

Supporting Information

Ts₂O Mediated Deoxygenative C2-dithiocarbamation of Quinoline *N*- oxides with CS₂ and Amines

Long-Yong Xie*, Chu Liu#, Si-Yu Wang#, Zhong-Ying Tian, and Sha Peng*

College of Chemistry and Bioengineering, Hunan University of Science and Engineering, Yongzhou

425100, China

longyongxie@yeah.net

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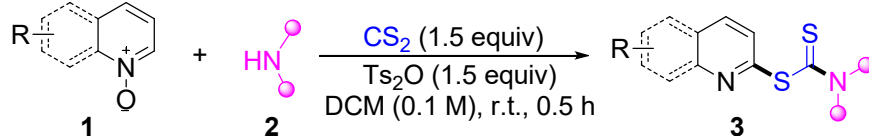
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1. General information

Unless otherwise noted, all solvents and reagents in this study were commercial and used without further purification. ^1H , ^{13}C and ^{19}F NMR spectra were recorded at 400, 100 and 376 MHz, respectively. Chemical shifts were quoted in ppm relative to CDCl_3 ($\delta_{\text{H}} = 7.26$, $\delta_{\text{C}} = 77.0$ ppm). Datas are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, etc. Azine *N*-oxides **1a**, **1t**, **1u**, **1v**, **1w** and **1y** are commercially available and other quinoline *N*-oxides were prepared according to the relevant literatures. The reactions were monitored by thin-layer chromatography (TLC) using GF254 silica gel-coated TLC plates. Mass spectra were performed on a spectrometer operating on ESI-TOF. Melting points were measured on a melting point apparatus and were uncorrected.

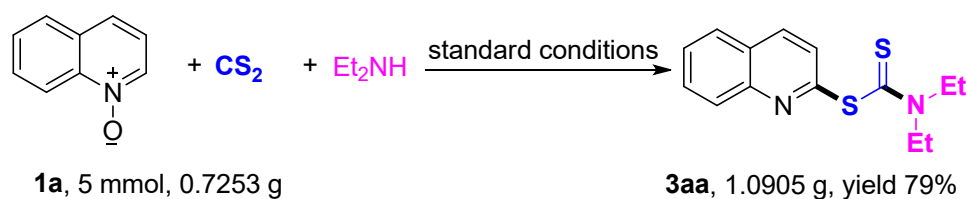
2. Experimental Section

General procedure for the synthesis of quinoline-dithiocarbamates **3**



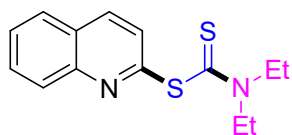
To a round bottom flask was consecutively added quinoline *N*-oxide **1** (0.3 mmol), CS_2 (0.45 mmol), amine **2** (0.45 mmol) and Ts_2O (0.45 mmol) in CH_2Cl_2 (3 mL). The reaction mixture was stirred at room temperature for about 0.5 h. The reaction was monitored by TLC. Upon completion, CH_2Cl_2 (10 mL) and water (10 mL) were added to the mixture, the organic layer was separated and the aqueous layer was further extracted with CH_2Cl_2 (2×10 mL). The organic phases were combined and dried with anhydrous Na_2SO_4 , followed by filtration and concentration under vacuo. The residue was purified by flash chromatography column over silica gel to afford the desired products **3**.

Procedure for gram-scale Synthesis of **3aa**

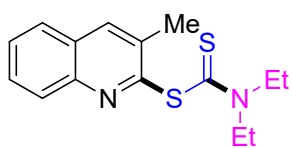


To a round bottom flask was consecutively added quinoline *N*-oxide **1a** (5 mmol, 0.7253 g), CS₂ (7.5 mmol, 0.5696 g), diethylamine **2a** (7.5 mmol, 0.5482 g) and Ts₂O (7.5 mmol, 2.4452 g) in CH₂Cl₂ (50 mL). The reaction mixture was stirred at room temperature for about 0.5 h. Upon completion, water (30 mL) was added to quench the reaction. The organic layer was separated and the aqueous layer was further extracted with CH₂Cl₂ (2 × 20 mL). The organic phases were combined and dried with anhydrous Na₂SO₄, followed by filtration and concentration under vacuo. The residue was purified by flash chromatography column over silica gel to afford 1.0905 g of **3aa**, yield: 79%.

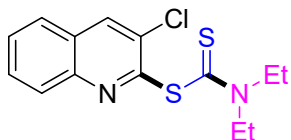
3. Characterization data of products



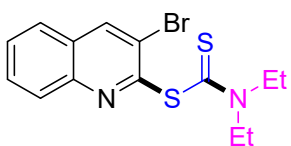
quinolin-2-yl diethylcarbamodithioate (3aa): Yellow solid (68.2 mg, 82%), mp: 118–119 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 8.4 Hz, 2H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.70 (t, *J* = 8.6 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 3.99 (q, *J* = 6.8 Hz, 2H), 3.83 (q, *J* = 6.8 Hz, 2H), 1.39 (t, *J* = 6.9 Hz, 3H), 1.26 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 192.8, 153.9, 148.2, 136.2, 129.6, 129.5, 129.3, 127.5, 127.4, 127.3, 49.1, 47.7, 12.7, 11.4; HRMS (ESI) *m/z* calcd. for C₁₄H₁₇N₂S₂ [M+H]⁺ : 277.0828, found 277.0829.



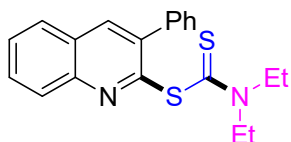
3-methylquinolin-2-yl diethylcarbamodithioate (3ba): Yellow solid (62.9 mg, 72%), mp: 122–123 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 8.5 Hz, 1H), 8.01 (s, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 4.00 (q, *J* = 7.0 Hz, 2H), 3.86 (q, *J* = 7.0 Hz, 2H), 2.60 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 192.0, 154.2, 147.1, 136.9, 136.1, 129.4, 128.8, 128.5, 127.6, 126.7, 48.9, 47.8, 20.5, 12.8, 11.5; HRMS (ESI) *m/z* calcd. for C₁₅H₁₉N₂S₂ [M+H]⁺ : 291.0984, found 291.0986.



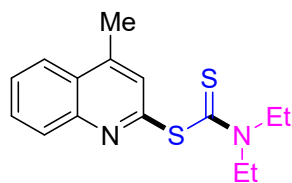
3-chloroquinolin-2-yl diethylcarbamodithioate (3ca): Yellow solid (63.2 mg, 68%), mp: 112–114 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.24 (s, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 7.81 – 7.68 (m, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 4.02 (q, *J* = 6.7 Hz, 2H), 3.87 (q, *J* = 6.7 Hz, 2H), 1.44 (t, *J* = 6.9 Hz, 3H), 1.30 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 190.7, 152.1, 146.5, 136.1, 133.4, 129.9, 129.6, 128.6, 128.5, 126.6, 49.1, 48.2, 12.9, 11.5; HRMS (ESI) *m/z* calcd. for C₁₄H₁₆ClN₂S₂ [M+H]⁺ : 311.0438, found 311.0440.



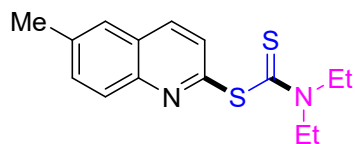
3-bromoquinolin-2-yl diethylcarbamodithioate (3da): Yellow solid (67.1 mg, 63%), mp: 116–117 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.44 (s, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 7.82 – 7.72 (m, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 4.04 (q, *J* = 7.0 Hz, 2H), 3.87 (q, *J* = 7.1 Hz, 2H), 1.45 (t, *J* = 7.1 Hz, 3H), 1.32 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 190.9, 153.4, 147.0, 139.9, 130.1, 129.7, 128.7, 128.6, 126.6, 124.1, 49.1, 48.3, 13.0, 11.5; HRMS (ESI) *m/z* calcd. for C₁₄H₁₆BrN₂S₂ [M+H]⁺ : 354.9933, found 354.9937.



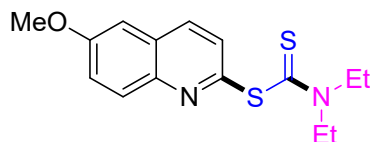
3-phenylquinolin-2-yl diethylcarbamodithioate (3ea): Yellow solid (81.3 mg, 77%), mp: 124–125 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.22 (d, *J* = 8.5 Hz, 1H), 8.10 (s, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.61 – 7.52 (m, 3H), 7.41 – 7.34 (m, 3H), 3.84 (q, *J* = 6.8 Hz, 2H), 3.60 (q, *J* = 6.9 Hz, 2H), 1.17 (t, *J* = 7.0 Hz, 3H), 1.09 (t, *J* = 6.9 Hz, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 192.0, 153.1, 147.5, 139.8, 139.0, 137.6, 129.8, 129.6, 129.4, 127.8, 127.5, 127.4, 127.4, 48.7, 47.8, 12.6, 11.3; HRMS (ESI) *m/z* calcd. for C₂₀H₂₁N₂S₂ [M+H]⁺ : 353.1141, found 353.1146.



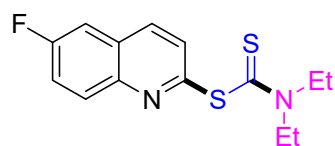
4-methylquinolin-2-yl diethylcarbamodithioate (3fa): Yellow solid (59.4 mg, 68%), mp: 116–117 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 8.3 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.64 – 7.54 (m, 2H), 4.02 (q, *J* = 6.6 Hz, 2H), 3.86 (q, *J* = 6.7 Hz, 2H), 2.71 (s, 3H), 1.41 (t, *J* = 6.9 Hz, 3H), 1.29 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 193.1, 153.6, 148.1, 144.8, 130.2, 129.7, 129.4, 127.6, 127.4, 123.7, 49.1, 47.8, 18.6, 12.7, 11.5; HRMS (ESI) *m/z* calcd. for C₁₅H₁₉N₂S₂ [M+H]⁺ : 291.0984, found 291.0986.



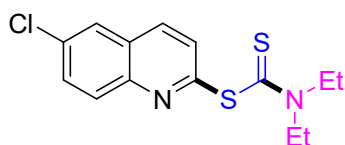
6-methylquinolin-2-yl diethylcarbamodithioate (3ga): Yellow solid (67.2 mg, 77%), mp: 127–128 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.12 – 7.99 (m, 2H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.58 (s, 1H), 7.54 (d, *J* = 8.7 Hz, 1H), 4.01 (q, *J* = 7.0 Hz, 2H), 3.85 (q, *J* = 7.0 Hz, 2H), 2.52 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.28 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 193.2, 152.8, 146.9, 137.7, 135.7, 131.9, 129.4, 129.3, 127.5, 126.4, 49.1, 47.7, 21.6, 12.7, 11.5; HRMS (ESI) *m/z* calcd. for C₁₅H₁₉N₂S₂ [M+H]⁺ : 291.0984, found 291.0987.



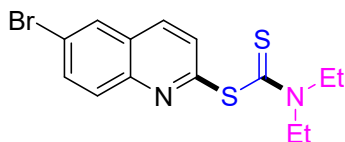
6-methoxyquinolin-2-yl diethylcarbamodithioate (3ha): Yellow solid (77.4 mg, 84%), mp: 121–122 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.05 (t, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.36 (d, *J* = 9.2 Hz, 1H), 7.09 (s, 1H), 4.02 (q, *J* = 6.9 Hz, 2H), 3.94 (s, 3H), 3.87 (q, *J* = 7.0 Hz, 2H), 1.43 (t, *J* = 7.0 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 193.7, 158.7, 150.9, 144.6, 135.2, 131.2, 130.0, 128.8, 122.5, 105.1, 55.6, 49.3, 47.7, 12.8, 11.5; HRMS (ESI) *m/z* calcd. for C₁₅H₁₉N₂OS₂ [M+H]⁺ : 307.0933, found 307.0933.



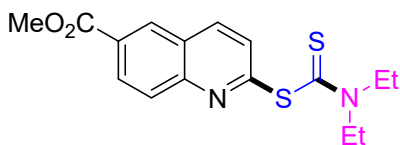
6-fluoroquinolin-2-yl diethylcarbamdithioate (3ia): Yellow solid (69.0 mg, 78%), mp: 101–102 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.22 – 8.06 (m, 2H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.55 – 7.39 (m, 2H), 4.02 (q, *J* = 7.0 Hz, 2H), 3.86 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H), 1.29 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 192.8, 161.1 (d, *J*_{C-F} = 248.4 Hz), 153.3 (d, *J*_{C-F} = 3.0 Hz), 145.4, 135.6 (d, *J*_{C-F} = 5.4 Hz), 132.2 (d, *J*_{C-F} = 9.2 Hz), 130.3, 128.3 (d, *J*_{C-F} = 10.2 Hz), 119.9 (d, *J*_{C-F} = 25.6 Hz), 110.7 (d, *J*_{C-F} = 21.8 Hz), 49.3, 47.9, 12.8, 11.5; ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -111.29; HRMS (ESI) *m/z* calcd. for C₁₄H₁₆FN₂S₂ [M+H]⁺ : 295.0733, found 295.0735.



6-chloroquinolin-2-yl diethylcarbamdithioate (3ja): Yellow solid (70.9 mg, 76%), mp: 122–123 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.11 – 8.00 (m, 2H), 7.80 (s, 1H), 7.73 (d, *J* = 8.6 Hz, 1H), 7.64 (d, *J* = 8.7 Hz, 1H), 4.01 (q, *J* = 6.9 Hz, 2H), 3.85 (q, *J* = 7.0 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.28 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 192.5, 154.4, 146.6, 135.2, 133.4, 131.1, 130.6, 130.3, 128.0, 126.2, 49.2, 47.9, 12.8, 11.5; HRMS (ESI) *m/z* calcd. for C₁₄H₁₆ClN₂S₂ [M+H]⁺ : 311.0438, found 311.0435.

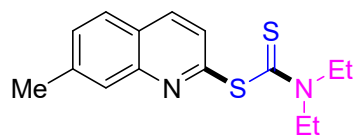


6-bromoquinolin-2-yl diethylcarbamdithioate (3ka): Yellow solid (89.5 mg, 84%), mp: 133–134 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 2H), 7.76 (dd, *J* = 14.2, 8.9 Hz, 2H), 4.01 (q, *J* = 6.9 Hz, 2H), 3.86 (q, *J* = 7.0 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H), 1.29 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 192.4, 154.6, 146.8, 135.1, 133.2, 131.3, 130.3, 129.6, 128.5, 121.7, 49.2, 47.9, 12.8, 11.5; HRMS (ESI) *m/z* calcd. for C₁₄H₁₆BrN₂S₂ [M+H]⁺ : 354.9933, found 354.9938.

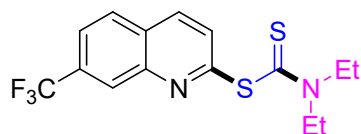


Methyl 2-((diethylcarbamoithiyl)thio)quinoline-6-carboxylate (3la): Yellow solid (63.1 mg, 63%), mp: 132–133 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.60 (s, 1H), 8.34 – 8.23 (m, 2H),

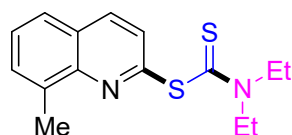
8.19 (dd, $J = 8.8, 3.0$ Hz, 1H), 7.82 (dd, $J = 8.4, 3.1$ Hz, 1H), 4.07 – 3.83 (m, 7H), 1.52 – 1.24 (m, 6H); ^{13}C NMR (100 MHz, Chloroform- d) δ 191.9, 166.4, 156.8, 149.8, 137.4, 130.6, 130.0, 129.7, 129.4, 129.0, 126.6, 52.5, 49.3, 48.1, 12.9, 11.5; HRMS (ESI) m/z calcd. for $\text{C}_{16}\text{H}_{19}\text{N}_2\text{O}_2\text{S}_2$ $[\text{M}+\text{H}]^+$: 335.0882, found 335.0885.



7-methylquinolin-2-yl diethylcarbamodithioate (3ma): Yellow solid (59.4 mg, 68%), mp: 126–127 °C. ^1H NMR (400 MHz, Chloroform- d) δ 8.11 (d, $J = 8.4$ Hz, 1H), 7.92 (s, 1H), 7.72 (d, $J = 8.3$ Hz, 1H), 7.65 (d, $J = 8.4$ Hz, 1H), 7.42 (d, $J = 8.3$ Hz, 1H), 4.02 (q, $J = 6.9$ Hz, 2H), 3.87 (q, $J = 7.0$ Hz, 2H), 2.55 (s, 3H), 1.42 (t, $J = 7.1$ Hz, 3H), 1.29 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, Chloroform- d) δ 193.2, 153.8, 148.6, 140.1, 136.1, 129.9, 128.6, 128.6, 127.2, 125.5, 49.2, 47.8, 21.9, 12.8, 11.5; HRMS (ESI) m/z calcd. for $\text{C}_{15}\text{H}_{19}\text{N}_2\text{S}_2$ $[\text{M}+\text{H}]^+$: 291.0984, found 291.0985.

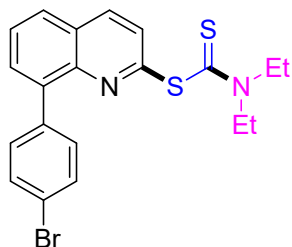


7-(trifluoromethyl)quinolin-2-yl diethylcarbamodithioate (3na): Yellow solid (74.3 mg, 72%), mp: 134–135 °C. ^1H NMR (400 MHz, Chloroform- d) δ 8.43 (s, 1H), 8.18 (d, $J = 8.5$ Hz, 1H), 7.93 (d, $J = 8.5$ Hz, 1H), 7.83 (d, $J = 8.5$ Hz, 1H), 7.73 (d, $J = 8.5$ Hz, 1H), 4.01 (q, $J = 6.9$ Hz, 2H), 3.86 (q, $J = 7.0$ Hz, 2H), 1.42 (t, $J = 7.1$ Hz, 3H), 1.29 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, Chloroform- d) δ 192.0, 156.0, 147.1, 135.9, 131.5, 131.2, 128.8, 128.7, 127.3 (q, $J_{\text{C-F}} = 4.4$ Hz), 123.7 (q, $J_{\text{C-F}} = 270.9$ Hz), 123.2 (q, $J_{\text{C-F}} = 3.0$ Hz), 49.2, 48.0, 12.8, 11.4; ^{19}F NMR (376 MHz, Chloroform- d) δ -62.73; HRMS (ESI) m/z calcd. for $\text{C}_{15}\text{H}_{16}\text{F}_3\text{N}_2\text{S}_2$ $[\text{M}+\text{H}]^+$: 345.0702, found 345.0706.

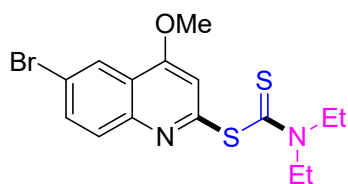


8-methylquinolin-2-yl diethylcarbamodithioate (3oa): Yellow solid (65.5 mg, 75%), mp: 71–72 °C. ^1H NMR (400 MHz, Chloroform- d) δ 8.11 (d, $J = 8.5$ Hz, 1H), 7.72 (d, $J = 8.5$ Hz, 1H), 7.66 (d, $J = 8.0$ Hz, 1H), 7.56 (d, $J = 6.9$ Hz, 1H), 7.46 (t, $J = 7.5$ Hz, 1H), 4.05 (q, $J = 6.9$ Hz, 2H), 3.89 (q, $J = 7.0$ Hz, 2H), 2.81 (s, 3H), 1.44 (t, $J = 7.1$ Hz, 3H), 1.32 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR

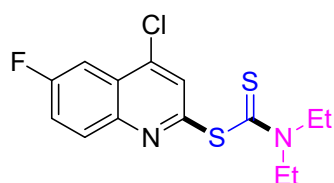
(100 MHz, Chloroform-*d*) δ 193.3, 153.3, 147.5, 137.6, 136.3, 129.8, 128.7, 127.4, 127.3, 125.5, 49.2, 47.9, 18.0, 12.9, 11.6; HRMS (ESI) m/z calcd. for $C_{15}H_{19}N_2S_2$ $[M+H]^+$: 291.0984, found 291.0987.



8-(4-bromophenyl)quinolin-2-yl diethylcarbamodithioate (3pa): Yellow solid (87.9 mg, 68%), mp: 74–75 °C. 1H NMR (400 MHz, Chloroform-*d*) δ 8.17 (d, J = 8.5 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.78 – 7.70 (m, 2H), 7.62 (dt, J = 26.1, 8.2 Hz, 5H), 4.03 (q, J = 6.9 Hz, 2H), 3.84 (q, J = 6.9 Hz, 2H), 1.37 (t, J = 7.0 Hz, 3H), 1.31 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.7, 154.6, 145.5, 139.3, 137.8, 136.4, 132.6, 130.9, 130.3, 128.5, 127.8, 127.6, 127.2, 121.7, 49.1, 48.1, 12.9, 11.5; HRMS (ESI) m/z calcd. for $C_{20}H_{20}BrN_2S_2$ $[M+H]^+$: 431.0246, found 431.0252.

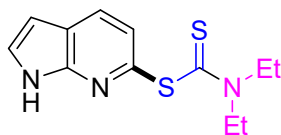


6-bromo-4-methoxyquinolin-2-yl diethylcarbamodithioate (3qa): Yellow solid (83.2 mg, 72%), mp: 124–125 °C. 1H NMR (400 MHz, Chloroform-*d*) δ 8.33 (s, 1H), 7.92 (d, J = 8.9 Hz, 1H), 7.75 (d, J = 9.3 Hz, 1H), 7.15 (s, 1H), 4.08 – 3.97 (m, 5H), 3.85 (q, J = 6.9 Hz, 2H), 1.41 (t, J = 7.0 Hz, 3H), 1.29 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.4, 161.1, 155.3, 147.4, 133.5, 130.8, 124.5, 122.0, 120.8, 109.2, 56.1, 49.2, 47.8, 12.8, 11.5; HRMS (ESI) m/z calcd. for $C_{15}H_{18}BrN_2OS_2$ $[M+H]^+$: 385.0038, found 385.0034.

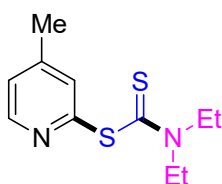


4-chloro-6-fluoroquinolin-2-yl diethylcarbamodithioate (3ra): Yellow solid (63.2 mg, 64%), mp: 126–127 °C. 1H NMR (400 MHz, Chloroform-*d*) δ 8.15 (dd, J = 9.1, 5.3 Hz, 1H), 7.83 (d, J = 8.3 Hz, 2H), 7.52 (t, J = 8.4 Hz, 1H), 4.00 (q, J = 7.1 Hz, 2H), 3.83 (q, J = 7.2 Hz, 2H), 1.41 (t, J =

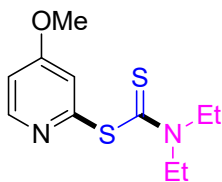
7.1 Hz, 3H), 1.28 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, Chloroform- d) δ 191.9, 161.8 (d, $J_{\text{C-F}} = 249.8$ Hz), 153.0, 145.7, 141.2 (d, $J = 5.7$ Hz), 132.7 (d, $J = 9.2$ Hz), 130.1, 129.7, 120.8 (d, $J = 25.8$ Hz), 108.1 (d, $J = 24.4$ Hz), 49.3, 47.9, 12.8, 11.4; ^{19}F NMR (376 MHz, Chloroform- d) δ -108.76; HRMS (ESI) m/z calcd. for $\text{C}_{14}\text{H}_{15}\text{ClFN}_2\text{S}_2$ $[\text{M}+\text{H}]^+$: 329.0344, found 329.0346.



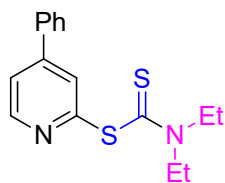
1H-pyrrolo[2,3-b]pyridin-6-yl diethylcarbamodithioate (3sa): Pale yellow solid (62.3 mg, 78%), mp: 174–4175 °C. ^1H NMR (400 MHz, Chloroform- d) δ 11.31 (s, 1H), 8.02 (d, $J = 8.0$ Hz, 1H), 7.41 (d, $J = 7.5$ Hz, 2H), 6.53 (s, 1H), 4.05 (q, $J = 6.9$ Hz, 2H), 3.90 (q, $J = 6.9$ Hz, 2H), 1.45 (t, $J = 7.0$ Hz, 3H), 1.31 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, Chloroform- d) δ 195.1, 149.0, 144.1, 129.6, 127.4, 125.0, 120.9, 100.7, 49.4, 47.5, 12.8, 11.6; HRMS (ESI) m/z calcd. for $\text{C}_{12}\text{H}_{16}\text{N}_3\text{S}_2$ $[\text{M}+\text{H}]^+$: 266.0780, found 266.0783.



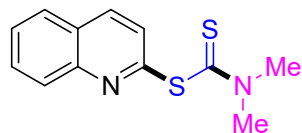
4-methylpyridin-2-yl diethylcarbamodithioate (3ta): Yellow oil (44.1 mg, 61%). ^1H NMR (400 MHz, Chloroform- d) δ 8.53 (s, 1H), 7.47 (s, 1H), 7.15 (s, 1H), 4.09 – 3.94 (m, 2H), 3.81 (s, 2H), 2.39 (s, 3H), 1.39 (t, $J = 5.6$ Hz, 3H), 1.31 – 1.24 (m, 3H); ^{13}C NMR (100 MHz, Chloroform- d) δ 193.8, 153.2, 150.1, 148.6, 134.0, 125.1, 49.4, 47.7, 20.9, 12.7, 11.5; HRMS (ESI) m/z calcd. for $\text{C}_{11}\text{H}_{17}\text{N}_2\text{S}_2$ $[\text{M}+\text{H}]^+$: 241.0828, found 241.0830.



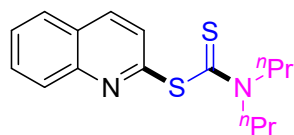
4-methoxypyridin-2-yl diethylcarbamodithioate (3ua): Yellow oil (28.5 mg, 37%). ^1H NMR (400 MHz, Chloroform- d) δ 8.47 (d, $J = 5.6$ Hz, 1H), 7.19 (s, 1H), 6.85 (d, $J = 4.5$ Hz, 1H), 4.00 (q, $J = 6.8$ Hz, 2H), 3.87 (s, 3H), 3.82 (q, $J = 7.1$ Hz, 2H), 1.38 (t, $J = 7.0$ Hz, 3H), 1.27 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, Chloroform- d) δ 193.3, 166.2, 154.6, 151.2, 119.0, 110.6, 55.4, 49.4, 12.7, 11.5; HRMS (ESI) m/z calcd. for $\text{C}_{11}\text{H}_{17}\text{N}_2\text{OS}_2$ $[\text{M}+\text{H}]^+$: 257.0777, found 257.0778.



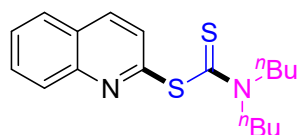
4-phenylpyridin-2-yl diethylcarbamodithioate (3va): Yellow oil (58.2 mg, 64%). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.70 (d, $J = 5.1$ Hz, 1H), 7.89 (s, 1H), 7.67 (d, $J = 7.1$ Hz, 2H), 7.54 (d, $J = 4.1$ Hz, 1H), 7.47 (q, $J = 10.0, 8.5$ Hz, 3H), 4.03 (q, $J = 6.6$ Hz, 2H), 3.86 (q, $J = 6.7$ Hz, 2H), 1.42 (t, $J = 6.9$ Hz, 3H), 1.29 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.4, 154.2, 150.6, 149.5, 137.3, 131.3, 129.3, 129.1, 127.1, 121.9, 49.5, 47.7, 12.7, 11.5; HRMS (ESI) m/z calcd. for $\text{C}_{16}\text{H}_{19}\text{N}_2\text{S}_2$ $[\text{M}+\text{H}]^+$: 303.0984, found 303.0989.



quinolin-2-yl dimethylcarbamodithioate (3ab): Yellow solid (62.0 mg, 83%), mp: 133–134 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.20 – 8.11 (m, 2H), 7.84 (d, $J = 8.1$ Hz, 1H), 7.73 (t, $J = 8.6$ Hz, 2H), 7.59 (t, $J = 7.5$ Hz, 1H), 3.54 (s, 3H), 3.51 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.5, 153.9, 148.3, 136.6, 129.8, 129.6, 129.1, 127.7, 127.6, 127.5, 45.0, 42.5; HRMS (ESI) m/z calcd. for $\text{C}_{12}\text{H}_{13}\text{N}_2\text{S}_2$ $[\text{M}+\text{H}]^+$: 249.0515, found 249.0516.

