Supporting Information

for

Dynamic kinetic asymmetric transfer hydrogenation-cyclization tandem reaction: an easy access to chiral 3,4-dihydro-2*H*-pyran-carbonitriles

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CONTENTS

1. General Information and Catalytic Experiments

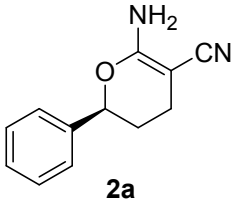
1.1. General. All reagents and solvents were purchased from commercial sources and used without further purification. All compounds are bought by commodity resources. Compounds (1 and 3) was synthesized according to the reported literatures (A. Russo, A. Perfetto, A. Lattanzi, *Adv. Synth. Catal*. **2009**, *351*, 3067–3071). Analytical HPLC was carried out with a Waters® Chromatography setup consisting of: Waters® 717plus Autosampler, Waters® 1525 Binary HPLC Pump, and Waters® 2478 Dual λ Absorbance Detector. The enantiomeric excesses (ee) were determined using a Daicel Chiralcel® column AD–H or OD–H or OJ–H with the above HPLC setup. Optical rotations were measured on a Rudolph Research Analytical Autopol VI automatic polarimeter using a 50 mm path-length cell at 589 nm.

1.2. General Procedure for ATH/Cyclization of Substituted 2-(3-oxo-1-arylpropyl)malononitriles. The catalyst **A** (2 μmol, S/C = 50), **1** (0.10 mmol), HCOONa (1.0 mmol, 68 mg, 10 equiv), and ^{i}PrOH/H_2O(v/v = 3/1) (4 mL) were added in a 10 mL round bottom flask in turn. The mixture was allowed to react at 60 °C for 1−5 h. The reaction was monitored constantly by TLC. After completion of the reaction, the solvent was removed by evaporation. The residue is dissolved in 2 mL water, and then the aqueous solution was extracted by ethyl acetate (3 × 3.0 mL). The combined ethyl acetate was washed with brine twice and dehydrated with Na_2SO_4. After the evaporation of EA, the residue was purified by silica gel flash column chromatography to afford the desired product. The *ee* value was determined by a Daicel Chiralcel® AD–H or OD–H or OJ–H column.

1.3. General Procedure for DKR-ATH/Cyclization of 2-(3-oxo-1,3-diarylpropyl)malononitriles. The catalyst **A** (2 μmol, S/C = 50), **3** (0.10 mmol), HCOONa (1.0 mmol, 68 mg, 10 equiv), Et_3N (0.10 mmol, 14.0 μL, 1.0 equiv) and ^{i}PrOH/H_2O (v/v = 3/1) (4 mL) were added in a 5 mL round bottom flask in turn. The mixture was allowed to react at 60 °C for 5-12 h. The reaction was monitored constantly by TLC. After completion of the reaction, the solvent was removed by evaporation. The residue is dissolved in 2 mL water, and then the aqueous solution was extracted by ethyl acetate(EA) (3 × 3.0 mL). The combined EA was washed with brine twice and dehydrated with Na_2SO_4. After the evaporation of EA, the residue was purified by silica gel flash column chromatography to afford the desired product. The *ee* value was determined by a Daicel Chiralcel® AD–H or OD–H or OJ–H column.

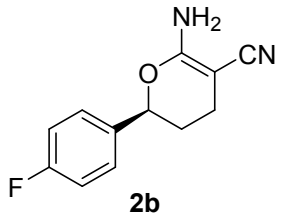
2. Characterizations of Chiral Products

2a: (*S*)-6-Amino-2-phenyl-3,4-dihydro-2*H*-pyran-5-carbonitrile. White solid, m. p. 123-124 °C, yield 99%, 97% *ee,* $[\alpha]_D^{25}$ = +42.6319 (c 0.7467, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.45–7.26 (m, 5H), 5.03 (dd, *J* = 10.5, 2.4 Hz, 1H), 4.38 (s, 2H), 2.47 (m, *J* = 14.7, 11.0, 6.1 Hz, 1H), 2.30 (m, *J* = 14.8, 6.0, 3.0 Hz, 1H), 2.16–2.06 (m, 1H), 2.01–1.89 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.84, 139.51, 128.94, 128.79, 126.13, 121.96, 80.05, 54.62, 29.27, 21.05. HRMS (ESI): m/z $[M+H]^+$ calculated for $C_{12}H_{12}N_2O$: 201.1022; found: 201.1021. HPLC (AD-H, elute: Hexanes/*i*-PrOH = 95/5, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C), t_1 = 29.9 min (major), t_2 = 35.5 min (minor).



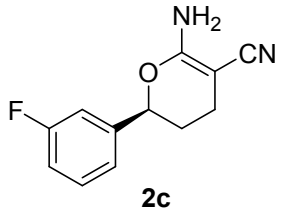
2a

2b: (*S*)-6-Amino-2-(4-fluorophenyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile. White solid, m. p. 138-139 °C, yield 97%, 97% *ee,* $[\alpha]_D^{25}$ = +44.6560 (c 1.0250, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 8.6, 5.2 Hz, 2H), 7.10 (t, *J* = 8.6 Hz, 2H), 5.00 (dd, *J* = 10.5, 2.3 Hz, 1H), 4.37 (s, 2H), 2.47 (m, *J* = 14.8, 11.0, 6.1 Hz, 1H), 2.30 (m, *J* = 14.8, 5.7, 2.6 Hz, 1H), 2.14–2.05 (m, 1H), 1.92 (m, *J* = 14.0, 10.9, 5.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.68, 161.70, 141.29, 135.35–135.32 (d, *J* = 3.2 Hz), 130.14–130.05 (d, *J* = 8.6 Hz), 128.04–127.95 (d, *J* = 8.4 Hz), 121.79, 115.99–115.77 (d, *J* = 21.7 Hz), 79.41, 54.70, 29.31, 21.04. HRMS (ESI): m/z $[M+H]^+$ calculated for $C_{12}H_{11}N_2OF$: 219.0928; found: 219.0928; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 95/5, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C), t_1 = 37.8 min (major), t_2 = 45.7 min (minor).



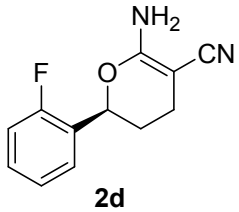
2b

2c: (*S*)-6-Amino-2-(3-fluorophenyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile. White solid, m. p. 58-59 °C, yield 95%, 95% *ee,* $[\alpha]_D^{25}$ = +30.2676 (c 0.3667, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.45–7.26 (m, 1H), 7.09 (dd, *J* = 17.7, 8.3 Hz, 3H), 5.02 (d, *J* = 10.4 Hz, 1H), 4.44 (s, 2H), 2.45 (m, *J* = 16.6, 10.9, 6.1 Hz, 1H), 2.28 (m, *J* = 14.9, 5.7, 3.0 Hz, 1H), 2.18–2.04 (m, 1H), 1.99–1.83 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.39, 163.54, 161.93, 142.08–142.01 (d, *J* = 7.2 Hz), 130.59–130.51 (d, *J* = 7.7 Hz), 121.65–121.62 (d, *J* = 3.2 Hz), 115.70–115.50 (d, *J* = 20.6 Hz), 113.24–113.02 (d, *J* = 22.6 Hz), 79.12, 54.73, 29.28, 20.87. HRMS (ESI): m/z $[M+H]^+$ calculated for $C_{12}H_{11}N_2OF$: 219.0928; found: 219.0929; HPLC (OJ-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C), t_1 = 41.4 min (major), t_2 = 46.7 min (minor).



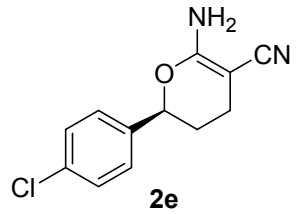
2c

2d: (*S*)-6-Amino-2-(2-fluorophenyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile. White solid, m. p. 108-110 °C, yield 83%, 90% *ee,* $[\alpha]_D^{25}$ = +22.7370 (c 0.1294, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.44–7.31 (m, 2H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.14–7.03 (m, 1H), 5.34 (dd, *J* = 10.4, 2.3 Hz, 1H), 4.41 (s, 2H), 2.48 (m, *J* = 14.9, 11.0, 6.1 Hz, 1H), 2.29 (m, *J* = 14.9, 5.8, 2.9 Hz, 1H), 2.18–2.09 (m, 2H), 2.00–1.87 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.68, 160.96, 158.49, δ 130.28–130.20 (d, *J* = 7.5 Hz), 127.37–127.34 (d, *J* = 3.7 Hz), 126.84–126.78 (d, *J* = 12.9 Hz), 124.6 , 121.73, 115.95–115.73 (d, *J* = 22.2 Hz), 74.14, 54.91, 28.19, 20.94. HRMS (ESI): m/z $[M+H]^+$ calculated for $C_{12}H_{11}N_2OF$: 219.0928; found: 219.0926; HPLC (OJ-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1mL/min, 25 °C), t_1 = 27.0 min (minor), t_2 = 35.0 min (major).



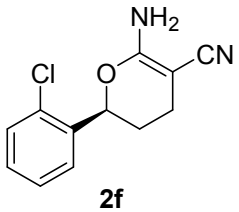
2d

2e: (*S*)-6-Amino-2-(4-chlorophenyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile. White solid, m. p. 135-137 °C, yield 96%, 97% *ee,* $[\alpha]_D^{25}$ = +15.3718 (c 0.1667, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.3 Hz, 2H), 7.29 (s, 1H), 7.27 (s, 1H), 5.00 (dd, *J* = 10.5, 2.1 Hz, 1H), 4.38 (s, 2H), 2.46 (m, *J* = 14.4, 11.0, 6.0 Hz, 1H), 2.29 (m, *J* = 14.7, 6.0, 2.9 Hz, 1H), 2.15–2.05 (m, 1H), 1.98–1.85 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.61, 138.02, 134.58, 129.13, 127.50, 121.75, 79.26, 54.70, 29.28, 20.94. HRMS (ESI): m/z $[M+H]^+$ calculated for $C_{12}H_{11}N_2OCl$: 235.0633; found: 235.0632; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 95/5, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C), t_1 = 41.1 min (major), t_2 = 46.8 min (minor).



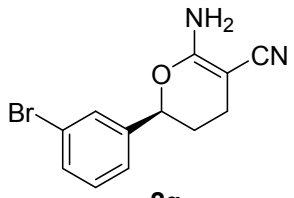
2e

2f: (*S*)-6-Amino-2-(2-chlorophenyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile. White solid, m. p. > 253 °C, yield 95%, 88% *ee,* $[\alpha]_D^{25}$ = -7.4857 (c 0.4000, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 7.5, 1.9 Hz, 1H), 7.40 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.38–7.29 (m, 2H), 5.42 (dd, *J* = 10.4, 2.3 Hz, 1H), 4.41 (s, 2H), 2.51 (m, *J* = 14.9, 11.3, 6.1 Hz, 2H), 2.30 (m, *J* = 14.7, 5.7, 2.7 Hz, 1H), 2.22 (m, *J* = 14.1, 5.7, 2.5 Hz, 2H), 1.79 (m, *J* = 14.0, 10.9, 5.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.73, 137.20, 131.84, 129.91, 129.66, 127.50, 127.09, 121.71, 76.82, 55.05, 28.12, 21.07. HRMS (ESI): m/z $[M+H]^+$ calculated for $C_{12}H_{11}N_2OCl$: 235.0633; found: 235.0632; HPLC (OJ-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1mL/min, 25 °C), t_1 = 25.3 min (minor), t_2 = 31.3 min (major).



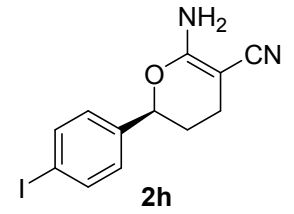
2f

2g: (*S*)-6-Amino-2-(3-bromophenyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile. White solid, m. p. 101-103 °C, yield 91%, 94% *ee,* $[\alpha]_D^{25}$ = +22.8927 (c 0.6800, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 3.0 Hz, 2H), 7.28 (d, *J* = 3.1 Hz, 3H), 4.99 (dd, *J* = 10.4, 2.3 Hz, 1H), 4.41 (s, 2H), 2.46 (m, *J* = 15.1, 11.0, 6.1 Hz, 1H), 2.30 (m, *J* = 15.0, 5.8, 2.9 Hz, 1H), 2.11 (m, *J* = 13.9, 5.9, 2.6 Hz, 1H), 1.97–1.83 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.49, 141.75, 131.81, 130.51, 129.19, 124.68, 123.02, 121.68, 79.08, 54.78, 29.34, 20.93. HRMS (ESI): m/z $[M+H]^+$ calculated for $C_{12}H_{11}N_2OBr$: 279.0128; found: 279.0128; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 0.5mL/min, 25 °C), t_1 = 50.9 min (minor), t_2 = 55.2 min (major).



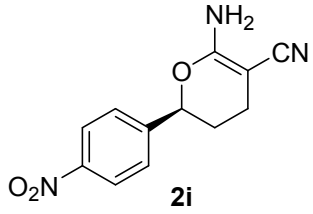
2g

2h: (*S*)-6-Amino-2-(4-iodophenyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile. White solid, m. p. 155-157 °C, yield 92%, 97% *ee,* $[\alpha]_D^{25}$ = +35.8177 (c 1.0533, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 4.97 (dd, *J* = 10.3, 2.3 Hz, 1H), 4.43 (s, 2H), 2.44 (m, *J* = 14.7, 10.9, 6.1 Hz, 1H), 2.27 (m, *J* = 14.9, 6.0, 3.0 Hz, 1H), 2.08 (m, *J* = 13.9, 5.9, 2.6 Hz, 1H), 1.95–1.81 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.58, 139.21, 138.04, 127.97, 121.74, 94.31, 79.34, 54.70, 29.23, 20.91. HRMS (ESI): m/z $[M+H]^+$ calculated for $C_{12}H_{11}N_2OI$: 326.9989; found: 326.9991; HPLC (OJ-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C), t_1 = 78.5 min (minor), t_2 = 93.8 min (major).



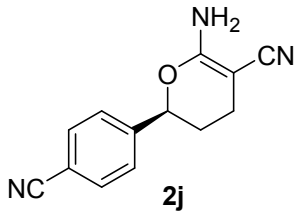
2h

2i: (*S*)-6-Amino-2-(4-nitrophenyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile. Light-yellow solid, m. p. 196-197 °C, yield 89%, 90% *ee,* $[\alpha]_D^{25}$ = +17.4540 (c 0.4867, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.7 Hz, 2H), 5.15 (dd, *J* = 10.3, 2.4 Hz, 1H), 4.45 (s, 2H), 2.49 (m, *J* = 14.9, 10.8, 6.2 Hz, 1H), 2.31 (m, *J* = 14.7, 5.8, 3.0 Hz, 1H), 2.17 (m, *J* = 13.8, 5.6, 3.0, 2.5 Hz, 1H), 2.01–1.85 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.08, 146.47, 141.86, 128.86, 126.79, 124.70, 124.21, 121.20, 78.68, 55.22, 29.45, 20.77. HRMS (ESI): m/z $[M+H]^+$ calculated for $C_{12}H_{11}N_3O_3$: 246.0873; found: 246.0875; HPLC (OJ-H, elute: Hexanes/*i*-PrOH = 80/20, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C), t_1 = 47.7 min (minor), t_2 = 61.5 min (major).



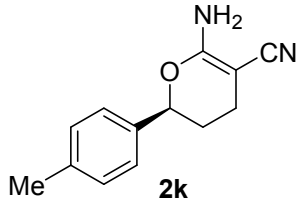
2i

2j: (*S*)-6-Amino-2-(4-cyanophenyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile. White solid, m. p. 150-152 °C, yield 94%, 92% *ee,* $[\alpha]_D^{25}$ = +28.2883 (c 0.7267, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 5.09 (dd, *J* = 10.3, 2.4 Hz, 1H), 4.45 (s, 2H), 2.47 (m, *J* = 15.0, 10.8, 6.2 Hz, 1H), 2.29 (m, *J* = 14.8, 5.8, 3.1 Hz, 1H), 2.13 (m, *J* = 14.0, 5.8, 2.7 Hz, 1H), 1.96–1.81 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.20, 144.63, 132.79, 126.65, 121.38, 118.59, 112.61, 78.85, 55.01, 29.34, 20.76. HRMS (ESI): m/z $[M+H]^+$ calculated for $C_{13}H_{11}N_3O$: 226.0975; found: 226.0975; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C), t_1 = 47.8 min (major), t_2 = 55.6 min (minor).



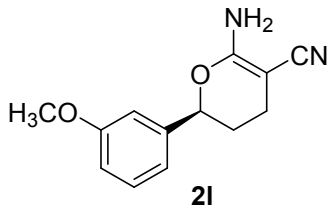
2j

2k: (*S*)-6-Amino-2-(p-tolyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile. White solid, m. p. 101-102 °C, yield 91%, 97% *ee,* $[\alpha]_D^{25}$ = +33.2835 (c 0.9333, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 20.0 Hz, 5H), 4.98 (dd, *J* = 10.3, 2.4 Hz, 1H), 4.37 (s, 2H), 2.46 (m, *J* = 14.7, 10.9, 6.1 Hz, 1H), 2.38 (s, 3H), 2.30 (m, *J* = 14.7, 5.8, 2.9 Hz, 1H), 2.09 (m, *J* = 13.7, 5.6, 2.6 Hz, 1H), 2.01–1.88 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.93, 138.71, 136.53, 130.35, 129.60, 127.80, 126.17, 122.04, 80.04, 54.51, 29.15, 21.39, 21.10. HRMS (ESI): m/z $[M+H]^+$ calculated for $C_{13}H_{14}N_2O$: 215.1179; found: 215.1177; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C), t_1 = 46.7 min (minor), t_2 = 66.1 min (major).



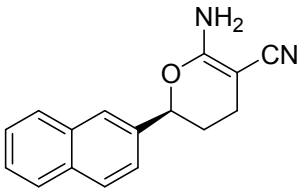
2k

2l: (*S*)-6-Amino-2-(3-methoxyphenyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile. White solid, m. p. 82-84 °C, yield 91%, 96% *ee,* $[\alpha]_D^{25}$ = +31.5671 (c 0.2200, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.42–7.24 (m, 1H), 7.07–6.77 (m, 3H), 4.99 (dd, *J* = 10.4, 2.4 Hz, 1H), 4.40 (s, 2H), 3.84 (s, 3H), 2.46 (m, *J* = 14.9, 11.0, 6.1 Hz, 1H), 2.29 (m, *J* = 14.7, 5.6, 2.8 Hz, 1H), 2.11 (m, *J* = 13.8, 5.8, 2.6 Hz, 1H), 1.93 (m, *J* = 13.9, 10.6, 5.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.76, 160.10, 141.08, 130.03, 121.91, 118.36, 113.96, 111.97, 79.91, 55.54, 29.27, 21.03. HRMS (ESI): m/z $[M+H]^+$ calculated for $C_{13}H_{14}N_2O_2$: 231.1128; found: 231.1128; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 95/5, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C), t_1 = 64.1 min (minor), t_2 = 74.8 min (major).



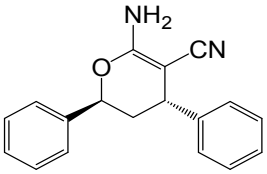
2l

2m: (*S*)-6-Amino-2-(naphthalen-2-yl)-3,4-dihydro-2*H*-pyran-5-carbonitrile. White solid, m. p. 106-108 °C, yield 90%, 95% *ee,* $[\alpha]_D^{25}$ = +46.2159 (c 0.7133, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.93–7.80 (m, 4H), 7.58–7.40 (m, 3H), 5.19 (dd, *J* = 10.5, 2.4 Hz, 1H), 4.43 (s, 2H), 2.52 (m, *J* = 14.9, 11.0, 6.1 Hz, 1H), 2.34 (m, *J* = 14.8, 5.8, 2.9 Hz, 1H), 2.19 (m, *J* = 11.3, 5.8, 2.9 Hz, 1H), 2.11–1.99 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.83, 136.84, 133.49, 133.35, 128.86, 128.27, 127.97, 126.76, 126.69, 125.29, 123.73, 80.19, 54.78, 29.32, 21.12. HRMS (ESI): m/z $[M+H]^+$ calculated for $C_{16}H_{14}N_2O$: 251.1179; found: 251.1179; HPLC (AD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C), t_1 = 27.2 min (major), t_2 = 35.6 min (minor).

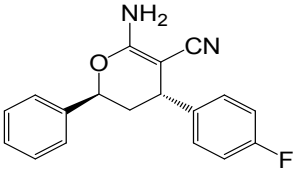


2m

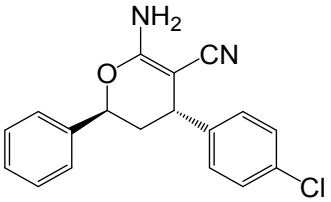
4a: (2*S*,4*S*)-6-Amino-2,4-diphenyl-3,4-dihydro-2*H*-pyran-5-carbonitrile. White solid, m. p. 120-121 °C, 78% yield, 99% *ee*, 96/4 *dr*. $[\alpha]_D^{25}$ = +7.2693 (c 0.6467, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.56–7.29 (m, 8H), 7.28–7.15 (m, 2H), 5.20–4.94 (m, 1H), 4.61 (d, *J* = 22.3 Hz, 2H), 3.94–3.79 (m, 1H), 2.35 (ddd, *J* = 14.0, 11.0, 6.0 Hz, 1H), 2.14–2.07 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.66, 143.84, 139.08, 129.03, 128.97, 128.89, 128.80, 128.09, 127.26, 126.25, 75.93, 57.16, 39.88, 37.25. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{18}H_{16}N_2ONa$ 299.1155; found: 299.1168. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 85/15, detector: 215 nm, flow rate: 1.0 mL/min, 25 °C).



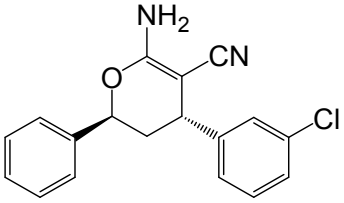
4b: (2*S*, 4*S*)-6-Amino-4-(4-fluorophenyl)-2-phenyl-3,4-dihydro-2*H*-pyran-5-carbonitrile. White solid, m. p. 146-147 °C, 79% yield, 99% *ee*, 94/6 *dr*. $[\alpha]_D^{25}$ = +6.0001 (c 1.3533, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.81–7.61 (m, 3H), 7.45–7.21 (m, 6H), 5.29–5.02 (m, 1H), 4.53 (d, *J* = 23.4 Hz, 2H), 3.90–3.70 (m, 1H), 2.36 (ddd, *J* = 14.0, 11.1, 6.0 Hz, 1H), 2.10 (ddd, *J* = 14.0, 9.7, 5.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.87, 160.97, 138.79, 138.42 (d, *J* = 3.1 Hz), 129.56 (d, *J* = 8.0 Hz), 129.12, 128.97 (d, *J* = 6.1 Hz), 126.25 (d, *J* = 8.8 Hz), 121.03, 115.73 (d, *J* = 6.8 Hz), 75.86, 57.10, 40.55, 39.20. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{16}FN_2O$ 295.1241; found: 295.1245. HPLC (Chiralpak OJ-H, elute: Hexanes/*i*-PrOH = 85/15, detector: 215 nm, flow rate: 1.0 mL/min, 25 °C).



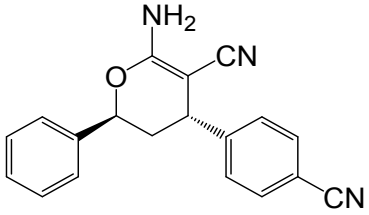
4c: (2*S*,4*S*)-6-Amino-4-(4-chlorophenyl)-2-phenyl-3,4-dihydro-2*H*-pyran-5-carbonitrile. White solid, m. p. 148-149 °C, 80% yield, 99% *ee*, 96/4 *dr*. $[\alpha]_D^{25}$ = +8.0321 (c 1.6467, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.49–7.44 (m, 2H), 7.32–7.28 (m, 3H), 7.25 (s, 1H), 7.21 (d, *J* = 2.1 Hz, 1H), 7.16 (t, *J* = 3.8 Hz, 1H), 7.05 (dd, *J* = 8.1, 5.5 Hz, 1H), 5.11–4.72 (m, 1H), 4.56 (s, 2H), 3.87–3.55 (m, 1H), 2.45–2.20 (m, 1H), 2.14–1.78 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.48, 141.08, 137.50, 131.82, 128.42, 128.18, 127.86, 127.69, 124.93, 120.13, 74.60, 55.41, 36.75, 35.47. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{16}ClN_2O$ 311.0946; found: 311.0947. HPLC (Chiralpak OJ-H, elute: Hexanes/*i*-PrOH = 82/20, detector: 215 nm, flow rate: 1.0 mL/min, 25 °C).



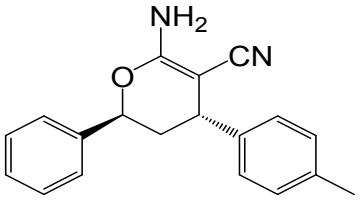
4d: (2*S*,4*S*)-6-Amino-4-(3-chlorophenyl)-2-phenyl-3,4-dihydro-2*H*-pyran-5-carbonitrile. White solid, m. p. 135-136 °C, 76% yield, 96% *ee*, 85/15 *dr*. $[\alpha]_D^{25}$ = +5.5691 (c 0.7200, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 75.0 Hz, 1H), 7.37 (dd, *J* = 15.4, 8.3 Hz, 3H), 7.33–7.10 (m, 5H), 5.16 (d, *J* = 11.5 Hz, 1H), 4.62 (d, *J* = 16.8 Hz, 2H), 3.92–3.77 (m, 1H), 2.43–2.28 (m, 1H), 2.11–2.01 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.10, 144.91, 142.60, 138.65, 130.78, 130.37, 129.44, 129.03, 127.74, 126.31, 126.03, 111.98, 80.02, 59.48, 42.57, 39.63. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{16}N_2OCl$ 311.0946; found: 311.0951. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 215 nm, flow rate: 1.0 mL/min, 25 °C).



4e: (2*S*,4*S*)-6-Amino-4-(4-cyanophenyl)-2-phenyl-3,4-dihydro-2*H*-pyran-5-carbonitrile. White solid, m. p. 167-168 °C, 83% yield, 89% *ee*, 82/18 *dr*. $[\alpha]_D^{25}$ = +8.5249 (c 1.1800, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.82–7.61 (m, 2H), 7.59–7.45 (m, 2H), 7.44–7.36 (m, 3H), 7.28–7.08 (m, 2H), 5.22–4.87 (m, 1H), 4.69 (d, *J* = 21.1 Hz, 2H), 4.02–3.83 (m, 1H), 2.47–2.32 (m, 1H), 2.09–2.05 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.95, 147.08, 137.09, 131.69, 127.98, 127.81, 127.20, 124.99, 119.36, 117.74, 110.12, 74.59, 54.65, 38.75, 36.17. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{16}N_3O$ 302.1288; found: 302.1297. HPLC (Chiralpak OD-H, elute: Hexanes/*i*-PrOH = 88/12, detector: 215 nm, flow rate: 1.0 mL/min, 25 °C).

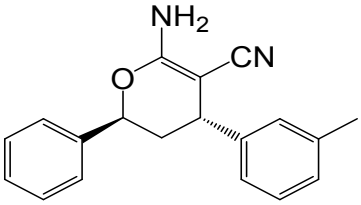


4f: (2*S*,4*S*)-6-Amino-2-phenyl-4-(p-tolyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile.



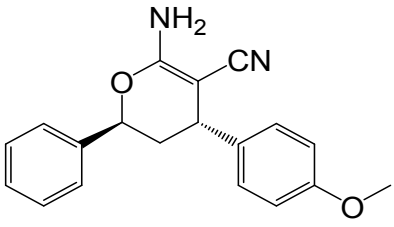
White solid, m. p. 122-123 °C, 73% yield, 99% *ee*, 97/3 *dr*. $[\alpha]_D^{25}$ = +6.1187 (c 1.5133, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 7.5, 2.1 Hz, 2H), 7.38 (dd, *J* = 5.0, 2.3 Hz, 2H), 7.35 (dd, *J* = 4.7, 2.9 Hz, 1H), 7.27–7.23 (m, 2H), 7.18 (d, *J* = 8.3 Hz, 2H), 5.17–4.94 (m, 1H), 4.62 (s, 2H), 3.91–3.71 (m, 1H), 2.37 (d, *J* = 5.9 Hz, 3H), 2.34–2.26 (m, 1H), 2.10–2.05 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.25, 143.08, 138.97, 137.07, 130.20, 129.05, 128.22, 127.56, 125.82, 112.53, 80.10, 60.87, 42.59, 39.44, 21.48. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{19}N_2O$ 291.1492; found: 291.1492. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 85/15, detector: 215 nm, flow rate: 1.0 mL/min, 25 °C).

4g: (2*S*,4*S*)-6-Amino-2-phenyl-4-(m-tolyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile.

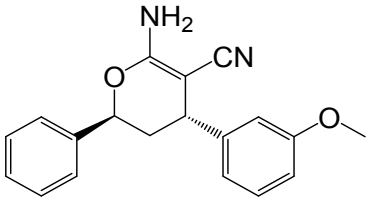


White solid, m. p. 117-118 °C, 72% yield, 98% *ee*, 80/20 *dr*. $[\alpha]_D^{25}$ = +7.5270 (c 1.9400, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.58–7.20 (m, 5H), 7.18–6.91 (m, 4H), 4.98 (dd, *J* = 70.7, 11.0 Hz, 1H), 4.47 (d, *J* = 20.8 Hz, 2H), 3.82–3.67 (m, 1H), 2.31 (s, 3H), 2.20 (ddd, *J* = 20.8, 11.6, 5.2 Hz, 1H), 2.05–1.97 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.54, 141.36, 137.67, 137.30, 128.66, 128.08, 127.69, 127.02, 125.08, 124.89, 123.33, 119.97, 74.66, 55.96, 41.66, 38.50, 20.46. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{19}N_2O$ 291.1492; found: 291.1494. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 215 nm, flow rate: 1.0 mL/min, 25 °C).

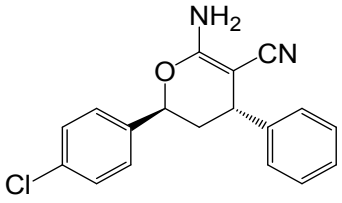
4h: (2*S*,4*S*)-6-Amino-4-(4-methoxyphenyl)-2-phenyl-3,4-dihydro-2*H*-pyran-5-carbonitrile. White solid, m. p. 129-130 °C, 72% yield, 99% *ee*, 95/5 *dr*. $[\alpha]_D^{25}$ = +19.1534 (c 0.8333, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (q, *J* = 6.2 Hz, 3H), 7.30–7.20 (m, 4H), 6.93 (d, *J* = 8.5 Hz, 2H), 5.05 (dd, *J* = 75.9, 10.5 Hz, 1H), 4.62 (s, 4H), 3.83 (s, 3H), 3.77 (dd, *J* = 5.7, 2.4 Hz, 1H), 2.31 (ddd, *J* = 13.9, 11.0, 5.9 Hz, 1H), 2.07 (d, *J* = 20.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.83, 143.95, 139.15, 128.90, 128.13, 127.28, 126.28, 121.78, 75.88, 56.89, 38.15, 37.28, 29.97. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{19}N_2O_2$ 307.1441; found: 307.1439. HPLC (Chiralpak OD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 215 nm, flow rate: 1.0 mL/min, 25 °C).



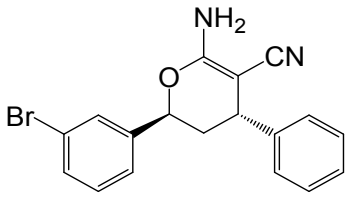
4i: (2*S*,4*S*)-6-Amino-4-(3-methoxyphenyl)-2-phenyl-3,4-dihydro-2*H*-pyran-5-carbonitrile. White solid, m. p. 125-126 °C, 71% yield, 96% *ee*, 94/6 *dr*. $[\alpha]_D^{25}$ = +7.5242 (c 1.8333, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.42–7.25 (m, 4H), 7.24–7.20 (m, 1H), 7.10 (d, *J* = 8.7 Hz, 2H), 6.86–6.78 (m, 2H), 5.05–4.80 (m, 1H), 4.46 (d, *J* = 20.7 Hz, 2H), 3.85–3.75 (m, 1H), 3.73 (s, 3H), 2.33–2.20 (m, 1H), 1.99–1.94 (m, 1H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 163.63, 158.84, 143.15, 137.63, 129.28, 128.76, 127.70, 125.07, 119.91, 118.65, 112.17, 111.42, 74.69, 58.86, 54.19, 41.74, 38.60. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{19}N_2O_2$ 307.1441; found: 307.1445. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 215 nm, flow rate: 1.0 mL/min, 25 °C).



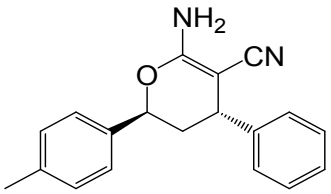
4j: (2*S*, 4*S*)-6-Amino-2-(4-chlorophenyl)-4-phenyl-3,4-dihydro-2*H*-pyran-5-carbonitrile. White solid, m. p. 140-141 °C, 84% yield, 97% *ee*, 98/2 *dr*. $[\alpha]_D^{25}$ = +58.2476 (c 1.0067, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.6 Hz, 1H), 7.43–7.36 (m, 3H), 7.35–7.29 (m, 4H), 7.19 (d, *J* = 8.4 Hz, 1H), 5.18–4.88 (m, 1H), 4.62 (s, 2H), 3.95–3.78 (m, 1H), 2.36–2.21 (m, 1H), 2.08–2.01 (m, 1H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 163.10, 142.34, 136.31, 133.33, 127.81, 127.76, 126.79, 126.36, 126.10, 120.08, 73.92, 56.03, 36.91, 35.91. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{16}N_2OCl$ 311.0946; found: 311.0949. HPLC (Chiralpak OD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 215 nm, flow rate: 1.0 mL/min, 25 °C).



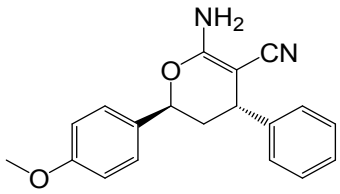
4k: (2*S*, 4*S*)-6-Amino-2-(3-bromophenyl)-4-phenyl-3,4-dihydro-2*H*-pyran-5-carbonitrile. White solid, m. p. 153-154 °C, 79% yield, 97% *ee*, 83/17 *dr*. $[\alpha]_D^{25}$ = -5.0934 (c 0.8800, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.49–7.28 (m, 4H), 7.28–7.23 (m, 2H), 7.23–7.20 (m, 1H), 7.13 (dt, *J* = 26.1, 7.2 Hz, 2H), 5.08–4.80 (m, 1H), 4.51 (d, *J* = 21.9 Hz, 2H), 3.85–3.67 (m, 1H), 2.30–2.12 (m, 1H), 2.03–1.98 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.95, 142.25, 130.76, 130.59, 129.21, 128.04, 127.79, 127.57, 126.78, 126.25, 126.14, 123.55, 73.80, 56.22, 36.98, 35.91. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{18}H_{15}N_2OBrNa$ 377.0260; found: 377.0273. HPLC (Chiralpak OJ-H, elute: Hexanes/*i*-PrOH = 85/15, detector: 215 nm, flow rate: 1.0 mL/min, 25 °C).



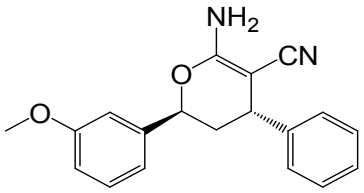
4l: (2*S*, 4*S*)-6-Amino-4-phenyl-2-(p-tolyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile. White solid, m. p. 128-129 °C, 82% yield, 99% *ee*, 93/7 *dr*. $[\alpha]_D^{25}$ = +5.7805 (c 1.6667, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (ddd, *J* = 15.7, 13.4, 7.8 Hz, 5H), 7.32–7.29 (m, 1H), 7.18 (dd, *J* = 14.6, 6.5 Hz, 3H), 5.16–4.90 (m, 1H), 4.57 (d, *J* = 21.6 Hz, 2H), 3.94–3.78 (m, 1H), 2.39 (t, *J* = 3.0 Hz, 1H), 2.36 (s, 3H), 2.09–2.05 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.64, 141.48, 137.71, 128.54, 128.36, 127.75, 126.82, 126.28, 125.14, 119.95, 74.59, 58.99, 41.80, 38.60, 20.13 HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{19}N_2O$ 291.1492; found: 291.1494. HPLC (Chiralpak OD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 215 nm, flow rate: 1.0 mL/min, 25 °C).



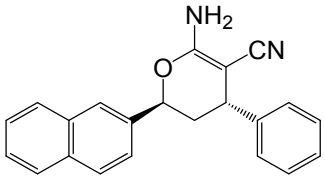
4m: (2*S*, 4*S*)-6-Amino-2-(4-methoxyphenyl)-4-phenyl-3,4-dihydro-2*H*-pyran-5-carbonitrile. White solid, m. p. 135-136 °C, 82% yield, 95% *ee*, 93/7 *dr*. $[\alpha]_D^{25}$ = +6.1324 (c 1.3067, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.50–7.24 (m, 4H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.18–7.16 (m, 1H), 6.96–6.66 (m, 3H), 5.09–4.87 (m, 1H), 4.48 (d, *J* = 20.0 Hz, 2H), 3.76 (s, 3H), 3.70 (dd, *J* = 5.9, 2.4 Hz, 1H), 2.25 (ddd, *J* = 13.9, 11.1, 6.0 Hz, 1H), 2.01 (dt, *J* = 14.1, 2.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.49, 158.77, 142.62, 129.76, 128.26, 127.68, 126.58, 126.23, 112.99, 111.03, 74.42, 55.67, 54.31, 41.92, 36.06. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{19}N_2O_2$ 307.1441; found: 307.1444. HPLC (Chiralpak OJ-H, elute: Hexanes/*i*-PrOH = 80/20, detector: 215 nm, flow rate: 1.0 mL/min, 25 °C).



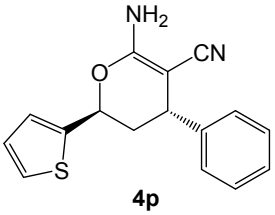
4n: (2*S*, 4*S*)-6-Amino-2-(3-methoxyphenyl)-4-phenyl-3,4-dihydro-2*H*-pyran-5-carbonitrile. White solid, m. p. 133-134 °C, 80% yield, 99% *ee*, 89/11 *dr*. $[\alpha]_D^{25}$ = +5.8710 (c 0.8733, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.77–7.29 (m, 5H), 7.28–7.10 (m, 1H), 7.10–6.73 (m, 3H), 5.17–4.90 (m, 1H), 4.58 (d, *J* = 20.9 Hz, 2H), 3.93–3.83 (m, 1H), 3.83–3.70 (m, 3H), 2.34 (ddd, *J* = 14.0, 10.9, 6.0 Hz, 1H), 2.14–2.07 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.43, 158.82 141.33, 139.13, 128.81, 127.77, 126.81, 126.26, 119.75, 117.30, 113.07, 110.70, 74.55, 59.26, 54.30, 38.55, 35.92. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{19}H_{18}N_2O_2Na$ 329.1260; found: 329.1278. HPLC (Chiralpak OJ-H, elute: Hexanes/*i*-PrOH = 85/15, detector: 215 nm, flow rate: 1.0 mL/min, 25 °C).



4o: (2*S*, 4*S*)-6-Amino-2-(naphthalen-2-yl)-4-phenyl-3,4-dihydro-2*H*-pyran-5-carbonitrile. White solid, m. p. 141-142 °C, 78% yield, 97% *ee*, 83/17 *dr*. $[\alpha]_D^{25}$ = +8.4712 (c 1.7133, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.61–7.51 (m, 2H), 7.43–7.37 (m, 3H), 7.35 (d, *J* = 9.2 Hz, 3H), 7.31 (t, *J* = 3.4 Hz, 1H), 7.25 (d, *J* = 5.2 Hz, 2H), 7.18–7.12 (m, 1H), 5.15 (d, *J* = 11.6 Hz, 1H), 4.62 (d, *J* = 22.9 Hz, 2H), 3.95–3.65 (m, 1H), 2.40–2.20 (m, 1H), 1.98 (ddd, *J* = 37.1, 18.6, 10.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.34, 142.53, 135.08, 132.16, 128.25, 127.94, 127.73, 127.53, 127.10, 126.95, 126.85, 126.68, 126.29, 126.03, 124.18, 122.50, 74.78, 55.94, 41.77, 36.00. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{19}N_2O$ 327.1492; found: 327.1501. HPLC (Chiralpak AD-H, elute: Hexanes/*i*-PrOH = 90/10, detector: 215 nm, flow rate: 1.0 mL/min, 25 °C).



4p: (*2S, 4S*)-6-Amino-4-phenyl-2-(thiophen-2-yl)-3,4-dihydro-2H-pyran-5-carbonitrile. white solid, mp 130-131°C, 81% yield (**2+3**), 97% *ee* (**2**), 87/13 *dr* (**2/3**). ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.22 (m, 6H), 7.20 – 6.94 (m, 2H), 5.45 – 5.17 (m, 1H), 4.61 (d, *J* = 16.5 Hz, 2H), 3.95 – 3.83 (m, 1H), 2.48 (ddd, *J* = 13.8, 10.9, 6.1 Hz, 1H), 2.23 (dt, *J* = 13.9, 2.5 Hz, 1H). $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.81, 142.23, 140.34, 127.75, 126.81, 126.09, 125.75, 125.16, 124.80, 120.03, 70.56, 56.04, 36.46, 35.91. HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{16}H_{14}N_2OSNa$ 305.0719; found: 305.0726. HPLC (Chiralpak AD-H, elute: Hexanes/i-PrOH = 90/10, detector: 215 nm, flow rate: 1.0 mL/min, 25 °C).



4p

4q: (*2S, 4S*)-6-Amino-4-ethyl-2-phenyl-3,4-dihydro-*2H*-pyran-5-carbonitrile. White solid, mp 141-142°C, 82% yield, 95% *ee*, 89/11 *dr*. ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.21 (m, 5H), 4.94 (ddd, *J* = 25.7, 10.8, 2.4 Hz, 1H), 4.34 (s, 2H), 2.54 – 2.13 (m, 1H), 2.12 – 1.73 (m, 2H), 1.57 – 1.10 (m, 2H), 0.89 (dt, *J* = 24.4, 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.02, 163.47, 139.42, 128.70, 128.59, 128.42, 126.04, 125.89, 121.93, 121.21, 79.90, 76.36, 35.73, 33.23, 33.04, 32.09, 28.84, 27.69, 11.36, 10.43. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{19}N_2O$ 327.1492; found: 327.1501. HPLC (Chiralpak AD-H, elute: Hexanes/i-PrOH = 95/5, detector: 254 nm, flow rate: 1.0 mL/min, 25 °C). HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{14}H_{16}N_2ONa$ 251.1155; found: 251.1157.

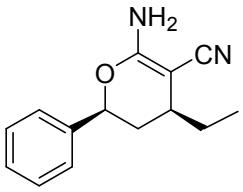
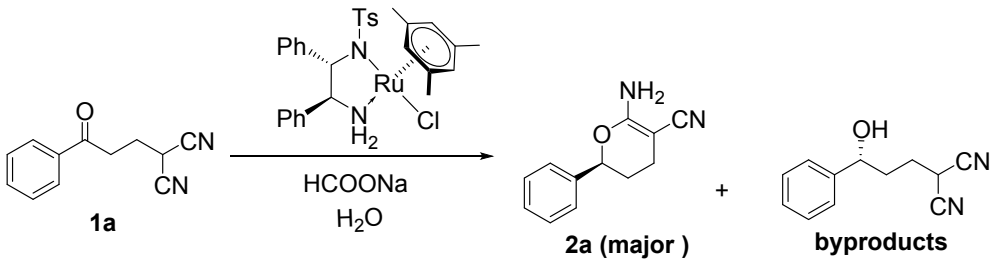


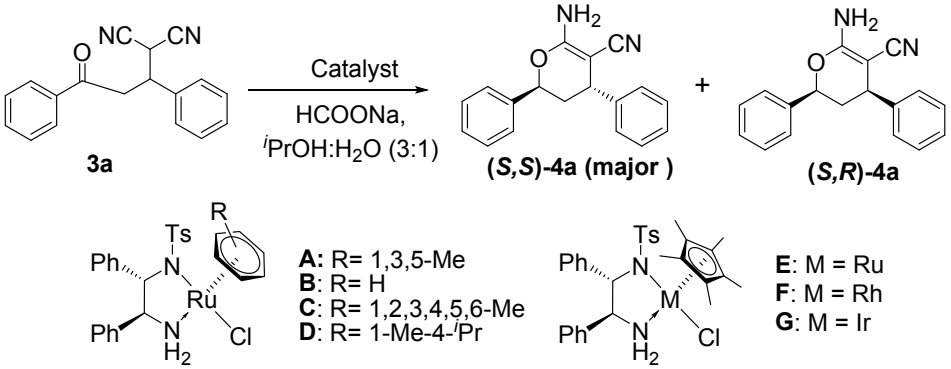
Table S1. Optimization of Reaction Temperature for the ATH/Cyclization Enantioselective Cascade Reaction of 2-(3-Oxo-3-phenylpropyl)malononitrile.[a]



Entry	Temperature	Time (h)	Yield. (%)[b]	*ee* (%)[c]	Selectivity [d]
1	40 °C	6	48	92	86%
2	50 °C	1	53	93	97%
3	60 °C	1	57	93	99%
4	70 °C	1	76	92	92%

[a] Reaction conditions: 0.10 mmol **1a**, 2.0 μmol catalyst **A** and 10 equivalent of H-resource were added into 4.0 mL of water and the mixture was stirred at different reaction temperature. [b] Yield was determined by ^{1}H-NMR analysis. [c] Determined by HPLC analysis using a Daicel Chiralcel® AD–H column. [d] (Yield/Conversion) ×100.

Table S2. Optimization of Bases and Catalysts for the DKR-ATH/Cyclization Enantioselective Cascade Reaction of 2-(3-oxo-1,3-diphenylpropyl)malononitrile. [a]

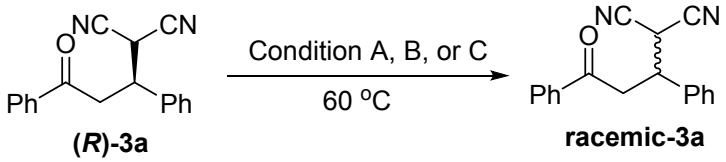


Entry	Catalyst/Base	Time (h)	Yield. (%)[b]	*ee* (%)[c]	*dr* [c]
1	**A**/morpholine	12	82	90	96:4
2	**A**/DBU[d]	12	66	92	93:7
3	**A**/DMAP[e]	12	81	83	91:19
4	**A**/pyridine	12	74	95	82:18
5	**A**/Et_3N	7	83	99	96:4
6	**A**/Et_3N	7	70	98	89:11
7	**B**/Et_3N	7	80	96	92:8
8	**C**/Et_3N	7	78	95	95:5
9	**D**/Et_3N	7	81	98	96:4
10	**E**/Et_3N	7	70	96	90:10
11	**F**/Et_3N	7	83	95	91:9
12	**G**/Et_3N	7	83	93	93:7

[a] 0.10 mmol **1a**, 2.0 μmol catalyst, 10 equivalent of HCOONa and 1 equivalent of base were added into 3.0 mL of co-solvent (^{i}PrOH: H_2O, v/v = 3: 1), and the mixture was stirred for 7-12 h. [b] Isolated yield. [c] Determined by HPLC analysis using a chiral stationary phase. [d] DBU = 1,8-diazabicyclo(5.4.0)undec-7-ene. [e] DMAP = 4-dimethylaminopyridine

3. Mechanistic Studies

Table S3. Results of reaction conditions A, B and C.



(*R*)-3a **racemic-3a**

Condition A: ^{i}PrOH:H_2O (3:1) (3.0 mL)
Condition B: ^{i}PrOH:H_2O (3:1) (3.0 mL) + HCOONa (10 eq)
Condition C: ^{i}PrOH:H_2O (3:1) (3.0 mL) + HCOONa (10 eq) + Et_3N (1eq)

Reaction Time/h	Condition A		Condition B		Condition C	
	ee[a]	Yield (%)[b]	ee[a]	yield (%)[b]	ee[a]	Yield (%)[b]
0	90	100%	90	100%	90	100%
3.5	88	95%	84	95%	36	85%
7.0	87	95%	71	85%	0	70%

[a] The *ee* value was determined by a Daicel Chiralcel® AD–H column. [b] Isolated yield.

Scheme S1. Proposed reaction mechanism.

