Visible-light-induced Decarboxylative Acylation of Quinoxalin-2(1*H*)-ones with α-Oxo Carboxylic Acids under Metal-, Strong Oxidant- and External Photocatalyst-Free Conditions

Long-Yong Xie[a], You-Shu Bai[a], Xiang-Qin Xu[a], Xia Peng[a], Hai-Shan Tang[a], Ying Huang[b], Ying-Wu Lin[c], Zhong Cao[b] and Wei-Min He*[a]

[a]Department of Chemistry，Hunan University of Science and Engineering, Yongzhou 425100, China

[b]Hunan Provincial Key Laboratory of Materials Protection for Electric Power and Transportation, Changsha University of Science and Technology, Changsha, 410114, China

[c]School of Chemistry and Chemical Engineering, University of South China, Hengyang 421001, China

E-mail: weiminhe2016@yeah.net

Table of Content

1. General Information

Unless otherwise specified, all reagents and solvents were obtained from commercial suppliers and used without further purification. ^{1}H 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 (^{1}H NMR: $CDCl_3$ 7.26 ppm, d^6-DMSO 2.50, ^{13}C NMR: $CDCl_3$ 77.0 ppm, d^6-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, brs = broad singlet. Mass spectra were performed on a spectrometer operating on ESI-TOF. Column chromatography was performed on silica gel (200-300 mesh). GC-MS were obtained by EI on a Shimadzu GC-MS 2010.

The Material of the Irradiation Vessel

Manufacturer： Xi 'an WATTECS experimental equipment co. LTD

Model： WP-VLH-1020

Broadband source： λ = 400-405 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

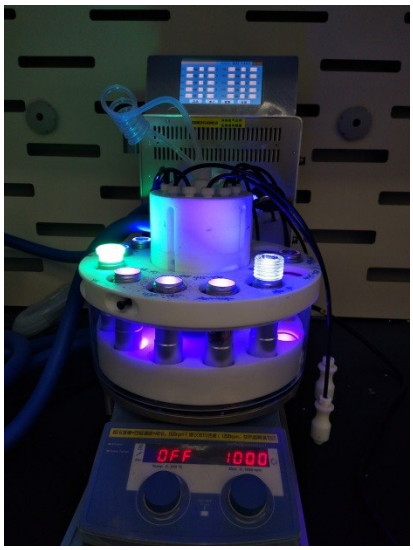
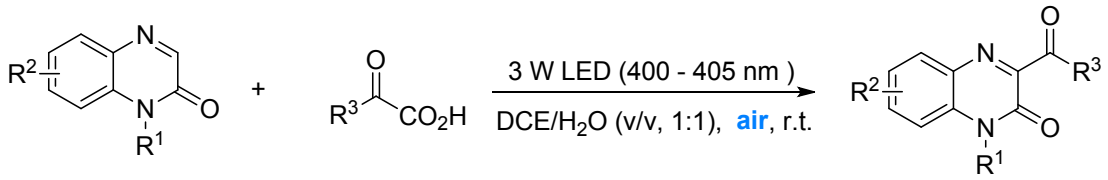


Figure S1（Photographed by author Long-Yong Xie）

2. Experimental Section

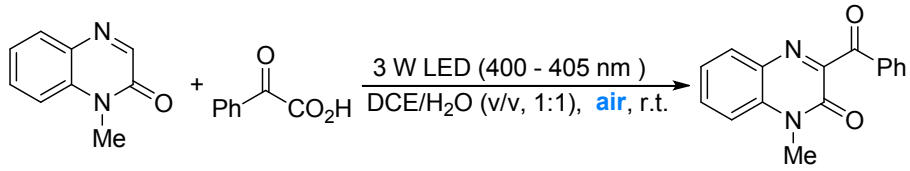
Typical Procedure for the Synthesis of 3-acylquinoxalin-2(1*H*)-ones 3.



1 **2** **3**

In a mixed solvent of DCE and H_2O (1.5 mL, V_{DCE}:V_{H2O} = 1:1) was added quinoxalin-2(1*H*)-ones **1** (0.3 mmol) and α-oxocarboxylic acid **2** (0.66 mmol). The reaction mixture was open to the air and stirred at room temperature under the irradiation of 3W LED lamps (400 – 405 nm) for 1 - 4 h. the reaction was monitored by TLC. After completion of the reaction, the resulting mixture was extracted with EtOAc (3 mL× 3) and the organic phase 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 product 3-acylquinoxalin-2(1*H*)-ones **3**.

Gram-scale synthesis of 3aa

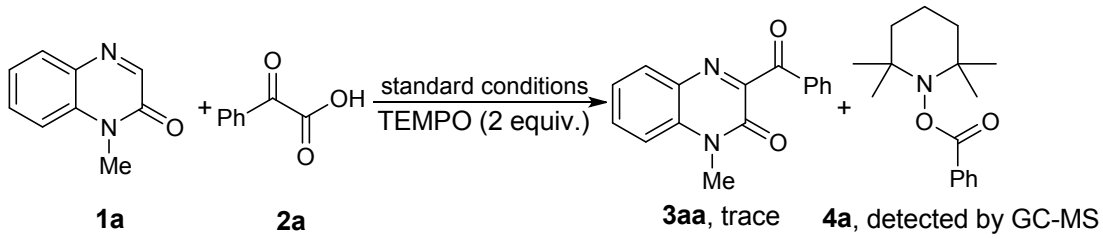


1a, (0.8 g, 5 mmol) **3aa**, (1.11 g, yield 84%)

In a mixed solvent of DCE and H_2O (25 mL, V_{DCE}:V_{H2O} = 1:1) was added quinoxalin-2(1*H*)-ones **1a** (0.8 g, 5 mmol) and 2-oxo-2-phenylacetic acid **2a** (1.65 g, 11 mmol) The reaction mixture was open to the air and stirred at room temperature under the irradiation of 3W LED lamps (400 – 405 nm) for about 3 h. After completion of the reaction, the resulting mixture was extracted with EtOAc (15 mL× 2) and the organic phase 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 1.11 gram of **3aa,** yield 84%.

3. Mechanism investigation

(a) Radical trapped experiment using TEMPO as radical scavenger



1a **2a** **3aa**, trace **4a**, detected by GC-MS

In a mixed solvent of DCE and H_2O (1.5 mL, V_{DCE}:V_{H2O} = 1:1) was added 1-methylquinoxalin-2(1H)-one **1a** (48 mg, 0.3 mmol), 2-oxo-2-phenylacetic acid **2a** (99 mg, 0.66 mmol) and TEMPO (94.2 mg, 0.6 mmol). The reaction mixture was open to the air and stirred at room temperature under the irradiation of 3W LED lamps (400 – 405 nm) for 4 h. the reaction was monitored by GC-MS, only trace of **3aa** formed and **4a** was detected by GC-MS shown in Figure S2, MS (EI) m/z calcd. for $C_{16}H_{23}NO_2$ $[M]^+$: 261.17, found 261.25.

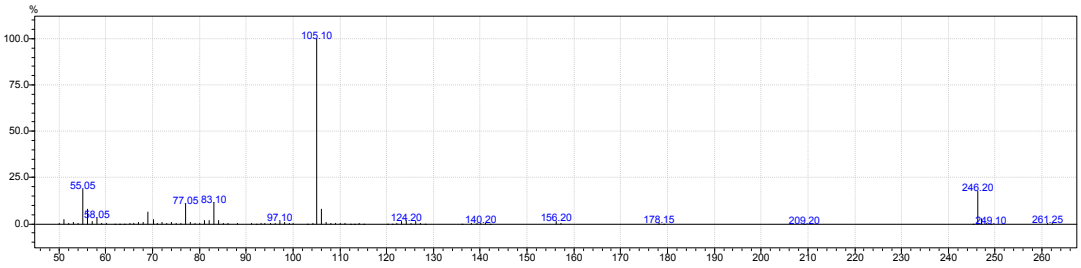
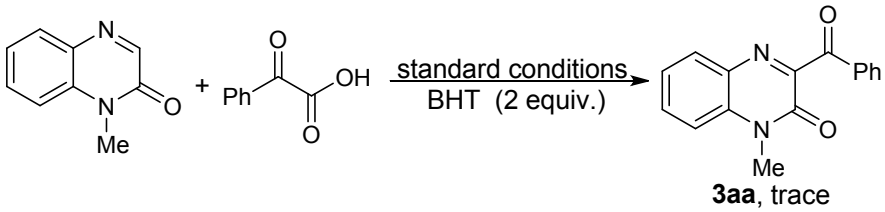


Figure S2 Mass spectra of 4a

(b) Radical trapped experiment using BHT as radical scavenger



3aa, trace

In a mixed solvent of DCE and H_2O (1.5 mL, V_{DCE}:V_{H2O} = 1:1) was added 1-methylquinoxalin-2(1H)-one **1a** (48 mg, 0.3 mmol), 2-oxo-2-phenylacetic acid **2a** (99 mg, 0.66 mmol) and BHT (132 mg, 0.6 mmol). The reaction mixture was open to the air and stirred at room temperature under the irradiation of 3W LED lamps (400 – 405 nm) for 4 h. the reaction was monitored by TLC, only trace of **3aa** was detected.

(c) H_2O_2 Detection Using Hydrogen Peroxides Strips

In a mixed solvent of DCE and H_2O (1.5 mL, V_{DCE}:V_{H2O} = 1:1) was added 1-methylquinoxalin-2(1H)-one **1a** (48 mg, 0.3 mmol) and 2-oxo-2-phenylacetic acid **2a** (99 mg, 0.66 mmol). The reaction mixture was open to the air and stirred at room temperature under the irradiation of 3W LED lamps (400 – 405 nm) for 1 h. When the reaction was complete, transfer 5 ul of the water solution into a 1.5ml centrifuge tube using a pipette. Add 1mL of deionized water to the centrifuge tube and mixed the solution evenly. Insert the hydrogen peroxide test strip into the mixture and let it rest for 2 seconds. After taking it out, let it rest for 10 seconds and compare it with the color chart. By comparing the color with the color

chart, we found that the hydrogen peroxide concentration was between 30mg/L and 100mg/L, so the content of hydrogen peroxide produced by this reaction was 4.5 mg - 15 mg.

Figure S3（Photographed by author Long-Yong Xie）

(d) UV/Vis Absorption Experiment

The UV/Vis absorption spectra of 1-methylquinoxalin-2(1H)-one (1a, 0.020 M) and 2-oxo-2-phenylacetic acid (2a, 0.044 M) in DCE were recorded in 1 cm path quartz cuvettes by using a SHIMADZU UV-2600 UV-visible spectrophotometer, respectively. The obtained bands in UV/vis absorption spectra were shown in Figure S4.

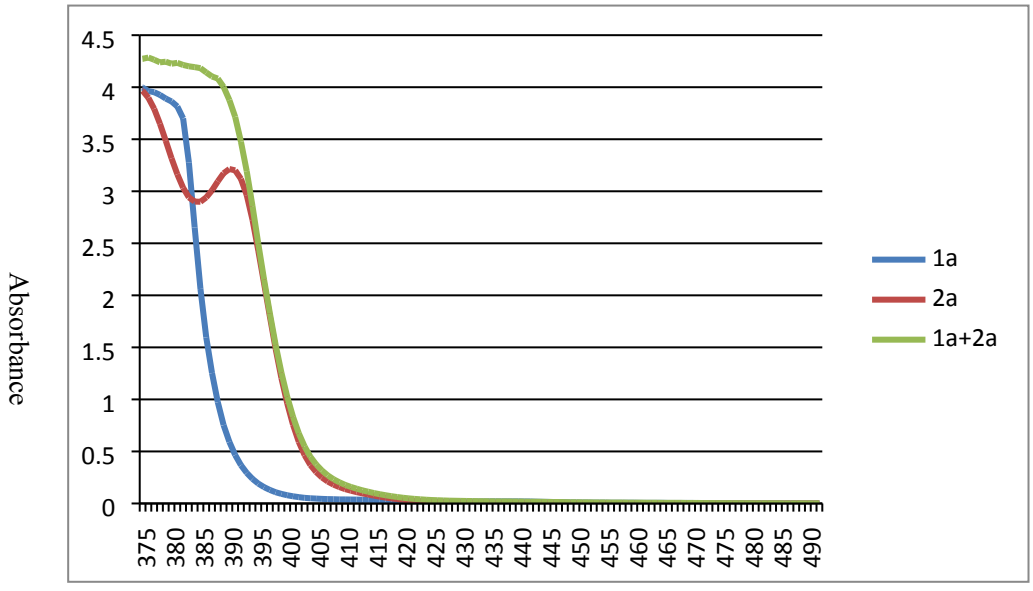
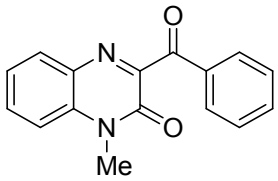


Figure S4. UV-Vis Spectroscopic Measurements on **1a**, **2a**, and Combinations of **1a** and **2a** in DCE

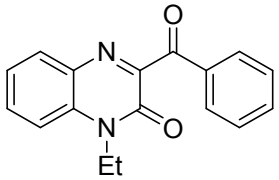
4. Characterization data of products

3-benzoyl-1-methylquinoxalin-2(1H)-one (3aa)[1]



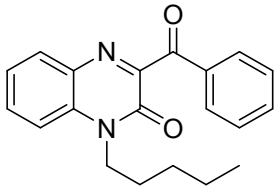
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 – 7.98 (m, 2 H), 7.94 – 7.92 (m, 1 H), 7.70 – 7.66 (m, 1 H), 7.65 – 7.60 (m, 1 H), 7.50 – 7.46 (m, 2 H), 7.44 – 7.40 (m, 2 H), 3.75 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.7, 154.6, 153.3, 134.8, 134.2, 133.9, 132.2, 132.0, 131.0, 130.0, 128.7, 124.2, 114.0, 29.0.

3-benzoyl-1-ethylquinoxalin-2(1H)-one (3ba)[2]



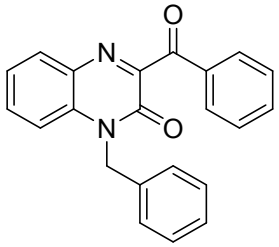
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 – 7.97 (m, 2 H), 7.92 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1 H), 7.69 – 7.59 (m, 2 H), 7.49 – 7.37 (m, 4 H), 4.36 (q, J = 7.2 Hz, 2 Hz), 1.41 (t, J = 7.2 Hz, 3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.8, 154.5, 152.8, 134.8, 134.2, 132.8, 132.4, 132.0, 131.1, 129.9, 128.6, 123.9, 113.8, 37.3, 12.4.

3-benzoyl-1-pentylquinoxalin-2(1H)-one (3ca)[2]



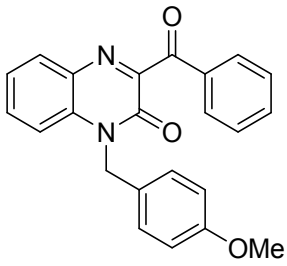
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 – 7.96 (m, 2 H), 7.92 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1 H), 7.68 – 7.58 (m, 2 H), 7.48 – 7.44 (m, 2 H), 7.41 – 7.36 (m, 2 H), 4.27 (t, J = 8.0 Hz, 2 Hz), 1.83 – 1.76 (m,2 H), 1.48 – 1.34 (m, 4 H), 0.91 (t, J = 7.2 Hz, 3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.9, 154.6, 153.0, 134.8, 134.1, 133.0, 132.4, 131.9, 131.1, 129.8, 128.6, 123.9, 113.9, 42.3, 28.9, 26.9, 22.2, 13.8.

3-benzoyl-1-benzylquinoxalin-2(1H)-one (3da)[3]



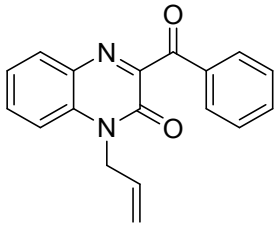
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 – 8.01 (m, 2 H), 7.94 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1 H), 7.66 – 7.62 (m, 1 H), 7.57 – 7.49 (m, 3 H), 7.38 – 7.28 (m, 7 H), 5.54 (s, 2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.7, 154.7, 153.4, 134.8, 134.8, 134.3, 133.2, 132.5, 132.0, 131.1, 130.0, 129.0, 128.7, 127.9, 127.1, 124.2, 114.8, 45.9.

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



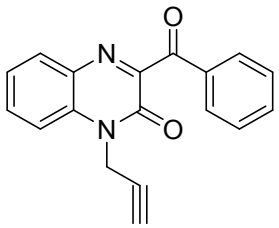
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 – 7.92 (m, 2 H), 7.83 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1 H), 7.56 – 7.53 (m, 1 H), 7.49 – 7.45 (m, 1 H), 7.43 – 7.39 (m, 2 H), 7.35 – 7.33 (m, 1 H), 7.28 – 7.25 (m, 1 H), 7.20 – 7.17 (m, 2 H), 6.77 – 6.75 (m, 2 H), 5.37 (s, 2 Hz), 3.67 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.7, 154.7, 153.4, 134.8, 134.2, 133.1, 132.4, 131.9, 131.0, 129.9, 128.7, 128.6, 128.3, 126.8, 124.1, 114.7, 114.3, 55.2, 45.3; HRMS (ESI) m/z calcd. for $C_{23}H_{19}N_2O_3[M+H]^+$: 371.1390, found 371.1387.

allyl-3-benzoylquinoxalin-2(1H)-one (3fa)



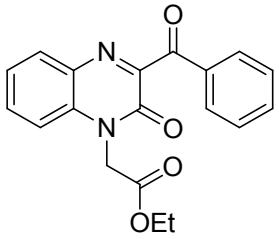
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 – 7.97 (m, 2 H), 7.92 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1 H), 7.65 – 7.59 (m, 2 H), 7.49 – 7.45 (m, 2 H), 7.40 – 7.37 (m,2 H), 5.99 – 5.89 (m, 1 Hz), 5.32 – 5.22 (m, 2 H), 4.95 – 4.93 (m, 2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.7, 154.6, 152.8, 134.7, 134.2, 133.0, 132.2, 131.9, 131.0, 130.2, 129.9, 128.6, 124.1, 118.7, 114.5, 44.4; HRMS (ESI) m/z calcd. for $C_{18}H_{15}N_2O_2[M+H]^+$: 291.1128, found 291.1126.

3-benzoyl-1-(prop-2-yn-1-yl)quinoxalin-2(1H)-one (3ga)



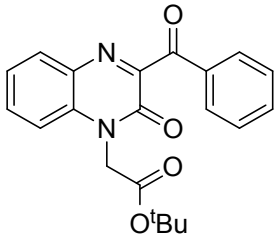
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 – 7.98 (m, 2 H), 7.94 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1 H), 7.73 – 7.69 (m, 1 H), 7.65 – 7.61 (m, 1 H), 7.59 – 7.56 (m,1 H), 7.51 – 7.42 (m, 3 H), 5.09 (d, J = 2.4 Hz, 2 H), 2.34 (t, J = 2.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.3, 154.3, 152.2, 134.6, 134.3, 132.3, 132.3, 132.2, 131.1, 130.0, 128.7, 124.5, 114.6, 76.3, 73.8, 31.4; HRMS (ESI) m/z calcd. for $C_{18}H_{13}N_2O_2[M+H]^+$: 289.0972, found 289.0966.

ethyl 2-(3-benzoyl-2-oxoquinoxalin-1(2H)-yl)acetate (3ha)[1]



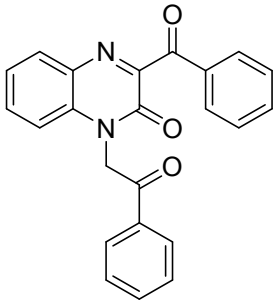
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 – 7.93 (m, 3 H), 7.66 – 7.60 (m, 2 H), 7.50 – 7.46 (m, 2 H), 7.42 – 7.39 (m, 1 H), 7.17 (dd, J_1 = 8.4 Hz, J_2 = 0.8 Hz, 1 H), 5.06 (s, 2 H), 4.25 (q, J = 7.2 Hz, 2 H), 1.27 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.3, 166.6, 154.3, 152.8, 134.7, 134.2, 133.0, 132.2, 132.2, 131.2, 130.0, 128.6, 124.4, 113.5, 62.2, 43.2, 14.0.

tert-butyl 2-(3-benzoyl-2-oxoquinoxalin-1(2H)-yl)acetate (3ia)



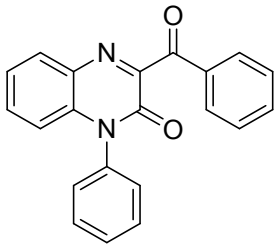
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 – 7.96 (m, 2 H), 7.93 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1 H), 7.66 – 7.59 (m, 2 H), 7.49 – 7.45 (m, 2 H), 7.42 – 7.38 (m, 1 H), 7.16 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1 H), 4.98 (s, 2 H), 1.46 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.3, 165.6, 154.3, 152.8, 134.2, 133.0, 132.1, 132.1, 131.2, 130.0, 130.0, 128.6, 124.3, 113.5, 83.4, 43.9, 27.9; HRMS (ESI) m/z calcd. for $C_{21}H_{21}N_2O_4[M+H]^+$: 365.1496, found 365.1499.

