Supporting Information

Electrochemical approach for upgrading the pollutant CS_2: three component N-H thiocarbamylation of sulfoximines

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General information:

All products were characterized by ^{1}H NMR and ^{13}C NMR, using TMS as an internal reference (^{1}H NMR: 400 MHz, ^{13}C NMR: 100 MHz). HRMS (ESI) data were recorded on a Q-TOF Premier. Flash column chromatography was performed using silica gel (200-300 mesh). All the compounds **1** were synthesized according to the previously reported procedures,[1] and compounds **2** were purchased from commercial supplies and used without purification.

Experimental section

Representative procedures for the electrochemical N-H thiocarbamylation (Synthesis of 3aa as an example): An undivided cell was equipped with a magnet stirrer, two platinum plates (1.0 x 1.0 cm^2) electrodes as the working electrode and counter electrode. In the electrolytic cell, a mixture of iminodiphenyl-λ^6-sulfanone **1a** (0.3 mmol, 65.1 mg, 1.0 equiv), pyrrolidine **2a** (0.6 mmol, 2.0 equiv), CS_2 (0.72 mmol, 2.4 equiv), *n*-Bu_4NI (0.30 mmol, 110.8 mg, 1.0 equiv), K_2CO_3 (0.60 mmol, 87.0 mg, 2.0 equiv), CH_3CN (3.0 mL) was allowed to stir and electrolyze at a constant current condition (5 mA) at room temperature. After the reaction was completed (about 6 h), the solvent was removed with a rotary evaporator and the residue was purified by column chromatography on silica gel to afford the desired product **3aa**. The product was dried under high vacuum for at least 0.5 h before it was weighed and characterized by NMR spectroscopy.

Gram-scale synthesis of 3aa: An undivided cell was equipped with a magnet stirrer, two platinum plates (1.5 x 1.5 cm^2) electrodes as the working electrode and counter electrode. In the electrolytic cell, a mixture of iminodiphenyl-λ^6-sulfanone **1a** (6 mmol, 1.30 g, 1.0 equiv), pyrrolidine **2a** (12 mmol, 2.0 equiv), CS_2 (14.4 mmol, 2.4 equiv), *n*-Bu_4NI (6 mmol, 2.22 g, 1.0 equiv), K_2CO_3 (12 mmol, 1.66 g, 2.0 equiv), CH_3CN (60.0 mL) was allowed to stir and electrolyze at a constant current condition (11 mA) at room temperature. After the reaction was completed (about 53 h), the solvent was removed with a rotary evaporator and the residue was purified by column chromatography on silica gel to afford the desired product **3aa**. The product was dried under high vacuum for at least 0.5 h before it was weighed and characterized by NMR spectroscopy (970 mg, 50%).

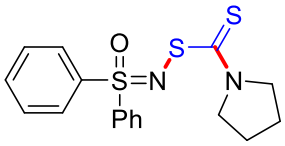
Photographic depiction of the electrolysis setup (3aa as an example):

Figure S1 Electrodes and electrolysis cell

Figure S2 Electrolysis setup

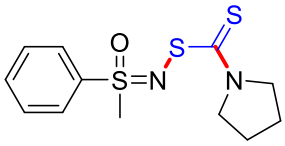
Detail descriptions for products

Diphenyl(((pyrrolidine-1-carbonothioyl)thio)imino)- λ^6-sulfanone (**3aa**)



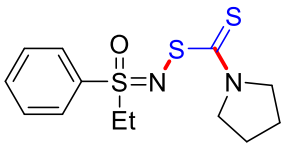
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 5:1) to give the product as a pale yellow solid in 74% yield (80.9 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.26-8.23 (m, 4H), 7.56-7.47 (m, 6H), 3.92 (t, J = 8.0 Hz, 2H), 3.44 (t, J = 8.0 Hz, 2H), 2.02-1.96 (m, 2H), 1.92-1.85 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 196.8, 139.3, 133.4, 129.4, 129.3, 55.1, 49.0, 26.4, 23.7. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{18}N_2OS_3Na$ 385.0479; Found: 385.0484.

Methyl(phenyl)(((pyrrolidine-1-carbonothioyl)thio)imino)- λ^6-sulfanone (**3ba**)



The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a pale yellow oil in 56% yield (50.0 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.36-8.33 (m, 2H), 7.68-7.63 (m, 1H), 7.60-7.56 (m, 2H), 3.94-3.91 (m, 2H), 3.60-3.50 (m, 2H), 3.35 (s, 3H), 2.10-2.02 (m, 2H), 1.96-1.89 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 197.8, 138.7, 134.0, 129.4, 128.9, 55.1, 48.8, 42.4, 26.4, 23.7. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{16}N_2OS_3Na$ 323.0322; Found: 323.0327.

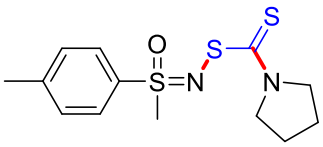
Ethyl(phenyl)(((pyrrolidine-1-carbonothioyl)thio)imino)-λ^6-sulfanone (**3ca**)



The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a pale yellow oil in 49% yield (46.4 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.22-8.19 (m, 2H), 7.66-7.63 (m, 1H), 7.58-7.55 (m, 2H), 3.93-3.90 (m, 2H), 3.75-3.66 (m, 1H), 3.53-3.50 (m, 2H), 3.48-3.39 (m, 1H), 2.07-2.00 (m, 2H), 1.94-1.87 (m, 2H), 1.24-1.21 (m,

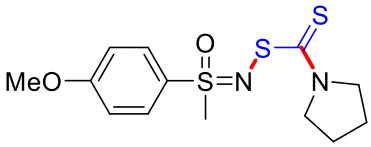
3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 198.0, 136.3, 133.9, 129.6, 129.3, 55.1, 49.3, 48.9, 26.4, 23.6, 8.1. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{18}N_2OS_3Na$ 337.0479; Found: 337.0484.

Methyl(((pyrrolidine-1-carbonothioyl)thio)imino)(p-tolyl)- λ^6-sulfanone (**3da**)



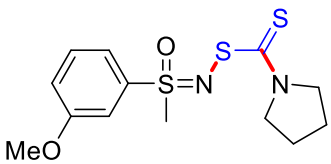
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a pale yellow solid in 92% yield (87.0 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.21 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 3.95-3.92 (m, 2H), 3.58-3.50 (m, 2H), 3.33 (s, 3H), 2.45 (s, 3H), 2.09-2.05 (m, 2H), 1.97-1.92 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 198.0, 145.0, 135.7, 130.0, 129.0, 55.1, 48.9, 42.6, 26.5, 23.7, 21.8. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{18}N_2OS_3Na$ 337.0479; Found: 337.0484.

(4-Methoxyphenyl)(methyl)(((pyrrolidine-1-carbonothioyl)thio)imino)-λ^6-sulfanone (**3ea**)



The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a pale yellow oil in 87% yield (86.2 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.28-8.24 (m, 2H), 7.04-7.01 (m, 2H), 3.93-3.90 (m, 2H), 3.86 (s, 3H), 3.58-3.51 (m, 2H), 3.31 (s, 3H), 2.09-2.03 (m, 2H), 1.95-1.89 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 198.0, 164.0, 131.2, 129.8, 114.6, 55.8, 55.1, 48.8, 42.5, 26.4, 23.7. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{18}N_2O_2S_3Na$ 353.0428; Found: 353.0433.

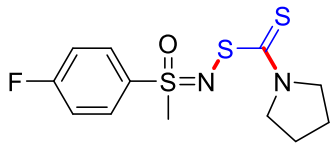
(3-Methoxyphenyl)(methyl)(((pyrrolidine-1-carbonothioyl)thio)imino)-λ^6-sulfanone (**3fa**)



The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a pale yellow oil in 73% yield (71.8 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.09-8.07 (m, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 8.0 Hz, 1H), 7.19-7.16 (m, 1H), 3.94-3.91 (m, 2H), 3.89 (s, 3H), 3.60-3.50 (m, 2H), 3.35 (s, 3H), 2.11-2.04 (m, 2H), 1.97-1.90 (m,

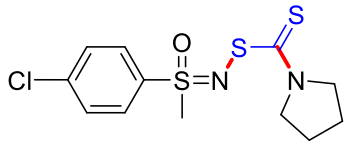
2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 197.9, 160.2, 139.8, 130.2, 121.4, 121.0, 113.0, 56.0, 55.1, 48.8, 42.3, 26.4, 23.7. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{18}N_2O_2S_3Na$ 353.0428; Found: 353.0433.

(4-Fluorophenyl)(methyl)(((pyrrolidine-1-carbonothioyl)thio)imino)-λ^6-sulfanone (**3ga**)



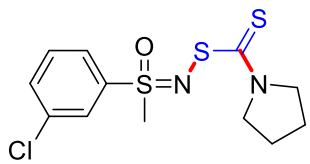
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a pale yellow oil in 75% yield (71.5 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.45-8.42 (m, 2H), 7.30-7.25 (m, 2H), 3.95 (t, J = 8.0 Hz, 2H), 3.62-3.51 (m, 2H), 3.38 (s, 3H), 2.13-2.08 (m, 2H), 2.00-1.94 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 197.6, 166.2 (d, J = 255.0 Hz), 134.5, 132.1 (d, J = 10.0 Hz), 116.7 (d, J = 22.0 Hz), 55.2, 48.9, 42.4, 26.4, 23.7. ^{19}F NMR ($CDCl_3$, 376 MHz, ppm): δ = 103.4. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{15}N_2OFS_3Na$ 341.0228; Found: 341.0232.

(4-Chlorophenyl)(methyl)(((pyrrolidine-1-carbonothioyl)thio)imino)-λ^6-sulfanone (**3ha**)



The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a pale yellow solid in 51% yield (51.0 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.34-8.31 (m, 2H), 7.57-7.54 (m, 2H), 3.94-3.91 (m, 2H), 3.59-3.49 (m, 2H), 3.35 (s, 3H), 2.11-2.04 (m, 2H), 1.97-1.90 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 197.4, 140.8, 137.2, 130.6, 129.7, 55.2, 48.8, 42.5, 26.4, 23.7. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{15}N_2OClS_3Na$ 356.9933; Found: 356.9937.

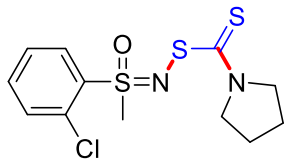
(3-Chlorophenyl)(methyl)(((pyrrolidine-1-carbonothioyl)thio)imino)-λ^6-sulfanone (**3ia**)



The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a pale yellow oil in 50% yield (49.6 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.36-8.35 (m, 1H), 8.29-8.26 (m, 1H), 7.64-7.61 (m, 1H), 7.53 (t, J = 8.0 Hz, 1H), 3.94-3.91 (m, 2H), 3.59-3.49 (m, 2H), 3.37 (s, 3H), 2.11-2.04 (m, 2H), 1.97-1.90 (m, 2H); ^{13}C NMR ($CDCl_3$,

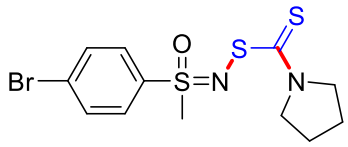
100 MHz, ppm): δ = 197.3, 140.5, 135.5, 134.2, 130.7, 129.0, 127.2, 55.2, 48.9, 42.5, 26.4, 23.7. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{15}N_2OClS_3Na$ 356.9933; Found: 356.9937.

(2-Chlorophenyl)(methyl)(((pyrrolidine-1-carbonothioyl)thio)imino)-λ^6-sulfanone (**3ja**)



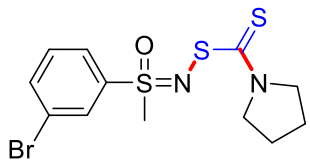
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 4:1) to give the product as a pale yellow oil in 39% yield (39.0 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.39-8.37 (m, 1H), 7.58-7.54 (m, 2H), 7.50-7.46 (m, 1H), 3.93-3.90 (m, 2H), 3.65-3.57 (m, 2H), 3.57 (s, 3H), 2.08-2.00 (m, 2H), 1.94-1.87 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 197.1, 136.7, 134.9, 132.7, 132.6, 132.3, 127.6, 55.3, 49.5, 42.3, 26.6, 23.7. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{15}N_2OClS_3Na$ 356.9933; Found: 356.9938.

(4-Bromophenyl)(methyl)(((pyrrolidine-1-carbonothioyl)thio)imino)-λ^6-sulfanone (**3ka**)



The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 4:1) to give the product as a pale yellow oil in 50% yield (57.1 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.26 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 8.0 Hz, 2H), 3.94 (t, J = 8.0 Hz, 2H), 3.60-3.50 (m, 2H), 3.36 (s, 3H), 2.12-2.06 (m, 2H), 1.99-1.92 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 197.5, 137.8, 132.7, 130.6, 129.6, 55.2, 48.9, 42.5, 26.5, 23.7. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{15}N_2OBrS_3Na$ 400.9428; Found: 400.9433.

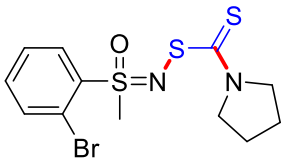
(3-Bromophenyl)(methyl)(((pyrrolidine-1-carbonothioyl)thio)imino)-λ^6-sulfanone (**3la**)



The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 4:1) to give the product as a pale yellow oil in 46% yield (52.4 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.50-8.49 (m, 1H), 8.34-8.31 (m, 1H), 7.79-7.76 (m, 1H), 7.46 (t, J = 8.0

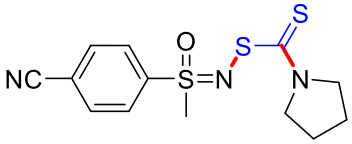
Hz, 1H), 3.94-3.91 (m, 2H), 3.58-3.51 (m, 2H), 3.37 (s, 3H), 2.11-2.04 (m, 2H), 1.97-1.90 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 197.3, 140.7, 137.1, 131.8, 130.9, 127.7, 123.2, 55.2, 48.9, 42.6, 26.4, 23.7. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{15}N_2OBrS_3Na$ 400.9428; Found: 400.9433.

(2-Bromophenyl)(methyl)(((pyrrolidine-1-carbonothioyl)thio)imino)- λ^6-sulfanone (**3ma**)



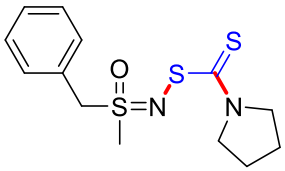
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 4:1) to give the product as a pale yellow oil in 31% yield (35.6 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.44-8.41 (m, 1H), 7.78-7.76 (m, 1H), 7.55-7.51 (m, 1H), 7.49-7.44 (m, 1H), 3.91 (t, J = 8.0 Hz, 2H), 3.62-3.59 (m, 2H), 3.57 (s, 3H), 2.07-1.99 (m, 2H), 1.93-1.86 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 197.0, 138.2, 135.9, 134.8, 133.1, 128.2, 120.8, 55.3, 49.5, 42.0, 26.5, 23.6. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{15}N_2OBrS_3Na$ 400.9428; Found: 400.9432.

4-(S-methyl-N-((pyrrolidine-1-carbonothioyl)thio)sulfonimidoyl)benzonitrile (**3na**)



The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a pale yellow oil in 27% yield (26.0 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.55 (d, J = 8.0 Hz, 2H), 7.90-7.87 (m, 2H), 3.94-3.91 (m, 2H), 3.59-3.49 (m, 2H), 3.40 (s, 3H), 2.13-2.06 (m, 2H), 1.99-1.92 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 196.9, 143.2, 133.1, 130.0, 117.8, 117.3, 55.3, 48.9, 42.3, 26.4, 23.7. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{15}N_3OS_3Na$ 348.0275; Found: 348.0280.

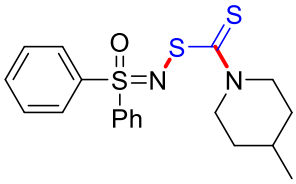
Benzyl(methyl)(((pyrrolidine-1-carbonothioyl)thio)imino)- λ^6-sulfanone (**3oa**)



The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 1:1) to give the product as a pale yellow oil in 45% yield (42.4

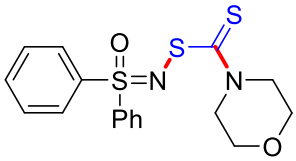
mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.42-7.46 (m, 2H), 7.41-7.38 (m, 3H), 4.76-4.66 (m, 2H), 3.94-3.91 (m, 2H), 3.57-3.54 (m, 2H), 3.01 (s, 3H), 2.12-2.05 (m, 2H), 1.97-1.90 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 198.7, 131.1, 129.3, 129.2, 128.2, 60.9, 55.3, 48.9, 38.2, 26.5, 23.7. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{18}N_2OS_3Na$ 337.0479; Found: 337.0482.

(((4-Methylpiperidine-1-carbonothioyl)thio)imino)diphenyl-λ^6-sulfanone (**3ab**)



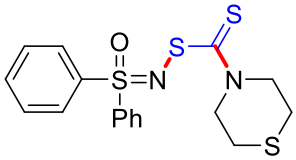
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 5:1) to give the product as pale yellow oil in 31% yield (35.3 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.23-8.21 (m, 4H), 7.57-7.47 (m, 6H), 3.07-3.00 (m, 2H), 1.67-1.62 (m, 4H), 1.19-1.08 (m, 2H), 0.99-0.95 (m, 1H), 0.90 (d, J = 8.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 200.2, 139.2, 133.4, 129.3, 129.2, 51.4, 33.8, 31.0, 21.5. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{22}N_2OS_3Na$ 413.0792; Found: 413.0795.

(((Morpholine-4-carbonothioyl)thio)imino)diphenyl-λ^6-sulfanone (**3ac**)



The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 4:1) to give the product as a pale yellow oil in 57% yield (65.0 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.16 (d, J = 8.0 Hz, 4H), 7.58-7.48 (m, 6H), 4.03 (s, 4H), 3.68 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 201.8, 139.1, 133.5, 129.4, 129.0, 66.4, 51.0. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{18}N_2O_2S_3Na$ 401.0428; Found: 401.0433.

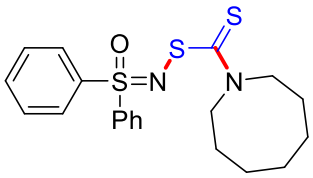
Diphenyl(((thiomorpholine-4-carbonothioyl)thio)imino)-λ^6-sulfanone (**3ad**)



The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 4:1) to give the product as a pale yellow solid in 63% yield

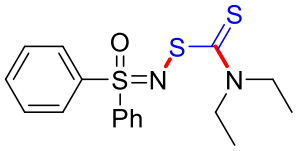
(74.0 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.19 (d, J = 8.0 Hz, 4H), 7.58-7.48 (m, 6H), 4.26 (s, 4H), 2.61 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 201.5, 139.0, 133.5, 129.4, 129.1, 53.8, 27.1. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{18}N_2OS_4Na$ 417.0204; Found: 417.0200.

(((Azocane-1-carbonothioyl)thio)imino)diphenyl-λ^6-sulfanone (**3ae**)



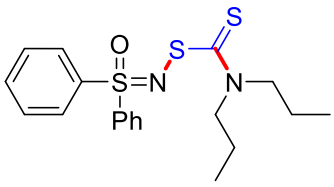
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 6:1) to give the product as a pale yellow oil in 42% yield (57.2 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.29-8.27 (m, 4H), 7.56-7.51 (m, 2H), 7.50-7.46 (m, 4H), 4.05-4.02 (m, 2H), 3.57-3.51 (m, 2H), 1.94-1.90 (m, 2H), 1.64-1.61 (m, 2H), 1.45-1.31 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 200.6, 139.0, 133.3, 129.4, 129.2, 56.4, 52.7, 26.7, 25.5. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{24}N_2OS_3Na$ 427.0948; Found: 427.0953.

(((Diethylcarbamothioyl)thio)imino)diphenyl-λ^6-sulfanone (**3af**)



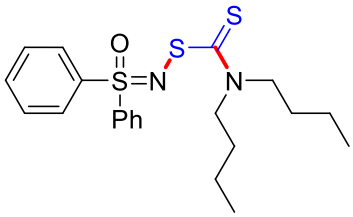
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a pale yellow solid in 64% yield (70.0 mg) ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.27-8.24 (m, 4H), 7.55-7.51 (m, 2H), 7.50-7.45 (m, 4H), 4.02-3.45 (m, 4H), 1.13 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 199.9, 139.1, 133.3, 129.3, 129.2, 12.2. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{20}N_2OS_3Na$ 387.0635; Found: 387.0640.

(((Dipropylcarbamothioyl)thio)imino)diphenyl-λ^6-sulfanone (**3ag**)



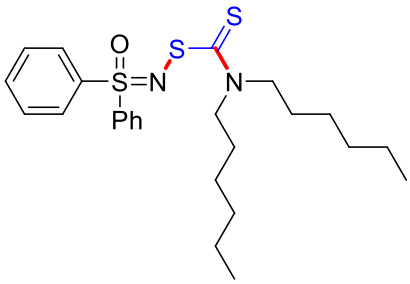
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 6:1) to give the product as a pale yellow oil in 41% yield (48.7 mg); ^{1}H NMR (CDCl3, 400 MHz, ppm): δ = 8.29-8.26 (m, 4H), 7.56-7.51 (m, 2H), 7.50-7.46 (m, 4H), 3.90-3.39 (m, 4H), 1.65-1.60 (m, 4H), 0.83-0.82 (m, 6H); ^{13}C NMR (CDCl3, 100 MHz, ppm): δ = 200.8, 139.0, 133.3, 129.4, 129.2, 11.2. HRMS (ESI-TOF) m/z: [M + Na]$^{+}$ Calcd for $C_{19}H_{24}N_2OS_3Na$ 415.0948; Found: 415.0953.

(((Dibutylcarbamothioyl)thio)imino)diphenyl-λ^{6}-sulfanone (**3ah**)



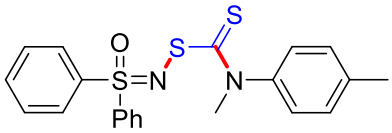
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 9:1) to give the product as a pale yellow oil in 81% yield (102.3 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8. 27 (d, J = 8.0 Hz, 4H), 7.54-7.45 (m, 6H), 3.88 (s, 2H), 3.37 (s, 2H), 1.60-1.46 (m, 4H), 1.27-1.19 (m, 4H), 0.85 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 200.5, 138.9, 133.3, 129.3, 129.2, 51.3, 28.9, 20.0, 13.8. HRMS (ESI-TOF) m/z: [M + Na]$^{+}$ Calcd for $C_{21}H_{28}N_2OS_3Na$ 443.1261; Found: 443.1261.

(((Dihexylcarbamothioyl)thio)imino)diphenyl-λ^{6}-sulfanone (**3ai**)



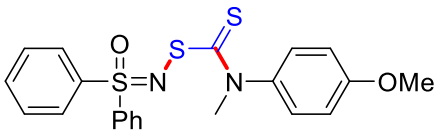
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 6:1) to give the product as a pale yellow solid in 49% yield (70.3 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.28 (d, J = 8.0 Hz, 4H), 7.55-7.46 (m, 6H), 3.92-3.88 (m, 2H), 3.41-3.38 (m, 2H), 1.49-1.42 (m, 2H), 1.30-1.22 (m, 14H), 0.87-0.84 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 200.4, 139.1, 133.3, 129.4, 129.2, 31.5, 26.5, 22.6, 14.1. HRMS (ESI-TOF) m/z: [M + Na]$^{+}$ Calcd for $C_{25}H_{36}N_2OS_3Na$ 499.1887; Found: 499.1892.

(((Methyl(p-tolyl)carbamothioyl)thio)imino)diphenyl-λ^{6}-sulfanone (**3aj**)



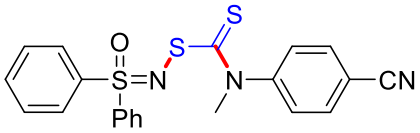
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 6:1) to give the product as a pale yellow oil in 63% yield (78.0 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.23-8.20 (m, 4H), 7.57-7.52 (m, 2H), 7.49-7.46 (m, 4H), 7.10 (d, J = 8.0 Hz, 2H), 6.87 (d, J = 8.0 Hz, 2H), 3.69 (s, 3H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 204.0, 140.9, 139.3, 139.2, 133.2, 130.3, 129.3, 129.2, 126.7, 46.0, 21.3. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{20}N_2OS_3Na$ 435.0635; Found: 435.0640.

