

Visible-Light-Promoted Direct C-H/S-H Cross-Coupling of Quinoxalin-2(1*H*)-ones with Thiols Leading to 3-Sulfenylated Quinoxalin-2(1*H*)-ones in Air

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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 NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra were recorded at 100 MHz by using a Bruker Avance 400 spectrometer. Chemical shifts were calibrated using residual undeuterated solvent as an internal reference (^1H NMR: CDCl_3 7.26 ppm, $\text{d}^6\text{-DMSO}$ 2.50, ^{13}C NMR: CDCl_3 77.0 ppm, $\text{d}^6\text{-DMSO}$ 40.0), the chemical shifts (δ) were expressed in ppm and J values were given in Hz. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, br = broad. Mass spectra were performed on a spectrometer operating on ESI-TOF. Column chromatography was performed on silica gel (200-300 mesh).

2. The Material of the Irradiation Vessel

Manufacturer: Xi'an WATTECS experimental equipment co. LTD

Model: WP-VLH-1020

Broadband source: $\lambda = 460\text{-}470\text{ nm}$

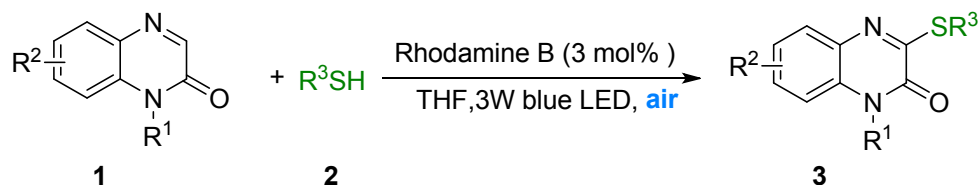
Material of the irradiation vessel: borosilicate reaction tube

Distance from the light source to the irradiation vessel: 2.0 cm

Not use any filters

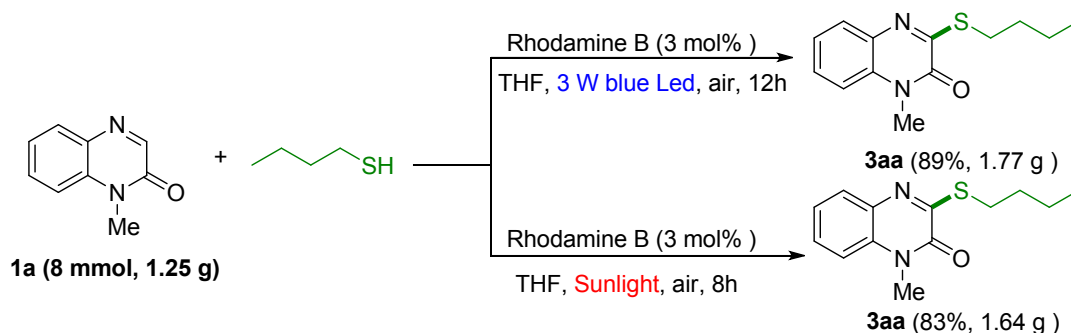
3. Experimental Section

3.1 Typical Procedure for the Synthesis of 3-Thioxyquinoxalin-2(1H)-ones.



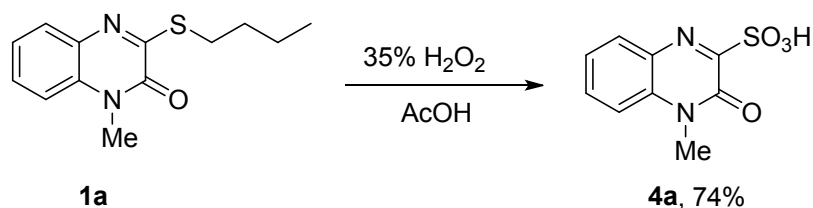
To a solution of quinoxalin-2(1H)-ones **1** (0.3 mmol) and thiols **2** (0.6 mmol) in THF (1.5 mL) was added Rhodamine B (4.32 mg, 0.009 mmol). The reaction mixture was open to the air and stirred at room temperature under the irradiation of 3 W blue LED lamps for about 12h. After completion of the reaction, the resulting mixture was extracted with EtOAc (3 mL \times 3) and the solvent was then removed under vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired products **3**.

3.2 Gram-scale synthesis of 3aa



To a solution of 1-methylquinoxalin-2(1H)-one (1.25 g, 8 mmol) and n-butyl thiol (1.44 g, 16 mmol) in THF (40 mL) was added Rhodamine B (0.12 g, 0.24 mmol). The reaction mixture was open to the air and stirred at room temperature under the irradiation of 3 W blue LED lamps or sunlight for about 12 h. After completion of the reaction, the resulting mixture was extracted with EtOAc (40 mL × 3) and the solvent was then removed under vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give **3aa**.

3.3 Synthesis of methyl-3-Sulfonylquinoxalin-2(1H)-one (**4a**)



To a solution of 3-(butylthio)-1-methylquinoxalin-2(1H)-one (0.25 g, 1 mmol) in acetic acid (2 mL) was added 35% H₂O₂ (0.29g, 3 mmol). The reaction mixture was stirred at 110°C for about 6 h. After completion of the reaction, the resulting mixture was vacuumed to remove the solvent, the residue was washed with n-hexane (5mL) to obtain 0.22 gram of the pure product **4a**, yield 93%. ¹H NMR (400 MHz, d⁶-DMSO): δ = 12.01 (s, 1 H), 7.36 – 7.34 (m, 1 H), 7.22 – 7.17 (m, 3 H), 3.51 (s, 3 H); ¹³C NMR (100 MHz, d⁶-DMSO): δ = 155.7, 154.1, 127.7, 126.0, 124.0, 123.7, 115.9, 115.5, 30.1; HRMS (ESI) m/z calcd. for C₉H₉N₂O₄[M+H]⁺: 241.0278, found 241.0273.

3.4 The UV-visible spectroscopy and Fluorescence quenching studies (Stern–VolmerStudies).

The fluorescence emission intensities were recorded on a Fluormax-4600 spespectrofluorimeter. The excitation wavelength was fixed at 578 nm, and the emission wavelength was measured at 560 nm (emission maximum). The samples were prepared by mixing by Rhodamine B (3.0 × 10⁻⁵ mol/L) and different amount of 1-methylquinoxalin-2(1H)-one **1a** in THF (total volume = 0.2 mL) in a light path quartz fluorescence cuvette. The concentration of 1-methylquinoxalin-2(1H)-one stock solution is 2.0 × 10⁻⁶ mol/L in THF. For each quenching experiment, 0.1mL different concentration of 1-methylquinoxalin-2(1H)-one stock solution was titrated to a mixed solution of 0.1 mL Rhodamine B (in a total volume = 0.2 mL). Then the emission intensity was collected and the results were presented in Figure S1.

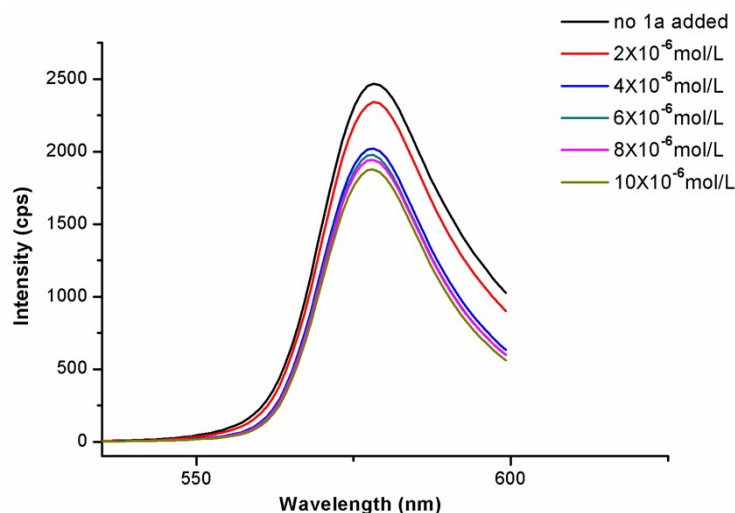


Figure S1. Quenching of Rhodamine B fluorescence emission in the presence of 1-methylquinoxalin-2(1H)-one.

An indeed fluorescence quenching phenomenon of Rhodamine B under various concentrations of 1-methylquinoxalin-2(1H)-one **1a** was demonstrated in a curve of $[I_0/I]$ vs $C[1a]$, as shown in Figure S4 (Stern-Volmer plots). For example, when $C[1a]$ is 2×10^{-6} mol/L, the non-linear Stern-Volmer plots indicated energy transfer process occurred between the excited state of Rhodamine B and 1-methylquinoxalin-2(1H)-one **1a**.

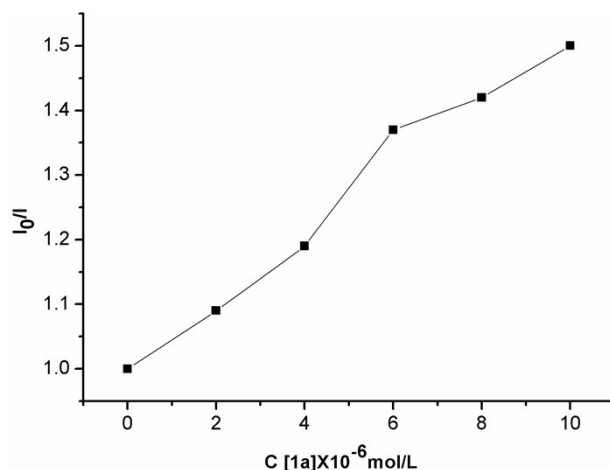


Figure S2. Stern-volmer plots. I_0 is the inherent fluorescence intensity of Rhodamine B. I is the fluorescence intensity of Rhodamine B in the presence of **1a**.

The fluorescence emission intensities were recorded on a Fluormax-4600 spespectrofluorimeter. The excitation wavelength was fixed at 578 nm, and the emission wavelength was measured at 560 nm (emission maximum). The samples were prepared by mixing by Rhodamine B (3.0×10^{-5} mol/L) and different amount of butane-1-thiol **2a** in THF (total volume = 0.2 mL) in a light path quartz fluorescence cuvette. The concentration of butane-1-thiol stock solution is 2.0×10^{-6} mol/L in THF. For each quenching experiment, 0.1 mL different concentration of butane-1-thiol stock solution was titrated to a mixed solution of 0.1 mL Rhodamine B (in a total volume = 0.2 mL). Then the emission intensity was collected and the results were presented in Figures S3 and S4 (Stern-Volmer plots).

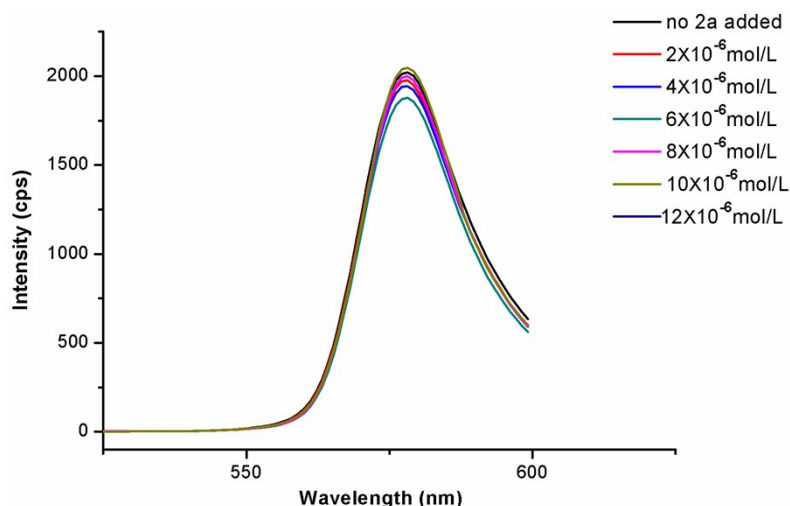


Figure S3. Quenching of Rhodamine B fluorescence emission in the presence of butane-1-thiol.

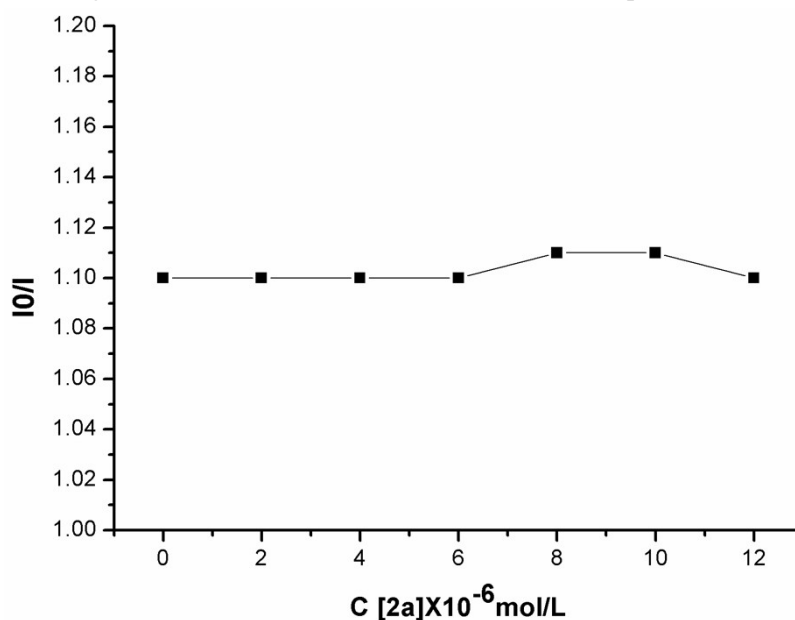
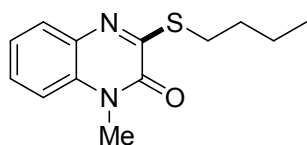


Figure S4. Stern-volmer plots.

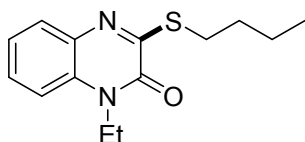
4. Characterization data of products

3-(butylthio)-1-methylquinoxalin-2(1H)-one (3aa)



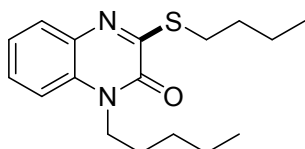
^1H NMR (400 MHz, CDCl_3): δ = 7.75 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1 H), 7.47 – 7.43 (m, 1 H), 7.34 – 7.27 (m, 2 H), 3.70 (s, 3 H), 3.18 (t, J = 7.2 Hz, 2 H), 1.78 – 1.70 (m, 2 H), 1.56 – 1.46 (m, 2 H), 0.97 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 160.1, 153.3, 133.4, 131.3, 128.2, 128.0, 123.7, 113.7, 30.6, 29.2, 29.2, 22.1, 13.6; HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{17}\text{N}_2\text{OS}[\text{M}+\text{H}]^+$: 249.1056, found 249.1053.

3-(butylthio)-1-ethylquinoxalin-2(1H)-one (3ba)



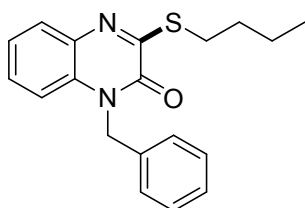
^1H NMR (400 MHz, CDCl_3): δ = 7.77 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1 H), 7.47 – 7.43 (m, 1 H), 7.33 – 7.29 (m, 2 H), 4.33 (q, J = 7.2 Hz, 2 H), 3.18 (t, J = 7.2 Hz, 2 H), 1.78 – 1.71 (m, 2 H), 1.54 – 1.47 (m, 2 H), 1.38 (t, J = 7.2 Hz, 3 H), 0.97 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 160.1, 152.9, 133.8, 130.2, 128.6, 128.1, 123.6, 113.6, 37.5, 30.7, 29.2, 22.1, 13.7, 12.3; HRMS (ESI) m/z calcd. for $\text{C}_{14}\text{H}_{19}\text{N}_2\text{OS}[\text{M}+\text{H}]^+$: 263.1213, found 263.1211.

3-(butylthio)-1-pentylquinoxalin-2(1H)-one (3ca)



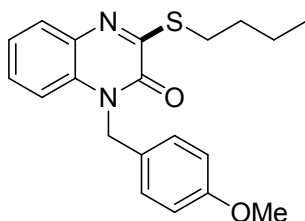
^1H NMR (400 MHz, CDCl_3): δ = 7.75 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1 H), 7.45 – 7.41 (m, 1 H), 7.31 – 7.27 (m, 2 H), 4.23 (t, J = 7.6 Hz, 2 H), 3.17 (t, J = 7.2 Hz, 2 H), 1.77 – 1.70 (m, 2 H), 1.53 – 1.46 (m, 2 H), 1.45 – 1.37 (m, 4 H), 0.98 – 0.89 (m, 6 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 160.1, 153.1, 133.8, 130.4, 128.5, 128.0, 123.5, 113.7, 42.5, 30.6, 29.2, 29.0, 26.8, 22.3, 22.1, 13.9, 13.7; HRMS (ESI) m/z calcd. for $\text{C}_{17}\text{H}_{25}\text{N}_2\text{OS}[\text{M}+\text{H}]^+$: 305.1682, found 305.1677.

benzyl-3-(butylthio)quinoxalin-2(1H)-one (3da)



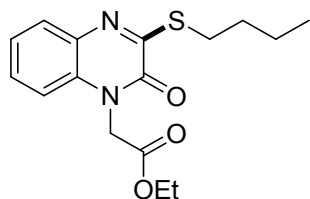
^1H NMR (400 MHz, CDCl_3): δ = 7.75 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1 H), 7.33 – 7.33 (m, 8 H), 5.49 (s, 2 H), 3.21 (t, J = 7.2 Hz, 2 H), 1.80 – 1.73 (m, 2 H), 1.58 – 1.48 (m, 2 H), 0.98 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 160.2, 153.5, 135.1, 133.7, 130.6, 128.9, 128.3, 128.0, 127.7, 127.0, 123.8, 114.6, 46.1, 30.6, 29.3, 22.2, 13.7; HRMS (ESI) m/z calcd. for $\text{C}_{19}\text{H}_{21}\text{N}_2\text{OS}[\text{M}+\text{H}]^+$: 325.1369, found 325.1365.

3-(butylthio)-1-(4-methoxybenzyl)quinoxalin-2(1H)-one (3ea)



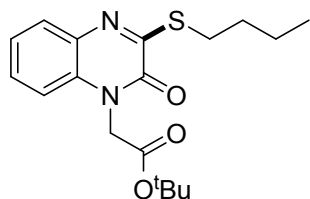
^1H NMR (400 MHz, CDCl_3): δ = 7.75 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1 H), 7.36 – 7.22 (m, 5 H), 6.83 (d, J = 8.4 Hz, 2 H), 5.42 (s, 2 H), 3.75 (s, 3 H), 3.21 (t, J = 7.2 Hz, 2 H), 1.80 – 1.73 (m, 2 H), 1.58 – 1.49 (m, 2 H), 0.99 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 160.2, 159.1, 153.5, 133.8, 130.6, 128.6, 128.4, 128.0, 127.2, 123.7, 114.5, 114.2, 55.2, 45.6, 30.6, 29.3, 22.2, 13.7; HRMS (ESI) m/z calcd. for $\text{C}_{20}\text{H}_{23}\text{N}_2\text{O}_2\text{S}[\text{M}+\text{H}]^+$: 355.1475, found 355.1471.

ethyl 2-(3-(butylthio)-2-oxoquinoxalin-1(2H)-yl)acetate (3fa)



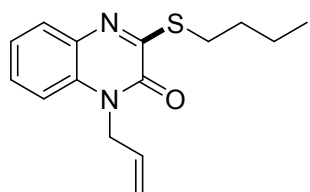
^1H NMR (400 MHz, CDCl_3): δ = 7.78 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1 H), 7.44 – 7.40 (m, 1 H), 7.34 – 7.30 (m, 1 H), 7.05 (dd, J_1 = 8.0 Hz, J_2 = 0.8 Hz, 1 H), 5.03 (s, 2 H), 4.24 (q, J = 7.2 Hz, 2 H), 3.20 (t, J = 7.2 Hz, 2 H), 1.79 – 1.72 (m, 2 H), 1.55 – 1.49 (m, 2 H), 1.26 (t, J = 7.2 Hz, 3 H), 0.98 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 166.9, 159.9, 153.1, 133.5, 130.5, 128.6, 128.2, 124.1, 113.2, 62.1, 43.6, 30.6, 29.3, 22.1, 14.1, 13.7; HRMS (ESI) m/z calcd. for $\text{C}_{16}\text{H}_{21}\text{N}_2\text{O}_3\text{S}[\text{M}+\text{H}]^+$: 321.1267, found 321.1268.

tert-butyl 2-(3-(butylthio)-2-oxoquinoxalin-1(2H)-yl)acetate (3ga)



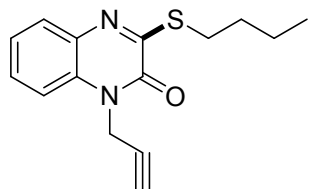
^1H NMR (400 MHz, CDCl_3): δ = 7.76 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1 H), 7.42 – 7.38 (m, 1 H), 7.32 – 7.28 (m, 1 H), 7.03 (dd, J_1 = 8.0 Hz, J_2 = 0.8 Hz, 1 H), 4.93 (s, 2 H), 3.19 (t, J = 7.2 Hz, 2 H), 1.78 – 1.70 (m, 2 H), 1.54 – 1.48 (m, 2 H), 1.44 (s, 9 H), 0.97 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 165.9, 159.8, 153.0, 133.5, 130.5, 128.5, 128.1, 123.9, 113.2, 83.1, 55.9, 44.2, 30.6, 29.2, 27.9, 22.1, 13.7; HRMS (ESI) m/z calcd. for $\text{C}_{18}\text{H}_{25}\text{N}_2\text{O}_3\text{S}[\text{M}+\text{H}]^+$: 349.1580, found 349.1578.

allyl 3-(butylthio)quinoxalin-2(1H)-one (3ha)



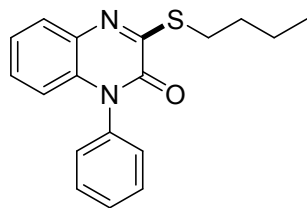
^1H NMR (400 MHz, CDCl_3): δ = 7.76 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1 H), 7.43 – 7.39 (m, 1 H), 7.32 – 7.28 (m, 2 H), 5.97 – 5.88 (m, 1 H), 5.28 – 5.17 (m, 2 H), 4.92 – 4.90 (m, 2 H), 3.19 (t, J = 7.2 Hz, 2 H), 1.79 – 1.71 (m, 2 H), 1.56 – 1.49 (m, 2 H), 0.98 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 160.1, 153.0, 133.7, 130.5, 128.4, 128.0, 123.8, 118.3, 114.3, 44.7, 30.6, 29.3, 22.1, 13.7; HRMS (ESI) m/z calcd. for $\text{C}_{15}\text{H}_{19}\text{N}_2\text{OS}[\text{M}+\text{H}]^+$: 275.1213, found 275.1216.

3-(butylthio)-1-(prop-2-yn-1-yl)quinoxalin-2(1H)-one (3ia)



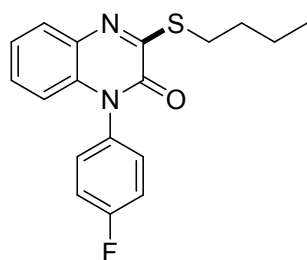
^1H NMR (400 MHz, CDCl_3): δ = 7.76 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1 H), 7.50 – 7.42 (m, 2 H), 7.36 – 7.31 (m, 1 H), 5.05 (d, J = 2.4 Hz, 2 H), 3.18 (t, J = 7.2 Hz, 2 H), 2.28 (t, J = 2.8 Hz, 2 H), 1.77 – 1.70 (m, 2 H), 1.55 – 1.46 (m, 2 H), 0.97 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 159.8, 152.4, 133.6, 129.7, 128.3, 128.1, 124.1, 114.2, 76.6, 73.3, 31.6, 30.5, 29.3, 22.1, 13.7; HRMS (ESI) m/z calcd. for $\text{C}_{15}\text{H}_{17}\text{N}_2\text{OS}[\text{M}+\text{H}]^+$: 273.1056, found 273.1049.

3-(butylthio)-1-phenylquinoxalin-2(1H)-one (3ja)



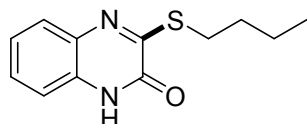
^1H NMR (400 MHz, CDCl_3): δ = 7.80 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.6$ Hz, 1 H), 7.62 – 7.53 (m, 3 H), 7.31 – 7.27 (3 H), 7.25 – 7.21 (1 H), 6.65 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.6$ Hz, 1 H), 3.24 (t, $J = 7.2$ Hz, 2 H), 1.82 – 1.75 (m, 2 H), 1.59 – 1.50 (m, 2 H), 1.00 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 160.8, 153.0, 135.6, 133.3, 132.3, 130.2, 129.4, 128.3, 127.9, 127.7, 123.9, 115.6, 30.7, 29.3, 22.2, 13.7; HRMS (ESI) m/z calcd. for $\text{C}_{18}\text{H}_{19}\text{N}_2\text{OS}[\text{M}+\text{H}]^+$: 311.1213, found 311.1207.

3-(butylthio)-1-(4-fluorophenyl)quinoxalin-2(1H)-one (3ka)



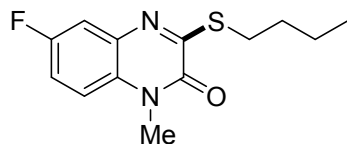
^1H NMR (400 MHz, CDCl_3): δ = 7.80 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1 H), 7.32 – 7.28 (m, 3 H), 7.27 – 7.23 (m, 3 H), 6.65 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1 H), 3.23 (t, $J = 7.2$ Hz, 2 H), 1.82 – 1.74 (m, 2 H), 1.57 – 1.51 (m, 2 H), 0.99 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 161.6, 160.7, 153.1, 133.3, 132.2, 131.4 ($J_{\text{C-F}} = 3.6$ Hz), 130.2, 129.0 ($J_{\text{C-F}} = 244.2$ Hz), 128.0, 124.1, 117.3 ($J_{\text{C-F}} = 22.6$ Hz), 115.3, 30.6, 29.3, 22.2, 13.7; ^{19}F NMR (376 MHz, CDCl_3): δ = -111.2; HRMS (ESI) m/z calcd. for $\text{C}_{18}\text{H}_{18}\text{FN}_2\text{OS}[\text{M}+\text{H}]^+$: 329.1118, found 329.1114.

3-(butylthio)quinoxalin-2(1H)-one (3la)



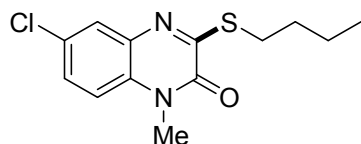
^1H NMR (400 MHz, CDCl_3): δ = 12.03 (s, 1 H), 7.75 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1 H), 7.44 – 7.38 (m, 2 H), 7.34 – 7.29 (m, 1 H), 3.24 (t, $J = 7.2$ Hz, 2 H), 1.81 – 1.73 (m, 2 H), 1.58 – 1.49 (m, 2 H), 0.99 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 159.9, 154.9, 133.5, 129.0, 128.2, 127.3, 124.4, 116.1, 30.6, 29.1, 22.1, 13.7; HRMS (ESI) m/z calcd. for $\text{C}_{12}\text{H}_{15}\text{N}_2\text{OS}[\text{M}+\text{H}]^+$: 235.0900, found 235.0897.

3-(butylthio)-6-fluoro-1-methylquinoxalin-2(1H)-one (3ma)



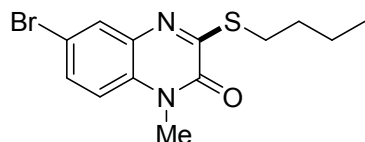
^1H NMR (400 MHz, CDCl_3): δ = 7.43 (dd, $J_1 = 8.8$ Hz, $J_2 = 2.4$ Hz, 1 H), 7.25 – 7.15 (m, 2 H), 3.69 (s, 3 H), 3.15 (t, $J = 7.2$ Hz, 2 H), 1.76 – 1.69 (m, 2 H), 1.55 – 1.46 (m, 2 H), 0.97 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 162.0, 158.9 (d, $J_{\text{C-F}} = 242.0$ Hz), 153.0, 134.0 (d, $J_{\text{C-F}} = 11.0$ Hz), 127.9 (d, $J_{\text{C-F}} = 2.2$ Hz), 115.5 (d, $J_{\text{C-F}} = 24.0$ Hz), 114.7 (d, $J_{\text{C-F}} = 9.5$ Hz), 113.8 (d, $J_{\text{C-F}} = 22.6$ Hz), 30.5, 29.5, 29.4, 22.1, 13.7; ^{19}F NMR (376 MHz, CDCl_3): δ = -119.1; HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{16}\text{FN}_2\text{OS}[\text{M}+\text{H}]^+$: 267.0962, found 267.0960.

3-(butylthio)-6-chloro-1-methylquinoxalin-2(1H)-one (3na)



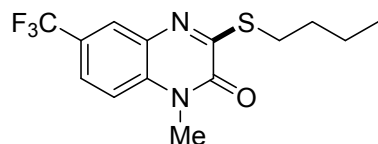
^1H NMR (400 MHz, CDCl_3): δ = 7.73 (d, J = 2.4 Hz, 1 H), 7.39 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1 H), 7.20 (d, J = 8.8 Hz, 1 H), 3.68 (s, 3 H), 3.15 (t, J = 7.2 Hz, 2 H), 1.76 – 1.69 (m, 2 H), 1.55 – 1.46 (m, 2 H), 0.97 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 161.9, 153.1, 133.9, 130.0, 129.1, 127.9, 127.6, 114.8, 30.5, 29.4, 29.4, 22.1, 13.7; HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{16}\text{ClN}_2\text{OS}[\text{M}+\text{H}]^+$: 283.0666, found 283.0661.

6-bromo-3-(butylthio)-1-methylquinoxalin-2(1H)-one (3oa)



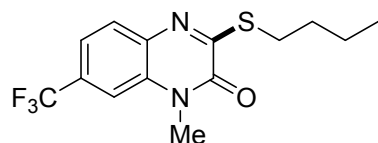
^1H NMR (400 MHz, CDCl_3): δ = 7.89 (d, J = 2.0 Hz, 1 H), 7.52 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1 H), 7.15 (d, J = 8.8 Hz, 1 H), 3.67 (s, 3 H), 3.15 (t, J = 7.2 Hz, 2 H), 1.76 – 1.68 (m, 2 H), 1.55 – 1.45 (m, 2 H), 0.97 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 161.8, 153.1, 134.2, 130.7, 130.6, 130.5, 116.4, 115.1, 30.5, 29.4, 22.1, 13.7; HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{16}\text{BrN}_2\text{OS}[\text{M}+\text{H}]^+$: 327.0161, found 327.0159.

3-(butylthio)-1-methyl-6-(trifluoromethyl)quinoxalin-2(1H)-one (3pa)



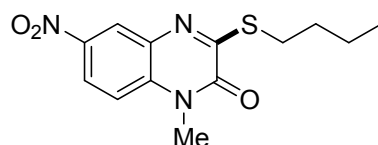
^1H NMR (400 MHz, CDCl_3): δ = 8.01 (d, J = 1.6 Hz, 1 H), 7.66 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1 H), 7.38 (d, J = 8.8 Hz, 1 H), 3.72 (s, 3 H), 3.18 (t, J = 7.2 Hz, 2 H), 1.78 – 1.70 (m, 2 H), 1.56 – 1.47 (m, 2 H), 0.98 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 162.2, 153.2, 133.6, 132.9, 126.1 (q, $J_{\text{C-F}}$ = 33.5 Hz), 125.5 (q, $J_{\text{C-F}}$ = 3.7 Hz), 124.3 (q, $J_{\text{C-F}}$ = 3.7 Hz), 123.8 (q, $J_{\text{C-F}}$ = 270.5 Hz), 114.3, 30.5, , 29.5, 29.5, 22.1, 13.7; ^{19}F NMR (376 MHz, CDCl_3): δ = -61.9; ^{19}F NMR (376 MHz, CDCl_3): δ = -61.9; HRMS (ESI) m/z calcd. for $\text{C}_{14}\text{H}_{16}\text{F}_3\text{N}_2\text{OS}[\text{M}+\text{H}]^+$: 317.0930, found 317.0926.