3-benzoyl-1-(2-oxo-2-phenylethyl)quinoxalin-2(1H)-one (3ja)[3]



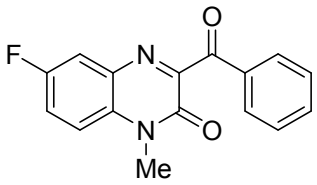
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 – 8.03 (m, 2 H), 8.00 – 7.98 (m, 2 H), 7.93 – 7.91 (m, 1 H), 7.65 – 7.58 (m, 2 H), 7.54 – 7.44 (m, 5 H), 7.37 – 7.34 (m, 1 H), 7.06 – 7.04 (m, 1 H), 5.76 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.5, 190.7, 154.1, 153.0, 134.7, 134.3, 134.2, 133.2, 132.2, 132.1, 131.0, 129.9, 129.0, 128.6, 128.1, 124.2, 113.9, 48.2;

3-benzoyl-1-phenylquinoxalin-2(1H)-one (3ka)[1]



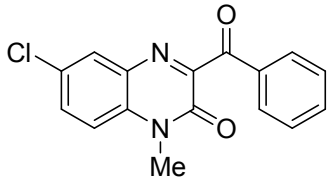
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 – 8.03 (m, 2 H), 7.96 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1 H), 7.64 – 7.59 (m, 3 H), 7.57 – 7.53 (m, 1 H), 7.51 – 7.44 (m, 3 H), 7.40 – 7.34 (m, 3 H), 6.79 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.5, 155.3, 152.9, 134.8, 134.8, 134.2, 132.0, 131.6, 130.5, 130.3, 130.0, 129.7, 128.6, 128.2, 127.3, 124.3, 115.7;

3-benzoyl-6-fluoro-1-methylquinoxalin-2(1H)-one (3la)[3]



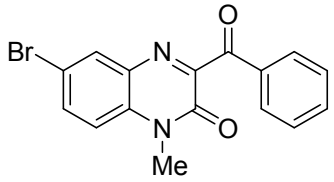
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 – 7.94 (m, 2 H), 7.64 – 7.59 (m, 2 H), 7.50 – 7.46 (m, 2 H), 7.42 – 7.36 (m, 2 H), 3.73 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.4, 158.7 (d, $J_{C\text{-}F}$ = 244.3 Hz), 156.0, 152.9, 134.5, 134.4, 132.6 (d, $J_{C\text{-}F}$ = 10.9 Hz), 130.5 (d, $J_{C\text{-}F}$ = 1.5 Hz), 129.9, 128.7, 119.9 (d, $J_{C\text{-}F}$ = 24.1 Hz), 116.1 (d, $J_{C\text{-}F}$ = 22.6 Hz), 115.2 (d, $J_{C\text{-}F}$ = 8.7 Hz), 29.3.

3-benzoyl-6-chloro-1-methylquinoxalin-2(1H)-one (3ma)[3]



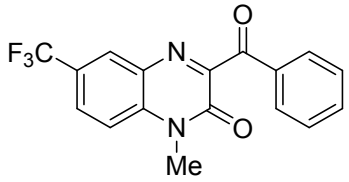
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 – 7.94 (m, 2 H), 7.91 – 7.89 (m, 1 H), 7.65 – 7.60 (m, 2 H), 7.50 – 7.46 (m, 2 H), 7.34 (d, J = 8.8 Hz, 1 H), 3.72 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.2, 155.7, 152.9, 134.5, 134.4, 132.5, 132.5, 132.0, 130.1, 129.9, 129.5, 128.7, 115.2, 29.2.

3-benzoyl-6-bromo-1-methylquinoxalin-2(1H)-one (3na)



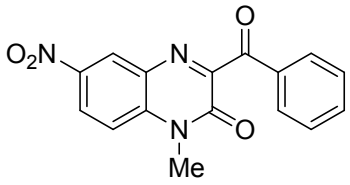
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, J = 2.4 Hz, 1 H), 7.98 – 7.95 (m, 2 H), 7.76 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1 H), 7.66 – 7.62 (m, 1 H), 7.49 (t, J = 8.0 Hz, 2 H), 7.29 (d, J = 9.2 Hz, 1 H), 3.73 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.2, 155.7, 152.9, 134.7, 134.5, 134.4, 133.2, 133.0, 132.9, 130.0, 128.7, 116.8, 115.4, 29.2; HRMS (ESI) m/z calcd. for $C_{16}H_{12}BrN_2O_2[M+H]^+$: 343.0077, found 343.0073.

3-benzoyl-1-methyl-6-(trifluoromethyl)quinoxalin-2(1H)-one (3oa)



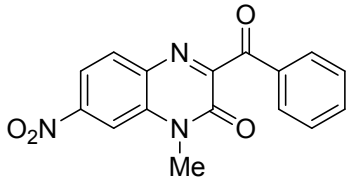
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (d, J = 1.6 Hz, 1 H), 7.98 – 7.96 (m, 2 H), 7.88 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz 1 H), 7.66 – 7.62 (m, 1 H), 7.53 – 7.47 (m, 3 H), 3.77 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.9, 156.0, 153.1, 136.1, 134.5, 134.4, 131.4, 129.9, 128.8, 128.3 (q, $J_{C\text{-}F}$ = 4.3 Hz), 128.2 (q, $J_{C\text{-}F}$ = 3.6 Hz), 126.5 (q, $J_{C\text{-}F}$ = 33.5 Hz), 123.4 (q, $J_{C\text{-}F}$ = 270.5 Hz), 114.8, 29.3; HRMS (ESI) m/z calcd. for $C_{17}H_{12}F_3N_2O_2[M+H]^+$: 333.0845, found 333.0843.

3-benzoyl-1-methyl-6-nitroquinoxalin-2(1H)-one (3pa)[4]



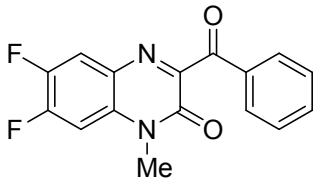
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.78 (d, J = 2.8 Hz, 1 H), 8.50 (dd, J_1 = 9.2 Hz, J_2 = 2.4 Hz, 1 H), 7.98 – 7.96 (m, 2 H), 7.68 – 7.64 (m, 1 H), 7.54 – 7.49 (m, 3 H), 3.80 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.5, 156.6, 152.3, 143.5, 138.2, 134.7, 134.0, 131.0, 129.8, 128.8, 126.0, 125.5, 114.9, 29.6.

3-benzoyl-1-methyl-7-nitroquinoxalin-2(1H)-one (3qa)[4]



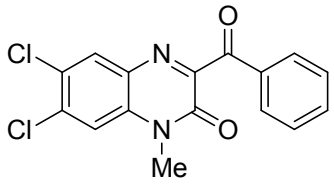
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (d, J = 2.4 Hz, 1 H), 8.22 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1 H), 8.07 (d, J = 8.4 Hz, 1 H), 7.97 – 7.95 (m, 2 H), 7.68 – 7.64 (m, 1 H), 7.53 – 7.49 (m, 2 H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.7, 158.1, 152.8, 148.9, 135.3, 134.7, 134.3, 132.1, 130.1, 129.9, 128.9, 118.5, 109.9, 29.5.

3-benzoyl-6,7-difluoro-1-methylquinoxalin-2(1H)-one (3ra)



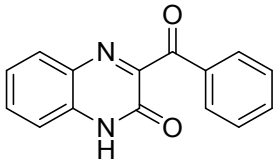
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 – 7.93 (m, 2 H), 7.75 – 7.71 (m, 1 H), 7.66 – 7.61 (m, 1 H), 7.50 – 7.47 (m, 2 H), 7.24 – 7.19 (m, 1 H), 3.70 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.1, 154.9 (d, $J_{C\text{-}F}$ = 3.7 Hz), 152.6 (dd, J_1 = 255.2 Hz, J_2 = 14.5 Hz), 152.8, 147.0 (dd, J_1 = 247.9 Hz, J_2 = 14.6 Hz), 134.4 (d, $J_{C\text{-}F}$ = 2.2 Hz), 131.3 (dd, J_1 = 8.8 Hz, J_2 = 2.2 Hz), 129.9, 128.7, 128.3 (dd, J_1 = 9.5 Hz, J_2 = 2.2 Hz), 118.4 (dd, J_1 = 18.3 Hz, J_2 = 2.2 Hz), 102.8, 102.6, 29.6; ^{19}F NMR (376 MHz, $CDCl_3$) : δ = -127.1 (d, $J_{F\text{-}F}$ = 21.8 Hz, 1 F), -140.5 (d, $J_{F\text{-}F}$ = 21.8 Hz, 1 F); HRMS (ESI) m/z calcd. for $C_{16}H_{11}F_2N_2O_2[M+H]^+$: 301.0783, found 301.0789.

3-benzoyl-6,7-dichloro-1-methylquinoxalin-2(1H)-one (3sa)[1]



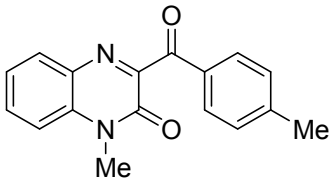
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (s, 1 H), 7.97 – 7.95 (m, 2 H), 7.65 – 7.62 (m, 1 H), 7.52 – 7.48 (m, 3 H), 3.71 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.9, 155.7, 152.7, 136.4, 134.5, 134.4, 133.2, 131.6, 130.2, 130.0, 128.8, 128.5, 115.5, 29.4;

3-benzoylquinoxalin-2(1H)-one (3ta)[3]



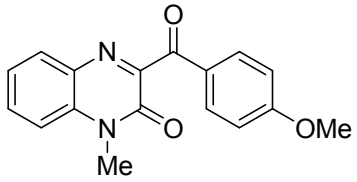
^{1}H NMR (400 MHz, d^6-DMSO): δ = 12.88 (s, 1 H), 7.98 – 7.95 (m, 2 H), 7.84 – 7.82 (m, 1 H), 7.76 – 7.72 (m, 1 H), 7.68 – 7.63 (m, 1 H), 7.59 – 7.55 (m, 2 H), 7.42 – 7.36 (m, 2 H); ^{13}C NMR (100 MHz, d^6-DMSO): δ = 193.1, 156.8, 154.0, 135.3, 135.1, 133.3, 132.4, 131.8, 130.3, 129.7, 129.6, 124.5, 116.5.

1-methyl-3-(4-methylbenzoyl)quinoxalin-2(1H)-one (3ab)[5]



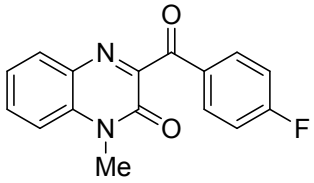
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1 H), 7.89 – 7.87 (m, 2 H), 7.70 – 7.65 (m, 1 H), 7.43 – 7.39 (m, 2 H), 7.28 (d, J = 8.0 Hz, 2 H), 3.75 (s, 3 H), 2.42 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.4, 154.9, 153.3, 145.4, 133.8, 132.4, 132.2, 131.9, 131.0, 130.1, 129.4, 124.2, 113.9, 29.0, 21.9.

3-(4-methoxybenzoyl)-1-methylquinoxalin-2(1H)-one (3ac)[3]



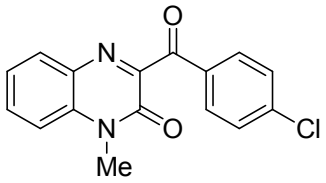
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 – 7.92 (m, 3 H), 7.67 (t, J = 7.2 Hz, 1 H), 7.43 – 7.39 (m, 2 H), 6.95 (d, J = 8.8 Hz, 2 H), 3.88 (s, 3 H), 3.75 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.2, 164.5, 155.0, 153.3, 133.8, 132.5, 132.2, 131.9, 130.9, 127.9, 124.1, 114.0, 113.9, 55.6, 29.1.

3-(4-fluorobenzoyl)-1-methylquinoxalin-2(1H)-one (3ad)[3]



^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 – 8.00 (m, 2 H), 7.93 – 7.91 (m, 1 H), 7.70 – 7.66 (m, 1 H), 7.43 – 7.40 (m, 2 H), 7.15 (t, J = 8.8 Hz, 2 H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.1, 166.4 (d, $J_{C\text{-}F}$ = 255.2 Hz), 154.1, 153.2, 133.8, 132.7 (d, $J_{C\text{-}F}$ = 9.5 Hz), 132.2, 132.1, 131.3 (d, $J_{C\text{-}F}$ = 2.9 Hz), 131.0, 124.2, 115.9 (d, $J_{C\text{-}F}$ = 21.9 Hz), 114.0, 29.1; ^{19}F NMR (376 MHz, $CDCl_3$) : δ = -102.8.

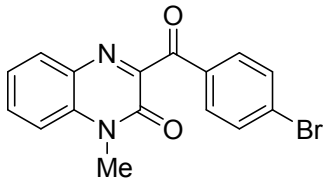
3-(4-chlorobenzoyl)-1-methylquinoxalin-2(1H)-one (3ae)[3]



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 – 7.91 (m, 3 H), 7.72 – 7.67 (m, 1 H), 7.48 – 7.41 (m, 4 H), 3.75

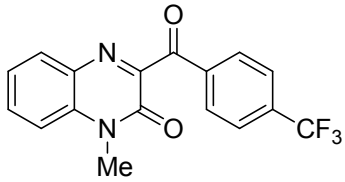
(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.4, 153.9, 153.2, 140.8, 133.9, 133.2, 132.3, 132.1, 131.3, 131.1, 129.0, 124.3, 114.0, 29.1.

3-(4-bromobenzoyl)-1-methylquinoxalin-2(1H)-one (3af)[3]



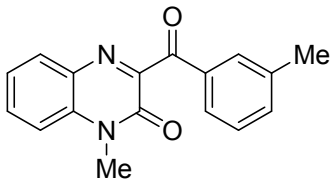
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 – 7.92 (m, 1 H), 7.87 – 7.84 (m, 2 H), 7.72 – 7.68 (m, 1 H), 7.65 – 7.62 (m, 2 H), 7.45 – 7.41 (m, 2 H), 3.76 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.6, 153.9, 153.2, 133.9, 133.6, 132.3, 132.1, 132.0, 131.4, 131.1, 129.7, 124.3, 114.0, 29.1.

methyl-3-(4-(trifluoromethyl)benzoyl)quinoxalin-2(1H)-one (3ag)



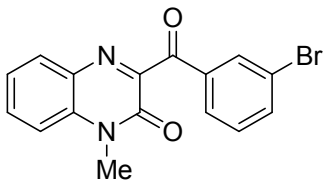
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, J = 8.0 Hz, 2 H), 7.95 – 7.92 (m, 1 H), 7.76 – 7.69 (m, 3 H), 7.46 – 7.42 (m, 2 H), 3.77 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.6, 153.4, 153.2, 137.6, 135.1 (q, $J_{C\text{-}F}$ = 32.8 Hz), 134.0, 132.6, 132.1, 131.2, 130.2, 125.7 (q, $J_{C\text{-}F}$ = 3.6 Hz), 124.4, 123.5 (q, $J_{C\text{-}F}$ = 271.2 Hz), 114.1, 29.1; ^{19}F NMR (376 MHz, $CDCl_3$) : δ = -63.2; HRMS (ESI) m/z calcd. for $C_{17}H_{12}F_3N_2O_2[M+H]^+$: 333.0845, found 333.0842.

methyl-3-(3-methylbenzoyl)quinoxalin-2(1H)-one (3ah)[1]



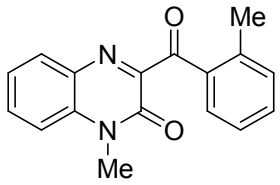
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1 H), 7.79 – 7.75 (m, 2 H), 7.70 – 7.65 (m, 1 H), 7.44 – 7.34 (m, 4 H), 3.75 (s, 3 H), 2.39 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.0, 154.9, 153.3, 138.5, 135.1, 134.8, 133.8, 132.2, 131.9, 130.9, 130.2, 128.5, 127.3, 124.1, 113.9, 29.0, 21.3.

3-(3-bromobenzoyl)-1-methylquinoxalin-2(1H)-one (3ai)[3]



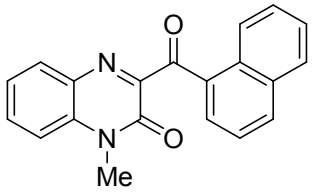
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 (s, 1 H), 7.94 – 7.90 (m, 2 H), 7.75 – 7.68 (m, 2 H), 7.45 – 7.35 (m, 3 H), 3.75 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.3, 153.6, 153.2, 137.0, 136.6, 133.9, 132.7, 132.4, 132.1, 131.1, 130.2, 128.5, 124.3, 122.9, 114.0, 29.1;

methyl-3-(2-methylbenzoyl)quinoxalin-2(1H)-one (3aj)[1]



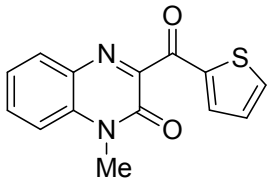
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 – 7.90 (m, 1 H), 7.69 – 7.64 (m, 1 H), 7.60 (d, *J* = 7.6 Hz, 1 H), 7.47 – 7.39 (m, 3 H), 7.33 (d, *J* = 7.6 Hz, 1 H), 7.23 (t, *J* = 7.6 Hz, 1 H), 3.74 (s, 3 H), 2.69 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.0, 155.6, 153.2, 140.7, 134.1, 133.7, 132.9, 132.2, 132.2, 131.9, 131.8, 130.9, 125.6, 124.1, 113.9, 28.9, 21.7.

3-(1-naphthoyl)-1-methylquinoxalin-2(1H)-one (3ak)[3]



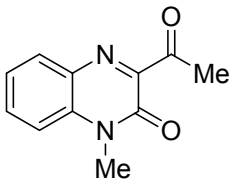
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.15 (d, *J* = 8.8, 1 H), 8.06 (d, *J* = 8.0, 1 H), 7.91 (d, *J* = 8.4, 2 H), 7.86 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1 H), 7.71 – 7.63 (m, 2 H), 7.60 – 7.57 (m, 1 H), 7.47 – 7.37 (m, 3 H), 3.72 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.0, 155.6, 153.4, 134.8, 134.0, 133.8, 132.9, 132.2, 131.9, 131.4, 131.0, 130.9, 128.8, 128.5, 126.7, 126.1, 124.2, 124.1, 113.9, 28.9.

methyl-3-(thiophene-2-carbonyl)quinoxalin-2(1H)-one (3al)[3]



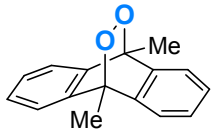
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1 H), 7.80 – 7.78 (m, 2 H), 7.71 – 7.67 (m, 1 H), 7.44 – 7.39 (m, 2 H), 7.17 – 7.15 (m, 1 H), 3.76 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 183.0, 152.9, 152.8, 141.5, 136.1, 136.1, 134.1, 132.4, 131.8, 131.1, 128.3, 124.2, 114.0, 29.1.

3-acetyl-1-methylquinoxalin-2(1H)-one (3am)[1]



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1 H), 7.70 – 7.66 (m, 1 H), 7.43 – 7.39 (m, 1 H), 7.36 (d, *J* = 8.4 Hz, 1 H), 3.73 (s, 3 H), 2.72 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.2, 152.9, 151.8, 134.4, 132.8, 131.9, 131.5, 124.2, 113.9, 29.0, 28.5.

9,10-dimethyl-9,10-dihydro-9,10-epidioxyanthracene (5b)



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 – 7.38 (m, 4 H), 7.31 – 7.27 (m, 4 H), 2.16 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.7, 127.4, 120.7, 79.5, 13.7.

4. References

1. Zeng, X.; Liu, C.; Wang, X.; Zhang, J.; Wang, X.; Hu, Y., Silver-catalyzed decarboxylative acylation of quinoxalin-2(1H)-ones with α-oxo-carboxylic acids. *Org. Biomol. Chem.* **2017,** *15* (42), 8929-8935.

2. Mamedov, V. A.; Kalinin, A. A.; Gubaidullin, A. T.; Chernova, A. V.; Litvinov, I. A.; Levin, Y. A.; Shagidullin, R. R., Ring contraction in reactions of 3-benzoylquinoxalin-2-ones with 1,2-phenylenediamines. Quinoxaline-benzoimidazole rearrangement. *Russ. Chem. Bull.* **2004,** *53* (1), 164-175.

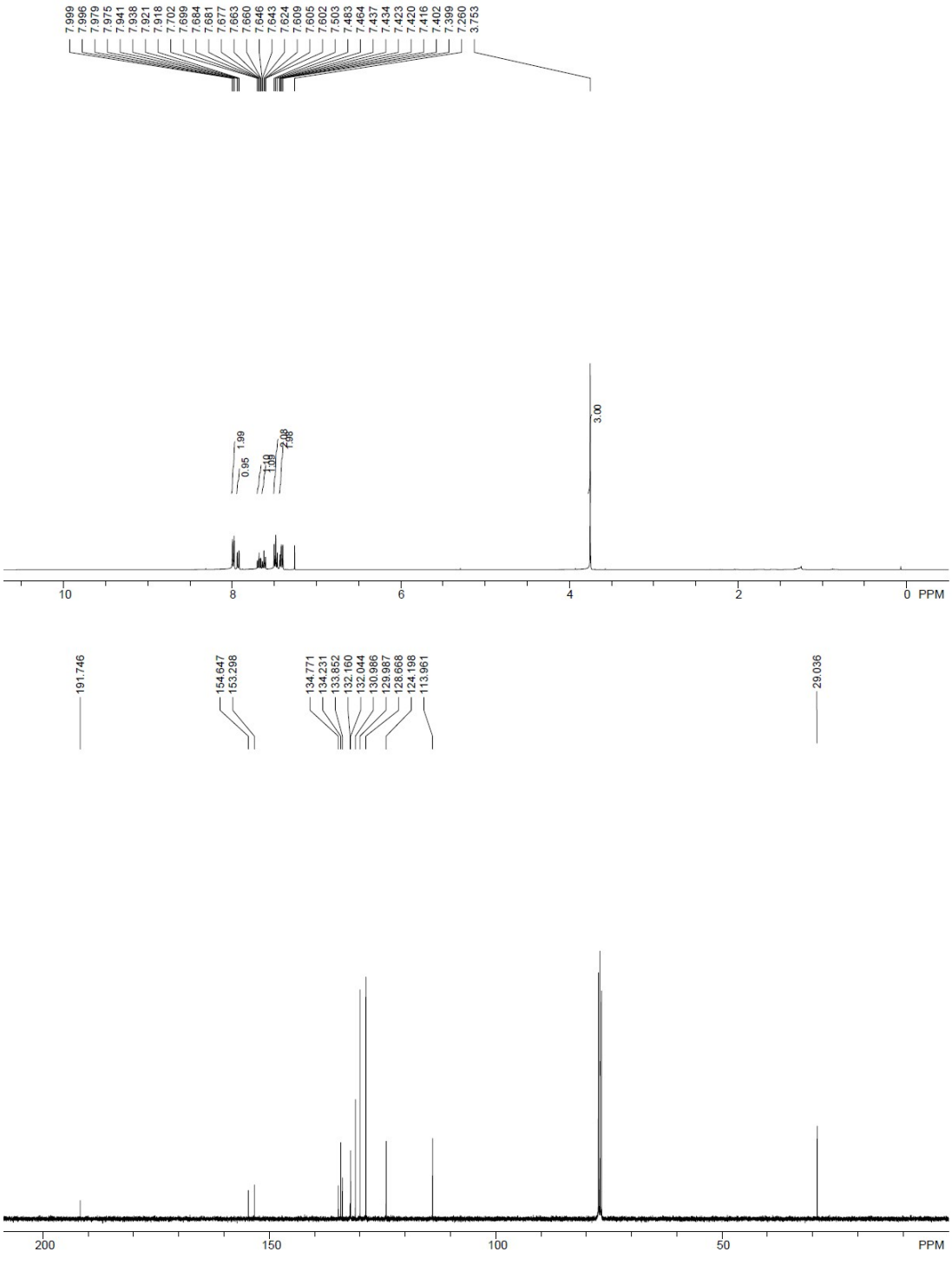
3. Yuan, J.-W.; Fu, J.-H.; Liu, S.-N.; Xiao, Y.-M.; Mao, P.; Qu, L.-B., Metal-free oxidative coupling of quinoxalin-2(1H)-ones with arylaldehydes leading to 3-acylated quinoxalin-2(1H)-ones. *Org. Biomol. Chem.* **2018,** *16* (17), 3203-3212.

