

Supporting Information

Tin Powder-Promoted One-Pot Synthesis of 3-Spiro-Fused or 3,3'-Disubstituted 2-Oxindoles

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Experimental Section

1 General

Flash chromatography was performed using silica gel 60 (230-400 mesh). Analytical thin layer chromatography (TLC) was done using Qingdao silica Gel (silica gel GF254). TLC plates were analyzed by an exposure to ultraviolet (UV) light and/or submersion in phosphomolybdic acid solution or in I₂ vapor. IR spectra were obtained using an Alpha Centauri FT-IR spectrophotometer and absorption frequencies were reported in reciprocal centimetres (cm⁻¹). High-resolution mass spectra were recorded on a Bruker APEX II Fourier transform ion cyclotron resonance mass spectrometer. ¹H NMR and ¹³C NMR spectra were recorded on Varian Mercury 400 plus or Agilent DD2 600 instrument in CDCl₃ or (CD₃)₂SO solution using TMS as an internal standard. The following abbreviations are used for the multiplicities: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, q = quadruplet, m = multiplet, br = broad signal for proton spectra; coupling constants (*J*) are reported in Hertz (Hz). Melting points were determined on a Beijing Taike X-4 apparatus and were uncorrected. The solvents were distilled by standard methods. Reagents were obtained from commercial suppliers and used without further purification unless otherwise noted.

2 General Experimental Procedures for the Synthesis of Compounds 4a–4x.

Isatins **1** (0.5 mmol, 1 equiv.), hydrazides **2** (0.5 mmol, 1.0 equiv.) and TfOH (0.05 mmol, 0.1 equiv.) were put into a dried roundbottom flask (50 mL) fitted with a magnetic bar. THF (4 mL) was then added. The mixture was stirred under reflux, and the reaction process was monitored by TLC. After formation of benzoyl hydrazone, tin powder (1.75 mmol, 3.5 equiv.) and ethyl 2-(bromomethyl)acrylate **3** (1.5 mmol, 3 equiv.) in 2 mL of THF were added to the flask. The resulting mixture was stirred under reflux for 3–13 h. The reaction mixture was cooled to room temperature. The saturated NH₄Cl solution (6 mL) was poured into the mixture and stirred for 10 min. The mixture was extracted with EtOAc (3 × 10 mL). The combined organic phases were dried (MgSO₄) and concentrated. Purification of the residue by silica gel column chromatography using hexane and EtOAc (1:1) as the eluent furnished the pure products compounds **4**.

N-(4'-Methylene-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)benzamide (4a). White solid, 143 mg, yield 86%. m.p. 251–253 °C; IR (KBr) ν 3406, 2986, 1656, 1404, 1308, 1017 cm⁻¹; ¹H NMR (600 MHz, (CD₃)₂SO) δ 10.67 (s, 1H), 10.62 (s, 1H), 7.66 (d, *J* = 7.8 Hz, 2H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.39–7.38 (m, 3H), 7.20 (t, *J* = 7.8 Hz, 1H), 6.94 (t, *J* = 7.8 Hz, 1H), 6.81 (d, *J* = 7.2 Hz, 1H), 6.00 (s, 1H), 5.56 (s, 1H), 3.16 (d, *J* = 17.4 Hz, 1H), 3.07 (d, *J* = 16.8 Hz, 1H); ¹³C NMR (150 MHz, (CD₃)₂SO) δ 176.2, 165.6, 165.1, 142.6, 136.0, 132.0, 131.7, 130.1, 128.3, 127.6, 126.2, 125.8, 121.8, 116.9, 109.8, 66.6, 35.5; HRMS (ESI-TOF) *m/z* calcd for C₁₉H₁₅N₃NaO₃ [M+Na⁺] 356.1006, Found: 356.0999.

2-Methyl-N-(4'-methylene-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)benzamide (4b). White solid, 101 mg, White solid, yield 58%. m.p. 229–231 °C; IR (KBr) ν 3406, 2236, 1719, 1002, 753 cm⁻¹; ¹H NMR (600 MHz, (CD₃)₂SO) δ 10.62 (s, 1H), 10.46 (s, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.28 (t, *J* = 7.8 Hz, 2H), 7.14 (t, *J* = 7.2 Hz, 2H), 7.00–6.98 (m, 2H), 6.85 (d, *J* = 7.8 Hz, 1H), 6.00 (s, 1H), 5.56 (s, 1H), 3.14 (d, *J* = 16.8 Hz, 1H), 3.08 (d, *J* = 17.4 Hz, 1H), 1.92 (s, 3H); ¹³C NMR (150 MHz, (CD₃)₂SO) δ 176.2, 167.7, 164.9, 142.9, 136.1, 135.5, 134.2, 130.3, 130.2, 129.9, 127.2, 126.1, 126.0, 125.3, 121.8, 116.9, 109.8, 66.4, 35.1, 18.5; HRMS (ESI-TOF) *m/z* calcd for C₂₀H₁₇N₃NaO₃ [M+Na⁺] 370.1162, Found: 370.1154.

3-Methyl-N-(4'-methylene-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)benzamide (4c). White solid, 121 mg, yield 70%. m.p. 256–258 °C; IR (KBr) ν 3406, 2986, 1656, 1404, 1308, 1017 cm⁻¹; ¹H NMR (600 MHz, (CD₃)₂SO) δ 10.62 (s, 1H), 10.60 (s, 1H), 7.52 (s, 1H), 7.46 (d, *J* = 7.2 Hz, 1H), 7.39 (d,

J = 7.2 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.26 (t, *J* = 7.2 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 6.94 (t, *J* = 7.2 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.00 (s, 1H), 5.55 (s, 1H), 3.15 (d, *J* = 16.8 Hz, 1H), 3.06 (d, *J* = 17.4 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (150 MHz, $(\text{CD}_3)_2\text{SO}$) δ 176.2, 165.5, 165.0, 142.6, 137.6, 136.0, 132.6, 131.6, 130.1, 128.2, 128.1, 126.2, 125.8, 124.8, 121.8, 116.8, 109.7, 66.6, 35.6, 20.8; HRMS (ESI-TOF) m/z calcd for $\text{C}_{20}\text{H}_{17}\text{N}_3\text{NaO}_3$ [M+Na $^+$] 370.1162, Found: 370.1155.

4-Methyl-N-(4'-methylene-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)benzamide (4d). White solid, 137 mg, yield 79%. m.p. 248–250 °C; IR (KBr) v 3412, 2236, 1653, 1020, 753 cm $^{-1}$; ^1H NMR (600 MHz, $(\text{CD}_3)_2\text{SO}$) δ 10.61 (s, 1H), 10.58 (s, 1H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 7.2 Hz, 1H), 7.21–7.18 (m, 3H), 6.93 (t, *J* = 7.8 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.00 (s, 1H), 5.55 (s, 1H), 3.15 (d, *J* = 16.8 Hz, 1H), 3.06 (d, *J* = 16.8 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (150 MHz, $(\text{CD}_3)_2\text{SO}$) δ 176.2, 165.4, 165.1, 142.6, 142.1, 136.0, 130.1, 128.8, 128.8, 127.7, 126.2, 125.8, 121.8, 116.8, 109.7, 66.6, 35.5, 21.0; HRMS (ESI-TOF) m/z calcd for $\text{C}_{20}\text{H}_{17}\text{N}_3\text{NaO}_3$ [M+Na $^+$] 370.1162, Found: 370.1154.

4-Methoxy-N-(4'-methylene-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)benzamide (4e). White solid 142 mg, yield 78%. m.p. 258–258 °C; IR (KBr) v 3412, 2236, 1719, 1470, 1248, 1002, 753 cm $^{-1}$; ^1H NMR (600 MHz, $(\text{CD}_3)_2\text{SO}$) δ 10.61 (s, 1H), 10.49 (s, 1H), 7.68 (s, 1H), 7.66 (s, 1H), 7.38 (d, *J* = 7.2 Hz, 1H), 7.20 (t, *J* = 7.8 Hz, 1H), 6.95–6.91 (m, 3H), 6.80 (d, *J* = 7.8 Hz, 1H), 5.99 (s, 1H), 5.55 (s, 1H), 3.76 (s, 3H), 3.15 (d, *J* = 17.4 Hz, 1H), 3.05 (d, *J* = 17.4 Hz, 1H); ^{13}C NMR (150 MHz, $(\text{CD}_3)_2\text{SO}$) δ 176.2, 165.2, 164.9, 162.1, 142.6, 136.1, 130.0, 129.6, 126.3, 125.8, 123.8, 121.8, 116.7, 113.5, 109.7, 66.6, 55.4, 35.6; HRMS (ESI-TOF) m/z calcd for $\text{C}_{20}\text{H}_{17}\text{N}_3\text{NaO}_4$ [M+Na $^+$] 386.1111, Found: 386.1105.

2-Chloro-N-(4'-methylene-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)benzamide (4h). White solid, 152 mg, yield 83%. m.p. 148–150 °C; IR (KBr) v 3406, 2158, 1656, 999, 753 cm $^{-1}$; ^1H NMR (600 MHz, $(\text{CD}_3)_2\text{SO}$) δ 10.67 (s, 1H), 10.63 (s, 1H), 7.41–7.36 (m, 3H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.27 (t, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 7.2 Hz, 1H), 6.98 (t, *J* = 7.2 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.01 (s, 1H), 5.57 (s, 1H), 3.14 (d, *J* = 16.8 Hz, 1H), 3.08 (d, *J* = 17.4 Hz, 1H); ^{13}C NMR (150 MHz, $(\text{CD}_3)_2\text{SO}$) δ 176.1, 165.0, 164.9, 142.4, 135.9, 134.0, 131.4, 130.1, 130.1, 129.5, 129.0, 126.8, 126.0, 125.9, 121.9, 117.0, 109.7, 66.4, 35.1; HRMS (ESI-TOF) m/z calcd for $\text{C}_{19}\text{H}_{15}\text{ClN}_3\text{O}_3$ [M+H $^+$] 368.0796, Found: 368.0799.

3-Chloro-N-(4'-methylene-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)benzamide (4i). White solid, 156 mg, yield 85%. m.p. 271–273 °C; IR (KBr) v 3406, 2992, 2122, 1656, 1404, 1308, 1017 cm $^{-1}$; ^1H NMR (600 MHz, $(\text{CD}_3)_2\text{SO}$) δ 10.80 (s, 1H), 10.65 (s, 1H), 7.70 (s, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 7.2 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 6.95 (t, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.01 (s, 1H), 5.57 (s, 1H), 3.16 (d, *J* = 16.8 Hz, 1H), 3.07 (d, *J* = 17.4 Hz, 1H); ^{13}C NMR (150 MHz, $(\text{CD}_3)_2\text{SO}$) δ 176.1, 165.0, 164.2, 142.6, 135.8, 133.5, 133.2, 131.9, 130.4, 130.2, 127.3, 126.4, 126.1, 125.7, 121.8, 117.1, 109.8, 66.5, 35.5; HRMS (ESI-TOF) m/z calcd for $\text{C}_{19}\text{H}_{14}\text{ClN}_3\text{NaO}_3$ [M+Na $^+$] 390.0616, Found: 390.0607.

4-Chloro-N-(4'-methylene-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)benzamide (4j). White solid, 167 mg, yield 91%. m.p. 285–287 °C; IR (KBr) v 3406, 2992, 1656, 1404, 1308, 1017 cm $^{-1}$; ^1H NMR (600 MHz, $(\text{CD}_3)_2\text{SO}$) δ 10.76 (s, 1H), 10.63 (s, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 6.94 (t, *J* = 7.8 Hz, 1H), 6.81 (d, *J* = 7.2 Hz, 1H), 6.00 (s, 1H), 5.56 (s, 1H), 3.16 (d, *J* = 16.8 Hz, 1H), 3.07 (d, *J* = 17.4 Hz, 1H); ^{13}C NMR (150 MHz, $(\text{CD}_3)_2\text{SO}$) δ 176.1, 165.0, 164.6, 142.6, 136.9, 135.9, 130.3, 130.1, 129.5, 128.5, 126.1, 125.7, 121.8, 117.0, 109.8, 66.6, 35.5; HRMS (ESI-TOF) m/z calcd for $\text{C}_{19}\text{H}_{14}\text{ClN}_3\text{NaO}_3$ [M+Na $^+$] 390.0616, Found: 386.0608.

4-Bromo-N-(4'-methylene-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)benzamide (4k). White solid, 146 mg, yield 71%. m.p. 269–271 °C; IR (KBr) v 3117, 1713, 1407, 1194, 745, 654 cm $^{-1}$; ^1H NMR (600 MHz, $(\text{CD}_3)_2\text{SO}$) δ 10.77 (s, 1H), 10.63 (s, 1H), 7.61 (dd, *J* = 13.2, *J* = 9.0 Hz, 4H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.20 (t, *J* = 7.8 Hz, 1H), 6.94 (t, *J* = 7.8 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.00 (s, 1H), 5.56 (s,

1H), 3.16 (d, J = 17.4 Hz, 1H), 3.07 (d, J = 17.4 Hz, 1H); ^{13}C NMR (150 MHz, $(\text{CD}_3)_2\text{SO}$) δ 176.1, 165.0, 164.7, 142.6, 135.9, 131.4, 130.7, 130.1, 129.7, 126.1, 125.9, 125.7, 121.8, 117.0, 109.7, 66.6, 35.5; HRMS (ESI-TOF) m/z calcd for $\text{C}_{19}\text{H}_{15}\text{BrN}_3\text{O}_3$ [M+H $^+$] 412.0291, Found: 412.0281.

4-Fluoro-N-(4'-methylene-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)benzamide (4l). White solid, 144 mg, yield 82%. m.p. 268–270 °C; IR (KBr) ν 3406, 2236, 1716, 1275, 1020, 753 cm^{-1} ; ^1H NMR (600 MHz, $(\text{CD}_3)_2\text{SO}$) δ 10.70 (s, 1H), 10.63 (s, 1H), 7.75 (s, 2H), 7.38 (d, J = 7.2 Hz, 1H), 7.25–7.20 (m, 3H), 6.94 (t, J = 7.2 Hz, 1H), 6.81 (d, J = 7.2 Hz, 1H), 6.00 (s, 1H), 5.57 (s, 1H), 3.16 (d, J = 17.4 Hz, 1H), 3.07 (d, J = 16.8 Hz, 1H); ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{SO}$) δ 176.2, 165.1, 164.5, 164.3 (d, J_{C-F} = 249.0 Hz), 142.6, 135.9, 130.4 (d, J_{C-F} = 10.0 Hz), 130.1, 128.1, 126.2, 125.7, 121.8, 117.0, 115.4 (d, J_{C-F} = 22.0 Hz), 109.8, 66.6, 35.5; HRMS (ESI-TOF) m/z calcd for $\text{C}_{19}\text{H}_{14}\text{FN}_3\text{NaO}_3$ [M+Na $^+$] 374.0911, Found: 374.0901.

Methyl 4-((4'-methylene-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)carbamoyl)benzoate (4n). White solid, 170 mg, yield 87%. m.p. 270–272 °C; IR (KBr) ν 3273, 1724, 1618, 1470, 1281, 1110, 722, 613 cm^{-1} ; ^1H NMR (600 MHz, $(\text{CD}_3)_2\text{SO}$) δ 10.90 (s, 1H), 10.65 (s, 1H), 7.96 (d, J = 8.4 Hz, 2H), 7.79–7.77 (m, 2H), 7.39 (s, 1H), 7.21 (t, J = 7.3 Hz, 1H), 6.95 (t, J = 7.2 Hz, 1H), 6.82 (d, J = 7.2 Hz, 1H), 6.02 (s, 1H), 5.57 (s, 1H), 3.85 (d, J = 3.0 Hz, 3H), 3.17 (d, J = 17.4 Hz, 1H), 3.08 (d, J = 17.4 Hz, 1H); ^{13}C NMR (150 MHz, $(\text{CD}_3)_2\text{SO}$) δ 176.1, 165.5, 165.0, 164.9, 142.6, 135.8, 135.6, 132.5, 130.2, 129.1, 128.0, 126.1, 125.7, 121.8, 117.1, 109.8, 66.6, 52.4, 35.5; HRMS (ESI-TOF) m/z calcd for $\text{C}_{21}\text{H}_{17}\text{N}_3\text{NaO}_5$ [M+Na $^+$] 414.1060, Found: 414.1061.

N-(4'-Methylene-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)-4-(trifluoromethyl)benzamide (4o). White solid, 166 mg, yield 83%. m.p. 259–261 °C; IR (KBr) ν 3273, 1724, 1618, 1281, 1110, 722, 613 cm^{-1} ; ^1H NMR (600 MHz, $(\text{CD}_3)_2\text{SO}$) δ 10.96 (s, 1H), 10.67 (s, 1H), 7.85 (d, J = 8.4 Hz, 2H), 7.80 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 7.2 Hz, 1H), 7.22 (t, J = 7.2 Hz, 1H), 6.96 (t, J = 7.2 Hz, 1H), 6.84 (d, J = 7.8 Hz, 1H), 6.03 (s, 1H), 5.59 (s, 1H), 3.19 (d, J = 16.8 Hz, 1H), 3.10 (d, J = 16.8 Hz, 1H); ^{13}C NMR (150 MHz, $(\text{CD}_3)_2\text{SO}$) δ 176.1, 165.0, 164.6, 142.6, 135.8, 135.4, 131.8 (q, J_{C-F} = 31.5 Hz), 130.2, 128.5, 126.0, 125.7, 125.4, 123.7 (q, J_{C-F} = 271.5 Hz), 121.8, 117.1, 109.8, 66.6, 35.5; HRMS (ESI-TOF) m/z calcd for $\text{C}_{20}\text{H}_{14}\text{F}_3\text{N}_3\text{NaO}_3$ [M+Na $^+$] 424.0879, Found: 424.0869.

4-Chloro-N-(5-methyl-4'-methylene-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)benzamide (4q). White solid, 162 mg, yield 85%. m.p. 233–235 °C; IR (KBr) ν 3406, 2986, 2902, 2194, 1653, 1404, 1305, 1017 cm^{-1} ; ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$) δ 10.74 (s, 1H), 10.53 (s, 1H), 7.68 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 7.20 (s, 1H), 7.01 (d, J = 7.6 Hz, 1H), 6.70 (d, J = 8.8 Hz, 1H), 6.00 (s, 1H), 5.56 (s, 1H), 3.14 (d, J = 16.4 Hz, 1H), 3.04 (d, J = 17.2 Hz, 1H), 2.19 (s, 3H); ^{13}C NMR (150 MHz, $(\text{CD}_3)_2\text{SO}$) δ 176.1, 165.0, 164.6, 140.1, 136.9, 135.9, 130.6, 130.4, 130.3, 129.6, 128.5, 126.3, 126.2, 117.0, 109.5, 66.6, 35.5, 20.7; HRMS (ESI-TOF) m/z calcd for $\text{C}_{20}\text{H}_{16}\text{ClN}_3\text{NaO}_3$ [M+Na $^+$] 404.0772, Found: 404.0762.

4-Chloro-N-(5-chloro-4'-methylene-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)benzamide (4r). White solid, 140 mg, yield 70%. m.p. 240–242 °C; IR (KBr) ν 3436, 2248, 1737, 1656, 1293, 1026, 825, 762, 624 cm^{-1} ; ^1H NMR (600 MHz, $(\text{CD}_3)_2\text{SO}$) δ 10.83 (s, 1H), 10.78 (s, 1H), 7.70 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H), 7.42 (s, 1H), 7.27 (d, J = 8.4 Hz, 1H), 6.83 (d, J = 8.4 Hz, 1H), 6.02 (s, 1H), 5.58 (s, 1H), 3.17 (s, 2H); ^{13}C NMR (150 MHz, $(\text{CD}_3)_2\text{SO}$) δ 175.8, 165.0, 164.8, 141.5, 137.1, 135.5, 130.2, 130.0, 129.5, 128.5, 128.1, 126.0, 125.7, 117.3, 111.2, 66.7, 35.1; HRMS (ESI-TOF) m/z calcd for $\text{C}_{19}\text{H}_{13}\text{Cl}_2\text{N}_3\text{NaO}_3$ [M+Na $^+$] 424.0226, Found: 424.0217.

N-(1-Benzyl-4'-methylene-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)-4-chlorobenzamide (4s). White solid, 153 mg, yield 67%. m.p. 271–273 °C; IR (KBr) ν 3256, 2989, 1690, 1615, 1489, 1364, 1272, 1097, 752 cm^{-1} ; ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$) δ 10.87 (s, 1H), 7.67 (d, J = 8.4 Hz, 2H), 7.51–7.40 (m, 5H), 7.30–7.28 (m, 3H), 7.20 (t, J = 7.6 Hz, 1H), 6.99 (t, J = 7.6 Hz, 1H), 6.82 (d, J = 7.6 Hz, 1H), 6.06 (s, 1H), 5.63 (s, 1H), 5.08 (d, J = 16.0 Hz, 1H), 4.77 (d, J = 16.0 Hz, 1H), 3.25 (d, J = 17.2 Hz, 1H), 3.17 (d,

$J = 17.2$ Hz, 1H); ^{13}C NMR (150 MHz, $(\text{CD}_3)_2\text{SO}$) δ 174.6, 165.1, 164.6, 142.9, 137.1, 135.8, 135.6, 130.2, 130.1, 129.6, 128.6, 128.4, 127.5, 127.3, 125.7, 122.6, 117.5, 109.3, 66.3, 43.0, 35.2; HRMS (ESI-TOF) m/z calcd for $\text{C}_{26}\text{H}_{20}\text{ClN}_3\text{NaO}_3$ [M+Na $^+$] 480.1085, Found: 480.1091.

N-(1-Butyl-4'-methylene-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)-4-chlorobenzamide (4t). White solid, 144 mg, yield 68%. 262–264 °C; IR (KBr) v 3406, 2986, 1656, 1404, 1020 cm^{-1} ; ^1H NMR (600 MHz, $(\text{CD}_3)_2\text{SO}$) δ 10.76 (s, 1H), 7.66 (d, $J = 8.4$ Hz, 2H), 7.47 (d, $J = 8.4$ Hz, 2H), 7.43 (d, $J = 7.2$ Hz, 1H), 7.30 (t, $J = 7.2$ Hz, 1H), 7.05 (d, $J = 7.8$ Hz, 1H), 7.02 (t, $J = 7.8$ Hz, 1H), 6.03 (s, 1H), 5.59 (s, 1H), 3.75–3.70 (m, 1H) 3.67–3.62 (m, 1H), 3.16–3.09 (m, 2H), 1.62–1.57 (m, 2H), 1.32–1.26 (m, 2H), 0.87 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, $(\text{CD}_3)_2\text{SO}$) δ 174.3, 165.0, 164.5, 143.4, 137.0, 135.7, 130.3, 130.2, 129.5, 128.4, 125.7, 125.6, 122.3, 117.2, 108.9, 66.1, 39.3, 35.3, 28.9, 19.5, 13.7; HRMS (ESI-TOF) m/z calcd for $\text{C}_{23}\text{H}_{22}\text{ClN}_3\text{NaO}_3$ [M+Na $^+$] 446.1242, Found: 446.1248.

N-(4'-Methylene-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)furan-2-carboxamide (4u). White solid, 99 mg, yield 61%. m.p. 282–284 °C; IR (KBr) v 3430, 2986, 2902, 1656, 1404, 1308, 1020 cm^{-1} ; ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$) δ 10.63 (s, 1H), 10.62 (s, 1H), 7.82 (s, 1H), 7.38 (d, $J = 7.2$ Hz, 1H), 7.24–7.21 (m, 2H), 6.96 (t, $J = 7.2$ Hz, 1H), 6.82 (d, $J = 7.6$ Hz, 1H), 6.57 (t, $J = 1.6$ Hz, 1H), 6.00 (s, 1H), 5.56 (s, 1H), 3.15 (d, $J = 17.2$ Hz, 1H), 3.04 (d, $J = 17.2$ Hz, 1H); ^{13}C NMR (150 MHz, $(\text{CD}_3)_2\text{SO}$) δ 176.1, 165.2, 156.8, 146.1, 145.1, 142.5, 135.8, 130.2, 126.3, 125.8, 121.9, 117.1, 115.4, 111.8, 109.8, 66.6, 35.6; HRMS (ESI-TOF) m/z calcd for $\text{C}_{17}\text{H}_{13}\text{N}_3\text{NaO}_4$ [M+Na $^+$] 346.0798, Found: 346.0789.

N-(4'-Methylene-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)-2-naphthamide (4v). White solid, 142 mg, yield 74%. m.p. 137–139 °C; IR (KBr) v 3200, 1721, 1657, 1619, 1457, 1286, 1192, 572, 473 cm^{-1} ; ^1H NMR (600 MHz, $(\text{CD}_3)_2\text{SO}$) δ 10.85 (s, 1H), 10.68 (s, 1H), 8.34 (s, 1H), 7.97–7.92 (m, 3H), 7.74 (d, $J = 9.0$ Hz, 1H), 7.61 (t, $J = 7.8$ Hz, 1H), 7.57 (t, $J = 7.2$ Hz, 1H), 7.44 (d, $J = 7.8$ Hz, 1H), 7.21 (t, $J = 7.8$ Hz, 1H), 6.96 (t, $J = 7.8$ Hz, 1H), 6.82 (d, $J = 7.8$ Hz, 1H), 6.03 (s, 1H), 5.59 (s, 1H), 3.19 (d, $J = 16.8$ Hz, 1H), 3.10 (d, $J = 17.4$ Hz, 1H); ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{SO}$) δ 176.2, 165.6, 165.1, 142.6, 136.0, 134.4, 131.8, 130.1, 128.9, 128.3, 128.0, 127.9, 127.60, 126.9, 126.2, 125.8, 124.1, 121.8, 116.9, 109.8, 66.7, 35.6; HRMS (ESI-TOF) m/z calcd for $\text{C}_{23}\text{H}_{17}\text{N}_3\text{NaO}_3$ [M+Na $^+$] 406.1162, Found: 406.1165.

N-(4'-Methylene-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)dodecanamide (4w). Colorless oil, 171 mg, yield 83%; IR (KBr) v 3208, 2914, 1719, 1617, 1464, 1374, 1248 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 9.35 (s, 1H), 8.95 (s, 1H), 7.51 (d, $J = 7.2$ Hz, 1H), 7.27–7.24 (m, 1H), 7.06 (t, $J = 7.2$ Hz, 1H), 6.90 (d, $J = 7.8$ Hz, 1H), 6.16 (s, 1H), 5.49 (s, 1H), 3.10 (s, 2H), 2.09–2.04 (m, 1H), 2.03–1.98 (m, 1H), 1.36–1.32 (m, 2H), 1.31–1.26 (m, 2H), 1.23–1.17 (m, 8H), 1.14–1.05 (m, 4H), 1.03–0.96 (m, 1H), 0.94–0.91 (m, 1H), 0.87 (t, $J = 7.8$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 177.9, 172.4, 167.2, 141.5, 134.6, 130.5, 126.2, 125.7, 123.4, 118.6, 110.6, 67.7, 35.2, 33.8, 31.9, 29.7, 29.6, 29.4, 29.3, 29.2, 28.6, 25.3, 22.6, 14.1; HRMS (ESI-TOF) m/z calcd for $\text{C}_{24}\text{H}_{33}\text{N}_3\text{NaO}_3$ [M+Na $^+$] 434.2414, Found: 434.2405.

N-(4'-Methylene-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)stearamide (4x). Colorless oil, 156 mg, yield 63%; IR (KBr) v 3208, 2914, 2848, 1719, 1617, 1464, 1251, cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 9.31 (s, 1H), 8.93 (s, 1H), 7.51 (d, $J = 7.2$ Hz, 1H), 7.27–7.24 (m, 1H), 7.06 (t, $J = 7.2$ Hz, 1H), 6.90 (d, $J = 7.8$ Hz, 1H), 6.17 (s, 1H), 5.49 (s, 1H), 3.10 (s, 2H), 2.09–2.04 (m, 1H), 2.02–1.97 (m, 1H), 1.35–0.87 (m, 33H); ^{13}C NMR (150 MHz, CDCl_3) δ 177.9, 172.4, 167.2, 141.5, 134.6, 130.5, 126.2, 125.8, 123.4, 118.7, 110.6, 67.7, 35.2, 33.9, 31.9, 29.7, 29.6, 29.4, 29.3, 28.6, 25.3, 22.7, 14.1; HRMS (ESI-TOF) m/z calcd for $\text{C}_{30}\text{H}_{45}\text{N}_3\text{NaO}_3$ [M+Na $^+$] 518.3353, Found: 518.3340.

3. General experimental procedures for the synthesis of compounds 6a–6s

Isatins **1** (0.5 mmol, 1 equiv.), amines **5** (0.75 mmol, 1.5 equiv.), $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (0.05 mmol, 0.1 equiv.) were put into a dried roundbottom flask (50 mL) fitted with a magnetic bar. THF (4 mL) was then added.

The mixture was stirred under reflux, and the reaction process was monitored by TLC. After reflux for 9 h, tin powder (1.75 mmol, 3.5 equiv.) and ethyl 2-(bromomethyl)acrylate **3** (1.5 mmol, 3 equiv.) in 2 mL of THF were added to the flask. The resulting mixture was stirred under reflux for another 3–19 h. The reaction mixture was cooled to room temperature. The saturated NH₄Cl solution (6 mL) was poured into the mixture and stirred for 10 min. The mixture was extracted with EtOAc (3 × 10 mL). The combined organic phases were dried (MgSO₄) and concentrated. Purification of the residue by silica gel column chromatography using hexane and EtOAc (3:1) as the eluent furnished the pure products **6**.

Ethyl 2-((2-oxo-3-(phenylamino)indolin-3-yl)methyl)acrylate (6a). Colorless oil, 139 mg, yield 83%; IR (KBr) ν 3274, 2152, 1701, 1599, 1467, 1311, 1182, 1014, 735 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 9.60 (s, 1H), 7.17 (t, *J* = 7.8 Hz, 1H), 7.13 (d, *J* = 7.2 Hz, 1H), 6.95–6.91 (m, 3H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.59 (t, *J* = 7.8 Hz, 1H), 6.30–6.19 (m, 3H), 5.43 (s, 1H), 5.41 (s, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.24 (d, *J* = 13.2 Hz, 1H), 2.69 (d, *J* = 13.2 Hz, 1H), 1.23 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 180.5, 167.5, 145.2, 139.7, 133.9, 130.4, 129.0, 128.9, 128.8, 124.9, 122.2, 118.4, 114.2, 110.8, 65.2, 61.2, 41.0, 14.0; HRMS (ESI–TOF) m/z calcd for C₂₀H₂₀N₂NaO₃ [M+Na⁺] 359.1366, Found: 359.1361.

Ethyl 2-((2-oxo-3-(phenylamino)indolin-3-yl)methyl)acrylate (6b). Colorless oil, 130 mg, yield 74%; IR (KBr) ν 3298, 1707, 1605, 1467, 1317, 1185, 744 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 9.44 (s, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.05 (d, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 7.2 Hz, 1H), 6.92 (d, *J* = 7.2 Hz, 1H), 6.86 (d, *J* = 7.2 Hz, 1H), 6.66 (t, *J* = 7.2 Hz, 1H), 6.52 (t, *J* = 7.2 Hz, 1H), 6.33 (s, 1H), 5.69 (d, *J* = 8.4 Hz, 1H), 5.40 (s, 1H), 5.17 (s, 1H), 4.20–4.18 (m, 2H), 3.29 (d, *J* = 13.8 Hz, 1H), 2.61 (d, *J* = 13.8 Hz, 1H), 2.26 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 180.7, 167.9, 143.3, 139.5, 139.4, 134.0, 130.6, 130.1, 129.1, 128.9, 126.69, 124.7, 123.3, 122.1, 117.9, 111.0, 64.9, 61.3, 41.3, 18.0, 14.1; HRMS (ESI–TOF) m/z calcd for C₂₁H₂₃N₂O₃ [M+H⁺] 351.1703, Found: 351.1698.

Ethyl 2-((2-oxo-3-(m-tolylamino)indolin-3-yl)methyl)acrylate (6c). White solid, 142 mg, yield 81%. m.p. 136–138 °C; IR (KBr) ν 3298, 1707, 1605, 1467, 1317, 1185, 744 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 9.32 (s, 1H), 7.20 (t, *J* = 7.8 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 6.95 (t, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.78 (t, *J* = 7.8 Hz, 1H), 6.43 (d, *J* = 7.2 Hz, 1H), 6.26 (s, 1H), 6.19 (s, 1H), 5.91 (d, *J* = 8.4 Hz, 1H), 5.43 (s, 1H), 5.27 (d, *J* = 4.8 Hz, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.24 (d, *J* = 13.2 Hz, 1H), 2.66 (d, *J* = 13.8 Hz, 1H), 2.08 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 180.4, 167.7, 145.1, 139.7, 138.6, 134.0, 130.4, 129.1, 129.0, 128.8, 125.0, 122.3, 119.5, 115.7, 110.8, 110.7, 65.1, 61.2, 41.1, 21.4, 14.1; HRMS (ESI–TOF) m/z calcd for C₂₁H₂₃N₂O₃ [M+H⁺] 351.1703, Found: 351.1697.

Ethyl 2-((2-oxo-3-(p-tolylamino)indolin-3-yl)methyl)acrylate (6d). Colorless oil, 145 mg, yield 83%. IR (KBr) ν 3280, 2974, 1701, 1614, 1509, 1467, 1305, 1182, 1014, 735 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 9.38 (br, 1H), 7.19–7.14 (m, 2H), 6.95 (t, *J* = 7.8 Hz, 1H), 6.80 (d, *J* = 7.8 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 2H), 6.24 (s, 1H), 6.17–6.15 (m, 2H), 5.44 (s, 1H), 5.14 (s, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.24 (d, *J* = 7.2 Hz, 1H), 2.68 (dd, *J* = 13.2, 3.6 Hz, 1H), 2.08 (s, 3H), 1.24 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 180.6, 167.5, 142.8, 139.8, 134.1, 130.1, 129.4, 129.1, 128.9, 127.8, 125.0, 122.2, 114.7, 110.8, 65.4, 61.1, 41.0, 20.3, 14.0; HRMS (ESI–TOF) m/z calcd for C₂₁H₂₃N₂O₃ [M+H⁺] 351.1703, Found: 359.1698.

Ethyl 2-((3-((4-methoxyphenyl)amino)-2-oxoindolin-3-yl)methyl)acrylate (6e). White solid, 119 mg, yield 65%. m.p. 126–128 °C; IR (KBr) ν 3274, 2176, 1707, 1617, 1506, 1464, 1299, 1179, 1020, 744 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 8.96 (s, 1H), 7.22–7.19 (m, 2H), 6.98 (t, *J* = 7.8 Hz, 1H), 6.80 (d, *J* = 7.8 Hz, 1H), 6.49 (d, *J* = 9.0 Hz, 2H), 6.26 (d, *J* = 9.0 Hz, 2H), 6.23 (s, 1H), 5.46 (s, 1H), 4.82 (s, 1H), 4.09 (q, *J* = 7.2 Hz, 2H), 3.57 (s, 3H), 3.25 (d, *J* = 13.2 Hz, 1H), 2.68 (d, *J* = 13.2 Hz, 1H), 1.23 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 180.5, 167.4, 167.4, 153.2, 140.0, 138.9, 134.3, 129.9, 129.2, 129.0, 125.3, 122.3, 117.5, 117.4, 114.3, 110.7, 66.2, 61.1, 55.4, 40.8, 14.1; HRMS (ESI–TOF) m/z calcd for C₂₁H₂₂N₂NaO₄ [M+Na⁺] 389.1472, Found: 389.1478.

Ethyl 2-((3-((2,6-dimethylphenyl)amino)-2-oxoindolin-3-yl)methyl)acrylate (6f). White solid, 138 mg, yield 76%. m.p. 149–151 °C; IR (KBr) ν 3313, 2983, 2255, 1724, 1513, 1238, 1186, 1040, 903, 733 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 9.40 (br, 1H), 7.08 (t, *J* = 7.8 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 2H), 6.78 (dd, *J* = 13.8, 7.2 Hz, 2H), 6.73 (t, *J* = 7.8 Hz, 1H), 6.62 (d, *J* = 7.8 Hz, 1H), 6.06 (s, 1H), 5.53 (s, 1H), 3.95–3.87 (m, 2H), 3.84 (d, *J* = 2.4 Hz, 1H), 3.44 (d, *J* = 12.6 Hz, 1H), 3.04 (d, *J* = 12.6 Hz, 1H), 2.11 (s, 6H), 1.11 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 180.8, 166.9, 142.2, 140.5, 134.5, 133.1, 128.8, 128.7, 128.2, 127.9, 126.3, 123.4, 121.5, 110.0, 67.9, 60.7, 42.1, 19.2, 13.9. HRMS (ESI–TOF) m/z calcd for C₂₂H₂₄N₂NaO₃ [M+Na⁺] 387.1679, Found: 387.1674.

Ethyl 2-((3-((4-fluorophenyl)amino)-2-oxoindolin-3-yl)methyl)acrylate (6h). White solid, 175 mg, yield 99%. m.p. 112–114 °C; IR (KBr) ν 3274, 2974, 1701, 1614, 1503, 1467, 1311, 1182, 1014, 744 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 9.40 (s, 1H), 7.24–7.19 (m, 1H), 7.16 (d, *J* = 7.2 Hz, 1H), 6.98 (t, *J* = 7.2 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.63 (t, *J* = 8.4 Hz, 2H), 6.26 (s, 1H), 6.21–6.19 (m, 2H), 5.43 (s, 1H), 5.26 (s, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.23 (d, *J* = 13.2 Hz, 1H), 2.67 (dd, *J* = 13.2, 7.8 Hz, 1H), 1.25–1.23 (m, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 180.3, 167.6, 156.5 (d, *J*_{C–F} = 234.0 Hz), 141.4, 139.7, 134.0, 130.3, 129.2, 128.8, 125.1, 122.5, 116.0 (d, *J*_{C–F} = 7.5 Hz), 115.4 (d, *J*_{C–F} = 22.5 Hz), 110.8, 65.7, 61.3, 41.0, 14.1; HRMS (ESI–TOF) m/z calcd for C₂₀H₁₉FN₂NaO₃ [M+Na⁺] 377.1272, Found: 377.1266.

Ethyl 2-((2-oxo-3-((4-(trifluoromethyl)phenyl)amino)indolin-3-yl)methyl)acrylate (6i). Colorless oil, 181 mg, yield 90%. IR (KBr) ν 3423, 3002, 2916, 1709, 1653, 1420, 1323, 1009, 964, 701 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 9.29 (s, 1H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 7.2 Hz, 1H), 6.98 (t, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.33 (s, 1H), 6.21 (d, *J* = 8.4 Hz, 2H), 6.09 (d, *J* = 10.2 Hz, 1H), 5.40 (s, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.22 (d, *J* = 13.2 Hz, 1H), 2.65 (d, *J* = 13.2 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 179.7, 168.1, 147.9, 139.4, 133.6, 131.3, 129.4, 128.2, 124.9, 124.7 (q, *J*_{C–F} = 268.0 Hz), 123.3, 122.6, 119.7 (q, *J*_{C–F} = 32.0 Hz), 113.1, 111.0, 64.8, 61.6, 41.2, 14.1; HRMS (ESI–TOF) m/z calcd for C₂₁H₂₀F₃N₂O₃ [M+H⁺] 405.1421, Found: 405.1416.

Ethyl 2-((3-((4-chlorophenyl)amino)-2-oxoindolin-3-yl)methyl)acrylate (6j). White solid, 172 mg, yield 93%. m.p. 147–149 °C; IR (KBr) ν 3340, 2164, 1707, 1599, 1488, 1311, 1182, cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 9.55 (s, 1H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.11 (d, *J* = 7.2 Hz, 1H), 6.97 (t, *J* = 7.2 Hz, 1H), 6.87–6.83 (m, 3H), 6.28 (s, 1H), 6.14 (d, *J* = 9.0 Hz, 2H), 5.60 (s, 1H), 5.42 (s, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.22 (d, *J* = 13.2 Hz, 1H), 2.66 (d, *J* = 13.2 Hz, 1H), 1.26 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 180.2, 167.8, 143.8, 139.6, 133.8, 130.7, 129.2, 128.8, 128.5, 124.9, 123.1, 122.5, 115.3, 110.9, 65.2, 61.4, 41.1, 14.1; HRMS (ESI–TOF) m/z calcd for C₂₀H₁₉ClN₂NaO₃ [M+Na⁺] 393.0976, Found: 393.0968.

Ethyl 2-((3-((4-bromophenyl)amino)-2-oxoindolin-3-yl)methyl)acrylate (6k). White solid, 126 mg, yield 61%. m.p. 143–145 °C; IR (KBr) ν 3334, 1707, 1590, 1467, 1311, 1182, 735 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 9.32 (s, 1H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.10 (d, *J* = 7.8 Hz, 1H), 7.01 (s, 1H), 6.99 (d, *J* = 3.0 Hz, 1H), 6.97 (d, *J* = 7.2 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 6.29 (s, 1H), 6.09 (d, *J* = 8.4 Hz, 2H), 5.59 (d, *J* = 2.4 Hz, 1H), 5.41 (s, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.21 (d, *J* = 13.2 Hz, 1H), 2.65 (d, *J* = 13.8 Hz, 1H), 1.27 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 180.1, 167.8, 144.3, 139.5, 133.8, 131.7, 130.8, 129.3, 128.5, 124.9, 122.5, 115.7, 110.9, 110.3, 65.1, 61.4, 41.1, 14.1; HRMS (ESI–TOF) m/z calcd for C₂₀H₁₉BrN₂NaO₃ [M+Na⁺] 437.0471, Found: 437.0464.

Ethyl 2-((3-((4-fluorophenyl)amino)-5-methyl-2-oxoindolin-3-yl)methyl)acrylate (6m). White solid, 166 mg, yield 90%. m.p. 176–178 °C; IR (KBr) ν 3380, 1716, 1626, 1510, 1305, 1226, 1172, 1026, 821 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 9.14 (s, 1H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.98 (s, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 6.64 (t, *J* = 8.4 Hz, 2H), 6.25 (s, 1H), 6.20 (dd, *J* = 8.4, 4.2 Hz, 2H), 5.45 (s, 1H), 5.21 (s, 1H), 4.15–4.09 (m, 2H), 3.19 (d, *J* = 13.2 Hz, 1H), 2.68 (d, *J* = 13.8 Hz, 1H), 2.26 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 179.1, 166.6, 155.9 (d, *J*_{C–F} = 235.5 Hz), 140.6, 136.3, 133.1, 131.0,

129.1, 128.6, 128.0, 124.6, 114.8 (d, $J_{C-F} = 7.5$ Hz), 114.4 (d, $J_{C-F} = 22.5$ Hz), 109.5, 64.7, 60.2, 40.1, 20.1, 13.1; HRMS (ESI-TOF) m/z calcd for $C_{21}H_{21}FN_2NaO_3$ [M+Na⁺] 391.1428, Found: 391.1432.

