

Supporting Information

Ball milling synthesis of *S*-quinolyl xanthates *via* coupling of haloquinolines with potassium *O*-alkyl xanthates

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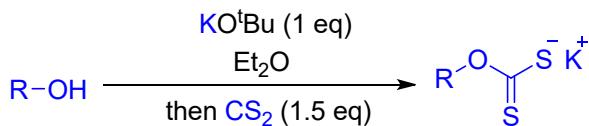
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1. General information

Unless otherwise specified, all reagents and solvents were obtained from commercial suppliers 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). Data are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, etc. 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.

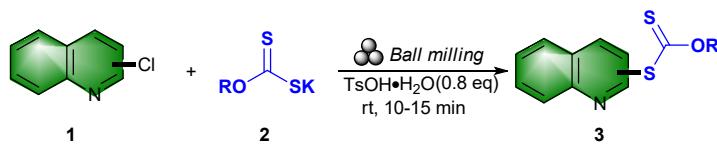
2. Experimental Section

General procedure for the preparation of *O*-alkyl xanthates 2



O-alkyl xanthates **2** were synthesized according to Wu's work.¹ In a N_2 -filled glovebox, an oven-dried 50 mL round-bottom flask equipped with a magnetic stir bar was charged sequentially with alcohol (2.0 mmol, 1.0 equiv.), $\text{KO}^\ddagger\text{Bu}$ (2.0 mmol, 1.0 equiv.), and dry Et_2O (20 mL). The flask was sealed with a septum cap and transferred out of the glovebox, and a balloon was attached. The reaction mixture was stirred at room temperature for 30 minutes, followed by the addition of CS_2 (3.0 mmol, 1.5 equiv.) via syringe and continued to be stirred for 3 hours at room temperature. The precipitate formed was collected by filtration, washed with Et_2O (2×10 mL), and dried in vacuo to afford the desired product.

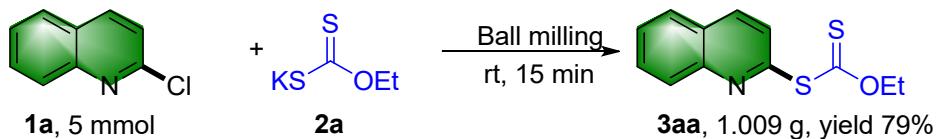
General procedure for the preparation of *S*-quinolyl xanthates



A mixture of chlorinated quinoline **1** (0.5 mmol, 1 eq), *O*-alkyl xanthate **2** (0.75 mmol, 1.5 eq) and p-toluene sulfonic acid (0.4 mmol, 0.8 eq) were milled in a stainless steel jar charged with 1 ball (10 mm) of the same material at 20 Hz for 10 – 15 min. After completion, ethyl acetate (10 mL) and water (10

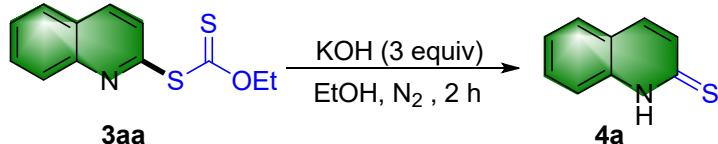
mL) were added to the mixture, the organic layer was separated and the aqueous layer was further extracted with ethyl acetate (2×10 mL). The combined organic layers were dried with anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The resulting organic residue was purified by flash chromatography column over silica gel to afford the desired S-quinolyl xanthates **3**.

Gram-scale synthesis of **3aa**



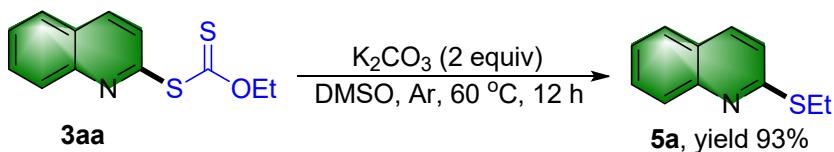
A mixture of 2-chloroquinoline **1a** (5 mmol, 0.815 g), potassium *O*-ethyl xanthate **2a** (7.5 mmol, 1.199 g) and p-toluene sulfonic acid (4 mmol, 0.761 g) were milled in a stainless steel jar charged with 1 ball (10 mm) of the same material at 20Hz for 15 min. After completion, ethyl acetate (30 mL) and water (30 mL) were added to the mixture, the organic layer was separated and the aqueous layer was further extracted with ethyl acetate (2×20 mL). The combined organic layers were dried with anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The resulting organic residue was purified by flash chromatography column over silica gel to afford 1.009 g of **3aa**, isolated yield 79%.

Synthesis of **4a** via hydrolysis of **3aa**



The experiment was carried out according to Karchava's work.² *O*-ethyl S-quinolin-2-yl carbonodithioate **3aa** (0.5 mmol, 0.1245 g) and KOH (1.5 mmol, 0.271 g) were dissolved in anhydrous ethanol (5 mL), the mixture was stirred at room temperature under N₂ atmosphere for 2 h. After completion, CH₂Cl₂ (10 mL) and water (10 mL) were added to the mixture, the organic layer was separated and the aqueous layer was further extracted with CH₂Cl₂ (2×10 mL). The combined organic layers were dried with anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The resulting organic residue was purified by flash chromatography column over silica gel (EA/PE 1:4 - 1:2) to afford 0.070 g of **4a**, isolated yield 87%.

Synthesis of **5a** via the release of carbonyl sulfide from **3aa**



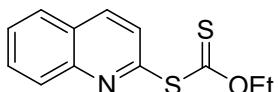
The experiment was carried out according to Wang's work.³ *O*-ethyl S-quinolin-2-yl carbonodithioate **3aa** (0.5 mmol, 0.1245 g) and K₂CO₃ (1 mmol, 0.138 g) were dissolved in DMSO (5 mL), the mixture was stirred at 60 °C under argon atmosphere for 12 h. After completion, CH₂Cl₂ (10 mL) and water (10 mL) were added to the mixture, the organic layer was separated and the aqueous layer was further extracted with CH₂Cl₂ (2 × 10 mL). The combined organic layers were dried with anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The resulting organic residue was purified by flash chromatography column over silica gel (EA/PE 1:20- 1:10) to afford 0.088 g f **5a**, isolated yield 93%.

Synthesis of **6a** via the coupling of **3aa** with 1-(4-bromophenyl)ethanone



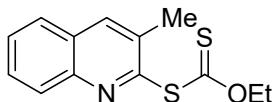
The experiment was carried out according to Karchava's work.² *O*-ethyl S-quinolin-2-yl carbonodithioate **3aa** (0.5 mmol, 0.1245 g), 1-(4-bromophenyl)ethanone (0.75 mmol, 0.148 g) and Cs₂CO₃ (1.5 mmol, 0.489 g) were dissolved in DMSO (5 mL), the reaction mixture was stirred at room temperature under the irradiation of 10 W blue LED lamps (440 – 445 nm) and N₂ atmosphere for 12 h. After completion, CH₂Cl₂ (10 mL) and water (10 mL) were added to the mixture, the organic layer was separated and the aqueous layer was further extracted with CH₂Cl₂ (2 × 10 mL). The combined organic layers were dried with anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The resulting organic residue was purified by flash chromatography column over silica gel (EA/PE 1:10- 1:6) to afford 0.095 g f **6a**, isolated yield 68%.

3. Characterization data of products

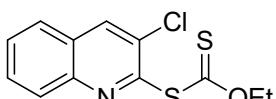


O-ethyl S-quinolin-2-yl carbonodithioate (3aa): Yellow oil (105.8 mg, 85%). ¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, *J* = 8.5 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 4.63 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz,

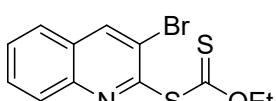
3H); ^{13}C NMR (100 MHz, CDCl_3) δ 210.5, 153.0, 148.3, 137.0, 130.2, 129.5, 127.8, 127.6, 127.3, 127.2, 70.3, 13.5; HRMS (ESI): m/z [M+H] $^+$ calcd for $\text{C}_{12}\text{H}_{12}\text{NOS}_2$: 250.0355; found: 250.0357.



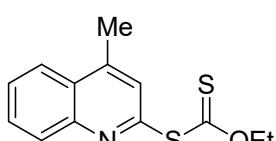
O-ethyl S-(3-methylquinolin-2-yl) carbonodithioate (3ba): Yellow oil (99.9 mg, 76%). ^1H NMR (400 MHz, CDCl_3) δ 8.10 (d, $J = 8.5$ Hz, 1H), 8.03 (s, 1H), 7.76 (d, $J = 8.1$ Hz, 1H), 7.67 (t, $J = 7.5$ Hz, 1H), 7.56 (t, $J = 7.4$ Hz, 1H), 4.57 (q, $J = 7.0$ Hz, 2H), 2.58 (s, 3H), 1.26 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 210.4, 153.0, 147.1, 137.1, 134.9, 129.3, 129.2, 128.4, 127.9, 126.7, 70.2, 20.2, 13.5; HRMS (ESI): m/z [M+H] $^+$ calcd for $\text{C}_{13}\text{H}_{14}\text{NOS}_2$: 264.0511; found: 264.0512.



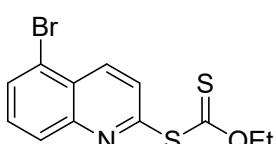
O-ethyl S-(3-chloroquinolin-2-yl) carbonodithioate (3ca): Yellow oil (90.5 mg, 64%). ^1H NMR (400 MHz, Chloroform- d) δ 8.26 (s, 1H), 8.11 (d, $J = 8.4$ Hz, 1H), 7.83 – 7.69 (m, 2H), 7.63 (t, $J = 7.5$ Hz, 1H), 4.58 (q, $J = 7.1$ Hz, 2H), 1.26 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, Chloroform- d) δ 208.7, 150.9, 146.5, 136.3, 132.6, 130.4, 129.7, 129.0, 128.6, 126.7, 70.6, 13.5; HRMS (ESI): m/z [M+H] $^+$ calcd for $\text{C}_{12}\text{H}_{11}\text{ClNOS}_2$: 283.9965; found: 283.9968.



O-ethyl S-(3-bromoquinolin-2-yl) carbonodithioate (3da): Yellow oil (101.4 mg, 62%). ^1H NMR (400 MHz, Chloroform- d) δ 8.47 (s, 1H), 8.12 (d, $J = 8.5$ Hz, 1H), 7.77 (t, $J = 7.7$ Hz, 2H), 7.64 (t, $J = 7.5$ Hz, 1H), 4.60 (q, $J = 7.1$ Hz, 2H), 1.28 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, Chloroform- d) δ 208.7, 152.1, 146.9, 140.1, 130.5, 129.7, 128.9, 128.7, 126.5, 122.8, 70.5, 13.5; HRMS (ESI): m/z [M+H] $^+$ calcd for $\text{C}_{12}\text{H}_{11}\text{BrNOS}_2$: 327.9459; found: 327.9462.

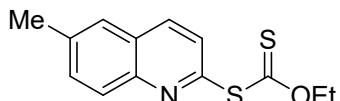


O-ethyl S-(4-methylquinolin-2-yl) carbonodithioate (3ea): Yellow oil (96.0 mg, 73%). ^1H NMR (400 MHz, Chloroform- d) δ 8.12 (d, $J = 8.4$ Hz, 1H), 8.00 (d, $J = 8.3$ Hz, 1H), 7.74 (t, $J = 7.6$ Hz, 1H), 7.62 (t, $J = 7.6$ Hz, 1H), 7.53 (s, 1H), 4.63 (q, $J = 7.1$ Hz, 2H), 2.72 (s, 3H), 1.32 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 210.7, 152.6, 148.1, 145.6, 130.1, 129.8, 127.6, 127.5, 127.4, 123.8, 70.2, 18.7, 13.5. HRMS (ESI): m/z [M+H] $^+$ calcd for $\text{C}_{12}\text{H}_{12}\text{NOS}_2$: 264.0511; found: 264.0513.

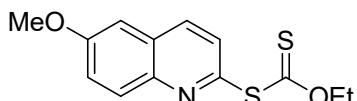


O-ethyl S-(5-bromoquinolin-2-yl) carbonodithioate (3fa): Yellow oil (109.5 mg, 67%). ^1H NMR (400 MHz, Chloroform- d) δ 8.53 (d, $J = 8.8$ Hz, 1H), 8.07 (d, $J = 8.5$ Hz, 1H), 7.85 (d, $J = 7.5$ Hz, 1H), 7.78 (d, $J = 8.7$ Hz, 1H), 7.58 (t, $J = 8.0$ Hz, 1H), 4.64 (q, $J = 7.1$ Hz, 2H), 1.34 (t, $J = 7.1$ Hz, 3H). ^{13}C

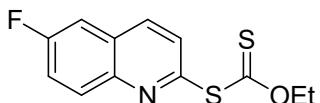
NMR (100 MHz, CDCl₃) δ 209.7, 154.3, 148.8, 136.4, 131.4, 130.4, 129.4, 128.1, 126.8, 121.7, 70.5, 13.5. HRMS (ESI): m/z [M+H]⁺ calcd for C₁₂H₁₁BrNOS₂: 327.9459; found: 327.9461.



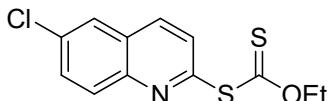
O-ethyl S-(6-methylquinolin-2-yl) carbonodithioate (3ga): Yellow oil (101.3 mg, 77%). ¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, *J* = 8.5 Hz, 1H), 8.01 (d, *J* = 8.5 Hz, 1H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.58 (d, *J* = 12.7 Hz, 2H), 4.62 (q, *J* = 7.1 Hz, 2H), 2.54 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 210.8, 151.8, 147.0, 138.0, 136.3, 132.4, 129.2, 127.3, 127.2, 126.4, 70.3, 21.6, 13.5; HRMS (ESI): m/z [M+H]⁺ calcd for C₁₂H₁₂NOS₂: 264.0511; found: 264.0514.



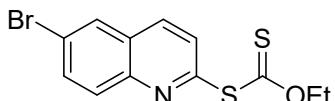
O-ethyl S-(6-methoxyquinolin-2-yl) carbonodithioate (3ha): Yellow oil (100.5 mg, 72%). ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J* = 8.5 Hz, 1H), 8.00 (d, *J* = 9.2 Hz, 1H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.38 (dd, *J* = 9.2, 2.3 Hz, 1H), 7.07 (d, *J* = 2.1 Hz, 1H), 4.61 (q, *J* = 7.1 Hz, 2H), 3.92 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 211.2, 158.8, 149.7, 144.5, 135.7, 131.0, 128.6, 127.7, 122.9, 104.9, 70.3, 55.6, 13.5; HRMS (ESI): m/z [M+H]⁺ calcd for C₁₃H₁₄NO₂S₂: 280.0460; found: 280.0464.



O-ethyl S-(6-fluoroquinolin-2-yl) carbonodithioate (3ia): Yellow oil (94.8 mg, 71%). ¹H NMR (400 MHz, CDCl₃) δ 8.13 (t, *J* = 8.5 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.56 – 7.43 (m, 2H), 4.63 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 210.4, 161.2 (d, *J*_{C-F} = 249.1 Hz), 152.4 (d, *J*_{C-F} = 2.9 Hz), 145.4, 136.3 (d, *J*_{C-F} = 5.4 Hz), 132.2 (d, *J*_{C-F} = 9.3 Hz), 128.2 (d, *J*_{C-F} = 10.3 Hz), 128.0, 120.5 (d, *J*_{C-F} = 25.7 Hz), 110.7 (d, *J*_{C-F} = 21.9 Hz), 70.4, 13.5; ¹⁹F NMR (376 MHz, CDCl₃) δ -110.76; HRMS (ESI): m/z [M+H]⁺ calcd for C₁₂H₁₁FNOS₂: 268.0261; found: 268.0262.

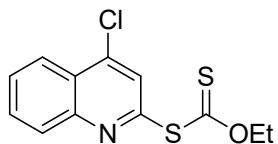


S-(6-chloroquinolin-2-yl) O-ethyl carbonodithioate (3ja): Yellow oil (103.3 mg, 73%). ¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, *J* = 8.5 Hz, 1H), 8.06 (d, *J* = 9.0 Hz, 1H), 7.83 (s, 1H), 7.70 (dd, *J* = 13.7, 8.8 Hz, 2H), 4.64 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 210.1, 153.5, 146.7, 135.9, 133.7, 131.1, 128.1, 127.9, 126.3, 70.5, 13.6; HRMS (ESI): m/z [M+H]⁺ calcd for C₁₂H₁₁ClNOS₂: 283.9965; found: 283.9963.

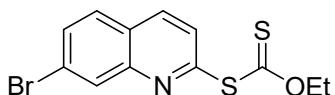


S-(6-bromoquinolin-2-yl) O-ethyl carbonodithioate (3ka): Yellow oil (104.6 mg, 64%). ¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, *J* = 8.3 Hz, 1H), 7.98 (d, *J* = 14.2 Hz, 2H), 7.80 (d, *J* = 8.8 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 1H), 4.63 (q, *J* = 6.4 Hz, 2H), 1.33 (t, *J* = 6.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ

210.0, 153.7, 146.8, 135.8, 133.7, 131.2, 129.6, 128.3, 128.0, 121.9, 70.5, 13.5; HRMS (ESI): m/z [M+H]⁺ calcd for C₁₂H₁₁BrNOS₂: 327.9460; found: 327.9462.



S-(4-chloroquinolin-2-yl) O-ethyl carbonodithioate (3la): Yellow oil (103.3 mg, 73%). ¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, *J* = 8.4 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.84 – 7.75 (m, 2H), 7.69 (t, *J* = 7.6 Hz, 1H), 4.64 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 209.3, 152.8, 148.7, 142.9, 131.0, 129.8, 128.7, 126.7, 125.5, 124.0, 70.5, 13.5; HRMS (ESI): m/z [M+H]⁺ calcd for C₁₂H₁₁ClNOS₂: 283.9965; found: 283.9968.



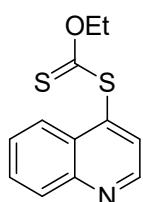
S-(7-bromoquinolin-2-yl) O-ethyl carbonodithioate (3ma): Yellow oil (111.2 mg, 68%). ¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, *J* = 8.5 Hz, 1H), 8.08 (d, *J* = 7.2 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 4.66 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 209.9, 154.9, 145.4, 137.2, 133.8, 128.6, 128.1, 127.8, 127.4, 124.9, 70.4, 13.6; HRMS (ESI): m/z [M+H]⁺ calcd for C₁₂H₁₁BrNOS₂: 327.9460; found: 327.9457.



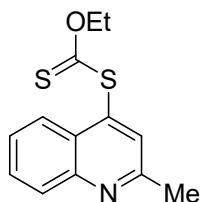
O-ethyl S-(8-methylquinolin-2-yl) carbonodithioate (3na): Yellow oil (107.8 mg, 82%). ¹H NMR (400 MHz, CDCl₃) δ 8.14 (d, *J* = 8.5 Hz, 1H), 7.68 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 7.0 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 4.66 (q, *J* = 7.2 Hz, 2H), 2.80 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 210.9, 152.1, 147.5, 137.7, 137.0, 130.2, 127.5, 127.3, 126.6, 125.5, 70.2, 17.8, 13.6; HRMS (ESI): m/z [M+H]⁺ calcd for C₁₃H₁₄NOS₂: 264.0511; found: 264.0511.



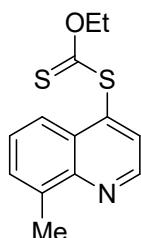
S-(8-bromoquinolin-2-yl) O-ethyl carbonodithioate (3oa): Yellow oil (91.5 mg, 56%). ¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, *J* = 8.5 Hz, 1H), 8.08 (d, *J* = 7.2 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 4.66 (q, *J* = 7.1 Hz), 1.36 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 209.9, 154.8, 145.4, 137.2, 133.8, 128.6, 128.1, 127.8, 127.4, 124.9, 70.4, 13.6; HRMS (ESI): m/z [M+H]⁺ calcd for C₁₂H₁₁BrNOS₂: 327.9460; found: 327.9466.



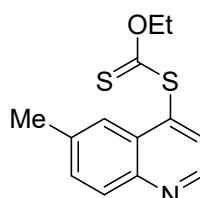
O-ethyl S-quinolin-4-yl carbonodithioate (3pa): Yellow oil (95.9 mg, 77%). ¹H NMR (400 MHz, CDCl₃) δ 8.93 (d, *J* = 3.9 Hz, 1H), 8.18 (dd, *J* = 22.0, 8.4 Hz, 2H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.60 (t, *J* = 7.1 Hz, 2H), 4.51 (q, *J* = 7.0 Hz, 2H), 1.13 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 208.8, 149.8, 148.7, 137.7, 130.0, 130.0, 128.5, 127.9, 127.7, 125.2, 70.6, 13.3; HRMS (ESI): m/z [M+H]⁺ calcd for C₁₂H₁₂NOS₂: 250.0355; found: 250.0357.



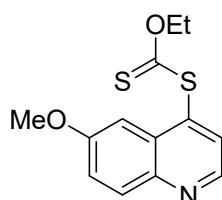
O-ethyl S-(2-methylquinolin-4-yl) carbonodithioate (3qa): Yellow oil (113.1 mg, 86%). ¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, *J* = 8.3 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.57 – 7.48 (m, 2H), 4.51 (q, *J* = 7.1 Hz, 2H), 2.75 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 209.1, 158.6, 148.4, 137.6, 129.9, 129.2, 128.7, 126.7, 126.6, 125.0, 70.5, 25.1, 13.3; HRMS (ESI): m/z [M+H]⁺ calcd for C₁₃H₁₄NOS₂: 264.0511; found: 264.0507.



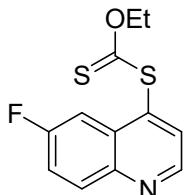
O-ethyl S-(8-methylquinolin-4-yl) carbonodithioate (3ra): Yellow oil (99.9 mg, 76%). ¹H NMR (400 MHz, CDCl₃) δ 8.98 – 8.88 (m, 1H), 8.08 (d, *J* = 8.3 Hz, 1H), 7.60 (t, *J* = 6.3 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 1H), 4.53 (q, *J* = 7.0 Hz, 2H), 2.83 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 209.2, 147.9, 148.5, 137.8, 137.7, 130.2, 128.5, 127.7, 127.3, 123.3, 70.5, 18.4, 13.3; HRMS (ESI): m/z [M+H]⁺ calcd for C₁₃H₁₄NOS₂: 264.0511; found: 264.0509.



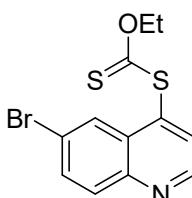
O-ethyl S-(6-methylquinolin-4-yl) carbonodithioate (3sa): Yellow oil (101.3 mg, 77%). ¹H NMR (400 MHz, CDCl₃) δ 8.77 (d, *J* = 4.3 Hz, 1H), 7.96 (d, *J* = 8.6 Hz, 1H), 7.88 (s, 1H), 7.49 (d, *J* = 5.0 Hz, 2H), 4.46 (q, *J* = 7.1 Hz, 2H), 2.46 (s, 3H), 1.08 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 209.2, 148.9, 147.5, 138.0, 136.9, 132.3, 129.8, 128.5, 128.1, 124.0, 70.6, 21.9, 13.4; HRMS (ESI): m/z [M+H]⁺ calcd for C₁₃H₁₄NOS₂: 264.0511; found: 264.0514.



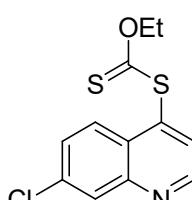
O-ethyl S-(6-methoxyquinolin-4-yl) carbonodithioate (3ta): Yellow oil (101.8 mg, 73%). ^1H NMR (400 MHz, CDCl_3) δ 8.77 (d, $J = 3.6$ Hz, 1H), 8.03 (d, $J = 9.1$ Hz, 1H), 7.57 (d, $J = 3.9$ Hz, 1H), 7.47 – 7.34 (m, 2H), 4.53 (q, $J = 7.1$ Hz, 2H), 3.91 (s, 3H), 1.17 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.8, 158.7, 147.1, 145.0, 135.9, 131.6, 129.9, 128.3, 122.8, 102.7, 70.5, 55.6, 13.4; HRMS (ESI): m/z [M+H] $^+$ calcd for $\text{C}_{13}\text{H}_{14}\text{NO}_2\text{S}_2$: 280.0460; found: 280.0465.



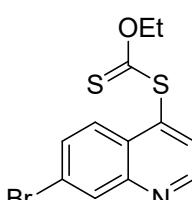
O-ethyl S-(6-fluoroquinolin-4-yl) carbonodithioate (3ua): Yellow oil (109.5 mg, 82%). ^1H NMR (400 MHz, CDCl_3) δ 8.89 (d, $J = 4.4$ Hz, 1H), 8.15 (dd, $J = 9.2, 5.4$ Hz, 1H), 7.82 (dd, $J = 9.7, 2.6$ Hz, 1H), 7.63 (d, $J = 4.3$ Hz, 1H), 7.56 – 7.47 (m, 1H), 4.54 (q, $J = 7.1$ Hz, 2H), 1.18 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.3, 161.2 (d, $J_{\text{C}-\text{F}} = 248.6$ Hz), 149.1 (d, $J_{\text{C}-\text{F}} = 2.9$ Hz), 145.9, 137.2 (d, $J_{\text{C}-\text{F}} = 5.9$ Hz), 132.7 (d, $J_{\text{C}-\text{F}} = 9.2$ Hz), 129.9 (d, $J_{\text{C}-\text{F}} = 10.3$ Hz), 128.7, 120.3 (d, $J_{\text{C}-\text{F}} = 25.7$ Hz), 108.9 (d, $J_{\text{C}-\text{F}} = 23.8$ Hz), 70.7, 13.3; ^{19}F NMR (376 MHz, CDCl_3) δ -110.25; HRMS (ESI): m/z [M+H] $^+$ calcd for $\text{C}_{12}\text{H}_{11}\text{FNOS}_2$: 268.0261; found: 268.0263.



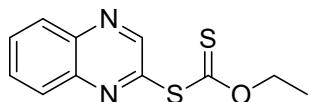
O-ethyl S-(6-bromoquinolin-4-yl) carbonodithioate (3va): Yellow oil (137.3 mg, 84%). ^1H NMR (400 MHz, CDCl_3) δ 8.92 (d, $J = 4.3$ Hz, 1H), 8.35 (d, $J = 1.4$ Hz, 1H), 8.00 (d, $J = 8.9$ Hz, 1H), 7.80 (dd, $J = 8.9$ Hz, 1.4 Hz, 1H), 7.62 (d, $J = 4.3$ Hz, 1H), 4.55 (q, $J = 7.1$ Hz, 2H), 1.20 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.1, 150.2, 147.4, 136.8, 133.5, 131.7, 129.7, 128.8, 127.5, 122.2, 70.8, 13.4; HRMS (ESI): m/z [M+H] $^+$ calcd for $\text{C}_{12}\text{H}_{11}\text{BrNOS}_2$: 327.9460; found: 327.9455.



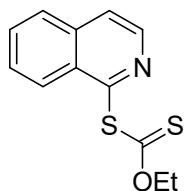
O-ethyl S-(7-chloroquinolin-4-yl)carbonodithioate (3wa): Yellow oil (117.4 mg, 83%). ^1H NMR (400 MHz, CDCl_3) δ 8.93 (d, $J = 4.3$ Hz, 1H), 8.31 – 8.06 (m, 1H), 7.60 (d, $J = 4.3$ Hz, 1H), 7.54 (d, $J = 9.0$ Hz, 1H), 4.53 (q, $J = 7.1$ Hz, 2H), 1.17 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.3, 151.0, 149.1, 137.9, 135.9, 128.9, 128.6, 128.1, 127.1, 126.8, 70.7, 13.4; HRMS (ESI): m/z [M+H] $^+$ calcd for $\text{C}_{12}\text{H}_{11}\text{ClNOS}_2$: 283.9965; found: 283.9967.



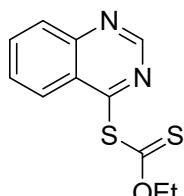
O-ethyl S-(7-bromoquinolin-4-yl) carbonodithioate (3xa): Yellow oil (143.9 mg, 88%). ¹H NMR (400 MHz, CDCl₃) δ 9.02 – 8.86 (m, 1H), 8.32 (s, 1H), 8.07 (d, *J* = 8.9 Hz, 1H), 7.67 (d, *J* = 8.9 Hz 1H), 7.62 (d, *J* = 4.2 Hz 1H), 4.52 (q, *J* = 7.1 Hz, 2H), 1.17 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 208.2, 150.9, 149.3, 138.0, 132.3, 131.1, 128.2, 127.3, 126.8, 124.2, 70.7, 13.4; HRMS (ESI): m/z [M+H]⁺ calcd for C₁₂H₁₁BrNOS₂: 327.9460; found: 327.9464.



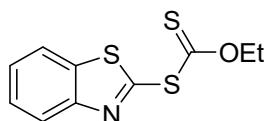
O-ethyl S-quinoxalin-2-yl carbonodithioate (3ya): Yellow oil (97.5 mg, 78%). ¹H NMR (400 MHz, CDCl₃) δ 8.99 (s, 1H), 8.10 (t, *J* = 6.3 Hz, 2H), 7.84 – 7.75 (m, 2H), 4.63 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 209.0, 149.6, 142.4, 141.0, 131.1, 130.6, 129.4, 129.2, 70.8, 13.5; HRMS (ESI): m/z [M+H]⁺ calcd for C₁₁H₁₁N₂OS₂: 251.0307; found: 251.0308.



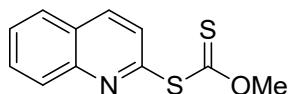
O-ethyl S-isoquinolin-1-yl carbonodithioate (3za): Yellow oil (79.1 mg, 63%). ¹H NMR (400 MHz, CDCl₃) δ 8.60 (d, *J* = 5.5 Hz, 1H), 8.38 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.79 – 7.71 (m, 2H), 7.67 (t, *J* = 7.6 Hz, 1H), 4.51 (q, *J* = 7.0 Hz, 2H), 1.13 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 210.2, 153.2, 142.8, 137.1, 130.9, 130.7, 128.5, 127.2, 127.1, 122.8, 70.3, 13.4; HRMS (ESI): m/z [M+H]⁺ calcd for C₁₂H₁₂NOS₂: 250.0355; found: 250.0358.



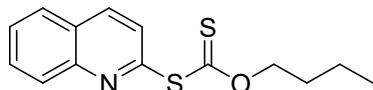
O-ethyl S-quinazolin-4-yl carbonodithioate (4aa): Yellow oil (95.0 mg, 76%). ¹H NMR (400 MHz, CDCl₃) δ 8.74 (d, *J* = 8.2 Hz, 1H), 8.27 (s, 1H), 7.80 (t, *J* = 7.5 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 4.76 (q, *J* = 7.1 Hz, 2H), 1.52 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 191.6, 184.6, 141.6, 141.6, 135.1, 129.9, 129.8, 129.2, 128.3, 72.3, 13.1; HRMS (ESI): m/z [M+H]⁺ calcd for C₁₁H₁₁N₂OS₂: 251.0307; found: 251.0309.



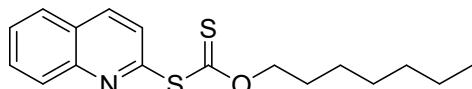
S-benzo[d]thiazol-2-yl O-ethyl carbonodithioate (4ba): Yellow oil (43.3 mg, 34%). ¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, *J* = 8.1 Hz, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.49 (dt, *J* = 25.5, 7.4 Hz, 2H), 4.71 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 206.1, 157.9, 152.4, 137.5, 126.6, 126.1, 123.8, 121.3, 71.2, 13.6; HRMS (ESI): m/z [M+H]⁺ calcd for C₁₀H₁₀NOS₃: 255.9919; found: 255.9923.



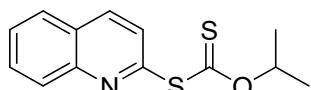
O-methyl S-quinolin-2-yl carbonodithioate (3ab): Yellow oil (97.5 mg, 83%). ^1H NMR (400 MHz, CDCl_3) δ 8.20 (d, $J = 8.5$ Hz, 1H), 8.13 (d, $J = 8.5$ Hz, 1H), 7.85 (d, $J = 8.1$ Hz, 1H), 7.76 (t, $J = 7.7$ Hz, 1H), 7.70 (d, $J = 8.5$ Hz, 1H), 7.62 (t, $J = 7.5$ Hz, 1H), 4.14 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 211.4, 152.9, 148.4, 137.2, 130.2, 129.6, 127.9, 127.6, 127.4, 127.1, 60.4; HRMS (ESI): m/z [M+H] $^+$ calcd for $\text{C}_{11}\text{H}_{10}\text{NOS}_2$: 236.0198; found: 236.0199.



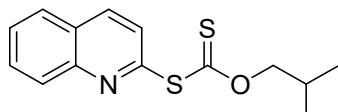
O-butyl S-quinolin-2-yl carbonodithioate (3ac): Yellow oil (113.6 mg, 82%). ^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, $J = 8.5$ Hz, 1H), 8.10 (d, $J = 8.5$ Hz, 1H), 7.82 (d, $J = 8.1$ Hz, 1H), 7.73 (t, $J = 7.7$ Hz, 1H), 7.66 (d, $J = 8.5$ Hz, 1H), 7.58 (t, $J = 7.5$ Hz, 1H), 4.53 (t, $J = 6.5$ Hz, 2H), 1.66 – 1.58 (m, 2H), 1.29 – 1.18 (m, 2H), 0.79 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 210.3, 152.8, 148.2, 136.9, 130.1, 129.4, 127.7, 127.5, 127.2, 127.0, 74.1, 29.8, 18.8, 13.4; HRMS (ESI): m/z [M+H] $^+$ calcd for $\text{C}_{14}\text{H}_{16}\text{NOS}_2$: 278.0668; found: 278.0671.



O-heptyl S-quinolin-2-yl carbonodithioate (3ad): Yellow oil (118.1 mg, 74%). ^1H NMR (400 MHz, CDCl_3) δ 8.18 (d, $J = 8.5$ Hz, 1H), 8.13 (d, $J = 8.5$ Hz, 1H), 7.85 (d, $J = 8.1$ Hz, 1H), 7.76 (t, $J = 7.7$ Hz, 1H), 7.69 (d, $J = 8.5$ Hz, 1H), 7.61 (t, $J = 7.5$ Hz, 1H), 4.54 (t, $J = 6.4$ Hz, 2H), 1.70 – 1.58 (m, 2H), 1.25 – 1.12 (m, 8H), 0.82 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 210.4, 152.8, 148.4, 136.9, 130.2, 129.6, 127.8, 127.5, 127.3, 127.2, 74.5, 31.5, 28.7, 28.0, 25.7, 22.4, 14.0; HRMS (ESI): m/z [M+H] $^+$ calcd for $\text{C}_{17}\text{H}_{22}\text{NOS}_2$: 320.1137; found: 320.1139.

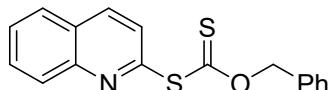


O-isopropyl S-quinolin-2-yl carbonodithioate (3ae): Yellow oil (119.7 mg, 91%). ^1H NMR (400 MHz, CDCl_3) δ 8.17 (d, $J = 8.4$ Hz, 1H), 8.12 (d, $J = 8.5$ Hz, 1H), 7.84 (d, $J = 8.1$ Hz, 1H), 7.74 (t, $J = 7.6$ Hz, 1H), 7.67 (d, $J = 8.4$ Hz, 1H), 7.60 (t, $J = 7.4$ Hz, 1H), 5.77 – 5.68 (m, 1H), 1.32 (d, $J = 6.2$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 209.7, 153.2, 148.2, 136.8, 130.1, 129.5, 127.7, 127.5, 127.2, 127.2, 78.6, 21.1; HRMS (ESI): m/z [M+H] $^+$ calcd for $\text{C}_{13}\text{H}_{14}\text{NOS}_2$: 264.0511; found: 264.0506.

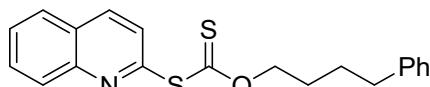


O-isobutyl S-quinolin-2-yl carbonodithioate (3af): Yellow oil (101.1 mg, 73%). ^1H NMR (400 MHz, CDCl_3) δ 8.19 (d, $J = 8.4$ Hz, 1H), 8.13 (d, $J = 8.4$ Hz, 1H), 7.85 (d, $J = 8.1$ Hz, 1H), 7.76 (t, $J = 7.6$ Hz, 1H), 7.70 (d, $J = 8.4$ Hz, 1H), 7.61 (t, $J = 7.4$ Hz, 1H), 4.32 (d, $J = 6.3$ Hz, 2H), 2.02 – 1.88 (m, 1H), 0.80 (d, $J = 6.7$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 210.4, 152.6, 148.3, 137.0, 130.2, 129.5,

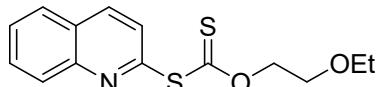
127.9, 127.5, 127.3, 127.2, 80.3, 27.4, 18.9; HRMS (ESI): m/z [M+H]⁺ calcd for C₁₄H₁₆NOS₂: 278.0668; found: 278.0666.



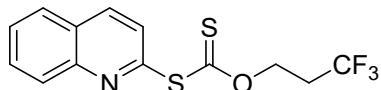
O-benzyl S-quinolin-2-yl carbonodithioate (3ag): Yellow oil (102.6 mg, 66%). ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.65 (t, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.22 – 7.08 (m, 5H), 5.49 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 210.3, 152.7, 148.4, 137.0, 134.0, 130.2, 129.5, 128.6, 128.4, 128.2, 127.8, 127.5, 127.3, 127.1, 75.3; HRMS (ESI): m/z [M+H]⁺ calcd for C₁₇H₁₄NOS₂: 312.0511; found: 312.0514.



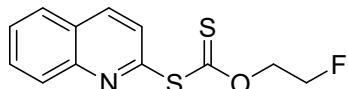
O-(4-phenylbutyl) S-quinolin-2-yl carbonodithioate (3ah): Yellow oil (146.5 mg, 83%). ¹H NMR (400 MHz, CDCl₃) δ 8.17 – 7.99 (m, 2H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.67 (t, *J* = 7.7 Hz, 1H), 7.63 – 7.49 (m, 2H), 7.11 (dt, *J* = 25.9, 7.5 Hz, 3H), 6.94 (d, *J* = 7.3 Hz, 2H), 4.49 (t, *J* = 6.3 Hz, 2H), 2.42 (t, *J* = 7.6 Hz, 2H), 1.62 (dt, *J* = 14.3, 6.4 Hz, 2H), 1.51 – 1.41 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 210.4, 152.7, 148.3, 141.6, 137.0, 130.2, 129.6, 128.2, 128.2, 127.9, 127.5, 127.3, 127.1, 125.8, 74.2, 35.2, 27.6, 27.5; HRMS (ESI): m/z [M+H]⁺ calcd for C₂₀H₂₀NOS₂: 354.0981; found: 354.0987.



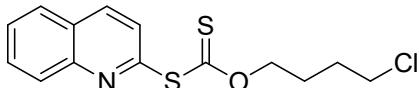
O-(2-ethoxyethyl) S-quinolin-2-yl carbonodithioate (3ai): Yellow oil (108.4 mg, 74%). ¹H NMR (400 MHz, CDCl₃) δ 8.16 (d, *J* = 8.5 Hz, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.80 – 7.69 (m, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 4.77 – 4.61 (m, 2H), 3.72 – 3.59 (m, 2H), 3.36 (q, *J* = 7.0 Hz, 2H), 1.08 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 210.4, 153.1, 148.2, 136.9, 130.1, 129.5, 127.8, 127.5, 127.3, 127.1, 73.1, 67.3, 66.6, 15.0; HRMS (ESI): m/z [M+H]⁺ calcd for C₁₄H₁₆NO₂S₂: 294.0617; found: 294.0622.



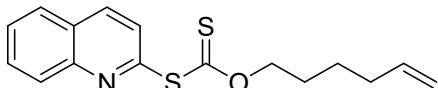
O-(3,3,3-trifluoropropyl) S-quinolin-2-yl carbonodithioate (3aj): Yellow oil (128.4 mg, 81%). ¹H NMR (400 MHz, CDCl₃) δ 8.20 (d, *J* = 8.5 Hz, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.77 (t, *J* = 7.7 Hz, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 4.76 (t, *J* = 6.2 Hz, 2H), 2.52 (qt, *J* = 10.7, 6.3 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 210.2, 152.2, 148.4, 137.3, 130.3, 129.5, 128.0, 127.6, 127.4, 127.1, 125.3 (q, *J*_{C-F} = 275.2 Hz), 65.9 (q, *J*_{C-F} = 3.5 Hz), 32.8 (q, *J*_{C-F} = 29.6 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -64.93; HRMS (ESI): m/z [M+H]⁺ calcd for C₁₃H₁₁F₃NOS₂: 318.0229; found: 318.0236.



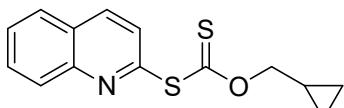
O-(2-fluoroethyl) S-quinolin-2-yl carbonodithioate (3ak): Yellow oil (88.1 mg, 66%). ^1H NMR (400 MHz, CDCl_3) δ 8.21 (d, $J = 8.5$ Hz, 1H), 8.13 (d, $J = 8.5$ Hz, 1H), 7.86 (d, $J = 8.1$ Hz, 1H), 7.81 – 7.69 (m, 2H), 7.62 (t, $J = 7.5$ Hz, 1H), 4.88 – 4.81 (m, 1H), 4.80 – 4.75 (m, 1H), 4.74 – 4.68 (m, 1H), 4.64 – 4.56 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 210.6, 152.8, 148.4, 137.2, 130.3, 129.5, 127.9, 127.6, 127.4, 127.1, 80.2 (d, $J_{\text{C}-\text{F}} = 171.4$ Hz), 72.1 (d, $J_{\text{C}-\text{F}} = 19.9$ Hz); HRMS (ESI): m/z [M+H] $^+$ calcd for $\text{C}_{12}\text{H}_{11}\text{FNOS}_2$: 268.0261; found: 268.0263.



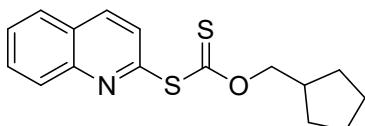
O-(4-chlorobutyl) S-quinolin-2-yl carbonodithioate (3al): Yellow oil (110.4 mg, 71%). ^1H NMR (400 MHz, CDCl_3) δ 8.21 (d, $J = 8.5$ Hz, 1H), 8.14 (d, $J = 8.5$ Hz, 1H), 7.87 (d, $J = 8.1$ Hz, 1H), 7.77 (t, $J = 7.7$ Hz, 1H), 7.69 (d, $J = 8.4$ Hz, 1H), 7.63 (t, $J = 7.5$ Hz, 1H), 4.59 (t, $J = 6.1$ Hz, 2H), 3.40 (t, $J = 6.3$ Hz, 2H), 1.88 – 1.80 (m, 2H), 1.75 – 1.67 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 210.4, 152.6, 148.4, 137.2, 130.3, 129.6, 128.0, 127.6, 127.4, 127.1, 73.2, 44.1, 28.9, 25.5; HRMS (ESI): m/z [M+H] $^+$ calcd for $\text{C}_{14}\text{H}_{15}\text{ClNOS}_2$: 312.0278; found: 312.0282.