((((4-Methoxyphenyl)(methyl)carbamothioyl)thio)imino)diphenyl-λ^6-sulfanone (**3ak**)



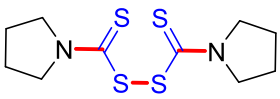
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1) to give the product as a pale yellow oil in 47% yield (60.9 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.22-8.19 (m, 4H), 7.56-7.52 (m, 2H), 7.50-7.45 (m, 4H), 6.92-6.88 (m, 2H), 6.81-6.77 (m, 2H), 3.77 (s, 3H), 3.67 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 204.3, 159.9, 139.2, 136.0, 133.2, 129.2, 129.2, 128.1, 114.8, 55.6, 46.1. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{20}N_2O_2S_3Na$ 451.0585; Found: 451.0589.

4-(Methyl((((oxodiphenyl-l6-sulfaneylidene)amino)thio)carbonothioyl)amino)benzonitrile (**3al**)



The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 4:1) to give the product as a pale yellow oil in 39% yield (49.6 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.10-8.08 (m, 4H), 7.59-7.55 (m, 4H), 7.51-7.47 (m, 4H), 7.21-7.19 (m, 2H), 3.69 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 204.0, 148.0, 139.1, 133.5, 133.5, 129.3, 128.9, 128.0, 118.0, 112.4, 45.5. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{17}N_3OS_3Na$ 446.0431; Found: 446.0434.

Pyrrolidine-1-carbothioic dithioperoxyanhydride (**4**) [2]



The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 10:1) to give the product as a white solid in 56% yield (48.7 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 3.98-3.92 (m, 8H), 2.18-2.11 (m, 4H), 2.03-1.96 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 189.2, 57.0, 51.0, 26.7, 24.3.

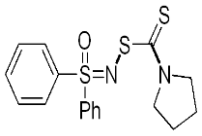
Reference

(1) J.-F. Lohier, T. Glachet, H. Marzag, A.-C. Gaumont, V. Reboul. *Chem. Commun*, 2017, **53**, 2064-2064.

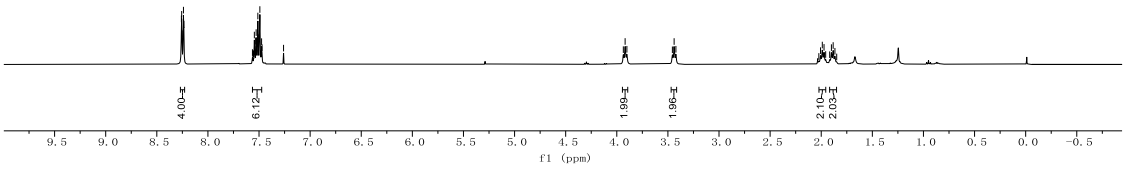
(2) Q. Wang, C.-H. Xu, Y.-C. Wang, Y.-M. Pan, W.-G. Duan, H.-T. Tang, *Green Chem*., 2022, **24**, 7362–7367.