Ethyl 2-((5-chloro-3-((4-fluorophenyl)amino)-2-oxoindolin-3-yl)methyl)acrylate (6n). White solid, 169 mg, yield 87%. m.p. 159–161 °C; IR (KBr) v 3368, 2924, 1714, 1621, 1513, 1184, 818 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 9.14 (s, 1H), 7.21 (d, $J = 6.0$ Hz, 1H), 7.15 (s, 1H), 6.79 (d, $J = 8.4$ Hz, 1H), 6.67 (t, $J = 9.0$ Hz, 2H), 6.30 (s, 1H), 6.19 (dd, $J = 9.0, 4.2$ Hz, 2H), 5.46 (s, 1H), 5.22 (s, 1H), 4.21–4.12 (m, 2H), 3.21 (d, $J = 13.2$ Hz, 1H), 2.65 (d, $J = 13.2$ Hz, 1H), 1.29 (t, $J = 7.2$ Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 179.7, 167.5, 156.6 (d, $J_{C-F} = 237.0$ Hz), 141.1, 141.0, 138.2, 133.8, 130.7, 129.3, 128.1, 125.4, 116.0 (d, $J_{C-F} = 7.5$ Hz), 115.6 (d, $J_{C-F} = 22.5$ Hz), 111.8, 65.8, 61.5, 41.0, 14.1; HRMS (ESI-TOF) m/z calcd for $C_{20}H_{18}ClFN_2NaO_3$ [M+Na⁺] 411.0882, Found: 411.0886.

Ethyl 2-((5-bromo-3-((4-fluorophenyl)amino)-2-oxoindolin-3-yl)methyl)acrylate (6o). White solid, 171 mg, yield 79%. m.p. 172–174 °C; IR (KBr) v 3368, 1718, 1621, 1508, 1466, 1192, 813 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 8.96 (s, 1H), 7.37 (dd, $J = 7.8, 1.8$ Hz, 1H), 7.29 (d, $J = 1.8$ Hz, 1H), 6.75 (d, $J = 7.8$ Hz, 1H), 6.67 (t, $J = 8.4$ Hz, 2H), 6.30 (s, 1H), 6.19 (dd, $J = 9.0, 4.0$ Hz, 2H), 5.47 (s, 1H), 5.18 (s, 1H), 4.21–4.12(m, 2H), 3.20 (d, $J = 13.2$ Hz, 1H), 2.66 (d, $J = 13.2$ Hz, 1H), 1.29 (t, $J = 7.2$ Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 179.4, 167.5, 156.7 (q, $J_{C-F} = 235.5$ Hz), 141.0, 138.6, 133.8, 132.2, 131.0, 130.6, 128.2, 116.0 (d, $J_{C-F} = 7.5$ Hz), 115.6 (d, $J_{C-F} = 22.5$ Hz), 115.4, 112.2, 65.7, 61.5, 41.0, 14.1; HRMS (ESI-TOF) m/z calcd for $C_{20}H_{18}BrFN_2NaO_3$ [M+Na⁺] 455.0377, Found: 455.0381.

Ethyl 2-((3-(naphthalen-2-ylamino)-2-oxoindolin-3-yl)methyl)acrylate (6p). White solid, 143 mg, yield 74%. m.p. 166–168 °C; IR (KBr) v 3304, 1717, 1627, 1536, 1470, 1317, 1189, 745 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 9.43 (s, 1H), 7.53 (d, $J = 7.8$ Hz, 1H), 7.43 (d, $J = 8.4$ Hz, 1H), 7.23–7.21 (m, 1H), 7.23–7.21 (m, 2H), 7.13–7.08 (m, 2H), 6.92 (t, $J = 7.8$ Hz, 1H), 6.88 (d, $J = 7.8$ Hz, 1H), 6.75 (d, $J = 9.0$ Hz, 1H), 6.27 (s, 1H), 6.20 (s, 1H), 5.69 (s, 1H), 5.42 (s, 1H), 4.17–4.12 (m, 2H), 3.28 (d, $J = 13.2$ Hz, 1H), 2.69 (d, $J = 13.2$ Hz, 1H), 1.24 (t, $J = 7.2$ Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 180.3, 167.8, 142.8, 139.7, 134.5, 133.9, 130.6, 129.1, 128.7, 128.6, 127.8, 127.3, 126.2, 125.9, 125.0, 122.4, 122.3, 118.5, 110.8, 106.9, 65.3, 61.3, 41.1, 14.0; HRMS (ESI-TOF) m/z calcd for $C_{24}H_{22}N_2NaO_3$ [M+Na⁺] 409.1523, Found: 409.1526.

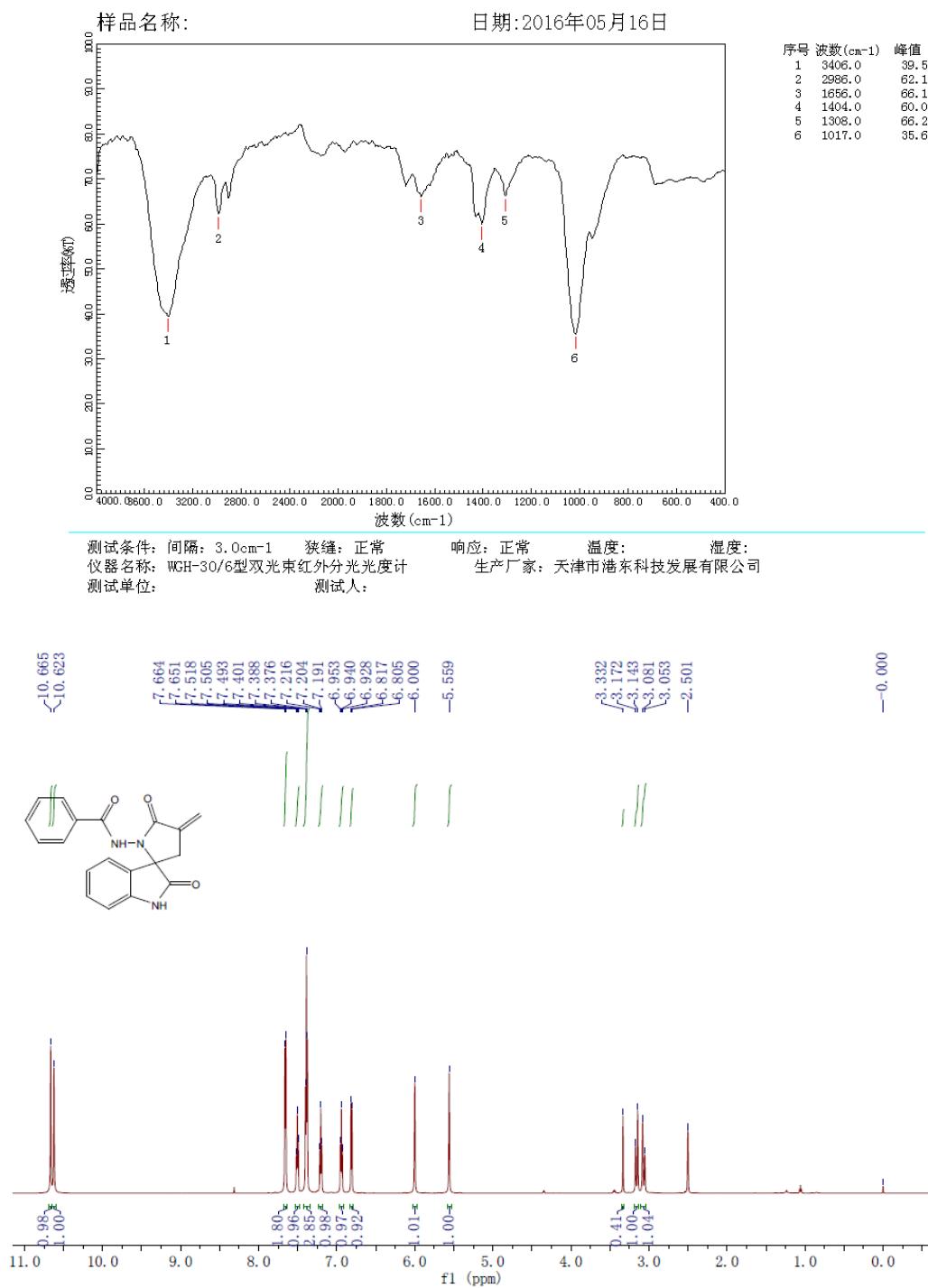
Ethyl 2-((1-benzyl-3-((4-fluorophenyl)amino)-2-oxoindolin-3-yl)methyl)acrylate (6q). Colorless oil, 198 mg, yield 89%. IR (KBr) v 3384, 1707, 1613, 1509, 1362, 1182, 752 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.27–7.24 (m, 4H), 7.19 (t, $J = 7.8$ Hz, 1H), 7.14 (d, $J = 7.2$ Hz, 2H), 6.99 (t, $J = 7.2$ Hz, 1H), 6.74 (d, $J = 7.8$ Hz, 1H), 6.60 (t, $J = 8.4$ Hz, 2H), 6.22 (s, 1H), 6.18 (dd, $J = 9.0, 4.2$ Hz, 2H), 5.43 (s, 1H), 5.06 (d, $J = 15.6$ Hz, 1H), 4.94 (s, 1H), 4.68 (d, $J = 15.6$ Hz, 1H), 4.11 (q, $J = 7.2$ Hz, 2H), 3.31 (d, $J = 13.2$ Hz, 1H), 2.67 (d, $J = 13.2$ Hz, 1H), 1.24 (t, $J = 7.2$ Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 177.2, 167.4, 157.1 (d, $J_{C-F} = 235.5$ Hz), 141.9, 141.3, 135.5, 134.4, 129.9, 129.1, 128.6, 128.2, 127.6, 127.5, 125.1, 122.4, 117.9 (d, $J_{C-F} = 7.5$ Hz), 115.3 (d, $J_{C-F} = 22.5$ Hz), 109.6, 65.6, 61.1, 43.9, 40.8, 14.1; HRMS (ESI-TOF) m/z calcd for $C_{27}H_{25}FN_2NaO_3$ [M+Na⁺] 467.1741, Found: 467.1747.

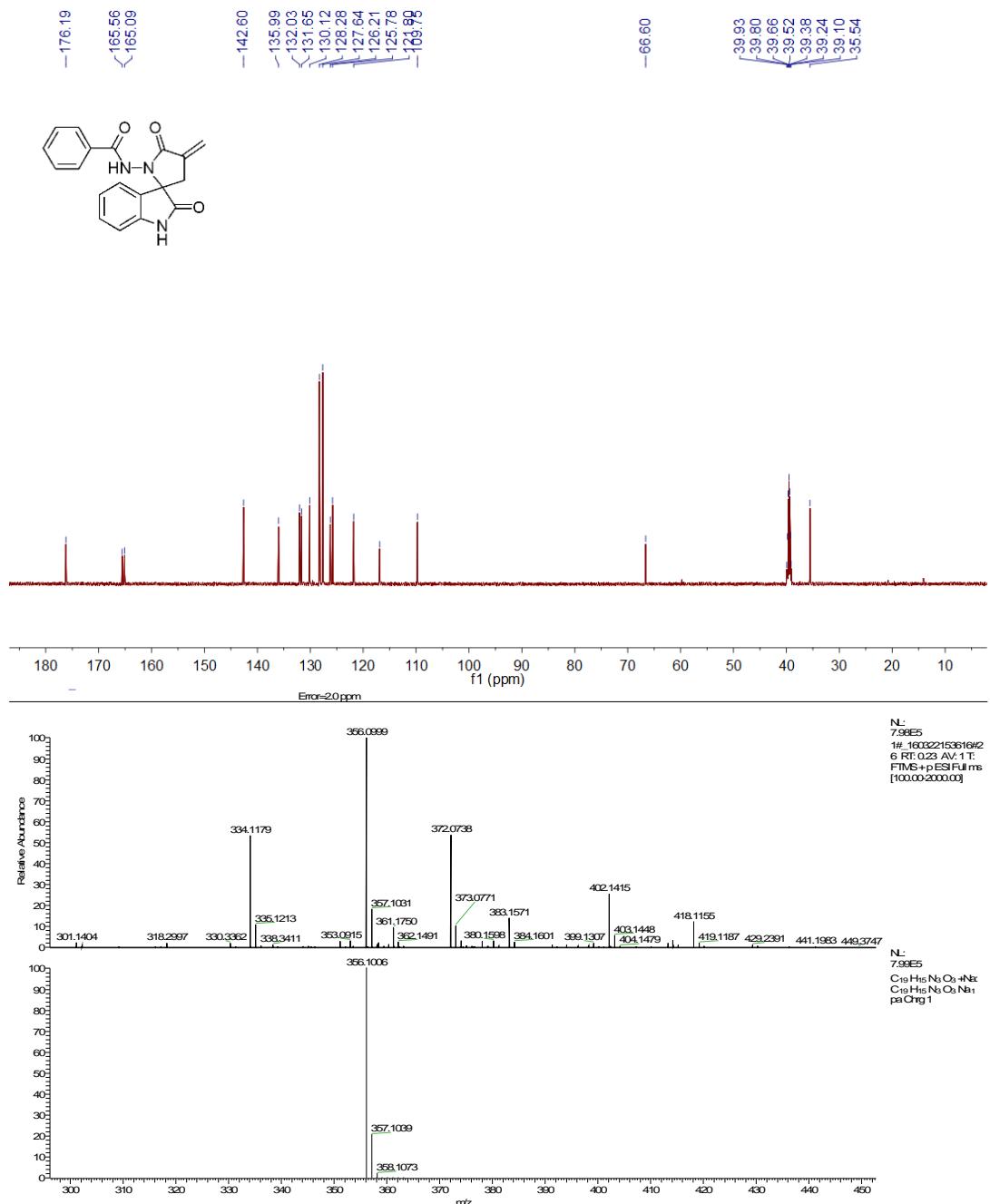
Ethyl 2-((1-ethyl-3-((4-fluorophenyl)amino)-2-oxoindolin-3-yl)methyl)acrylate (6r). White solid, 159 mg, yield 83%. m.p. 128–129 °C; IR (KBr) v 3377, 2924, 1714, 1607, 1505, 1371, 752 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.31 (t, $J = 7.8$ Hz, 1H), 7.24 (d, $J = 7.2$ Hz, 1H), 7.02 (t, $J = 7.8$ Hz, 1H), 6.88 (d, $J = 7.8$ Hz, 1H), 6.64 (t, $J = 9.0$ Hz, 2H), 6.21 (s, 1H), 6.15 (dd, $J = 9.0, 4.8$ Hz, 2H), 5.42 (s, 1H), 4.89 (s, 1H), 4.14–4.07 (m, 2H), 3.77–3.73 (m, 2H), 3.25 (d, $J = 13.2$ Hz, 1H), 2.61 (d, $J = 13.2$ Hz, 1H), 1.24 (t, $J = 7.2$ Hz, 3H), 1.20 (t, $J = 7.2$ Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 176.8, 167.4, 156.75 (d, $J_{C-F} = 237.0$ Hz), 141.8, 141.4, 134.3, 129.9, 129.2, 128.4, 125.3, 122.2, 116.8 (d, $J_{C-F} = 7.5$ Hz), 115.3 (d, $J_{C-F} = 22.5$ Hz), 108.6, 65.2, 61.1, 40.8, 34.7, 14.1, 12.5.; HRMS (ESI-TOF) m/z calcd for $C_{22}H_{23}FN_2O_3Na$ [M+Na⁺] 405.1585, Found: 405.1587.

Ethyl 2-((1-butyl-3-((4-fluorophenyl)amino)-2-oxoindolin-3-yl)methyl)acrylate (6s). White solid, 164 mg, yield 80%. m.p. 104–105 °C; IR (KBr) ν 3358, 2956, 1705, 1615, 1510, 1331, 1186, 826, 752, 518 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.30 (t, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.01 (t, *J* = 7.8 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 6.63 (t, *J* = 9.0 Hz, 2H), 6.21 (s, 1H), 6.16 (dd, *J* = 9.0, 4.8 Hz, 2H), 5.41 (s, 1H), 4.91 (s, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.73–3.63 (m, 2H), 3.25 (d, *J* = 13.2 Hz, 1H), 2.60 (d, *J* = 13.2 Hz, 1H), 1.63–1.53 (m, 2H), 1.33–1.28 (m, 2H), 1.24 (t, *J* = 7.2 Hz, 3H), 0.92 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 176.9, 167.4, 156.8 (d, *J*_{C-F} = 237.0 Hz), 142.3, 141.4, 134.3, 129.8, 129.1, 128.3, 125.2, 122.1, 117.1 (d, *J*_{C-F} = 7.5 Hz), 115.2 (d, *J*_{C-F} = 22.5 Hz), 108.7, 65.3, 61.1, 40.7, 39.8, 29.4, 20.1, 14.1, 13.7; HRMS (ESI-TOF) *m/z* calcd for C₂₄H₂₇FN₂NaO₃ [M+Na⁺] 433.1898, Found: 433.1900.

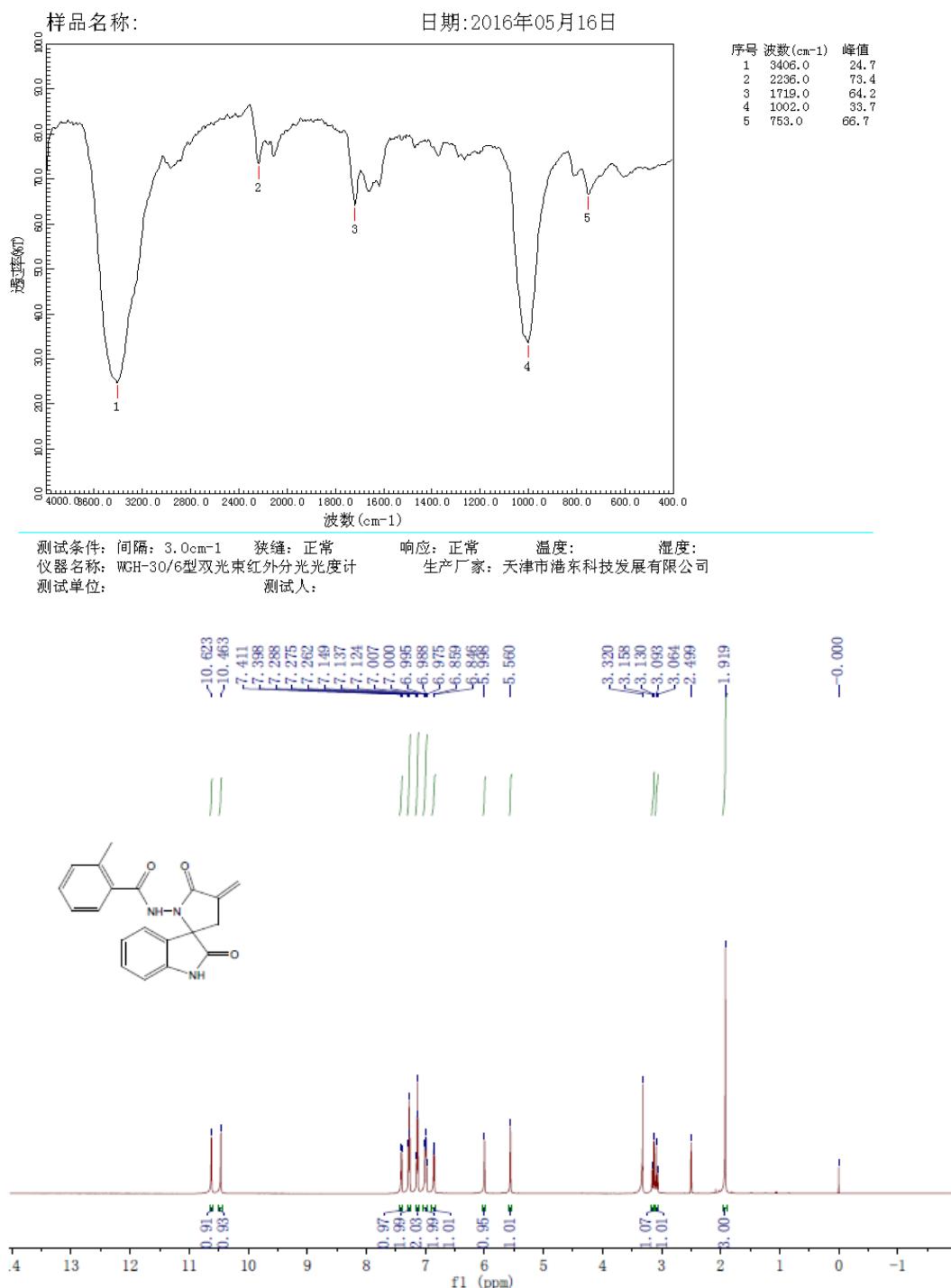
IR, NMR and HRMS Spectra of Compounds 4 and 6

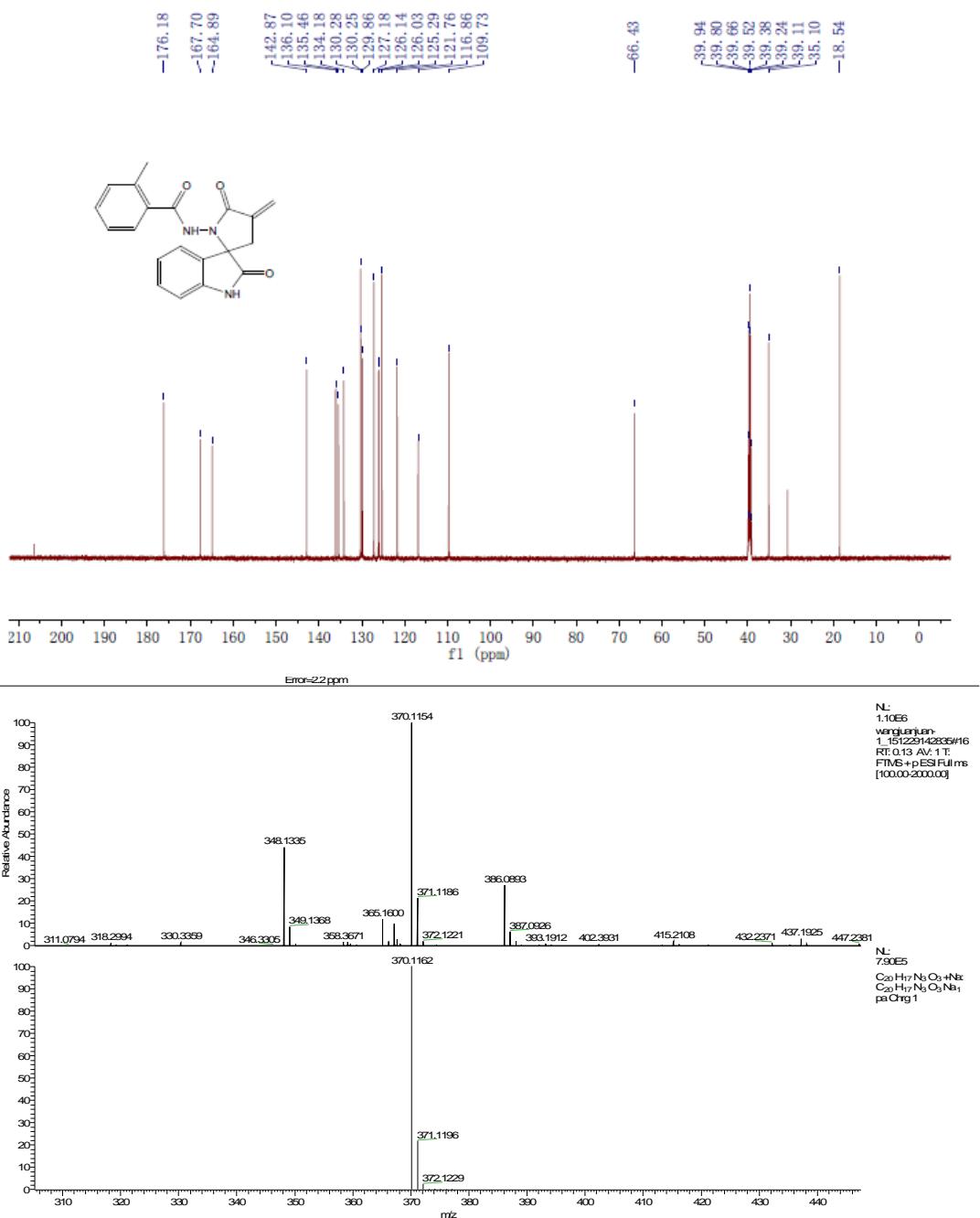
N-(4'-methylene-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)benzamide (4a)



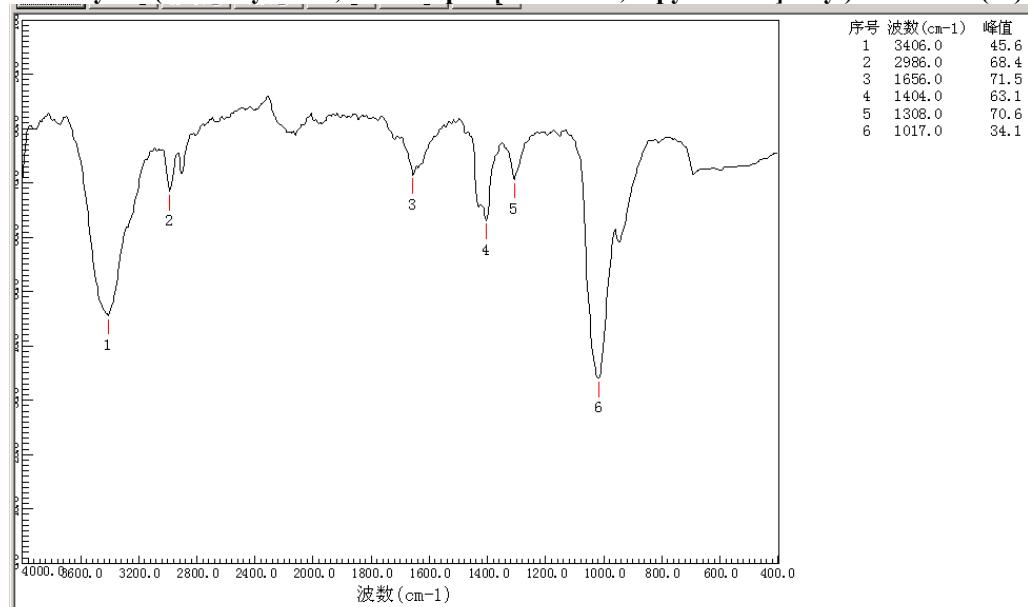


2-Methyl-N-(4'-methylene-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)benzamide (4b)





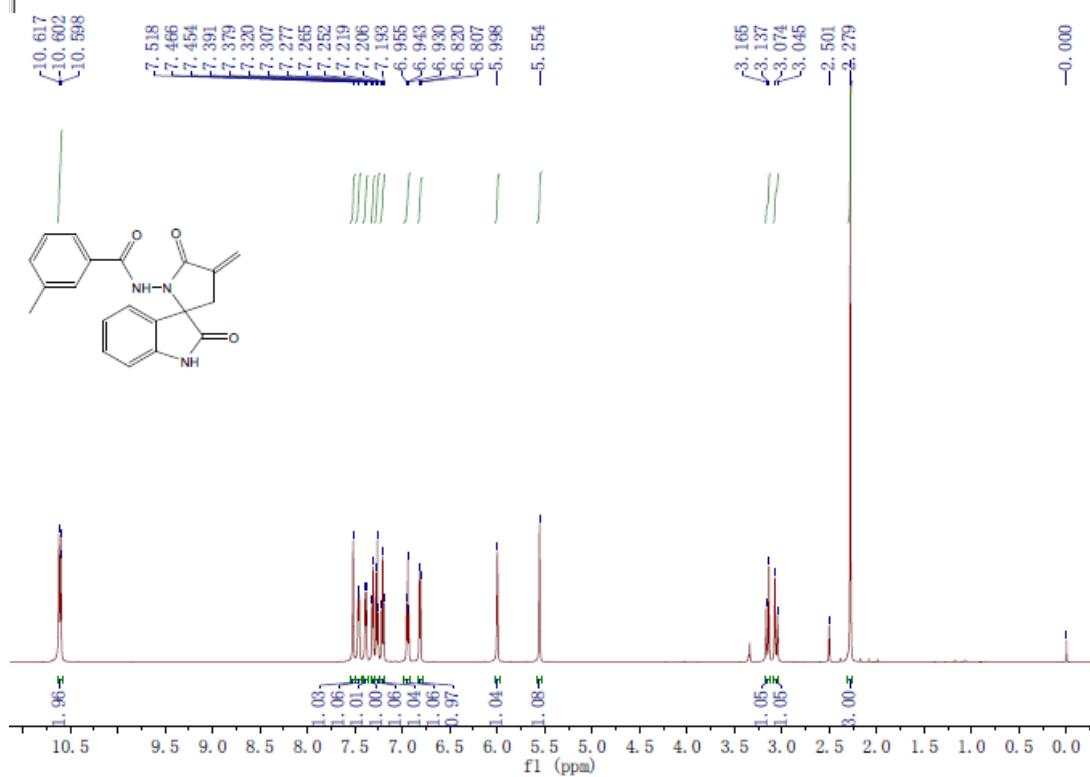
3-Methyl-N-(4'-methylene-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)benzamide(4c)

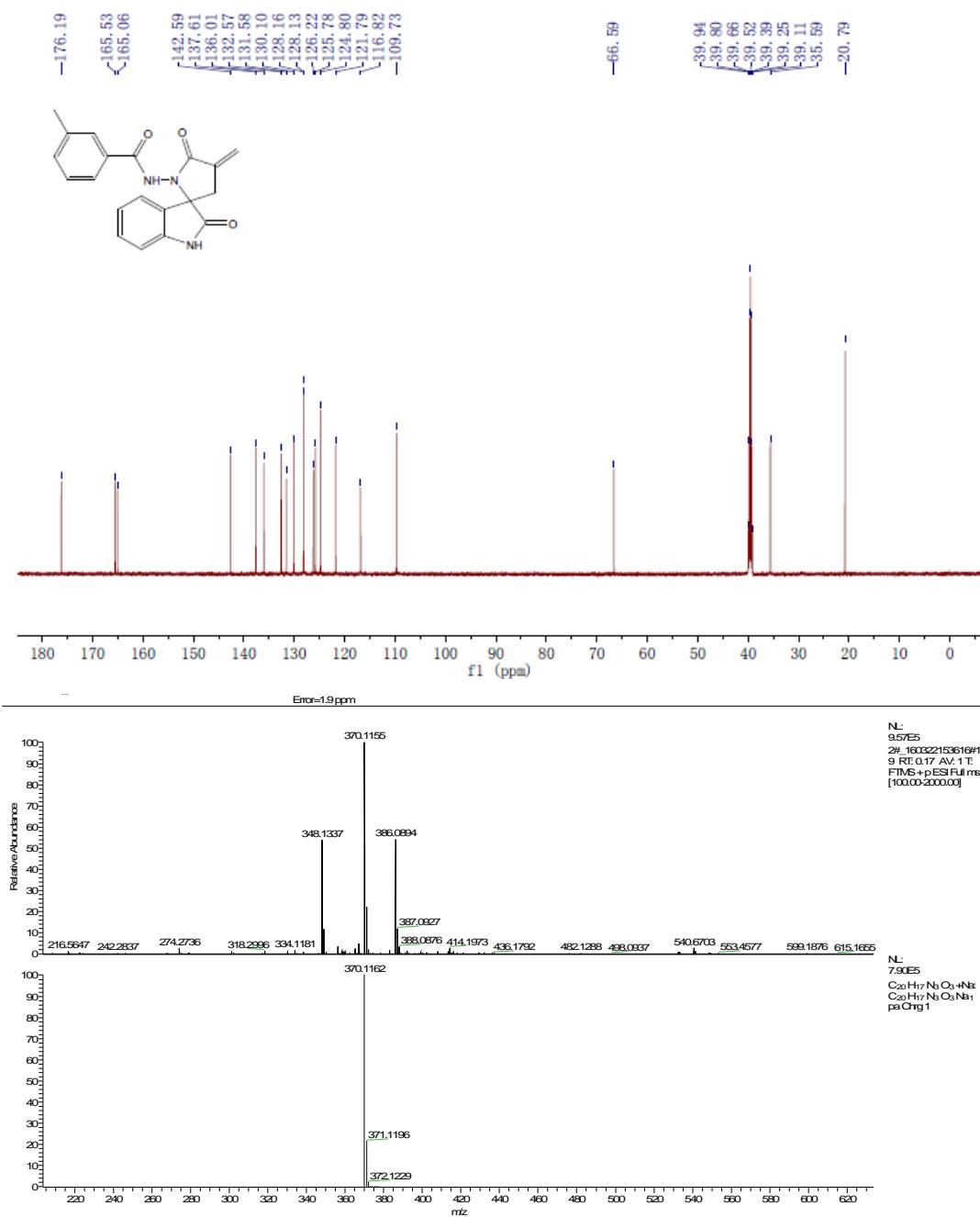


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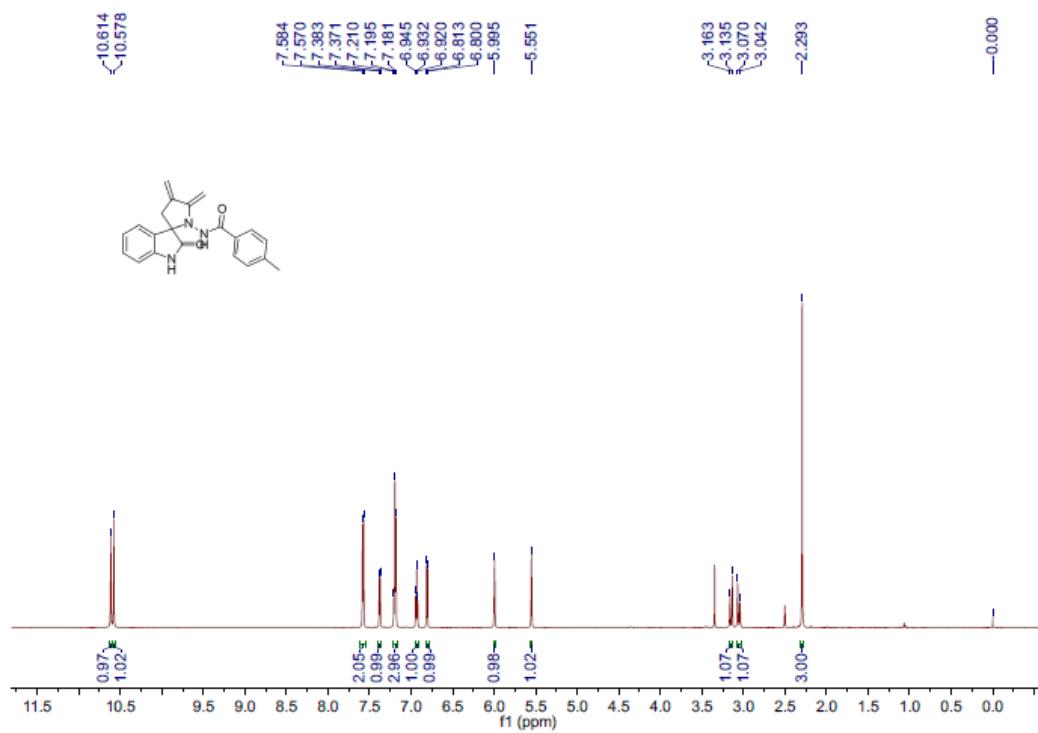
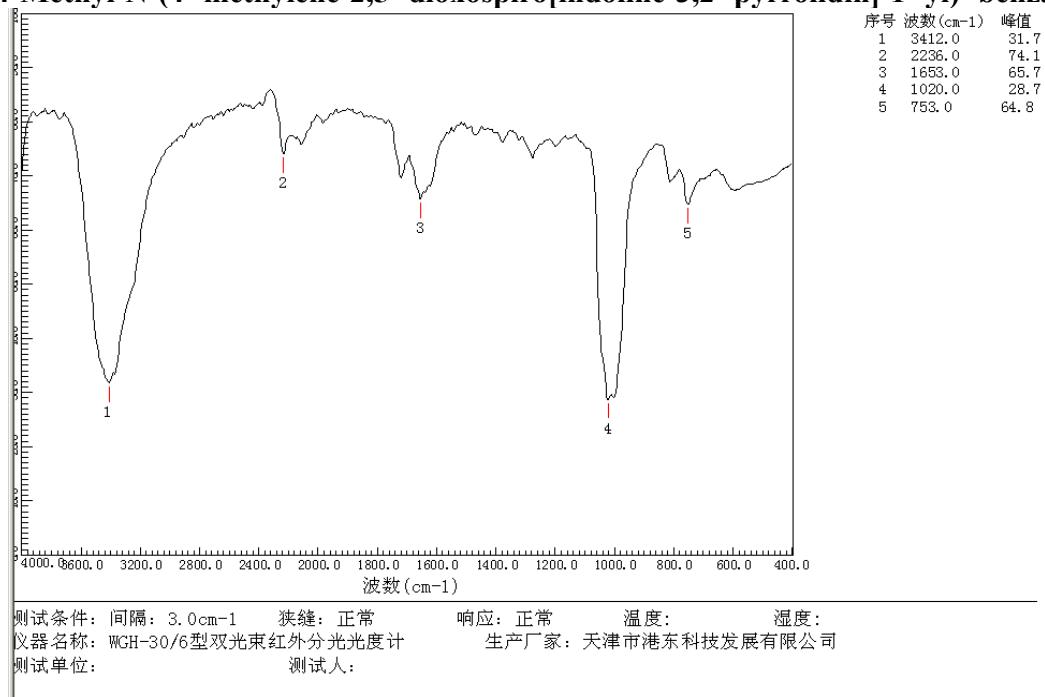
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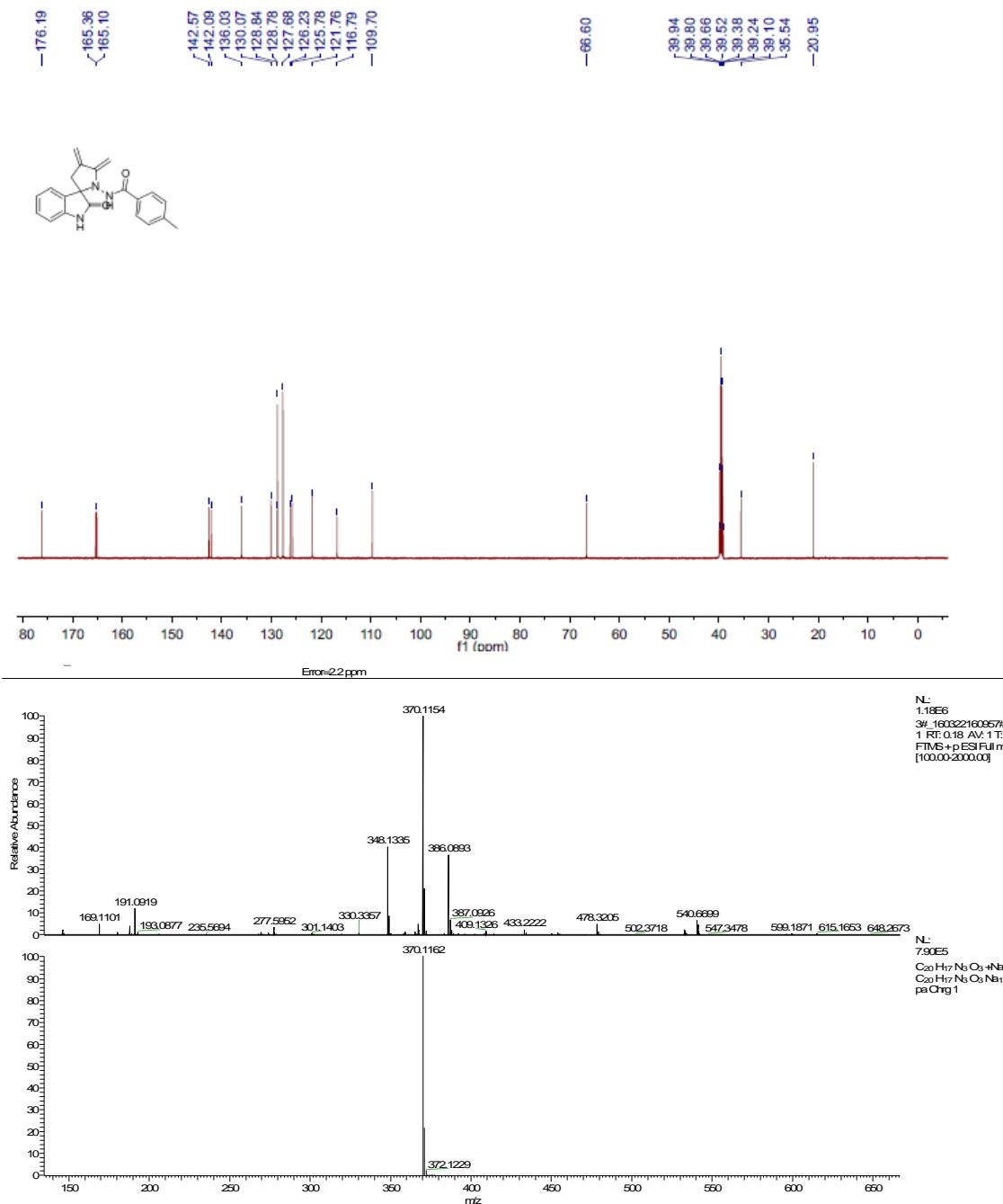
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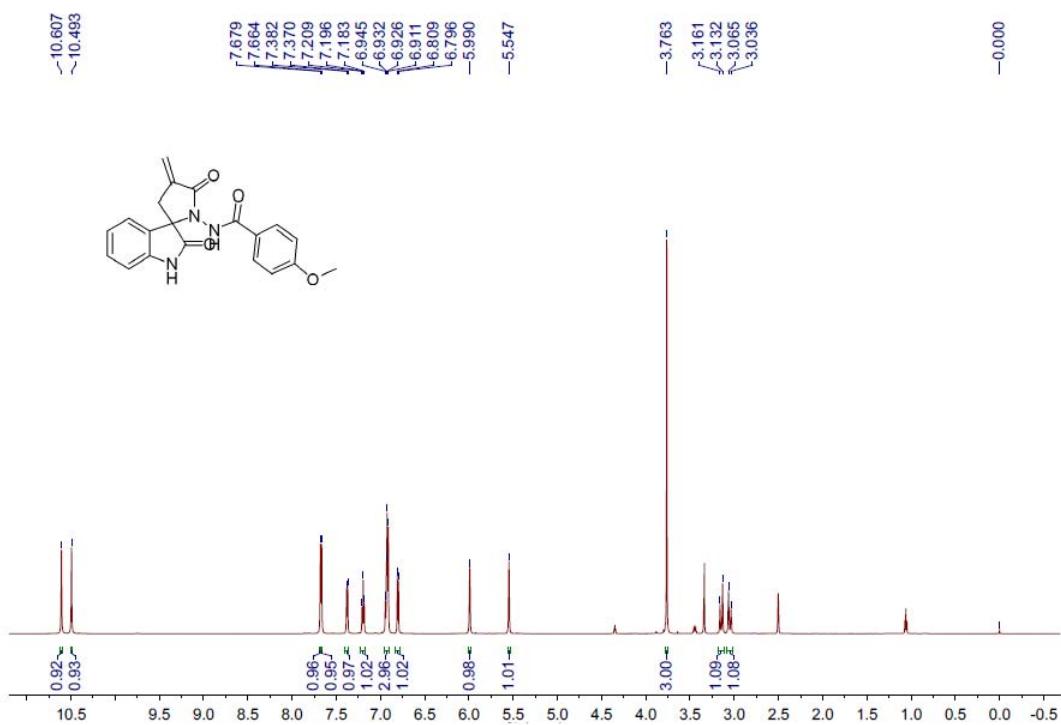
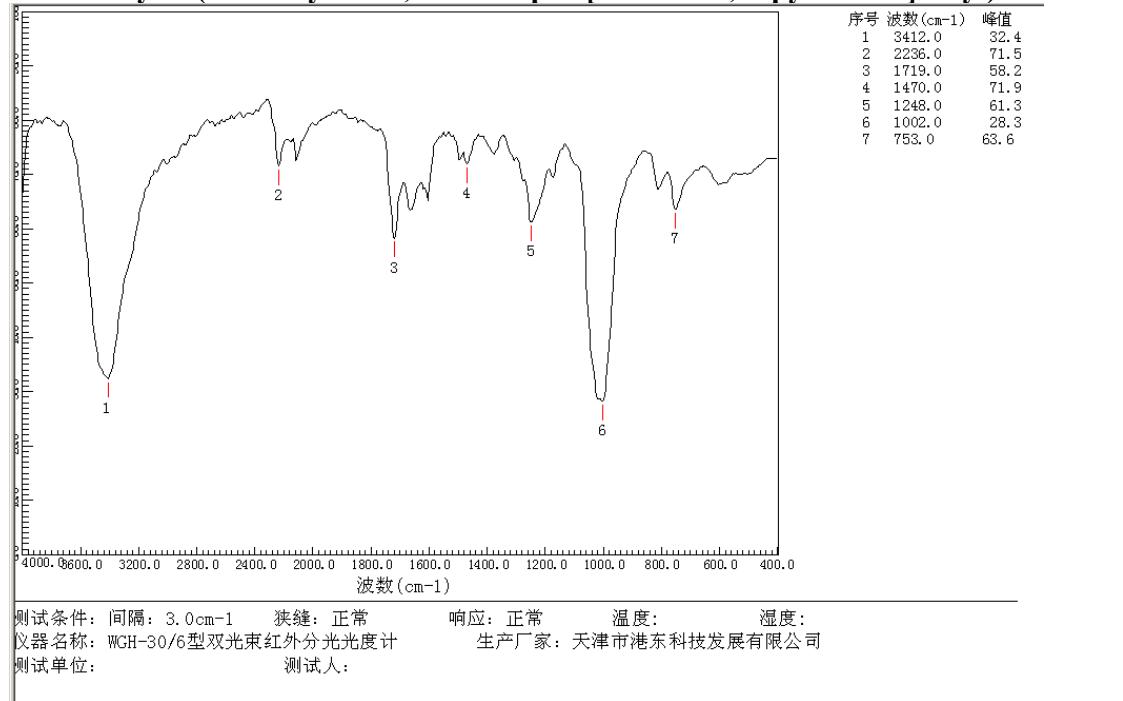


