Supporting Information

Asymmetric Construction of Spirocyclohexanonerhodanines Catalyzed by Simple Diamine Derived from Chiral tert-Leucine

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A: General Information and Starting Materials

General Information. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker AV-400 spectrometer (400 MHz and 100 MHz). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CDCl_3$: δ 7.26) Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$: δ 77.16). Data are represented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz). High resolution mass spectrometry (EI) were carried out using a Waters Quatro Macro triple quadrupole mass spectrometer Mass spectra (EI) were measured on a Waters Micromass GCT spectrometer. Optical rotations were measured on an Autopol III automatic polarimeter (Rudolph Research analytical). Melting points were measured on a XT3A apparatus. High Performance Liquid Chromatography (HPLC) was performed on an Agilent 1200 Series chromatographs using chiral columns (DAICEL CHIRALPAK IA, AD, IC) as noted.

Starting Materials. All solvents and inorganic reagents were from commercial sources and used without purification unless otherwise noted. Substrates 5,8,9 was synthesized following the literature procedure[1-4]. Catalyst 4a-4e was synthesized following the literature procedure[5].

Reference.

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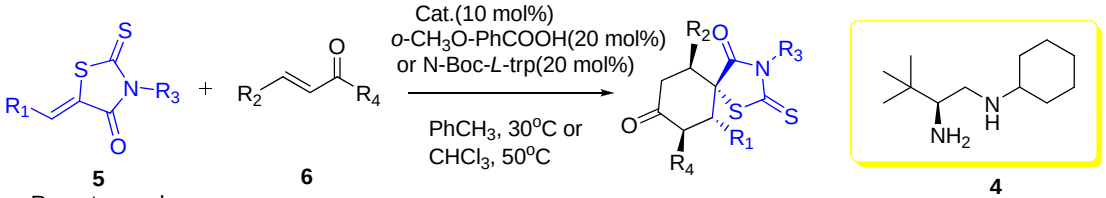
4 N. Faucher, P. Martres, A. Laroze, O. Pineau, F. Potvain, D. Grillot. *Bioorg. Med. Chem. Lett.* **2008**, *18*, 710.

5 a) F. Yu, H. Hu, X. Gu, J. Ye. *Org. Lett.* **2012**, *12*, 1008; b) Y.-Q, Yang, G. Zhao, *Chem. Eur. J.*, **2008**, *14*, 10888; c) J. Li, S. Luo, J.-P. Cheng. *J. Org. Chem.* **2009**, *74*, 1747; d) Y. Gao, Q. Ren, L. Wang, J. Wang, *Chem. Eur. J.*, **2010**, *16*, 13068.

B: Experimental Sections:



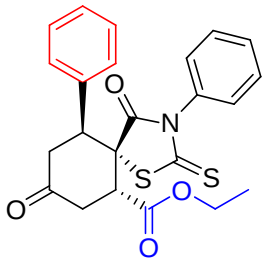
5 **6** **4**

R_1=ester, aryl
R_3=H, alkyl, aryl

25 examples
up to 99% ee and >20/1 dr

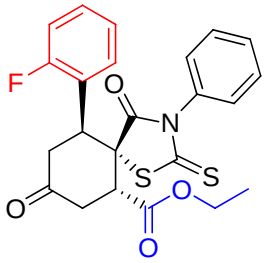
To a solution of **6** (0.45 mmol, 1.5 equiv.) in solvent (0.6 mL) was added catalyst **4** (0.03 mmol, 0.10 equiv.) and acid (0.06 mmol, 0.20 equiv.), then substrate 5 (0.30 mmol, 1.0 equiv.) was added. The reaction mixture was stirred at 30°C or 50°C for 1-3 days and then the solvent was removed under vacuum. The residue was purified by silica gel chromatography to yield the desired product.

C: Characterization of Cascade Reaction Products



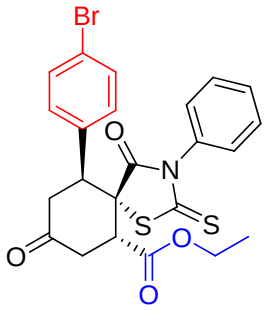
7a: (5S,6S,10S)-ethyl 4,8-dioxo-3,10-diphenyl-2-thioxo-1-thia-3-azaspiro[4.5]decane-6-carboxylate

The product was obtained in 86% yield, light yellow solid. Mp 105-106°C; $[\alpha]^{20}_{D}$ -40.8 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, CDCl3): (ppm) δ1.32 (t, J = 7.2 Hz, 3H), 2.64 (dd, J = 4.0, 15.6 Hz, 1H), 2.83 (dd, J = 6.8, 16.0 Hz, 1H), 3.46-3.60 (m, 2H), 3.95-3.81 (t, J = 6.0 Hz, 1H), 4.11 (dd, J = 4.0, 14.0 Hz, 1H), 4.21-4.35 (m, 2H), 6.68-6.92 (m, 2H), 7.33-7.44 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 39.5, 42.6, 47.9, 48.4, 62.5, 63.9, 128.1, 128.8, 128.9, 129.4, 129.5, 129.8, 134.7, 135.6, 170.7, 175.9, 198.4, 206.2; HRMS (EI): Exact mass calcd for $(C_{23}H_{21}NO_4S_2)^+$: 439.0912. Found: 439.0914. The enantiomeric ratio was determined by Daicel Chiralpak IA (25 cm), n-Hexane / EtOH= 4:1, 1.0 mL/min^{-1}, λ = 240 nm, 19.2 min (major), 22.8 min (minor), ee 98%.



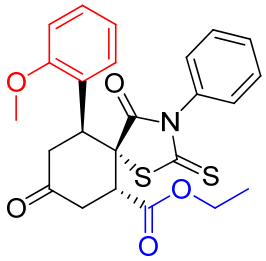
7b: (5S,6S,10S)-ethyl 10-(2-fluorophenyl)-4,8-dioxo-3-phenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-6-carboxylate

The product was obtained in 83% yield, yellow solid. Mp 92-93°C; $[\alpha]^{20}_{D}$ -42.3 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, CDCl3): (ppm)δ1.34 (t, J = 7.2 Hz, 3H), 2.72-2.85 (m, 2H);3.39 (dd, J = 10.4, 15.6 Hz, 1H), 3.54 (dd, J = 6.4, 16.0 Hz, 1H), 3.85 (t, J = 6.4 Hz, 1H), 4.29 (q, J = 6.8 Hz, 1H), 4.67 (dd, J = 5.2, 10.0 Hz, 1H),7.03-7.25 (m, 5H), 7.35-7.40 (m, 1H), 7.49-7.54 (m, 3H); 13C NMR (100 MHz, $CDCl_3$) δ14.2, 40.2, 42.7, 47.6, 62.6, 63.5, 116.1, 116.3, 124.5, 124.6, 128.2, 129.6, 129.9, 130.4, 130.5, 135.0, 170.4, 175.5, 196.4, 205.4; HRMS (EI): Exact mass calcd for $(C_{23}H_{20}FNO_4S_2)^+$: 457.0818. Found: 457.0819. The enantiomeric ratio was determined by Daicel Chiralpak AD (25 cm), n-Hexane / EtOH= 4:1, 0.8 mL/min^{-1}, λ = 240 nm, 10.5 min (minor), 22.2 min (major), ee 92%.



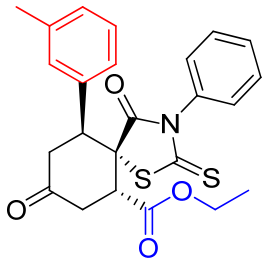
7c: (5S,6S,10S)-ethyl 10-(4-bromophenyl)-4,8-dioxo-3-phenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-6-carboxylate

The product was obtained in 81% yield, light yellow solid. Mp 147-148°C; $[\alpha]^{20}_{D}$ -27.8 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): (ppm)δ1.34 (t, J = 7.2 Hz, 3H), 2.62 (d, J = 16.0 Hz, 2H), 2.83 (dd, J = 6.0, 16.0 Hz, 1H), 3.48-3.56 (m, 2H), 3.94 (t, J = 5.6 Hz, 1H), 4.09-4.12 (m, 1H), 4.25-4.32(m, 2H), 6.72 (bs, 2H),7.23-7.29 (m, 2H), 7.49-7.54 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$)δ14.3, 39.5, 42.6, 47.4, 48.4, 62.7, 63.6, 123.2, 128.0, 129.7, 130.0, 131.0, 131.9, 134.6, 134.8, 170.7, 175.7, 197.9, 205.6; HRMS (EI): Exact mass calcd for $(C_{23}H_{20}BrNO_4S_2)^+$: 517.0017, Found: 517.0020. The enantiomeric ratio was determined by Daicel Chiralpak IA (25 cm), n-Hexane / EtOH= 7:3, 1.0 mL/min^{-1}, λ = 240 nm, 13.9 min (minor), 20.4 min (major), ee 87%.



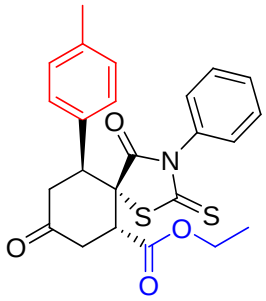
7d: 6S,10S)-ethyl 10-(2-methoxyphenyl)-4,8-dioxo-3-phenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-6-carboxylate

The product was obtained in 79% yield, light yellow solid. Mp 143-145°C; $[\alpha]^{20}_{D}$ -43.5 (*c* 1.0, CH_2Cl_2);^{1}H NMR (400 MHz, $CDCl_3$): (ppm) δ1.30 (t, J = 6.8 Hz, 3H), 2.70-2.78 (m, 2H), 3.27 (dd, J = 9.2, 14.8 Hz, 1H), 3.43 (dd, J = 5.2, 16.0 Hz, 1H), 3.78 (s, 3H), 3.84-3.86 (m, 1H), 4.24 (t, J = 7.2 Hz, 1H), 4.79 (bs, 1H), 6.87-6.89 (m, 1H), 6.93-6.97 (m, 1H), 7.07-7.08 (m, 3H), 7.29-7.33 (m, 1H), 7.44-7.52 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$)δ14.2, 40.3, 43.2, 47.3, 55.5, 55.6, 62.3, 64.0, 111.3, 120.8, 125.6, 128.3, 129.5, 129.7, 129.8, 135.3, 157.5, 170.4, 175.6, 192.9, 199.2; HRMS (EI): Exact mass calcd for $(C_{24}H_{23}NO_5S_2)^+$: 469.1018, Found: 469.1016. The enantiomeric ratio was determined by Daicel Chiralpak IA (25 cm), n-Hexane / EtOH= 7:3, 0.8 mL/min^{-1}, λ = 254 nm, 10.2 min (minor), 12.6 min (major), ee 88%.



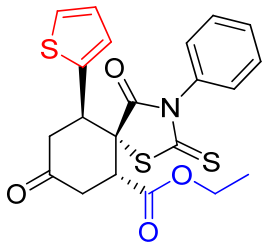
7e: (5S,6S,10S)-ethyl 4,8-dioxo-3-phenyl-2-thioxo-10-m-tolyl-1-thia-3-azaspiro[4.5] decane-6-carboxylate

The product was obtained in 80% yield, light yellow solid. Mp 138-139°C; $[\alpha]^{20}_{D}$ -58.4 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): (ppm) δ1.35 (t, J = 7.2 Hz, 3H), 2.37 (s, 3H), 2.64 (dd, J = 3.6, 15.2 Hz, 1H), 2.84 (dd, J =6.4, 16.0 Hz, 1H), 3.49-3.60 (m, 2H), 3.96 (t, J = 6.4 Hz, 1H), 4.10 (dd, J =4.4, 14.0 Hz, 1H), 4.23-4.37 (m, 2H), 6.71 (bs, 2H), 7.15-7.17 (m, 2H), 7.23-7.31 (m, 2H), 7.45-7.47 (m, 3H);^{13}C NMR (100 MHz, $CDCl_3$)δ14.2, 21.5, 39.5, 42.6, 47.8, 48.3, 62.5, 63.8, 126.7, 128.1, 128.6, 129.5, 129.6, 129.8, 129.9, 134.7, 135.5, 138.4, 170.8, 175.8, 198.6, 206.2; HRMS (EI): Exact mass calcd for $(C_{24}H_{23}NO_4S_2)^+$: 453.1068, Found: 453.1069; The enantiomeric ratio was determined by Daicel Chiralpak IA (25 cm), n-Hexane / ^{i}PrOH= 7:3, 0.8 mL/min^{-1}, λ = 254 nm, 12.8 min (minor), 14.0 min (major), ee 98%.



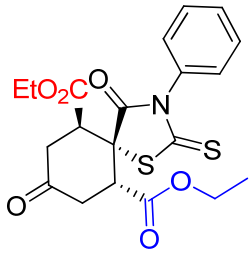
7f: (5S,6S,10S)-ethyl 4,8-dioxo-3-phenyl-2-thioxo-10-p-tolyl-1-thia-3-azaspiro[4.5] decane-6-carboxylate

The product was obtained in 80% yield, yellow solid. Mp 83-84°C ; $[\alpha]^{20}_{D}$ -62.1 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): (ppm)δ1.32 (t, J = 7.2 Hz, 3H), 2.39 (s, 3H), 2.61 (dd, J = 4.0, 15.6 Hz, 1H), 2.80 (dd, J =6.8, 16.4 Hz, 1H), 3.43-3.56 (m, 2H), 3.93 (t, J = 6.4 Hz, 1H), 4.06 (dd, J =4.0, 13.6 Hz, 1H), 4.20-4.34 (m, 2H), 6.69 (bs, 2H), 7.17-7.23 (m, 4H), 7.42-7.49 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$)δ14.3, 21.2, 39.4, 42.8, 47.6, 48.2, 62.5, 64.0, 129.1, 129.2, 129.4, 129.5, 129.8, 132.6, 134.8, 138.8, 170.7, 175.9, 198.6, 206.3; HRMS (EI): Exact mass calcd for $(C_{24}H_{23}NO_4S_2)^+$: 453.1068, Found: 453.1069; The enantiomeric ratio was determined by Daicel Chiralpak IA (25 cm), n-Hexane / ^{i}PrOH= 7:3, 0.8 mL/min^{-1}, λ = 254 nm, 10.2 min (major), 14.5 min (minor), ee >99%.



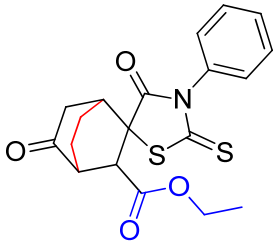
7g:(5R,6S,10S)-ethyl 4,8-dioxo-3-phenyl-10-(thiophen-2-yl)-2-thioxo-1-thia-3-azaspiro[4.5] decane-6-carboxylate

The product was obtained in 90% yield, light yellow solid. Mp 82-83°C; $[\alpha]^{20}_{D}$ -82.9 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): (ppm)δ1.33 (t, J = 7.2 Hz, 3H), 2.75-2.81 (m, 2H), 3.47-3.54 (m, 2H), 3.90 (t, J = 6.0 Hz, 1H), 4.23-4.31 (m, 2H), 4.44 (dd, J = 4.4, 13.6 Hz, 2H), 6.75 (bs, 2H), 7.04-7.06 (m, 1H), 7.34-7.35 (m, 1H), 7.44-7.46 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$)δ14.2, 39.7, 43.6, 44.0, 48.5, 62.7, 63.8, 126.0, 127.0, 127.5, 128.1, 129.6, 129.9, 134.7, 138.6, 170.9, 175.6, 198.6, 205.0; HRMS (EI): Exact mass calcd for $(C_{21}H_{19}NO_4S_3)^+$: 445.0476, Found: 445.0477; The enantiomeric ratio was determined by Daicel Chiralpak IA (25 cm), n-Hexane / ^{i}PrOH = 7:3, 0.8 mL/min^{-1}, λ = 254 nm, 12.9 min (minor), 13.4 min (major), ee 90%.



7h: (6S,10S)-diethyl 4,8-dioxo-3-phenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-6,10-dicarboxylate

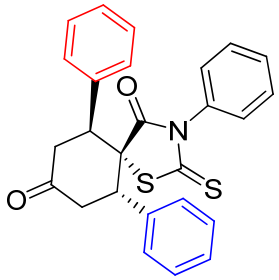
The product was obtained in 35% yield, yellow oil. $[\alpha]^{20}_{D}$ -160.4 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): (ppm)δ1.26 (t, J = 7.2 Hz, 3H), 1.30 (t, J = 7.2 Hz, 3H), 2.61 (dd, J = 6.8, 16.0 Hz, 1H), 2.73 (dd, J = 5.2, 15.2 Hz, 1H), 3.04 (dd, J = 8.4, 15.2 Hz, 1H), 3.37 (dd, J = 6.0, 15.6 Hz, 1H), 3.88-3.97 (m, 2H), 4.18-4.26(m, 3H), 7.34-7.36 (m, 2H), 7.49-7.58 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$)δ14.1, 14.2, 39.9, 40.4, 48.0, 49.1, 59.8, 62.4, 62.6, 128.4, 129.8, 130.0, 135.3, 170.6, 175.9, 196.2, 203.1; HRMS (EI): Exact mass calcd for $(C_{20}H_{21}NO_6S_2)^+$: 435.0810, Found: 435.0811; The enantiomeric ratio was determined by Daicel Chiralpak IC (25 cm), n-Hexane / ^{i}PrOH= 7:3, 0.8 mL/min^{-1}, λ = 254 nm, 19.8 min (major), 23.9 min (minor), ee 94%.



7i: ethyl 4',5-dioxo-3'-phenyl-2'-thioxospiro[bicyclo[2.2.2] octane-2,5'-thiazolidine]-3-carboxylate

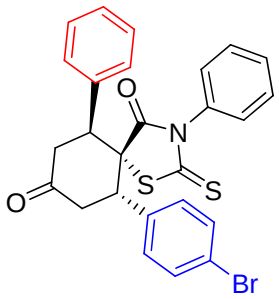
The product was obtained in 95% yield, yellow solid. Mp 166-167°C; ^{1}H NMR (400

MHz, $CDCl_3$): (ppm)δ1.28 (t, J = 7.2 Hz, 3H), 1.59-1.68 (m, 2H), 1.92-1.99 (m, 1H), 2.09-2.17 (m, 1H), 2.22-2.32 (m, 2H), 2.76-2.77 (m, 1H), 2.93-2.94 (m, 1H), 3.36-3.41 (m, 1H), 3.76 (bs, 1H), 4.15-4.30 (m, 2H), 7.19-7.21 (m, 2H), 7.51-7.57 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$)δ14.4, 18.5, 24.7, 39.0, 41.2, 43.9, 48.3, 62.3, 128.3, 129.8, 130.1, 168.4, 178.3, 198.6, 210.4; HRMS (EI): Exact mass calcd for $(C_{19}H_{19}NO_4S_2)^+$: 389.0755, Found: 389.0753.



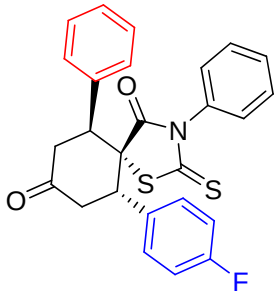
7j: (6S,10S)-3,6,10-triphenyl-2-thioxo-1-thia-3-azaspiro[4.5]decane-4,8-dione

The product was obtained in 70% yield, light yellow solid. Mp 157-158°C; $[\alpha]^{20}_D$ -118.0 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): (ppm)δ2.80-2.84 (m, 1H), 3.02 (dd, J = 8.4, 16.4 Hz, 1H), 3.37(dd, J = 4.8, 16.8 Hz, 1H), 3.67-3.74 (m, 1H), 3.87-3.91(m, 1H), 4.31-4.34(m, 1H), 6.61 (bs, 2H), 7.26-7.43 (m, 13H); ^{13}C NMR (100 MHz, $CDCl_3$)δ42.4, 42.6, 46.8, 48.1, 69.3, 128.0, 128.6, 128.7, 128.9, 129.2, 129.3, 129.5, 129.7, 134.8, 135.9, 138.2, 176.4, 197.7, 208.2; HRMS (EI): Exact mass calcd for $(C_{26}H_{21}NO_2S_2)^+$: 443.1014, Found: 443.1016; The enantiomeric ratio was determined by Daicel Chiralpak IA (25 cm), n-Hexane / ^{i}PrOH= 7:3, 0.8 mL/min^{-1}, λ = 254 nm, 11.7 min (minor), 22.0 min (major), ee 94%.



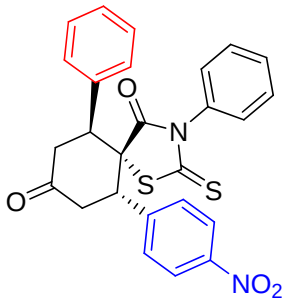
7k: (5S,6S,10S)-6-(4-bromophenyl)-3,10-diphenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-4,8-dione

The product was obtained in 94% yield, yellow solid. Mp 101-103°C; $[\alpha]^{20}_D$ -75.8 (*c* 1.0, CH_2Cl_2);^{1}H NMR (400 MHz, $CDCl_3$): (ppm)δ2.78 (dd, J = 4.0, 16.4 Hz, 1H), 2.95 (dd, J = 8.8, 16.4 Hz, 1H), 3.28(dd, J = 4.8, 16.4 Hz, 1H), 3.65 (dd, J = 13.2, 16.4 Hz, 1H), 3.81(dd, J = 3.6, 12.8 Hz, 1H), 4.27(dd, J = 4.8, 8.8 Hz, 1H), 6.55 (bs, 2H), 7.10-7.12(m, 1H), 7.28-7.29(m, 2H), 7.34-7.42(m, 6H), 7.51-7.53 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$)δ42.3, 42.6, 46.2, 48.3, 69.0, 122.9, 128.0, 128.8, 128.9, 129.3, 129.6, 129.8, 130.8, 132.1, 134.7, 135.8, 137.2, 176.3, 197.0, 207.8; HRMS (EI): Exact mass calcd for $(C_{26}H_{20}BrNO_2S_2)^+$: 521.0119, Found: 521.0119; The enantiomeric ratio was determined by Daicel Chiralpak IA (25 cm), n-Hexane / ^{i}PrOH = 7:3, 0.8 mL/min^{-1}, λ = 254 nm, 11.0 min (minor), 17.2 min (major), ee 98%.



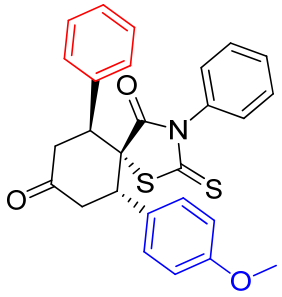
7l: (5S,6S,10S)-6-(4-fluorophenyl)-3,10-diphenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-4,8-dione

The product was obtained in 86% yield, yellow solid. Mp 197-198°C; $[\alpha]^{20}_{D}$ -126.5(*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): (ppm)δ2.79 (dd, J = 4.0, 16.4 Hz, 1H), 2.95 (dd, J = 8.8, 16.4 Hz, 1H), 3.29(dd, J = 4.8, 16.8 Hz, 1H), 3.66 (dd, J = 13.2, 16.0 Hz, 1H), 3.82(dd, J = 4.0, 13.2 Hz, 1H), 4.30(dd, J = 4.8, 8.8 Hz, 1H), 6.55 (bs, 2H), 7.07-7.11(m, 1H), 7.20-7.24(m, 2H), 7.28-7.30(m, 2H), 7.35-7.42 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$)δ42.5, 42.6, 46.1, 48.2, 69.4, 115.8, 116.0, 128.0, 128.8, 129.3, 129.5, 129.8, 130.9, 131.0, 134.0, 134.7, 135.9, 161.5, 163.9, 176.3, 197.2, 207.9; HRMS (EI): Exact mass calcd for $(C_{26}H_{20}FNO_2S_2)^+$: 461.0919, Found: 461.0920; The enantiomeric ratio was determined by Daicel Chiralpak IA (25 cm), n-Hexane / ^{i}PrOH = 7:3, 0.8 mL/min^{-1}, λ = 254 nm, 13.3 min (minor), 20.9 min (major), ee 95%.



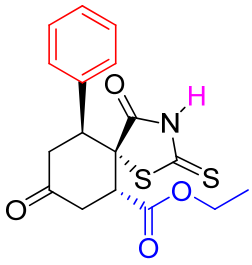
7m: (5S,6S,10S)-6-(4-nitrophenyl)-3,10-diphenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-4,8-dione

The product was obtained in 85% yield, yellow solid. Mp 214-215°C; $[\alpha]^{20}_{D}$ -187.5 (*c* 1.0, CH_2Cl_2);^{1}H NMR (400 MHz, $CDCl_3$): (ppm)δ2.81 (dd, J = 3.6, 16.4 Hz, 1H), 3.04 (dd, J = 10.0, 16.8 Hz, 1H), 3.23(dd, J = 4.4, 16.4 Hz, 1H), 3.68 (dd, J = 13.2, 16.4 Hz, 1H), 3.84(dd, J = 3.6, 13.2 Hz, 1H), 4.49(dd, J = 4.4, 10.0 Hz, 1H), 6.48 (bs, 2H), 7.30-7.32(m, 2H), 7.36-7.43(m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$)δ41.8, 42.3, 46.0, 48.6, 68.7, 124.1, 127.9, 128.9, 129.0, 129.3, 129.6, 129.9, 130.1, 134.4, 135.3, 145.2, 147.9, 176.1, 196.2, 207.0; HRMS (EI): Exact mass calcd for $(C_{26}H_{20}N_2O_4S_2)^+$: 488.0864, Found: 488.0865; The enantiomeric ratio was determined by Daicel Chiralpak IA (25 cm), n-Hexane / ^{i}PrOH = 7:3, 0.8 mL/min^{-1}, λ = 254 nm, 21.9 min (minor), 25.6 min (major), ee 98%.



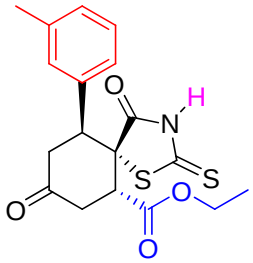
7n: (5S,6S,10S)-6-(4-methoxyphenyl)-3,10-diphenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-4,8-dione

The product was obtained in 68% yield, yellow solid. $[\alpha]^{20}_{D}$ -155.4 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): (ppm)δ2.77 (dd, J = 3.6, 16.0 Hz, 1H), 2.93 (dd, J = 8.0, 16.4 Hz, 1H), 3.35(dd, J = 5.2, 16.4 Hz, 1H), 3.62-3.70 (m, 1H), 3.80-3.81(m, 1H), 3.83(s, 1H), 4.22(dd, J = 5.2, 7.6 Hz, 1H), 6.61 (bs, 2H), 6.89-6.92(m, 2H), 7.15-7.17(m, 2H), 7.26-7.28 (m, 2H), 7.35-7.42 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$)δ42.7, 42.8, 46.4, 48.1, 55.5, 69.7, 114.2, 128.1, 128.8, 129.3, 129.5, 129.8, 130.4, 134.9, 136.1, 159.7, 176.5, 197.8, 208.5; HRMS (EI): Exact mass calcd for $(C_{27}H_{23}NO_3S_2)^+$: 473.1119, Found: 473.1123; The enantiomeric ratio was determined by Daicel Chiralpak IA (25 cm), n-Hexane / iPrOH = 7:3, 0.8 mL/min^{-1}, λ = 254 nm, 16.4 min (minor), 25.4 min (major), ee 99%.



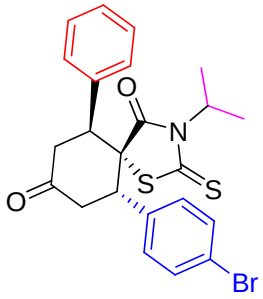
7o: (5S,6S,10S)-ethyl 4,8-dioxo-10-phenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-6-carboxylate

The product was obtained in 88% yield, yellow oil. $[\alpha]^{20}_{D}$ -58.2 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): (ppm)δ1.31 (t, J = 7.2 Hz, 3H), 2.65 (dd, J = 4.0, 15.2 Hz, 1H), 2.78(dd, J = 5.2, 16.0 Hz, 1H), 3.51-3.58 (m, 2H), 3.80 (t, J = 5.6 Hz, 1H), 4.09(dd, J = 4.0, 12.8 Hz, 1H), 4.19-4.32 (m,2H), 7.29-7.30(m, 2H), 7.33-7.34(m, 3H), 8.91 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$)δ14.1, 39.8, 42.9, 47.8, 48.3, 62.7, 66.8, 128.8, 128.9, 129.2, 135.9, 170.9, 176.4, 197.8, 206.1; HRMS (EI): Exact mass calcd for $(C_{17}H_{17}NO_4S_2)^+$: 363.0599, Found: 363.0598; The enantiomeric ratio was determined by Daicel Chiralpak IA (25 cm), n-Hexane / ^{i}PrOH= 7:3, 0.8 mL/min^{-1}, λ = 254 nm, 20.9 min (major), 32.8 min (minor), ee 99%.



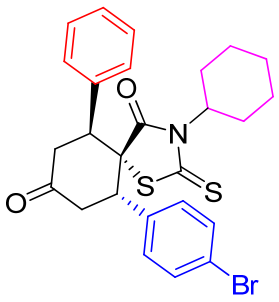
7p:(5S,6S,10S)-ethyl 4,8-dioxo-2-thioxo-10-m-tolyl-1-thia-3-azaspiro[4.5] decane-6-carboxylate

The product was obtained in 77% yield, yellow oil. $[\alpha]^{20}_{D}$ -75.2 (*c* 0.5, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$): (ppm)δ1.28 (t, J = 7.2 Hz, 3H), 2.31(s, 3H), 2.61 (dd, J = 3.6, 15.2 Hz, 1H), 2.75 (dd, J = 5.2, 16.0 Hz, 1H), 3.45-3.53 (m, 2H), 3.77 (t, J = 6.0 Hz, 1H), 4.01 (dd, J = 4.4, 12.8 Hz, 1H), 4.16-4.26 (m, 2H), 7.04-7.05 (m, 2H), 7.10-7.12(m, 1H), 7.17-7.20(m, 1H), 9.20(bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$)δ14.1, 21.6, 39.8, 43.0, 47.7, 48.2, 62.6, 66.8, 125.9, 128.6, 129.6, 130.1, 135.8, 138.4, 170.9, 176.6, 198.1, 206.4; HRMS (EI): Exact mass calcd for $(C_{18}H_{19}NO_4S_2)^+$: 377.0755, Found: 377.0753; The enantiomeric ratio was determined by Daicel Chiralpak IA (25 cm), n-Hexane / ^{i}PrOH= 7:3, 0.8 mL/min^{-1}, λ = 254 nm, 8.5 min (minor), 12.8 min (major), ee 89%.



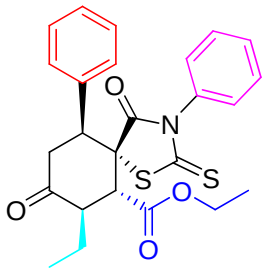
7q: (5S,6S,10S)-6-(4-bromophenyl)-3-isopropyl-10-phenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-4,8-dione

The product was obtained in 88% yield, light yellow solid. Mp 85-86°C; $[\alpha]^{20}_{D}$ -138.7 (*c* 1.0, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$): (ppm)δ1.03(d, J = 6.8 Hz, 3H), 1.16(d, J = 6.8 Hz, 3H), 2.75 (dd, J = 4.0, 16.0 Hz, 1H), 2.89 (dd, J = 10.4, 16.4 Hz, 1H), 3.08 (dd, J = 4.4, 16.8 Hz, 1H), 3.55(dd, J = 12.0, 16.4 Hz, 1H), 3.68(dd, J = 4.0, 11.6 Hz, 1H), 4.11(dd, J = 4.4, 10.4 Hz, 1H), 4.82-4.88 (m, 1H), 7.00-7.03 (m, 2H), 7.18-7.20 (m, 2H), 7.28-7.30 (m, 3H), 7.41-7.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$)δ17.7, 18.1, 42.4, 42.7, 45.5, 48.4, 50.2, 65.6, 122.6, 128.5, 128.6, 129.2, 130.8, 131.8, 135.9, 136.6, 176.6, 197.9, 207.8; HRMS (EI): Exact mass calcd for $(C_{23}H_{22}BrNO_2S_2)^+$: 487.0275, Found: 487.0275; The enantiomeric ratio was determined by Daicel Chiralpak IA (25 cm), n-Hexane / ^{i}PrOH= 7:3, 0.8 mL/min^{-1}, λ = 254 nm, 10.6 min (major), 12.3 min (minor), ee 98%.



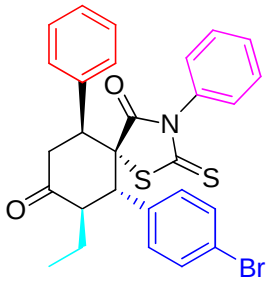
7r: (5S,6S,10S)-6-(4-bromophenyl)-3-cyclohexyl-10-phenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-4,8-dione

The product was obtained in 87% yield, white solid. Mp 149-150°C; $[\alpha]^{30}_{D}$ -153.9 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): (ppm)δ0.95-0.98(m, 1H), 1.13-1.26(m, 4H), 1.59-1.63 (m, 1H), 1.74-2.09 (m, 4H), 2.75 (dd, J = 3.6, 16.0 Hz, 1H), 2.89(dd, J = 10.4, 16.8 Hz, 1H), 3.09(dd, J = 4.4, 16.8 Hz, 1H), 3.55(dd, J = 12.0, 16.4 Hz, 1H), 3.66 (dd, J = 4.0, 12.0 Hz, 1H), 4.10 (dd, J = 4.4, 10.4 Hz, 1H), 4.49(t, J = 11.6 Hz, 1H), 7.00-7.02 (m, 2H), 7.18-7.19 (m, 2H), 7.28-7.30 (m, 3H), 7.41-7.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$)δ25.0, 25.9, 26.0, 27.0, 27.4, 42.4, 42.7, 45.6, 48.4, 58.2, 122.6, 128.5, 128.6, 129.2, 130.8, 131.8, 135.9, 136.7, 176.8, 196.2, 207.9; HRMS (EI): Exact mass calcd for $(C_{26}H_{26}BrNO_2S_2)^+$: 527.0588, Found: 527.0589; The enantiomeric ratio was determined by Daicel Chiralpak IA (25 cm), n-Hexane / ^{i}PrOH= 7:3, 0.8 mL/min^{-1}, λ = 254 nm, 9.8 min (minor), 12.0 min (major), ee 98%.



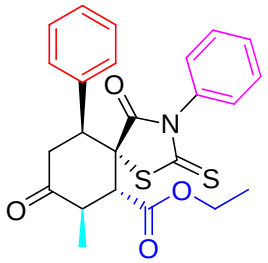
7s: (5S,6S,7R,10S)-ethyl 7-ethyl-4,8-dioxo-3,10-diphenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-6-carboxylate

The product was obtained in 75% yield, yellow solid. Mp 84-85°C; $[\alpha]^{20}_{D}$ -6.6 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): (ppm)δ1.03(t, J = 7.2 Hz, 3H), 1.27-1.31 (m, 2H), 1.36(t, J = 7.2 Hz, 3H), 1.87-1.94(m, 1H), 2.68 (dd, J = 4.8, 14.0 Hz, 1H), 3.59-3.69 (m, 2H), 3.80 (d, J = 6.4 Hz, 2H), 4.28-4.31 (m, 2H), 4.37 (dd, J = 4.4, 13.6 Hz, 1H), 6.78(bs, 2H), 7.35-7.46 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$)δ12.0, 14.3, 20.0, 43.3, 48.3, 48.8, 55.3, 62.2, 64.0, 128.1, 128.7, 128.9, 129.6, 129.9, 134.6, 135.9, 170.5, 197.4, 206.7; HRMS (EI): Exact mass calcd for $(C_{25}H_{25}NO_4S_2)^+$: 467.1225, Found: 467.1223; The enantiomeric ratio was determined by Daicel Chiralpak IA (25 cm), n-Hexane / ^{i}PrOH= 7:3, 0.8 mL/min^{-1}, λ = 254 nm, 5.6 min (major), 7.5 min (minor), ee 95%.



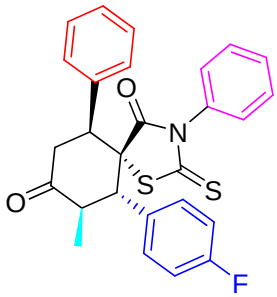
7t:(5S,6S,7R,10S)-10-(4-bromophenyl)-7-ethyl-3,6-diphenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-4,8-dione

The product was obtained in 85% yield, yellow oil. $[\alpha]^{20}_{D}$ -114.7 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): (ppm)δ0.78(t, J = 7.2 Hz, 3H), 1.38-1.48 (m, 1H), 1.92-2.02 (m, 1H), 2.90 (dd, J = 4.8, 16.4 Hz, 1H), 2.94-2.98 (m, 1H), 3.38 (dd, J = 8.8, 16.0 Hz, 1H), 3.92 (dd, J = 4.4, 8.8 Hz, 1H) , 4.24 (d, J = 13.6 Hz, 1H), 6.27-6.29(m, 2H), 7.22-7.24 (m, 2H), 7.32-7.37 (m, 7H), 7.44-7.52 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$)δ9.8, 19.4, 43.5, 48.0, 49.7, 49.9, 71.2, 122.6, 127.9, 128.5, 128.7, 129.3, 129.5, 129.7, 131.7, 134.2, 134.6, 136.7, 175.2, 196.7, 208.7; HRMS (EI): Exact mass calcd for $(C_{28}H_{24}BrNO_2S_2)^+$: 549.0432, Found: 549.0429; The enantiomeric ratio was determined by Daicel Chiralpak IA (25 cm), n-Hexane / ^{i}PrOH= 7:3, 0.8 mL/min^{-1}, λ = 254 nm, 11.9 min (minor), 13.6 min (major), ee 99%.



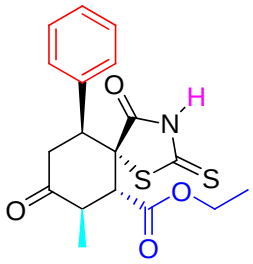
7u: (5S,6S,7R,10S)-ethyl 7-methyl-4,8-dioxo-3,10-diphenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-6-carboxylate

The product was obtained in 87% yield, yellow solid. Mp 69-70°C; $[\alpha]^{20}_{D}$ -20.5 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): (ppm)δ1.15(d, J = 6.8 Hz, 3H), 1.36 (t, J = 7.2 Hz, 3H), 2.71 (dd, J = 4.8, 14.4 Hz, 1H), 3.62 (t, J = 14.0 Hz, 1H), 3.76 (d, J = 6.0 Hz, 1H), 3.87-3.90 (m, 1H) , 4.30 (q, J = 7.2 Hz, 1H), 4.37 (dd, J = 4.4, 13.6 Hz, 1H), 6.77 (bs, 2H), 7.35-7.45 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$)δ11.9, 14.3, 41.9, 42.8, 48.0, 56.5, 62.2, 63.9, 128.1, 128.7, 128.9, 129.5, 129.9, 134.6, 135.9, 170.5, 197.3, 207.0; HRMS (EI): Exact mass calcd for $(C_{24}H_{23}NO_4S_2)^+$: 453.1068, Found: 453.1070; The enantiomeric ratio was determined by Daicel Chiralpak IA (25 cm), n-Hexane / ^{i}PrOH= 7:3, 0.8 mL/min^{-1}, λ = 254 nm, 6.1 min (major), 8.5 min (minor), ee 98%.