3-(butylthio)-1-methyl-7-(trifluoromethyl)quinoxalin-2(1H)-one (3qa)



^1H NMR (400 MHz, CDCl_3): δ = 7.83 (d, J = 8.4 Hz, 1 H), 7.55 – 7.51 (m, 2 H), 3.73 (s, 3 H), 3.18 (t, J = 7.2 Hz, 2 H), 1.77 – 1.70 (m, 2 H), 1.55 – 1.48 (m, 2 H), 0.97 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 163.3, 153.1, 135.0 (q, $J_{\text{C-F}}$ = 1.5 Hz), 131.3, 129.5 (q, $J_{\text{C-F}}$ = 32.8 Hz), 128.7, 123.7 (q, $J_{\text{C-F}}$ = 270.6 Hz), 120.4 (q, $J_{\text{C-F}}$ = 3.6 Hz), 111.2 (q, $J_{\text{C-F}}$ = 3.6 Hz), 30.4, , 29.5, 29.4, 22.1, 13.6; ^{19}F NMR (376 MHz, CDCl_3): δ = -62.0; HRMS (ESI) m/z calcd. for $\text{C}_{14}\text{H}_{16}\text{F}_3\text{N}_2\text{OS}[\text{M}+\text{H}]^+$: 317.0930, found 317.0925.

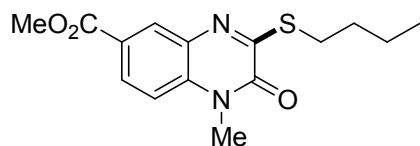
3-(butylthio)-1-methyl-6-nitroquinoxalin-2(1H)-one (3ra)



^1H NMR (400 MHz, CDCl_3): δ = 8.61 (d, J = 2.8 Hz, 1 H), 8.30 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1 H), 7.39 (d, J = 9.2

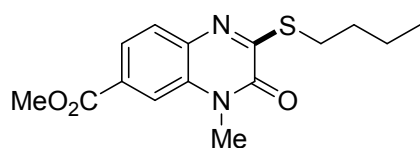
Hz, 1 H), 3.76 (s, 3 H), 3.20 (t, $J = 7.2$ Hz, 2 H), 1.79 – 1.71 (m, 2 H), 1.57 – 1.48 (m, 2 H), 0.98 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 163.4, 153.1, 143.6, 136.0, 132.7, 123.7, 122.6, 114.3, 30.4, 29.8, 29.6, 22.1, 13.7$; HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{16}\text{N}_3\text{O}_3\text{S}[\text{M}+\text{H}]^+$: 294.0907, found 294.0903.

methyl 3-(butylthio)-1-methyl-2-oxo-1,2-dihydroquinoxaline-6-carboxylate (3sa)



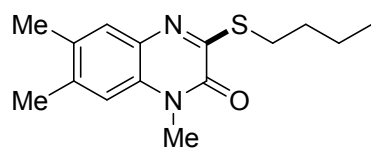
^1H NMR (400 MHz, CDCl_3): $\delta = 8.41$ (d, $J = 2.0$ Hz, 1 H), 8.09 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.0$ Hz, 1 H), 7.32 (d, $J = 8.4$ Hz, 1 H), 3.96 (s, 3 H), 3.72 (s, 3 H), 3.18 (t, $J = 7.2$ Hz, 2 H), 1.78 – 1.70 (m, 2 H), 1.56 – 1.47 (m, 2 H), 0.97 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 166.2, 161.3, 153.3, 134.7, 132.9, 129.9, 128.9, 125.7, 113.8, 52.3, 30.6, 29.5, 29.4, 22.1, 13.7$; HRMS (ESI) m/z calcd. for $\text{C}_{15}\text{H}_{19}\text{N}_2\text{O}_3\text{S}[\text{M}+\text{H}]^+$: 307.1111, found 307.1108.

methyl 2-(butylthio)-4-methyl-3-oxo-3,4-dihydroquinoxaline-6-carboxylate (3ta)



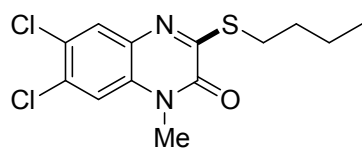
^1H NMR (400 MHz, CDCl_3): $\delta = 7.99 - 7.95$ (m, 2 H), 7.77 (d, $J = 8.0$ Hz, 1 H), 3.97 (s, 3 H), 3.75 (s, 3 H), 3.19 (t, $J = 7.2$ Hz, 2 H), 1.78 – 1.70 (m, 2 H), 1.56 – 1.46 (m, 2 H), 0.97 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 166.3, 163.3, 153.2, 136.1, 131.1, 129.0, 128.1, 124.7, 115.6, 52.5, 30.5, 29.5, 29.5, 22.1, 13.7$; HRMS (ESI) m/z calcd. for $\text{C}_{15}\text{H}_{19}\text{N}_2\text{O}_3\text{S}[\text{M}+\text{H}]^+$: 307.1111, found 307.1106.

3-(butylthio)-1,6,7-trimethylquinoxalin-2(1H)-one (3ua)



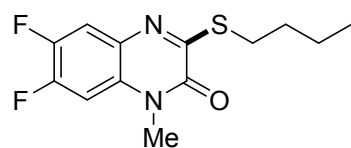
^1H NMR (400 MHz, CDCl_3): $\delta = 7.50$ (s, 1 H), 7.03 (s, 1 H), 3.66 (s, 3 H), 3.15 (t, $J = 7.2$ Hz, 2 H), 2.38 (s, 3 H), 2.33 (s, 3 H), 1.76 – 1.67 (m, 2 H), 1.55 – 1.46 (m, 2 H), 0.97 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 158.6, 153.4, 137.6, 132.6, 131.9, 129.2, 128.4, 114.3, 30.7, 29.2, 29.1, 22.1, 20.4, 19.1, 13.7$; HRMS (ESI) m/z calcd. for $\text{C}_{15}\text{H}_{21}\text{N}_2\text{OS}[\text{M}+\text{H}]^+$: 277.1369, found 277.1367.

3-(butylthio)-6,7-dichloro-1-methylquinoxalin-2(1H)-one (3va)



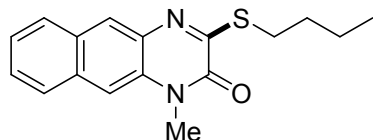
^1H NMR (400 MHz, CDCl_3): $\delta = 7.82$ (s, 1 H), 7.36 (s, 1 H), 3.65 (s, 3 H), 3.14 (t, $J = 7.2$ Hz, 2 H), 1.75 – 1.68 (m, 2 H), 1.54 – 1.45 (m, 2 H), 0.97 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 162.1, 152.8, 132.5, 131.7, 130.8, 128.9, 127.5, 115.2, 30.4, 29.5, 29.5, 22.1, 13.7$; HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{15}\text{Cl}_2\text{N}_2\text{OS}[\text{M}+\text{H}]^+$: 317.0277, found 317.0272.

3-(butylthio)-6,7-difluoro-1-methylquinoxalin-2(1H)-one (3wa)



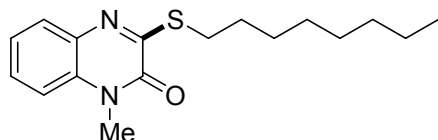
^1H NMR (400 MHz, CDCl_3): δ = 7.57 – 7.53 (m, 1 H), 7.11 – 7.06 (m, 1 H), 3.65 (s, 3 H), 3.13 (t, J = 7.2 Hz, 2 H), 1.75 – 1.68 (m, 2 H), 1.54 – 1.45 (m, 2 H), 0.97 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 161.0 (d, $J_{\text{C-F}}$ = 3.0 Hz), 153.0, 149.8 (dd, J_1 = 249.3 Hz, J_2 = 14.5 Hz), 146.7 (dd, J_1 = 245.0 Hz, J_2 = 13.8 Hz), 129.8 (dd, J_1 = 6.6 Hz, J_2 = 2.2 Hz), 128.2 (dd, J_1 = 8.6 Hz, J_2 = 2.2 Hz), 115.8 (dd, J_1 = 18.3 Hz, J_2 = 1.5 Hz), 102.4 (d, $J_{\text{C-F}}$ = 23.3 Hz), 30.5, 29.7, 29.4, 22.1, 13.7; ^{19}F NMR (376 MHz, CDCl_3): δ = -134.0 (d, $J_{\text{F-F}}$ = 21.8 Hz, 1 F), -142.2 (d, $J_{\text{F-F}}$ = 23.3 Hz, 1 F); HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{15}\text{F}_2\text{N}_2\text{OS}[\text{M}+\text{H}]^+$: 285.0868, found 285.0861.

3-(butylthio)-1-methylbenzo[*g*]quinoxalin-2(1H)-one (3xa)



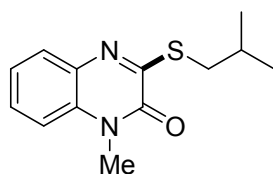
^1H NMR (400 MHz, CDCl_3): δ = 8.20 (s, 1 H), 7.93 (d, J = 8.0 Hz, 1 H), 7.87 (d, J = 8.0 Hz, 1 H), 7.56 – 7.45 (m, 3 H), 3.75 (s, 3 H), 3.22 (t, J = 7.6 Hz, 2 H), 1.81 – 1.74 (m, 2 H), 1.59 – 1.50 (m, 2 H), 1.00 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 160.6, 153.3, 132.7, 132.4, 130.5, 130.0, 128.0, 127.2, 127.0, 126.4, 125.3, 110.2, 30.6, 29.4, 29.3, 22.2, 13.7; HRMS (ESI) m/z calcd. for $\text{C}_{17}\text{H}_{19}\text{N}_2\text{OS}[\text{M}+\text{H}]^+$: 299.1213, found 299.1214.

methyl-3-(octylthio)quinoxalin-2(1H)-one (3ab)



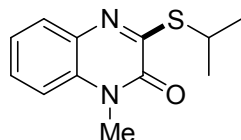
^1H NMR (400 MHz, CDCl_3): δ = 7.74 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1 H), 7.47 – 7.42 (m, 1 H), 7.33 – 7.27 (m, 2 H), 3.70 (s, 3 H), 3.17 (t, J = 7.2 Hz, 2 H), 1.79 – 1.71 (m, 2 H), 1.52 – 1.44 (m, 2 H), 1.36 – 1.25 (m, 8 H), 0.88 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 160.1, 153.4, 133.5, 131.3, 128.2, 128.0, 123.7, 113.7, 31.8, 29.6, 29.2, 29.1, 29.1, 29.0, 28.5, 22.6, 14.1; HRMS (ESI) m/z calcd. for $\text{C}_{17}\text{H}_{25}\text{N}_2\text{OS}[\text{M}+\text{H}]^+$: 305.1682, found 305.1681.

3-(isobutylthio)-1-methylquinoxalin-2(1H)-one (3ac)



^1H NMR (400 MHz, CDCl_3): δ = 7.73 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1 H), 7.46 – 7.41 (m, 1 H), 7.33 – 7.26 (m, 2 H), 3.69 (s, 3 H), 3.09 (d, J = 6.8 Hz, 2 H), 2.08 – 1.98 (m, 1 H), 1.08 (d, J = 6.8 Hz, 6 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 160.1, 153.4, 133.4, 131.3, 128.1, 128.0, 123.7, 113.7, 38.0, 29.2, 28.0, 22.1; HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{17}\text{N}_2\text{OS}[\text{M}+\text{H}]^+$: 249.1056, found 249.1052.

3-(isopropylthio)-1-methylquinoxalin-2(1H)-one (3ad)



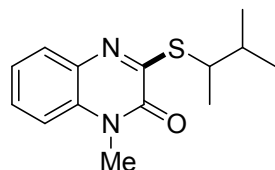
^1H NMR (400 MHz, CDCl_3): δ = 7.73 (d, J = 8.0 Hz, 1 H), 7.46 – 7.42 (m, 1 H), 7.32 – 7.28 (m, 2 H), 4.02 – 3.94 (m, 1 H), 3.68 (s, 3 H), 1.45 (d, J = 6.8 Hz, 6 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 159.9, 153.2, 133.5, 131.2, 128.2, 128.0, 123.7, 113.7, 34.4, 29.2, 22.5; HRMS (ESI) m/z calcd. for $\text{C}_{12}\text{H}_{15}\text{N}_2\text{OS}[\text{M}+\text{H}]^+$: 235.0900, found 235.0902.

3-(tert-butylthio)-1-methylquinoxalin-2(1H)-one (3ae)



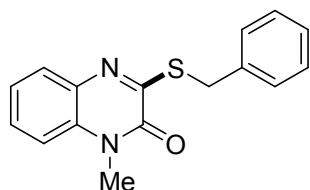
^1H NMR (400 MHz, CDCl_3): δ = 7.75 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1 H), 7.46 – 7.42 (m, 1 H), 7.33 – 7.28 (m, 2 H), 3.68 (s, 3 H), 1.67 (s, 9 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 160.5, 153.3, 133.2, 131.1, 128.2, 128.1, 123.7, 113.7, 47.2, 29.5, 29.2; HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{17}\text{N}_2\text{OS}[\text{M}+\text{H}]^+$: 249.1056, found 249.1053.

methyl-3-(3-methylbutan-2-yl)thioquinoxalin-2(1H)-one (3af)



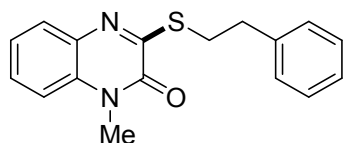
^1H NMR (400 MHz, CDCl_3): δ = 7.73 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1 H), 7.45 – 7.41 (m, 1 H), 7.32 – 7.25 (m, 2 H), 4.01 – 3.94 (m, 1 H), 3.69 (s, 3 H), 2.11 – 2.02 (m, 1 H), 1.38 (d, J = 7.2 Hz, 3 H), 1.07 (d, J = 6.8 Hz, 3 H), 1.04 (d, J = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 160.0, 153.4, 133.4, 131.2, 128.1, 127.9, 123.7, 113.6, 45.2, 32.7, 29.2, 19.7, 19.2, 17.2; HRMS (ESI) m/z calcd. for $\text{C}_{14}\text{H}_{19}\text{N}_2\text{OS}[\text{M}+\text{H}]^+$: 263.1213, found 263.1208.

3-(benzylthio)-1-methylquinoxalin-2(1H)-one (3ag)



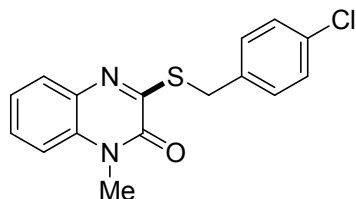
^1H NMR (400 MHz, CDCl_3): δ = 7.80 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1 H), 7.47 – 7.43 (m, 3 H), 7.35 – 7.23 (m, 5 H), 4.41 (s, 2 H), 3.68 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 159.3, 153.2, 137.3, 133.3, 131.5, 129.3, 128.4, 128.3, 128.2, 127.1, 123.8, 113.7, 34.0, 29.2; HRMS (ESI) m/z calcd. for $\text{C}_{16}\text{H}_{15}\text{N}_2\text{OS}[\text{M}+\text{H}]^+$: 283.0900, found 283.0895.

methyl-3-(phenethylthio)quinoxalin-2(1H)-one (3ah)



^1H NMR (400 MHz, CDCl_3): δ = 7.80 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1 H), 7.50 – 7.45 (m, 1 H), 7.37 – 7.30 (m, 5 H), 7.26 – 7.22 (m, 2 H), 3.72 (s, 3 H), 3.43 – 3.39 (m, 2 H), 3.07 – 3.03 (m, 2 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 159.7, 153.4, 140.6, 133.5, 131.4, 128.7, 128.5, 128.3, 128.3, 126.4, 123.9, 113.8, 35.1, 31.0, 29.3; HRMS (ESI) m/z calcd. for $\text{C}_{17}\text{H}_{17}\text{N}_2\text{OS}[\text{M}+\text{H}]^+$: 297.1056, found 297.1052.

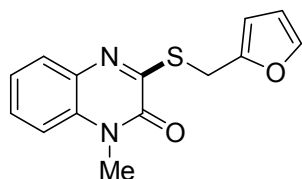
3-((4-chlorobenzyl)thio)-1-methylquinoxalin-2(1H)-one (3ai)



^1H NMR (400 MHz, CDCl_3): δ = 7.78 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1 H), 7.50 – 7.45 (m, 1 H), 7.41 – 7.28 (m, 5

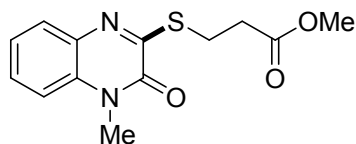
H), 7.25 – 7.23 (m, 1 H), 4.36 (s, 2 H), 3.69 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 158.9, 153.2, 136.0, 133.3, 133.0, 131.5, 130.6, 128.5, 128.2, 124.0, 113.8, 33.2, 29.3; HRMS (ESI) m/z calcd. for $\text{C}_{16}\text{H}_{14}\text{ClN}_2\text{OS}[\text{M}+\text{H}]^+$: 317.0510, found 317.0504.

3-((furan-2-ylmethyl)thio)-1-methylquinoxalin-2(1H)-one (3aj)



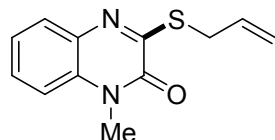
^1H NMR (400 MHz, CDCl_3): δ = 7.81 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1 H), 7.50 – 7.46 (m, 1 H), 7.37 – 7.29 (m, 3 H), 6.34 – 6.32 (m, 1 H), 6.29 – 6.27 (m, 1 H), 4.46 (s, 2 H), 3.70 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 158.8, 153.2, 150.5, 142.0, 133.3, 131.5, 128.5, 128.3, 123.9, 113.8, 110.5, 108.1, 29.2, 26.4; HRMS (ESI) m/z calcd. for $\text{C}_{14}\text{H}_{13}\text{N}_2\text{O}_2\text{S}[\text{M}+\text{H}]^+$: 273.0692, found 273.0689.

methyl 3-((4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)thio)propanoate (3ak)



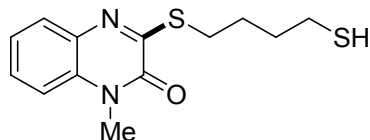
^1H NMR (400 MHz, CDCl_3): δ = 7.77 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1 H), 7.50 – 7.45 (m, 1 H), 7.35 – 7.29 (m, 2 H), 3.72 (s, 3 H), 3.71 (s, 3 H), 3.43 (d, J = 7.2 Hz, 2 H), 2.83 (d, J = 7.2 Hz, 2 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 172.4, 159.2, 153.3, 133.4, 131.4, 128.5, 128.4, 123.9, 113.8, 51.9, 33.5, 29.3, 24.5; HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{15}\text{N}_2\text{O}_3\text{S}[\text{M}+\text{H}]^+$: 279.0798, found 279.0789.

3-(allylthio)-1-methylquinoxalin-2(1H)-one (3al)



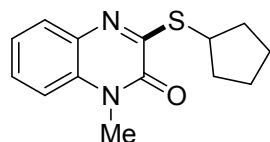
^1H NMR (400 MHz, CDCl_3): δ = 7.77 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1 H), 7.49 – 7.44 (m, 1 H), 7.35 – 7.28 (m, 2 H), 6.04 – 5.94 (m, 1 H), 5.41 – 5.35 (m, 1 H), 5.17 – 5.14 (m, 1 H), 3.86 – 3.84 (m, 2 H), 3.71 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 159.2, 153.3, 133.4, 132.9, 131.4, 128.3, 123.9, 118.2, 113.8, 32.4, 29.3; HRMS (ESI) m/z calcd. for $\text{C}_{12}\text{H}_{13}\text{N}_2\text{OS}[\text{M}+\text{H}]^+$: 233.0743, found 233.0746.

3-((4-mercaptobutyl)thio)-1-methylquinoxalin-2(1H)-one (3am)



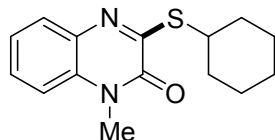
^1H NMR (400 MHz, CDCl_3): δ = 7.78 – 7.73 (m, 1 H), 7.48 – 7.43 (m, 1 H), 7.35 – 7.27 (m, 2 H), 4.91 (br, 1H), 3.70 (s, 3 H), 3.20 – 3.18 (m, 2 H), 2.76 – 2.74 (m, 2 H), 1.88 – 1.85 (m, 4 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 159.7, 153.3, 133.4, 131.3, 128.3, 128.2, 123.8, 113.7, 38.5, 29.3, 28.9, 28.4, 27.5; HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{17}\text{N}_2\text{OS}_2[\text{M}+\text{H}]^+$: 281.0777, found 281.0772.

3-(cyclopentylthio)-1-methylquinoxalin-2(1H)-one (3an)



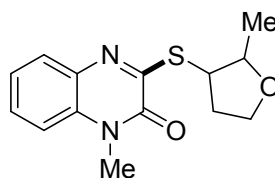
^1H NMR (400 MHz, CDCl_3): δ = 7.71 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1 H), 7.43 – 7.39 (m, 1 H), 7.30 – 7.23 (m, 2 H), 4.06 – 3.99 (m, 1 H), 3.66 (s, 3 H), 2.31 – 2.22 (m, 2 H), 1.80 – 1.63 (m, 6 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 160.7, 153.2, 133.5, 131.2, 128.2, 127.9, 123.7, 113.6, 42.4, 32.9, 29.1, 24.9; HRMS (ESI) m/z calcd. for $\text{C}_{14}\text{H}_{17}\text{N}_2\text{OS}[\text{M}+\text{H}]^+$: 261.1056, found 261.1055.

3-(cyclohexylthio)-1-methylquinoxalin-2(1H)-one (3ao)



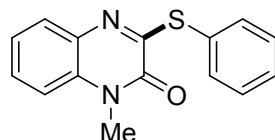
^1H NMR (400 MHz, CDCl_3): δ = 7.74 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1 H), 7.46 – 7.41 (m, 1 H), 7.33 – 7.26 (m, 2 H), 3.92 – 3.85 (m, 1 H), 3.69 (s, 3 H), 2.15 – 2.10 (m, 2 H), 1.82 – 1.77 (m, 2 H), 1.67 – 1.46 (m, 6 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 159.7, 153.3, 133.5, 131.2, 128.2, 128.0, 123.7, 113.6, 42.1, 32.5, 29.2, 25.9, 25.8; HRMS (ESI) m/z calcd. for $\text{C}_{15}\text{H}_{19}\text{N}_2\text{OS}[\text{M}+\text{H}]^+$: 275.1213, found 275.1211.

1-methyl-3-((2-methyltetrahydrofuran-3-yl)thio)quinoxalin-2(1H)-one (3ap)



^1H NMR (400 MHz, CDCl_3): δ = 7.73 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1 H), 7.49 – 7.45 (m, 1 H), 7.35 – 7.29 (m, 2 H), 4.47 – 4.39 (m, 2 H), 4.07 – 4.02 (m, 1 H), 3.86 – 3.80 (m, 1 H), 3.71 (s, 3 H), 2.62 – 2.53 (m, 1 H), 2.13 – 2.05 (m, 1 H), 1.28 (d, J = 5.6 Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 159.6, 153.2, 133.3, 131.4, 128.4, 128.3, 123.9, 113.8, 76.5, 66.0, 45.8, 32.9, 29.3, 17.0; HRMS (ESI) m/z calcd. for $\text{C}_{14}\text{H}_{17}\text{N}_2\text{O}_2\text{S}[\text{M}+\text{H}]^+$: 277.1005, found 277.1009.

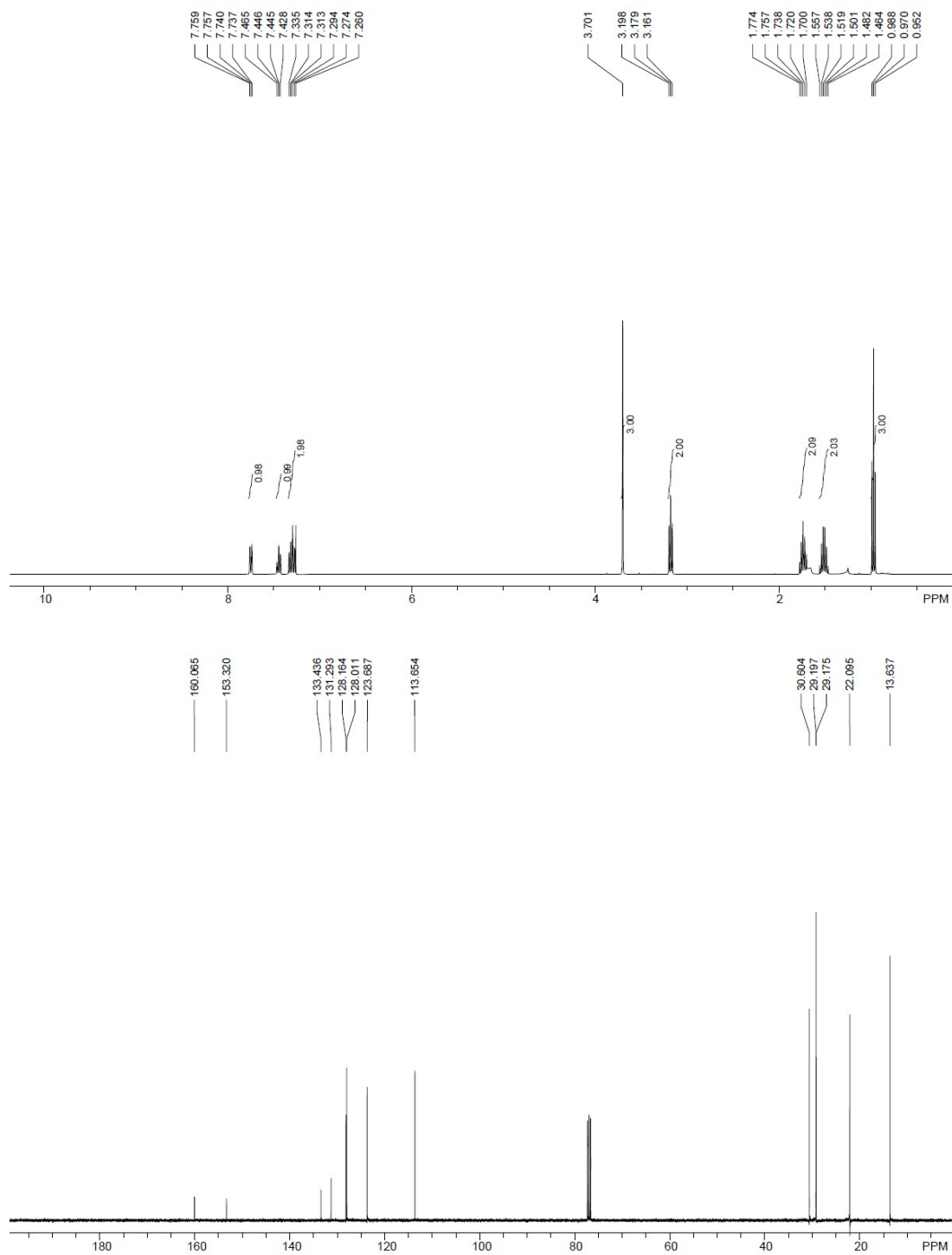
methyl-3-(phenylthio)quinoxalin-2(1H)-one (3aq)



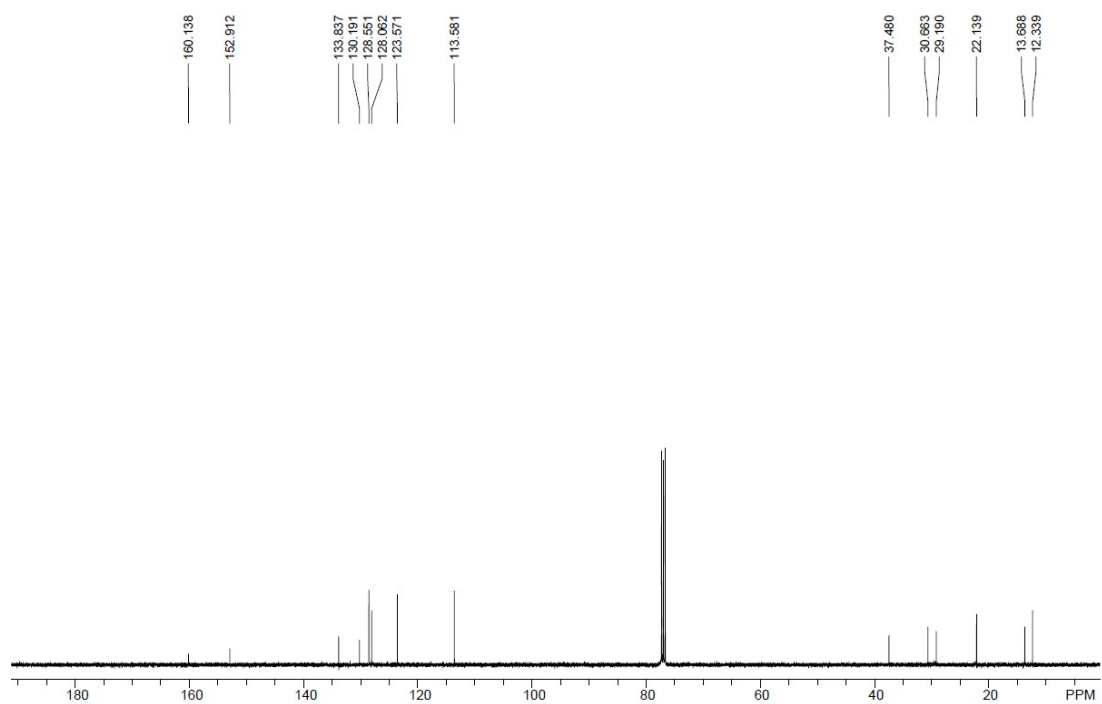
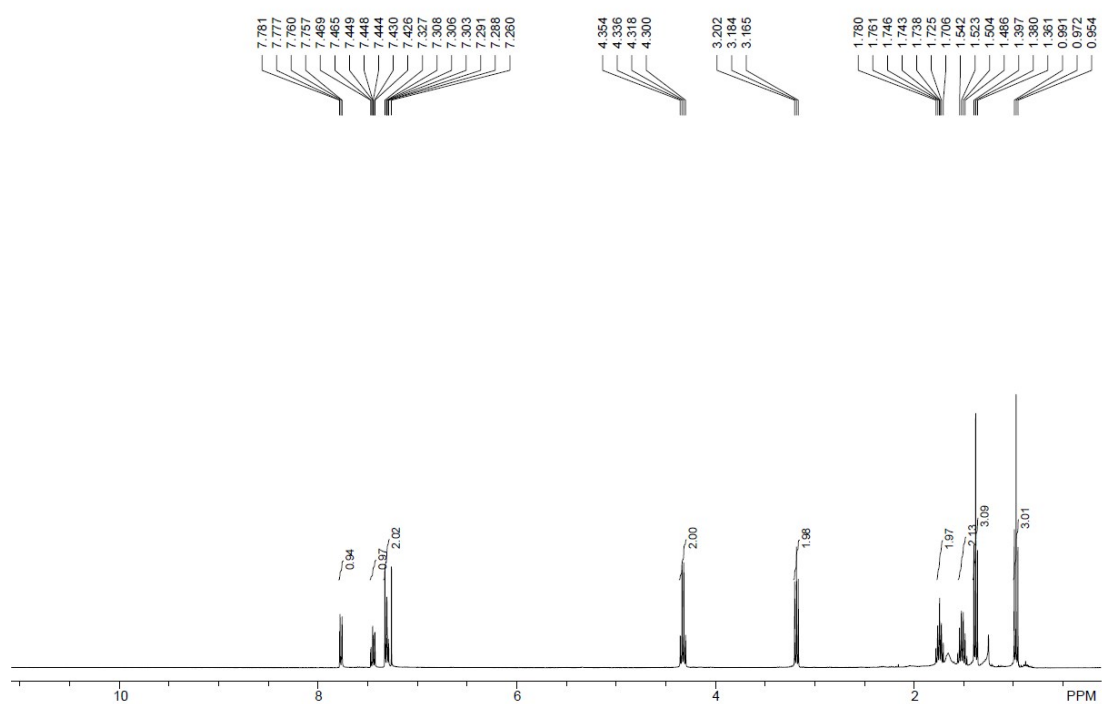
^1H NMR (400 MHz, CDCl_3): δ = 7.63 – 7.61 (m, 2 H), 7.53 – 7.51 (m, 1 H), 7.47 – 7.42 (m, 4 H), 7.29 – 7.27 (m, 1 H), 7.26 – 7.22 (m, 1 H), 3.75 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 159.6, 153.1, 135.4, 133.3, 131.7, 129.4, 129.1, 129.0, 128.8, 128.6, 123.8, 113.6, 29.3; HRMS (ESI) m/z calcd. for $\text{C}_{15}\text{H}_{13}\text{N}_2\text{OS}[\text{M}+\text{H}]^+$: 269.0743, found 269.0736.