NMR Spectra of products

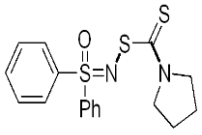
3aa-^{1}H NMR



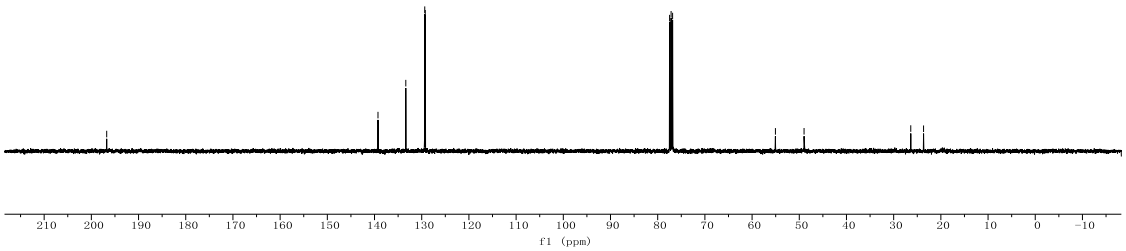
400 MHz, $CDCl_3$



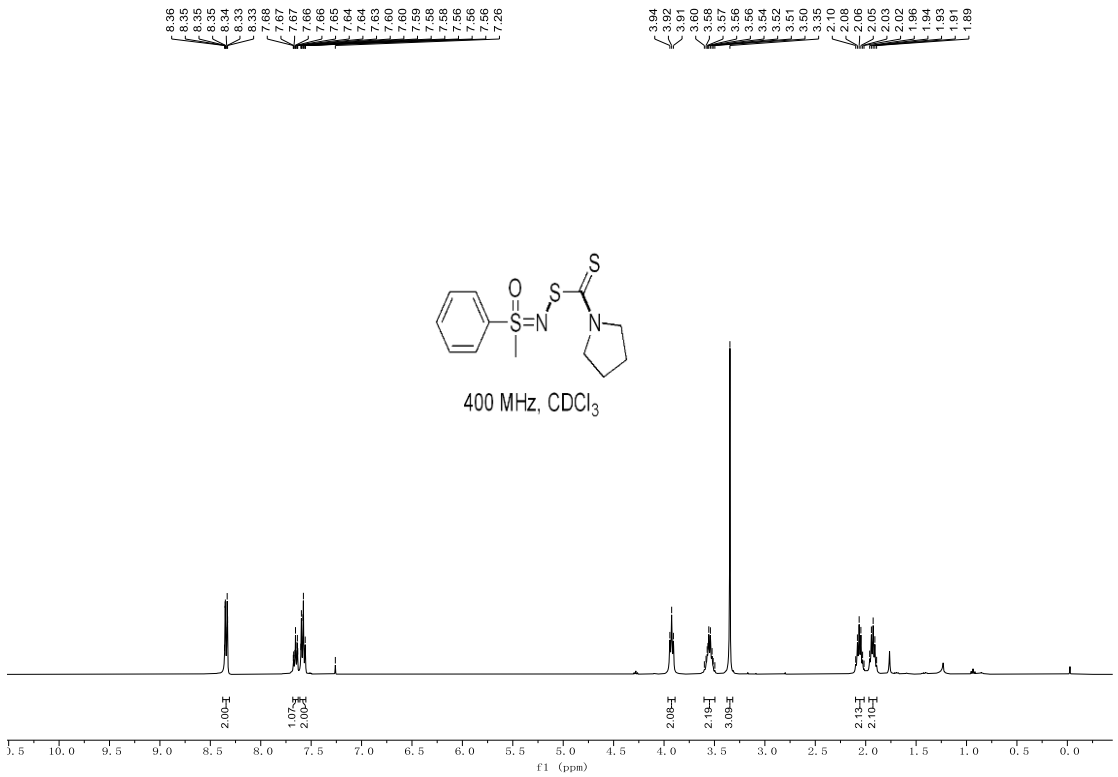
3aa-^{13}C NMR



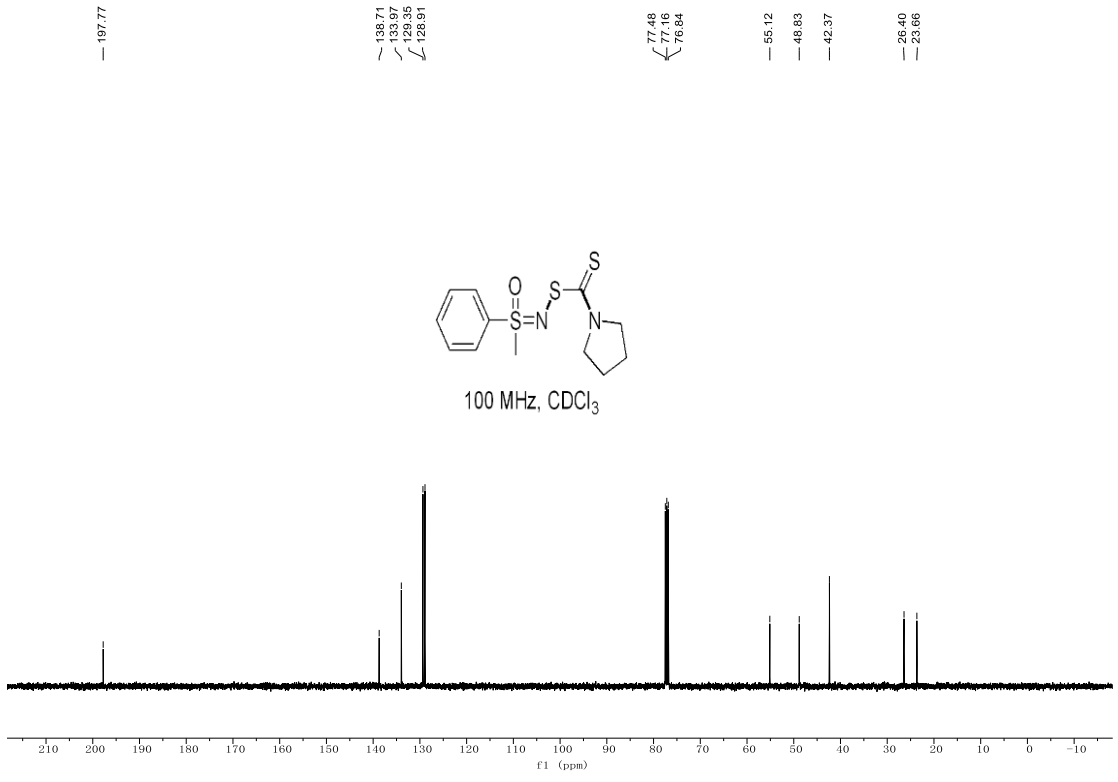
100 MHz, $CDCl_3$



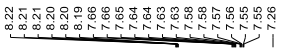
3ba-^{1}H NMR

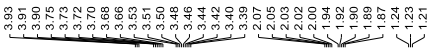


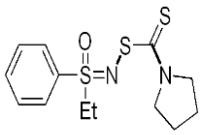
3ba -^{13}C NMR



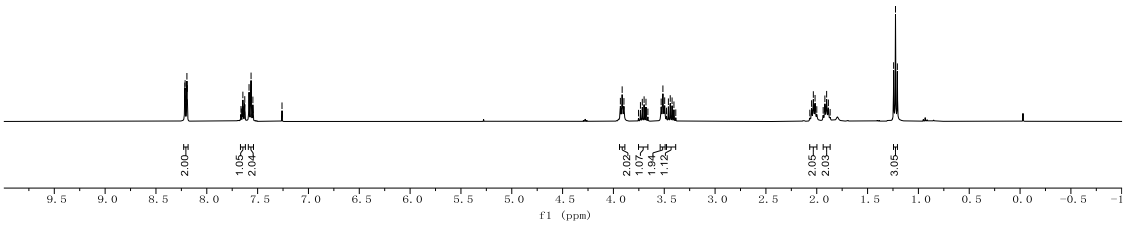
3ca-^{1}H NMR



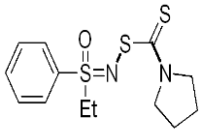




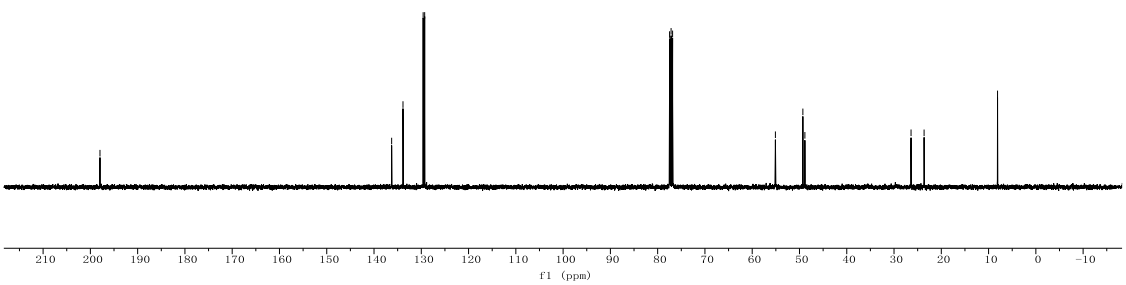
400 MHz, $CDCl_3$



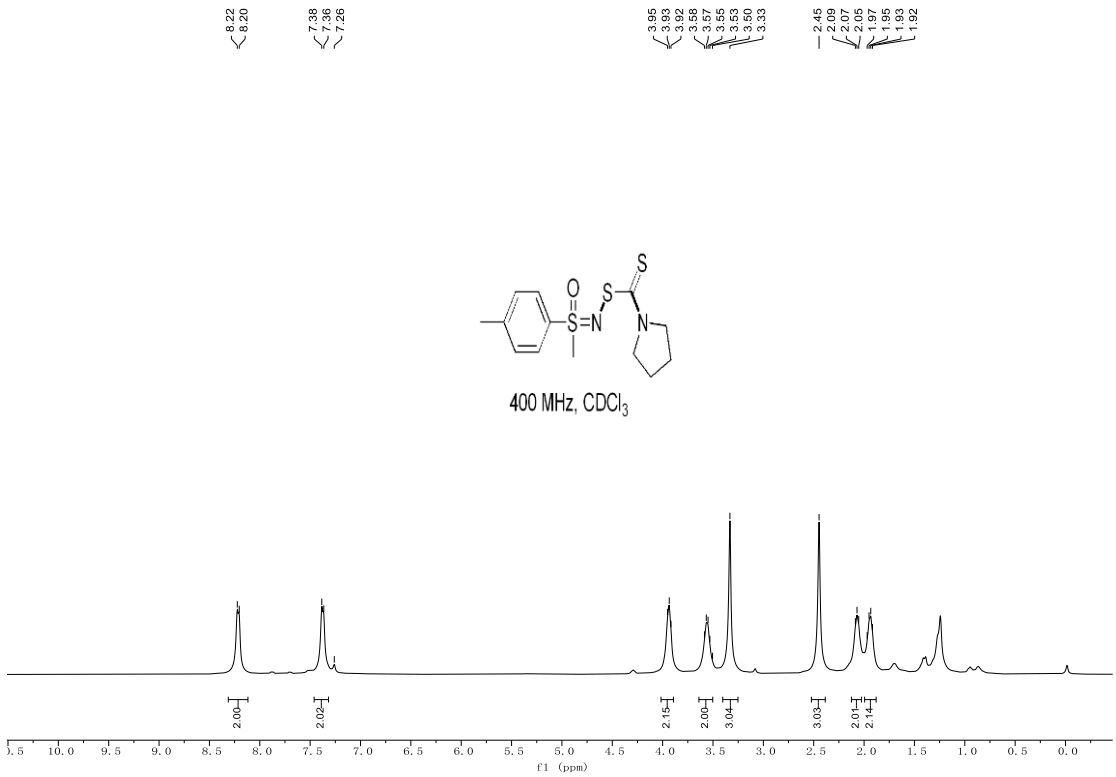
3ca -^{13}C NMR



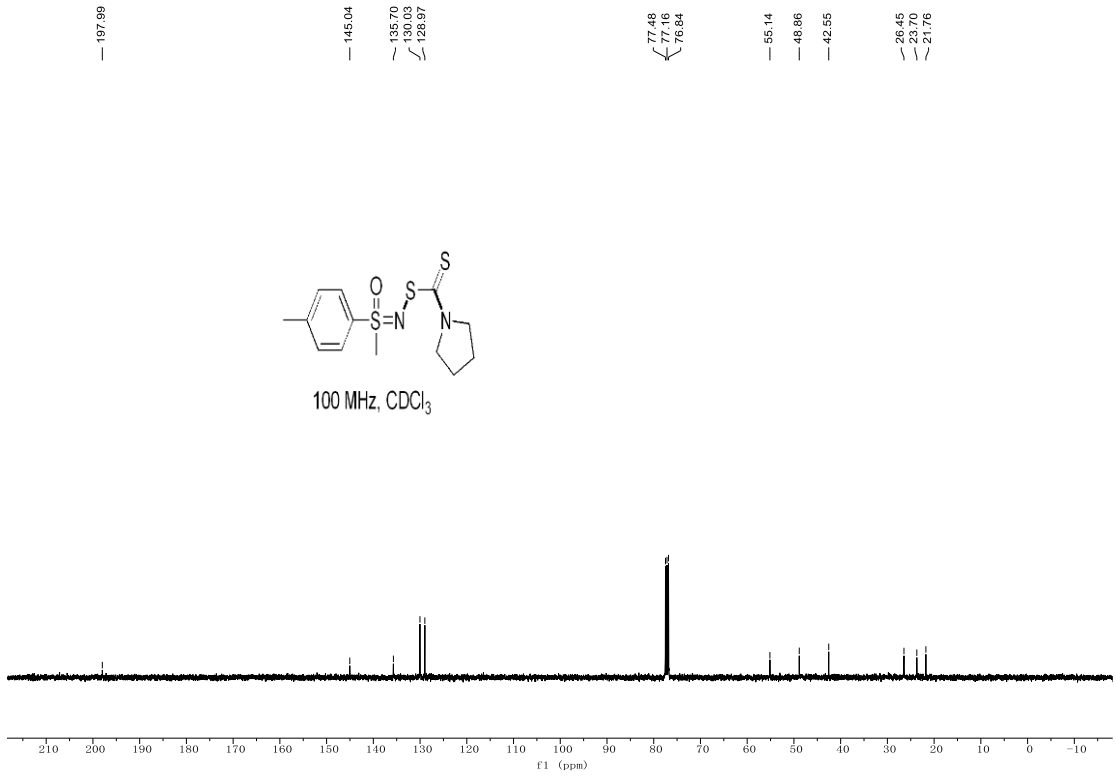
100 MHz, $CDCl_3$



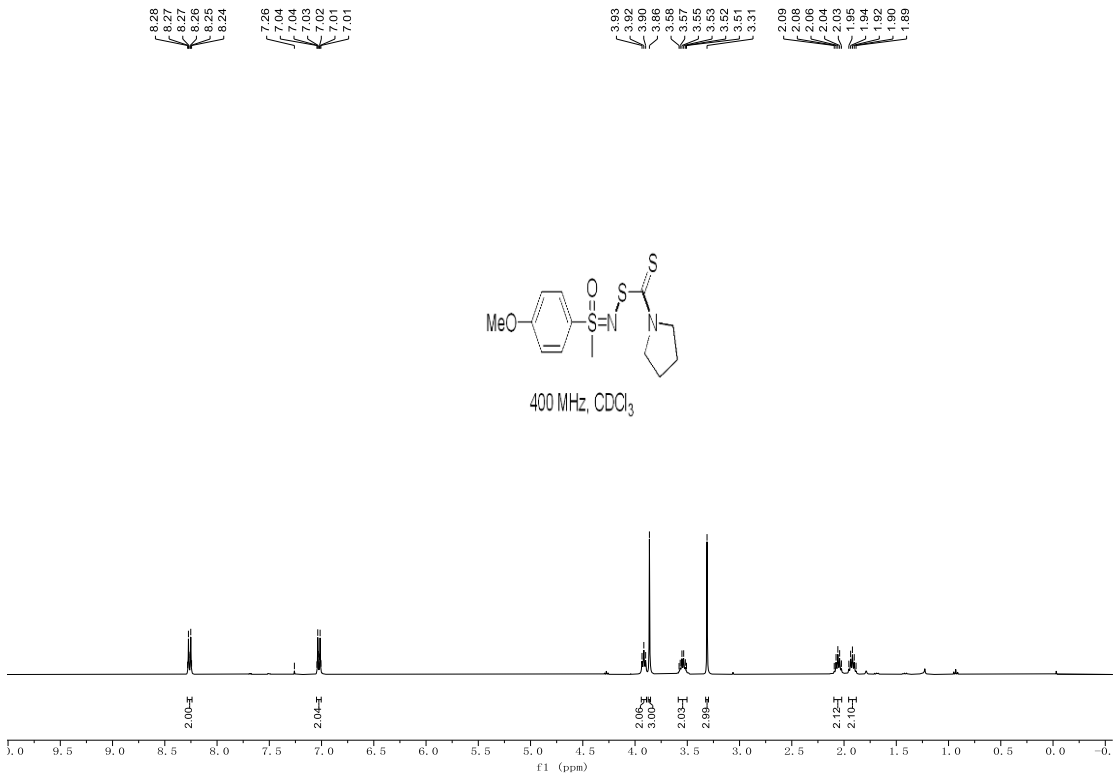
3da-^{1}H NMR



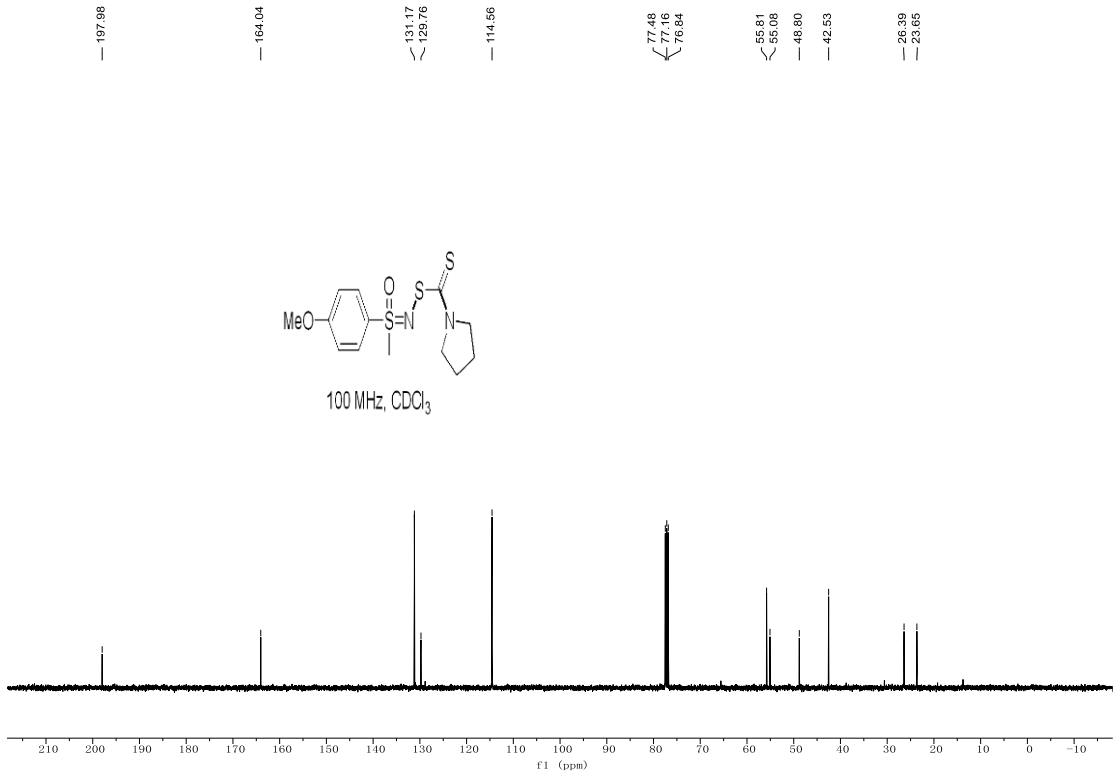
3da -^{13}C NMR



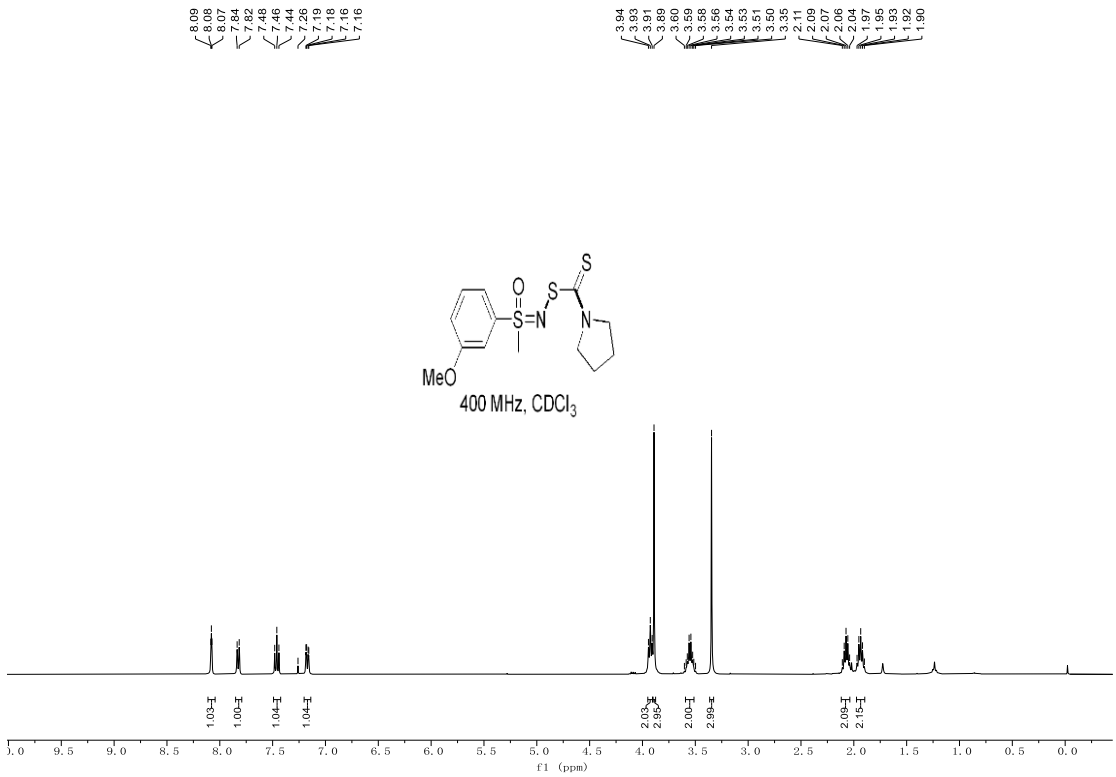
3ea-^{1}H NMR



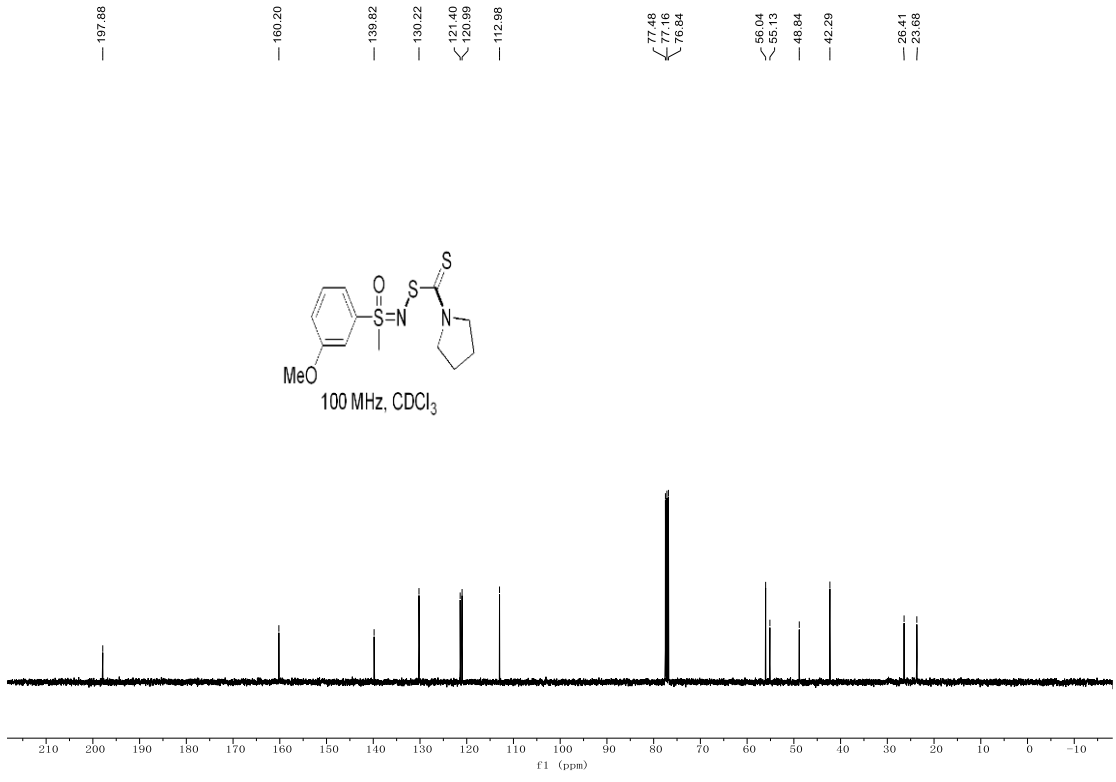