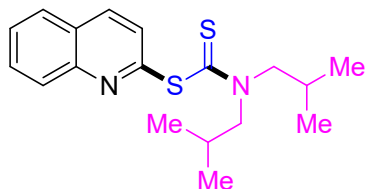


quinolin-2-yl dipropylcarbamodithioate (3ac): Yellow oil (78.7 mg, 86%). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.12 (d, $J = 8.4$ Hz, 2H), 7.80 (d, $J = 8.0$ Hz, 1H), 7.69 (t, $J = 9.1$ Hz, 2H), 7.55 (t, $J = 7.4$ Hz, 1H), 3.94 – 3.81 (m, 2H), 3.79 – 3.66 (m, 2H), 1.95 – 1.71 (m, 4H), 1.00 (t, $J = 7.1$ Hz, 3H), 0.91 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.2, 154.1, 148.1, 136.1, 129.6, 129.4, 129.2, 127.5, 127.4, 127.3, 56.3, 55.3, 20.9, 19.5, 11.1; HRMS (ESI) m/z calcd. for $\text{C}_{16}\text{H}_{21}\text{N}_2\text{S}_2$ $[\text{M}+\text{H}]^+$: 305.1141, found 305.1144.

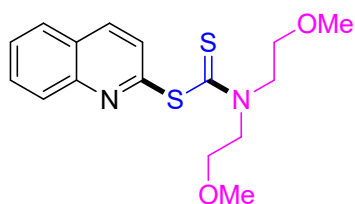


quinolin-2-yl dibutylcarbamodithioate (3ad): Yellow oil (80.9 mg, 81%). ^1H NMR (400 MHz,

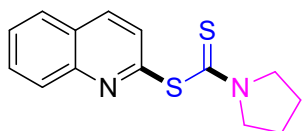
Chloroform-*d*) δ 8.14 (d, $J = 8.4$ Hz, 2H), 7.82 (d, $J = 8.1$ Hz, 1H), 7.71 (t, $J = 9.6$ Hz, 2H), 7.57 (t, $J = 7.5$ Hz, 1H), 4.02 – 3.86 (m, 2H), 3.86 – 3.71 (m, 2H), 1.91 – 1.67 (m, 4H), 1.51 – 1.29 (m, 4H), 1.00 (t, $J = 7.3$ Hz, 3H), 0.93 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.1, 154.2, 148.2, 136.2, 129.6, 129.6, 129.3, 127.5, 127.5, 127.4, 54.7, 53.6, 29.6, 28.3, 20.0, 13.8, 13.6; HRMS (ESI) m/z calcd. for $\text{C}_{18}\text{H}_{25}\text{N}_2\text{S}_2$ $[\text{M}+\text{H}]^+$: 333.1454, found 333.1455.



quinolin-2-yl diisobutylcarbamodithioate (3ae): Yellow oil (72.9 mg, 73%). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.13 (d, $J = 8.4$ Hz, 2H), 7.82 (d, $J = 8.1$ Hz, 1H), 7.76 – 7.64 (m, 2H), 7.57 (t, $J = 7.5$ Hz, 1H), 3.86 (d, $J = 7.3$ Hz, 2H), 3.70 (d, $J = 7.4$ Hz, 2H), 2.52 – 2.39 (m, 2H), 1.04 (d, $J = 6.5$ Hz, 6H), 0.95 (d, $J = 6.5$ Hz, 6H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.3, 154.6, 148.2, 136.1, 129.6, 129.6, 129.2, 127.5, 127.5, 127.3, 62.7, 62.1, 28.0, 26.2, 20.3, 20.2; HRMS (ESI) m/z calcd. for $\text{C}_{18}\text{H}_{25}\text{N}_2\text{S}_2$ $[\text{M}+\text{H}]^+$: 333.1454, found 333.1452.

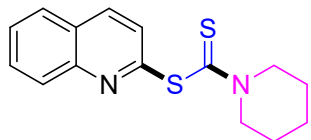


quinolin-2-yl bis(2-methoxyethyl)carbamodithioate (3af): Yellow oil (62.7 mg, 62%). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.15 (t, $J = 8.7$ Hz, 2H), 7.83 (d, $J = 8.1$ Hz, 1H), 7.72 (d, $J = 8.3$ Hz, 2H), 7.58 (t, $J = 7.5$ Hz, 1H), 4.29 (t, $J = 4.9$ Hz, 2H), 4.18 (t, $J = 5.5$ Hz, 2H), 3.79 (t, $J = 5.5$ Hz, 2H), 3.72 (t, $J = 4.9$ Hz, 2H), 3.40 (s, 3H), 3.33 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.8, 153.8, 148.3, 136.5, 129.8, 129.6, 129.3, 127.7, 127.5, 127.5, 70.0, 70.0, 59.0, 58.9, 55.5, 54.7; HRMS (ESI) m/z calcd. for $\text{C}_{16}\text{H}_{21}\text{N}_2\text{O}_2\text{S}_2$ $[\text{M}+\text{H}]^+$: 337.1039, found 337.1034.

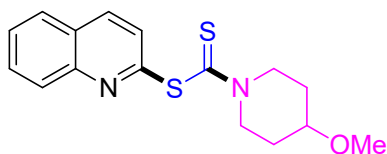


quinolin-2-yl pyrrolidine-1-carbodithioate (3ag): Yellow solid (71.8 mg, 87%), mp: 135–136 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.18 (d, $J = 8.5$ Hz, 1H), 8.13 (d, $J = 8.5$ Hz, 1H), 7.83 (d, $J = 8.1$ Hz, 1H), 7.79 – 7.68 (m, 2H), 7.58 (t, $J = 7.5$ Hz, 1H), 3.91 (t, $J = 6.9$ Hz, 2H), 3.81 (t, $J =$

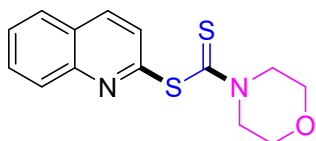
6.8 Hz, 2H), 2.15 – 2.07 (m, 2H), 2.04 – 1.95 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 190.0, 153.5, 148.3, 136.4, 129.7, 129.6, 129.1, 127.7, 127.6, 127.5, 54.8, 51.5, 26.3, 24.4; HRMS (ESI) m/z calcd. for $\text{C}_{14}\text{H}_{15}\text{N}_2\text{S}_2$ $[\text{M}+\text{H}]^+$: 275.0671, found 275.0674.



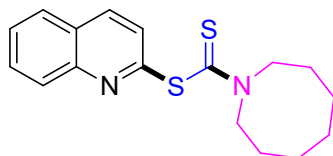
quinolin-2-yl piperidine-1-carbodithioate (3ah): Yellow solid (72.0 mg, 83%), mp: 107–108 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.23 – 8.08 (m, 2H), 7.83 (d, $J = 8.1$ Hz, 1H), 7.72 (t, $J = 7.8$ Hz, 2H), 7.58 (t, $J = 7.4$ Hz, 1H), 4.26 (s, 2H), 3.98 (s, 2H), 1.73 (s, 6H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.6, 154.1, 148.3, 136.3, 129.7, 129.6, 129.1, 127.6, 127.5, 127.4, 52.6, 52.4, 26.2, 25.3, 24.0; HRMS (ESI) m/z calcd. for $\text{C}_{15}\text{H}_{17}\text{N}_2\text{S}_2$ $[\text{M}+\text{H}]^+$: 289.0828, found 289.0833.



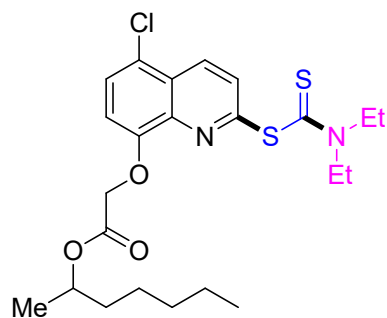
quinolin-2-yl 4-methoxypiperidine-1-carbodithioate (3ai): Yellow solid (77.5 mg, 81%), mp: 100–101 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.26 – 8.08 (m, 2H), 7.84 (d, $J = 8.1$ Hz, 1H), 7.77 – 7.65 (m, 2H), 7.59 (t, $J = 7.5$ Hz, 1H), 4.52 – 3.94 (m, 4H), 3.62 – 3.53 (m, 1H), 3.38 (s, 3H), 2.04 – 1.74 (m, 4H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 193.1, 153.9, 148.3, 136.4, 129.8, 129.6, 129.1, 127.7, 127.6, 127.4, 73.8, 56.0, 48.0, 47.9, 30.6, 29.7; HRMS (ESI) m/z calcd. for $\text{C}_{16}\text{H}_{19}\text{N}_2\text{OS}_2$ $[\text{M}+\text{H}]^+$: 319.0933, found 319.0941.



quinolin-2-yl morpholine-4-carbodithioate (3aj): Yellow solid (72.5 mg, 83%), mp: 167–168 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.21 – 8.12 (m, 2H), 7.85 (d, $J = 8.1$ Hz, 1H), 7.78 – 7.66 (m, 2H), 7.60 (t, $J = 7.5$ Hz, 1H), 4.43 – 3.96 (m, 4H), 3.85 – 3.76 (m, 4H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.5, 153.4, 148.4, 136.6, 129.9, 129.6, 128.9, 127.8, 127.6, 127.5, 66.3, 66.0, 51.4, 51.0; HRMS (ESI) m/z calcd. for $\text{C}_{14}\text{H}_{15}\text{N}_2\text{OS}_2$ $[\text{M}+\text{H}]^+$: 291.0620, found 291.0624.

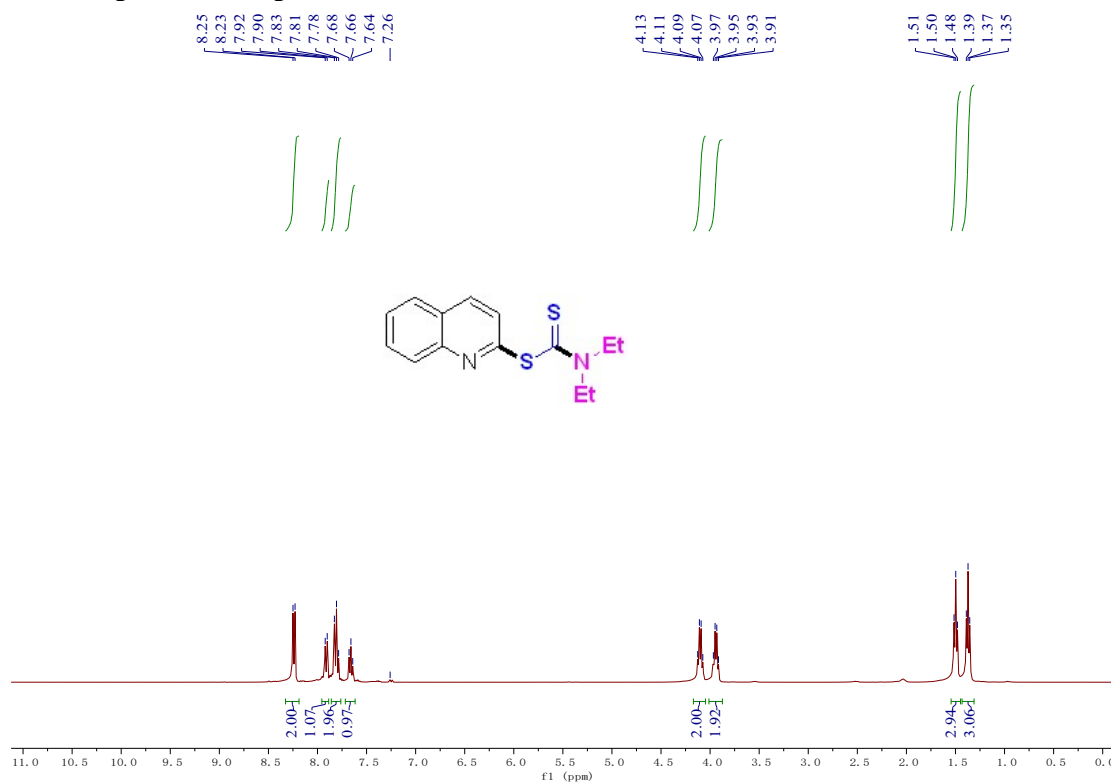


quinolin-2-yl azocane-1-carbodithioate (3ak): Yellow solid (72.3 mg, 76%), mp: 79–80 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 8.4 Hz, 2H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.72 (t, *J* = 9.1 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 4.20 – 4.08 (m, 2H), 4.04 – 3.94 (m, 2H), 2.05 – 1.91 (m, 4H), 1.79 – 1.52 (m, 8H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 193.7, 154.2, 148.3, 136.2, 129.7, 129.6, 129.4, 127.6, 127.5, 127.4, 56.1, 55.0, 26.6, 25.6, 25.3, 25.1; HRMS (ESI) *m/z* calcd. for C₁₇H₂₁N₂S₂ [M+H]⁺ : 317.1141, found 317.1140.

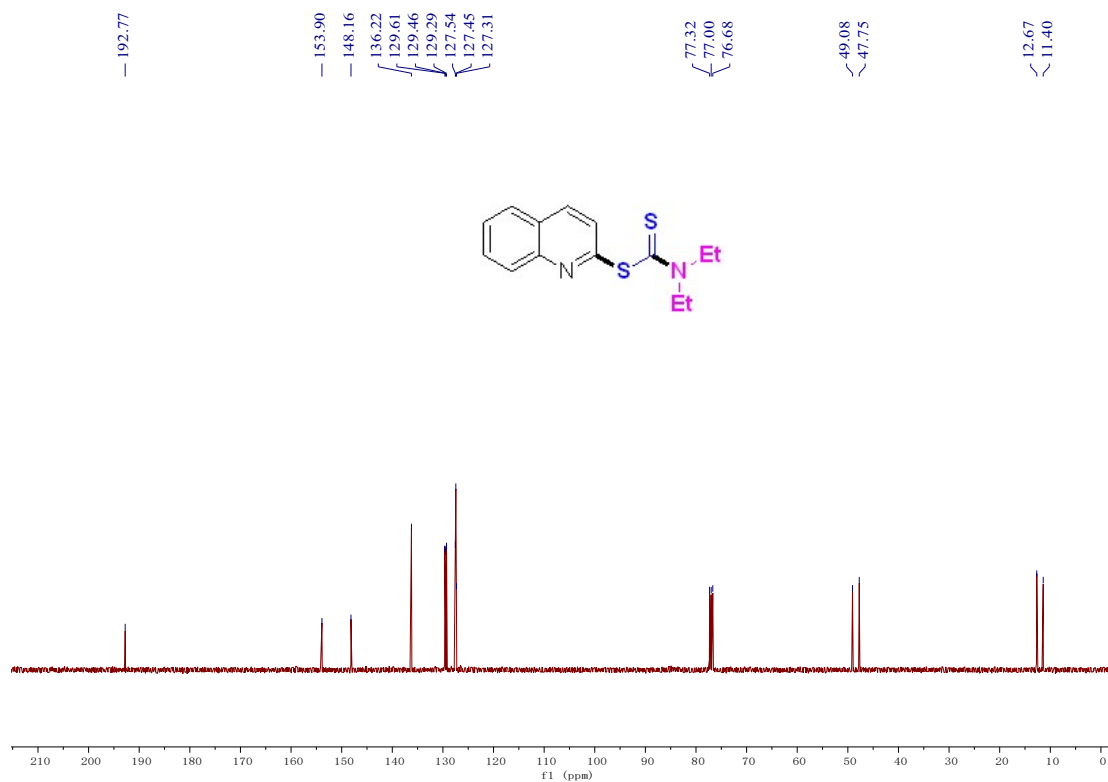


heptan-2-yl2-((5-chloro-2-((diethylcarbamothioyl)thio)quinolin-8-yl)oxy)acetate (4ca): Yellow solid (107.3 mg, 74%), mp: 55–56 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.47 (d, *J* = 8.7 Hz, 1H), 7.88 (d, *J* = 8.7 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 4.98 (q, *J* = 6.2 Hz, 1H), 4.91 (s, 2H), 3.99 (q, *J* = 6.6 Hz, 2H), 3.83 (q, *J* = 6.7 Hz, 2H), 1.59 – 1.48 (m, 1H), 1.44 – 1.34 (m, 4H), 1.28 – 1.08 (m, 12H), 0.86 – 0.78 (m, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 192.4, 168.2, 154.4, 152.9, 140.4, 132.9, 130.8, 127.0, 126.4, 123.3, 110.6, 72.5, 66.7, 49.1, 47.8, 35.5, 31.4, 24.8, 22.4, 19.8, 13.8, 12.8, 11.4; HRMS (ESI) *m/z* calcd. for C₂₃H₃₂ClN₂O₃S₂ [M+H]⁺ : 483.1537, found 483.1542.