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

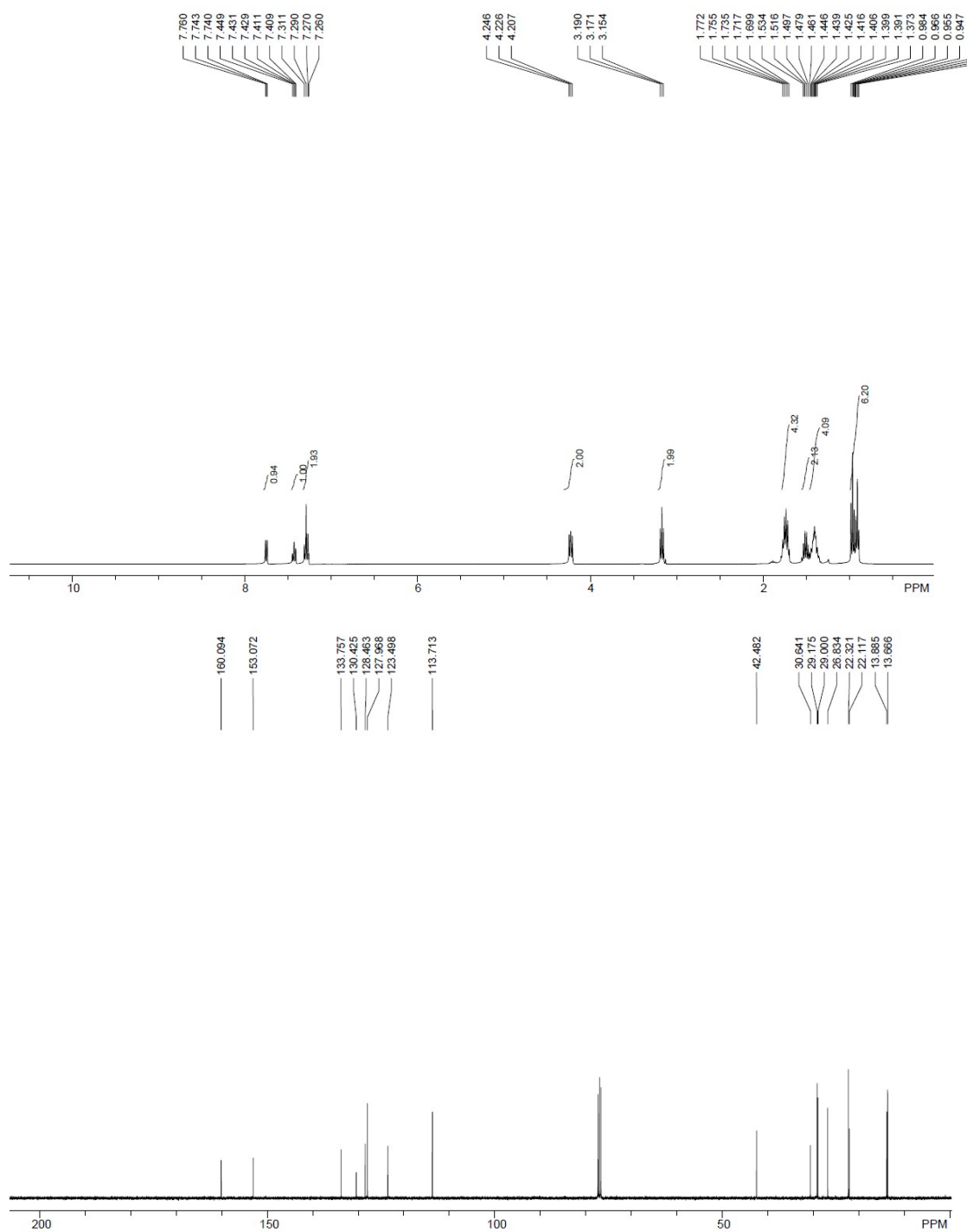
3-(butylthio)-1-methylquinoxalin-2(1H)-one (3aa)



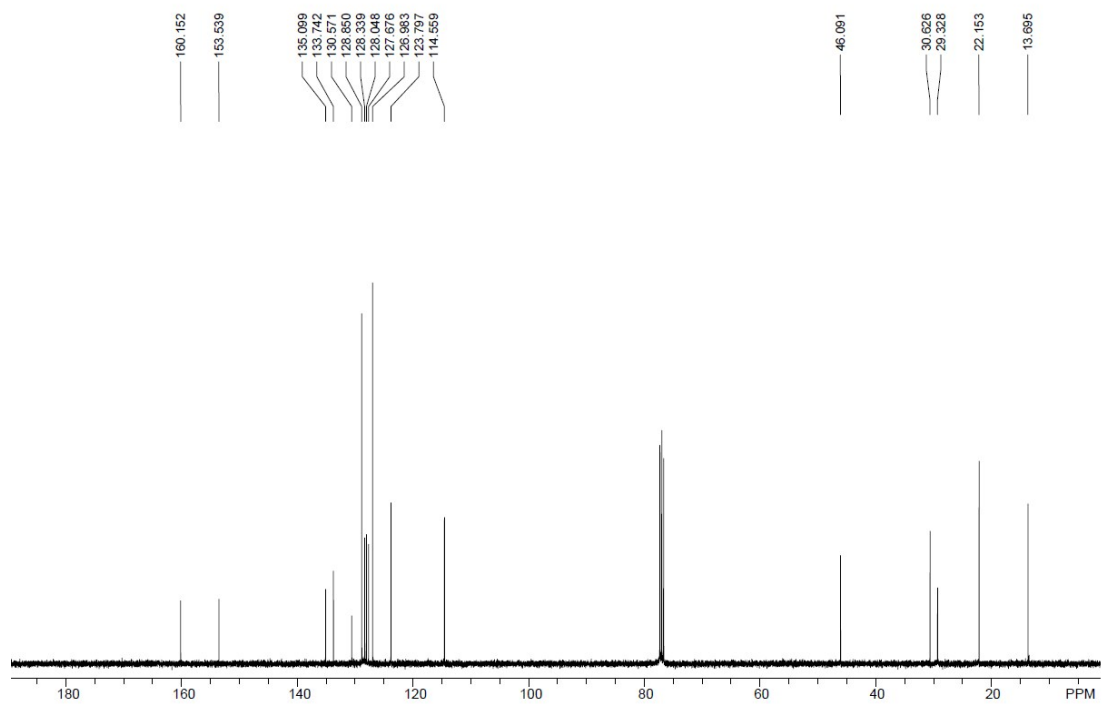
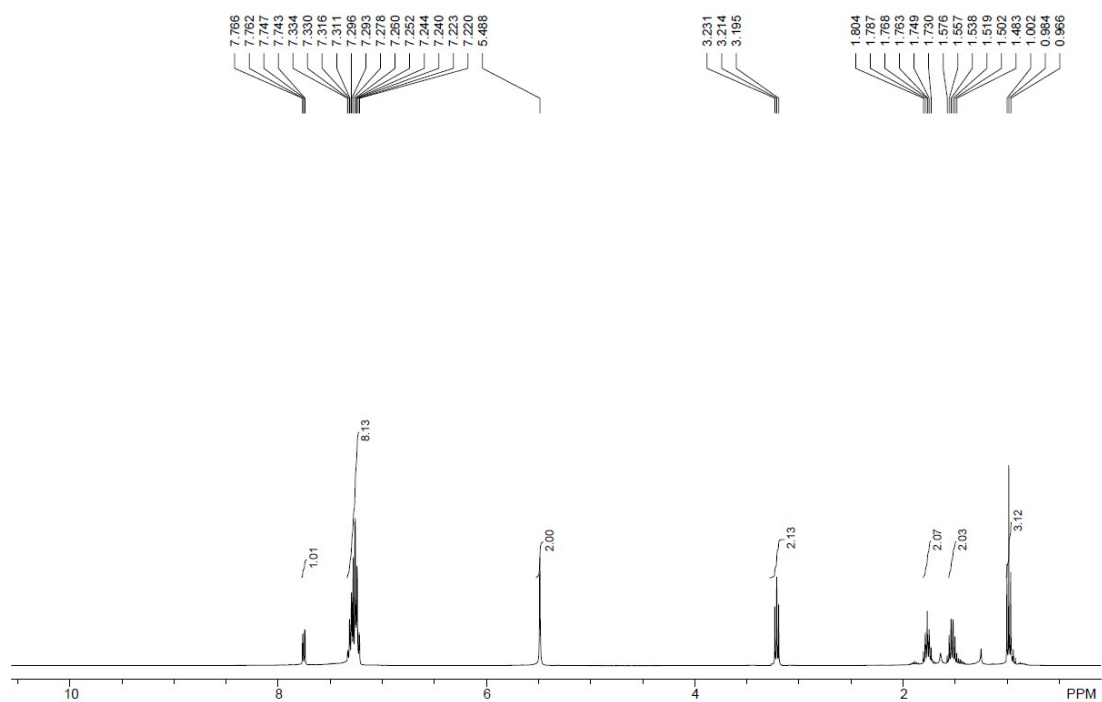
3-(butylthio)-1-ethylquinoxalin-2(1H)-one (3ba)



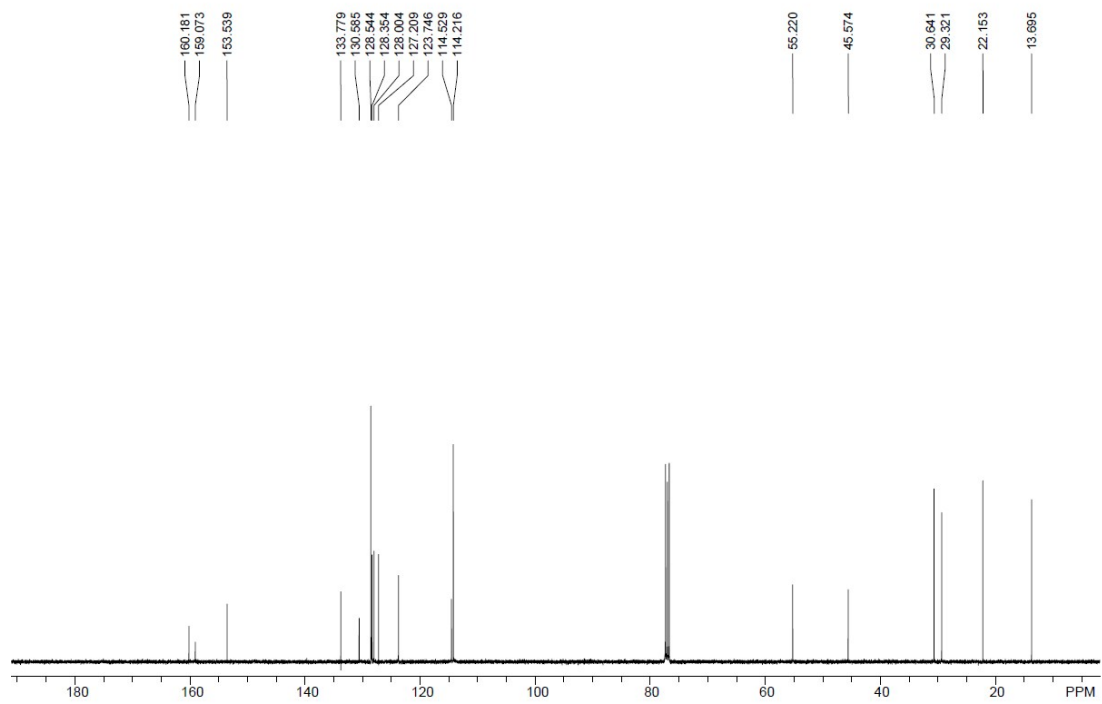
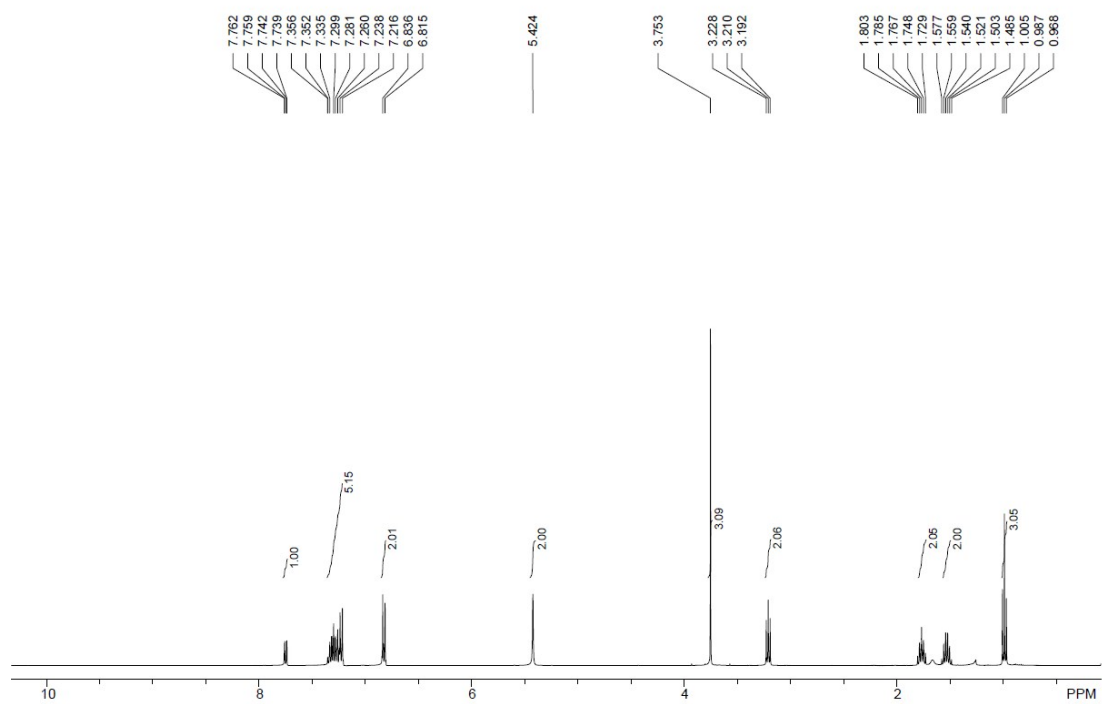
3-(butylthio)-1-pentylquinoxalin-2(1H)-one (3ca)



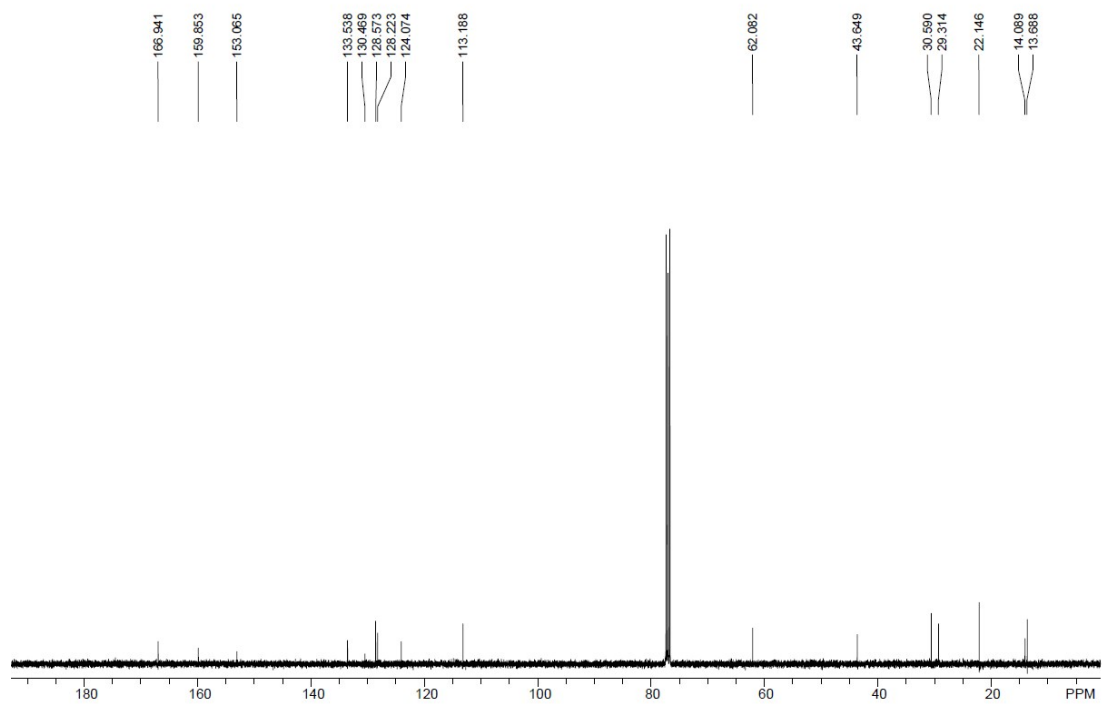
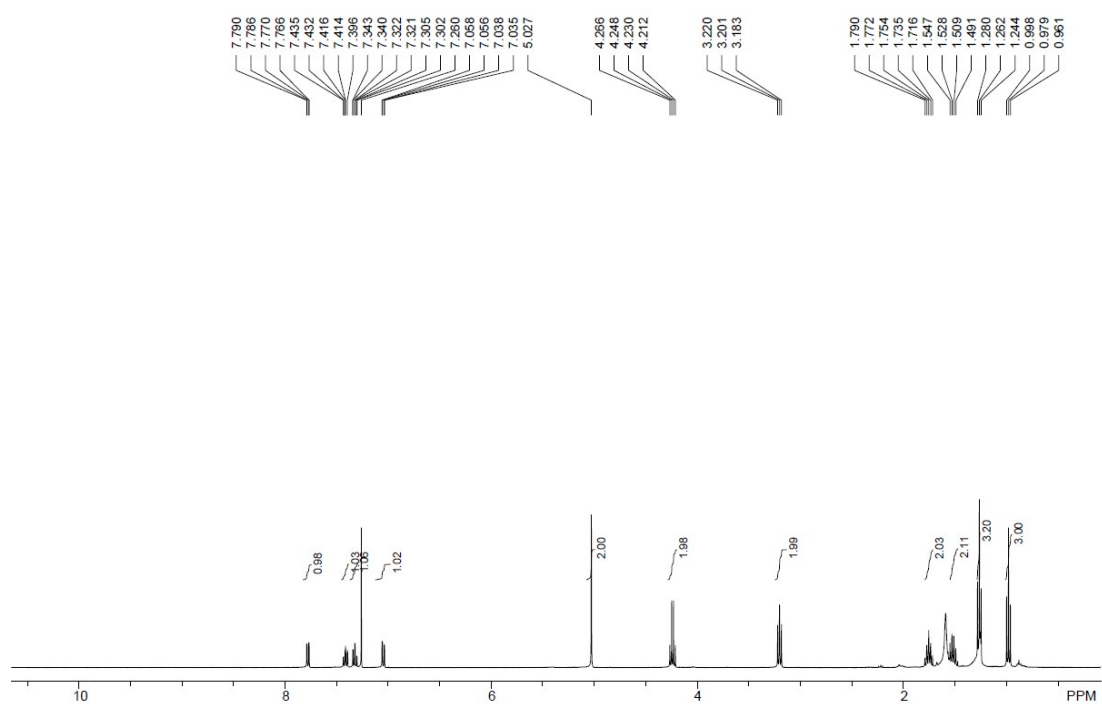
benzyl-3-(butylthio)quinoxalin-2(1H)-one (3da)



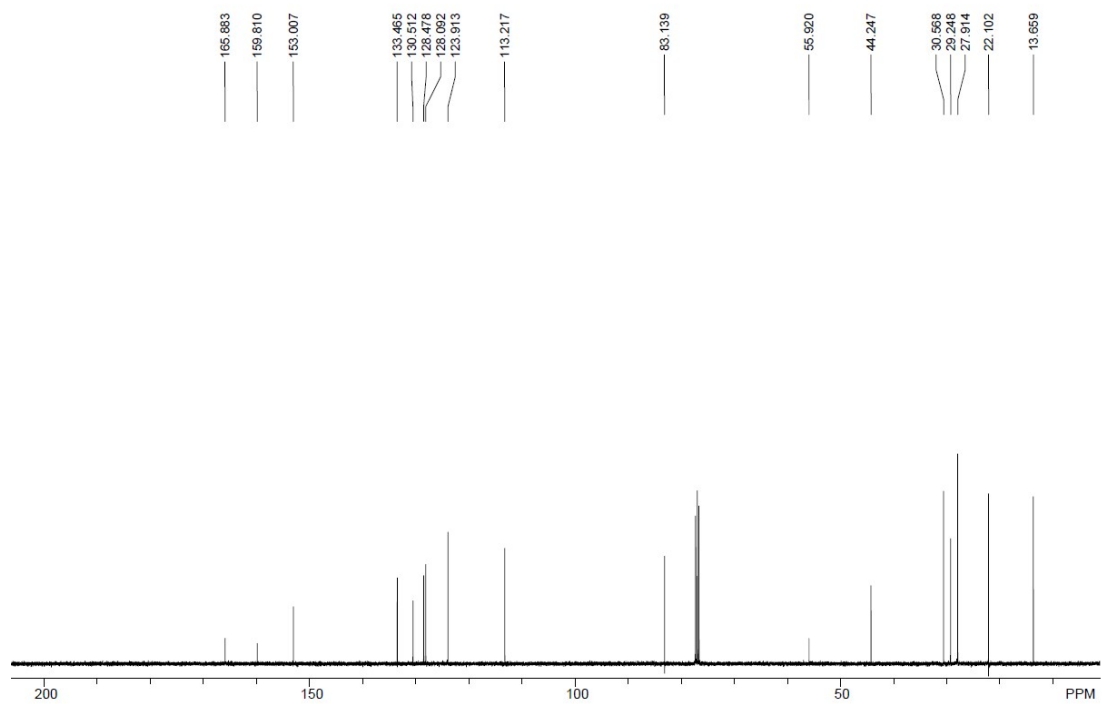
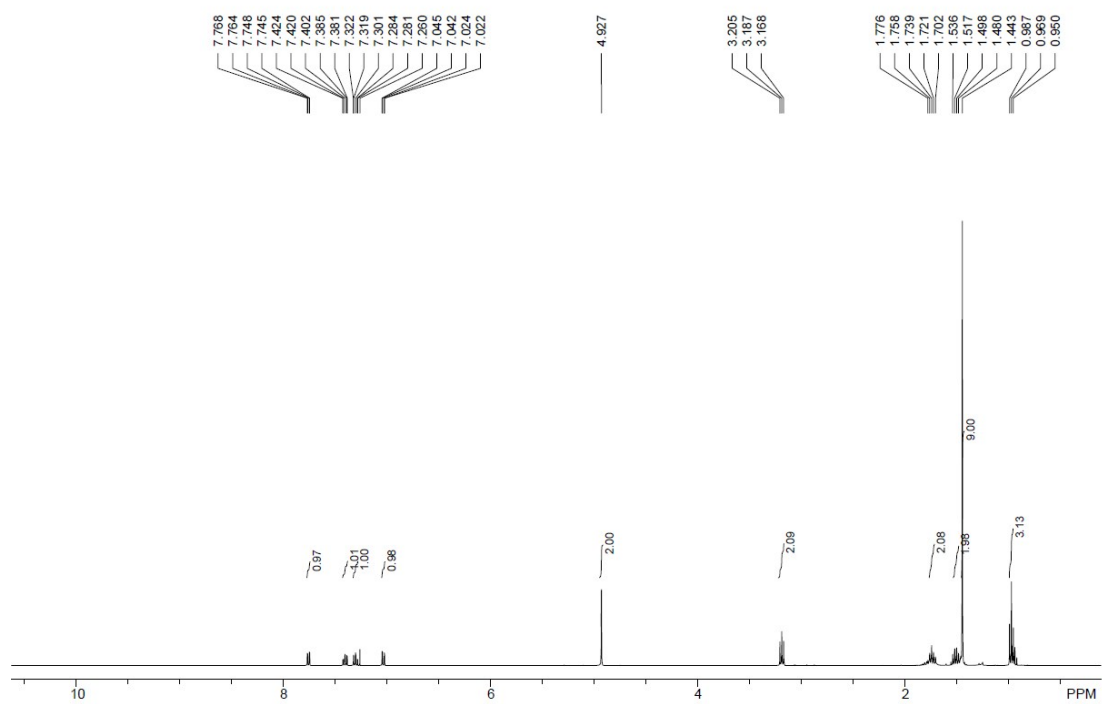
3-(butylthio)-1-(4-methoxybenzyl)quinoxalin-2(1H)-one (3ea)



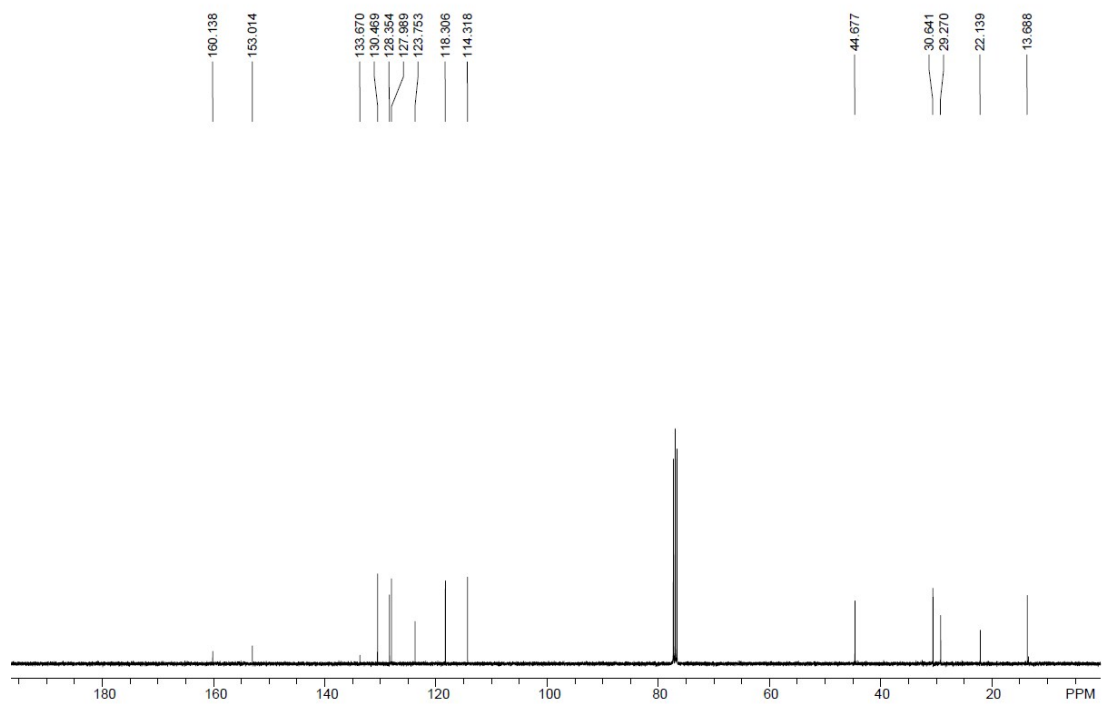
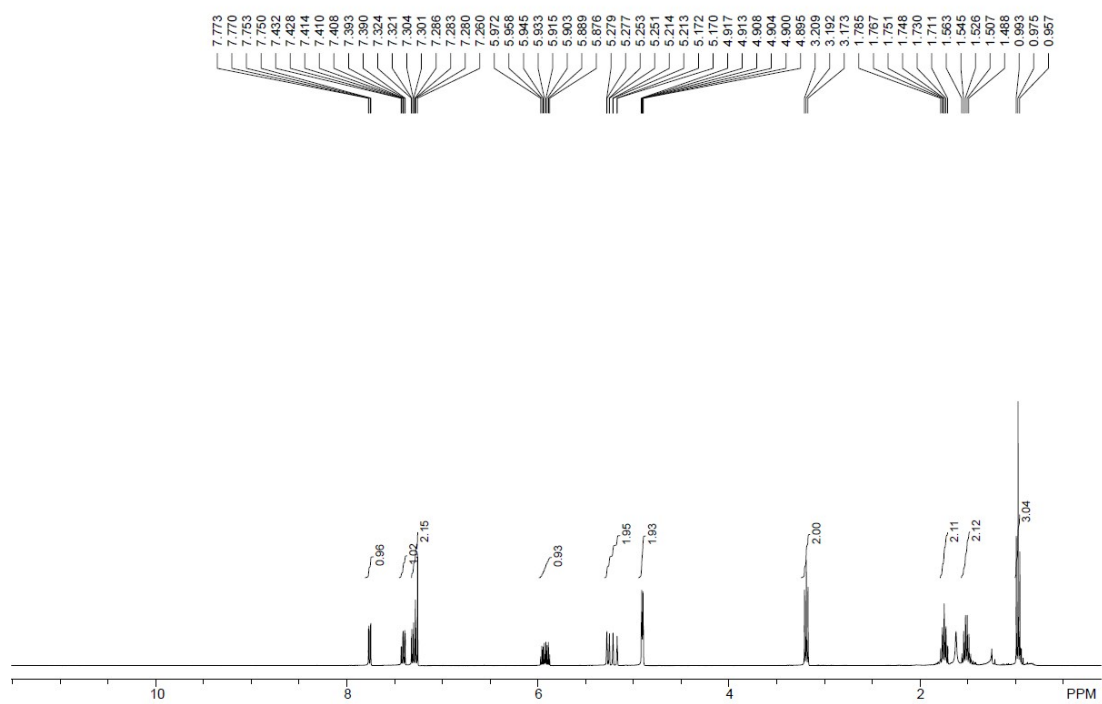
ethyl 2-(3-(butylthio)-2-oxoquinoxalin-1(2H)-yl)acetate (3fa)