O-hex-5-en-1-yl S-quinolin-2-yl carbonodithioate (3am): Yellow oil (115.2 mg, 76%). ^1H NMR (400 MHz, CDCl_3) δ 8.17 (d, $J = 8.5$ Hz, 1H), 8.12 (d, $J = 8.5$ Hz, 1H), 7.84 (d, $J = 8.1$ Hz, 1H), 7.74 (t, $J = 7.6$ Hz, 1H), 7.67 (d, $J = 8.5$ Hz, 1H), 7.60 (t, $J = 7.5$ Hz, 1H), 5.61 (td, $J = 16.9, 6.7$ Hz, 1H), 4.95 – 4.83 (m, 2H), 4.54 (t, $J = 6.4$ Hz, 2H), 1.92 (q, $J = 7.1$ Hz, 2H), 1.66 (dt, $J = 14.4, 6.6$ Hz, 2H), 1.30 (q, $J = 7.6$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 210.3, 152.7, 148.3, 137.8, 137.0, 130.2, 129.5, 127.8, 127.5, 127.2, 127.1, 114.8, 74.2, 32.9, 27.3, 24.9; HRMS (ESI): m/z [M+H] $^+$ calcd for $\text{C}_{16}\text{H}_{18}\text{NOS}_2$: 304.0824; found: 304.0827.

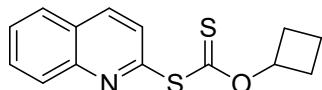


O-(cyclopropylmethyl) S-quinolin-2-yl carbonodithioate (3an): Yellow oil (101.8 mg, 74%). ^1H NMR (400 MHz, CDCl_3) δ 8.18 (d, $J = 8.5$ Hz, 1H), 8.12 (d, $J = 8.5$ Hz, 1H), 7.84 (d, $J = 8.1$ Hz, 1H), 7.79 – 7.69 (m, 2H), 7.60 (t, $J = 7.5$ Hz, 1H), 4.42 (d, $J = 7.4$ Hz, 2H), 1.19 (tt, $J = 8.0, 4.8$ Hz, 1H), 0.55 (q, $J = 5.4$ Hz, 2H), 0.28 (q, $J = 5.1$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 210.6, 153.2, 148.3, 136.9, 130.1, 129.5, 127.8, 127.5, 127.3, 127.2, 79.2, 9.1, 3.4; HRMS (ESI): m/z [M+H] $^+$ calcd for $\text{C}_{14}\text{H}_{14}\text{NOS}_2$: 276.0511; found: 276.0508.

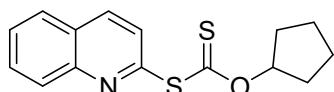


O-(cyclopentylmethyl) S-quinolin-2-yl carbonodithioate (3ao): Yellow oil (130.3 mg, 86%). ^1H NMR (400 MHz, CDCl_3) δ 8.17 (d, $J = 8.5$ Hz, 1H), 8.11 (d, $J = 8.5$ Hz, 1H), 7.84 (d, $J = 8.1$ Hz, 1H), 7.74 (t, $J = 7.7$ Hz, 1H), 7.68 (d, $J = 8.4$ Hz, 1H), 7.60 (t, $J = 7.5$ Hz, 1H), 4.42 (d, $J = 6.9$ Hz, 2H), 2.24 – 2.15 (m, 1H), 1.59 (dd, $J = 11.8, 6.7$ Hz, 2H), 1.42 (s, 4H), 1.13 (dt, $J = 12.3, 7.3$ Hz, 2H); ^{13}C

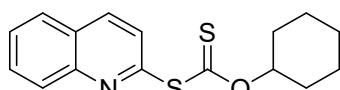
NMR (100 MHz, CDCl₃) δ 210.3, 152.7, 148.3, 136.9, 130.1, 129.5, 127.8, 127.5, 127.2, 127.1, 78.1, 37.9, 29.1, 25.2; HRMS (ESI): m/z [M+H]⁺ calcd for C₁₆H₁₈NOS₂: 304.0824; found: 304.0826.



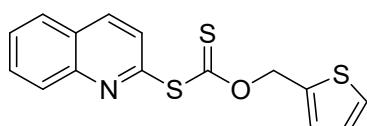
O-cyclobutyl S-quinolin-2-yl carbonodithioate (3ap): Yellow oil (107.3 mg, 78%). ¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, *J* = 8.5 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.77 – 7.66 (m, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 5.55 – 5.46 (m, 1H), 2.47 – 2.36 (m, 2H), 5.55 – 5.46 (m, 2H), 1.85 – 1.74 (m, 1H), 1.66 – 1.55 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 208.8, 153.2, 148.2, 136.9, 130.1, 129.5, 127.8, 127.5, 127.2, 127.1, 77.8, 29.9, 13.5; HRMS (ESI): m/z [M+H]⁺ calcd for C₁₄H₁₄NOS₂: 276.0511; found: 276.0506.



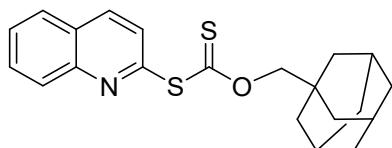
O-cyclopentyl S-quinolin-2-yl carbonodithioate (3aq): Yellow oil (124.3 mg, 86%). ¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, *J* = 8.5 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 5.92 – 5.77 (m, 1H), 1.90 – 1.75 (m, 4H), 1.61 – 1.45 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 209.4, 153.1, 148.3, 136.8, 130.2, 129.5, 127.8, 127.5, 127.2, 127.0, 88.0, 32.4, 23.7; HRMS (ESI): m/z [M+H]⁺ calcd for C₁₅H₁₆NOS₂: 290.0668; found: 290.0667.



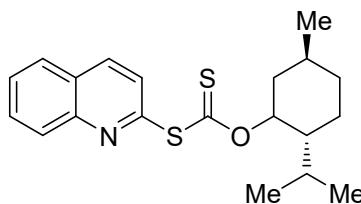
O-cyclohexyl S-quinolin-2-yl carbonodithioate (3ar): Yellow oil (125.8 mg, 83%). ¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, *J* = 8.5 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 5.59 – 5.52 (m, 1H), 1.93 – 1.79 (m, 2H), 1.60 – 1.17 (m, 8H); ¹³C NMR (100 MHz, CDCl₃) δ 209.4, 153.0, 148.3, 136.8, 130.1, 129.5, 127.7, 127.5, 127.2, 127.1, 82.9, 30.5, 25.0, 23.0; HRMS (ESI): m/z [M+H]⁺ calcd for C₁₆H₁₈NOS₂: 304.0824; found: 304.0827.



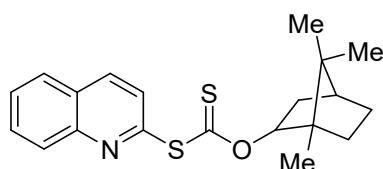
O-(thiophen-2-ylmethyl) S-quinolin-2-yl carbonodithioate (3as): Yellow oil (101.4 mg, 64%). ¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, *J* = 8.5 Hz, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.75 (t, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 5.1 Hz, 1H), 6.99 (s, 1H), 6.91 (t, *J* = 4.1 Hz, 1H), 4.47 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 186.9, 151.3, 148.5, 138.6, 137.2, 130.3, 129.4, 127.8, 127.6, 127.5, 127.3, 127.0, 126.4, 125.7, 29.7; HRMS (ESI): m/z [M+H]⁺ calcd for C₁₅H₁₂NOS₃: 318.0076; found: 318.0079.



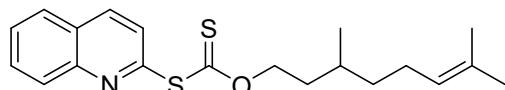
O-(adamantan-1-ylmethyl) S-quinolin-2-yl carbonodithioate (3at): Yellow oil (144.0 mg, 78%). ^1H NMR (400 MHz, CDCl_3) δ 8.21 (d, $J = 8.4$ Hz, 1H), 8.15 (d, $J = 8.5$ Hz, 1H), 7.86 (d, $J = 8.1$ Hz, 1H), 7.77 (t, $J = 7.7$ Hz, 1H), 7.71 (d, $J = 8.4$ Hz, 1H), 7.62 (t, $J = 7.5$ Hz, 1H), 4.03 (s, 2H), 1.79 – 1.71 (m, 3H), 1.60 – 1.49 (m, 3H), 1.33 – 1.20 (m, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 210.1, 152.0, 148.4, 137.1, 130.3, 129.6, 128.0, 127.5, 127.4, 127.4, 83.7, 38.8, 36.5, 33.3, 27.7; HRMS (ESI): m/z [M+H] $^+$ calcd for $\text{C}_{21}\text{H}_{24}\text{NOS}_2$: 370.1294; found: 370.1299.



O-((2R,5S)-2-isopropyl-5-methylcyclohexyl) S-quinolin-2-yl carbonodithioate (3au): Yellow oil (129.3 mg, 72%). ^1H NMR (400 MHz, CDCl_3) δ 8.18 (d, $J = 8.5$ Hz, 1H), 8.12 (d, $J = 8.5$ Hz, 1H), 7.84 (d, $J = 8.1$ Hz, 1H), 7.75 (t, $J = 7.7$ Hz, 1H), 7.69 (d, $J = 8.5$ Hz, 1H), 7.60 (t, $J = 7.5$ Hz, 1H), 5.45 (td, $J = 10.8, 4.4$ Hz, 1H), 2.28 – 2.20 (m, 1H), 1.84 – 1.74 (m, 1H), 1.69 – 1.58 (m, 2H), 1.52 – 1.34 (m, 2H), 1.10 – 0.72 (m, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 209.9, 152.9, 148.3, 136.7, 130.1, 129.6, 127.8, 127.5, 127.3, 127.3, 85.0, 47.0, 39.4, 33.9, 31.2, 26.2, 23.4, 21.9, 20.5, 16.7; HRMS (ESI): m/z [M+H] $^+$ calcd for $\text{C}_{20}\text{H}_{26}\text{NOS}_2$: 360.1450; found: 360.1457.

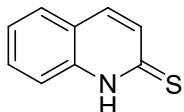


O-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl) S-quinolin-2-yl carbonodithioate (3av): Yellow oil (150.0 mg, 84%). ^1H NMR (400 MHz, CDCl_3) δ 8.20 (d, $J = 8.4$ Hz, 1H), 8.14 (d, $J = 8.5$ Hz, 1H), 7.86 (d, $J = 8.1$ Hz, 1H), 7.76 (t, $J = 7.6$ Hz, 1H), 7.70 (d, $J = 8.4$ Hz, 1H), 7.62 (t, $J = 7.5$ Hz, 1H), 5.42 (d, $J = 9.5$ Hz, 1H), 2.47 – 2.36 (m, 1H), 1.69 – 1.63 (m, 1H), 1.62 – 1.49 (m, 1H), 1.23 – 1.18 (m, 1H), 1.11 – 0.95 (m, 3H), 0.86 (s, 3H), 0.77 (d, $J = 5.9$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 210.0, 152.6, 148.4, 136.9, 130.2, 129.6, 127.8, 127.6, 127.3, 127.2, 91.0, 49.3, 47.8, 44.7, 36.3, 27.5, 27.0, 19.4, 18.8, 13.5; HRMS (ESI): m/z [M+H] $^+$ calcd for $\text{C}_{20}\text{H}_{24}\text{NOS}_2$: 358.1294; found: 358.1298.

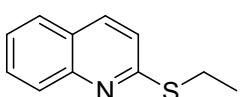


O-(3,7-dimethyloct-6-en-1-yl) S-quinolin-2-yl carbonodithioate (3aw): Yellow oil (104.2 mg, 58%). ^1H NMR (400 MHz, CDCl_3) δ 8.18 (d, $J = 8.5$ Hz, 1H), 8.12 (d, $J = 8.5$ Hz, 1H), 7.84 (d, $J = 8.1$ Hz, 1H), 7.75 (t, $J = 7.6$ Hz, 1H), 7.68 (d, $J = 8.4$ Hz, 1H), 7.60 (t, $J = 7.5$ Hz, 1H), 4.99 (t, $J = 6.6$ Hz, 1H), 4.64 – 4.54 (m, 2H), 1.88 – 1.76 (m, 2H), 1.73 – 1.67 (m, 1H), 1.65 (s, 3H), 1.55 (s, 3H), 1.50 – 1.32 (m, 2H), 1.26 – 1.16 (m, 1H), 1.13 – 1.02 (m, 1H), 0.79 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (100 MHz,

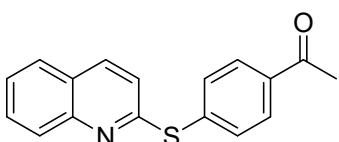
CDCl_3) δ 210.4, 152.8, 148.3, 136.9, 131.3, 130.2, 129.5, 127.8, 127.5, 127.3, 127.1, 124.3, 72.9, 36.8, 34.7, 29.3, 25.6, 25.3, 19.1, 17.6; HRMS (ESI): m/z [M+H]⁺ calcd for $\text{C}_{20}\text{H}_{26}\text{NOS}_2$: 360.1450; found: 360.1454.



quinoline-2(1H)-thione (4a): Yellow solid (70.0 mg, 87%). mp: 172–174 °C. ¹H NMR (400 MHz, CDCl_3) δ 13.29 (s, 1H), 7.66 (d, J = 8.6 Hz, 2H), 7.61 (d, J = 7.9 Hz, 1H), 7.56 (t, J = 7.6 Hz, 1H), 7.46 (d, J = 8.9 Hz, 1H), 7.32 (t, J = 7.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl_3) δ 180.5, 139.0, 135.7, 131.4, 127.7, 124.9, 122.9, 116.1. The compound spectra data is in accord with the previous literature.⁴



2-(ethylthio)quinoline (5a): Yellow oil (87.9 mg, 93%). ¹H NMR (400 MHz, CDCl_3) δ 7.94 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 8.6 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.64 (t, J = 7.6 Hz, 1H), 7.42 (t, J = 7.4 Hz, 1H), 7.20 (d, J = 8.6 Hz, 1H), 3.36 (q, J = 7.3 Hz, 2H), 1.45 (t, J = 7.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl_3) δ 159.5, 148.3, 135.2, 129.5, 128.0, 127.6, 125.9, 125.1, 121.0, 24.2, 14.6. The compound spectra data is in accord with the previous literature.⁵

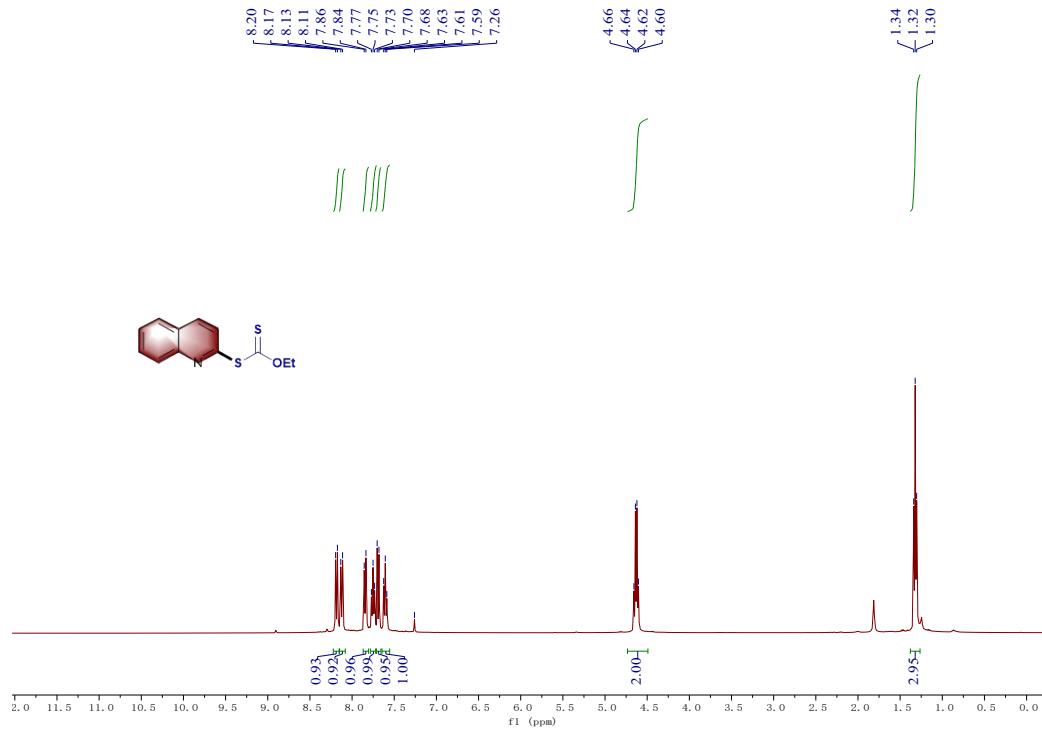


1-(4-(quinolin-2-ylthio)phenyl)ethanone (6a): Yellow solid (94.9 mg, 68%). mp: 112–113 °C. ¹H NMR (400 MHz, CDCl_3) δ 7.96 (t, J = 9.6 Hz, 4H), 8.00 – 7.93 (m, 4H), 7.49 (t, J = 7.4 Hz, 1H), 7.15 (d, J = 8.7 Hz, 1H), 2.63 (s, 3H); ¹³C NMR (100 MHz, CDCl_3) δ 197.3, 158.9, 148.1, 138.1, 136.8, 136.7, 133.3, 130.2, 129.1, 128.5, 127.6, 126.3, 126.2, 120.8, 26.6; HRMS (ESI): m/z [M+H]⁺ calcd for $\text{C}_{17}\text{H}_{14}\text{NOS}$: 280.0791; found: 280.0793.

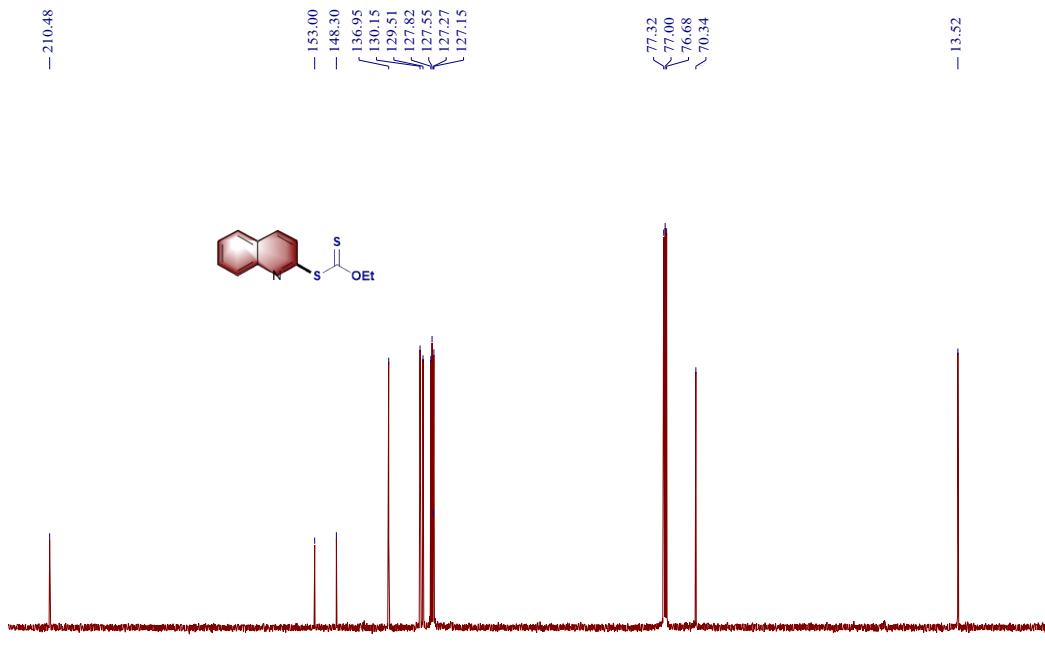
4. References

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5. R. Beugelmans, M. Bois-Choussy and B. Boudet, *Tetrahedron*, 1983, **39**, 4153-4161.

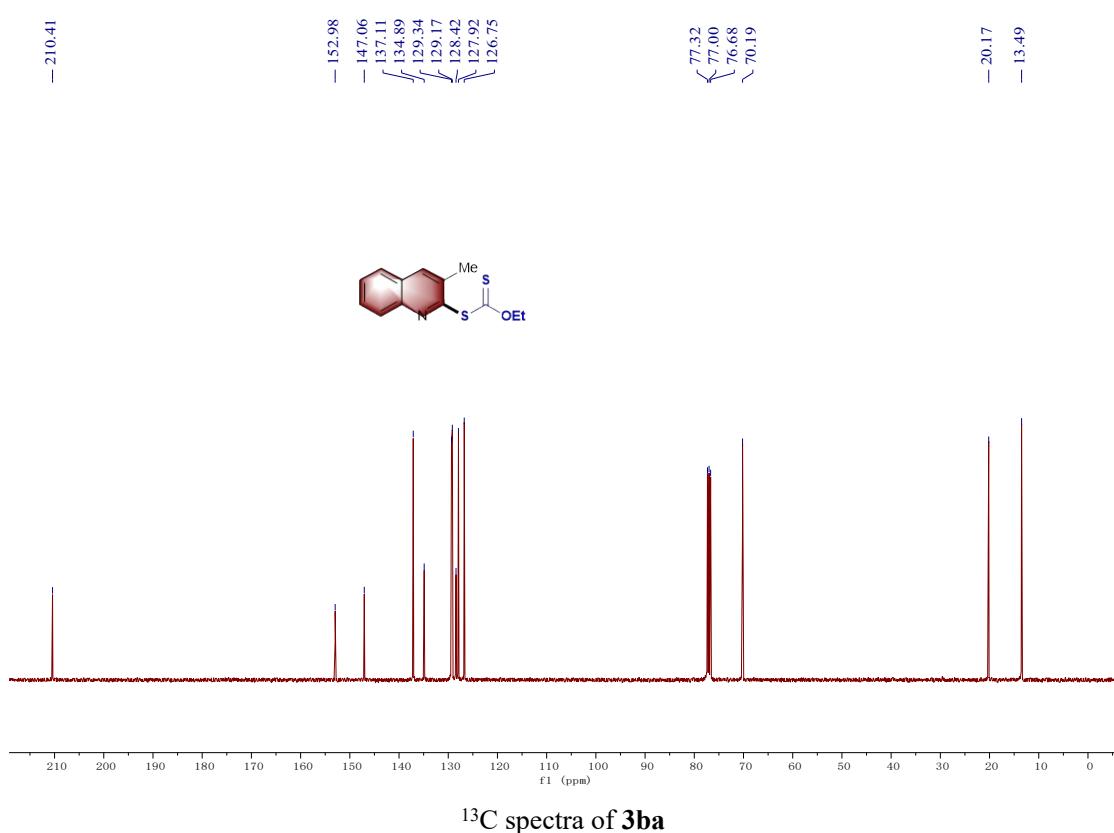
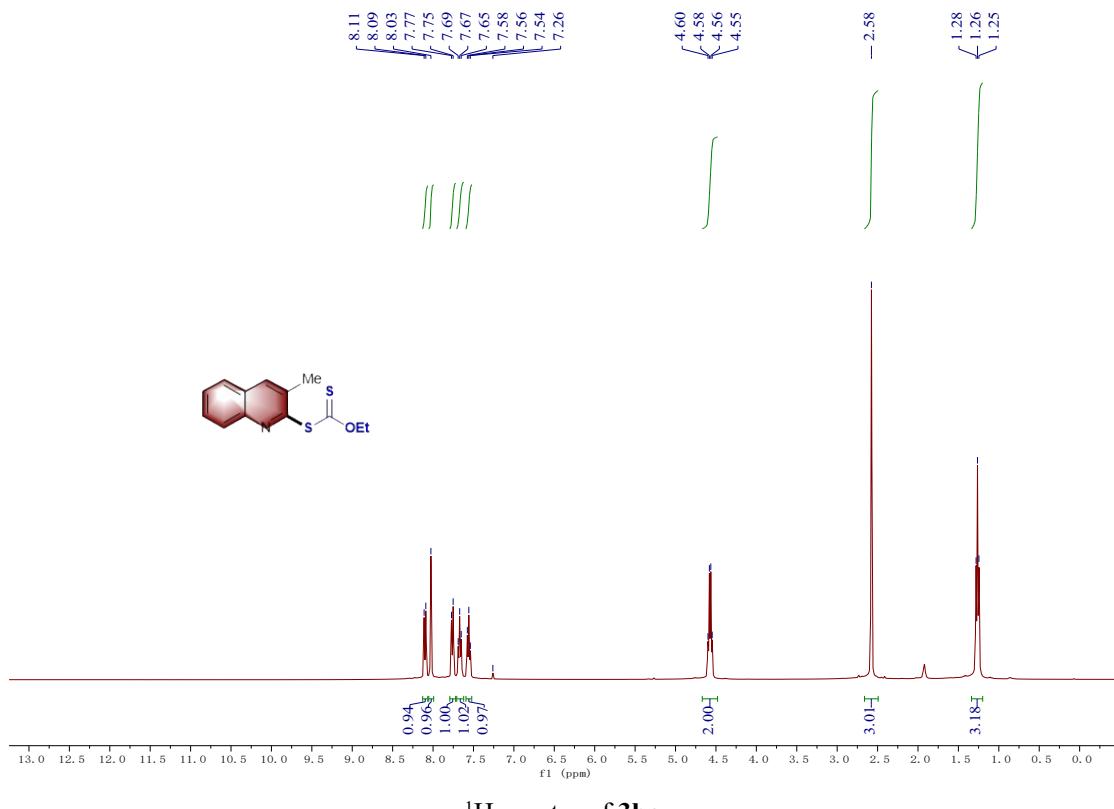
5. ^1H and ^{13}C NMR spectra of products

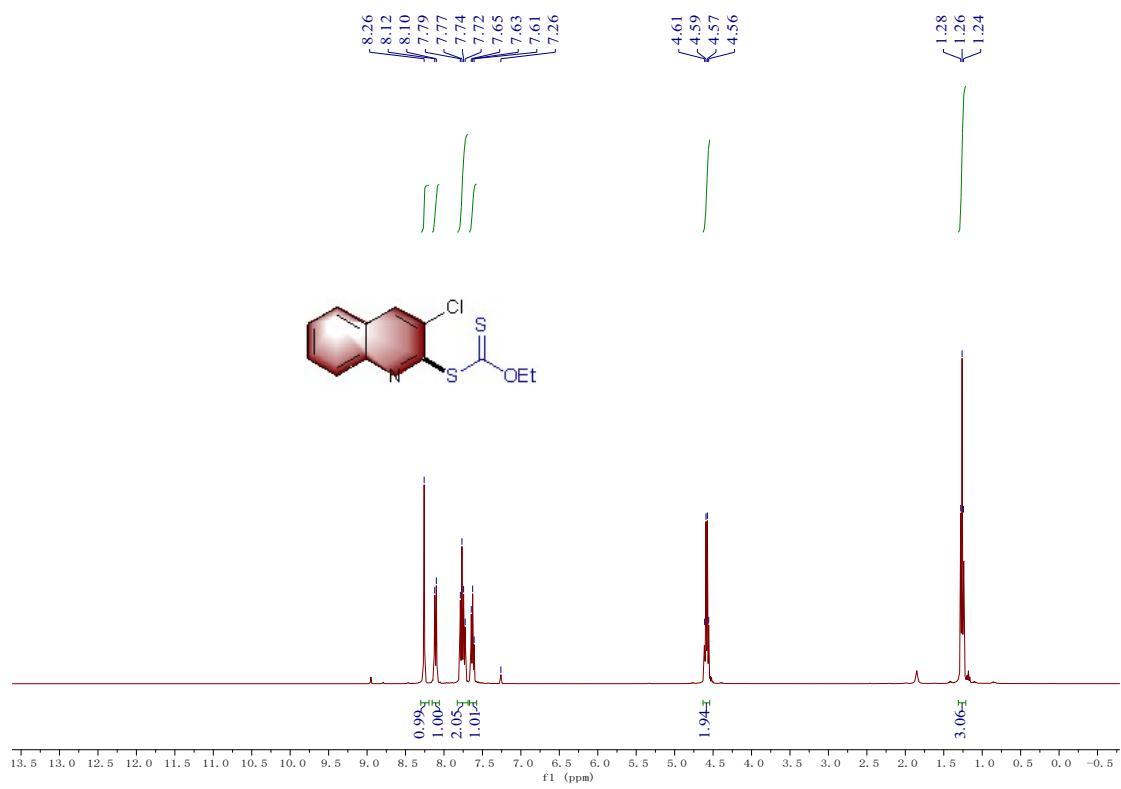


^1H spectra of **3aa**

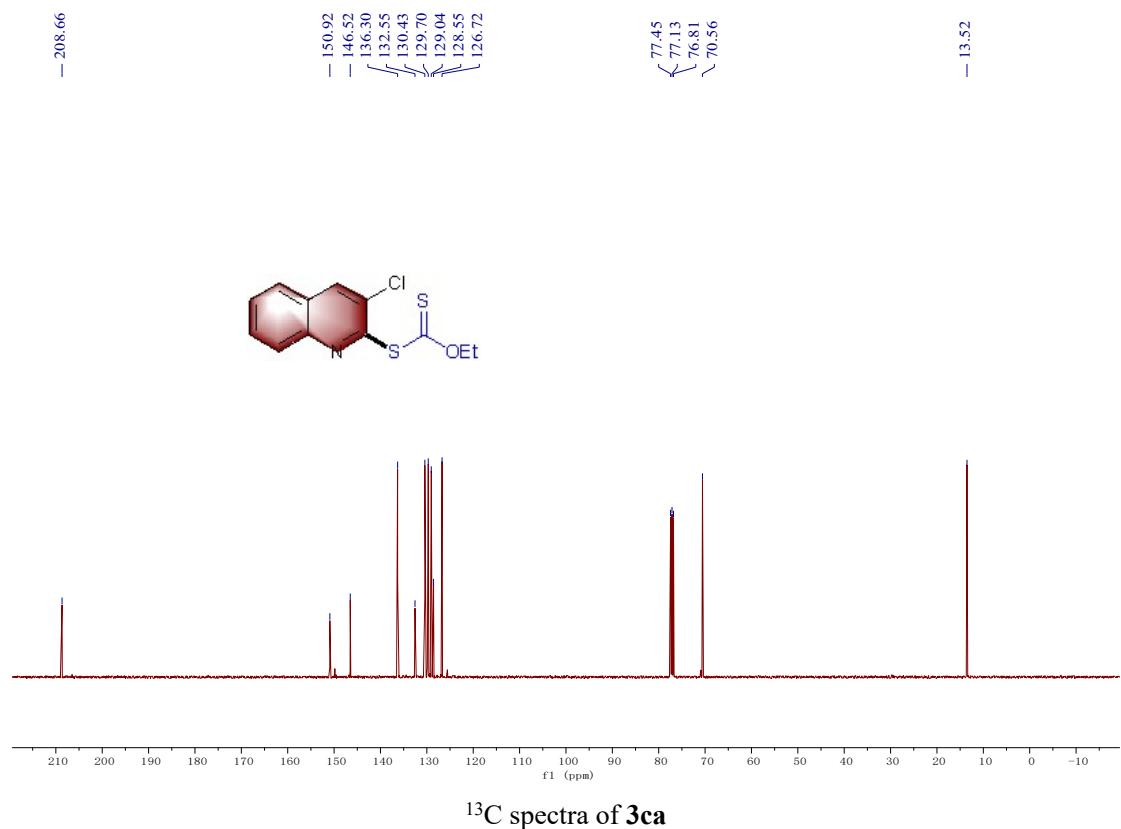


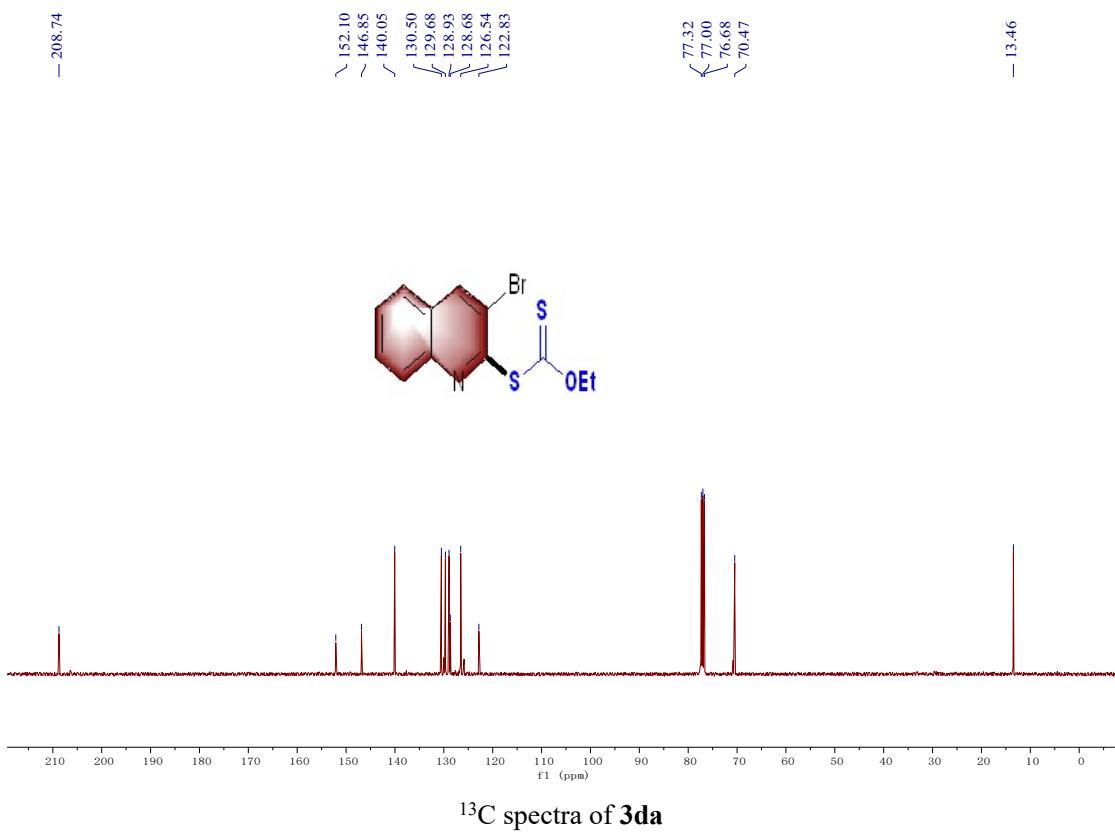
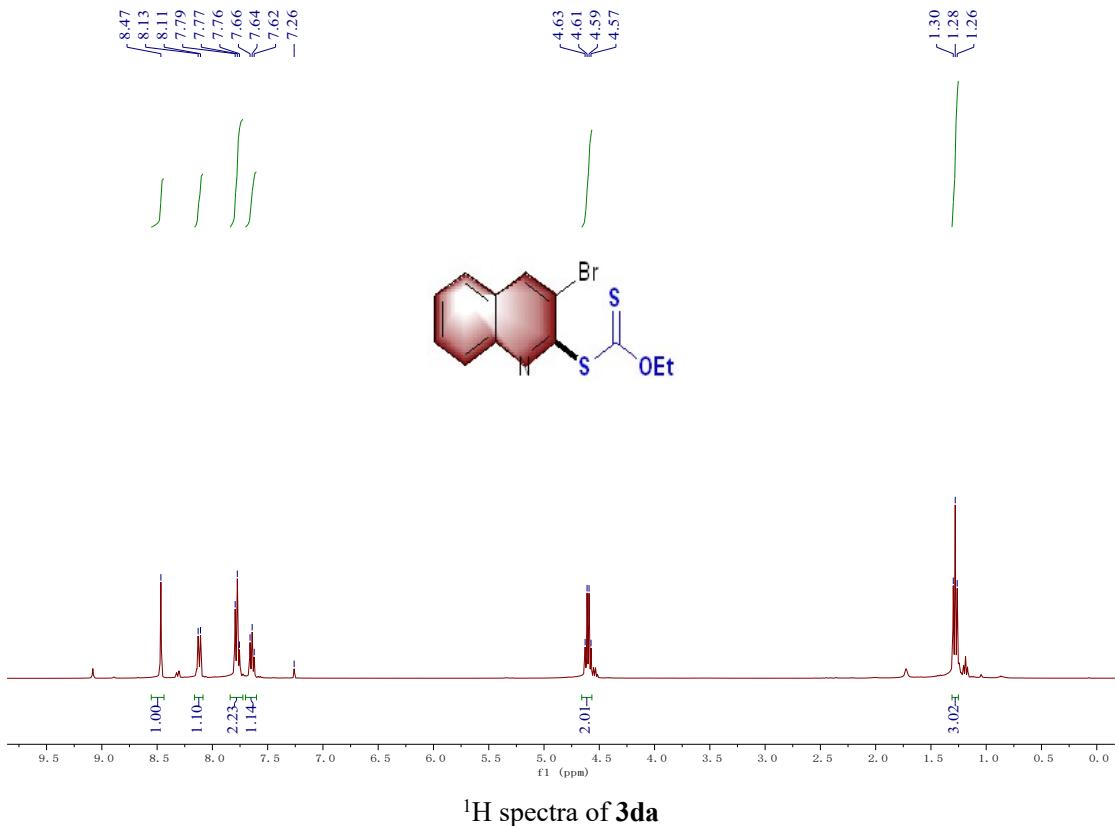
^{13}C spectra of **3aa**

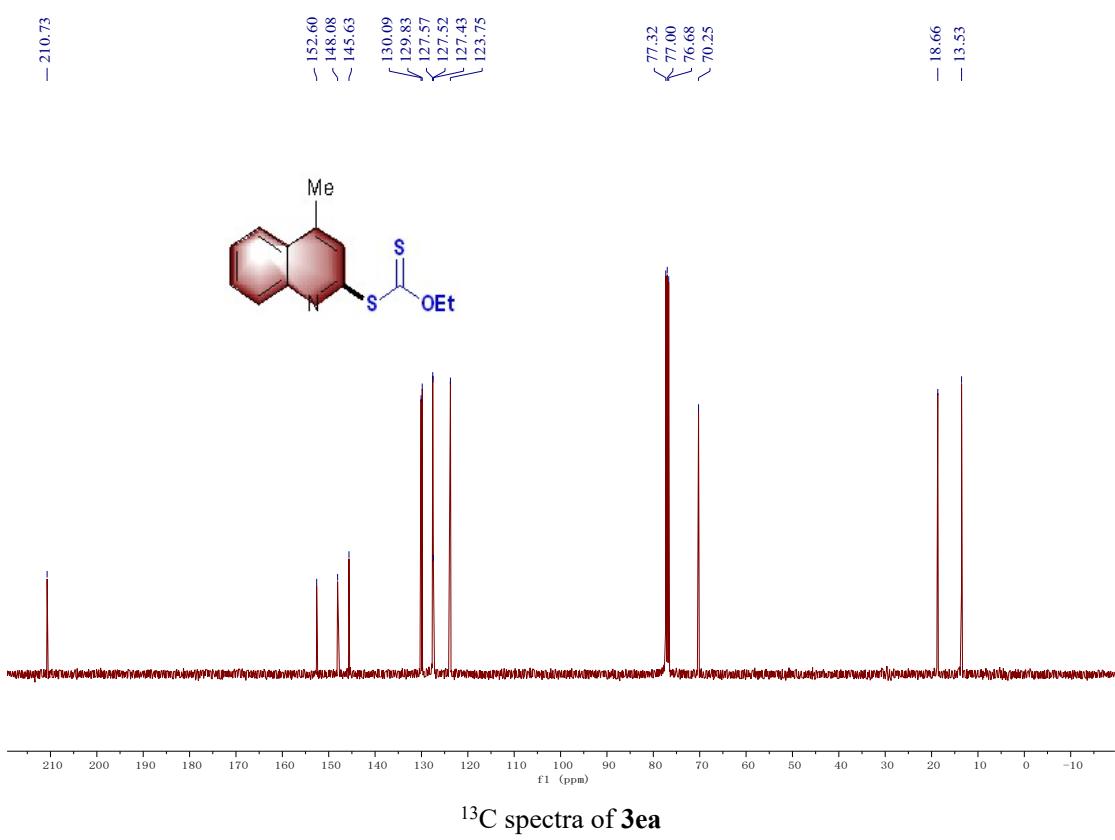
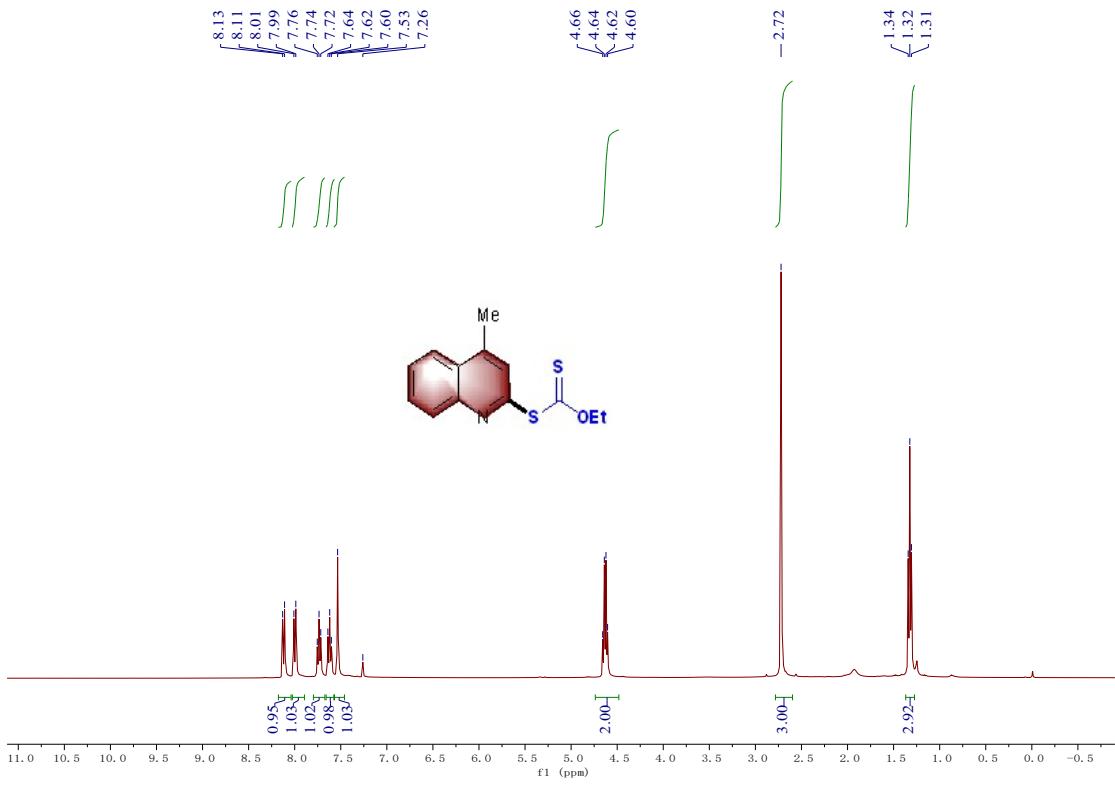


