

Supporting Information

Synthesis of optically active 2-amino-1'-benzyl-2',5-dioxo-5H-spiro[indeno[1,2-b]pyran-4,3'-indoline]-3-carbonitriles catalyzed by a bifunctional squaramide derived from quinine
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
1. General Methods.

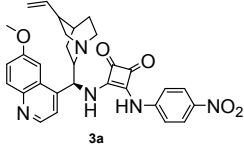
Unless otherwise stated, all reagents were purchased from commercial suppliers and used without purification. All solvents were obtained from commercial sources and were purified according to standard procedures. TLC was carried out on silica gel plates (HSGF 254), which were visualized with UV light and/or staining with phosphomolybdic acids solution. Purification of reaction products was carried out by column chromatography using silica gel (200-300 mesh). ¹H, ¹³C NMR, and ¹⁹F NMR spectra were recorded on a Varian Mercury-300BB (300 MHz) and a Bruker NMR Spectrometer (400 MHz). All chemical shifts (δ) were given in ppm. Chemical shifts are relative to the resonance of the deuterated solvent as the internal standard (CDCl₃, δ7.26 ppm for proton NMR, δ77.16 ppm for carbon NMR; DMSO, δ2.50 ppm for proton NMR, δ39.52 ppm for carbon NMR). Data are presented as follows: chemical shift, integration, multiplicity (s = singlet, d = double, t = triplet, q = quartet, m = multiplet), and coupling constant in hertz. Mass spectra were recorded on a Bruker Agilent 1290 MicrOTOF-Q II instrument. Melting points were measured on a melting points apparatus and were uncorrected. The enantioselectivity value determination was carried out using chiral HPLC (Waters) instrumentation with a Chiracel OD-H column and IC-3 column. Optical rotations were measured on a Shanghai ShenGuang SGW-2 polarimeter at λ = 589 nm. Optical rotations are reported as follows: [α]_D²⁵ (c = g/100mL, solvent).

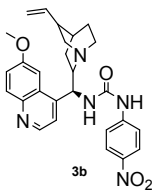
2. Starting Materials.

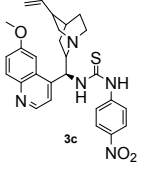
1a-1q, 1t-1v were prepared according to literature procedures^(1,2); catalysts **3a-3h**⁽³⁻⁵⁾ and substrate **2b**⁽⁶⁾ were prepared according to the reported procedures. Synthesis of racemates based on previous literature report⁽⁷⁾.

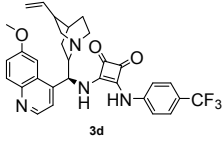
3. Characterization Data of Products **2b, 3a-3h** and **4a-4u,4o-1**.

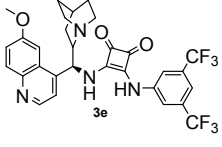
 **4-fluoro-1H-indene-1,3(2H)-dione (2b)**. White solid, 128.6 mg, 51% yield. ¹H NMR (400 MHz, DMSO) δ 8.06 – 7.88 (m, 1H), 7.80 – 7.65 (m, 2H), 3.37 (s, 2H). HRMS (ESI) calculated for C₉H₅FO₂ [M+H]⁺: 165.0307, found 165.0274.

 **3-(((1S)-(6-methoxyquinolin-4-yl)(5-vinylquinuclidin-2-yl)methyl)amino)-4-((4-nitrophenyl)amino)cyclobut-3-ene-1,2-dione (3a)**. Yellow solid, 189.0 mg, 78% yield, m. p. = 212-214 °C, [α]_D²⁵ = 0.1, CHCl₃. ¹H NMR (400 MHz, DMSO) δ 10.23 (s, 1H), 8.83 (d, J = 9.2 Hz, 1H), 8.42 (s, 1H), 8.29 – 8.09 (m, 2H), 7.99 (d, J = 9.2 Hz, 1H), 7.68 (d, J = 4.6 Hz, 1H), 7.57 (m, 2H), 7.46 (m, 1H), 6.24 – 5.70 (m, 2H), 5.16 – 4.90 (m, 2H), 4.42 (s, 1H), 3.95 (s, 3H), 3.48 (s, 1H), 3.30 – 3.09 (m, 2H), 2.85 – 2.55 (m, 2H), 2.30 (s, 1H), 1.57 (d, J = 29.8 Hz, 4H), 0.68 (s, 1H). HRMS (ESI) calculated for C₃₀H₂₉N₅O₅ [M+H]⁺: 540.2202, found 540.5804.

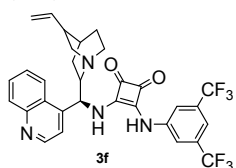
 **1-(((1S)-(6-methoxyquinolin-4-yl)(5-vinylquinuclidin-2-yl)methyl)-3-(4-nitrophenyl)urea (3b)**. Yellow solid, 102.8 mg, 82% yield, m. p. = 216-218 °C, [α]_D²⁵ = -62.8 (c = 0.1, CHCl₃). ¹H NMR (400 MHz, DMSO) δ 9.67 (s, 1H), 8.73 (d, J = 4.5 Hz, 1H), 8.26 – 8.01 (m, 2H), 7.97 (d, J = 9.2 Hz, 1H), 7.82 – 7.67 (m, 1H), 7.62 – 7.48 (m, 3H), 7.48 – 7.38 (m, 1H), 7.16 (s, 1H), 6.03 – 5.76 (m, 1H), 5.38 (s, 1H), 5.10– 4.84 (m, 2H), 3.95 (s, 3H), 3.51 – 3.32 (m, 2H), 3.27 – 3.19 (m, 1H), 2.76 (d, J = 11.8 Hz, 2H), 2.34 (s, 1H), 1.86 – 1.50 (m, 3H), 1.39 (s, 1H), 1.02 – 0.71 (m, 1H). HRMS (ESI) calculated for C₂₇H₂₉N₅O₄ [M+H]⁺: 488.2253, found 488.2257.

 **1-(((1S)-(6-methoxyquinolin-4-yl)(5-vinylquinuclidin-2-yl)methyl)-3-(4-nitrophenyl)thiourea (3c)**. Yellow solid, 135.0 mg, 73% yield, m. p. = 220-222 °C, [α]_D²⁵ = -54.8 (c = 0.1, CHCl₃). ¹H NMR (400 MHz, DMSO) δ 10.43 (s, 1H), 9.00 (s, 1H), 8.76 (d, J = 4.2 Hz, 1H), 8.15 (d, J = 9.2 Hz, 2H), 8.00 – 7.77 (m, 4H), 7.61 (d, J = 4.3 Hz, 1H), 7.45 (m, 1H), 6.34 – 5.67 (m, 2H), 5.17 – 4.82 (m, 2H), 3.97 (s, 3H), 3.27 – 3.08 (m, 1H), 2.91 – 2.62 (m, 2H), 2.39 – 2.10 (m, 1H), 1.76 – 1.16 (m, 5H), 0.98 – 0.73 (m, 2H). HRMS (ESI) calculated for C₂₇H₂₉N₅O₃S [M+H]⁺: 504.2025, found 504.2017.

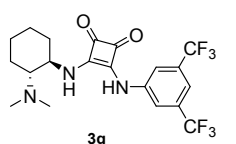
 **3-(((1S)-(6-methoxyquinolin-4-yl)(5-vinylquinuclidin-2-yl)methyl)amino)-4-((4-(trifluoromethyl)phenyl)amino)cyclobut-3-ene-1,2-dione (3d)**. White solid, 216.0 mg, 83% yield, m. p. = 211-213 °C, [α]_D²⁵ = -70.6 (c = 0.1, DMSO). ¹H NMR (400 MHz, DMSO) δ 9.96 (s, 1H), 8.83 (d, J = 4.5 Hz, 1H), 8.32 (s, 1H), 7.99 (d, J = 9.2 Hz, 1H), 7.76 (s, 1H), 7.72 – 7.62 (m, 3H), 7.56 (d, J = 8.4 Hz, 2H), 7.51 – 7.42 (m, 1H), 6.24 – 5.81 (m, 2H), 5.18 – 4.86 (m, 2H), 3.96 (s, 3H), 3.48 (d, J = 7.7 Hz, 1H), 3.32 – 3.12 (m, 2H), 2.90 – 2.57 (m, 2H), 2.29 (s, 1H), 1.56 (d, J = 30.8 Hz, 4H), 0.67 (s, 1H). ¹⁹F NMR (377 MHz, DMSO) δ -60.20. HRMS (ESI) calculated for C₃₁H₂₉F₃N₄O₃ [M+H]⁺: 563.2225, found 563.2214.

 **3-(((3,5-bis(trifluoromethyl)phenyl)amino)-4-(((1S)-(6-methoxyquinolin-4-yl)(5-vinylquinuclidin-2-yl)methyl)amino)cyclobut-3-ene-1,2-dione (3e)**. White solid, 206 mg, 77% yield, m. p. = 225-227 °C, [α]_D²⁵ = -50.6 (c = 0.1, DMSO). ¹H NMR (400 MHz, DMSO) δ 10.18 (s, 1H), 8.82 (d, J = 4.5 Hz, 1H), 8.32 (s, 1H), 8.08 – 7.86 (m, 3H), 7.75 (s, 1H), 7.70 – 7.59 (m, 2H), 7.46 (m, 1H), 6.22 – 5.87 (m, 2H), 5.02 (m, 2H), 3.95 (s, 3H), 3.48 (d, J = 8.3 Hz, 1H), 3.20 (m, 2H), 2.68 (m,

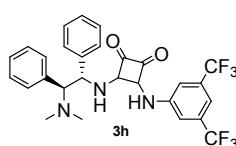
2H), 2.30 (s, 1H), 1.57 (d, J = 29.8 Hz, 4H), 0.67 (s, 1H). ¹⁹F NMR (377 MHz, DMSO) δ -61.74. HRMS (ESI) calculated for C₃₂H₂₈F₆N₄O₃ [M+H]⁺: 631.2099, found 631.5981.



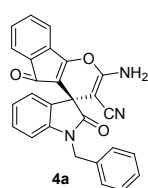
3-((3,5-bis(trifluoromethyl)phenyl)amino)-4-(((1S)-quinolin-4-yl(5-vinylquinuclidin-2-yl)methyl)amino)cyclobut-3-ene-1,2-dione (3f). White solid, 236.0 mg, 83% yield, m. p. = 233-235 °C, [α]_D²⁵ = -89.8 (c = 0.1, DMSO). ¹H NMR (400 MHz, DMSO) δ 10.26 (s, 1H), 8.98 (d, J = 4.5 Hz, 1H), 8.45 (m, 2H), 8.09 (d, J = 8.0 Hz, 1H), 7.98 (s, 2H), 7.82 (m, 1H), 7.78 – 7.68 (m, 2H), 7.66 (s, 1H), 6.22 – 5.73 (m, 2H), 5.19 – 4.83 (m, 2H), 3.53 – 3.37 (m, 1H), 3.20 (m, 2H), 2.83 – 2.59 (m, 2H), 2.29 (s, 1H), 1.55 (d, J = 33.3 Hz, 3H), 1.38 (s, 1H), 0.74 (s, 1H). ¹⁹F NMR (377 MHz, DMSO) δ -61.74. HRMS (ESI) calculated for C₃₁H₂₆F₆N₄O₂ [M+H]⁺: 601.1994, found 601.5799.



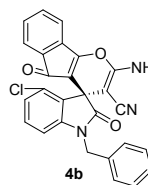
3-((3,5-bis(trifluoromethyl)phenyl)amino)-4-(((1R,2R)-2-dimethylamino)cyclohexyl)amino)cyclobut-3-ene-1,2-dione (3g). White solid, 196.0 mg, 52% yield, m. p. = 223-225 °C, [α]_D²⁵ = +59.8 (c = 0.1, DMSO). ¹H NMR (400 MHz, DMSO) δ 10.47 (s, 1H), 8.08 (s, 2H), 7.94 (s, 1H), 7.66 (s, 1H), 3.89 (s, 1H), 2.25 (s, 6H), 2.10 (d, J = 12.3 Hz, 1H), 1.95 – 1.81 (m, 1H), 1.81 – 1.59 (m, 2H), 1.46 – 1.11 (m, 5H). ¹⁹F NMR (377 MHz, DMSO) δ -61.74. HRMS (ESI) calculated for C₂₀H₂₁F₆N₃O₂ [M+H]⁺: 450.1572, found 450.1580.



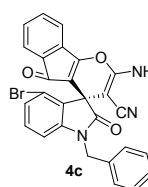
3-((3,5-bis(trifluoromethyl)phenyl)amino)-4-(((1S,2S)-2-(dimethylamino)-1,2-diphenylethyl)amino)cyclobutane-1,2-dione (3h). White solid, 256.0 mg, 68% yield, m. p. = 226-228 °C, [α]_D²⁵ = -52.6 (c = 0.1, DMSO). ¹H NMR (400 MHz, DMSO) δ 10.34 (s, 1H), 8.48 (s, 1H), 8.07 (s, 2H), 7.67 (s, 1H), 7.26 (m, 4H), 7.22 – 7.14 (m, 5H), 7.10 (m, 1H), 5.94 – 5.63 (m, 1H), 4.20 (d, J = 11.3 Hz, 1H), 2.13 (s, 6H). ¹⁹F NMR (377 MHz, DMSO) δ -61.72. HRMS (ESI) calculated for C₂₈H₂₅F₆N₃O₂ [M+H]⁺: 550.1885, found 550.1767.



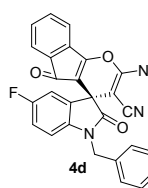
(R)-2-amino-1'-benzyl-2',5-dioxo-5H-spiro[indeno[1,2-b]pyran-4,3'-indoline]-3-carbonitrile (4a). Yellow solid, 39.7 mg, 92% yield, after recrystallization (85% yield), m. p. = 173-175 °C, [α]_D²⁵ = +224.8 (c = 0.1, CHCl₃). ee = 76% (Chiralpak IC-3, hexane/EtOH = 80:20, 254 nm, 1 mL/min, t_{major} = 12.070 min, t_{minor} = 20.155 min). ¹H NMR (400 MHz, DMSO) δ 7.79 (s, 2H), 7.58 (m, 1H), 7.52 – 7.15 (m, 10H), 7.03 (m, 1H), 6.86 (d, J = 7.8 Hz, 1H), 5.18 – 4.79 (m, 2H). ¹³C NMR (101 MHz, DMSO) δ 189.84, 175.83, 168.60, 161.23, 141.67, 135.85, 135.66, 134.16, 133.74, 131.93, 131.03, 129.61, 129.01, 127.89, 127.80, 127.41, 125.48, 122.82, 119.50, 117.78, 111.37, 106.73, 56.86, 46.73, 43.81. HRMS (ESI) calculated for C₂₇H₁₇N₃O₃ [M+H]⁺: 432.1343, found 432.1367. recrystallized 4q



(R)-2-amino-1'-benzyl-4'-chloro-2',5-dioxo-5H-spiro[indeno[1,2-b]pyran-4,3'-indoline]-3-carbonitrile (4b). Yellow solid, 41.5 mg, 89% yield, after recrystallization (80% yield), m. p. = 158-160 °C, [α]_D²⁵ = +186.4 (c = 0.1, CHCl₃). ee = 61% (Chiralpak IC-3, hexane/EtOH = 80:20, 254 nm, 1 mL/min, t_{major} = 9.626 min, t_{minor} = 17.856 min). ¹H NMR (400 MHz, DMSO) δ 7.92 (s, 2H), 7.62 (m, 1H), 7.54 – 7.22 (m, 9H), 7.06 (d, J = 8.2 Hz, 1H), 6.90 (d, J = 7.5 Hz, 1H), 5.10 – 4.95 (m, 2H). ¹³C NMR (101 MHz, DMSO) δ 189.66, 175.16, 169.02, 161.83, 144.59, 135.80, 135.13, 134.38, 132.19, 131.59, 130.83, 130.58, 129.02, 127.94, 127.45, 126.54, 124.12, 123.05, 119.60, 117.48, 109.24, 105.48, 54.85, 46.92, 43.98. HRMS (ESI) calculated for C₂₇H₁₆ClN₃O₃ [M+H]⁺: 466.0953, found 466.4237.

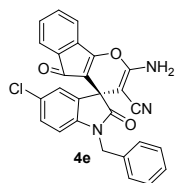


(R)-2-amino-1'-benzyl-4'-bromo-2',5-dioxo-5H-spiro[indeno[1,2-b]pyran-4,3'-indoline]-3-carbonitrile (4c). Yellow solid, 44.4 mg, 87% yield, after recrystallization (81% yield), m. p. = 218-220 °C, [α]_D²⁵ = +179.6 (c = 0.1, CHCl₃). ee = 60% (Chiralpak IC-3, hexane/EtOH = 80:20, 254 nm, 1 mL/min, t_{major} = 10.052 min, t_{minor} = 18.735 min). ¹H NMR (400 MHz, DMSO) δ 7.93 (s, 2H), 7.60 (m, 1H), 7.54 – 7.14 (m, 10H), 7.02 – 6.86 (m, 1H), 5.76 (s, 1H), 5.20 – 4.84 (m, 2H). ¹³C NMR (101 MHz, DMSO) δ 189.62, 175.19, 169.18, 161.91, 144.80, 135.78, 135.16, 134.38, 132.20, 131.76, 130.83, 129.02, 127.95, 127.93, 127.43, 127.16, 123.04, 119.60, 119.46, 117.48, 109.67, 105.39, 54.85, 48.12, 43.89. HRMS (ESI) calculated for C₂₇H₁₆BrN₃O₃ [M+H]⁺: 510.0448, found 510.3886.

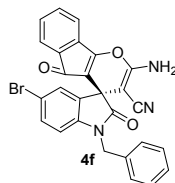


(R)-2-amino-1'-benzyl-5'-fluoro-2',5-dioxo-5H-spiro[indeno[1,2-b]pyran-4,3'-indoline]-3-carbonitrile (4d). Yellow solid, 40.9 mg, 91% yield, after recrystallization (85% yield), m. p. = 148-150 °C, [α]_D²⁵ = +214.4 (c = 0.1, CHCl₃). ee = 78% (Chiralpak IC-3, hexane/EtOH = 80:20, 254 nm, 1 mL/min, t_{major} = 10.201 min, t_{minor} = 17.233 min). ¹H NMR (400 MHz, DMSO) δ 7.89 (s, 2H), 7.61 (m, 1H), 7.54 – 7.20 (m, 9H), 7.19 – 7.03 (m, 1H), 6.88 (m, 1H), 5.16 – 4.87 (m, 2H). ¹³C NMR (101 MHz, DMSO) δ 189.82, 176.01, 168.51, 161.21, 158.30, 138.98, 135.98, 135.61, 134.14, 133.56 (d, J = 8.0 Hz),

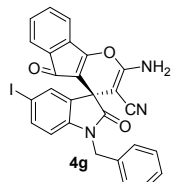
131.92, 131.01, 129.00, 127.87, 127.44, 122.81, 119.48, 117.79, 116.04 (d, J = 23.6 Hz), 113.19 (d, J = 25.2 Hz), 110.82 (d, J = 8.0 Hz), 106.90, 57.03, 46.95, 43.86. ¹⁹F NMR (377 MHz, DMSO) δ -120.02. HRMS (ESI) calculated for C₂₇H₁₆FN₃O₃ [M+H]⁺: 450.1248, found 510.3886.



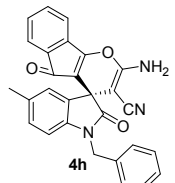
(R)-2-amino-1'-benzyl-5'-chloro-2',5-dioxo-5H-spiro[indeno[1,2-b]pyran-4,3'-indoline]-3-carbonitrile (4e). Yellow solid, 41.9 mg, 90% yield, after recrystallization (84% yield), m. p. = 155-158 °C, [α]_D²⁵ = +246.8 (c = 0.1, CHCl₃). ee = 76% (Chiralpak IC-3, hexane/EtOH = 80:20, 254 nm, 1 mL/min, t_{major} = 8.566 min, t_{minor} = 14.477 min). ¹H NMR (400 MHz, DMSO) δ 7.86 (s, 2H), 7.68 – 7.53 (m, 2H), 7.52 – 7.20 (m, 9H), 6.88 (d, J = 8.4 Hz, 1H), 5.12 – 4.90 (m, 2H). ¹³C NMR (101 MHz, DMSO) δ 189.84, 175.83, 168.60, 161.23, 141.67, 135.85, 135.66, 134.16, 133.74, 131.93, 131.03, 129.61, 129.01, 127.89, 127.80, 127.41, 125.48, 122.82, 119.50, 117.78, 111.37, 106.73, 56.86, 46.73, 43.81. HRMS (ESI) calculated for C₂₇H₁₆ClN₃O₃ [M+H]⁺: 466.0953, found 466.0971.



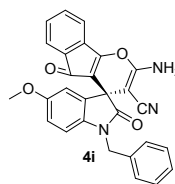
(R)-2-amino-1'-benzyl-5'-bromo-2',5-dioxo-5H-spiro[indeno[1,2-b]pyran-4,3'-indoline]-3-carbonitrile (4f). Yellow solid, 46.9 mg, 92% yield, after recrystallization (82% yield), m. p. = 169-171 °C, [α]_D²⁵ = +273.6 (c = 0.1, CHCl₃). ee = 73% (Chiralpak IC-3, hexane/EtOH = 80:20, 254 nm, 1 mL/min, t_{major} = 8.853 min, t_{minor} = 15.038 min). ¹H NMR (400 MHz, DMSO) δ 7.86 (s, 2H), 7.69 (d, J = 2.0 Hz, 1H), 7.63 – 7.55 (m, 1H), 7.53 – 7.20 (m, 9H), 6.83 (d, J = 8.4 Hz, 1H), 5.10 – 4.90 (m, 2H). ¹³C NMR (101 MHz, DMSO) δ 189.86, 175.71, 168.62, 161.22, 142.08, 135.82, 135.68, 134.17, 134.06, 132.46, 131.93, 131.03, 129.01, 128.17, 127.89, 127.40, 122.82, 119.51, 117.80, 115.55, 111.88, 106.71, 56.85, 46.66, 43.77. HRMS (ESI) calculated for C₂₇H₁₆BrN₃O₃ [M+H]⁺: 510.0448, found 510.3676.



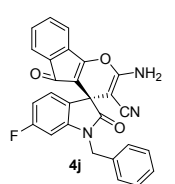
(R)-2-amino-1'-benzyl-5'-iodo-2',5-dioxo-5H-spiro[indeno[1,2-b]pyran-4,3'-indoline]-3-carbonitrile (4g). Yellow solid, 51.3 mg, 92% yield, after recrystallization (84% yield), m. p. = 163-165 °C, [α]_D²⁵ = +278.0 (c = 0.1, CHCl₃). ee = 77% (Chiralpak IC-3, hexane/EtOH = 80:20, 254 nm, 1 mL/min, t_{major} = 9.572 min, t_{minor} = 16.746 min). ¹H NMR (400 MHz, DMSO) δ 7.85 (s, 2H), 7.79 (d, J = 1.6 Hz, 1H), 7.59 (m, 2H), 7.54 – 7.22 (m, 8H), 6.71 (d, J = 8.3 Hz, 1H), 5.16 – 4.82 (m, 2H). ¹³C NMR (101 MHz, DMSO) δ 189.86, 175.51, 168.57, 161.18, 142.56, 138.23, 135.81, 135.69, 134.17, 134.14, 133.46, 131.89, 131.02, 128.98, 127.86, 127.36, 122.79, 119.48, 117.81, 112.32, 106.75, 86.92, 56.91, 46.45, 43.70. HRMS (ESI) calculated for C₂₇H₁₆IN₃O₃ [M+H]⁺: 558.0309, found 558.3913.



(R)-2-amino-1'-benzyl-5'-methyl-2',5-dioxo-5H-spiro[indeno[1,2-b]pyran-4,3'-indoline]-3-carbonitrile (4h). Yellow solid, 41.9 mg, 94% yield, after recrystallization (85% yield), m. p. = 181-183 °C, [α]_D²⁵ = +272.4 (c = 0.1, CHCl₃). ee = 72% (Chiralpak IC-3, hexane/EtOH = 80:20, 254 nm, 1 mL/min, t_{major} = 11.776 min, t_{minor} = 21.937 min). ¹H NMR (400 MHz, DMSO) δ 7.76 (s, 2H), 7.66 – 7.52 (m, 1H), 7.51 – 7.21 (m, 8H), 7.16 (s, 1H), 7.03 (d, J = 7.3 Hz, 1H), 6.72 (d, J = 8.0 Hz, 1H), 5.11 – 4.83 (m, 2H), 2.21 (s, 3H). ¹³C NMR (101 MHz, DMSO) δ 189.83, 175.88, 168.16, 161.03, 140.40, 136.26, 135.59, 134.18, 132.72, 131.85, 131.82, 130.97, 129.90, 128.92, 127.74, 127.41, 125.52, 122.78, 119.38, 117.87, 109.68, 107.56, 57.67, 46.62, 43.74, 20.98. HRMS (ESI) calculated for C₂₈H₁₉N₃O₃ [M+H]⁺: 446.1499, found 446.1886.

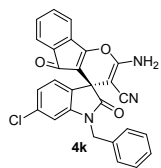


(R)-2-amino-1'-benzyl-5'-methoxy-2',5-dioxo-5H-spiro[indeno[1,2-b]pyran-4,3'-indoline]-3-carbonitrile (4i). Yellow solid, 42.5 mg, 92% yield, after recrystallization (83% yield), m. p. = 156-158 °C, [α]_D²⁵ = +249.6 (c = 0.1, CHCl₃). ee = 72% (Chiralpak IC-3, hexane/EtOH = 80:20, 254 nm, 1 mL/min, t_{major} = 11.776 min, t_{minor} = 21.937 min). ¹H NMR (400 MHz, DMSO) δ 7.78 (s, 2H), 7.67 – 7.54 (m, 1H), 7.53 – 7.16 (m, 8H), 7.05 (d, J = 2.5 Hz, 1H), 6.78 (m, 2H), 5.16 – 4.80 (m, 2H), 3.67 (s, 3H). ¹³C NMR (101 MHz, DMSO) δ 189.84, 175.77, 168.28, 161.06, 156.53, 136.28, 136.05, 135.68, 134.11, 133.05, 131.84, 131.05, 128.93, 127.74, 127.42, 122.74, 119.36, 117.90, 114.28, 112.02, 110.39, 107.44, 57.64, 55.99, 46.99, 43.78. HRMS (ESI) calculated for C₂₈H₁₉N₃O₄ [M+H]⁺: 462.1448, found 462.4724.

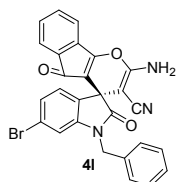


(R)-2-amino-1'-benzyl-6'-fluoro-2',5-dioxo-5H-spiro[indeno[1,2-b]pyran-4,3'-indoline]-3-carbonitrile (4j). Yellow solid, 41.8 mg, 93% yield, after recrystallization (86% yield), m. p. = 145-147 °C, [α]_D²⁵ = +136.8 (c = 0.1, CHCl₃). ee = 79% (Chiralpak IC-3, hexane/EtOH = 80:20, 254 nm, 1 mL/min, t_{major} = 8.735 min, t_{minor} = 13.176 min). ¹H NMR (400 MHz, DMSO) δ 7.82 (s, 2H), 7.59 (m, 1H), 7.52 – 7.22 (m, 9H), 7.02 – 6.67 (m, 2H), 5.00 (s, 2H). ¹³C NMR (101 MHz, DMSO) δ 189.80, 176.46, 168.33, 161.12, 144.55 (d, J = 12.4 Hz), 135.90, 135.55, 134.20, 131.94, 130.94, 128.99, 127.91, 127.52, 126.69 (d, J = 12.0 Hz), 122.82, 119.47, 117.74, 109.71, 109.59 (d, J = 22.5 Hz), 107.08, 98.70,

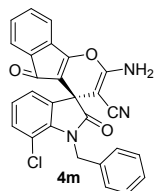
98.56 (d, $J = 27.9$ Hz), 57.16, 46.22, 43.81. ^{19}F NMR (377 MHz, DMSO) δ -111.07. HRMS (ESI) calculated for $\text{C}_{27}\text{H}_{16}\text{FN}_3\text{O}_3$ $[\text{M}+\text{H}]^+$: 450.1248, found 450.4484.



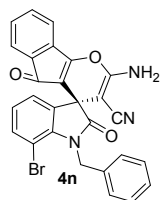
(R)-2-amino-1'-benzyl-6'-chloro-2',5-dioxo-5H-spiro[indeno[1,2-b]pyran-4,3'-indoline]-3-carbonitrile (4k). Yellow solid, 44.3 mg, 95% yield, after recrystallization (85% yield), m. p. = 178-180 °C, $[\alpha]_{\text{D}}^{25} = +168.0$ ($c = 0.1$, CHCl_3). ee = 75% (Chiralpak IC-3, hexane/EtOH = 80:20, 254 nm, 1 mL/min, $t_{\text{major}} = 8.617$ min, $t_{\text{minor}} = 13.442$ min). ^1H NMR (400 MHz, DMSO) δ 7.86 (s, 2H), 7.50 – 7.43 (m, 2H), 7.43 – 7.34 (m, 5H), 7.34 – 7.25 (m, 3H), 7.09 (m, 1H), 7.01 (d, $J = 1.8$ Hz, 1H), 5.02 (s, 2H). ^{13}C NMR (101 MHz, DMSO) δ 189.79, 176.14, 168.45, 161.18, 144.27, 135.85, 135.52, 134.22, 134.10, 131.98, 130.94, 130.52, 129.02, 127.93, 127.45, 126.66, 123.33, 122.85, 119.52, 117.72, 110.24, 106.85, 56.85, 46.31, 43.72. HRMS (ESI) calculated for $\text{C}_{27}\text{H}_{16}\text{ClN}_3\text{O}_3$ $[\text{M}+\text{H}]^+$: 466.0953, found 466.0964.



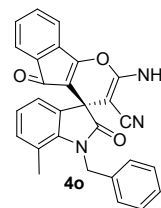
(R)-2-amino-1'-benzyl-6'-bromo-2',5-dioxo-5H-spiro[indeno[1,2-b]pyran-4,3'-indoline]-3-carbonitrile (4l). Yellow solid, 47.0 mg, 92% yield, after recrystallization (80% yield), m. p. = 155-157 °C, $[\alpha]_{\text{D}}^{25} = +281.2$ ($c = 0.1$, CHCl_3). ee = 71% (Chiralpak IC-3, hexane/EtOH = 80:20, 254 nm, 1 mL/min, $t_{\text{major}} = 8.754$ min, $t_{\text{minor}} = 13.796$ min). ^1H NMR (400 MHz, DMSO) δ 7.87 (s, 2H), 7.68 – 7.53 (m, 1H), 7.54 – 7.17 (m, 10H), 7.14 (d, $J = 1.6$ Hz, 1H), 5.20 – 4.86 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ 189.79, 176.77, 168.46, 161.14, 138.66, 137.73, 135.47, 134.85, 134.26, 132.03, 132.00, 130.90, 128.88, 127.41, 126.30, 125.13, 124.54, 122.91, 119.60, 117.78, 114.66, 106.87, 57.07, 46.46, 45.38. HRMS (ESI) calculated for $\text{C}_{27}\text{H}_{16}\text{BrN}_3\text{O}_3$ $[\text{M}+\text{H}]^+$: 510.0448, found 510.3895.



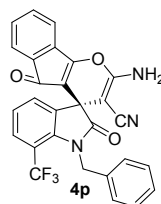
(R)-2-amino-1'-benzyl-7'-chloro-2',5-dioxo-5H-spiro[indeno[1,2-b]pyran-4,3'-indoline]-3-carbonitrile (4m). Yellow solid, 43.8 mg, 94% yield, after recrystallization (81% yield), m. p. = 150-152 °C, $[\alpha]_{\text{D}}^{25} = +166.8$ ($c = 0.1$, CHCl_3). ee = 71% (Chiralpak IC-3, hexane/EtOH = 80:20, 254 nm, 1 mL/min, $t_{\text{major}} = 8.478$ min, $t_{\text{minor}} = 18.664$ min). ^1H NMR (400 MHz, DMSO) δ 7.91 (s, 2H), 7.59 (m, 1H), 7.55 – 7.16 (m, 10H), 7.09 (m, 1H), 5.49 – 5.06 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ 189.84, 175.83, 168.60, 161.23, 141.67, 135.85, 135.66, 134.16, 133.74, 131.93, 131.03, 129.61, 129.01, 127.89, 127.80, 127.41, 125.48, 122.82, 119.50, 117.78, 111.37, 106.73, 56.86, 46.73, 43.81. HRMS (ESI) calculated for $\text{C}_{27}\text{H}_{16}\text{ClN}_3\text{O}_3$ $[\text{M}+\text{H}]^+$: 466.0953, found 466.4251.



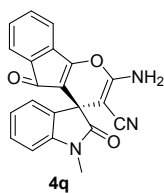
(R)-2-amino-1'-benzyl-7'-bromo-2',5-dioxo-5H-spiro[indeno[1,2-b]pyran-4,3'-indoline]-3-carbonitrile (4n). Yellow solid, 48.0 mg, 94% yield, after recrystallization (79% yield), m. p. = 221-223 °C, $[\alpha]_{\text{D}}^{25} = +212.4$ ($c = 0.1$, CHCl_3). ee = 65% (Chiralpak IC-3, hexane/EtOH = 80:20, 254 nm, 1 mL/min, $t_{\text{major}} = 8.559$ min, $t_{\text{minor}} = 20.833$ min). ^1H NMR (400 MHz, DMSO) δ 7.90 (s, 2H), 7.65 – 7.54 (m, 1H), 7.52 – 7.18 (m, 10H), 7.02 (m, 1H), 5.33 (d, $J = 16.9$ Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 189.78, 176.94, 168.46, 161.14, 140.11, 137.67, 135.47, 135.38, 135.17, 134.27, 132.04, 130.89, 128.85, 127.35, 126.31, 125.51, 125.05, 122.91, 119.60, 117.78, 106.90, 102.05, 57.12, 46.40, 45.10. HRMS (ESI) calculated for $\text{C}_{27}\text{H}_{16}\text{BrN}_3\text{O}_3$ $[\text{M}+\text{H}]^+$: 510.0448, found 510.3890.



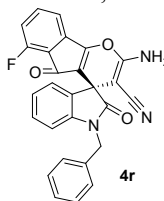
(R)-2-amino-1'-benzyl-7'-methyl-2',5-dioxo-5H-spiro[indeno[1,2-b]pyran-4,3'-indoline]-3-carbonitrile (4o). Yellow solid, 42.3 mg, 95% yield, after recrystallization (87% yield), m. p. = 223-225 °C, $[\alpha]_{\text{D}}^{25} = +207.6$ ($c = 0.1$, CHCl_3). ee = 82% (Chiralpak IC-3, hexane/EtOH = 80:20, 254 nm, 1 mL/min, $t_{\text{major}} = 11.415$ min, $t_{\text{minor}} = 31.109$ min). ^1H NMR (400 MHz, DMSO) δ 7.79 (s, 2H), 7.57 (m, 1H), 7.51 – 7.14 (m, 9H), 6.98 (m, 2H), 5.39 – 5.07 (m, 2H), 2.21 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 189.88, 176.99, 168.18, 160.99, 140.78, 138.22, 135.56, 134.18, 133.51, 132.63, 131.88, 130.94, 129.11, 127.49, 126.04, 123.67, 123.17, 122.78, 119.97, 119.41, 117.99, 107.66, 57.96, 46.11, 45.34, 18.38. HRMS (ESI) calculated for $\text{C}_{28}\text{H}_{19}\text{N}_3\text{O}_3$ $[\text{M}+\text{H}]^+$: 446.1499, found 446.4718.



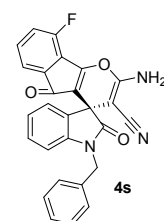
(R)-2-amino-1'-benzyl-2',5-dioxo-7'-(trifluoromethyl)-5H-spiro[indeno[1,2-b]pyran-4,3'-indoline]-3-carbonitrile (4p). Yellow solid, 45.9 mg, 92% yield, after recrystallization (78% yield), m. p. = 221-223 °C, $[\alpha]_{\text{D}}^{25} = +158.6$ ($c = 0.1$, CHCl_3). ee = 64% (Chiralpak OD-H, hexane/EtOH = 90:10, 254 nm, 1 mL/min, $t_{\text{major}} = 12.293$ min, $t_{\text{minor}} = 20.889$ min). ^1H NMR (300 MHz, dmsO) δ 7.97 (s, 2H), 7.86 – 7.75 (m, 1H), 7.74 – 7.64 (m, 1H), 7.65 – 7.55 (m, 1H), 7.53 – 7.38 (m, 2H), 7.38 – 7.15 (m, 7H), 5.15 (s, 2H). ^{13}C NMR (101 MHz, DMSO) δ 189.74, 177.53, 168.70, 161.31, 140.78, 136.41, 135.44, 134.74, 134.30, 132.09, 130.87, 130.12, 128.65, 127.82 (q, $J = 11.1, 5.5$ Hz), 127.14, 125.69, 123.89, 122.94, 119.67, 117.72, 111.80, 111.47, 106.59, 56.72, 46.11, 45.27. ^{19}F NMR (377 MHz, DMSO) δ -53.50. HRMS (ESI) calculated for $\text{C}_{28}\text{H}_{16}\text{F}_3\text{N}_3\text{O}_3$ $[\text{M}+\text{H}]^+$: 500.1177, found 500.1802.



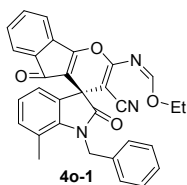
(R)-2-amino-1'-methyl-2',5-dioxo-5H-spiro[indeno[1,2-b]pyran-4,3'-indoline]-3-carbonitrile (4q). Yellow solid, 33.1 mg, 93% yield, after recrystallization (86% yield), m. p. = 209-211 °C, $[\alpha]_D^{25} = +78.4$ (c = 0.1, CHCl₃). ee = 80% (Chiralpak IC-3, hexane/EtOH = 80:20, 254 nm, 1 mL/min, t_{major} = 24.583 min, t_{minor} = 33.464 min). ¹H NMR (400 MHz, DMSO) δ 7.74 (s, 2H), 7.57 (m, 1H), 7.49 – 7.22 (m, 5H), 7.15 – 7.00 (m, 2H), 3.21 (s, 3H). ¹³C NMR (101 MHz, DMSO) δ 189.69, 175.68, 168.02, 161.08, 143.75, 135.55, 134.15, 131.84, 131.66, 130.93, 129.80, 124.77, 123.46, 122.67, 119.35, 117.68, 109.23, 107.55, 57.26, 46.50, 27.03. HRMS (ESI) calculated for C₂₁H₁₃N₃O₃ [M+H]⁺: 356.1030, found 356.3911.



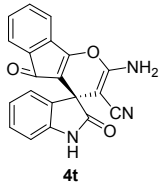
(R)-2-amino-1'-benzyl-6-fluoro-2',5-dioxo-5H-spiro[indeno[1,2-b]pyran-4,3'-indoline]-3-carbonitrile (4r). Yellow solid, 17.5 mg, 39% yield, m. p. = 155-157 °C, $[\alpha]_D^{25} = +176.2$ (c = 0.1, CHCl₃). ee = 35% (Chiralpak IC-3, hexane/EtOH = 80:20, 254 nm, 1 mL/min, t_{major} = 13.069 min, t_{minor} = 21.281 min). ¹H NMR (400 MHz, DMSO) δ 7.80 (s, 2H), 7.58 – 7.40 (m, 4H), 7.40 – 7.15 (m, 6H), 7.11 – 6.93 (m, 1H), 6.86 (d, J = 7.8 Hz, 1H), 5.18 – 4.81 (m, 2H). ¹³C NMR (101 MHz, DMSO) δ 188.63, 175.87, 166.90, 160.94, 155.73, 153.18, 142.75, 136.18, 135.03 (d, J = 6.7 Hz), 133.20, 131.63, 129.75, 128.96, 127.80, 127.43, 125.14, 123.54 (d, J = 11.6 Hz), 120.38 (d, J = 12.8 Hz), 119.41, 117.69, 109.90, 107.78, 57.2, 46.47, 43.74. ¹⁹F NMR (377 MHz, DMSO) δ -117.86. HRMS (ESI) calculated for C₂₇H₁₆FN₃O₃ [M+H]⁺: 450.1209, found 450.1174.



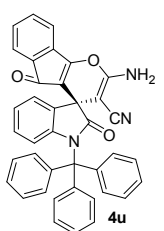
(R)-2-amino-1'-benzyl-9-fluoro-2',5-dioxo-5H-spiro[indeno[1,2-b]pyran-4,3'-indoline]-3-carbonitrile (4s). Yellow solid, 22.5 mg, 50% yield, m. p. = 145-147 °C, $[\alpha]_D^{25} = +184.4$ (c = 0.1, CHCl₃). ee = 38% (Chiralpak IC-3, hexane/EtOH = 80:20, 254 nm, 1 mL/min, t_{major} = 12.423 min, t_{minor} = 20.031 min). ¹H NMR (400 MHz, DMSO) δ 7.82 (s, 2H), 7.74 – 7.54 (m, 1H), 7.43 (d, J = 7.3 Hz, 2H), 7.38 – 7.12 (m, 7H), 7.09 – 6.96 (m, 1H), 6.86 (d, J = 7.8 Hz, 1H), 4.99 (s, 2H). ¹³C NMR (101 MHz, DMSO) δ 186.21, 175.82, 166.96, 160.97, 157.95, 155.35, 142.76, 137.59 (d, J = 18.9, 6.3 Hz), 136.17, 131.50, 129.77, 128.96, 127.81, 127.43, 125.11, 123.60, 121.28 (d, J = 21.3 Hz), 117.72, 116.29, 115.36 (d, J = 14.0 Hz), 109.93, 107.99, 57.40, 46.59, 43.75. ¹⁹F NMR (377 MHz, DMSO) δ -114.24. HRMS (ESI) calculated for C₂₇H₁₆FN₃O₃ [M+H]⁺: 450.1209, found 450.2005.



Ethyl (R, Z)-N-(1'-benzyl-3-cyano-7'-methyl-2',5-dioxo-5H-spiro[indeno[1,2-b]pyran-4,3'-indolin]-2-yl)formimidate (4o-1). Compound **4o** (1.0 eq, 44.6 mg) was put into a round bottom flask, added triethoxymethane (1.5 eq, 22.5 mg) and 0.5 mL AcOH, heated and stirred at 120 °C for about 4 hours. After the reaction was complete, the solvent was evaporated in vacuo, Separation and purification of compound **4o-1** by column chromatography. Yellow solid, 49.1 mg, 98% yield, m. p. = 209-211 °C, $[\alpha]_D^{25} = +198.2$ (c = 0.1, CHCl₃), ee = 95% (Chiralpak IC-3, hexane/EtOH = 80:20, 254 nm, 1 mL/min, t_{major} = 14.755 min, t_{minor} = 22.287 min). ¹H NMR (300 MHz, CDCl₃) δ 8.51 (s, 1H), 7.51 – 7.18 (m, 9H), 7.18 – 6.81 (m, 3H), 5.31 (q, J = 17.1 Hz, 2H), 4.44 (q, J = 7.1 Hz, 2H), 2.28 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 189.26, 175.57, 167.90, 160.43, 158.92, 140.83, 137.09, 135.56, 134.14, 133.00, 131.27, 131.10, 130.92, 128.96, 127.19, 125.84, 123.63, 122.65, 122.60, 120.60, 118.96, 114.95, 107.37, 83.03, 64.99, 47.66, 46.08, 18.67, 13.88. HRMS (ESI) calculated for C₃₁H₂₃N₃O₄ [M+H]⁺: 502.1722, found 502.1809.

