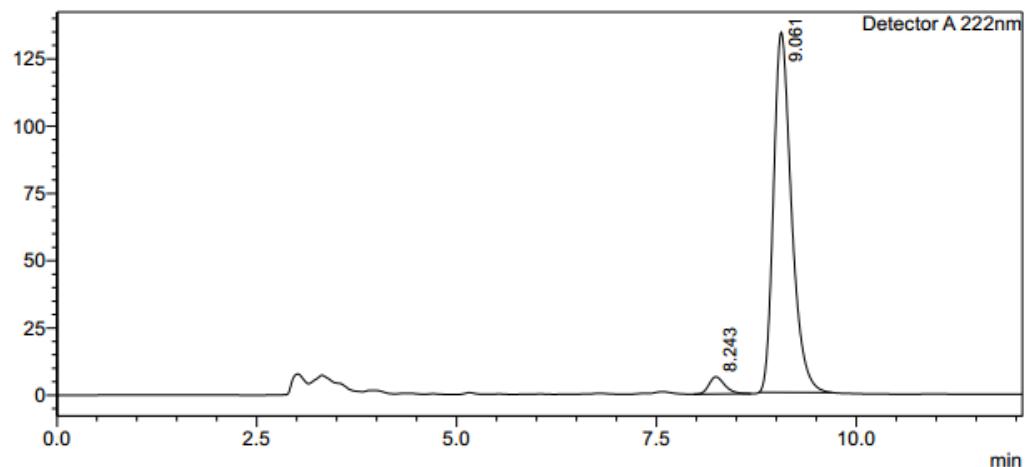
<Peak Table>

Detector A 222nm

Peak#	Name	Ret. Time	Area	Area%	Height	Unit	Mark
1		8.242	6944739	49.695	501895		M
2		9.061	7030028	50.305	453404		M
Total			13974767	100.000	955299		

<Chromatogram>

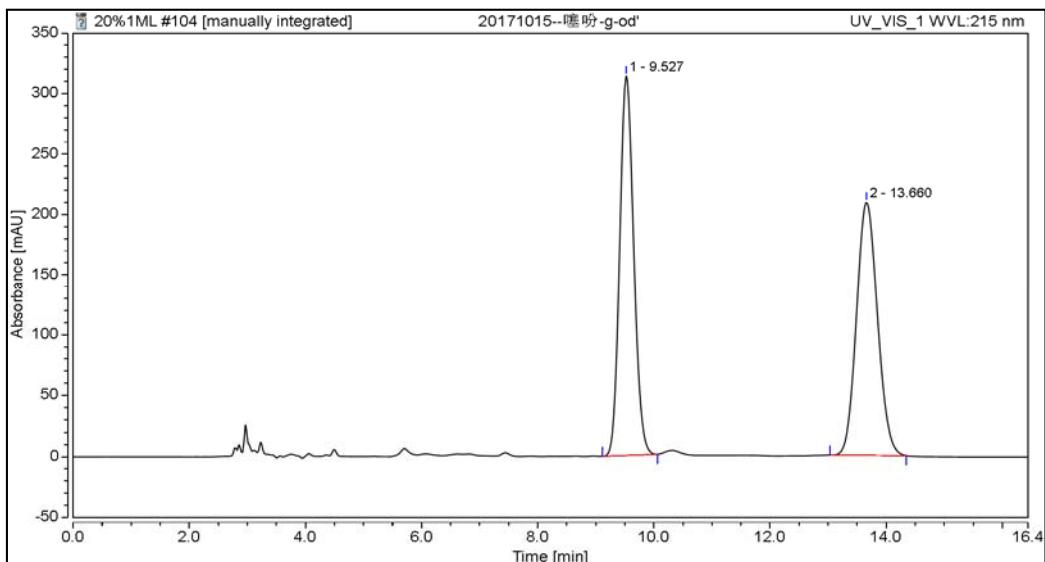
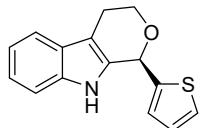
mV



