Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

For

Unusual C_3-Acetylation of Quinoxalin-2(1*H*)-one via Oxidative C–C and C–O Bond Cleavages of PEG-400.

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(1) General Information

^{1}H, ^{13}C, and DEPT NMR spectra were recorded on a 400 MHz Varian Unity Plus or Varian Mercury plus spectrometer. The chemical shift (δ) values are reported in parts per million (ppm), and the coupling constants (J) are given in Hz. The spectra were recorded using $CDCl_3$ as a solvent. ^{1} H NMR chemical shifts are referenced to tetramethylsilane (TMS) (0 ppm). ^{13}C NMR was referenced to $CDCl_3$ (77.0 ppm) or DMSO-d_6 (39.51 ppm). The abbreviations used are as follows: s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublet; ddd, doublet of doublet; dt, doublet of triplets; td, triplet of doublet; m, multiplet. Mass spectra and high-resolution mass spectra (HRMS) were measured using the ESI (FT-MS solariX) at National Sun Yat-Sen University, Kaohsiung, Taiwan. Melting points were determined on an EZ-Melt (Automated melting point apparatus). All products reported showed ^{1}H NMR spectra in agreement with the assigned structures. Reaction progress and product mixtures were routinely monitored by TLC using Merck TLC aluminum sheets (silica gel 60 F254). Column chromatography was carried out with 230–400 mesh silica gel 60 (Merck) and a mixture of hexane/ethyl acetate or hexane as eluent. Preparative TLC was run on Merck TLC aluminum sheets (silica gel 60 F254).

(2) Mechanistic studies:

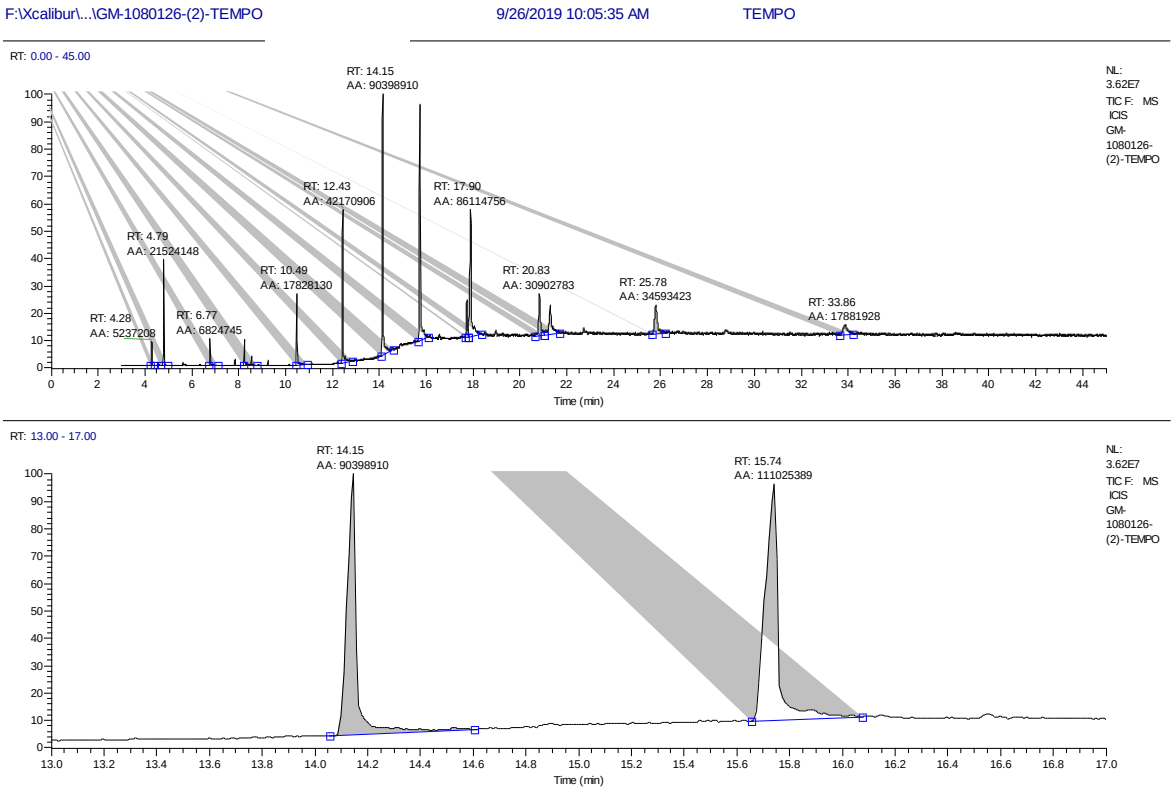


Fig S1: GC-MS with different retention times generated from PEG-400 in the presence of oxidant & radical scavenger.

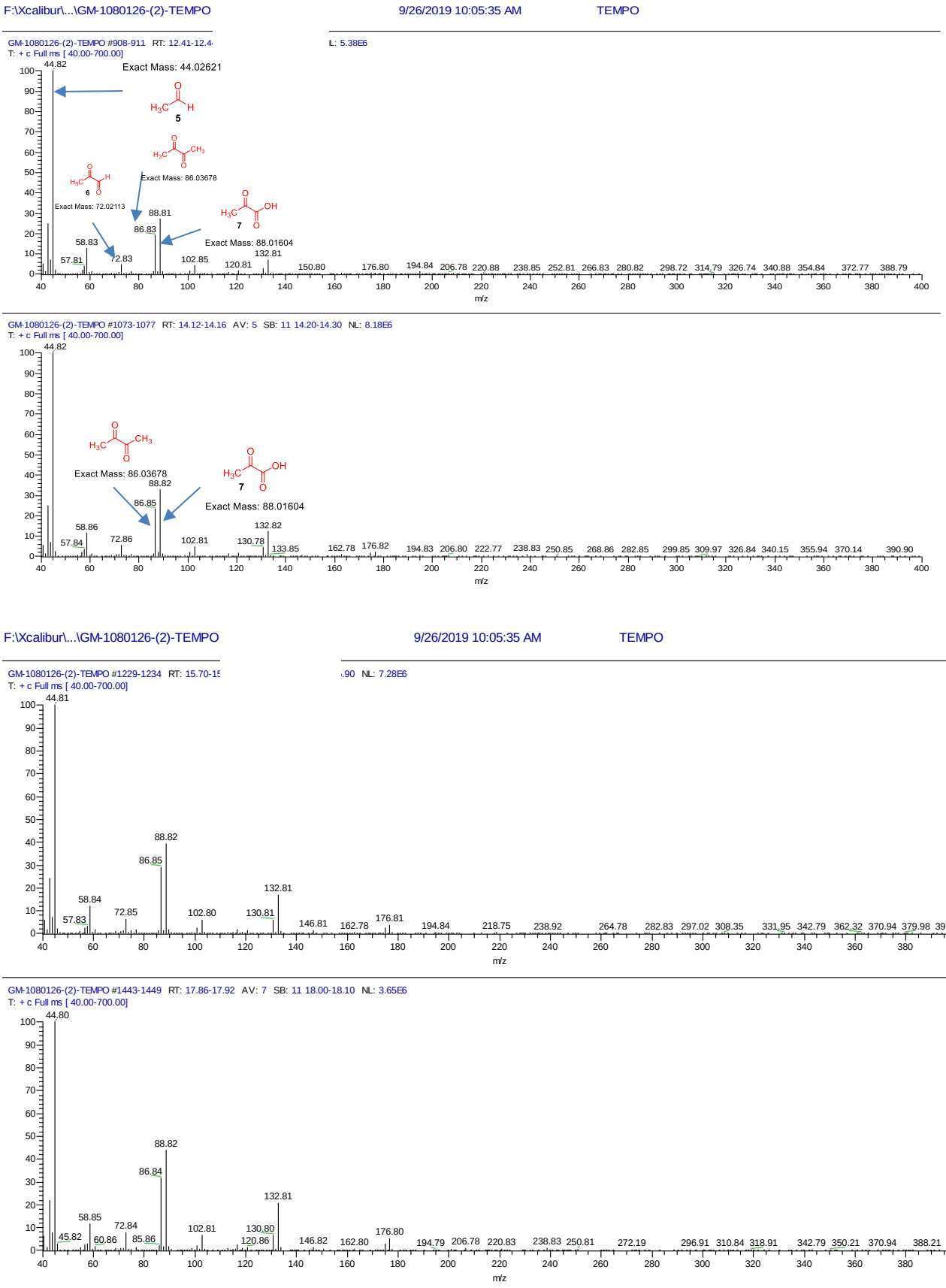
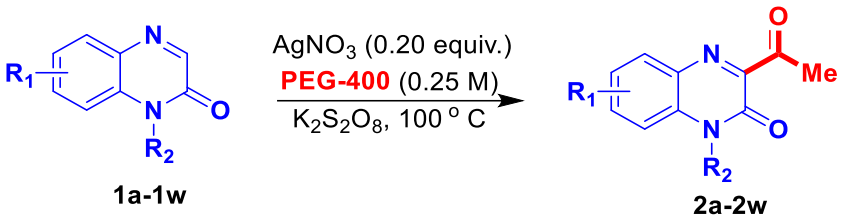


Fig S2: GC-MS observed fragments of acetaldehyde, 2-oxopropanal, 2-oxopropanoic acid from PEG-400.

