Photocatalytic Three-component Reaction for Synthesis of Dithiocarbamates

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1. General Information

General Remarks. Catalytic reactions were performed under air using pre-dried glasswares. Analytical TLC was performed with silica gel GF254 plates. For column chromatography, a 200-300 mesh silica gel was employed. Organic solutions were concentrated under reduced pressure using a rotary evaporator. Room temperature (r.t.) is 23-25 °C.

Materials. Unless otherwise noted below, all other compounds have been reported in the literature or are commercially available. Commercial reagents and analytical grade or anhydrous solvents were used without further purification. All photocatalysts are purchased from laajoo.com.

Instrumentation. Deuterated solvents were purchased from Cambridge Isotope Laboratories. ^{1}H NMR spectra were recorded on Bruker AVANCE III 400 and INOVA instruments with 400 MHz frequencies, and ^{13}C NMR spectra were recorded on Bruker AVANCE III 400 with 100 MHz frequencies. ^{19}F NMR spectra were recorded on a Bruker AVANCE III 400 spectrometer with a ^{19}F operating frequency of 376 MHz. Chemical shifts (δ) were reported in ppm relative to the residual solvent signal ($CDCl_3$ δ = 7.26 for ^{1}H NMR and δ = 77.0 for ^{13}C NMR; DMSO δ = 2.53 for ^{1}H NMR and δ =40.01 for ^{13}C NMR). Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), td (triplet of doublets) or m (multiplet). HRMS was obtained using a Q-TOF instrument equipped with an ESI source.

Light source in detail. The light source used for the photochemical experiments is a UV LED curing system (Figure S1), purchased from Shenzhen Heshengbang Technology Co., LTD (Product model: PLS-LED 100). The reaction vessel is borosilicate glass test tubes and no filters were applied. The distance from the light source to the irradiation vessel is 0.5-1 cm.

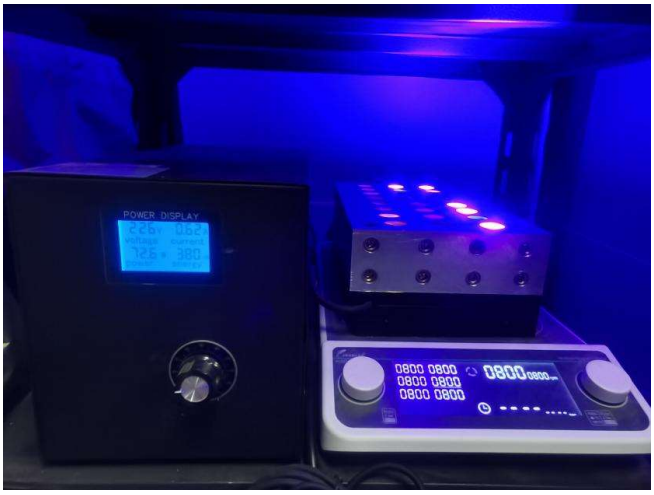


Figure S1. Reaction device

LED fixed lamp (Figure S2), 15-40 W ($\lambda = 420 \pm 15$ nm). Product model: PLS-LED 100. 3 W blue LED, purchased from taobao.COM. Manufacturer: Beijing Perfect light Technology Co., Ltd. (China). The reaction vessel is borosilicate glass test tubes and no filters were applied. The distance from the light source to the irradiation vessel is 4-5 cm.

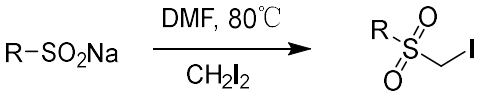
Figure S2. Photoreaction set-up for scale-up reaction.

2. General Procedures for the Synthesis of Products 4a

Mix the raw materials 1- [(iodomethyl)sulfonyl] -4-methylbenzene **1a** (0.1 mmol), carbon disulfide **2a** (0.4 mmol), morpholine **3a** (0.12 mmol), Cs_2CO_3 (0.2 mmol), and DMSO (2 mL) in a 4 mL transparent glass bottle, and react for 30 minutes under the illumination of a 3 W blue LED light. After 30 minutes, the mixture was concentrated

by rotary evaporation and the crude mixture was directly charged on silica gel and purified by column chromatography with petroleum ether/ethyl acetate as eluents to afford product **4a**.

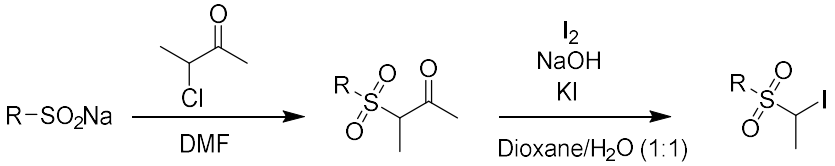
3. General Procedures A for the Synthesis of Compounds 1



1

Add sodium metabisulfite (5 mmol, 1 equiv) to a round-bottom flask containing 20 mL of N, N-dimethylformamide (DMF), stir at room temperature for 15 minutes, then add methylene iodide (6 mmol, 1.2 equiv). Stir the reaction at 80 °C for 20 hours. After the reaction is complete, quench the reaction mixture by adding it to 100 mL of water and extract the mixture three times, each with 50 mL of ethyl acetate (EA) The remaining organic phase is then extracted and washed separately with 50 mL of saturated brine and 50 mL of saturated sodium thiosulfate solution, taking the upper organic phase. Remove most of the solvent by rotary evaporation, and dry in an oven at 50 °C for 24 hours to obtain the product **1**. (**1a-1g**,**1i**)

4. General Procedures B for the Synthesis of Compounds 1

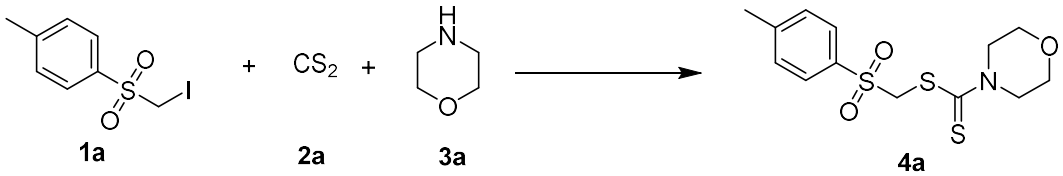


Add an equimolar amount of 3-chloroacetone (5 mmol, 1 equiv.) and sodium p-toluenesulfinate to a round-bottom flask containing 10 mL of DMF, stir at room temperature for 24 hours, then quench the reaction mixture by adding it to 50 mL of water and extract with 30 mL of ethyl acetate (EA) each for three times, retaining the organic phase. Drying and evaporation of solvent give the product.

In a beaker containing 5 mL of a 1,4-dioxane/water (1:1) mixture, add materials

synthesized in the previous step (2.5 mmol, 1 equiv), potassium iodide (20 mmol, 8 equiv), and iodine (10 mmol, 4 equiv.), then NaOH aqueous solution (1 M) was added until the color of iodine disappeared Stir the mixture for 30 minutes, then extract with 20 mL of dichloromethane each for three times. Evaporation of solvent from the organic phase and drying of the crude product in an oven at 50 °C for 24 hours afford the product **1h**.

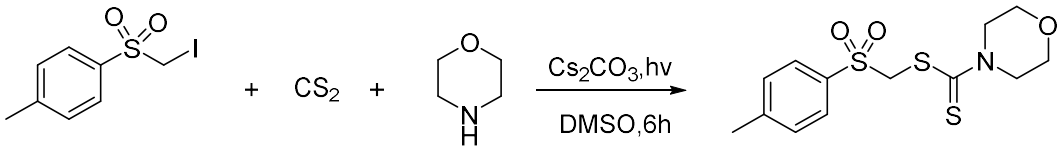
5. Condition optimization[a]



entry	base (n)	yield (%)[b]
1	0.1mmol	80
2	0.2mmol	88
3	0.3mmol	86
4	0.4mmol	87
5	0.5mmol	77

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.4 mmol), **3a** (0.12 mmol), Cs_2CO_3, DMSO (2 mL), r.t., 3 W blue LEDs, 30 minutes reaction time. [b]Isolated yield.

6. Gram-Scale Reaction



1a, 2.2195 g **2a**, 2.2783 g **3a**, 0.7836 g **4a**, 1.4648 g,59%

In a 250 ml round bottom flask, **1a** (2.2195 g, 7.5 mmol), **2a** (2.2783 g, 30 mmol), **3a** (0.7836 g, 9 mmol), and Cs_2CO_3 (4.8873 g, 15 mmol) were dissolved in DMSO (150 ml). The reactants were mixed evenly and then reacted under irradiation from a 42 W blue LEDs for 6h. After reaction, the mixture was extracted with ethyl acetate (3×100 mL), and the combined organic extract was washed with saline (300 mL), dried with

anhydrous sodium sulfate and then concentrated in vacuo. The crude mixture was directly purified by column chromatography on silica gel (EA: PE =1:1) by flash column to obtain the desired product **4a** (1.4648 g, 59%).

7. Sunlight reaction

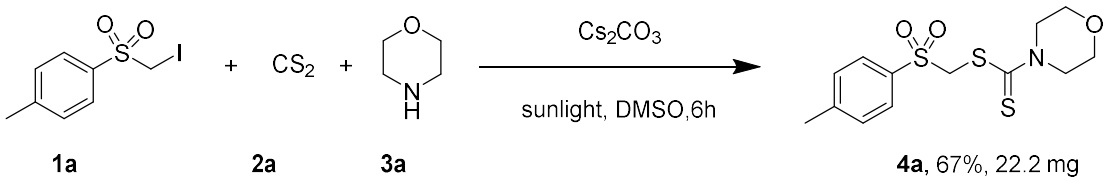
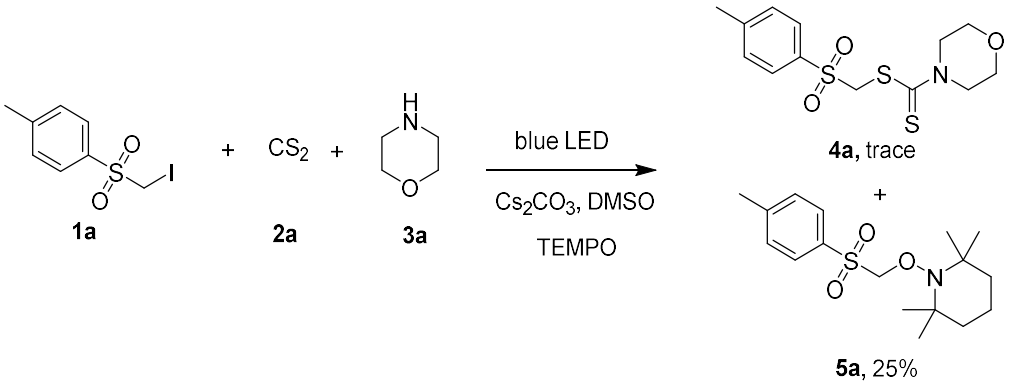


Figure S3. Sunlight reaction

Compound **1a** (0.1 mmol, 1.0 equiv), **2a** (0.4 mmol, 2.0 equiv), **3a** (0.12 mmol, 1.2 equiv), and cesium carbonate (Cs_2CO_3, 0.2 mmol, 2.0 equiv) was added to a 4 mL transparent glass vial containing a magnetic stir bar. Anhydrous dimethyl sulfoxide (2.0 mL) was then added to the vial using a syringe. The reaction mixture was stirred under direct sunlight for 6 hours (location: Hangzhou, longitude 118° E, latitude 29° N, starting at 10:00 a.m. in January). After 6 hours, the reaction mixture was extracted with ethyl acetate (3×10 mL), washed twice with water (40 mL each time), and then washed with brine (40 mL). The organic layer was dried over anhydrous sodium sulfate, and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel, eluting with hexane/ethyl acetate, to afford the desired product **4a** (67%, 22.2mg).

8. Control experiments

a) The radical trapping experiments



The raw materials 1-[(iodomethyl) sulfonyl] -4-methylbenzene **1a** (0.1 mmol), carbon disulfide **2a** (0.4 mmol), morpholine **3a** (0.12 mmol), Cs_2CO_3 (0.2 mmol), TEMPO (1 mmol) and DMSO (2 mL) were mixed in a 4 mL transparent glass bottle, and reacted for 30 minutes under the illumination of a 3 W blue LED light. After the reaction, only a little target product **4a** was detected, and the reaction was basically inhibited.

9. Mechanistic investigation

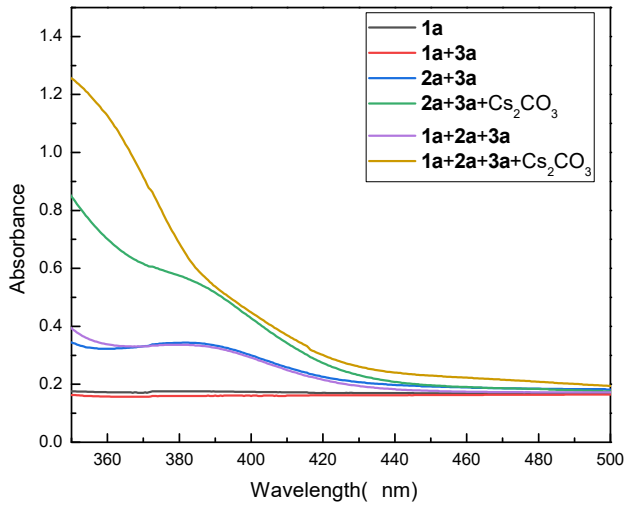
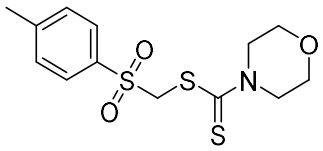


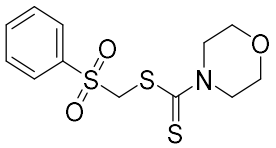
Figure S4. UV-vis Spectroscopic Measurements on Various Combinations of **1a** (0.05M)**, 2a** (0.2M)**, 3a** (0.06M) and Cs_2CO_3 (0.1M) in DMSO

The UV/Vis absorption spectra of different combinations of 1-[(iodomethyl) sulfonyl]-4-methylbenzene (**1a**), carbon disulfide (**2a**) with and morpholine (**3a**) in DMSO were recorded in 1 cm path quartz cuvettes by using a SHIMADZU UV-3600 UV-visible spectrophotometer, respectively. The long wavelength bands in UV/vis absorption spectra were shown in Figure S4.

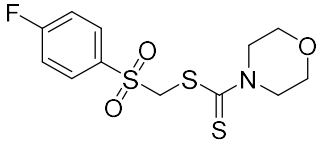
10. Characterization Data



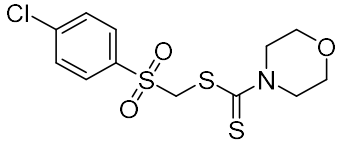
tosylmethyl morpholine-4-carbodithioate (4a). brown oil (88%, 29.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.25 (s, 2H), 4.21 (s, 2H), 3.99 (s, 2H), 3.74-3.66 (m, 4H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.2, 145.3, 134.8, 129.7, 129.2, 66.2, 59.5, 21.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{17}NO_3S_3$ 332.0444; Found: 332.0458.



(phenylsulfonyl)methyl morpholine-4-carbodithioate (4b). brown oil (91%, 28.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.2 Hz, 2H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 5.28 (s, 2H), 4.19 (s, 2H), 3.98 (s, 2H), 3.74-3.62 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.1, 137.7, 134.2, 129.3, 129.1, 66.2, 59.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{15}NO_3S_3$ 318.0287; Found: 318.0290.

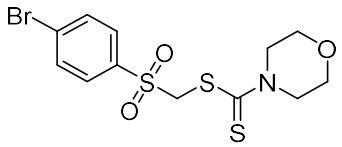


((4-fluorophenyl) sulfonyl) methyl morpholine-4-carbodithioate (4c). yellow solid (74%, 28.8 mg), m.p. 114-115℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-7.85 (m, 2H), 7.21 (t, *J* = 8.5 Hz, 2H), 5.27 (s, 2H), 4.19 (s, 2H), 3.97 (s, 2H), 3.75-3.69 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 167.5, 165.0, 133.6, 132.3, 132.2, 116.5, 116.3, 66.1, 59.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.57. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{14}FNO_3S_3$ 336.0193; Found: 336.0203.

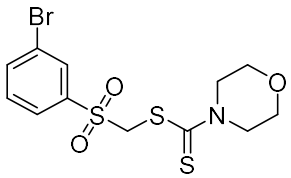


((4-chlorophenyl) sulfonyl) methyl morpholine-4-carbodithioate (4d). yellow solid (88%, 33.4 mg), m.p. 107-108℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.6 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 2H), 5.29 (s, 2H), 4.21 (s, 2H), 3.96 (s, 2H), 3.79-3.66 (m,

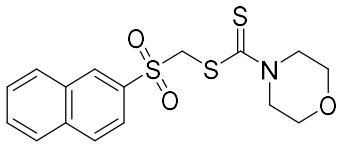
4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 141.1, 136.0, 130.8, 129.3, 59.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{14}ClNO_3S_3$ 351.9898; Found: 351.9899.



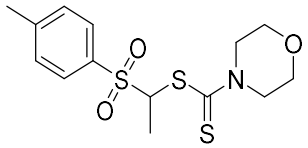
((4-bromophenyl) sulfonyl) methyl morpholine-4-carbodithioate (4e). yellow solid (75%, 29.7 mg), m.p. 142-143℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.6 Hz, 2H), 7.68 (d, *J* = 8.6 Hz, 2H), 5.28 (s, 2H), 4.21 (s, 2H), 3.96 (s, 2H), 3.80-3.60 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 136.5, 132.3, 130.9, 129.7, 59.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{14}BrNO_3S_3$ 395.9392; Found: 395.9393.



((3-bromophenyl) sulfonyl) methyl morpholine-4-carbodithioate (4f). yellow solid (69%, 29.7 mg), m.p. 121-122℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.42 (t, *J* = 7.9 Hz, 1H), 5.28 (s, 2H), 4.18 (s, 2H), 3.98 (s, 2H), 3.72 (t, *J* = 4.9 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.4, 139.3, 137.2, 132.3, 130.6, 128.0, 122.8, 66.2, 59.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{14}BrNO_3S_3$ 395.9392; Found: 395.9390.

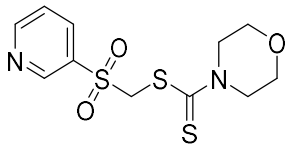


(naphthalen-2-ylsulfonyl) methyl morpholine-4-carbodithioate (4g). yellow solid (83%, 35.0 mg), m.p. 103-104℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 1.7 Hz, 1H), 8.08-7.86 (m, 4H), 7.77-7.46 (m, 2H), 5.35 (s, 2H), 3.99 (d, *J* = 45.5 Hz, 4H), 3.56 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 135.6, 134.4, 131.9, 131.4, 129.6, 129.5, 129.3, 128.1, 127.8, 123.7, 66.1, 59.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{17}NO_3S_3$ 368.0444; Found: 368.0451.

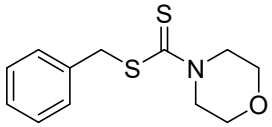


1-tosylethyl morpholine-4-carbodithioate (4h). brown oil (39%, 16.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 5.92 (q, *J* = 7.3

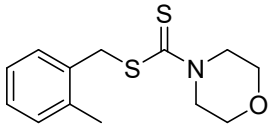
Hz, 1H), 4.41-3.84 (m, 4H), 3.70 (s, 4H), 2.45 (s, 4H), 1.76 (d, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.7, 145.1, 133.9, 129.9, 129.7, 129.6, 129.3, 68.6, 66.2, 21.8, 15.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{19}NO_3S_3$ 346.0600; Found: 346.0604.



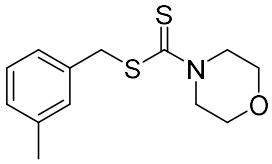
(pyridin-3-ylsulfonyl) methyl morpholine-4-carbodithioate (4i). yellow solid (93%, 30.0 mg), m.p. 99-100℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (s, 1H), 8.84 (d, J = 5.1 Hz, 1H), 8.23 (d, J = 8.1 Hz, 1H), 7.48 (dd, J = 8.0, 4.8 Hz, 1H), 5.31 (s, 2H), 4.12 (s, 2H), 3.97 (s, 2H), 3.69 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.1, 154.5, 150.3, 137.2, 133.8, 123.7, 66.1, 59.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{11}H_{14}N_2O_3S_3$ 319.0240; Found: 319.0250.



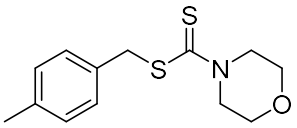
benzyl morpholine-4-carbodithioate(4j). yellow oil (50%, 12.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, J = 8.0, 1.6 Hz, 2H), 7.30-7.21 (m, 3H), 4.53 (s, 2H), 4.28 (s, 2H), 3.88 (s, 2H), 3.69 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.2, 135.8, 129.5, 128.7, 127.7, 66.3, 42.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{15}NOS_2$ 254.0668; Found: 254.0675.



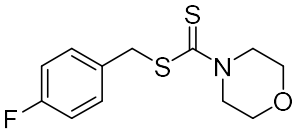
2-methylbenzyl morpholine-4-carbodithioate(4k). yellow oil (82%, 21.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 7.4 Hz, 1H), 7.18 (dhept, J = 9.1, 1.8 Hz, 3H), 4.54 (s, 2H), 4.35 (s, 2H), 3.93 (s, 2H), 3.75 (s, 4H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 137.5, 133.1, 130.6, 130.5, 128.2, 126.3, 66.3, 40.8, 19.42. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{17}NOS_2$ 268.0824; Found: 268.0832.



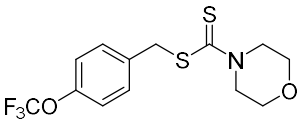
3-methylbenzyl morpholine-4-carbodithioate(4l). yellow oil (63%, 16.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.22 (m, 3H), 7.15 (d, *J* = 7.0 Hz, 1H), 4.61 (s, 2H), 4.40 (s, 2H), 4.00 (s, 2H), 3.81 (s, 4H), 2.41(s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.3, 138.4, 135.6, 130.2, 128.6, 128.5, 126.5, 66.3, 42.2, 21.6. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{17}NOS_2$ 268.0824; Found: 268.0830.



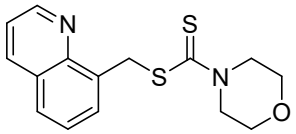
4-methylbenzyl morpholine-4-carbodithioate(4m). yellow oil (45%, 12.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 4.54 (s, 2H), 4.33 (s, 2H), 3.93 (s, 2H), 3.75 (s, 4H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 137.5, 132.6, 129.4, 129.3, 66.3, 41.9, 21.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{17}NOS_2$ 268.0824; Found: 268.0831.



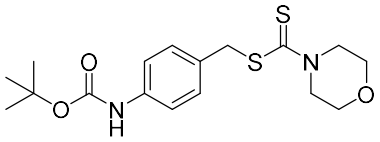
4-fluorobenzyl morpholine-4-carbodithioate(4n). yellow oil (44%, 11.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 8.4, 5.5 Hz, 2H), 6.99 (t, *J* = 8.6 Hz, 2H), 4.55 (s, 2H), 4.32 (s, 2H), 3.92 (s, 2H), 3.74 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 163.5, 161.0, 131.8, 131.7, 131.1, 131.0, 115.4, 66.3, 41.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.6. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{14}FNOS_2$ 272.0574; Found: 272.0579.



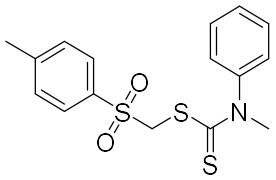
4-(trifluoromethoxy) benzyl morpholine-4-carbodithioate(4o). yellow oil (77%, 26.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 8.6 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 4.55 (s, 2H), 4.34 (s, 2H), 3.92 (s, 2H), 3.76 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6, 148.6, 135.0, 130.8, 121.8, 121.1, 119.20, 66.3, 40.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{14}F_3NO_2S_2$ 338.0491; Found: 338.0494.



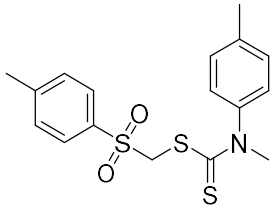
quinolin-8-ylmethyl morpholine-4-carbodithioate(4p). yellow oil (74%, 22.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.14 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.97 (d, *J* = 7.1 Hz, 1H), 7.75 (d, *J* = 6.8 Hz, 1H), 7.53-7.37 (m, 2H), 5.31 (s, 2H), 4.31 (s, 2H), 3.92 (s, 2H), 3.70 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.3, 149.8, 146.6, 136.5, 135.2, 130.6, 128.5, 127.9, 126.5, 121.3, 66.3, 37.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{16}N_2OS_2$ 305.0777; Found: 305.0784.



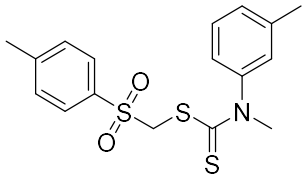
4-((tert-butoxycarbonyl) amino) benzyl morpholine-4-carbodithioate(4q). yellow oil (57%, 21.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.32-7.26 (m, 2H), 7.09 (d, *J* = 7.0 Hz, 1H), 6.60 (s, 1H), 4.58 (s, 2H), 4.37 (s, 2H), 3.97 (s, 2H), 3.79 (s, 4H), 1.55(s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 137.5, 132.6, 129.4, 129.3, 66.3, 41.9, 21.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{24}N_2O_3S_2$ 369.1301; Found: 369.1308.



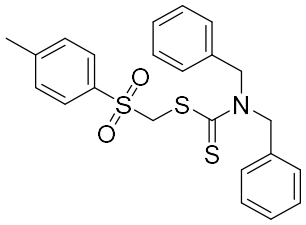
tosylmethyl methyl(phenyl)carbamodithioate (4r). brown oil (85%, 29.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.52-7.43 (m, 3H), 7.36-7.29 (m, 2H), 7.18 (d, *J* = 9.7 Hz, 2H), 5.09 (s, 2H), 3.68 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.2, 145.0, 135.1, 130.0, 129.6, 129.5, 129.3, 126.9, 60.8, 21.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{17}NO_2S_3$ 352.0495; Found: 352.0512.



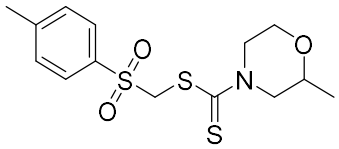
tosylmethyl methyl(p-tolyl) carbamodithioate (4s). yellow solid (86%, 33.0 mg), m.p. 150-151℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 7.28 (s, 1H), 7.05 (d, *J* = 8.3 Hz, 2H), 5.09 (s, 2H), 3.65 (s, 3H), 2.44 (d, *J* = 13.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.2, 145.0, 135.0, 130.6, 129.5, 129.3, 126.6, 60.8, 47.3, 21.8, 21.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{19}NO_2S_3$ 366.0651; Found: 366.0659.



tosylmethyl methyl(m-tolyl) carbamodithioate (4t). yellow solid (64%, 23.0 mg), m.p. 108-109℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.34 (t, *J* = 8.2 Hz, 3H), 7.28 (s, 1H), 6.97 (s, 2H), 5.10 (s, 2H), 3.66 (s, 3H), 2.44 (d, *J* = 17.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.0, 145.0, 140.3, 135.0, 130.4, 129.8, 129.5, 129.3, 127.3, 123.8, 60.8, 21.8, 21.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{19}NO_2S_3$ 366.0651; Found: 366.0659.

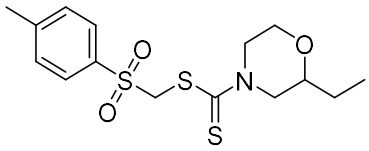


tosylmethyl dibenzylcarbamodithioate (4u). yellow solid (50%, 21.1 mg), m.p. 120-121℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.35 (dd, *J* = 16.6, 7.9 Hz, 9H), 7.13 (d, *J* = 6.2 Hz, 3H), 5.33 (s, 2H), 5.22 (s, 2H), 4.89 (s, 2H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.5, 145.1, 134.7, 134.0, 129.6, 129.4, 129.1, 128.9, 128.3, 128.1, 127.9, 127.1, 60.4, 58.1, 54.2, 21.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{23}NO_2S_3$ 442.0964; Found: 442.0965.

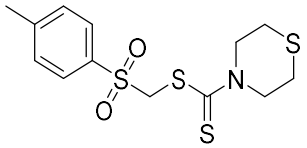


tosylmethyl 2-methylmorpholine-4-carbodithioate (4v). brown oil (82%, 28.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 5.24 (d, *J* = 21.8 Hz, 3H), 4.46 (s, 1H), 3.95 (d, J = 3.6 Hz, 1H), 3.65-3.50 (m, 2H), 3.28 (d, *J* = 40.7 Hz, 1H), 3.03 (s, 1H), 2.44 (s, 3H), 1.28-1.17 (m, 3H)). ^{13}C NMR (101 MHz,

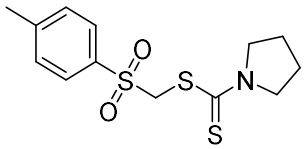
$CDCl_3$) δ 192.0, 145.3, 134.8, 129.7, 129.2, 71.6, 65.7, 59.5, 21.8, 18.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{19}NO_3S_3$ 346.0600; Found: 346.0610.



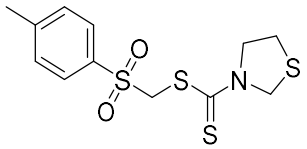
tosylmethyl 2-ethylmorpholine-4-carbodithioate (4w). brown oil (80%, 28.9 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.45-7.26 (m, 2H), 5.24 (d, *J* = 17.9 Hz, 3H), 4.45 (s, 1H), 3.95 (d, *J* = 13.6 Hz, 1H), 3.52 (t, *J* = 11.8 Hz, 1H), 3.42-3.20 (m, 2H), 2.98 (d, *J* = 32.3 Hz, 1H), 2.44 (s, 3H), 1.66-1.41 (m, 2H), 0.98 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 145.2, 134.8, 129.7, 129.2, 65.7, 59.5, 26.0, 21.8, 9.6. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{21}NO_3S_3$ 360.0757; Found: 360.0764.



tosylmethyl thiomorpholine-4-carbodithioate (4x). brown oil (79%, 27.3 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.26 (s, 2H), 4.46 (s, 2H), 4.25 (s, 2H), 2.65 (s, 4H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.4, 145.3, 134.6, 129.7, 129.4, 59.6, 21.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{17}NO_2S_4$ 348.0215; Found: 348.0226.

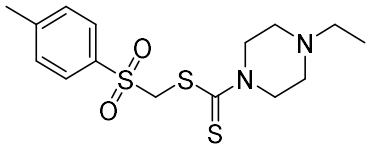


tosylmethyl pyrrolidine-1-carbodithioate (4y). brown oil (64%, 20.3 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 5.22 (s, 2H), 3.83 (t, *J* = 7.5 Hz, 2H), 3.70 (t, *J* = 6.9 Hz, 2H), 2.44 (s, 3H), 2.07 (q, *J* = 6.6 Hz, 2H), 1.96 (p, *J* = 6.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.7, 145.1, 135.1, 129.7, 129.1, 59.4, 56.2, 50.8, 26.1, 24.2, 21.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{17}NO_2S_3$ 316.0495; Found: 316.0506.

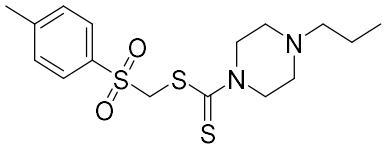


tosylmethyl thiazolidine-3-carbodithioate (4z). yellow solid (80%, 26.6 mg), m.p. 95-96°C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 7.9 Hz,

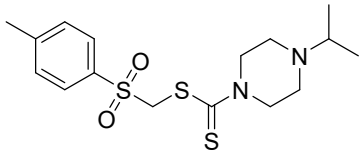
2H), 5.22 (s, 2H), 3.47 (s, 3H), 3.39 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.1, 145.2, 135.0, 129.7, 129.0, 60.6, 46.7, 41.6, 21.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{15}NO_2S_4$ 334.0059; Found: 334.0074.



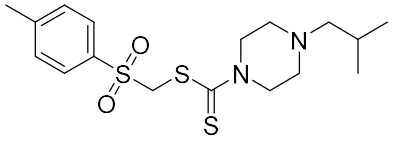
tosylmethyl 4-ethylpiperazine-1-carbodithioate (4aa). yellow solid (70%, 25.4 mg), m.p. 98-99℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 5.25 (s, 2H), 4.27 (s, 2H), 4.01 (s, 2H), 2.58-2.45 (m, 6H), 2.44 (s, 3H), 1.12 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.6, 145.2, 134.8, 129.7, 129.3, 59.7, 51.9, 21.8, 11.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{22}N_2O_2S_3$ 359.0917; Found: 359.0923.



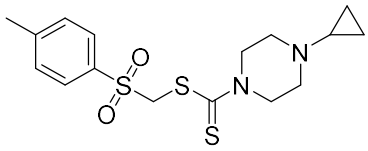
tosylmethyl 4-propylpiperazine-1-carbodithioate (4ab). brown oil (46%, 17.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 5.25 (s, 2H), 4.23 (s, 2H), 3.97 (s, 2H), 2.47 (d, *J* = 10.0 Hz, 4H), 2.44 (s, 3H), 2.37-2.29 (m, 2H), 1.51 (h, *J* = 7.4 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.4, 145.1, 134.8, 129.7, 129.3, 60.0, 59.7, 52.4, 21.8, 19.9, 11.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{24}N_2O_2S_3$ 373.1073; Found: 373.1081.