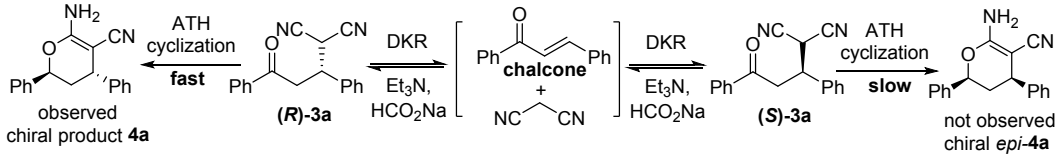
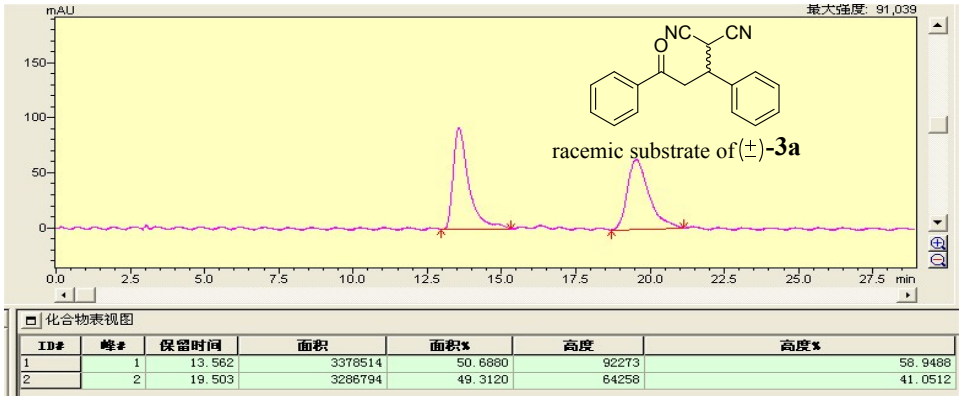
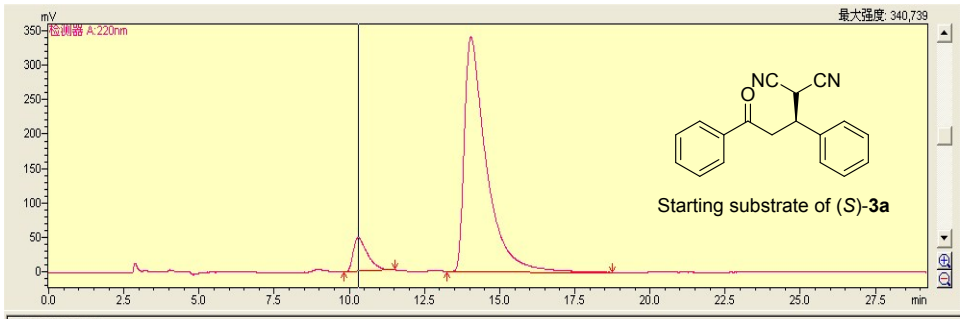


Figure S1. The **A**-catalyzed DKR-ATH-cyclization tandem reactions of (*R*)-**3a** or (*S*)-**3a.**



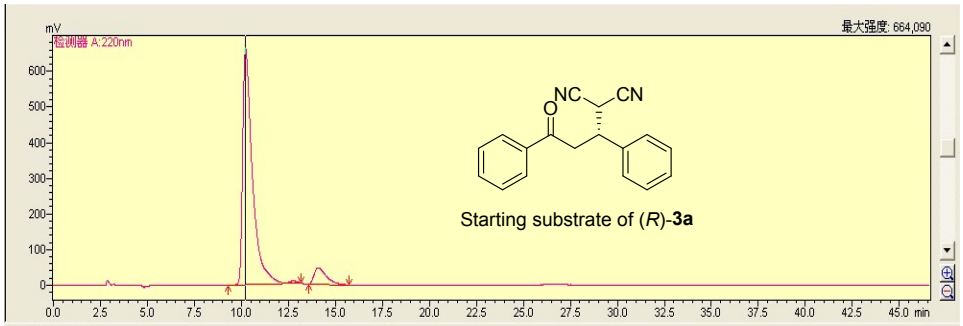
化合物表视图

ID#	峰#	保留时间	面积	面积%	高度	高度%
1	1	13.562	3378514	50.6880	92273	58.9488
2	2	19.503	3286794	49.3120	64258	41.0512



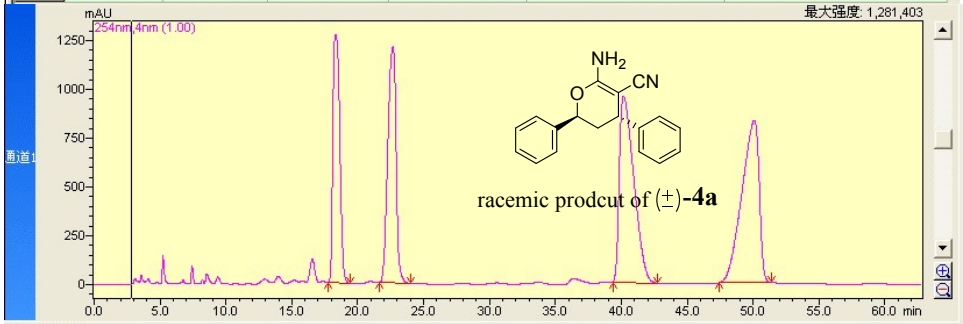
化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT10.294	10.294	1	1613442	48971	8.5753
2	RT14.041	14.041	2	17201655	339826	91.4247



化合物表视图

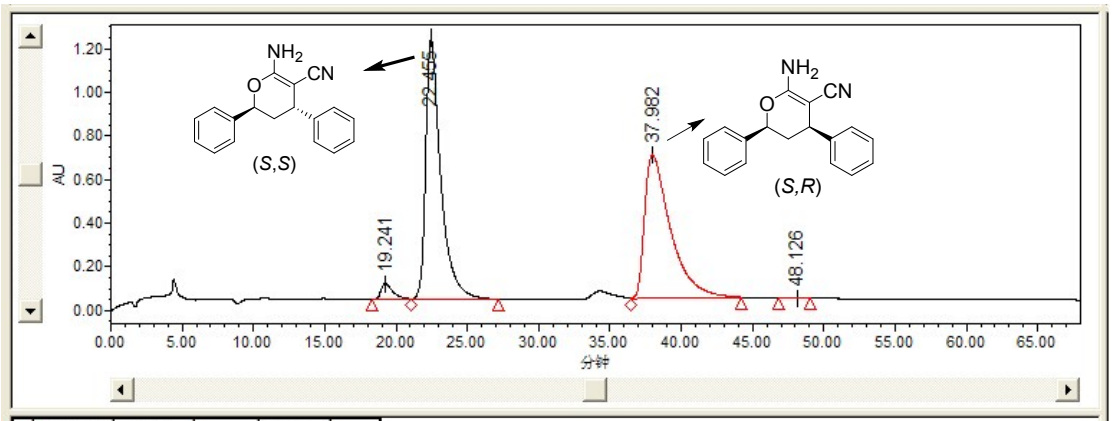
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT10.225	10.225	1	24160704	662815	91.9449
2	RT14.079	14.079	2	2116661	47061	8.0551



化合物表视图

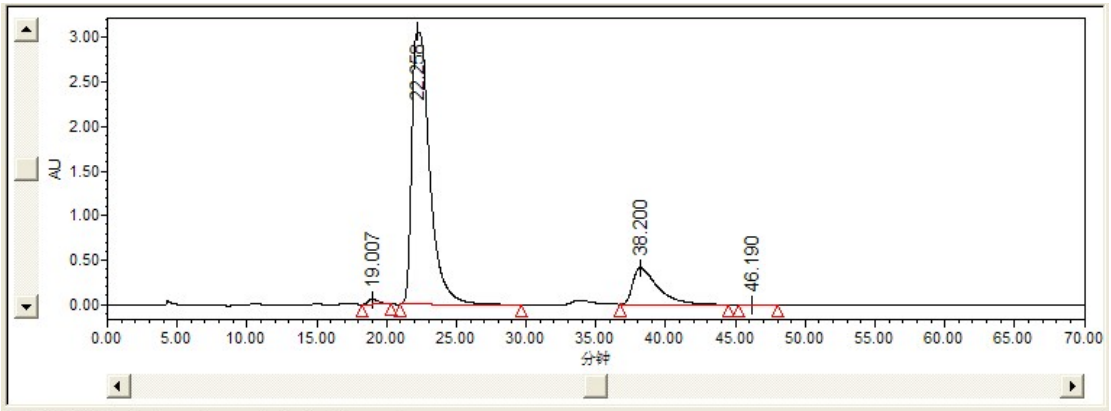
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT18.326	18.326	1	46299539	1272824	18.6774
2	RT22.661	22.661	2	52718969	1210678	21.2670
3	RT40.169	40.169	3	72849412	954352	29.3877
4	RT50.077	50.077	4	76023201	831949	30.6680

The **A**-catalyzed DKR-ATH-cyclization tandem reactions of (*S*)-**3a** (reaction time 7 h).



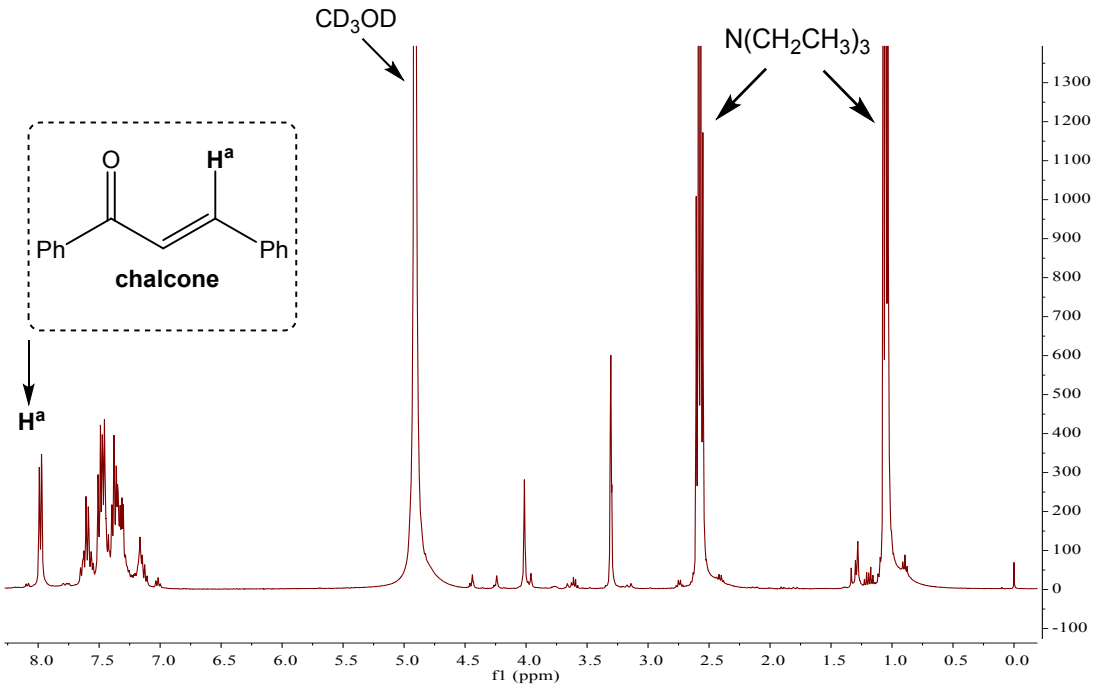
	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	% 高
1	19.241	4171343	2.38	71116	3.69
2	22.455	87716733	50.08	1194903	62.08
3	37.982	83255433	47.53	658491	34.21
4	48.126	23549	0.01	-357	0.02

The **A**-catalyzed DKR-ATH-cyclization tandem reactions of (*S*)-**3a** (reaction time 3.5 h, reaction time 7h see supporting information).



	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	% 高
1	19.007	3000746	0.91	58398	1.65
2	22.258	274194872	83.54	3060180	86.67
3	38.200	50735732	15.46	409378	11.59
4	46.190	274102	0.08	2712	0.08

Figure S2. Captured intermediate of chalcone in the ^{1}H NMR spectrum by the treatment of (*S*)-**3a** with NEt_3 in CD_3OD in a NMR-tube experiement.



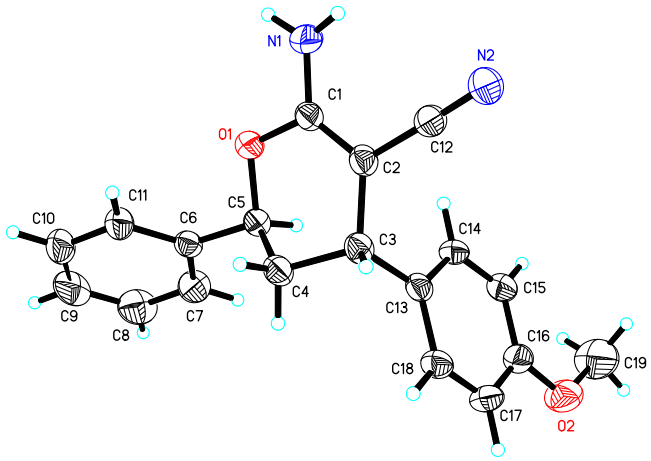
4. Procedure for growing X-ray crystal structures of chiral **4h**

Crystals of compound (2*S*, 4*S*)-**4h** was grown by liquid–liquid diffusion. Compound **4h** (0.10 g) was dissolved in 3.0 mL of $CHCl_3$. Toluene (1.0 mL) was then slowly added via a pipette along the sides of the tube so that the solution was not disturbed, forming a layer of toluene. The tube was then covered and the solvents were allowed to slowly diffuse at room temperature. The resultant crystals were separated from the solution by decanting.

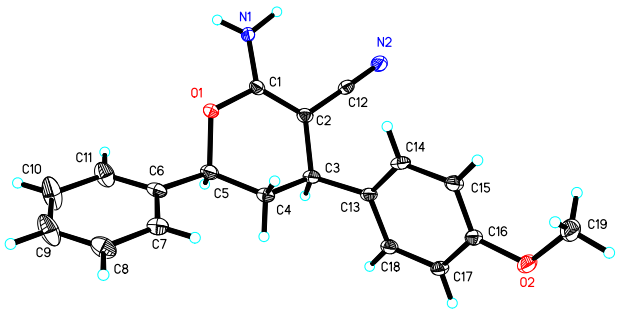
Suitable X-ray quality crystals were recovered and mounted using epoxy glue. Data were collected using on a Bruker SMART APEX CCD area detector diffractometer. SAINT (Bruker, 1998), SHELXTL (Bruker, 1998), and SHELXS 97 were used for cell refinement, data reduction and structure solving, and refinement of structure. Molecular graphics and publication materials were prepared using SHELXTL.

Figure S3. X-Ray crystal structures of chiral **4h** and its 1:1 mixture of (*S*, *S*) and (*S, R*) epimeric form**.**

Chiral **4h**

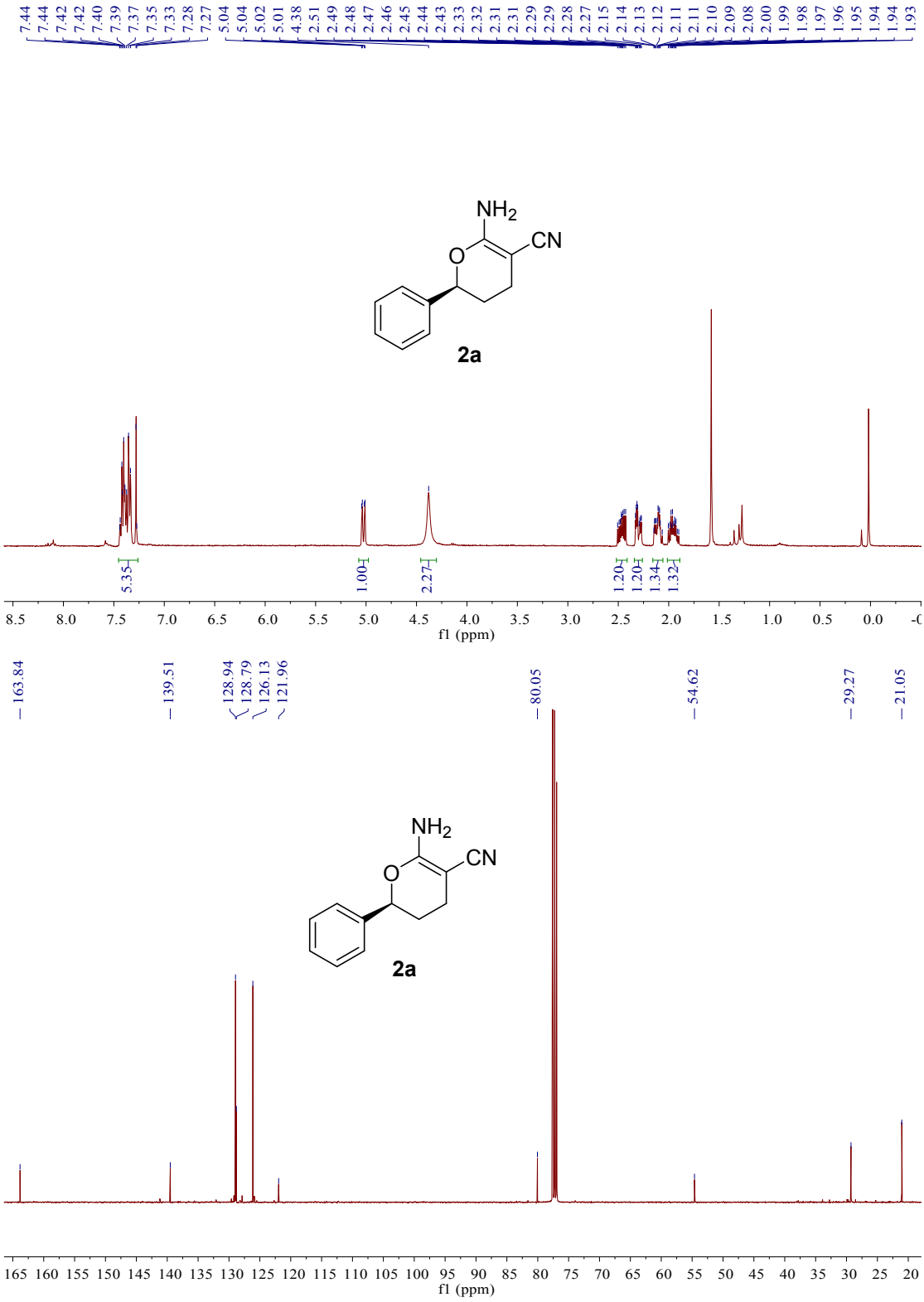


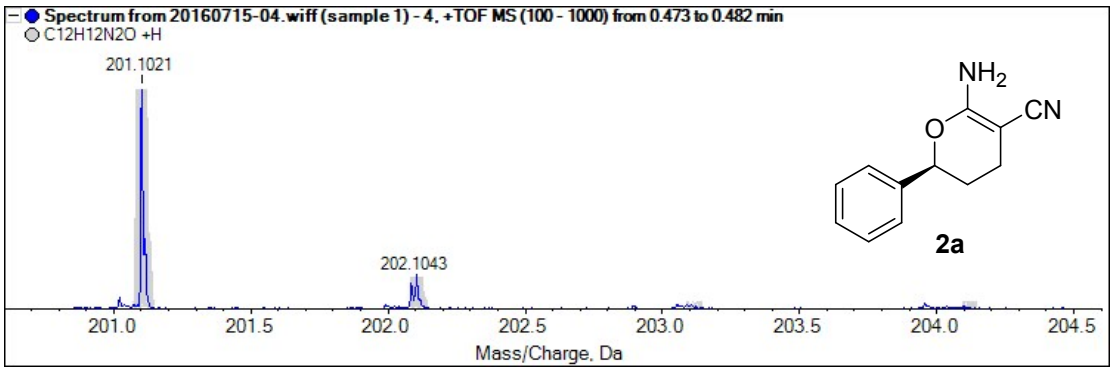
1:1 mixture of (*S*, *S*) and (*S, R*) **4h**



5. ^{1}H NMR, ^{13}C NMR and HRMS of Chiral Products

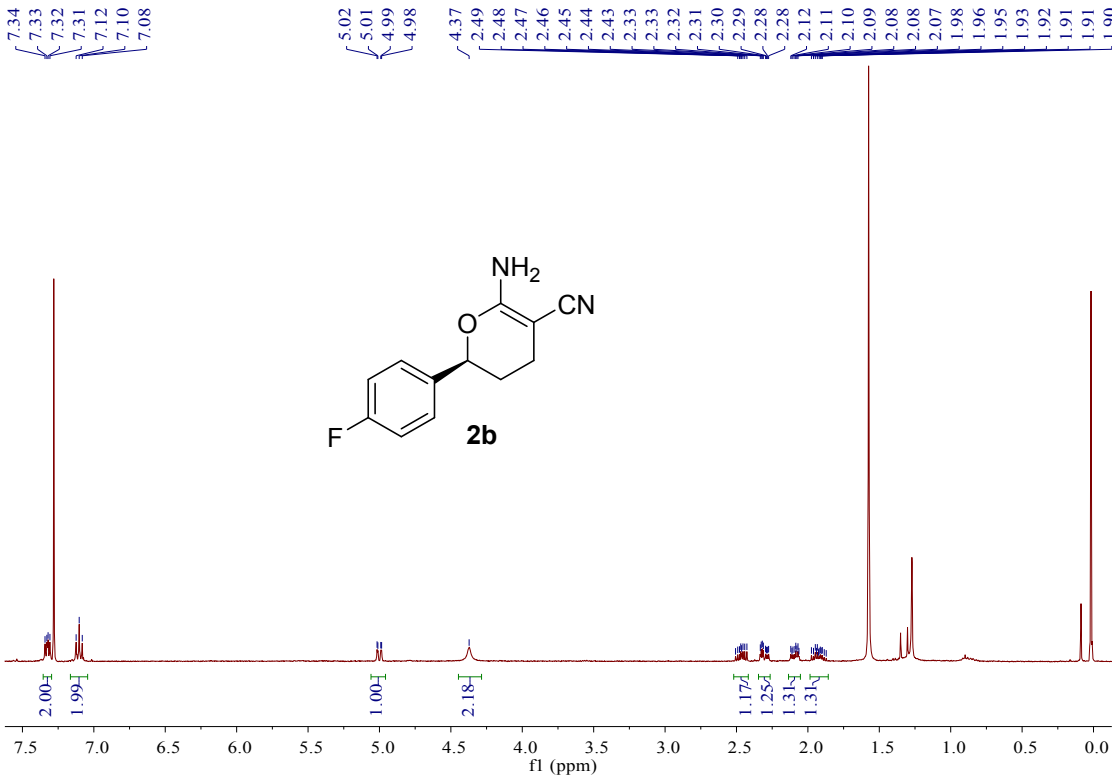
2a: (*S*)-6-Amino-2-phenyl-3,4-dihydro-2*H*-pyran-5-carbonitrile.

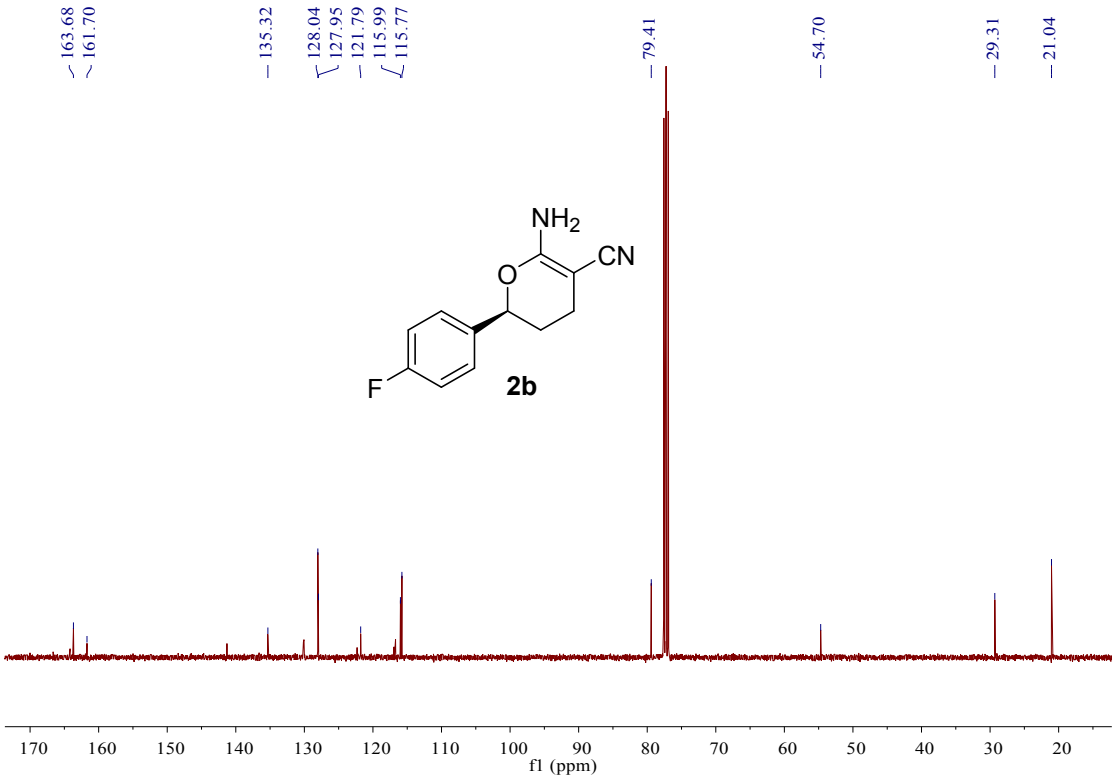


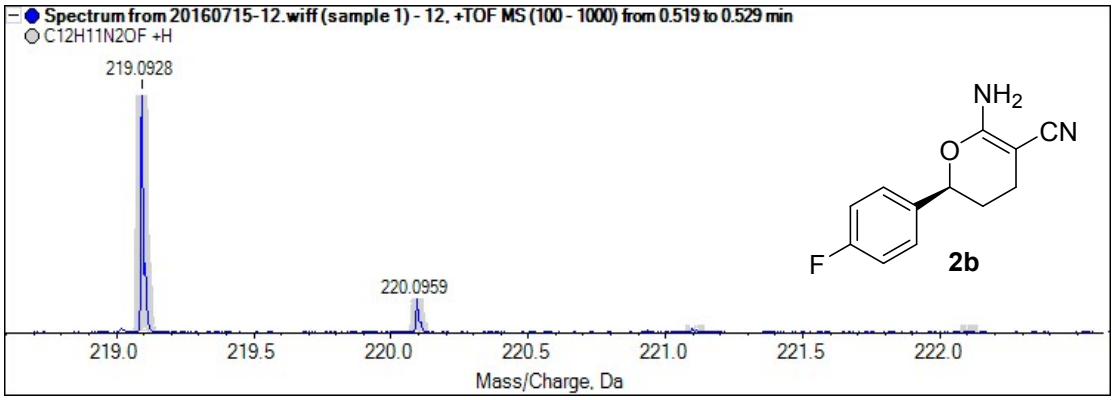


Formula	Intensity	Threshold	Expected m/z	Found at m/z	Error (ppm)
C12H12N2O	**624577**	**100**	**201.1022**	**201.1021**	**-0.8**

2b: (*S*)-6-amino-2-(4-fluorophenyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile.

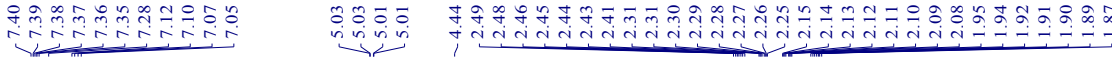


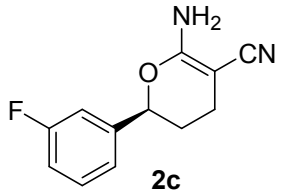




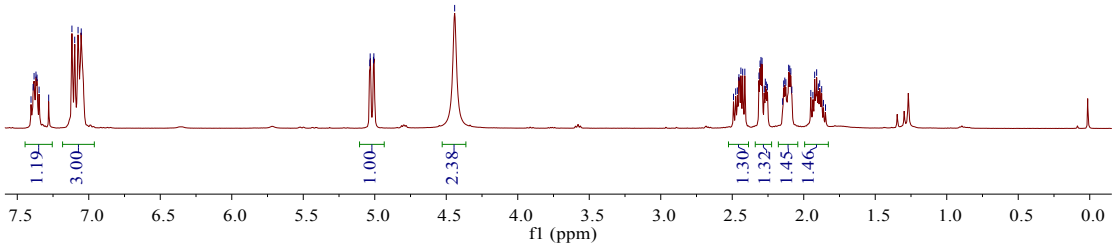
Formula	Intensity	Threshold	Expected m/z	Found at m/z	Error (ppm)
C12H11N2OF	**759275**	**100**	**219.0928**	**219.0928**	**-0.1**

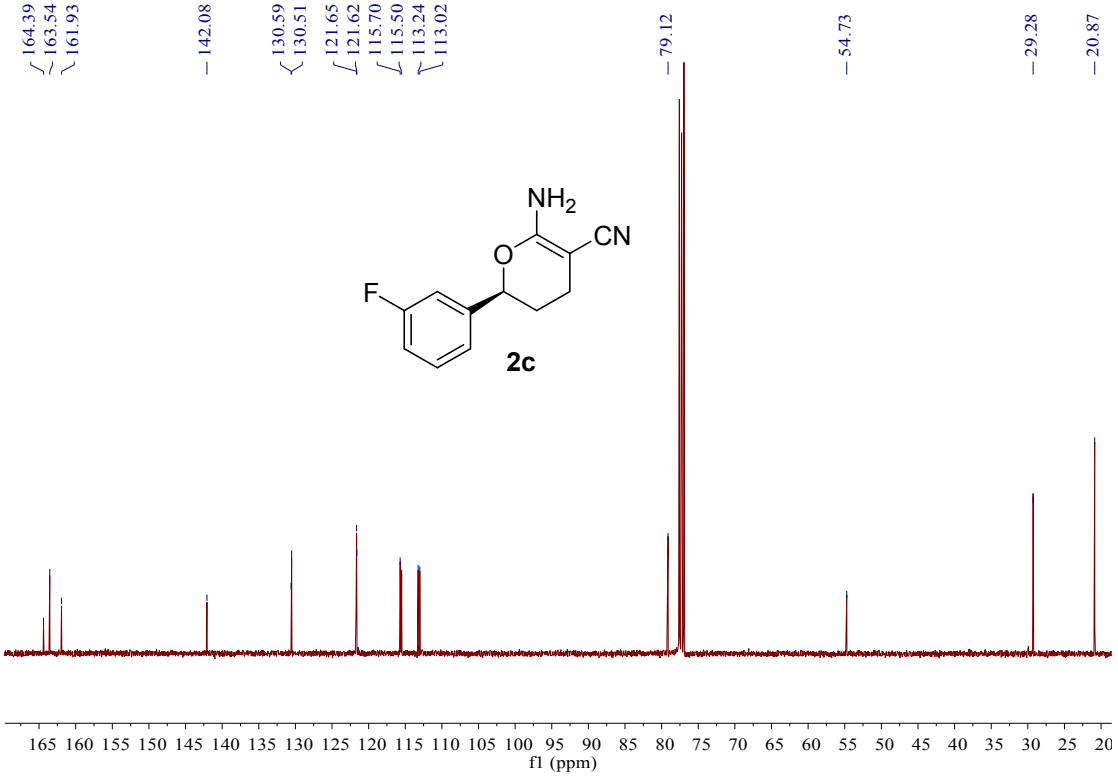
2c: (*S*)-6-amino-2-(3-fluorophenyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile.



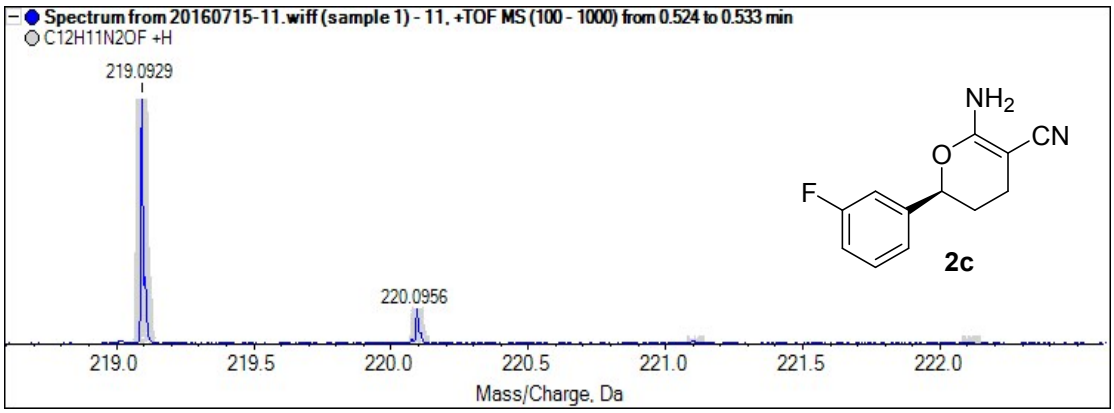


2c



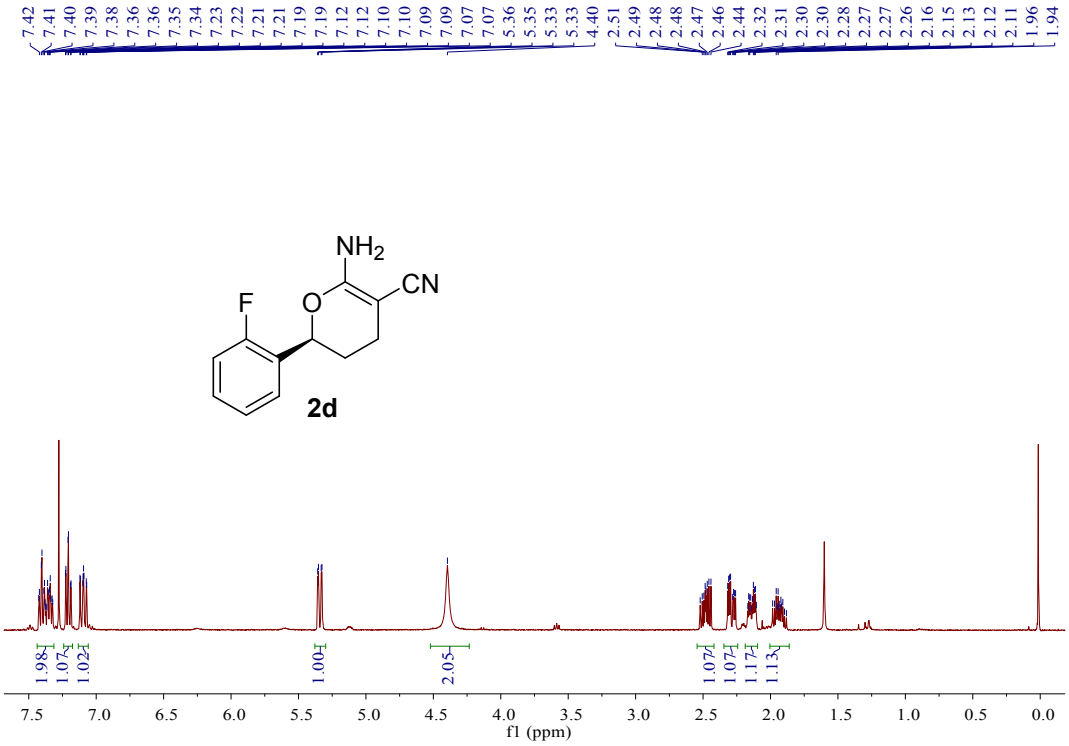


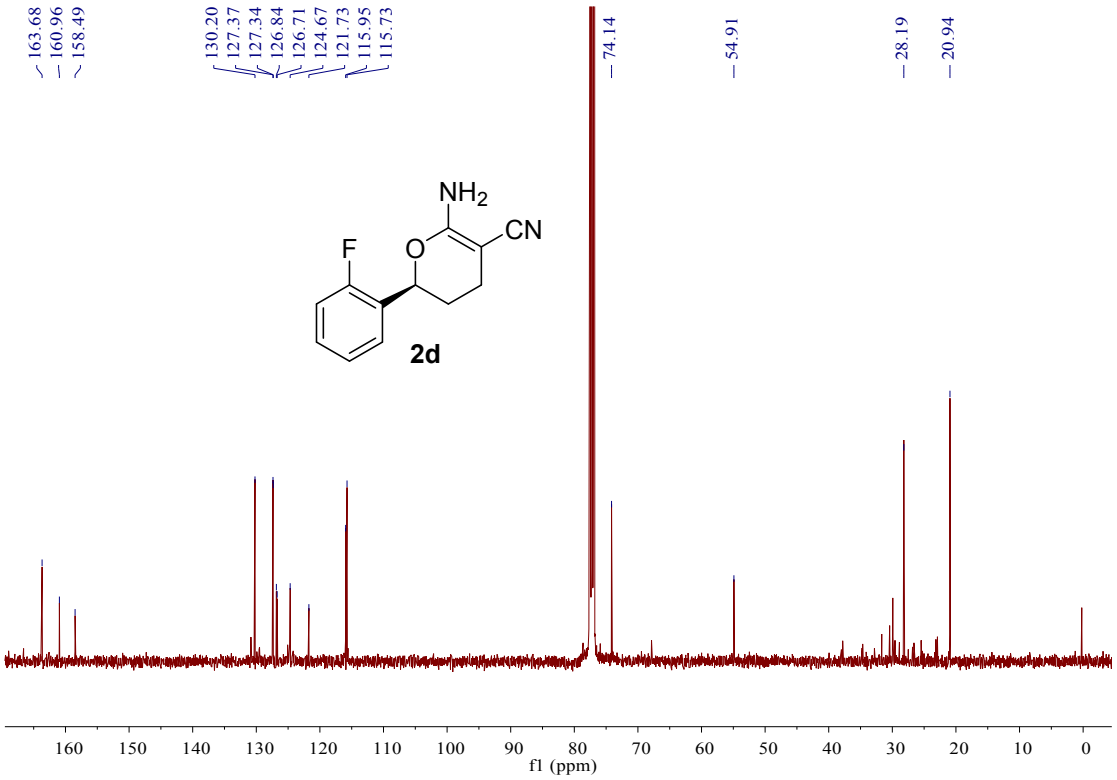
2c

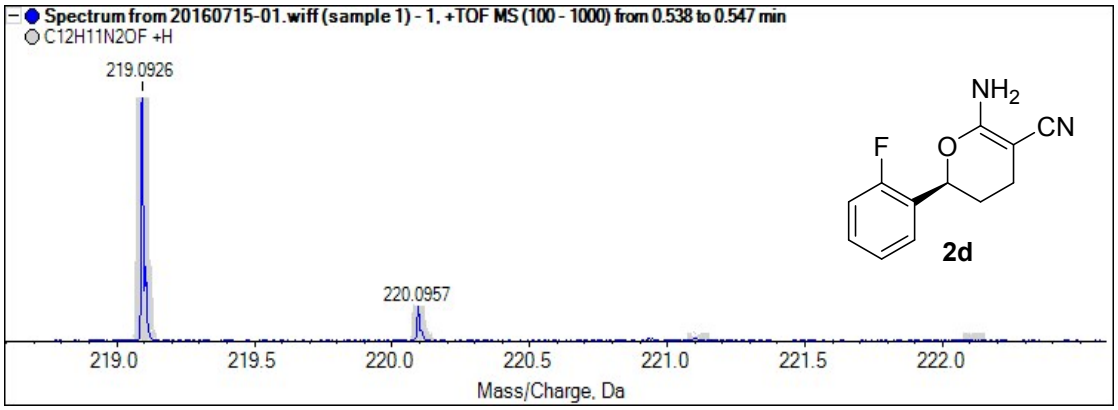


Formula	Intensity	Threshold	Expected m/z	Found at m/z	Error (ppm)
C12H11N2OF	**1547752**	**100**	**219.0928**	**219.0929**	**0.5**

2d: (*S*)-6-amino-2-(2-fluorophenyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile.

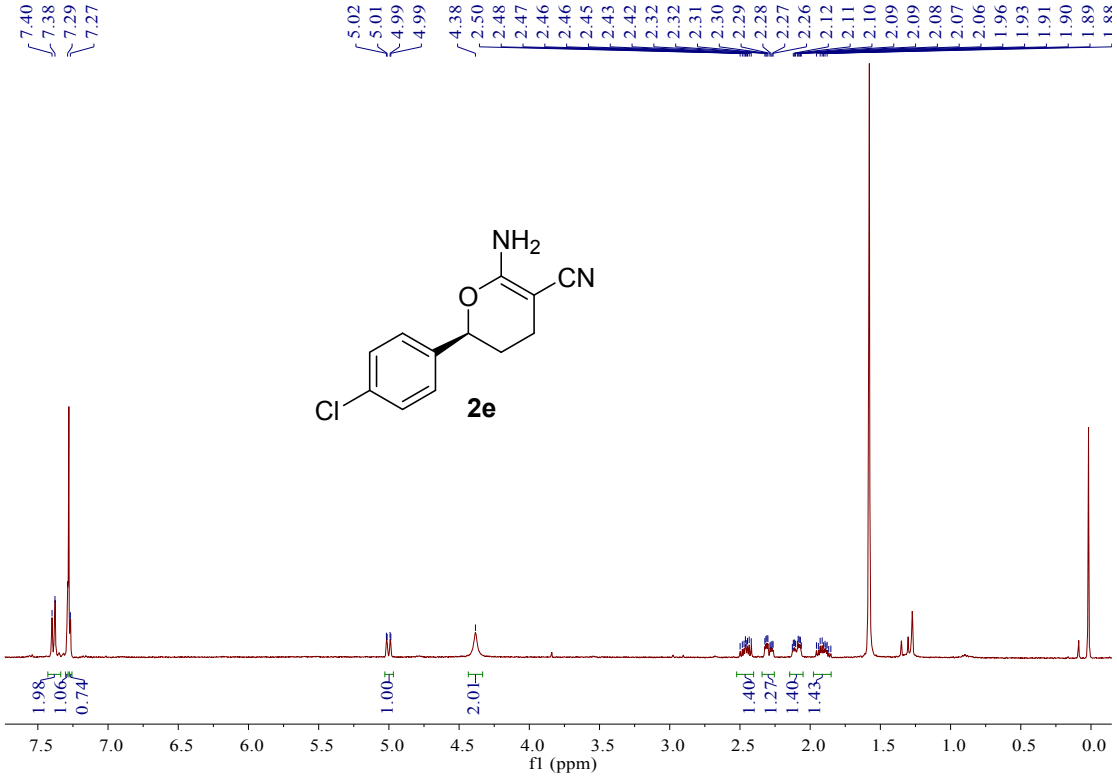


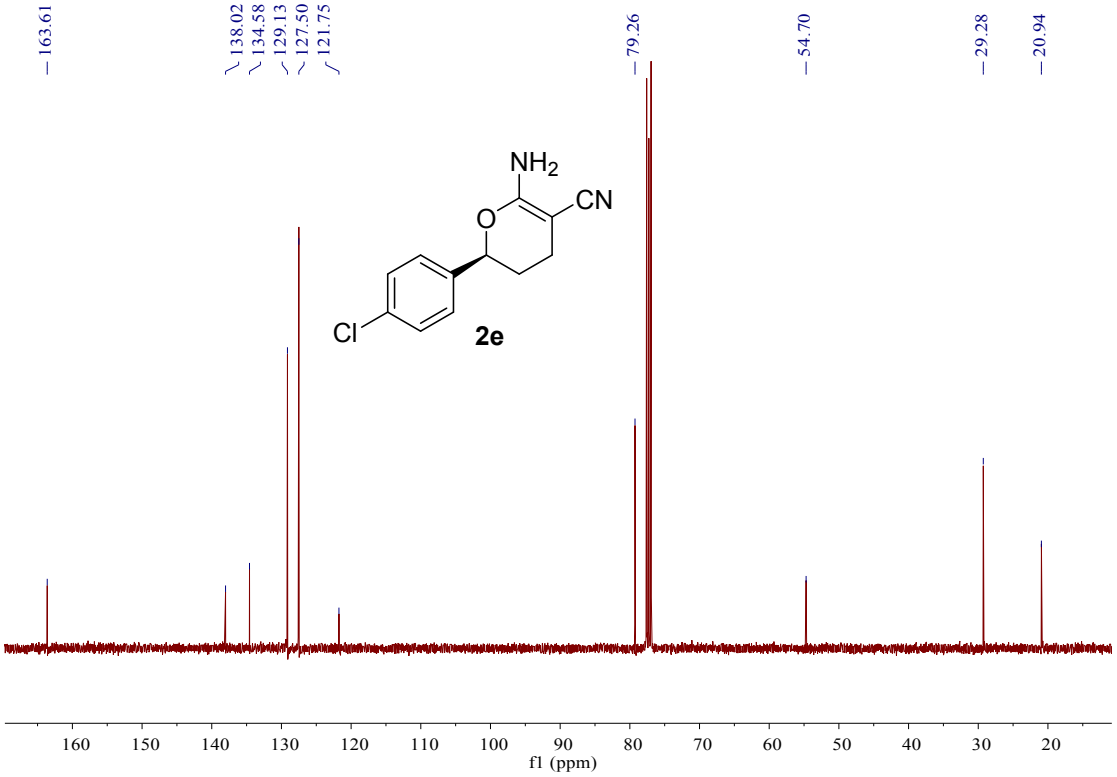


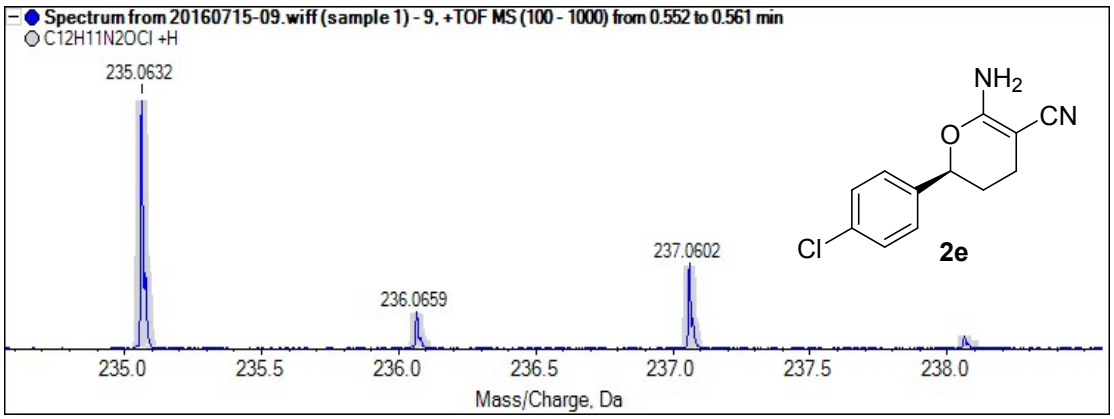


C12H11N2OF	**1041434**	**100**	**219.0928**	**219.0926**	**-1.0**

2e: (*S*)-6-amino-2-(4-chlorophenyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile.

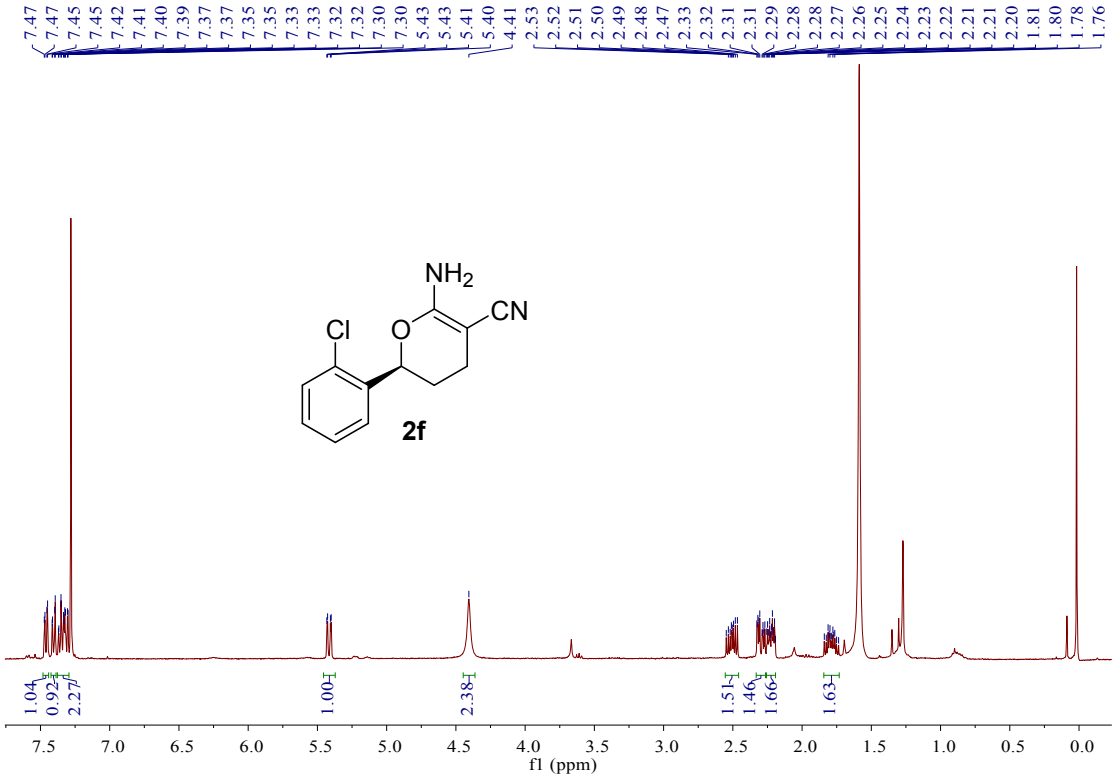


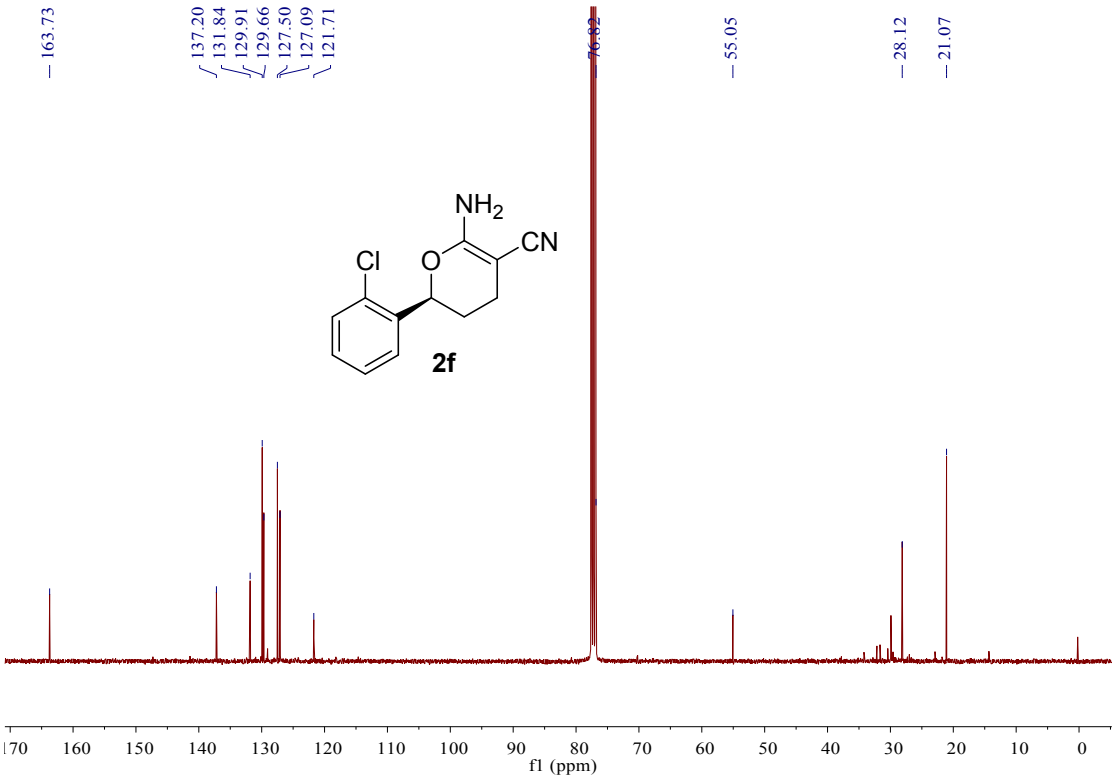


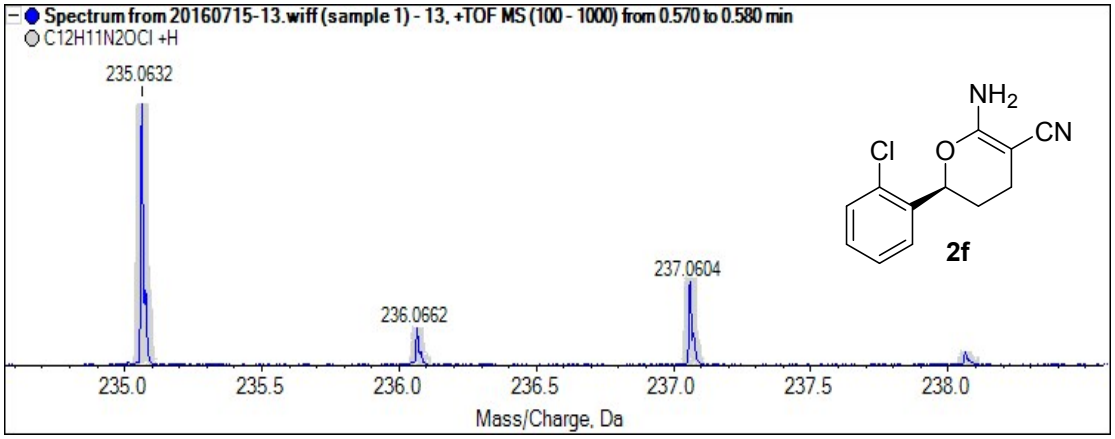


Formula	Intensity	Threshold	Expected m/z	Found at m/z	Error (ppm)
C12H11N2OCl	**1181211**	**100**	**235.0633**	**235.0632**	**-0.1**

2f: (*S*)-6-amino-2-(2-chlorophenyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile.