(3) Experimental Procedures

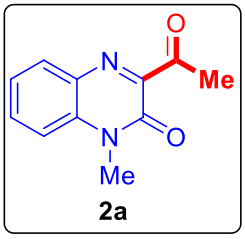
(i) General Experimental Procedure and Spectral Characterization for the Synthesis of 1-quinoxalin-2(1H)-one acetylation with PEG-400 as "CH_3CO" Source



To an oven-dried sealed tube was charged with 1-methylquinoxalin-2(1*H*)-one **1a-1w** [1] (0.25 mmol), PEG-400 (0.25 M), and $AgNO_3$ (0.25 mmol) and allowed to stir at 100° C until the completion of the reaction (7 ~ 24 h) by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 5.0 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate, and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 8/2) to afford pure heteroaryl acetylation **2a-2u** in 48%-76% yields.

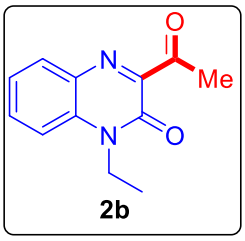
(4) Spectral Characterization

3-acetyl-1-methylquinoxalin-2(1*H*)-one (**2a**) [2]: Following the general procedure, a 15 mL reaction tube was

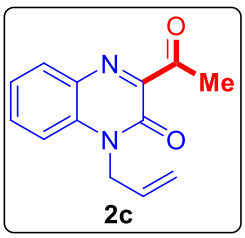


charged with 1-methylquinoxalin-2(1*H*)-one (1b) (35 mg, 0.2 mmol), PEG-400 (0.20 M), $AgNO_3$ (25 mol %) and $K_2S_2O_8$ (2.0 equiv) allowed to stir at 100° C until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 8/2) to afford the corresponding 3-acetyl-1-methylquinoxalin-2(1*H*)-one (2a) as a yellow solid (30 mg, yield = 76 %); Mp. 116.2-116.9 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.97-7.94 (m, 1H), 7.69 (ddd, *J* = 8.4, 7.2 ,1.6 Hz, 1H), 7.41 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.36 (dd, *J* = 8.4, 0.8 Hz, 1H), 3.73 (s, 3H), 2.72 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.16, 152.83, 151.77, 134.42, 132.77, 131.88, 131.52, 124.15, 113.84, 29.02, 28.51.

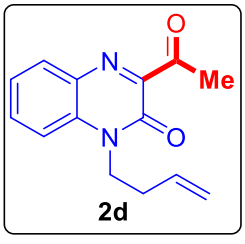
3-acetyl-1-ethylquinoxalin-2(1*H*)-one (**2b**): Following the general procedure, a 15 mL reaction tube was charged with 1-ethylquinoxalin-2(1*H*)-one (1b) (37 mg, 0.2 mmol), PEG-400 (0.25 M), $AgNO_3$ (20 mol %) and $K_2S_2O_8$ (2.0 equiv) allowed to stir at 100° C until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 8/2) to afford the corresponding 3-acetyl-1-ethylquinoxalin-2(1*H*)-one (2b) as a yellow solid (31 mg, yield = 73 %); Mp. 122-122.5 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.96 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.70-7.65 (m, 1H), 7.41-7.37 (m, 2H), 4.35 (q, *J* = 7.2 Hz, 1H), 2.72 (s, 3H), 1.40 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ198.22, 152.34, 151.69, 133.42, 132.71, 132.17, 131.75, 123.93, 113.67, 37.39, 28.52, 12.34. HRMS (ESI) calcd for C_{12} H_{12} N_2 O_2 Na [M + Na] $^+$: 239.0796; found: 239.0799.



3-acetyl-1-allylquinoxalin-2(1*H*)-one (**2c**): Following the general procedure, a 15 mL reaction tube was charged with 1-allylquinoxalin-2(1*H*)-one (1c) (40 mg, 0.2 mmol), PEG-400 (0.25 M), $AgNO_3$ (20 mol %) and $K_2S_2O_8$ (2.0 equiv) allowed to stir at 100° C until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 8/2) to afford the corresponding 3-acetyl-1-allylquinoxalin-2(1*H*)-one (2c) as a yellow solid (29 mg, yield = 65 %); Mp. 136.1-137 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.96 (ddd, *J* = 8.0, 1.2, 0.4 Hz, 1H), δ 7.65 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.42-7.37 (m, 1H), 7.34 (dd, *J* = 8.4,1.2, 1H), 5.97-5.90 (m, 1H), 5.32-5.28 (m, 1H), 5.23-5.18 (m, 1H), 4.93 (dt, *J* = 3.6, 2.0, 2H), 2.72 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.01, 152.36, 151.61, 133.69, 132.68, 132.00, 131.56, 130.13, 124.11, 118.57, 114.39, 44.44, 28.51. HRMS (ESI) calcd for C_{13} H_{12} N_2 O_2 Na [M + Na] $^+$: 251.0796; found: 251.0799.

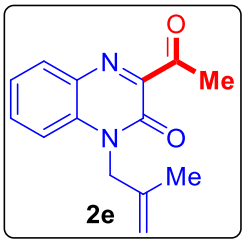


3-acetyl-1-(but-3-en-1-yl)quinoxalin-2(1*H*)-one (**2d**): Following the general procedure, a 15 mL reaction tube was charged with 1-(but-3-en-1-yl)quinoxalin-2(1*H*)-one (1d) (43 mg, 0.2 mmol), PEG-400 (0.25 M), $AgNO_3$ (20 mol %) and $K_2S_2O_8$ (2.0 equiv) allowed to stir at 100° C until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10

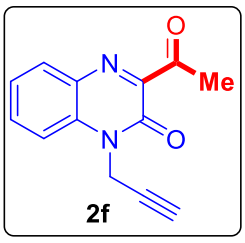


mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 8/2) to afford the corresponding 3-acetyl-1-(but-3-en-1-yl)quinoxalin-2(1*H*)-one (2d) as a yellow solid (30 mg, yield = 63 %); Mp. 140.5-141.2°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.96 (dd, *J* = 8.0, 1.2 Hz, 1H), δ 7.68 (ddd, *J* = 8.4, 7.8, 1.6 Hz, 1H), 7.42-7.35 (m, 2H), 5.93-5.83 (m, 1H), 5.15-5.09 (m, 2H), 4.39-4.33 (m, 2H), 2.72 (s, 3H) 2.56-2.50 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.11, 152.53, 151.68, 133.56, 132.70, 132.14, 131.81, 124.01, 117.92, 113.78, 41.60, 31.42, 28.51.HRMS (ESI) calcd for C_{12} H_{12} N_2 O_2 Na [M + Na] $^{+}$: 265.0796; found: 265.0799.

3-acetyl-1-(2-methylallyl)quinoxalin-2(1*H*)-one (**2e**): Following the general procedure, a 15 mL reaction tube was charged with 1-(2-methylallyl)quinoxalin-2(1*H*)-one (1e) (43 mg, 0.2 mmol), PEG-400 (0.25 M), $AgNO_3$ (20 mol %) and $K_2S_2O_8$ (2.0 equiv) allowed to stir at 100° C until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 8/2) to afford the corresponding 3-acetyl-1-(2-methylallyl)quinoxalin-2(1*H*)-one (2e) as a yellow solid (28 mg, yield = 58 %); Mp. 132.5-132.9 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.96 (ddd, *J* = 8.0, 1.2, 0.4 Hz, 1H), δ 7.62 (ddd, *J* = 6.8, 3.6, 1.6 Hz, 1H), 7.41-7.37 (m, 1H), 7.28-7.26 (m, 1H), 4.84 (s, 2H), 4.62 (dt, *J* = 1.6, 0.8 Hz 1H), 2.73 (s, 3H), 1.83 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.03, 152.56, 151.82, 137.82, 133.93, 132.61, 132.01, 131.50, 124.15, 114.68, 112.20, 77.31, 76.99, 76.68, 47.55, 28.58, 20.17.HRMS (ESI) calcd for C_{12} H_{12} N_2 O_2 Na [M + Na] $^{+}$: 266.1693; found: 266.1696.