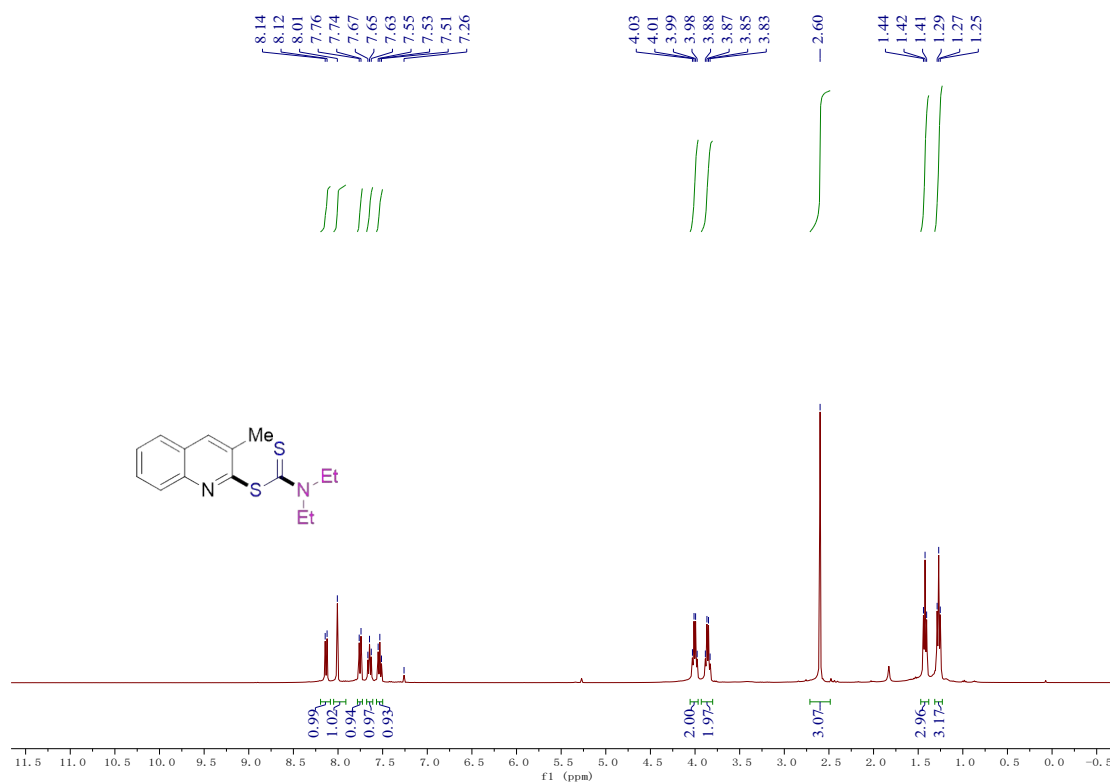
4. NMR spectrum of products



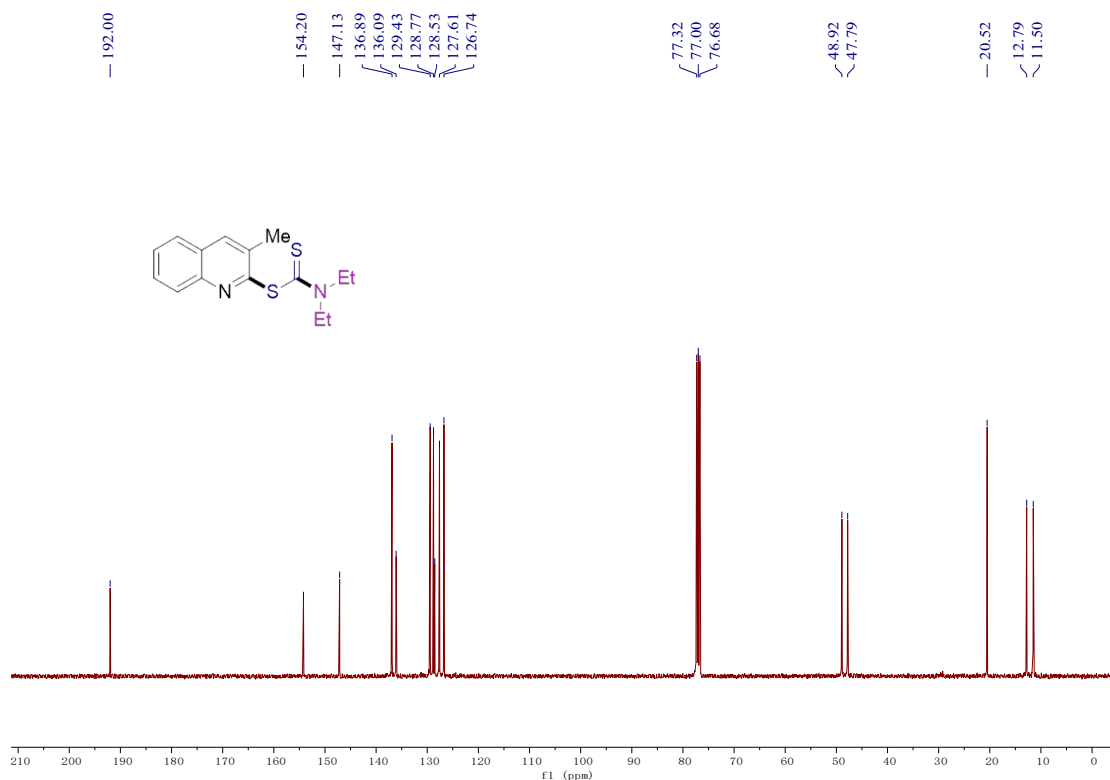
¹H spectrum of compound **3aa**



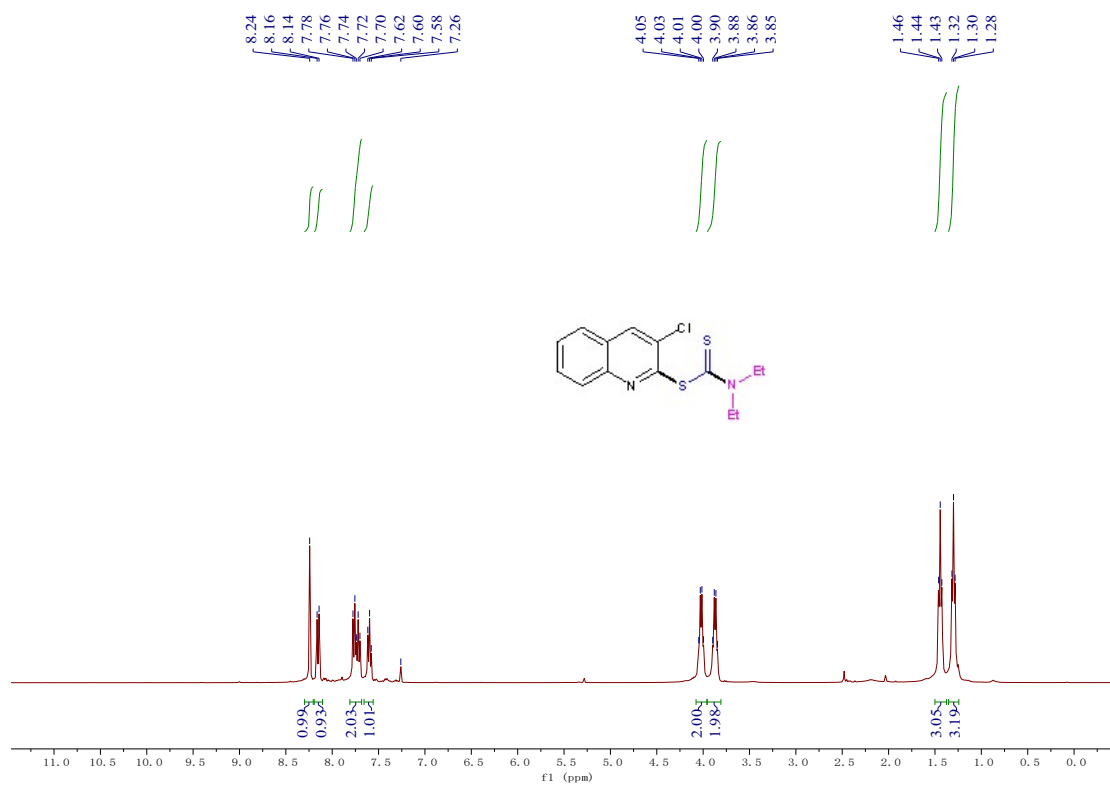
¹³C spectrum of compound **3aa**



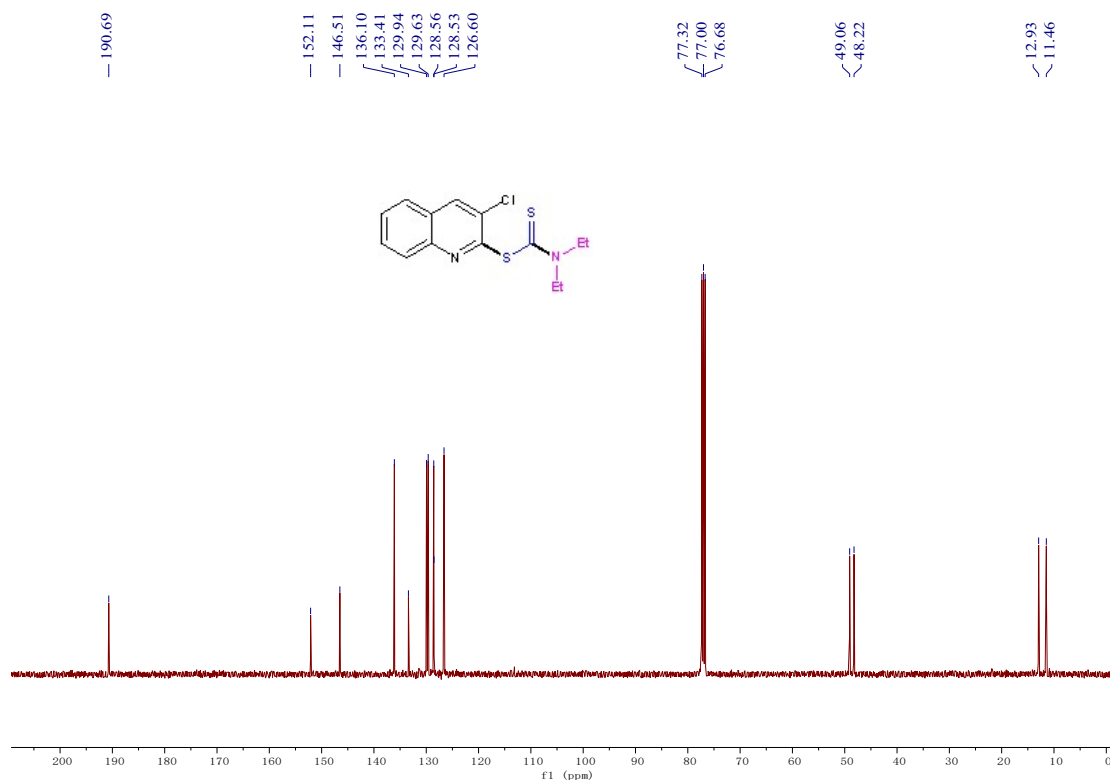
¹H spectrum of compound 3ba



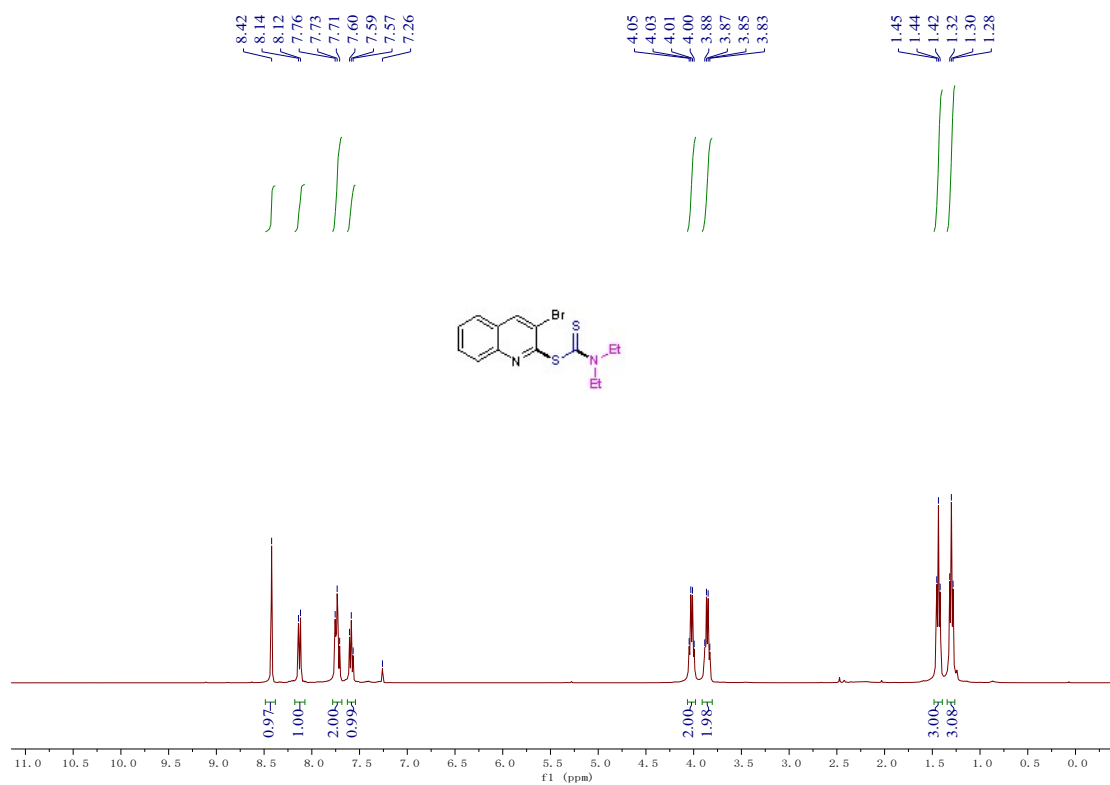
¹³C spectrum of compound 3ba



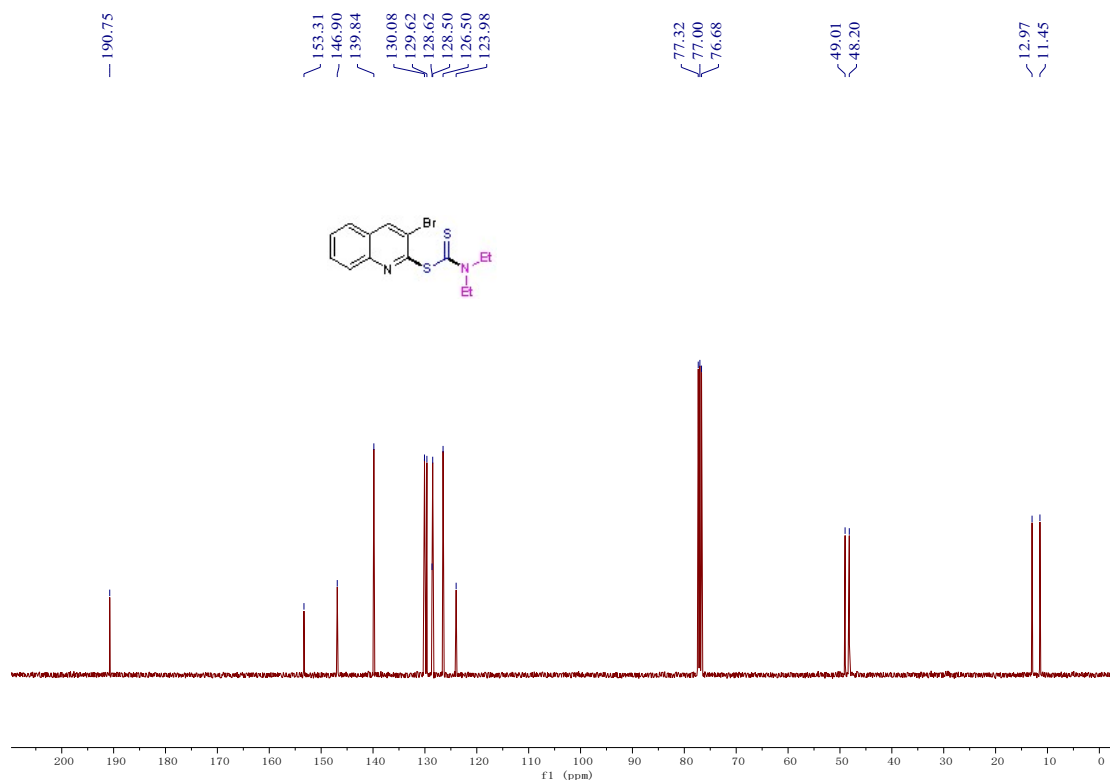
¹H spectrum of compound 3ca



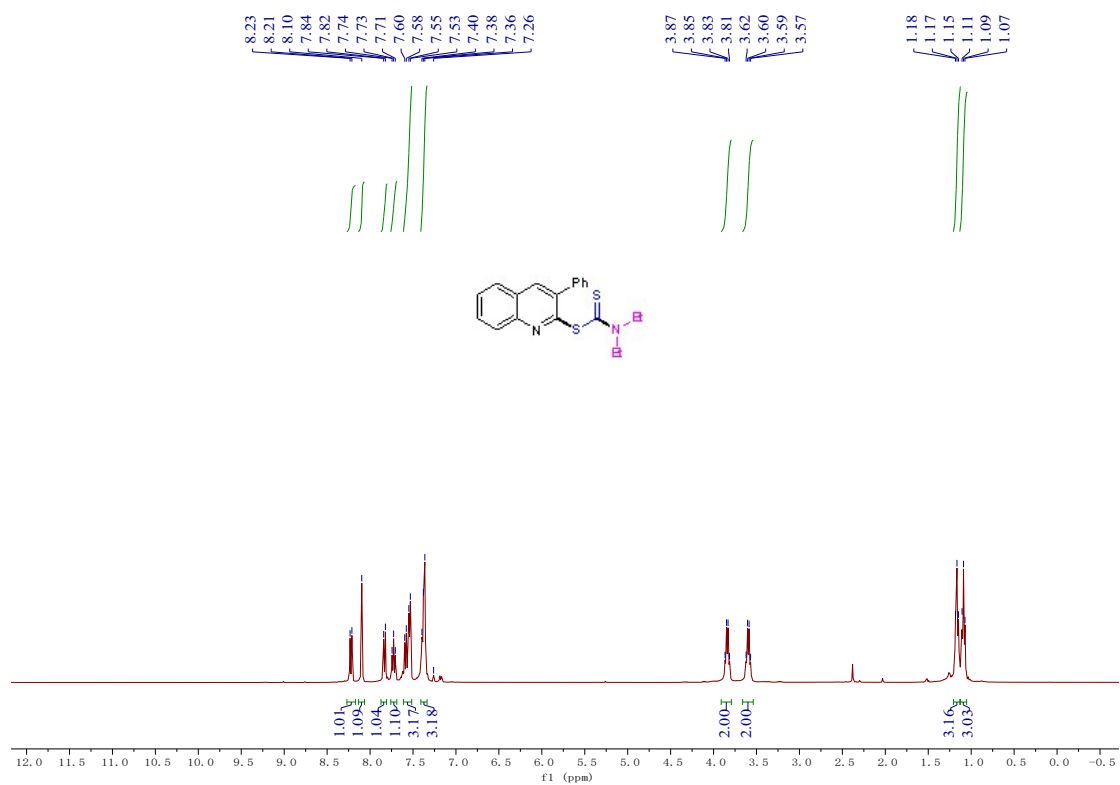
¹³C spectrum of compound 3ca



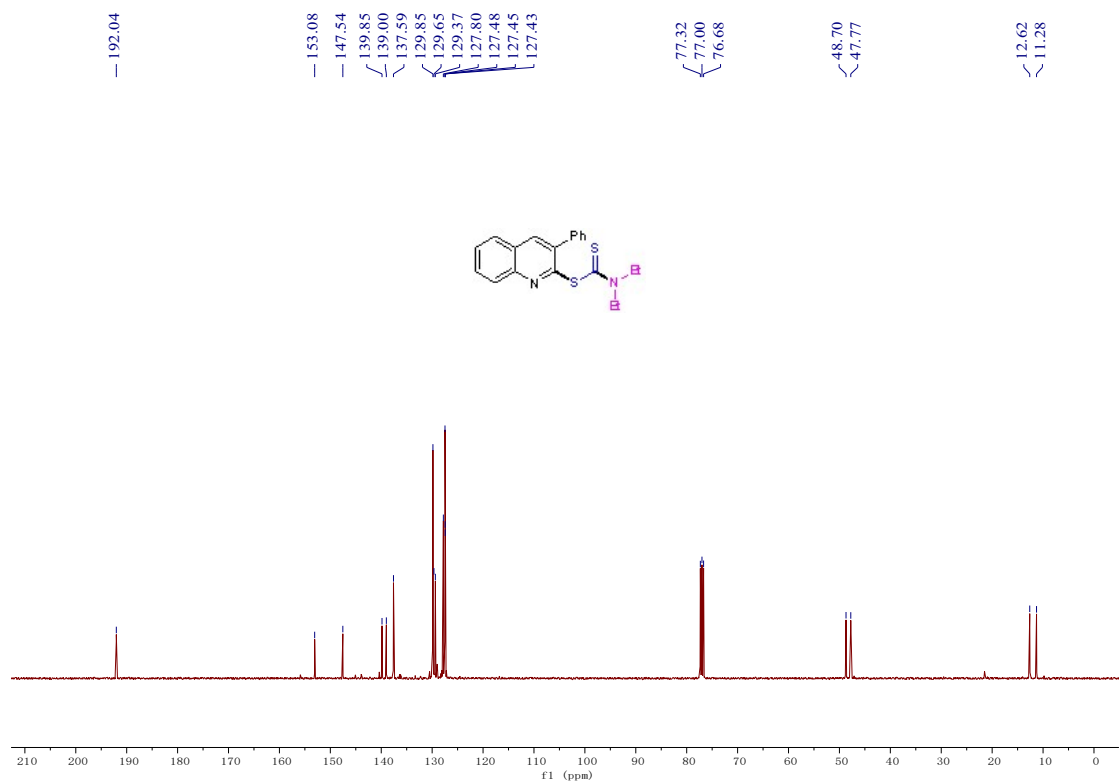
¹H spectrum of compound 3da



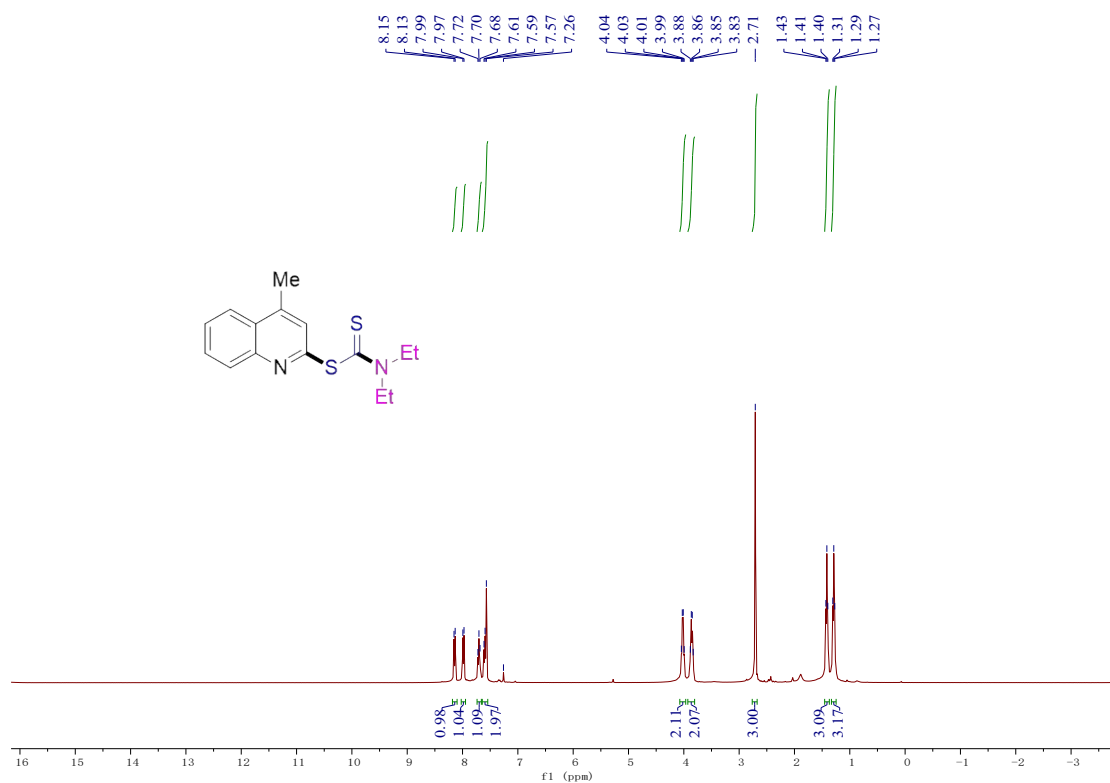
¹³C spectrum of compound 3da



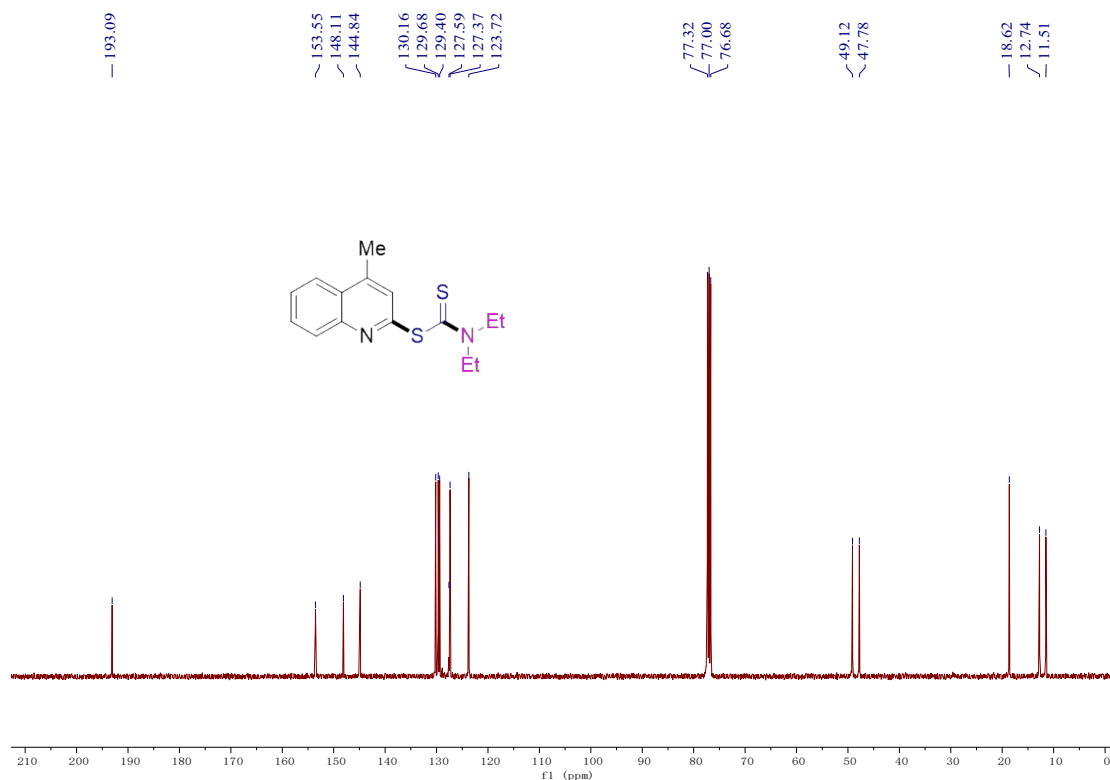
¹H spectrum of compound 3ea



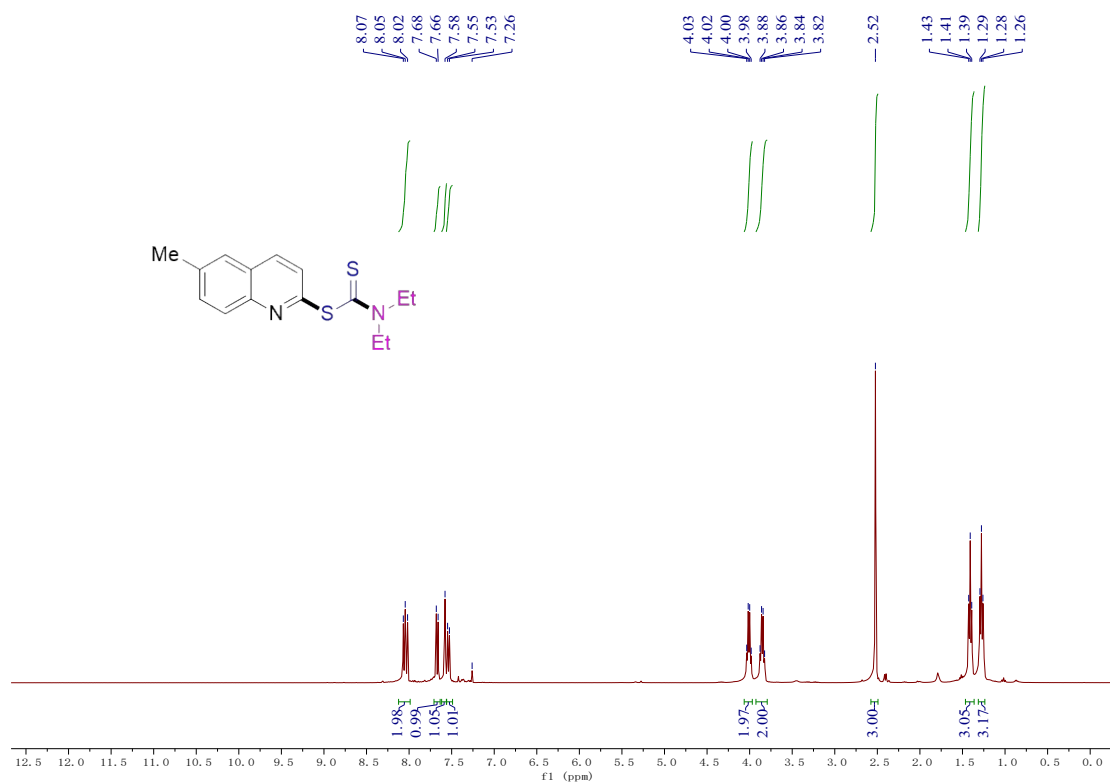
¹³C spectrum of compound 3ea



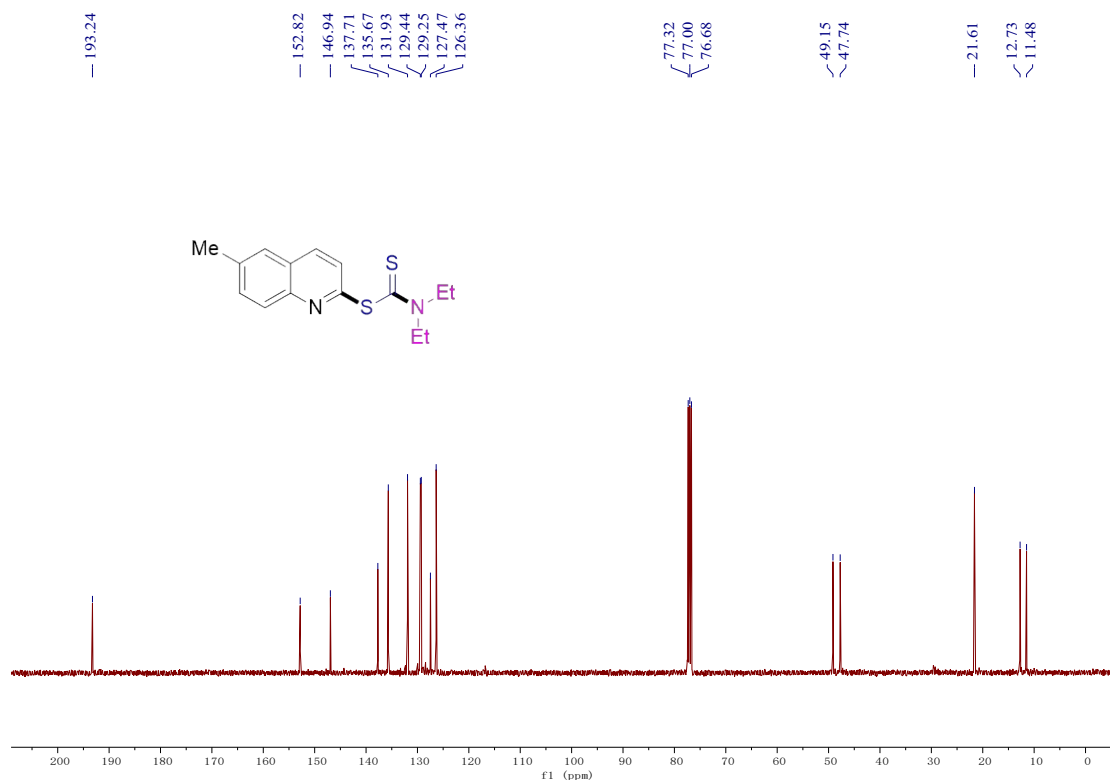
¹H spectrum of compound 3fa



