

Supporting Information for

The Organocatalytic Two-step Synthesis of Diversely Functionalized Tricyclic Tetrazoles

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1. General methods

2. Asymmetric Michael addition and intramolecular 1,3-dipolar cycloaddition of functionalized α,β -unsaturated ketones 2 to malononitrile

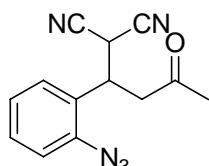
1. General Methods:

Column chromatography was performed using silica gel (200-300 mesh) eluting with ethyl acetate and petroleum ether. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker DRX 400 spectrometer at room temperature in CDCl_3 as solvent. Chemical shifts for protons are reported using residual CHCl_3 as internal reference ($=7.26$ ppm). Carbon spectra were referenced to the shift of the ^{13}C signal of CDCl_3 ($=77.0$ ppm). Coupling constants (J) are given in Hz. IR spectra were recorded using a Perkin-Elmer 1600 Series FTIR. ESI-HRMS spectrometer was measured with a Finnigan LCQ^{DECA} ion trap mass spectrometer. Optical rotations were measured at 589 nm at 25 °C in a 1 dm cell and specific rotations are given in 10^{-1} deg $\text{cm}^2 \text{ g}^{-1}$. Enantiomeric excess were determined by HPLC analysis (Waters-Breeze 2487, dual absorbance detector and 1525 Binary HPLC Pump) using Daicel Chiralpak AS column (4.6mm*250mm, 5μm) and Daicel Chiralpak AD column (4.6mm*250mm,

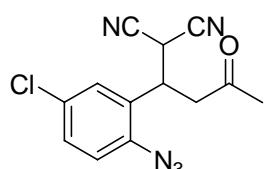
5μm). Commercial grade solvents were dried and purified by standard procedures as specified in Purification of Laboratory Chemicals, 4th Ed (Armarego, W. L. F.; Perrin, D. D. Butterworth Heinemann: 1997).

2. Asymmetric Michael addition and intramolecular 1,3-dipolar cycloaddition of functionalized α,β-unsaturated ketones 2 to malononitrile

General procedure: **2a** 18.7 mg (0.1 mmol), malononitrile 13.2 mg (0.2 mmol), **1a** 6.5 mg (0.02 mol) and TFA 3.0 μL (0.04 mol) were stirred in DCM (1 mL) at 25 °C for 96 h. and flash chromatography on silica gel (8% ethyl acetate/petroleum ether) gave **3a** as a white solid (21.5 mg, 85%). The product **3a** (0.1 mmol) was refluxed in CH₃CN (1.5 mL) for 12h, then the solvent was removed and flash column chromatography (citation to Clark Still's paper) was performed (monitored by TLC, 15% ethyl acetate/petroleum ether as eluent) to give **4a** as a yellow solid (19.7 mg, 92%).

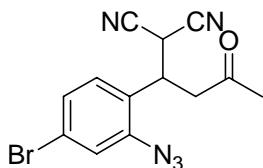


3a, 85% yield. pale yellow solid, m.p. 84-85 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.44-7.35 (m, 2H), 7.24-7.17 (m, 2H), 4.51 (d, *J* = 6.3Hz, 1H), 4.24-4.18 (m, 1H), 3.14 (d, *J* = 7.0Hz, 1H), 2.20 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 204.6, 138.2, 130.2, 128.6, 127.2, 125.5, 118.8, 111.8, 111.5, 43.9, 35.4, 30.3, 27.2; ESI-HRMS: calcd. for C₁₃H₁₁N₅O+H 254.10376, found 254.10364; 96% ee; The enantiomeric ratio was determined by HPLC on Chiraldak AD column (30% 2-propanol/hexane, 1.0 mL/min, detection at 254 nm), t_{minor} = 5.06 min, t_{major} = 5.64 min.

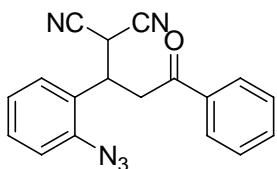


3b, 72% yield. pale yellow solid, m.p. 91-92 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.28-7.21 (m, 1H), 7.12-7.09 (m, 1H), 6.98 (d, *J* = 2.5 Hz, 1H),

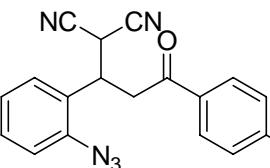
4.52 (d, $J = 6.5$ Hz, 1H), 4.21-4.15 (m, 1H), 3.13 (d, $J = 7.0$ Hz, 2H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 204.3, 137.4, 134.6, 128.8, 120.6, 120.2, 119.5, 111.5, 111.3, 43.7, 35.4, 30.2, 26.9; ESI-HRMS: calcd. for $\text{C}_{13}\text{H}_{10}\text{ClN}_5\text{O}+\text{Na}$ 310.04743, found 310.04768; 94% ee; The enantiomeric ratio was determined by HPLC on Chiralpak aD column (20% 2-propanol/hexane, 1.0 mL/min, detection at 254 nm), $t_{\text{minor}} = 11.20$ min, $t_{\text{major}} = 13.51$ min.



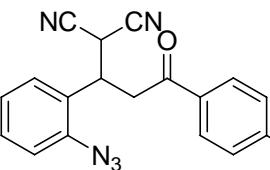
3c, 82% yield. yellow solid, m.p. 97-99 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.37-7.34 (m, 1H), 6.90-6.88 (m, 1H), 6.81 (d, $J = 2.2$ Hz, 1H), 4.50 (d, $J = 6.4$ Hz, 1H), 4.20-4.15 (m, 1H), 3.13 (d, $J = 7.0$ Hz, 2H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 204.5, 142.2, 138.8, 130.0, 123.6, 115.8, 111.6, 111.4, 109.4, 43.9, 35.0, 30.2, 27.2; IR (KBr) cm^{-1} 2226, 1715; ESI-HRMS: calcd. for $\text{C}_{13}\text{H}_{10}\text{BrN}_5\text{O}+\text{Na}$ 353.99612, found 353.99704; 97% ee; The enantiomeric ratio was determined by HPLC on Chiralpak AD column (10% 2-propanol/hexane, 1.0 mL/min, detection at 254 nm), $t_{\text{minor}} = 20.17$ min, $t_{\text{major}} = 22.50$ min.



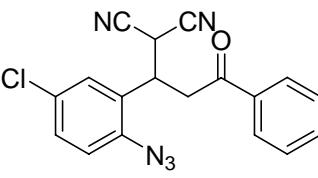
3d, 73% yield. yellow solid, m.p. 101-103 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.96 (d, $J = 7.8$ Hz, 2H), 7.65-7.61 (m, 1H), 7.52-7.40 (m, 4H), 7.25-7.17 (m, 2H), 4.66 (d, $J = 6.2$ Hz, 1H), 4.47-4.42 (m, 1H), 3.80-3.57 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 196.0, 138.2, 135.8, 134.1, 130.2, 128.9, 128.6, 128.6, 128.1, 128.1, 127.4, 125.5, 118.8, 111.9, 111.6, 38.2, 36.7, 27.4; ESI-HRMS: calcd. for $\text{C}_{18}\text{H}_{13}\text{N}_5\text{O}+\text{Na}$ 338.10087, found 338.10123; 93% ee; The enantiomeric ratio was determined by HPLC on Chiralpak AD column (20% 2-propanol/hexane, 1.0 mL/min, detection at 254 nm), $t_{\text{major}} = 12.94$ min, $t_{\text{minor}} = 15.61$ min.

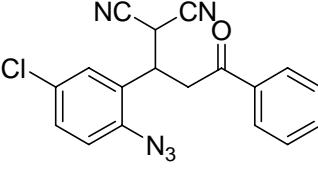

3e, 76% yield. yellow solid, m.p. 110-112 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.85 (d, $J = 8.1$ Hz, 2H), 7.45-7.38 (m, 2H), 7.29-7.16 (m, 4H), 4.65 (d, $J = 6.1$ Hz, 1H), 4.45-4.40 (m, 1H), 3.75-3.56 (m, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 195.6, 145.1, 138.2, 133.3, 130.1, 129.5, 129.5, 128.6, 128.2, 128.2, 127.5, 125.5, 118.8, 111.9, 111.5, 39.0, 35.6, 27.4, 21.7; ESI-HRMS: calcd. for $\text{C}_{19}\text{H}_{15}\text{N}_5\text{O}+\text{H}$ 330.13560, found 330.13494; 93% ee; The enantiomeric ratio was determined by HPLC on Chiralpak AD column (20% 2-propanol/hexane, 1.0 mL/min, detection at 254 nm), $t_{\text{major}} = 15.57$ min, $t_{\text{minor}} = 18.20$ min.

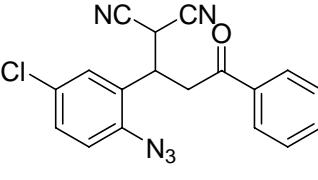

3f, 81% yield. yellow solid, m.p. 121-122 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.89 (d, $J = 8.6$ Hz, 2H), 7.48-7.40 (m, 4H), 7.25-7.17 (m, 2H), 4.62 (d, $J = 6.3$, 1H), 4.42-4.40 (m, 1H), 3.75-3.56 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 194.8, 140.6, 138.2, 134.1, 130.3, 130.2, 129.5, 129.4, 129.2, 128.6, 127.2, 125.5, 118.8, 111.8, 111.5, 38.2, 36.8, 27.3; ESI-HRMS: calcd. for $\text{C}_{18}\text{H}_{12}\text{ClN}_5\text{O}+\text{Na}$ 372.06224, found 372.06226; 91% ee; The enantiomeric ratio was determined by HPLC on Chiralpak AD column (20% 2-propanol/hexane, 1.0 mL/min, detection at 254 nm), $t_{\text{major}} = 14.86$ min, $t_{\text{minor}} = 17.37$ min.


3g, 80% yield. yellow solid, m.p. 129-130 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.81 (d, $J = 8.6$ Hz, 2H), 7.63 (d, $J = 8.6$, 2H), 7.44-7.40 (m, 2H), 7.25-7.16 (m, 2H), 4.62 (d, $J = 6.3$, 1H), 4.42-4.40 (m, 1H), 3.74-3.55 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 195.0, 138.2, 134.5, 132.2, 132.2, 130.3, 129.6, 129.5, 129.4, 128.6, 127.2, 125.5, 118.9, 111.8, 111.5, 39.2, 35.8, 27.3; ESI-HRMS: calcd. for $\text{C}_{18}\text{H}_{12}\text{BrN}_5\text{O}+\text{Na}$ 416.01224, found 416.01174; 90% ee; The enantiomeric

ratio was determined by HPLC on Chiralpak AD column (20% 2-propanol/hexane, 1.0 mL/min, detection at 254 nm), $t_{\text{major}} = 16.88$ min, $t_{\text{minor}} = 19.66$ min.


3h, 69% yield. yellow solid, m.p. 135-136 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.85 (d, $J = 8.1$ Hz, 2H), 7.30-7.26 (m, 2H), 7.23-7.17 (m, 1H), 7.10-7.04 (m, 2H), 4.63 (d, $J = 6.3$ Hz, 1H), 4.41-4.36 (m, 1H), 3.71-3.54 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 195.3, 145.3, 137.4, 134.7, 133.2, 129.6, 129.5, 129.2, 129.2, 128.2, 127.2, 120.2, 119.6, 111.6, 111.4, 38.9, 36.8, 27.2, 21.7; ESI-HRMS: calcd. for $\text{C}_{19}\text{H}_{14}\text{ClN}_5\text{O}+\text{Na}$ 386.07715, found 386.07664; 90% ee; The enantiomeric ratio was determined by HPLC on Chiralpak AD column (20% 2-propanol/hexane, 1.0 mL/min, detection at 254 nm), $t_{\text{minor}} = 17.31$ min, $t_{\text{major}} = 24.82$ min.


3i, 61% yield. yellow solid, m.p. 141-143 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.89-7.81 (m, 2H), 7.67-7.64 (m, 3H), 7.12-7.09 (m, 1H), 7.03-7.02 (m, 1H), 4.62 (d, $J = 6.5$ Hz, 1H), 4.40-4.35 (m, 1H), 3.71-3.55 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 194.7, 138.6, 132.3, 132.3, 132.0, 130.1, 129.6, 129.5, 129.5, 129.4, 124.1, 122.0, 120.6, 119.6, 111.5, 39.0, 35.8, 27.2; ESI-HRMS: calcd. for $\text{C}_{18}\text{H}_{11}\text{BrClN}_5\text{O}+\text{Na}$ 449.97320, found 449.97296; 83% ee; The enantiomeric ratio was determined by HPLC on Chiralpak AD column (20% 2-propanol/hexane, 1.0 mL/min, detection at 254 nm), $t_{\text{minor}} = 22.12$ min, $t_{\text{major}} = 36.70$ min.


3j, 62% yield. yellow solid, m.p. 146-147 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.97-7.89 (m, 2H), 7.51-7.47 (m, 3H), 7.13-7.03 (m, 2H), 4.62 (d, $J = 6.5$ Hz, 1H), 4.39-4.37 (m, 1H), 3.67-3.60 (m, 2H); ^{13}C NMR (100 MHz,

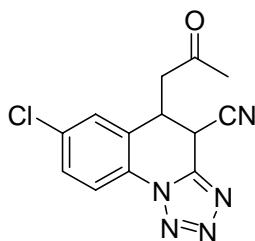
CDCl_3 δ (ppm) 194.4, 142.0, 138.5, 130.0, 130.0, 129.3, 129.3, 129.1, 129.0, 124.1, 120.6, 120.3, 120.2, 118.4, 111.5, 39.0, 35.4, 27.2; ESI-HRMS: calcd. for $\text{C}_{18}\text{H}_{11}\text{Cl}_2\text{N}_5\text{O}+\text{Na}$ 406.02374, found 406.02369; 84% ee; The enantiomeric ratio was determined by HPLC on Chiralpak AD column (20% 2-propanol/hexane, 1.0 mL/min, detection at 254 nm), $t_{\text{minor}} = 20.65$ min, $t_{\text{major}} = 30.34$ min.

3k, 60% yield. yellow solid, m.p. 139-140 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.84 (d, $J = 7.7$ Hz, 2H), 7.42 (d, $J = 8.3$ Hz, 1H), 7.30-7.26 (m, 2H), 6.88-6.80 (m, 2H), 4.61 (d, $J = 6.1$ Hz, 1H), 4.39-4.35 (m, 1H), 3.71-3.55 (m, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 195.4, 145.2, 142.1, 138.1, 133.2, 130.0, 130.0, 129.6, 128.2, 128.2, 124.0, 115.8, 111.7, 111.5, 109.4, 39.0, 35.4, 27.4, 21.7; ESI-HRMS: calcd. for $\text{C}_{19}\text{H}_{14}\text{BrN}_5\text{O}+\text{Na}$ 430.02786, found 430.02774; 95% ee; The enantiomeric ratio was determined by HPLC on Chiralpak AS column (20% 2-propanol/hexane, 1.0 mL/min, detection at 254 nm), $t_{\text{major}} = 17.31$ min, $t_{\text{minor}} = 22.57$ min.

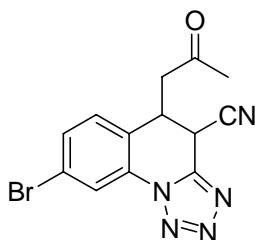
3l, 68% yield. yellow solid, m.p. 157-158 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.81 (d, $J = 8.5$ Hz, 2H), 7.63 (d, $J = 8.5$ Hz, 2H), 7.39 (d, $J = 8.5$ Hz, 1H), 6.88-6.80 (m, 2H), 4.57 (d, $J = 6.3$ Hz, 1H), 4.38-4.33 (m, 1H), 3.70-3.53 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 194.8, 142.3, 139.8, 134.4, 134.3, 132.3, 132.3, 130.0, 129.5, 129.5, 123.7, 115.9, 111.7, 111.5, 109.5, 39.1, 35.5, 27.4; ESI-HRMS: calcd. for $\text{C}_{18}\text{H}_{11}\text{Br}_2\text{N}_5\text{O}+\text{Na}$ 495.92068, found 495.92061; 91% ee; The enantiomeric ratio was determined by HPLC on Chiralpak AS column (20% 2-propanol/hexane, 1.0 mL/min, detection at 254 nm), $t_{\text{major}} = 21.56$ min, $t_{\text{minor}} = 23.92$ min.

3m, 66% yield. yellow solid, m.p. 151-152 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.92 (d, J = 8.6 Hz, 2H), 7.54-7.43 (m, 3H), 6.93-6.85 (m, 2H), 4.62 (d, J = 6.3 Hz, 1H), 4.43-4.38 (m, 1H), 3.76-3.58 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 194.6, 142.3, 140.7, 139.8, 134.0, 130.0, 130.0, 129.5, 129.4, 129.3, 123.7, 115.9, 111.7, 111.5, 109.5, 39.1, 35.5, 27.4; ESI-HRMS: calcd. for $\text{C}_{18}\text{H}_{11}\text{BrClN}_5\text{O}+\text{Na}$ 449.97321, found 449.97315; 93% ee; The enantiomeric ratio was determined by HPLC on Chiralpak AD column (20% 2-propanol/hexane, 1.0 mL/min, detection at 254 nm), $t_{\text{major}} = 19.11$ min, $t_{\text{minor}} = 21.87$ min.

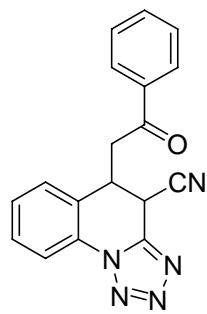
4a, 92% yield. yellow solid, m.p. 197-198 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.07-8.03 (m, 1H), 7.60-7.45 (m, 3H), 4.93-4.89 (m, 1H), 4.16-4.11 (m, 1H), 3.17-2.92 (m, 1H), 2.71 (d, J = 6.8 Hz, 1H), 2.18 (d, J = 33.6 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 204.3, 204.0, 145.7, 144.9, 130.3, 130.2, 130.1, 130.0, 129.8, 129.7, 129.2, 128.7, 126.3, 126.2, 118.1, 118.1, 114.4, 113.3, 45.5, 43.8, 36.7, 34.0, 30.4, 30.1, 28.6, 27.0; IR (KBr) cm^{-1} 3425, 3127, 2779, 2116, 1719, 1401, 825, 770; ESI-HRMS: calcd. for $\text{C}_{13}\text{H}_{11}\text{N}_5\text{O}+\text{H}$ 254.10349, found 254.10364; $[\alpha]^{25}_{\text{D}} = +60.0$ (c 1.12, EtOAc), 56/44 dr, the enantiomeric ratio was determined by HPLC on Chiralpak AD column (30% 2-propanol/hexane, 1.0 mL/min, detection at 254 nm), 95% ee, $t_{\text{minor}} = 7.38$ min, $t_{\text{major}} = 8.86$ min; 96% ee, $t_{\text{minor}} = 12.32$ min, $t_{\text{major}} = 26.11$ min.



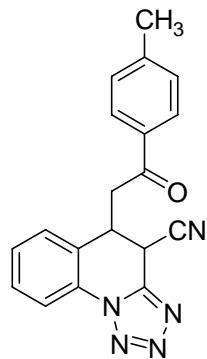
4b, 83% yield. yellow solid, m.p. 209-211 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.07-8.01 (m, 1H), 7.25-7.22 (m, 1H), 7.16-7.14 (m, 1H), 4.93-4.88 (m, 1H), 4.13-4.09 (m, 1H), 3.18-2.90 (m, 1H), 2.70-2.68 (m, 1H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 204.0, 203.8, 145.3, 144.5, 142.1, 141.8, 128.4, 128.3, 127.0, 126.8, 120.4, 120.2, 119.8, 119.7, 119.4, 114.2, 113.1, 45.3, 43.6, 36.8, 34.1, 30.3, 30.1, 30.0, 28.4, 26.9; IR (KBr) cm^{-1} 3426, 3127, 2779, 1717, 1400, 827, 776; ESI-HRMS: calcd. for $\text{C}_{13}\text{H}_{10}\text{ClN}_5\text{O}+\text{Na}$ 310.04731, found 310.04768; $[\alpha]^{25}_D = +42.3$ (c 0.6, EtOAc), 95/5 dr, the enantiomeric ratio was determined by HPLC on Chiraldak AD column (30% 2-propanol/hexane, 1.0 mL/min, detection at 254 nm), 94% ee, $t_{\text{major}} = 10.83$ min, $t_{\text{minor}} = 13.07$ min; 99% ee, $t_{\text{major}} = 26.23$ min, $t_{\text{minor}} = 36.88$ min.



4c, 81% yield. yellow solid, m.p. 215-216 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.72-7.71 (m, 1H), 7.62-7.49 (m, 1H), 7.16-7.11 (m, 1H), 4.92-4.87 (m, 1H), 4.14-4.08 (m, 1H), 3.17-2.88 (m, 1H), 2.69 (d, $J = 6.5$ Hz, 1H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 204.1, 203.9, 145.9, 145.1, 142.6, 142.5, 133.1, 131.3, 131.1, 130.8, 130.4, 122.3, 122.2, 120.3, 119.8, 114.2, 113.2, 108.9, 45.5, 43.8, 36.3, 33.9, 33.8, 30.4, 30.1, 28.6, 27.1, 27.0; IR (KBr) cm^{-1} 3420, 3109, 2780, 2114, 1720, 1400, 823, 769; ESI-HRMS: calcd. for $\text{C}_{13}\text{H}_{10}\text{BrN}_5\text{O}+\text{Na}$ 353.99600, found 353.99744; $[\alpha]^{25}_D = +71.9$ (c 0.7, EtOAc), 53/47 dr, the enantiomeric ratio was determined by HPLC on Chiraldak AD column (30% 2-propanol/hexane, 1.0 mL/min, detection at 254 nm), 88% ee, $t_{\text{minor}} = 9.76$ min, $t_{\text{major}} = 11.55$ min; 98% ee, $t_{\text{minor}} = 22.38$ min, $t_{\text{major}} = 26.20$ min.

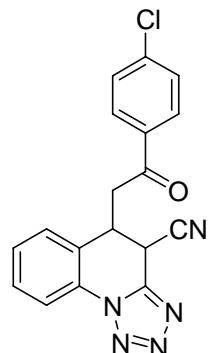


4d, 94% yield. yellow solid, m.p. 207-209 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.09-8.03 (m, 1H), 7.95-7.81 (m, 2H), 7.60-7.41 (m, 5H), 5.00-4.96 (m, 1H), 4.35 (m, 1H), 3.63-3.51 (m, 1H), 3.23-3.16 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 195.5, 145.8, 145.0, 135.7, 135.4, 134.2, 134.1, 130.3, 130.2, 130.1, 130.0, 129.7, 129.4, 128.9, 128.1, 128.0, 126.6, 118.2, 114.5, 113.4, 41.0, 39.1, 37.1, 34.4, 28.9, 27.2; IR (KBr) cm^{-1} 3427, 3122, 2779, 2110, 1720, 1683, 1400, 689; ESI-HRMS: calcd. for $\text{C}_{18}\text{H}_{13}\text{N}_5\text{O}+\text{H}$ 316.11936, found 316.11929; $[\alpha]^{25}_D = +43.2$ (c 0.6, EtOAc), 60/40 dr, the enantiomeric ratio was determined by HPLC on Chiralpak AD column (30% 2-propanol/hexane, 1.0 mL/min, detection at 254 nm), 90% ee, $t_{\text{major}} = 22.85$ min, $t_{\text{minor}} = 26.56$ min.

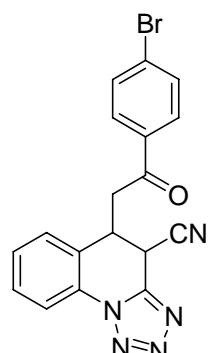


4e, 93% yield. yellow solid, m.p. 211-212 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.10-8.04 (m, 1H), 7.86-7.83 (m, 2H), 7.59-7.44 (m, 3H), 7.29-7.22 (m, 2H), 5.01-4.97 (m, 1H), 4.35-4.34 (m, 1H), 3.60-3.50 (m, 1H), 3.19-3.11 (m, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 195.0, 194.9, 145.8, 145.3, 145.2, 145.0, 133.3, 133.0, 130.5, 130.5, 130.4, 130.3, 130.2, 130.1, 130.0, 129.6, 129.6, 129.5, 129.5, 129.4, 129.3, 129.2, 128.8, 128.3, 128.1, 126.7, 126.3, 118.1, 114.5, 113.4, 40.8, 38.9, 37.1, 34.4, 28.9, 27.2, 21.8, 21.7; IR (KBr) cm^{-1} 3425, 3123, 2779, 2110, 1720, 1679, 1400, 765; ESI-HRMS: calcd. for $\text{C}_{19}\text{H}_{15}\text{N}_5\text{O}+\text{Na}$ 352.11724, found 352.116884; $[\alpha]^{25}_D = +54.8$ (c 0.7, EtOAc), 63/37 dr, the enantiomeric ratio was determined by HPLC on Chiralpak AD column (10% 2-propanol/hexane, 1.0

mL/min, detection at 254 nm), 99% ee, $t_{\text{minor}} = 50.12$ min, $t_{\text{major}} = 54.32$ min; 99% ee, $t_{\text{major}} = 84.63$ min, $t_{\text{minor}} = 112.09$ min.

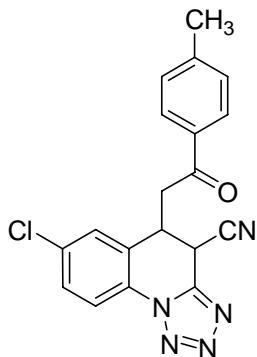


4f, 87% yield. yellow solid, m.p. 223-224 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.07-8.01 (m, 1H), 7.88-7.77 (m, 2H), 7.60-7.38 (m, 5H), 5.01-4.95 (m, 1H), 4.39-4.32 (m, 1H), 3.64-3.41 (m, 1H), 3.22 (d, $J = 6.7$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 194.4, 194.3, 145.7, 145.0, 140.7, 140.6, 134.0, 133.7, 130.4, 130.3, 130.2, 130.1, 130.1, 129.7, 129.6, 129.6, 129.6, 129.5, 129.4, 129.2, 129.1, 129.0, 126.4, 126.3, 116.2, 114.5, 113.5, 41.0, 38.4, 36.9, 34.3, 29.0, 27.2; IR (KBr) cm^{-1} 3422, 3120, 2780, 2111, 1718, 1681, 1400, 784; ESI-HRMS: calcd. for $\text{C}_{18}\text{H}_{12}\text{ClN}_5\text{O}+\text{Na}$ 372.06212, found 372.06246; $[\alpha]^{25}_D = +89.6$ (c 1.1, EtOAc), 61/39 dr, the enantiomeric ratio was determined by HPLC on Chiralpak AD column (20% 2-propanol/hexane, 0.5 mL/min), 92% ee, $t_{\text{minor}} = 44.49$ min, $t_{\text{major}} = 49.72$ min; 93% ee, $t_{\text{major}} = 93.62$ min, $t_{\text{minor}} = 100.62$ min.

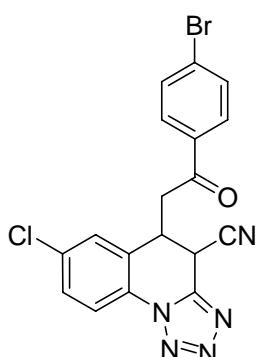


4g, 88% yield. yellow solid, m.p. 230-231 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.15-8.08 (m, 1H), 7.85-7.72 (m, 2H), 7.67-7.48 (m, 5H), 5.03-4.88 (m, 1H), 4.38-4.35 (m, 1H), 3.66-3.44 (m, 1H), 3.20-3.16 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 194.5, 194.3, 145.6, 144.9, 134.1, 132.2, 132.2, 130.4, 130.4, 130.3, 130.3, 130.2, 130.2, 129.7, 129.7, 129.6, 129.6, 129.5, 129.5, 129.4, 129.3, 128.9, 126.4, 126.2, 126.1, 118.3, 118.2, 114.3, 113.3, 41.0, 39.2, 37.0, 34.4, 28.9, 27.2; IR (KBr) cm^{-1} 3429, 3121, 2781, 2116, 1713, 1400, 824, 775; ESI-HRMS: calcd.

for $C_{18}H_{12}BrN_5O+Na$ 416.01198, found 416.01174; $[\alpha]^{25}_D = +34.3$ (c 0.6, EtOAc), 57/43 dr, the enantiomeric ratio was determined by HPLC on Chiraldak AD column (30% 2-propanol/hexane, 1.0 mL/min, detection at 254 nm), 90% ee, $t_{\text{minor}} = 26.28$ min, $t_{\text{major}} = 30.70$ min; 92% ee, $t_{\text{major}} = 53.29$ min, $t_{\text{minor}} = 56.84$ min.

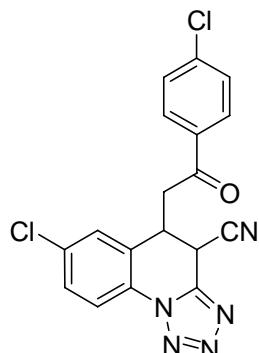


4h, 86% yield. yellow solid, m.p. 231-233 °C; 1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.09-8.04 (m, 1H), 7.86-7.68 (m, 2H), 7.30-7.28 (m, 1H), 7.24-7.17 (m, 3H), 4.99-4.95 (m, 1H), 4.33-4.29 (m, 1H), 3.63-3.41 (m, 1H), 3.19-3.03 (m, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 194.6, 145.5, 144.6, 142.2, 141.8, 132.8, 129.6, 128.7, 128.4, 128.3, 128.1, 126.9, 120.4, 120.1, 119.8, 119.7, 119.5, 114.3, 113.1, 40.7, 38.7, 37.3, 34.6, 28.7, 27.1, 21.7; IR (KBr) cm^{-1} 3426, 3120, 2779, 2113, 1718, 1685, 1400, 756, 667; ESI-HRMS: calcd. for $C_{19}H_{14}ClN_5O+Na$ 386.07706, found 386.07664; $[\alpha]^{25}_D = 0.5$ (c 1.4, EtOAc), 62/38 dr, the enantiomeric ratio was determined by HPLC on Chiraldak AD column (30% 2-propanol/hexane, 1.0 mL/min, detection at 254 nm), 86% ee, $t_{\text{minor}} = 14.82$ min, $t_{\text{major}} = 16.48$ min; 83% ee, $t_{\text{major}} = 33.52$ min, $t_{\text{minor}} = 92.37$ min.

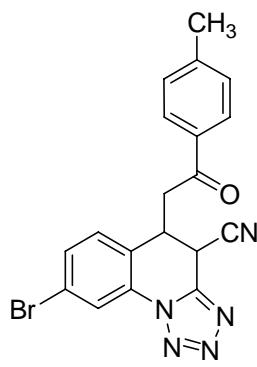


4i, 85% yield. yellow solid, m.p. 245-247 °C; 1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.10-8.04 (m, 1H), 7.82-7.80 (m, 1H), 7.73-7.68 (m, 1H), 7.64-7.57 (m, 2H), 7.27-7.18 (m, 2H), 4.98-4.94 (m, 1H), 4.34-4.31 (m, 1H), 3.65-3.36 (m, 1H), 3.16-3.10 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 194.5, 194.5, 144.5, 142.3,

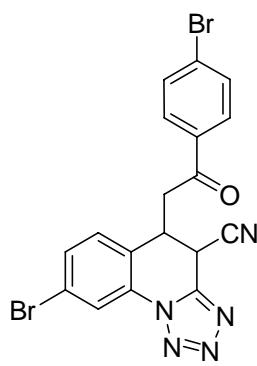
140.2, 133.9, 133.9, 133.8, 133.6, 133.5, 132.3, 132.1, 132.0, 129.8, 129.6, 129.5, 129.5, 129.4, 129.3, 128.4, 125.9, 125.8, 125.6, 120.5, 120.2, 119.9, 119.8, 119.6, 119.1, 118.4, 40.9, 39.0, 37.1, 34.5, 28.8, 27.1; IR (KBr) cm^{-1} 3425, 3120, 2778, 2113, 1719, 1685, 1400, 756, 660; ESI-HRMS: calcd. for $\text{C}_{18}\text{H}_{11}\text{BrClN}_5\text{O}+\text{Na}$ 449.97316, found 449.97307; $[\alpha]^{25}_D = +18$ (c 0.7, EtOAc), 60/40 dr, the enantiomeric ratio was determined by HPLC on Chiralpak AD column (30% 2-propanol/hexane, 1.0 mL/min, detection at 254 nm), 82% ee, $t_{\text{minor}} = 16.06$ min, $t_{\text{major}} = 18.01$ min; 81% ee, $t_{\text{major}} = 44.40$ min, $t_{\text{minor}} = 86.34$ min.



4j, 89% yield. yellow solid, m.p. 243-245 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.08-8.02 (m, 1H), 7.91-7.75 (m, 2H), 7.47-7.40 (m, 2H), 7.25-7.18 (m, 2H), 5.00-4.94 (m, 1H), 4.36-4.30 (m, 1H), 3.65-3.37 (m, 1H), 3.22-3.09 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 194.0, 145.3, 144.5, 142.2, 140.9, 133.8, 133.6, 129.6, 129.4, 129.3, 128.5, 128.3, 127.0, 126.8, 120.5, 120.2, 119.9, 119.8, 119.7, 114.2, 40.9, 39.1, 37.1, 34.5, 28.8, 27.1; IR (KBr) cm^{-1} 3427, 3126, 2778, 2110, 1717, 1679, 1400, 827, 779; ESI-HRMS: calcd. for $\text{C}_{18}\text{H}_{11}\text{Cl}_2\text{N}_5\text{O}+\text{Na}$ 406.02368, found 406.02347; $[\alpha]^{25}_D = +3.0$ (c 0.5, EtOAc), 55/45, the enantiomeric ratio was determined by HPLC on Chiralpak AD column (20% 2-propanol/hexane, 1.0 mL/min, detection at 254 nm), 81% ee; $t_{\text{minor}} = 17.13$ min, $t_{\text{major}} = 20.05$ min; 88% ee, $t_{\text{major}} = 43.30$ min, $t_{\text{minor}} = 85.80$ min.

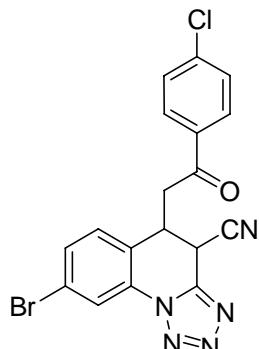


4k, 91% yield. yellow solid, m.p. 238-240 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.84-7.82 (m, 1H), 7.75-7.68 (m, 2H), 7.58-7.51 (m, 1H), 7.28-7.27 (m, 1H), 7.25-7.22 (m, 1H), 7.15-7.08 (m, 1H), 4.88-4.84 (m, 1H), 4.33-4.31 (m, 1H), 3.58-3.45 (m, 1H), 3.14-3.10 (m, 1H), 2.41 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 194.7, 145.5, 142.6, 142.5, 132.9, 131.3, 130.9, 130.4, 129.6, 128.3, 128.1, 122.6, 120.3, 119.7, 114.3, 108.9, 40.8, 38.9, 36.8, 34.2, 28.8, 27.4, 21.7; IR (KBr) cm⁻¹ 3427, 3125, 2778, 2115, 1721, 1400, 824, 773; ESI-HRMS: calcd. for C₁₉H₁₄BrN₅O+Na 430.02780, found 430.02774; [α]²⁵_D = +48.3 (c 0.7, EtOAc),, 58/42 dr, the enantiomeric ratio was determined by HPLC on Chiraldak AD column (30% 2-propanol/hexane, 1.0 mL/min, detection at 254 nm), 92% ee; t_{minor} = 16.00 min, t_{major} = 17.98 min; 95% ee, t_{major} = 25.04 min, t_{minor} = 32.29 min.