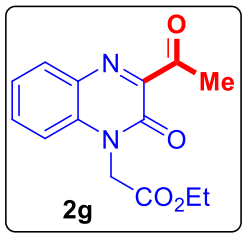


3-acetyl-1-(prop-2-yn-1-yl)quinoxalin-2(1*H*)-one (**2f**): Following the general procedure, a 15 mL reaction tube was charged with 1-(prop-2-yn-1-yl)quinoxalin-2(1*H*)-one (1f) (40 mg, 0.2 mmol), PEG-400 (0.25 M), $AgNO_3$ (20 mol %) and $K_2S_2O_8$ (2.0 equiv) allowed to stir at 100° C until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 8/2) to afford the corresponding 3-acetyl-1-(prop-2-yn-1-yl)quinoxalin-2(1*H*)-one (2f) as a yellow solid (32 mg, yield = 71 %); Mp. 106.2-106.7 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.97 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.74-7.69 (m, 1H), 7.52 (d, *J* = 8.8, 1H), 7.46-7.42 (m, 1H), 5.08 (d, *J* = 2.8, 2H), 2.72 (s, 3H); ^{13}C NMR



($CDCl_3$, 100 MHz) δ 13C NMR (101 MHz, cdcl3) δ 197.64, 151.75, 151.42, 132.95, 132.91, 132.05, 131.66, 124.52, 114.39, 76.27, 73.58, 31.33, 28.46. HRMS (ESI) calcd for C_{13} H_{10} N_2 O_2 Na [M + Na] $^+$: 249.0640; found: 249.0642.

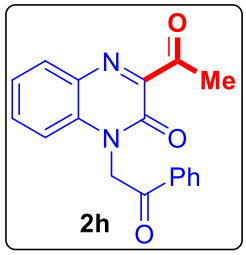
ethyl 2-(3-acetyl-2-oxoquinoxalin-1(2*H*)-yl)acetate (2g)[2]: Following the general procedure, a 15 mL



2g

reaction tube was charged with ethyl 2-(2-oxoquinoxalin-1(2*H*)-yl)acetate (1g) (49 mg, 0.2 mmol), PEG-400 (0.25 M), $AgNO_3$ (20 mol %) and $K_2S_2O_8$ (2.0 equiv) allowed to stir at 100^o C until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 8/2) to afford the corresponding ethyl 2-(3-acetyl-2-oxoquinoxalin-1(2*H*)-yl)acetate (2g) as a yellow solid (37 mg, yield = 67 %); Mp. 107.1-107.6 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.98 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.65 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 7.42 (ddd, *J* = 8.47.6,1.2 Hz, 1H), 7.12 (dd, *J* = 8.4,0.8 Hz, 1H), 5.02 (s, 2H), 4.26 (q, *J* = 7.2 Hz, 2H), 2.72 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.57, 166.65, 152.30, 151.14, 133.68, 133.00, 131.90, 131.85, 124.42, 113.34, 62.24, 43.30, 28.41, 14.06.

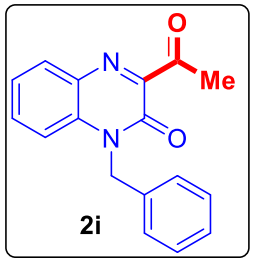
3-acetyl-1-(2-oxo-2-phenylethyl)quinoxalin-2(1*H*)-one (2h): Following the general procedure, a 15 mL



2h

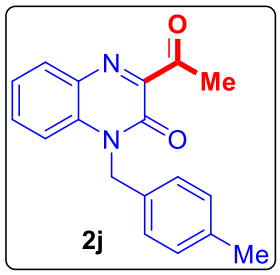
reaction tube was charged with 1-(2-oxo-2-phenylethyl)quinoxalin-2(1*H*)-one (1h) (55 mg, 0.2 mmol), PEG-400 (0.25 M), $AgNO_3$ (20 mol %) and $K_2S_2O_8$ (2.0 equiv) allowed to stir at 100^o C until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 8/2) to afford the corresponding 3-acetyl-1-(2-oxo-2-phenylethyl)quinoxalin-2(1*H*)-one (2h) as a yellow solid (29 mg, yield = 48 %); Mp. 138.2-139.1 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.07-8.05 (m, 1H), 8.02-8.00 (m, 2H), 7.68-7.57 (m, 4H), 7.53-7.50 (m, 2H), 5.86 (s, 2H), 2.85 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.39, 192.77, 153.89, 141.67, 140.96, 137.93, 134.46, 133.74, 131.99, 129.65, 128.81, 127.80, 127.56, 126.79, 68.02, 28.43. HRMS (ESI) calcd for $C_{18}H_{14}$ N2 O_3 Na [M + Na] $^+$: 329.0902; found: 329.0905.

3-acetyl-1-benzylquinoxalin-2(1*H*)-one (**2i**): Following the general procedure, a 15 mL reaction tube was



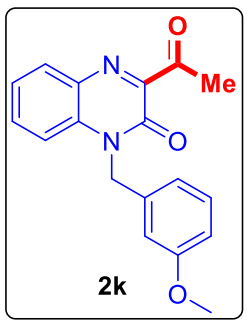
charged with 1-benzylquinoxalin-2(1*H*)-one (1i) (50 mg, 0.2 mmol), PEG-400 (0.25 M), $AgNO_3$ (20 mol %) and $K_2S_2O_8$ (2.0 equiv) allowed to stir at 100° C until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 8/2) to afford the corresponding 3-acetyl-1-benzylquinoxalin-2(1*H*)-one (2i) as a yellow solid (38 mg, yield = 69 %); Mp. 129.7-130.1 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.96 (ddd, *J* = 8.0, 1.6, 0.4 Hz, 1H), 7.55 (ddd, *J* = 8.8, 7.2, 1.6 Hz, 1H), 7.38-7.35 (m, 1H), 7.34-7.31 (m, 2H), 7.29-7.25 (m, 4H), 5.51 (s, 2H) 2.75 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.01, 152.90, 151.70, 134.74, 133.82, 132.75, 132.12, 131.61, 128.96, 127.85, 126.96, 124.18, 114.63, 45.83, 28.52. HRMS (ESI) calcd for C_{17} H_{14} N_2 O_2 Na [M + Na] $^+$: 301.0953; found: 301.0956.

3-acetyl-1-(4-methylbenzyl)quinoxalin-2(1*H*)-one (**2j**): Following the general procedure, a 15 mL reaction



tube was charged with 1-(4-methylbenzyl)quinoxalin-2(1*H*)-one (1j) (53 mg, 0.2 mmol), PEG-400 (0.25 M), $AgNO_3$ (20 mol %) and $K_2S_2O_8$ (2.0 equiv) allowed to stir at 100° C until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 8/2) to afford the corresponding 3-acetyl-1-(4-methylbenzyl)quinoxalin-2(1*H*)-one (2j) as a yellow solid (38 mg, yield = 66 %); Mp. 132.4-133.6 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.96-7.93 (m, 1H), 7.55 (ddd, *J* = 8.8, 7.6, 1.6 Hz, 1H), 7.37-7.32 (m, 2H), 7.18-7.11 (m, 4H), 5.47 (s, 2H), 2.75 (s, 3H), 2.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) 13C NMR (101 MHz, cdcl3) δ 198.07, 152.93, 151.76, 137.65, 133.86, 132.71, 132.14, 131.75, 131.59, 129.61, 127.01, 124.12, 114.66, 45.64, 28.55, 21.05. HRMS (ESI) calcd for C_{18} H_{16} N_2 O_2 Na [M + Na] $^+$: 315.1109; found: 315.1109.