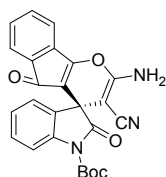


(R)-2-amino-2',5-dioxo-5H-spiro[indeno[1,2-b]pyran-4,3'-indoline]-3-carbonitrile (4t). Yellow solid, 32.0 mg, 94% yield, after recrystallization (84% yield), m. p. = 178-180 °C, $[\alpha]_D^{25} = +198.6$ (c = 0.1, CHCl₃). ee = 66% (Chiralpak IC-3, hexane/*i*-PrOH = 90:10, 254 nm, 1 mL/min, t_{major} = 26.254 min, t_{minor} = 38.945 min). ¹H NMR (400 MHz, DMSO) δ 10.69 (s, 1H), 7.71 (s, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.4 Hz, 1H), 7.37 (d, J = 7.1 Hz, 1H), 7.31 (d, J = 7.2 Hz, 1H), 7.24 (t, J = 7.6 Hz, 2H), 6.97 (t, J = 7.5 Hz, 1H), 6.89 (d, J = 7.6 Hz, 1H). ¹³C NMR (101 MHz, DMSO) δ 189.82, 177.31, 167.96, 160.93, 142.30, 135.58, 134.11, 132.49, 131.78, 130.96, 129.62, 125.06, 122.73, 122.66, 119.27, 117.82, 110.22, 107.71, 57.68, 46.86.



(R)-2-amino-2',5-dioxo-1'-trityl-5H-spiro[indeno[1,2-b]pyran-4,3'-indoline]-3-carbonitrile (4u). Yellow solid, 59.9 mg, 96% yield, after recrystallization (82% yield), m. p. = 165-167 °C, $[\alpha]_D^{25} = +242.4$ (c = 0.1, CHCl₃). ee = 63% (Chiralpak IC-3, hexane/EtOH = 90:10, 254 nm, 1 mL/min, t_{major} = 20.150 min, t_{minor} = 45.032 min). ¹H NMR (400 MHz, DMSO) δ 7.76 (s, 2H), 7.60 – 7.53 (m, 1H), 7.53 – 7.41 (m, 8H), 7.35 – 7.17 (m, 11H), 7.01 – 6.85 (m, 2H), 6.31 – 6.19 (m, 1H). ¹³C NMR (101 MHz, DMSO) δ 189.93, 176.87, 168.14, 161.06, 143.20, 142.23, 135.56, 134.15, 131.98, 131.90, 130.93,

129.57, 128.06, 127.23, 124.65, 123.10, 122.90, 119.37, 118.19, 115.99, 107.71, 74.73, 58.00, 47.32.

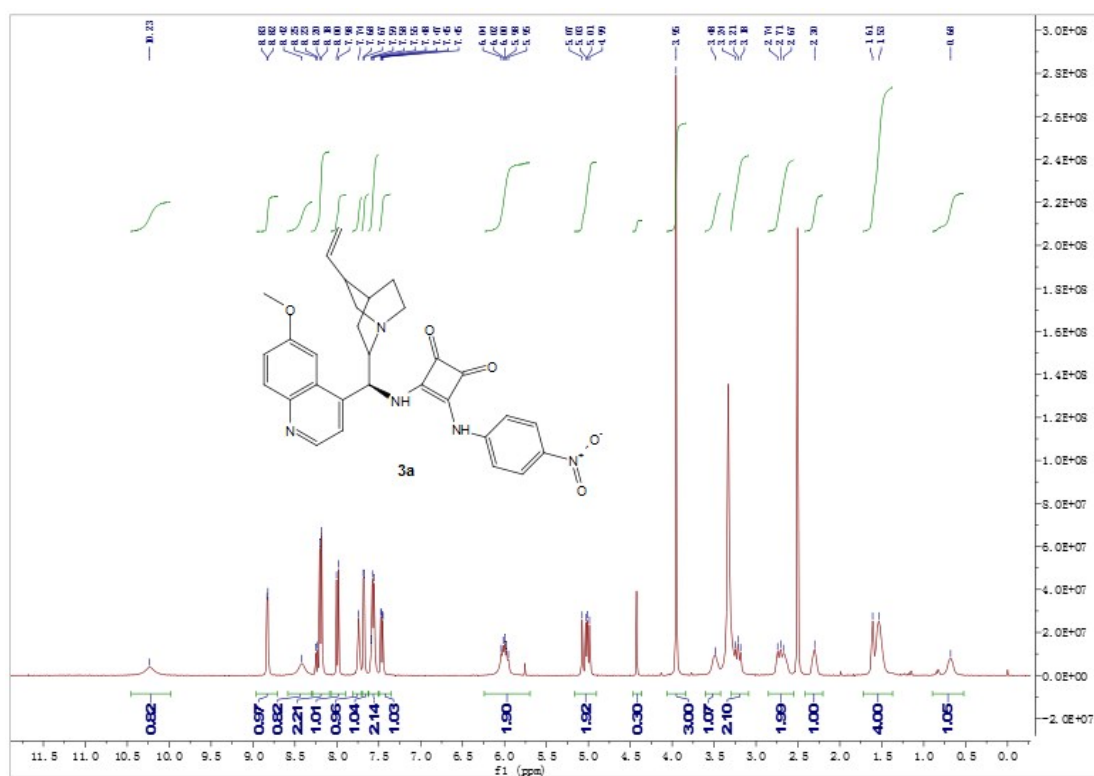
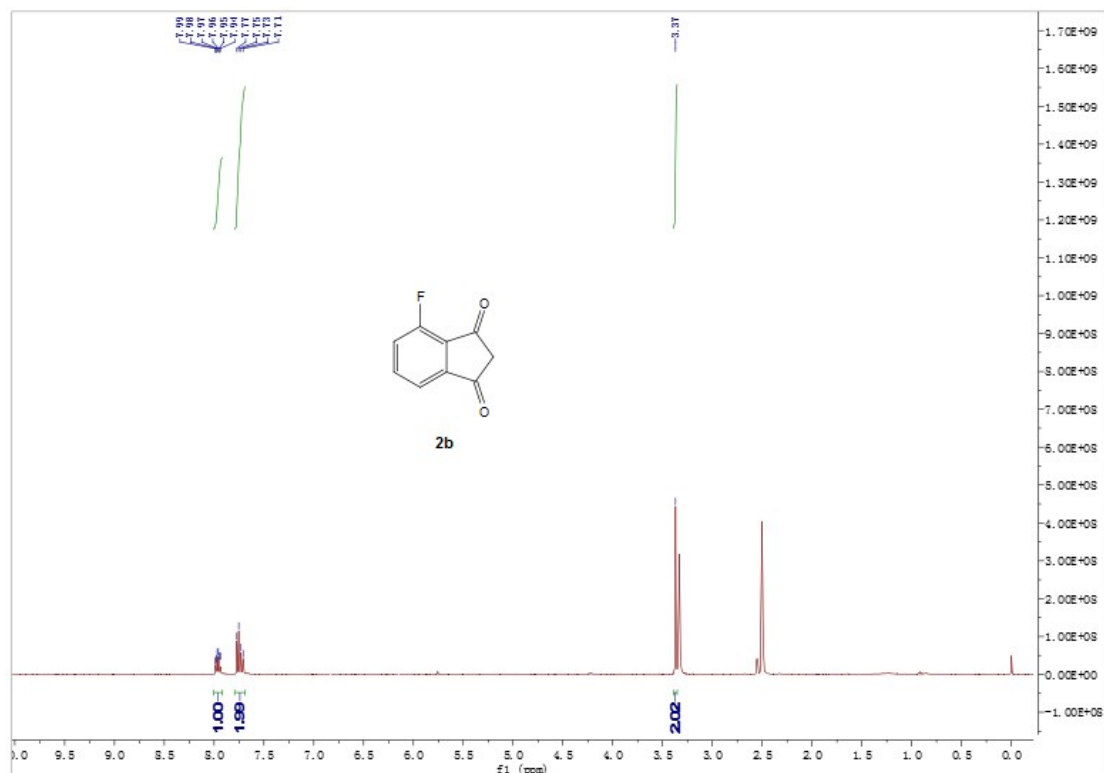


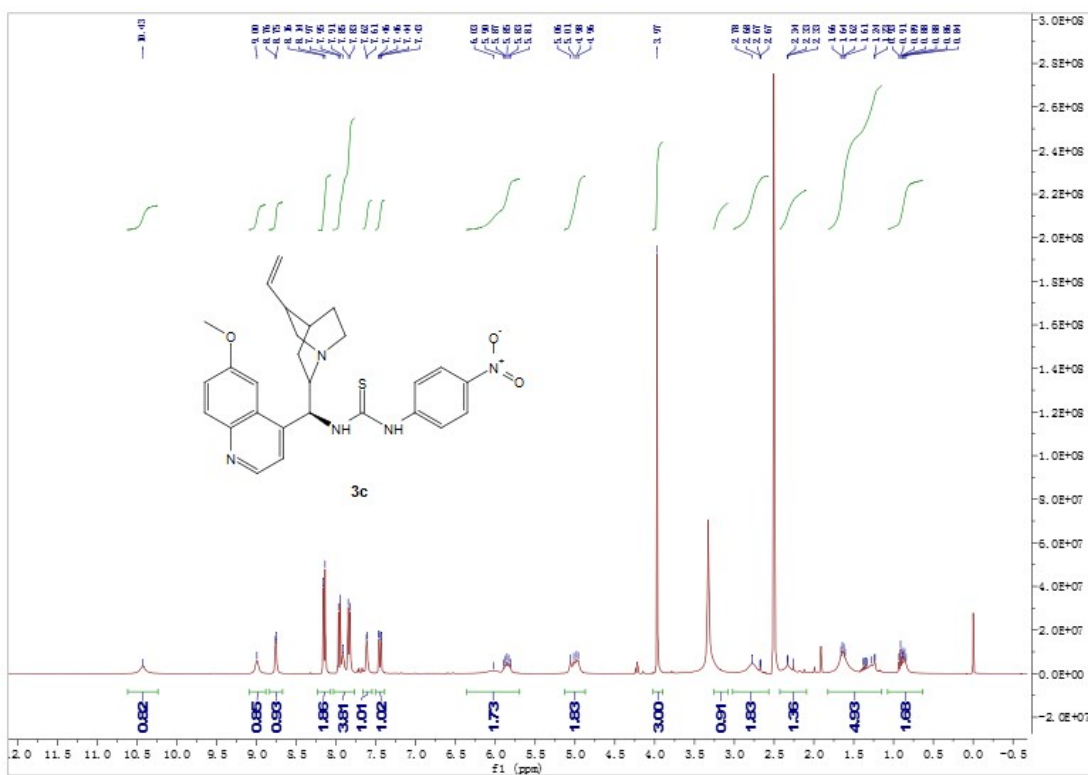
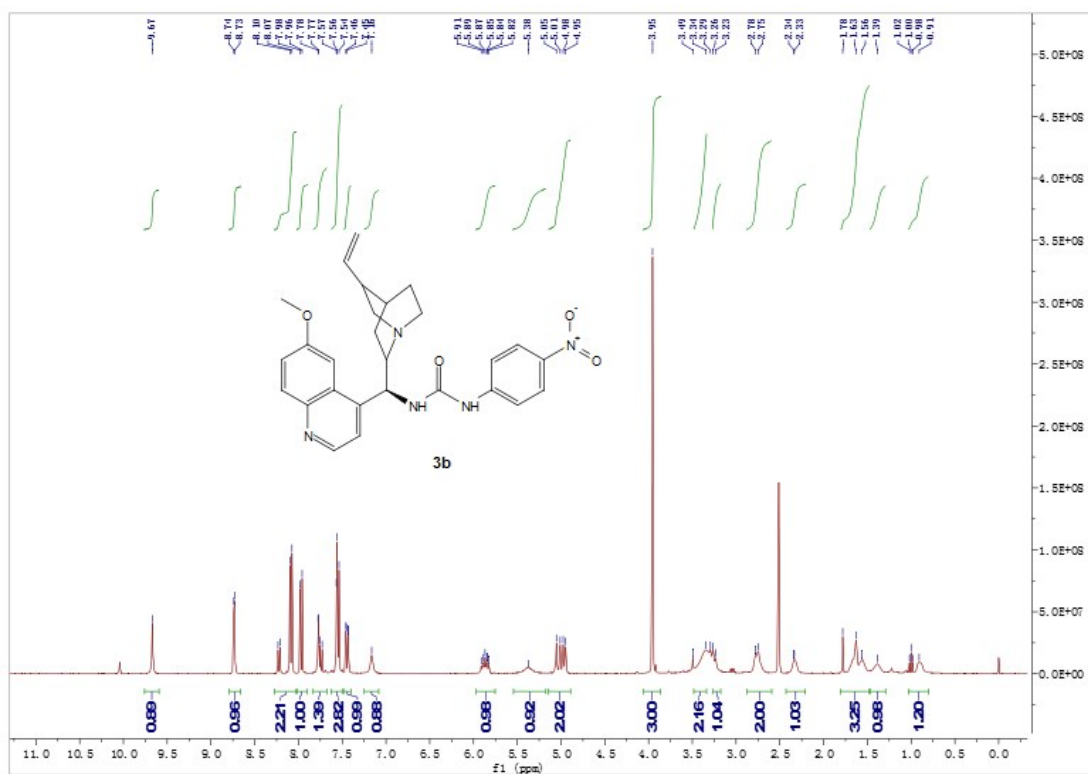
tert-butyl (R)-2-amino-3-cyano-2',5-dioxo-5H-spiro[indeno[1,2-b]pyran-4,3'-indoline]-1'-carboxylate. Yellow solid, 22.9 mg, 52% yield, m. p. = 179-181 °C, $[\alpha]_{\text{D}}^{25} = +166.2$ (c = 0.1, CHCl₃). ee = 14% (Chiralpak IA, hexane/EtOH = 95:5, 254 nm, 1 mL/min, t_{major} = 32.394 min, t_{minor} = 35.553 min). ¹H NMR (400 MHz, DMSO) δ 7.93 (s, 2H), 7.80 (d, J = 8.2 Hz, 1H), 7.59 (t, J = 7.2 Hz, 1H), 7.51 – 7.31 (m, 5H), 7.21 (t, J = 7.4 Hz, 1H), 1.59 (s, 9H). ¹³C NMR (101 MHz, DMSO) δ 189.75, 174.65, 168.12, 161.03, 148.74, 139.26, 135.38, 134.28, 132.08, 130.77, 130.35, 130.08, 125.69, 125.41, 122.88, 119.68, 117.61, 114.96, 107.15, 84.98, 57.33, 47.34, 28.07.

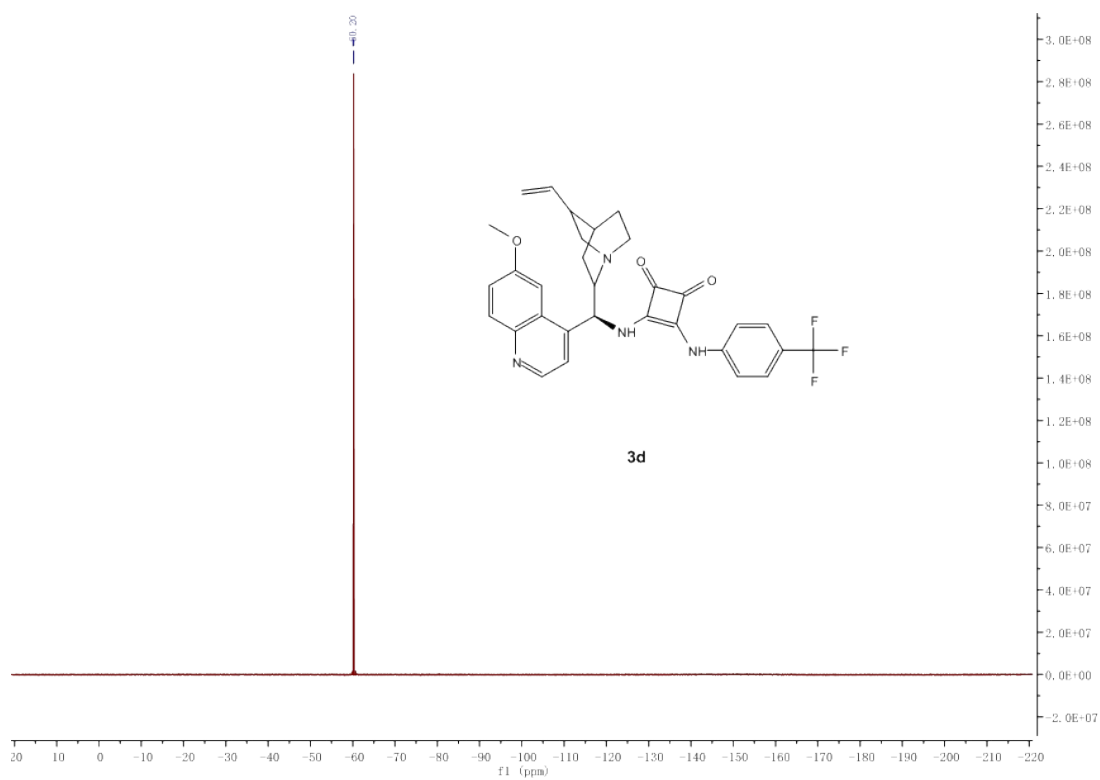
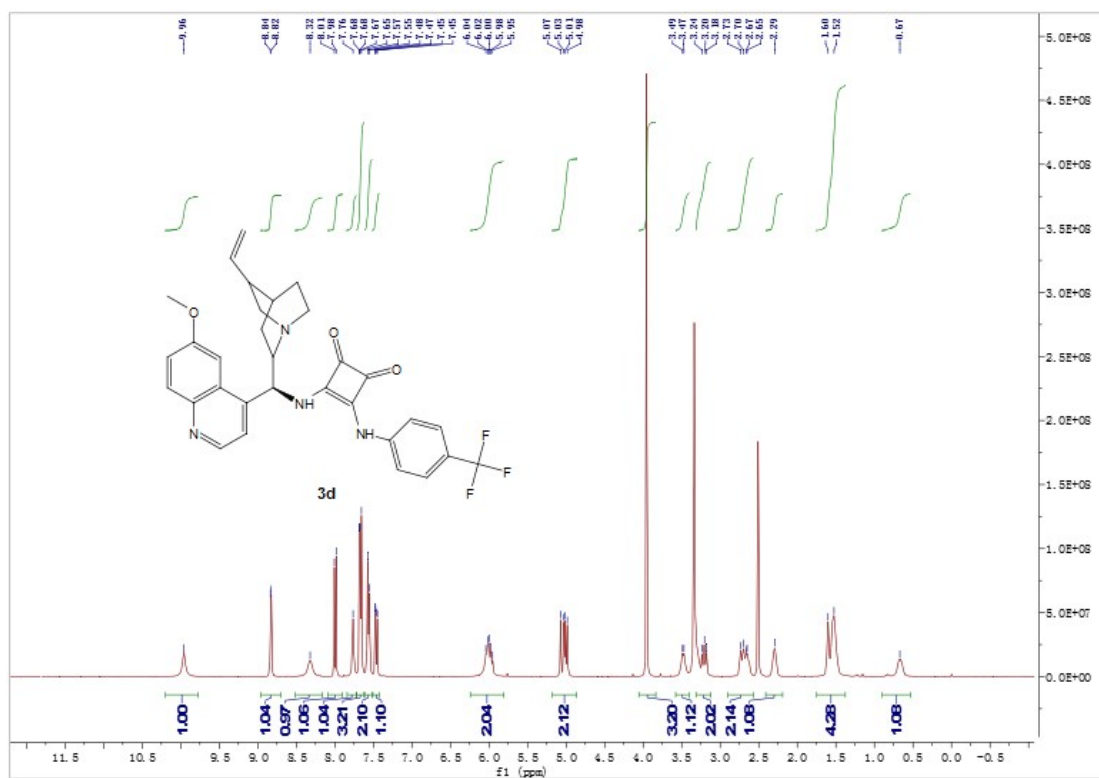
4. References

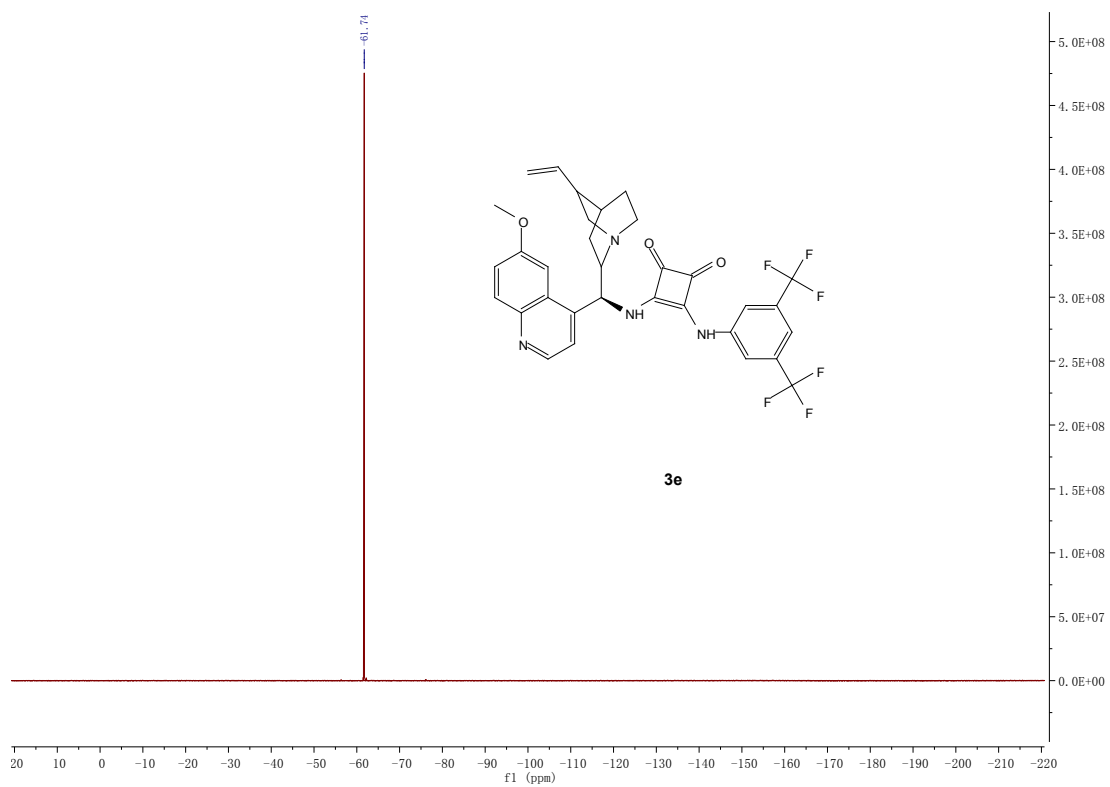
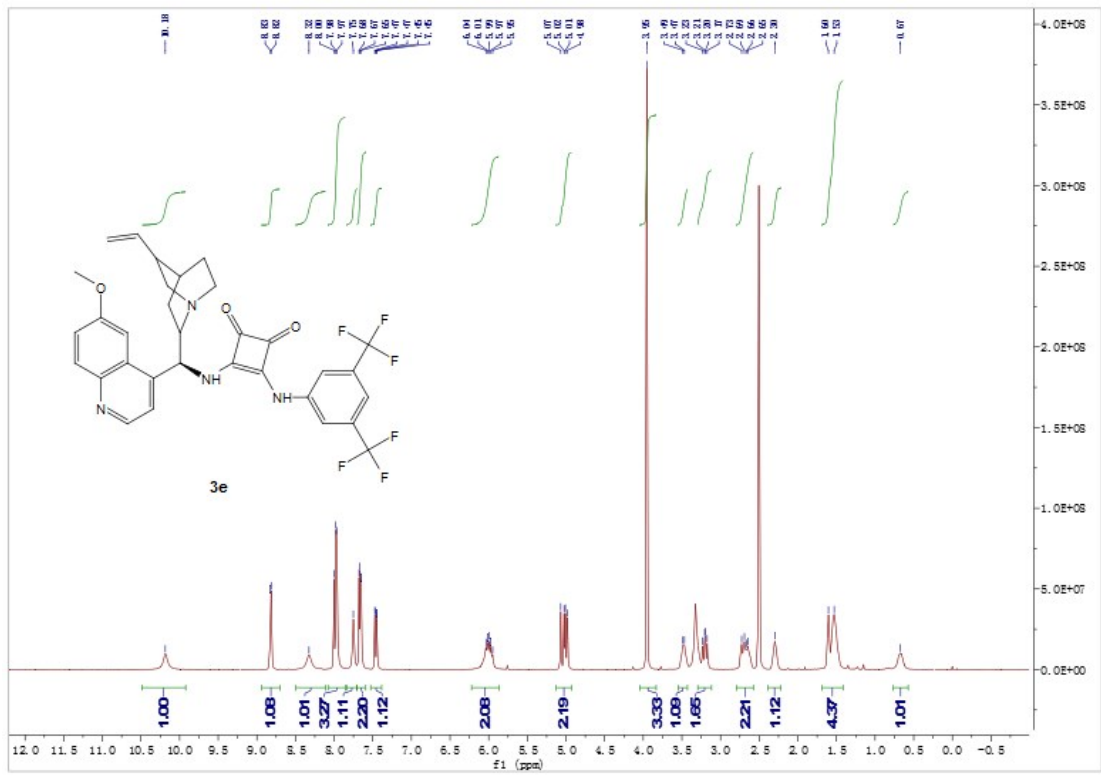
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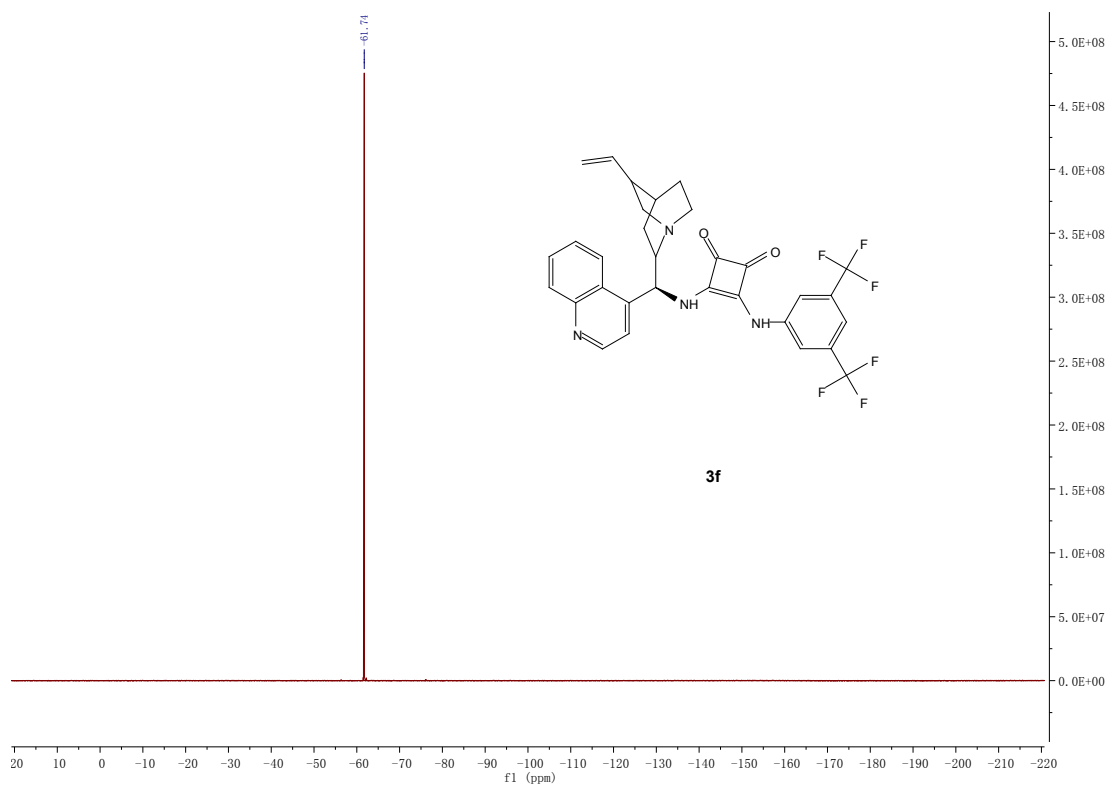
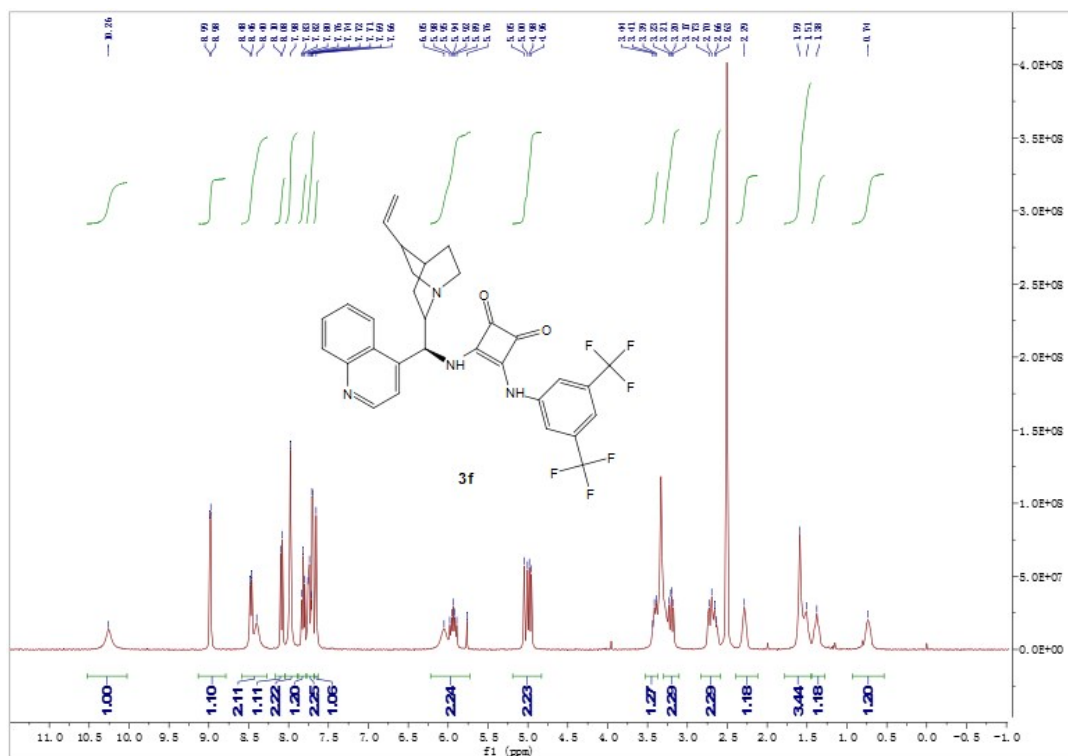
5. NMR spectra of catalyst, substrate 2b and addition products 4a-4u,4o-1

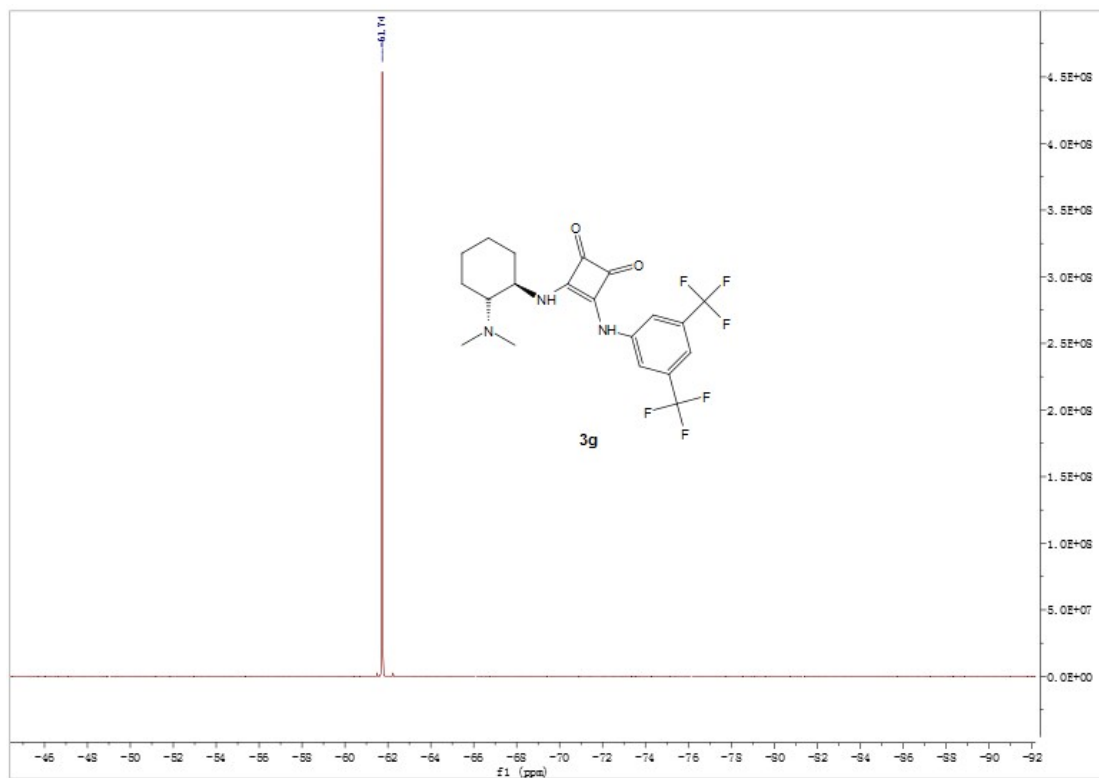
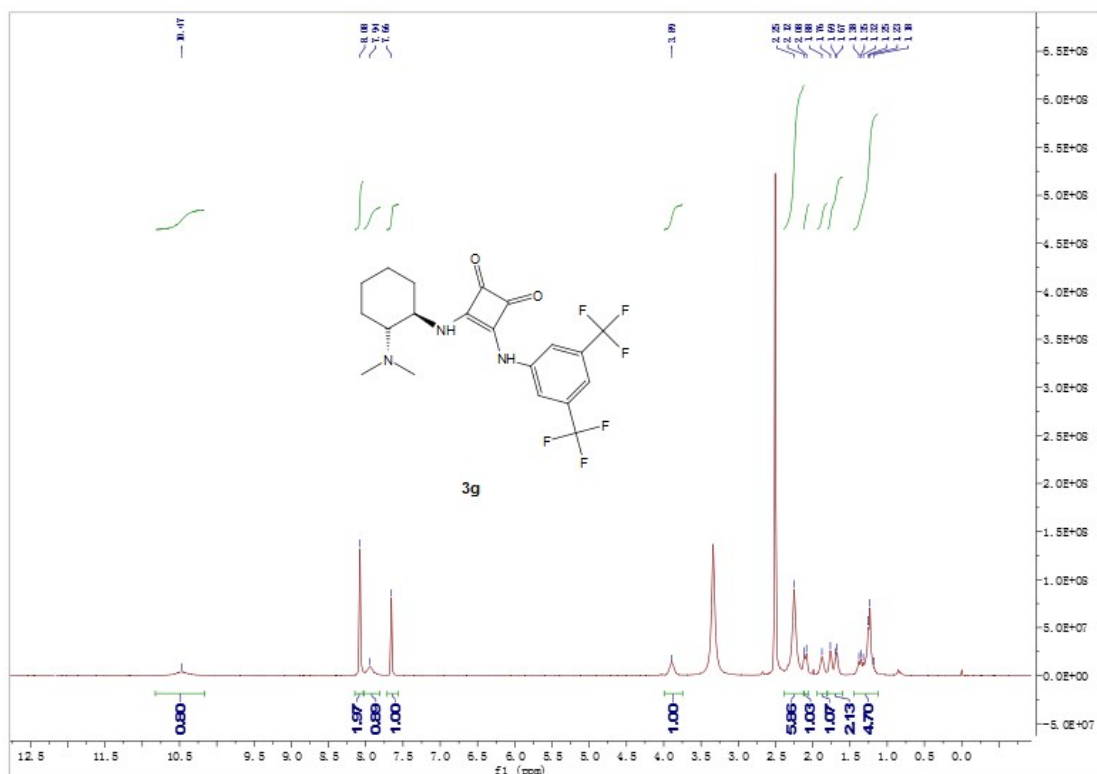


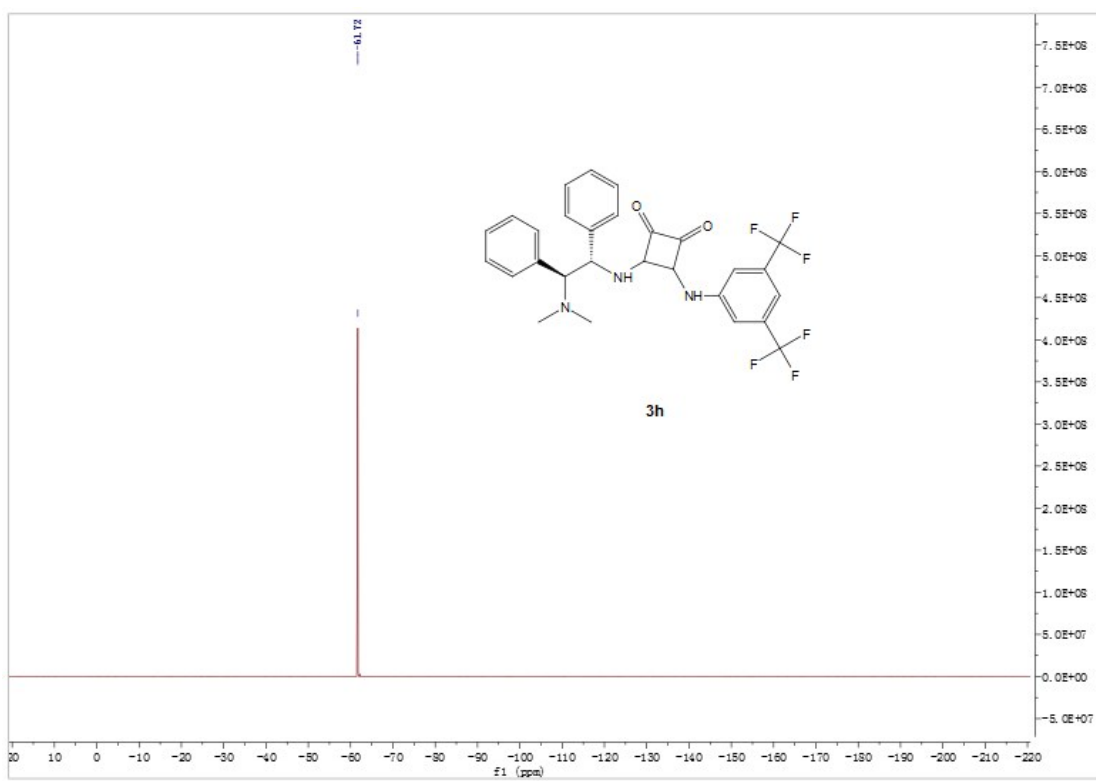
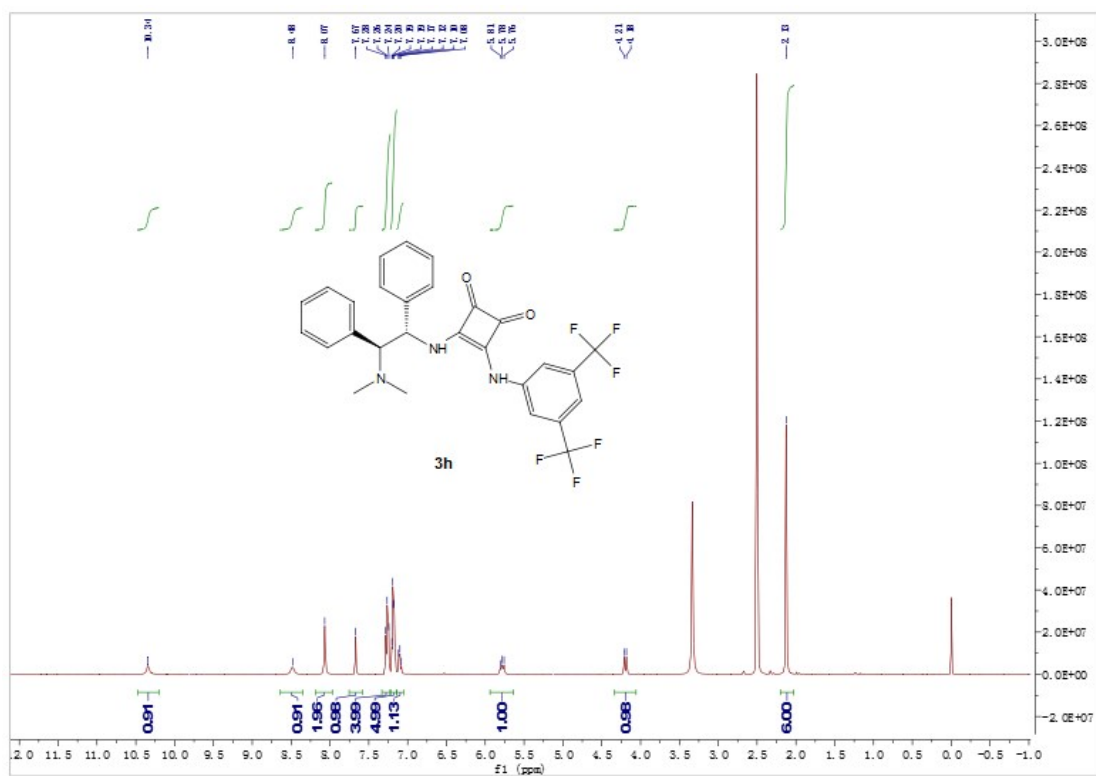


