

Supporting Information

Lingkai Kong, Peng Wang, Chunzhi Ju, Guangliang Zhang* and Suoqin Zhang*

College of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, People's Republic of China.

*Fax: (+86)-431-8515-5252;
phone: (+86)-431-8515-5252;
e-mail: suoqin@jlu.edu.cn.*

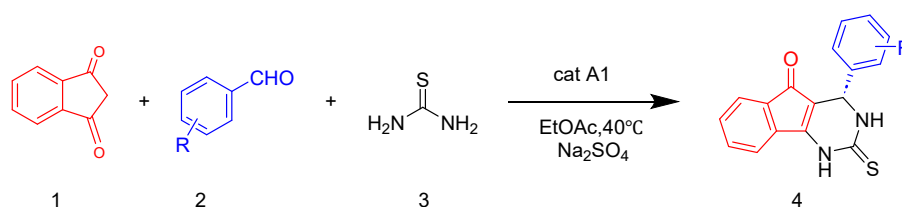
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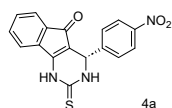
1. General Experimental Information

All reagents were used without purification. All solvents were purified and dried according to standard methods. The reaction products were purified by flash column chromatography on 200–300 mesh silica gel. Optical rotations were measured with a Jasco-P-2000 digital polarimeter at 25 °C and concentrations (*c*) are given in g (100 mL)⁻¹. ¹H and ¹³C NMR spectra were recorded with Bruker 400 MHz spectrometers (400 MHz for ¹H NMR, 101 MHz for ¹³C NMR); chemical shifts (δ), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, td = triplet of doublet, dt = doublet of triplet, dd = doublet of doublet), coupling constants (Hz), and integration. Enantiomeric excess values were measured by analytical HPLC with Daicel ChiralPak AD-H, Daicel ChiralPak AS-H or Daicel Chiralcel OD-H columns.

2. Experimental Procedures and Characterization Data

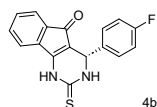


General Procedure for the Organocatalytic Biginelli Reaction: A solution of aldehyde (0.2 mmol), thiourea (0.2 mmol), and catalyst (10 mol%, 0.01 mmol) and Na₂SO₄ (200 mg) in EtOAc (2.0 mL) was stirred at 25 °C for 2 h, then 1,3-indanedione (0.1 mmol) was added. The reaction mixture was stirred at 40 °C for 48 h (reaction progress monitored by TLC). EtOAc and silica gel were added and, after removal of the solvent, the residue was purified by flash column chromatography on silica gel to afford the pure products.



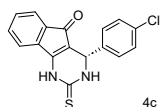
(S)-4-(4-nitrophenyl)-2-thioxo-1,2,3,4-tetrahydro-5H-indeno[1,2-d]pyrimidin-5-one (**4a**)

The crude product was purified by flash column chromatography (DCM/EA = 40/1) on silicagel. Red solid, 65% yield (21.93 mg), $[\alpha]_D^{25} = -1070$ (*c* = 0.10, EtOH), 96% ee [Daicel Chiralcel OJ-H column, *n*-hexane/EtOH = 50 / 50, 1.0 ml/min, $\lambda = 254$ nm, *t*(major) = 28.5 min, *t*(minor) = 16.1 min]; ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.92 (s, 1H), 10.01 (s, 1H), 8.25 (d, *J* = 8.8 Hz, 2H), 7.84 (d, *J* = 7.2 Hz, 1H), 7.60 (d, *J* = 8.8 Hz, 2H), 7.46 (t, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.33 (d, *J* = 6.9 Hz, 1H), 5.56 (s, 1H). ¹³C NMR (101 MHz, DMSO) δ 189.33, 175.81, 153.16, 149.54, 147.56, 135.70, 133.26, 132.82, 131.39, 128.67, 124.42, 121.80, 121.27, 104.79, 53.58. HRMS (ESI) *m/z* calcd for C₁₇H₁₂N₃O₃S ([M+H]⁺): 338.0594, found: 338.0595.



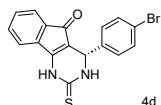
(S)-4-(4-fluorophenyl)-2-thioxo-1,2,3,4-tetrahydro-5H-indeno[1,2-d]pyrimidin-5-one (**4b**)

The crude product was purified by flash column chromatography (DCM/EA = 40/1) on silicagel. Red solid, 51% yield (15.80 mg), $[\alpha]_D^{25} = -980$ (c = 0.10, EtOH), 92% ee [Daicel Chiralcel AD column, *n*-hexane/ *i*-PrOH = 85 / 35, 1.0 ml/min, $\lambda = 254$ nm, t(major)= 10.9 min, t(minor) = 6.6 min]; **¹H NMR (400 MHz, DMSO-*d*₆)** δ 11.81 (s, 1H), 9.91 (s, 1H), 7.83 (d, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.9 Hz, 1H), 7.42 – 7.27 (m, 4H), 7.20 (t, *J* = 8.8 Hz, 2H), 5.39 (s, 1H). **¹³C NMR (101 MHz, DMSO-*d*₆)** δ 189.51 , 175.37 , 152.89 , 138.97 , 135.84 , 133.31 , 132.75 , 131.22 , 129.40 , 129.32 , 121.71 , 121.11 , 116.01 , 115.79 , 105.72 , 79.64 , 53.39 . HRMS (ESI) *m/z* calcd for C₁₇H₁₂FN₂OS ([M+H]⁺): 311.0649, found: 311.0644.



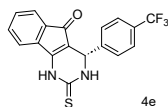
(S)-4-(4-chlorophenyl)-2-thioxo-1,2,3,4-tetrahydro-5H-indeno[1,2-d]pyrimidin-5-one (**4c**)

The crude product was purified by flash column chromatography (DCM/EA = 40/1) on silicagel. Red solid, 67% yield (21.90 mg), $[\alpha]_D^{25} = -1170$ (c = 0.10, EtOH), 94 % ee [Daicel Chiralcel AD column, *n*-hexane/ *i*-PrOH = 80 / 20, 1.0 ml/min, $\lambda = 254$ nm, t(major)= 16.8 min, t(minor) = 9.1 min]; **¹H NMR (400 MHz, DMSO-*d*₆)** δ 11.83 (s, 1H), 9.92 (s, 1H), 7.83 (d, *J* = 7.2 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 3H), 7.40 – 7.30 (m, 4H), 5.39 (s, 1H). **¹³C NMR (101 MHz, DMSO-*d*₆)** δ 189.46 , 175.50 , 152.95 , 141.60 , 135.80 , 133.30 , 132.98 , 132.75 , 131.25 , 129.18 , 129.10 , 121.72 , 121.13 , 105.47 , 53.46 . HRMS (ESI) *m/z* calcd for C₁₇H₁₂ClN₂OS ([M+H]⁺): 327.0353, found: 327.0349.



(S)-4-(4-bromophenyl)-2-thioxo-1,2,3,4-tetrahydro-5H-indeno[1,2-d]pyrimidin-5-one (**4d**)

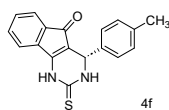
The crude product was purified by flash column chromatography (DCM/EA = 40/1) on silicagel. Red solid, 49% yield (18.20 mg), $[\alpha]_D^{25} = -1060$ (c = 0.10, EtOH), 92% ee [Daicel Chiralcel AD column, *n*-hexane/ *i*-PrOH = 80 / 20, 1.0 ml/min, $\lambda = 254$ nm, t(major)= 18.2 min, t(minor) = 9.8 min]; **¹H NMR (400 MHz, DMSO-*d*₆)** δ 11.83 (s, 1H), 9.92 (s, 1H), 7.82 (d, *J* = 7.2 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.40 – 7.25 (m, 4H), 5.38 (s, 1H). **¹³C NMR (101 MHz, DMSO-*d*₆)** δ 189.46 , 175.48 , 152.95 , 142.01 , 135.79 , 133.29 , 132.76 , 132.03 , 131.27 , 129.52 , 121.74 , 121.55 , 121.14 , 105.40 , 53.53 . HRMS (ESI) *m/z* calcd for C₁₇H₁₂BrN₂OS ([M+H]⁺): 370.9848, found: 370.9850.



(S)-2-thioxo-4-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydro-5H-indeno[1,2-d]pyrimidin-5-one (**4e**)

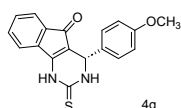
The crude product was purified by flash column chromatography (DCM/EA = 40/1) on silicagel. Red solid, 31% yield (11.30 mg), $[\alpha]_D^{25} = -960$ (c = 0.10, EtOH), 90% ee [Daicel Chiralcel AD column, *n*-hexane/ *i*-PrOH = 85 / 35, 1.0 ml/min, $\lambda = 254$ nm, t(major)= 5.4 min, t(minor) = 8.3 min]; **¹H NMR (400 MHz, DMSO-*d*₆)** δ 11.89 (s, 1H), 9.98 (s, 1H), 7.83 (d, *J* = 7.2 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.45 (t, *J* = 6.9 Hz, 1H), 7.41 – 7.29 (m, 2H), 5.51 (s, 1H). **¹³C NMR (101 MHz, DMSO-*d*₆)** δ 189.41 , 175.72 , 153.07 , 147.01 , 135.74 , 133.27 , 132.76 , 131.30 , 128.17 , 126.13 ,

121.75 , 121.20 , 105.15 , 53.73 . HRMS (ESI) m/z calcd for C₁₈H₁₂F₃N₂OS ([M+H]⁺): 361.0617, found: 361.0620.



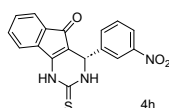
(S)-2-thioxo-4-(*p*-tolyl)-1,2,3,4-tetrahydro-5H-indeno[1,2-*d*]pyrimidin-5-one (**4f**)

The crude product was purified by flash column chromatography (DCM/EA = 40/1) on silicagel. Red solid, 71% yield (21.70 mg), $[\alpha]_D^{25} = -1190$ (c = 0.10, EtOH), 89% ee [Daicel Chiralcel AD column, *n*-hexane/ *i*-PrOH = 80 / 20, 1.0 ml/min, $\lambda = 254$ nm, t(major)= 17.0 min, t(minor) = 10.5 min]; **¹H NMR (400 MHz, DMSO-*d*₆)** δ 11.77 (s, 1H), 9.89 (s, 1H), 7.82 (d, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.40 – 7.30 (m, 2H), 7.18 (s, 4H), 5.31 (d, *J* = 2.4 Hz, 1H), 2.28 (s, 3H). **¹³C NMR (101 MHz, DMSO)** δ 189.56, 175.31, 152.76, 139.88, 137.70, 135.92, 133.36, 132.72, 131.16, 129.81, 129.64, 127.13, 121.67, 121.01, 106.11, 53.81, 21.17. HRMS (ESI) m/z calcd for C₁₈H₁₅N₂OS ([M+H]⁺): 307.0900, found: 307.0898.



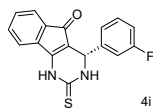
(S)-4-(4-methoxyphenyl)-2-thioxo-1,2,3,4-tetrahydro-5H-indeno[1,2-*d*]pyrimidin-5-one (**4g**)

The crude product was purified by flash column chromatography (DCM/EA = 40/1) on silicagel. Red solid, 75% yield (24.00 mg), $[\alpha]_D^{25} = -910$ (c = 0.10, EtOH), 80% ee [Daicel Chiralcel AD column, *n*-hexane/ *i*-PrOH = 85 / 35, 1.0 ml/min, $\lambda = 254$ nm, t(major)= 17.2 min, t(minor) = 8.9 min]; **¹H NMR (400 MHz, DMSO-*d*₆)** δ 11.74 (s, 1H), 9.85 (s, 1H), 7.82 (d, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.38 – 7.28 (m, 2H), 7.21 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 5.29 (s, 1H), 3.72 (s, 3H). **¹³C NMR (101 MHz, DMSO-*d*₆)** δ 189.59 , 175.12 , 159.44 , 152.70 , 135.93 , 134.90 , 133.36 , 132.69 , 131.11 , 128.49 , 121.63 , 120.99 , 114.46 , 106.18 , 79.64 , 55.62 , 53.53 . HRMS (ESI) m/z calcd for C₁₈H₁₅N₂O₂S ([M+H]⁺): 323.0849, found: 323.0847.



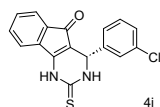
(S)-4-(3-nitrophenyl)-2-thioxo-1,2,3,4-tetrahydro-5H-indeno[1,2-*d*]pyrimidin-5-one (**4h**)

The crude product was purified by flash column chromatography (DCM/EA = 40/1) on silicagel. Red solid, 85% yield (28.60 mg), $[\alpha]_D^{25} = -990$ (c = 0.10, EtOH), 97% ee [Daicel Chiralcel OJ-H column, *n*-hexane/ EtOH = 50 / 50, 1.0 ml/min, $\lambda = 254$ nm, t(major)= 19.4 min, t(minor) = 14.8 min]; **¹H NMR (400 MHz, DMSO-*d*₆)** δ 11.94 (s, 1H), 10.03 (s, 1H), 8.19 (d, *J* = 7.4 Hz, 2H), 7.83 (dd, *J* = 16.7, 7.4 Hz, 2H), 7.70 (t, *J* = 7.9 Hz, 1H), 7.51 – 7.31 (m, 3H), 5.64 (s, 1H). **¹³C NMR (101 MHz, DMSO)** δ 189.44, 175.79, 153.26, 148.31, 144.60, 135.70, 134.04, 133.25, 132.83, 131.39, 130.87, 123.40, 122.02, 121.83, 121.28, 104.79, 53.44. HRMS (ESI) m/z calcd for C₁₇H₁₂N₃O₃S ([M+H]⁺): 338.0594, found: 338.0591.



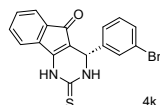
(S)-4-(3-fluorophenyl)-2-thioxo-1,2,3,4-tetrahydro-5H-indeno[1,2-*d*]pyrimidin-5-one (**4i**)

The crude product was purified by flash column chromatography (DCM/EA = 40/1) on silicagel. Red solid, 88% yield (27.30 mg), $[\alpha]_D^{25} = -980$ (c = 0.10, EtOH), 91%ee [Daicel Chiralcel AD column, *n*-hexane/ *i*-PrOH = 80 / 20, 1.0 ml/min, $\lambda = 254$ nm, t(major)= 14.2 min, t(minor) = 9.6 min]; **¹H NMR (400 MHz, DMSO-*d*₆)** δ 11.83 (s, 1H), 9.94 (s, 1H), 7.82 (d, *J* = 7.2 Hz, 1H), 7.39 (ddt, *J* = 33.3, 15.0, 6.9 Hz, 4H), 7.14 (dd, *J* = 13.4, 8.6 Hz, 3H), 5.42 (s, 1H). **¹³C NMR (101 MHz, DMSO)** δ 189.47, 175.65, 163.84, 161.41, 153.05, 145.41, 135.79, 133.30, 132.74, 131.27, 123.21, 121.74, 121.16, 115.30, 113.94, 105.32, 53.54. HRMS (ESI) *m/z* calcd for C₁₇H₁₂FN₂OS ([M+H]⁺): 311.0649, found: 311.0652.



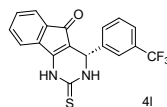
(S)-4-(3-chlorophenyl)-2-thioxo-1,2,3,4-tetrahydro-5H-indeno[1,2-*d*]pyrimidin-5-one (**4j**)

The crude product was purified by flash column chromatography (DCM/EA = 40/1) on silicagel. Red solid, 74% yield (24.30 mg), $[\alpha]_D^{25} = -1090$ (c = 0.10, EtOH), 94%ee [Daicel Chiralcel AD column, *n*-hexane/ *i*-PrOH = 80 / 20, 1.0 ml/min, $\lambda = 254$ nm, t(major)= 13.8 min, t(minor) = 9.3 min]; **¹H NMR (400 MHz, DMSO-*d*₆)** δ 11.80 (s, 1H), 9.81 (s, 1H), 7.84 (d, *J* = 7.2 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.41 – 7.32 (m, 4H), 7.28 (d, *J* = 6.9 Hz, 1H), 5.73 (s, 1H). **¹³C NMR (101 MHz, DMSO)** δ 189.14, 175.59, 153.25, 139.09, 135.84, 133.35, 132.67, 132.60, 131.24, 130.32, 130.26, 128.11, 121.59, 121.10, 104.67, 52.61. HRMS (ESI) *m/z* calcd for C₁₇H₁₂ClN₂OS ([M+H]⁺): 327.0353, found: 327.0350.



(S)-4-(3-bromophenyl)-2-thioxo-1,2,3,4-tetrahydro-5H-indeno[1,2-*d*]pyrimidin-5-one (**4k**)

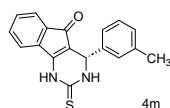
The crude product was purified by flash column chromatography (DCM/EA = 40/1) on silicagel. Red solid, 70% yield (25.90 mg), $[\alpha]_D^{25} = -1200$ (c = 0.10, EtOH), 94%ee [Daicel Chiralcel AD column, *n*-hexane/ *i*-PrOH = 80 / 20, 1.0 ml/min, $\lambda = 254$ nm, t(major)= 14.9 min, t(minor) = 9.5 min]; **¹H NMR (400 MHz, DMSO-*d*₆)** δ 11.85 (s, 1H), 9.93 (s, 1H), 7.82 (d, *J* = 7.2 Hz, 1H), 7.52 – 7.43 (m, 3H), 7.41 – 7.29 (m, 4H), 5.41 (s, 1H). **¹³C NMR (101 MHz, DMSO)** δ 189.46, 175.59, 153.08, 145.21, 135.77, 133.28, 132.78, 131.45, 131.30, 131.27, 130.05, 126.33, 122.22, 121.78, 121.19, 105.20, 53.51. HRMS (ESI) *m/z* calcd for C₁₇H₁₂BrN₂OS ([M+H]⁺): 370.9848, found: 370.9846.



(S)-2-thioxo-4-(3-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydro-5H-indeno[1,2-*d*]pyrimidin-5-one (**4l**)

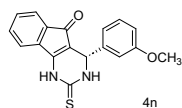
The crude product was purified by flash column chromatography (DCM/EA = 40/1) on silicagel. Red solid, 44% yield (15.80 mg), $[\alpha]_D^{25} = -1150$ (c = 0.10, EtOH), 96%ee [Daicel Chiralcel AD column, *n*-hexane/ *i*-PrOH = 80 / 20, 1.0 ml/min, $\lambda = 254$ nm, t(major)= 10.2 min, t(minor) = 6.8 min]; **¹H NMR (400 MHz, DMSO-*d*₆)** δ 11.86 (s, 1H), 9.95 (s, 1H), 7.83 (d, *J* = 7.2 Hz, 1H), 7.77 – 7.57 (m, 4H), 7.52 – 7.29 (m, 3H), 5.55 (s, 1H). **¹³C NMR (101 MHz, DMSO)** δ 189.46, 175.77, 153.15, 143.88, 135.75, 133.28, 132.76, 131.37, 131.29, 130.40, 125.19, 123.99, 121.77, 121.21, 105.07, 53.69. HRMS (ESI)

m/z calcd for C₁₈H₁₂F₃N₂OS ([M+H]⁺): 361.0617, found: 361.0620.



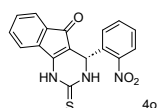
(S)-2-thioxo-4-(*m*-tolyl)-1,2,3,4-tetrahydro-5H-indeno[1,2-*d*]pyrimidin-5-one (**4m**)

The crude product was purified by flash column chromatography (DCM/EA = 40/1) on silicagel. Red solid, 78% yield (23.80 mg), $[\alpha]_D^{25} = -1150$ (c = 0.10, EtOH), 91%ee [Daicel Chiralcel AD column, *n*-hexane/ *i*-PrOH = 80 / 20, 1.0 ml/min, $\lambda = 254$ nm, t(major) = 14.7 min, t(minor) = 9.8 min]; **¹H NMR (400 MHz, DMSO-*d*₆)** δ 11.76 (s, 1H), 9.87 (s, 1H), 7.82 (d, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.40 – 7.22 (m, 3H), 7.18 – 7.03 (m, 3H), 5.31 (s, 1H), 2.29 (s, 3H). **¹³C NMR (101 MHz, DMSO)** δ 189.53, 175.37, 152.79, 142.73, 138.26, 135.88, 133.35, 132.73, 131.18, 129.05, 127.65, 124.38, 121.70, 121.03, 105.98, 54.08, 21.54. HRMS (ESI) m/z calcd for C₁₈H₁₅N₂OS ([M+H]⁺): 307.0900, found: 307.0897.



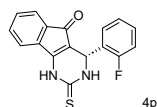
(S)-2-thioxo-4-(3-methoxyphenyl)-1,2,3,4-tetrahydro-5H-indeno[1,2-*d*]pyrimidin-5-one (**4n**)

The crude product was purified by flash column chromatography (DCM/EA = 40/1) on silicagel. Red solid, 81% yield (26.10 mg), $[\alpha]_D^{25} = -1160$ (c = 0.10, EtOH), 99%ee [Daicel Chiralcel AD column, *n*-hexane/ *i*-PrOH = 80 / 20, 1.0 ml/min, $\lambda = 254$ nm, t(major) = 20.8 min, t(minor) = 13.4 min]; **¹H NMR (400 MHz, DMSO-*d*₆)** δ 11.79 (s, 1H), 9.91 (s, 1H), 7.82 (d, *J* = 7.2 Hz, 1H), 7.52 – 7.25 (m, 4H), 6.96 – 6.74 (m, 3H), 5.34 (s, 1H), 3.75 (s, 3H). **¹³C NMR (101 MHz, DMSO)** δ 189.52, 175.56, 159.83, 152.87, 144.25, 135.83, 133.33, 132.75, 131.21, 130.35, 121.73, 121.05, 119.04, 113.36, 113.21, 105.85, 55.56, 53.83. HRMS (ESI) m/z calcd for C₁₈H₁₅N₂O₂S ([M+H]⁺): 323.0849, found: 323.0844.



(S)-4-(2-nitrophenyl)-2-thioxo-1,2,3,4-tetrahydro-5H-indeno[1,2-*d*]pyrimidin-5-one (**4o**)

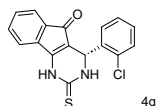
The crude product was purified by flash column chromatography (DCM/EA = 40/1) on silicagel. Red solid, 43% yield (14.30 mg), $[\alpha]_D^{25} = -970$ (c = 0.10, EtOH), 91%ee [Daicel Chiralcel OJ-H column, *n*-hexane/ EtOH = 50 / 50, 1.0 ml/min, $\lambda = 254$ nm, t(major) = 28.5 min, t(minor) = 16.1 min]; **¹H NMR (400 MHz, DMSO-*d*₆)** δ 11.90 (s, 1H), 9.85 (s, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.84 (d, *J* = 7.2 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 2H), 7.42 (dt, *J* = 34.2, 7.5 Hz, 2H), 7.29 (d, *J* = 7.0 Hz, 1H), 6.21 (s, 1H). **¹³C NMR (101 MHz, DMSO)** δ 189.10, 175.68, 153.17, 148.21, 136.30, 135.72, 134.53, 133.23, 132.77, 131.36, 130.96, 129.86, 125.14, 121.72, 121.25, 104.49, 49.68. HRMS (ESI) m/z calcd for C₁₇H₁₂N₃O₃S ([M+H]⁺): 338.0594, found: 338.0588.



(S)-4-(2-fluorophenyl)-2-thioxo-1,2,3,4-tetrahydro-5H-indeno[1,2-*d*]pyrimidin-5-one (**4p**)

The crude product was purified by flash column chromatography (DCM/EA = 40/1) on silicagel. Red

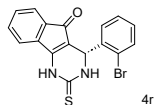
solid, 78% yield (24.30 mg), $[\alpha]_D^{25} = -960$ (c = 0.10, EtOH), 96% ee [Daicel Chiralcel AD column, *n*-hexane/ *i*-PrOH = 80 / 20, 1.0 ml/min, $\lambda = 254$ nm, t(major) = 19.6 min, t(minor) = 10.2 min]; **¹H NMR (400 MHz, DMSO-*d*₆)** δ 11.80 (s, 1H), 9.84 (s, 1H), 7.84 (d, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.42 – 7.27 (m, 4H), 7.19 (q, *J* = 8.7, 7.8 Hz, 2H), 5.55 (s, 1H). **¹³C NMR (101 MHz, DMSO)** δ 189.21, 175.59, 159.22, 153.03, 135.85, 133.35, 132.69, 131.22, 130.71, 130.62, 130.31, 129.43, 129.30, 125.17, 121.63, 121.09, 116.33, 116.12, 104.71, 49.25, 40.64, 40.43, 40.22, 40.01, 39.80, 39.60, 39.39, 21.52. HRMS (ESI) *m/z* calcd for C₁₇H₁₂FN₂OS ([M+H]⁺): 311.0649, found: 311.0641.



(S)-4-(2-chlorophenyl)-2-thioxo-1,2,3,4-tetrahydro-5H-indeno[1,2-d]pyrimidin-5-one (**4q**)

The crude product was purified by flash column chromatography (DCM/EA = 40/1) on silicagel. Red

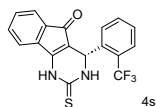
solid, 71% yield (23.20 mg), $[\alpha]_D^{25} = -1100$ (c = 0.10, EtOH), 98% ee [Daicel Chiralcel AD column, *n*-hexane/ *i*-PrOH = 80 / 20, 1.0 ml/min, $\lambda = 254$ nm, t(major) = 16.2 min, t(minor) = 10.6 min]; **¹H NMR (400 MHz, DMSO-*d*₆)** δ 11.81 (s, 1H), 9.82 (s, 1H), 7.84 (d, *J* = 7.2 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.40 – 7.32 (m, 4H), 7.28 (d, *J* = 6.9 Hz, 1H), 5.73 (s, 1H). **¹³C NMR (101 MHz, DMSO)** δ 189.14, 175.58, 153.25, 139.08, 135.83, 133.34, 132.68, 132.60, 131.25, 130.32, 130.26, 128.11, 121.59, 121.11, 104.66, 52.61. HRMS (ESI) *m/z* calcd for C₁₇H₁₂ClN₂OS ([M+H]⁺): 327.0353, found: 327.0359.



(S)-4-(2-bromophenyl)-2-thioxo-1,2,3,4-tetrahydro-5H-indeno[1,2-d]pyrimidin-5-one (**4r**)

The crude product was purified by flash column chromatography (DCM/EA = 40/1) on silicagel. Red

solid, 67% yield (24.80 mg), $[\alpha]_D^{25} = -1020$ (c = 0.10, EtOH), 96% ee [Daicel Chiralcel AD column, *n*-hexane/ *i*-PrOH = 80 / 20, 1.0 ml/min, $\lambda = 254$ nm, t(major) = 16.2 min, t(minor) = 10.9 min]; **¹H NMR (400 MHz, DMSO-*d*₆)** δ 11.80 (s, 1H), 9.82 (s, 1H), 7.85 (d, *J* = 7.2 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.46 – 7.33 (m, 4H), 7.26 (dd, *J* = 15.9, 7.1 Hz, 2H), 5.74 (s, 1H). **¹³C NMR (101 MHz, DMSO)** δ 189.08, 175.53, 153.25, 140.66, 135.85, 133.54, 133.35, 132.65, 131.46, 131.22, 130.50, 128.71, 122.60, 121.57, 121.13, 104.87, 54.80. HRMS (ESI) *m/z* calcd for C₁₇H₁₂BrN₂OS ([M+H]⁺): 370.9848, found: 370.9842.

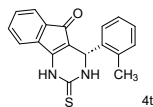


(S)-2-thioxo-4-(2-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydro-5H-indeno[1,2-d]pyrimidin-5-one (**4s**)

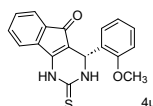
The crude product was purified by flash column chromatography (DCM/EA = 40/1) on silicagel. Red

solid, 42% yield (15.00 mg), $[\alpha]_D^{25} = -1120$ (c = 0.10, EtOH), 94% ee [Daicel Chiralcel AD column, *n*-hexane/ *i*-PrOH = 80 / 20, 1.0 ml/min, $\lambda = 254$ nm, t(major) = 9.7 min, t(minor) = 7.5 min]; **¹H NMR (400 MHz, DMSO-*d*₆)** δ 11.84 (s, 1H), 9.88 (s, 1H), 7.88 (d, *J* = 7.2 Hz, 1H), 7.74 – 7.65 (m, 2H), 7.59 – 7.44 (m, 3H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.27 (d, *J* = 7.0 Hz, 1H), 5.68 (s, 1H). **¹³C NMR (101 MHz, DMSO)** δ 188.85, 175.28, 170.76, 153.05, 141.41, 135.76, 133.63, 133.24, 132.66, 131.25, 131.04,

129.03, 125.89, 121.57, 121.16, 105.30, 60.20, 50.55, 21.20, 14.54. HRMS (ESI) m/z calcd for $C_{18}H_{12}F_3N_2OS$ ($[M+H]^+$): 361.0617, found: 361.0610.