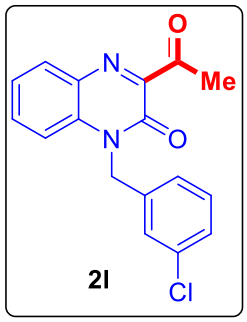
3-acetyl-1-(3-methoxybenzyl)quinoxalin-2(1*H*)-one (**2k**): Following the general procedure, a 15 mL



reaction tube was charged with 1-(3-methoxybenzyl)quinoxalin-2(1*H*)-one (1k) (56 mg, 0.2 mmol), PEG-400 (0.25 M), $AgNO_3$ (20 mol %) and $K_2S_2O_8$ (2.0 equiv) allowed to stir at 100° C until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water

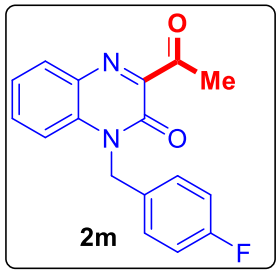
layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 8/2) to afford the corresponding 3-acetyl-1-(3-methoxybenzyl)quinoxalin-2(1*H*)-one (2k) as a yellow solid (34 mg, yield = 55 %); Mp. 142.1-143 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.96 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.57-7.53 (m, 1H), 7.38-7.34 (m, 1H), 7.31-7.29 (m, 1H),), 7.24-7.22 (m, 1H),), 6.84- 6.78 (m, 3H), 5.48 (s, 2H), 3.76 (s, 3H), 2.75 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.00, 160.05, 151.73, 136.36, 133.88, 132.78, 132.15, 131.64, 130.08, 124.21, 119.14, 114.68, 113.04, 112.79, 77.31, 76.99, 76.67, 55.26, 45.81, 28.56. HRMS (ESI) calcd for C_{18} H_{16} N_2 O_3 Na [M + Na] $^{+}$: 331.1059; found: 331.1060.

3-acetyl-1-(3-chlorobenzyl)quinoxalin-2(1*H*)-one (**2l**): Following the general procedure, a 15 mL reaction



tube was charged with 1-(3-chlorobenzyl)quinoxalin-2(1*H*)-one (1l) (57 mg, 0.2 mmol), PEG-400 (0.25 M), $AgNO_3$ (20 mol %) and $K_2S_2O_8$ (2.0 equiv) allowed to stir at 100^{o} C until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 8/2) to afford the corresponding 3-acetyl-1-(3-chlorobenzyl)quinoxalin-2(1*H*)-one (2l) as a yellow solid (38 mg, yield = 61 %); Mp. 136.4-137 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.98-7.95 (m, 1H), 7.59-7.54 (m, 1H), 7.40-7.36 (m, 1H), 7.30-7.26 (m, 3H), 7.23-7.20 (m, 2H), 5.47 (s, 2H), 2.75 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) 13C NMR (101 MHz, cdcl3) ^{13}C NMR (101 MHz, $cdcl_3$) δ 197.84, 152.80, 151.58, 133.83, 133.66, 133.29, 132.86, 132.13, 131.79, 129.18, 128.49, 124.35, 114.37, 45.26. 28.45. HRMS (ESI) calcd for C_{17} H_{13} N_2 O_2 Cl Na [M + Na] $^{+}$: 335.0563; found: 335.0567.

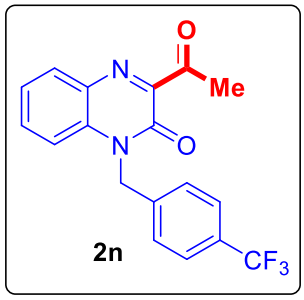
3-acetyl-1-(4-fluorobenzyl)quinoxalin-2(1*H*)-one (**2m**): Following the general procedure, a 15 mL reaction



tube was charged with 1-(4-fluorobenzyl)quinoxalin-2(1*H*)-one (1m) (54 mg, 0.2 mmol), PEG-400 (0.25 M), $AgNO_3$ (20 mol %) and $K_2S_2O_8$ (2.0 equiv) allowed to stir at 100^{o} C until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 8/2) to afford the corresponding 3-acetyl-1-(4-

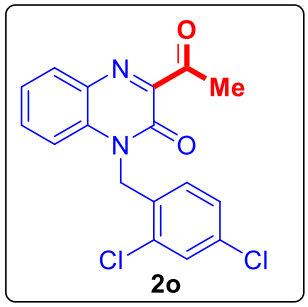
fluorobenzyl)quinoxalin-2(1*H*)-one (2m) as a yellow solid (32 mg, yield = 54 %); Mp. 129.1-130 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.97 (dd, *J* = 8.0, 0.4 Hz, 1H), 7.58 (ddd, *J* = 8.8, 7.2, 0.4 Hz, 1H), 7.38 (ddd, *J* = 8.0, 7.2, 0.8 Hz, 1H), 7.31-7.25 (m, 3H), 7.03-6.99 (m, 2H), 5.47 (s, 2H), 2.74 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.89, 163.51, (d, J_F = 245 Hz), 161.06, 152.84 (d, J_F = 119 Hz), 151.65, 133.72, 132.82, 132.15, 131.77, 130.56, 130.53, 128.97, (d, J_F = 8 Hz), 128.89, 124.30, 116.06, (d, J_F = 21.7 Hz),115.85, 114.40, 45.22, 28.47. HRMS (ESI) calcd for C_{17} H_{13} N_2 O_2 F Na [M + Na] $^{+}$: 319.0859; found: 319.0863

3-acetyl-1-(4-(trifluoromethyl)benzyl)quinoxalin-2(1*H*)-one (**2n**): Following the general procedure, a 15



mL reaction tube was charged with 1-(4-(trifluoromethyl)benzyl)quinoxalin-2(1*H*)-one (1n) (64 mg, 0.2 mmol), PEG-400 (0.25 M), $AgNO_3$ (20 mol %) and $K_2S_2O_8$ (2.0 equiv) allowed to stir at 100^{o} C until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 8/2) to afford the corresponding 3-acetyl-1-(4-(trifluoromethyl)benzyl)quinoxalin-2(1*H*)-one (2n) as a yellow solid (36 mg, yield = 52 %); Mp. 130.1-131.3 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.99 (dd, *J* = 8.0, 0.4 Hz, 1H), 7.58 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 3H), 7.40 (ddd, *J* = 8.0, 7.2, 1.2 Hz, 3H), 7.23 (dd, *J* = 8.8, 1.2 Hz, 1H), 5.56 (s, 2H), 2.75 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.74, 152.76, 151.51, 138.78, 133.61, 132.98, 132.12, 131.86, 130.44, 130.11(q, *J* = 28.6 Hz), 127.32, 126.05, 126.01, 125.98, 125.94 (q, *J* = 3.7 Hz), 124.47, 122.449 (q, *J* = 270.4 Hz), 114.25, 45.45, 29.67, 28.41. HRMS (ESI) calcd for C_{18} H_{13} N_2 F_3 O_2 Na [M + Na] $^{+}$: 369.0827; found: 369.0831.

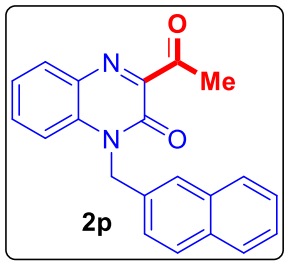
3-acetyl-1-(2,4-dichlorobenzyl)quinoxalin-2(1*H*)-one (**2o**): Following the general procedure, a 15 mL



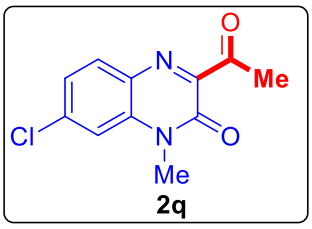
reaction tube was charged with 1-(2,4-dichlorobenzyl)quinoxalin-2(1*H*)-one (1o) (63 mg, 0.2 mmol), PEG-400 (0.25 M), $AgNO_3$ (20 mol %) and $K_2S_2O_8$ (2.0 equiv) allowed to stir at 100^{o} C until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 8/2) to afford the corresponding 3-acetyl-1-(2,4-dichlorobenzyl)quinoxalin-2(1*H*)-one (2o) as a yellow solid (42 mg, yield = 61 %); Mp. 125.2-126 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.00-7.98 (m, 1H), 7.57 (ddd, *J* = 8.4,

7.2, 1.6 Hz, 1H), 7.48 (d, *J* =2.0 Hz, 1H), 7.40 (ddd, *J* = 8.4, 7.6, 1.2 Hz, 1H), 7.09 (ddd, *J* = 8.4, 7.2, 2.4 Hz, 2H), 6.75 (dd, *J* = 8.4 Hz, 1H),5.53 (s, 2H), 2.75 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.67, 152.81, 151.48, 134.28, 133.40, 133.29, 133.12, 132.10, 131.78, 130.54, 129.67, 128.04, 127.75, 124.58, 114.31, 77.31, 76.99, 76.67, 43.00, 28.44. HRMS (ESI) calcd for C_{12} H_{12} N_2 O_2 Cl_2 Na [M + Na] $^+$: 369.0174; found 369.0173.