4. Mtiraoui, H.; Renault, K.; Sanselme, M.; Msaddek, M.; Renard, P.-Y.; Sabot, C., Metal-free oxidative ring contraction of benzodiazepinones: an entry to quinoxalinones. *Org. Biomol. Chem.* **2017,** *15* (14), 3060-3068.

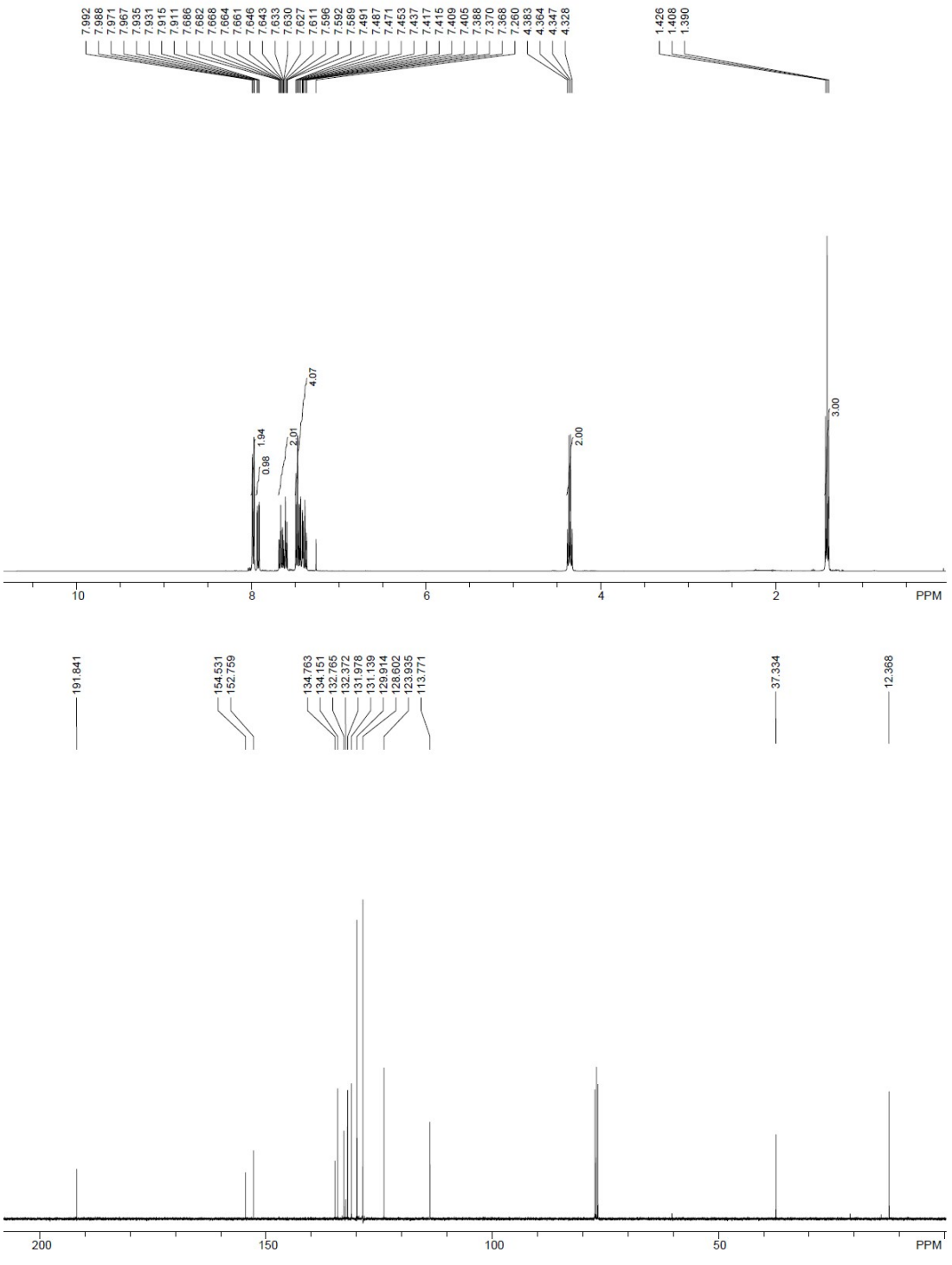
5. Xie, L.-Y.; Peng, S.; Fan, T.-G.; Liu, Y.-F.; Sun, M.; Jiang, L.-L.; Wang, X.-X.; Cao, Z.; He, W.-M., Metal-free C3-alkoxycarbonylation of quinoxalin-2(1H)-ones with carbazates as ecofriendly ester sources. *Sci. China Chem.* **2019,** *62* (4), 460-464.

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

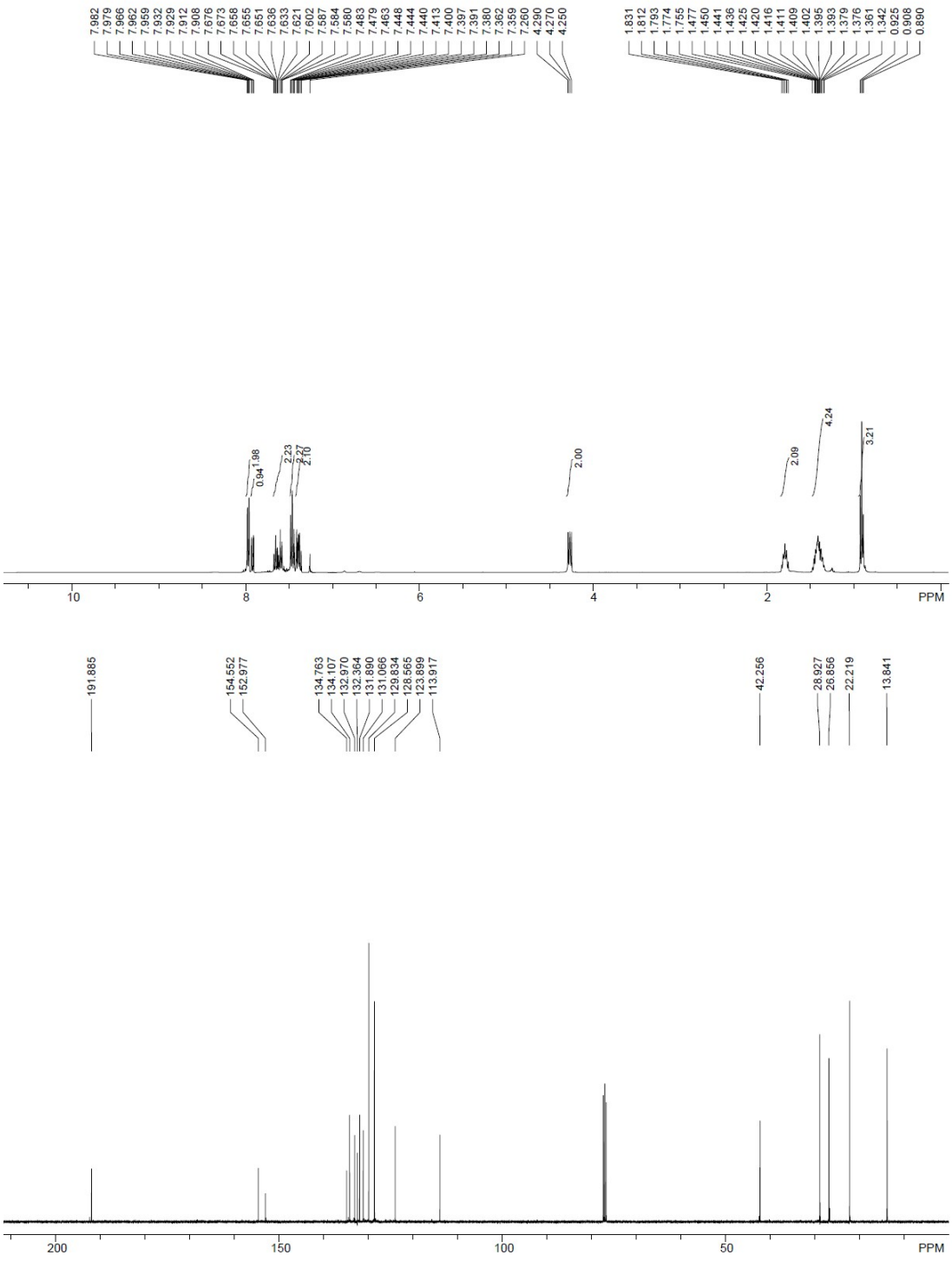
3-benzoyl-1-methylquinoxalin-2(1H)-one (3aa)



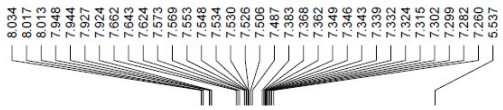
3-benzoyl-1-ethylquinoxalin-2(1H)-one (3ba)

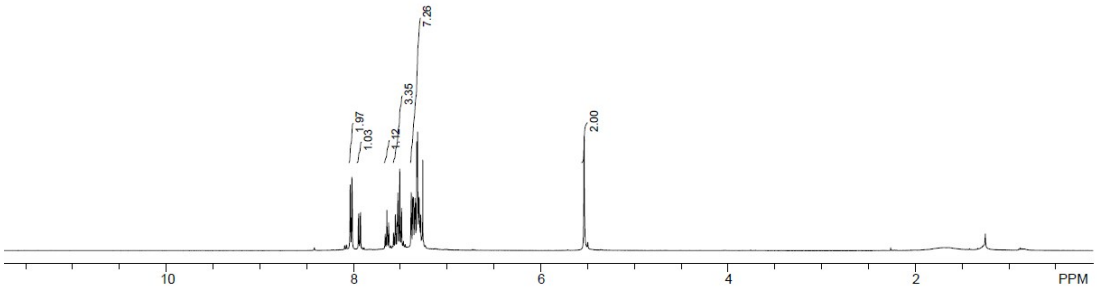


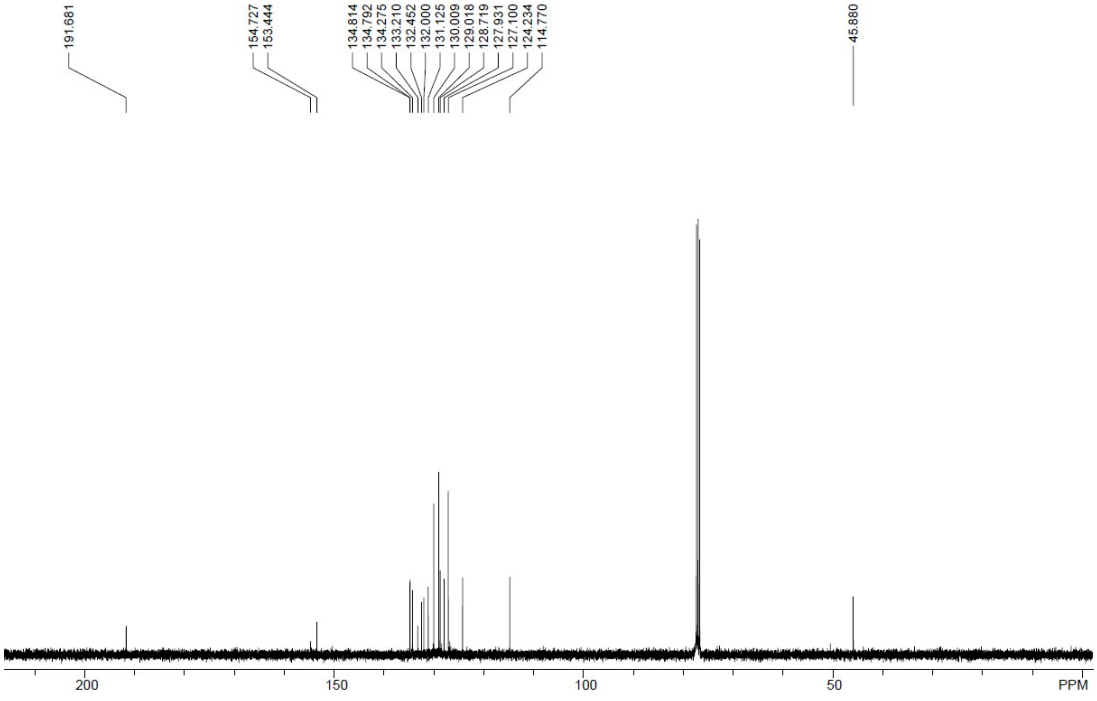
3-benzoyl-1-pentylquinoxalin-2(1H)-one (3ca)



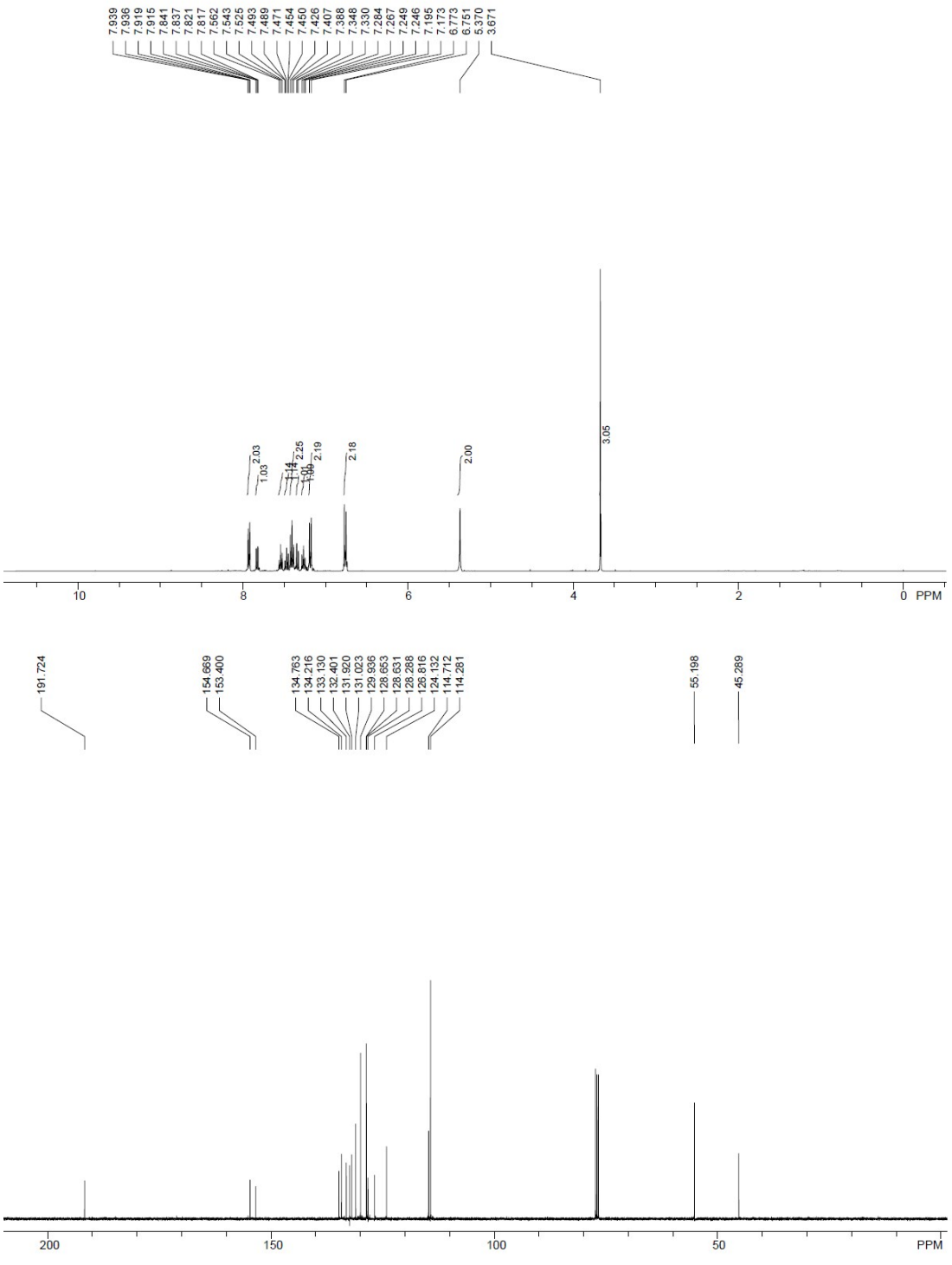
3-benzoyl-1-benzylquinoxalin-2(1H)-one (3da)



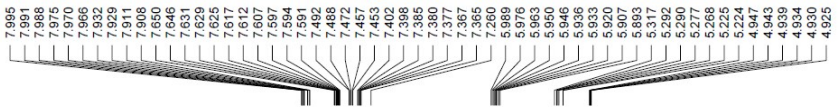


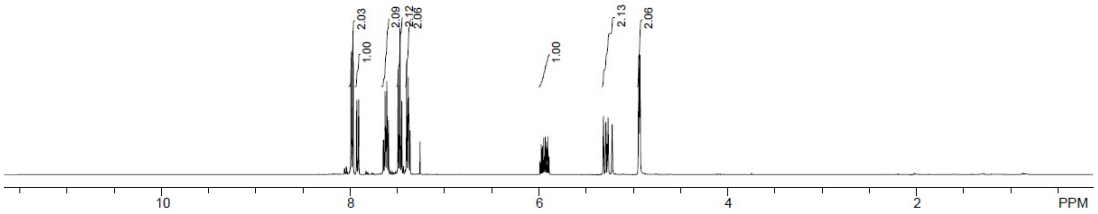


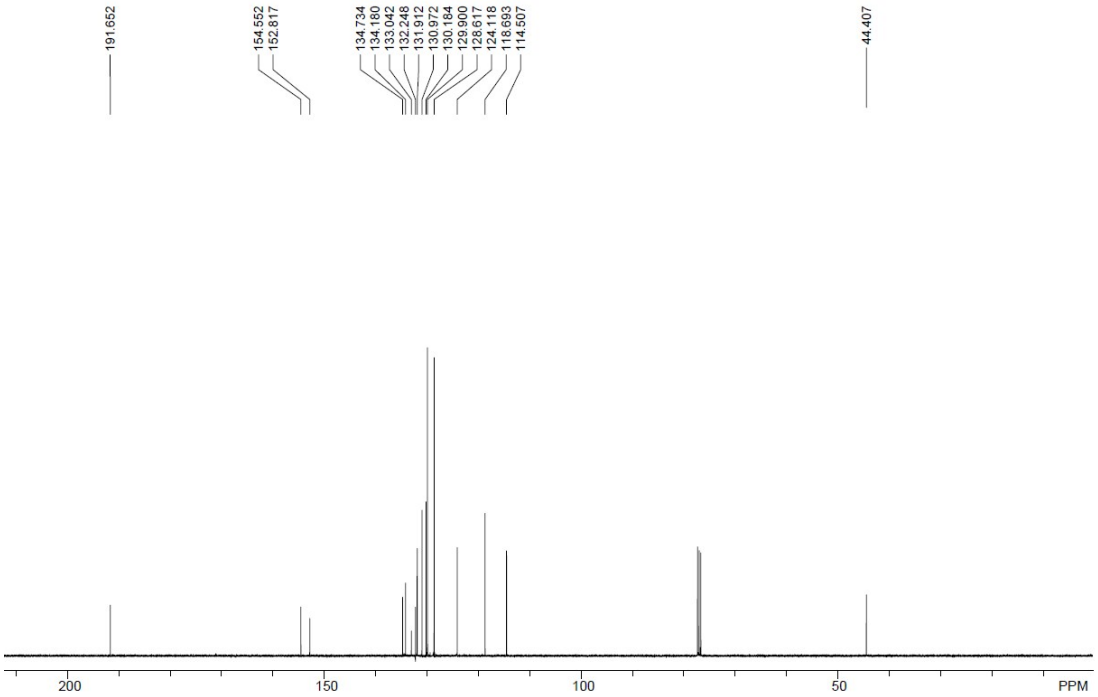
3-benzoyl-1-(4-methoxybenzyl)quinoxalin-2(1H)-one (3ea)



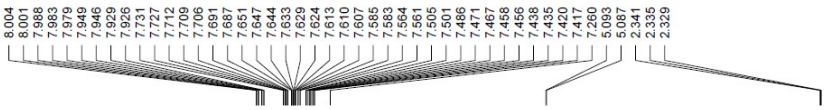
allyl-3-benzoylquinoxalin-2(1H)-one (3fa)