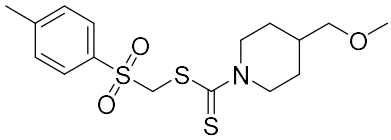
tosylmethyl 4-isopropylpiperazine-1-carbodithioate (4ac). brown oil (44%, 16.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 5.25 (s, 2H), 4.23 (s, 2H), 3.97 (s, 2H), 2.75 (s, 1H), 2.56 (s, 4H), 2.44 (s, 3H), 1.06 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.3, 145.1, 134.8, 129.7, 129.3, 59.7, 54.5, 48.0, 21.8, 18.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{24}N_2O_2S_3$ 373.1073; Found: 373.1084.



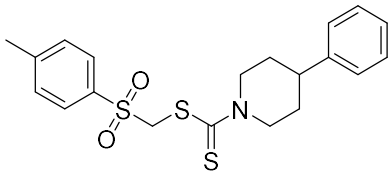
tosylmethyl 4-isobutylpiperazine-1-carbodithioate (4ad). brown oil (93%, 36.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 5.26 (s, 2H), 4.23 (s, 2H), 3.96 (s, 2H), 2.45 (s, 7H), 2.13 (s, 2H), 1.78 (t, *J* = 6.7 Hz, 1H), 0.91 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.4, 145.1, 134.8, 130.0, 129.7, 129.3, 77.3, 66.2, 59.7, 52.7, 25.4, 21.8, 20.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{26}N_2O_2S_3$ 387.1230; Found: 387.1235.



tosylmethyl 4-cyclopropylpiperazine-1-carbodithioate (4ae). yellow solid (65%, 29.6 mg), m.p. 142-143℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 5.25 (s, 2H), 4.18 (s, 2H), 3.90 (s, 2H), 2.66 (d, *J* = 20.8 Hz, 4H), 2.44 (s, 3H), 1.63 (s, 1H), 0.53-0.41 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.4, 186.4, 145.1, 134.8, 129.7, 129.3, 59.7, 53.4, 52.5, 51.9, 50.4, 38.1, 37.9, 21.8, 6.2, 6.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{22}N_2O_2S_3$ 371.0917; Found: 371.0930.

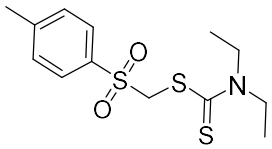


tosylmethyl 4-(methoxymethyl) piperidine-1-carbodithioate (4af). brown oil (25%, 9.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 9.7 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.25 (d, *J* = 31.1 Hz, 3H), 4.60 (s, 1H), 3.32 (s, 3H), 3.22 (d, *J* = 6.1 Hz, 3H), 3.08 (s, 1H), 2.43 (s, 3H), 2.15-1.54 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.5, 145.0, 134.7, 129.6, 129.6, 129.3, 129.3, 59.8, 59.0, 53.6, 50.6, 36.3, 21.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{23}NO_3S_3$ 374.0913; Found: 374.0929.

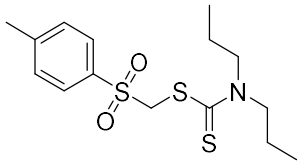


tosylmethyl 4-phenylpiperidine-1-carbodithioate (4ag). yellow solid (67%, 27.1 mg), m.p. 135-136℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.28 (s, 1H), 7.24 (s, 2H), 7.23-7.14 (m, 2H), 7.11 (d, *J* = 6.8 Hz, 2H), 5.42 (s, 1H), 5.23 (d, *J* = 28.1 Hz, 2H), 4.72 (s, 1H), 3.16 (d, *J* = 62.5 Hz, 2H), 2.88-2.74 (m, 1H), 2.36 (s, 3H), 1.90 (s, 2H), 1.68-1.57 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.8, 145.1, 144.0,

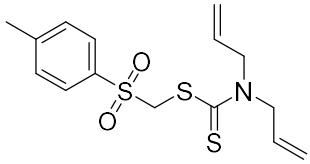
134.9, 129.7, 129.3, 128.8, 126.9, 126.7, 60.0, 42.4, 21.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{23}NO_2S_3$ 406.0964; Found: 406.0969.



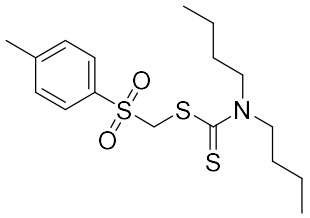
tosylmethyl diethylcarbamodithioate (4ah). brown oil (75%, 23.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.24 (s, 2H), 3.88 (q, *J* = 7.1 Hz, 2H), 3.72 (q, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.12 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.3, 145.1, 134.7, 129.5, 129.4, 59.8, 51.1, 47.1, 21.7, 12.8, 11.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{19}NO_2S_3$ 318.0651; Found: 318.0663.



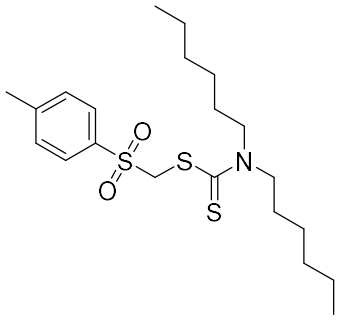
tosylmethyl dipropylcarbamodithioate (4ai). brown oil (72%, 24.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.25 (s, 2H), 3.82-3.71 (m, 2H), 3.64-3.55 (m, 2H), 2.42 (s, 3H), 1.70 (h, *J* = 7.5 Hz, 2H), 1.57 (h, *J* = 7.5 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.85 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.9, 145.0, 134.6, 129.5, 129.4, 59.9, 58.3, 54.5, 21.7, 21.1, 19.4, 11.2, 11.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{23}NO_2S_3$ 346.0964; Found: 346.0972.



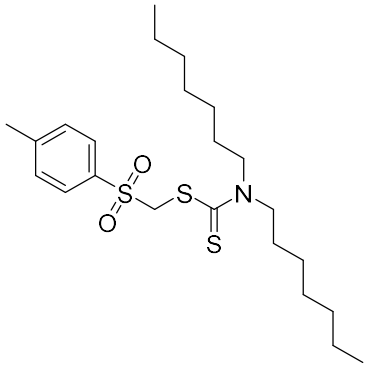
tosylmethyl diallylcarbamodithioate (4aj). brown oil (48%, 16.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 5.84-5.59 (m, 2H), 5.29 (d, *J* = 10.4 Hz, 1H), 5.24 (s, 2H), 5.22-5.03 (m, 3H), 4.50 (d, *J* = 6.1 Hz, 2H), 4.29 (d, *J* = 5.4 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.0, 145.1, 134.6, 130.2, 129.8, 129.6, 129.4, 119.0, 118.7, 60.1, 58.1, 53.9, 21.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{19}NO_2S_3$ 342.0651; Found: 342.0657.



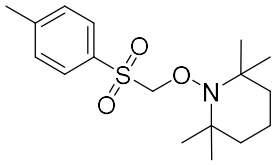
tosylmethyl 4-phenylpiperidine-1-carbodithioate (4ak). brown oil (77%, 28.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 5.25 (s, 2H), 3.84-3.75 (m, 2H), 3.68-3.57 (m, 2H), 2.42 (s, 3H), 1.68-1.60 (m, 2H), 1.57 - 1.46 (m, 2H), 1.40-1.32 (m, 2H), 1.30-1.22 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H), 0.91 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.6, 145.0, 134.6, 129.5, 129.4, 59.9, 56.5, 52.7, 29.7, 28.1, 21.8, 20.1, 20.0, 13.9, 13.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{27}NO_2S_3$ 374.1277; Found: 374.1291.



tosylmethyl dihexylcarbamodithioate (4al). brown oil (42%, 18.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.3 Hz, 2H), 5.25 (s, 2H), 3.82-3.73 (m, 2H), 3.66-3.56 (m, 2H), 2.42 (s, 3H), 1.65 (t, *J* = 7.7 Hz, 2H), 1.50 (q, *J* = 7.5 Hz, 2H), 1.29 (d, *J* = 23.5 Hz, 12H), 0.89 (dd, *J* = 12.1, 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.5, 145.0, 134.6, 129.5, 129.4, 59.9, 56.8, 53.0, 31.5, 31.4, 27.6, 26.5, 26.4, 25.9, 22.6, 21.7, 14.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{35}NO_2S_3$ 430.1903; Found: 430.1921.



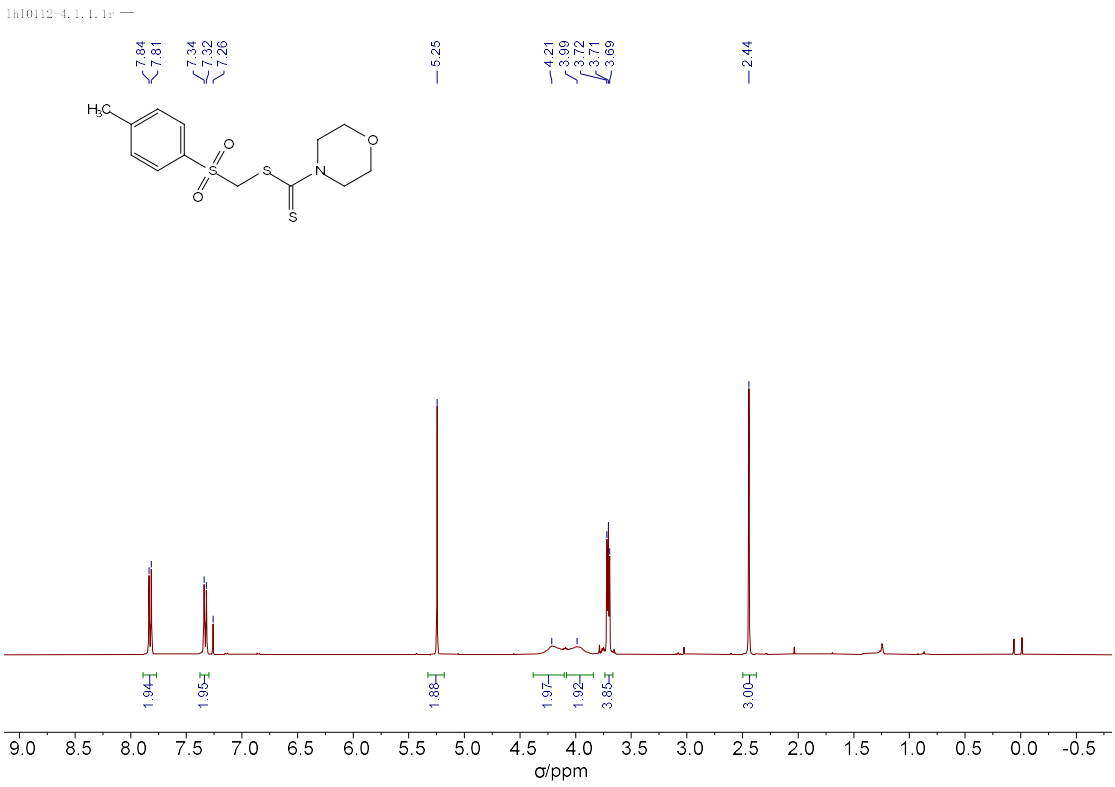
tosylmethyl diheptylcarbamodithioate (4am). brown oil (51%, 25.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 5.25 (s, 2H), 3.84-3.70 (m, 2H), 3.64-3.53 (m, 2H), 2.42 (s, 3H), 1.66 (q, *J* = 7.4 Hz, 2H), 1.51 (p, *J* = 7.7 Hz, 2H), 1.33-1.23 (m, 16H), 0.92-0.86 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.5, 145.0, 134.6, 129.5, 129.4, 59.9, 56.8, 53.0, 31.8, 31.7, 29.0, 28.9, 27.7, 26.8, 26.7, 26.0, 22.6, 21.8, 14.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{39}NO_2S_3$ 458.2216; Found: 458.2218.



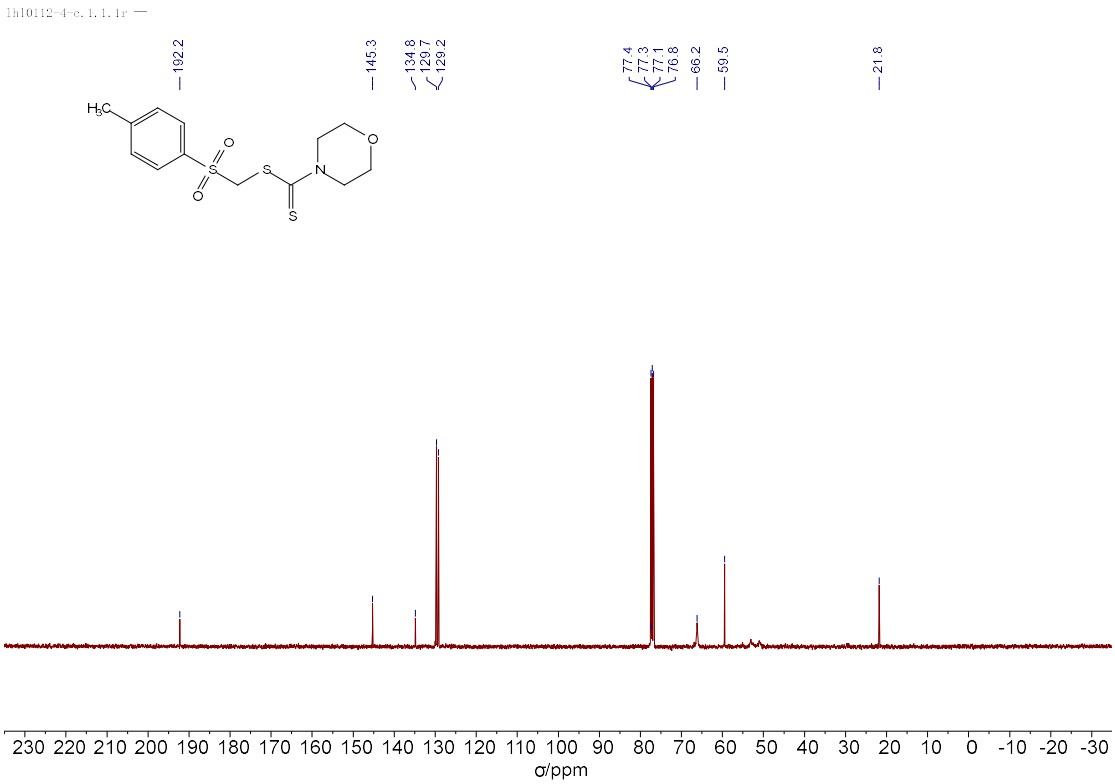
2,2,6,6-tetramethyl-1-(tosylmethoxy)piperidine (5a). yellow solid (25%, 25.0 mg), m.p. 113-114℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.3 Hz, 2H), 4.78 (s, 2H), 2.46 (s, 3H), 1.70 (s, 1H), 1.54 (s, 1H), 1.41-1.36 (m, 4H), 0.98 (d, J = 7.9 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 129.7, 129.0, 89.6, 60.8, 39.7, 32.4, 21.8, 20.1, 16.8. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{27}NO_3S$ 348.1604; Found: 348.162

11. NMR spectra

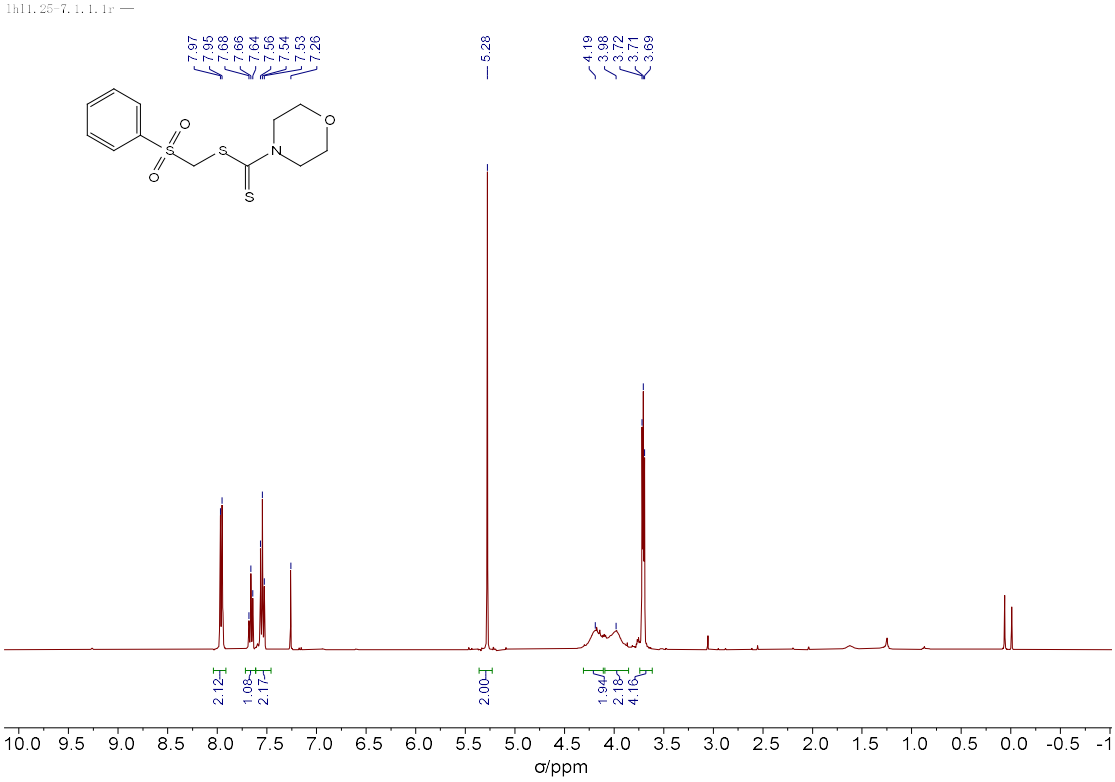
^{1}H NMR-spectrum of **4a**



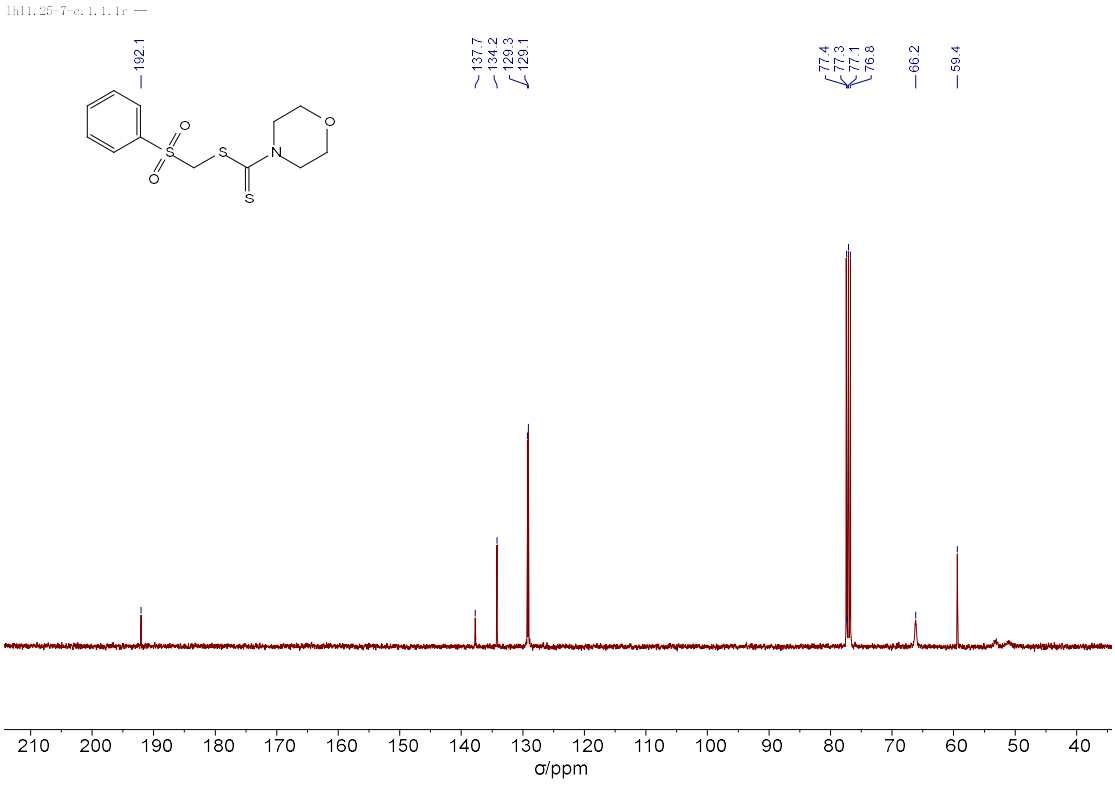
^{13}C NMR-spectrum of **4a**


192.2
145.3
134.8
129.7
129.2
77.4
77.3
77.1
76.8
66.2
59.5
21.8
H3C
O
S
O
S
N
O
S
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
σ/ppm