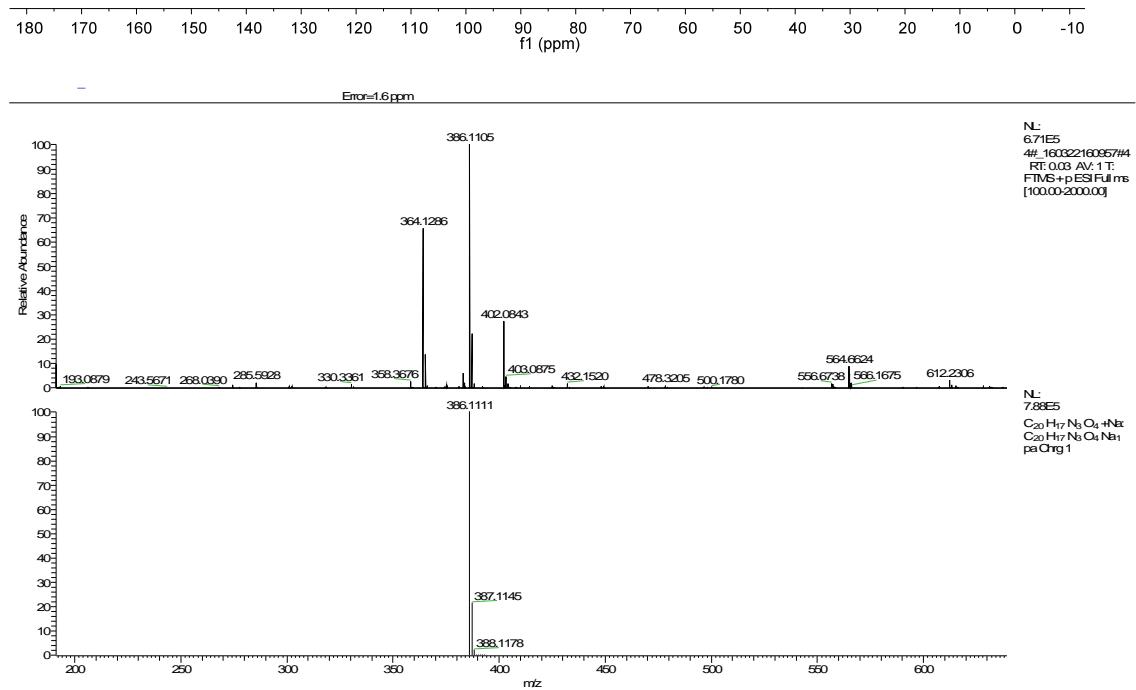
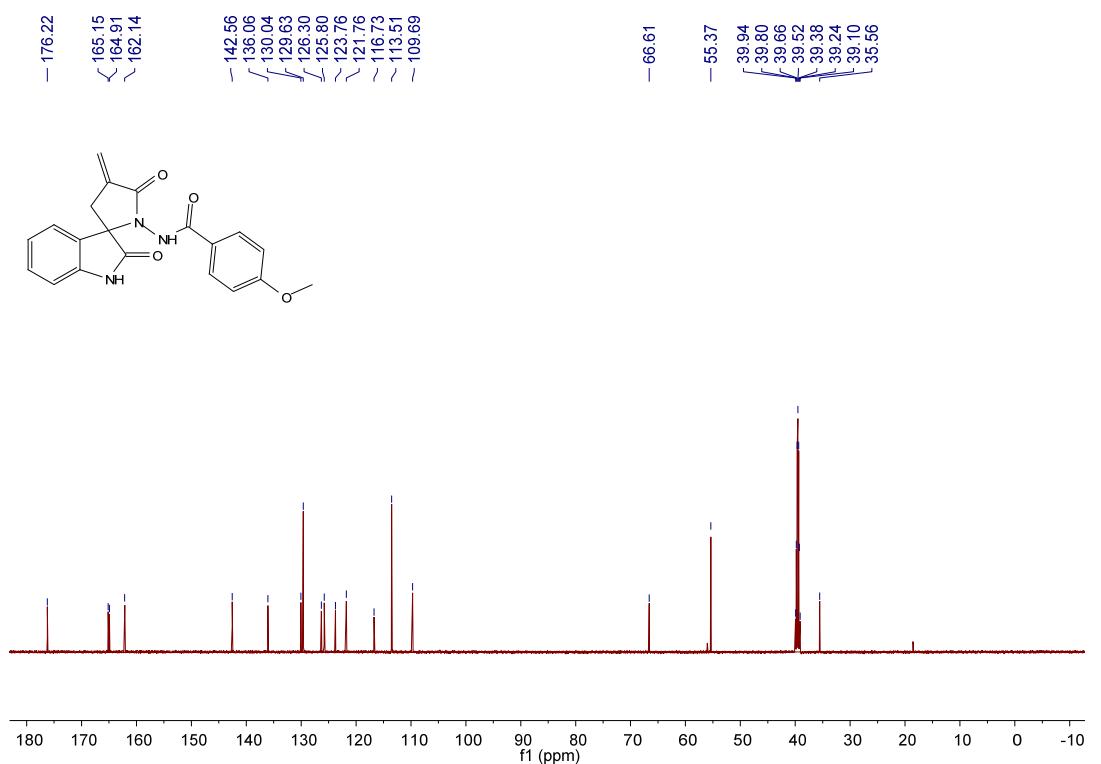
4-Methyl-N-(4'-methylen-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)-benzamide(4d)



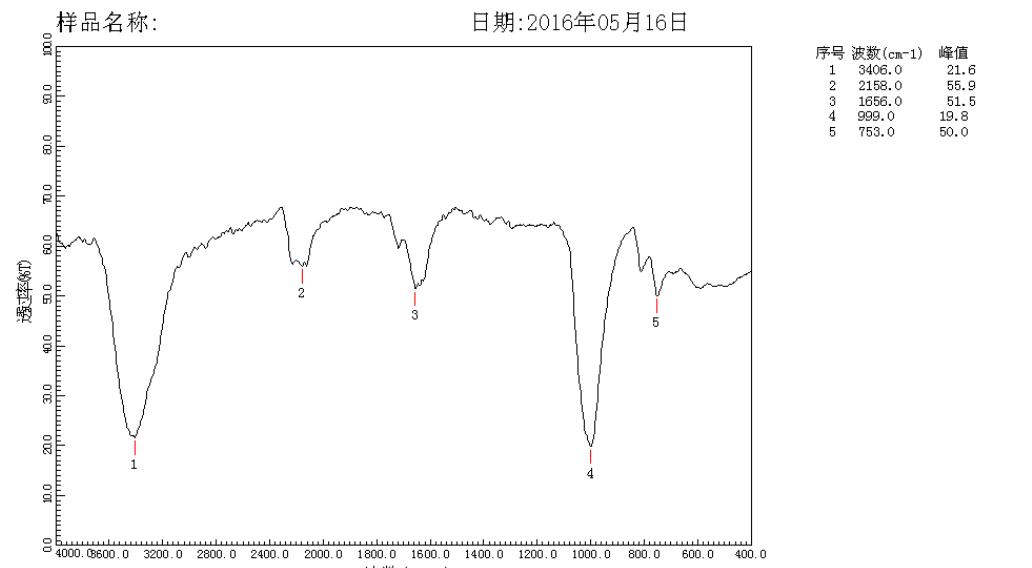


4-Methoxy-N-(4'-methylen-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)-benzamide(4e)

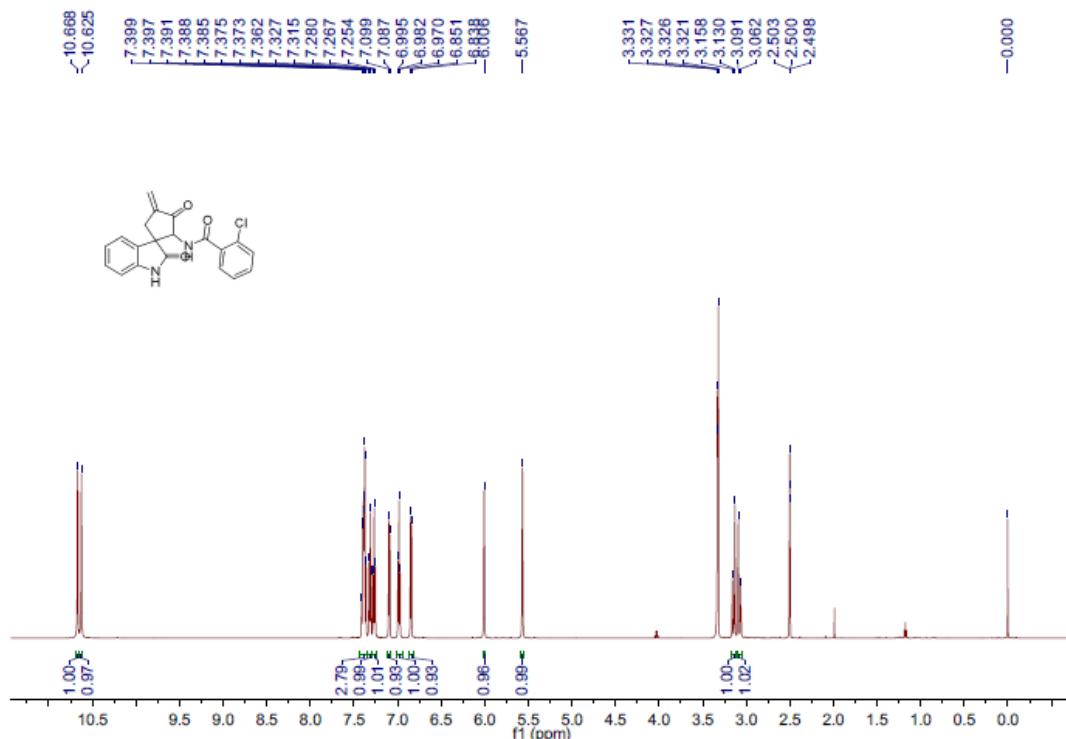


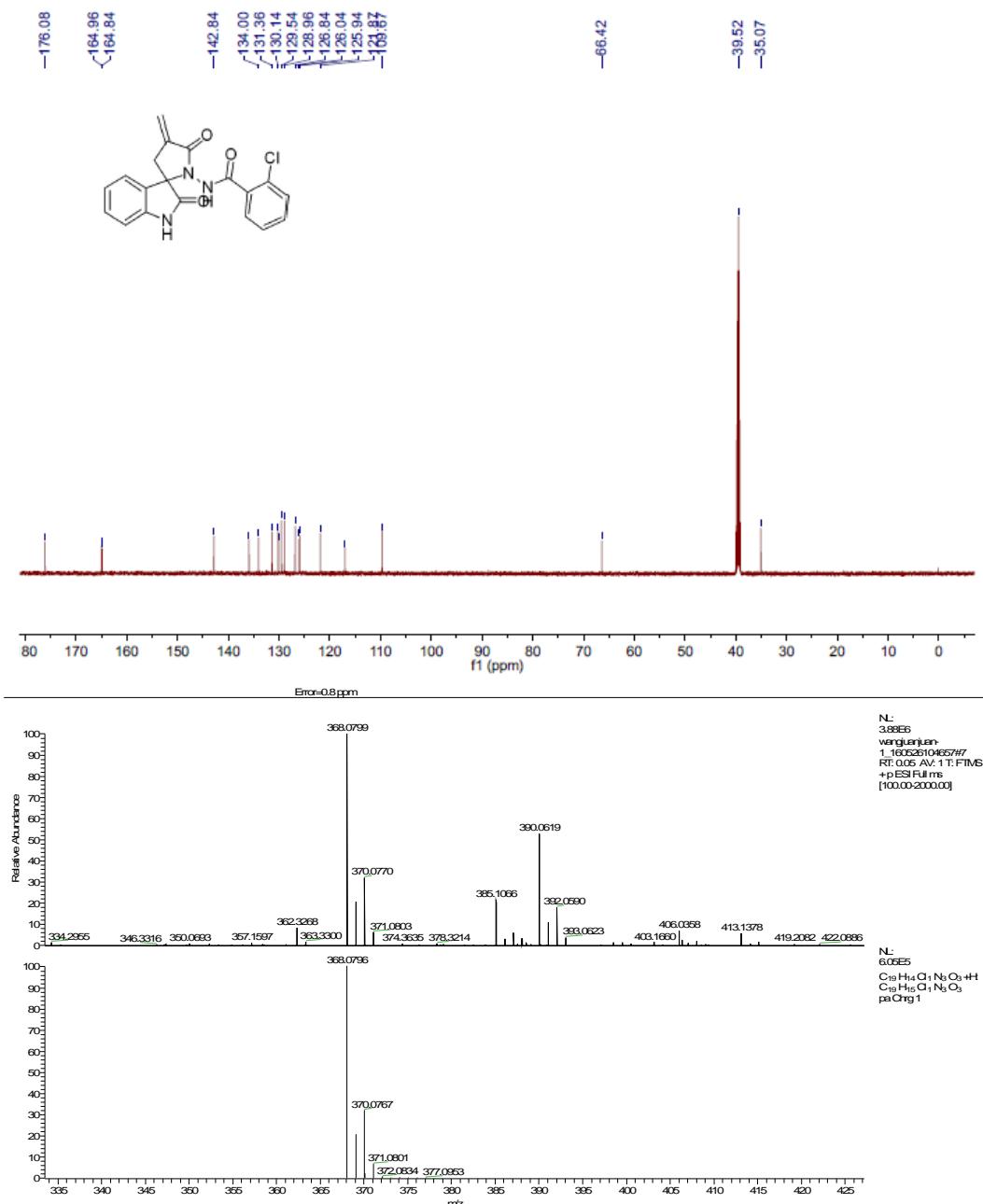


2-Chloro-N-(4'-methylen-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)-benzamide(4h)



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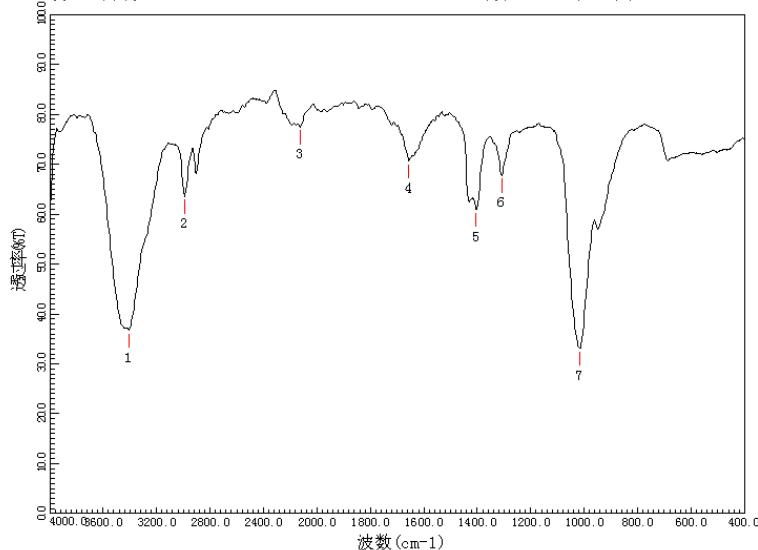




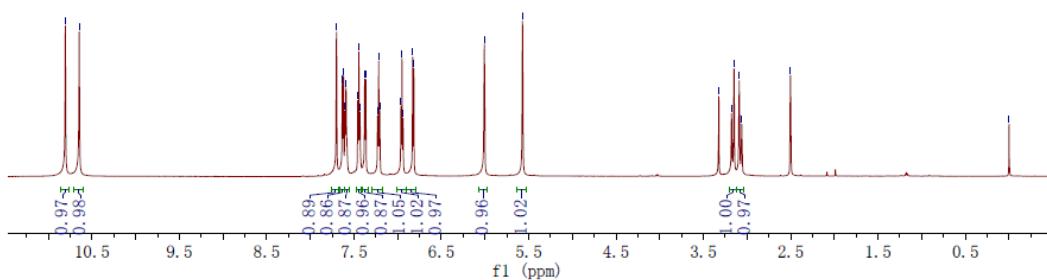
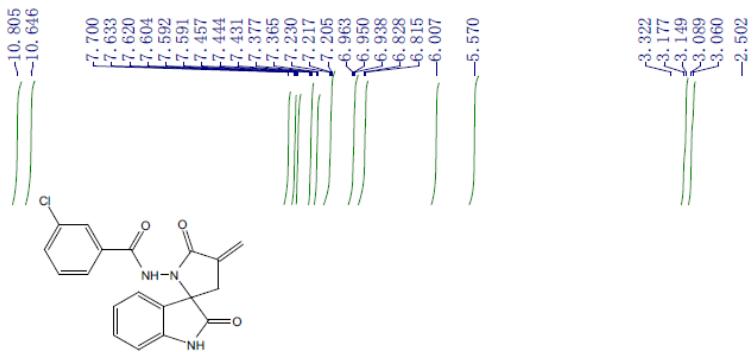
3-Chloro-N-(4'-methylen-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)-benzamide(4i)

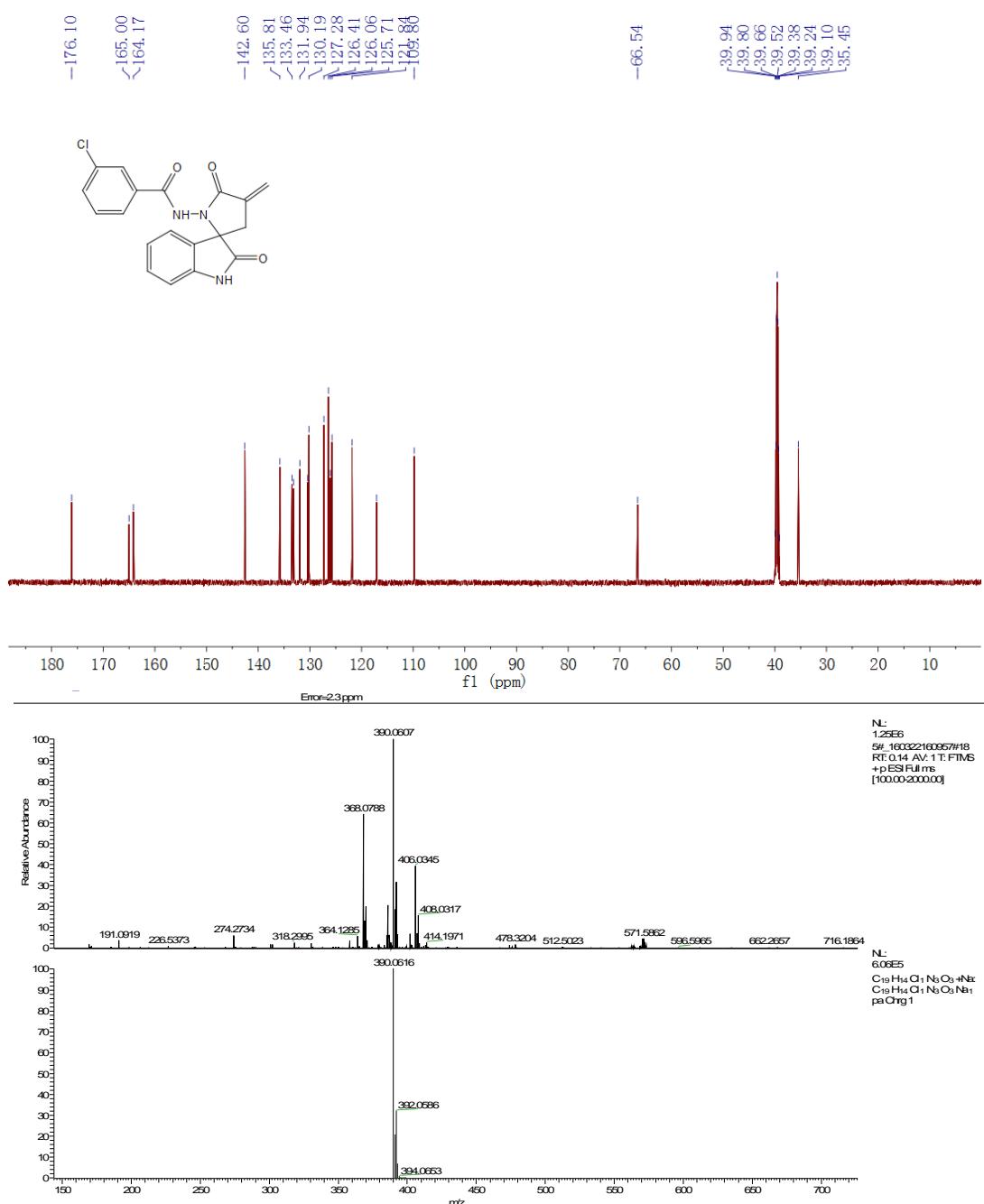
样品名称：

日期:2016年05月16日

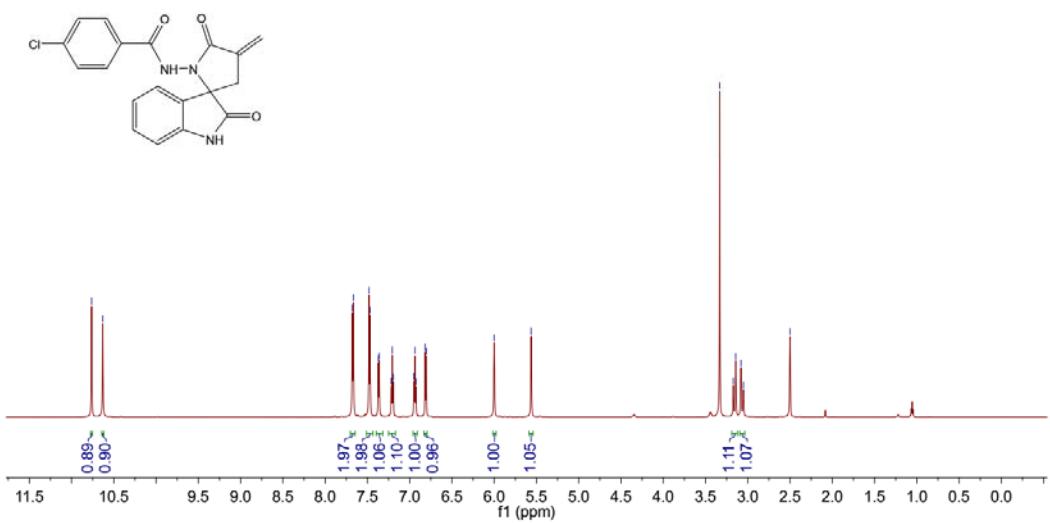
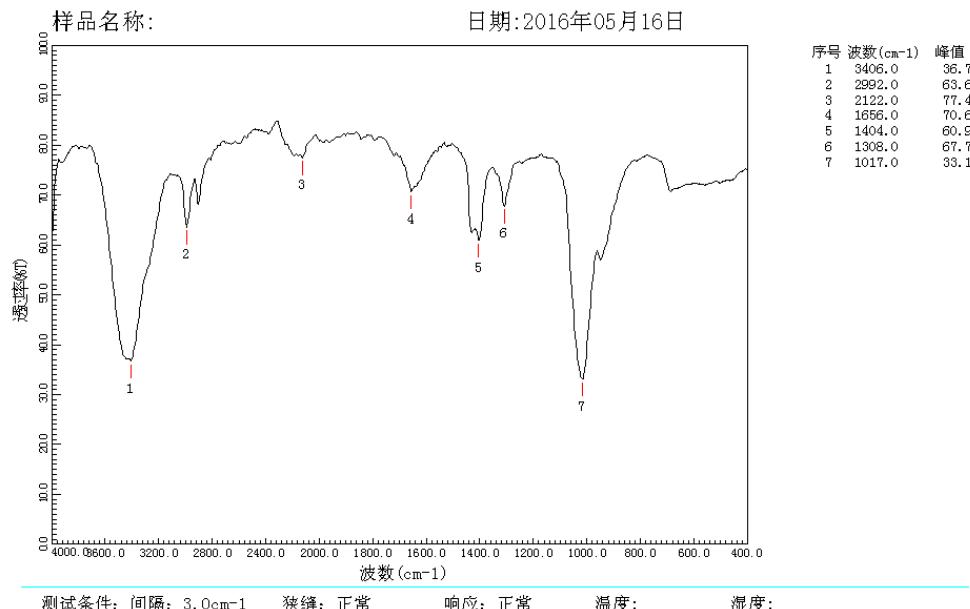


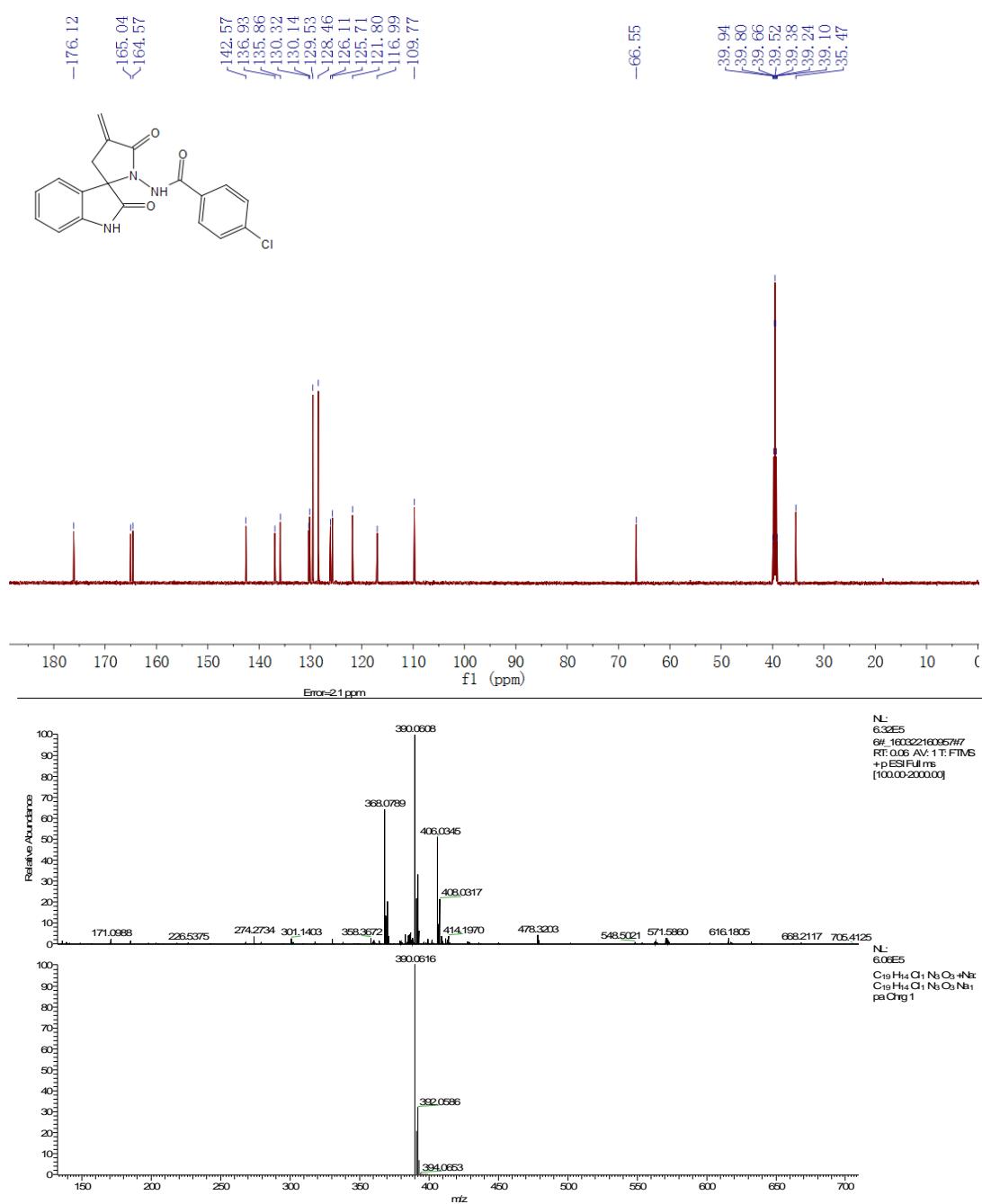
测试条件：间隔: 3.0cm⁻¹ 狭缝: 正常 响应: 正常 温度: 湿度:
仪器名称: WGH-30/6型双光束红外分光光度计 生产厂家: 天津市浦东科技发展有限公司
测试人: 测试单位:



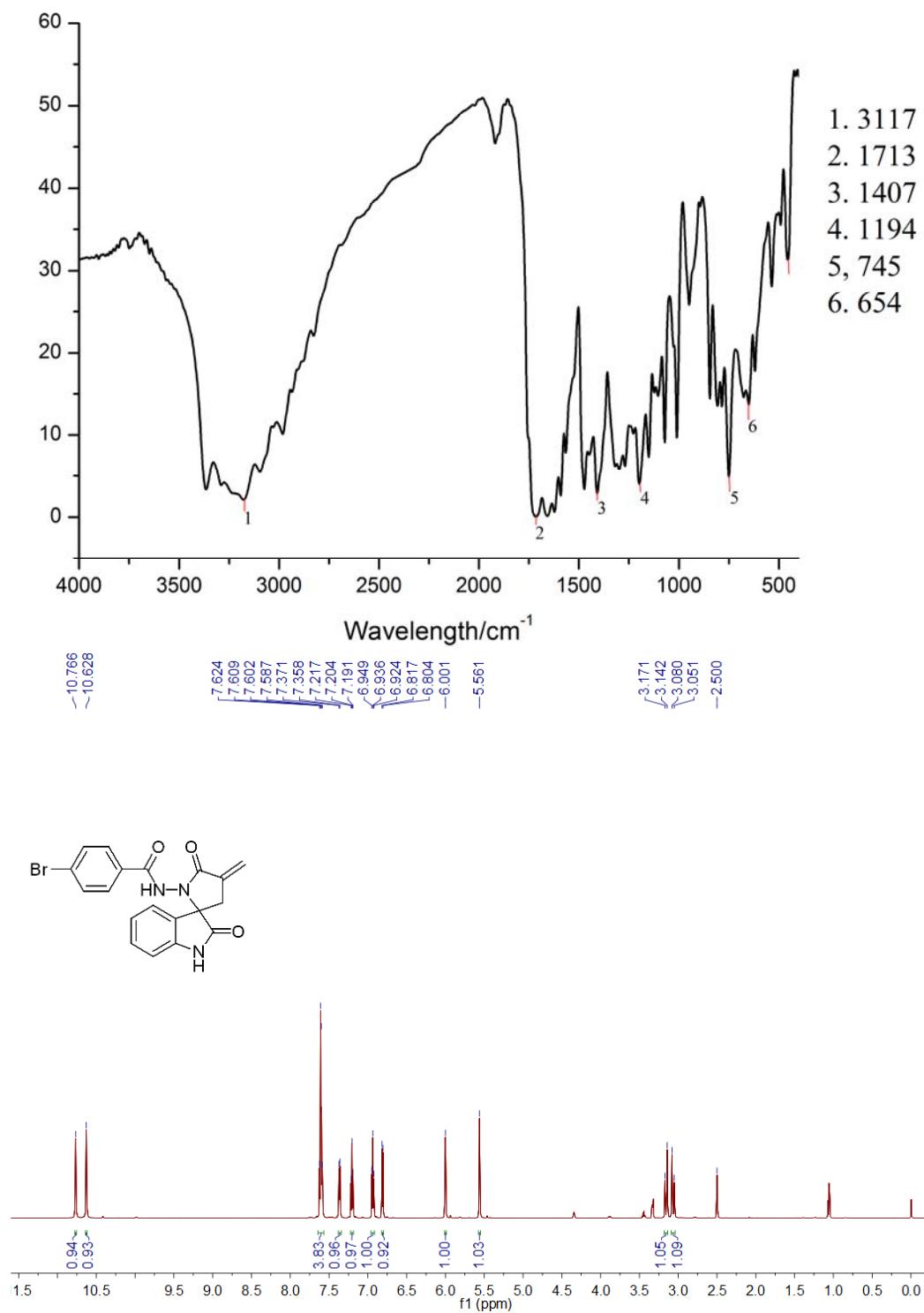


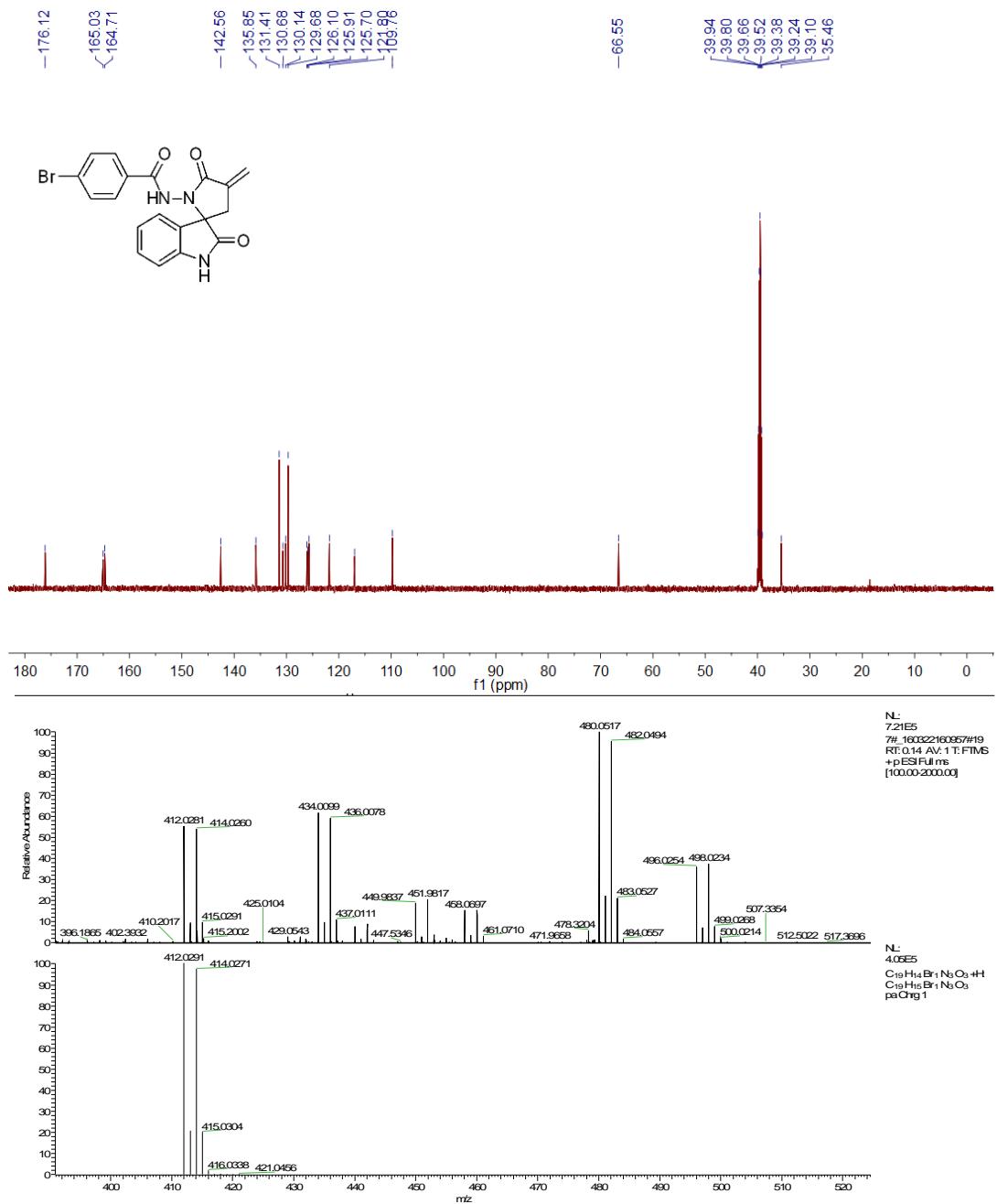
4-Chloro-N-(4'-methylene-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)-benzamide(4j)