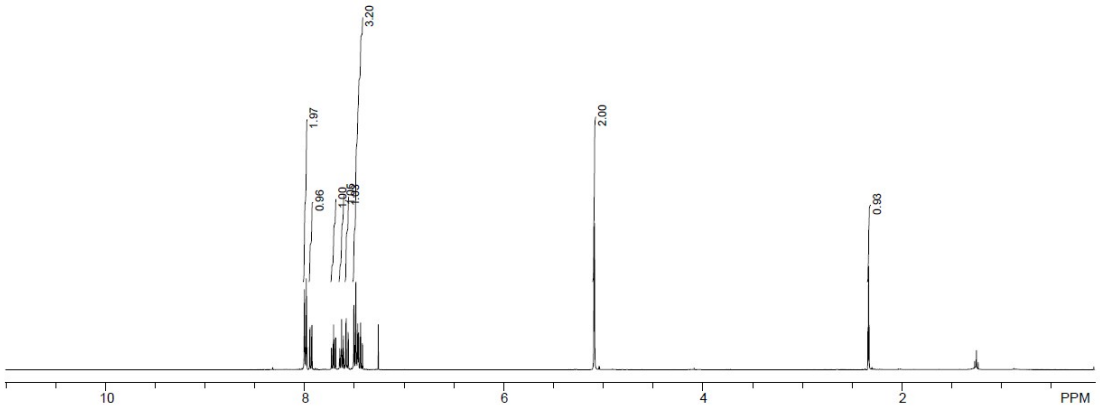


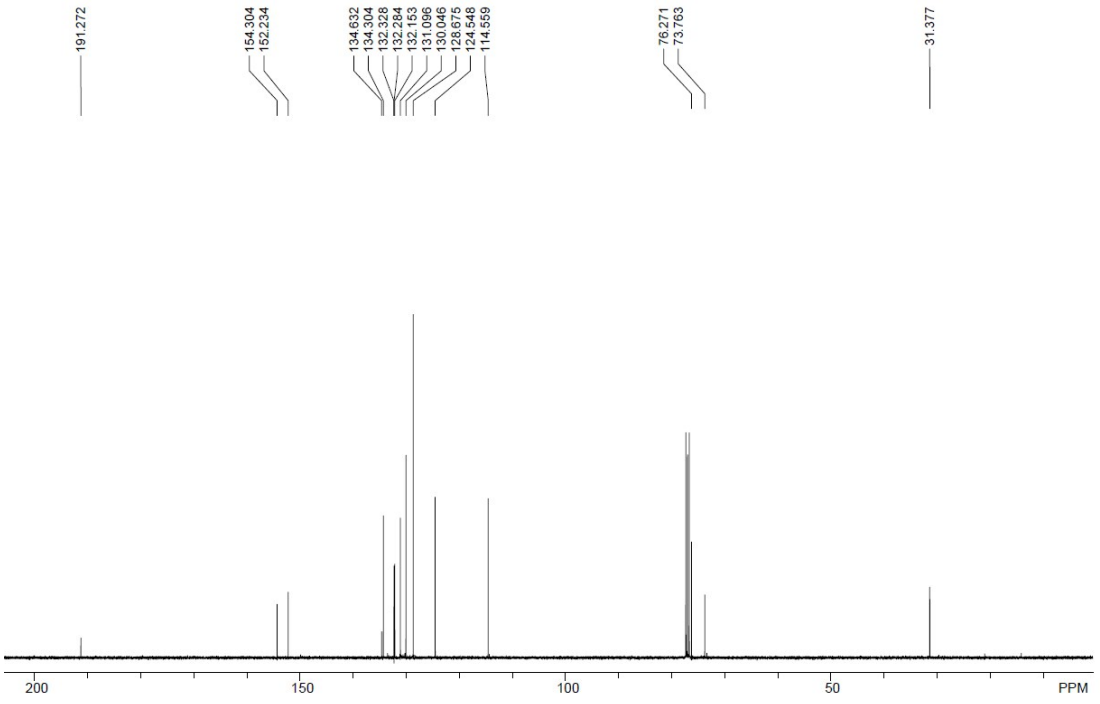




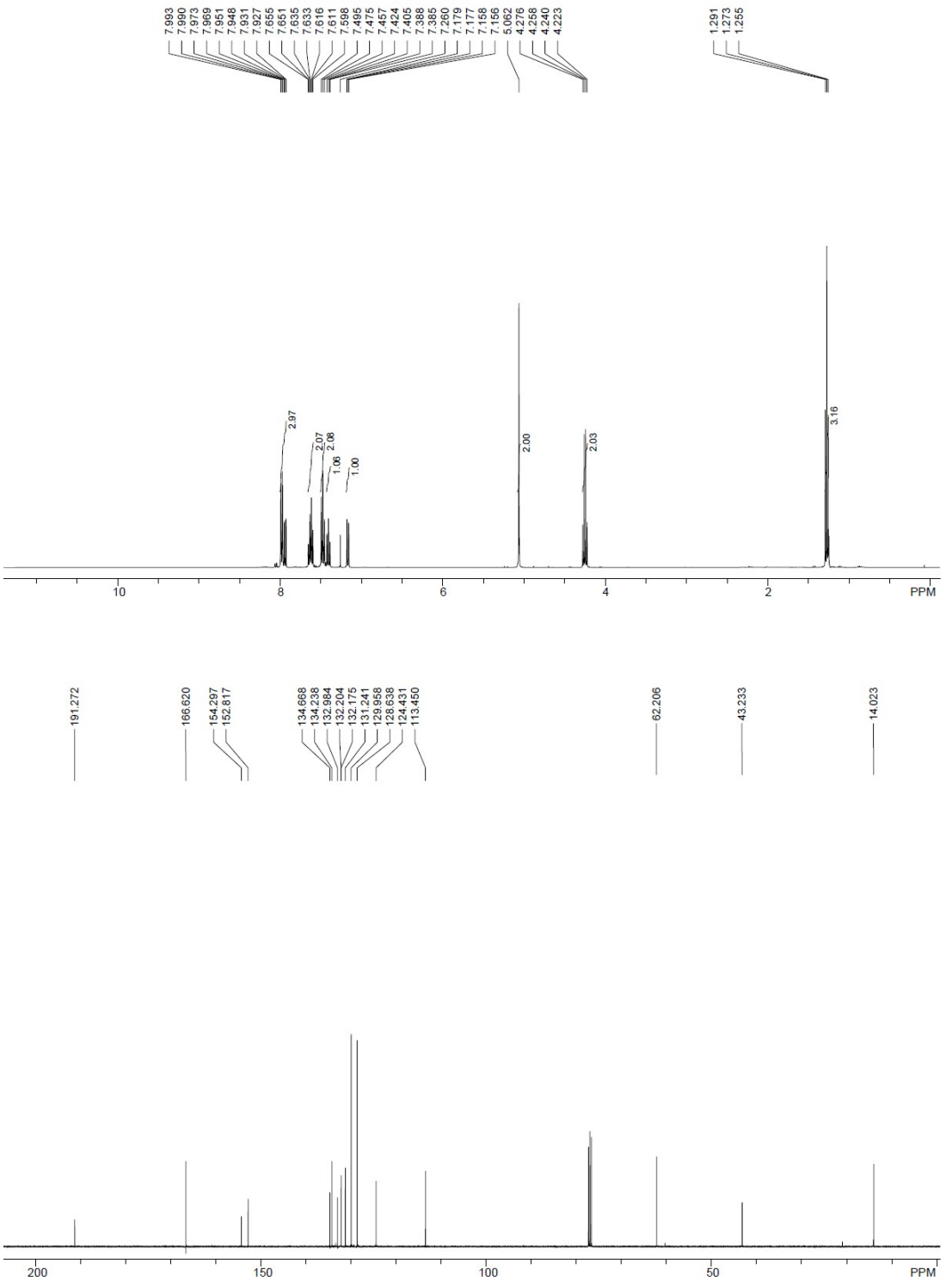
3-benzoyl-1-(prop-2-yn-1-yl)quinoxalin-2(1H)-one (3ga)



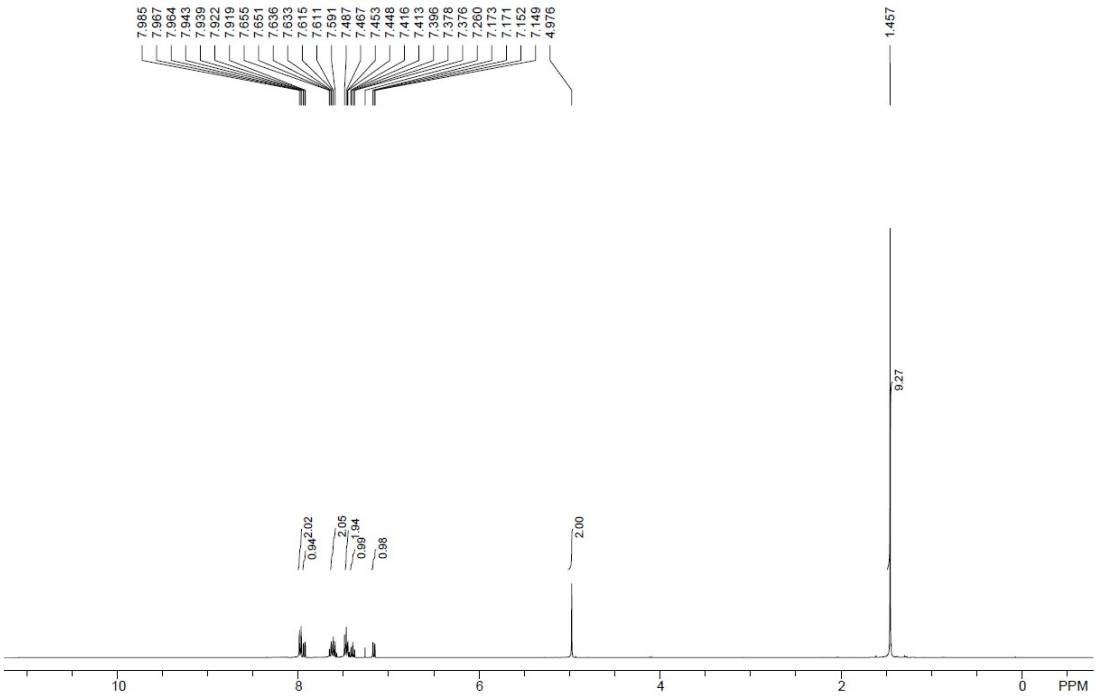


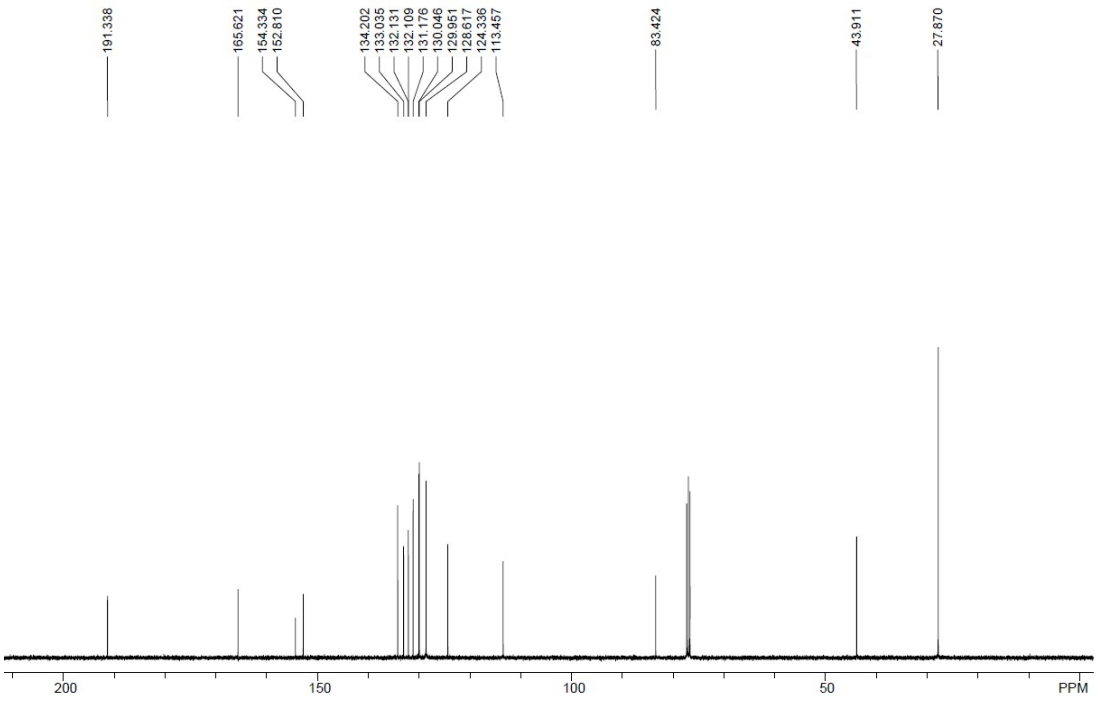


ethyl 2-(3-benzoyl-2-oxoquinoxalin-1(2H)-yl)acetate (3ha)

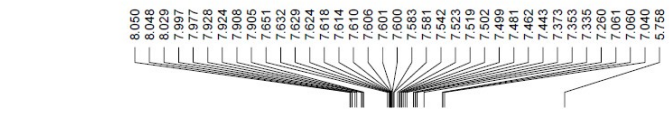


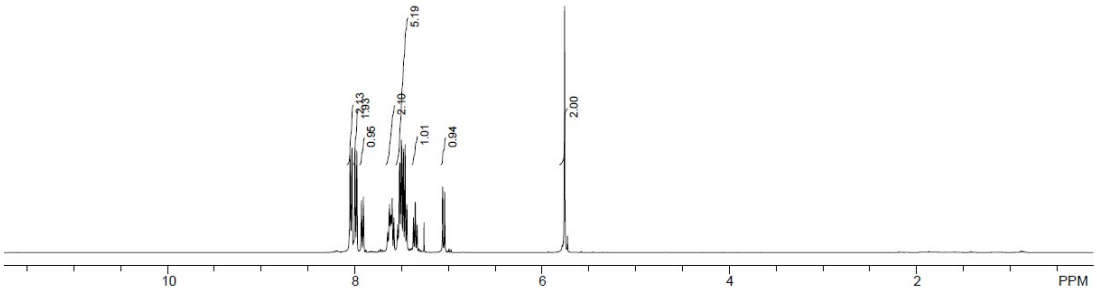
tert-butyl 2-(3-benzoyl-2-oxoquinoxalin-1(2H)-yl)acetate (3ia)

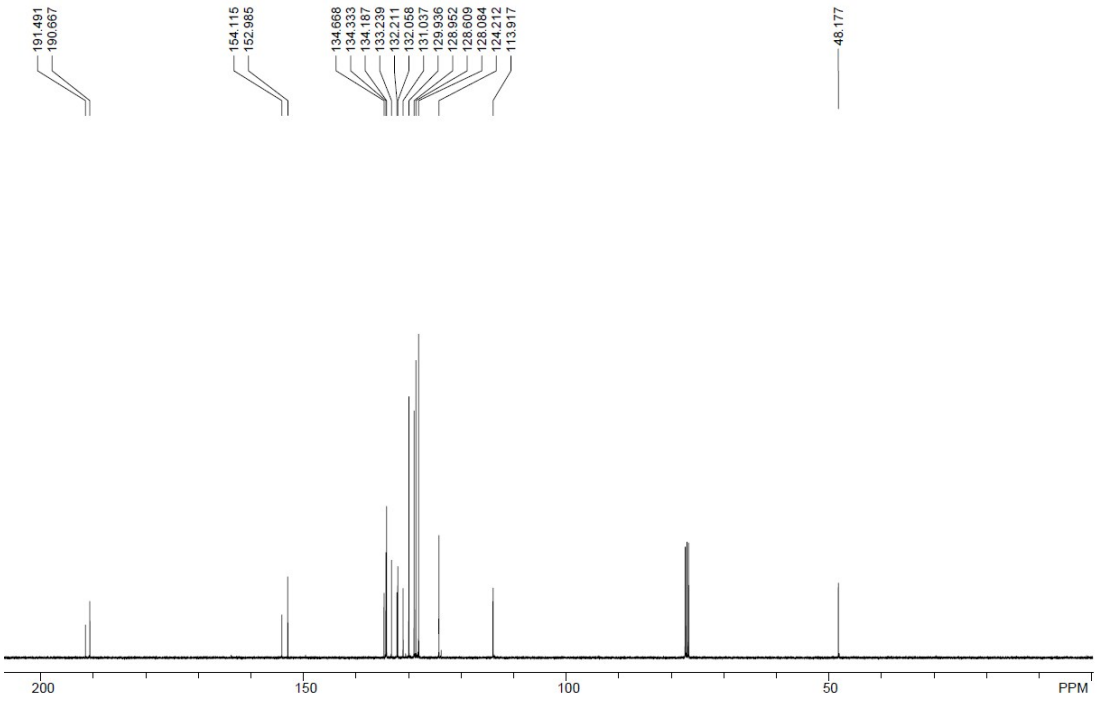




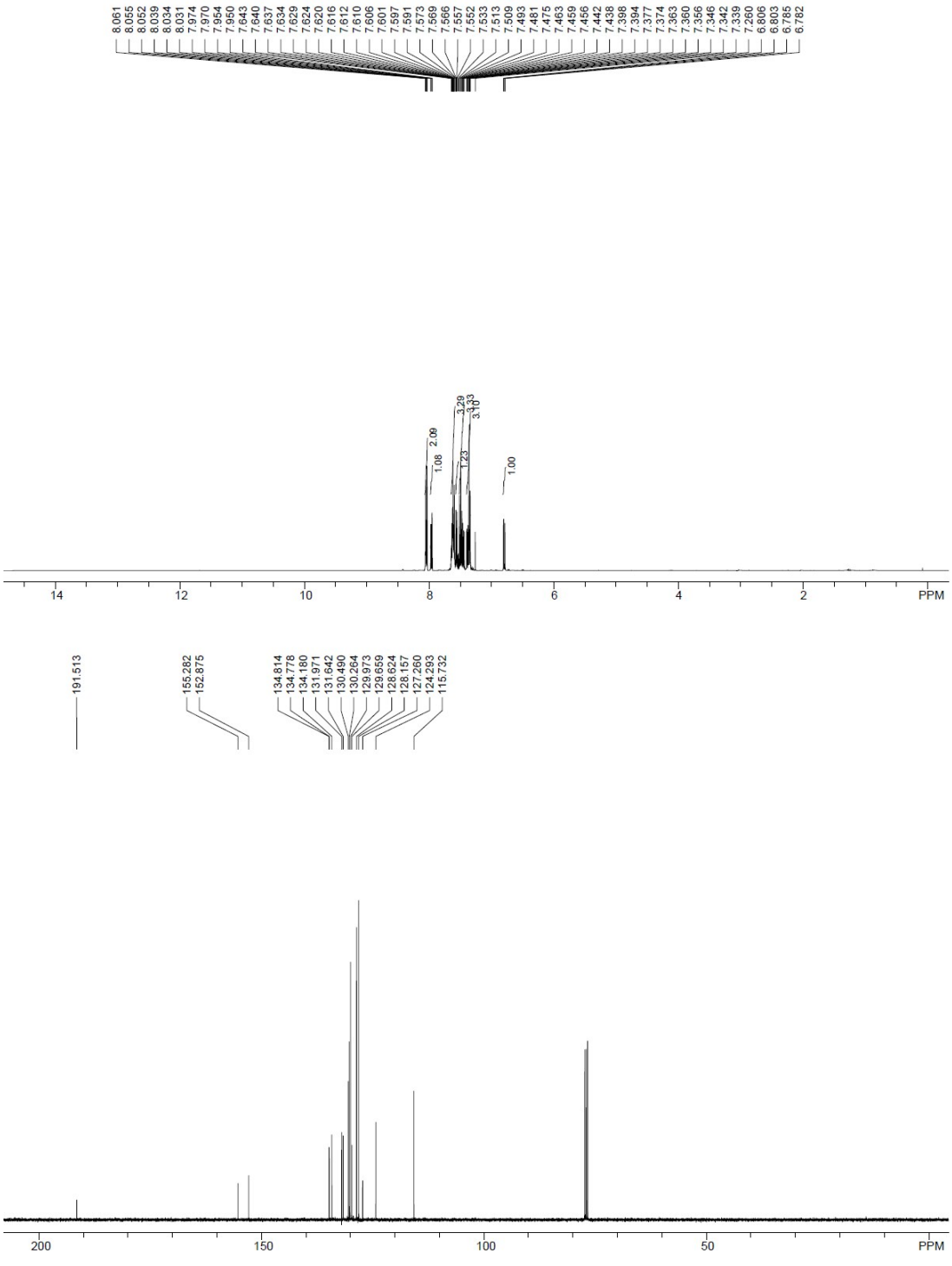
3-benzoyl-1-(2-oxo-2-phenylethyl)quinoxalin-2(1H)-one (3ja)