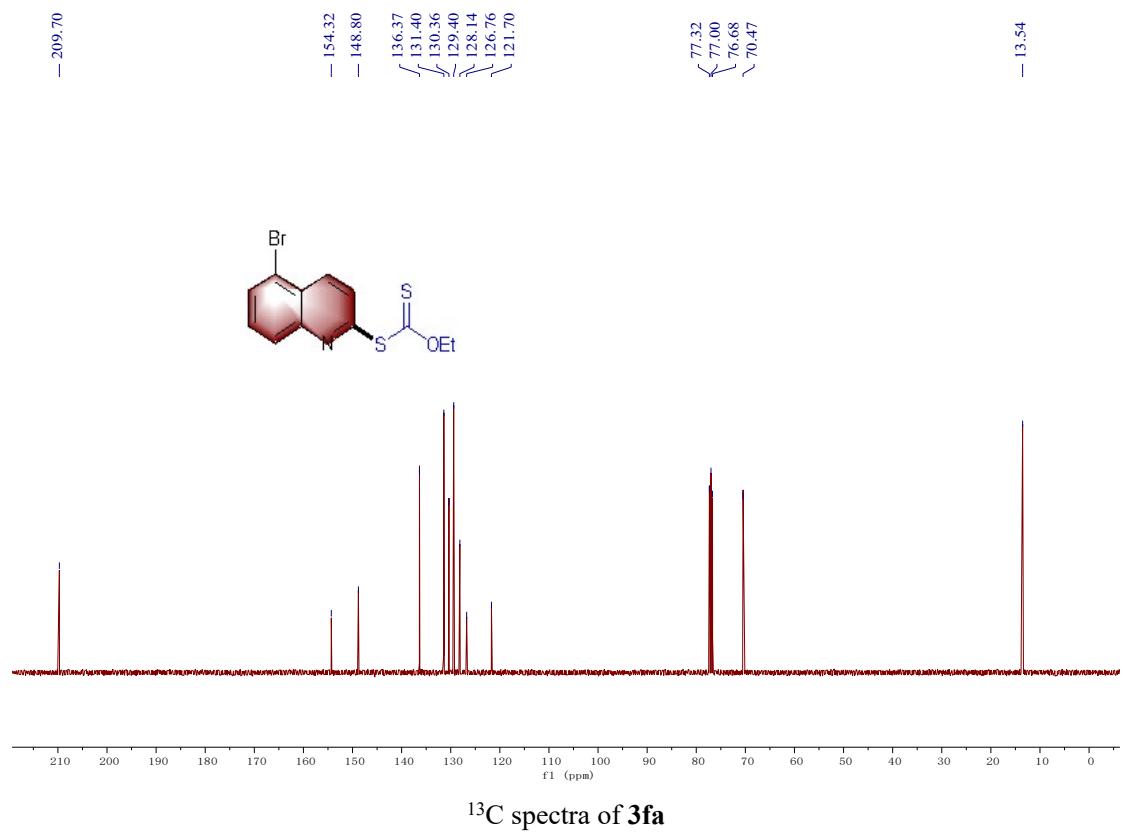
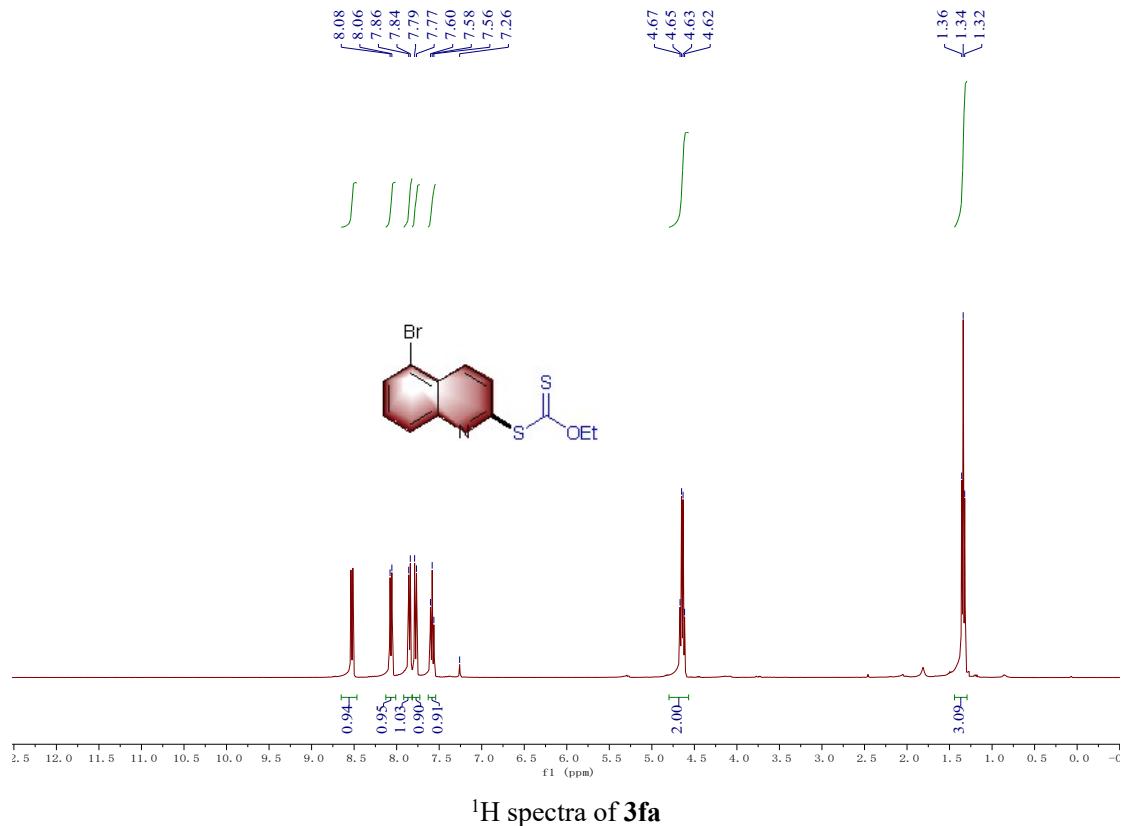


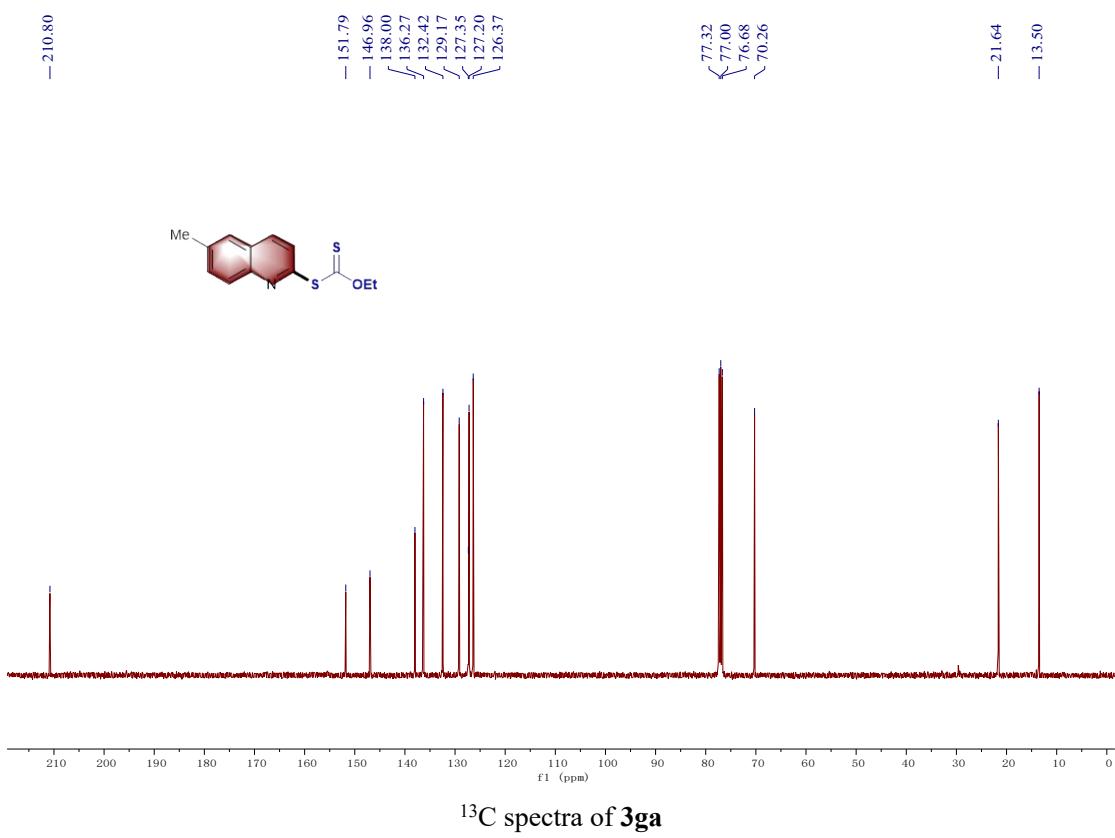
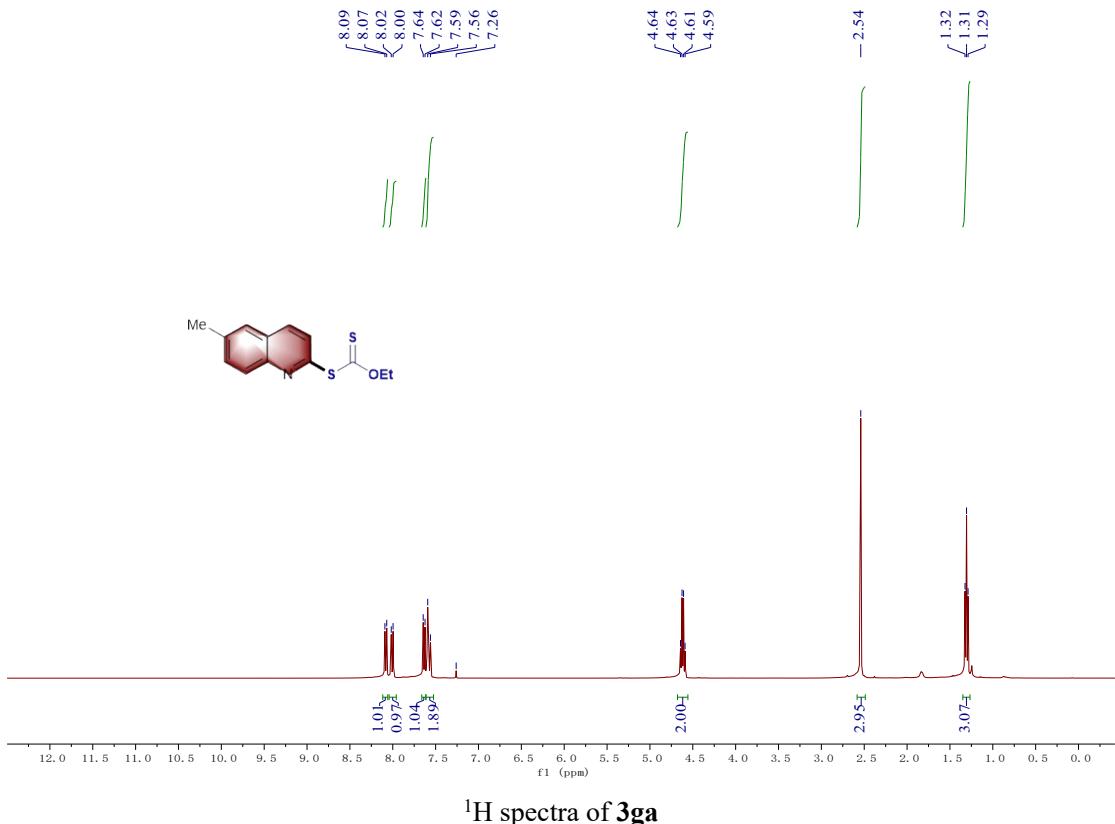
— 208.66

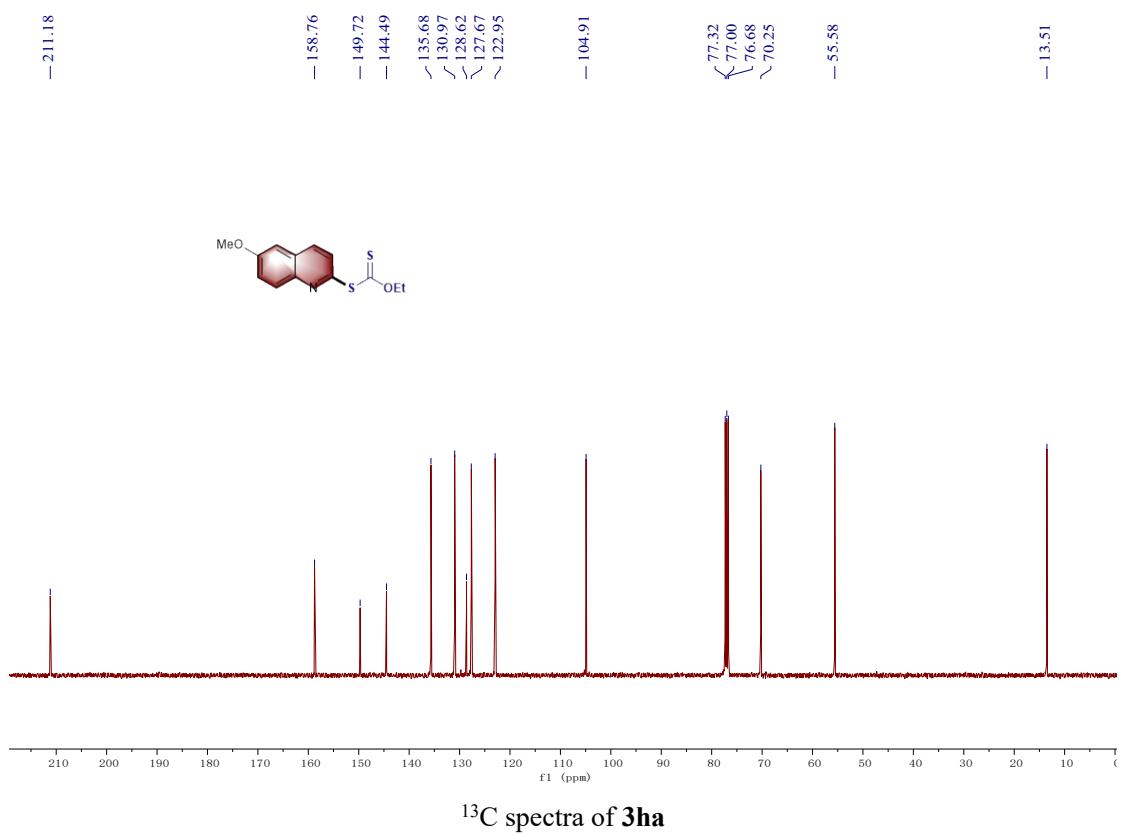
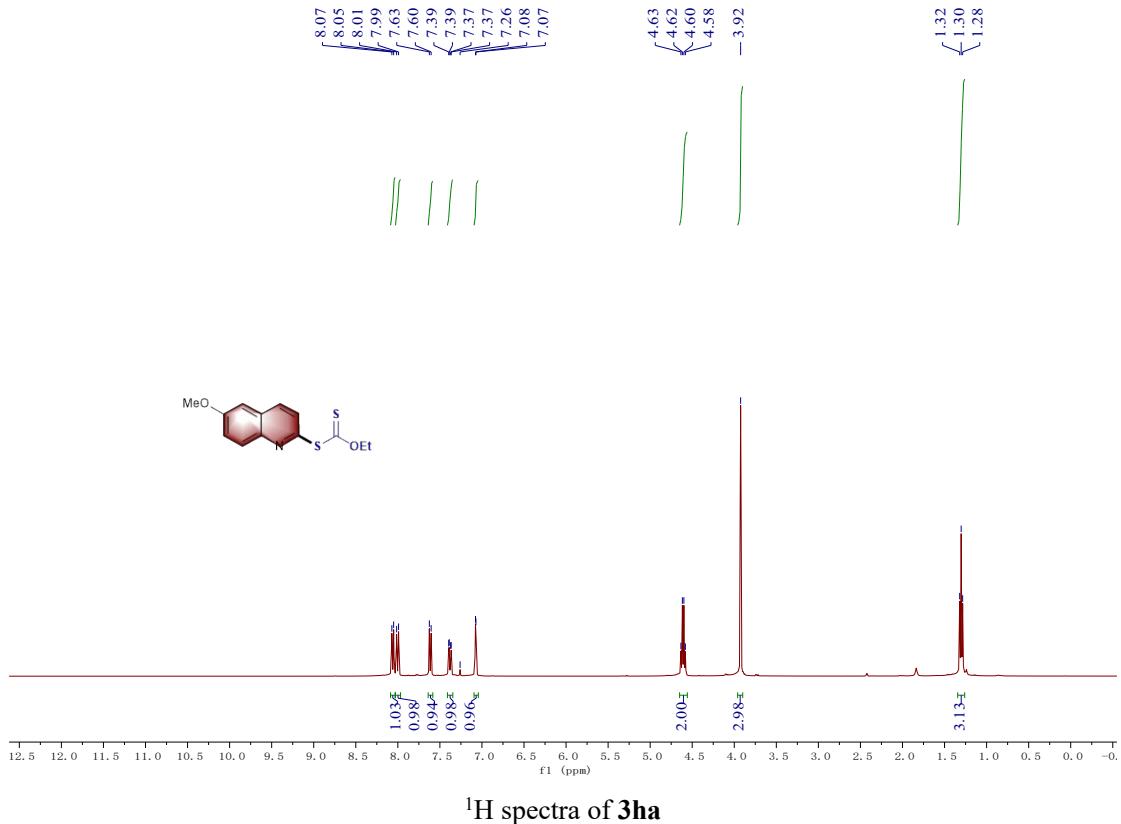


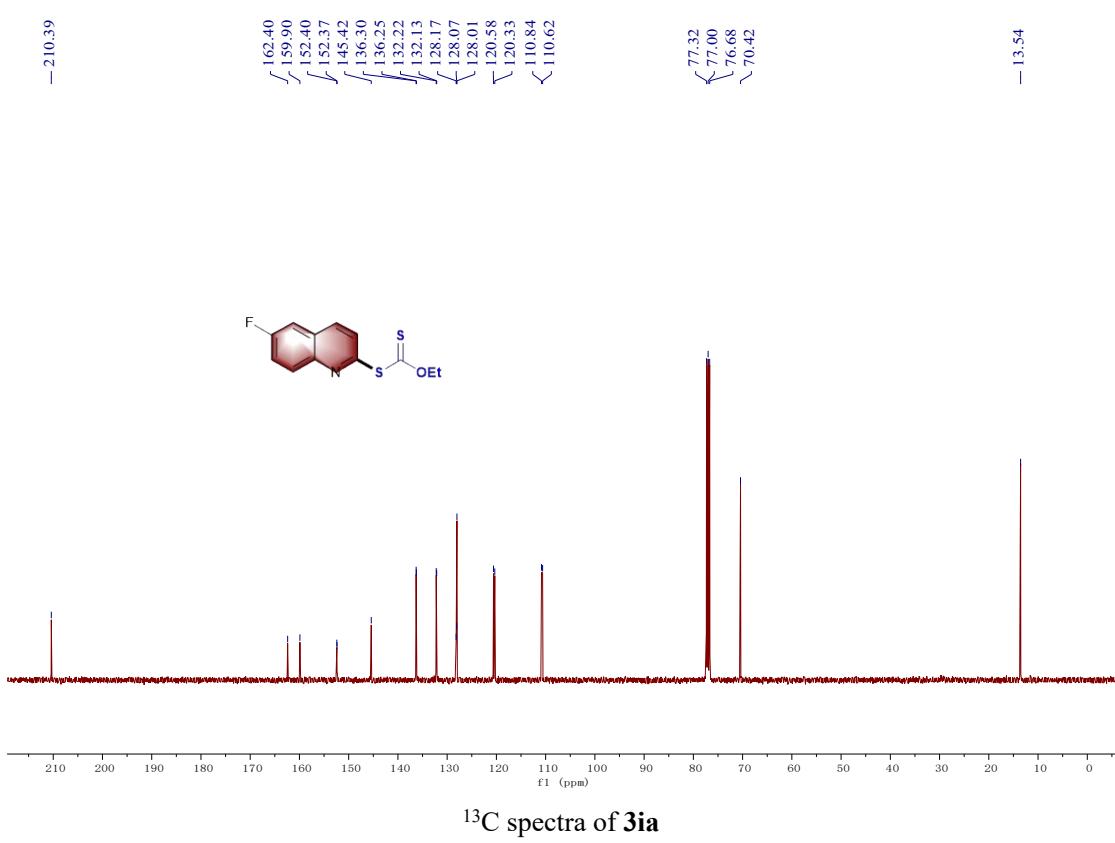
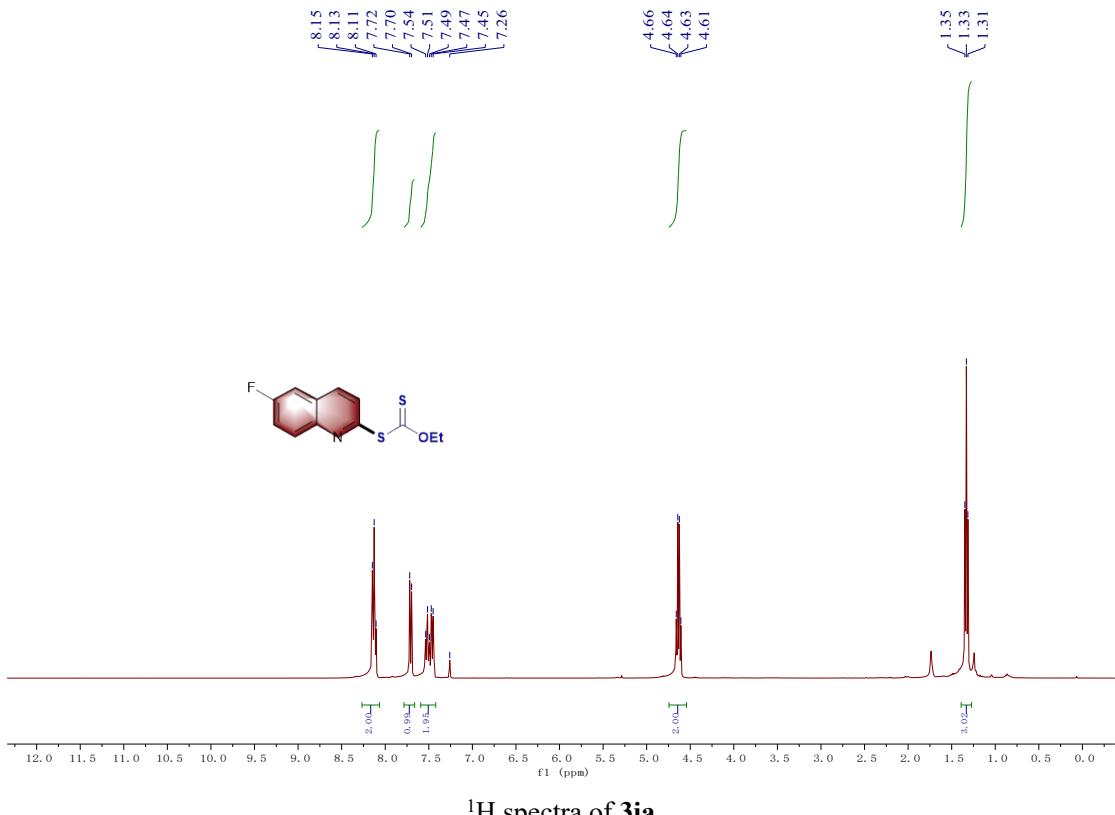


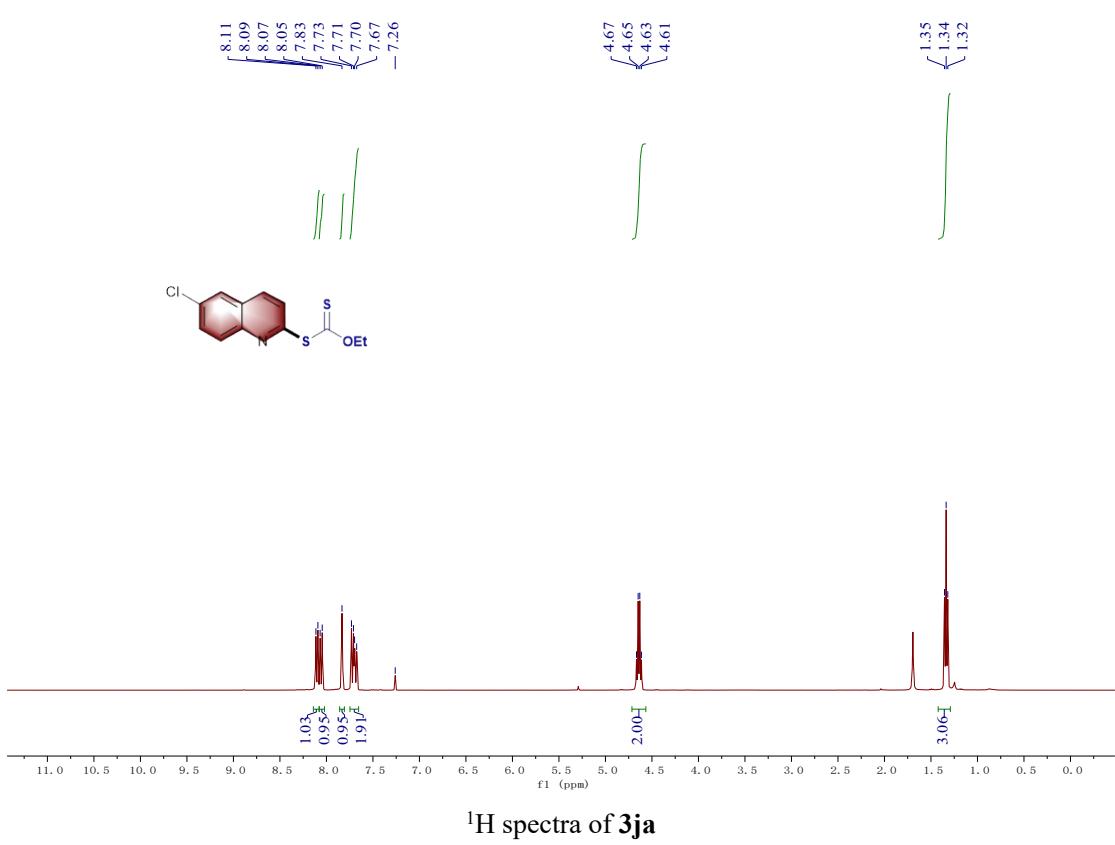
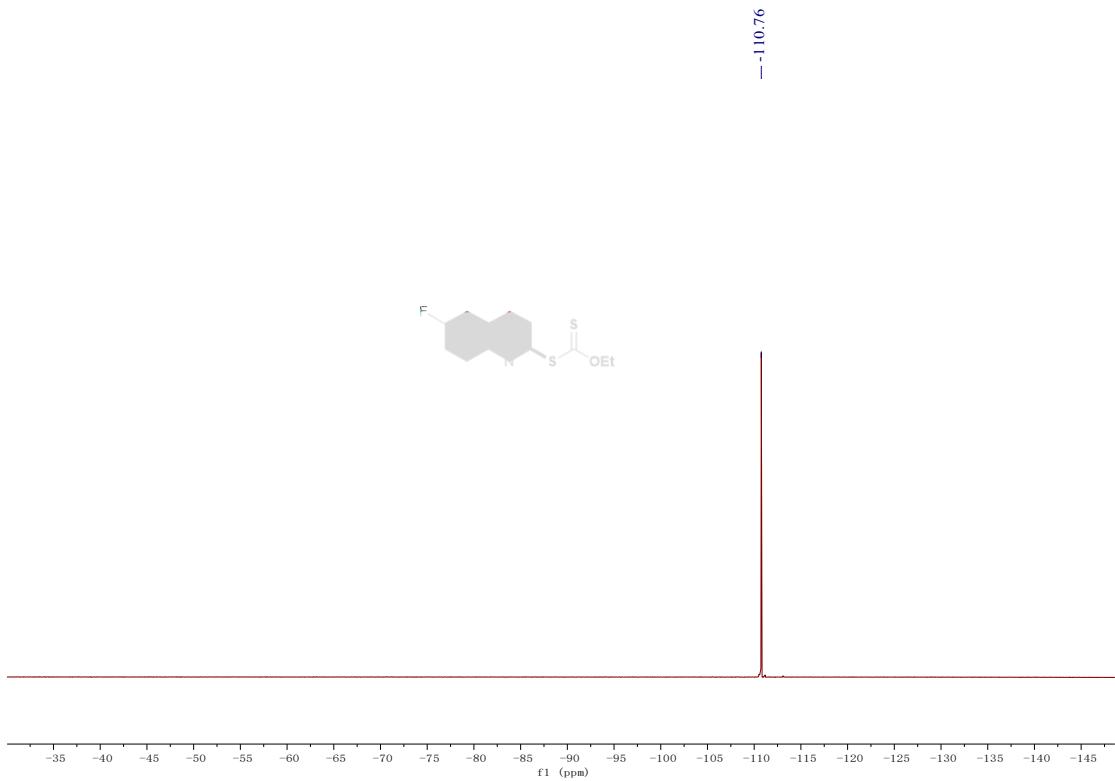


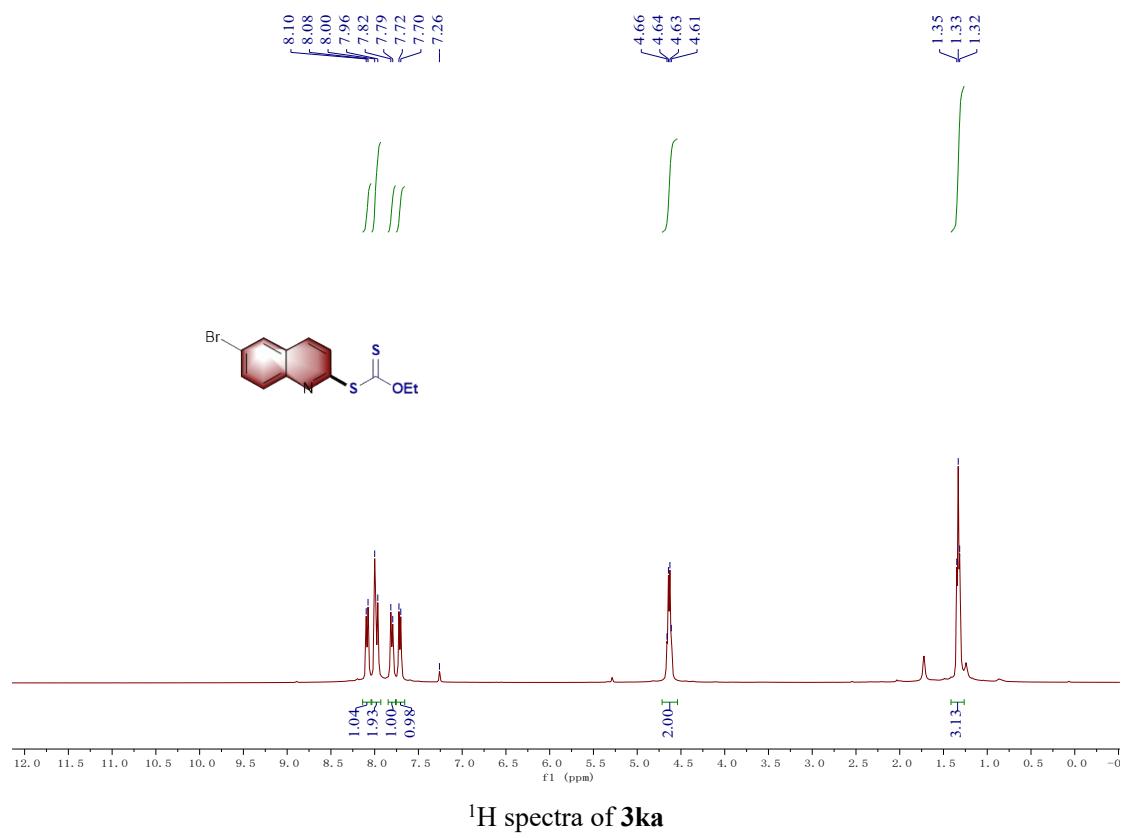
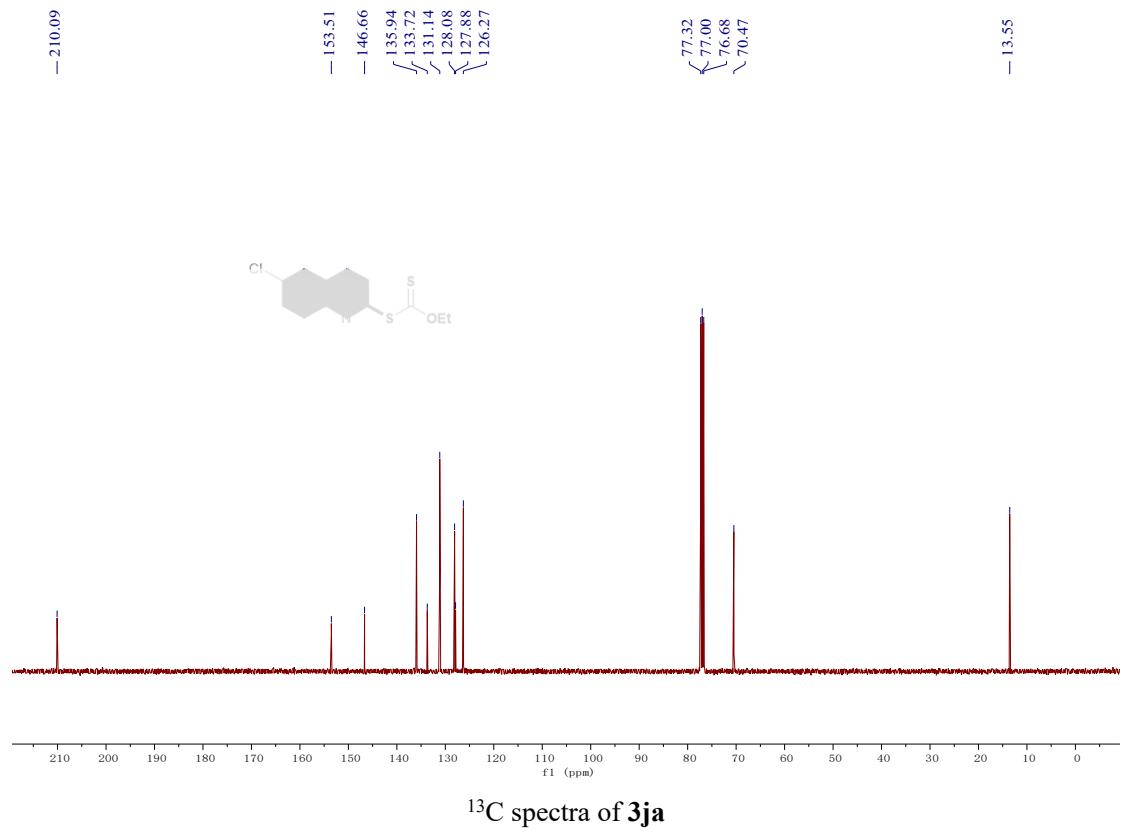










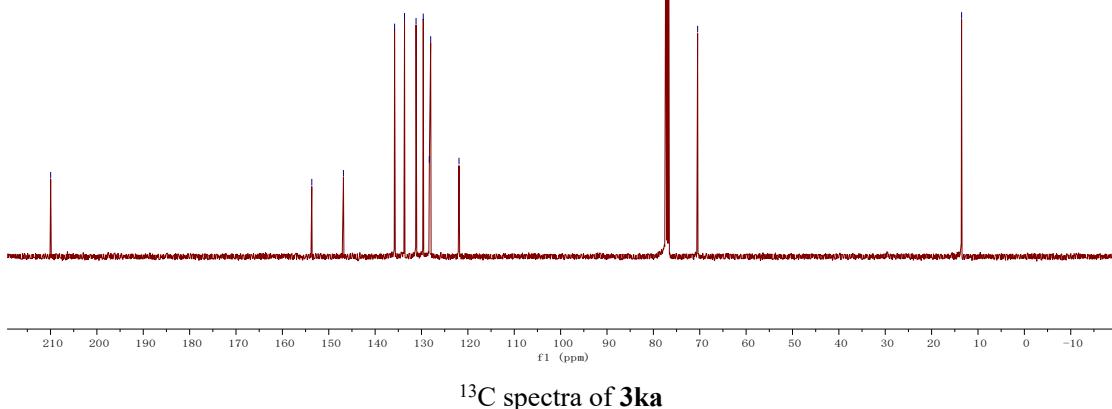


— 209.97

— 153.66
— 146.83
— 135.80
— 133.66
— 131.18
— 129.62
— 128.31
— 128.02
— 121.92

— 77.32
— 77.00
— 76.68
— 70.46

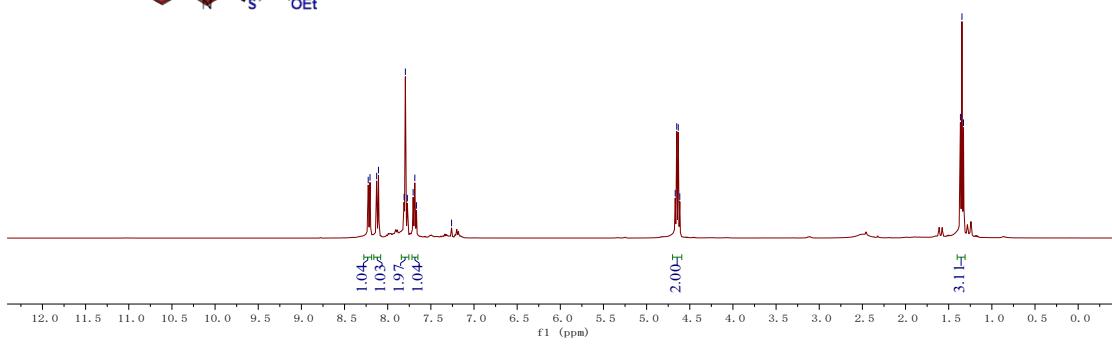
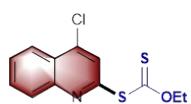
— 13.54



8.23
8.20
8.13
8.11
7.81
7.80
7.77
7.71
7.69
7.67
7.26

4.67
4.65
4.63
4.62

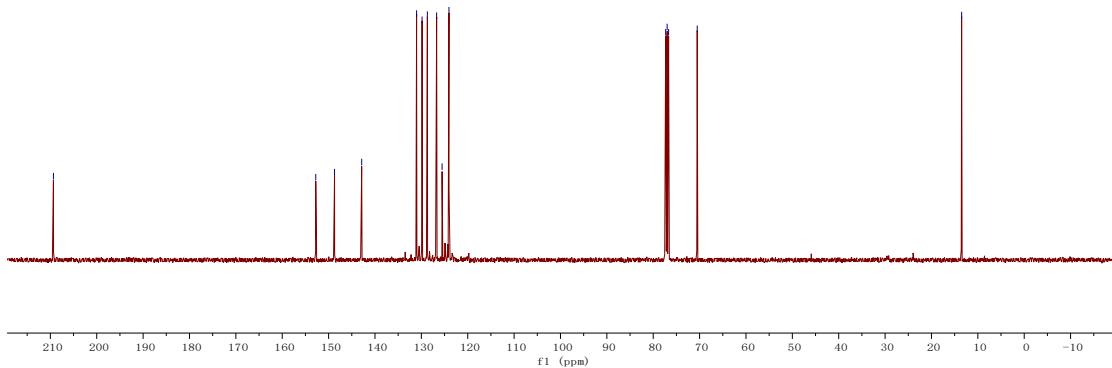
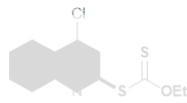
1.36
1.35
1.33



- 209.34

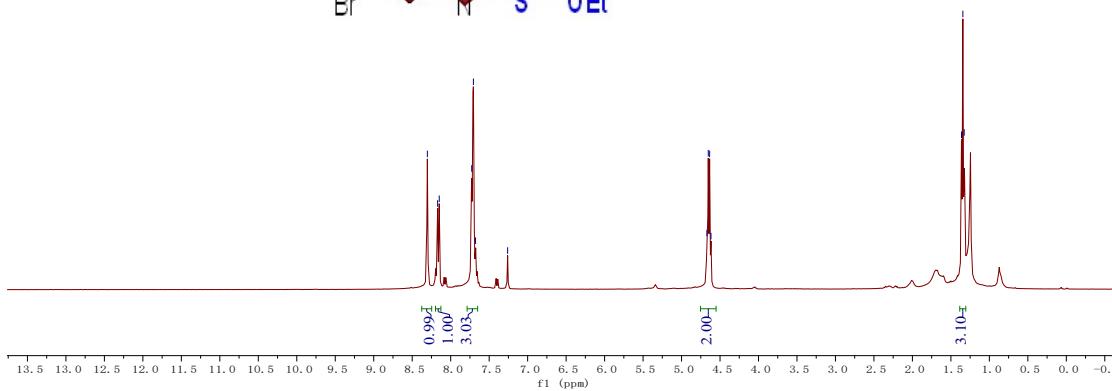
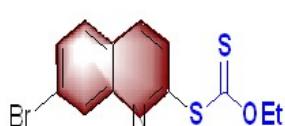
~ 152.77
~ 148.72
~ 142.87
131.03
129.85
128.70
126.70
125.53
124.04