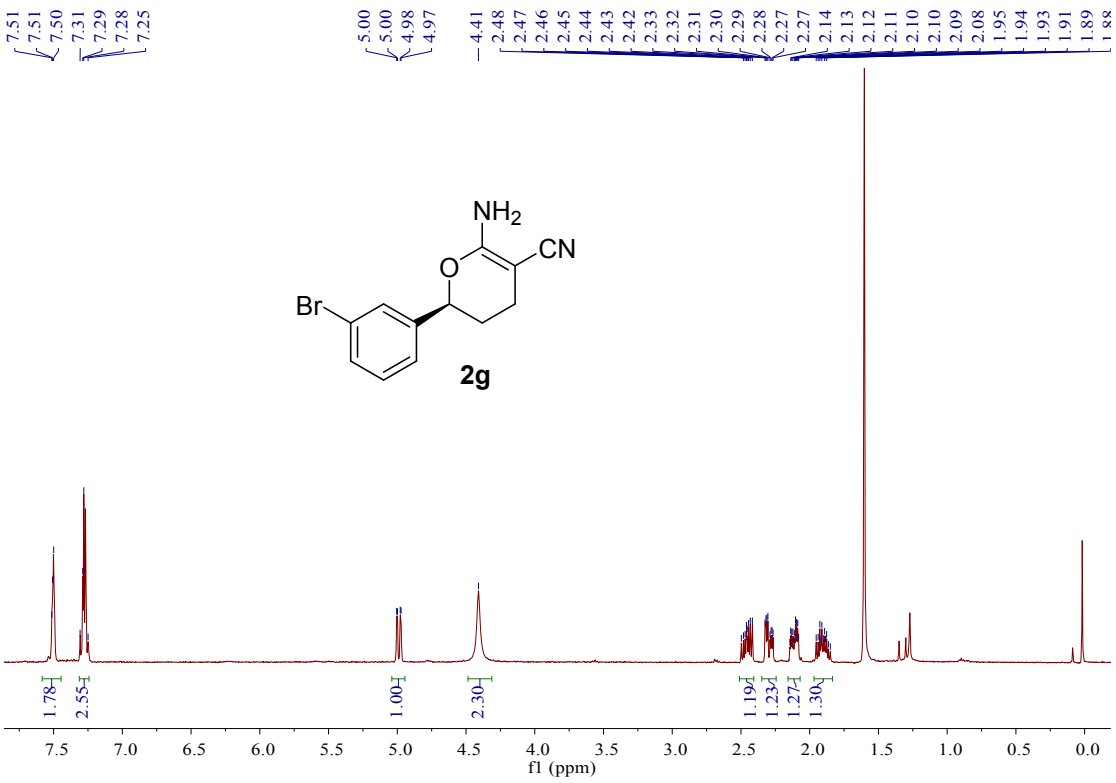


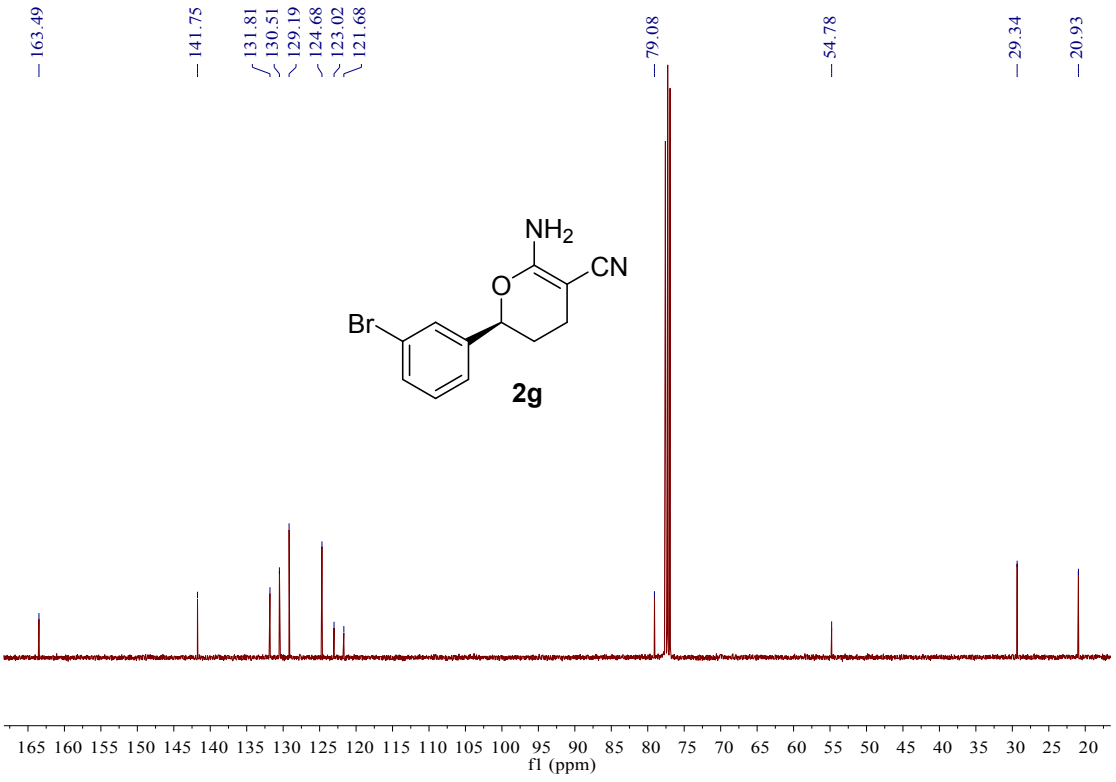


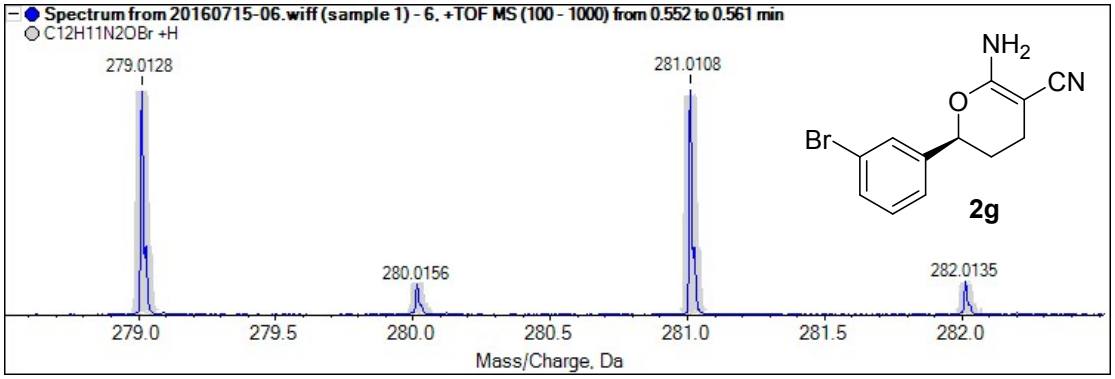


Formula	Intensity	Threshold	Expected m/z	Found at m/z	Error (ppm)
C12H11N2OCl	**746126**	**100**	**235.0633**	**235.0632**	**-0.1**

2g: (*S*)-6-amino-2-(3-bromophenyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile.

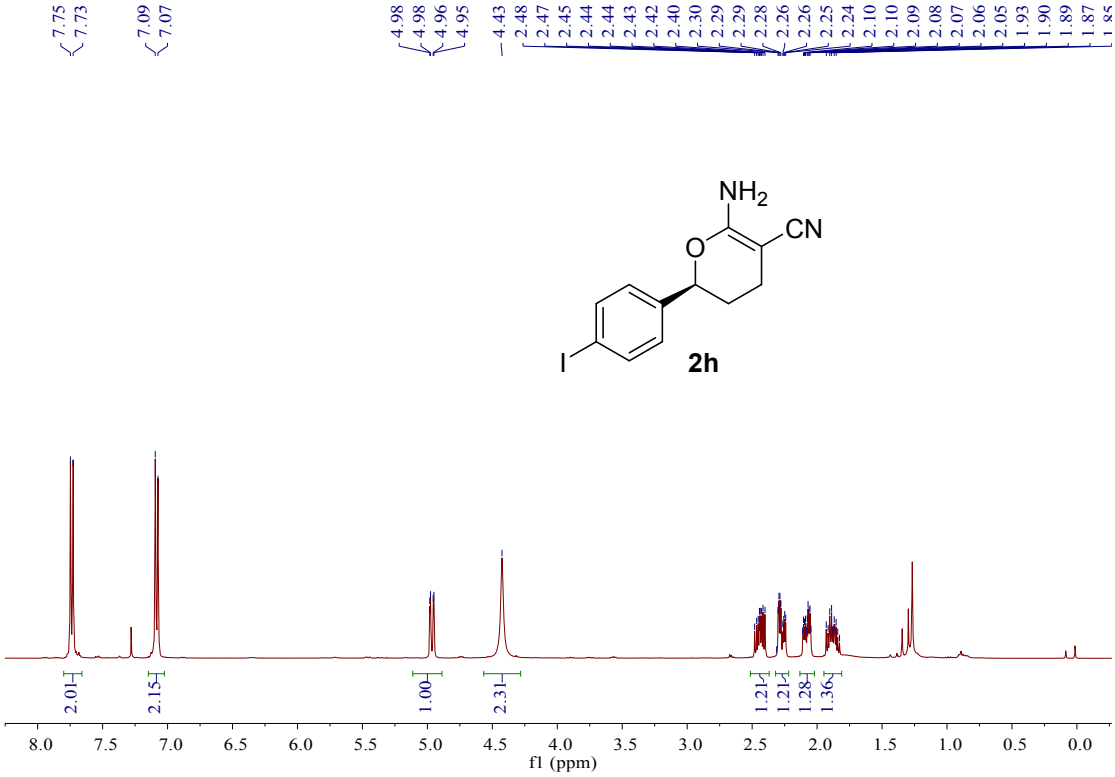


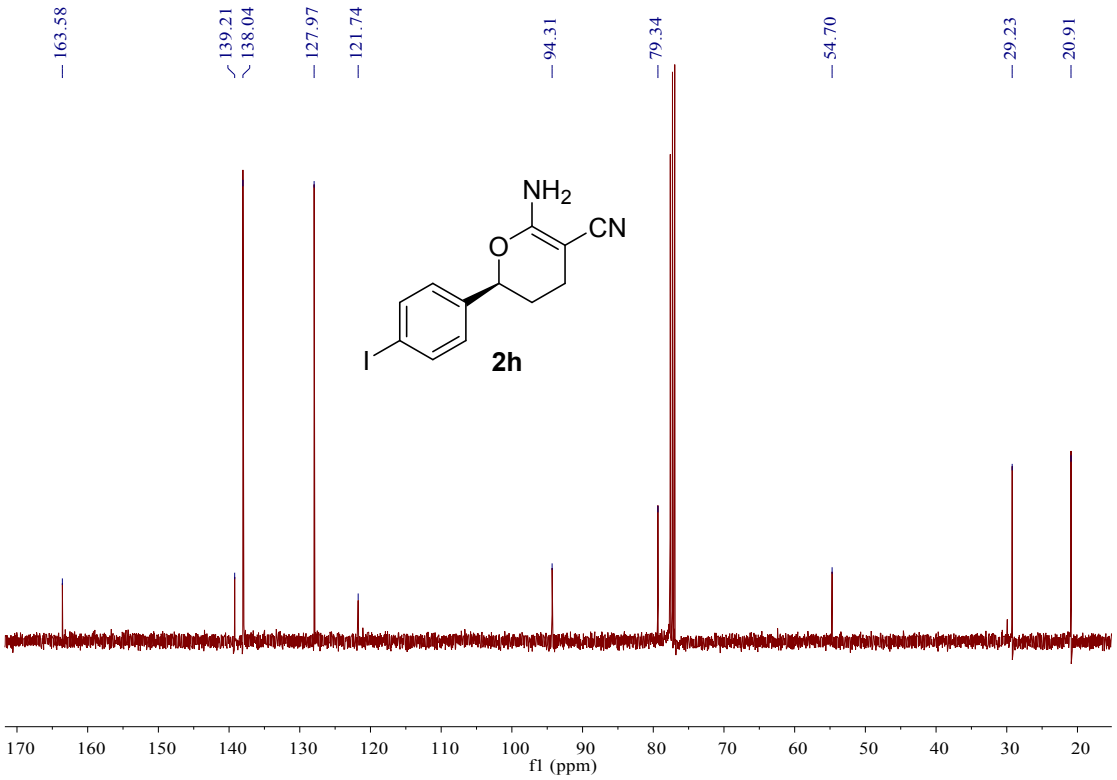


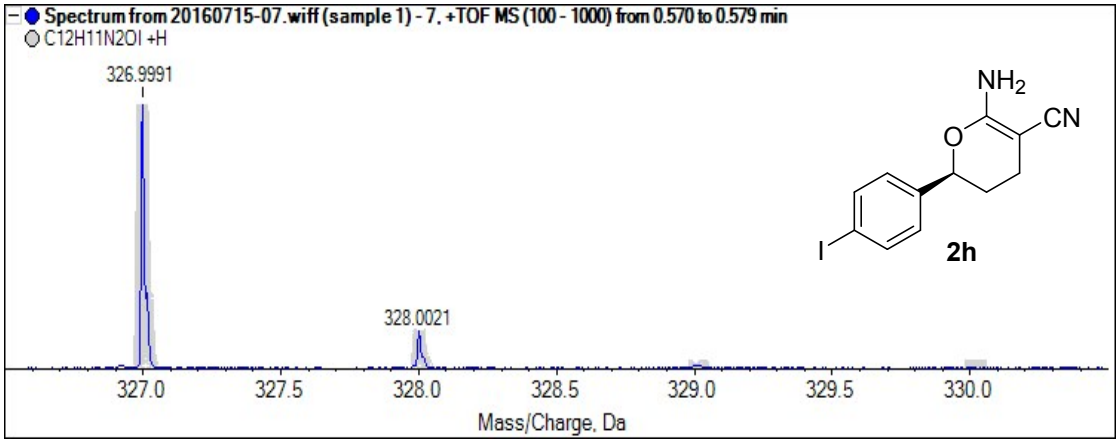


Formula	Intensity	Threshold	Expected m/z	Found at m/z	Error (ppm)
C12H11N2OBr	**1241905**	**100**	**279.0128**	**279.0128**	**0.0**

2h: (*S*)-6-amino-2-(4-iodophenyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile.

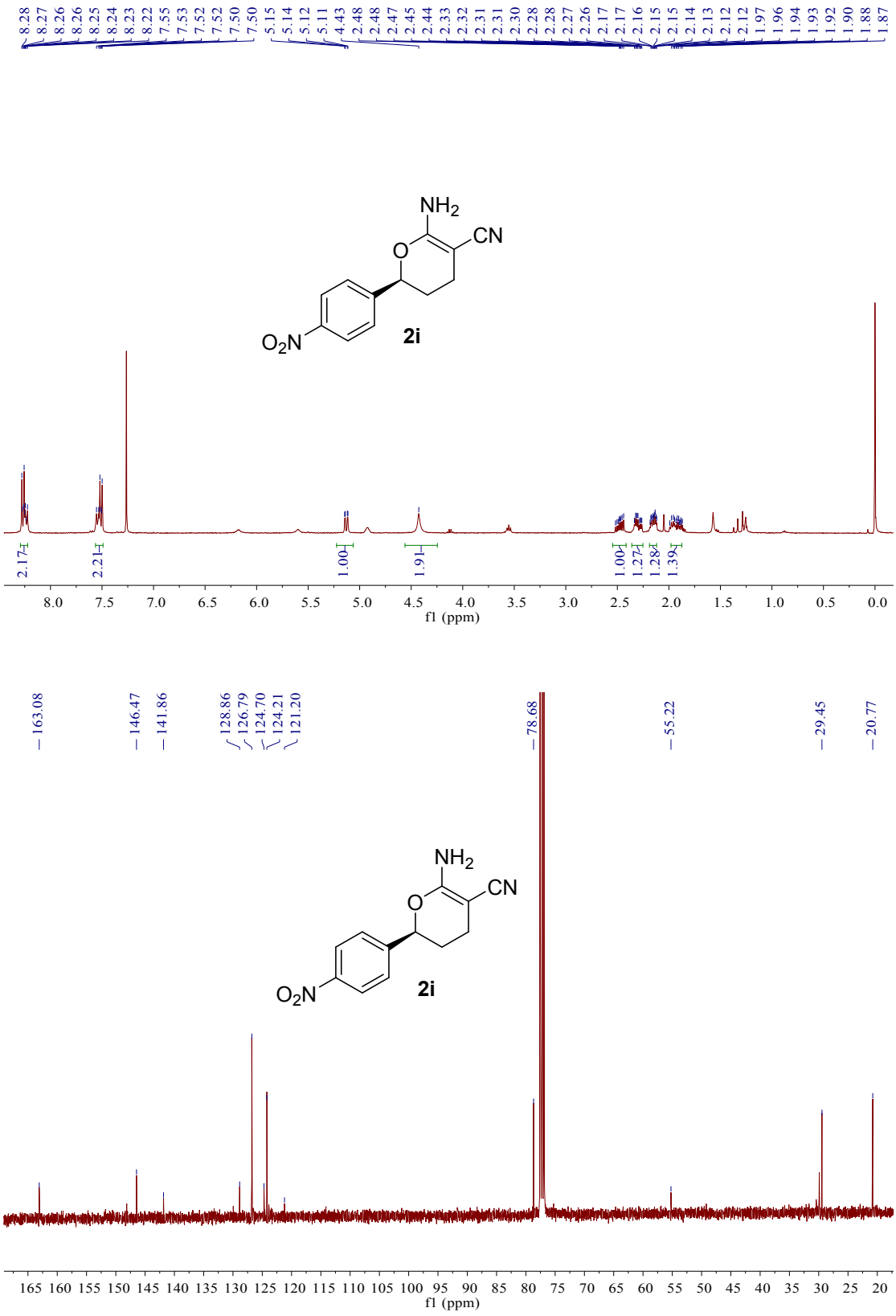


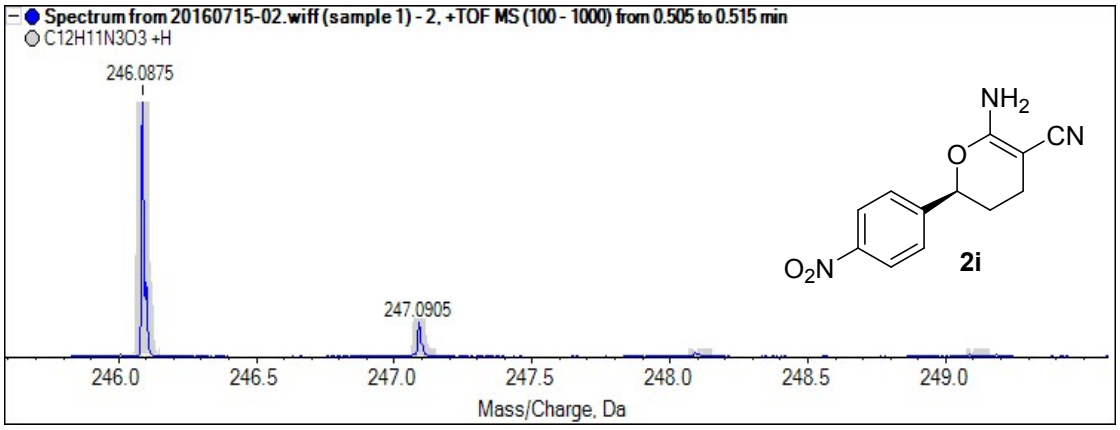




Formula	Intensity	Threshold	Expected m/z	Found at m/z	Error (ppm)
C12H11N2OI	**954119**	**100**	**326.9989**	**326.9991**	**0.7**

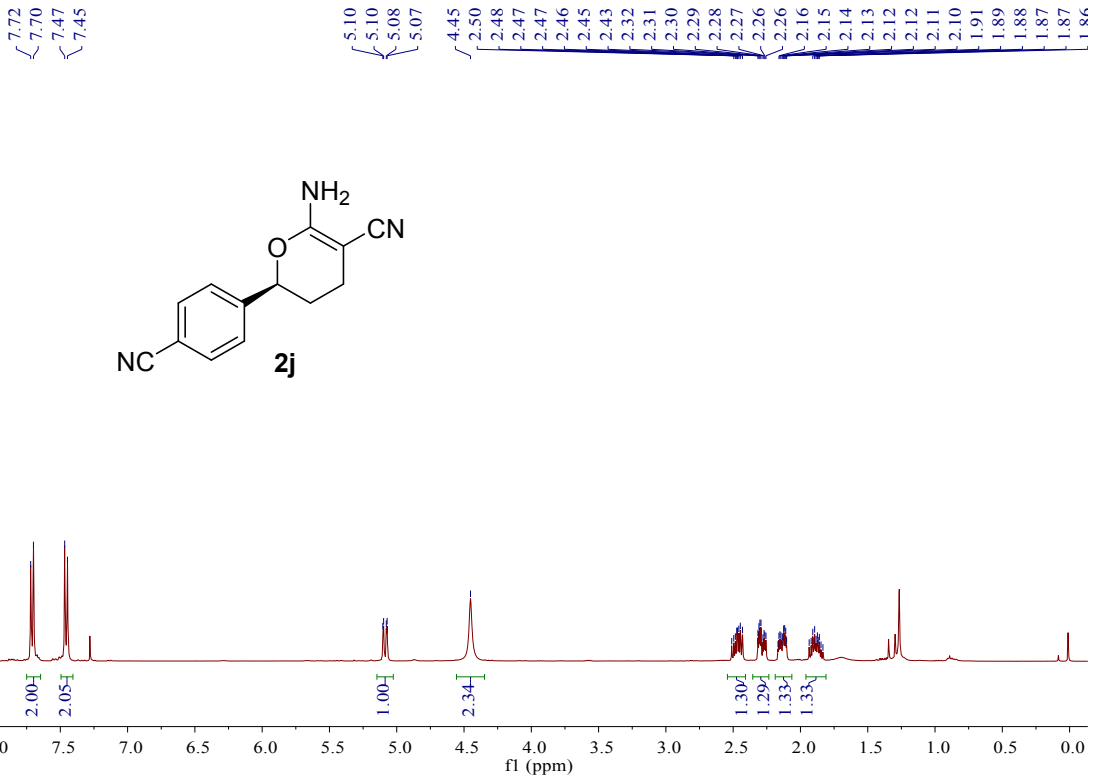
2i: (*S*)-6-amino-2-(4-nitrophenyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile.

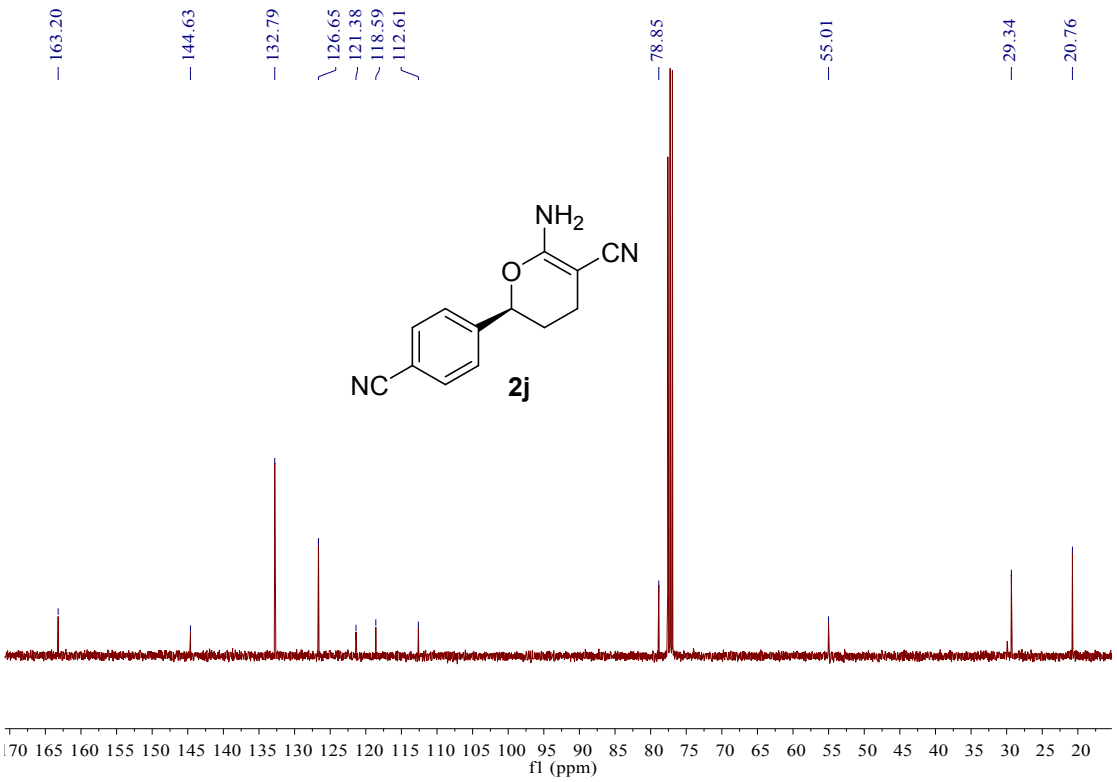


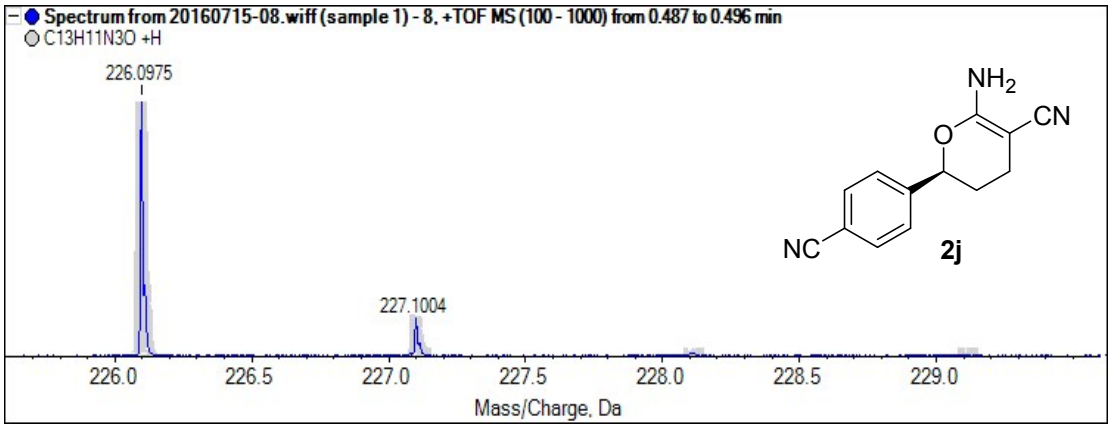


Formula	Intensity	Threshold	Expected m/z	Found at m/z	Error (ppm)
C12H11N3O3	**166622**	**100**	**246.0873**	**246.0875**	**0.6**

2j: (*S*)-6-amino-2-(4-cyanophenyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile.

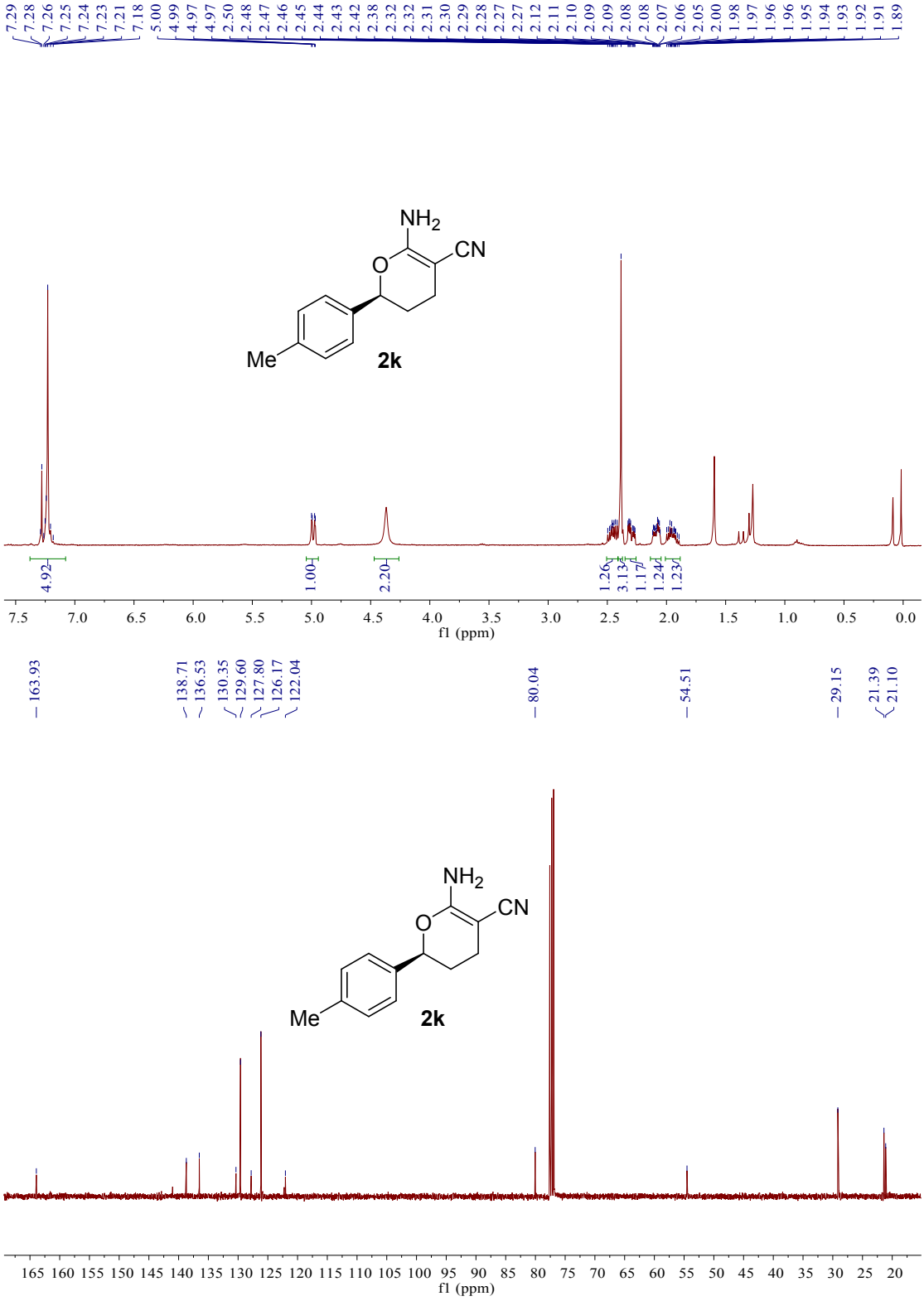


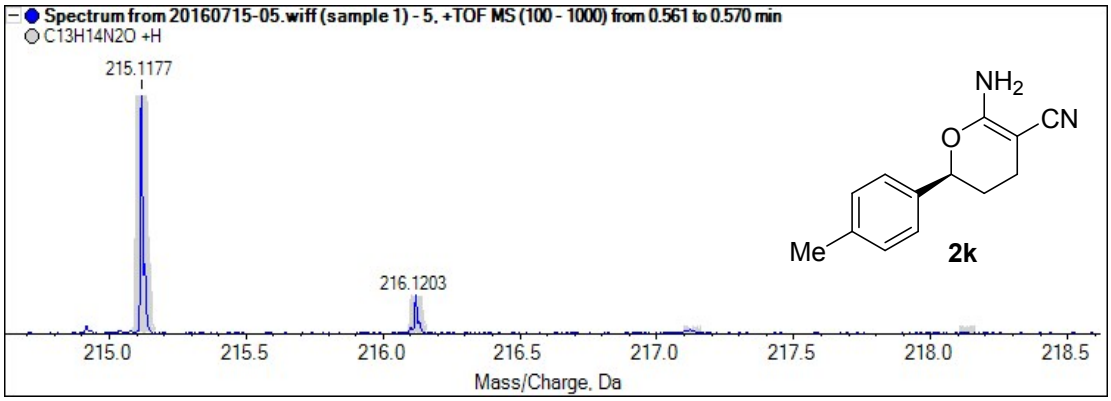




Formula	Intensity	Threshold	Expected m/z	Found at m/z	Error (ppm)
C13H11N3O	**700535**	**100**	**226.0975**	**226.0975**	**0.2**

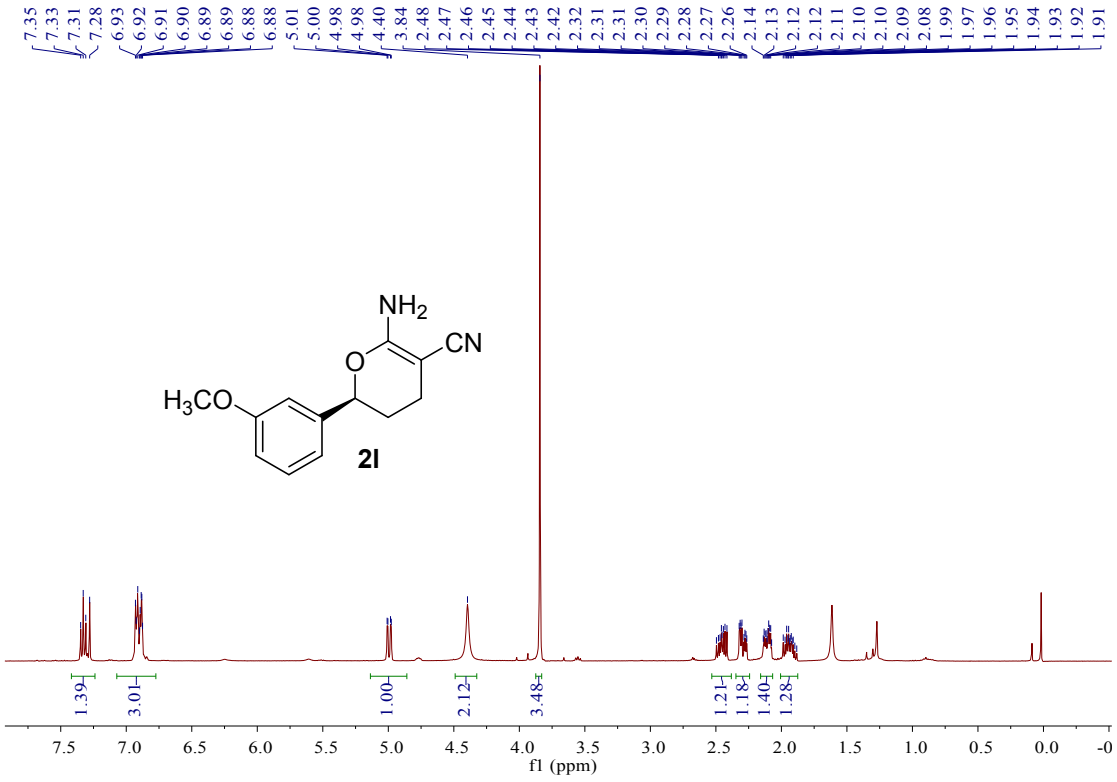
2k: (*S*)-6-amino-2-(p-tolyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile.

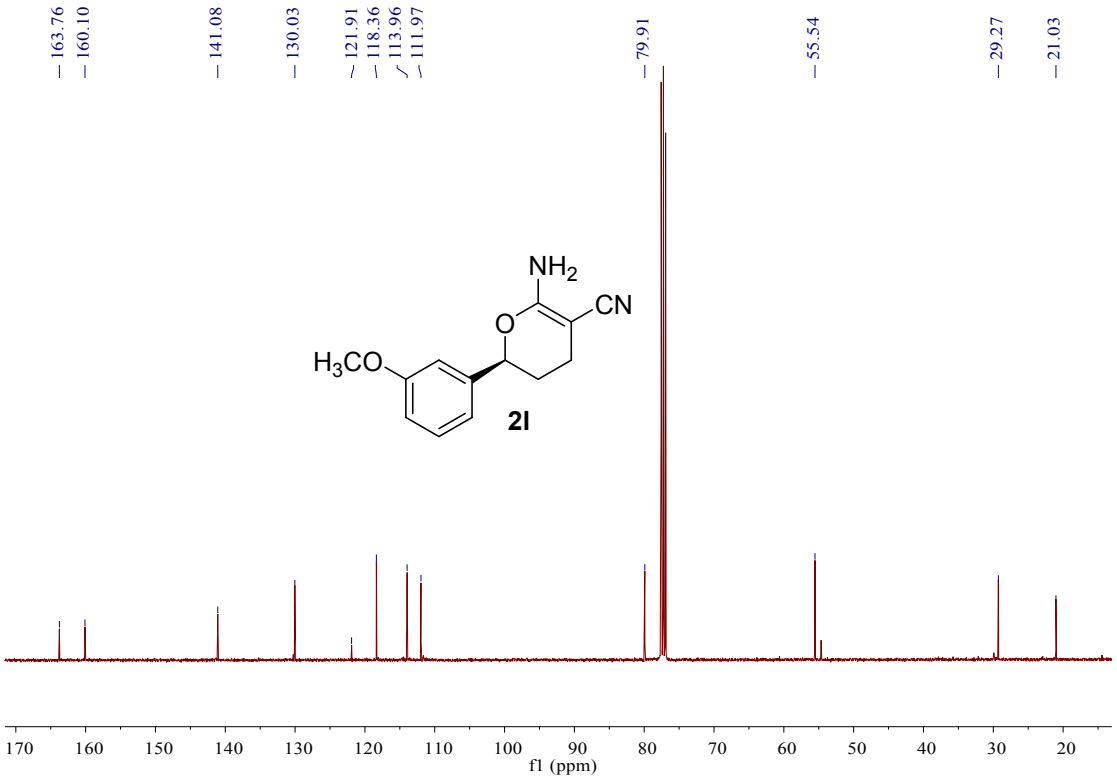


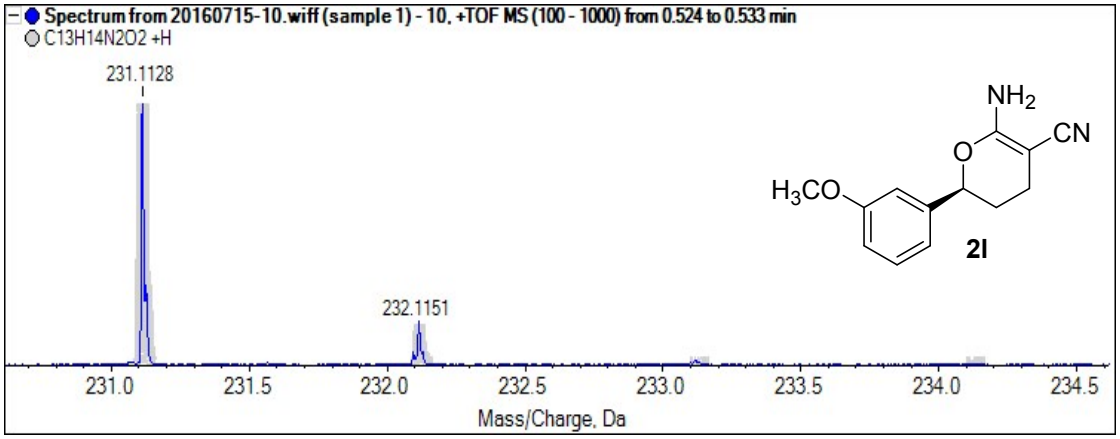


Formula	Intensity	Threshold	Expected m/z	Found at m/z	Error (ppm)
C13H14N2O	**629726**	**100**	**215.1179**	**215.1177**	**-0.9**

2l: (*S*)-6-amino-2-(3-methoxyphenyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile.

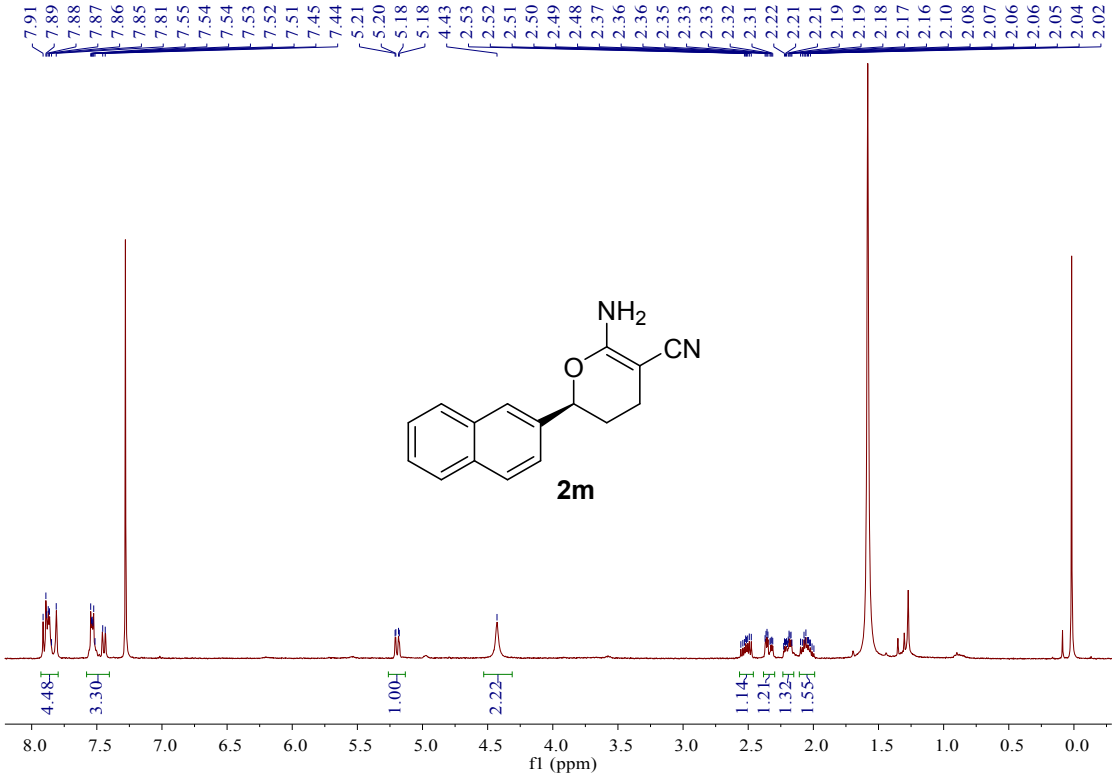


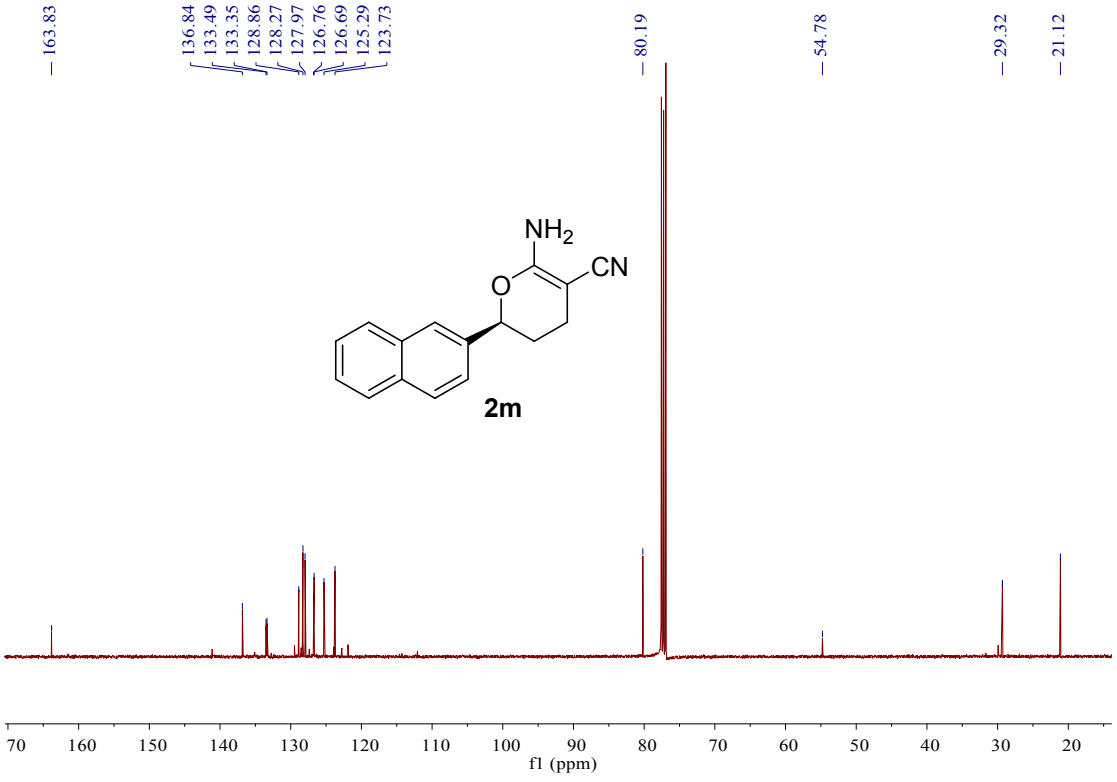


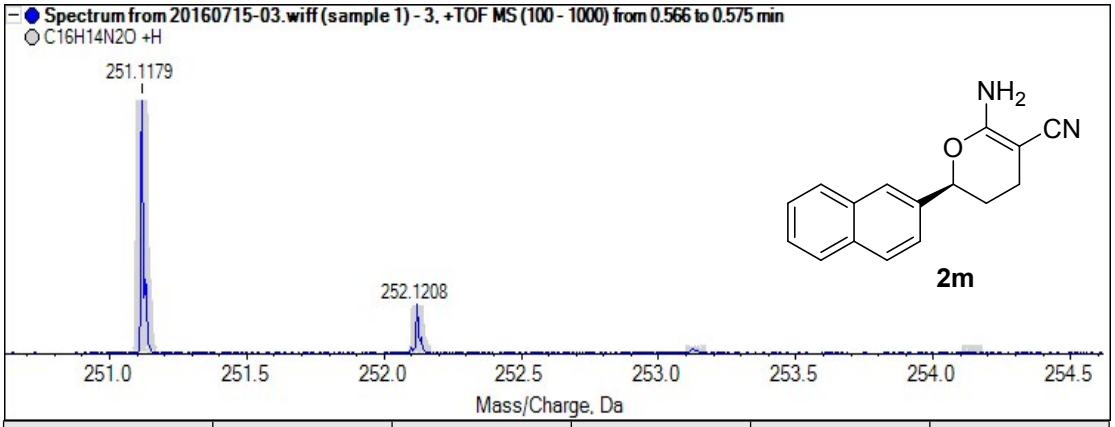


Formula	Intensity	Threshold	Expected m/z	Found at m/z	Error (ppm)
C13H14N2O2	**1701483**	**100**	**231.1128**	**231.1128**	**0.1**

2m: (*S*)-6-amino-2-(naphthalen-2-yl)-3,4-dihydro-2*H*-pyran-5-carbonitrile.

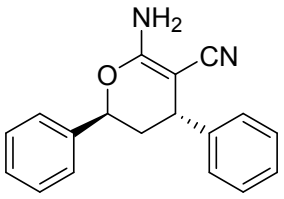




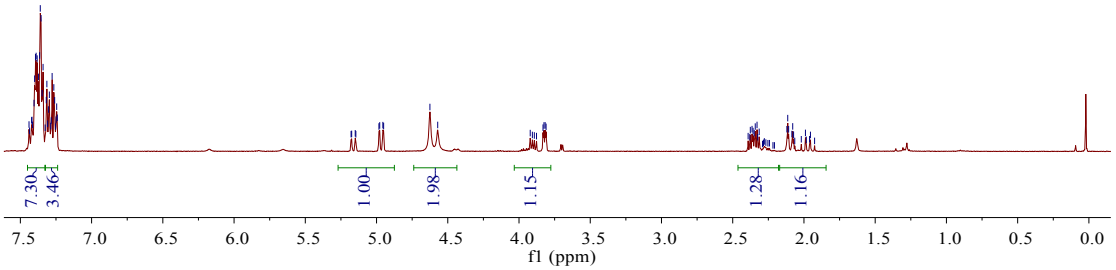


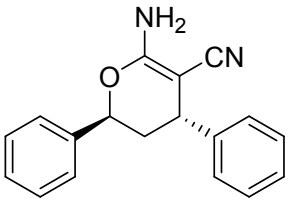
Formula	Intensity	Threshold	Expected m/z	Found at m/z	Error (ppm)
C16H14N2O	**1294479**	**100**	**251.1179**	**251.1179**	**0.2**

4a. (2*S*,4*S*)-6-amino-2,4-diphenyl-3,4-dihydro-2*H*-pyran-5 -carbonitrile.