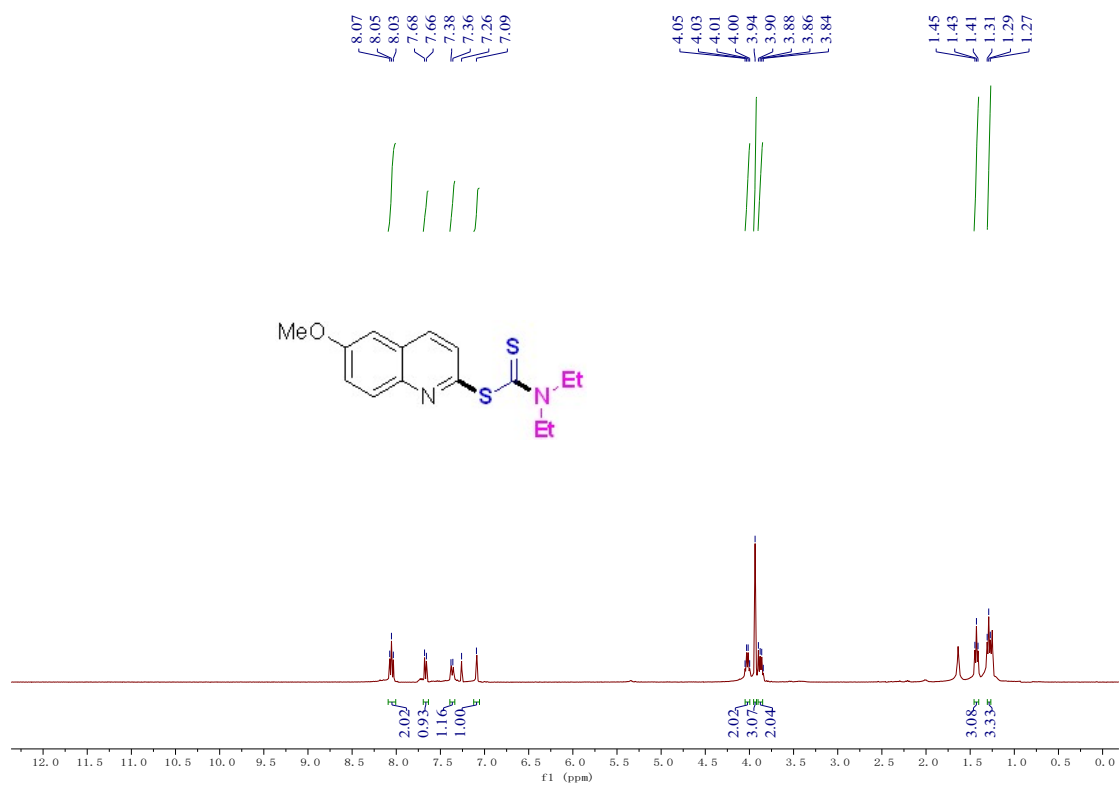
¹³C spectrum of compound 3fa



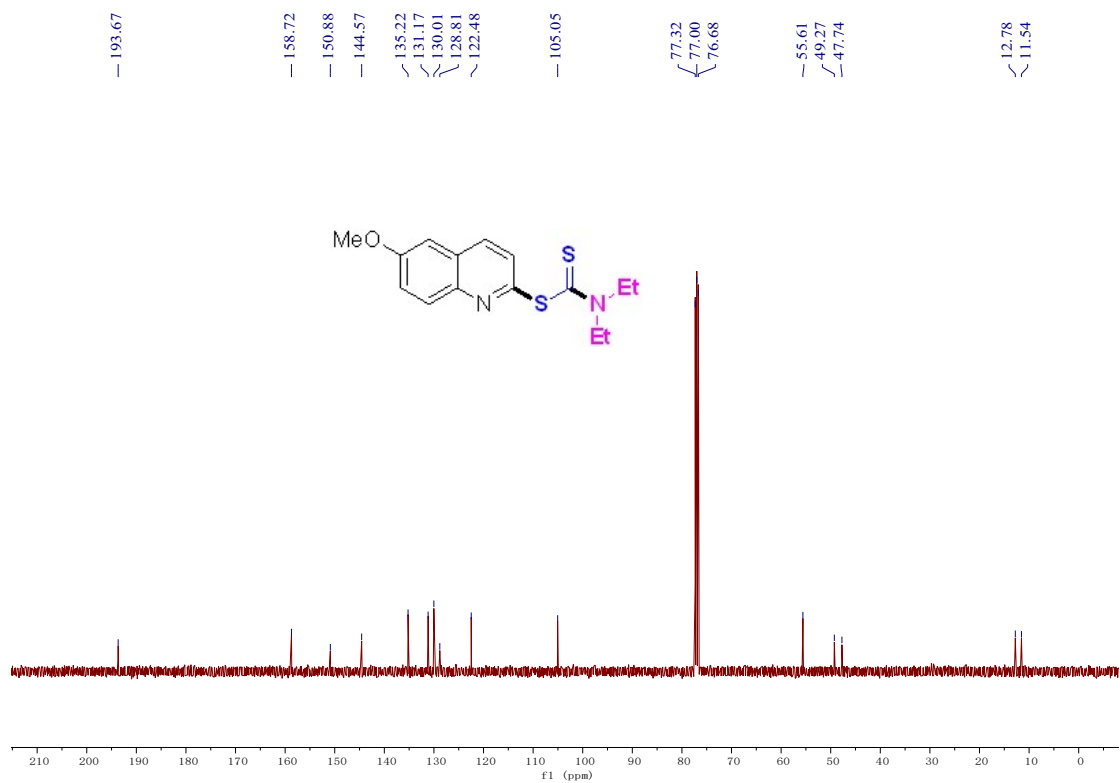
¹H spectrum of compound 3ga



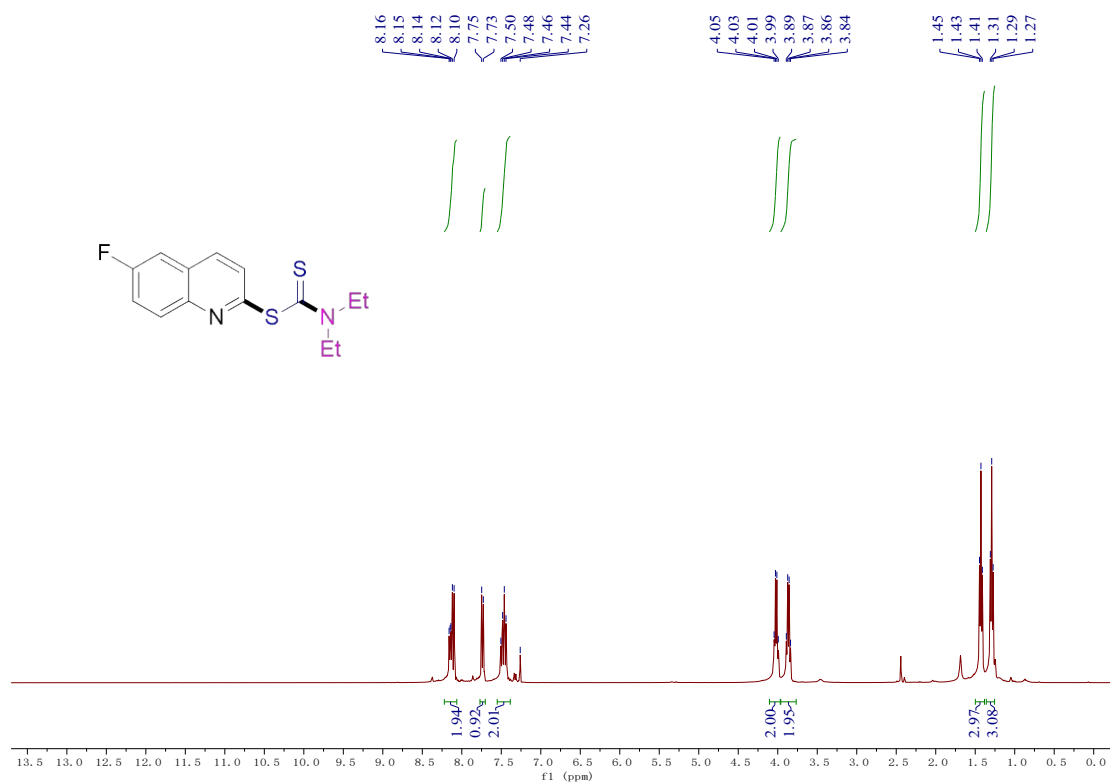
¹³C spectrum of compound 3ga



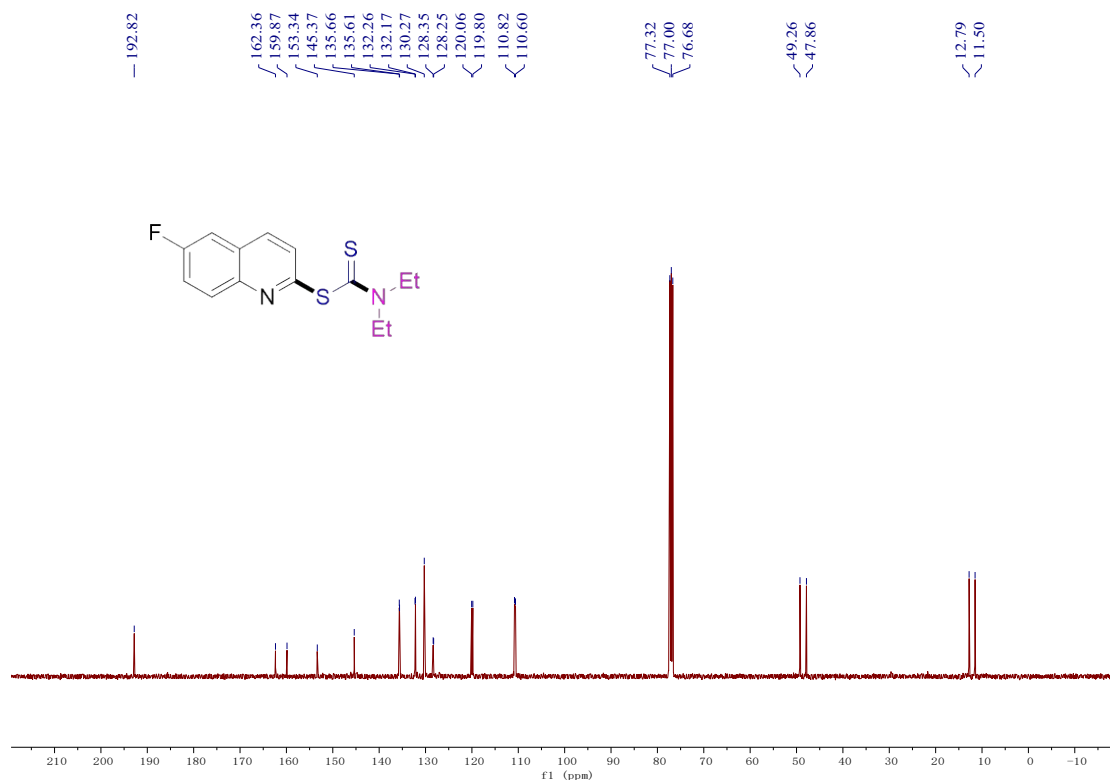
¹H spectrum of compound 3ha



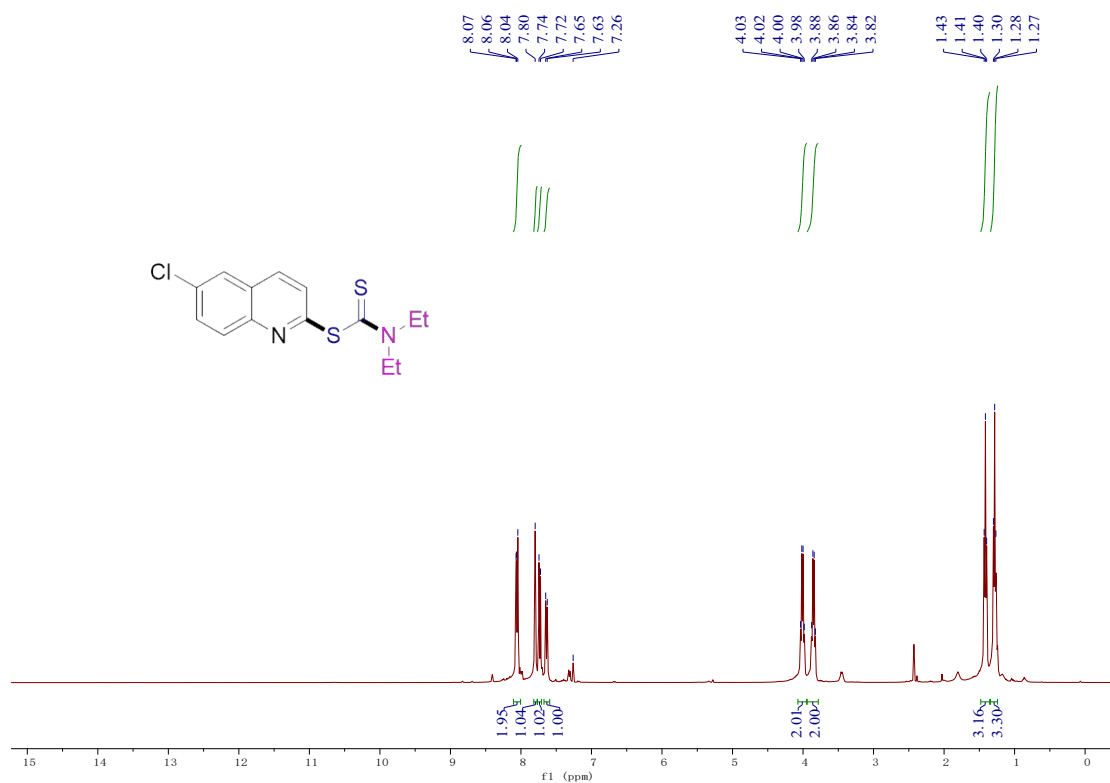
¹³C spectrum of compound 3ha



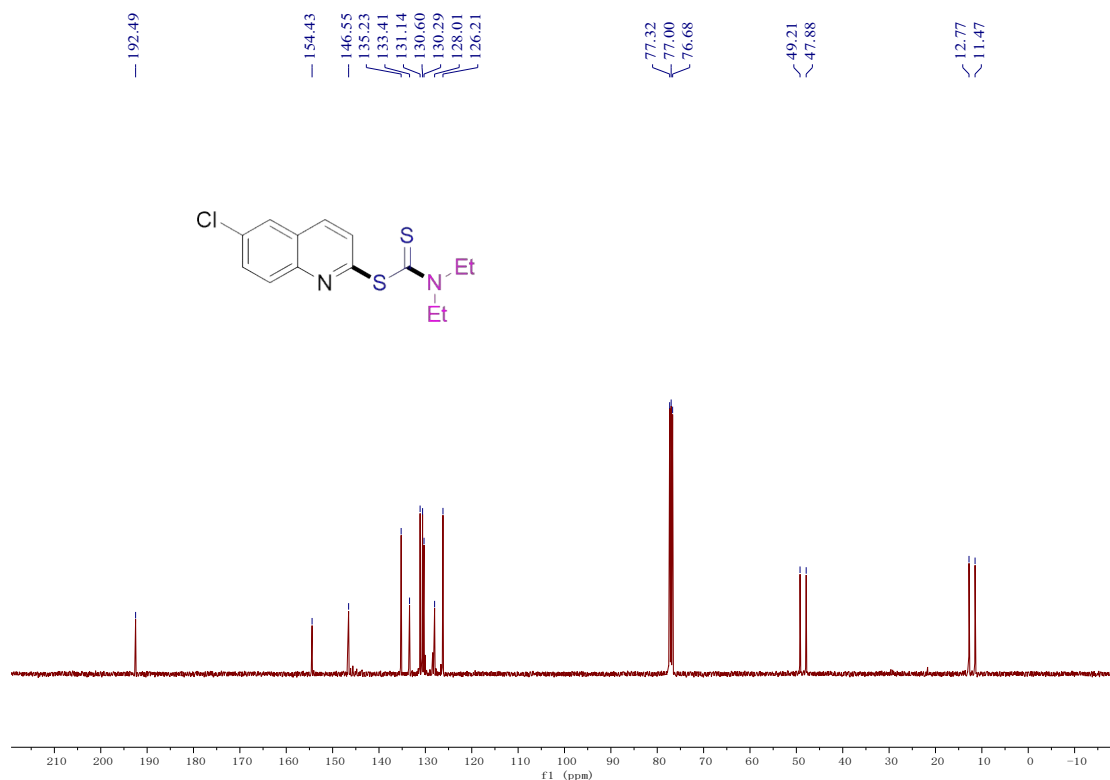
¹H spectrum of compound **3ia**



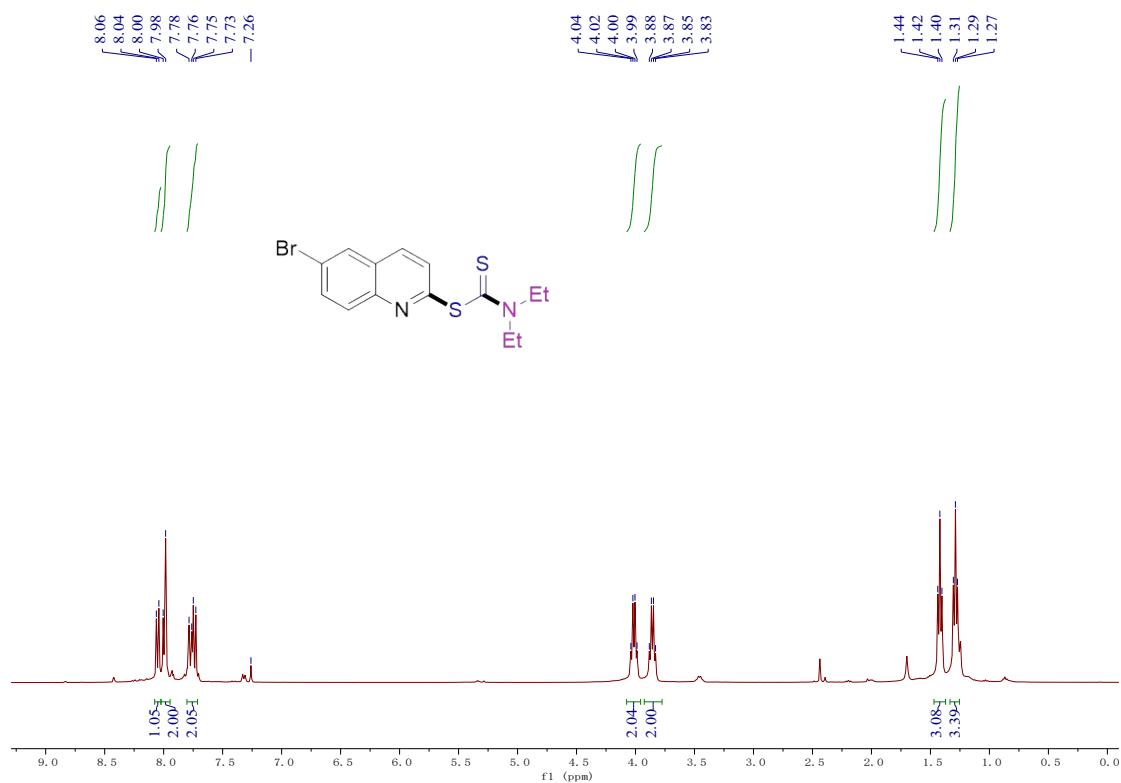
¹³C spectrum of compound **3ia**



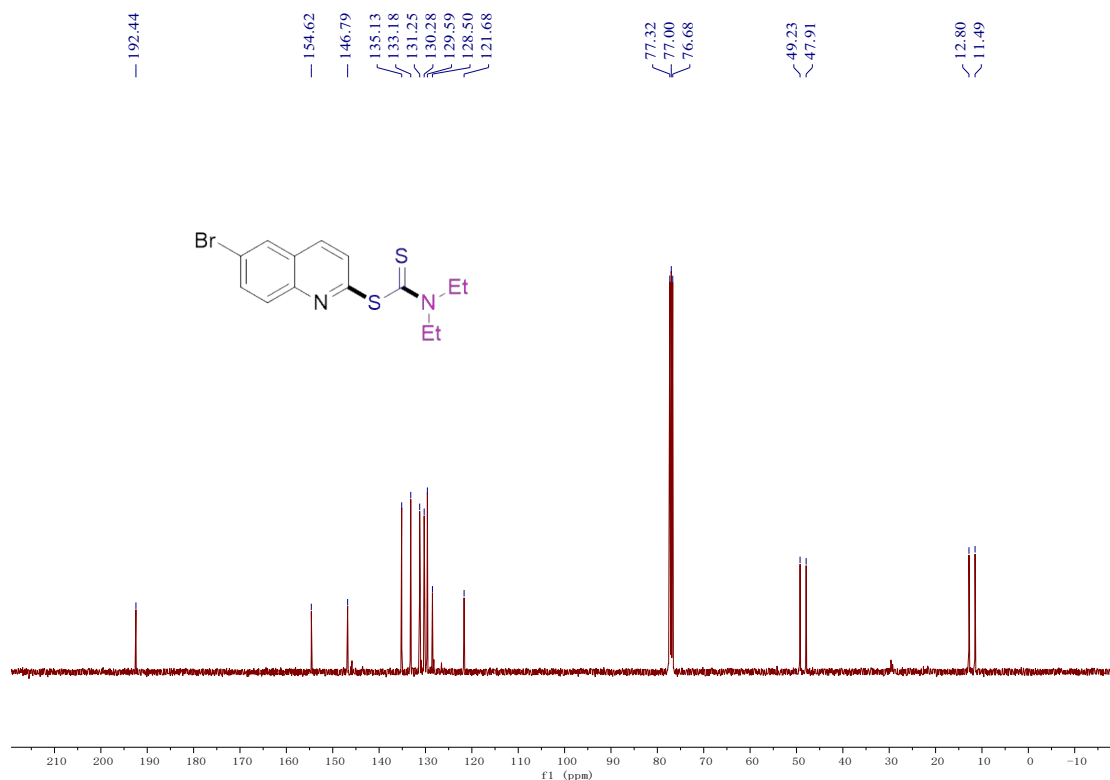
¹H spectrum of compound **3ja**



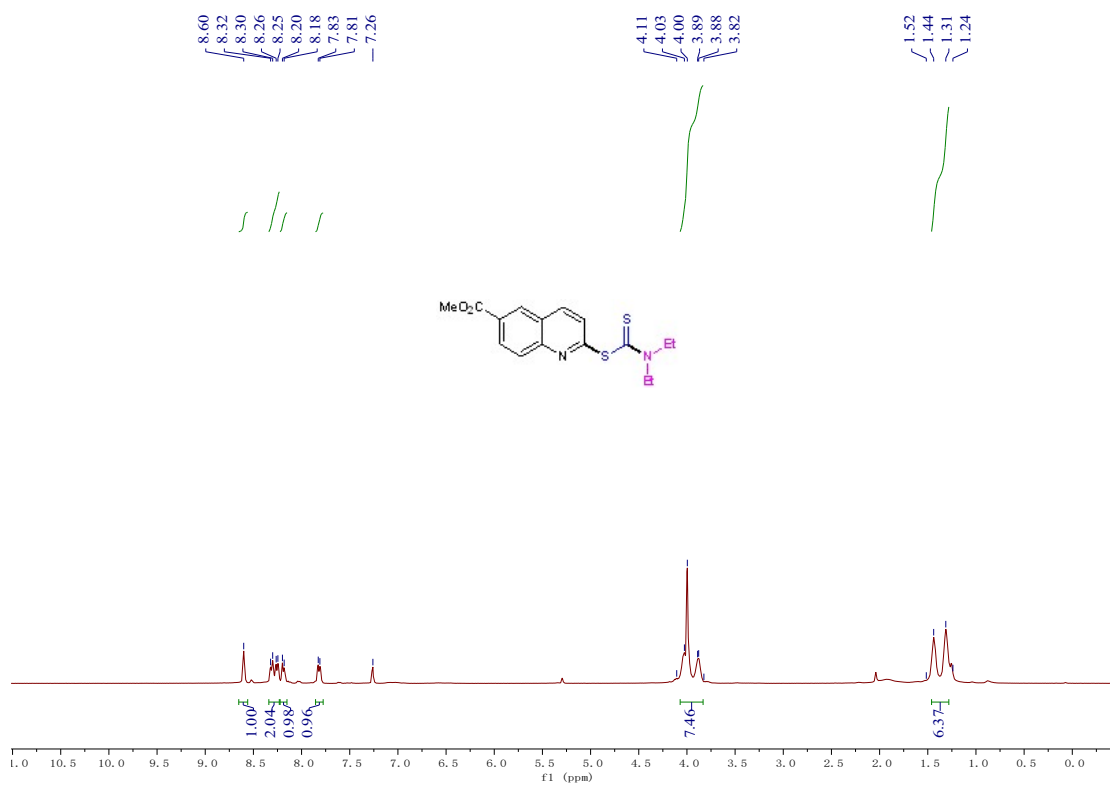
¹³C spectrum of compound **3ja**



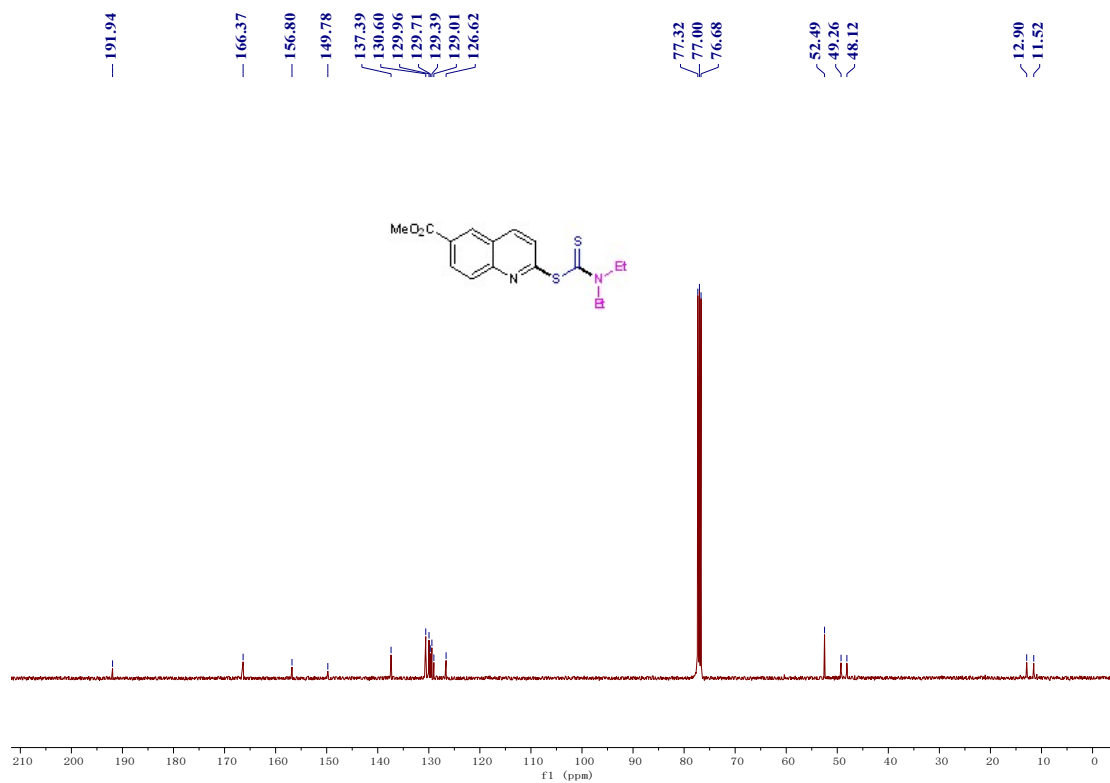
¹H spectrum of compound 3ka



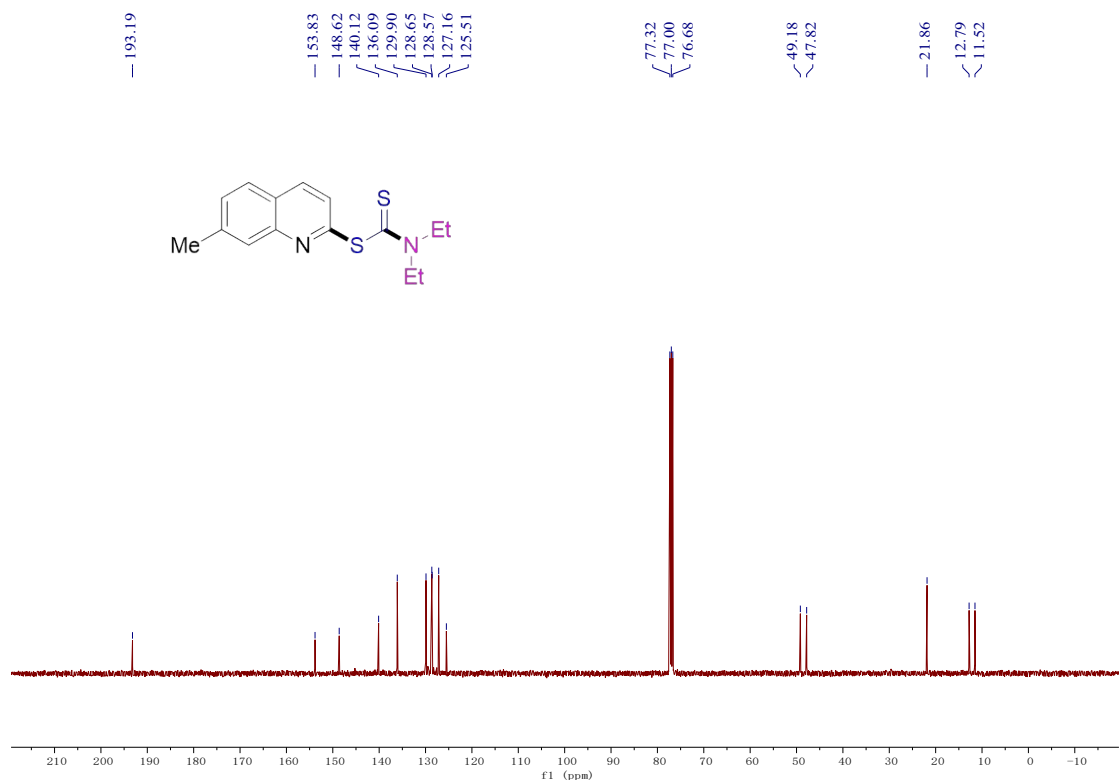
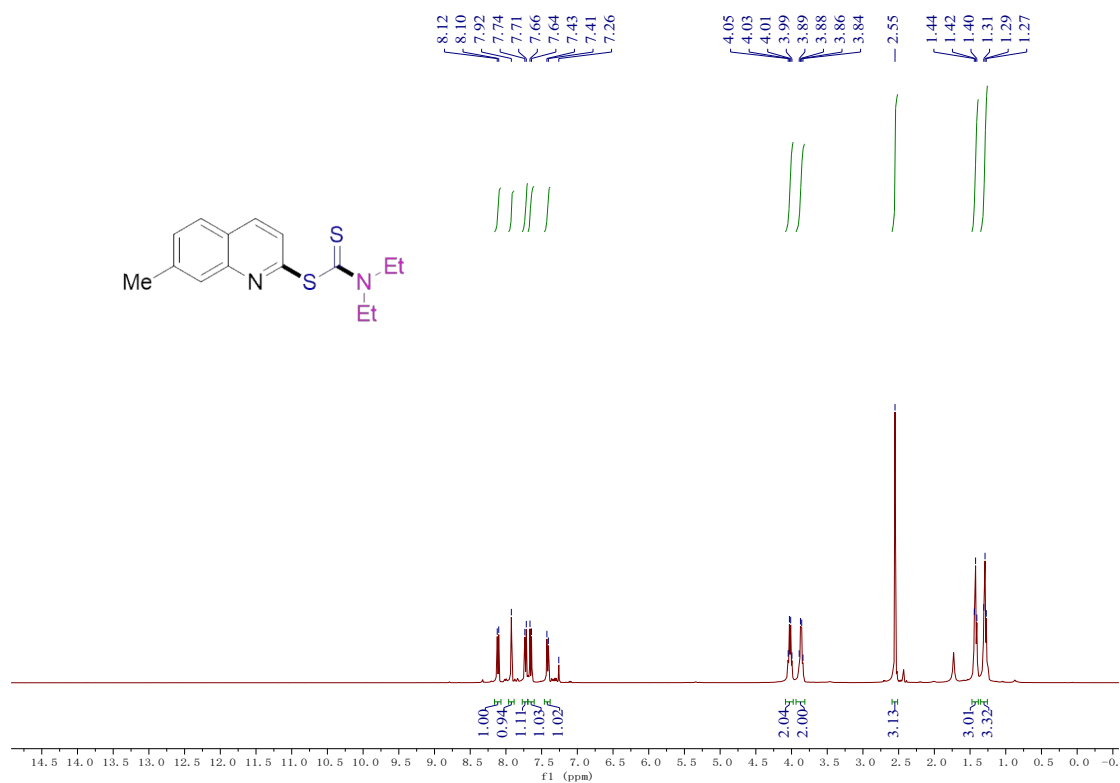
¹³C spectrum of compound 3ka