3-acetyl-1-(naphthalen-2-ylmethyl)quinoxalin-2(1*H*)-one (**2p**): Following the general procedure, a 15 mL reaction tube was charged with 1-(naphthalen-2-ylmethyl)quinoxalin-2(1*H*)-one (1o) (60 mg, 0.2 mmol), PEG-400 (0.25 M), $AgNO_3$ (20 mol %) and $K_2S_2O_8$ (2.0 equiv) allowed to stir at 100^o C until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 8/2) to afford the corresponding 3-acetyl-1-(naphthalen-2-ylmethyl)quinoxalin-2(1*H*)-one (2p) as a yellow solid (43 mg, yield = 65 %); Mp 167.9-168.3 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.98-7.95 (m, 1H), 7.82-7.79 (m, 2H), 7.75 (dd, *J* = 8.8, 3.2 Hz, 1H), 7.66 (s, 1H) 7.54-7.49 (m, 1H), 7.47-7.45 (m, 2H), 7.41 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.37 (s, 1H), 7.35 (d, *J* =1.2 Hz, 1H), 5. 67(s, 2H) 2.78 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.03, 153.02, 151.75, 133.89, 133.26, 132.80, 132.25, 132.20, 131.67, 129.01, 127.71, 126.51, 126.24, 125.82, 124.71, 124.23. 46.10, 28.55. HRMS (ESI) calcd for C_{21} H_{16} N_2 O_2 Na [M + Na] $^+$: 351.1109; found: 351.1108.

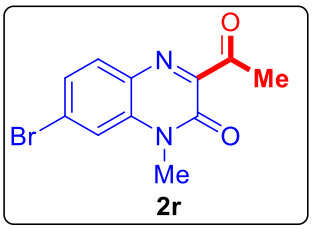


3-acetyl-7-chloro-1-methylquinoxalin-2(1*H*)-one (**2q**): Following the general procedure, a 15 mL reaction tube was charged with 7-chloro-1-methylquinoxalin-2(1*H*)-one (1p) (41 mg, 0.2 mmol), PEG-400 (0.25 M), $AgNO_3$ (20 mol %) and $K_2S_2O_8$ (2.0 equiv) allowed to stir at 100^o C until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 8/2) to afford the corresponding 3-acetyl-7-chloro-1-methylquinoxalin-2(1*H*)-one (2q) as a yellow solid (28 mg, yield = 59 %); Mp. 191.4-192 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.94 (d, *J* = 2.4 Hz, 1H), 7.63 (dd, *J* = 9.2, 2.4 Hz, 1H), 7.30 (d, *J* = 8.8 Hz, 1H), 3.71 (s, 3H), 2.69 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.72, 152.88, 152.38, 133.07, 132.68, 132.28, 130.51,



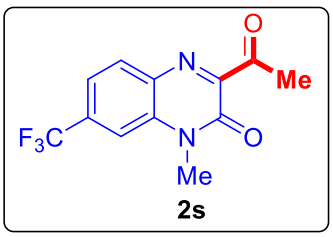
129.54, 115.03, 29.22, 28.38. HRMS (ESI) calcd for C_{11} H_{09} N_2 O_2 Cl Na [M + Na] $^+$: 259.0250; found: 259.0252.

3-acetyl-7-Bromo-1-methylquinoxalin-2(1*H*)-one (**2r**): Following the general procedure, a 15 mL reaction tube was charged with 7-Bromo-1-methylquinoxalin-2(1*H*)-one (1q) (51 mg, 0.2 mmol), PEG-400 (0.25 M), $AgNO_3$ (20 mol %) and $K_2S_2O_8$ (2.0 equiv) allowed to stir at 100^o C until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate, and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 8/2) to afford the corresponding 3-acetyl-7-Bromo-1-methylquinoxalin-2(1*H*)-one (2r) as a yellow solid (35 mg, yield = 63 %); Mp 188-189.2 °C;^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.10 (d, *J* = 2.4 Hz, 1H), 7.76 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.24 (d, *J* = 9.2 Hz, 1H), 3.70 (s, 3H), 2.69 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.65, 152.80, 152.38, 135.39, 133.62, 133.53, 132.59, 116.71, 115.29, 29.19, 28.35. HRMS (ESI) calcd for C_{11} H_{09} N_2 O_2 Br Na [M + Na] $^+$: 302.9745; found: 302.9746.



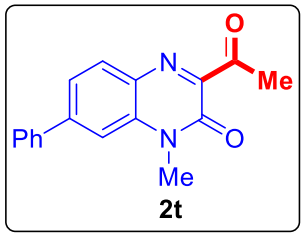
2r

3-acetyl-1-methyl-7-(trifluoromethyl)quinoxalin-2(1*H*)-one (**2s**): Following the general procedure, a 15 mL reaction tube was charged with 1-methyl-7-(trifluoromethyl)quinoxalin-2(1*H*)-one (1r) (48 mg, 0.2 mmol), PEG-400 (0.25 M), $AgNO_3$ (20 mol %) and $K_2S_2O_8$ (2.0 equiv) allowed to stir at 100^o C until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 8/2) to afford the corresponding 3-acetyl-1-methyl-7-(trifluoromethyl)quinoxalin-2(1*H*)-one (2s) as a yellow solid (32 mg, yield = 59 %); Mp. 170-170.6 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.23 (d, *J* = 1.6 Hz, 1H), 7.89 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.48 (d, *J* = 8.8 Hz, 1H), 3.75 (s, 3H), 2.70 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.36, 153.07, 152.44, 136.61, 131.09, 128.85, 128.81, 128.77, 128.73 (q, *J* = 3.4 Hz), 127.44(q, *J* = 41.6 Hz), 126.66, 126.33, 124.72,125.99 (q, *J* = 33.7 Hz), 122.02(q, *J* = 270.1 Hz), 114.66, 29.30, 28.25. HRMS (ESI) calcd for C_{12} H_{10} N_2 O_2 F_3 [M + H] $^+$: 271.0694; found: 271.0697.



2s

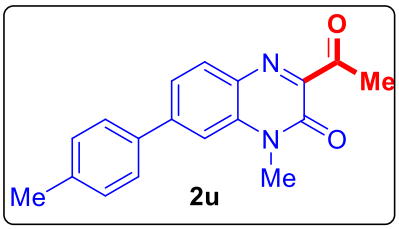
3-acetyl-1-methyl-7-phenylquinoxalin-2(1*H*)-one (**2t**): Following the general procedure, a 15 mL reaction tube was charged with 1-methyl-7-phenylquinoxalin-2(1*H*)-one (1s) (50 mg, 0.2 mmol), PEG-400 (0.25 M), $AgNO_3$ (20 mol %) and $K_2S_2O_8$ (2.0 equiv) allowed to



2t

stir at 100° C until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 8/2) to afford the corresponding 3-acetyl-1-methyl-7-phenylquinoxalin-2(1*H*)-one (2t) as a yellow solid (32 mg, yield = 58 %); Mp 178-178.9 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.19 (d, *J* = 2.4 Hz, 1H), 7.93 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.67-7.64 (m, 2H), 7.52-7.47 (m, 2H), 7.44-7.38 (m, 2H), 3.76 (s, 3H), 2.73 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.07, 152.78, 152.12, 138.72, 137.34, 133.55, 132.17, 131.63, 129.29, 129.11, 127.95, 126.89, 114.28, 29.15, 28.54. HRMS (ESI) calcd for C_{12} H_{12} N_2 O_2 Na [M + Na] $^{+}$: 301.1106; found: 301.1107.

3-acetyl-1-methyl-7-(p-tolyl)quinoxalin-2(1*H*)-one (**2u**): Following the general procedure, a 15 mL reaction tube was charged with 1-methyl-7-(p-tolyl)quinoxalin-2(1*H*)-one (1t) (53 mg, 0.2 mmol), PEG-400 (0.25 M), $AgNO_3$ (20 mol %) and $K_2S_2O_8$ (2.0 equiv) and allowed to stir at 100° C until the completion of reaction by TLC. After completion, the reaction mixture was cooled to room temperature and diluted with 10 mL of water. The water layer was extracted with (3X10 mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X10 mL). The final ethyl acetate layer was dried over sodium sulfate and concentrated under reduced pressure to get the crude compound. The obtained crude was purified using column chromatography by eluting from (Hex/EA = 8/2) to afford the corresponding 3-acetyl-1-methyl-7-(p-tolyl)quinoxalin-2(1*H*)-one (2u) as a yellow solid (35 mg, yield = 60 %); Mp 183-184.6 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.16 (d, *J* = 2.4 Hz, 1H), 7.91 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.56-7.54 (m, 2H), 7.40 (d, *J* = 8.8 Hz, 1H), 7.31-7.28 (m, 2H), 3.75 (s, 3H), 2.73 (s, 3H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.09, 152.76, 152.04, 137.89, 137.28, 135.79, 133.32, 132.17, 131.48, 129.81, 128.95, 126.68, 114.20, 29.11, 28.54, 21.10. HRMS (ESI) calcd for C_{18} H_{16} N_2 O_2 Na [M + Na] $^{+}$: 315.1109; found: 315.1111.