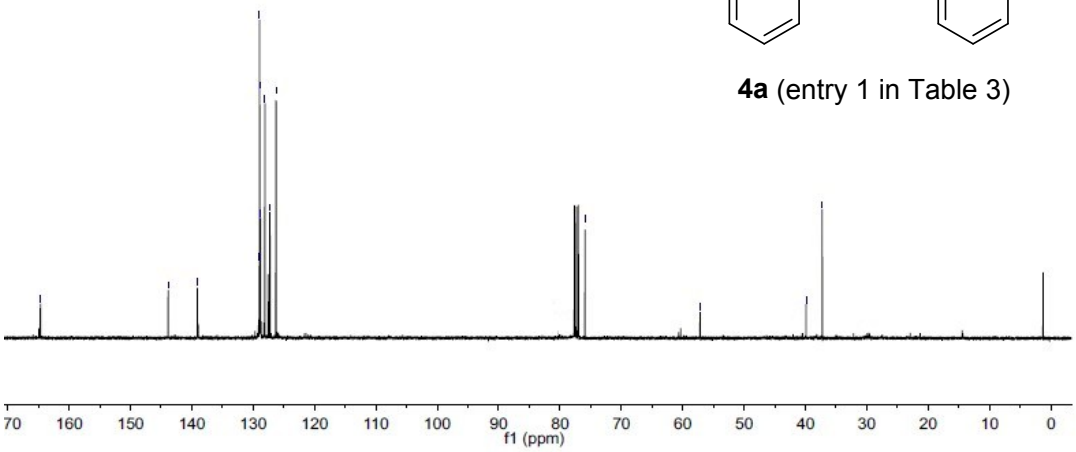


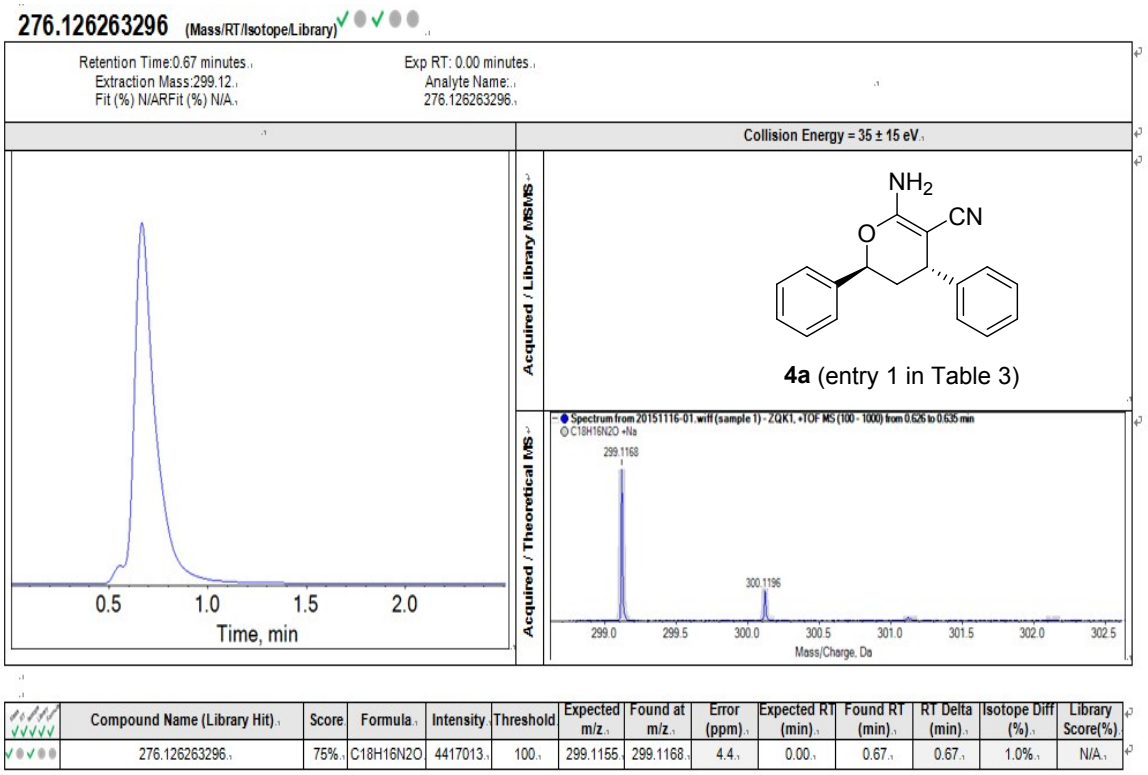
4a (entry 1 in Table 3)





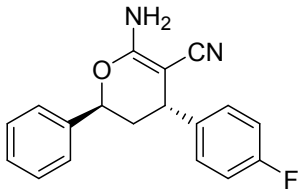
4a (entry 1 in Table 3)



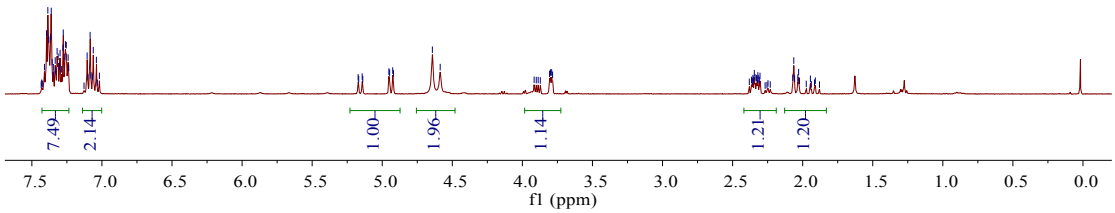


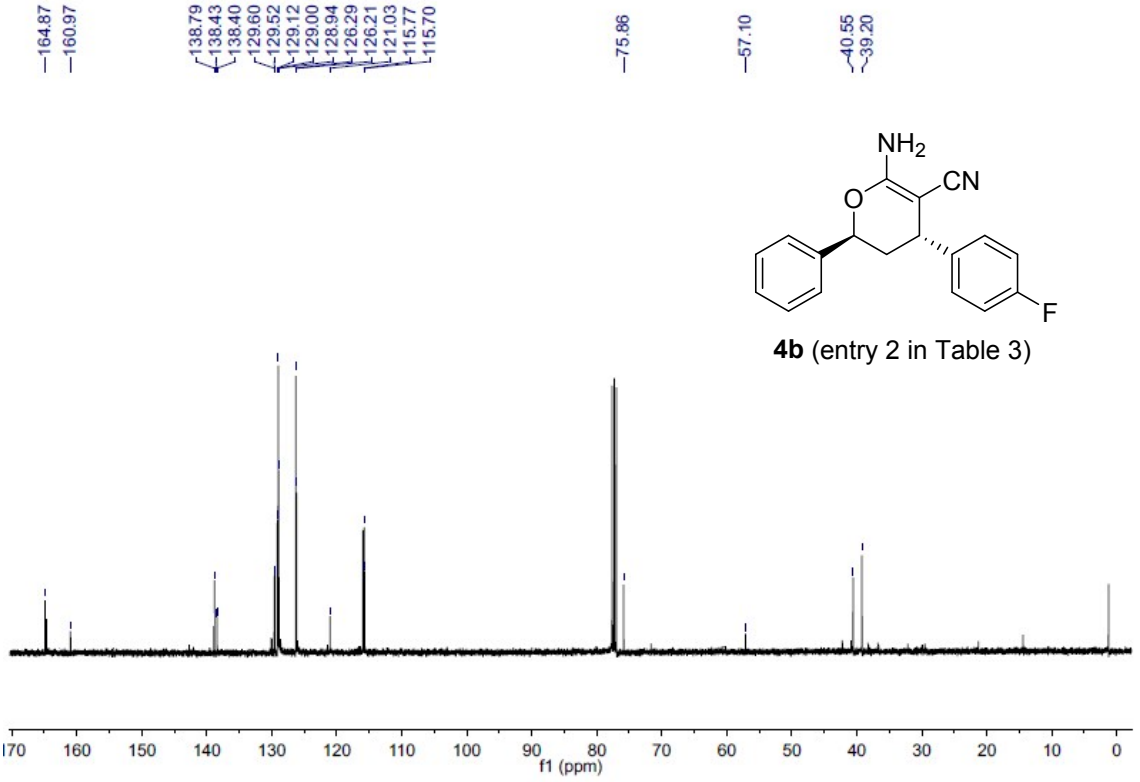
Compound Name (Library Hit)	Score	Formula	Intensity	Threshold	Expected m/z	Found at m/z	Error (ppm)	Expected RT (min)	Found RT (min)	RT Delta (min)	Isotope Diff (%)	Library Score(%)
276.126263296	75%	C18H16N2O	4417013	100	299.1155	299.1168	4.4	0.00	0.67	0.67	1.0%	N/A

4b. (2*S*,4*S*)-6-amino-4-(4-fluorophenyl)-2-phenyl-3,4-dihydro-2*H*- pyran-5-carbonitrile.

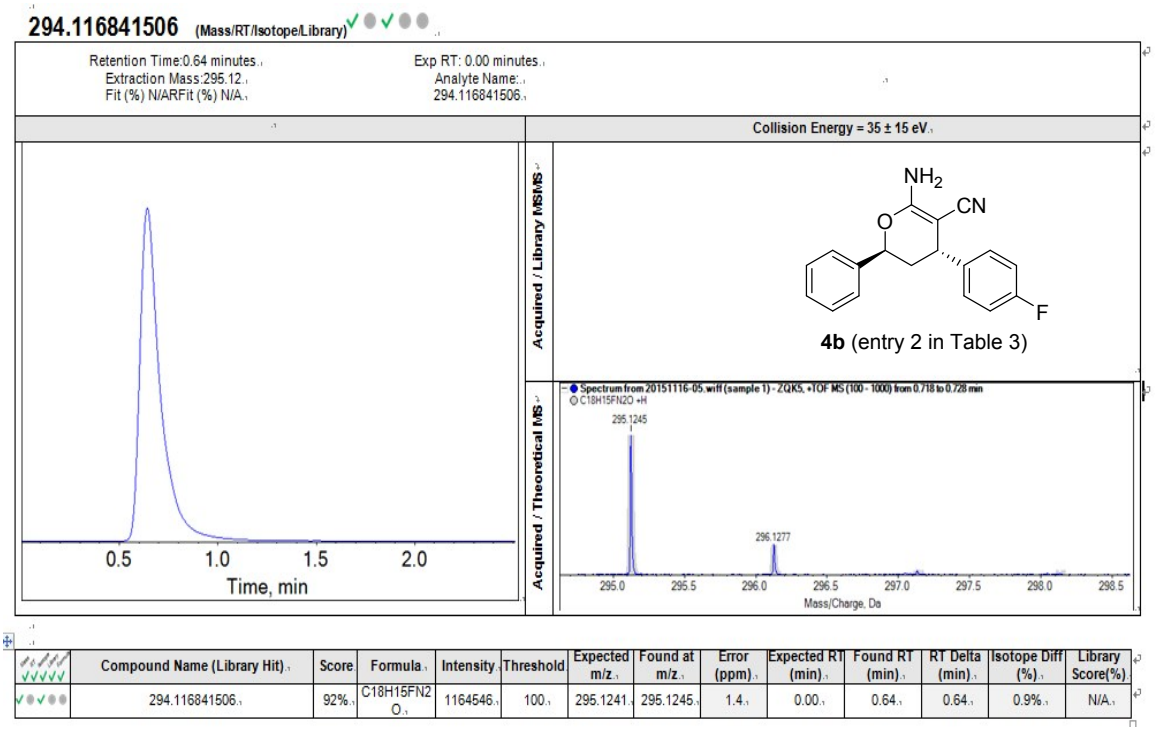


4b (entry 2 in Table 3)





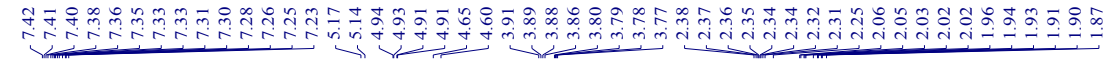
4b (entry 2 in Table 3)

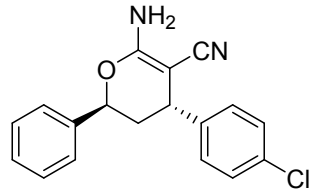


4b (entry 2 in Table 3)

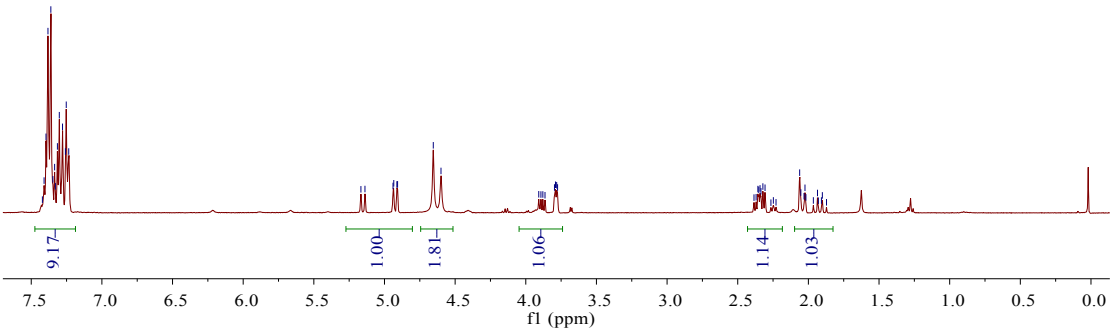
	Compound Name (Library Hit)	Score	Formula	Intensity	Threshold	Expected m/z	Found at m/z	Error (ppm)	Expected RT (min)	Found RT (min)	RT Delta (min)	Isotope Diff (%)	Library Score(%)
✓✓✓✓✓	294.116841506	92%	C18H15FN2O	1164546	100	295.1241	295.1245	1.4	0.00	0.64	0.64	0.9%	N/A

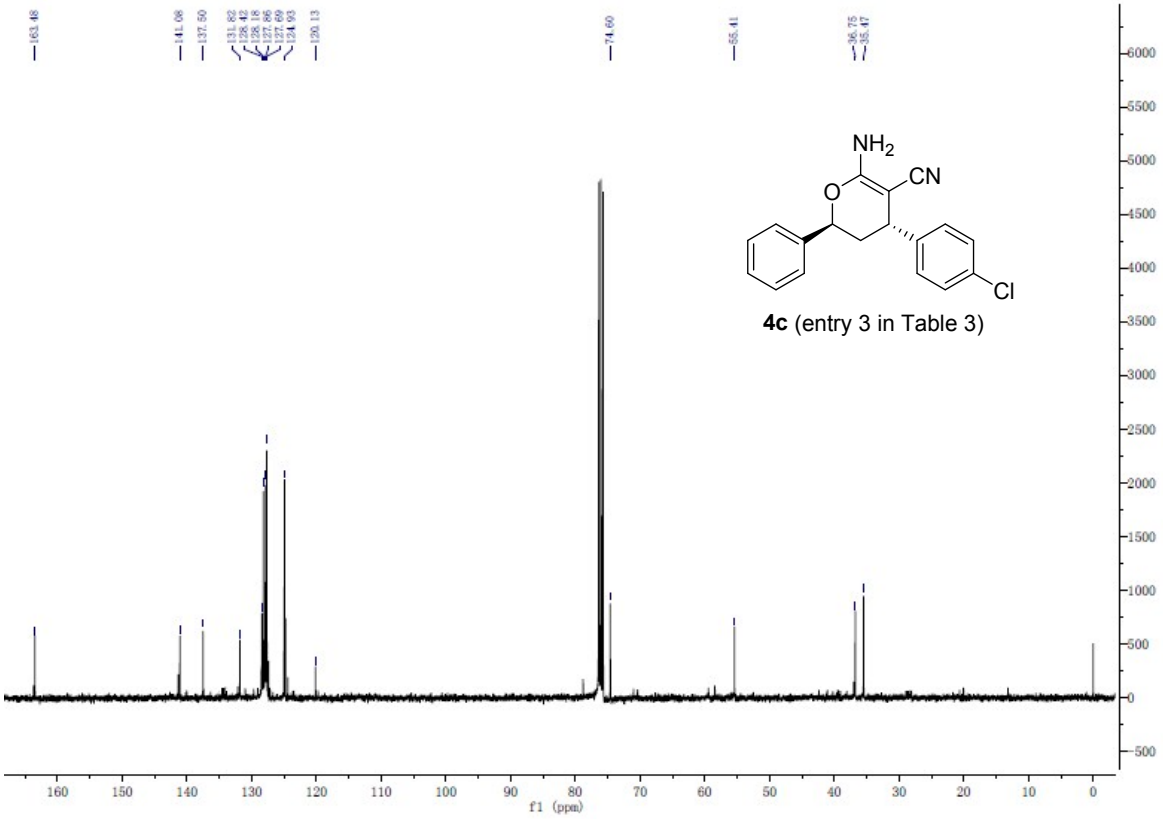
4c. (2*S*,4*S*)-6-amino-4-(4-chlorophenyl)-2-phenyl-3,4-dihydro-2*H*-pyran-5-carbonitrile.



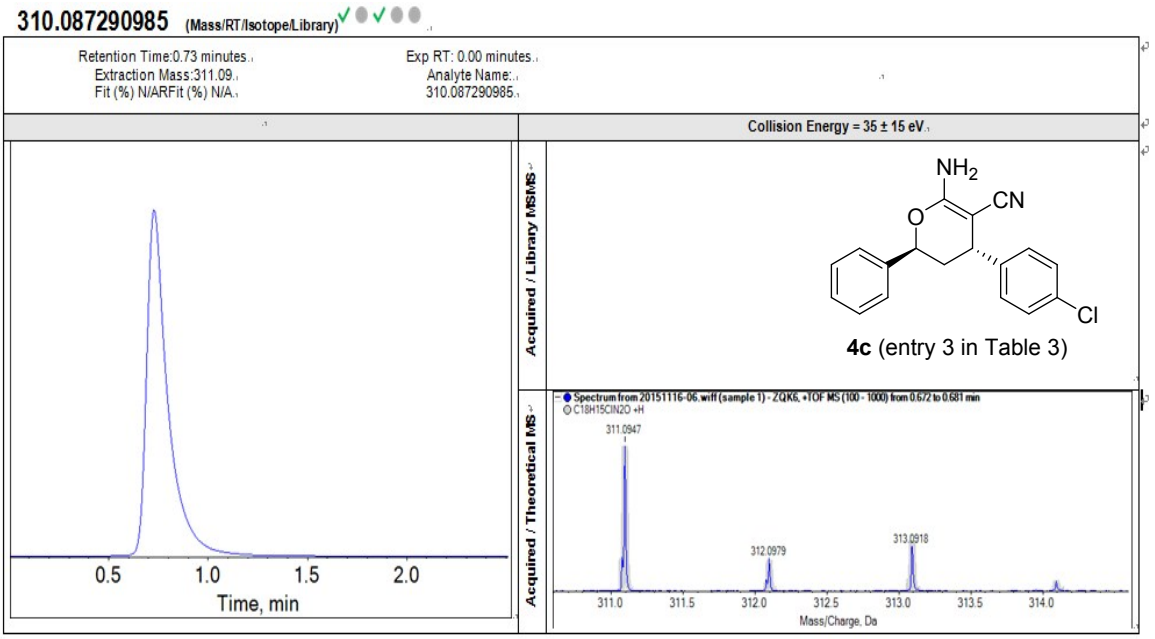


4c (entry 3 in Table 3)



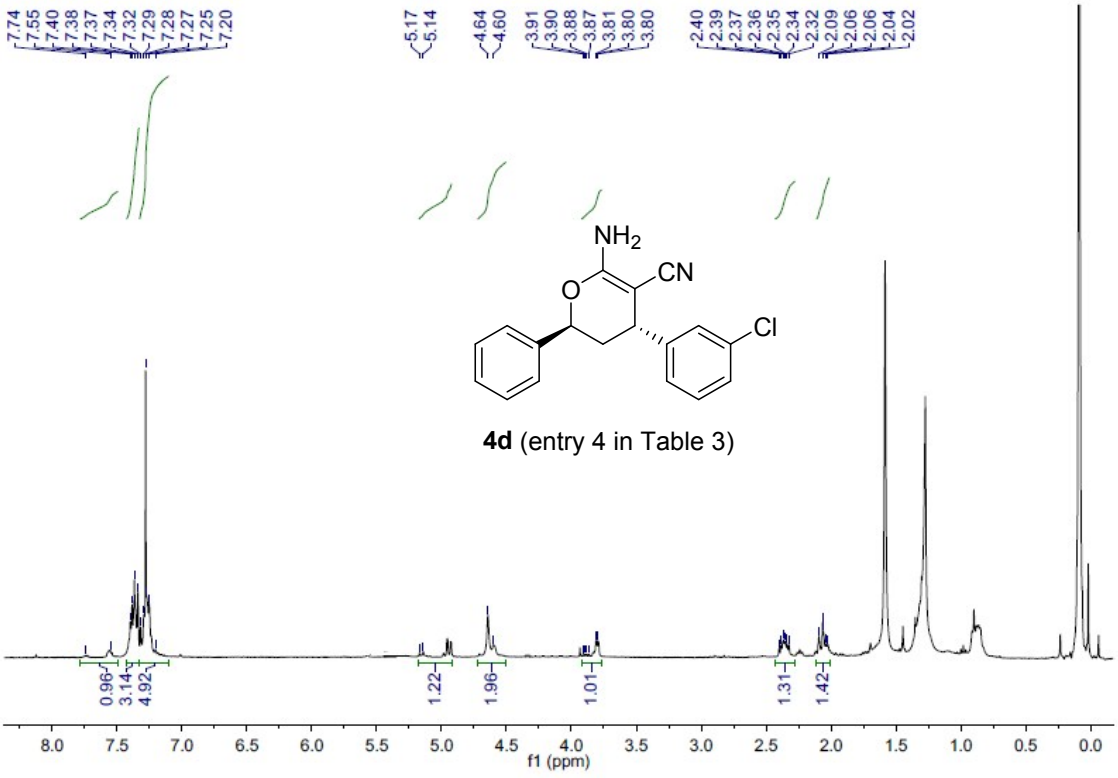


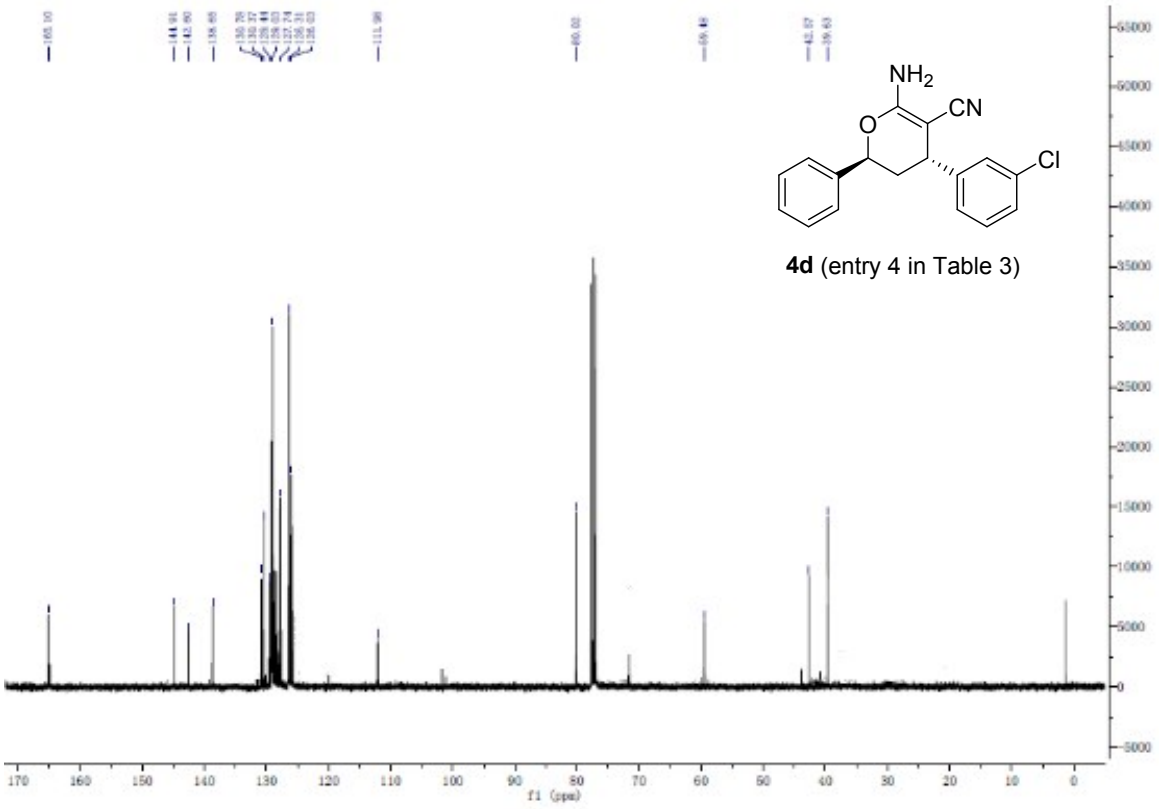
4c (entry 3 in Table 3)



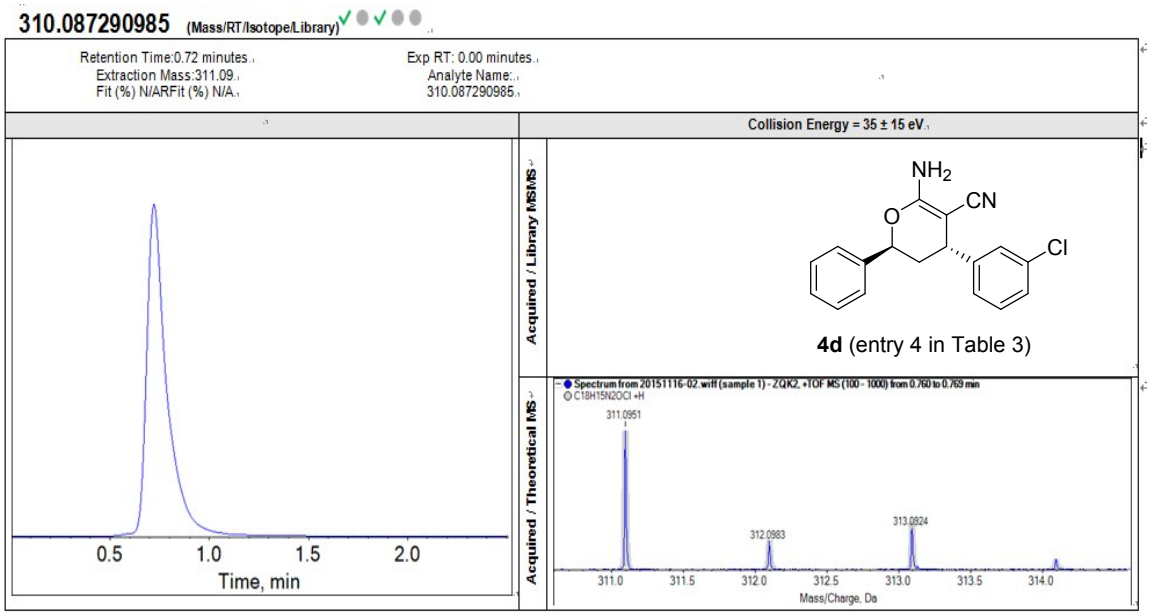
	Compound Name (Library Hit)	Score	Formula	Intensity	Threshold	Expected m/z	Found at m/z	Error (ppm)	Expected RT (min)	Found RT (min)	RT Delta (min)	Isotope Diff (%)	Library Score(%)
✓●✓●●	310.087290985	92%	C18H15ClN2O	1613639	100	311.0946	311.0947	0.5	0.00	0.73	0.73	3.5%	N/A

4d. (2*S*,4*S*)-6-amino-4-(3-chlorophenyl)-2-phenyl-3,4-dihydro-2*H*-pyran-5-carbonitrile.





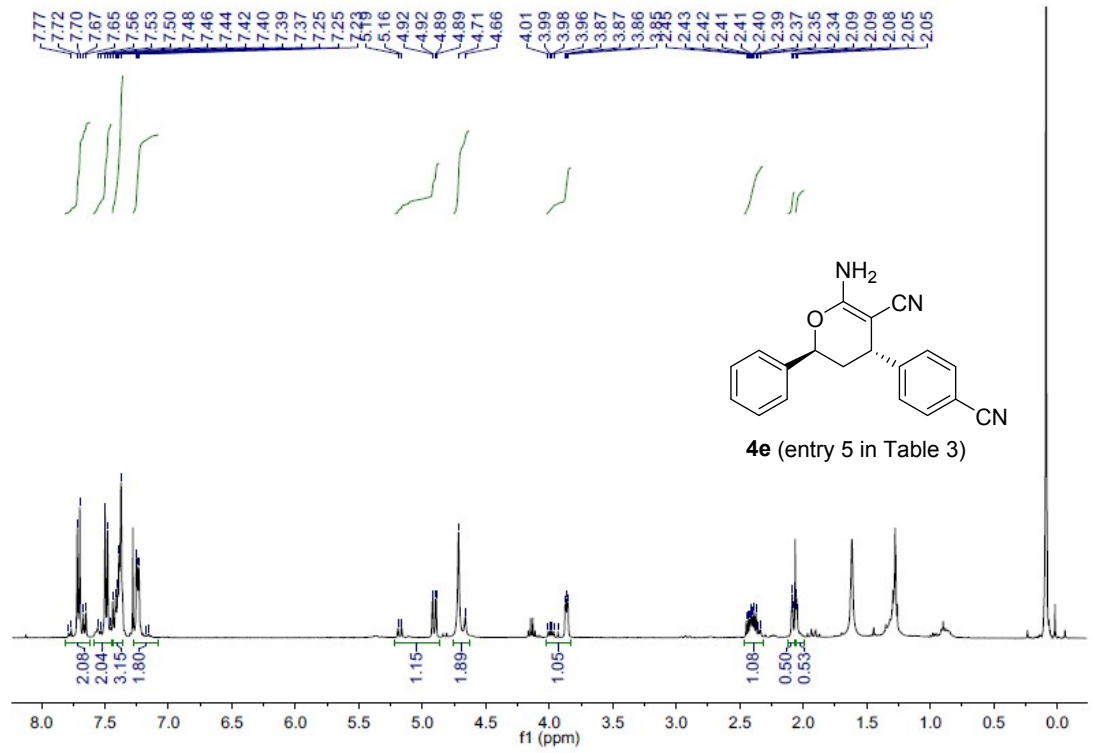
4d (entry 4 in Table 3)

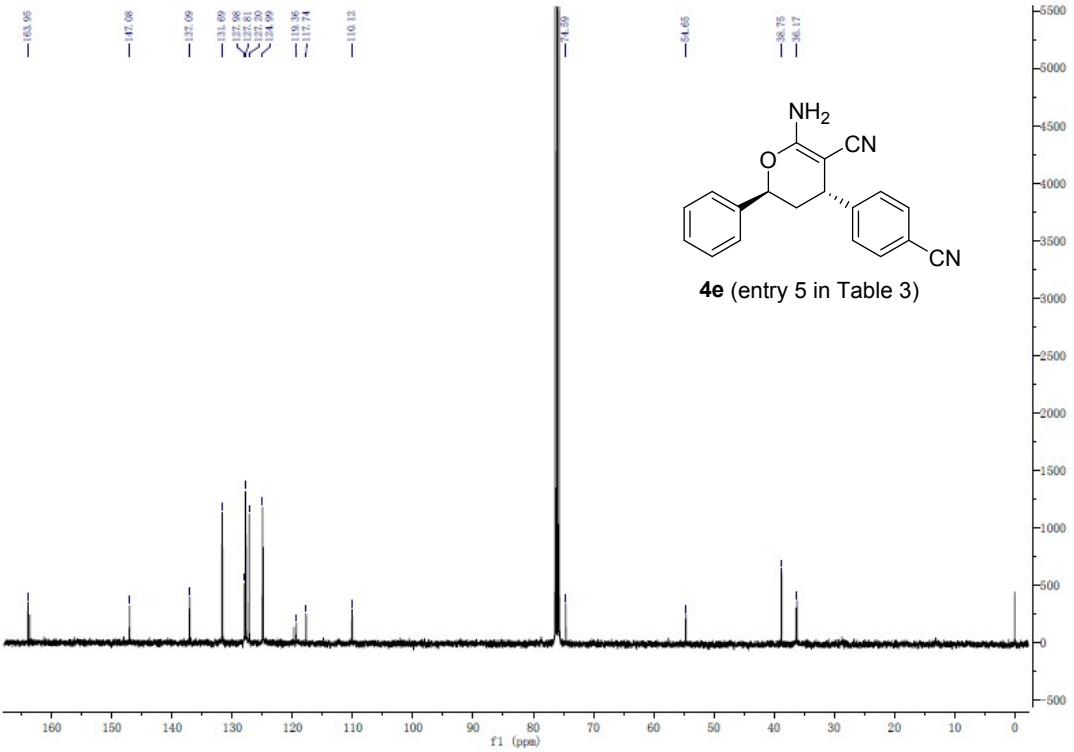


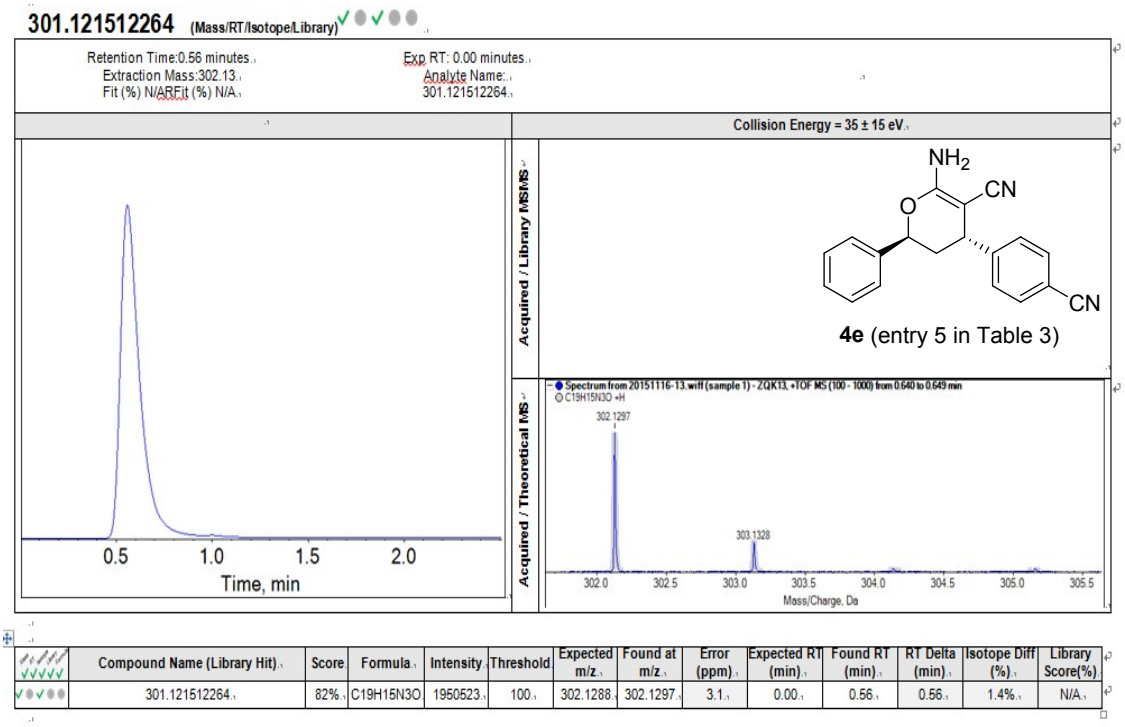
4d (entry 4 in Table 3)

	Compound Name (Library Hit)	Score	Formula	Intensity	Threshold	Expected m/z	Found at m/z	Error (ppm)	Expected RT (min)	Found RT (min)	RT Delta (min)	Isotope Diff (%)	Library Score(%)
✓●✓●●	310.087290985	80%	C18H15N2OCl	746860	100	311.0946	311.0951	1.9	0.00	0.72	0.72	4.4%	N/A

4e. (2*S*,4*S*)-6-amino-4-(4-cyanophenyl)-2-phenyl-3,4-dihydro-2*H*- pyran-5-carbonitrile.

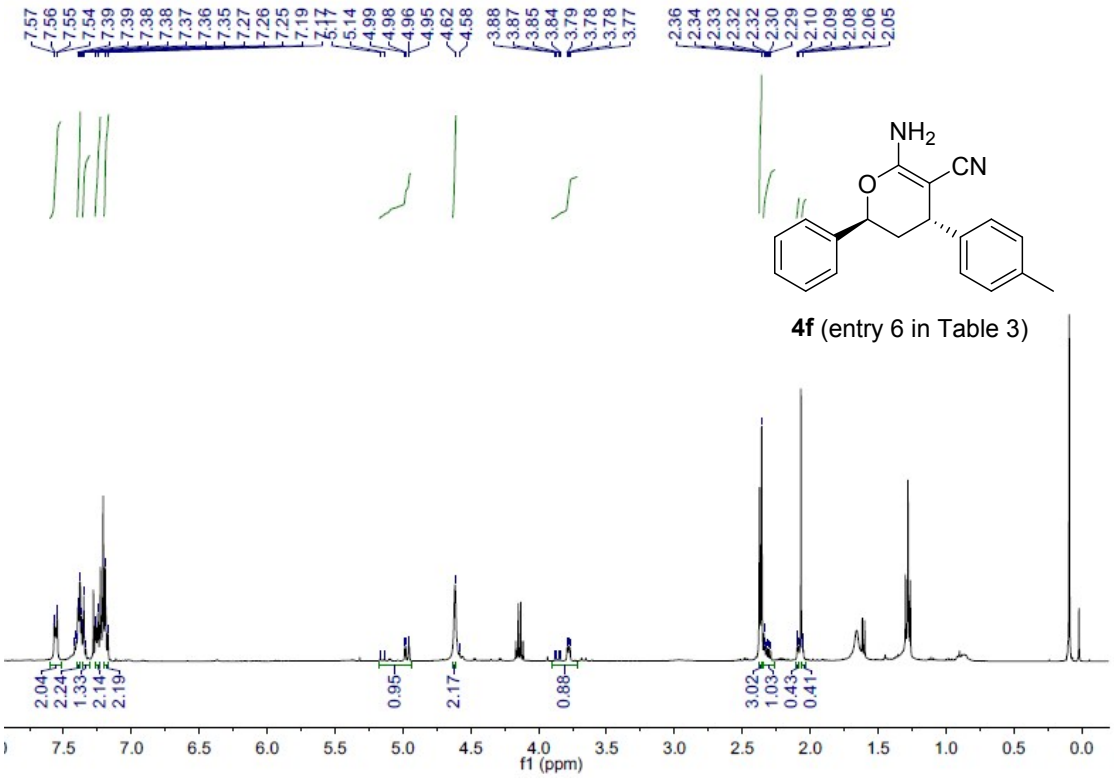


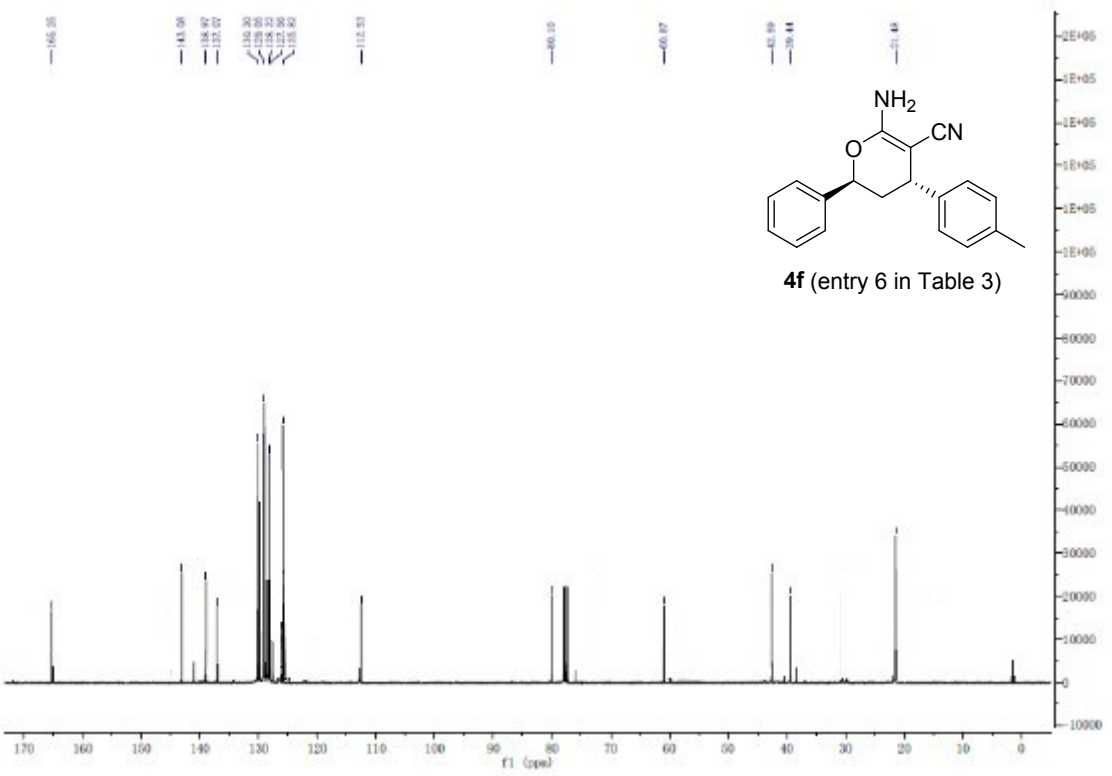




Compound Name (Library Hit)	Score	Formula	Intensity	Threshold	Expected m/z	Found at m/z	Error (ppm)	Expected RT (min)	Found RT (min)	RT Delta (min)	Isotope Diff (%)	Library Score(%)
301.121512264	82%	C19H15N3O	1950523	100	302.1288	302.1297	3.1	0.00	0.56	0.56	1.4%	N/A

4f. (2*S*,4*S*)-6-amino-2-phenyl-4-(p-tolyl)-3,4-dihydro-2*H*- pyran-5-carbonitrile.





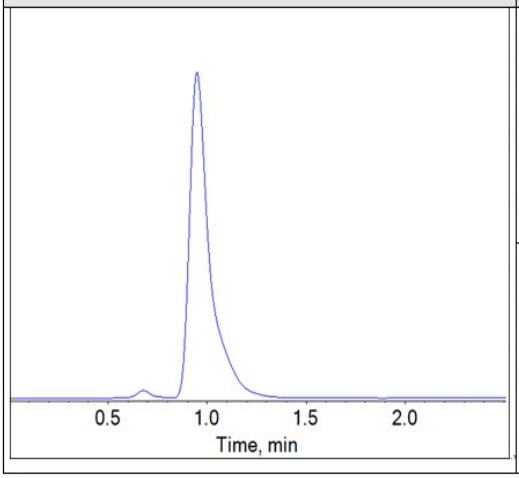
4f (entry 6 in Table 3)

290.141913376 (Mass/RT/Isotope/Library)

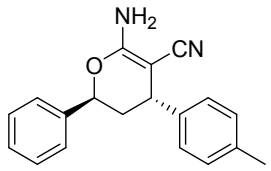
Retention Time:0.95 minutes
Extraction Mass:291.15
Fit (%) N/ARFit (%) N/A

Exp RT: 0.00 minutes
Analyte Name:
290.141913376

Collision Energy = 35 ± 15 eV

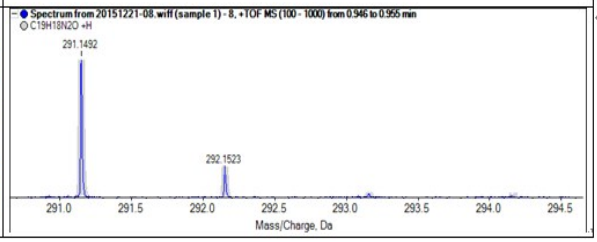


Acquired / Library MSMS



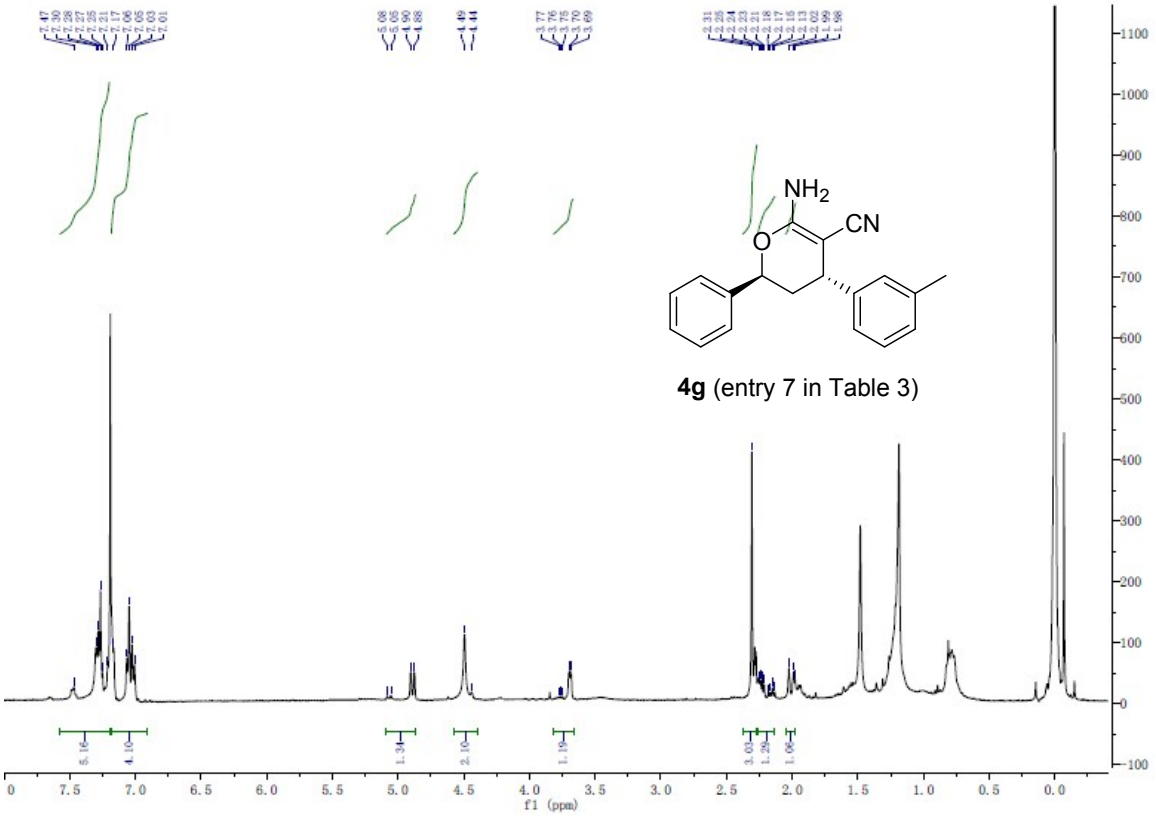
4f (entry 6 in Table 3)

Acquired / Theoretical MS

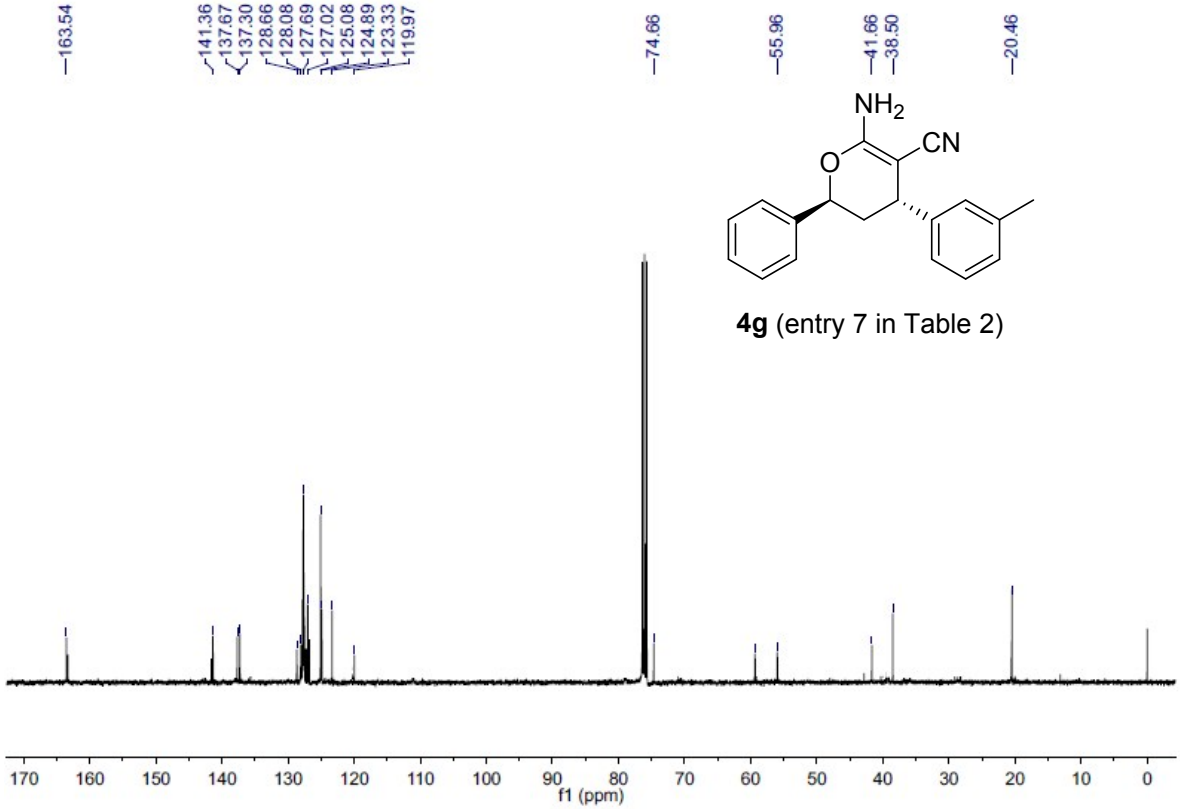


Compound Name (Library Hit)	Score	Formula	Intensity	Threshold	Expected m/z	Found at m/z	Error (ppm)	Expected RT (min)	Found RT (min)	RT Delta (min)	Isotope Diff (%)	Library Score(%)
290.141913376	99%	C19H18N2O	244276	100	291.1492	291.1492	0.1	0.00	0.95	0.95	0.3%	N/A

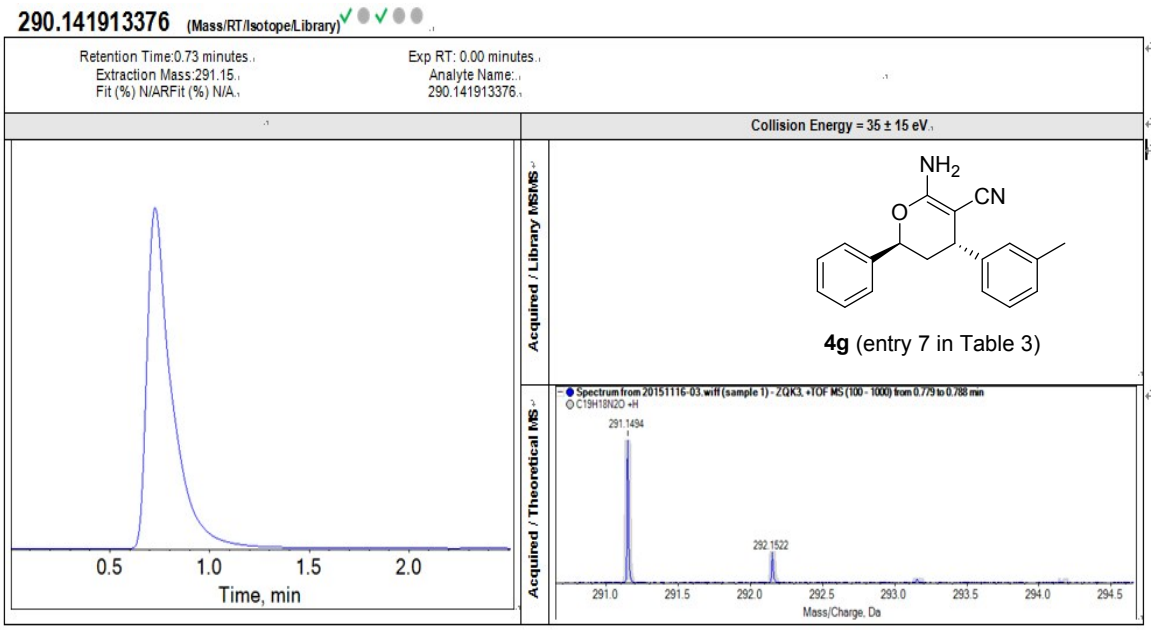
4g. (2*S*,4*S*)-6-amino-2-phenyl-4-(m-tolyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile.