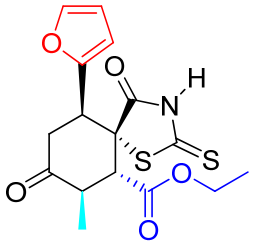
7v:(5S,6S,7R,10S)-6-(4-fluorophenyl)-7-methyl-3,10-diphenyl-2-thioxo-1-thia-3-azaspiro [4.5]decane-4,8-dione

The product was obtained in 80% yield, yellow oil. $[\alpha]^{20}_{D}$ -138.4 (*c* 0.5, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$): (ppm)δ1.09 (d, J = 6.4 Hz, 3H), 2.90-3.03 (m, 2H), 3.40 (dd, J = 8.8, 16.4 Hz, 1H), 3.96 (dd, J = 4.8, 8.4 Hz, 1H), 4.06 (d, J = 13.2 Hz, 1H) , 6.31-6.33(m, 2H), 7.07-7.23 (m, 5H), 7.35-7.37 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$)δ12.9, 42.8, 45.3, 49.7, 50.9, 71.4, 115.5, 127.9, 128.5, 129.4, 129.5, 129.7, 131.21, 131.25, 134.7, 134.8, 175.1, 196.8, 209.2; HRMS (EI): Exact mass calcd for $(C_{27}H_{22}FNO_2S_2)^+$: 475.1076, Found: 475.1077; The enantiomeric ratio was determined by Daicel Chiralpak IA (25 cm), n-Hexane / ^{i}PrOH= 7:3, 0.8 mL/min^{-1}, λ = 254 nm, 11.8 min (major), 12.6 min (minor), ee 93%.



7w: (5S,6S,7R,10S)-ethyl 7-methyl-4,8-dioxo-10-phenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-6-carboxylate

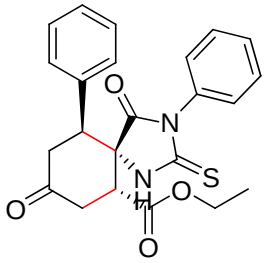
The product was obtained in 78% yield, yellow oil. $[\alpha]^{20}_{D}$ -42.2 (*c* 0.5, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$): (ppm)δ1.11 (d, J = 6.8 Hz, 3H), 1.33(t, J = 6.8 Hz, 3H), 2.68 (dd, J = 4.8, 14.4 Hz, 1H), 3.52-3.66 (m, 2H), 3.78-3.81 (m, 1H), 4.20-4.28 (m, 3H), 7.29-7.31 (m, 5H), 8.80 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$)δ11.9, 14.3, 41.7, 43.1, 47.8, 56.5, 62.3, 67.2, 128.7, 128.8, 128.9, 129.0, 129.1, 129.4, 136.1, 170.5, 176.2, 196.6, 207.0; HRMS (EI): Exact mass calcd for $(C_{18}H_{19}NO_4S_2)^+$: 377.0755, Found: 377.0758; The enantiomeric ratio was determined by Daicel Chiralpak IA (25 cm), n-Hexane / ^{i}PrOH= 7:3, 0.8 mL/min^{-1}, λ = 254 nm, 10.8 min (minor), 14.3 min (majr), ee 97%.



7x:(5S,6S,7R,10S)-ethyl 10-(furan-2-yl)-7-methyl-4,8-dioxo-2-thioxo-1-thia-3-azaspiro[4.5]decane-6-carboxylate

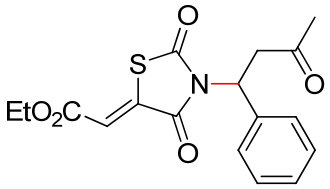
The product was obtained in 82% yield, yellow oil. $[\alpha]^{20}_{D}$ -56.9 (*c* 1.0, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$): (ppm)δ1.08 (d, J = 7.2 Hz, 3H), 1.31(t, J = 7.2 Hz, 3H), 2.71 (dd, J = 4.8, 14.4 Hz, 1H), 3.49-3.62 (m, 2H), 3.72-3.80 (m, 1H), 4.23 (q, J = 7.2 Hz, 2H), 4.41(dd, J = 4.8, 13.2 Hz, 1H), 6.26-6.27 (m, 1H), 6.31-6.34 (m, 1H), 7.33-7.35 (m, 1H), 9.18 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$)δ11.9, 14.3, 41.6, 42.1, 42.3, 55.8, 62.3, 65.6, 109.7, 110.8, 143.0, 150.6, 170.5, 176.0, 196.9, 206.2; HRMS (EI): Exact mass calcd for $(C_{16}H_{17}NO_5S_2)^+$: 367.0548, Found: 367.0549; The

enantiomeric ratio was determined by Daicel Chiralpak IC (25 cm), n-Hexane / EtOH= 4:1, 0.5 mL/min^{-1}, λ = 254 nm, 9.4 min (minor), 10.6 min (majr), ee 96%.



10: (5S,6R,10S)-ethyl 4,8-dioxo-3,10-diphenyl-2-thioxo-1,3-diazaspiro[4.5] decane-6-carboxylate

The product was obtained in 31% yield, yellow oil. $[\alpha]^{20}_{D}$ -90.0 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): (ppm)δ1.33 (t, J = 7.2 Hz, 3H), 2.61(dd, J = 2.8, 14.4 Hz, 1H), 2.94(dd, J = 4.4, 15.6 Hz, 1H), 3.49-3.64 (m, 3H), 3.99 (dd, J = 4.0, 14.4 Hz, 1H), 4.29 (q, J = 7.2 Hz, 2H), 6.70-6.71 (m, 2H), 7.29-7.30 (m, 2H), 7.39-7.40 (m, 6H), 8.33 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$)δ14.2, 38.8, 41.1, 46.1, 46.3, 60.6, 62.7, 66.6, 128.0, 129.0, 129.2, 129.5, 132.0, 135.0, 171.0, 173.1, 182.3, 206.2; HRMS (EI): Exact mass calcd for $(C_{23}H_{22}N_2O_4S)^+$: 422.1300, Found: 422.1299; The enantiomeric ratio was determined by Daicel Chiralpak IA (25 cm), n-Hexane / ^{i}PrOH= 7:3, 0.8 mL/min^{-1}, λ = 254 nm, 10.7 min (minor), 13.9 min (majr), ee 99%.

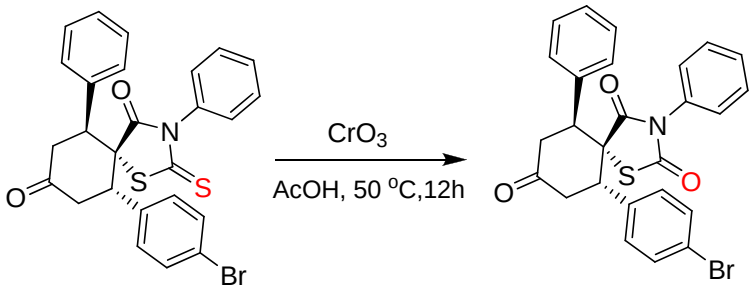


11:(Z)-ethyl 2-(2,4-dioxo-3-(3-oxo-1-phenylbutyl)thiazolidin-5-ylidene)acetate

The product was obtained in 93% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): (ppm)δ1.32 (t, J = 6.8 Hz, 3H), 2.18 (s, 3H), 3.27 (dd, J = 5.6, 18.4 Hz, 1H), 3.95 (dd, J = 9.6, 18.0 Hz, 1H), 4.28 (t, J = 7.2 Hz, 1H), 5.89 (dd, J = 5.6, 10.0 Hz, 1H), 6.97 (s, 1H), 7.29-7.38 (m, 3H), 7.44-7.46 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$)δ14.3, 30.2, 43.8, 53.5, 62.1, 119.6, 128.0. 128.8, 129.0, 137.4, 140.1, 164.9, 165.4, 169.2, 204.841.1, 63.2, 64.8, 65.2, 76.1, 93.2, 127.8, 127.9, 128.5, 133.4, 137.8, 145.1, 196.2; HRMS (EI): Exact mass calcd for $(C_{17}H_{17}NO_5S)^+$: 347.0827, Found: 347.0828；

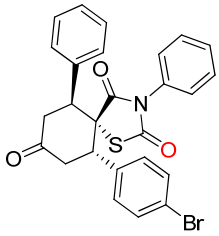
D: Elaboration of spiro-Products

（a）



7k **12** 85% yield

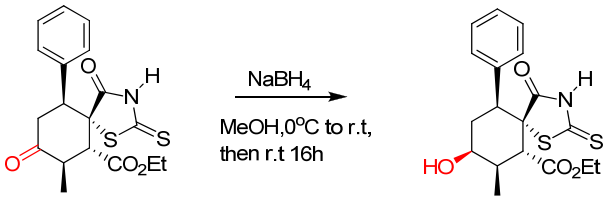
To a solution of compound 7k (52.2 mg, 0.10 mmol) in acetic acid (1.0 mL) was added chromium trioxide (30.0 mg, 0.30 mmol) in three portions over 30 mintutes at room temperature. The solution was stirred at 50 °C for 12 h. The mixture was treated with H_2O (10 mL) and extracted with EtOAc (3 *10 mL). The combined organic extracts was washed by brine, dried over Na_2SO_4, and the solvent was removed under vacuum. The residue was purified by silica gel chromatography to yield the desired product.



12:(5S,6S,10S)-6-(4-bromophenyl)-3,10-diphenyl-1-thia-3-azaspiro[4.5]decane-2,4,8-trione

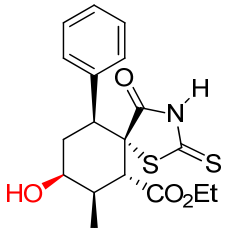
The product was obtained in 85% yield, white solid. Mp 198-200°C; $[\alpha]^{20}_D$ -112.8 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): (ppm)δ2.81 (dd, J = 2.4, 16.0 Hz, 1H), 2.97 (dd, J = 9.2, 16.4 Hz, 1H), 3.28 (dd, J = 4.4, 16.8 Hz, 1H), 3.65-3.72 (m, 1H), 3.79-3.83 (m, 1H), 4.31-4.34 (m, 1H), 6.57-6.71 (m, 2H), 7.12-7.20 (m, 2H), 7.53-7.55 (m, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$)δ42.4, 42.8, 46.2, 48.6, 67.4, 122.8, 127.2, 128.7, 128.8, 128.9, 129.4, 129.6, 130.9, 132.0, 135.9, 137.4, 168.1, 174.6, 208.0; HRMS (EI): Exact mass calcd for $(C_{26}H_{20}BrNO_3S)^+$: 505.0347, Found: 505.0346;

（b）



7x **14** 86% yield

To a solution of compound 7x (37.7 mg, 0.10 mmol) in MeOH (0.5 mL) was added $NaBH_4$ (113.4 mg, 0.30 mmol) at 0°C. The solution was stirred at room temperature for 16 h. The solvent was removed under vacuum and the residue was purified by silica gel chromatography to yield the desired product.

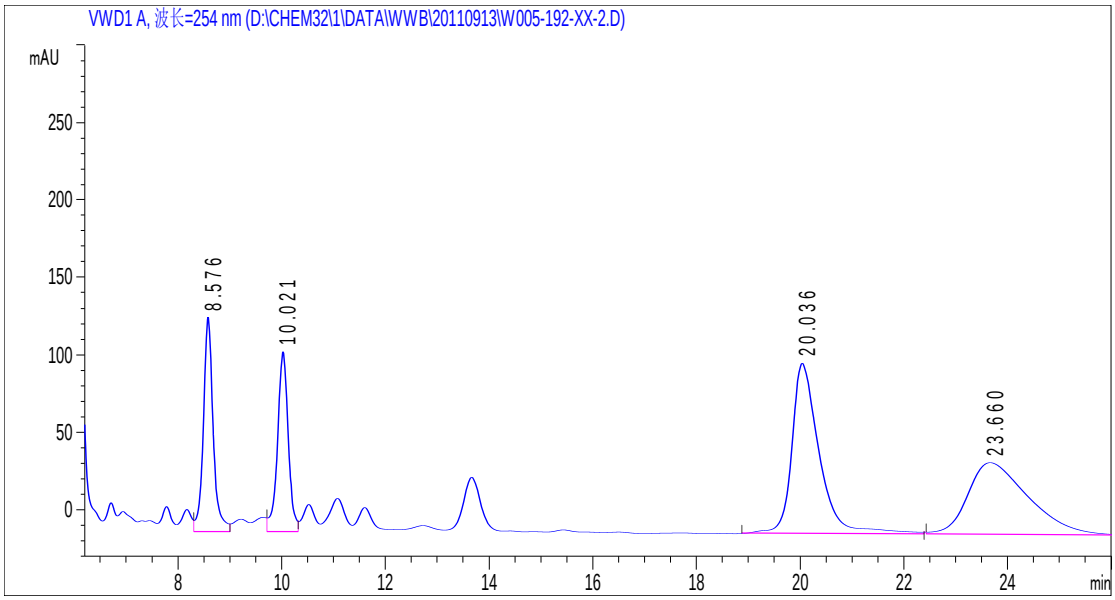


13: (5S,6S,7R,8R,10S)-ethyl 8-hydroxy-7-methyl-4-oxo-10-phenyl-2-thioxo-1-thia-3-azaspiro [4.5]decane-6-carboxylate

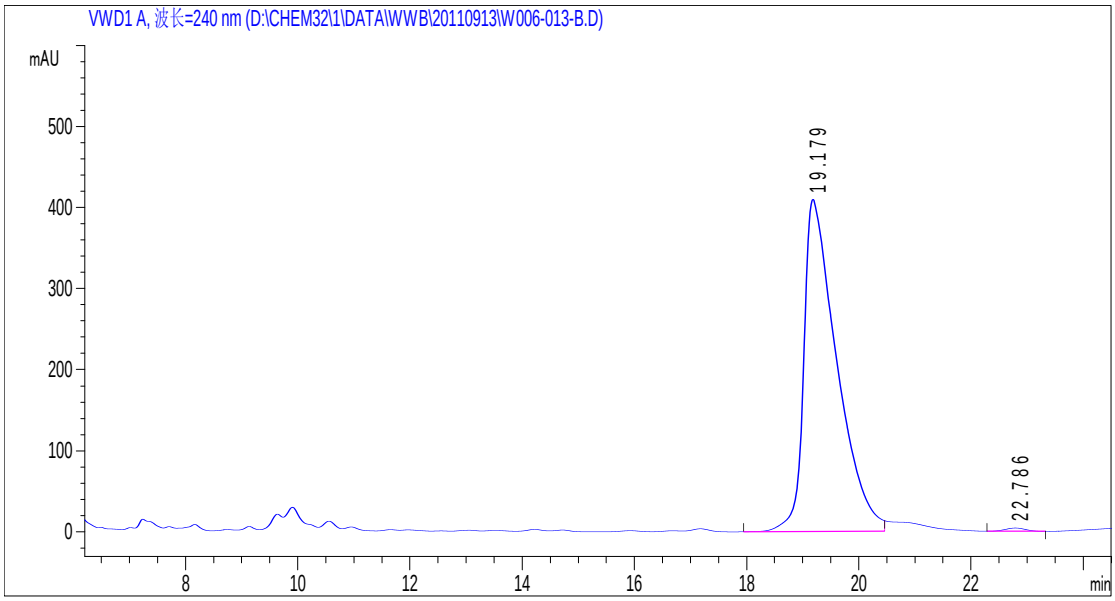
The product was obtained in 86% yield, yellow solid. Mp 162-163°C; $[\alpha]^{20}_{D}$ -15.5 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): (ppm)δ1.20 (d, J = 7.2 Hz, 3H), 1.38 (t, J = 7.2 Hz, 3H), 2.11-2.15 (m, 1H), 2.88-3.00 (m, 2H), 3.28-3.30 (m, 1H), 3.99-4.02 (m, 2H), 4.26-4.36 (m, 2H), 7.26-7.32 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$)δ14.3, 16.1, 33.3, 35.4, 40.9, 52.5, 62.5, 67.9, 69.8, 128.2, 128.5, 129.7, 137.5, 175.2, 176.7, 198.4; HRMS (ESI): Exact mass calcd for $(C_{18}H_{21}NO_4S_2)^+$: 379.0912, Found: 379.0910;

E: HPLC Charts of Products

7a: (5S,6S,10S)-ethyl 4,8-dioxo-3,10-diphenyl-2-thioxo-1-thia-3-azaspiro[4.5]decane-6-carboxylate

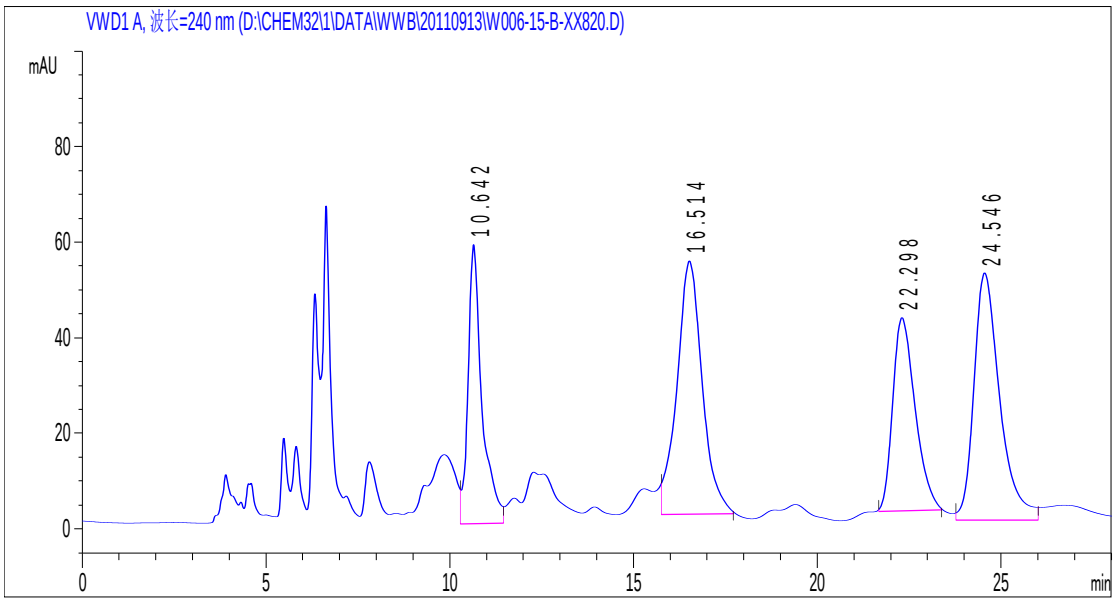


#	Time	Area	Height	Width	Symmetry	Area %
1	8.576	1826.7	138.6	0.196	0.872	16.054
2	10.021	1689.3	116.4	0.2202	1.005	14.847
3	20.036	4089.3	110.1	0.5438	0.575	35.939
4	23.66	3773.2	46.5	1.2097	0.566	33.161

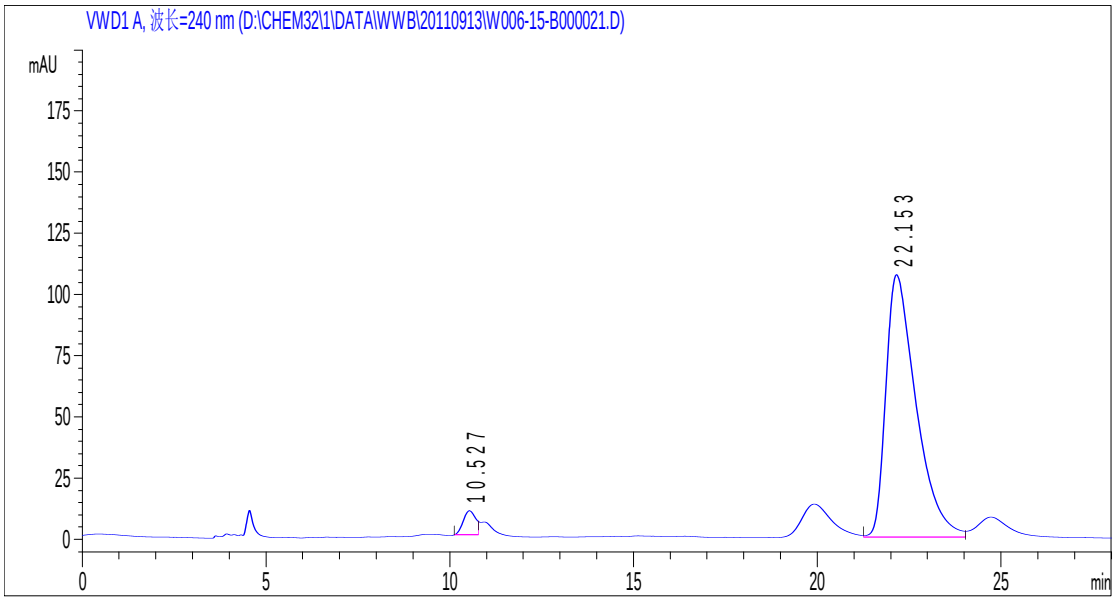


#	Time	Area	Height	Width	Symmetry	Area %
1	19.179	16772.2	409.9	0.6819	0.391	99.246
2	22.786	127.4	4.5	0.432	1.041	0.754

7b: (5S,6S,10S)-ethyl 10-(2-fluorophenyl)-4,8-dioxo-3-phenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-6-carboxylate

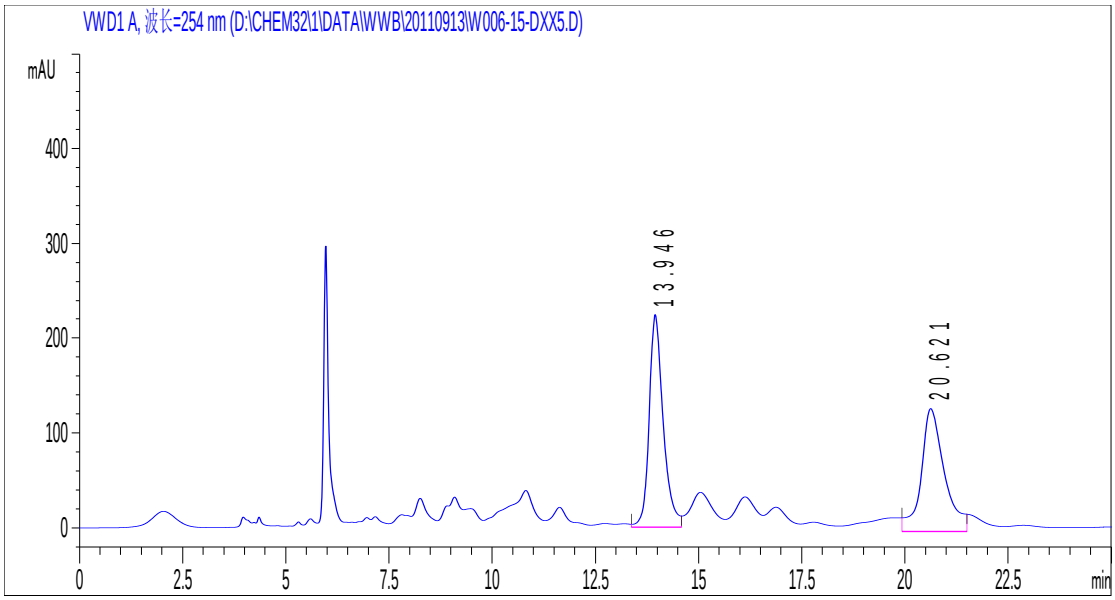


#	Time	Area	Height	Width	Symmetry	Area %
1	10.642	1541.4	58.5	0.4391	0.626	18.455
2	16.514	2542.3	53.2	0.7971	0.933	30.439
3	22.298	1721.8	40.5	0.7078	0.683	20.614
4	24.546	2546.8	51.9	0.8184	0.672	30.492

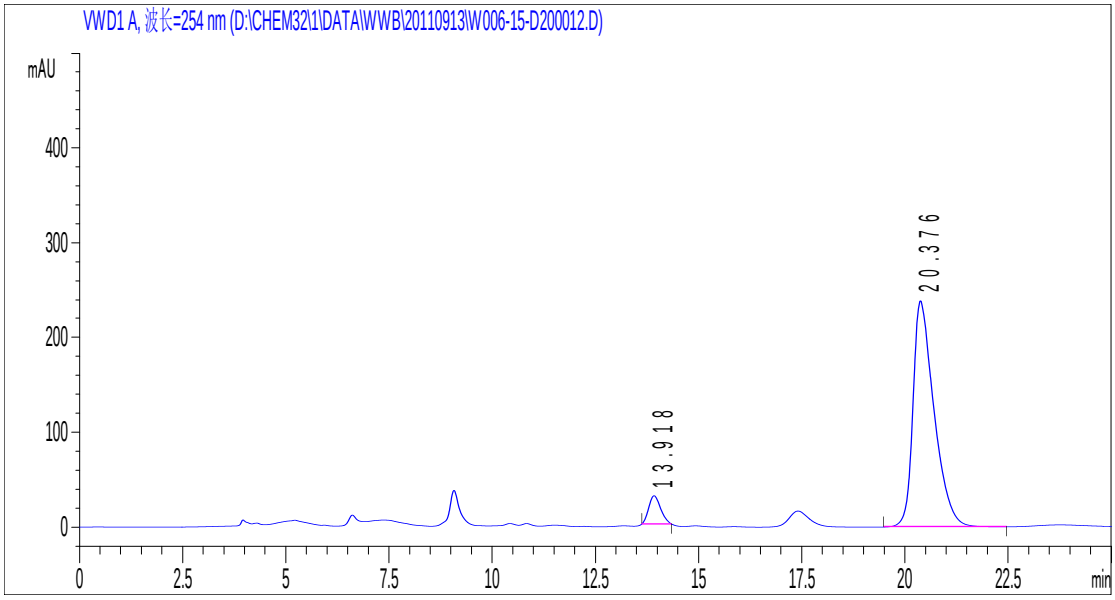


#	Time	Area	Height	Width	Symmetry	Area %
1	10.527	242.8	10.1	0.402	0.955	3.813
2	22.153	6124.7	107.3	0.858	0.515	96.187

7c: (5S,6S,10S)-ethyl 10-(4-bromophenyl)-4,8-dioxo-3-phenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-6-carboxylate

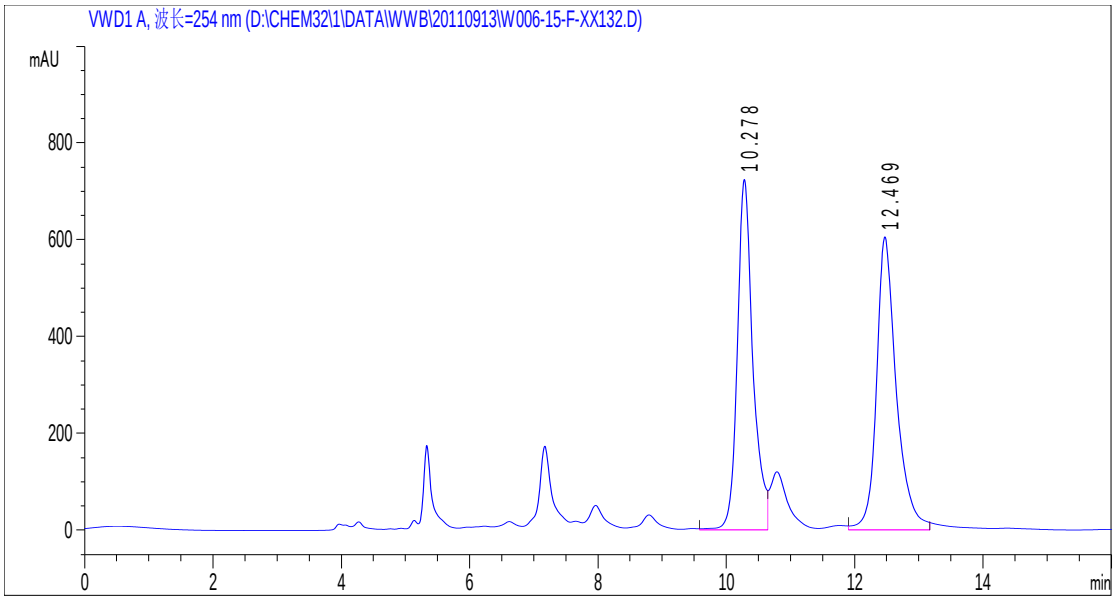


#	Time	Area	Height	Width	Symmetry	Area %
1	13.946	5380.3	224.9	0.3548	0.72	51.371
2	20.621	5093.1	130	0.6527	0.665	48.629

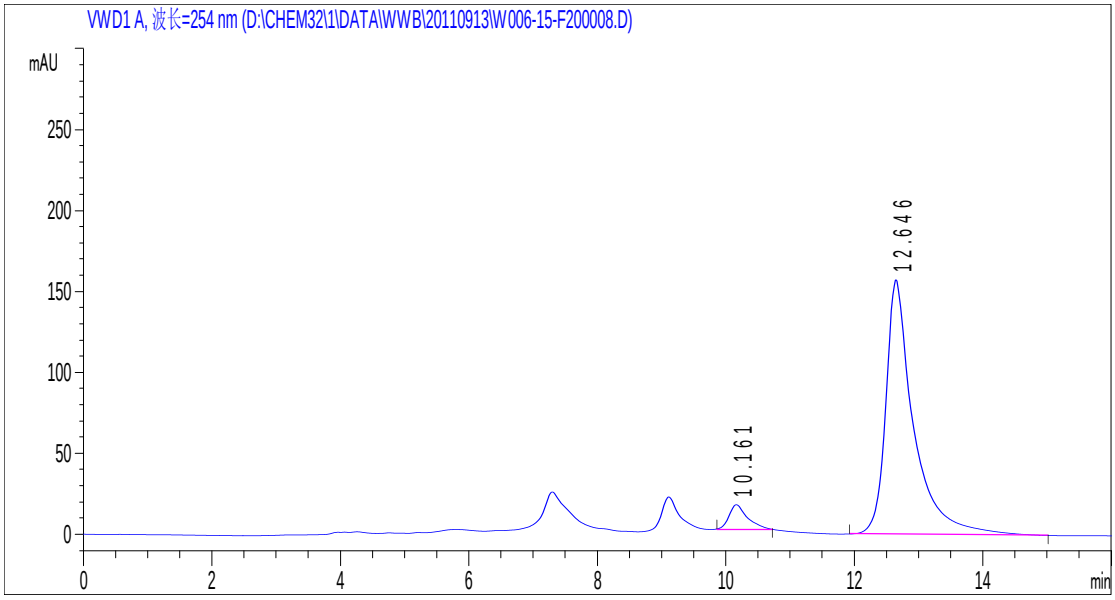


#	Time	Area	Height	Width	Symmetry	Area %
1	13.918	624.3	30.5	0.3415	0.796	6.823
2	20.376	8525.6	239	0.5269	0.535	93.177

7d: 6S,10S)-ethyl 10-(2-methoxyphenyl)-4,8-dioxo-3-phenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-6-carboxylate

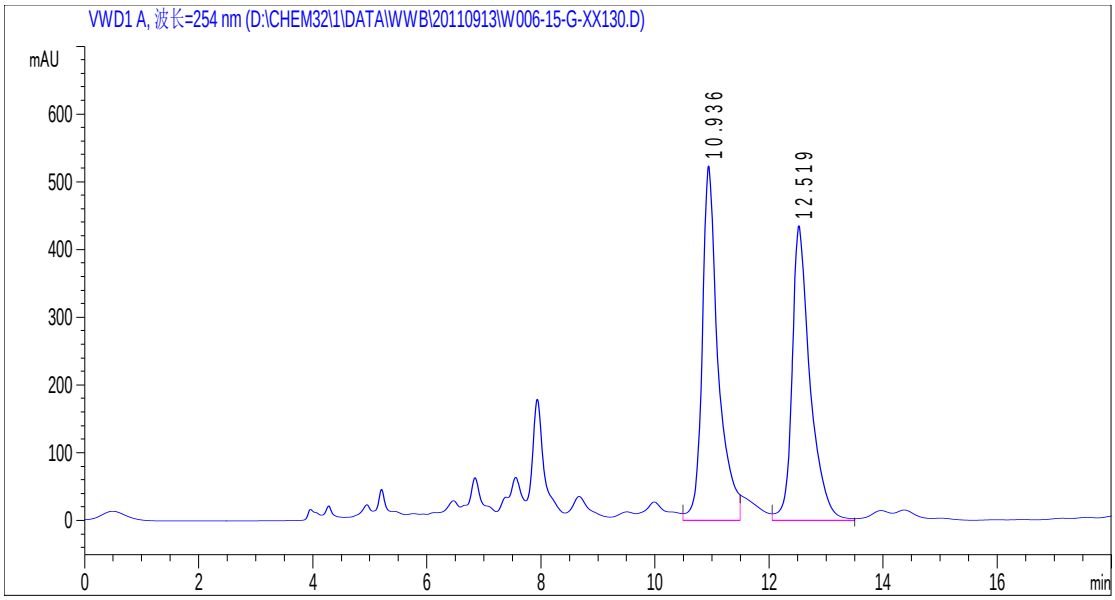


#	Time	Area	Height	Width	Symmetry	Area %
1	10.278	12324.4	725.3	0.2521	0.775	48.506
2	12.469	13083.6	607	0.3592	0.709	51.494

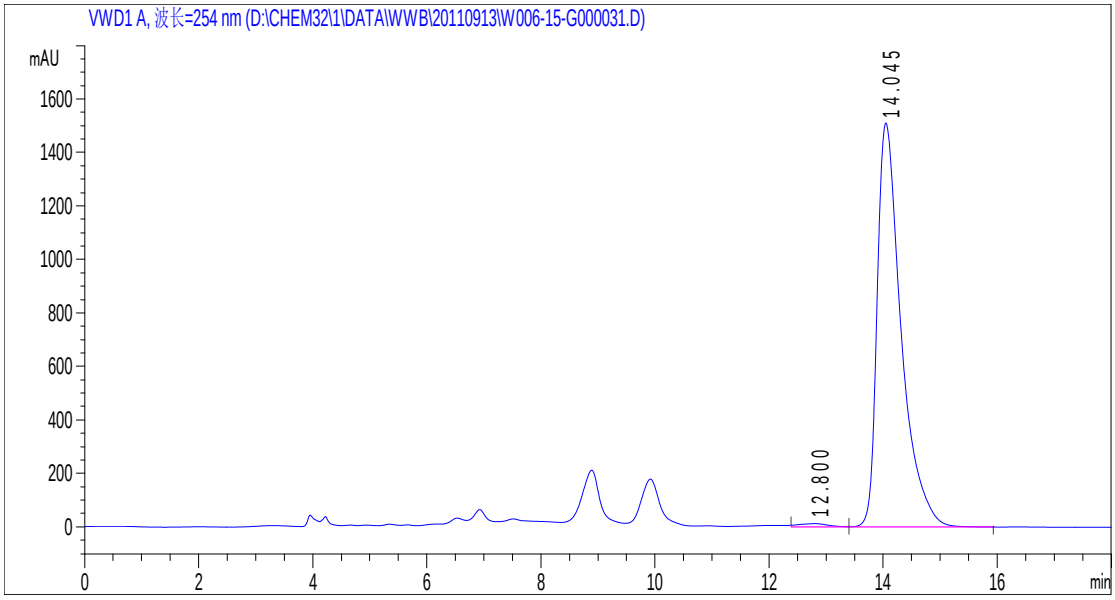


#	Time	Area	Height	Width	Symmetry	Area %
1	10.161	315.5	15.5	0.3398	0.635	6.229
2	12.646	4749.8	157.4	0.4264	0.527	93.771

7e: (5S,6S,10S)-ethyl 4,8-dioxo-3-phenyl-2-thioxo-10-m-tolyl-1-thia-3-azaspiro[4.5] decane-6-carboxylate

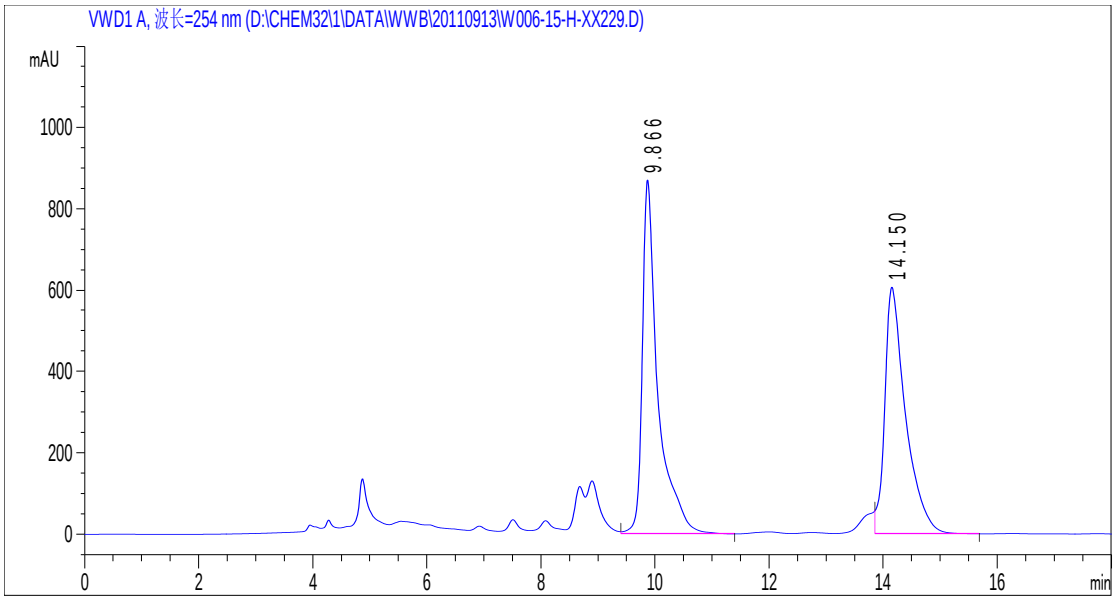


#	Time	Area	Height	Width	Symmetry	Area %
1	10.936	10204	523.7	0.3247	0.649	51.635
2	12.519	9557.7	435.2	0.3174	0.578	48.365

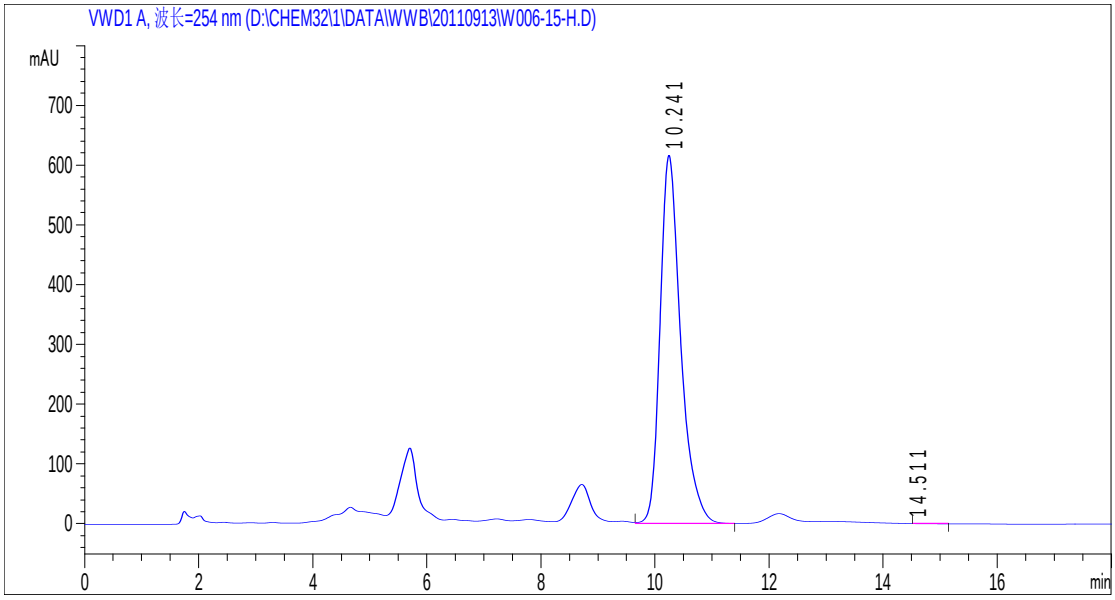


#	Time	Area	Height	Width	Symmetry	Area %
1	12.8	472	12.8	0.6142	1.158	1.058
2	14.045	44124.5	1510.4	0.4384	0.528	98.942

7f: (5S,6S,10S)-ethyl 4,8-dioxo-3-phenyl-2-thioxo-10-p-tolyl-1-thia-3-azaspiro[4.5] decane-6-carboxylate