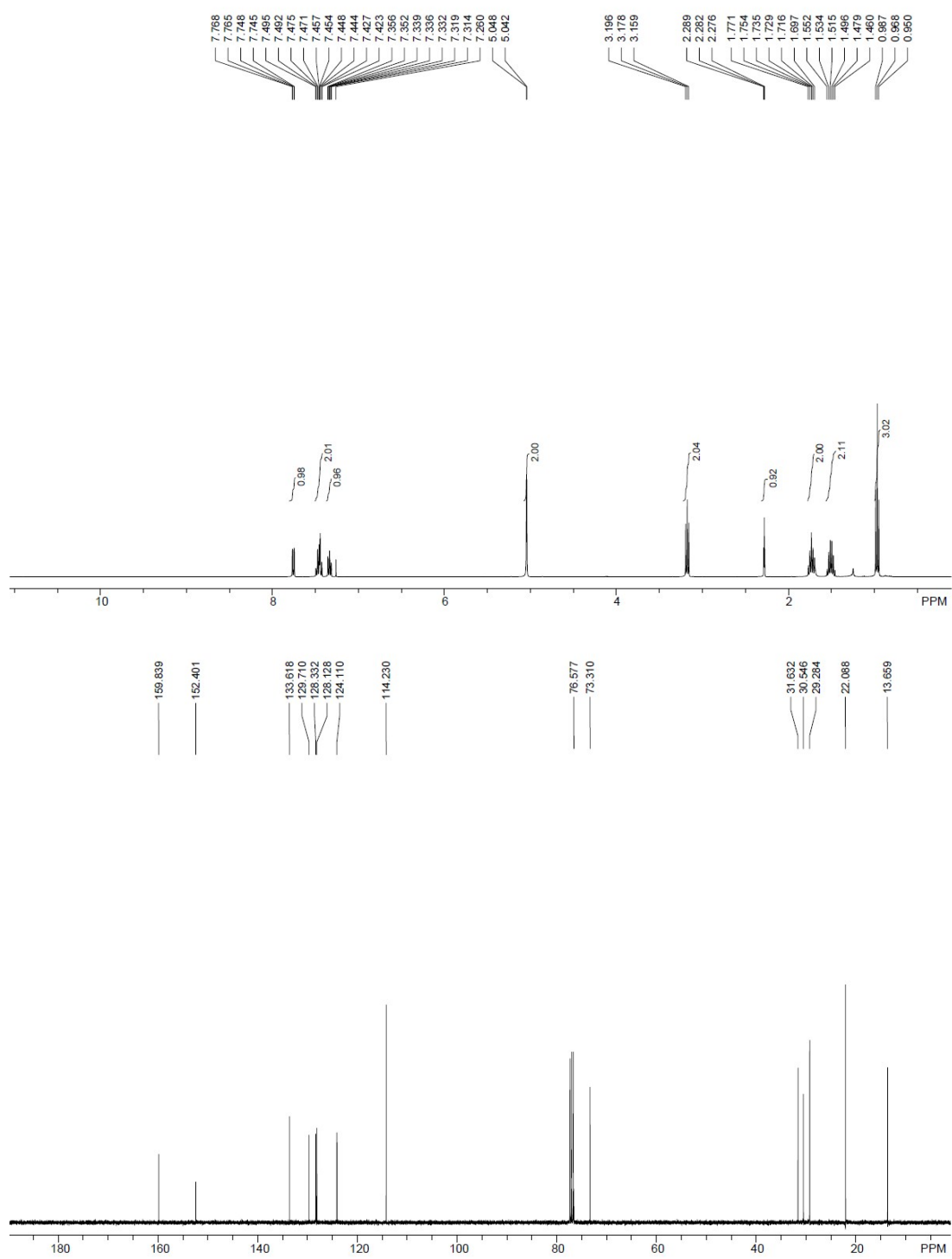
tert-butyl 2-(3-(butylthio)-2-oxoquinoxalin-1(2H)-yl)acetate (3ga)



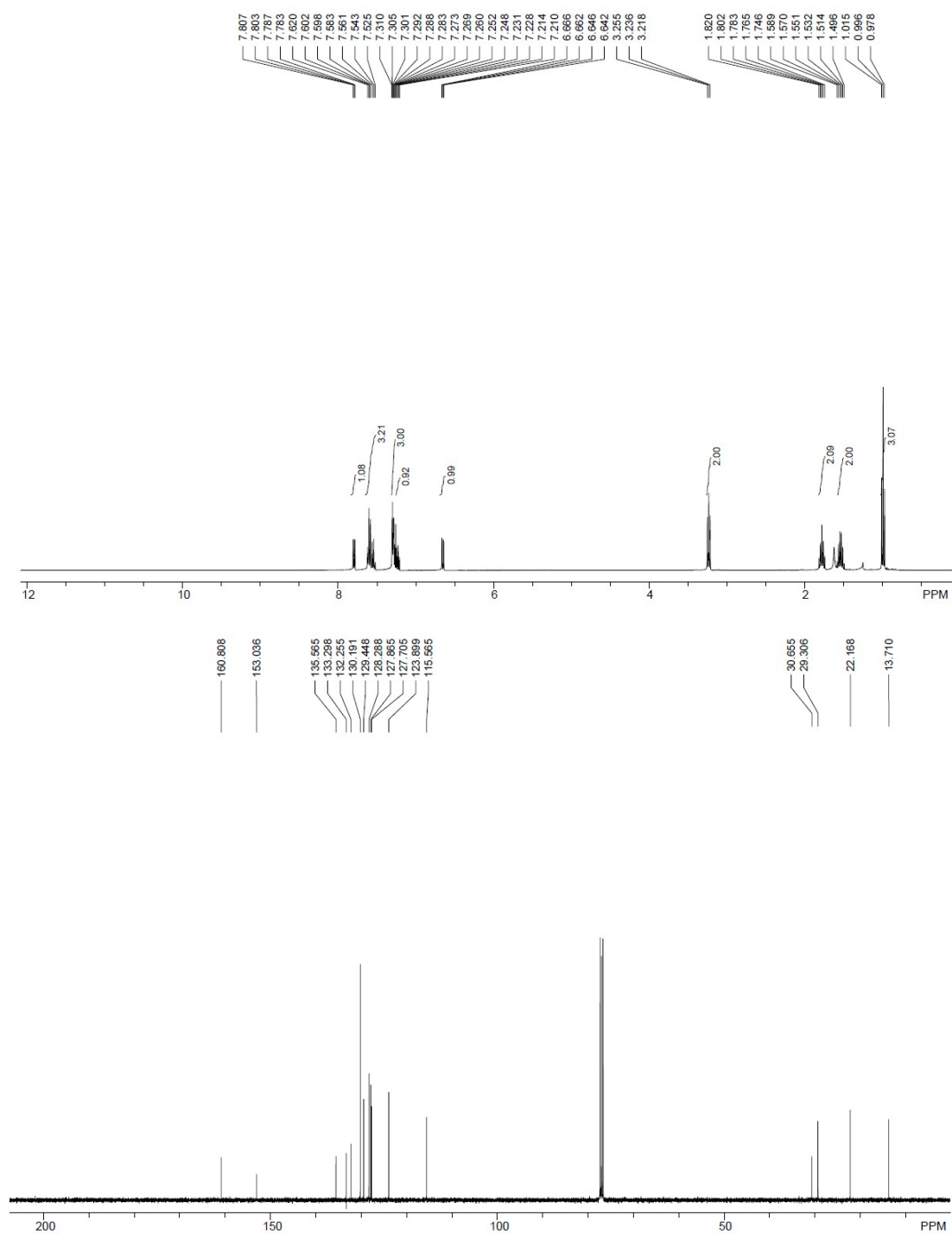
allyl-3-(butylthio)quinoxalin-2(1H)-one (3ha)



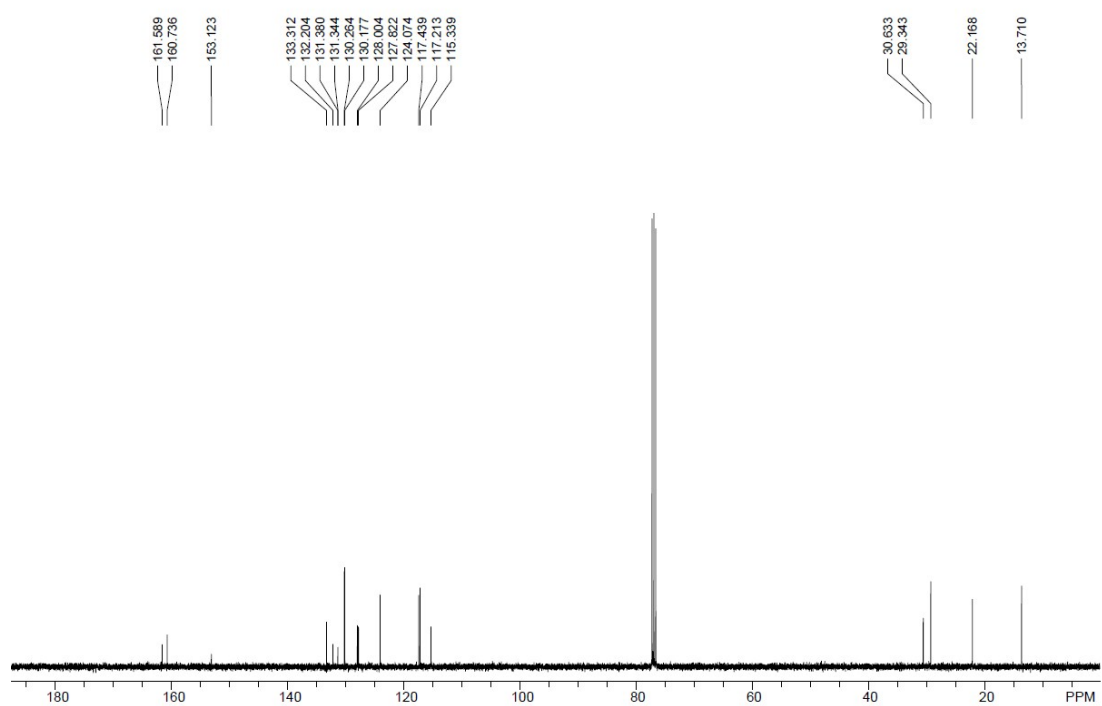
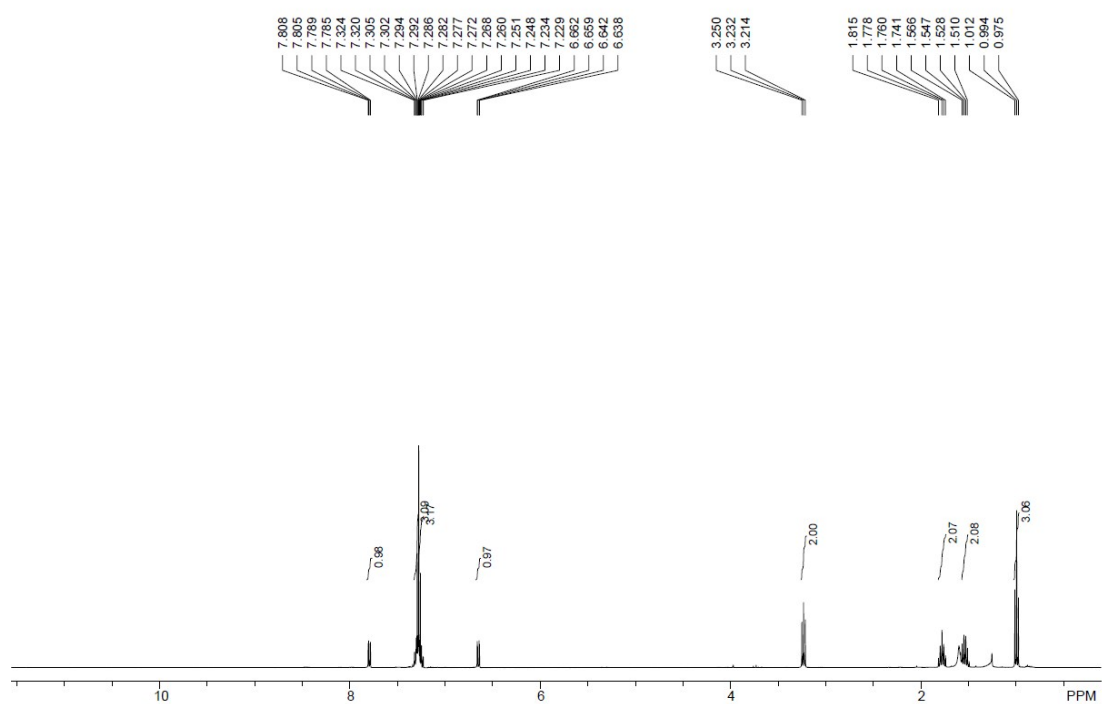
3-(butylthio)-1-(prop-2-yn-1-yl)quinoxalin-2(1H)-one (3ia)



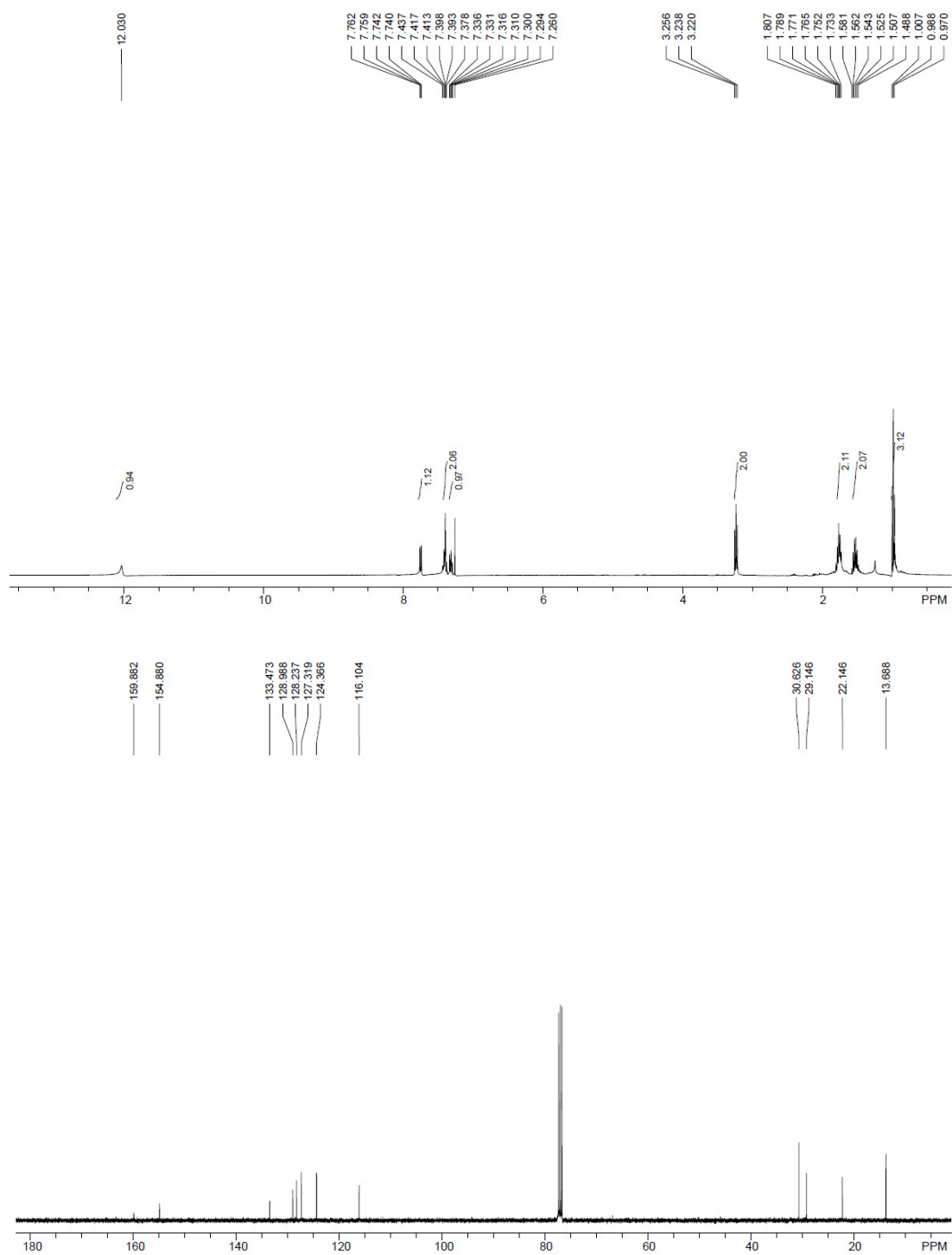
3-(butylthio)-1-phenylquinoxalin-2(1H)-one (3ja)



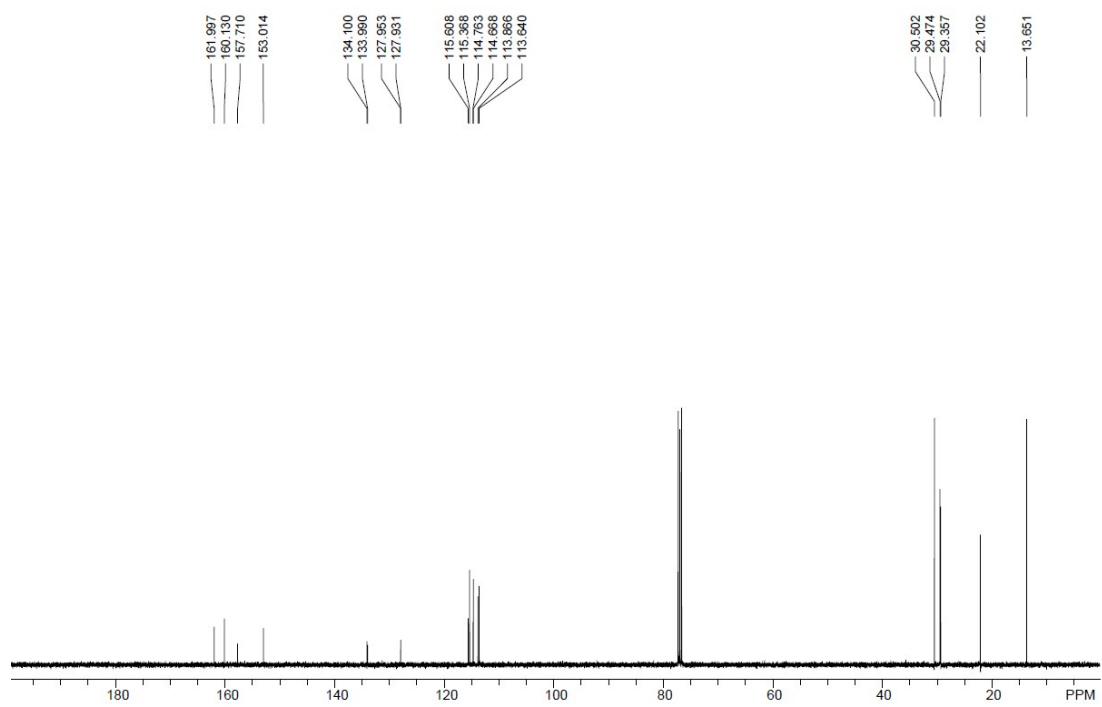
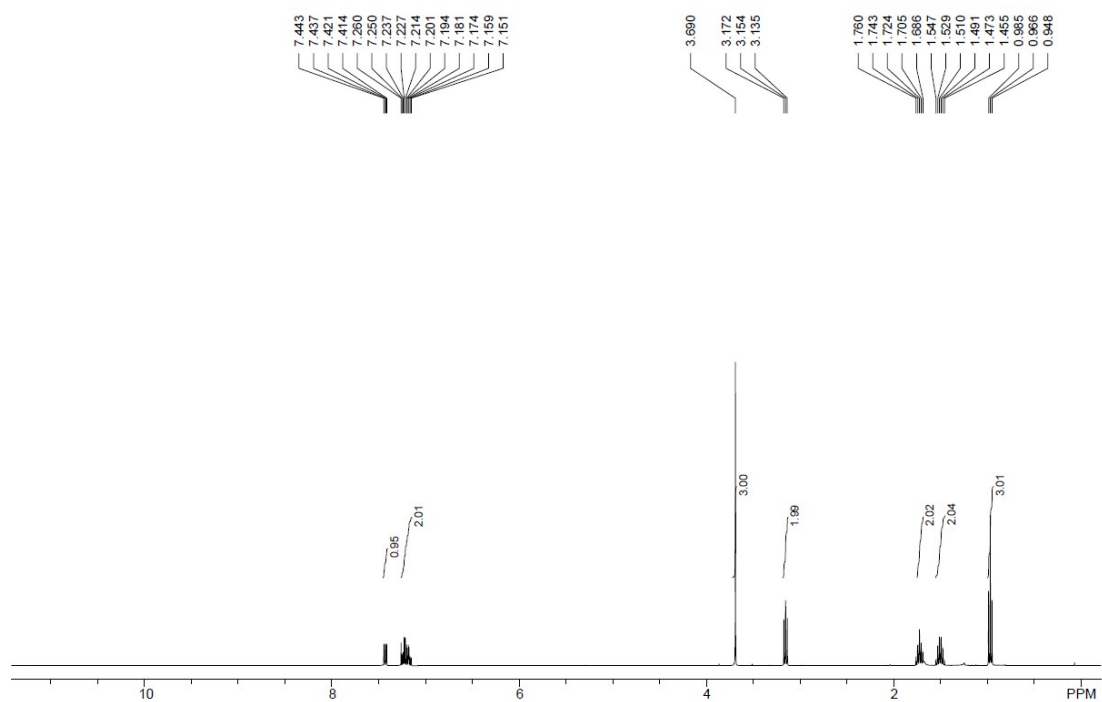
3-(butylthio)-1-(4-fluorophenyl)quinoxalin-2(1H)-one (3ka)



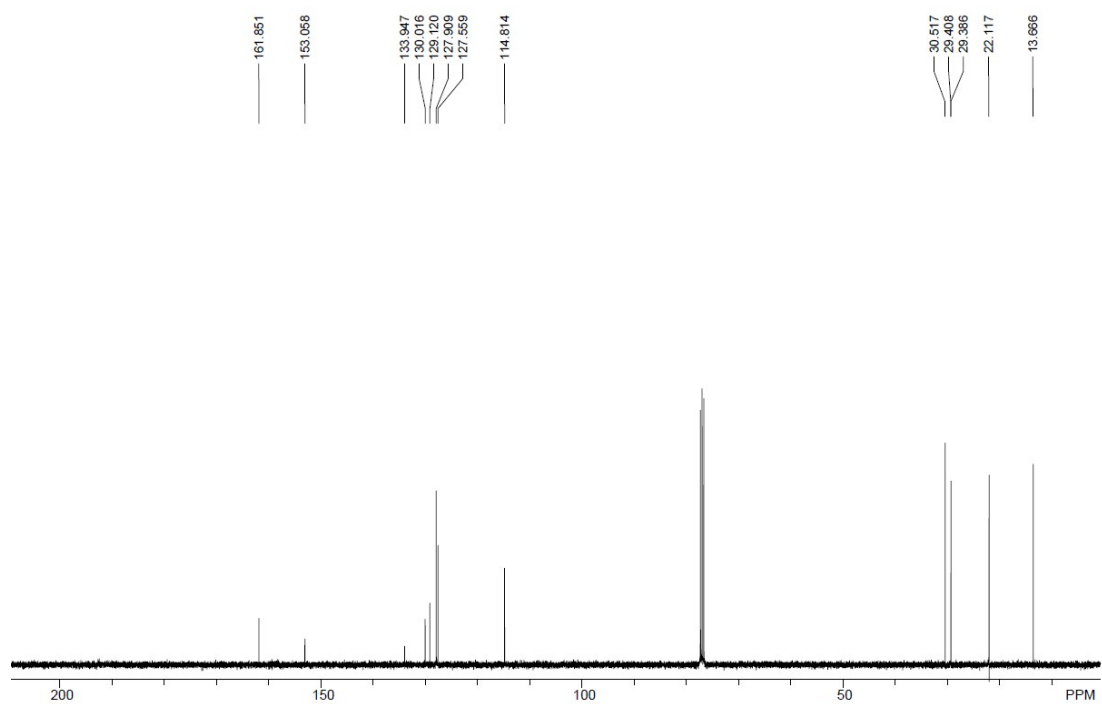
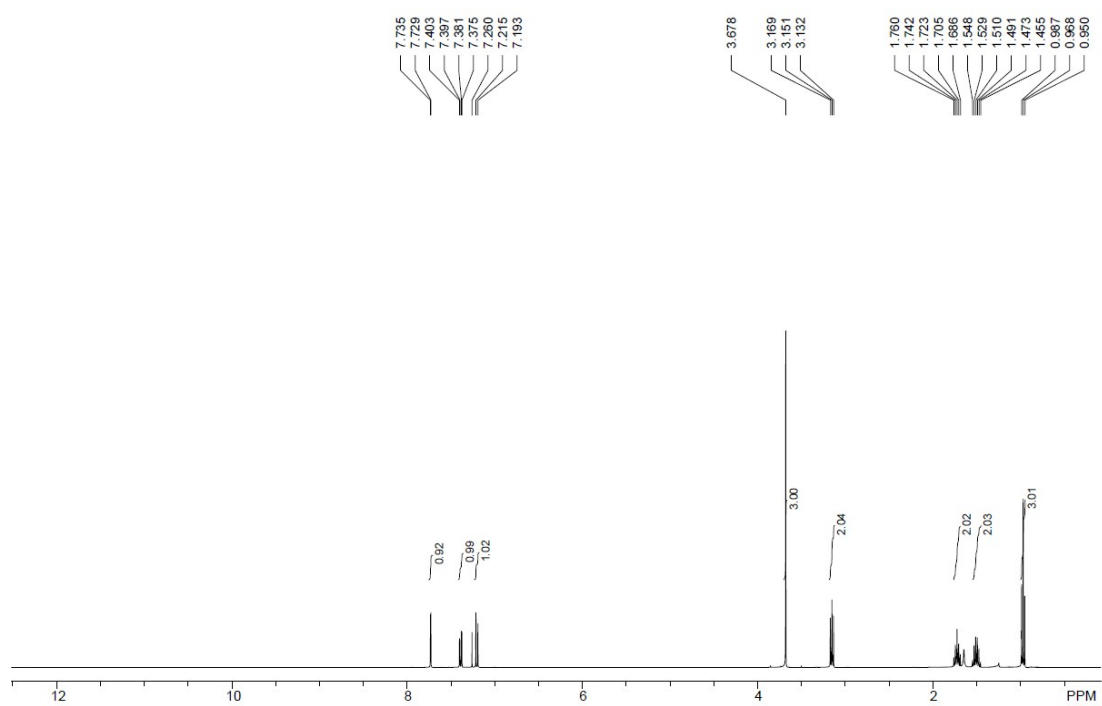
3-(butylthio)quinoxalin-2(1H)-one (31a)



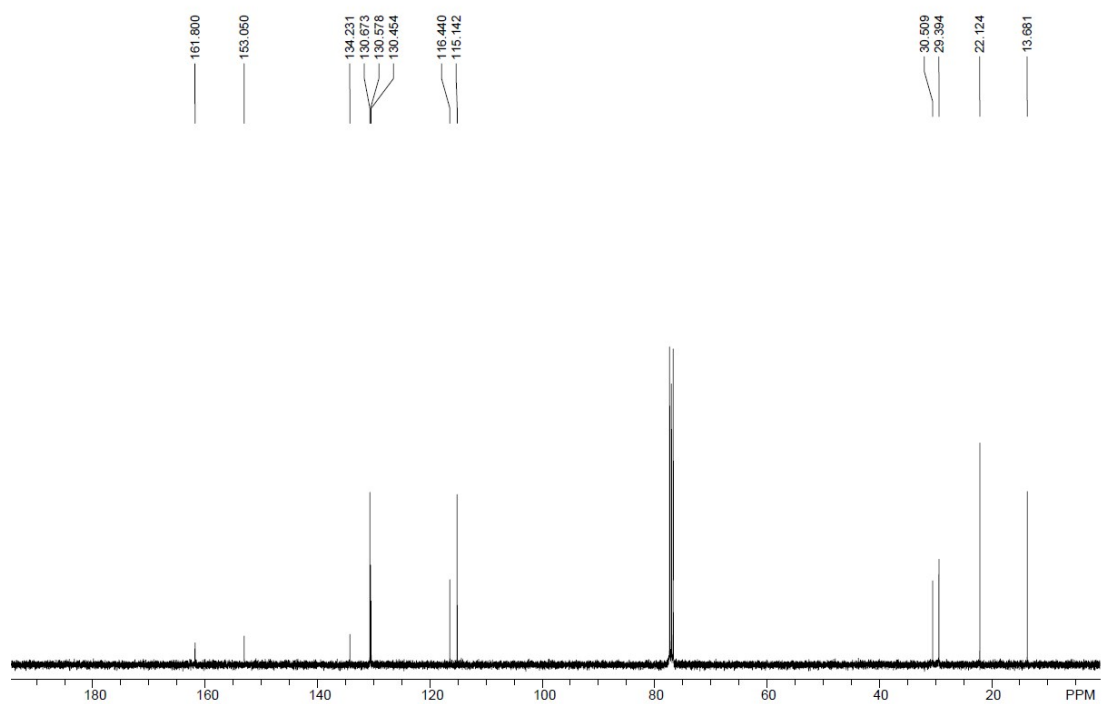
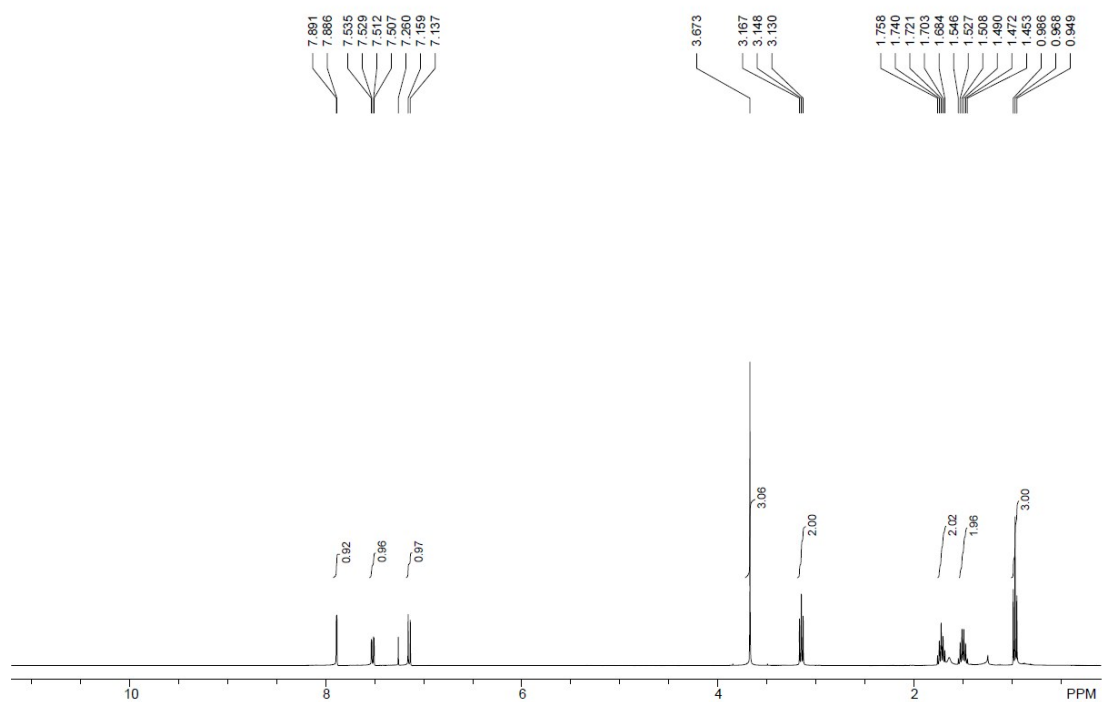
3-(butylthio)-6-fluoro-1-methylquinoxalin-2(1H)-one (3ma)