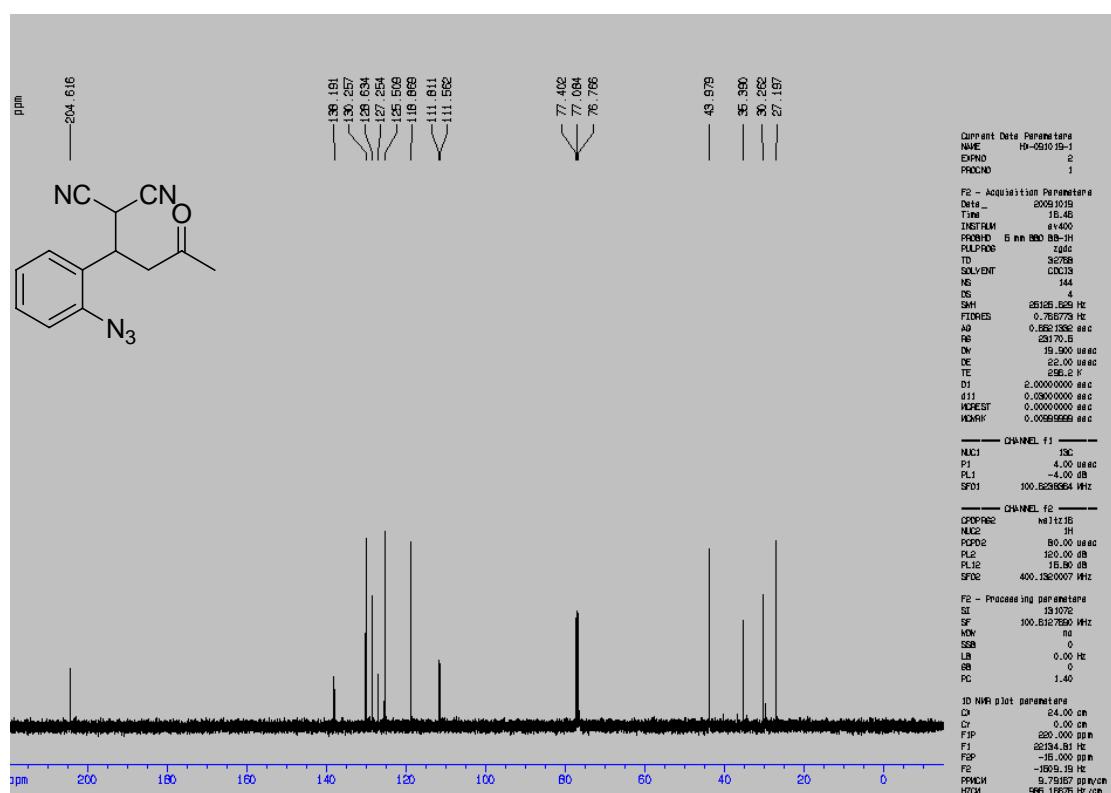
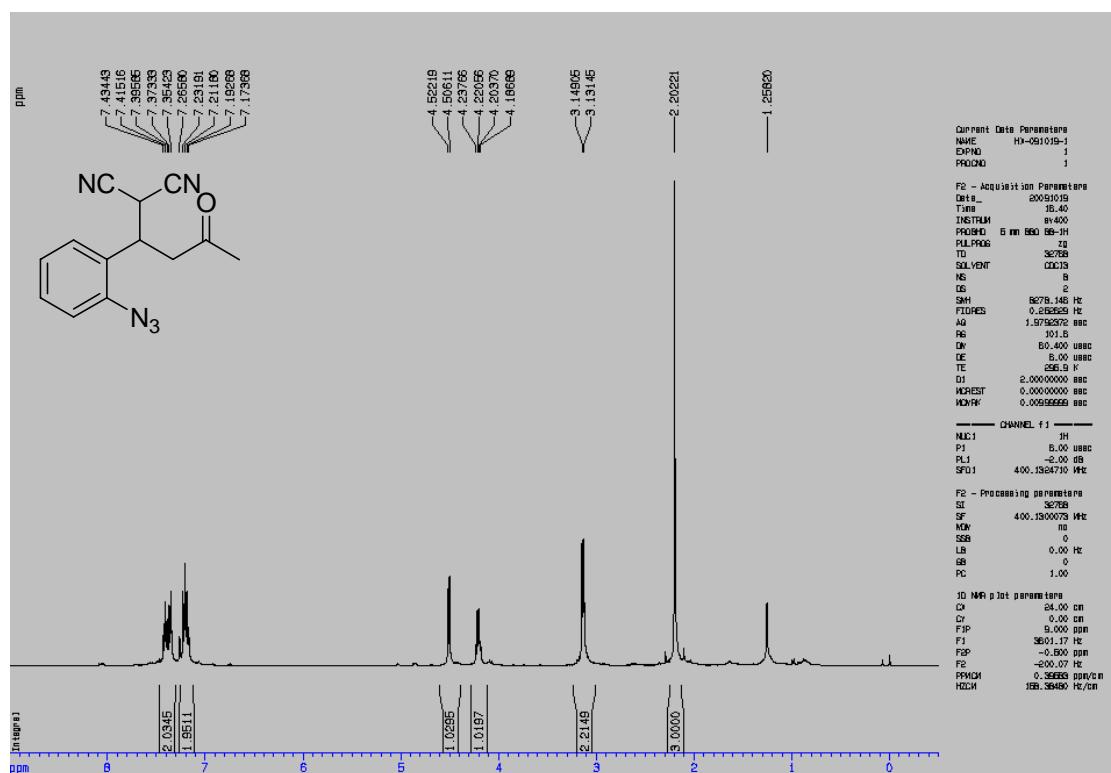
4l, 79% yield. yellow solid, m.p. 257-259 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.82-7.80 (m, 1H), 7.75-7.70 (m, 2H), 7.65-7.54 (m, 3H), 7.17-7.11 (m, 1H), 5.00-4.84 (m, 1H), 4.38-4.33 (m, 1H), 3.65-3.38 (m, 1H), 3.17 (d, *J* = 3.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 194.4, 194.3, 145.1, 142.7, 142.6, 134.2, 134.0, 132.3, 131.4, 131.2, 130.9, 130.6, 129.7, 129.6, 129.5, 122.3, 122.1, 120.3, 119.8, 114.2, 113.2, 108.9, 41.0, 39.3, 36.6, 34.1, 29.0, 27.3; IR (KBr) cm⁻¹ 3427, 3126, 2776, 2114, 1719, 1683, 1400, 826, 779; ESI-HRMS: calcd. for C₁₈H₁₁Br₂N₅NaO+Na 495.92068, found 495.92061; [α]²⁵_D = +31.0 (c 0.8, EtOAc), 60/40 dr, the enantiomeric ratio was determined by HPLC on Chiraldak AD column

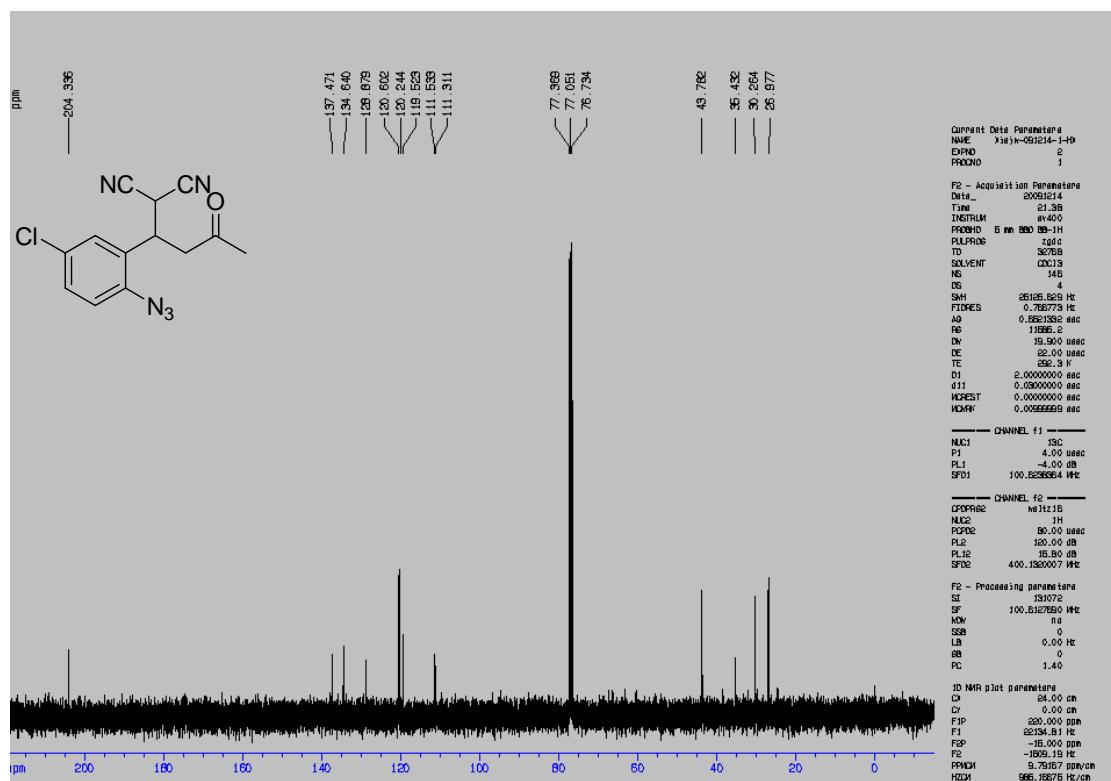
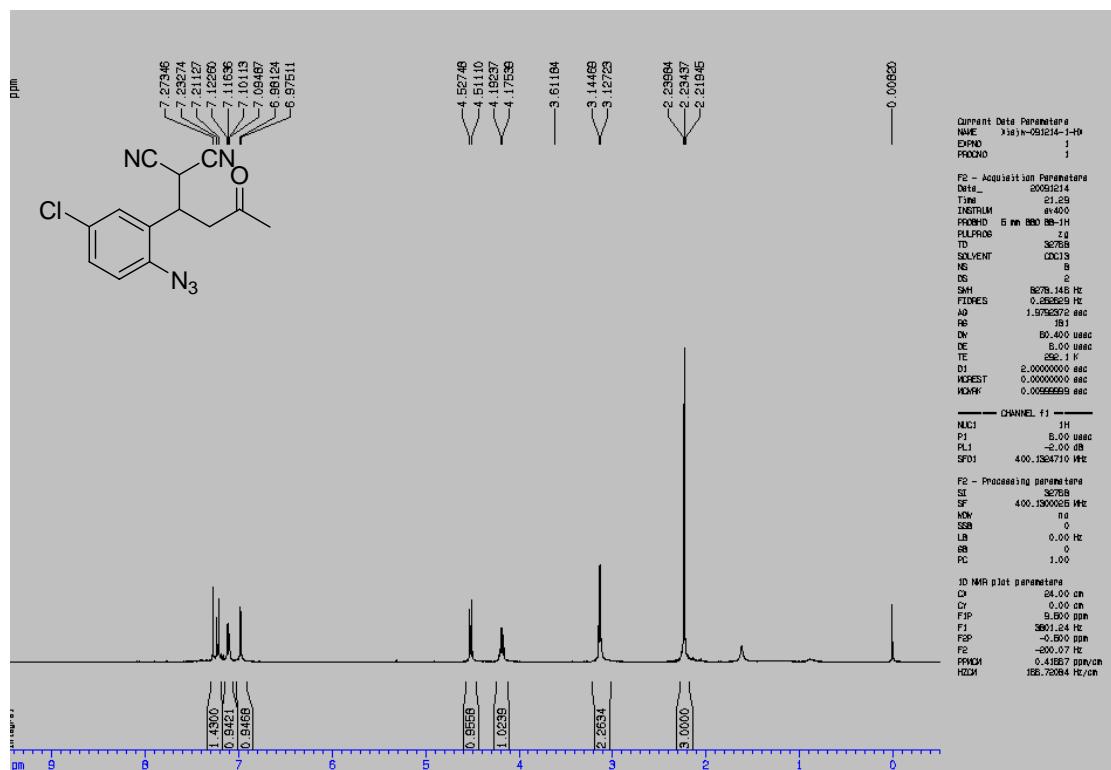
(30% 2-propanol/hexane, 1.0 mL/min, detection at 254 nm), 90% ee, $t_{\text{minor}} = 35.90$ min, $t_{\text{major}} = 39.51$ min.

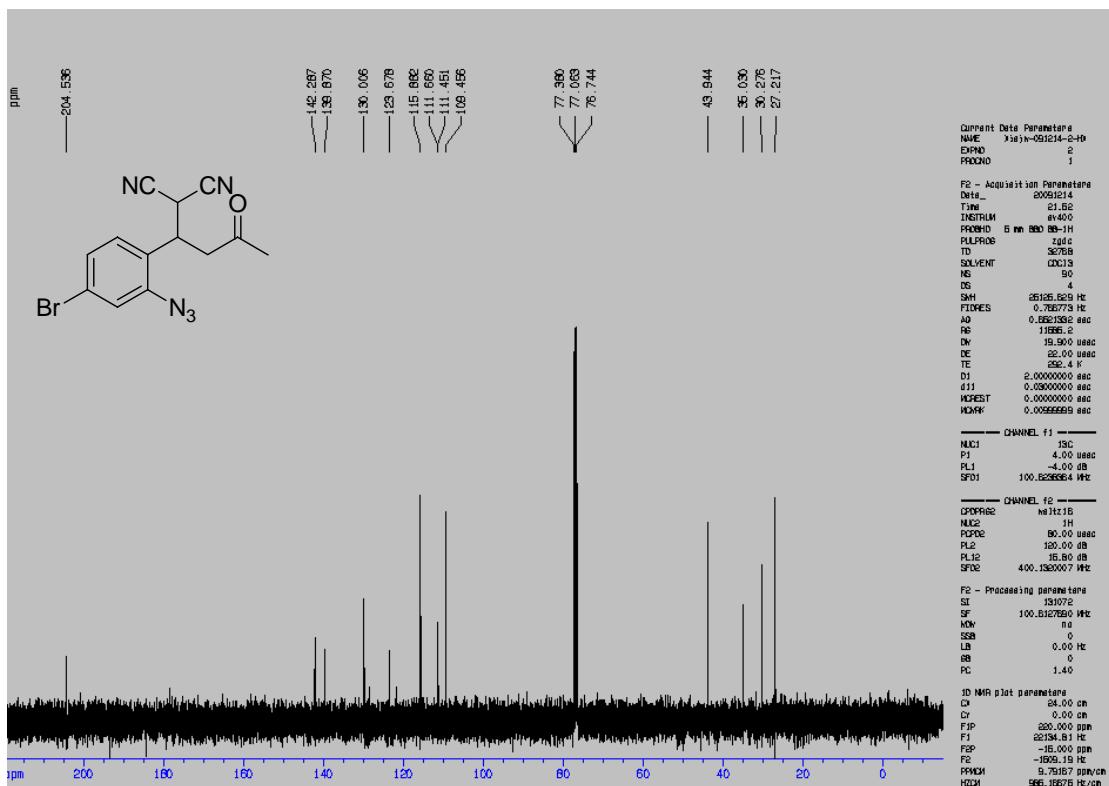
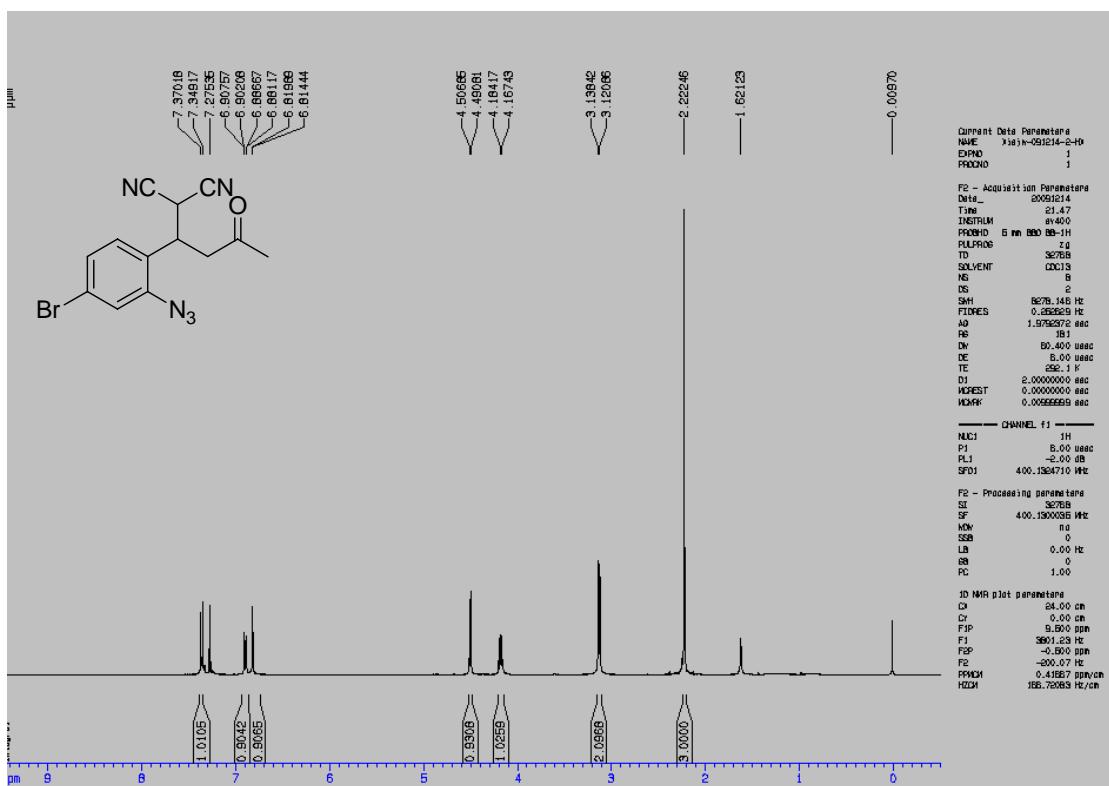


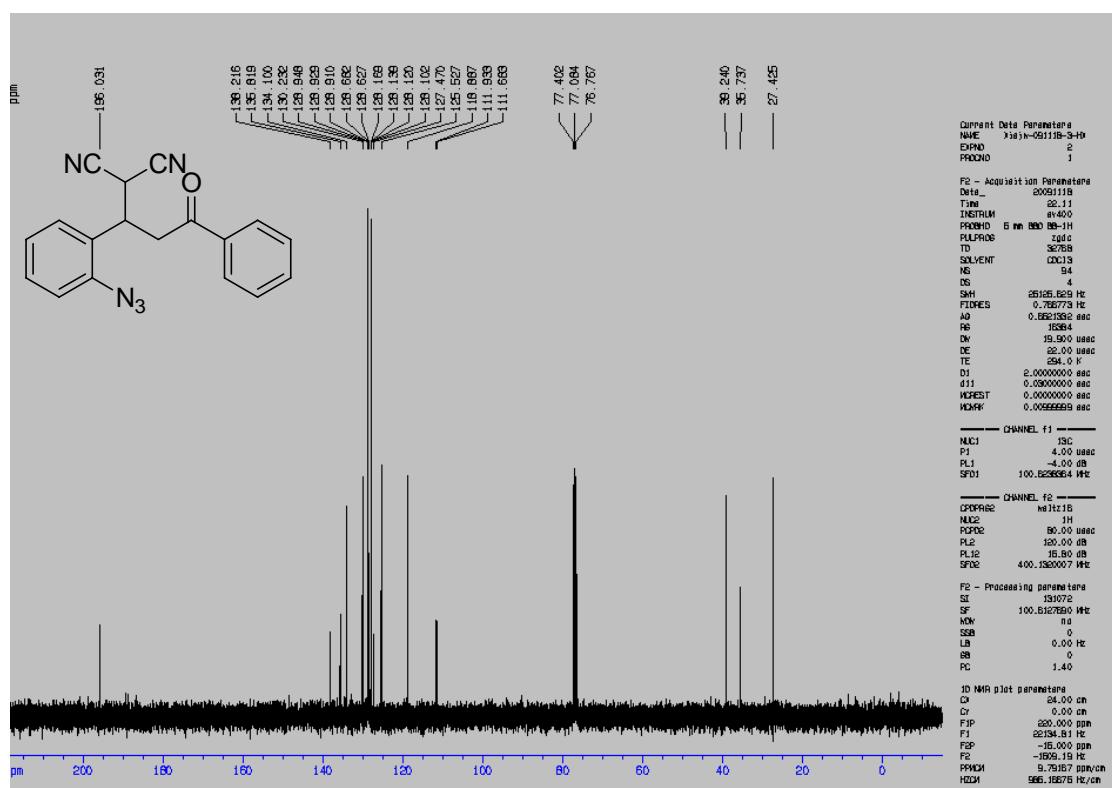
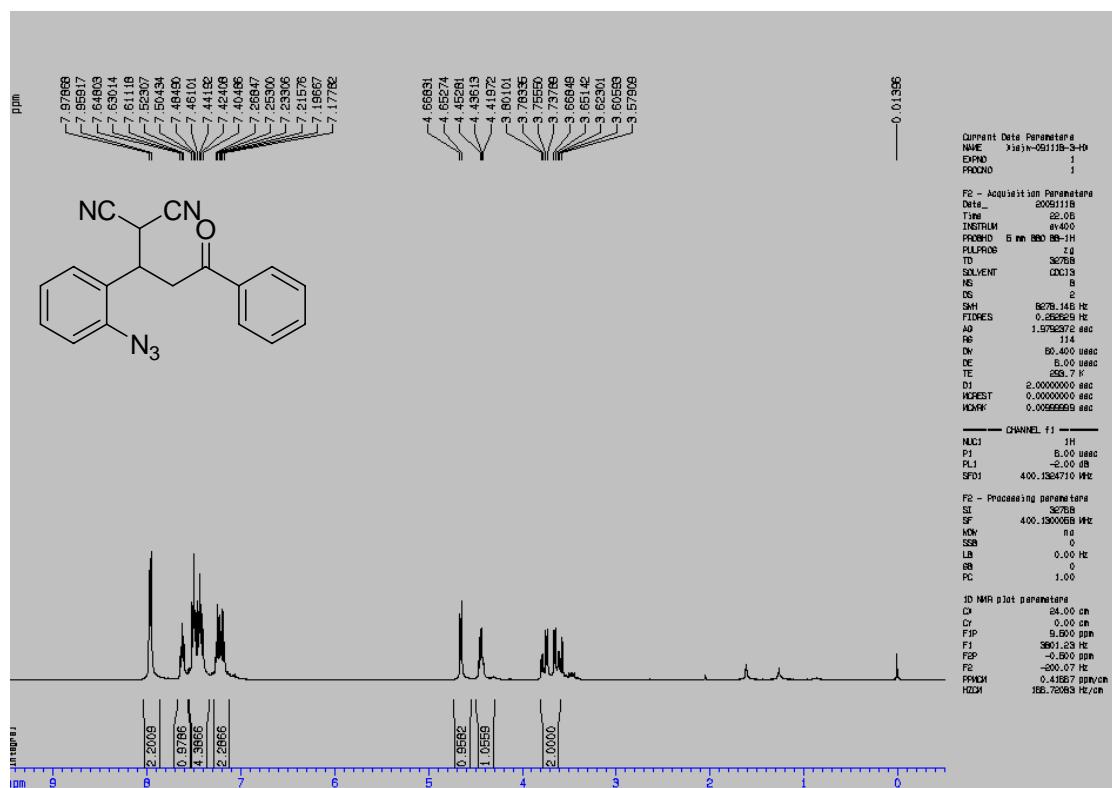
4m, 88% yield. yellow solid, m.p. 251-252 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.89-7.86 (m, 1H), 7.79-7.68 (m, 2H), 7.60-7.52 (m, 1H), 7.46-7.40 (m, 2H), 7.16-7.09 (m, 1H), 4.88-4.83 (m, 1H), 4.36-4.32 (m, 1H), 3.64-3.38 (m, 1H), 3.18 (d, $J = 6.3$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 194.2, 194.1, 145.9, 145.1, 142.7, 142.6, 140.9, 140.8, 133.6, 131.4, 131.2, 130.9, 130.6, 129.6, 129.4, 129.3, 122.3, 122.2, 120.3, 119.8, 114.2, 108.9, 41.0, 38.3, 36.6, 34.1, 29.0, 27.3; IR (KBr) cm^{-1} 3426, 3125, 2775, 2114, 1724, 1682, 1400, 756; ESI-HRMS: calcd. for $\text{C}_{18}\text{H}_{11}\text{BrClN}_5\text{O}+\text{Na}$ 449.97316, found 449.97305; $[\alpha]^{25}_{\text{D}} = +2$ (c 0.3, EtOAc), 61/39 dr, the enantiomeric ratio was determined by HPLC on Chiralpak AD column (30% 2-propanol/hexane, 1.0 mL/min, detection at 254 nm), 92% ee, $t_{\text{minor}} = 31.86$ min, $t_{\text{major}} = 39.65$ min.

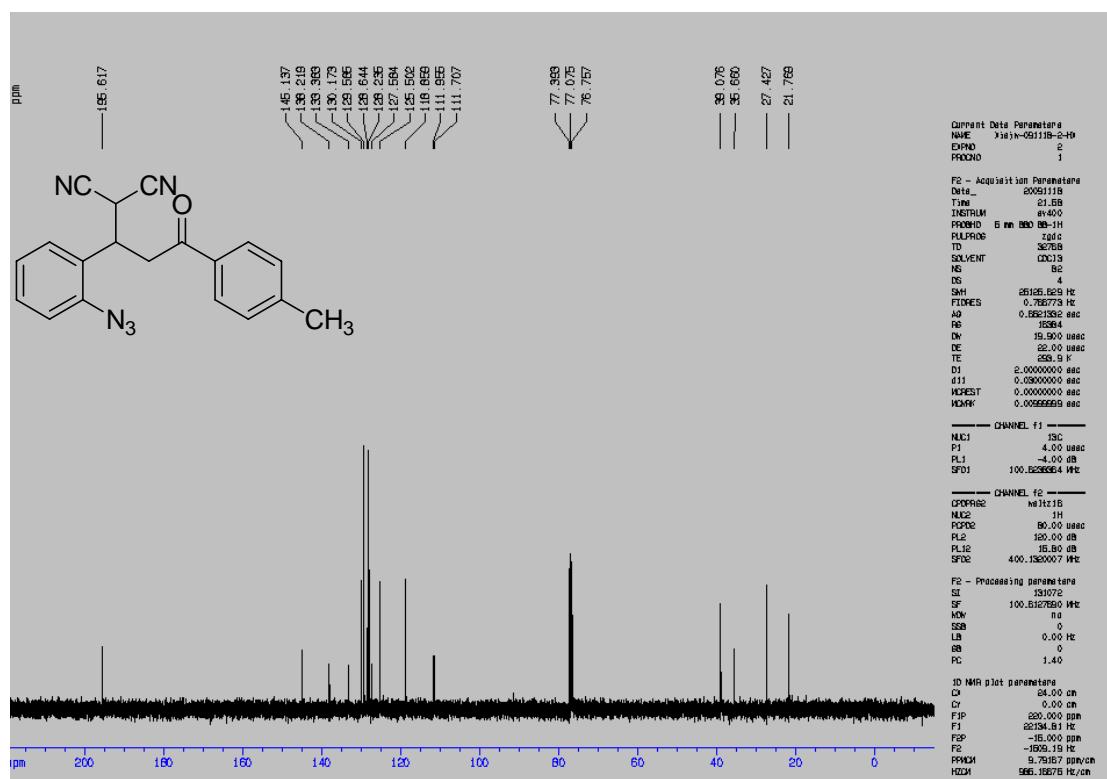
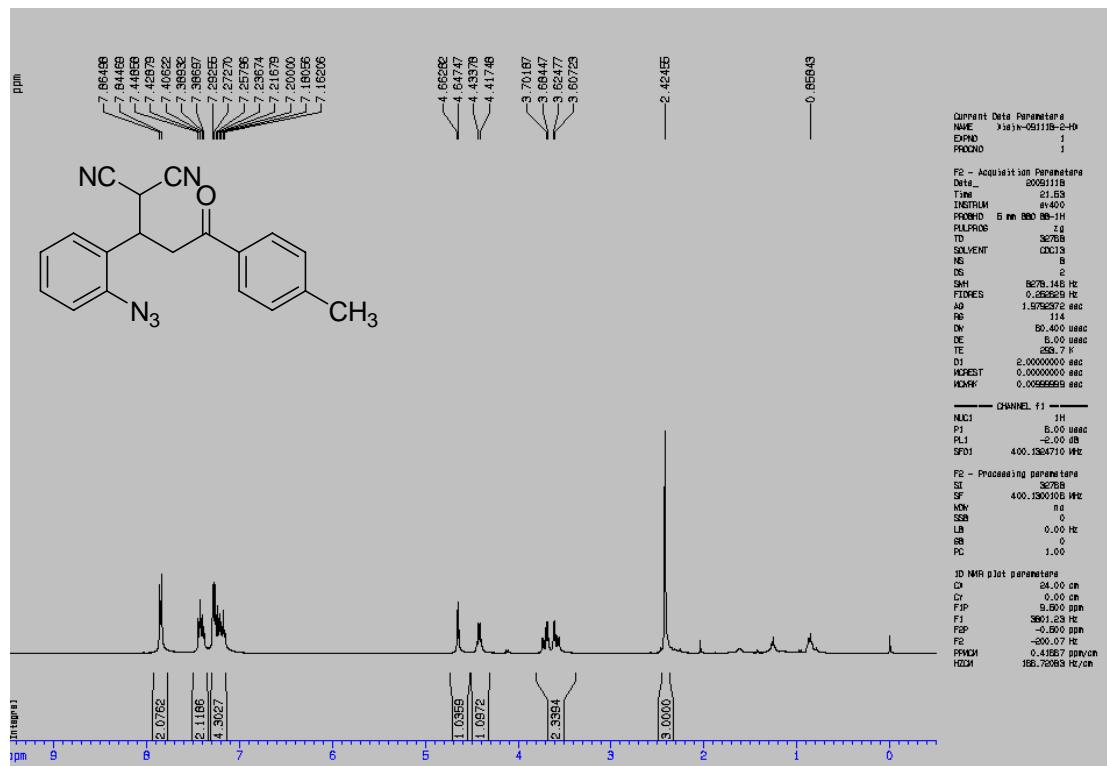
NMR Spectra

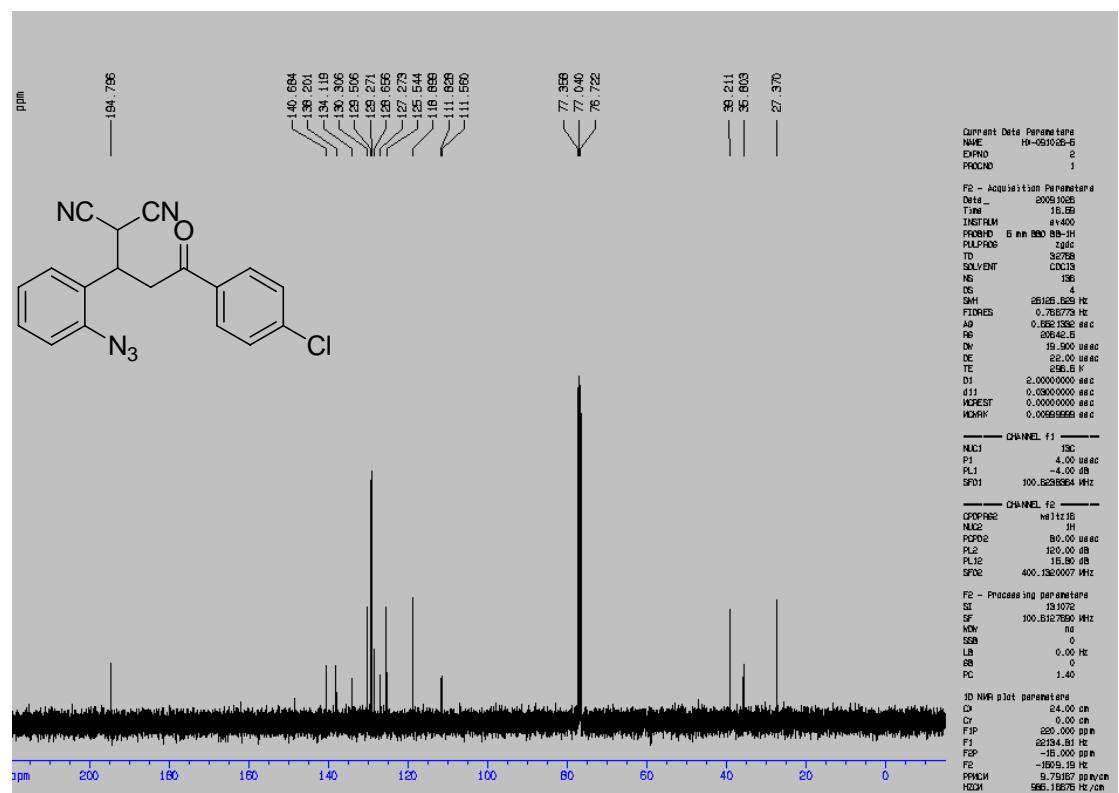
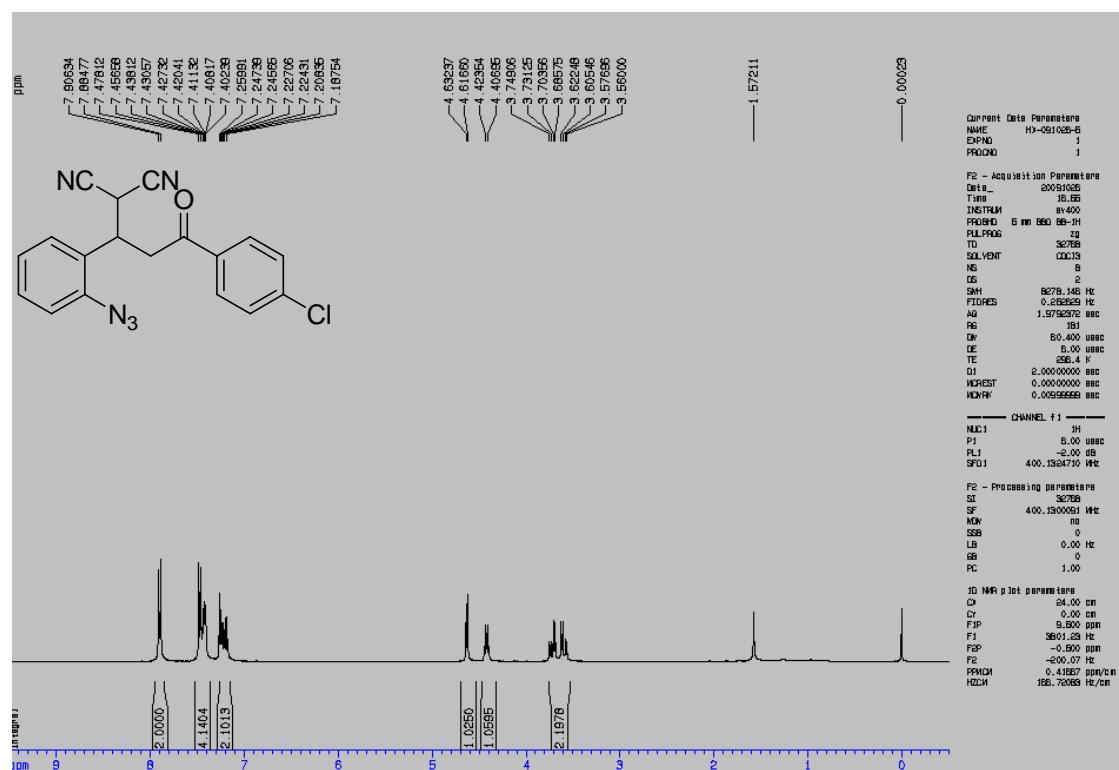