- 13.49

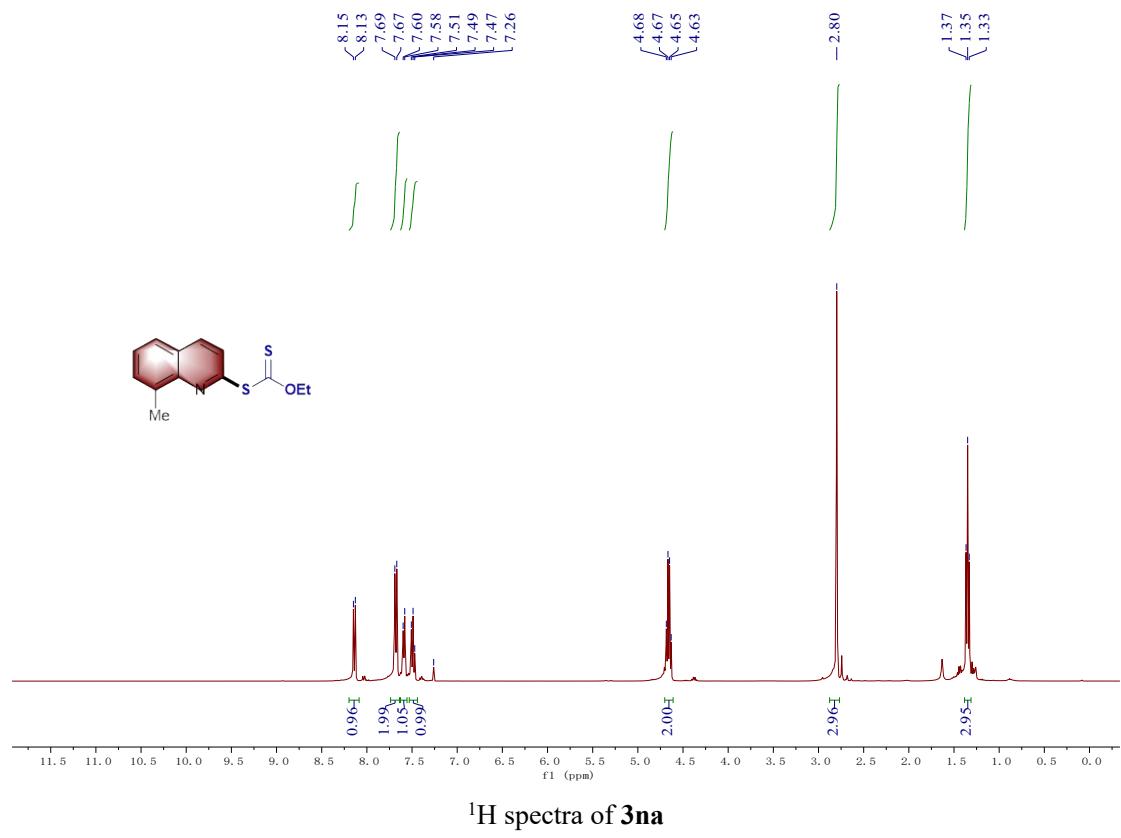
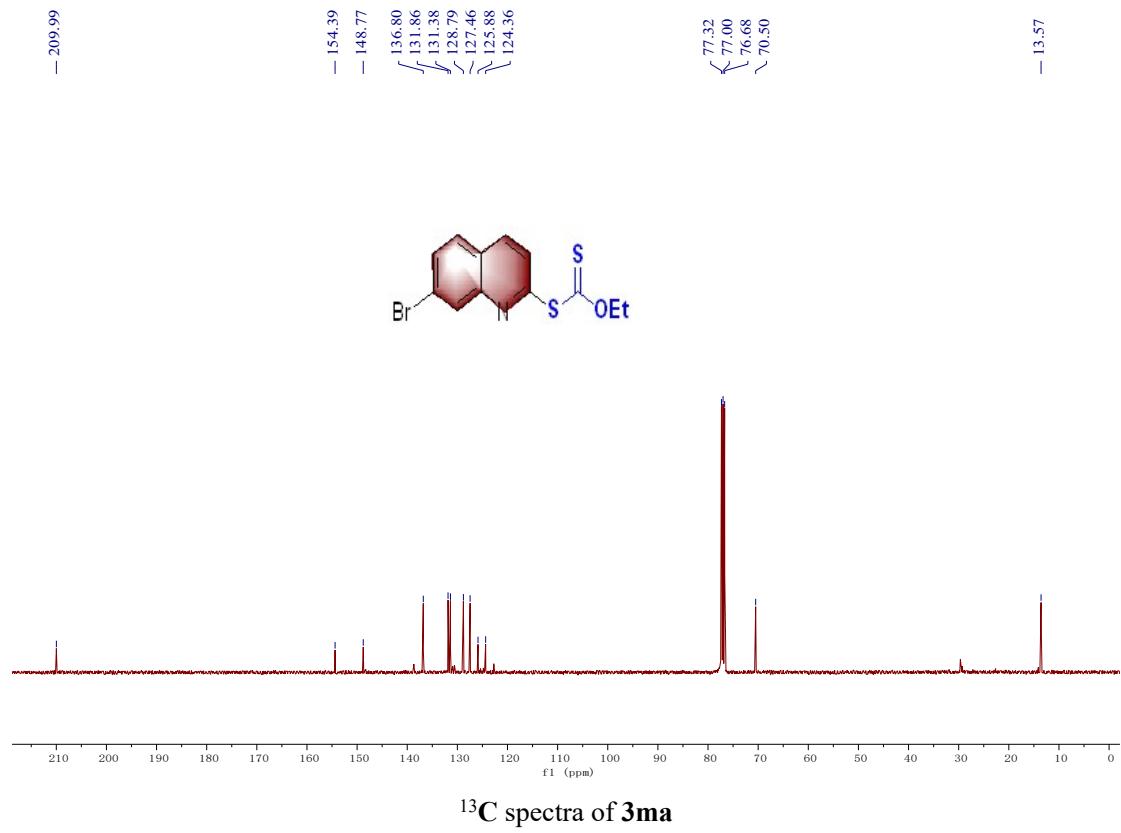


¹³C spectra of 3la

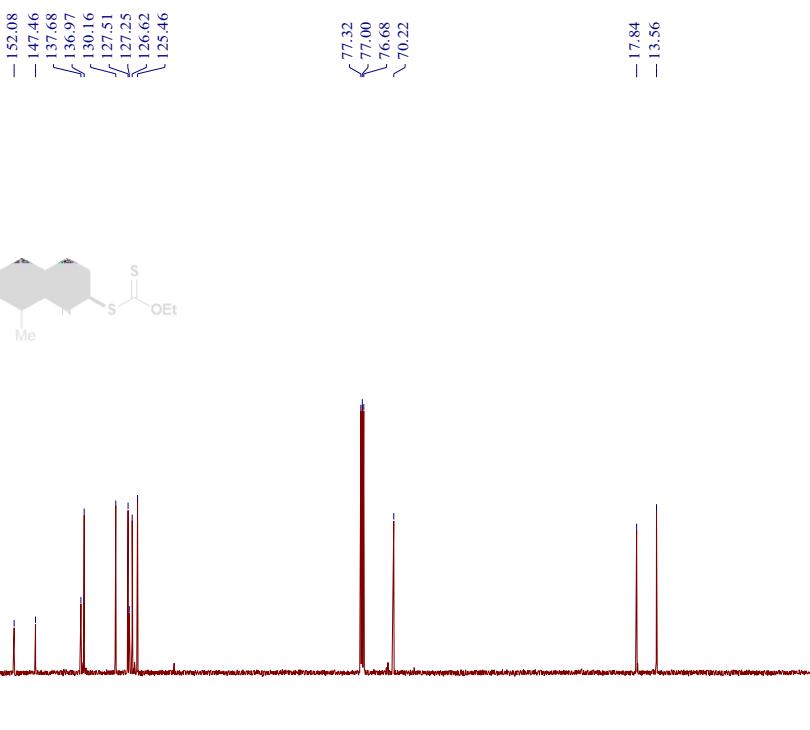
8.30
8.17
8.15
7.73
7.70
7.68
7.26
4.67
4.65
4.64
4.62
1.36
1.34
1.33



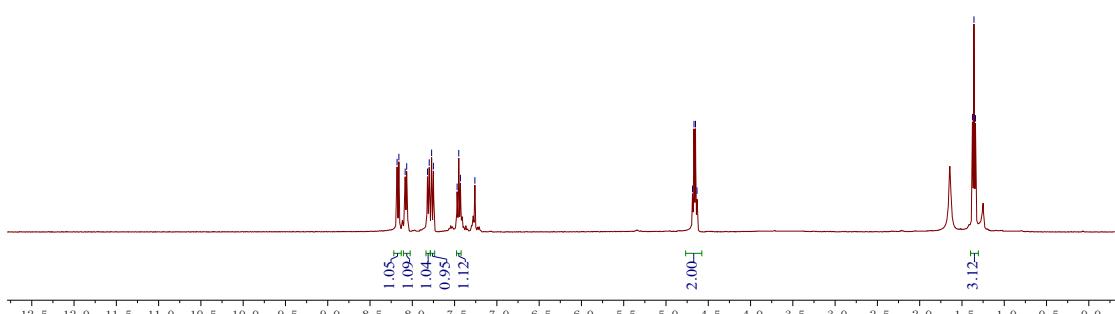
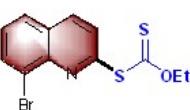
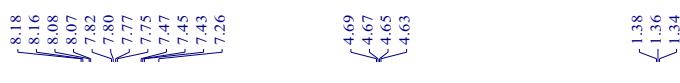
¹H spectra of 3ma



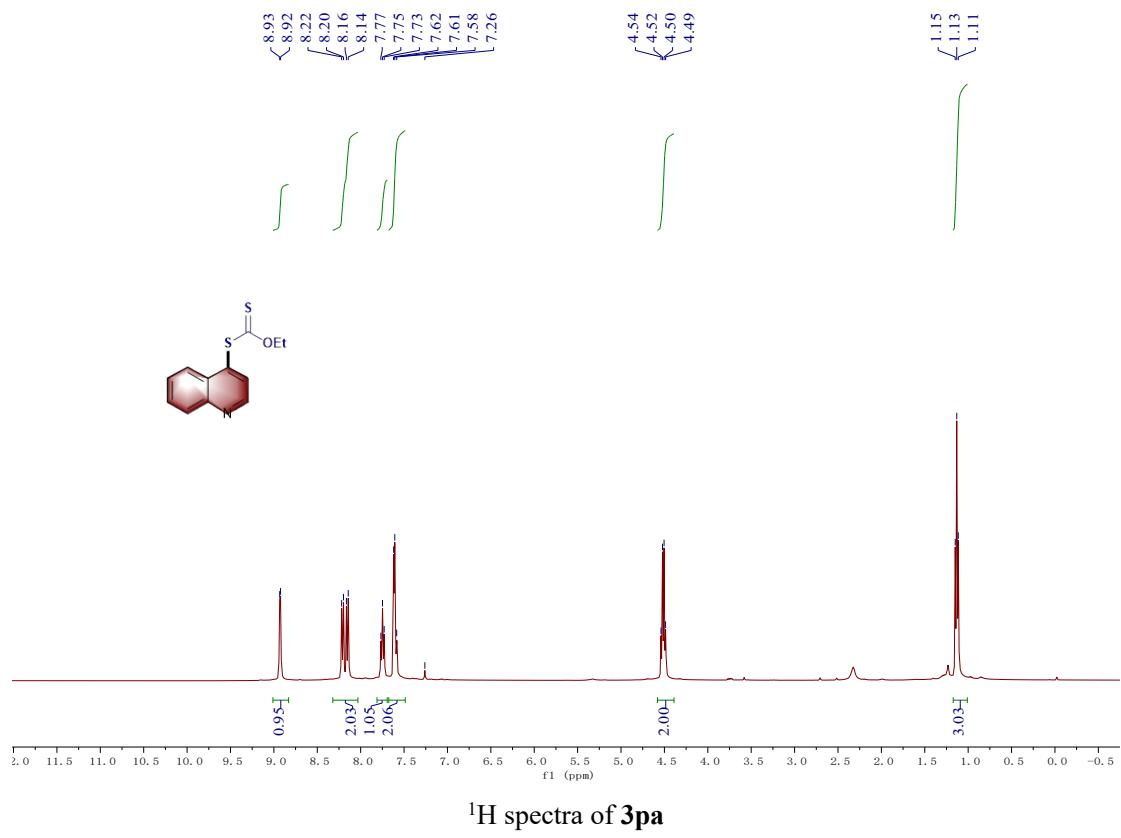
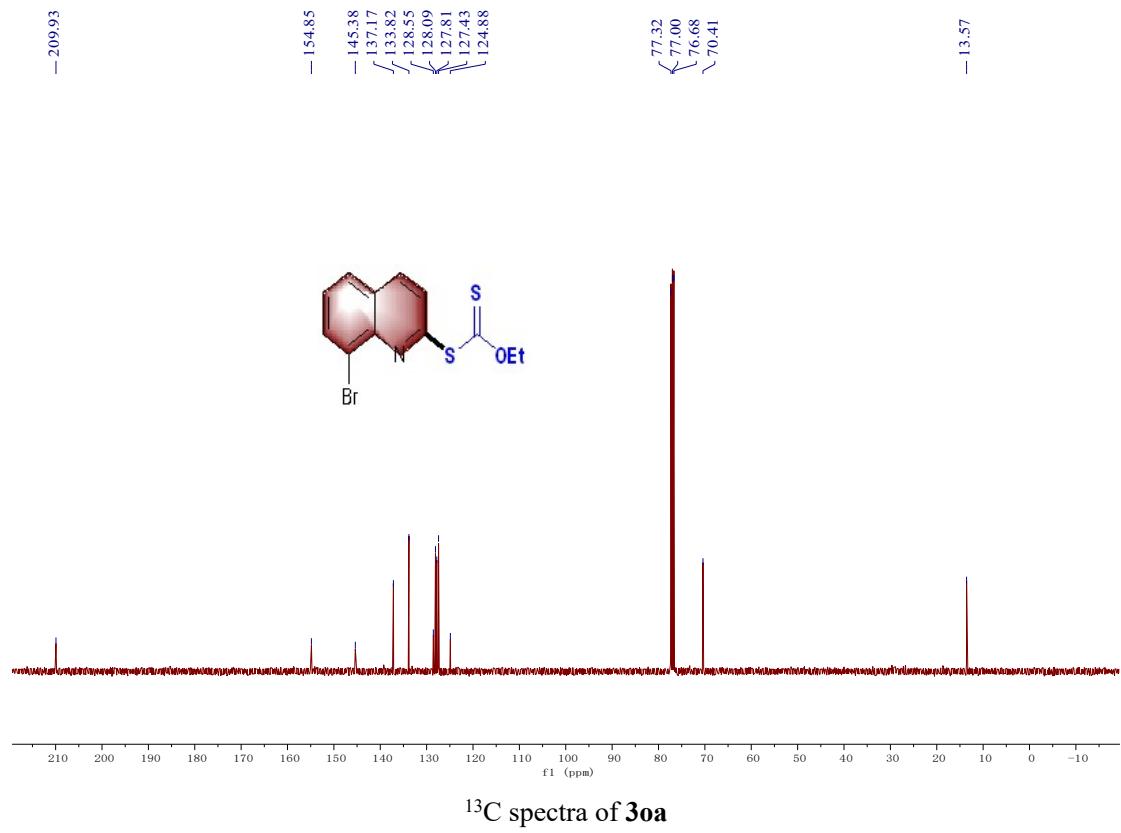
— 210.95

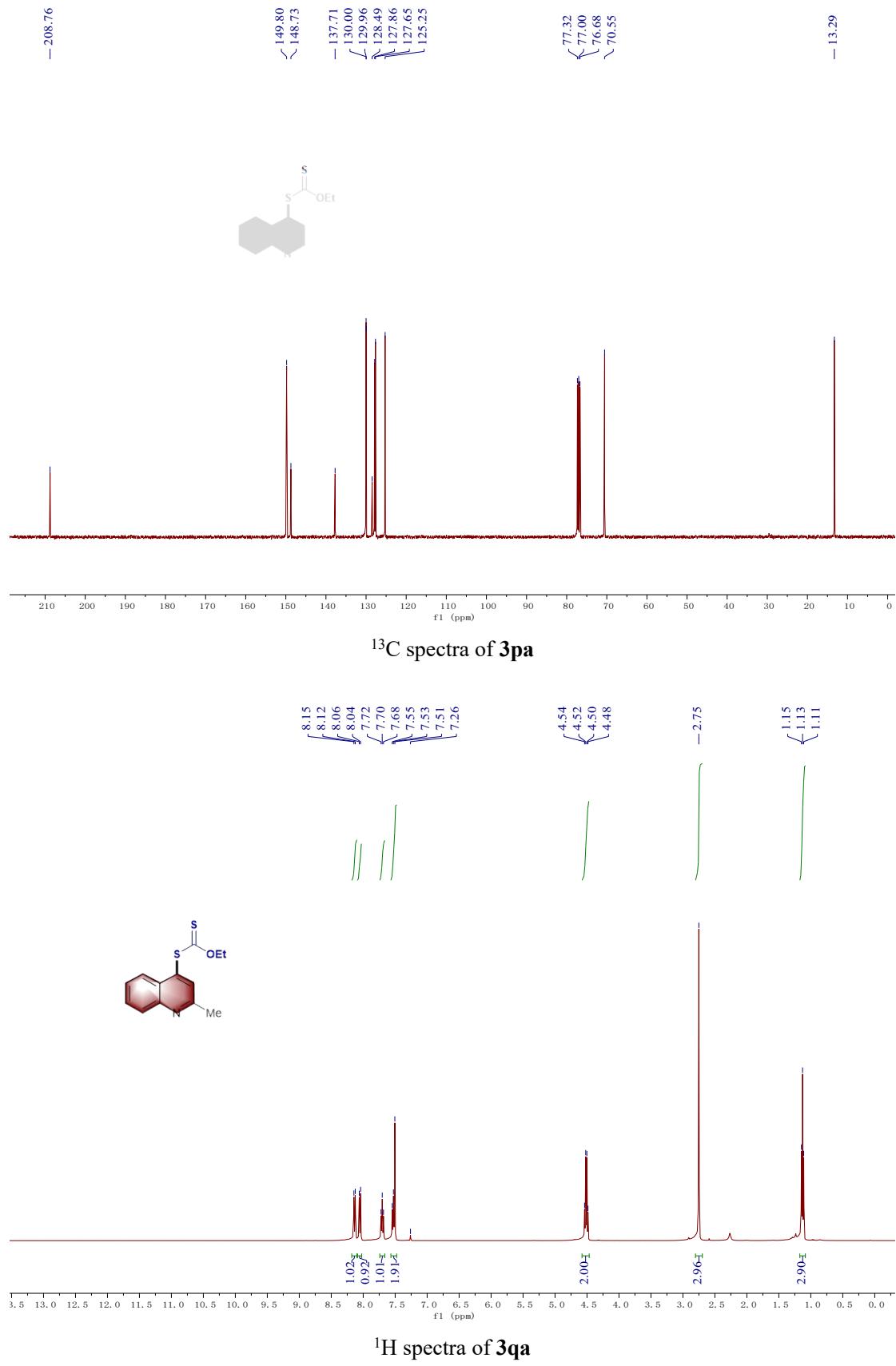


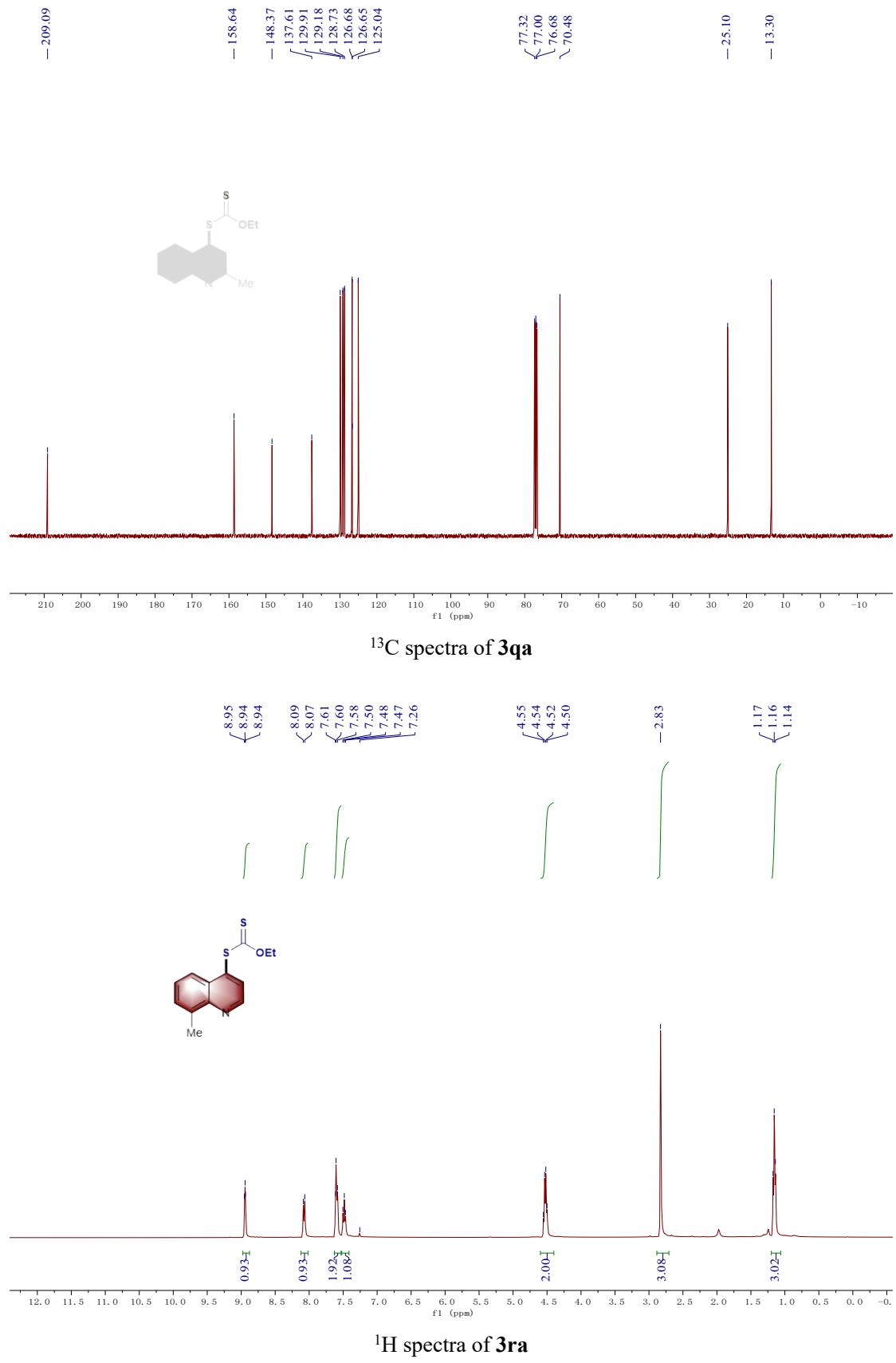
¹³C spectra of **3na**



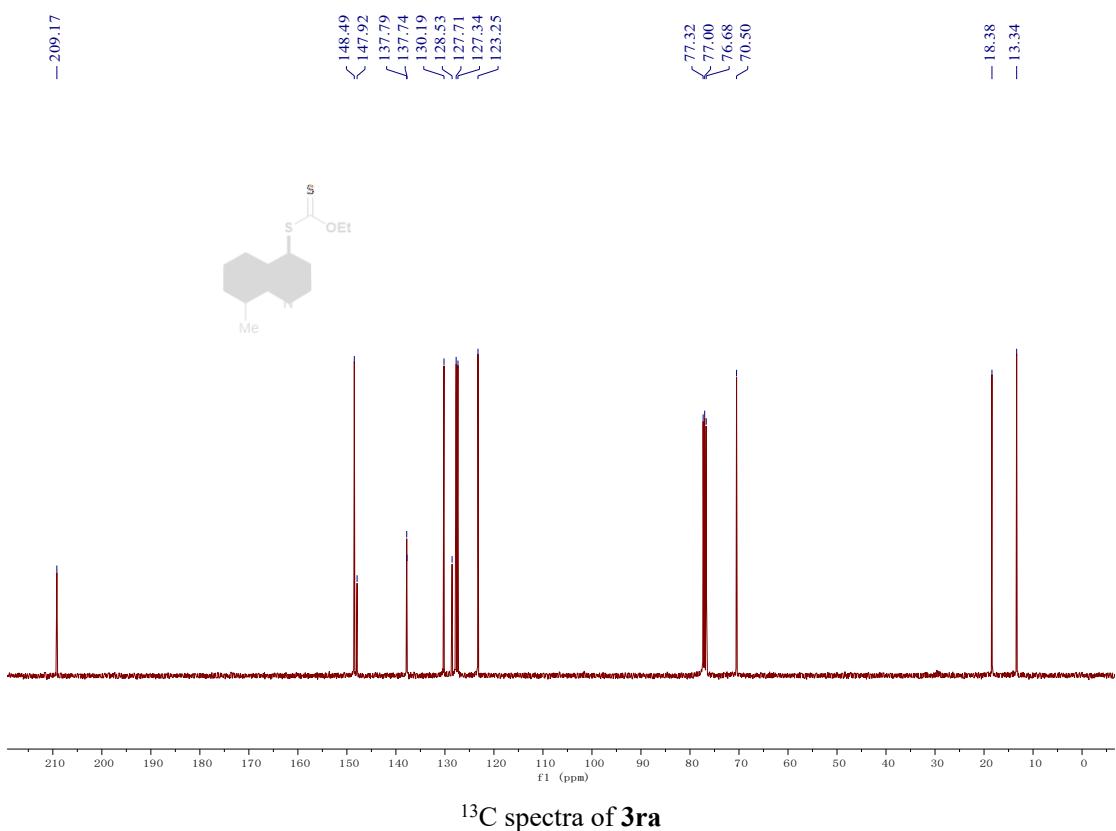
¹H spectra of **3oa**



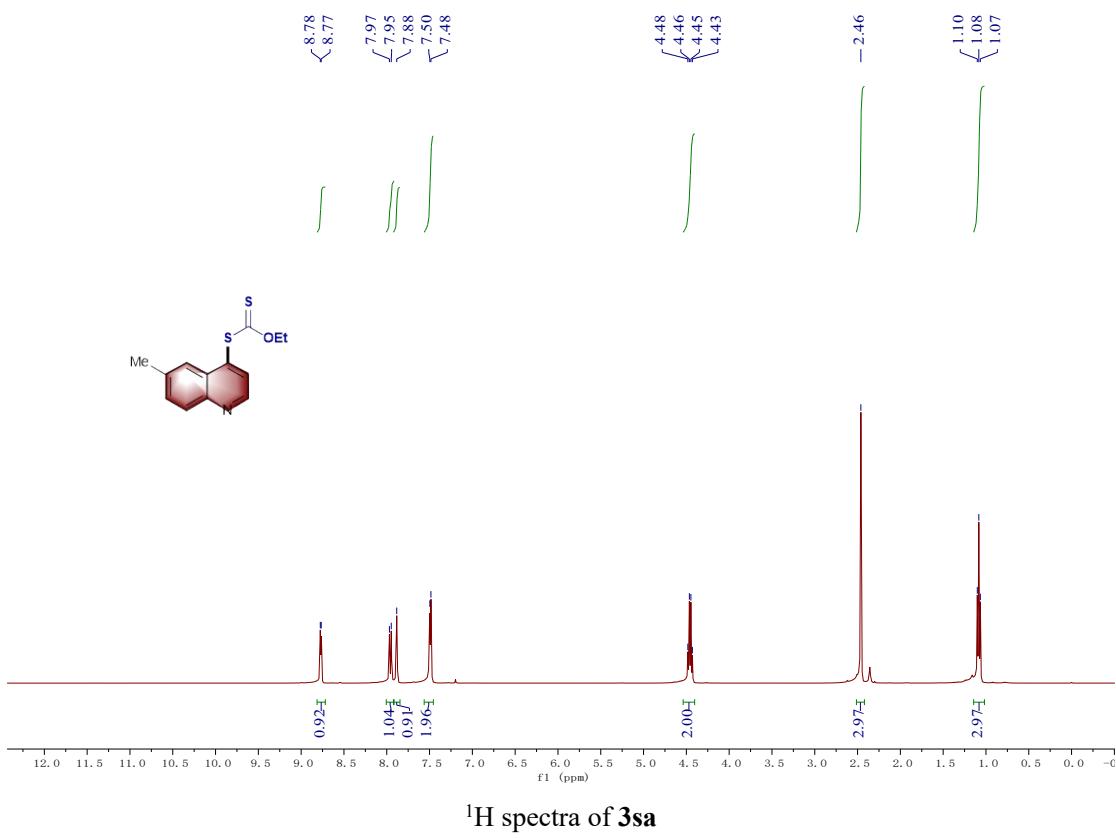




- 209.17

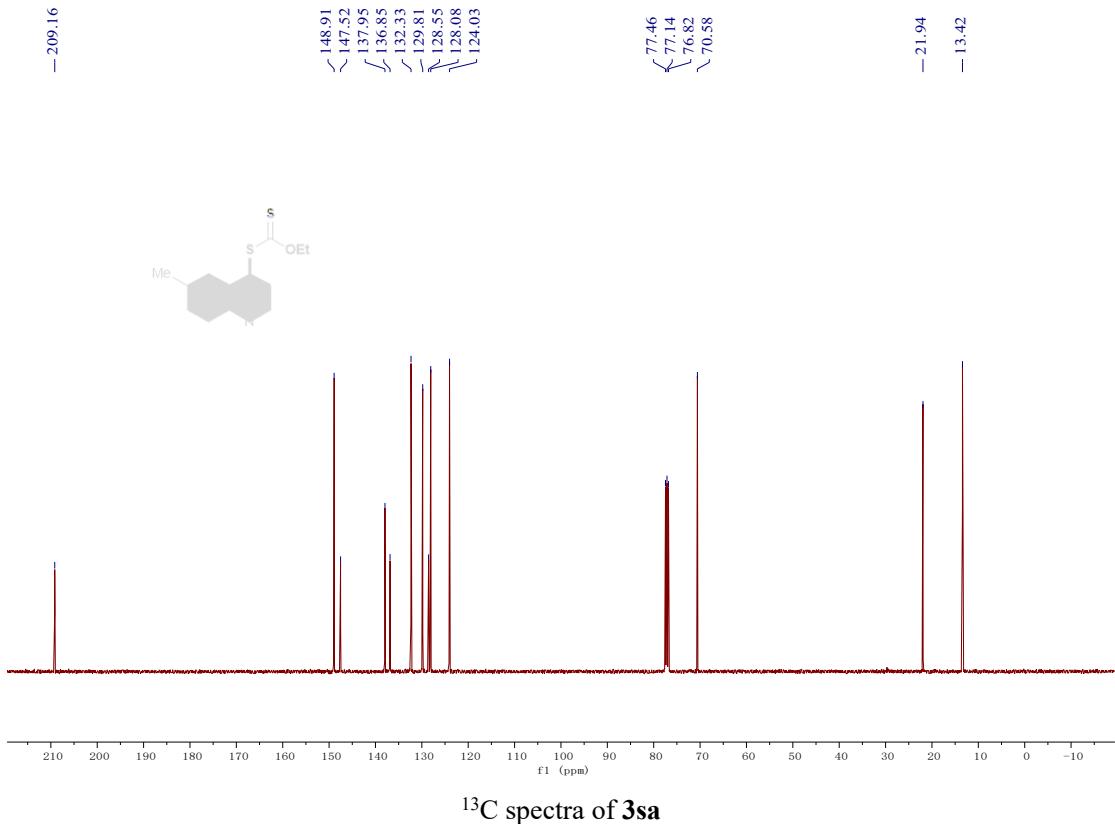


^{13}C spectra of **3ra**

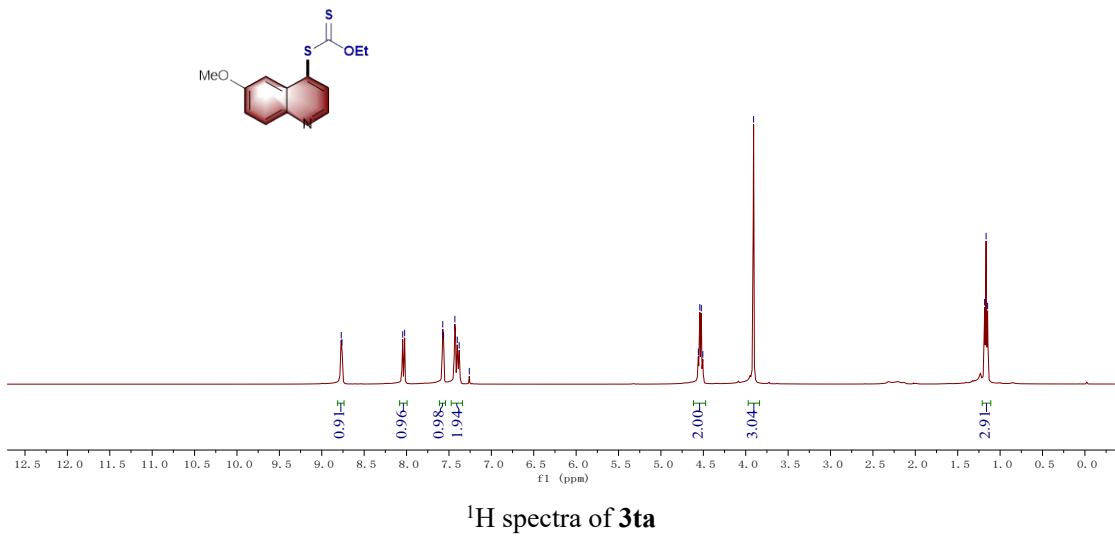
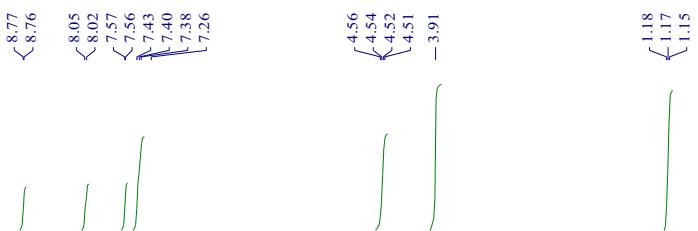


^1H spectra of **3sa**

- 209.16



¹³C spectra of 3sa



¹H spectra of 3ta

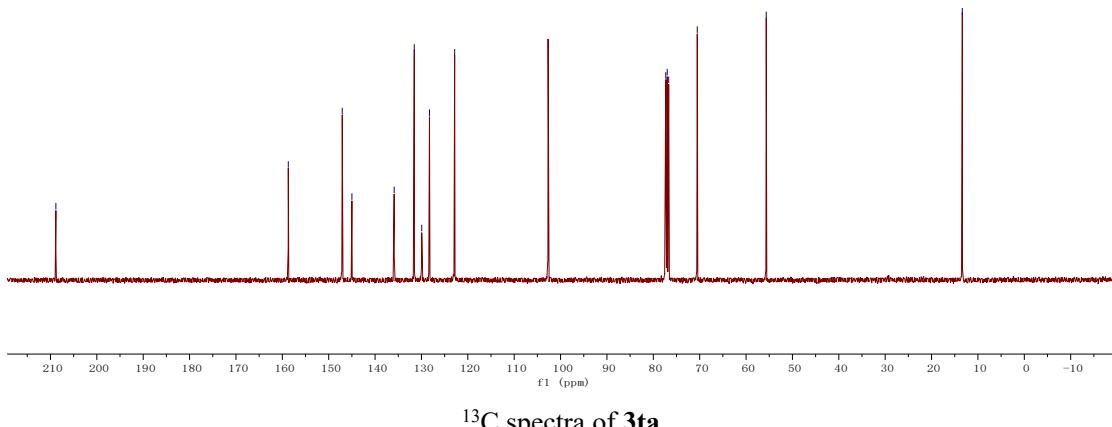
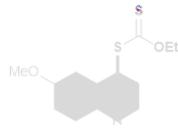
-208.83

-158.72

147.08
~145.00
135.88
131.55
129.93
128.27
~122.84

-55.65

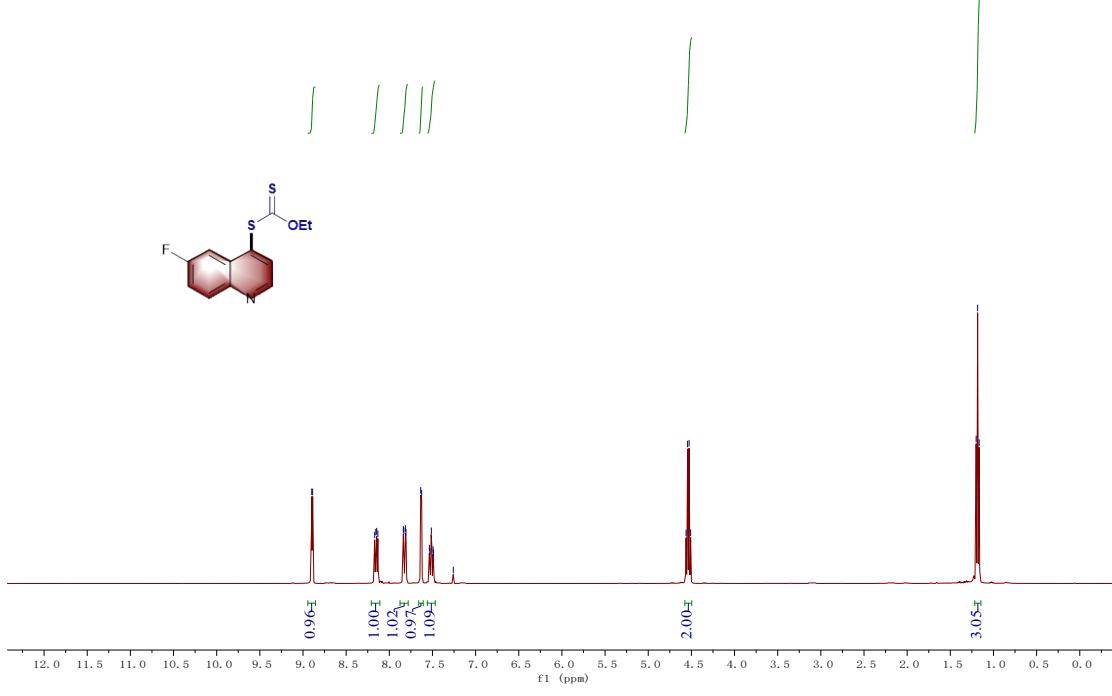
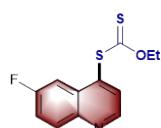
-13.37

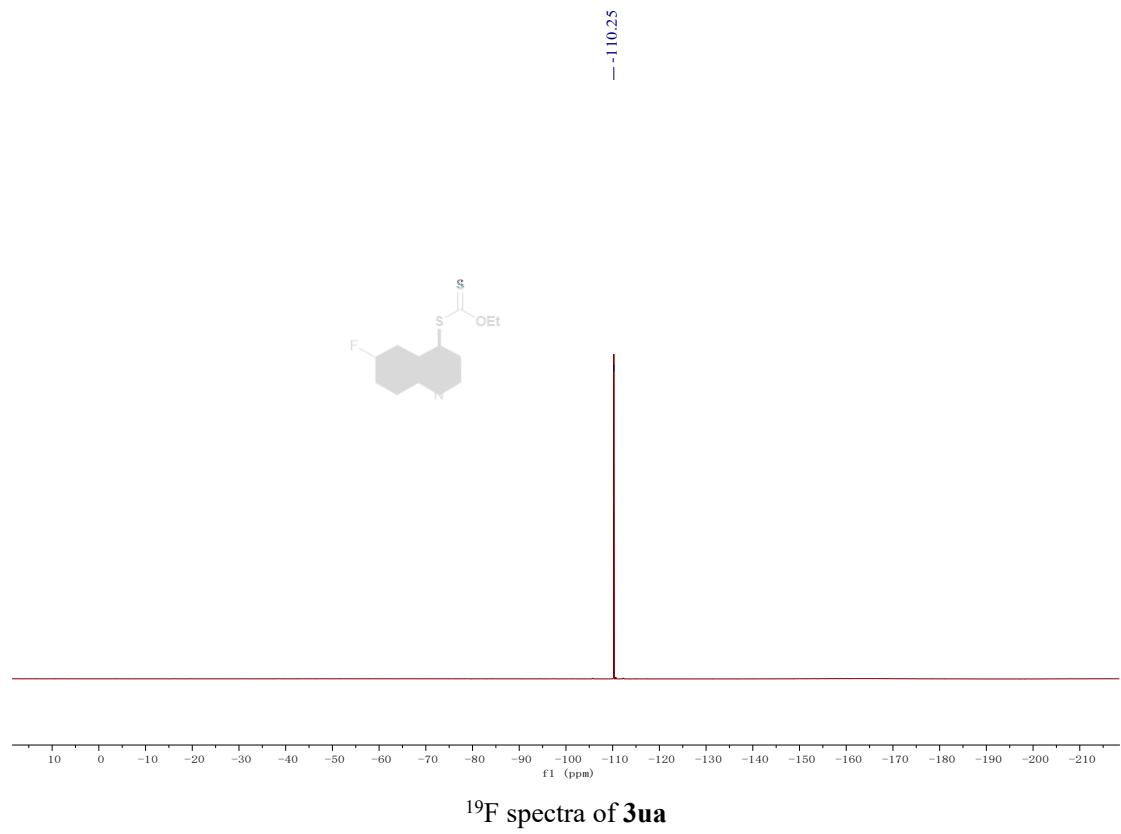
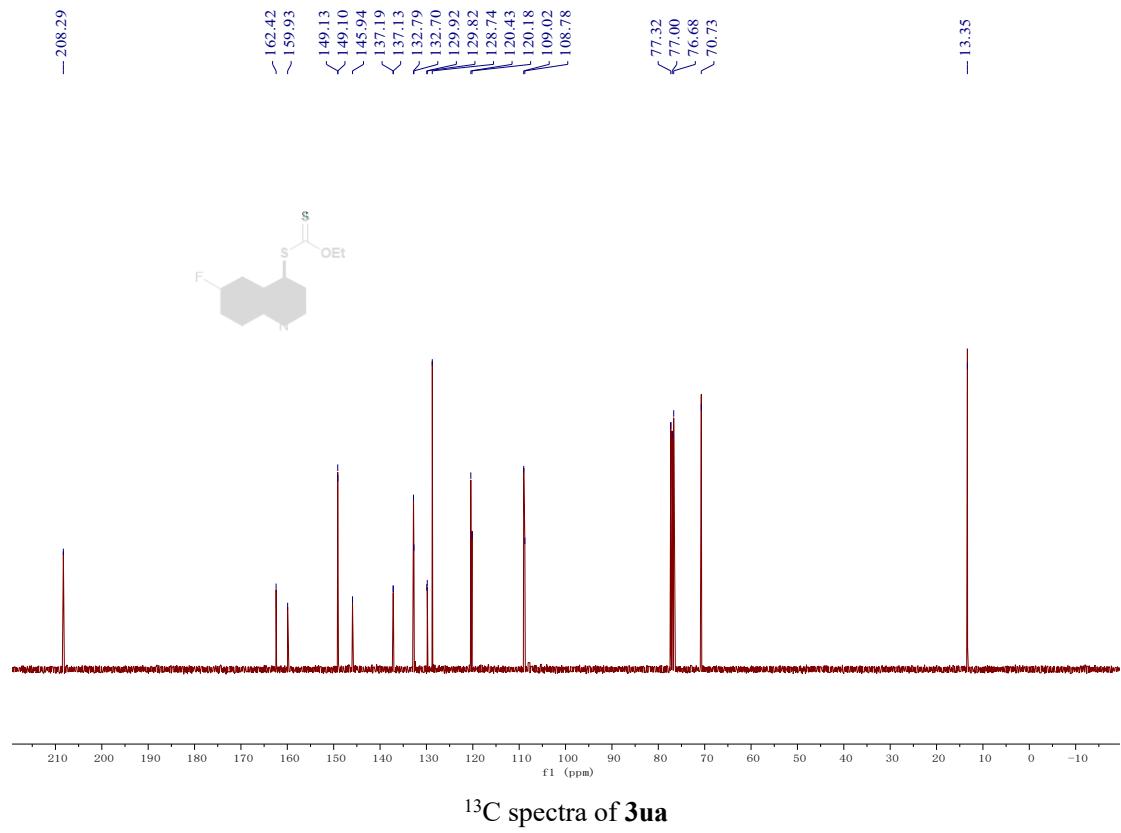