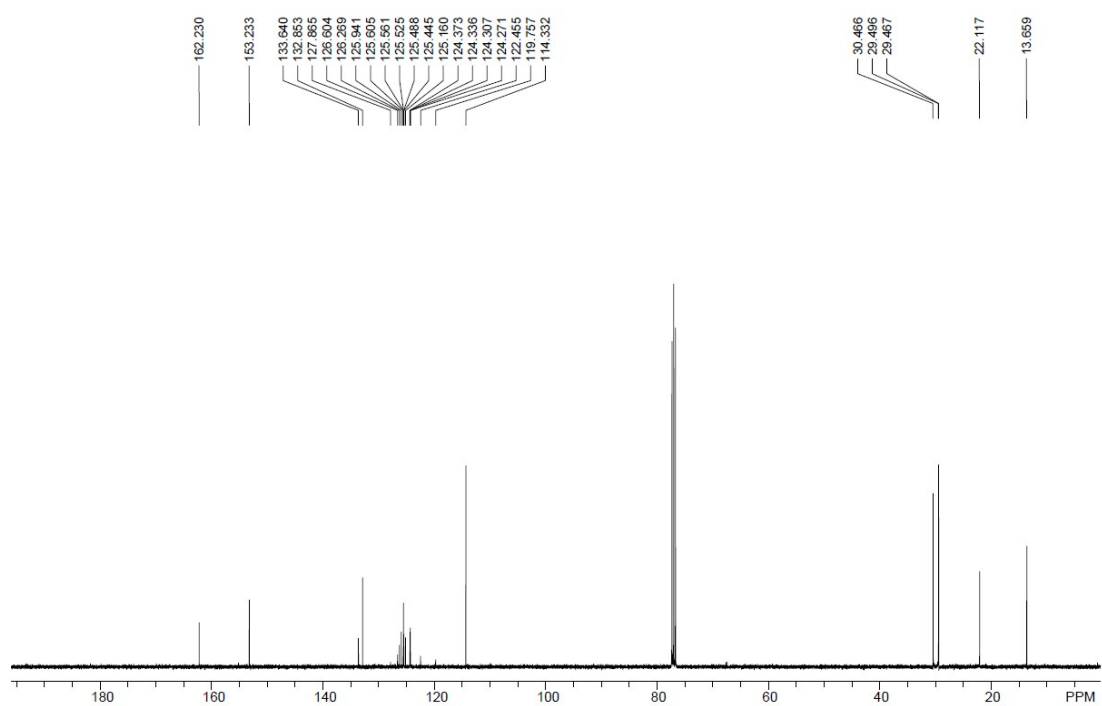
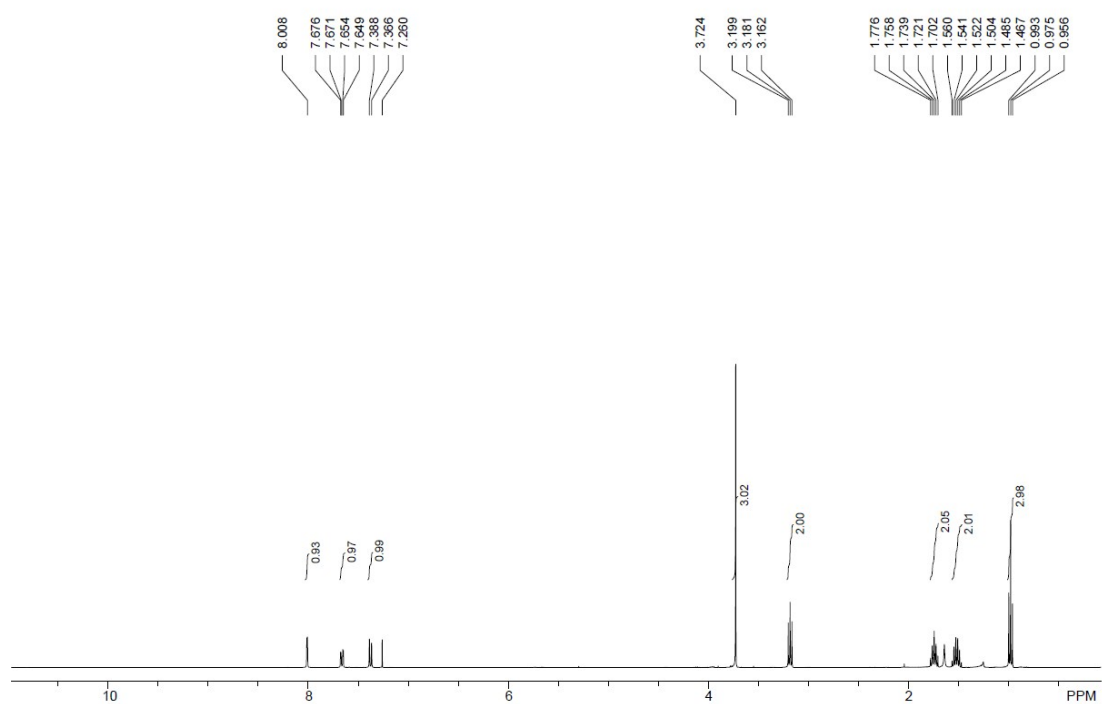
3-(butylthio)-6-chloro-1-methylquinoxalin-2(1H)-one (3na)



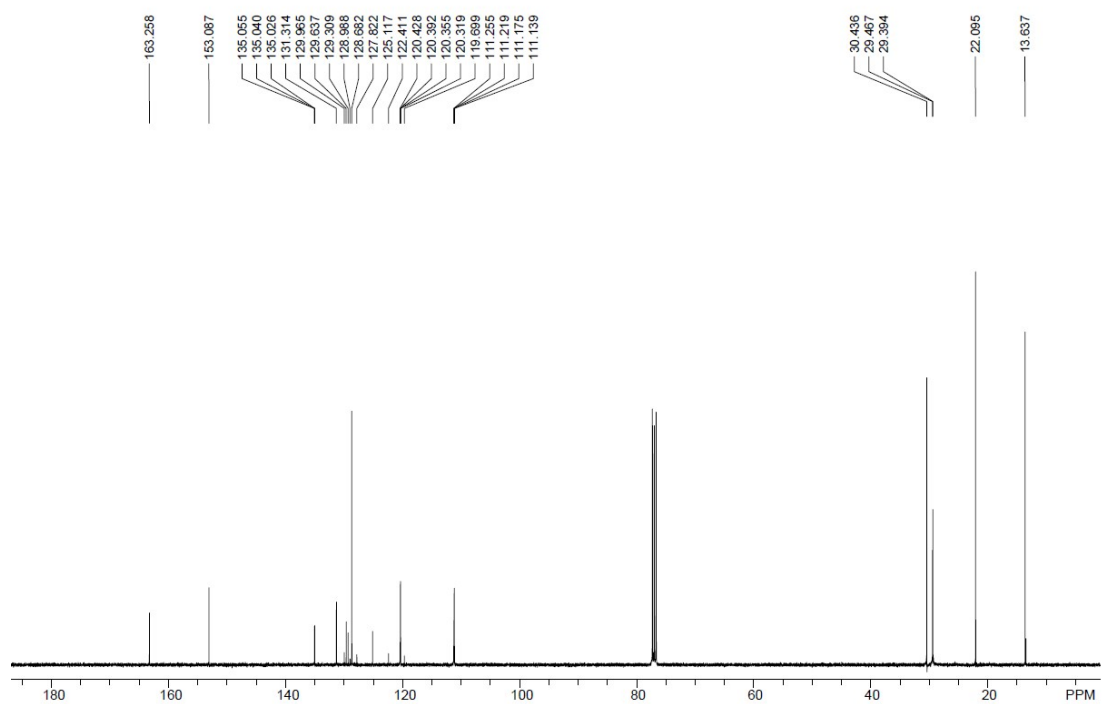
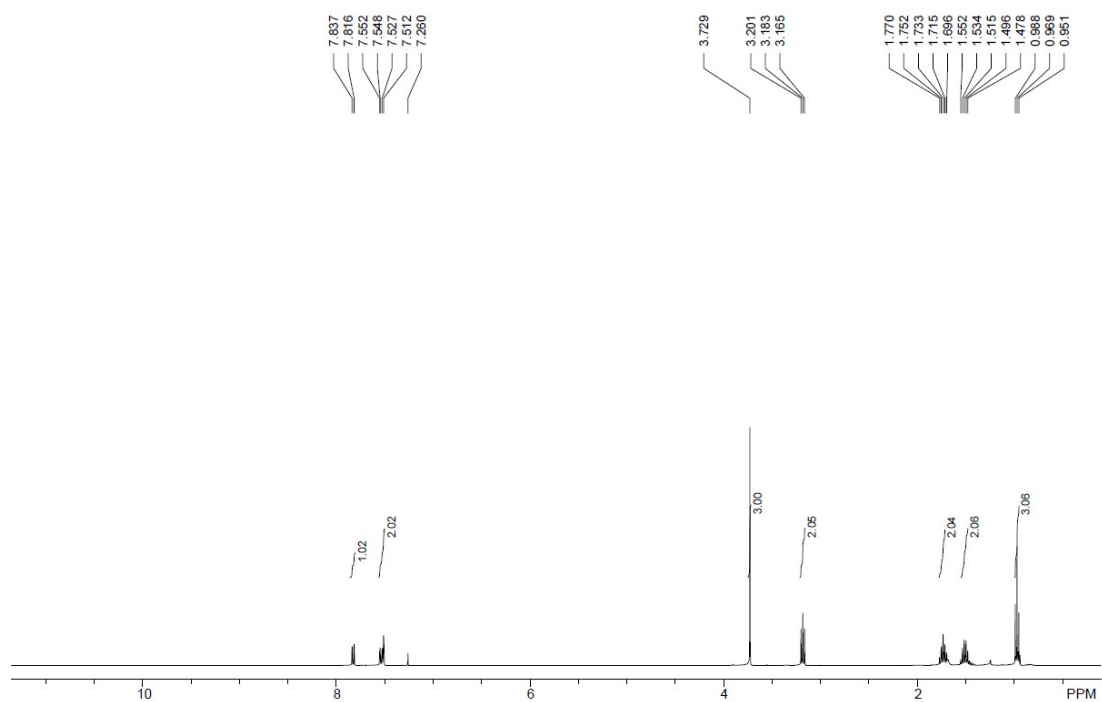
6-bromo-3-(butylthio)-1-methylquinoxalin-2(1H)-one (30a)



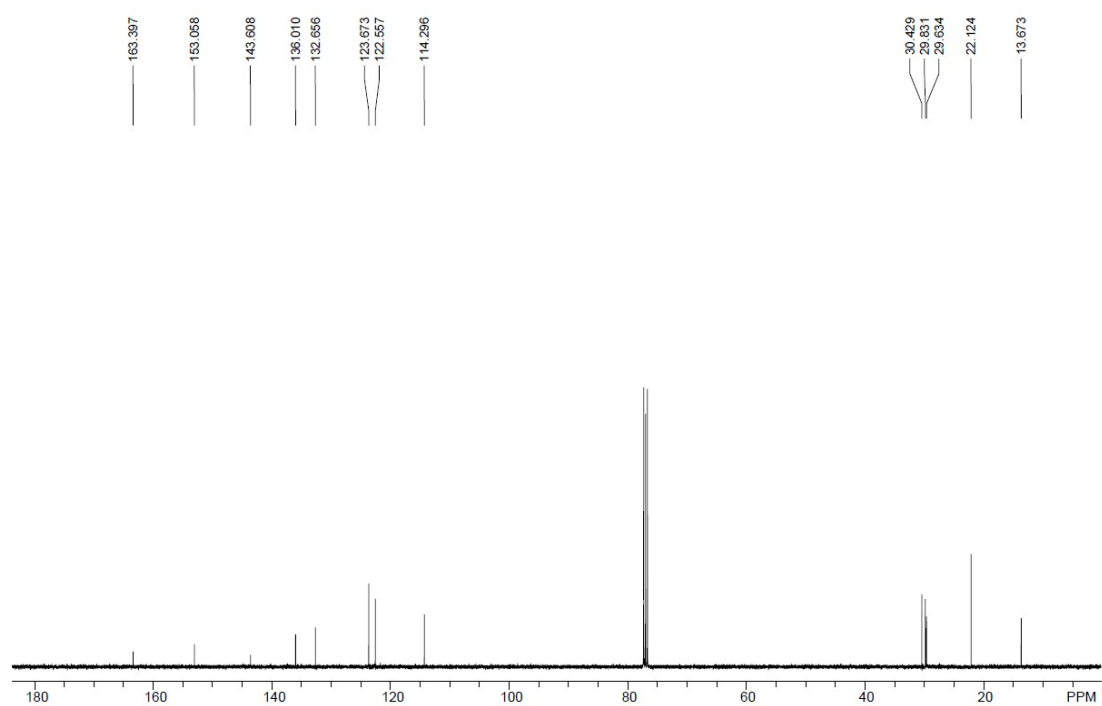
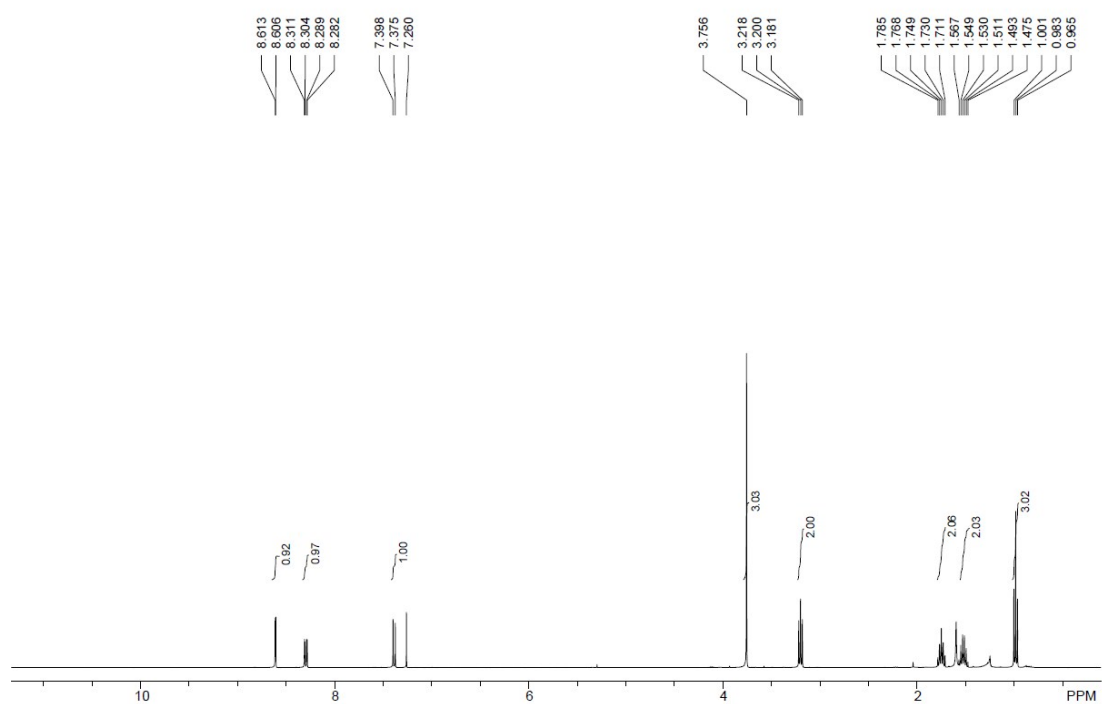
3-(butylthio)-1-methyl-6-(trifluoromethyl)quinoxalin-2(1H)-one (3pa)



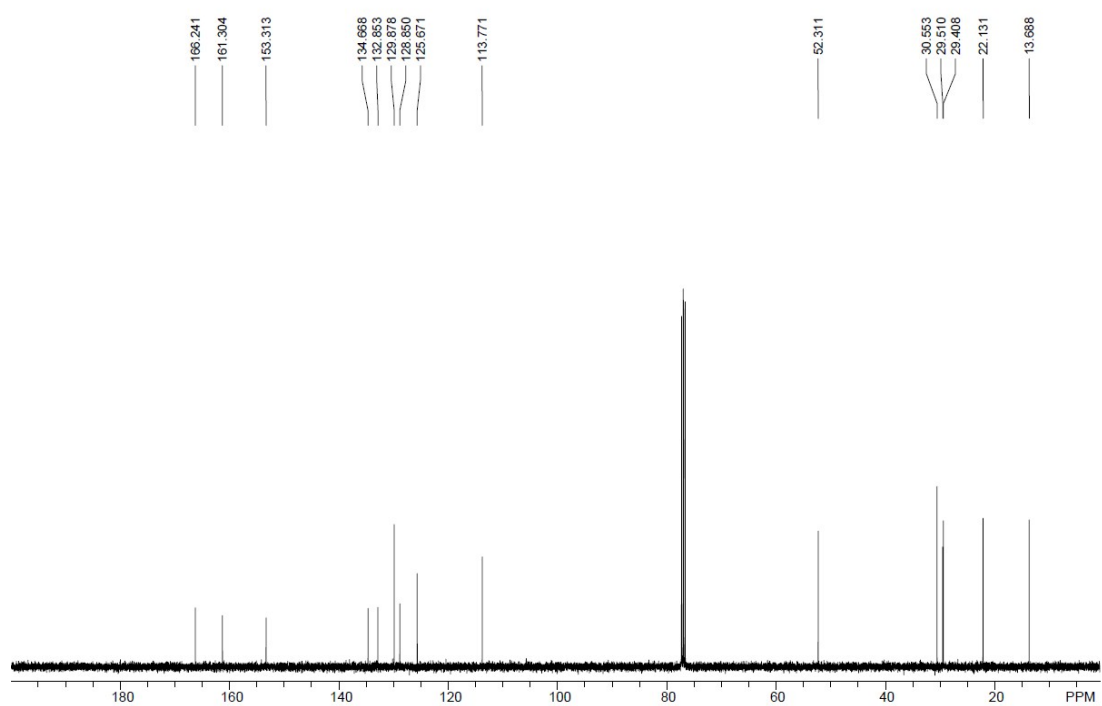
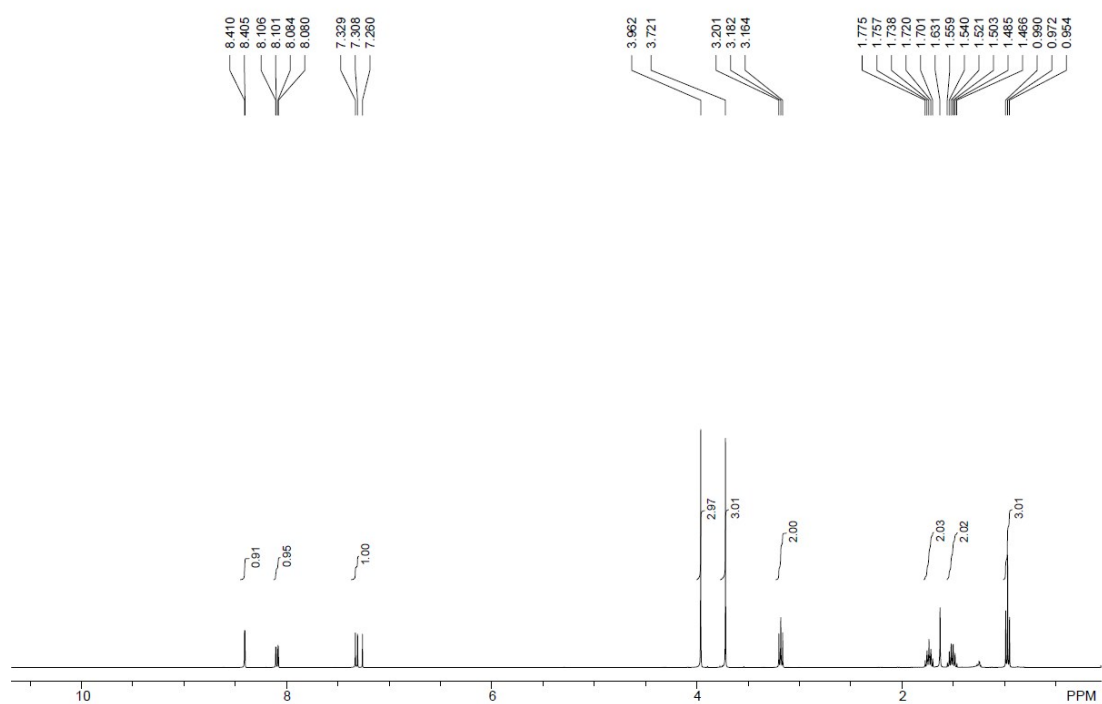
3-(butylthio)-1-methyl-7-(trifluoromethyl)quinoxalin-2(1H)-one (3qa)



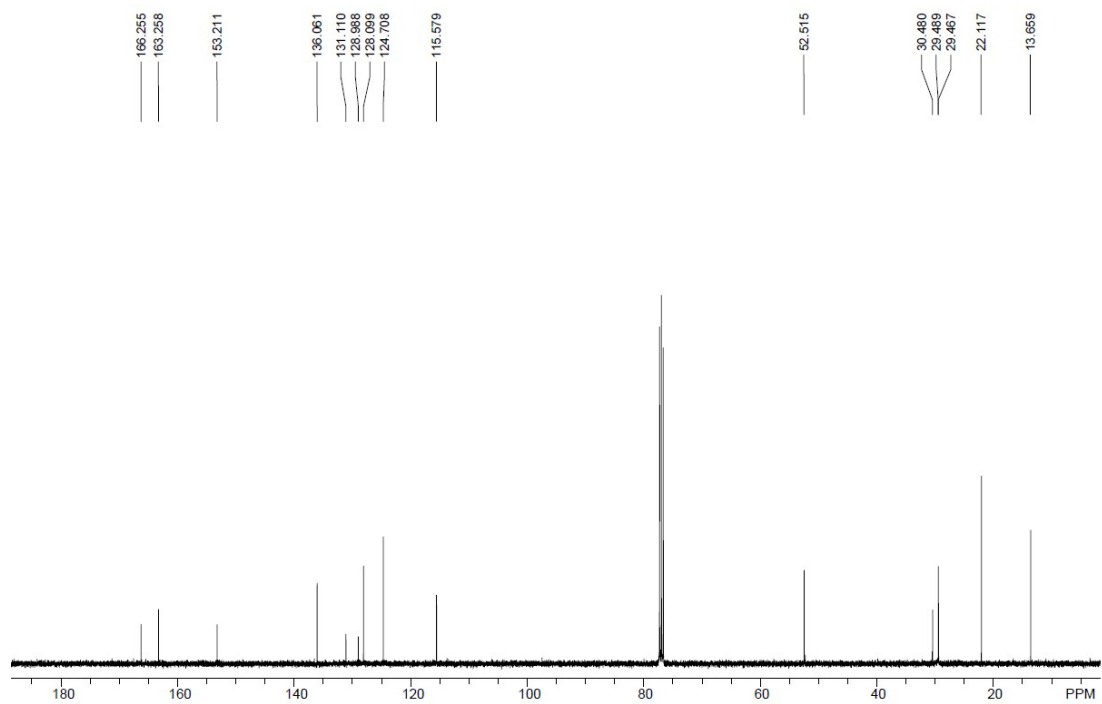
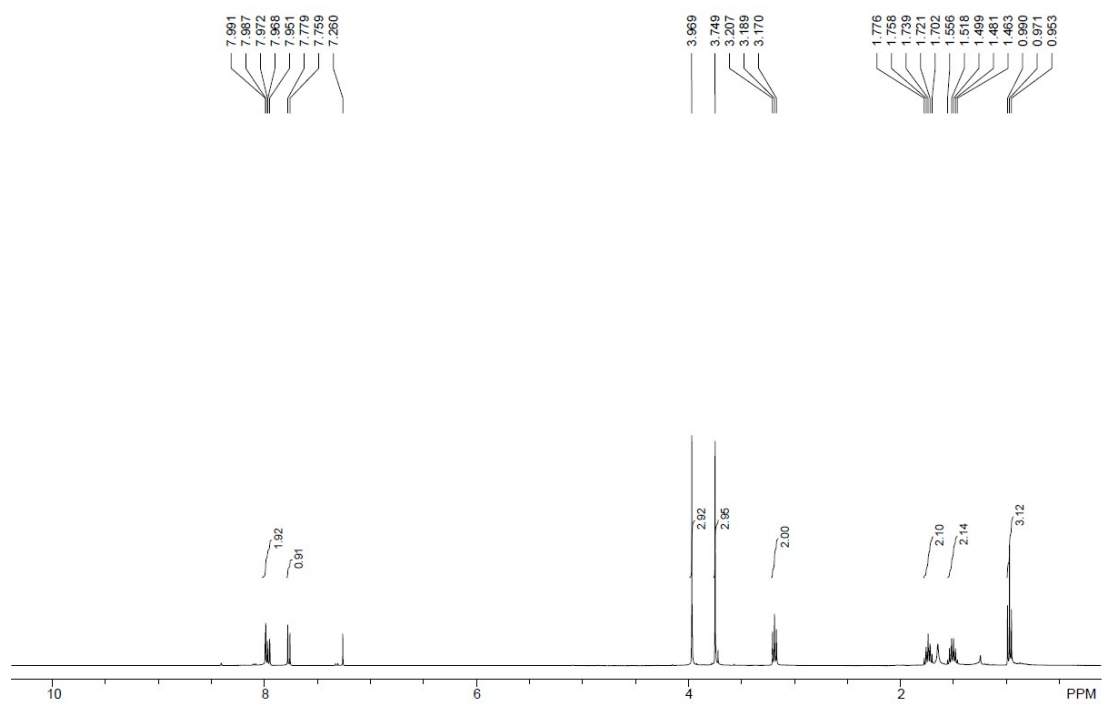
3-(butylthio)-1-methyl-6-nitroquinoxalin-2(1H)-one (3ra)



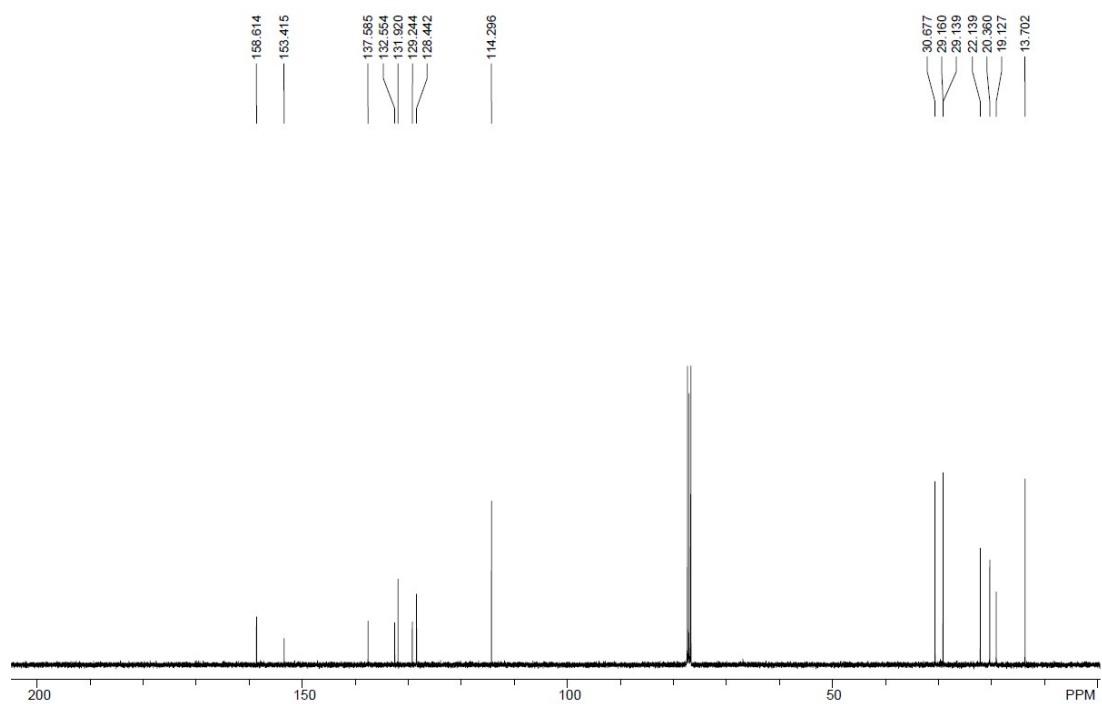
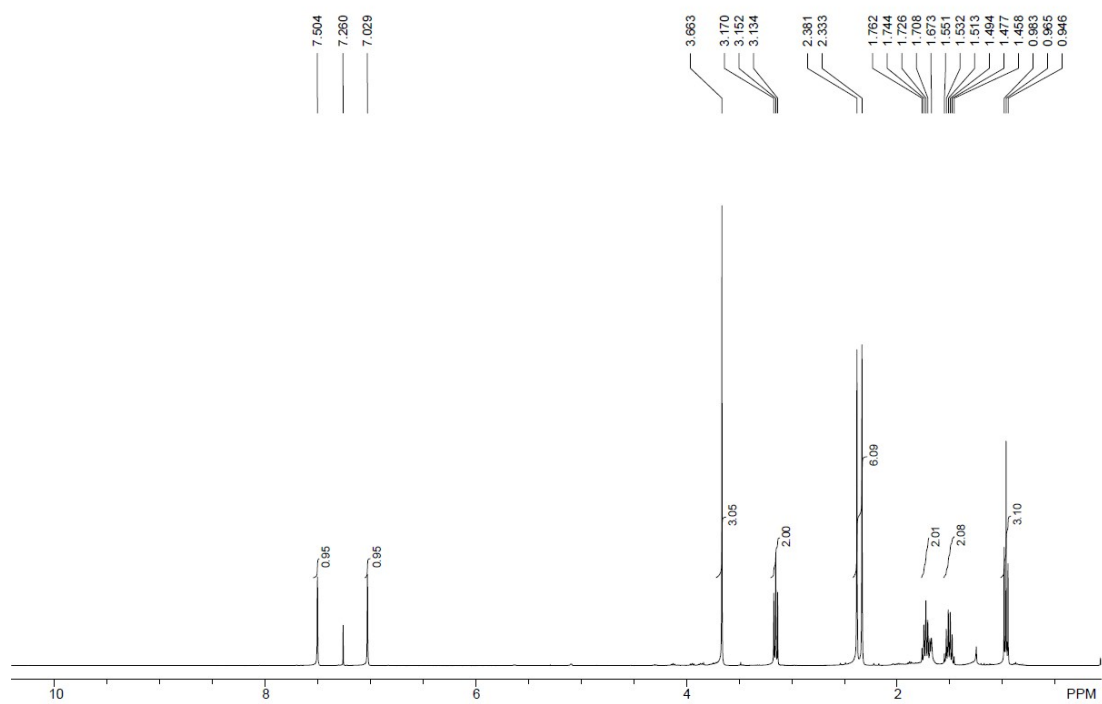
methyl 3-(butylthio)-1-methyl-2-oxo-1,2-dihydroquinoxaline-6-carboxylate (3sa)