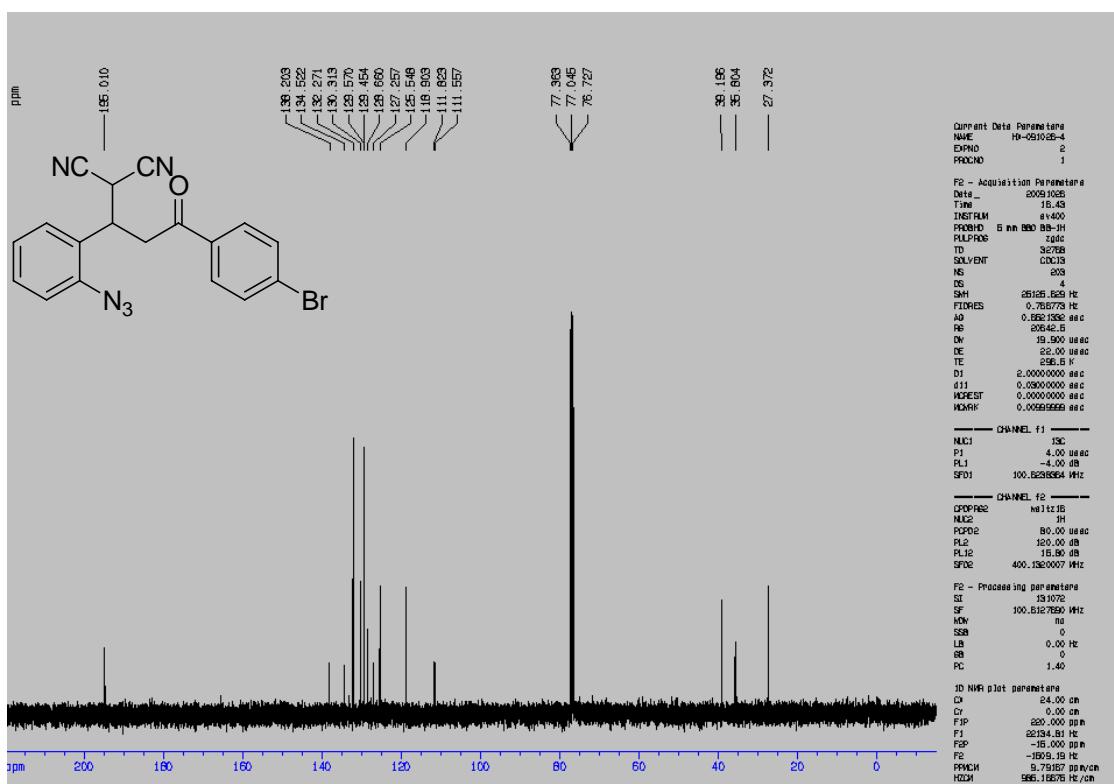
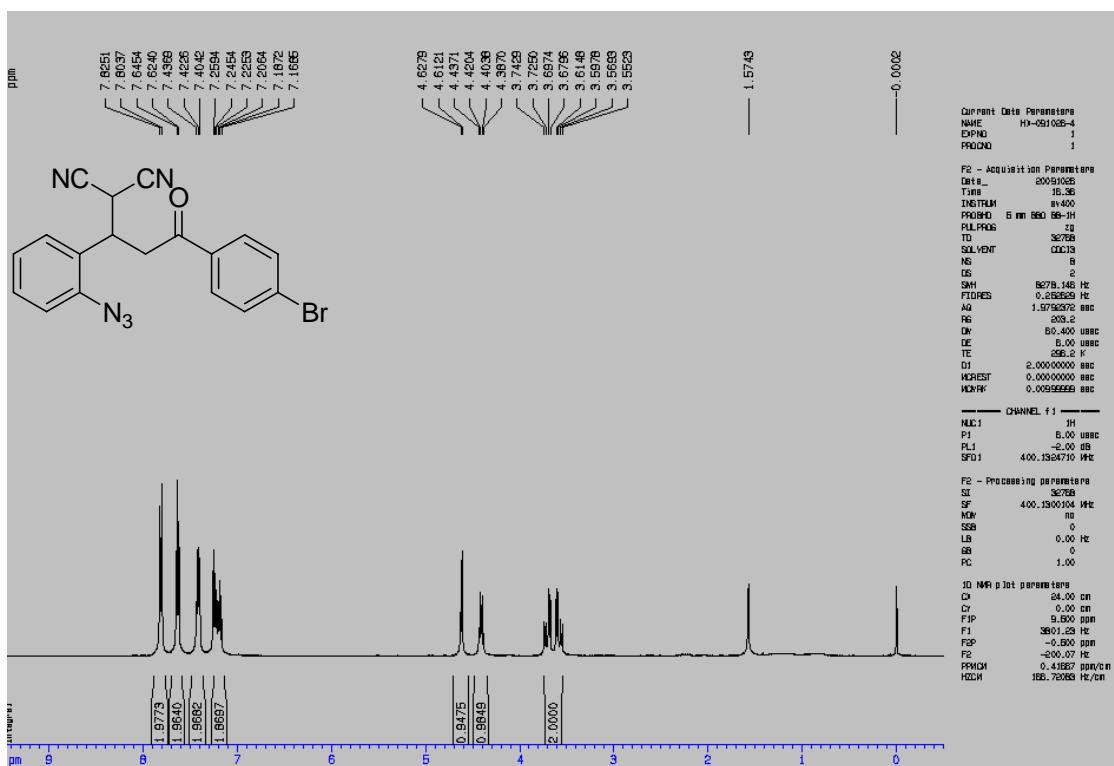


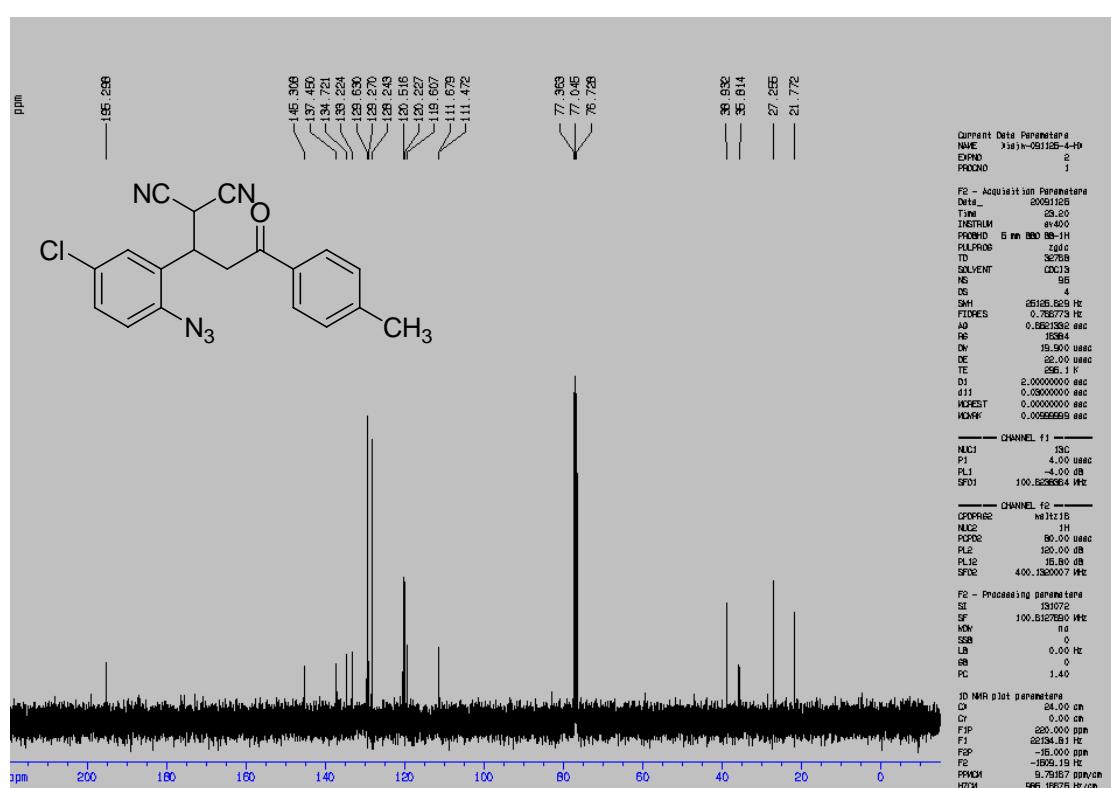
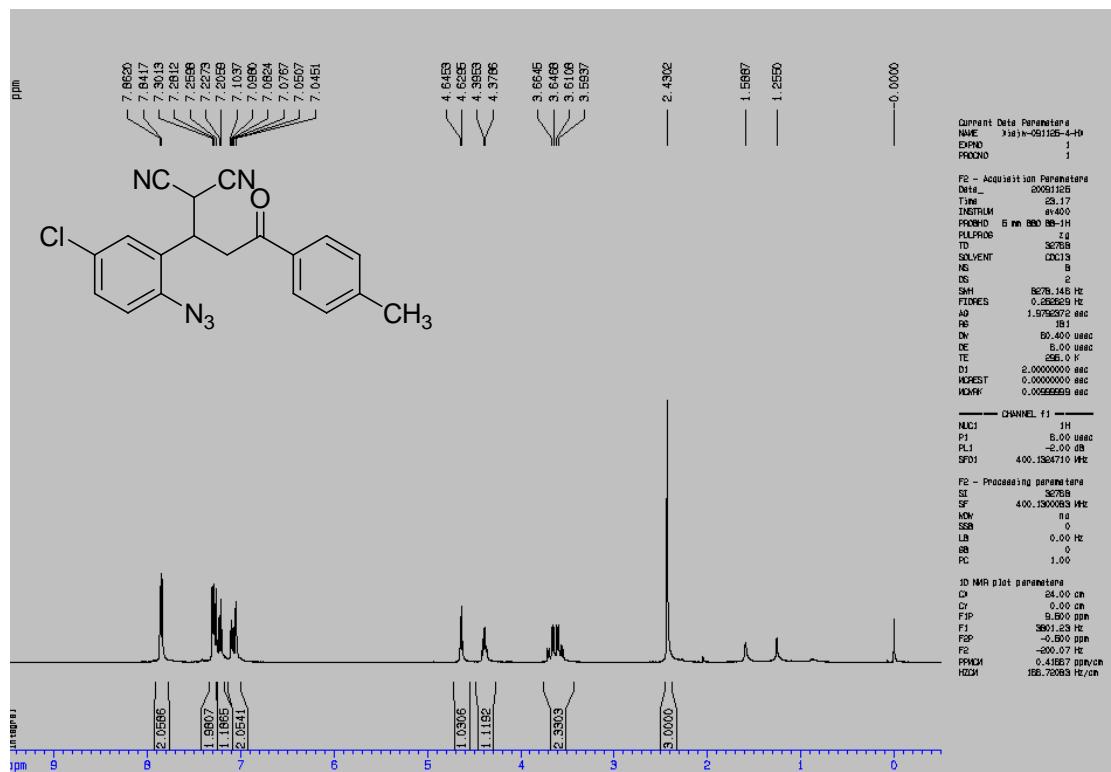


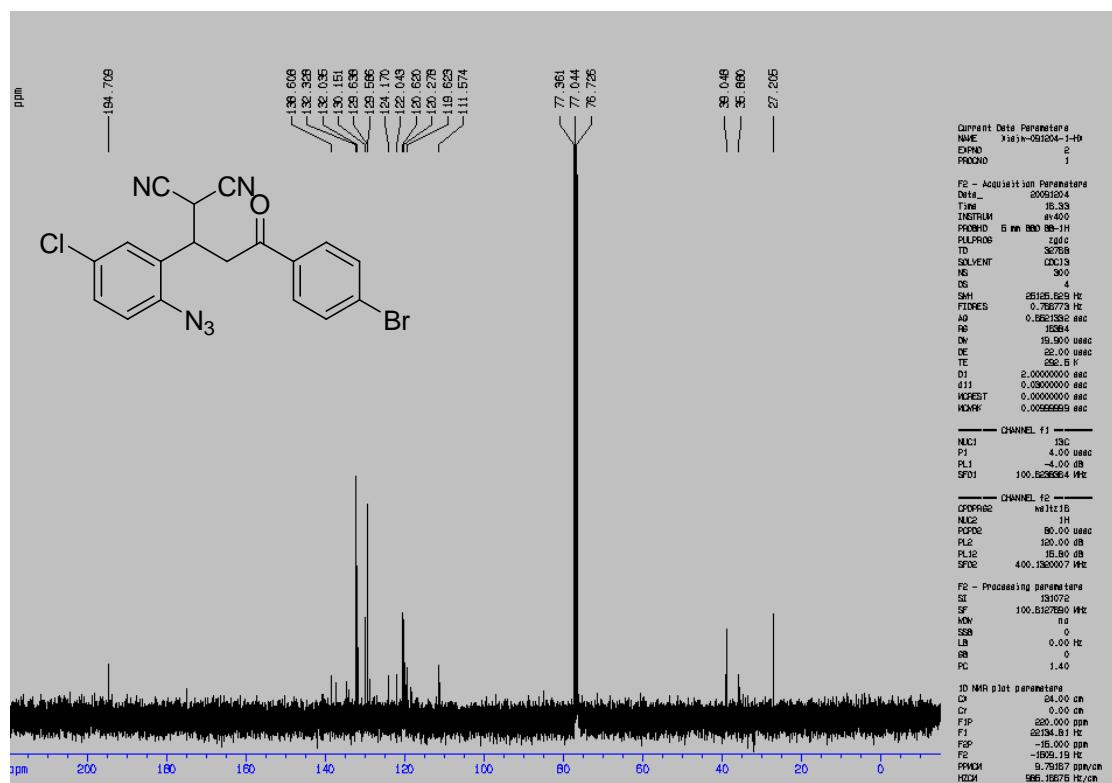
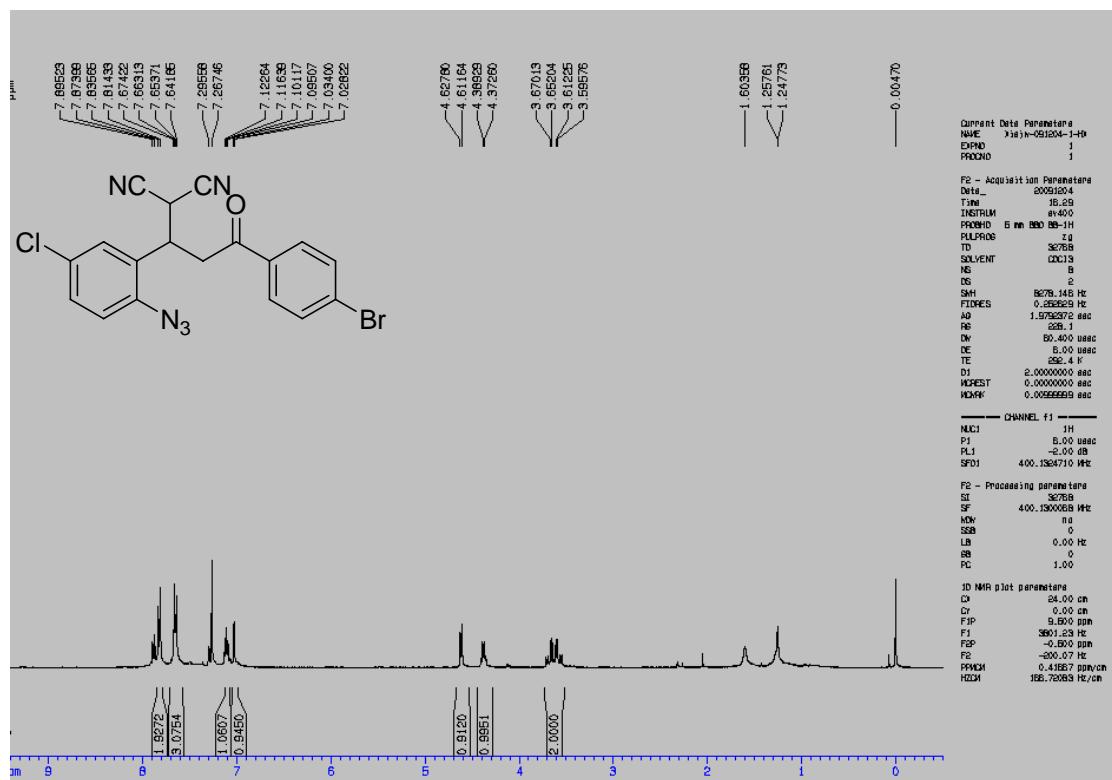


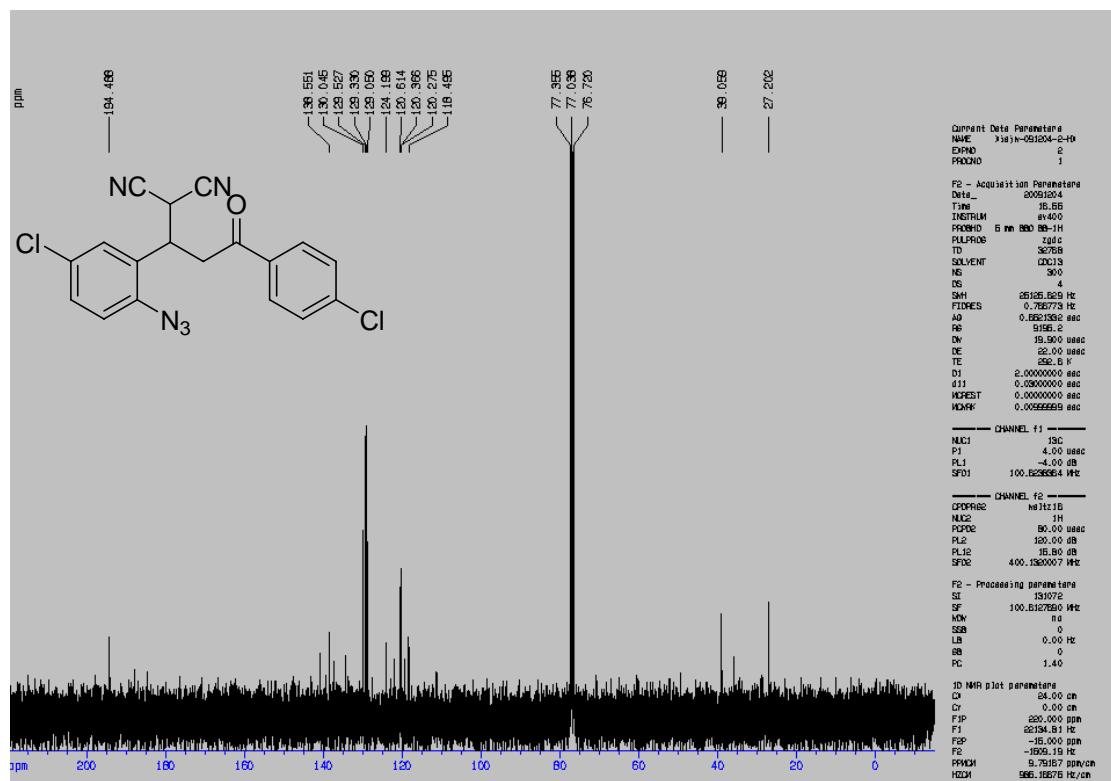
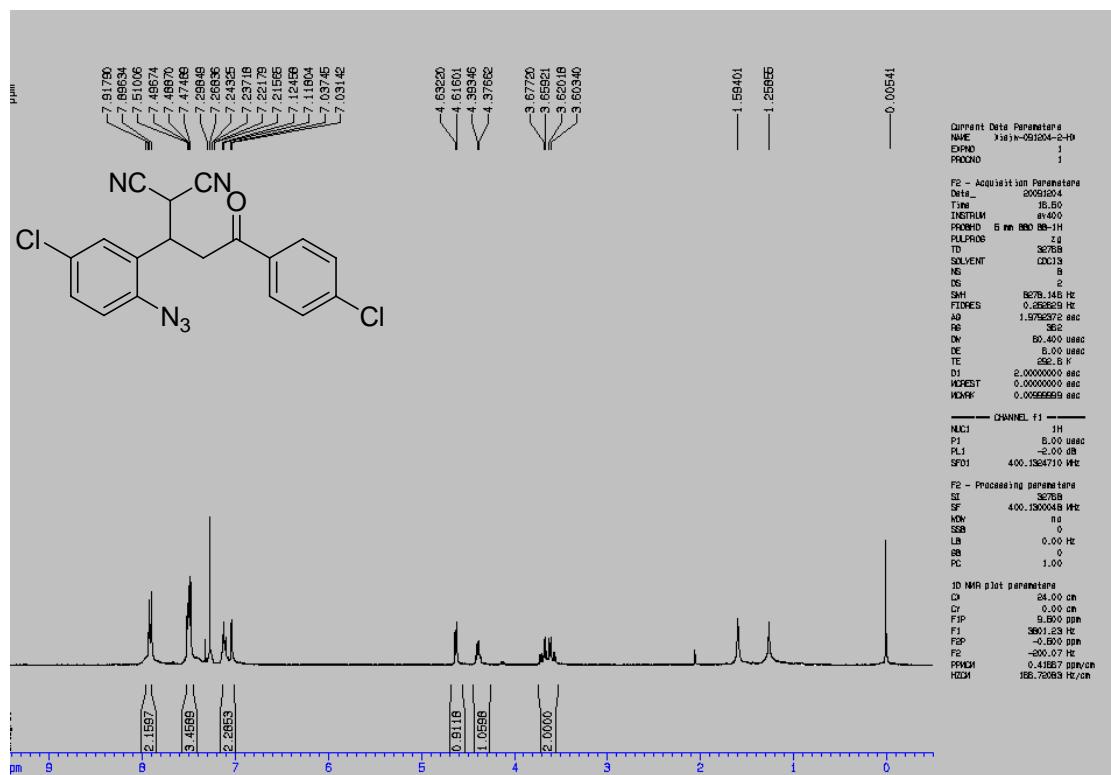


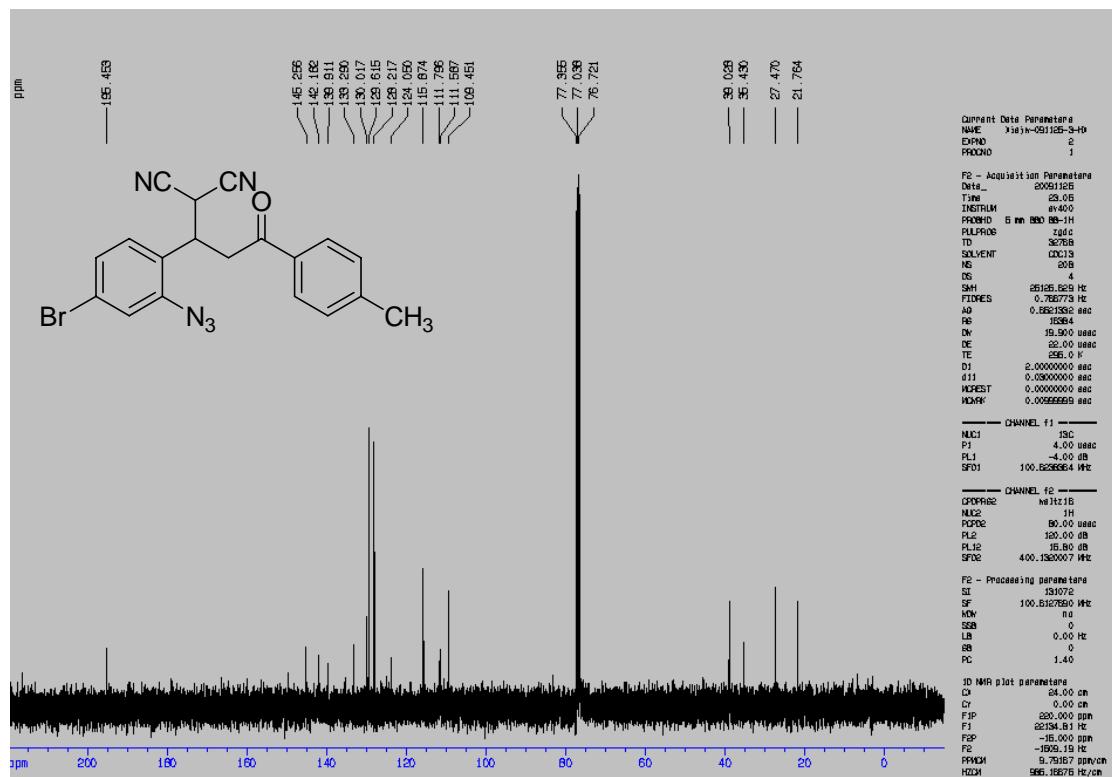
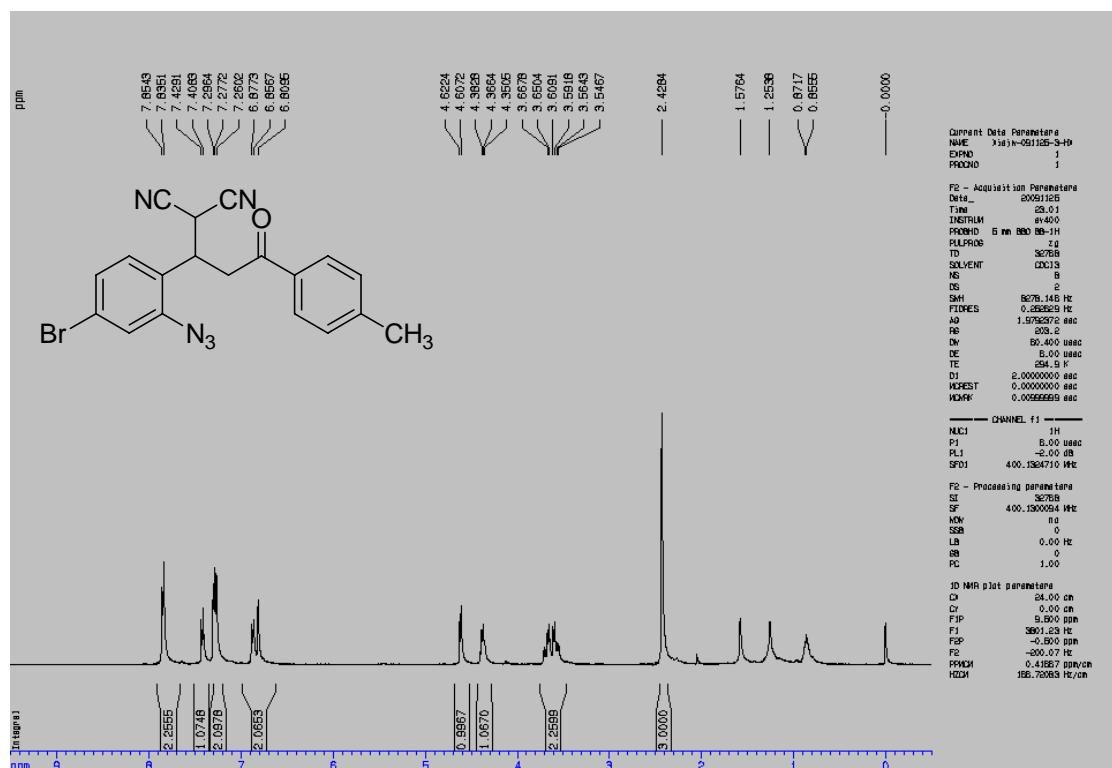


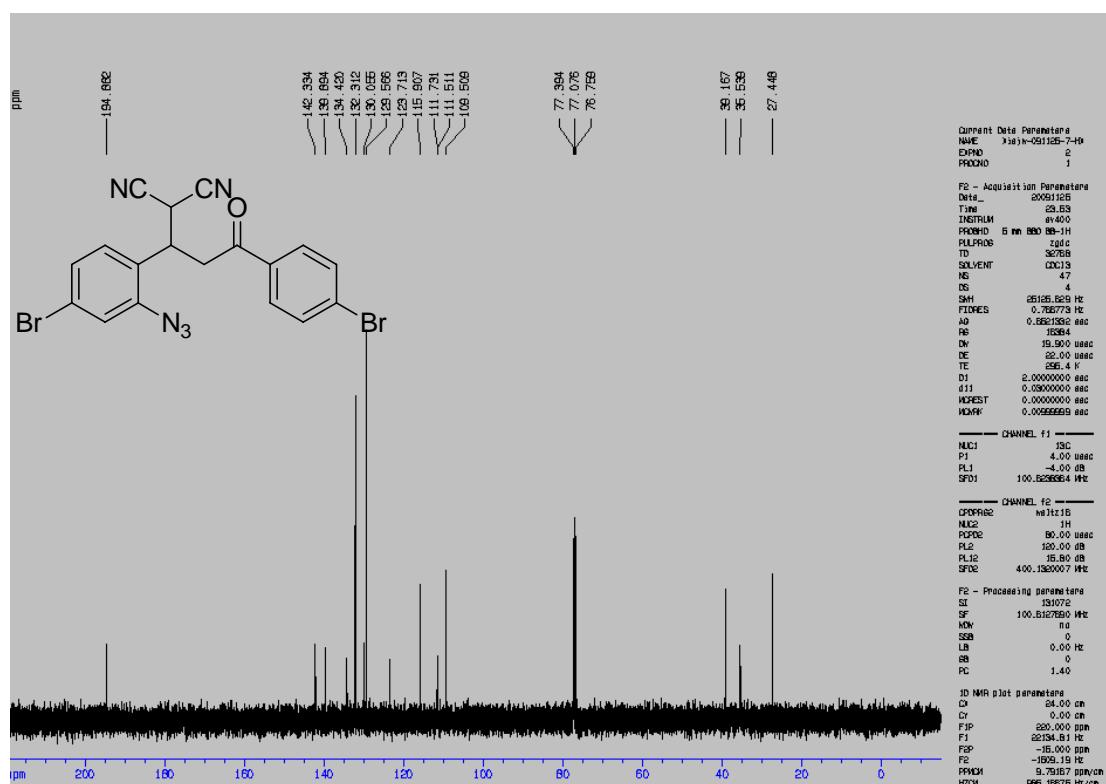
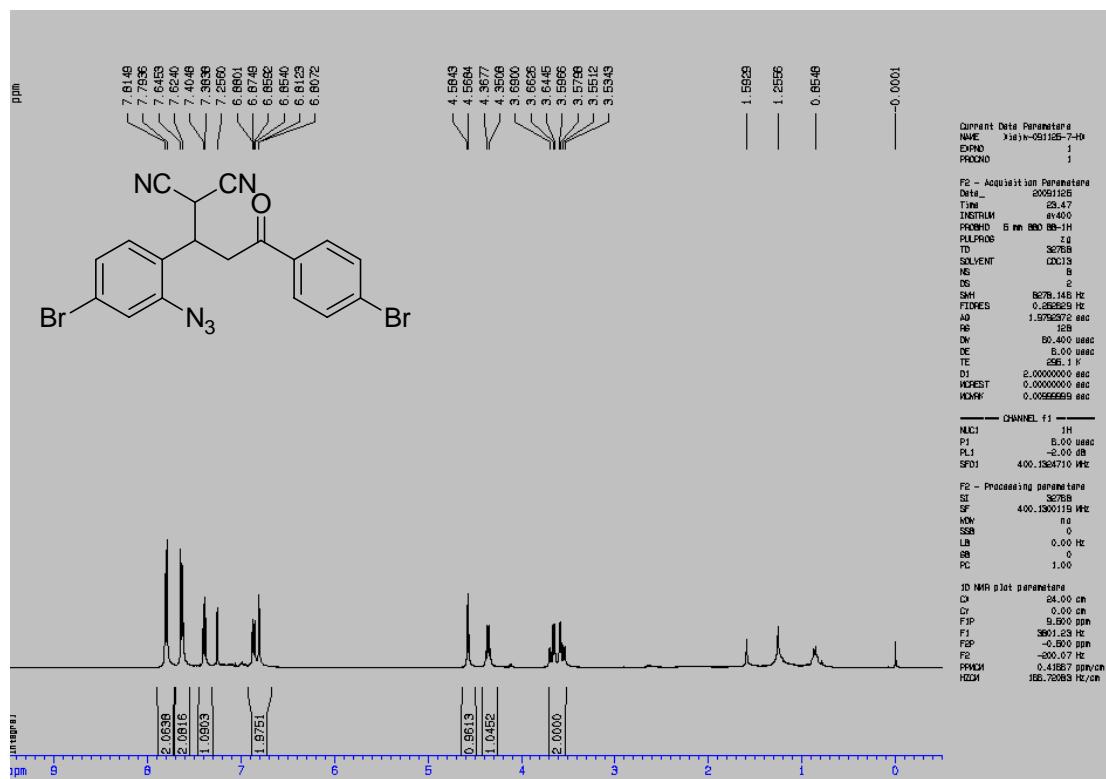


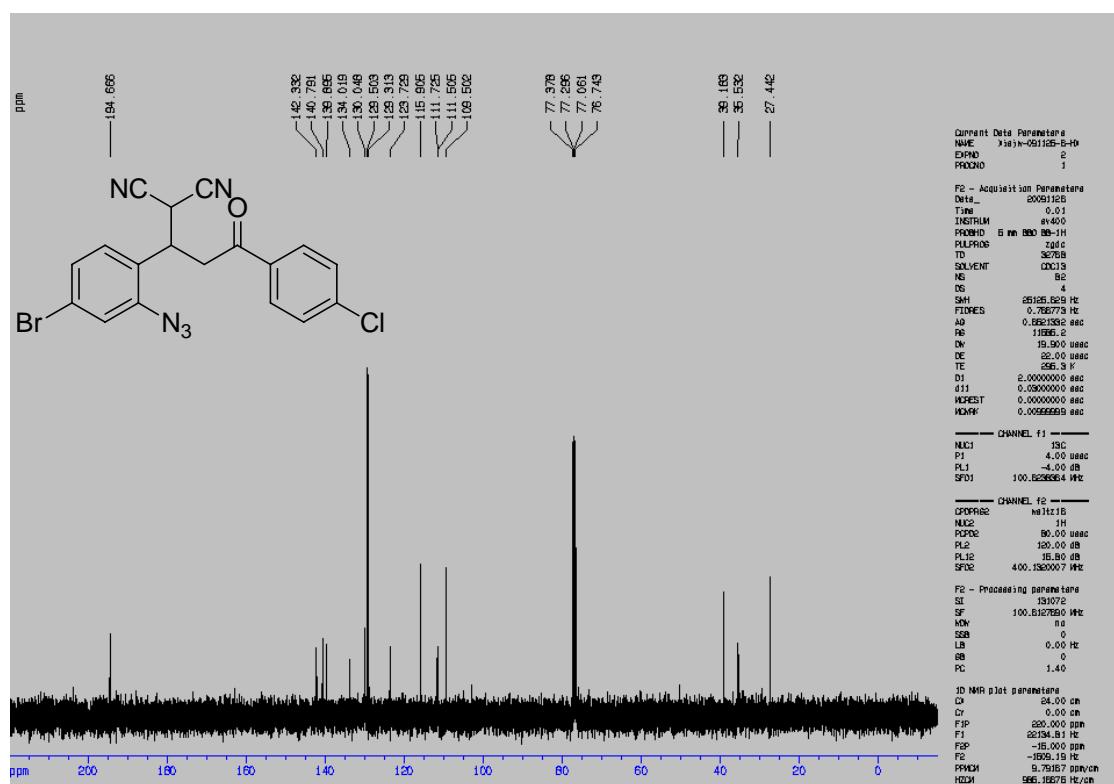
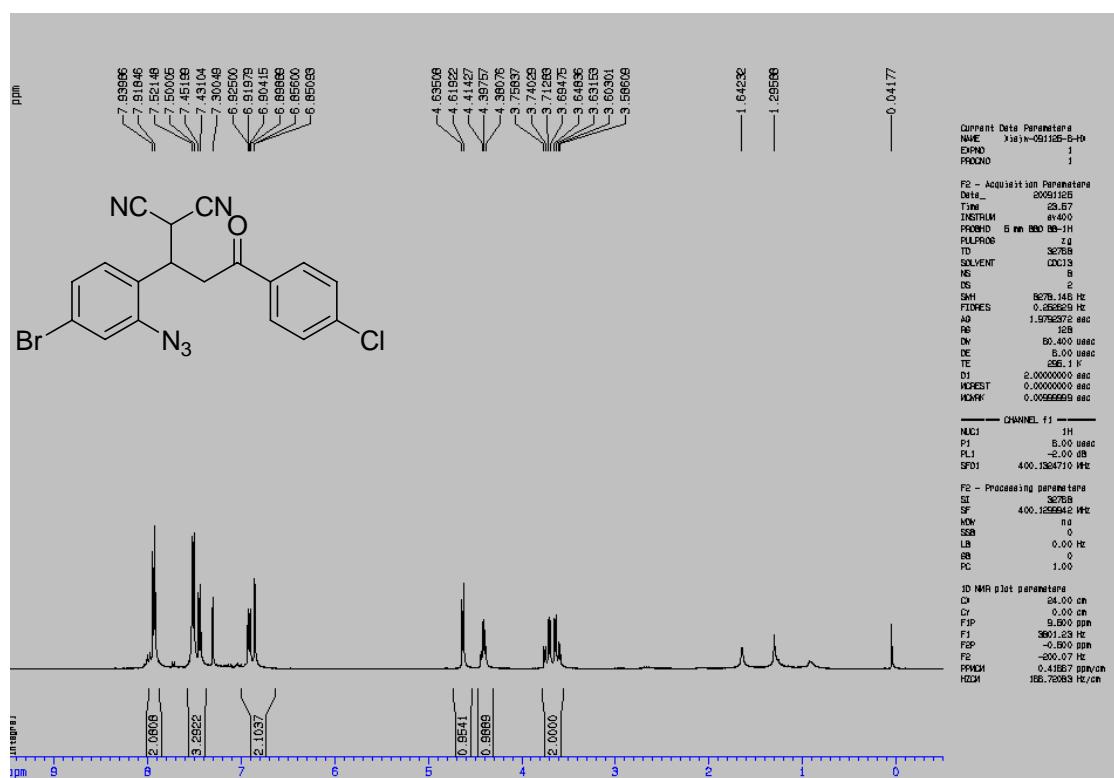