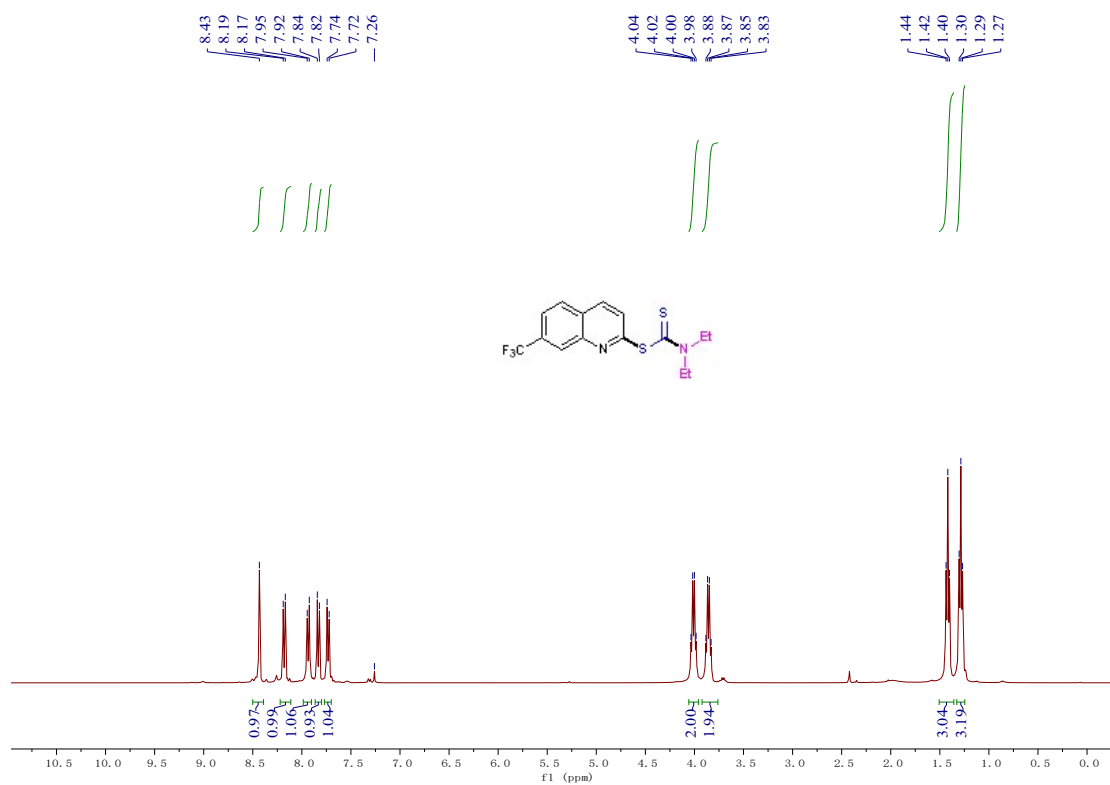


¹H spectrum of compound 3la

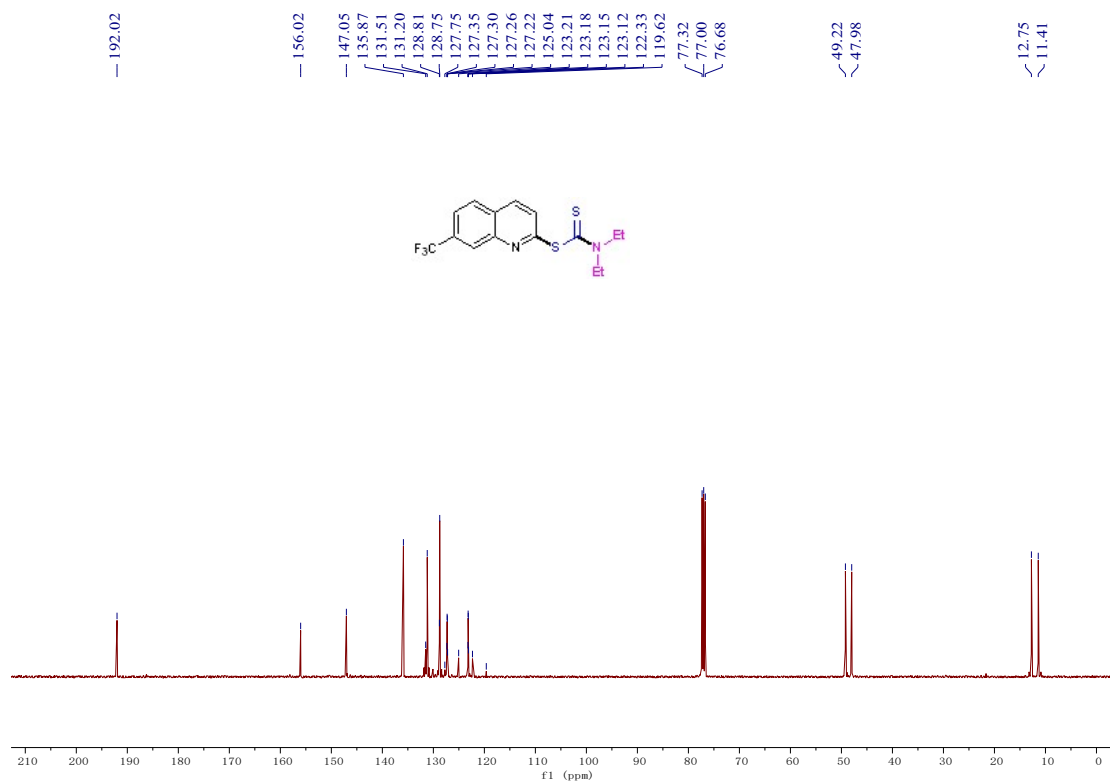


¹³C spectrum of compound 3la

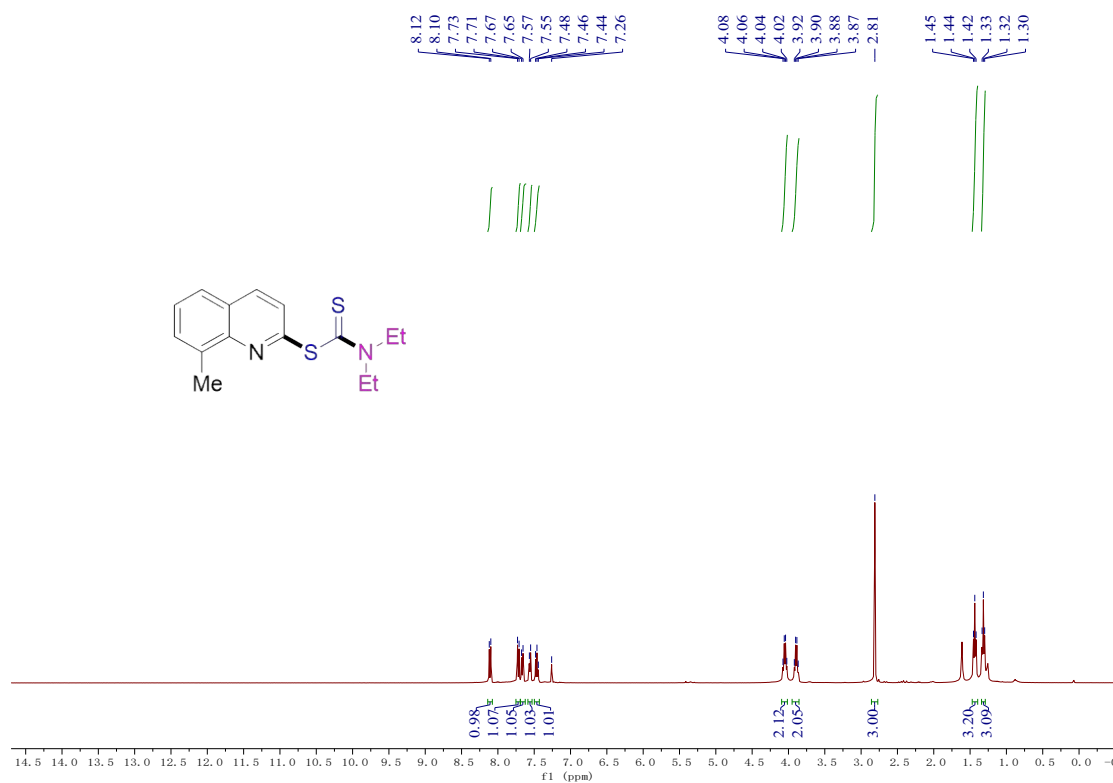




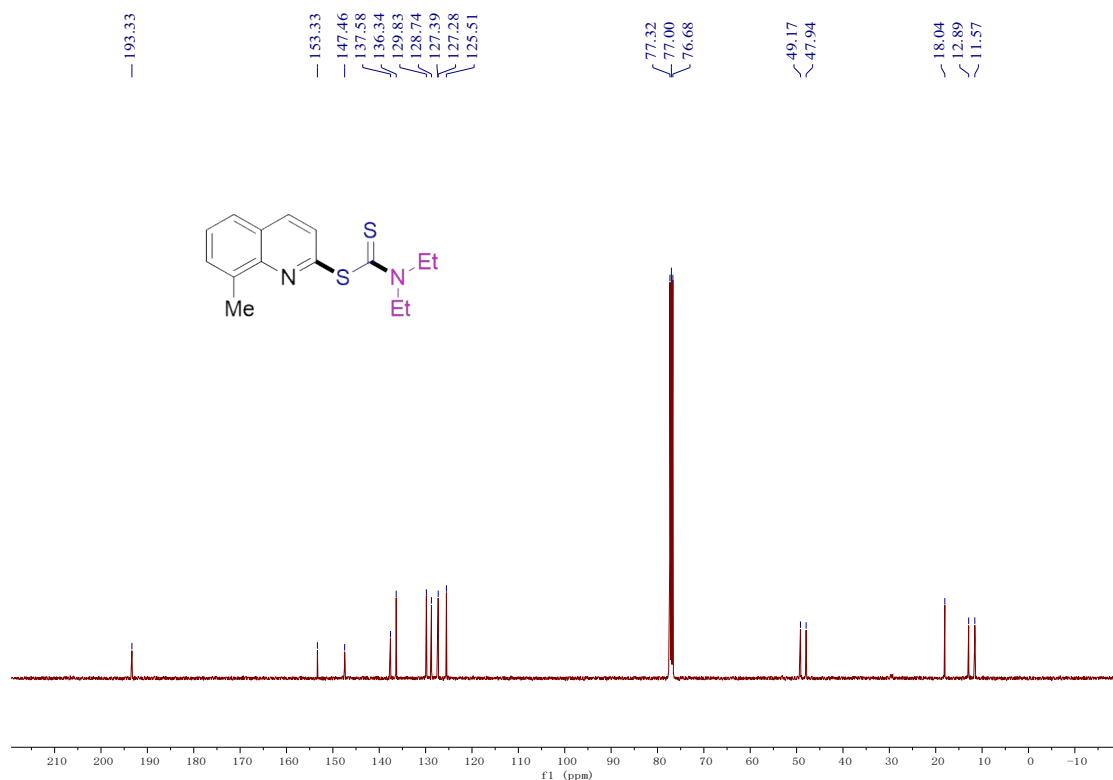
¹H spectrum of compound 3na



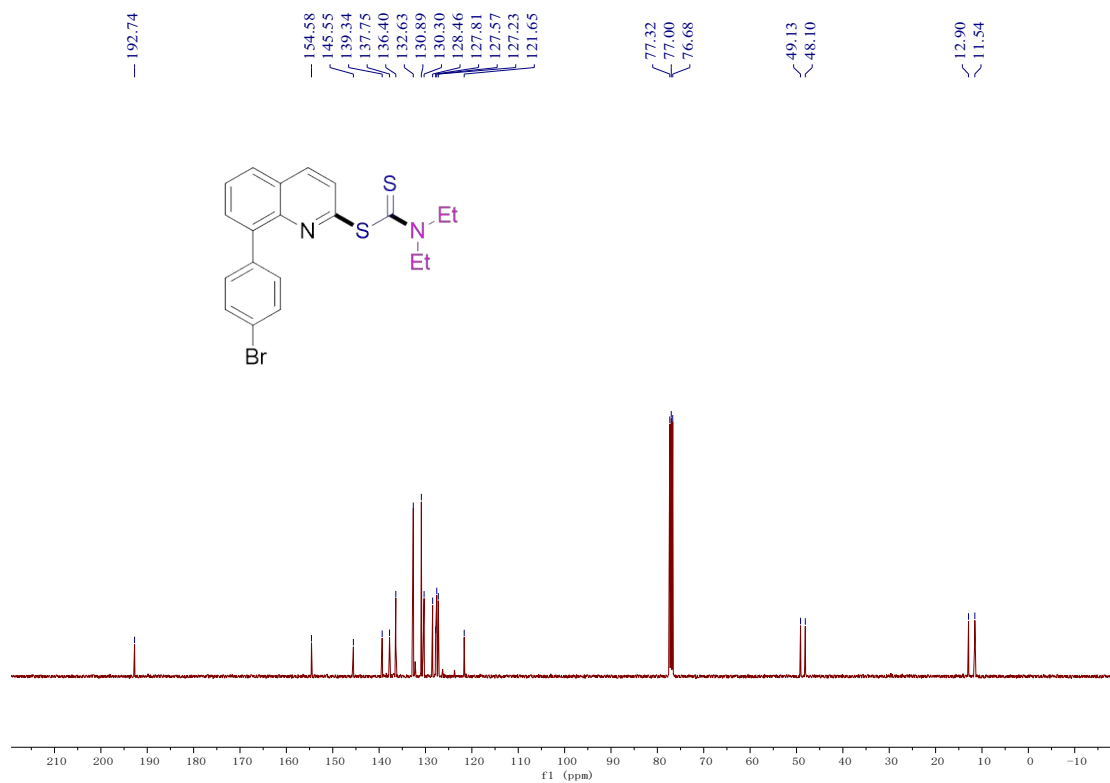
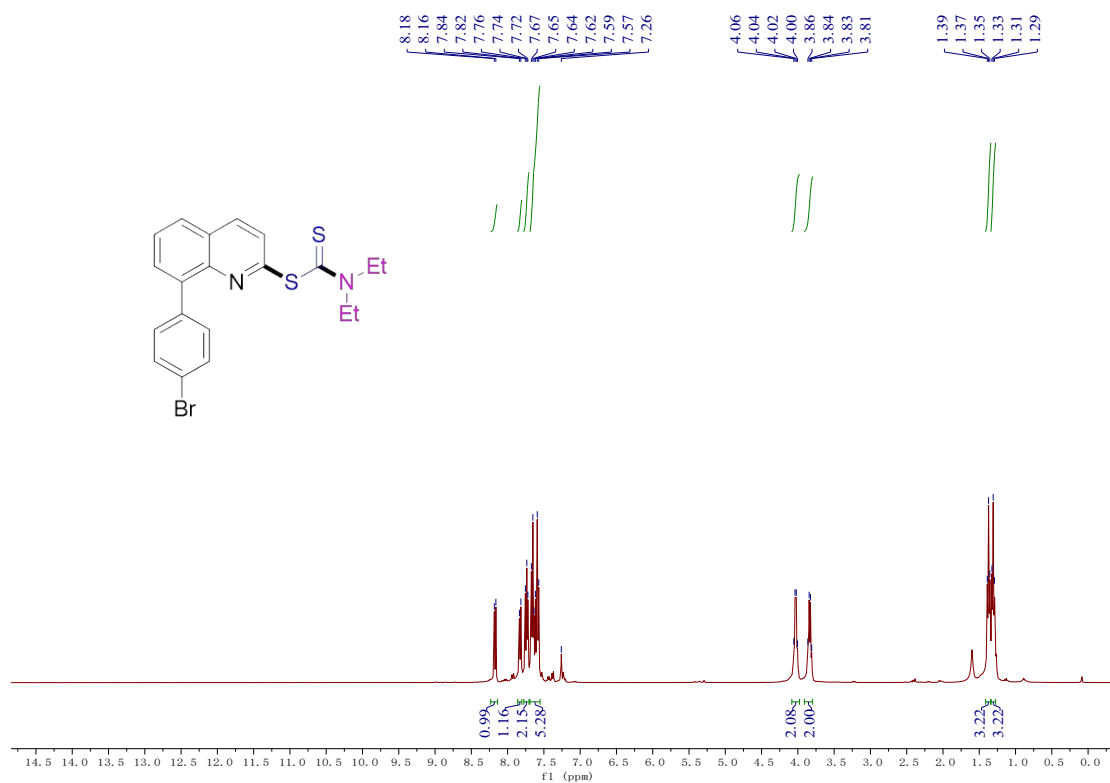
¹³C spectrum of compound 3na