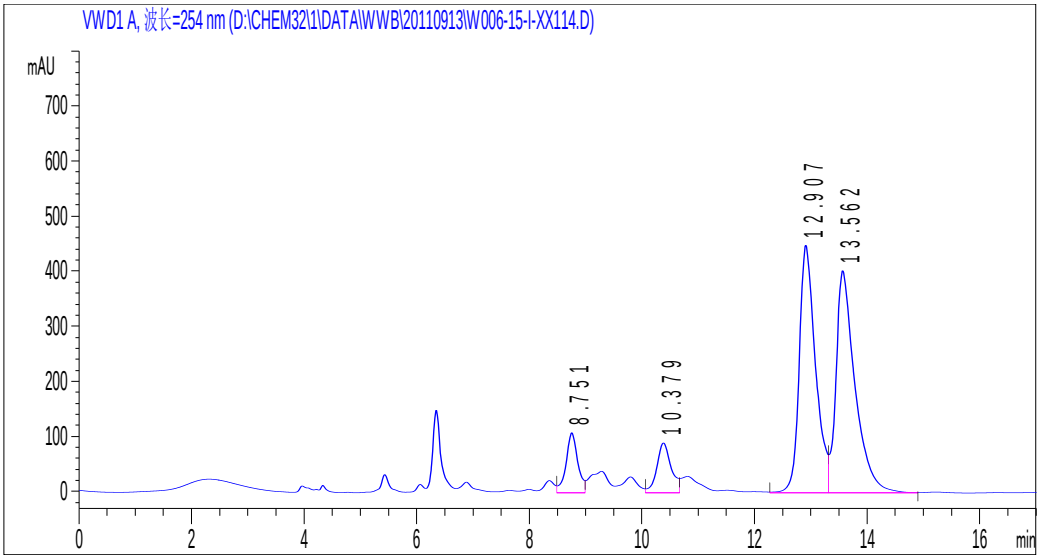


#	Time	Area	Height	Width	Symmetry	Area %
1	9.866	16534.8	870.7	0.2711	0.465	51.812
2	14.15	15378.1	606.7	0.4225	0.501	48.188

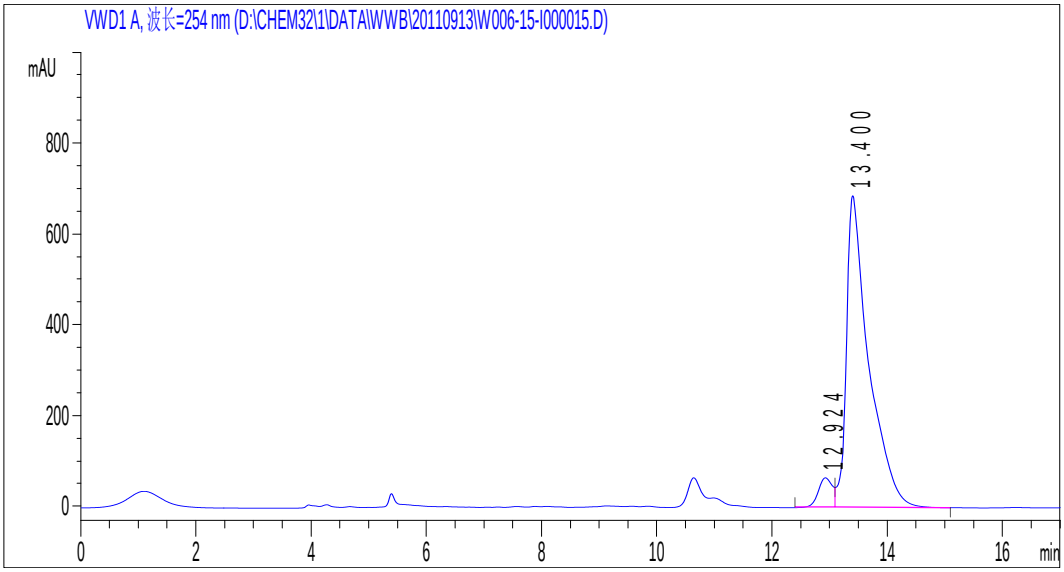


#	Time	Area	Height	Width	Symmetry	Area %
1	10.241	15471.4	616	0.3804	0.706	99.882
2	14.511	18.2	7.8E-1	0.278	0	0.118

7g: (5R,6S,10S)-ethyl 4,8-dioxo-3-phenyl-10-(thiophen-2-yl)-2-thioxo-1-thia-3-azaspiro[4.5] decane-6-carboxylate

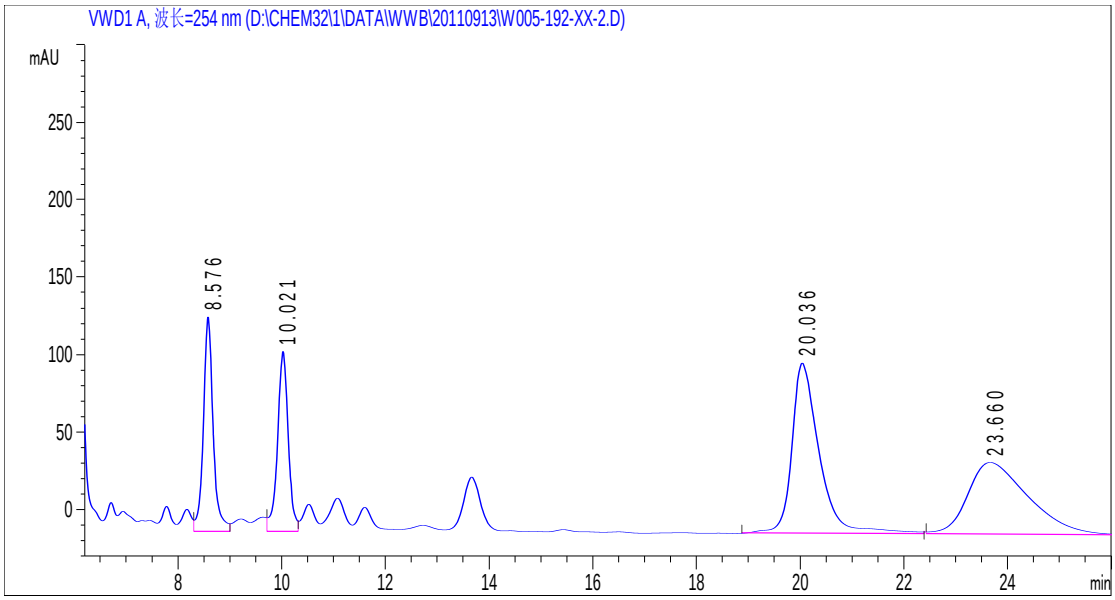


#	Time	Area	Height	Width	Symmetry	Area %
1	8.751	1592.1	109.1	0.2153	0.923	7.302
2	10.379	1622	90.8	0.2637	0.818	7.439
3	12.907	9093.4	449.8	0.2999	0.648	41.704
4	13.562	9497	403.8	0.3414	0.495	43.555

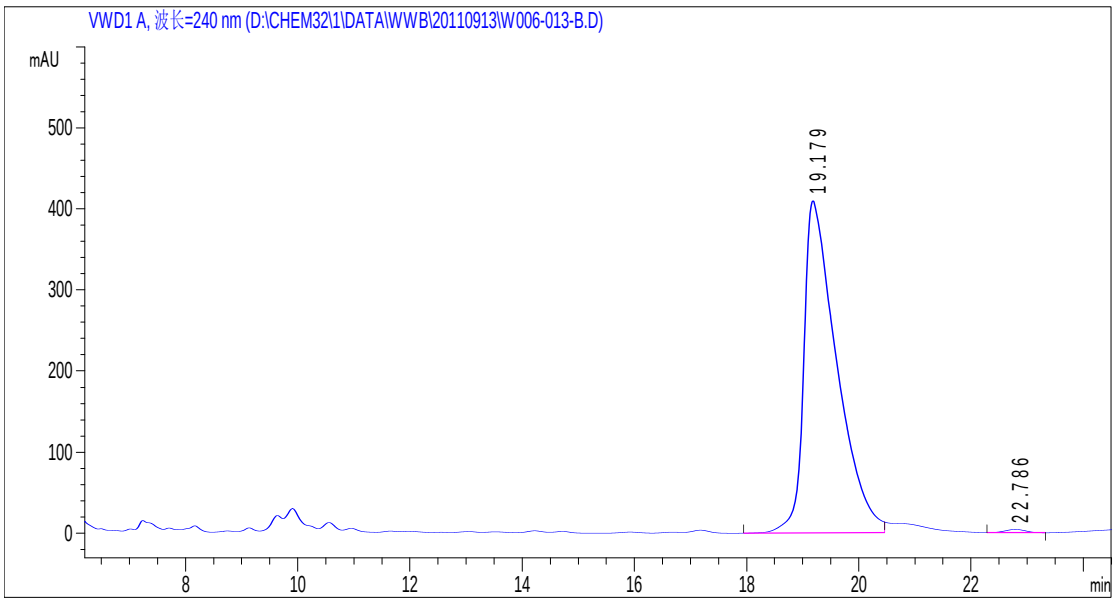


#	Time	Area	Height	Width	Symmetry	Area %
1	12.924	1001.7	62.4	0.2676	0.968	5.221
2	13.399	18185	683.5	0.4434	0.39	94.779

7h: (6S,10S)-diethyl 4,8-dioxo-3-phenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-6,10-dicarboxylate

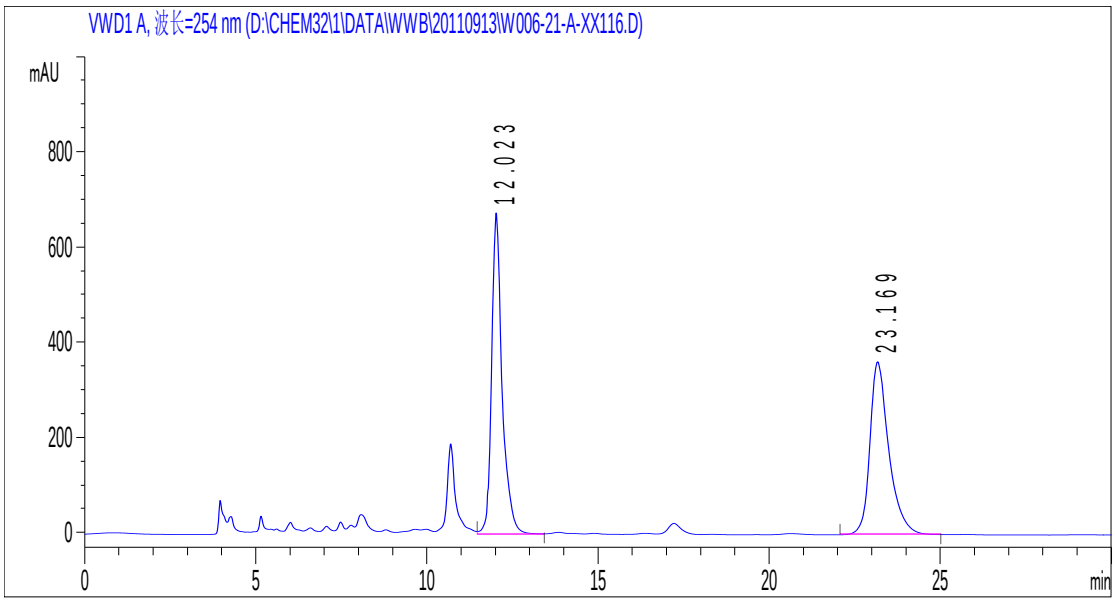


#	Time	Area	Height	Width	Symmetry	Area %
1	8.576	1826.7	138.6	0.196	0.872	16.054
2	10.021	1689.3	116.4	0.2202	1.005	14.847
3	20.036	4089.3	110.1	0.5438	0.575	35.939
4	23.66	3773.2	46.5	1.2097	0.566	33.161

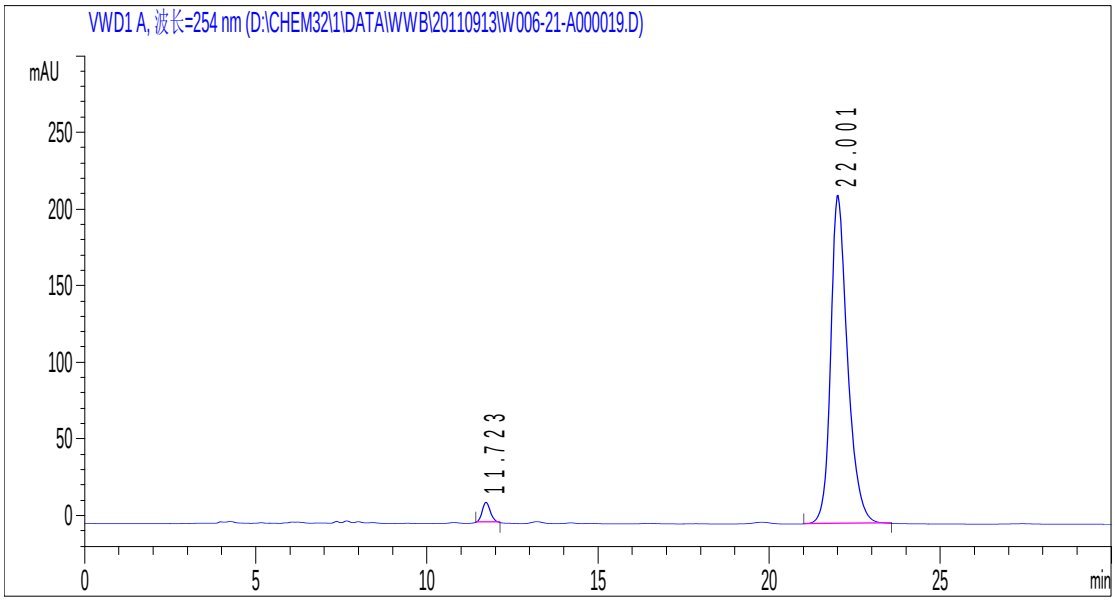


#	Time	Area	Height	Width	Symmetry	Area %
1	19.179	16772.2	409.9	0.6819	0.391	99.246
2	22.786	127.4	4.5	0.432	1.041	0.754

7j: (6S,10S)-3,6,10-triphenyl-2-thioxo-1-thia-3-azaspiro[4.5]decane-4,8-dione

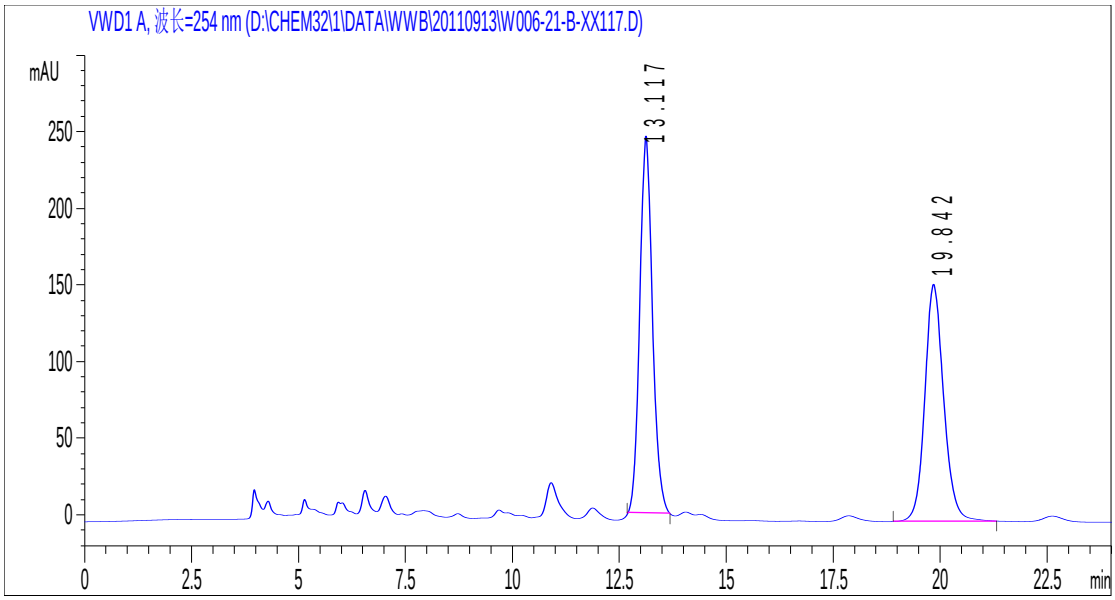


#	Time	Area	Height	Width	Symmetry	Area %
1	12.023	14490.4	675.3	0.3188	0.722	50.880
2	23.169	13989	363.2	0.5761	0.659	49.120

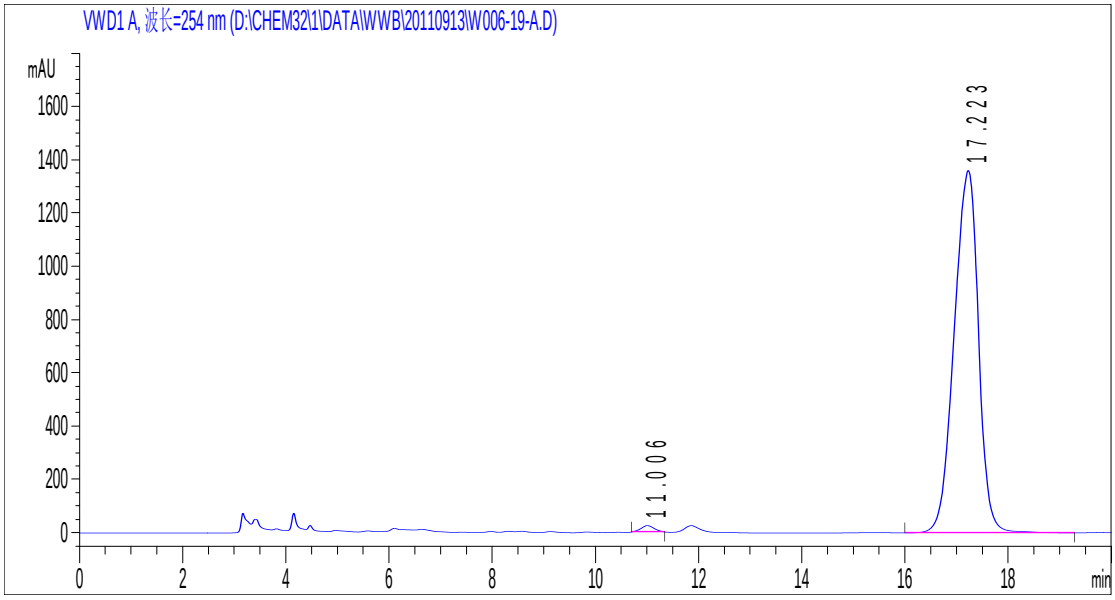


#	Time	Area	Height	Width	Symmetry	Area %
1	11.723	215.9	13.1	0.2748	0.843	2.850
2	22.001	7359.5	214.4	0.5139	0.683	97.150

7k: (5S,6S,10S)-6-(4-bromophenyl)-3,10-diphenyl-2-thioxo-1-thia-3-azaspiro[4.5]decane-4,8-dione

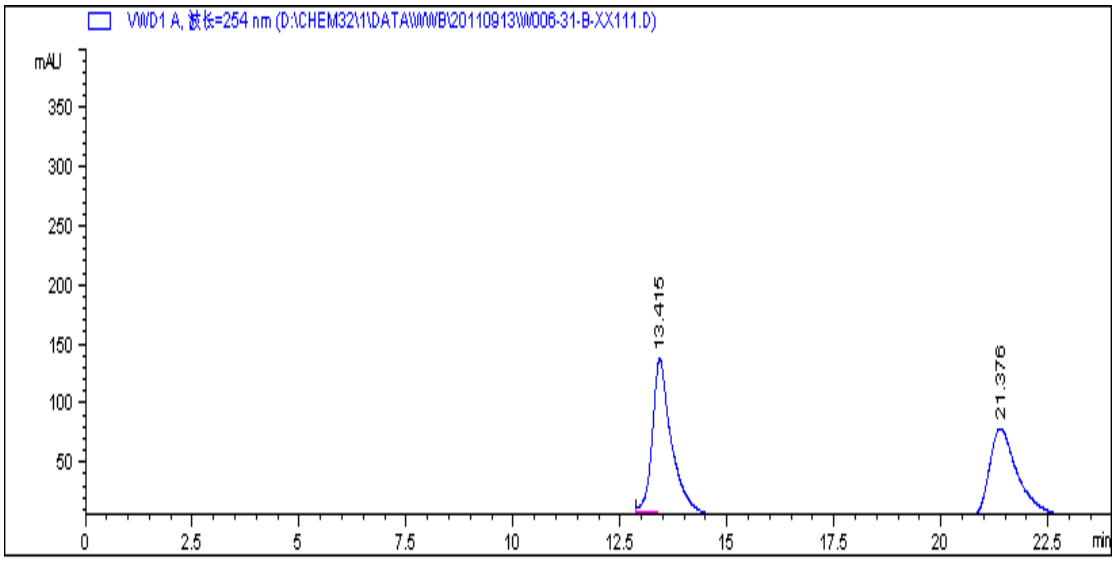


#	Time	Area	Height	Width	Symmetry	Area %
1	13.117	5089.8	246.1	0.3447	0.91	51.687
2	19.842	4757.6	154.8	0.4677	0.826	48.313

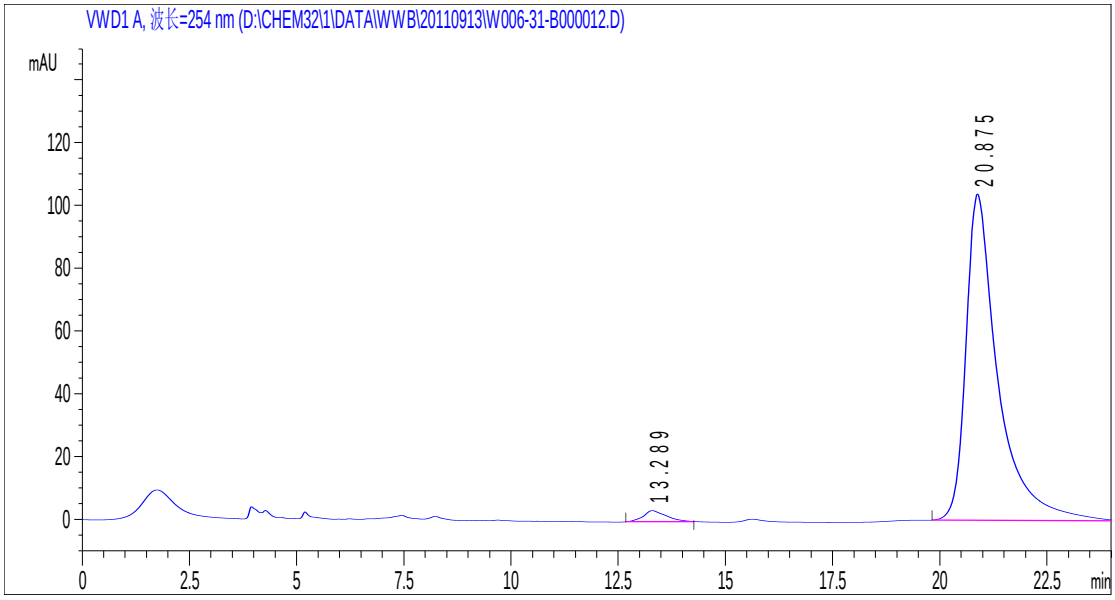


#	Time	Area	Height	Width	Symmetry	Area %
1	11.006	430.7	24	0.2988	0.954	0.956
2	17.223	44609.9	1360.6	0.5223	1.282	99.044

7l: (5S,6S,10S)-6-(4-fluorophenyl)-3,10-diphenyl-2-thioxo-1-thia-3-azaspiro[4.5]decane-4,8-dione

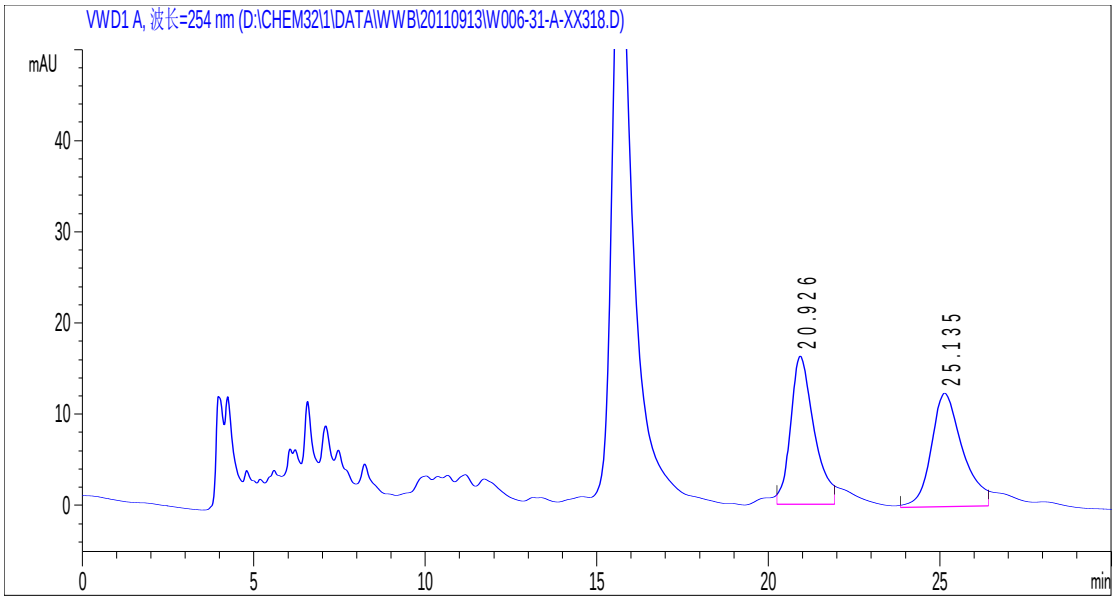


#	Time	Area	Height	Width	Symmetry	Area %
1	13.414	4277.8	133.1	0.5358	0.599	50.568
2	21.376	4181.7	79.1	0.7624	0.522	49.432

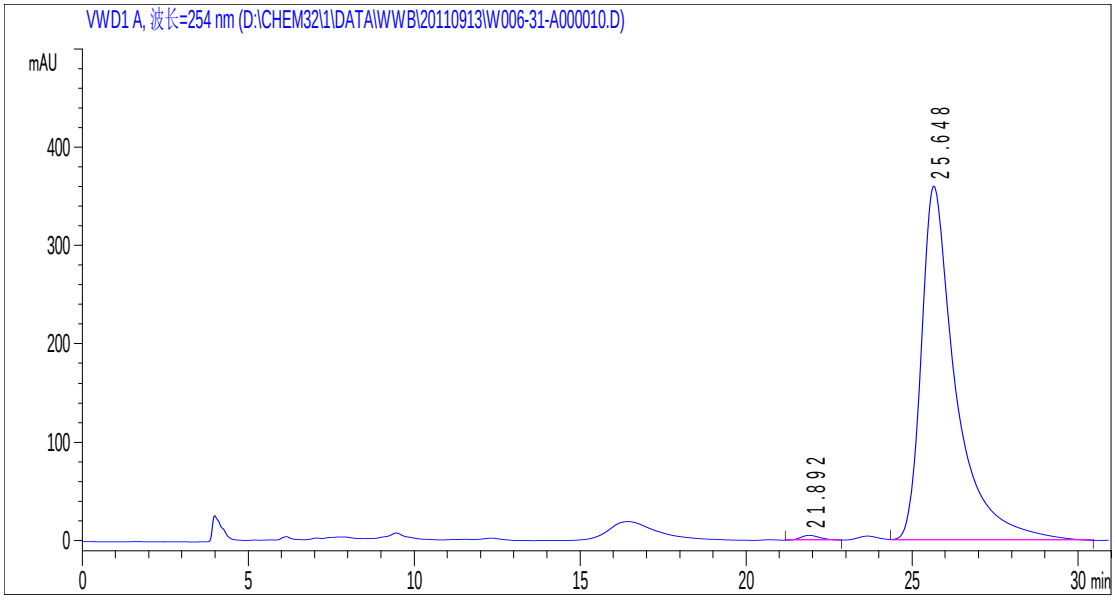


#	Time	Area	Height	Width	Symmetry	Area %
1	13.289	137.2	3.6	0.5158	0.638	2.469
2	20.875	5420.2	104.1	0.7558	0.516	97.531

7m: (5S,6S,10S)-6-(4-nitrophenyl)-3,10-diphenyl-2-thioxo-1-thia-3-azaspiro[4.5]decane-4,8-dione

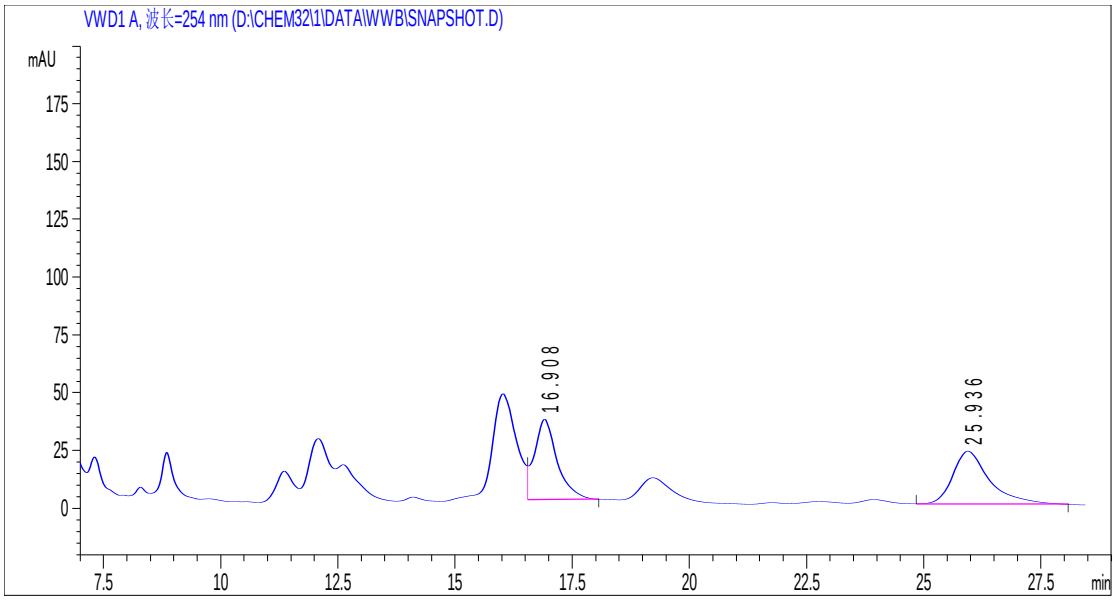


#	Time	Area	Height	Width	Symmetry	Area %
1	20.926	775.9	16.3	0.7939	0.675	49.230
2	25.135	800.2	12.5	1.0666	0.725	50.770

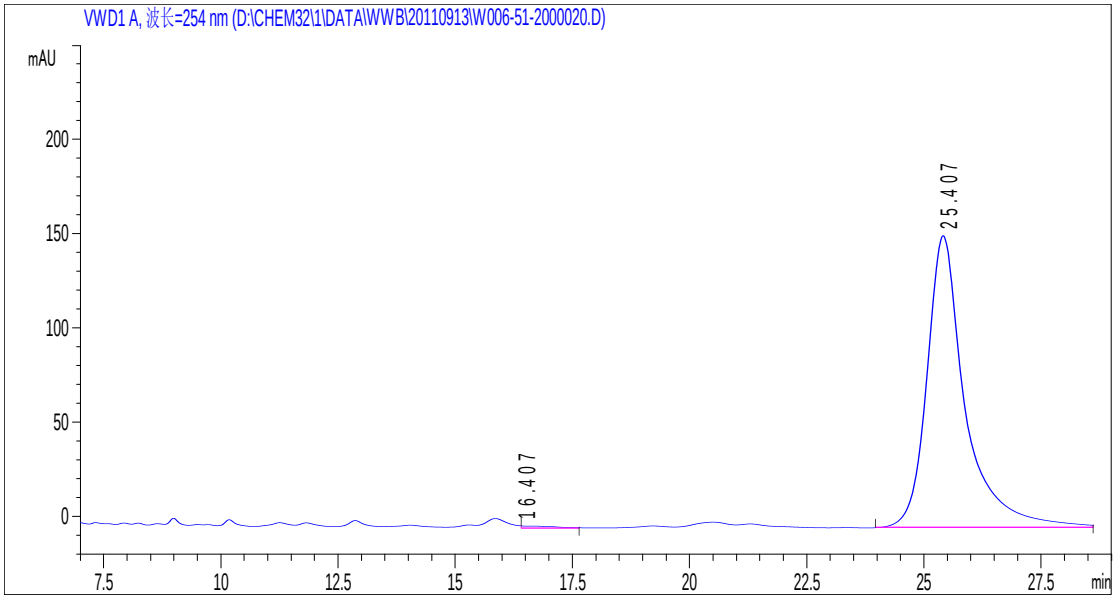


#	Time	Area	Height	Width	Symmetry	Area %
1	21.892	216.6	5	0.6344	0.732	0.826
2	25.648	25998	360.1	1.0431	0.525	99.174

7n: (5S,6S,10S)-6-(4-methoxyphenyl)-3,10-diphenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-4,8-dione

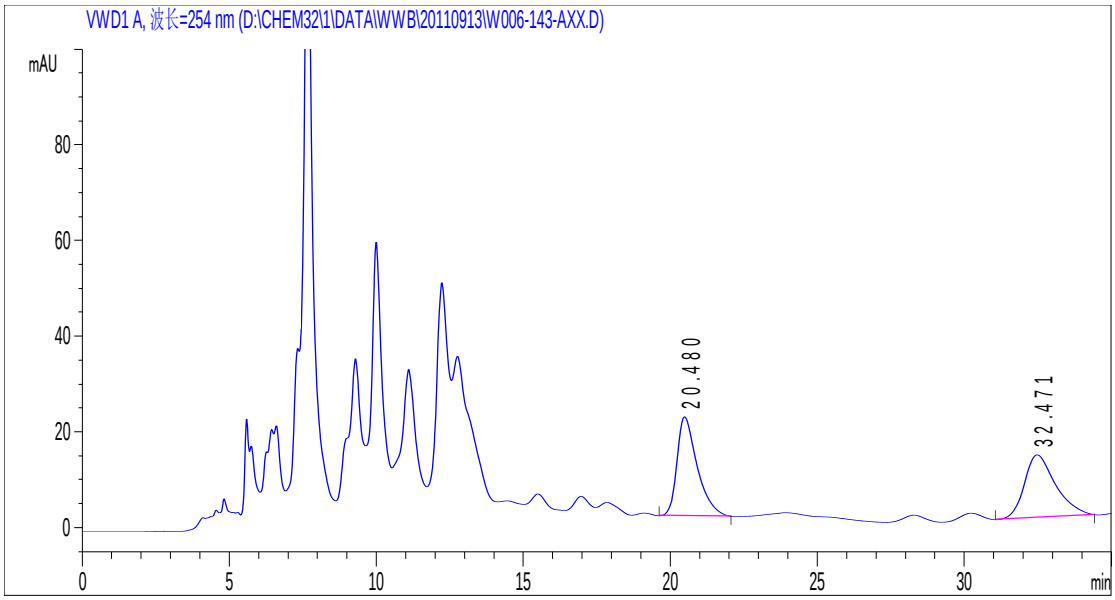


#	Time	Area	Height	Width	Symmetry	Area %
1	16.908	1184.1	35	0.4906	0.742	47.918
2	25.936	1287	23.1	0.8178	0.641	52.082

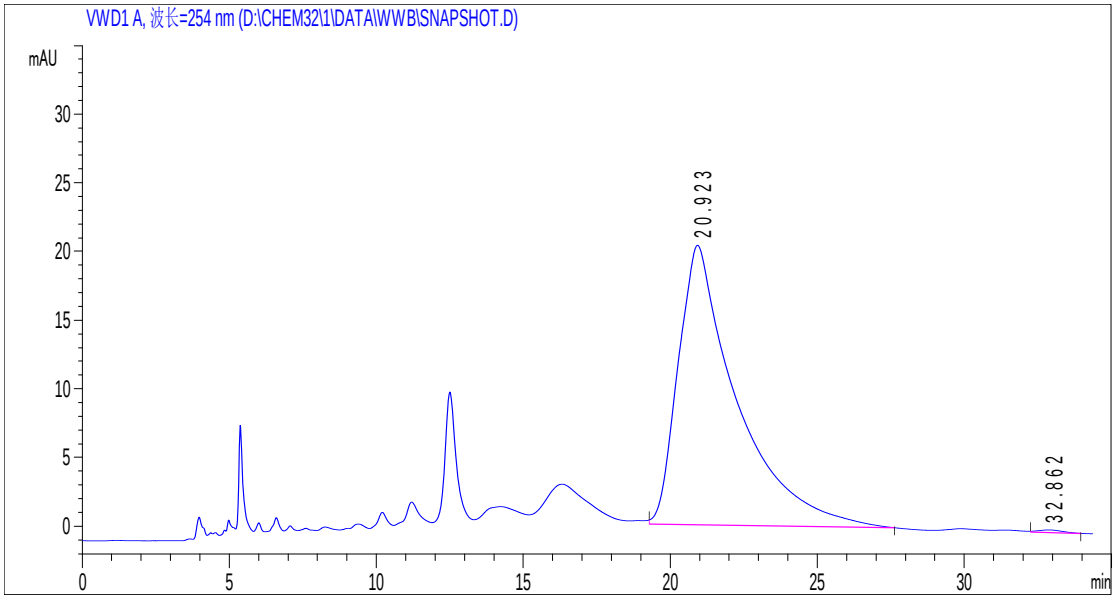


#	Time	Area	Height	Width	Symmetry	Area %
1	16.407	51.3	1.1	0.5363	8.14E-3	0.578
2	25.407	8827.5	155.1	0.8271	0.675	99.422

7o: (5S,6S,10S)-ethyl 4,8-dioxo-10-phenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-6-carboxylate