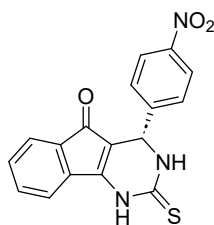


(S)-2-thioxo-4-(*o*-tolyl)-1,2,3,4-tetrahydro-5H-indeno[1,2-*d*]pyrimidin-5-one (**4t**) The crude product was purified by flash column chromatography (DCM/EA = 40/1) on silicagel. Red solid, 68% yield (23.80 mg), $[\alpha]_D^{25} = -930$ (c = 0.10, EtOH), 92% ee [Daicel Chiralcel AD column, *n*-hexane/ *i*-PrOH = 80 / 20, 1.0 ml/min, $\lambda = 254$ nm, t(major) = 12.2 min, t(minor) = 8.8 min]; 1H NMR (400 MHz, DMSO- d_6) δ 11.75 (s, 1H), 9.75 (s, 1H), 7.83 (d, $J = 7.2$ Hz, 1H), 7.44 (t, $J = 7.4$ Hz, 1H), 7.35 (t, $J = 7.4$ Hz, 1H), 7.28 (d, $J = 7.0$ Hz, 1H), 7.17 (t, $J = 4.2$ Hz, 4H), 5.56 (s, 1H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 189.49, 175.18, 152.60, 141.33, 135.99, 135.66, 133.33, 132.68, 131.10, 130.84, 128.31, 128.24, 127.07, 121.56, 121.00, 106.60, 51.14, 19.32. HRMS (ESI) m/z calcd for $C_{18}H_{15}N_2OS$ ($[M+H]^+$): 307.0900, found: 307.0898.

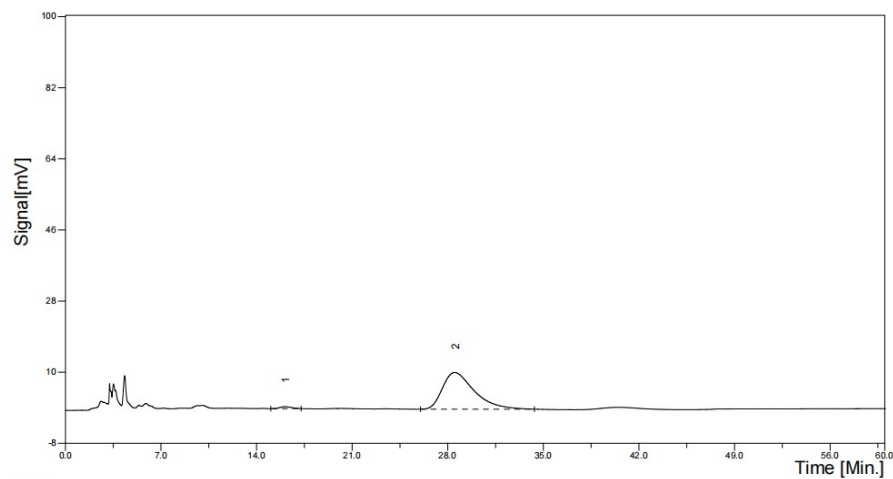


(S)-4-(2-methoxyphenyl)-2-thioxo-1,2,3,4-tetrahydro-5H-indeno[1,2-*d*]pyrimidin-5-one (**4u**) The crude product was purified by flash column chromatography (DCM/EA = 40/1) on silicagel. Red solid, 54% yield (17.30 mg), $[\alpha]_D^{25} = -1050$ (c = 0.10, EtOH), 90% ee [Daicel Chiralcel AD column, *n*-hexane/ *i*-PrOH = 80 / 20, 1.0 ml/min, $\lambda = 254$ nm, t(major) = 20.9 min, t(minor) = 10.7 min]; 1H NMR (400 MHz, DMSO- d_6) δ 11.67 (s, 1H), 9.53 (s, 1H), 7.82 (d, $J = 7.2$ Hz, 1H), 7.44 (t, $J = 7.5$ Hz, 1H), 7.32 (dt, $J = 27.0, 7.3$ Hz, 3H), 7.15 (d, $J = 7.5$ Hz, 1H), 7.02 (d, $J = 8.2$ Hz, 1H), 6.92 (t, $J = 7.4$ Hz, 1H), 5.53 (s, 1H), 3.78 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 189.36, 175.62, 157.63, 153.39, 136.05, 133.53, 132.57, 131.02, 129.99, 129.28, 121.48, 120.92, 120.81, 112.25, 105.16, 56.27, 50.24. HRMS (ESI) m/z calcd for $C_{18}H_{15}N_2O_2S$ ($[M+H]^+$): 323.0849, found: 323.0850.

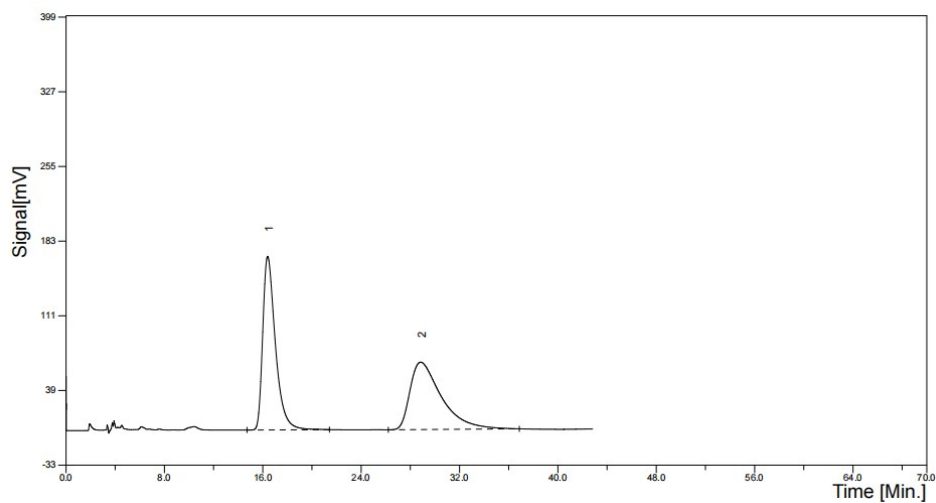
3. Copies of HPLC spectra.



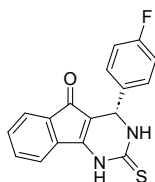
4a



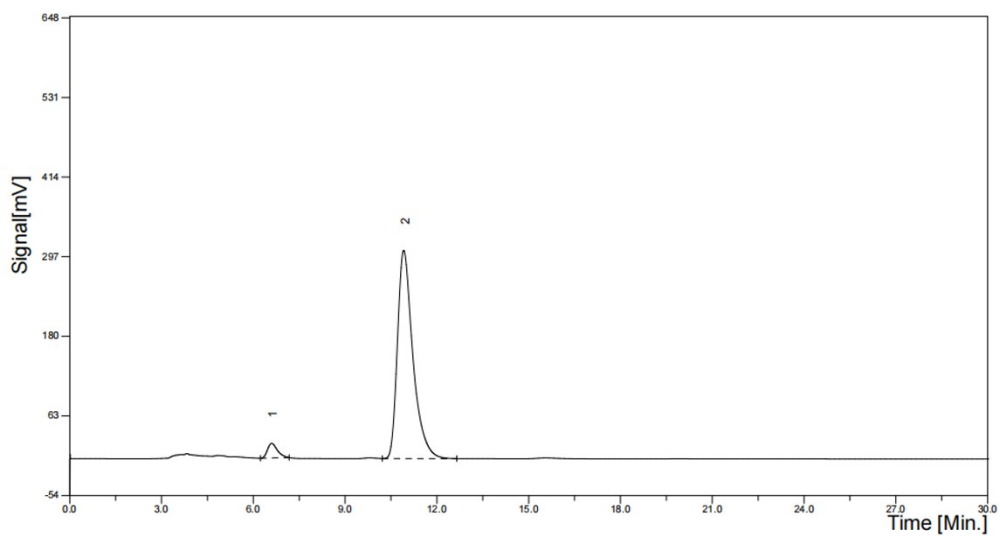
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
	16.055	0.490	28.57	1.8667
	28.491	9.29	1502.20	98.1333



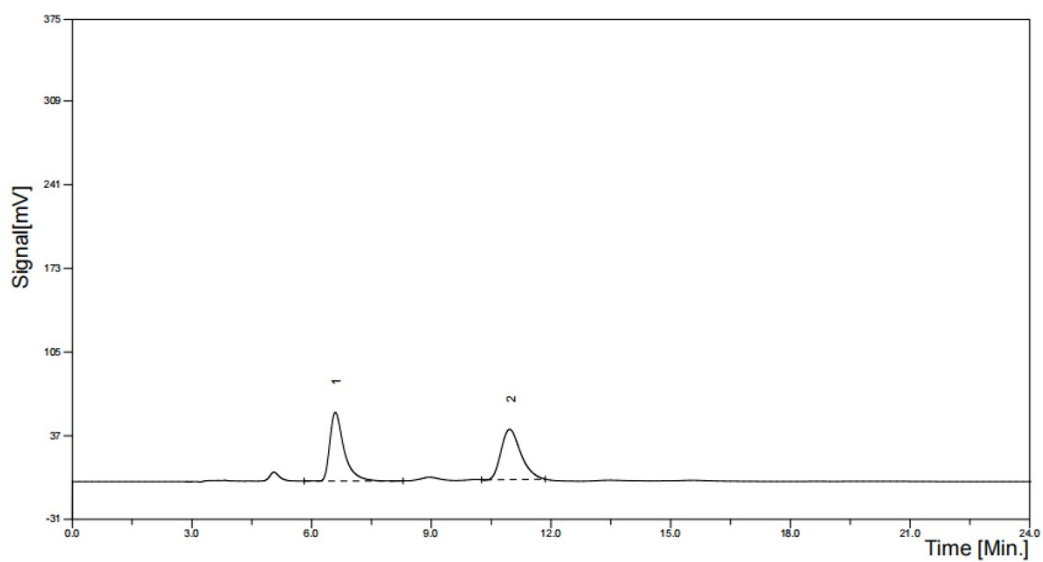
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
	16.398	167.43	11961.08	50.9686
	28.842	65.04	11506.48	49.0314



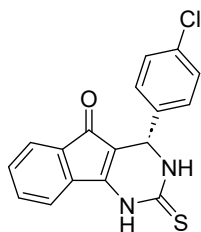
4b



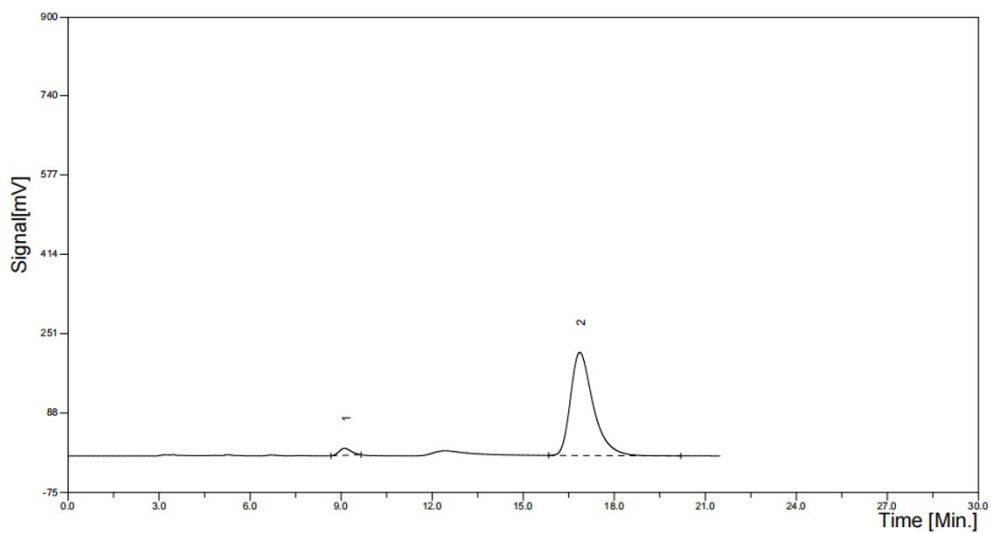
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
1	6.600	21.46	482.00	4.3043
2	10.917	65.04	10715.99	95.6957



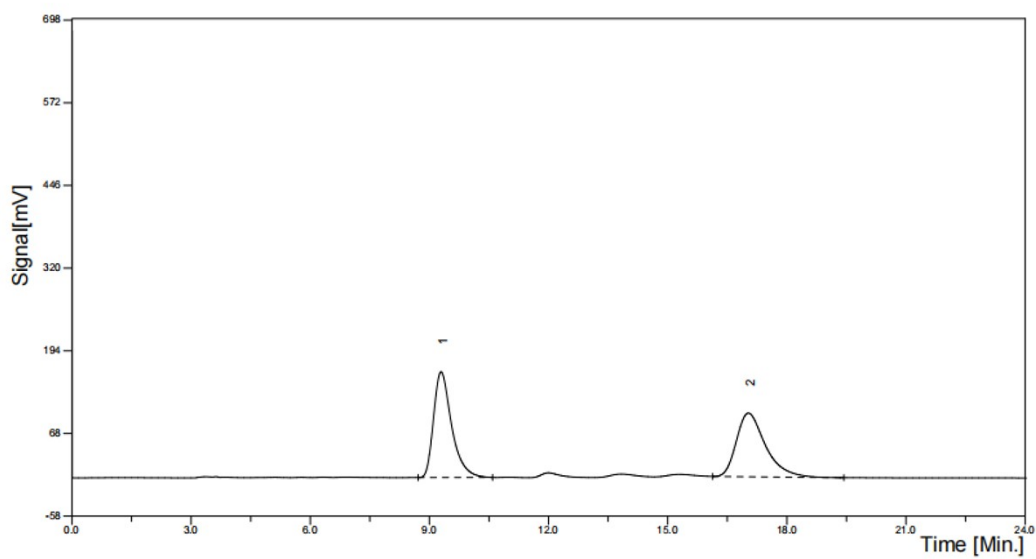
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
1	6.595	55.79	1370.00	49.5167
2	10.962	40.77	1396.74	50.4833



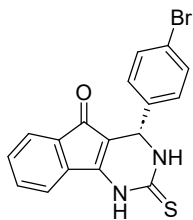
4c



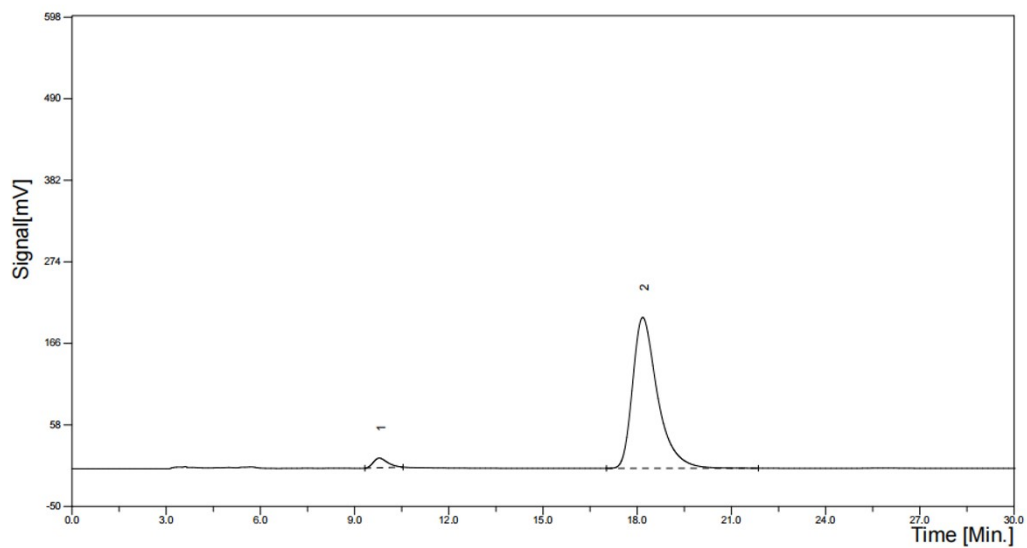
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
1	9.112	14.17	387.28	3.4206
2	16.864	211.79	10934.72	96.5794



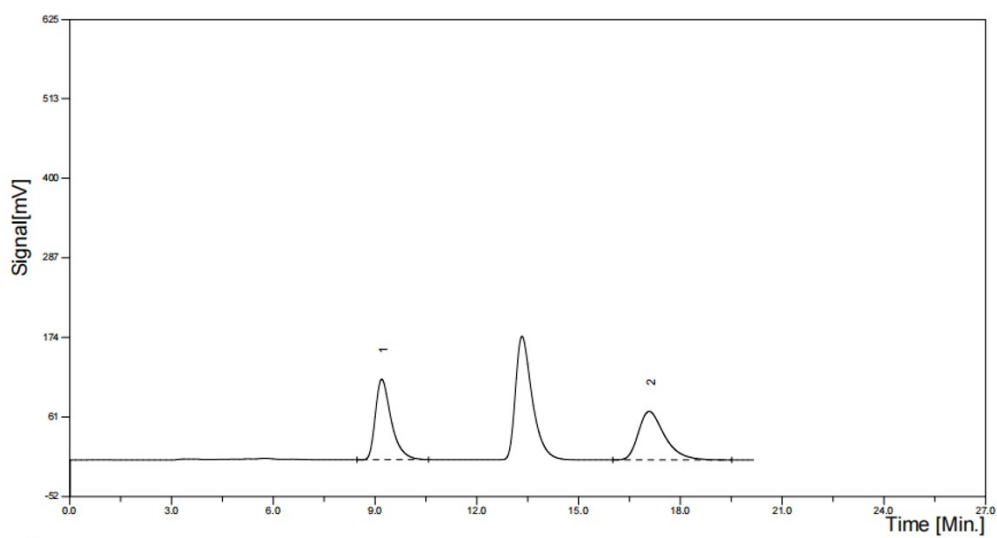
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
1	9.295	161.23	5085.06	50.7738
2	17.032	97.06	4930.07	49.2262



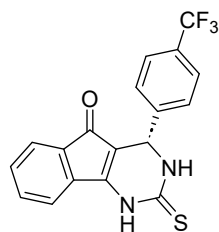
4d



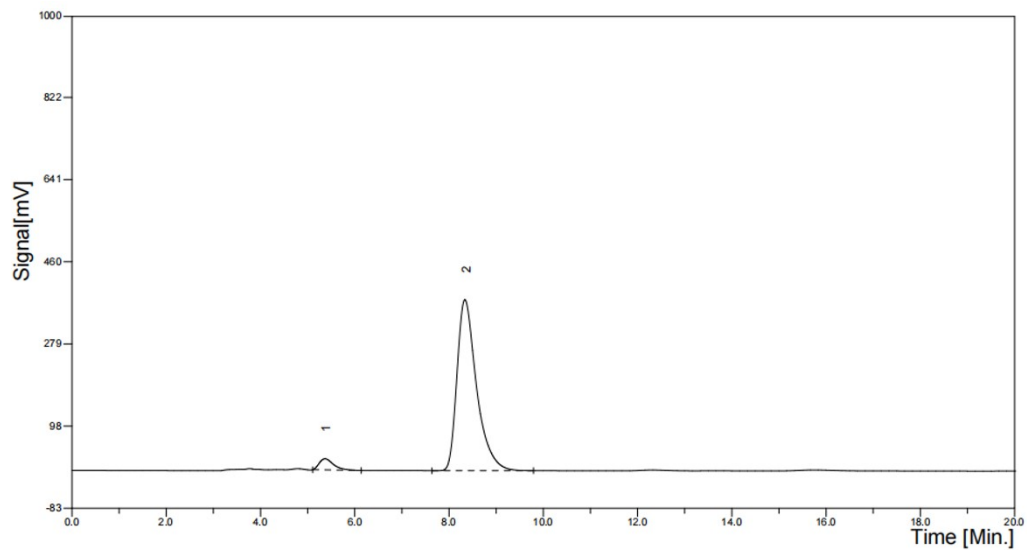
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
	9.787	12.80	402.99	3.5309
	18.175	199.90	11010.14	96.4691



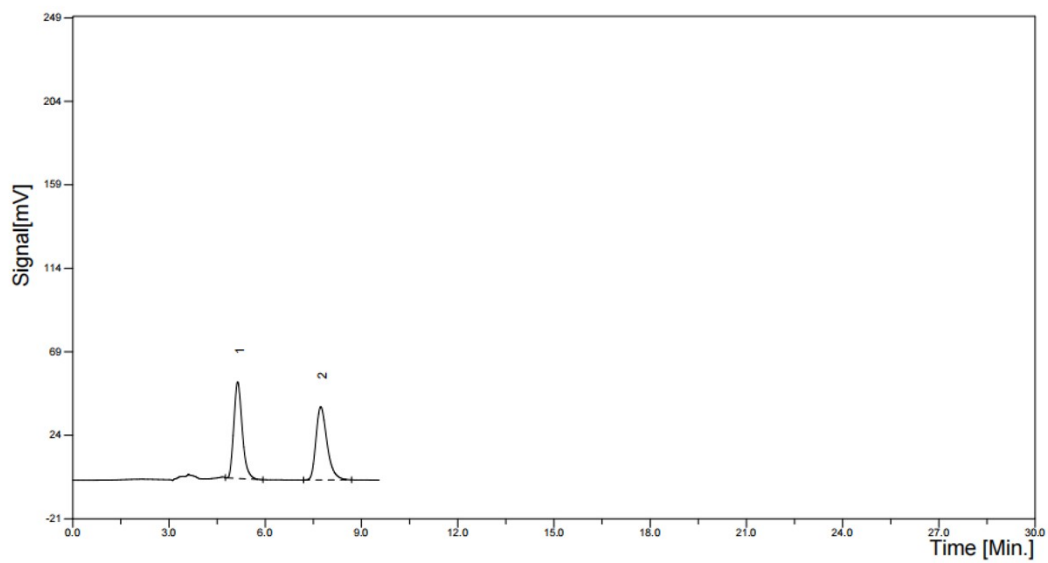
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
	9.196	114.19	3692.82	50.0277
	17.080	68.83	3688.73	49.9723



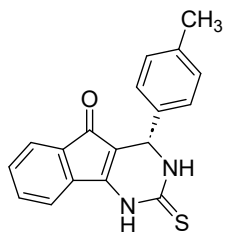
4e



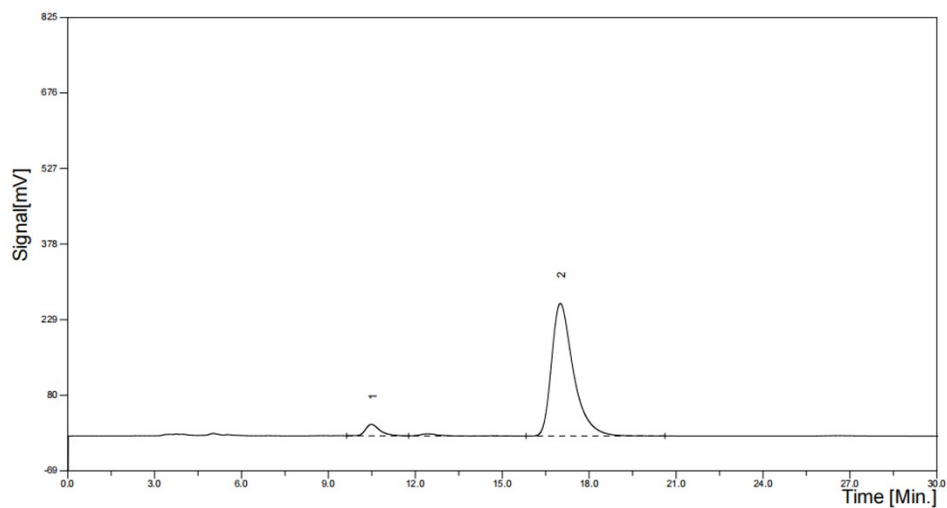
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
1	5.368	24.70	517.33	4.5529
2	8.337	376.74	10845.29	95.4471



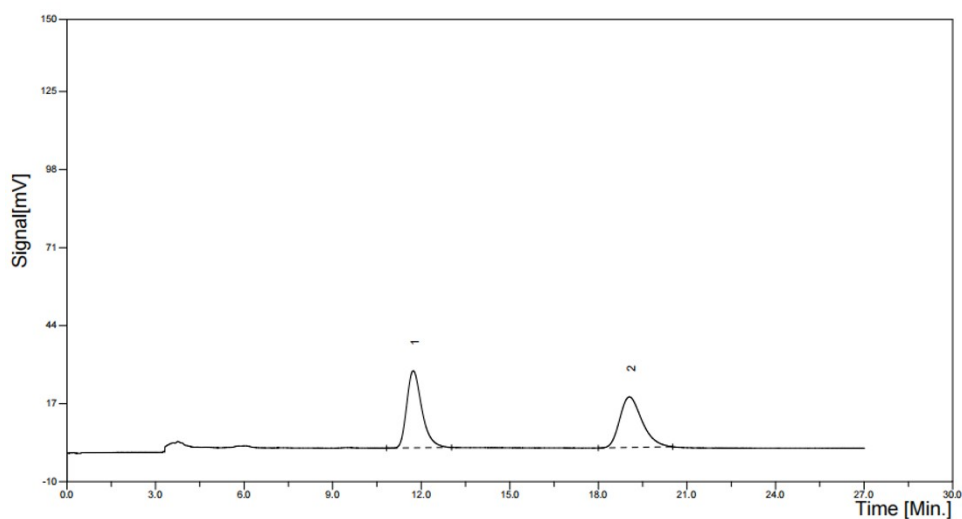
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
1	5.141	52.04	943.16	49.9602
2	7.729	39.42	944.67	50.0398



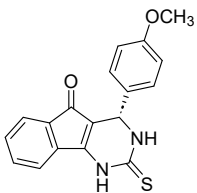
4f



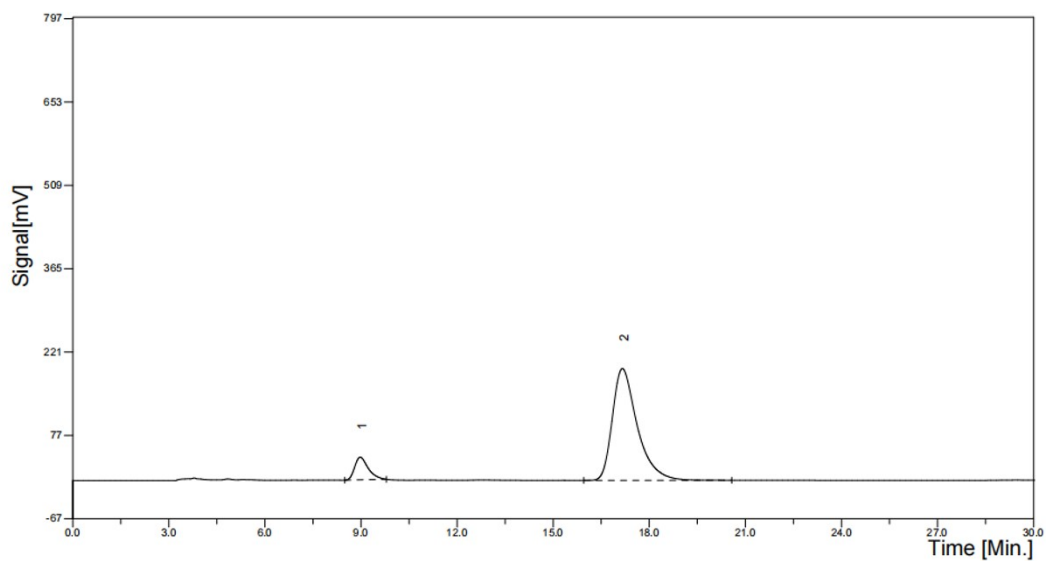
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
	10.485	22.54	767.81	5.3355
	17.005	261.39	13622.72	94.6645



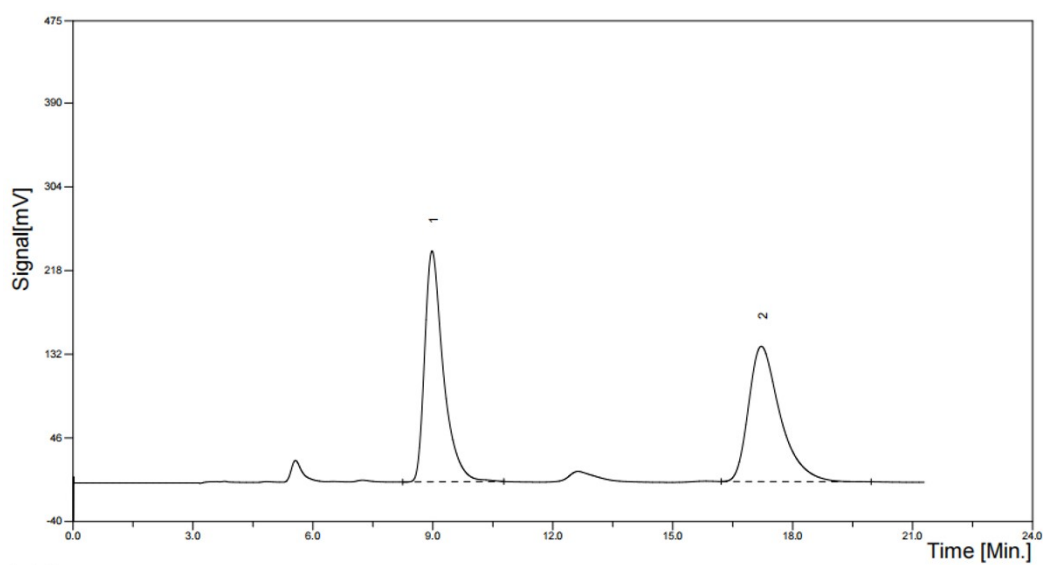
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
	11.732	26.70	946.08	50.6712
	19.052	17.55	921.02	49.3288