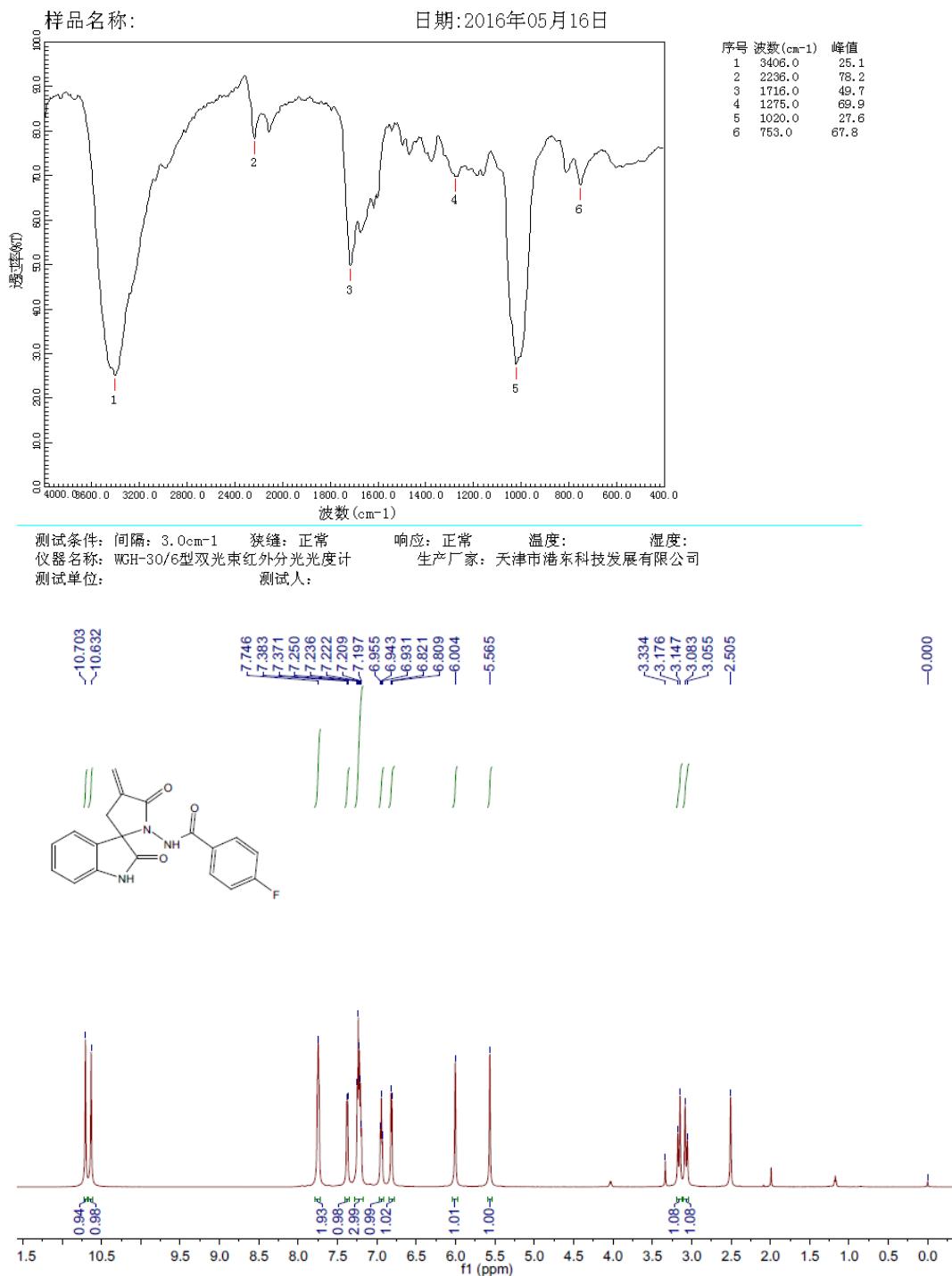


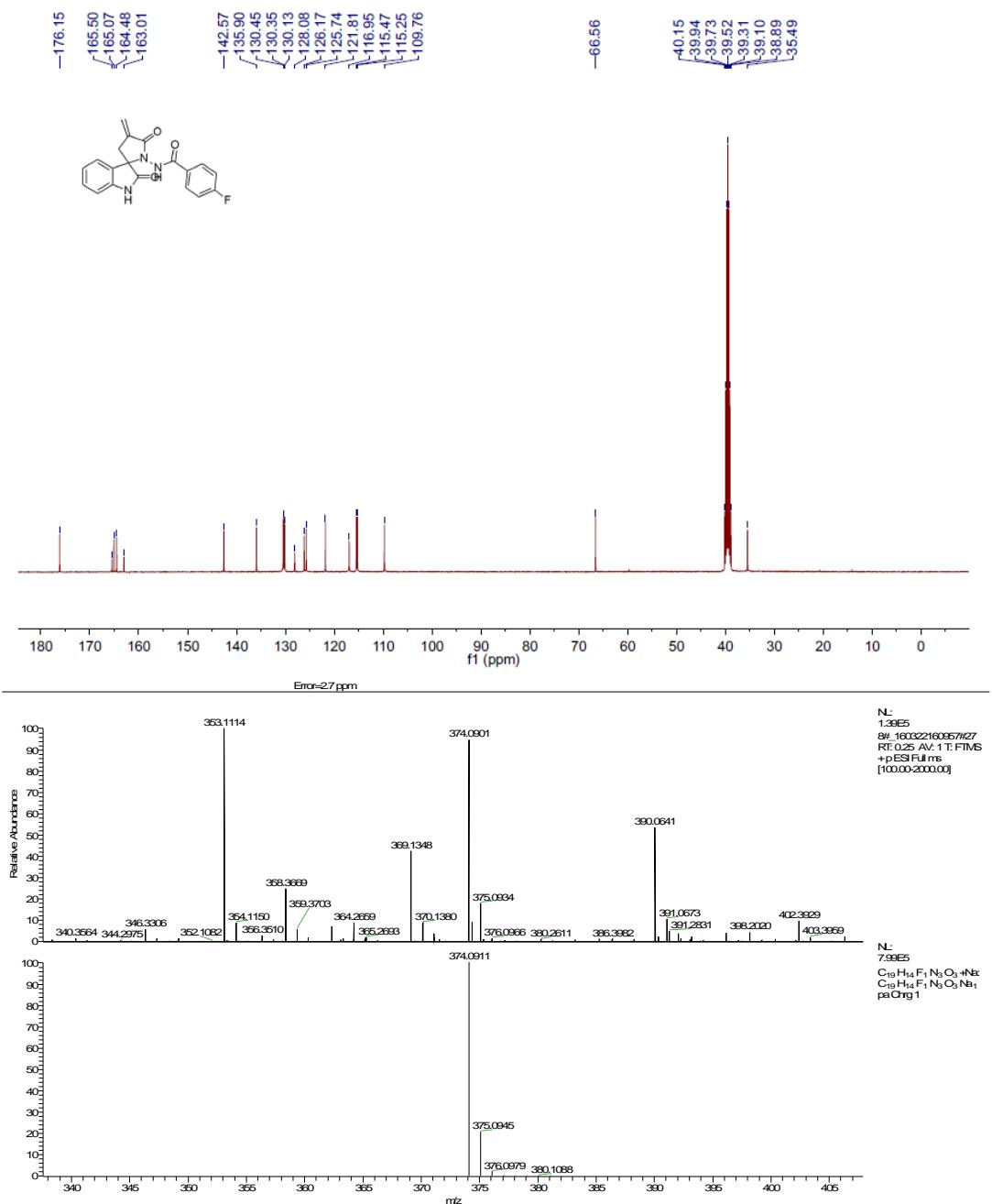
4-Bromo-N-(4'-methylene-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl) -benzamide(4k)



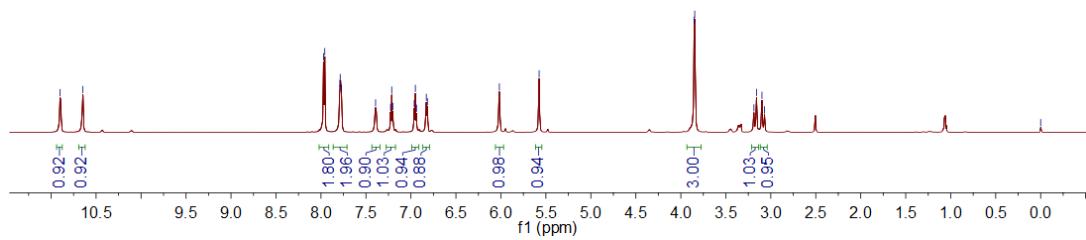
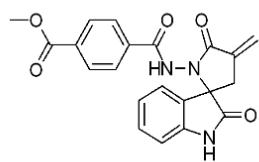
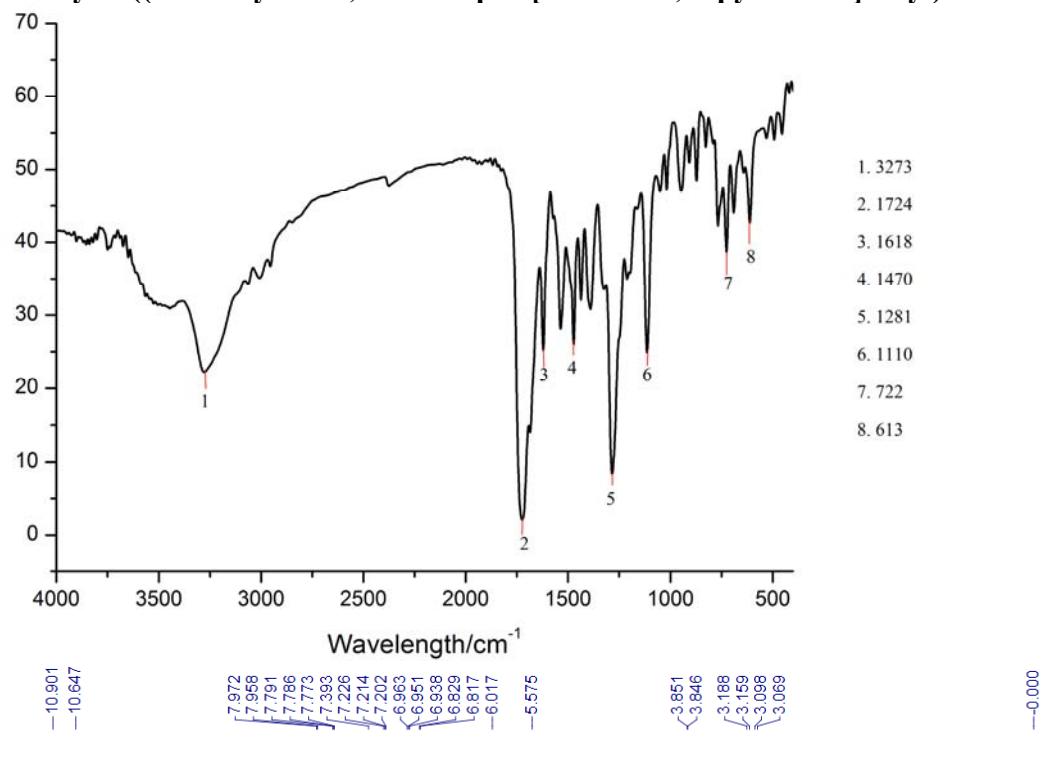


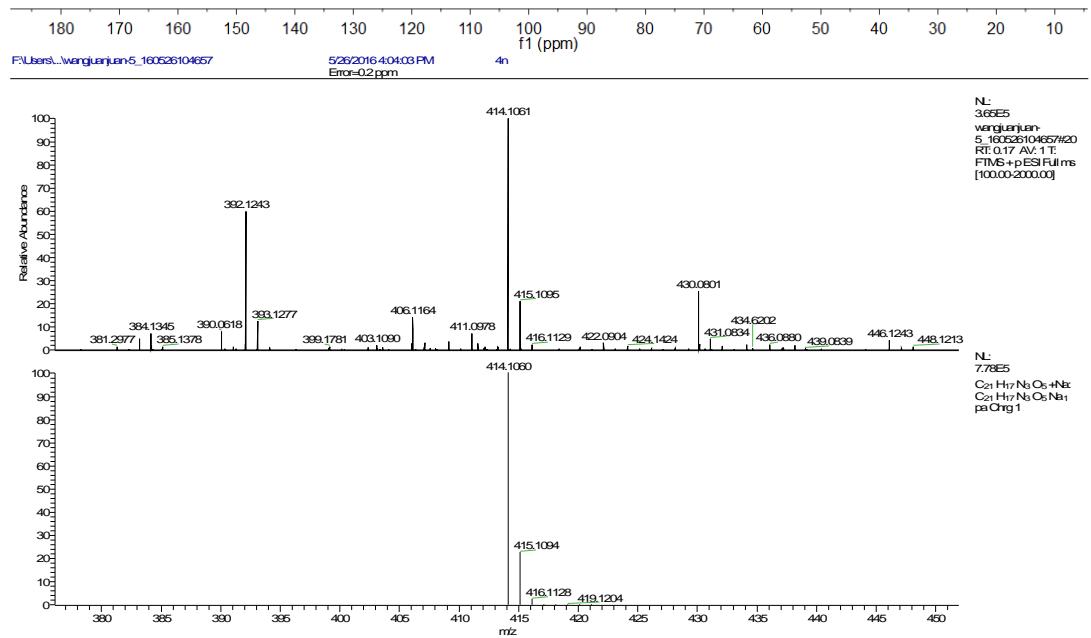
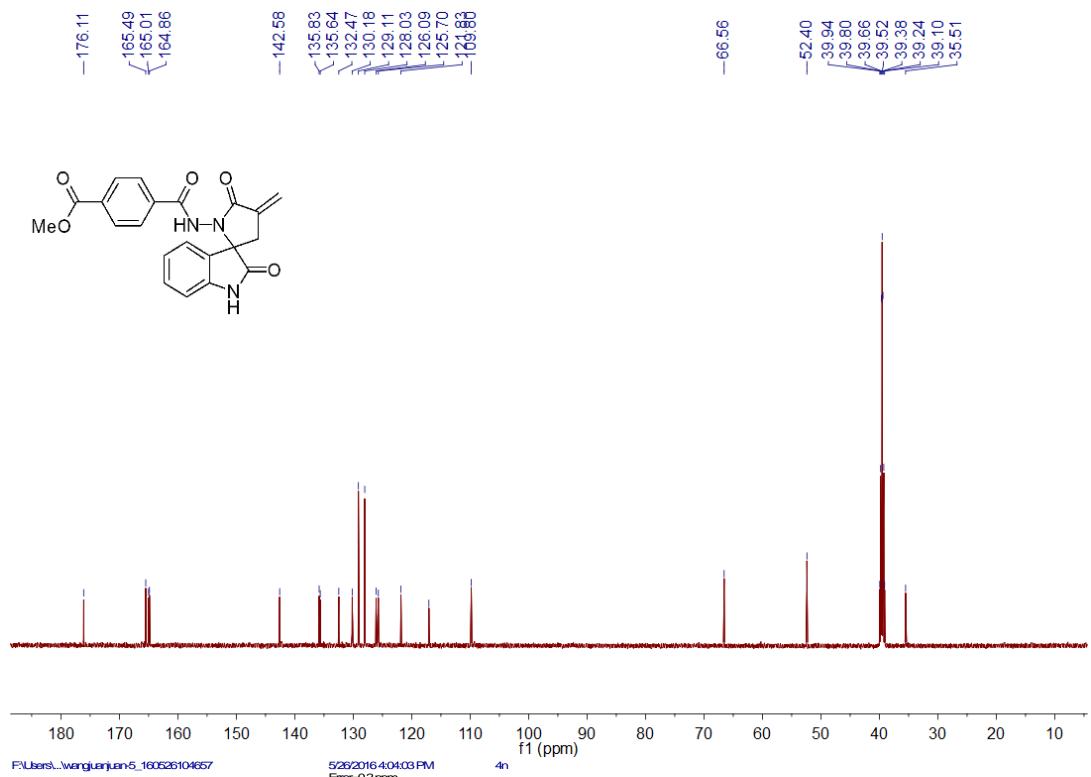
4-Fluoro-N-(4'-methylene-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)benzamide(4l)



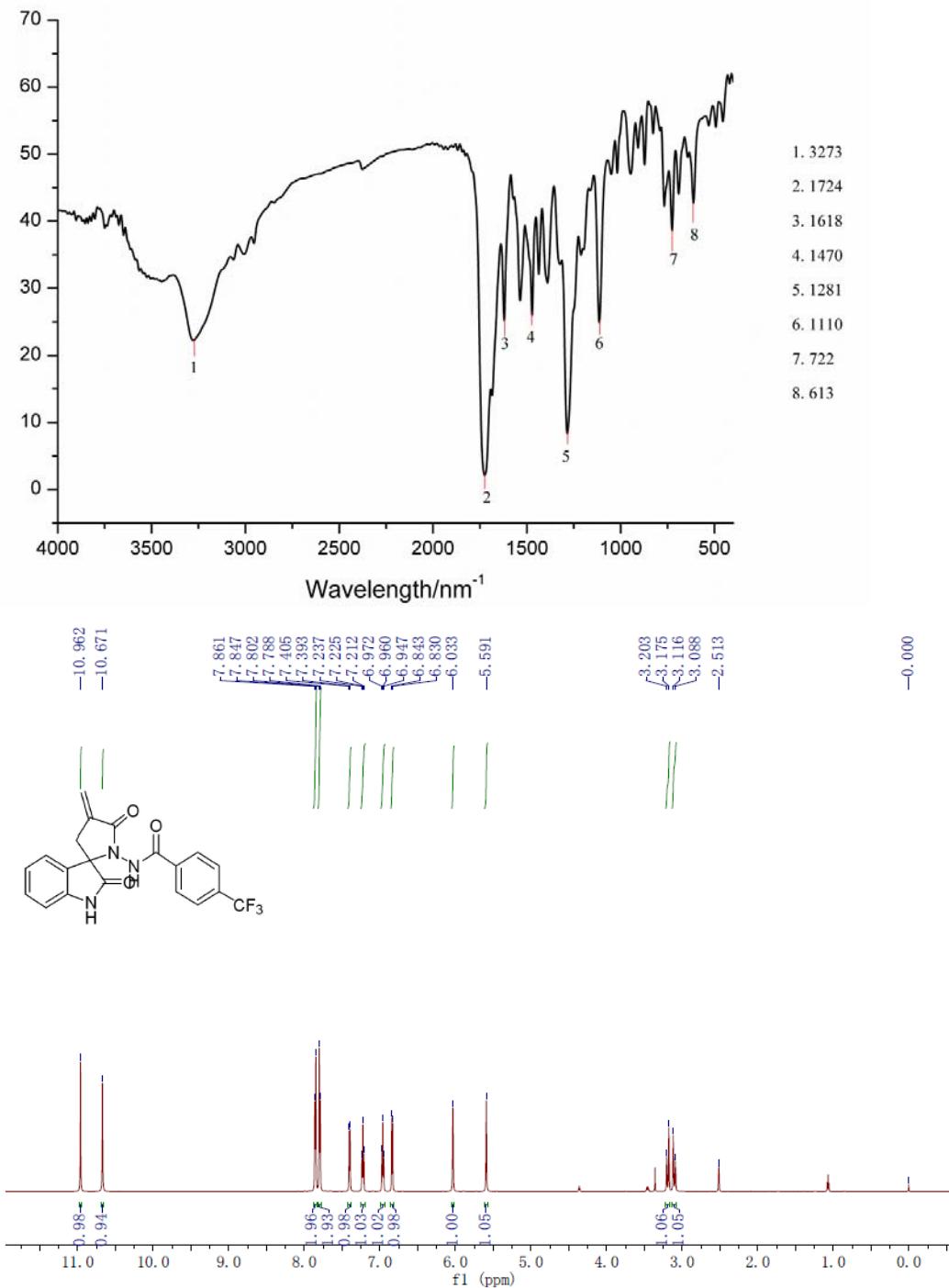


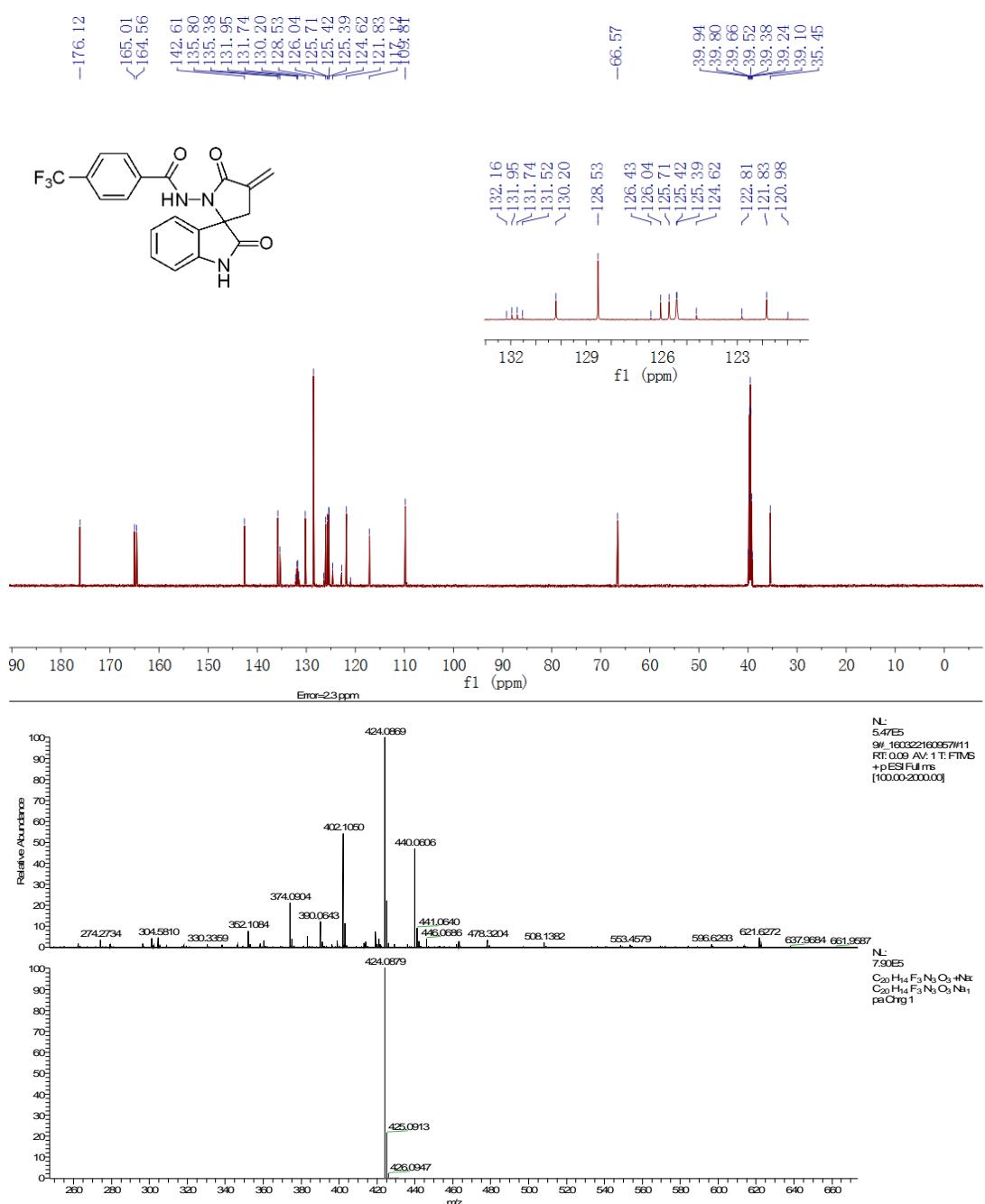
Methyl 4-((4'-methylene-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)carbamoyl)- benzoate(4n)





N-(4'-Methylene-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)-4-(trifluoromethyl)benzamide(4o)

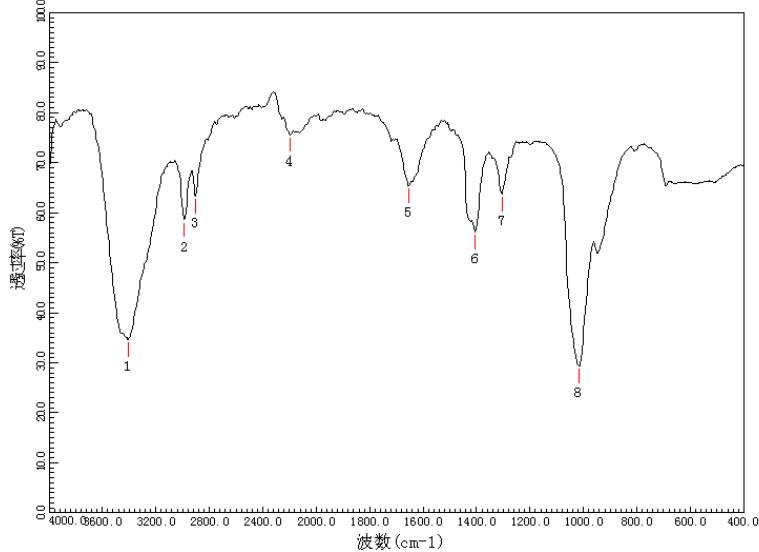




4-Chloro-N-(5-methyl-4'-methylen-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)-benzamide(4q)

样品名称:

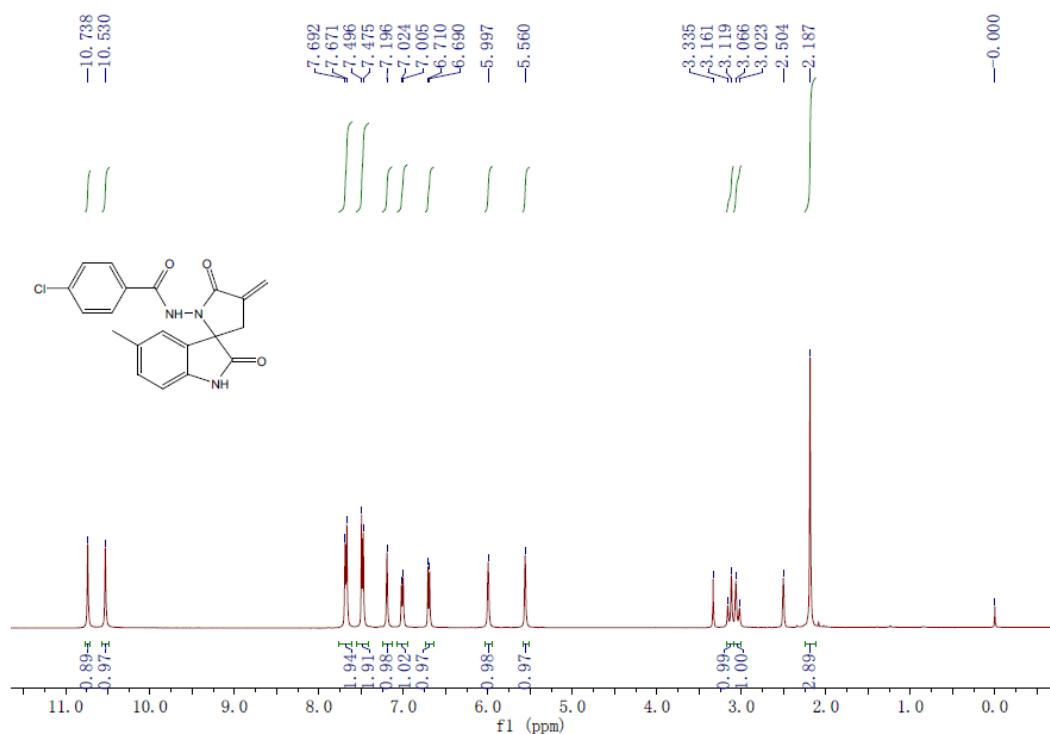
日期:2016年05月16日

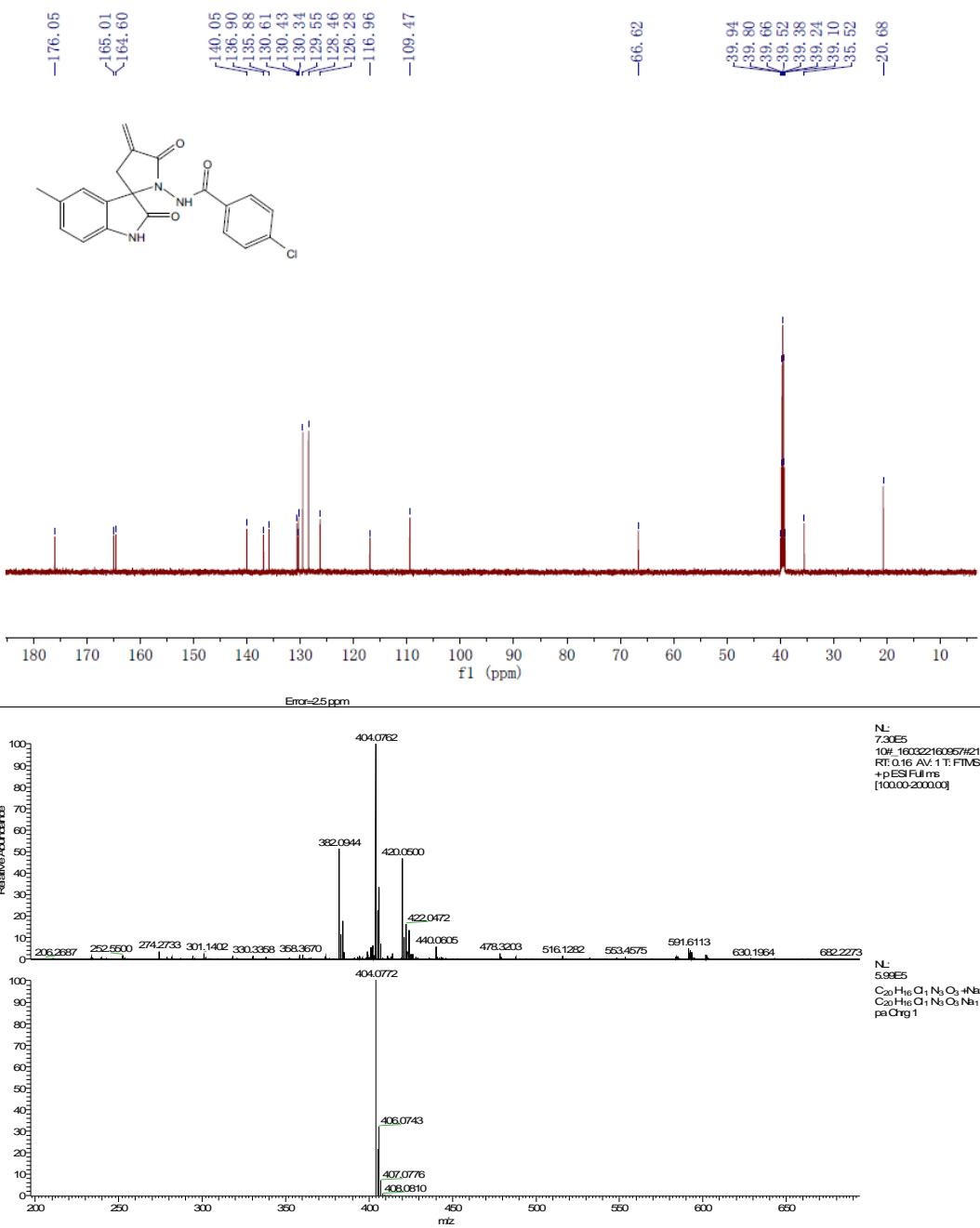


序号	波数(cm⁻¹)	峰值
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2	2986.0	58.6
3	2902.0	63.3
4	2194.0	75.6
5	1653.0	65.4
6	1404.0	56.1
7	1305.0	63.7
8	1017.0	29.4

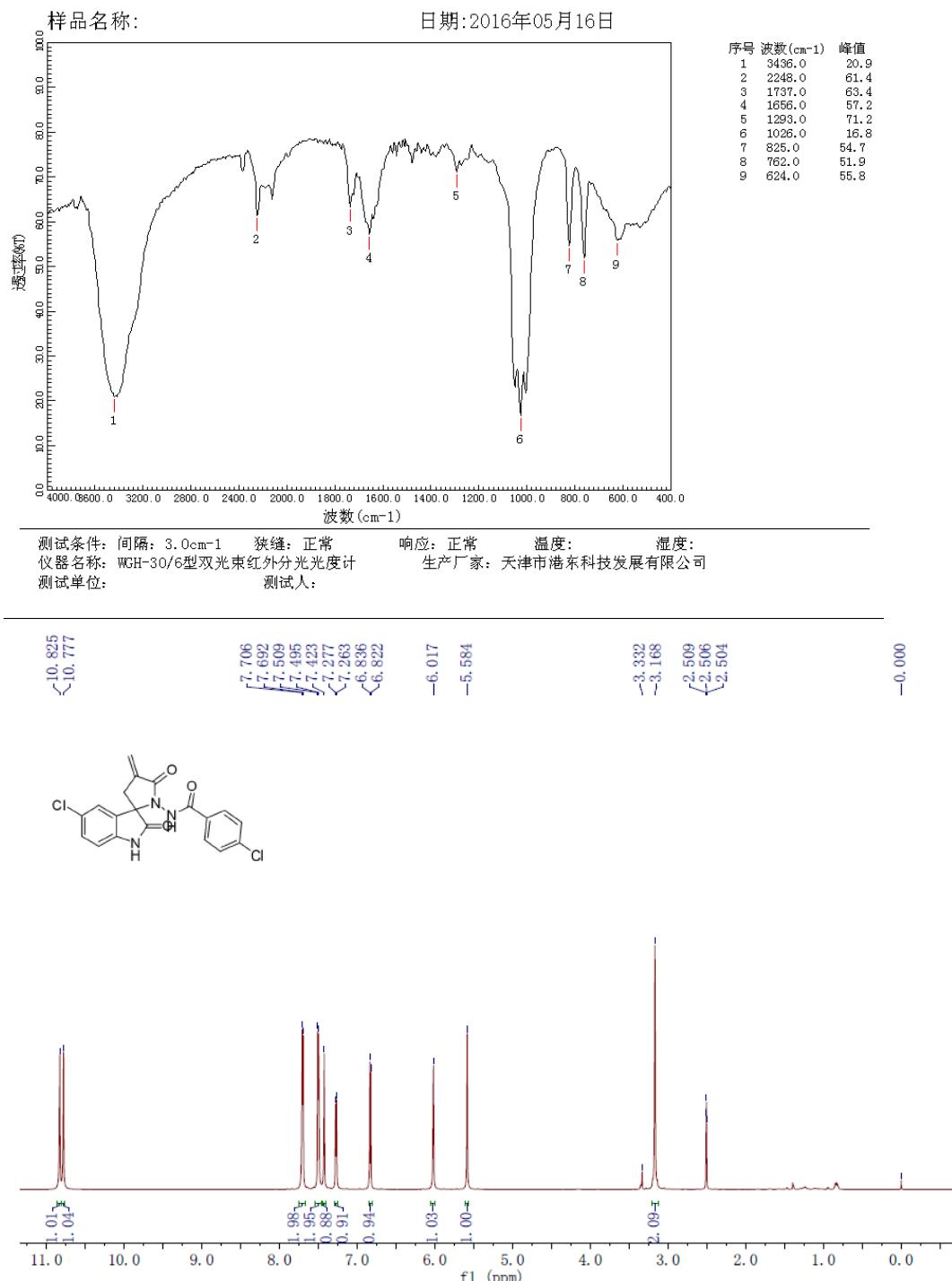
测试条件: 间隔: 3.0cm⁻¹ 狭缝: 正常
仪器名称: WGH-30/6型双光束红外分光光度计
测试单位:

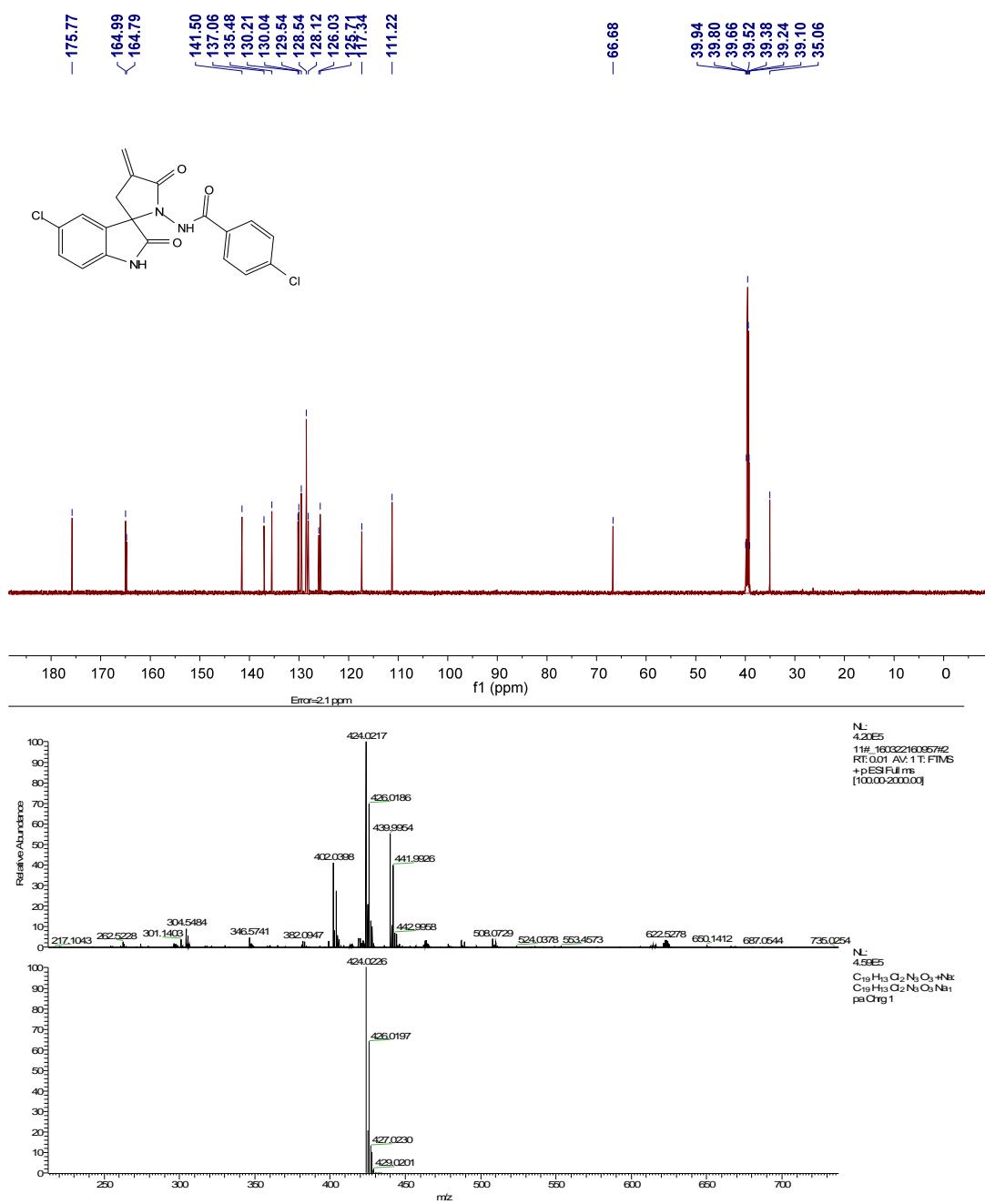
响应: 正常 温度: 湿度:
生产厂家: 天津市浦东科技发展有限公司
测试人:



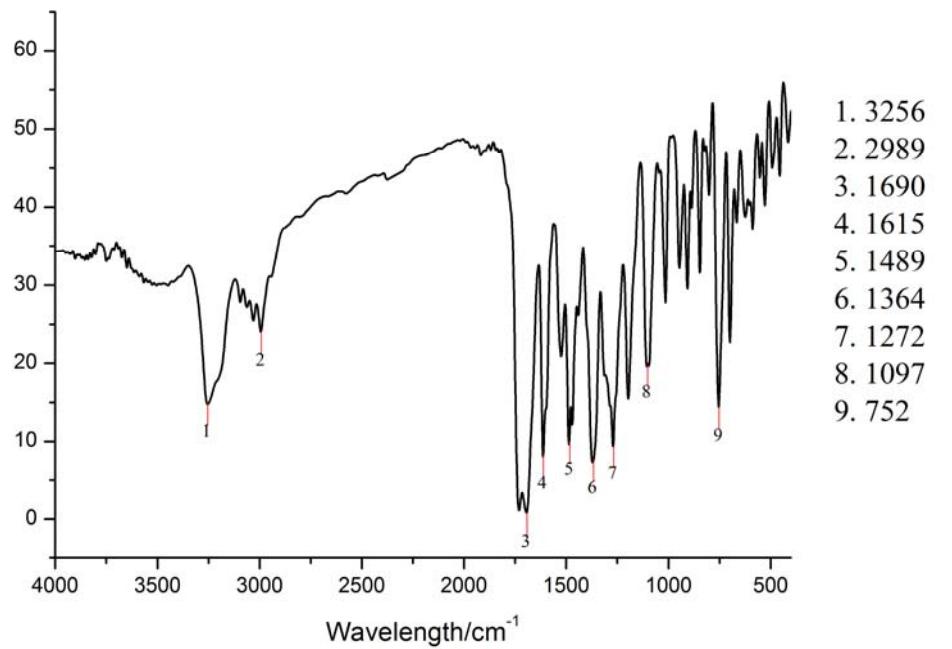


4-Chloro-N-(5-chloro-4'-methylen-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl) -benzamide(4r)

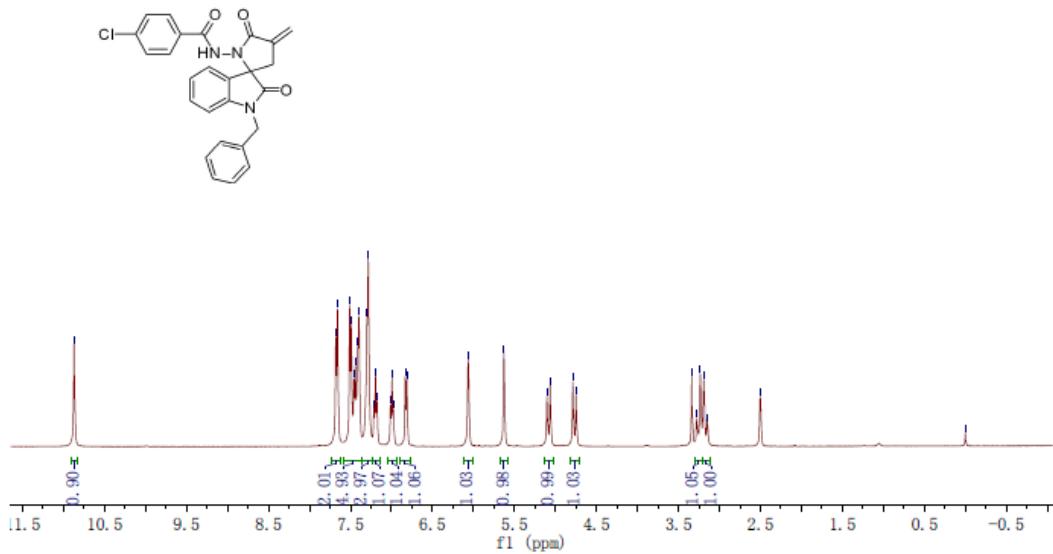
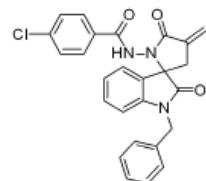


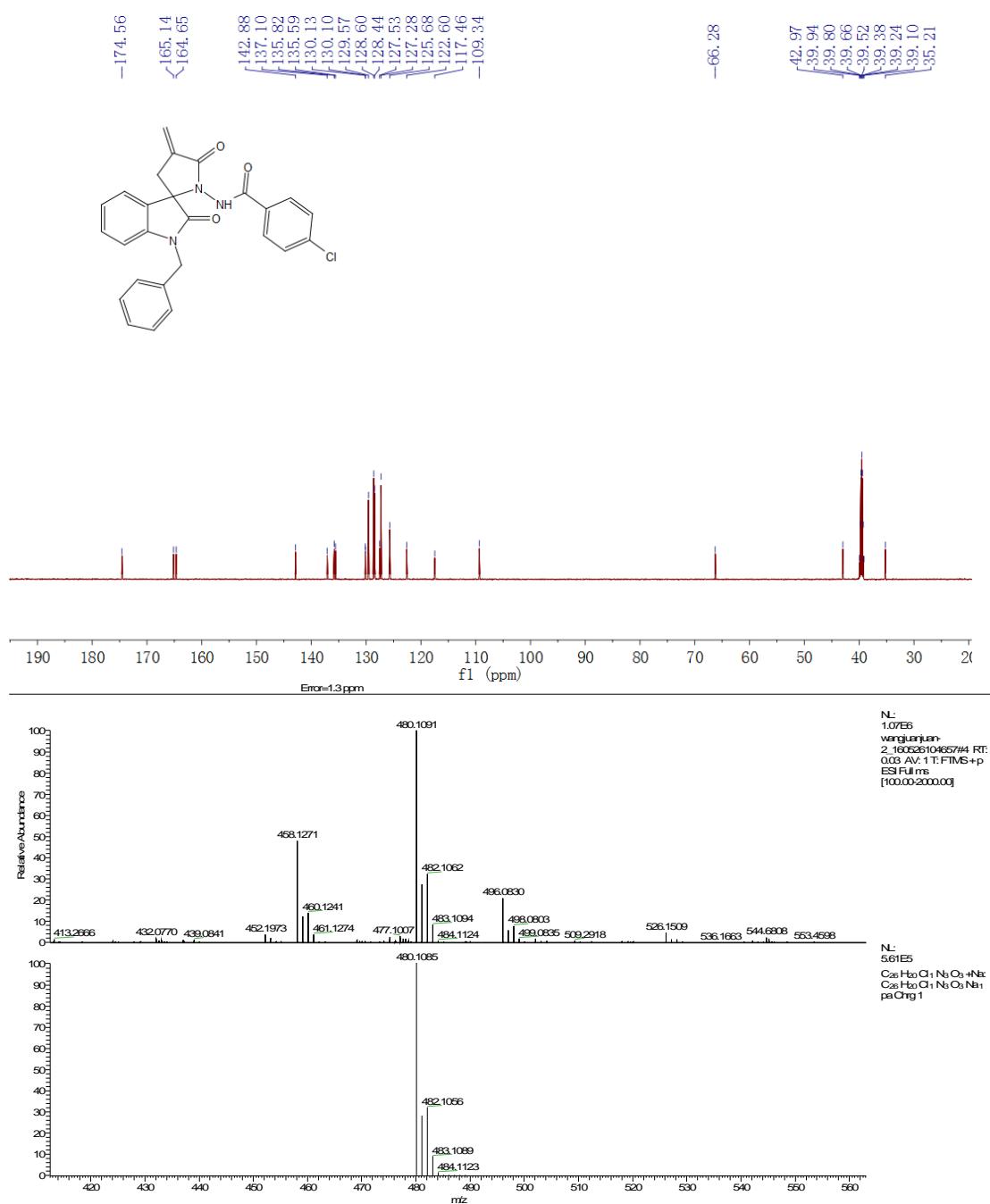


N-(1-Benzyl-4'-methylene-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)-4-chlorobenzamide(4s)