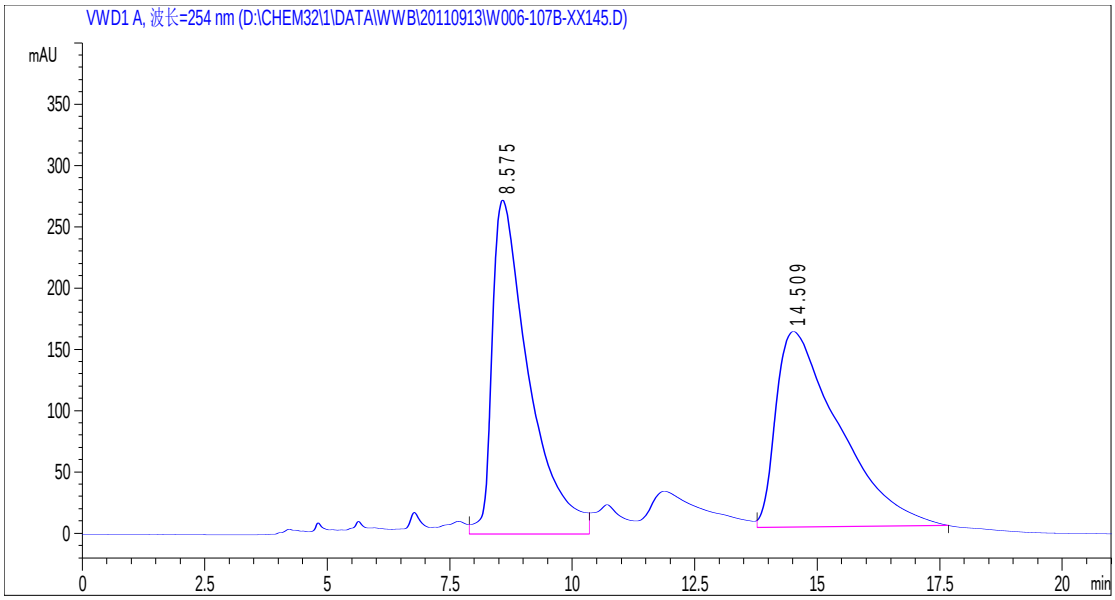


#	Time	Area	Height	Width	Symmetry	Area %
1	20.48	995	20.8	0.7077	0.566	50.538
2	32.471	973.8	13.2	1.0586	0.655	49.462

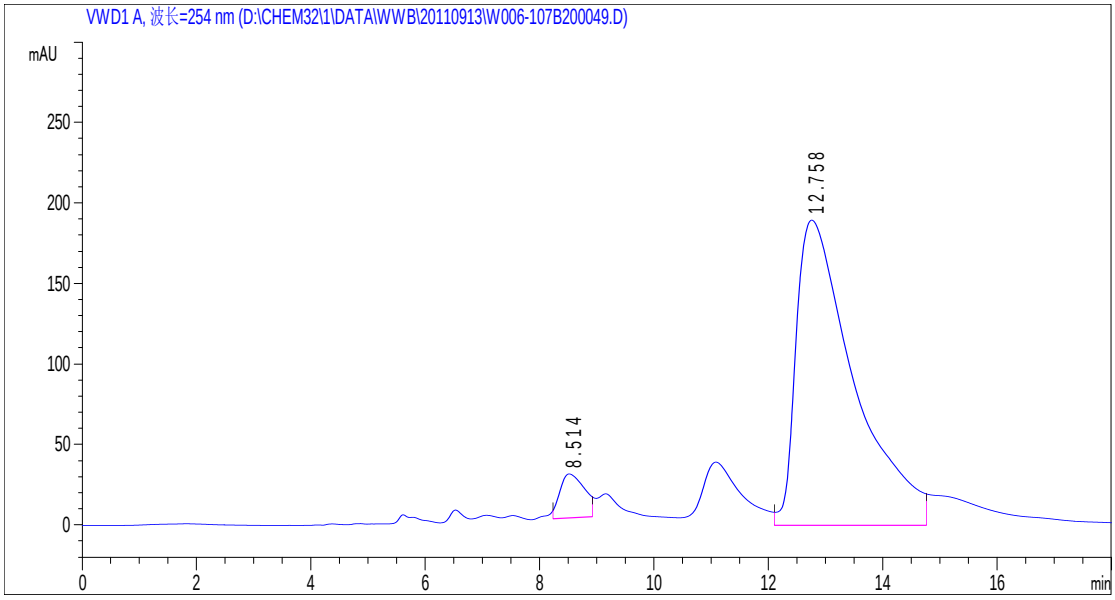


#	Time	Area	Height	Width	Symmetry	Area %
1	20.923	2815	20.4	2.3047	0.48	99.505
2	32.862	14	2.2E-1	1.0388	0.728	0.495

7p:(5S,6S,10S)-ethyl 4,8-dioxo-2-thioxo-10-m-tolyl-1-thia-3-azaspiro[4.5] decane-6-carboxylate

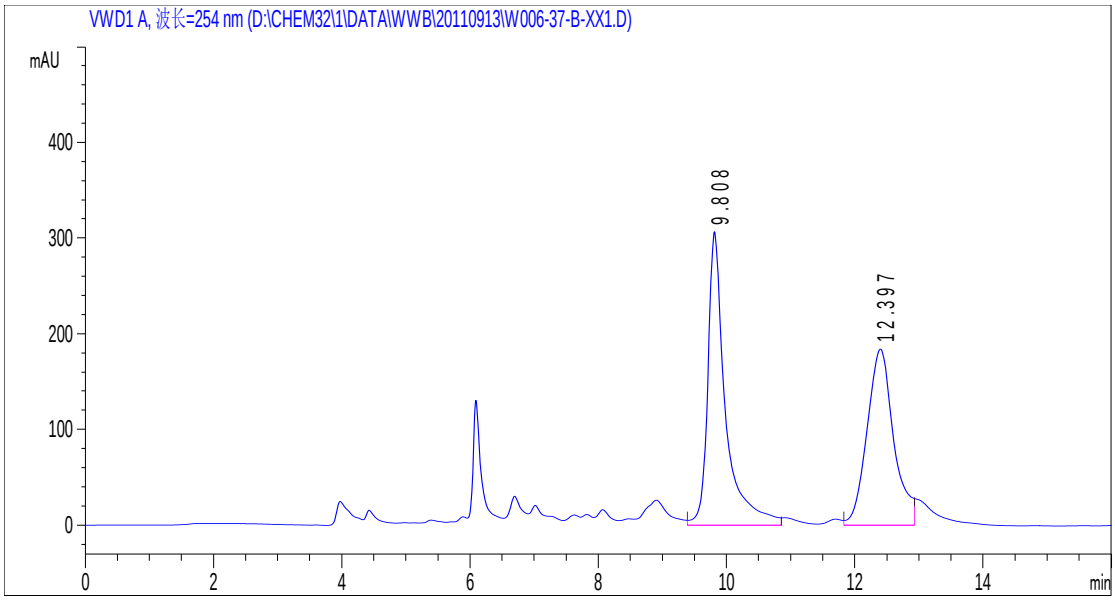


#	Time	Area	Height	Width	Symmetry	Area %
1	8.575	14198	272.5	0.7534	0.376	49.764
2	14.509	14332.7	159.6	1.4971	0.372	50.236

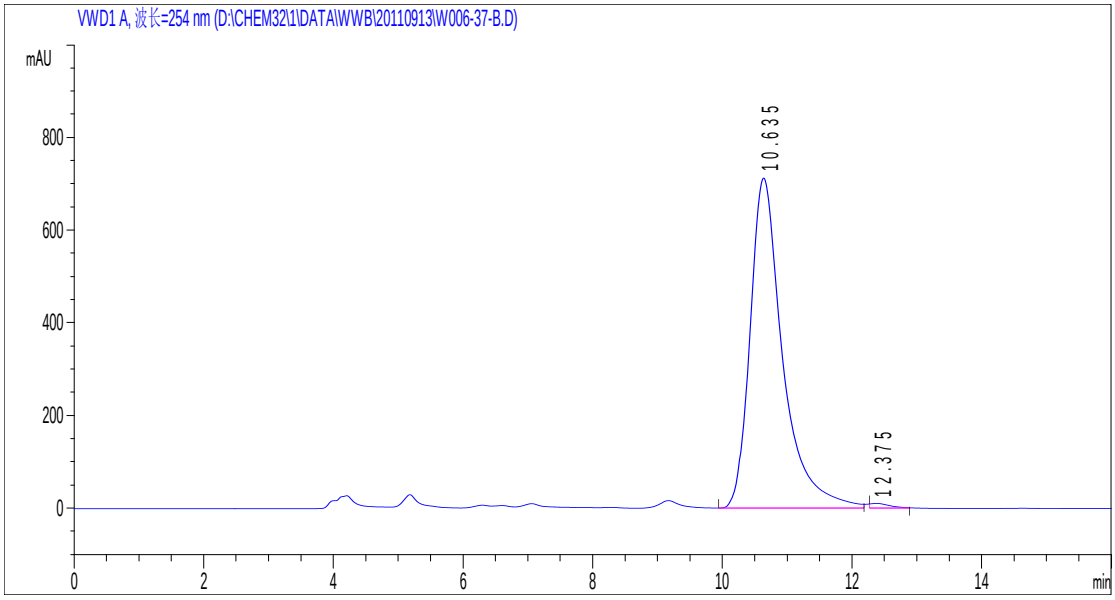


#	Time	Area	Height	Width	Symmetry	Area %
1	8.514	818.7	27.5	0.4953	0.581	5.788
2	12.758	13326.4	189.7	1.1706	0.355	94.212

7q: (5S,6S,10S)-6-(4-bromophenyl)-3-isopropyl-10-phenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-4,8-dione

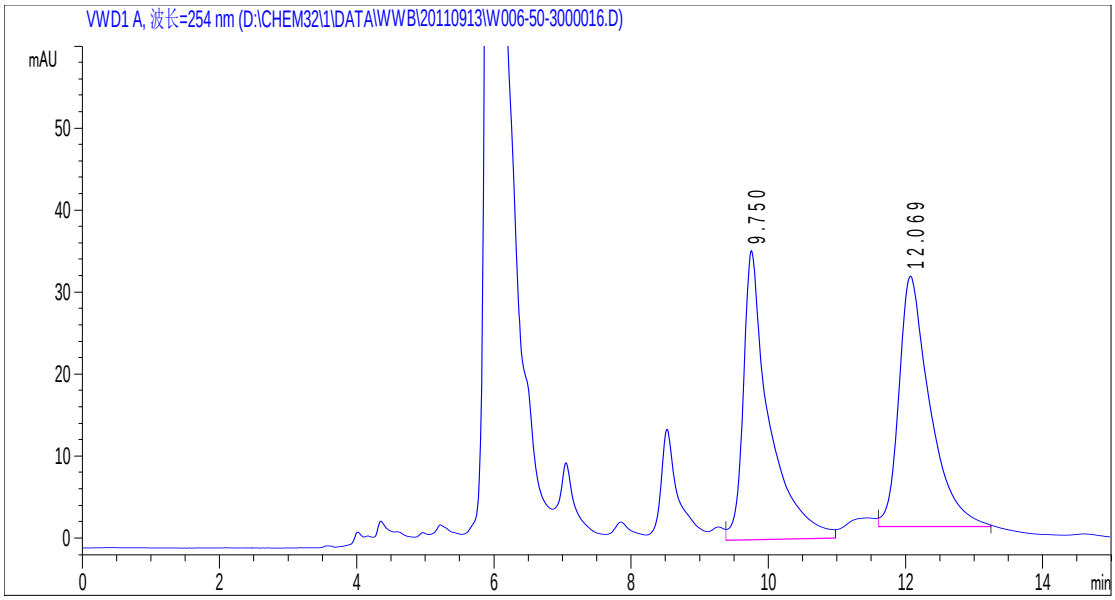


#	Time	Area	Height	Width	Symmetry	Area %
1	9.808	5909.6	307.3	0.2739	0.547	52.477
2	12.397	5351.6	184.7	0.483	0.969	47.523

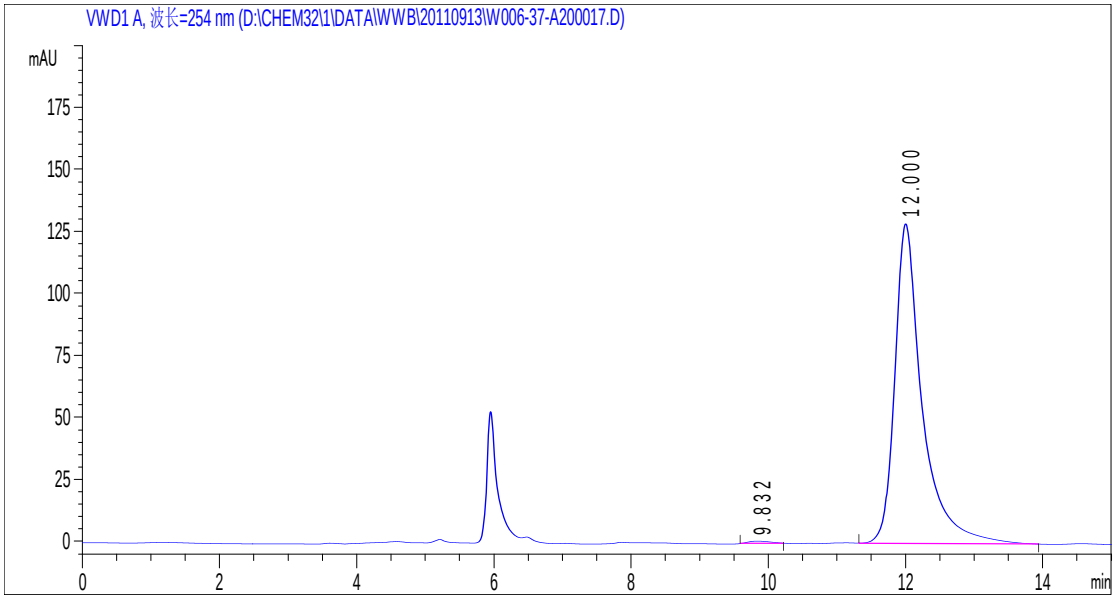


#	Time	Area	Height	Width	Symmetry	Area %
1	10.635	24883.2	713.3	0.5147	0.652	99.074
2	12.375	232.7	10.8	0.3578	0.374	0.926

7r: (5S,6S,10S)-6-(4-bromophenyl)-3-cyclohexyl-10-phenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-4,8-dione

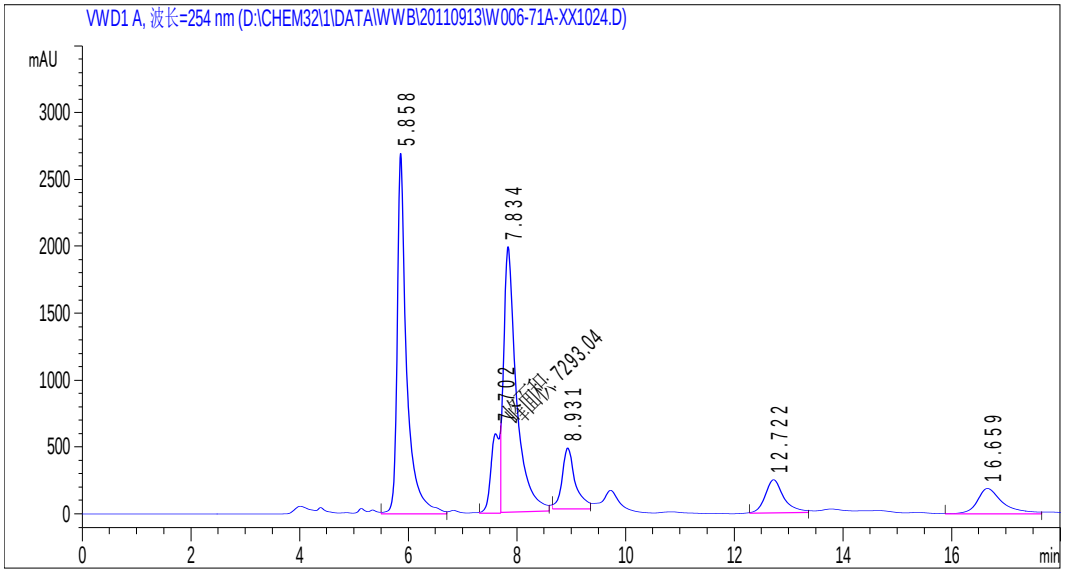


#	Time	Area	Height	Width	Symmetry	Area %
1	9.75	923.1	35.3	0.3606	0.421	48.931
2	12.069	963.4	30.6	0.5247	0.572	51.069

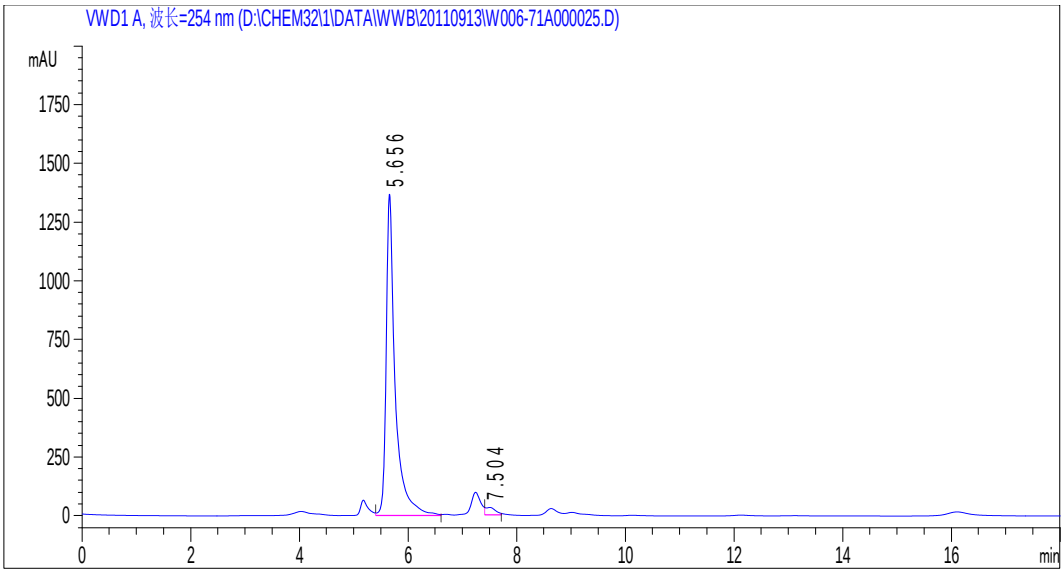


#	Time	Area	Height	Width	Symmetry	Area %
1	9.832	20.2	9.3E-1	0.3624	0.659	0.558
2	12	3593.8	129	0.4035	0.602	99.442

7s: (5S,6S,7R,10S)-ethyl 7-ethyl-4,8-dioxo-3,10-diphenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-6-carboxylate

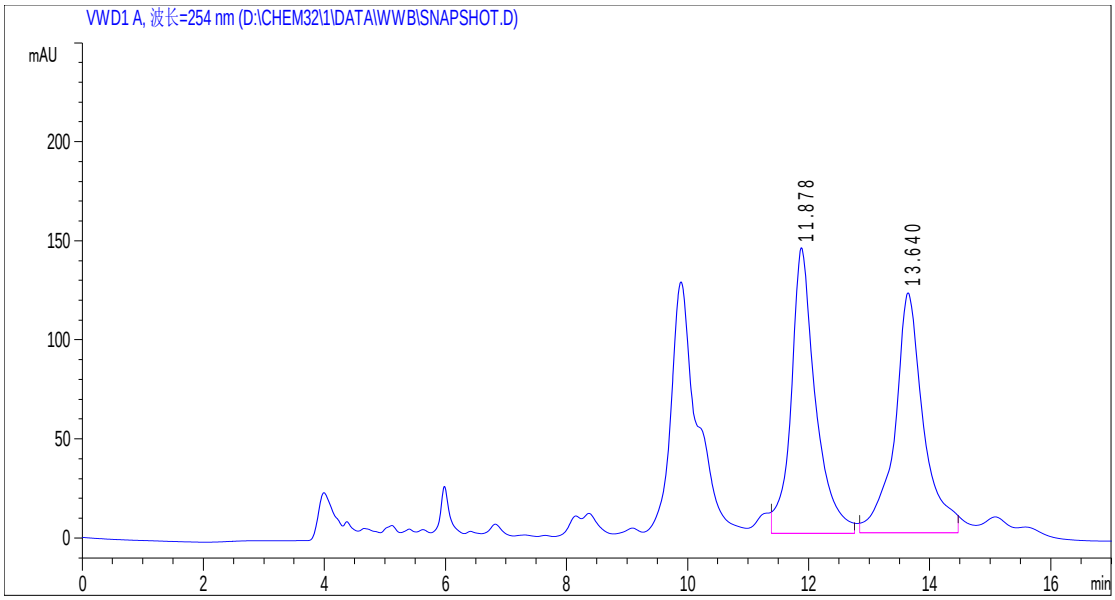


#	Time	Area	Height	Width	Symmetry	Area %
1	5.858	32644.3	2694.9	0.1719	0.516	35.212
2	7.702	7293	641.9	0.1894	8084.96	7.867
3	7.834	32479.4	1987.2	0.2724	0.481	35.034
4	8.931	7837.8	460.1	0.2839	0.698	8.454
5	12.722	6104.5	250.9	0.4056	0.778	6.585
6	16.659	6348.8	190.8	0.4828	0.627	6.848

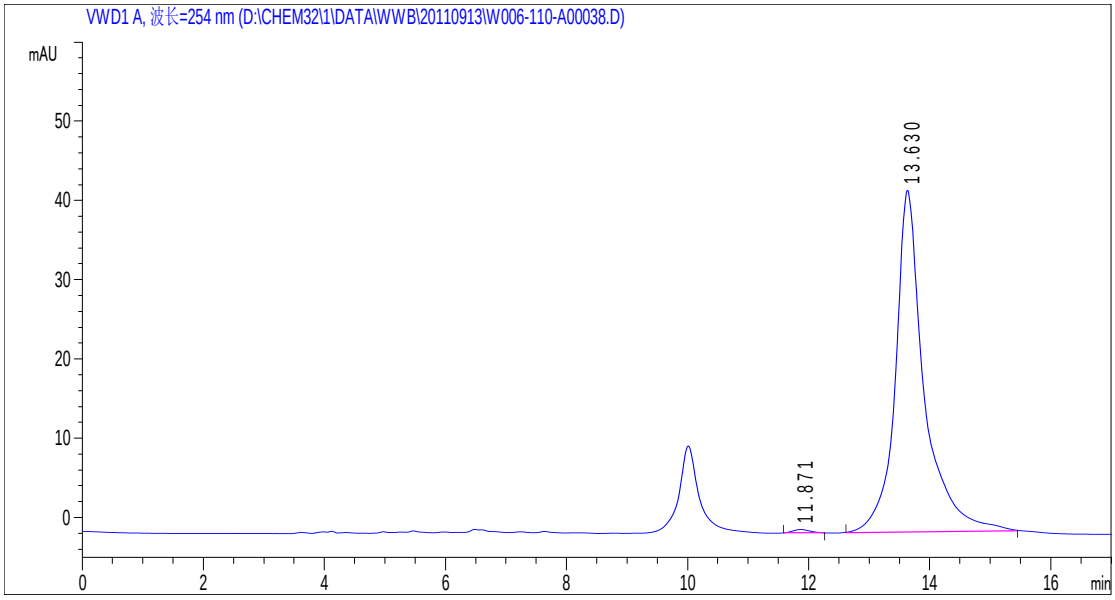


#	Time	Area	Height	Width	Symmetry	Area %
1	5.656	15882.9	1370.1	0.1644	0.518	97.499
2	7.504	407.3	32.4	0.2095	0.629	2.501

7t:(5S,6S,7R,10S)-10-(4-bromophenyl)-7-ethyl-3,6-diphenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-4,8-dione

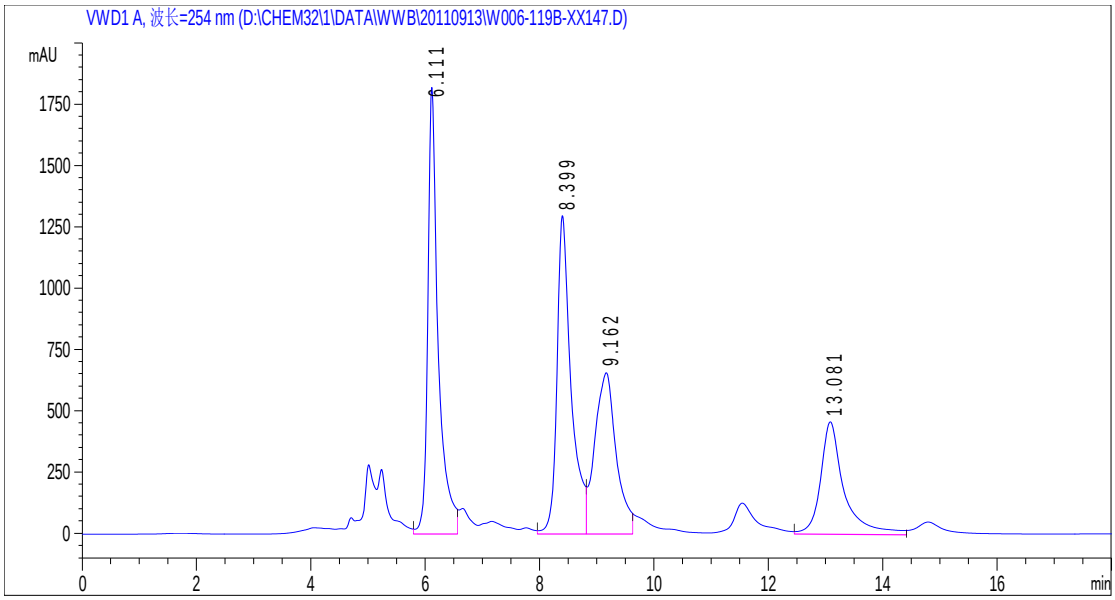


#	Time	Area	Height	Width	Symmetry	Area %
1	11.878	4057.4	144.5	0.4679	0.709	50.236
2	13.64	4019.2	121.4	0.5517	0.854	49.764

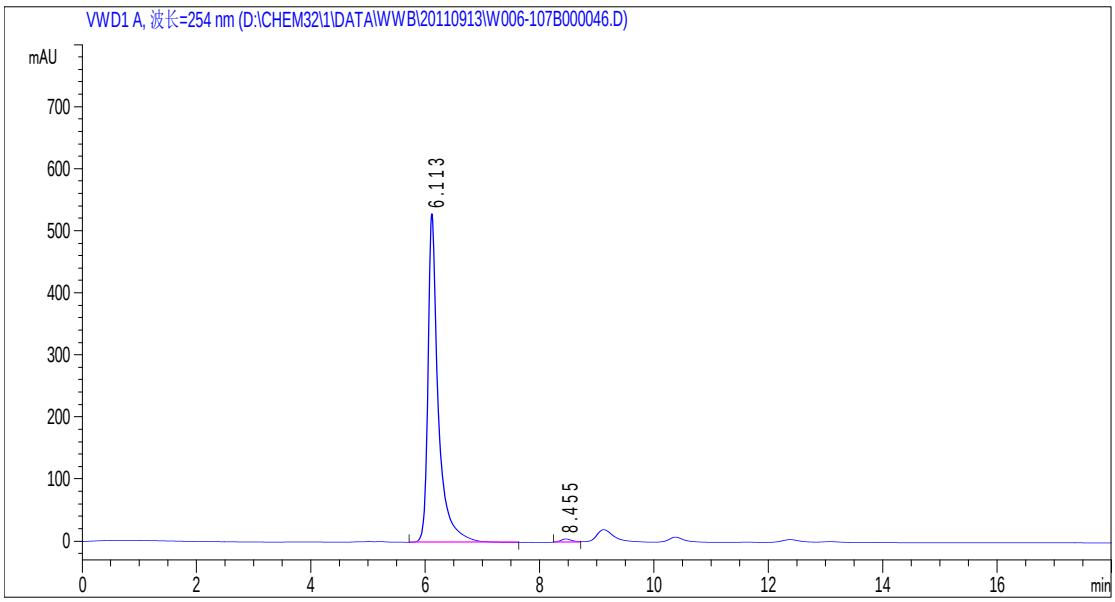


#	Time	Area	Height	Width	Symmetry	Area %
1	11.871	9.8	4.6E-1	0.3528	0.814	0.679
2	13.63	1430.5	43.1	0.47	0.69	99.321

7u: (5S,6S,7R,10S)-ethyl 7-methyl-4,8-dioxo-3,10-diphenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-6-carboxylate

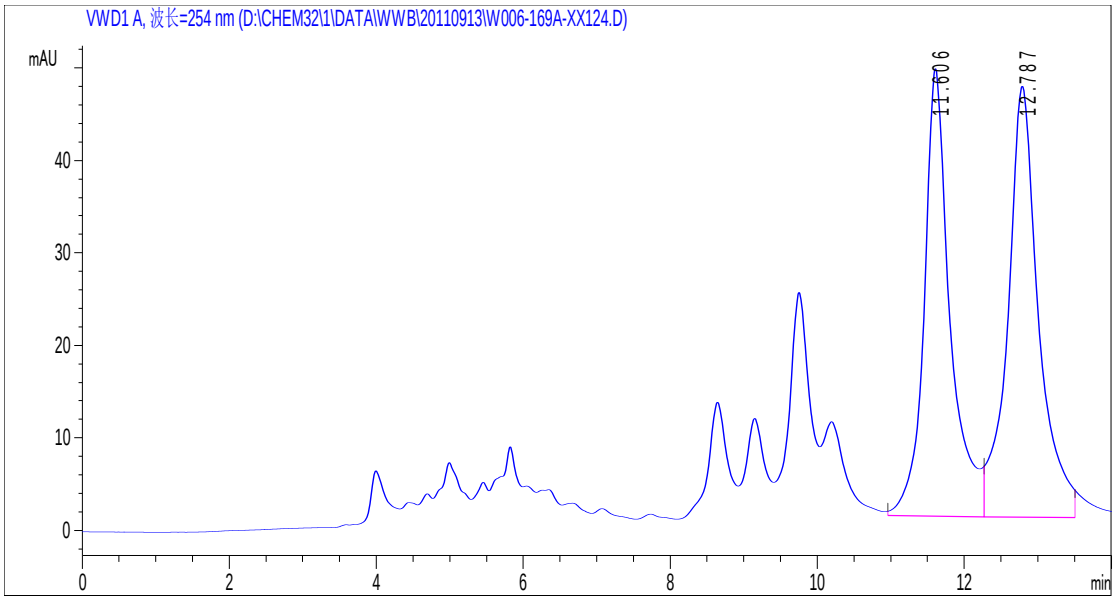


#	Time	Area	Height	Width	Symmetry	Area %
1	6.111	22774.2	1828.7	0.2076	0.566	29.765
2	8.399	22457.4	1297.8	0.2543	0.613	29.351
3	9.162	17028.1	659	0.4307	1.126	22.255
4	13.081	14253.4	475	0.5001	0.713	18.629

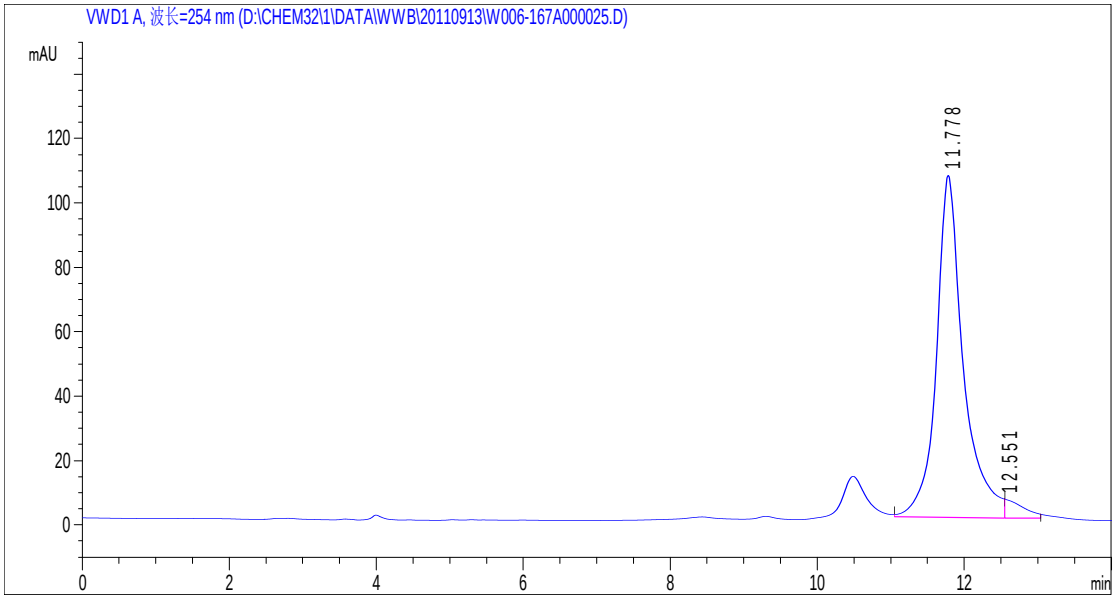


#	Time	Area	Height	Width	Symmetry	Area %
1	6.113	6614.2	528.5	0.181	0.554	98.933
2	8.455	71.4	5.2	0.2298	0.817	1.067

7v:(5S,6S,7R,10S)-6-(4-fluorophenyl)-7-methyl-3,10-diphenyl-2-thioxo-1-thia-3-azaspiro [4.5]decane-4,8-dione

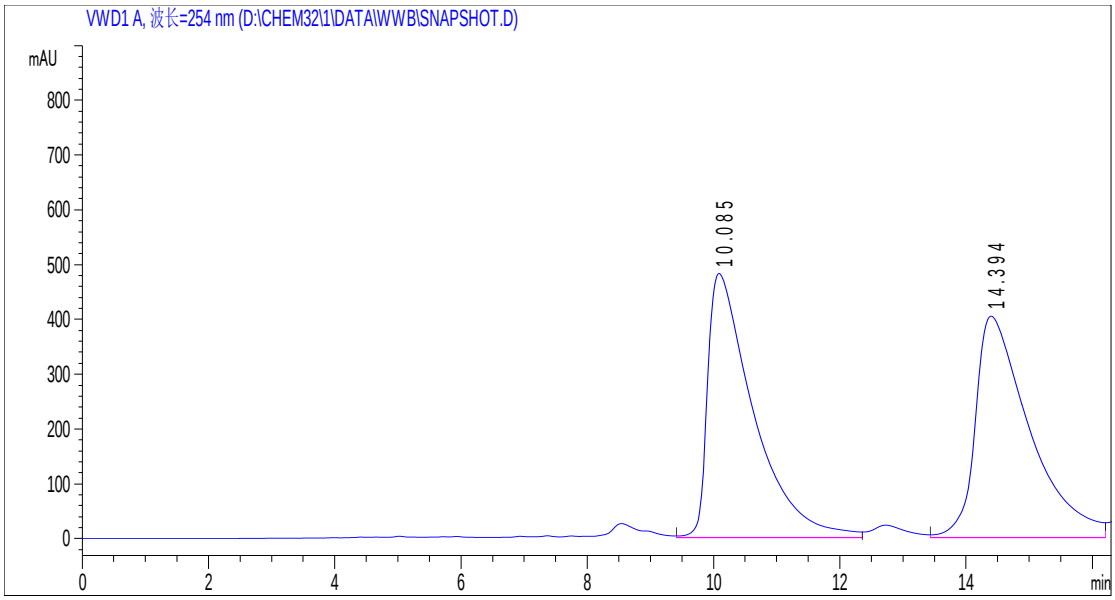


#	Time	Area	Height	Width	Symmetry	Area %
1	11.606	1203.8	48.8	0.3534	0.774	46.866
2	12.787	1364.8	46.8	0.4861	0.912	53.134

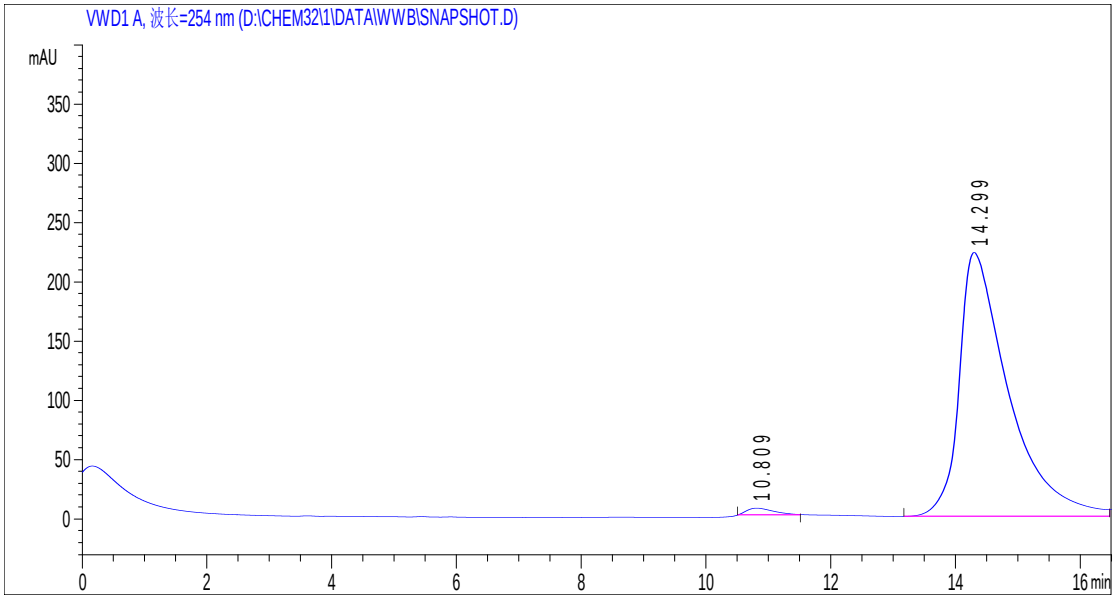


#	Time	Area	Height	Width	Symmetry	Area %
1	11.778	2713.6	106.3	0.4255	0.763	96.387
2	12.551	101.7	5.9	0.2016	0	3.613

7w: (5S,6S,7R,10S)-ethyl 7-methyl-4,8-dioxo-10-phenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-6-carboxylate

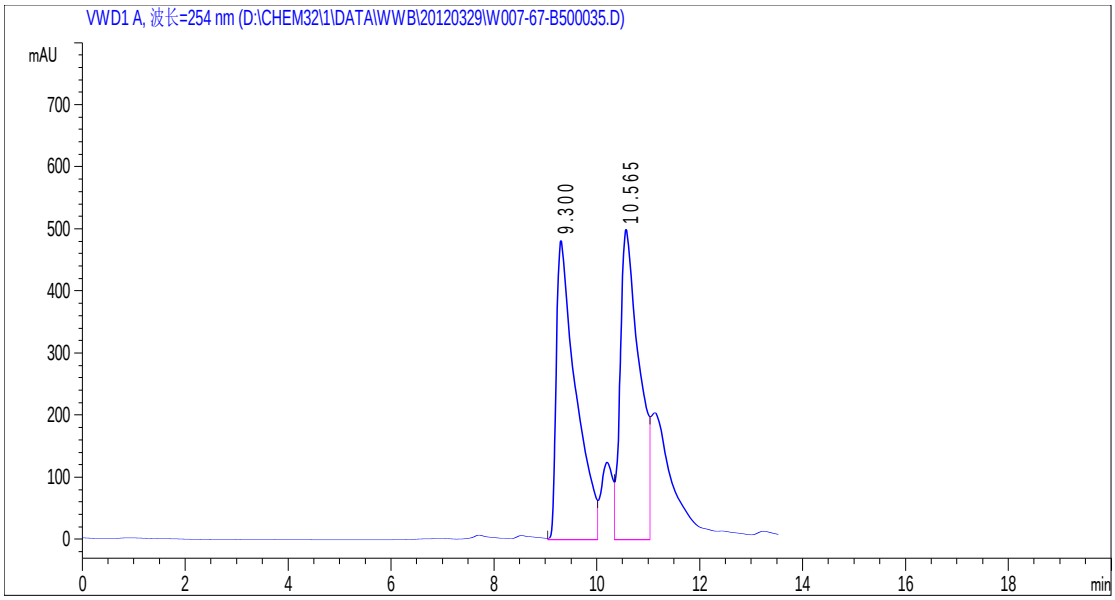


#	Time	Area	Height	Width	Symmetry	Area %
1	10.085	24450.8	482.9	0.7406	0.308	50.155
2	14.394	24299.6	405.1	0.8803	0.398	49.845

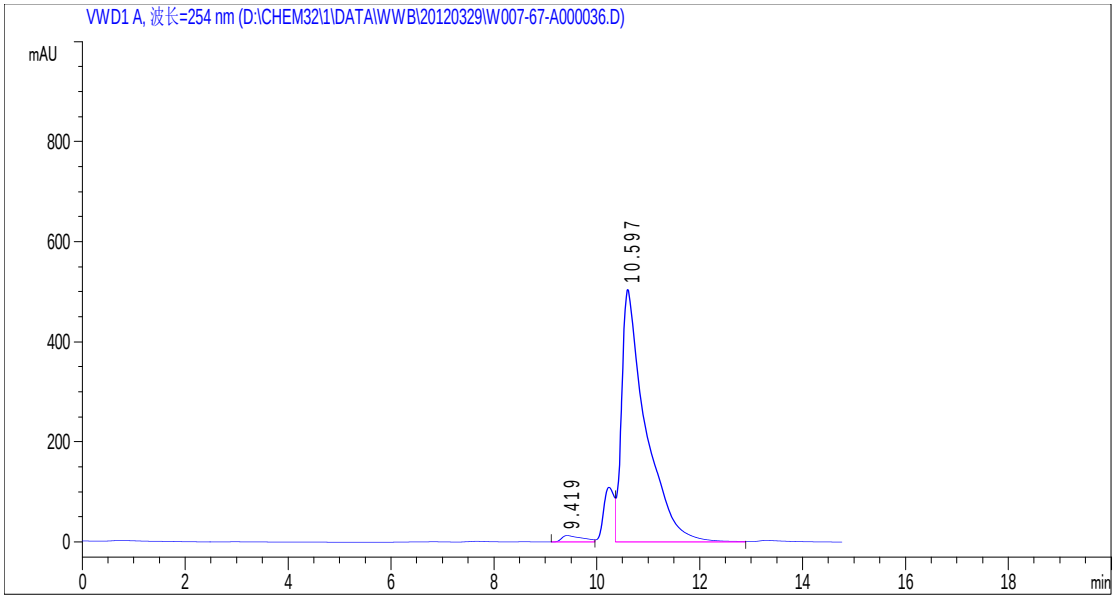


#	Time	Area	Height	Width	Symmetry	Area %
1	10.809	196	6.1	0.5353	0.544	1.577
2	14.299	12230.9	222.7	0.8009	0.416	98.423

7x: (5S,6S,7R,10S)-ethyl 10-(furan-2-yl)-7-methyl-4,8-dioxo-2-thioxo-1-thia-3-azaspiro[4.5] decane-6-carboxylate