4g (entry 7 in Table 3)

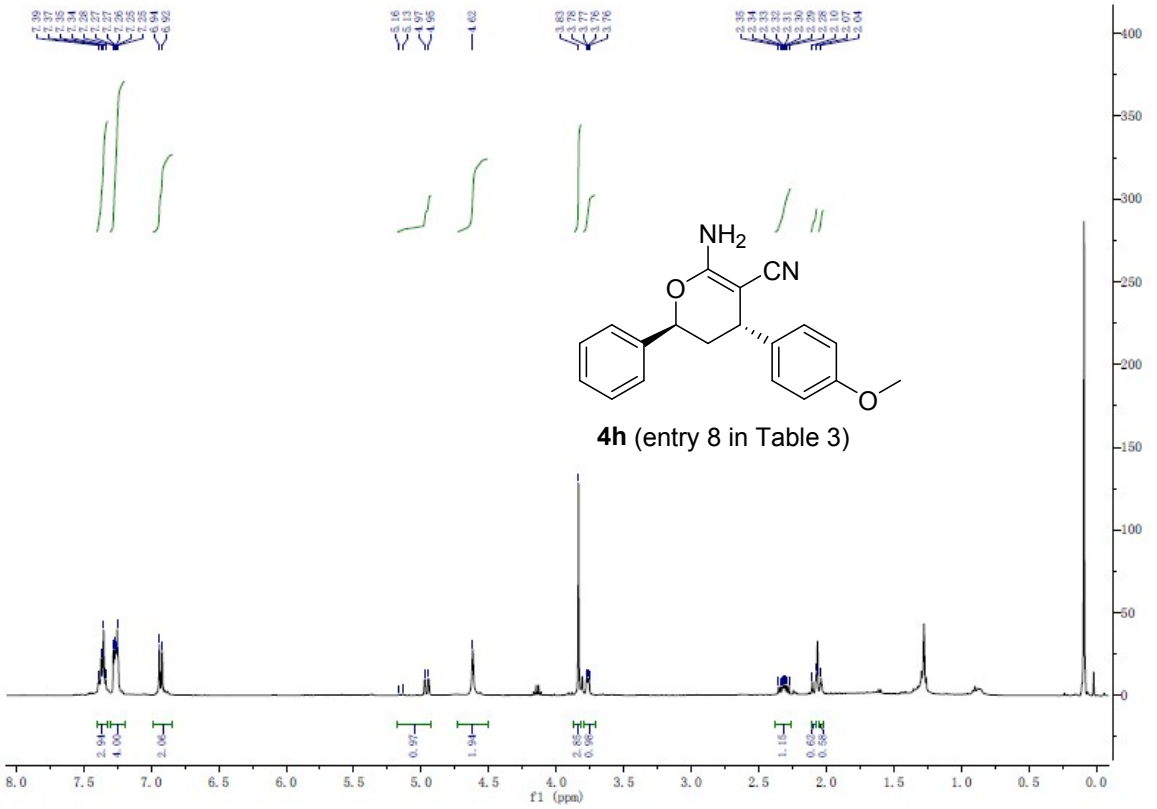


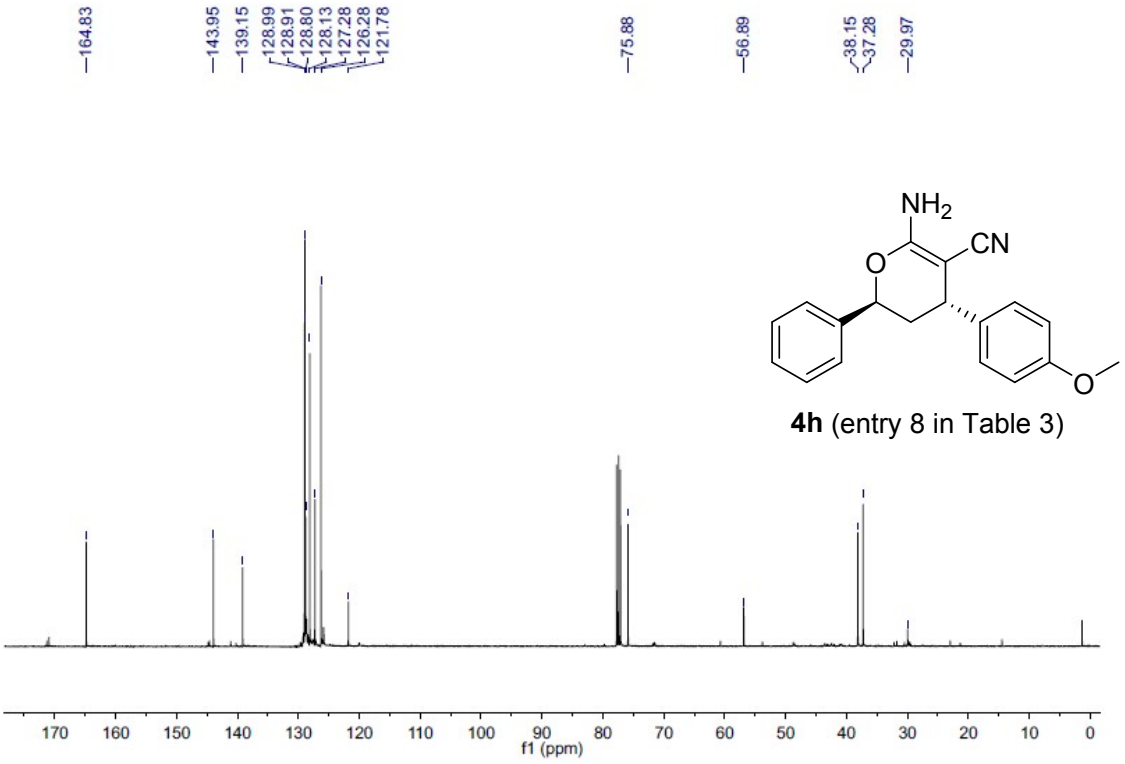
4g (entry 7 in Table 2)

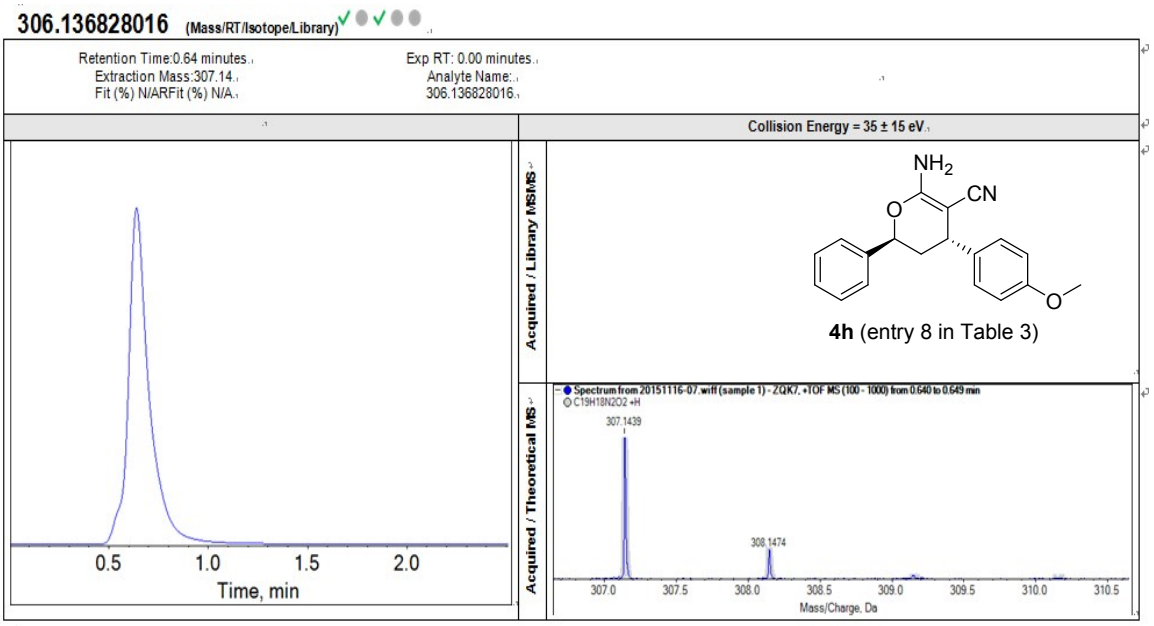


Compound Name (Library Hit)	Score	Formula	Intensity	Threshold	Expected m/z	Found at m/z	Error (ppm)	Expected RT (min)	Found RT (min)	RT Delta (min)	Isotope Diff (%)	Library Score(%)
290.141913376	93%	C19H18N2O	3173390	100	291.1492	291.1494	0.8	0.00	0.73	0.73	1.0%	N/A

4h.(2*S*,4*S*)-6-amino-4-(4-methoxyphenyl)-2-phenyl-3,4-dihydro-2*H*-pyran-5-carbonitrile.

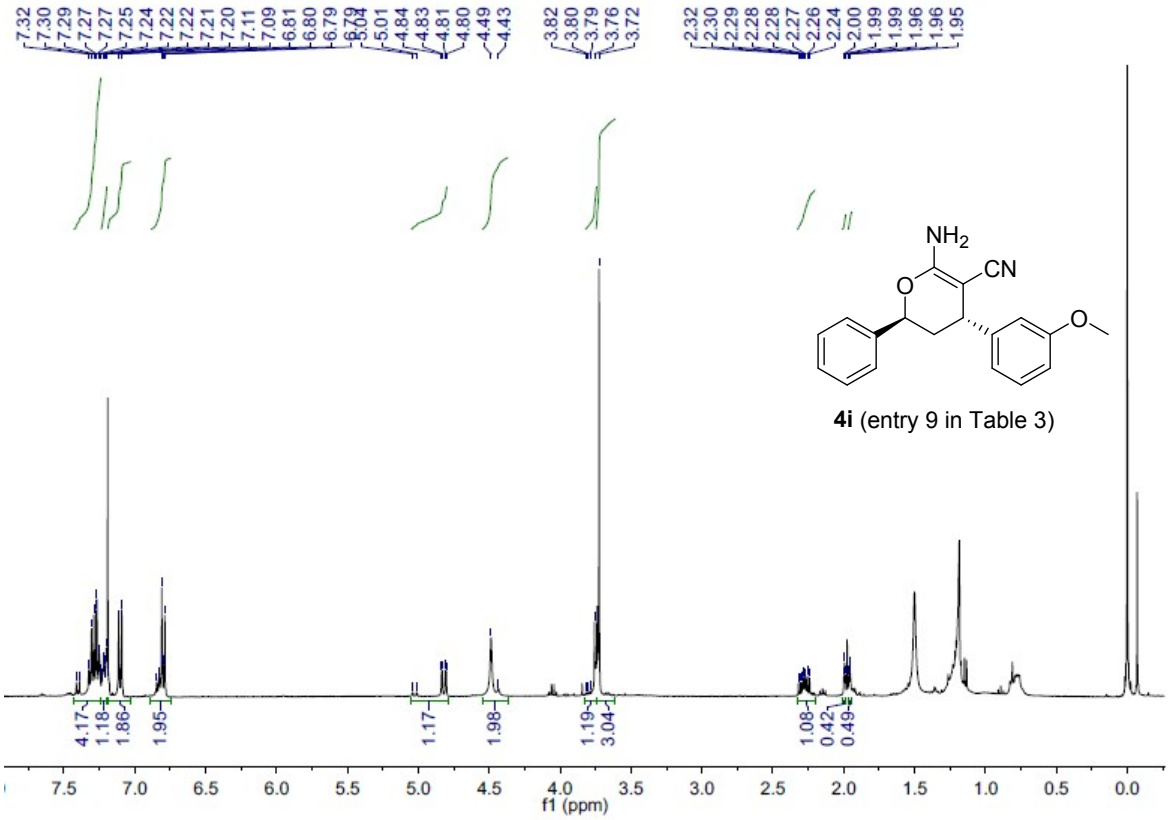




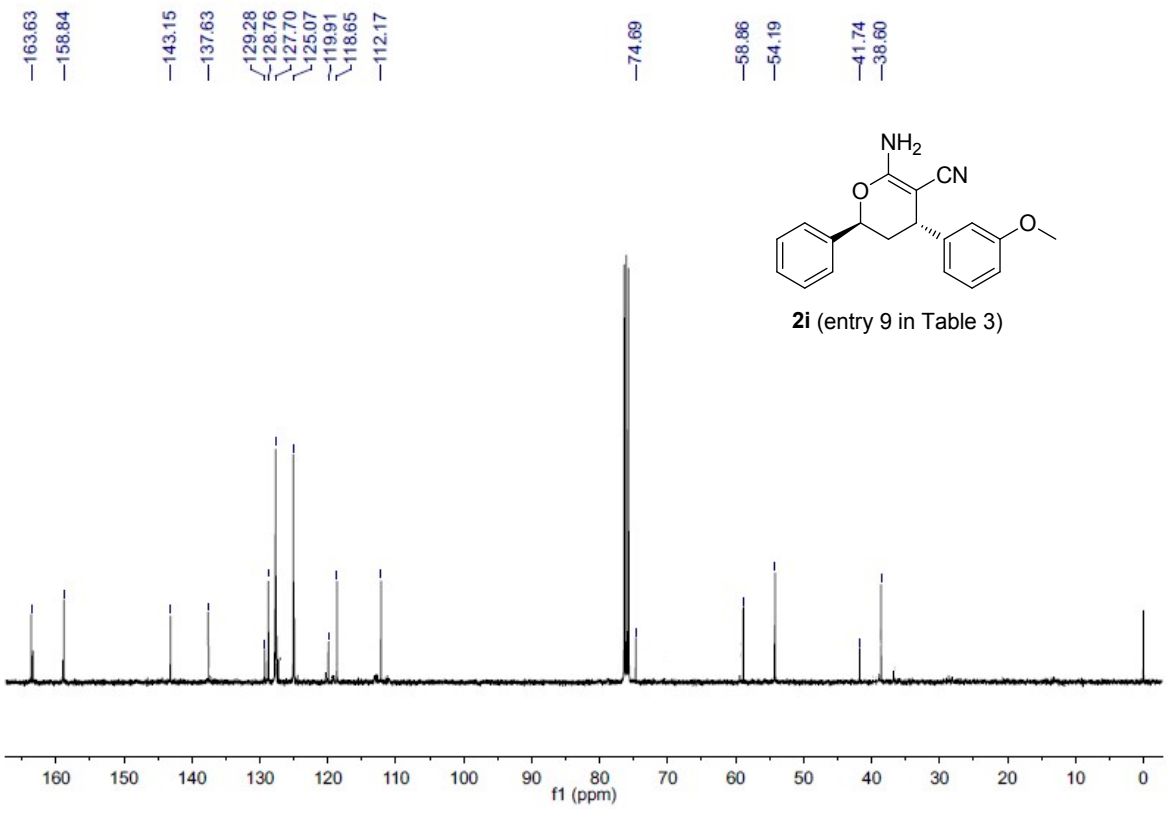


	Compound Name (Library Hit)	Score	Formula	Intensity	Threshold	Expected m/z	Found at m/z	Error (ppm)	Expected RT (min)	Found RT (min)	RT Delta (min)	Isotope Diff (%)	Library Score(%)
✓●✓●●	306.136828016	93%	C19H18N2O2	324626	100	307.1441	307.1439	-0.8	0.00	0.64	0.64	1.5%	N/A

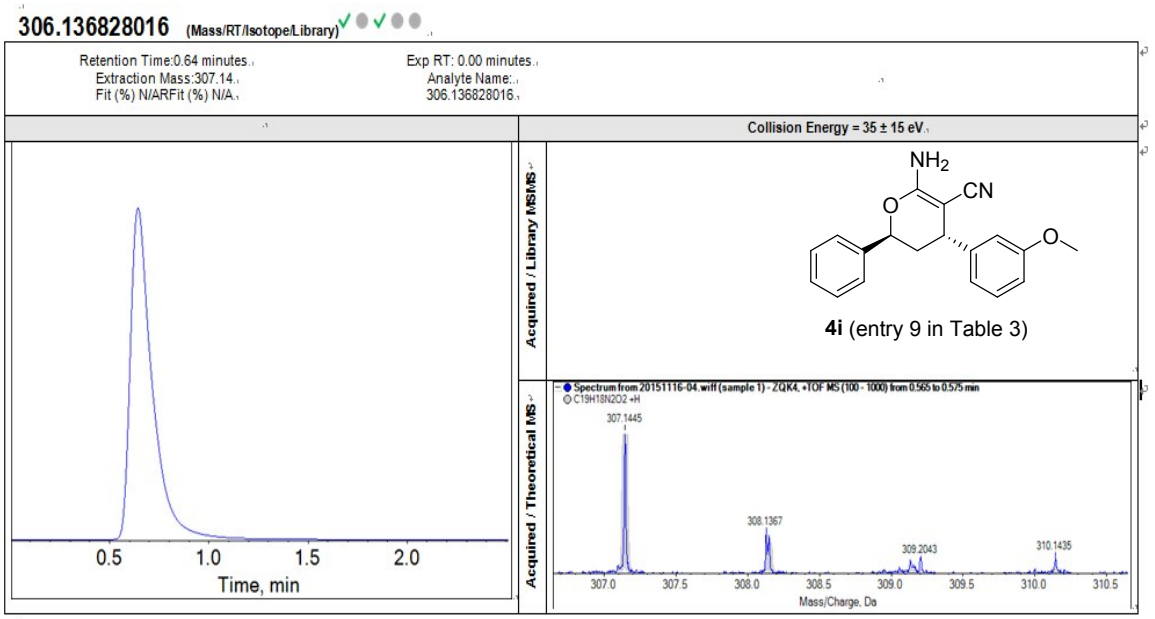
4i. (2*S*,4*S*)-6-amino-4-(3-methoxyphenyl)-2-phenyl-3,4-dihydro-2*H*-pyran-5-carbonitrile.



4i (entry 9 in Table 3)

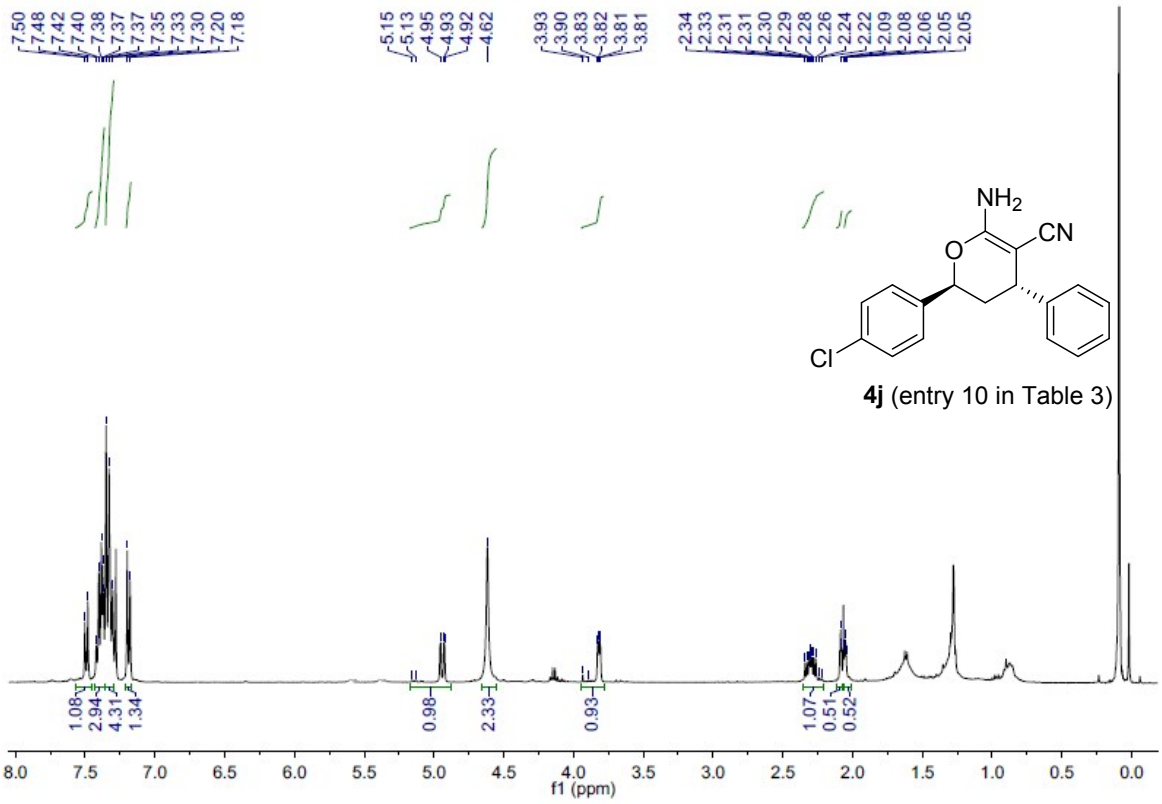


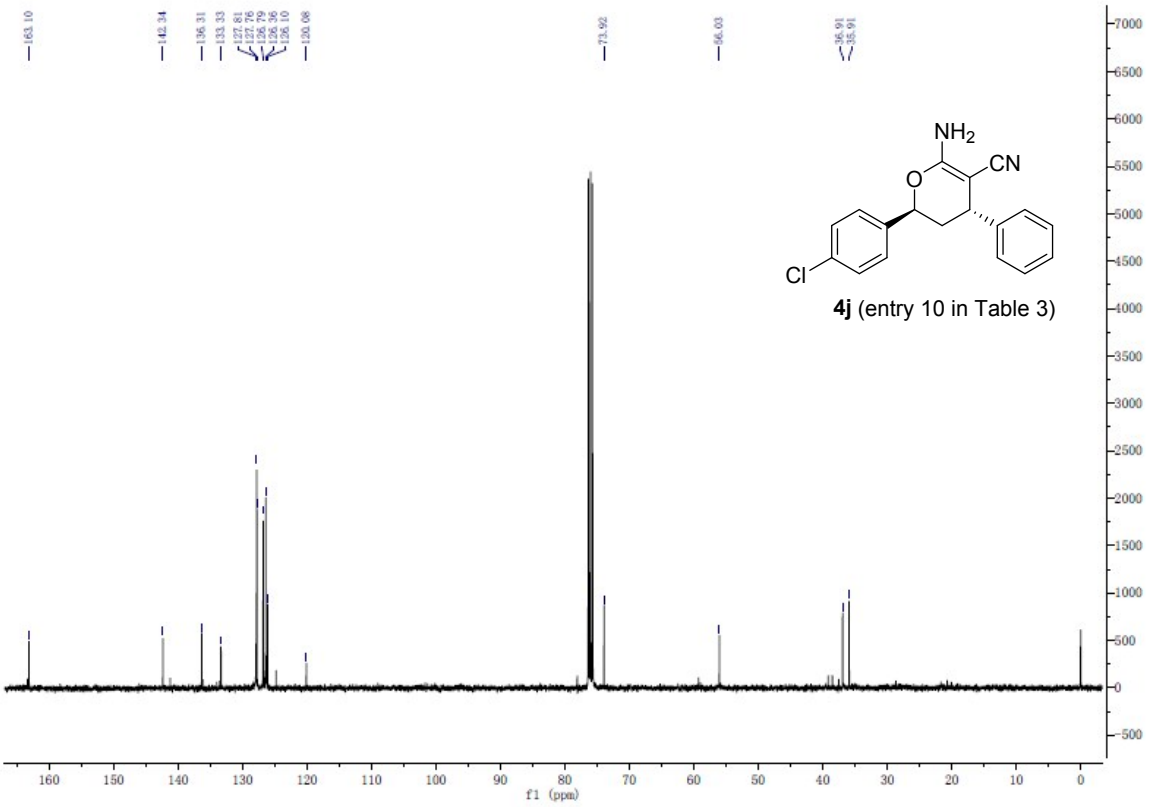
2i (entry 9 in Table 3)



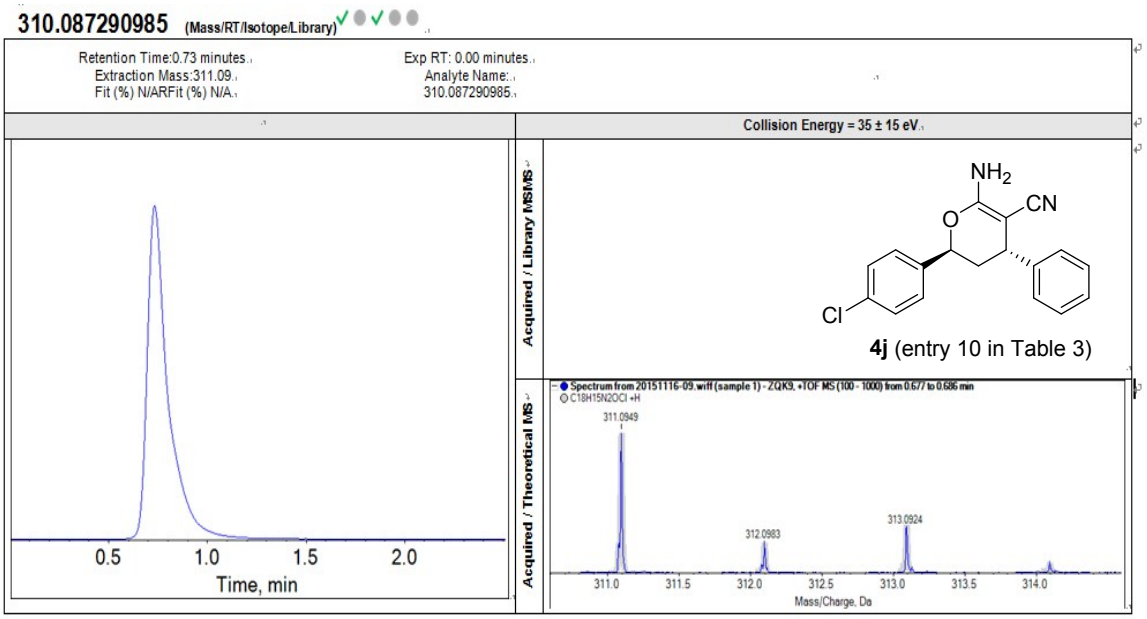
Compound Name (Library Hit)	Score	Formula	Intensity	Threshold	Expected m/z	Found at m/z	Error (ppm)	Expected RT (min)	Found RT (min)	RT Delta (min)	Isotope Diff (%)	Library Score(%)
306.136828016	57%	C19H18N2O2	4841174	100	307.1441	307.1445	1.2	0.00	0.64	0.64	22.1%	N/A

4j.(2*S*,4*S*)-6-amino-2-(4-chlorophenyl)-4-phenyl-3,4-dihydro-2*H*-pyran-5-carbonitrile.



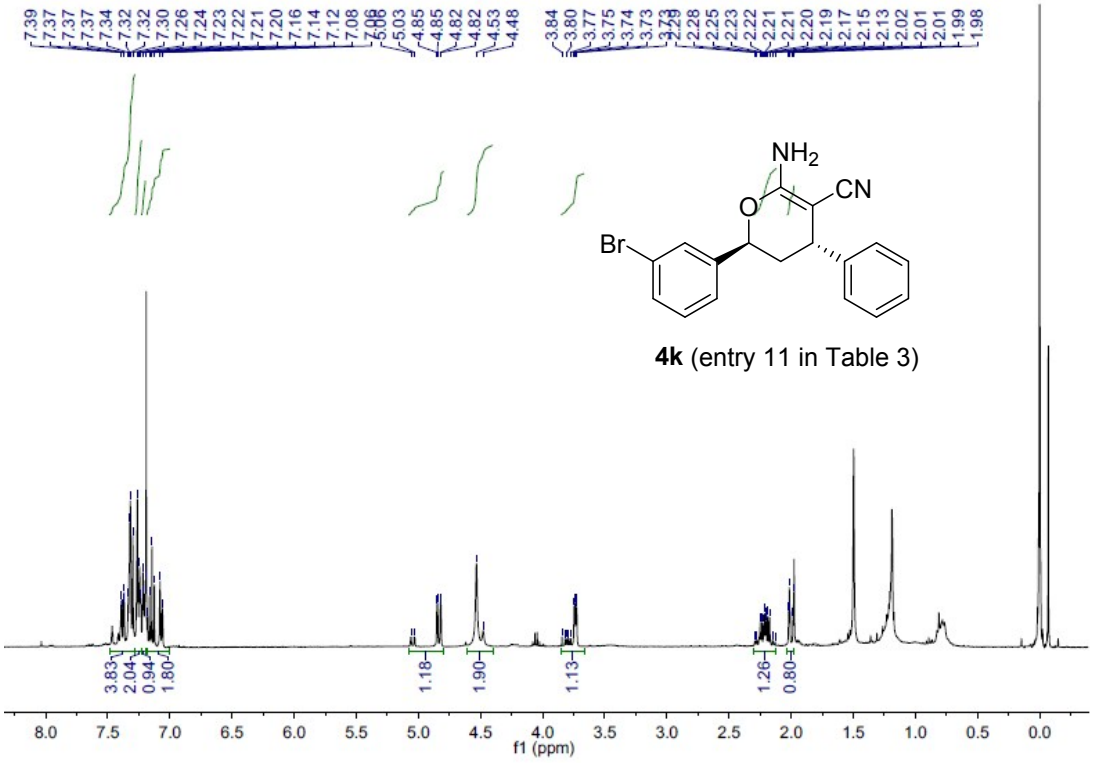


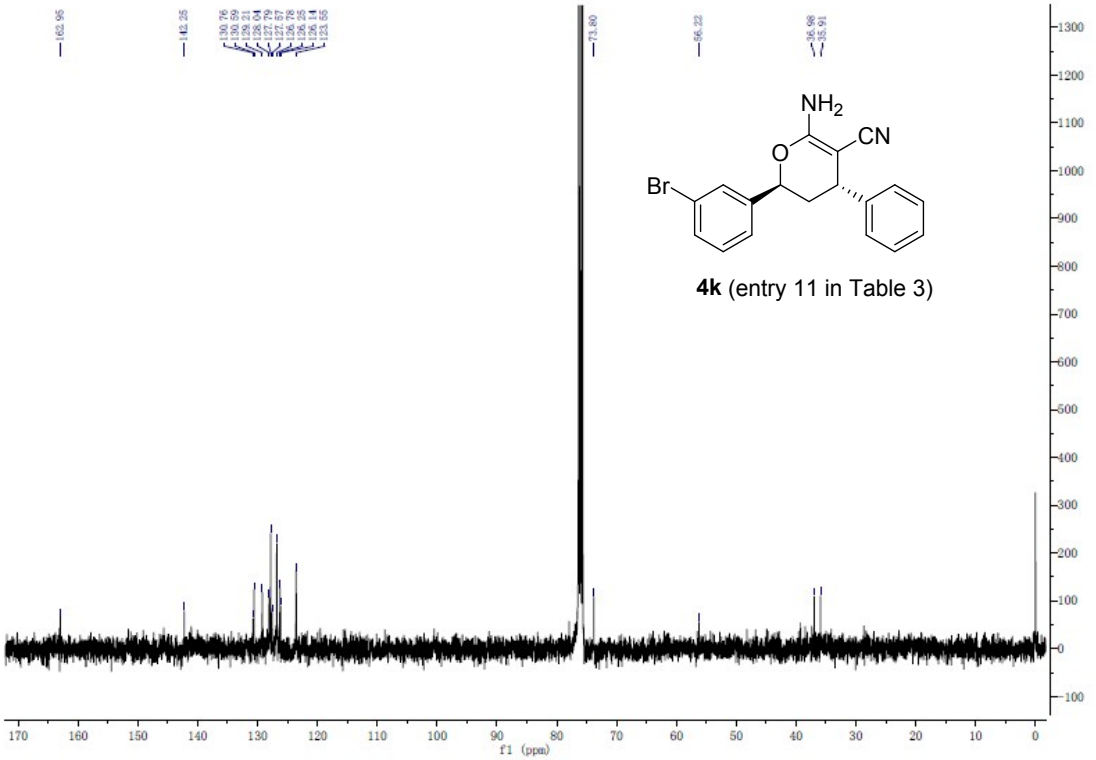
4j (entry 10 in Table 3)

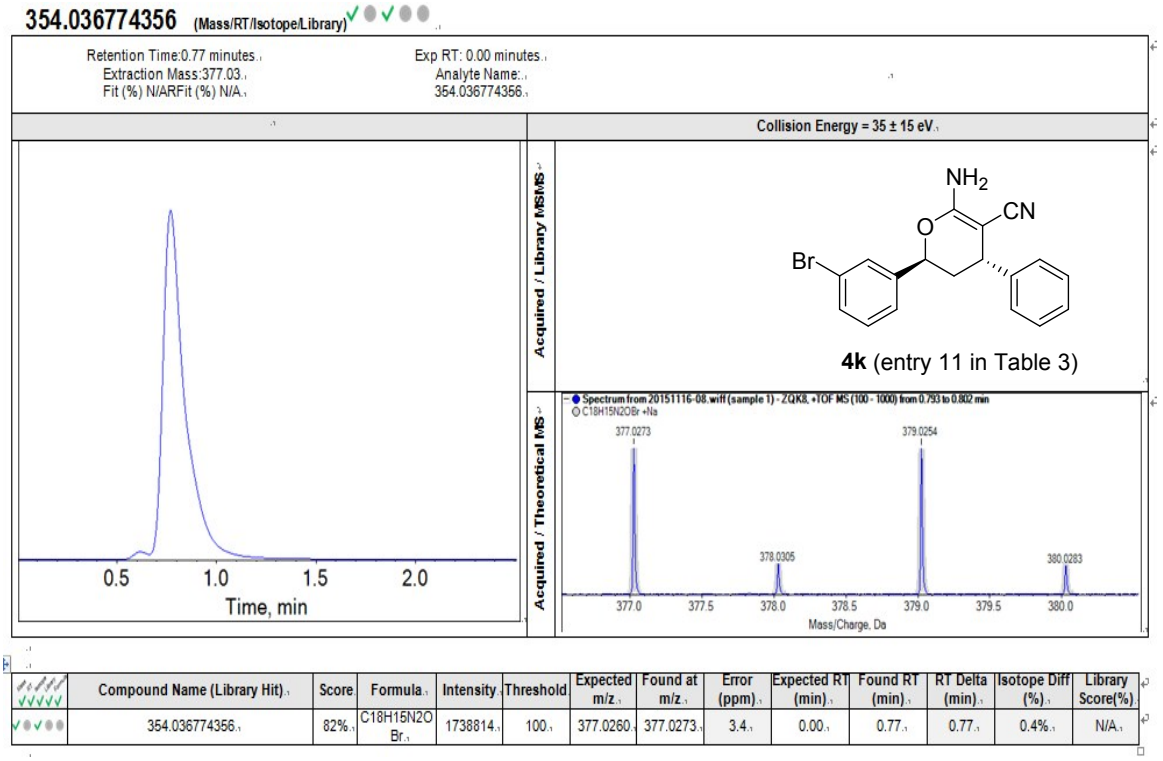


Compound Name (Library Hit)	Score	Formula	Intensity	Threshold	Expected m/z	Found at m/z	Error (ppm)	Expected RT (min)	Found RT (min)	RT Delta (min)	Isotope Diff (%)	Library Score(%)
310.087290985	91%	C18H15N2OCl	818124	100	311.0946	311.0949	1.2	0.00	0.73	0.73	1.6%	N/A

4k. (2*S*,4*S*)-6-amino-2-(3-bromophenyl)-4-phenyl-3,4-dihydro-2*H*-pyran-5-carbonitrile.

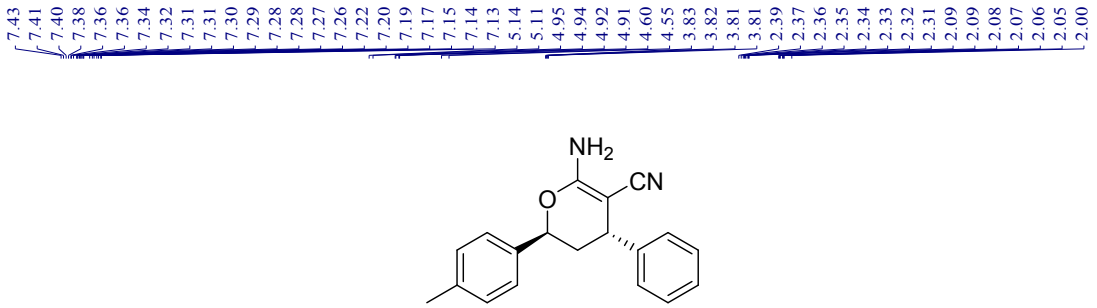




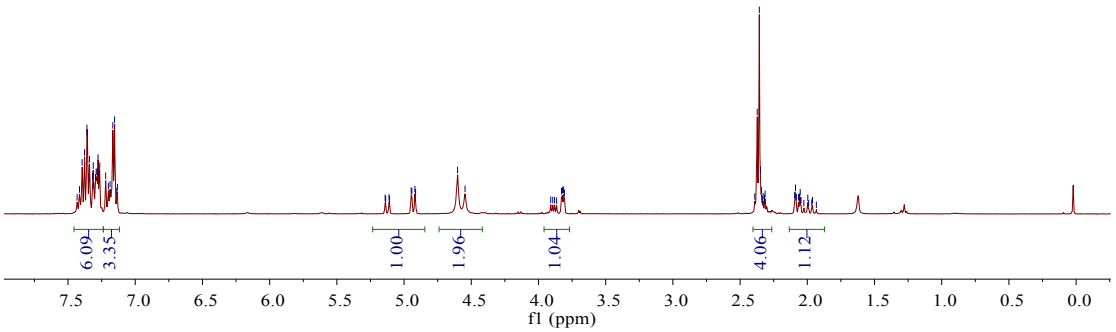


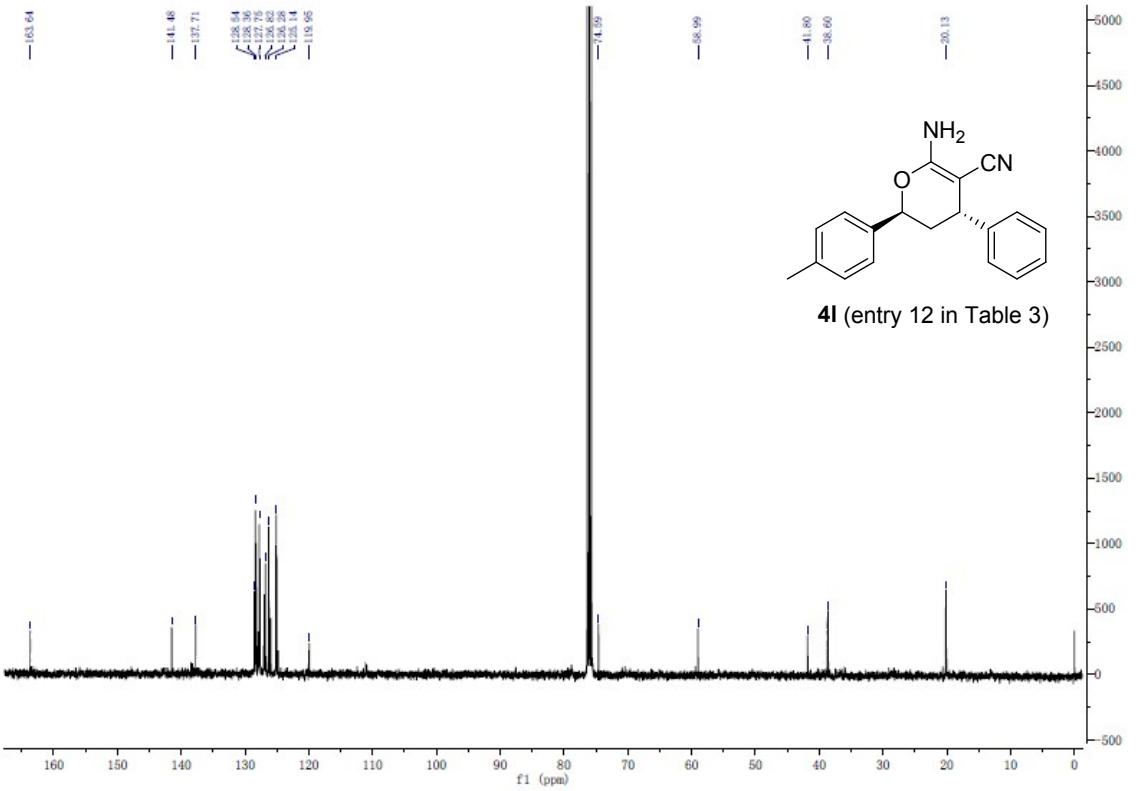
	Compound Name (Library Hit)	Score	Formula	Intensity	Threshold	Expected m/z	Found at m/z	Error (ppm)	Expected RT (min)	Found RT (min)	RT Delta (min)	Isotope Diff (%)	Library Score(%)
✓●✓●●	354.036774356	82%	C18H15N2OBr	1738814	100	377.0260	377.0273	3.4	0.00	0.77	0.77	0.4%	N/A

4l. (2*S*,4*S*)-6-amino-4-phenyl-2-(p-tolyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile.

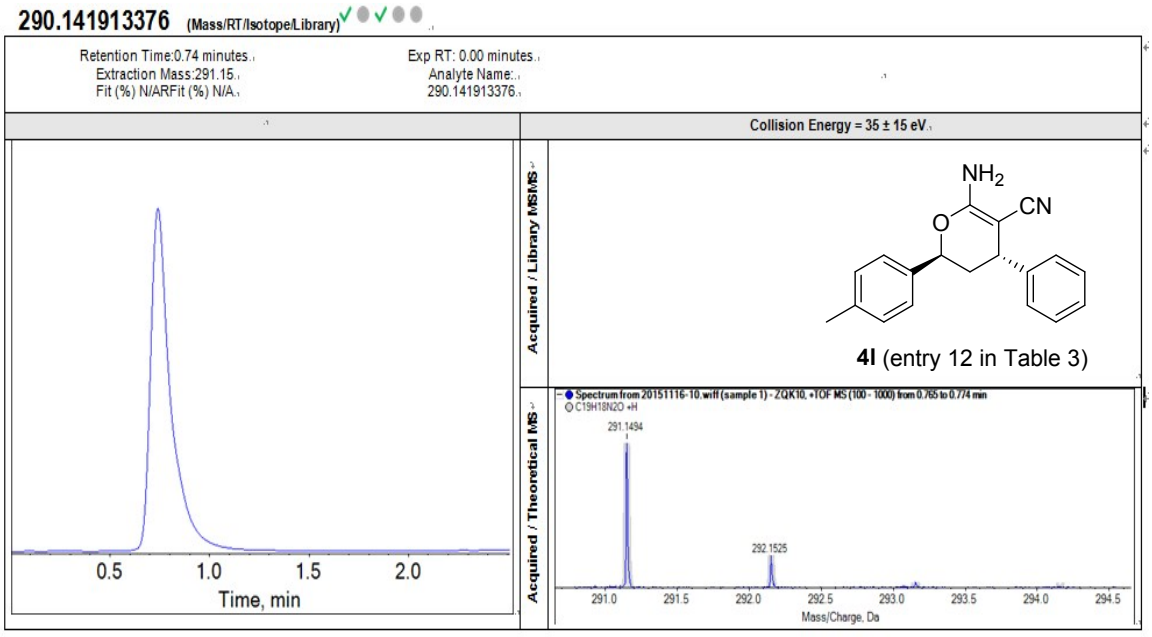


4l (entry 12 in Table 3)





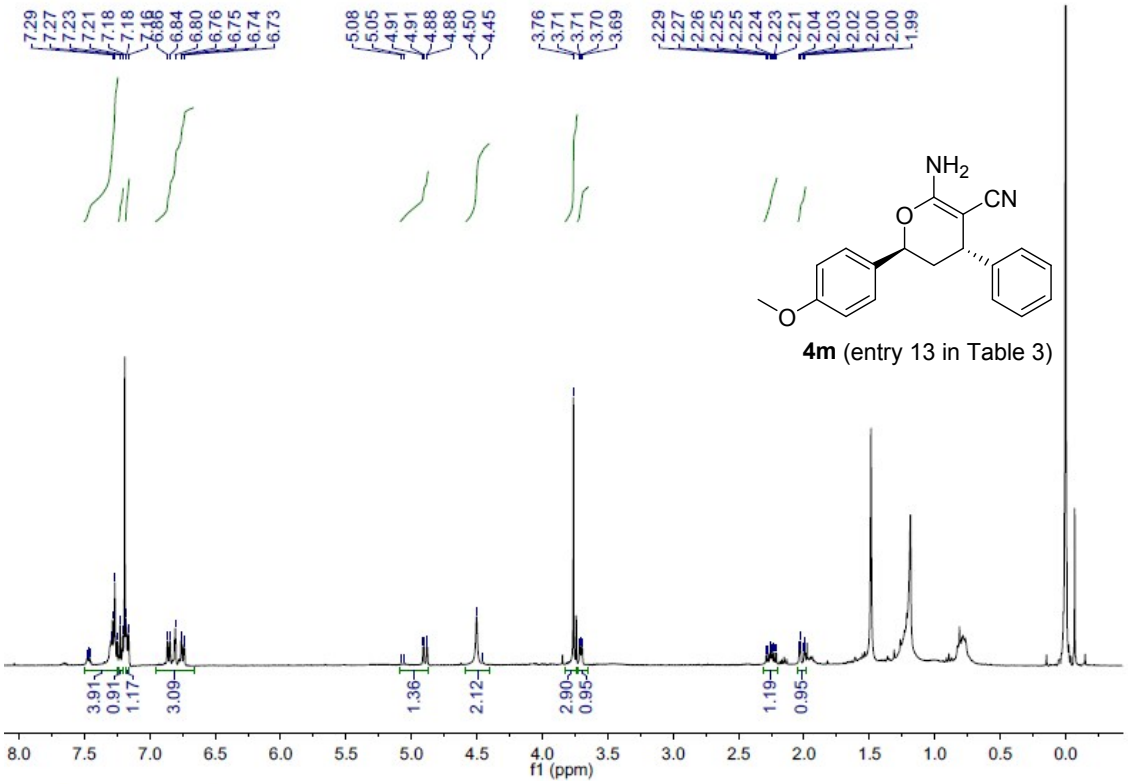
4l (entry 12 in Table 3)

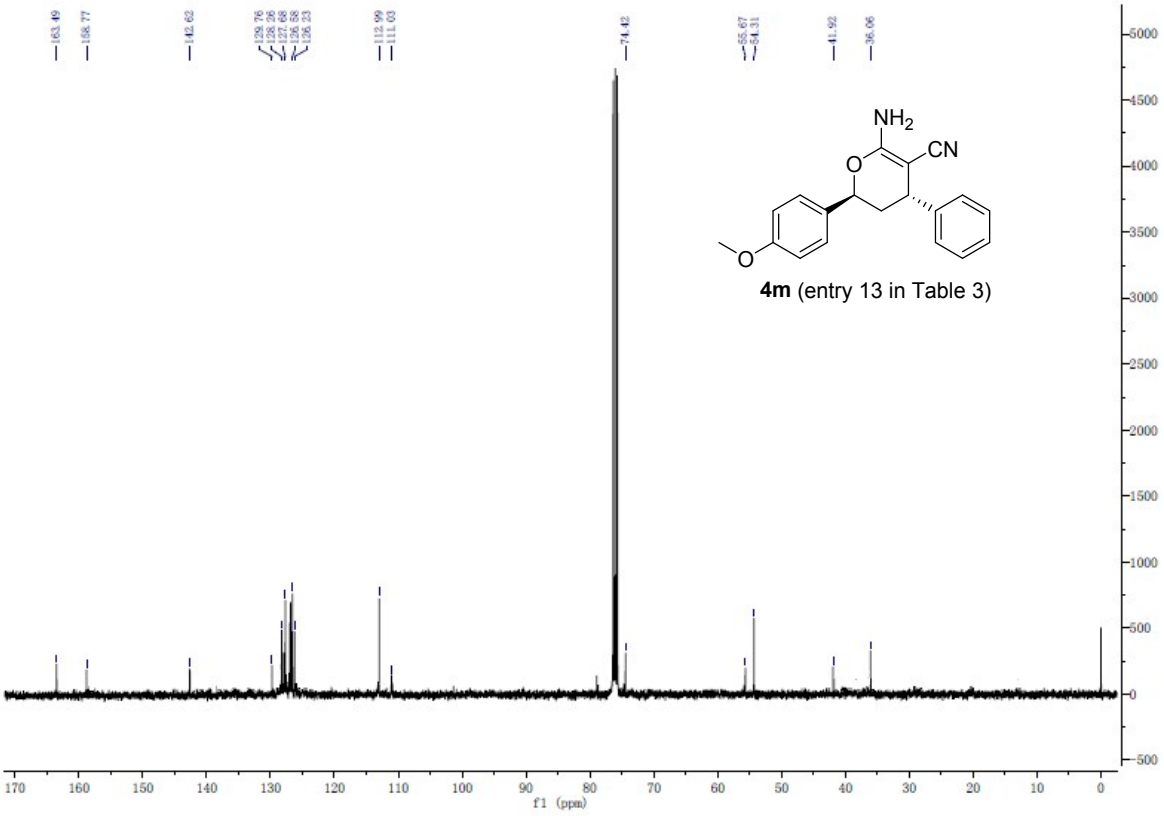


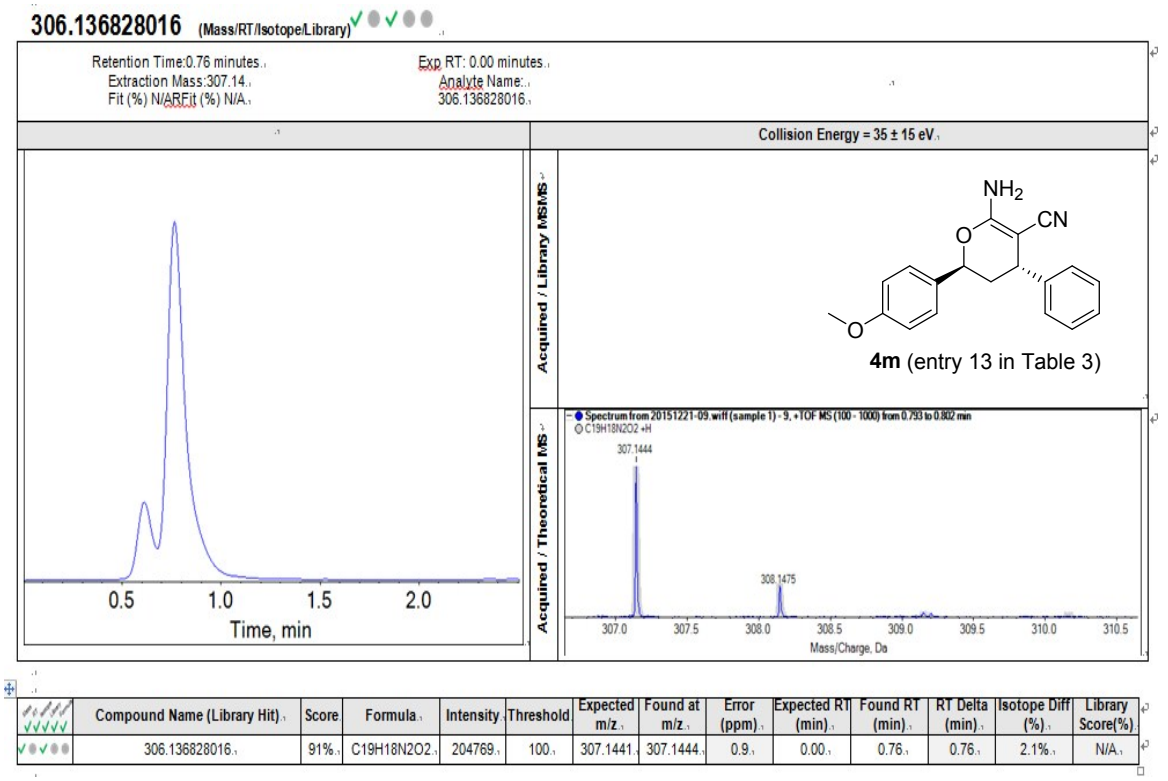
4l (entry 12 in Table 3)

	Compound Name (Library Hit)	Score	Formula	Intensity	Threshold	Expected m/z	Found at m/z	Error (ppm)	Expected RT (min)	Found RT (min)	RT Delta (min)	Isotope Diff (%)	Library Score(%)
✓✓✓✓✓	290.141913376	94%	C19H18N2O	374361	100	291.1492	291.1494	0.9	0.00	0.74	0.74	0.8%	N/A

4m. (2*S*,4*S*)-6-amino-2-(4-methoxyphenyl)-4-phenyl-3,4-dihydro-2*H*-pyran-5-carbonitrile.