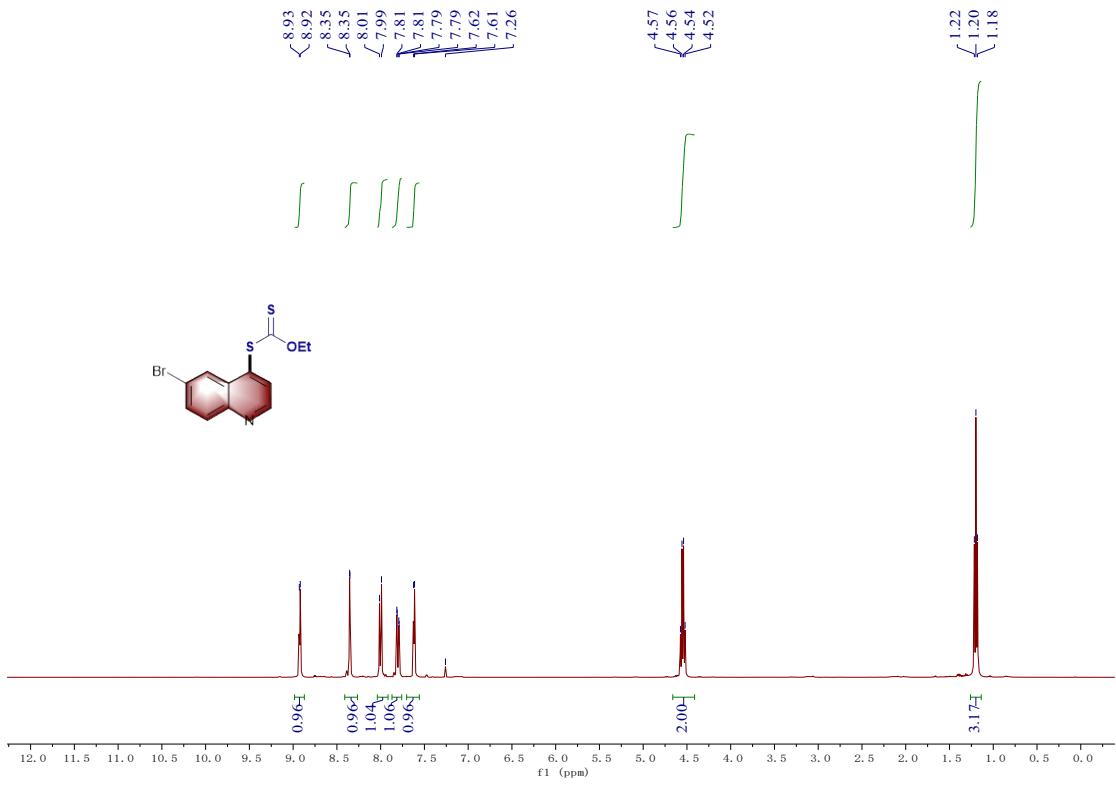
8.90
<8.89
8.17
8.16
8.15
8.13
8.13
7.84
7.83
7.81
7.81
7.64
7.63
7.54
7.53
7.51
7.49
7.49
7.26

4.56
4.54
4.53
4.51

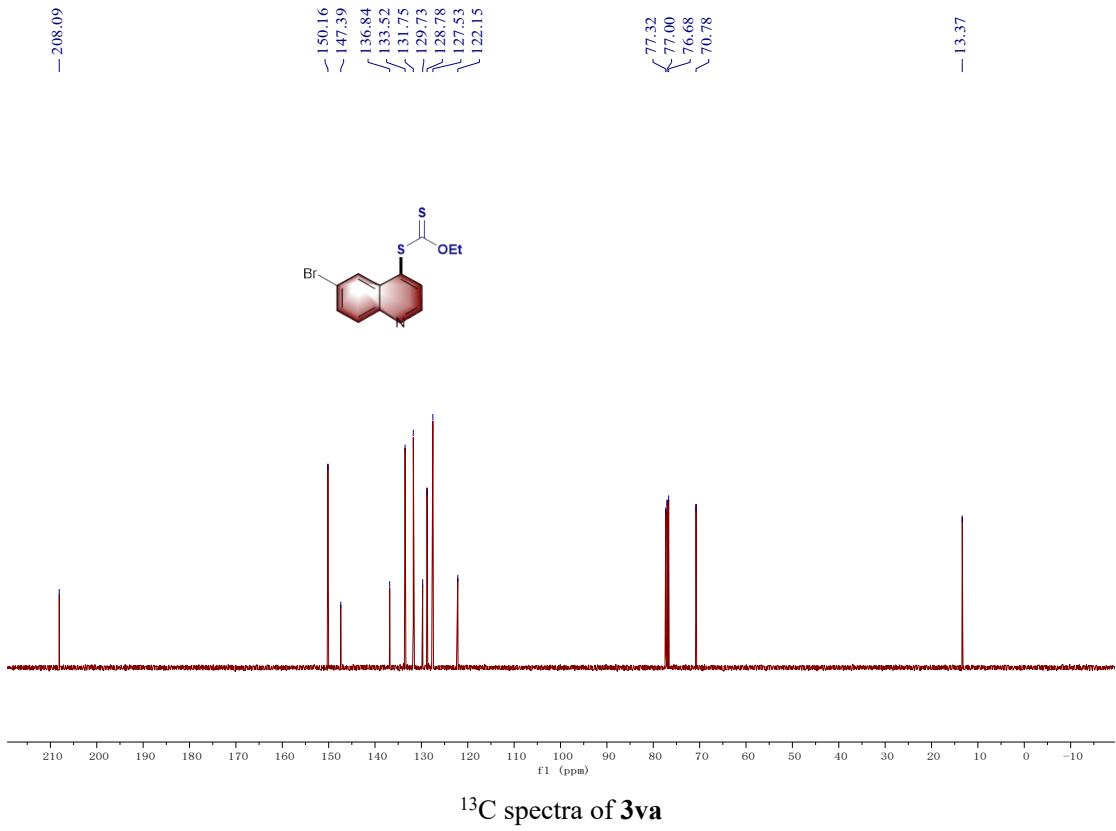
1.20
1.18
1.17



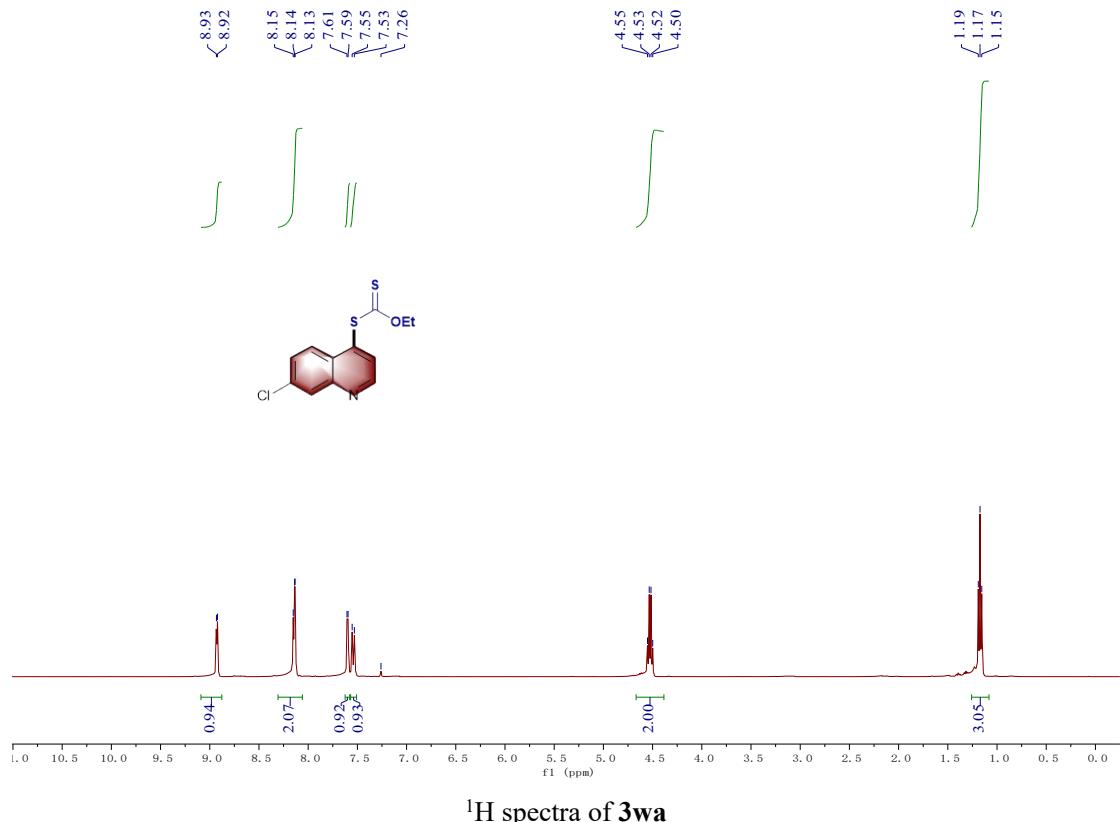




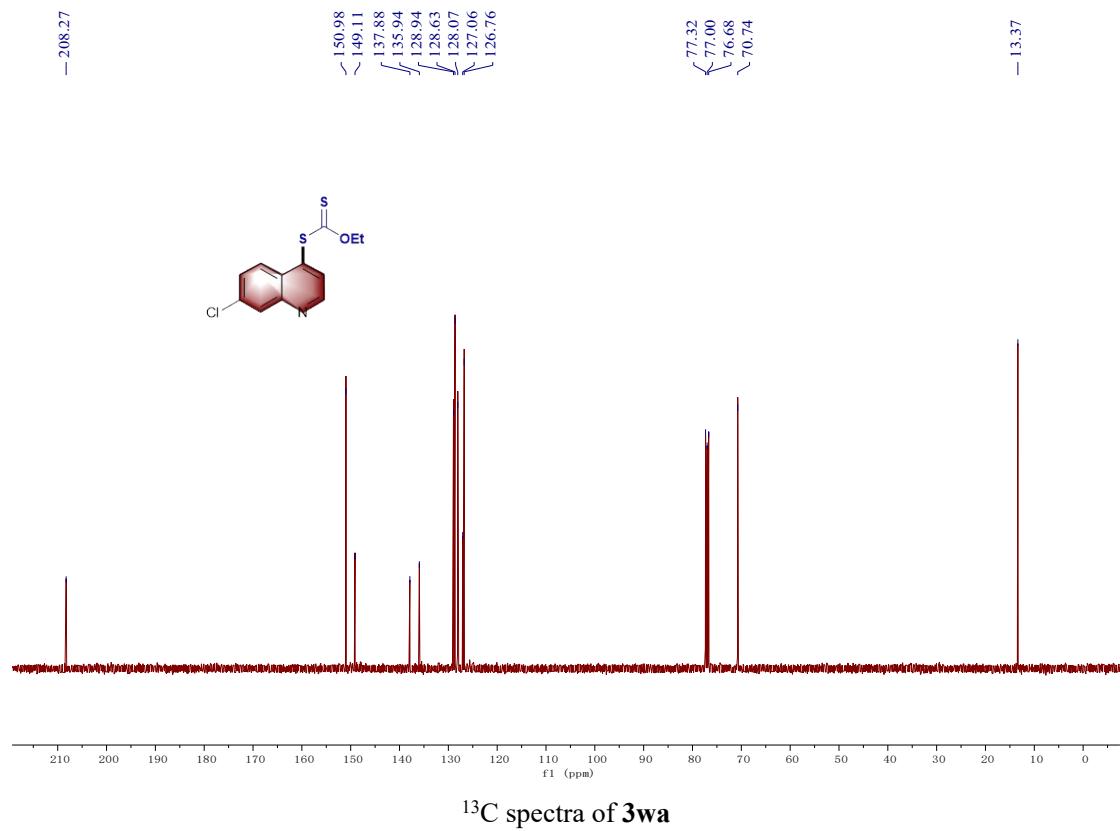
¹H spectra of **3va**



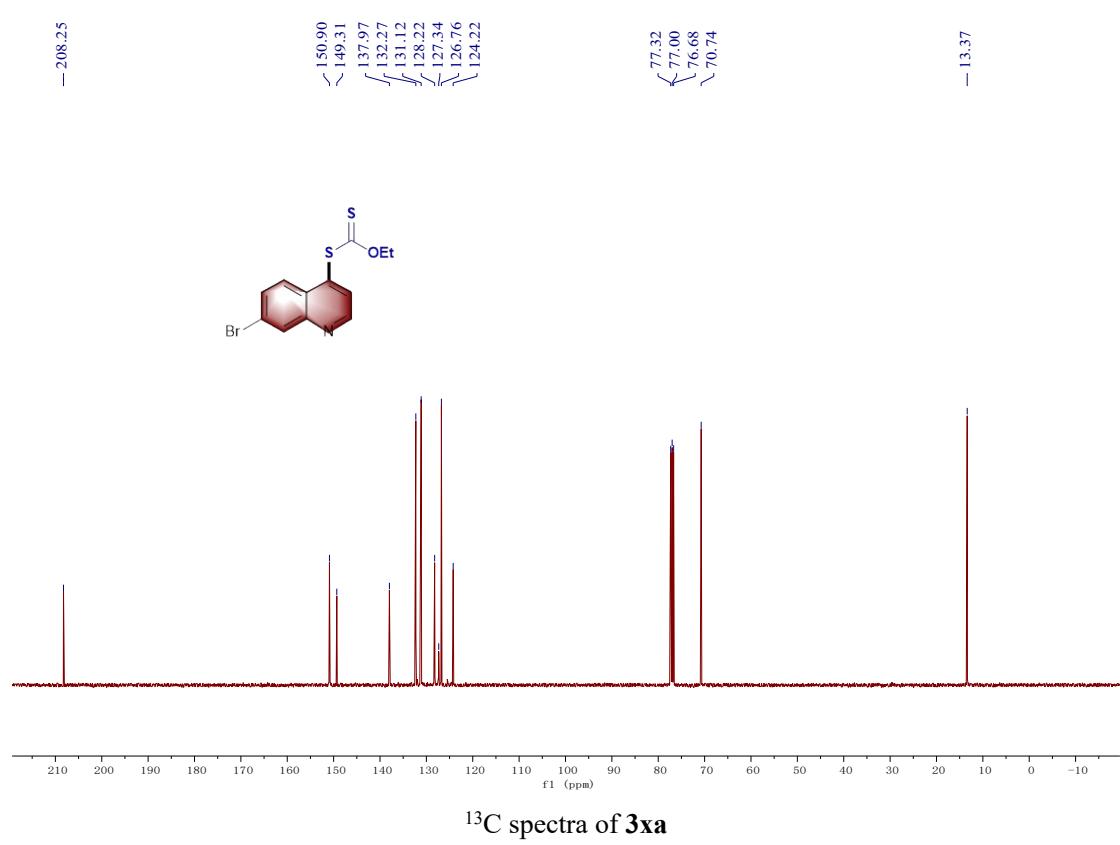
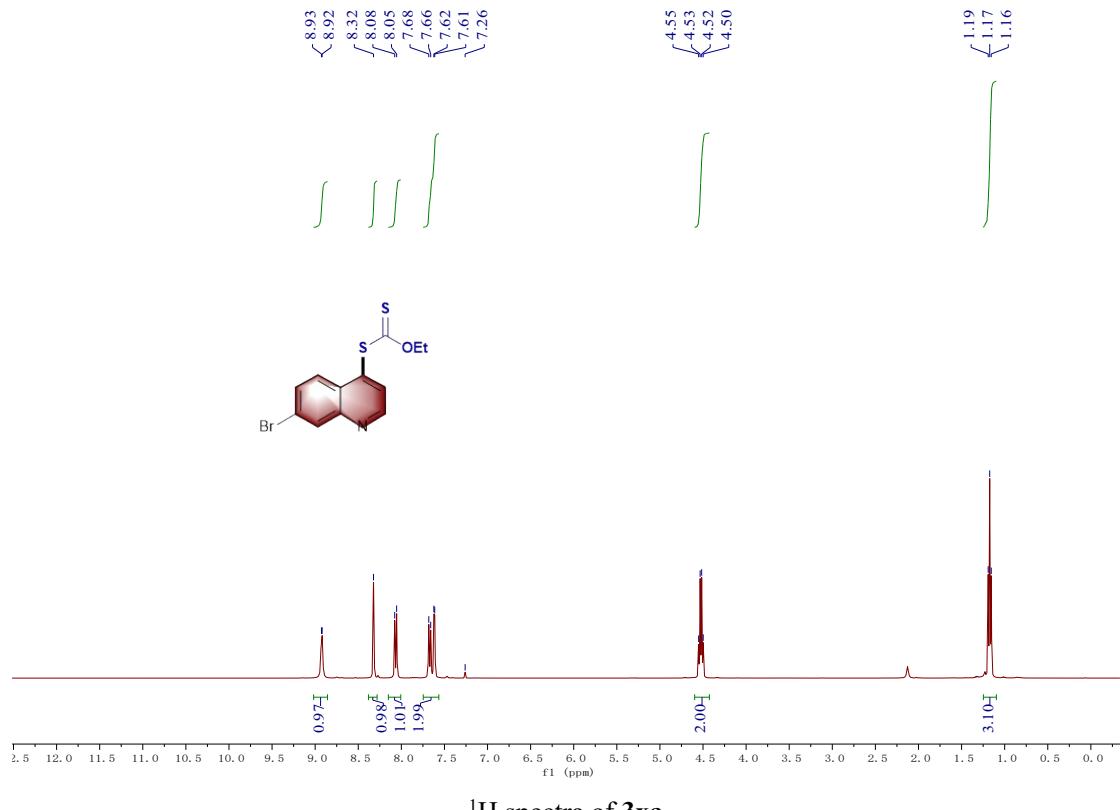
¹³C spectra of **3va**

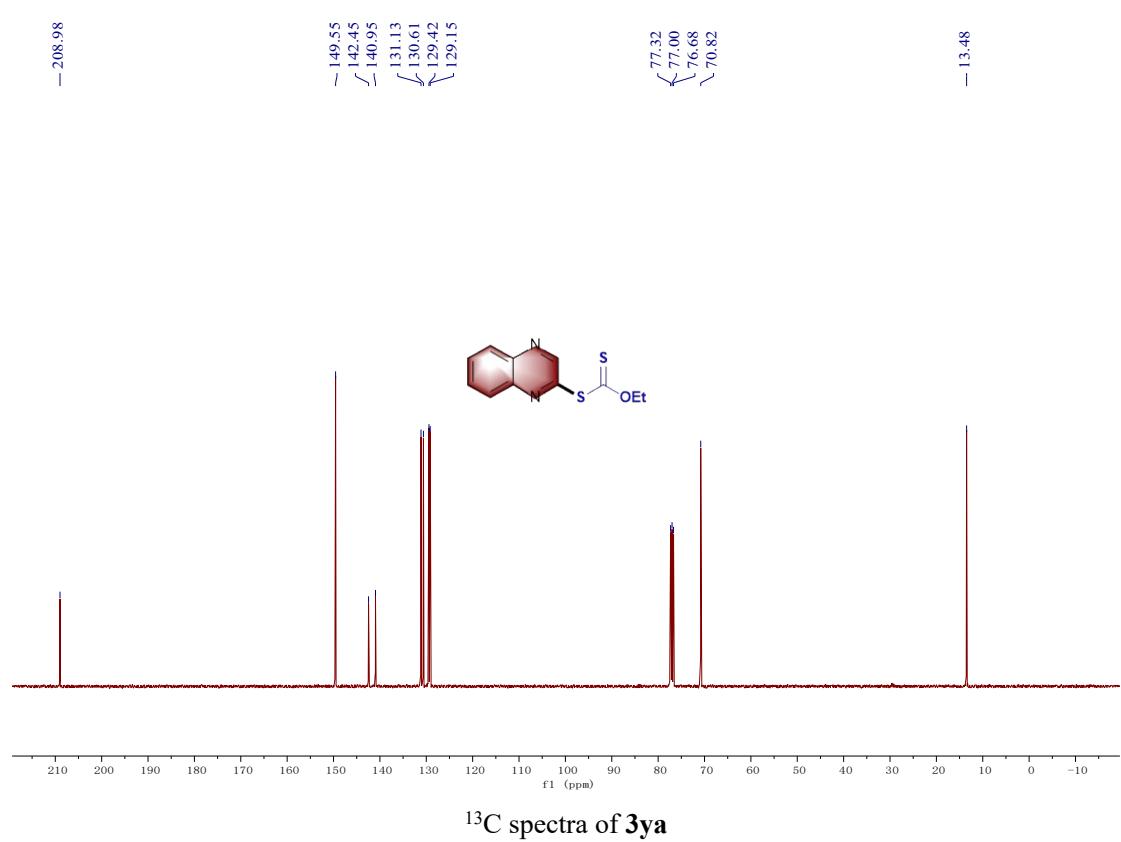
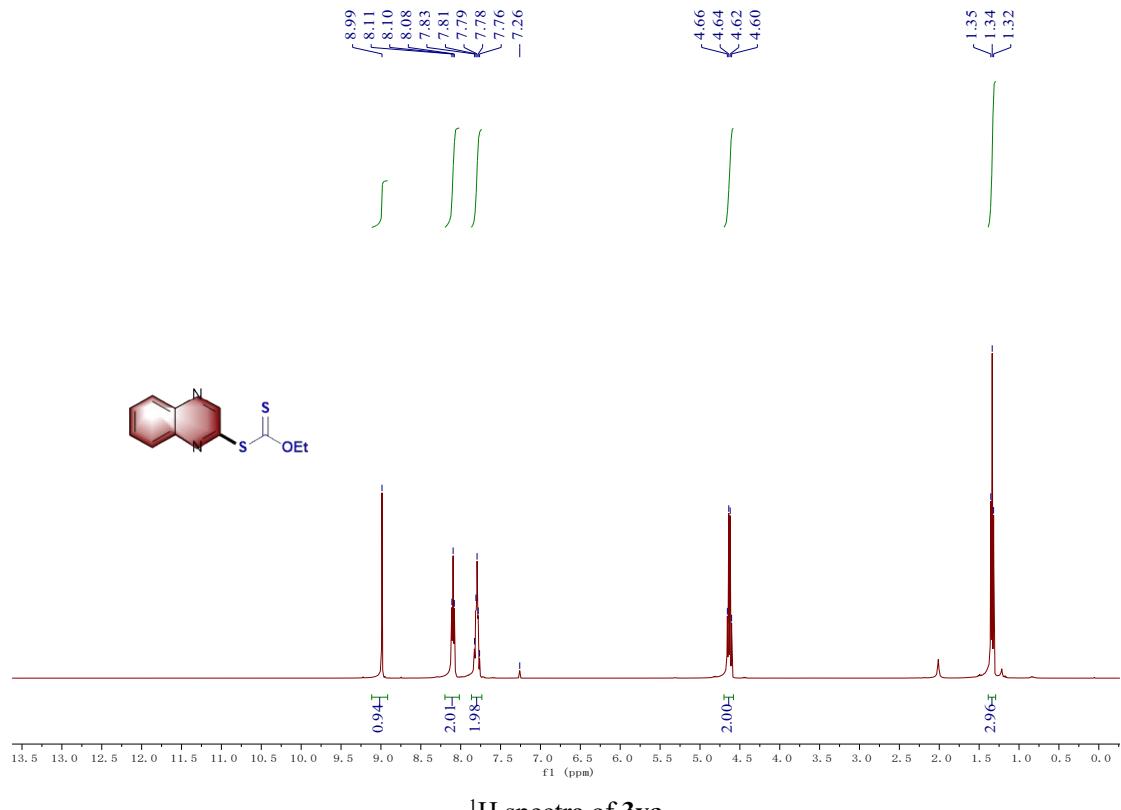


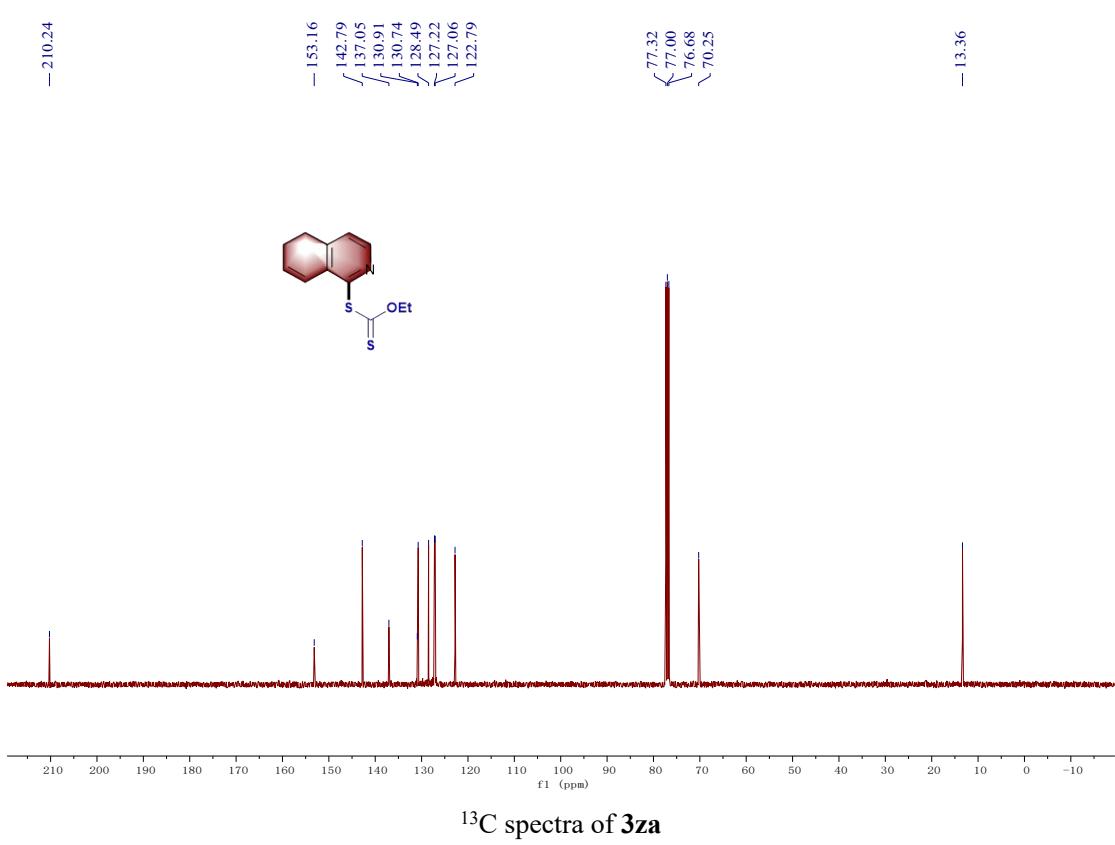
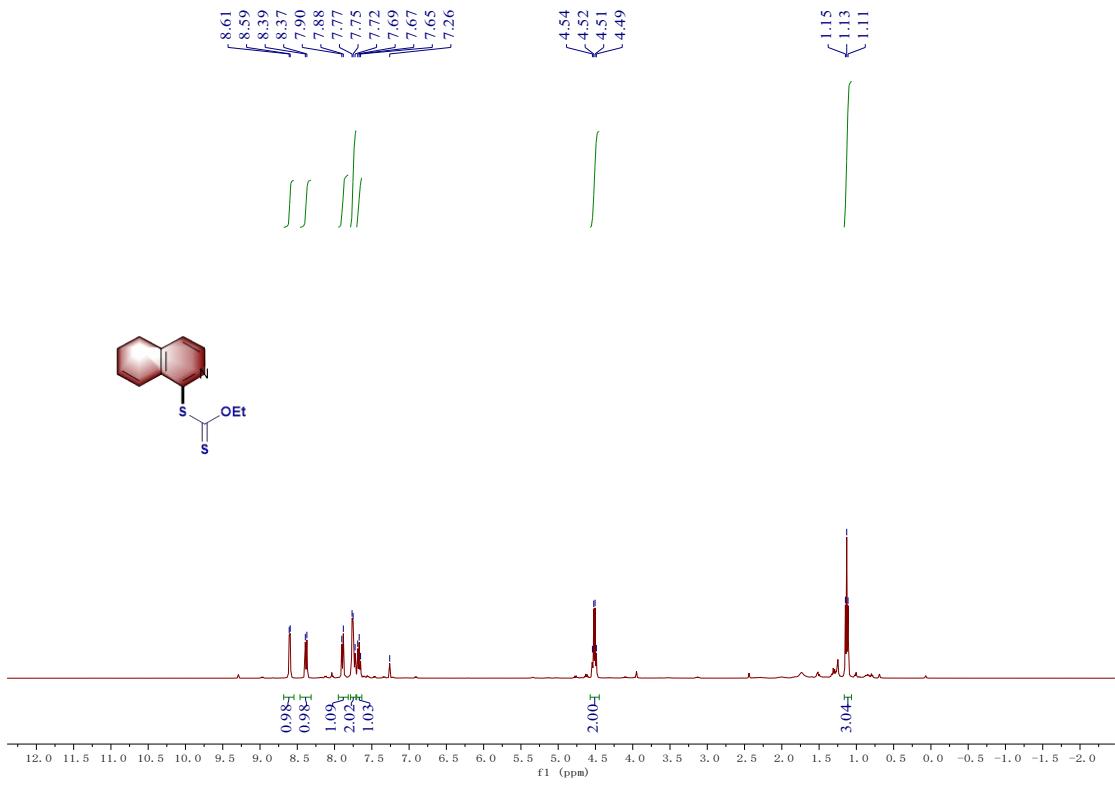
¹H spectra of **3wa**

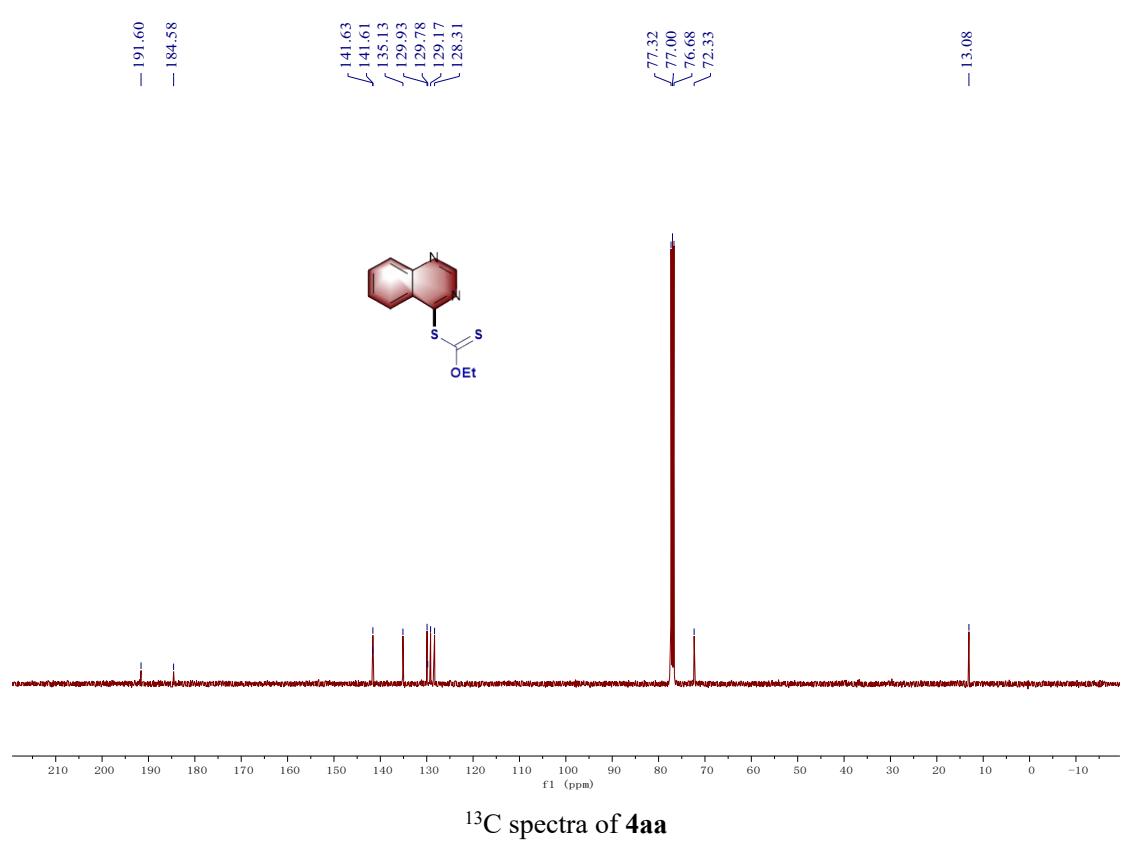
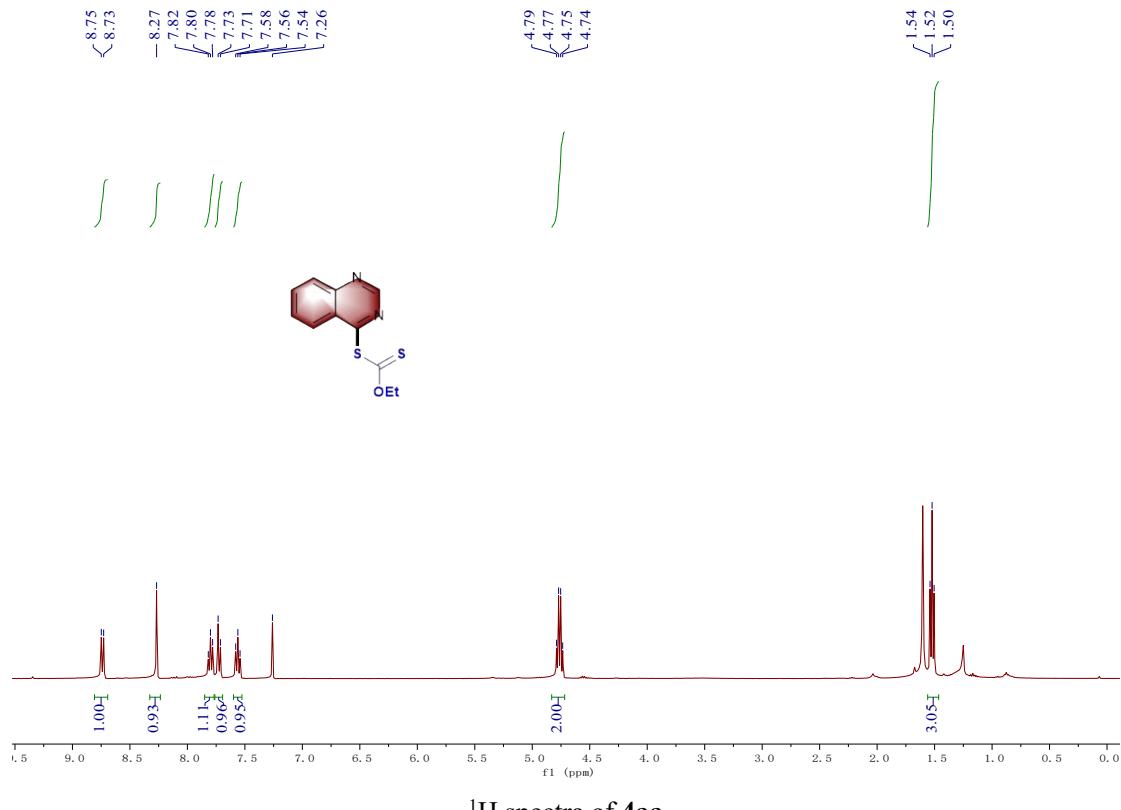


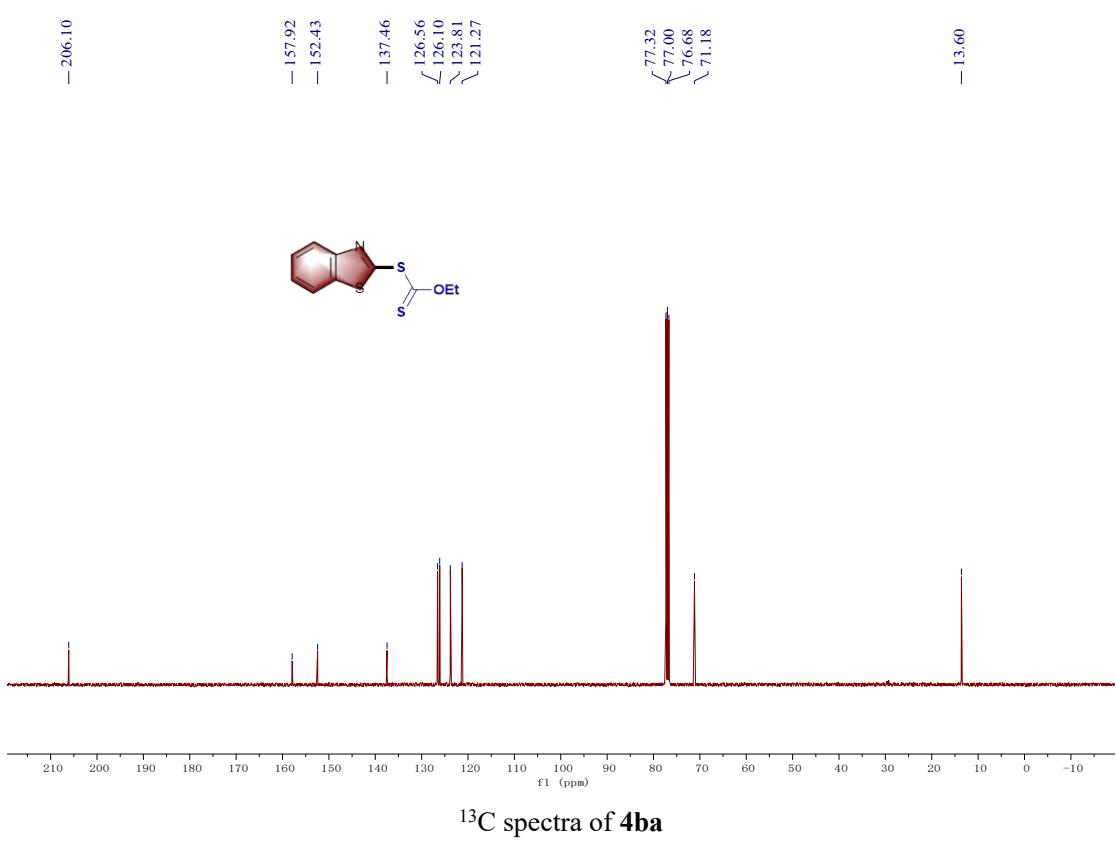
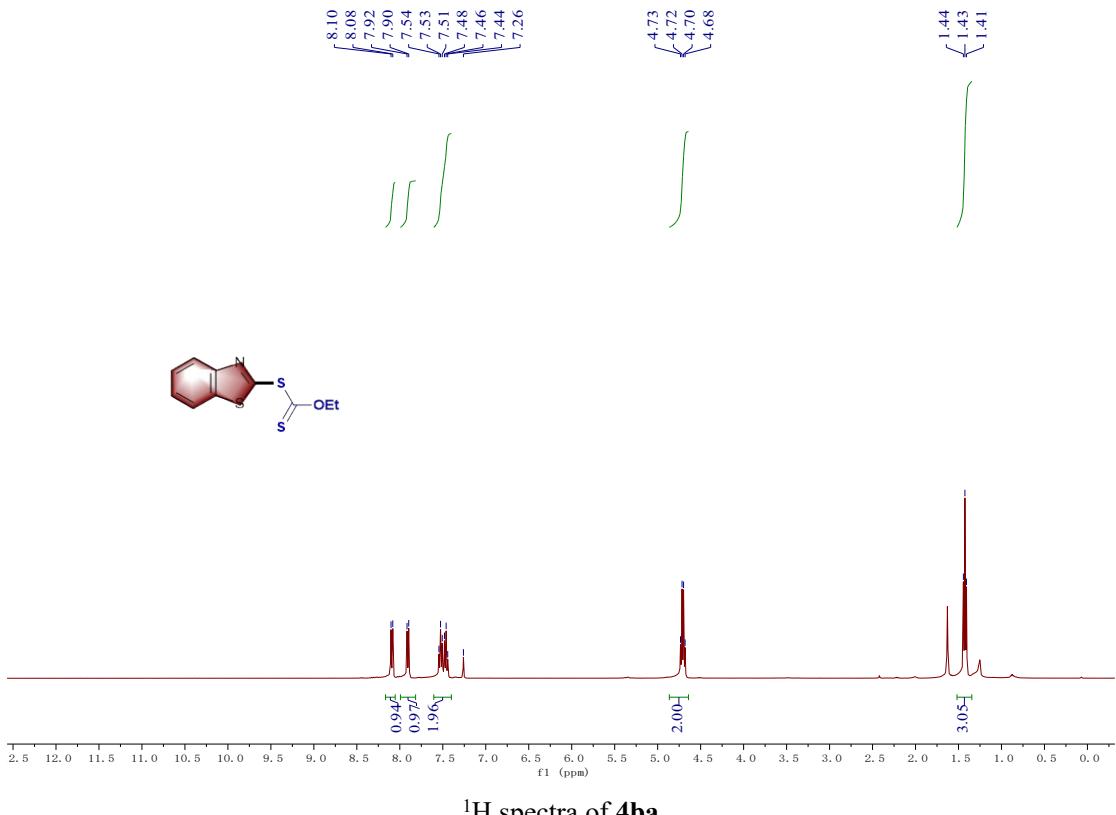
¹³C spectra of **3wa**