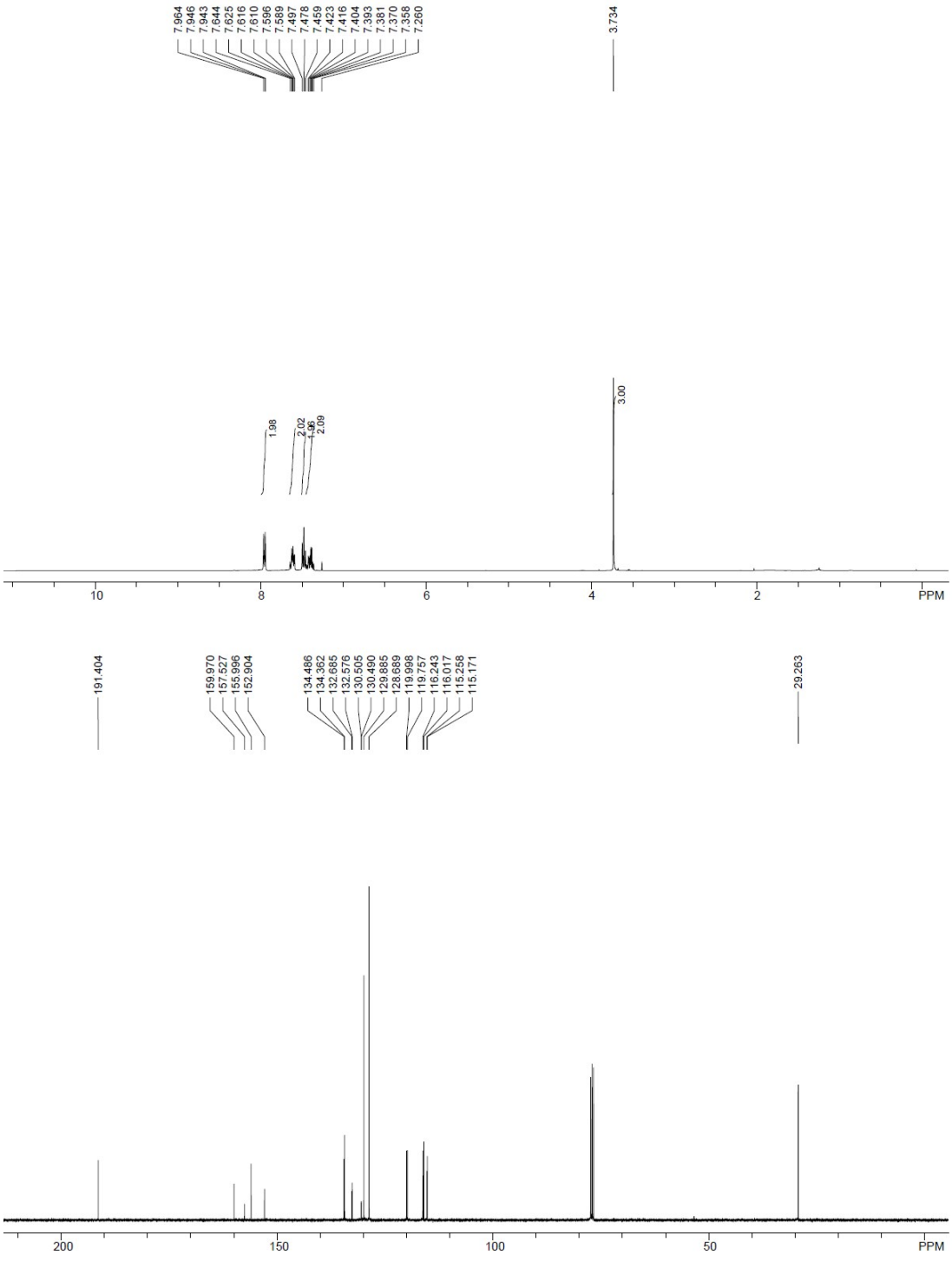




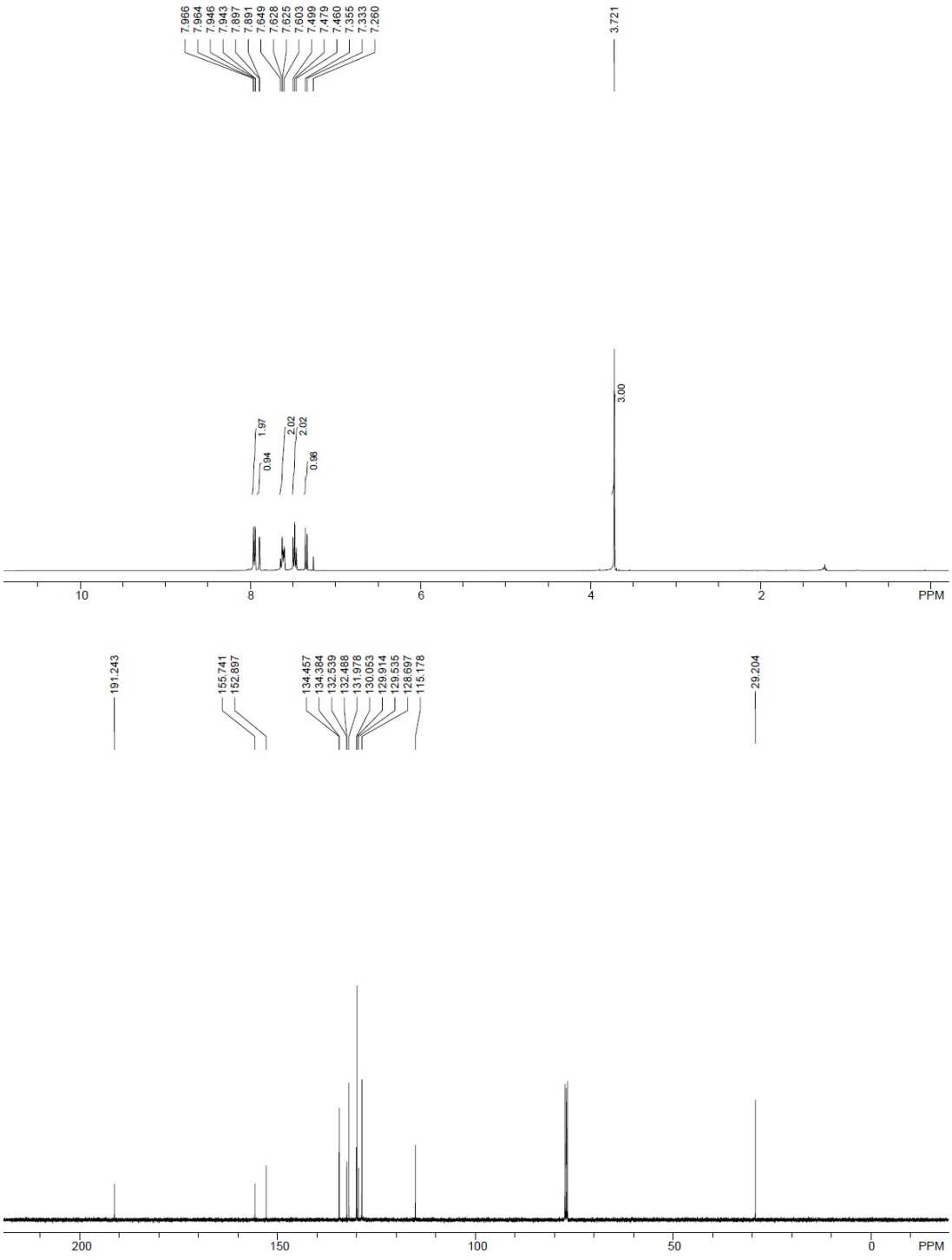
3-benzoyl-1-phenylquinoxalin-2(1H)-one (3ka)



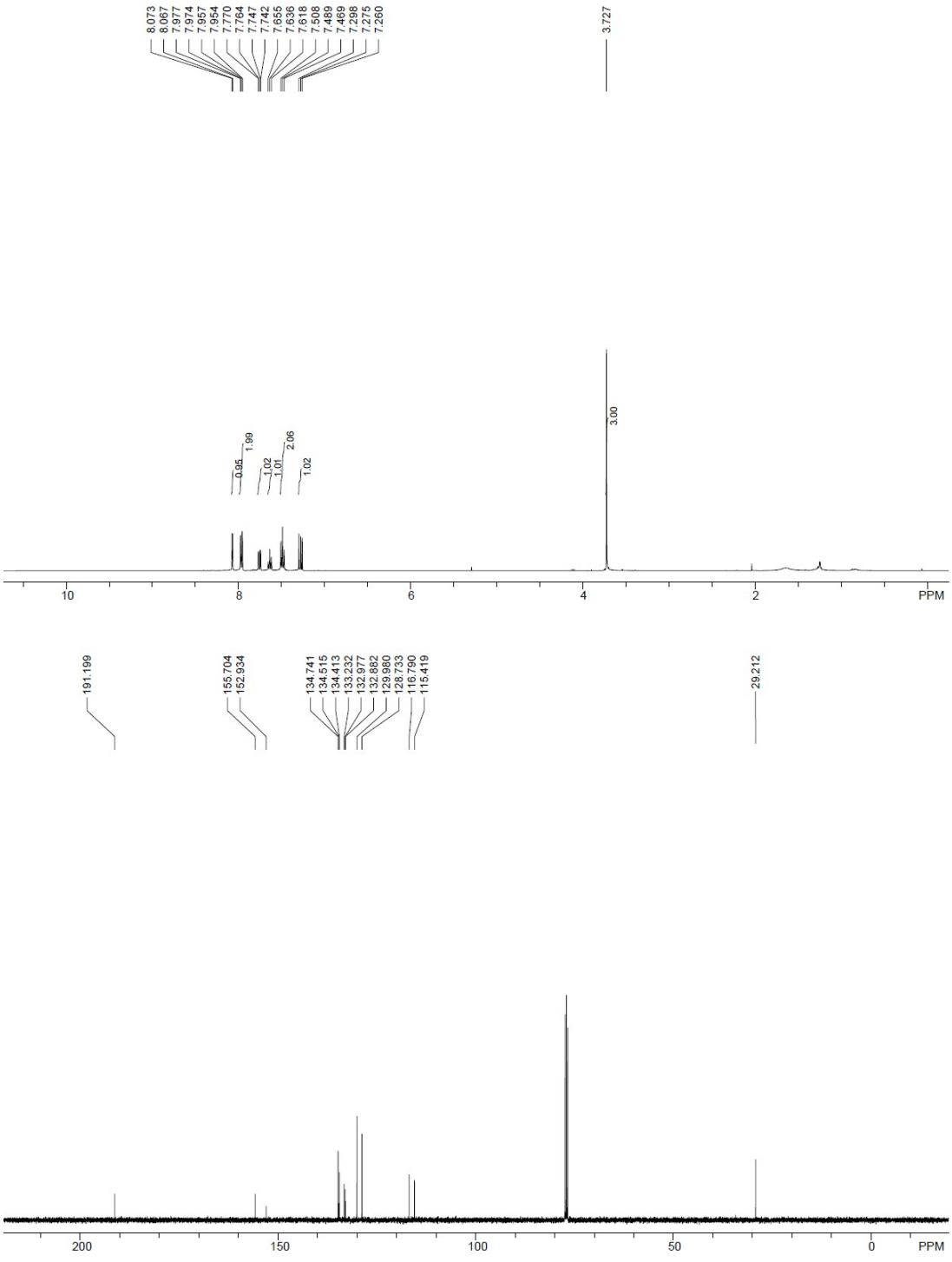
3-benzoyl-6-fluoro-1-methylquinoxalin-2(1H)-one (3la)



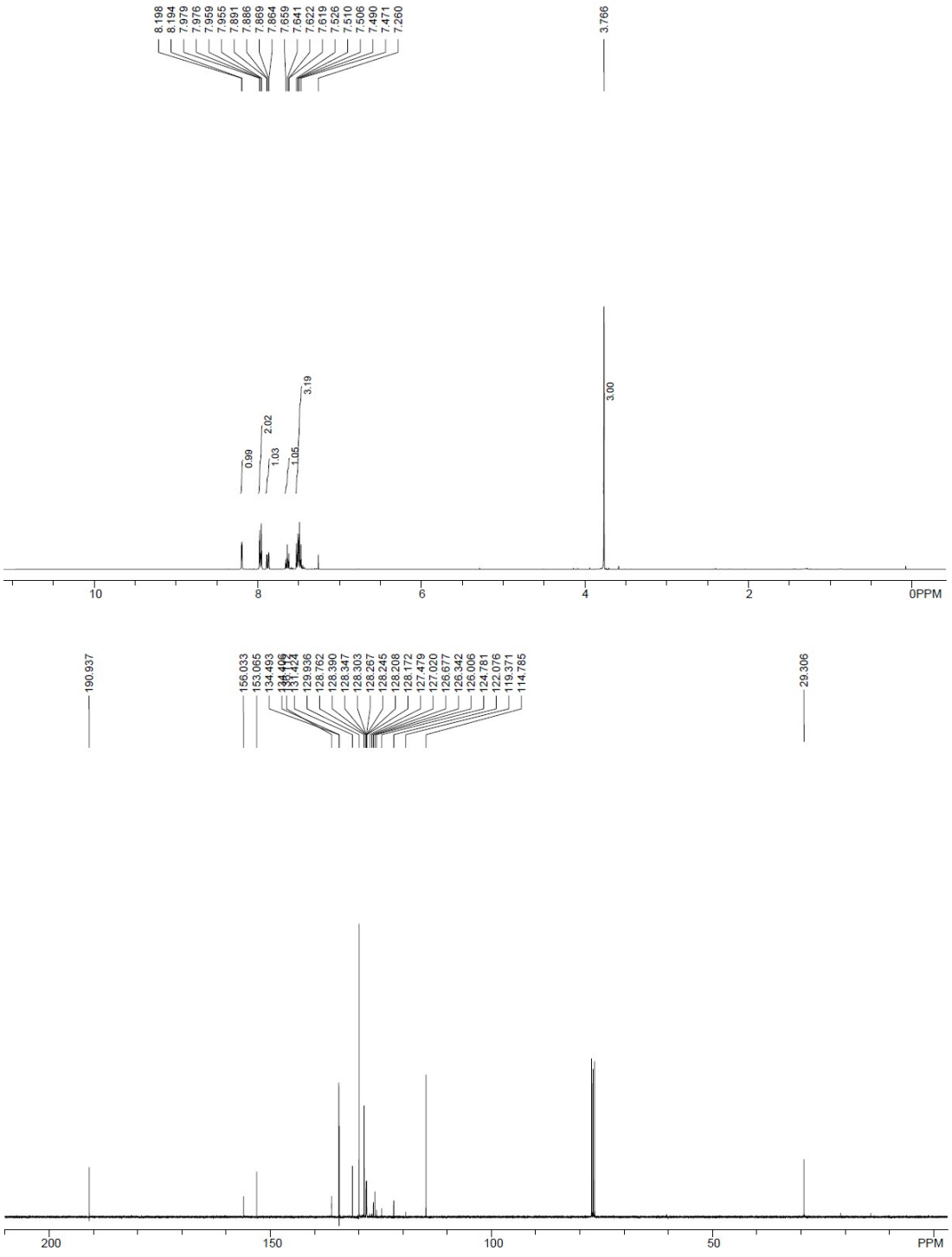
3-benzoyl-6-chloro-1-methylquinoxalin-2(1H)-one (3ma)



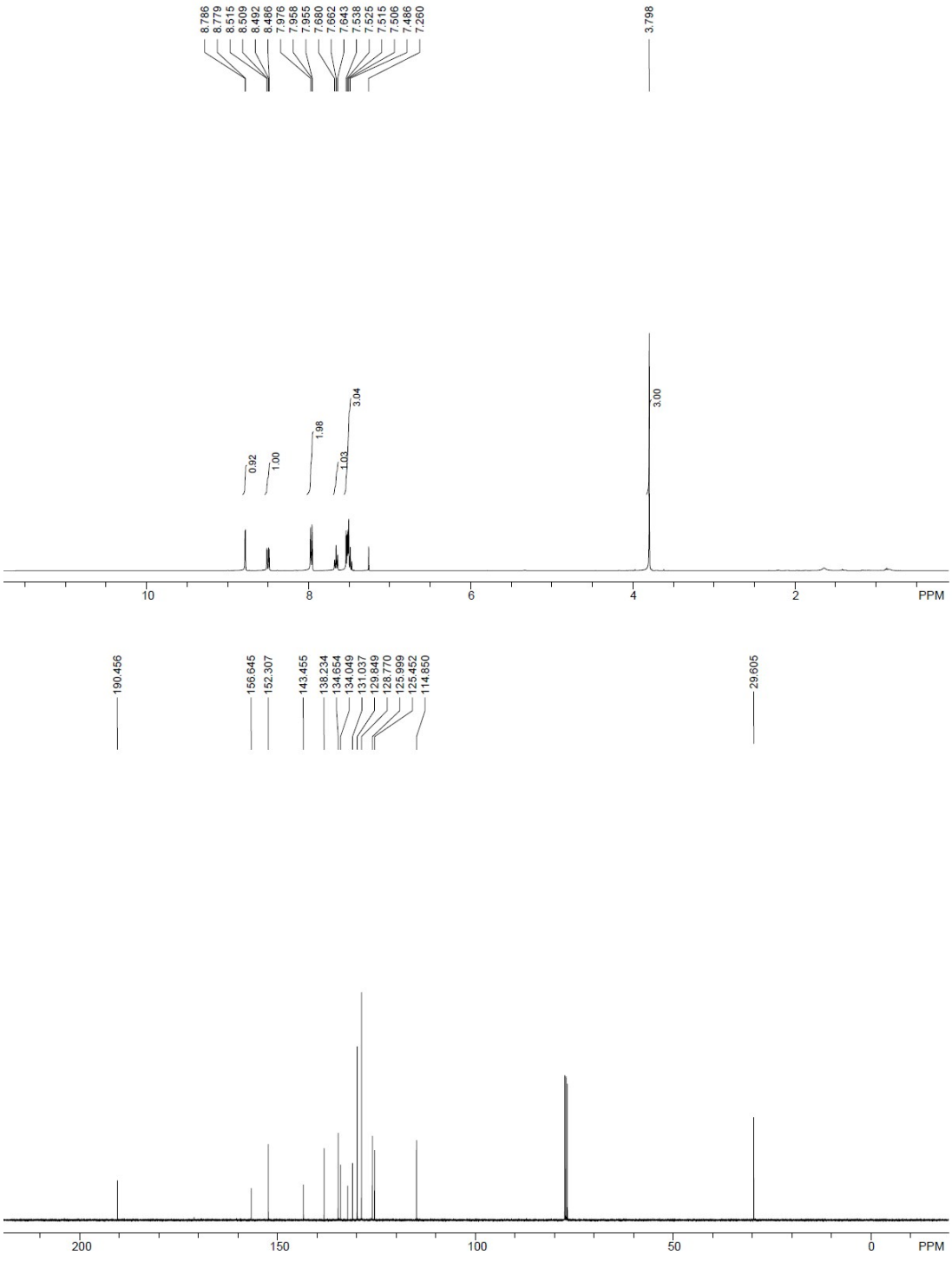
3-benzoyl-6-bromo-1-methylquinoxalin-2(1H)-one (3na)



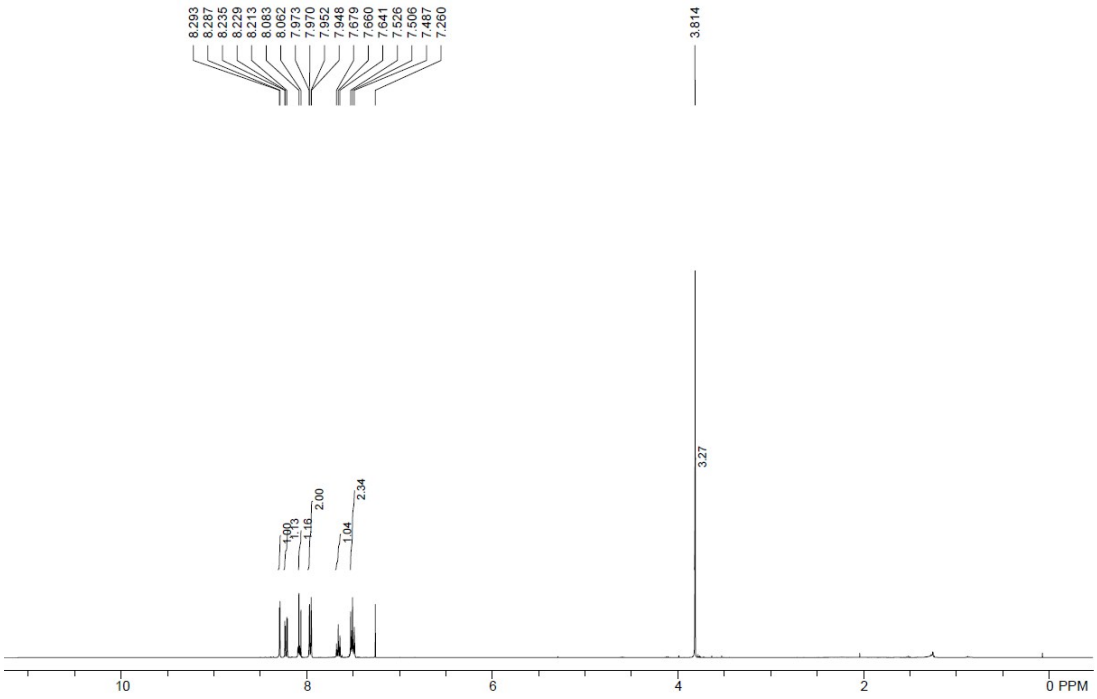
3-benzoyl-1-methyl-6-(trifluoromethyl)quinoxalin-2(1H)-one (3oa)

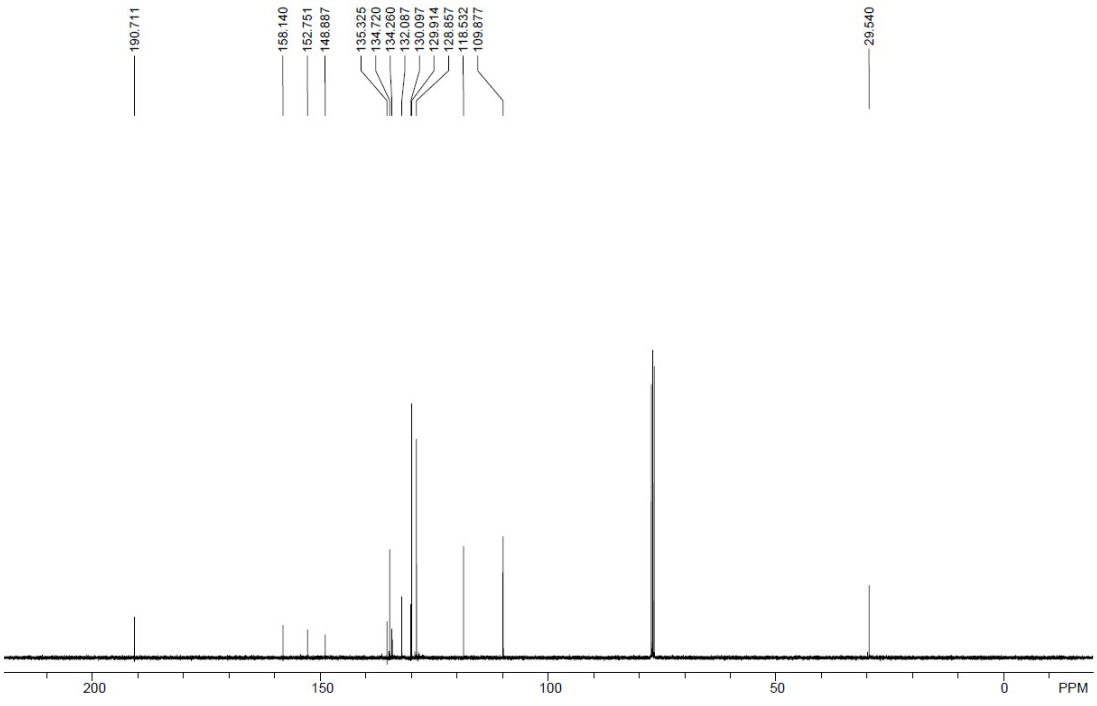


3-benzoyl-1-methyl-6-nitroquinoxalin-2(1H)-one (3pa)