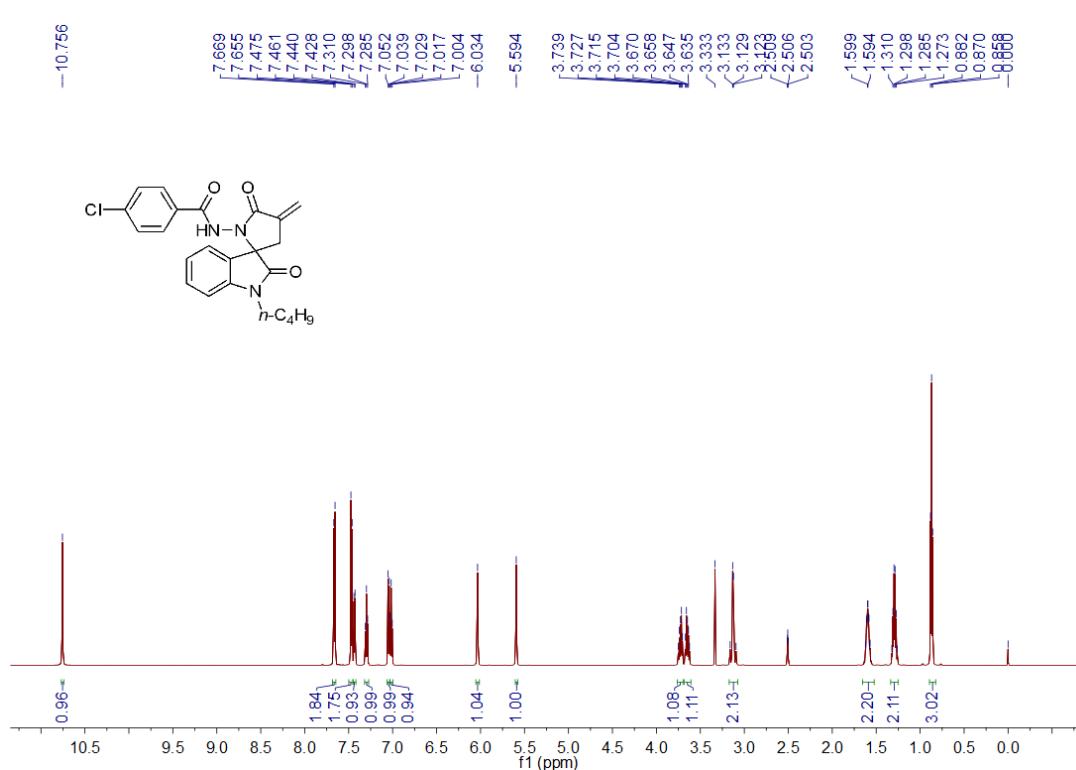
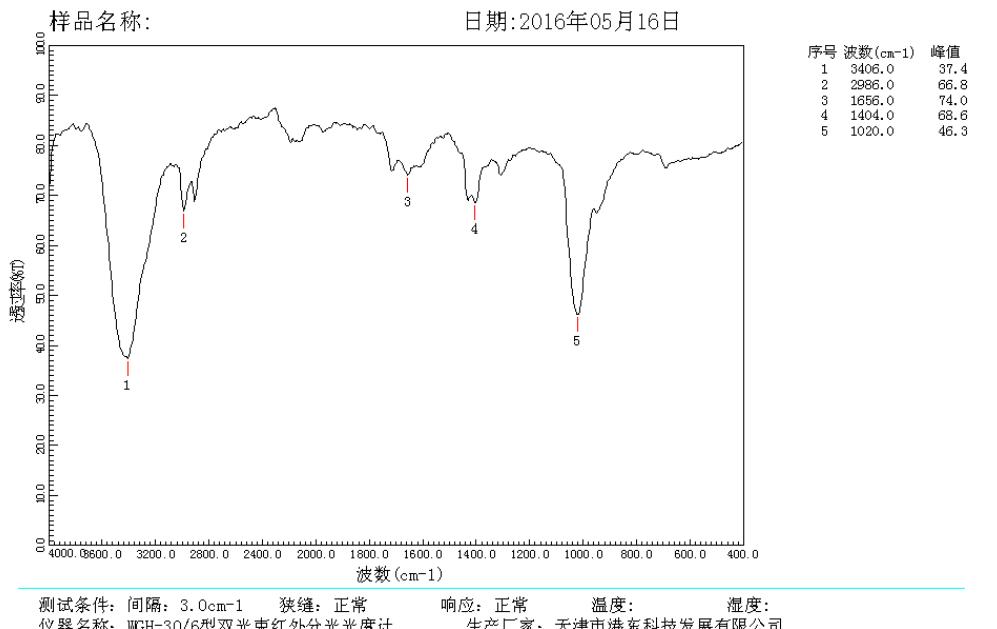


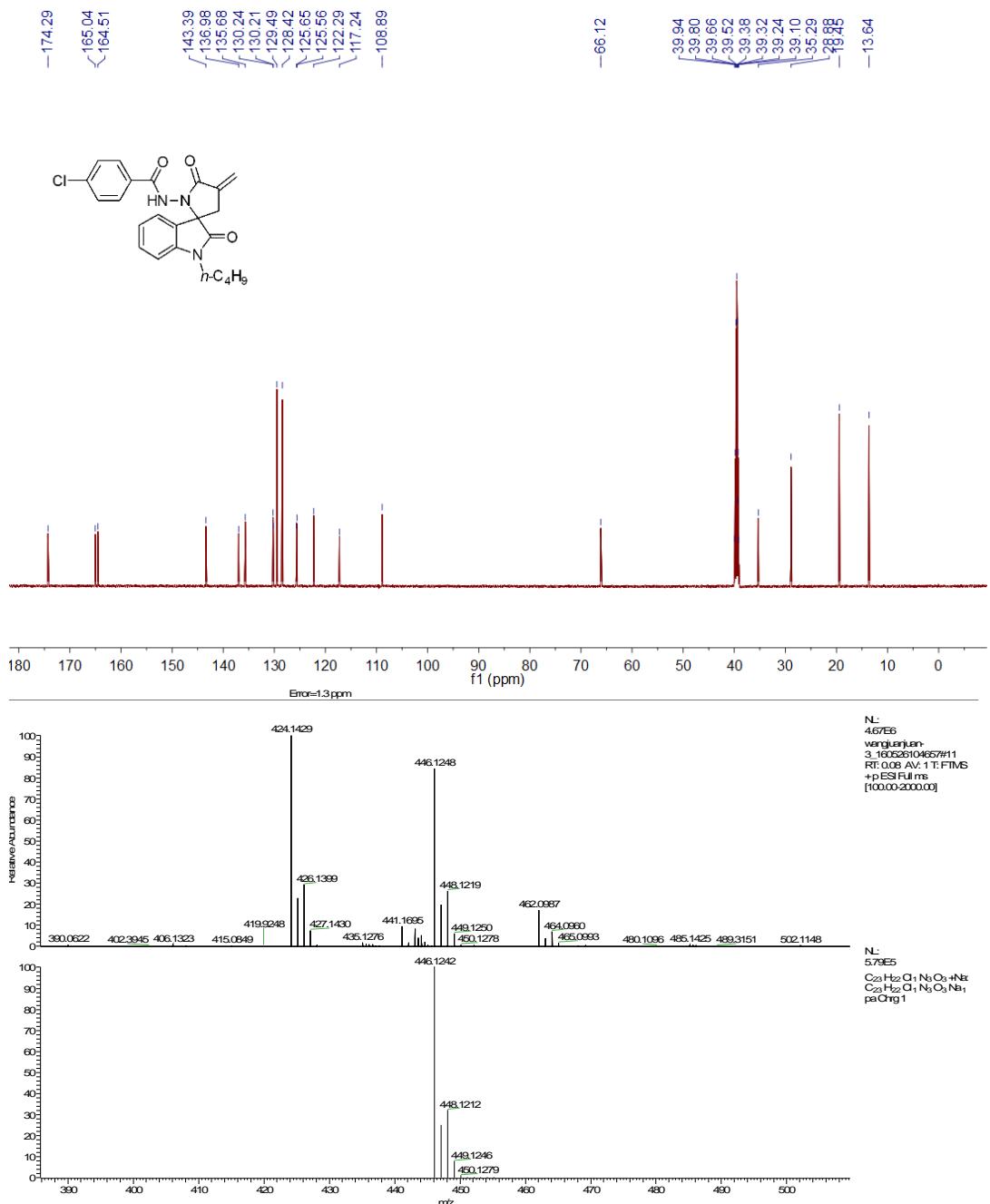
Wavenumbers/cm⁻¹: 3388, 2976, 2333, 1911, 1483, 1252, 1000



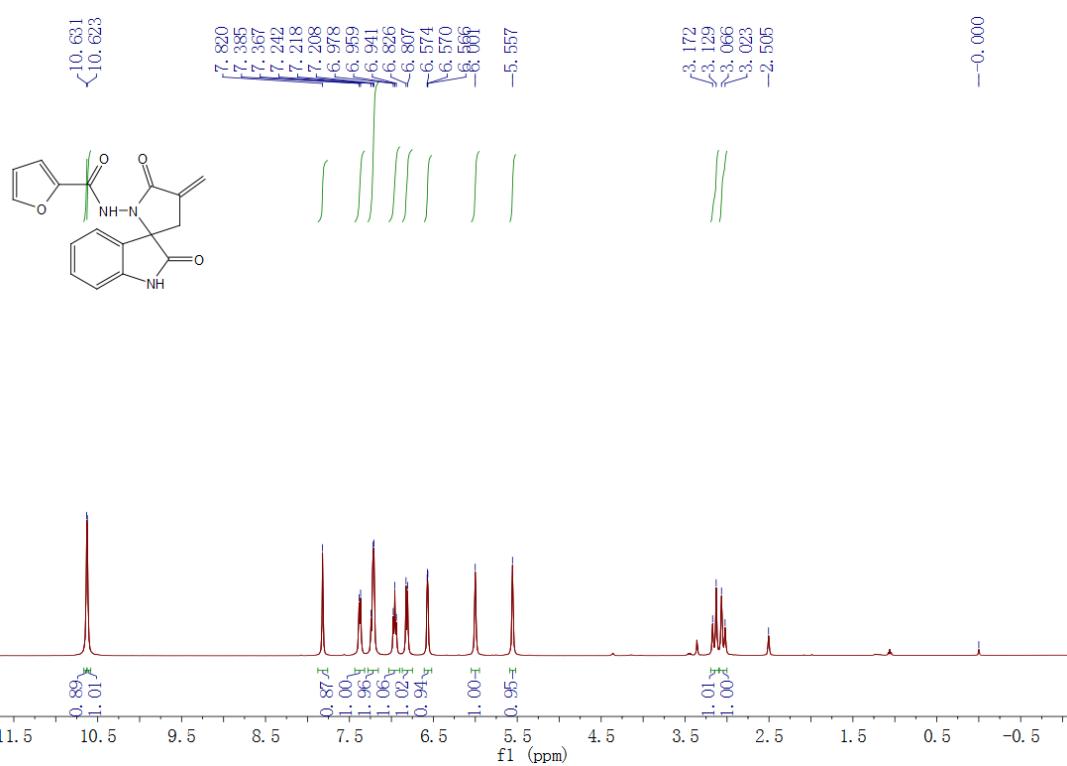
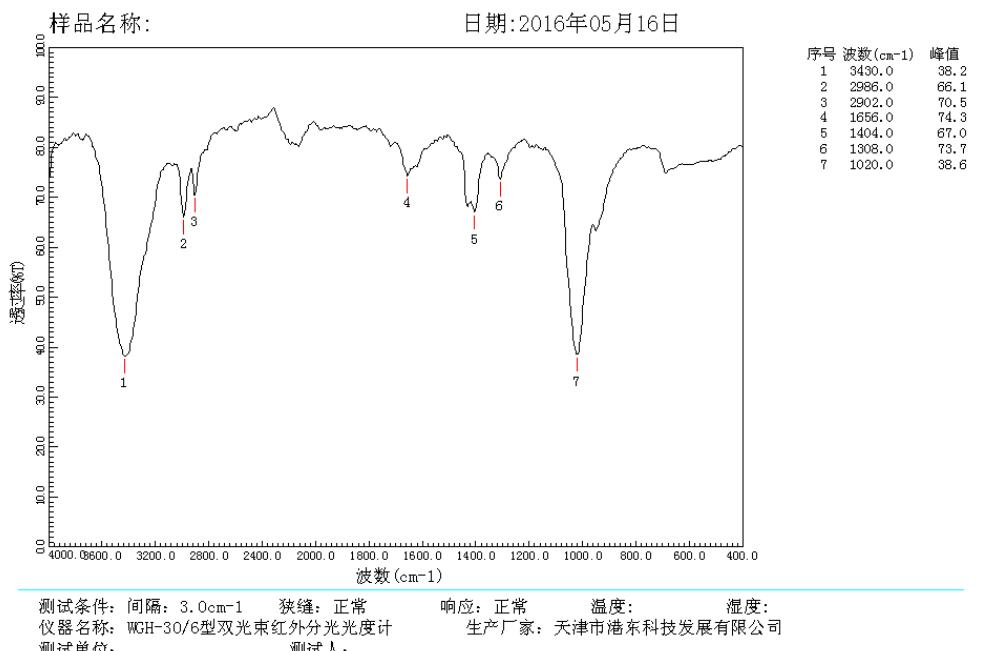


N-(1-Butyl-4'-methylene-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)-4-chlorobenzamide(4t)

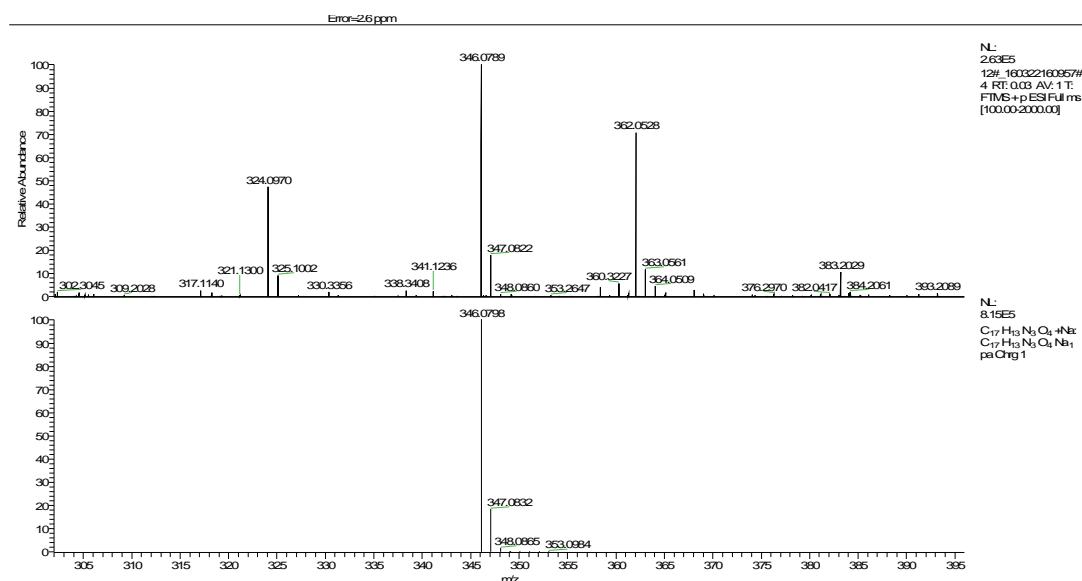
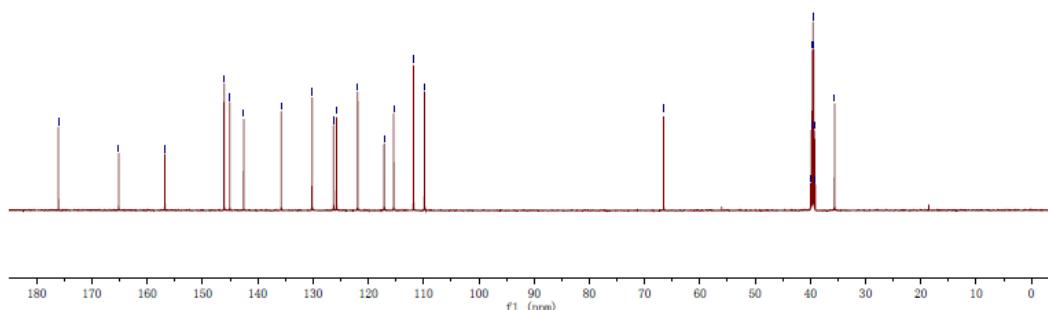
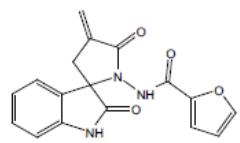




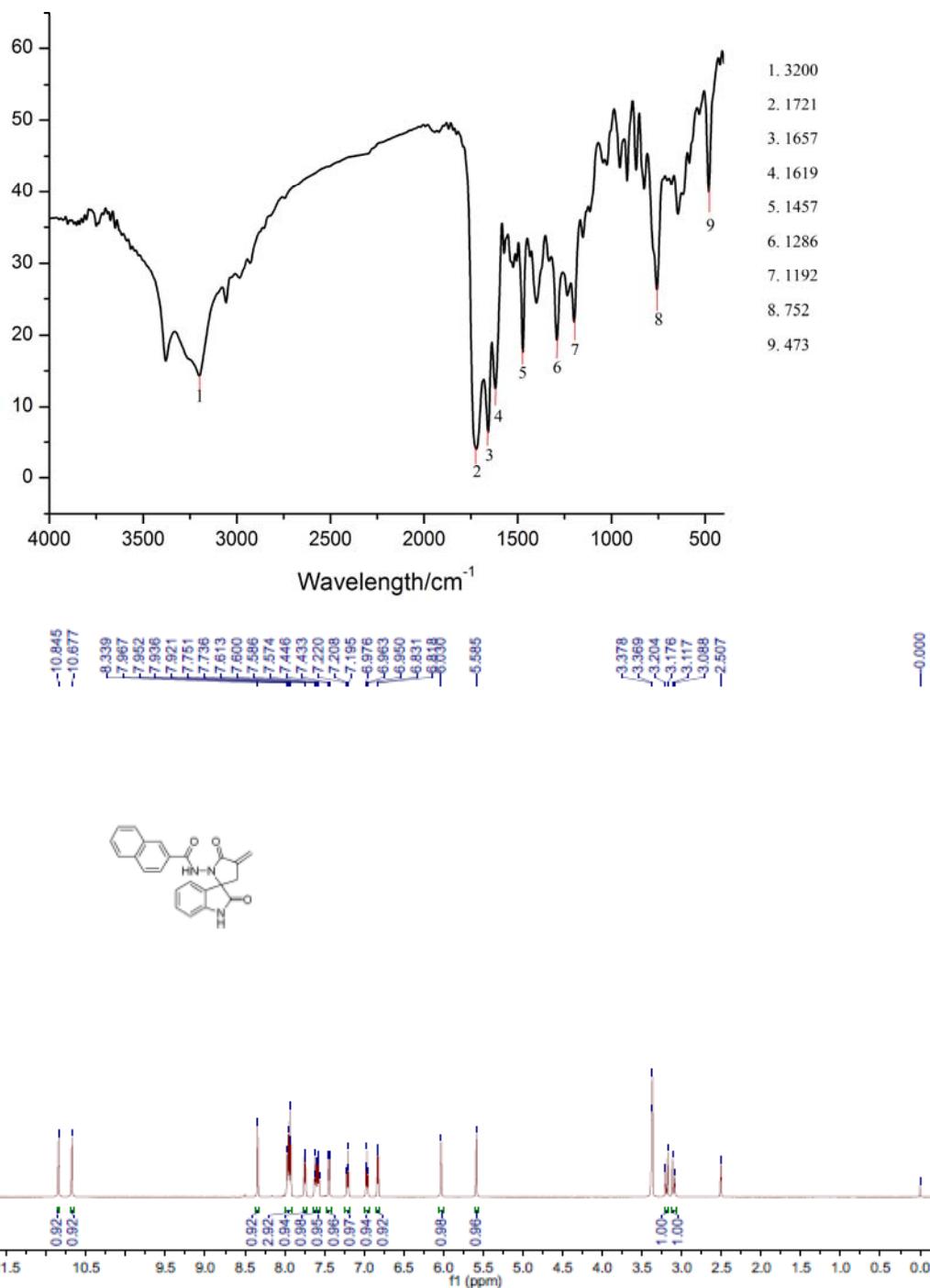
N-(4'-Methylene-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)furan -2-carboxamide(4u)

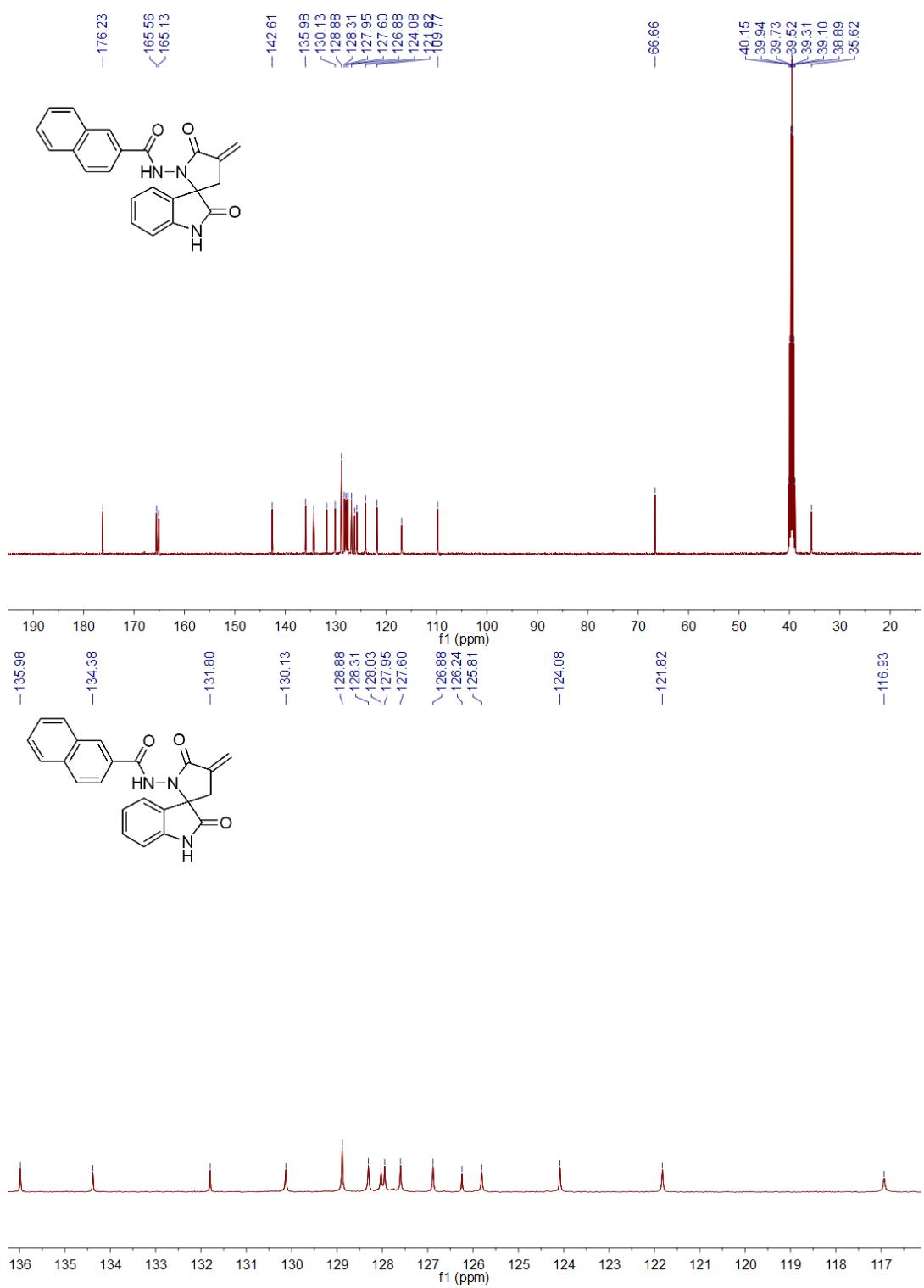


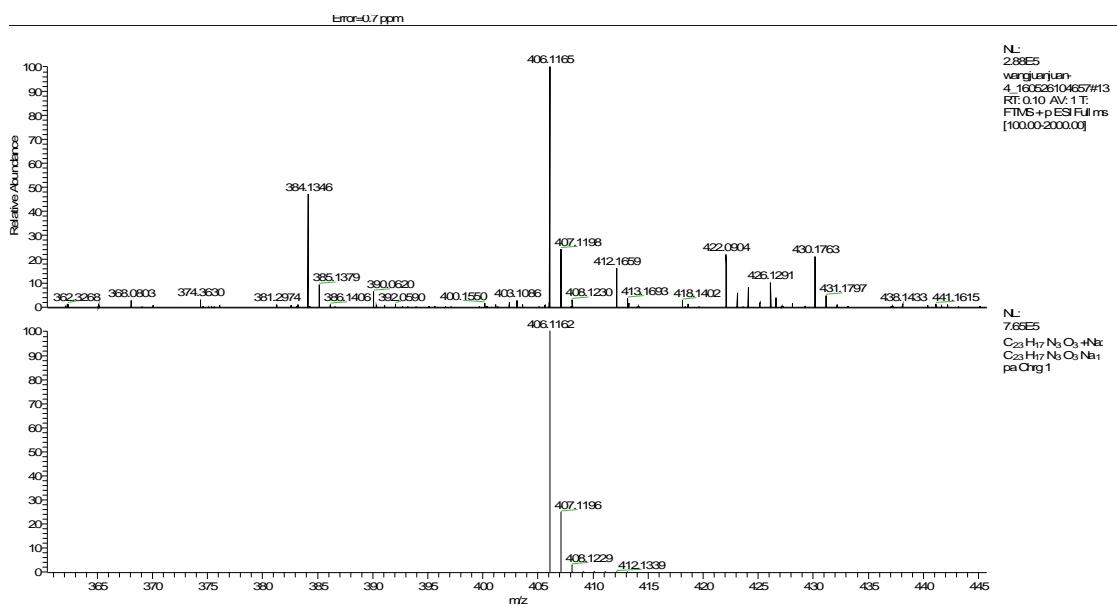
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 -156.81
 146.09
 145.07
 142.54
 135.75
 130.16
 126.29
 125.75
 121.91
 117.12
 115.40
 111.81
 109.83



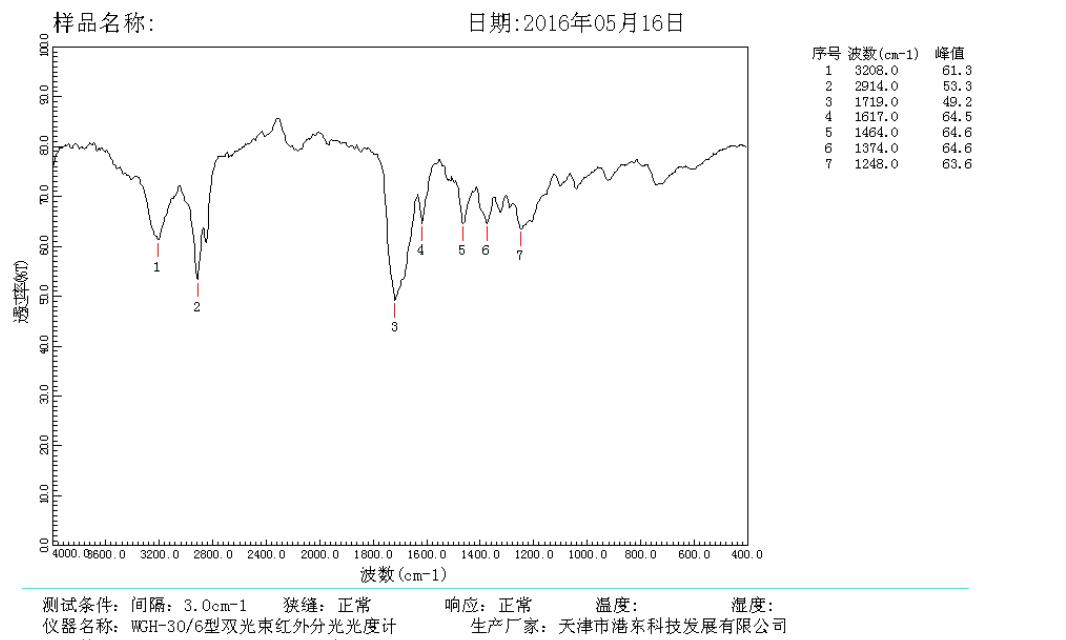
N-(4'-Methylene-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)-2-naphthamide (4v)



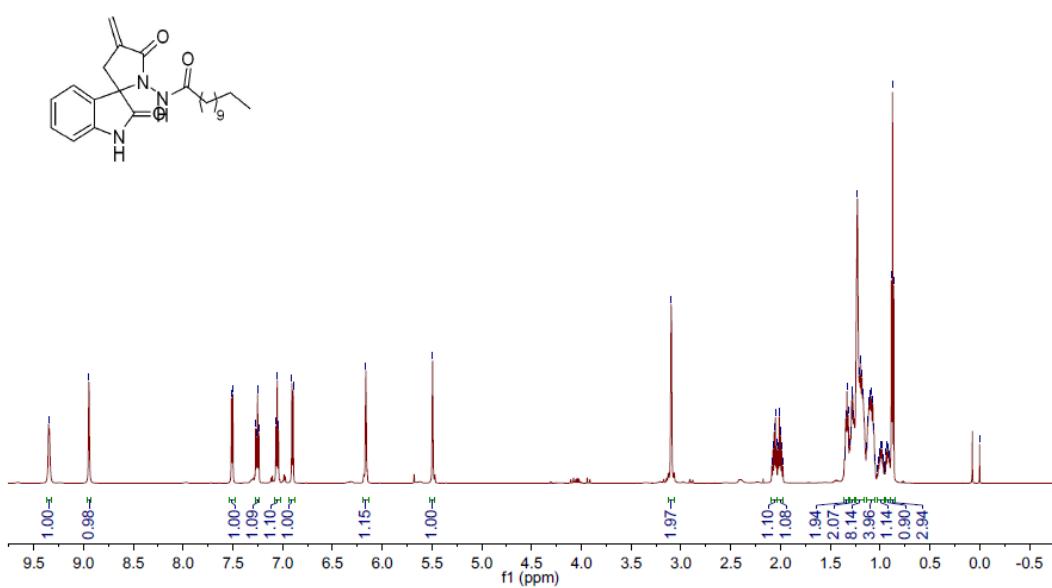


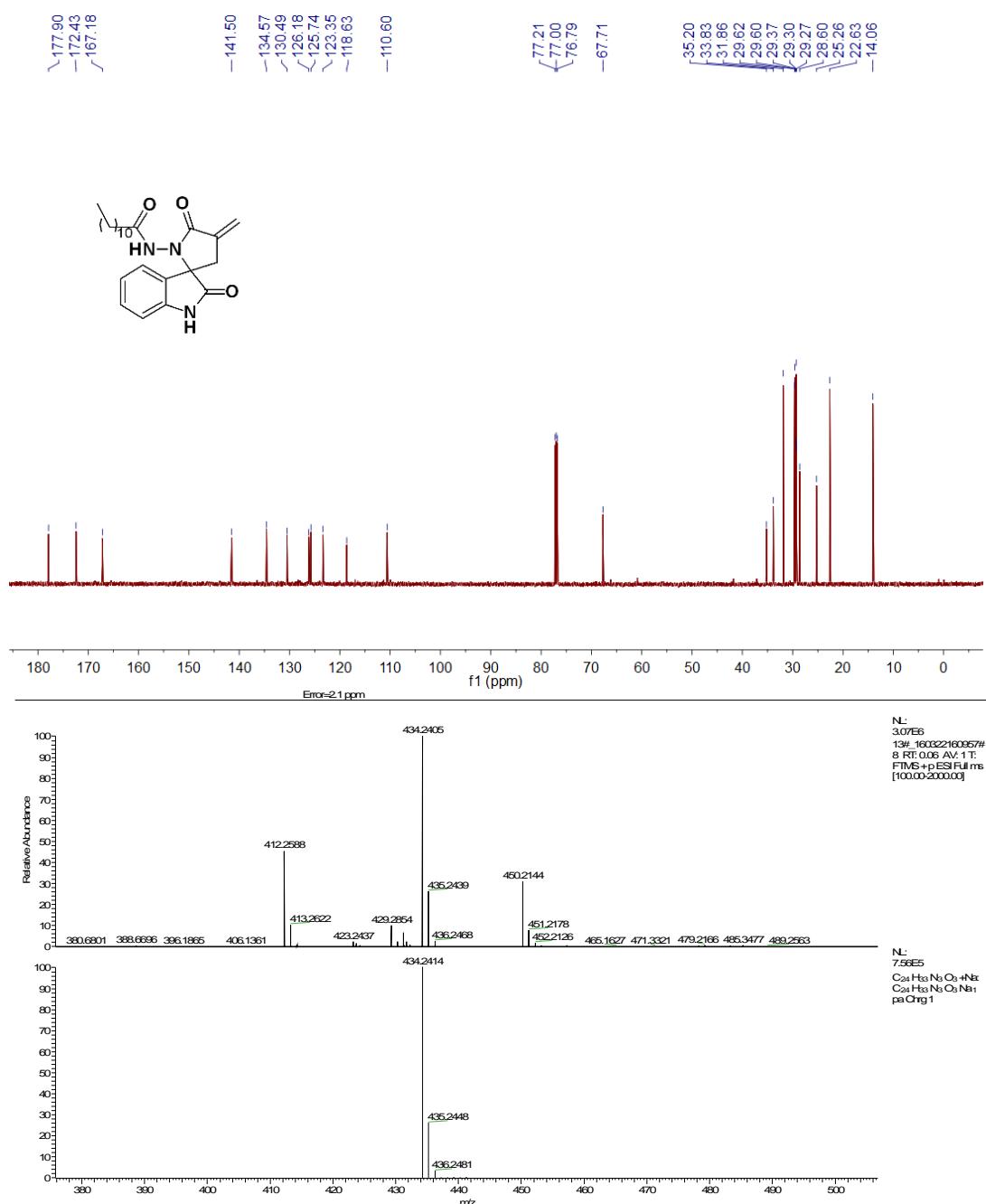


N-(4'-Methylene-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)dodecanamide (4w)

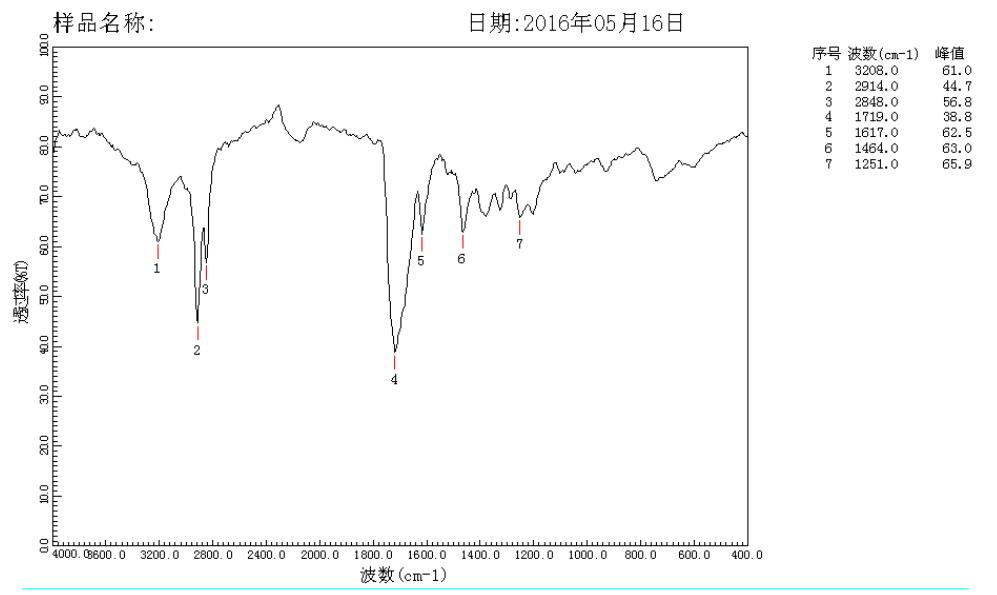


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8.513
7.501
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7.239
7.067
7.055
7.042
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6.894
6.164
5.494
3.098
2.000
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1.356
1.344
1.332
1.320
1.205
1.306
1.193
1.182
1.172
1.175
1.126
1.127
1.125
1.111
1.100
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1.073
1.065
1.051
1.004
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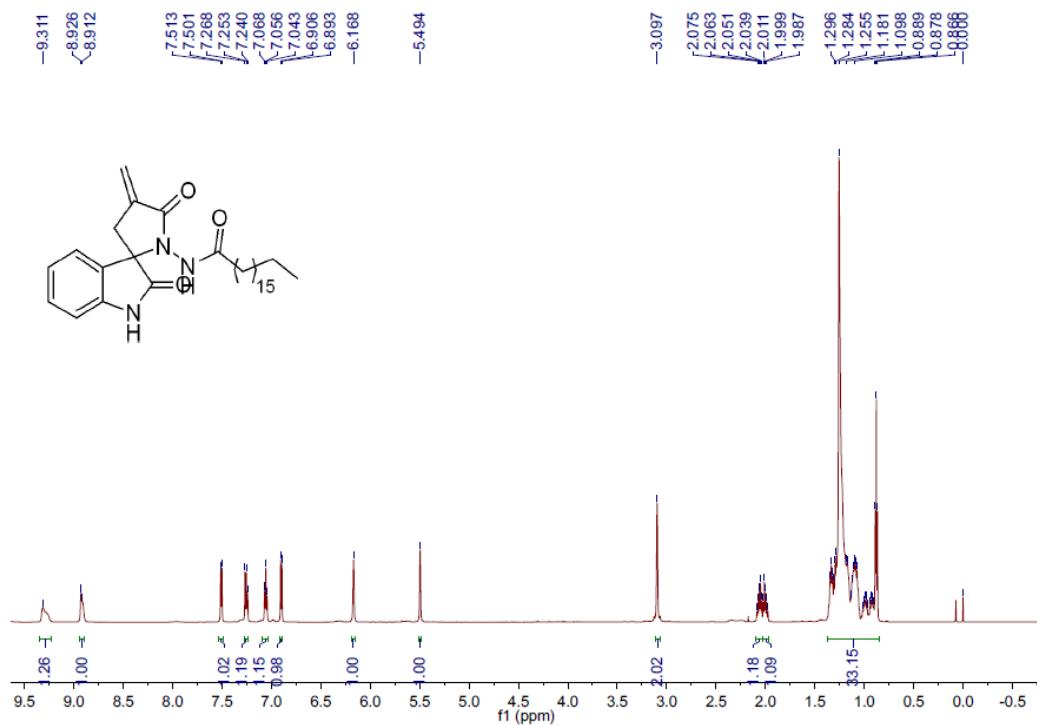


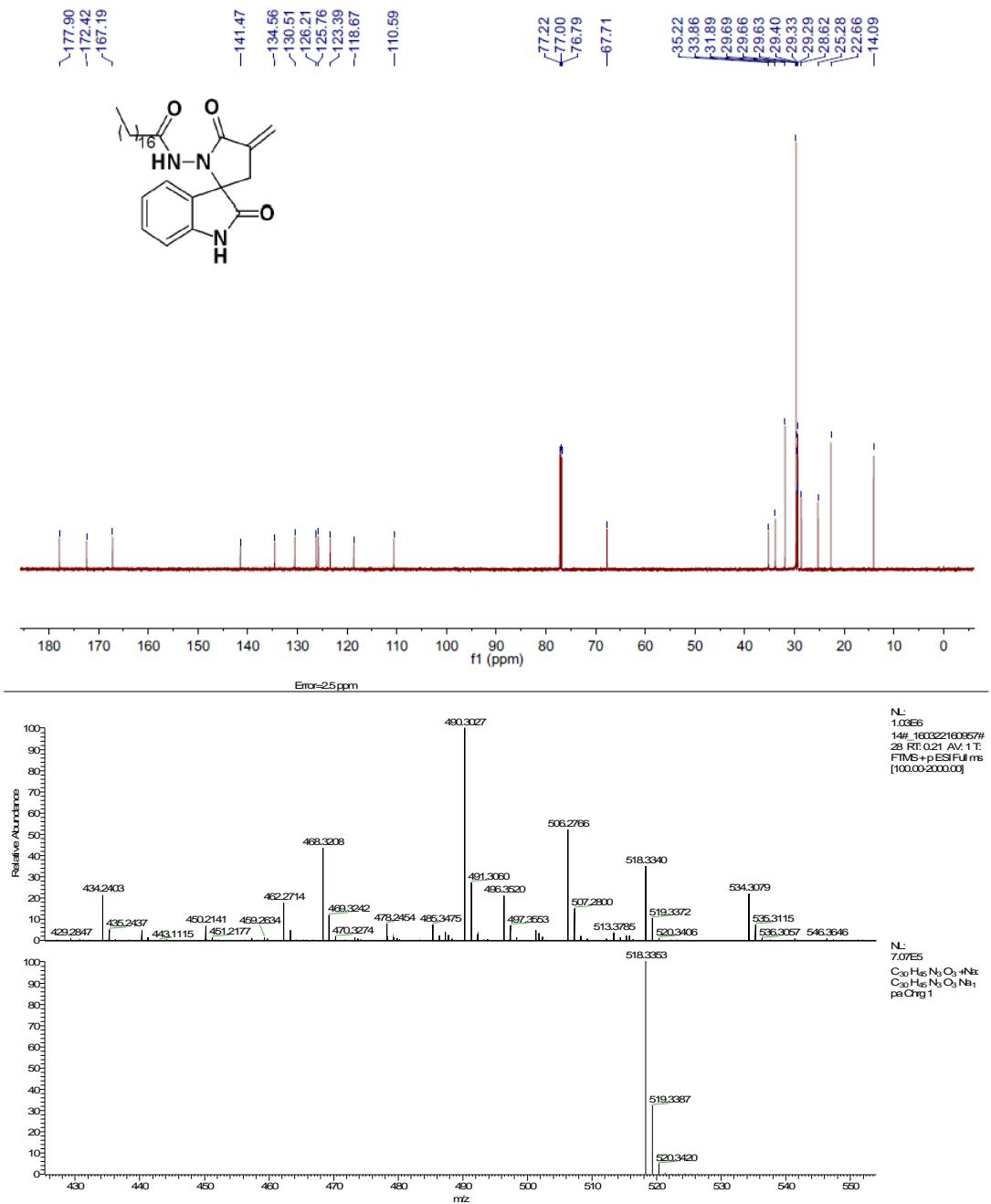


N-(4'-Methylene-2,5'-dioxospiro[indoline-3,2'-pyrrolidin]-1'-yl)stearamide (4x)