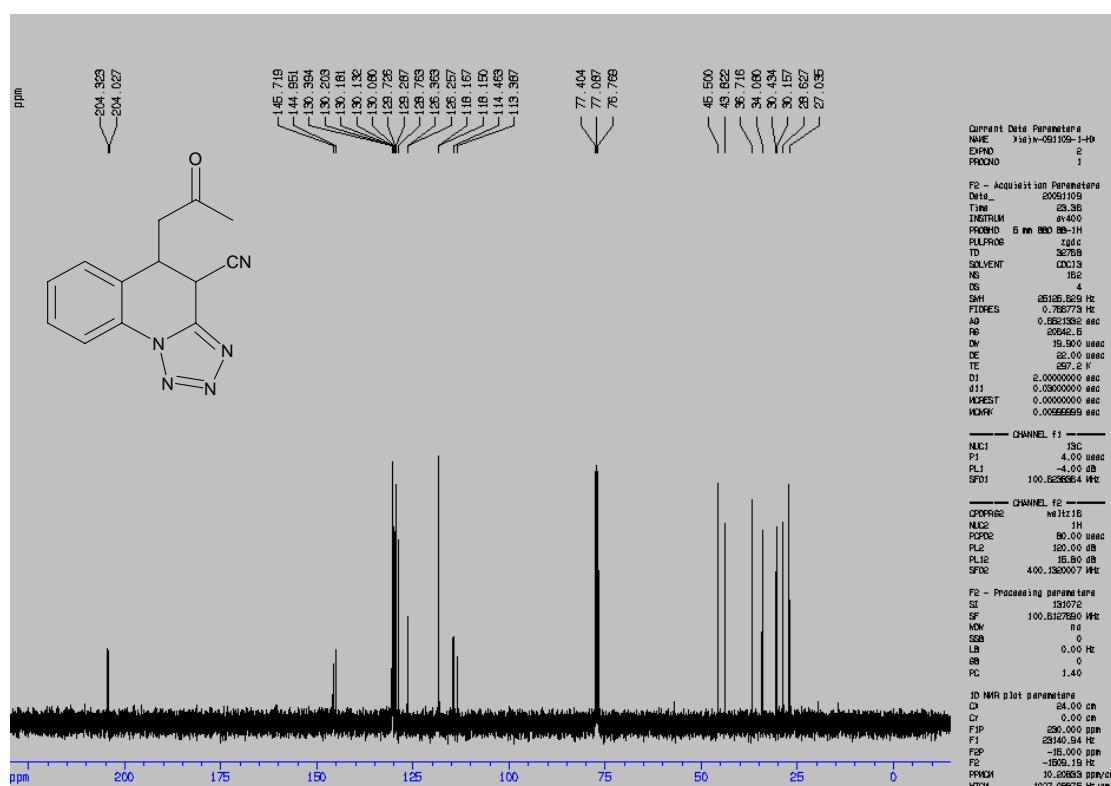
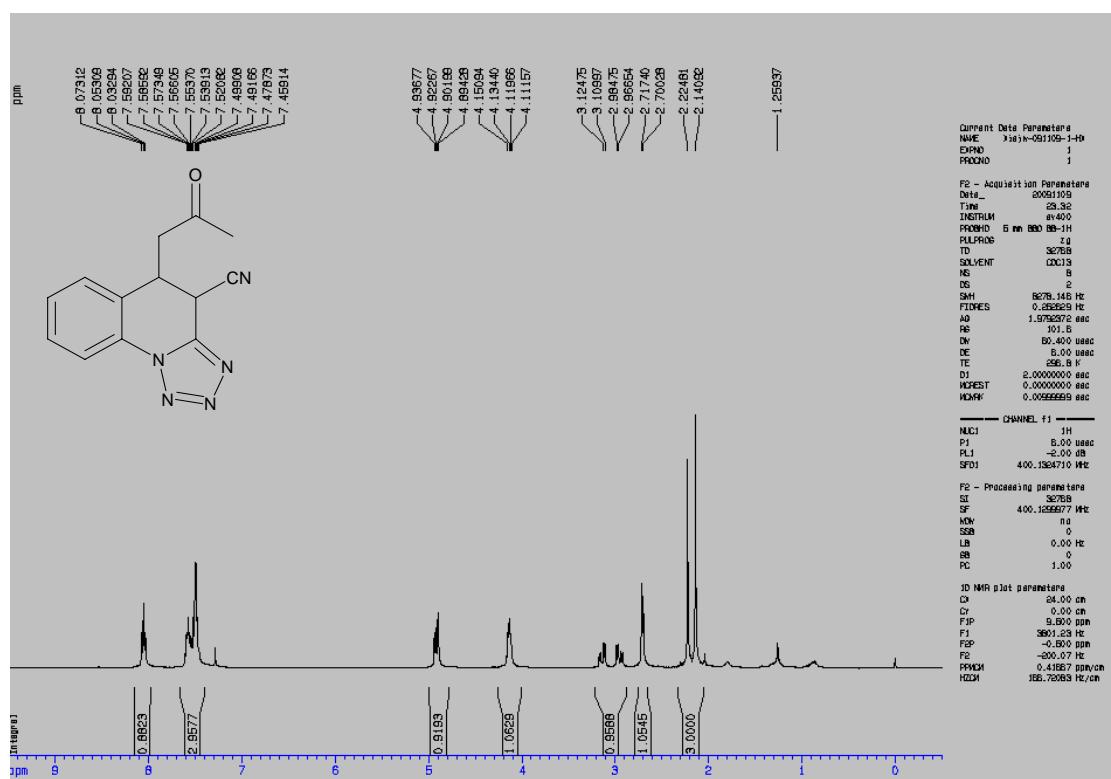


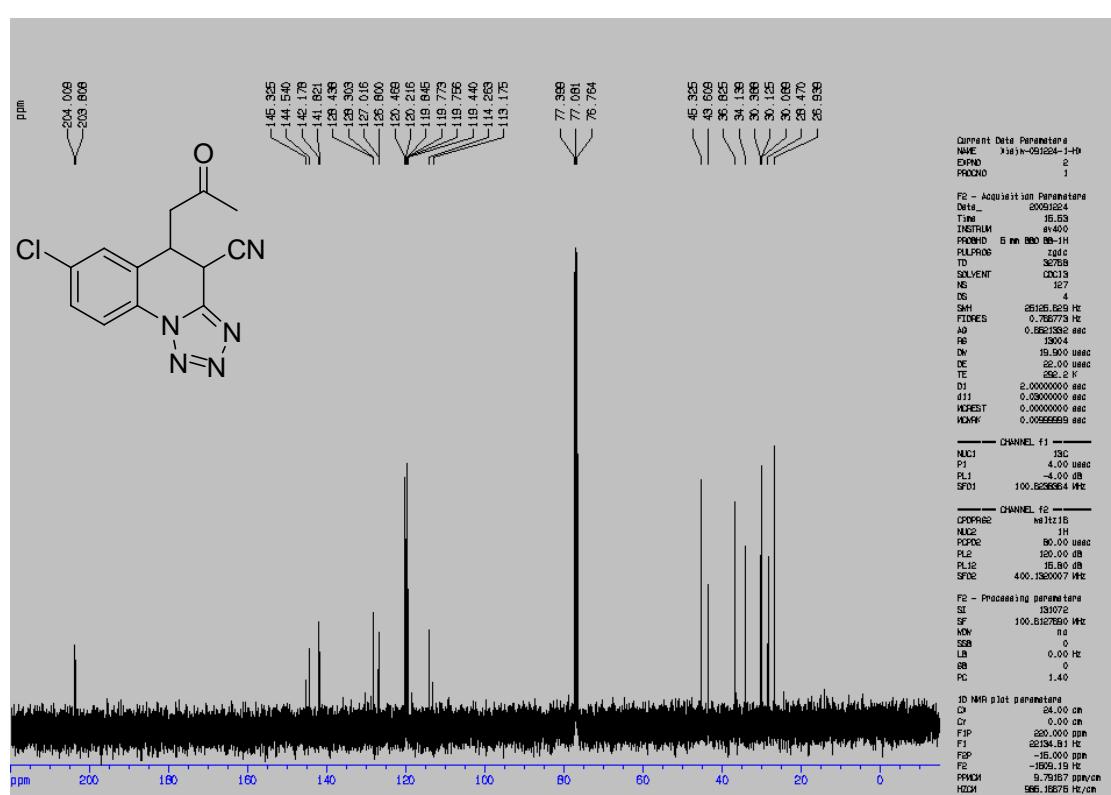
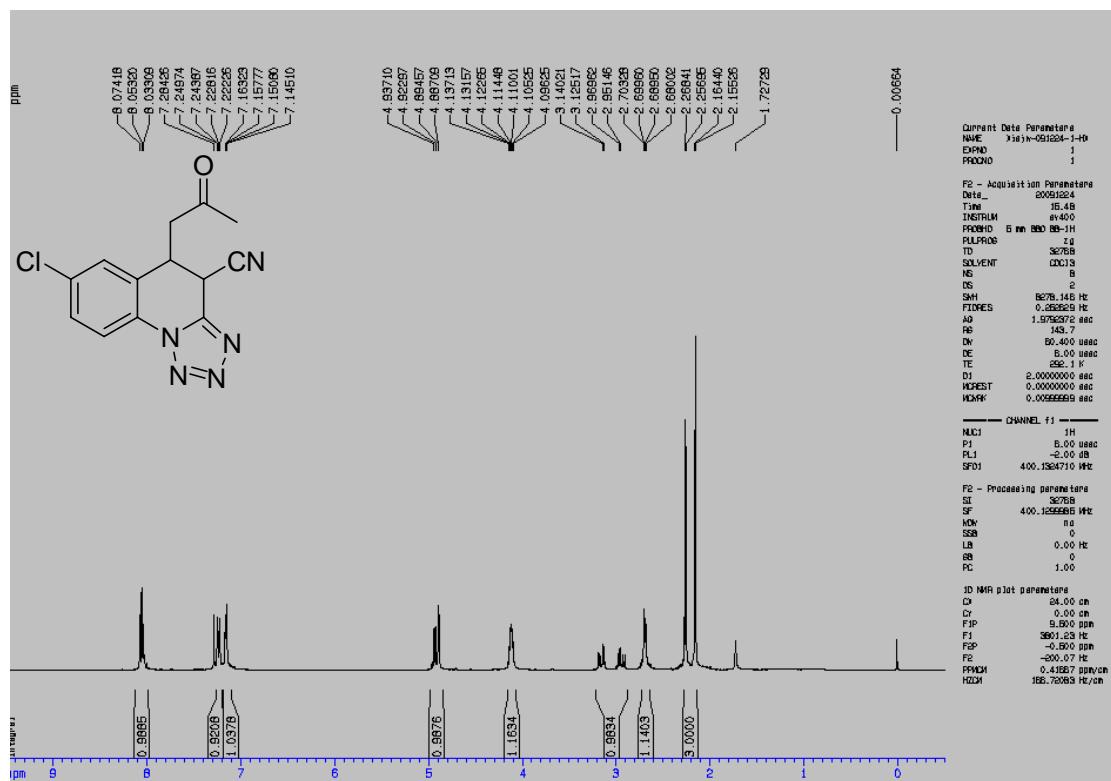


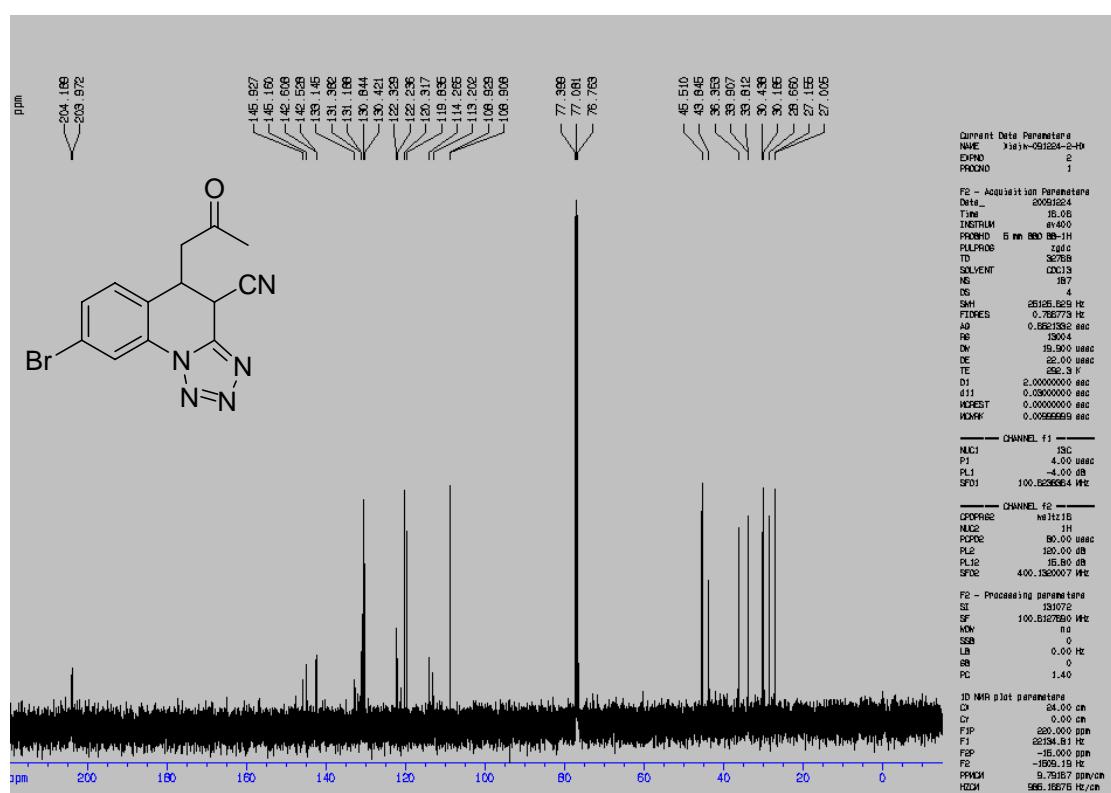
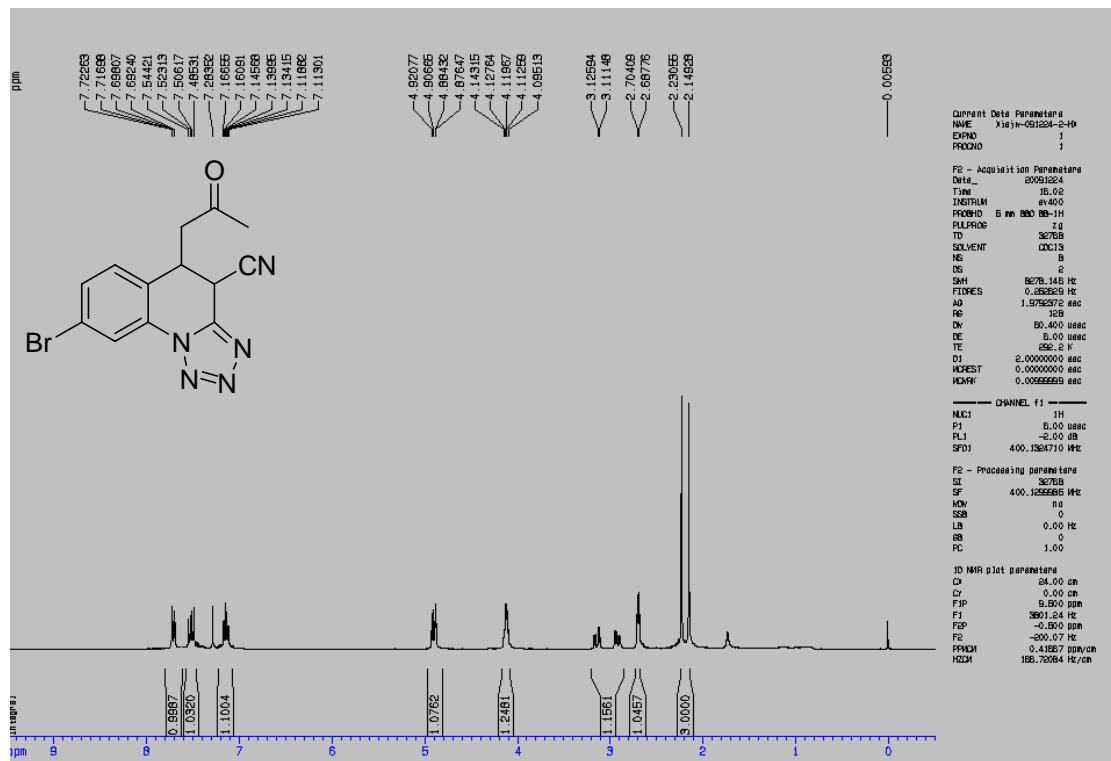


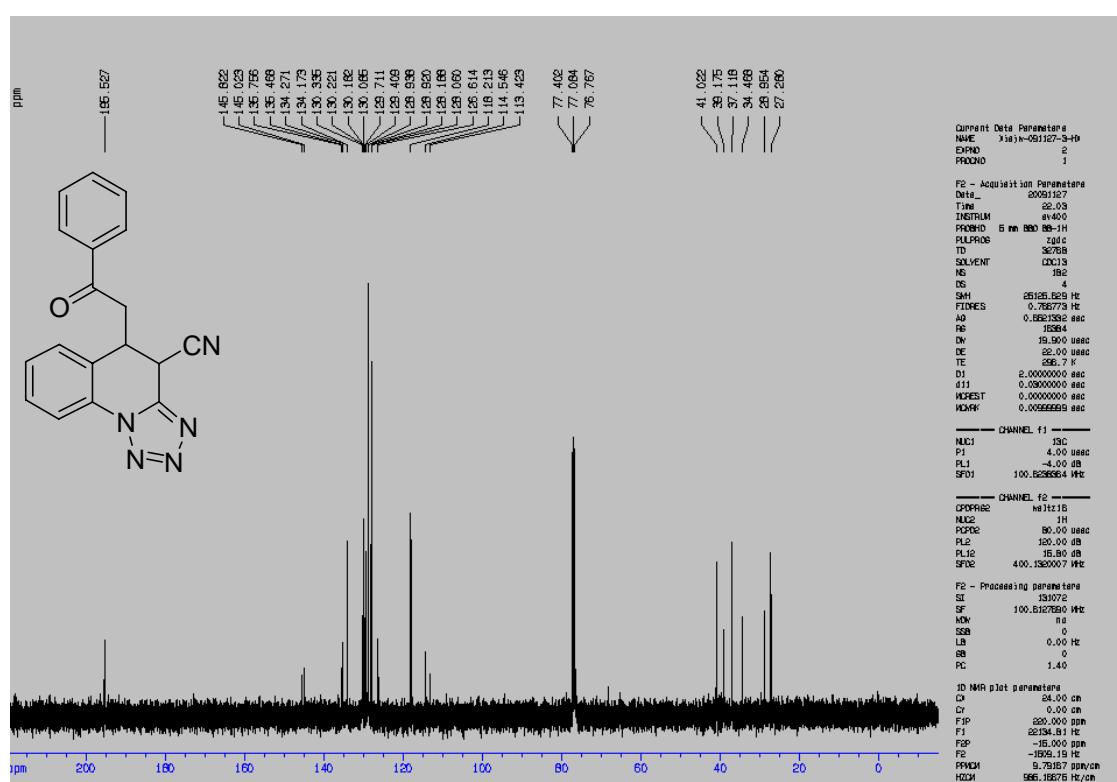
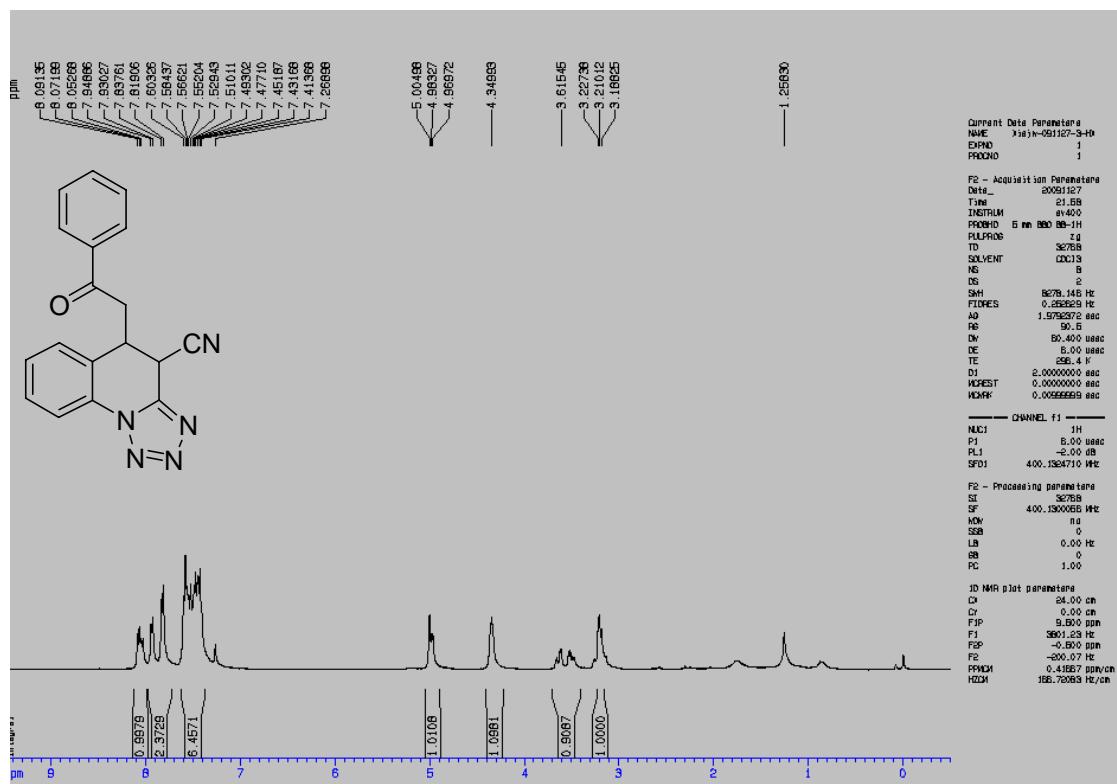


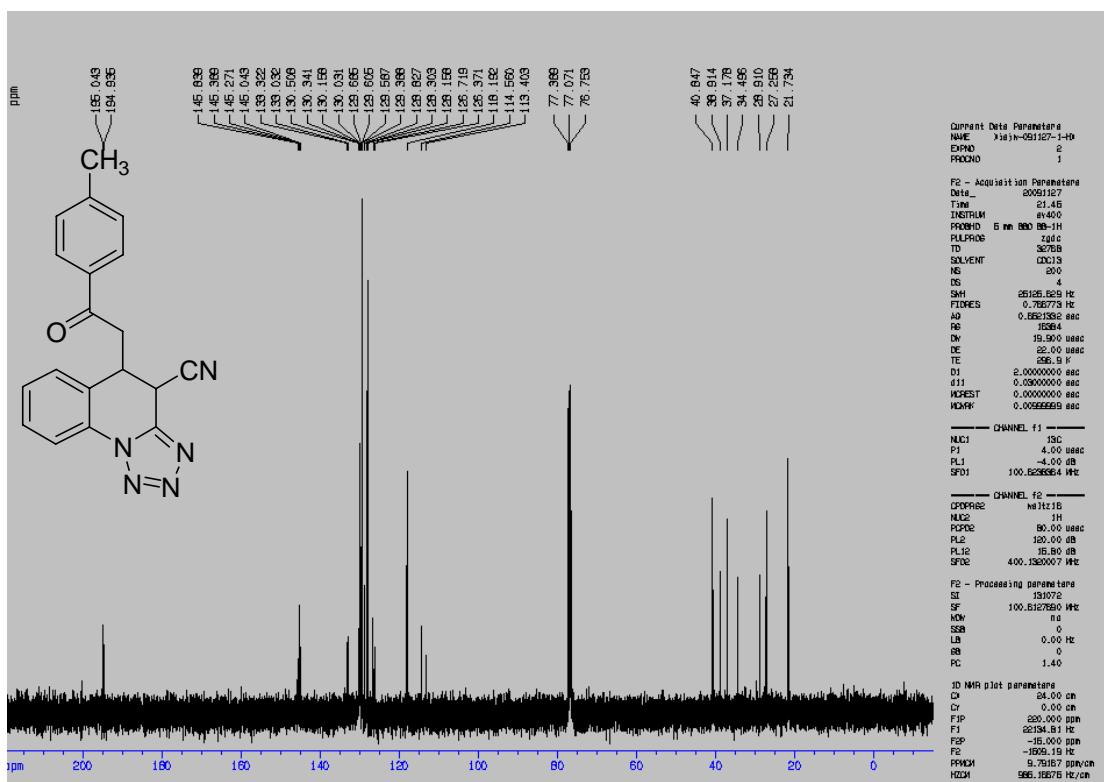
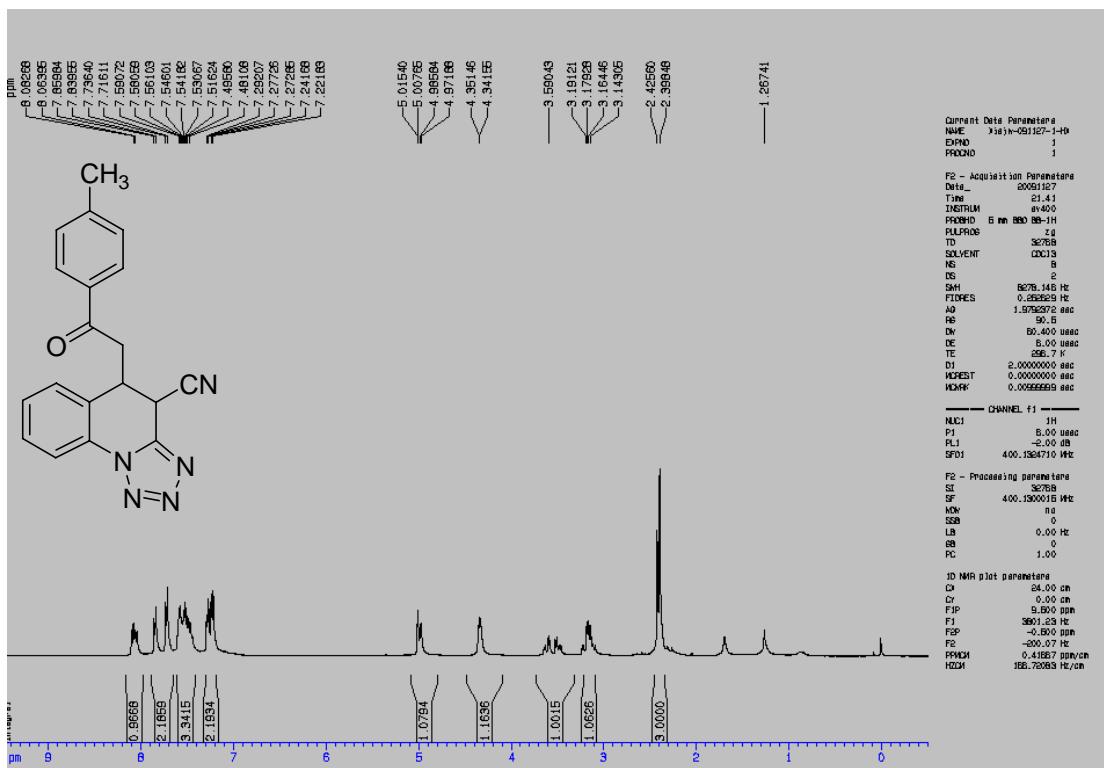


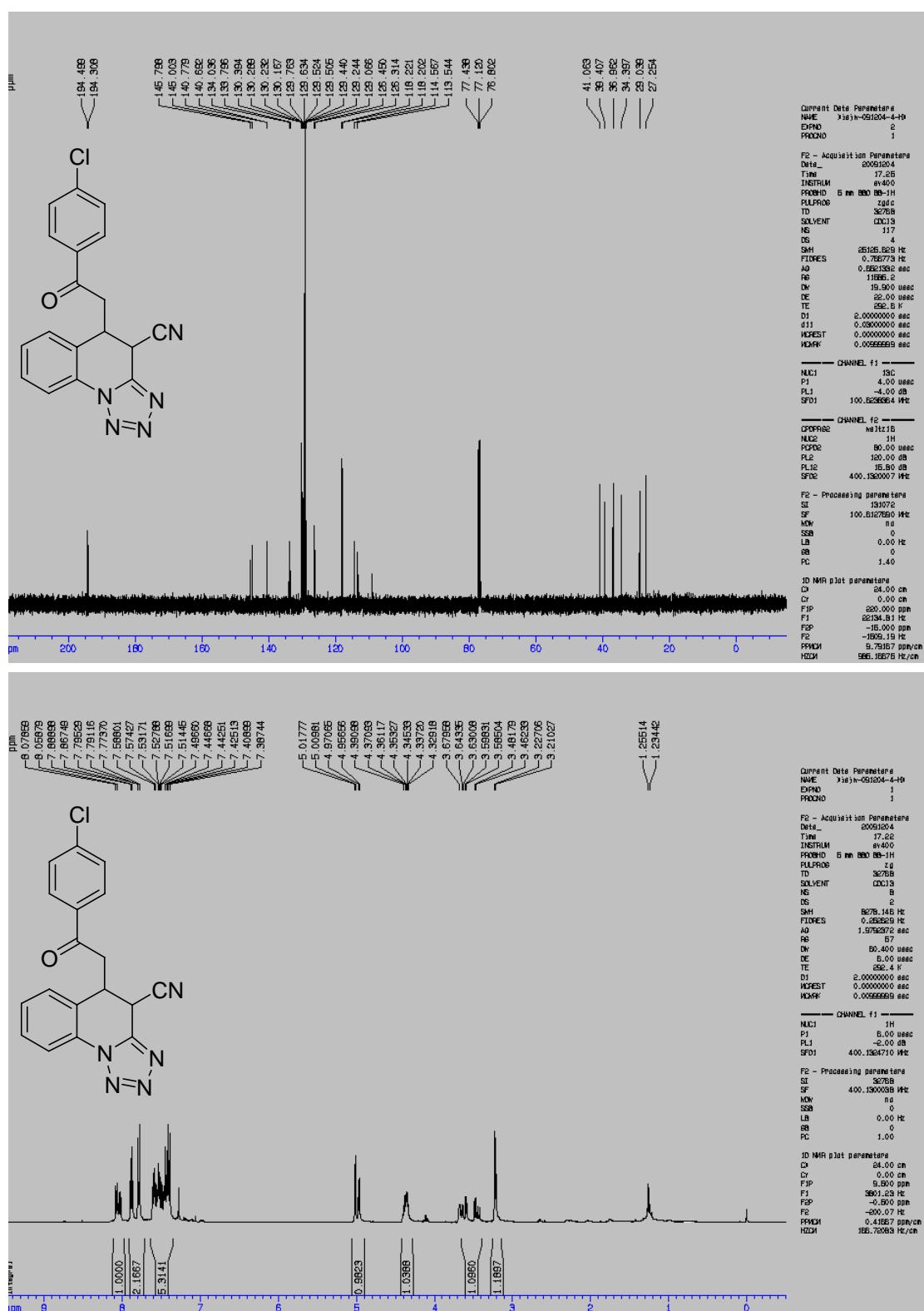


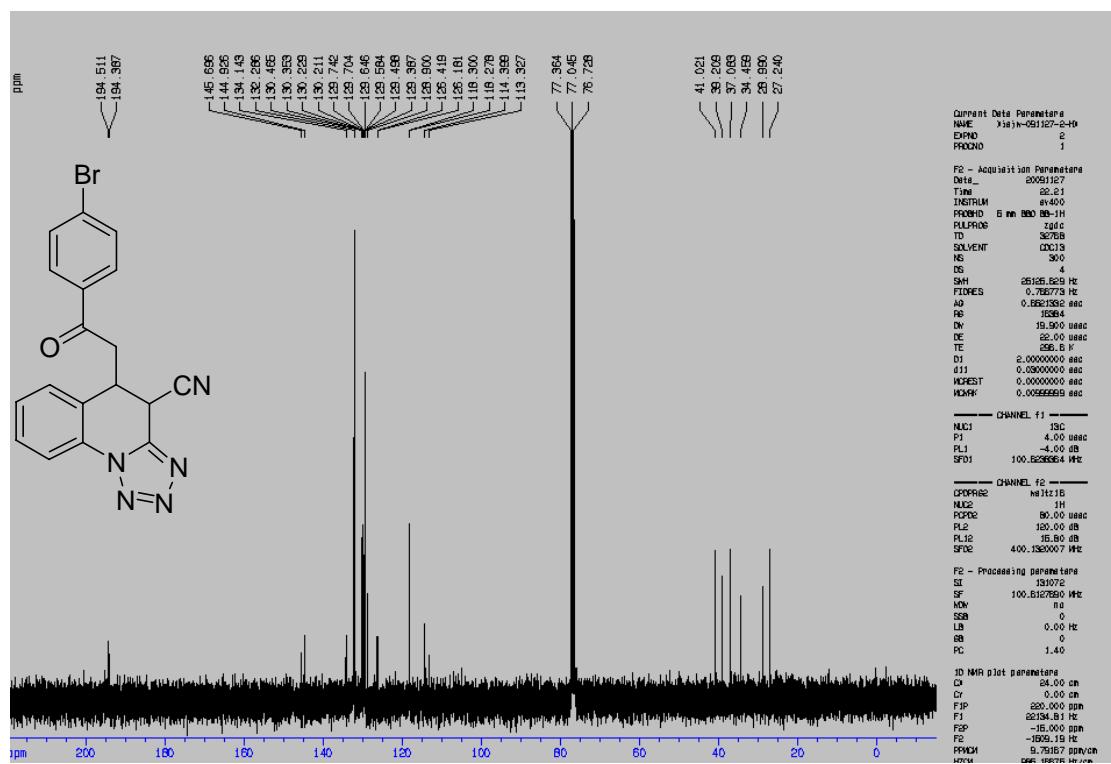
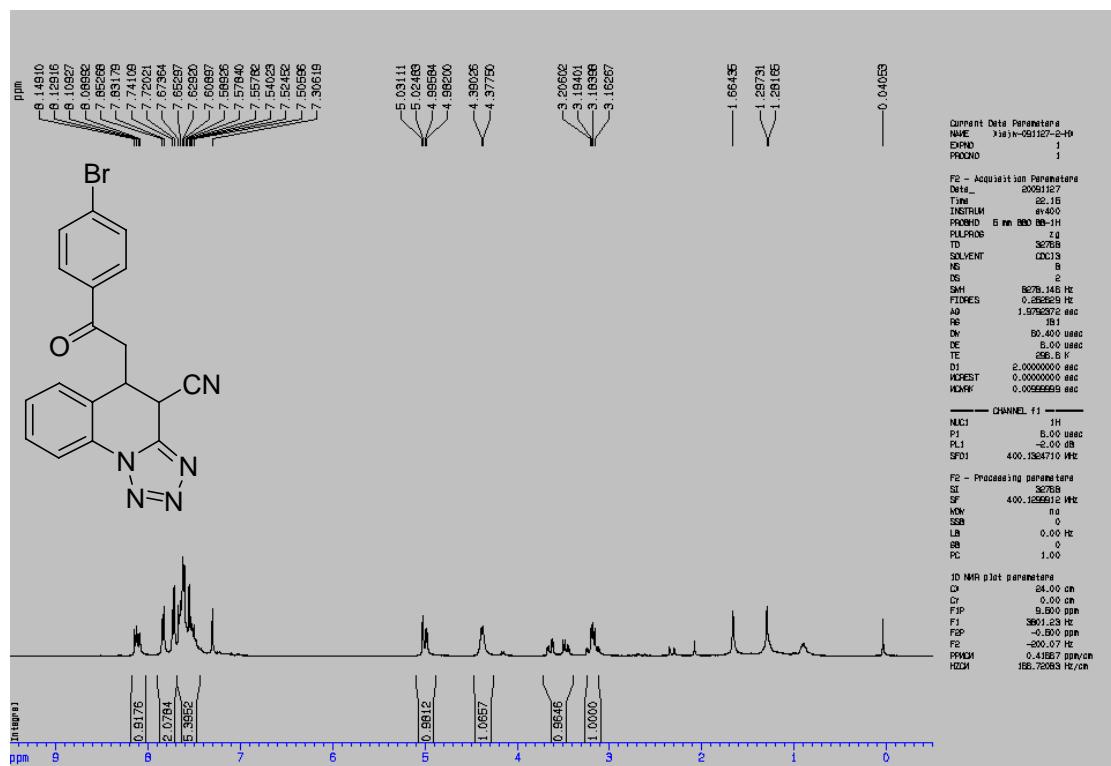