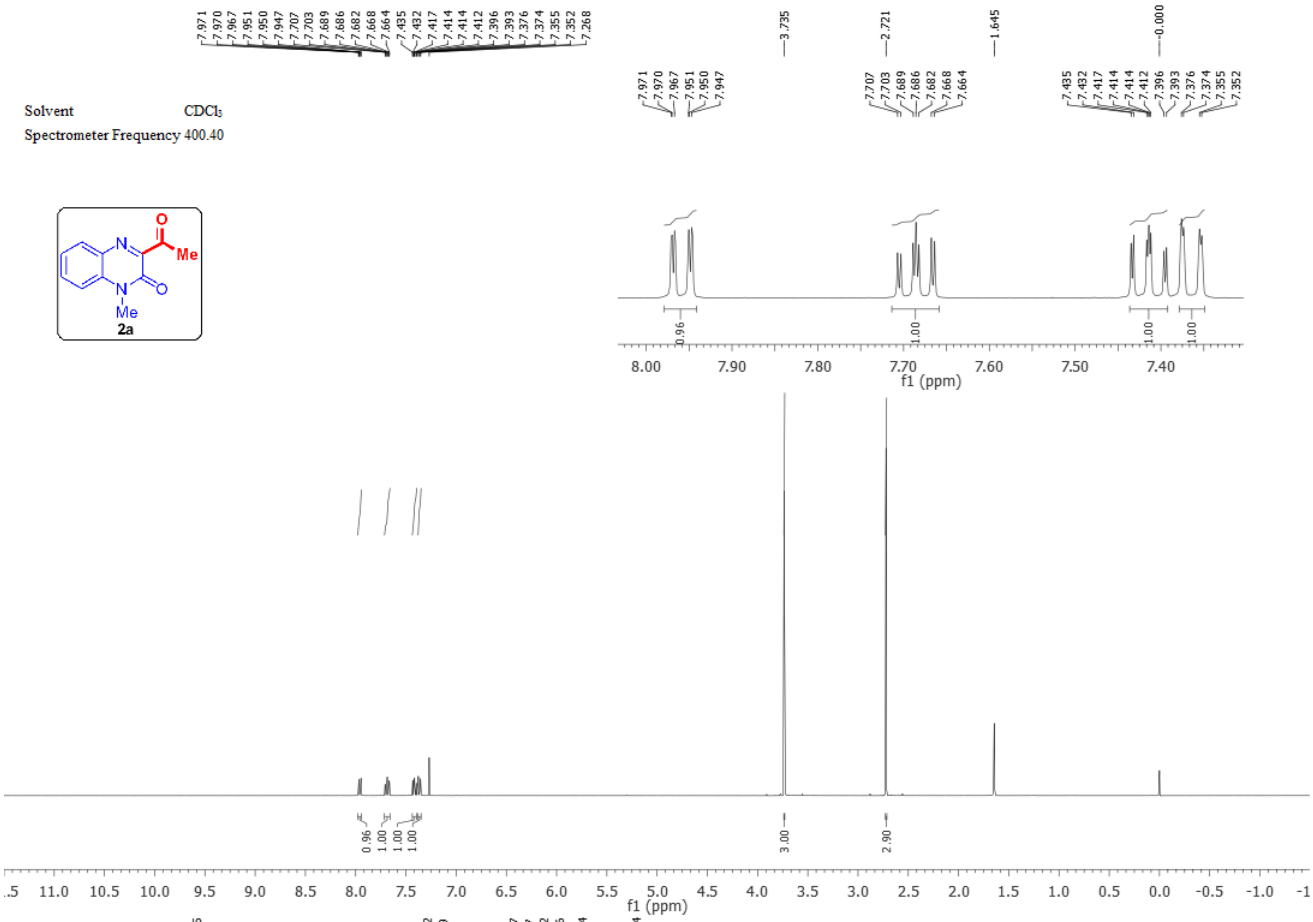


2u

(5) References:

1. M. I. Shahin, D. A. Abou El Ella, N. S. M. Ismail, K. A. M. Abouzid. *Bioorg. Chem.* 2014**, 56,** 16-26.

2. X. Zeng, C. Liu, X. Wang, J. Zhang, X. Wang, Y. Hu. *Organic & Biomolecular Chemistry*. 2017, **15**, 8929-8935.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Me
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O
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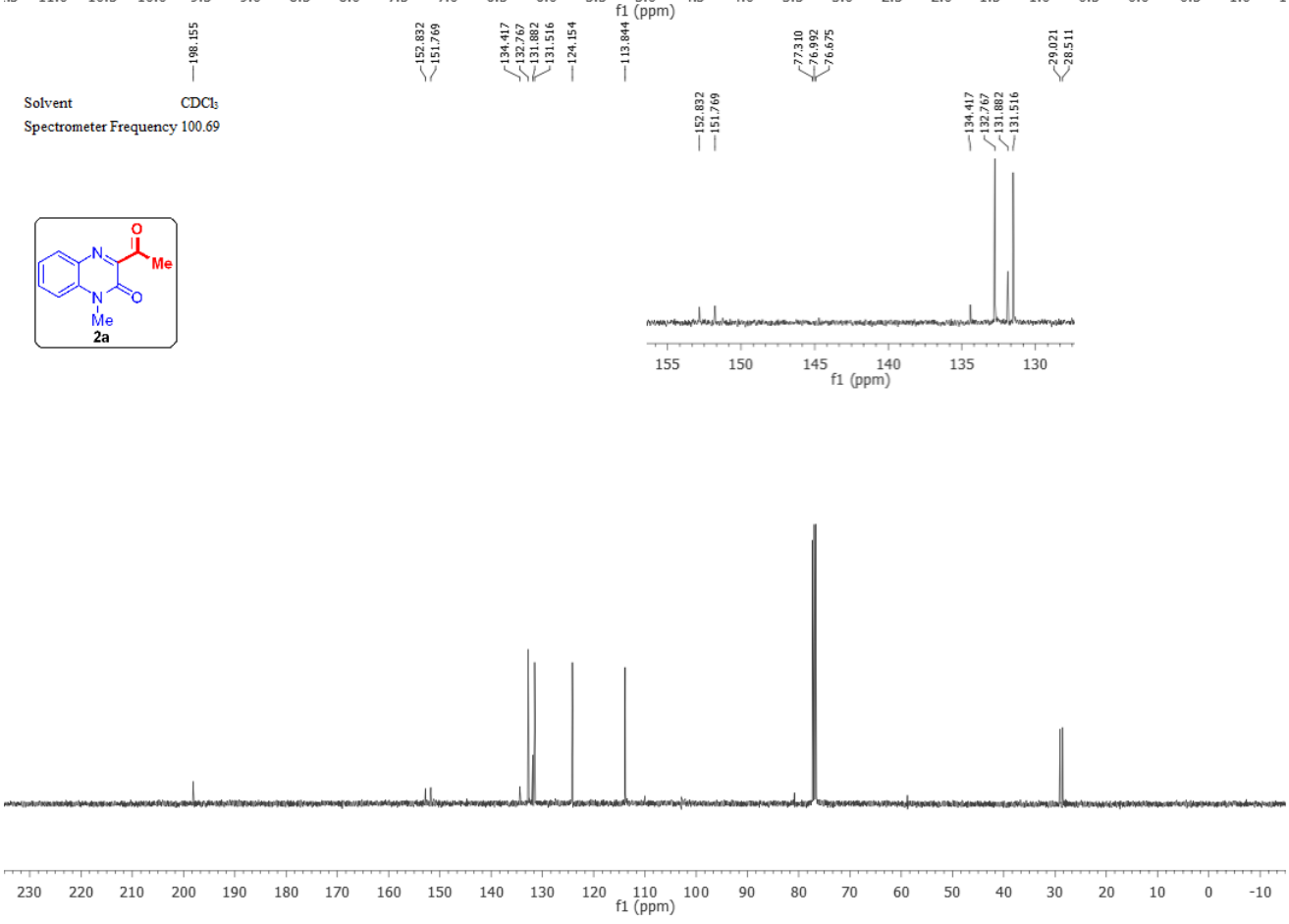
7.40
f1 (ppm)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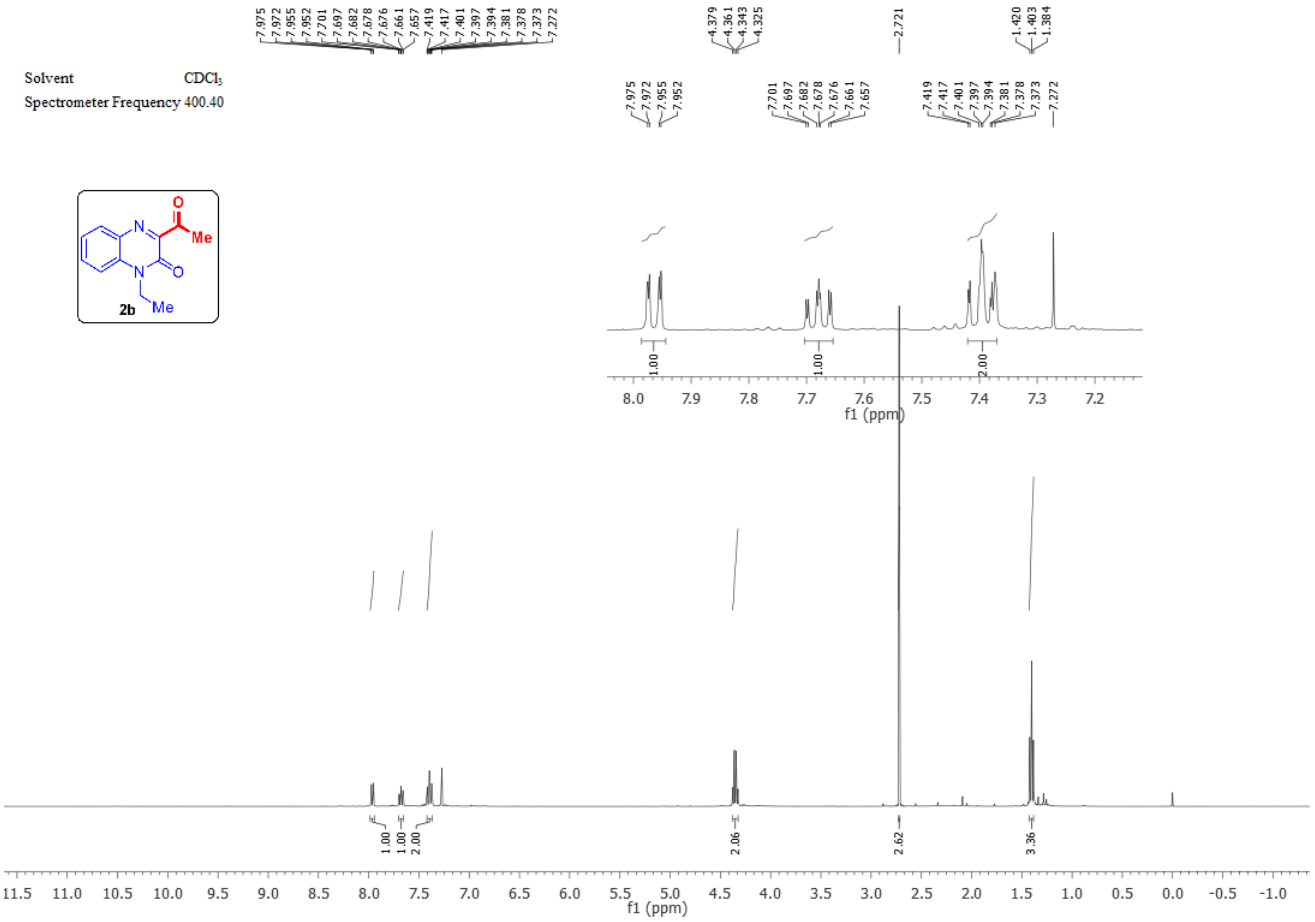
Me
N
O
Me
2a
155
150
145
140
135
130
f1 (ppm)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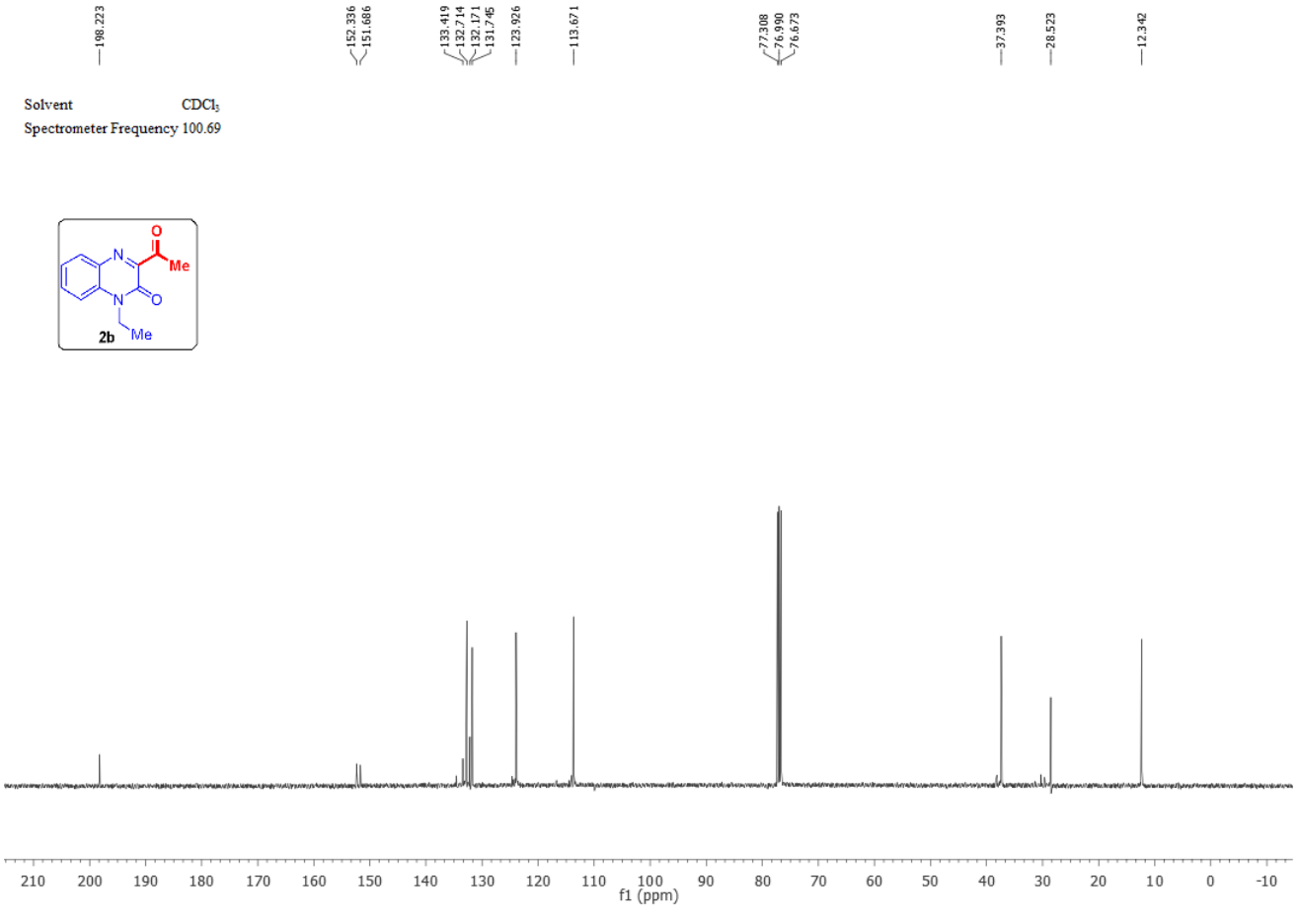
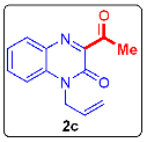
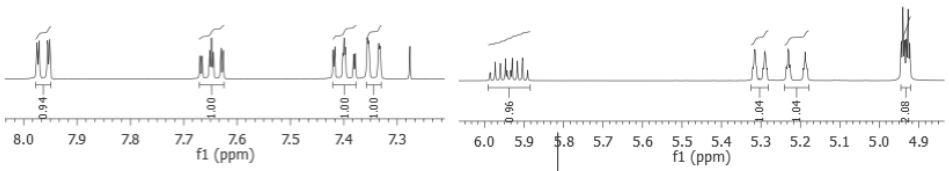
7.972
7.955
7.952
7.701
7.697
7.682
7.678
7.676
7.661
7.657
7.419
7.417
7.401
7.397
7.394
7.381
7.378
7.373
7.272
4.379
4.361
4.343
4.325
2.721
1.420
1.403
1.384
Solvent CDCl3
Spectrometer Frequency 400.40
2b
1.00
1.00
2.00
2.06
2.62
3.36
f1 (ppm)