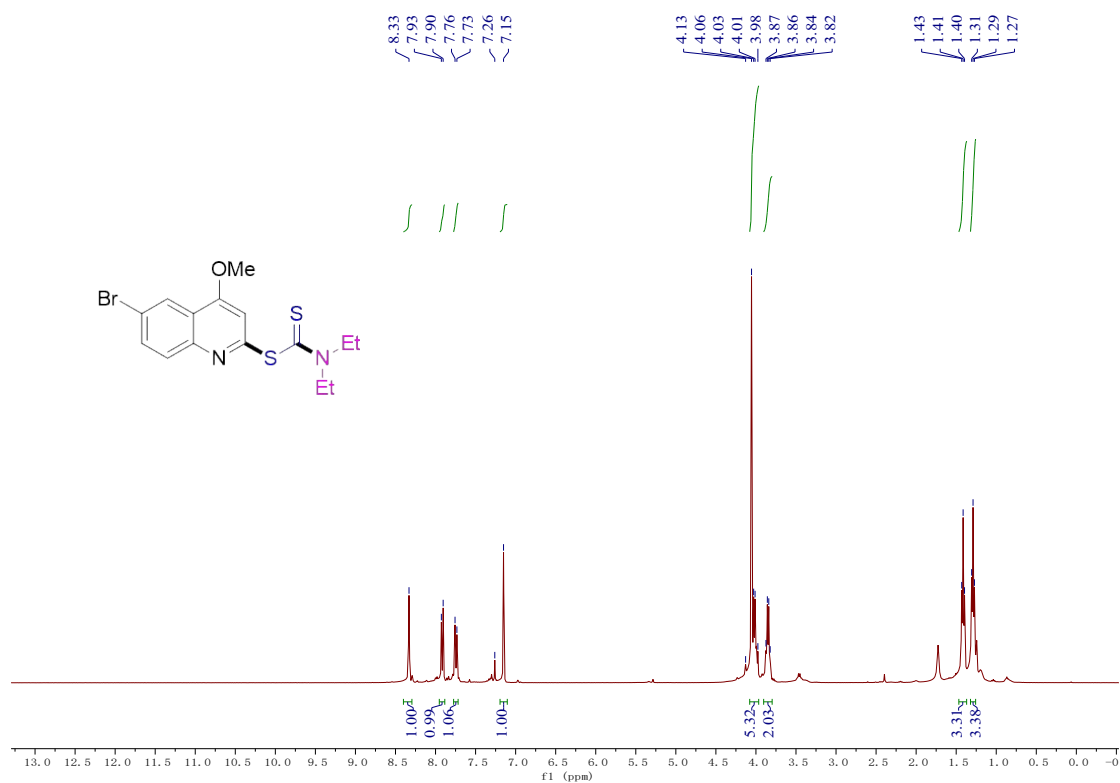


¹H spectrum of compound 30a

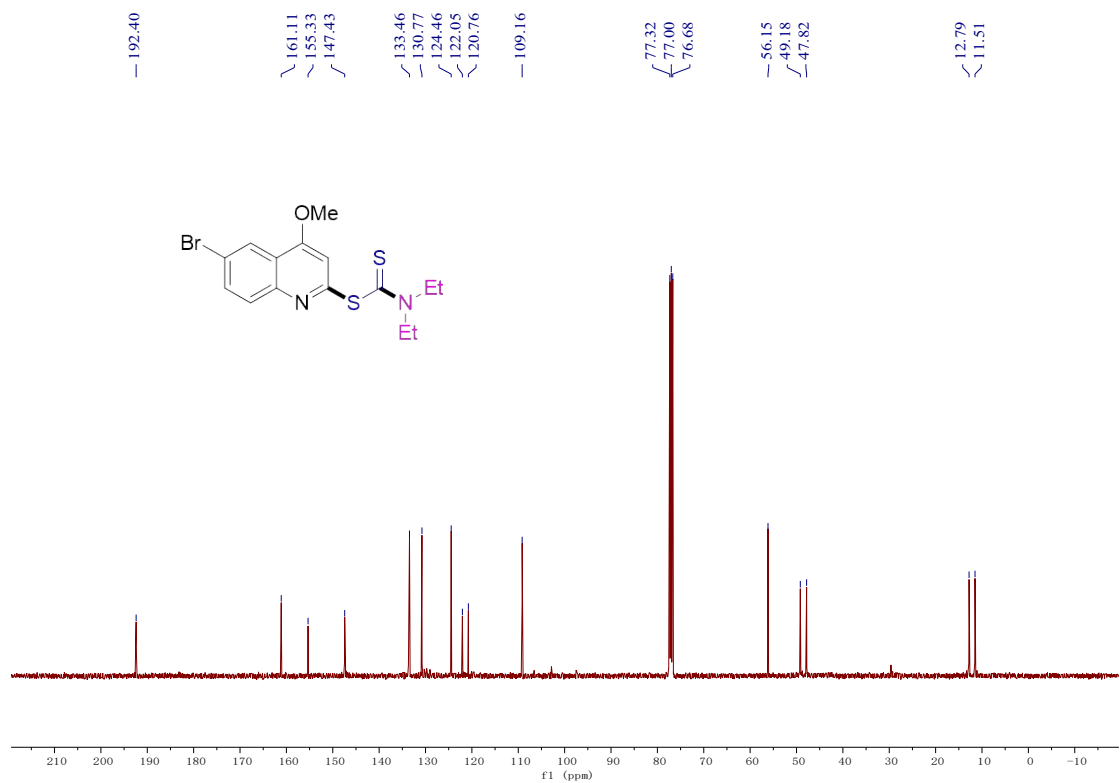


¹³C spectrum of compound 30a

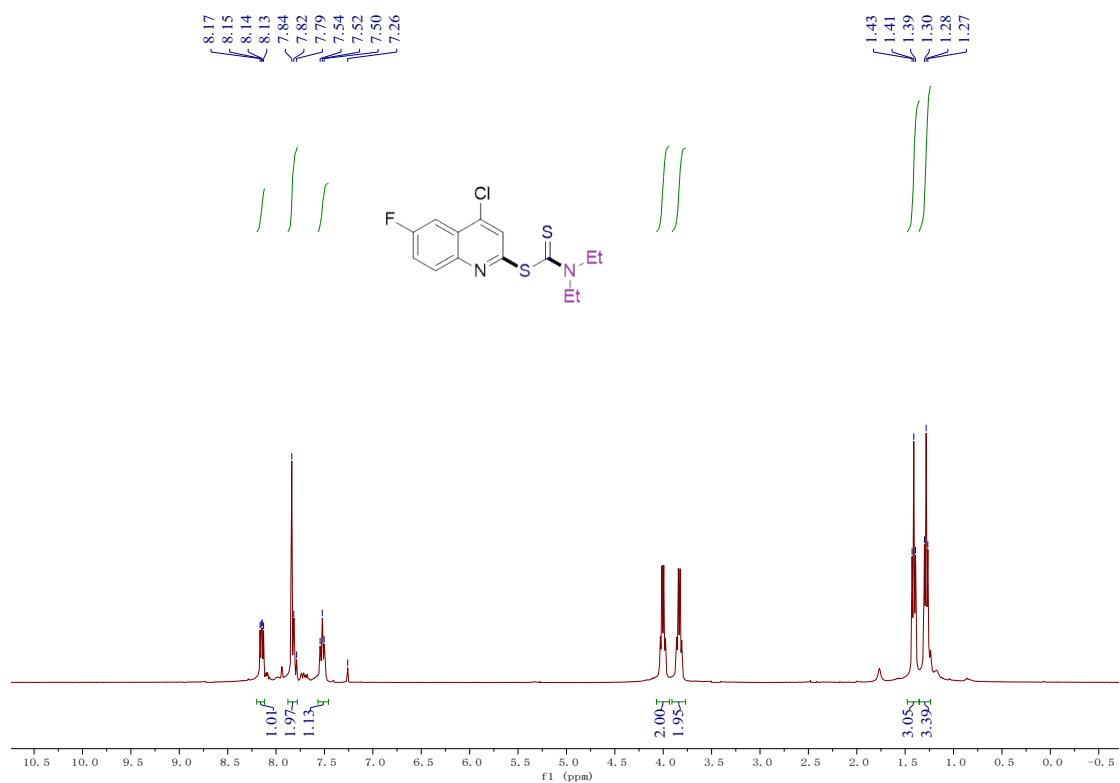




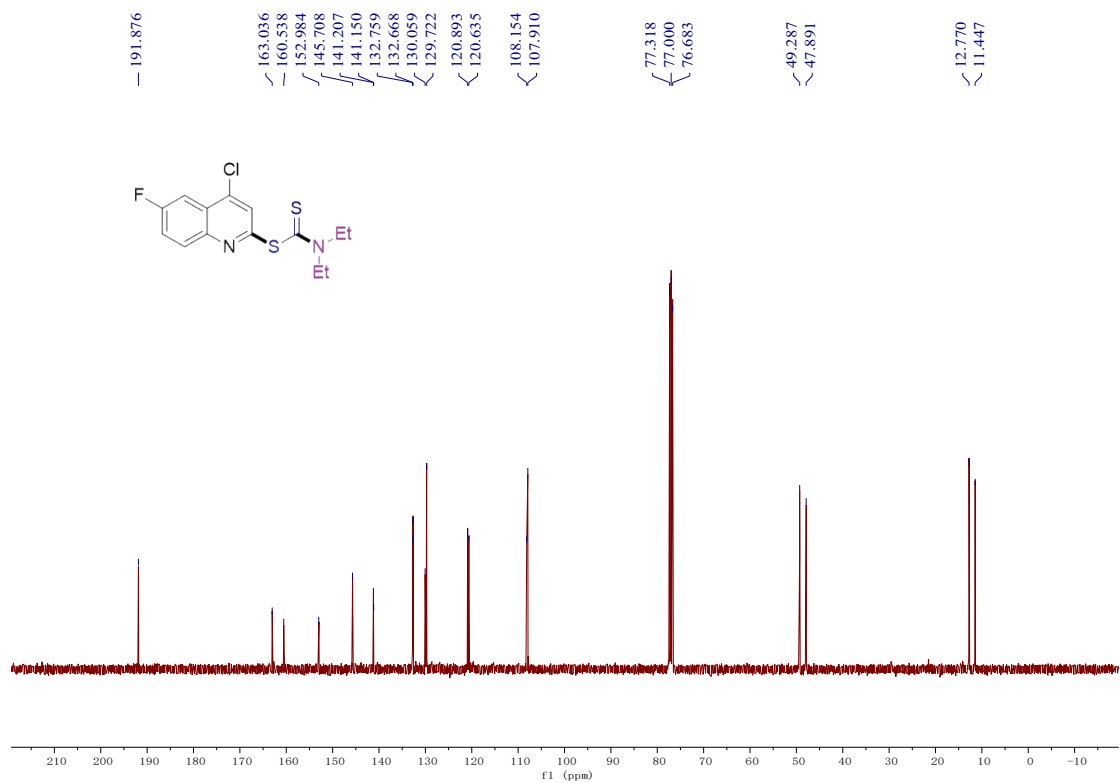
¹H spectrum of compound 3qa



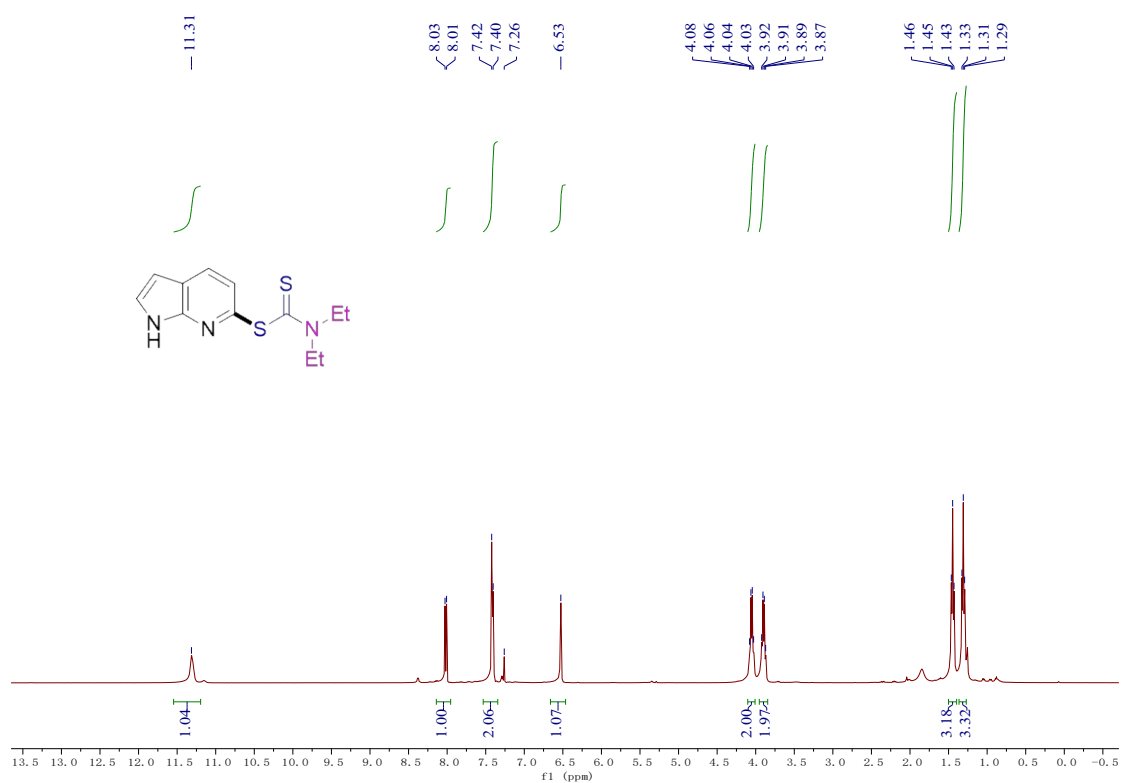
¹³C spectrum of compound 3qa



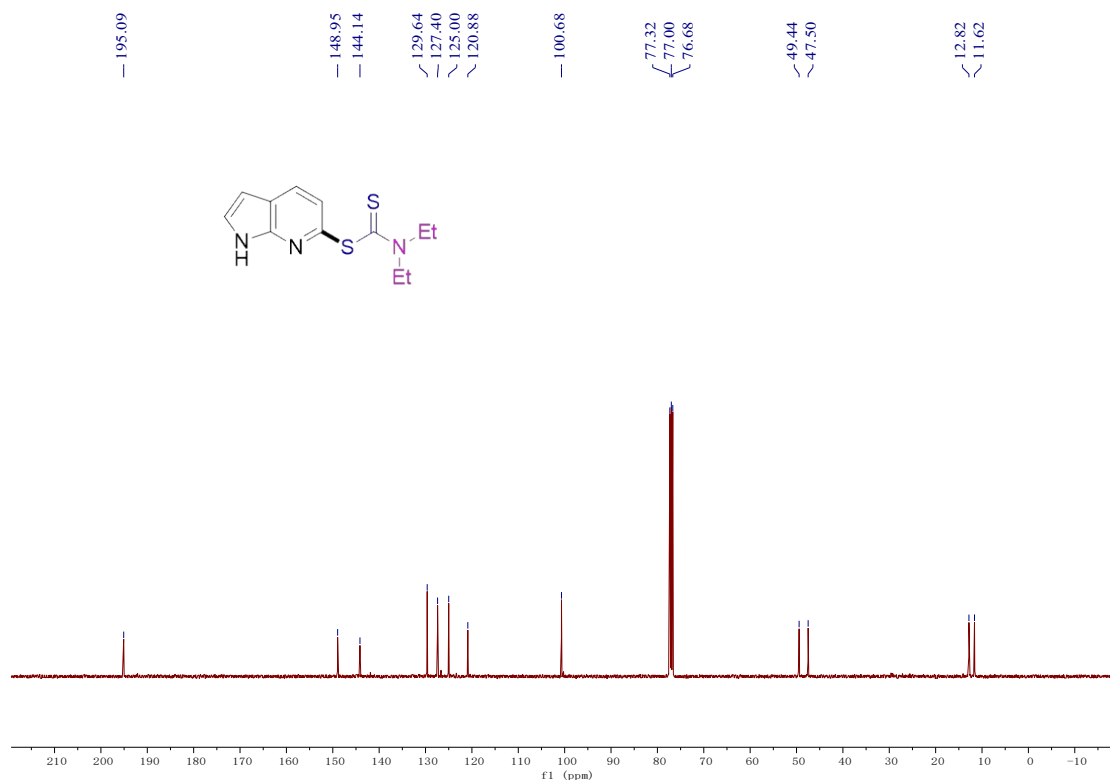
¹H spectrum of compound 3ra



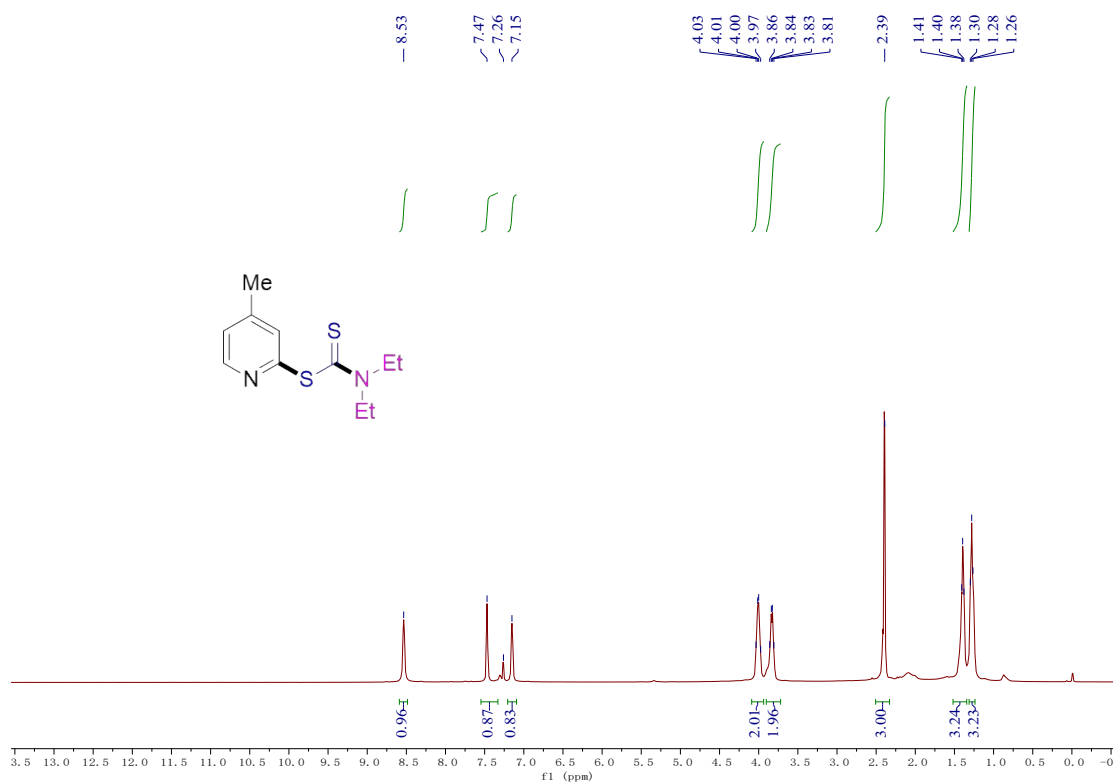
¹³C spectrum of compound 3ra



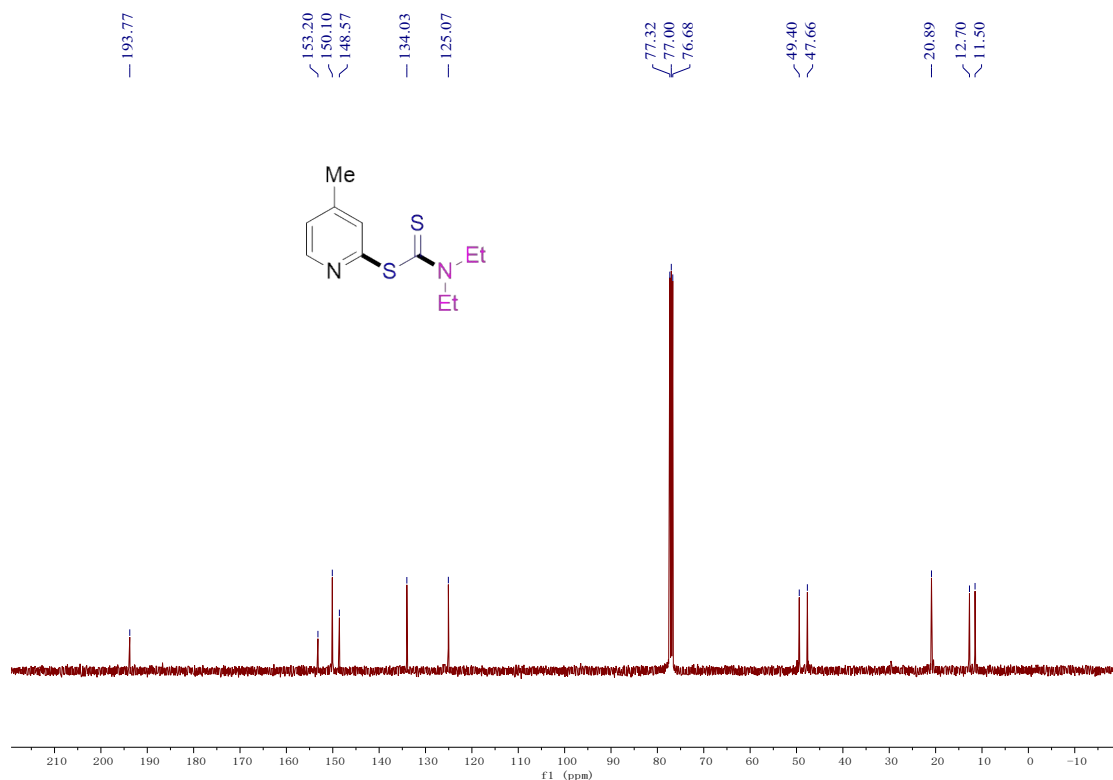
¹H spectrum of compound 3sa



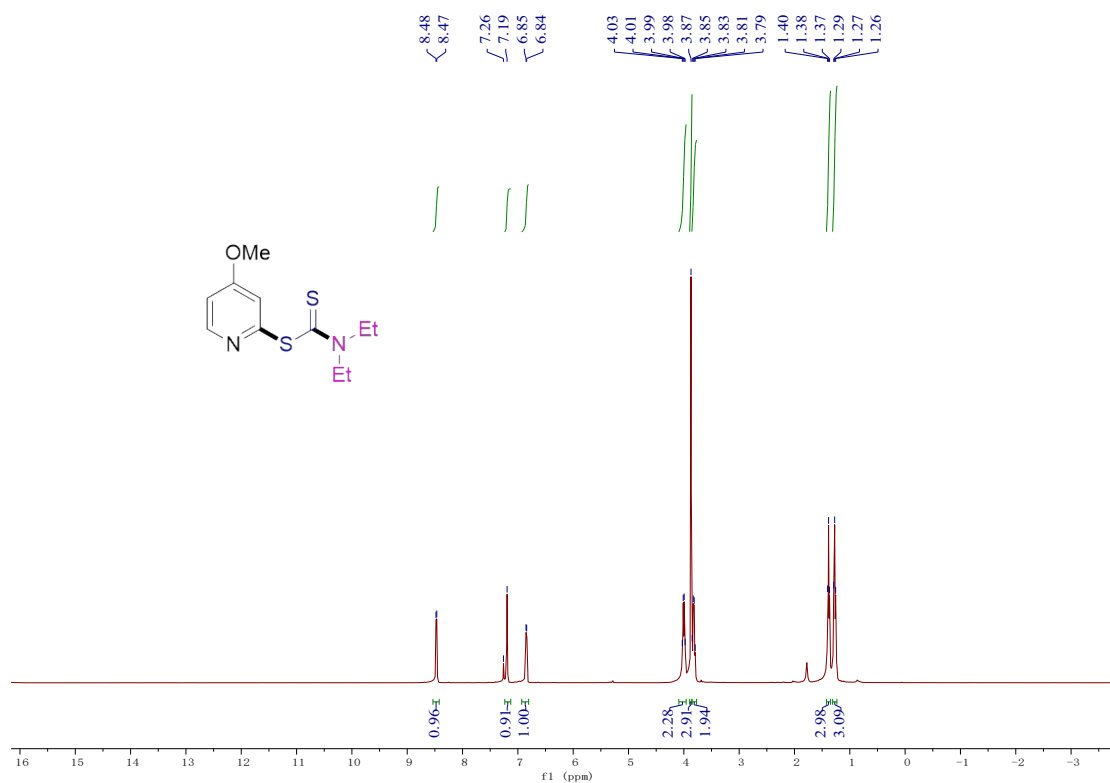
¹³C spectrum of compound 3sa



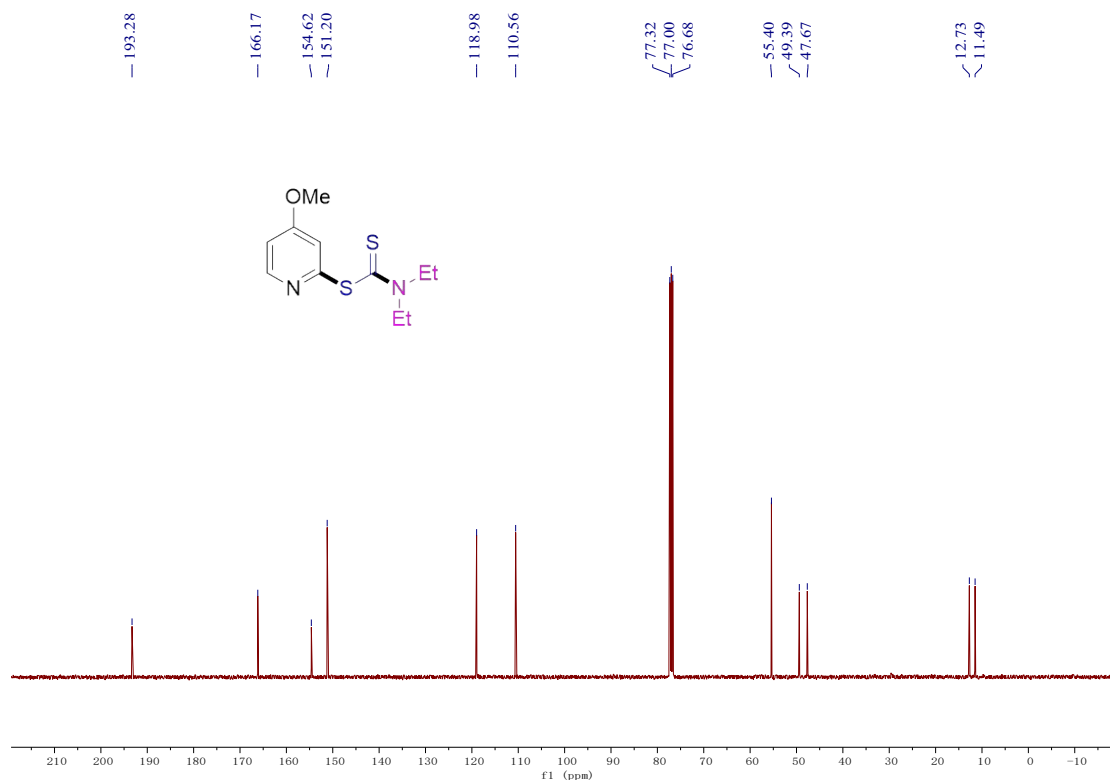
¹H spectrum of compound 3ta



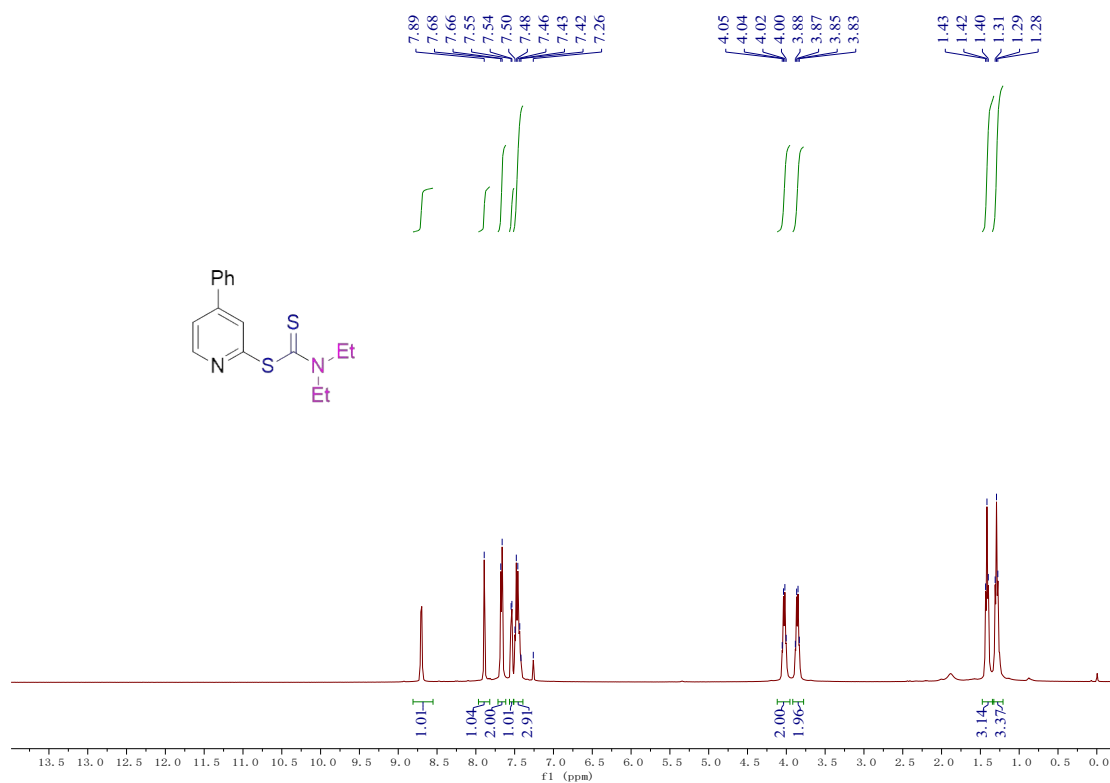
¹³C spectrum of compound 3ta