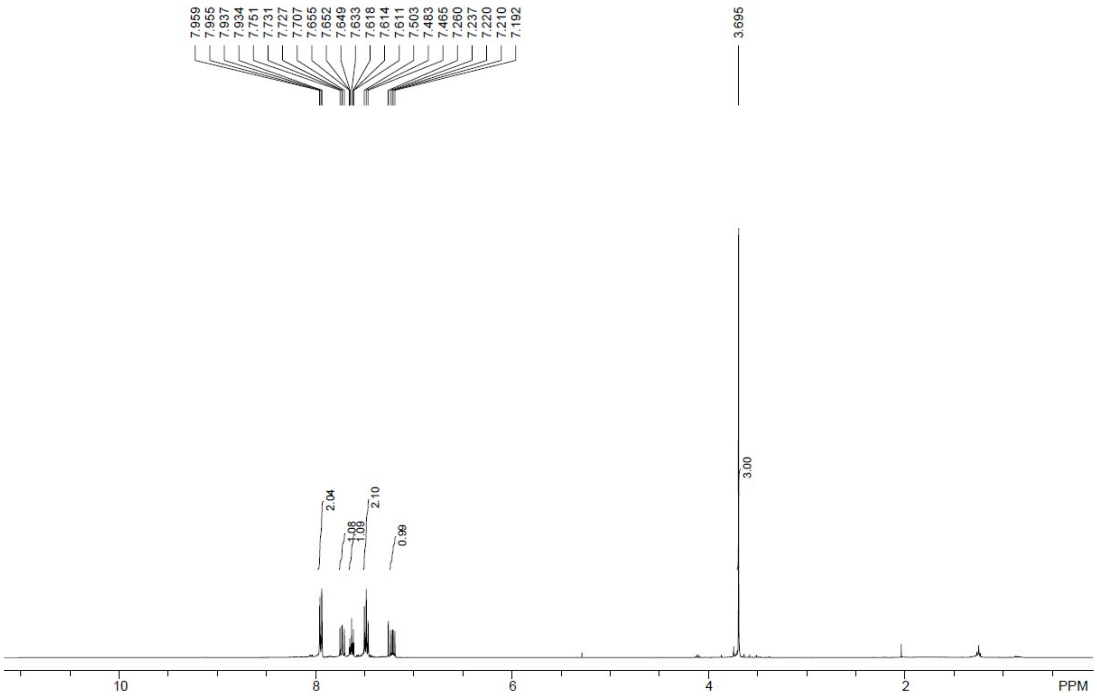


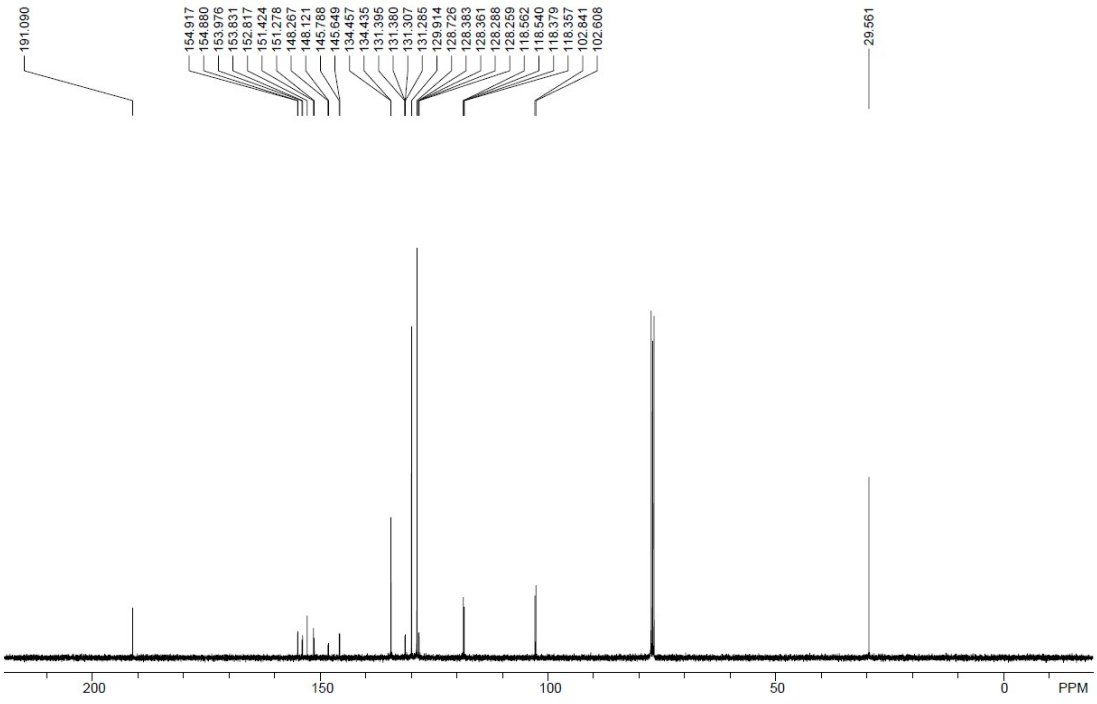
3-benzoyl-1-methyl-7-nitroquinoxalin-2(1H)-one (3qa)



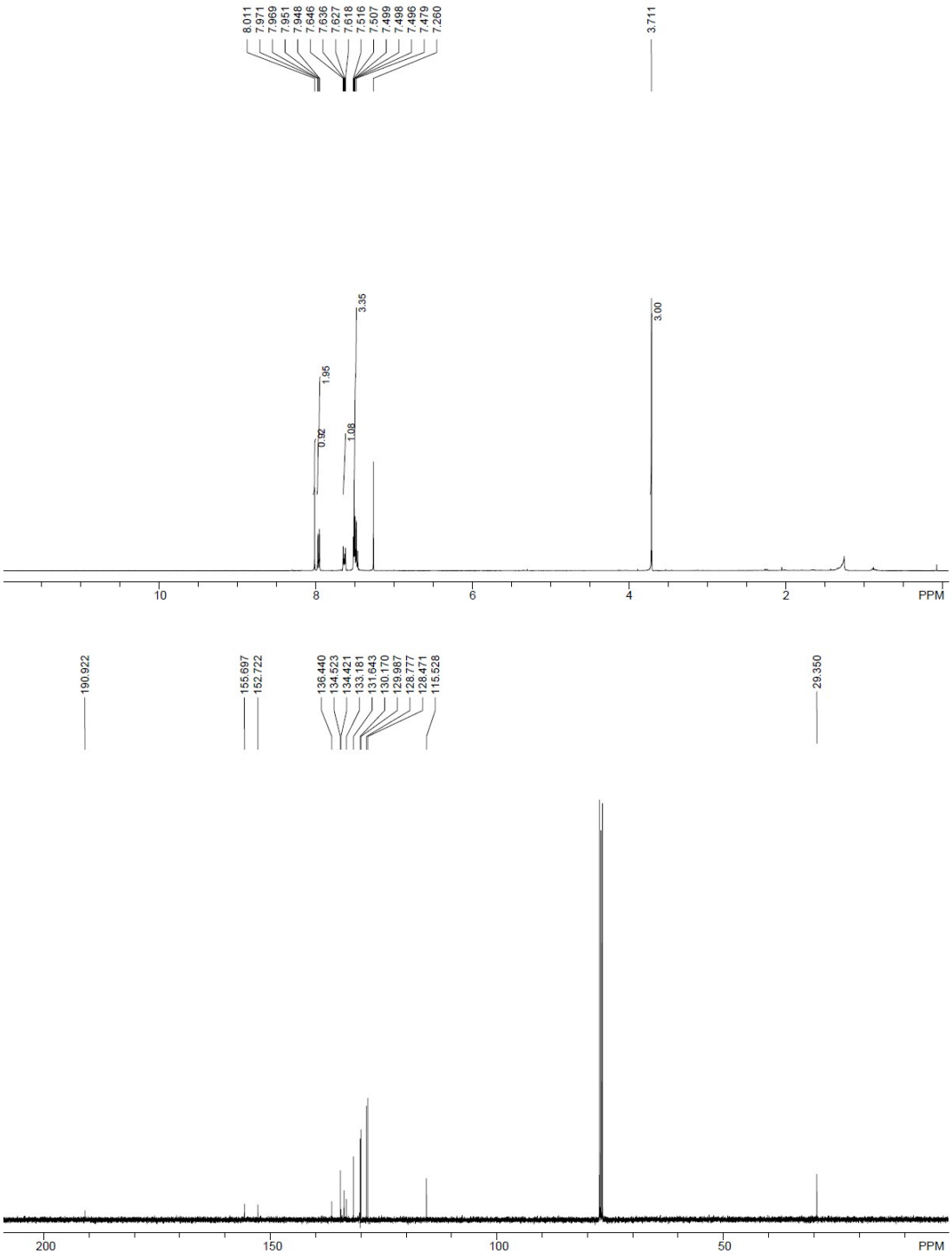


3-benzoyl-6,7-difluoro-1-methylquinoxalin-2(1H)-one (3ra)

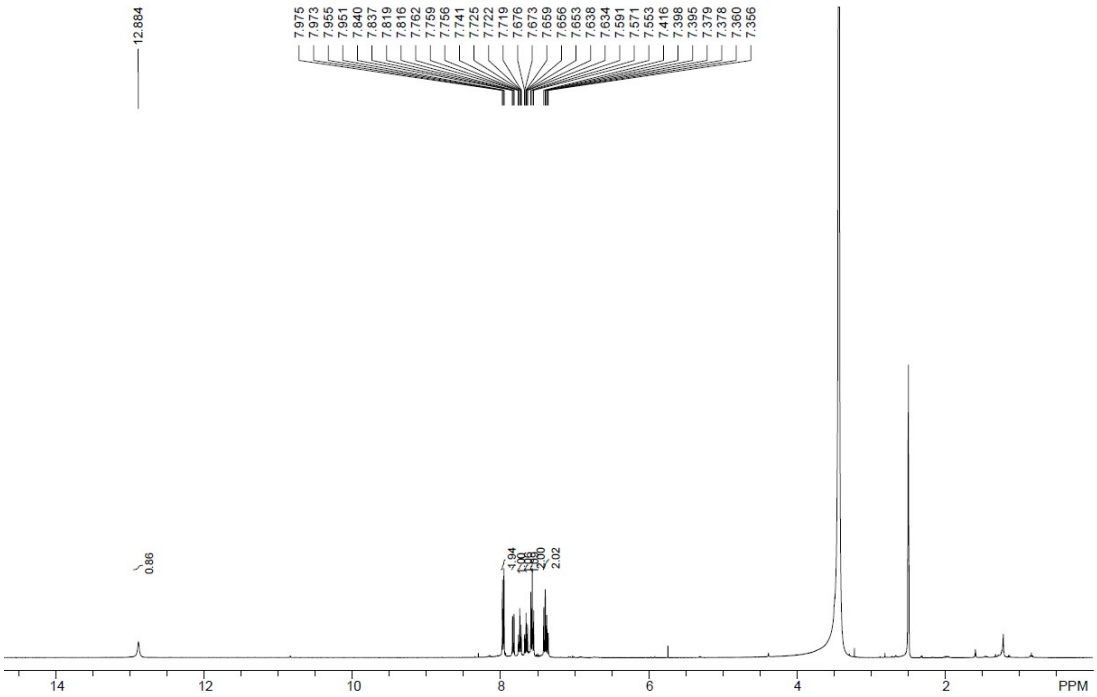


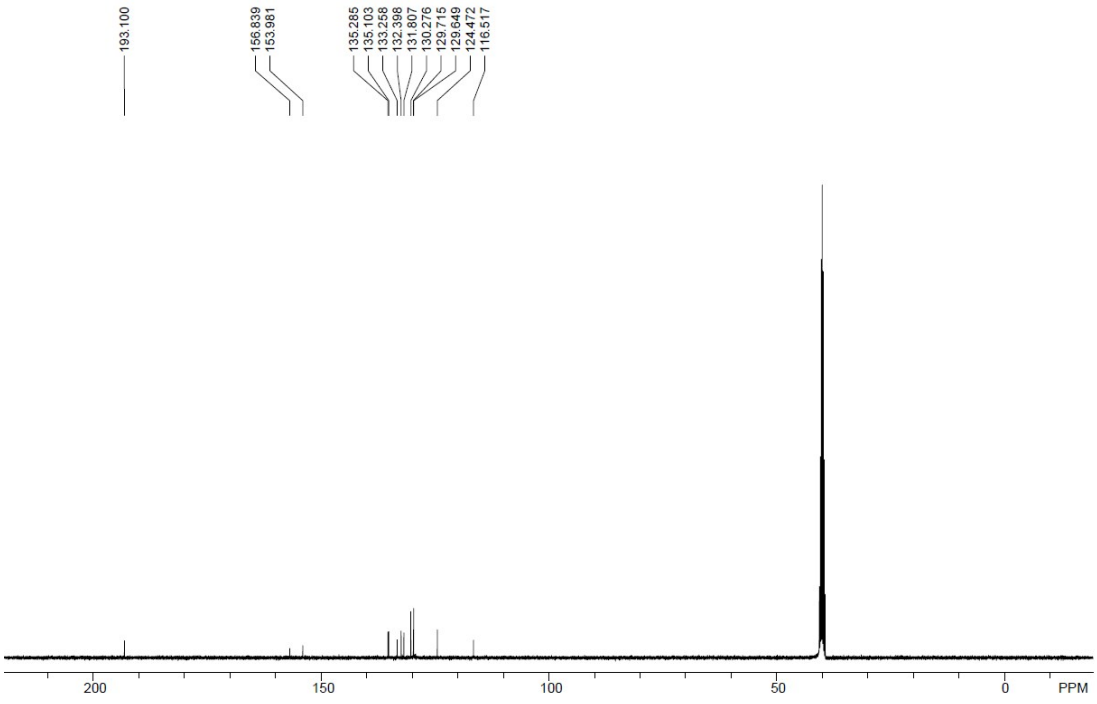


3-benzoyl-6,7-dichloro-1-methylquinoxalin-2(1H)-one (3sa)

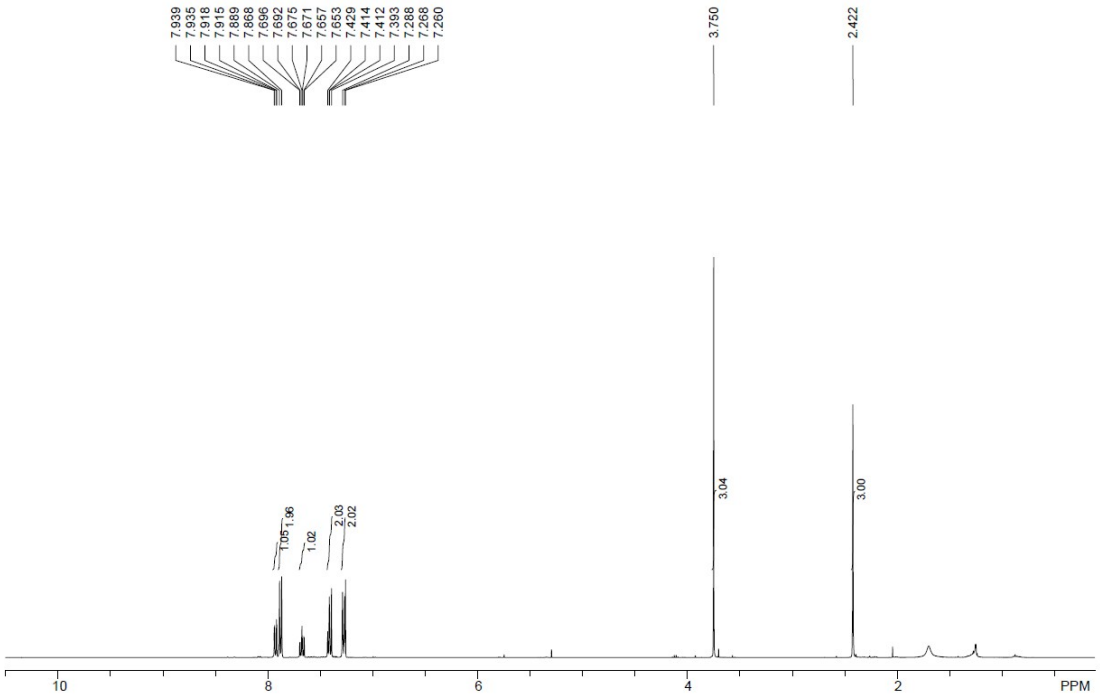


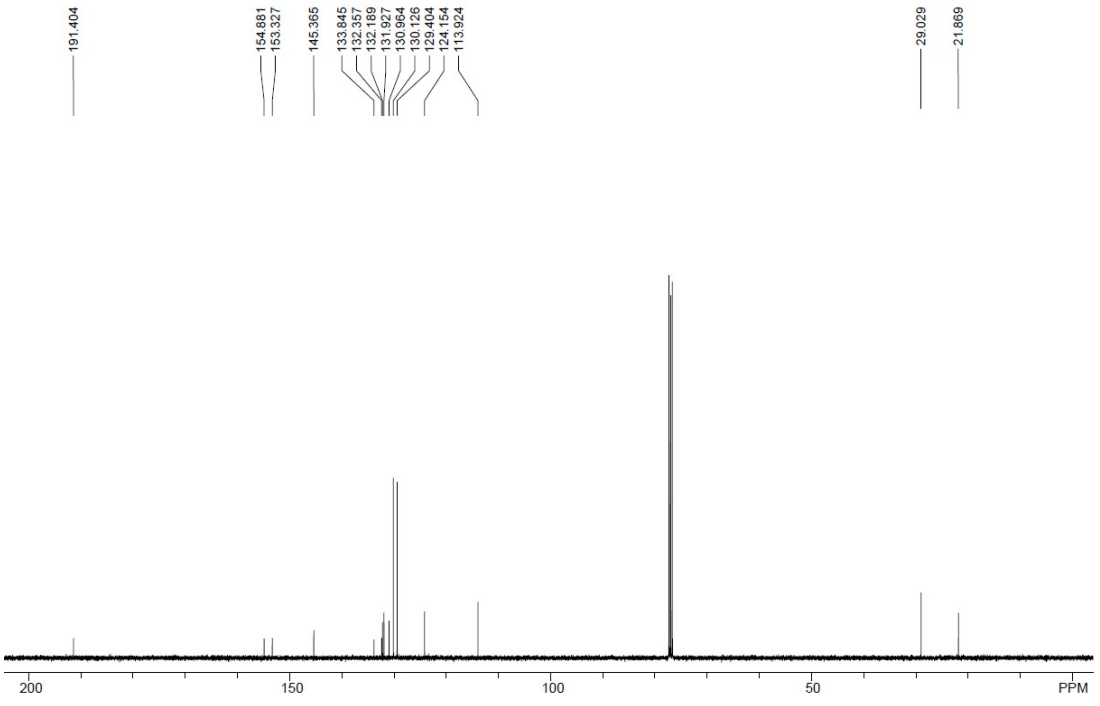
3-benzoylquinoxalin-2(1H)-one (3ta)



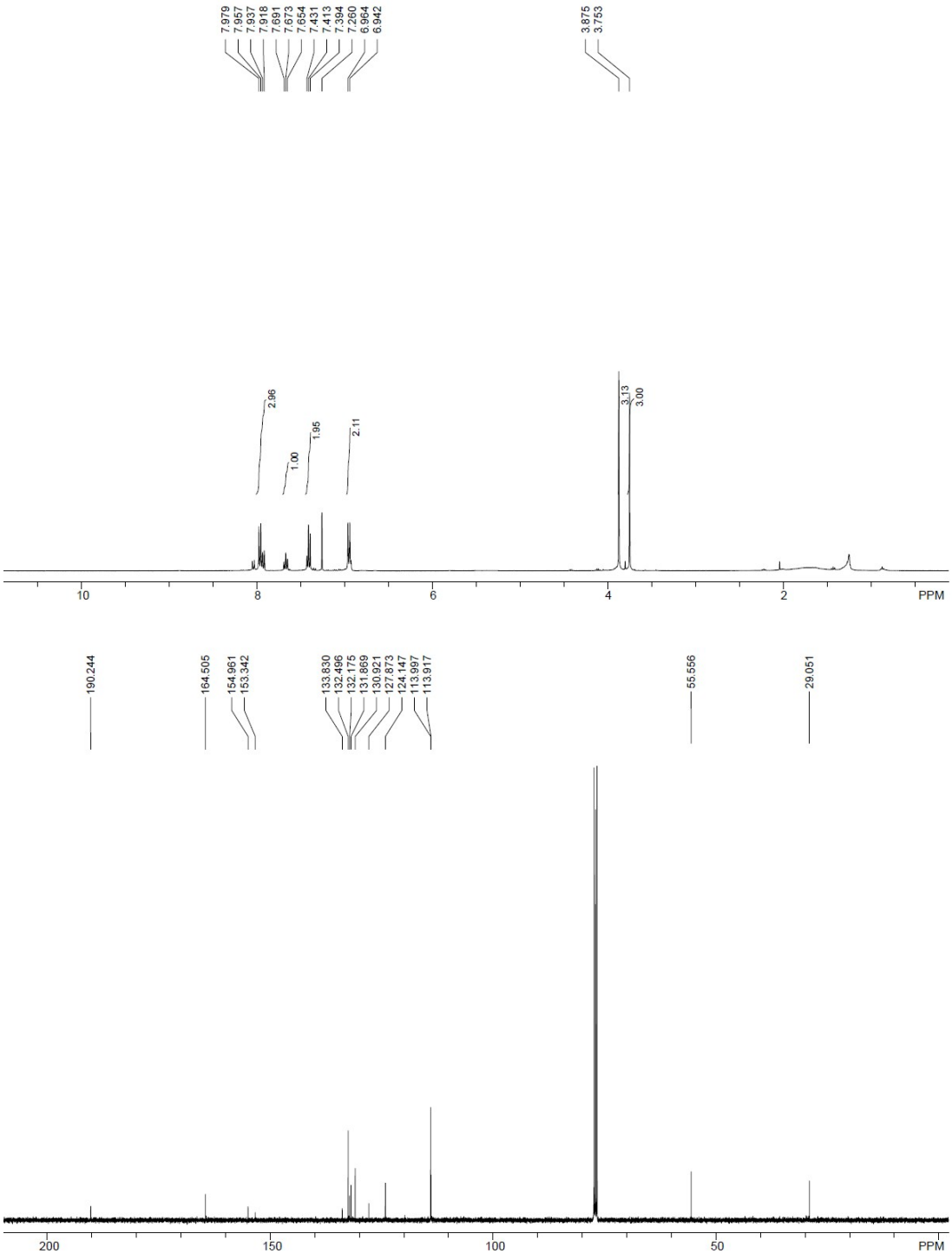


1-methyl-3-(4-methylbenzoyl)quinoxalin-2(1H)-one (3ab)