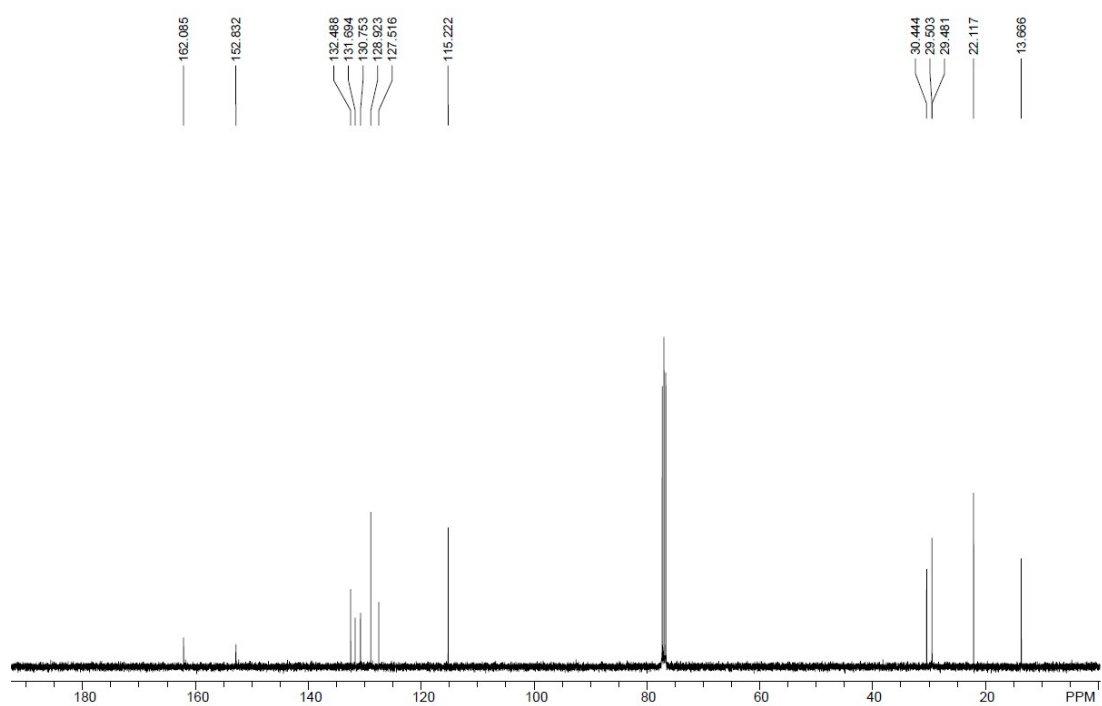
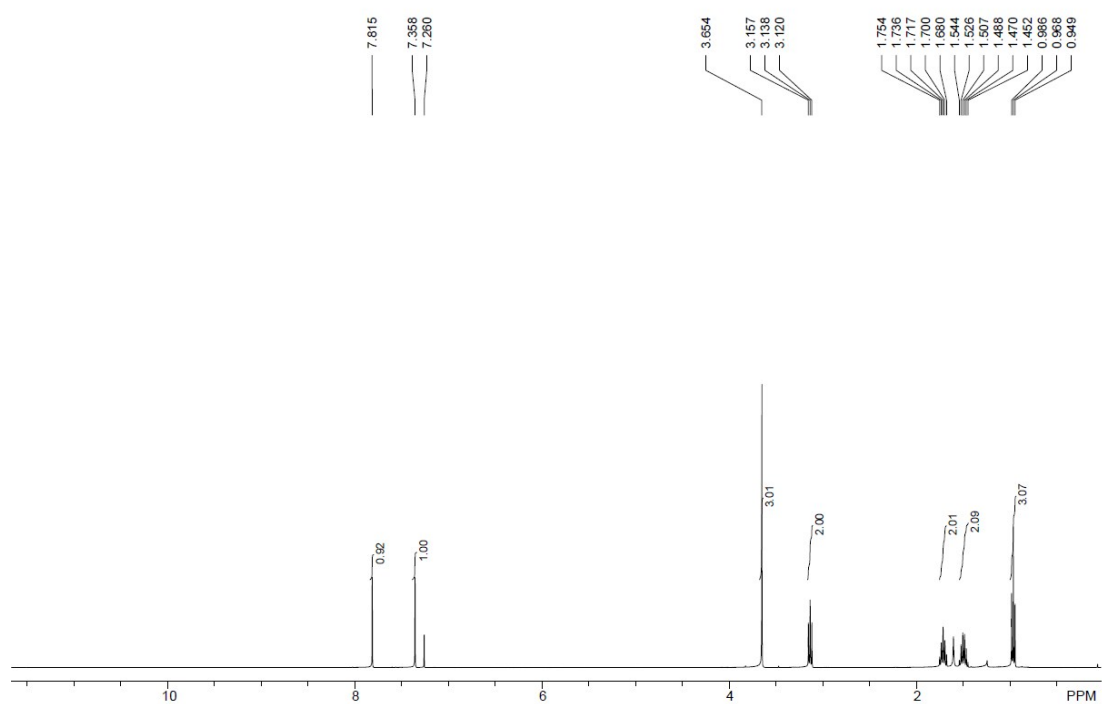
methyl 2-(butylthio)-4-methyl-3-oxo-3,4-dihydroquinoxaline-6-carboxylate (3ta)



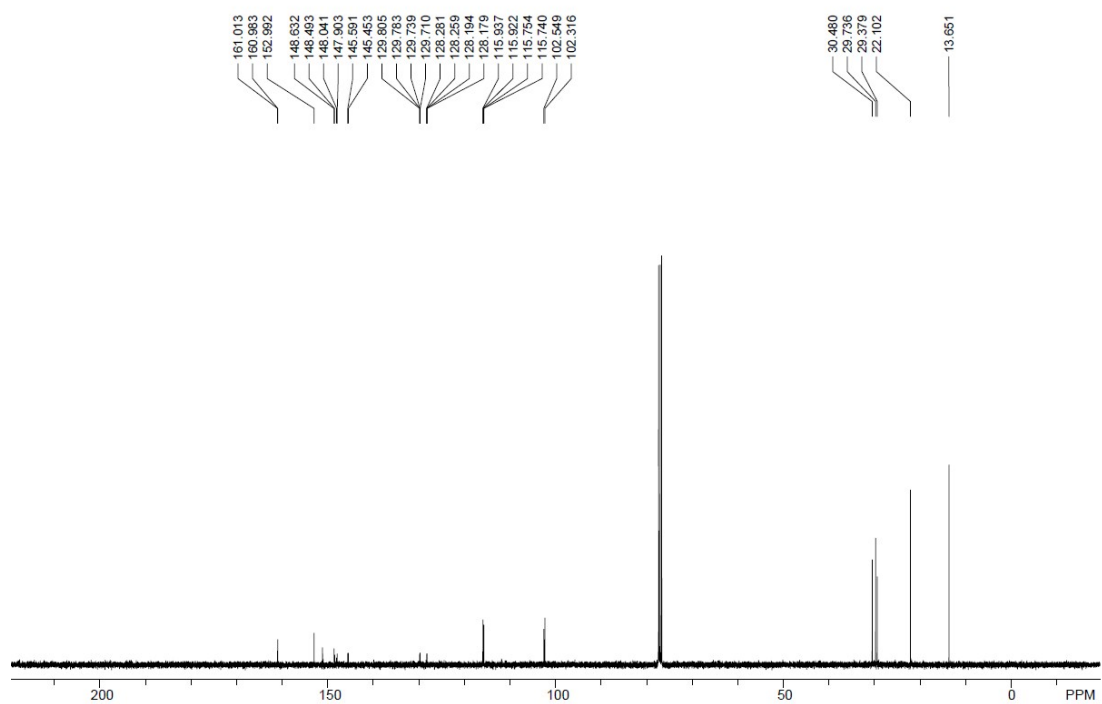
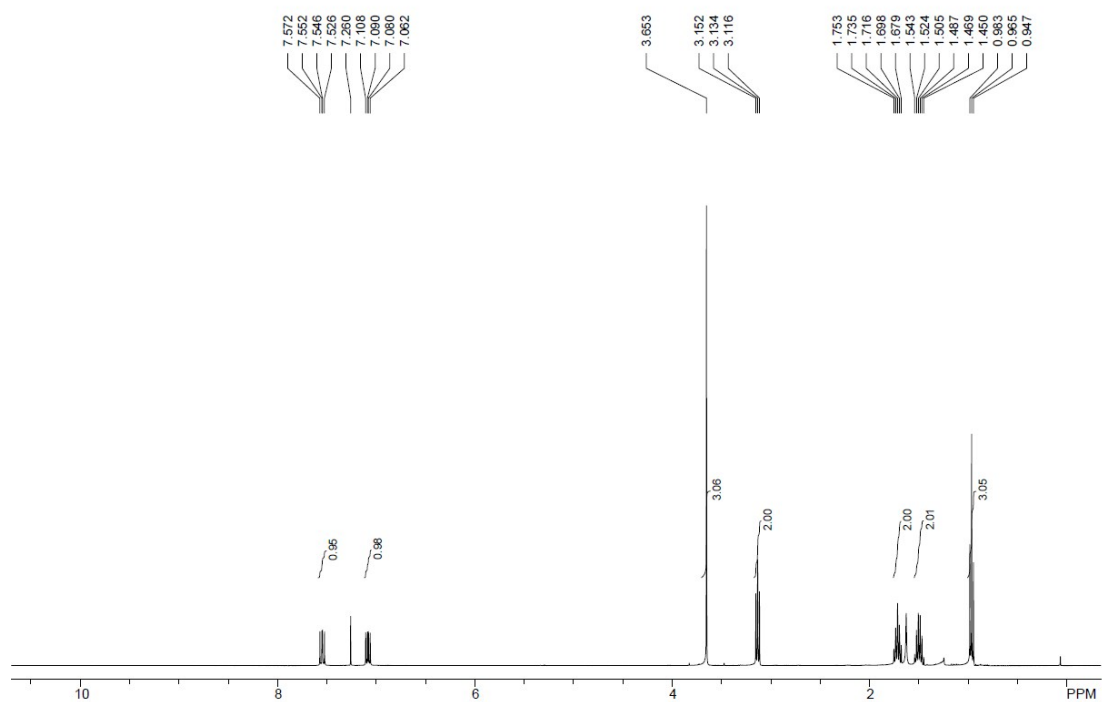
3-(butylthio)-1,6,7-trimethylquinoxalin-2(1H)-one (3ua)



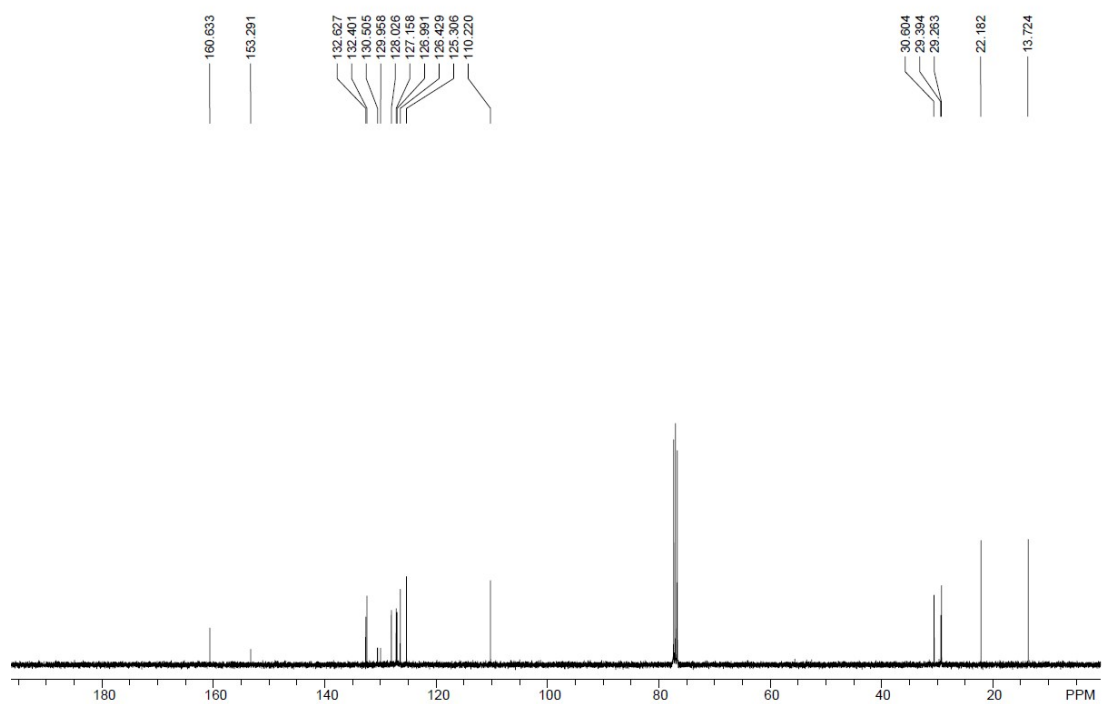
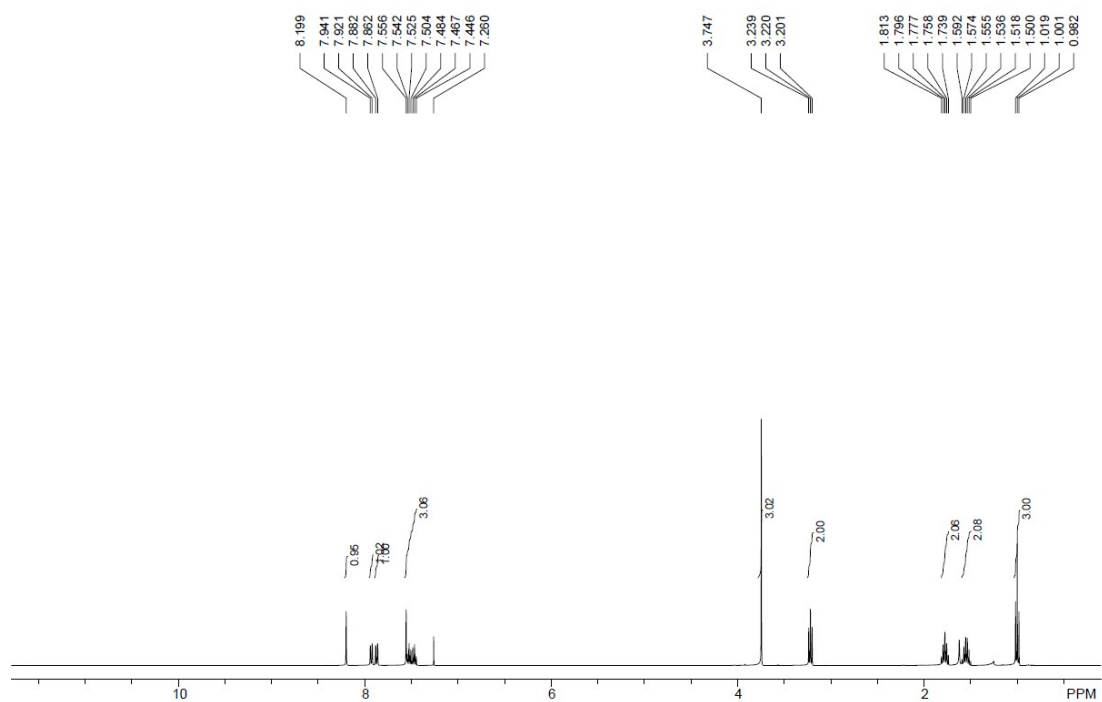
3-(butylthio)-6,7-dichloro-1-methylquinoxalin-2(1H)-one (3va)



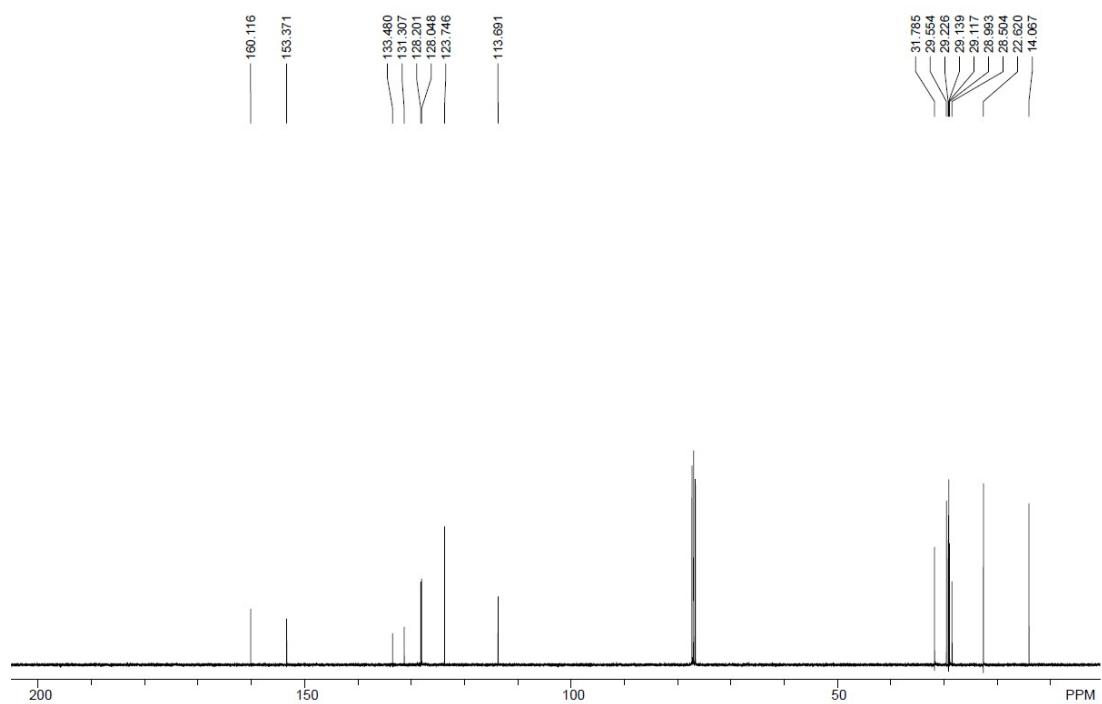
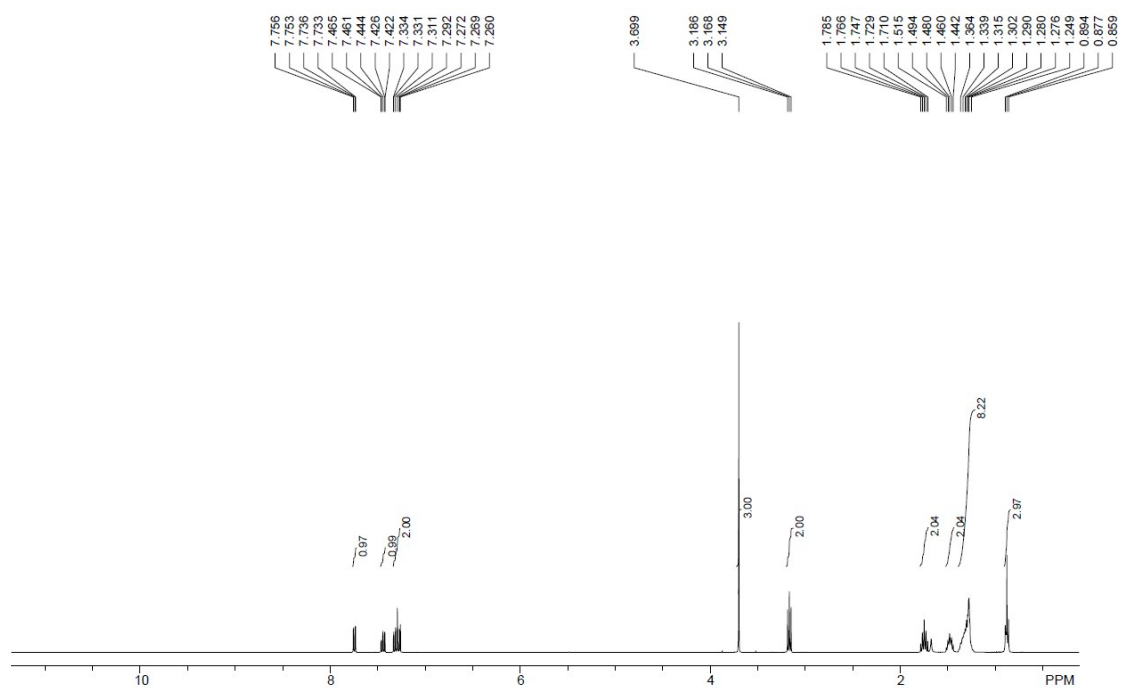
3-(butylthio)-6,7-difluoro-1-methylquinoxalin-2(1H)-one (3wa)



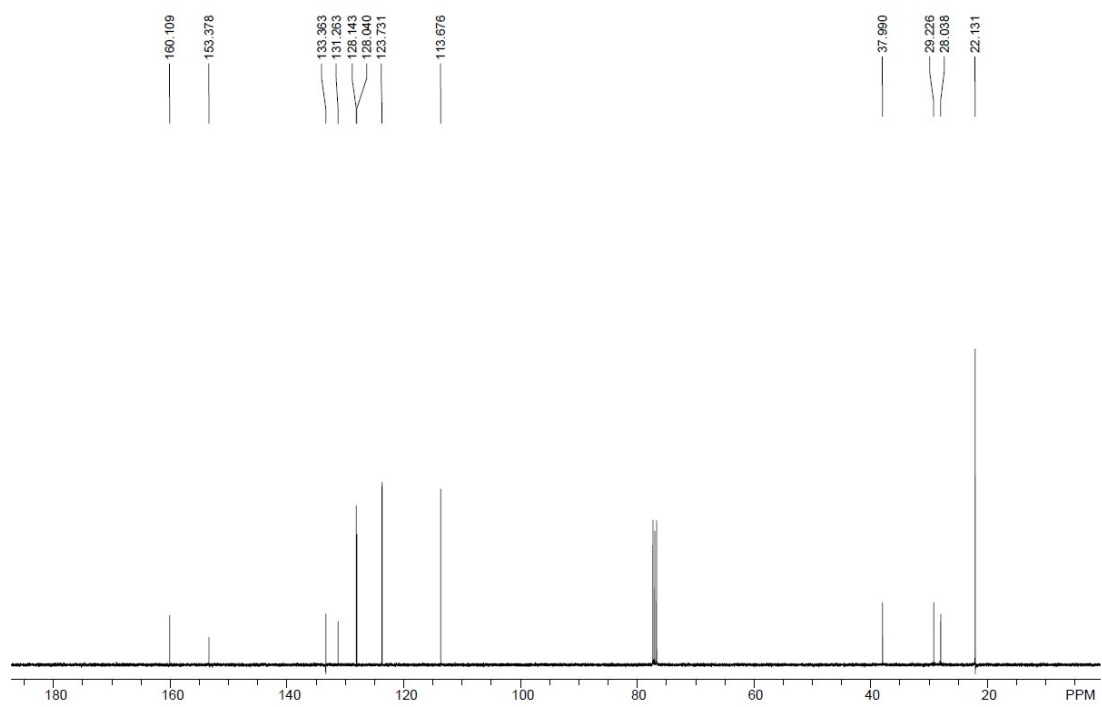
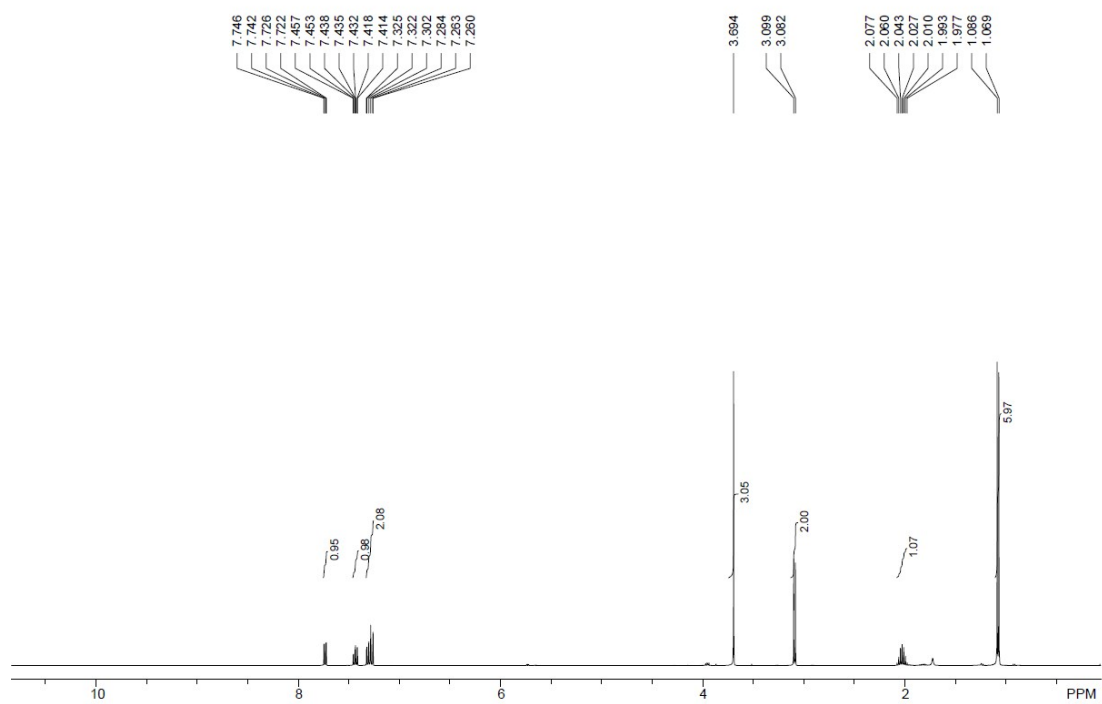
3-(butylthio)-1-methylbenzo[g]quinoxalin-2(1H)-one (3xa)



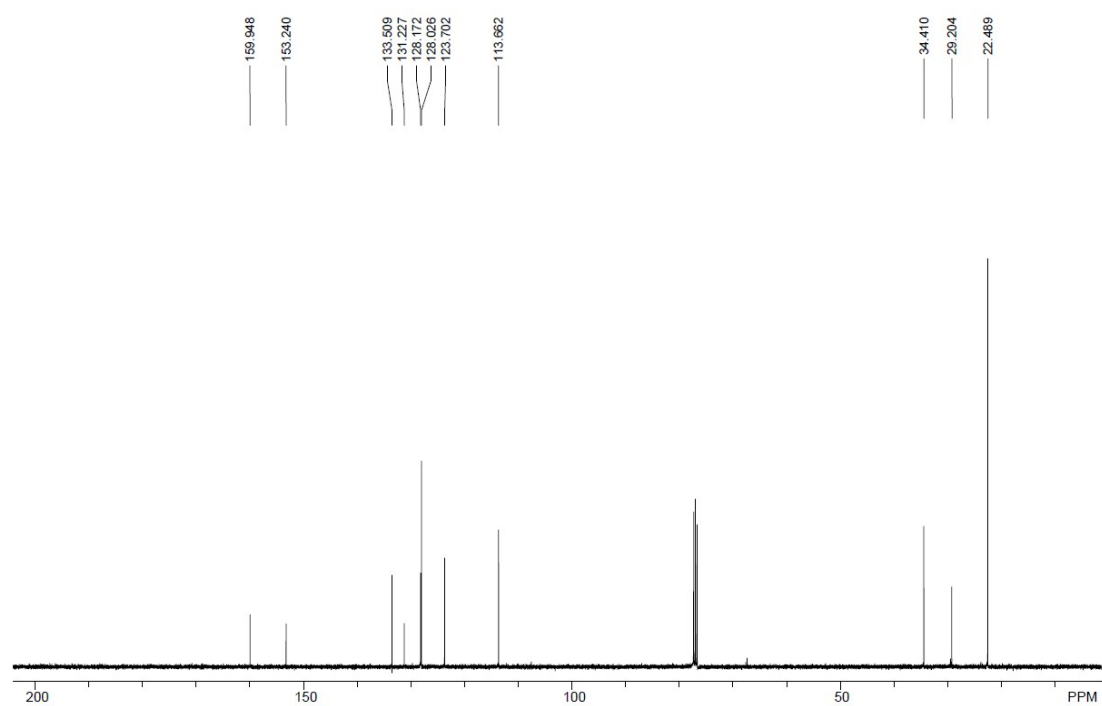
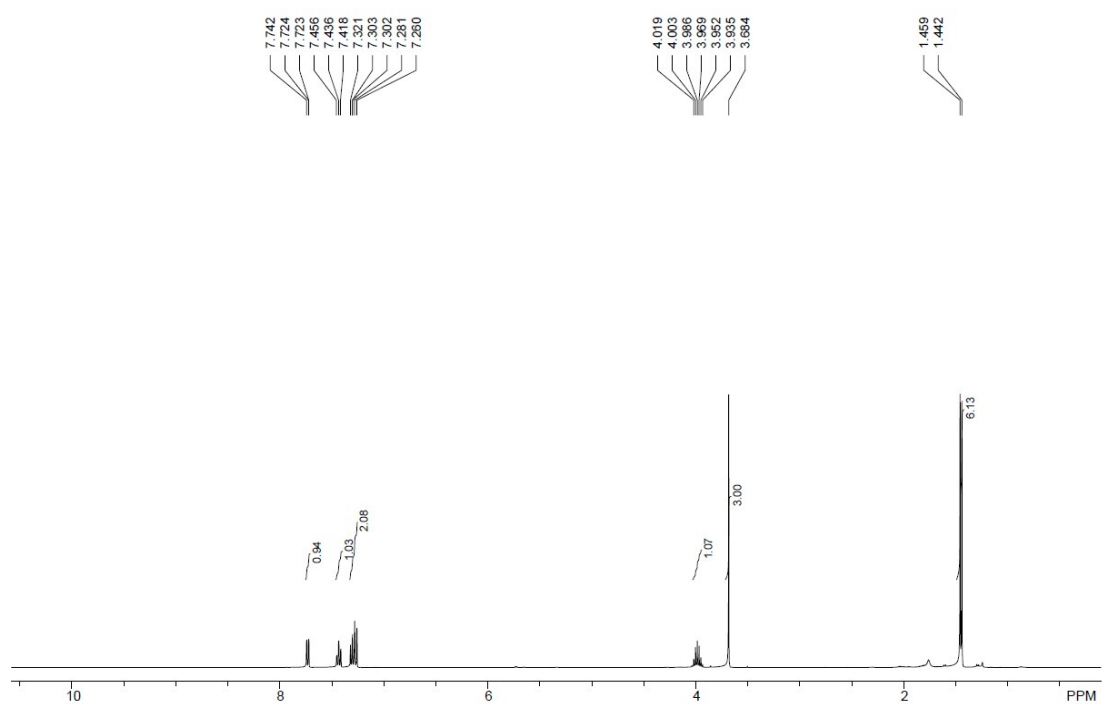
methyl-3-(octylthio)quinoxalin-2(1H)-one (3ab)