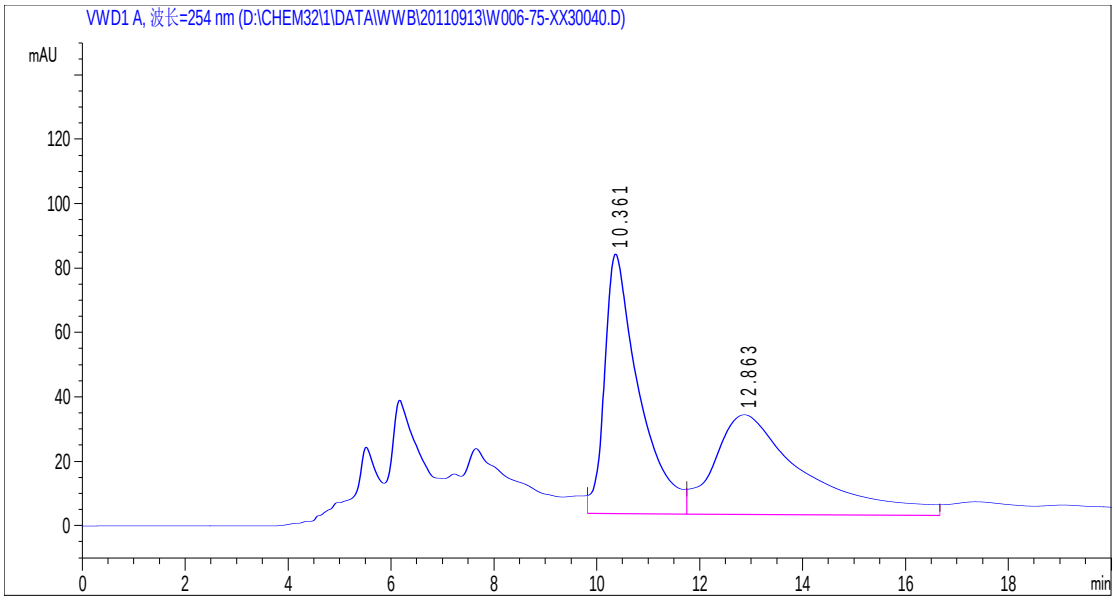


#	Time	Area	Height	Width	Symmetry	Area %
1	9.3	12658.1	481.6	0.3649	0.287	49.535
2	10.565	12895.9	499.7	0.3637	0.416	50.465

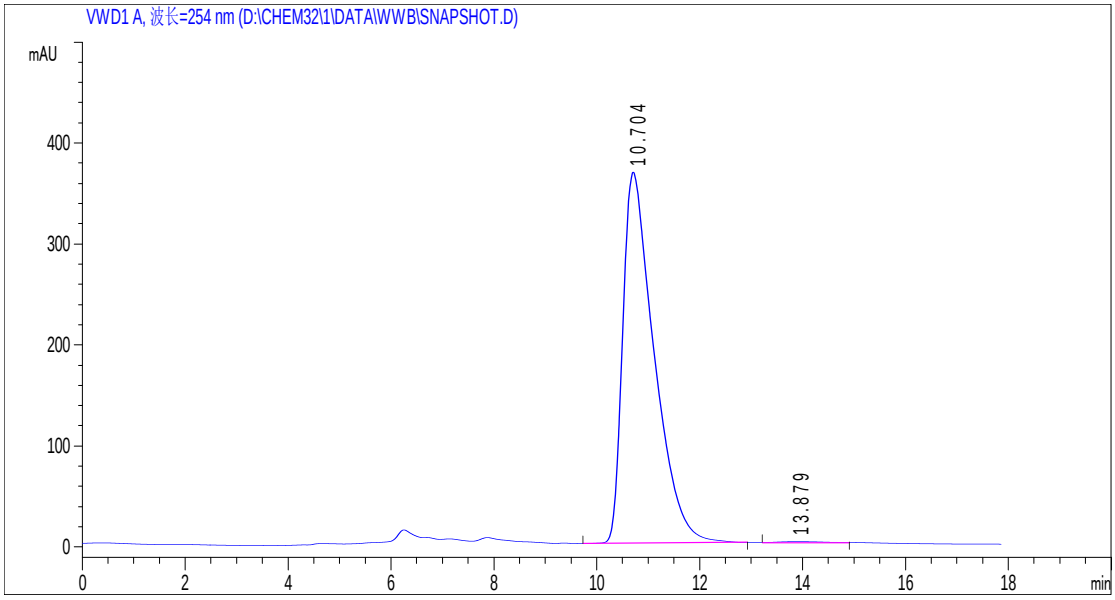


#	Time	Area	Height	Width	Symmetry	Area %
1	9.419	363.7	12.9	0.3834	0.326	2.166
2	10.597	16432.4	504.7	0.4497	0.311	97.834

10: (5S,6R,10S)-ethyl 4,8-dioxo-3,10-diphenyl-2-thioxo-1,3-diazaspiro[4.5] decane-6-carboxylate



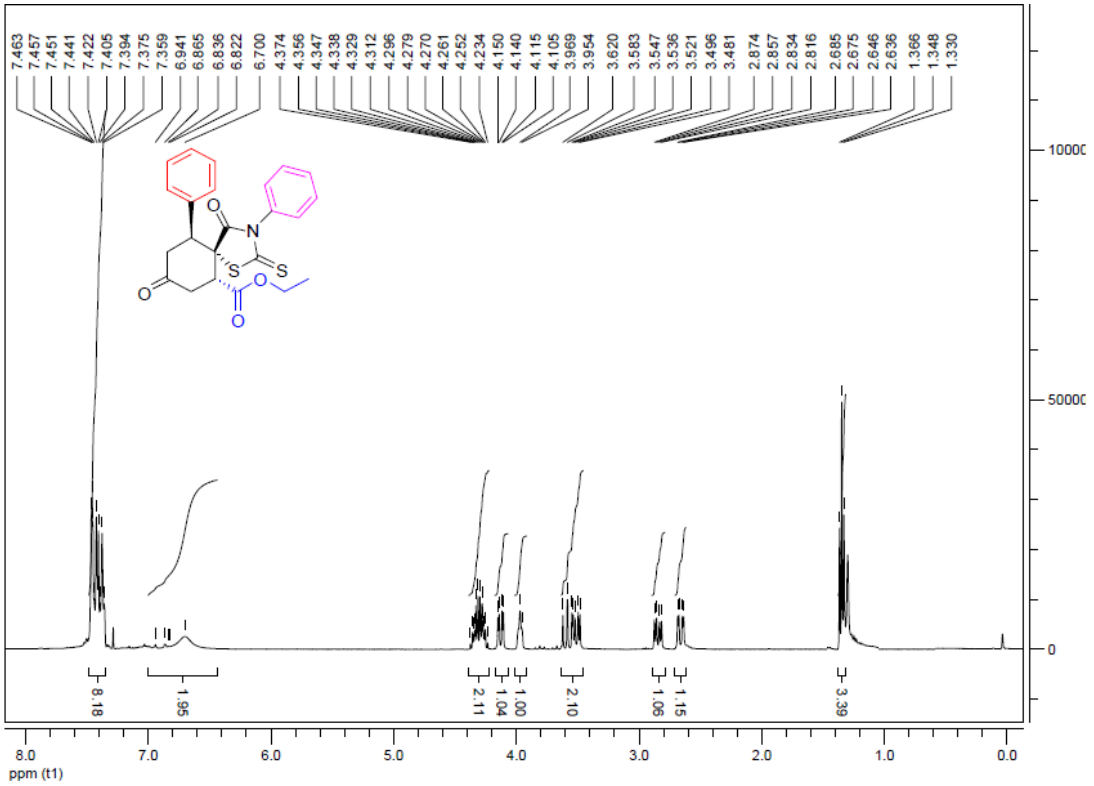
#	Time	Area	Height	Width	Symmetry	Area %
1	10.361	3770.6	80.8	0.7773	0	50.022
2	12.863	3767.3	31.1	2.0212	0.481	49.978

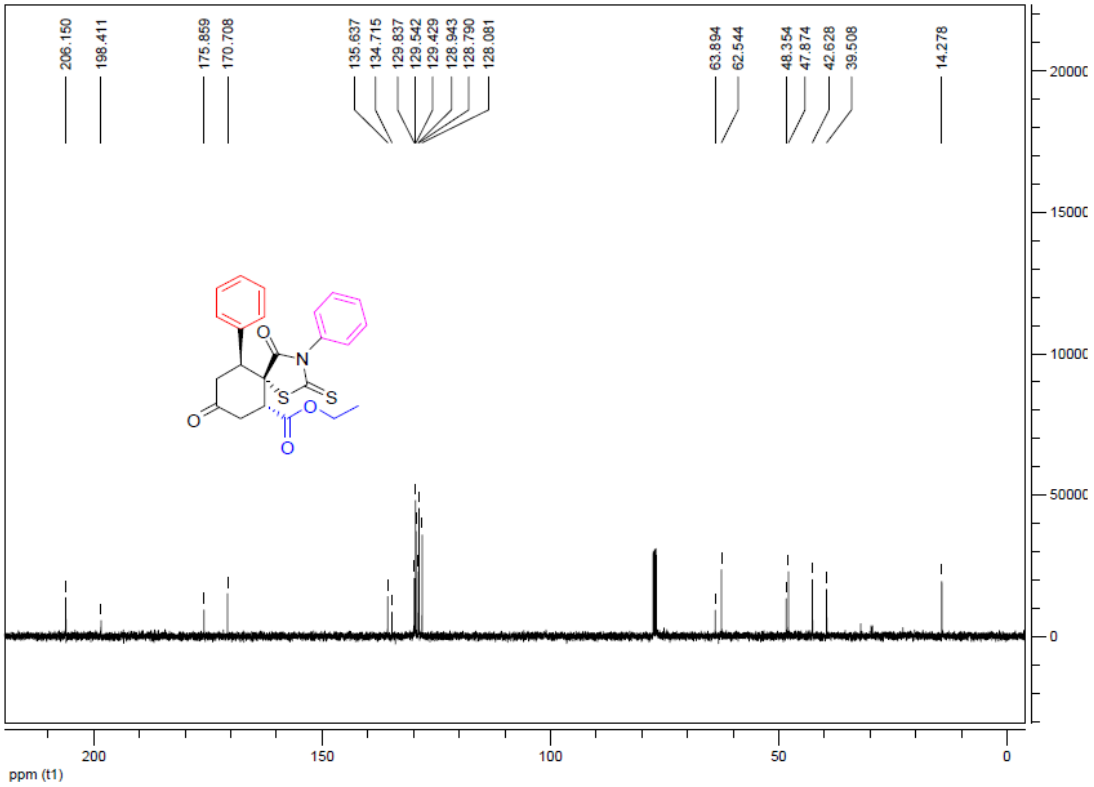


#	Time	Area	Height	Width	Symmetry	Area %
1	10.704	15581.3	367.6	0.6211	0.462	99.483
2	13.879	80.9	1.2	1.0847	0.715	0.517

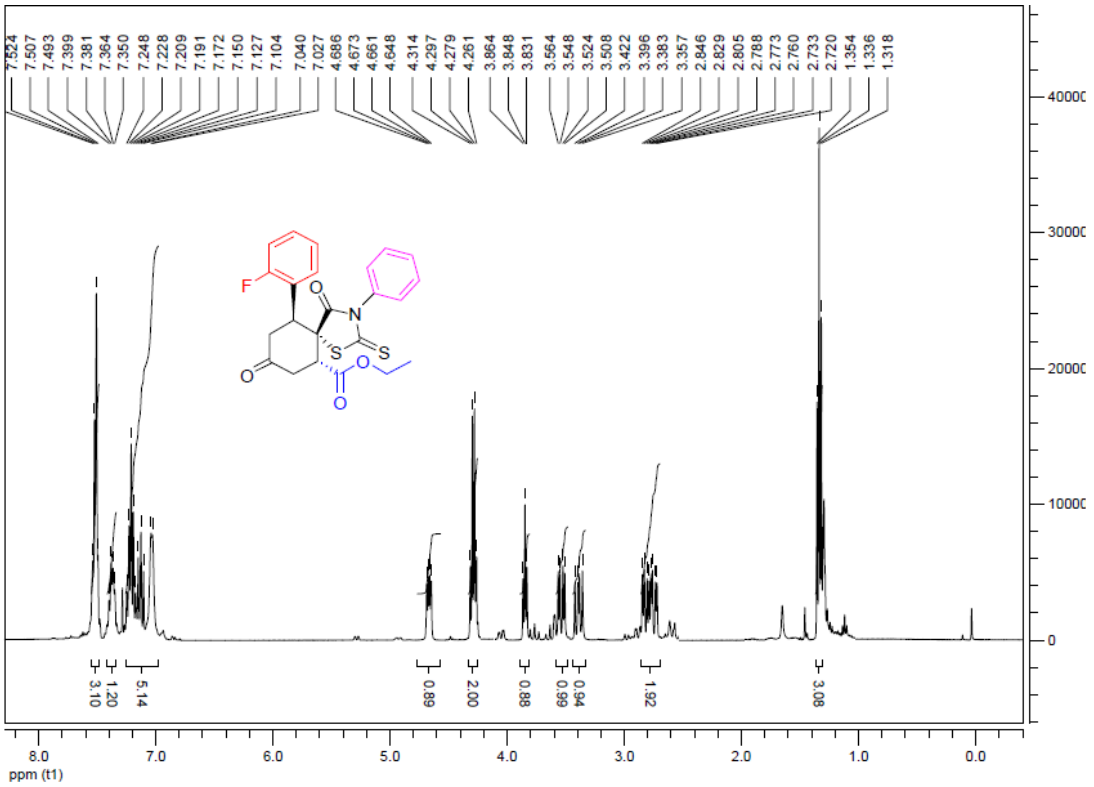
F: NMR Spectra of Products

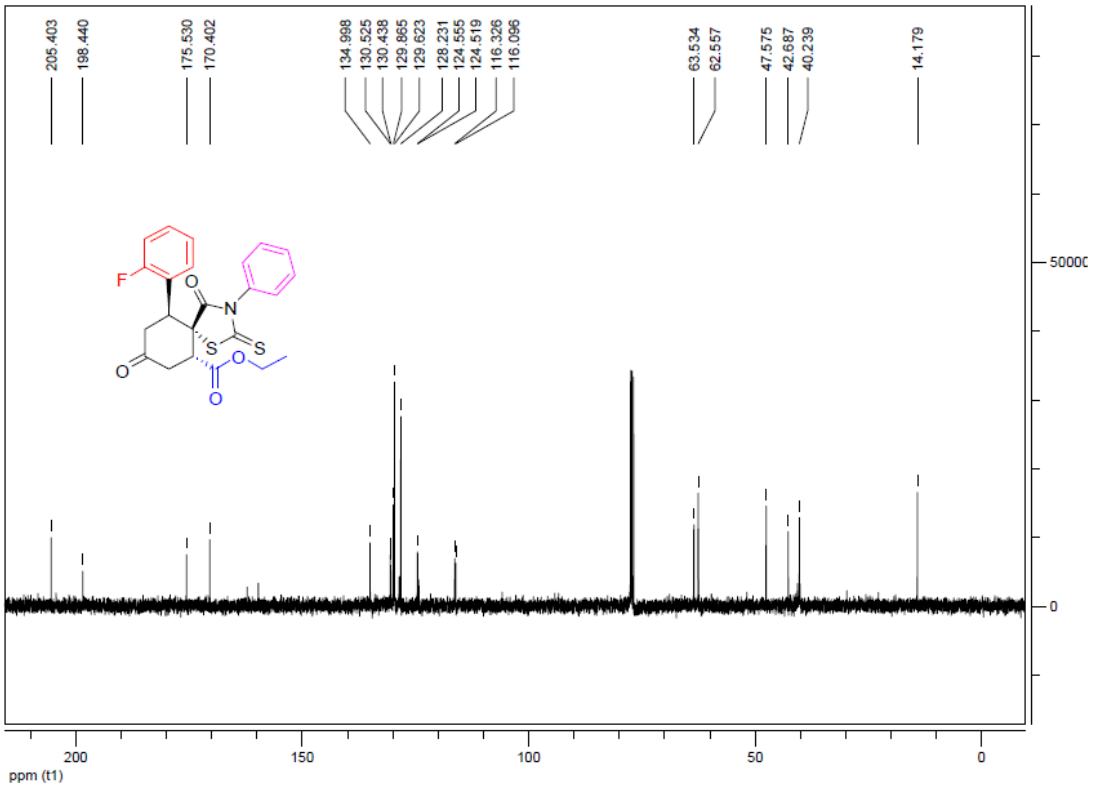
7a: (5S,6S,10S)-ethyl 4,8-dioxo-3,10-diphenyl-2-thioxo-1-thia-3-azaspiro[4.5]decane-6-carboxylate



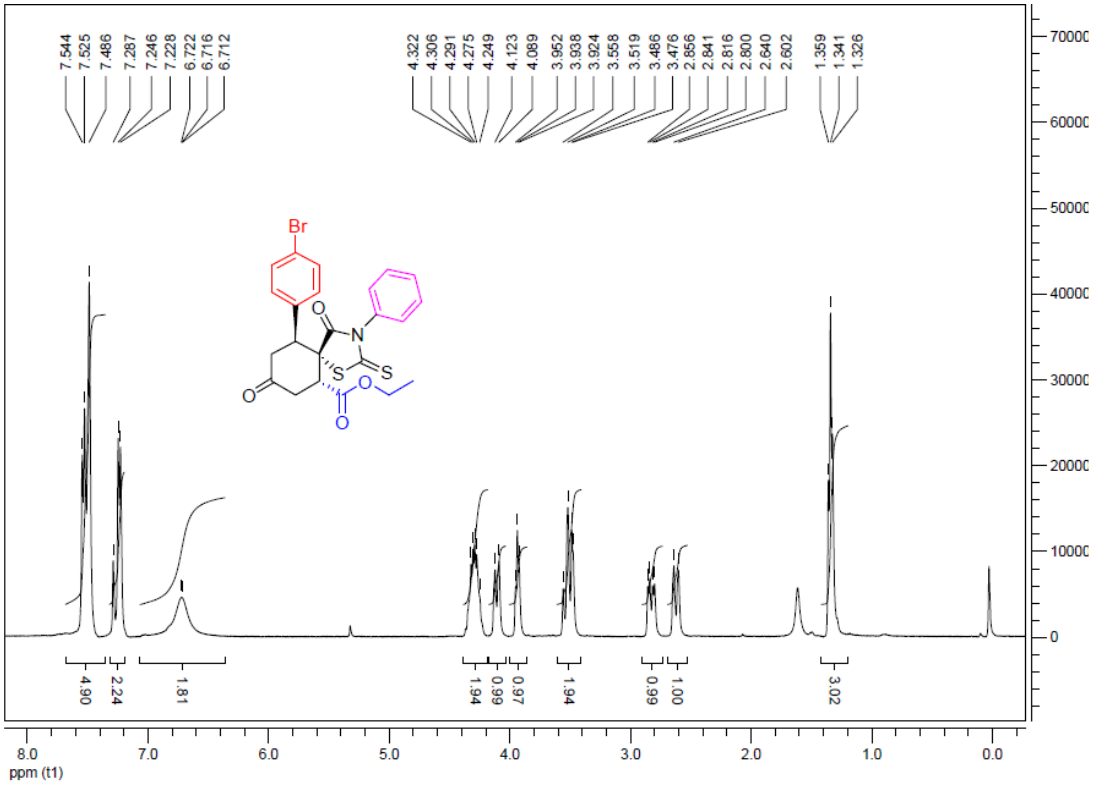


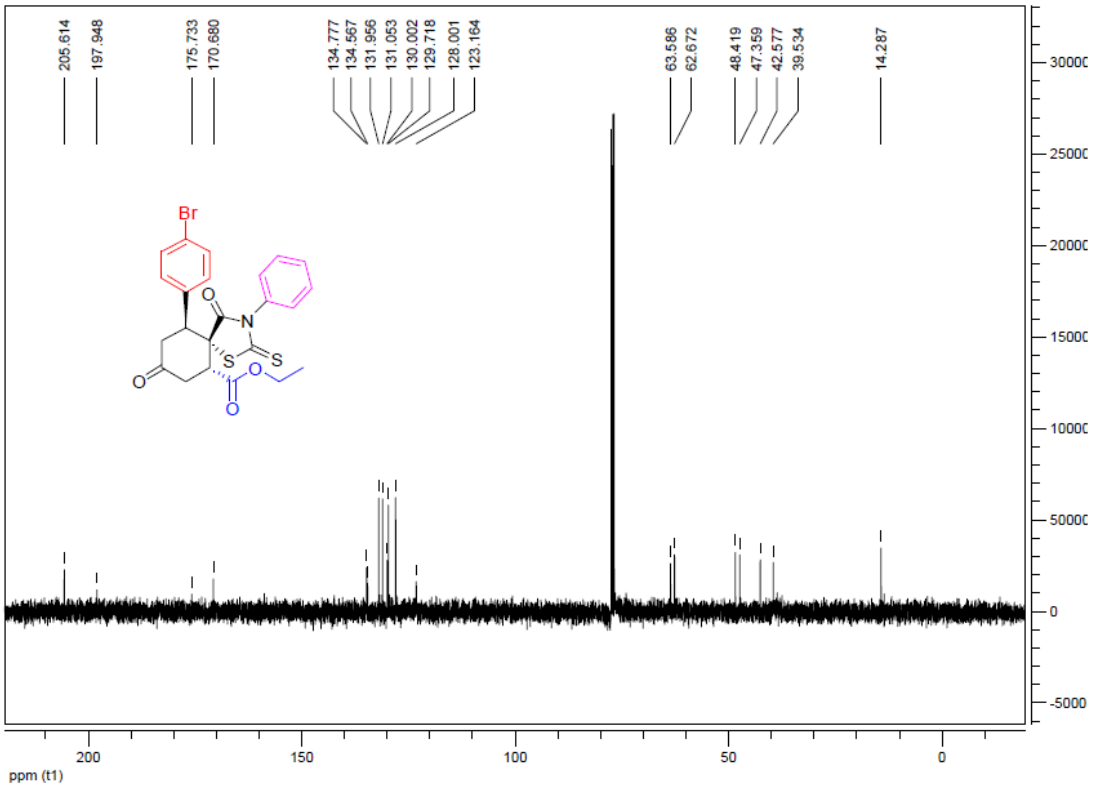
7b: (5S,6S,10S)-ethyl 10-(2-fluorophenyl)-4,8-dioxo-3-phenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-6-carboxylate



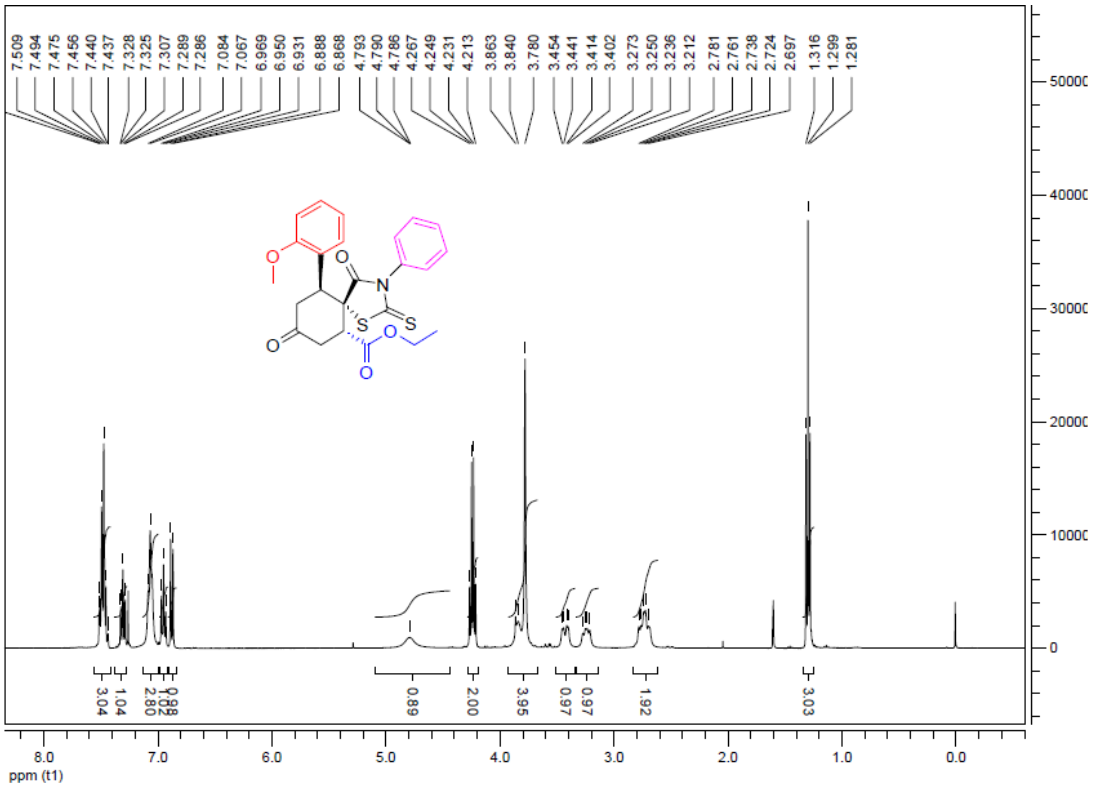


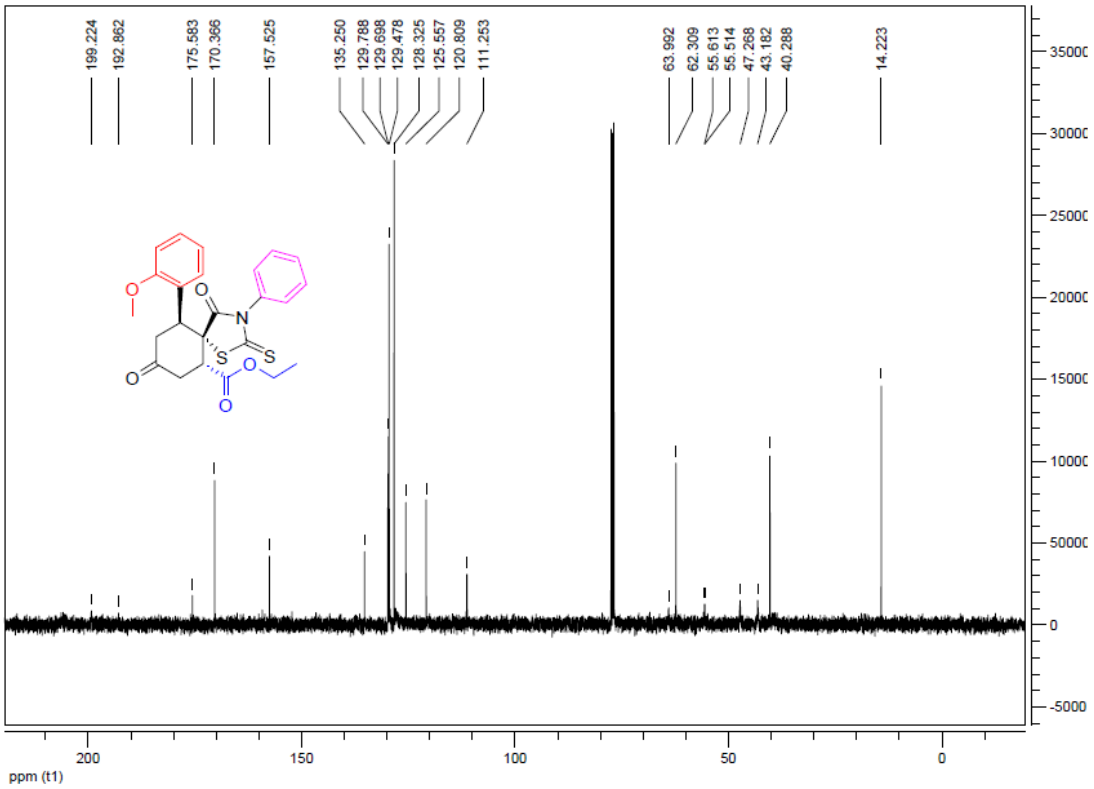
7c: (5S,6S,10S)-ethyl 10-(4-bromophenyl)-4,8-dioxo-3-phenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-6-carboxylate



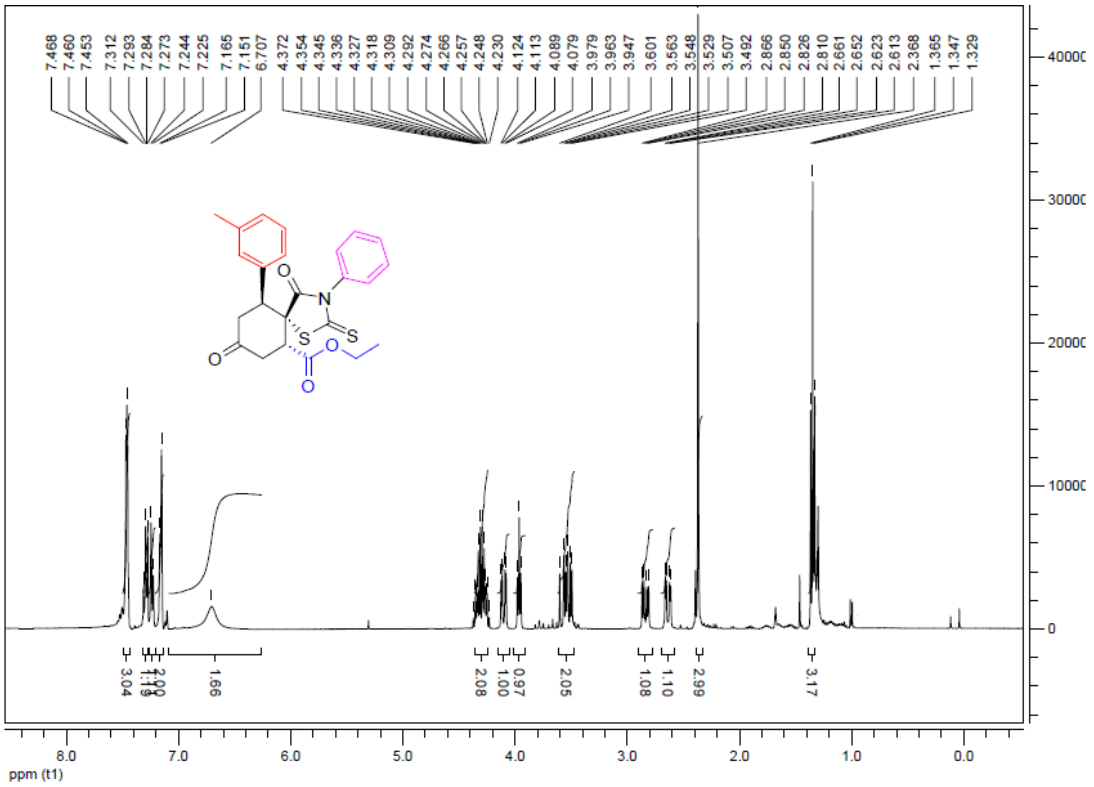


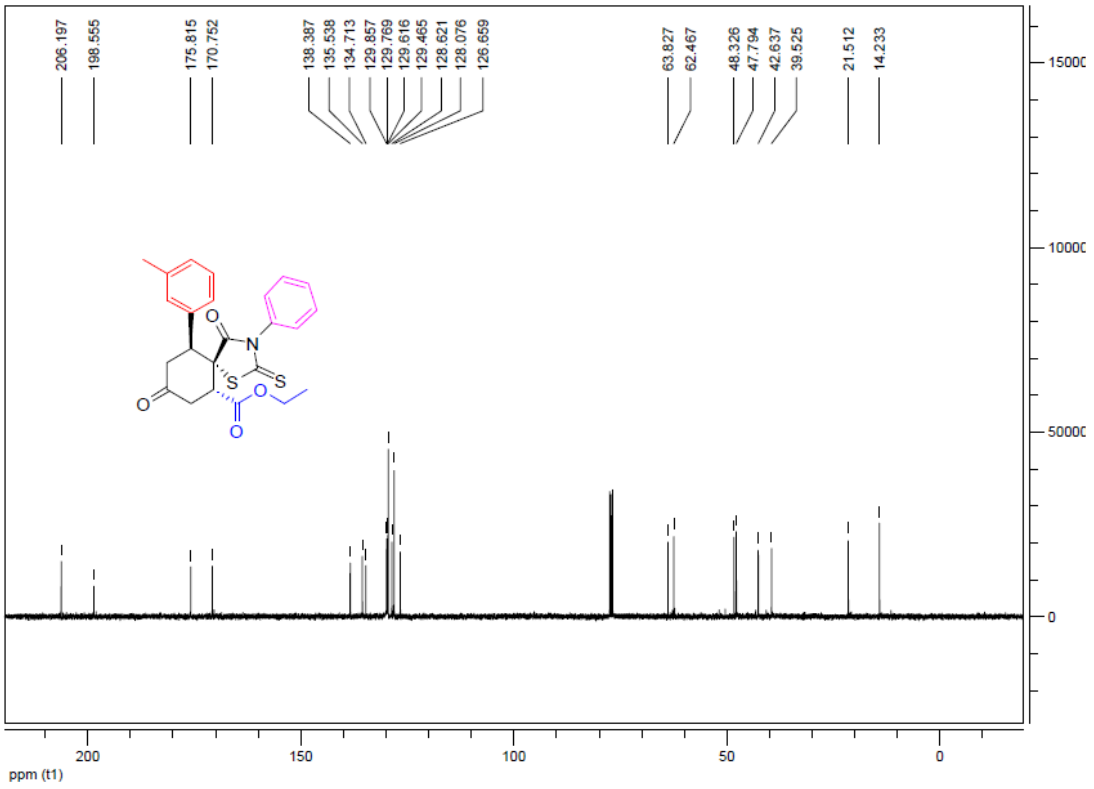
7d：(5S,6S,10S)-ethyl 10-(2-methoxyphenyl)-4,8-dioxo-3-phenyl-2-thioxo-1-thia-3-azaspiro [4.5]decane-6-carboxylate



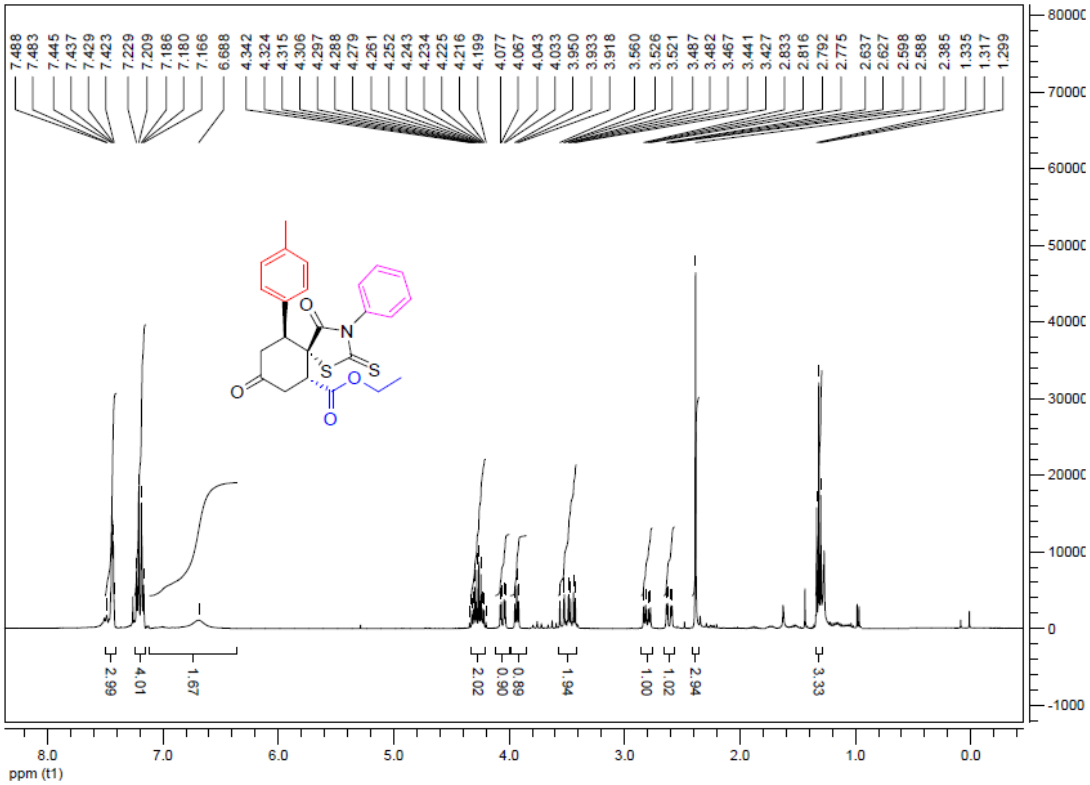


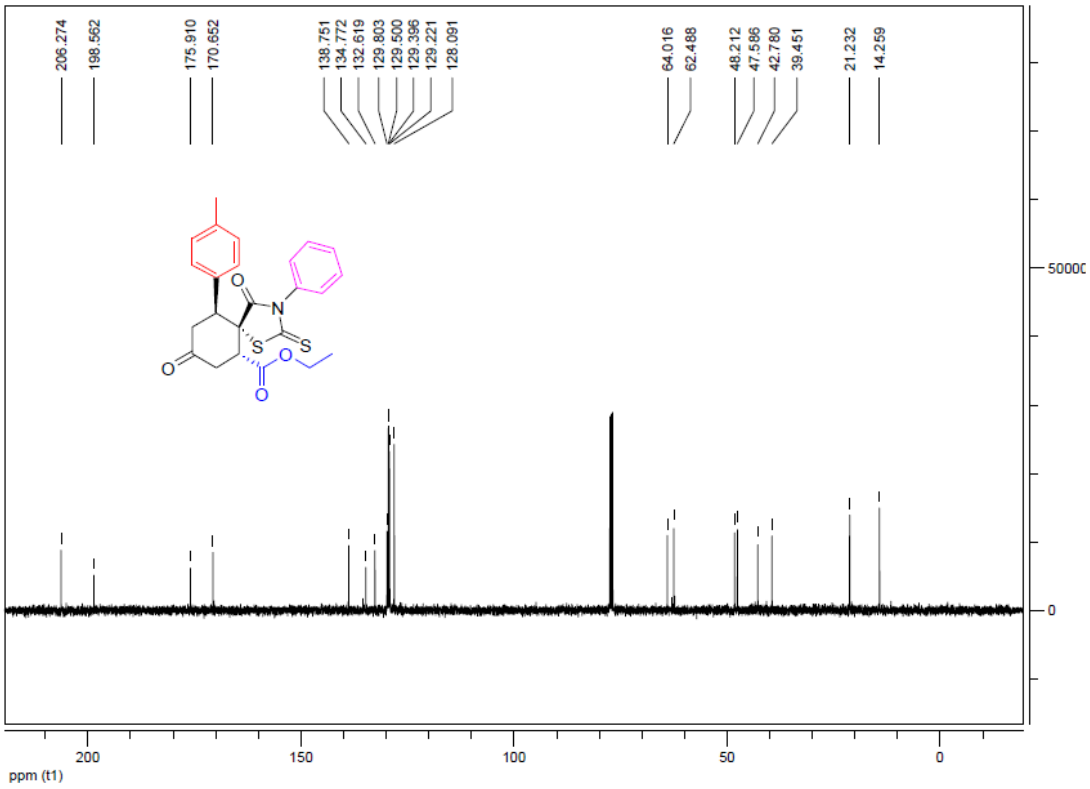
7e：(5S,6S,10S)-ethyl 4,8-dioxo-3-phenyl-2-thioxo-10-m-tolyl-1-thia-3-azaspiro [4.5]decane-6-carboxylate