3ea -^{13}C NMR



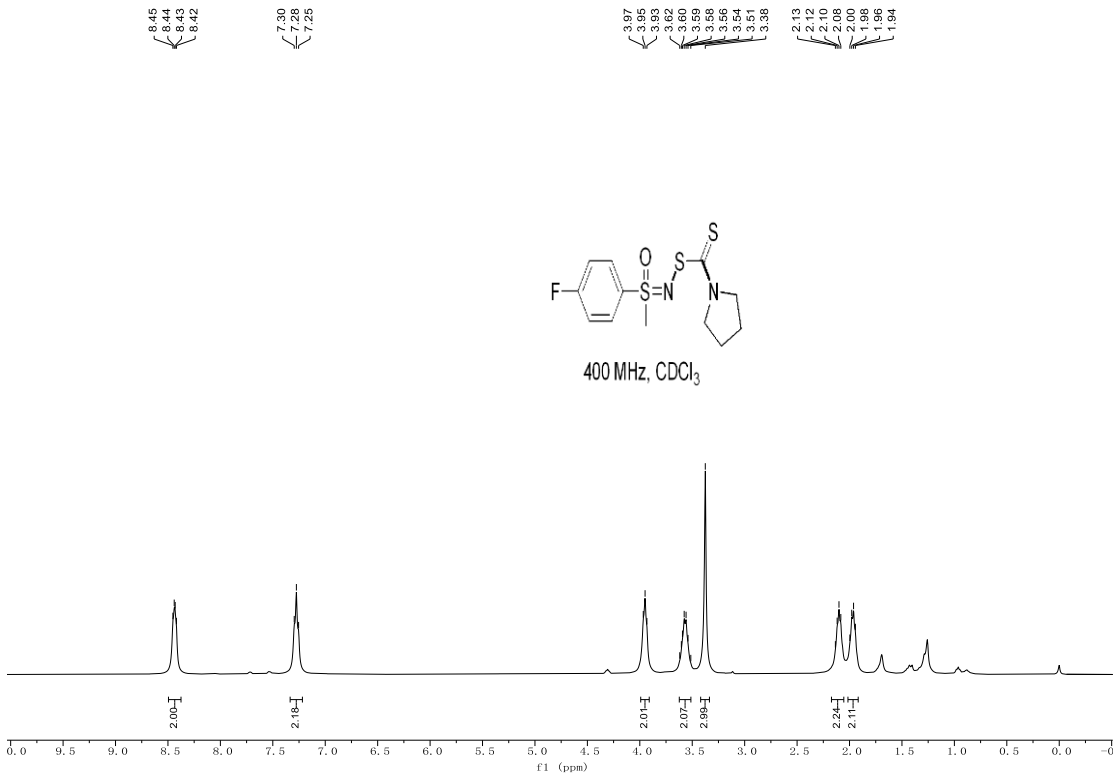
3fa-^{1}H NMR



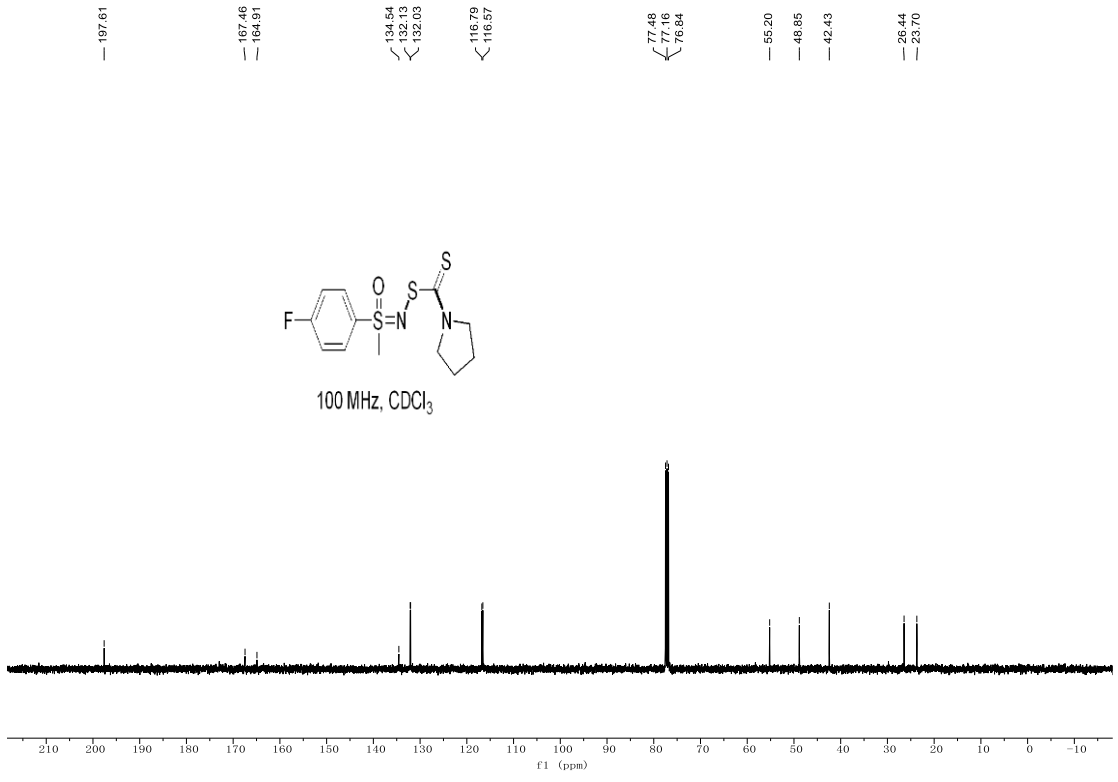
3fa -^{13}C NMR



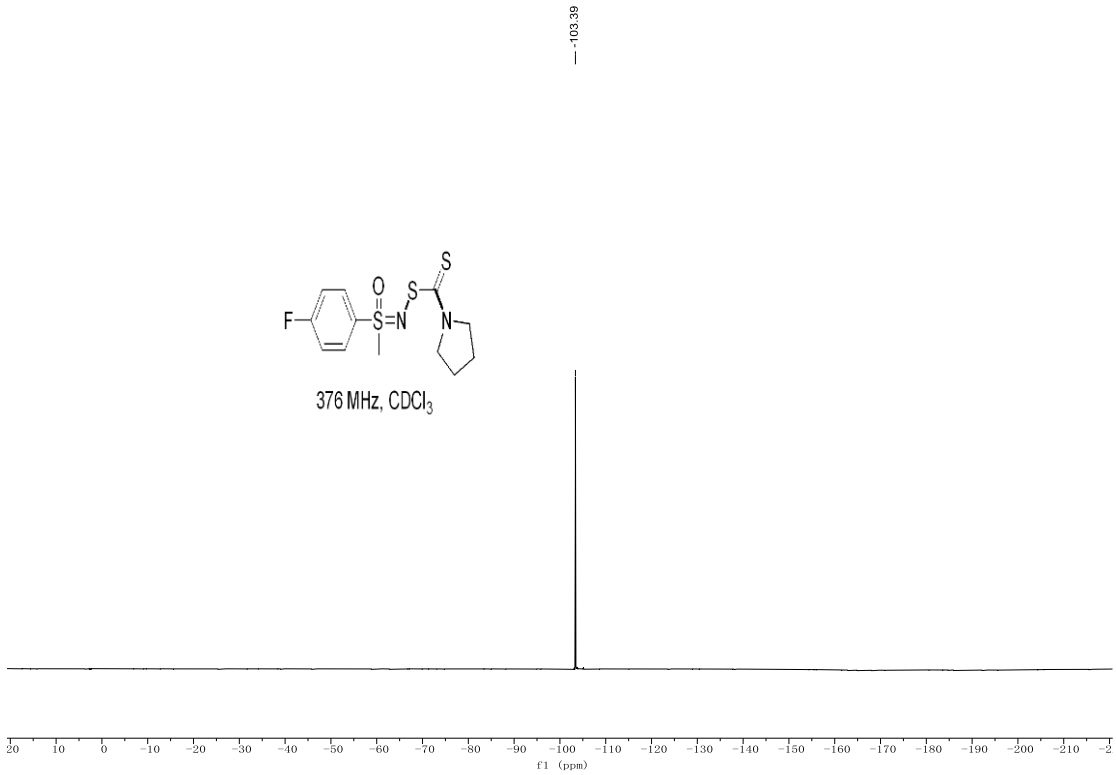
3ga-^{1}H NMR



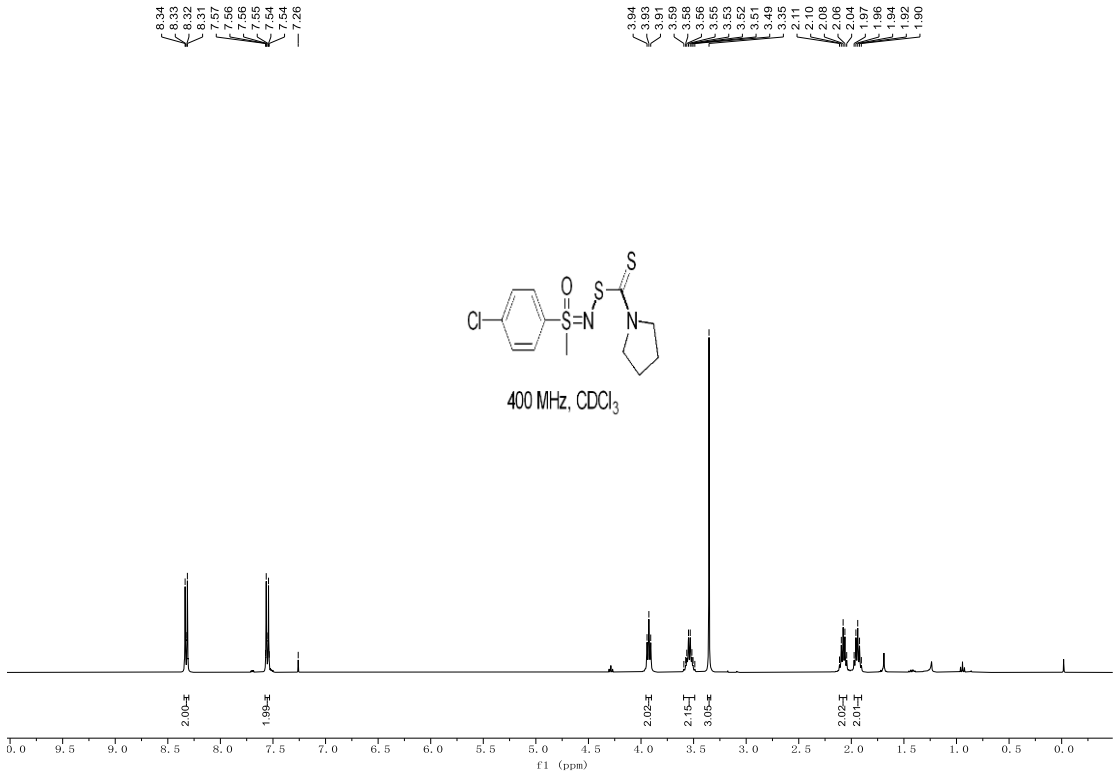
3ga -^{13}C NMR



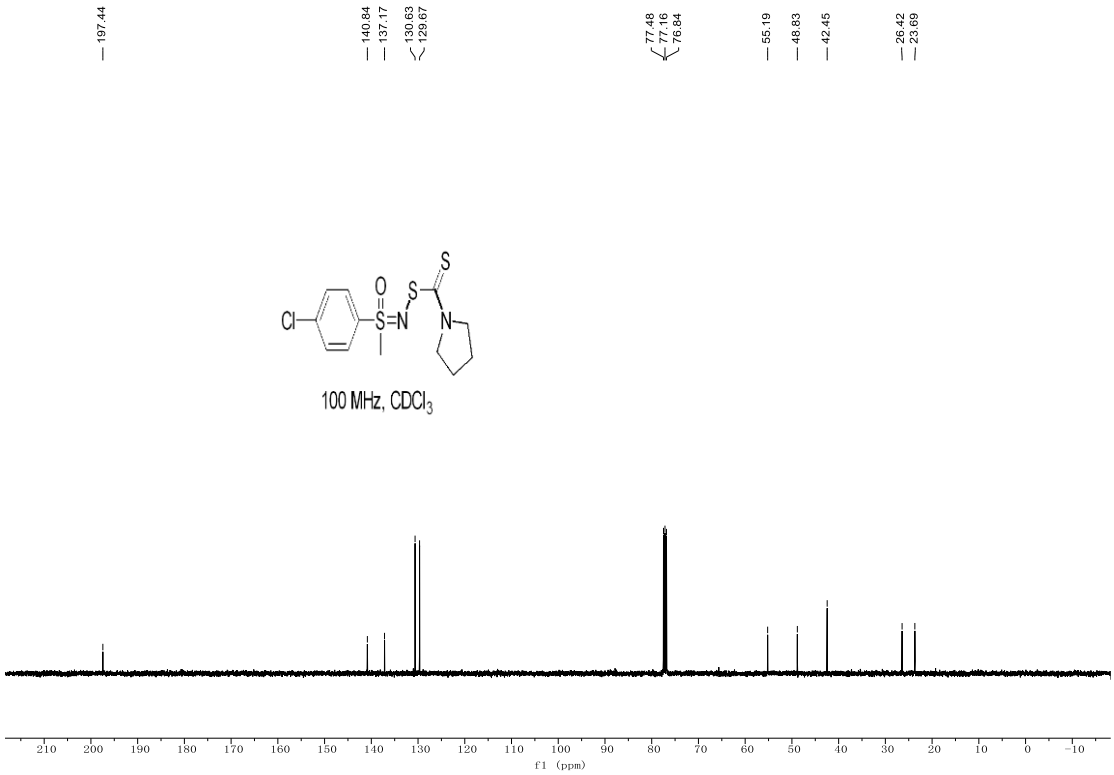
3ga -^{19}F NMR



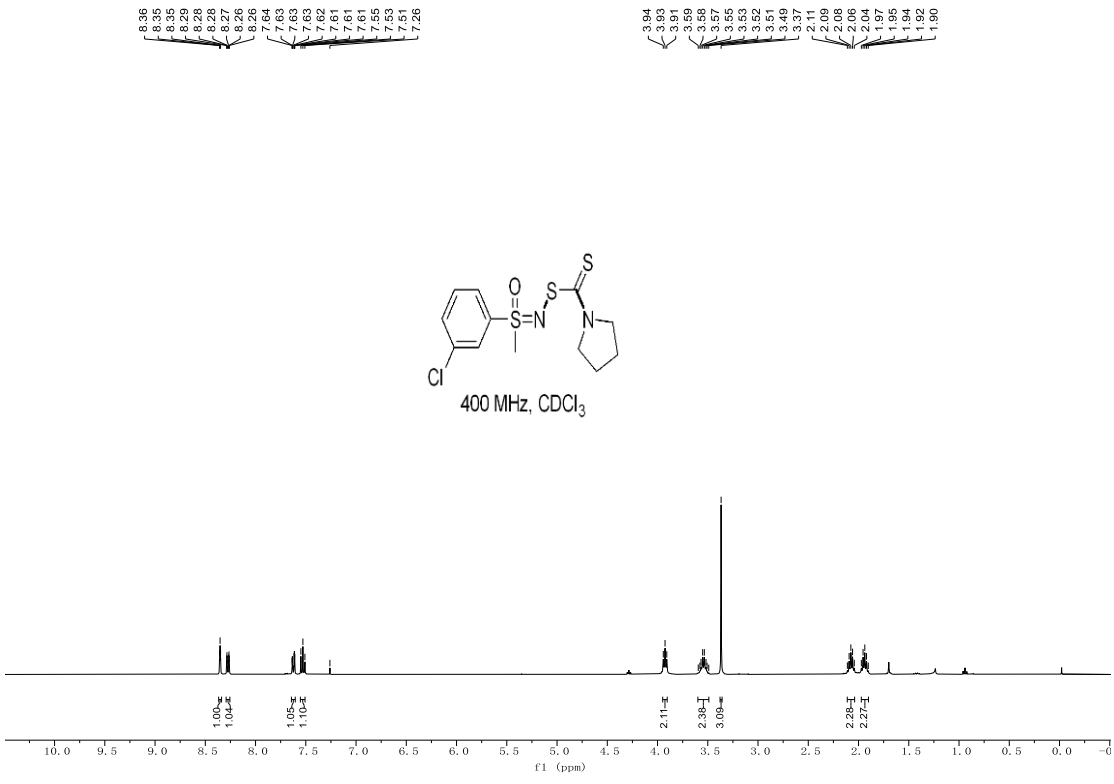
3ha-^{1}H NMR



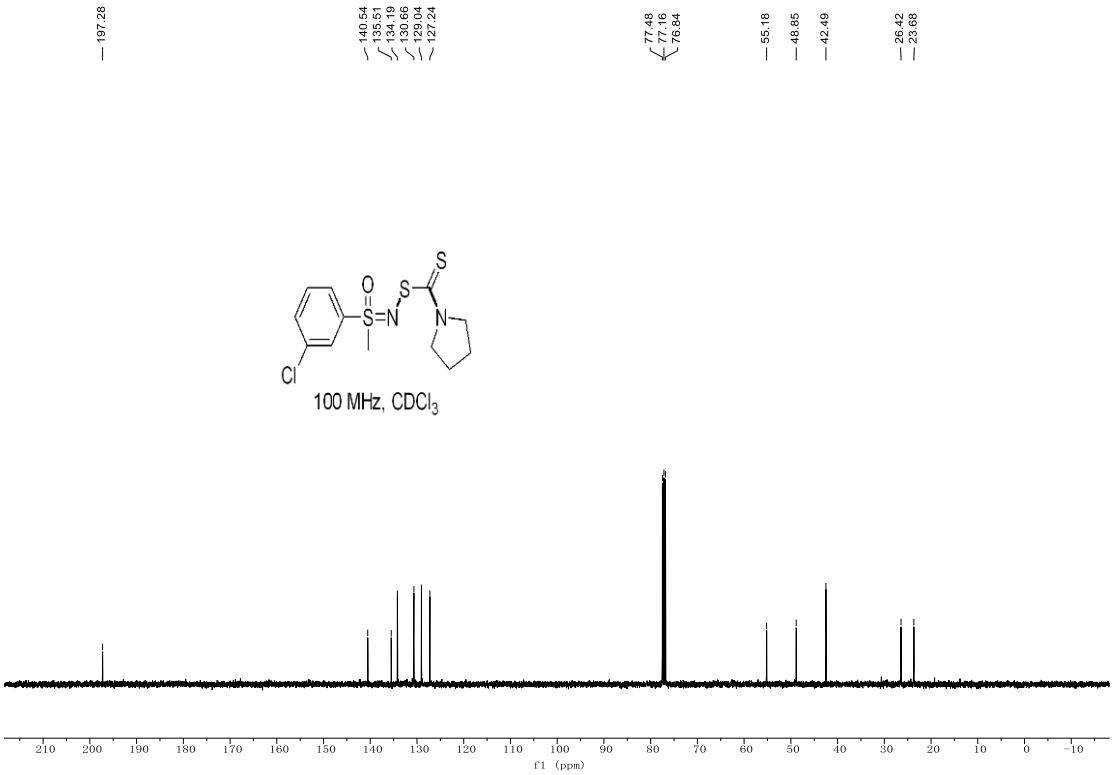
3ha -^{13}C NMR



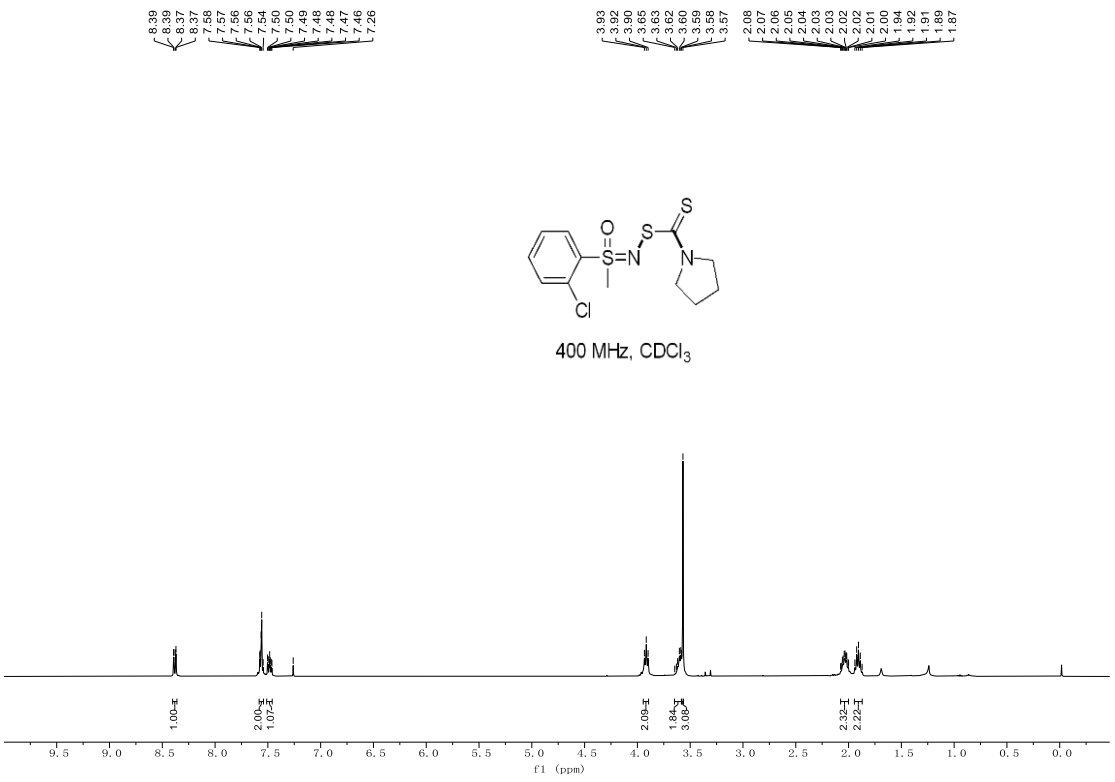
3ia-^{1}H NMR



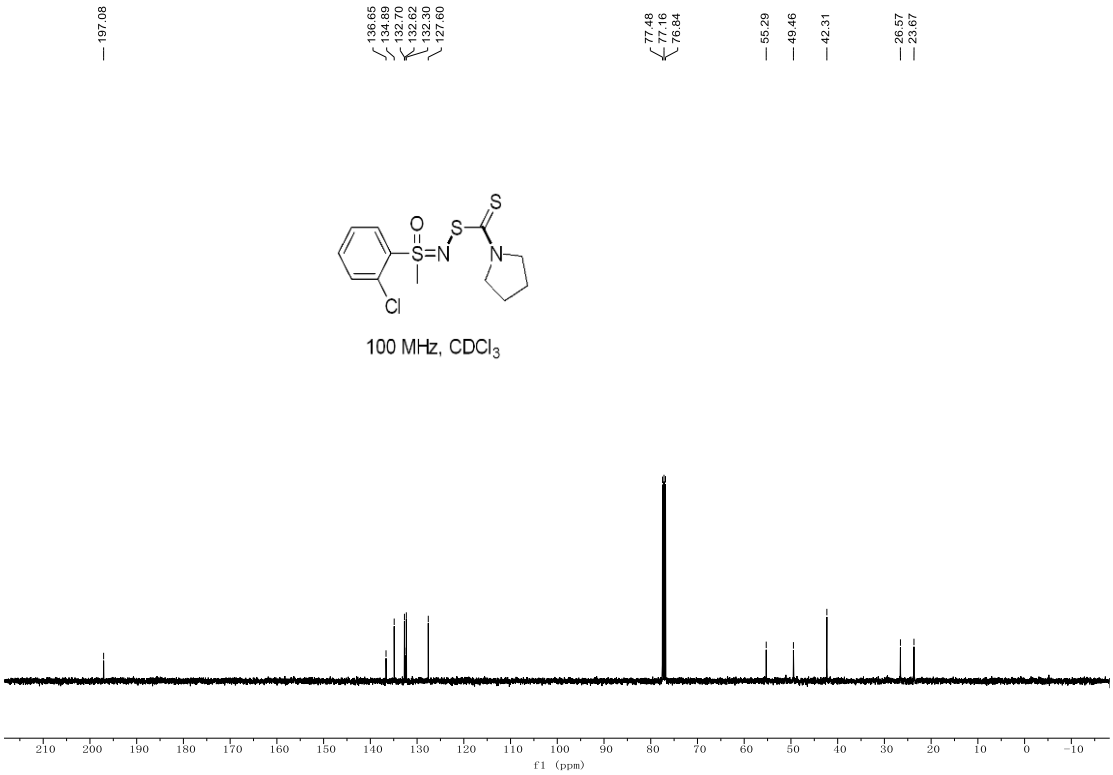
3ia -^{13}C NMR



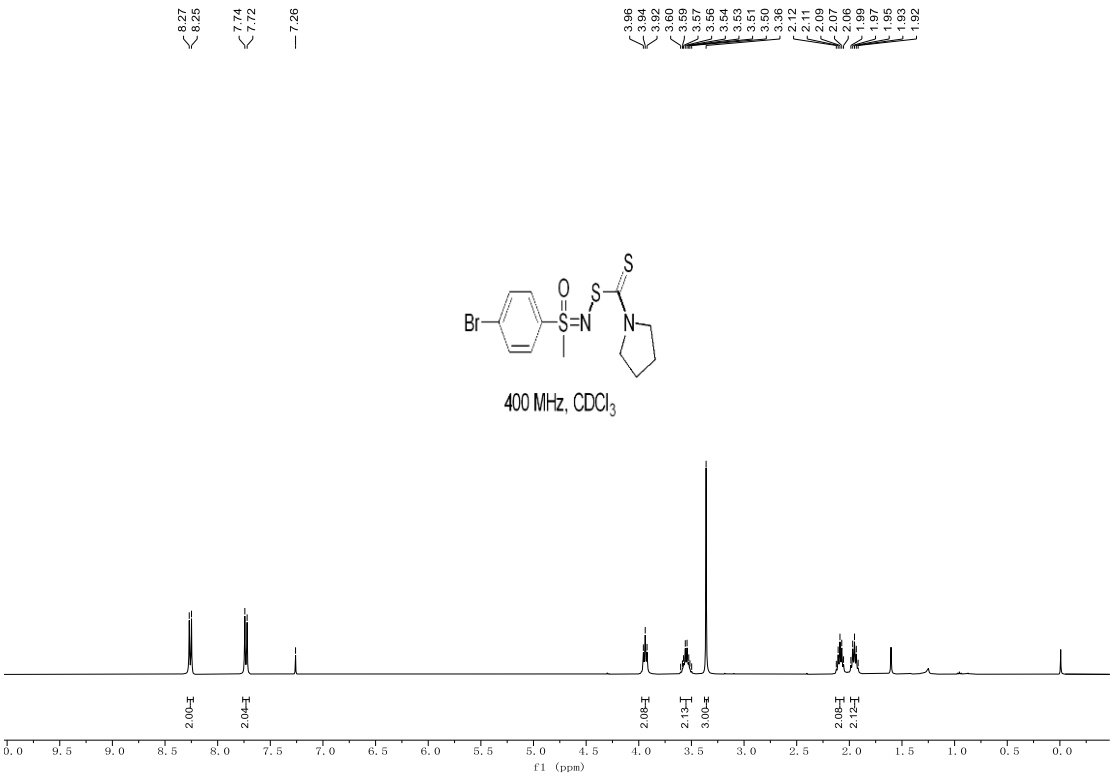
3ja-^{1}H NMR



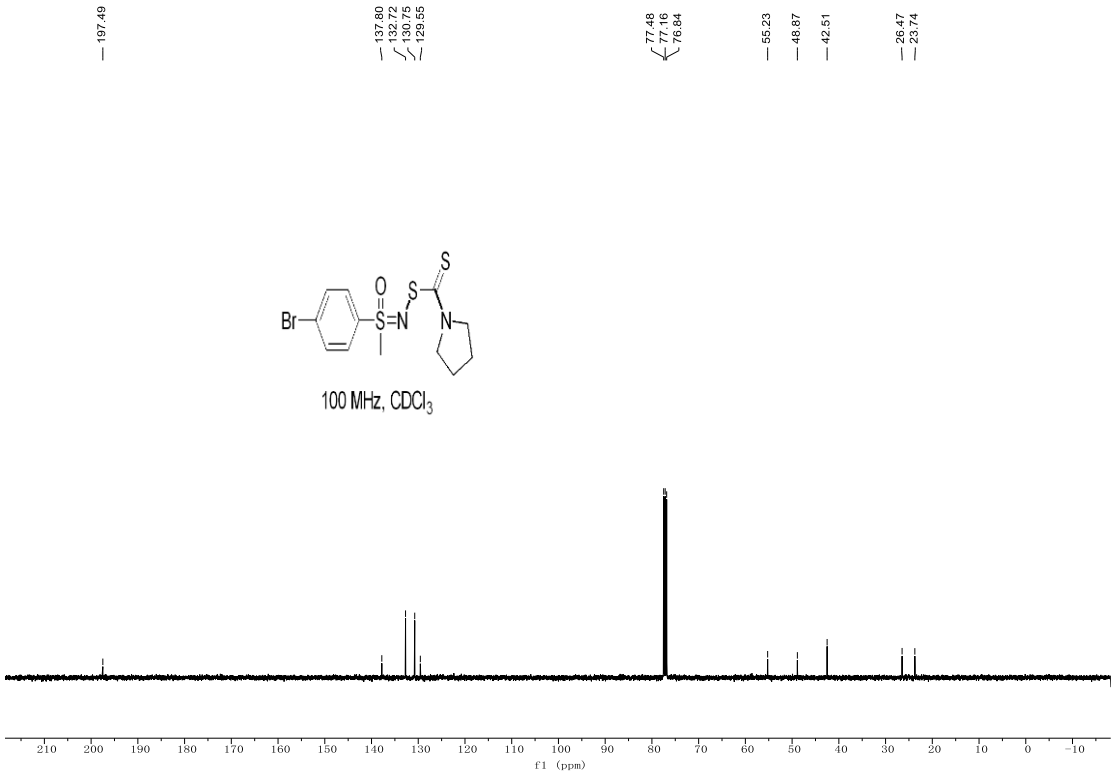
3ja-^{13}C NMR



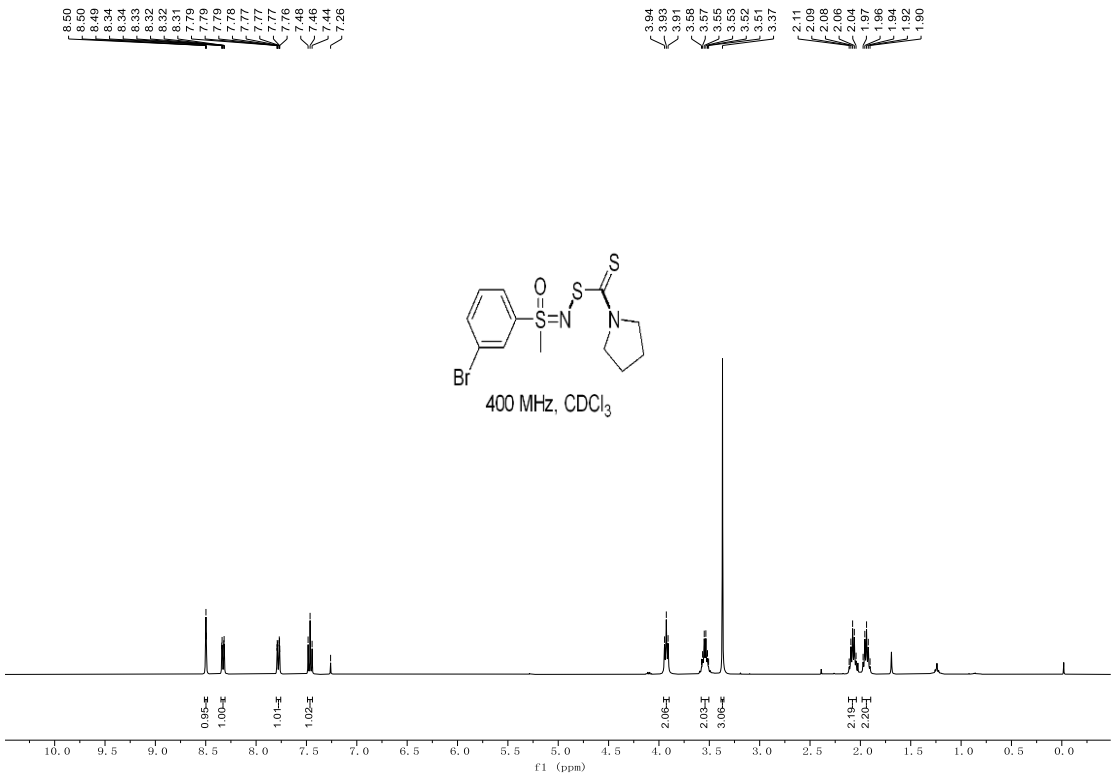
3ka-^{1}H NMR



3ka-^{13}C NMR



3la-^{1}H NMR



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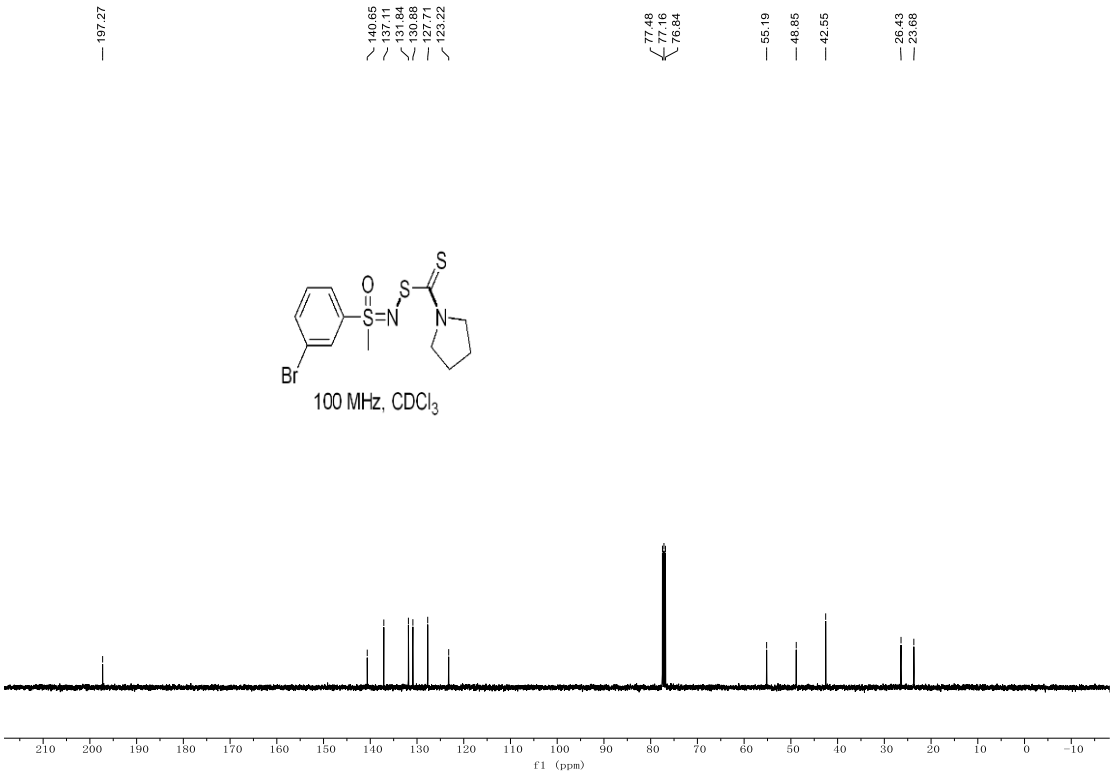
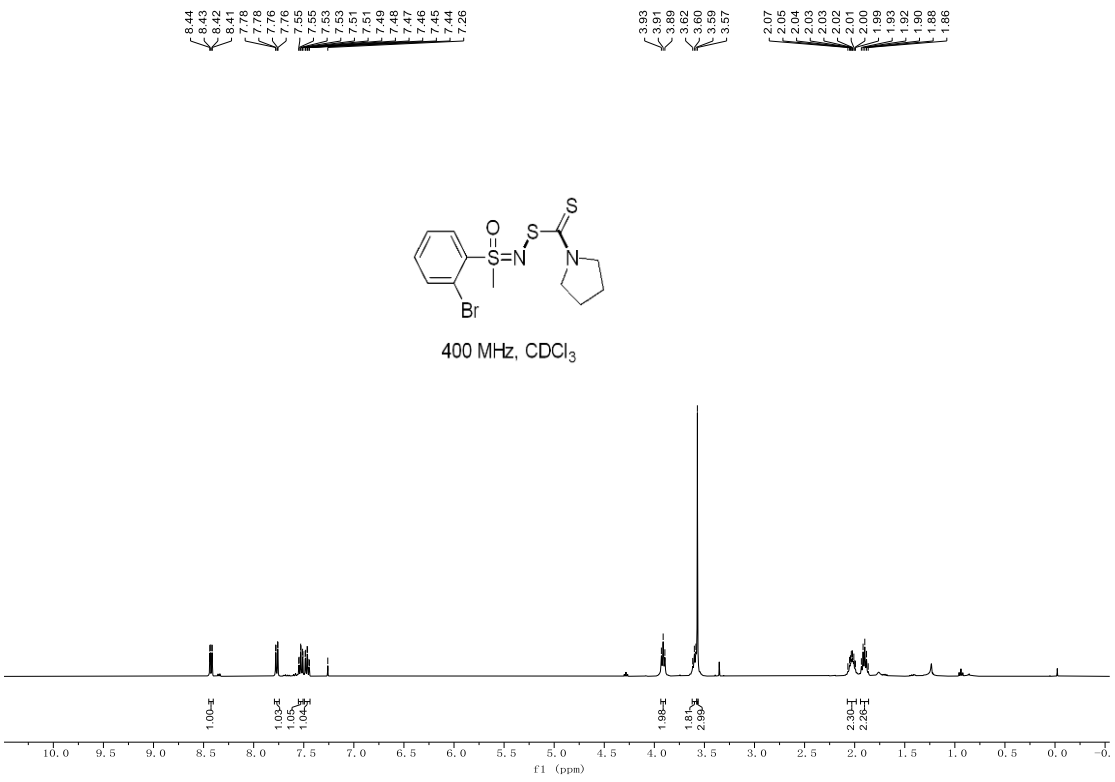
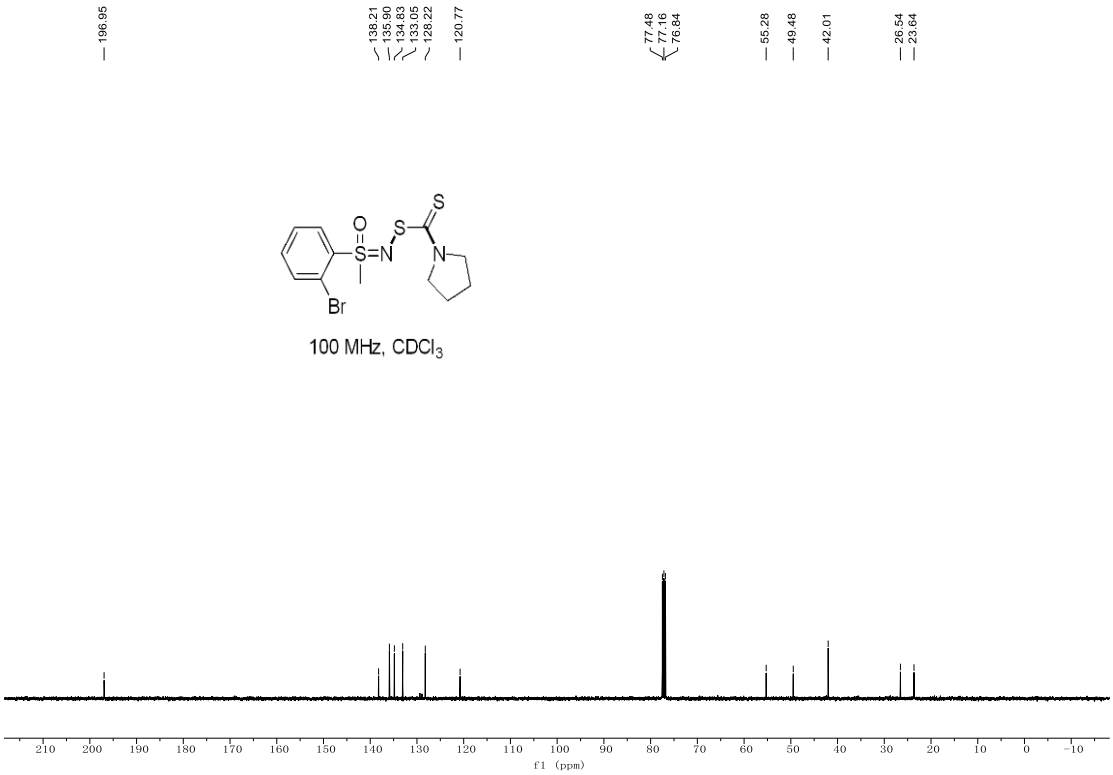