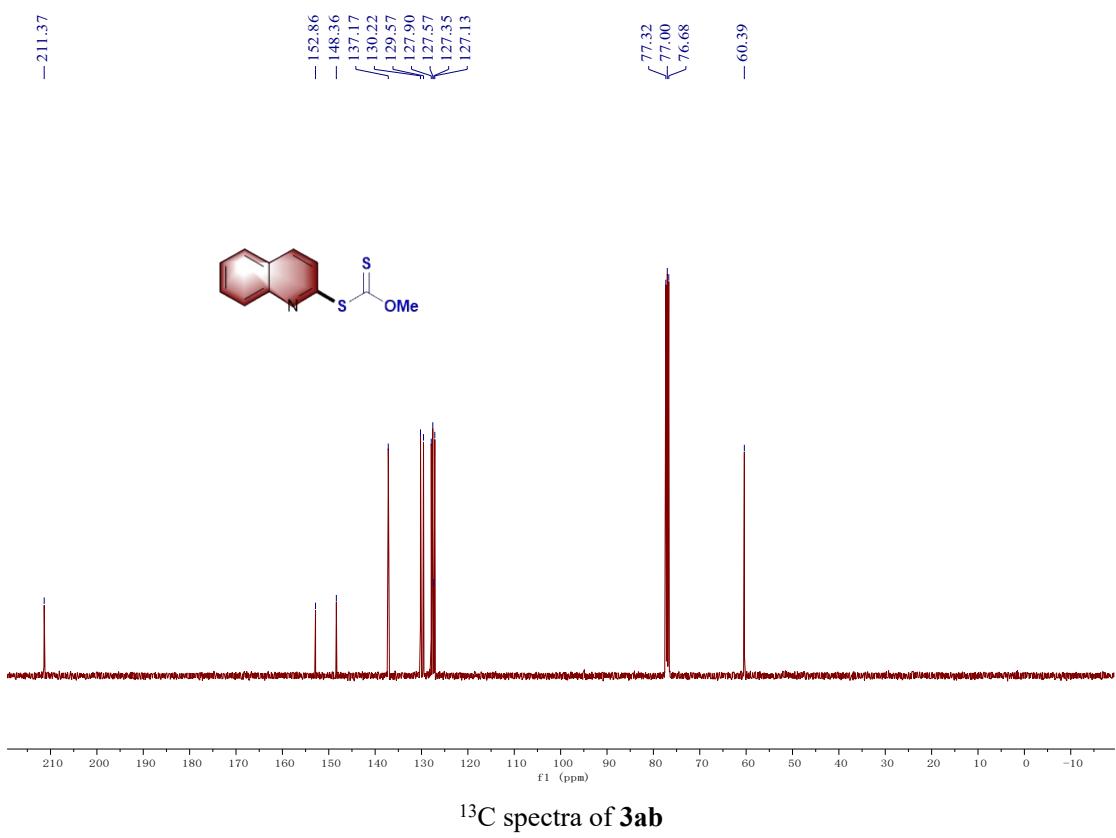
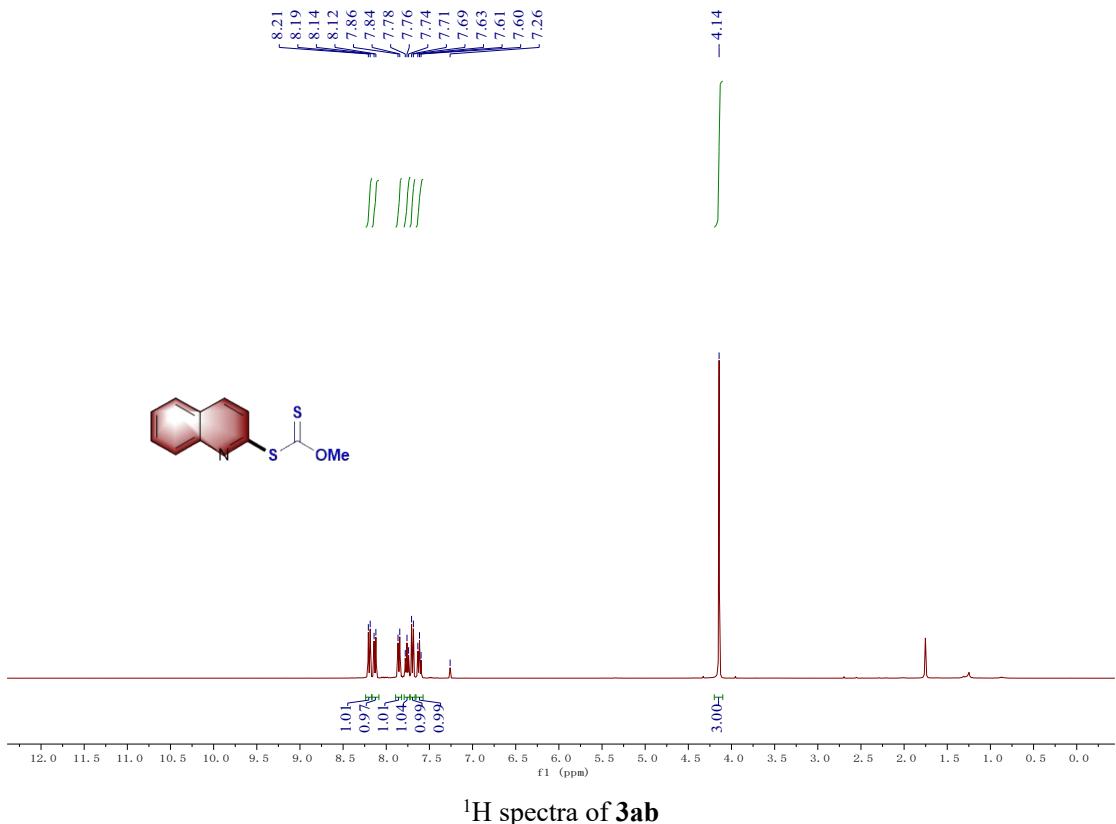


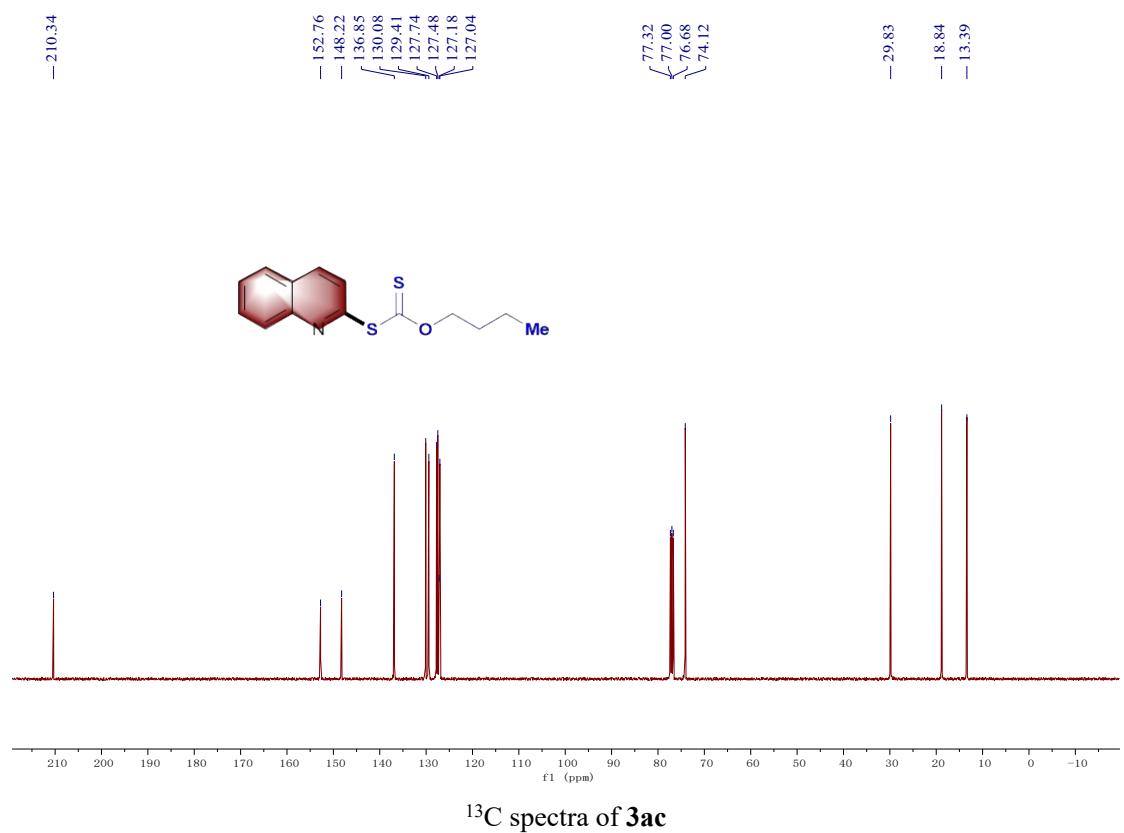
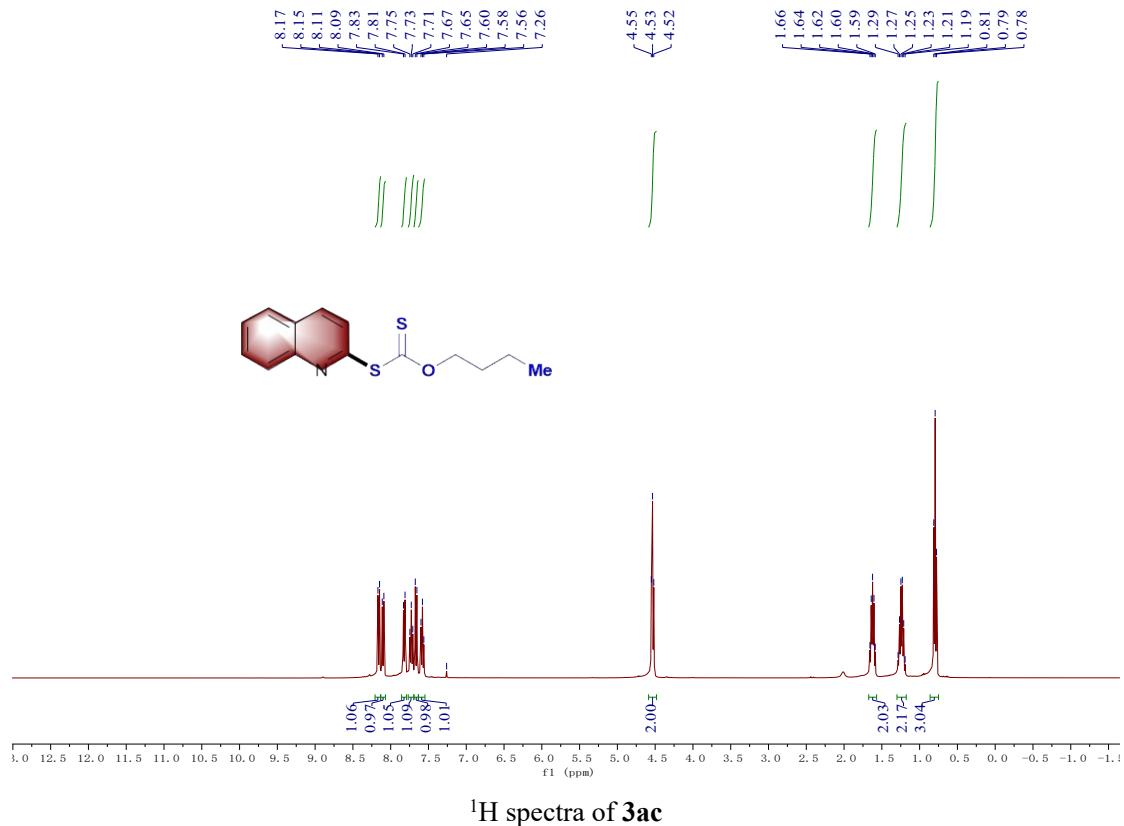


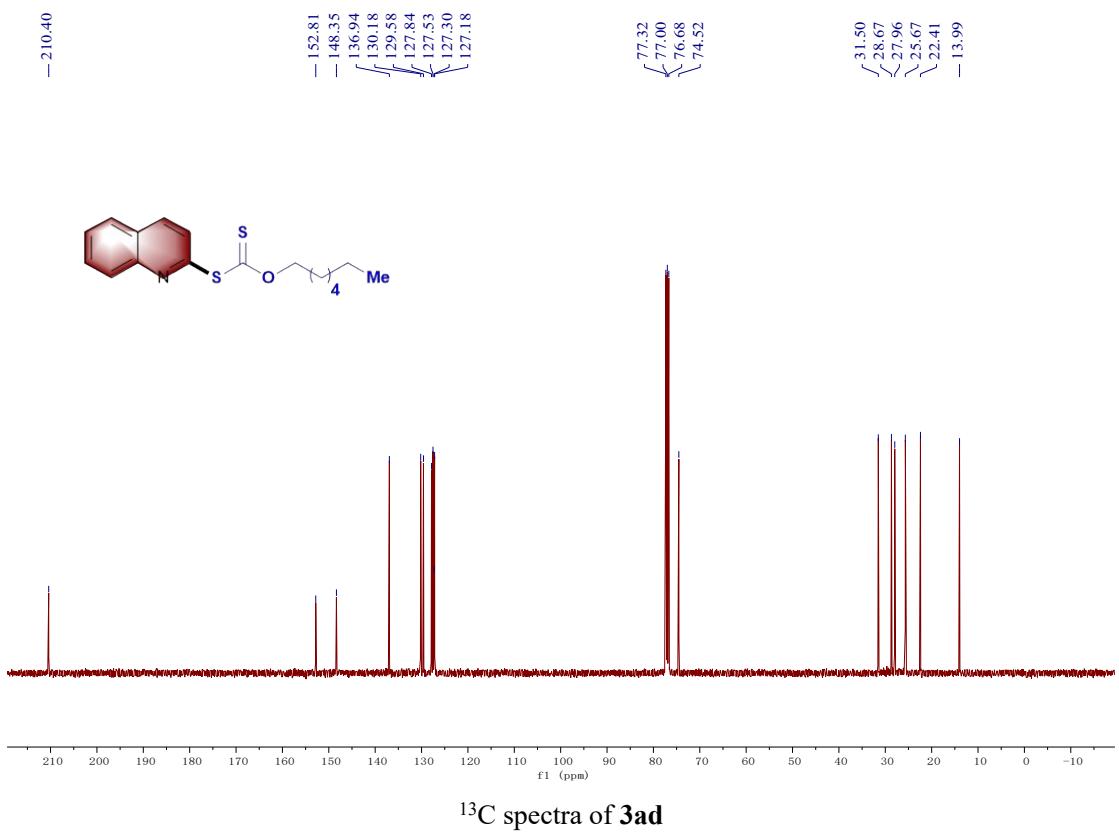
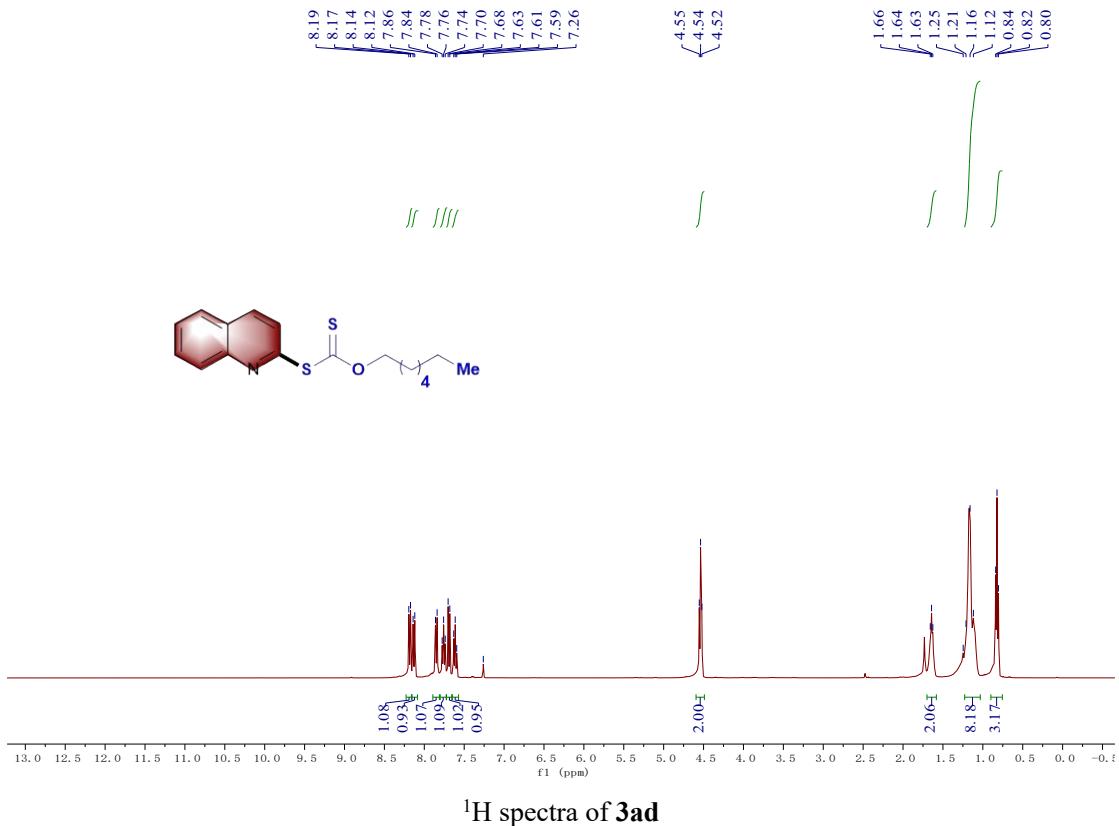


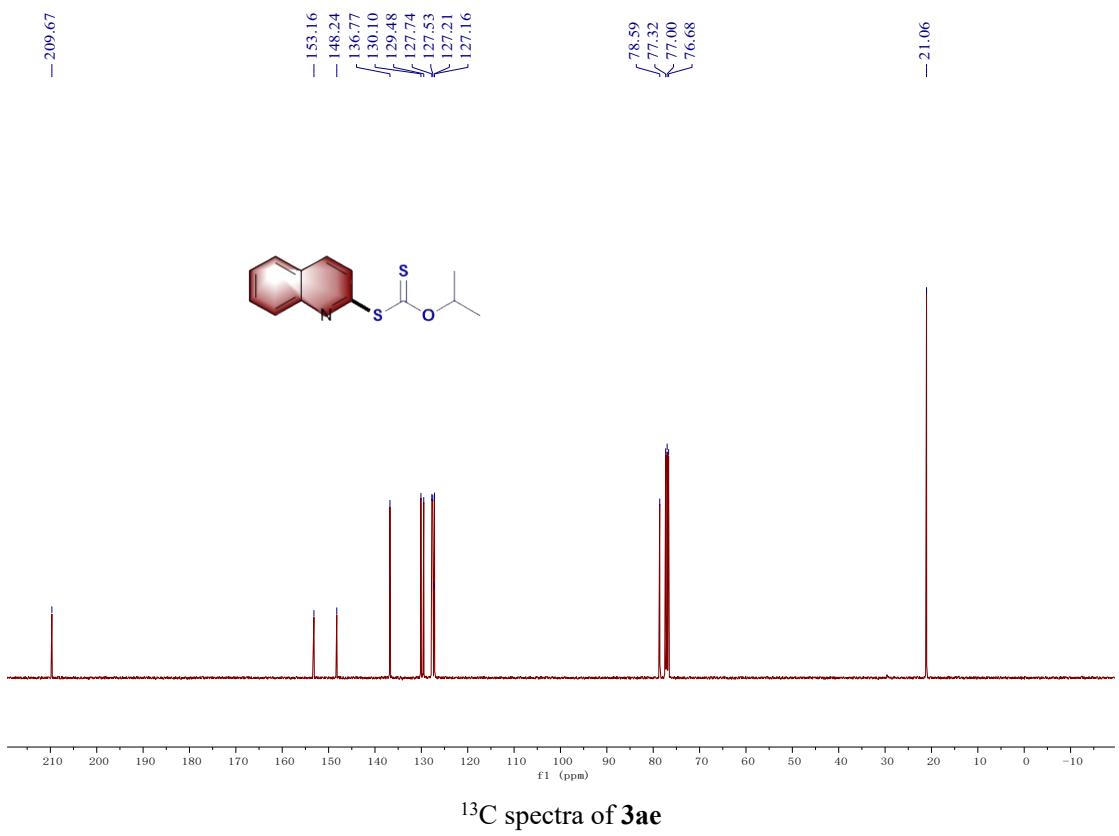
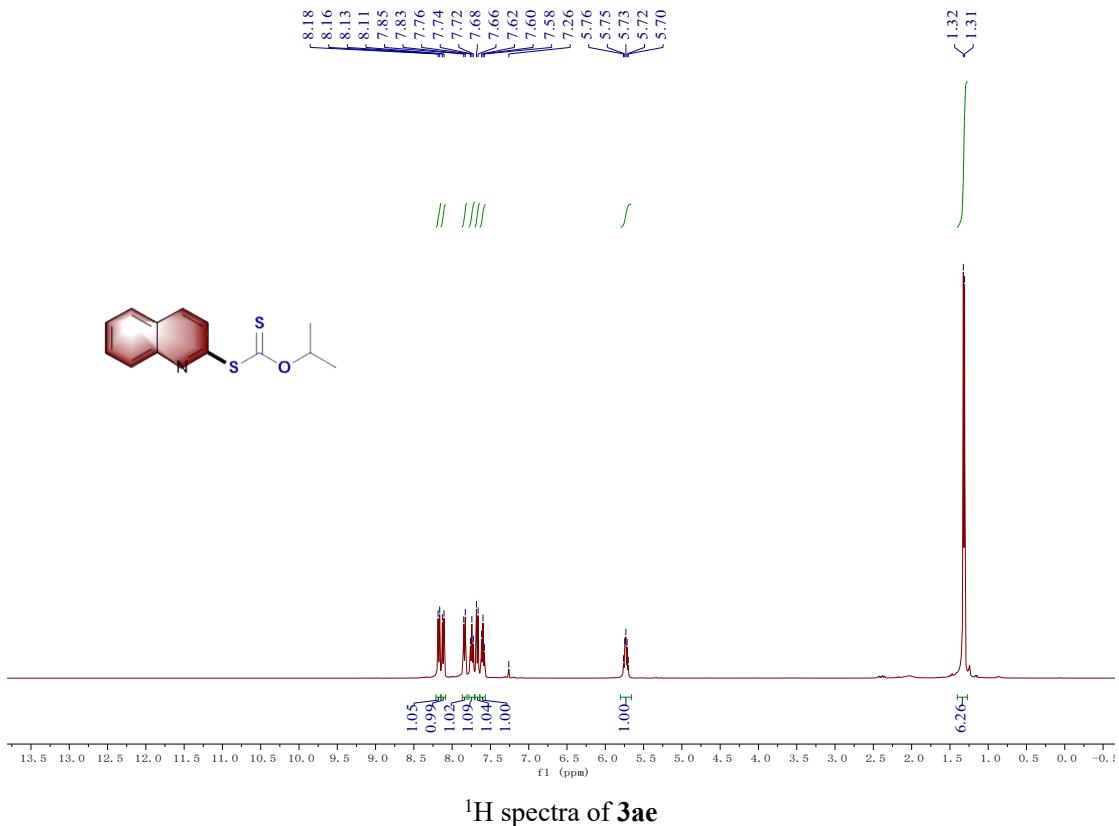


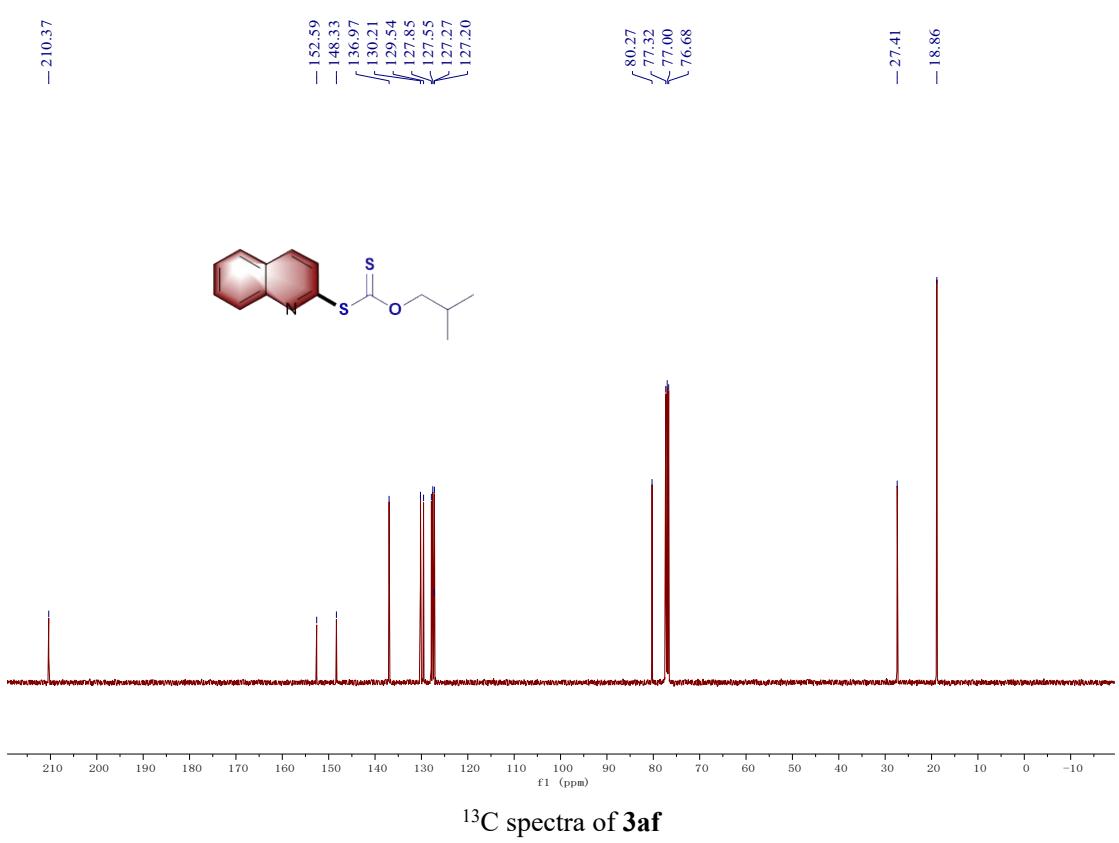
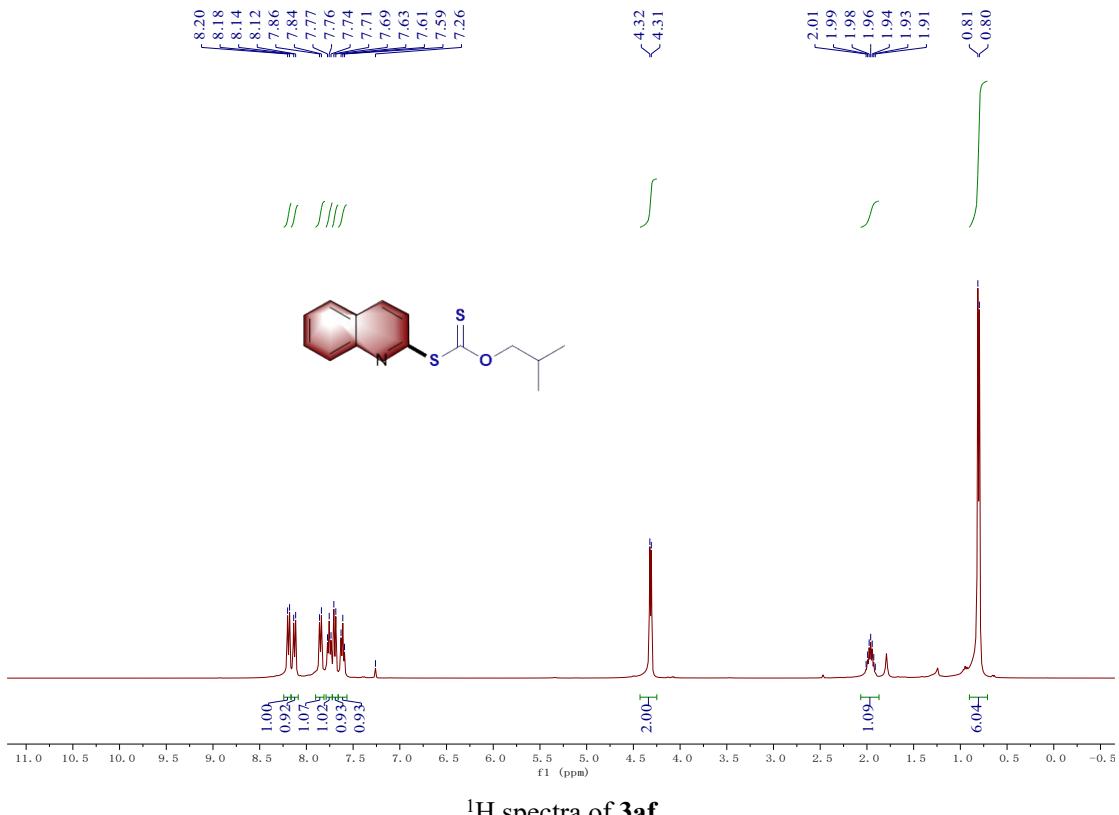


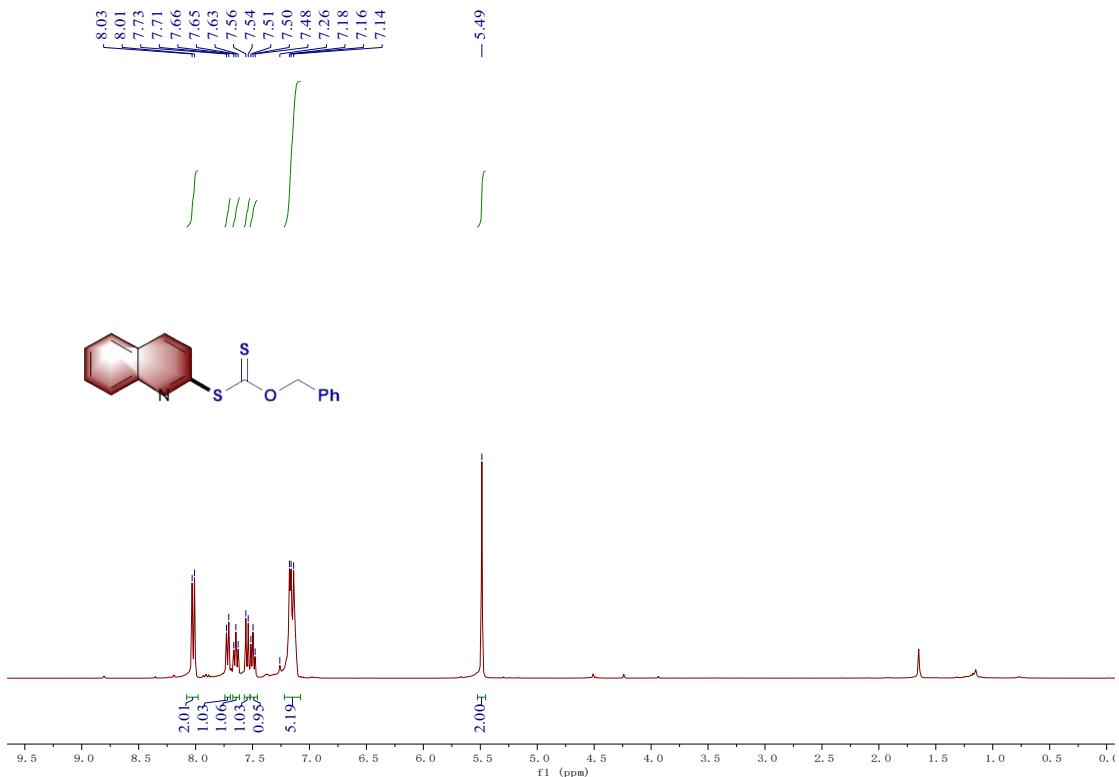




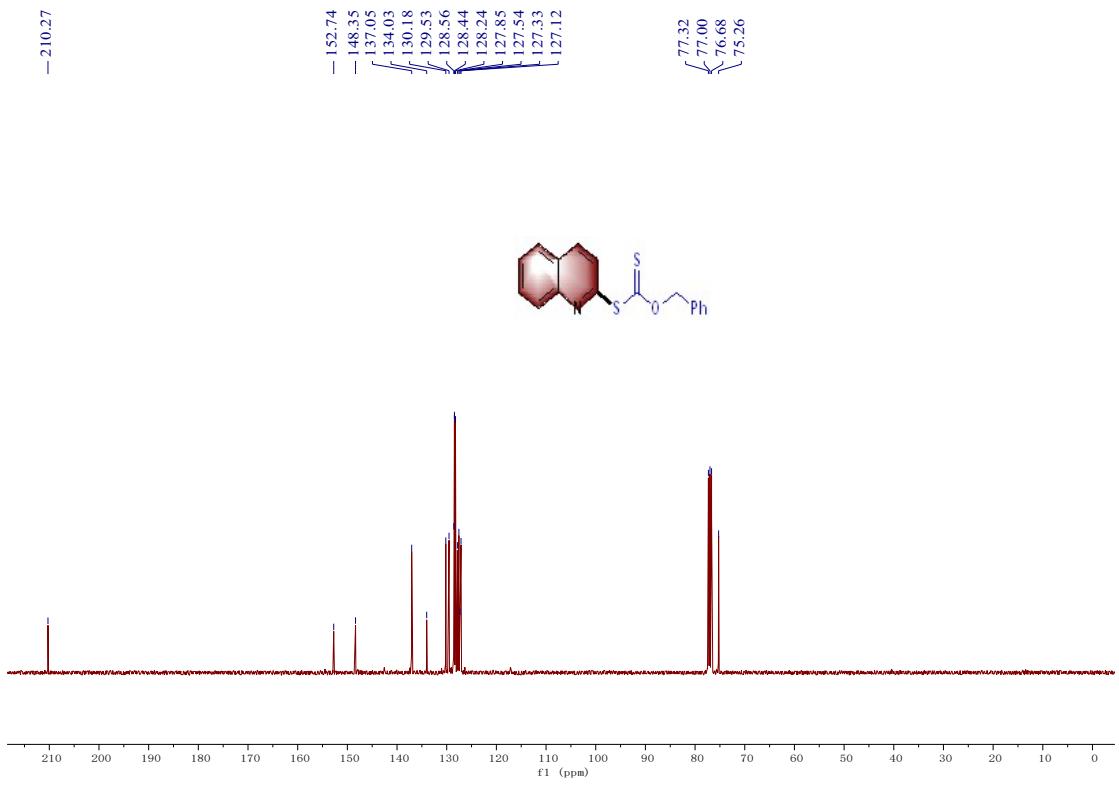




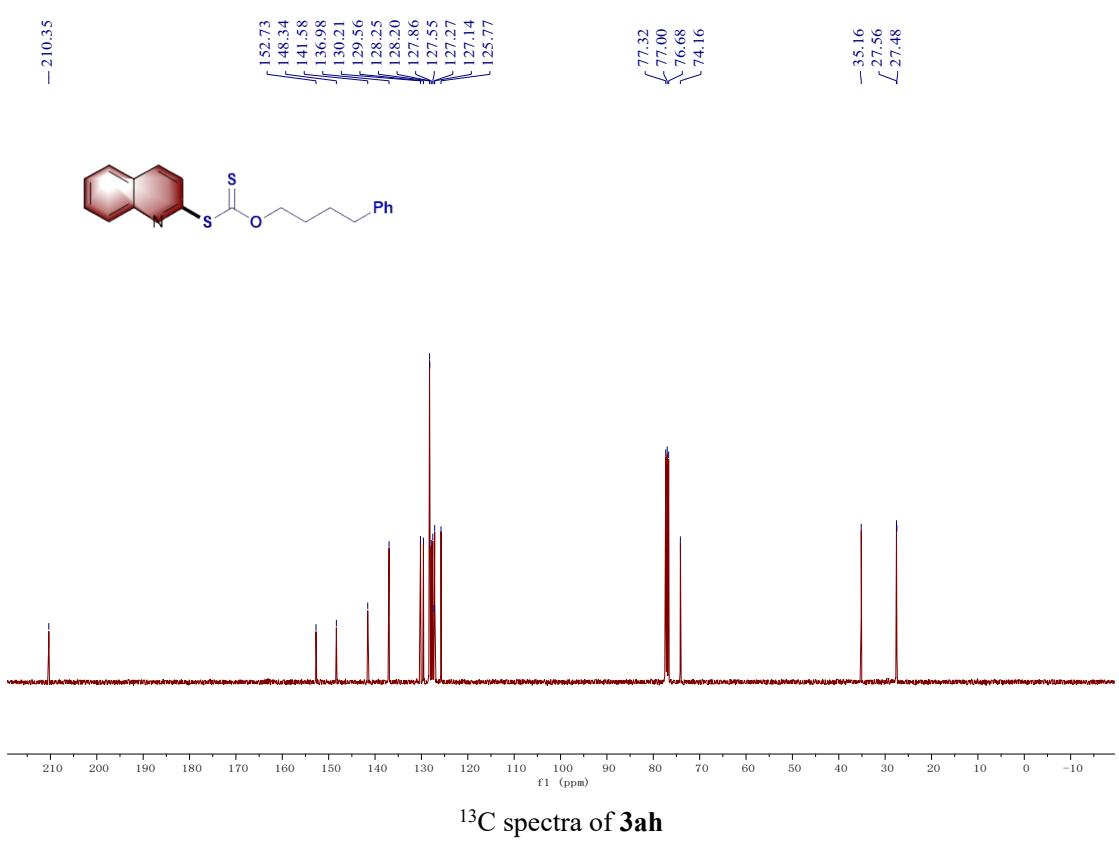
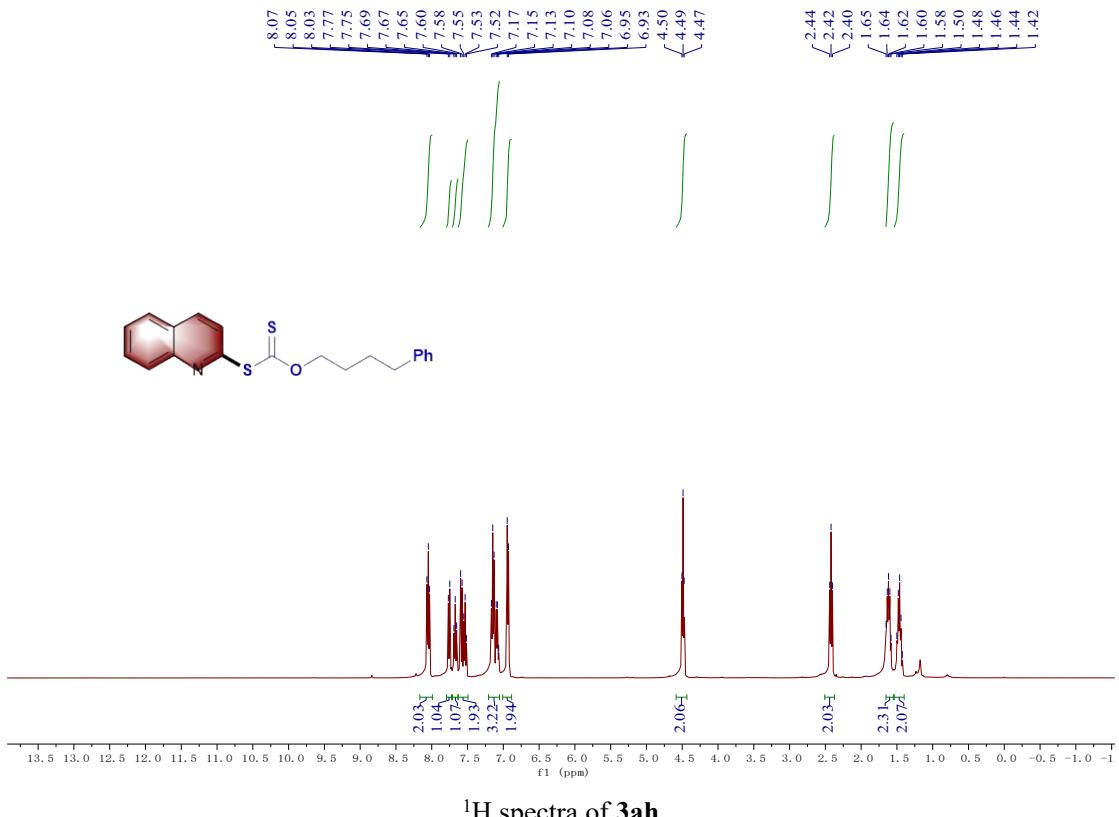


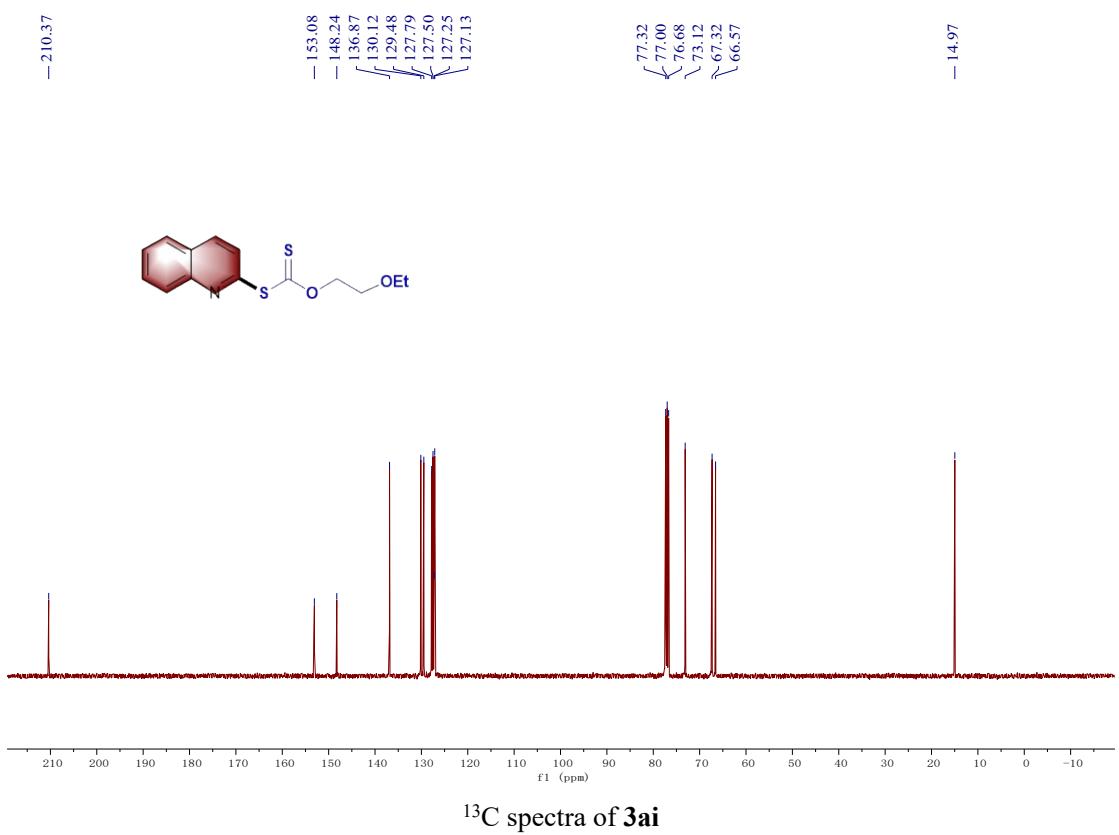
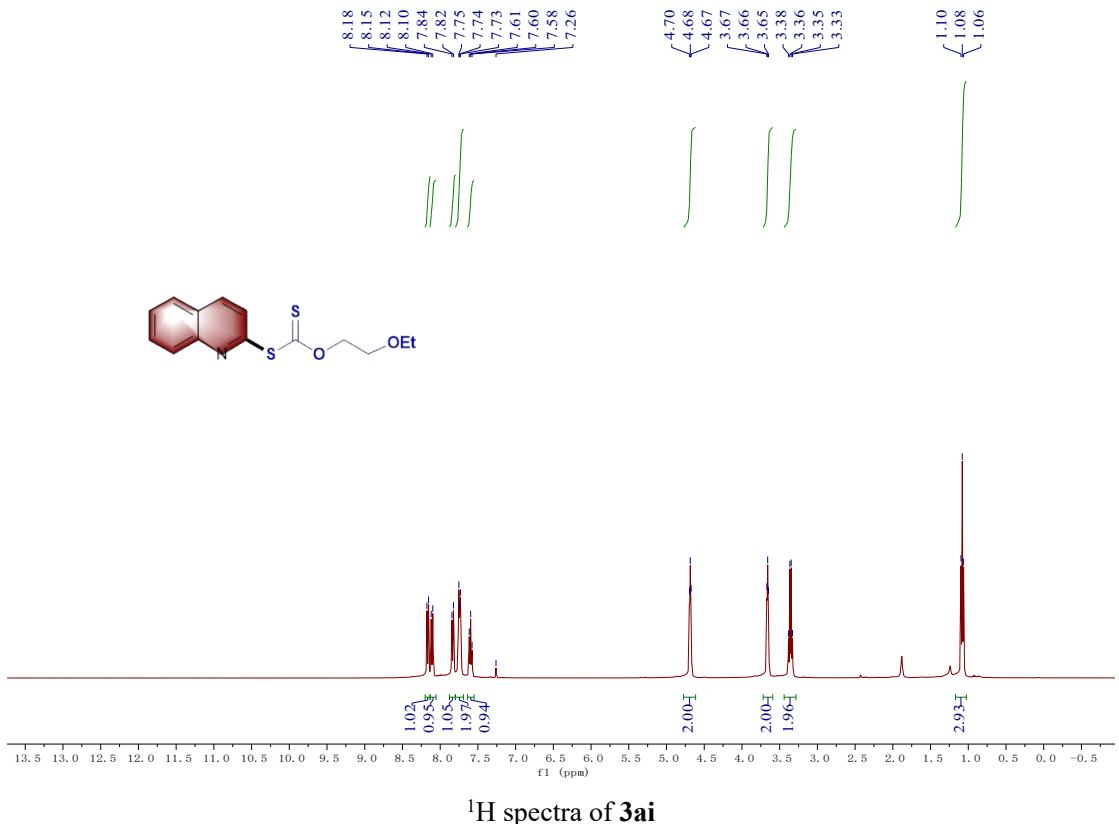