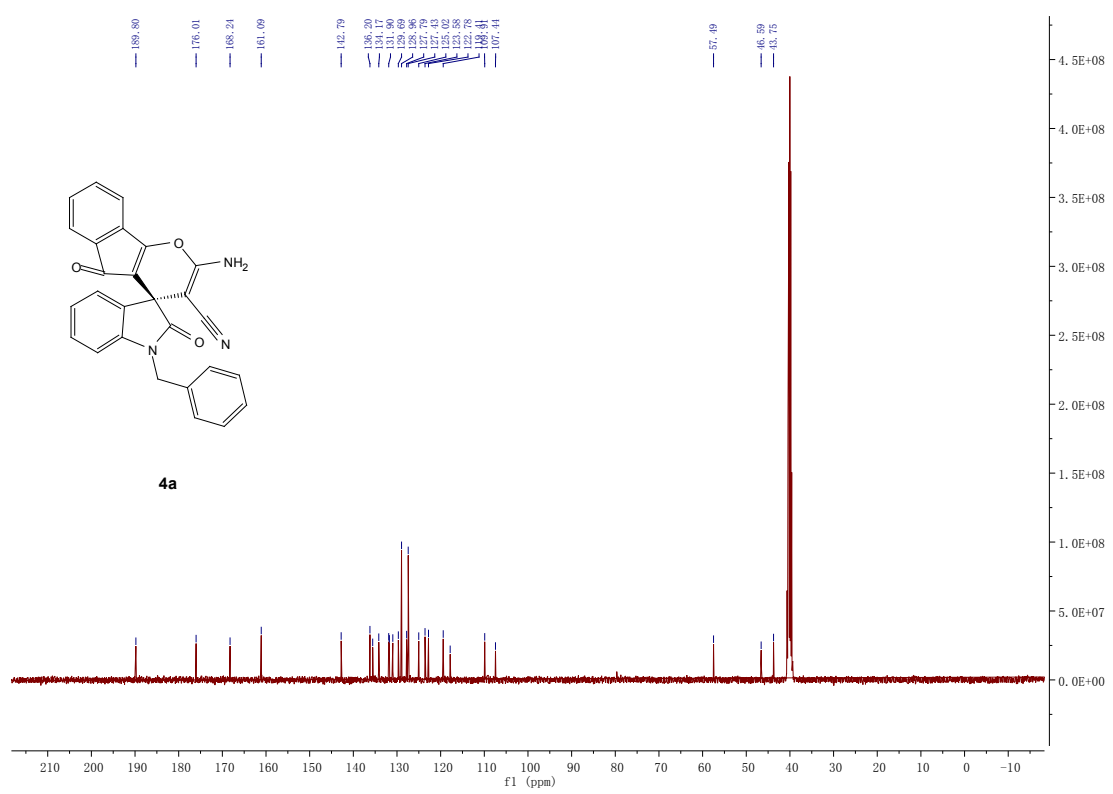
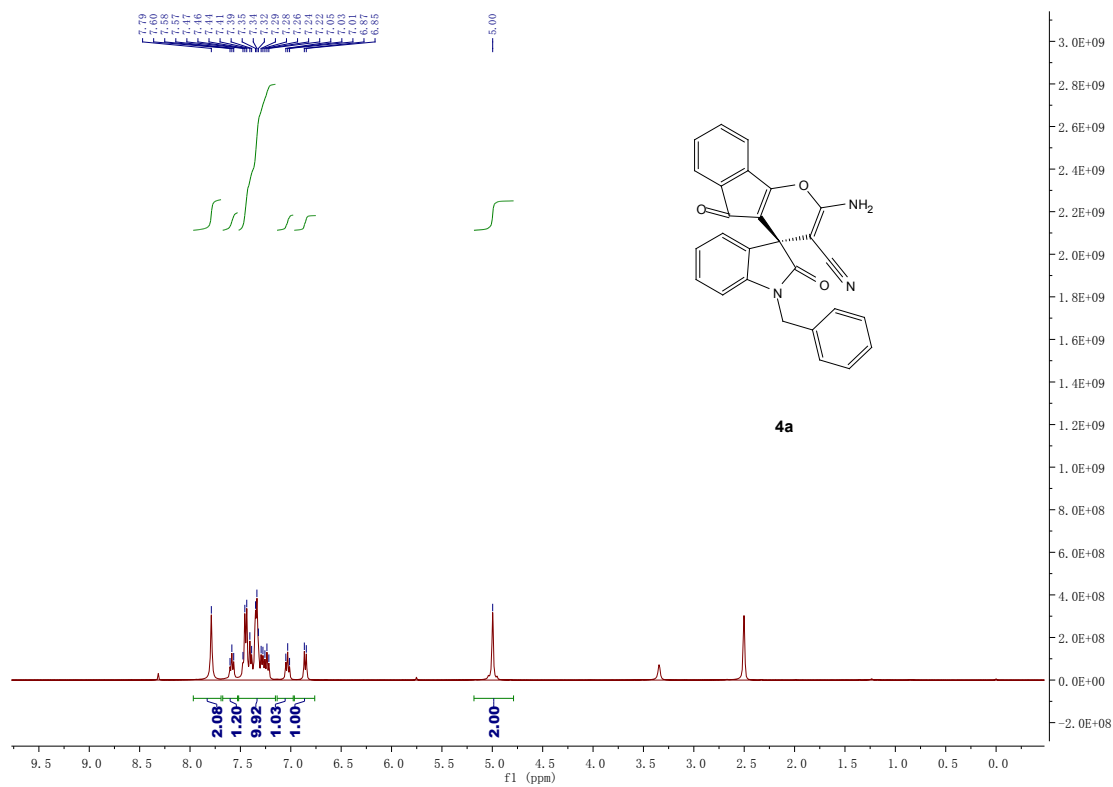


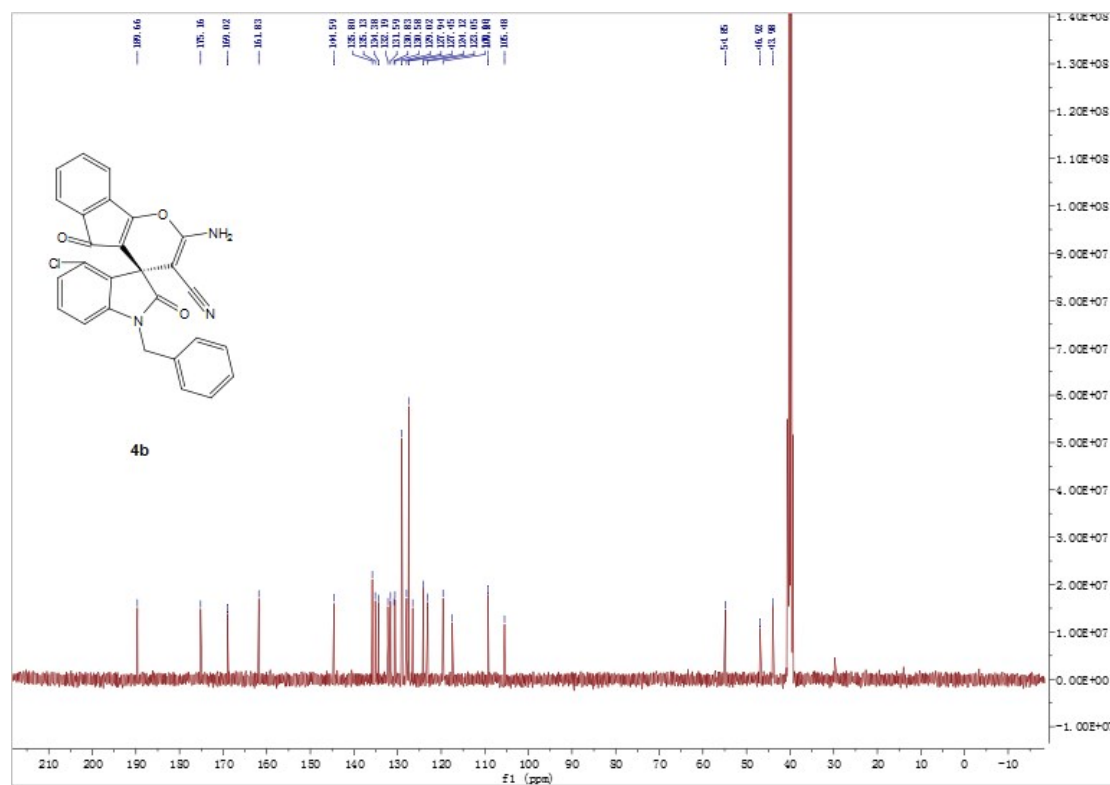
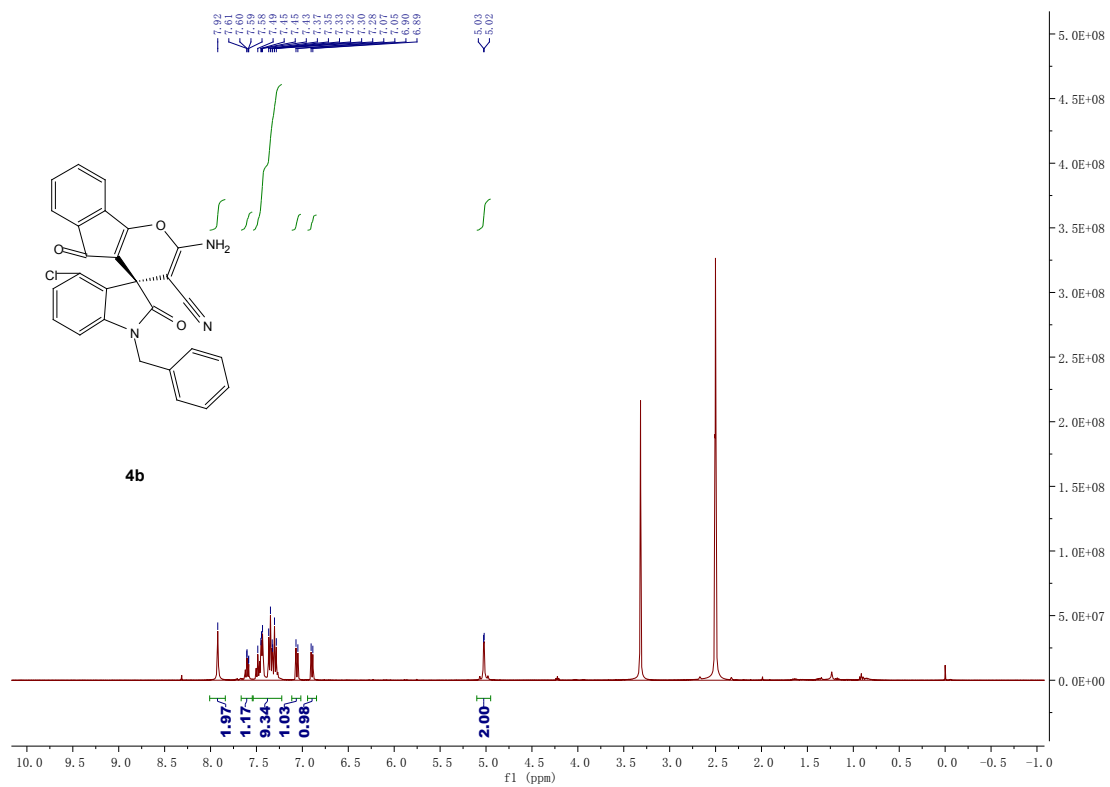


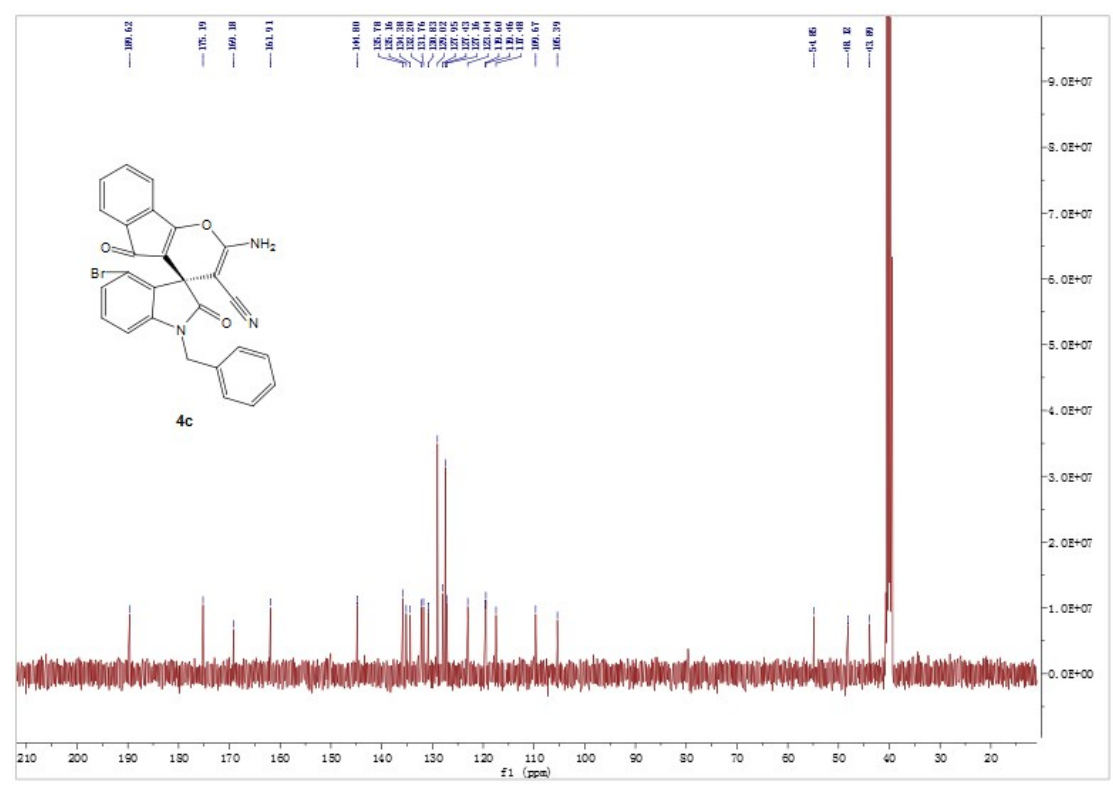
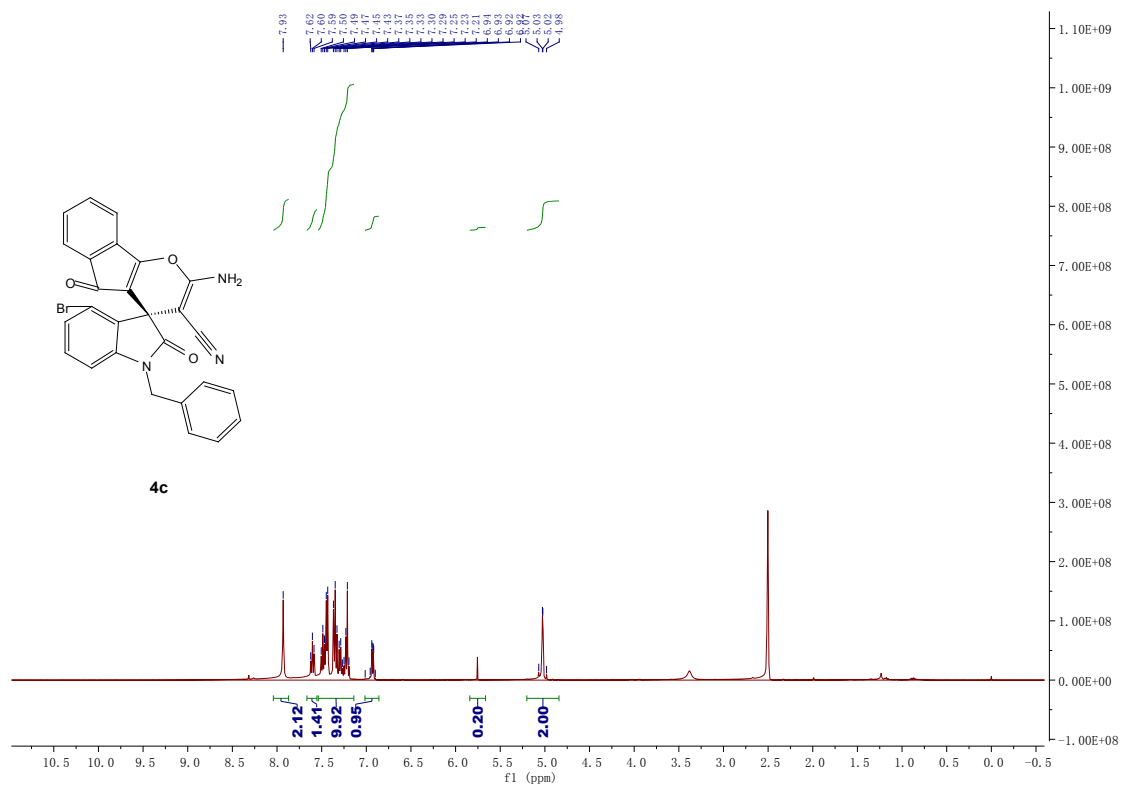


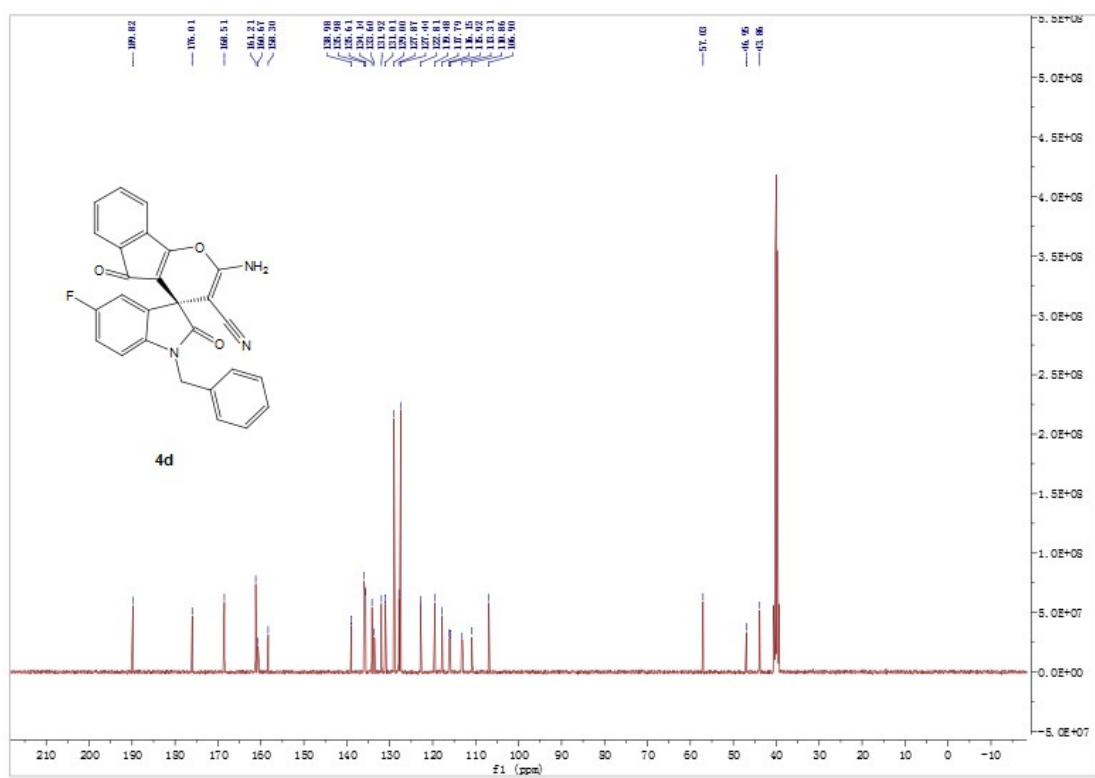
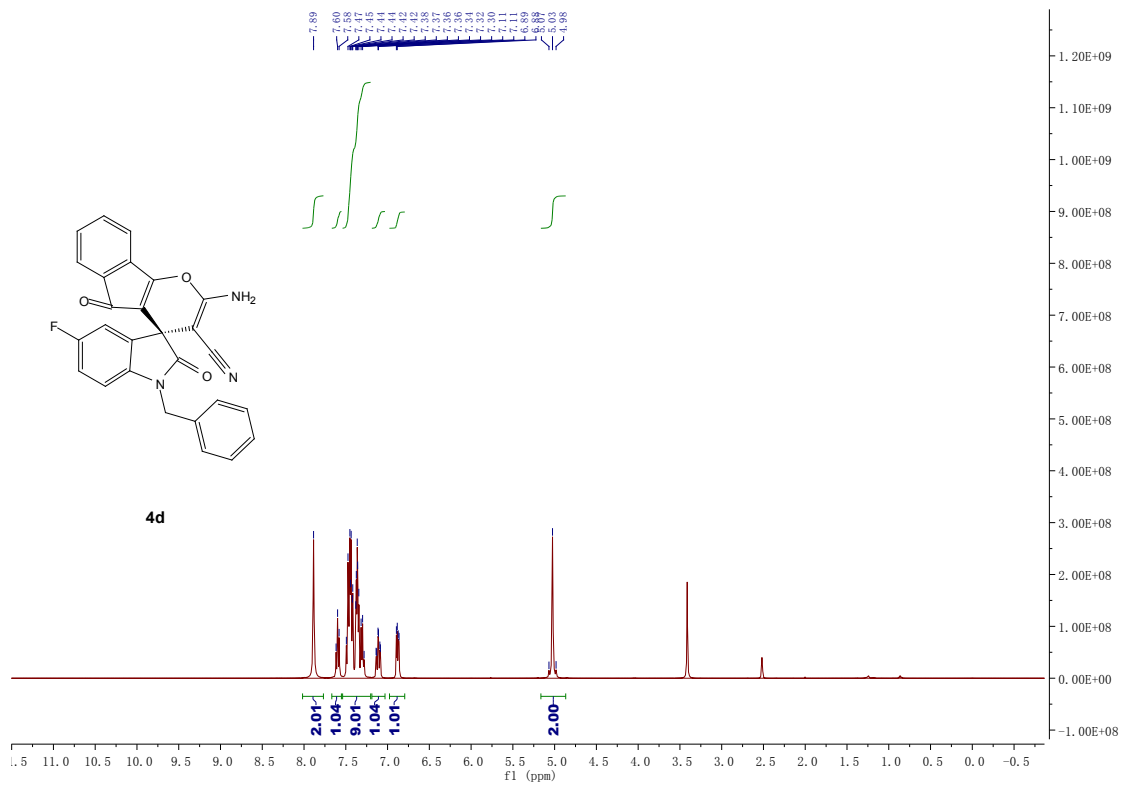


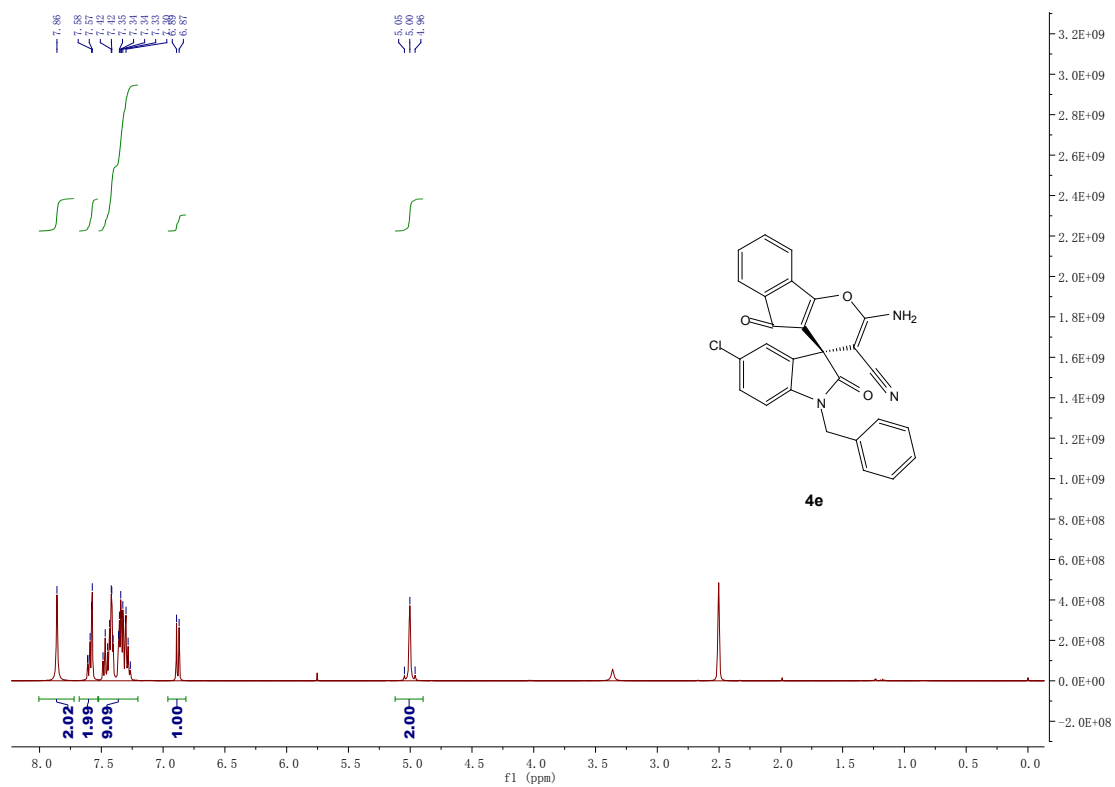
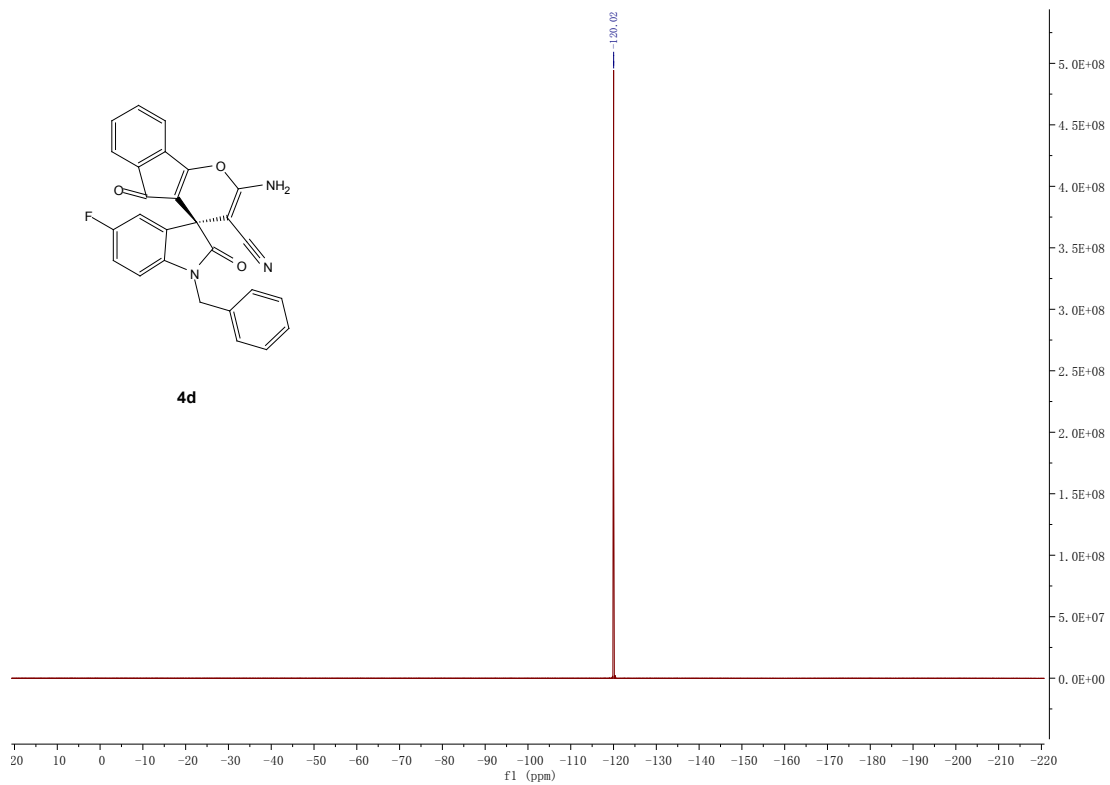


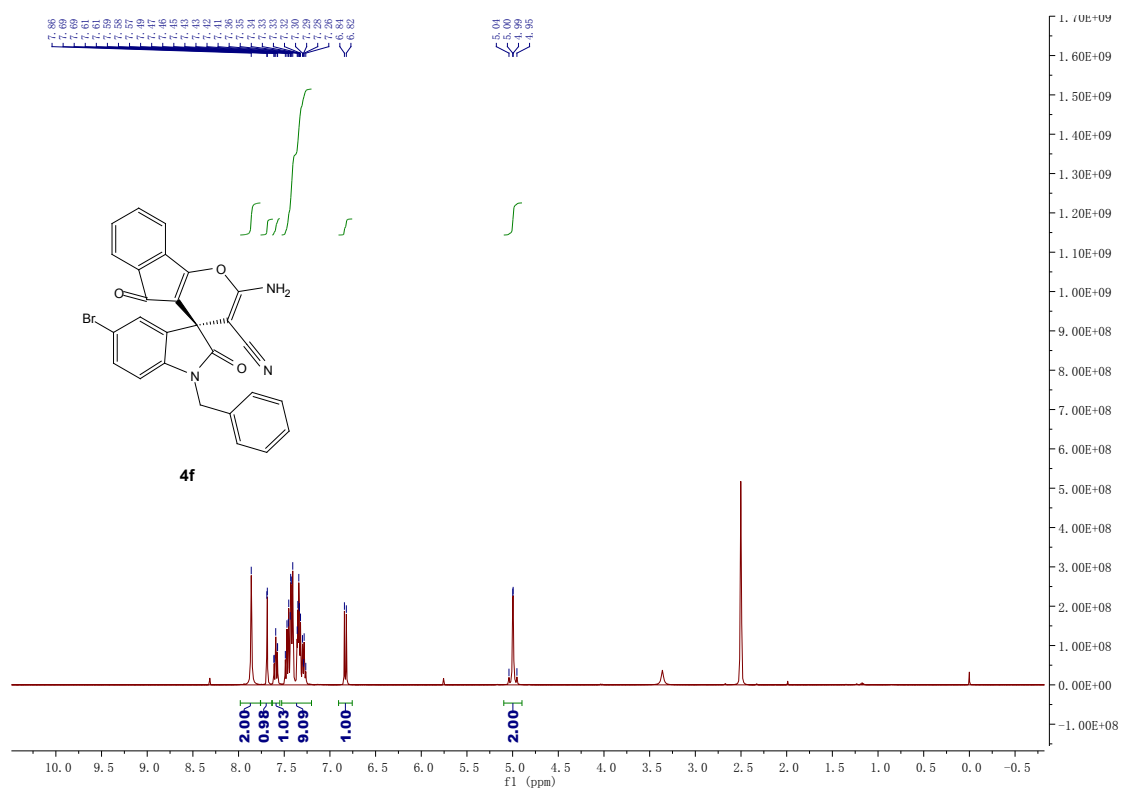
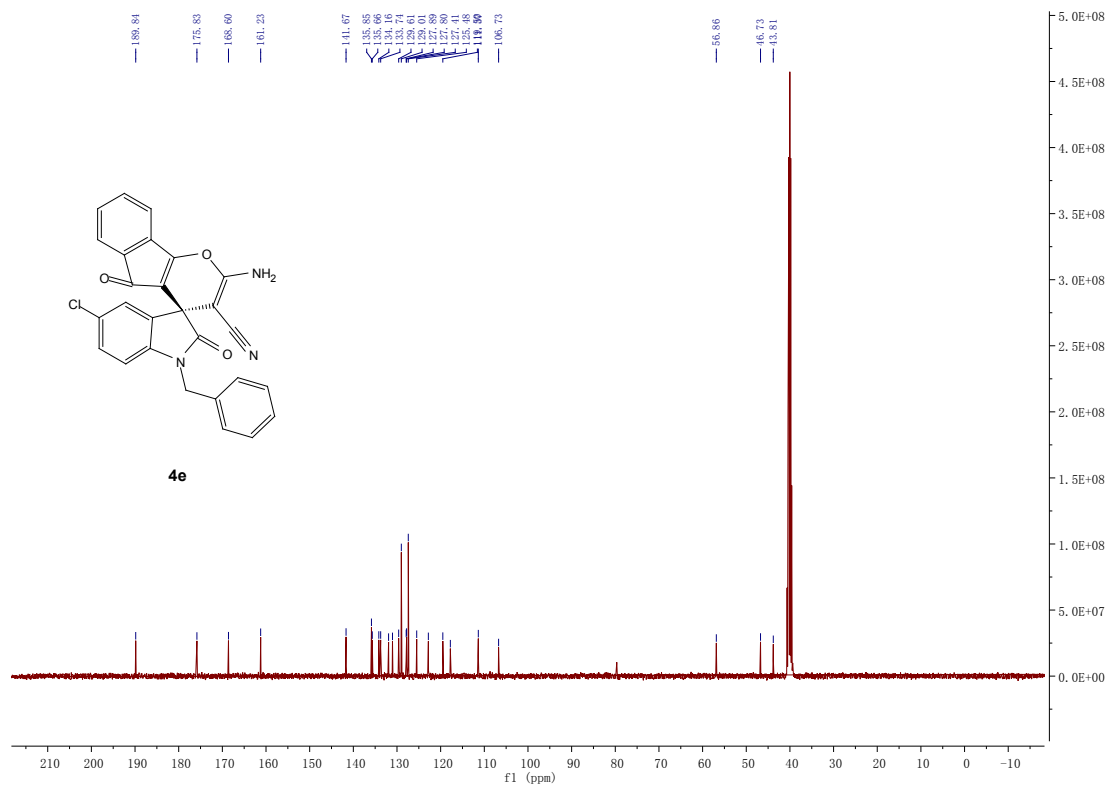


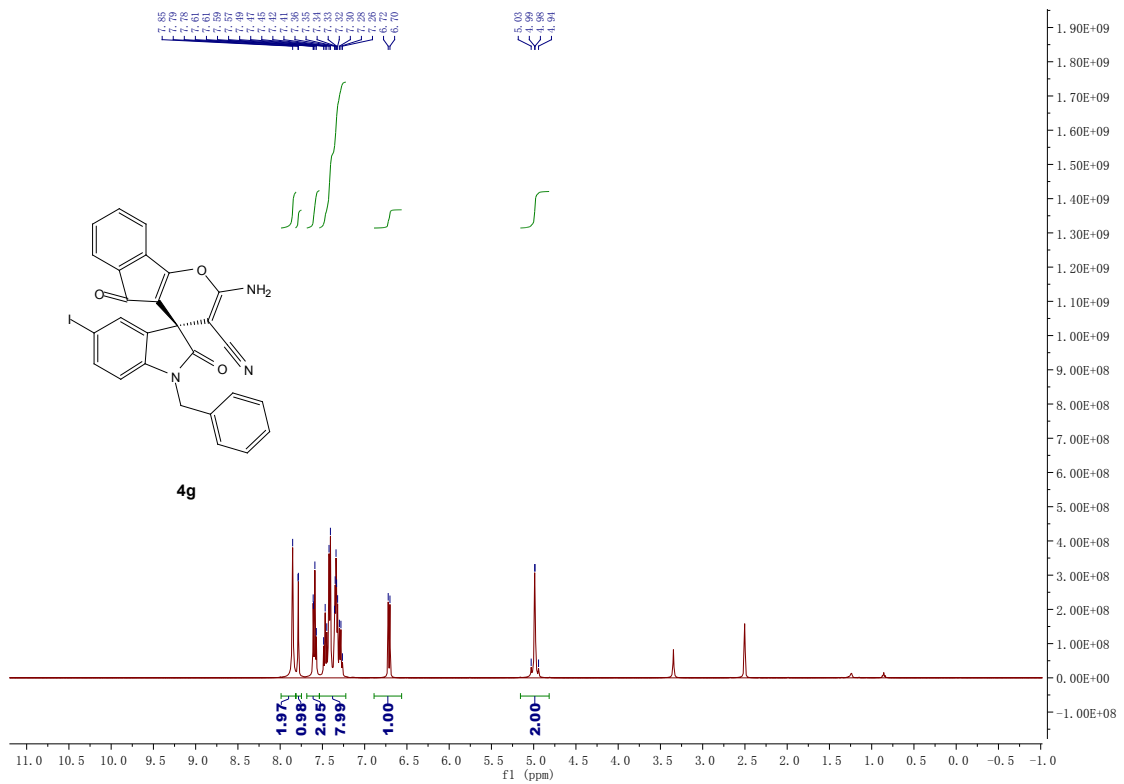
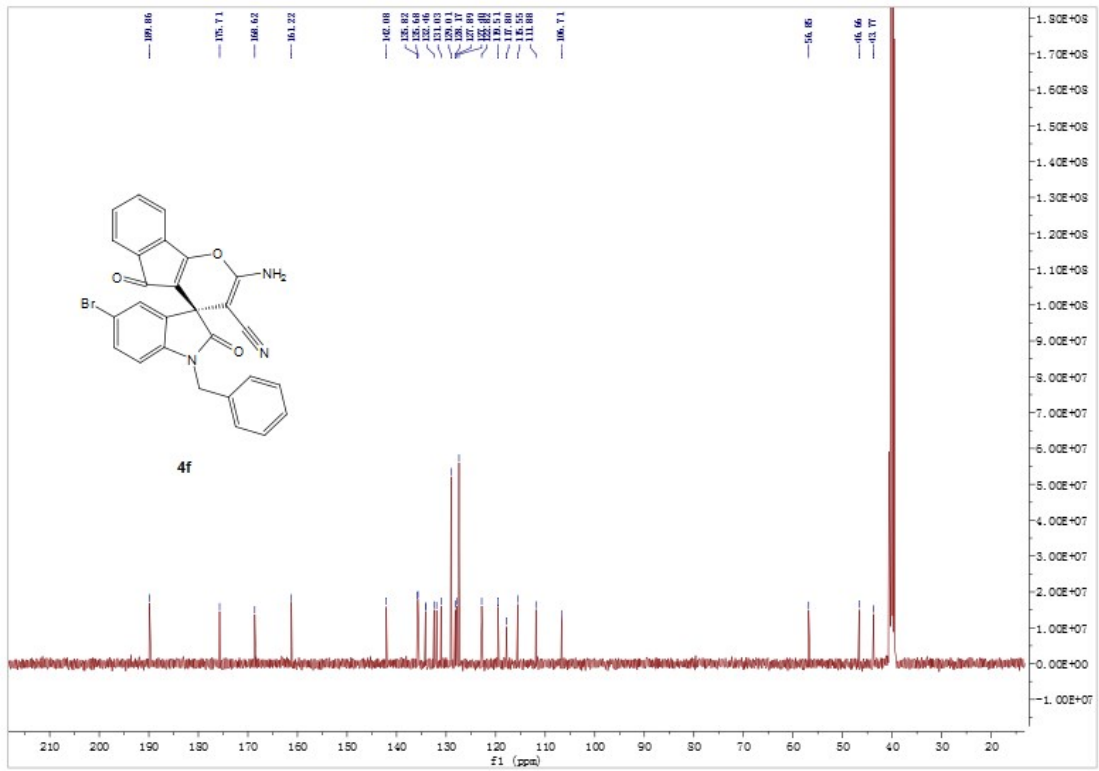


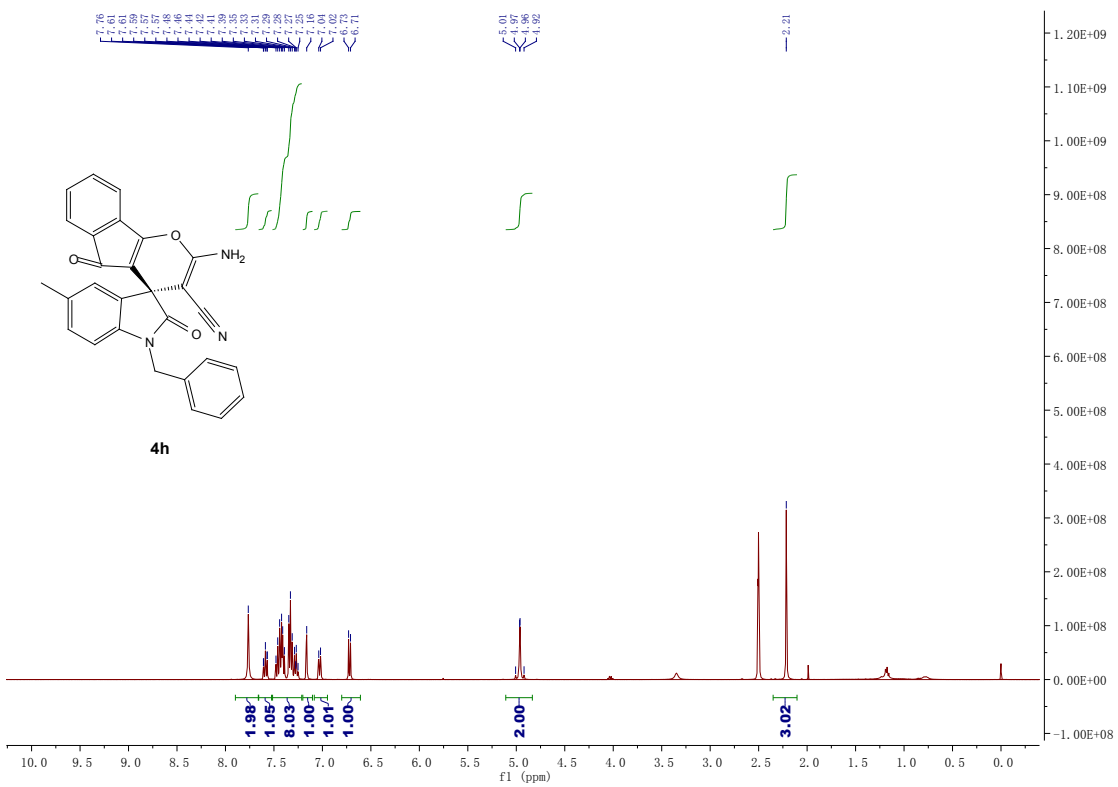
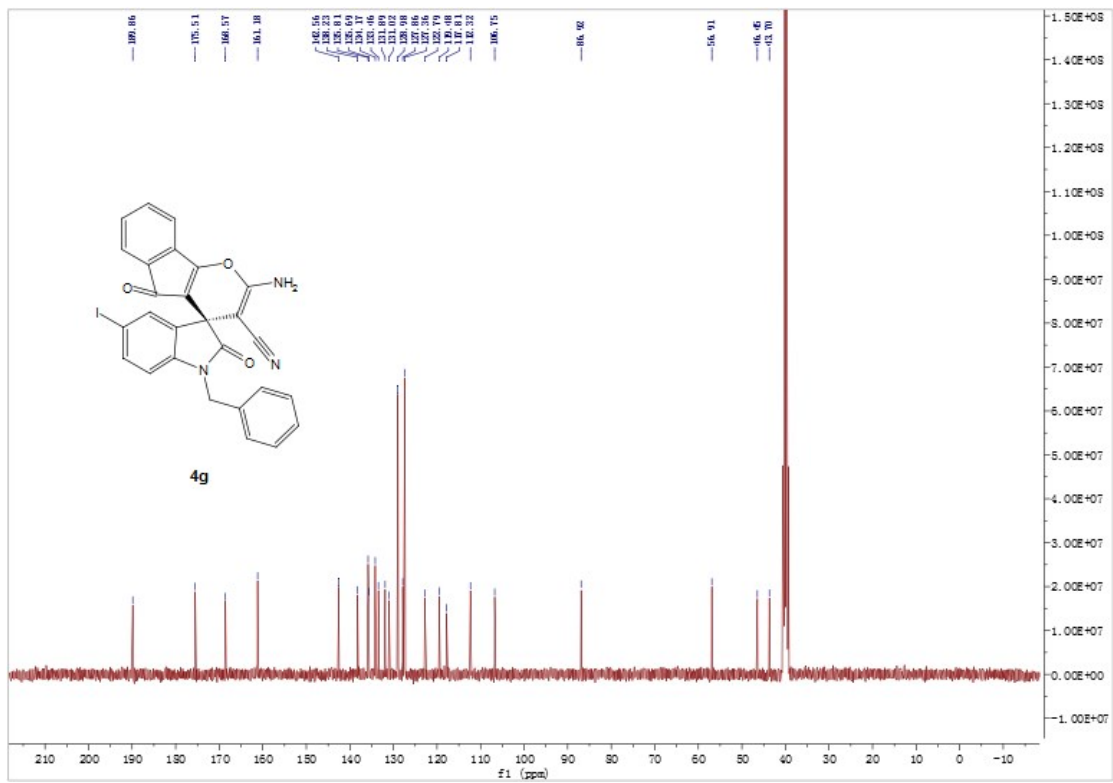