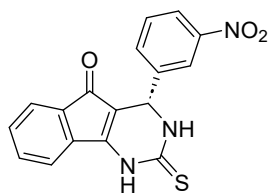
4g



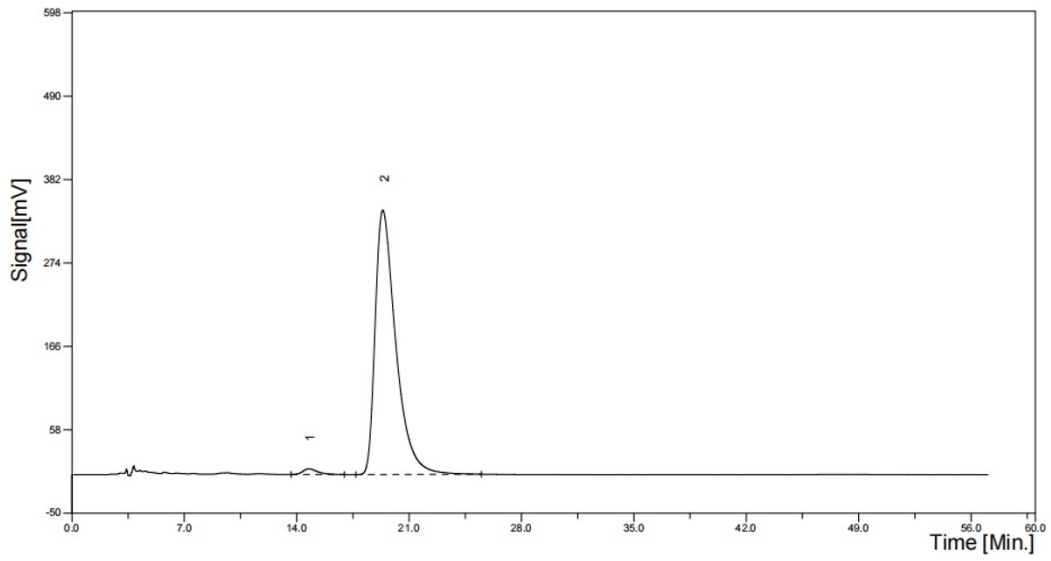
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
	8.976	39.27	1152.51	9.9479
	17.160	193.17	10432.96	90.0521



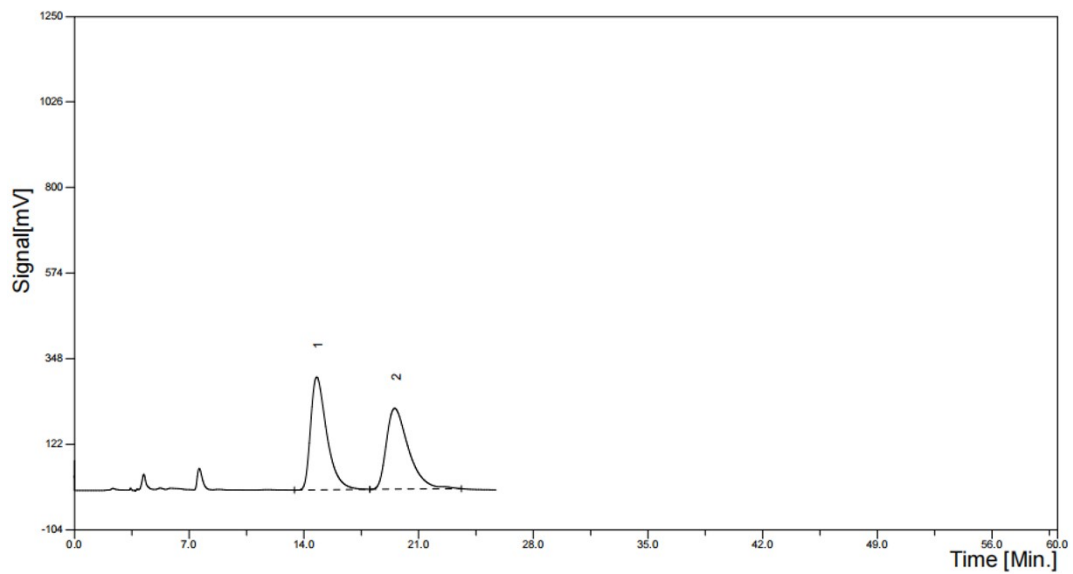
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
	8.980	237.38	7696.11	50.2200
	17.216	139.05	7628.69	49.7800



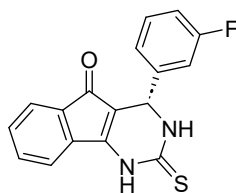
4h



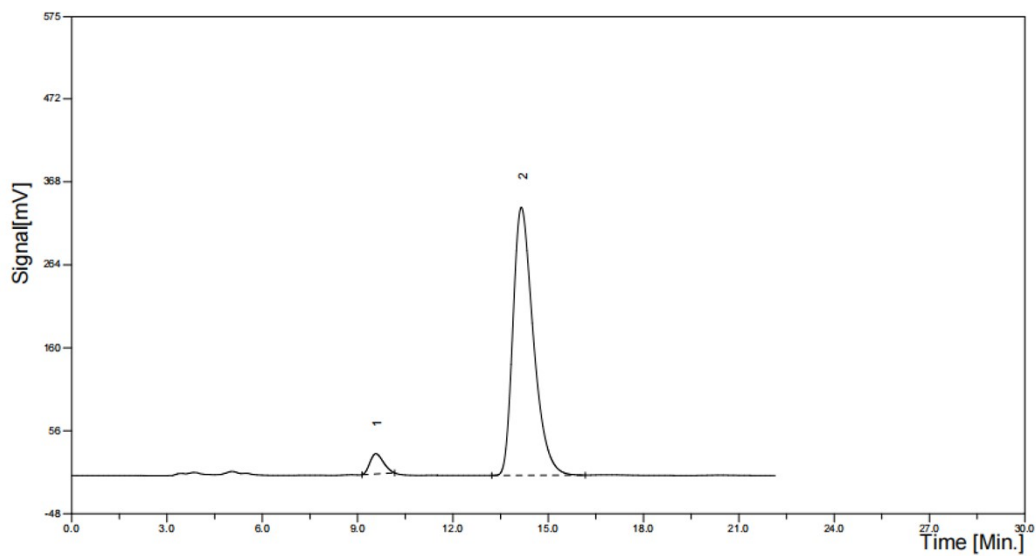
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
	14.758	7.28	458.59	1.4784
	19.362	342.26	30560.55	98.5216



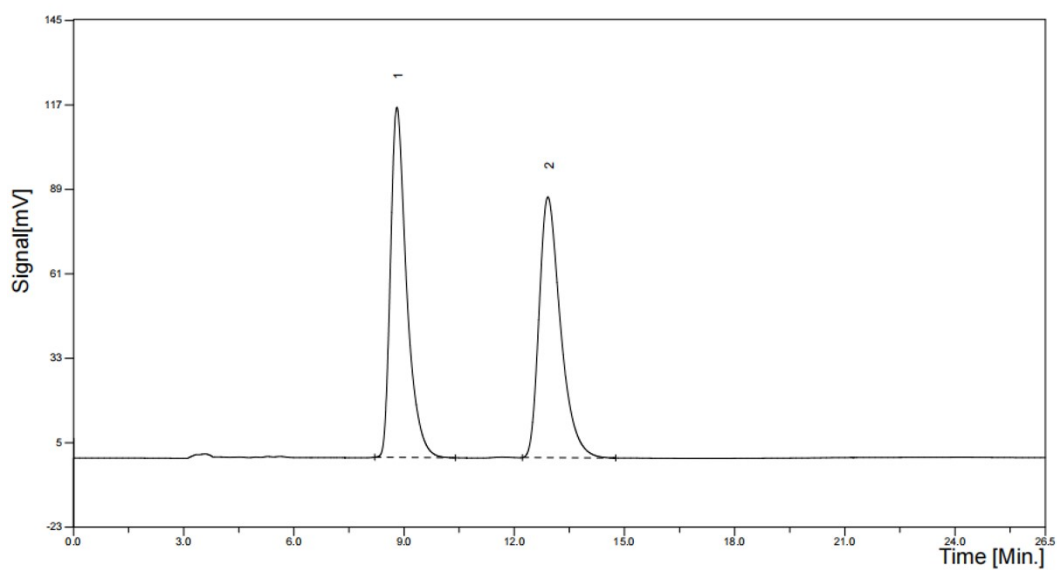
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
	14.787	297.89	20369.09	50.3861
	19.543	213.53	20056.88	49.6139



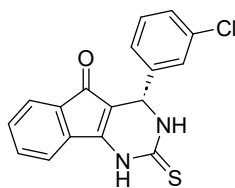
4i



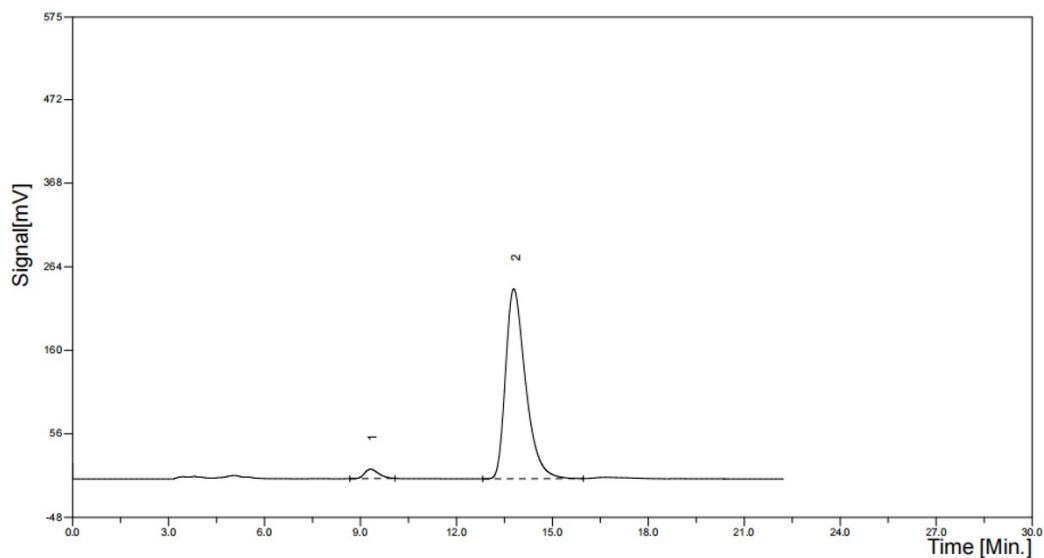
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
	9.578	25.38	742.99	4.7254
	14.153	335.92	14980.41	95.2746



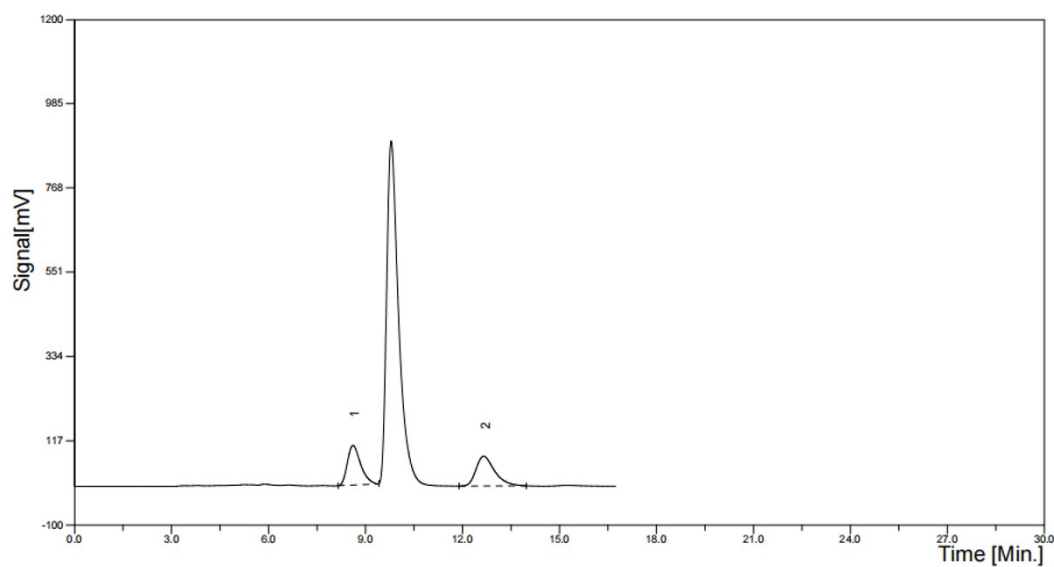
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
	8.806	116.14	3536.67	50.2620
	12.916	86.48	3499.80	49.7380



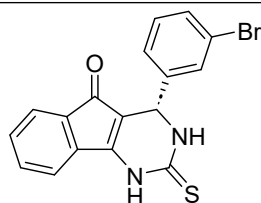
4j



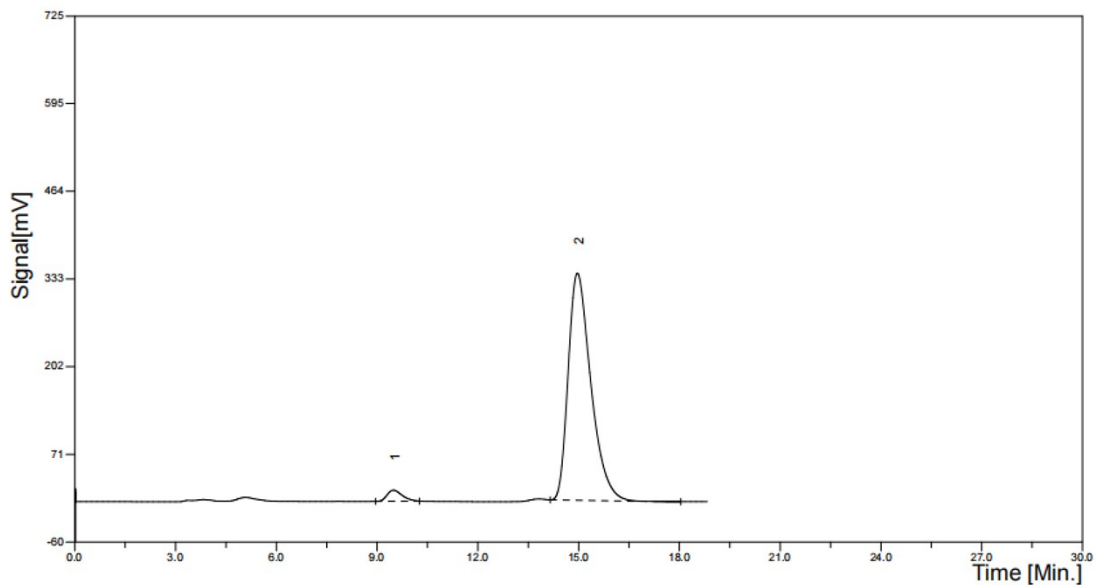
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
	9.313	11.66	354.43	3.3353
	13.793	236.60	10272.23	96.6647



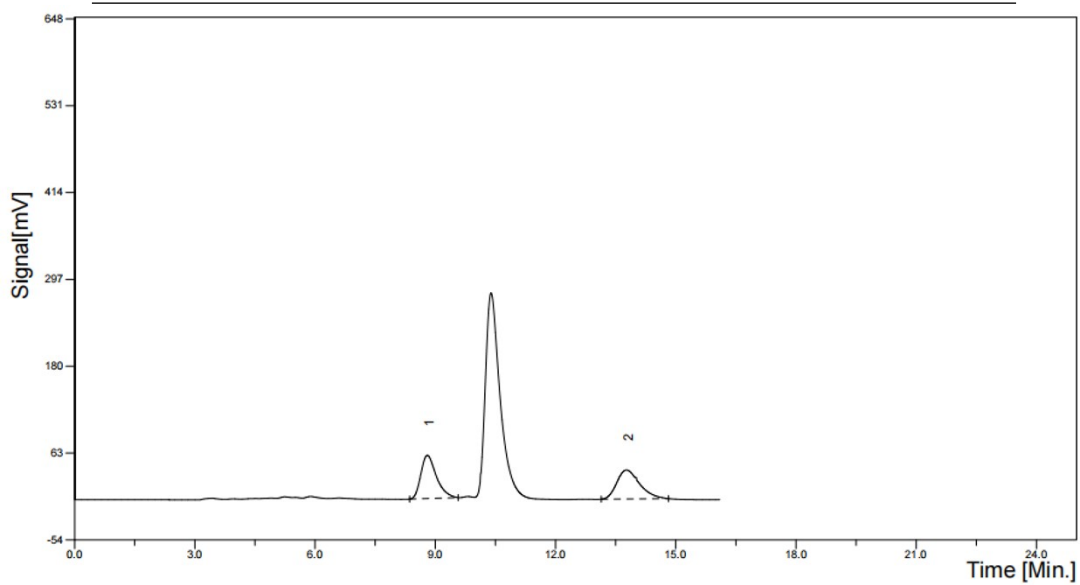
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
	8.613	101.70	2855.82	48.2942
	12.653	76.45	3057.57	51.7058



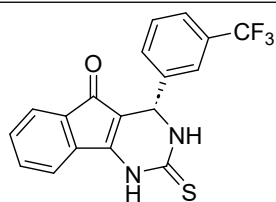
4k



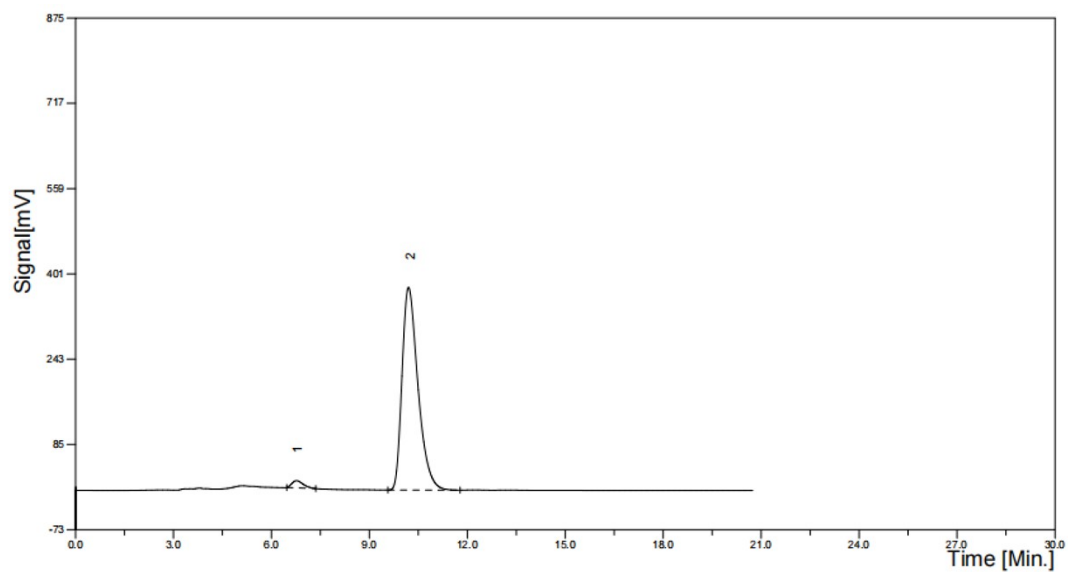
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
1	9.485	16.56	514.45	3.1396
2	14.963	339.24	15871.30	96.8604



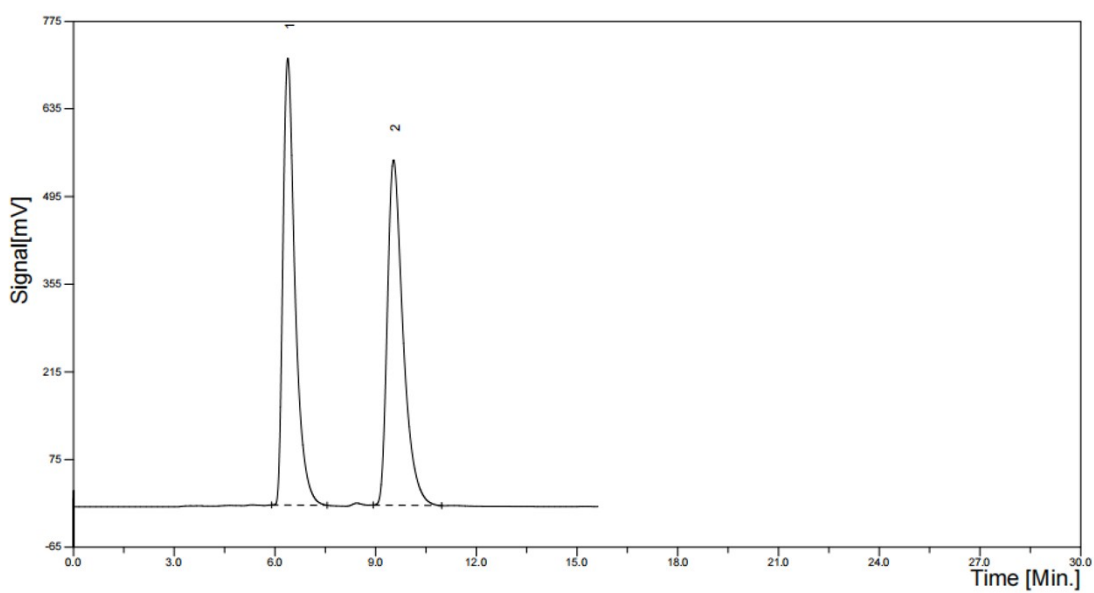
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
1	8.800	58.29	1565.28	50.3595
2	13.7768	39.04	1542.93	49.6405



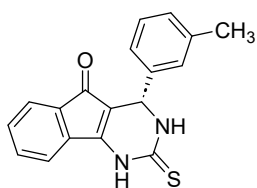
41



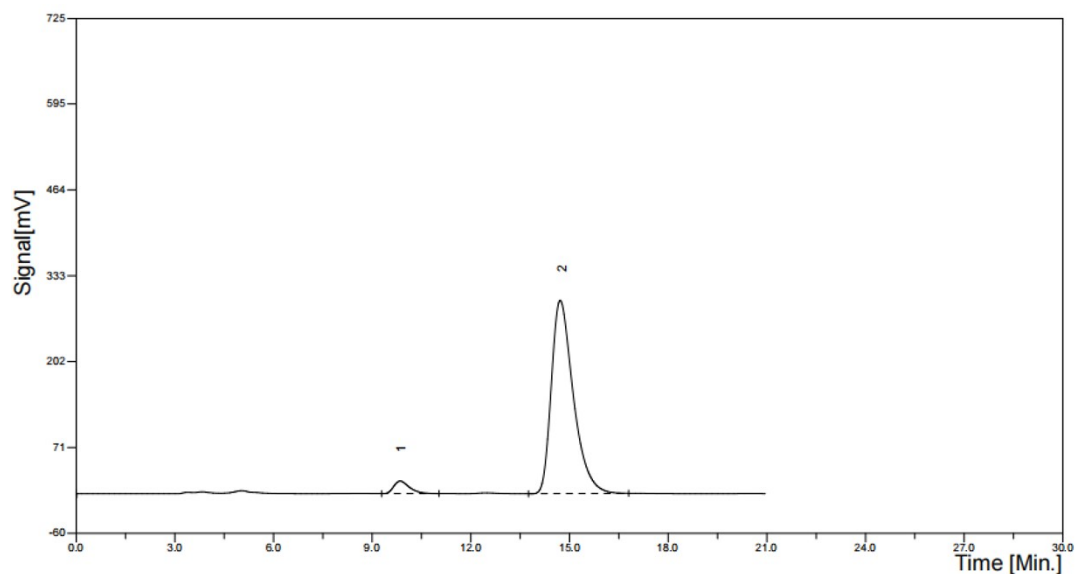
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
1	6.768	13.26	318.69	2.4473
2	10.201	375.42	12703.26	97.5527



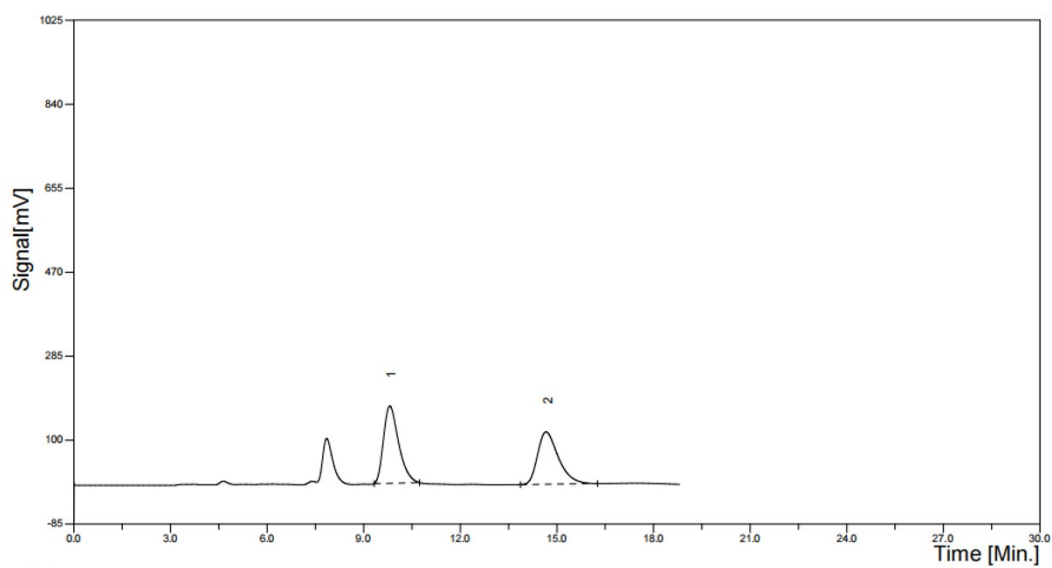
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
1	6.384	713.55	17826.56	49.8957
2	9.536	551.26	17901.12	50.1043



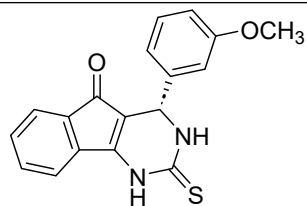
4m



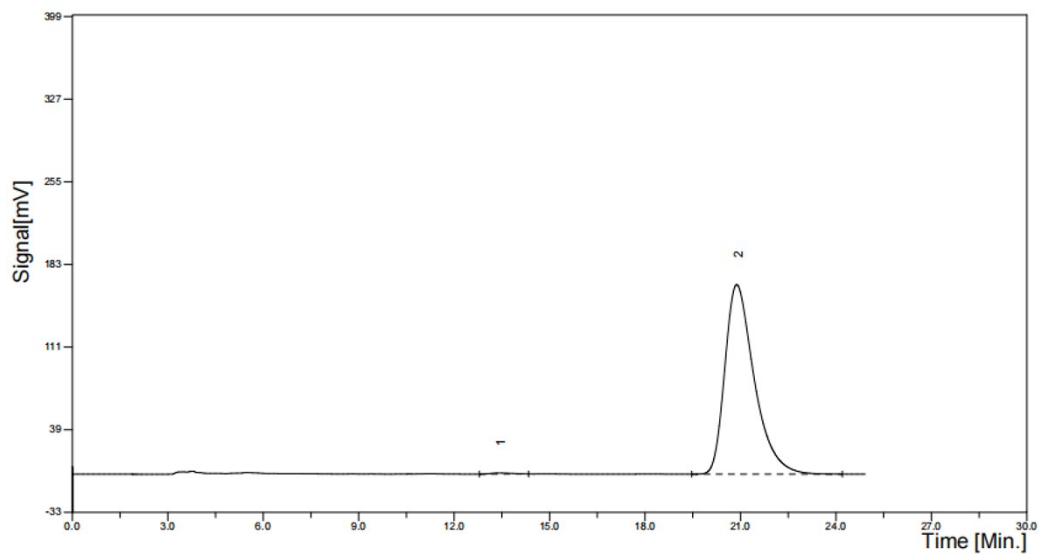
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
	9.848	19.18	635.31	4.4432
	14.717	294.98	13663.01	95.5568