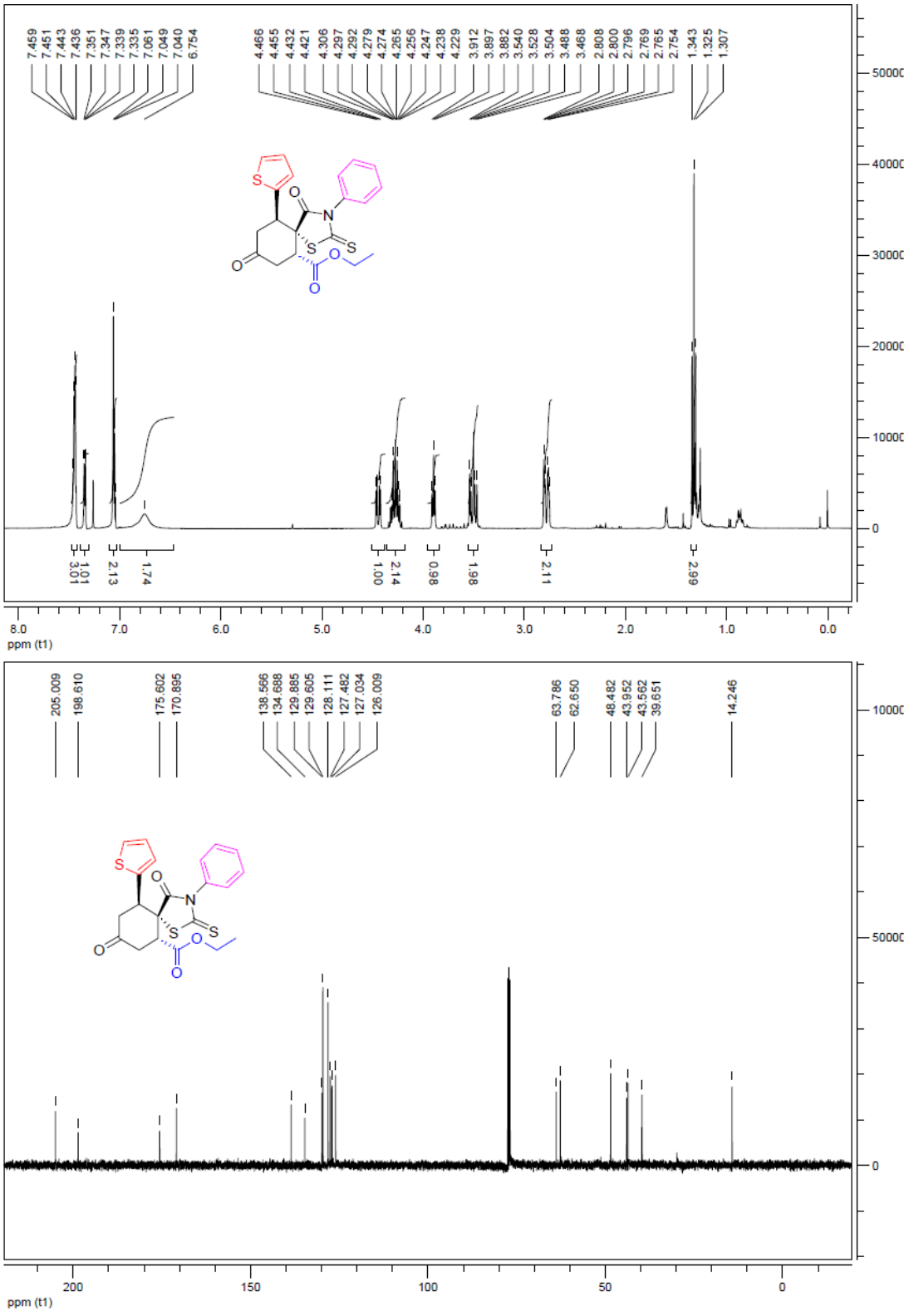


7f：(5S,6S,10S)-ethyl 4,8-dioxo-3-phenyl-2-thioxo-10-p-tolyl-1-thia-3-azaspiro [4.5]decane-6-carboxylate

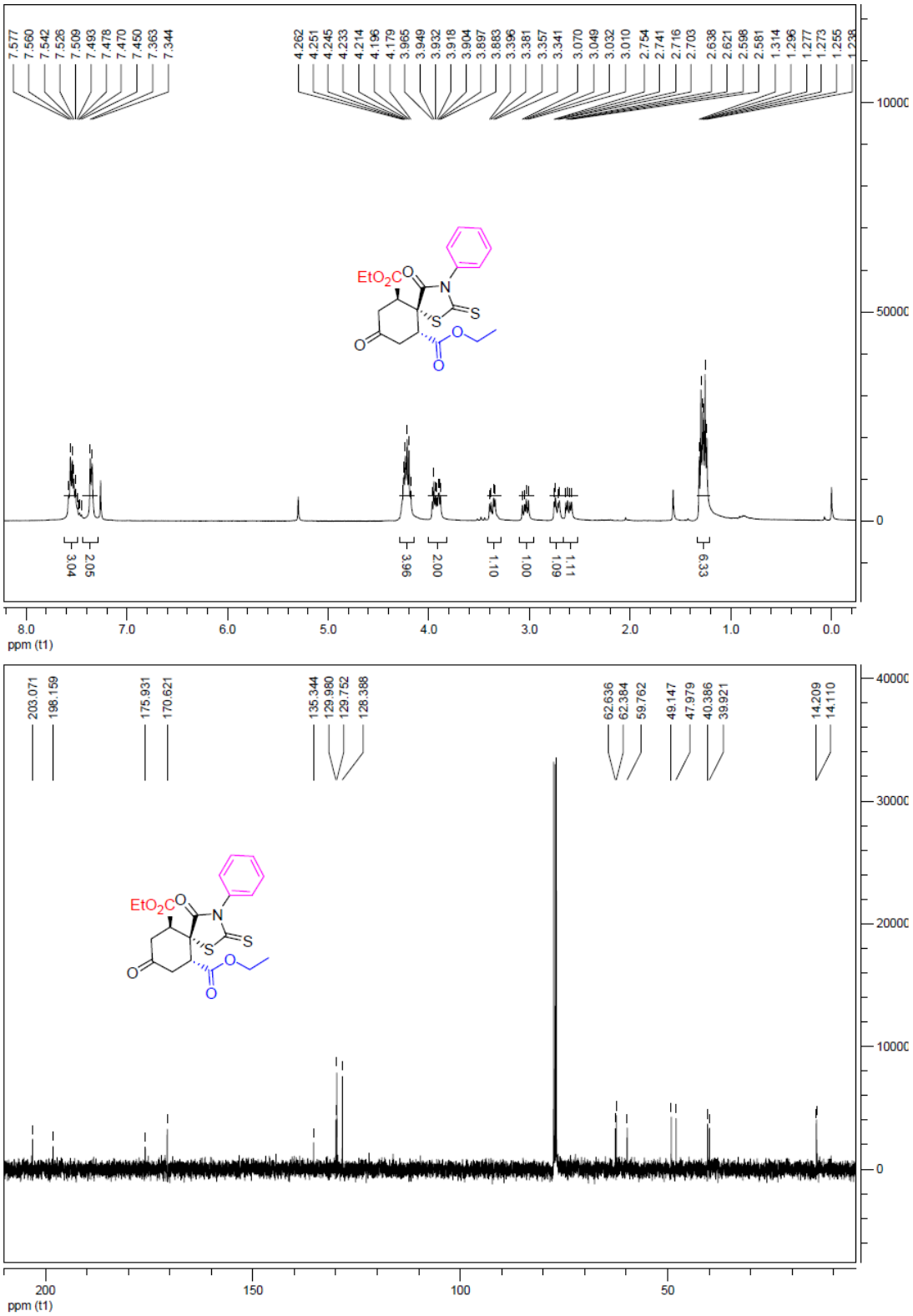




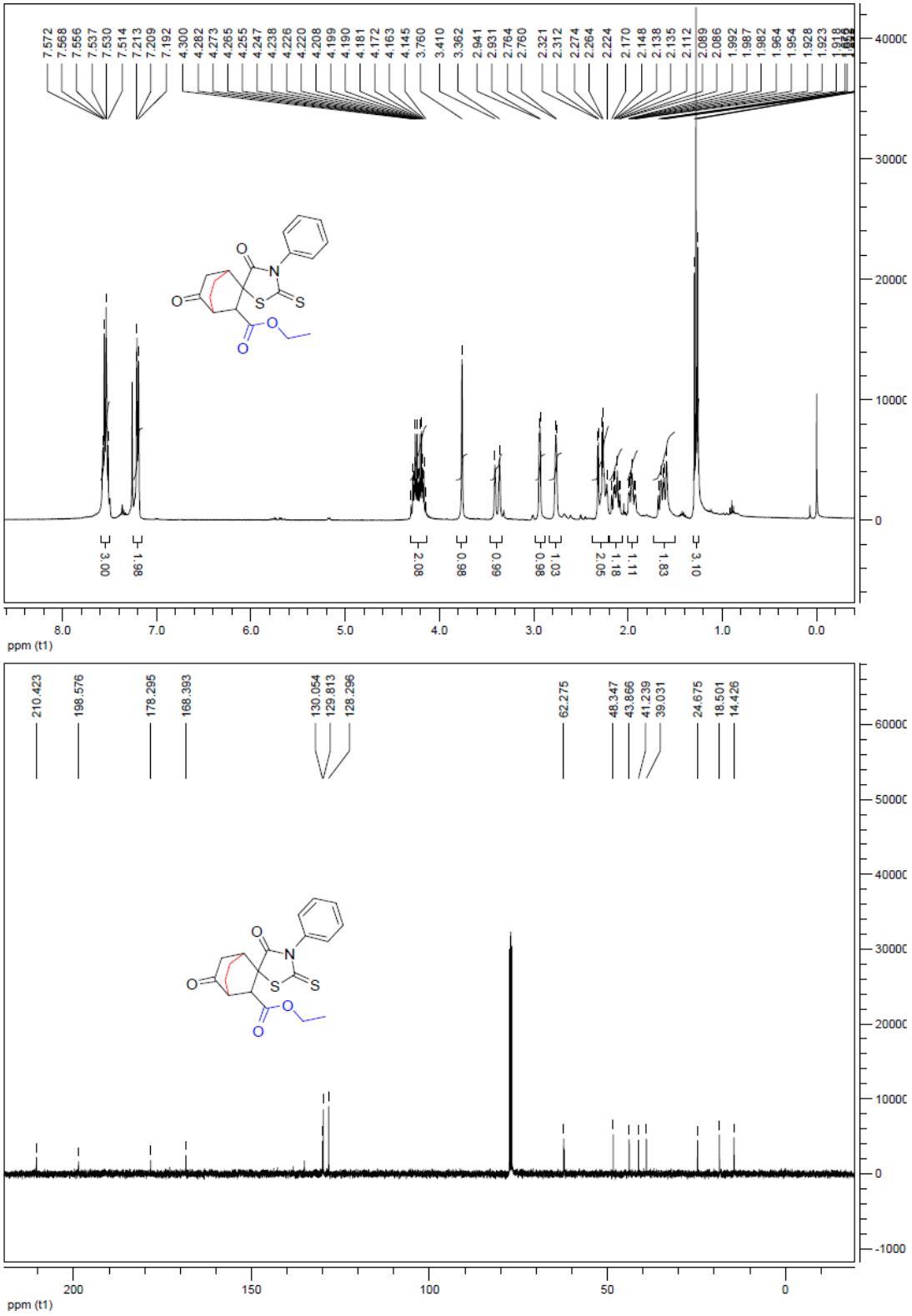
7g：(5R,6S,10S)-ethyl 4,8-dioxo-3-phenyl-10-(thiophen-2-yl)-2-thioxo-1-thia-3-azaspiro [4.5]decane-6-carboxylate



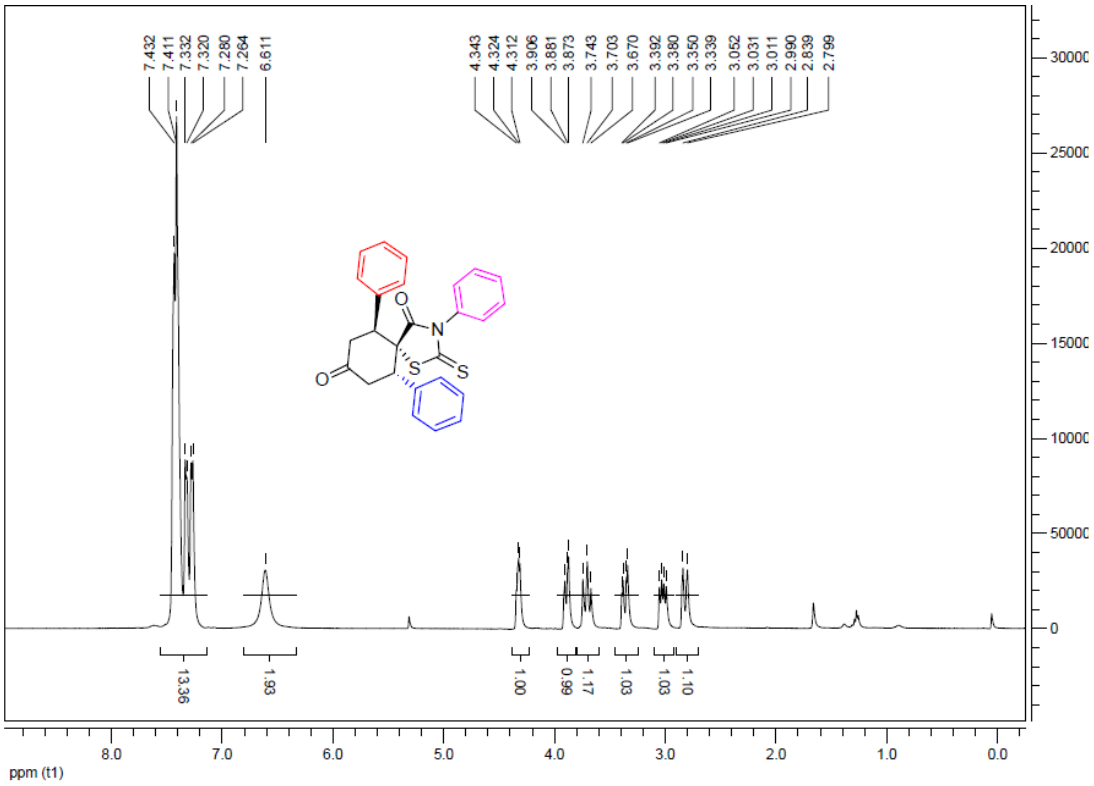
7h: (6S,10S)-diethyl 4,8-dioxo-3-phenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-6,10-dicarboxylate

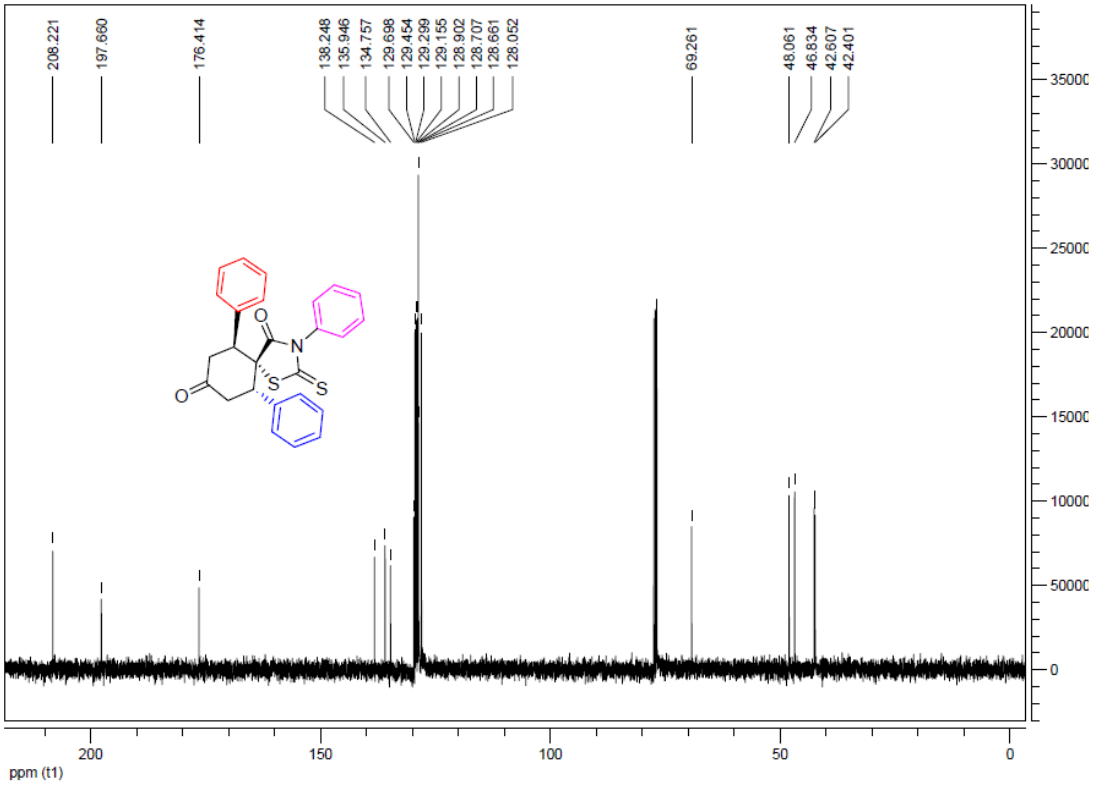


7i:ethyl 4',5-dioxo-3'-phenyl-2'-thioxospiro[bicyclo[2.2.2]octane-2,5'-thiazolidine]-3-carboxylate

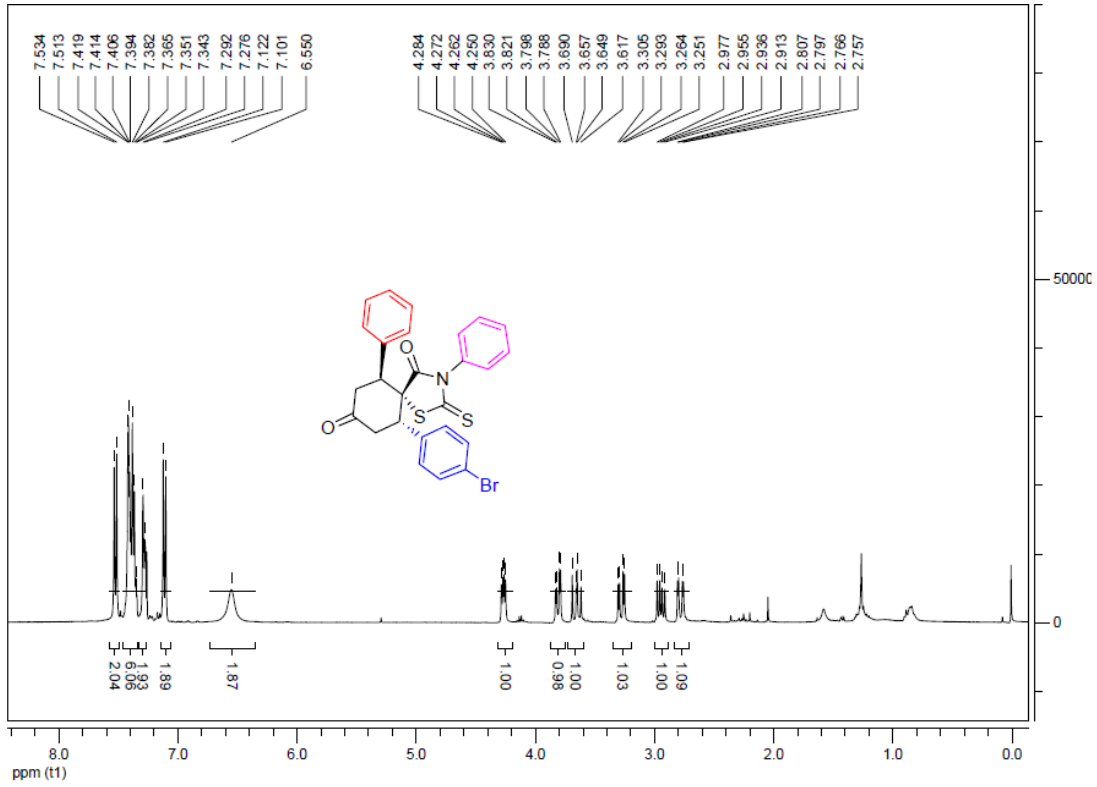


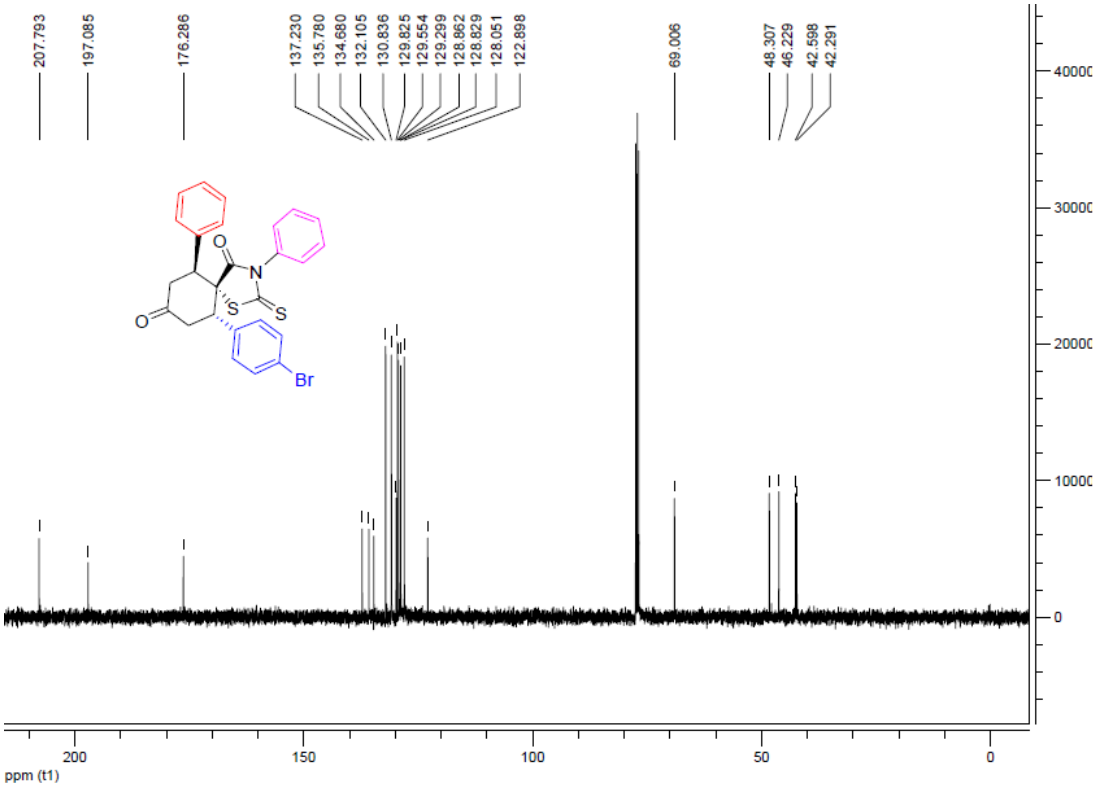
7j: (6S,10S)-3,6,10-triphenyl-2-thioxo-1-thia-3-azaspiro[4.5]decane-4,8-dione



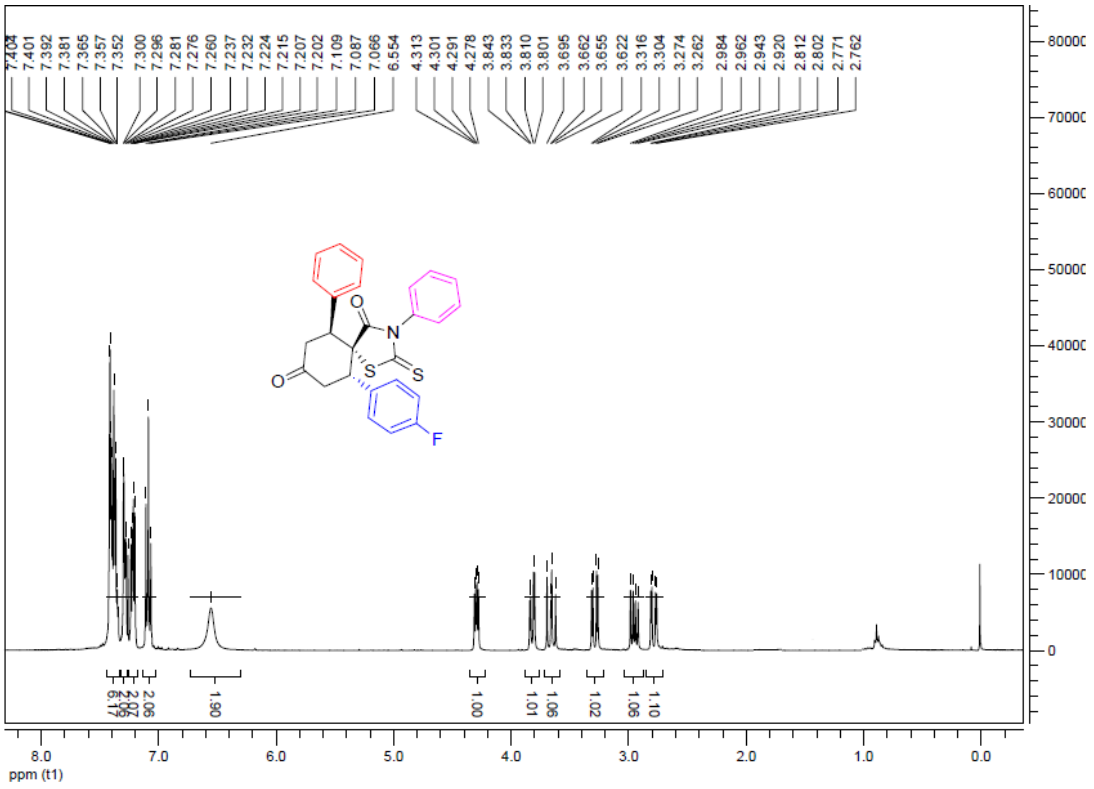


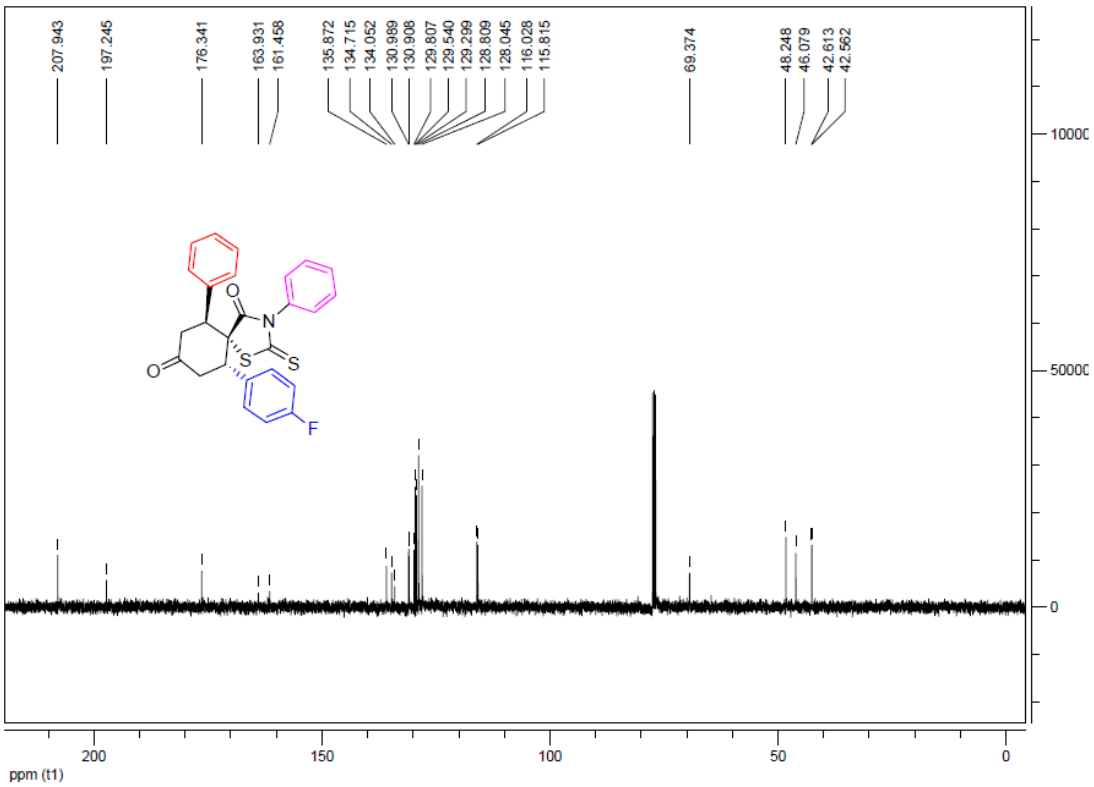
7k: (5S,6S,10S)-6-(4-bromophenyl)-3,10-diphenyl-2-thioxo-1-thia-3-azaspiro[4.5]decane-4,8-dione



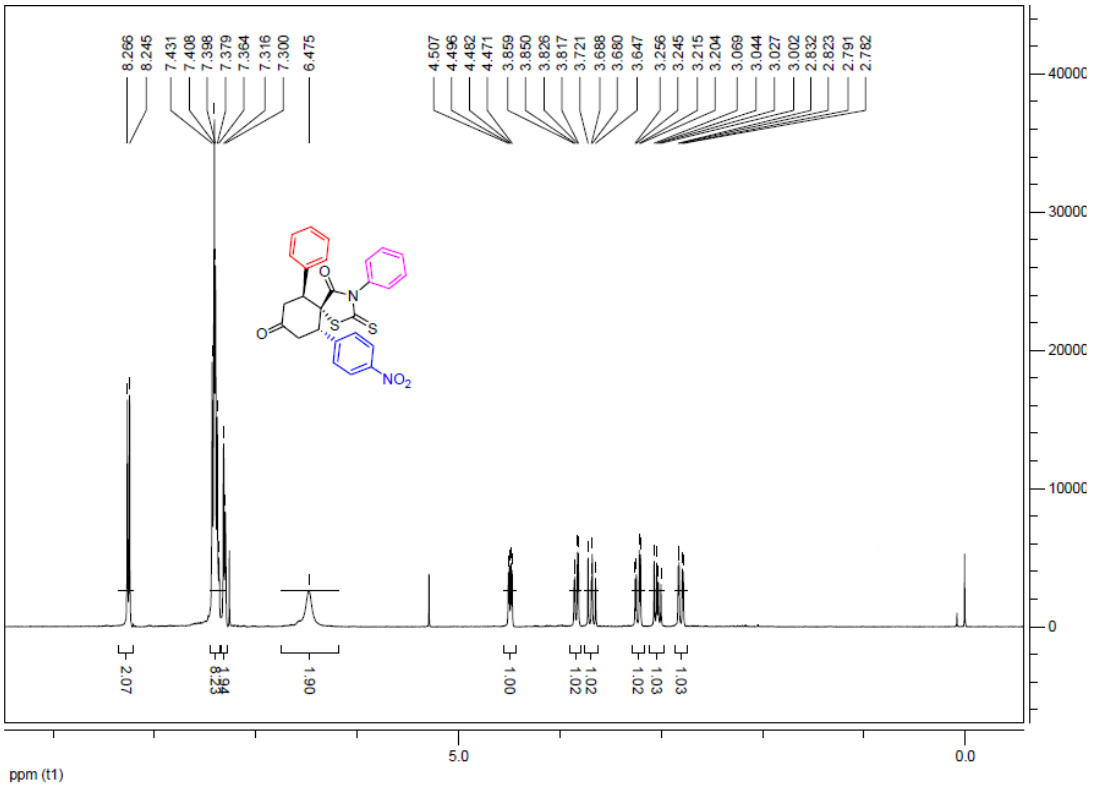


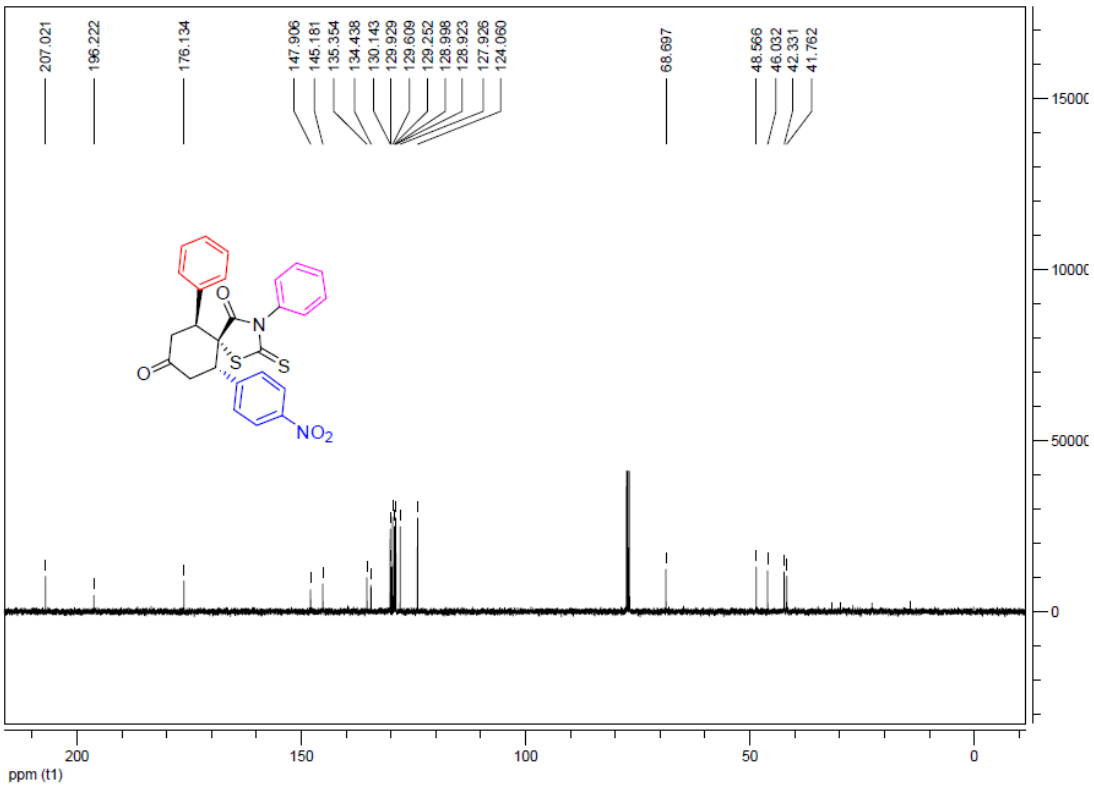
7l: (5S,6S,10S)-6-(4-fluorophenyl)-3,10-diphenyl-2-thioxo-1-thia-3-azaspiro[4.5]decane-4,8-dione



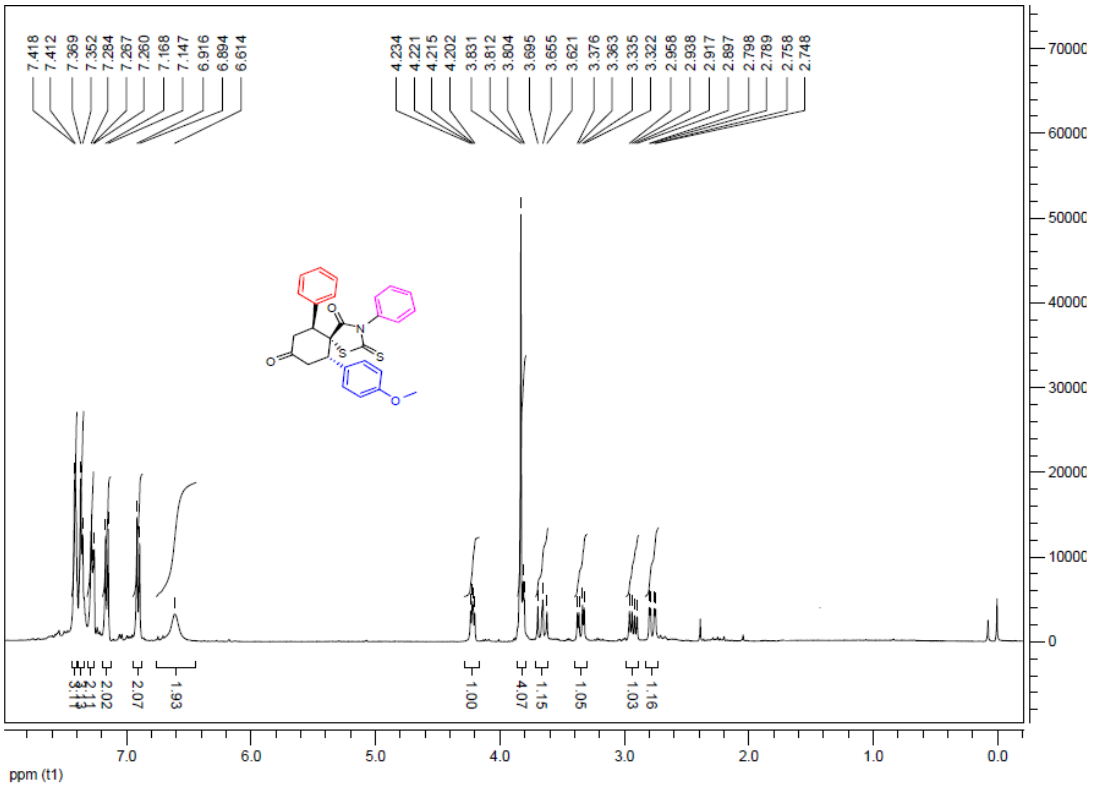


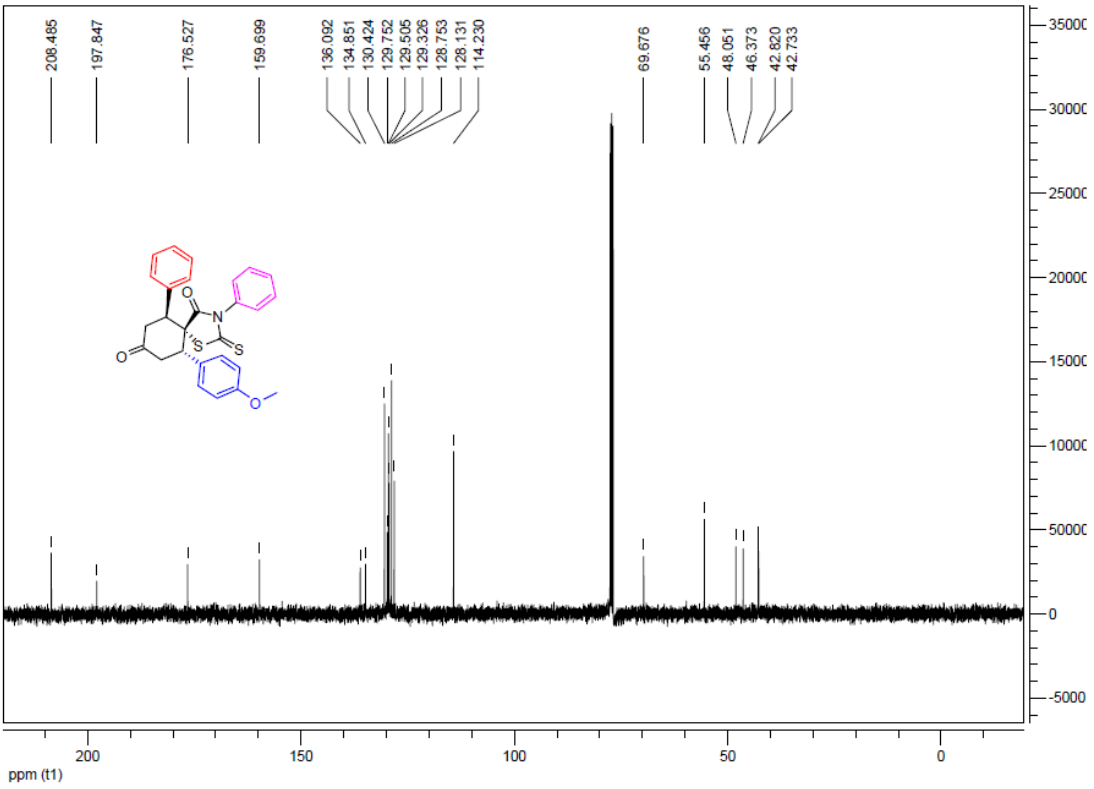
7m: (5S,6S,10S)-6-(4-nitrophenyl)-3,10-diphenyl-2-thioxo-1-thia-3-azaspiro[4.5]decane-4,8-dione