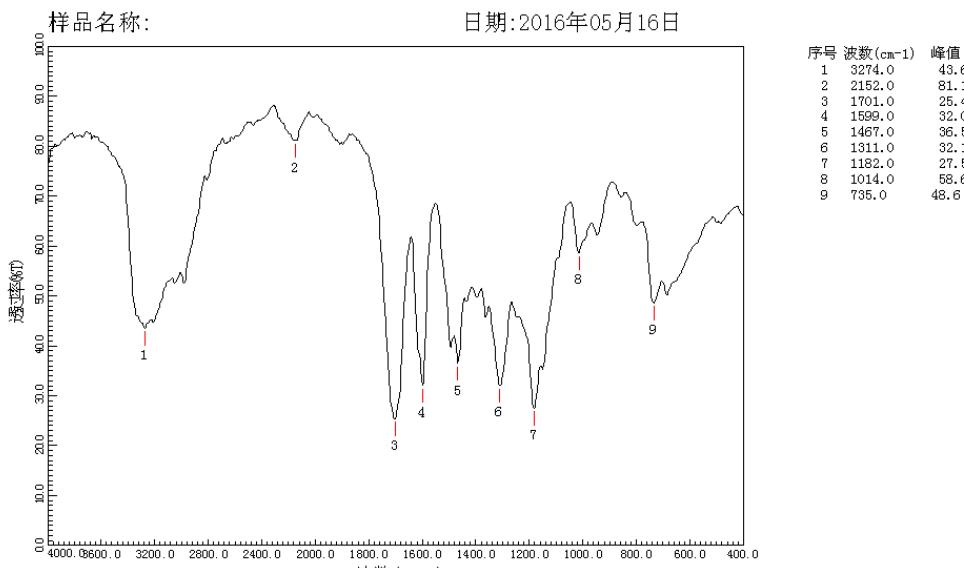


测试条件: 间隔: 3.0 cm^{-1} 狹缝: 正常 响应: 正常 温度: 湿度:
仪器名称: WGH-30/6型双光束红外分光光度计 生产厂家: 天津市浦东科技发展有限公司
测试单位: 测试人:

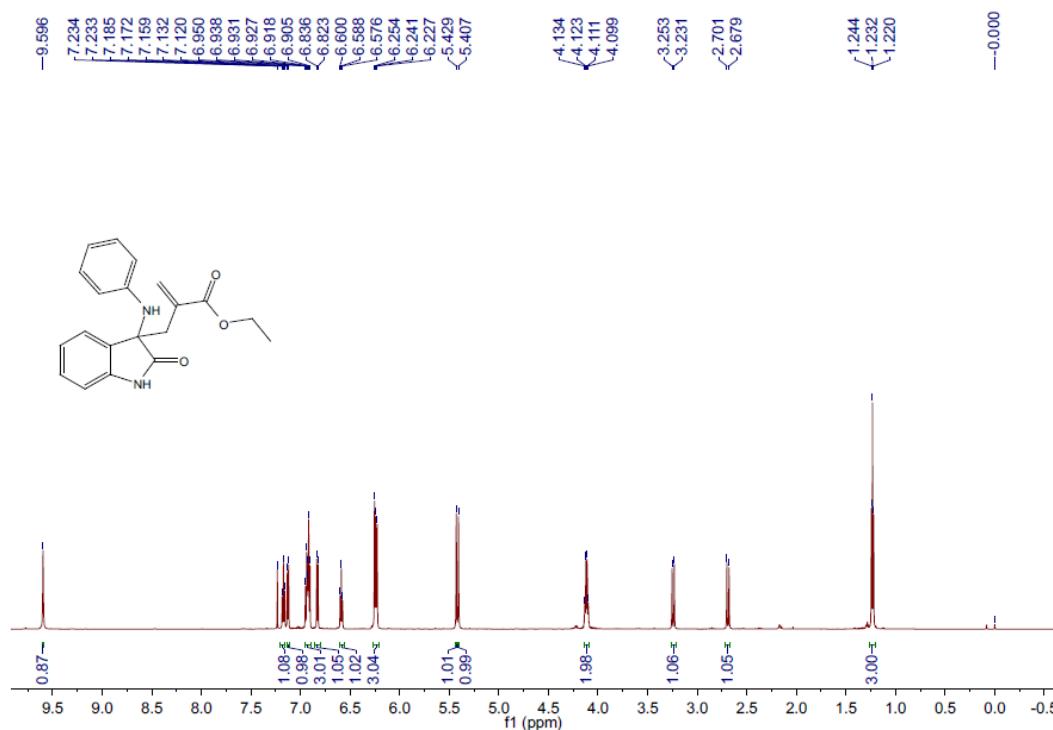


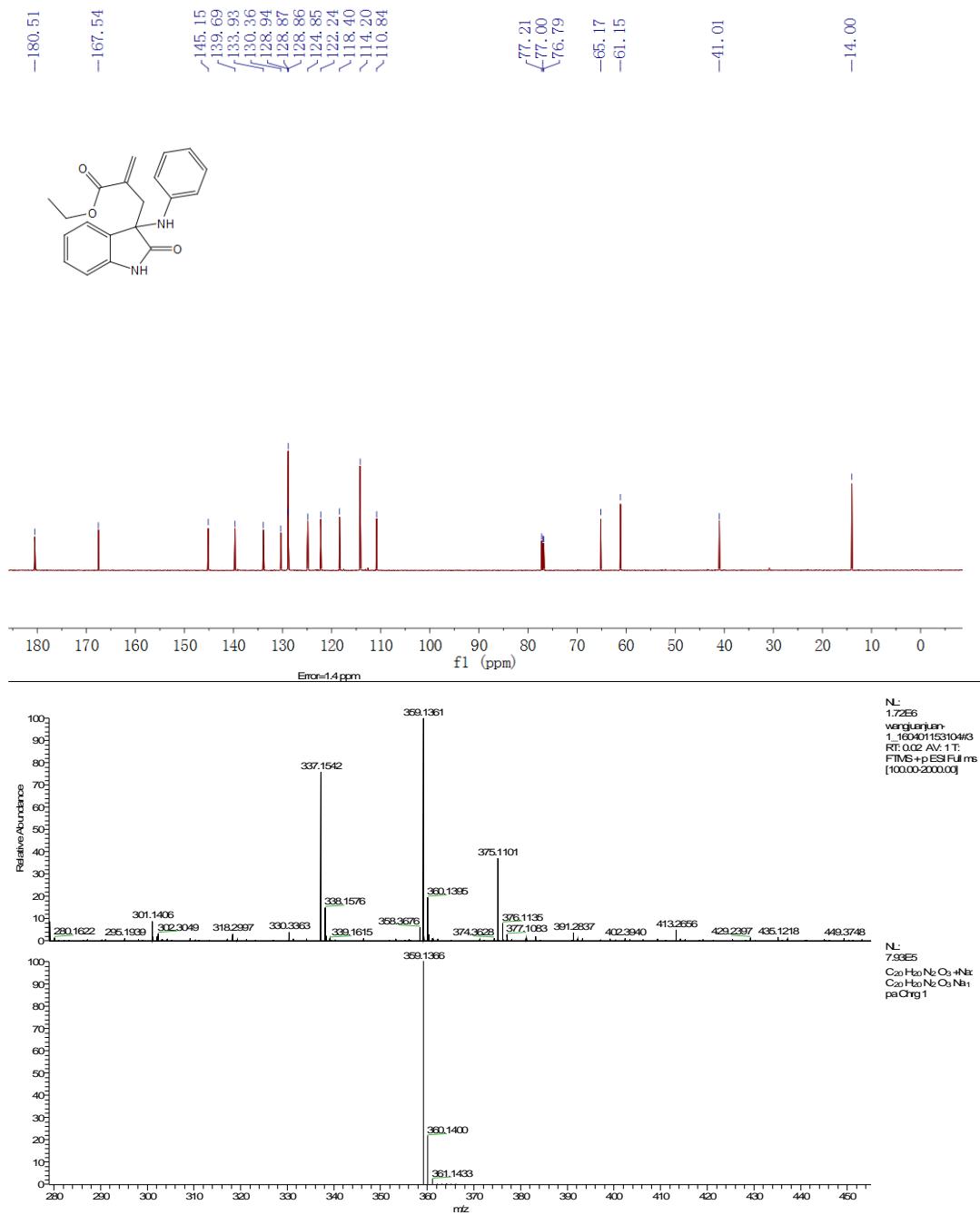


Ethyl 2-((2-oxo-3-(phenylamino)indolin-3-yl)methyl)acrylate(6a)

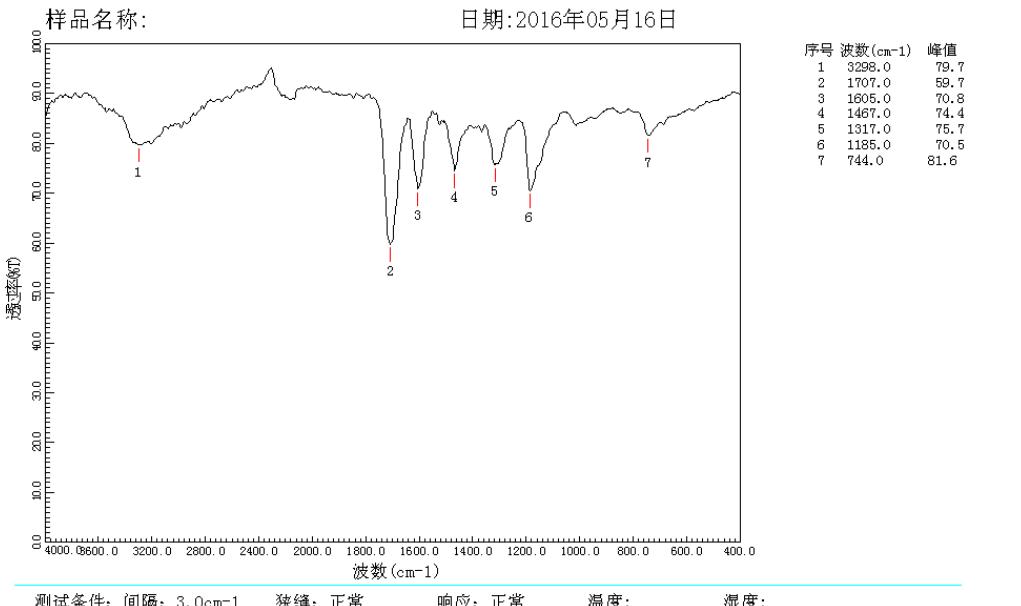


测试条件: 间隔: 3.0cm⁻¹ 狭缝: 正常 响应: 正常 温度: 湿度:
仪器名称: WGH-30/6型双光束红外分光光度计 生产厂家: 天津市港东科技发展有限公司
测试单位: 测试人:

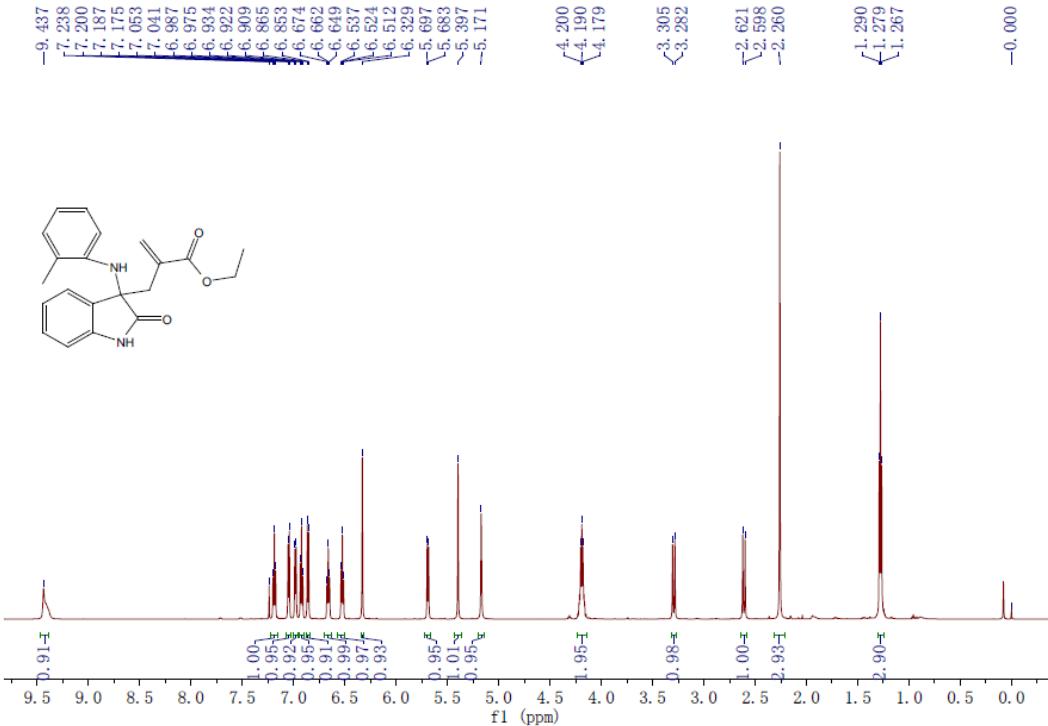


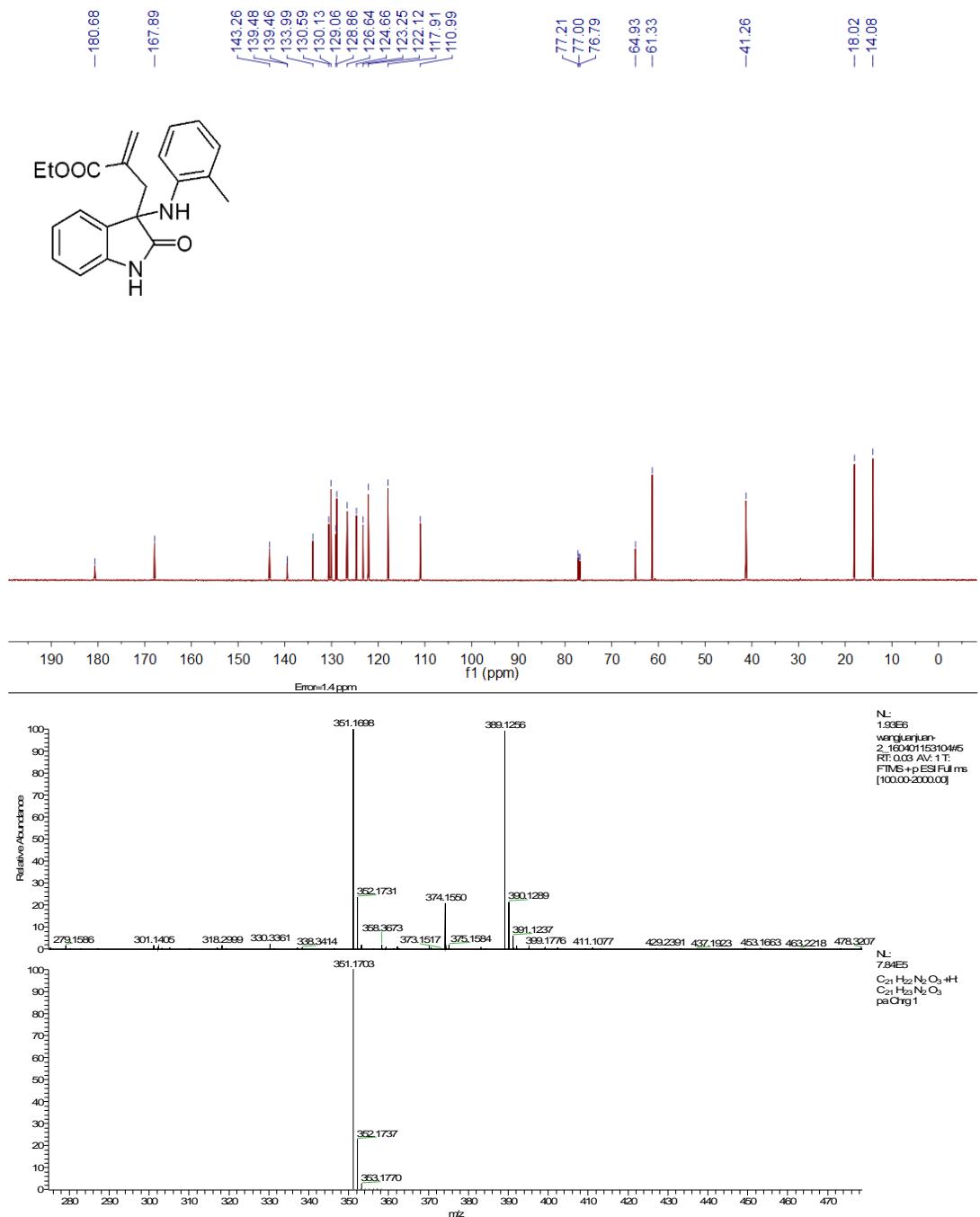


Ethyl 2-((2-oxo-3-(phenylamino)indolin-3-yl)methyl)acrylate(6b)

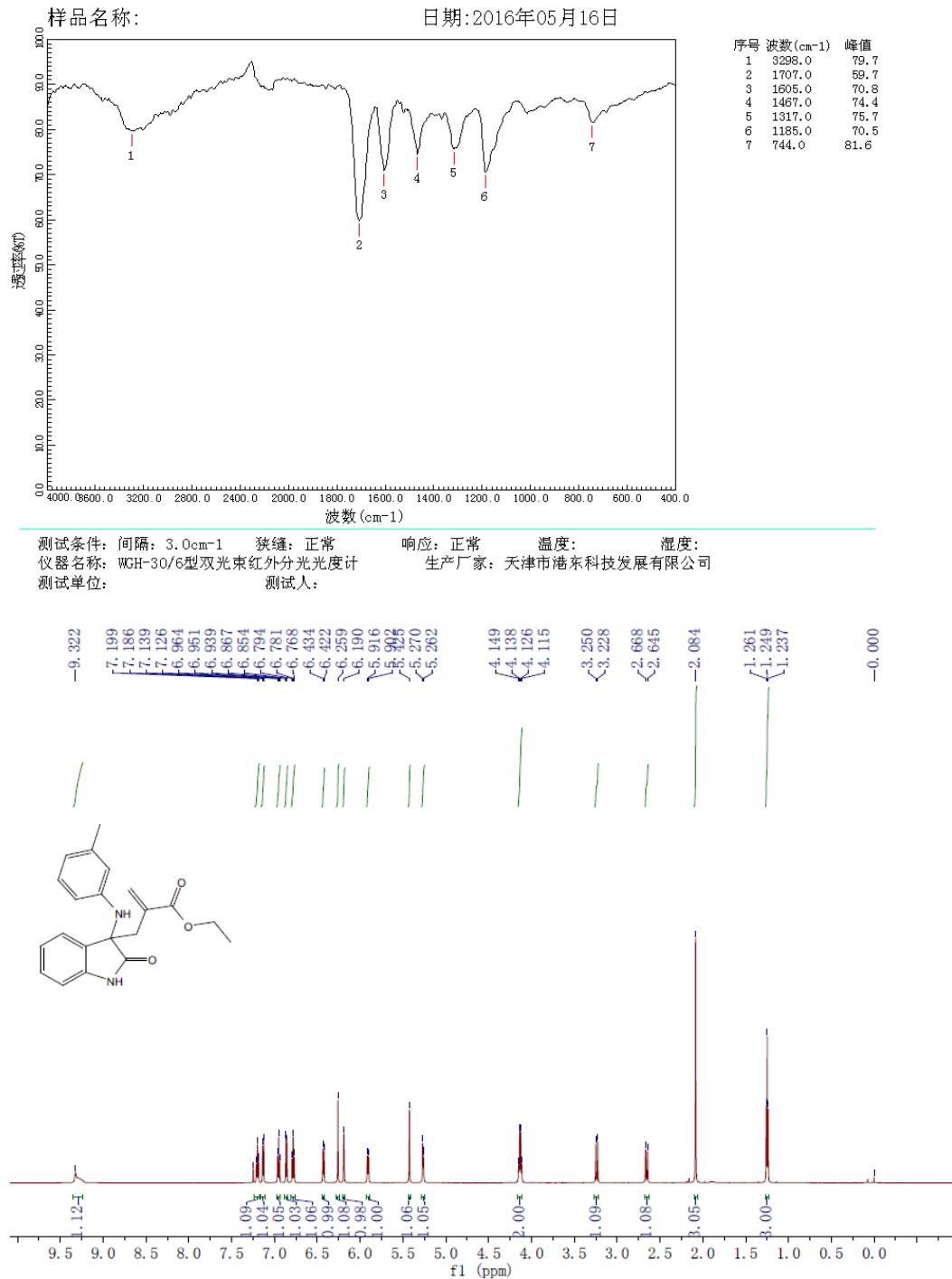


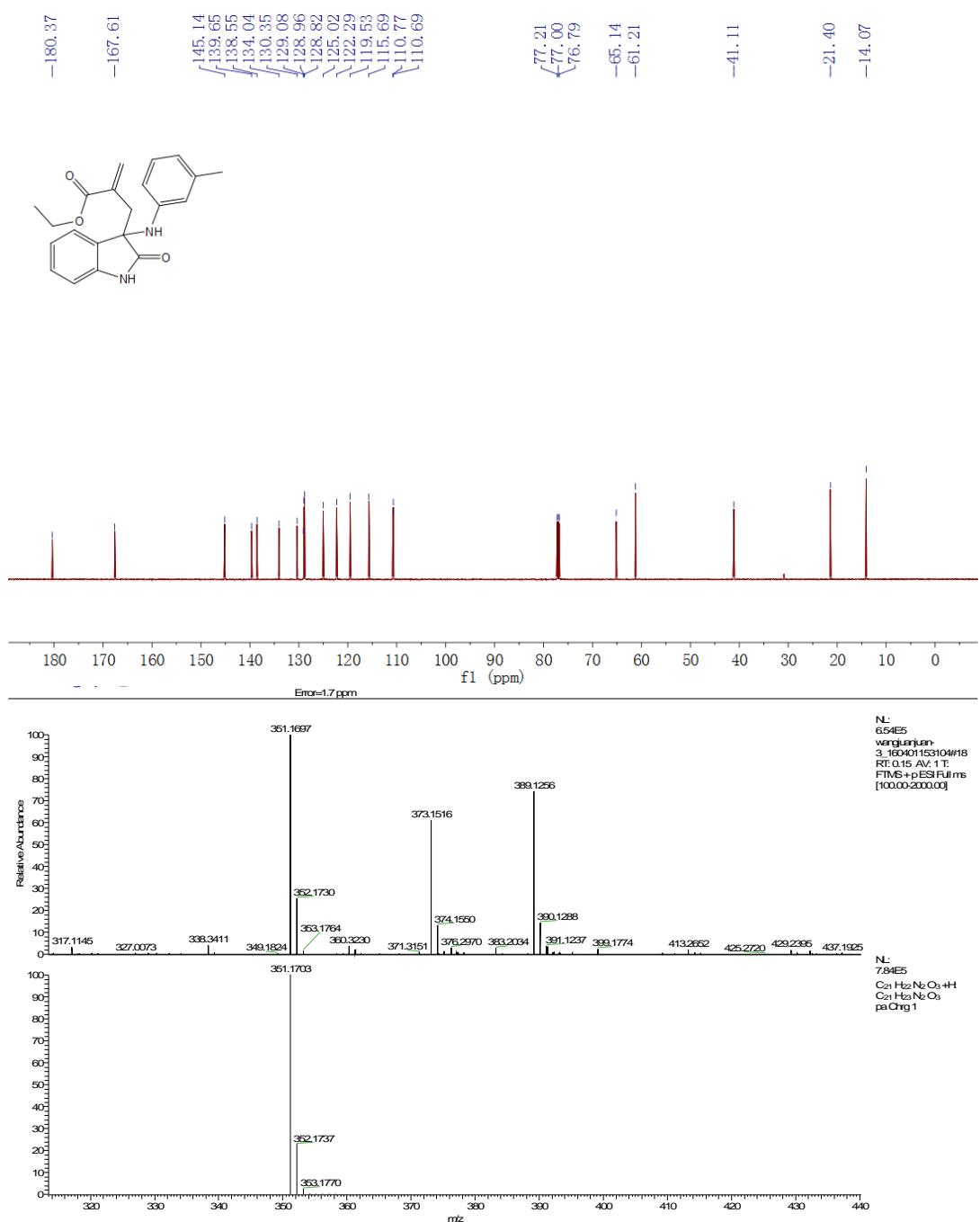
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仪器名称：WQH-30/6型双光束红外分光光度计 生产厂家：天津市浦东科技发展有限公司
测试单位： 测试人：



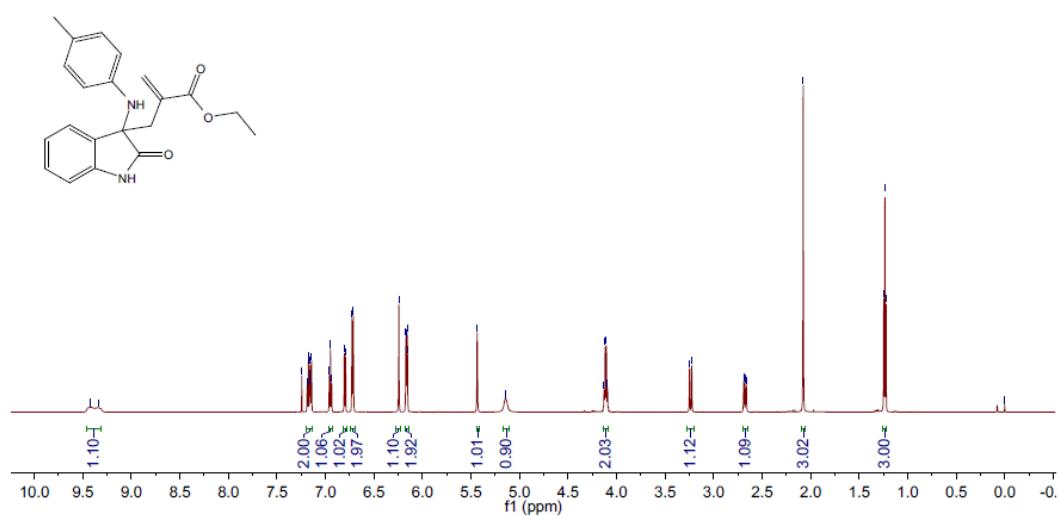
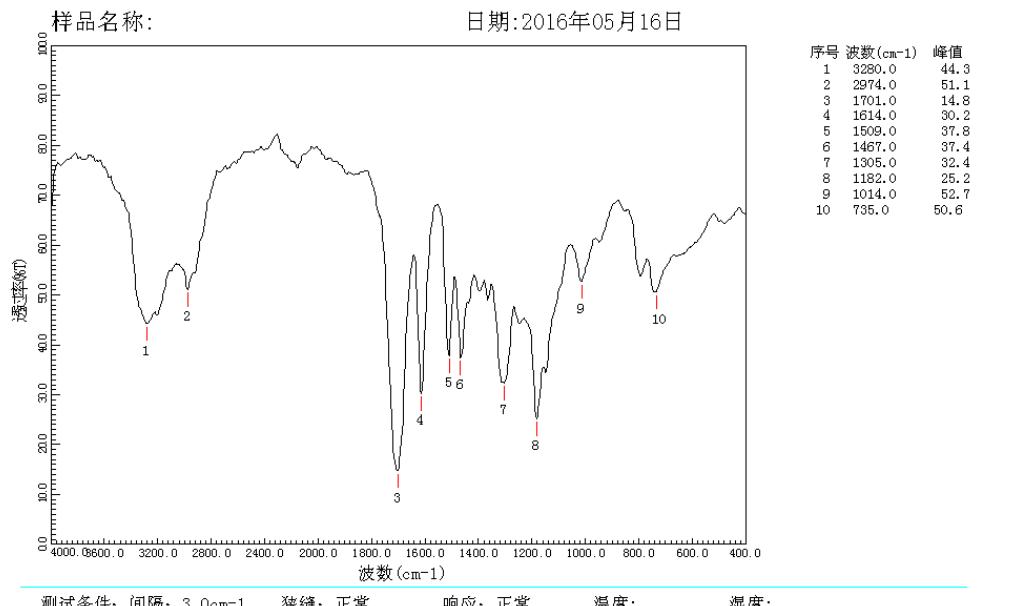


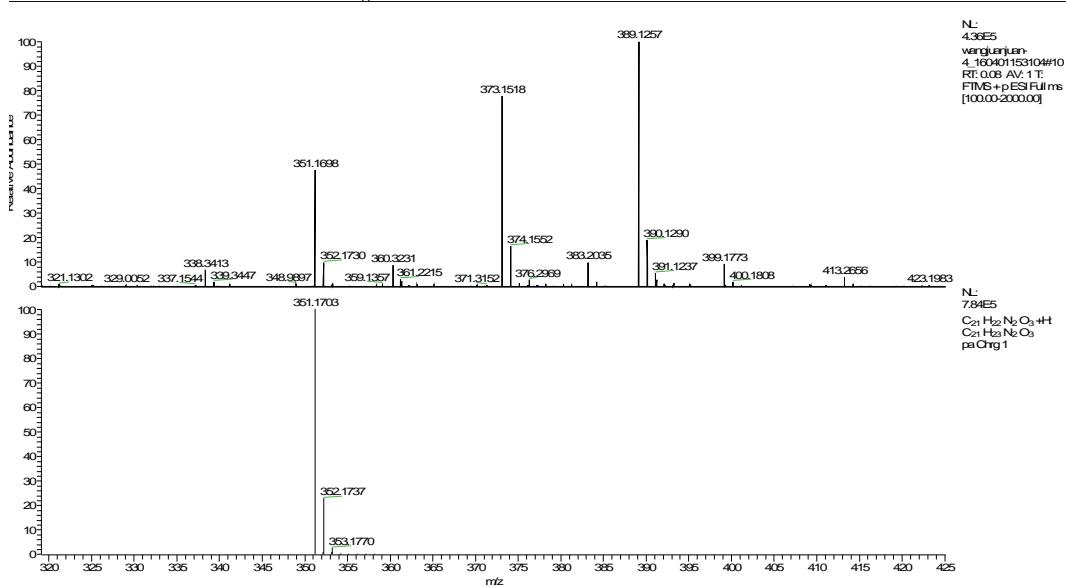
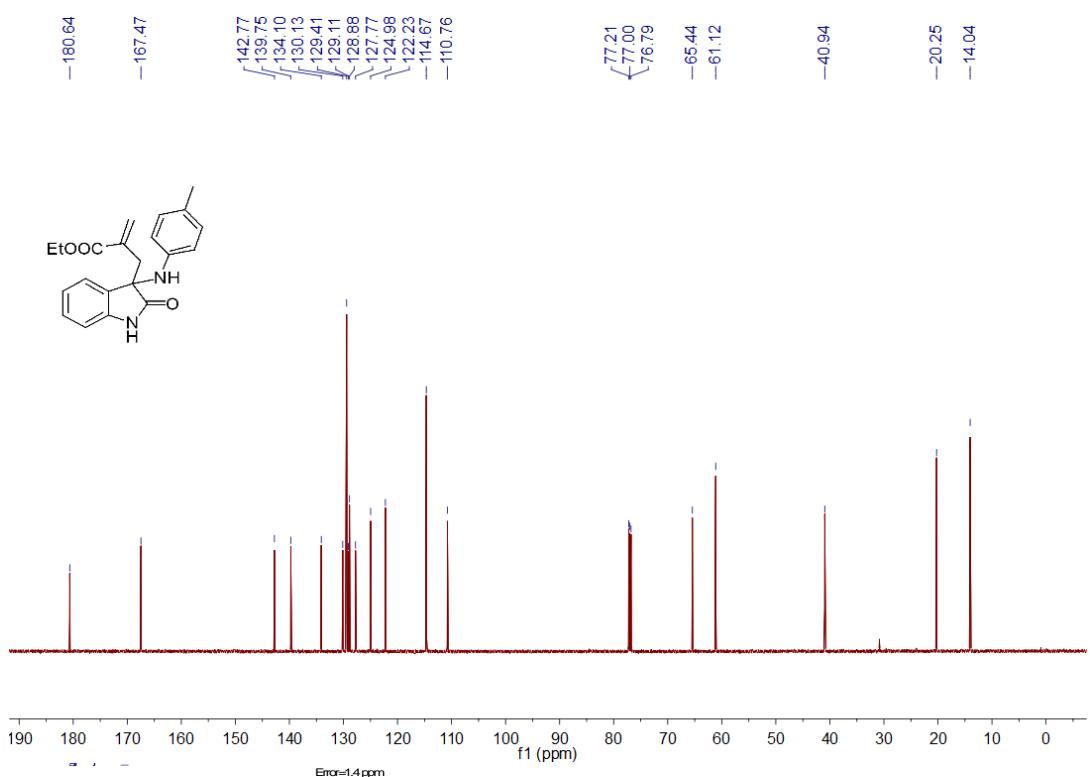
Ethyl 2-((2-oxo-3-(m-tolylamino)indolin-3-yl)methyl)acrylate(6c)



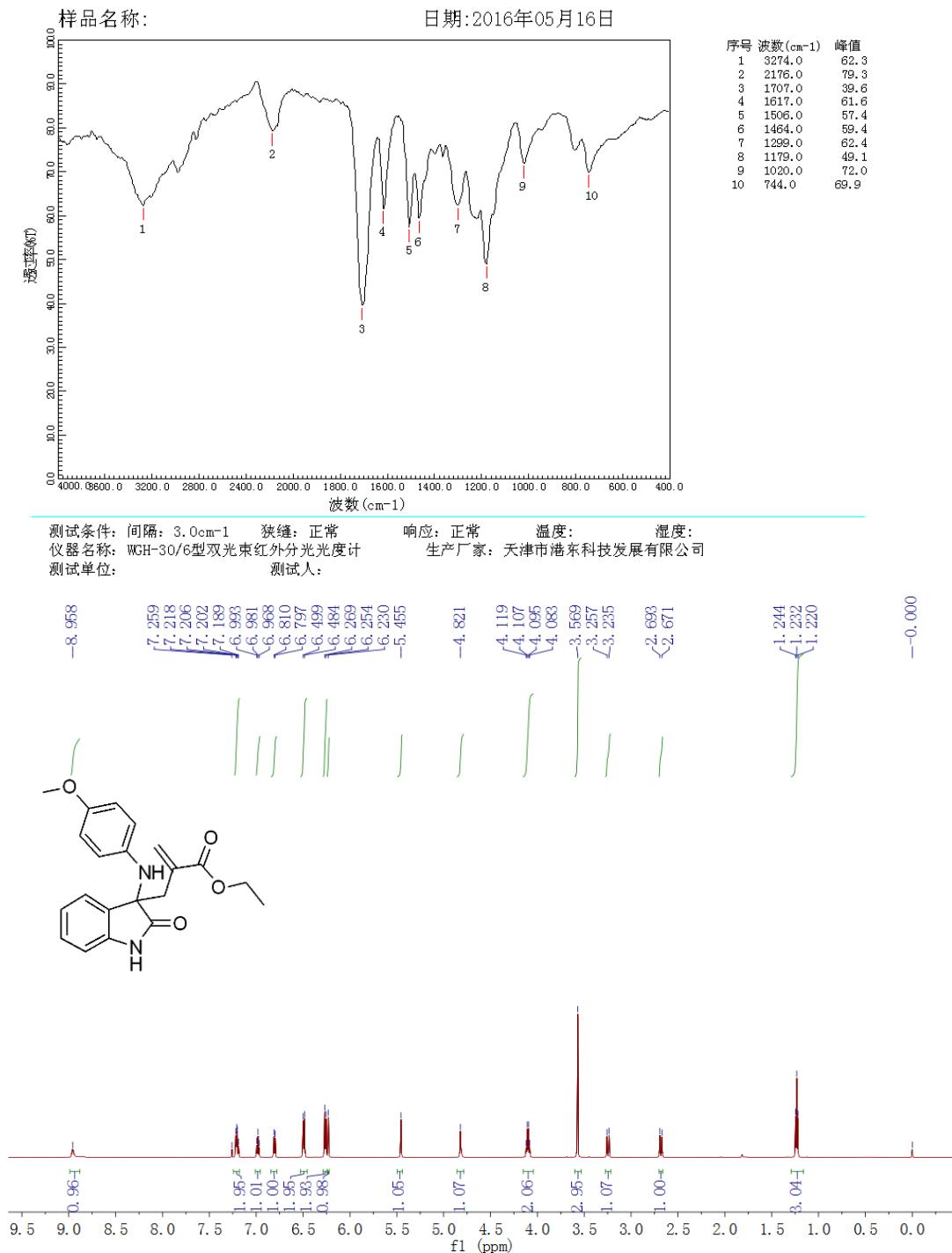


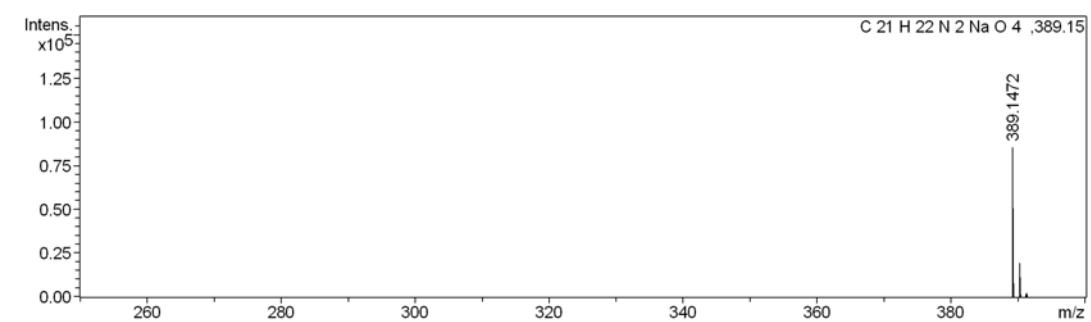
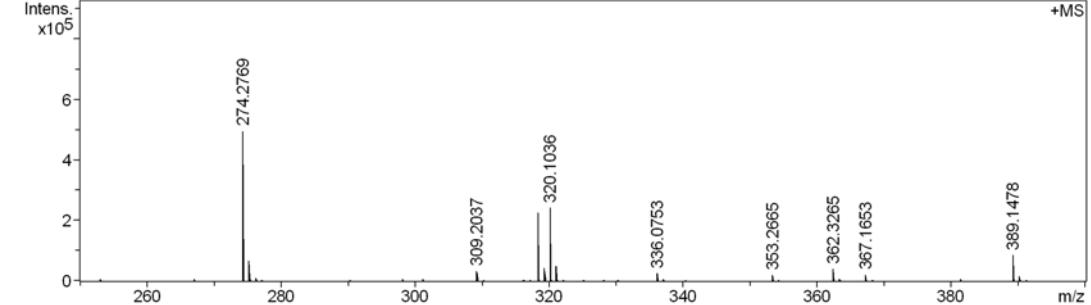
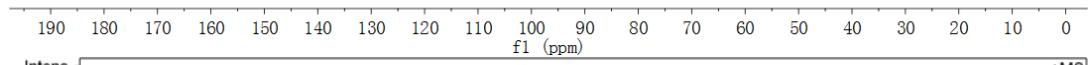
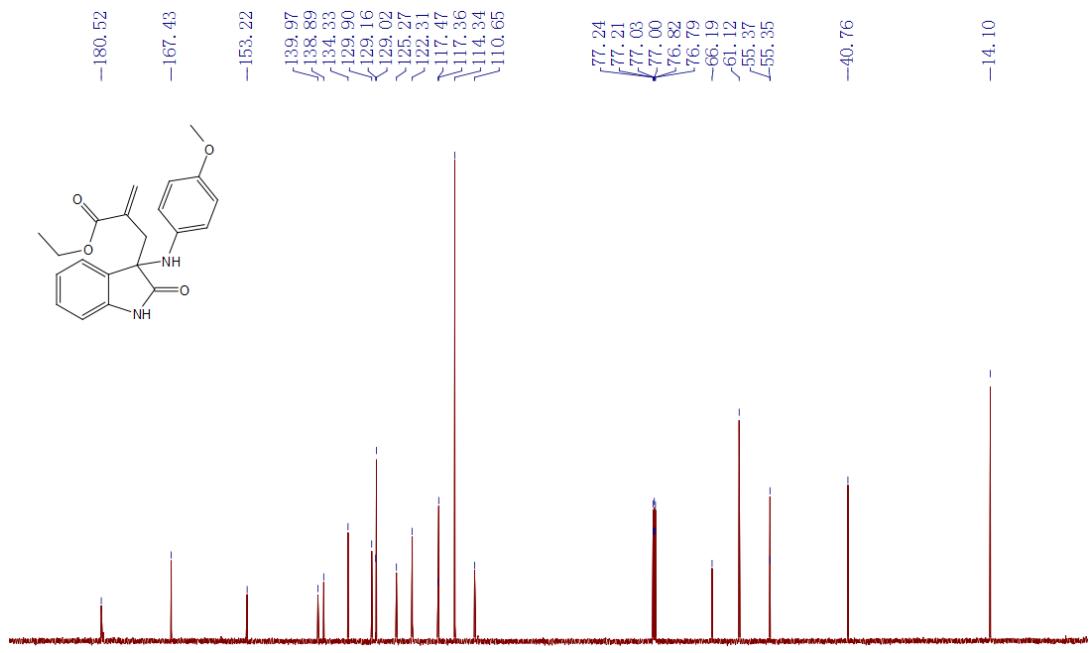
Ethyl 2-((2-oxo-3-(p-tolylamino)indolin-3-yl)methyl)acrylate(6d)