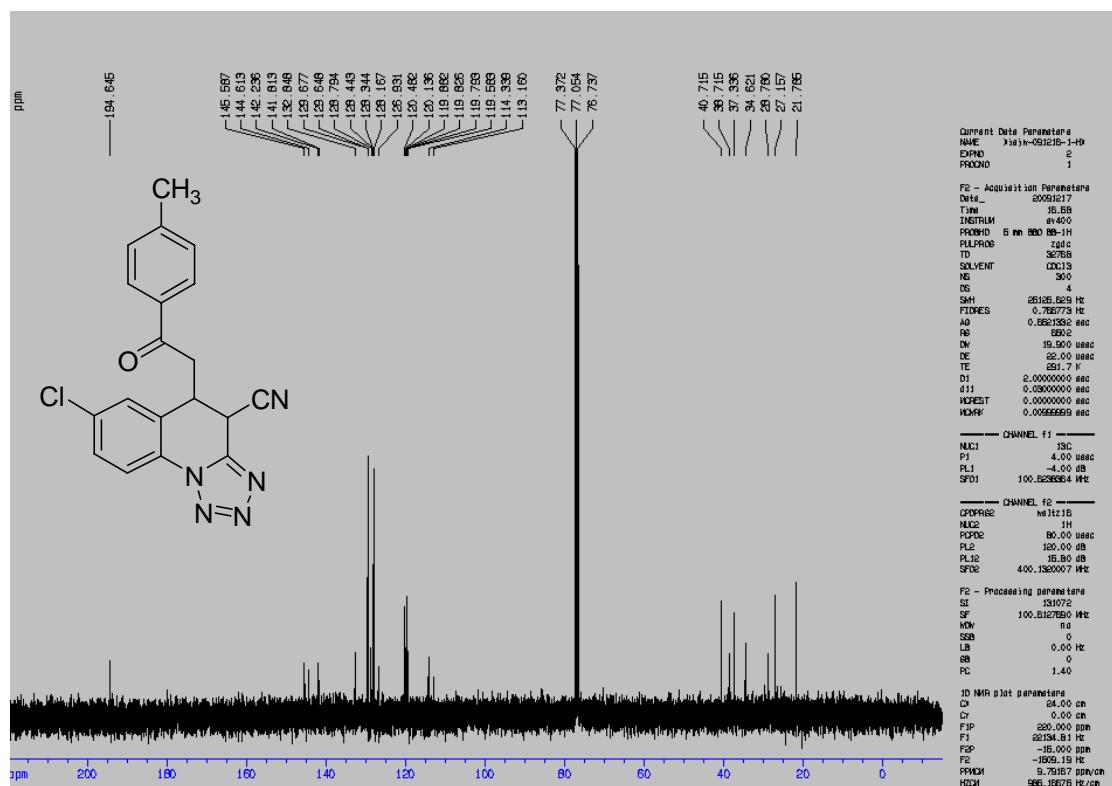
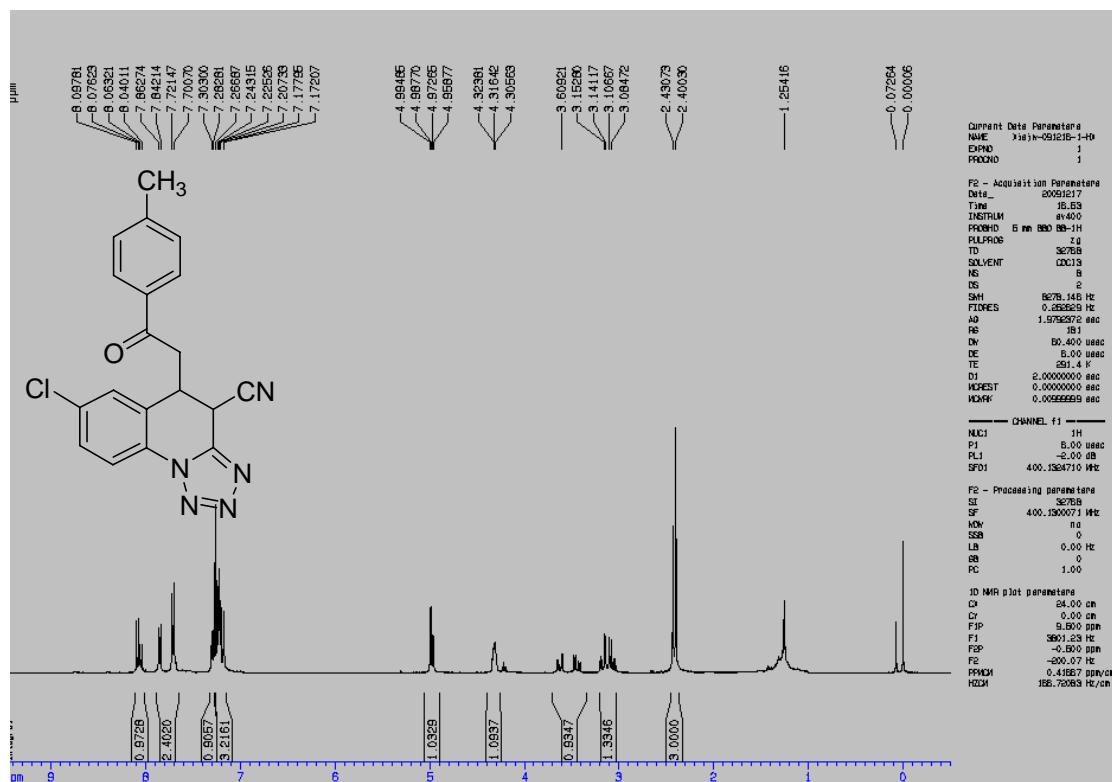


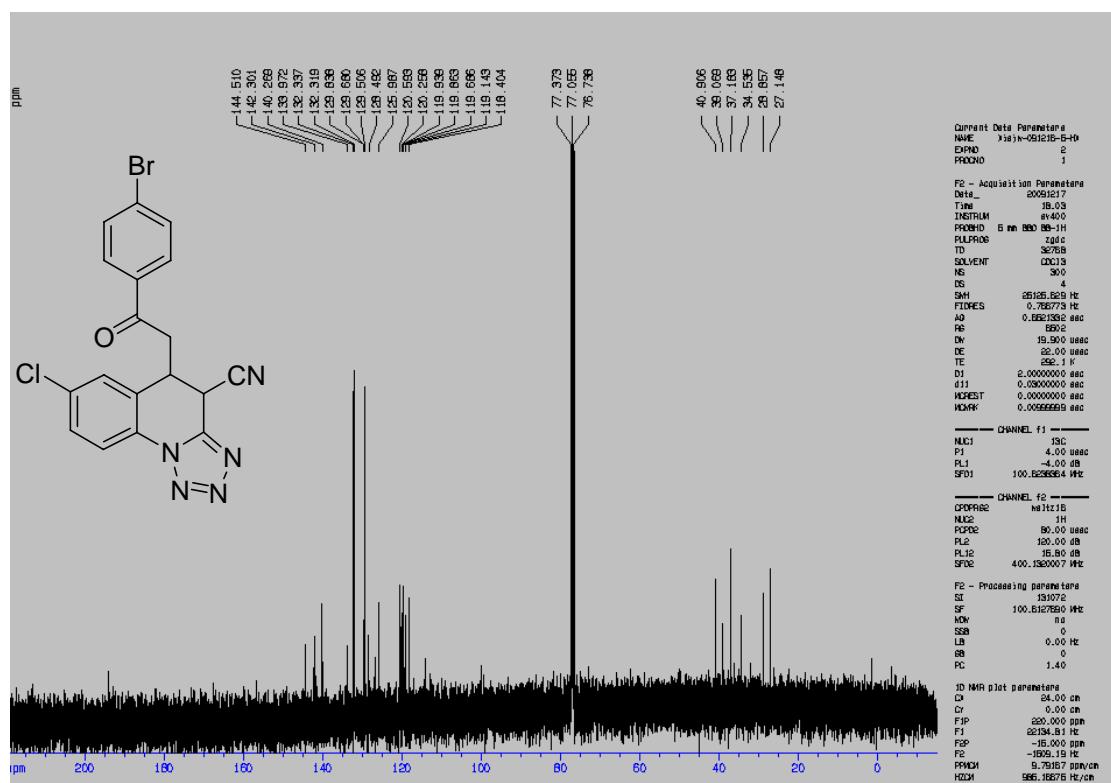
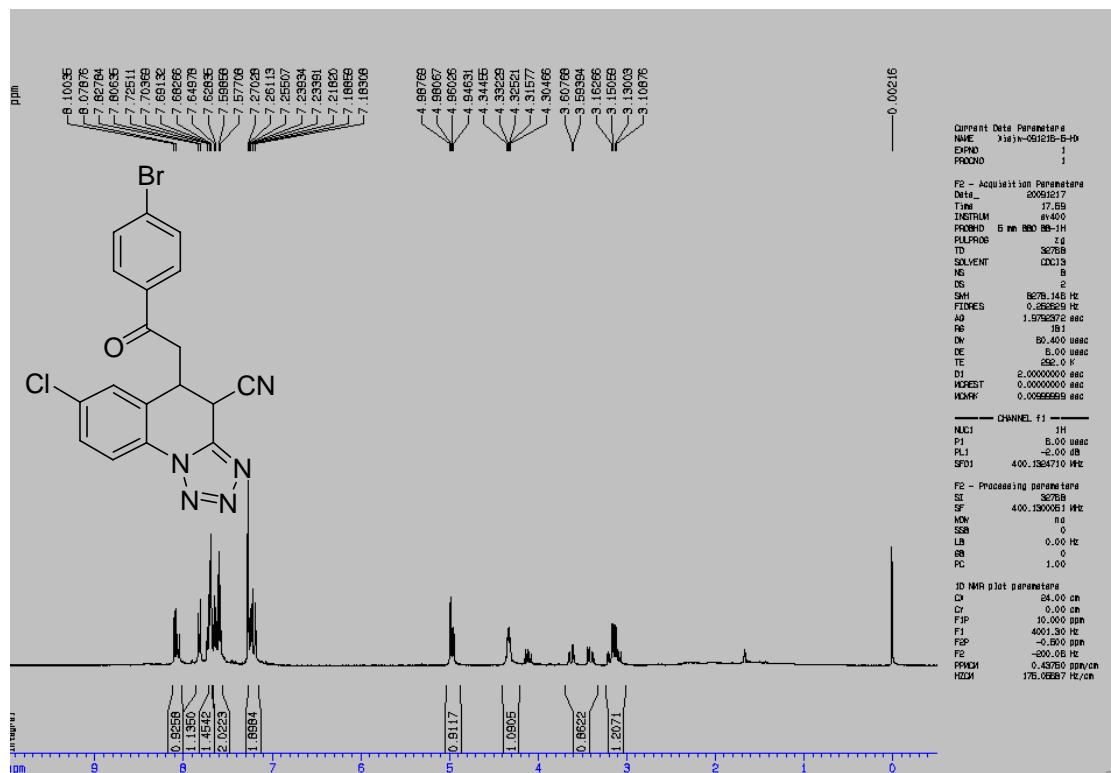


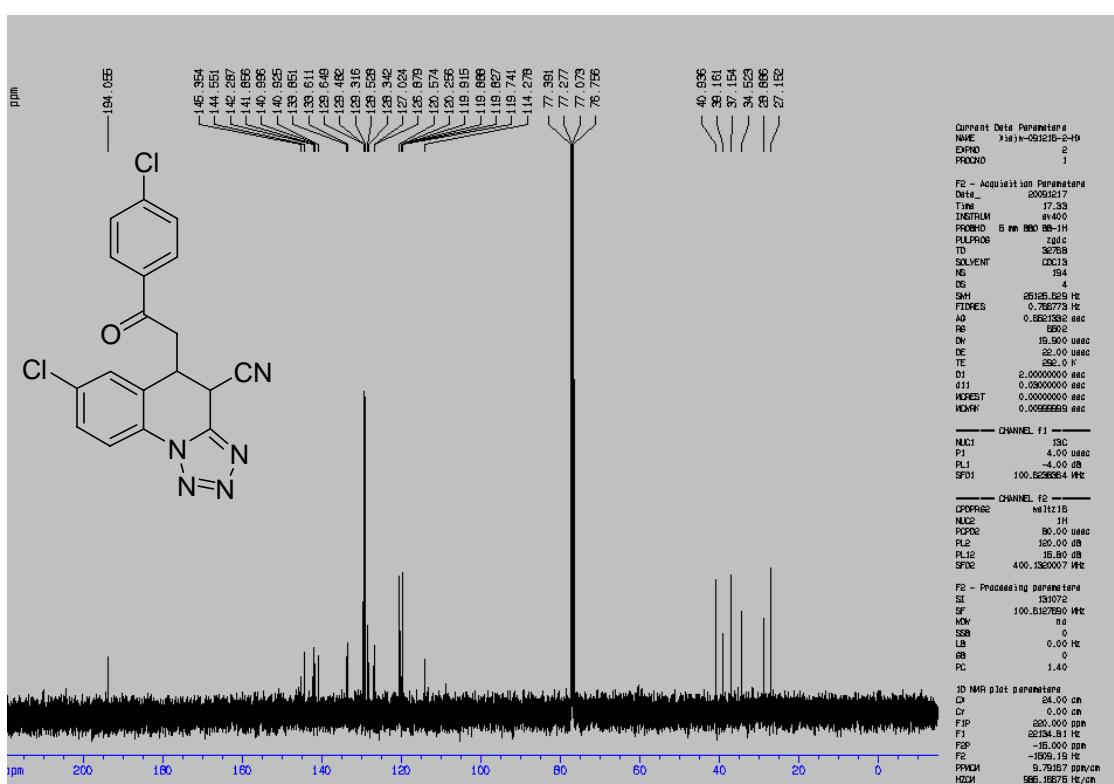
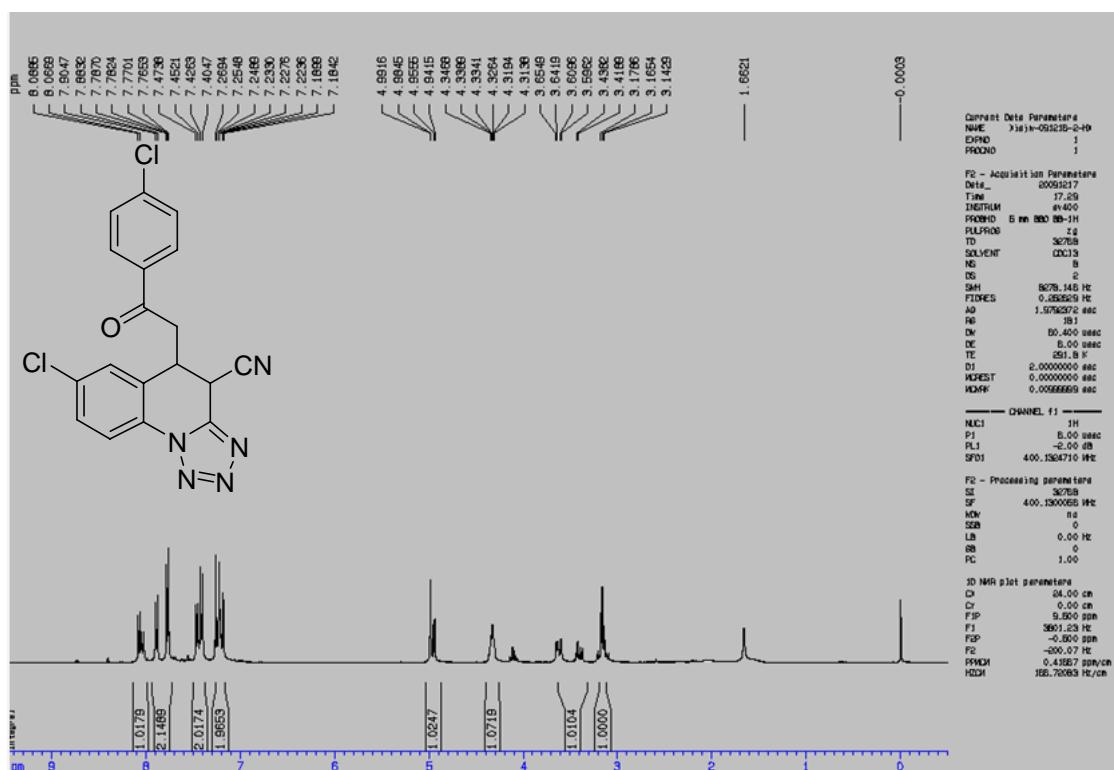


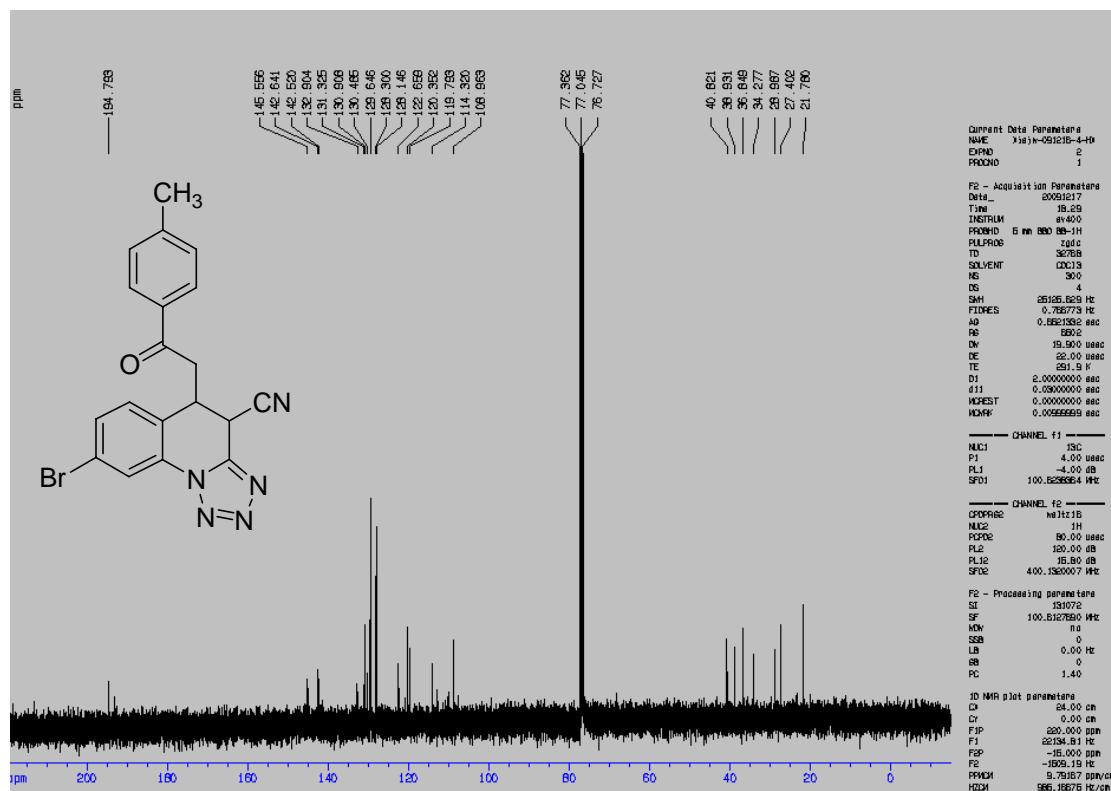
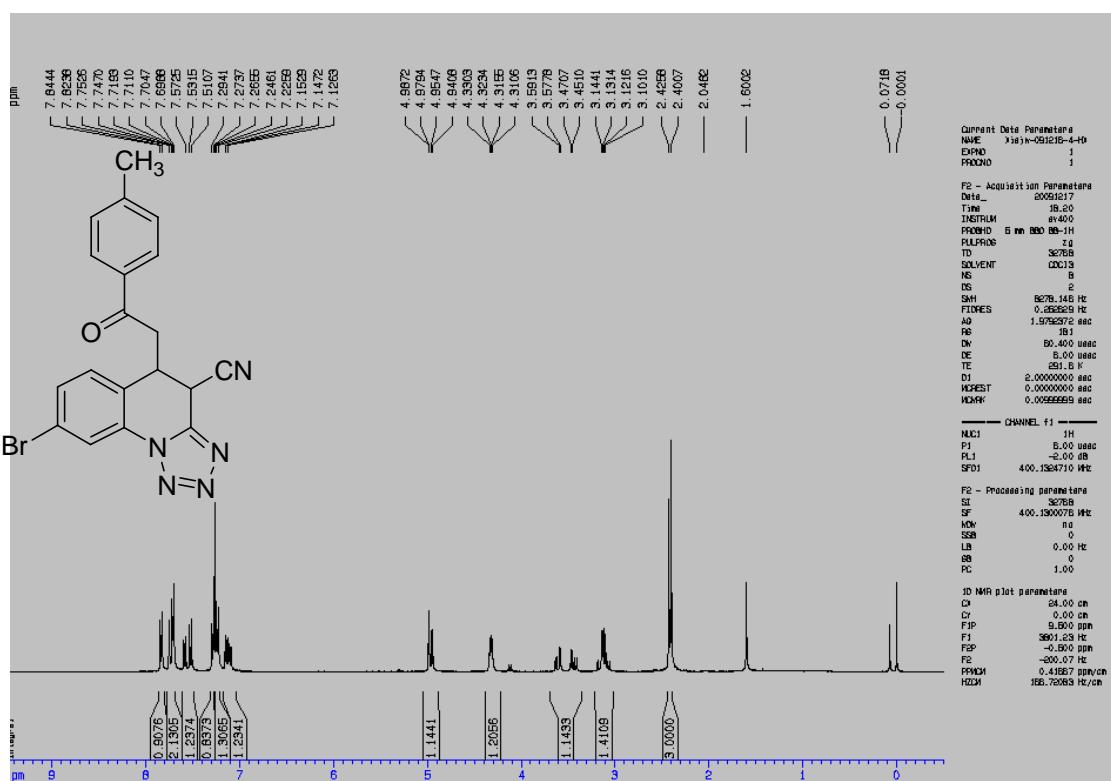


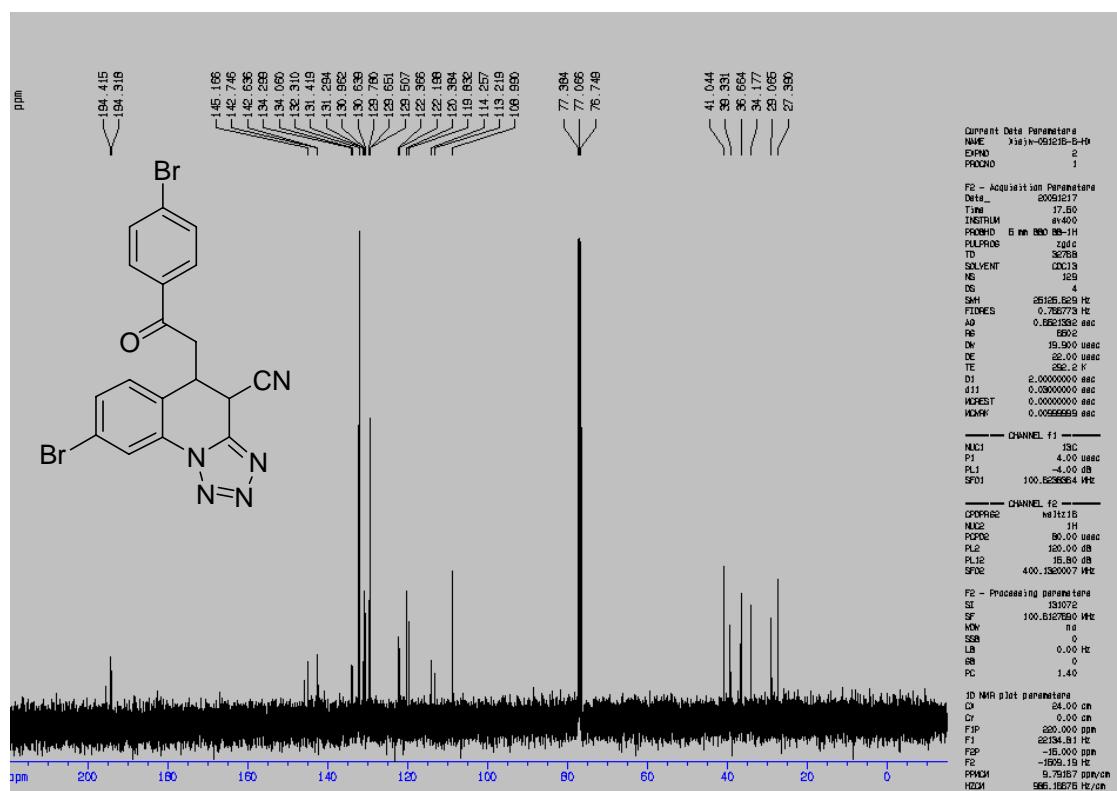
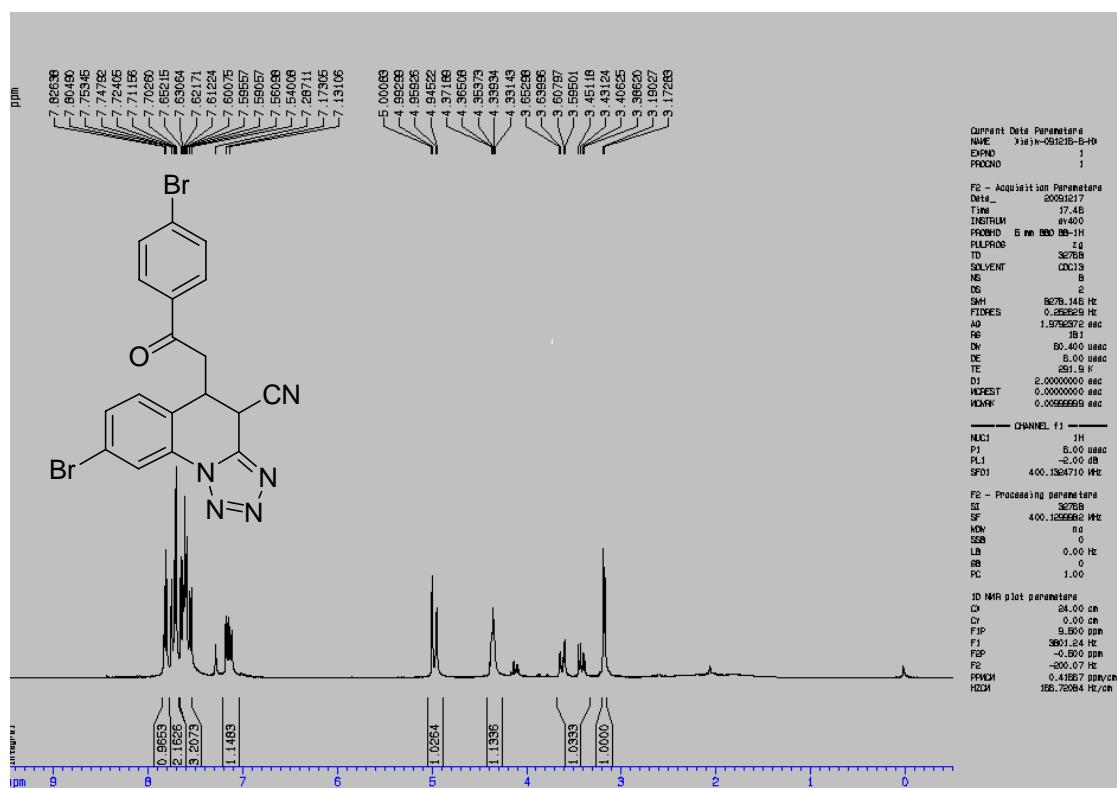


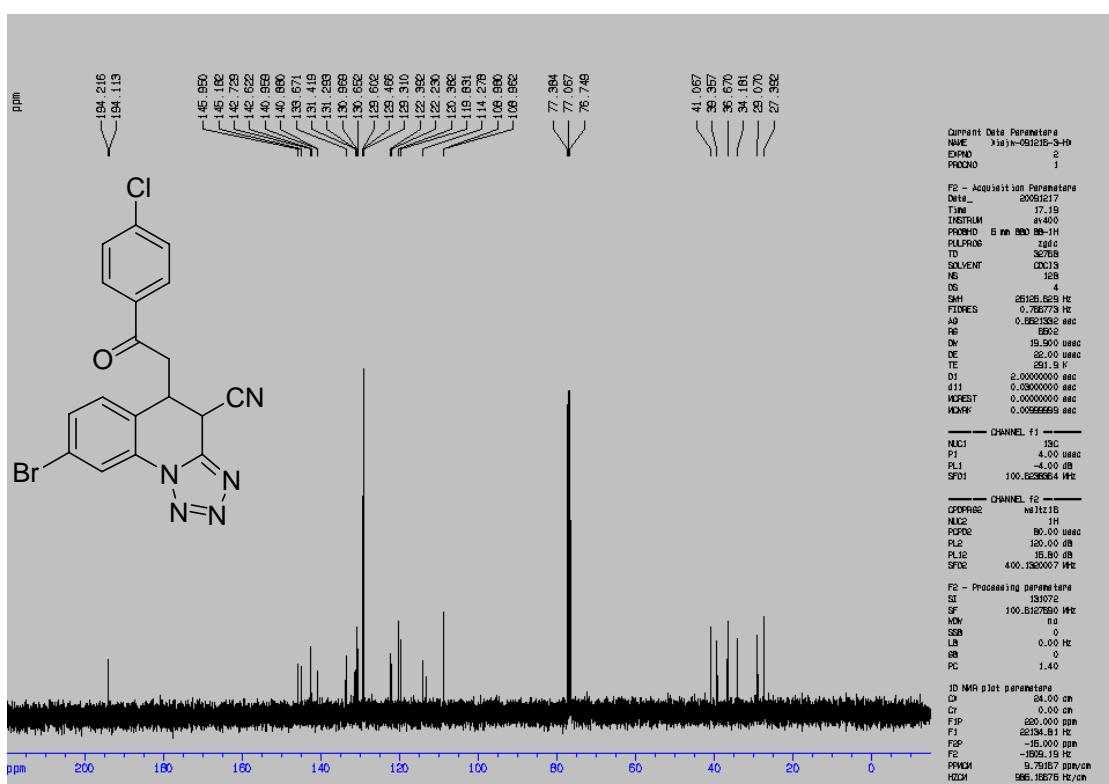
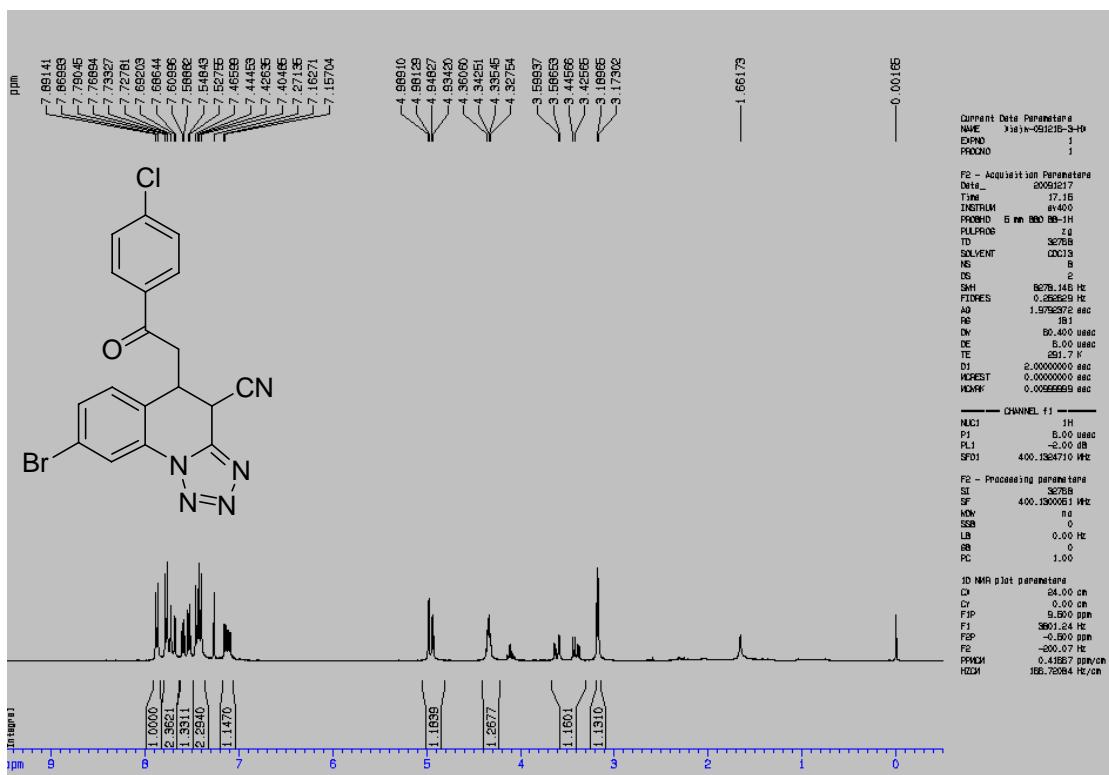