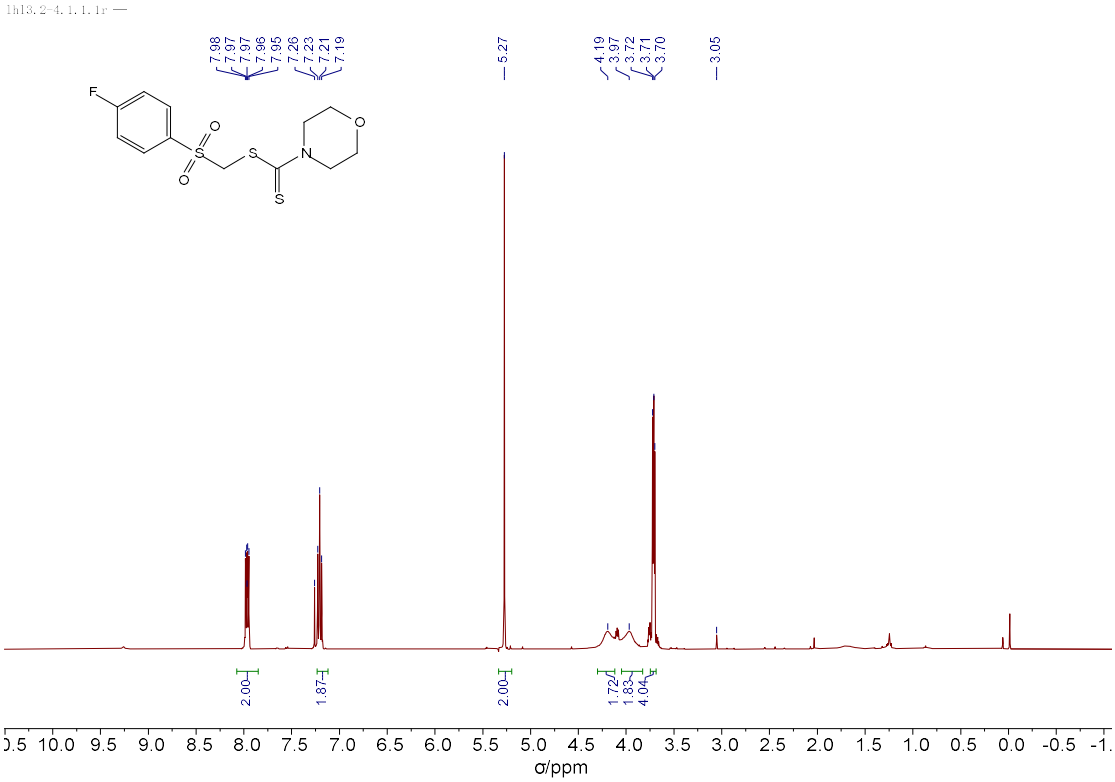
^{1}H NMR-spectrum of **4b**



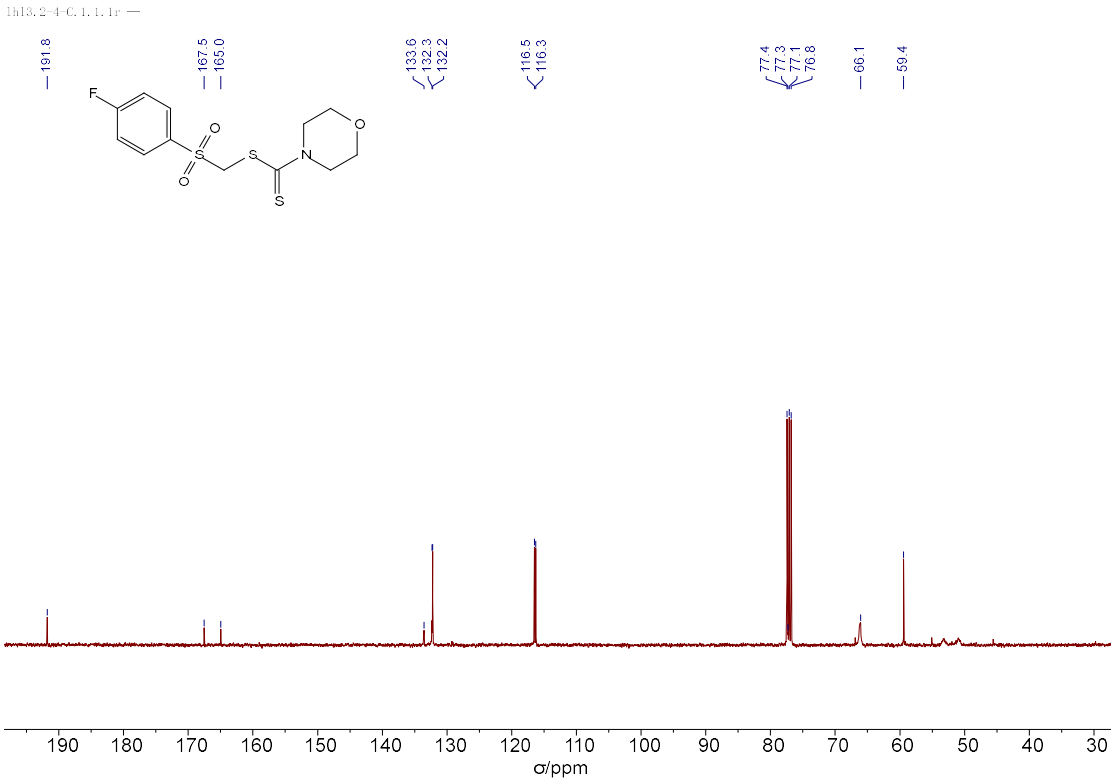
^{13}C NMR-spectrum of **4b**



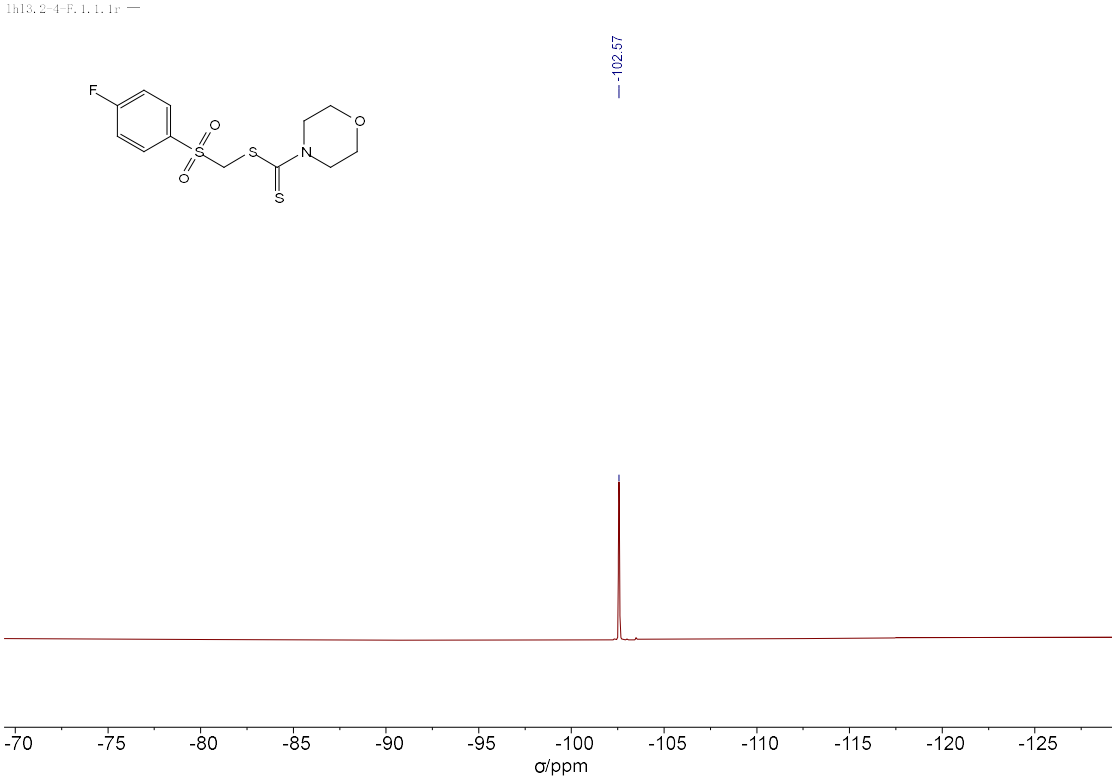
^{1}H NMR-spectrum of **4c**



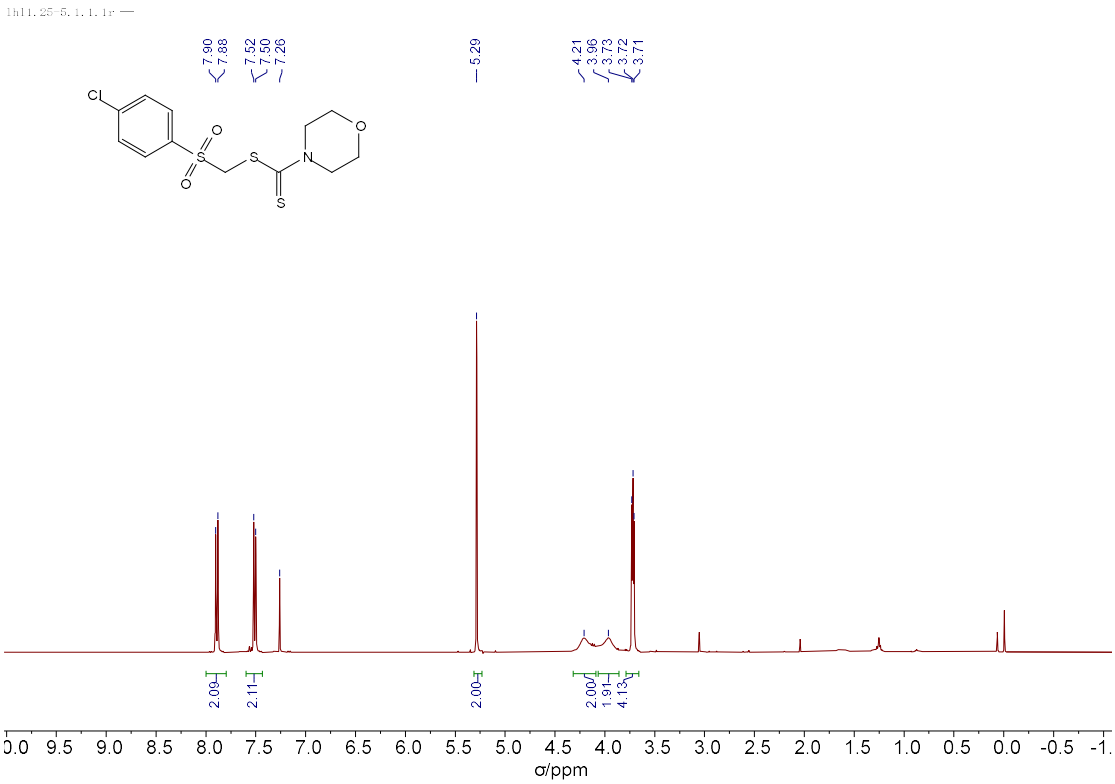
^{13}C NMR-spectrum of **4c**



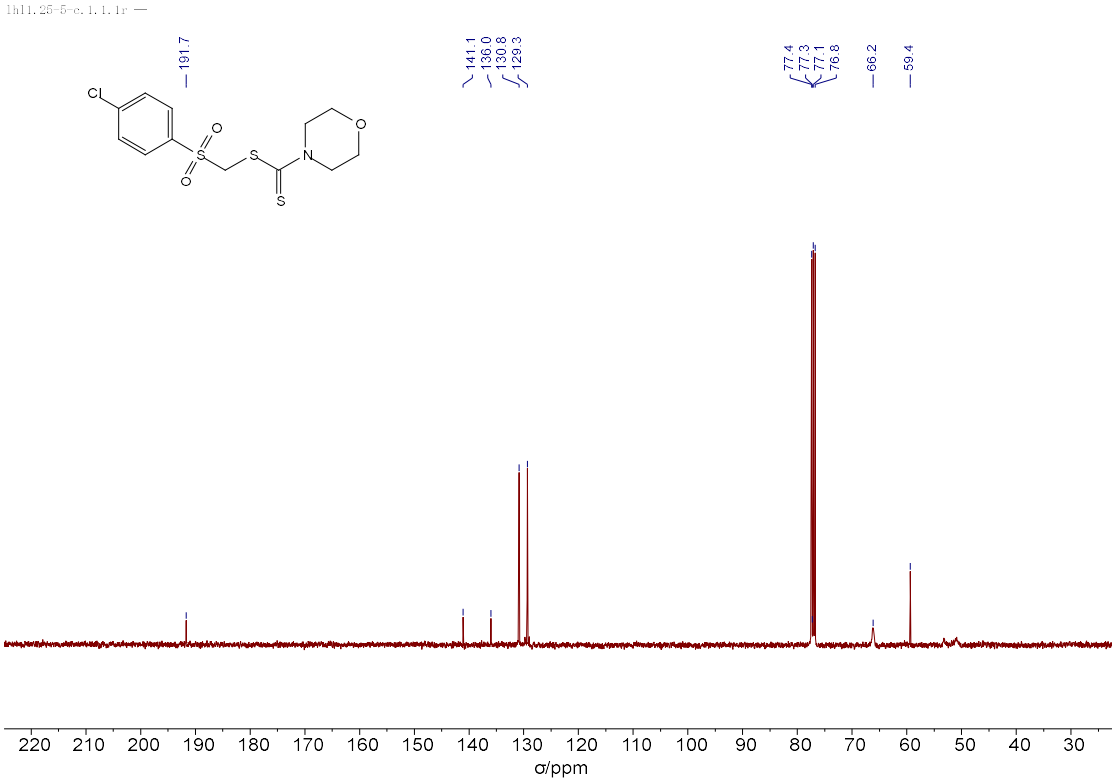
^{19}F NMR-spectrum of **4c**



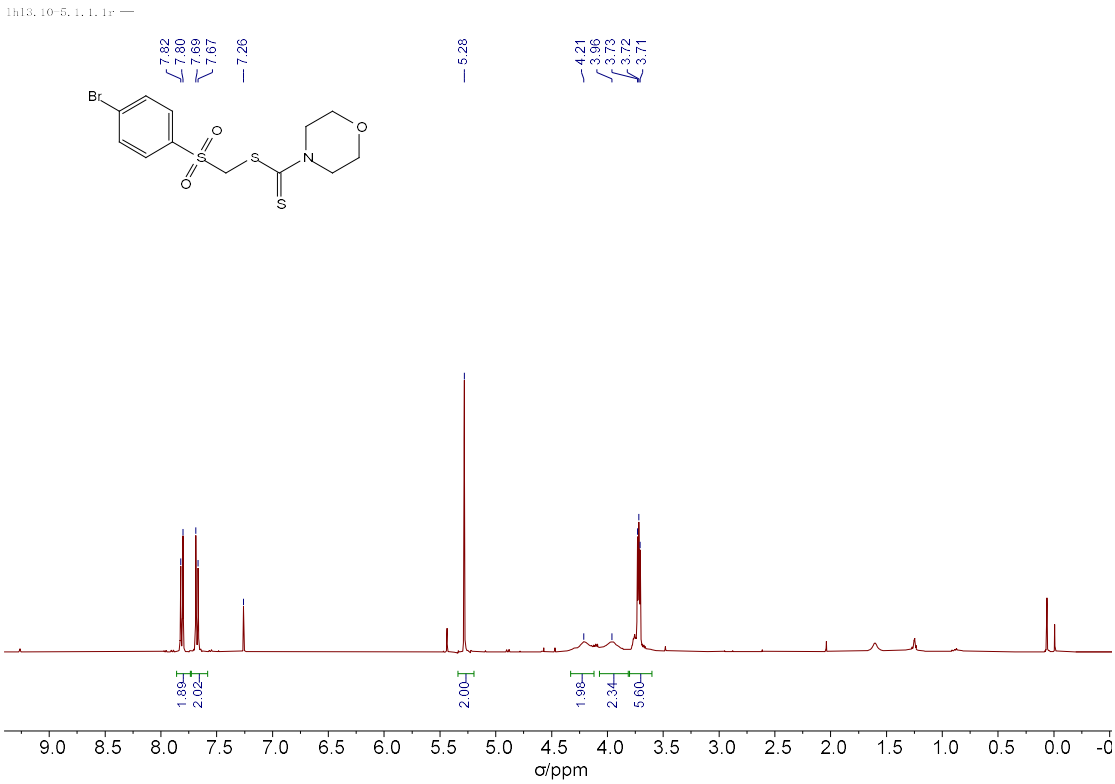
^{1}H NMR-spectrum of **4d**



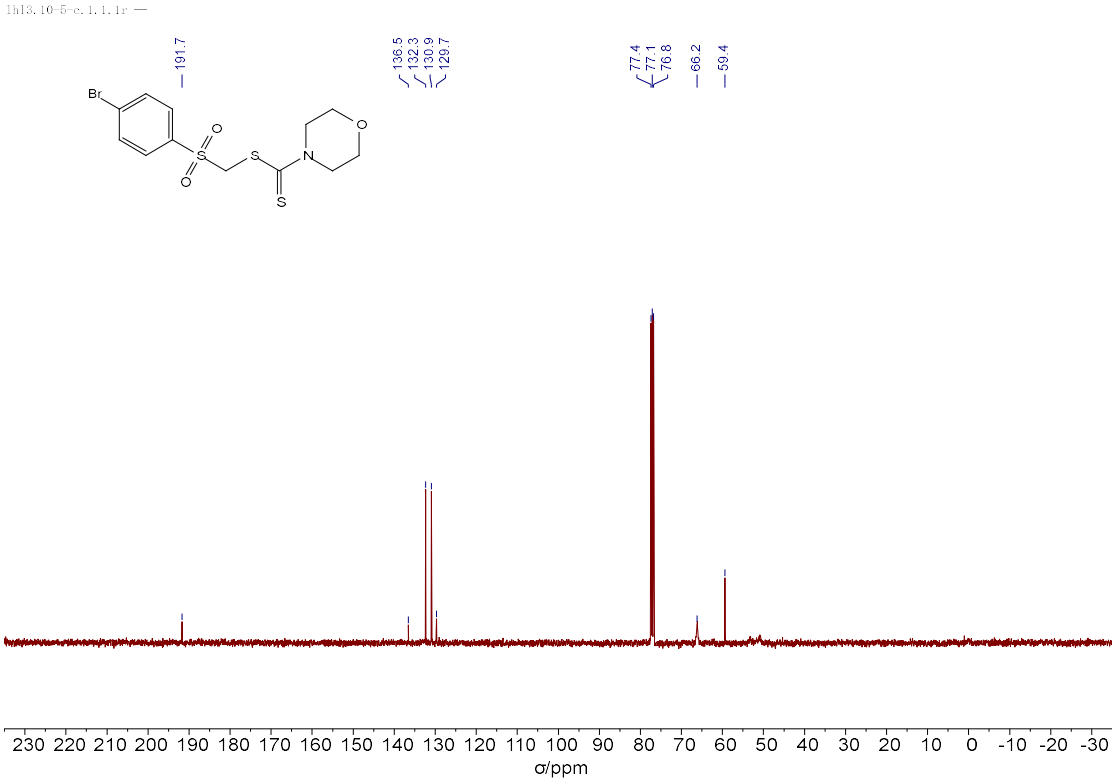
^{13}C NMR-spectrum of **4d**



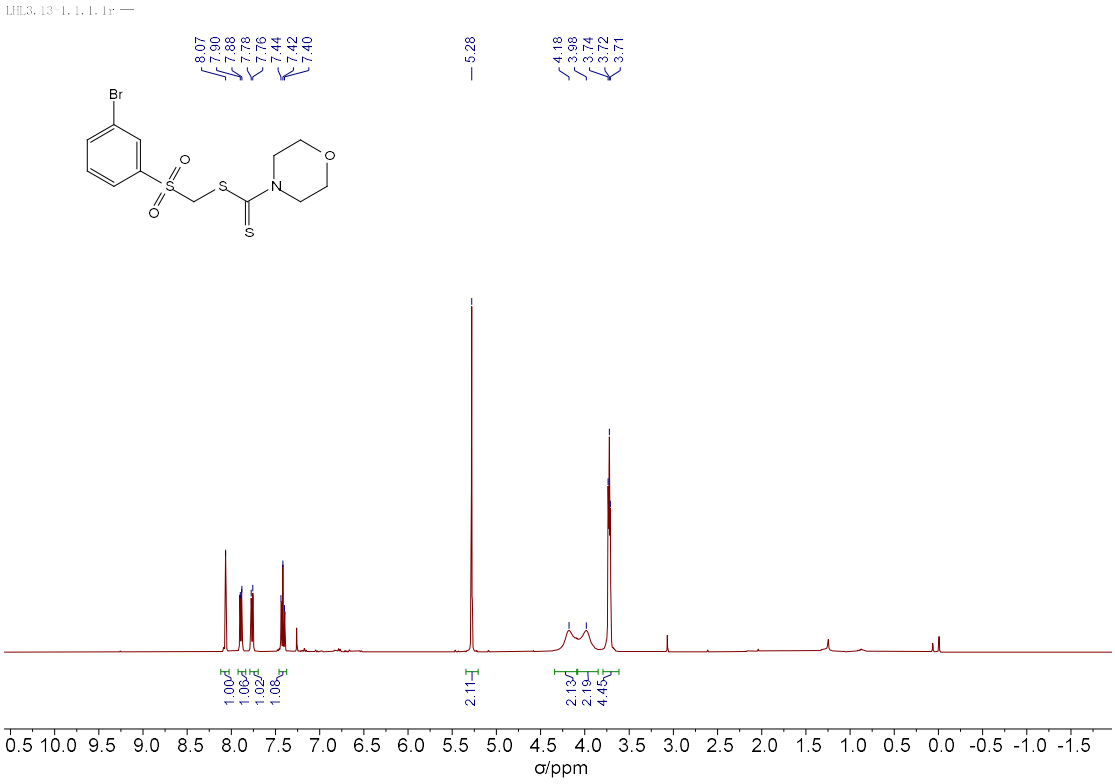
^{1}H NMR-spectrum of **4e**



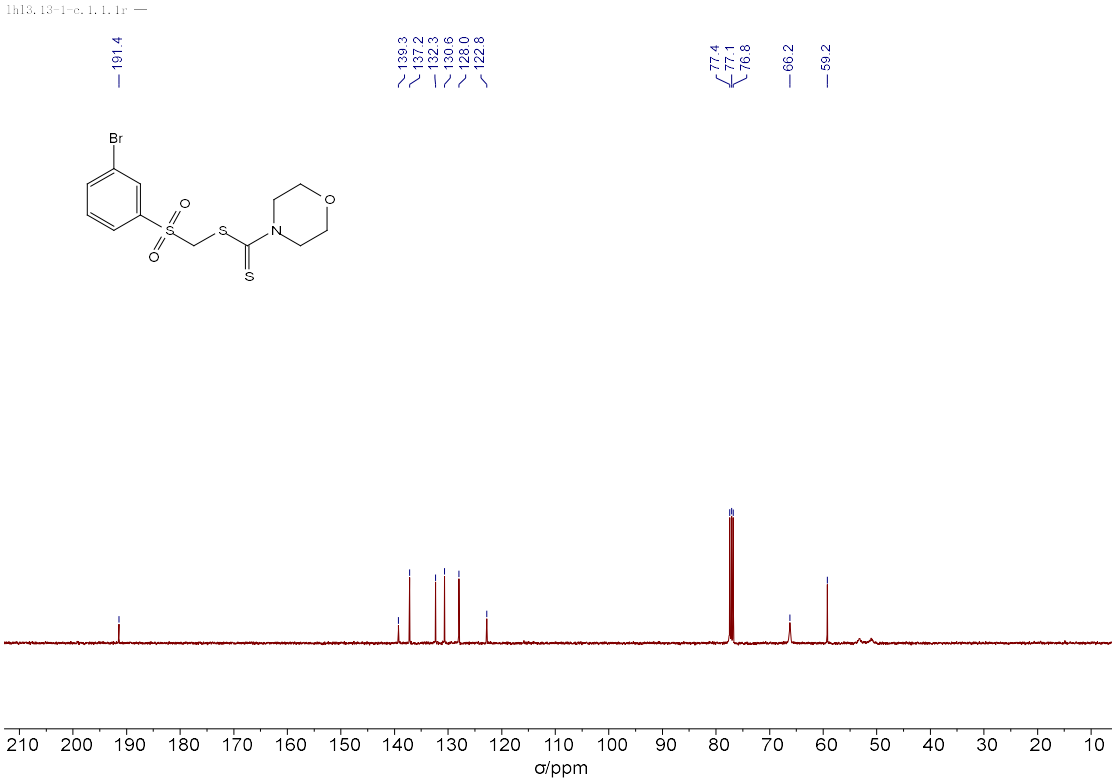
^{13}C NMR-spectrum of **4e**



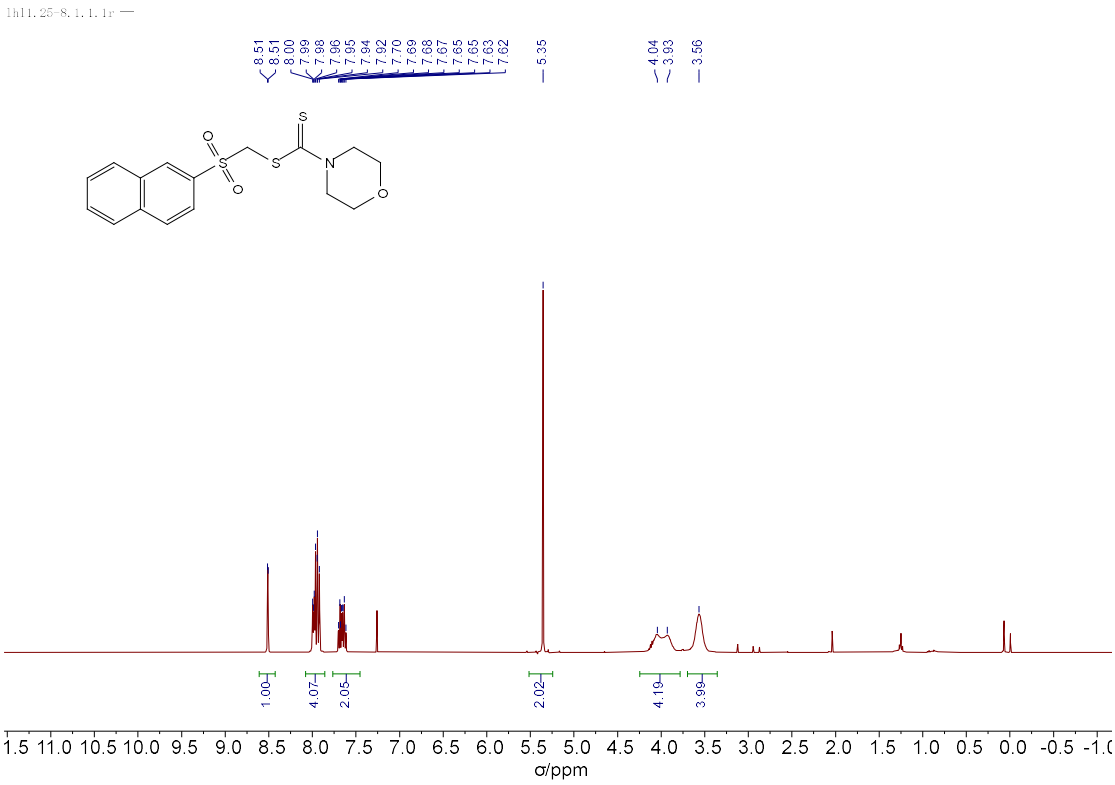
^{1}H NMR-spectrum of **4f**



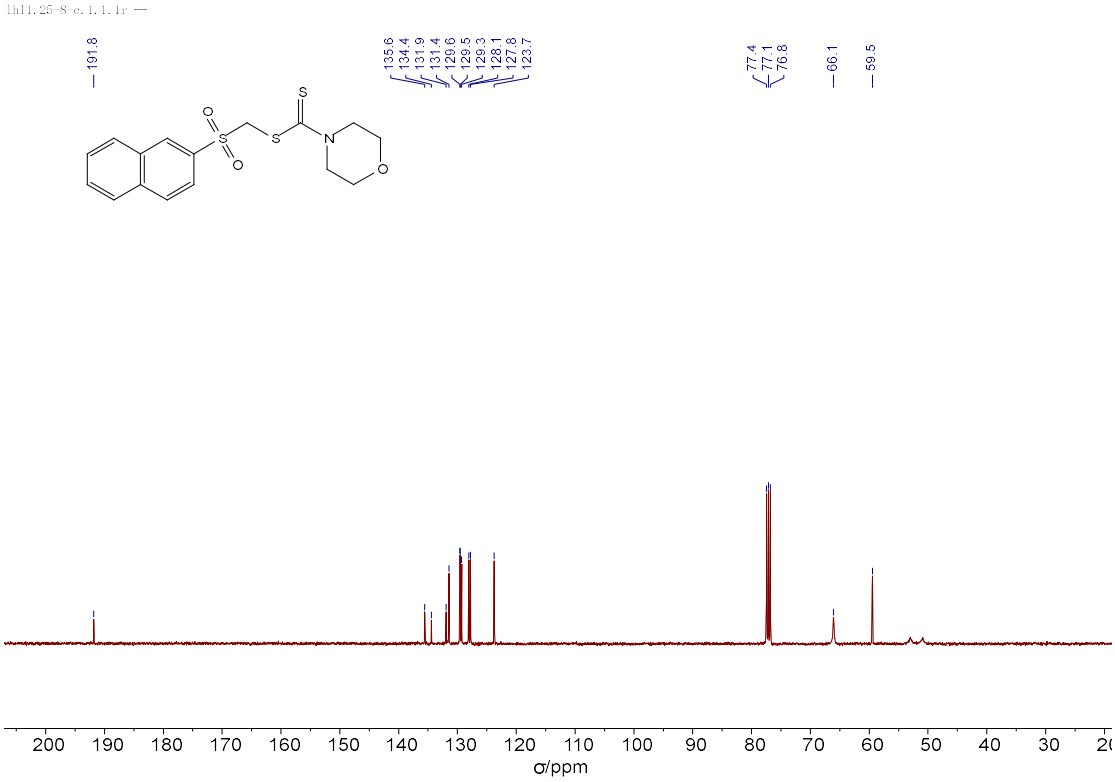
^{13}C NMR-spectrum of **4f**



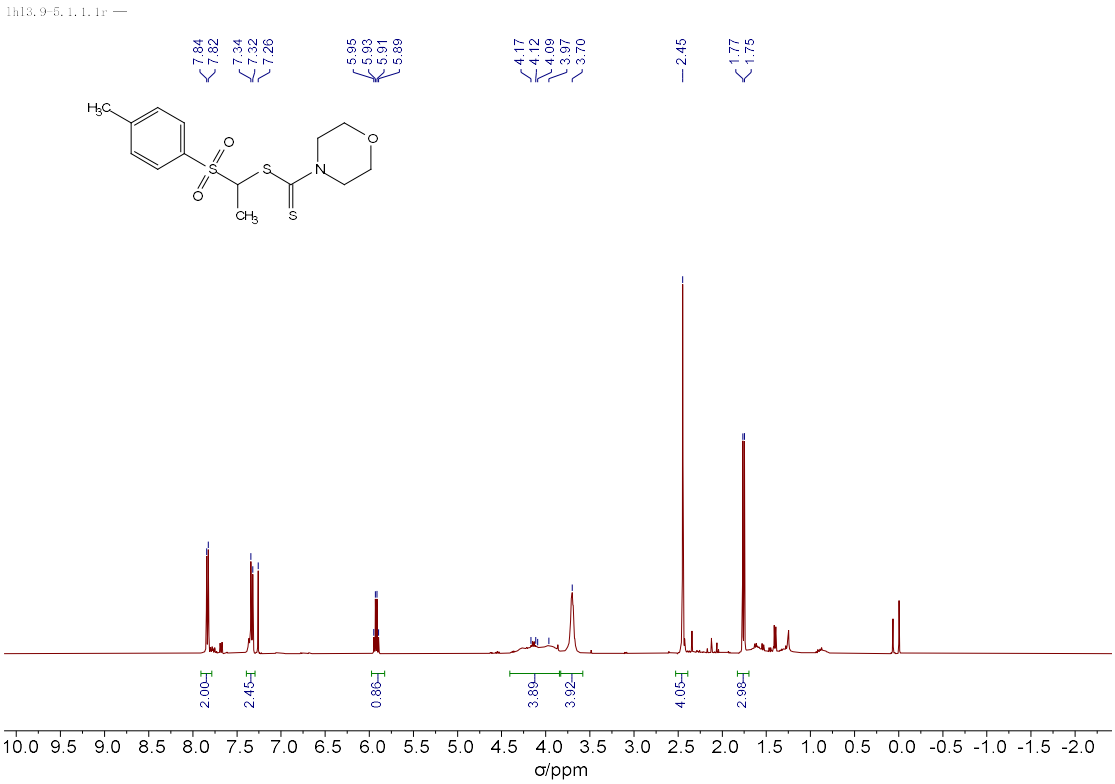
^{1}H NMR-spectrum of **4g**



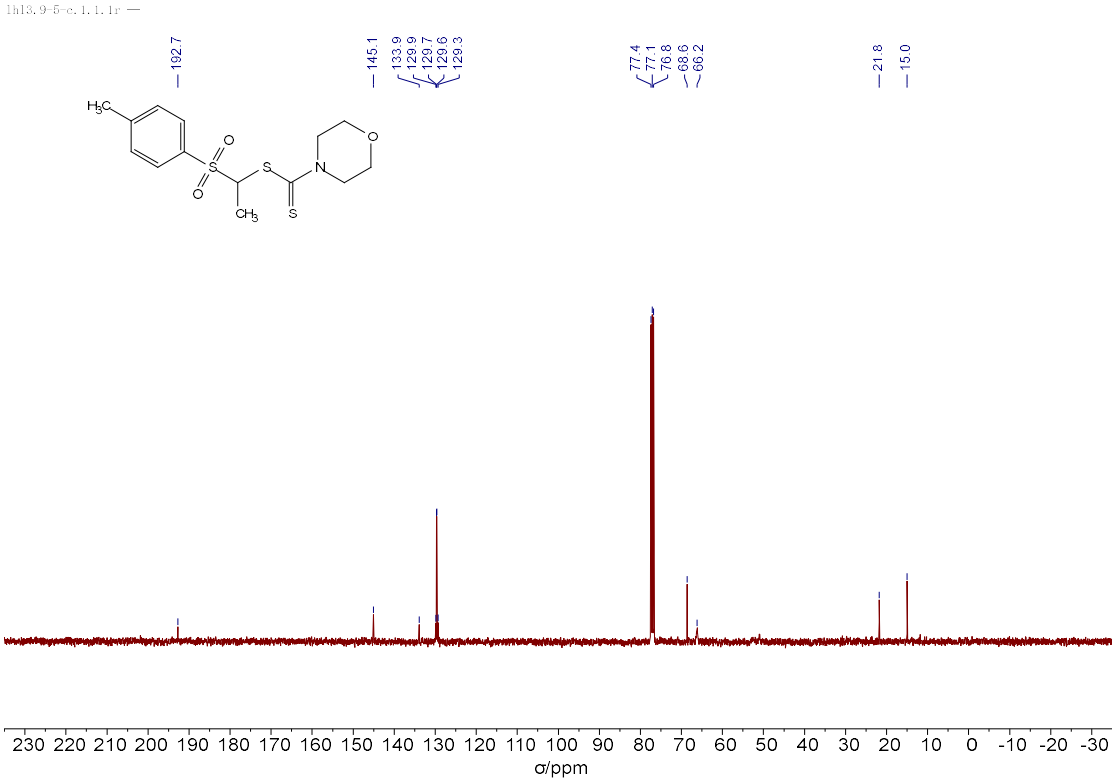
^{13}C NMR-spectrum of **4g**