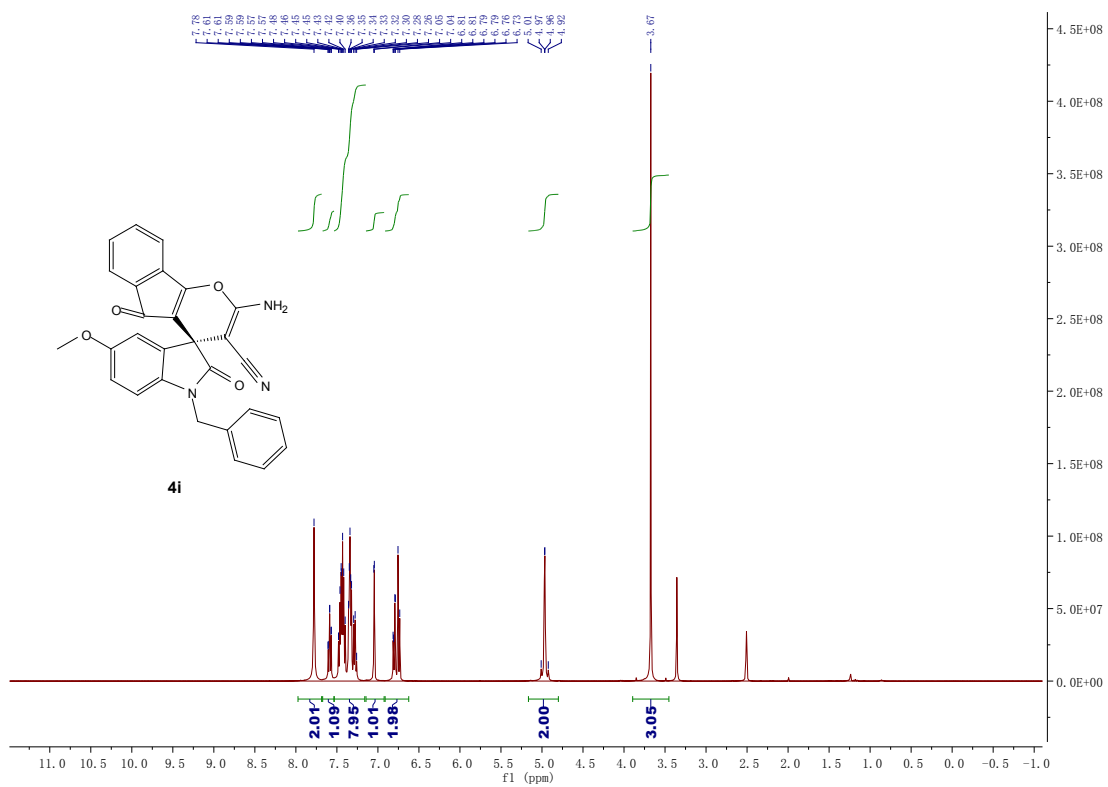
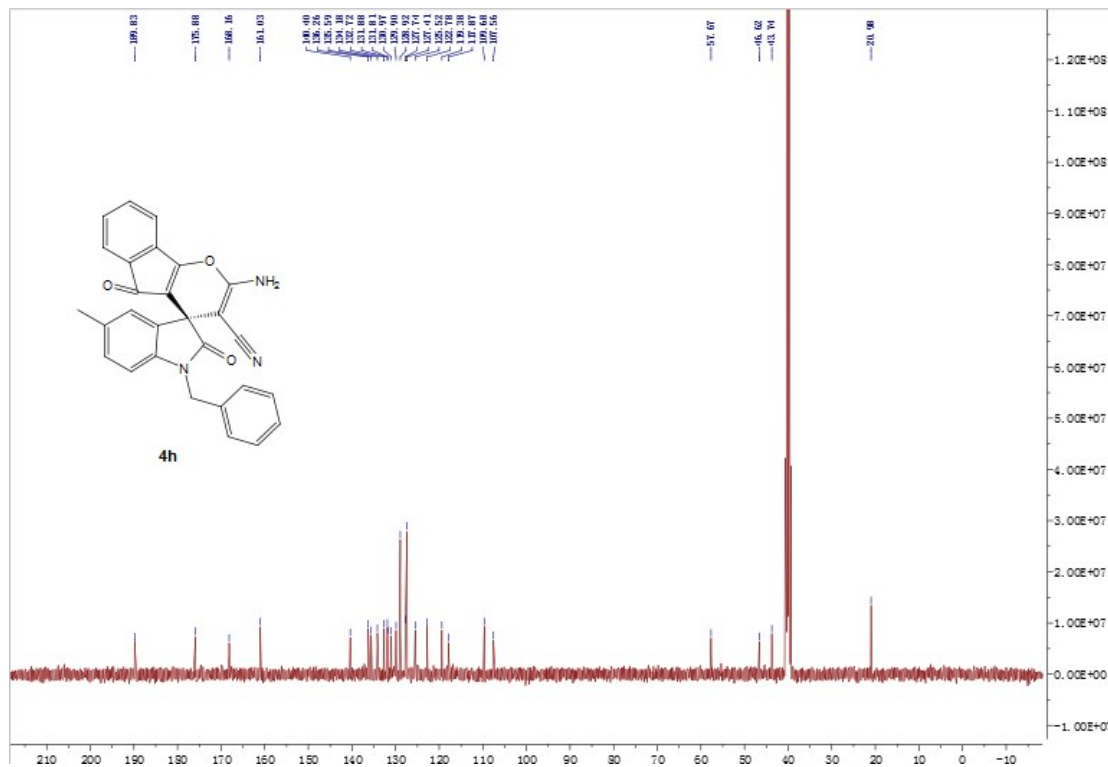


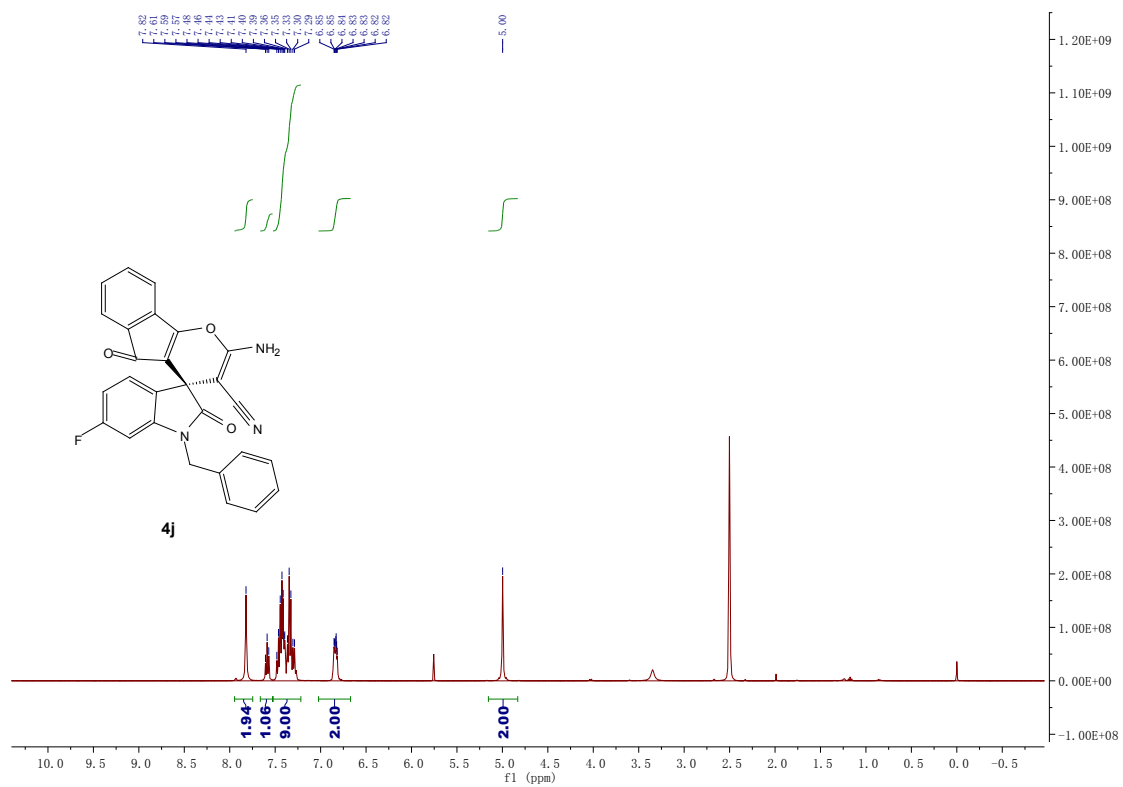
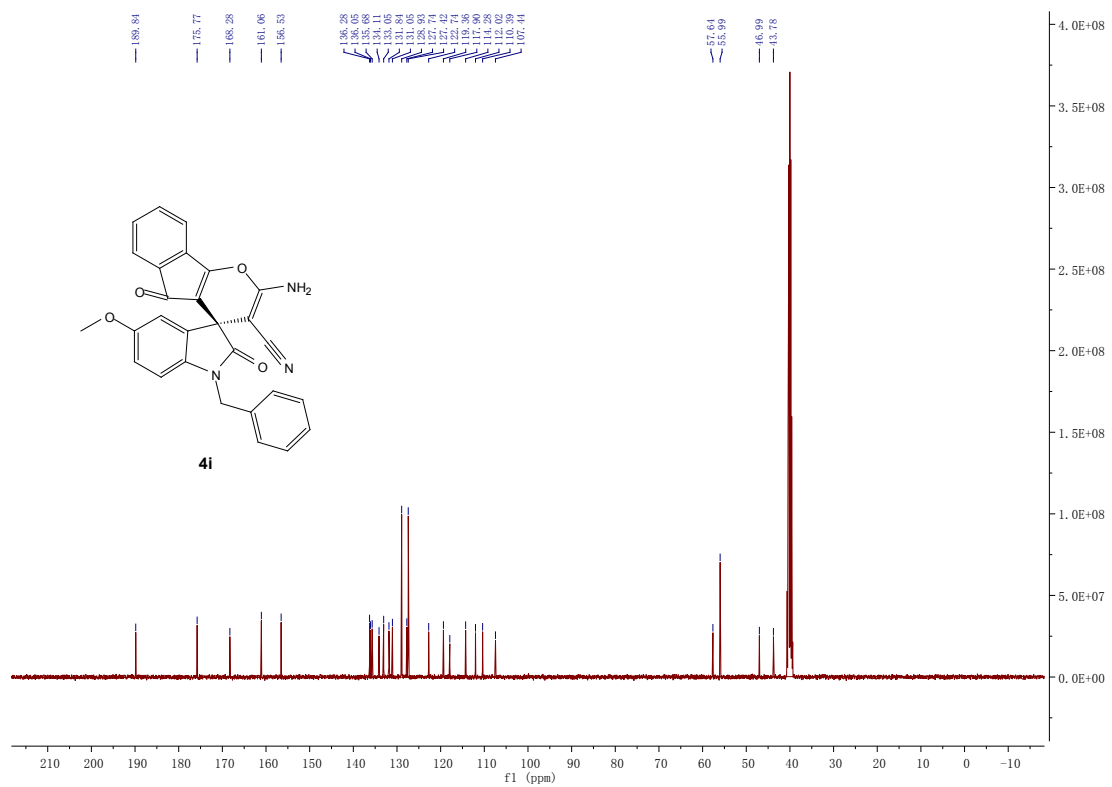


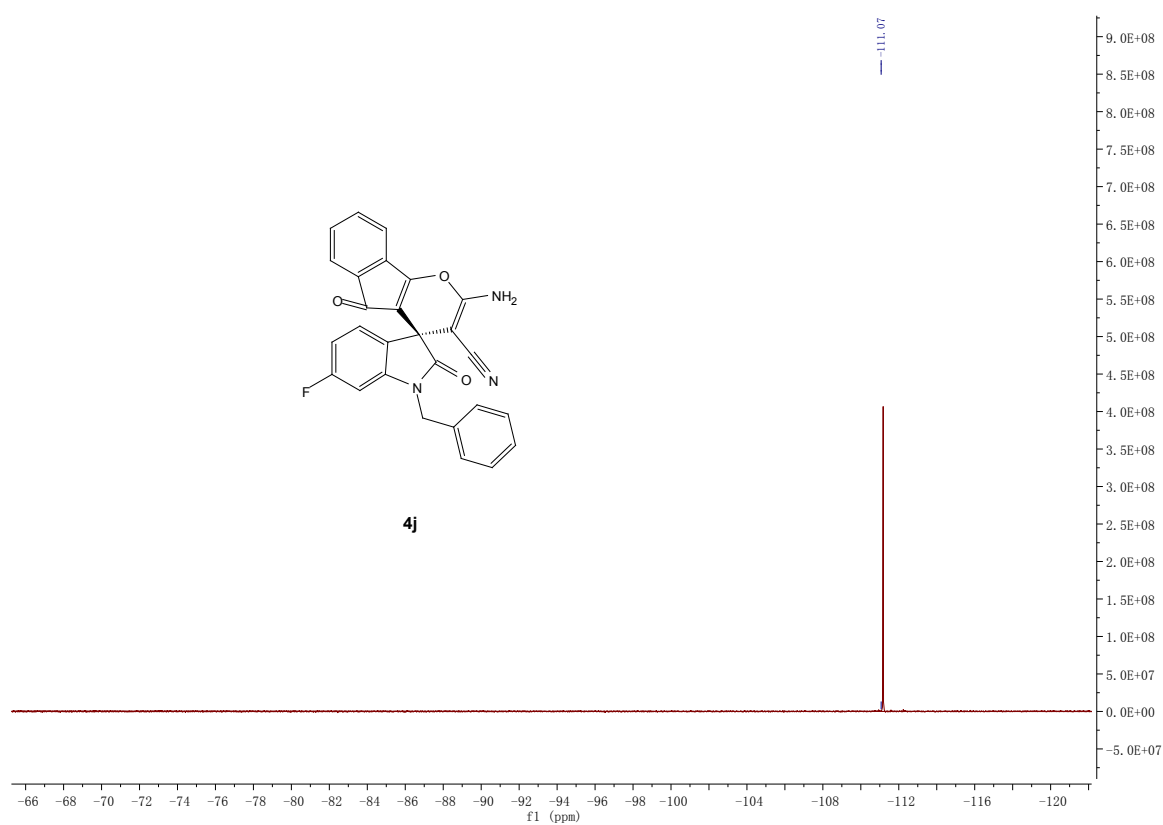
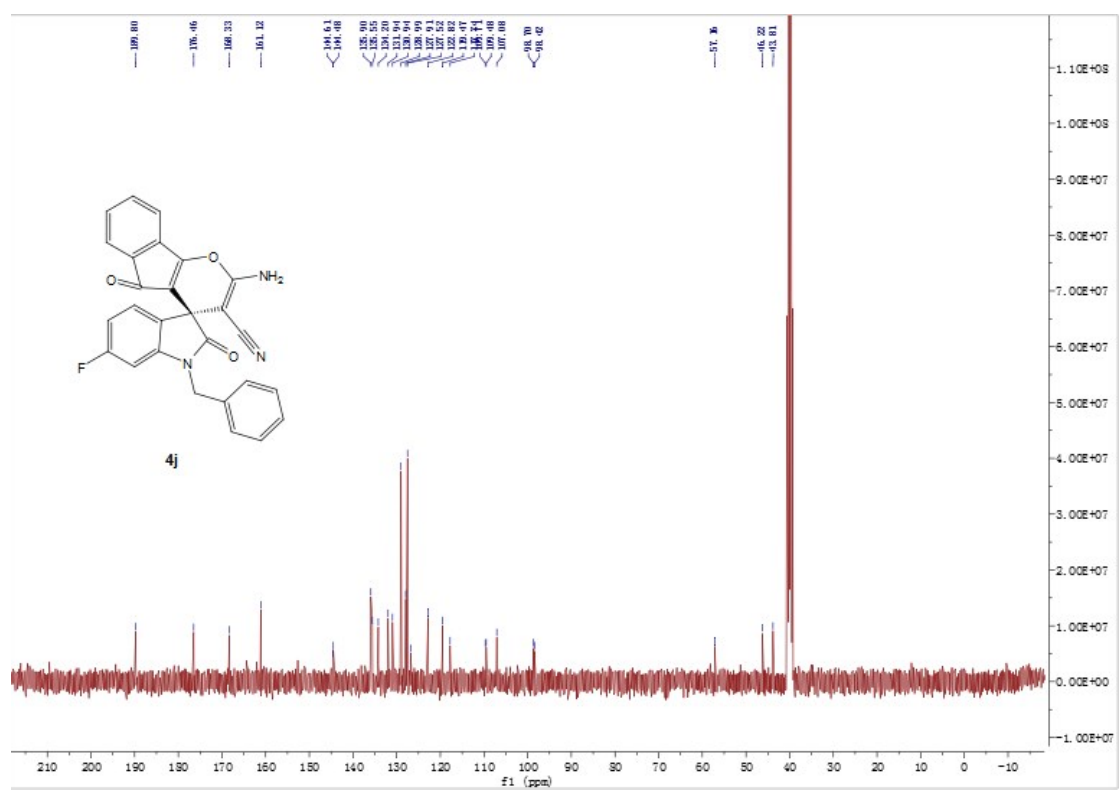


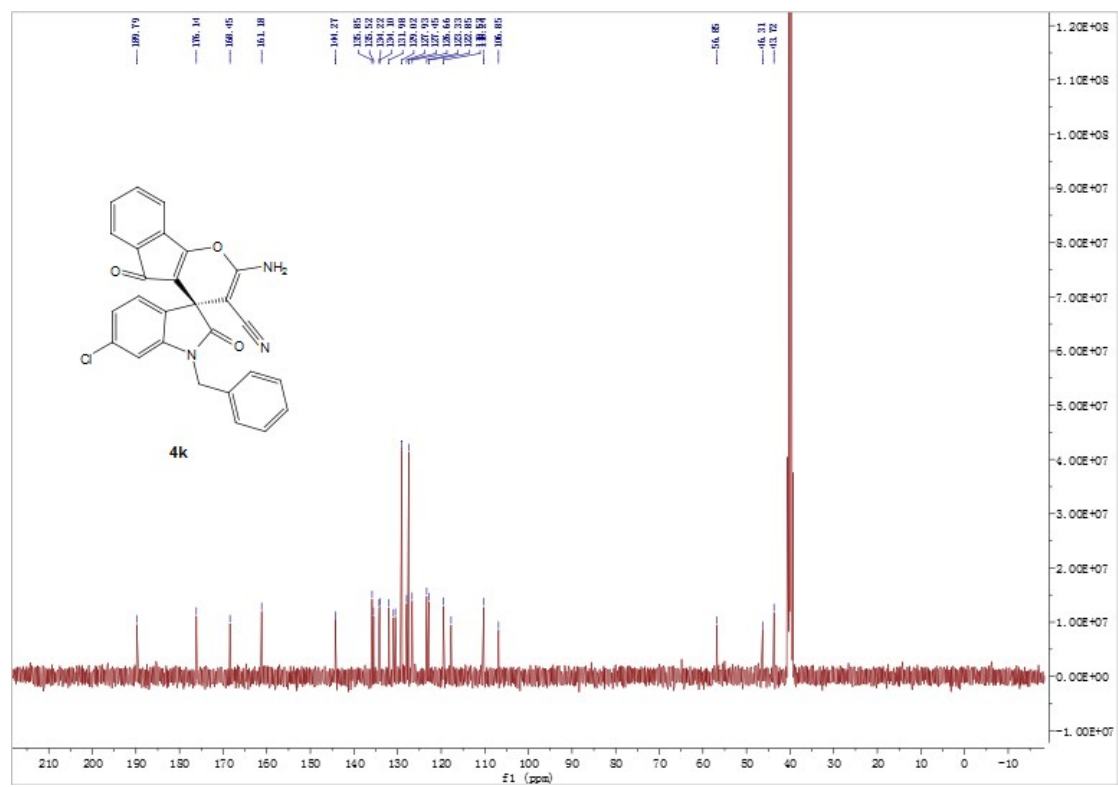
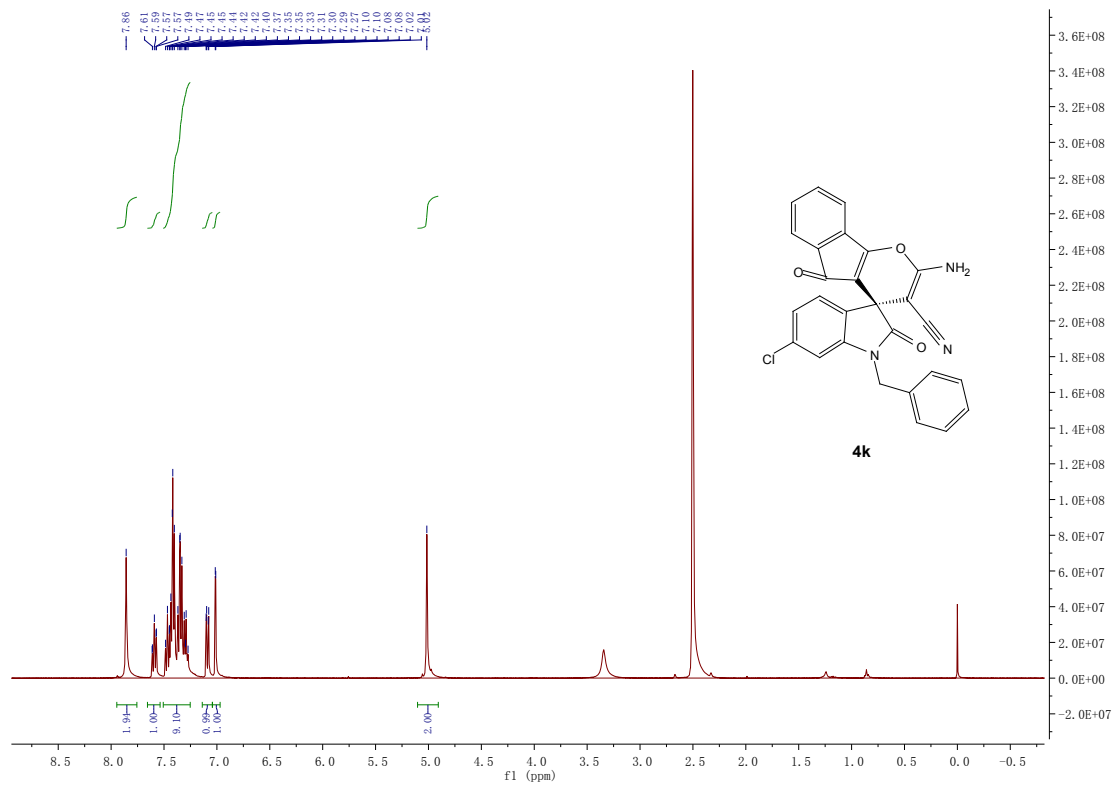


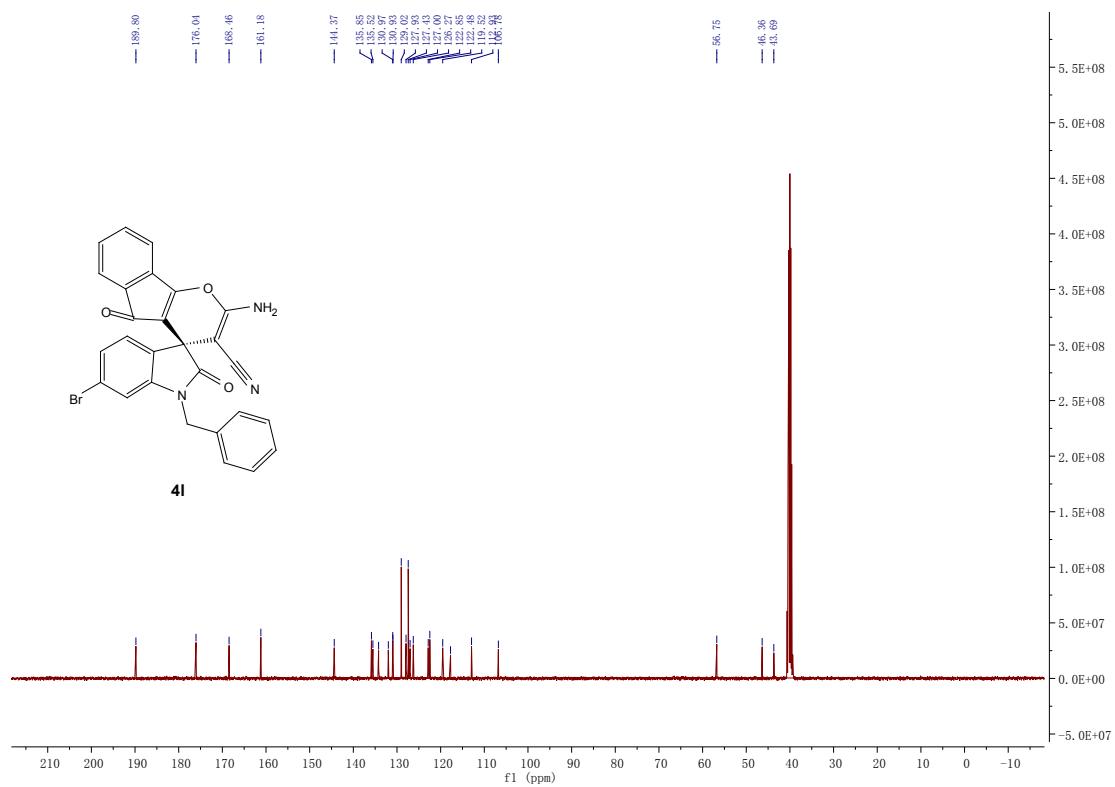
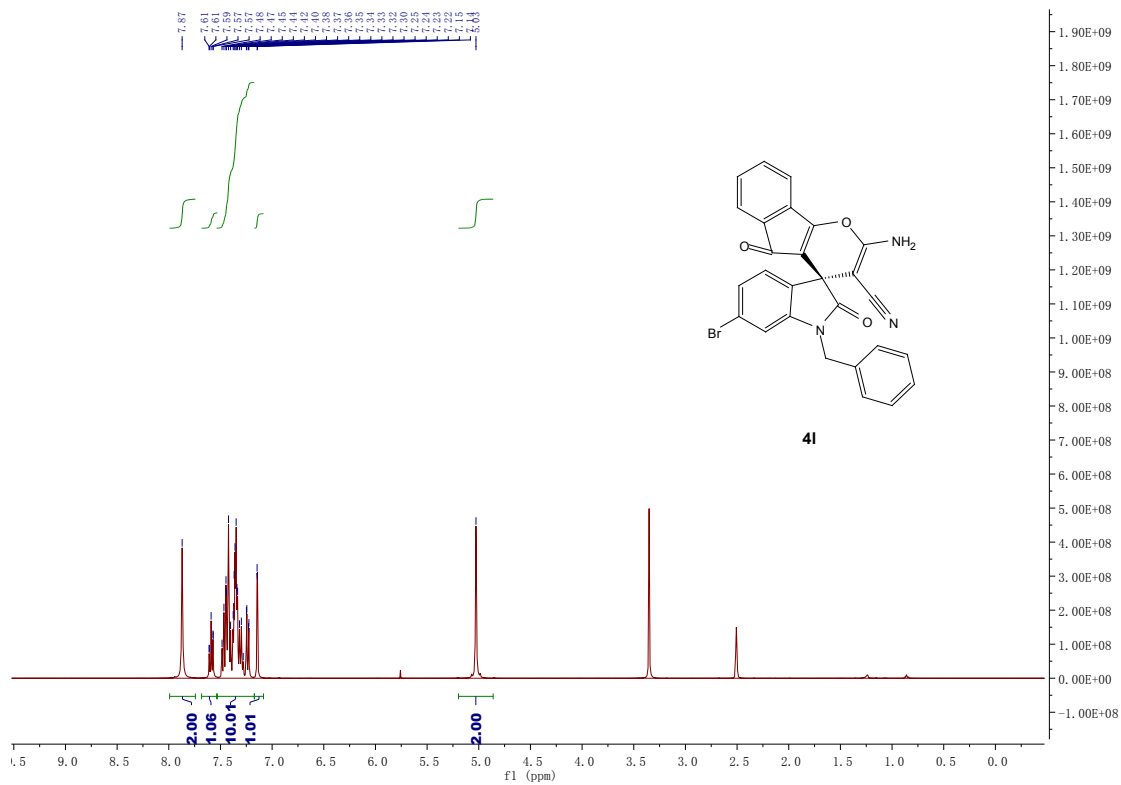


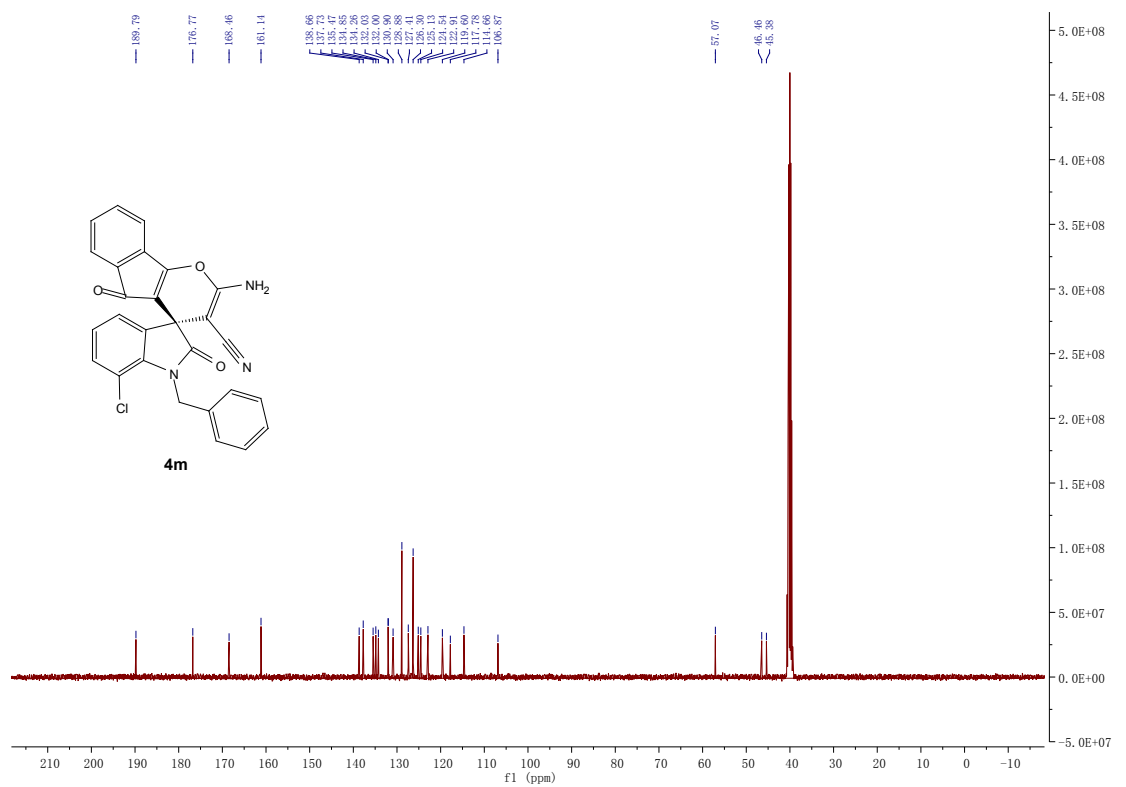
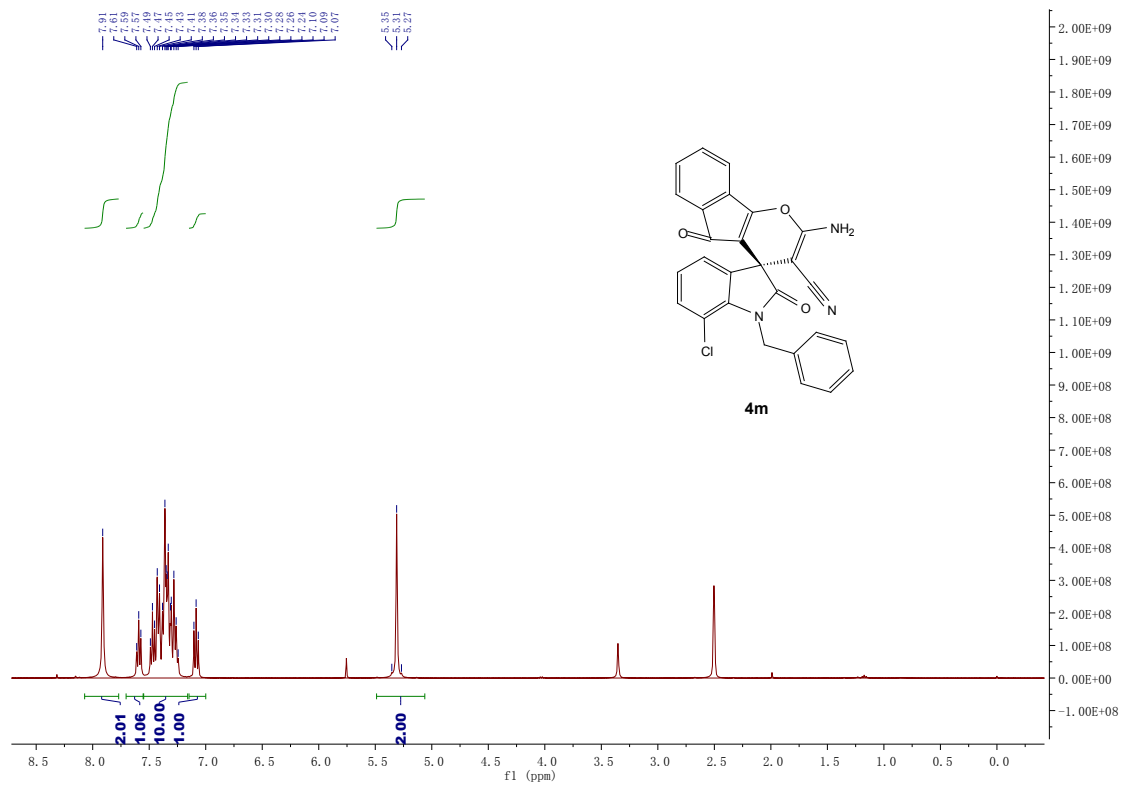


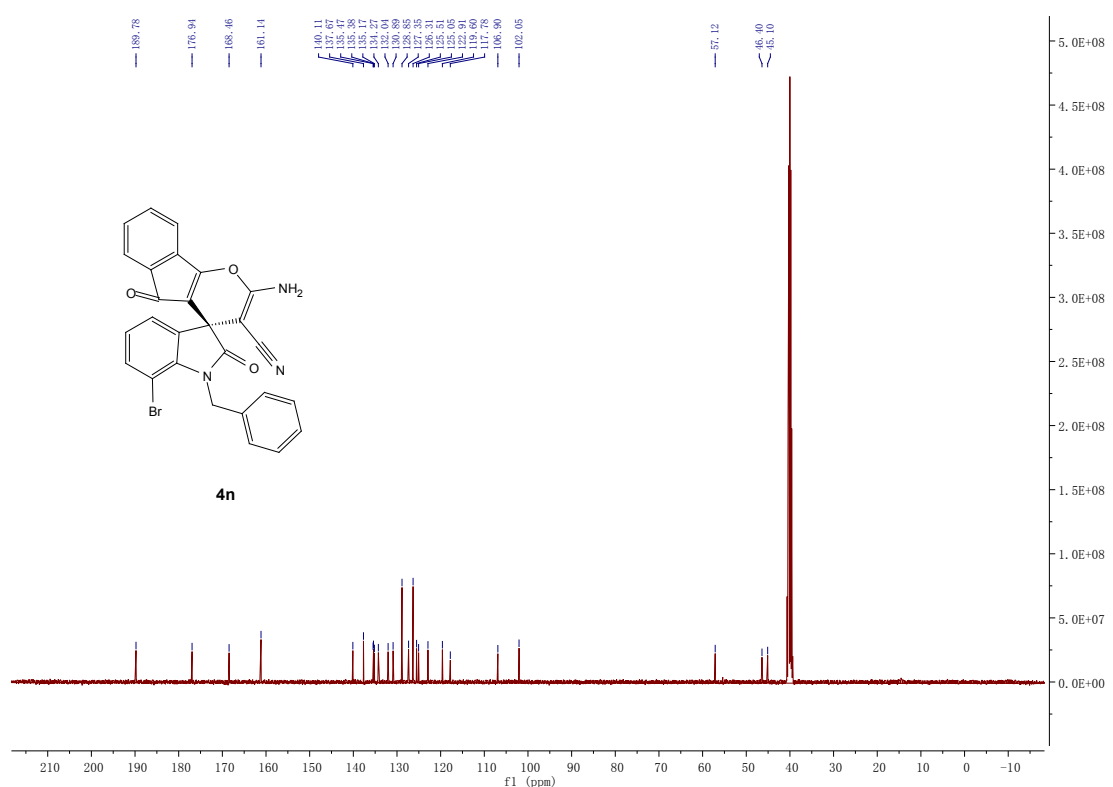
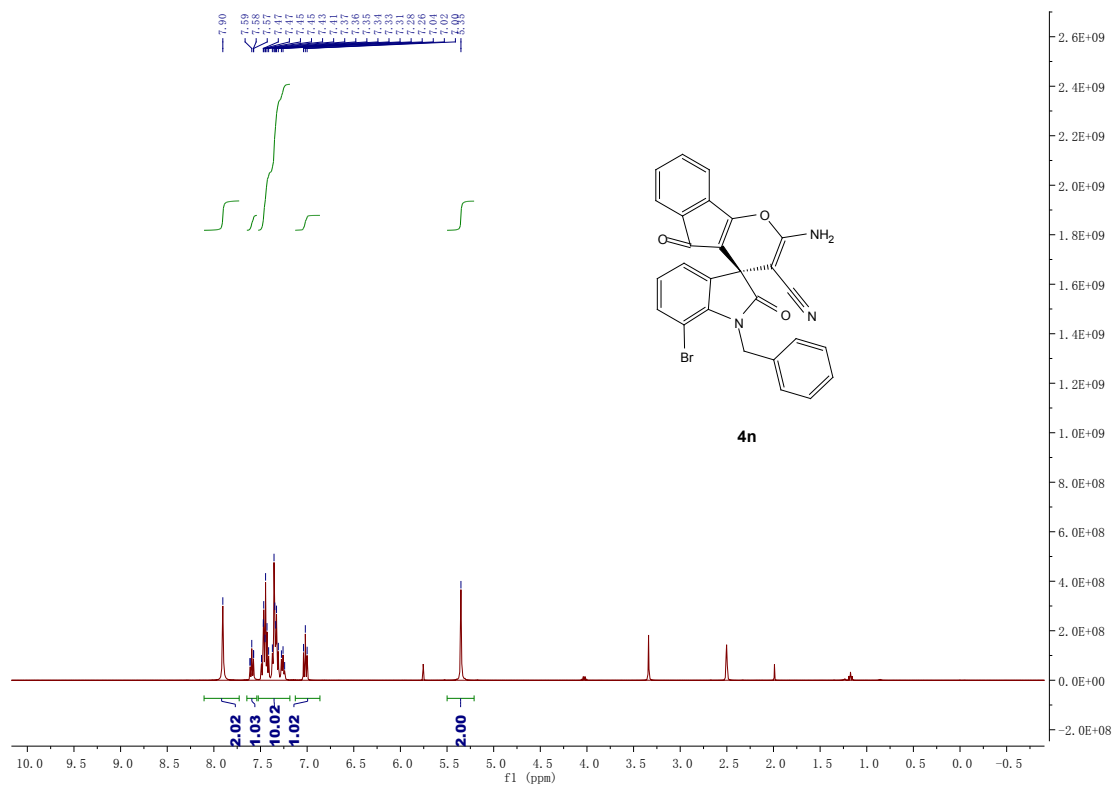


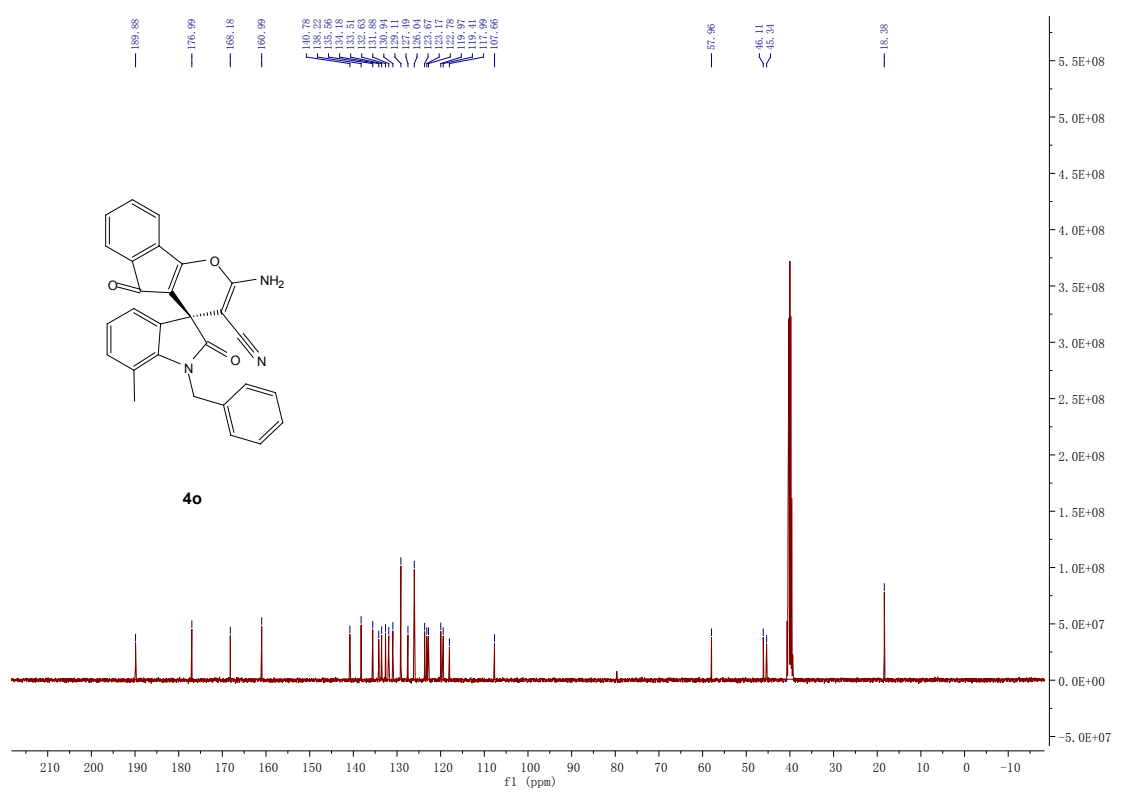
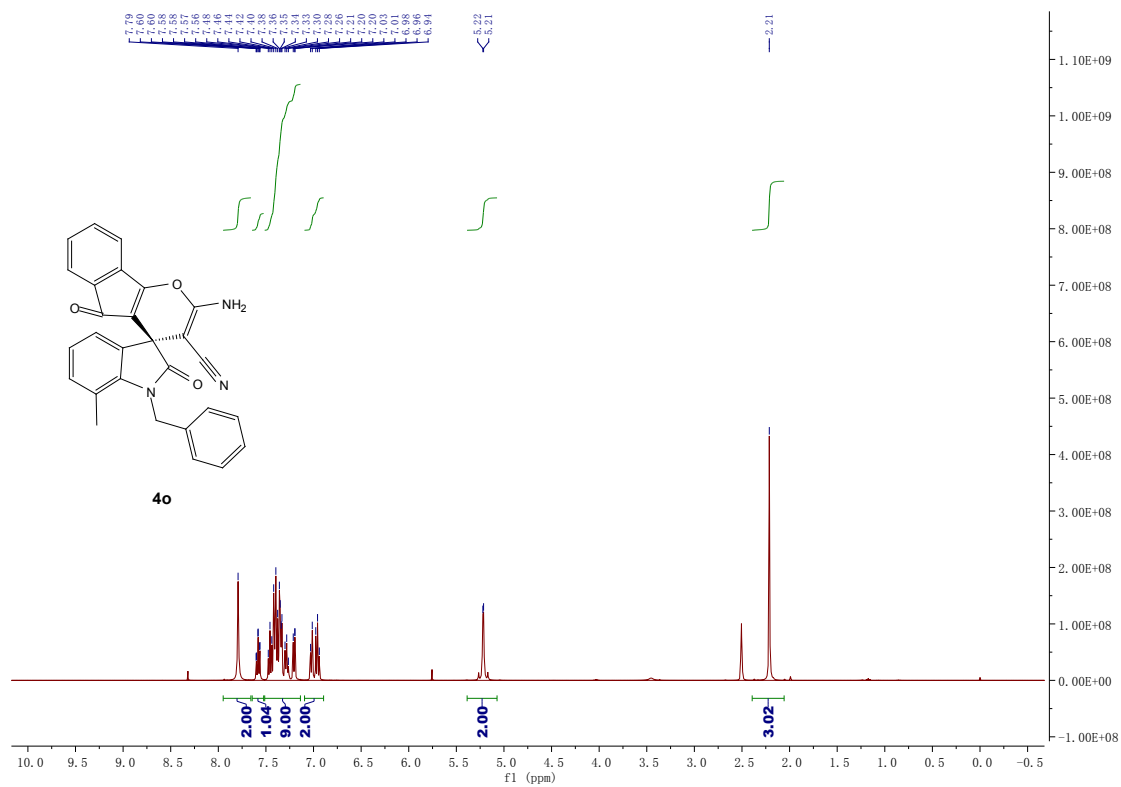