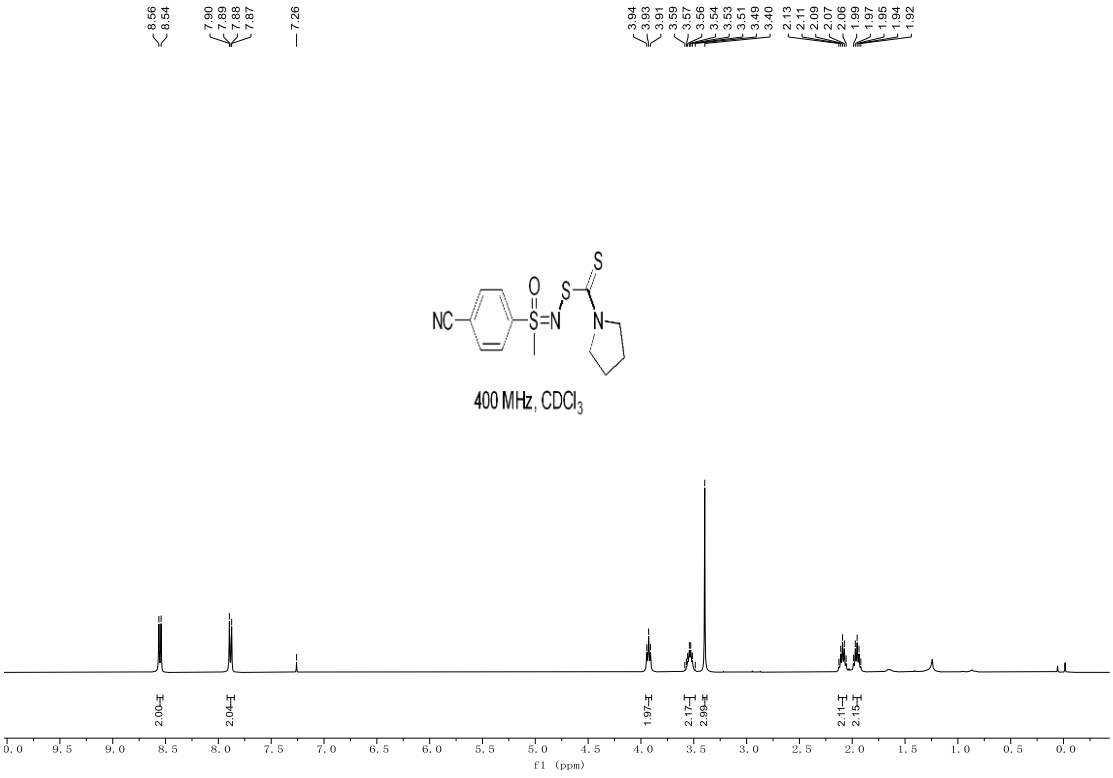
3ma-^{1}H NMR



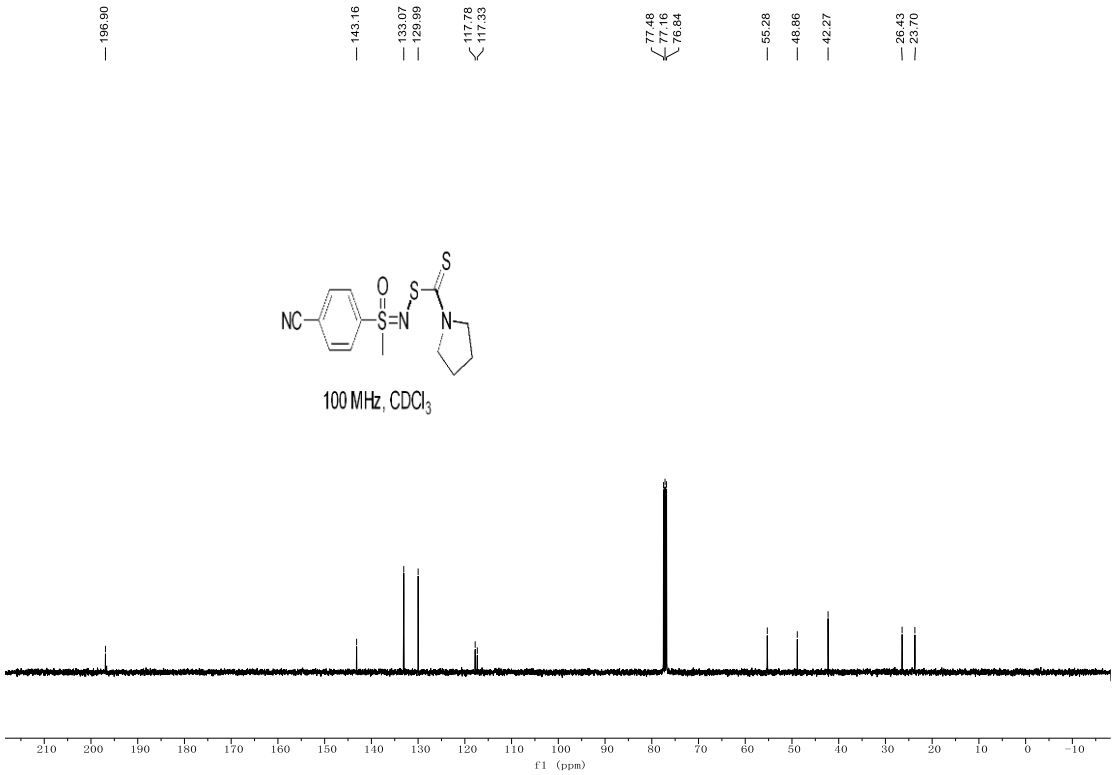
3ma -^{13}C NMR



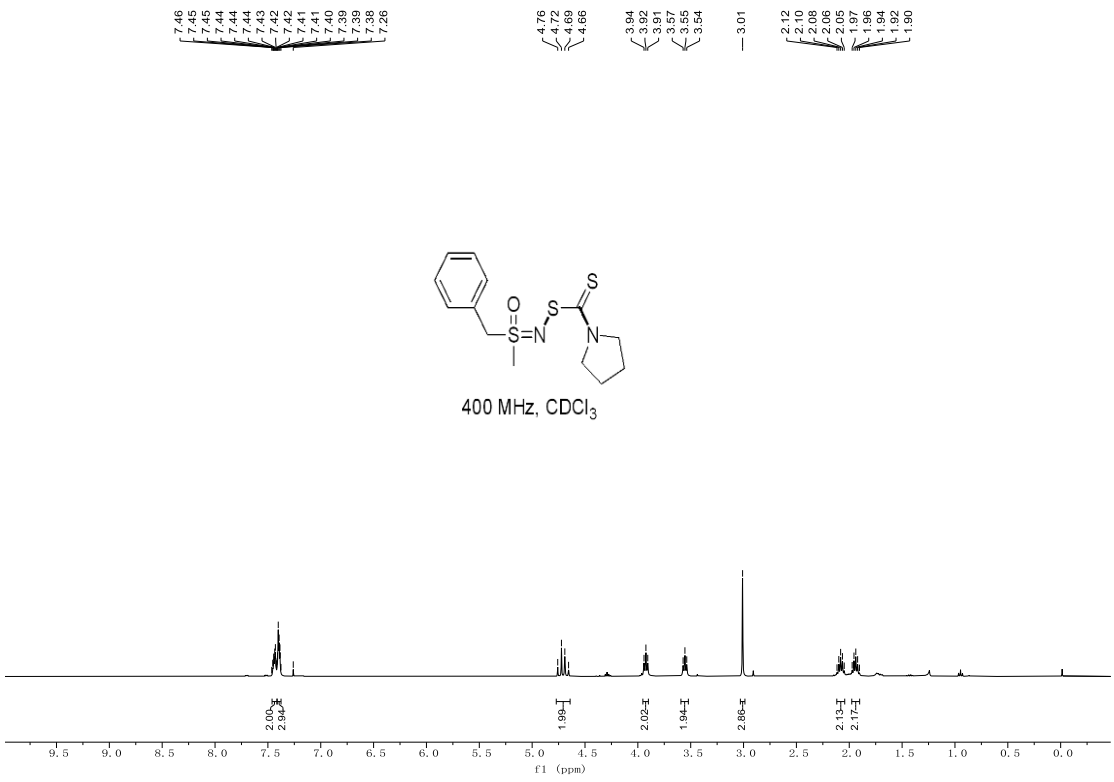
3na-^{1}H NMR



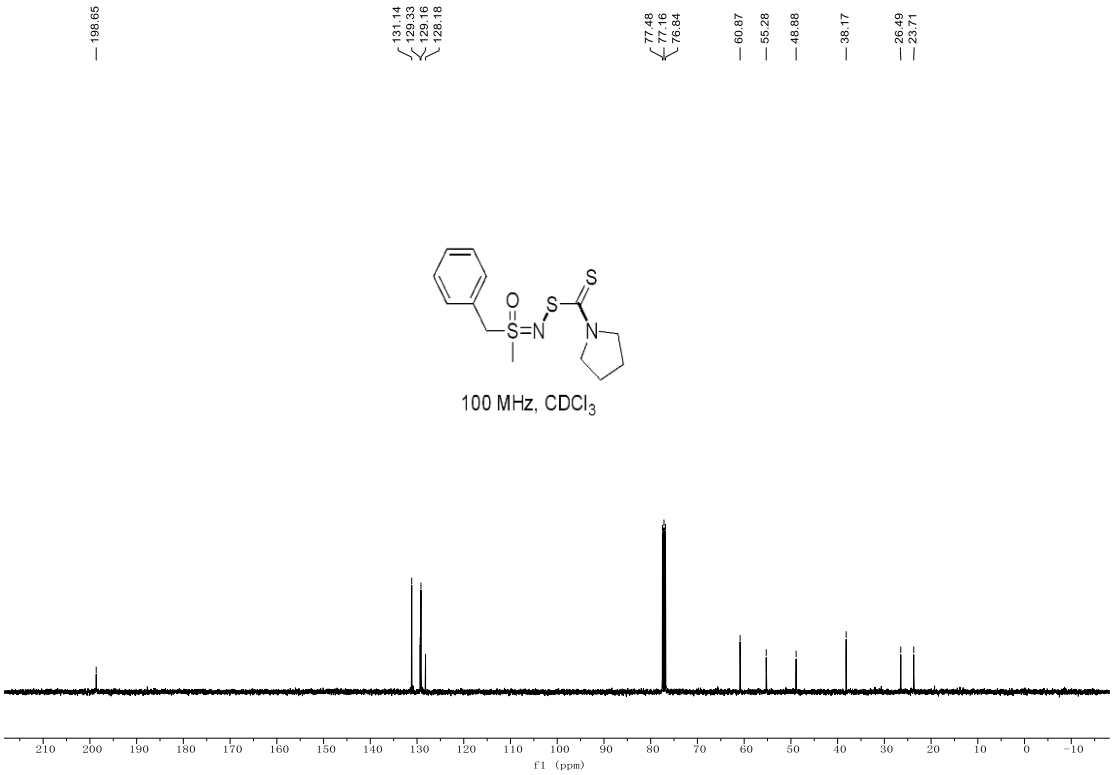
3na-^{13}C NMR



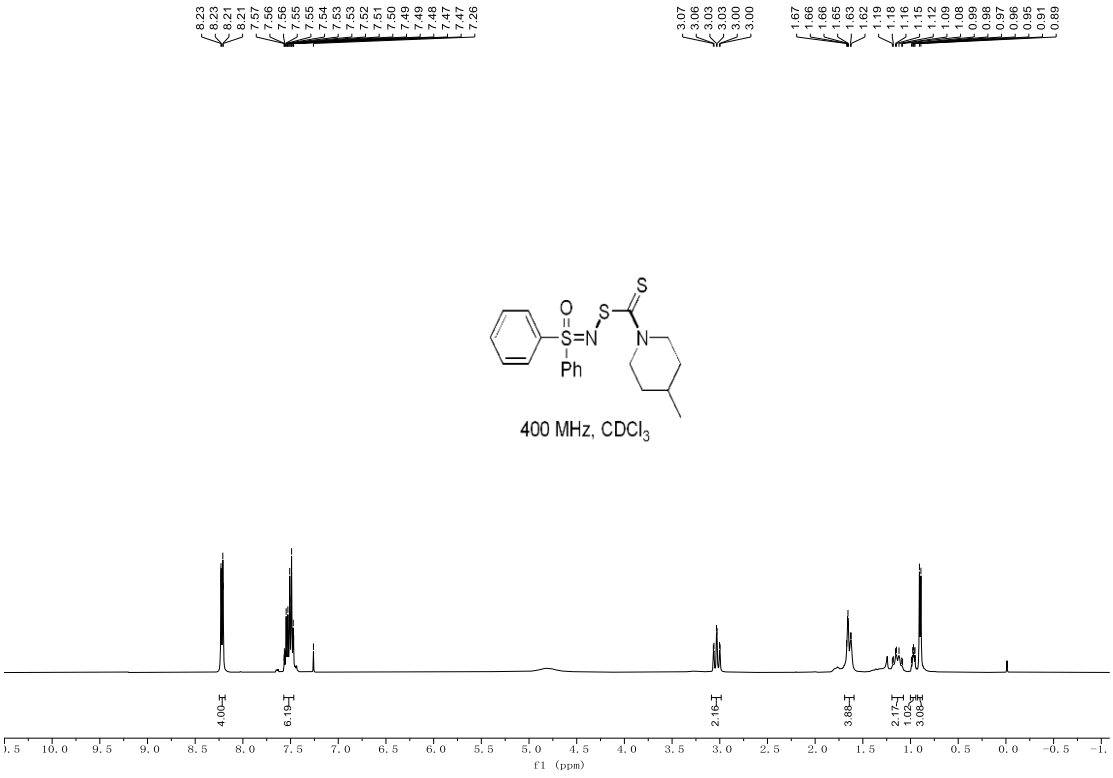
3oa-^{1}H NMR



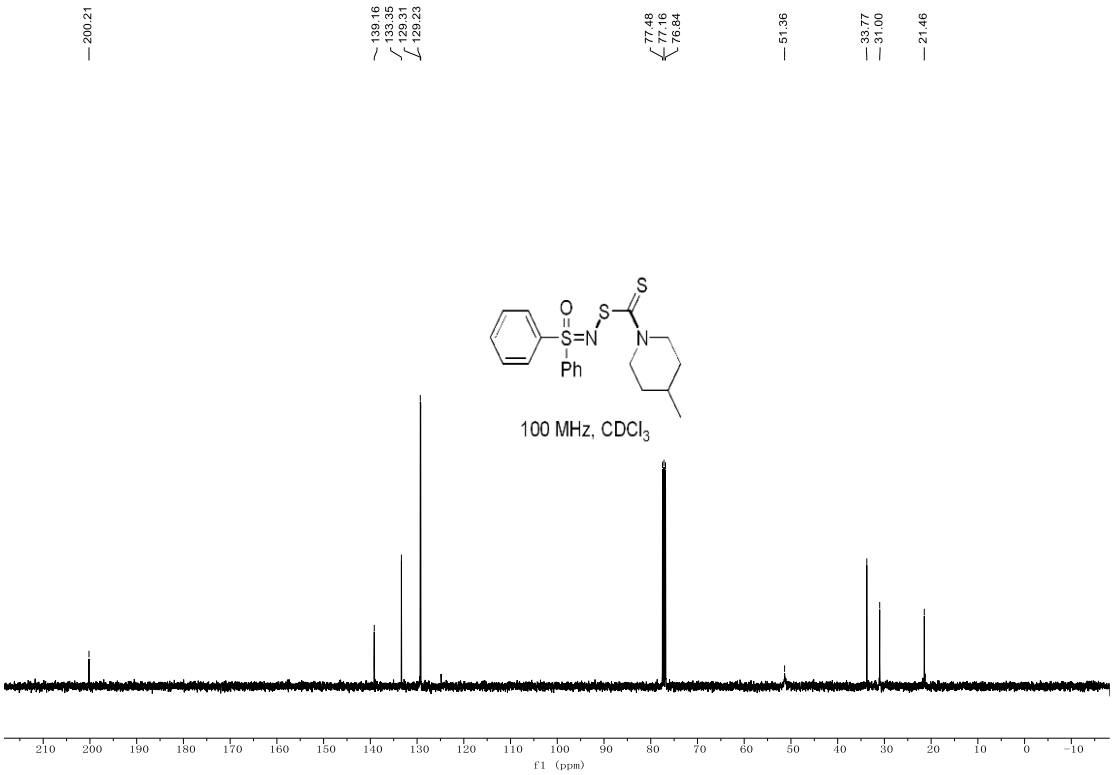
3oa-^{13}C NMR



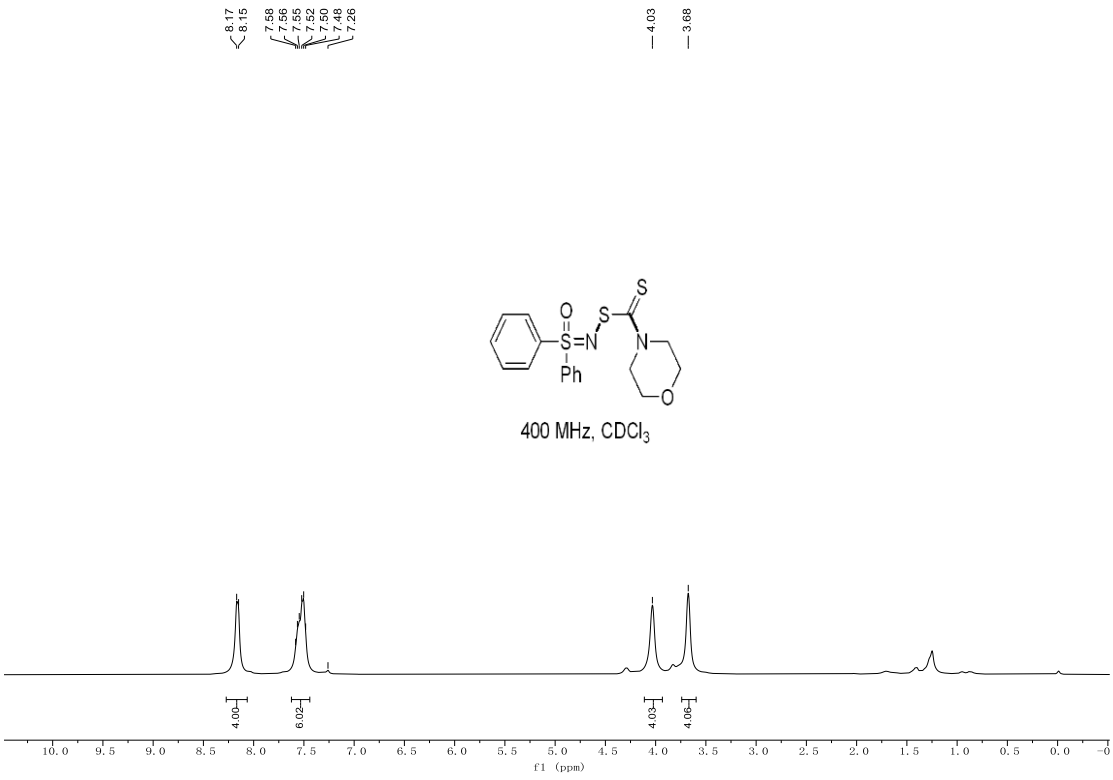
3ab-^{1}H NMR



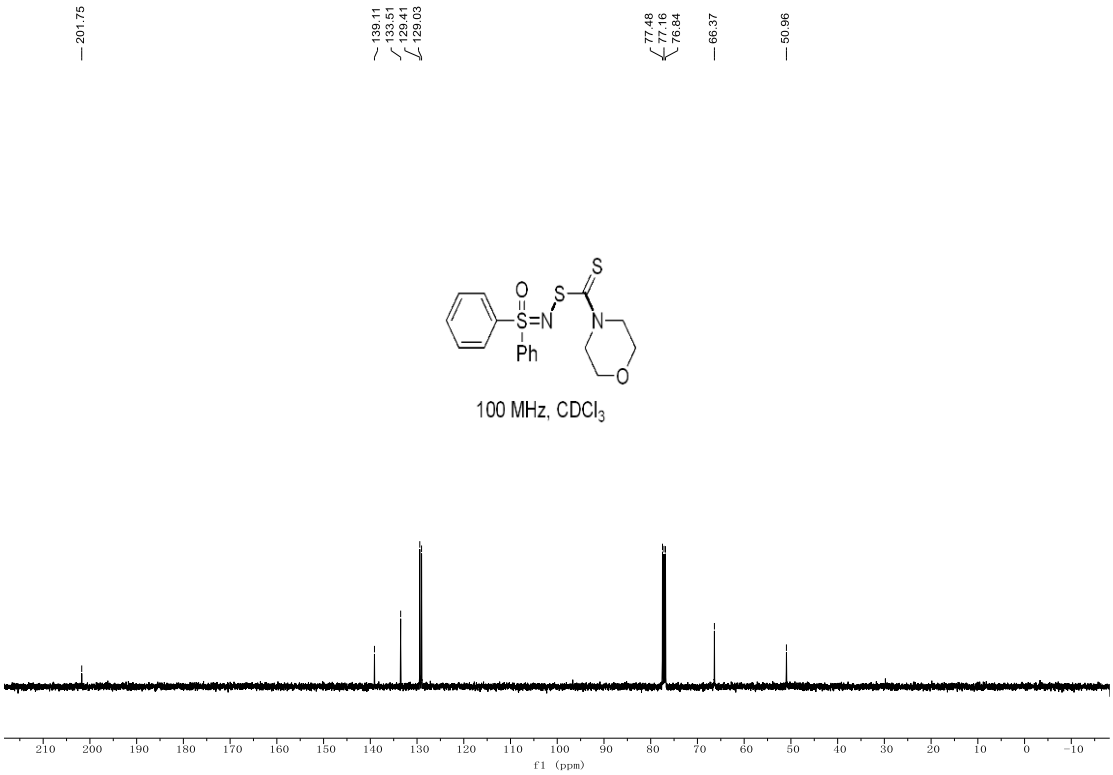
3ab-^{13}C NMR



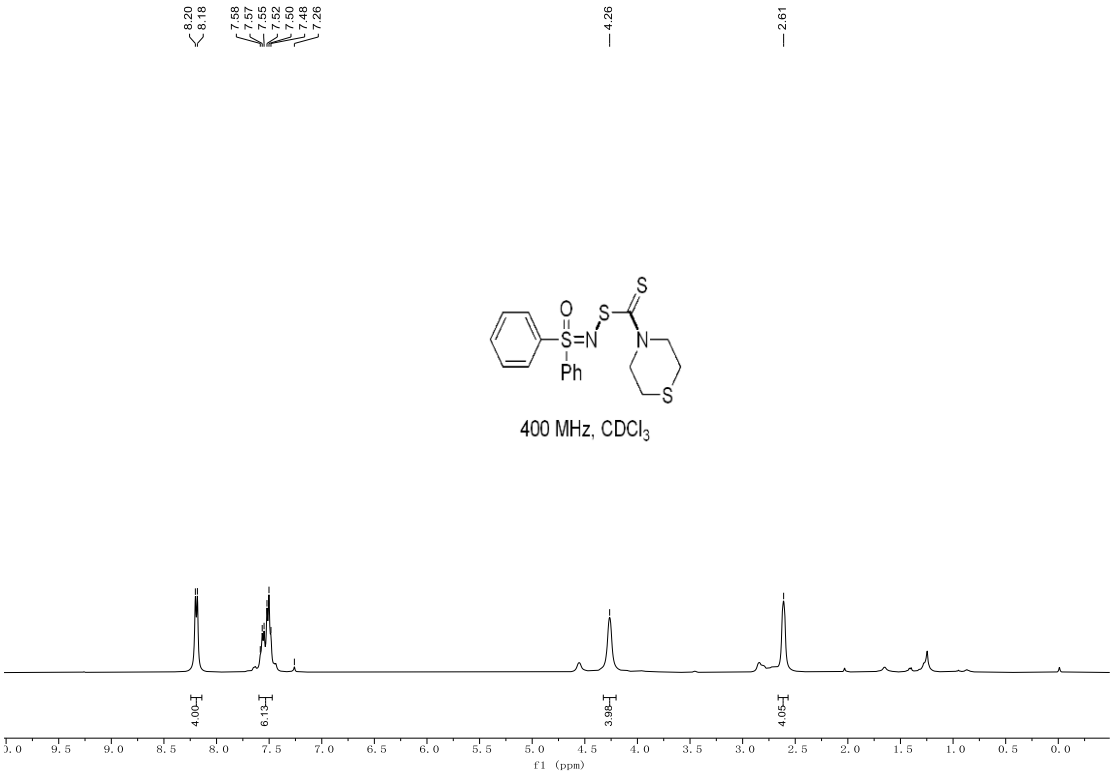
3ac-^{1}H NMR



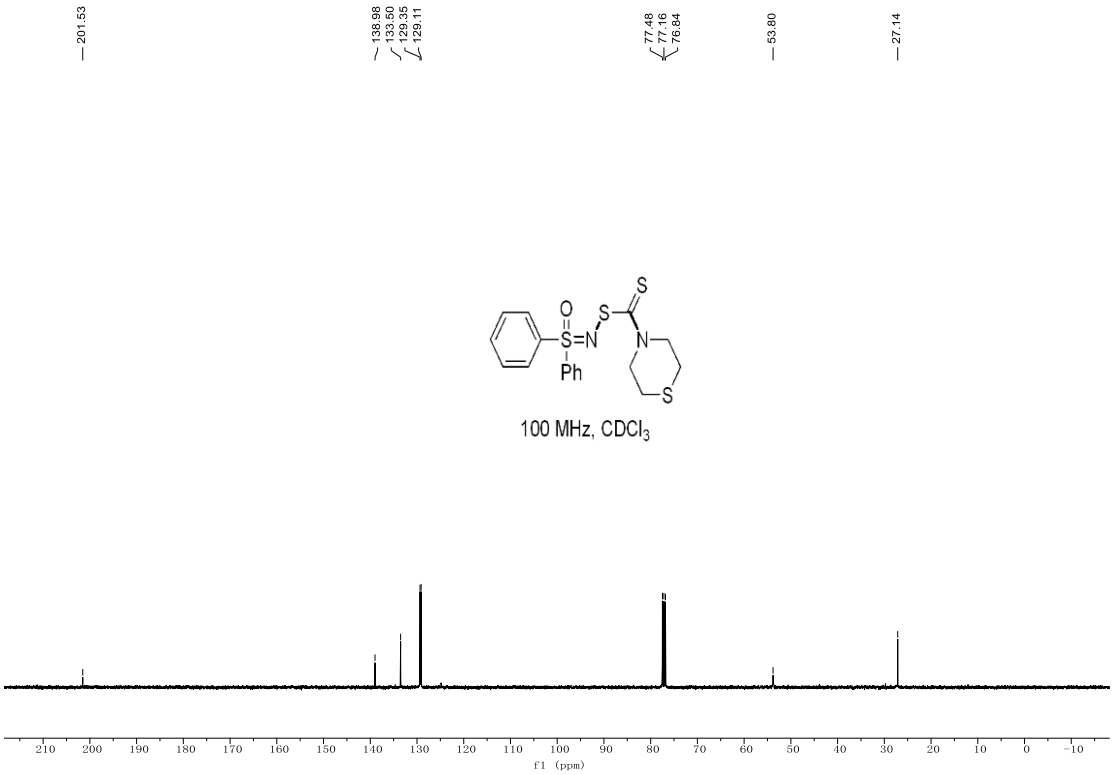