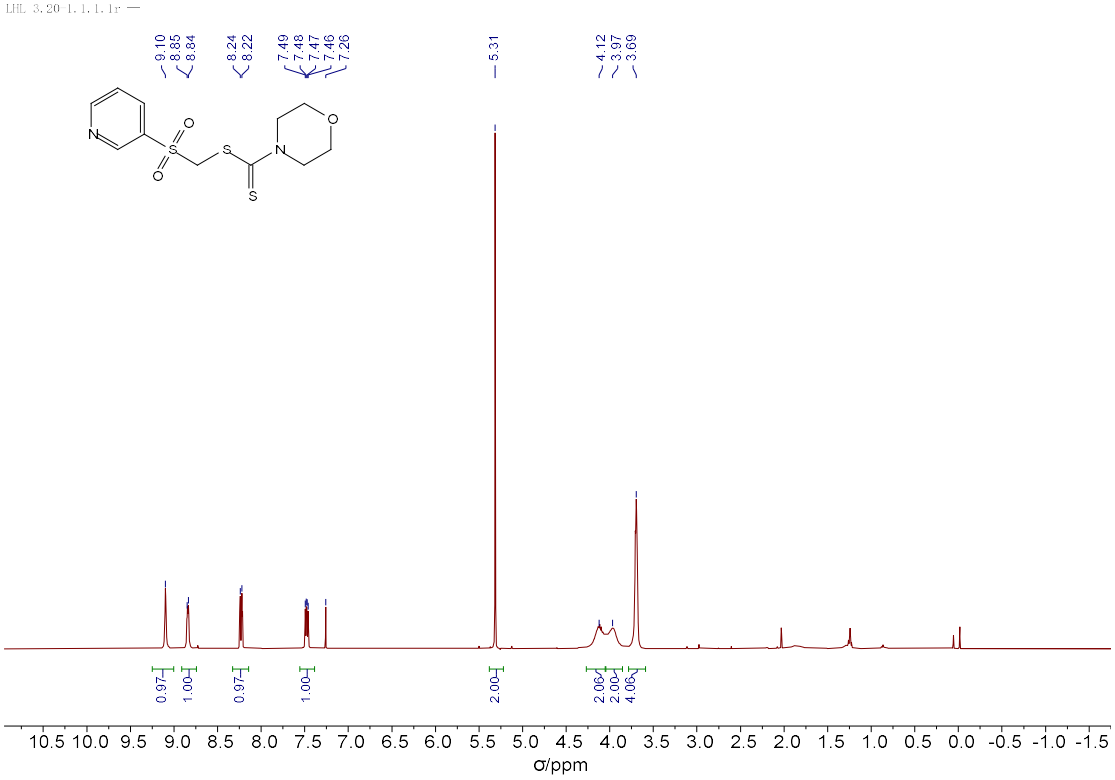
^{1}H NMR-spectrum of **4h**



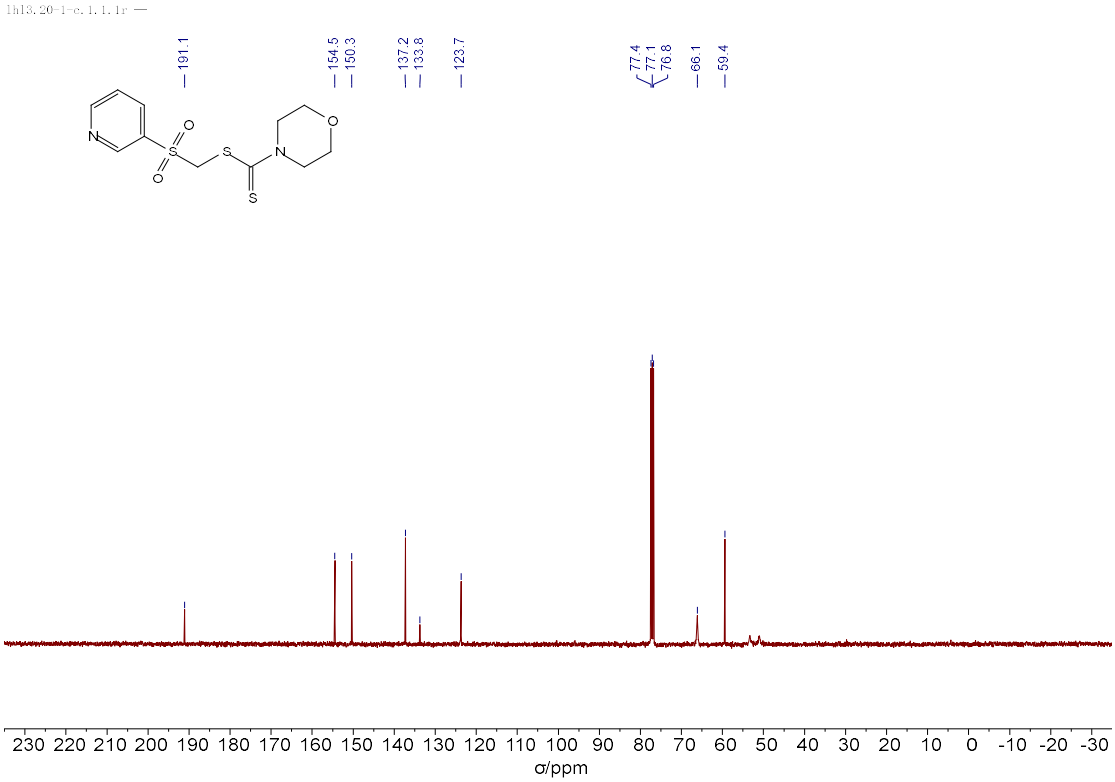
^{13}C NMR-spectrum of **4h**



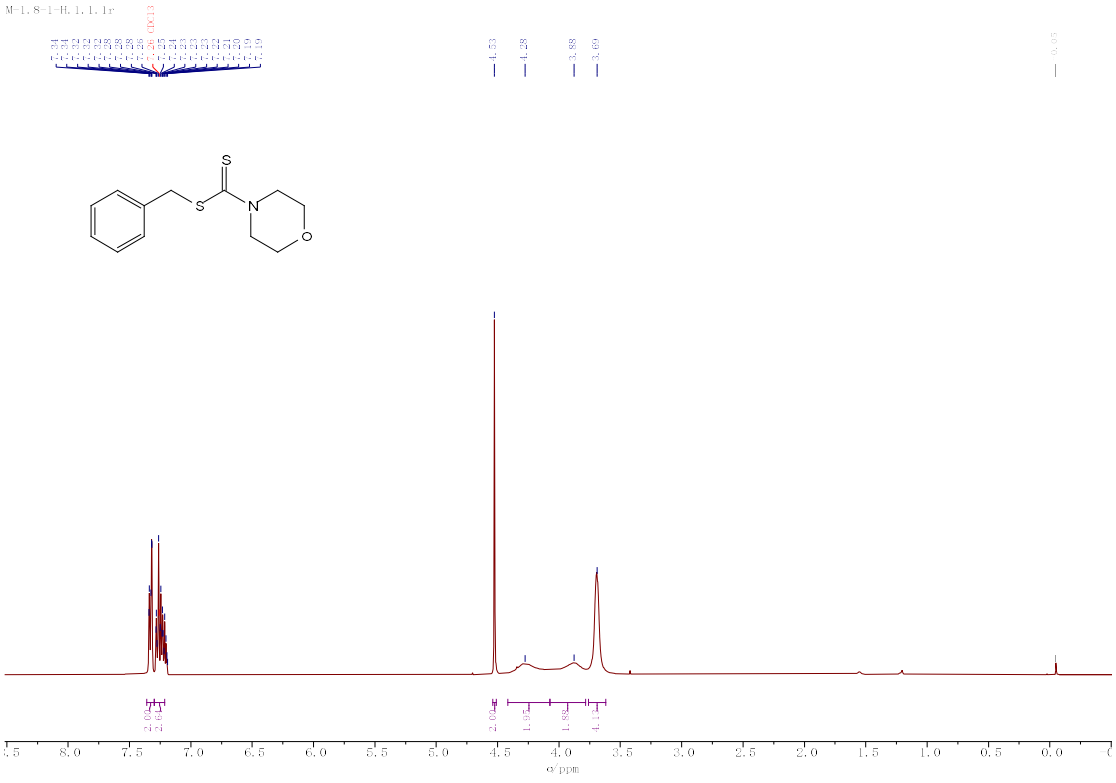
^{1}H NMR-spectrum of **4i**



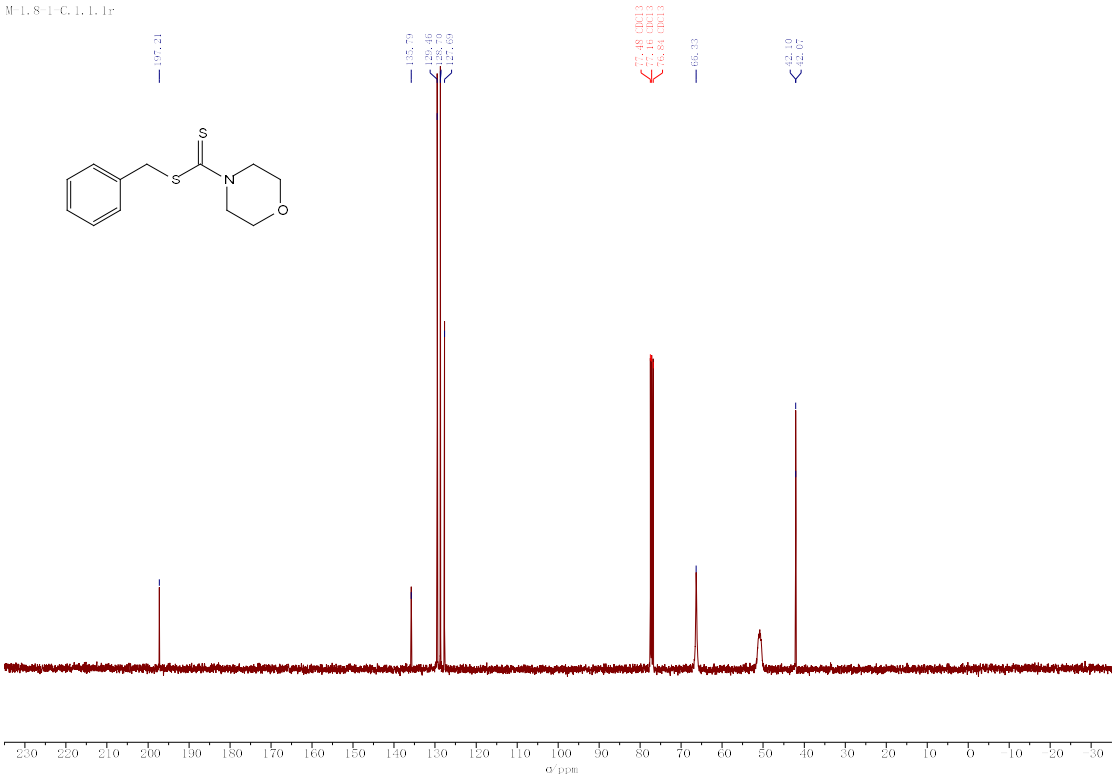
^{13}C NMR-spectrum of **4i**



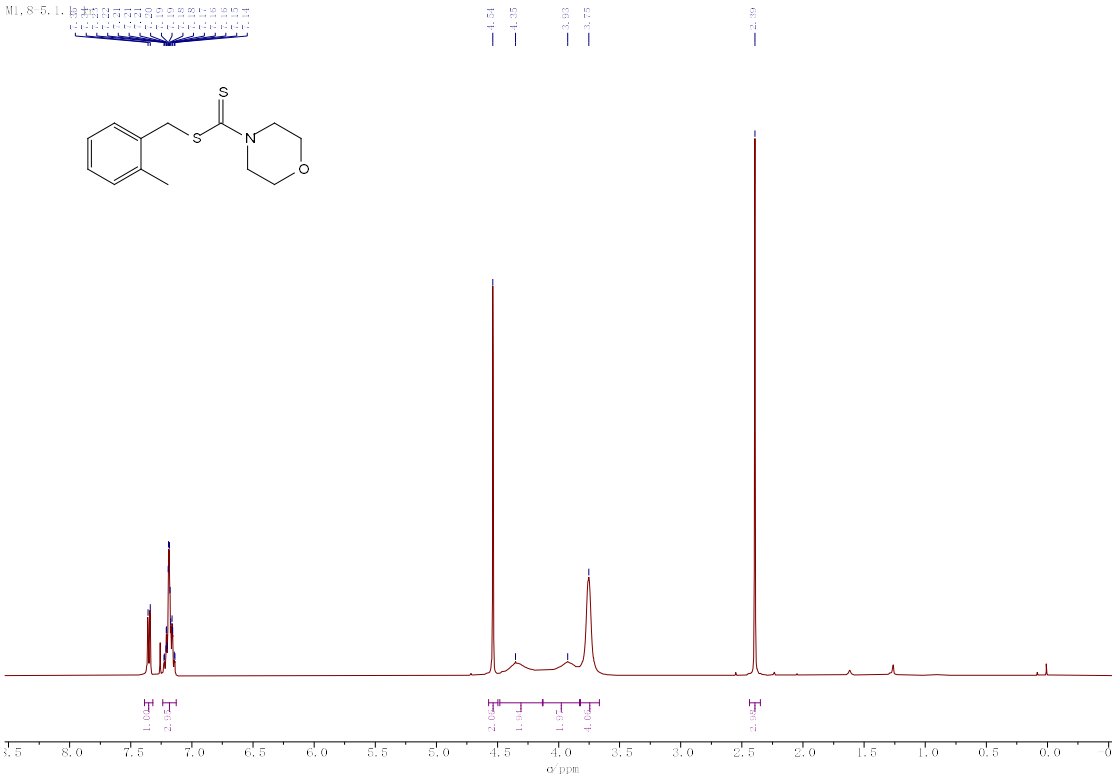
^{1}H NMR-spectrum of **4j**



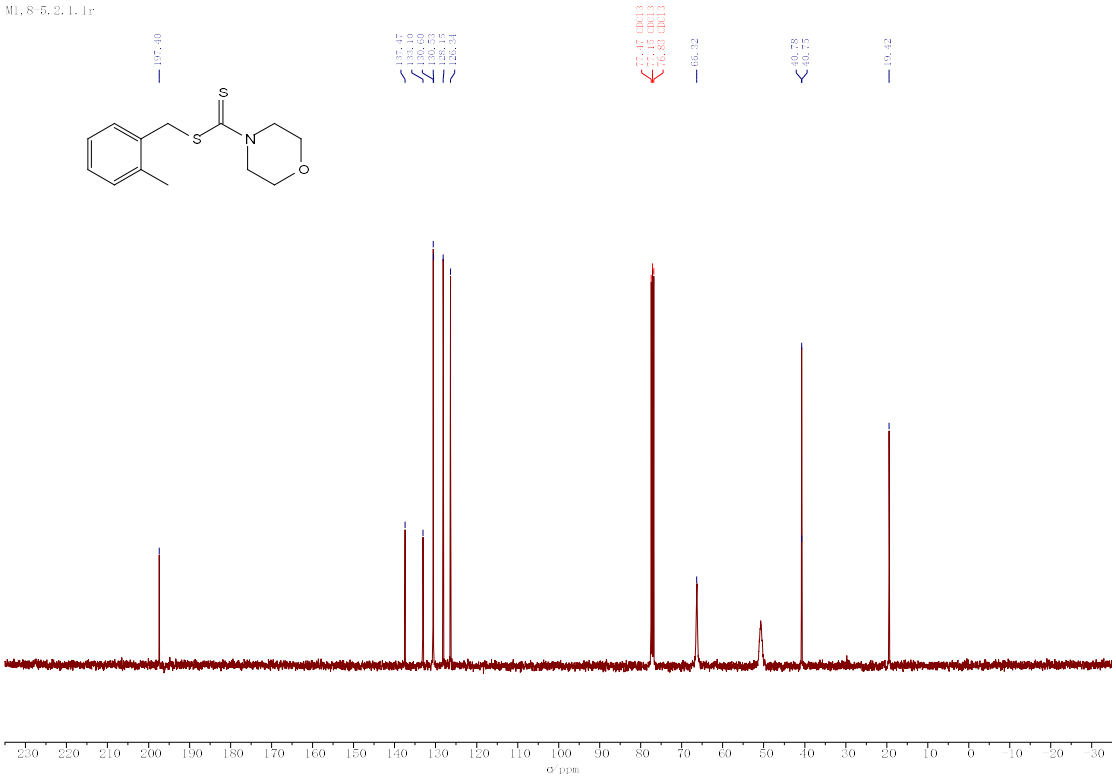
^{13}C NMR-spectrum of **4j**



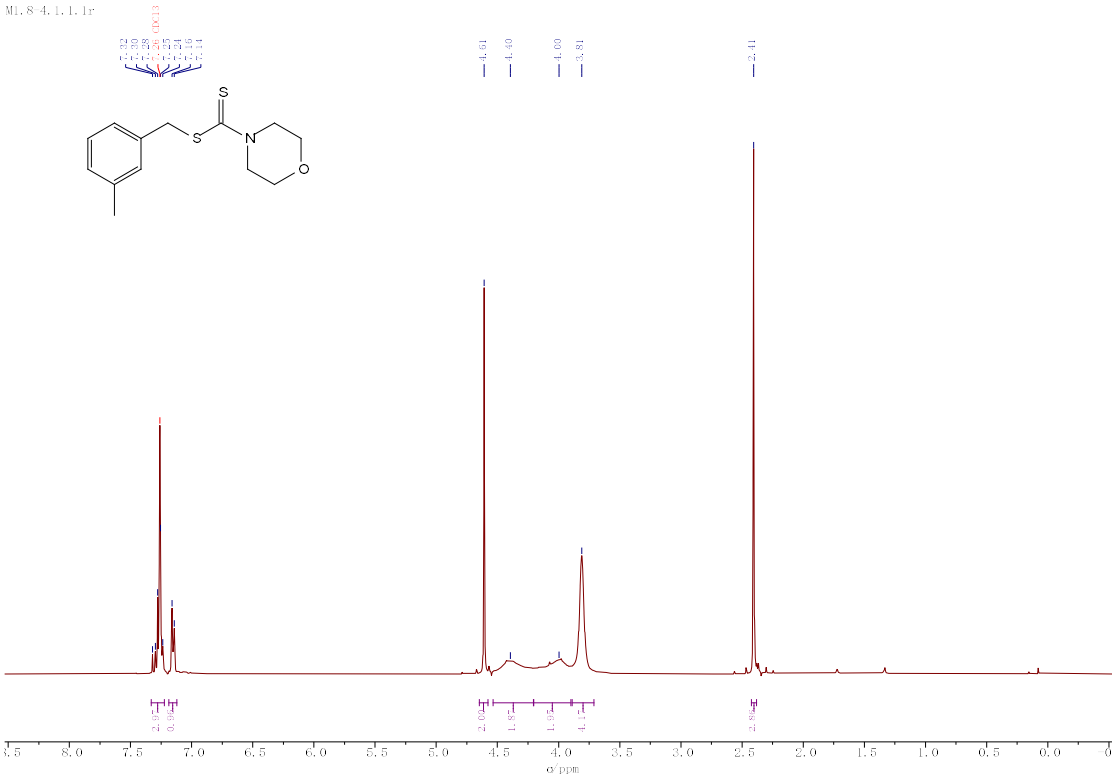
^{1}H NMR-spectrum of **4k**



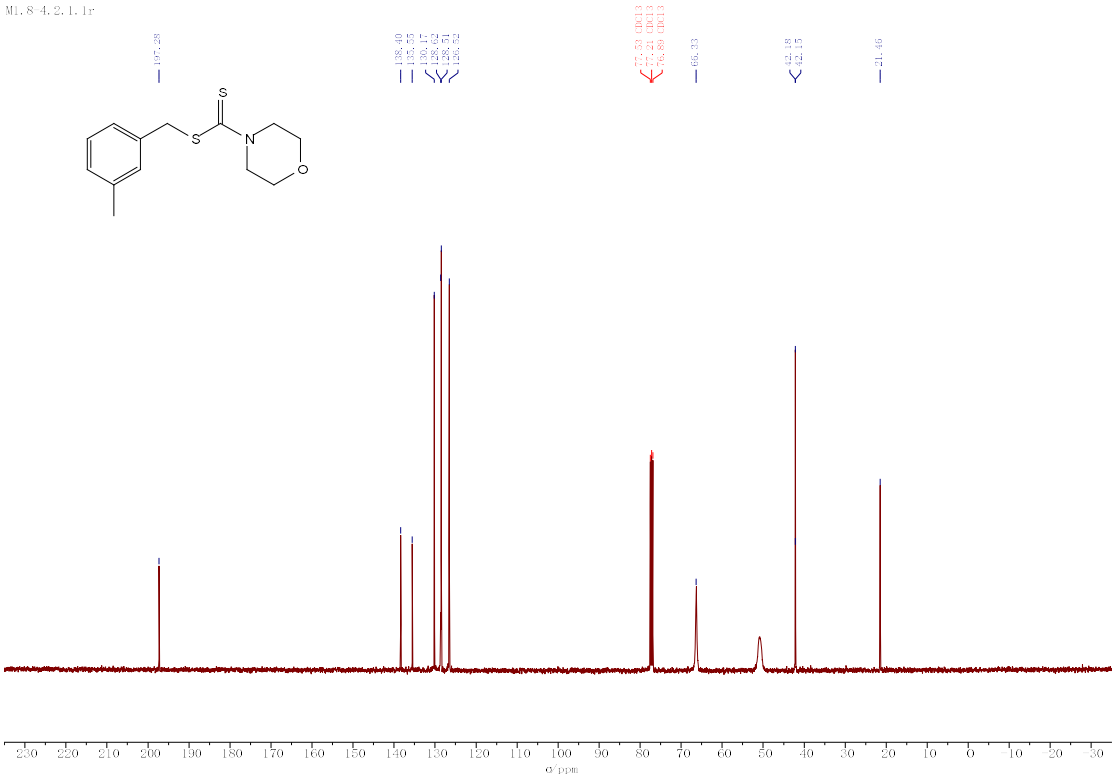
^{13}C NMR-spectrum of **4k**



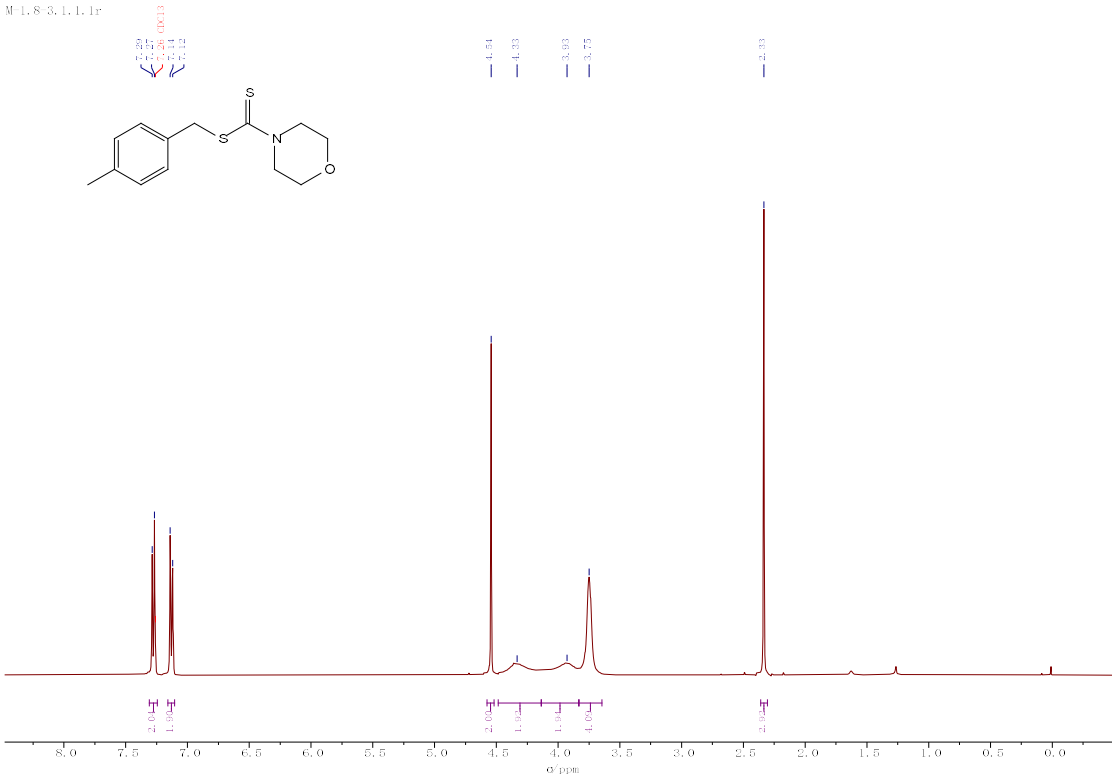
^{1}H NMR-spectrum of **4l**



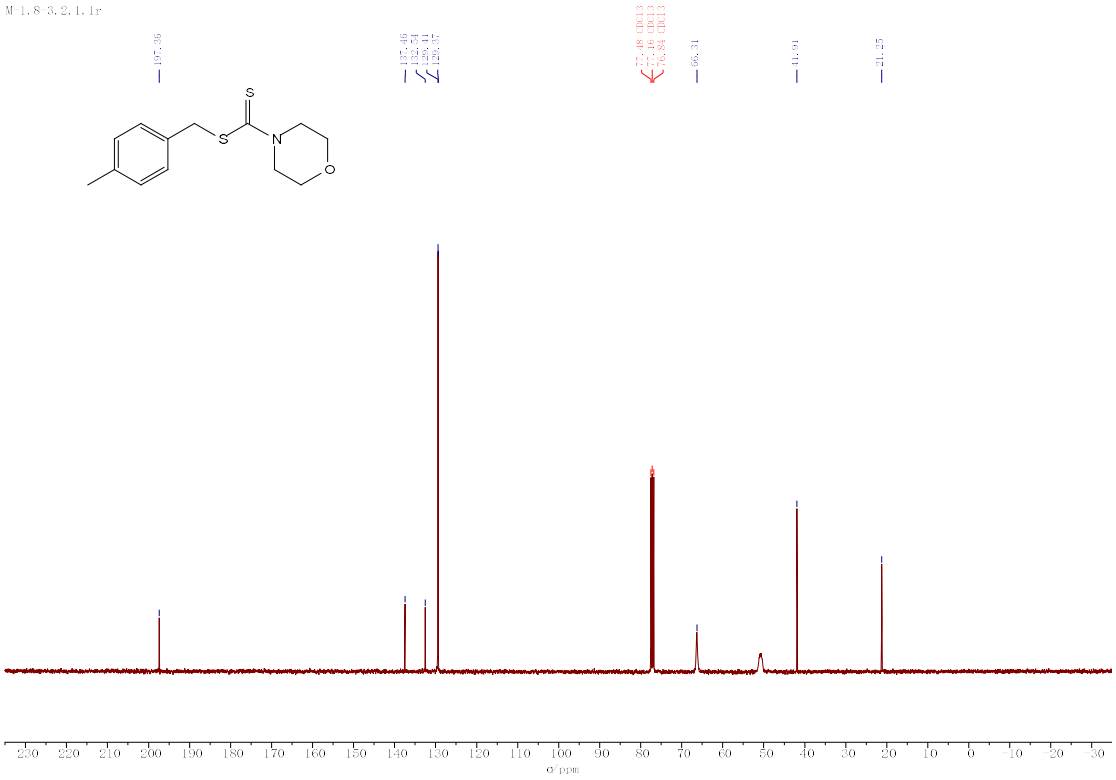
^{13}C NMR-spectrum of **4l**



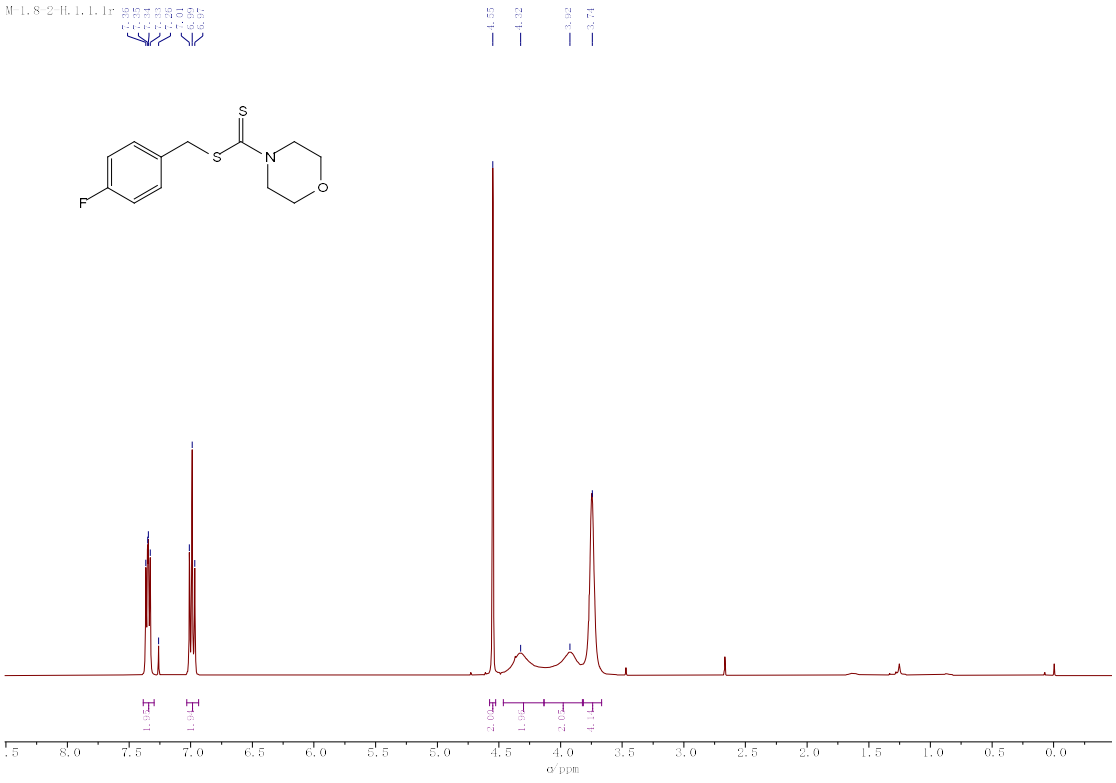
^{1}H NMR-spectrum of **4m**



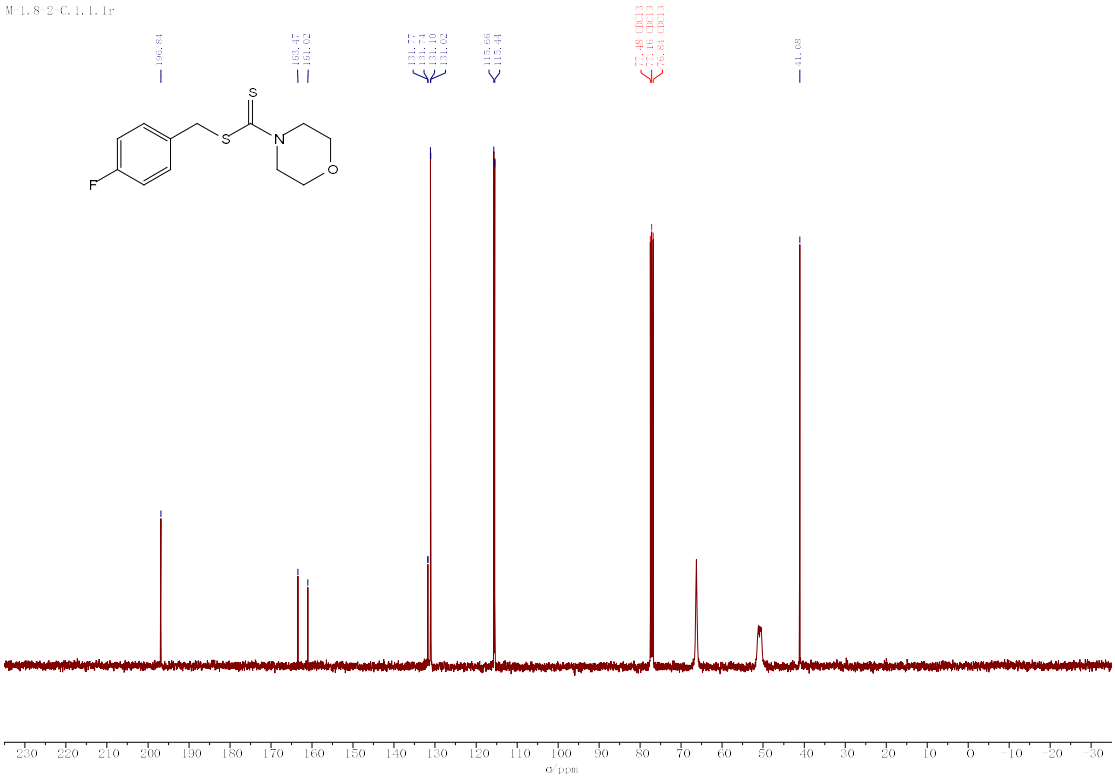
^{13}C NMR-spectrum of **4m**



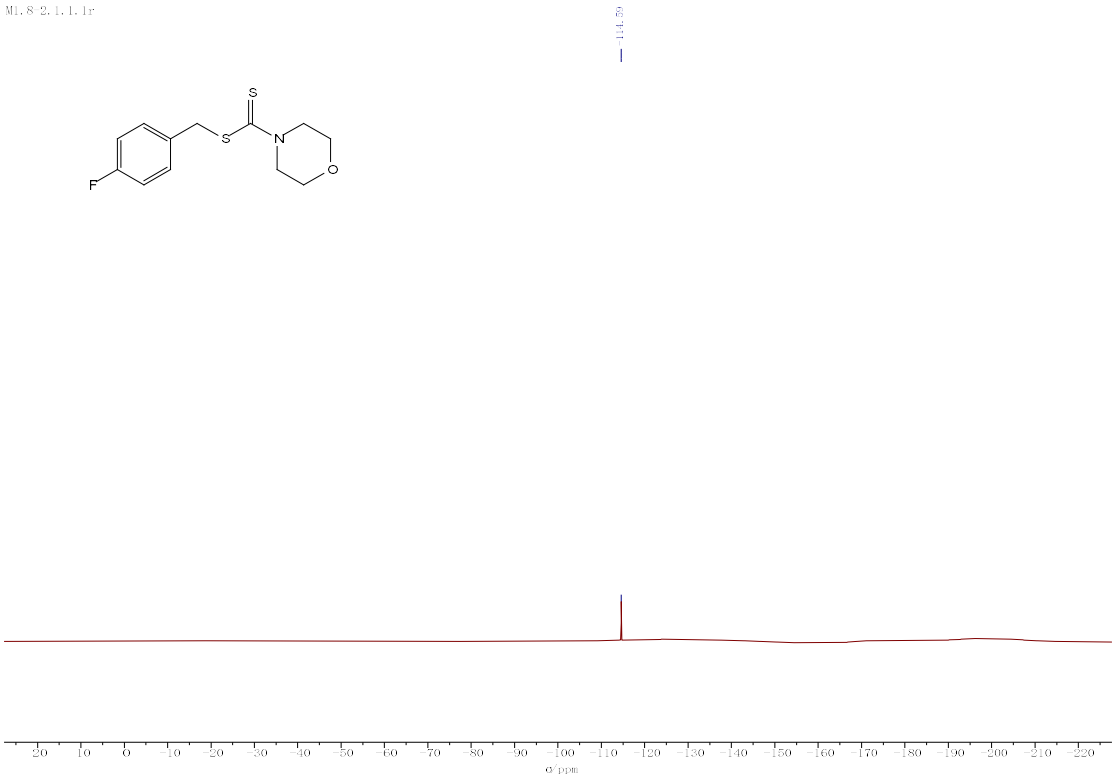
^{1}H NMR-spectrum of **4n**



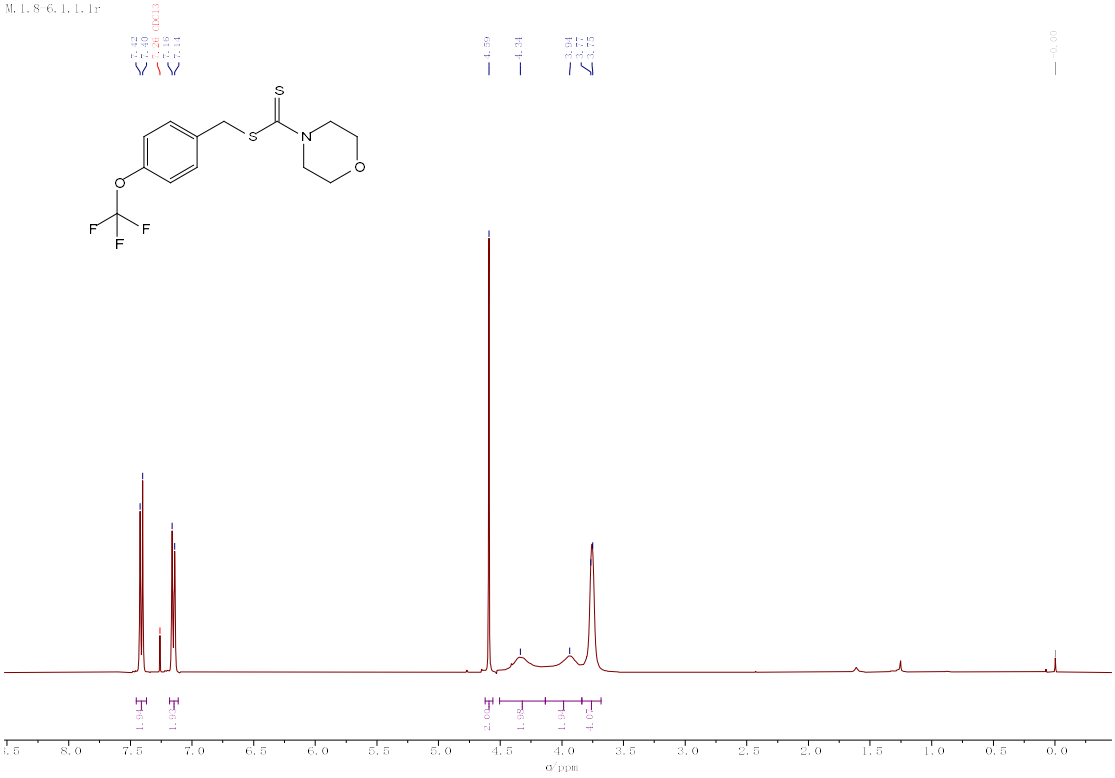