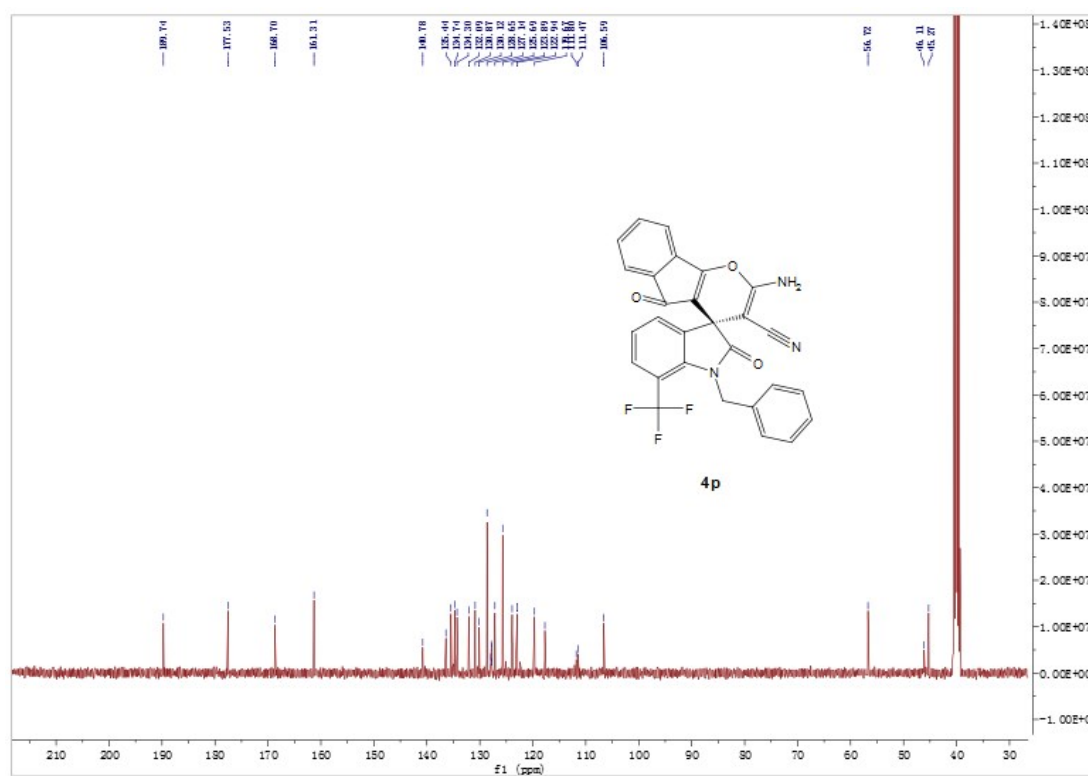
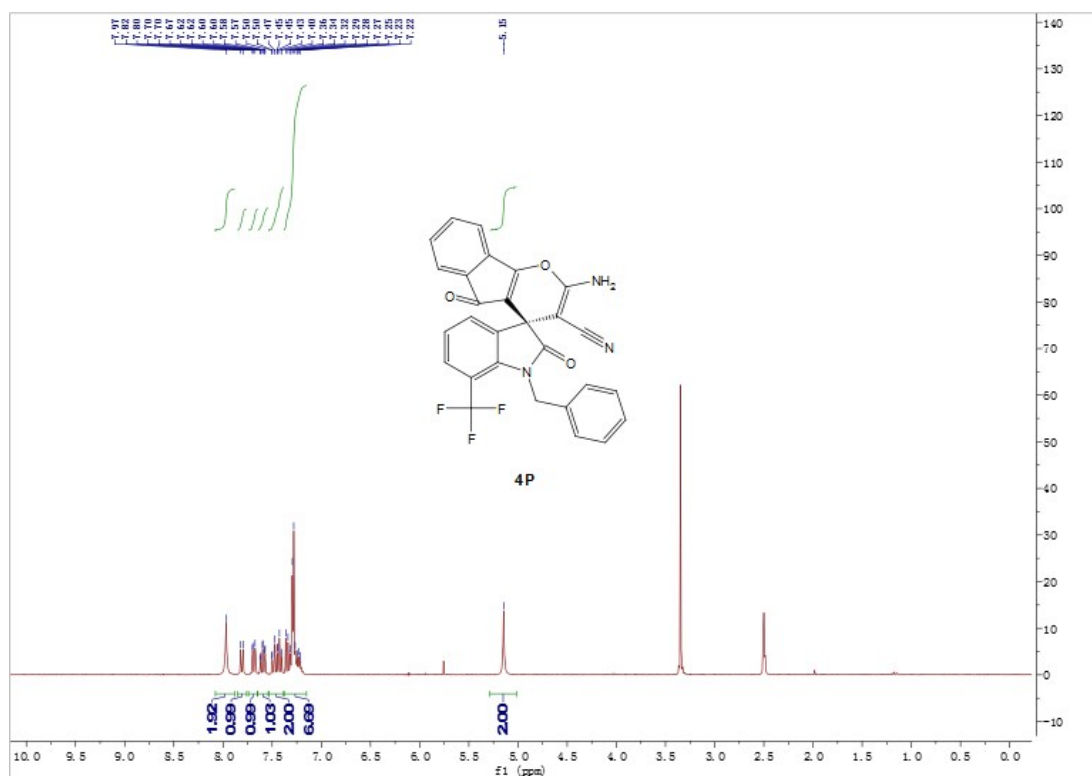


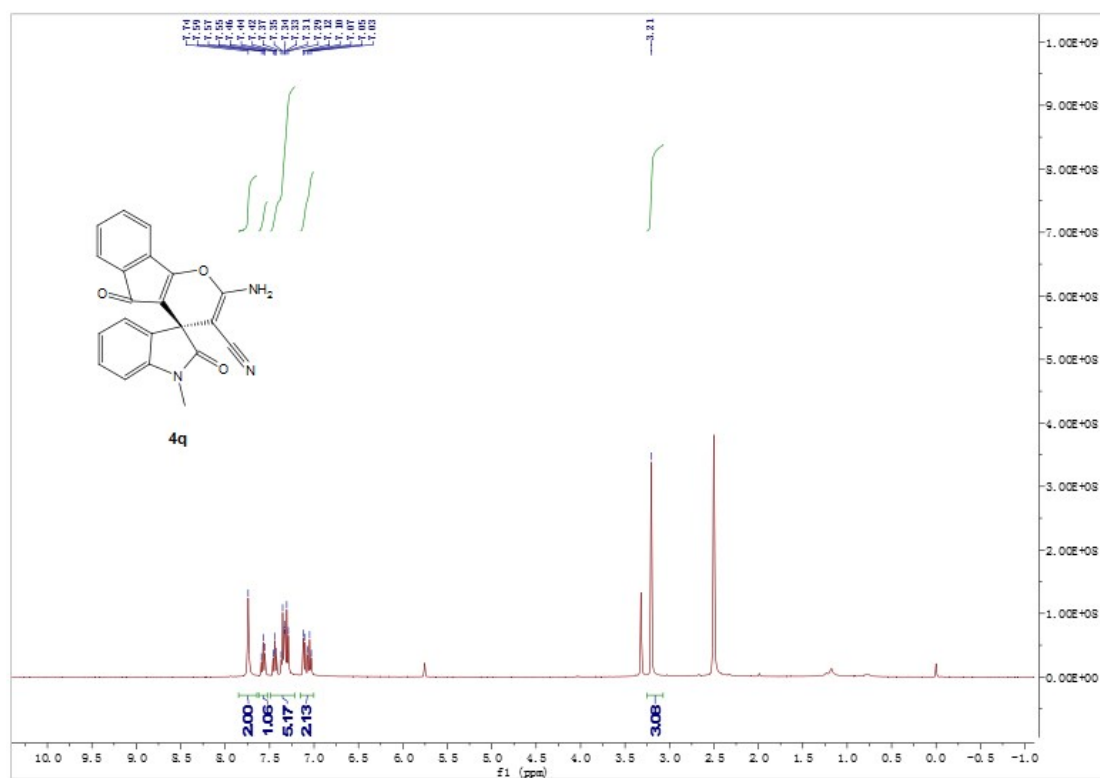
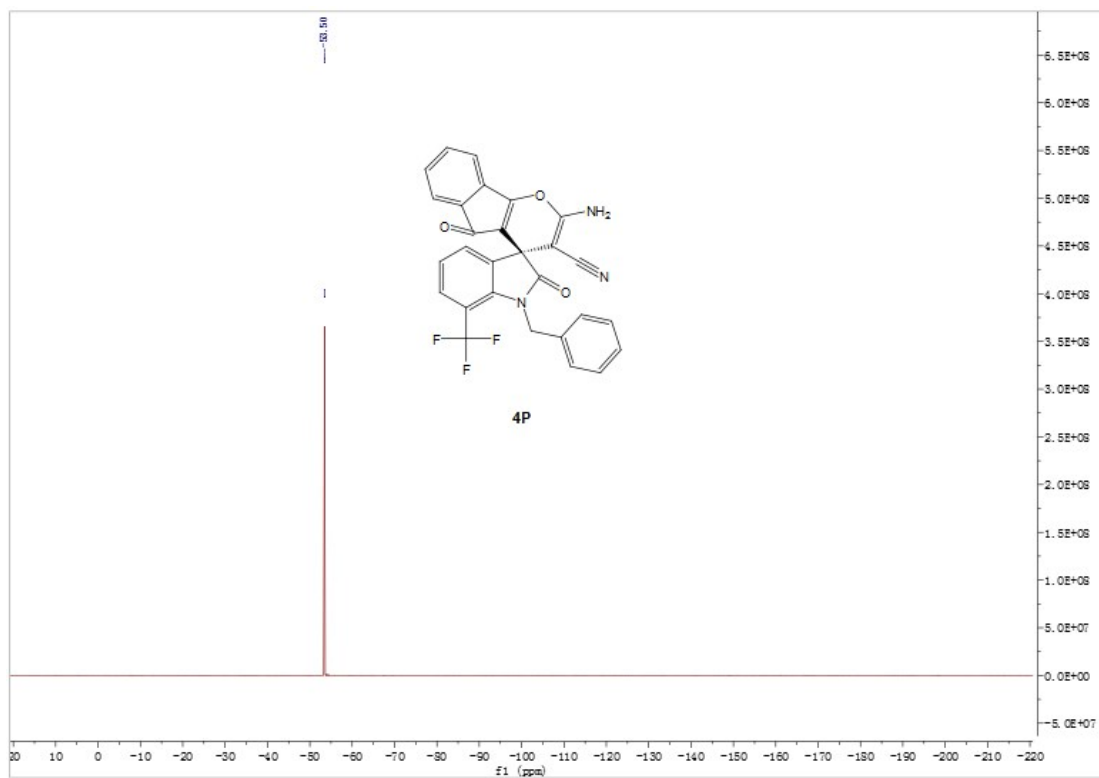


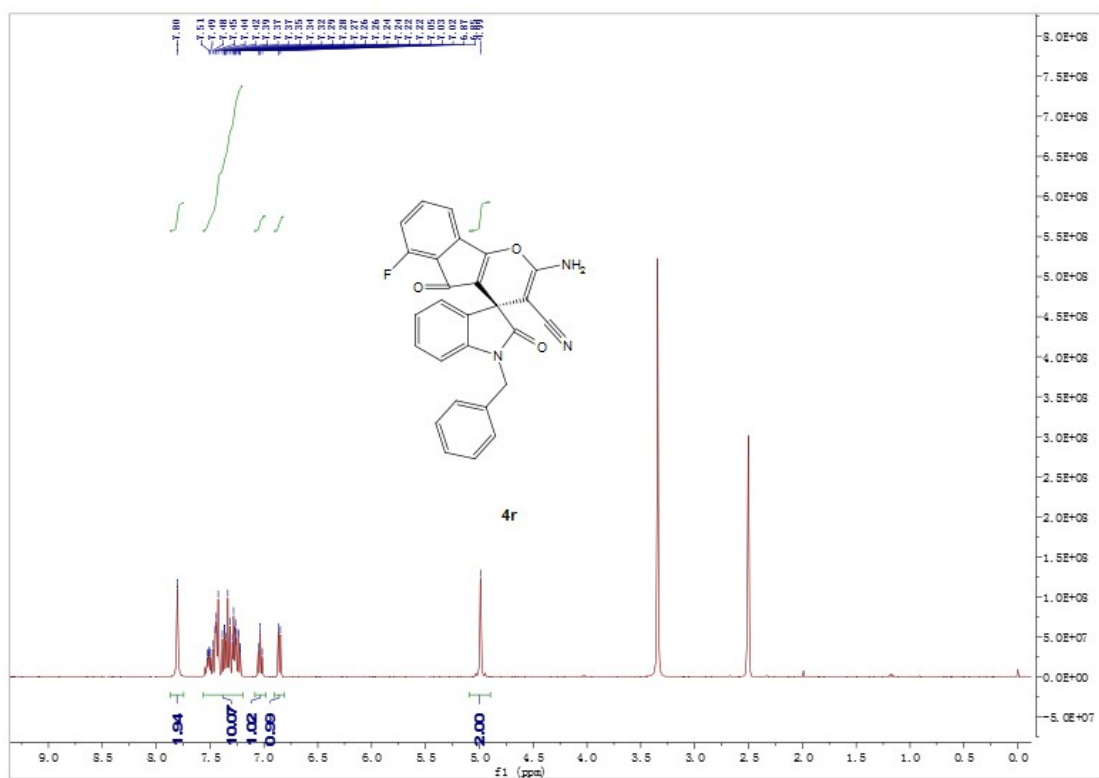
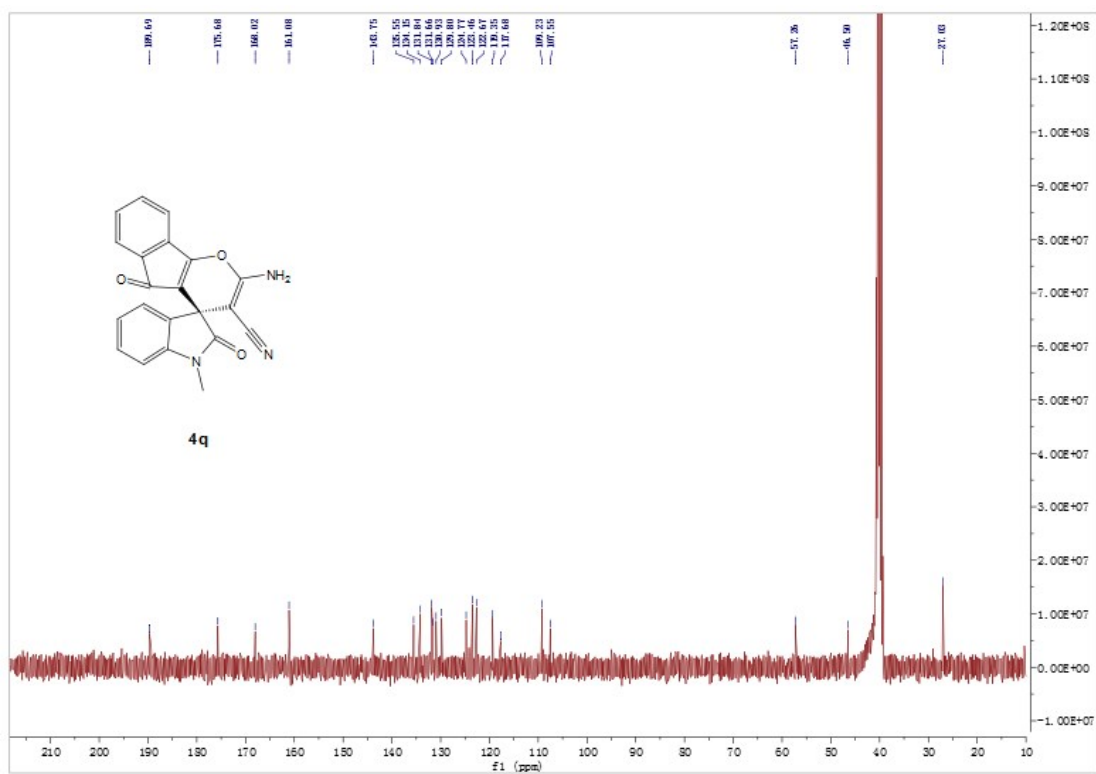


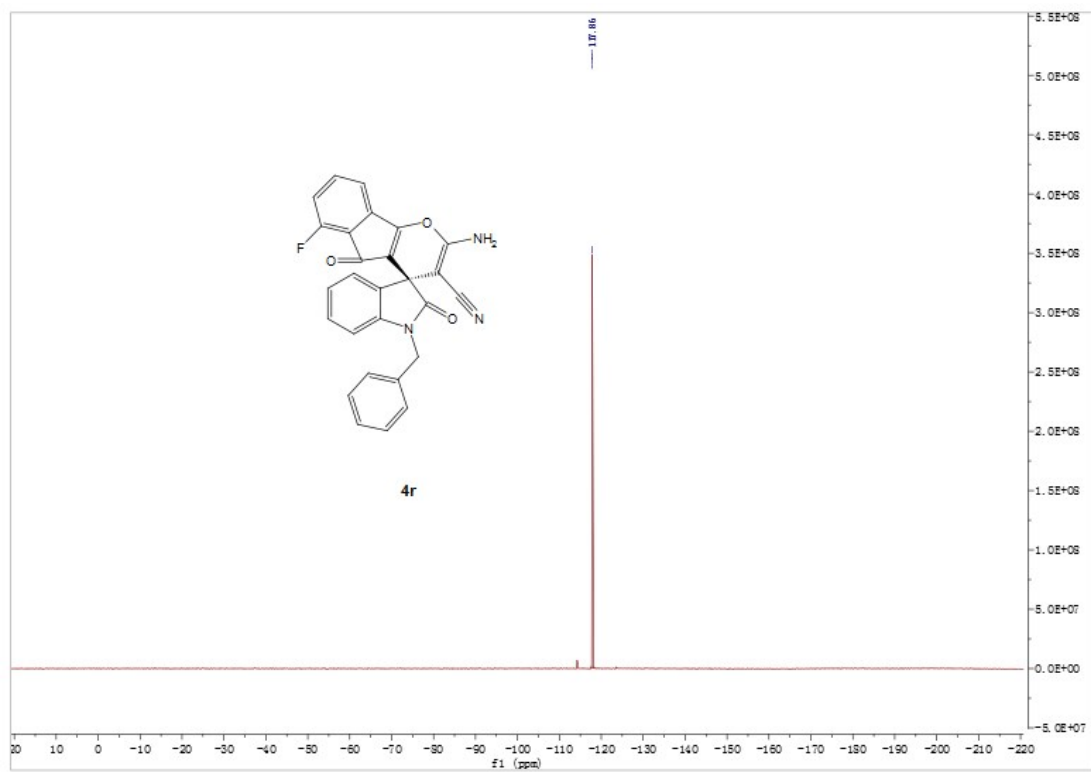
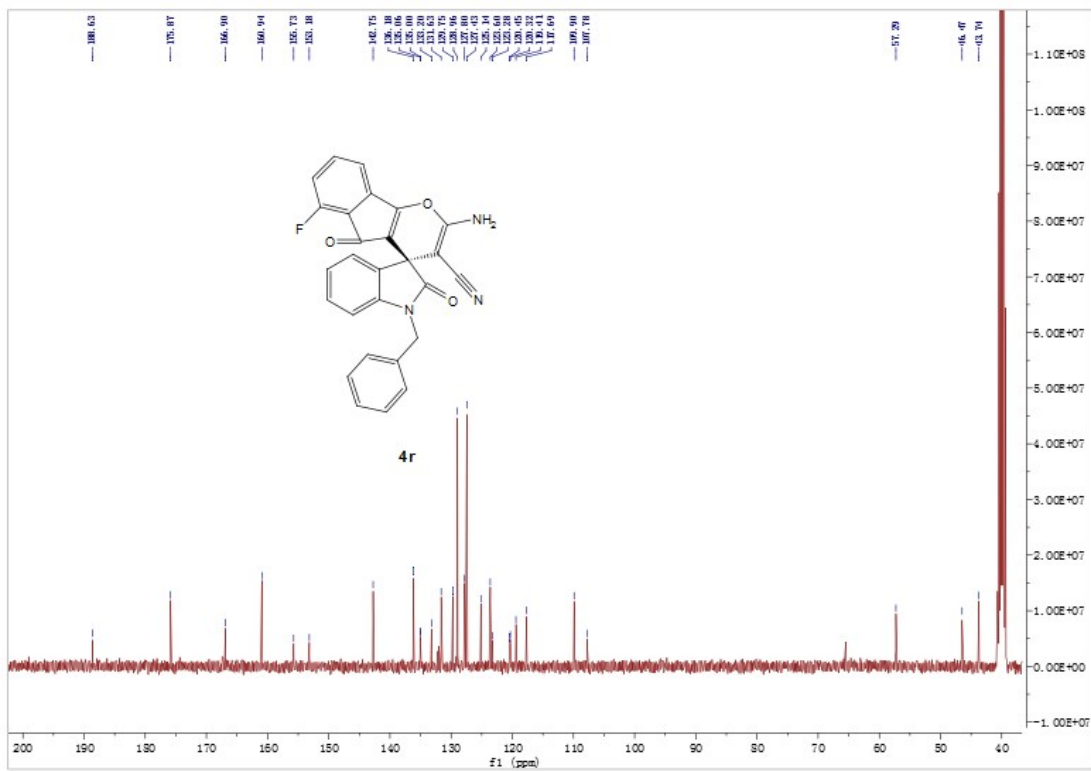


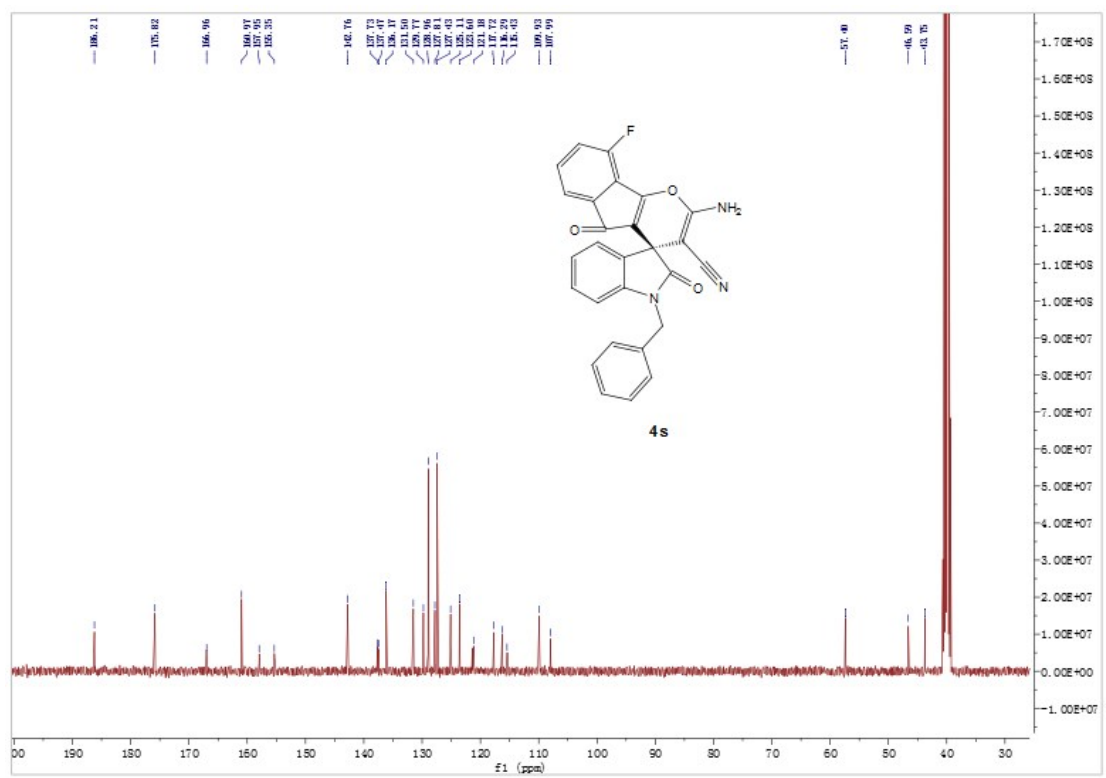
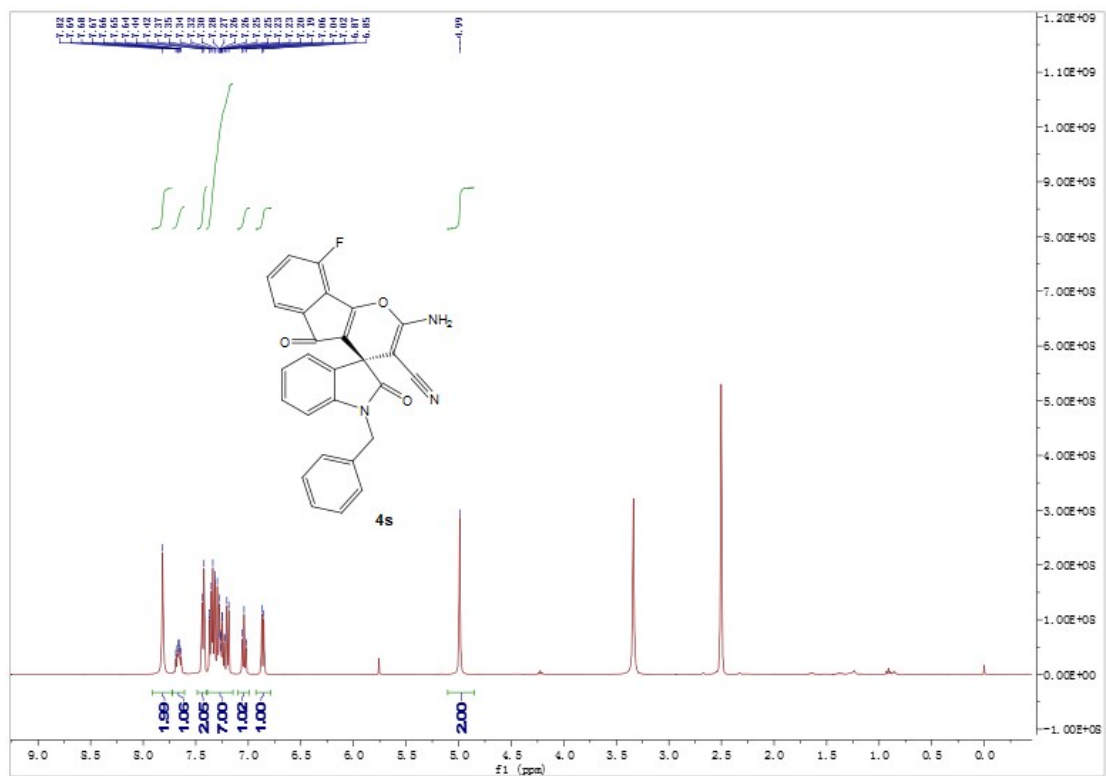


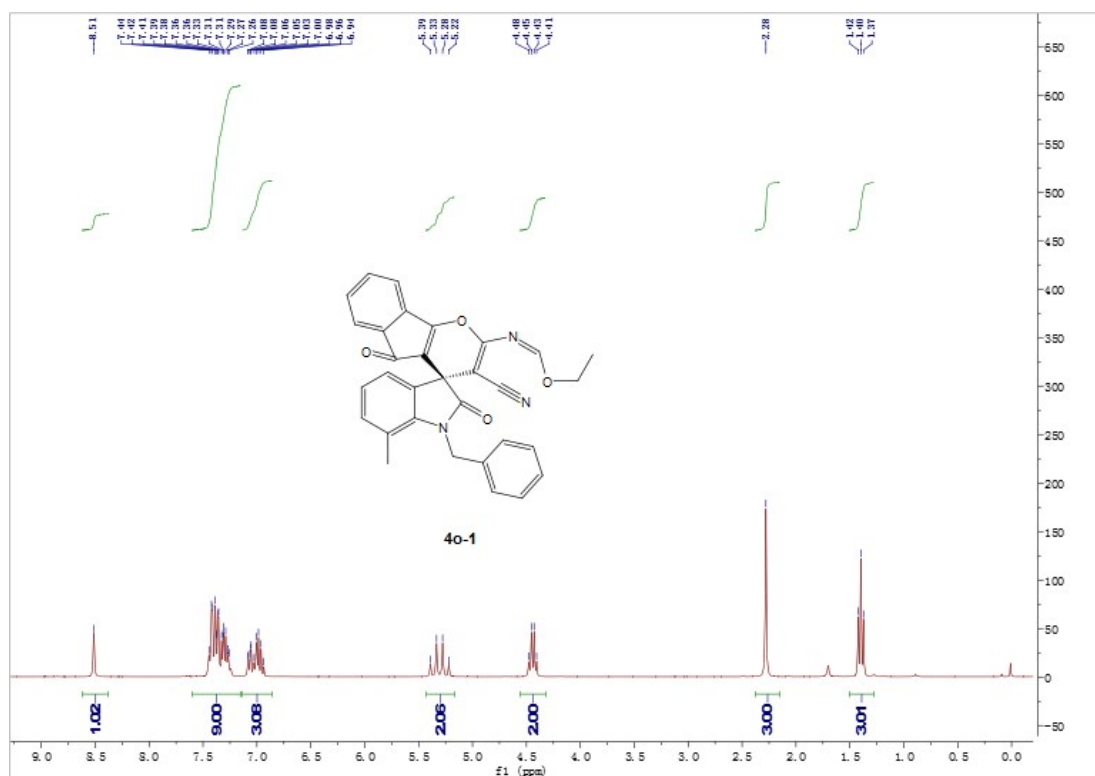
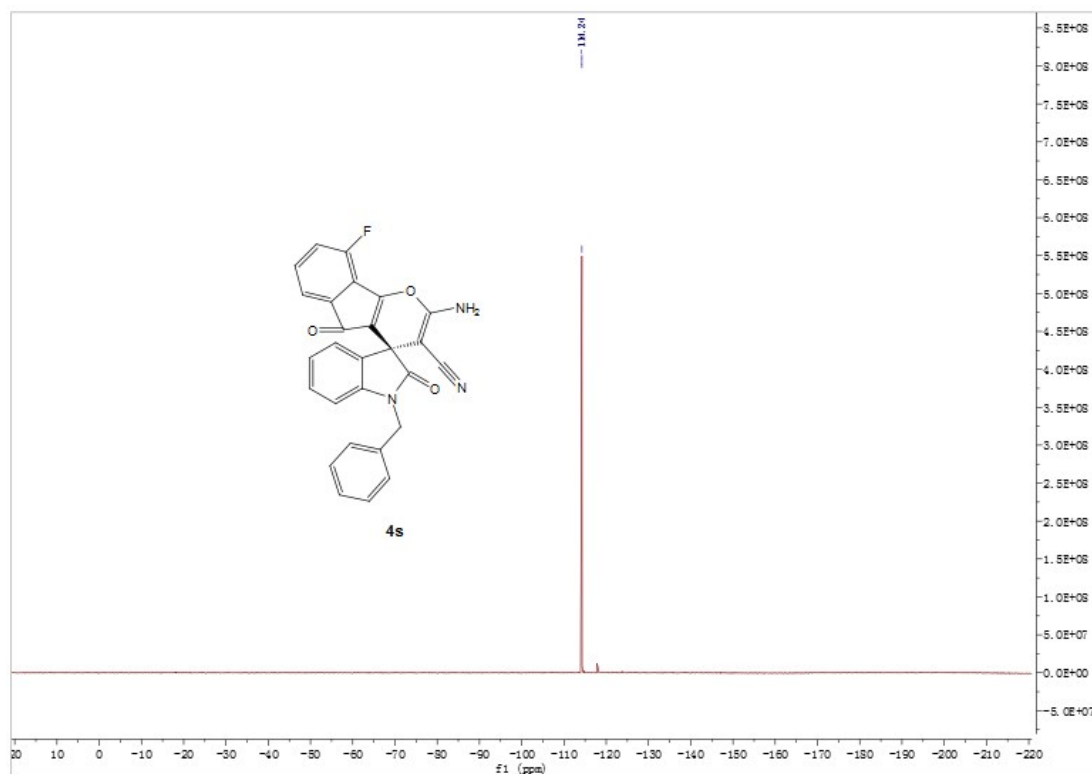


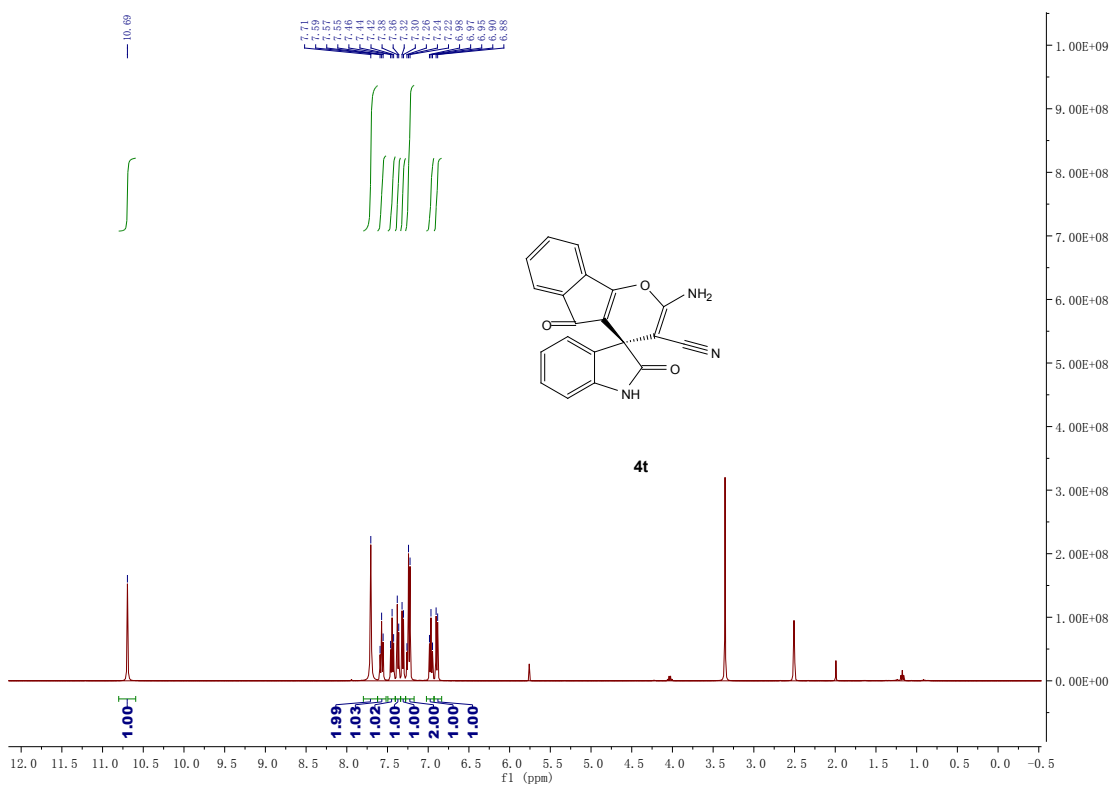
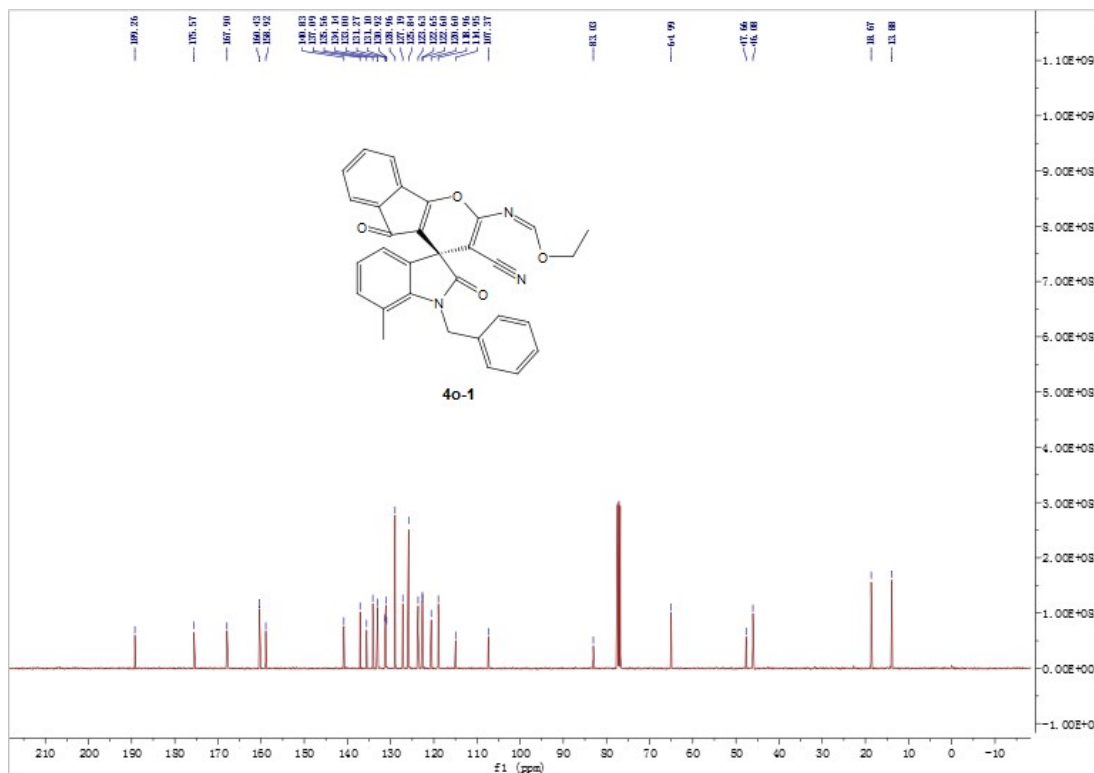


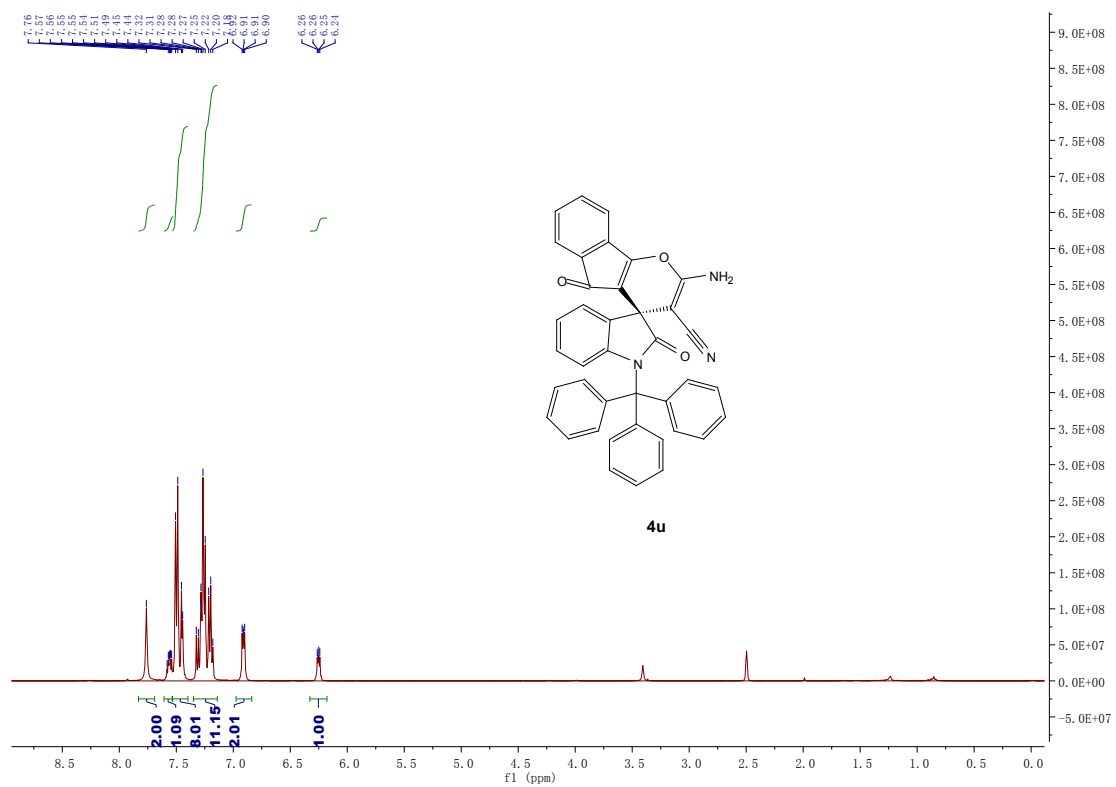
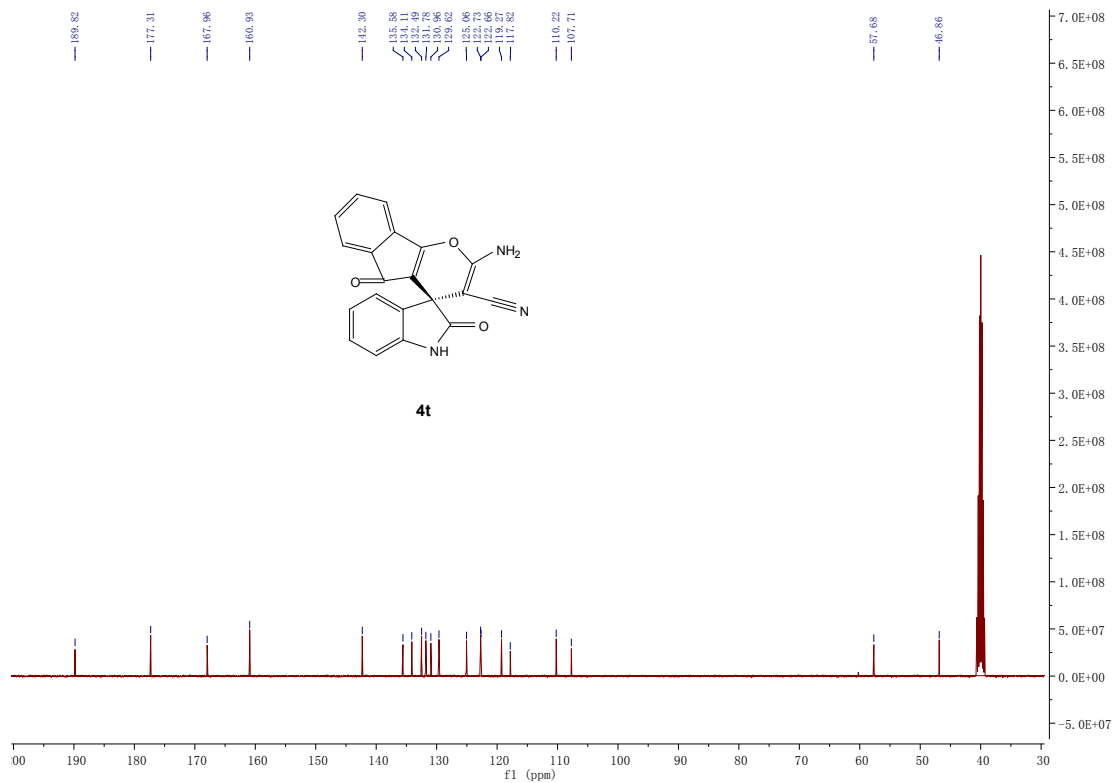