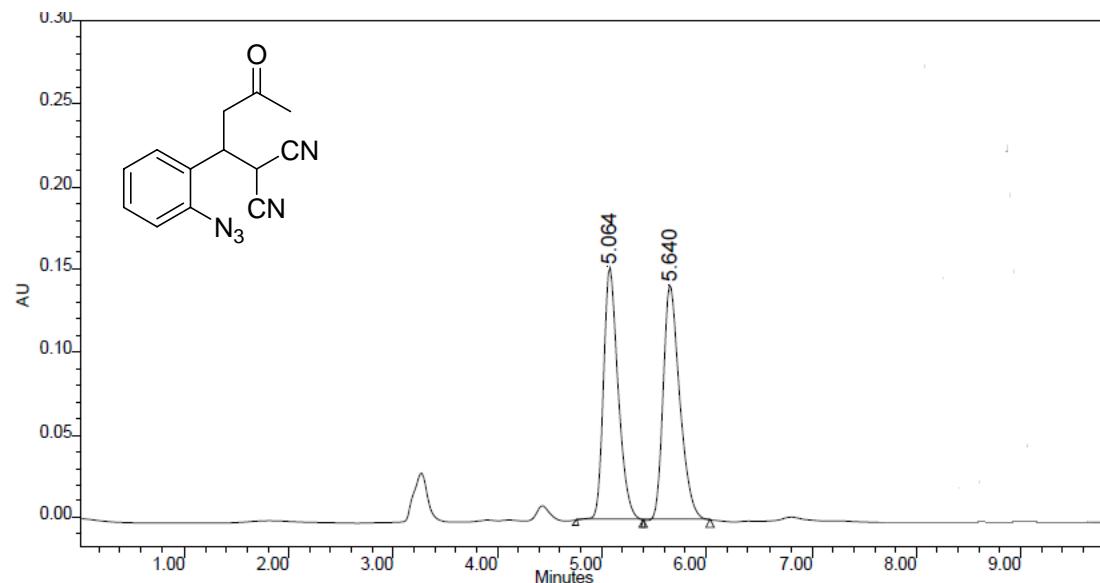




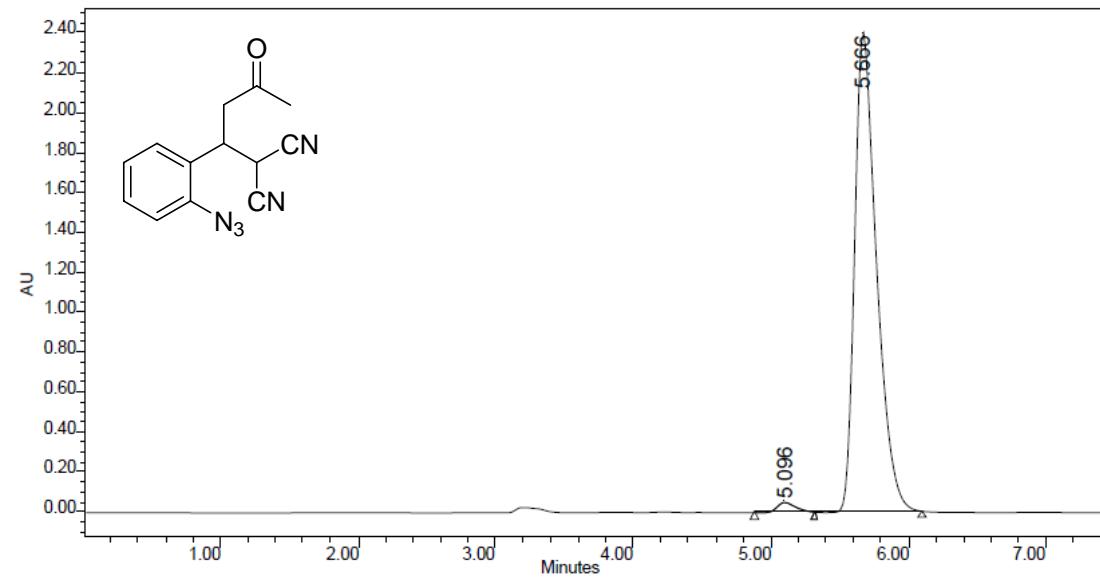




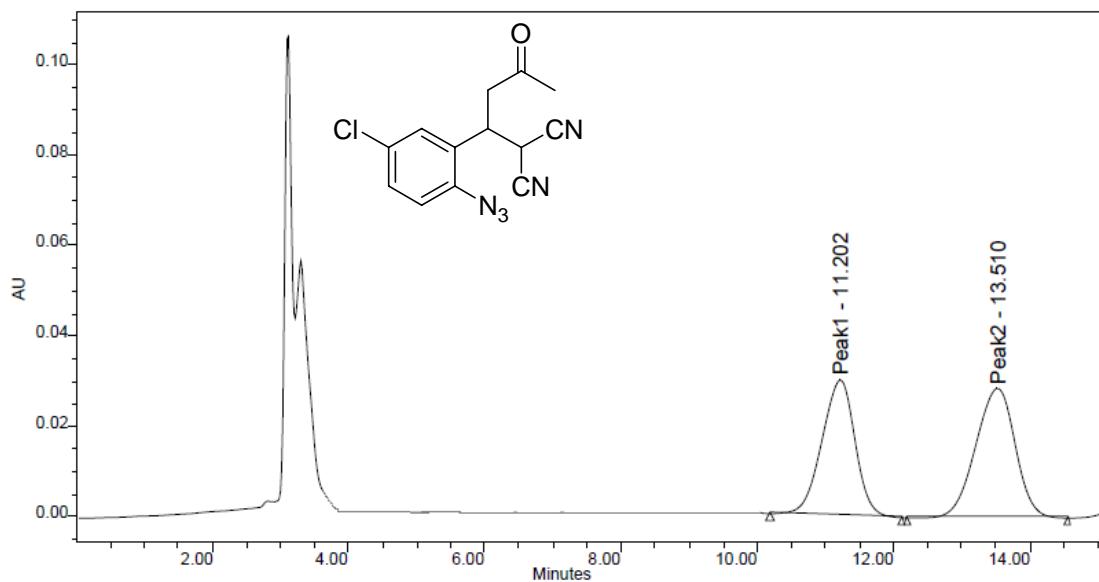
HPLC Spectra



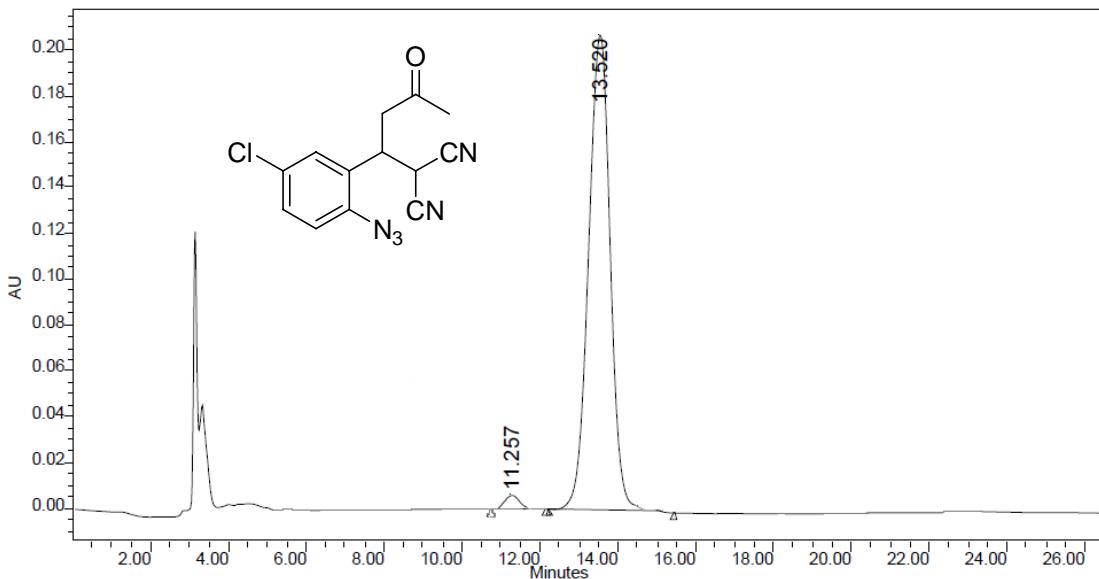
	RT (min)	Area ($\text{mV}^{\ast}\text{sec}$)	% Area	Height (mV)	% Height
1	5.064	1485705	48.74	152183	51.66
2	5.640	1562304	51.26	142393	48.34



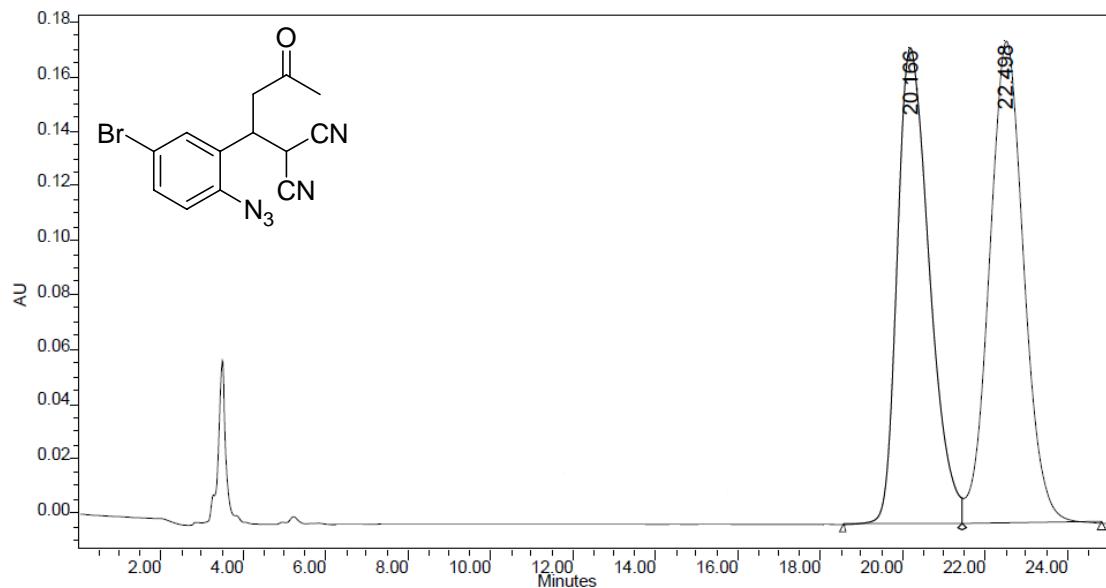
	RT (min)	Area ($\text{mV}^{\ast}\text{sec}$)	% Area	Height (mV)	% Height
1	5.096	463701	1.72	49940	2.04
2	5.666	26478827	98.28	2393238	97.96



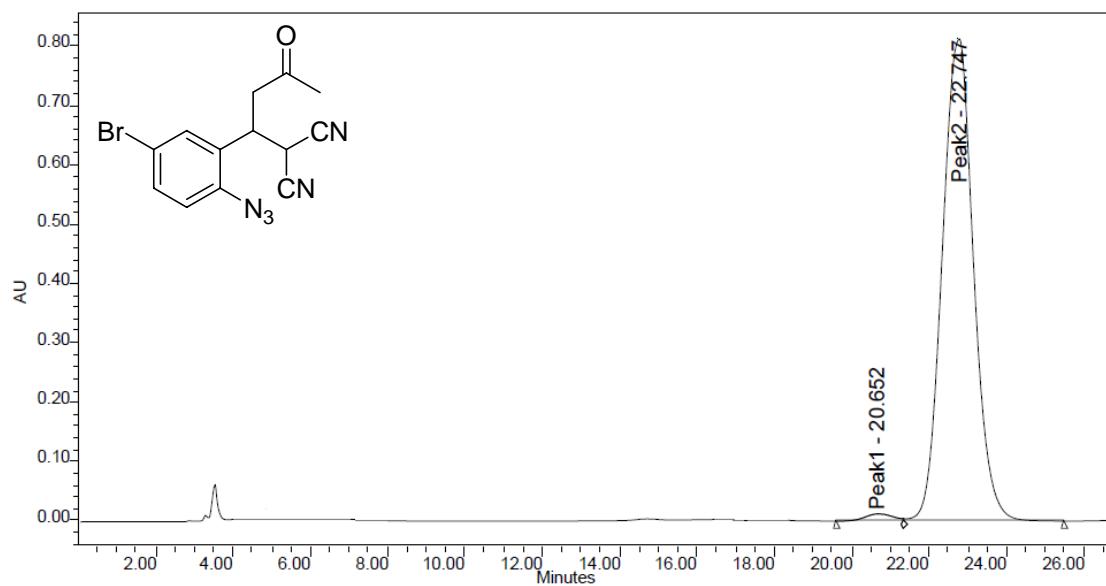
	Peak Name	RT (min)	Area (V^*sec)	% Area	Height (V)	% Height
1	Peak1	11.202	1022602	46.83	30003	51.17
2	Peak2	13.510	1160958	53.17	28634	48.83



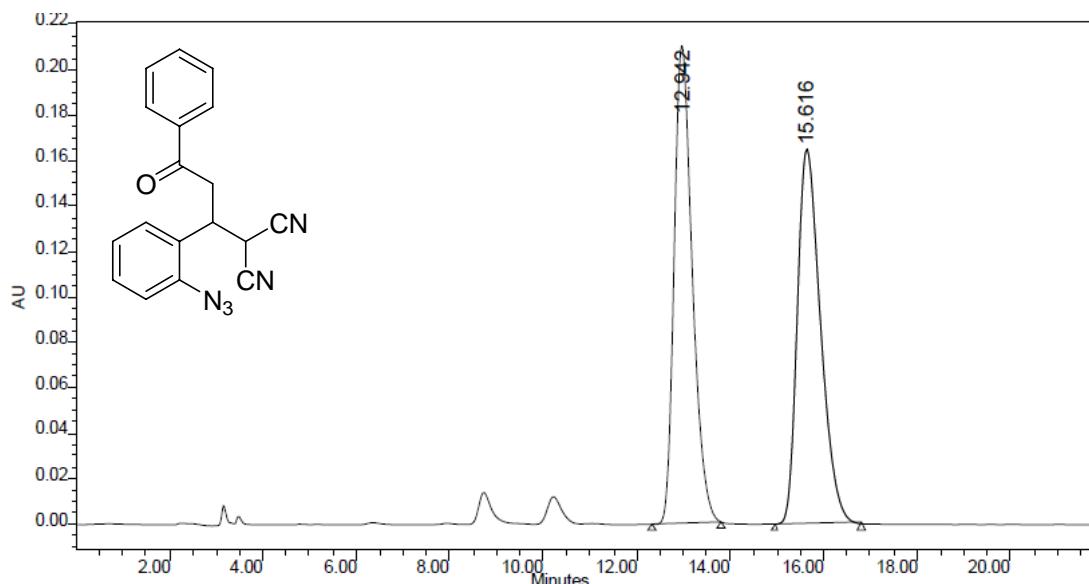
	RT (min)	Area (V^*sec)	% Area	Height (V)	% Height
1	11.257	225497	2.71	6853	3.20
2	13.520	8098821	97.29	207634	96.80



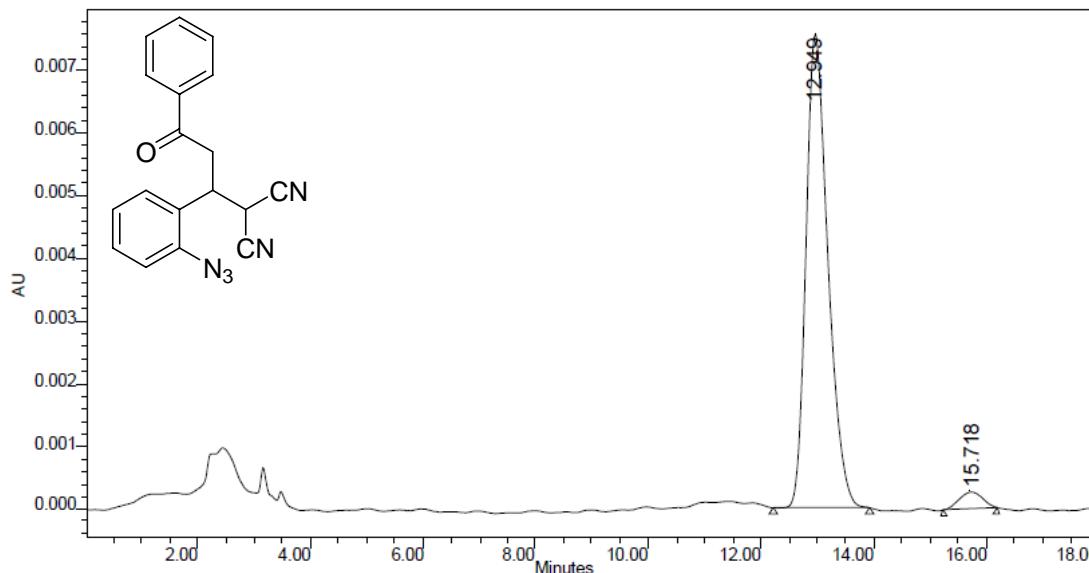
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	20.166	9478895	48.03	174661	49.68
2	22.498	10258330	51.97	176913	50.32



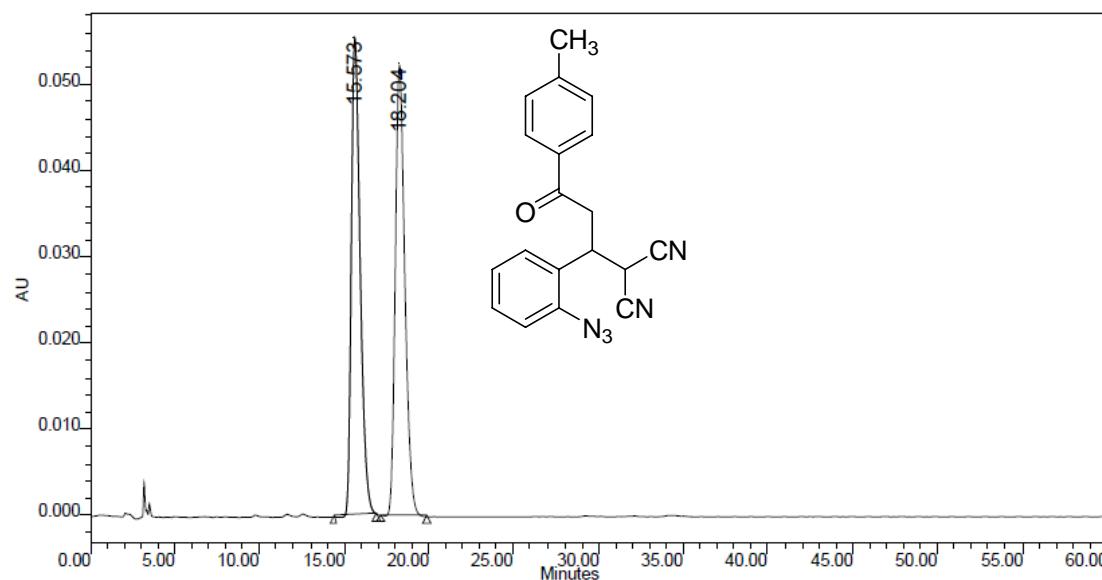
	Peak Name	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	Peak1	20.652	620098	1.34	12110	1.47
2	Peak2	22.747	45629904	98.66	812493	98.53



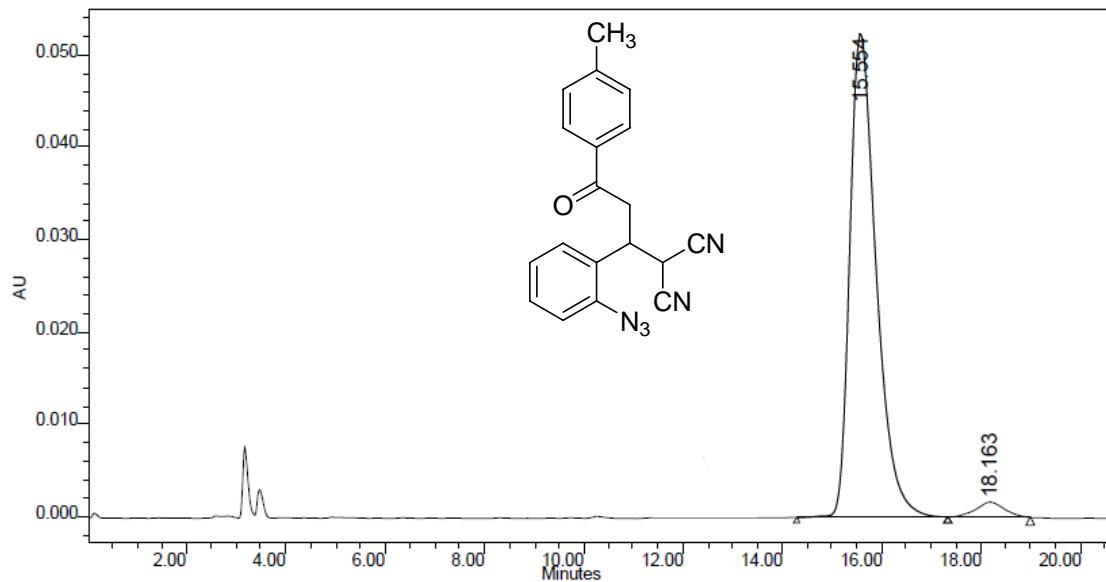
	RT (min)	Area (V^*sec)	% Area	Height (V)	% Height
1	12.942	5687228	49.95	210505	56.06
2	15.616	5698148	50.05	165008	43.94



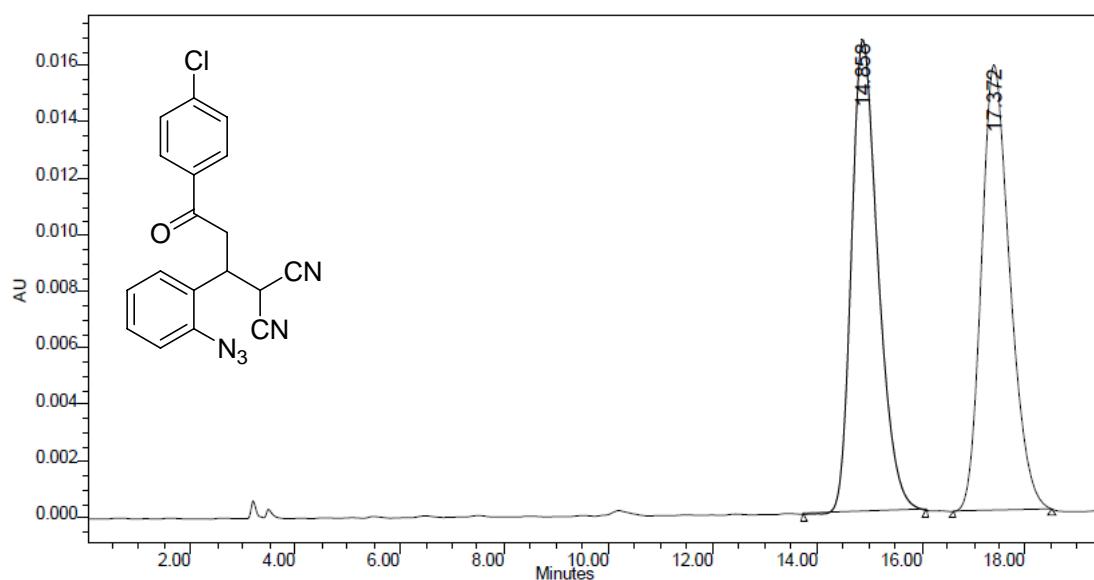
	RT (min)	Area (V^*sec)	% Area	Height (V)	% Height
1	12.949	205228	96.42	7572	96.62
2	15.718	7628	3.58	265	3.38



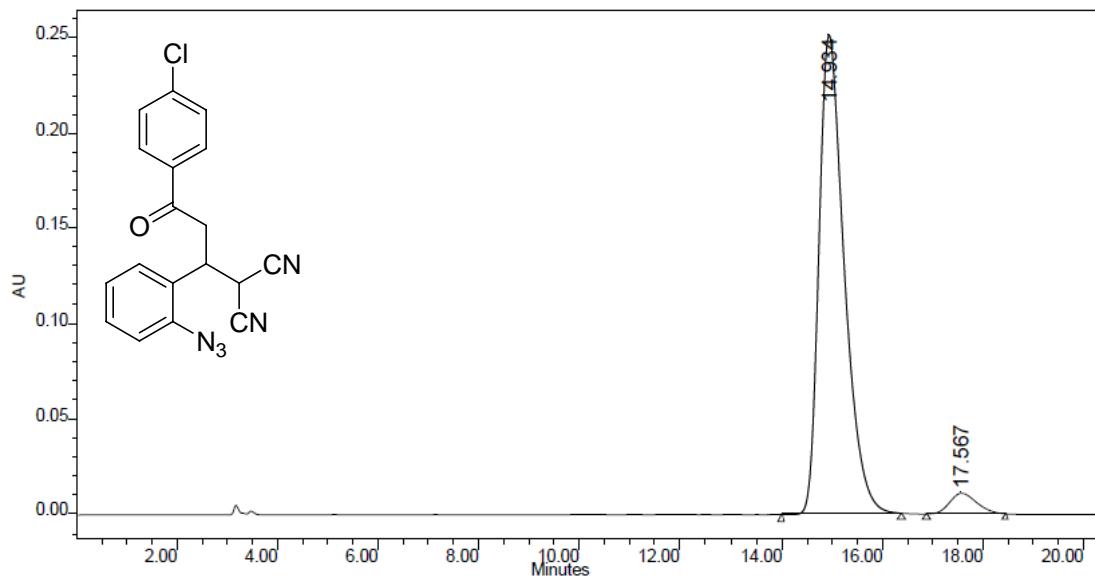
	RT (min)	Area (V^*sec)	% Area	Height (V)	% Height
1	15.573	2018480	49.56	55489	51.45
2	18.204	2053968	50.44	52353	48.55



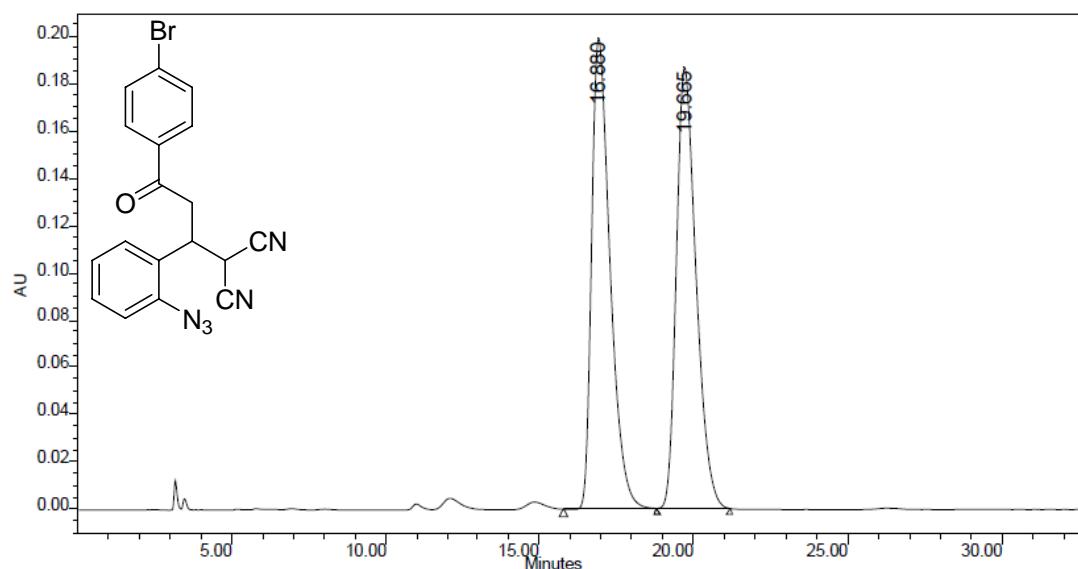
	RT (min)	Area (V^*sec)	% Area	Height (V)	% Height
1	15.554	1926673	96.67	52273	96.96
2	18.163	66406	3.33	1640	3.04



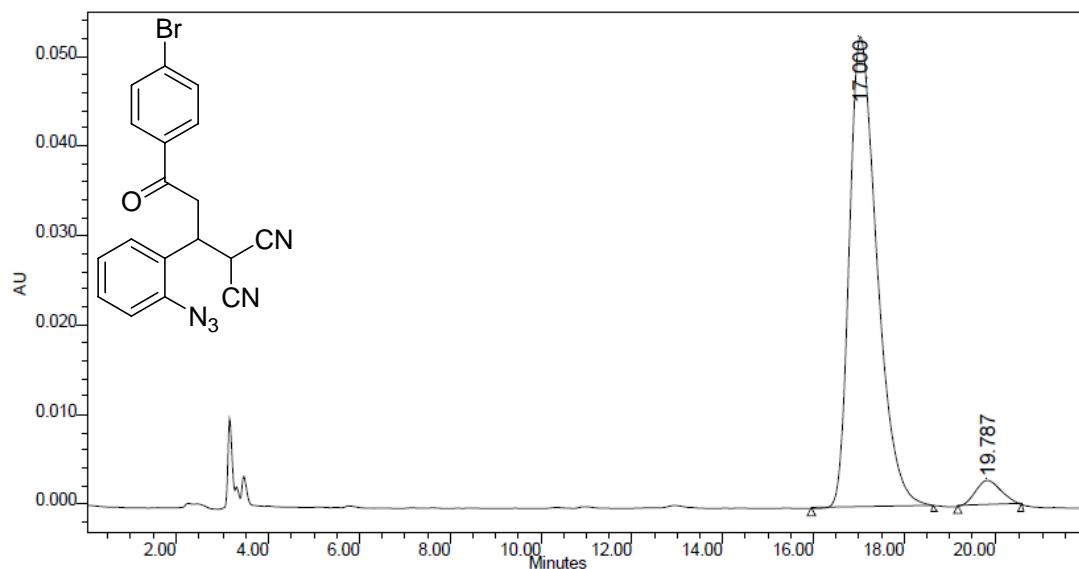
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	14.858	593766	49.75	16733	51.47
2	17.372	599688	50.25	15779	48.53



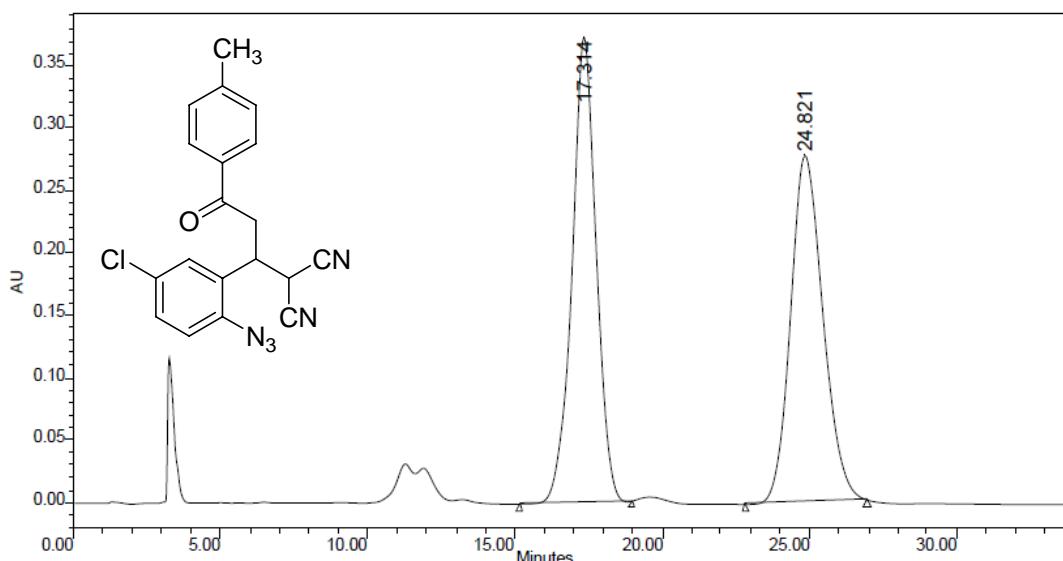
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	14.934	8741829	95.56	251433	95.87
2	17.567	406314	4.44	10842	4.13



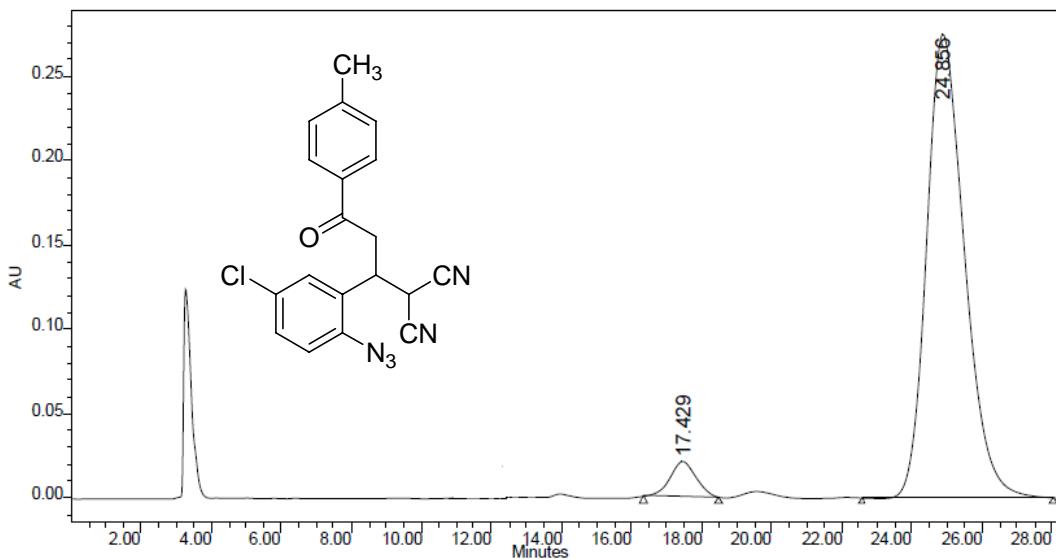
	RT (min)	Area (V^*sec)	% Area	Height (V)	% Height
1	16.880	8239418	49.94	198790	51.63
2	19.665	8258958	50.06	186257	48.37



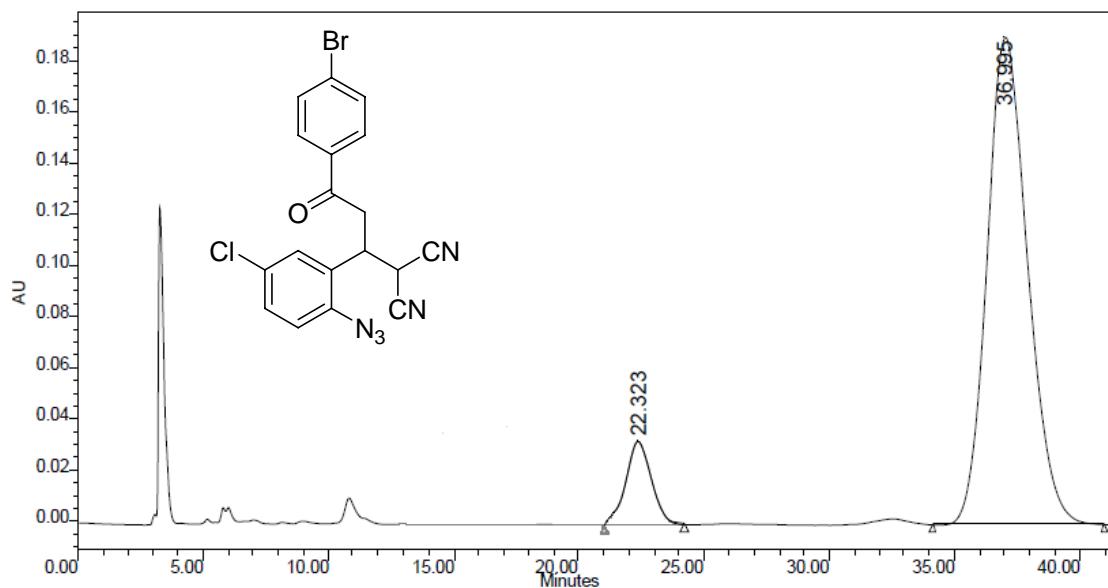
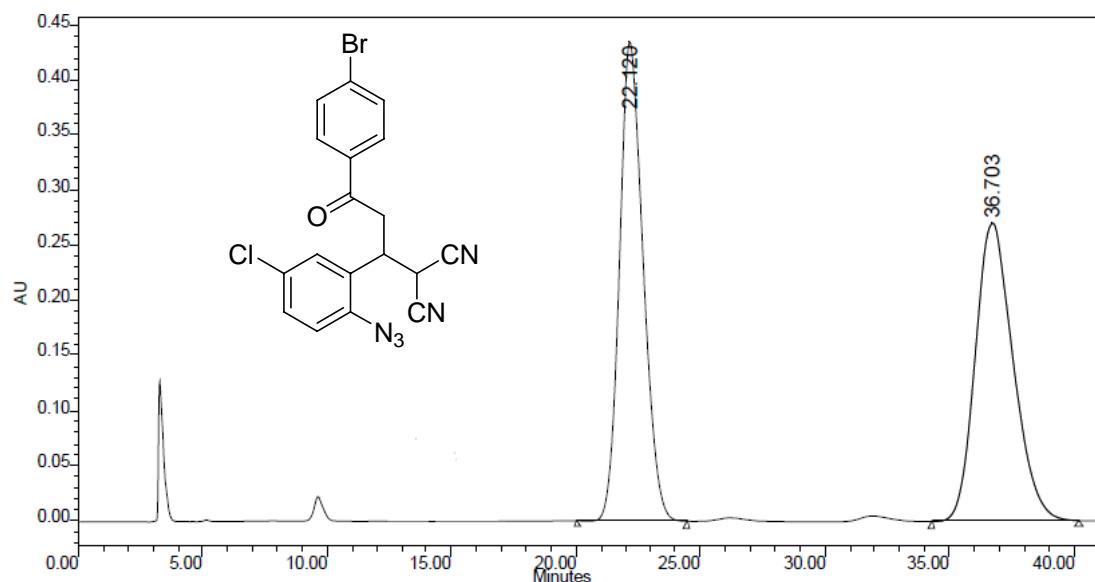
	RT (min)	Area (V^*sec)	% Area	Height (V)	% Height
1	17.000	2218009	95.21	52595	94.96
2	19.787	111554	4.79	2793	5.04