^{13}C NMR-spectrum of **4n**



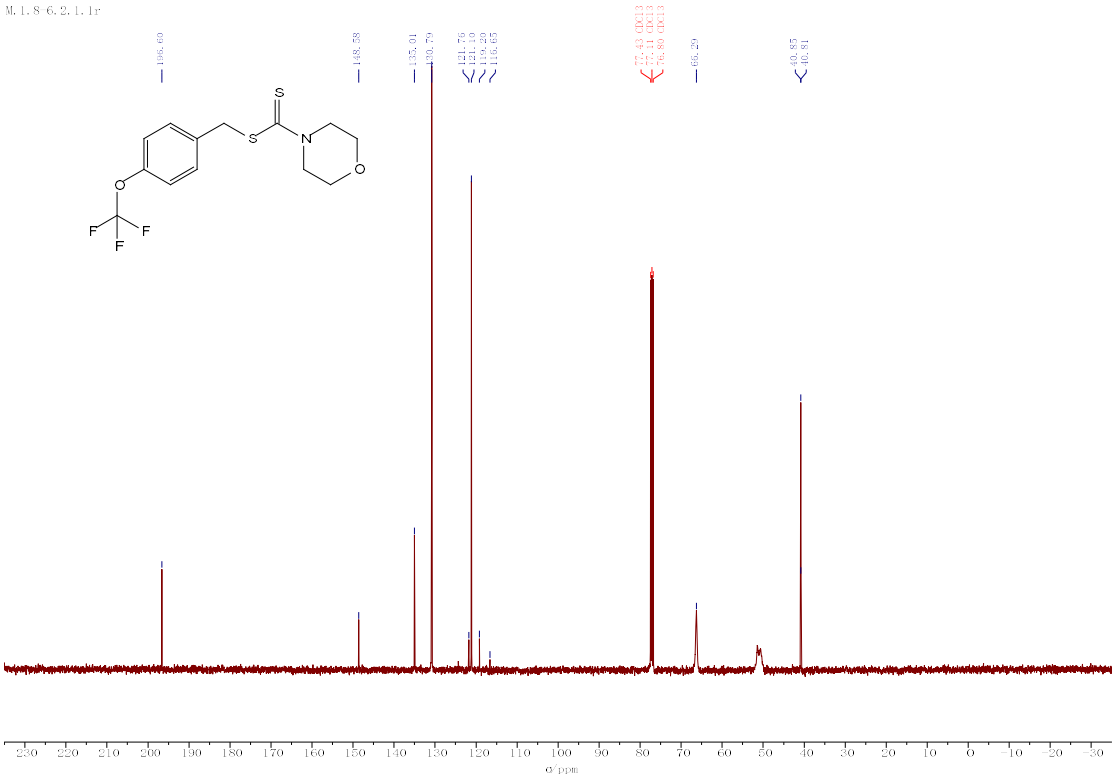
^{19}F NMR-spectrum of **4n**



^{1}H NMR-spectrum of **4o**

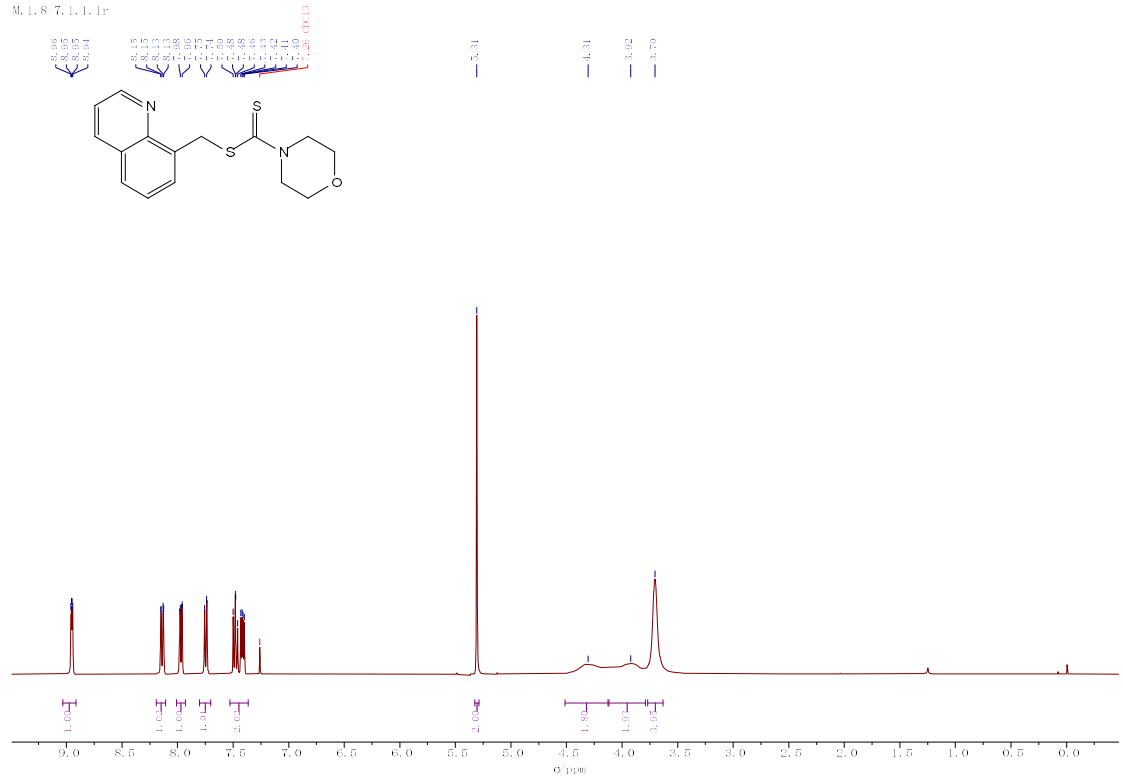


^{13}C NMR-spectrum of **4o**

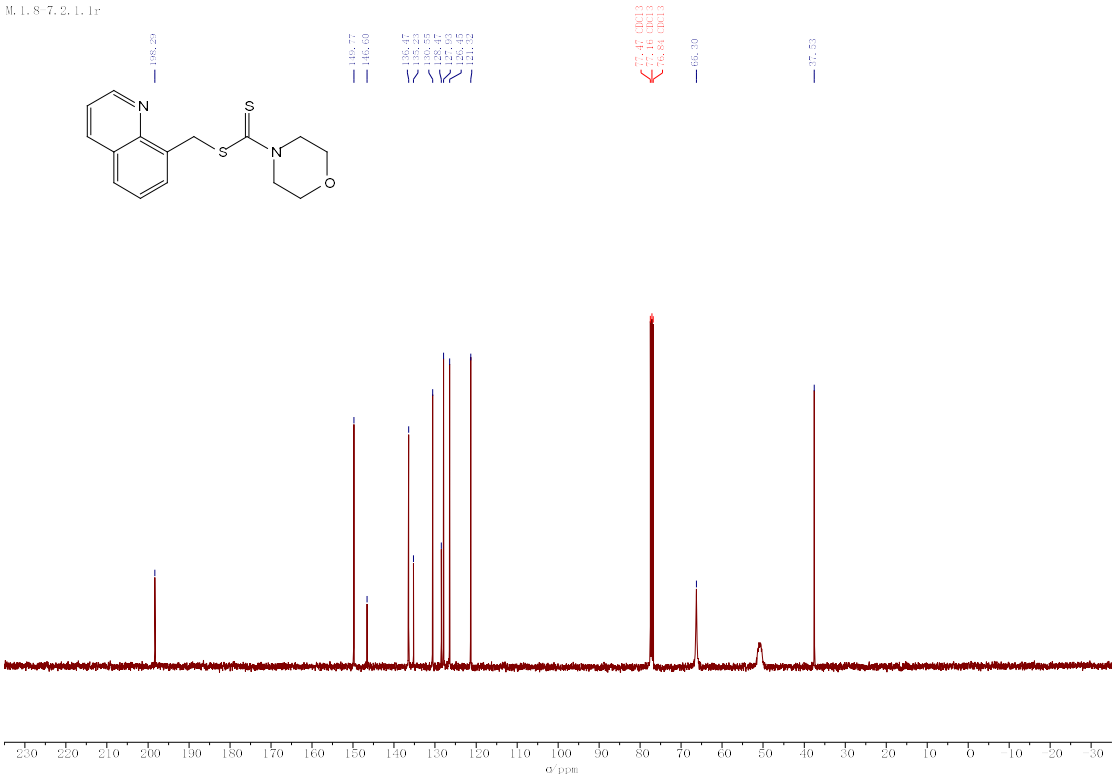


^{19}F NMR-spectrum of **4o**

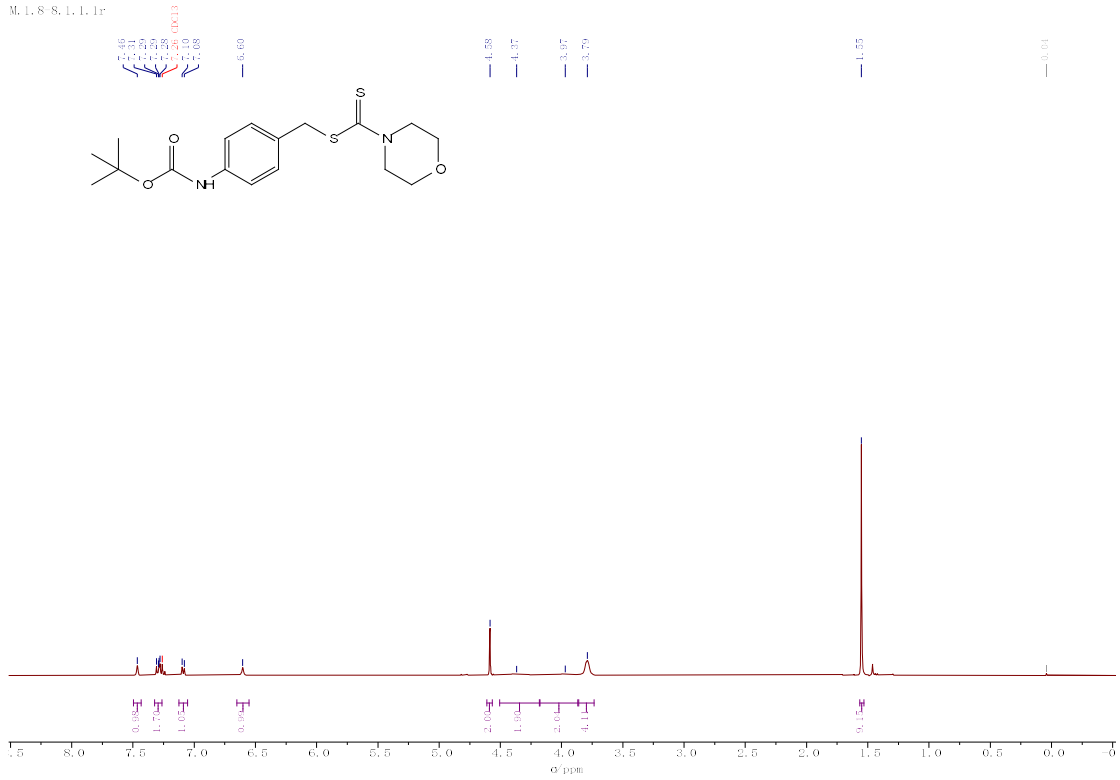
^{1}H NMR-spectrum of **4p**



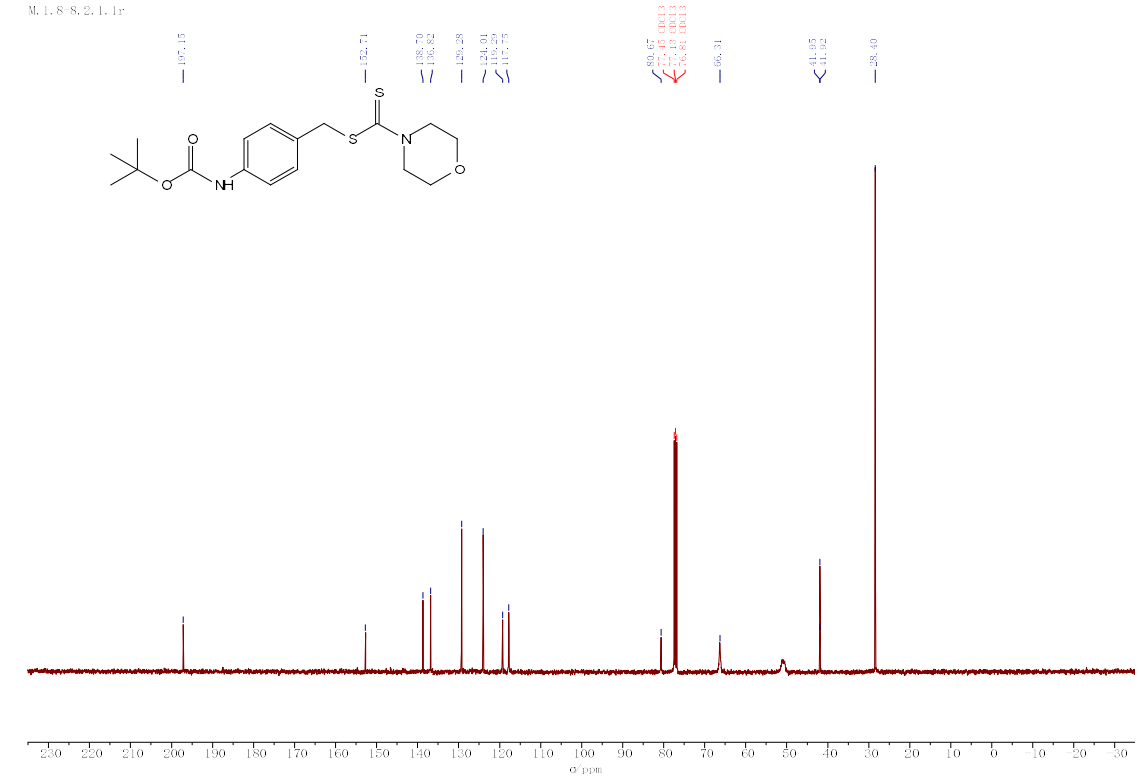
^{13}C NMR-spectrum of **4p**



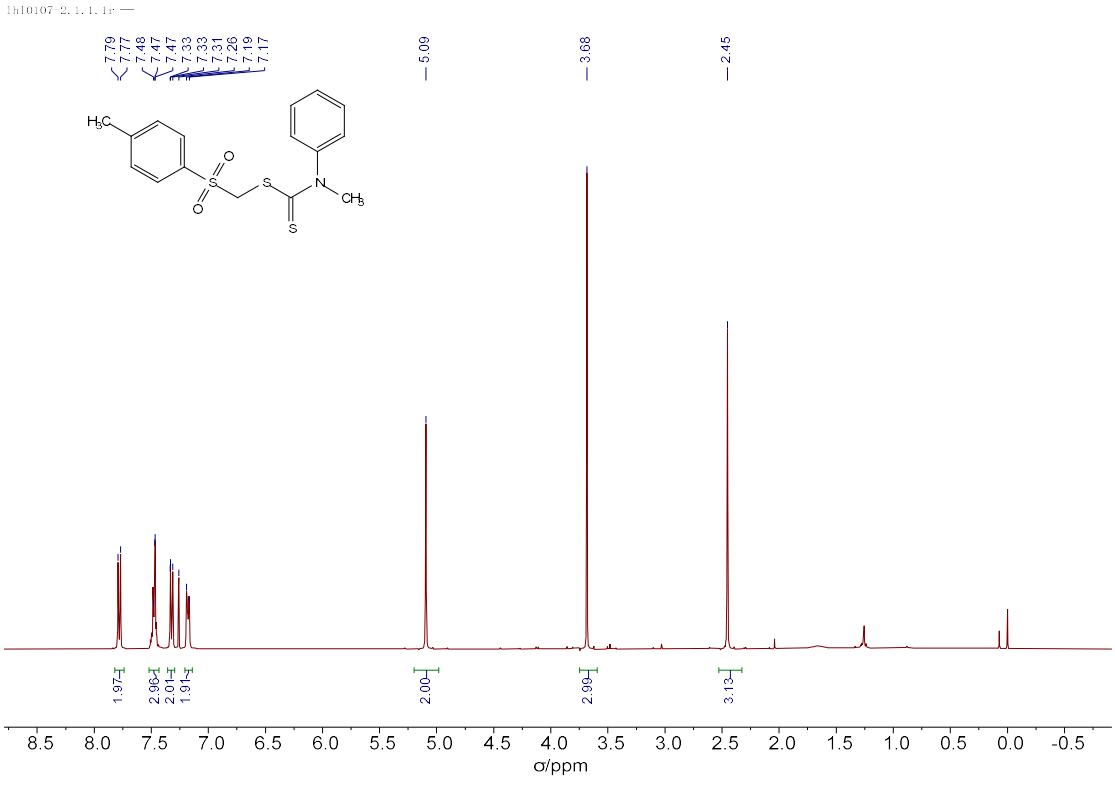
^{1}H NMR-spectrum of **4q**



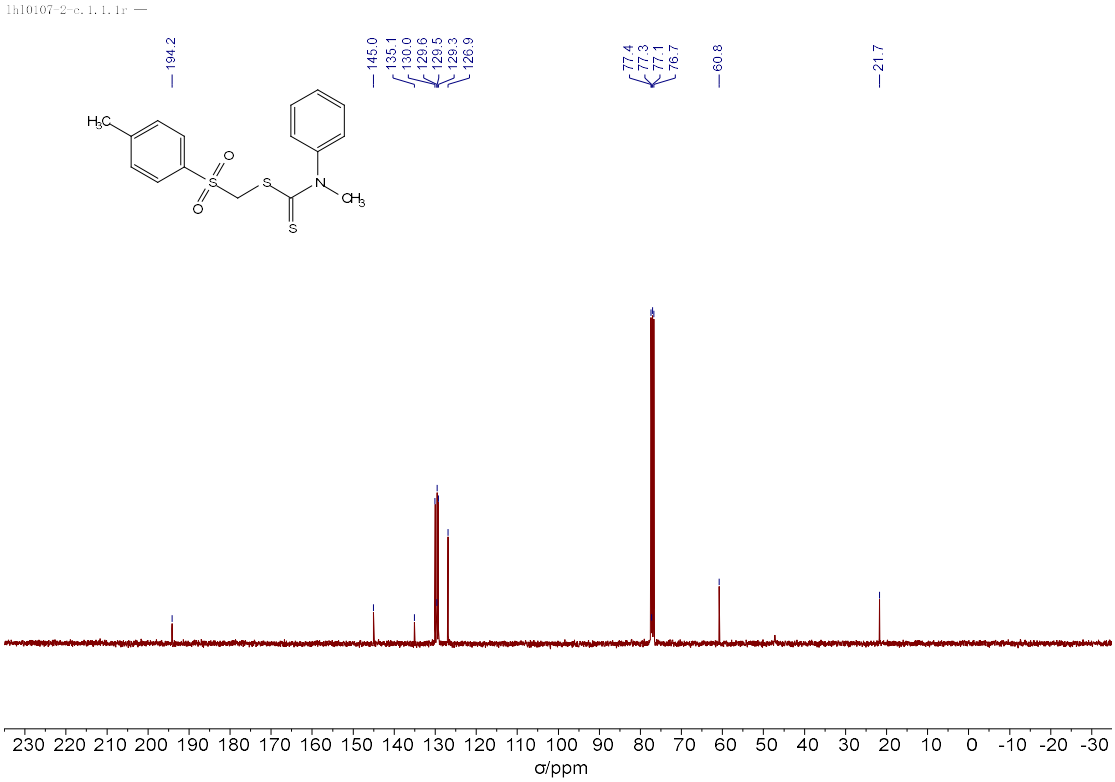
^{13}C NMR-spectrum of **4q**



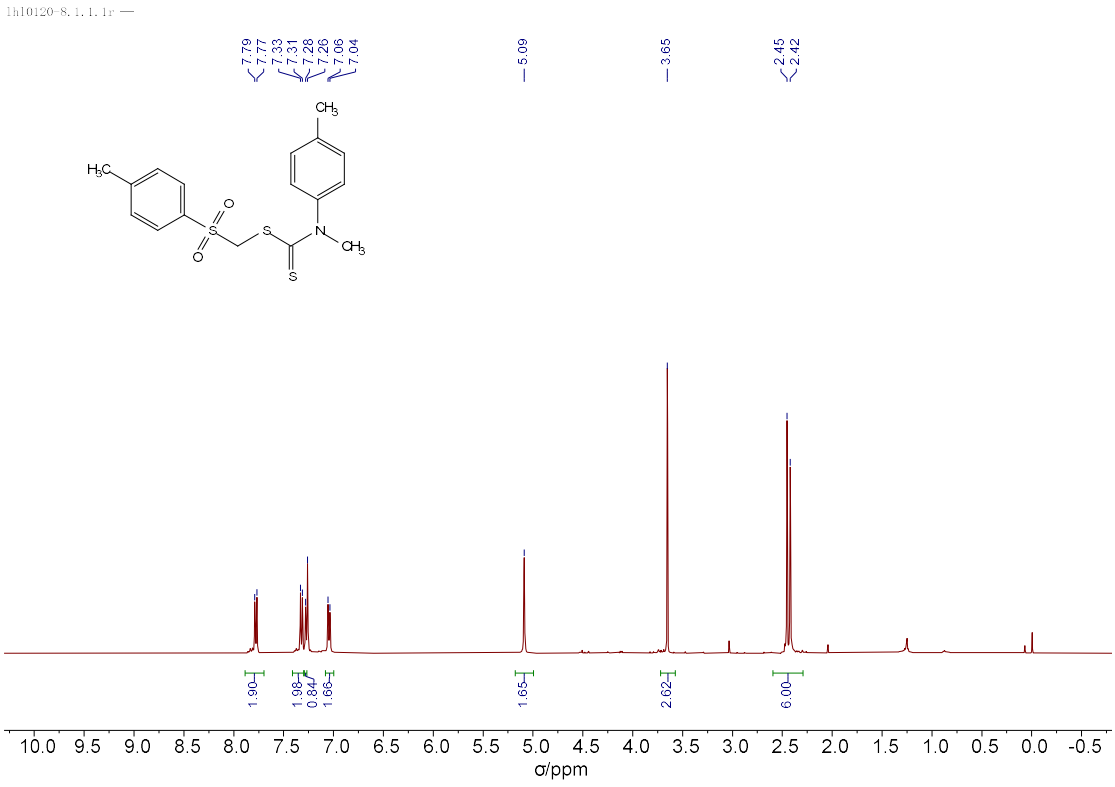
^{1}H NMR-spectrum of **4r**



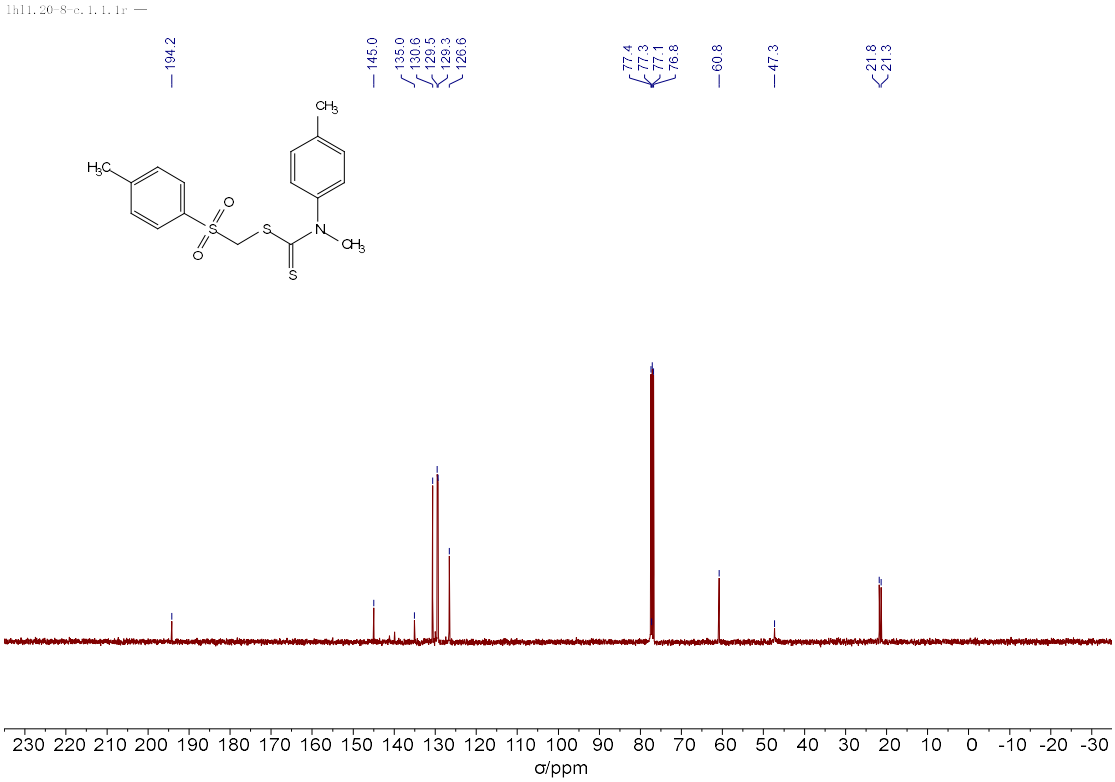
^{13}C NMR-spectrum of **4r**



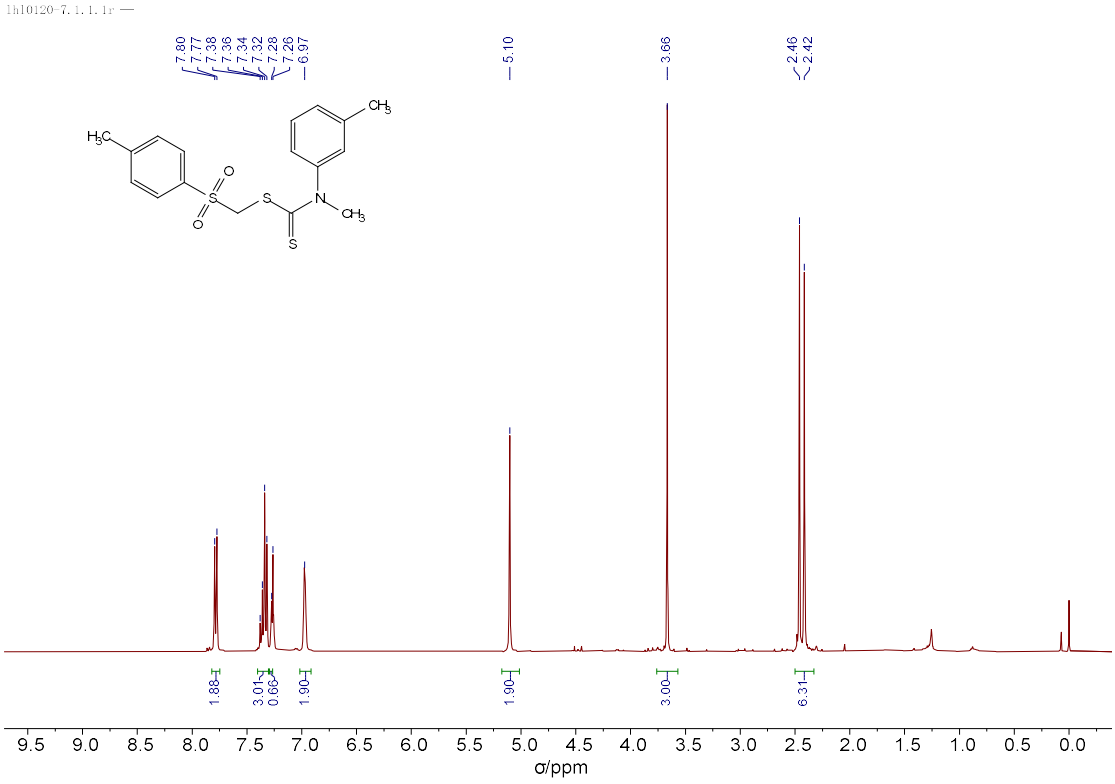
^{1}H NMR-spectrum of **4s**



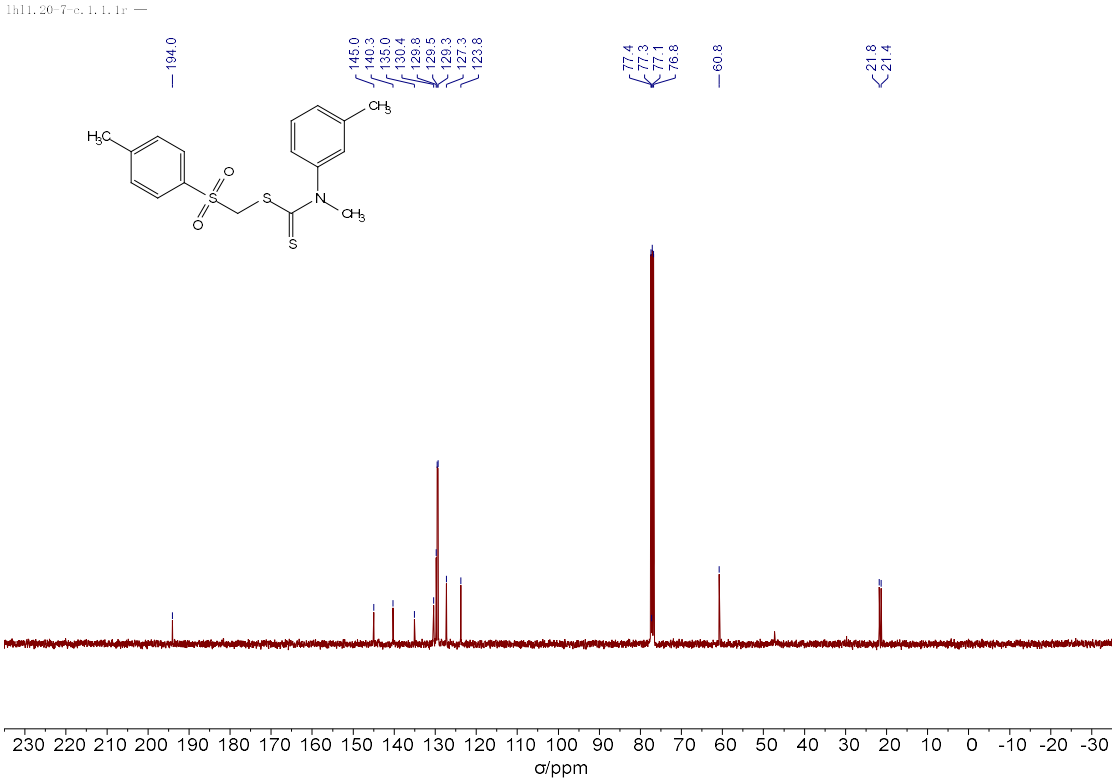
^{13}C NMR-spectrum of **4s**



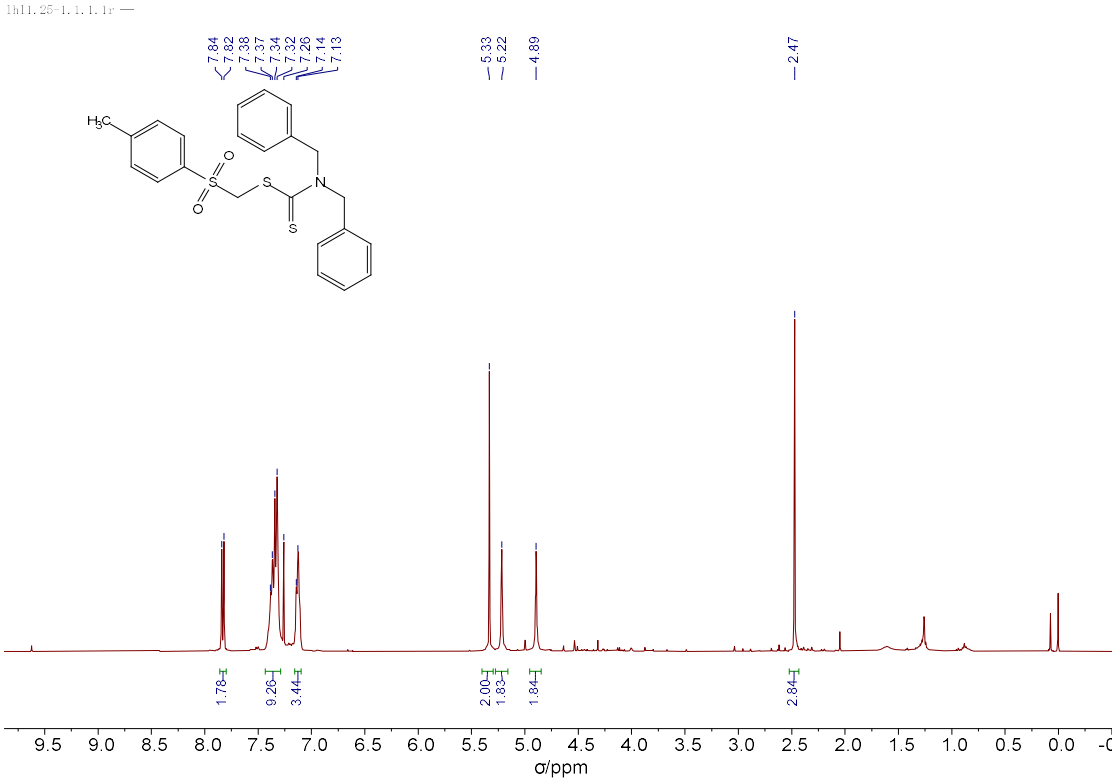
^{1}H NMR-spectrum of **4t**