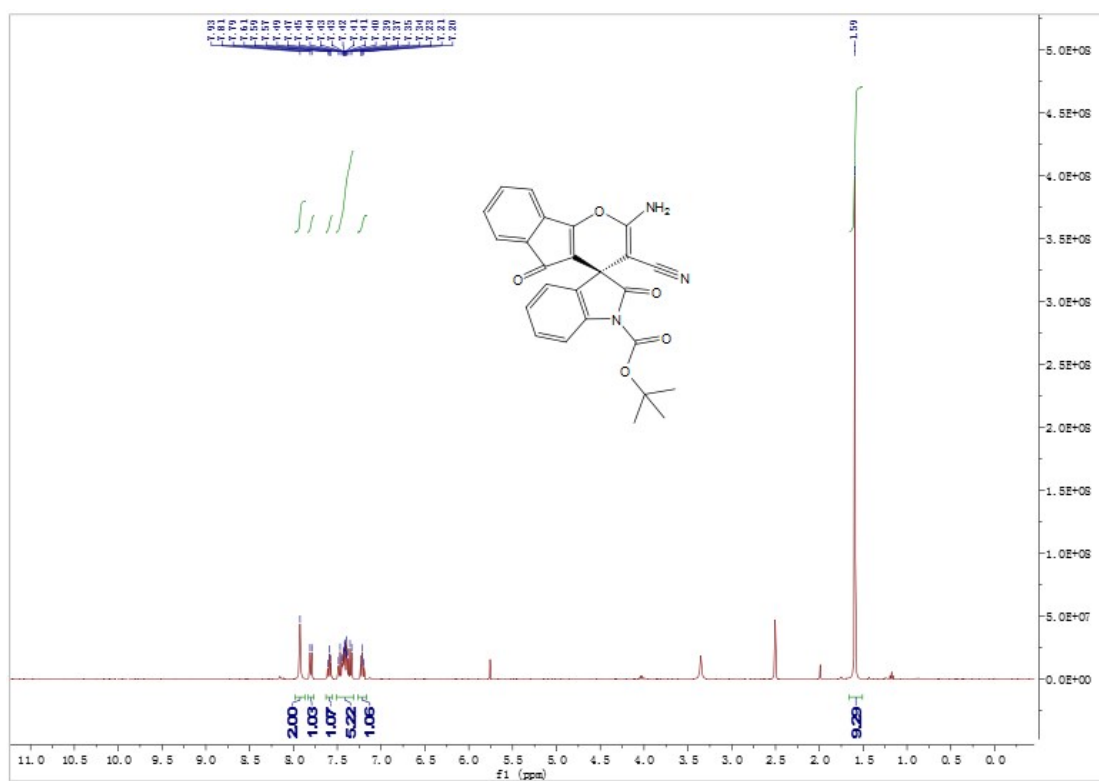
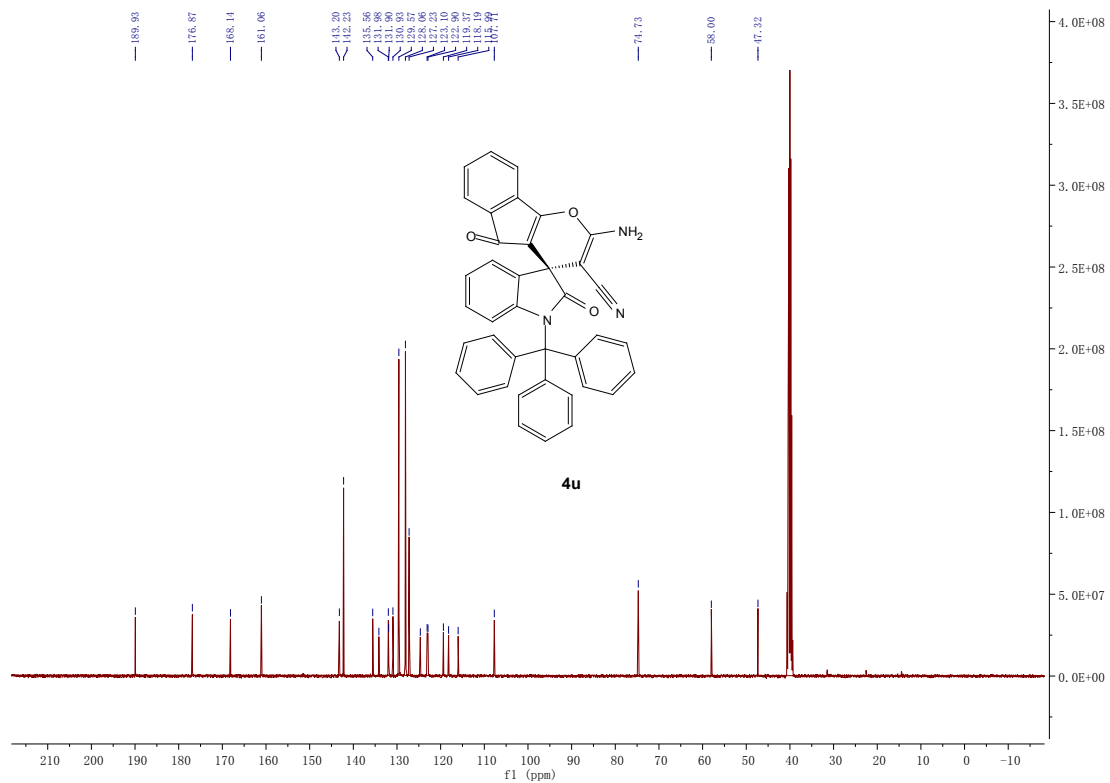


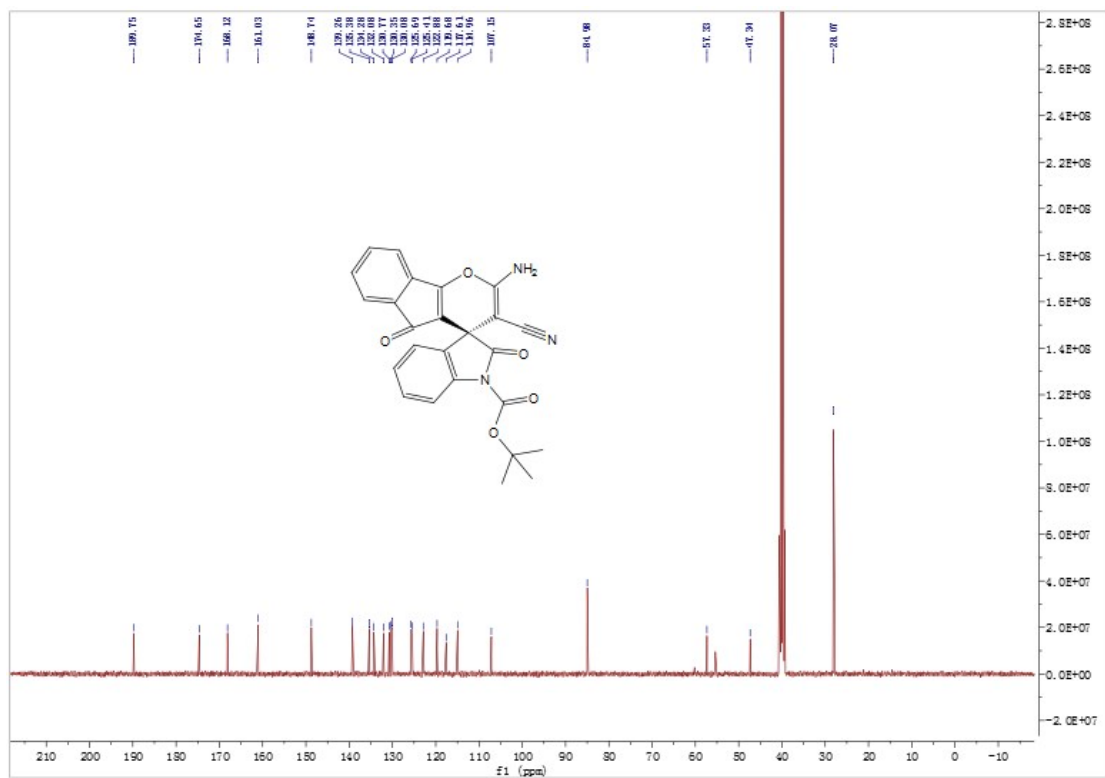




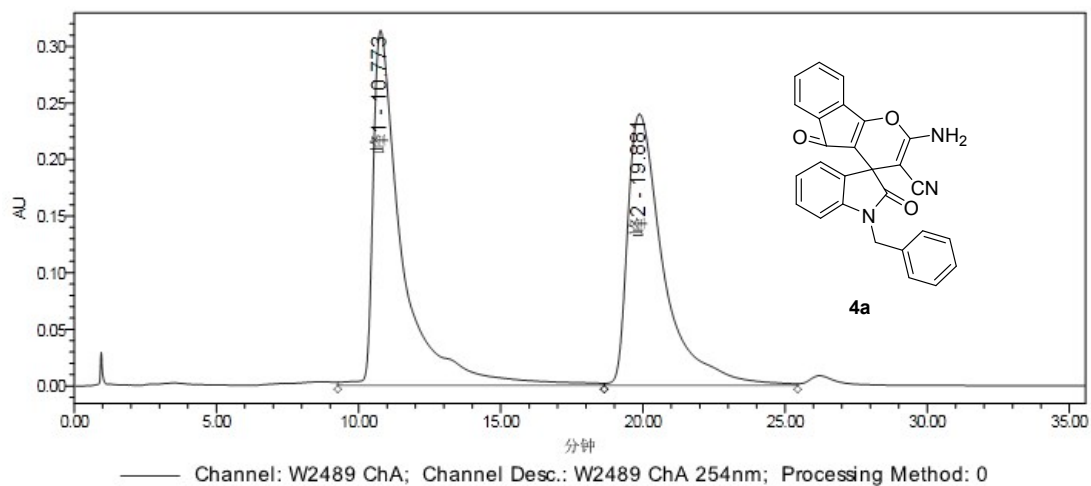






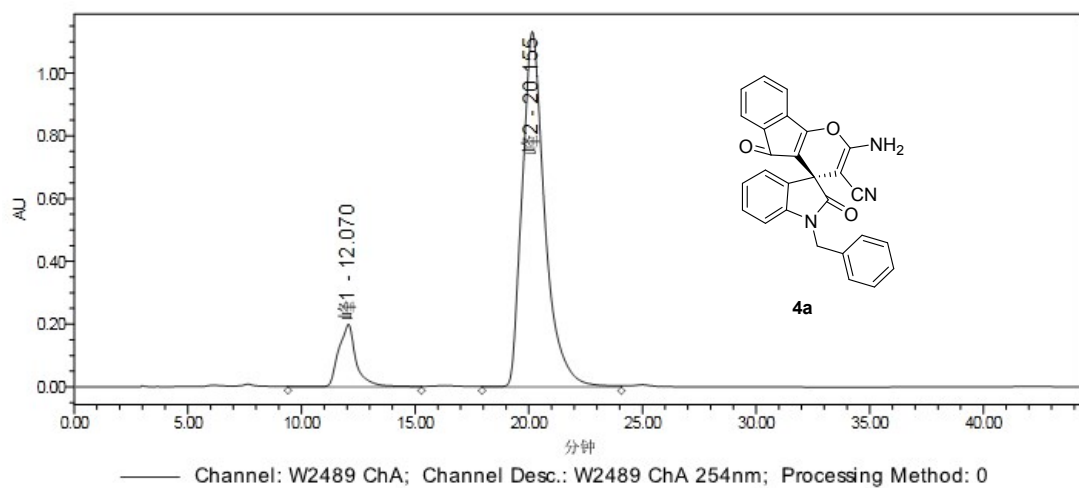


6. HPLC traces of compounds 4a-4u, 4o-1

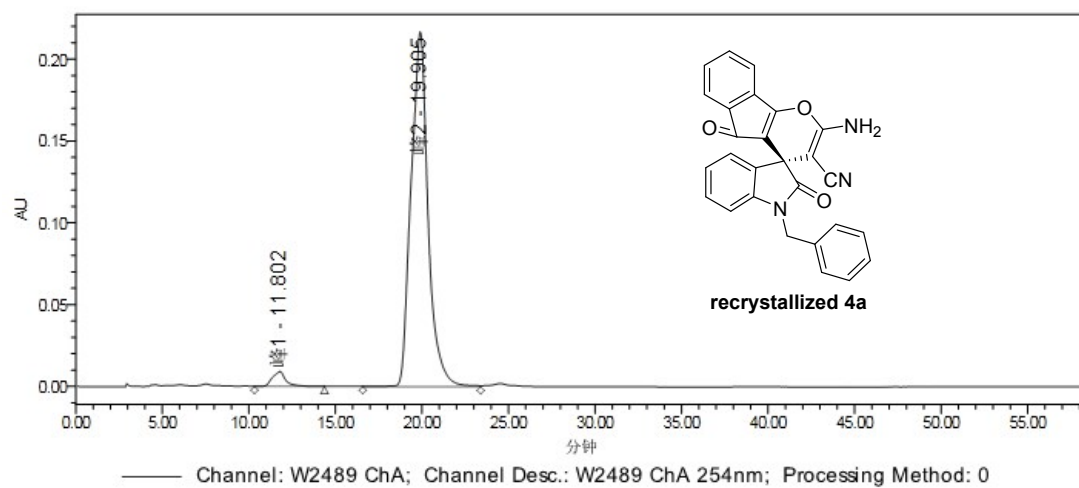


	Channel Description	Peak Name	RT (min)	Area (磷*sec)	% Area	Height (磷)
1	W2489 ChA 254nm	峰1	10.773	22245436	51.36	313401
2	W2489 ChA 254nm	峰2	19.881	21063149	48.64	239706

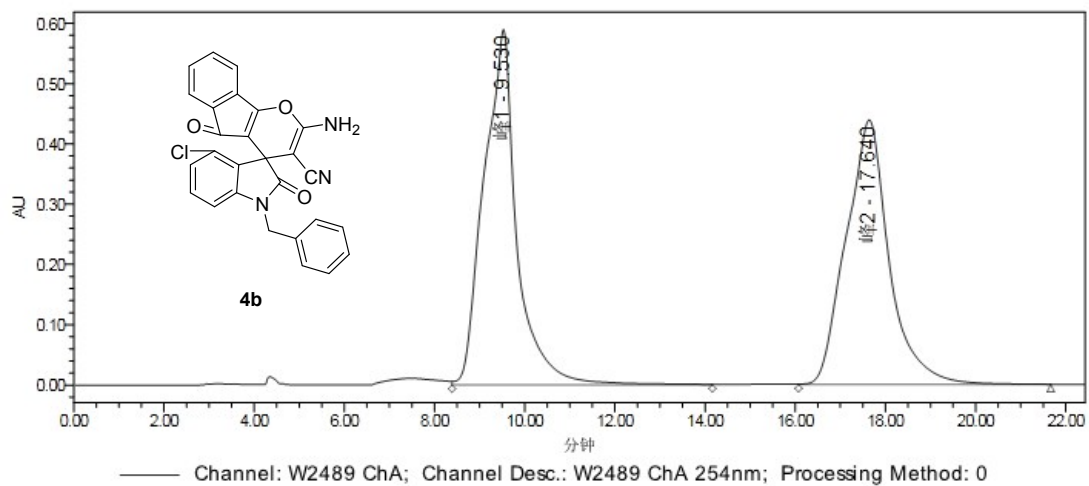
remark: 峰→Peak
分钟→time(min)
磷→mAU



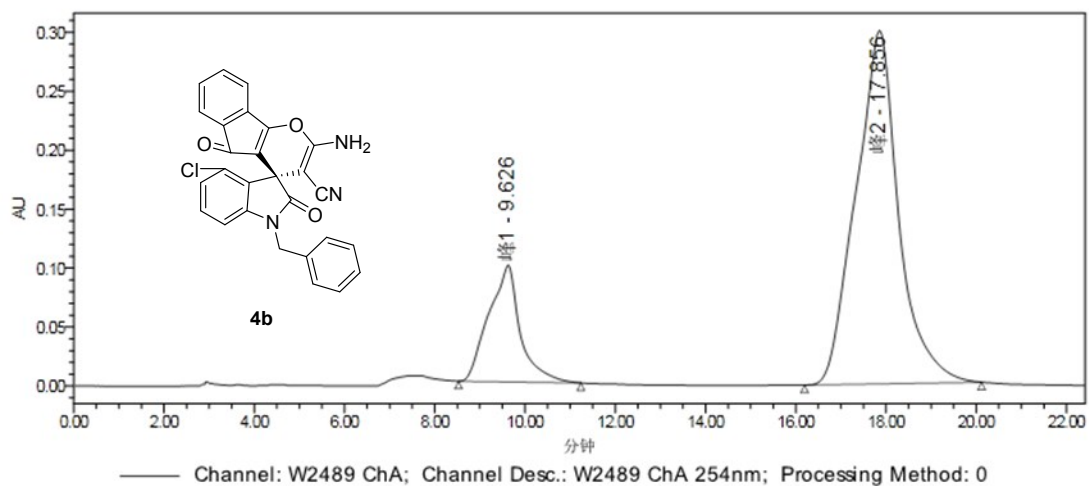
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1	W2489 ChA 254nm	峰1	12.070	10588812	11.92	198429
2	W2489 ChA 254nm	峰2	20.155	78224476	88.08	1131232



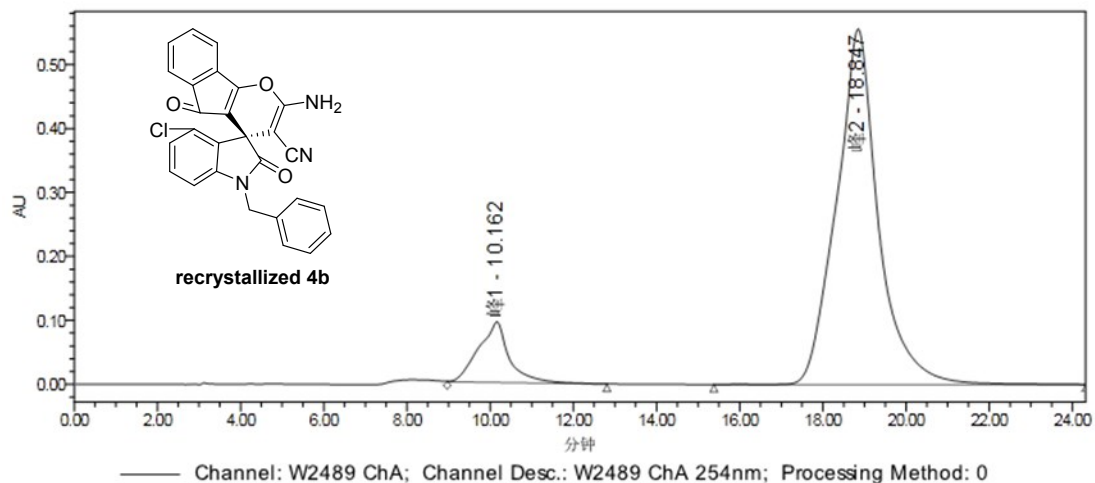
	Channel Description	Peak Name	RT (min)	Area (磷*sec)	% Area	Height (磷)
1	W2489 ChA 254nm	峰1	11.802	473776	3.11	9007
2	W2489 ChA 254nm	峰2	19.905	14759605	96.89	216489



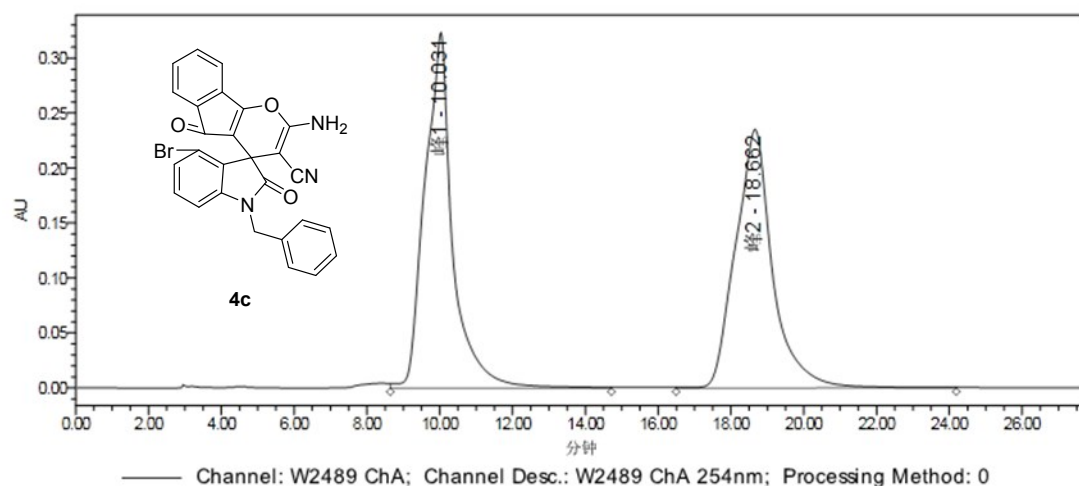
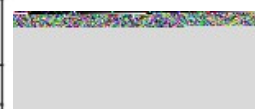
	Channel Description	Peak Name	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	峰1	9.530	29902180	50.67	588853
2	W2489 ChA 254nm	峰2	17.640	29114383	49.33	438640



	Channel Description	Peak Name	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	峰1	9.626	4794168	19.54	98831
2	W2489 ChA 254nm	峰2	17.856	19740517	80.46	299369

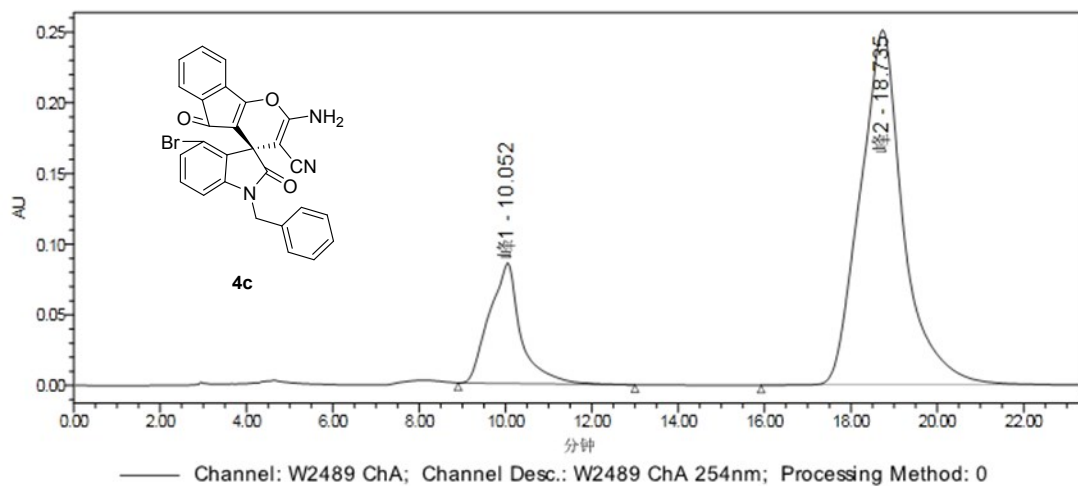


	Channel Description	Peak Name	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	峰1	10.162	4845339	11.09	94571
2	W2489 ChA 254nm	峰2	18.847	38840847	88.91	555441

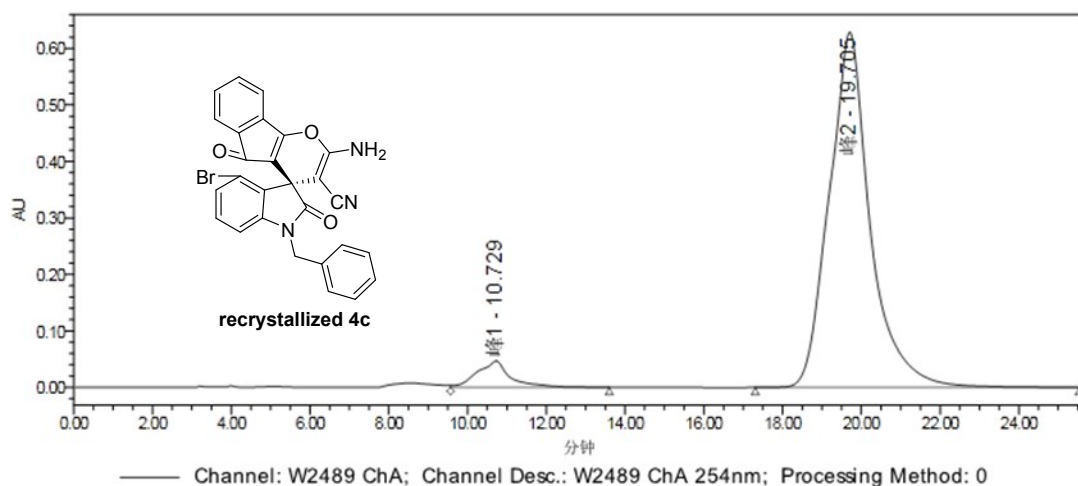
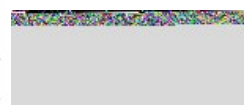


	Channel Description	Peak Name	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	峰1	10.031	17140167	50.75	323197
2	W2489 ChA 254nm	峰2	18.662	16636876	49.25	235185

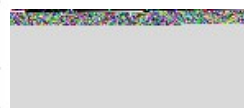


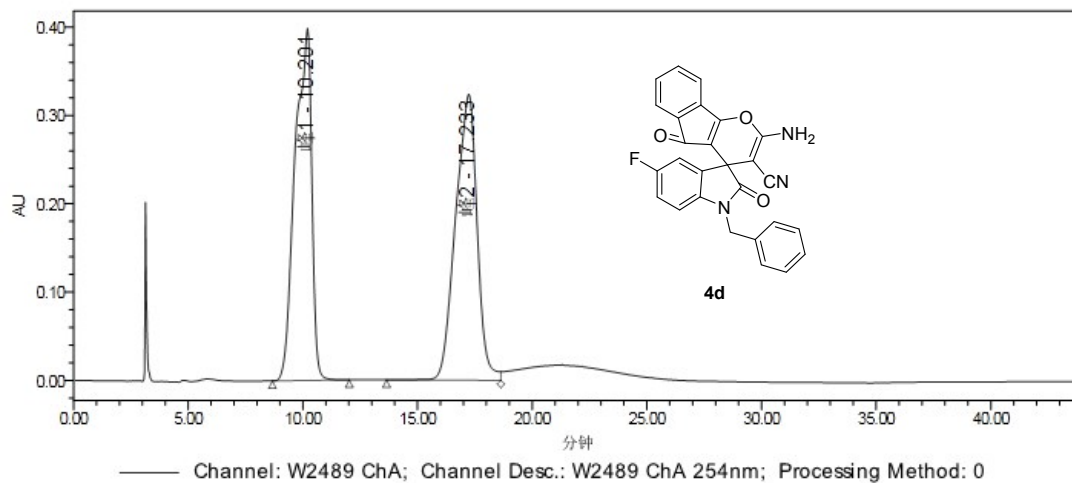


	Channel Description	Peak Name	RT (min)	Area (面积*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	峰1	10.052	4320070	19.79	85060
2	W2489 ChA 254nm	峰2	18.735	17511677	80.21	251231

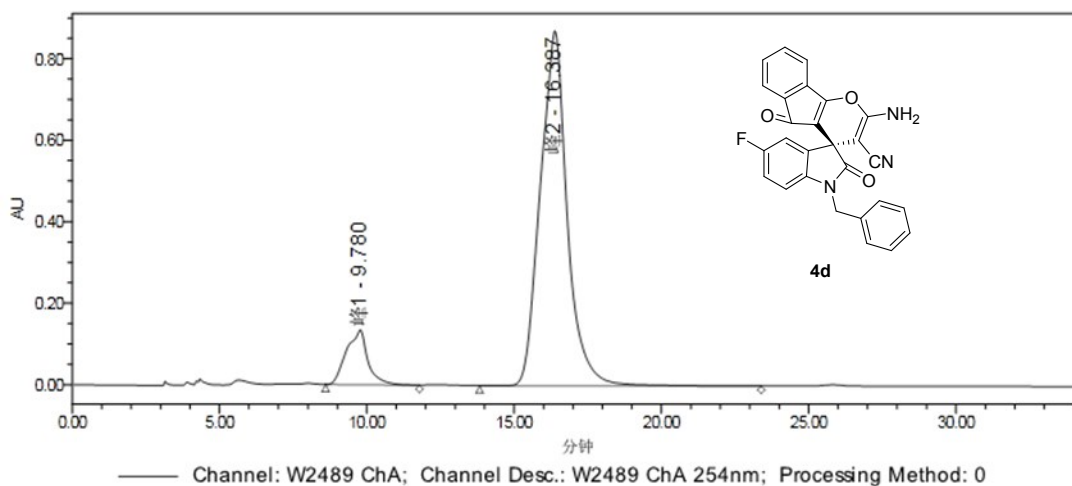
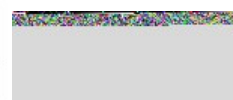


	Channel Description	Peak Name	RT (min)	Area (面积*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	峰1	10.729	2732516	5.66	46886
2	W2489 ChA 254nm	峰2	19.705	45519870	94.34	628809



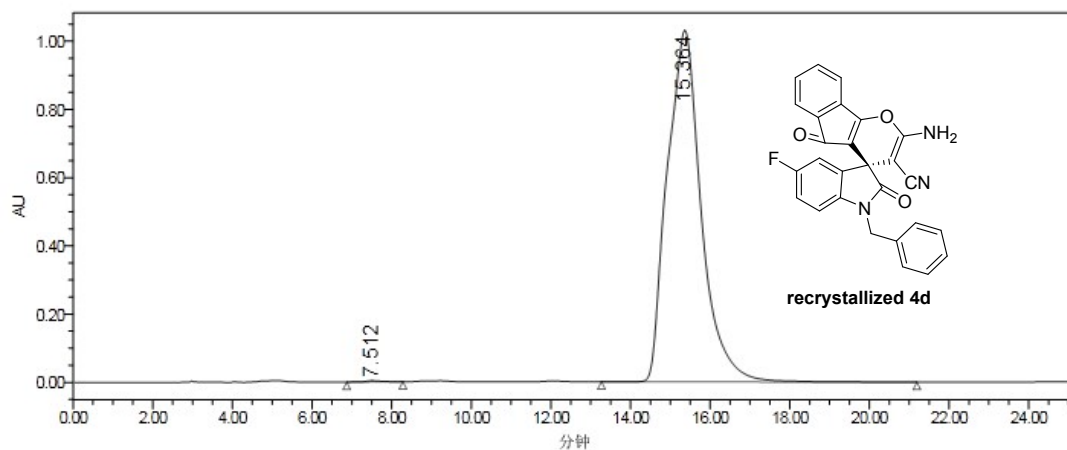


	Channel Description	Peak Name	RT (min)	Area (磷*sec)	% Area	Height (磷)
1	W2489 ChA 254nm	峰1	10.201	20167573	48.81	398356
2	W2489 ChA 254nm	峰2	17.233	21150002	51.19	323723



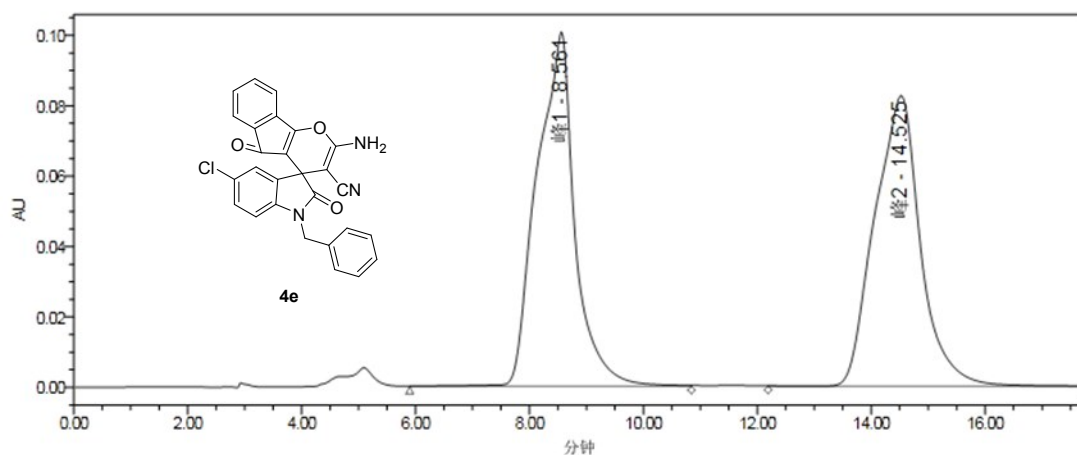
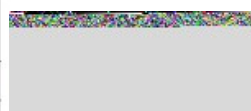
	Channel Description	Peak Name	RT (min)	Area (磷*sec)	% Area	Height (磷)
1	W2489 ChA 254nm	峰1	9.780	6827208	10.99	134019
2	W2489 ChA 254nm	峰2	16.387	55284752	89.01	870067





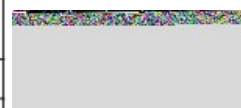
Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 0

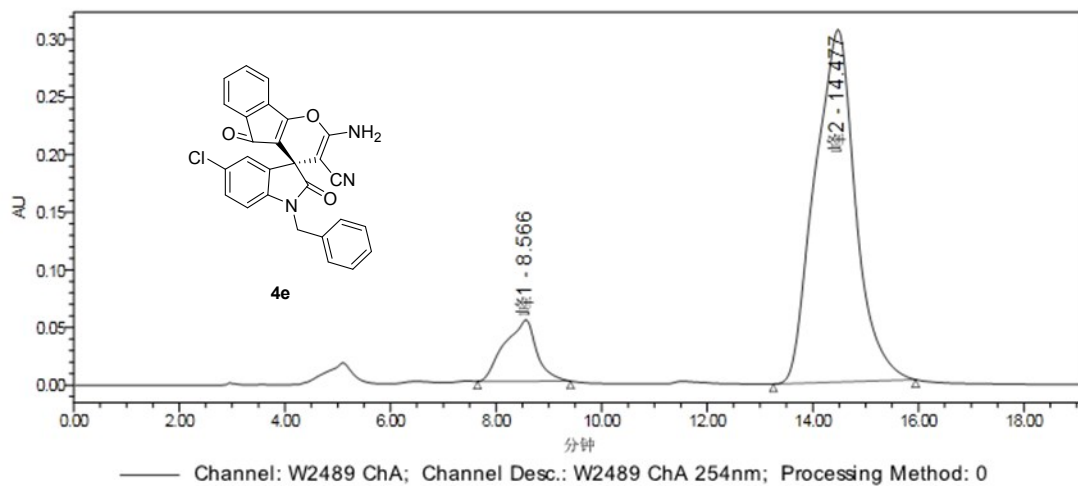
	Channel Description	RT (min)	Area (磺*sec)	% Area	Height (磺)
1	W2489 ChA 254nm	7.512	89265	0.15	3333
2	W2489 ChA 254nm	15.364	6111606E	99.85	1030271



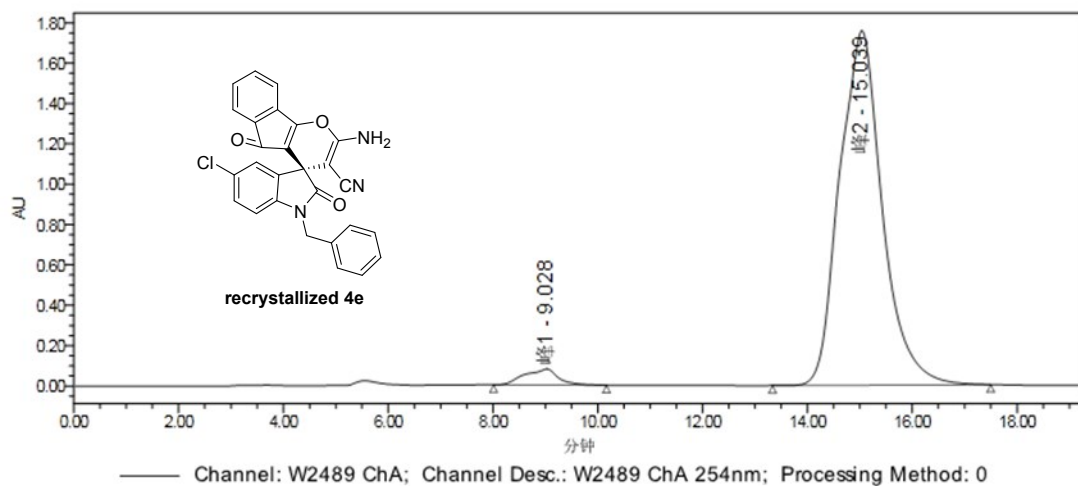
Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 0

	Channel Description	Peak Name	RT (min)	Area (磺*sec)	% Area	Height (磺)
1	W2489 ChA 254nm	峰1	8.561	4655373	50.25	100590
2	W2489 ChA 254nm	峰2	14.525	4608586	49.75	82499

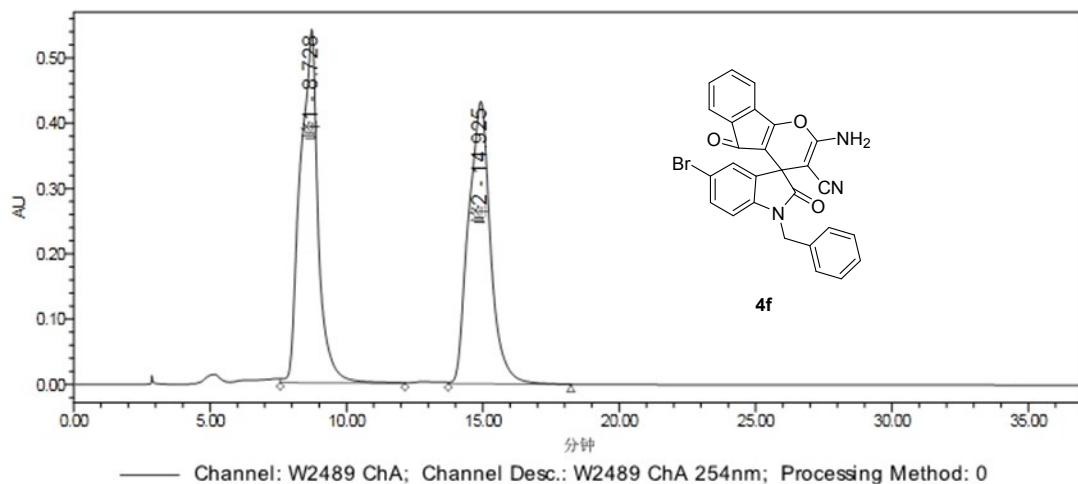




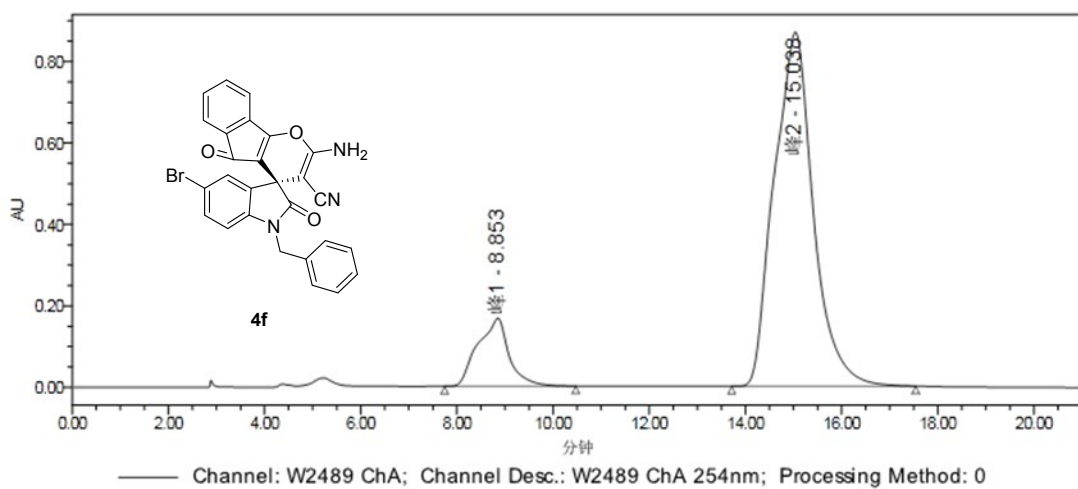
	Channel Description	Peak Name	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	峰1	8.566	2245919	12.03	53147
2	W2489 ChA 254nm	峰2	14.477	16426376	87.97	305839



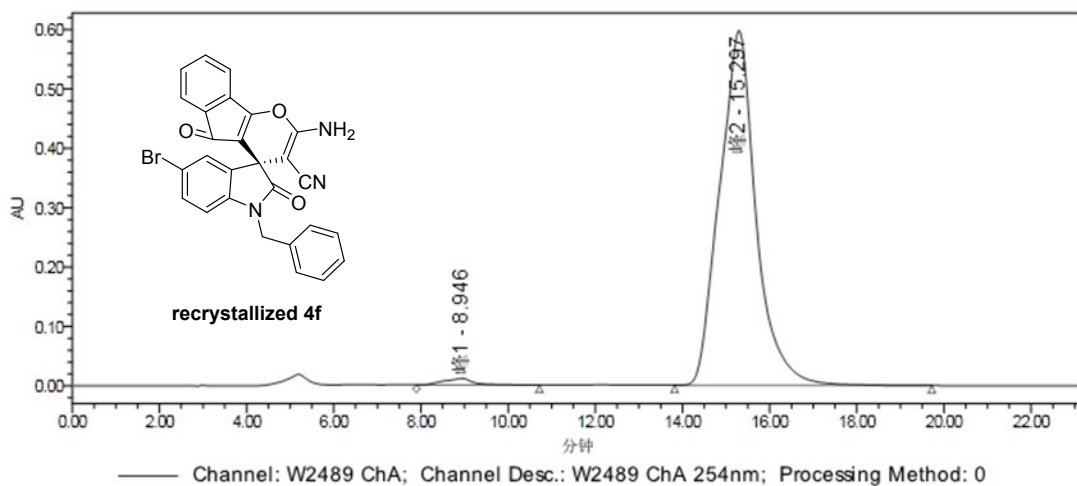
	Channel Description	Peak Name	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	峰1	9.028	3542185	3.44	79492
2	W2489 ChA 254nm	峰2	15.039	99428755	96.56	1757052



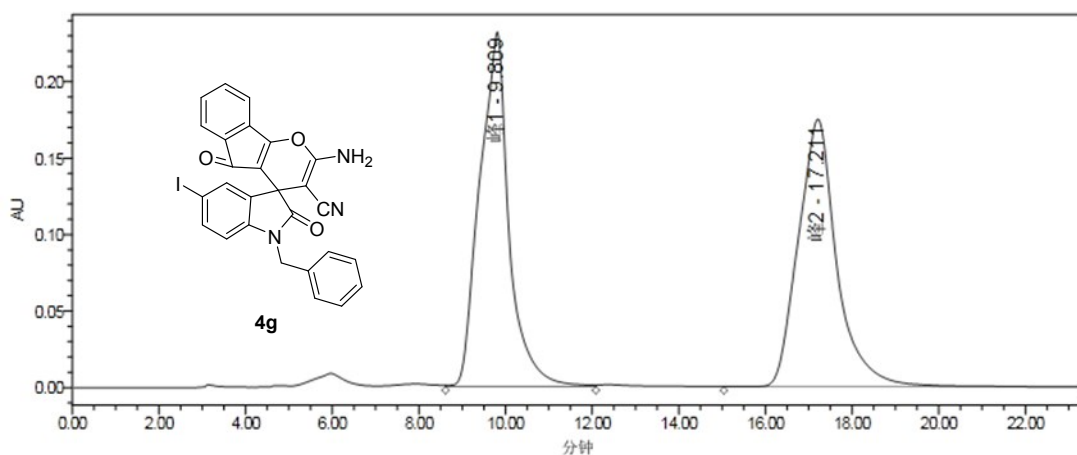
	Channel Description	Peak Name	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	峰1	8.728	24637788	50.51	540216
2	W2489 ChA 254nm	峰2	14.925	24143264	49.49	432288