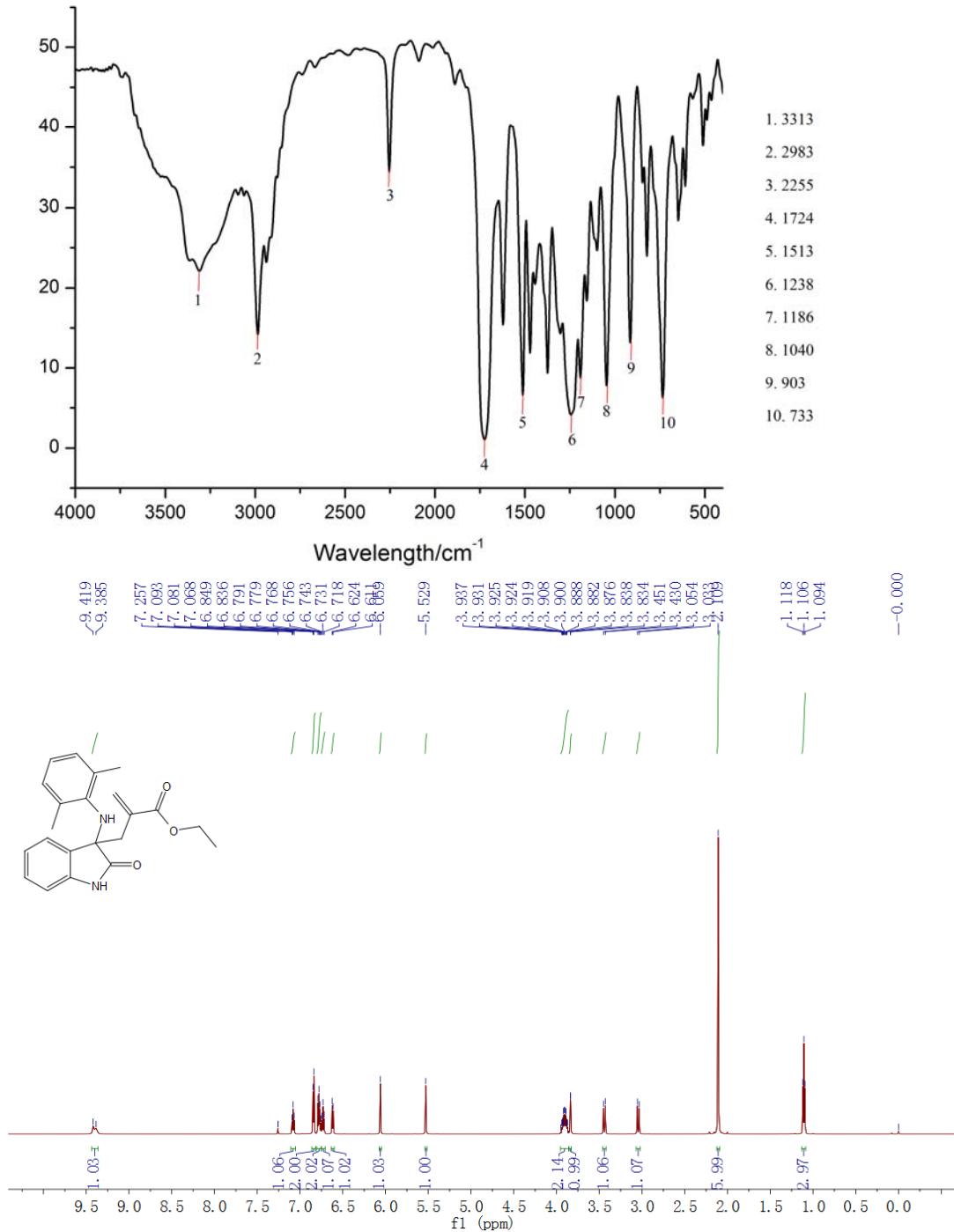


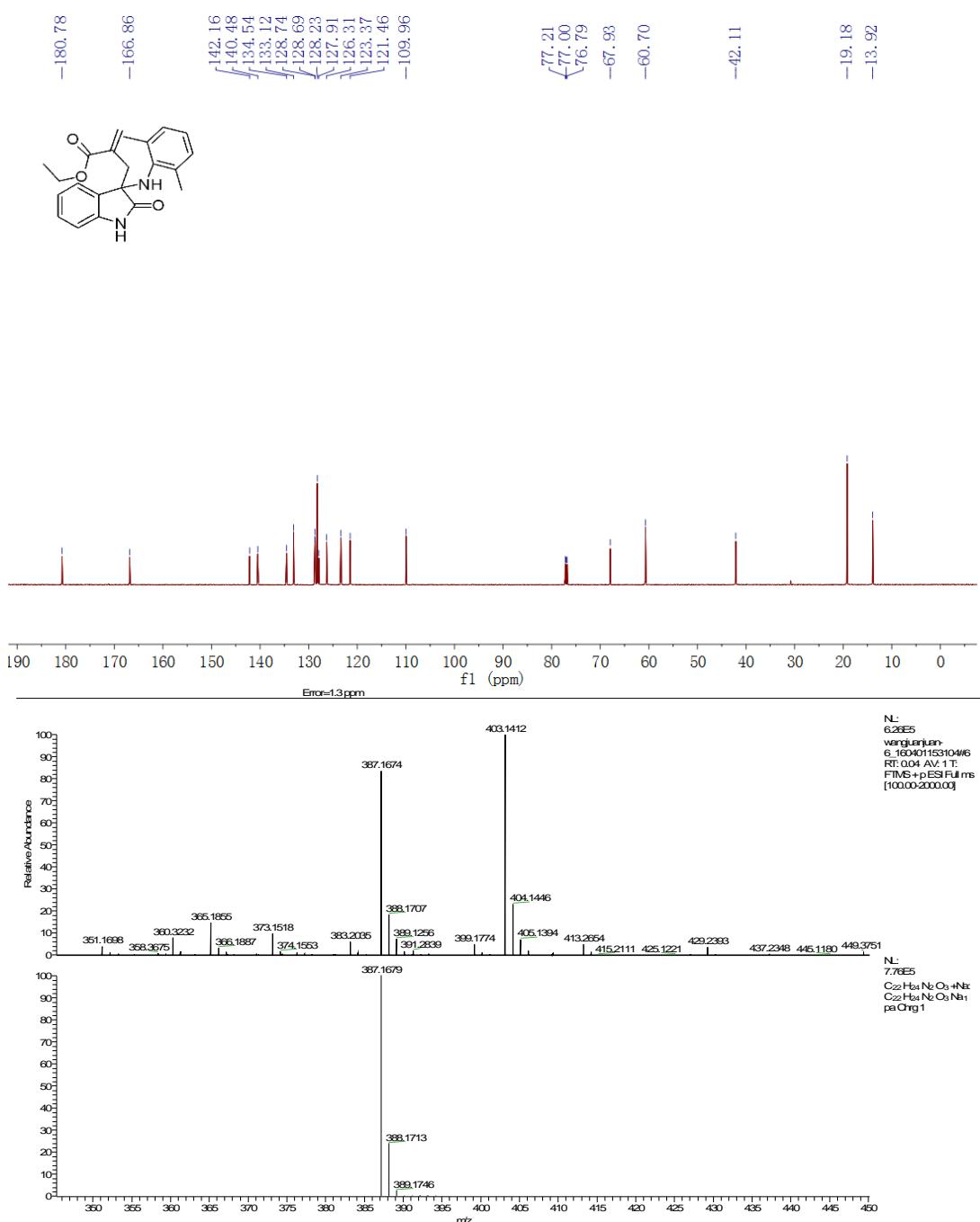
Ethyl 2-((3-((4-methoxyphenyl)amino)-2-oxoindolin-3-yl)methyl)acrylate(6e)





Ethyl 2-((3-((2,6-dimethylphenyl)amino)-2-oxoindolin-3-yl)methyl)acrylate(6f)

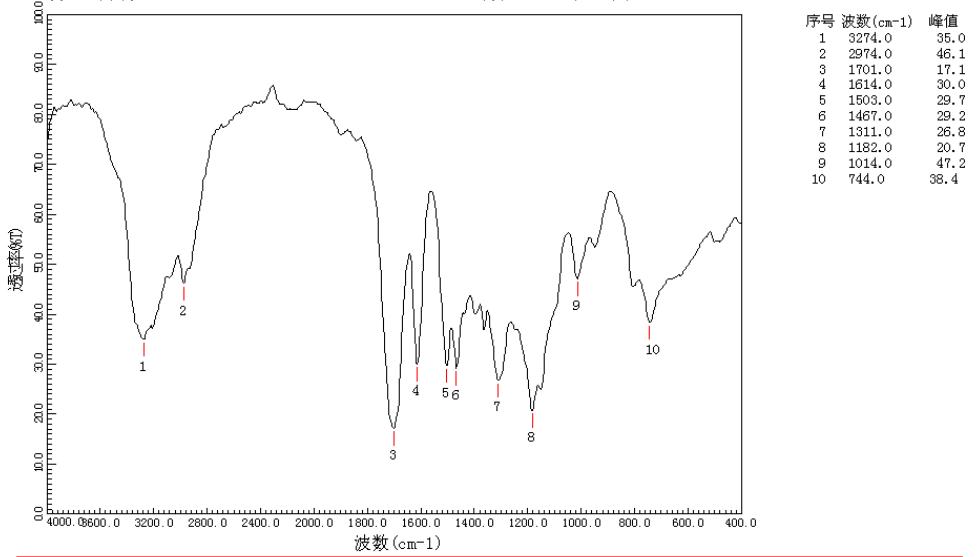




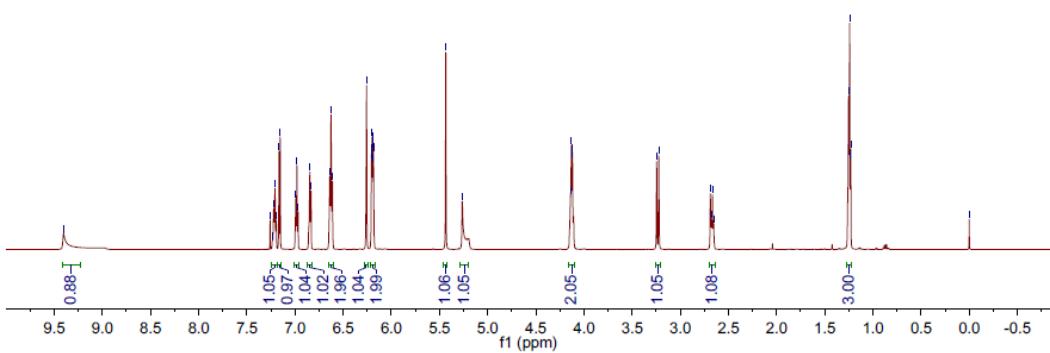
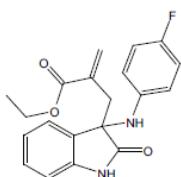
Ethyl 2-((3-((4-fluorophenyl)amino)-2-oxoindolin-3-yl)methyl)acrylate(6h)

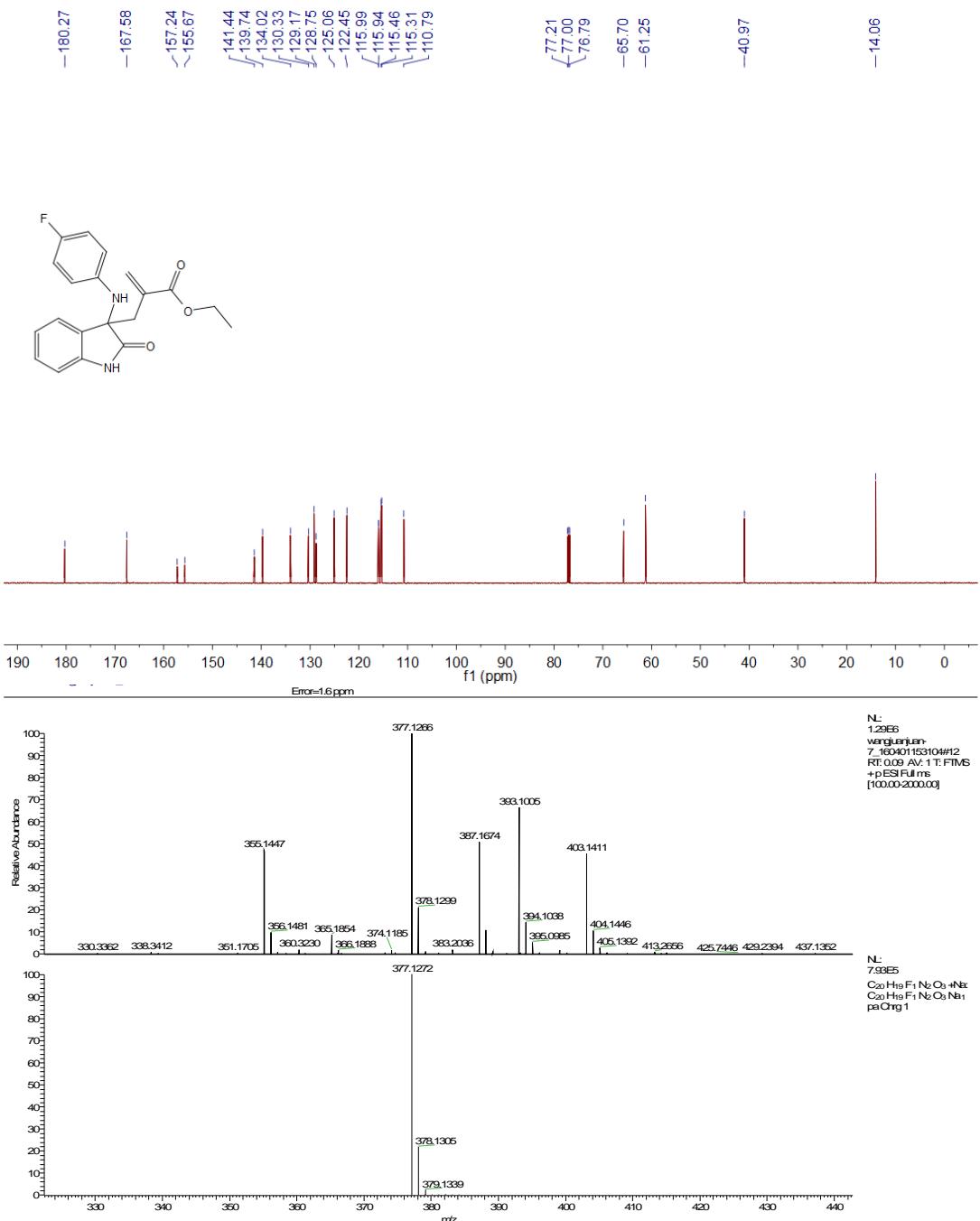
样品名称:

日期:2016年05月16日

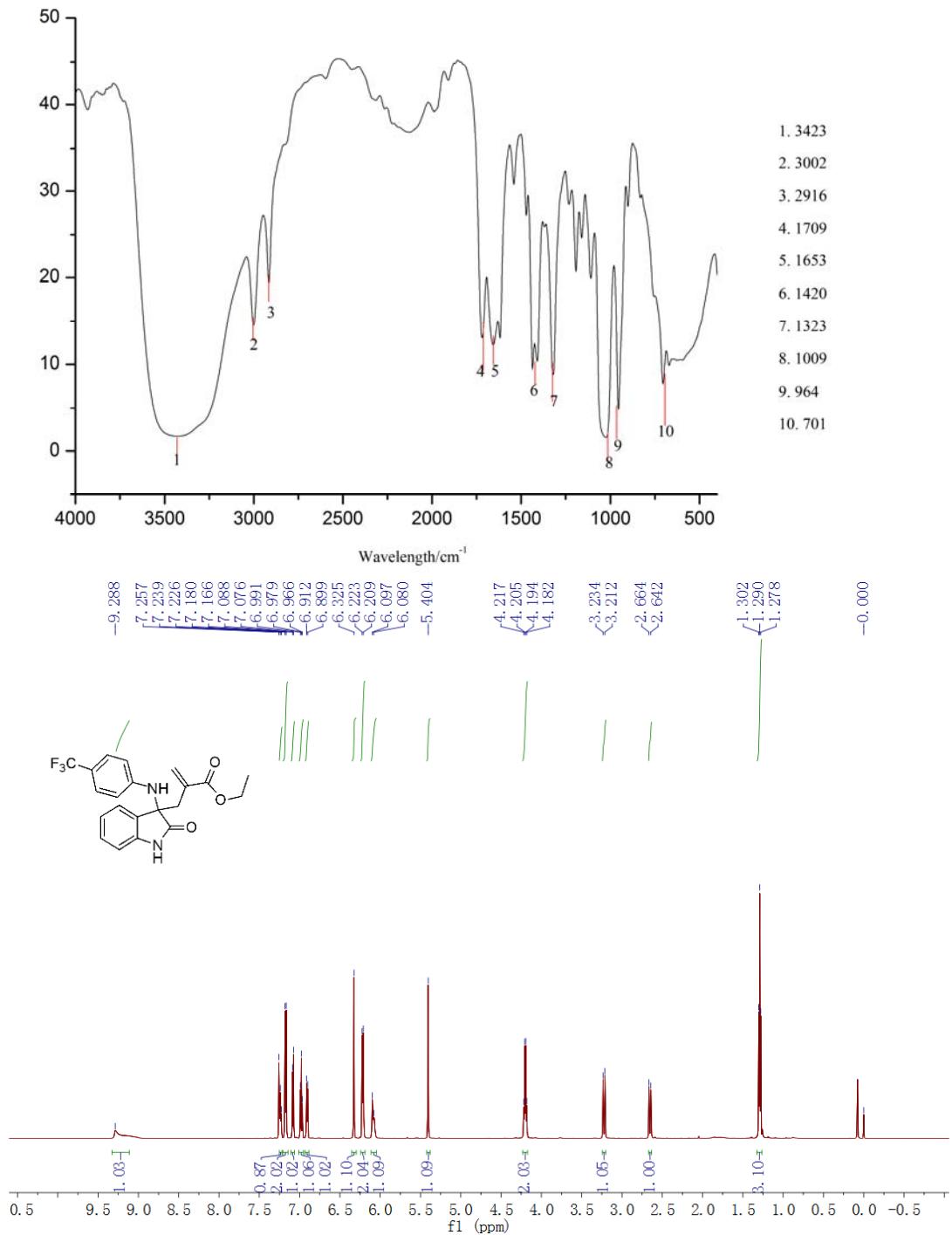


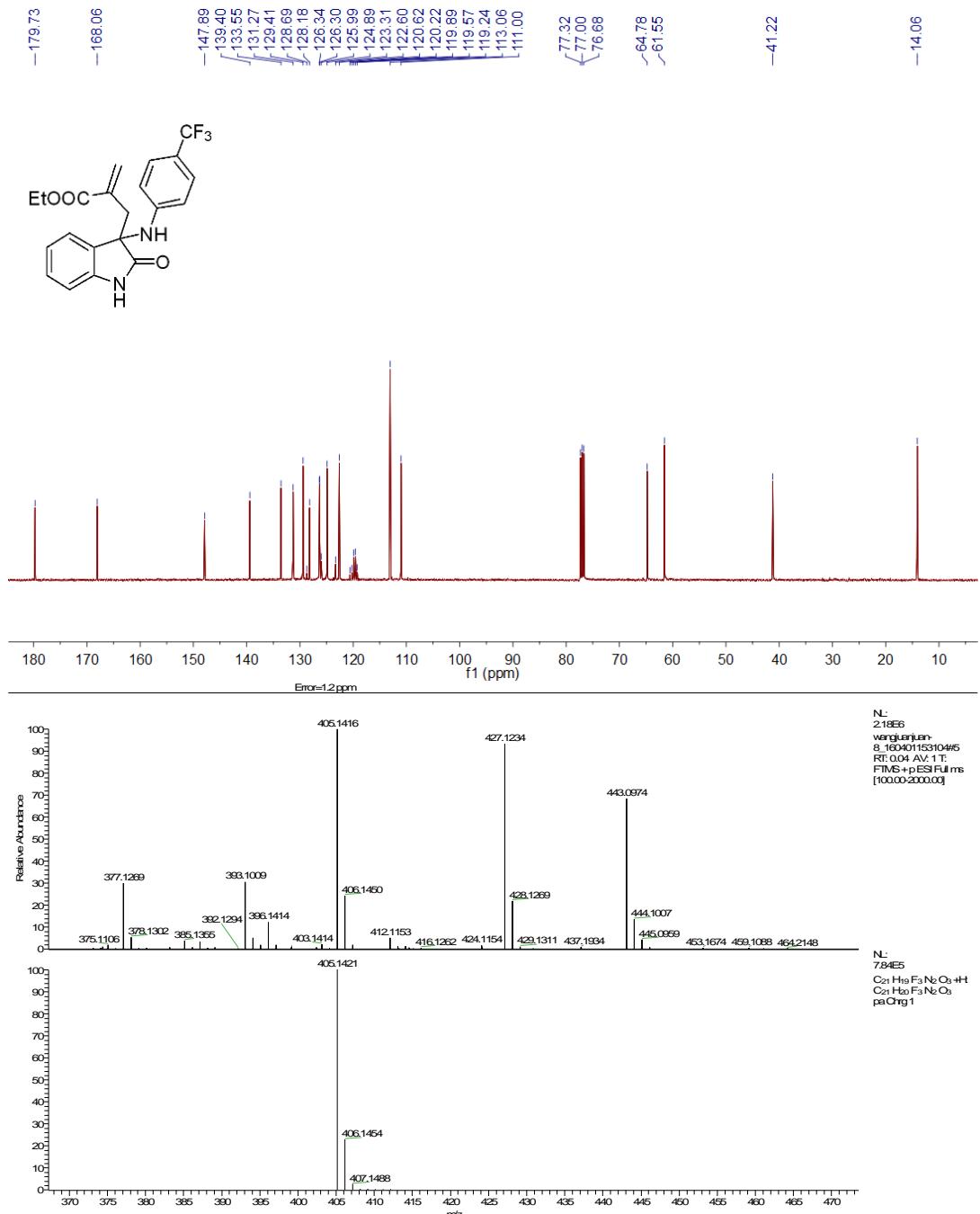
测试条件：间隔：3.0cm⁻¹ 狹缝：正常 响应：正常 温度： 湿度：
仪器名称：WGH-30/6型双光束红外分光光度计 生产厂家：天津市港东科技发展有限公司
测试单位： 测试人：



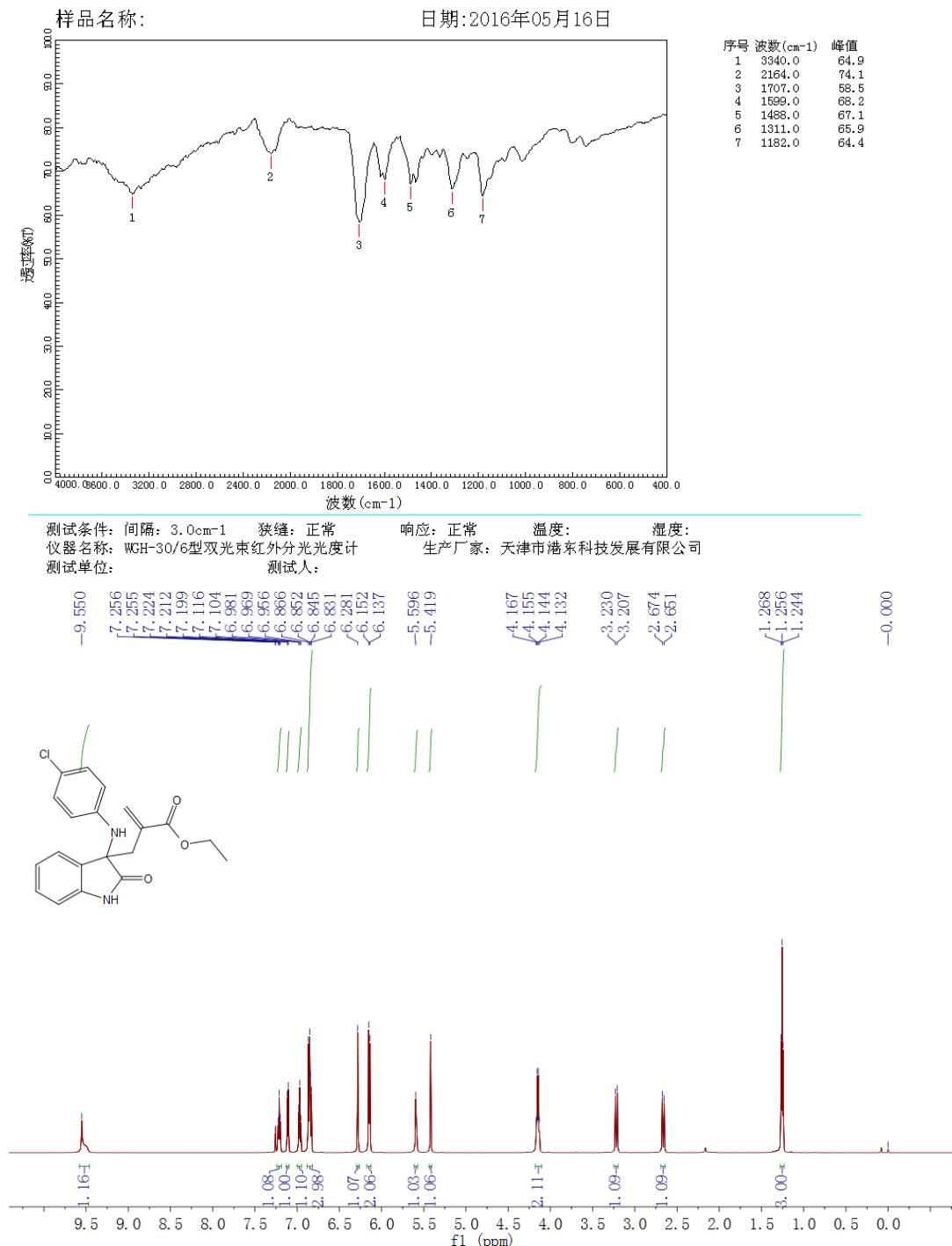


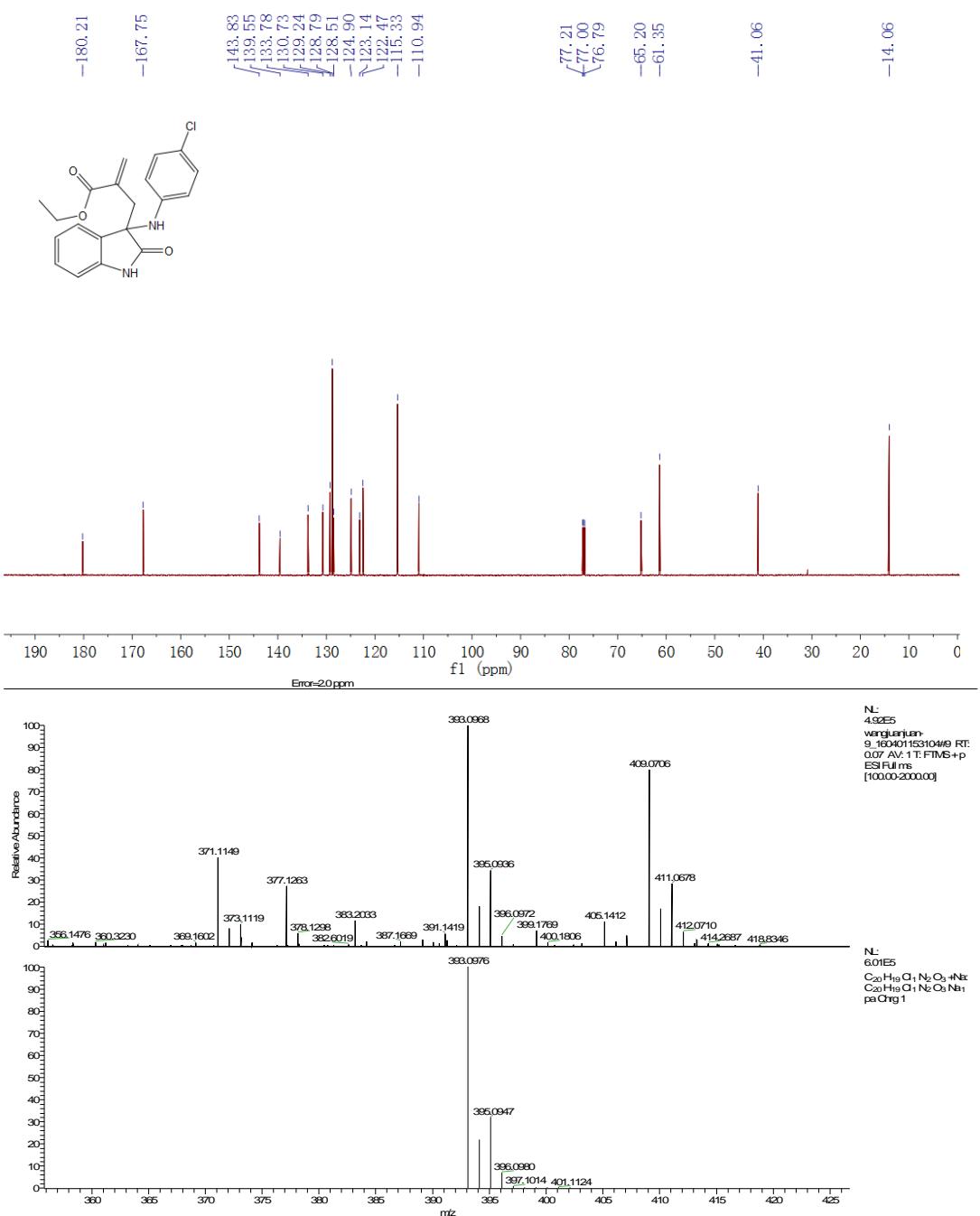
Ethyl 2-((2-oxo-3-((4-(trifluoromethyl)phenyl)amino)indolin-3-yl)methyl) -acrylate(6i)



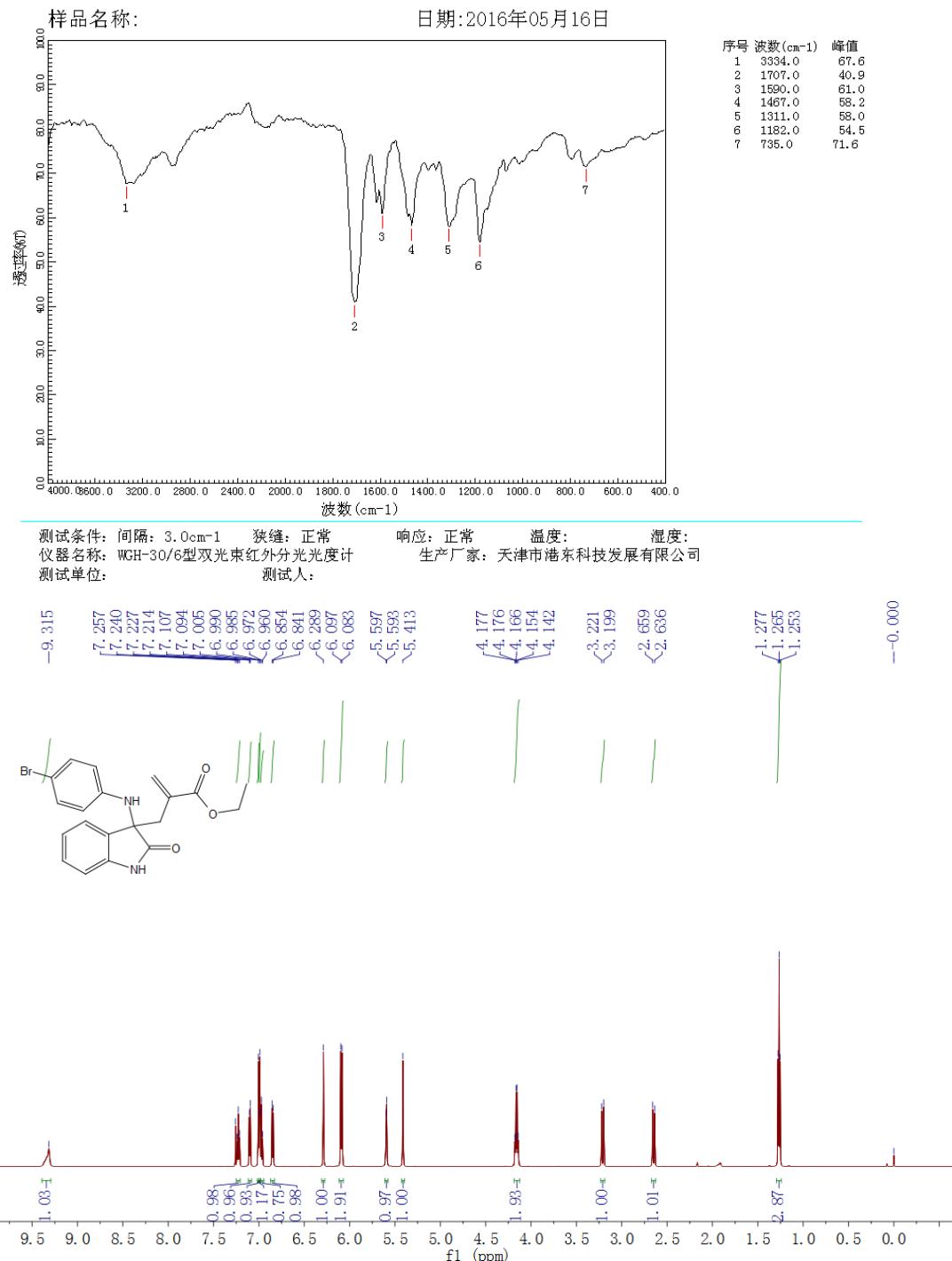


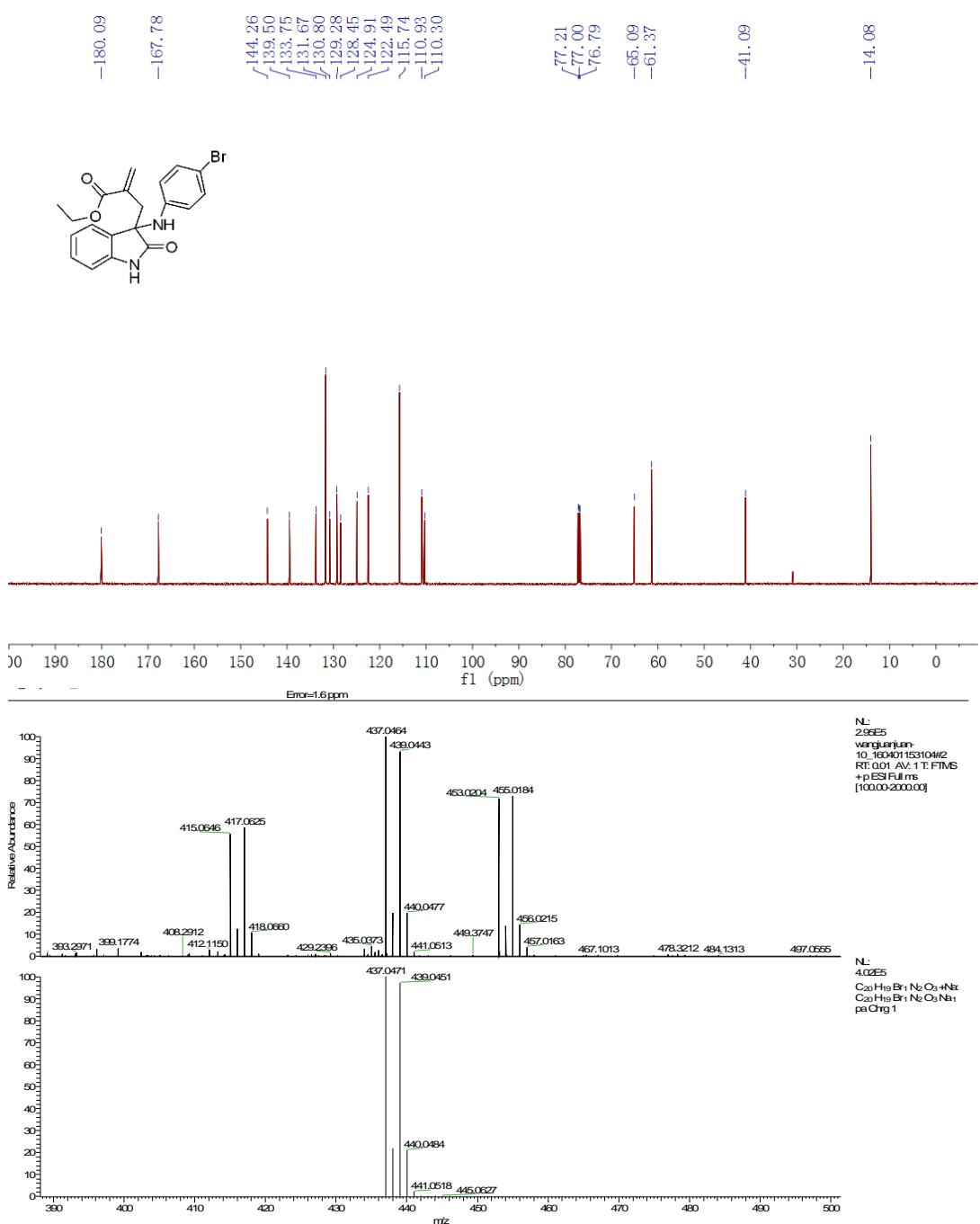
Ethyl 2-((3-((4-chlorophenyl)amino)-2-oxoindolin-3-yl)methyl)acrylate(6j)



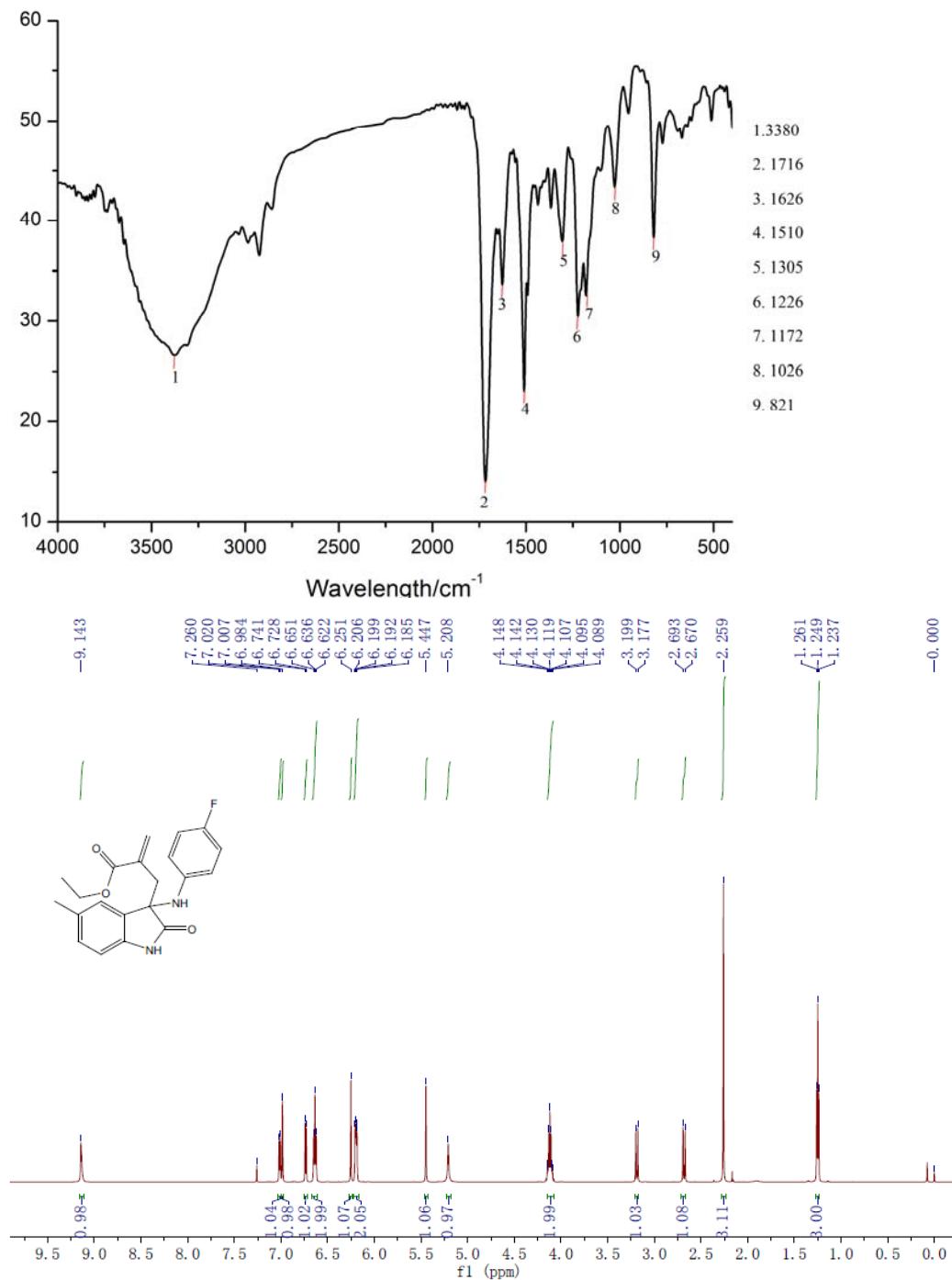


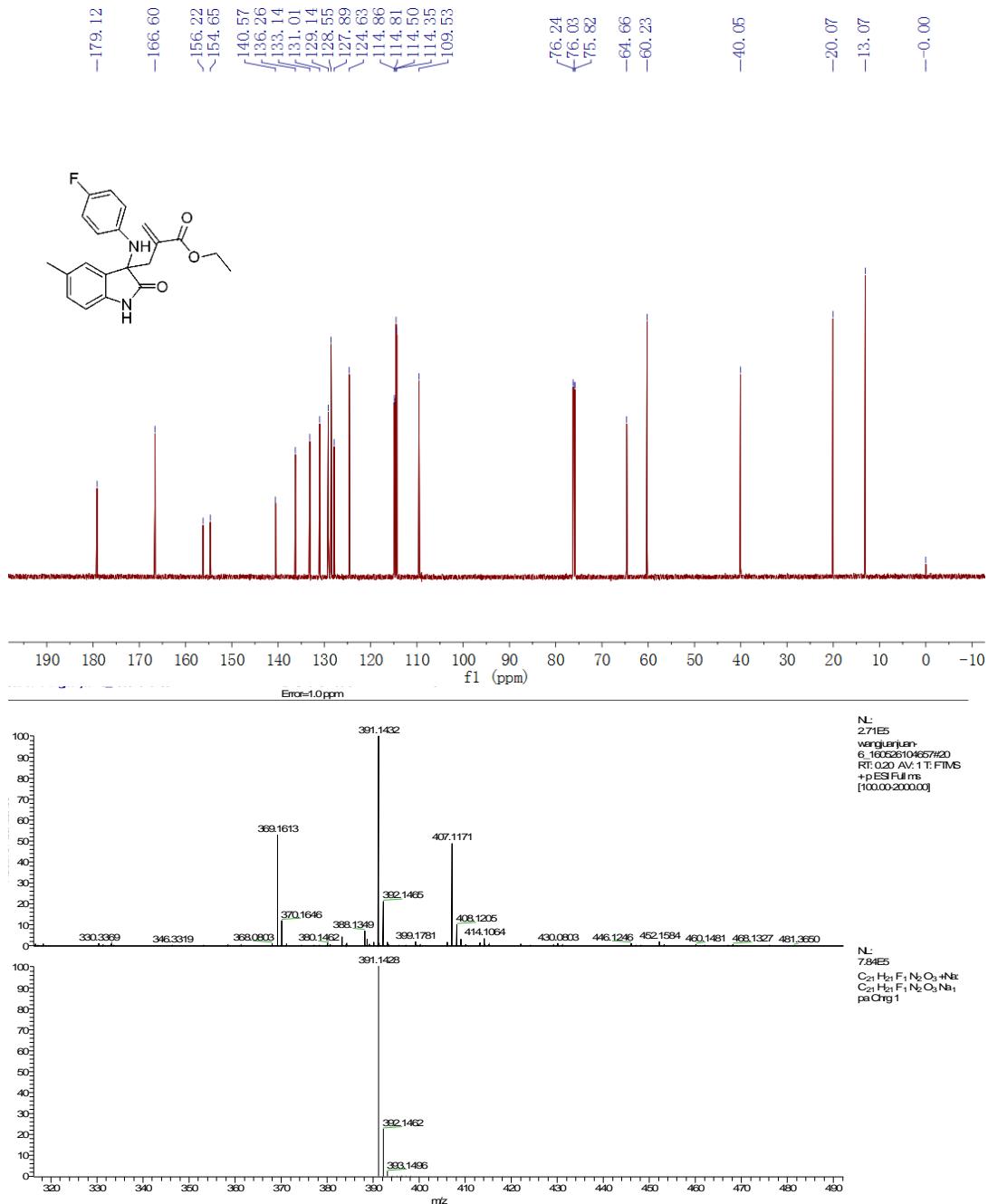
Ethyl 2-((3-((4-bromophenyl)amino)-2-oxoindolin-3-yl)methyl)acrylate(6k)