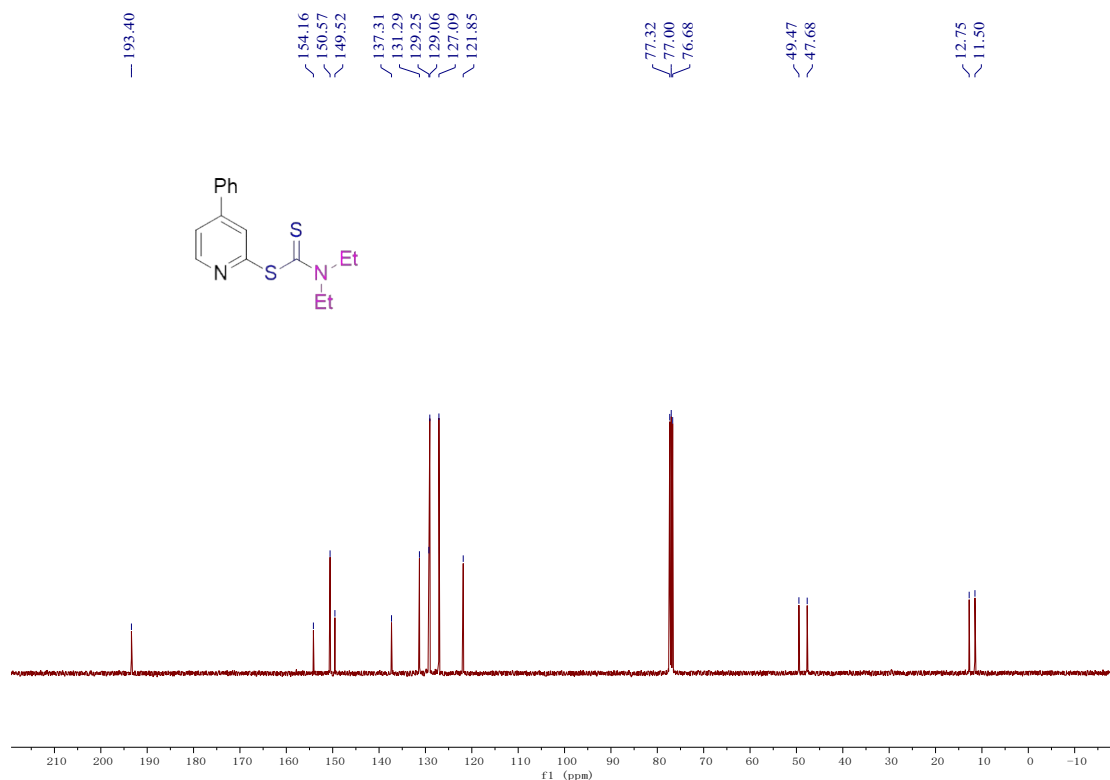
¹H spectrum of compound 3ua



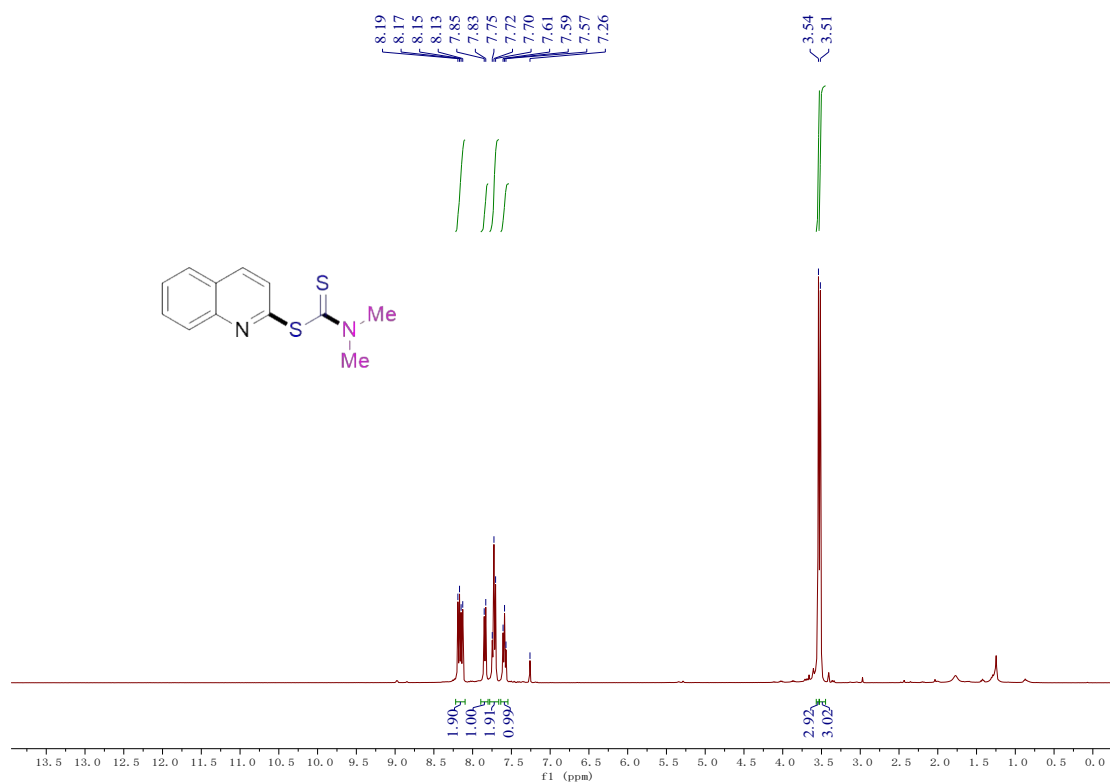
¹³C spectrum of compound 3ua



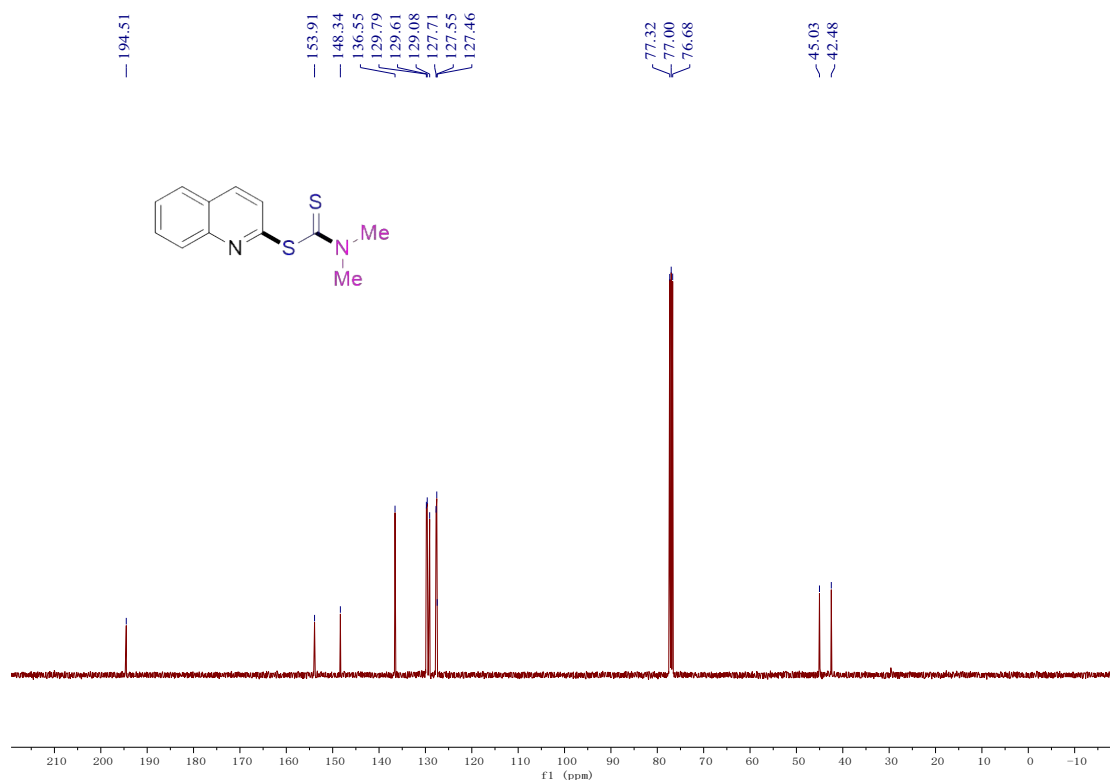
¹H spectrum of compound **3va**



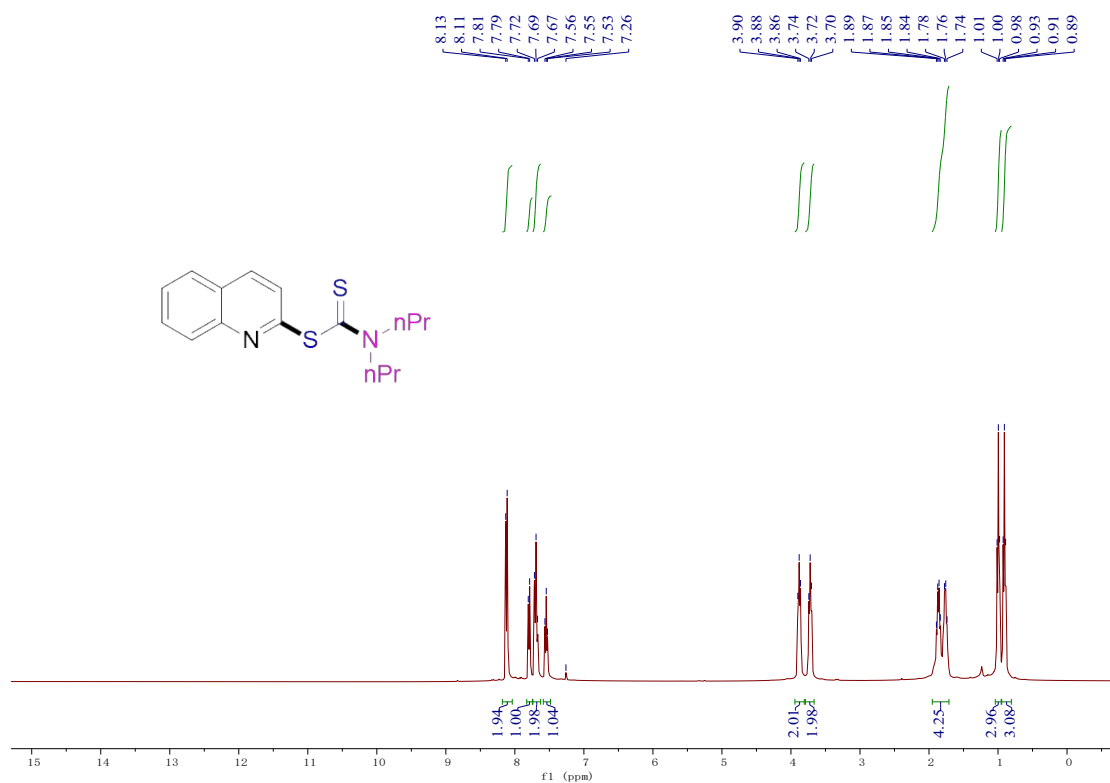
¹³C spectrum of compound **3va**



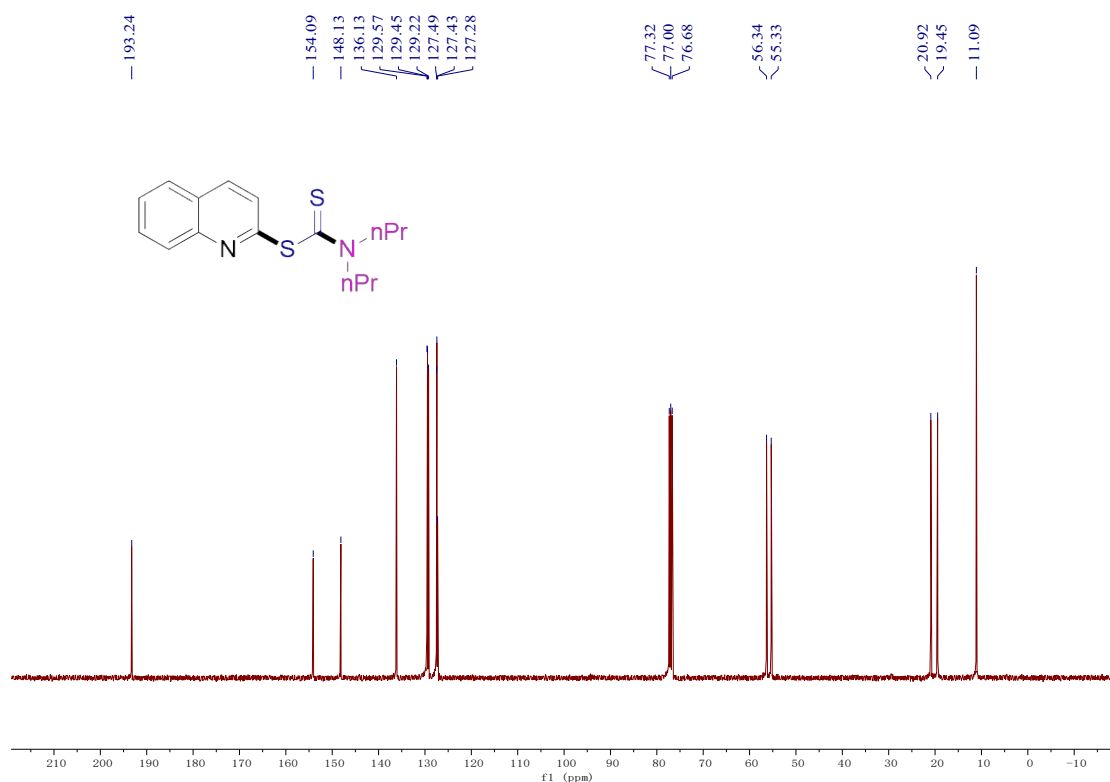
¹H spectrum of compound 3ab



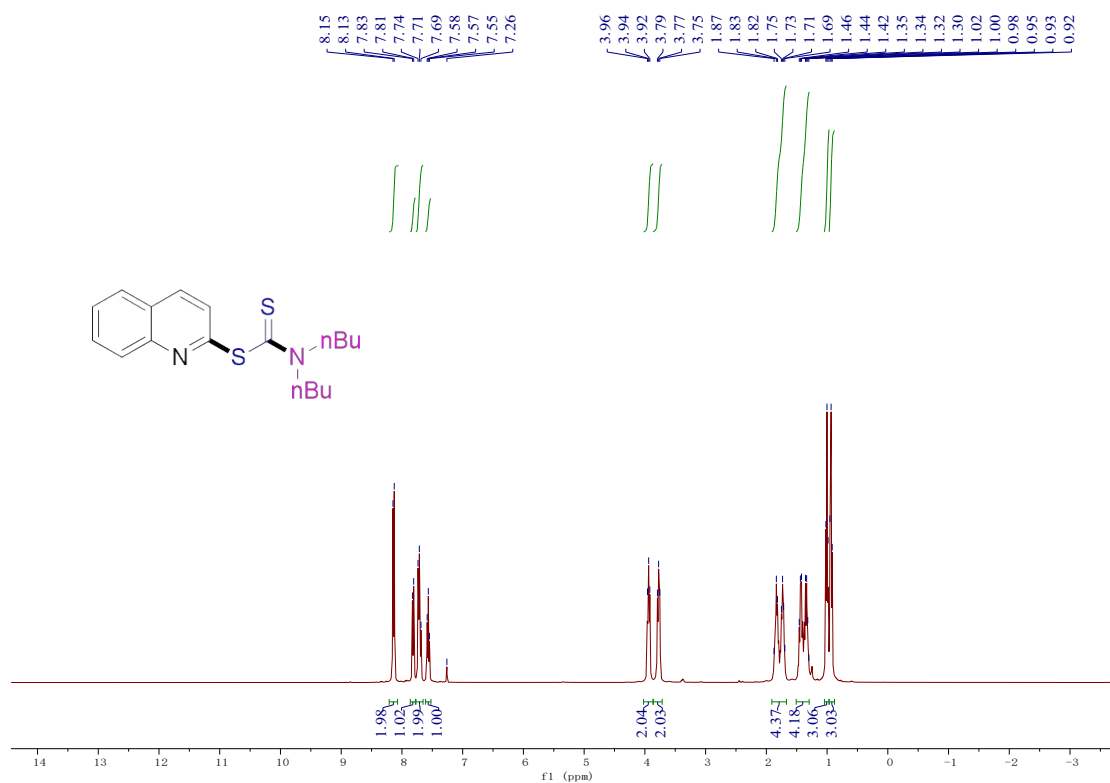
¹³C spectrum of compound 3ab



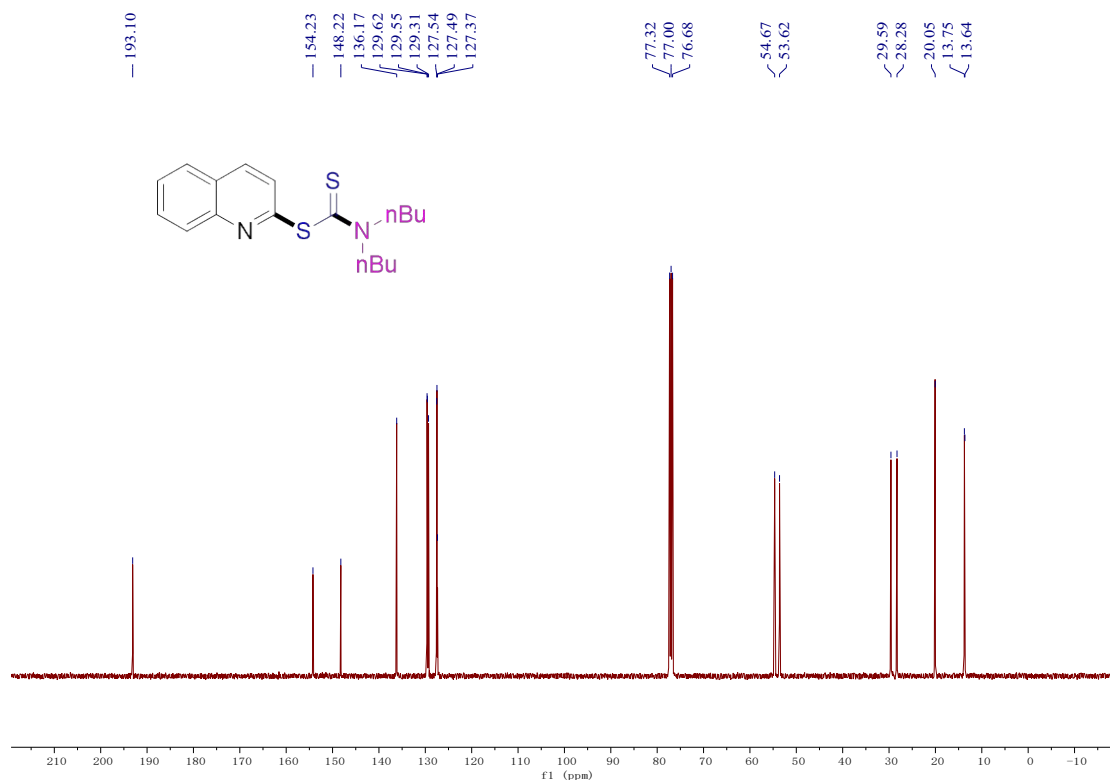
¹H spectrum of compound **3ac**



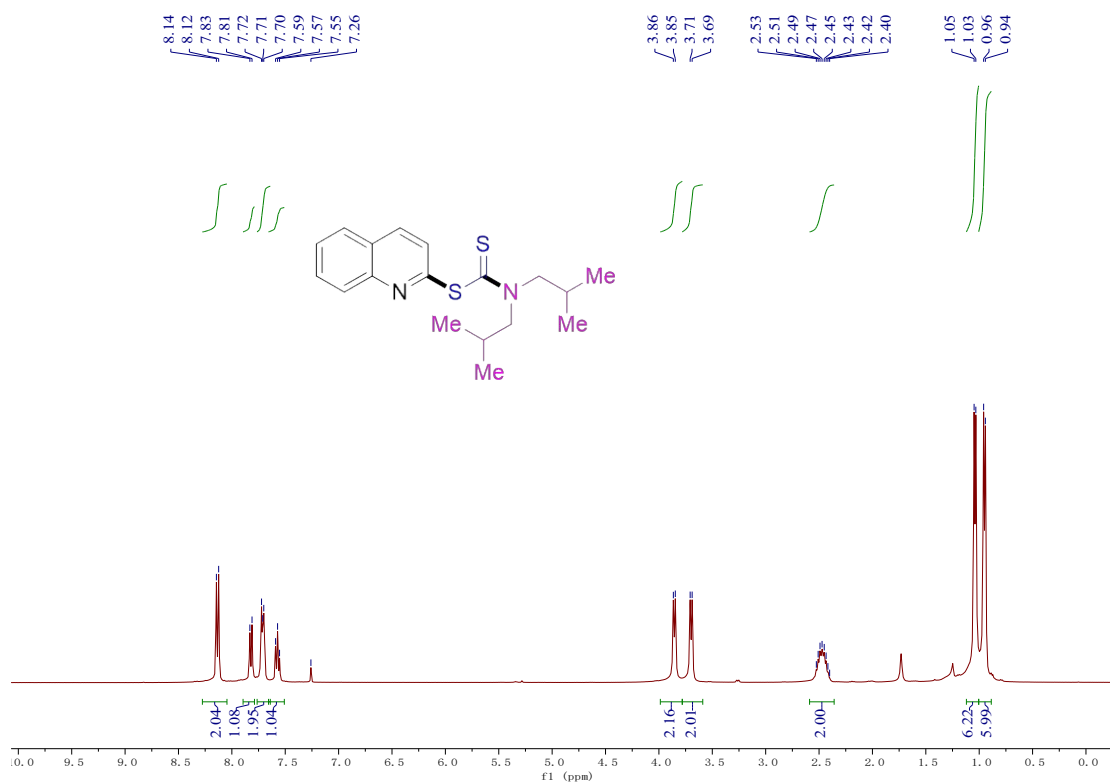
¹³C spectrum of compound **3ac**



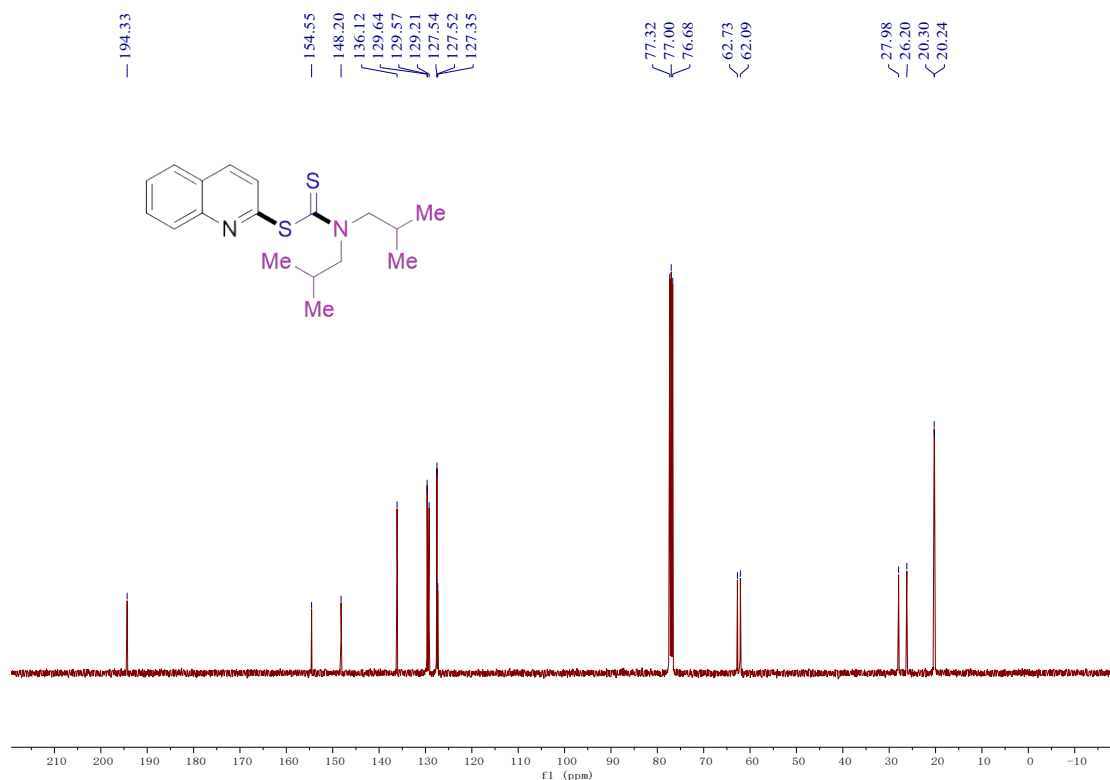
¹H spectrum of compound 3ad



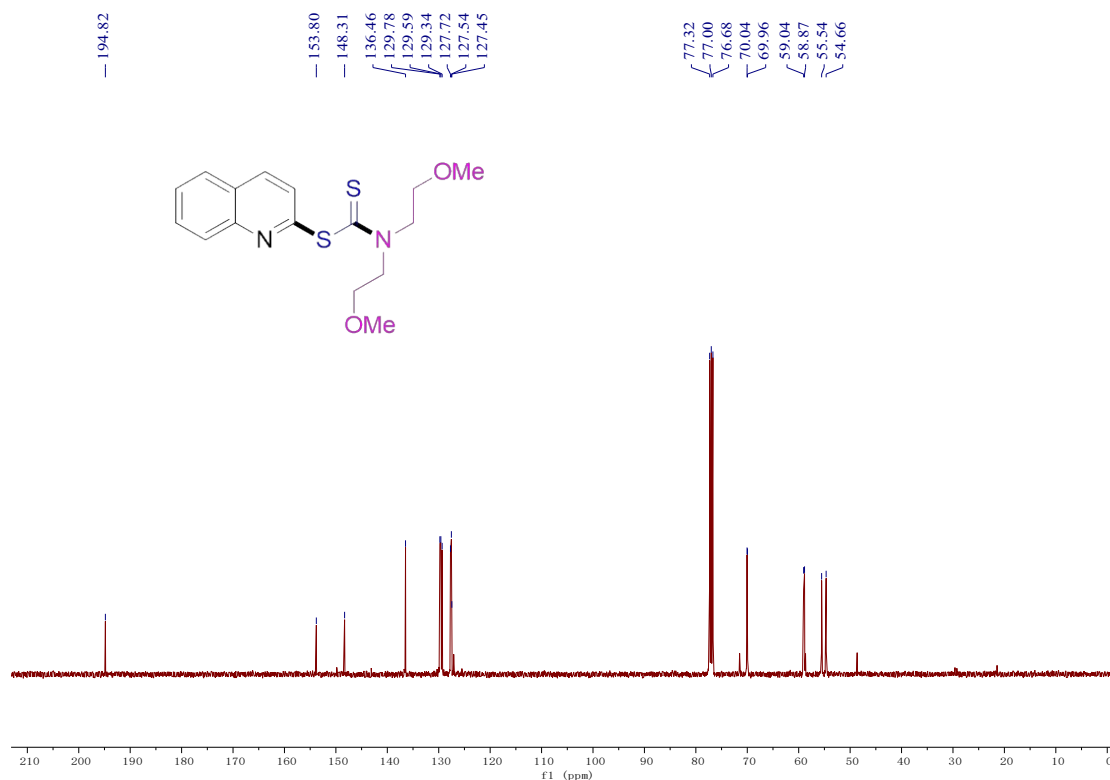
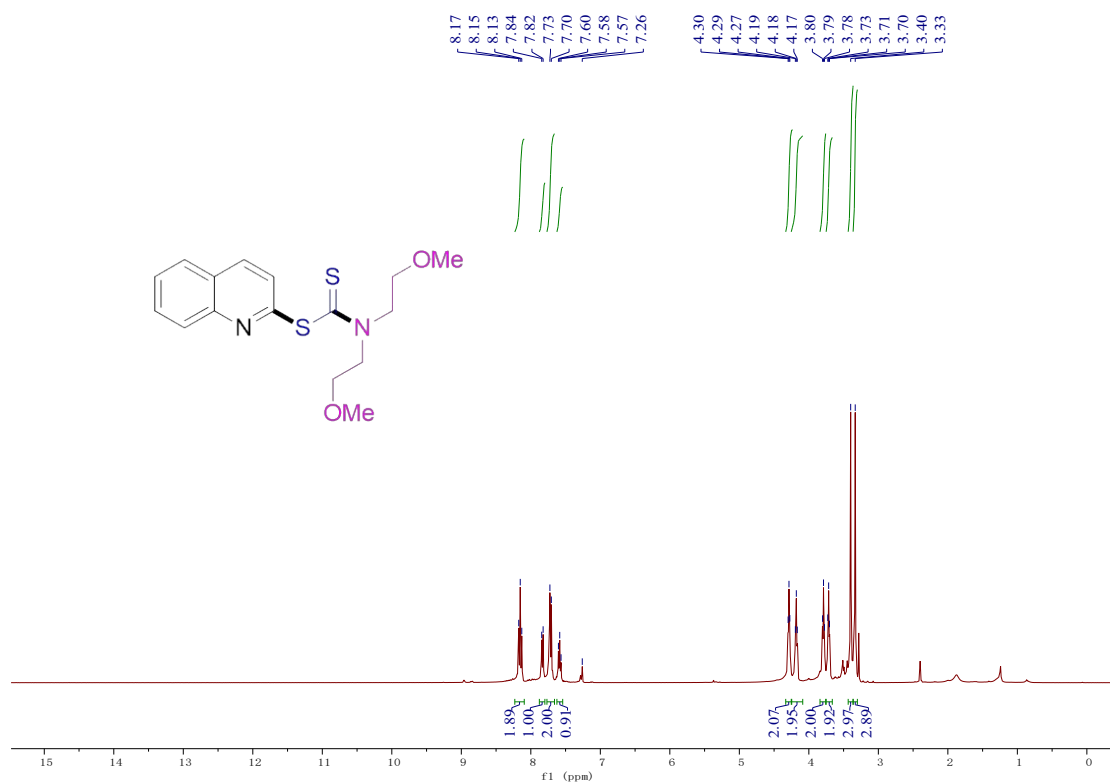
¹³C spectrum of compound 3ad