3ac-^{13}C NMR



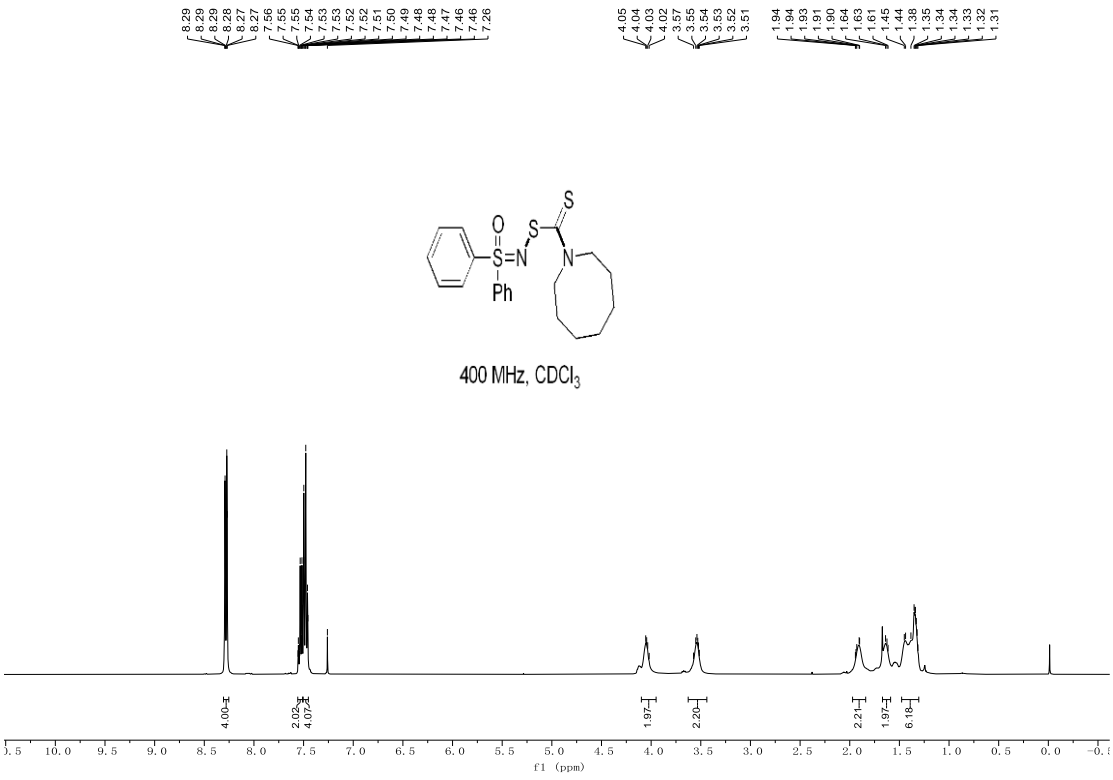
3ad-^{1}H NMR



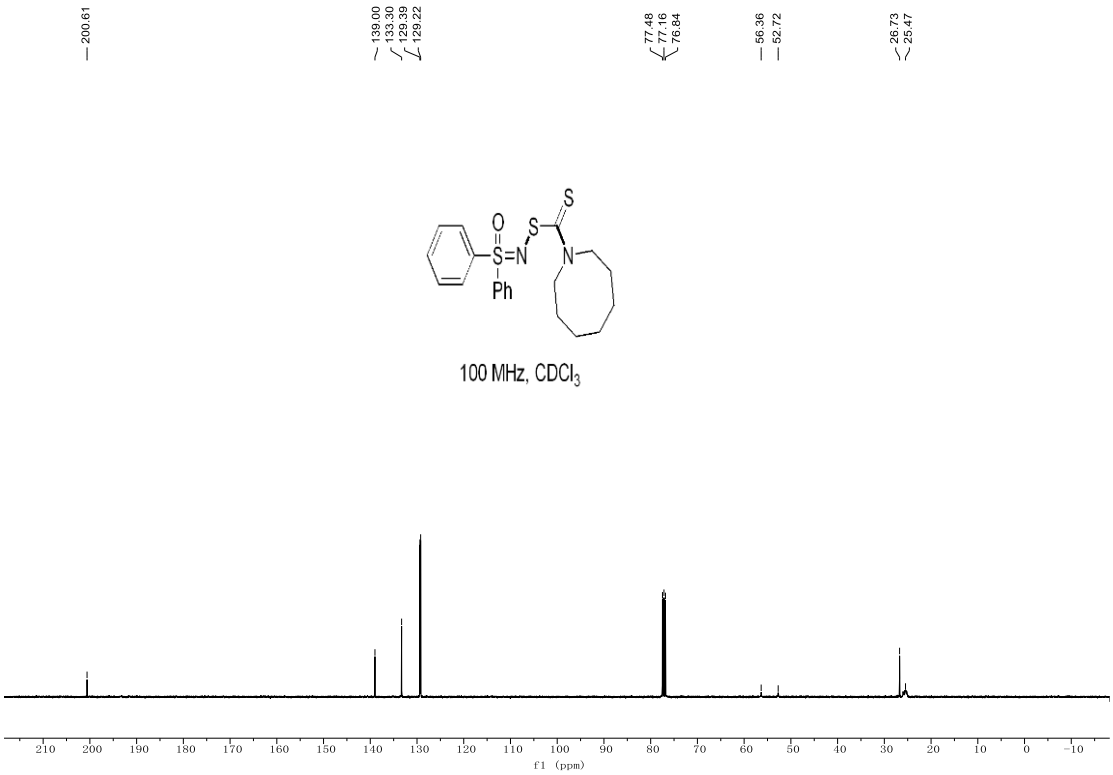
3ad-^{13}C NMR



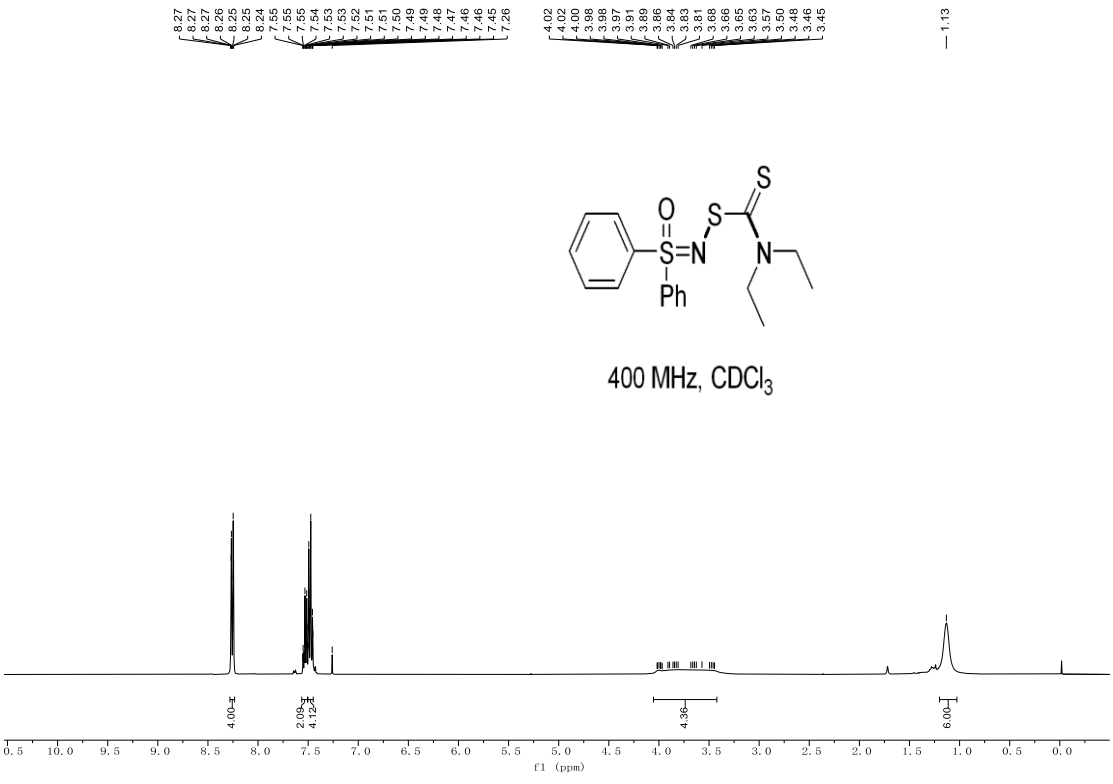
3ae-^{1}H NMR



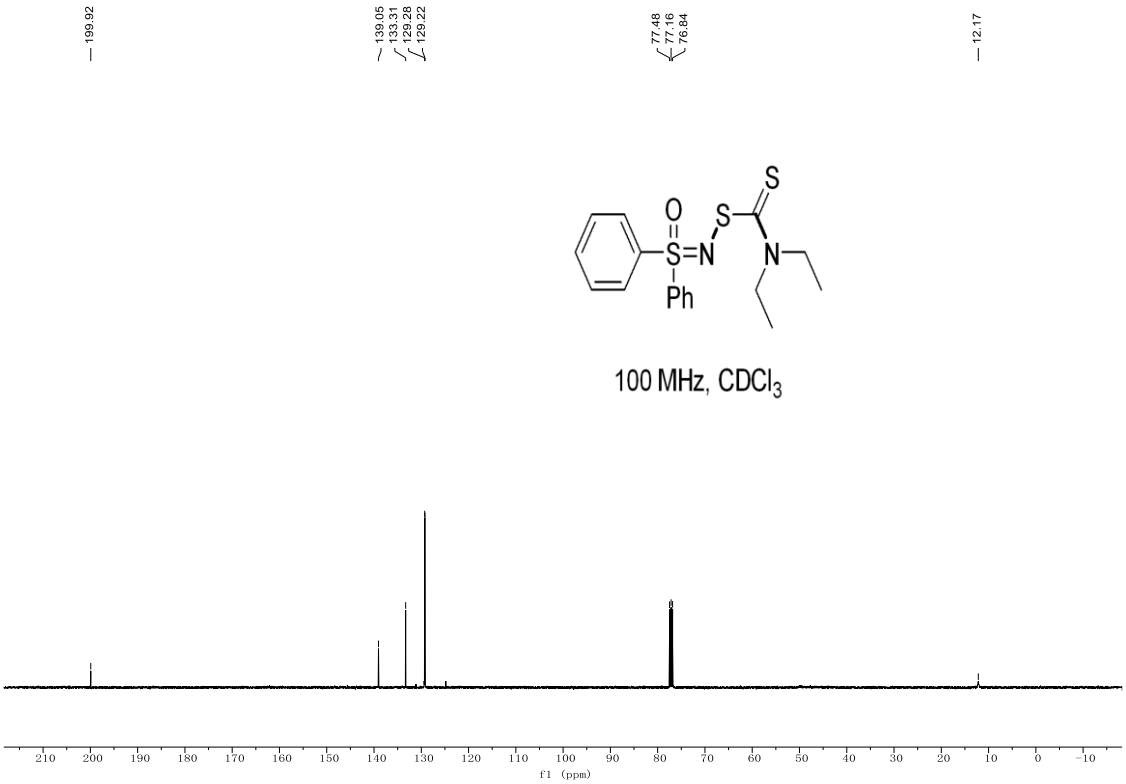
3ae-^{13}C NMR



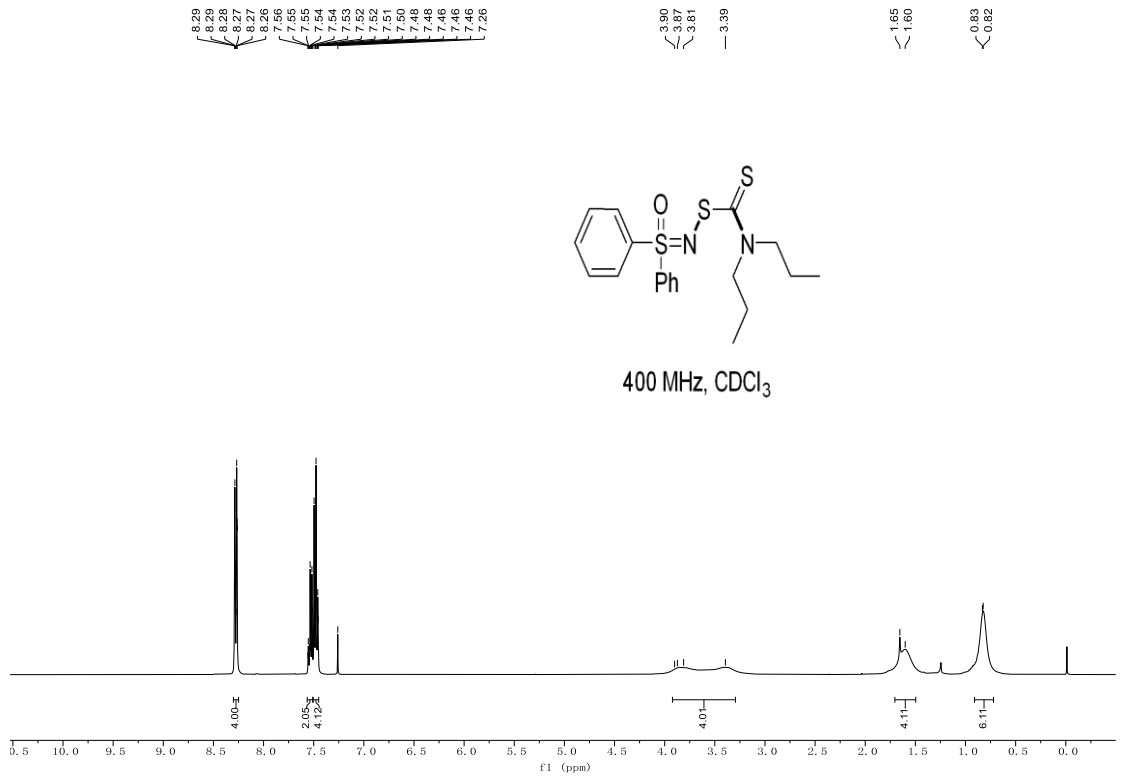
3af-^{1}H NMR



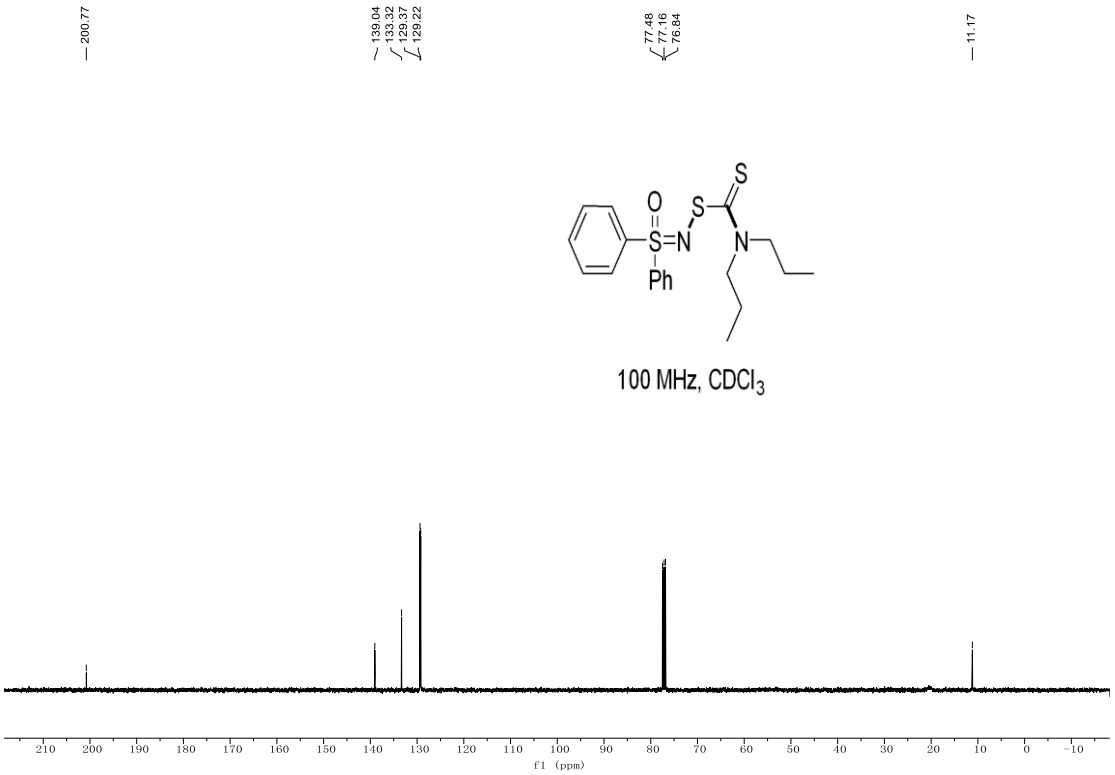
3af-^{13}C NMR



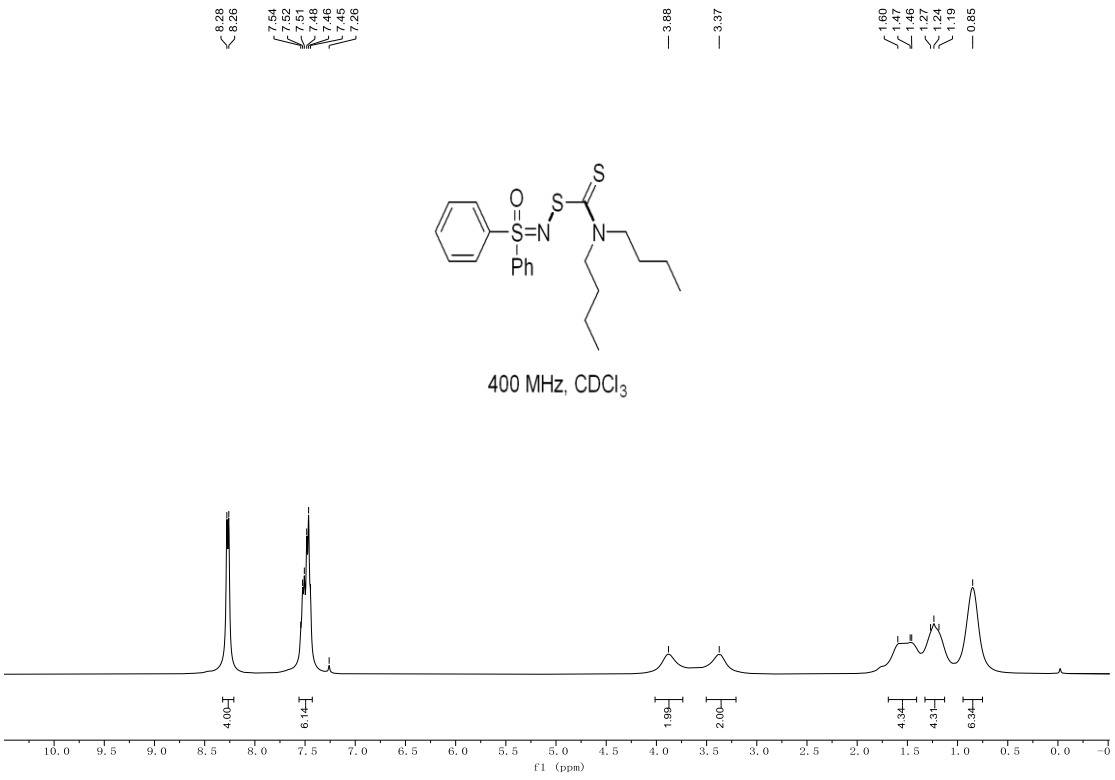
3ag-^{1}H NMR



3ag-^{13}C NMR



3ah-^{1}H NMR



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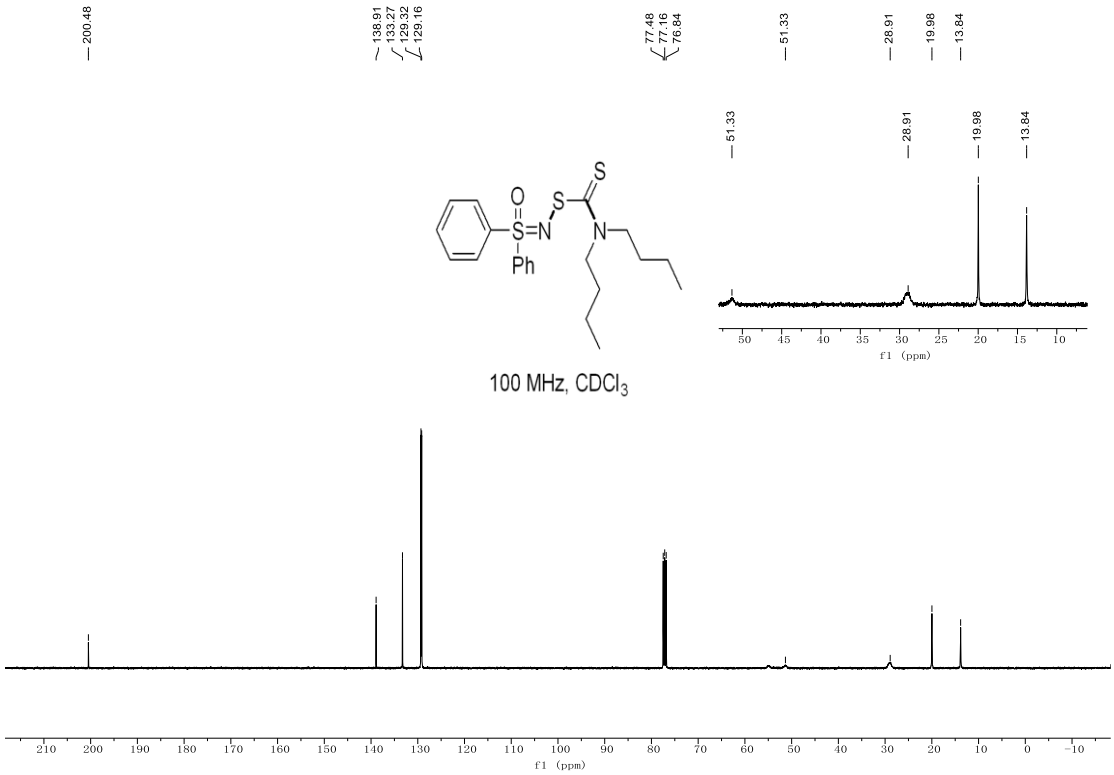