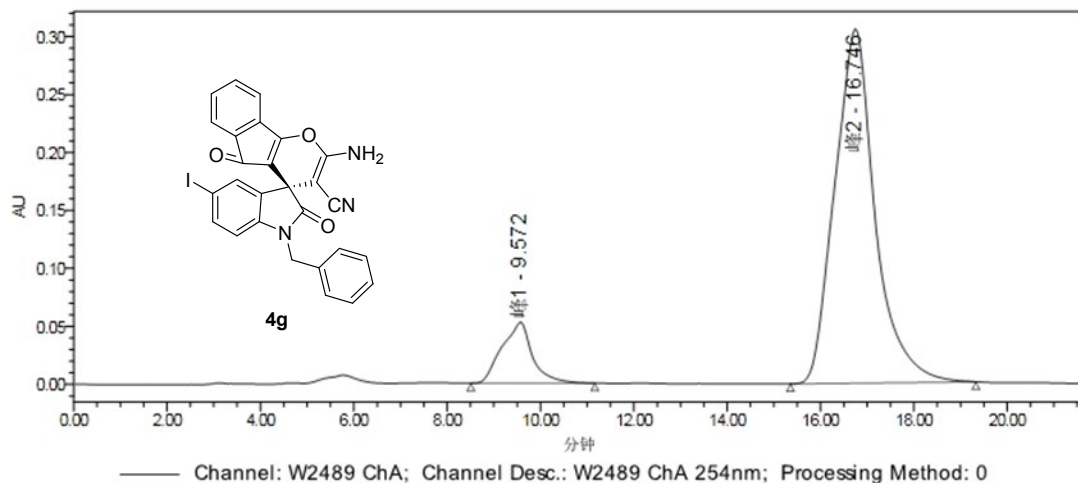
	Channel Description	Peak Name	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	峰1	8.853	7552481	13.31	167138
2	W2489 ChA 254nm	峰2	15.038	49183619	86.69	869499



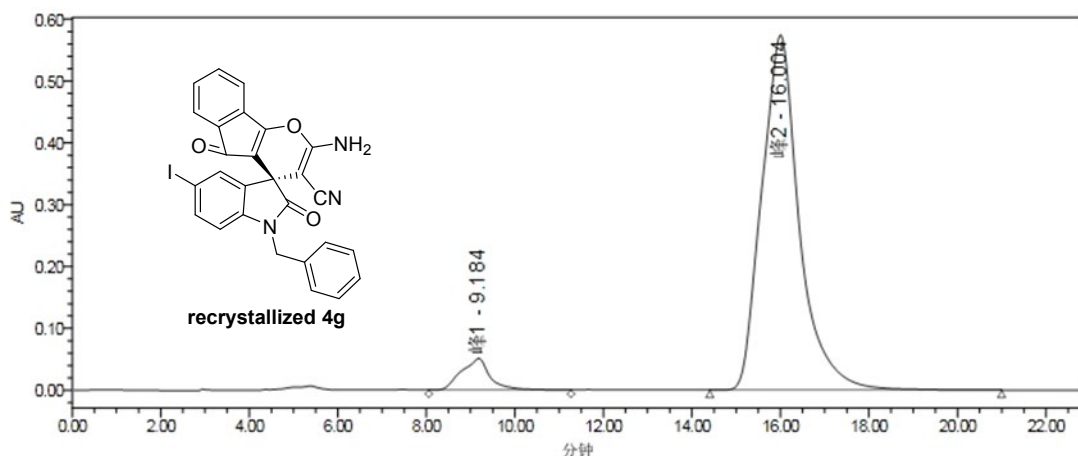
	Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
1	W2489 ChA 254nm	峰1	8.946	527142	1.50	11341
2	W2489 ChA 254nm	峰2	15.297	34642920	98.50	596901



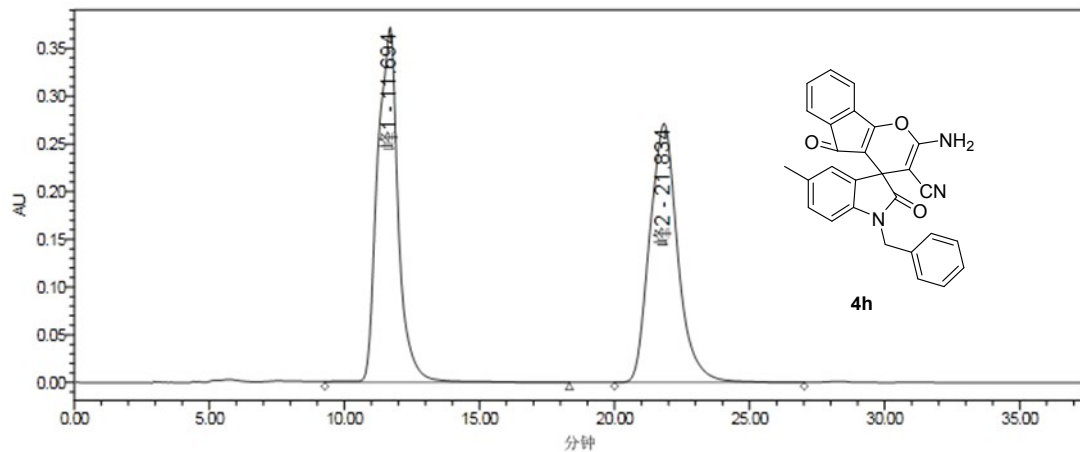
	Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
1	W2489 ChA 254nm	峰1	9.809	10878117	50.12	231694
2	W2489 ChA 254nm	峰2	17.211	10826489	49.88	174968



	Channel Description	Peak Name	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	峰1	9.572	2393569	11.54	52599
2	W2489 ChA 254nm	峰2	16.746	18343850	88.46	305212

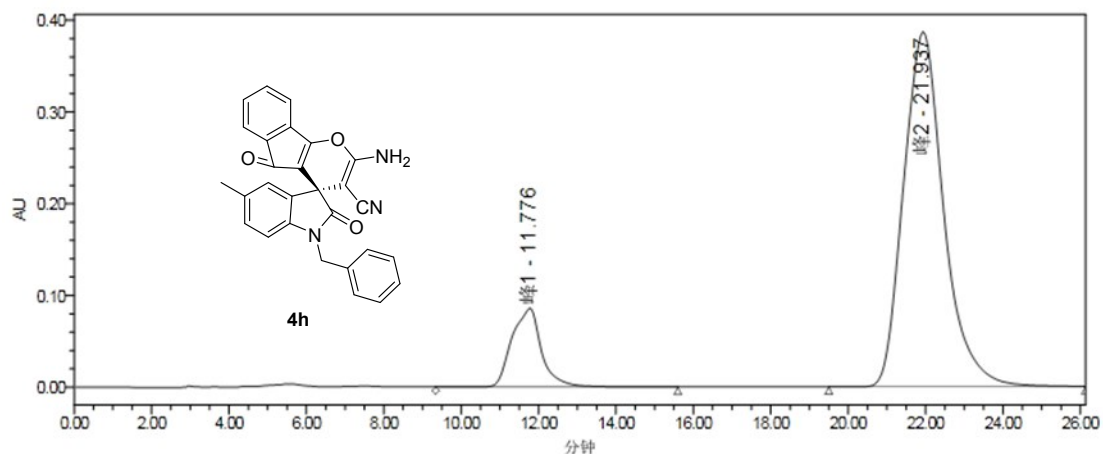


	Channel Description	Peak Name	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	峰1	9.184	2301821	6.37	51099
2	W2489 ChA 254nm	峰2	16.004	33818398	93.63	573780



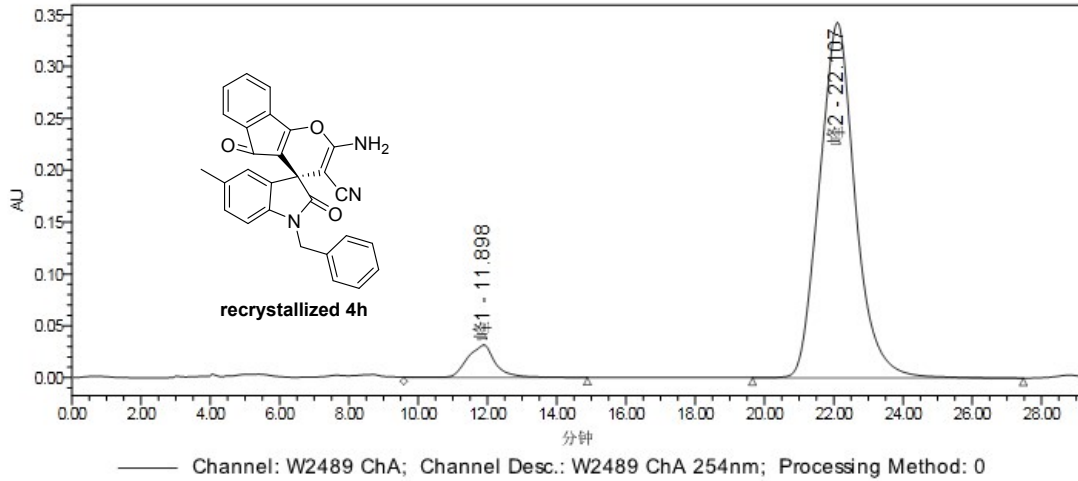
Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 0

	Channel Description	Peak Name	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	峰1	11.694	19858123	50.35	371616
2	W2489 ChA 254nm	峰2	21.834	19579514	49.65	271071

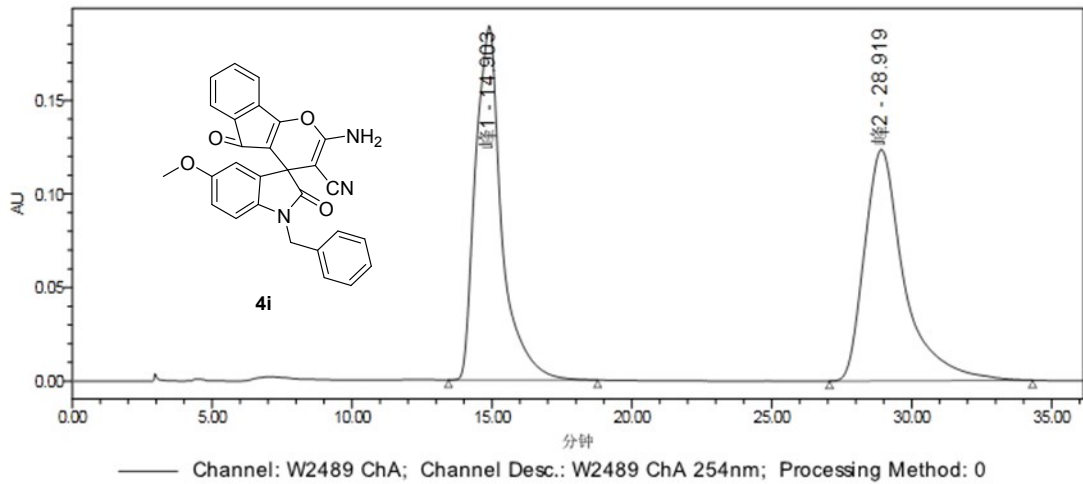


Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 0

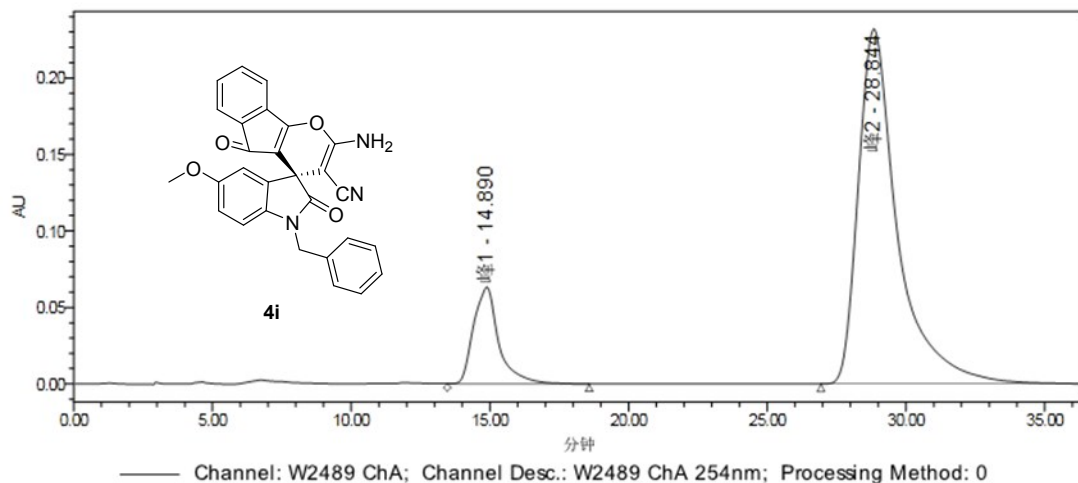
	Channel Description	Peak Name	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	峰1	11.776	4538717	13.99	85526
2	W2489 ChA 254nm	峰2	21.937	27903545	86.01	386566



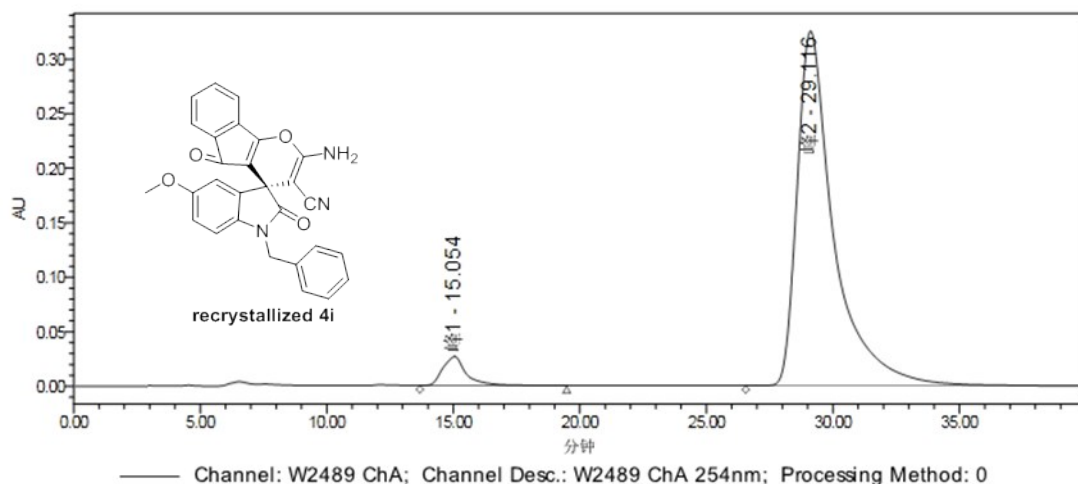
	Channel Description	Peak Name	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	峰1	11.898	1733877	6.57	31242
2	W2489 ChA 254nm	峰2	22.107	24645604	93.43	342326



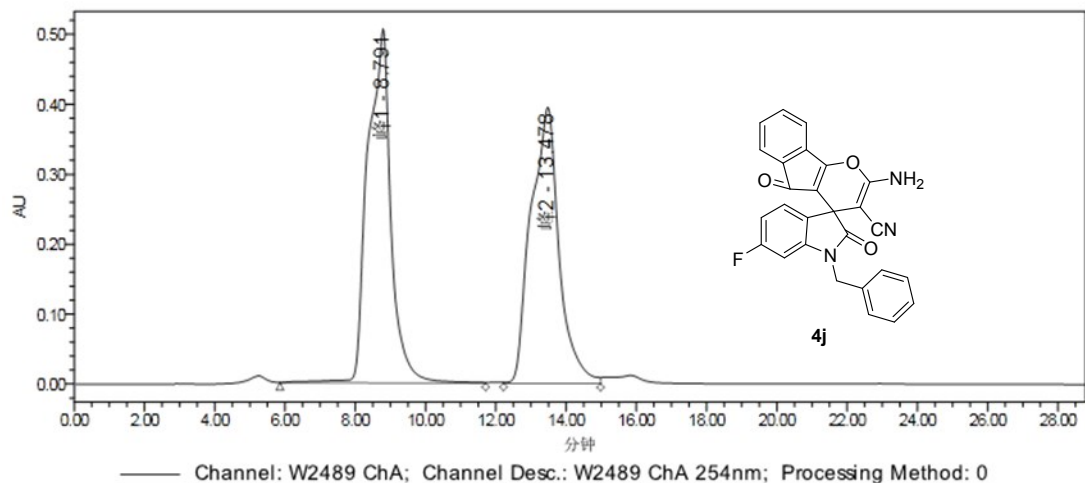
	Channel Description	Peak Name	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	峰1	14.903	12295599	50.25	188983
2	W2489 ChA 254nm	峰2	28.919	12174058	49.75	123500



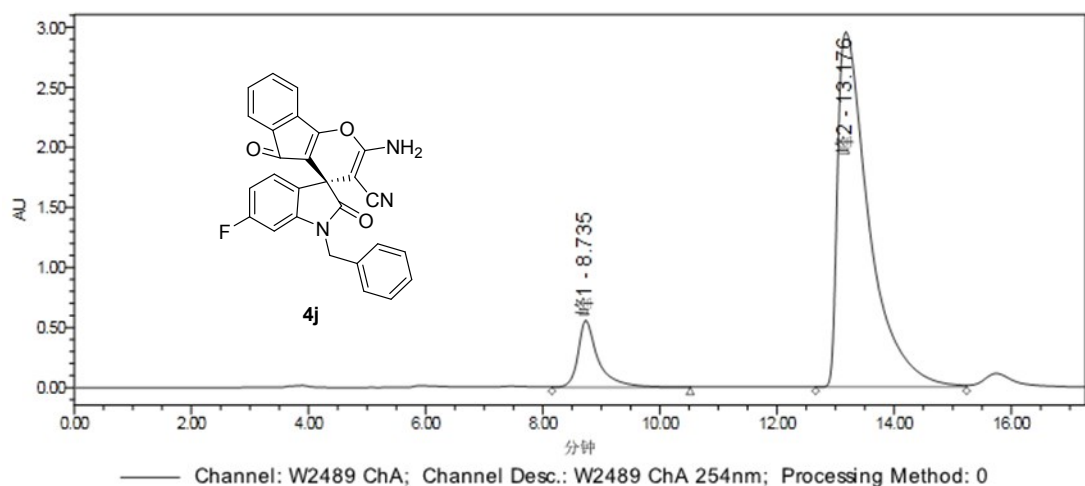
	Channel Description	Peak Name	RT (min)	Area (磺*sec)	% Area	Height (磺)
1	W2489 ChA 254nm	峰1	14.890	3981506	14.85	63060
2	W2489 ChA 254nm	峰2	28.844	22828033	85.15	231822



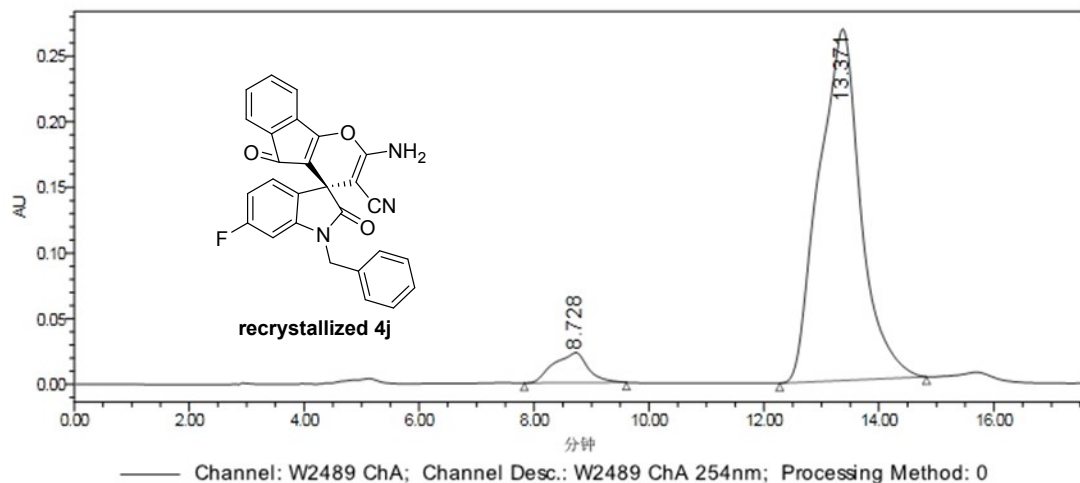
	Channel Description	Peak Name	RT (min)	Area (磺*sec)	% Area	Height (磺)
1	W2489 ChA 254nm	峰1	15.054	1710033	4.96	26698
2	W2489 ChA 254nm	峰2	29.116	32749635	95.04	325099



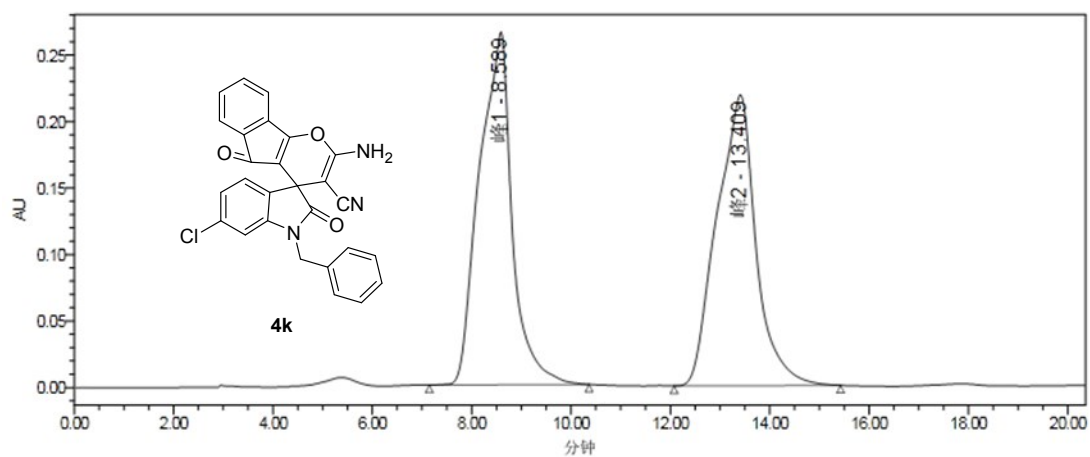
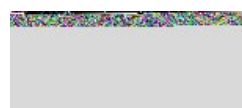
	Channel Description	Peak Name	RT (min)	Area (响*sec)	% Area	Height (响)
1	W2489 ChA 254nm	峰1	8.791	23319305	51.46	505711
2	W2489 ChA 254nm	峰2	13.478	21992223	48.54	394643



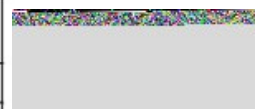
	Channel Description	Peak Name	RT (min)	Area (响*sec)	% Area	Height (响)
1	W2489 ChA 254nm	峰1	8.735	13222145	10.74	553649
2	W2489 ChA 254nm	峰2	13.176	109879853	89.26	2953574

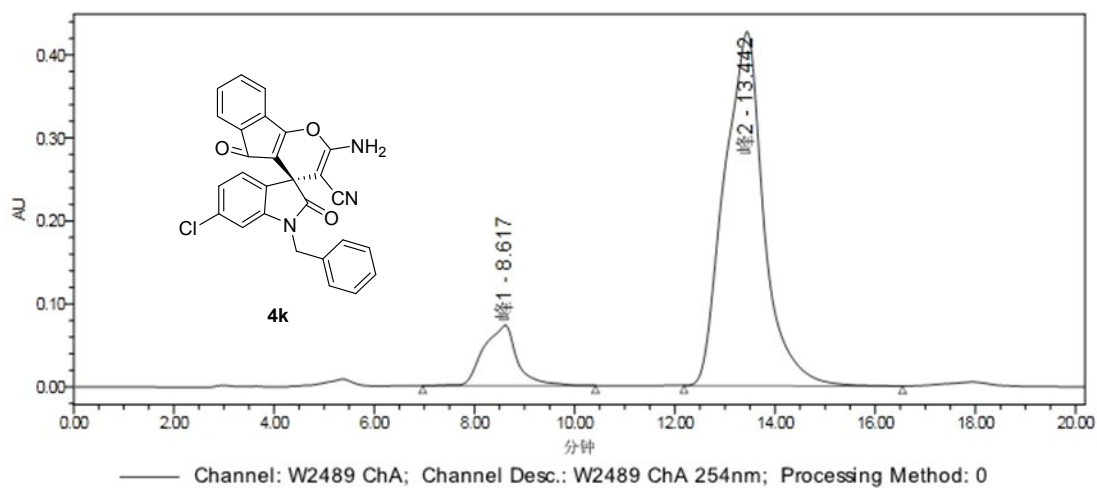


	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	8.728	947700	6.55	22879
2	W2489 ChA 254nm	13.371	13517745	93.45	267484

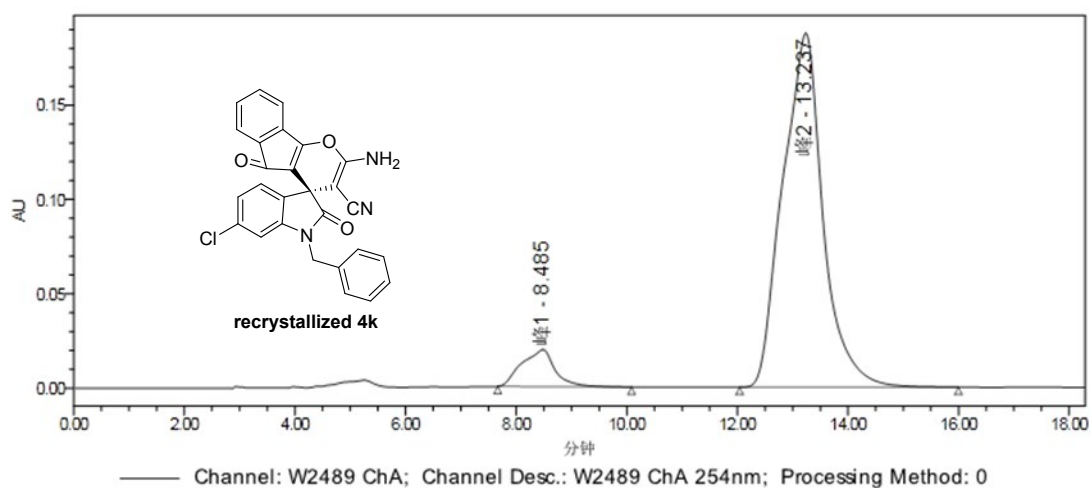


	Channel Description	Peak Name	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	峰1	8.589	12162676	50.40	265029
2	W2489 ChA 254nm	峰2	13.409	11971836	49.60	218598

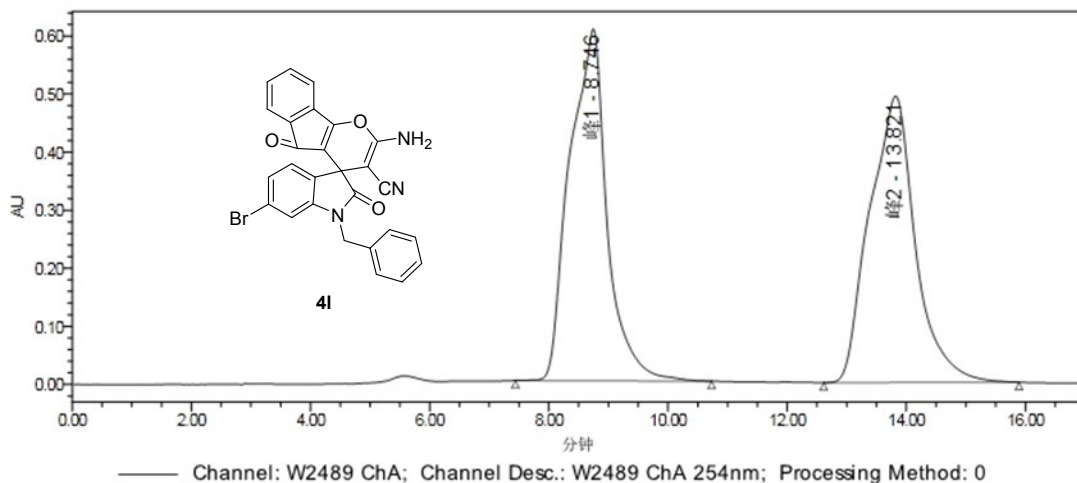




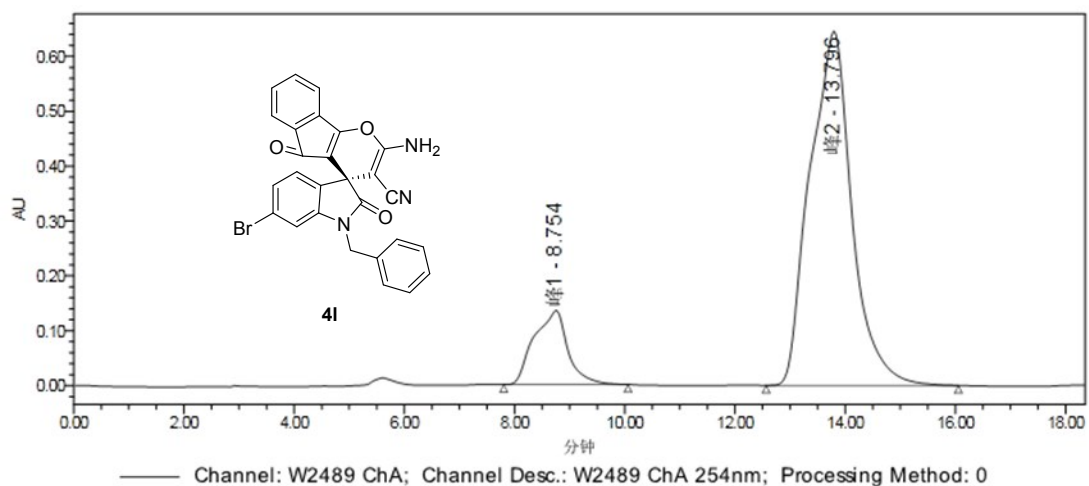
	Channel Description	Peak Name	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	峰1	8.617	3372501	12.63	72834
2	W2489 ChA 254nm	峰2	13.442	23339964	87.37	426426



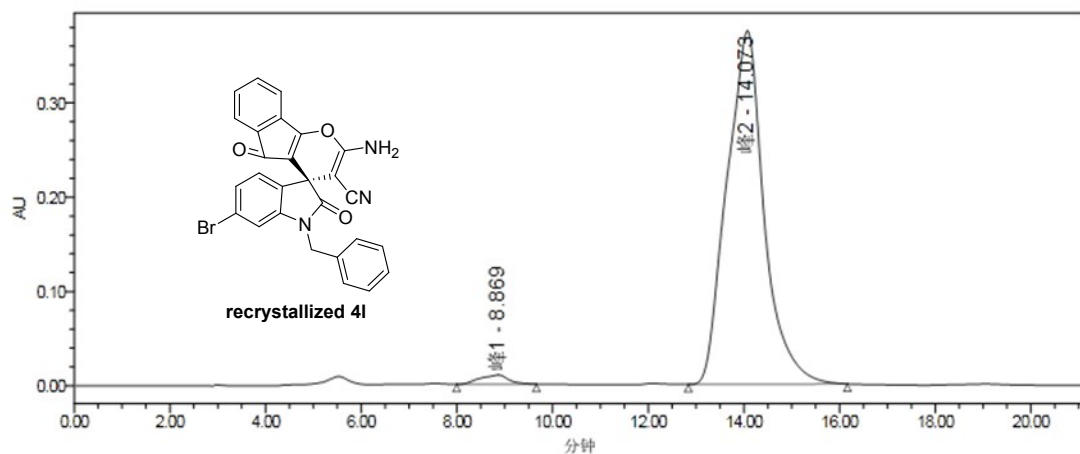
	Channel Description	Peak Name	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	峰1	8.485	817844	7.94	19623
2	W2489 ChA 254nm	峰2	13.237	9479336	92.06	187634



	Channel Description	Peak Name	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	峰1	8.746	26444712	50.10	605518
2	W2489 ChA 254nm	峰2	13.821	26337291	49.90	493153

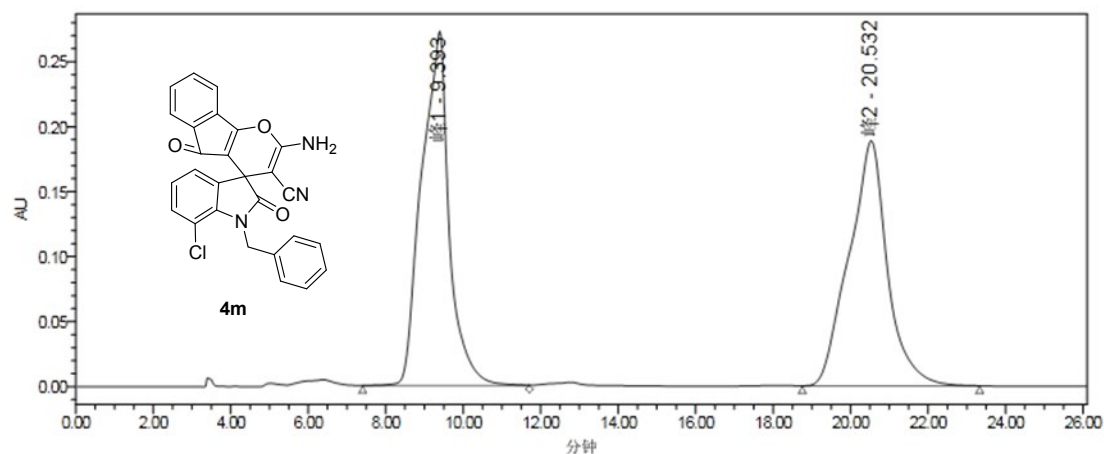


	Channel Description	Peak Name	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	峰1	8.754	5733642	14.37	134702
2	W2489 ChA 254nm	峰2	13.796	34158716	85.63	644653



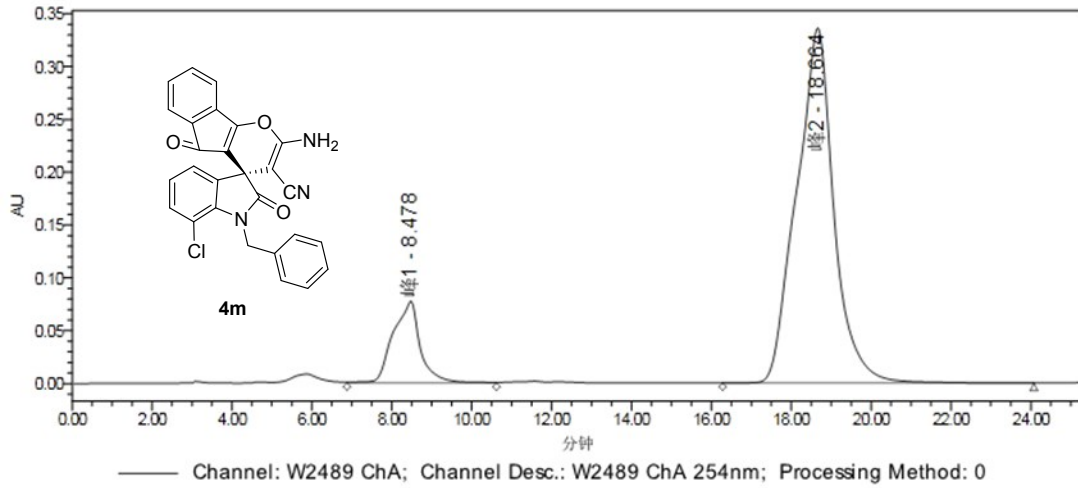
Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 0

	Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
1	W2489 ChA 254nm	峰1	8.869	404916	1.96	9811
2	W2489 ChA 254nm	峰2	14.073	20258546	98.04	374835

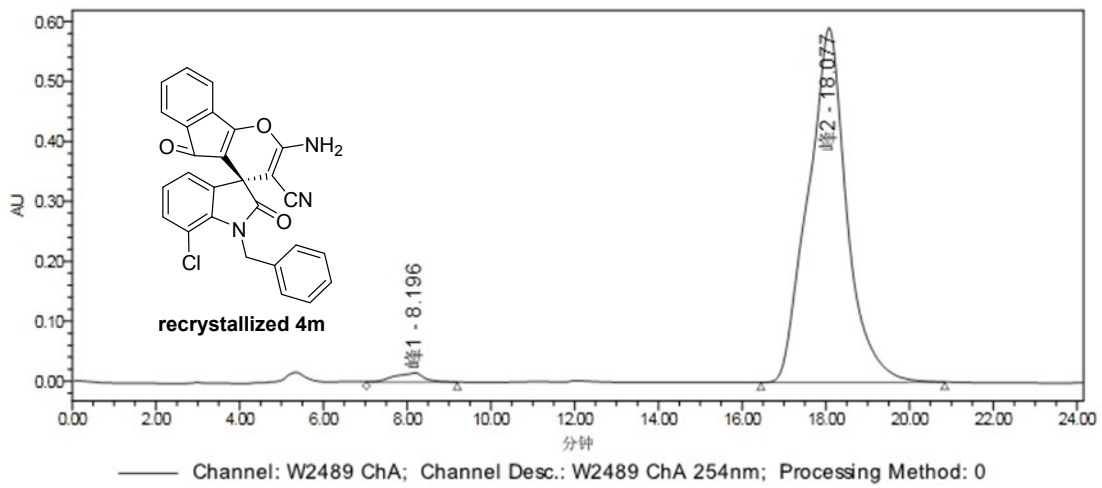


Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 0

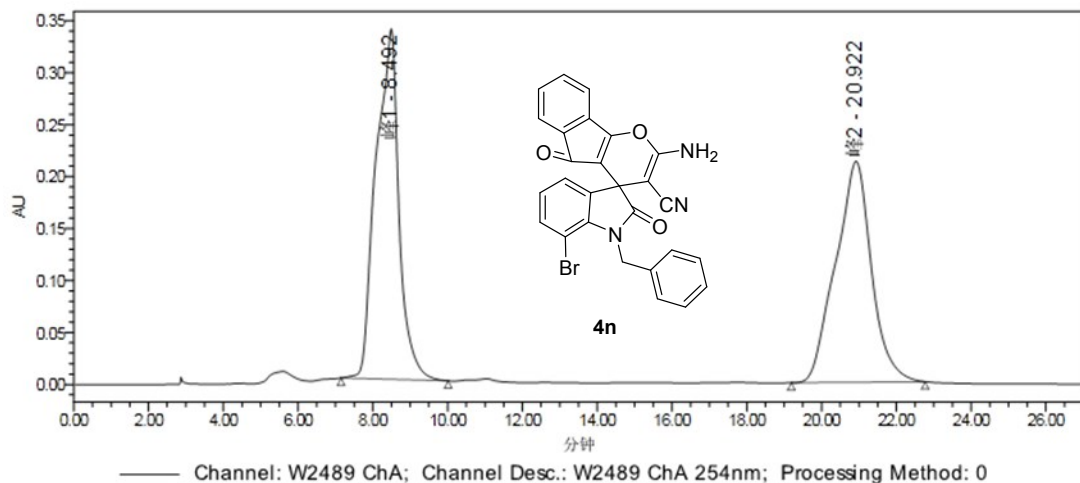
	Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
1	W2489 ChA 254nm	峰1	9.393	13460854	50.89	272318
2	W2489 ChA 254nm	峰2	20.532	12988336	49.11	188528



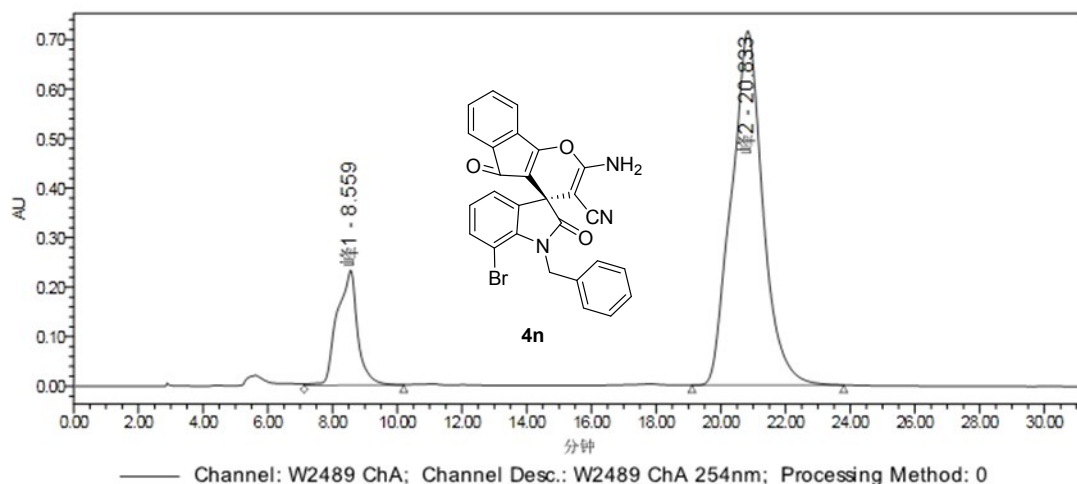
	Channel Description	Peak Name	RT (min)	Area (磺*sec)	% Area	Height (磺)
1	W2489 ChA 254nm	峰1	8.478	3656173	14.35	77136
2	W2489 ChA 254nm	峰2	18.664	21817669	85.65	335764



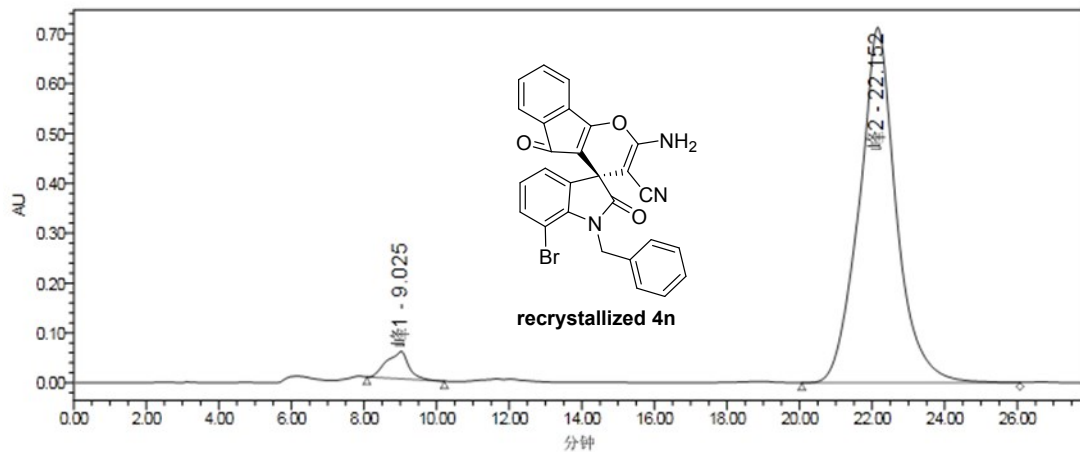
	Channel Description	Peak Name	RT (min)	Area (磺*sec)	% Area	Height (磺)
1	W2489 ChA 254nm	峰1	8.196	773717	2.00	15418
2	W2489 ChA 254nm	峰2	18.077	37911355	98.00	590957



	Channel Description	Peak Name	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	峰1	8.492	14465988	50.50	336970
2	W2489 ChA 254nm	峰2	20.922	14180544	49.50	212529