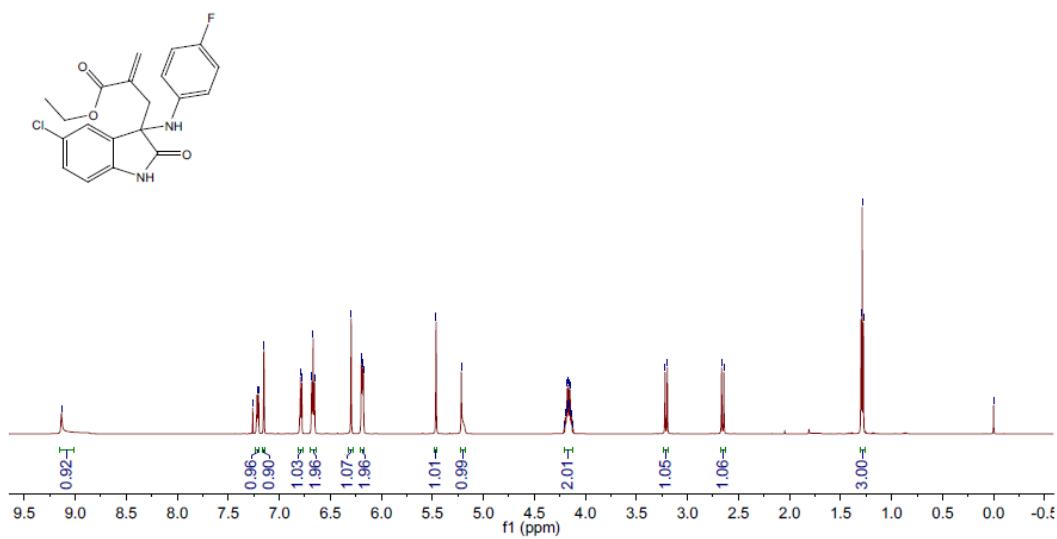
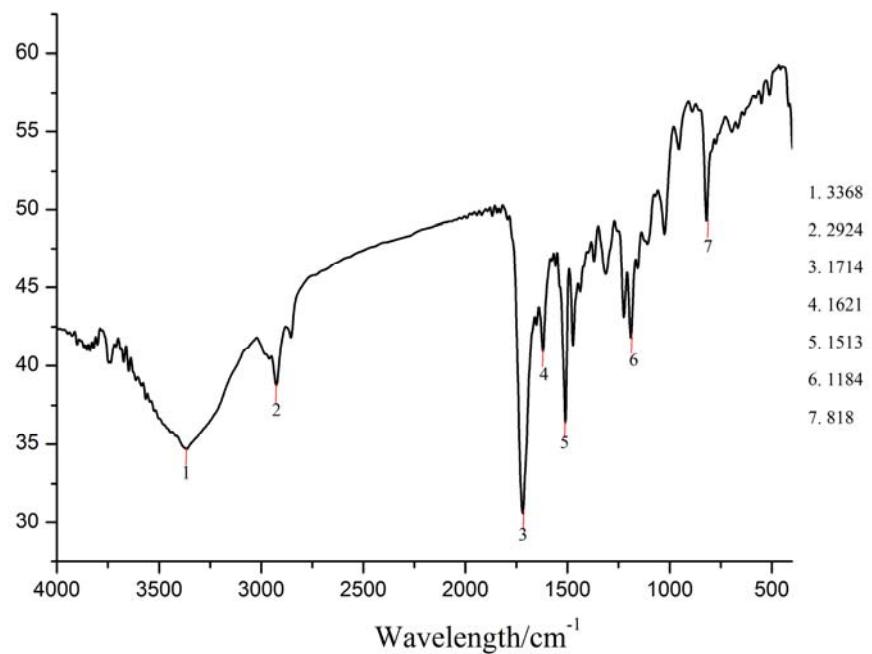


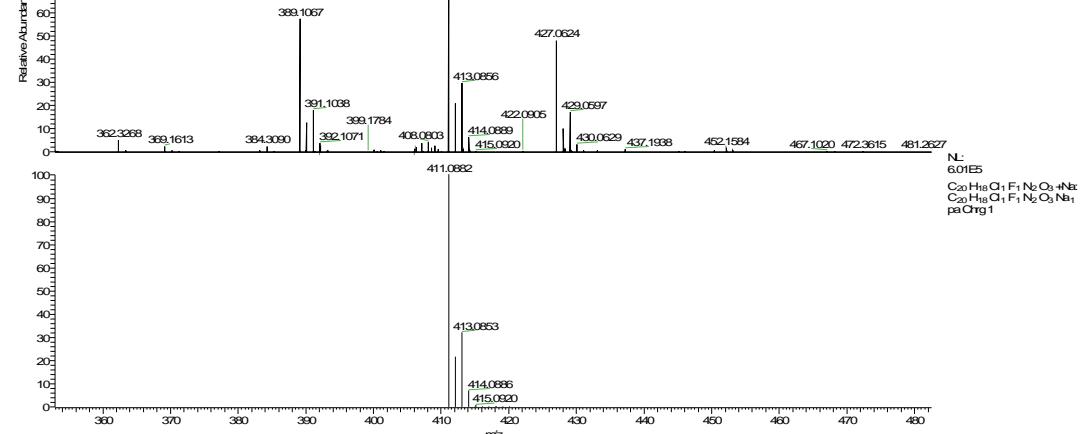
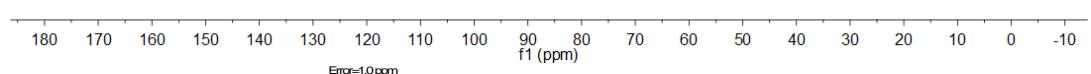
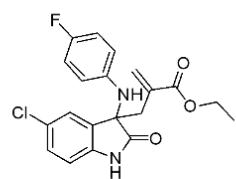
Ethyl 2-((3-((4-fluorophenyl)amino)-5-methyl-2-oxoindolin-3-yl)methyl)acrylate(6m)



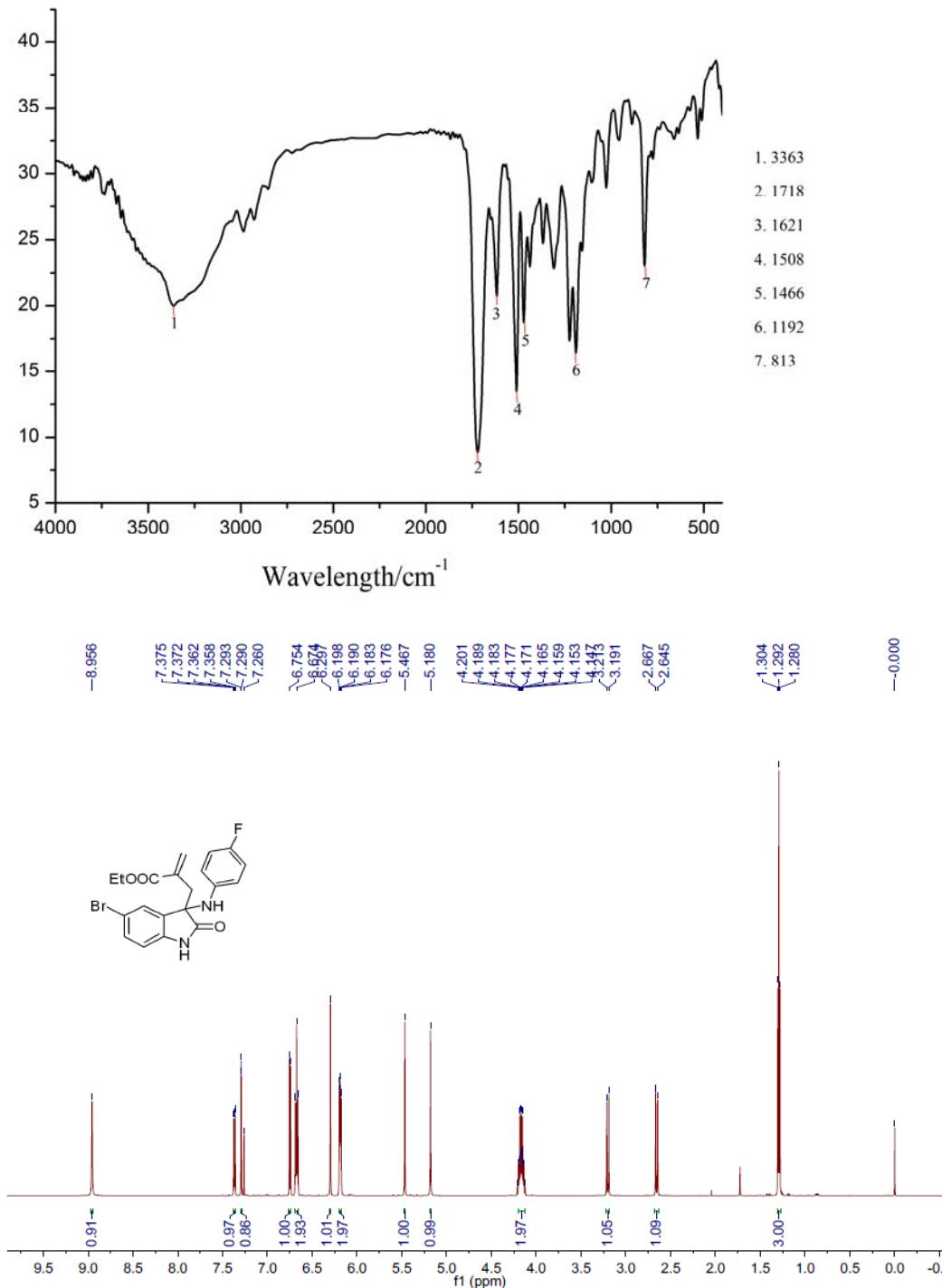


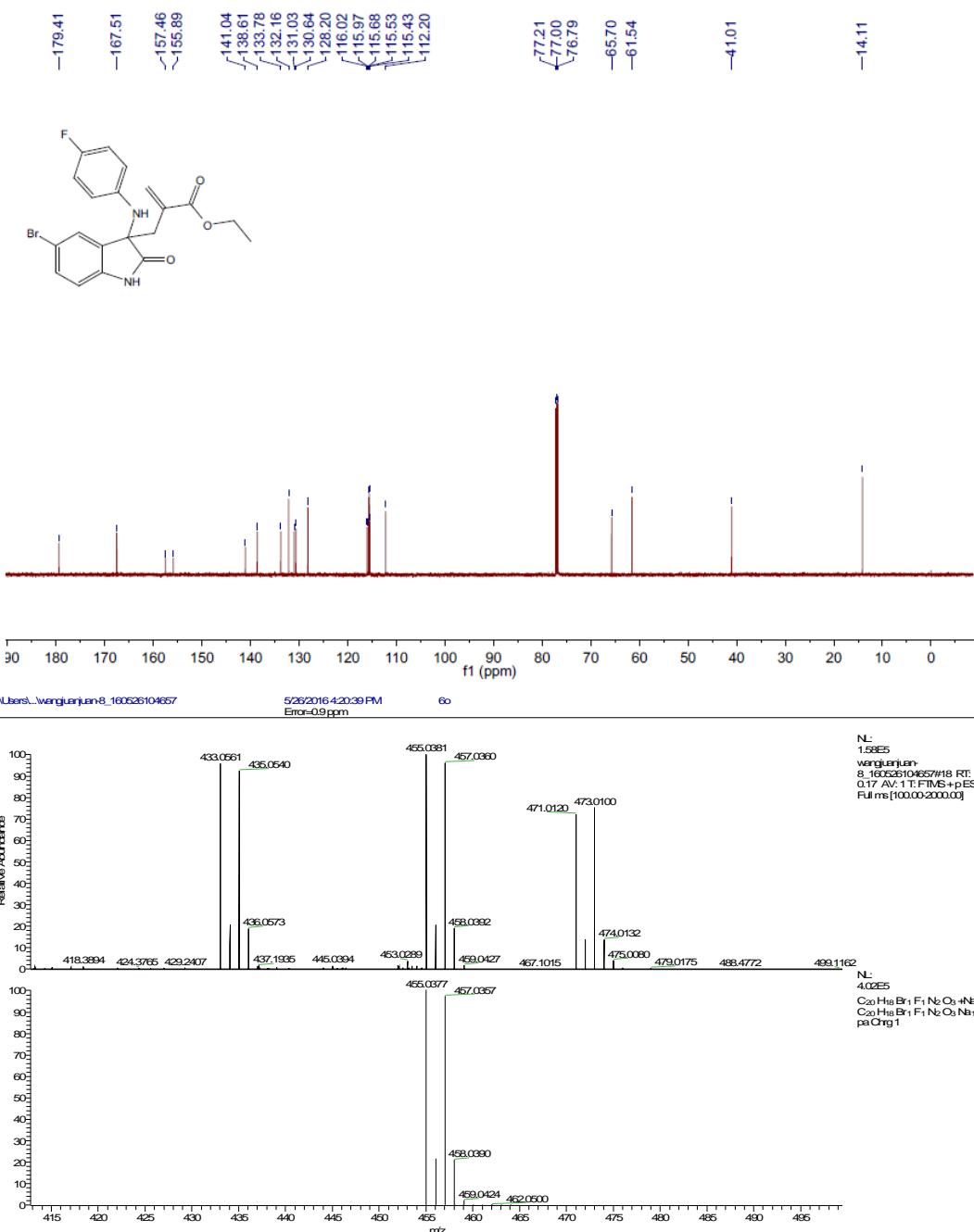
Ethyl 2-((5-chloro-3-((4-fluorophenyl)amino)-2-oxoindolin-3-yl)methyl)acrylate(6n)



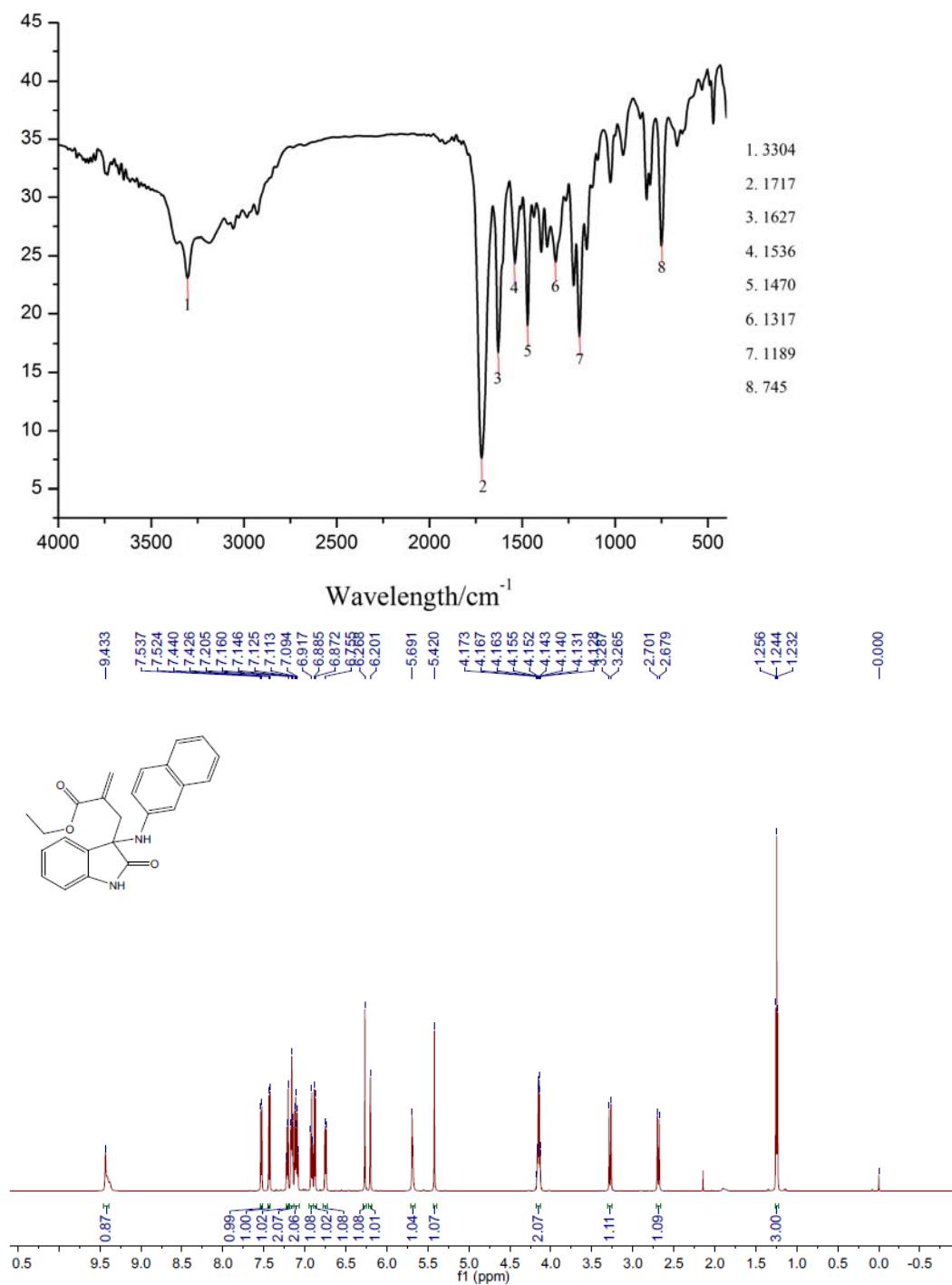


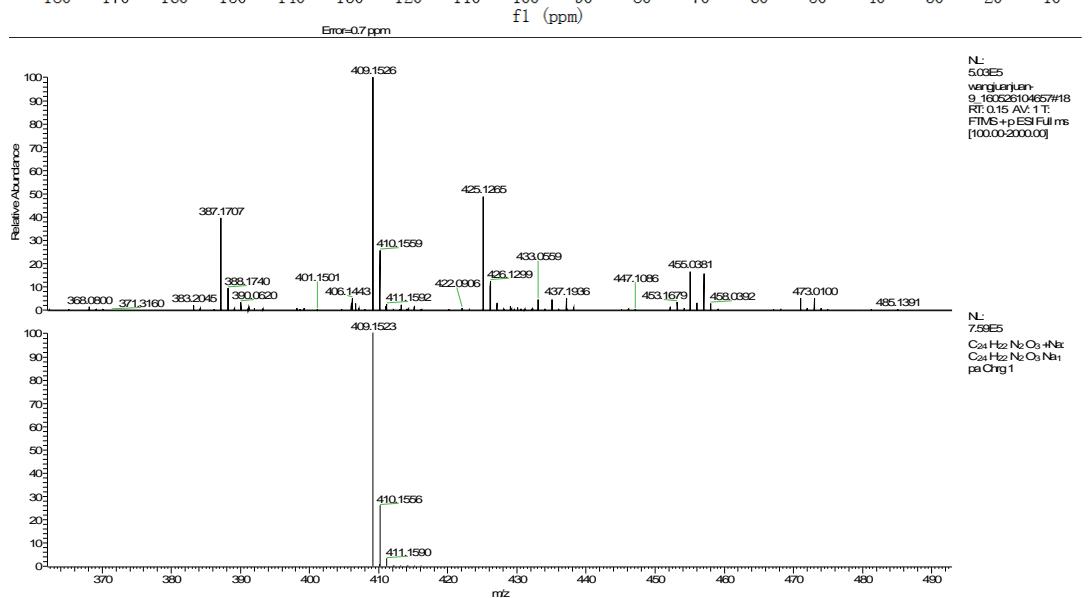
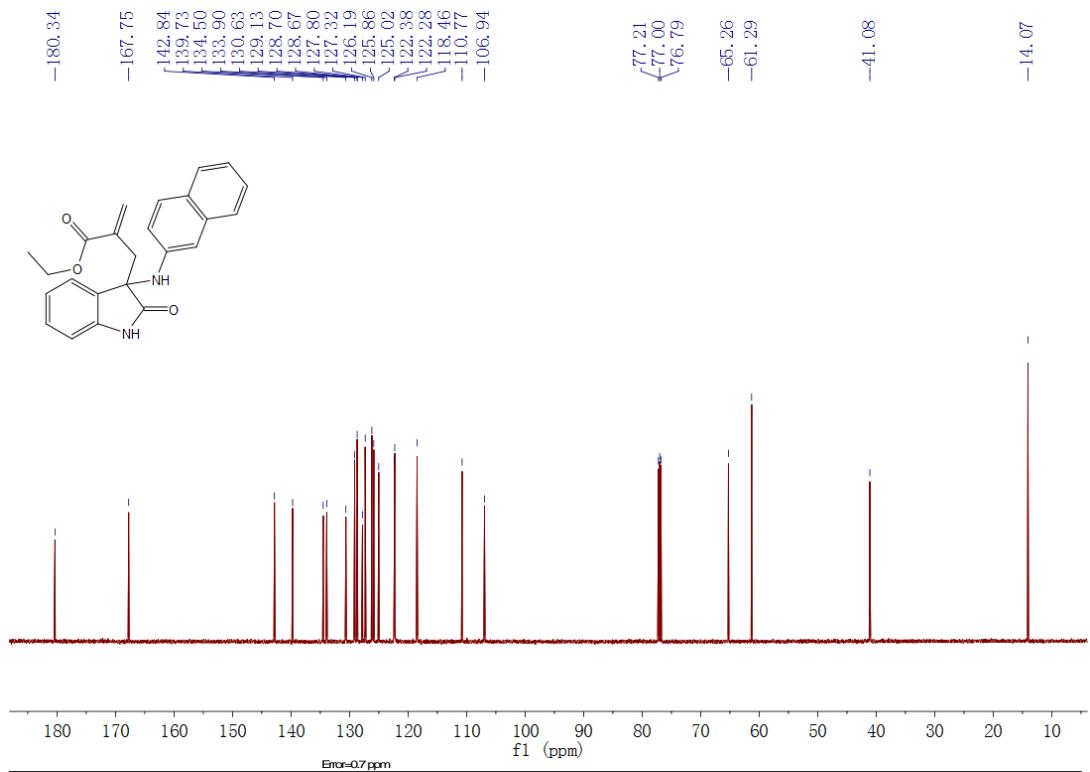
Ethyl 2-((5-bromo-3-((4-fluorophenyl)amino)-2-oxoindolin-3-yl)methyl)acrylate(6o)



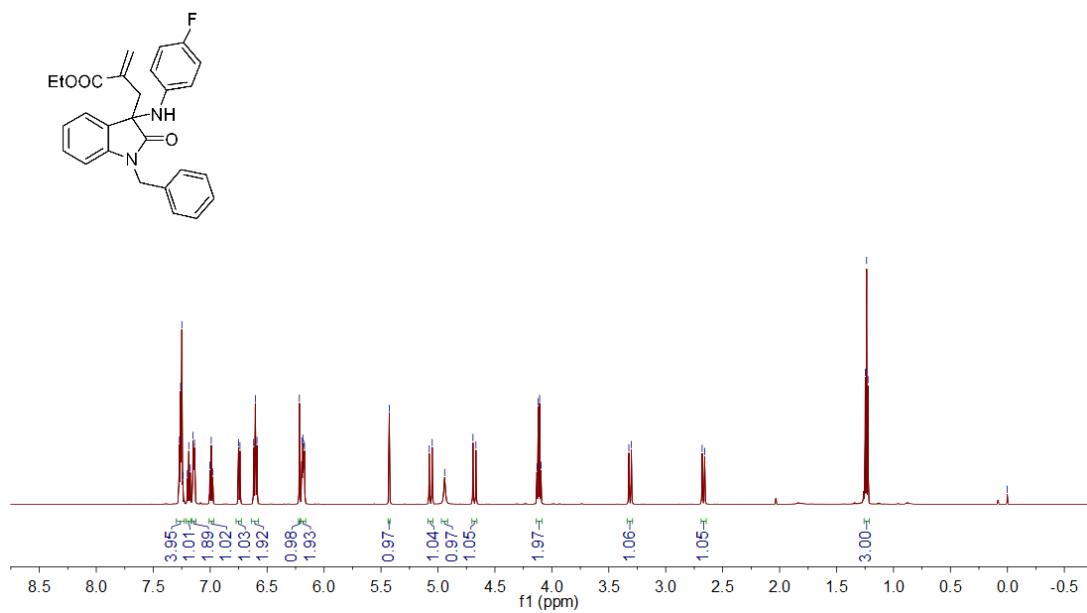
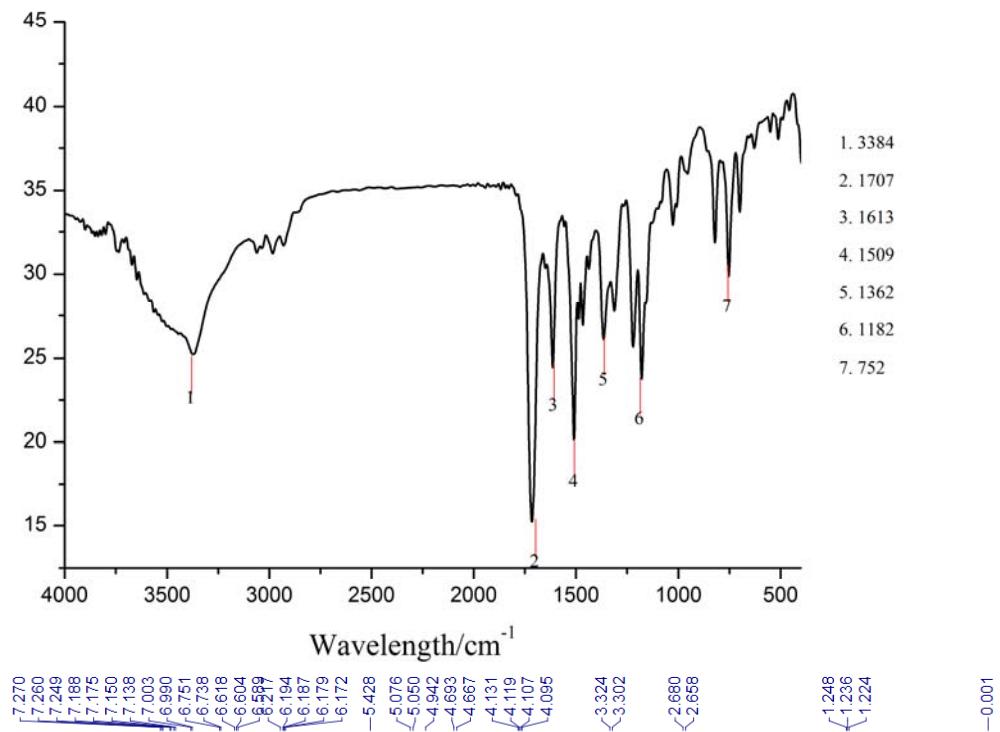


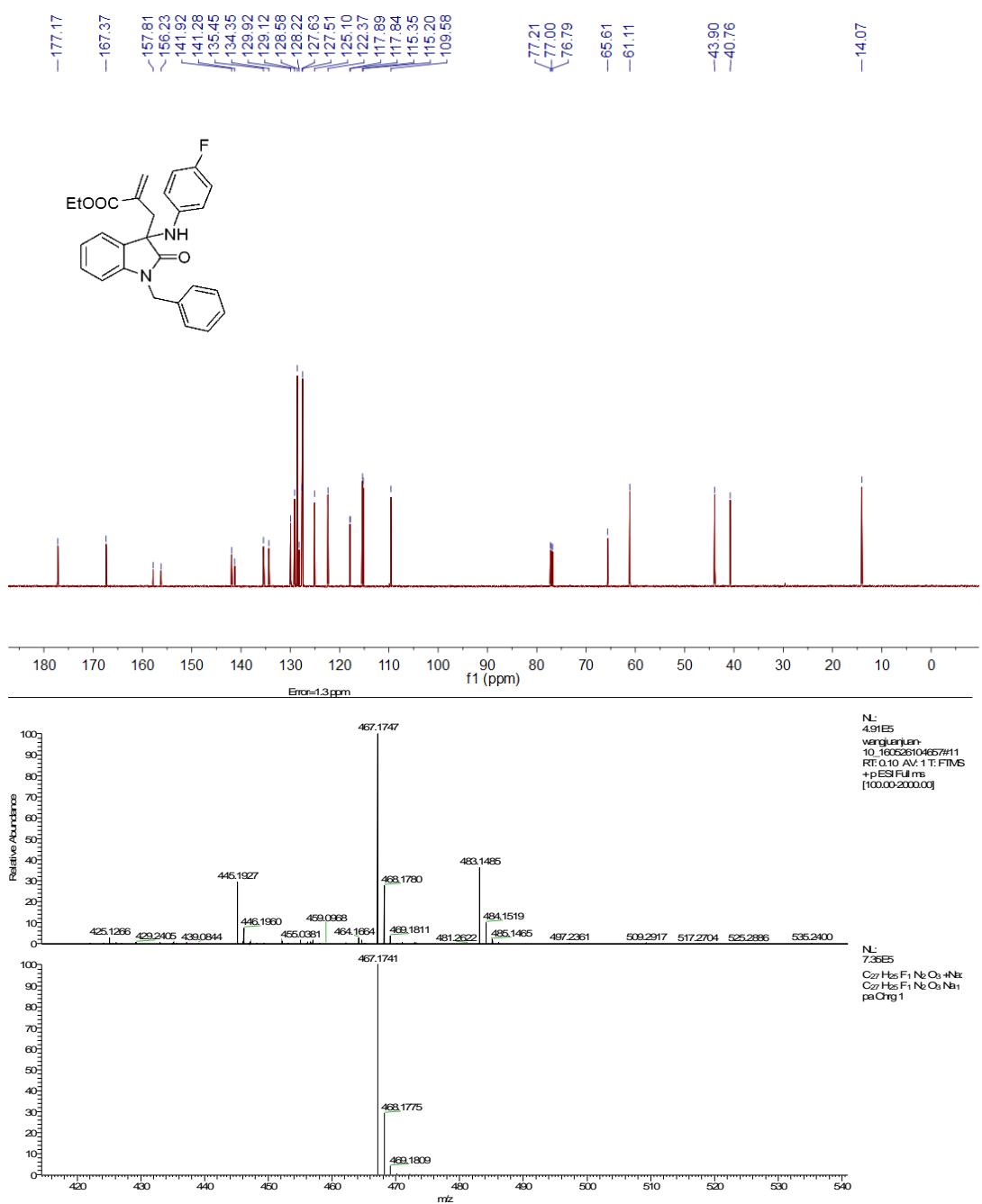
Ethyl 2-((3-(naphthalen-2-ylamino)-2-oxoindolin-3-yl)methyl)acrylate(6p)



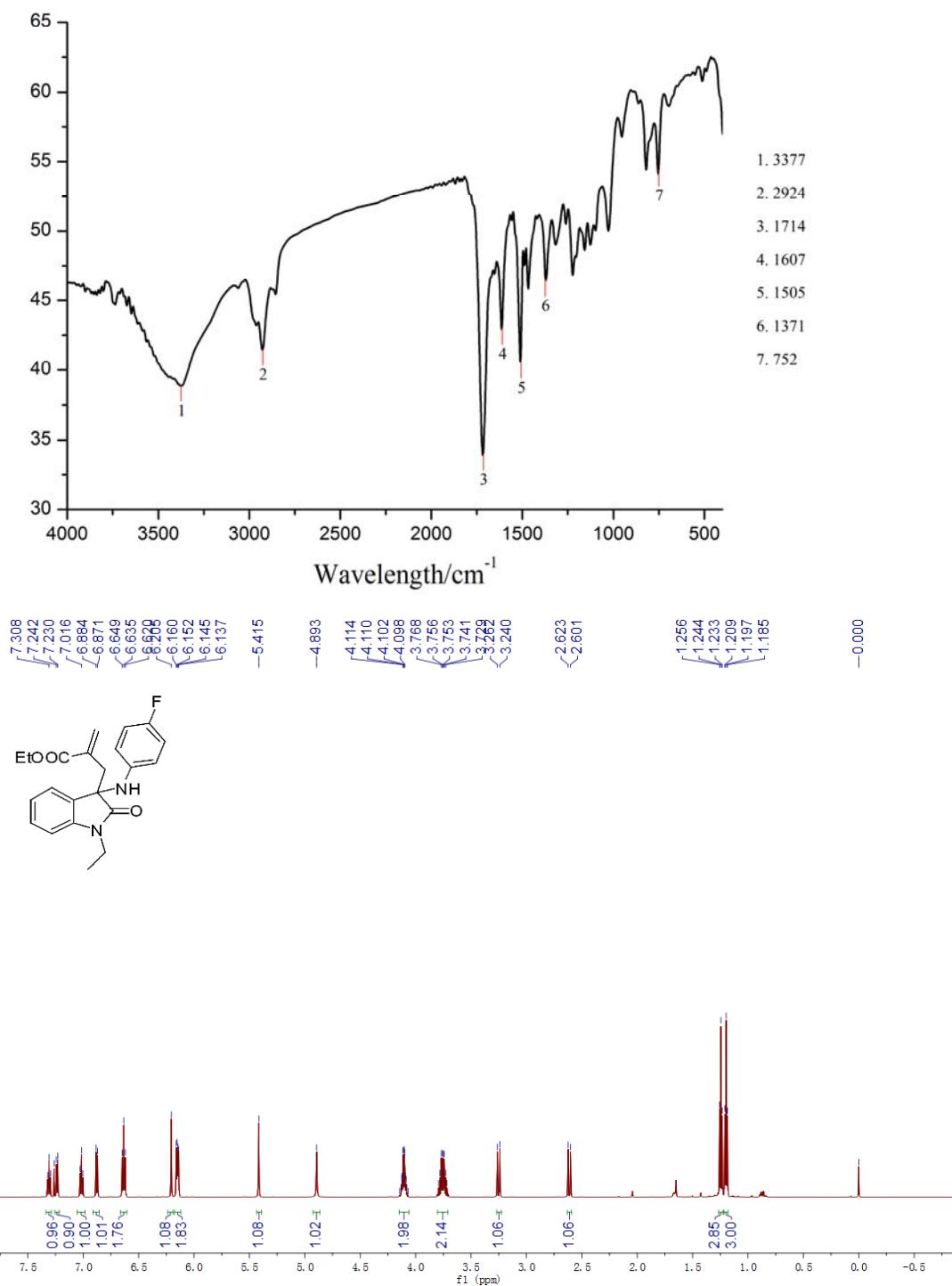


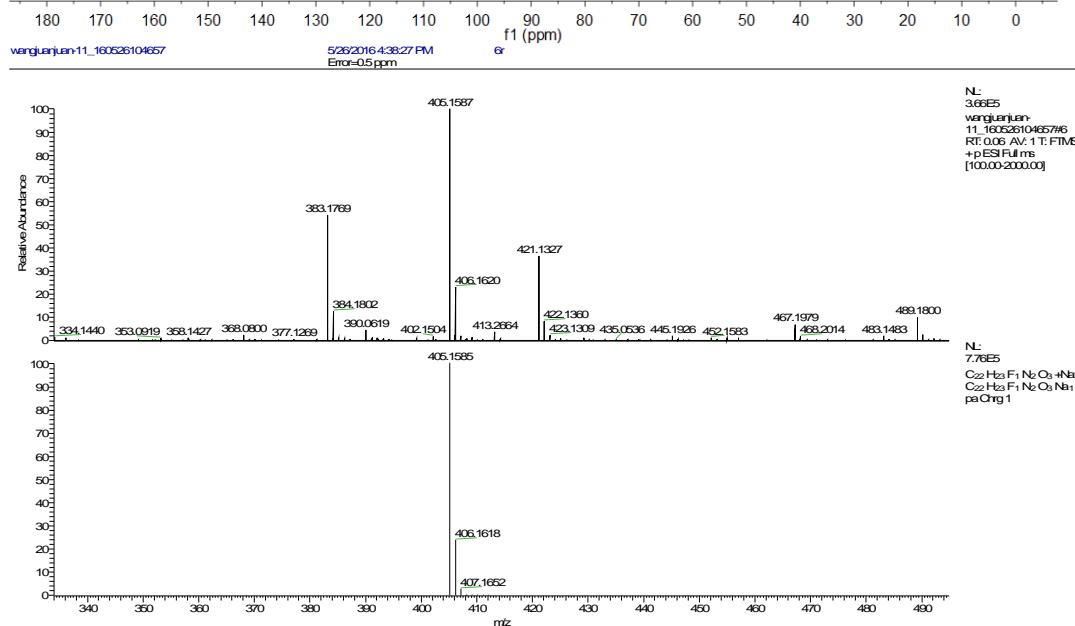
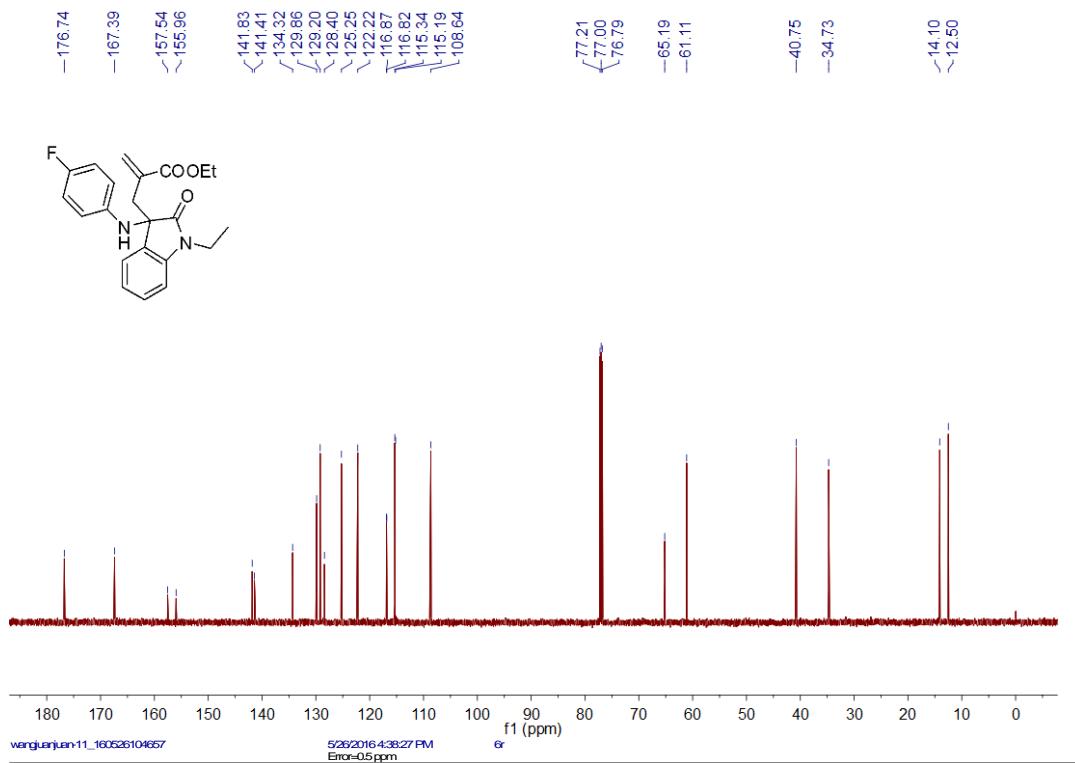
Ethyl 2-((1-benzyl-3-((4-fluorophenyl)amino)-2-oxoindolin-3-yl)methyl)acrylate(6q)





Ethyl 2-((1-ethyl-3-((4-fluorophenyl)amino)-2-oxoindolin-3-yl)methyl)acrylate(6r)





Ethyl 2-((1-butyl-3-((4-fluorophenyl)amino)-2-oxoindolin-3-yl)methyl)acrylate(6s)