<Peak Table>

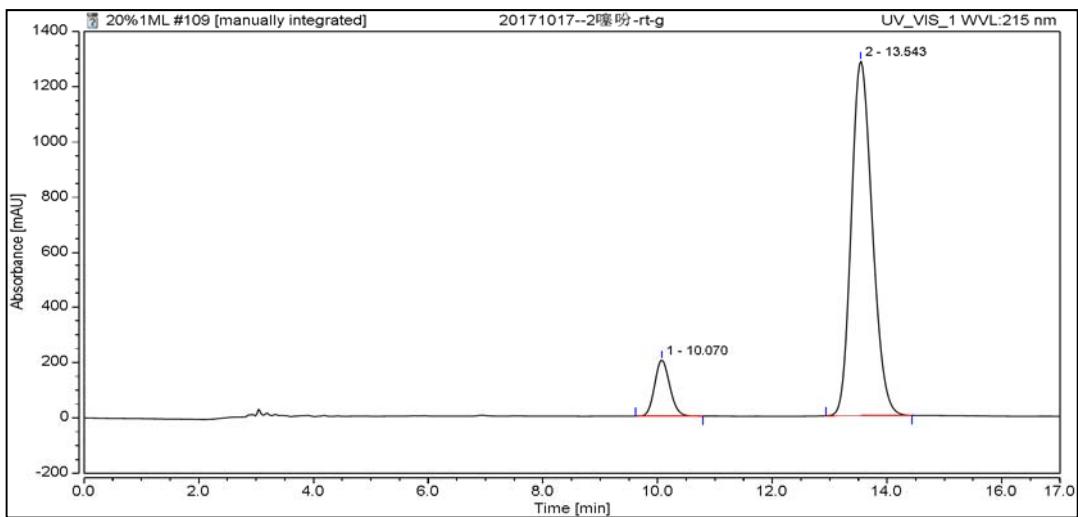
Detector A 222nm

Peak#	Name	Ret. Time	Area	Area%	Height	Unit	Mark
1		8.243	87249	3.997	6347		M
2		9.061	2095854	96.003	133823		M
Total			2183102	100.000	140169		



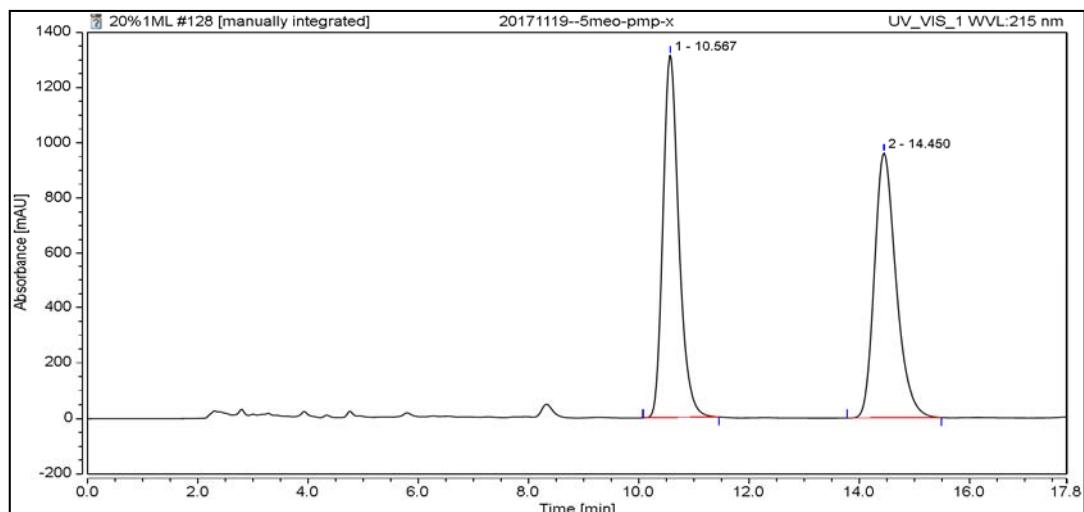
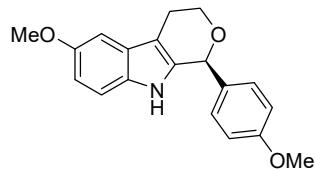
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Relative Area %	Amount
1		9.527	87.617	50.16	n.a.
2		13.660	87.066	49.84	n.a.
Total:	174.684				100.00



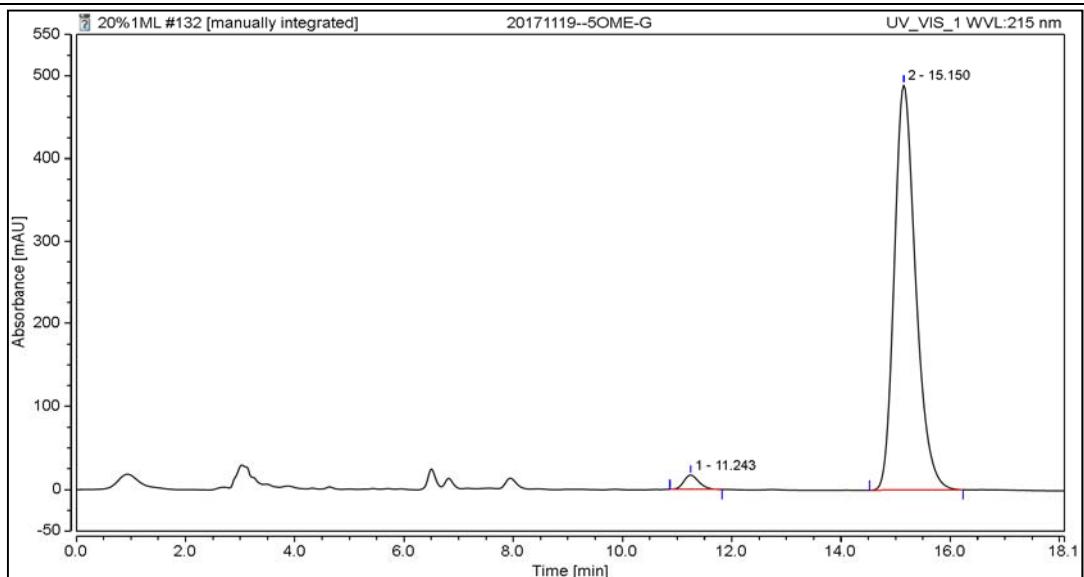
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Relative Area %	Amount
1		10.070	61.839	10.20	n.a.
2		13.543	544.255	89.80	n.a.
Total:	606.094				100.00