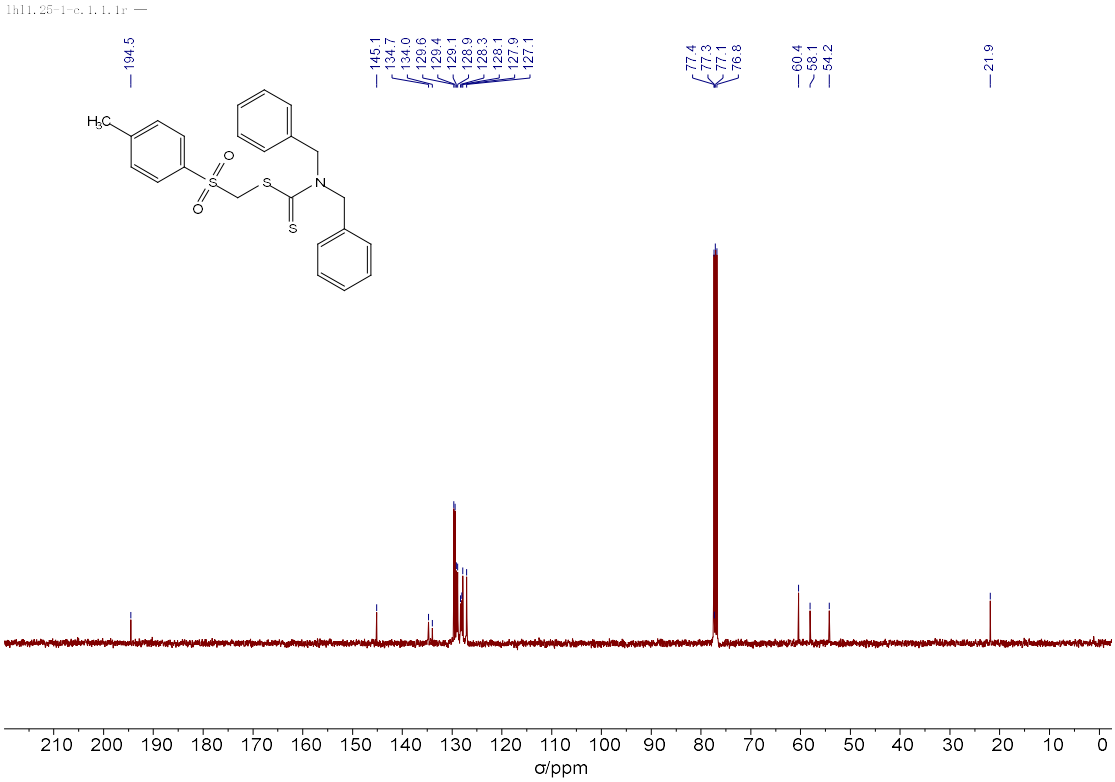
^{13}C NMR-spectrum of **4t**



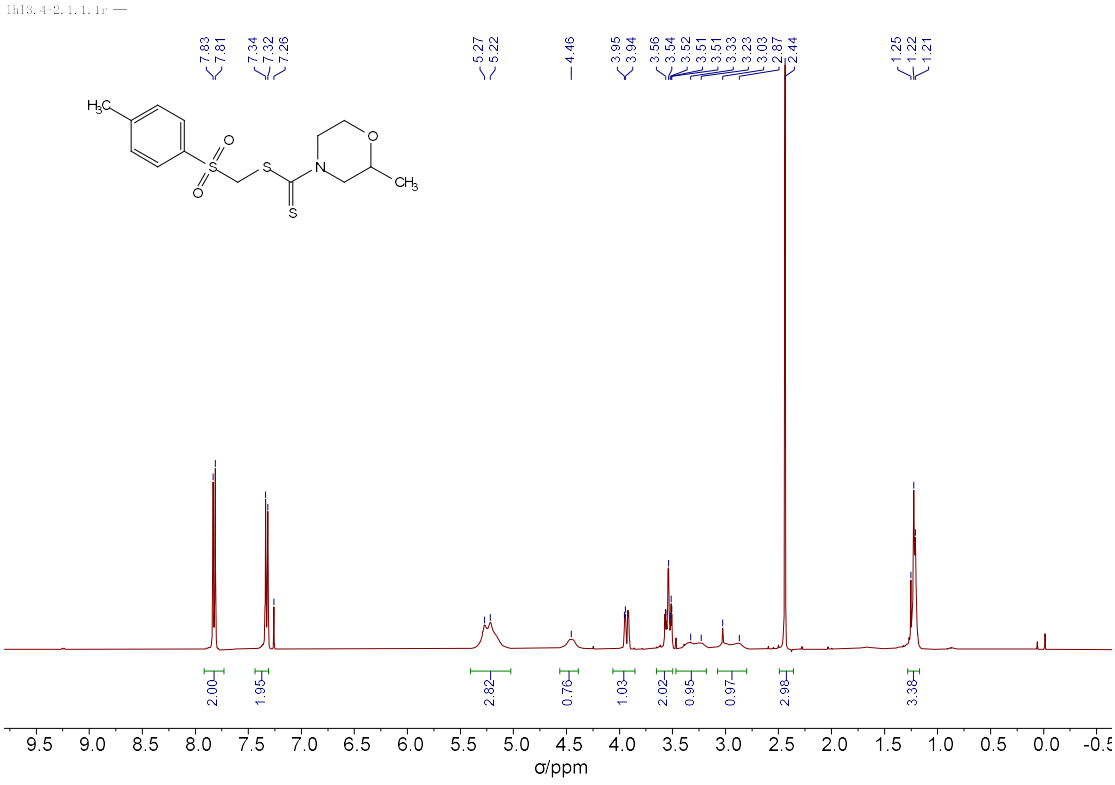
^{1}H NMR-spectrum of **4u**



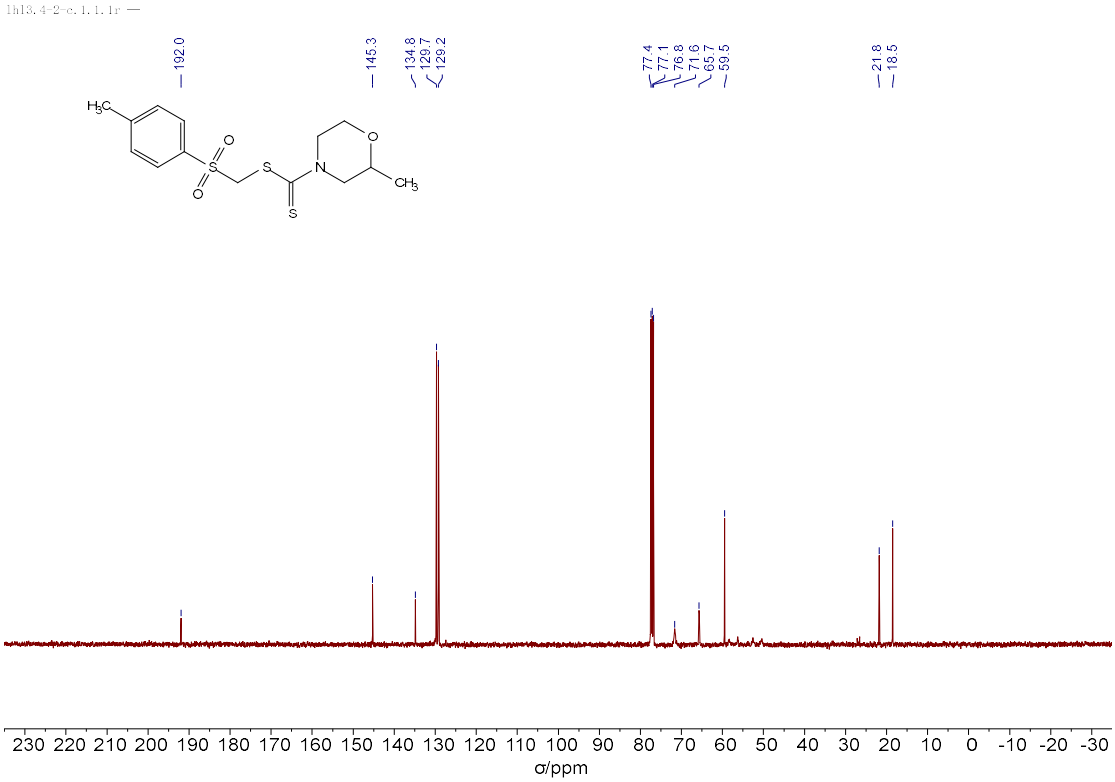
^{13}C NMR-spectrum of **4u**



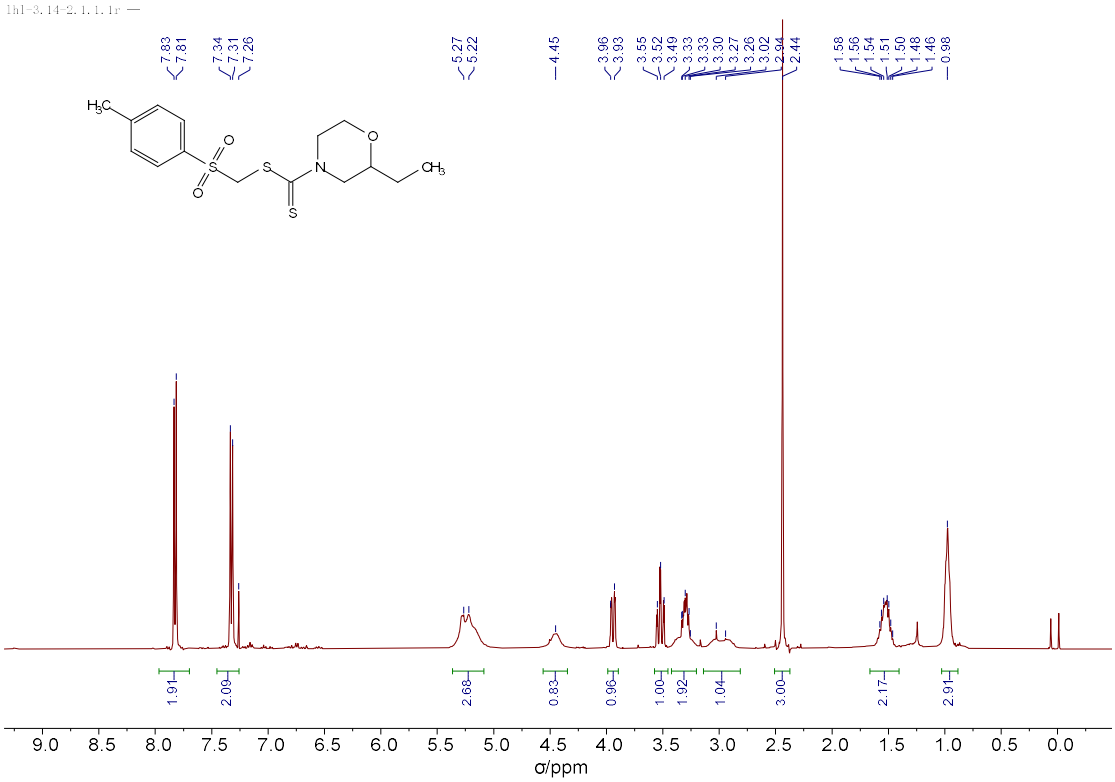
^{1}H NMR-spectrum of **4v**



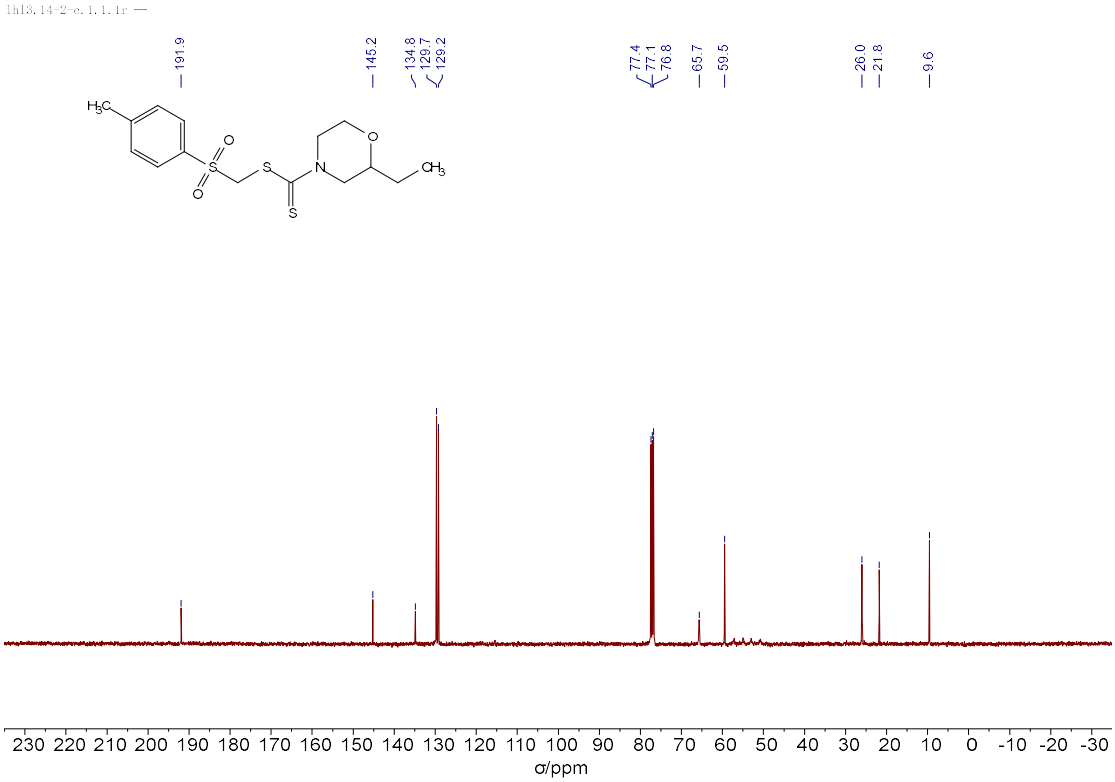
^{13}C NMR-spectrum of **4v**



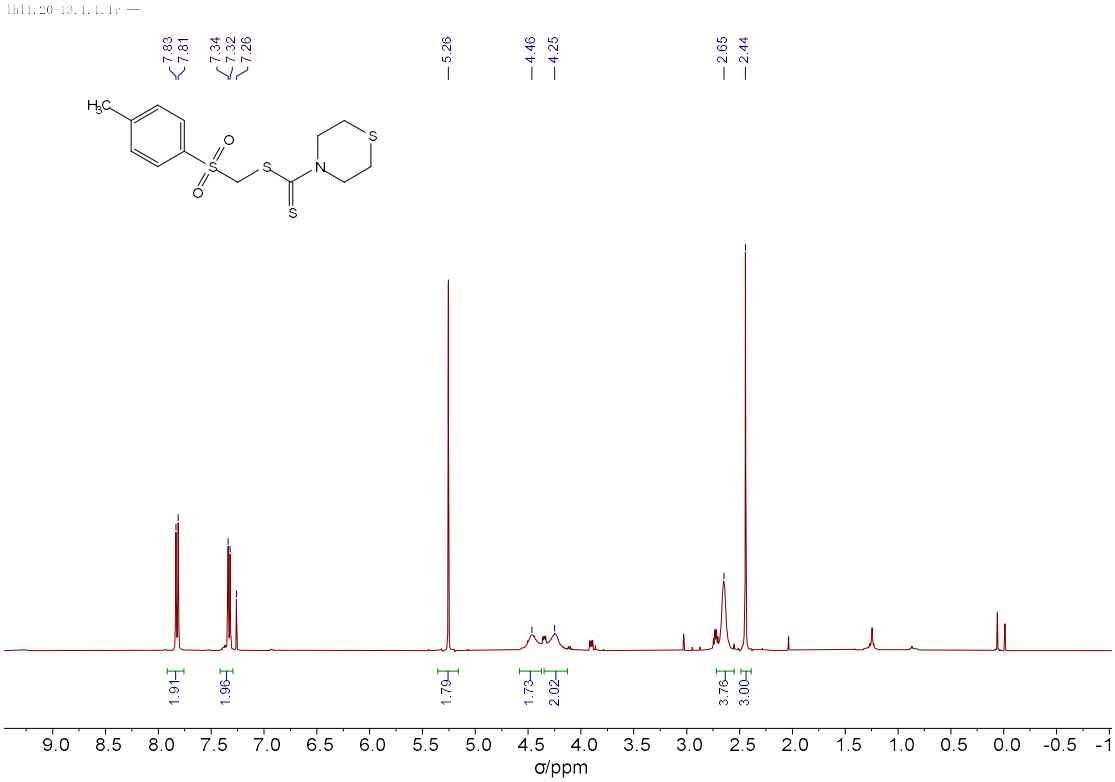
^{1}H NMR-spectrum of **4w**



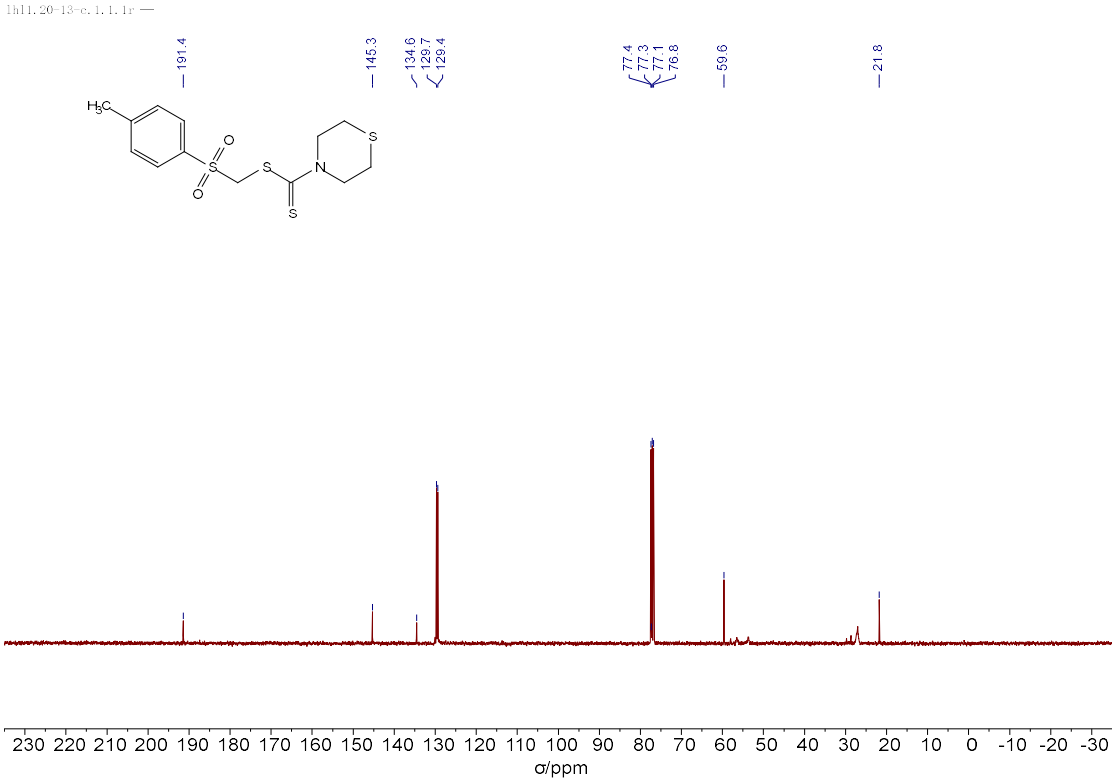
^{13}C NMR-spectrum of **4w**



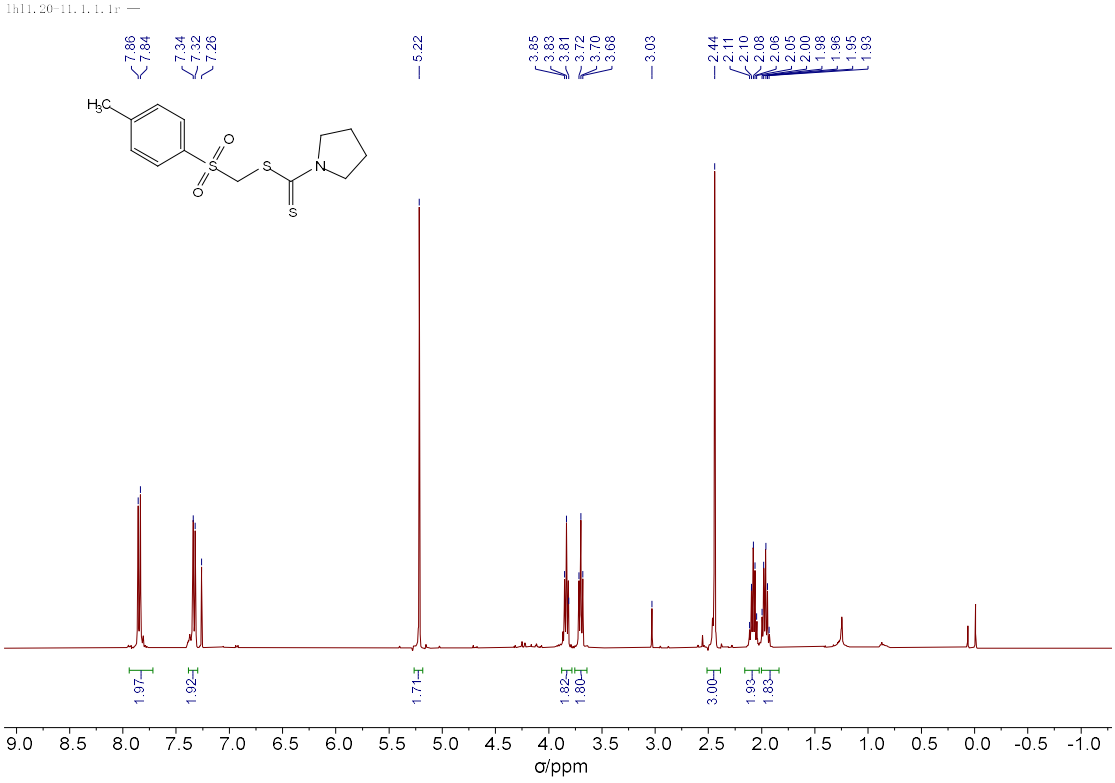
^{1}H NMR-spectrum of **4x**



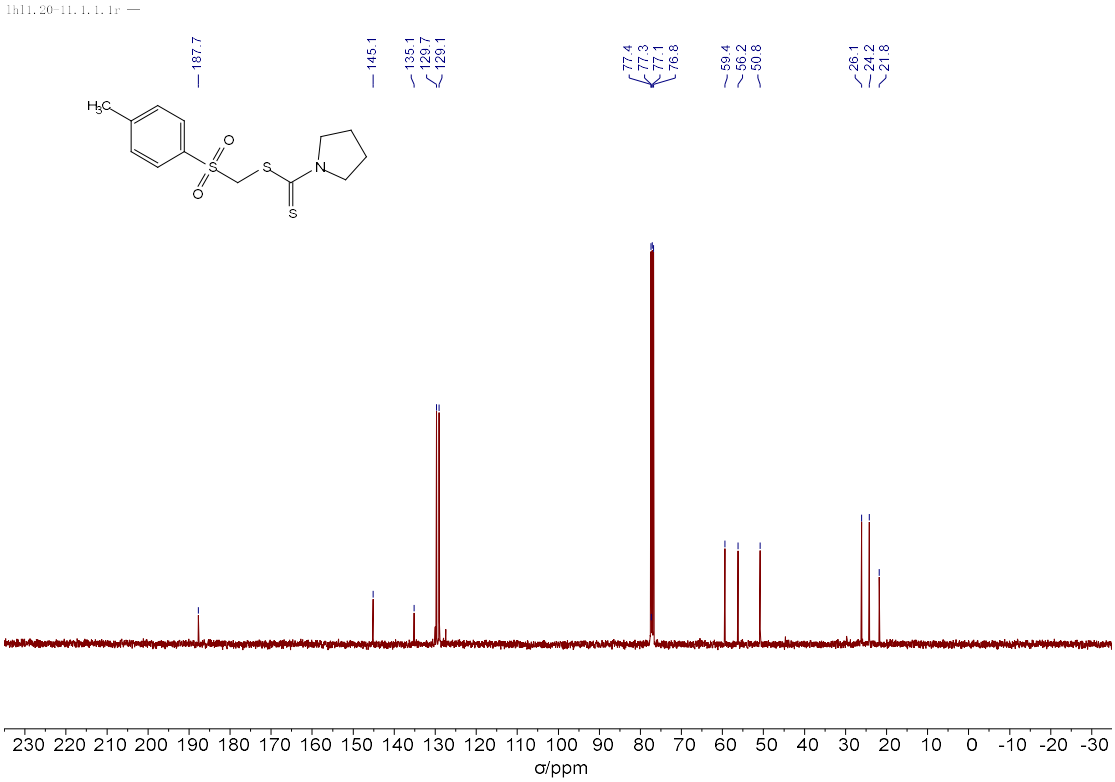
^{13}C NMR-spectrum of **4x**



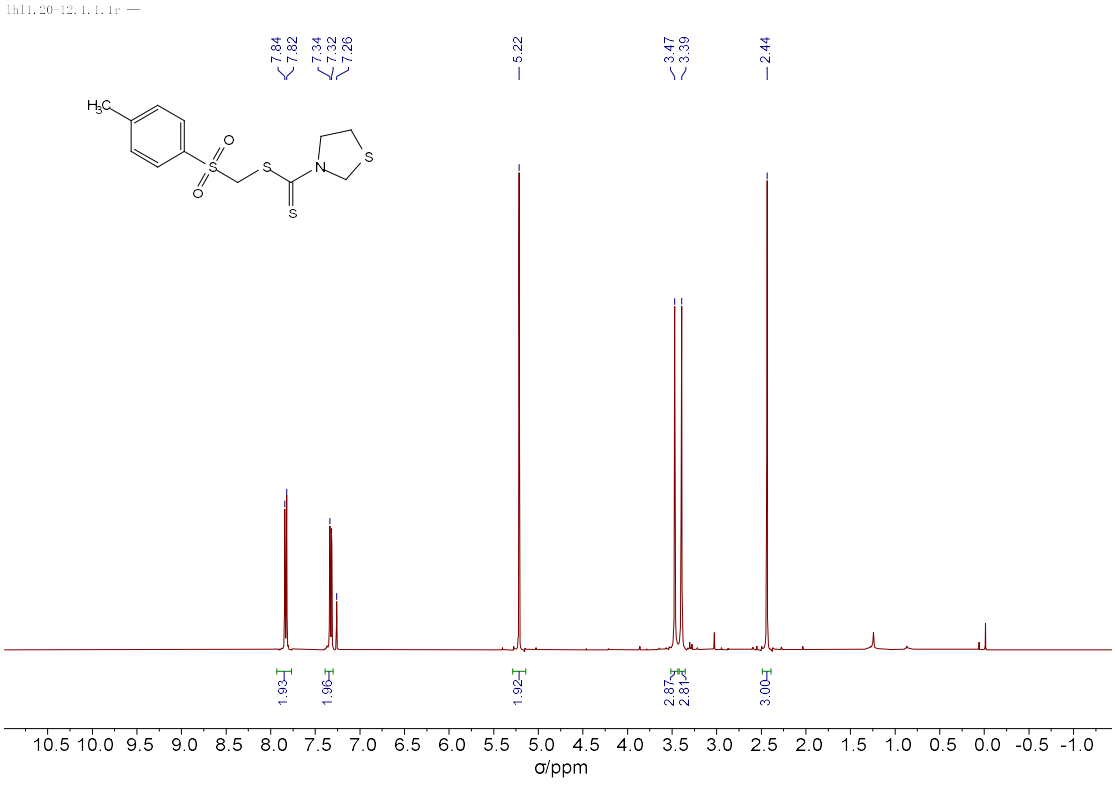
^{1}H NMR-spectrum of **4y**



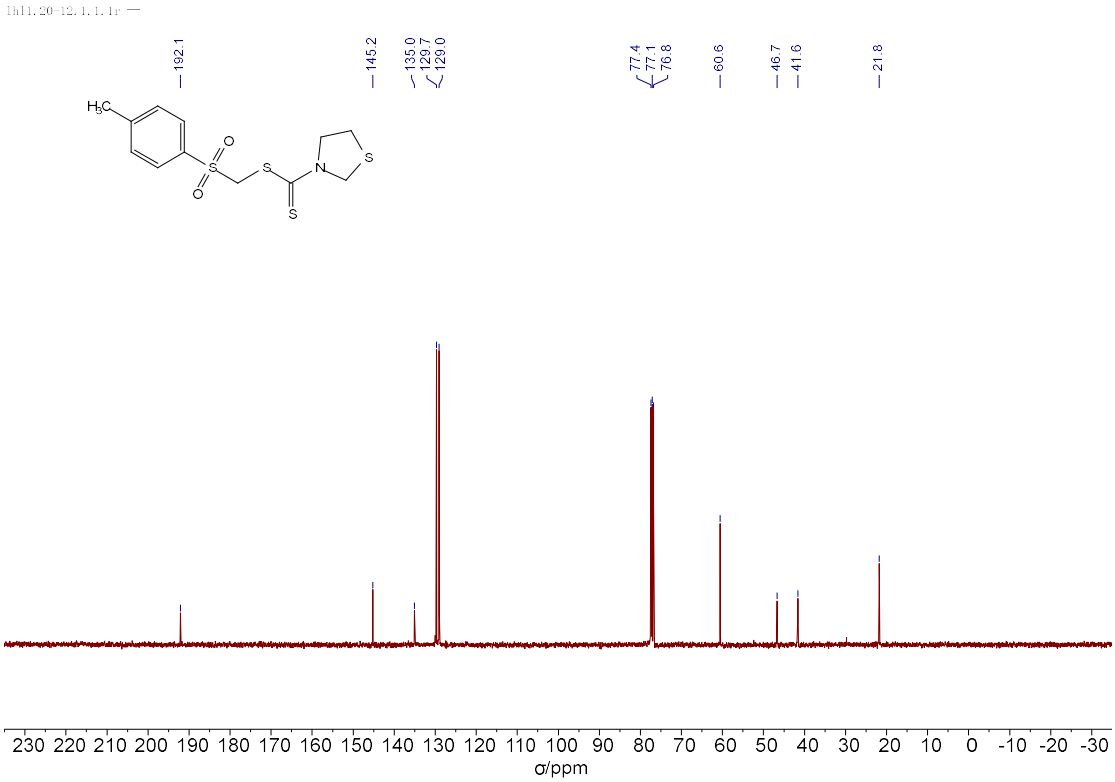
^{13}C NMR-spectrum of **4y**



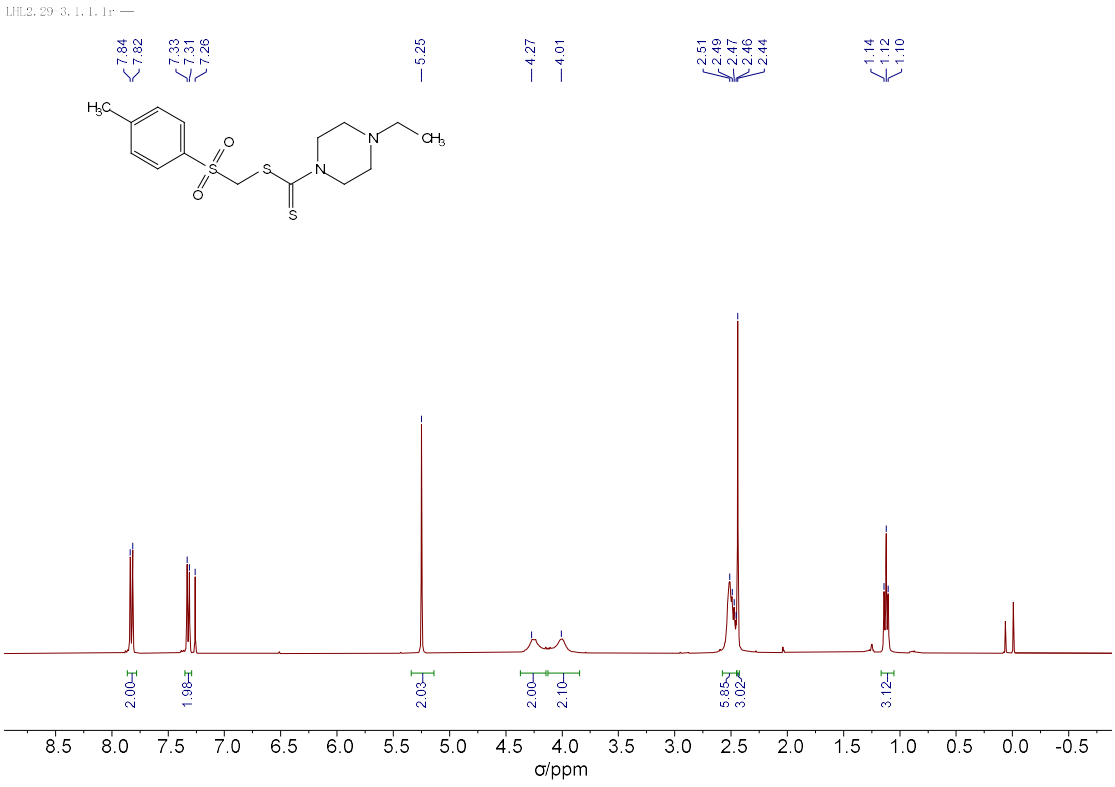
^{1}H NMR-spectrum of **4z**



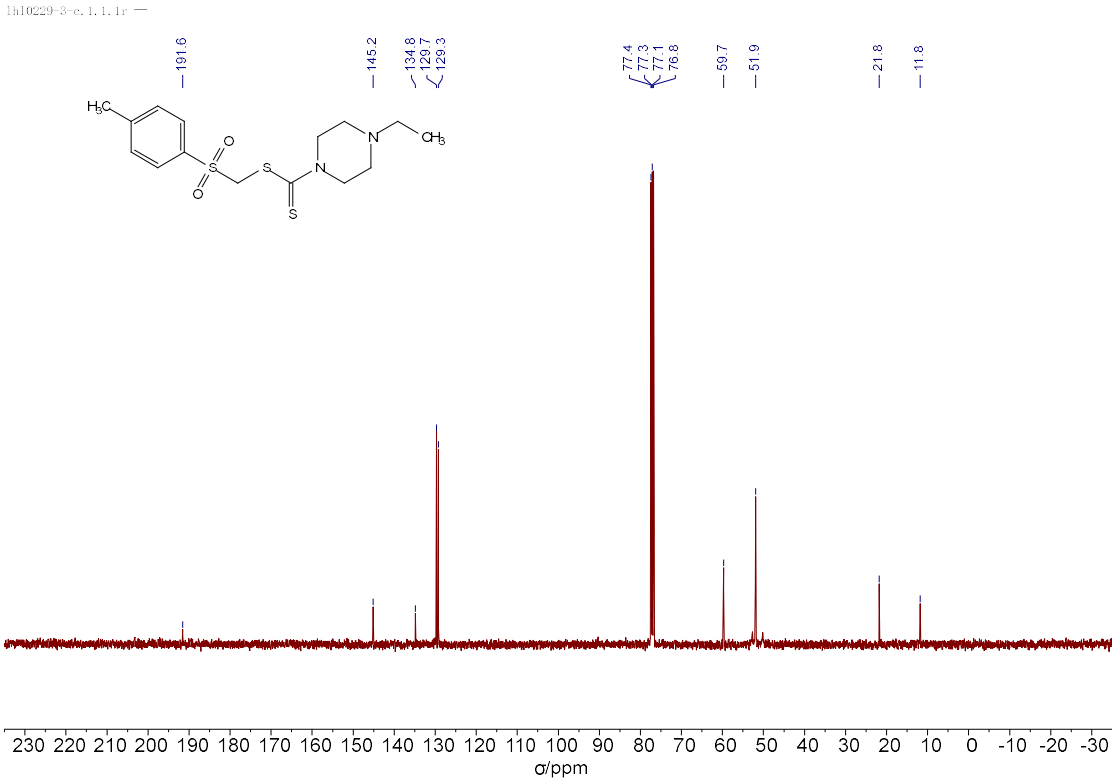
^{13}C NMR-spectrum of **4z**