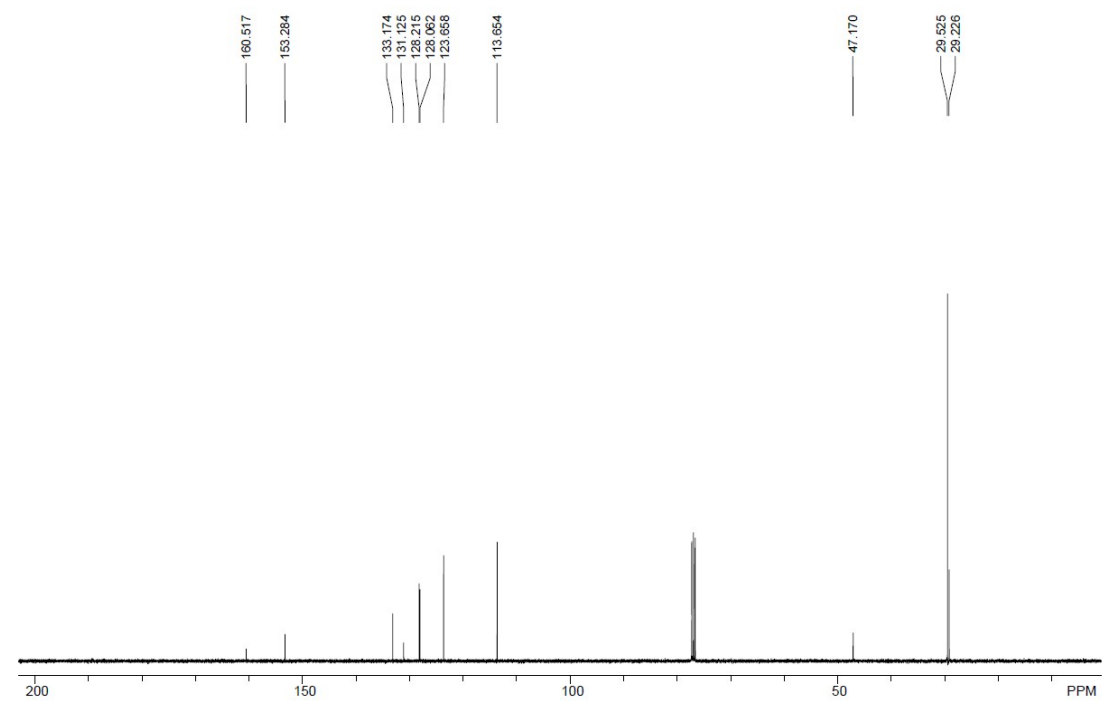
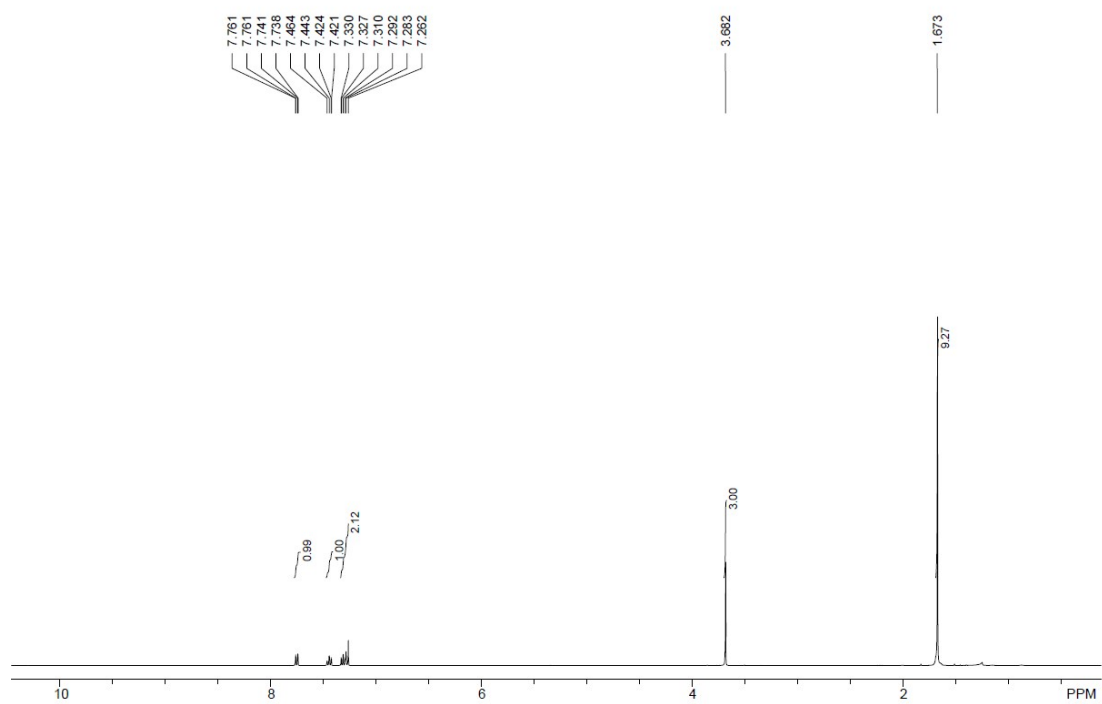
3-(isobutylthio)-1-methylquinoxalin-2(1H)-one (3ac)



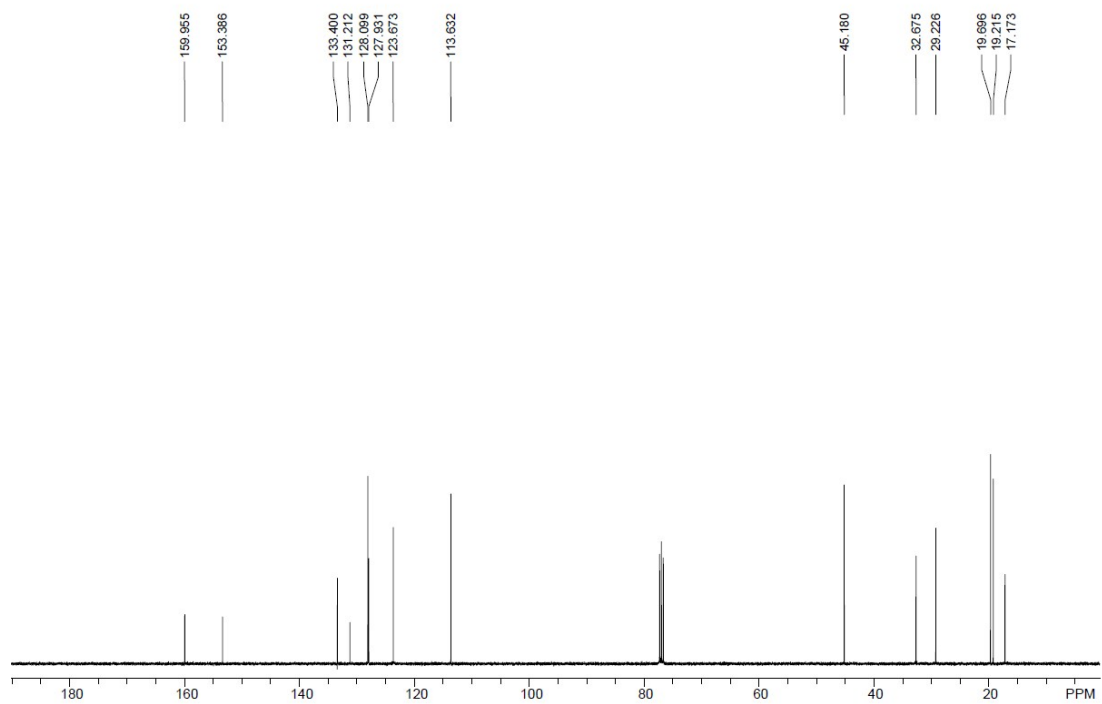
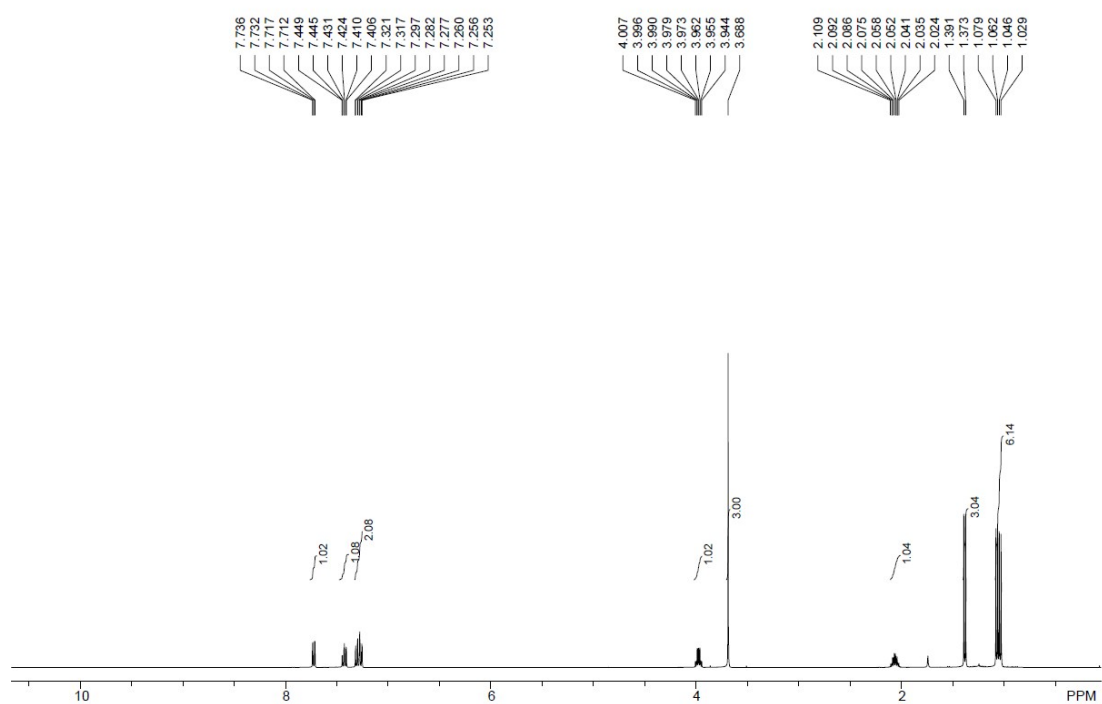
3-(isopropylthio)-1-methylquinoxalin-2(1H)-one (3ad)



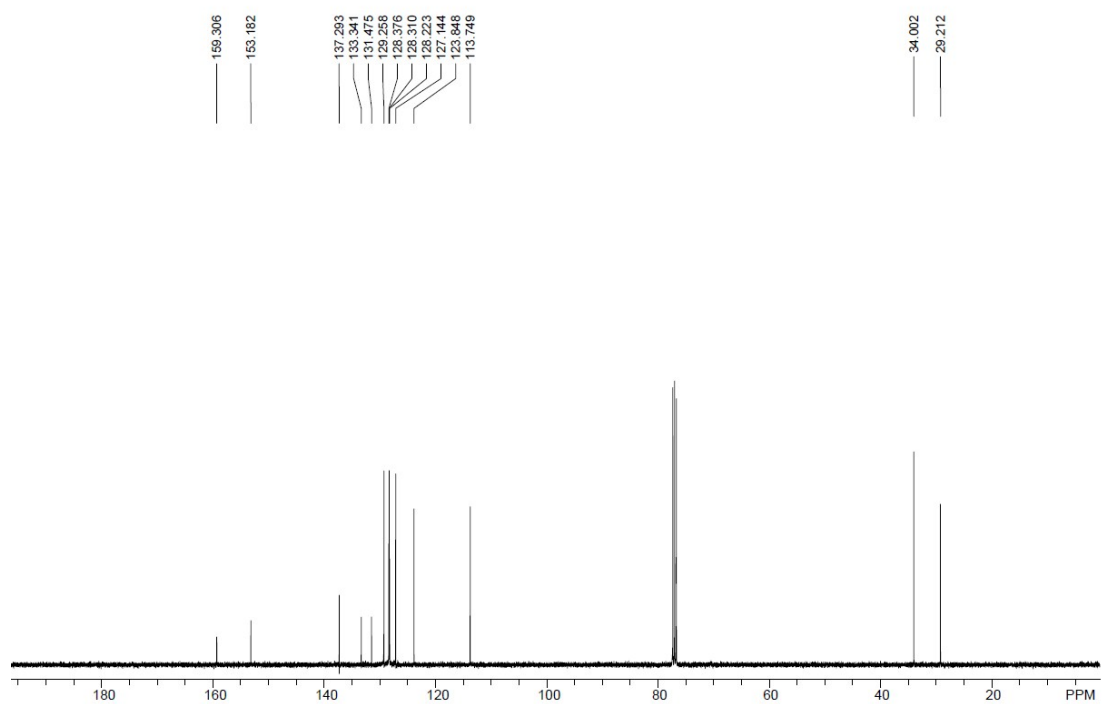
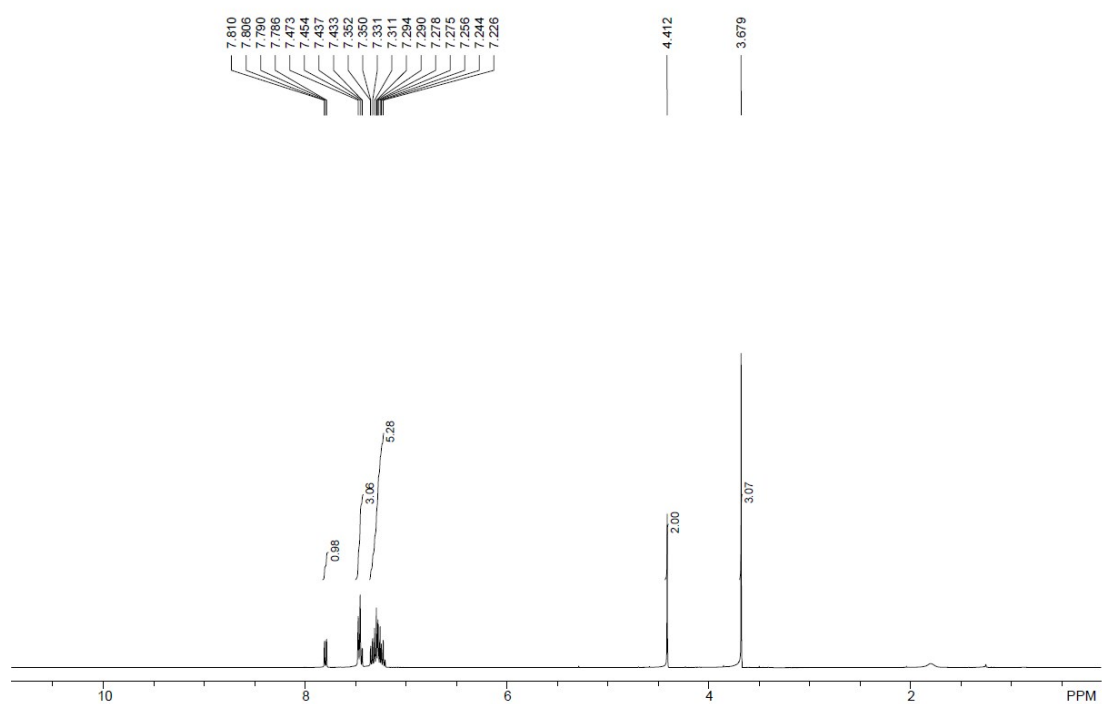
3-(tert-butylthio)-1-methylquinoxalin-2(1H)-one (3ae)



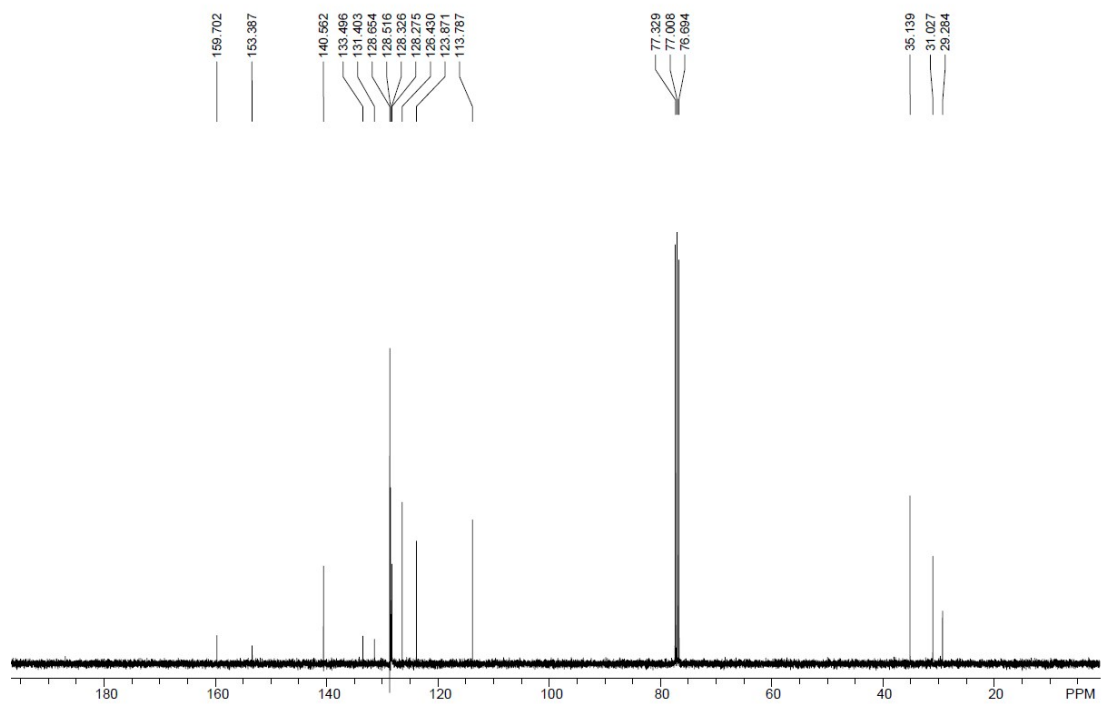
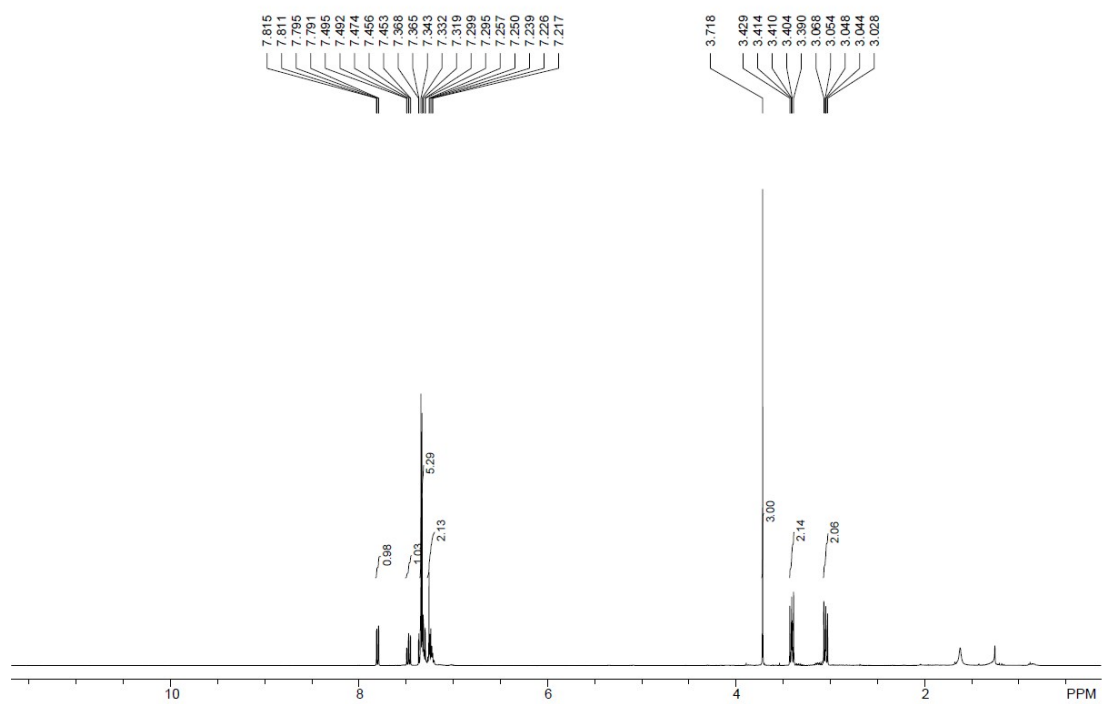
methyl-3-((3-methylbutan-2-yl)thio)quinoxalin-2(1H)-one (3af)



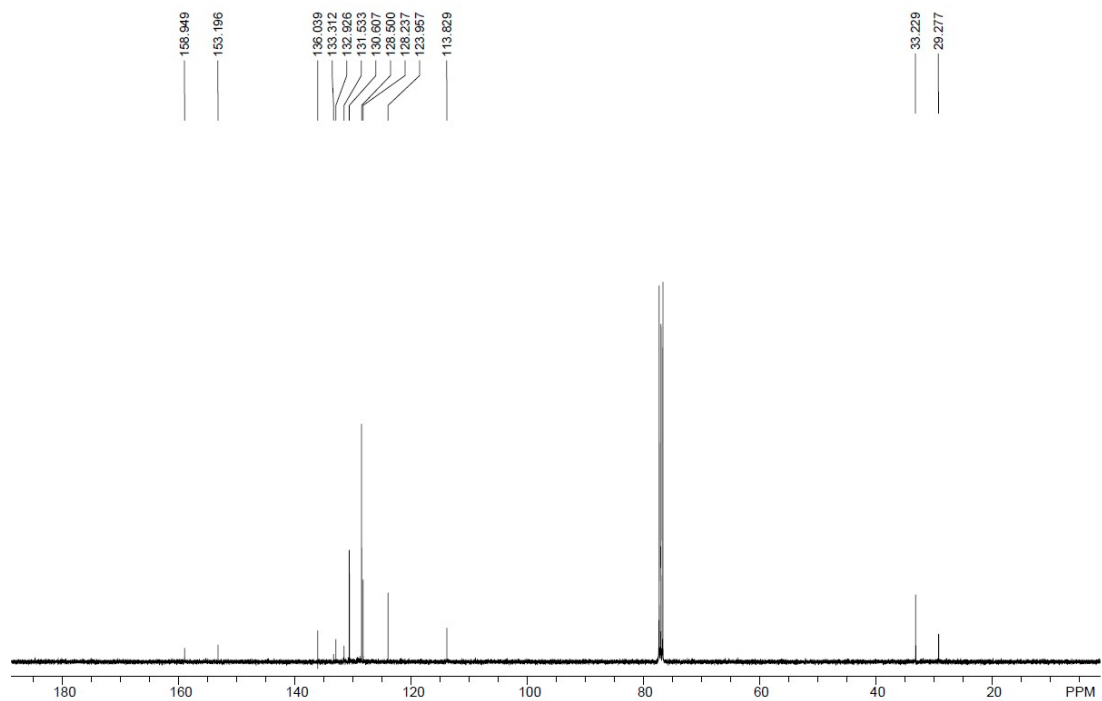
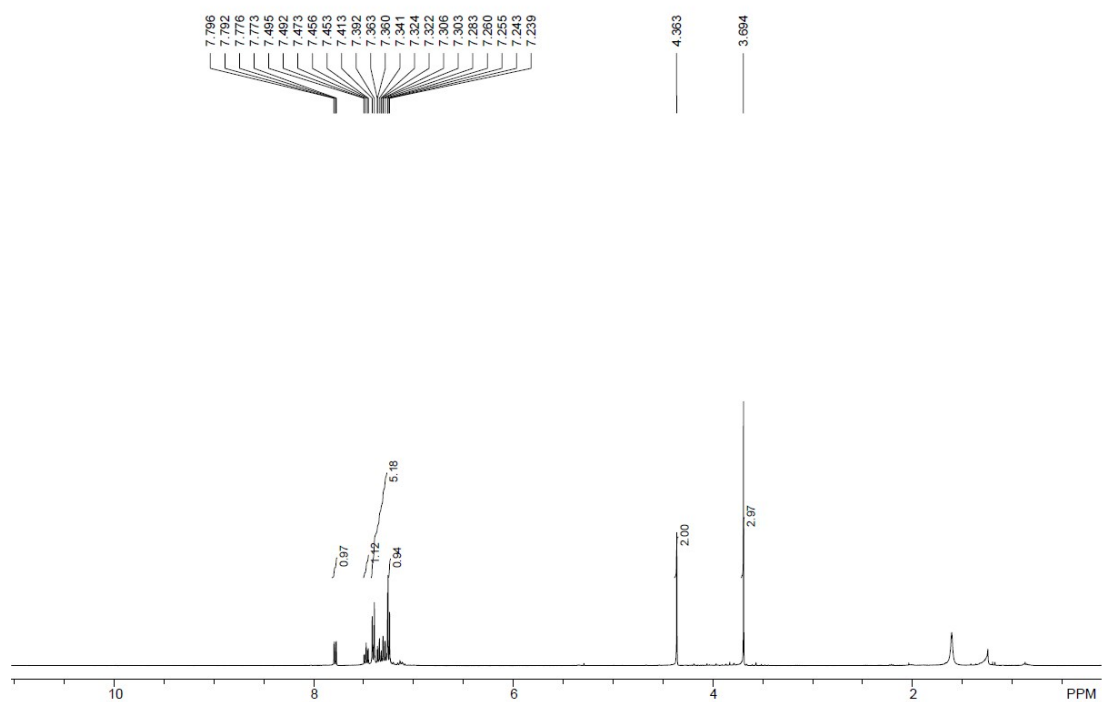
3-(benzylthio)-1-methylquinoxalin-2(1H)-one (3ag)



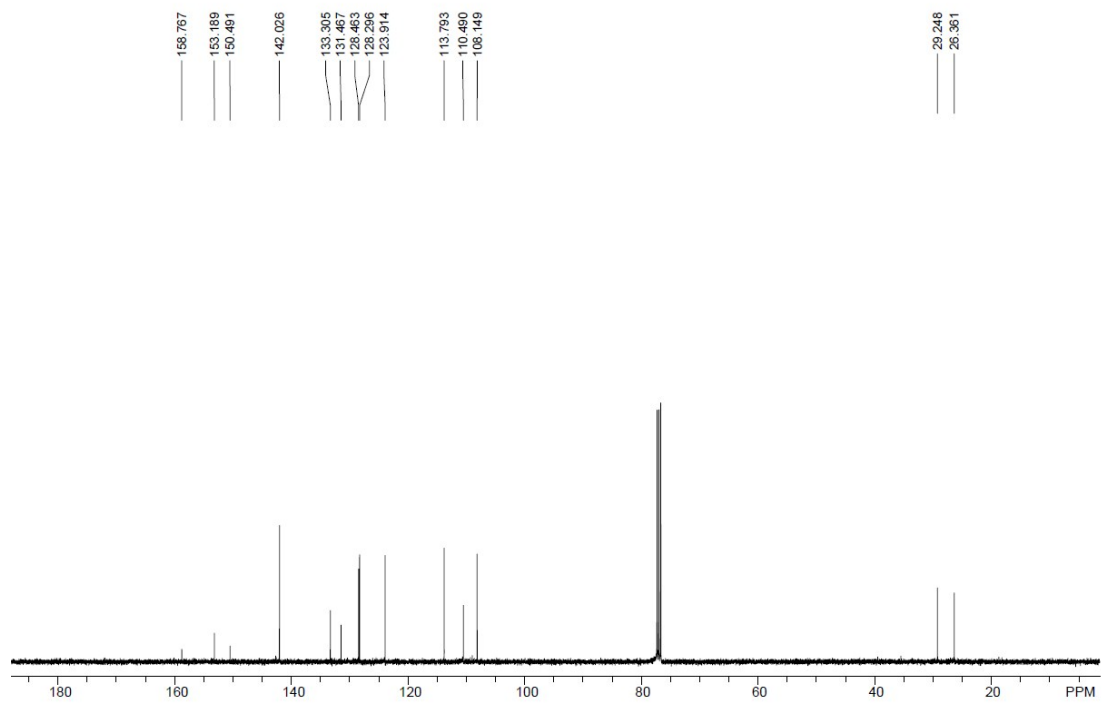
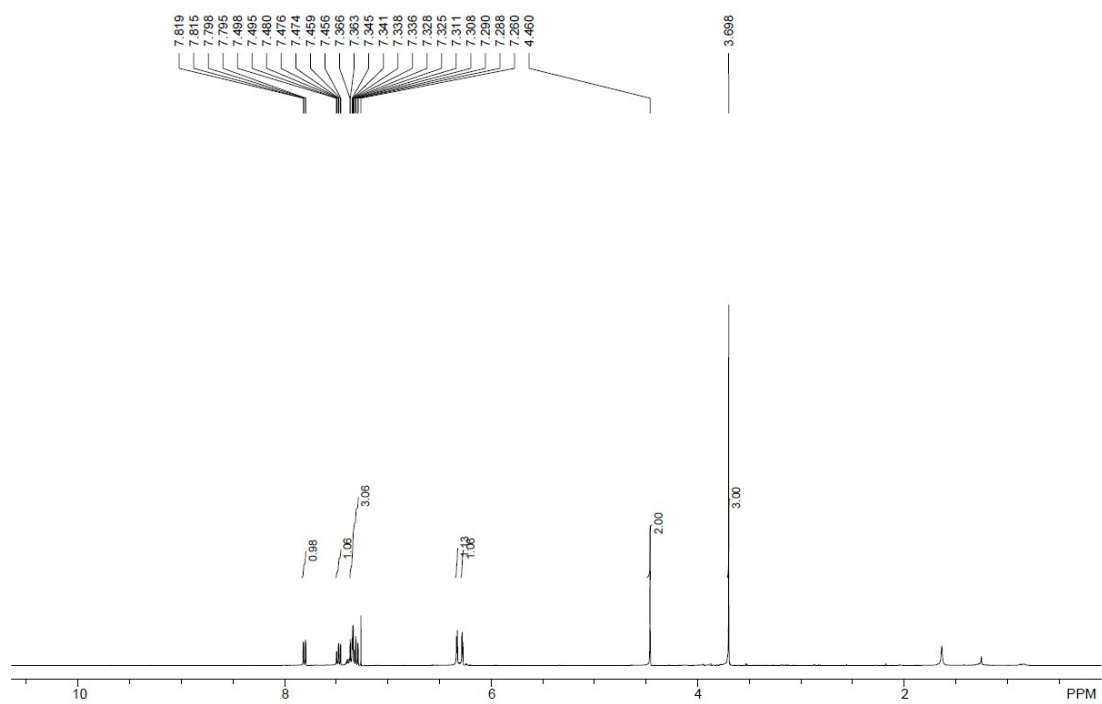
methyl-3-(phenethylthio)quinoxalin-2(1H)-one (3ah)



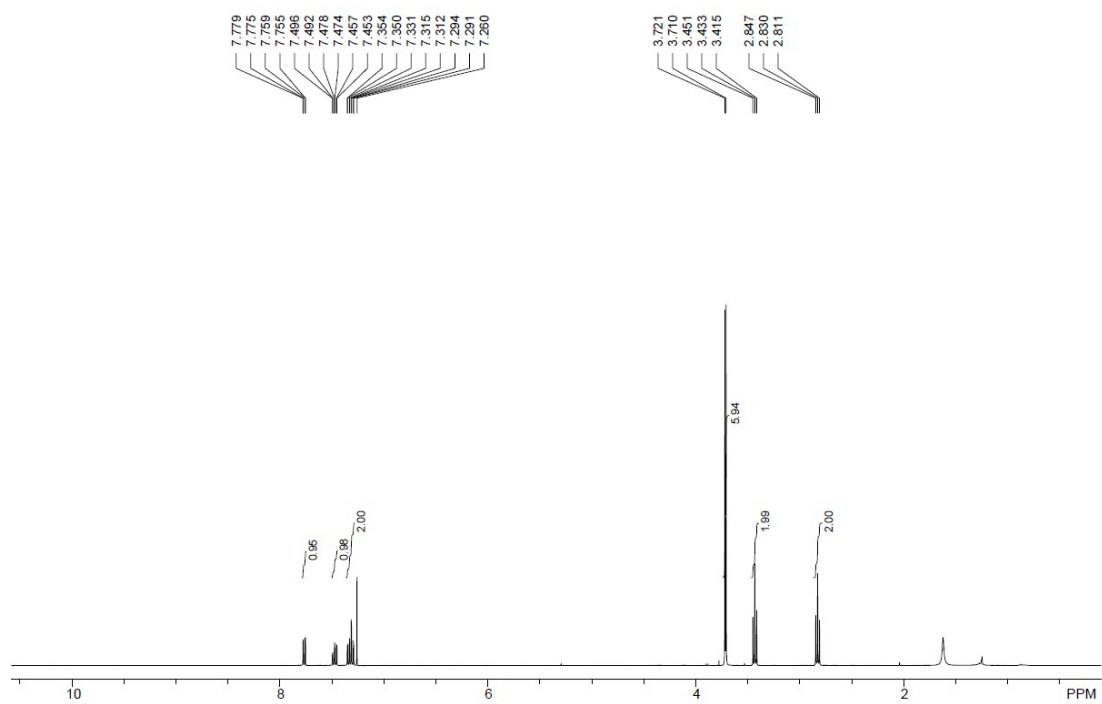
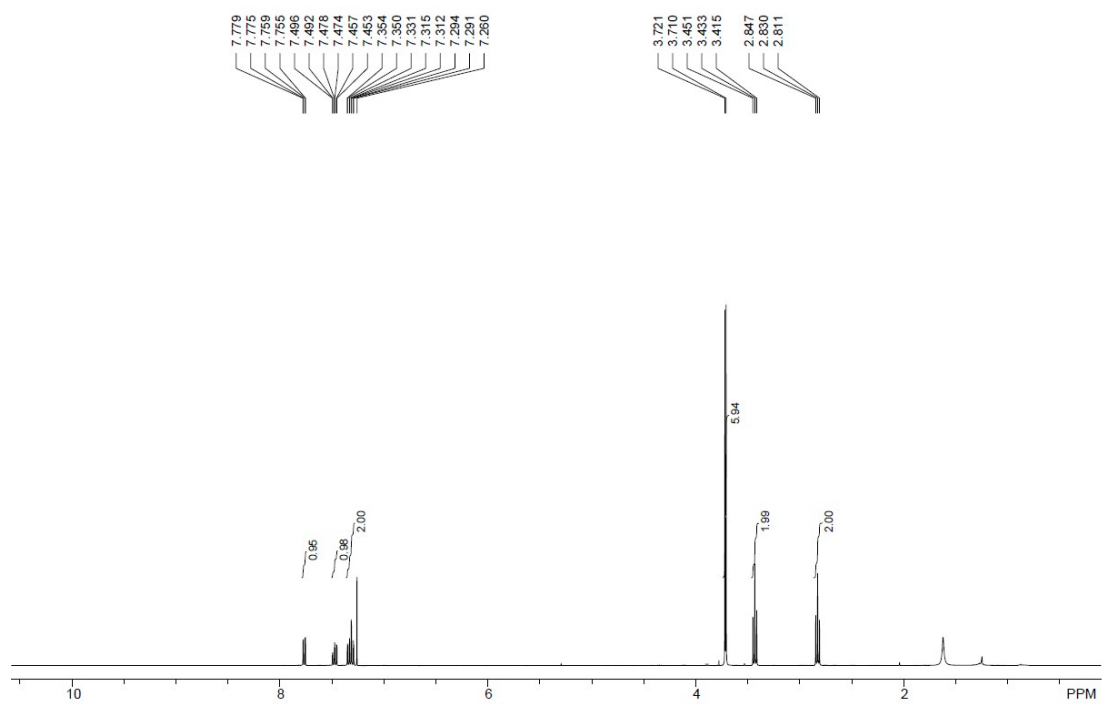
3-((4-chlorobenzyl)thio)-1-methylquinoxalin-2(1H)-one (3ai)