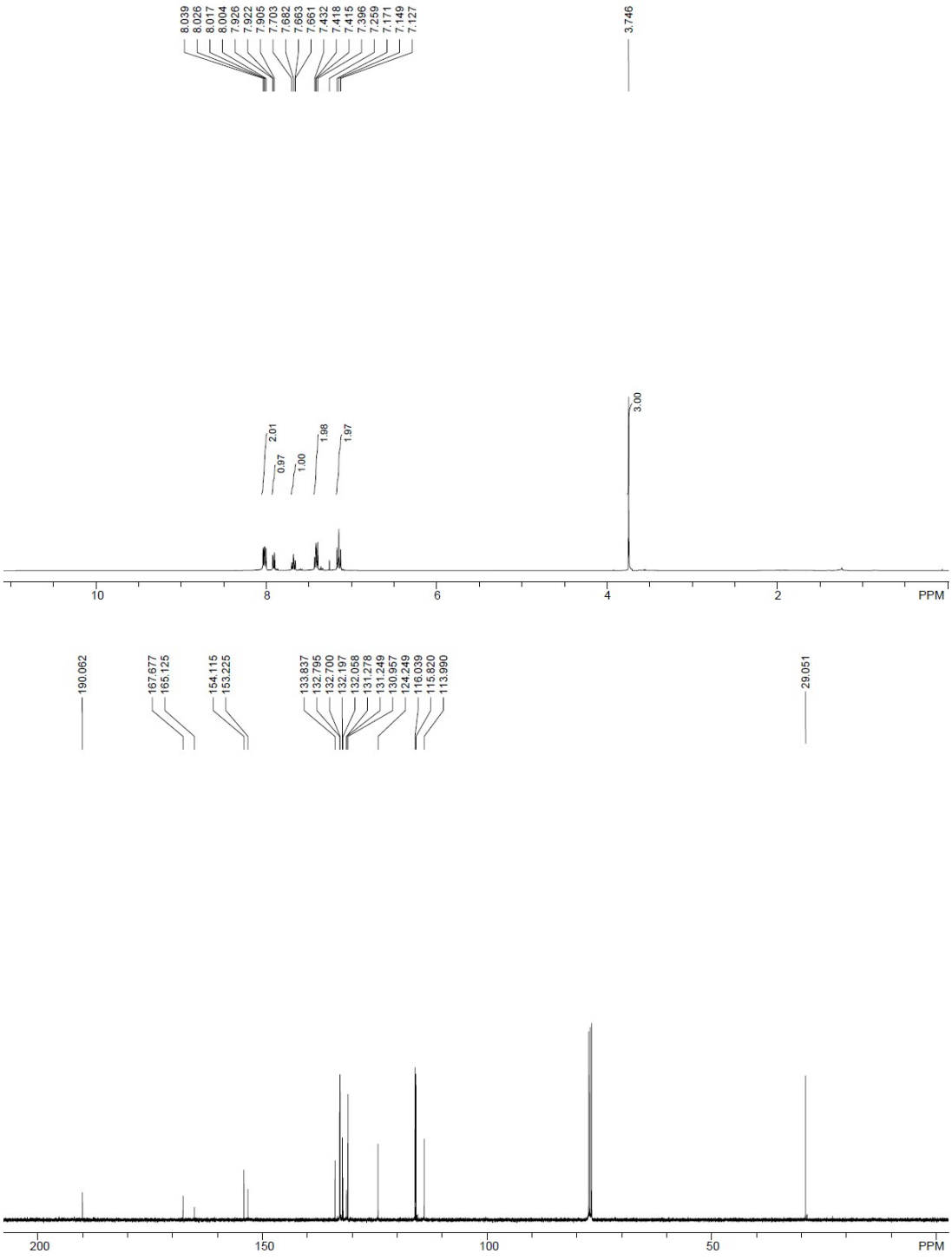




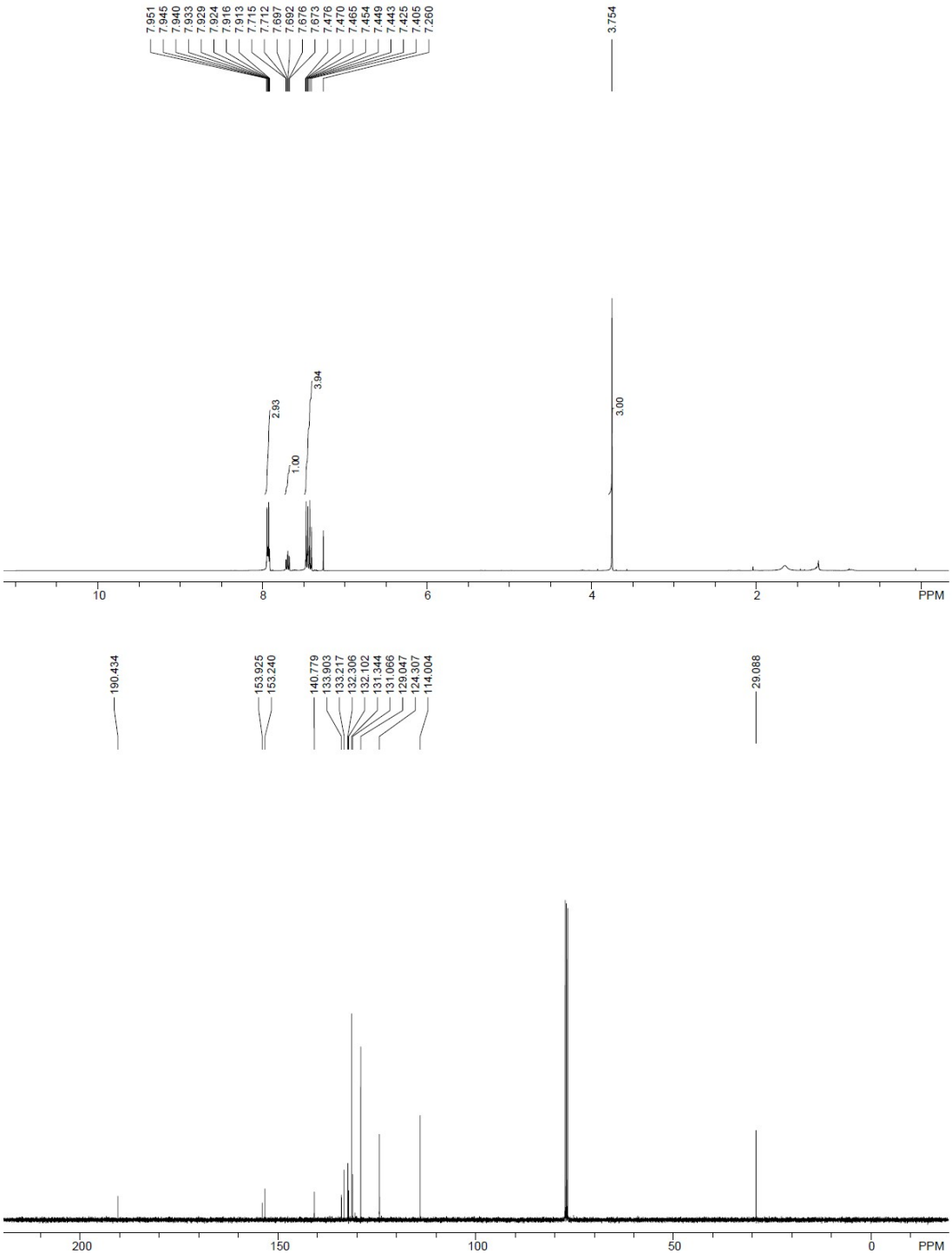
3-(4-methoxybenzoyl)-1-methylquinoxalin-2(1H)-one (3ac)



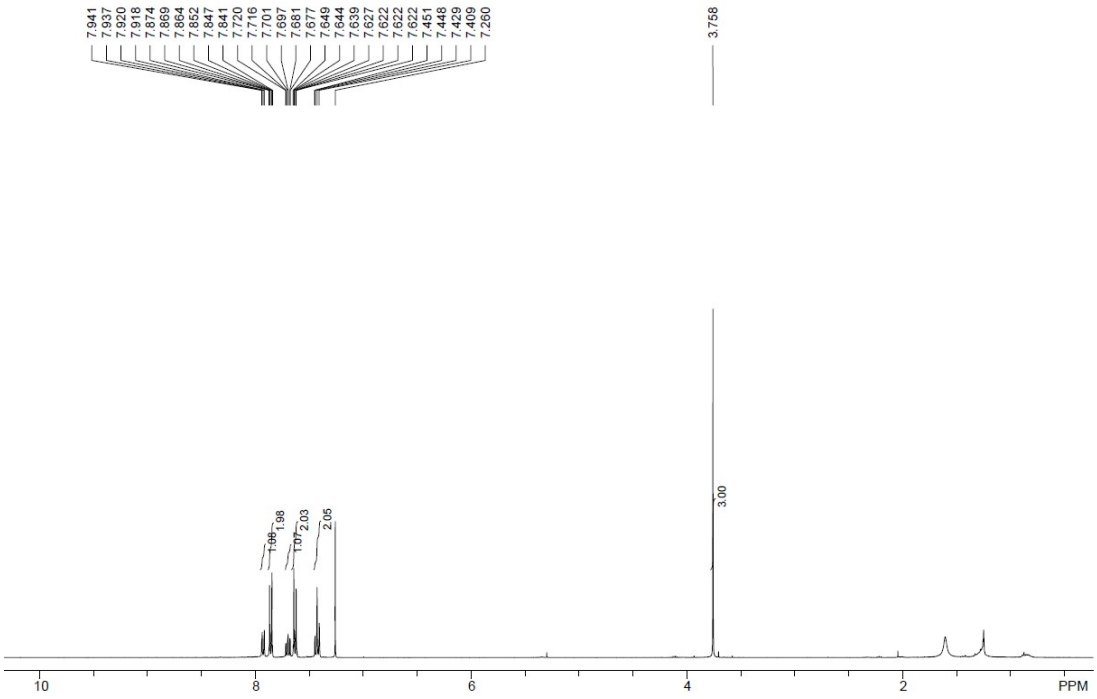
3-(4-fluorobenzoyl)-1-methylquinoxalin-2(1H)-one (3ad)

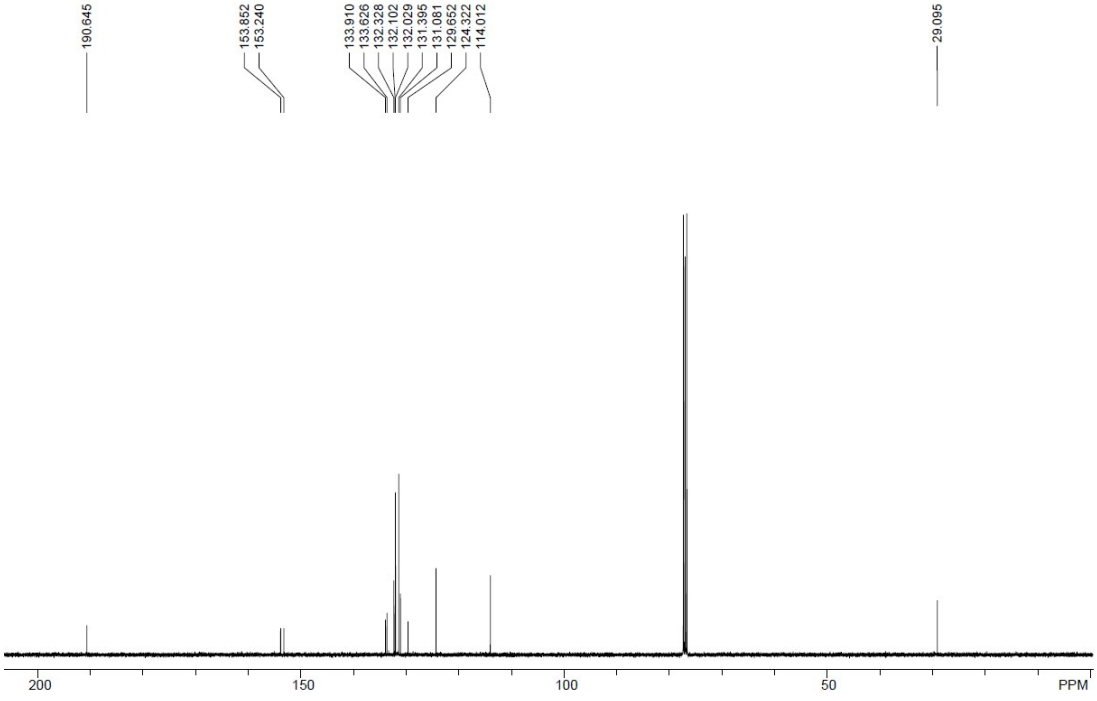


3-(4-chlorobenzoyl)-1-methylquinoxalin-2(1H)-one (3ae)

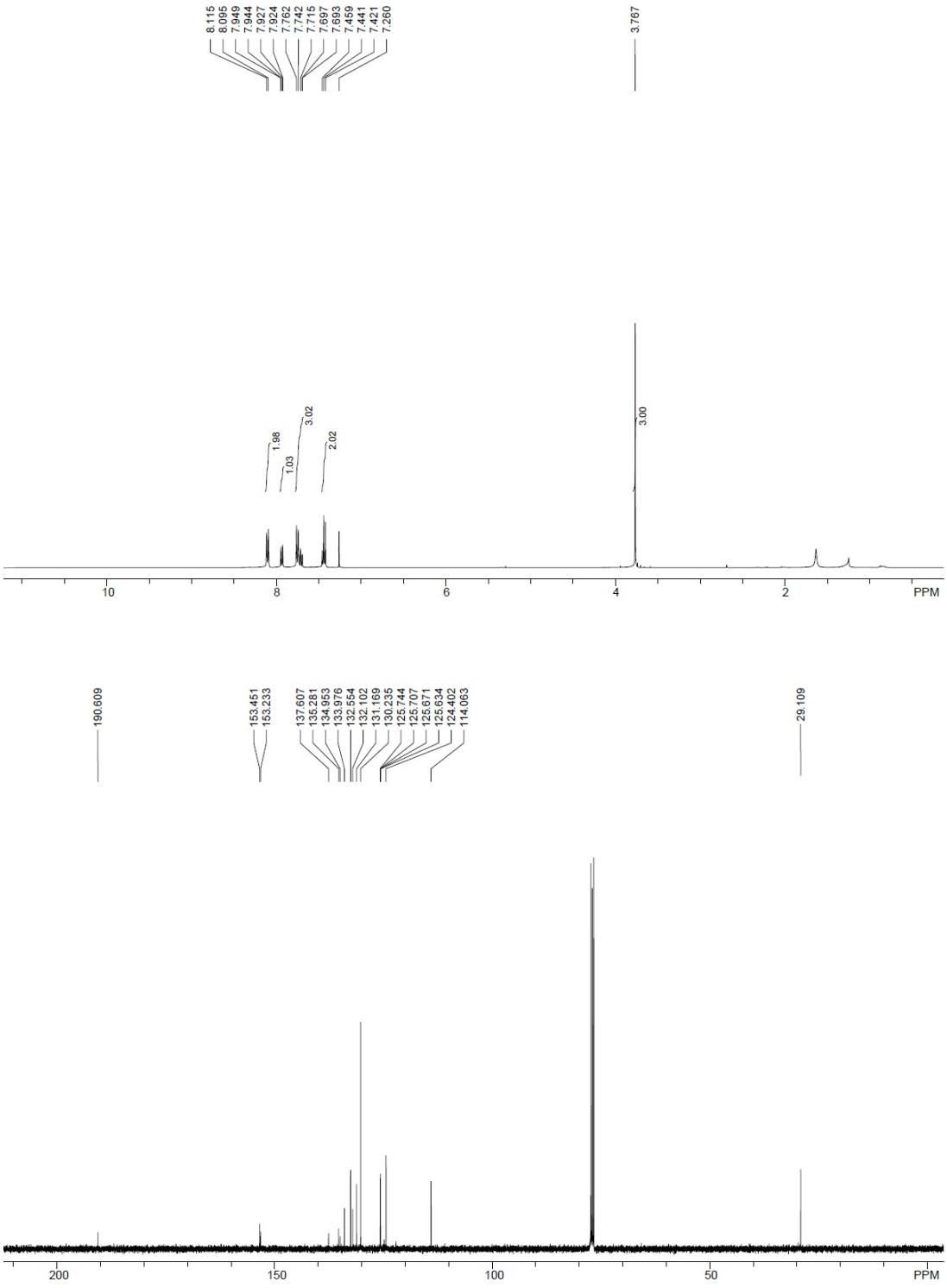


3-(4-bromobenzoyl)-1-methylquinoxalin-2(1H)-one (3af)

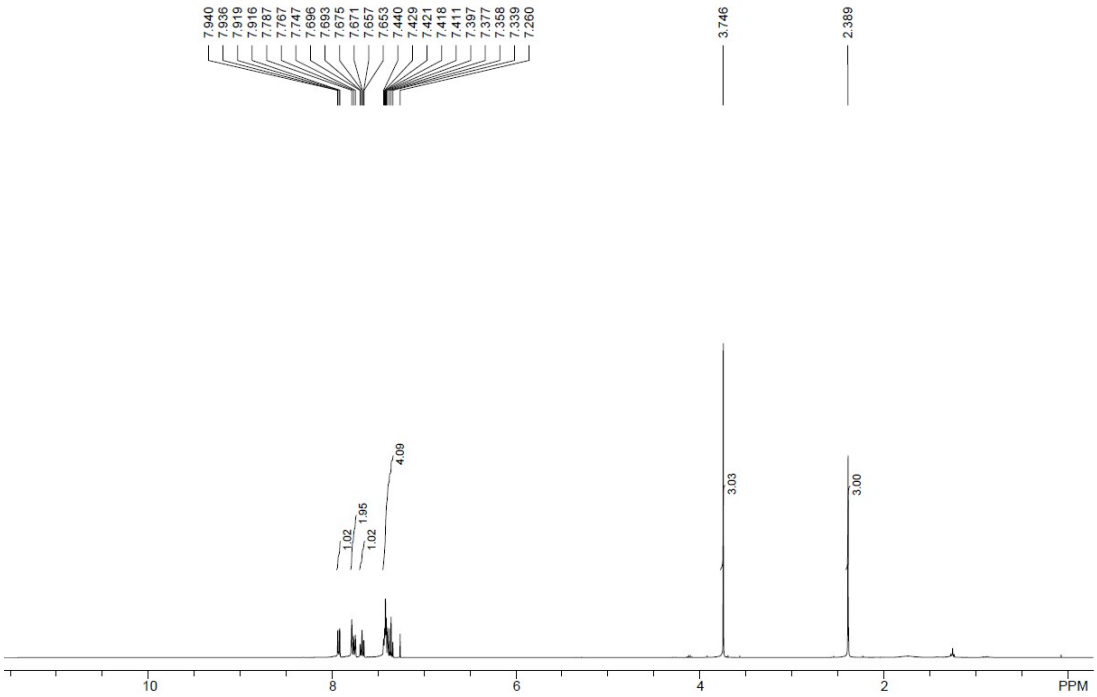


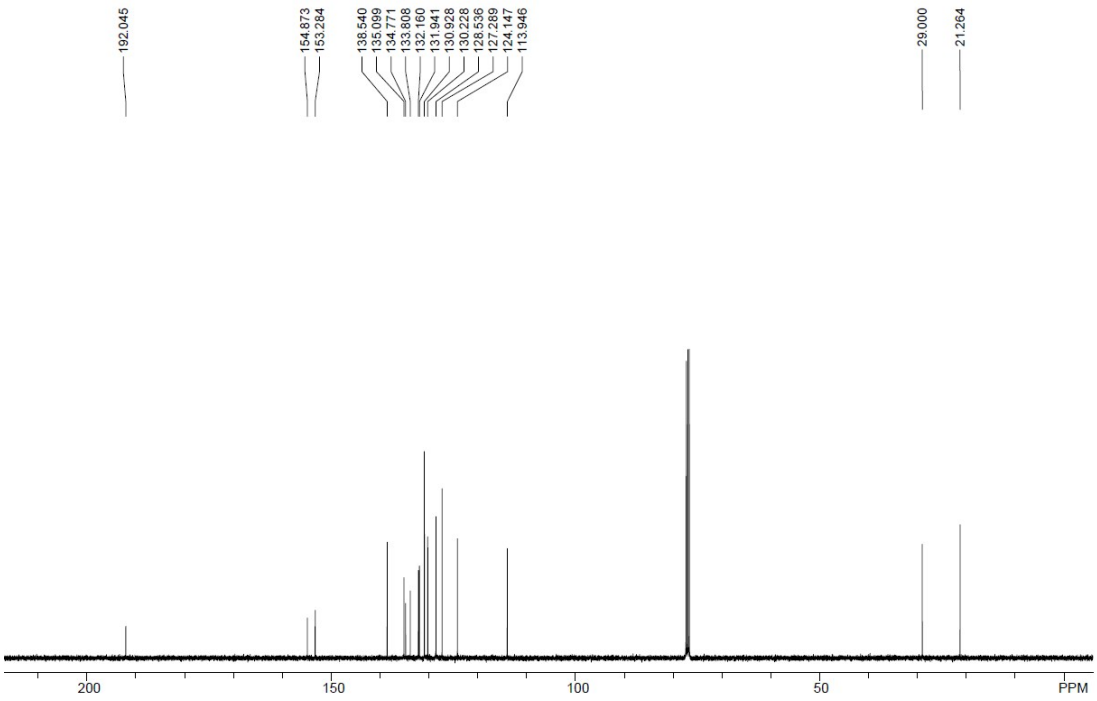


methyl-3-(4-(trifluoromethyl)benzoyl)quinoxalin-2(1H)-one (3ag)