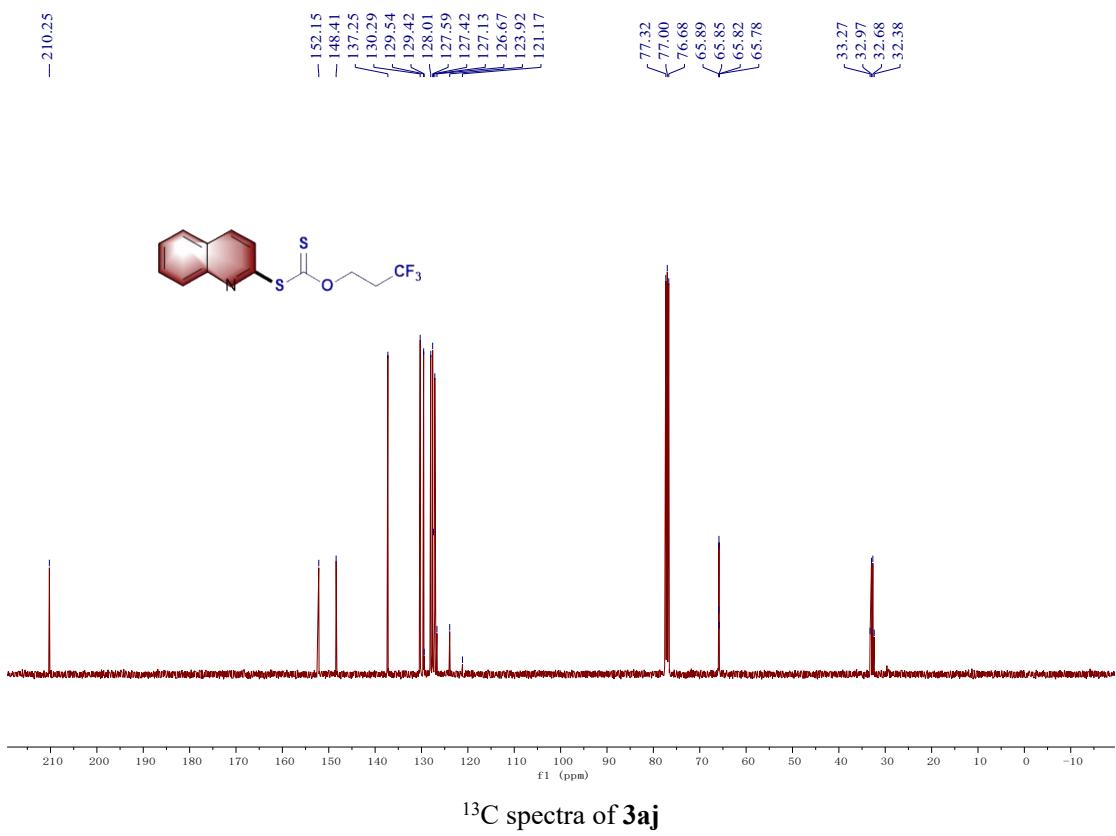
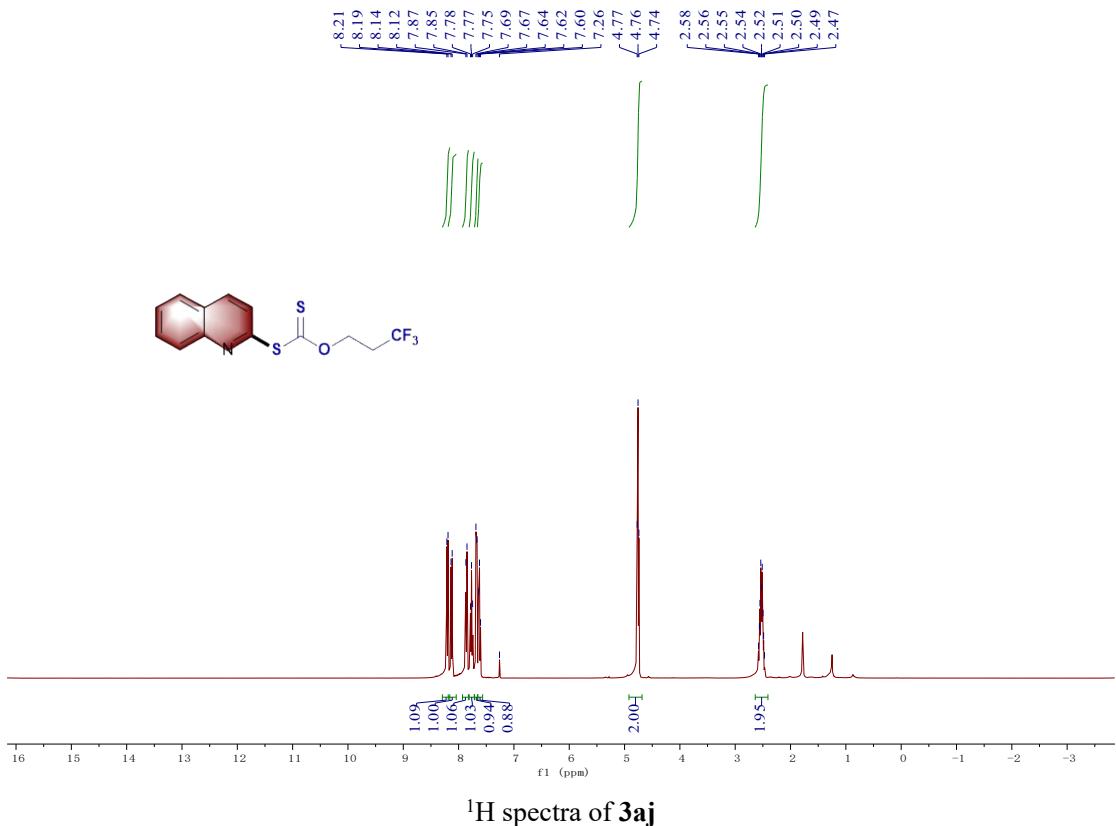
¹H spectra of 3ag

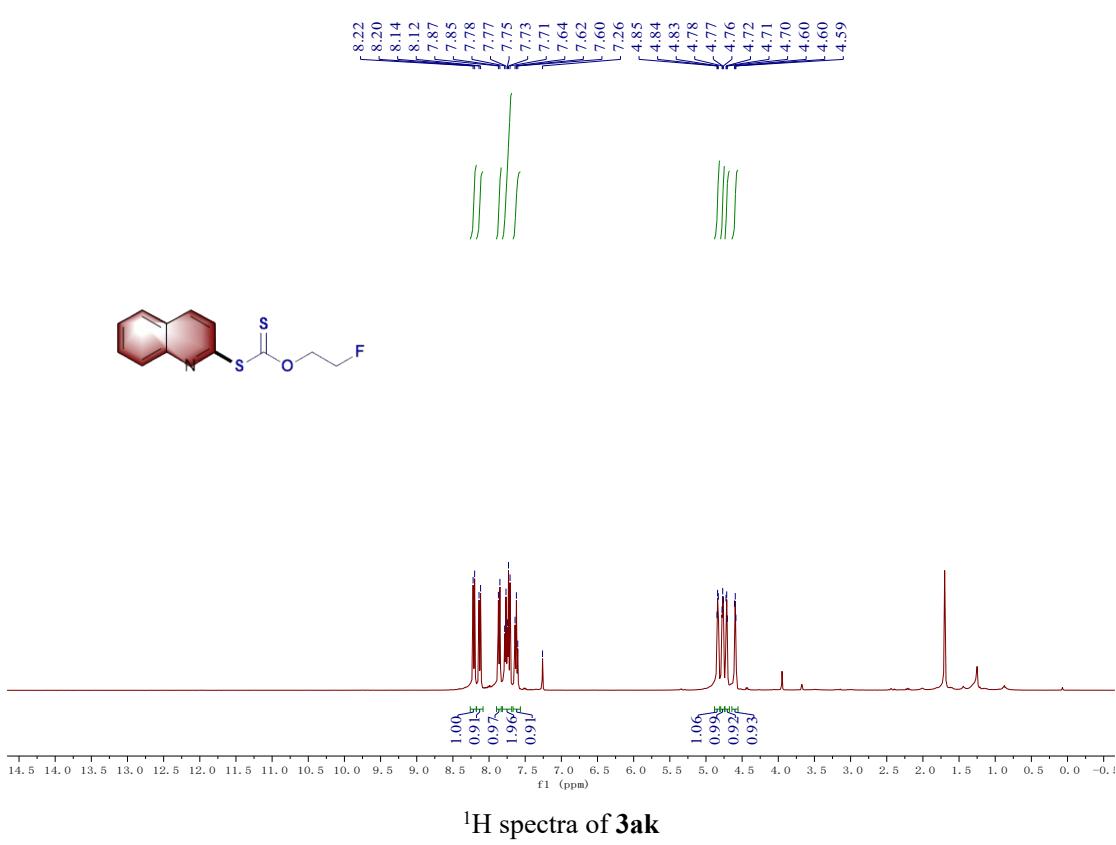
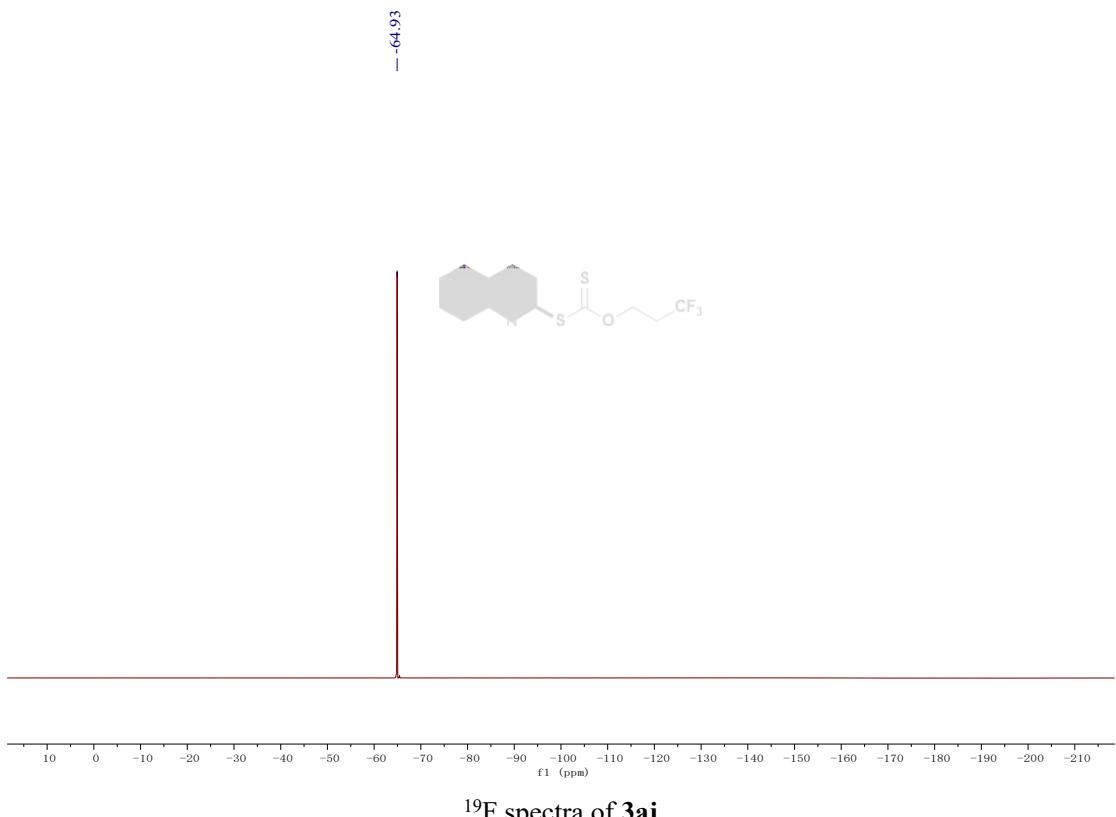


¹³C spectra of 3ag

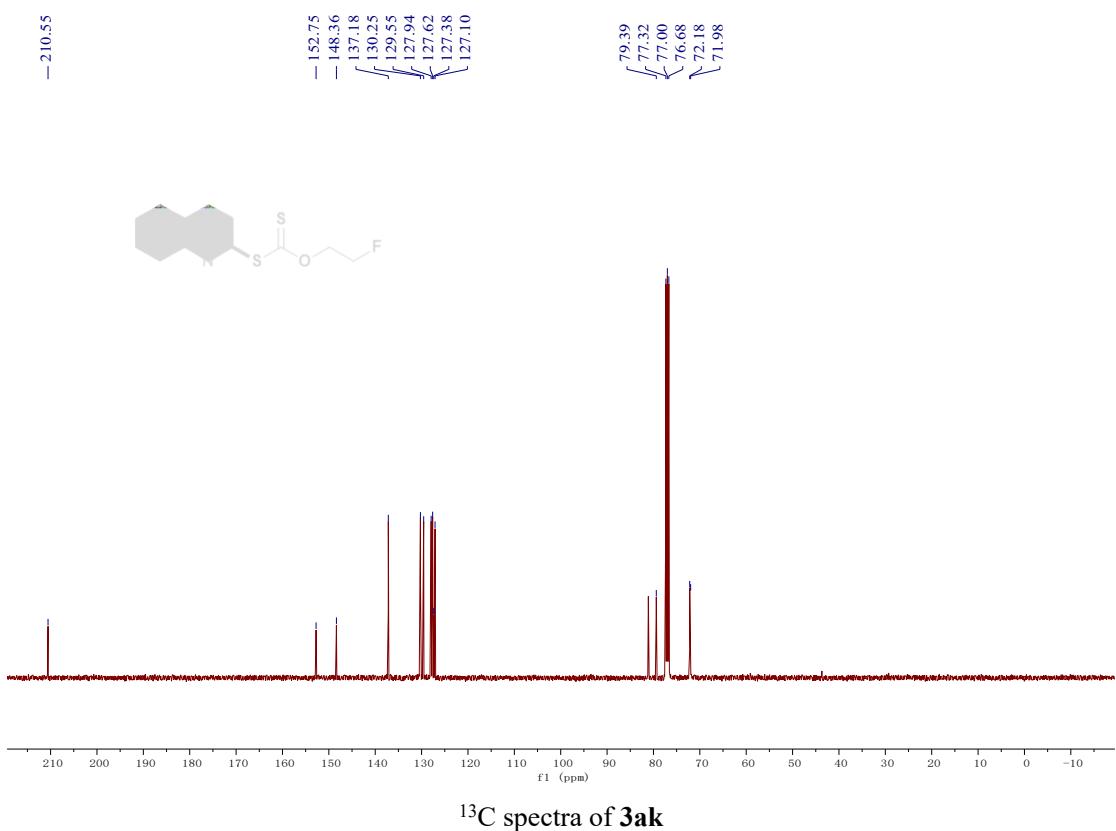




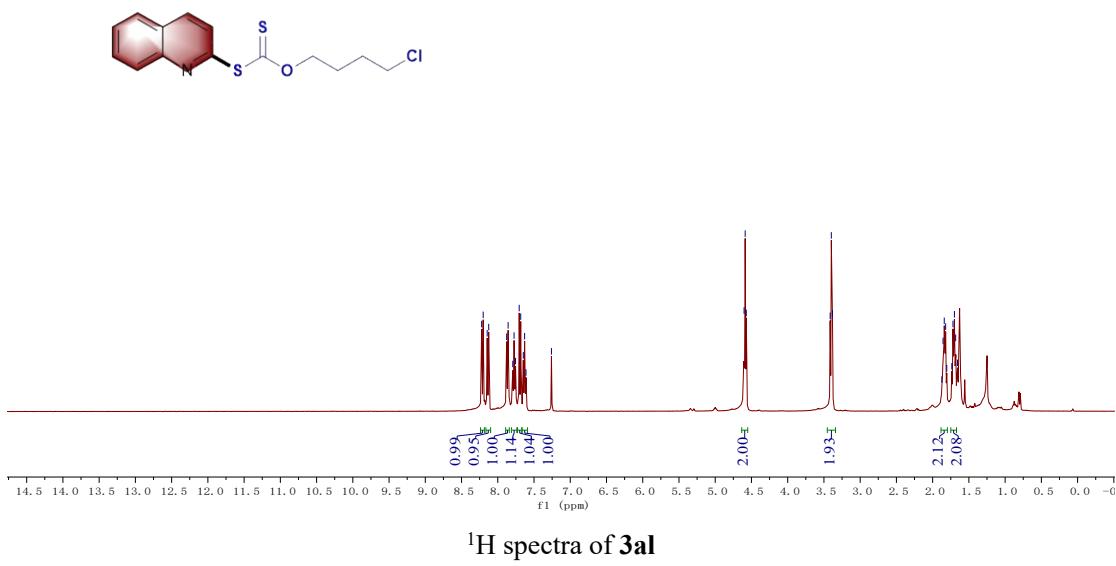
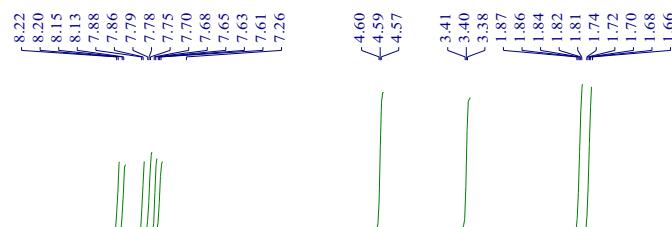




— 210.55

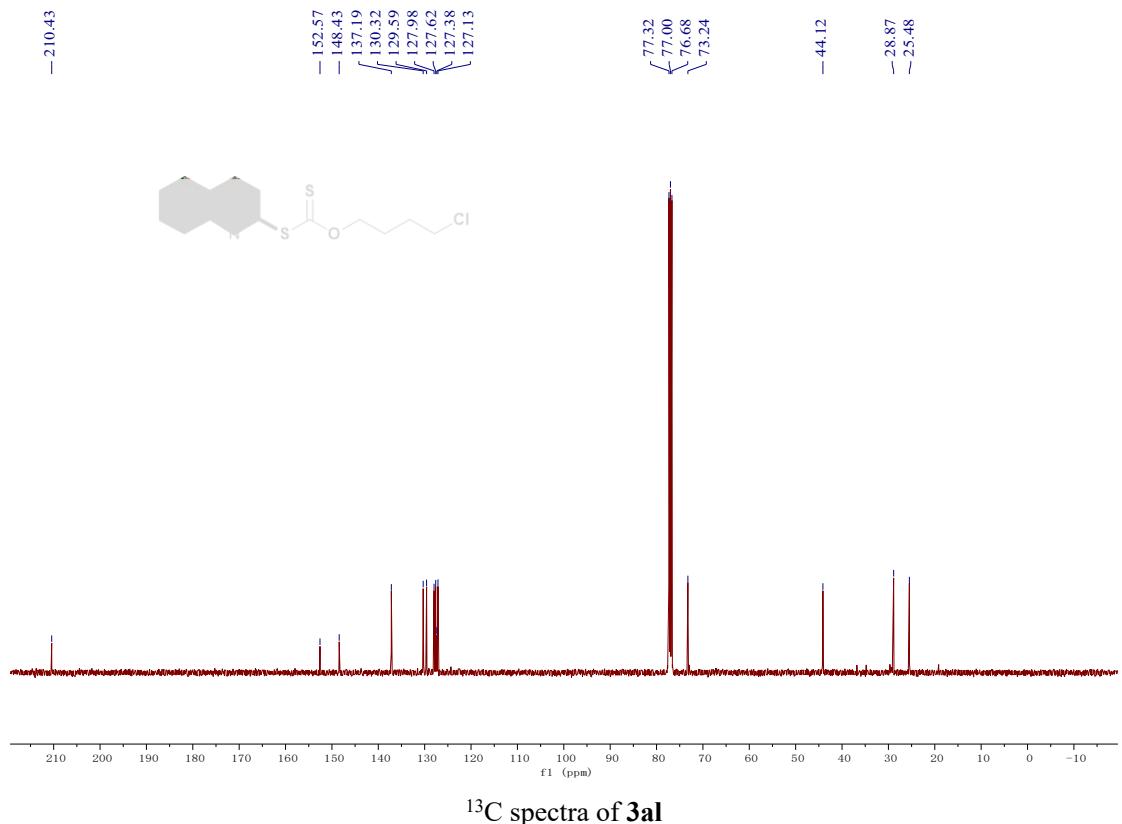


¹³C spectra of 3ak

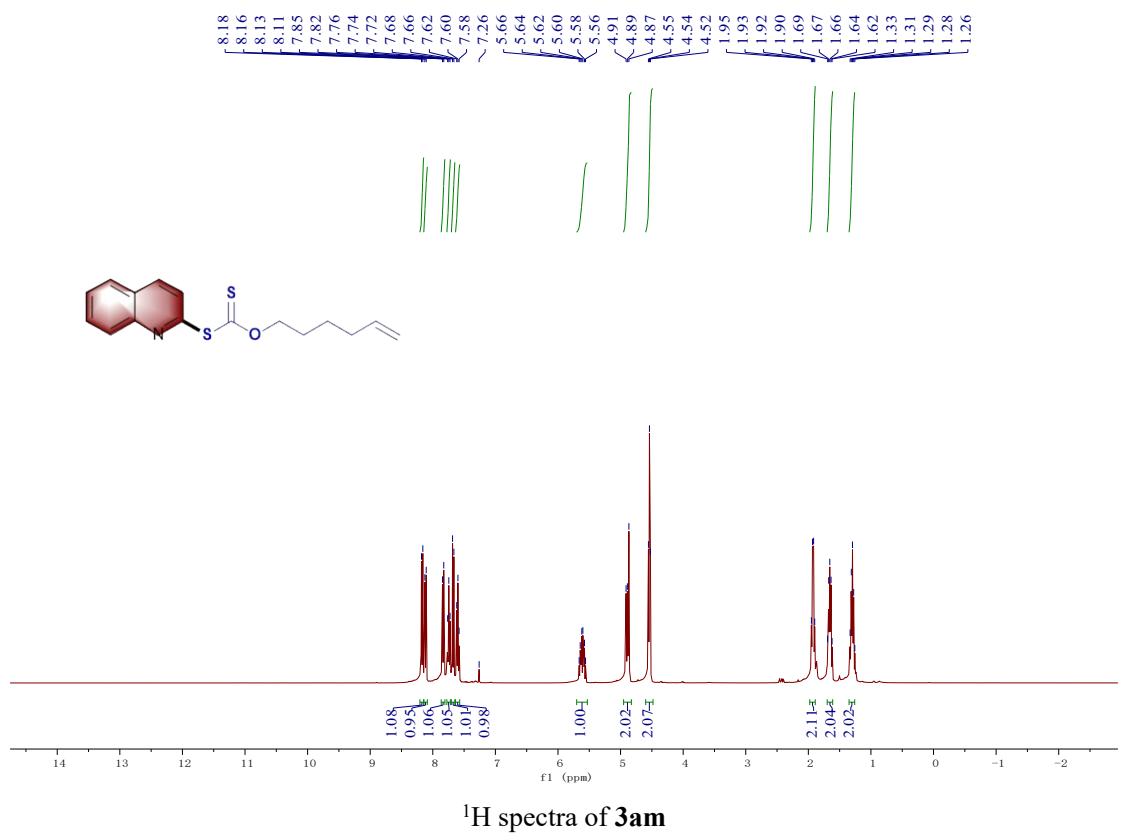


¹H spectra of 3al

- 210.43



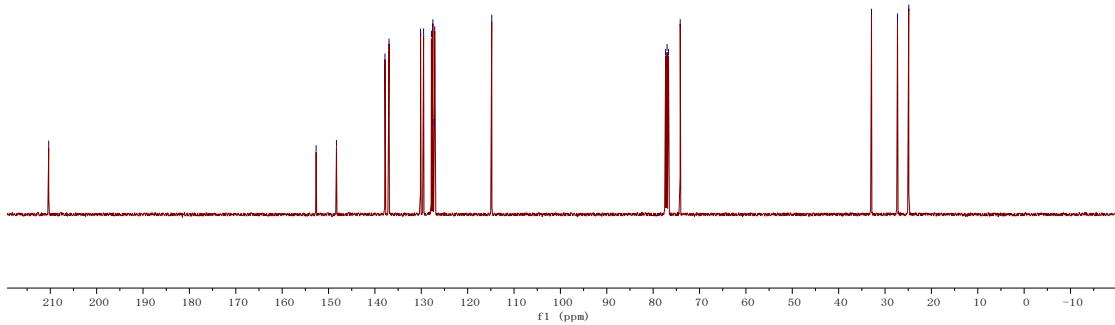
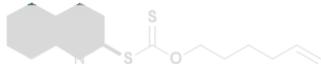
¹³C spectra of **3al**



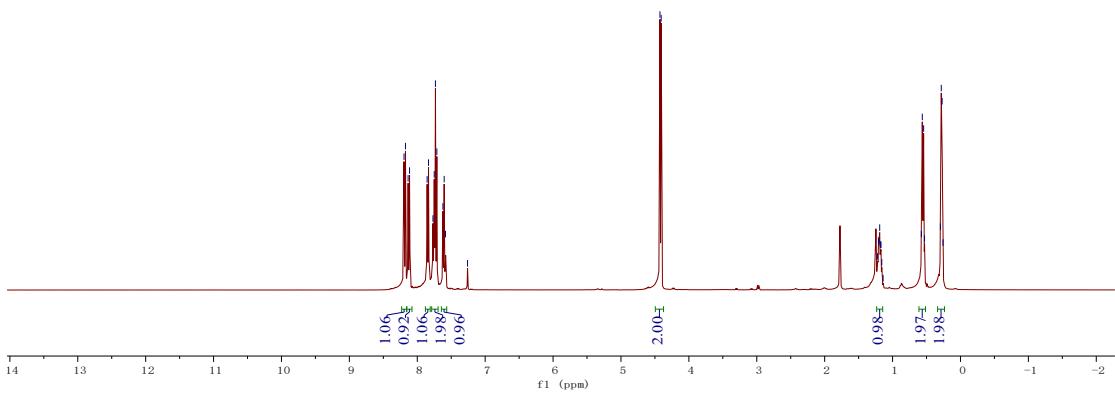
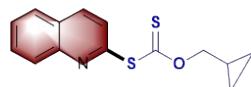
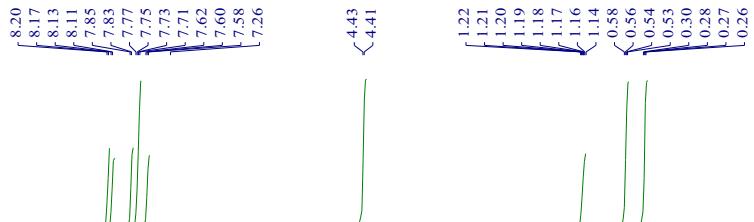
¹H spectra of **3am**

— 210.34

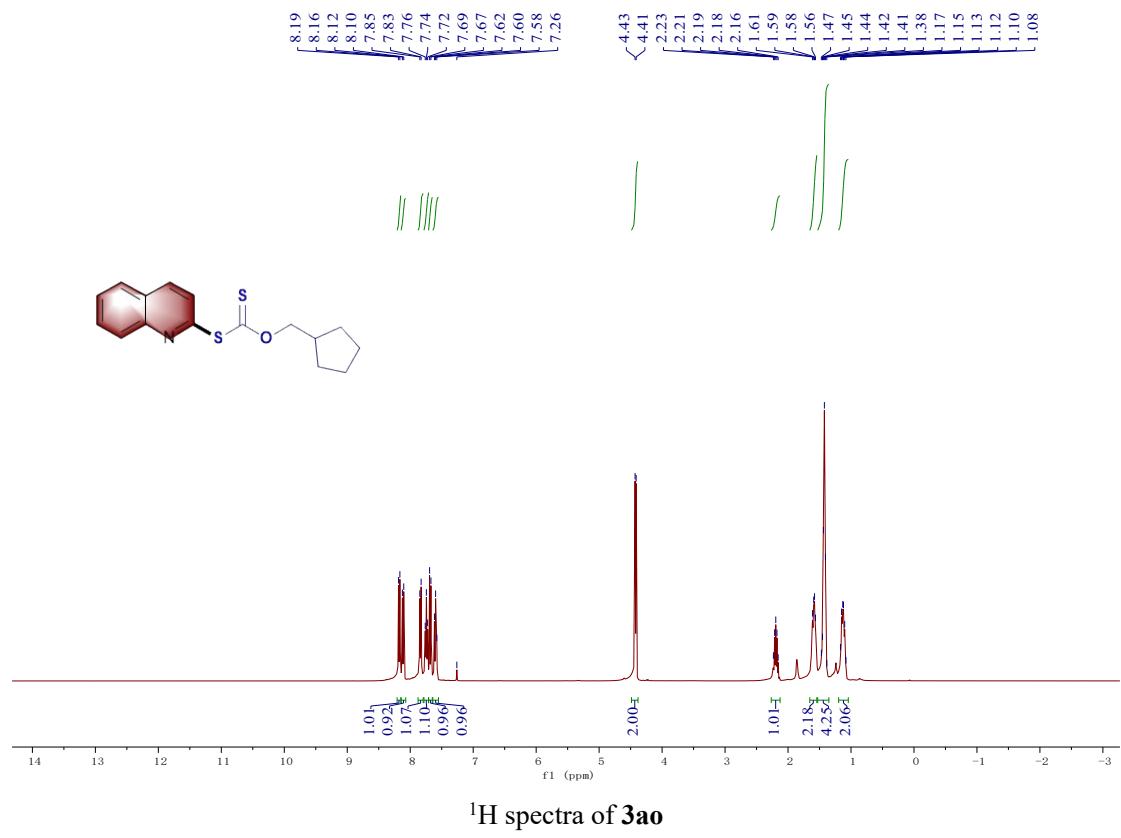
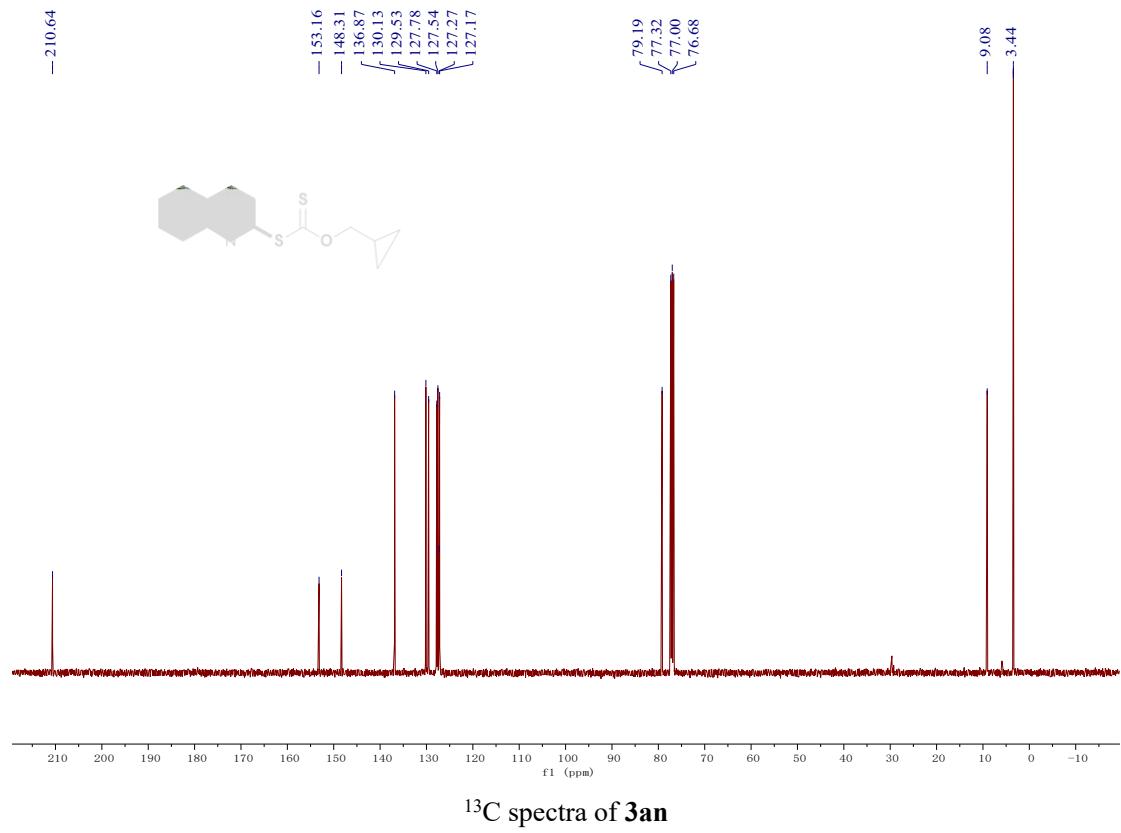
152.68
148.29
137.83
136.95
130.15
129.50
127.81
127.51
127.24
127.10
— 114.80

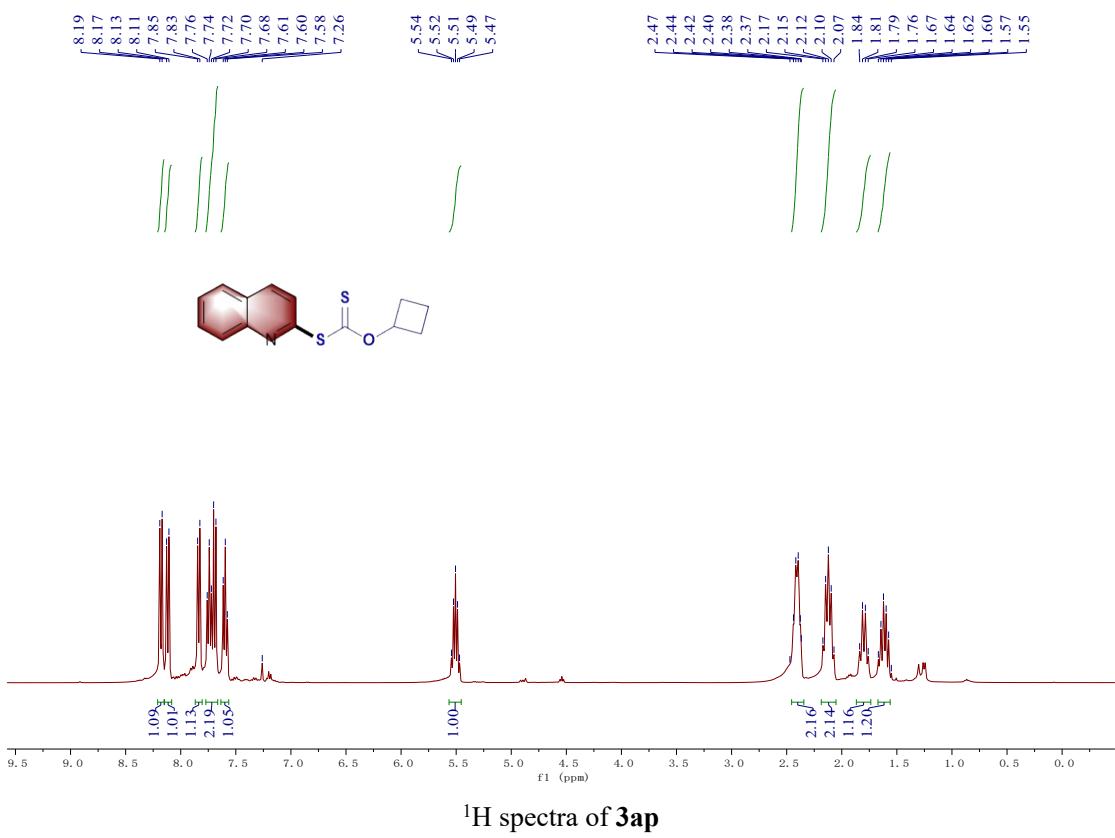
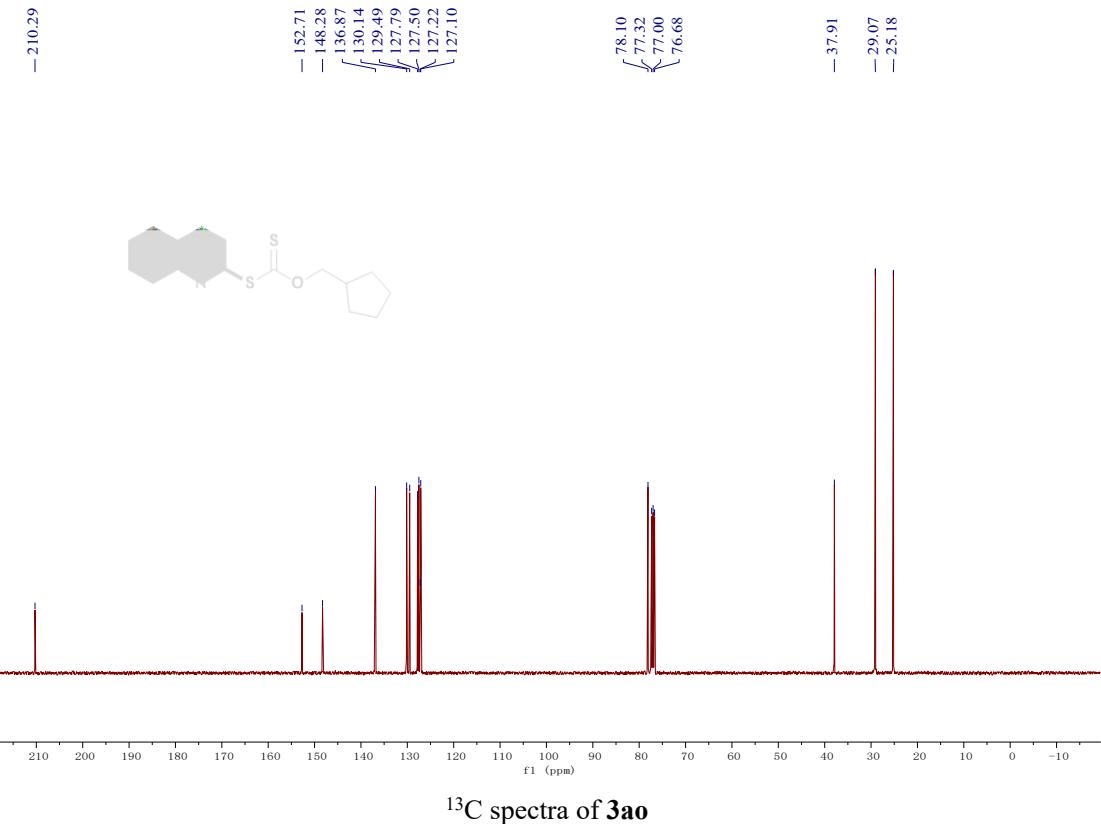