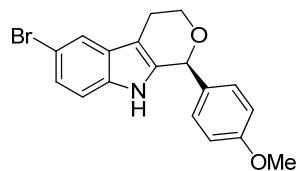
Integration Results

No.	Peak Name	Retention Time min	Height mAU	Relative Area %	Amount
1		10.567	1313.452	50.01	n.a.
2		14.450	960.842	49.99	n.a.
Total:			2274.294	100.00	



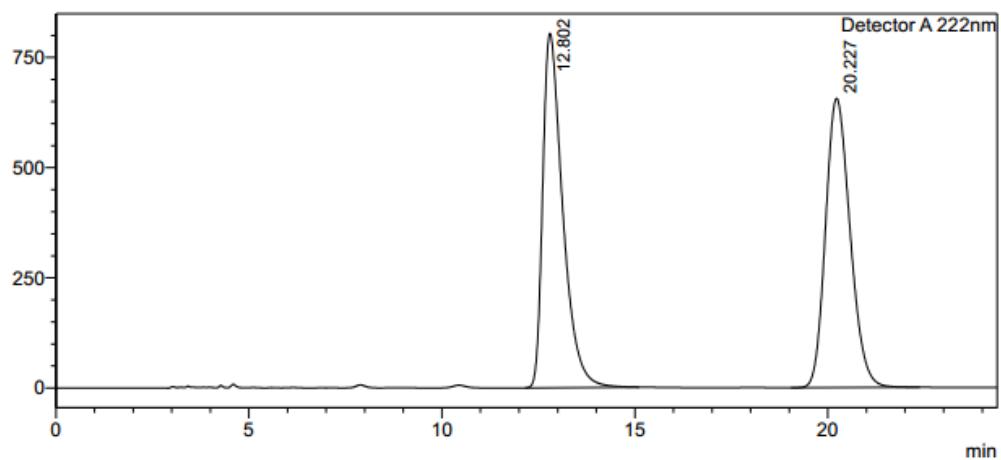
Integration Results

No.	Peak Name	Retention Time min	Height mAU	Relative Area %	Amount
1		11.243	17.179	2.43	n.a.
2		15.150	489.678	97.57	n.a.
Total:			506.857	100.00	



<Chromatogram>

mV



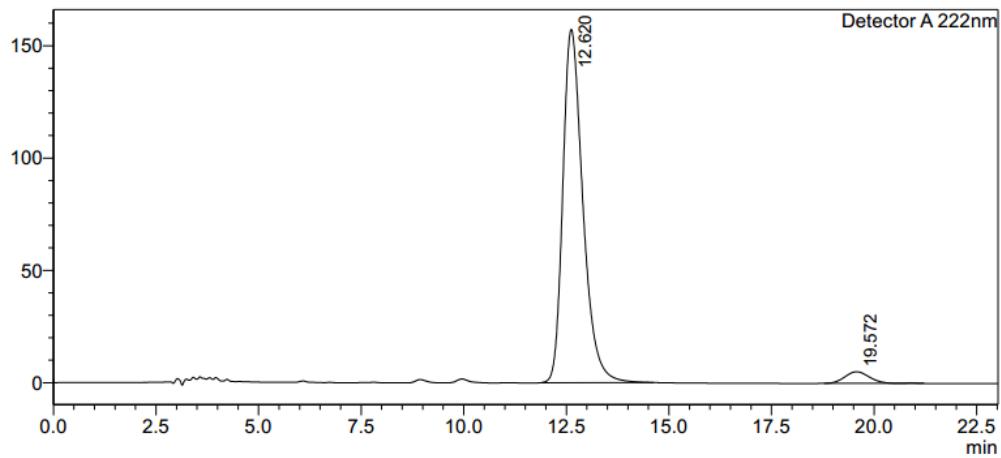
<Peak Table>

Detector A 222nm

Peak#	Name	Ret. Time	Area	Area%	Height	Unit	Mark
1		12.802	28954598	49.933	803500		M
2		20.227	29032669	50.067	655860		M
Total			57987267	100.000	1459359		

<Chromatogram>

mV



<Peak Table>

Detector A 222nm

Peak#	Name	Ret. Time	Area	Area%	Height	Unit	Mark
1		12.620	5348559	96.098	157257		M
2		19.572	217153	3.902	5168		M
Total			5565712	100.000	162425		