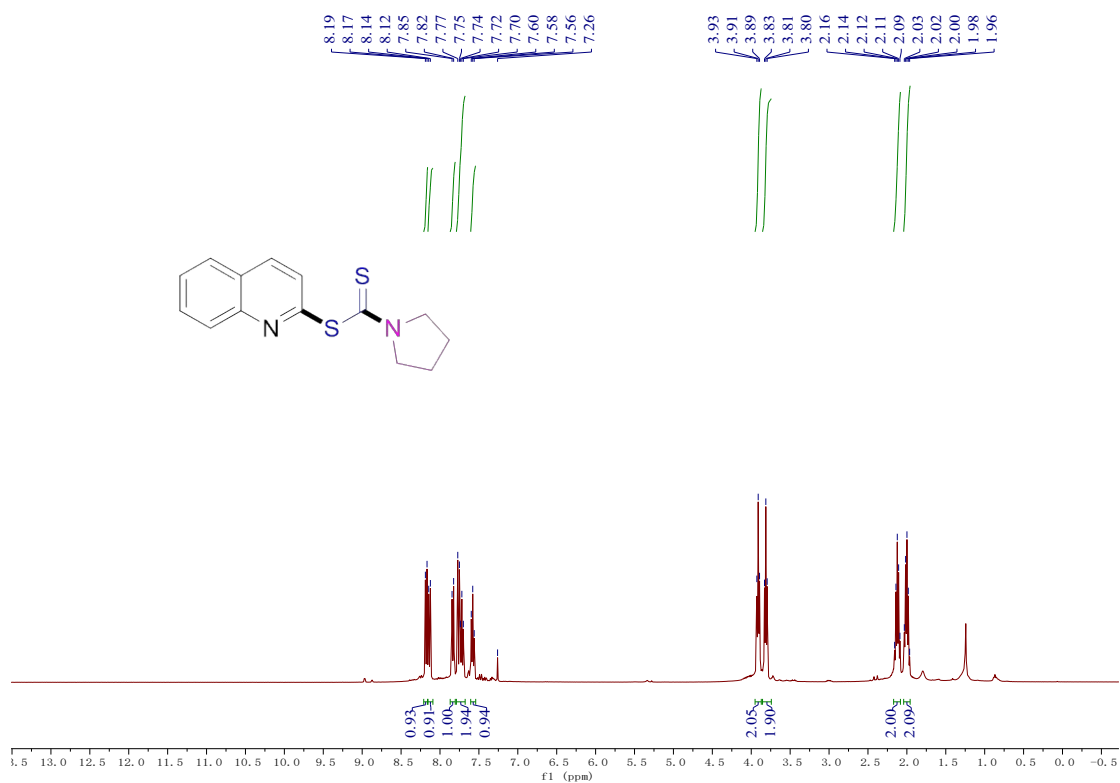


¹H spectrum of compound 3ae

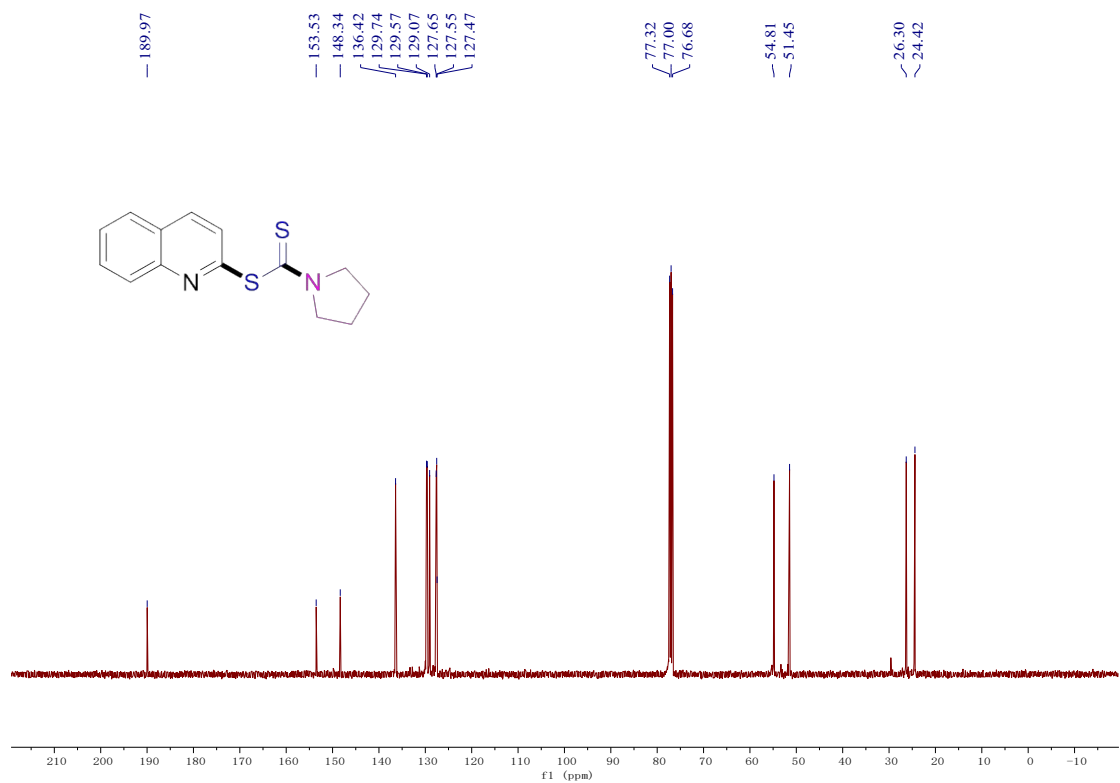


¹³C spectrum of compound 3ae

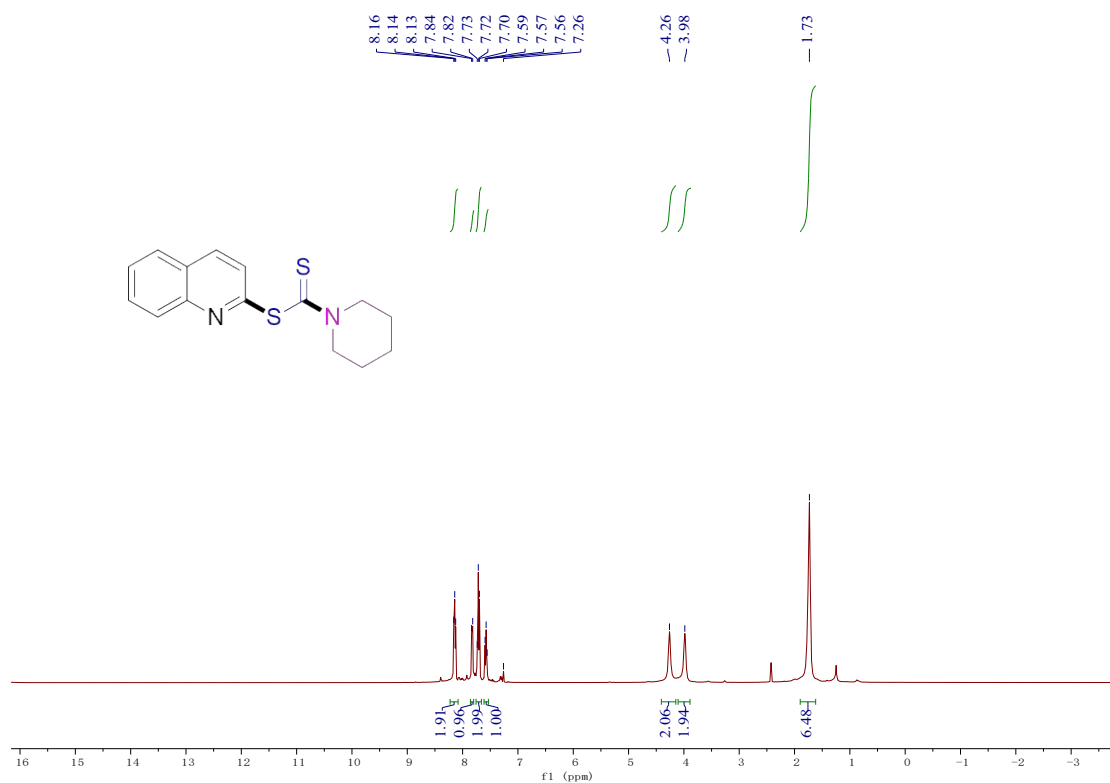




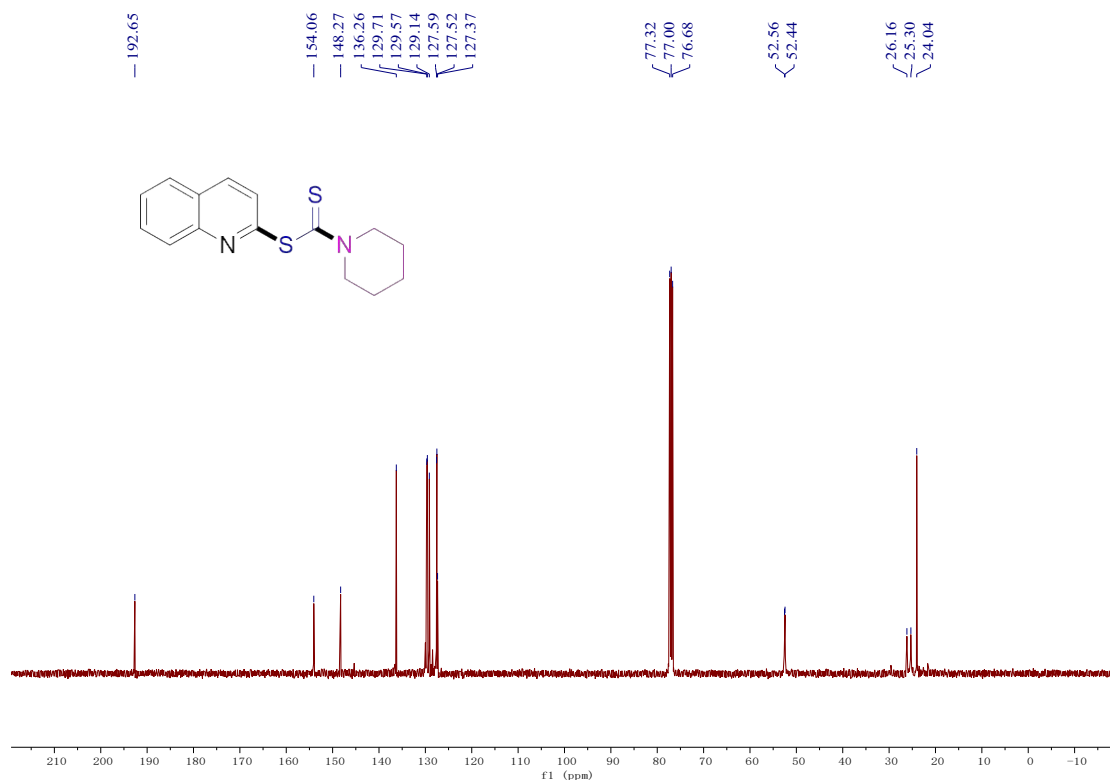
¹H spectrum of compound **3ag**



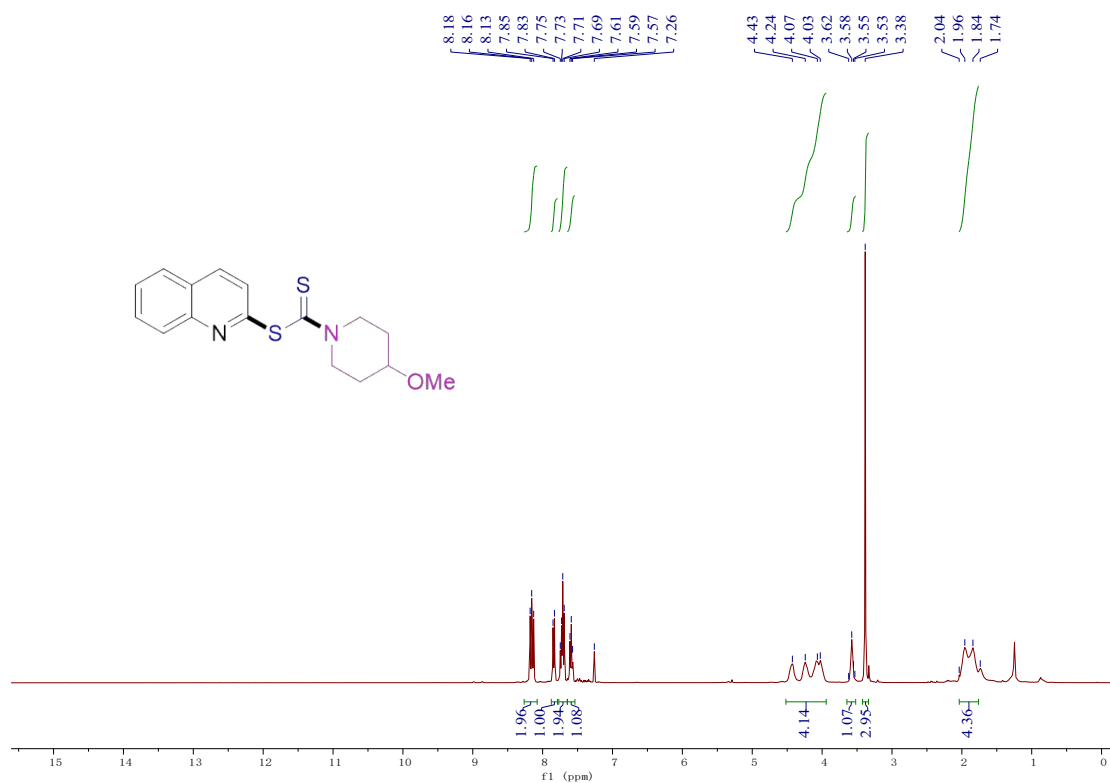
¹³C spectrum of compound **3ag**



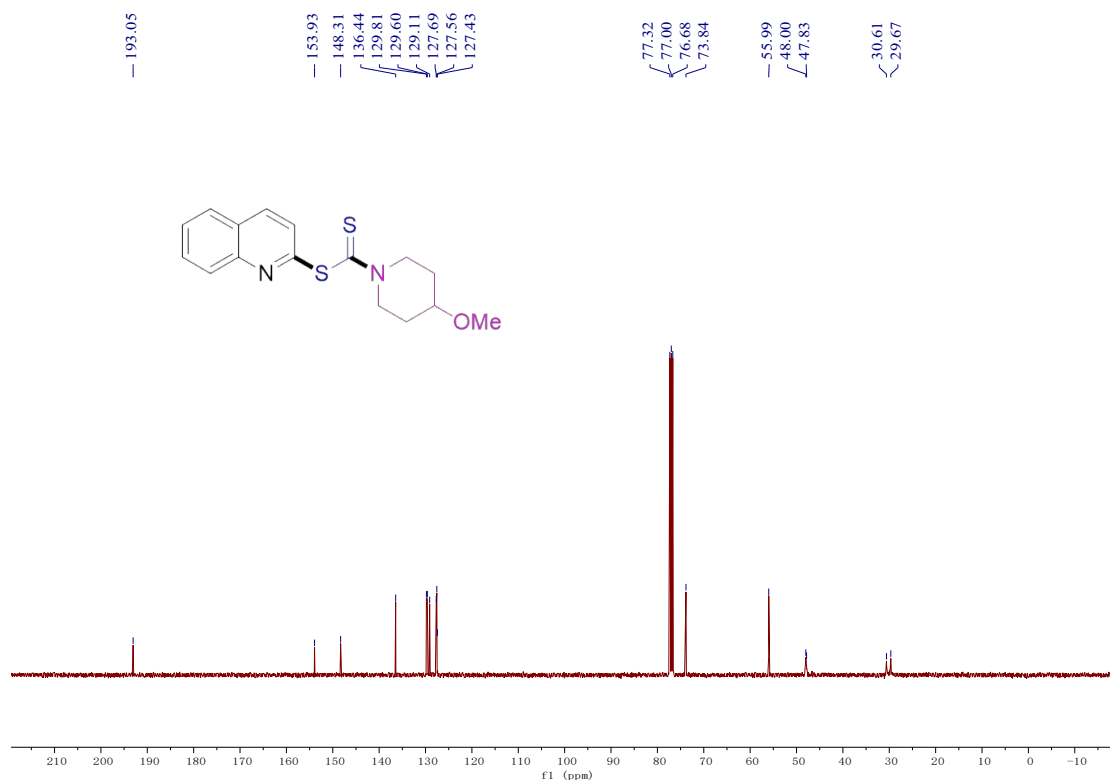
¹H spectrum of compound **3ah**



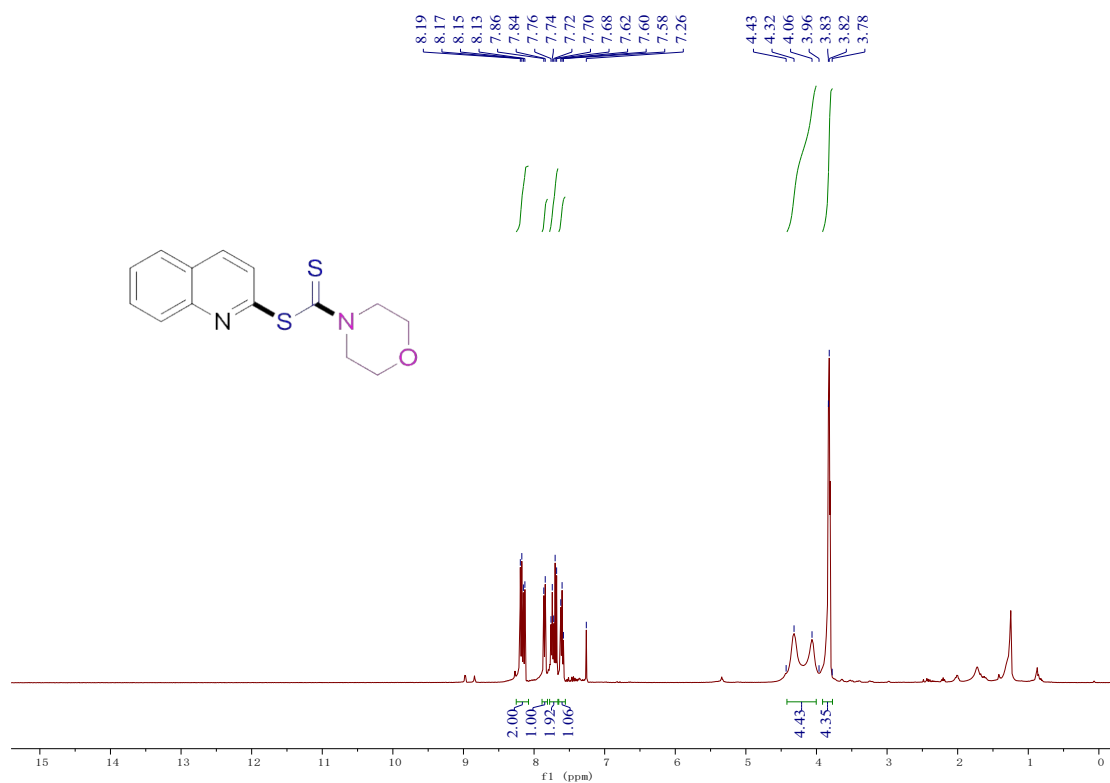
¹³C spectrum of compound **3ah**



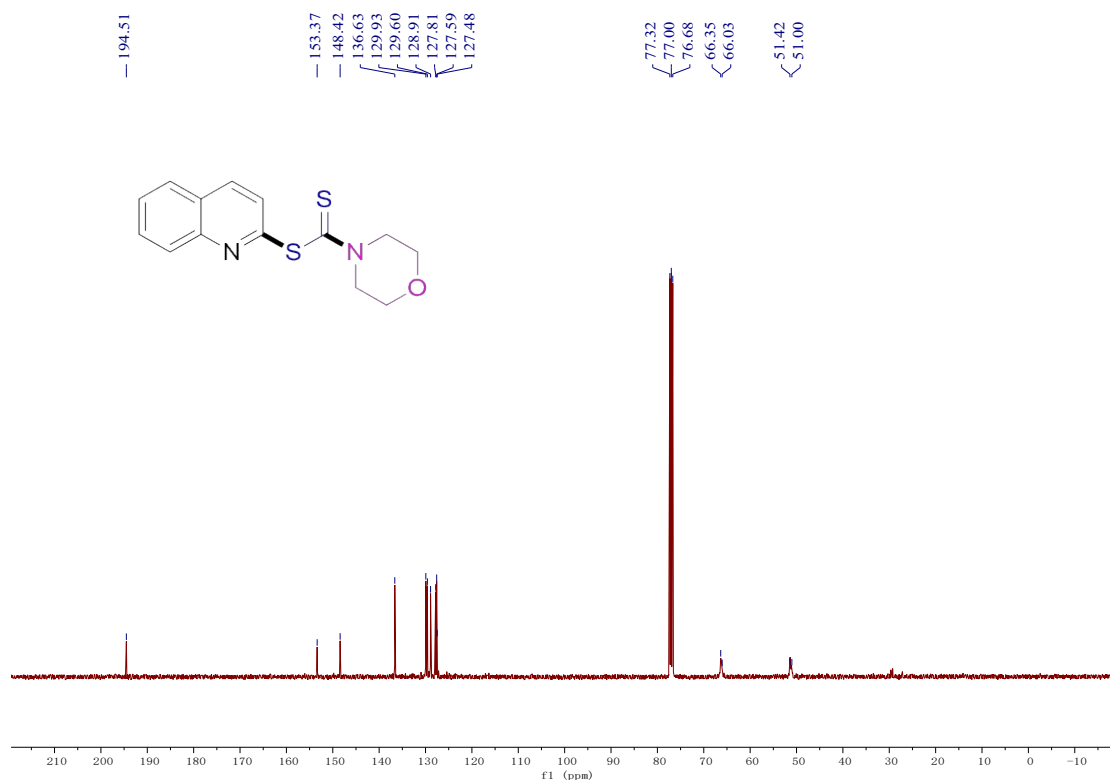
¹H spectrum of compound 3ai



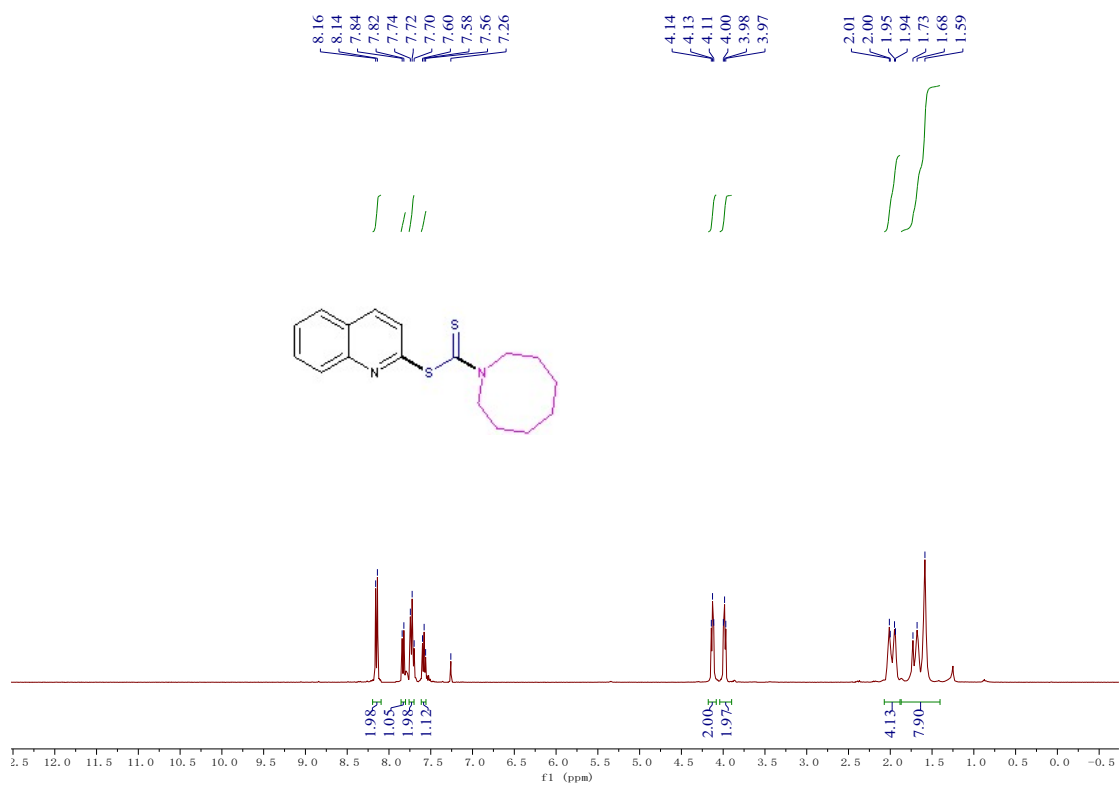
¹³C spectrum of compound 3ai



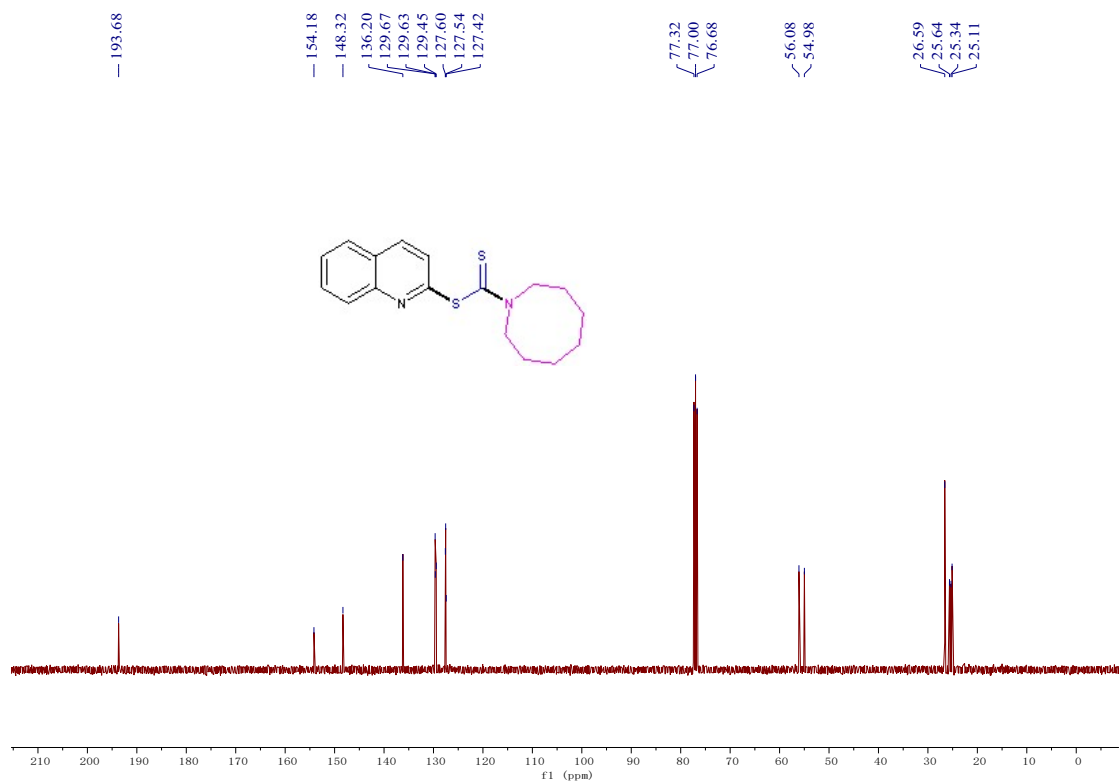
¹H spectrum of compound **3aj**



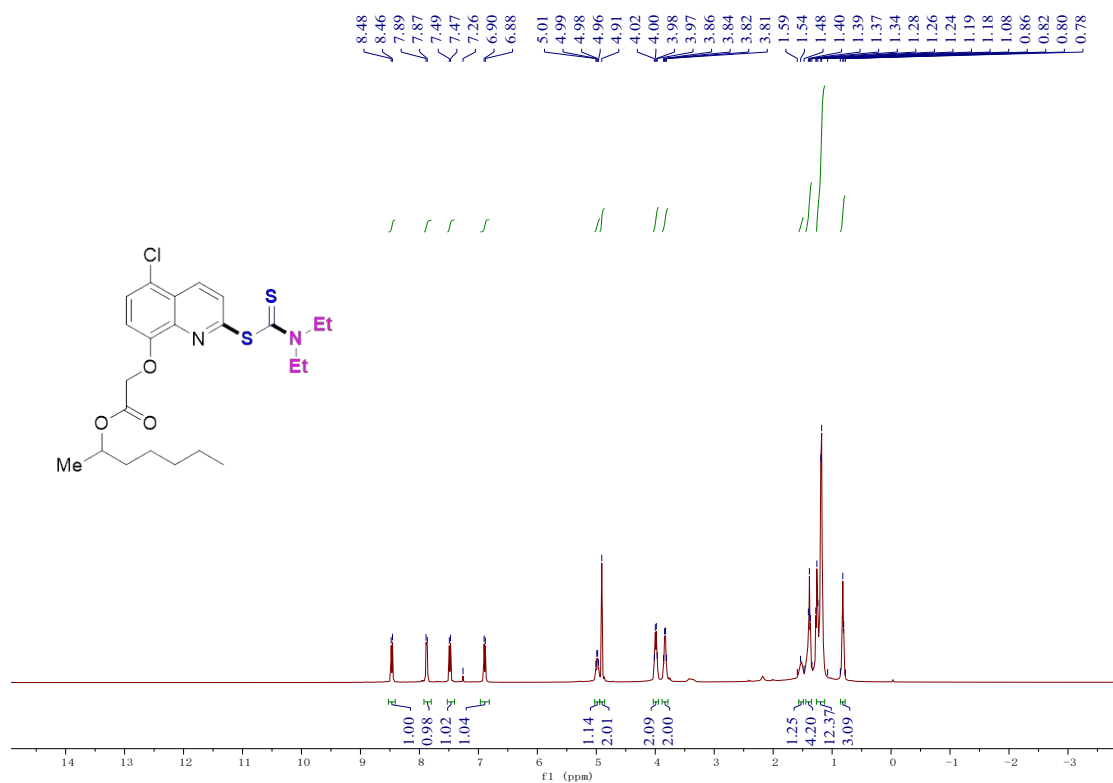
¹³C spectrum of compound **3aj**



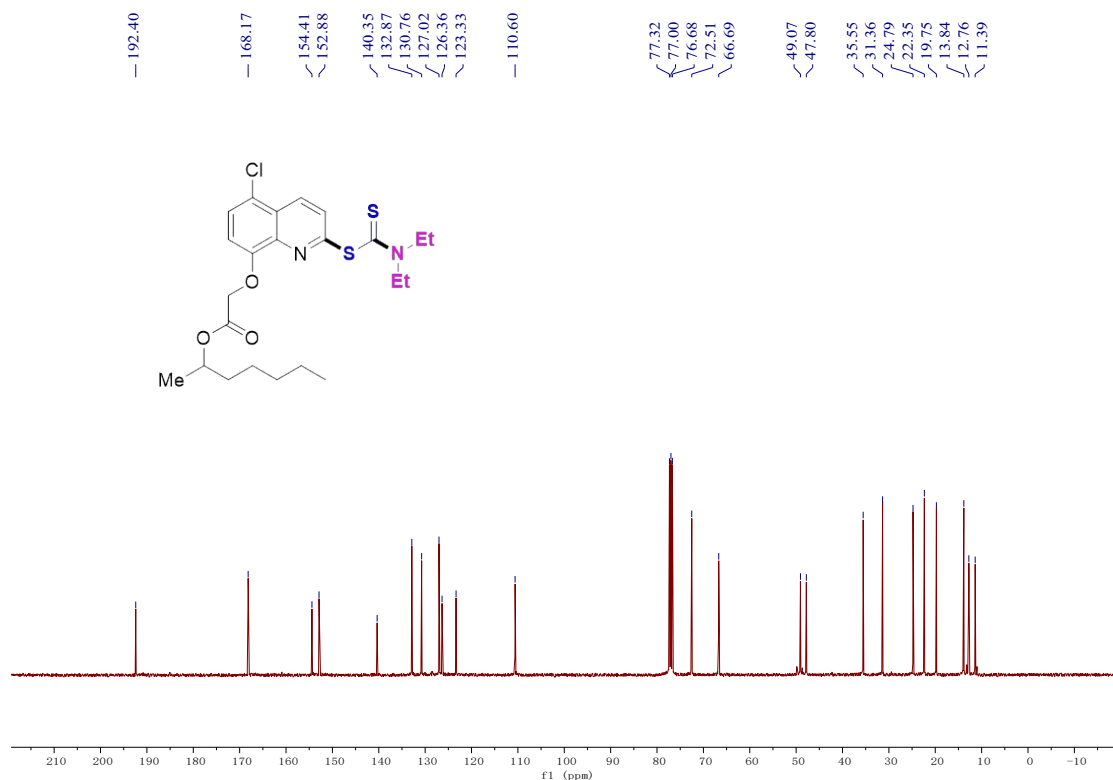
¹H spectrum of compound **3ak**



¹³C spectrum of compound **3ak**



¹H spectrum of compound 4ca



¹³C spectrum of compound 4ca