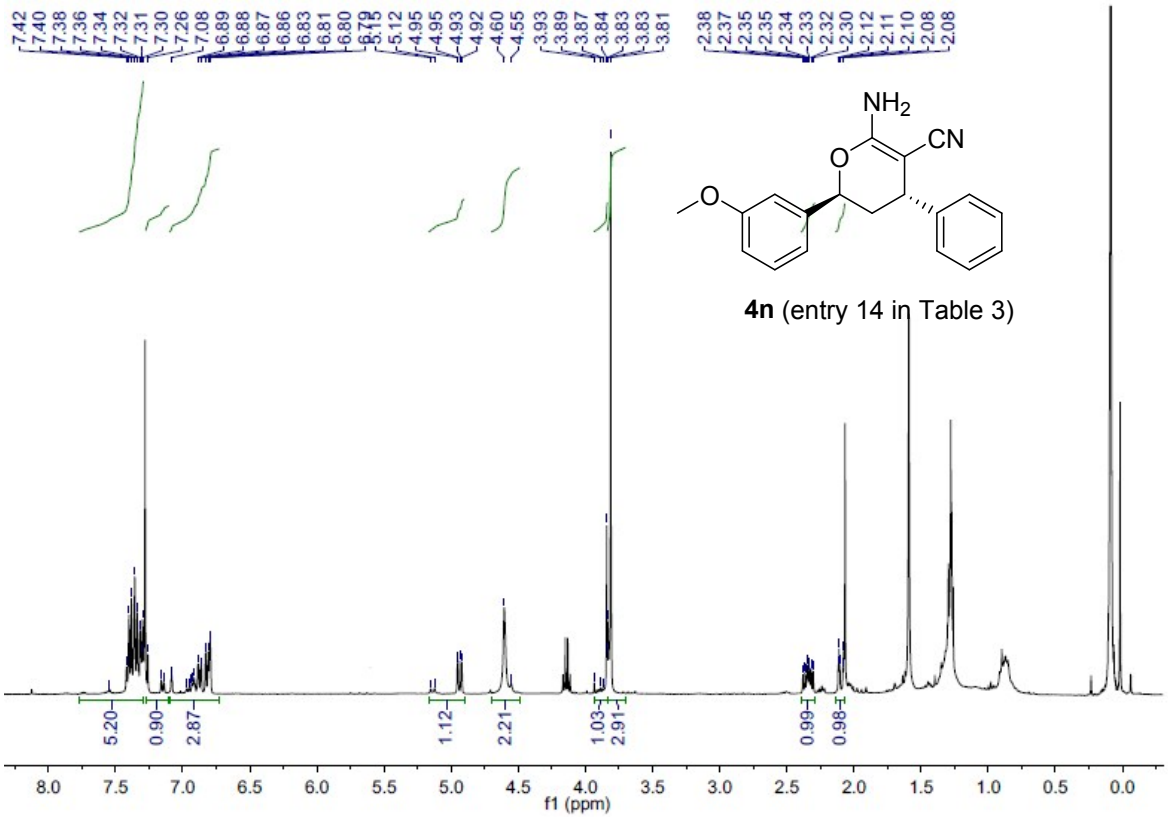


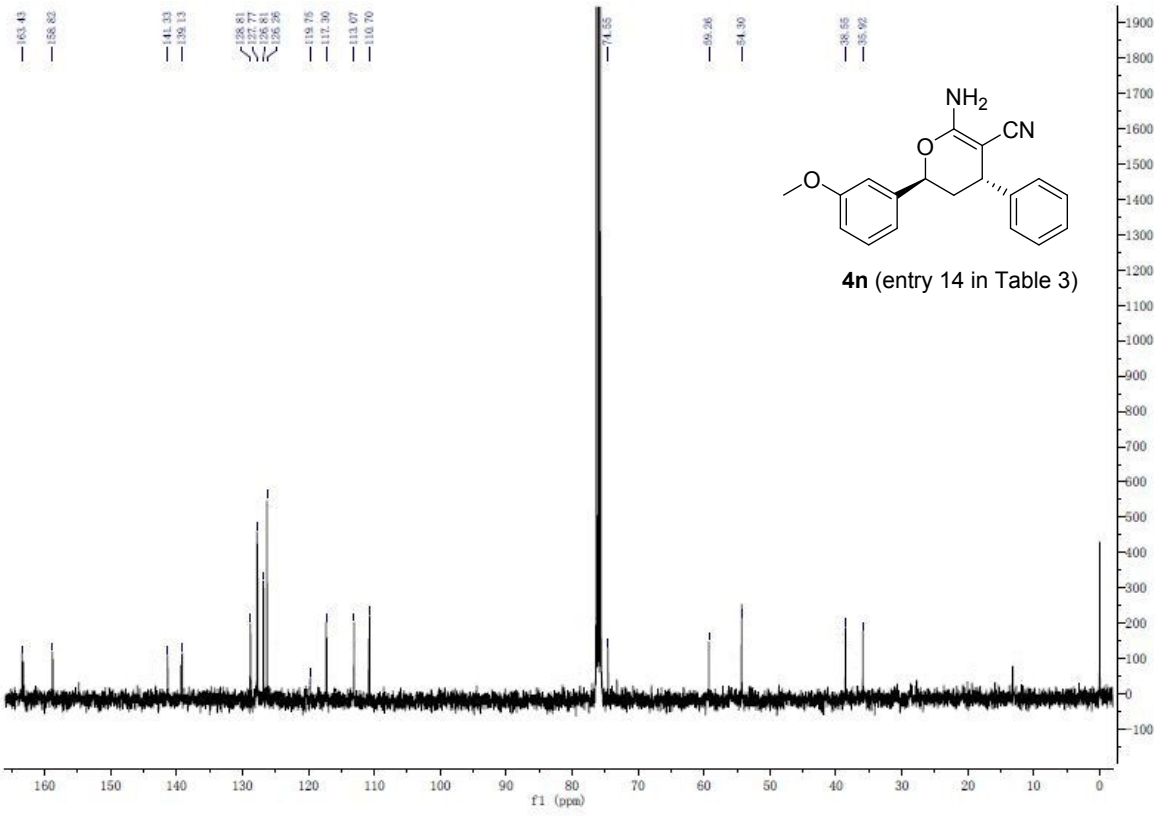




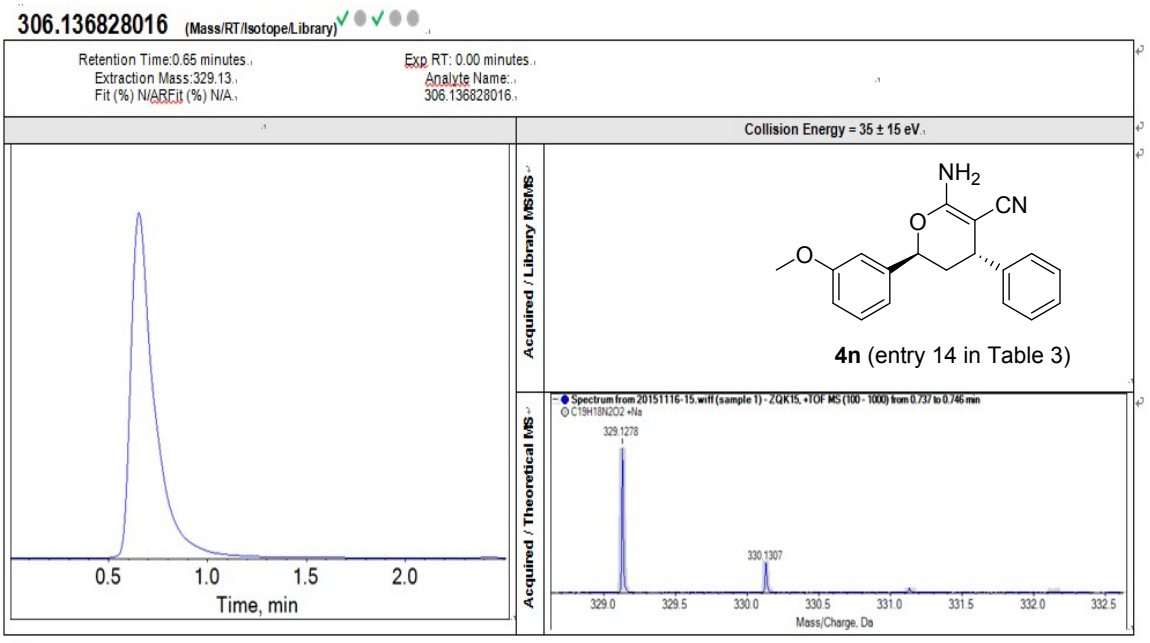
Compound Name (Library Hit)	Score	Formula	Intensity	Threshold	Expected m/z	Found at m/z	Error (ppm)	Expected RT (min)	Found RT (min)	RT Delta (min)	Isotope Diff (%)	Library Score(%)
306.136828016	91%	C19H18N2O2	204769	100	307.1441	307.1444	0.9	0.00	0.76	0.76	2.1%	N/A

4n. (2*S*,4*S*)-6-amino-2-(3-methoxyphenyl)-4-phenyl-3,4-dihydro-2*H*-pyran-5-carbonitrile.





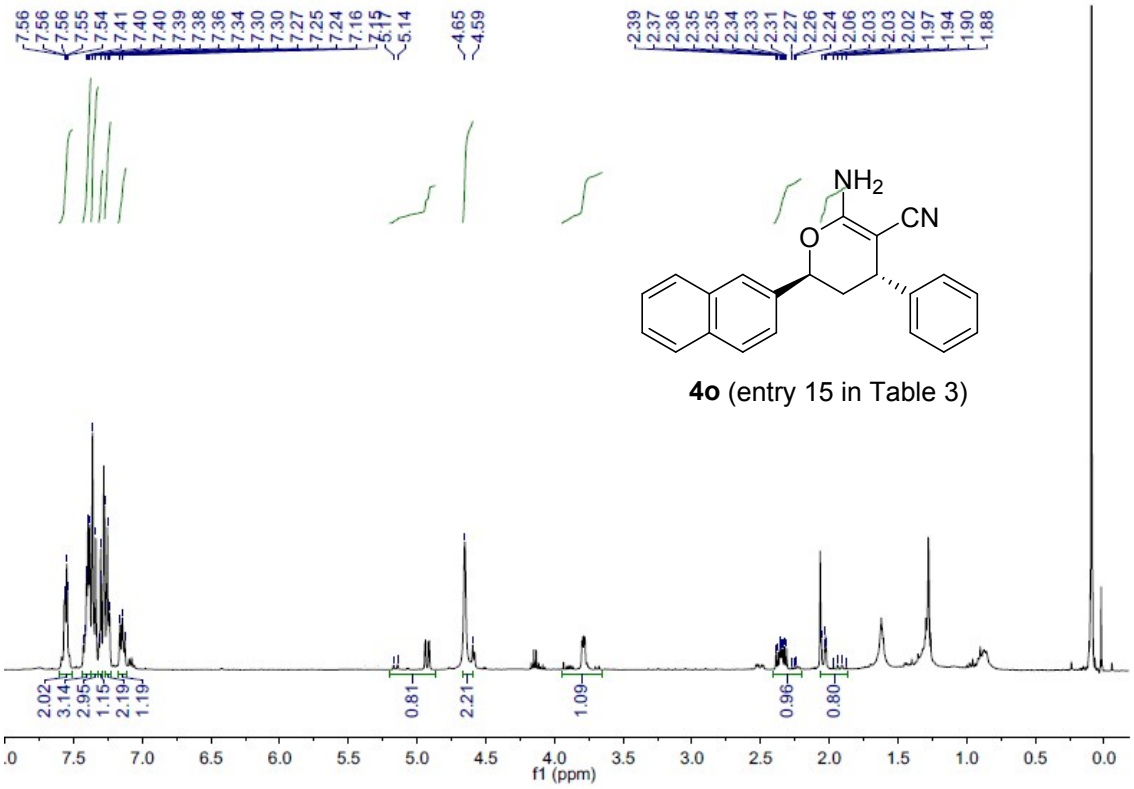
4n (entry 14 in Table 3)



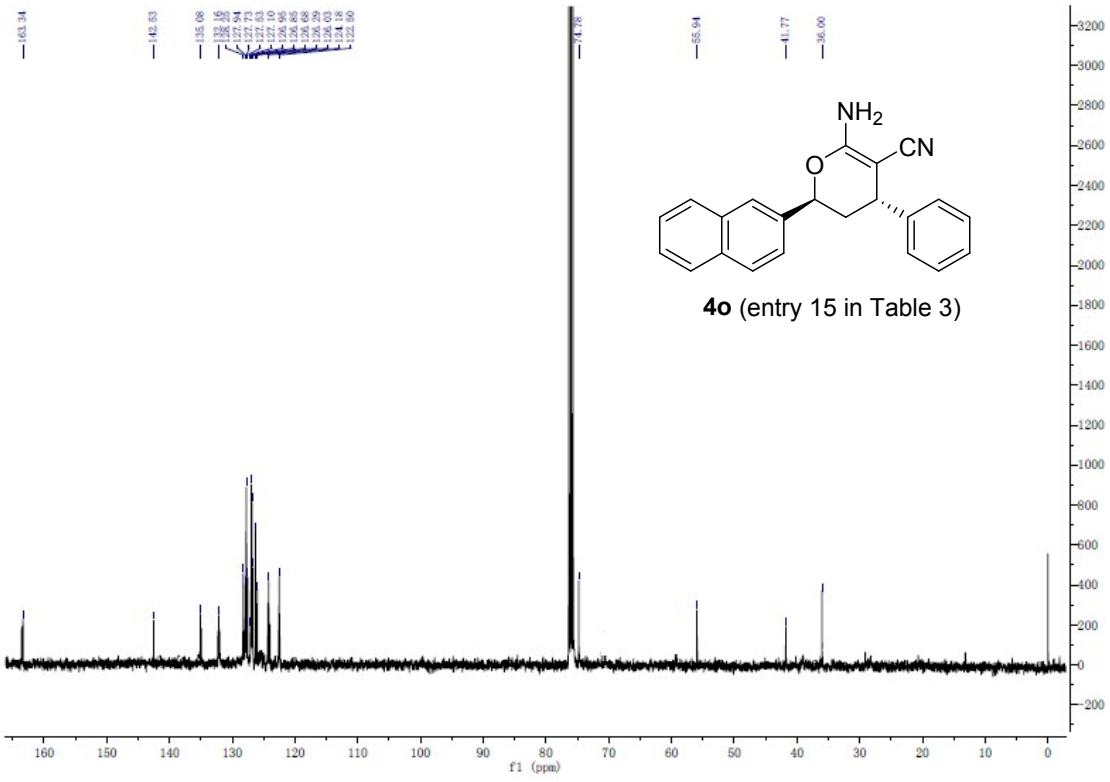
4n (entry 14 in Table 3)

Compound Name (Library Hit)	Score	Formula	Intensity	Threshold	Expected m/z	Found at m/z	Error (ppm)	Expected RT (min)	Found RT (min)	RT Delta (min)	Isotope Diff (%)	Library Score(%)
306.136828016	72%	C19H18N2O2	9815249	100	329.1260	329.1278	5.2	0.00	0.65	0.65	1.4%	N/A

4o. (2*S*,4*S*)-6-amino-2-(naphthalen-2-yl)-4-phenyl-3,4-dihydro-2*H*-pyran-5-carbonitrile.



4o (entry 15 in Table 3)



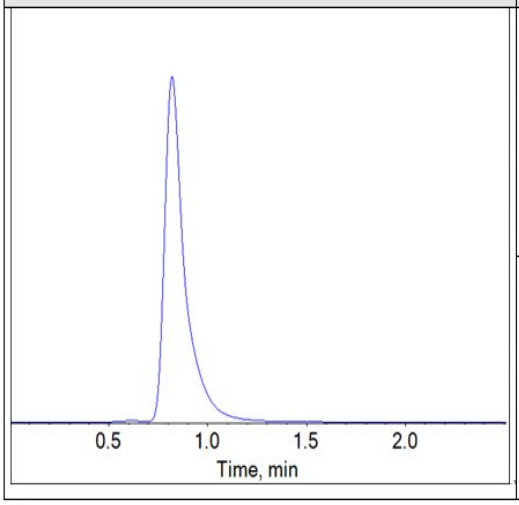
4o (entry 15 in Table 3)

326.141913376 (Mass/RT/Isotope/Library) ✓ ● ✓ ● ●

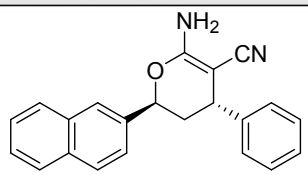
Retention Time:0.82 minutes
Extraction Mass:327.15
Fit (%) N/ARFit (%) N/A

Exp RT: 0.00 minutes
Analyte Name:
326.141913376

Collision Energy = 35 ± 15 eV

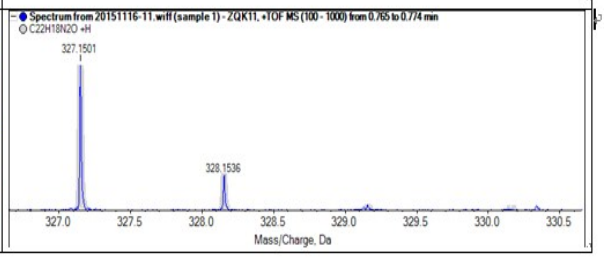


Acquired / Library MSMS



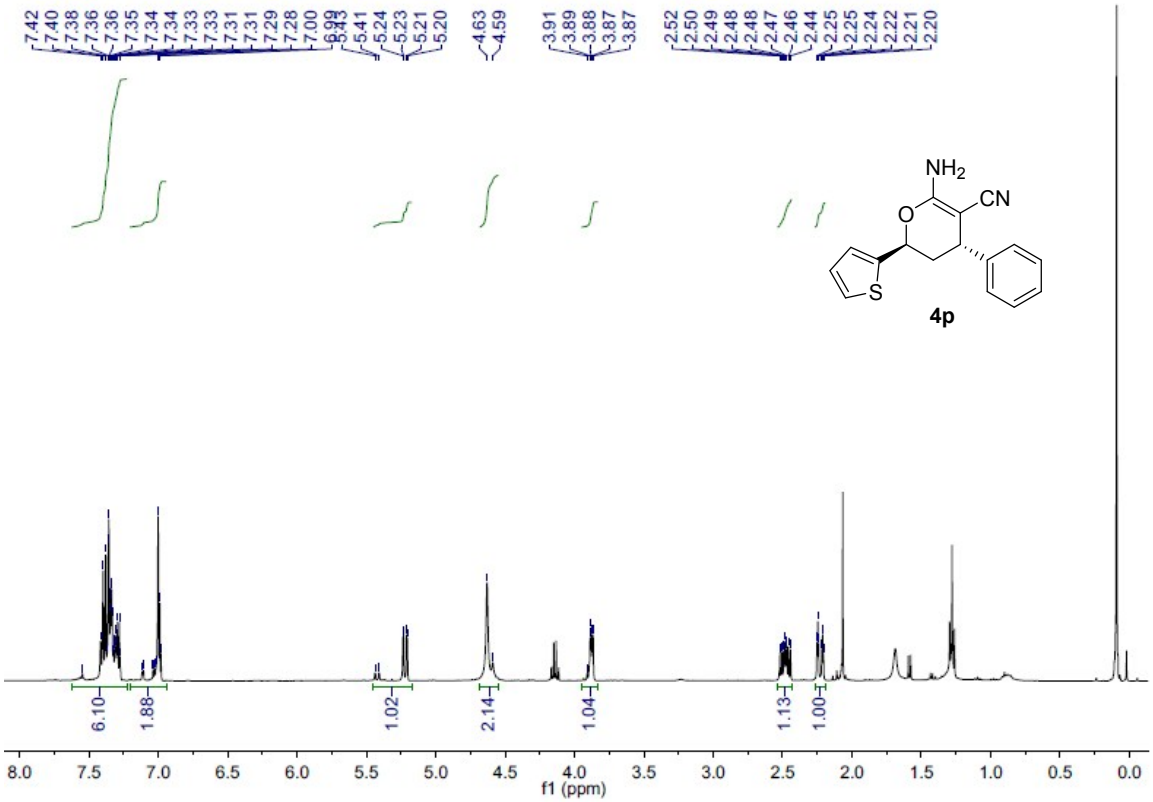
4o (entry 15 in Table 3)

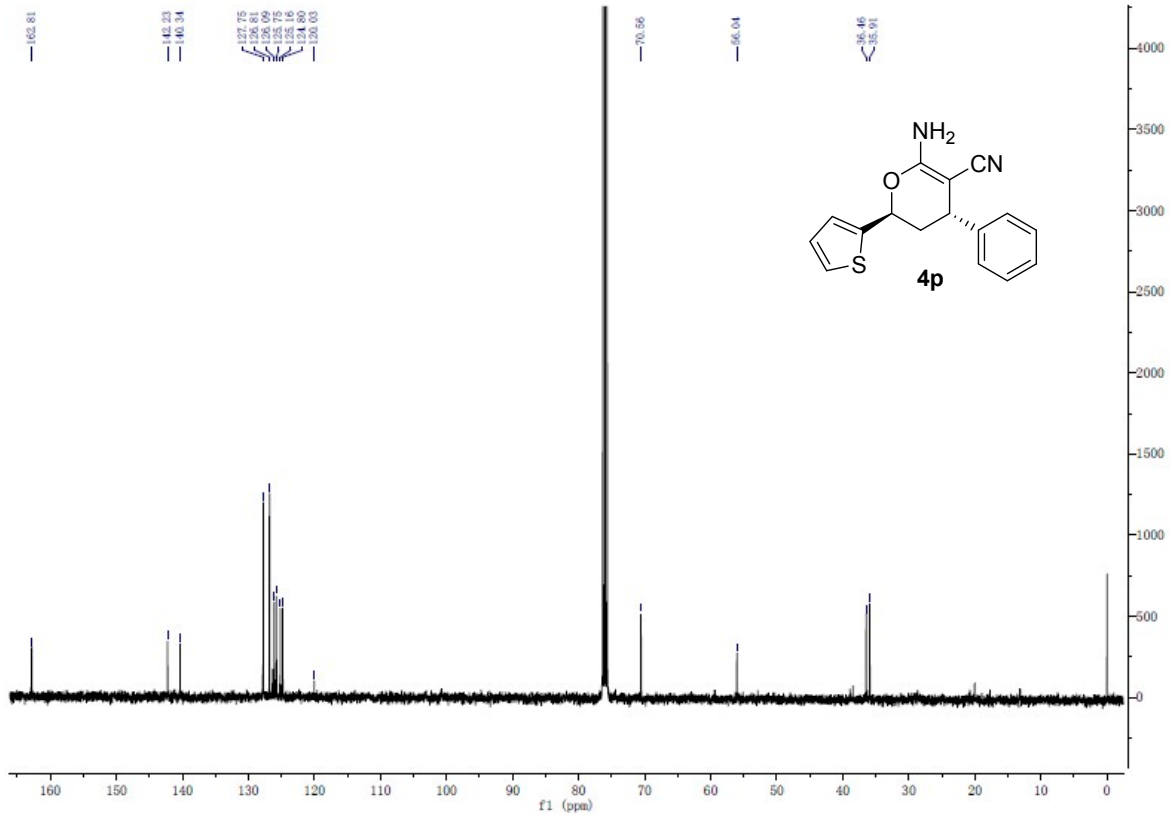
Acquired / Theoretical MS



✓✓✓✓✓	Compound Name (Library Hit)	Score	Formula	Intensity	Threshold	Expected m/z	Found at m/z	Error (ppm)	Expected RT (min)	Found RT (min)	RT Delta (min)	Isotope Diff (%)	Library Score(%)
✓●✓●●	326.141913376	84%	C22H18N2O	1225840	100	327.1492	327.1501	2.7	0.00	0.82	0.82	1.5%	N/A

4p: (2*S*,4*S*)-6-amino-4-phenyl-2-(thiophen-2-yl)-3,4-dihydro-*2H*-pyran-5-carbonitrile



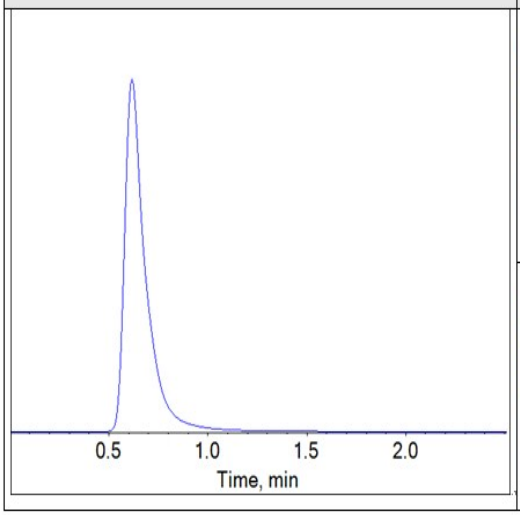


282.082685016 (Mass/RT/Isotope/Library)

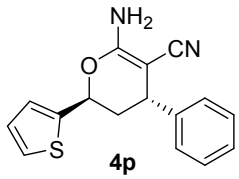
Retention Time:0.62 minutes
Extraction Mass:305.07
Fit (%) N/ARFit (%) N/A

Exp RT: 0.00 minutes
Analyte Name:
282.082685016

Collision Energy = 35 ± 15 eV

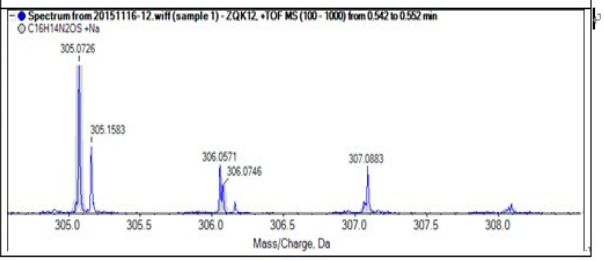


Acquired / Library MSMS



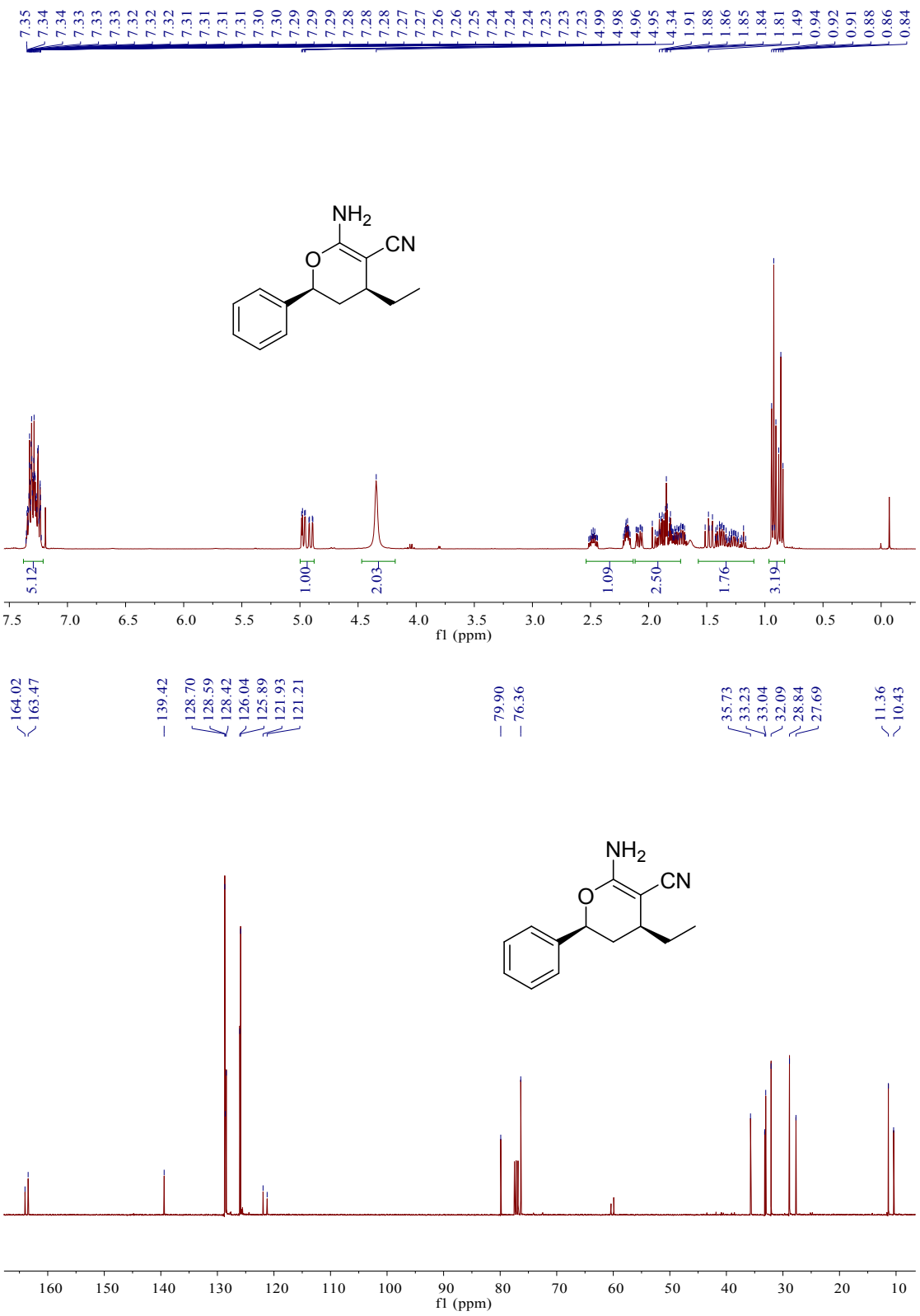
4p

Acquired / Theoretical MS

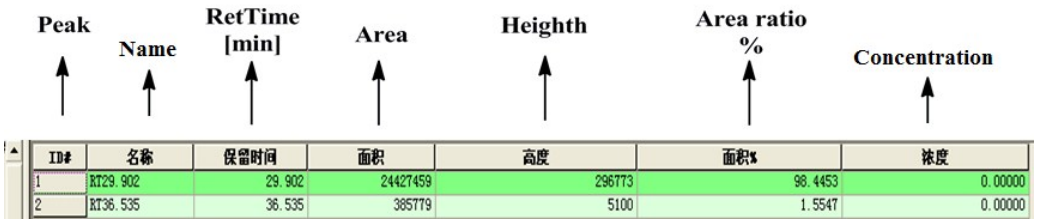


	Compound Name (Library Hit)	Score	Formula	Intensity	Threshold	Expected m/z	Found at m/z	Error (ppm)	Expected RT (min)	Found RT (min)	RT Delta (min)	Isotope Diff (%)	Library Score(%)
✓●✓●●	282.082685016	86%	C16H14N2OS	3610569	100	305.0719	305.0726	2.3	0.00	0.62	0.62	1.1%	N/A

4q: (2*S*,4*S*)-6-amino-4-ethyl-2-phenyl-3,4-dihydro-2H-pyran-5-carbonitrile

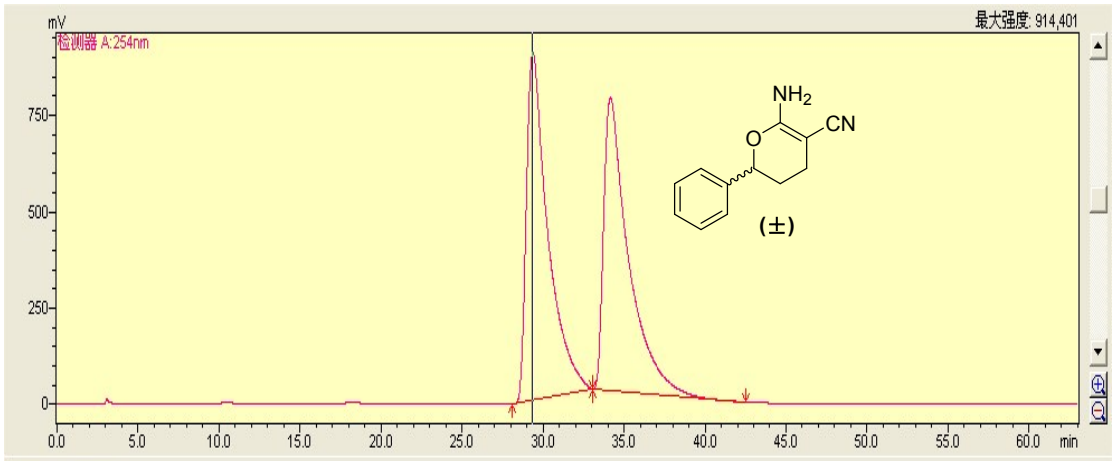


6. HPLC Trace Analyses for Chiral Products



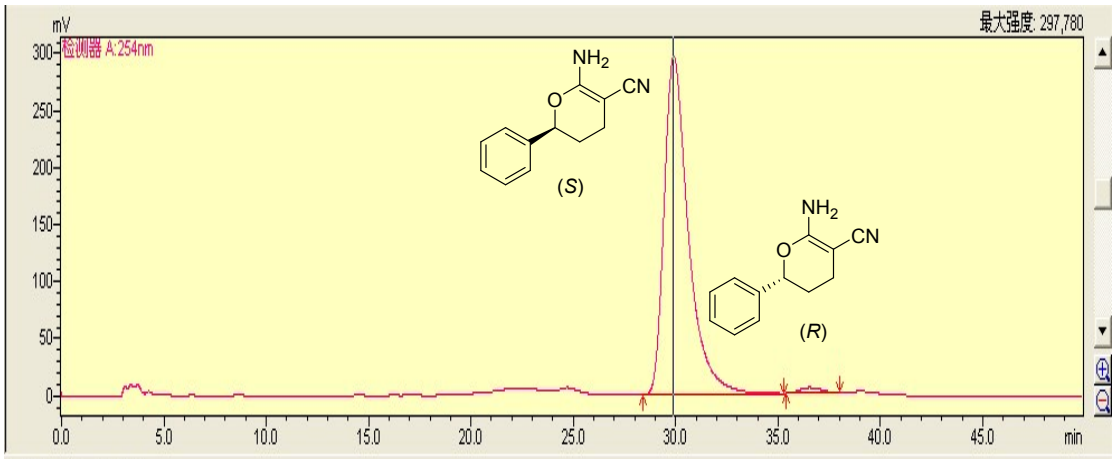
ID#	名称	保留时间	面积	高度	面积%	浓度
1	RT29.902	29.902	24427459	296773	98.4453	0.00000
2	RT36.535	36.535	385779	5100	1.5547	0.00000

2a: (*S*)-6-amino-2-phenyl-3,4-dihydro-2*H*-pyran-5-carbonitrile.



化合物表视图

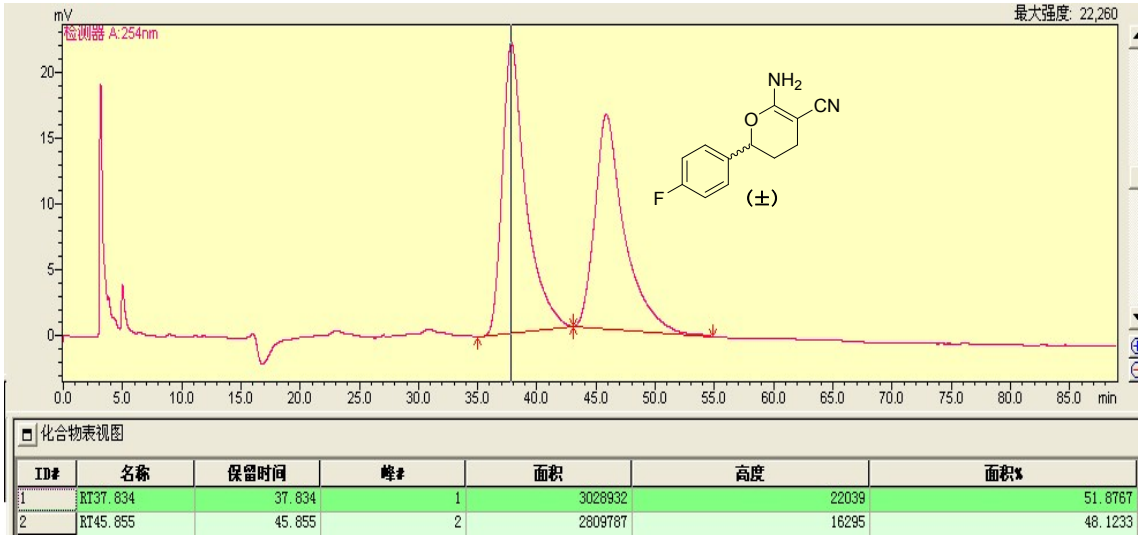
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT29.368	29.368	1	83282329	903655	50.6264
2	RT34.159	34.159	2	81221331	761746	49.3736



化合物表视图

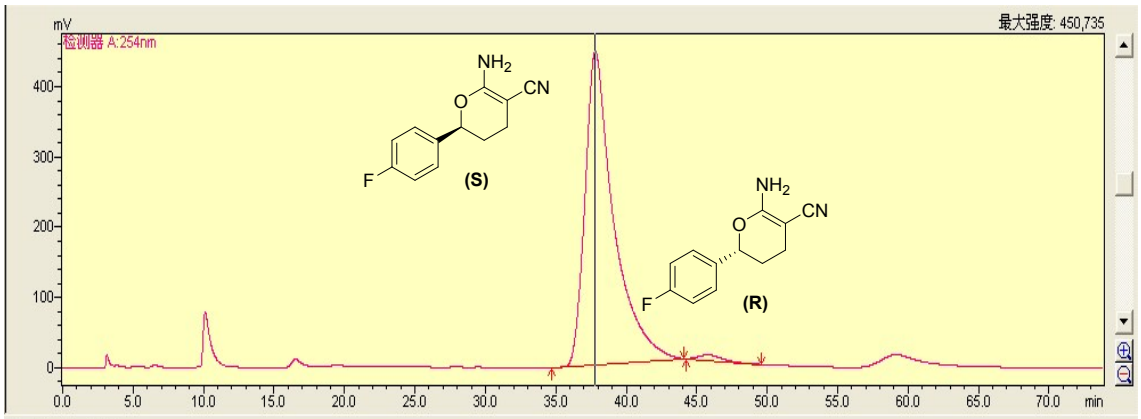
ID#	名称	保留时间	面积	高度	面积%	浓度
1	RT29.902	29.902	24427459	296773	98.4453	0.00000
2	RT36.535	36.535	385779	5100	1.5547	0.00000

2b: (*S*)-6-amino-2-(4-fluorophenyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile.



化合物表视图

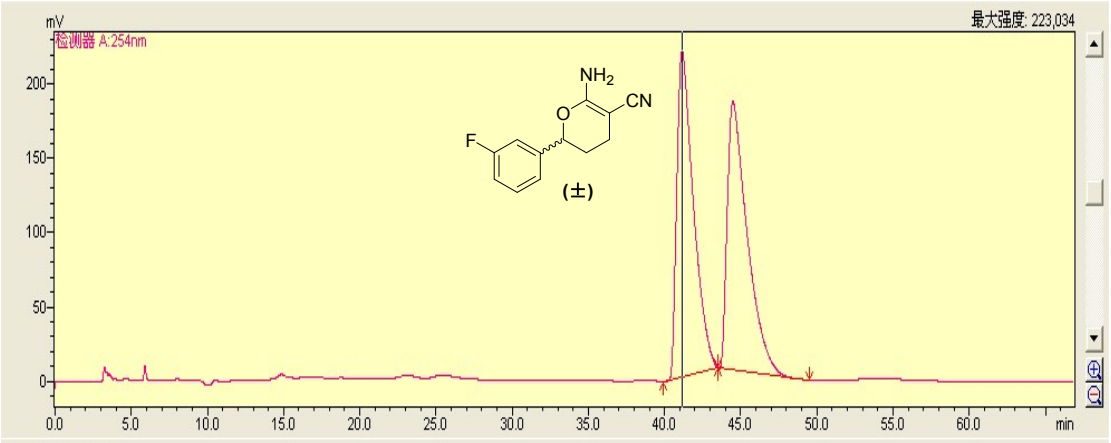
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT37.834	37.834	1	3028932	22039	51.8767
2	RT45.855	45.855	2	2809787	16295	48.1233



化合物表视图

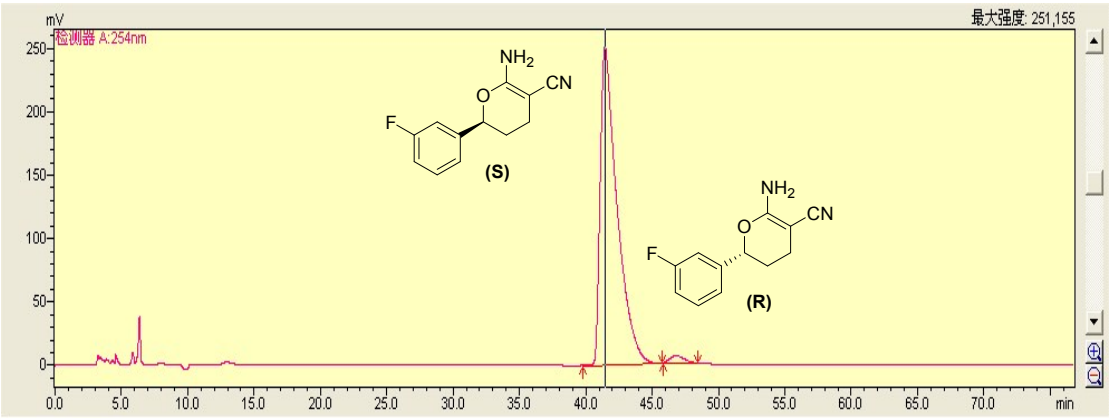
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT37.801	37.801	1	63122721	446268	98.6915
2	RT45.790	45.790	2	836905	7899	1.3085

2c:(*S*)-6-amino-2-(3-fluorophenyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile.



化合物表视图

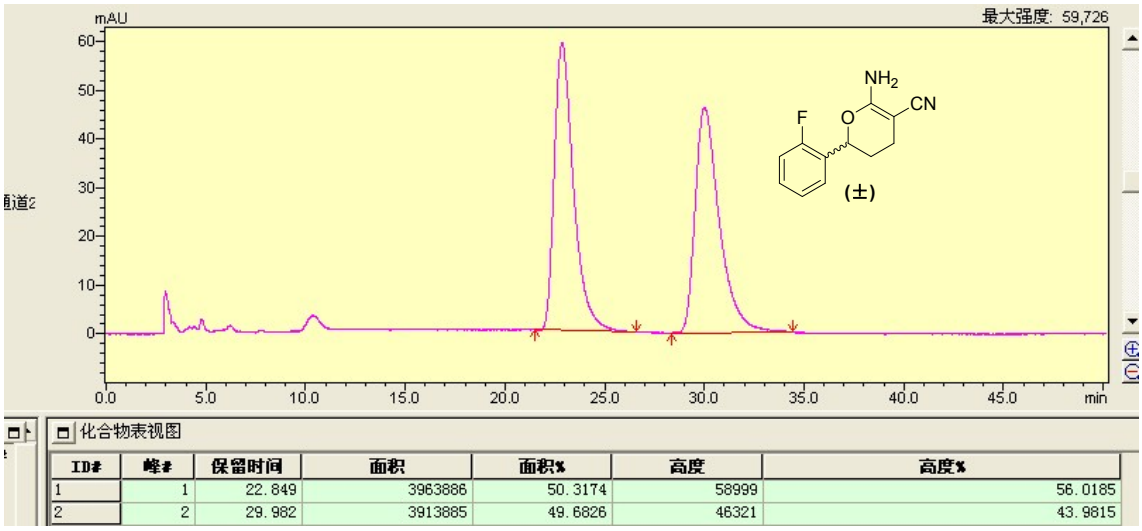
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT41.153	41.153	1	16637469	220197	50.1847
2	RT44.488	44.488	2	16514989	181319	49.8153



化合物表视图

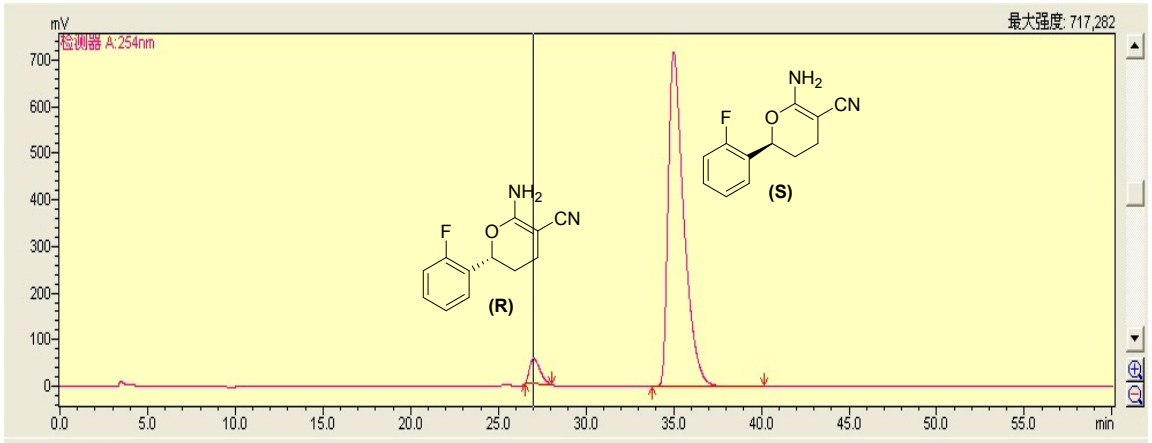
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT41.447	41.447	1	22198955	251014	98.0746
2	RT46.796	46.796	2	435818	5877	1.9254

2d: (*S*)-6-amino-2-(2-fluorophenyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile.