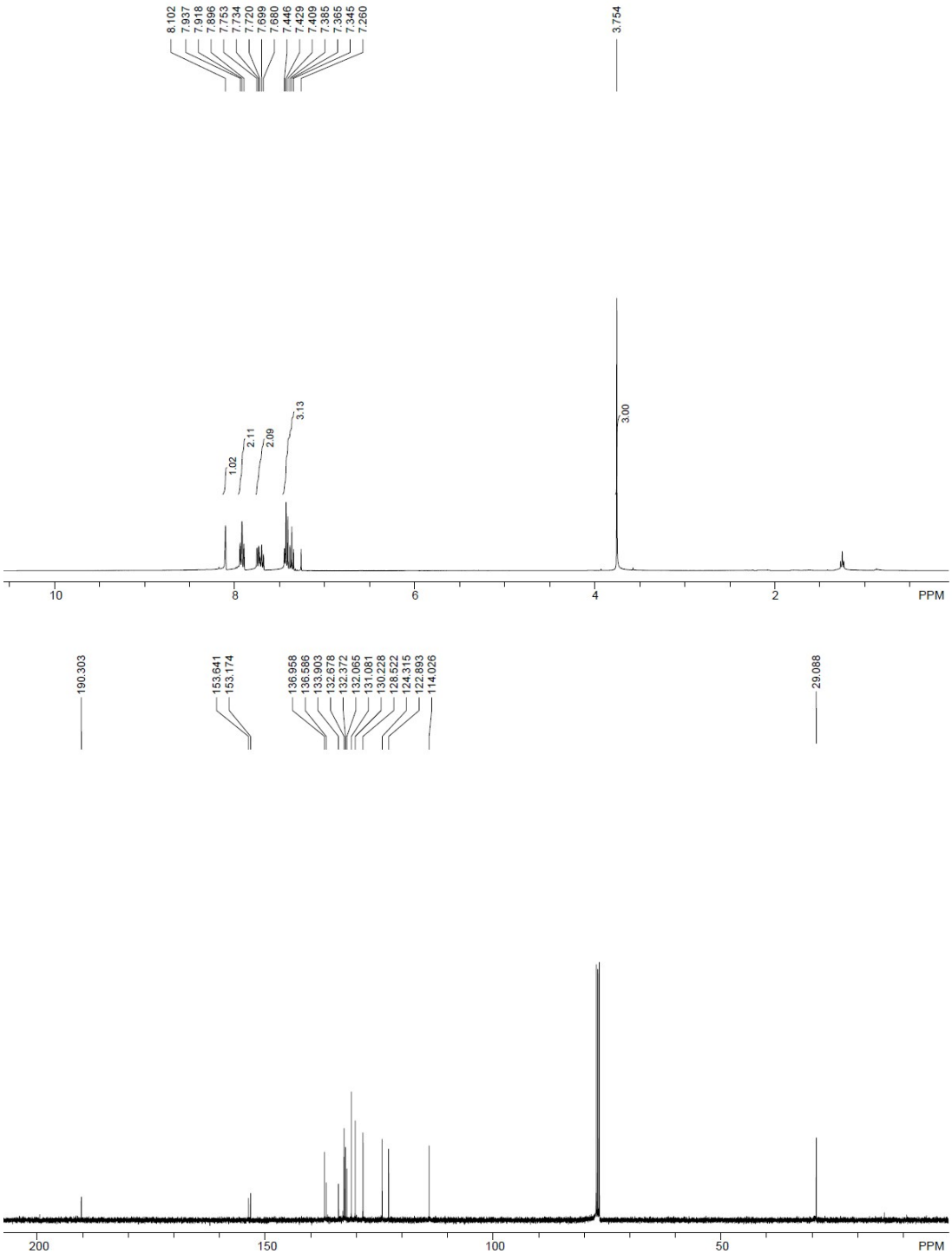


methyl-3-(3-methylbenzoyl)quinoxalin-2(1H)-one (3ah)

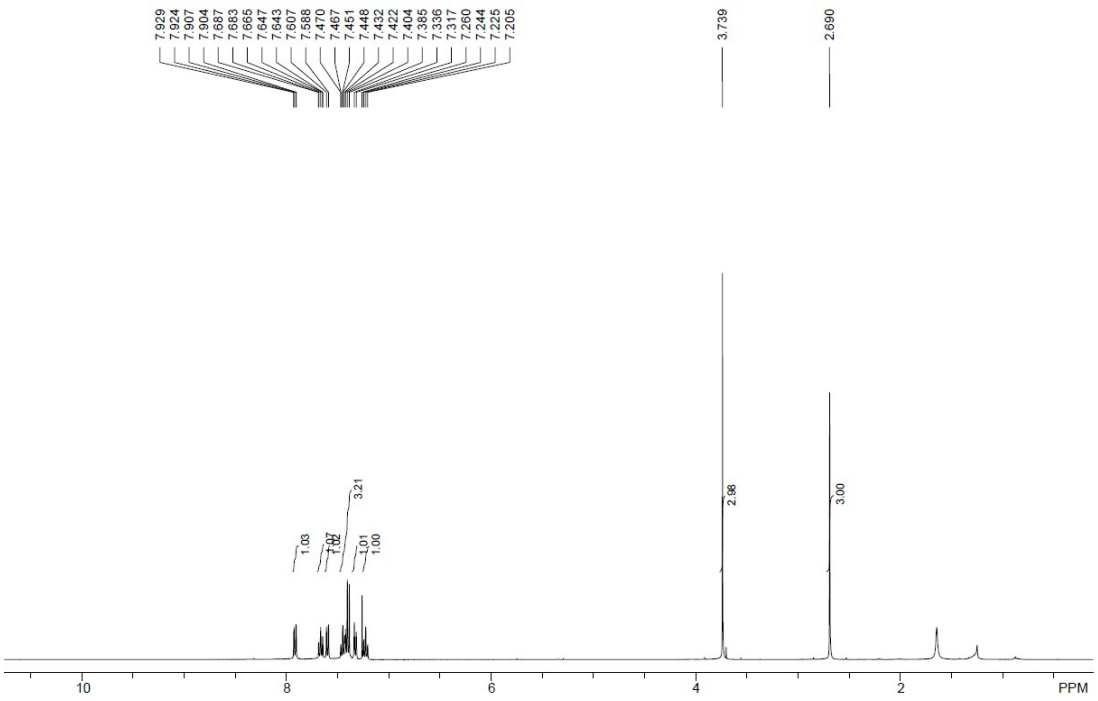


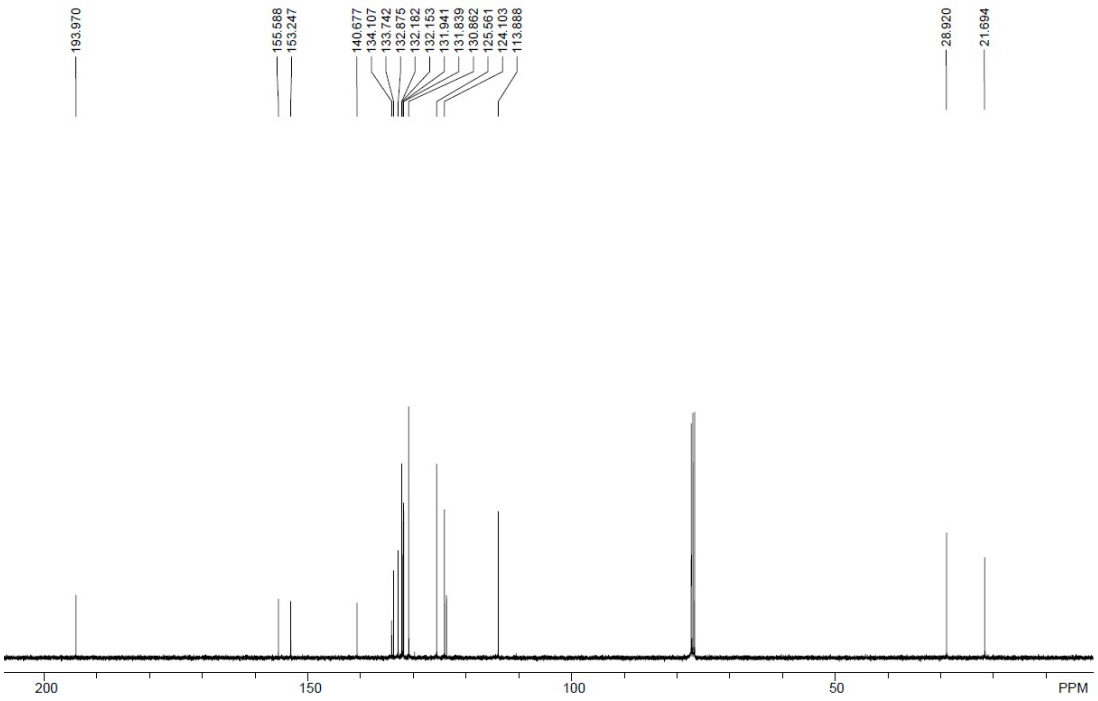


3-(3-bromobenzoyl)-1-methylquinoxalin-2(1H)-one (3ai)

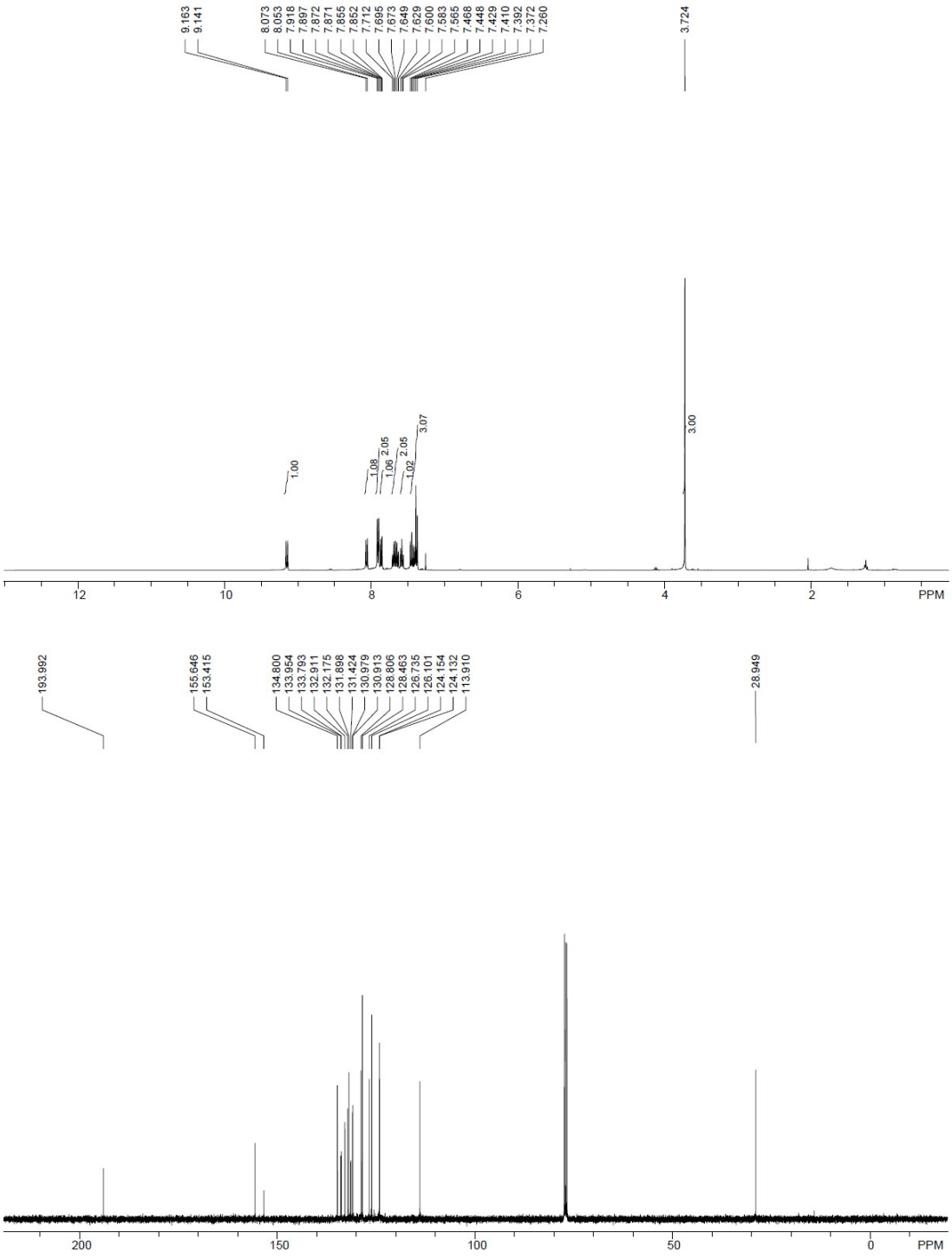


methyl-3-(2-methylbenzoyl)quinoxalin-2(1H)-one (3aj)

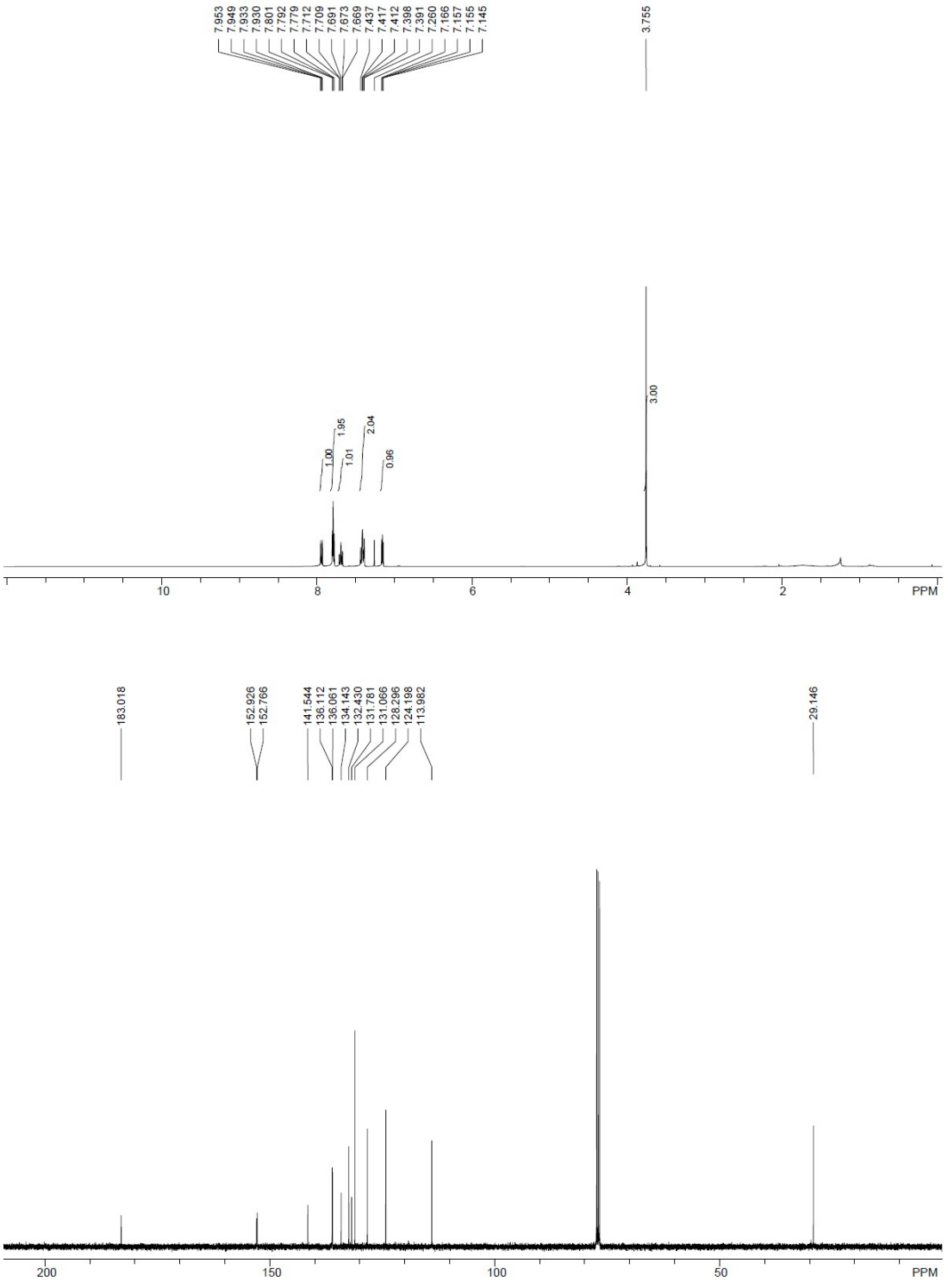




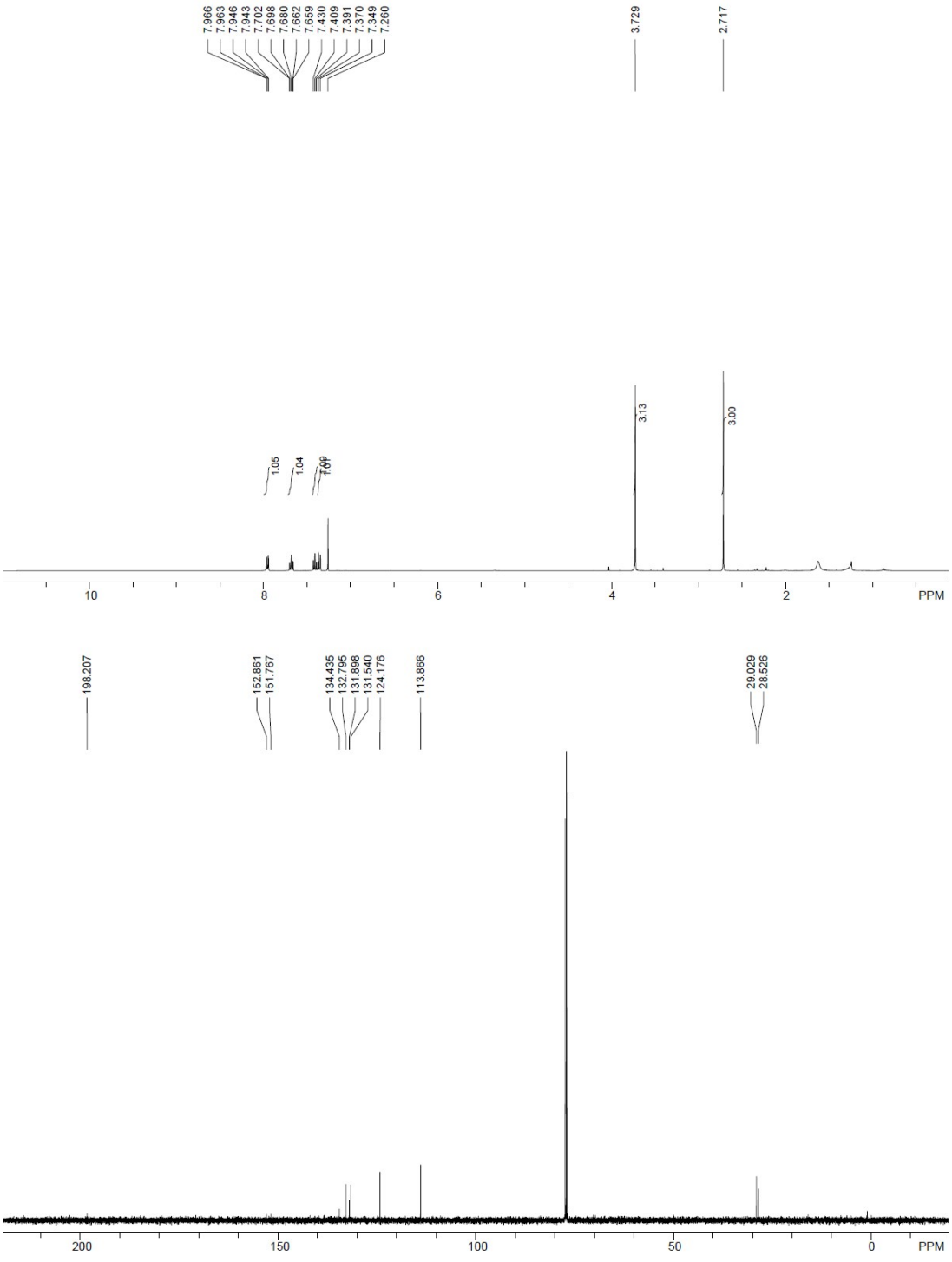
3-(1-naphthoyl)-1-methylquinoxalin-2(1H)-one (3ak)



methyl-3-(thiophene-2-carbonyl)quinoxalin-2(1H)-one (3al)



3-acetyl-1-methylquinoxalin-2(1H)-one (3am)



9,10-dimethyl-9,10-dihydro-9,10-epidioxyanthracene (5b)