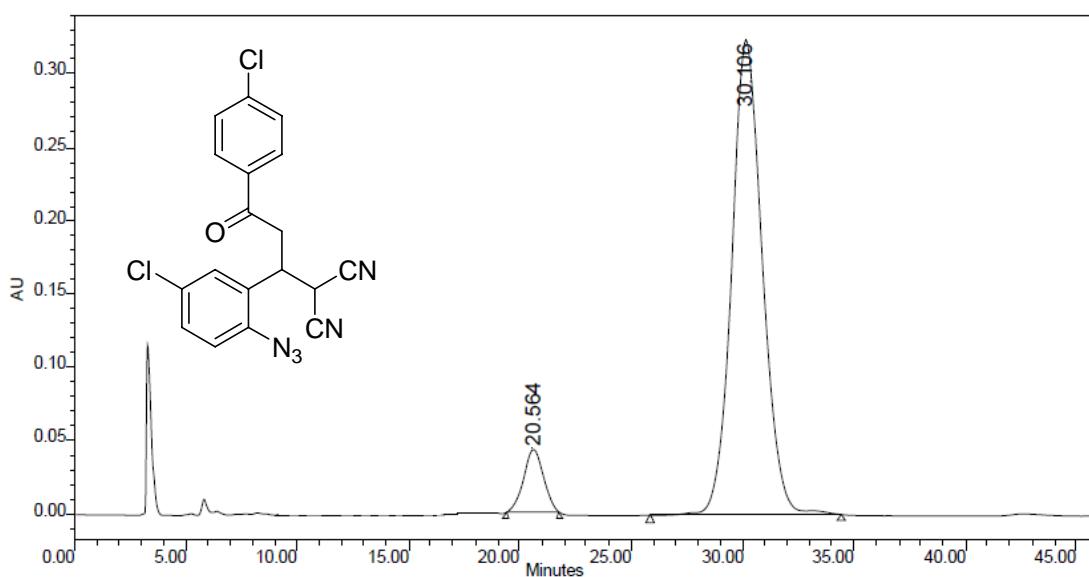
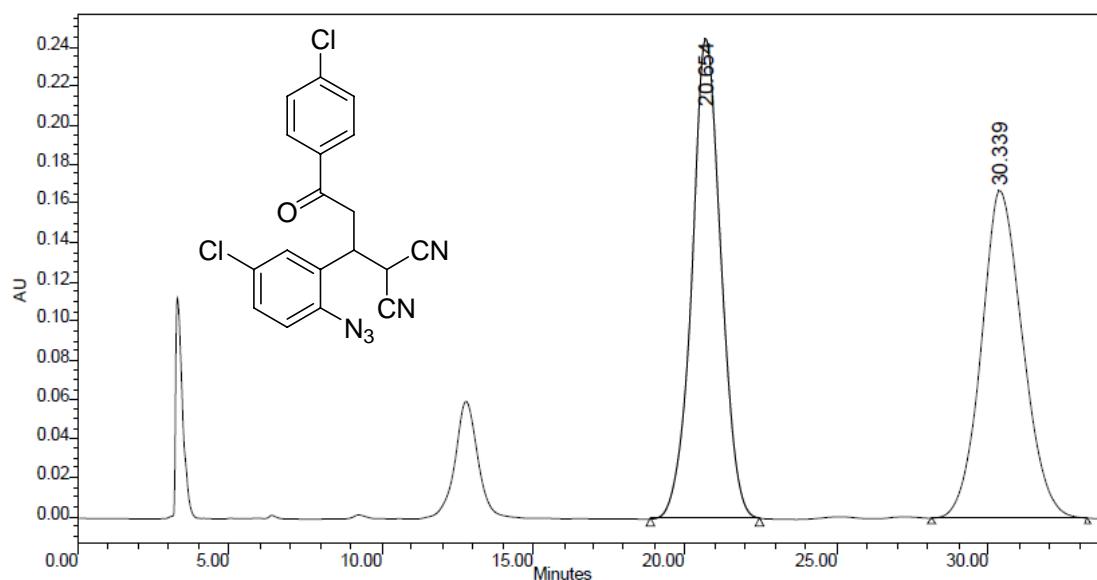


	RT (min)	Area (m^3sec)	% Area	Height (m)	% Height
1	17.314	21170478	49.86	372748	57.28
2	24.821	21293482	50.14	277969	42.72

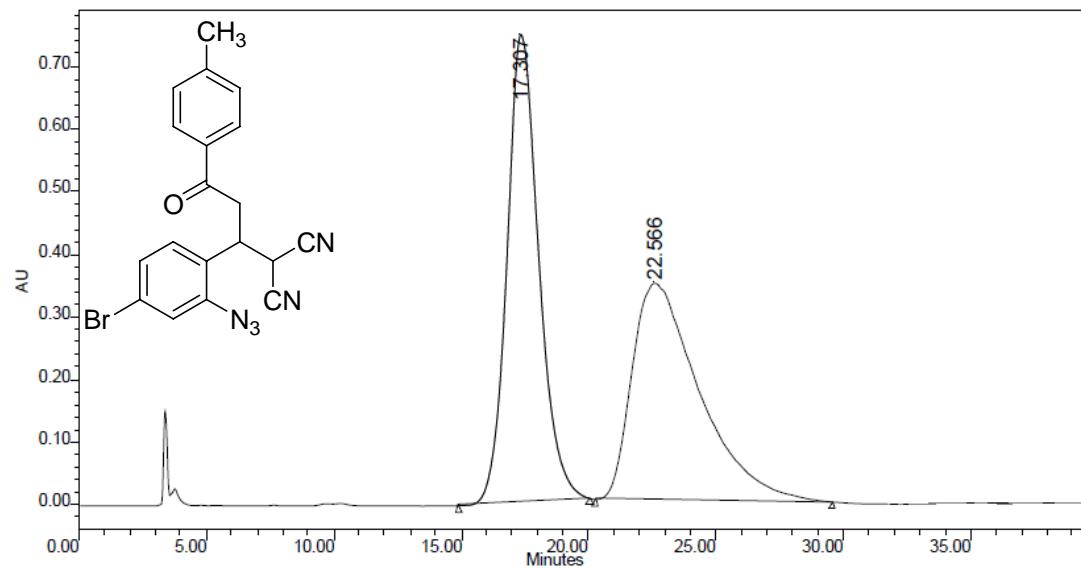


	RT (min)	Area (m^3sec)	% Area	Height (m)	% Height
1	17.429	1082533	4.99	20894	7.06
2	24.856	20616130	95.01	274954	92.94

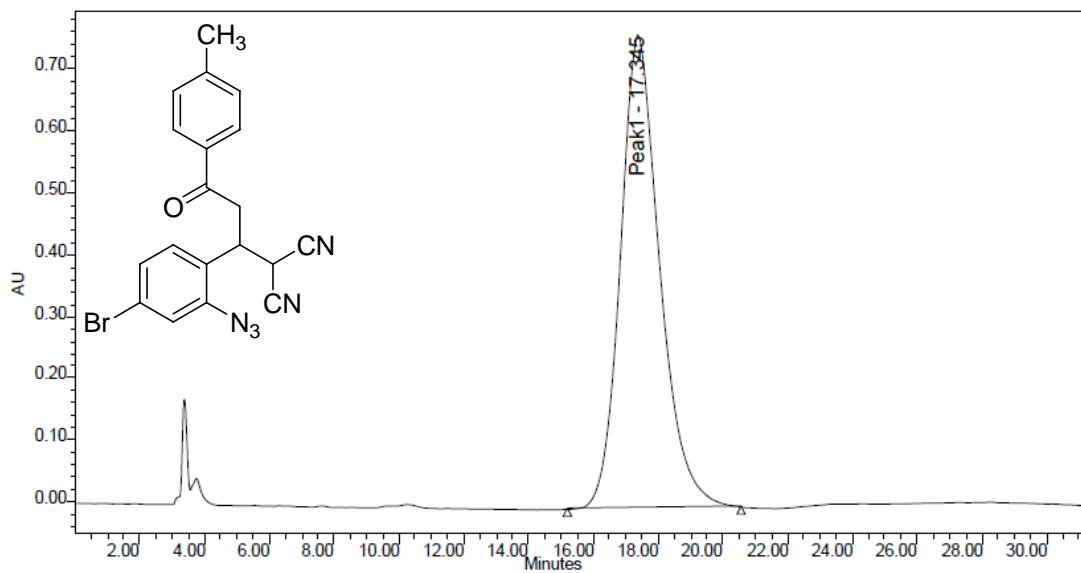




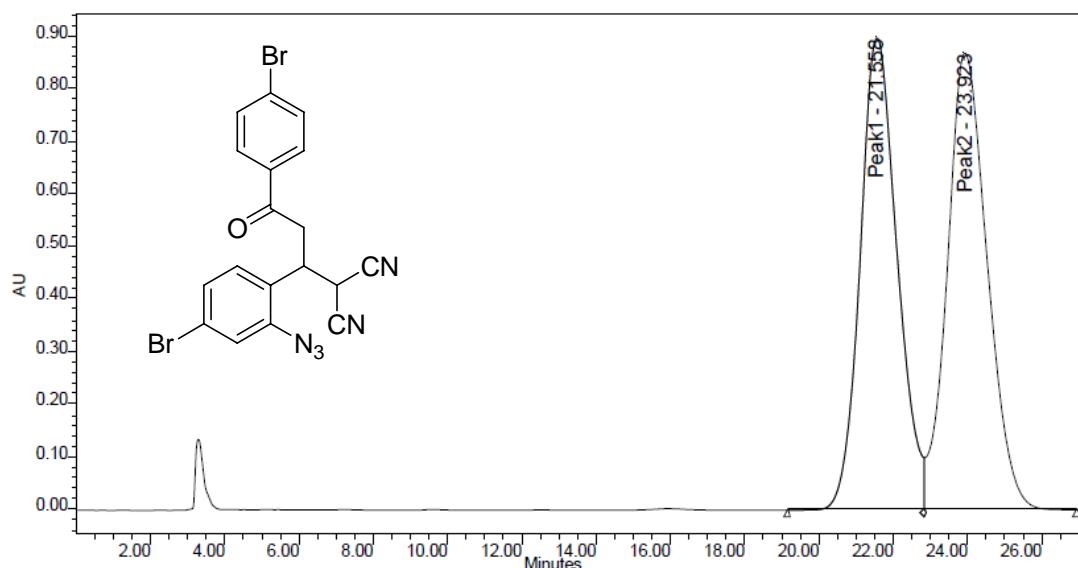
	RT (min)	Area ($\text{mV}^{\star}\text{sec}$)	% Area	Height (mV)	% Height
1	20.564	2693535	7.98	42884	11.69
2	30.106	31061744	92.02	324047	88.31



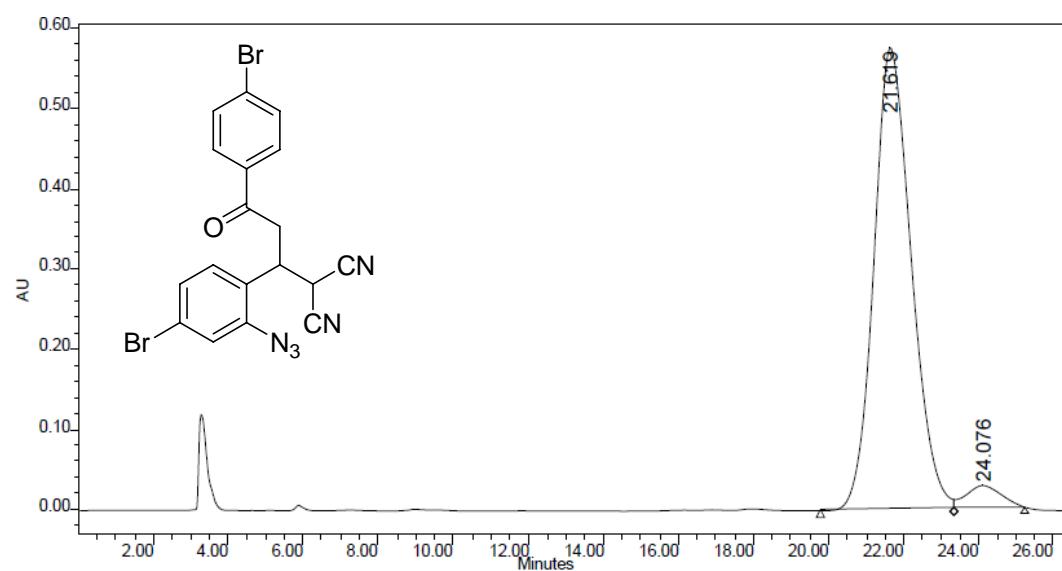
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	17.307	64647322	50.33	747131	68.35
2	22.566	63805351	49.67	346031	31.65



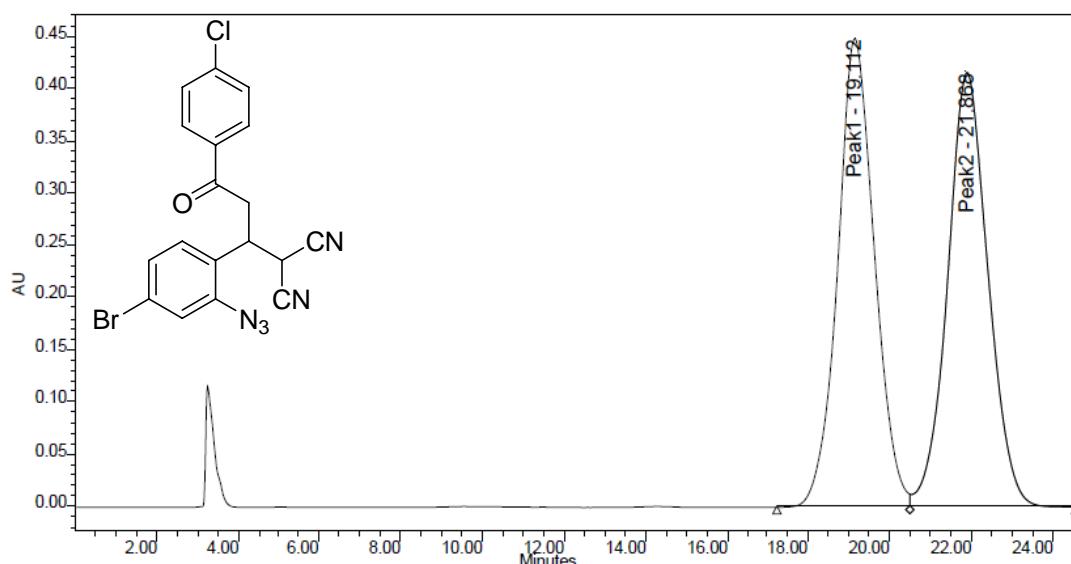
	Peak Name	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	Peak1	17.345	64429856	100.00	762761	100.00



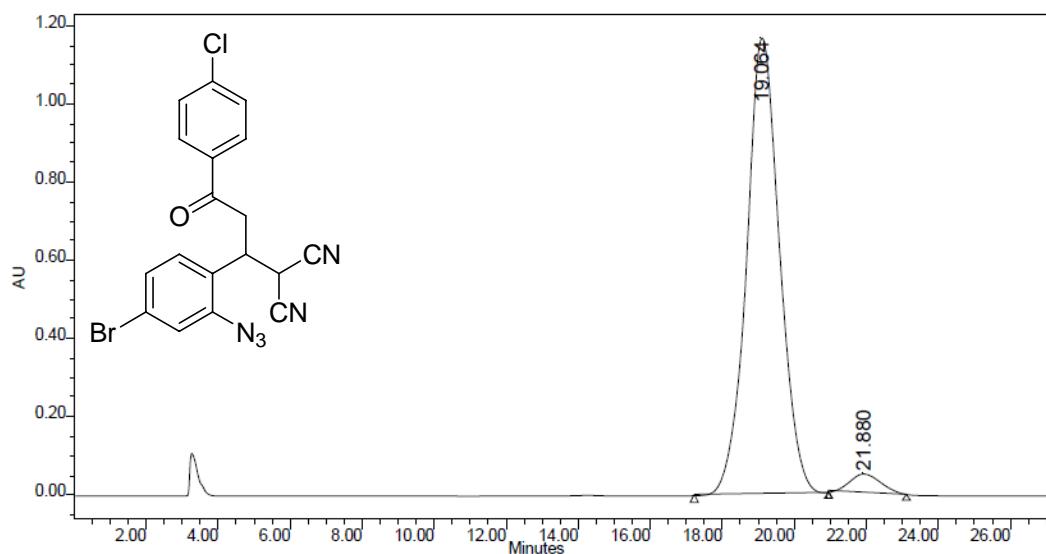
	Peak Name	RT (min)	Area ($\text{mV}^{\star}\text{sec}$)	% Area	Height (mV)	% Height
1	Peak1	21.558	62190040	48.89	896966	50.80
2	Peak2	23.923	65006954	51.11	868693	49.20



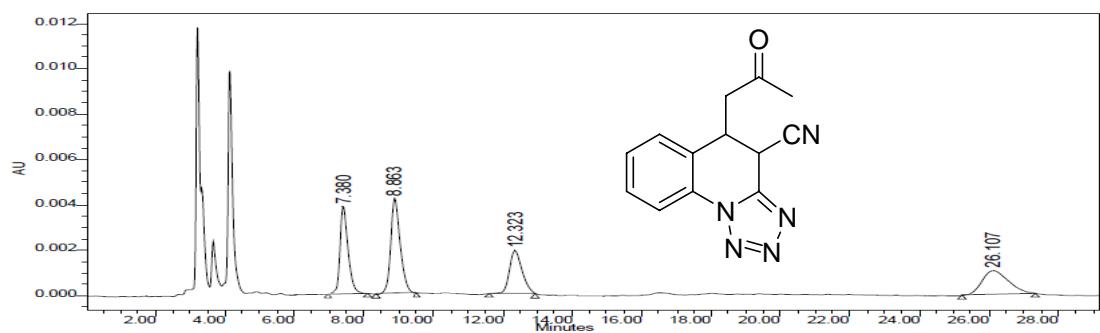
	RT (min)	Area ($\text{mV}^{\star}\text{sec}$)	% Area	Height (mV)	% Height
1	21.619	39941734	95.61	576041	95.35
2	24.076	1831893	4.39	28089	4.65



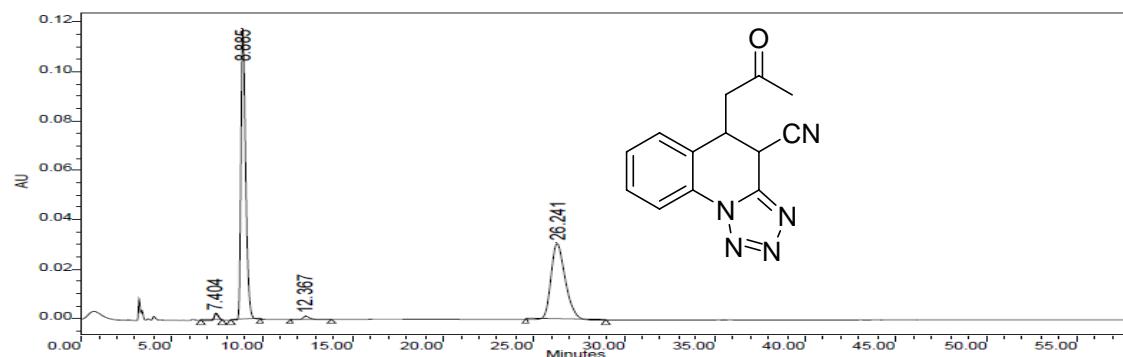
	Peak Name	RT (min)	Area (V^*sec)	% Area	Height (V)	% Height
1	Peak1	19.112	28126439	49.57	448190	51.88
2	Peak2	21.868	28609382	50.43	415785	48.12



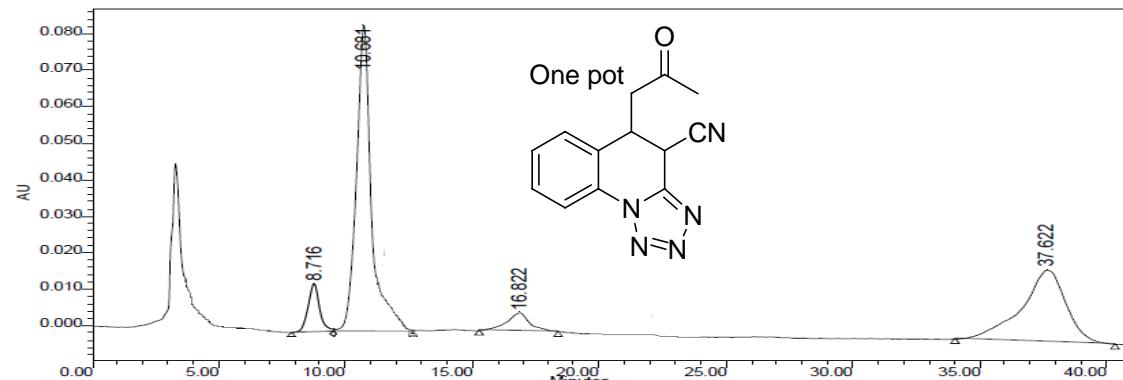
	RT (min)	Area (V^*sec)	% Area	Height (V)	% Height
1	19.064	74036589	96.12	1165586	95.95
2	21.880	2992189	3.88	49162	4.05



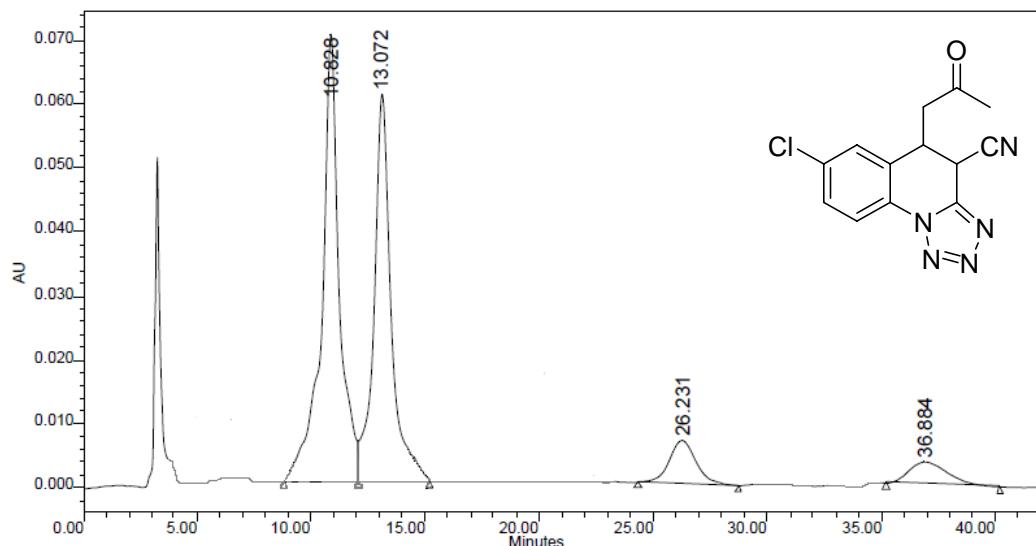
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.380	69328	27.20	3860	35.07
2	8.863	80019	31.39	4188	38.06
3	12.323	49101	19.26	1903	17.29
4	26.107	56478	22.15	1054	9.58



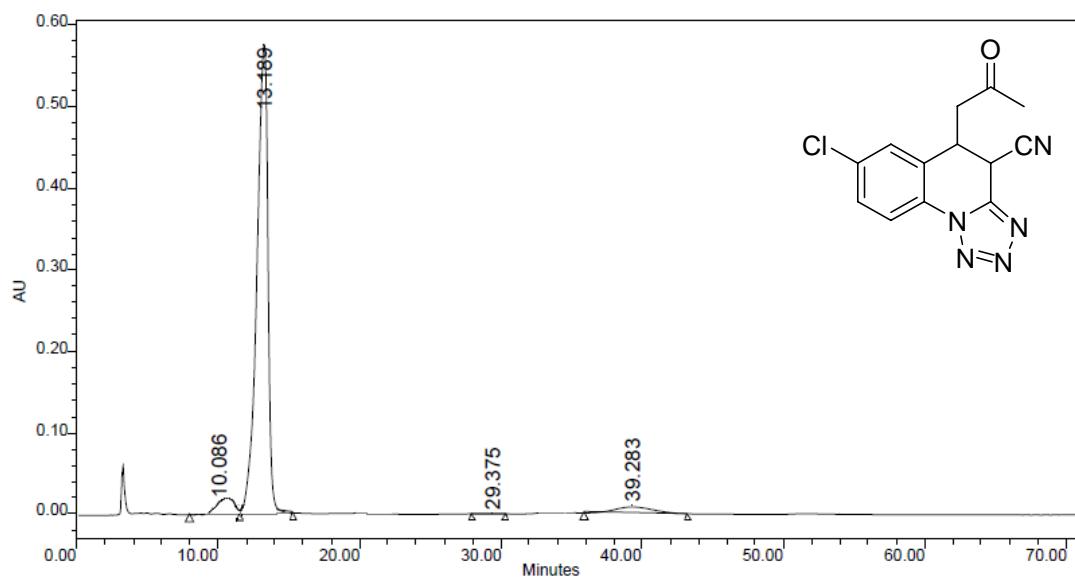
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.404	43624	1.12	2811	1.84
2	8.885	2113661	54.37	118111	77.22
3	12.367	34035	0.88	1272	0.83
4	26.241	1696415	43.64	30768	20.11



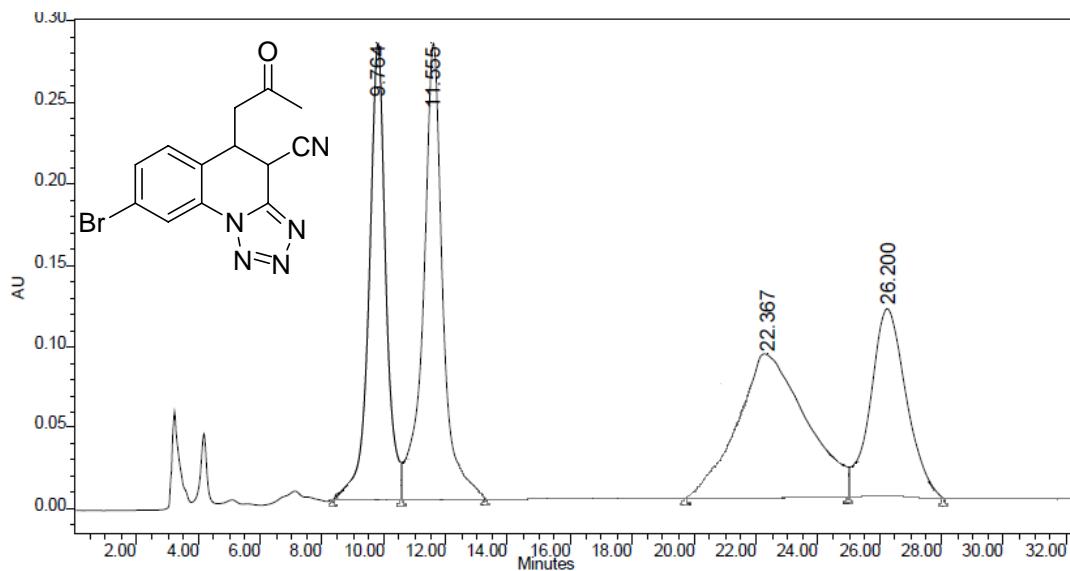
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	8.716	425781	6.75	13323	10.92
2	10.681	3133804	49.66	83948	68.78
3	16.822	323901	5.13	5036	4.13
4	37.622	2426575	38.46	19746	16.18



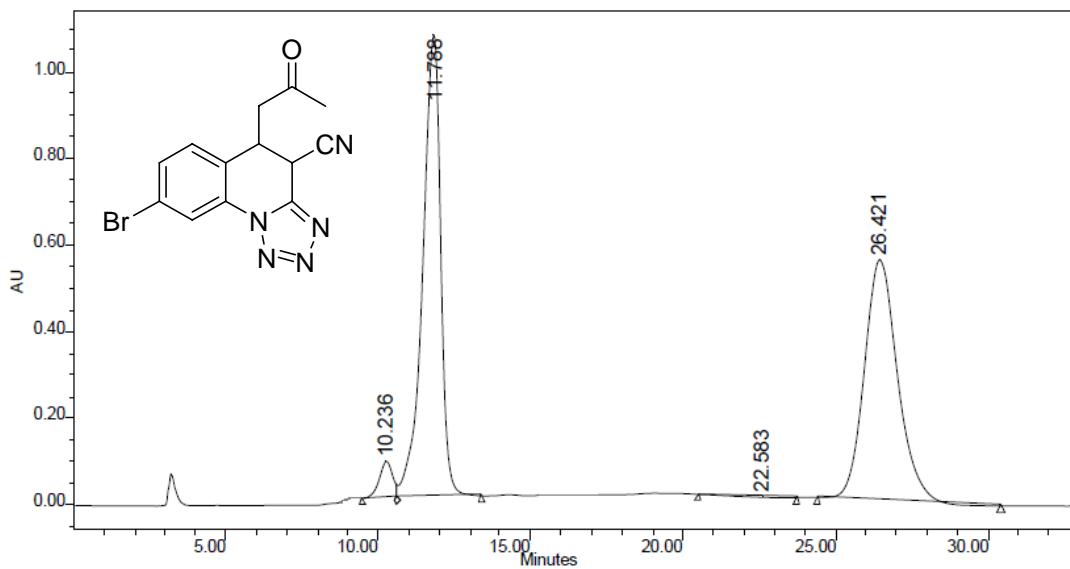
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	10.828	3224919	45.46	66988	49.59
2	13.072	2898384	40.86	57826	42.81
3	26.231	554883	7.82	6761	5.01
4	36.884	415508	5.86	3499	2.59



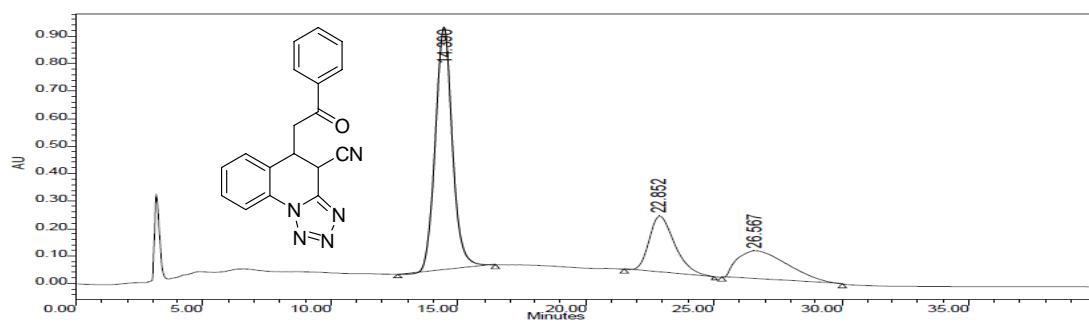
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	10.086	905919	2.78	11047	1.88
2	13.189	30196139	92.57	569654	96.77
3	29.375	4165	0.01	-62	0.01
4	39.283	1512776	4.64	7900	1.34



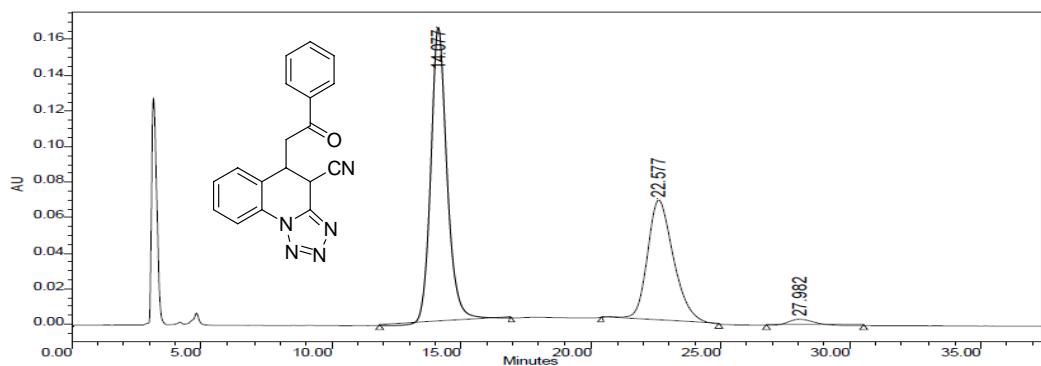
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.764	9025966	29.36	265300	40.17
2	11.555	9290104	30.22	258065	39.08
3	22.367	5612470	18.26	37325	5.65
4	26.200	6809787	22.15	99708	15.10



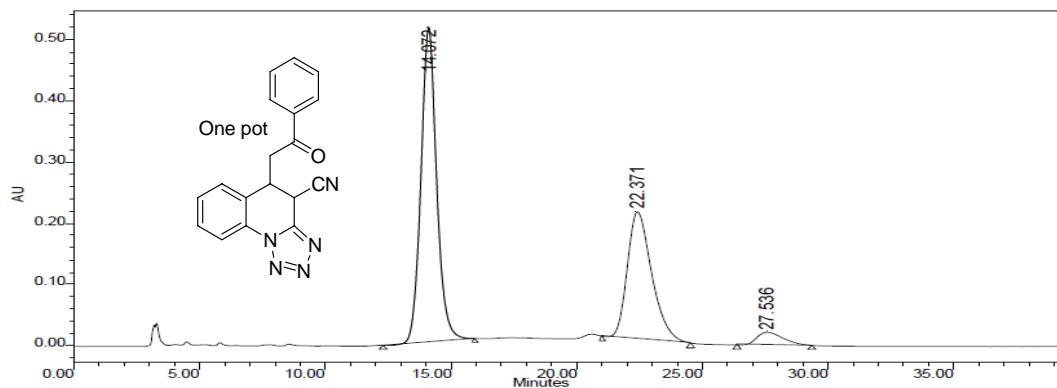
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	10.236	2625586	2.95	84396	4.94
2	11.788	43780938	49.24	1067015	62.42
3	22.583	259136	0.29	-2160	0.13
4	26.421	42249043	47.52	555833	32.52