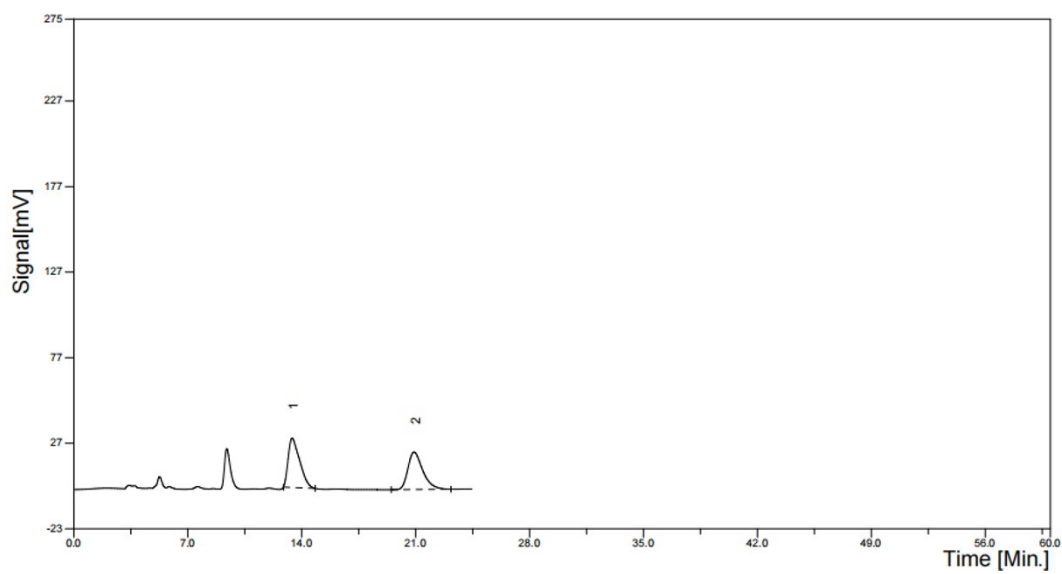
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
	9.811	170.20	5561.75	51.8126
	14.663	115.50	5172.60	48.1874



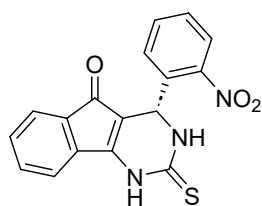
4n



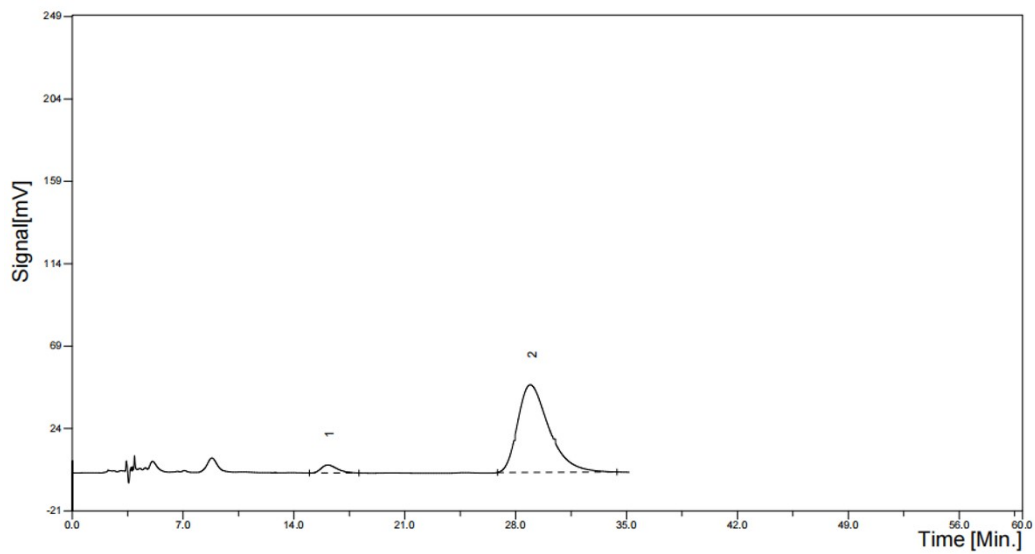
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
	13.409	0.94	41.78	0.3935
	20.882	165.10	10574.91	99.6065



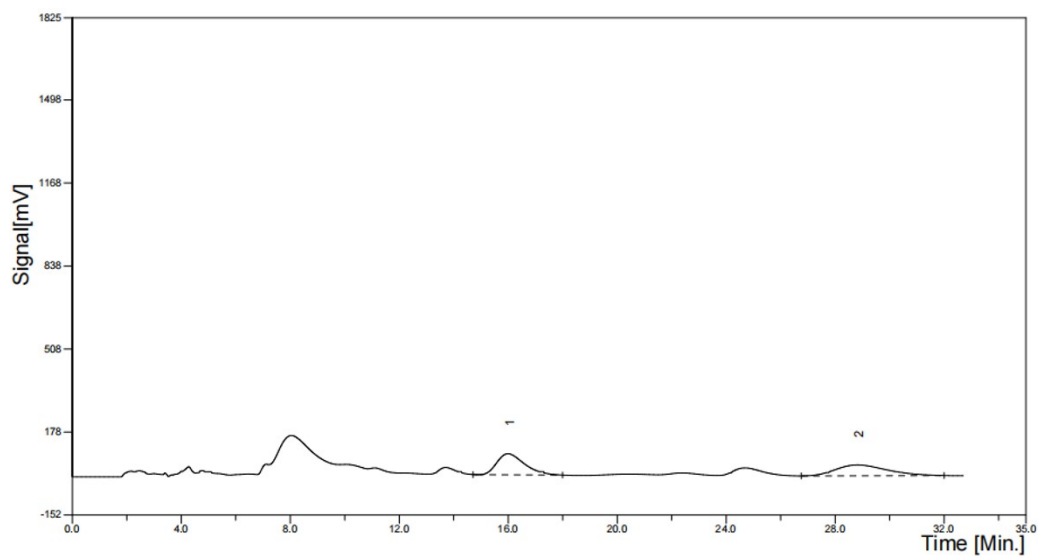
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
	13.411	28.90	1412.98	50.5988
	20.902	21.88	1379.54	49.4012



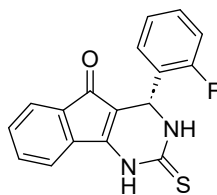
4o



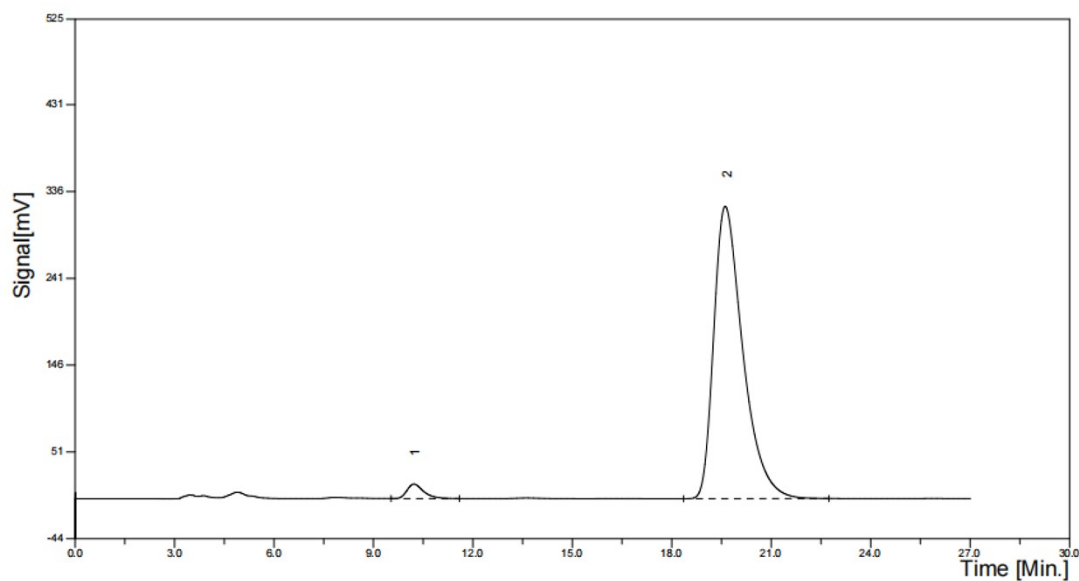
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
1	16.133	4.36	305.58	4.4471
2	28.915	47.82	6565.98	95.5529



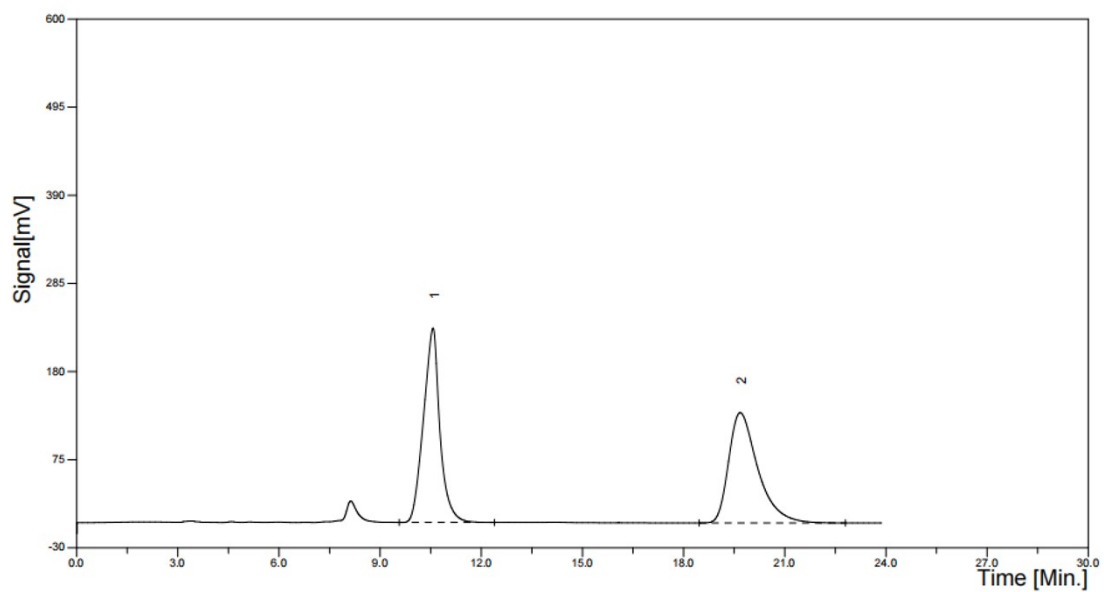
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
1	15.992	83.49	5862.31	51.1588
2	28.815	42.96	5596.73	48.8412



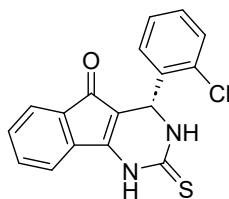
4p



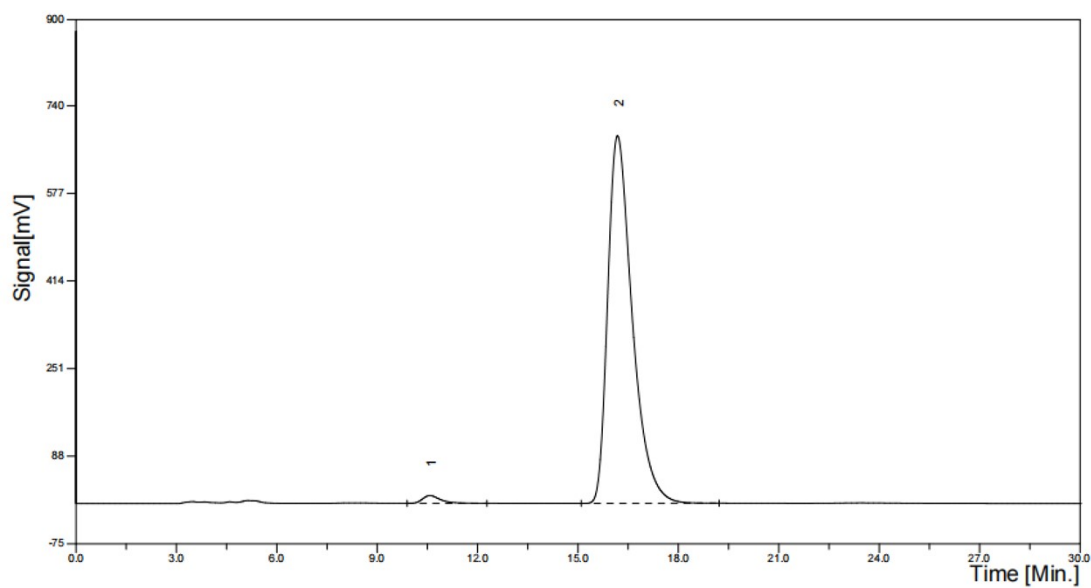
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
	10.224	15.86	554.43	2.7665
	19.613	320.10	19486.60	97.2335



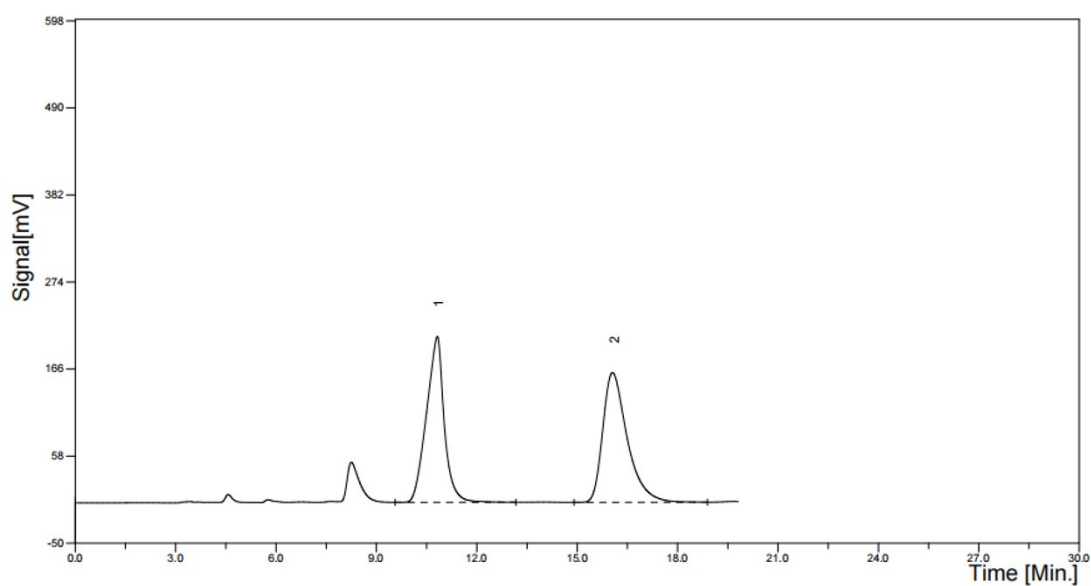
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
	10.568	231.66	7837.64	49.8018
	19.680	131.44	7900.04	50.1982



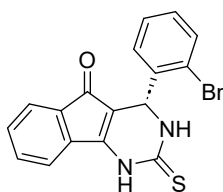
4q



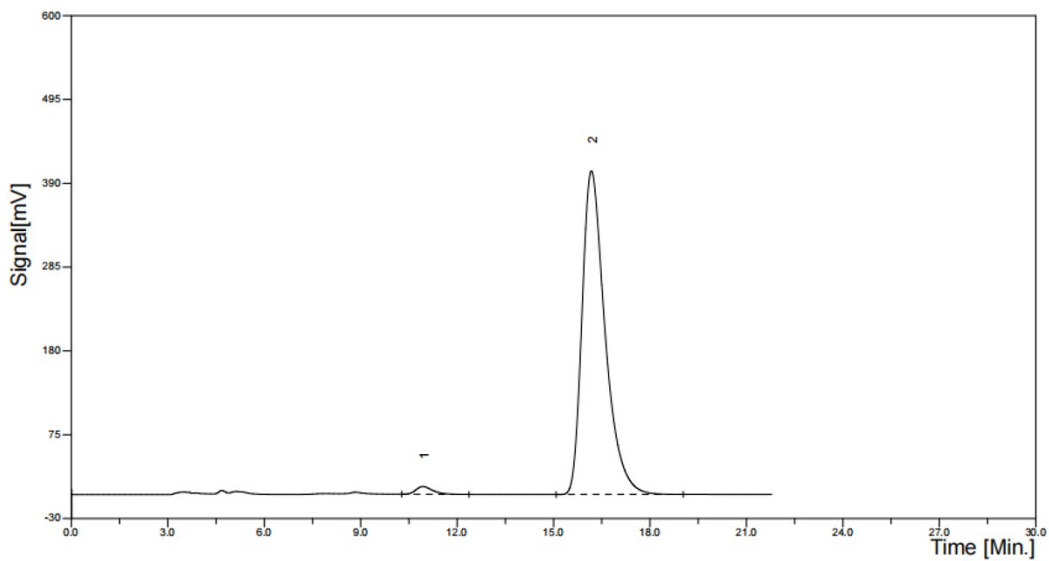
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
	10.577	14.58	540.98	1.5310
	16.182	683.75	34793.59	98.4690



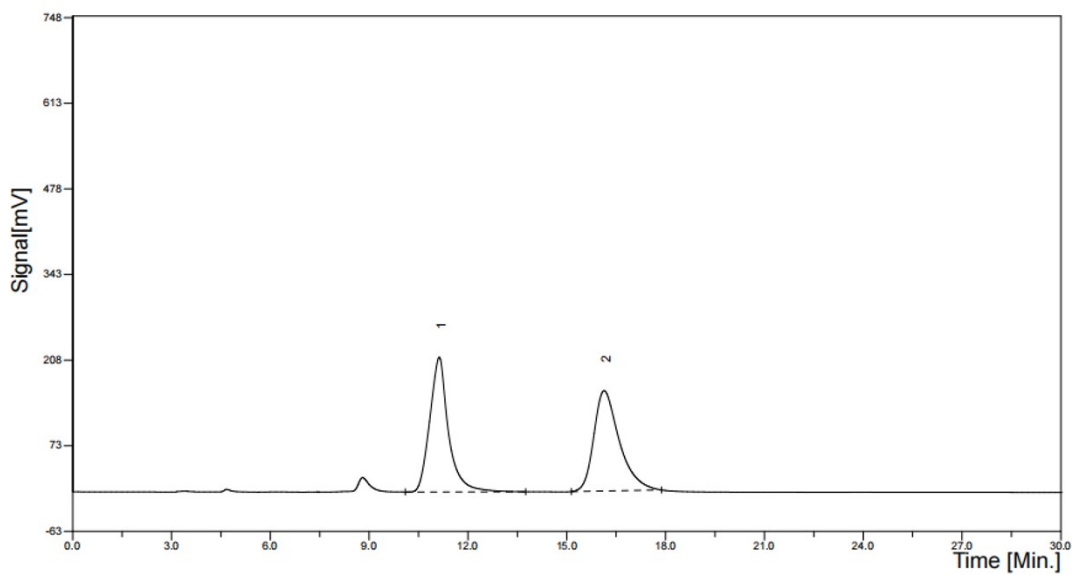
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
	10.820	205.79	7575.11	48.0845
	16.056	161.06	8178.63	51.9155



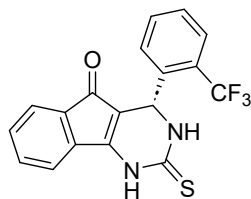
4r



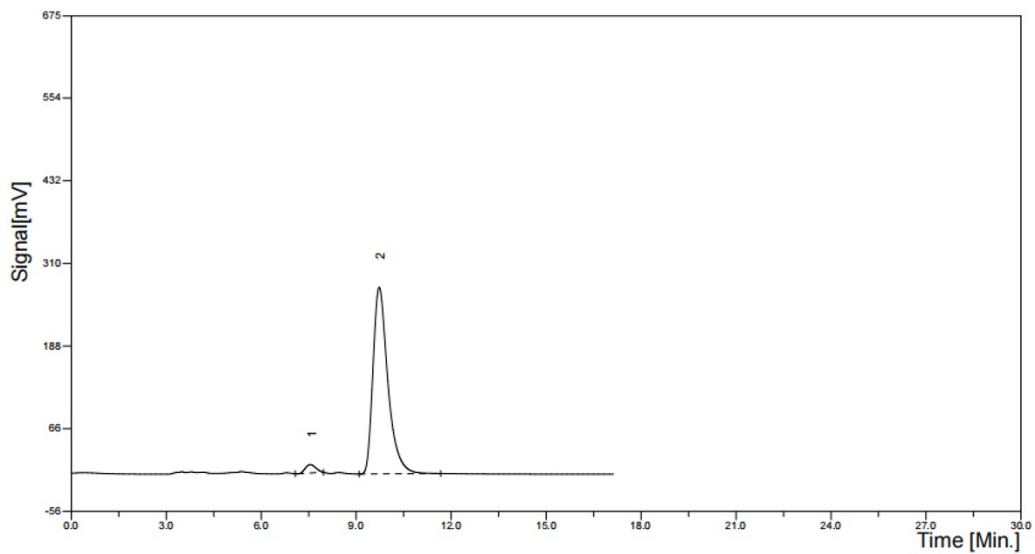
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
	10.936	9.78	353.11	1.7206
	16.177	405.41	20169.49	98.2794



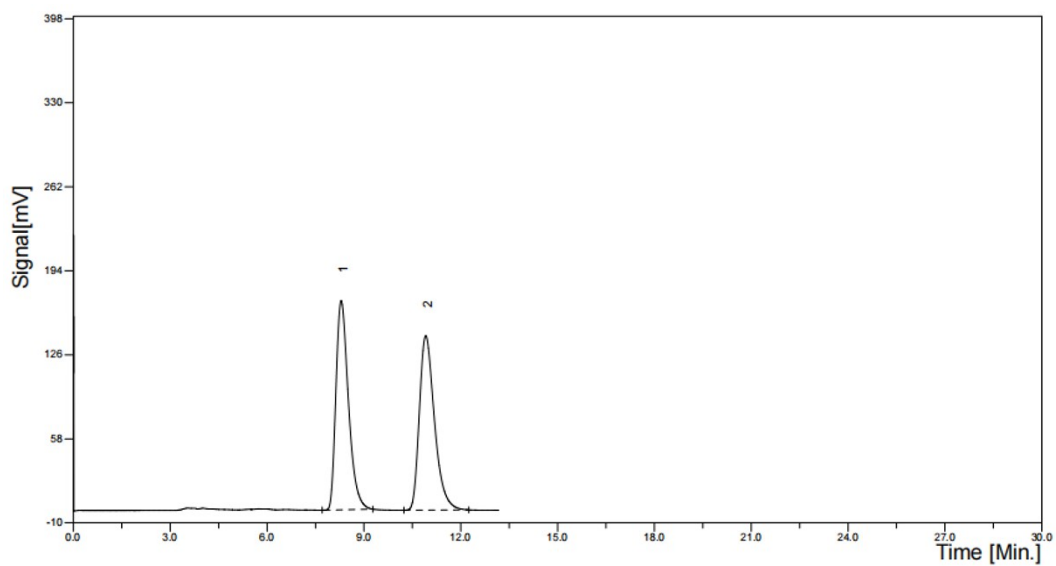
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
	11.129	212.48	8359.00	49.5915
	16.133	158.20	8496.70	50.4085



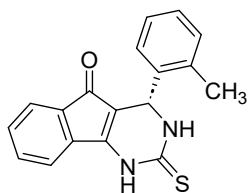
4s



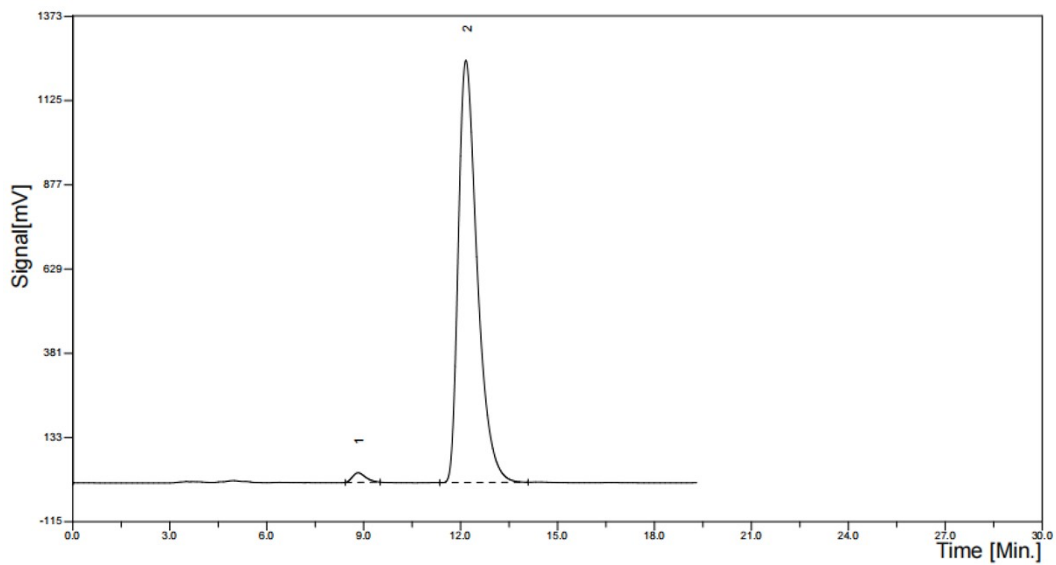
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
1	7.549	12.37	280.97	3.0228
2	9.728	275.64	9013.87	96.9772



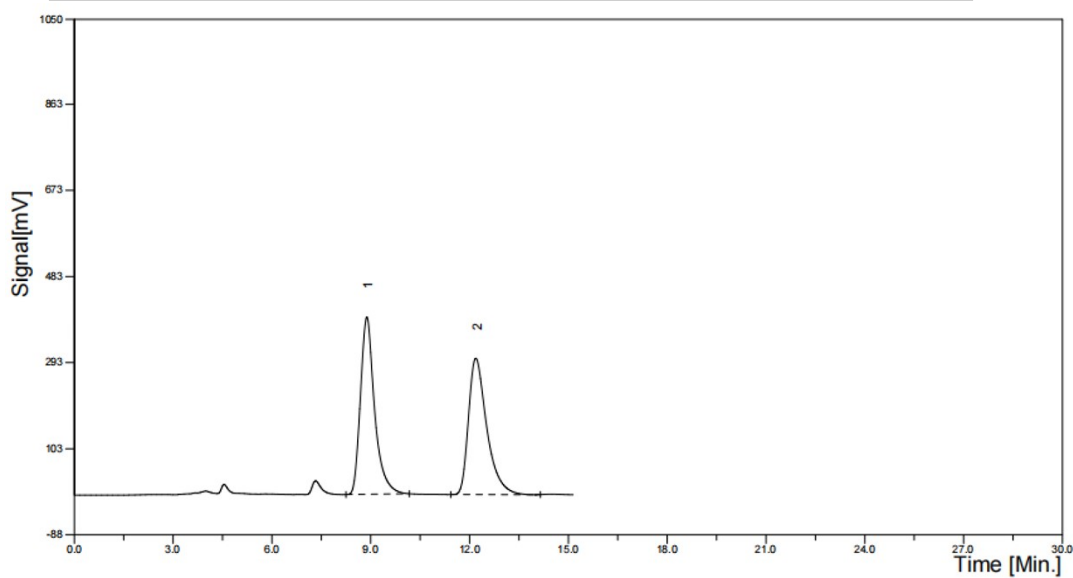
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
1	8.298	169.23	4551.60	49.7955
2	10.916	141.07	4588.99	50.2045



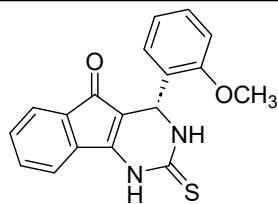
4t



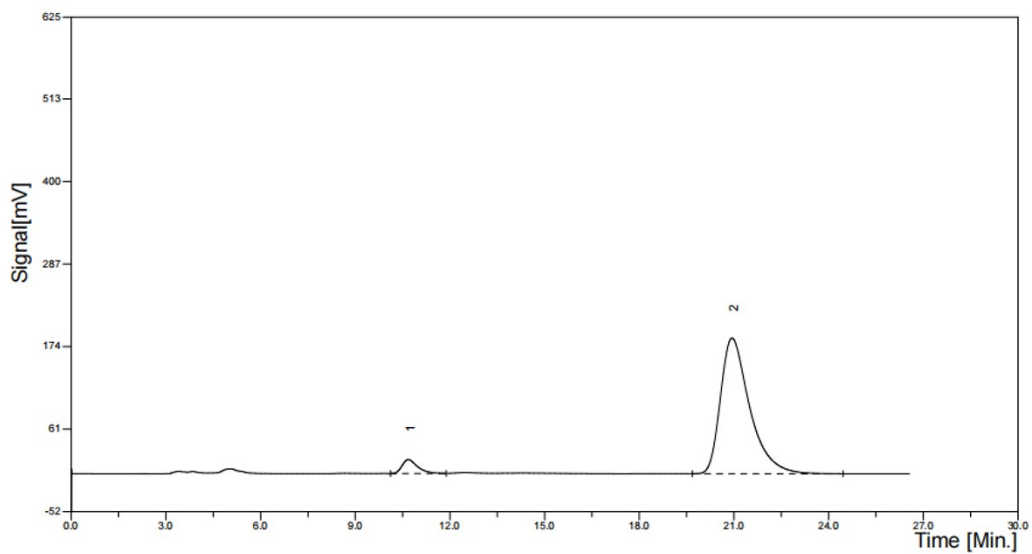
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
	8.828	28.17	793.52	1.5502
	12.165	1242.67	50394.09	98.4498