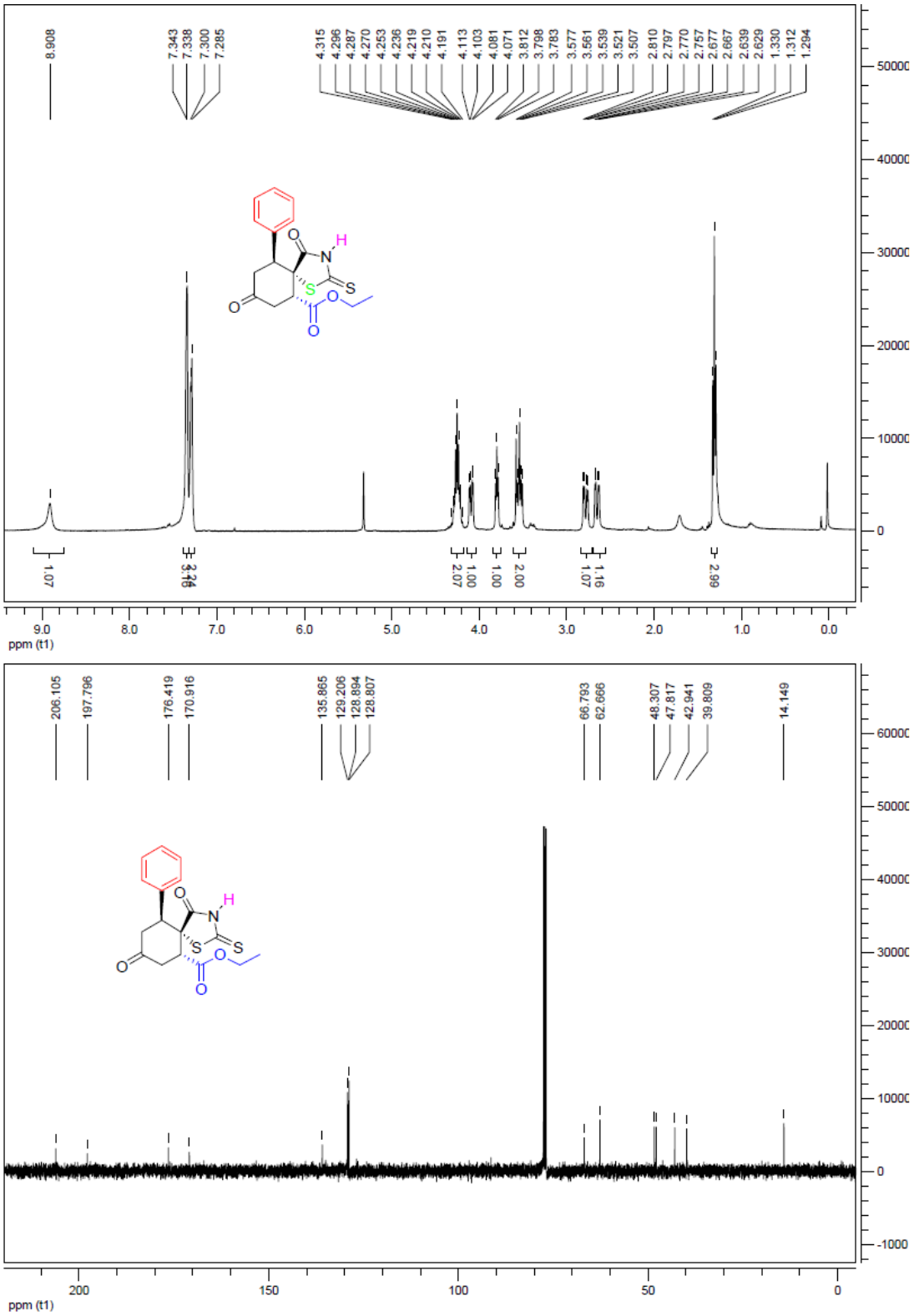


7n: (5S,6S,10S)-6-(4-methoxyphenyl)-3,10-diphenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-4,8-dione

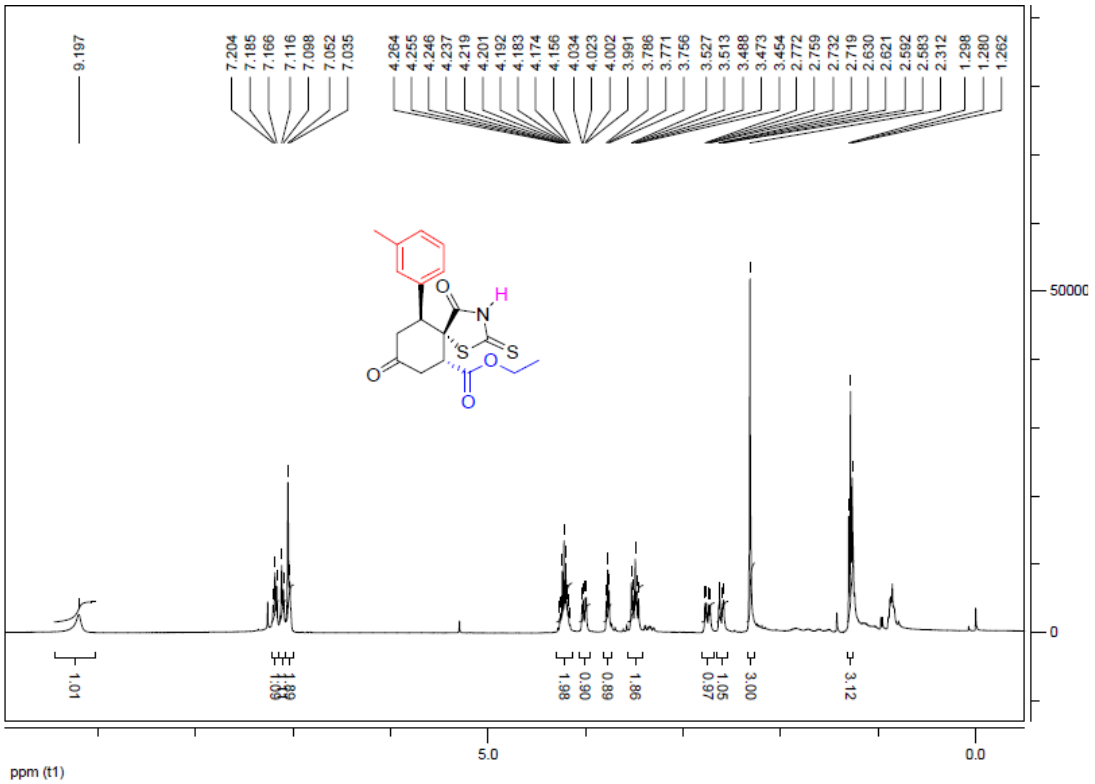


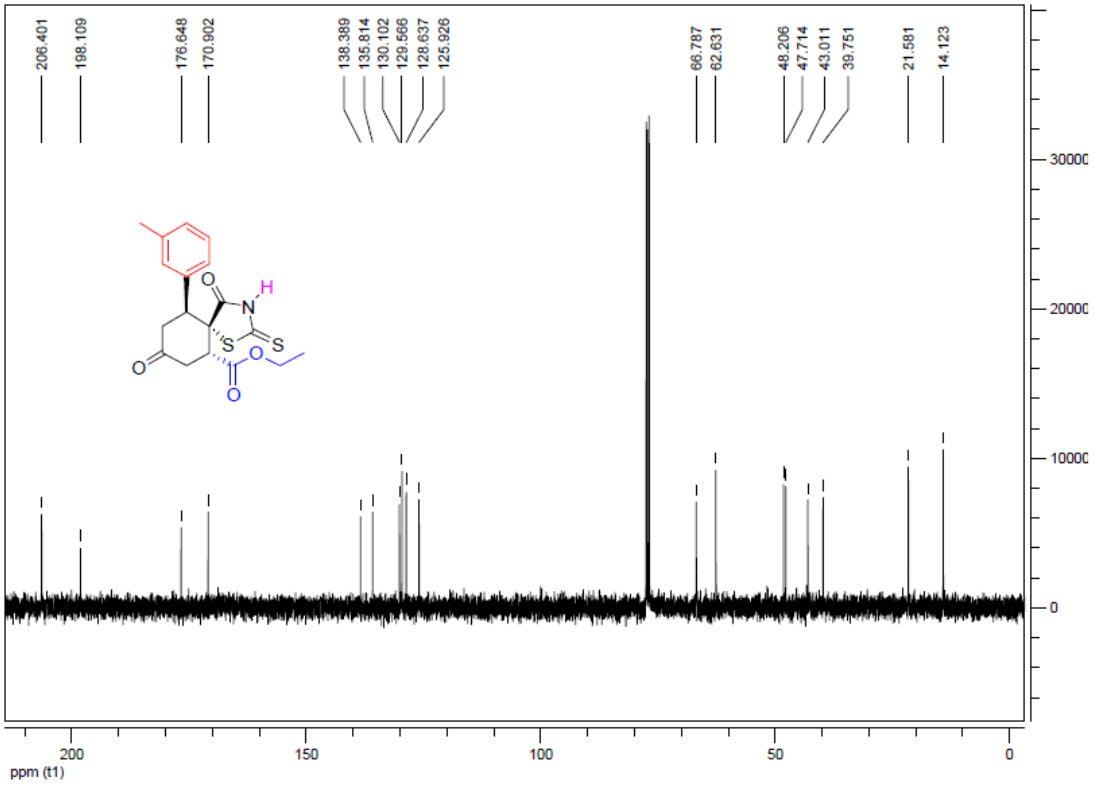


7o: (5S,6S,10S)-ethyl 4,8-dioxo-10-phenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-6-carboxylate

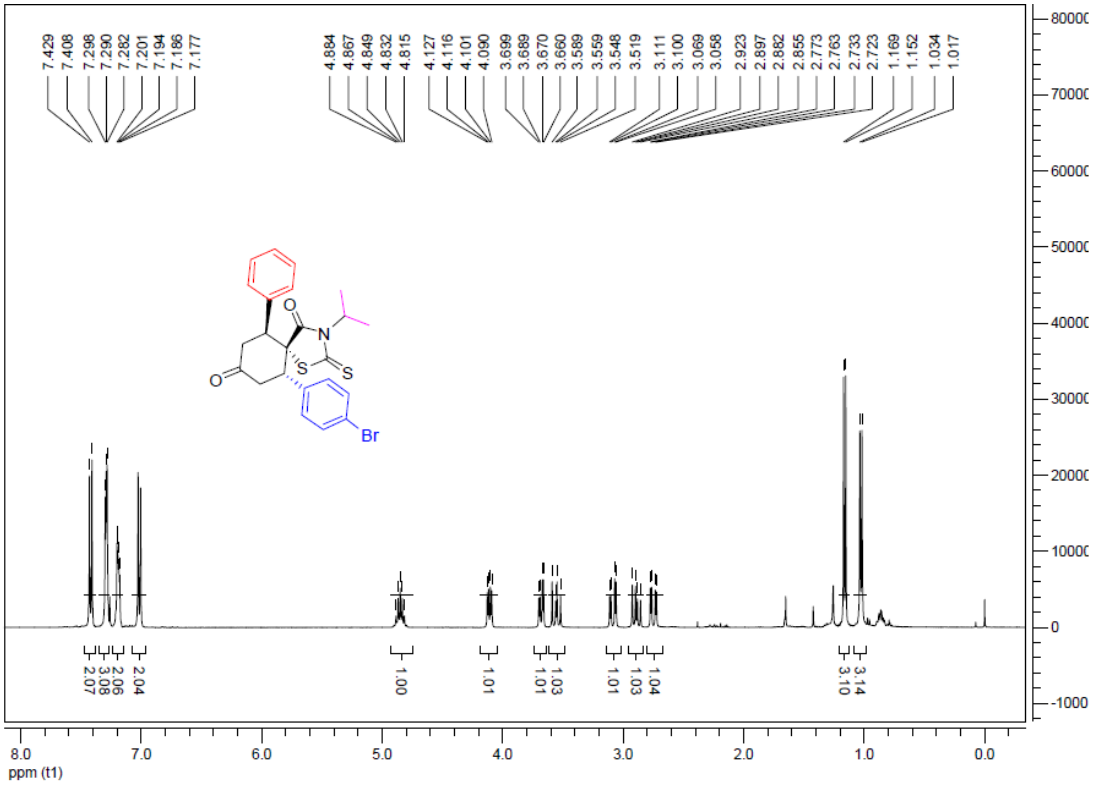


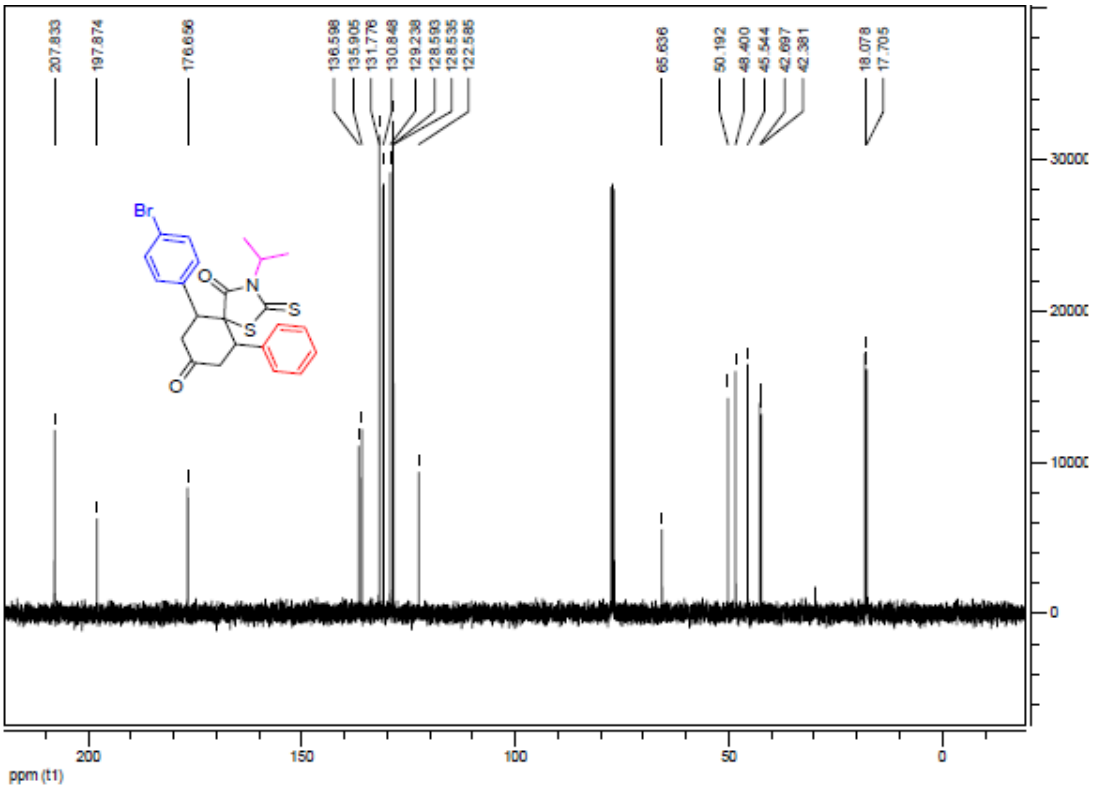
7p:(5S,6S,10S)-ethyl 4,8-dioxo-2-thioxo-10-m-tolyl-1-thia-3-azaspiro[4.5] decane-6-carboxylate



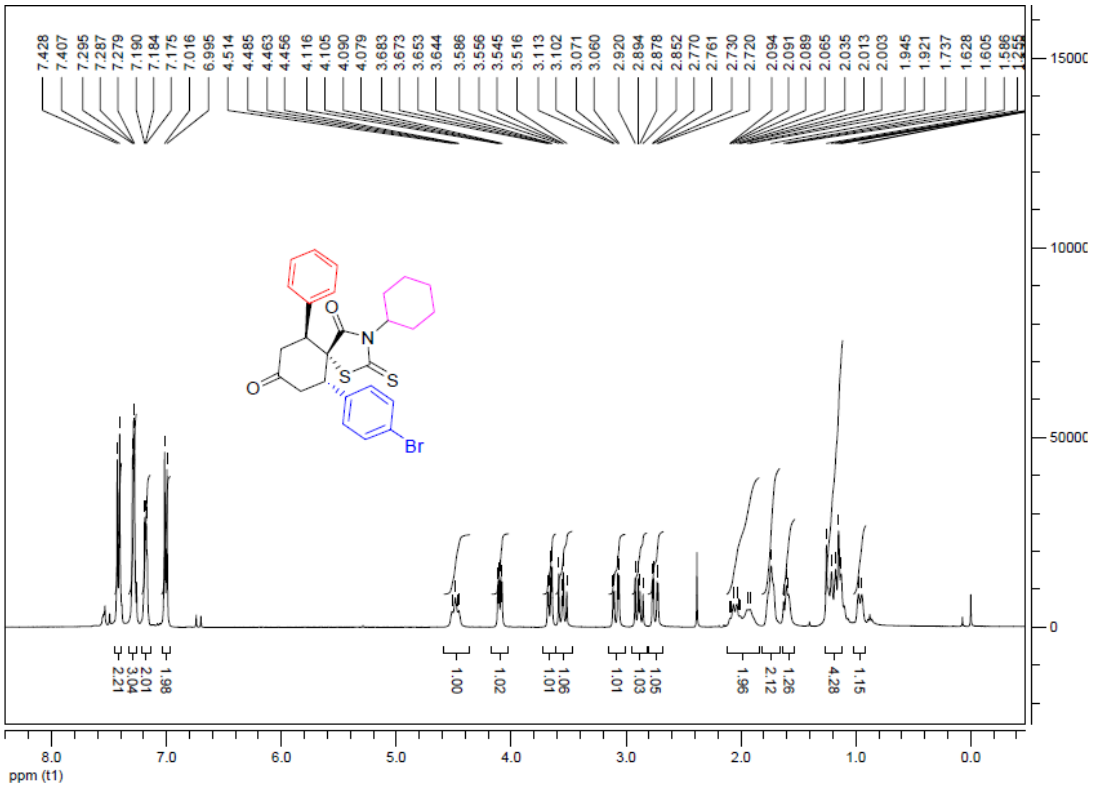


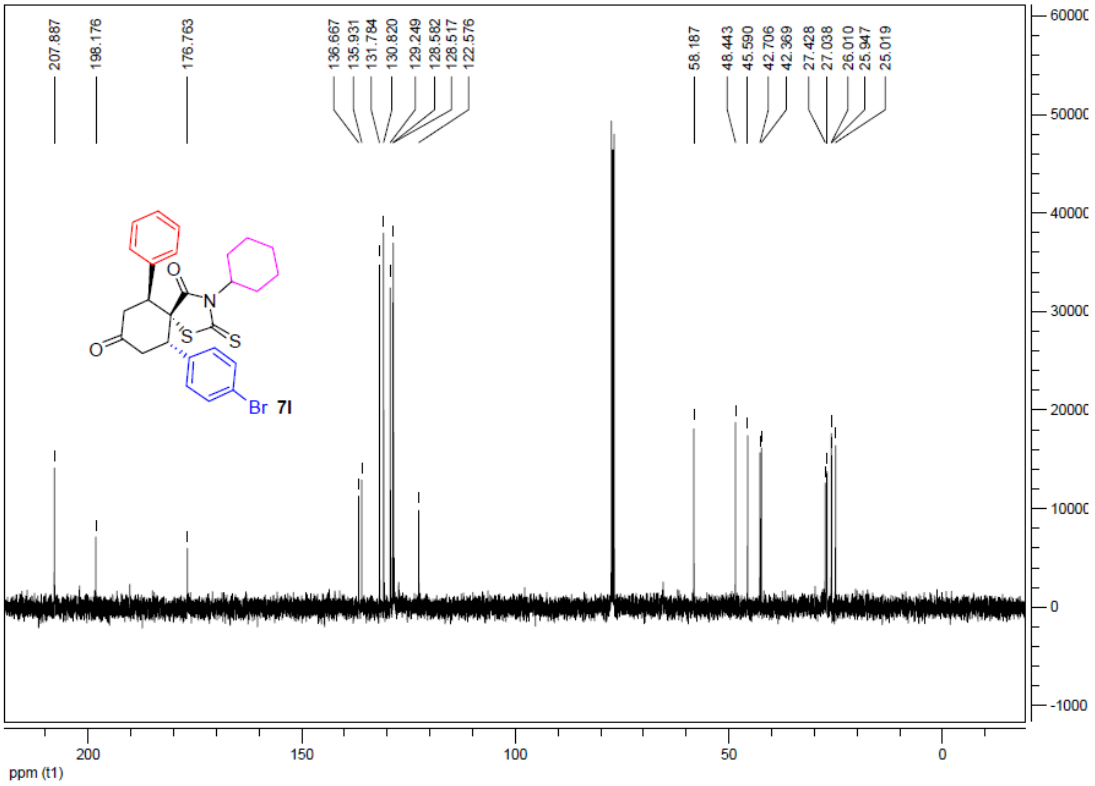
7q: (5S,6S,10S)-6-(4-bromophenyl)-3-isopropyl-10-phenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-4,8-dione



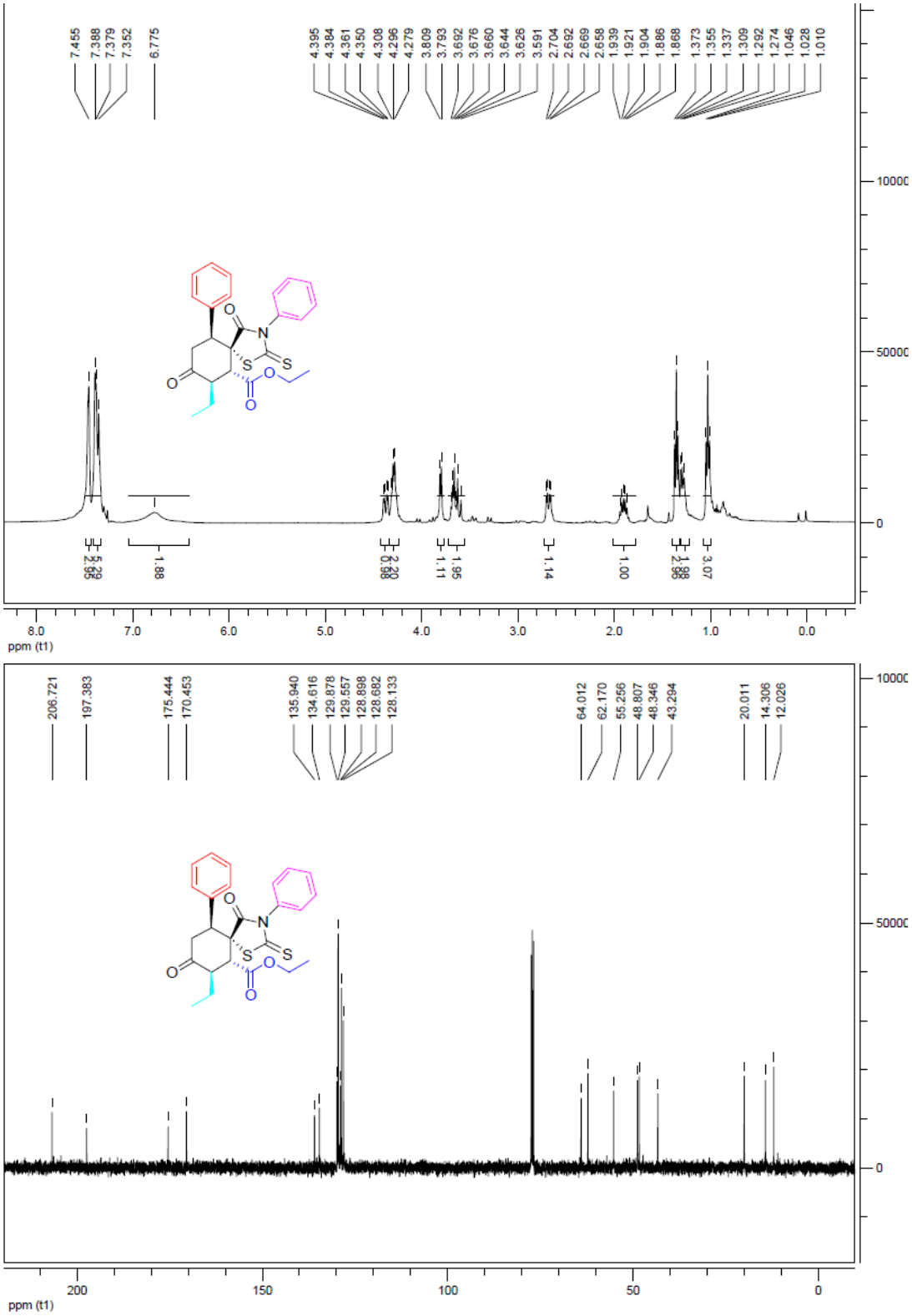


7r: (5S,6S,10S)-6-(4-bromophenyl)-3-cyclohexyl-10-phenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-4,8-dione

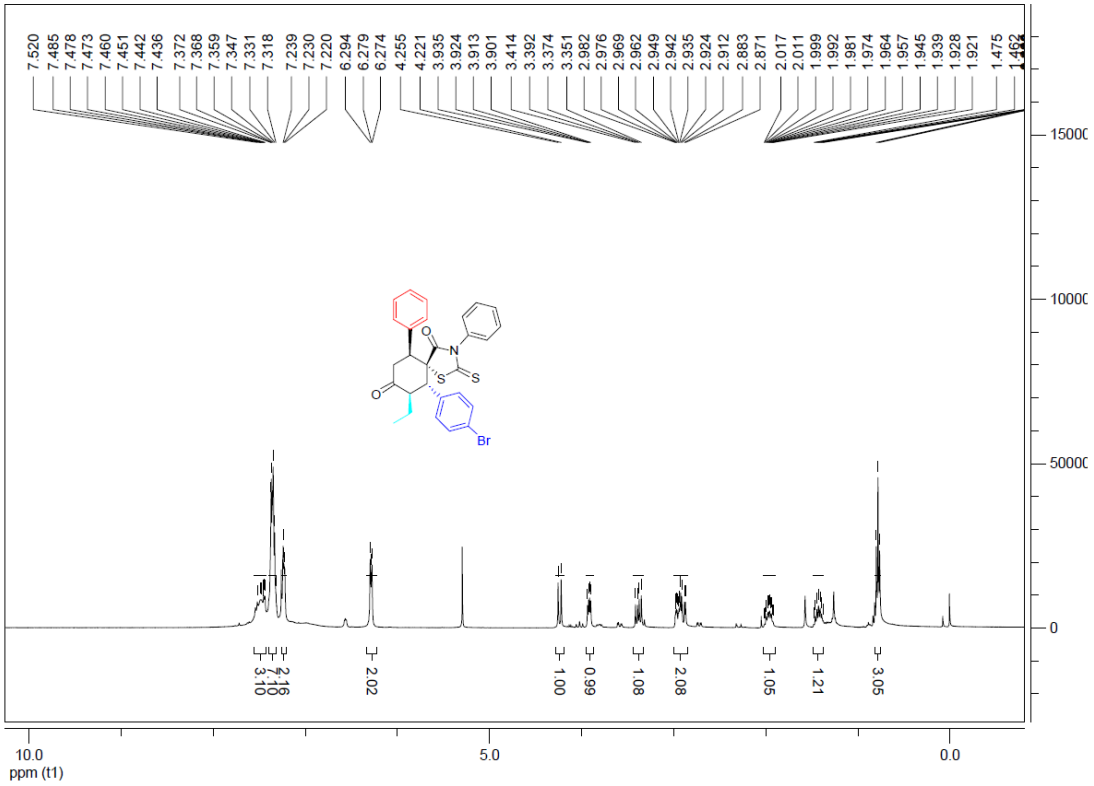


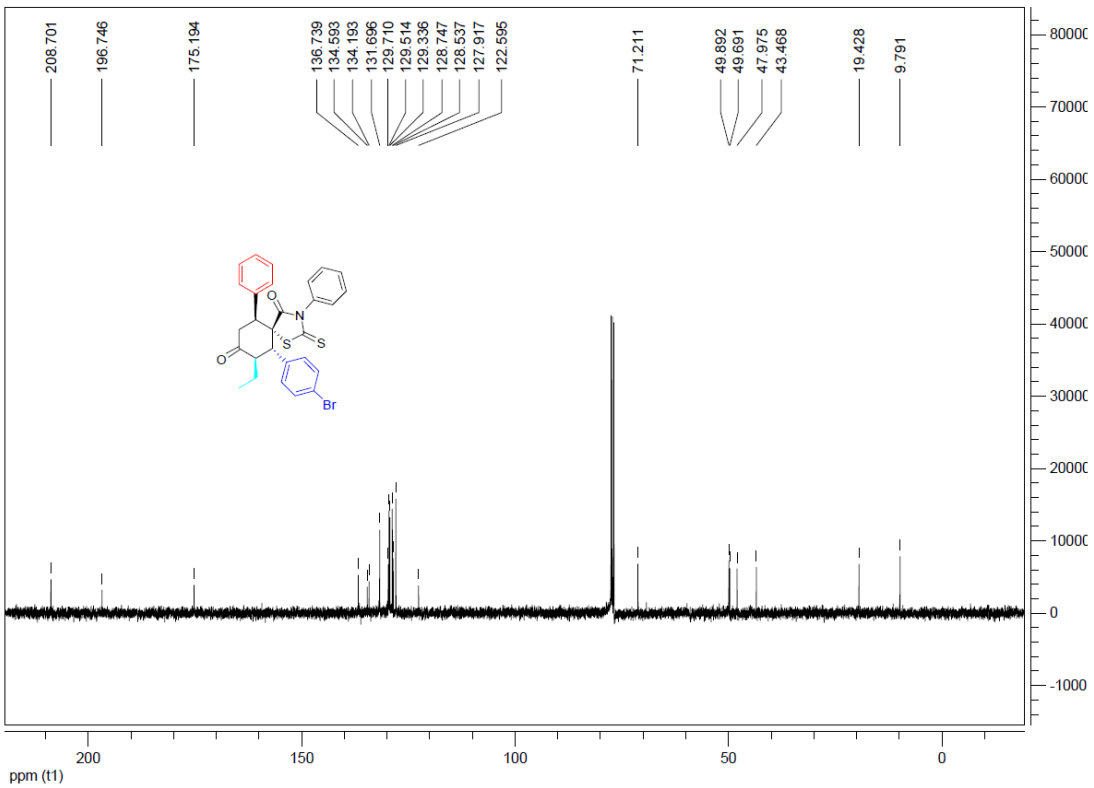


7s: (5S,6S,7R,10S)-ethyl 7-ethyl-4,8-dioxo-3,10-diphenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-6-carboxylate

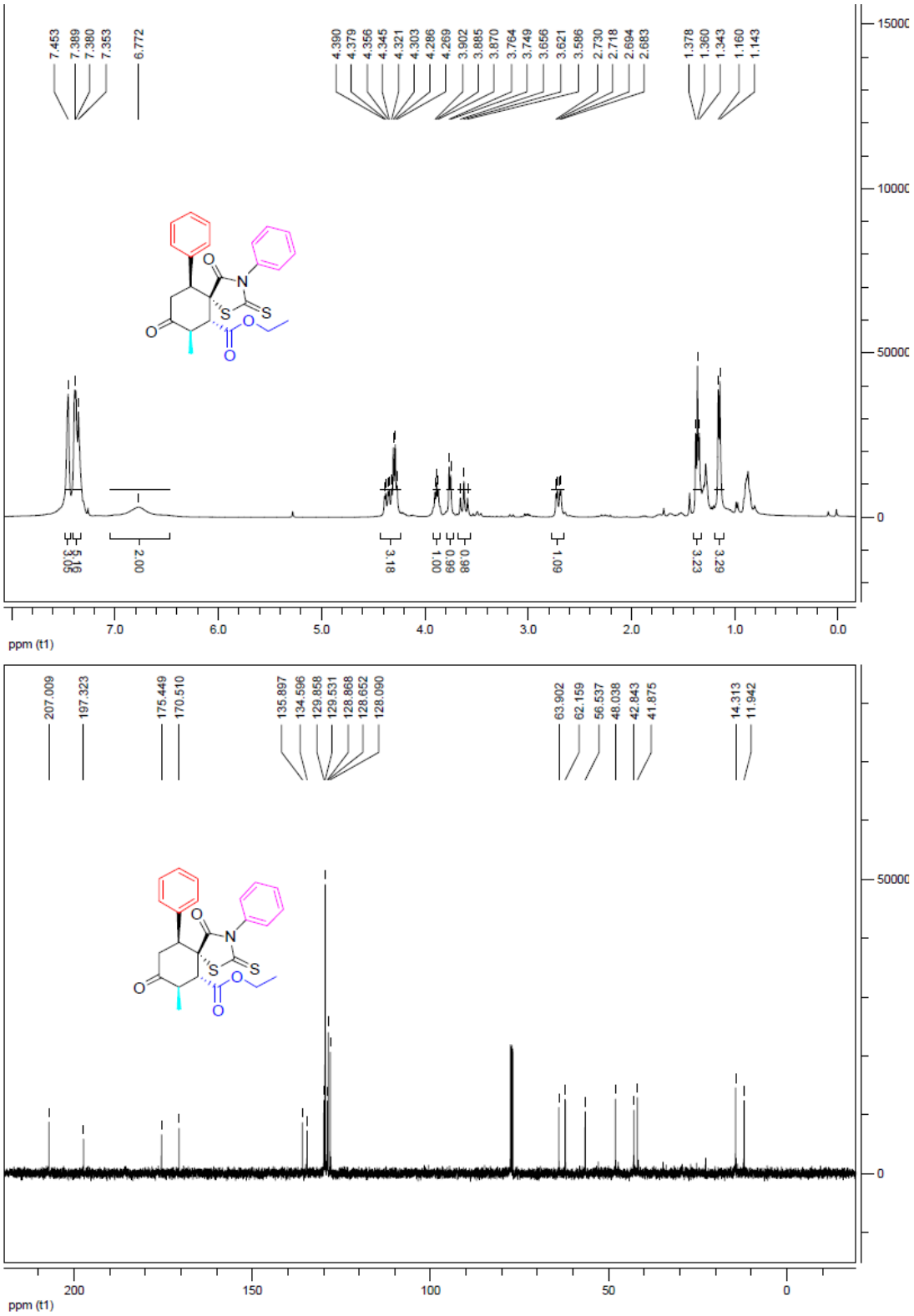


7t:(5S,6S,7R,10S)-10-(4-bromophenyl)-7-ethyl-3,6-diphenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-4,8-dione

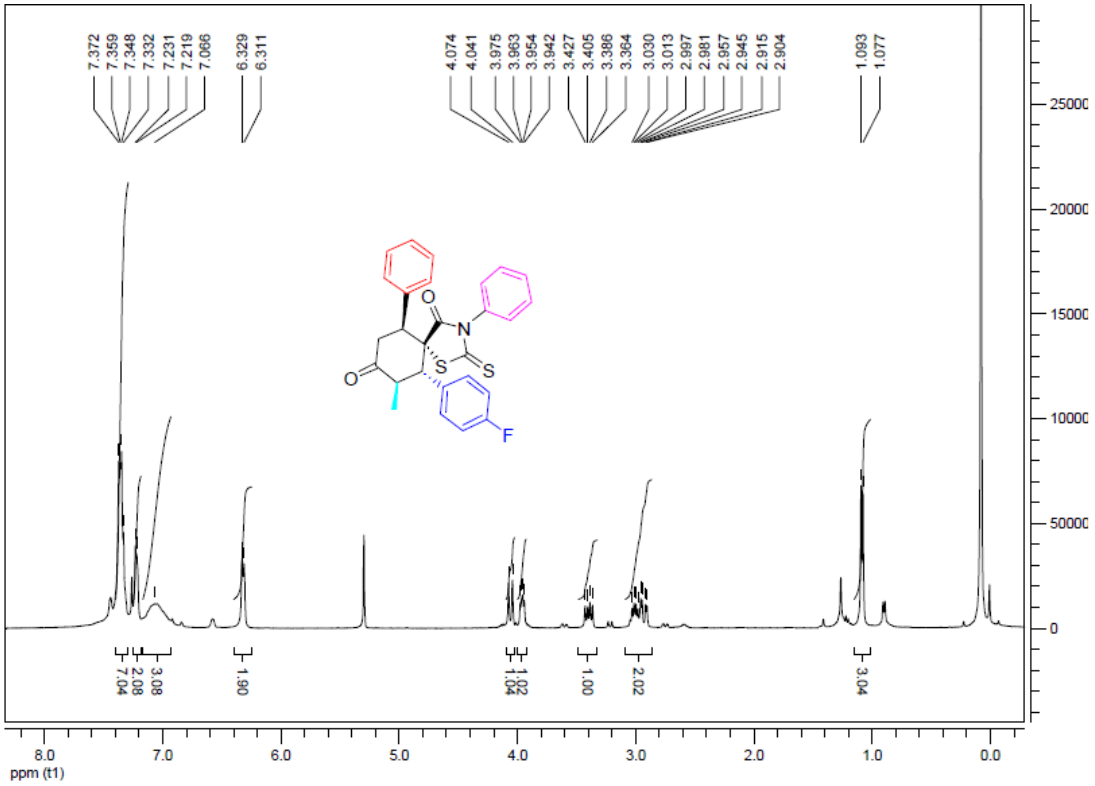


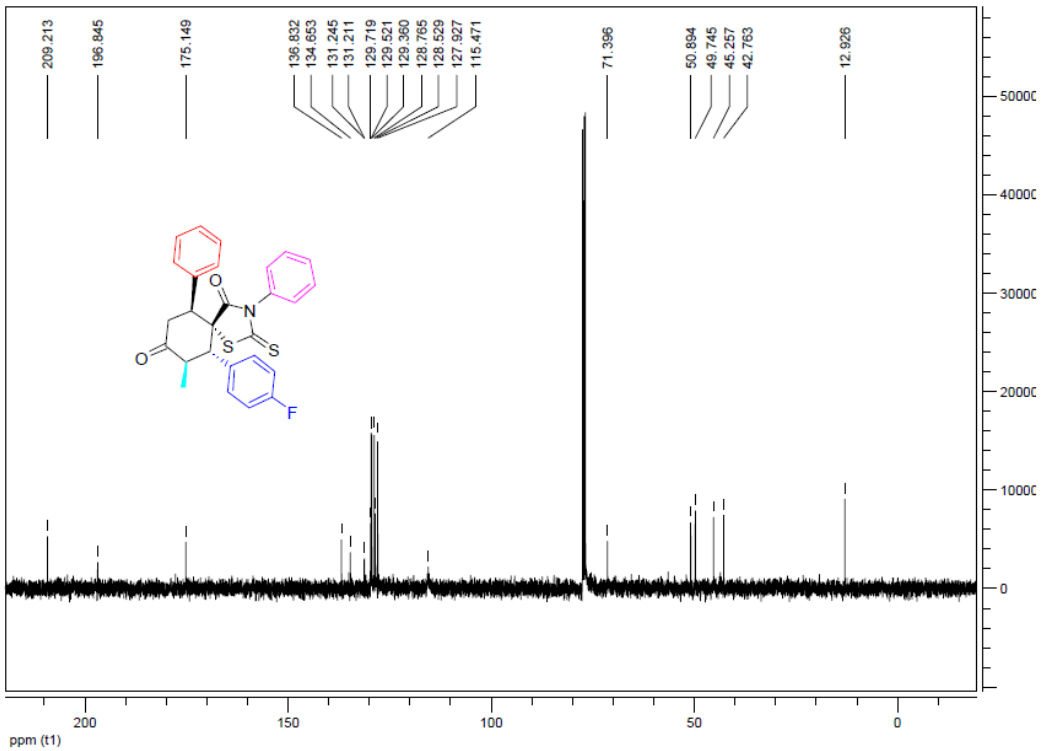


7u: (5S,6S,7R,10S)-ethyl 7-methyl-4,8-dioxo-3,10-diphenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-6-carboxylate