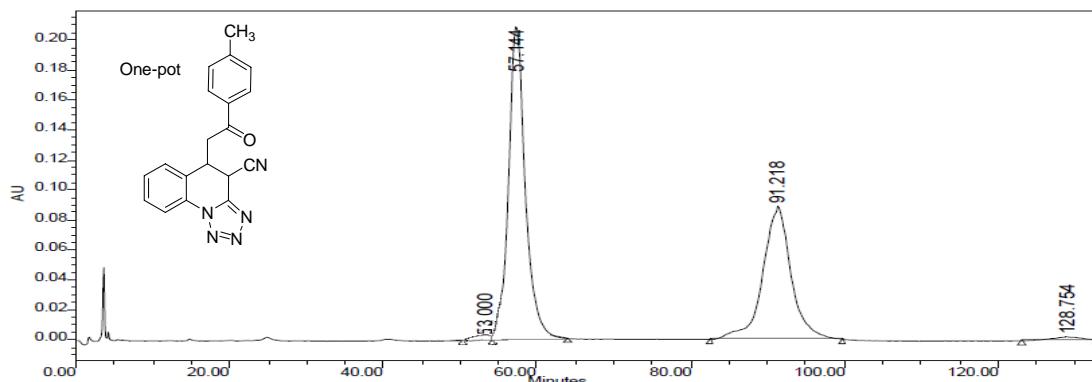
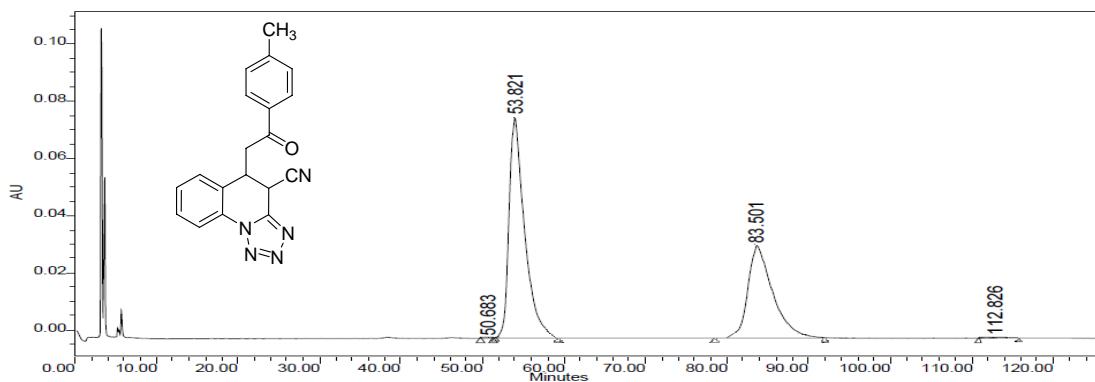
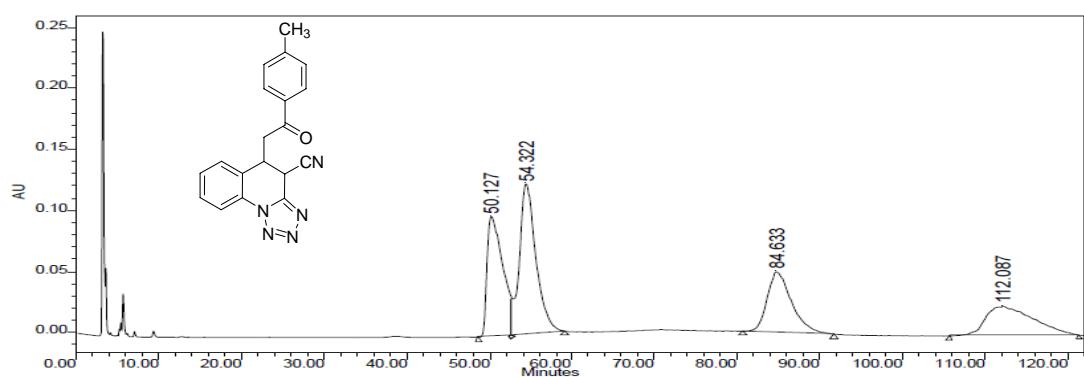
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	14.390	41433802	59.07	884268	74.15
2	22.852	14256358	20.33	204045	17.11
3	26.567	14451804	20.60	104171	8.74

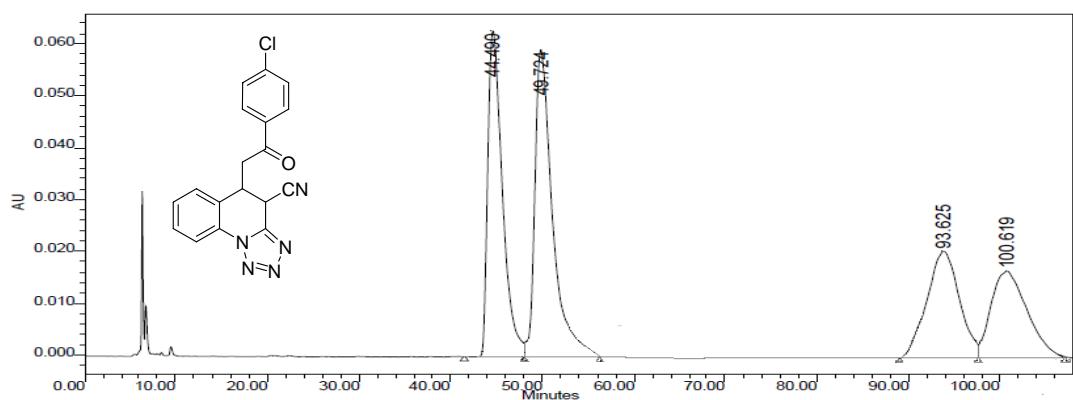


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	14.077	7268453	59.22	165697	69.94
2	22.577	4767066	38.84	67792	28.61
3	27.982	238169	1.94	3434	1.45

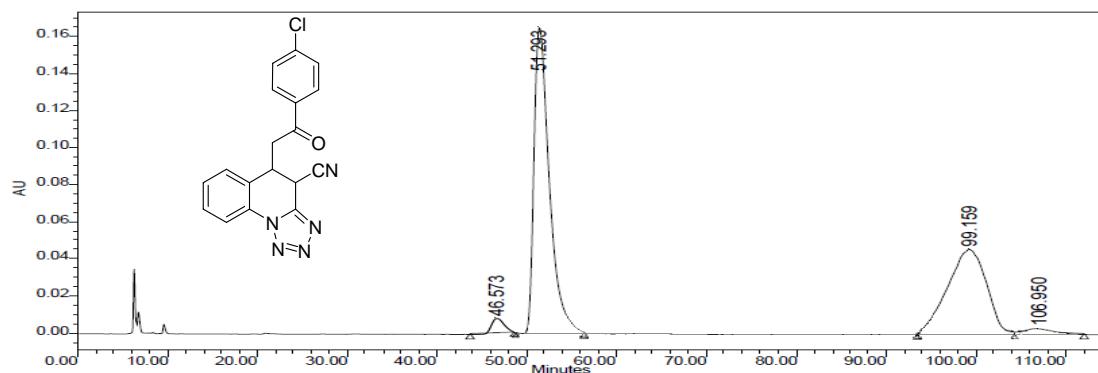


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	14.072	22295521	58.97	514354	69.23
2	22.371	14004944	37.04	207921	27.98
3	27.536	1506955	3.99	20712	2.79

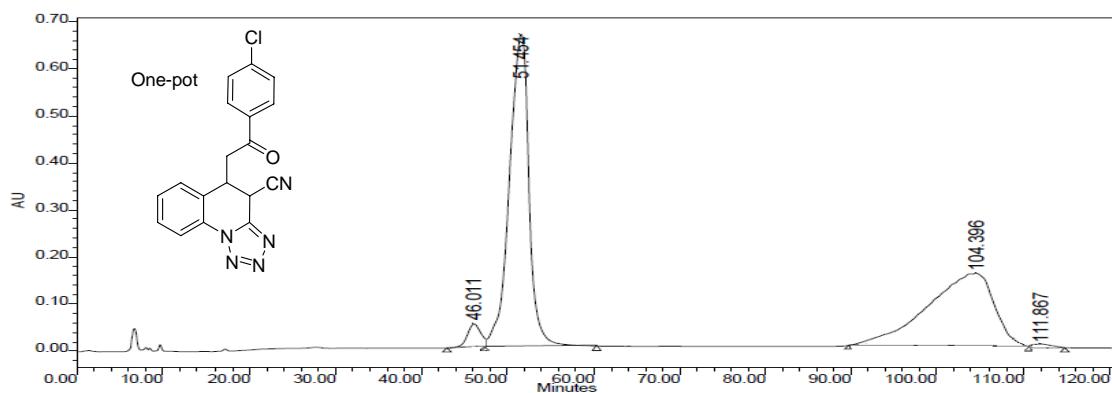




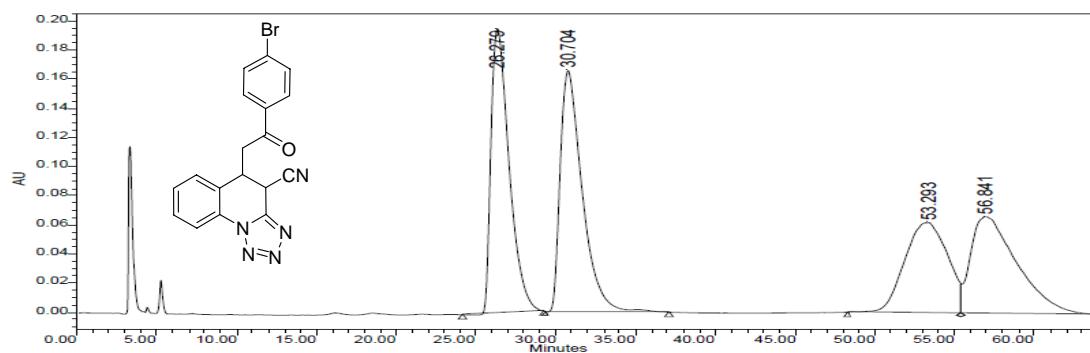
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	44.490	6526826	32.67	61421	41.41
2	49.724	6393603	32.00	55601	37.48
3	93.625	3474825	17.39	16864	11.37
4	100.619	3584029	17.94	14450	9.74



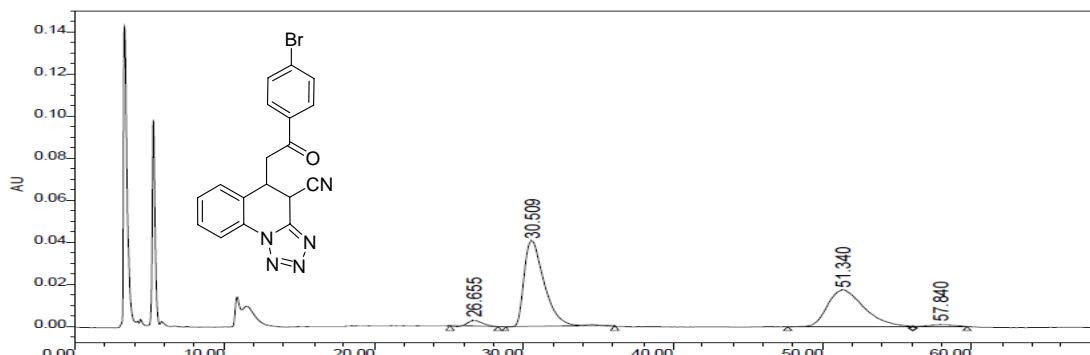
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	46.573	778445	2.44	7896	3.66
2	51.293	18699253	58.56	162568	75.43
3	99.159	12071855	37.80	42966	19.94
4	106.950	384191	1.20	2095	0.97



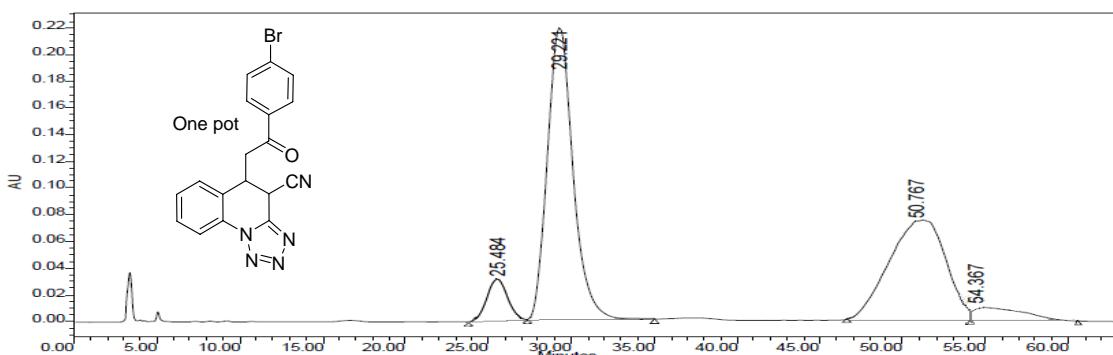
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	46.011	4315826	2.33	50605	5.87
2	51.454	107219257	57.82	664808	77.11
3	104.396	72826638	39.27	141862	16.45
4	111.867	1077993	0.58	4875	0.57



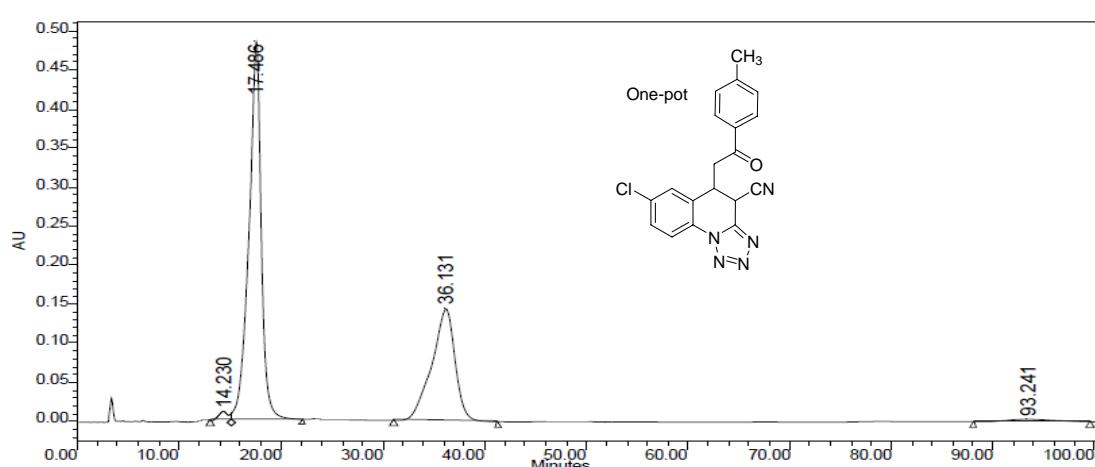
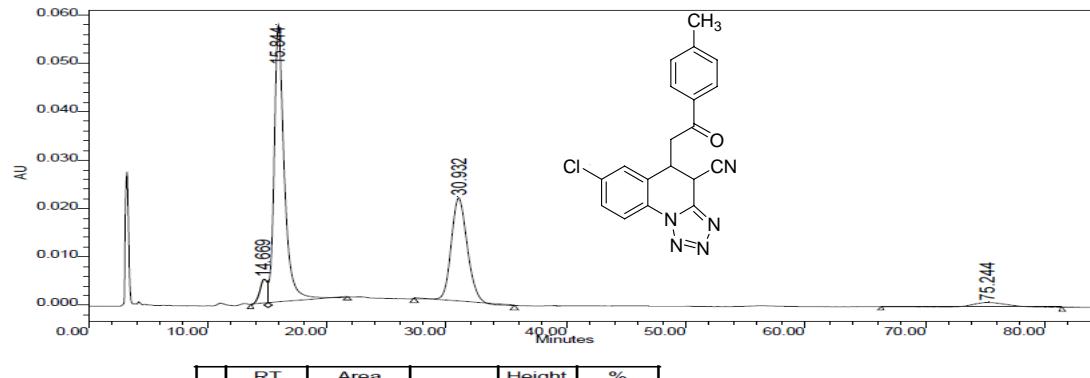
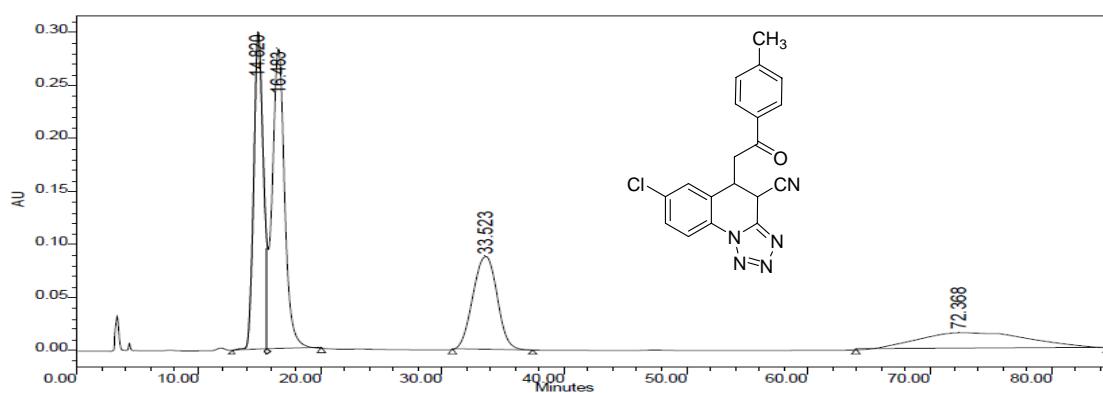
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	26.279	15519000	27.52	195439	39.95
2	30.704	15867754	28.14	165505	33.83
3	53.293	11657246	20.68	61934	12.66
4	56.841	13339232	23.66	66383	13.57

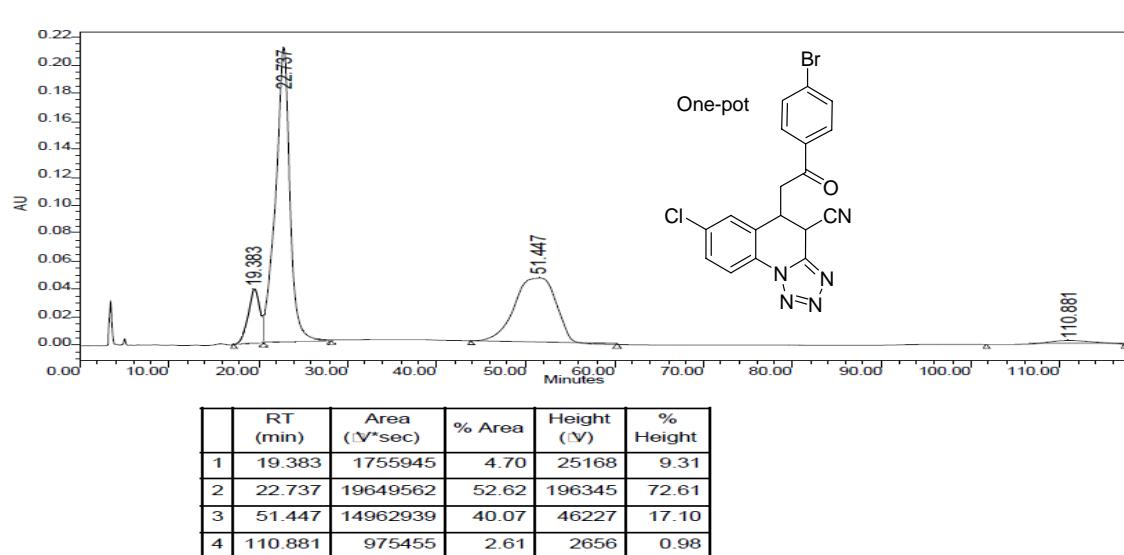
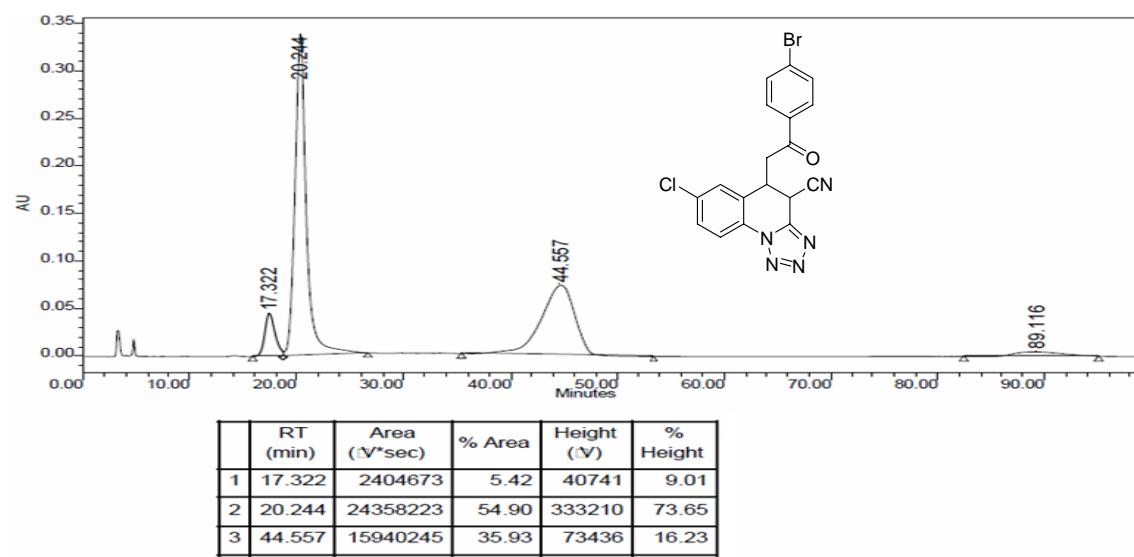
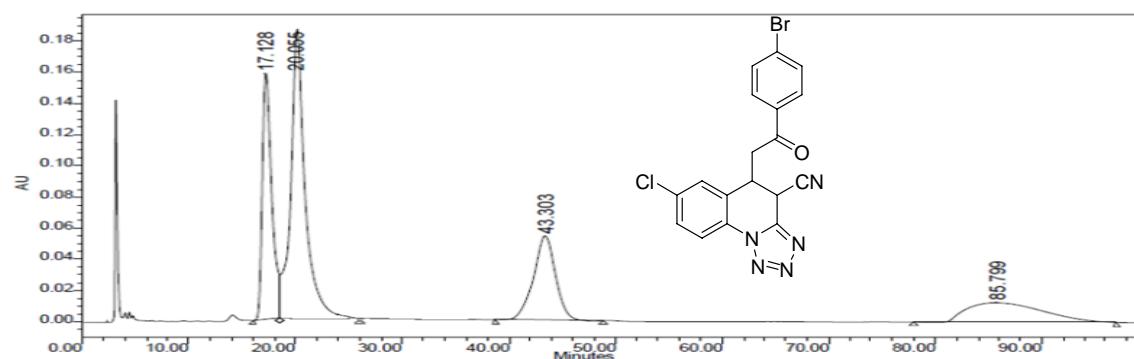


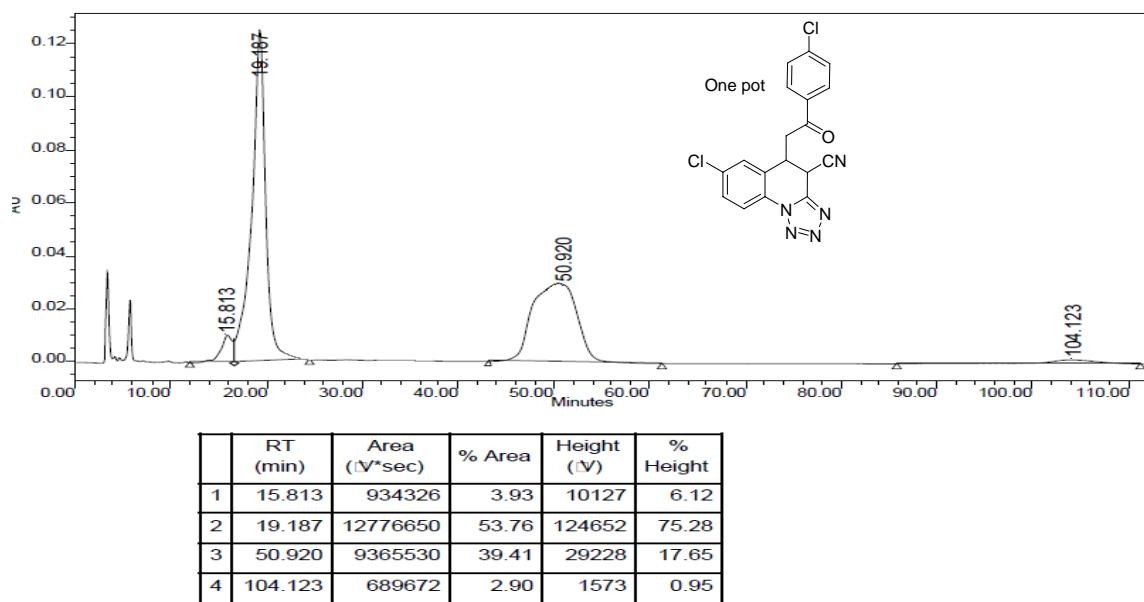
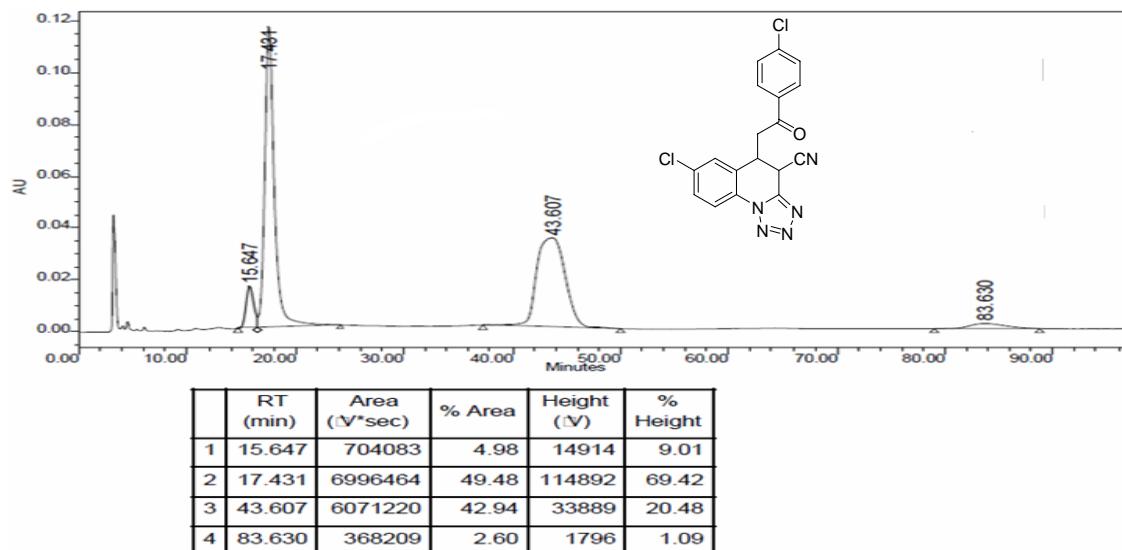
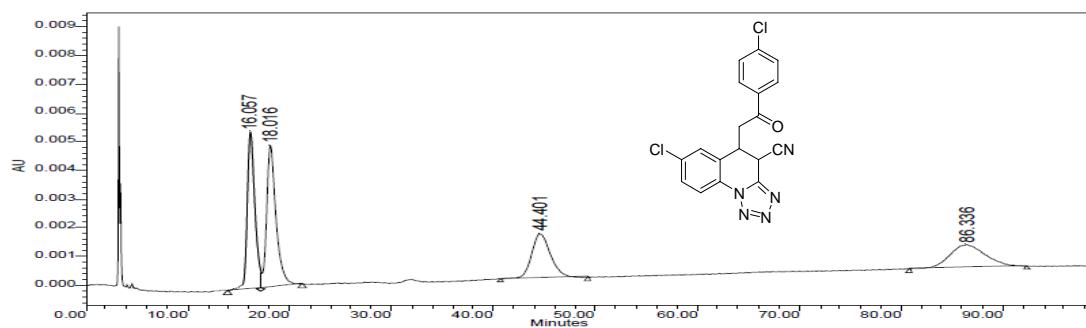
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	26.655	201518	2.79	2808	4.52
2	30.509	3910673	54.08	40735	65.61
3	51.340	2998688	41.47	17573	28.30
4	57.840	120931	1.67	973	1.57

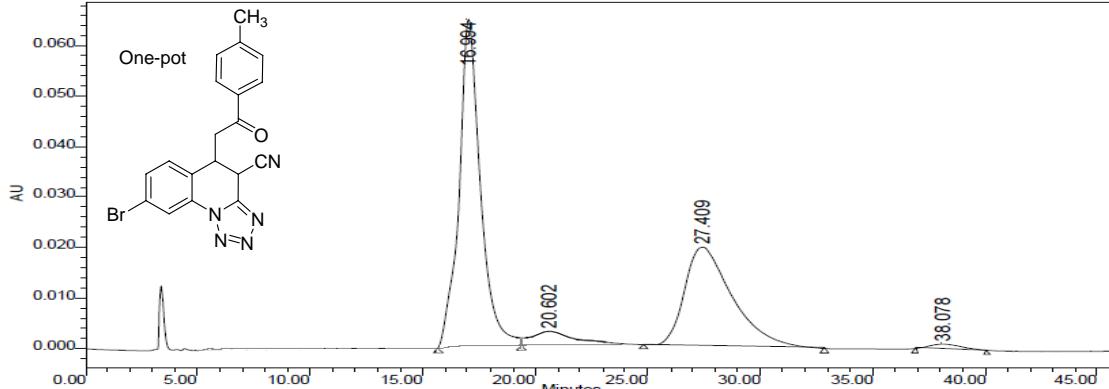
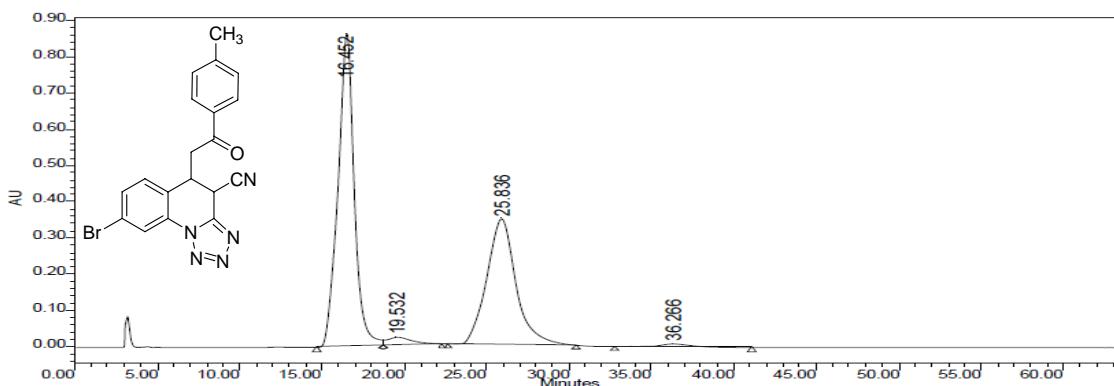
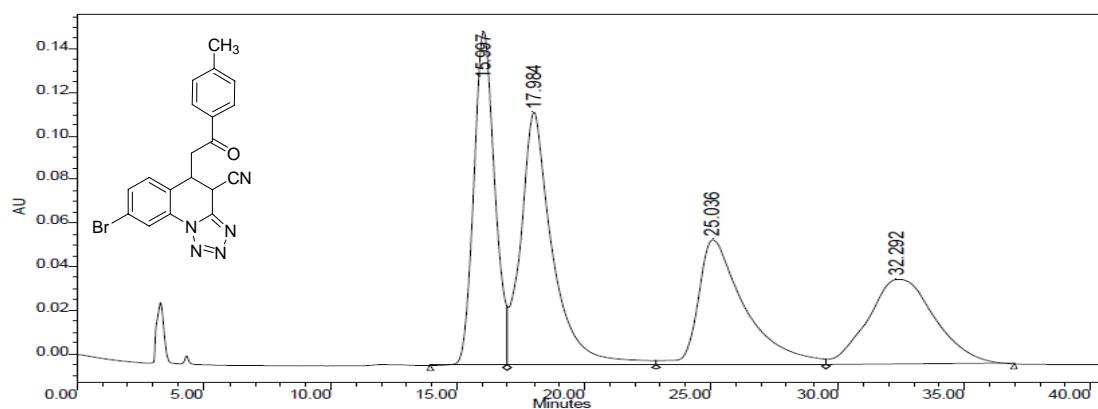


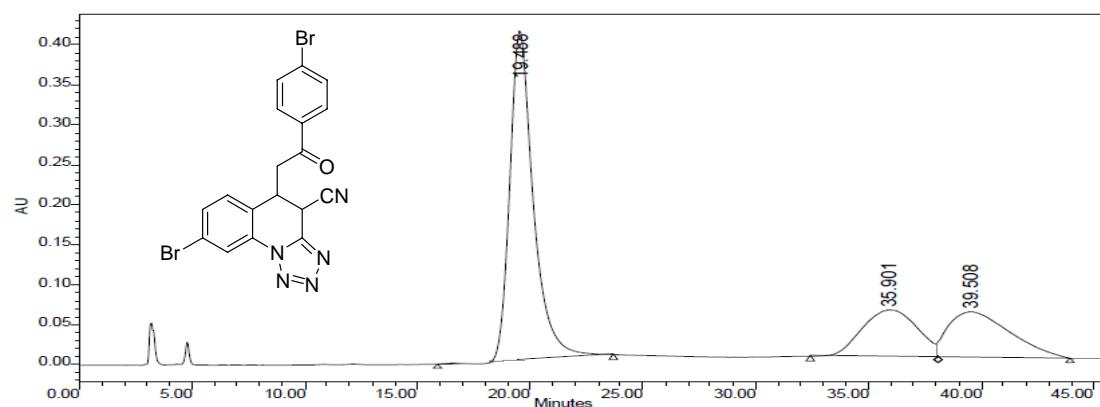
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	25.484	2212527	5.49	28431	9.07
2	29.221	23290643	57.81	217374	69.31
3	50.767	13330552	33.09	61910	19.74
4	54.367	1453236	3.61	5895	1.88



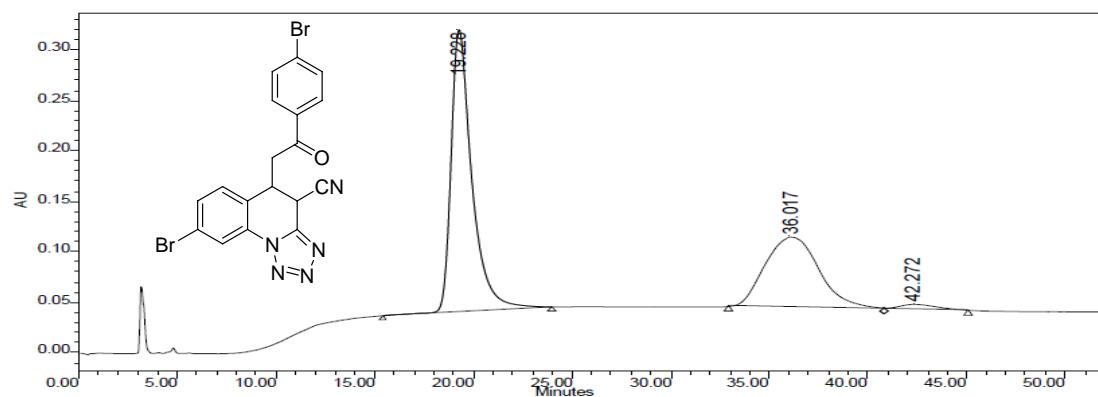




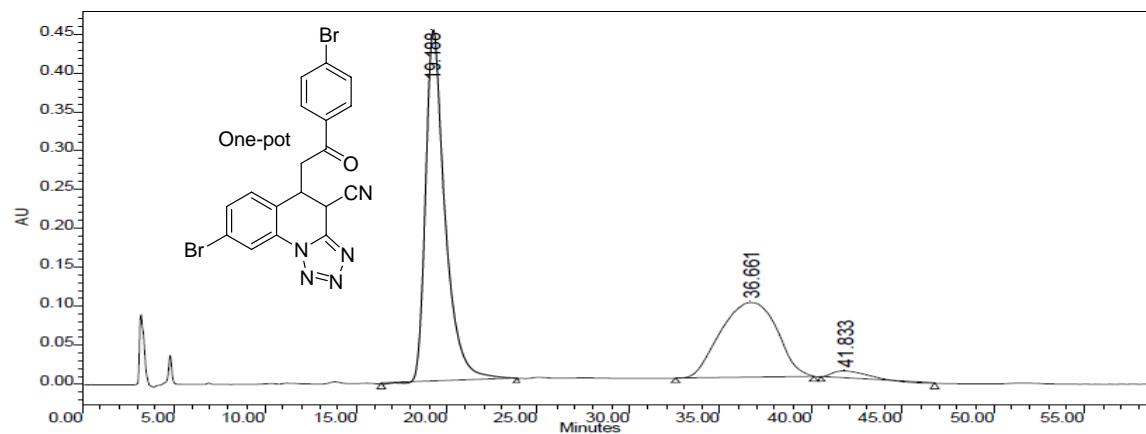




	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	19.488	29996885	58.80	411139	77.95
2	35.901	10143243	19.88	58721	11.13
3	39.508	10873053	21.31	57581	10.92



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	19.228	20434903	59.48	279247	78.93
2	36.017	13261415	38.60	69664	19.69
3	42.272	658673	1.92	4894	1.38



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	19.188	33621925	60.37	452724	81.13
2	36.661	20805334	37.36	96147	17.23
3	41.833	1267856	2.28	9136	1.64