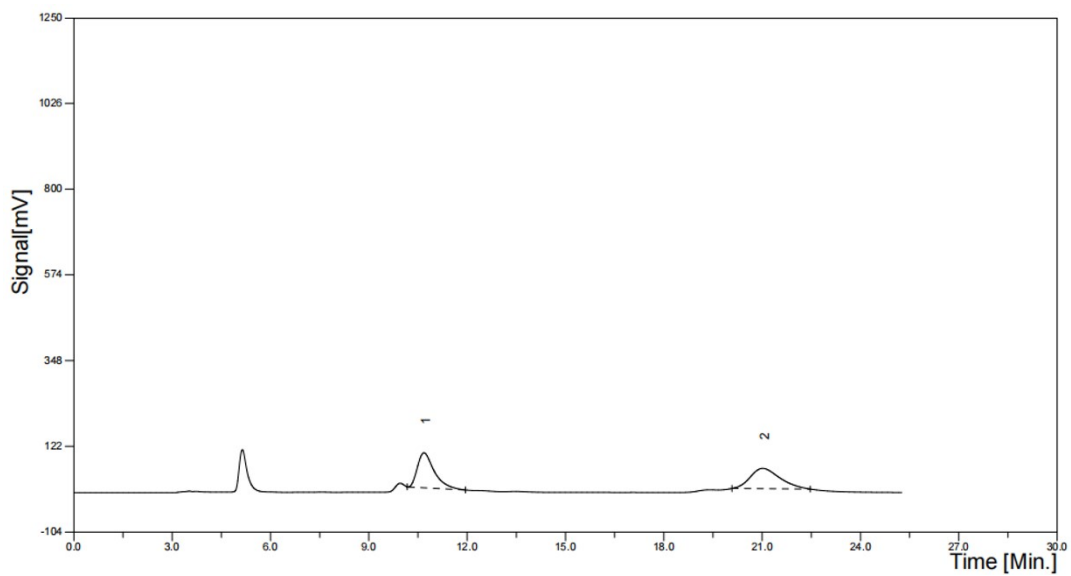
Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
	8.882	391.30	11683.31	50.1949
	12.189	300.82	11592.60	49.8051



4u

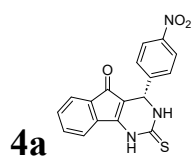


Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
	10.683	19.04	643.83	5.1162
	20.940	185.73	11940.39	94.8838

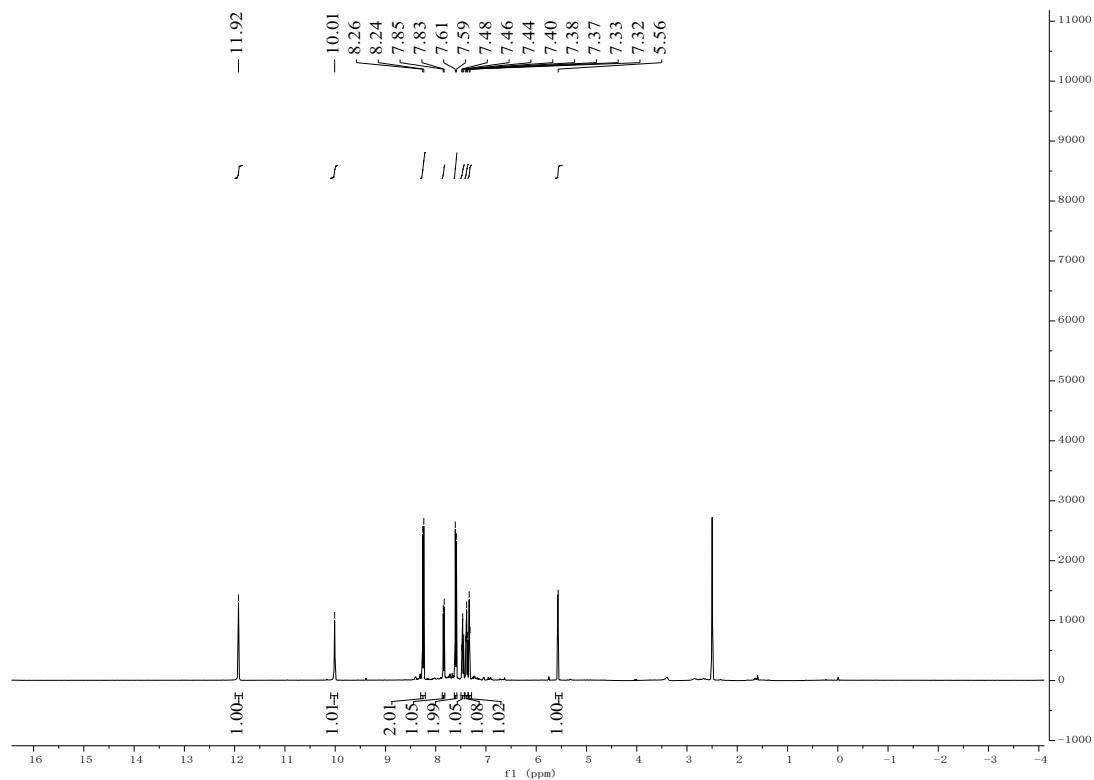


Peak #	RetTime [min]	Heigh [mV]	Area [mV*s]	Area %
	10.683	92.16	3278.91	49.2808
	21.013	53.55	3374.62	50.7192

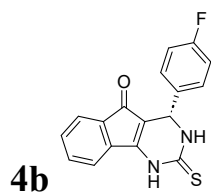
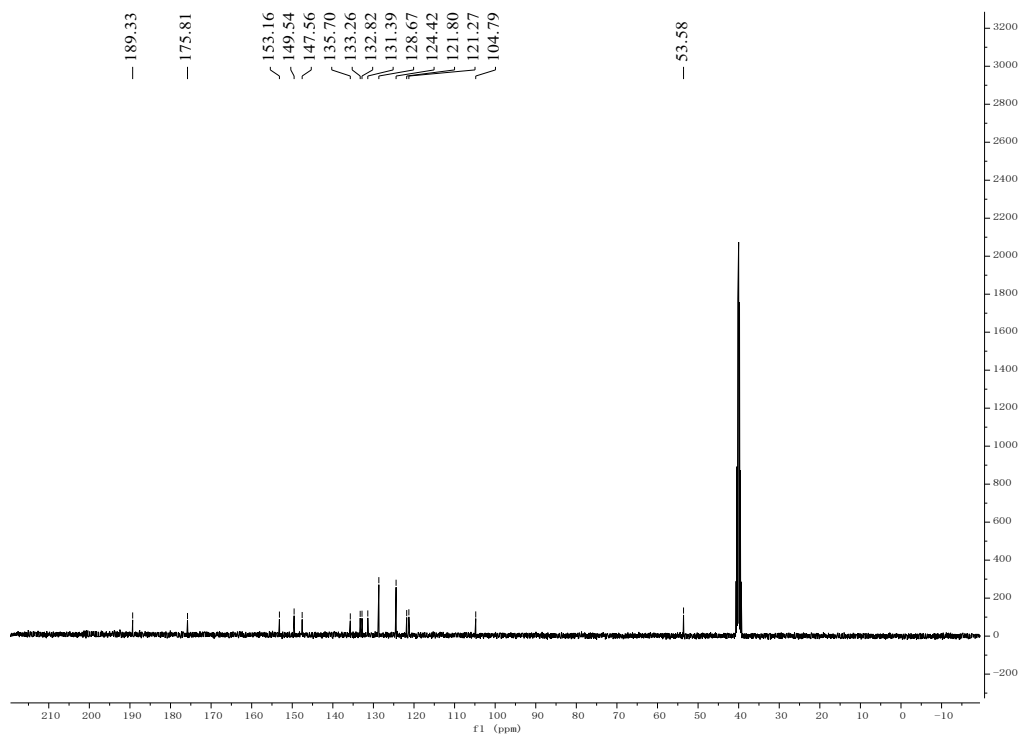
4. Copies of NMR spectra.



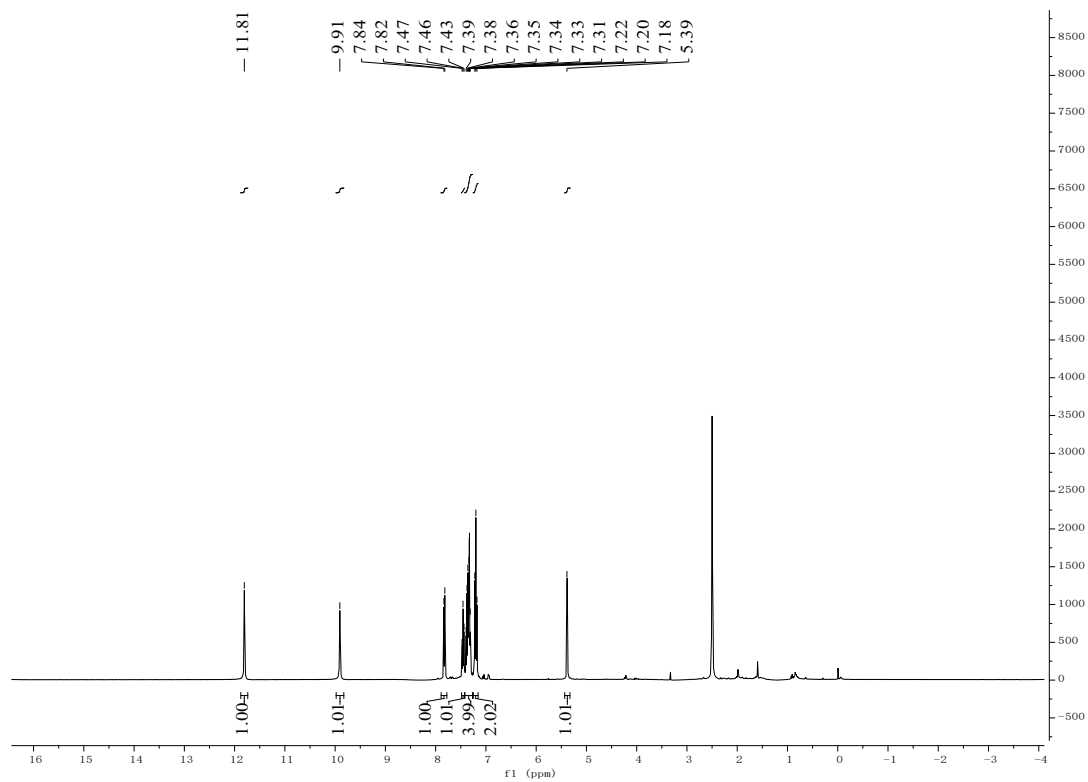
^1H NMR (400 MHz, DMSO- d_6)



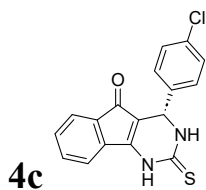
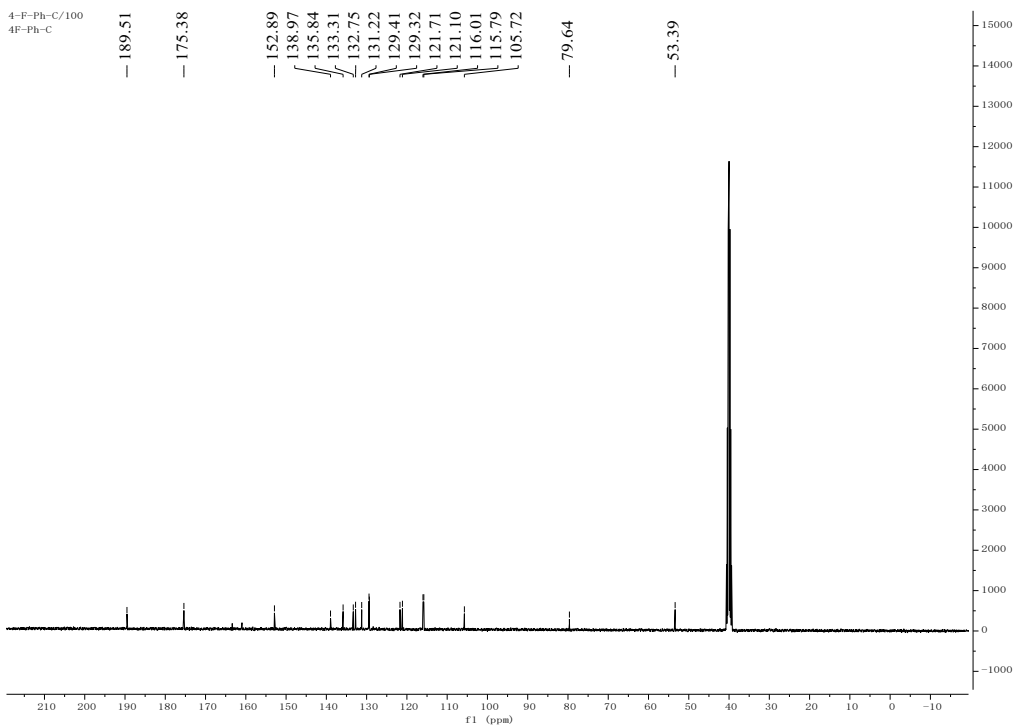
^{13}C NMR (101 MHz, DMSO- d_6)



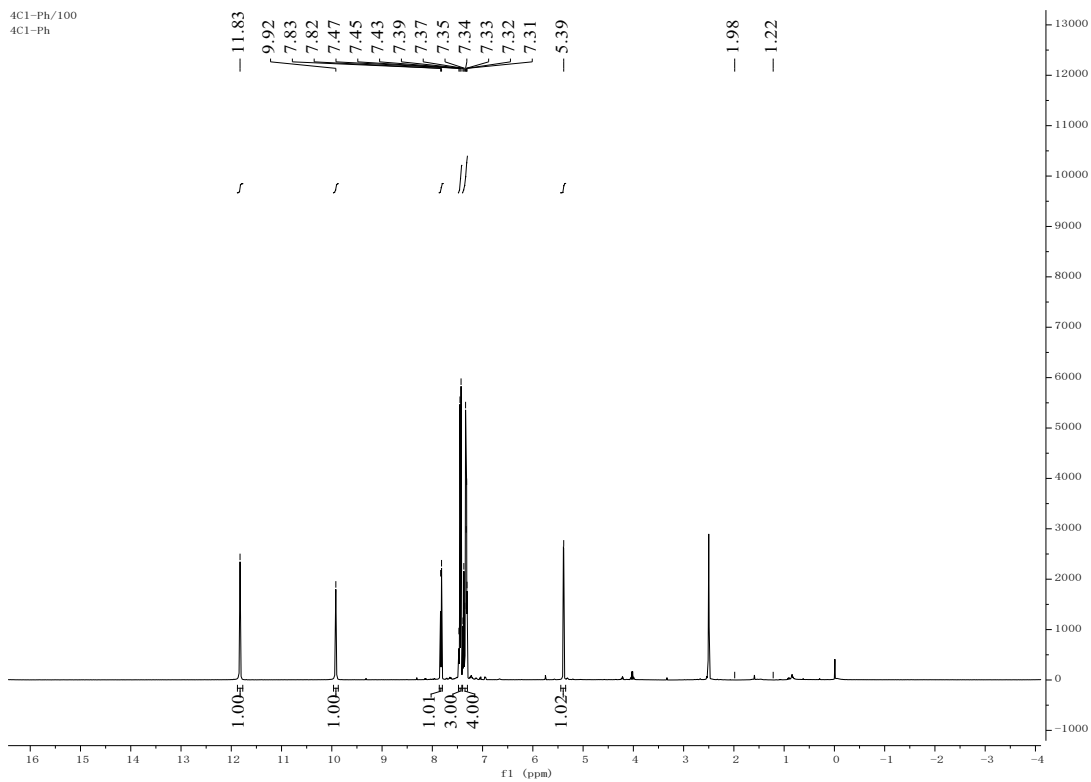
¹H NMR (400 MHz, DMSO-d₆)



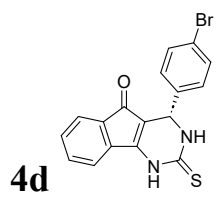
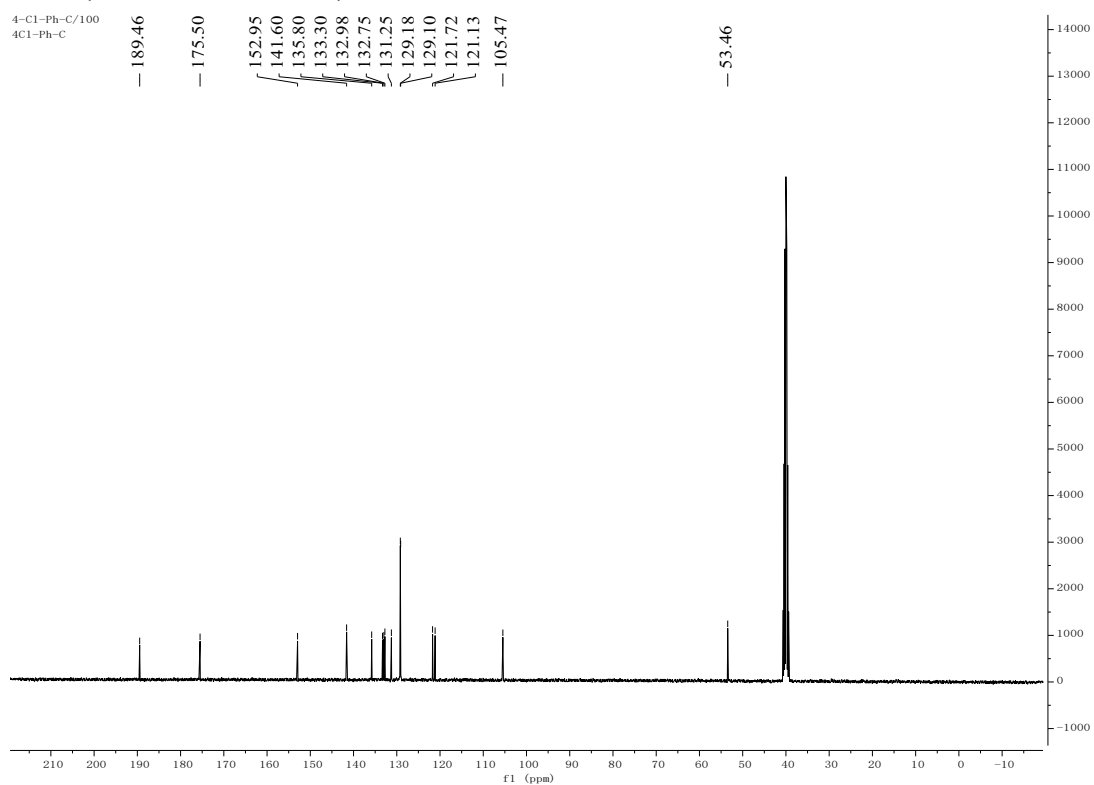
¹³C NMR (101 MHz, DMSO-d₆)



¹H NMR (400 MHz, DMSO-d₆)

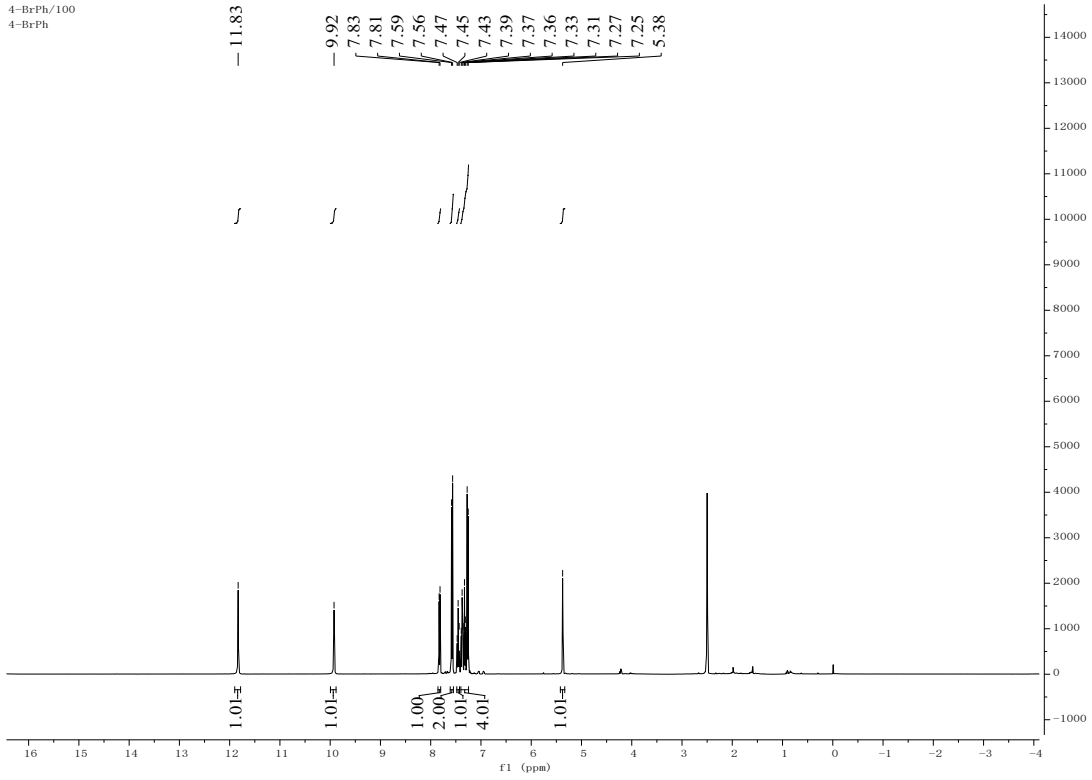


¹³C NMR (101 MHz, DMSO-d6)



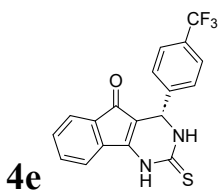
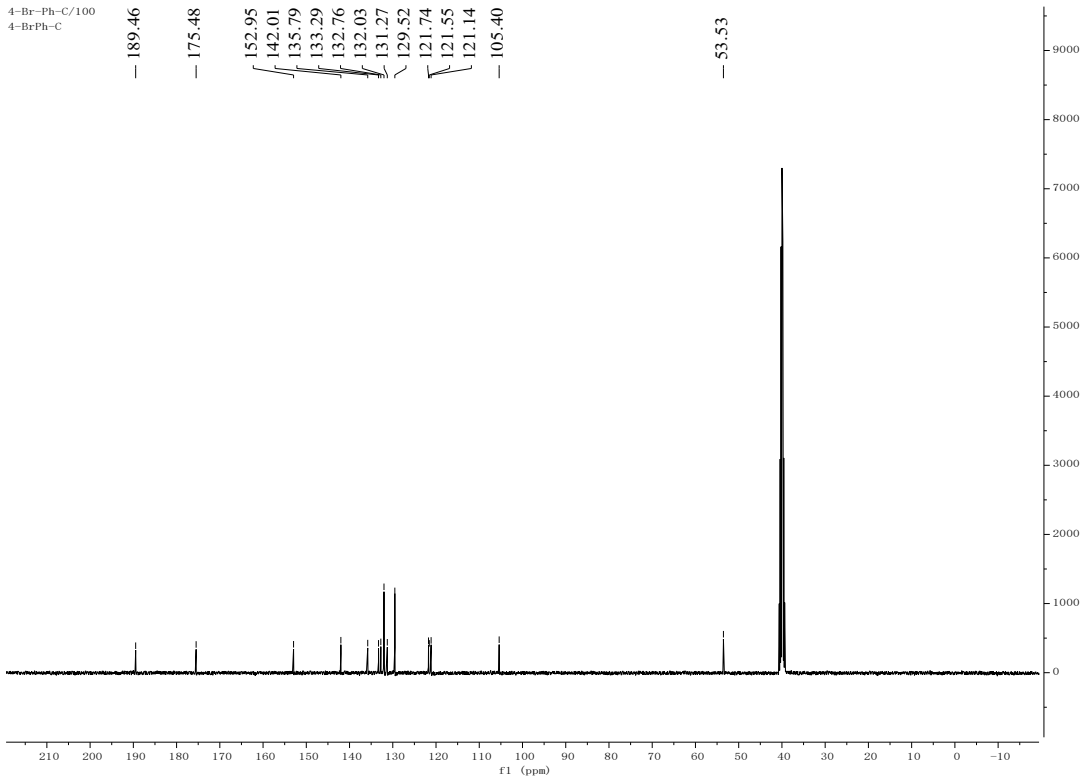
¹H NMR (400 MHz, DMSO-d6)

4-BrPh/100
4-BrPh



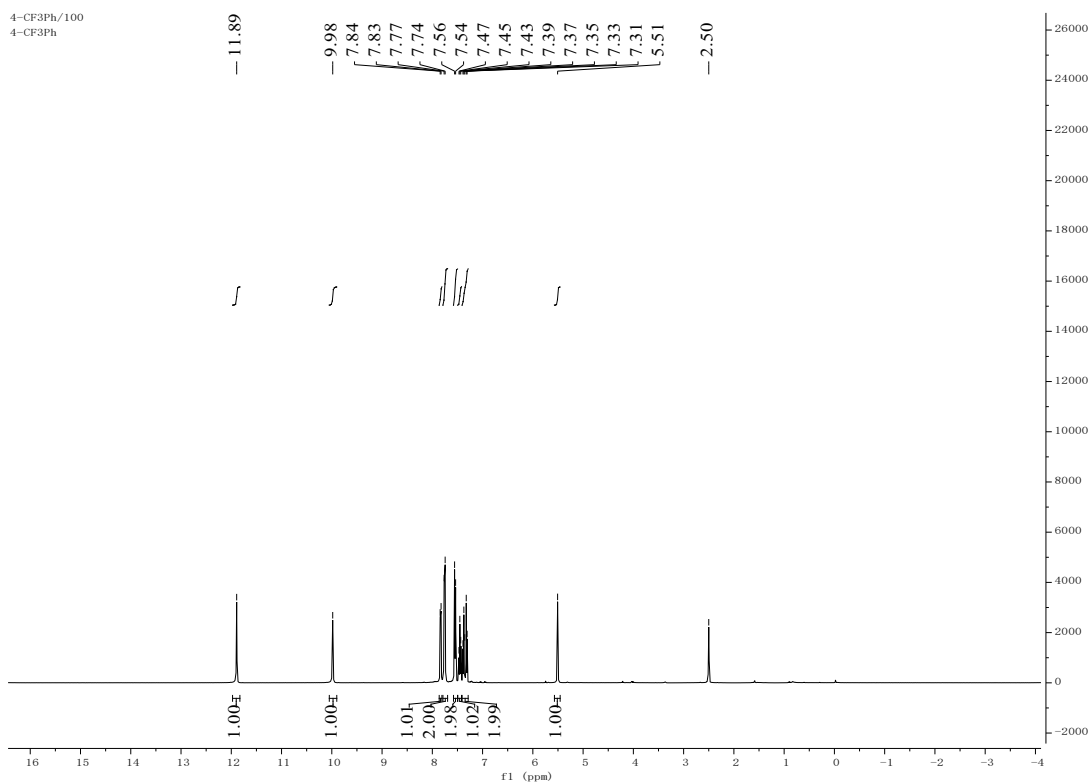
¹³C NMR (101 MHz, DMSO-d6)

4-Br-Ph-C/100
4-BrPh-C



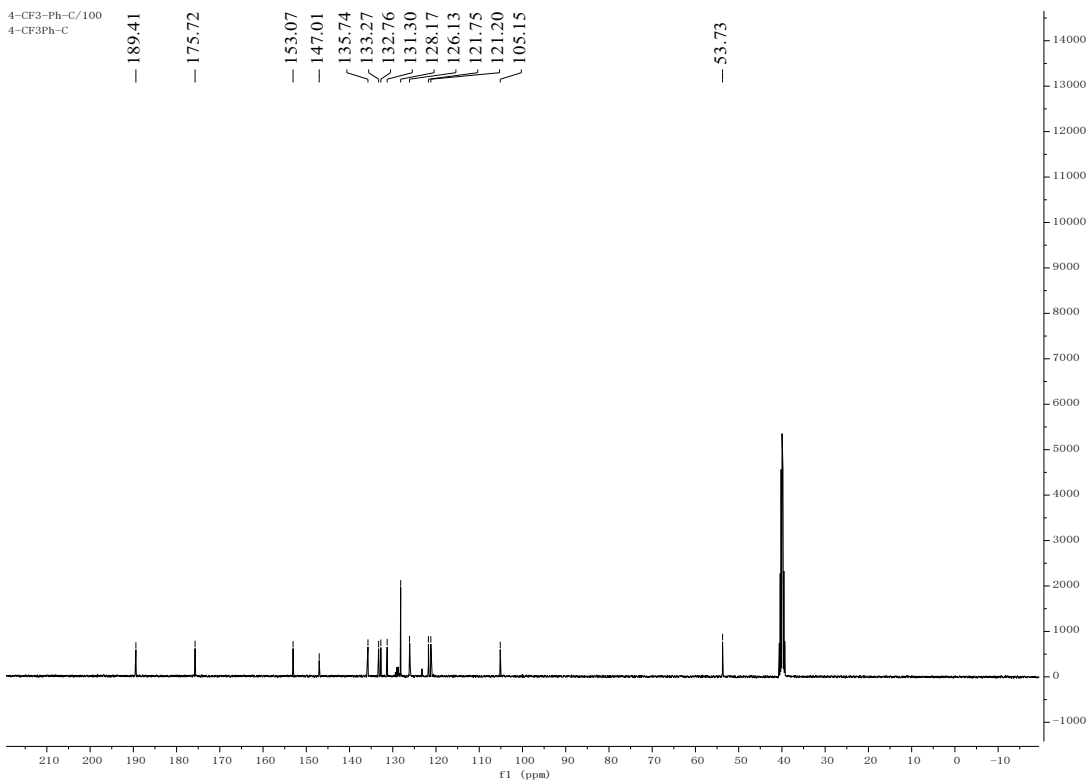
¹H NMR (400 MHz, DMSO-d6)