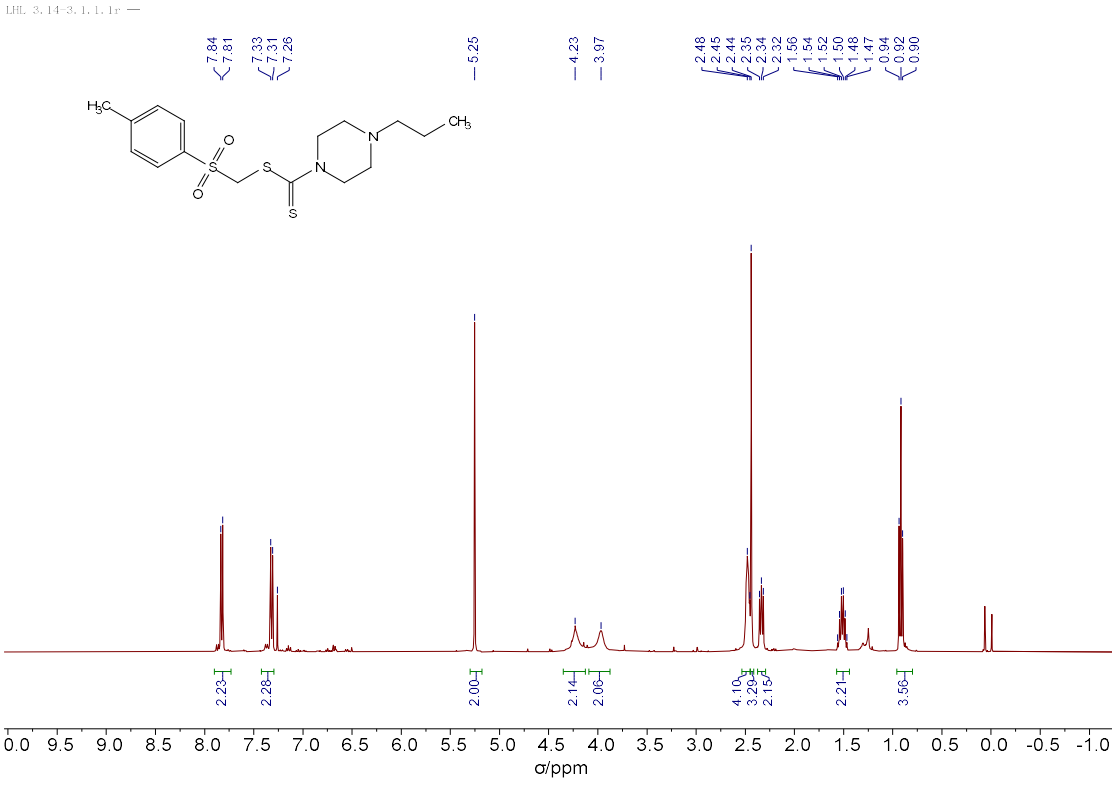
^{1}H NMR-spectrum of **4aa**



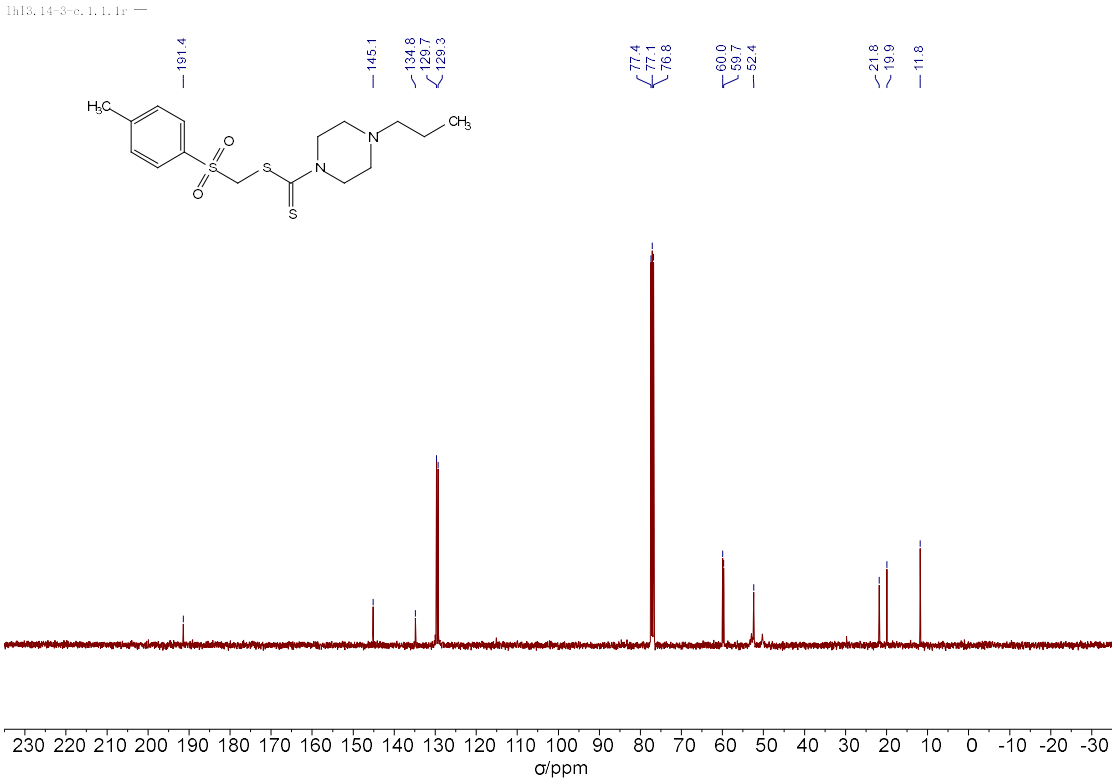
^{13}C NMR-spectrum of **4aa**



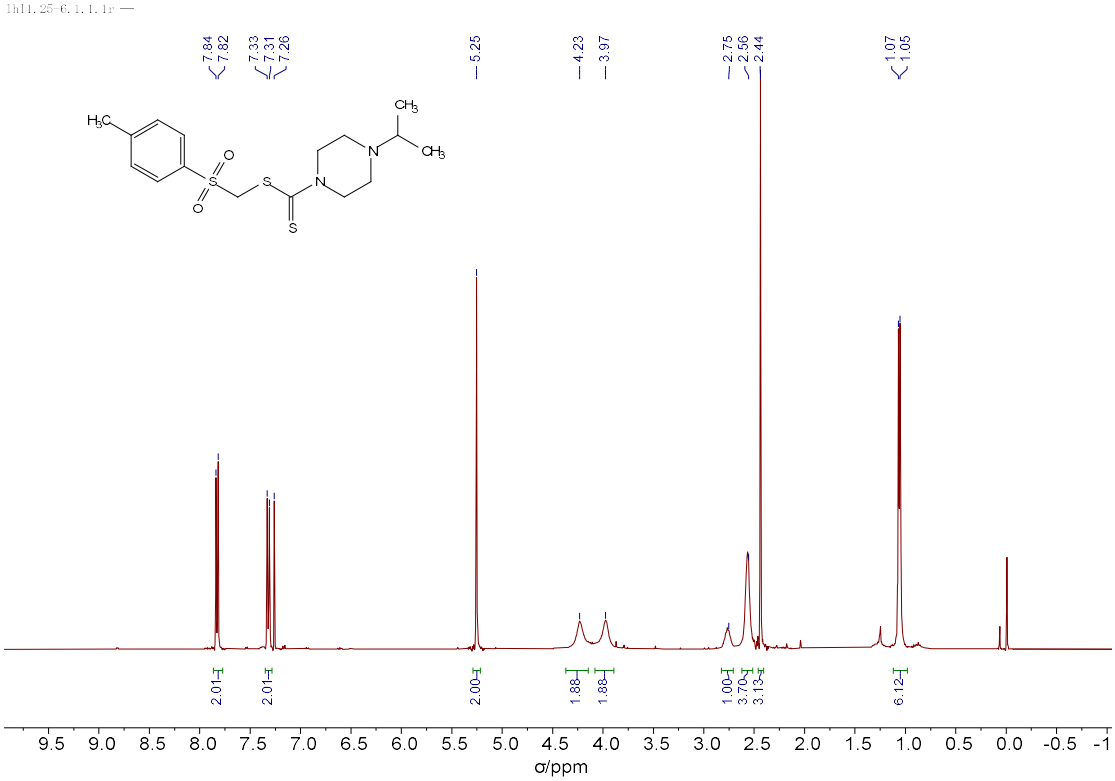
^{1}H NMR-spectrum of **4ab**



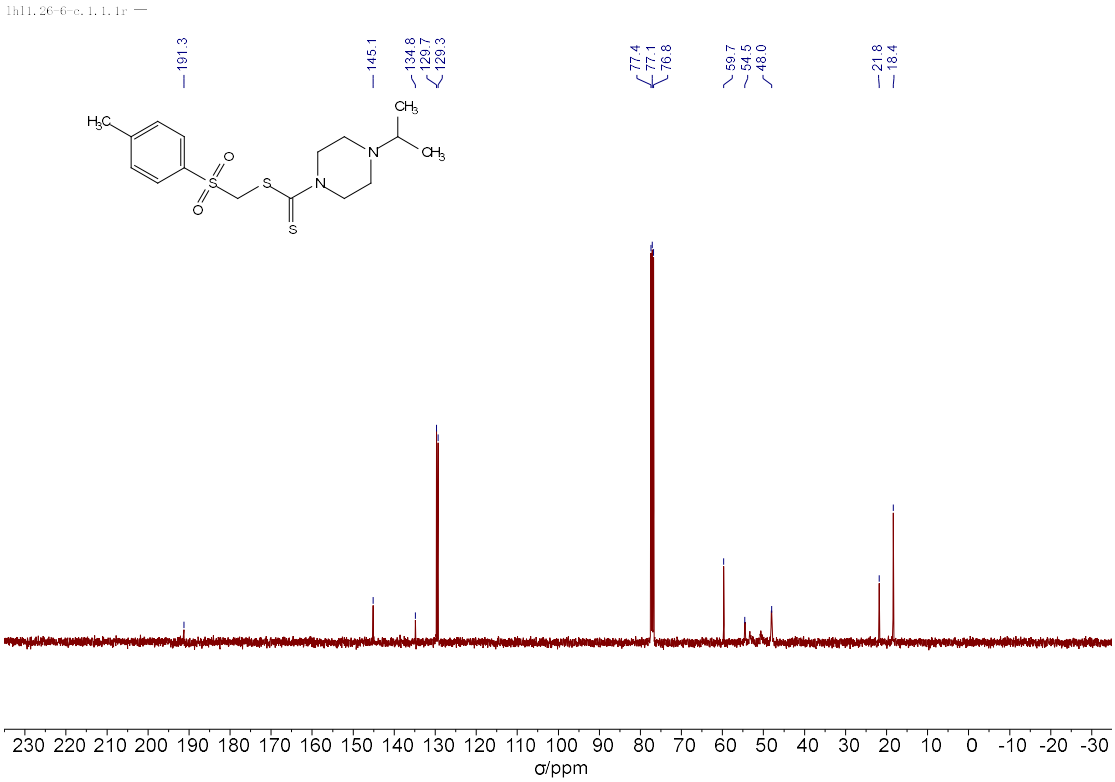
^{13}C NMR-spectrum of **4ab**



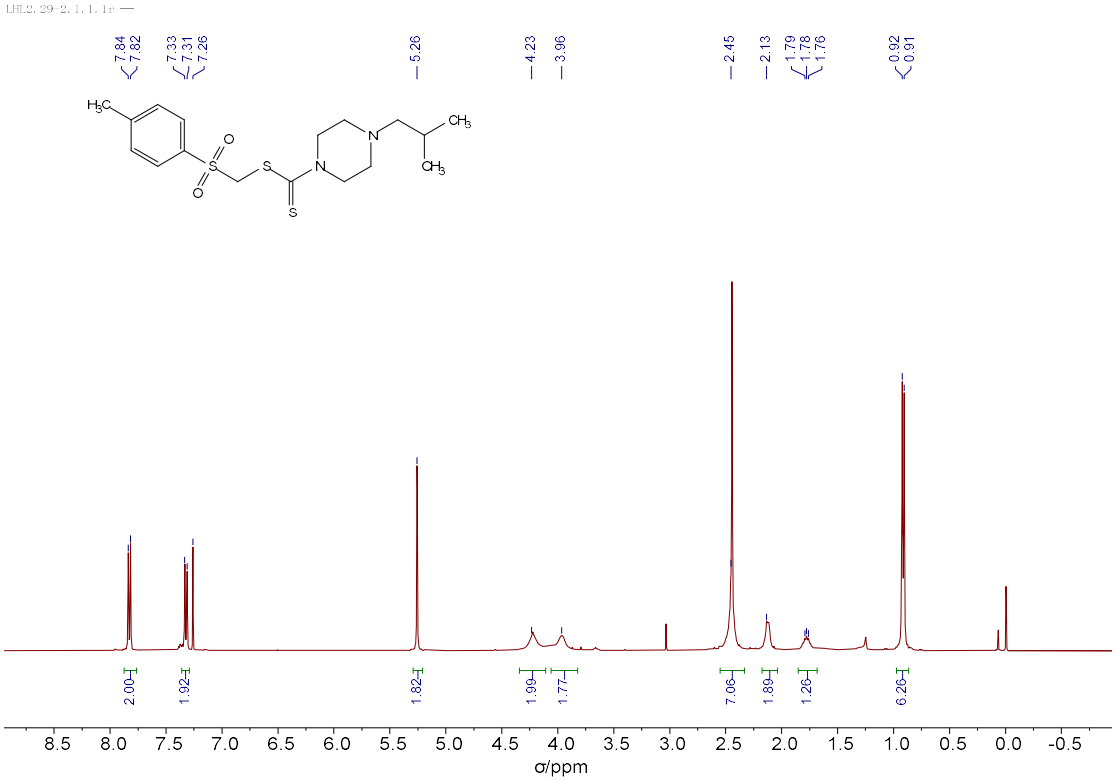
^{1}H NMR-spectrum of **4ac**



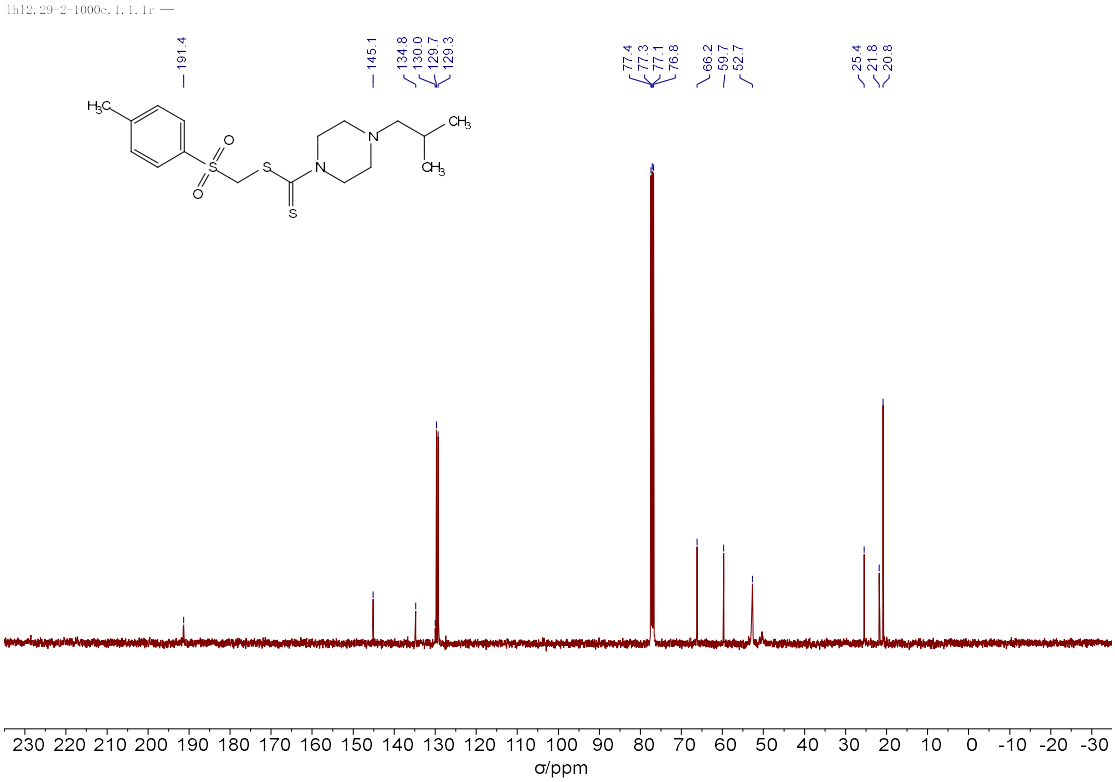
^{13}C NMR-spectrum of **4ac**



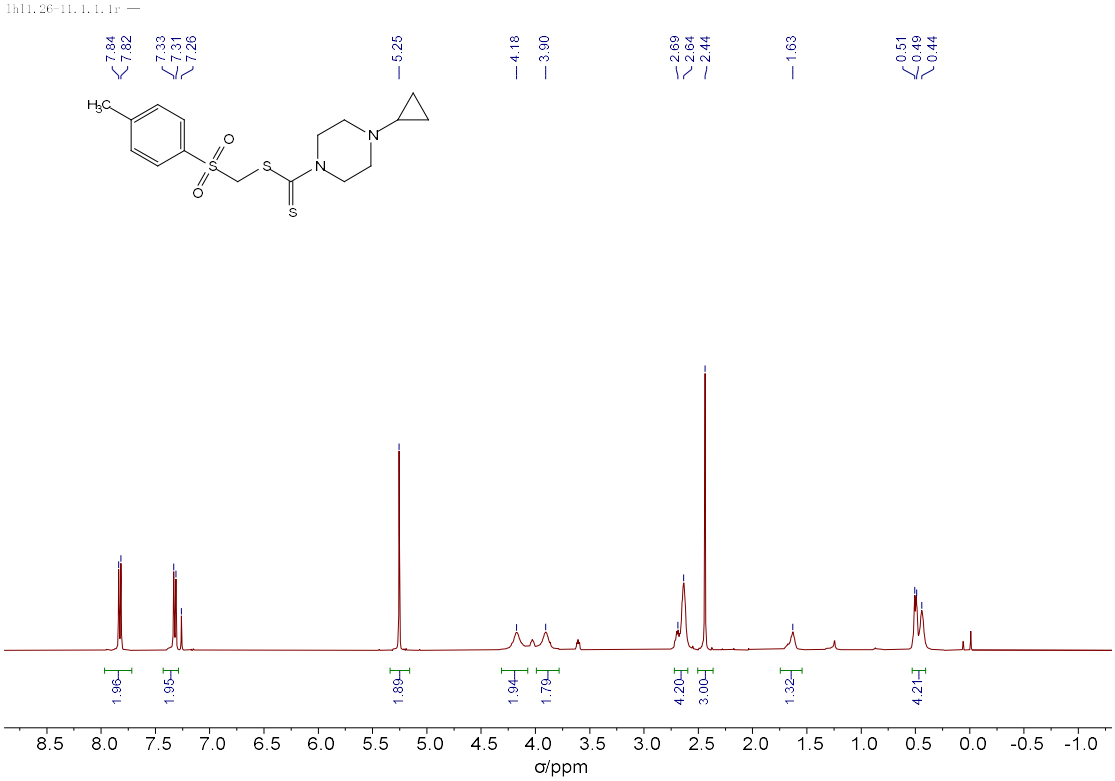
^{1}H NMR-spectrum of **4ad**



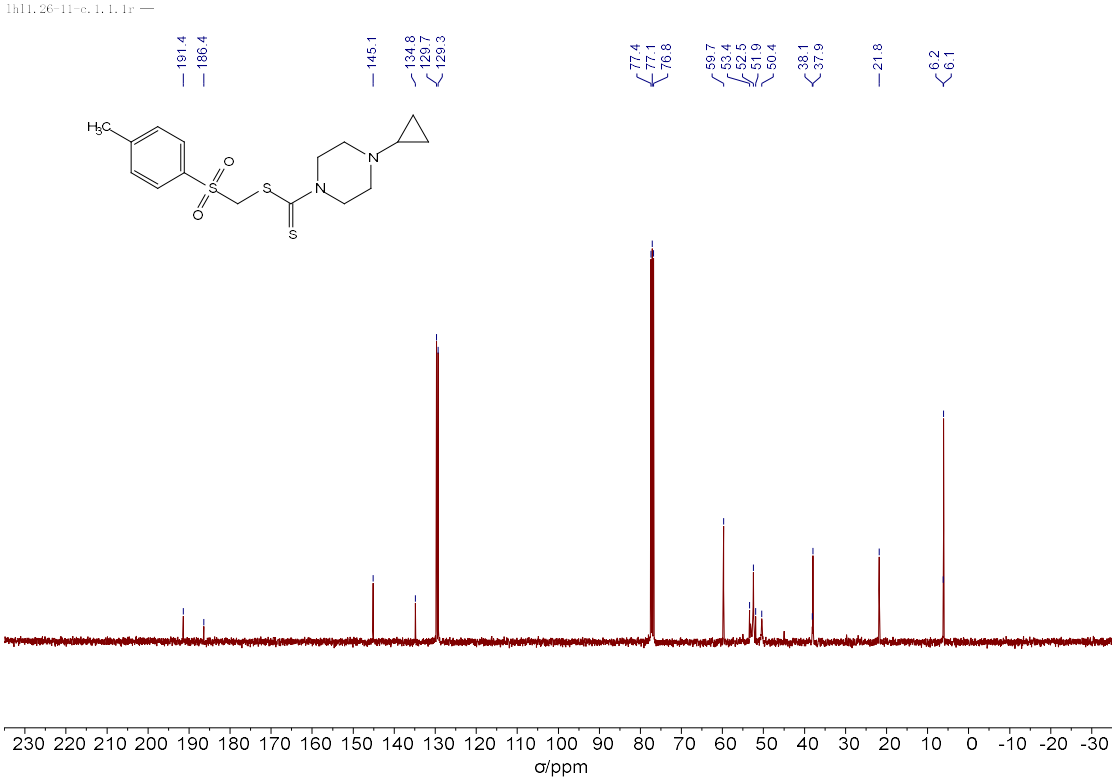
^{13}C NMR-spectrum of **4ad**



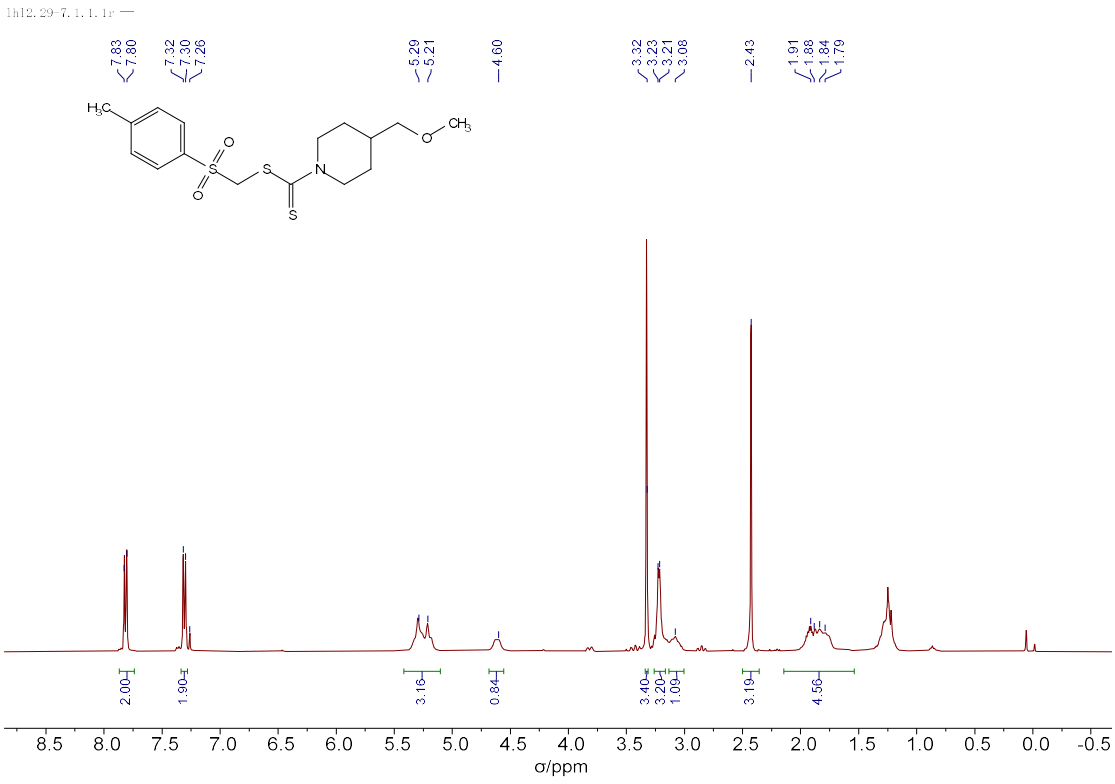
^{1}H NMR-spectrum of **4ae**



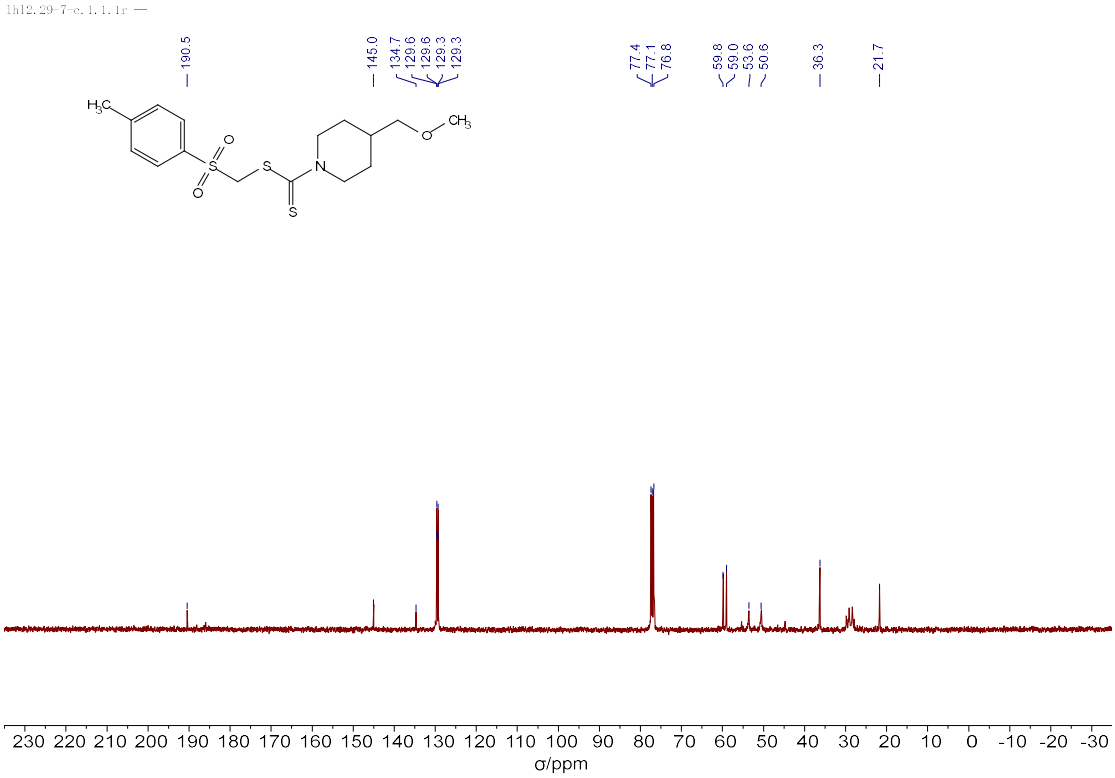
^{13}C NMR-spectrum of **4ae**



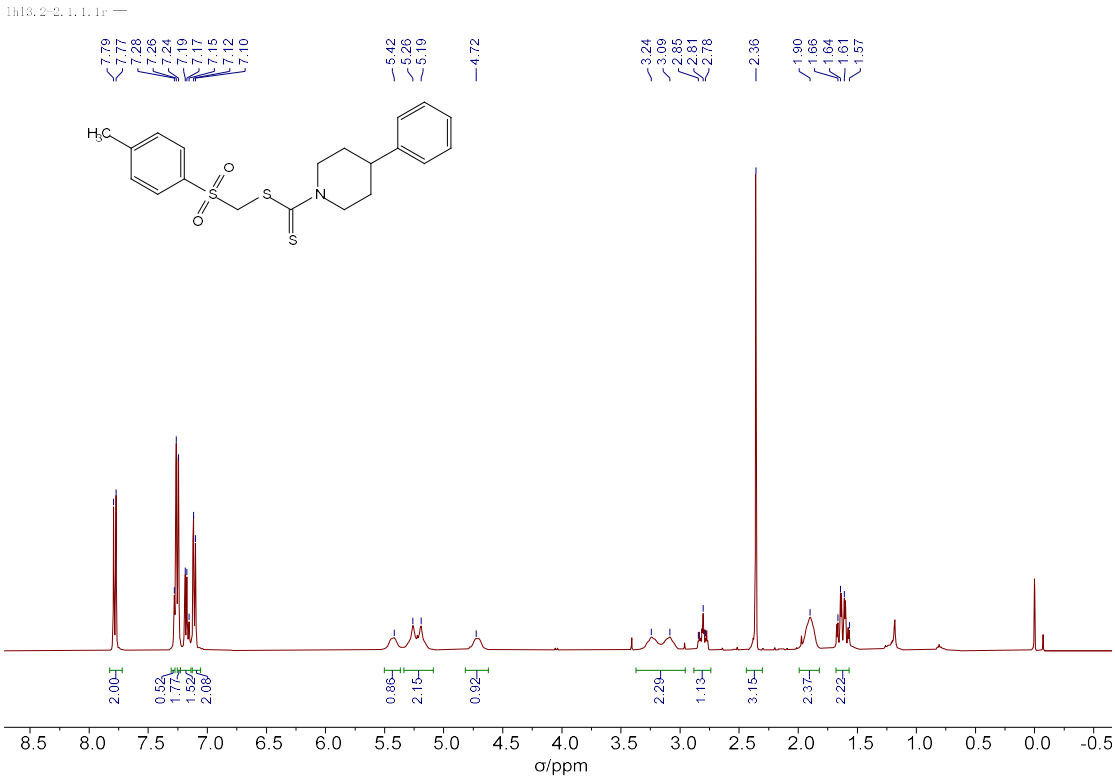
^{1}H NMR-spectrum of **4af**



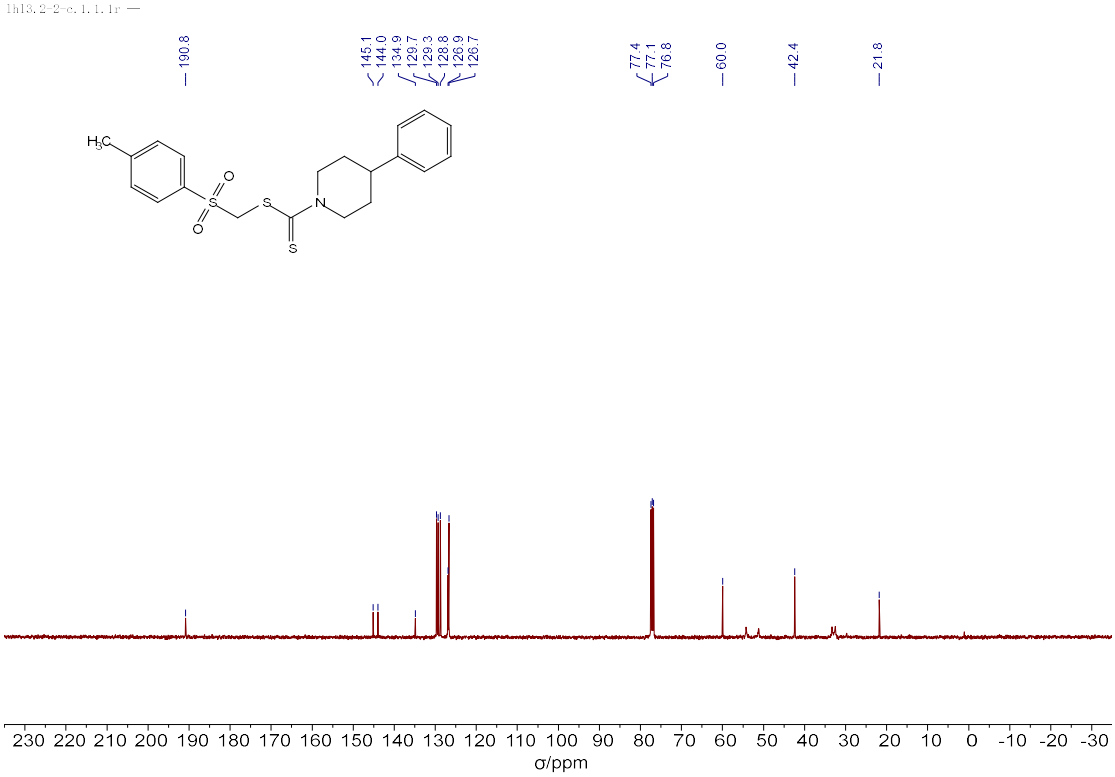
^{13}C NMR-spectrum of **4af**



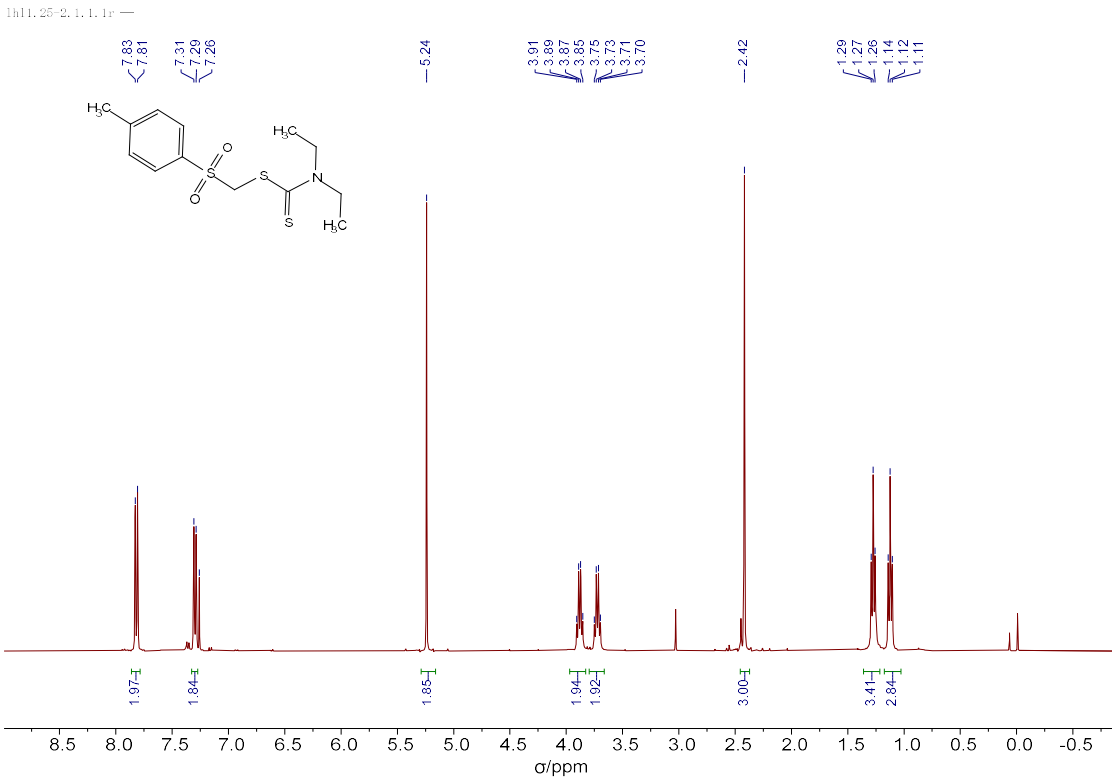
^{1}H NMR-spectrum of **4ag**