¹³C spectra of 3am

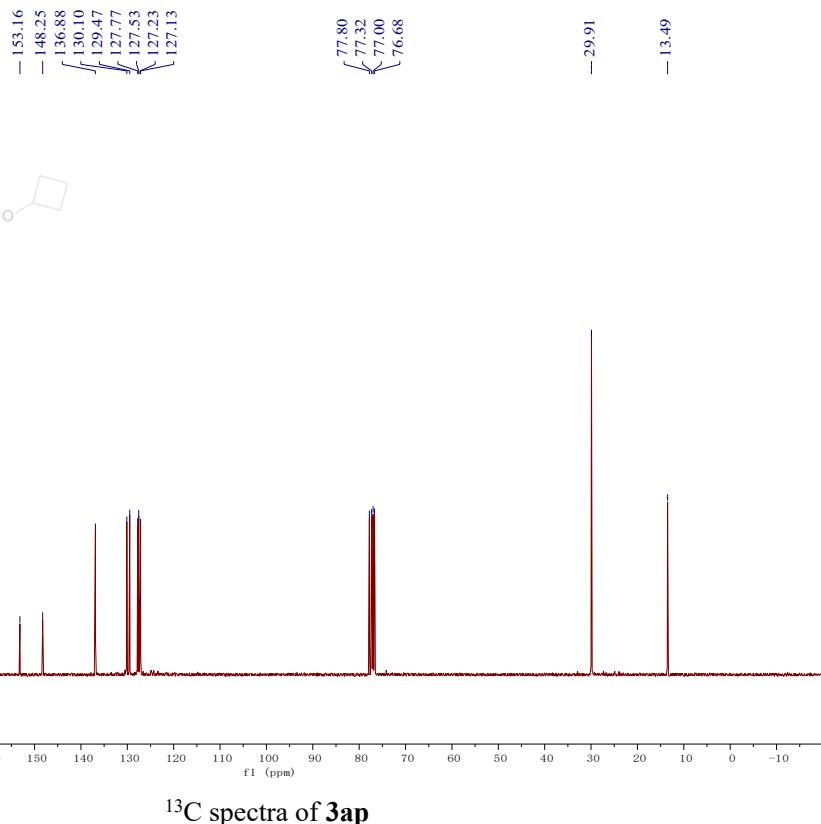


¹H spectra of 3an

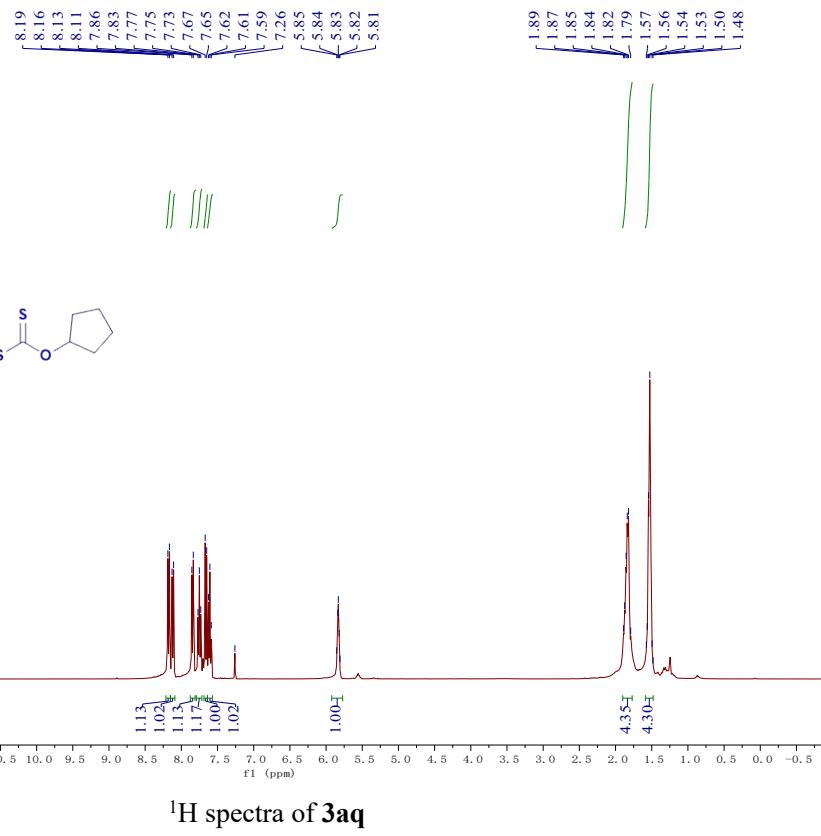




- 208.83

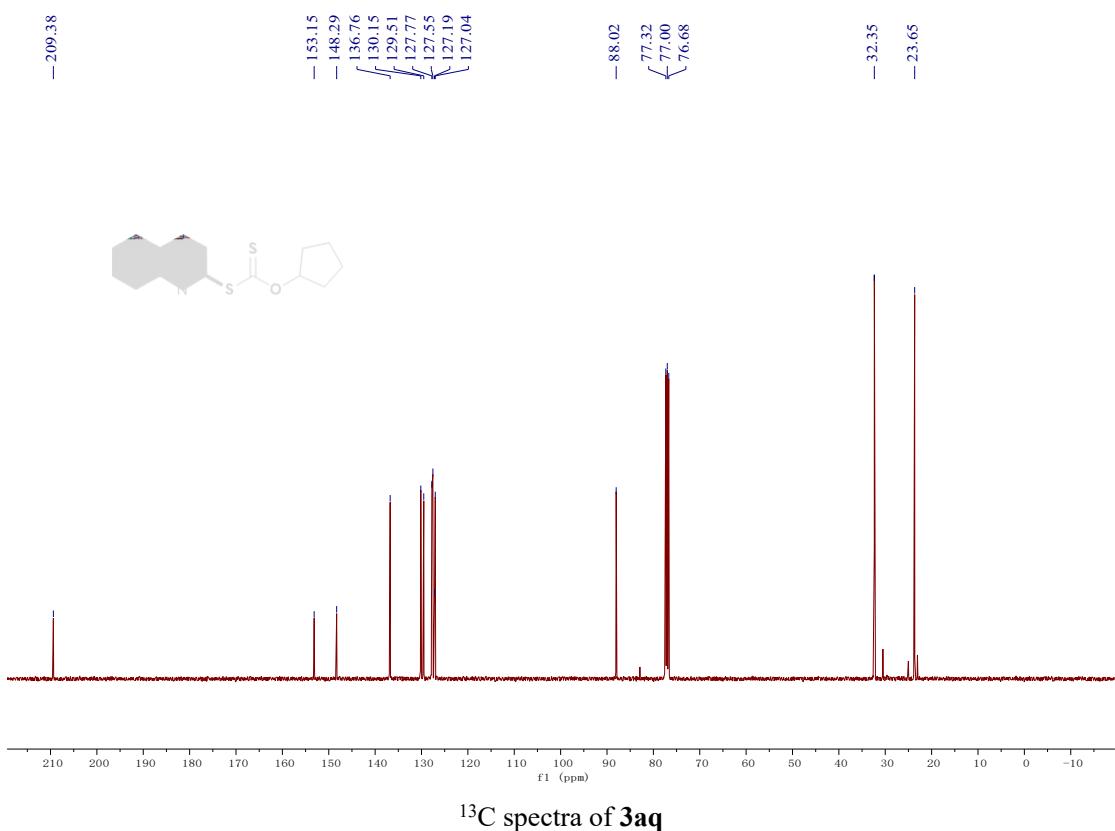


^{13}C spectra of 3ap

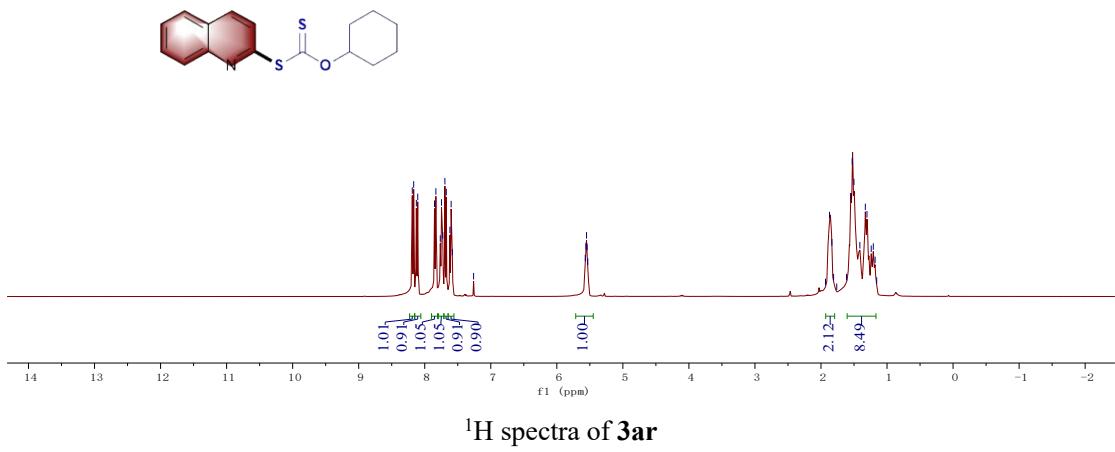
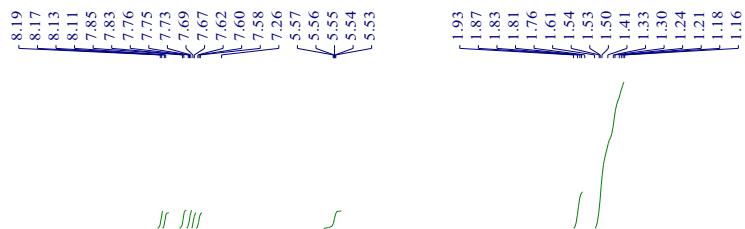


^1H spectra of 3aq

- 209.38



¹³C spectra of 3aq

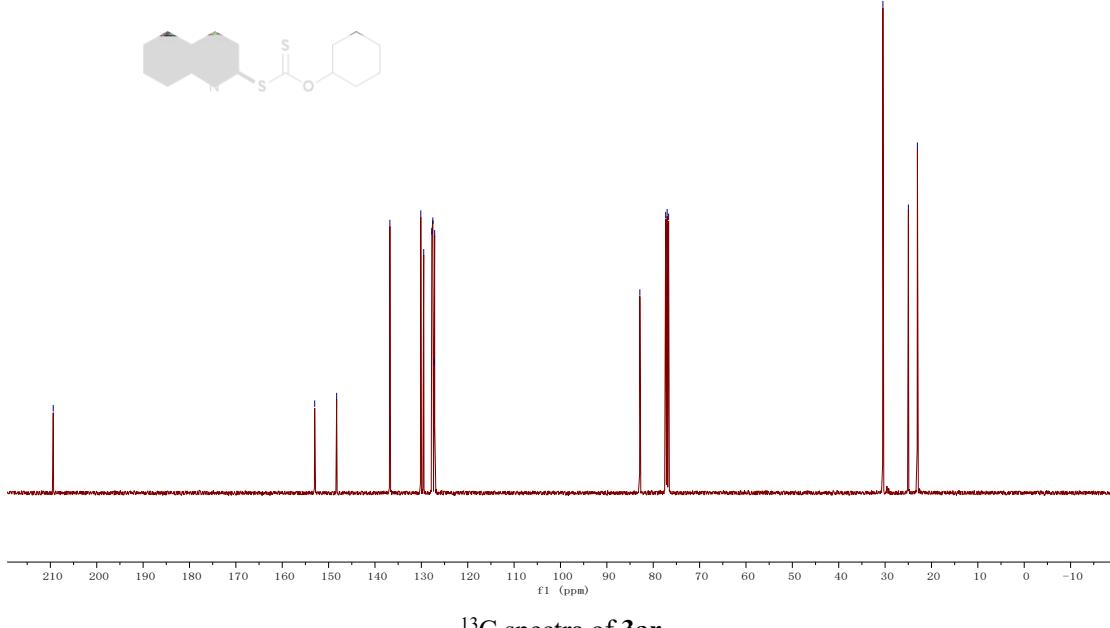


¹H spectra of 3ar

- 209.38

- 153.00
- 148.27
- 136.78
- 130.12
- 129.49
- 127.75
- 127.53

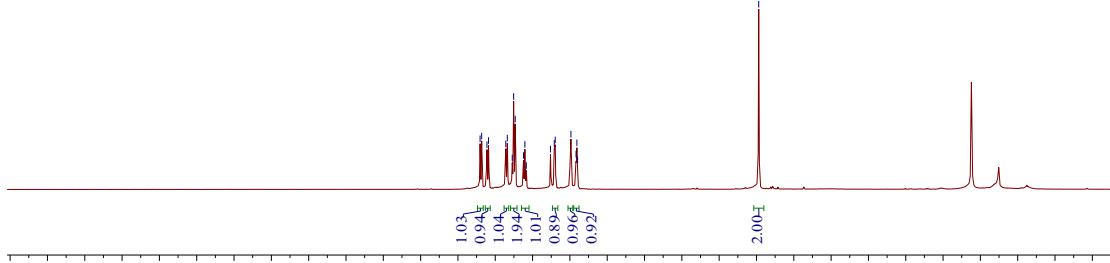
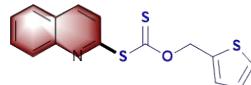
- 127.19
- 127.13
- 82.88
- 77.32
- 76.00
- 76.58



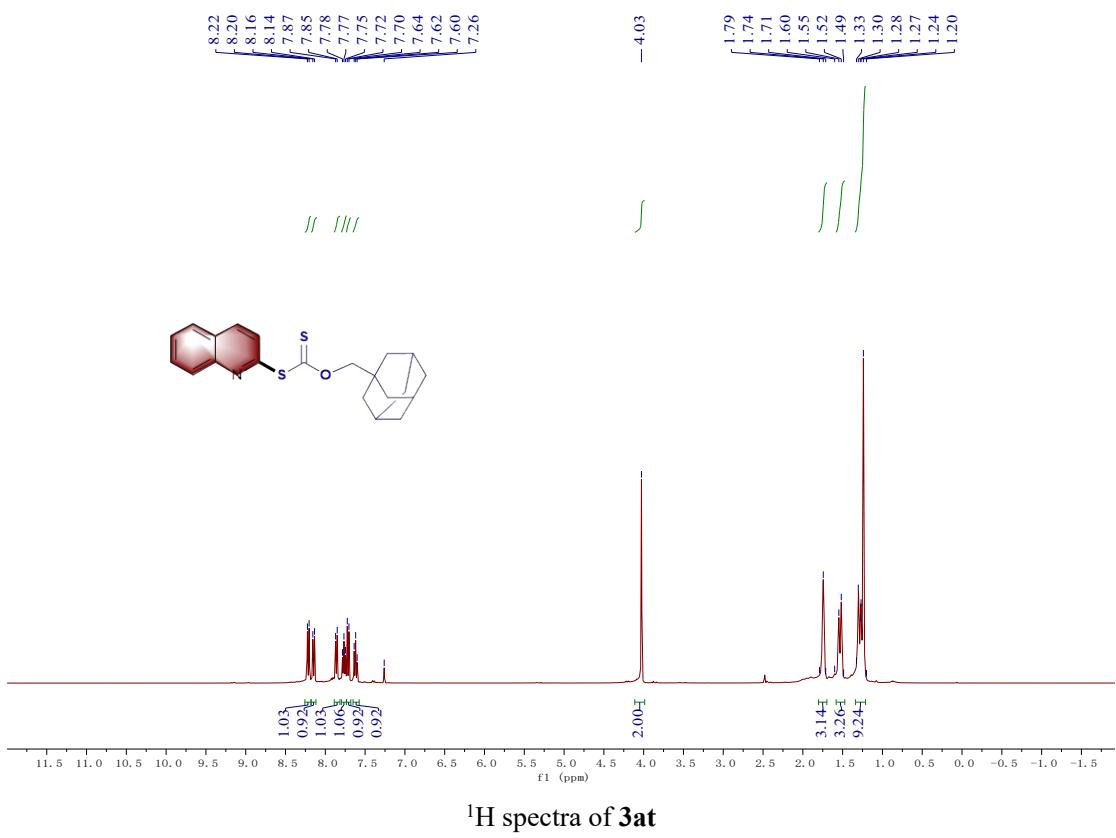
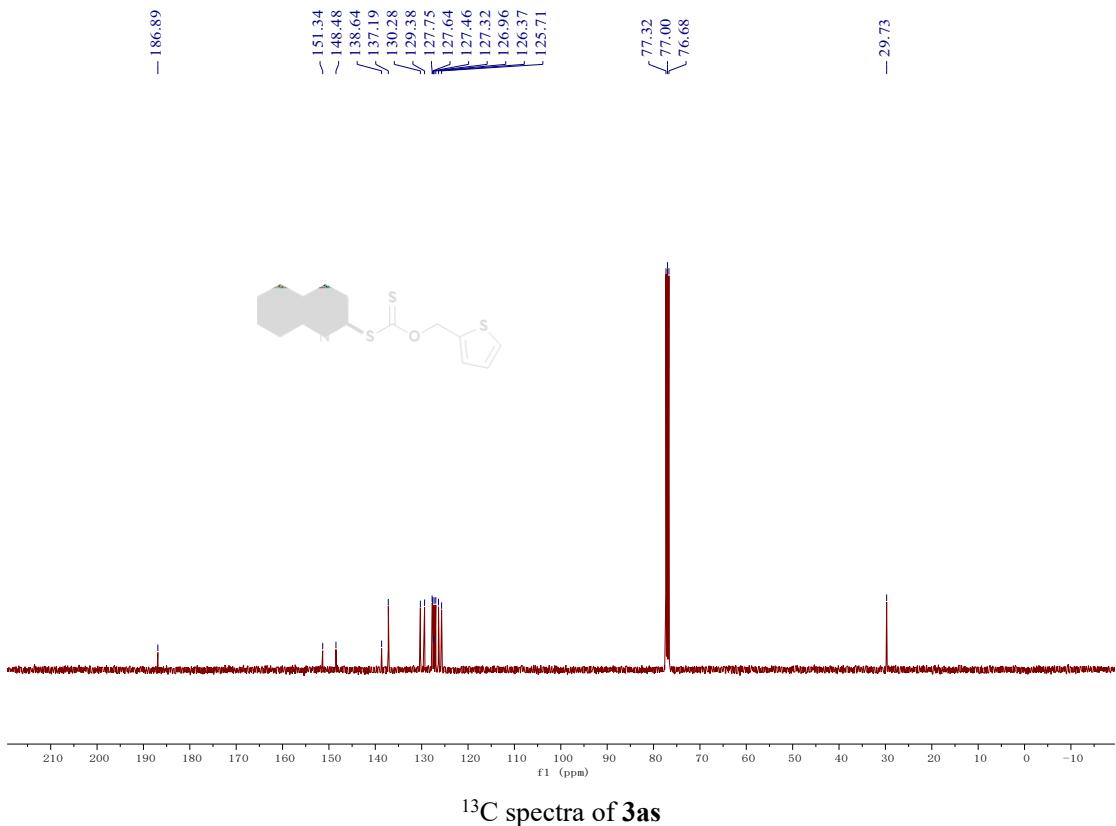
¹³C spectra of 3ar

8.20
8.18
8.11
8.09
8.09
7.86
7.84
7.77
7.75
7.73
7.73
7.62
7.60
7.58
7.26
7.21
7.20
7.20
6.99
6.92
6.91
6.90

-4.47

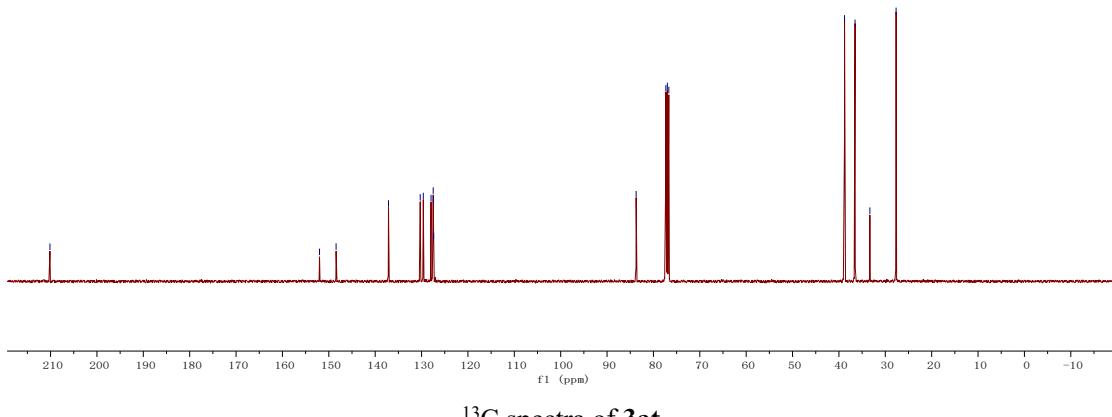
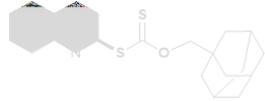


¹H spectra of 3as



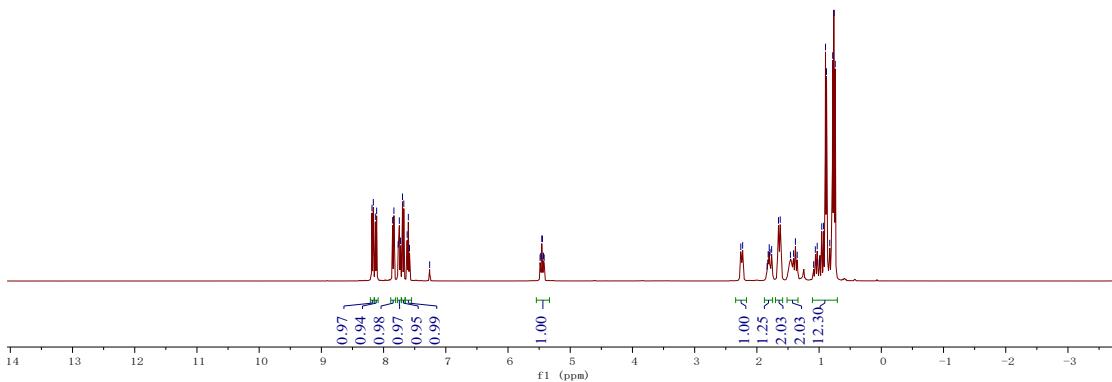
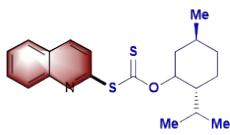
- 210.13

- 152.00
- 148.43
- 137.13
/ 130.29
/ 129.62
/ 127.95
/ 127.49
/ 127.42
/ 127.40



¹³C spectra of 3at

8.19
7.77
7.75
7.73
7.70
7.68
7.62
7.60
7.58
7.56
7.26
5.48
5.47
5.46
5.45
5.43
5.42
2.26
2.23
1.84
1.82
1.80
1.79
1.76
1.65
1.62
1.46
1.41
1.38
1.35
1.09
1.06
1.03
1.00
0.96
0.93
0.90
0.88
0.83
0.78
0.76
0.74

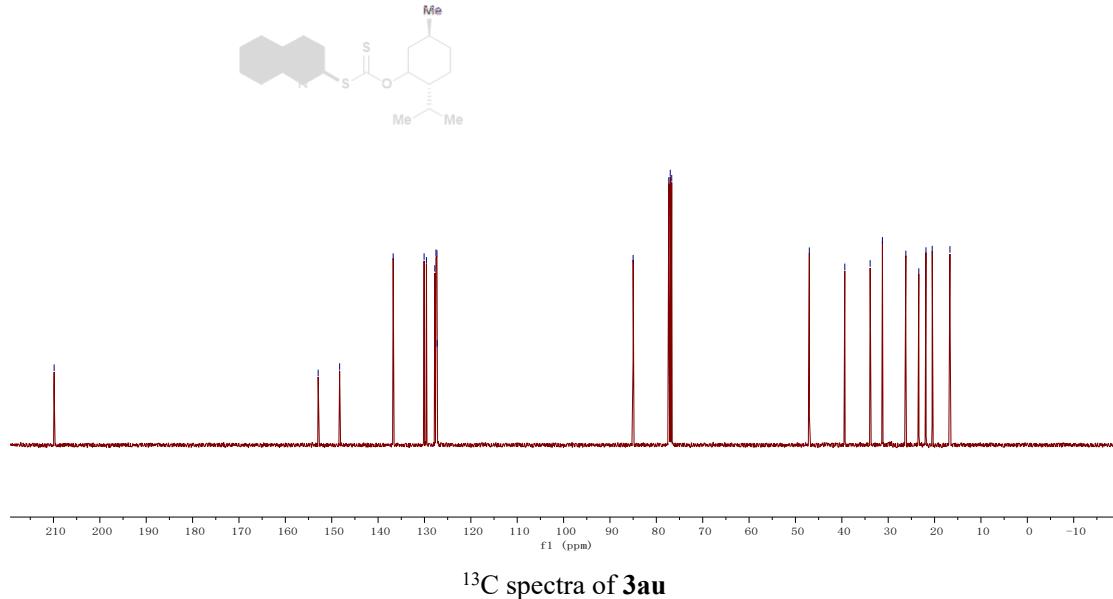


¹H spectra of 3au

— 209.86

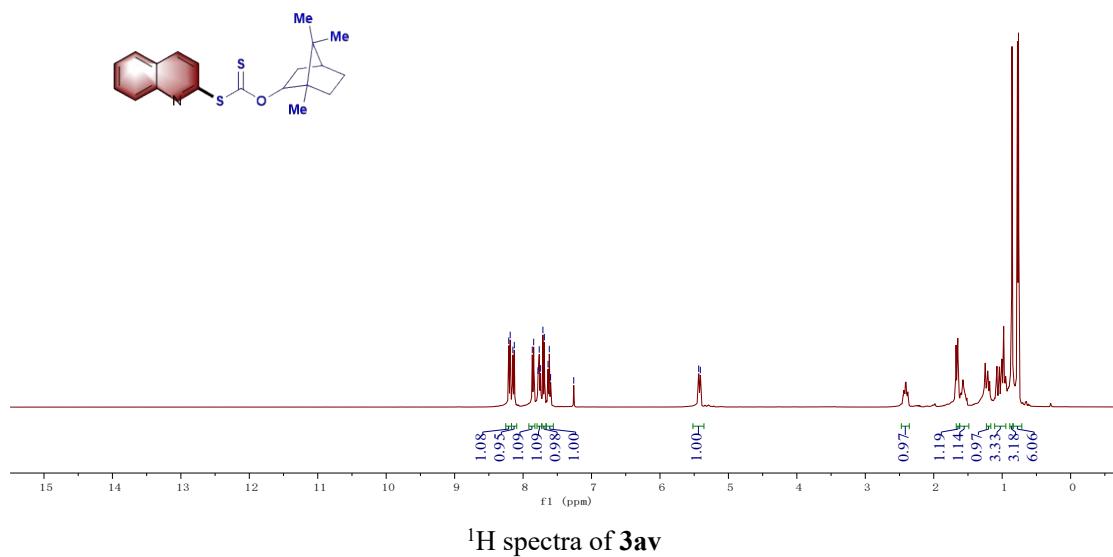
— 152.93
— 148.29
— 136.75
— 130.08
— 129.57
— 127.77
— 127.52
— 127.31
— 127.26

— 85.01
— 77.32
— 77.00
— 76.68

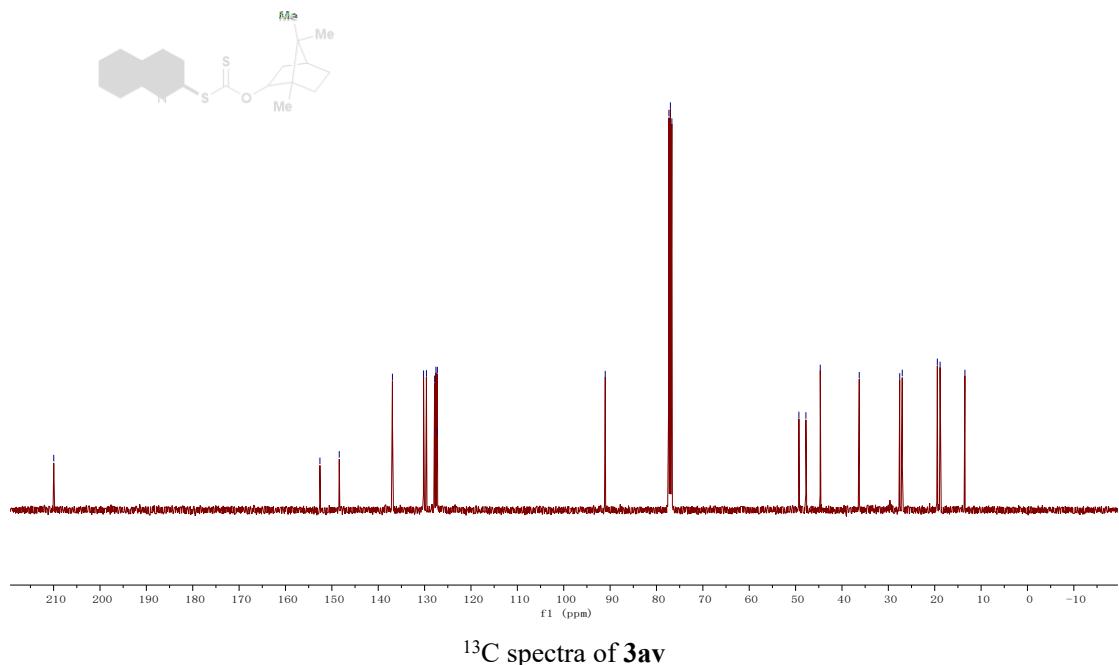


8.21
8.19
8.15
8.13
7.87
7.85
7.78
7.76
7.74
7.71
7.69
7.64
7.62
7.60
7.26
5.43
5.41

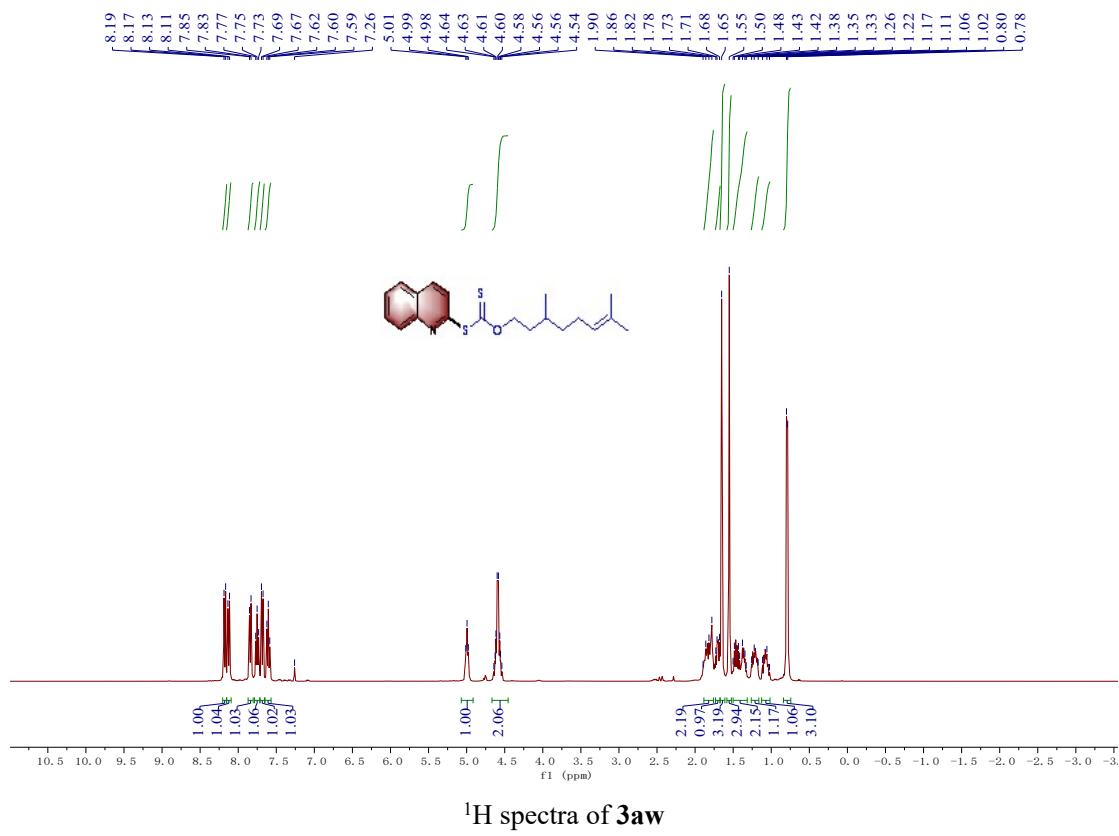
11 10 9 8 7 6 5 4 3 2 1 0



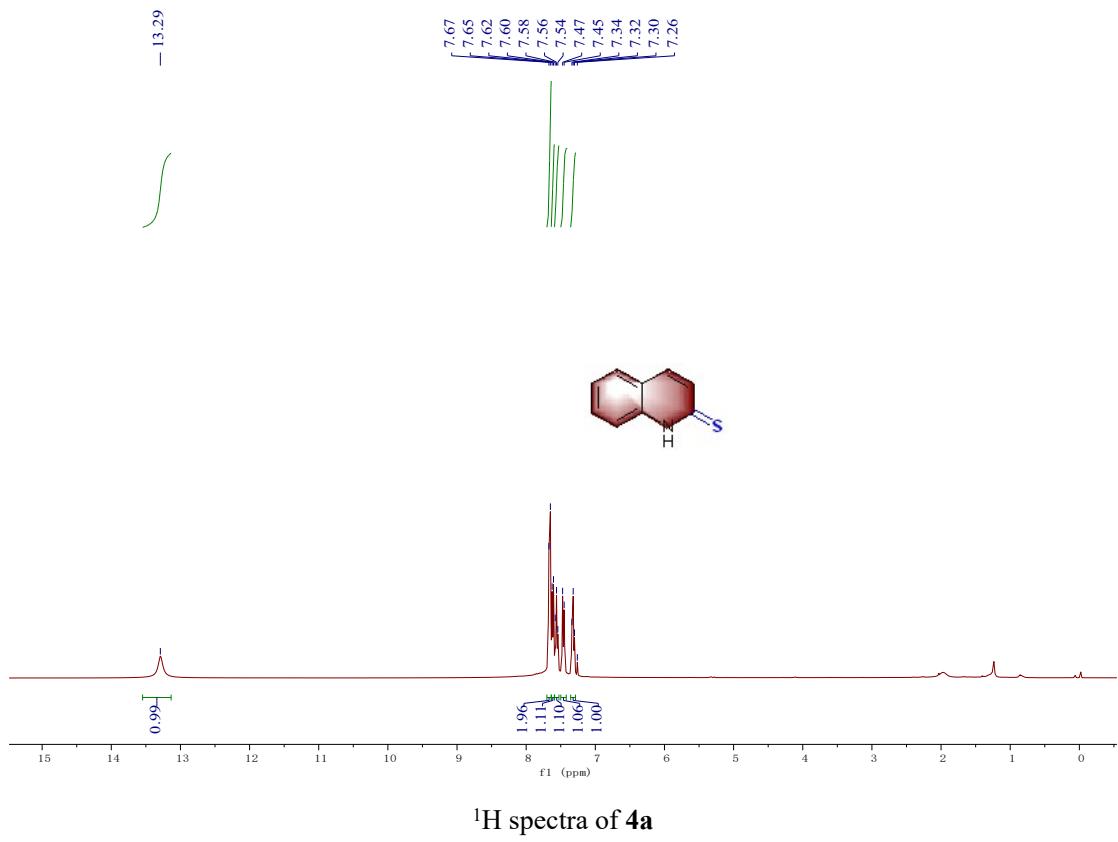
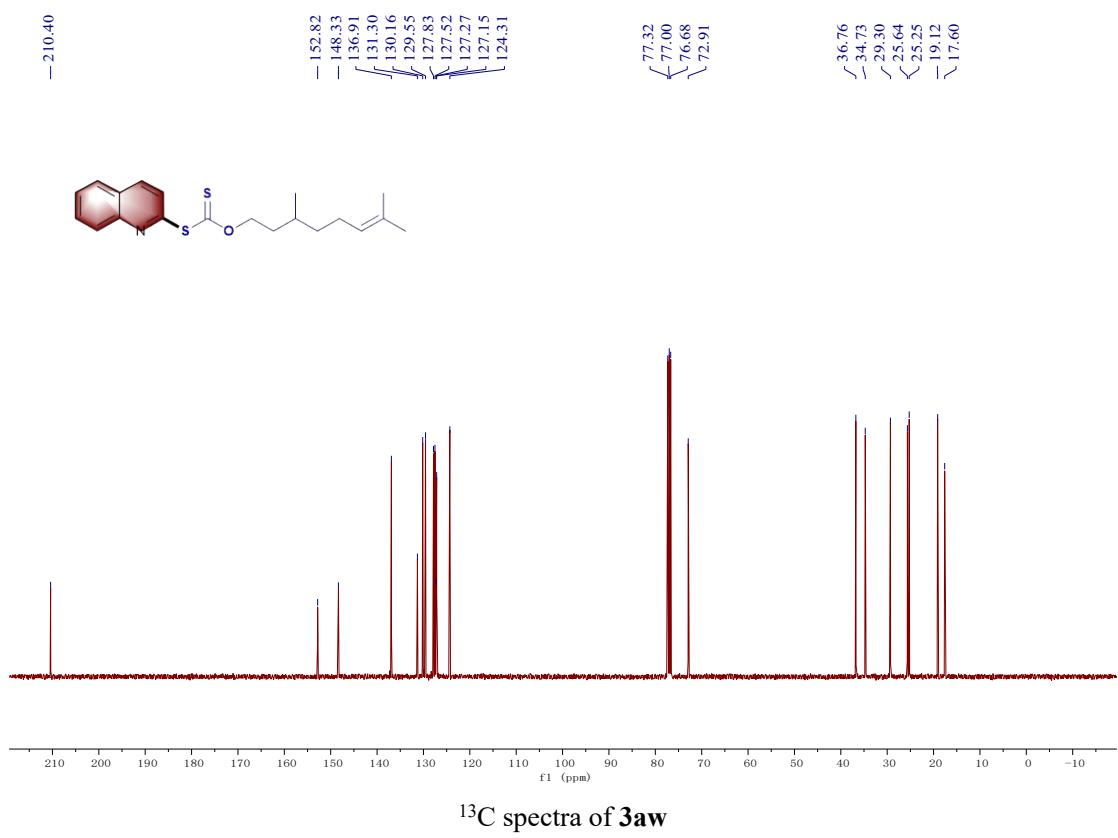
— 209.97



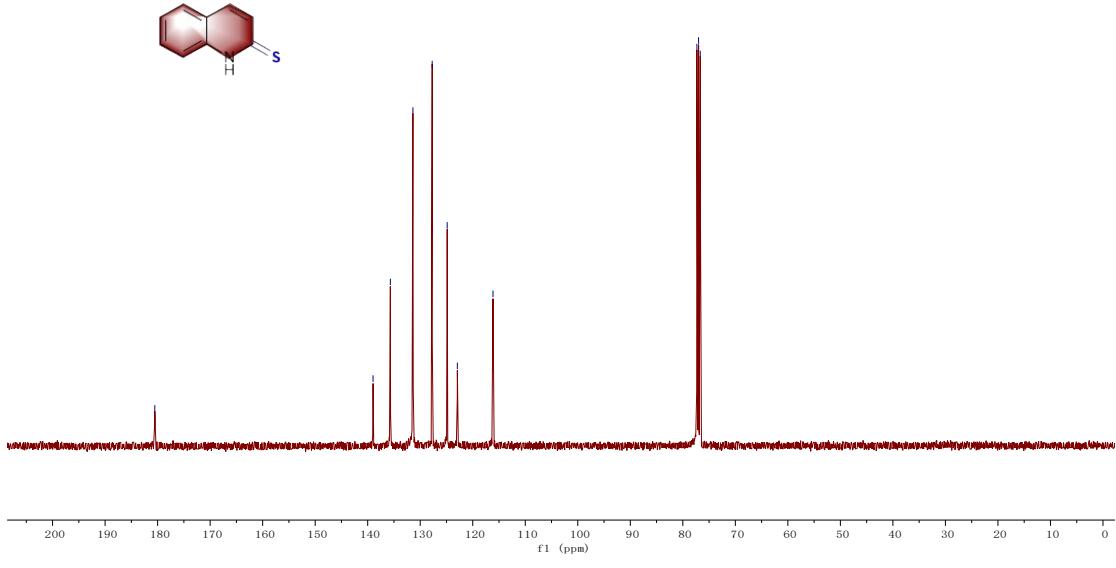
¹³C spectra of 3av



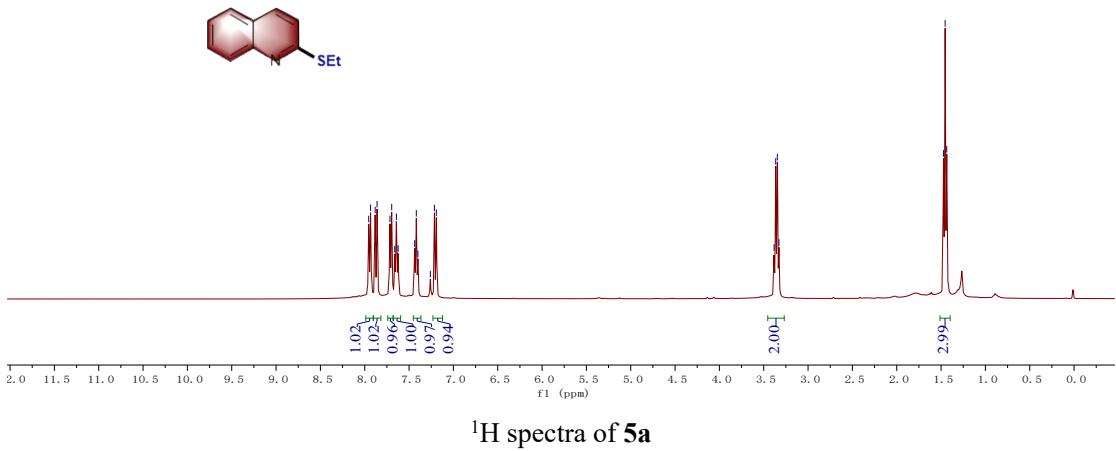
¹H spectra of 3aw



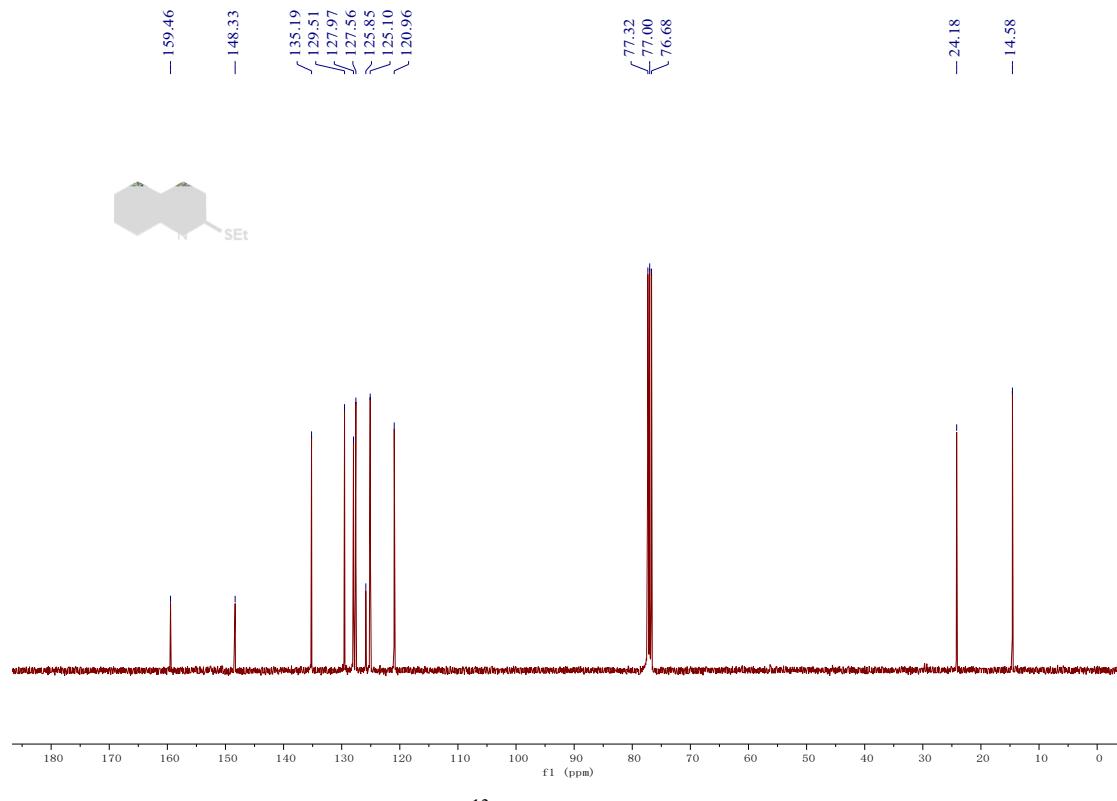
— 180.54



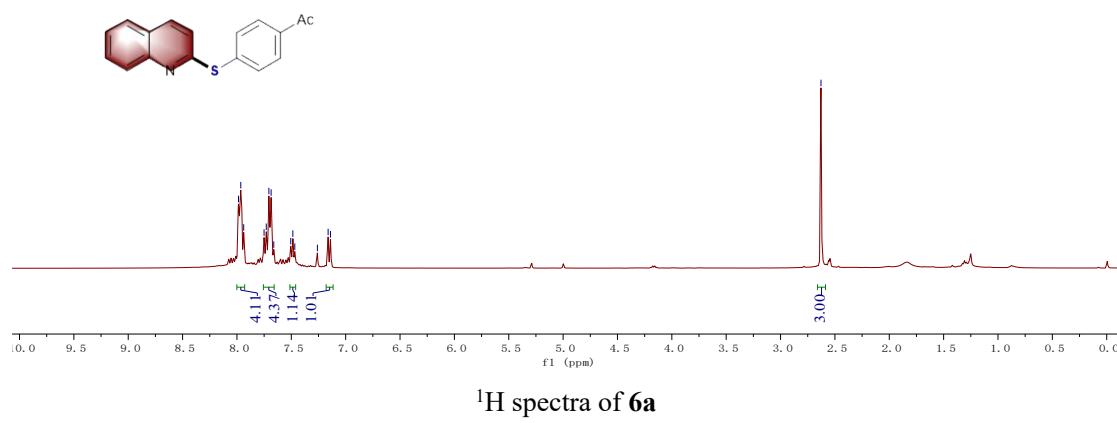
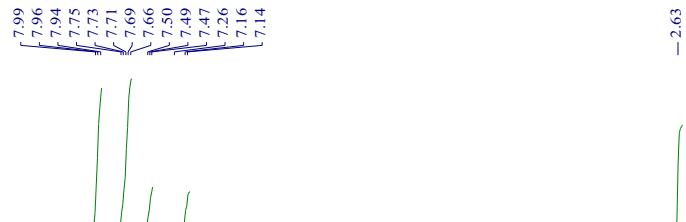
¹³C spectra of **4a**



¹H spectra of **5a**



¹³C spectra of **5a**



¹H spectra of **6a**