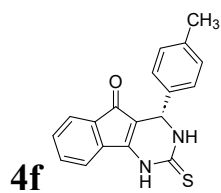
4-CF3Ph/100
4-CF3Ph



¹³C NMR (101 MHz, DMSO-d6)

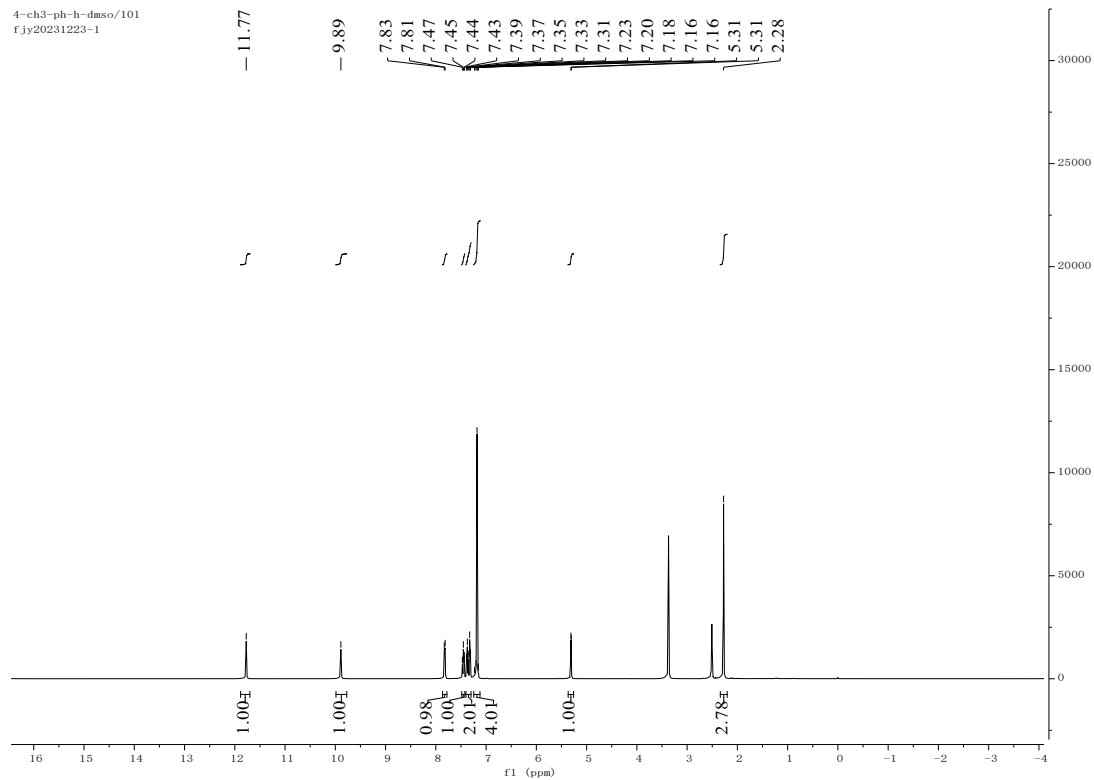
4-CF3-Ph-C/100
4-CF3Ph-C





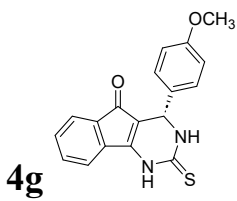
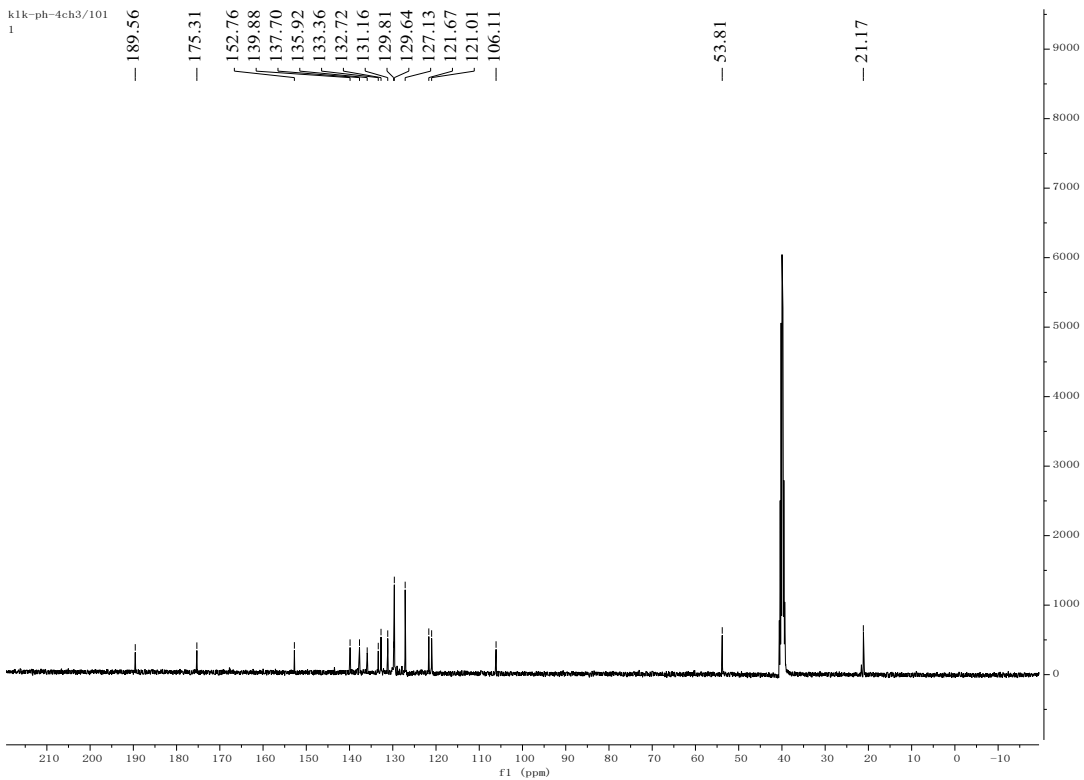
¹H NMR (400 MHz, DMSO-d₆)

4-ch3-ph-h-dms0/101
fjy20231223-1



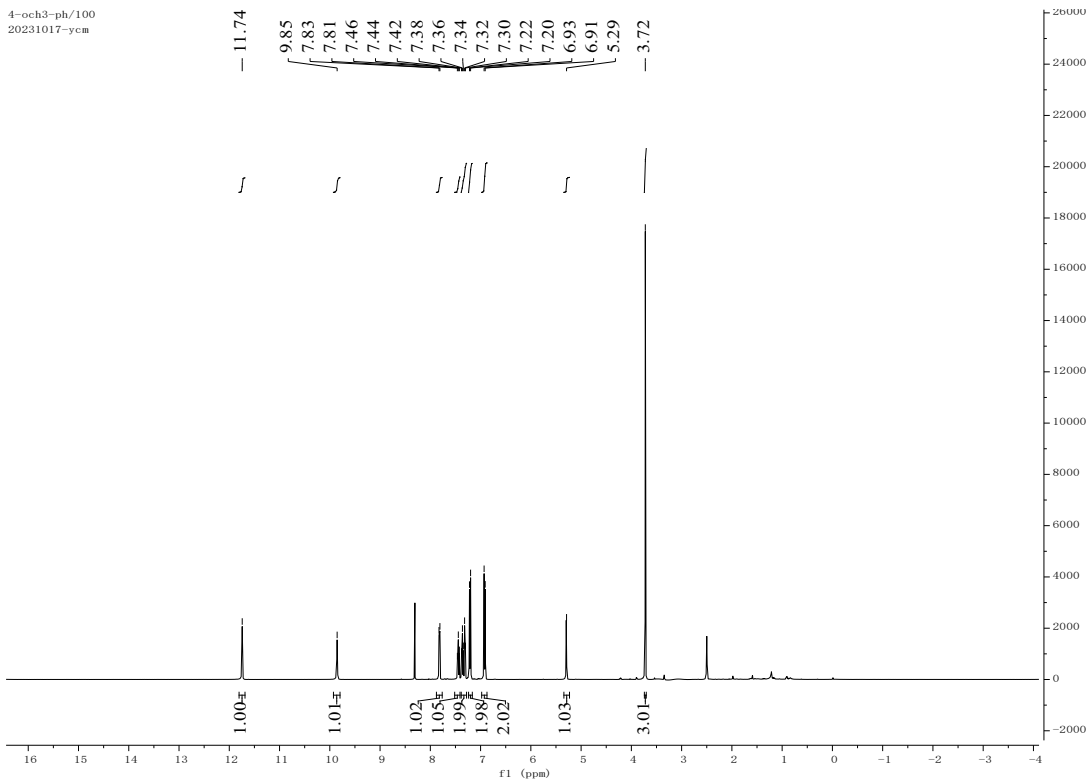
¹³C NMR (101 MHz, DMSO-d₆)

k1k-ph-4ch3/101
1

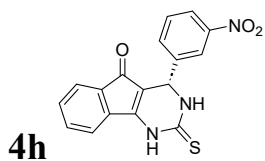
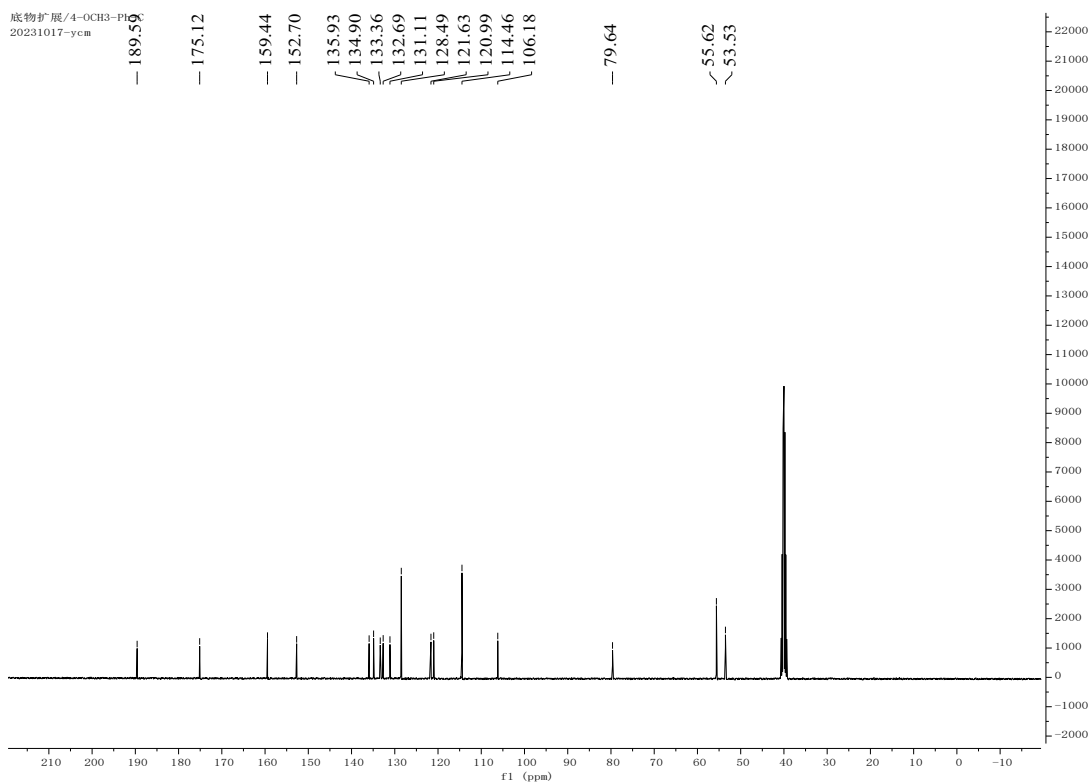


¹H NMR (400 MHz, DMSO-d₆)

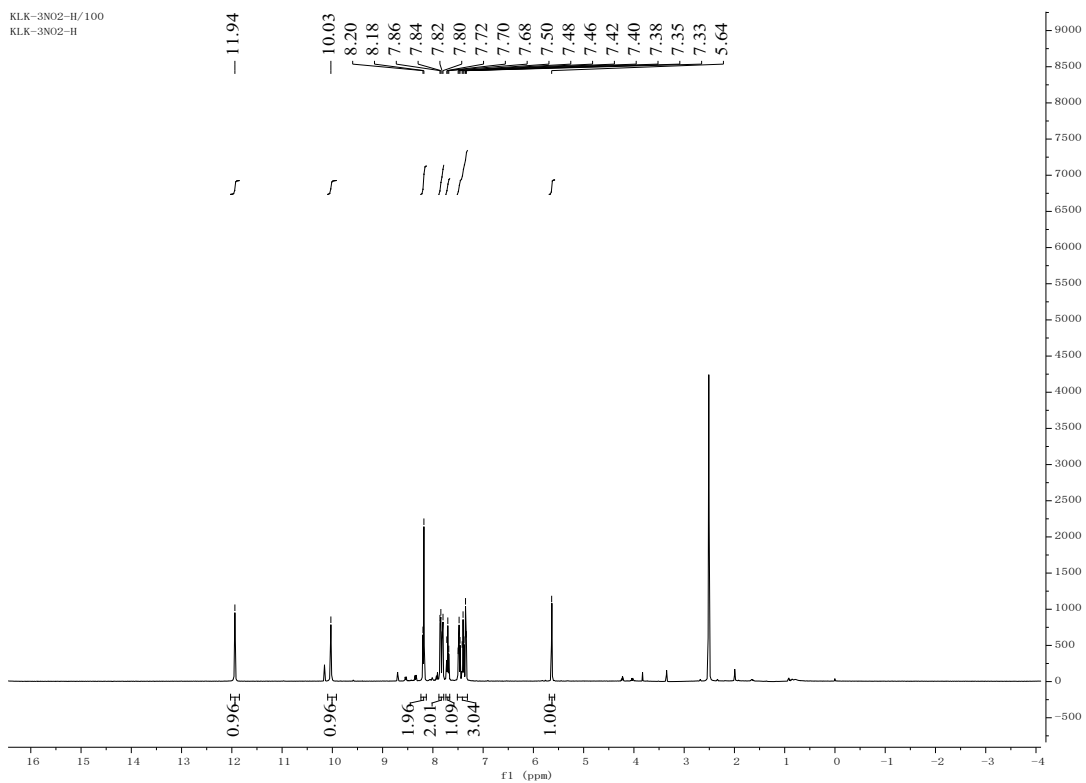
4-och3-ph/100
20231017-ycm



¹³C NMR (101 MHz, DMSO-d6)

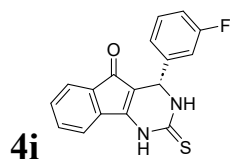
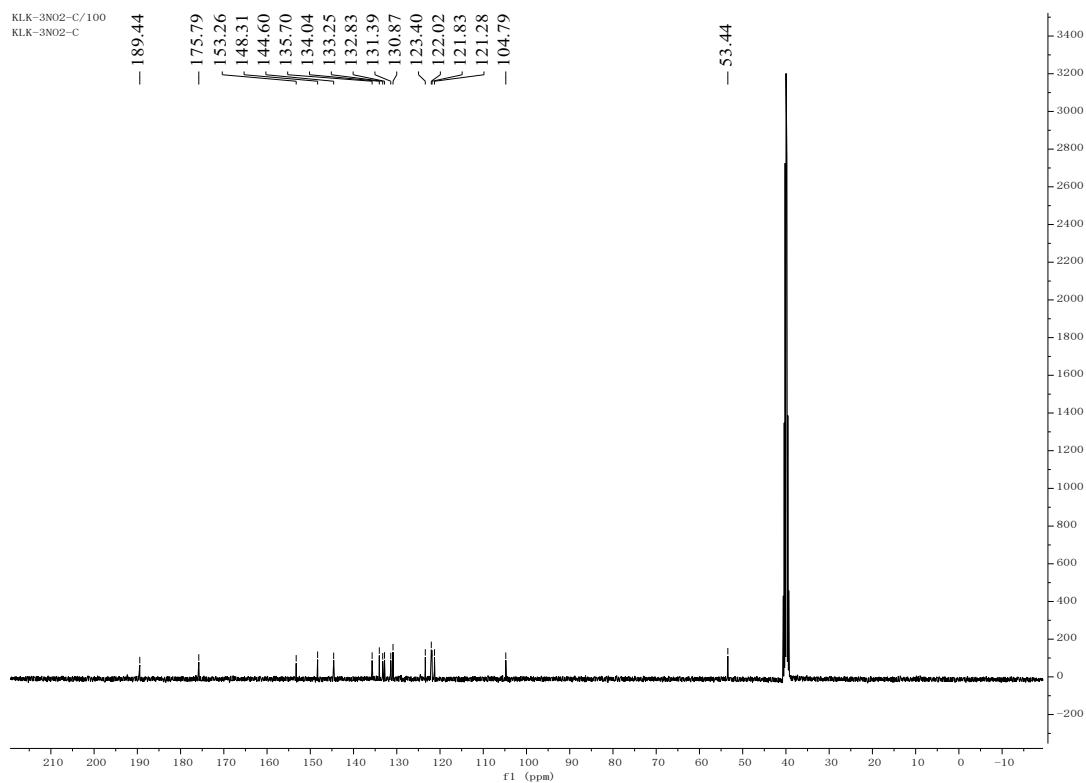


¹H NMR (400 MHz, DMSO-d6)



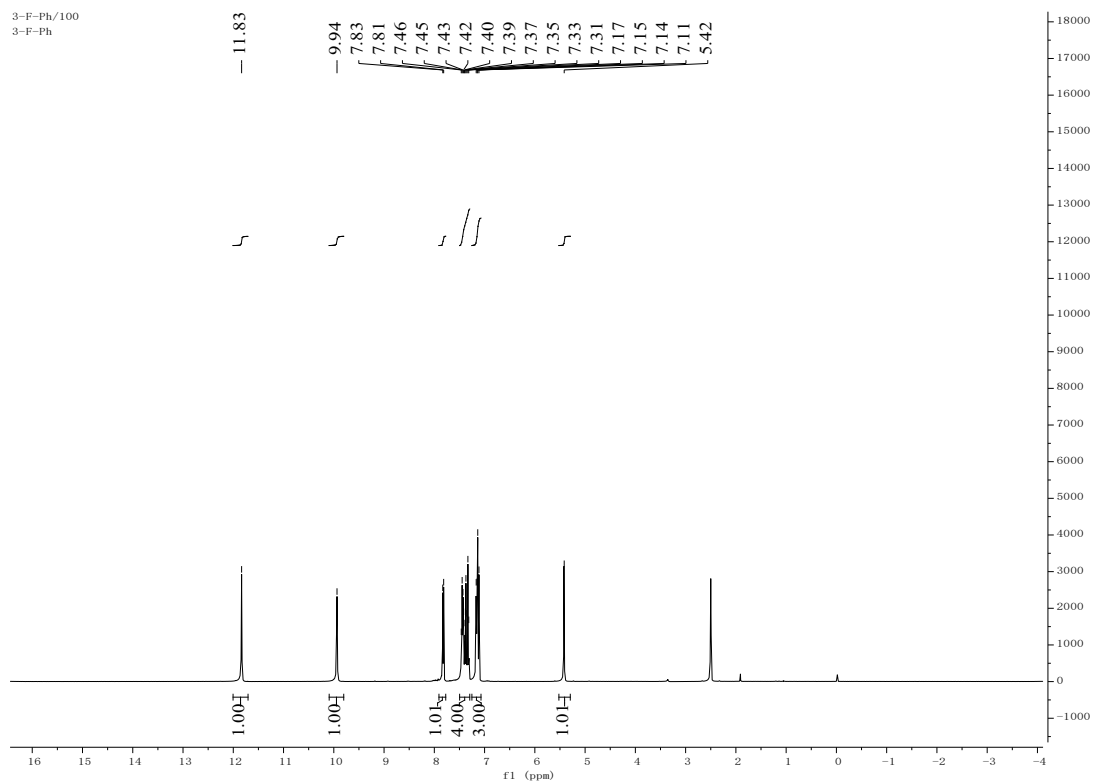
¹³C NMR (101 MHz, DMSO-d6)

KLK-3N02-C/100
KLK-3N02-C



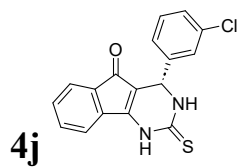
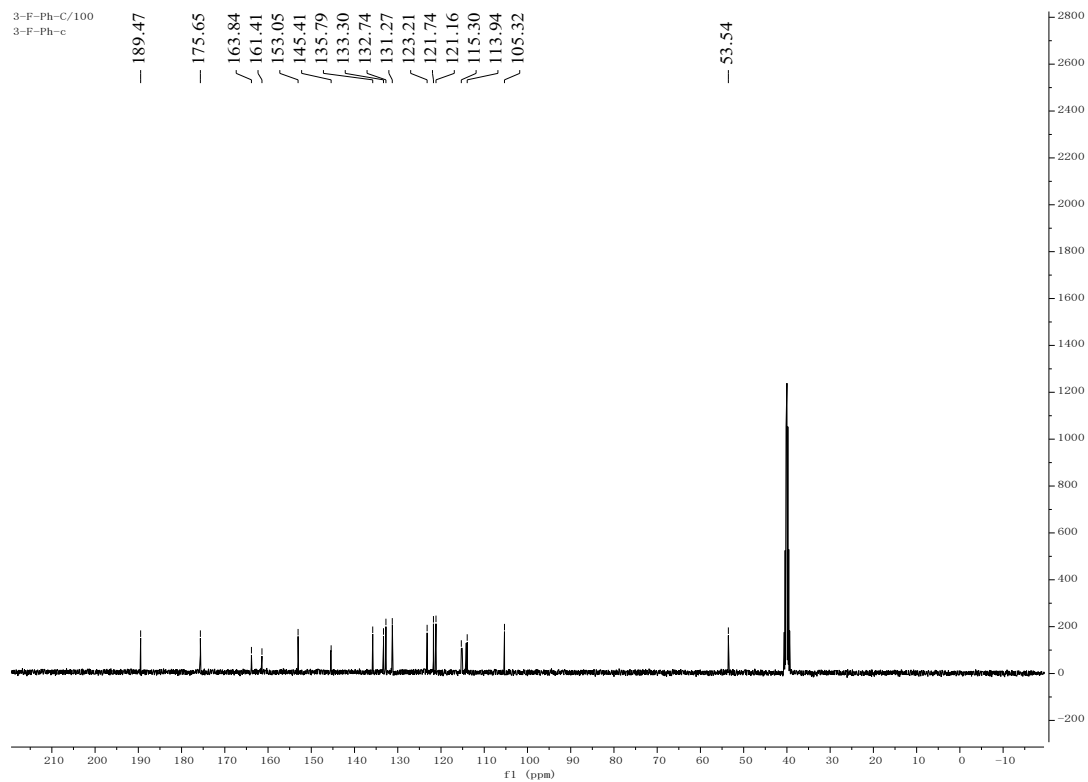
¹H NMR (400 MHz, DMSO-d6)

3-F-Ph/100
3-F-Ph



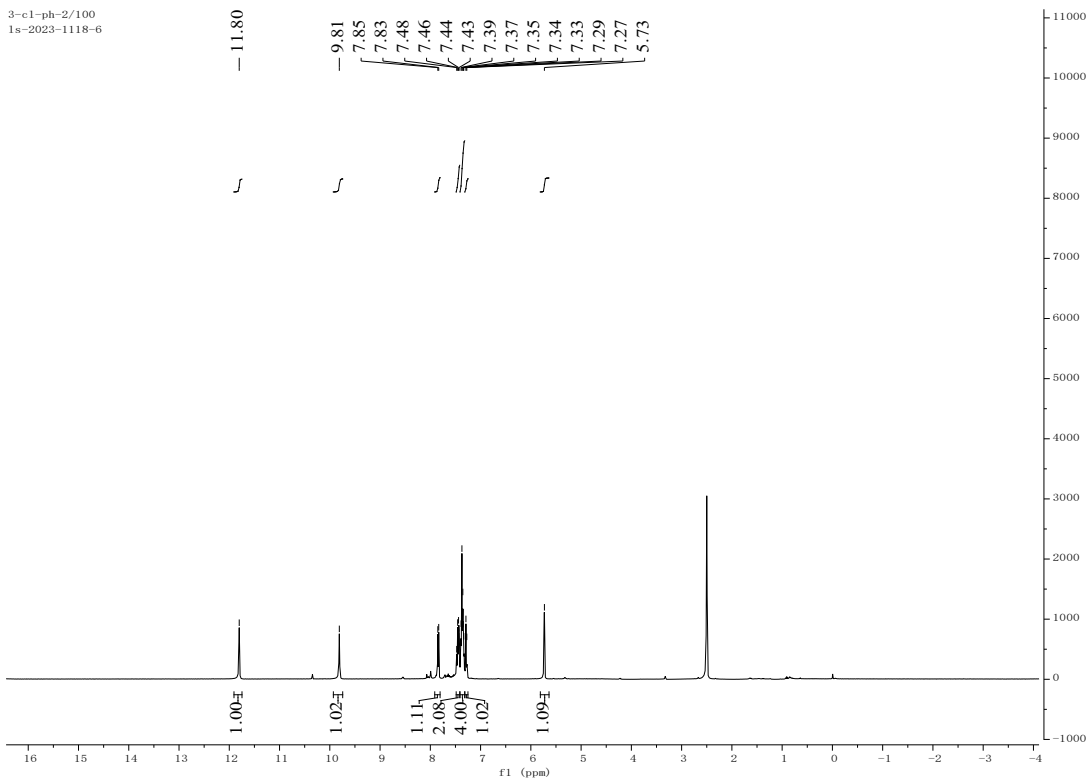
¹³C NMR (101 MHz, DMSO-d6)

3-F-Ph-C/100
3-F-Ph-c



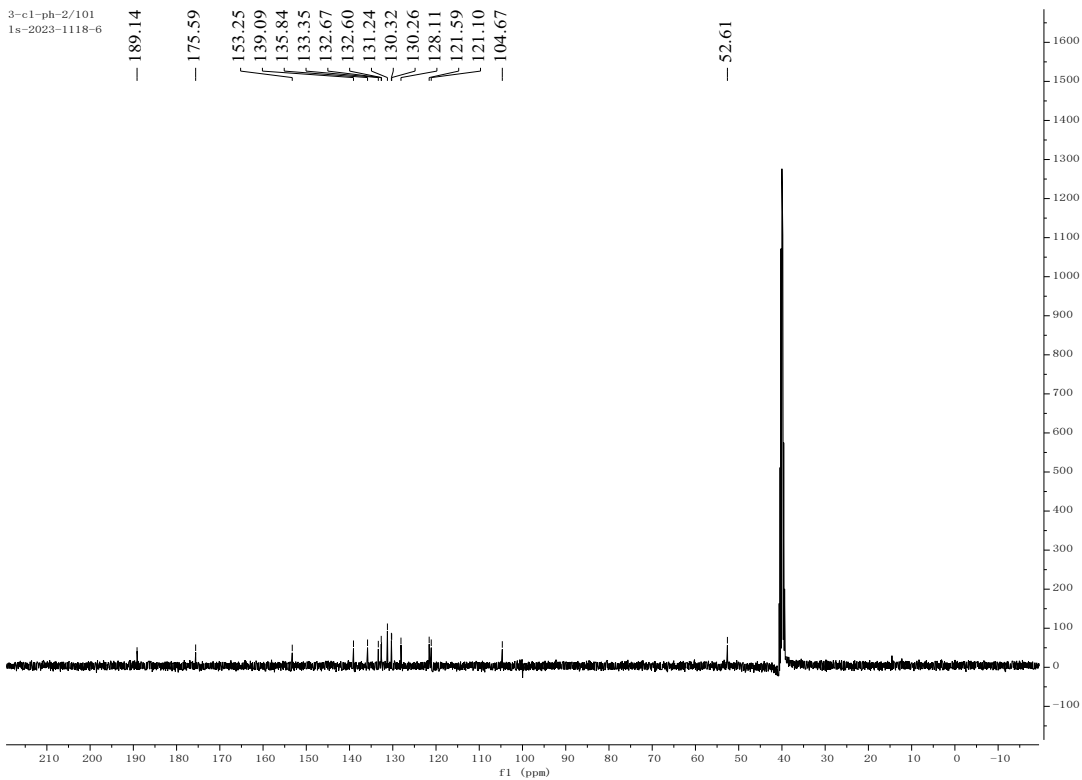
¹H NMR (400 MHz, DMSO-d6)

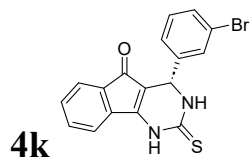
3-c1-ph-2/100
1s-2023-1118-6



¹³C NMR (101 MHz, DMSO-d6)