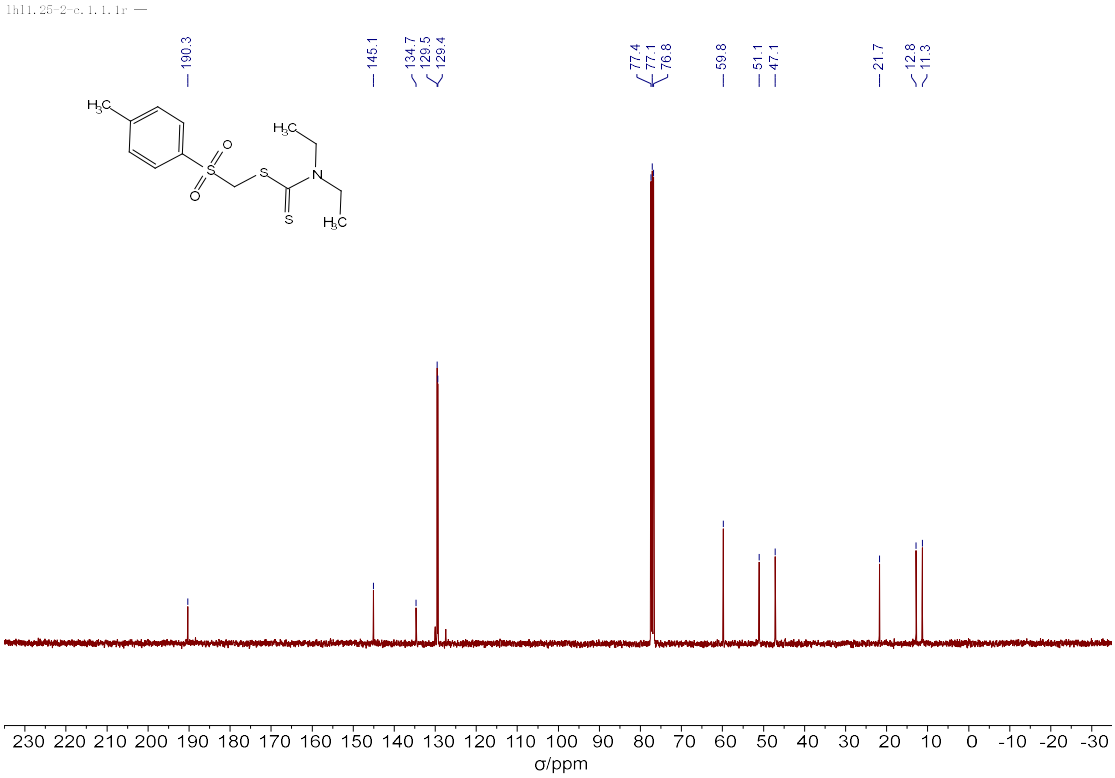
^{13}C NMR-spectrum of **4ag**



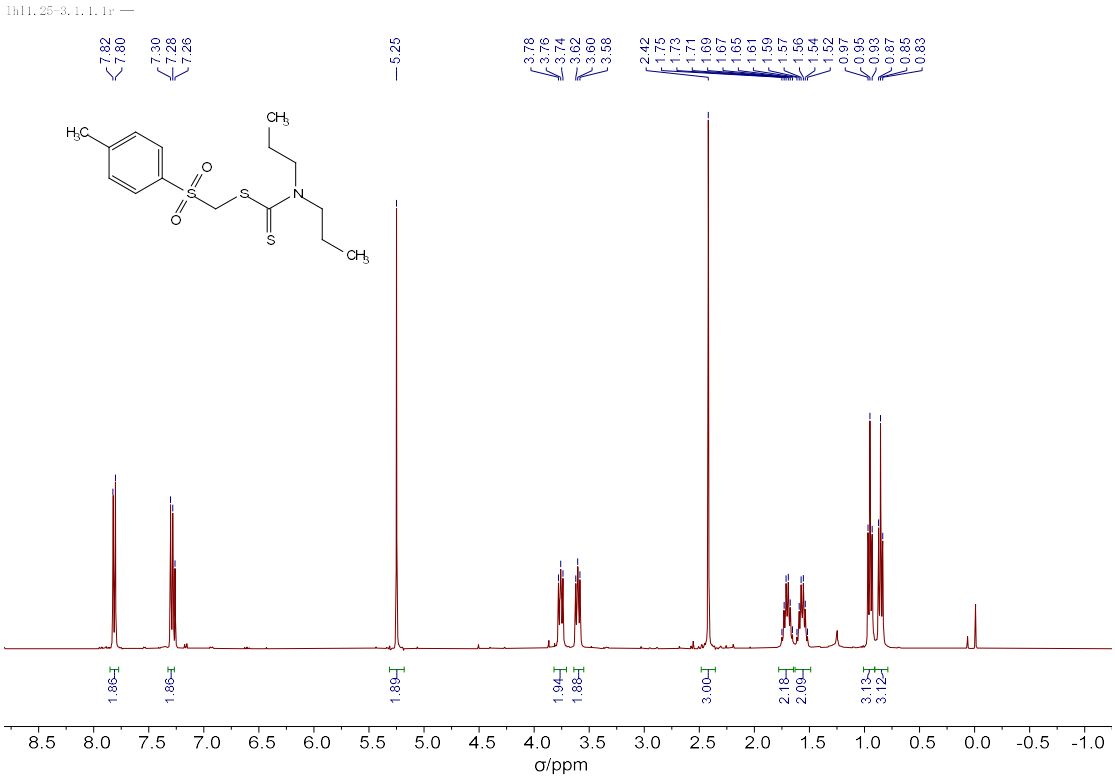
^{1}H NMR-spectrum of **4ah**



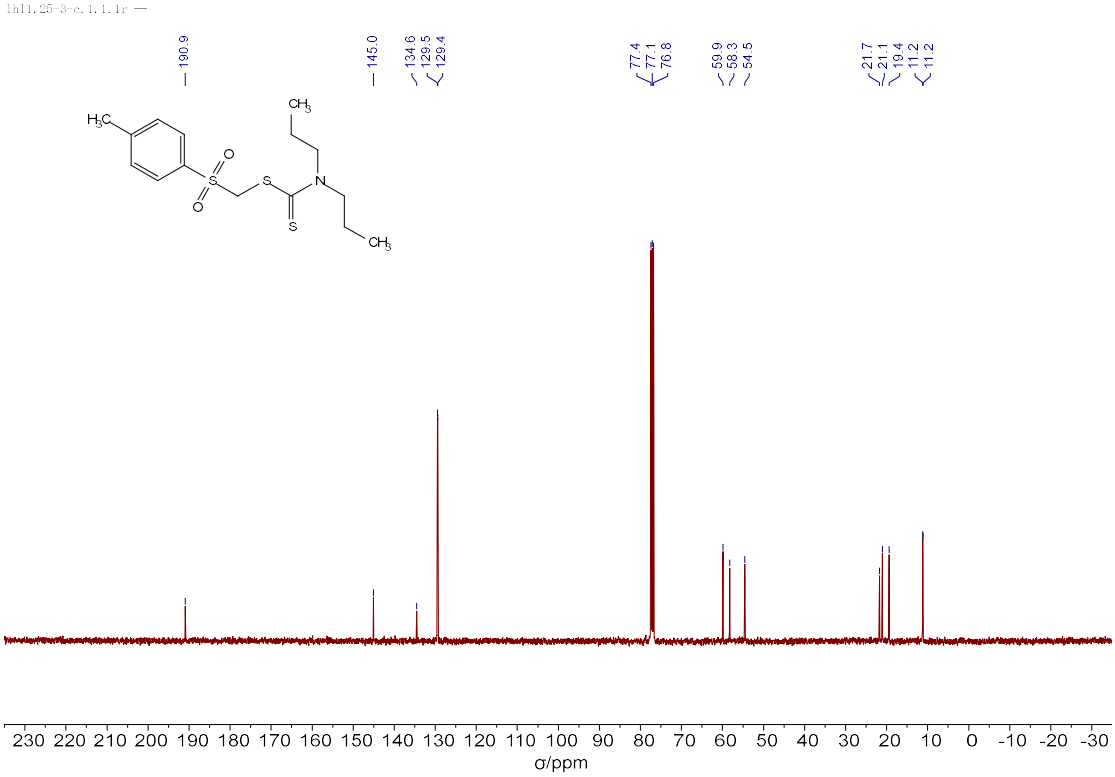
^{13}C NMR-spectrum of **4ah**



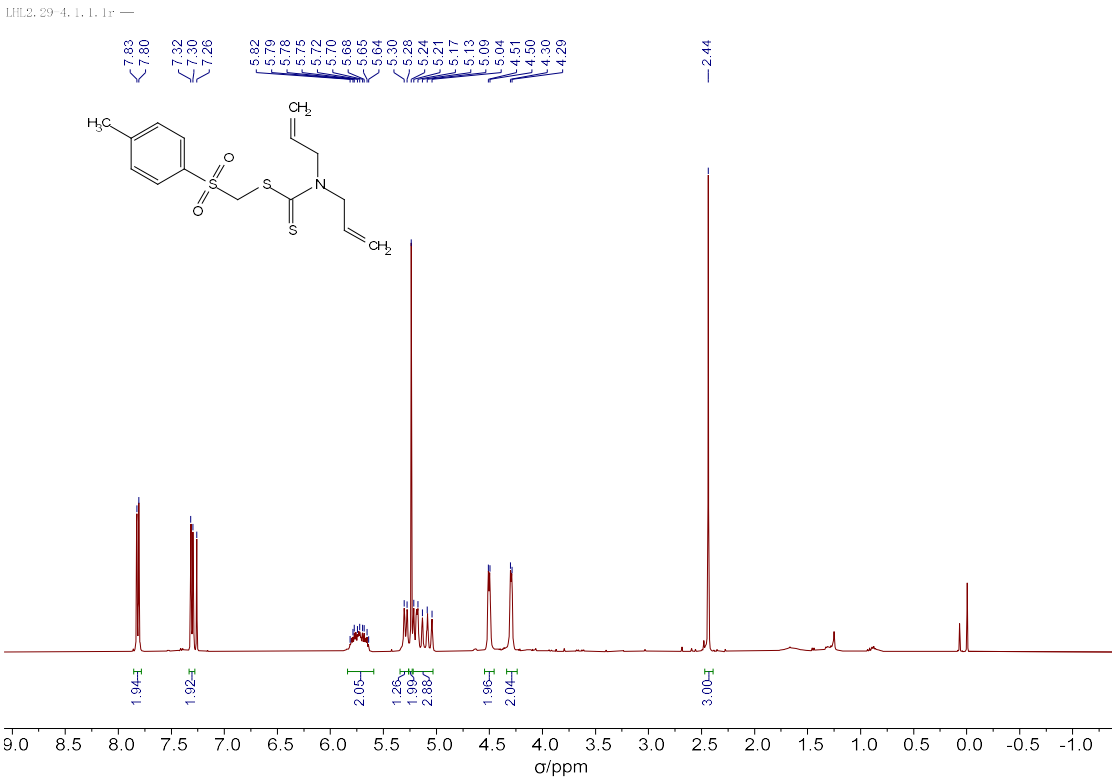
^{1}H NMR-spectrum of **4ai**



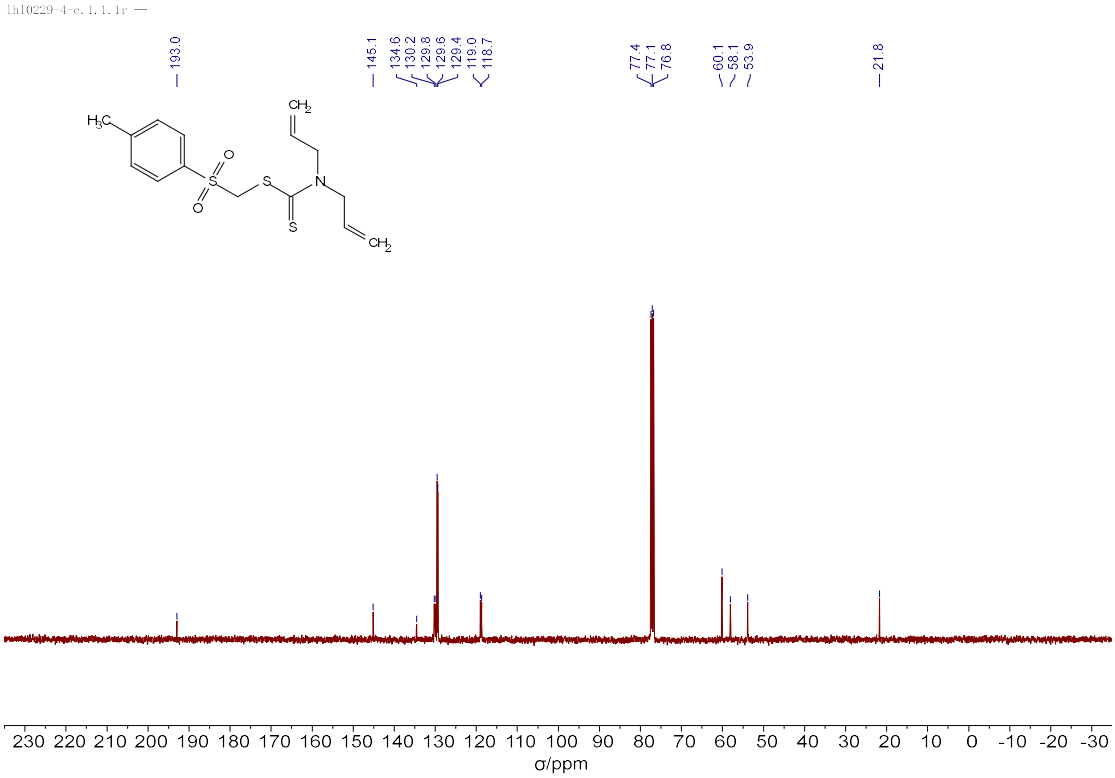
^{13}C NMR-spectrum of **4ai**



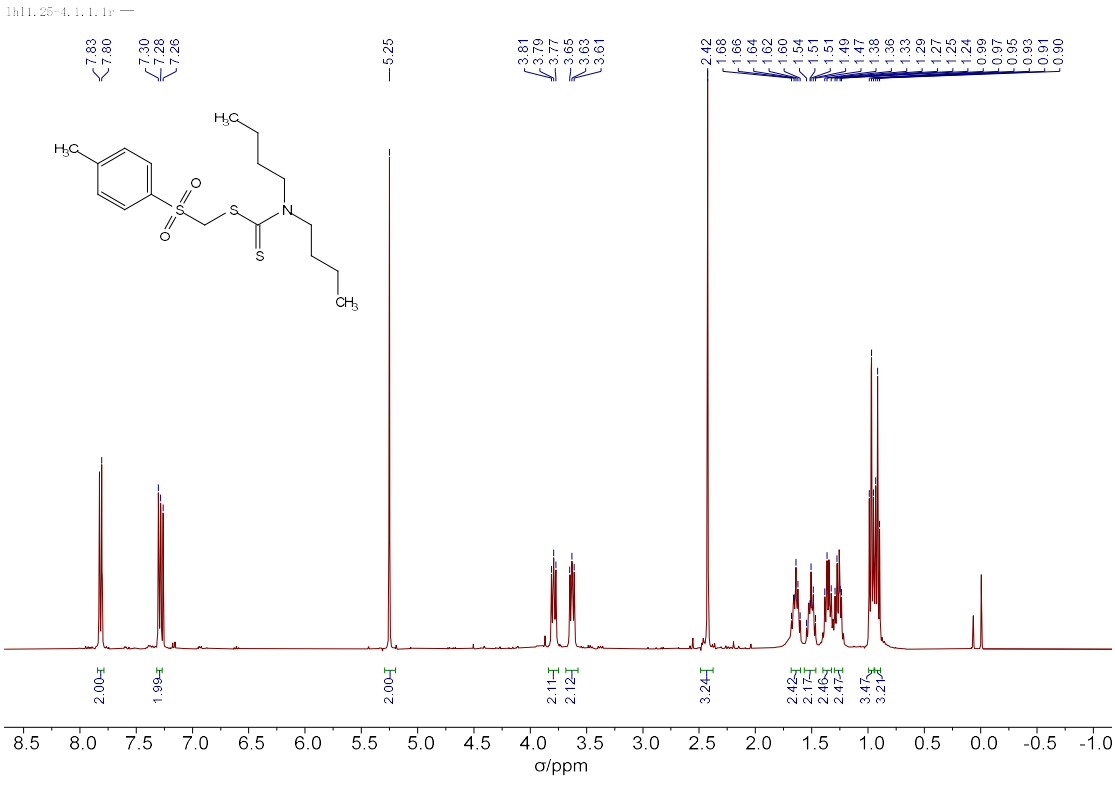
^{1}H NMR-spectrum of **4aj**



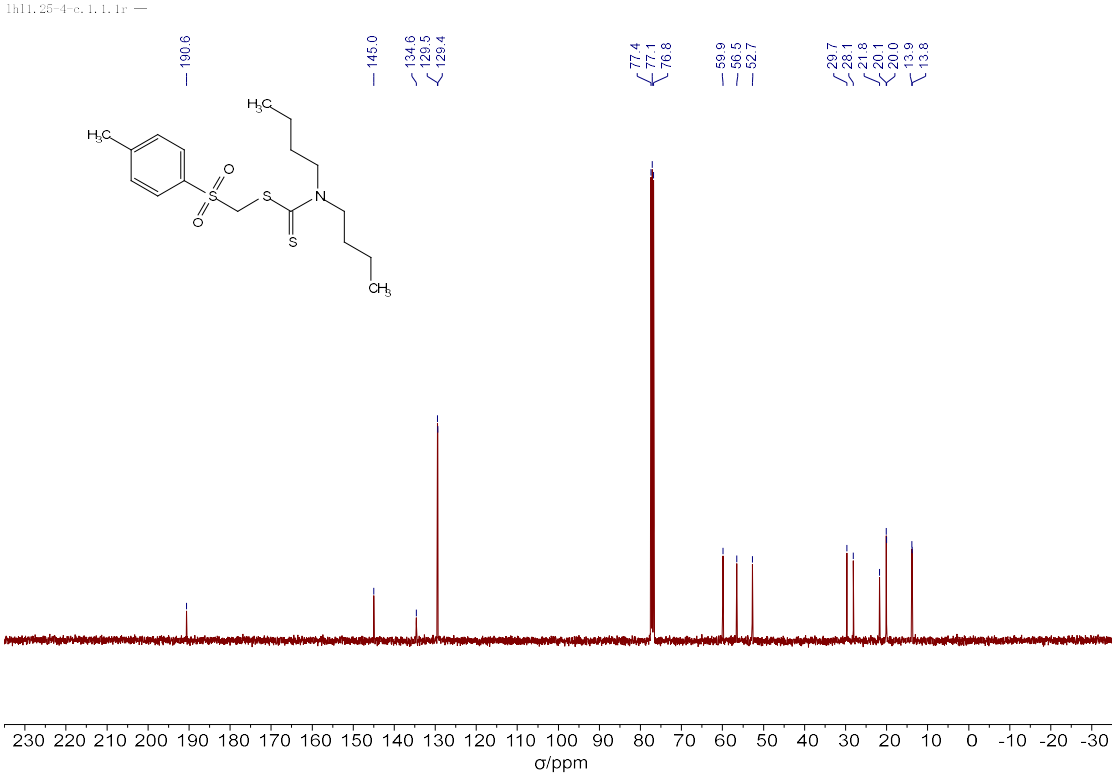
^{13}C NMR-spectrum of **4aj**



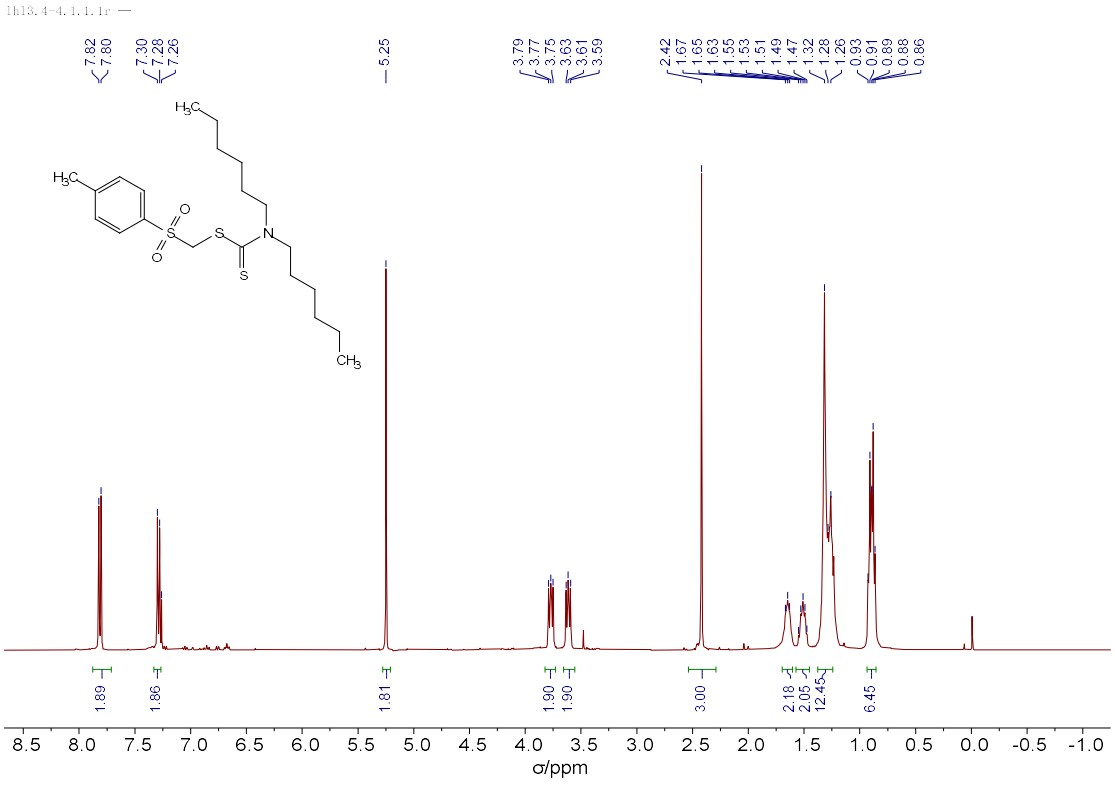
^{1}H NMR-spectrum of **4ak**



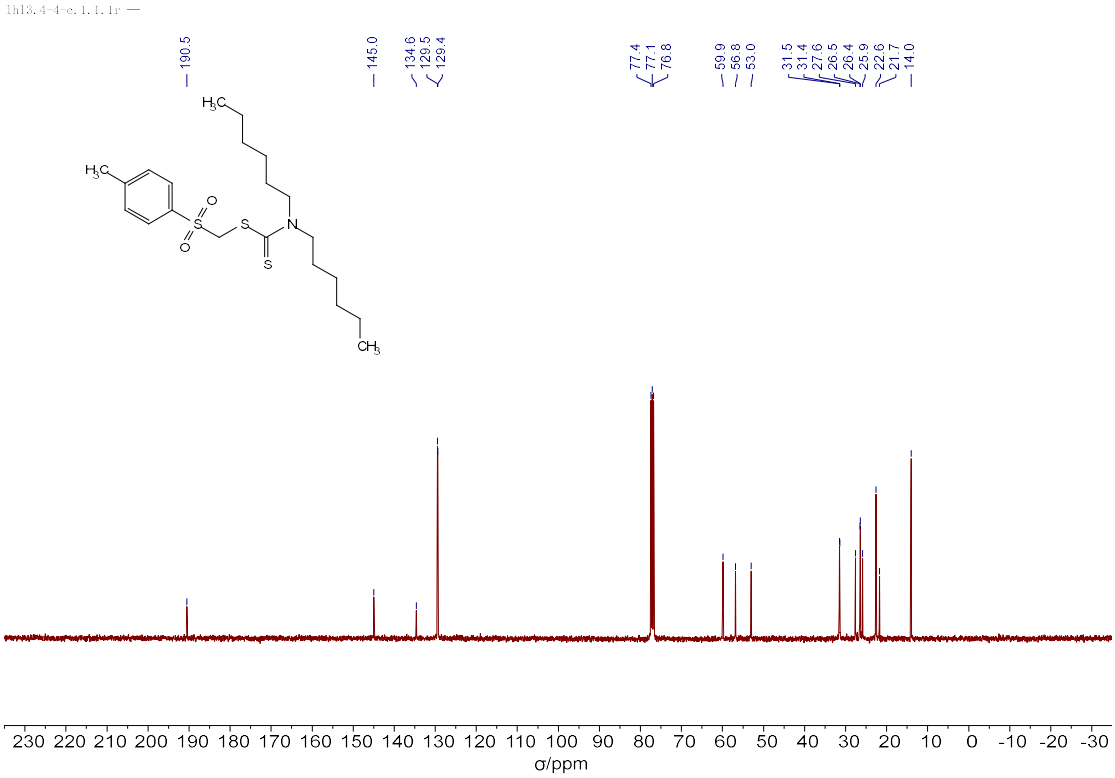
^{13}C NMR-spectrum of **4ak**



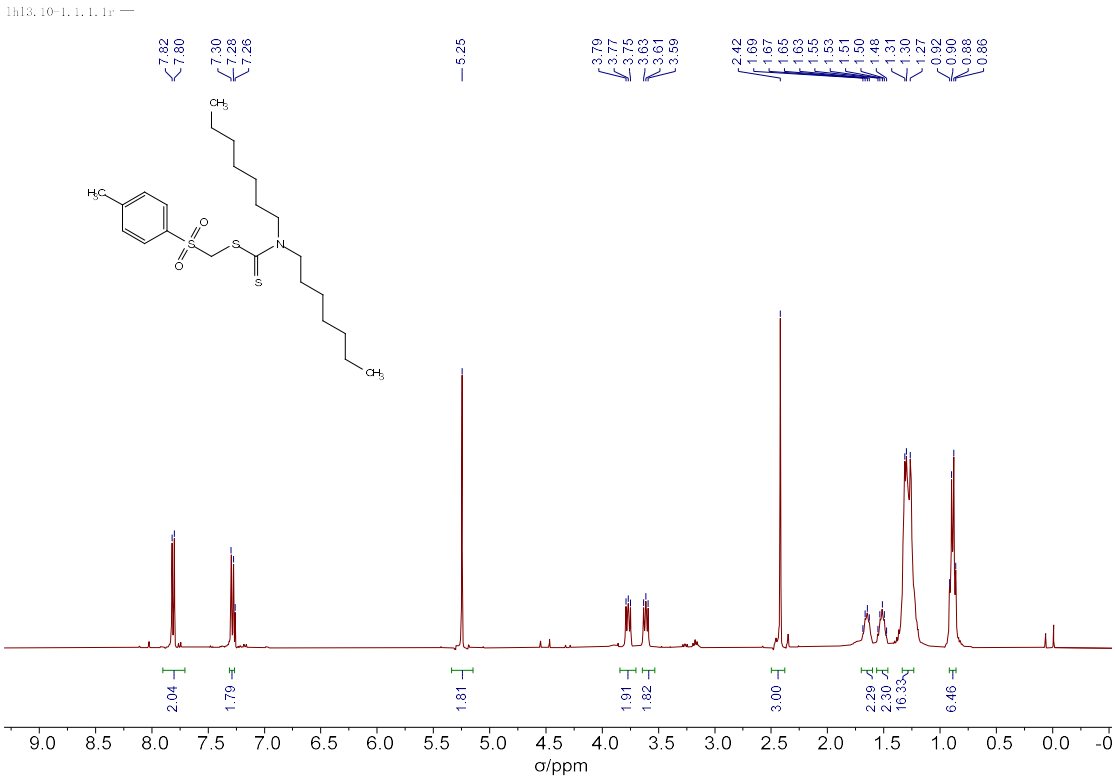
^{1}H NMR-spectrum of **4al**



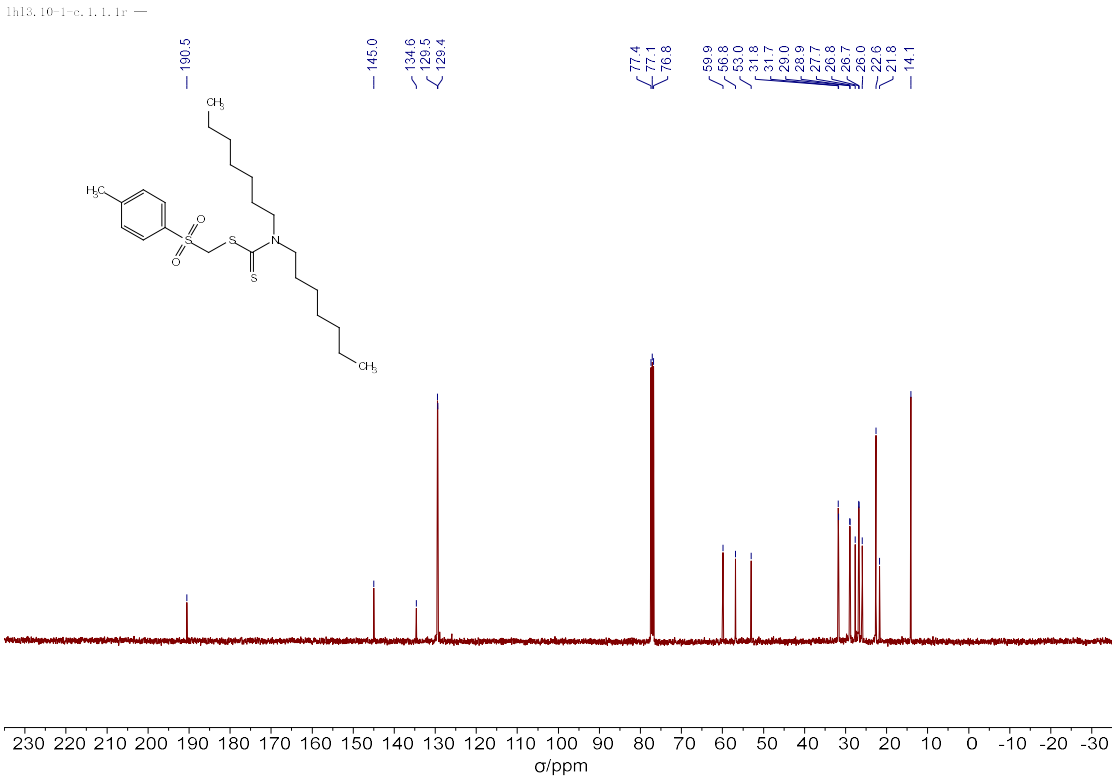
^{13}C NMR-spectrum of **4al**



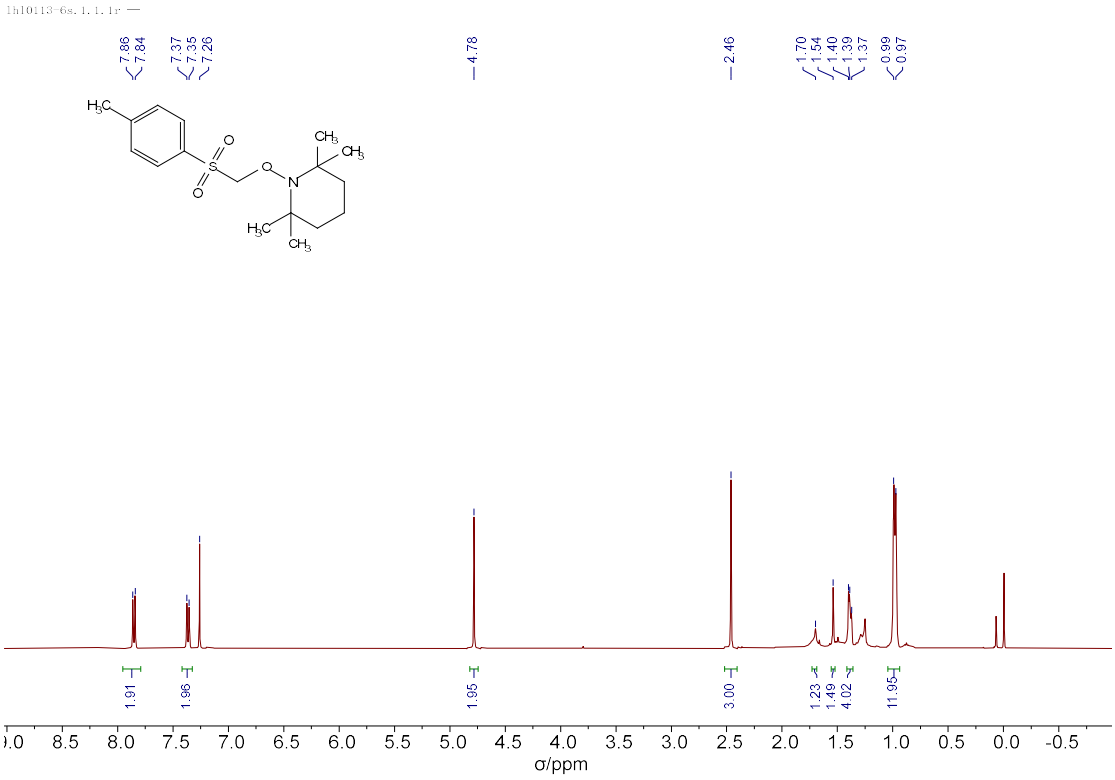
^{1}H NMR-spectrum of **4am**



^{13}C NMR-spectrum of **4am**



^{1}H NMR-spectrum of **5a**



^{13}C NMR-spectrum of **5a**