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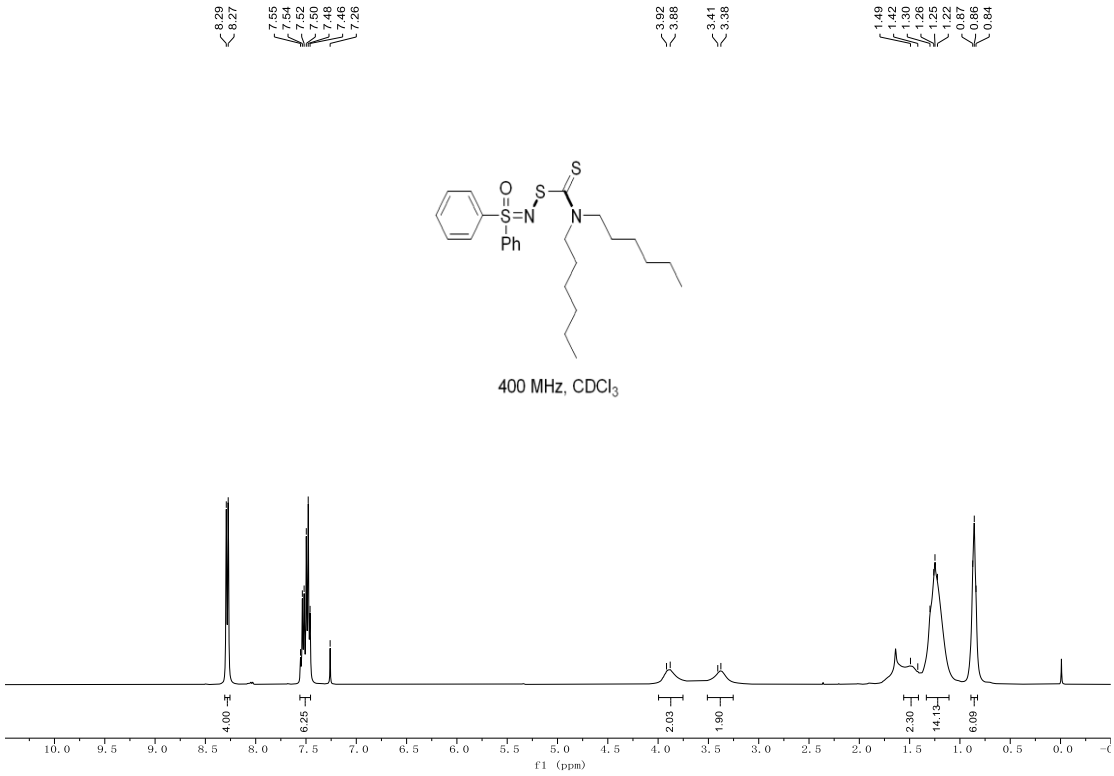
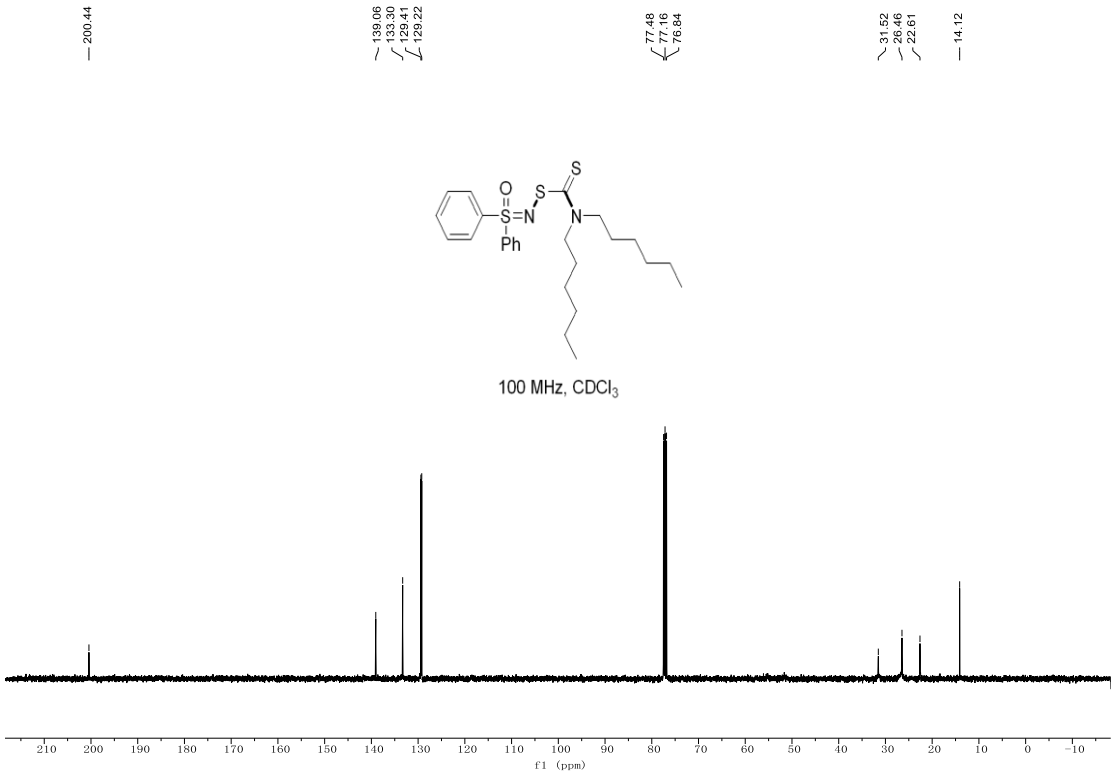
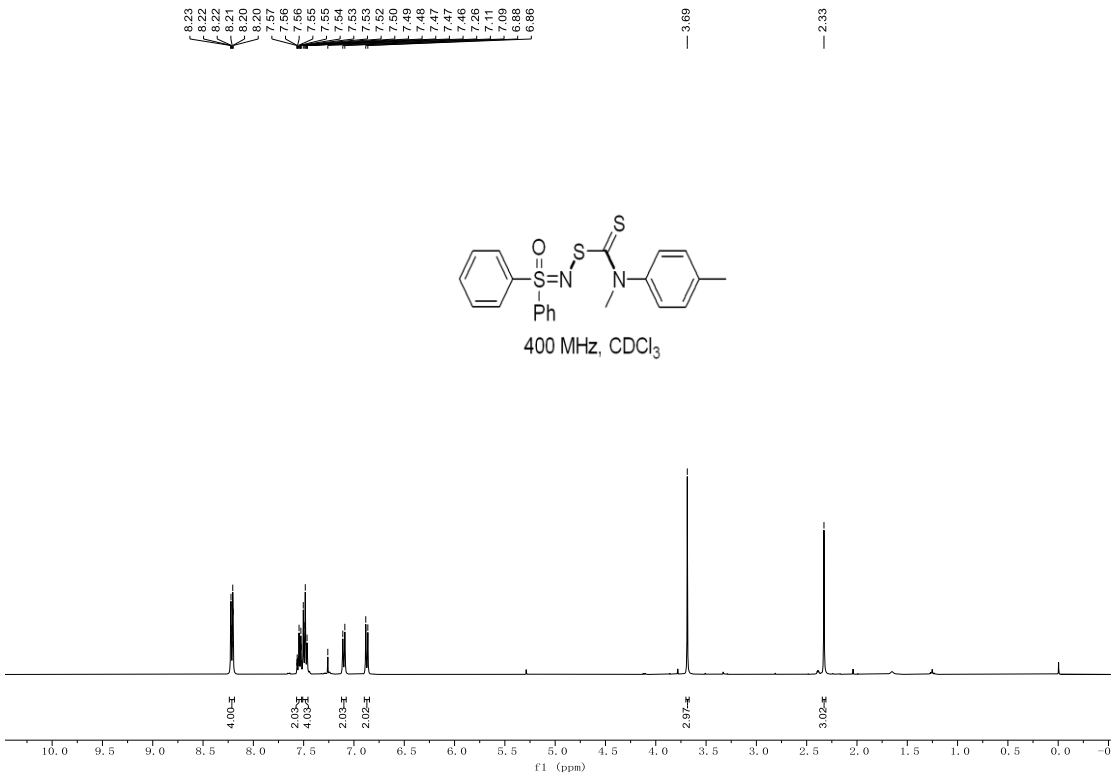


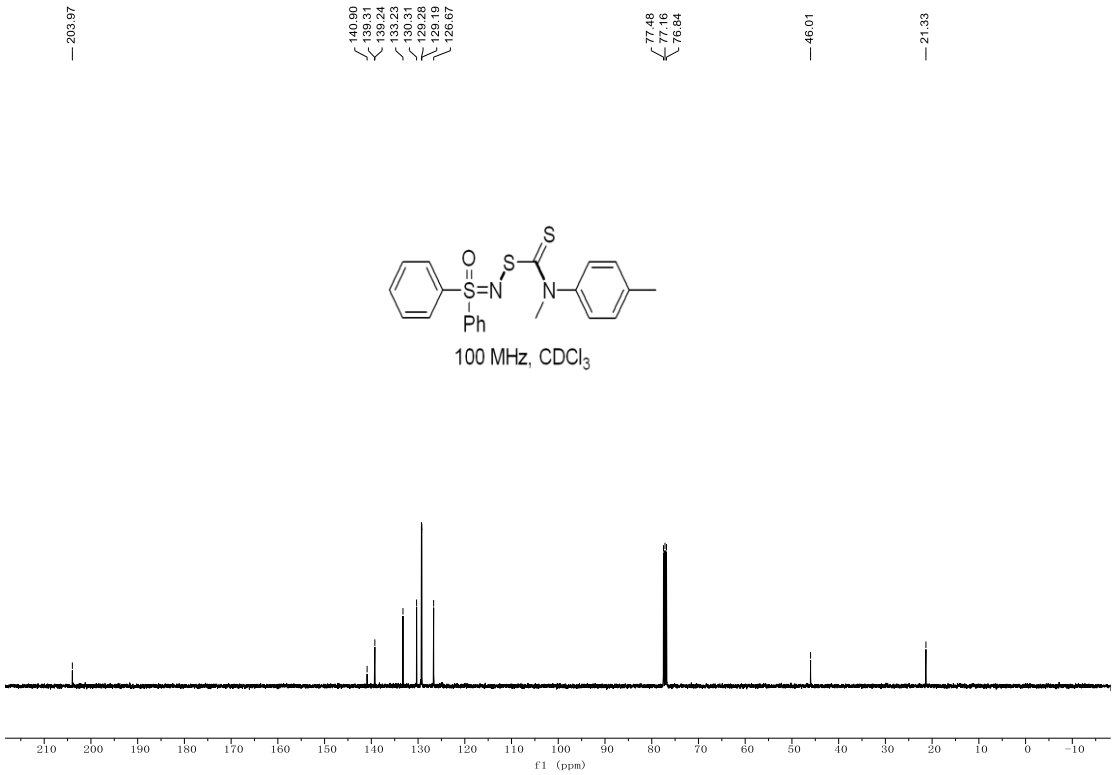
3ai-^{13}C NMR



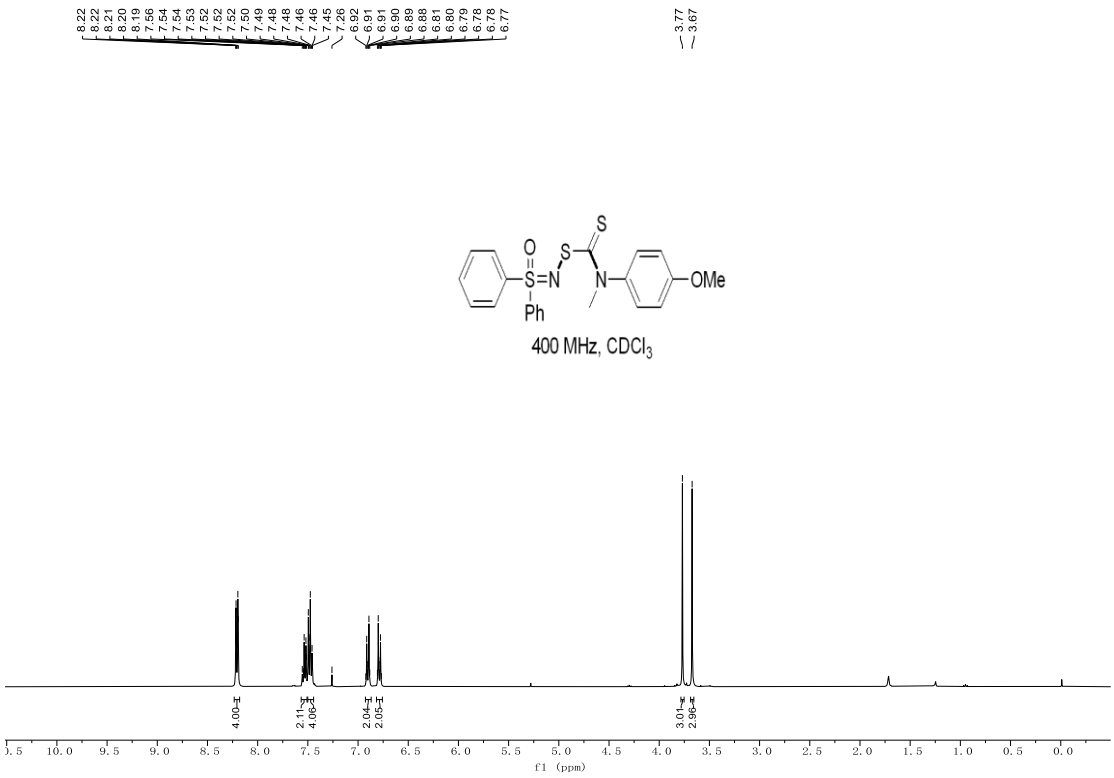
3aj-^{1}H NMR



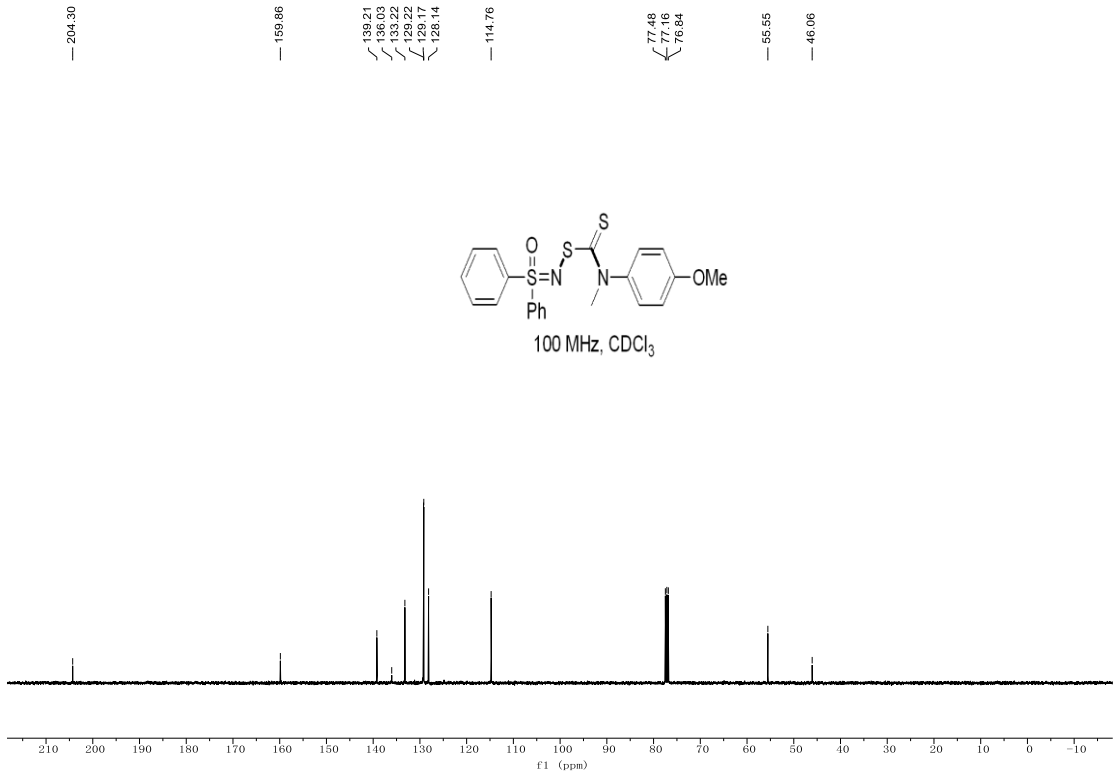
3aj-^{13}C NMR



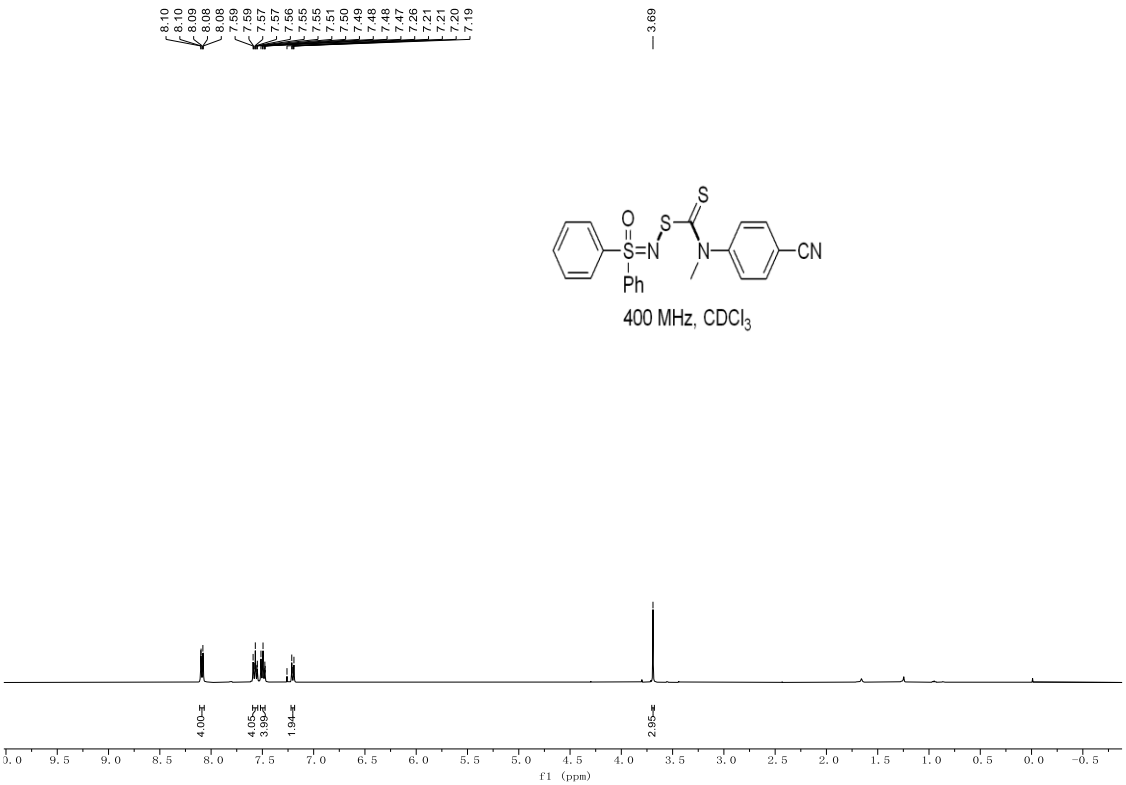
3ak-^{1}H NMR



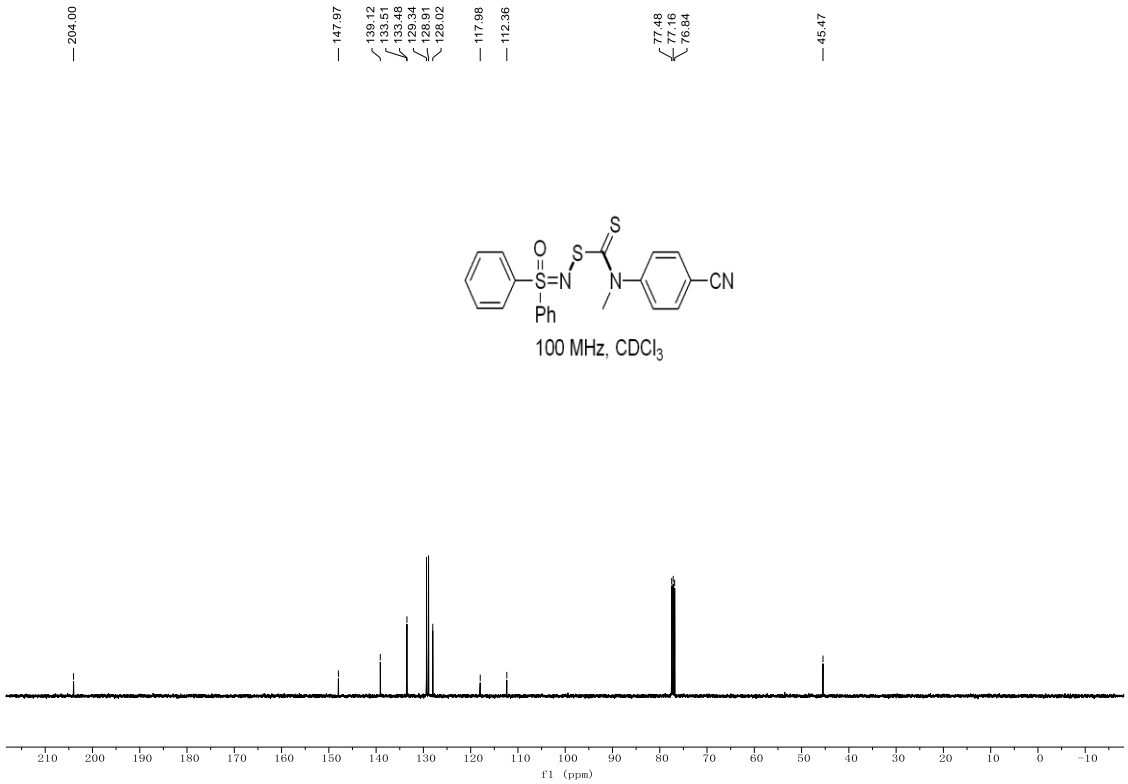
3ak-^{13}C NMR



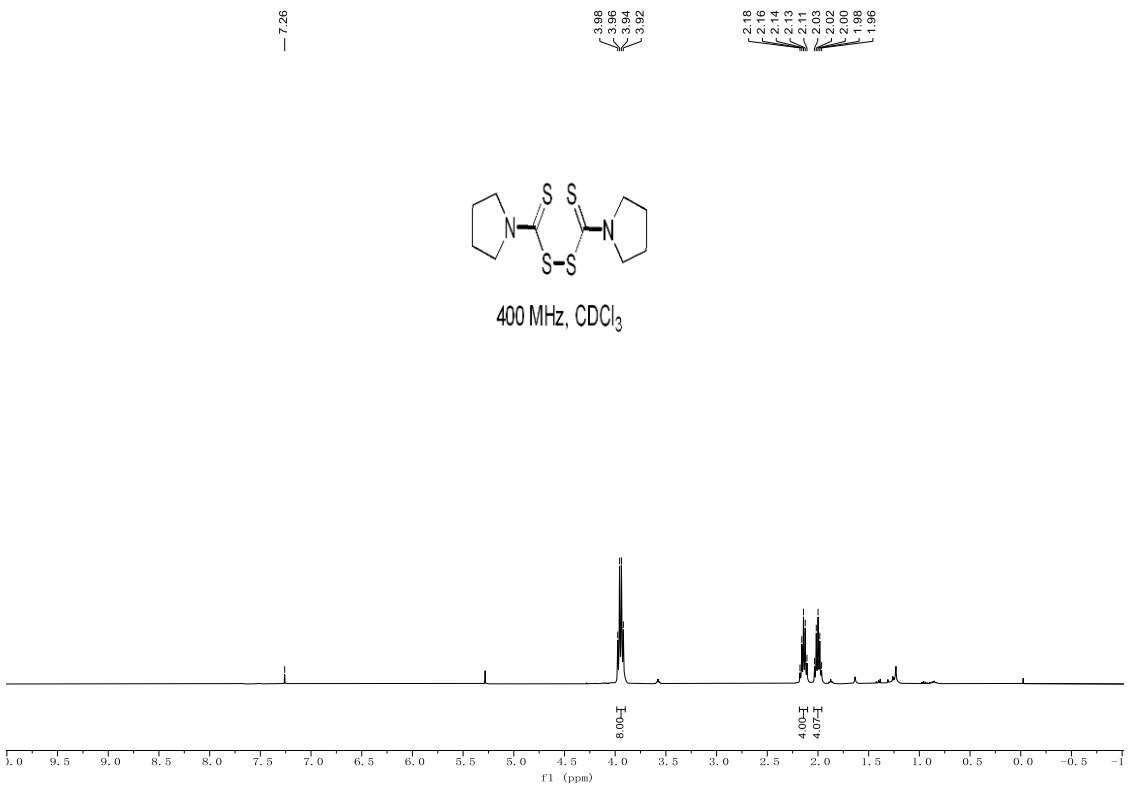
3al-^{1}H NMR



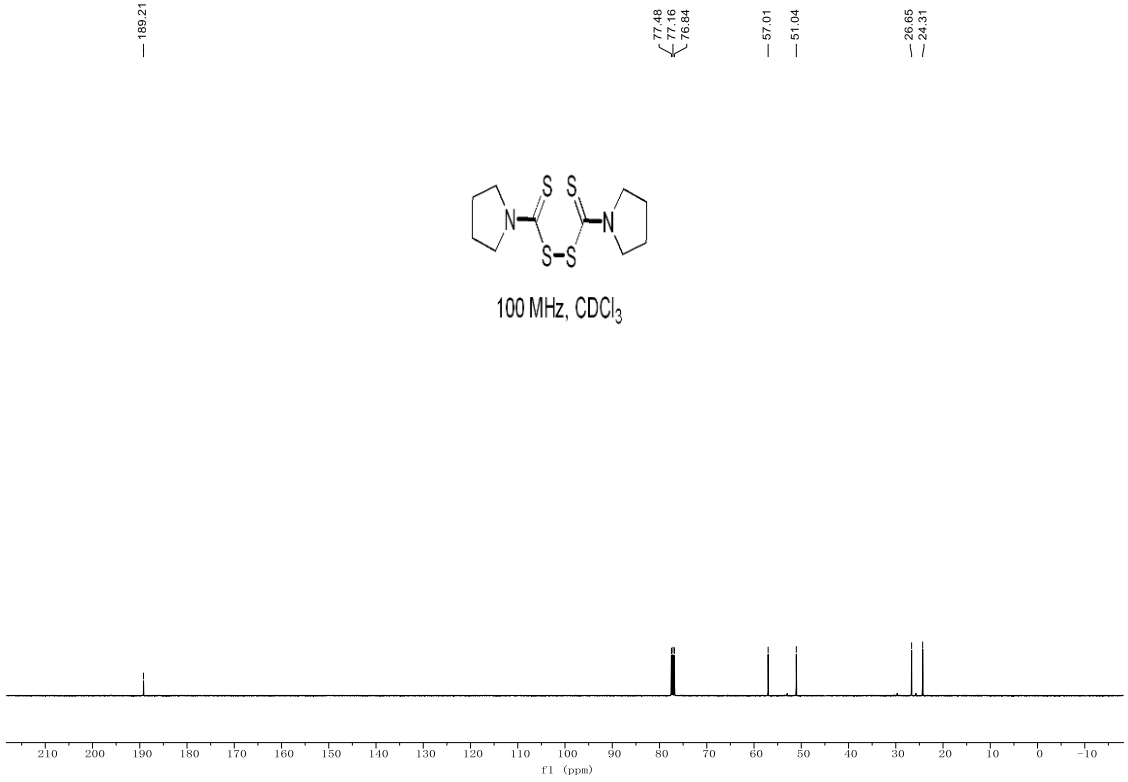
3al-^{13}C NMR



4-^{1}H NMR



4-^{13}C NMR


189.21
77.48
77.16
76.84
57.01
51.04
26.65
24.31
S
S
N
N
S
S
100 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

Crystal data and refinement results

A single crystal for X-ray analysis of **3aa** was obtained by recrystallation from CH_2Cl_2.