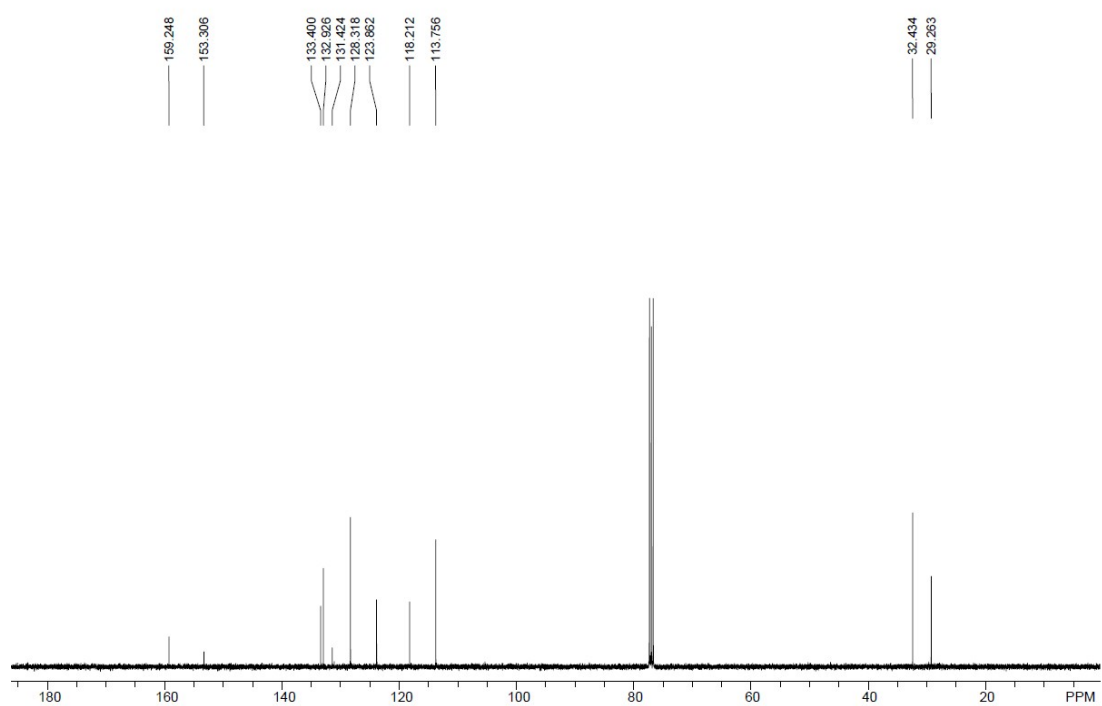
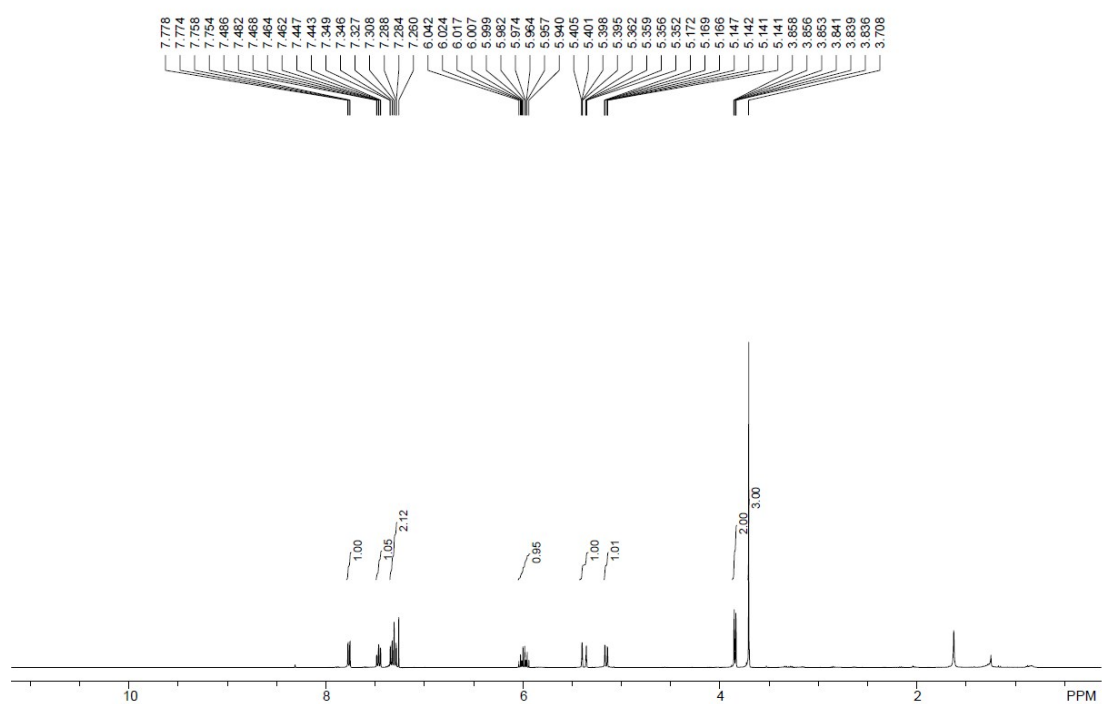
3-((furan-2-ylmethyl)thio)-1-methylquinoxalin-2(1H)-one (3aj)



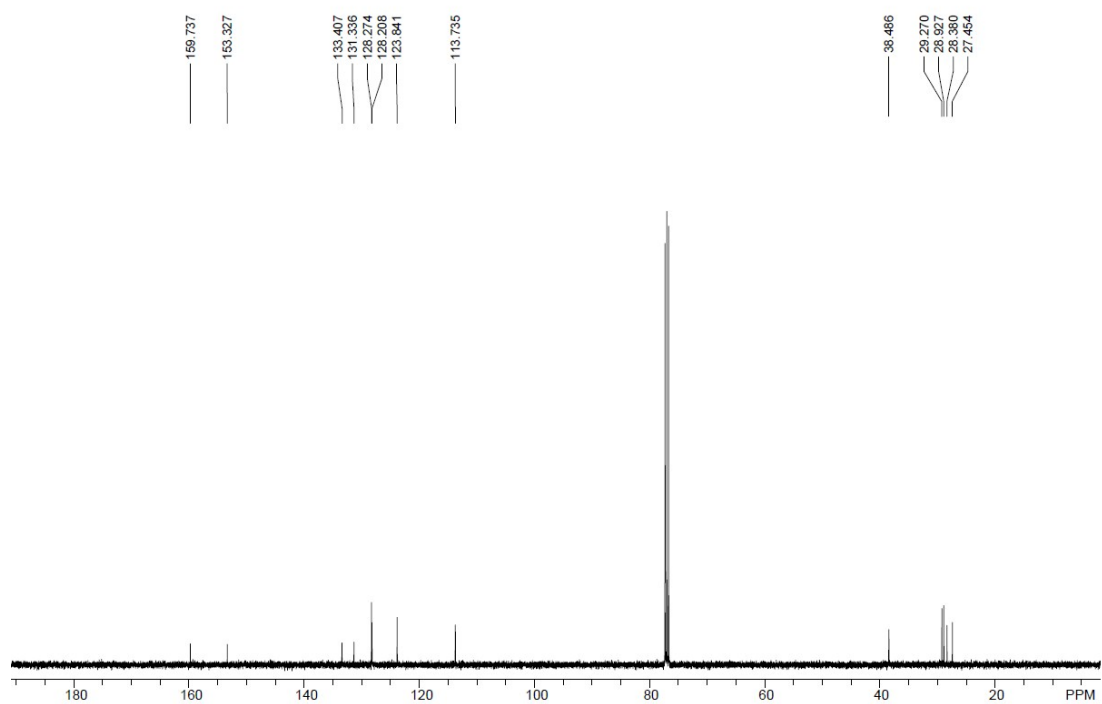
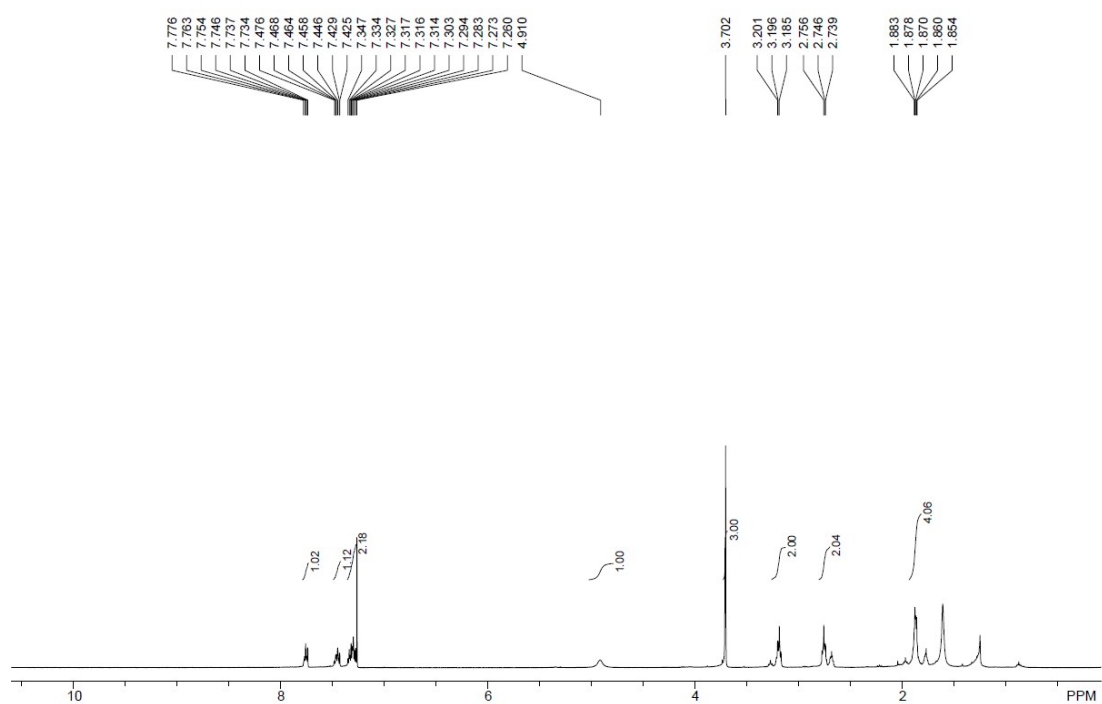
methyl 3-((4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)thio)propanoate (3ak)



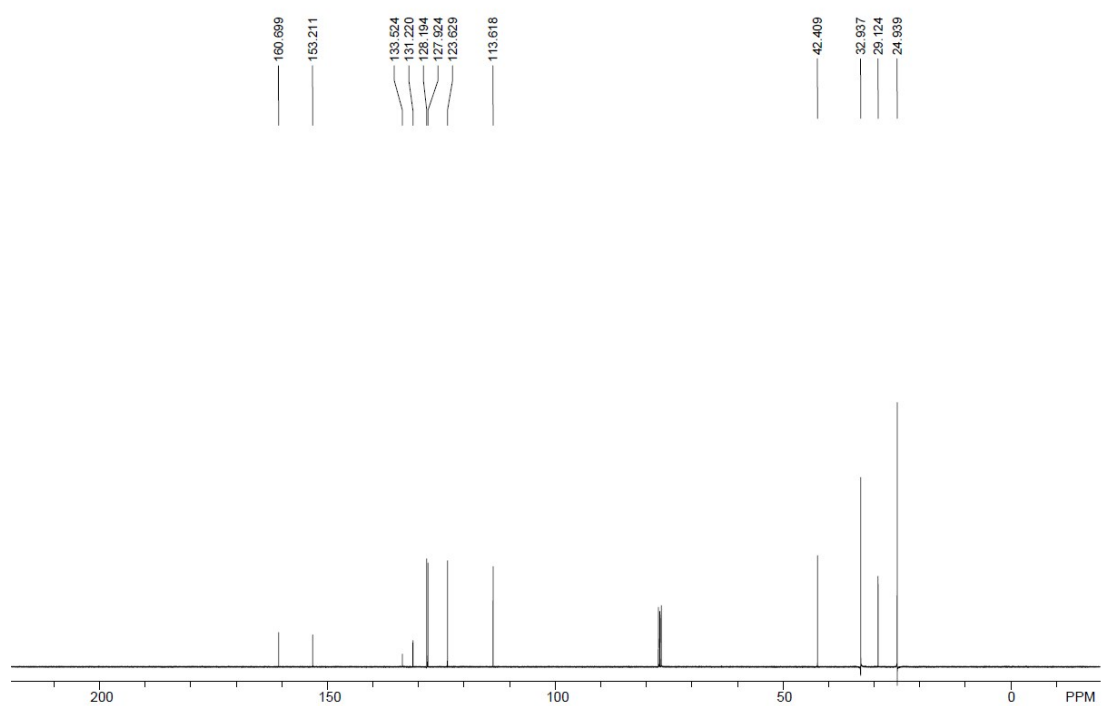
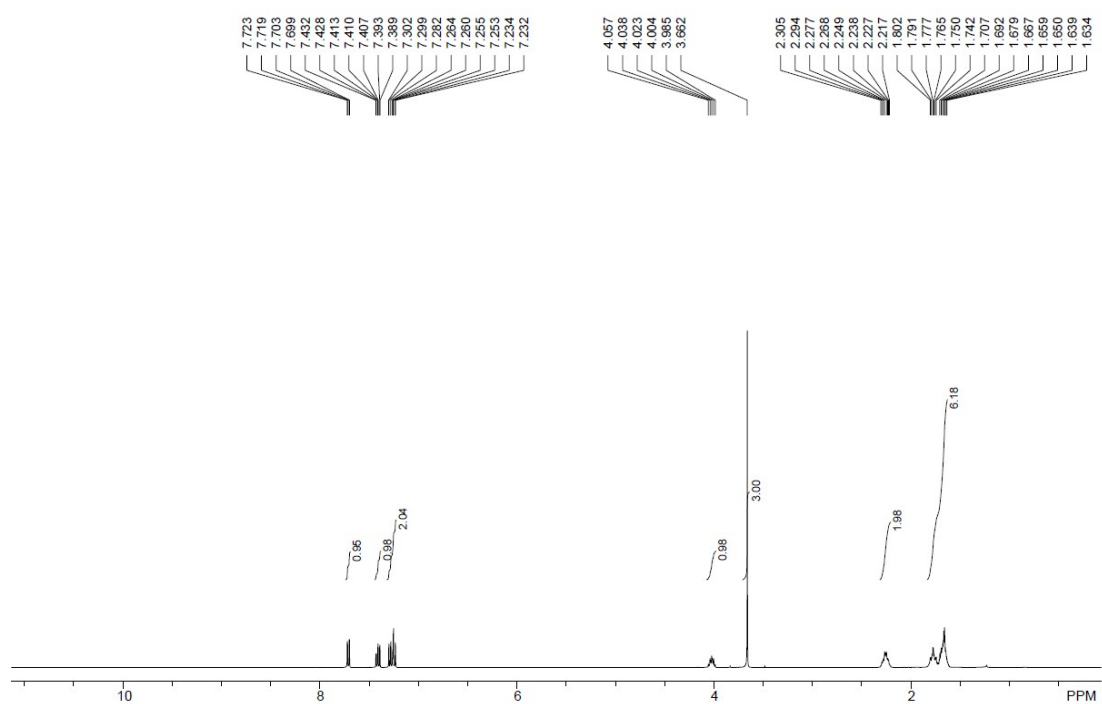
3-(allylthio)-1-methylquinoxalin-2(1H)-one (3al)



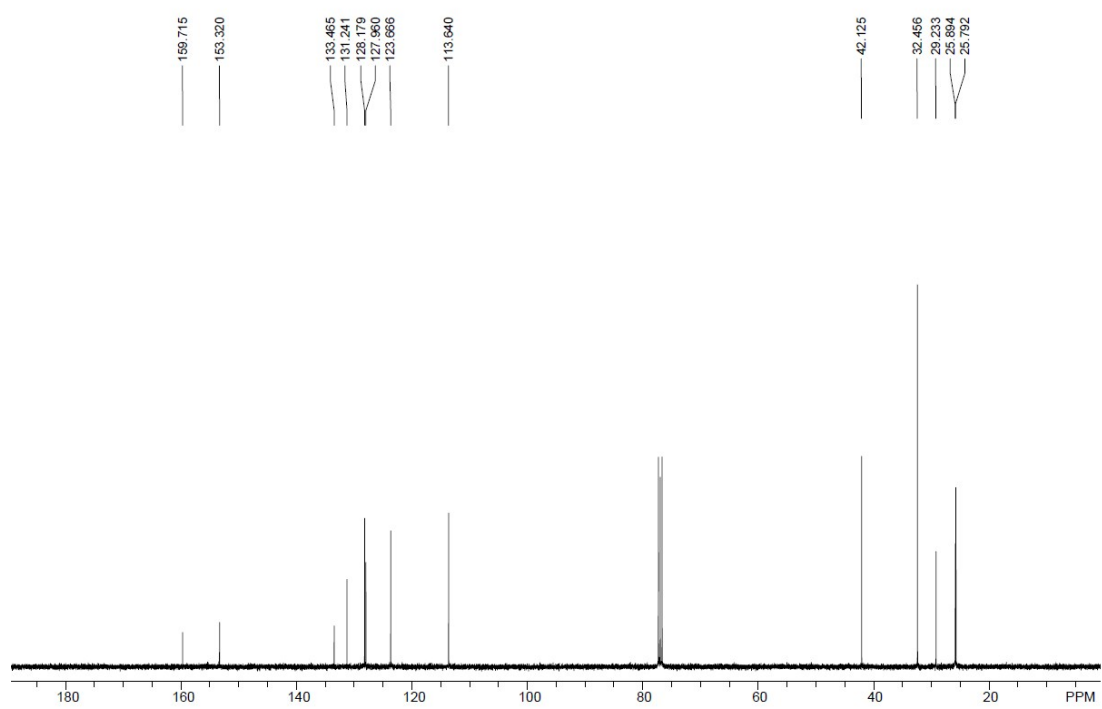
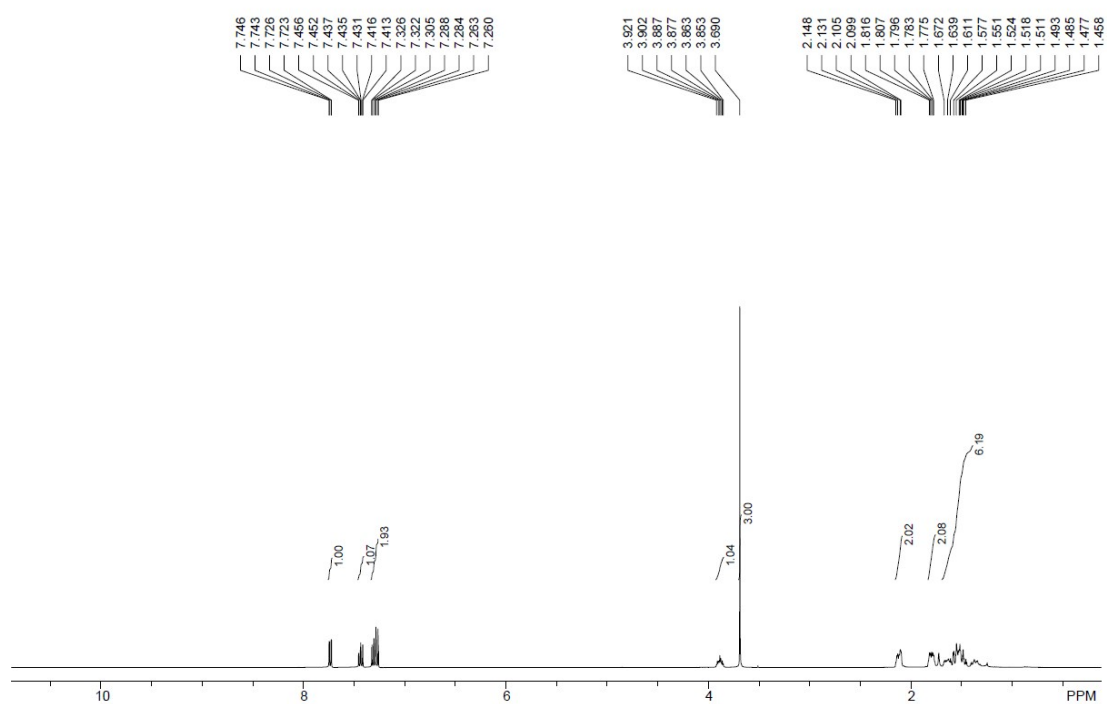
3-((4-mercaptobutyl)thio)-1-methylquinoxalin-2(1H)-one (3am)



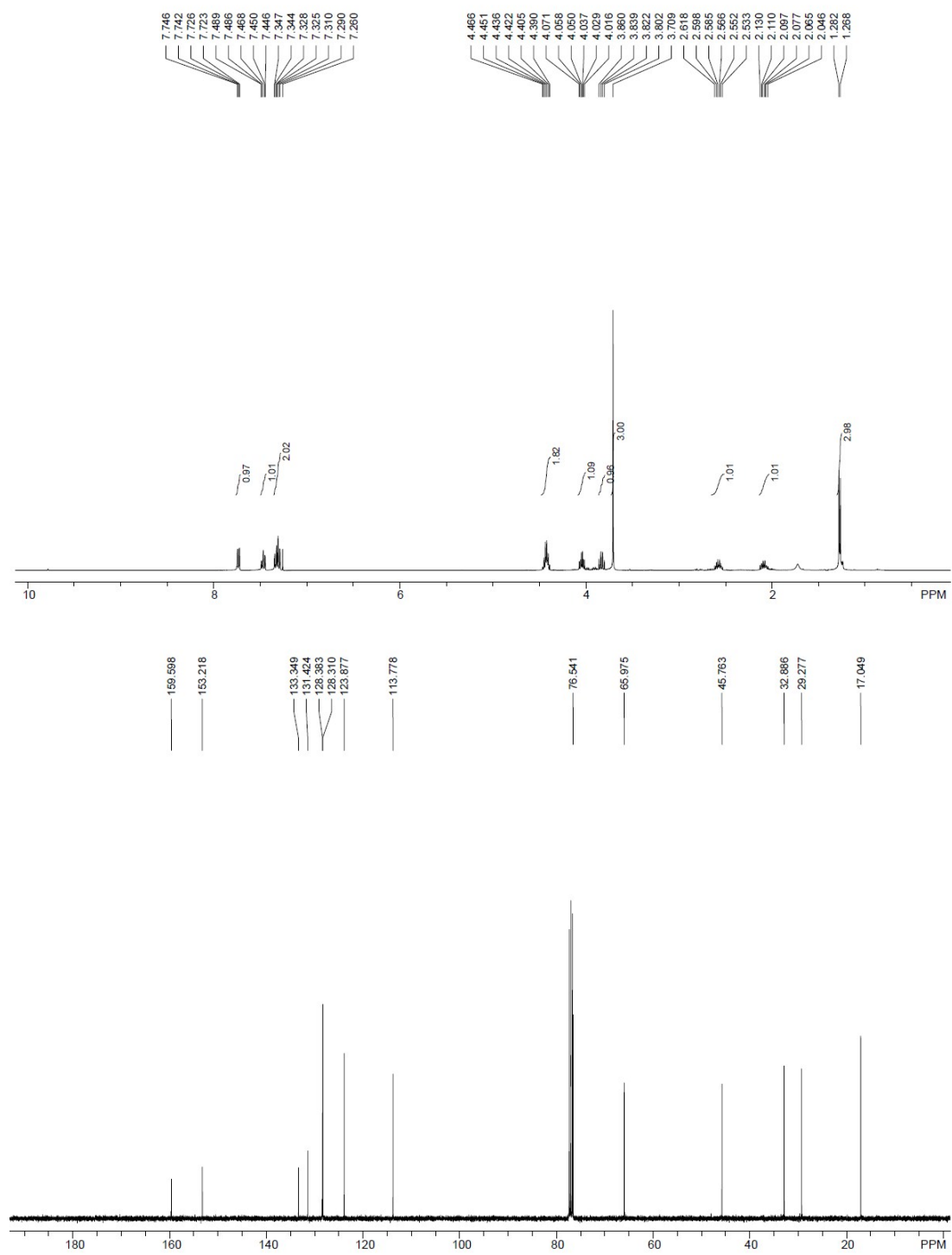
3-(cyclopentylthio)-1-methylquinoxalin-2(1H)-one (3an)



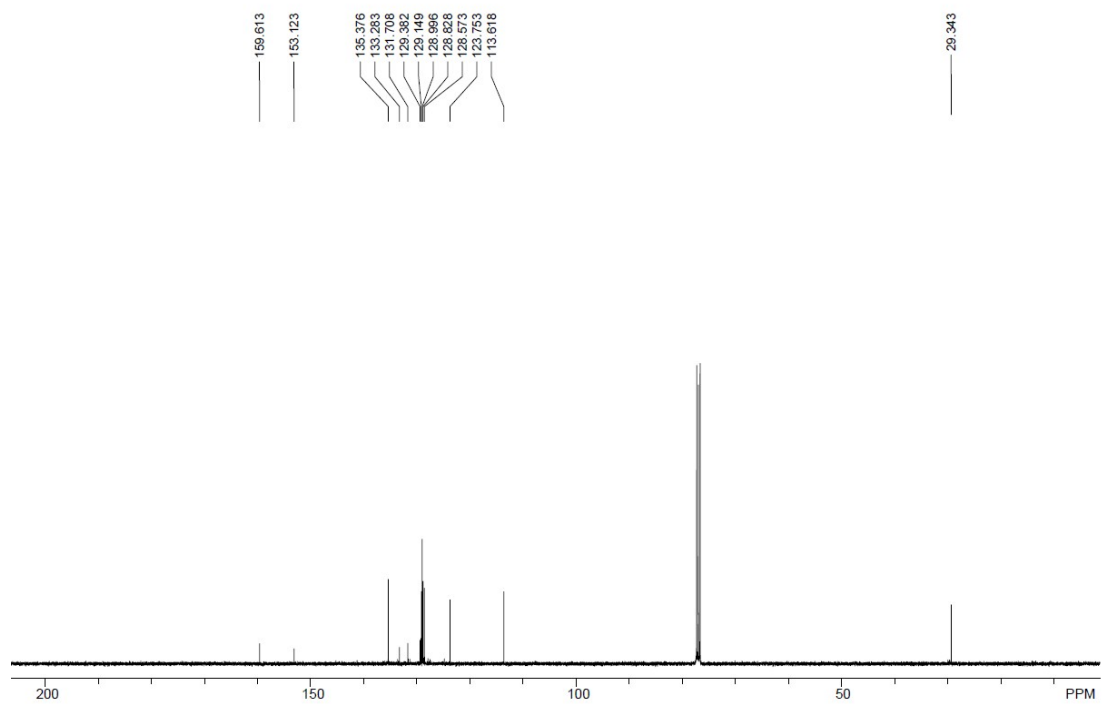
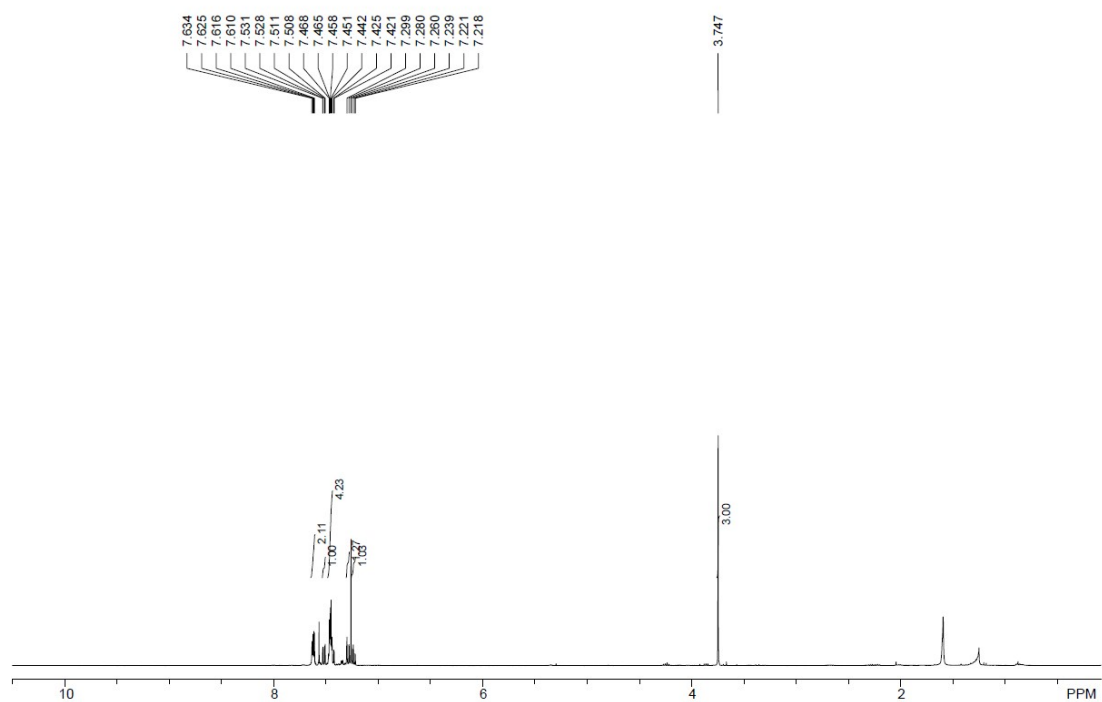
3-(cyclohexylthio)-1-methylquinoxalin-2(1H)-one (3ao)



1-methyl-3-((2-methyltetrahydrofuran-3-yl)thio)quinoxalin-2(1H)-one (3ap)



methyl-3-(phenylthio)quinoxalin-2(1H)-one (3aq)



methyl-3-Sulfonylquinoxalin-2(1H)-one (4a)