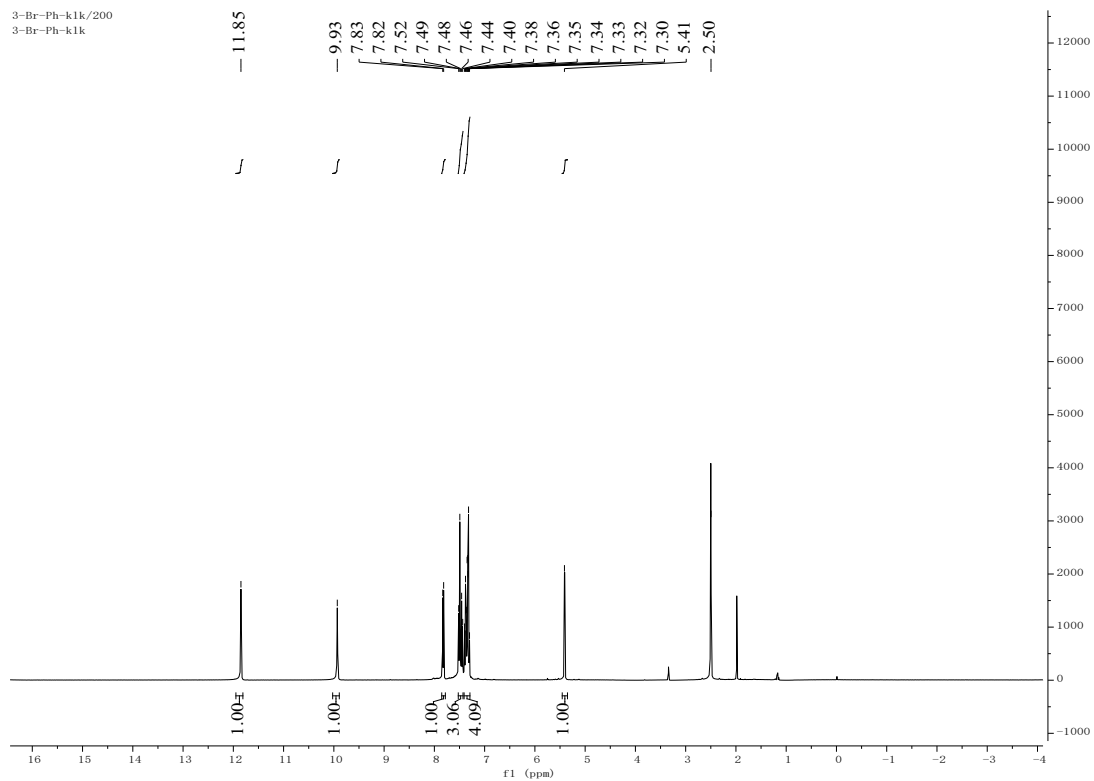
3-c1-ph-2/101
1s-2023-1118-6



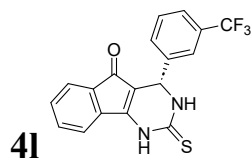
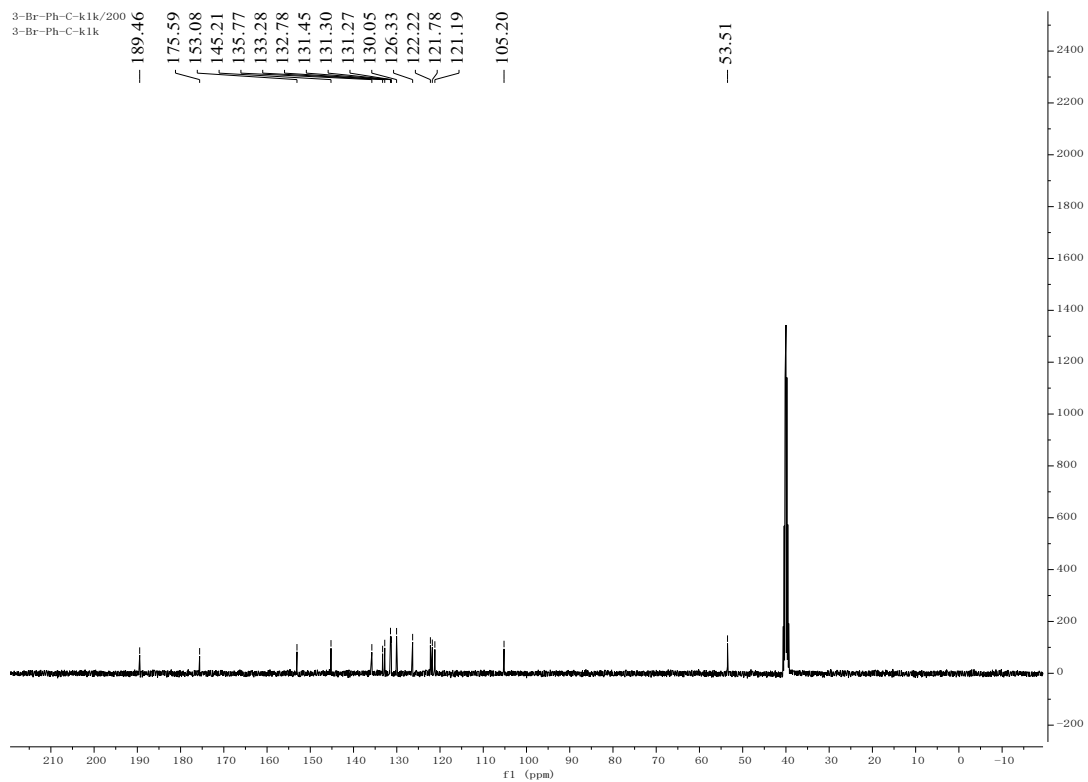


¹H NMR (400 MHz, DMSO-d₆)

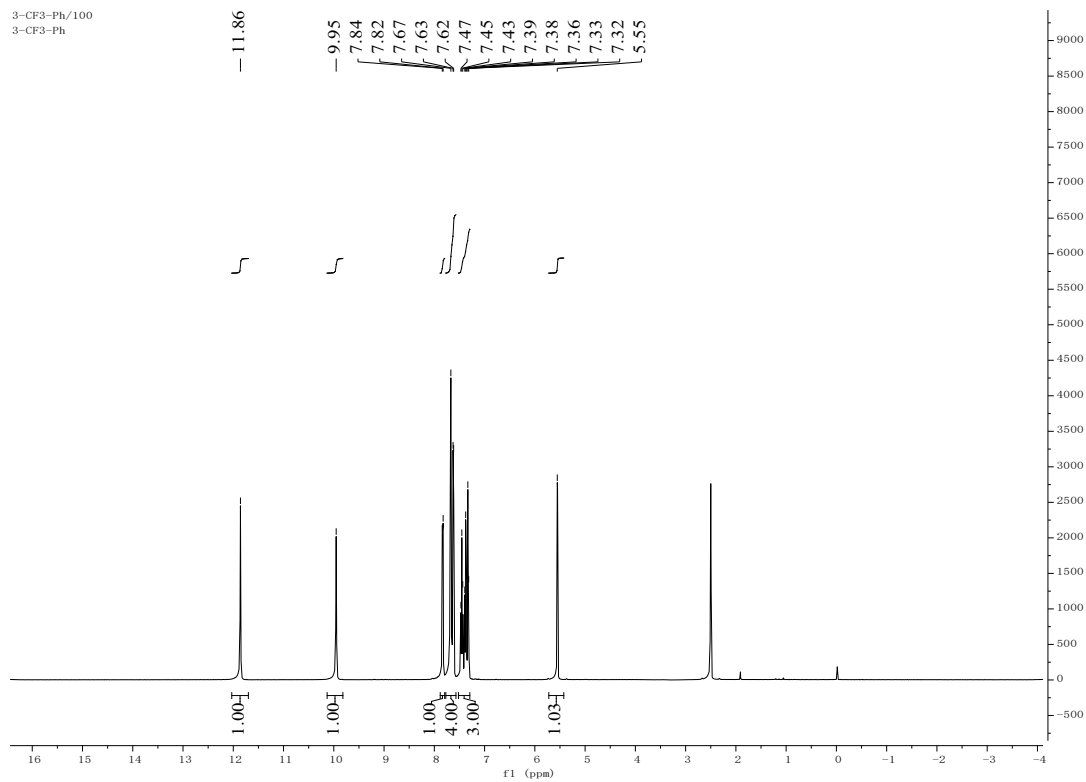
3-Br-Ph-k1k/200
3-Br-Ph-k1k



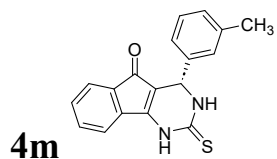
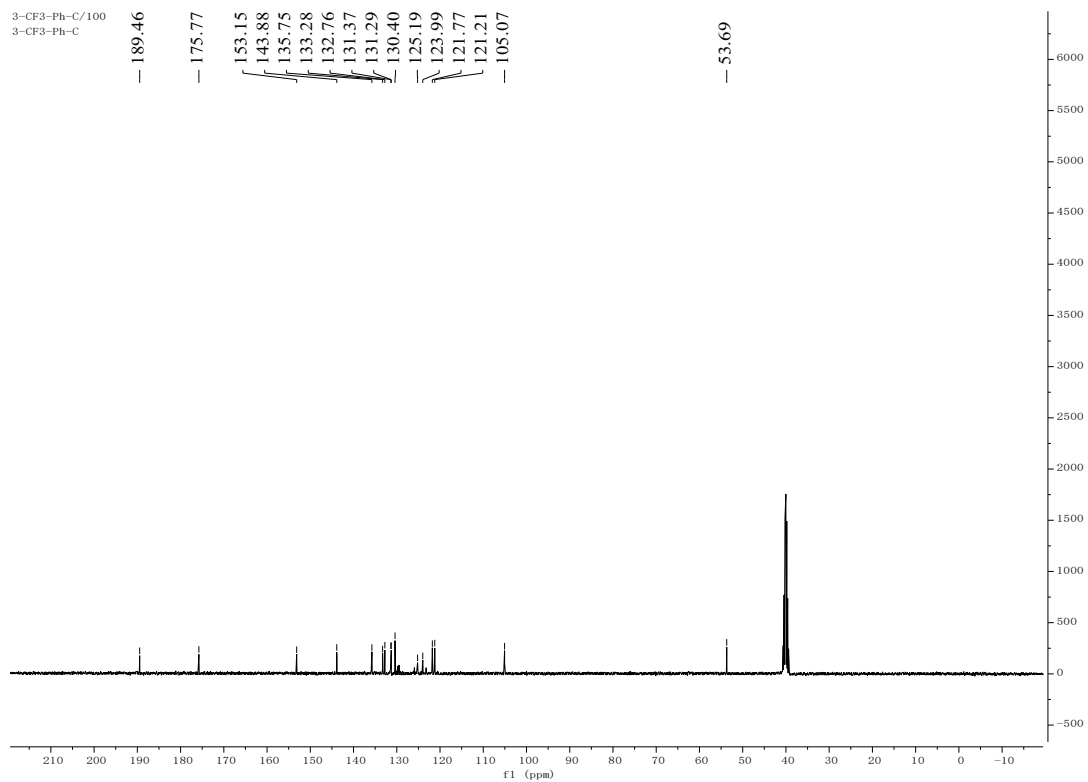
¹³C NMR (101 MHz, DMSO-d₆)



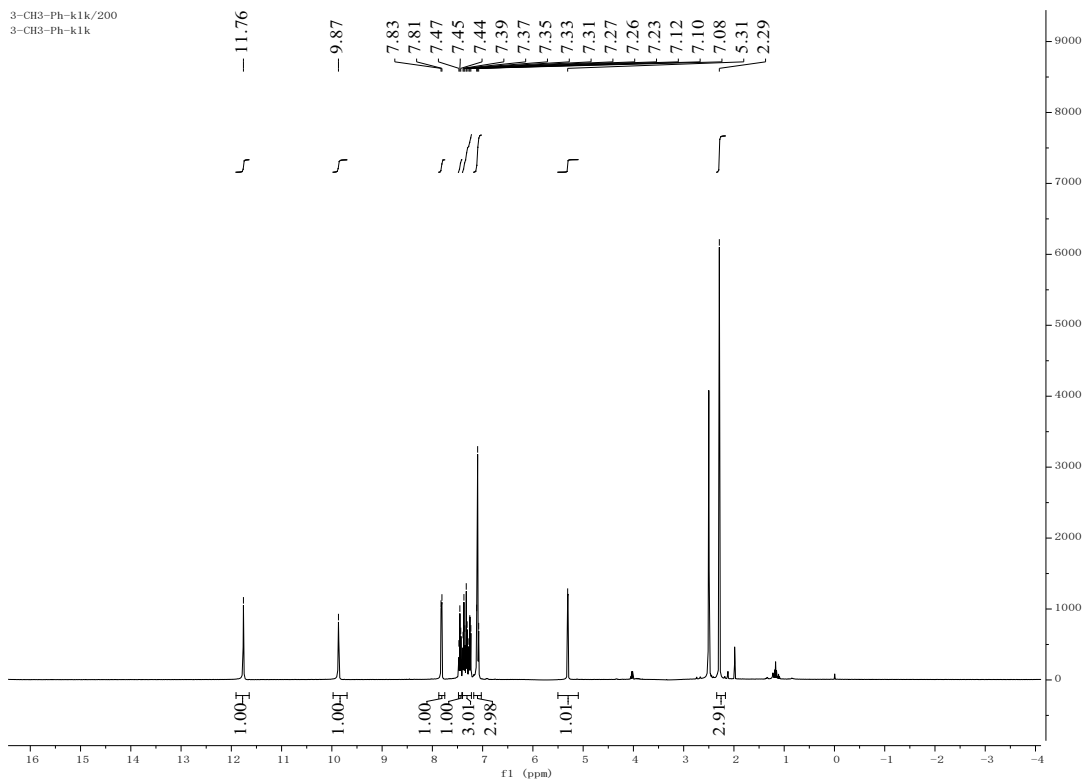
¹H NMR (400 MHz, DMSO-d₆)



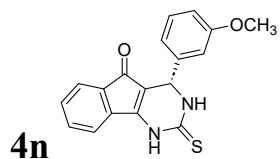
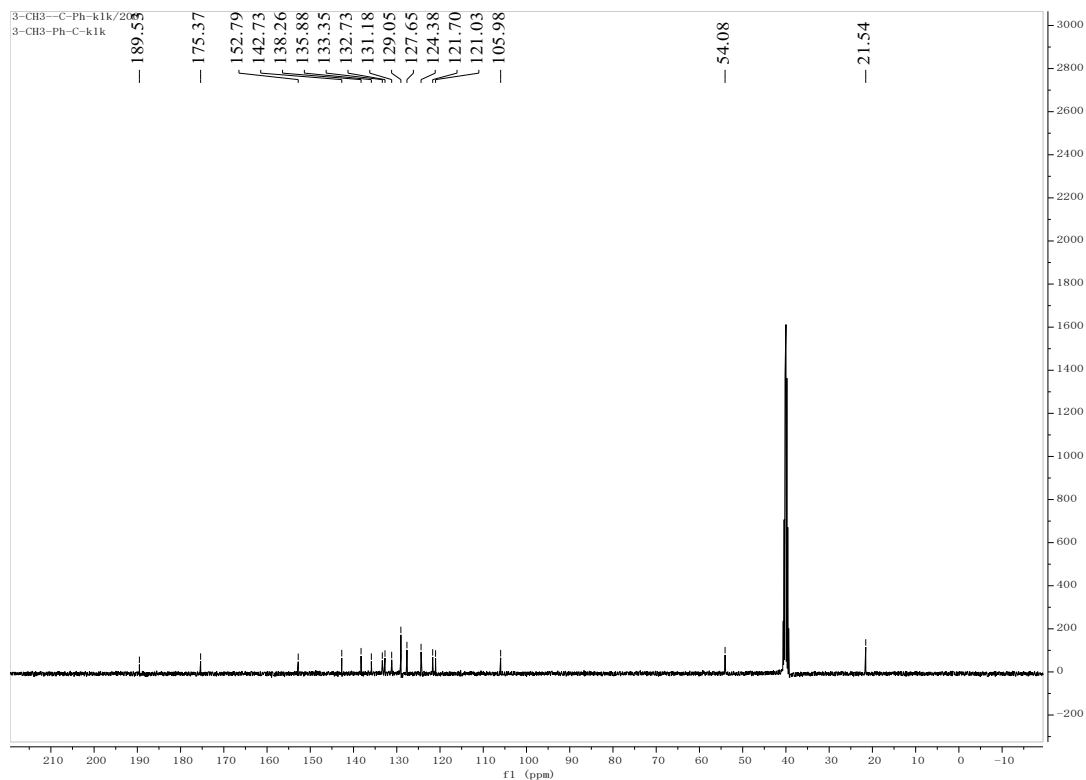
¹³C NMR (101 MHz, DMSO-d₆)



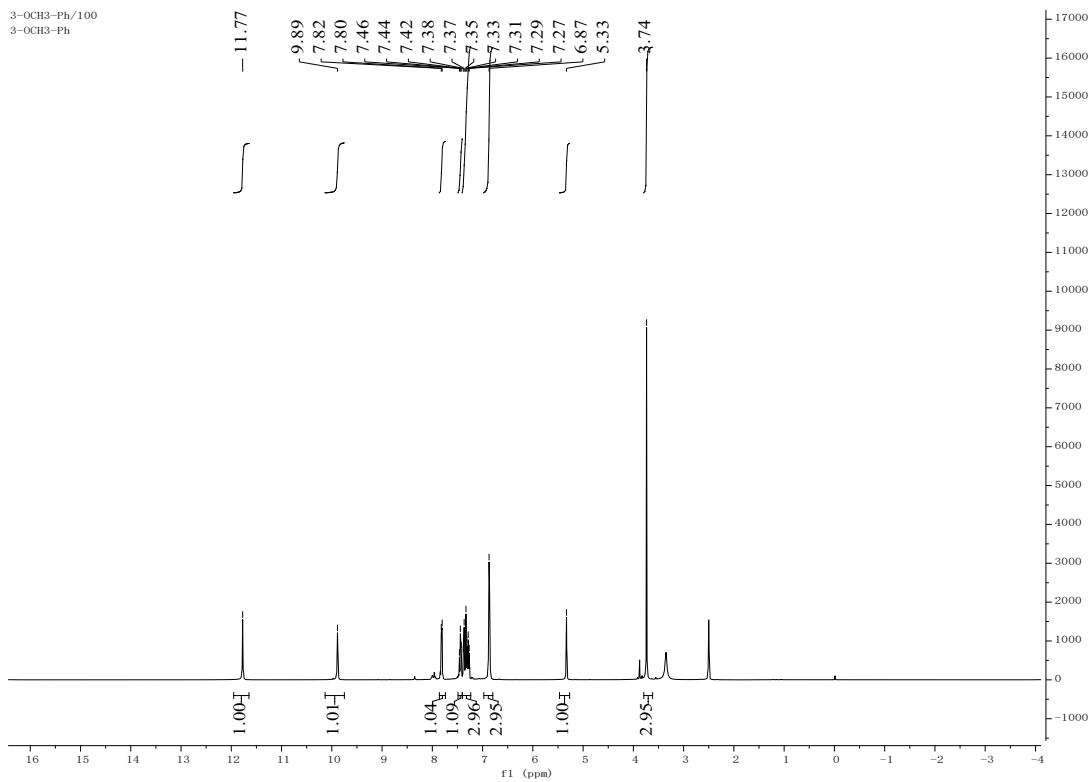
¹H NMR (400 MHz, DMSO-d6)



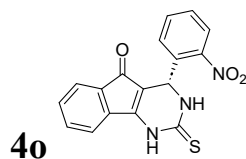
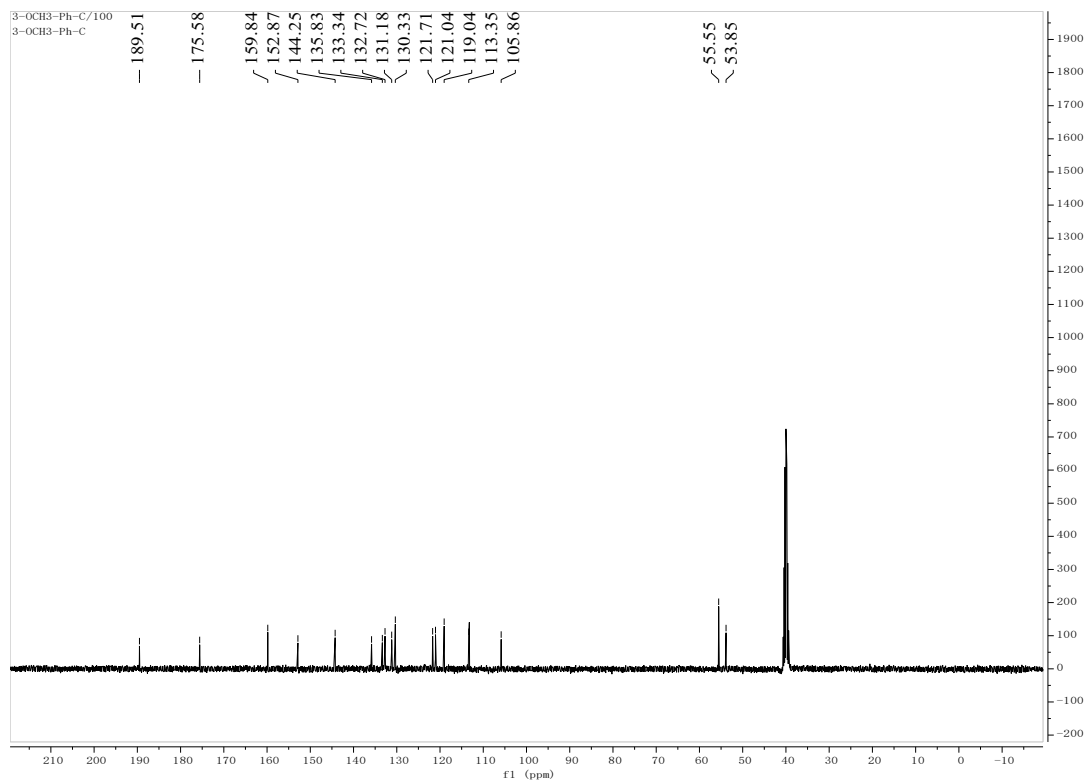
¹³C NMR (101 MHz, DMSO-d6)



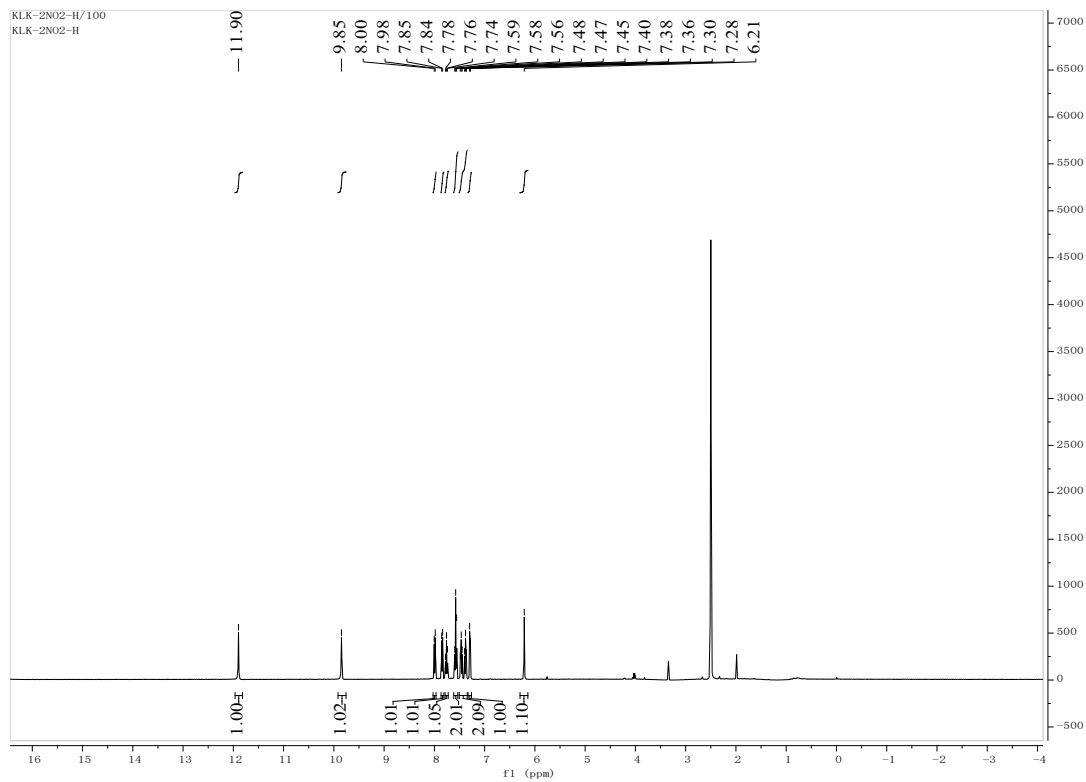
¹H NMR (400 MHz, DMSO-d₆)



¹³C NMR (101 MHz, DMSO-d₆)

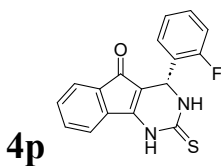
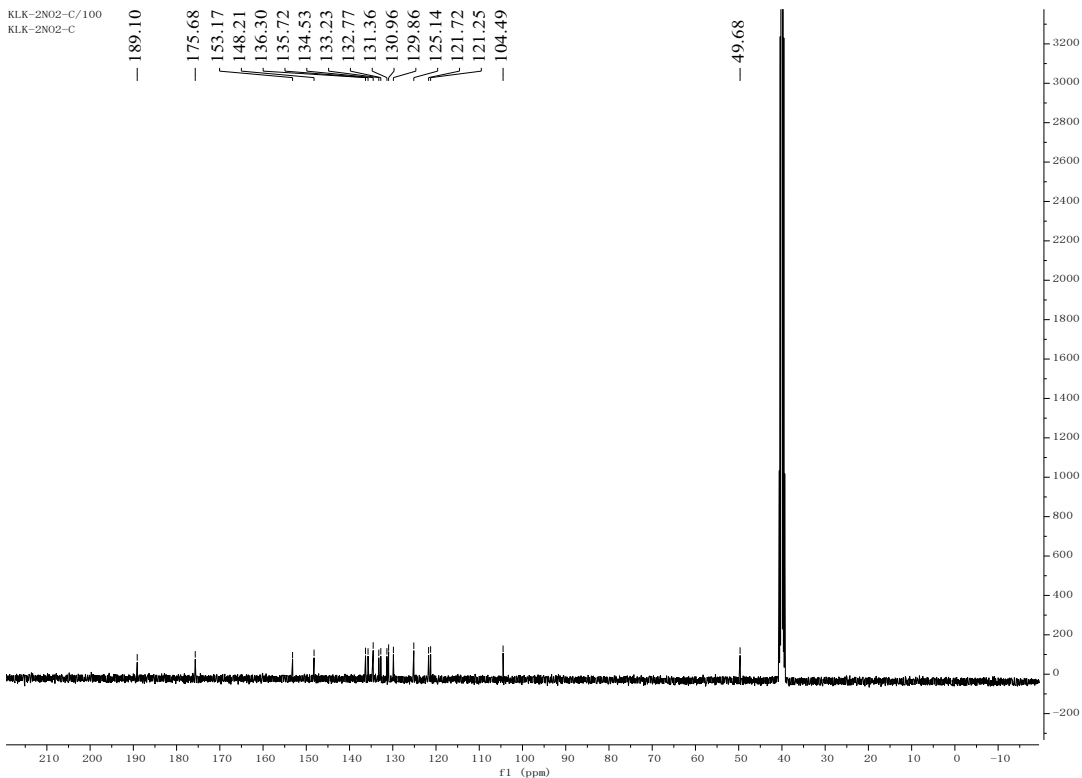


¹H NMR (400 MHz, DMSO-d₆)



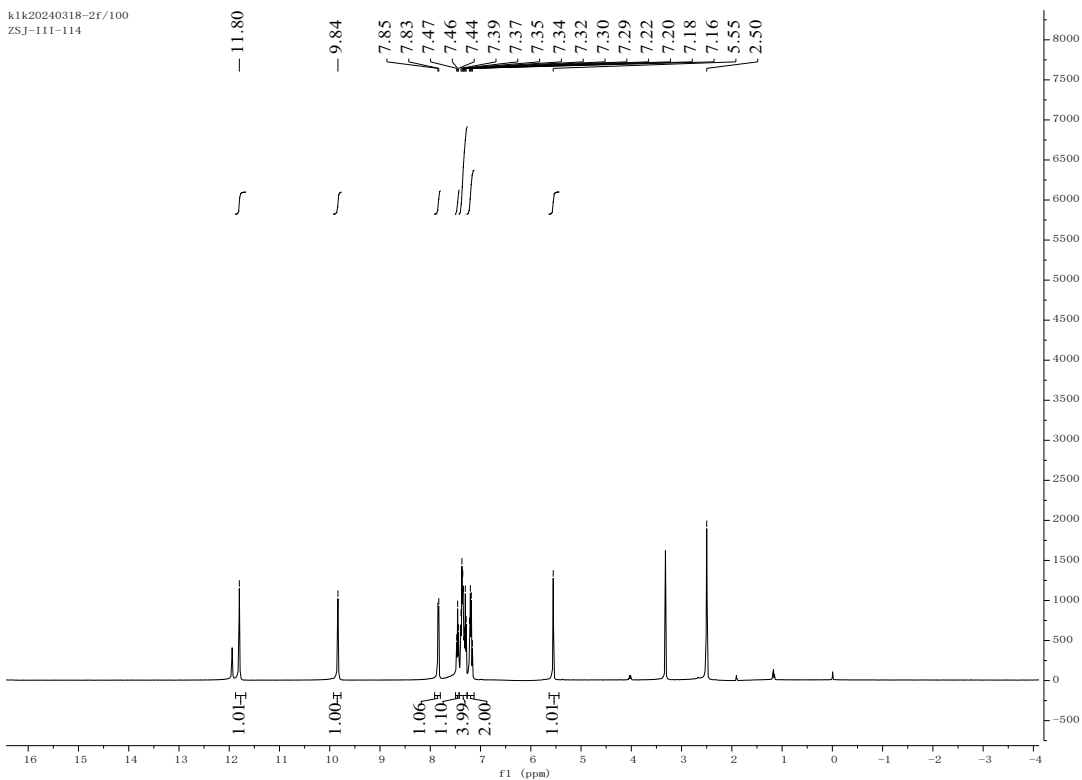
¹³C NMR (101 MHz, DMSO-d₆)