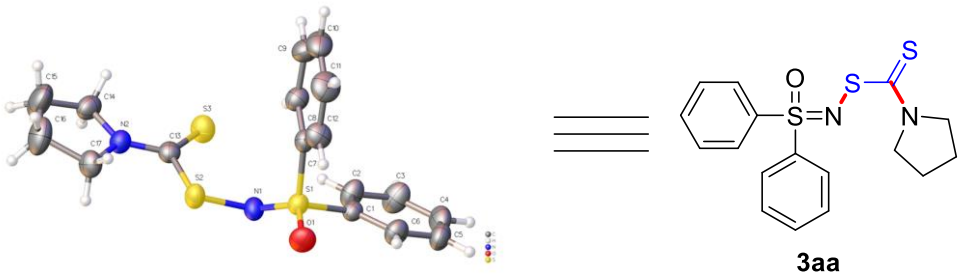


Figure S3. Crystal structure of **3aa (CCDC: 2367753)**

Table S1 Crystal data and structure refinement for 3aa.

Identification code	**3aa**
Empirical formula	$C_{17}H_{18}N_2OS_3$
Formula weight	362.51
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	Pbca
a/Å	15.7490(13)
b/Å	17.8448(12)
c/Å	25.1694(15)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	7073.6(9)
Z	16
ρ_{calc}g/cm^3	1.362
μ/mm^{-1}	0.424
F(000)	3040.0
Crystal size/mm^3	0.18 × 0.14 × 0.08
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.73 to 49.998
Index ranges	-18 ≤ h ≤ 18, -21 ≤ k ≤ 20, -29 ≤ l ≤ 29
Reflections collected	27330
Independent reflections	6220 [R_{int} = 0.0551, R_{sigma} = 0.0567]

Data/restraints/parameters	6220/0/415
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0493, wR_2 = 0.0975
Final R indexes [all data]	R_1 = 0.0846, wR_2 = 0.1133
Largest diff. peak/hole / e $Å^{-3}$	0.30/-0.27

Table S2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$×10^3) for 3aa. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C1	1836.2(19)	1206.0(16)	4272.6(11)	30.4(7)
C2	1718(2)	1172.6(18)	3732.1(12)	45.8(9)
C3	1814(3)	493.4(19)	3477.6(13)	55.2(10)
C4	2023(2)	-142.1(18)	3762.8(14)	49.9(9)
C5	2136(2)	-101.7(18)	4300.4(14)	48.9(9)
C6	2053(2)	577.2(18)	4559.8(12)	43.2(9)
C7	2803(2)	2473.5(16)	4556.9(11)	33.1(7)
C8	3074(2)	2731.7(17)	4069.0(12)	41.2(8)
C9	3895(2)	2993.2(19)	4019.4(15)	52.5(9)
C10	4428(2)	3007(2)	4454.0(17)	58.4(10)
C11	4144(3)	2753(2)	4937.3(16)	61.4(11)
C12	3329(2)	2479(2)	4995.1(13)	47.9(9)
C13	1001(2)	3861.3(17)	3829.1(11)	35.1(8)
C14	785(2)	5104.7(17)	3423.3(13)	47.2(9)
C15	693(3)	5866(2)	3680.3(16)	78.8(14)
C16	529(3)	5775(2)	4239.5(16)	73.2(13)
C17	580(2)	4956.7(17)	4377.4(12)	45.8(9)
C18	1864(2)	3819.2(17)	6432.5(12)	35.7(8)
C19	1830(2)	3175.5(18)	6131.7(13)	44.3(9)
C20	1745(2)	2491.2(19)	6386.2(14)	55.0(10)
C21	1708(3)	2459(2)	6926.5(15)	61.9(11)
C22	1737(3)	3105(2)	7221.1(15)	78.7(15)
C23	1805(3)	3792.7(19)	6976.9(13)	63.9(12)

C24	3051(2)	4984.8(18)	6241.8(13)	41.3(8)
C25	3666(2)	4883(2)	5854.8(14)	57.0(10)
C26	4500(3)	5111(2)	5966.7(18)	68.5(12)
C27	4686(3)	5413(2)	6453(2)	69.5(12)
C28	4077(3)	5502(2)	6831.9(17)	61.4(11)
C29	3247(2)	5296.6(18)	6727.4(14)	46.5(9)
C30	1209(2)	6447.3(18)	6956.3(12)	40.3(8)
C31	847(2)	7638.7(18)	6501.0(13)	47.8(9)
C32	479(4)	8328(2)	6738.6(18)	89.1(16)
C33	681(4)	8363(2)	7283.3(18)	115(2)
C34	862(3)	7580(2)	7465.8(14)	68.2(12)
N1	1086.6(16)	2487.8(14)	4282.0(10)	37.2(6)
N2	813.5(17)	4585.4(14)	3877.3(9)	37.4(6)
N3	1323.2(17)	5170.0(14)	6407.5(11)	44.8(7)
N4	1014.4(18)	7168.4(14)	6970.6(10)	41.7(7)
O1	1629.4(15)	1920.5(12)	5171.6(8)	47.2(6)
O2	1925.2(16)	4586.6(13)	5539.6(8)	53.6(7)
S1	1764.9(5)	2070.1(4)	4613.0(3)	33.2(2)
S2	951.9(6)	3399.2(5)	4458.4(3)	40.3(2)
S3	1231.1(6)	3429.5(5)	3262.6(3)	47.1(2)
S4	1985.3(5)	4695.3(5)	6108.2(3)	38.1(2)
S5	1318.9(6)	6103.3(5)	6296.8(3)	44.4(2)
S6	1321.7(8)	5913.6(6)	7493.4(4)	64.5(3)

Table S3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 3aa. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	29.3(17)	29.3(16)	32.5(17)	1.1(13)	-3.6(14)	-2.2(15)
C2	64(2)	36.1(19)	36.8(19)	1.1(15)	-10.2(17)	0.5(19)
C3	84(3)	45(2)	36.6(19)	-7.8(16)	-7.0(19)	-5(2)
C4	52(2)	31.9(19)	66(2)	-12.4(17)	-1.4(19)	-1.4(18)
C5	53(2)	32.4(19)	61(2)	4.6(16)	-4.7(19)	3.3(18)

C6	54(2)	39.9(19)	36.3(18)	5.2(15)	-5.2(16)	0.4(18)
C7	35.5(18)	28.4(16)	35.4(18)	-2.8(14)	-2.1(14)	3.5(15)
C8	44(2)	38.3(19)	41.1(19)	1.0(15)	-4.8(16)	-2.4(17)
C9	52(2)	46(2)	59(2)	4.0(18)	8(2)	-8(2)
C10	38(2)	50(2)	87(3)	-3(2)	-8(2)	-6(2)
C11	50(2)	69(3)	66(3)	1(2)	-22(2)	0(2)
C12	47(2)	55(2)	42(2)	1.9(17)	-7.2(17)	2(2)
C13	31.5(18)	34.9(18)	38.9(18)	-1.5(14)	-3.3(14)	-2.6(16)
C14	47(2)	44(2)	50(2)	11.9(16)	-4.4(17)	-1.7(18)
C15	112(4)	37(2)	87(3)	8(2)	13(3)	5(3)
C16	100(4)	40(2)	80(3)	-10(2)	-17(3)	12(2)
C17	54(2)	40.3(19)	43.3(19)	-10.2(15)	-0.9(17)	3.6(18)
C18	35.6(19)	34.8(17)	36.8(18)	-1.6(14)	1.4(15)	-1.1(16)
C19	54(2)	40.0(19)	39.2(18)	-4.9(15)	-1.3(17)	2.3(18)
C20	78(3)	36(2)	51(2)	-10.7(17)	2(2)	1(2)
C21	88(3)	36(2)	62(2)	4.4(18)	16(2)	-8(2)
C22	142(5)	53(2)	42(2)	3.1(18)	22(3)	-15(3)
C23	111(4)	39(2)	42(2)	-9.4(17)	12(2)	-14(2)
C24	41(2)	36.2(18)	47(2)	12.5(15)	0.5(17)	1.5(17)
C25	54(2)	67(3)	49(2)	18.1(19)	6(2)	3(2)
C26	43(2)	77(3)	85(3)	32(2)	18(2)	3(2)
C27	47(3)	54(3)	107(4)	22(3)	-12(3)	-12(2)
C28	56(3)	43(2)	86(3)	0(2)	-21(2)	1(2)
C29	40(2)	41(2)	58(2)	-2.3(17)	-7.8(18)	2.0(18)
C30	41(2)	40(2)	39.7(18)	3.3(14)	-0.7(16)	0.2(17)
C31	54(2)	41(2)	49(2)	13.3(16)	2.5(18)	2.7(19)
C32	131(5)	46(3)	90(3)	0(2)	-15(3)	31(3)
C33	204(7)	57(3)	85(4)	-6(3)	16(4)	34(4)
C34	97(3)	57(2)	51(2)	-6.3(19)	4(2)	13(3)
N1	35.3(16)	31.4(14)	44.9(15)	-2.2(12)	-2.1(12)	3.1(13)
N2	41.3(16)	33.0(15)	37.9(15)	-1.0(12)	-1.5(13)	0.9(13)
N3	37.5(16)	33.9(15)	63.0(18)	-0.8(13)	1.5(15)	0.6(14)
N4	49.7(18)	36.0(16)	39.3(15)	4.4(12)	0.1(13)	-0.7(14)

O1	61.4(16)	50.9(14)	29.5(11)	-0.7(10)	9.0(11)	0.4(13)
O2	68.1(17)	59.8(15)	33.0(12)	3.7(11)	-7.0(12)	-5.0(14)
S1	38.2(5)	31.1(4)	30.4(4)	-0.9(3)	0.6(4)	0.5(4)
S2	50.1(5)	33.4(4)	37.5(4)	-1.6(4)	4.4(4)	7.4(4)
S3	58.7(6)	45.7(5)	37.0(5)	-7.3(4)	0.9(4)	5.2(5)
S4	38.3(5)	38.3(5)	37.8(5)	2.6(4)	-3.0(4)	-1.6(4)
S5	53.6(6)	38.2(5)	41.5(5)	4.2(4)	-5.8(4)	5.0(5)
S6	91.1(9)	58.4(6)	44.1(5)	18.3(4)	5.9(5)	20.1(6)

Table S4 Bond Lengths for 3aa.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.374(4)	C19	C20	1.385(4)
C1	C6	1.378(4)	C20	C21	1.362(5)
C1	S1	1.768(3)	C21	C22	1.373(5)
C2	C3	1.379(4)	C22	C23	1.376(5)
C3	C4	1.382(5)	C24	C25	1.385(5)
C4	C5	1.367(4)	C24	C29	1.378(4)
C5	C6	1.382(4)	C24	S4	1.788(3)
C7	C8	1.379(4)	C25	C26	1.404(5)
C7	C12	1.379(4)	C26	C27	1.369(5)
C7	S1	1.793(3)	C27	C28	1.362(5)
C8	C9	1.380(5)	C28	C29	1.382(5)
C9	C10	1.379(5)	C30	N4	1.323(4)
C10	C11	1.373(5)	C30	S5	1.778(3)
C11	C12	1.381(5)	C30	S6	1.663(3)
C13	N2	1.331(4)	C31	C32	1.486(5)
C13	S2	1.787(3)	C31	N4	1.473(4)
C13	S3	1.661(3)	C32	C33	1.409(5)
C14	C15	1.512(5)	C33	C34	1.498(5)
C14	N2	1.472(4)	C34	N4	1.466(4)
C15	C16	1.440(5)	N1	S1	1.546(3)
C16	C17	1.503(5)	N1	S2	1.699(3)

C17	N2	1.469(4)	N3	S4	1.540(3)
C18	C19	1.377(4)	N3	S5	1.689(3)
C18	C23	1.374(4)	O1	S1	1.447(2)
C18	S4	1.774(3)	O2	S4	1.447(2)

Table S5 Bond Angles for 3aa.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C2	C1	C6	121.2(3)	C24	C25	C26	118.4(4)
C2	C1	S1	120.6(2)	C27	C26	C25	119.6(4)
C6	C1	S1	118.2(2)	C28	C27	C26	121.4(4)
C1	C2	C3	118.9(3)	C27	C28	C29	120.1(4)
C2	C3	C4	120.4(3)	C24	C29	C28	119.2(4)
C5	C4	C3	120.1(3)	N4	C30	S5	112.6(2)
C4	C5	C6	120.1(3)	N4	C30	S6	124.0(2)
C1	C6	C5	119.3(3)	S6	C30	S5	123.4(2)
C8	C7	S1	119.1(2)	N4	C31	C32	102.6(3)
C12	C7	C8	121.7(3)	C33	C32	C31	109.9(4)
C12	C7	S1	119.1(2)	C32	C33	C34	107.5(4)
C7	C8	C9	118.9(3)	N4	C34	C33	103.7(3)
C10	C9	C8	120.3(3)	S1	N1	S2	114.00(15)
C11	C10	C9	119.9(4)	C13	N2	C14	123.2(2)
C10	C11	C12	120.9(3)	C13	N2	C17	124.9(2)
C7	C12	C11	118.4(3)	C17	N2	C14	111.9(2)
N2	C13	S2	111.0(2)	S4	N3	S5	117.67(17)
N2	C13	S3	125.2(2)	C30	N4	C31	125.0(3)
S3	C13	S2	123.80(19)	C30	N4	C34	123.2(3)
N2	C14	C15	103.7(3)	C34	N4	C31	111.6(3)
C16	C15	C14	109.5(3)	C1	S1	C7	104.72(14)
C15	C16	C17	109.0(3)	N1	S1	C1	101.72(14)
N2	C17	C16	104.7(3)	N1	S1	C7	113.22(14)
C19	C18	S4	119.1(2)	O1	S1	C1	108.63(13)
C23	C18	C19	121.1(3)	O1	S1	C7	106.58(14)

C23	C18	S4	119.8(2)	O1	S1	N1	120.70(14)
C18	C19	C20	119.0(3)	N1	S2	C13	101.80(13)
C21	C20	C19	120.2(3)	C18	S4	C24	105.61(15)
C20	C21	C22	120.1(3)	N3	S4	C18	100.76(15)
C21	C22	C23	120.7(4)	N3	S4	C24	112.62(15)
C18	C23	C22	118.8(3)	O2	S4	C18	109.27(14)
C25	C24	S4	119.1(3)	O2	S4	C24	106.63(15)
C29	C24	C25	121.3(3)	O2	S4	N3	120.87(15)
C29	C24	S4	119.6(3)	N3	S5	C30	100.76(14)

Table S6 Torsion Angles for 3aa.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
C1	C2	C3	C4	0.3(6)	C25	C24	S4	N3	-150.5(3)
C2	C1	C6	C5	-1.3(5)	C25	C24	S4	O2	-15.7(3)
C2	C1	S1	C7	-85.4(3)	C25	C26	C27	C28	-0.2(6)
C2	C1	S1	N1	32.7(3)	C26	C27	C28	C29	-1.1(6)
C2	C1	S1	O1	161.0(3)	C27	C28	C29	C24	1.6(5)
C2	C3	C4	C5	-0.1(6)	C29	C24	C25	C26	-0.4(5)
C3	C4	C5	C6	-0.8(6)	C29	C24	S4	C18	-78.9(3)
C4	C5	C6	C1	1.4(5)	C29	C24	S4	N3	30.1(3)
C6	C1	C2	C3	0.4(5)	C29	C24	S4	O2	164.9(3)
C6	C1	S1	C7	91.5(3)	C31	C32	C33	C34	-23.1(7)
C6	C1	S1	N1	-150.4(3)	C32	C31	N4	C30	167.7(4)
C6	C1	S1	O1	-22.1(3)	C32	C31	N4	C34	-7.0(4)
C7	C8	C9	C10	-1.1(5)	C32	C33	C34	N4	17.5(6)
C8	C7	C12	C11	0.2(5)	C33	C34	N4	C30	179.2(4)
C8	C7	S1	C1	70.4(3)	C33	C34	N4	C31	-6.0(5)
C8	C7	S1	N1	-39.5(3)	N2	C13	S2	N1	173.1(2)
C8	C7	S1	O1	-174.6(2)	N2	C14	C15	C16	-9.5(5)
C8	C9	C10	C11	0.6(6)	N4	C30	S5	N3	-167.0(3)
C9	C10	C11	C12	0.3(6)	N4	C31	C32	C33	18.5(5)
C10	C11	C12	C7	-0.7(6)	S1	C1	C2	C3	177.3(3)

C12	C7	C8	C9	0.7(5)	S1	C1	C6	C5	-178.2(3)
C12	C7	S1	C1	-105.9(3)	S1	C7	C8	C9	-175.5(3)
C12	C7	S1	N1	144.1(3)	S1	C7	C12	C11	176.4(3)
C12	C7	S1	O1	9.1(3)	S1	N1	S2	C13	131.01(17)
C14	C15	C16	C17	4.6(6)	S2	C13	N2	C14	-178.7(2)
C15	C14	N2	C13	-171.0(3)	S2	C13	N2	C17	-1.2(4)
C15	C14	N2	C17	11.1(4)	S2	N1	S1	C1	-172.55(15)
C15	C16	C17	N2	2.2(5)	S2	N1	S1	C7	-60.75(19)
C16	C17	N2	C13	173.7(3)	S2	N1	S1	O1	67.3(2)
C16	C17	N2	C14	-8.6(4)	S3	C13	N2	C14	0.1(5)
C18	C19	C20	C21	-1.0(6)	S3	C13	N2	C17	177.6(3)
C19	C18	C23	C22	2.1(6)	S3	C13	S2	N1	-5.7(2)
C19	C18	S4	C24	-107.3(3)	S4	C18	C19	C20	179.3(3)
C19	C18	S4	N3	135.4(3)	S4	C18	C23	C22	-178.0(4)
C19	C18	S4	O2	7.1(3)	S4	C24	C25	C26	-179.7(3)
C19	C20	C21	C22	1.4(7)	S4	C24	C29	C28	178.4(3)
C20	C21	C22	C23	-0.1(8)	S4	N3	S5	C30	-135.98(19)
C21	C22	C23	C18	-1.6(7)	S5	C30	N4	C31	3.9(4)
C23	C18	C19	C20	-0.8(6)	S5	C30	N4	C34	178.0(3)
C23	C18	S4	C24	72.8(3)	S5	N3	S4	C18	170.44(17)
C23	C18	S4	N3	-44.6(3)	S5	N3	S4	C24	58.4(2)
C23	C18	S4	O2	-172.8(3)	S5	N3	S4	O2	-69.2(2)
C24	C25	C26	C27	0.9(6)	S6	C30	N4	C31	-175.1(3)
C25	C24	C29	C28	-0.9(5)	S6	C30	N4	C34	-0.9(5)
C25	C24	S4	C18	100.5(3)	S6	C30	S5	N3	12.0(3)

Table S7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3aa.

Atom	*x*	*y*	*z*	U(eq)
H2	1575	1601	3541	55
H3	1739	463	3112	66
H4	2086	-598	3589	60
H5	2270	-531	4492	59

H6	2142	609	4924	52
H8	2709	2730	3778	49
H9	4089	3161	3691	63
H10	4979	3188	4420	70
H11	4504	2766	5230	74
H12	3139	2302	5322	58
H14A	305	4996	3194	57
H14B	1304	5076	3216	57
H15A	1210	6154	3630	95
H15B	228	6138	3516	95
H16A	-31	5967	4325	88
H16B	944	6054	4444	88
H17A	1007	4869	4648	55
H17B	37	4775	4506	55
H19	1864	3200	5763	53
H20	1713	2053	6188	66
H21	1664	1997	7096	74
H22	1711	3079	7590	94
H23	1810	4231	7177	77
H25	3529	4670	5529	68
H26	4924	5056	5712	82
H27	5240	5561	6526	83
H28	4220	5701	7162	74
H29	2827	5368	6982	56
H31A	448	7399	6262	57
H31B	1367	7748	6310	57
H32A	703	8766	6558	107
H32B	-133	8325	6694	107
H33A	209	8571	7482	138
H33B	1175	8679	7338	138
H34A	1359	7566	7694	82
H34B	382	7373	7657	82

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) exp_14482_auto

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FORPUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: exp_14482_auto

Bond precision:	C-C = 0.0051 A	Wavelength=0.71073	
Cell:	a=15.7490(13)	b=17.8448(12)	c=25.1694(15)
	alpha=90	beta=90	gamma=90
Temperature:	293 K		

	Calculated	Reported
Volume Space	7073.6(9)	7073.6(9)
groupHall group	P b c a	P b c a
Moiety formula	-P 2ac 2abC17 H18 N2 O S3	-P 2ac 2ab C17 H18 N2 O S3
Sum formula	C17 H18 N2 O S3	C17 H18 N2 O S3
Mr	362.51	362.51
Dx,g cm-3	1.362	1.362
Z	16	16
Mu (mm-1)	0.424	0.424
F000	3040.0	3040.0
F000’	3046.83	
h,k,lmax	18,21,29	18,21,29
Nref	6226	6220
Tmin,Tmax	0.931,0.967	0.901,1.000

Tmin’ 0.927

Correction method= # Reported T Limits: Tmin=0.901 Tmax=1.000AbsCorr = MULTI-SCAN

Data completeness= 0.999 Theta(max)= 24.999

R(reflections)= 0.0493(4296) wR2(reflections)= 0.1133(6220)

S = 1.025 Npar= 415

The following ALERTS were generated. Each ALERT has the format

test-name_ALERT_alert-type_alert-level.

Click on the hyperlinks for more details of the test.

Alert level A

PLAT902_ALERT_1_A No (Interpretable) Reflections Found in FCF .... Please Check

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Alert level C

PLAT220_ALERT_2_C NonSolvent Resd 2 C Ueq(max)/Ueq(min) Range 3.2 Ratio

PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C15 Check

PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C22 Check

PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C33 Check

PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of C31 Check

PLAT340_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.00513 Ang. PLAT360_ALERT_2_C Short C(sp3)-C(sp3) Bond C32 - C33 . 1.41 Ang.

Alert level G

PLAT012_ALERT_1_G No _shelx_res_checksum Found in CIF ..... Please Check

PLAT199_ALERT_1_G Reported _cell_measurement_temperature ..... (K) 293 Check

PLAT200_ALERT_1_G Reported _diffrn_ambient_temperature ..... (K) 293 Check

PLAT967_ALERT_5_G Note: Two-Theta Cutoff Value in Embedded .res .. 50.0 Degree

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1 **ALERT level A** = Most likely a serious problem - resolve or explain

0 **ALERT level B** = A potentially serious problem, consider carefully

7 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight

4 **ALERT level G** = General information/check it is not something unexpected

4 ALERT type 1 CIF construction/syntax error, inconsistent or missing data

6 ALERT type 2 Indicator that the structure model may be wrong or deficient

1 ALERT type 3 Indicator that the structure quality may be low

0 ALERT type 4 Improvement, methodology, query or suggestion

1 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problemsit may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needingattention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks arerun on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

Validation response form

Please find below a validation response form (VRF) that can be filled in and pasted into your CIF.

start Validation Reply Form
_vrf_PLAT902_exp_14482_auto
;
PROBLEM: No (Interpretable) Reflections Found in FCF .... Please Check

RESPONSE: ...

;

_vrf_PLAT220_exp_14482_auto

;

PROBLEM: NonSolvent Resd 2 C Ueq(max)/Ueq(min) Range 3.2 Ratio

RESPONSE: ...

;

_vrf_PLAT241_exp_14482_auto

;

PROBLEM: High 'MainMol' Ueq as Compared to Neighbors of C15 Check

RESPONSE: ...

;

_vrf_PLAT242_exp_14482_auto

;

PROBLEM: Low 'MainMol' Ueq as Compared to Neighbors of C31 Check

RESPONSE: ...

;

_vrf_PLAT340_exp_14482_auto

;

PROBLEM: Low Bond Precision on C-C Bonds ..... 0.00513 Ang.

RESPONSE: ...

;

_vrf_PLAT360_exp_14482_auto

;

PROBLEM: Short C(sp3)-C(sp3) Bond C32 - C33 . 1.41 Ang.

RESPONSE: ...

;

end Validation Reply Form

PLATON version of 13/05/2024; check.def file version of 04/05/2024

Datablock exp_14482_auto - ellipsoid plot