化合物表视图

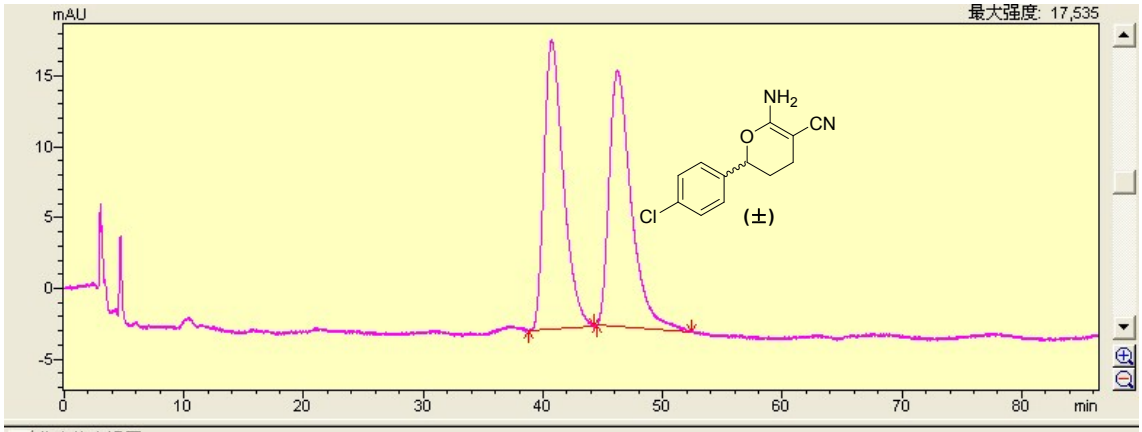
ID#	峰#	保留时间	面积	面积%	高度	高度%
1	1	22.849	3963886	50.3174	58999	56.0185
2	2	29.982	3913885	49.6826	46321	43.9815



化合物表视图

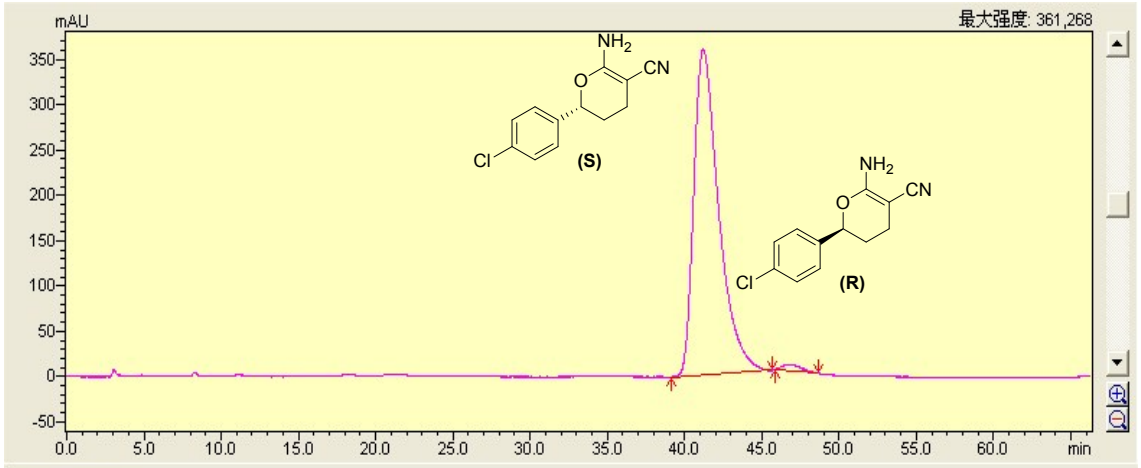
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT27.011	27.011	1	2316982	55238	4.9174
2	RT35.000	35.000	2	44801421	718459	95.0826

2e: (*S*)-6-amino-2-(4-chlorophenyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile.



化合物表视图

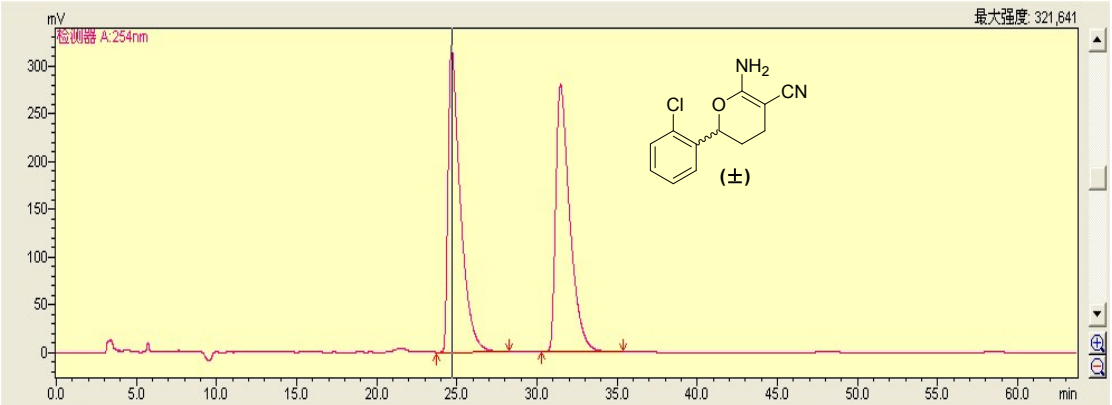
ID#	峰#	保留时间	面积	面积%	高度	高度%
1	1	40.729	2284450	49.6386	20411	52.9640
2	2	46.217	2317714	50.3614	18127	47.0360



化合物表视图

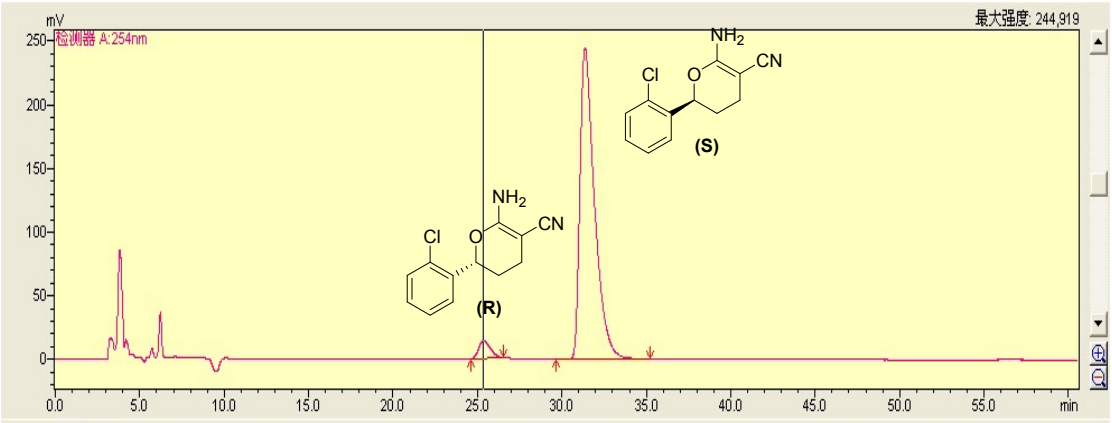
ID#	峰#	保留时间	面积	面积%	高度	高度%
1	1	41.194	40281109	98.4285	359309	98.0064
2	2	46.807	643125	1.5715	7309	1.9936

2f: (*S*)-6-amino-2-(2-chlorophenyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile.



化合物表视图

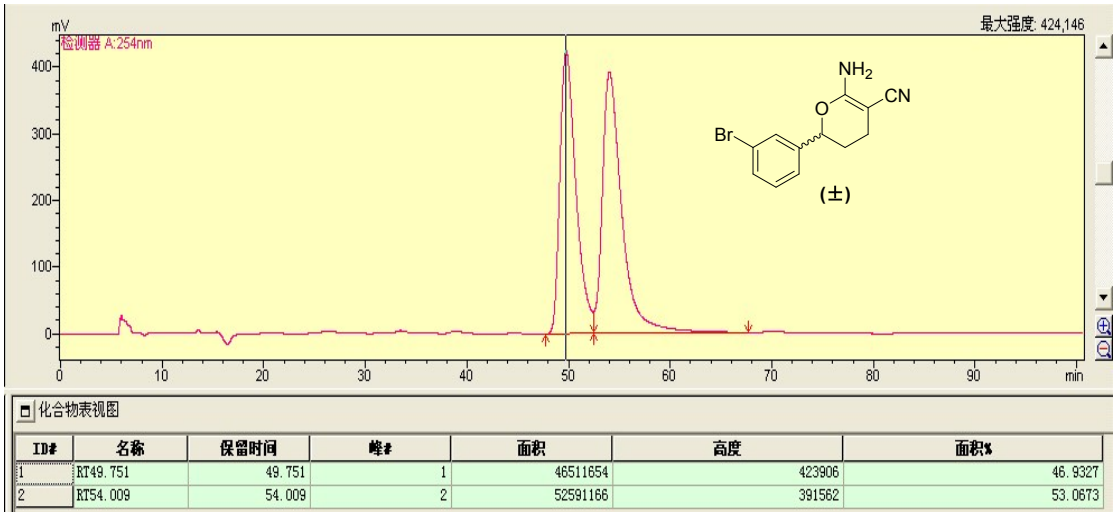
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT24.667	24.667	1	17049949	321440	49.9130
2	RT31.468	31.468	2	17109388	280325	50.0870



化合物表视图

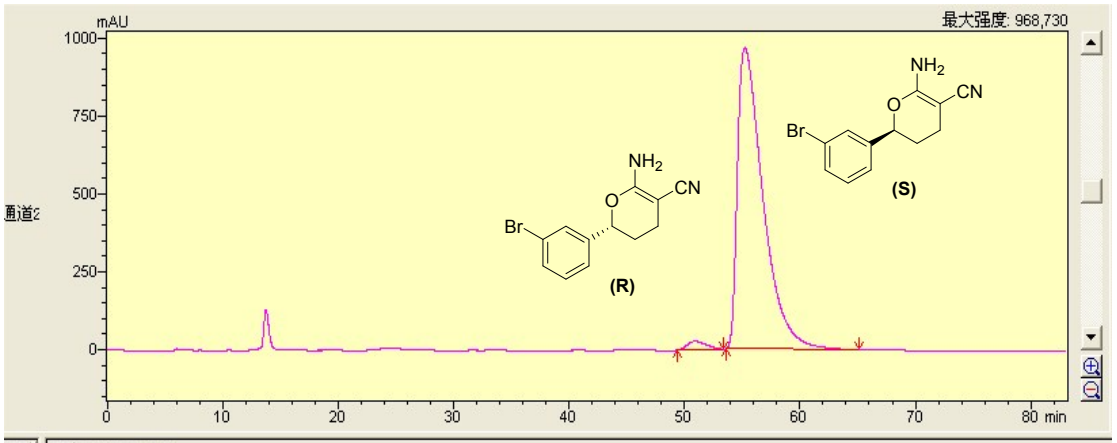
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT25.368	25.368	1	666955	14018	4.3486
2	RT31.370	31.370	2	14677356	244720	95.6534

2g: (*S*)-6-amino-2-(3-bromophenyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile.



化合物表视图

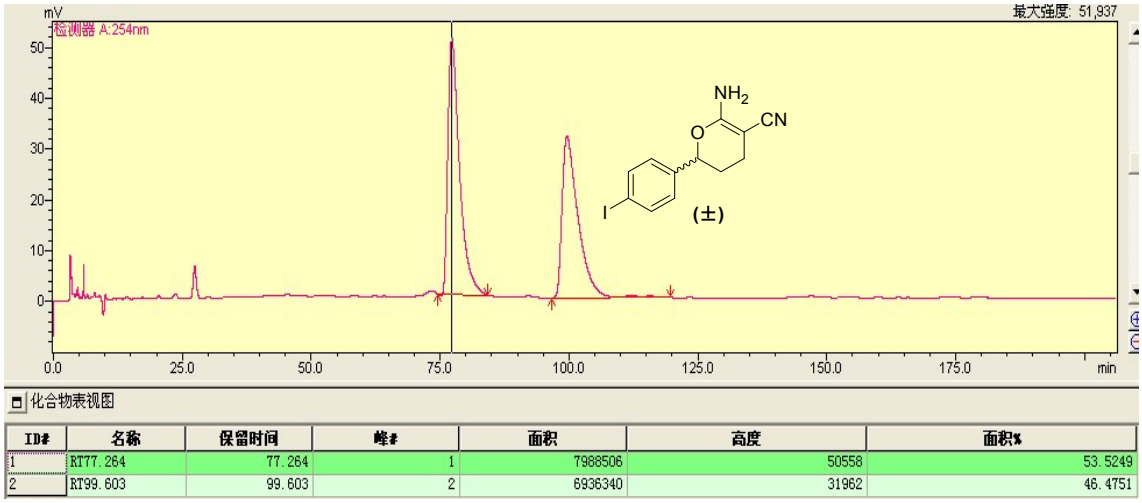
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT49.751	49.751	1	46511654	423906	46.9327
2	RT54.009	54.009	2	52591166	391562	53.0673



化合物表视图

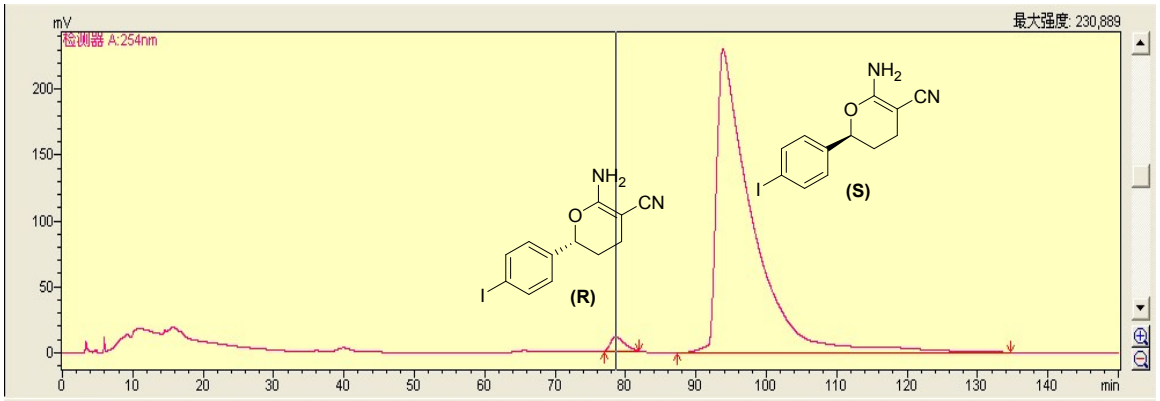
ID#	峰#	保留时间	面积	面积%	高度	高度%
1	1	50.916	3161328	2.0784	27253	2.7440
2	2	55.217	148944744	97.9216	965923	97.2560

2h: (*S*)-6-amino-2-(4-iodophenyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile.



化合物表视图

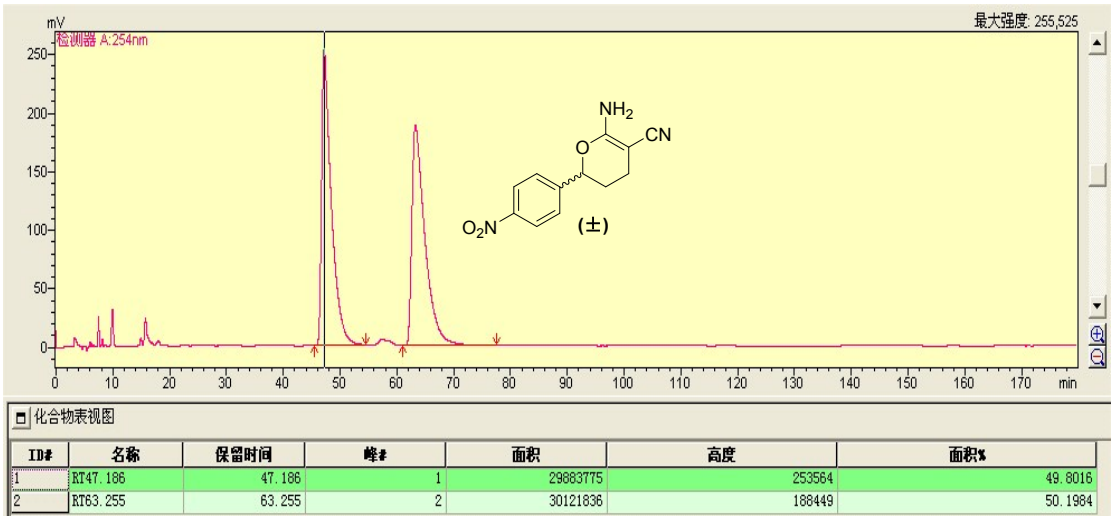
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT77.264	77.264	1	7988506	50558	53.5249
2	RT99.603	99.603	2	6936340	31962	46.4751



化合物表视图

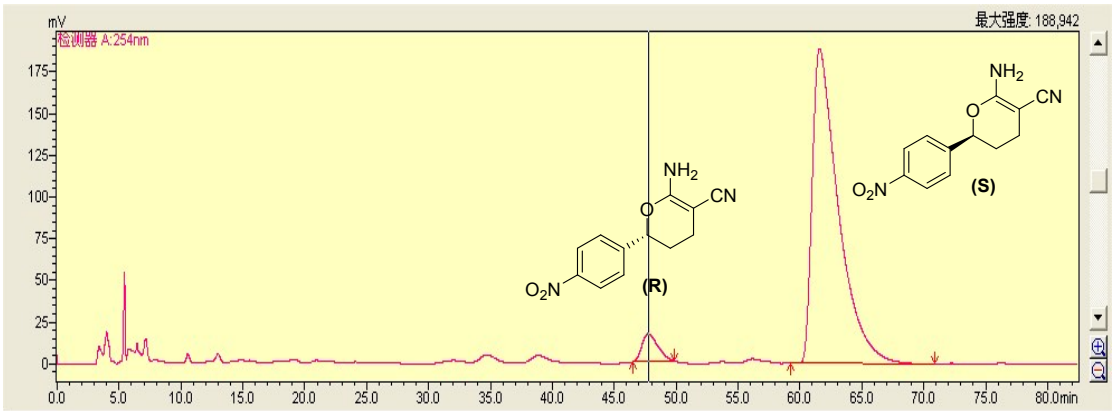
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT78.594	78.594	1	1532617	11185	1.8742
2	RT93.825	93.825	2	80242637	230839	98.1258

2i: (*S*)-6-amino-2-(4-nitrophenyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile.



化合物表视图

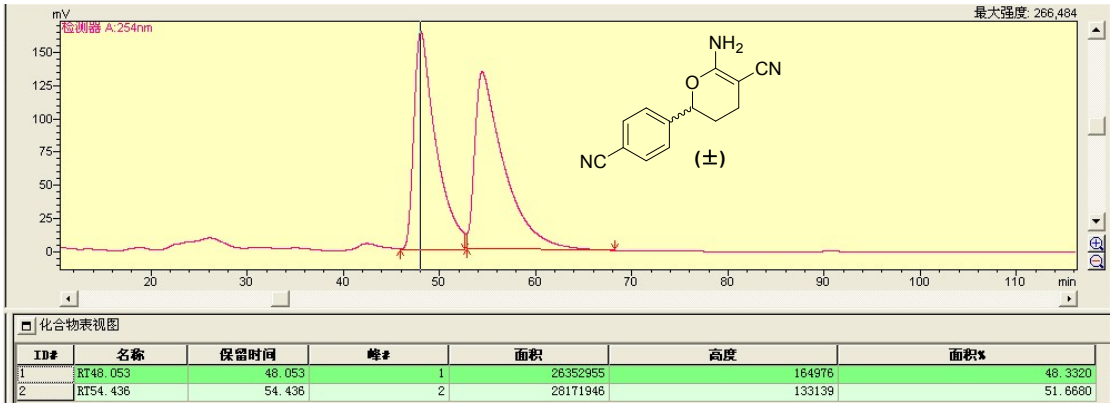
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT47.186	47.186	1	29883775	253564	49.8016
2	RT63.255	63.255	2	30121836	188449	50.1984



化合物表视图

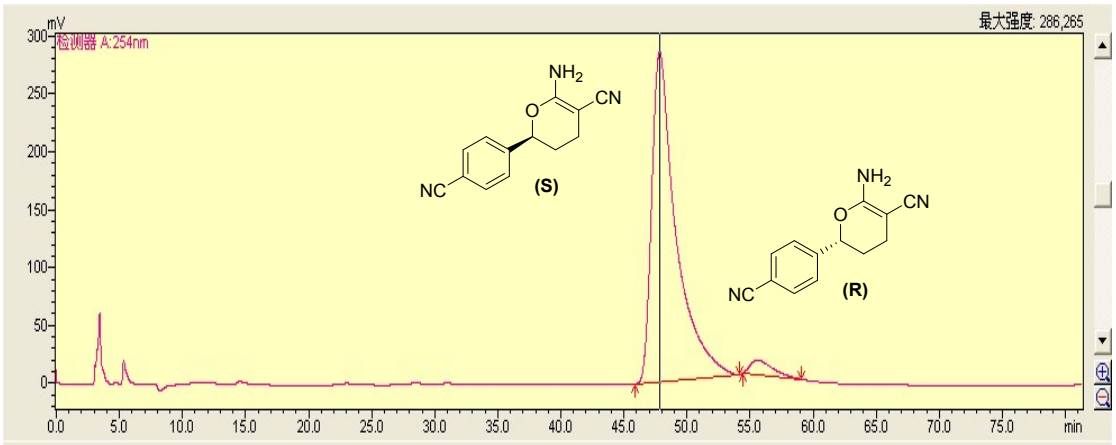
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT47.741	47.741	1	1451069	16537	4.9631
2	RT61.584	61.584	2	27786093	188647	95.0369

2j: (*S*)-6-amino-2-(4-cyanophenyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile.



化合物表视图

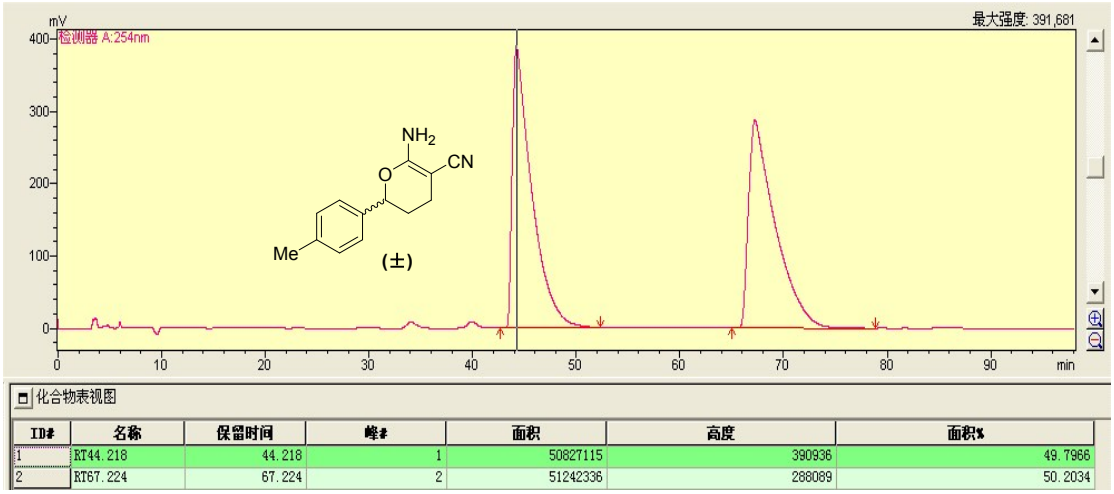
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT48.053	48.053	1	26352955	164976	48.3320
2	RT54.436	54.436	2	28171946	133139	51.6680



化合物表视图

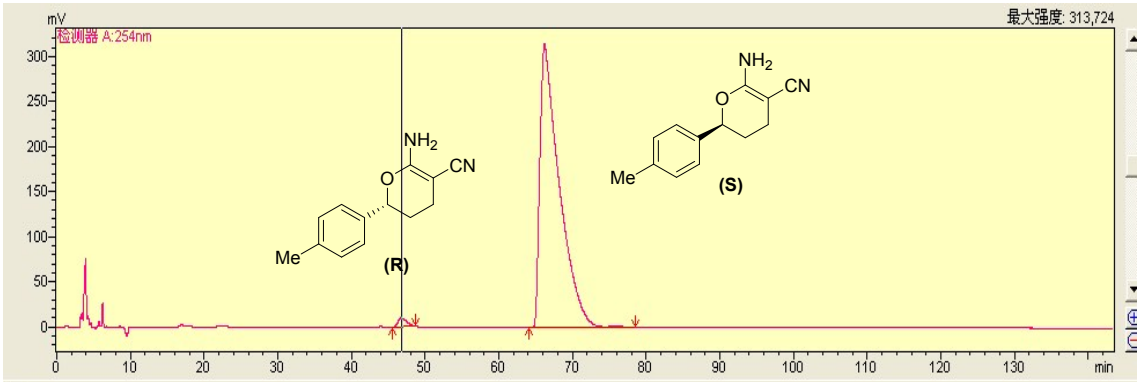
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT47.833	47.833	1	38196363	285009	96.0852
2	RT55.607	55.607	2	1556246	12504	3.9148

2k: (*S*)-6-amino-2-(p-tolyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile.



化合物表视图

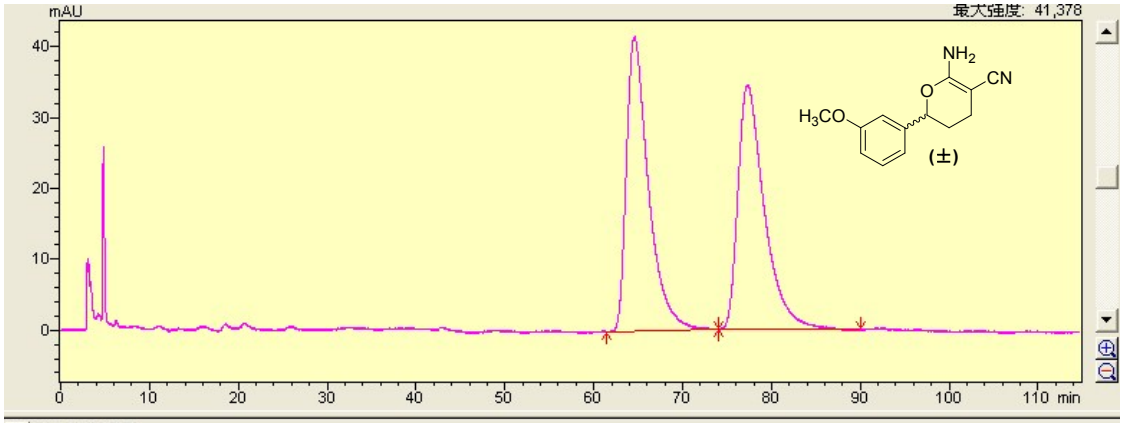
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT44.218	44.218	1	50827115	390936	49.7966
2	RT67.224	67.224	2	51242336	288089	50.2034



化合物表视图

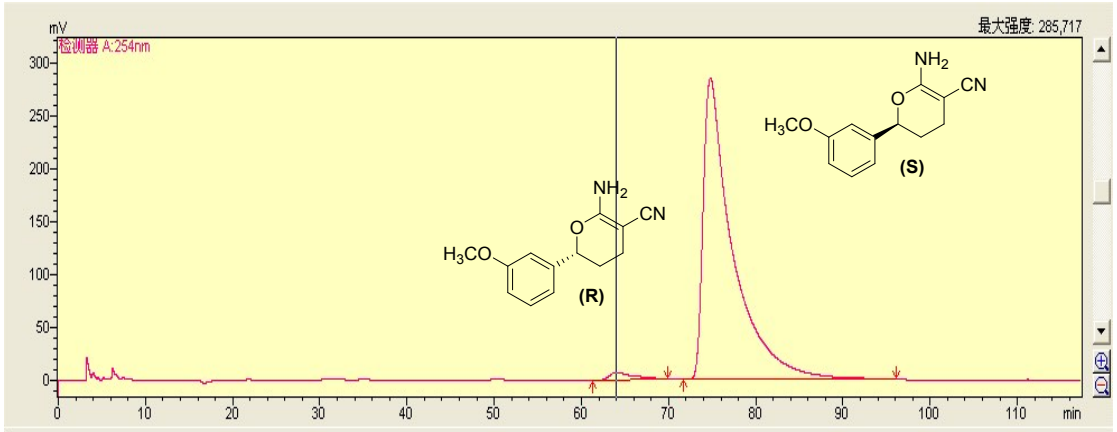
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT46.759	46.759	1	848341	10166	1.4480
2	RT66.190	66.190	2	57740621	314723	98.5520

2l: (*S*)-6-amino-2-(3-methoxyphenyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile.



化合物表视图

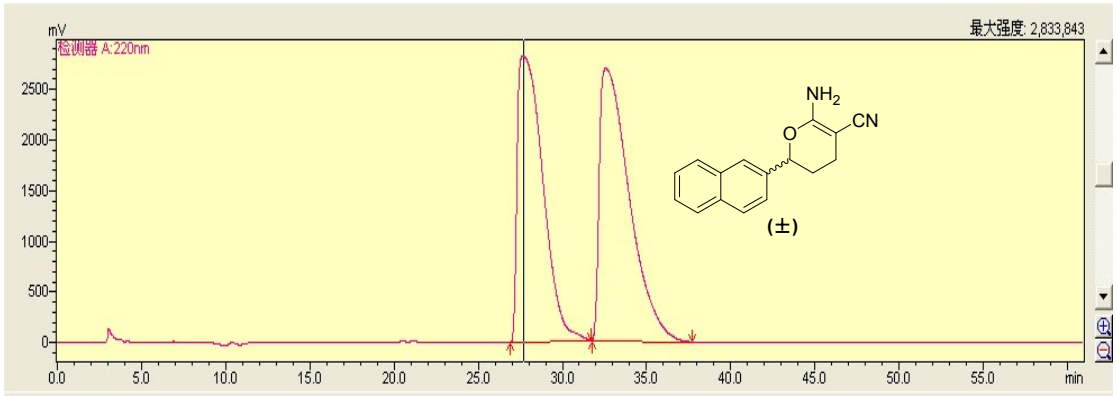
ID#	峰#	保留时间	面积	面积%	高度	高度%
1	1	64.592	7157591	50.1362	41469	54.5628
2	2	77.289	7118711	49.8638	34533	45.4372



化合物表视图

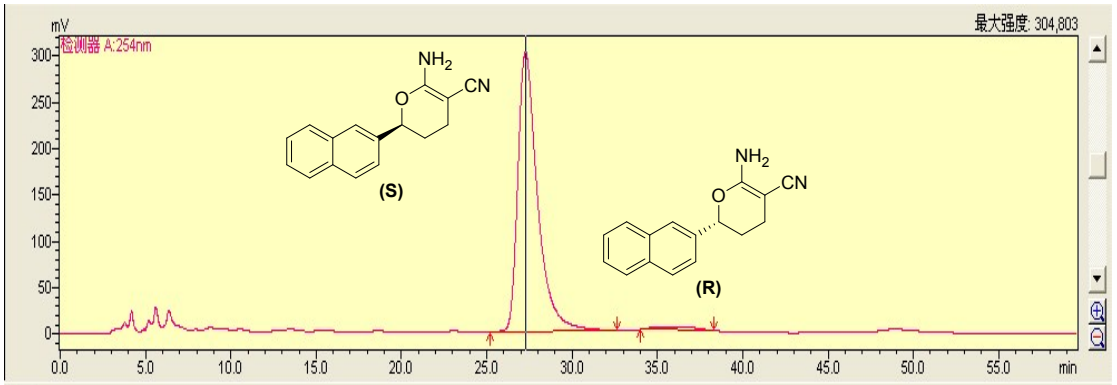
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT64.046	64.046	1	1296687	7035	1.9109
2	RT74.800	74.800	2	66561241	284206	98.0891

2m: (*S*)-6-amino-2-(naphthalen-2-yl)-3,4-dihydro-2*H*-pyran-5-carbonitrile.



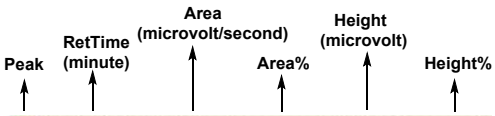
化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT27.687	27.687	1	299152648	2832007	47.3742
2	RT32.573	32.573	2	332314228	2691320	52.6258



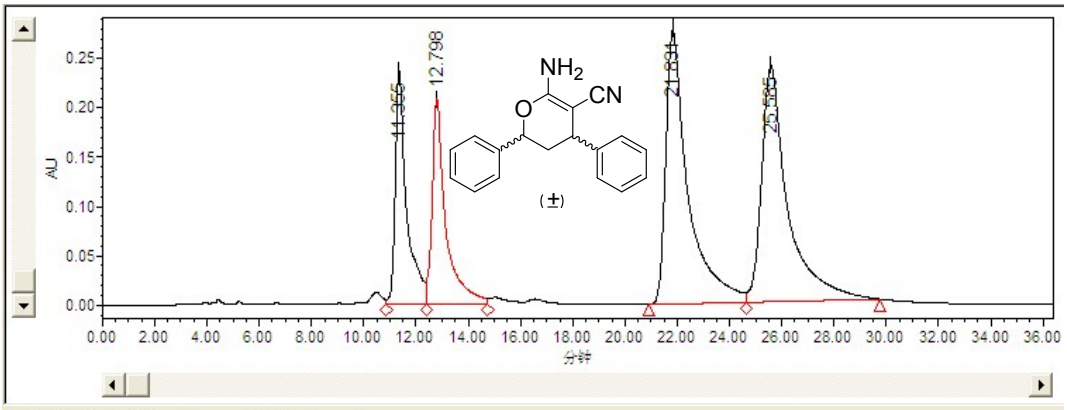
化合物表视图

ID#	名称	保留时间	面积	高度	面积%	浓度
1	RT27.263	27.263	24258948	302281	97.5081	0.00000
2	RT35.624	35.624	619953	3565	2.4919	0.00000

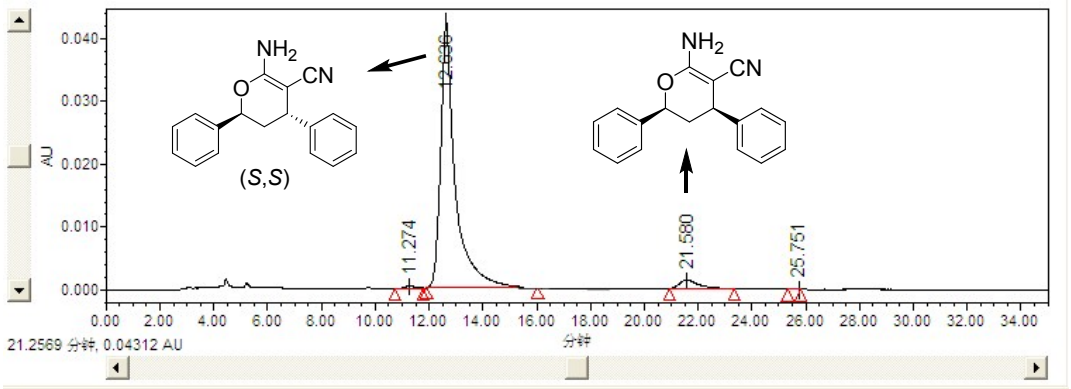


	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	% 高
1	9.212	54421487	49.64	2755344	52.56
2	10.141	55206565	50.36	2487434	47.44

4a. (2*S*,4*S*)-6-amino-2,4-diphenyl-3,4-dihydro-2*H*-pyran-5-carbonitrile.

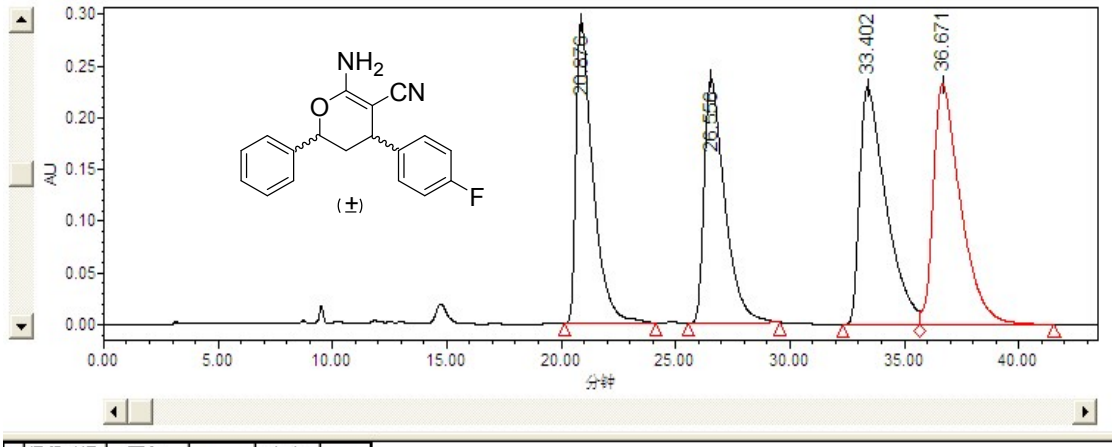


	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	% 高
1	11.355	7123451	14.93	236086	24.52
2	12.798	7483373	15.68	207895	21.59
3	21.831	16440025	34.45	279378	29.01
4	25.585	16677010	34.94	239611	24.88

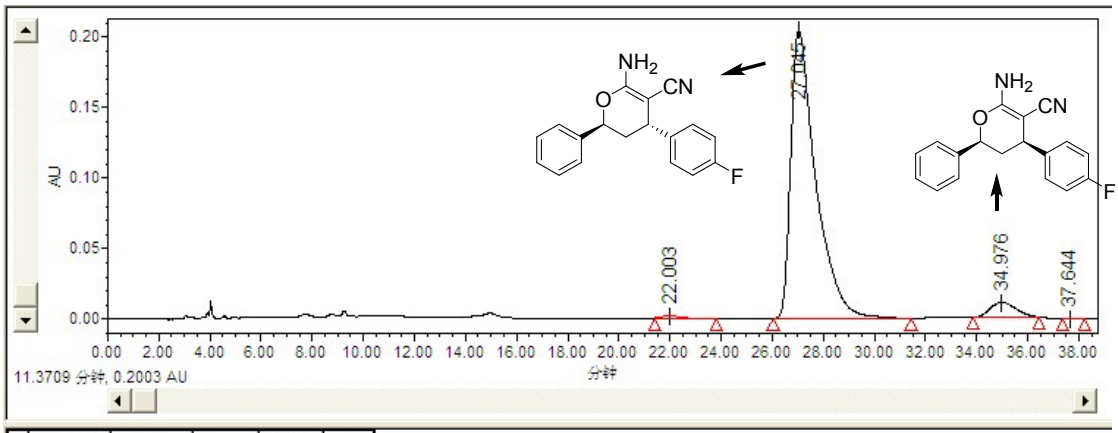


	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	% 高
1	11.274	11996	0.72	451	1.02
2	12.636	1588951	95.20	42244	95.86
3	21.580	67901	4.07	1361	3.09
4	25.751	150	0.01	11	0.03

4b. (2*S*,4*S*)-6-amino-4-(4-fluorophenyl)-2-phenyl-3,4-dihydro-2*H*- pyran-5-carbonitrile.

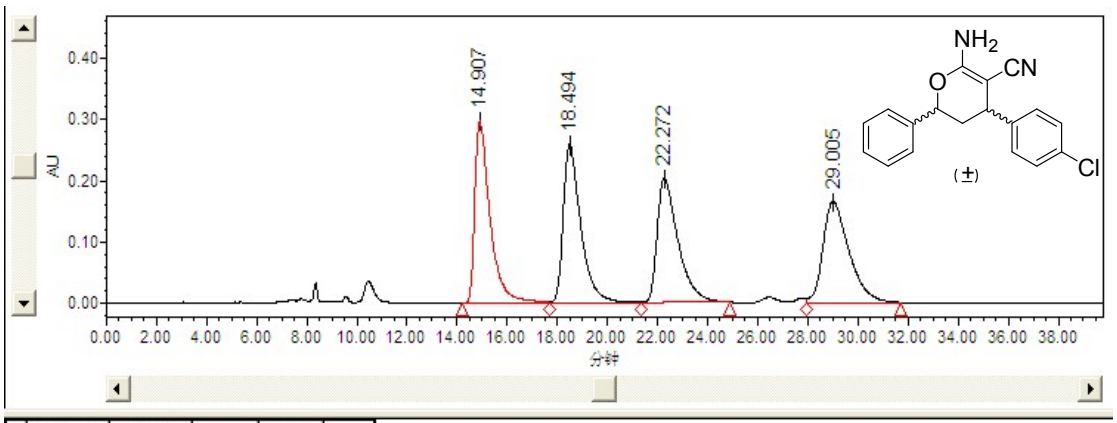


	保留时间 (分钟)	面积 (微伏·秒)	% 面积	高度 (微伏)	% 高
1	20.876	15099602	22.34	290406	29.39
2	26.556	14814750	21.92	236352	23.92
3	33.402	18396217	27.22	228999	23.18
4	36.671	19269293	28.51	232298	23.51

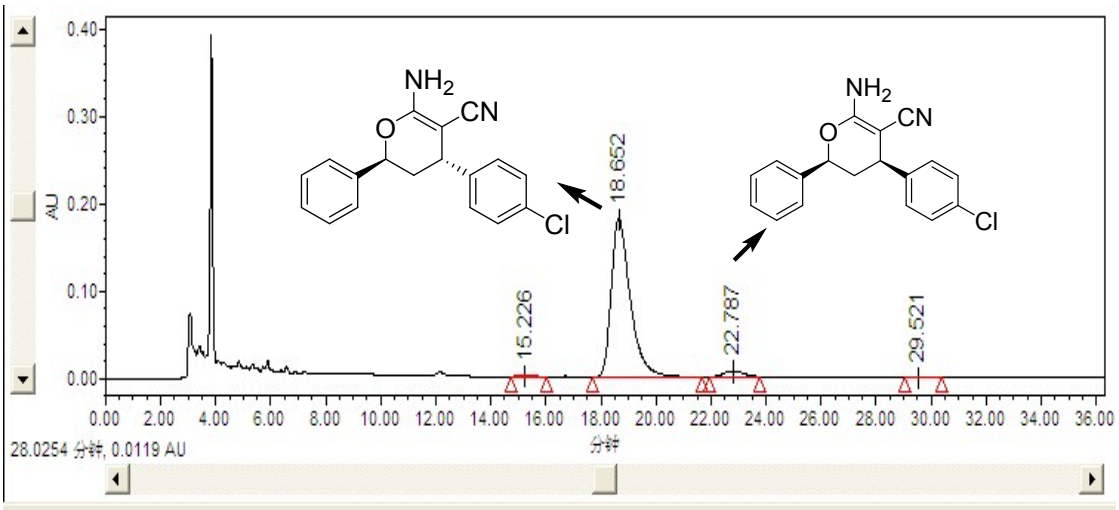


	保留时间 (分钟)	面积 (微伏·秒)	% 面积	高度 (微伏)	% 高
1	22.003	83714	0.57	1610	0.74
2	27.045	13850626	94.22	204351	94.28
3	34.976	763451	5.19	10728	4.95
4	37.644	2022	0.01	-66	0.03

4c. (2*S*,4*S*)-6-amino-4-(4-chlorophenyl)-2-phenyl-3,4-dihydro-2*H*-pyran-5-carbonitrile.

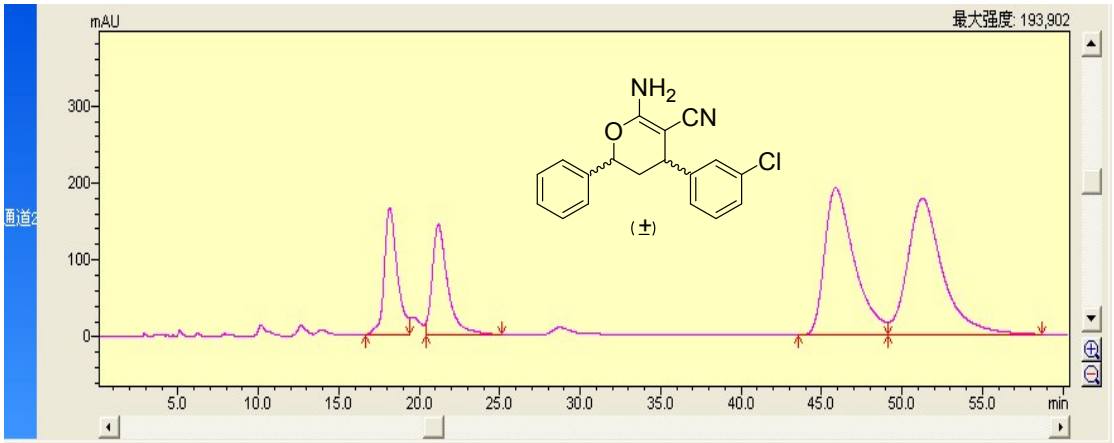


	保留时间 (分钟)	面积 (微伏·秒)	% 面积	高度 (微伏)	% 高
1	14.907	12545401	25.81	296811	32.21
2	18.494	12466723	25.65	257720	27.97
3	22.272	11712443	24.09	202189	21.94
4	29.005	11886576	24.45	164719	17.88



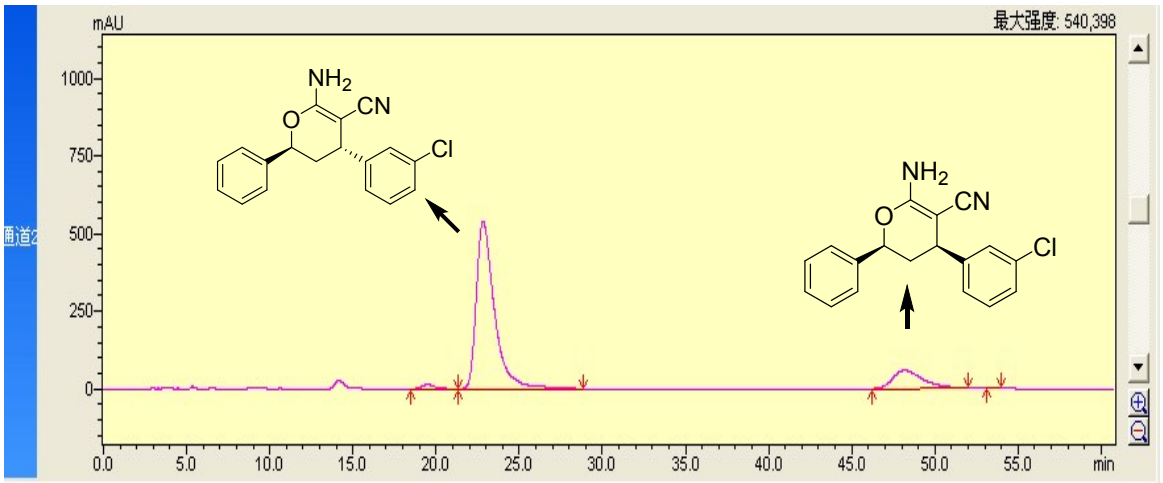
	保留时间 (分钟)	面积 (微伏·秒)	% 面积	高度 (微伏)	% 高
1	15.226	65834	0.71	1703	0.90
2	18.652	8813940	95.45	181580	95.49
3	22.787	352122	3.81	6801	3.58
4	29.521	2292	0.02	82	0.04

4d. (2*S*,4*S*)-6-amino-4-(3-chlorophenyl)-2-phenyl-3,4-dihydro-2*H*-pyran-5-carbonitrile.



化合物表视图

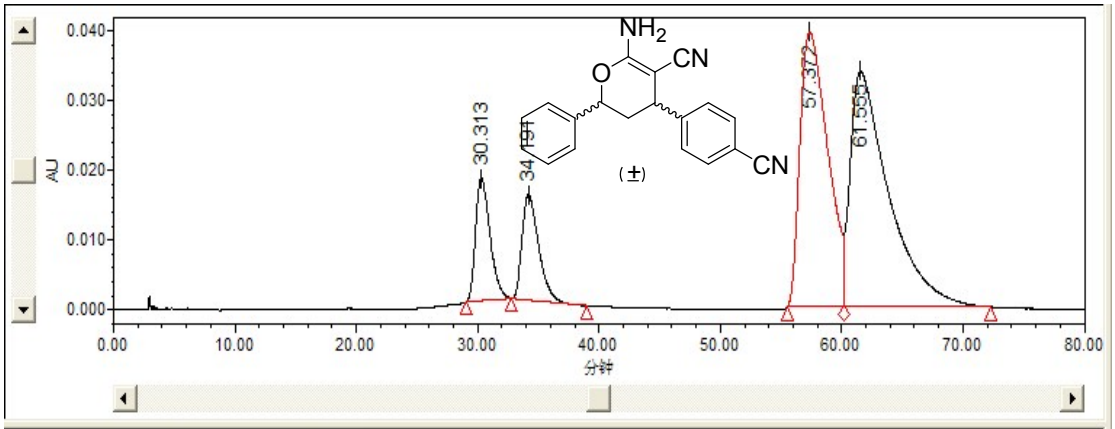
ID#	峰#	保留时间	面积	面积%	高度	高度%
1	1	18.153	9378814	13.2658	165708	24.4141
2	2	21.179	9662817	13.6676	143683	21.1691
3	3	45.871	24720777	34.9663	191723	28.2470
4	4	51.269	26936521	38.1003	177624	26.1697



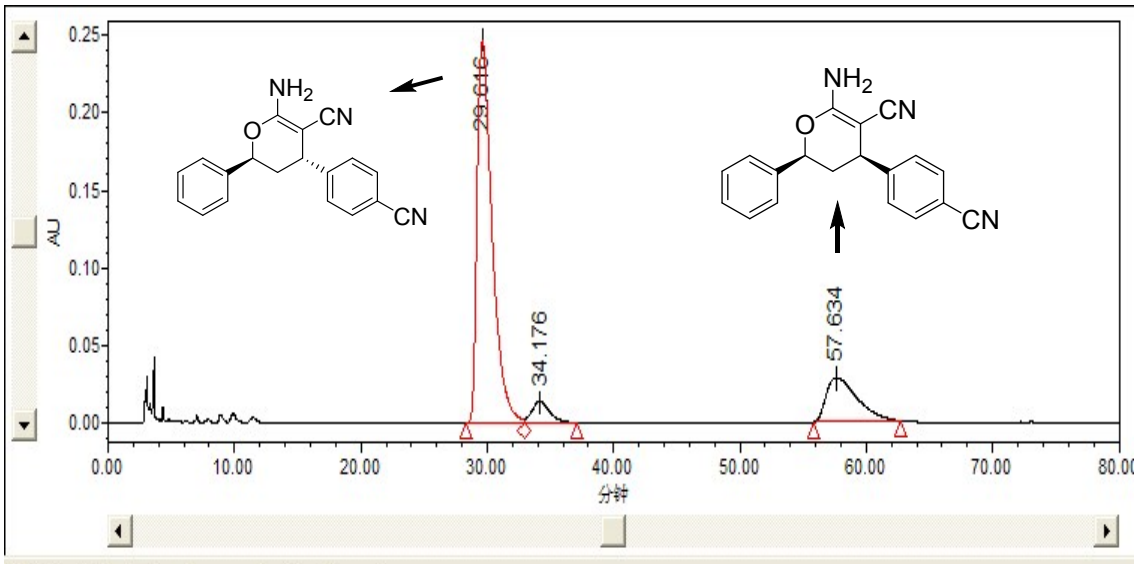
化合物表视图

ID#	峰#	保留时间	面积	面积%	高度	高度%
1	1	19.479	791209	1.6144	14081	2.2998
2	2	22.824	40889184	83.4291	539807	88.1635
3	3	48.175	7327055	14.9499	58348	9.5297
4	4	53.136	3271	0.0067	43	0.0070

4e. (2*S*,4*S*)-6-amino-4-(4-cyanophenyl)-2-phenyl-3,4-dihydro-2*H*- pyran-5-carbonitrile.