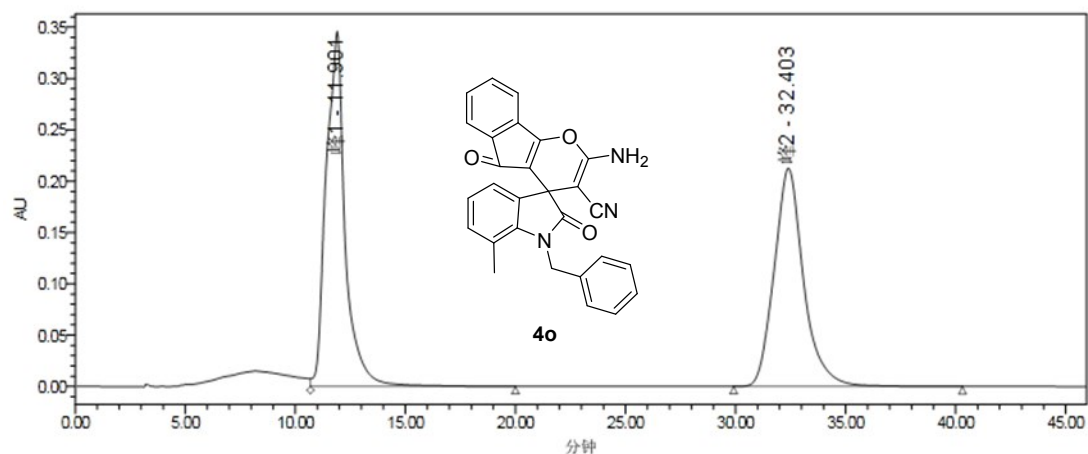


	Channel Description	Peak Name	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	峰1	8.559	10194203	17.41	231710
2	W2489 ChA 254nm	峰2	20.833	48355291	82.59	714843



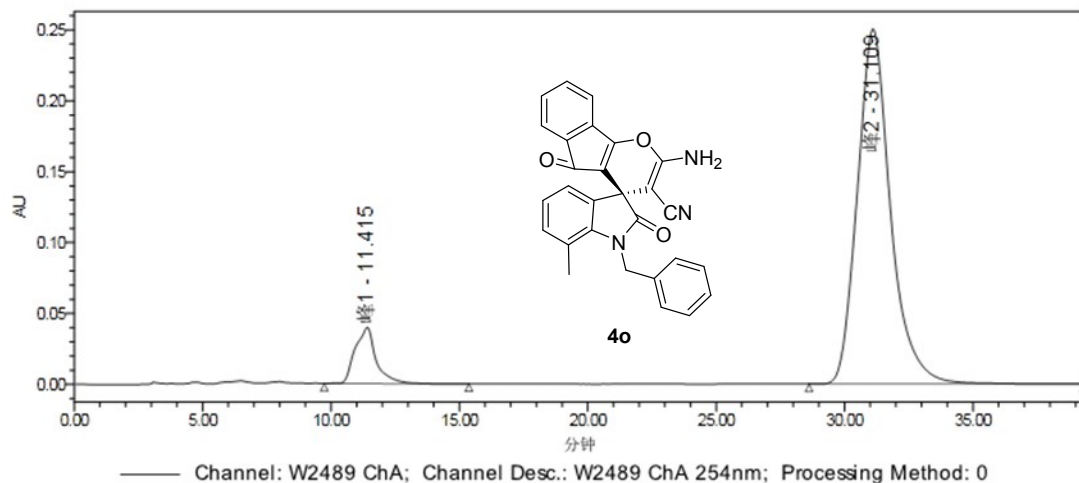
Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 0

	Channel Description	Peak Name	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	峰1	9.025	2319126	4.37	54984
2	W2489 ChA 254nm	峰2	22.152	50734084	95.63	712325

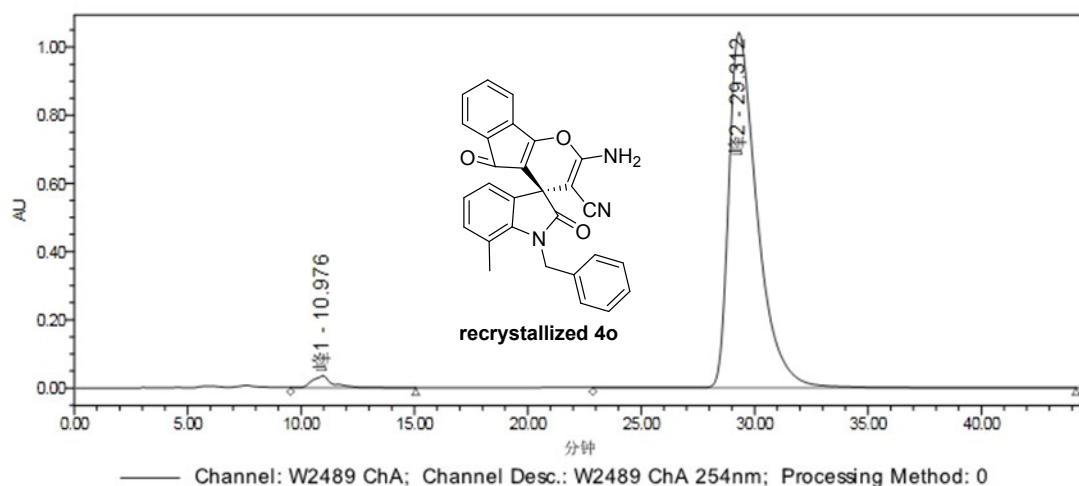


Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 0

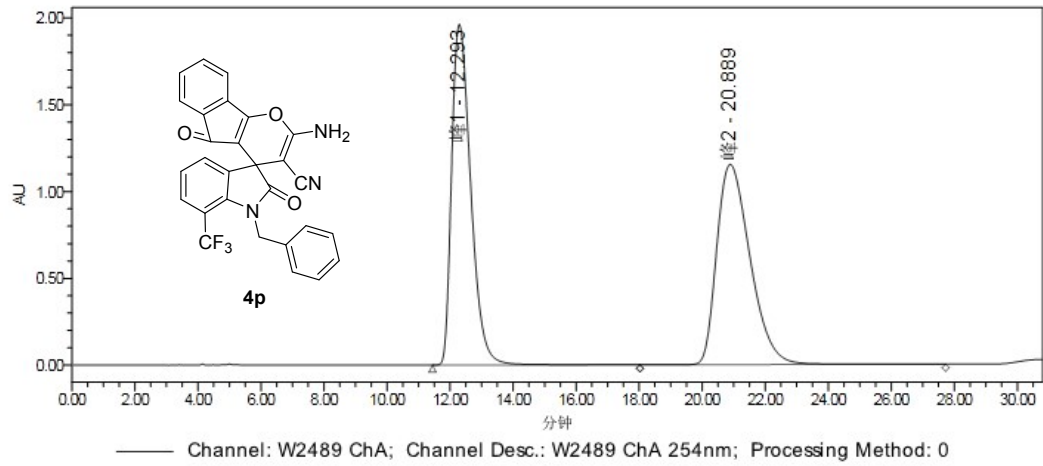
	Channel Description	Peak Name	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	峰1	11.901	20727602	51.19	345515
2	W2489 ChA 254nm	峰2	32.403	19762246	48.81	212412



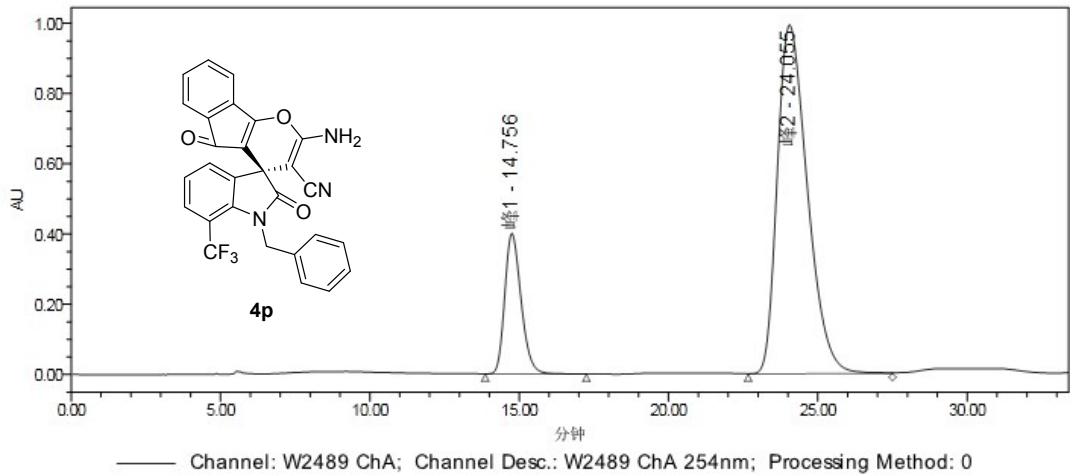
	Channel Description	Peak Name	RT (min)	Area (磷*sec)	% Area	Height (磷)
1	W2489 ChA 254nm	峰1	11.415	2252849	9.10	39597
2	W2489 ChA 254nm	峰2	31.109	22496791	90.90	250258



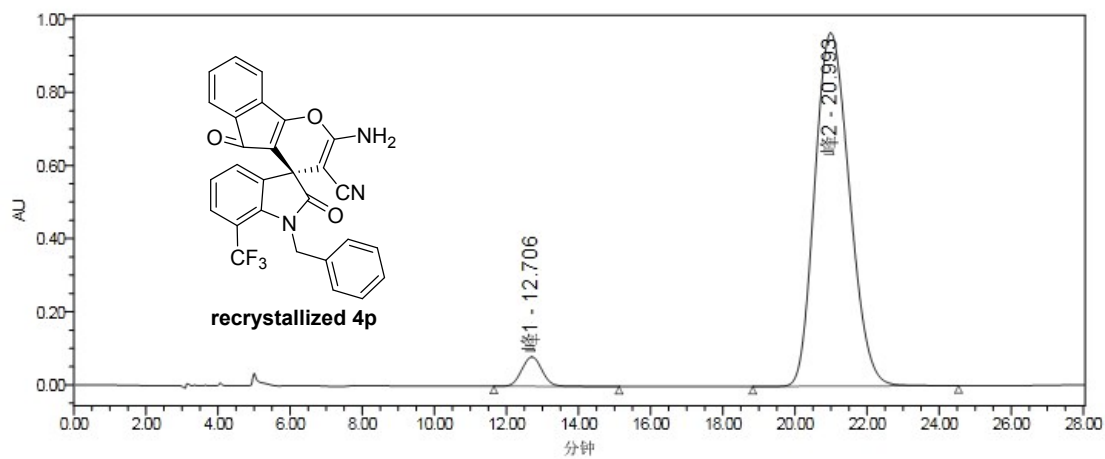
	Channel Description	Peak Name	RT (min)	Area (磷*sec)	% Area	Height (磷)
1	W2489 ChA 254nm	峰1	10.976	2166400	2.33	35167
2	W2489 ChA 254nm	峰2	29.312	90915263	97.67	1041566



	Channel Description	Peak Name	RT (min)	Area (磷*sec)	% Area	Height (磷)
1	W2489 ChA 254nm	峰1	12.293	82408468	49.27	1961496
2	W2489 ChA 254nm	峰2	20.889	84864490	50.73	1153026

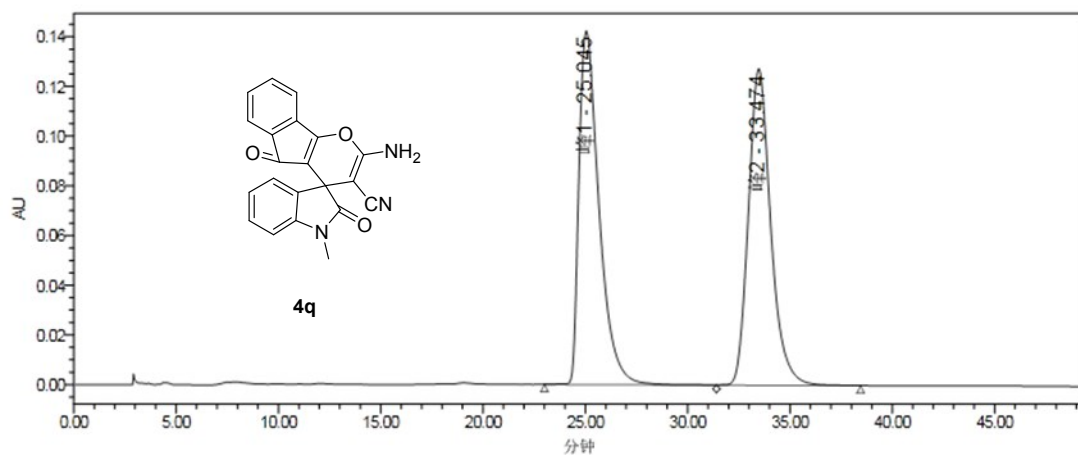


	Channel Description	Peak Name	RT (min)	Area (磷*sec)	% Area	Height (磷)
1	W2489 ChA 254nm	峰1	14.756	15247701	17.98	399593
2	W2489 ChA 254nm	峰2	24.055	69562176	82.02	992423



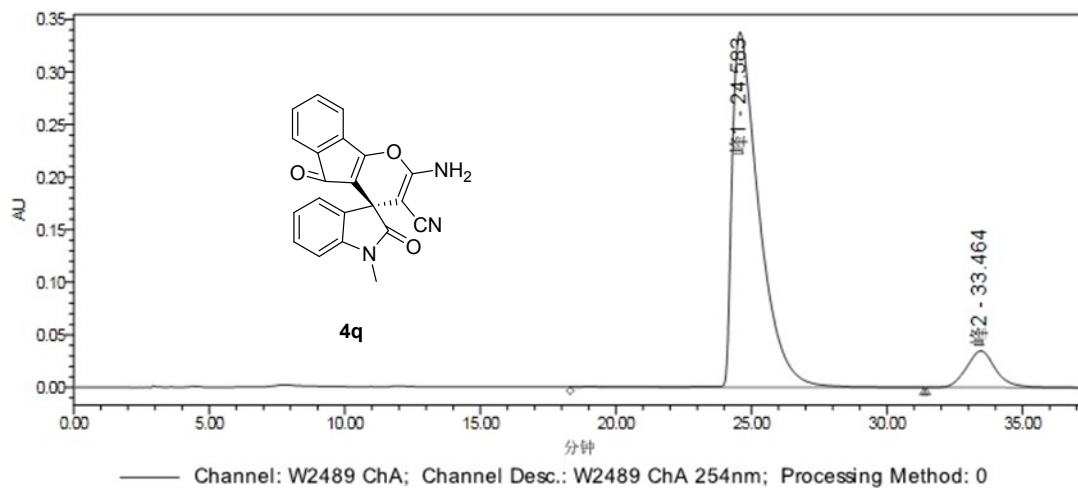
Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 0

	Channel Description	Peak Name	RT (min)	Area (磺*sec)	% Area	Height (磺)
1	W2489 ChA 254nm	峰1	12.706	3128710	4.63	80205
2	W2489 ChA 254nm	峰2	20.993	64393356	95.37	965637

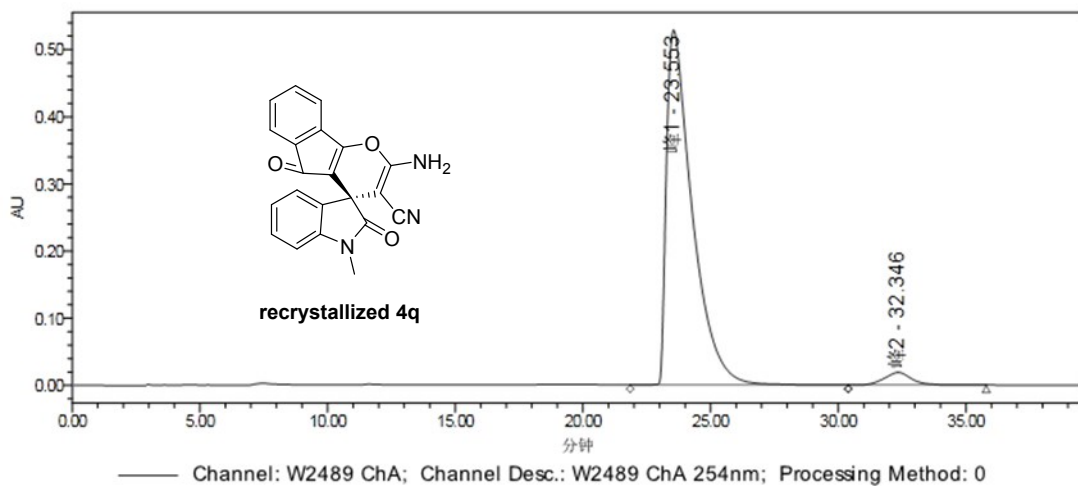


Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 0

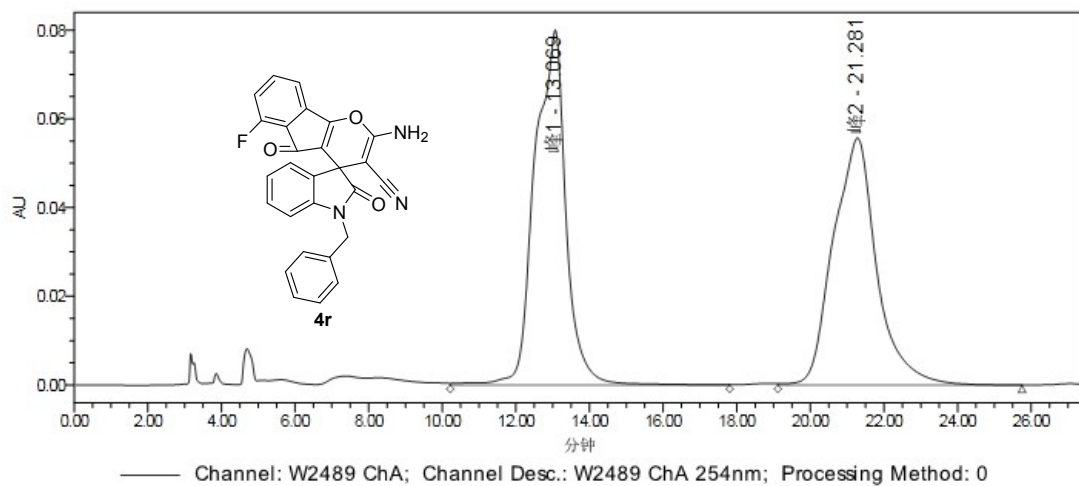
	Channel Description	Peak Name	RT (min)	Area (磺*sec)	% Area	Height (磺)
1	W2489 ChA 254nm	峰1	25.045	9699741	50.15	142185
2	W2489 ChA 254nm	峰2	33.474	9642030	49.85	127336



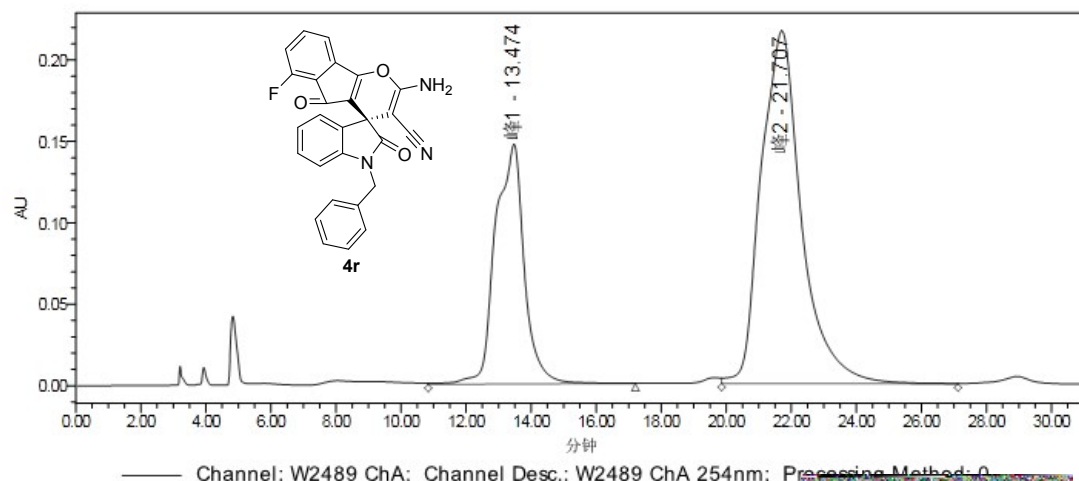
	Channel Description	Peak Name	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	峰1	24.583	23304470	89.98	337436
2	W2489 ChA 254nm	峰2	33.464	2595128	10.02	34835



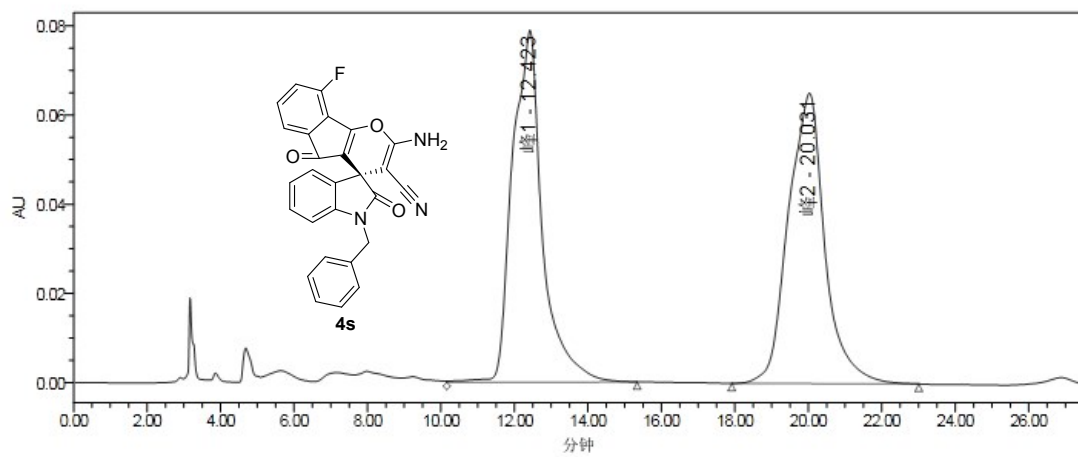
	Channel Description	Peak Name	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	峰1	23.553	37058631	96.34	528286
2	W2489 ChA 254nm	峰2	32.346	1406268	3.66	18802



	Channel Description	Peak Name	RT (min)	Area (礦*sec)	% Area	Height (礦)
1	W2489 ChA 254nm	峰1	13.069	4728232	50.76	80010
2	W2489 ChA 254nm	峰2	21.281	4586430	49.24	55690

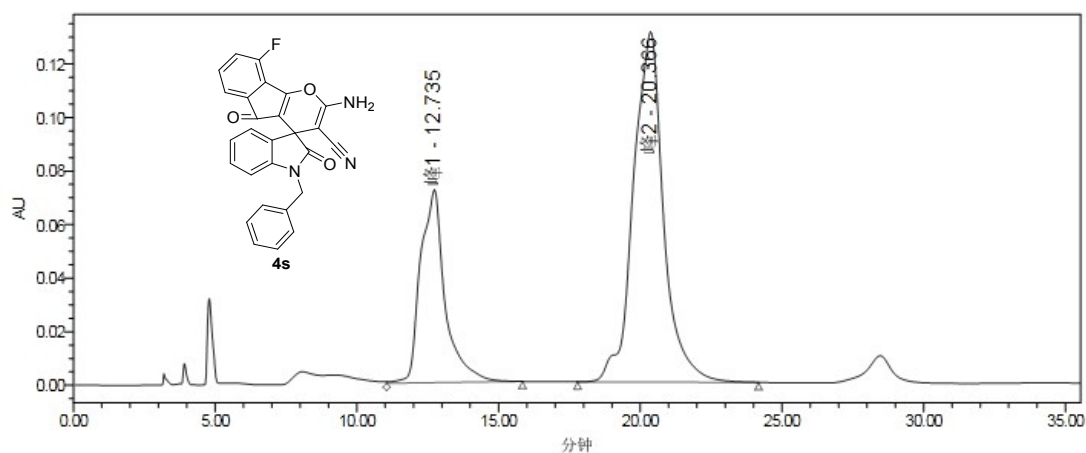


	Channel Description	Peak Name	RT (min)	Area (礦*sec)	% Area	Height (礦)
1	W2489 ChA 254nm	峰1	13.474	9121540	32.76	147233
2	W2489 ChA 254nm	峰2	21.707	18722313	67.24	216631



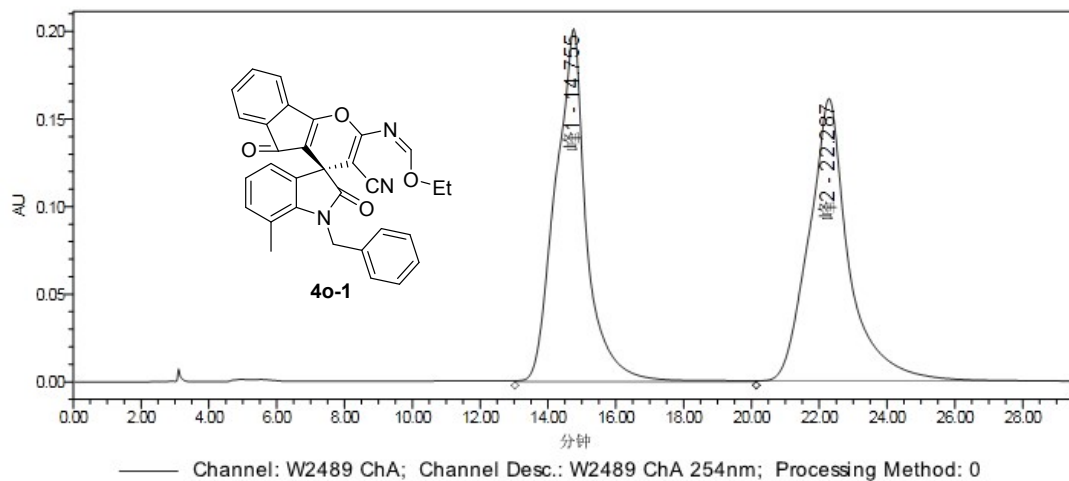
Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 0

Peak	Channel Description	Peak Name	RT (min)	Area (面积*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	峰1	12.423	4477410	49.99	78838
2	W2489 ChA 254nm	峰2	20.031	4480025	50.01	65063

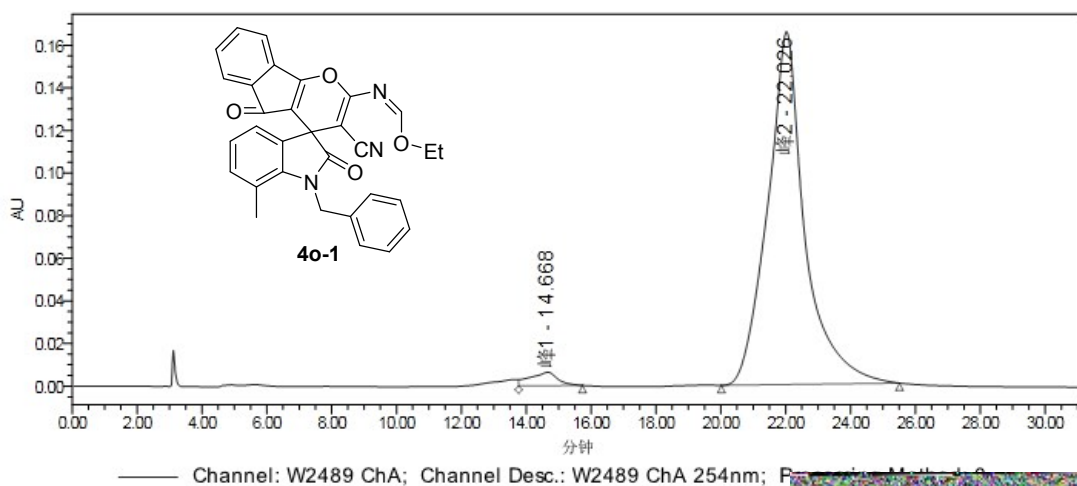


Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 0

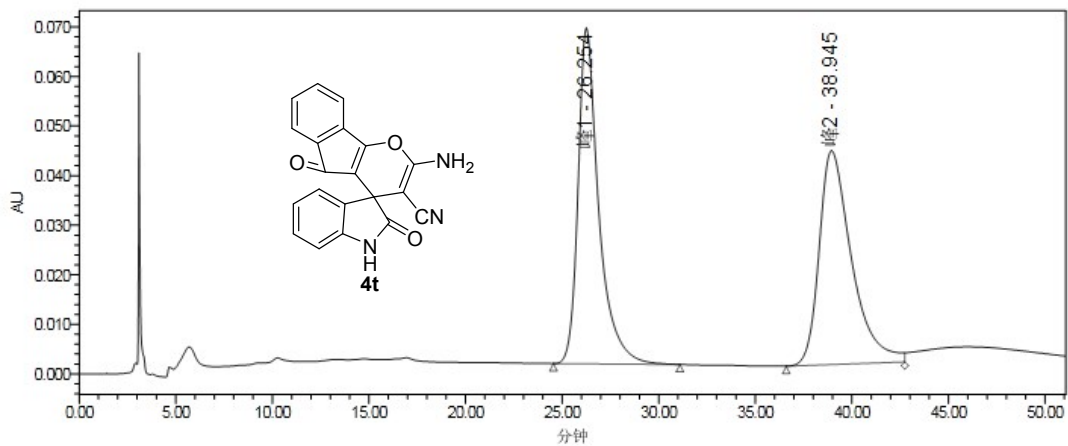
Peak	Channel Description	Peak Name	RT (min)	Area (面积*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	峰1	12.735	4354420	31.00	71992
2	W2489 ChA 254nm	峰2	20.366	9694094	69.00	130713



	Channel Description	Peak Name	RT (min)	Area (磷*sec)	% Area	Height (磷)
1	W2489 ChA 254nm	峰1	14.755	12801690	49.13	201177
2	W2489 ChA 254nm	峰2	22.287	13257268	50.87	161414

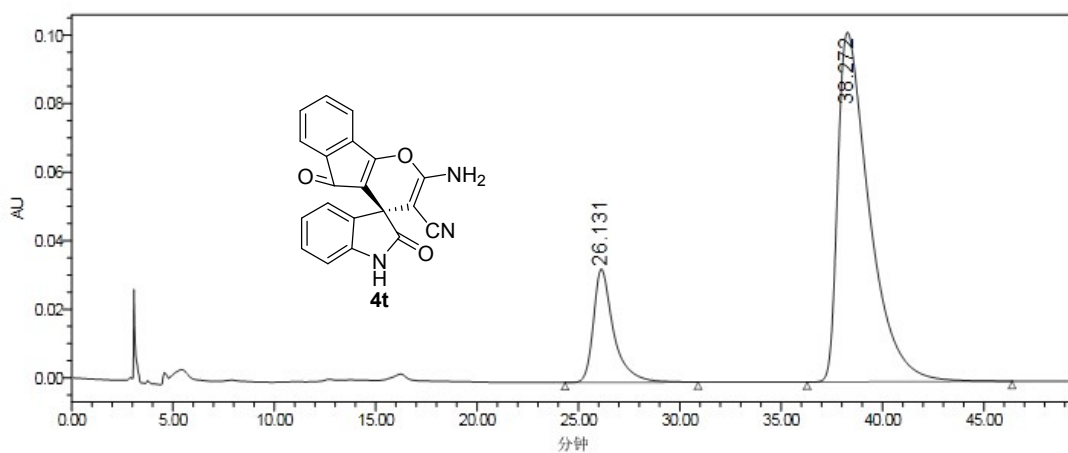
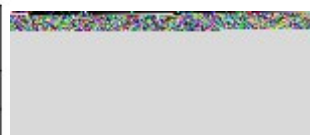


	Channel Description	Peak Name	RT (min)	Area (磷*sec)	% Area	Height (磷)
1	W2489 ChA 254nm	峰1	14.668	378332	2.79	6348
2	W2489 ChA 254nm	峰2	22.026	13202188	97.21	165436



Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 0

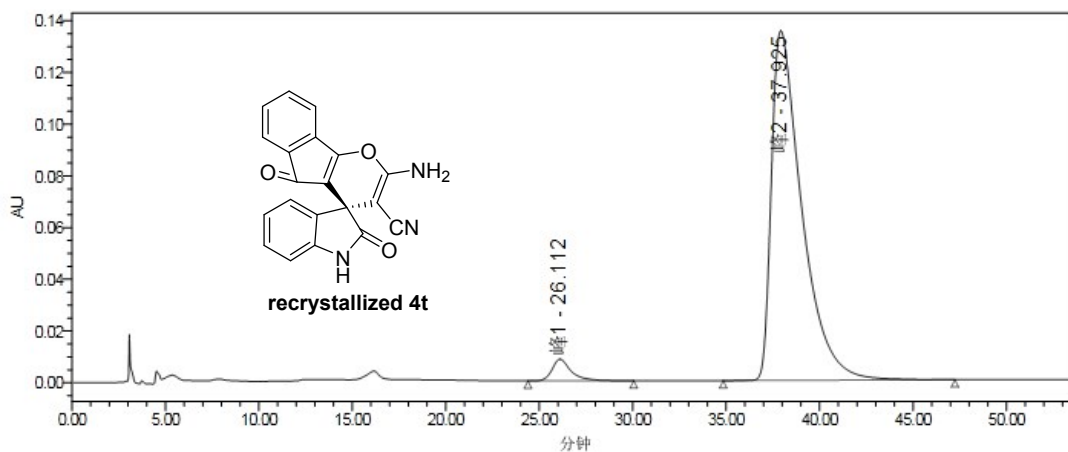
	Channel Description	Peak Name	RT (min)	Area (AU*sec)	% Area	Height (AU)
1	W2489 ChA 254nm	峰1	26.254	5043214	50.05	67751
2	W2489 ChA 254nm	峰2	38.945	5034109	49.95	43147



Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 0

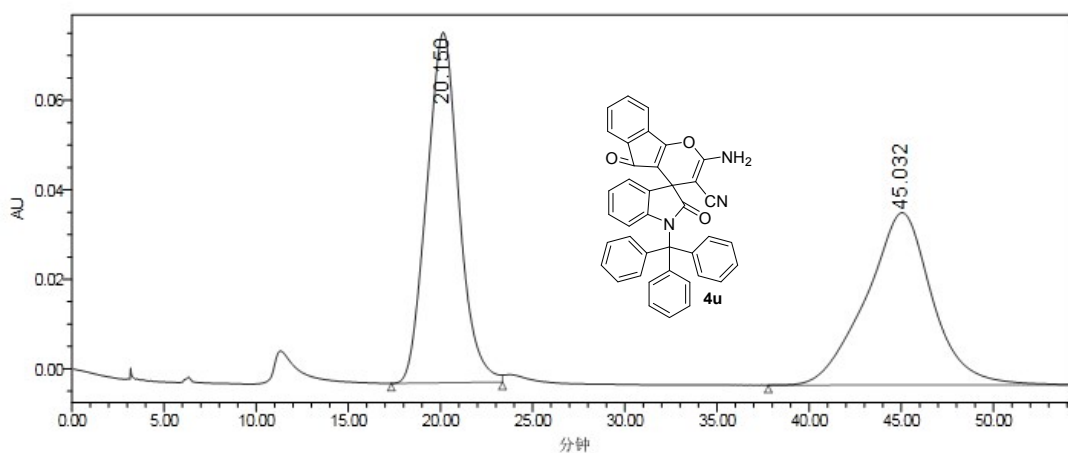
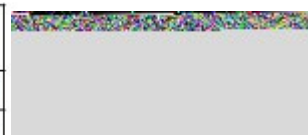
	Channel Description	RT (min)	Area (AU*sec)	% Area	Height (AU)
1	W2489 ChA 254nm	26.131	2283797	17.16	33013
2	W2489 ChA 254nm	38.272	11022930	82.84	101924





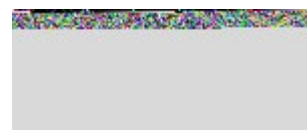
Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 0

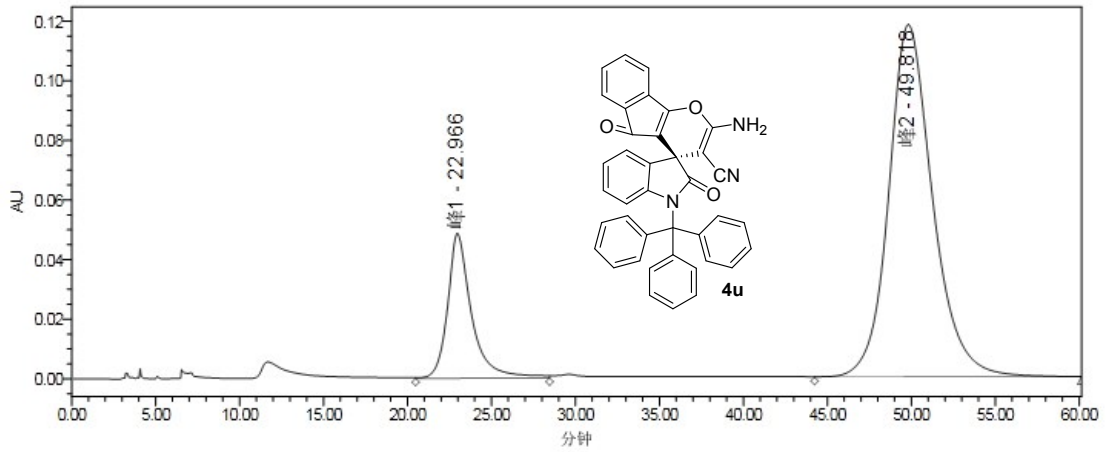
	Channel Description	Peak Name	RT (min)	Area (磷*sec)	% Area	Height (磷)
1	W2489 ChA 254nm	峰1	26.112	597842	3.76	8423
2	W2489 ChA 254nm	峰2	37.925	15282990	96.24	135273



Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 0

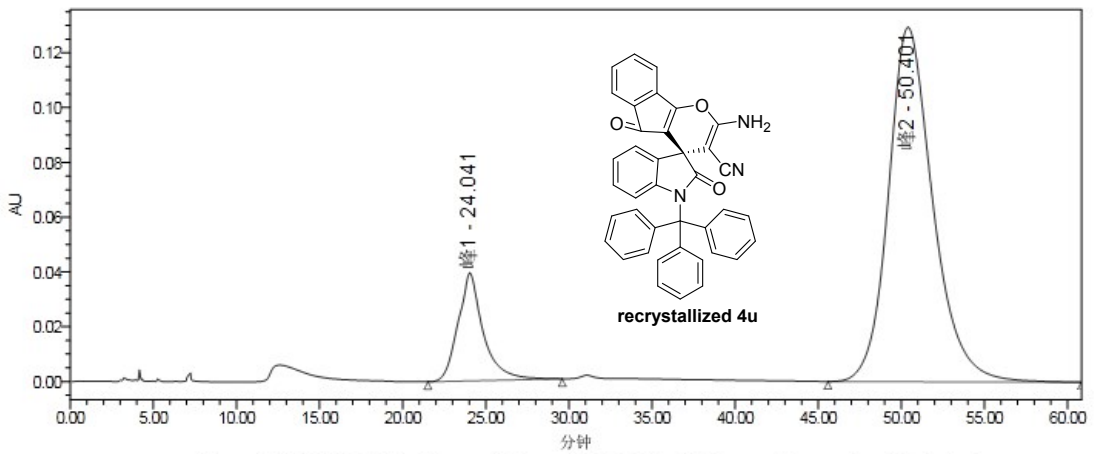
	Channel Description	RT (min)	Area (磷*sec)	% Area	Height (磷)
1	W2489 ChA 254nm	20.150	9484595	49.71	78244
2	W2489 ChA 254nm	45.032	9593380	50.29	38468





Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 0

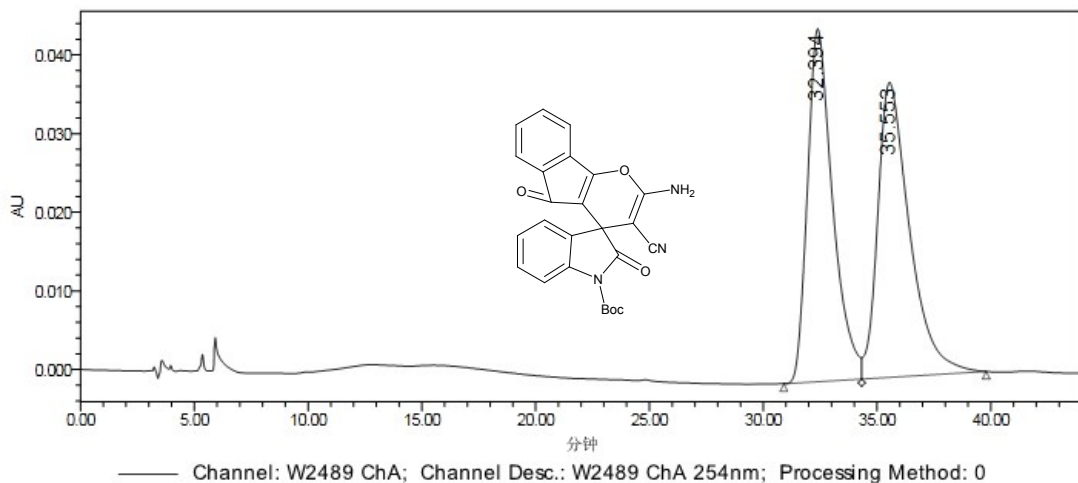
	Channel Description	Peak Name	RT (min)	Area (磺*sec)	% Area	Height (磺)
1	W2489 ChA 254nm	峰1	22.966	4808650	18.23	48515
2	W2489 ChA 254nm	峰2	49.818	21571741	81.77	118239



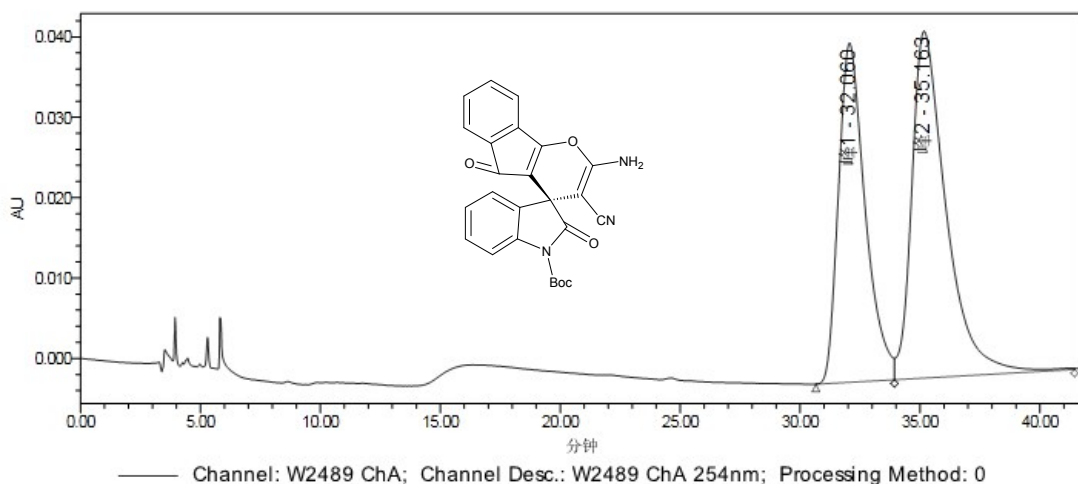
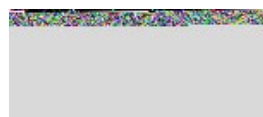
Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 0

	Channel Description	Peak Name	RT (min)	Area (磺*sec)	% Area	Height (磺)
1	W2489 ChA 254nm	峰1	24.041	4155979	14.71	39420
2	W2489 ChA 254nm	峰2	50.401	24089363	85.29	129400





	Channel Description	RT (min)	Area (磺*sec)	% Area	Height (磺)
1	W2489 ChA 254nm	32.394	3452806	48.56	44848
2	W2489 ChA 254nm	35.553	3657250	51.44	37470



	Channel Description	Peak Name	RT (min)	Area (磺*sec)	% Area	Height (磺)
1	W2489 ChA 254nm	峰1	32.060	3259838	43.16	42158
2	W2489 ChA 254nm	峰2	35.163	4292925	56.84	43132