KLK-2N02-C/100
KLK-2N02-C



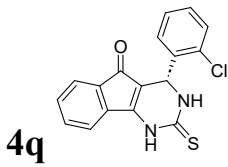
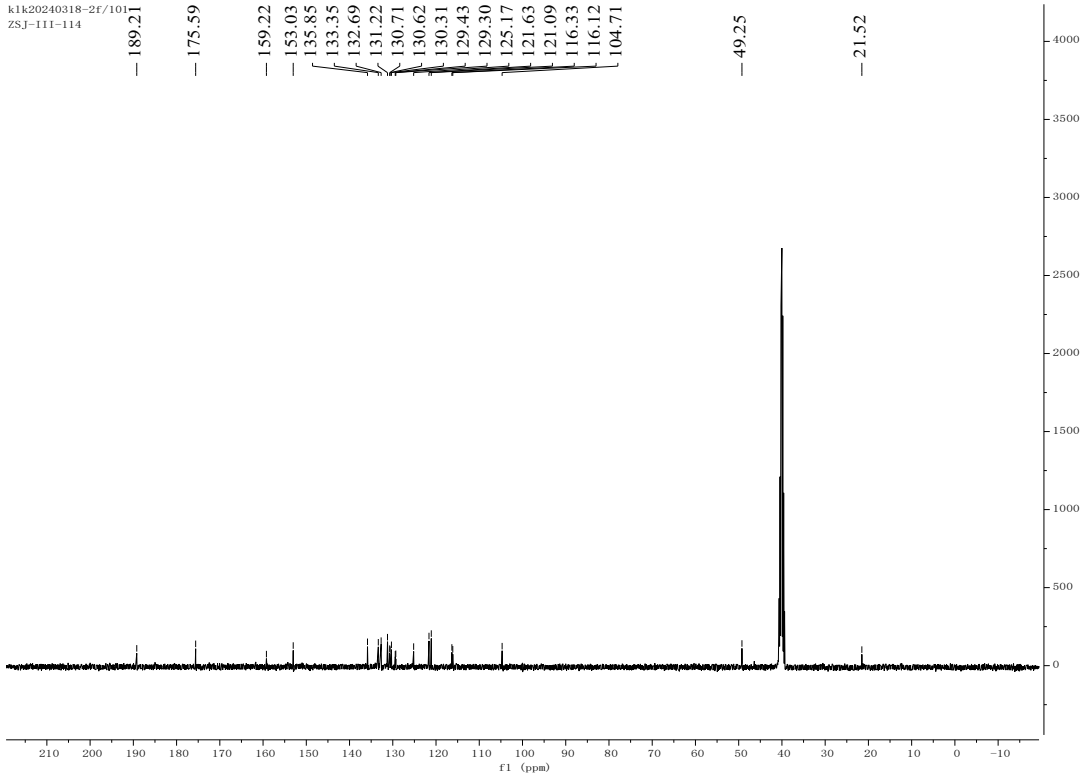
¹H NMR (400 MHz, DMSO-d₆)

klk20240318-2f/100
ZSJ-1117-114

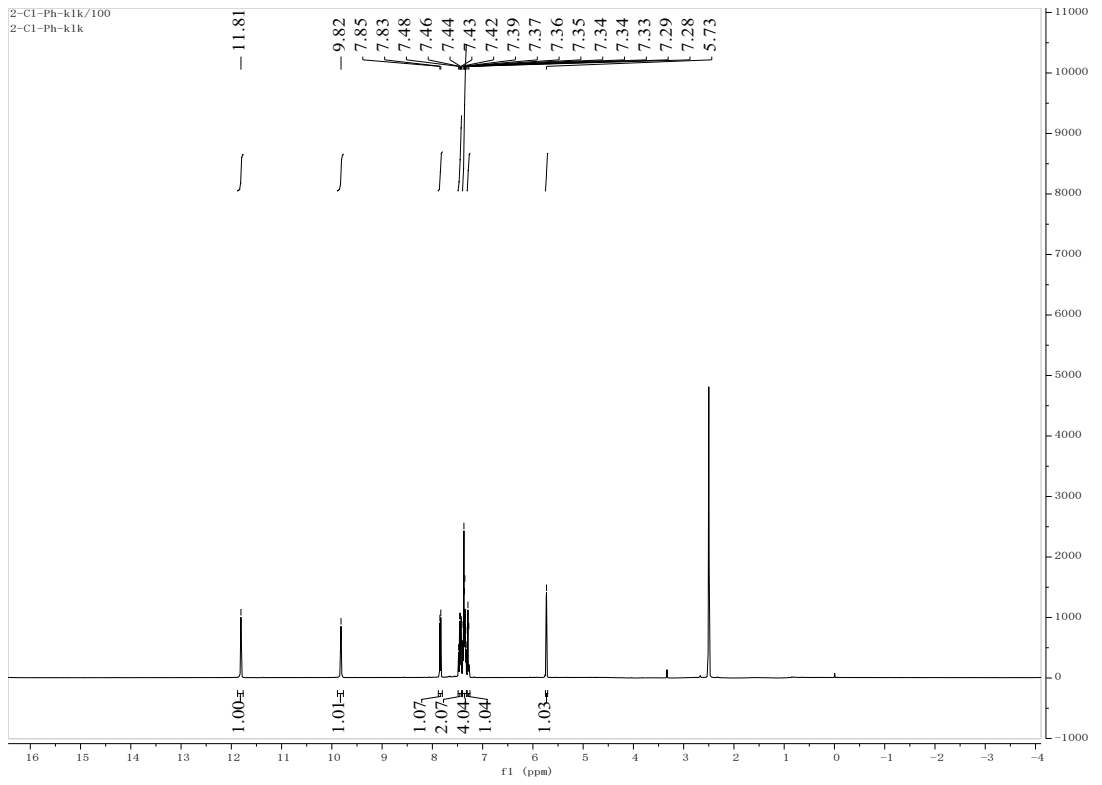


¹³C NMR (101 MHz, DMSO-d₆)

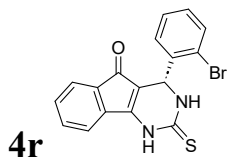
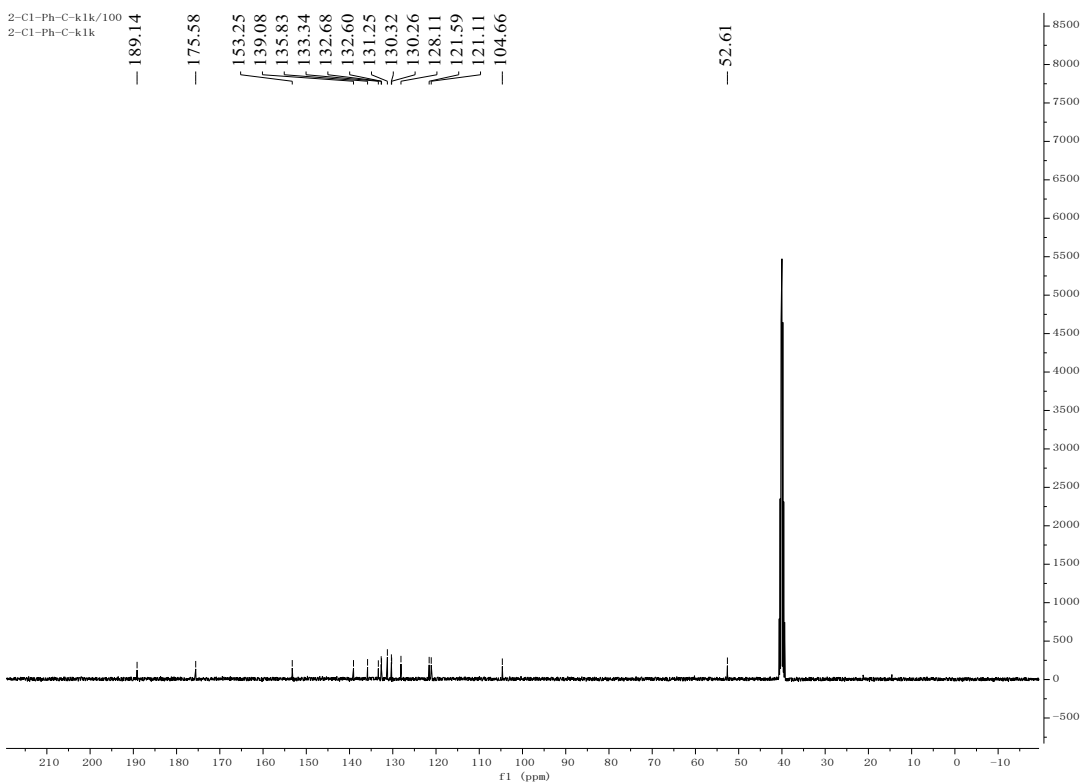
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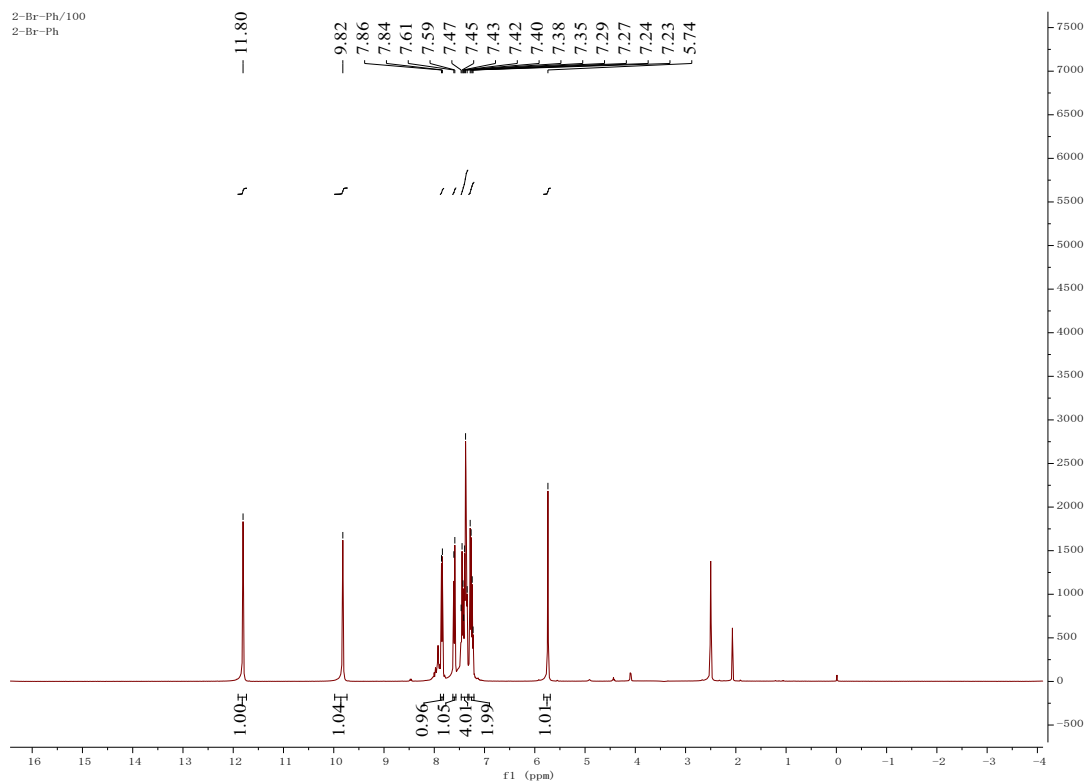
¹H NMR (400 MHz, DMSO-d₆)



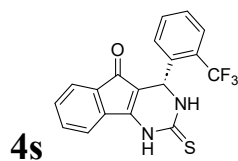
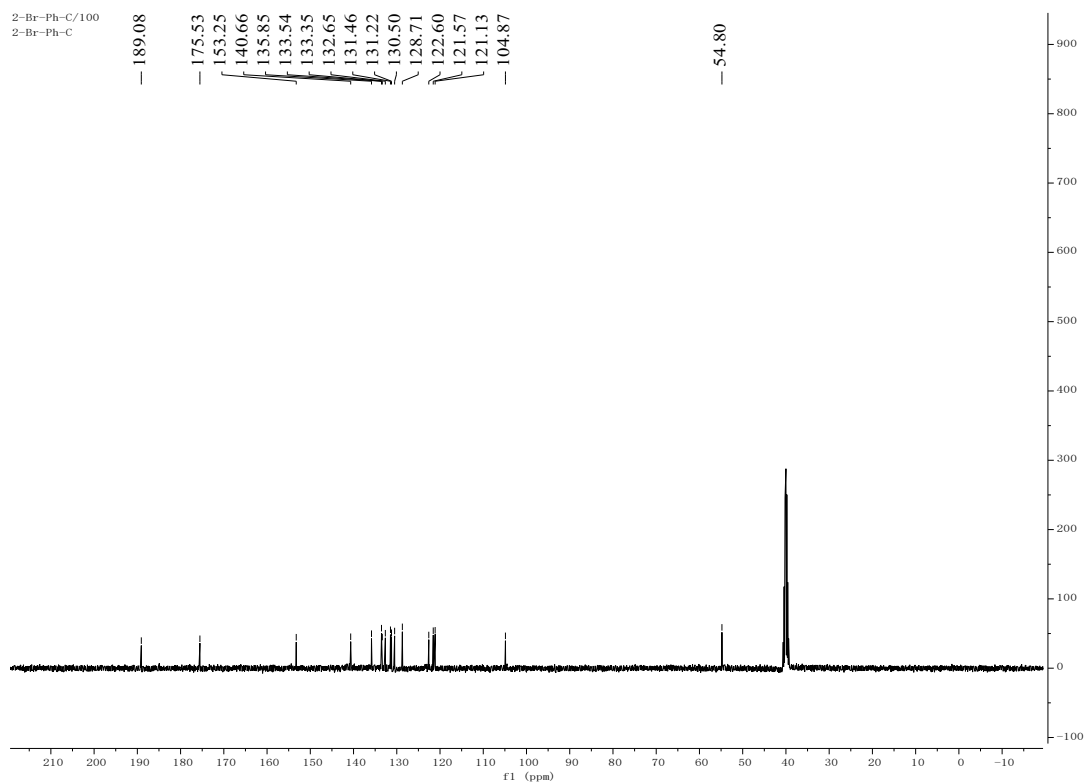
¹³C NMR (101 MHz, DMSO-d6)



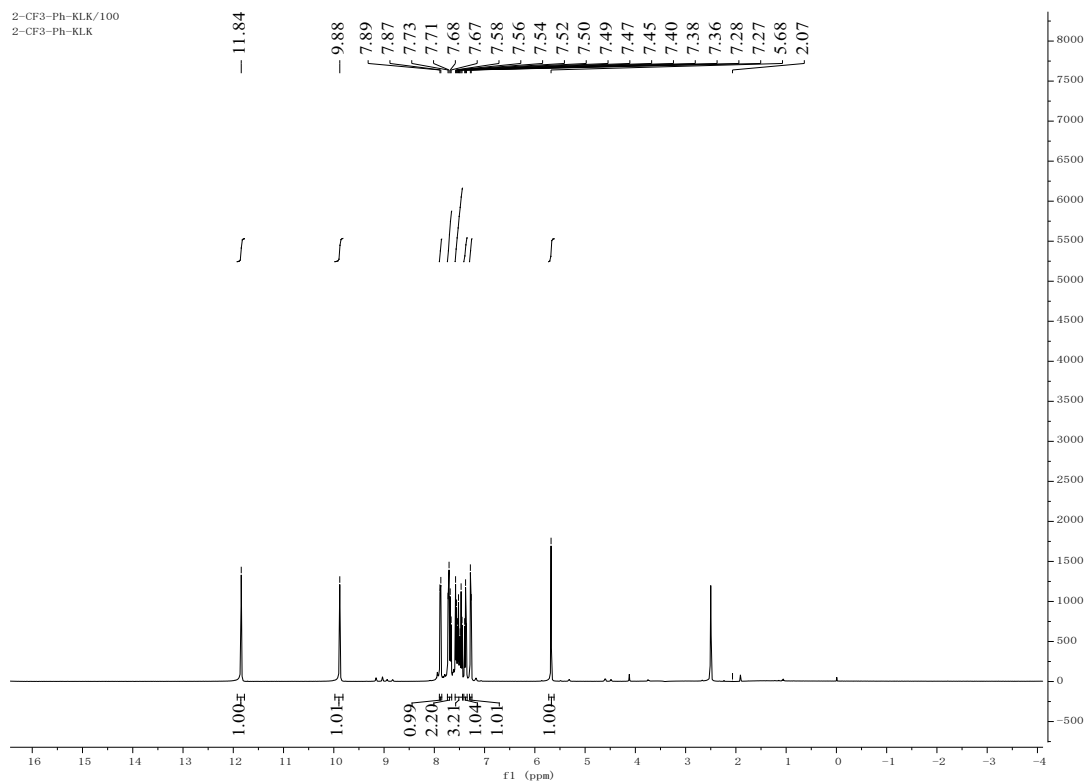
¹H NMR (400 MHz, DMSO-d6)



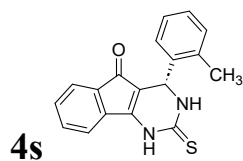
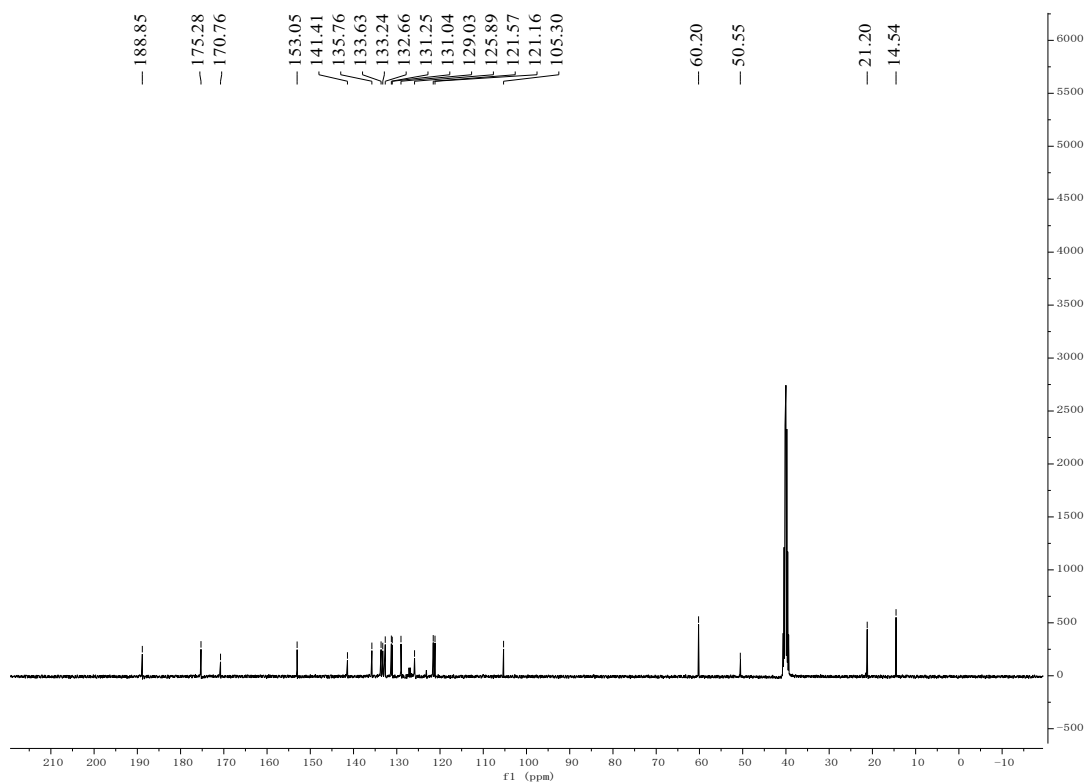
¹³C NMR (101 MHz, DMSO-d₆)



¹H NMR (400 MHz, DMSO-d₆)

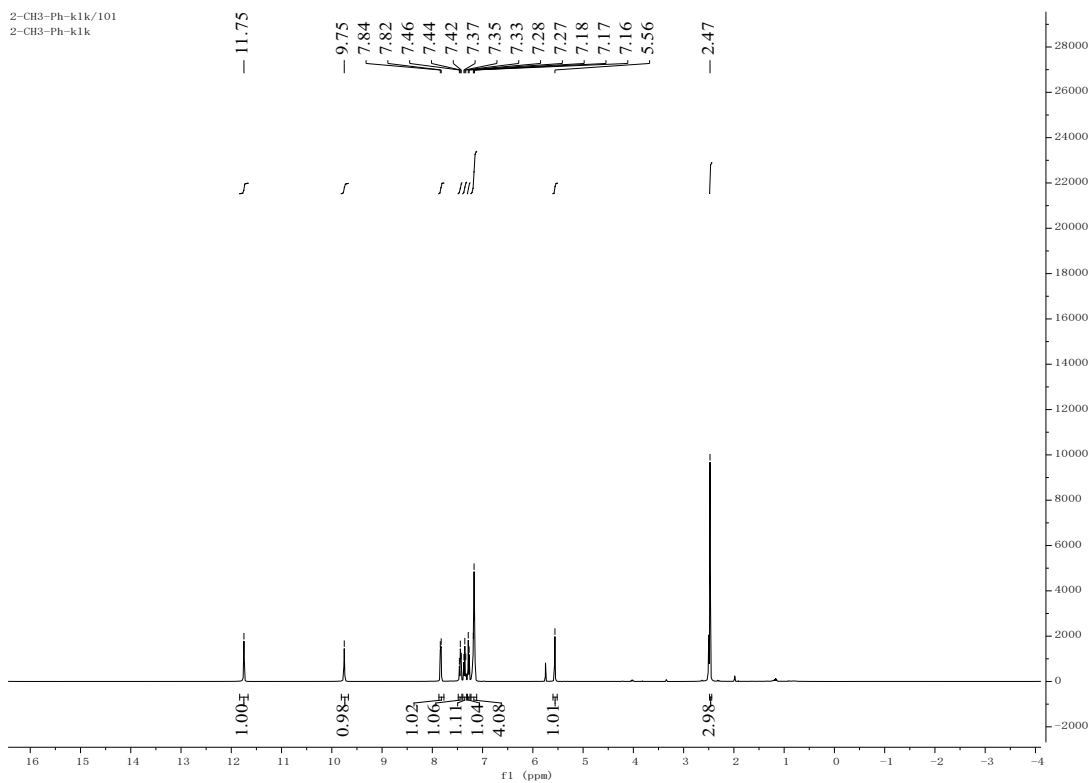


¹³C NMR (101 MHz, DMSO-d6)

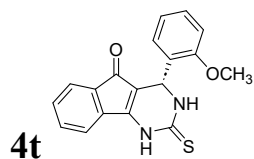
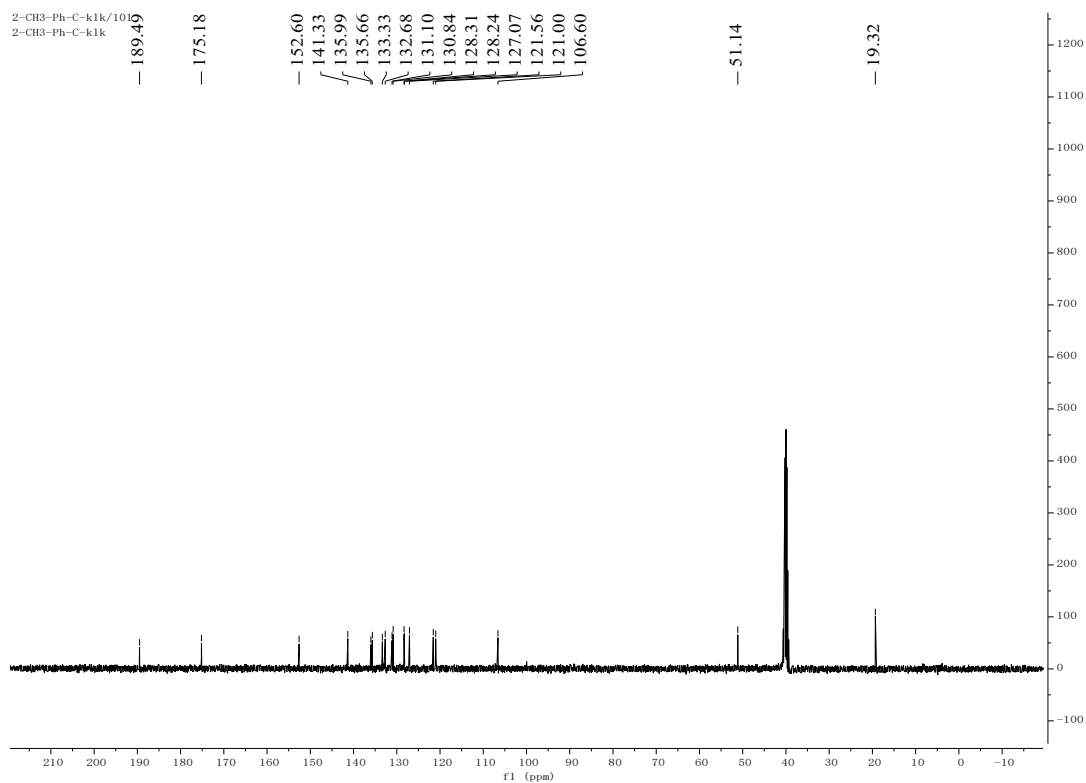


¹H NMR (400 MHz, DMSO-d6)

2-CH3-Ph-k1k/101
2-CH3-Ph-k1k

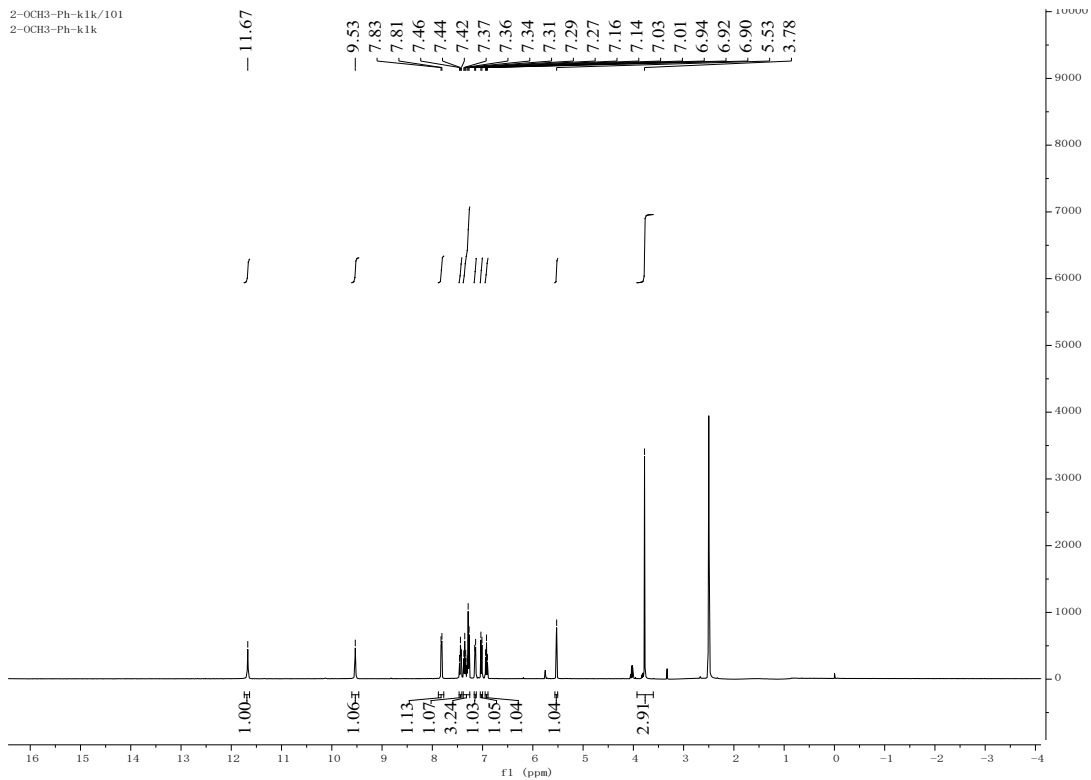


¹³C NMR (101 MHz, DMSO-d₆)



¹H NMR (400 MHz, DMSO-d₆)

2-OCH3-Ph-k1k/101
2-OCH3-Ph-k1k



¹³C NMR (101 MHz, DMSO-d6)

2-OCH3-Ph-C-k1k/101
2-OCH3-Ph-C-k1k