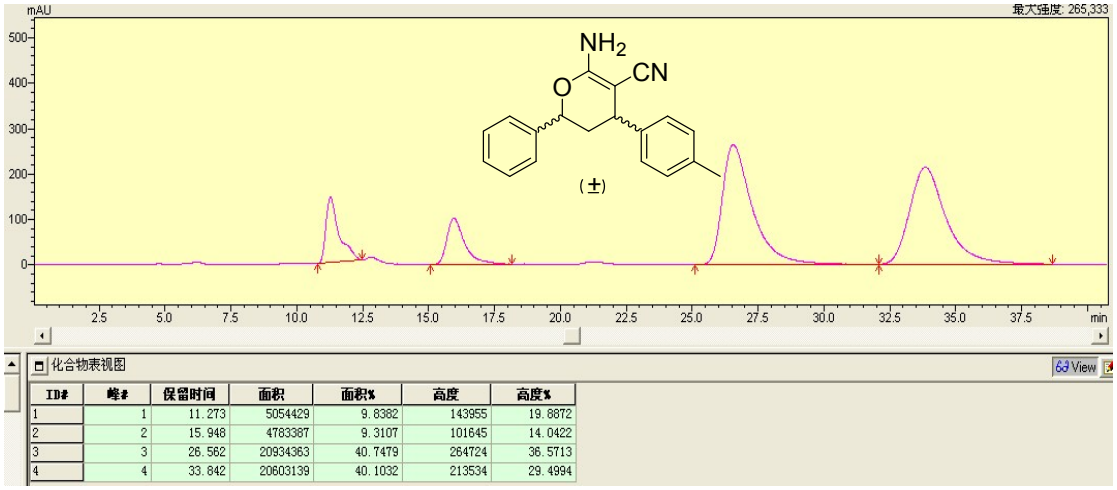


	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	% 高
1	30.313	1446140	8.72	17630	16.61
2	34.191	1433805	8.65	15191	14.31
3	57.372	6234609	37.60	39468	37.18
4	61.555	7464856	45.02	33863	31.90



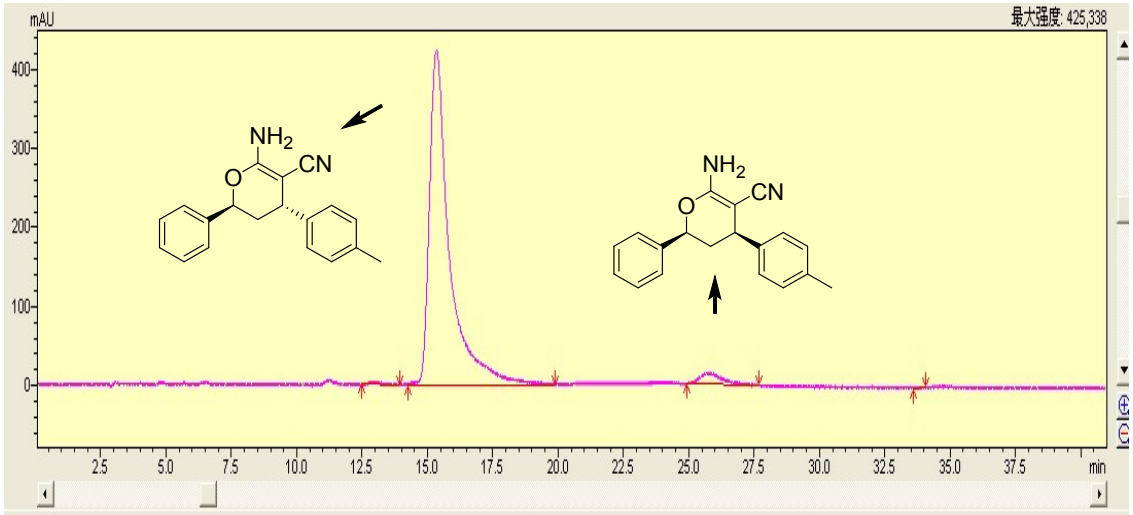
	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	% 高
1	29.616	20441301	76.70	246036	85.34
2	34.176	1346739	5.05	13881	4.81
3	57.634	4863409	18.25	28384	9.85

4f. (2*S*,4*S*)-6-amino-2-phenyl-4-(p-tolyl)-3,4-dihydro-2*H*- pyran-5-carbonitrile.



化合物表视图

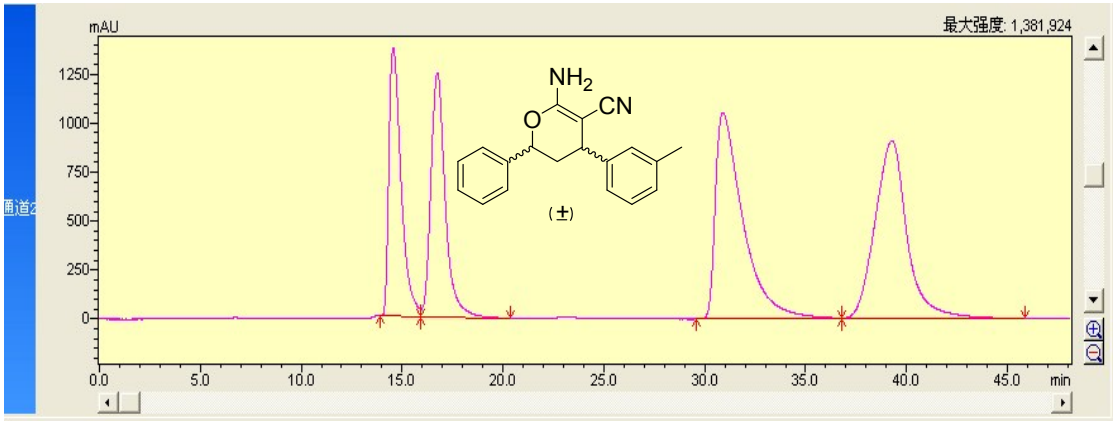
ID#	峰#	保留时间	面积	面积%	高度	高度%
1	1	11.273	5054429	9.8382	143955	19.8872
2	2	15.948	4783387	9.3107	101645	14.0422
3	3	26.562	20934363	40.7479	264724	36.5713
4	4	33.842	20603139	40.1032	213534	29.4994



化合物表视图

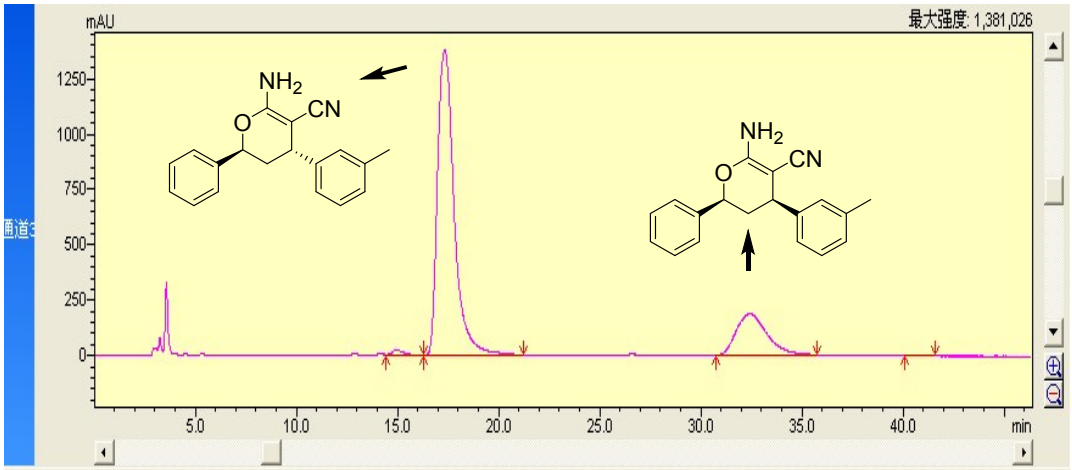
ID#	峰#	保留时间	面积	面积%	高度	高度%
1	1	12.947	78697	0.3354	4163	0.9359
2	2	15.355	22602698	96.3244	424420	95.4121
3	3	25.806	754056	3.2135	14197	3.1915
4	4	33.948	29728	0.1267	2048	0.4605

4g. (2*S*,4*S*)-6-amino-2-phenyl-4-(m-tolyl)-3,4-dihydro-2*H*- pyran-5-carbonitrile.



化合物表视图

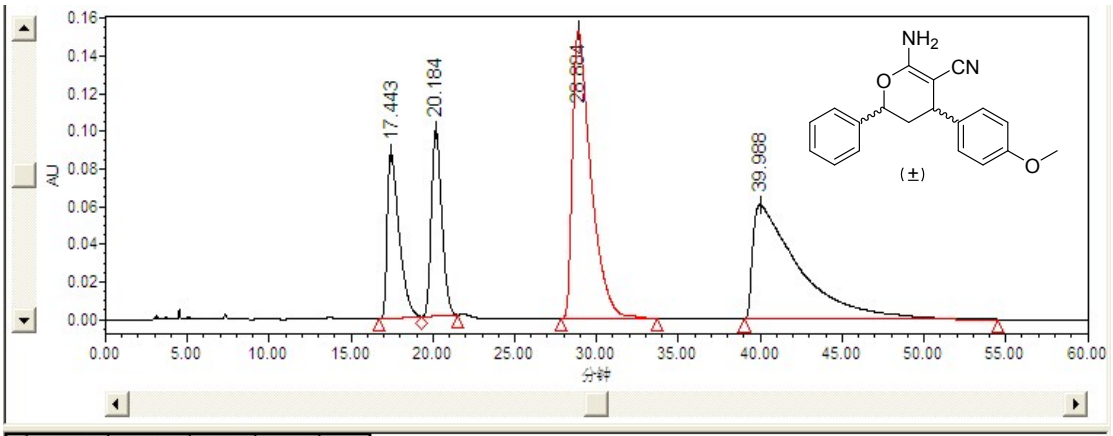
ID#	峰#	保留时间	面积	面积%	高度	高度%
1	1	14.552	57626702	17.9510	1367860	29.8634
2	2	16.744	62041453	19.3262	1248358	27.2545
3	3	30.888	100499245	31.3060	1054122	23.0138
4	4	39.267	100854779	31.4168	910044	19.8683



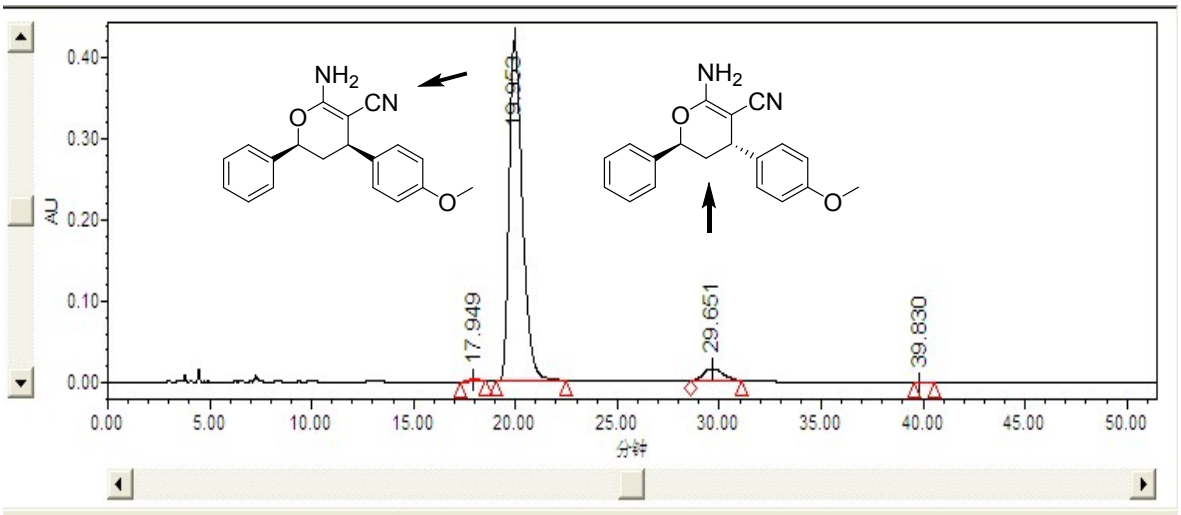
化合物表视图

ID#	峰#	保留时间	面积	面积%	高度	高度%
1	1	14.956	830596	0.8344	22432	1.4107
2	2	17.315	78907870	79.2668	1379340	86.7436
3	3	32.413	19782289	19.8723	187815	11.8113
4	4	40.264	26377	0.0265	548	0.0344

4h. (2*S*,4*S*)-6-amino-4-(4-methoxyphenyl)-2-phenyl-3,4-dihydro-2*H*-pyran-5-carbonitrile.

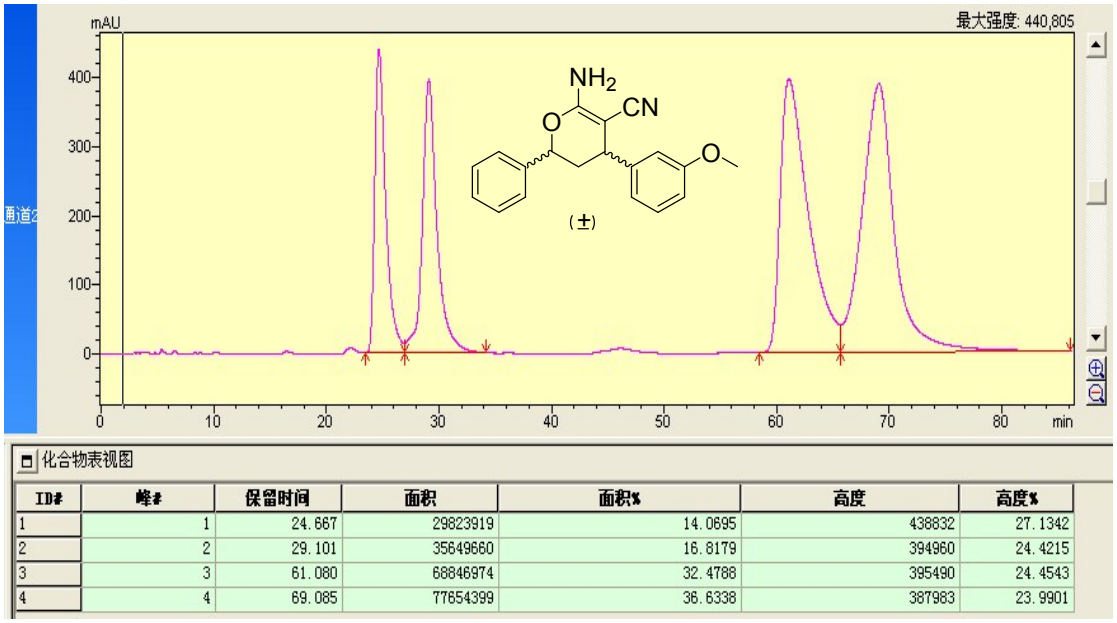


	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	% 高
1	17.443	4416671	13.42	88452	22.05
2	20.184	4364522	13.26	98907	24.65
3	28.884	12106703	36.78	153059	38.15
4	39.988	12025042	36.54	60809	15.16



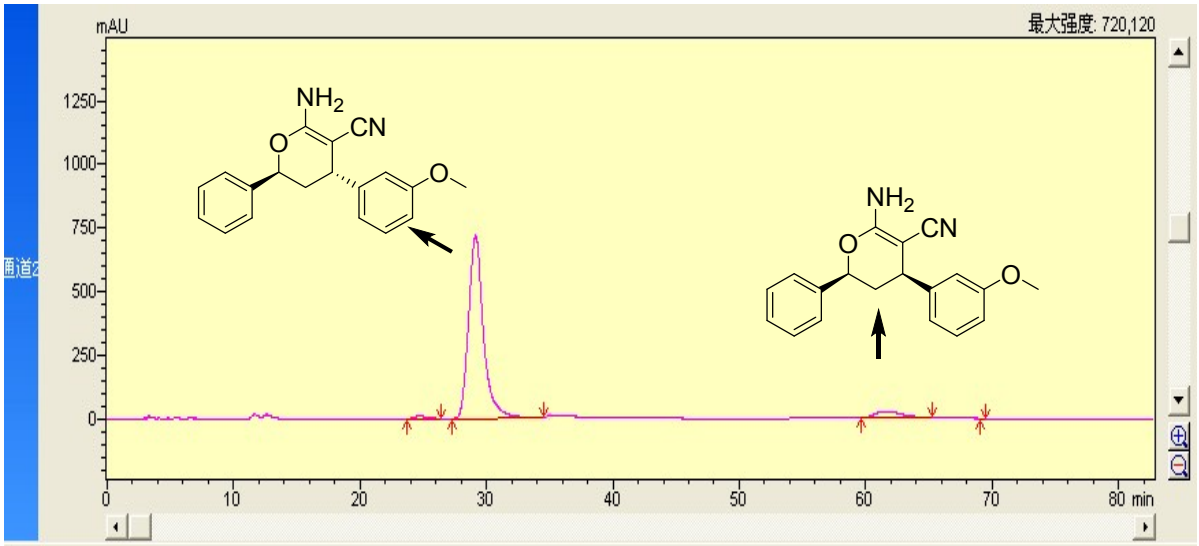
	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	% 高
1	17.949	109859	0.54	2763	0.63
2	19.953	19127457	94.23	420796	95.90
3	29.651	1061743	5.23	15168	3.46
4	39.830	537	0.00	41	0.01

4i. (2*S*,4*S*)-6-amino-4-(3-methoxyphenyl)-2-phenyl-3,4-dihydro-2*H*-pyran-5-carbonitrile.



化合物表视图

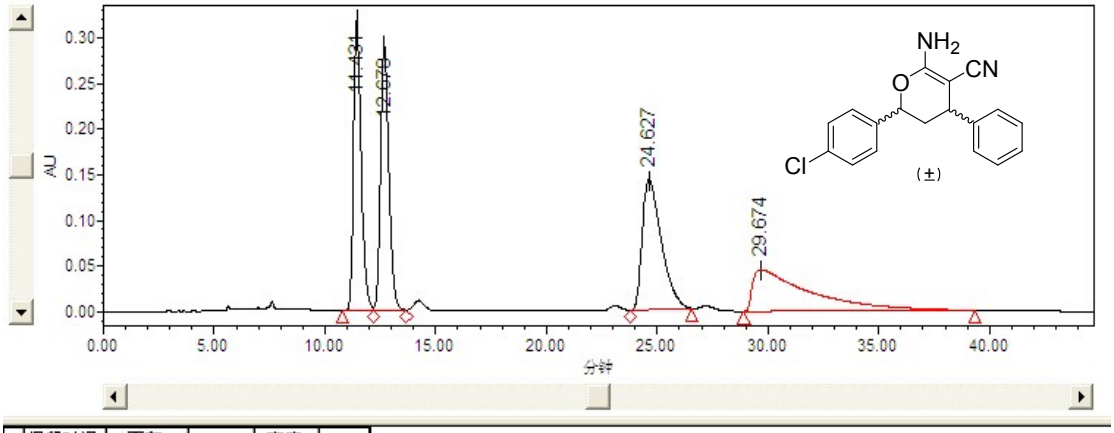
ID#	峰#	保留时间	面积	面积%	高度	高度%
1	1	24.667	29823919	14.0695	438832	27.1342
2	2	29.101	35649660	16.8179	394960	24.4215
3	3	61.080	68846974	32.4788	395490	24.4543
4	4	69.085	77654399	36.6338	387983	23.9901



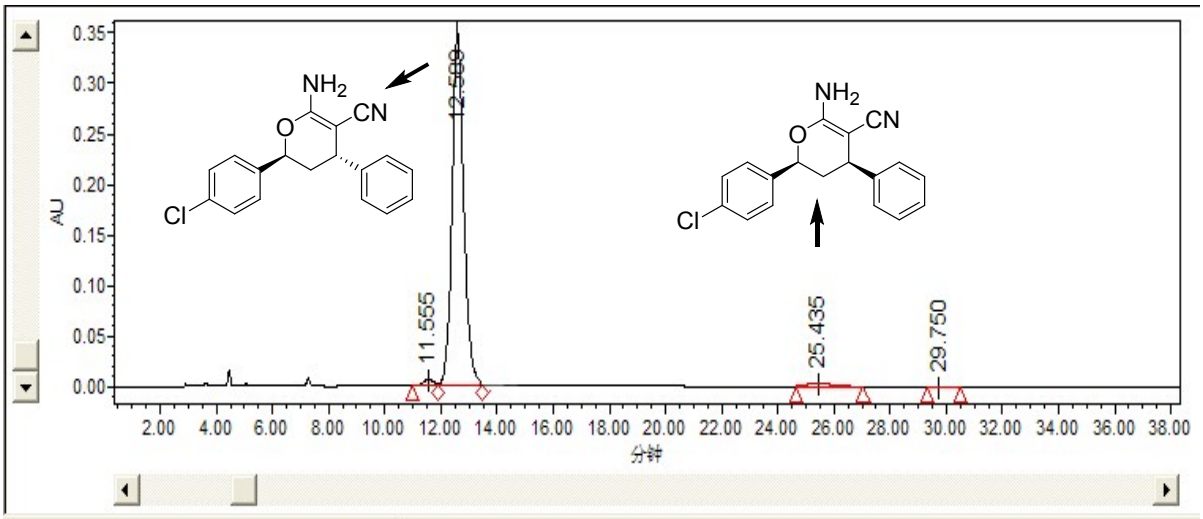
化合物表视图

ID#	峰#	保留时间	面积	面积%	高度	高度%
1	1	24.729	644556	1.0149	10161	1.3462
2	2	29.142	59032199	92.9462	718641	95.2092
3	3	61.639	3834894	6.0380	25955	3.4386
4	4	69.012	562	0.0009	46	0.0061

4j. (2*S*,4*S*)-6-amino-2-(4-chlorophenyl)-4-phenyl-3,4-dihydro-2*H*-pyran-5-carbonitrile.

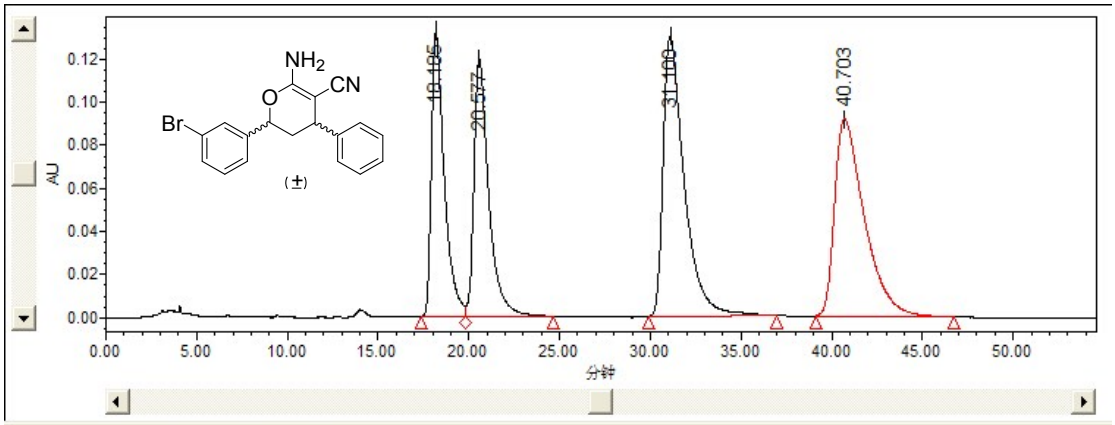


	保留时间 (分钟)	面积 (微伏·秒)	% 面积	高度 (微伏)	% 高
1	11.431	7617250	23.72	317839	39.95
2	12.678	7651127	23.82	290229	36.48
3	24.627	8556932	26.64	141787	17.82
4	29.674	8291673	25.82	45648	5.74

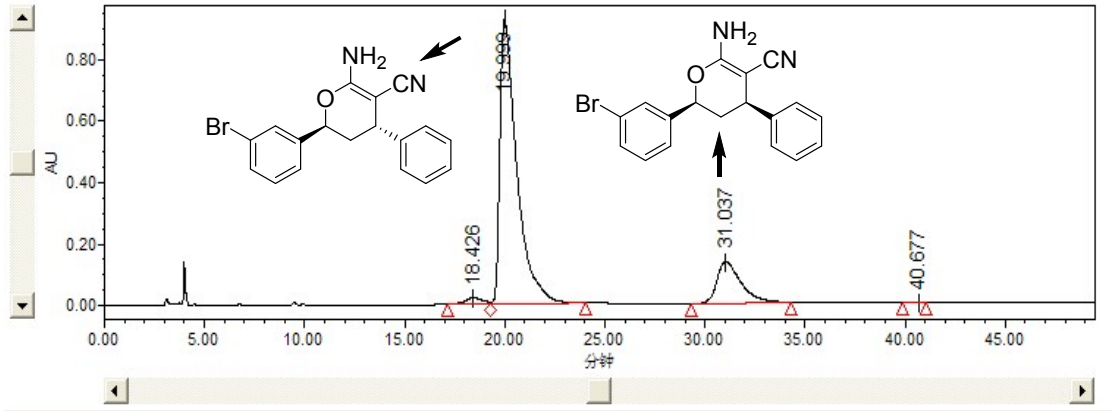


	保留时间 (分钟)	面积 (微伏·秒)	% 面积	高度 (微伏)	% 高
1	11.555	151187	1.44	5766	1.61
2	12.589	10137546	96.57	348852	97.42
3	25.435	207388	1.98	3416	0.95
4	29.750	1439	0.01	41	0.01

4k. (2*S*,4*S*)-6-amino-2-(3-bromophenyl)-4-phenyl-3,4-dihydro-2*H*-pyran-5-carbonitrile.

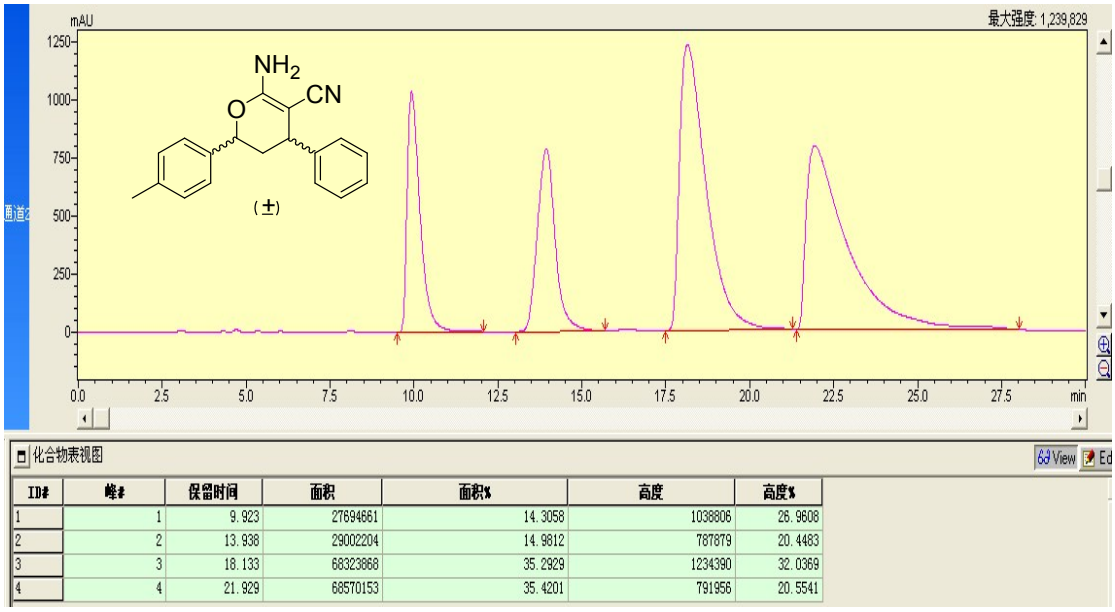


	保留时间 (分钟)	面积 (微伏·秒)	% 面积	高度 (微伏)	% 高
1	18.185	6529398	19.05	132517	27.99
2	20.577	6802703	19.84	119464	25.23
3	31.100	10501692	30.64	129748	27.40
4	40.703	10445402	30.47	91759	19.38



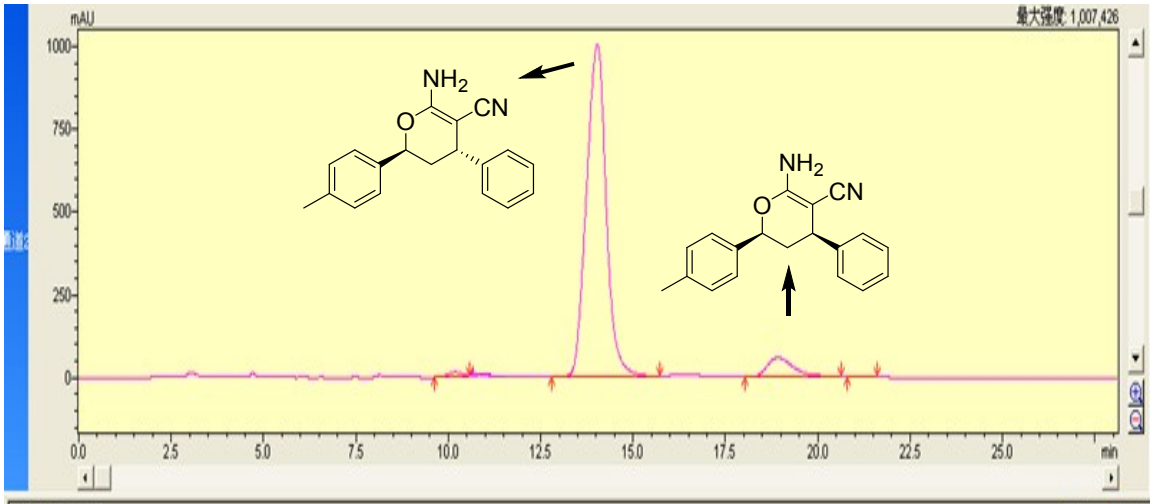
	保留时间 (分钟)	面积 (微伏·秒)	% 面积	高度 (微伏)	% 高
1	18.426	1161083	1.73	19116	1.77
2	19.999	54456503	81.21	924576	85.51
3	31.037	11435958	17.05	137482	12.72
4	40.677	1935	0.00	-76	0.01

4l. (2*S*,4*S*)-6-amino-4-phenyl-2-(p-tolyl)-3,4-dihydro-2*H*-pyran-5-carbonitrile.



化合物表视图

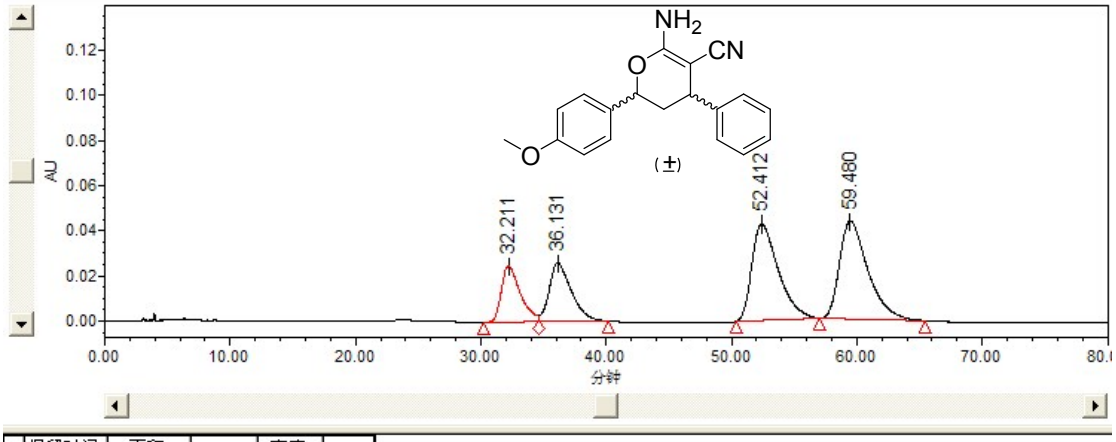
ID#	峰#	保留时间	面积	面积%	高度	高度%
1	1	9.923	27694661	14.3058	1038806	26.9608
2	2	13.938	29002204	14.9812	787879	20.4483
3	3	18.133	68323868	35.2929	1234390	32.0369
4	4	21.929	68570153	35.4201	791956	20.5541



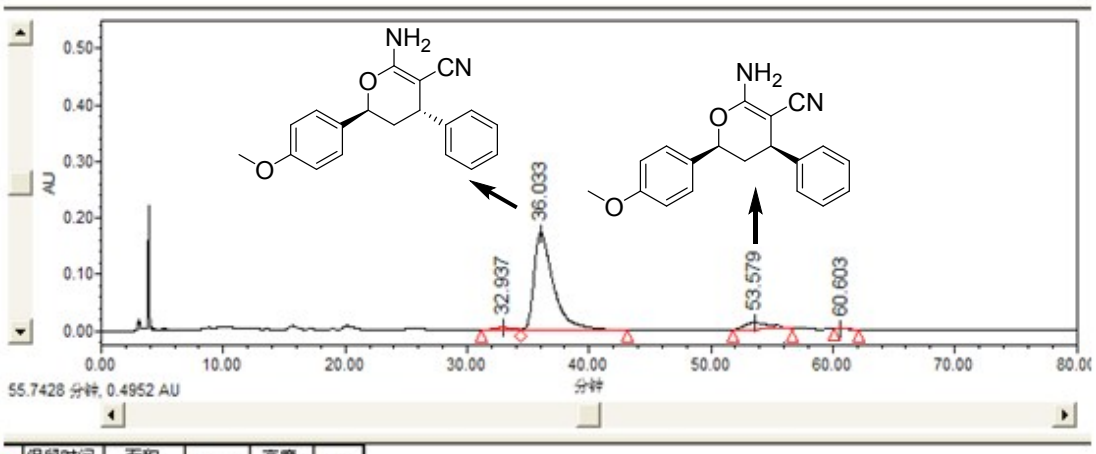
化合物表视图

ID#	峰#	保留时间	面积	面积%	高度	高度%
1	1	10.189	312439	0.7726	13032	1.2106
2	2	14.032	37203764	91.9951	1003951	93.2597
3	3	18.914	2880926	7.1238	58021	5.3898
4	4	21.049	43888	0.1085	1507	0.1400

4m. (2*S*,4*S*)-6-amino-2-(4-methoxyphenyl)-4-phenyl-3,4-dihydro-2*H*-pyran-5-carbonitrile.

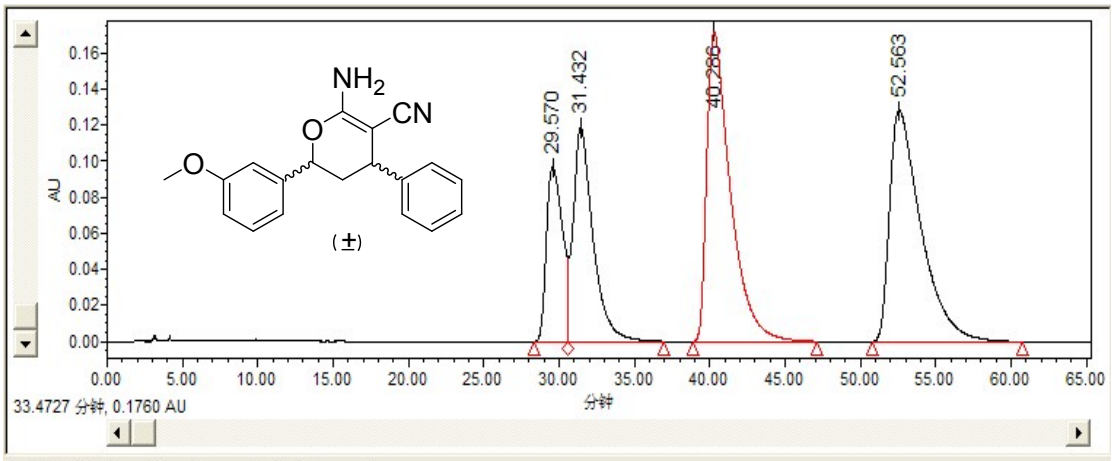


	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	% 高
1	32.211	2601631	13.74	24819	18.09
2	36.131	3193375	16.86	26082	19.01
3	52.412	6284086	33.18	42904	31.27
4	59.480	6858893	36.22	43403	31.63

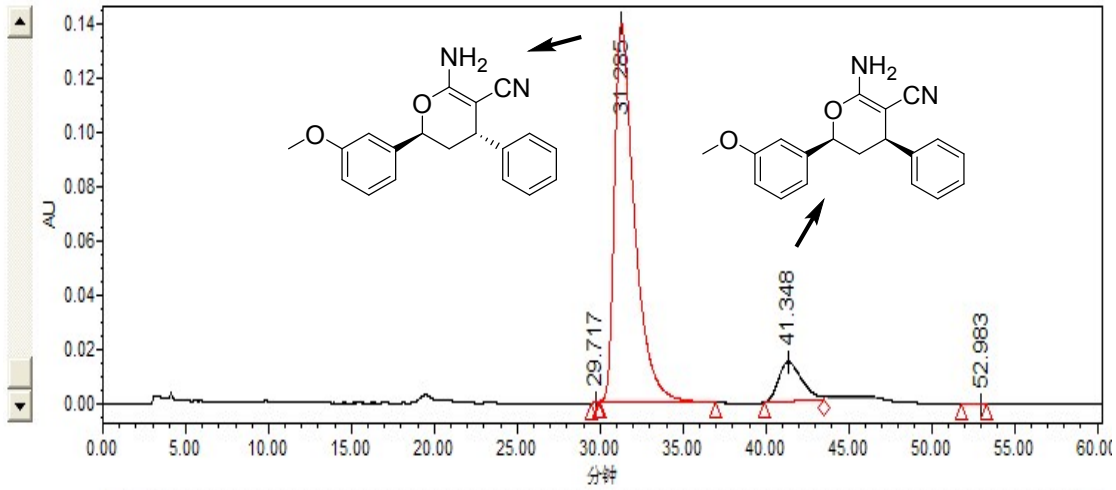


	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	% 高
1	32.937	534253	2.53	4635	2.45
2	36.033	19121016	90.47	172950	91.37
3	53.579	1471847	6.96	11561	6.11
4	60.603	9051	0.04	-149	0.08

4n. (2*S*,4*S*)-6-amino-2-(3-methoxyphenyl)-4-phenyl-3,4-dihydro-2*H*-pyran-5-carbonitrile.

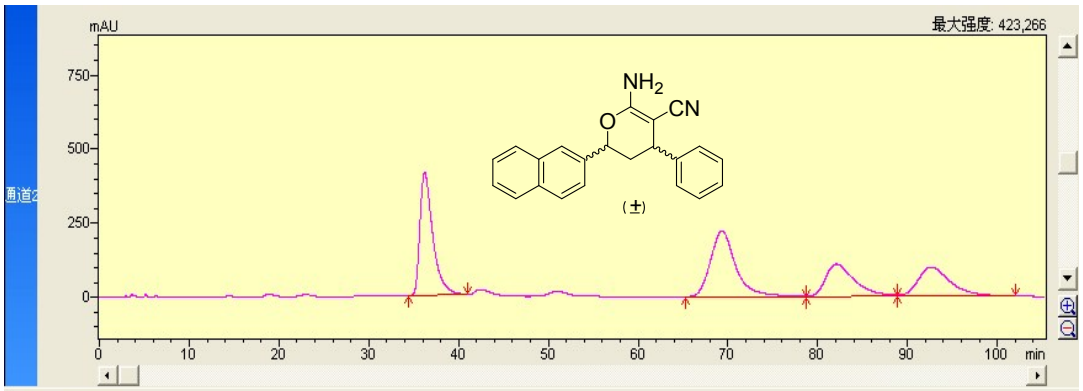


	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	% 高
1	29.570	7279964	13.08	97113	18.78
2	31.432	10865866	19.53	119104	23.03
3	40.286	18788585	33.76	172114	33.28
4	52.563	18712028	33.63	128771	24.90



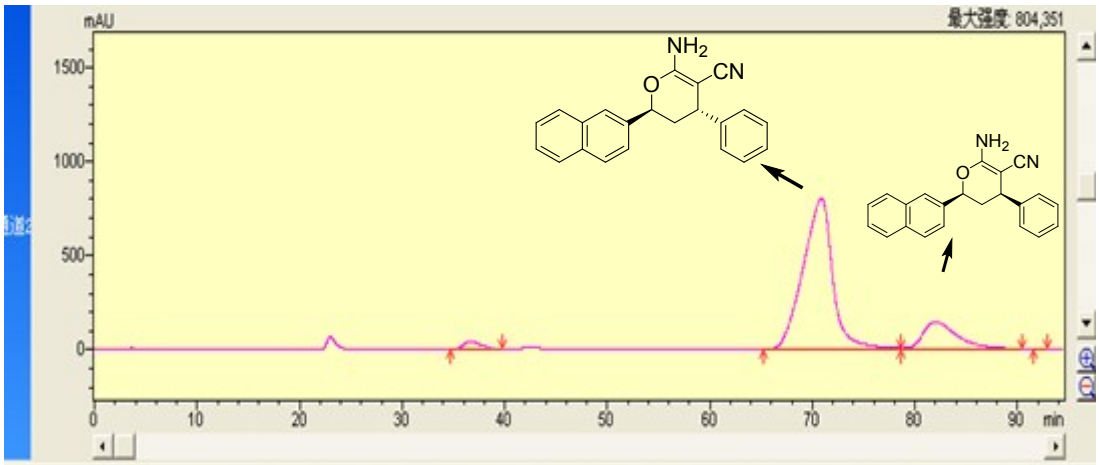
	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	% 高
1	29.717	1481	0.01	-85	0.06
2	31.285	11702800	89.08	139532	90.46
3	41.348	1430597	10.89	14599	9.46
4	52.983	1825	0.01	-39	0.03

4o. (2*S*,4*S*)-6-amino-2-(naphthalen-2-yl)-4-phenyl-3,4-dihydro-2*H*-pyran-5-carbonitrile.



化合物表视图

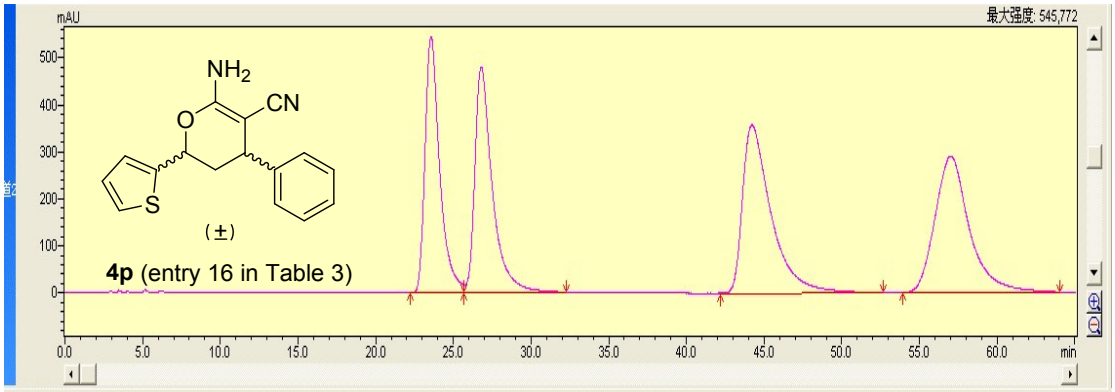
ID#	峰#	保留时间	面积	面积%	高度	高度%
1	1	36.219	41752884	30.9954	416899	49.3020
2	2	69.347	43299987	32.1439	221097	26.1467
3	3	82.042	24790136	18.4030	109223	12.9166
4	4	92.625	24863849	18.4577	98383	11.6347



化合物表视图

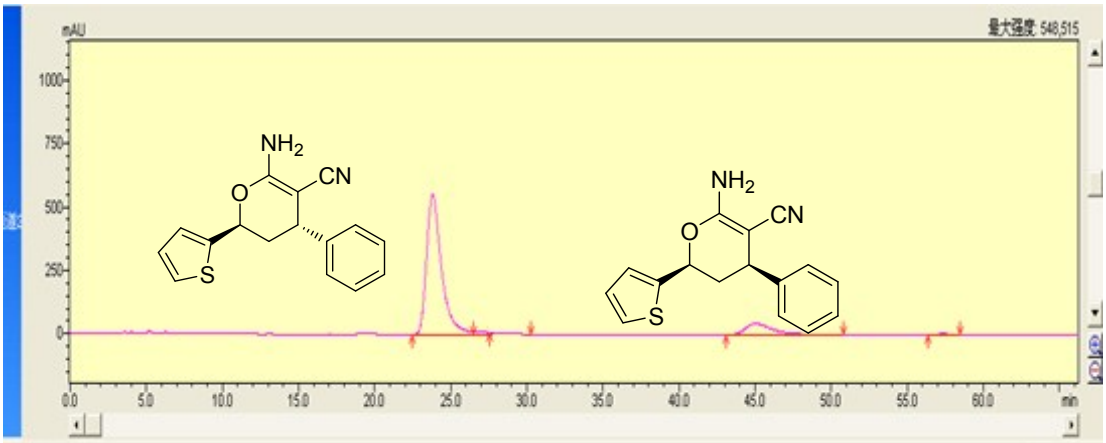
ID#	峰#	保留时间	面积	面积%	高度	高度%
1	1	37.184	2078299	1.0445	29724	3.0274
2	2	70.868	162593499	81.7127	803186	81.8033
3	3	81.996	34047288	17.1108	145311	14.7998
4	4	91.580	262735	0.1320	3628	0.3696

4p: (2*S*,4*S*)-6-amino-4-phenyl-2-(thiophen-2-yl)-3,4-dihydro-*2H*-pyran-5-carbonitrile



化合物表视图

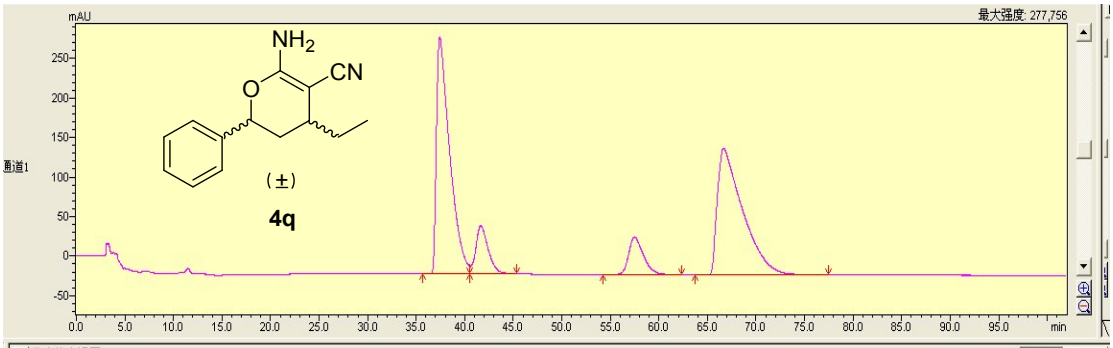
ID#	峰#	保留时间	面积	面积%	高度	高度%
1	1	23.560	35824337	21.9650	545516	32.6188
2	2	26.789	37453397	22.9638	479802	28.6895
3	3	44.204	45434235	27.8571	357147	21.3554
4	4	57.018	44385389	27.2140	289934	17.3384



化合物表视图

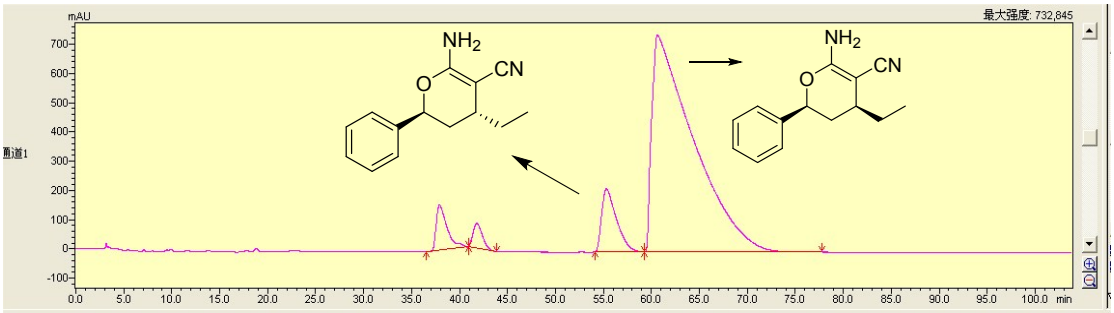
ID#	峰#	保留时间	面积	面积%	高度	高度%
1	1	23.801	37642928	85.6453	551647	90.7327
2	2	26.995	661723	1.5056	10321	1.6975
3	3	45.022	5520116	12.5594	44332	7.2915
4	4	57.339	127360	0.2898	1692	0.2783

4q: (2*S*,4*S*)-6-amino-4-ethyl-2-phenyl-3,4-dihydro-2H-pyran-5-carbonitrile



化合物表视图 View Edit

ID#	名称	保留时间	峰#	面积	面积%	高度	高度%
1	RT37.423	37.423	1	28177190	41.8901	299770	52.8149
2	RT41.650	41.650	2	5292330	7.8679	60401	10.6417
3	RT57.475	57.475	3	4941273	7.3460	47144	8.3060
4	RT66.659	66.659	4	28853704	42.8959	160271	28.2373



化合物表视图 View Edit

ID#	名称	保留时间	峰#	面积	面积%	高度	高度%
1	RT37.905	37.905	1	12015965	4.5344	155852	12.9900
2	RT41.798	41.798	2	5694569	2.1490	84308	7.0269
3	RT55.304	55.304	3	23072836	8.7070	216428	18.0389
4	RT60.609	60.609	4	224209492	84.6096	743200	61.9443