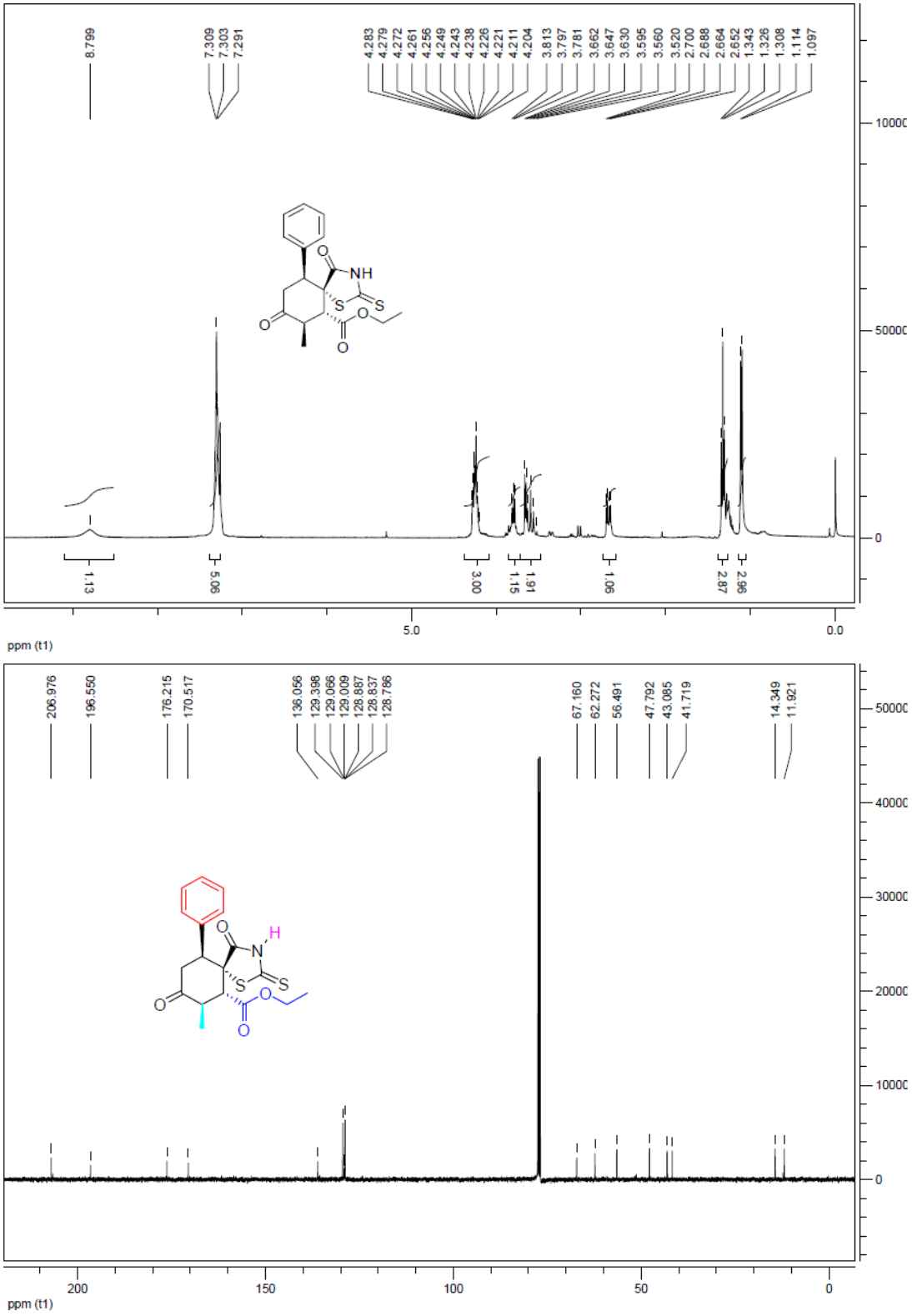


7v:(5S,6S,7R,10S)-6-(4-fluorophenyl)-7-methyl-3,10-diphenyl-2-thioxo-1-thia-3-azaspiro [4.5]decane-4,8-dione

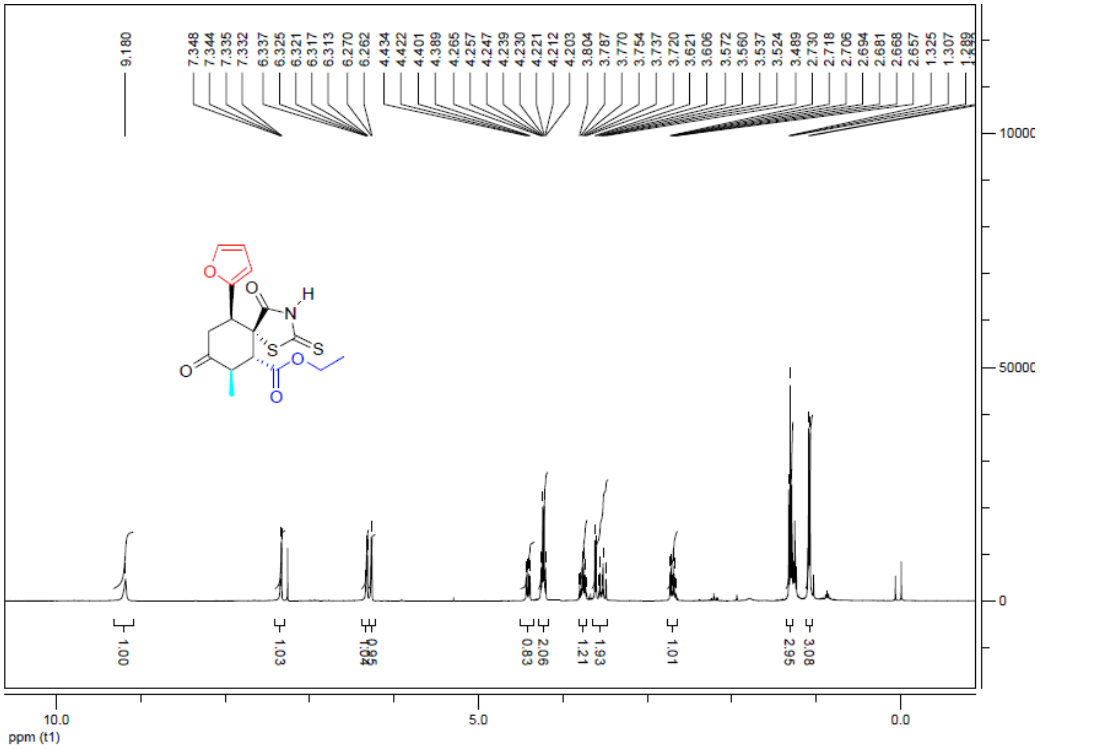


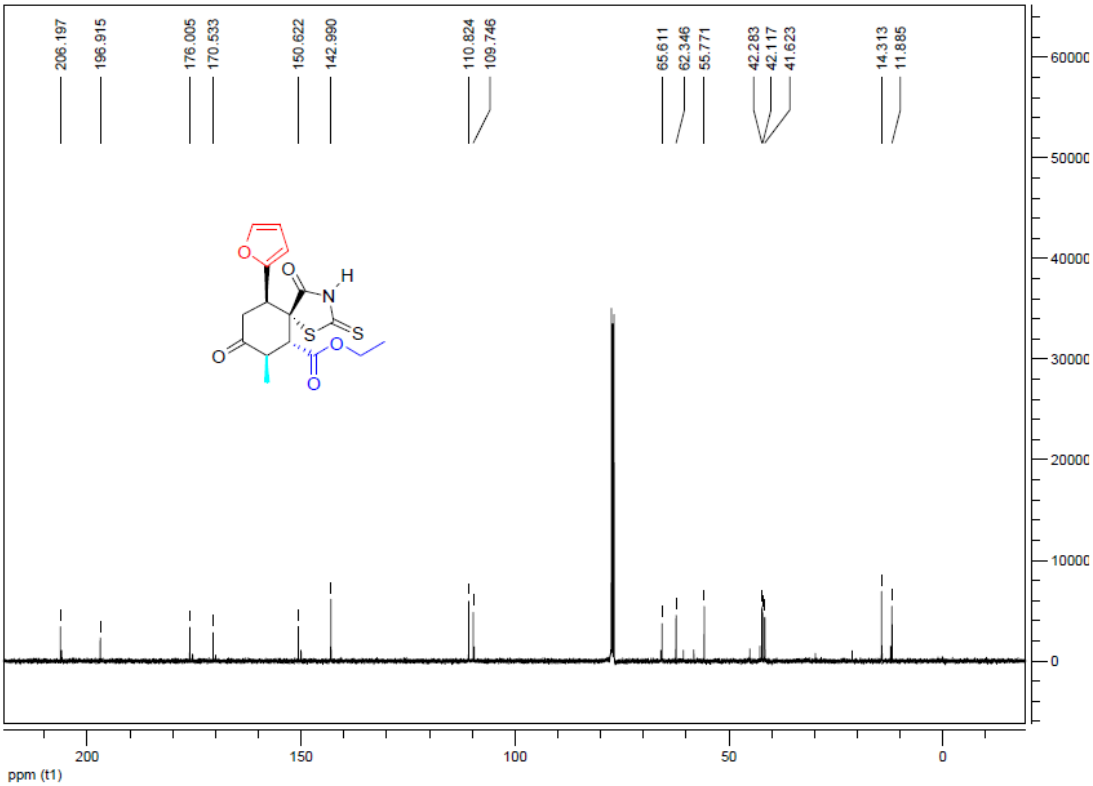


7w: (5S,6S,7R,10S)-ethyl 7-methyl-4,8-dioxo-10-phenyl-2-thioxo-1-thia-3-azaspiro[4.5] decane-6-carboxylate

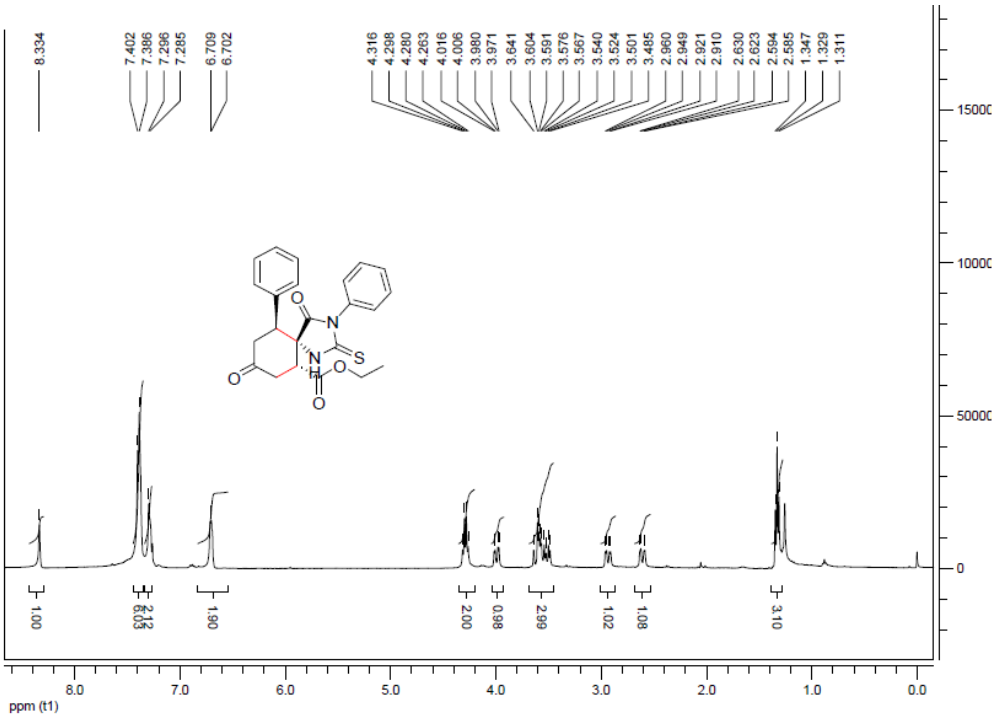


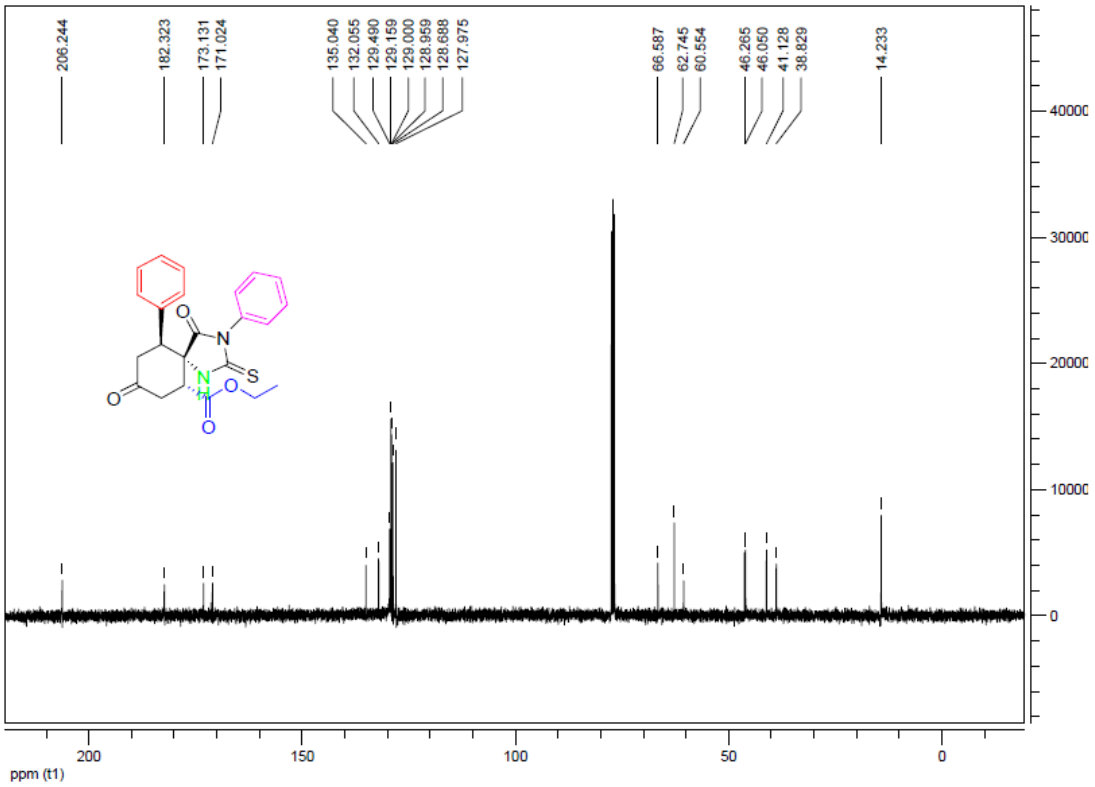
7x:(5S,6S,7R,10S)-ethyl 10-(furan-2-yl)-7-methyl-4,8-dioxo-2-thioxo-1-thia-3-azaspiro[4.5] decane-6-carboxylate



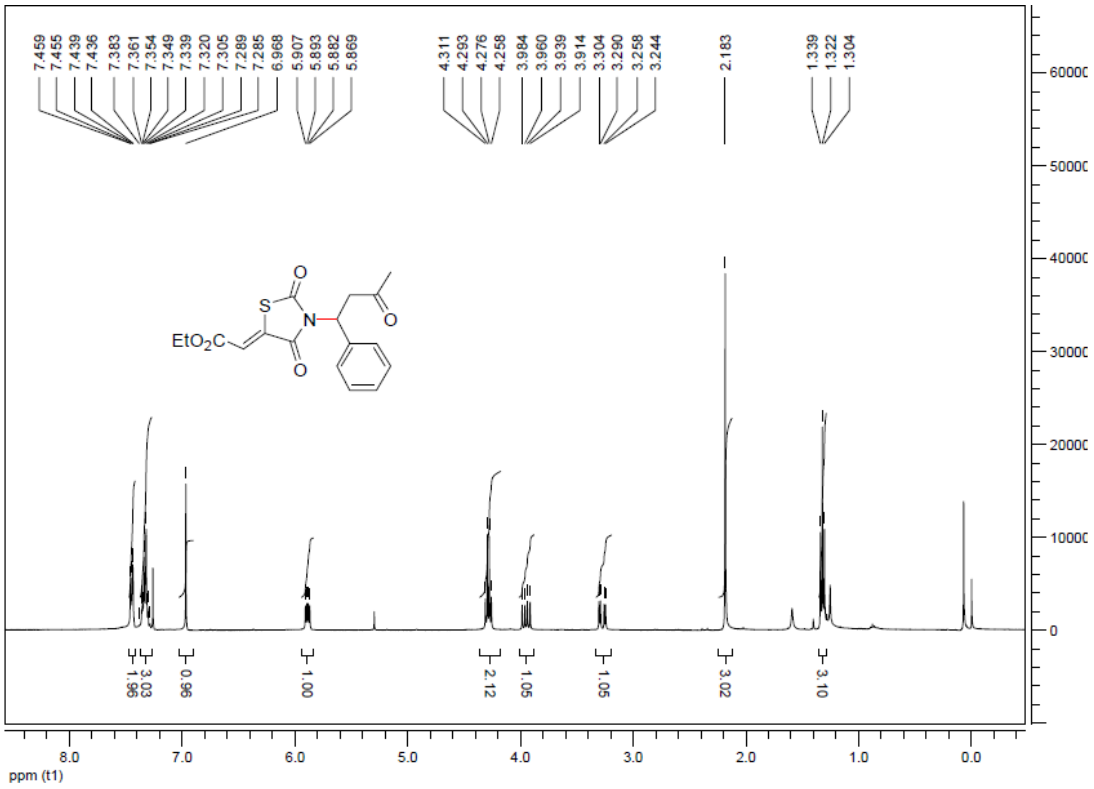


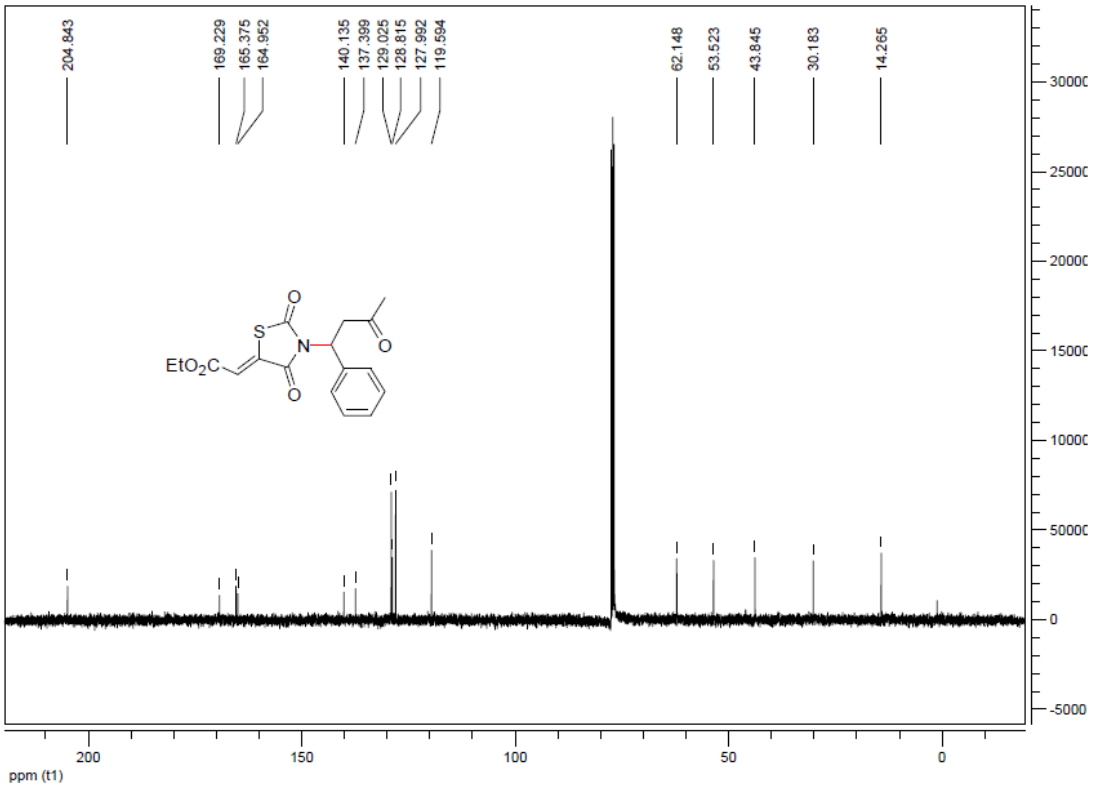
10: (5S,6R,10S)-ethyl 4,8-dioxo-3,10-diphenyl-2-thioxo-1,3-diazaspiro[4.5] decane-6-carboxylate



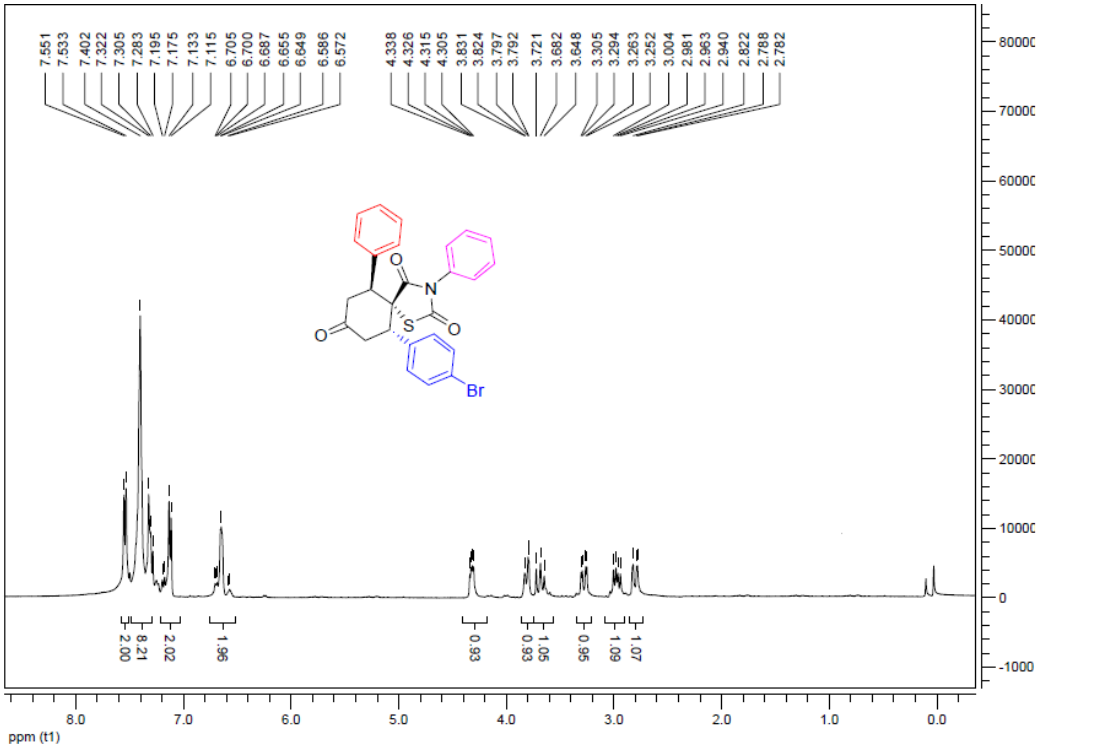


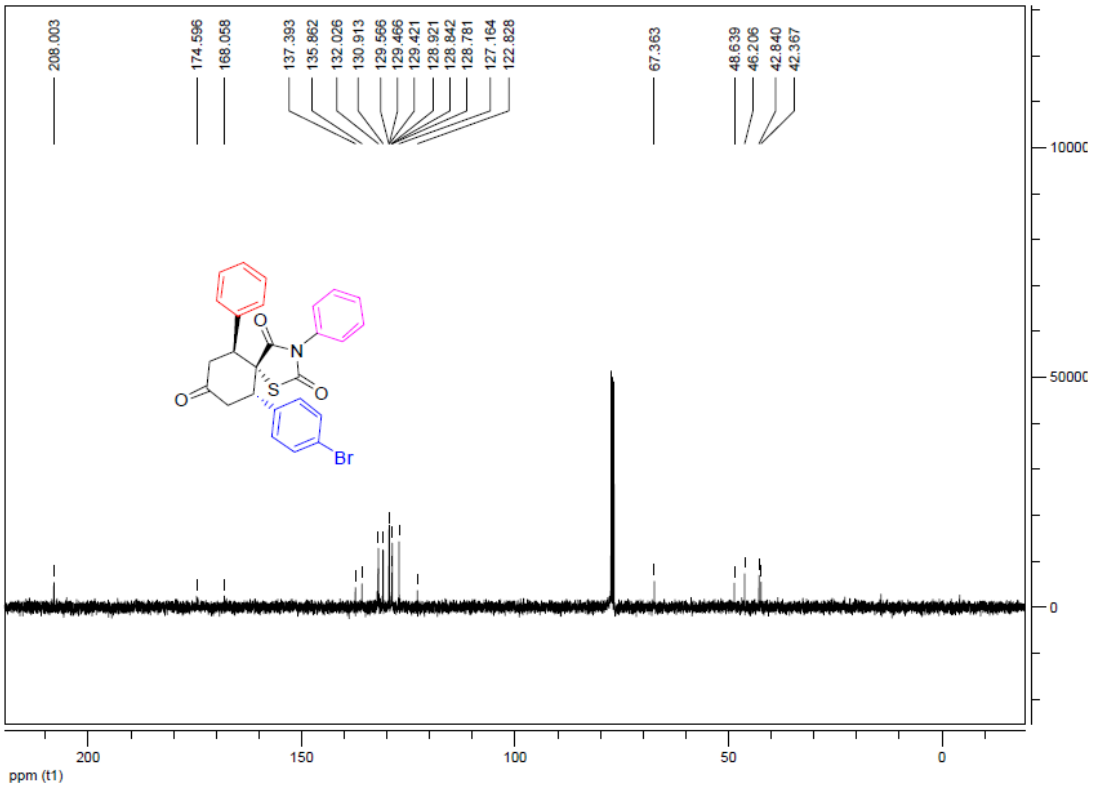
11:(Z)-ethyl 2-(2,4-dioxo-3-(3-oxo-1-phenylbutyl)thiazolidin-5-ylidene)acetate



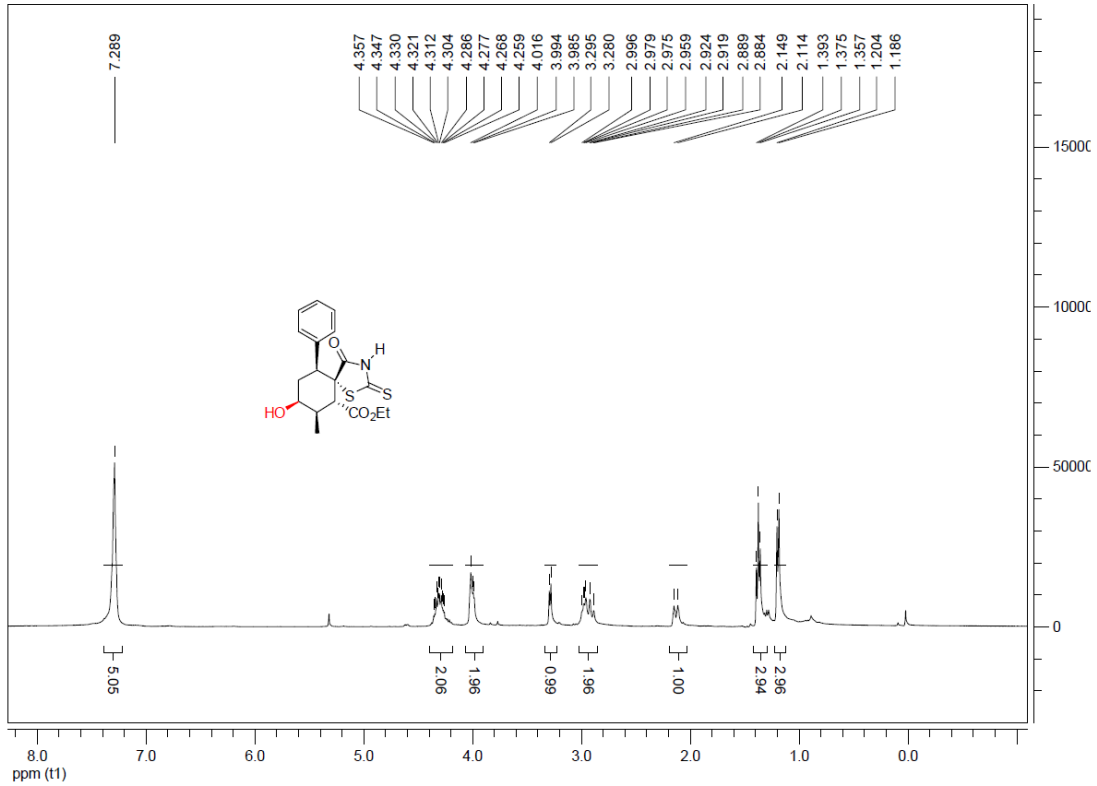


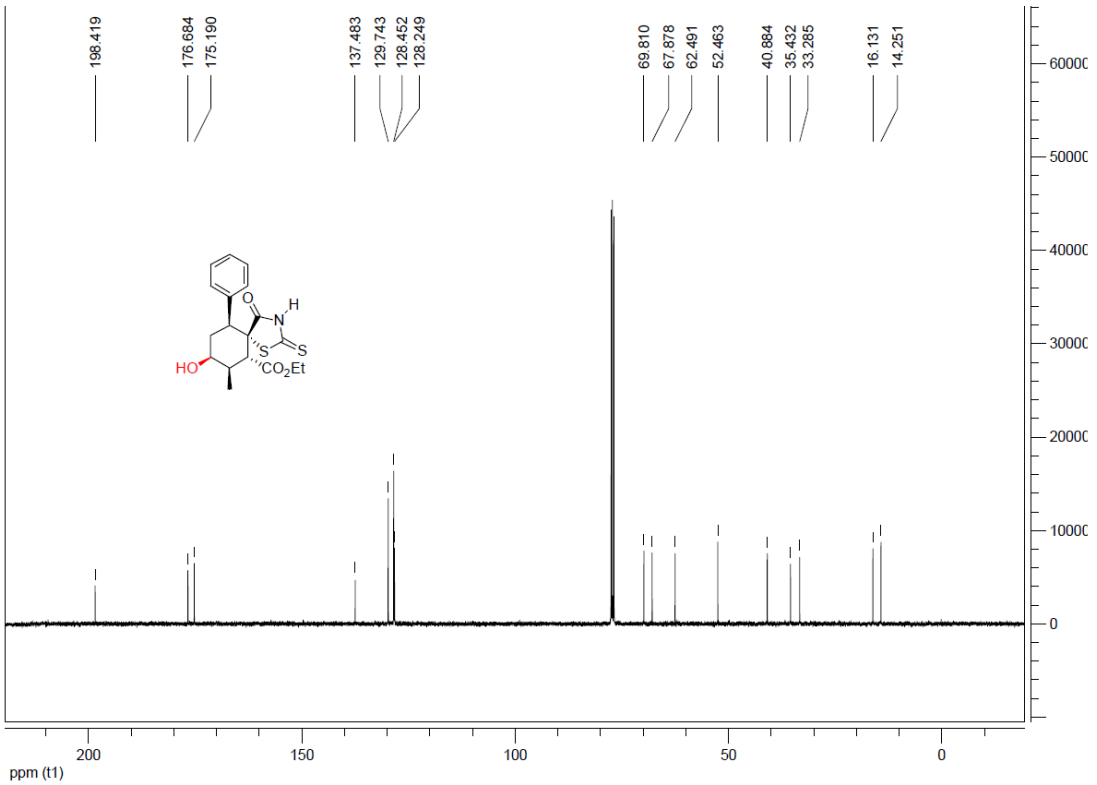
12:(5S,6S,10S)-6-(4-bromophenyl)-3,10-diphenyl-1-thia-3-azaspiro[4.5]decane-2,4,8-trione





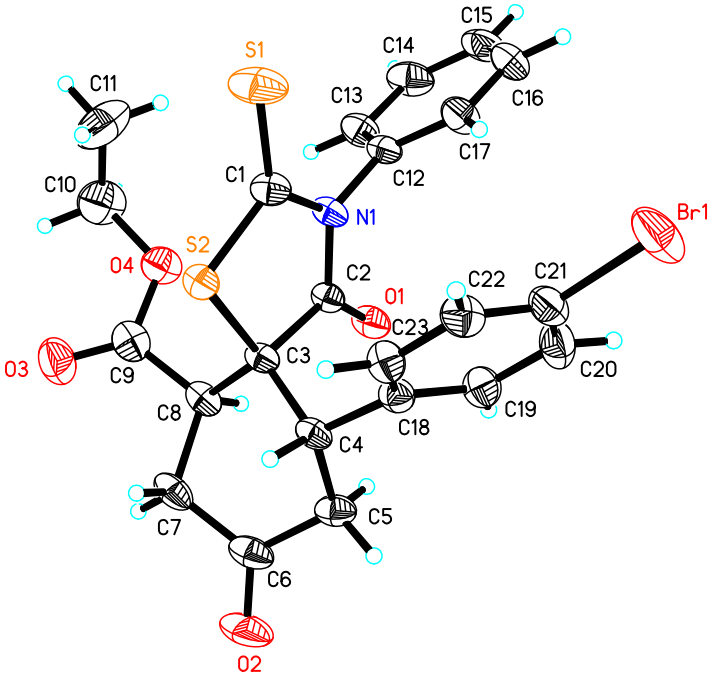
13:(5S,6S,7R,8R,10S)-ethyl 8-hydroxy-7-methyl-4-oxo-10-phenyl-2-thioxo-1-thia-3-azaspiro [4.5]decane-6-carboxylate

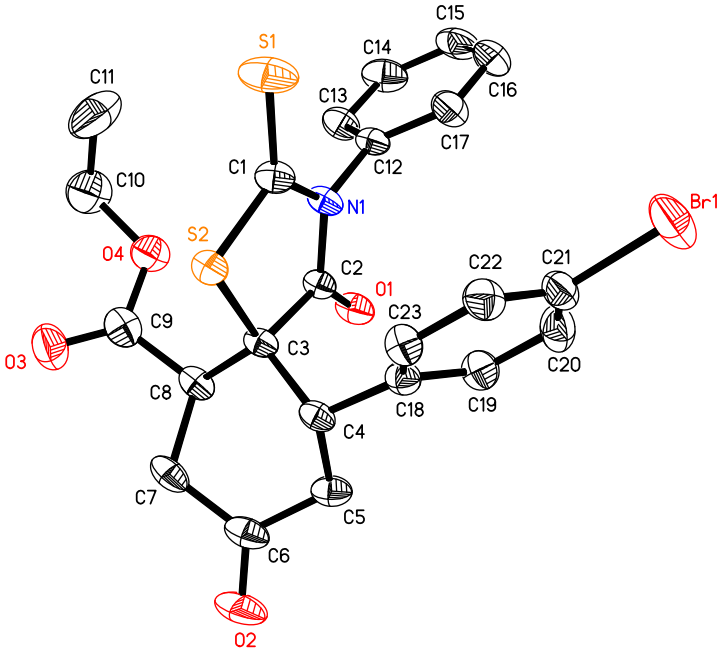


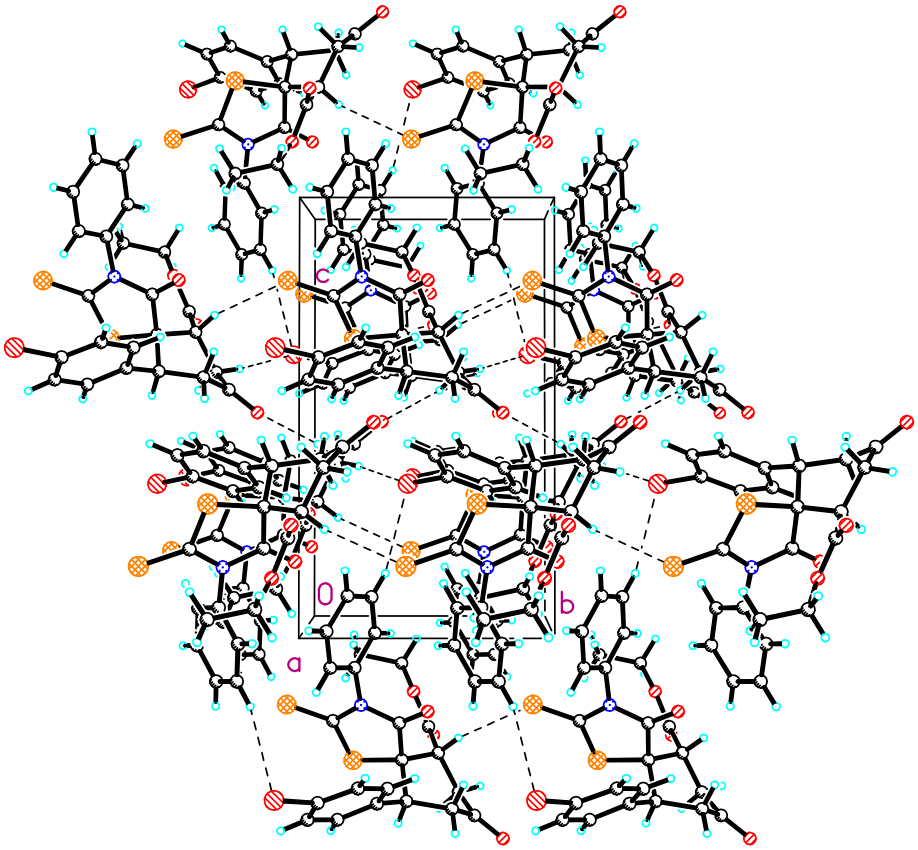


G: Absolute Configuration and X-Ray Analysis Data

7c: (5S,6S,10S)-ethyl 10-(4-bromophenyl)-4,8-dioxo-3-phenyl-2-thioxo-1-thia-3-azaspiro[4.5]decane-6-carboxylate







Crystal data and structure refinement for 7c.

Identification code	7c
Empirical formula	$C_{23}H_{20}BrNO_4S_2$
Formula weight	518.43
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic,
Space group	P2(1)
Unit cell dimensions	a = 9.9316(8) Å α = 90 °.
	b = 8.1197(7) Å β = 92.344(2) °.
	c = 14.0243(12) Å γ = 90 °.
Volume	1130.00(16) $Å^3$
Z,	2
Calculated density	1.524 Mg/m^3
Absorption coefficient	2.034 mm^{-1}
F(000)	528
Crystal size	0.281 x 0.269 x 0.157 mm^3
θ range for data collection	2.05 to 26.00 °.
Limiting indices	-10≤h≤12, -9≤k≤9, -17≤l≤13
Reflections collected / unique	5863 / 4267 [R_{int} = 0.0178]
Completeness to θ = 26.00°	99.9 %
Absorption correction（μ）	Empirical
Max. and min. transmission	1.00000 and 0.59422
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4267 / 2 / 281
Goodness-of-fit on F^2	0.982
Final R indices [I>2σ(I)]	R_1 = 0.0350, wR_2 = 0.0843
R indices (all data)	R_1 = 0.0404, wR_2 = 0.0867
Absolute structure parameter	0.024(7)
Largest diff. peak and hole	0.387 and -0.437 e^-. $Å^{-3}$