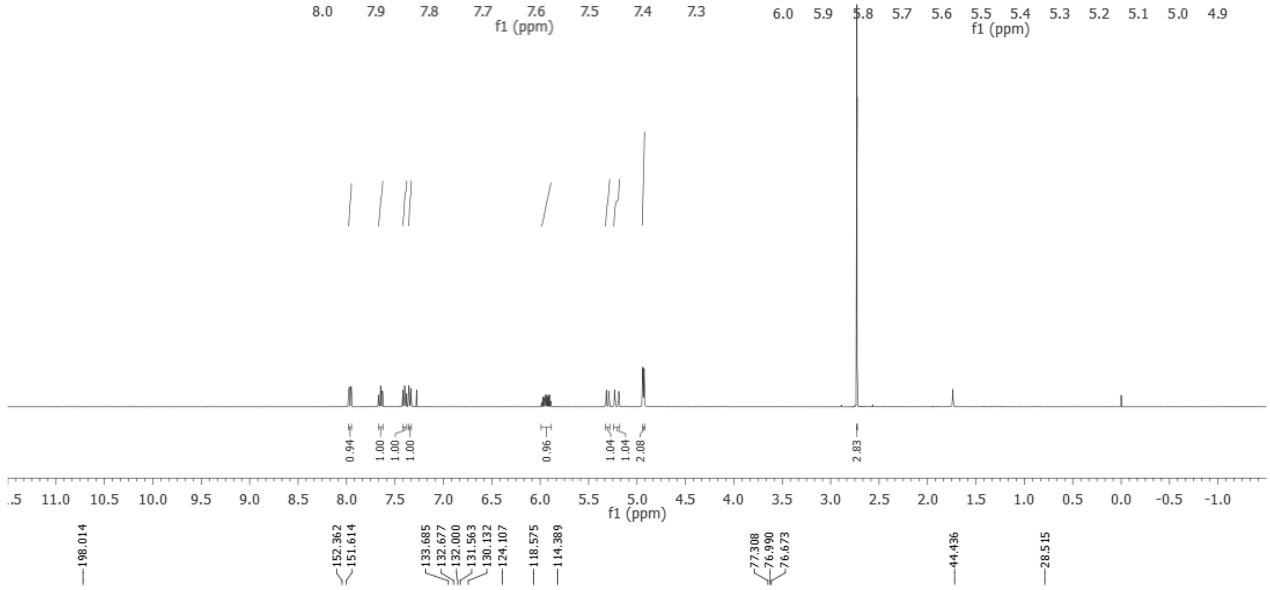

198.223
152.336
151.686
133.419
132.714
132.171
131.745
123.926
113.671
77.308
76.990
76.673
37.393
28.523
12.342
Solvent CDCl3
Spectrometer Frequency 100.69
2b
f1 (ppm)

Solvent $CDCl_3$

Spectrometer Frequency 400.40

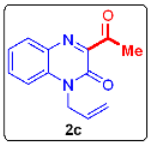


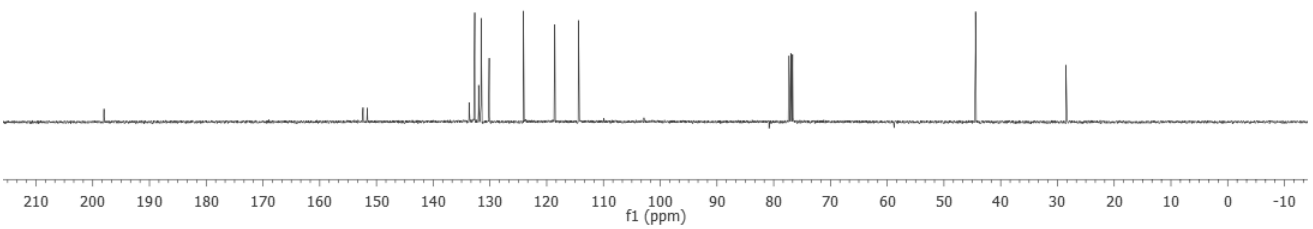


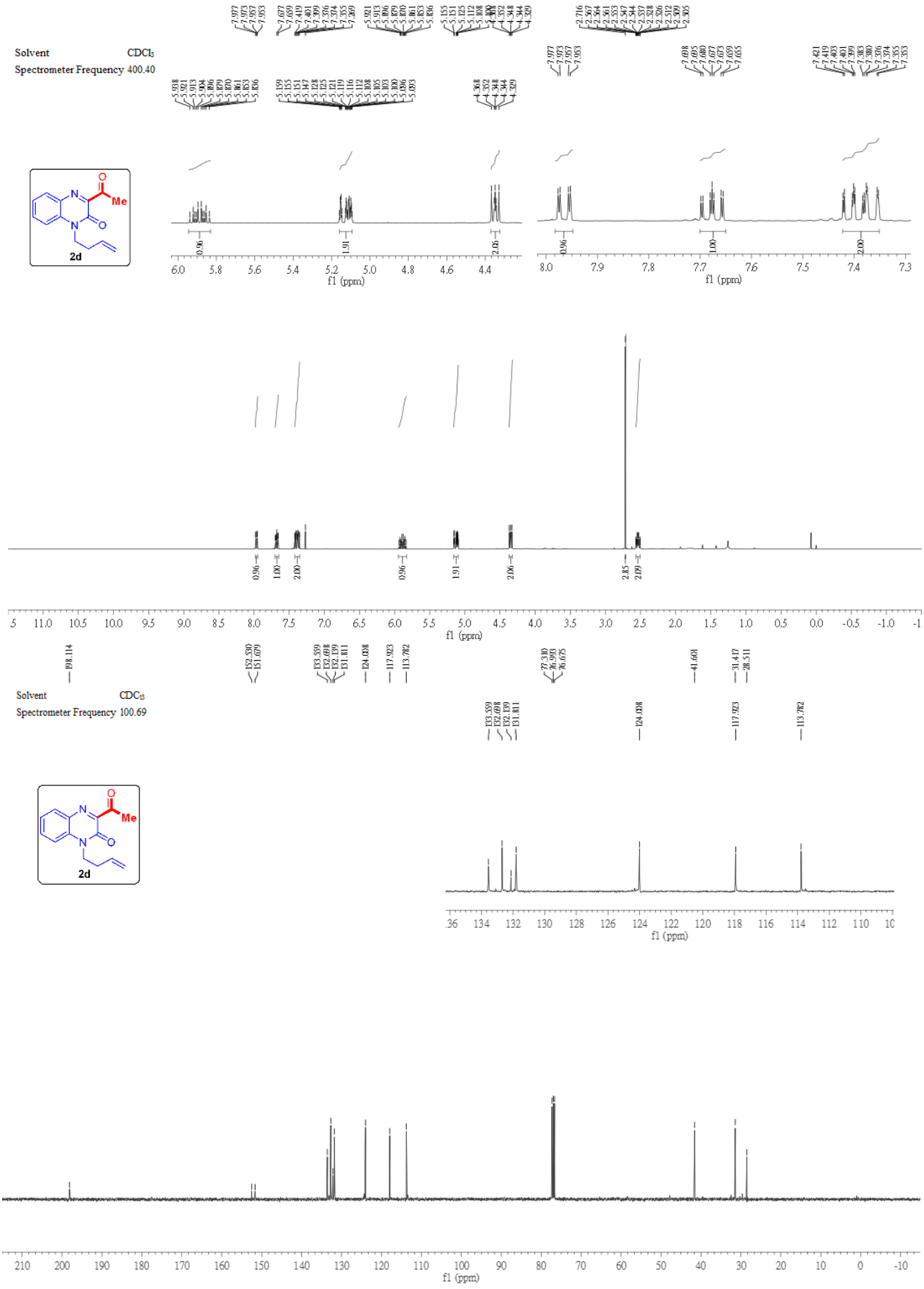


Solvent $CDCl_3$

Spectrometer Frequency 100.69



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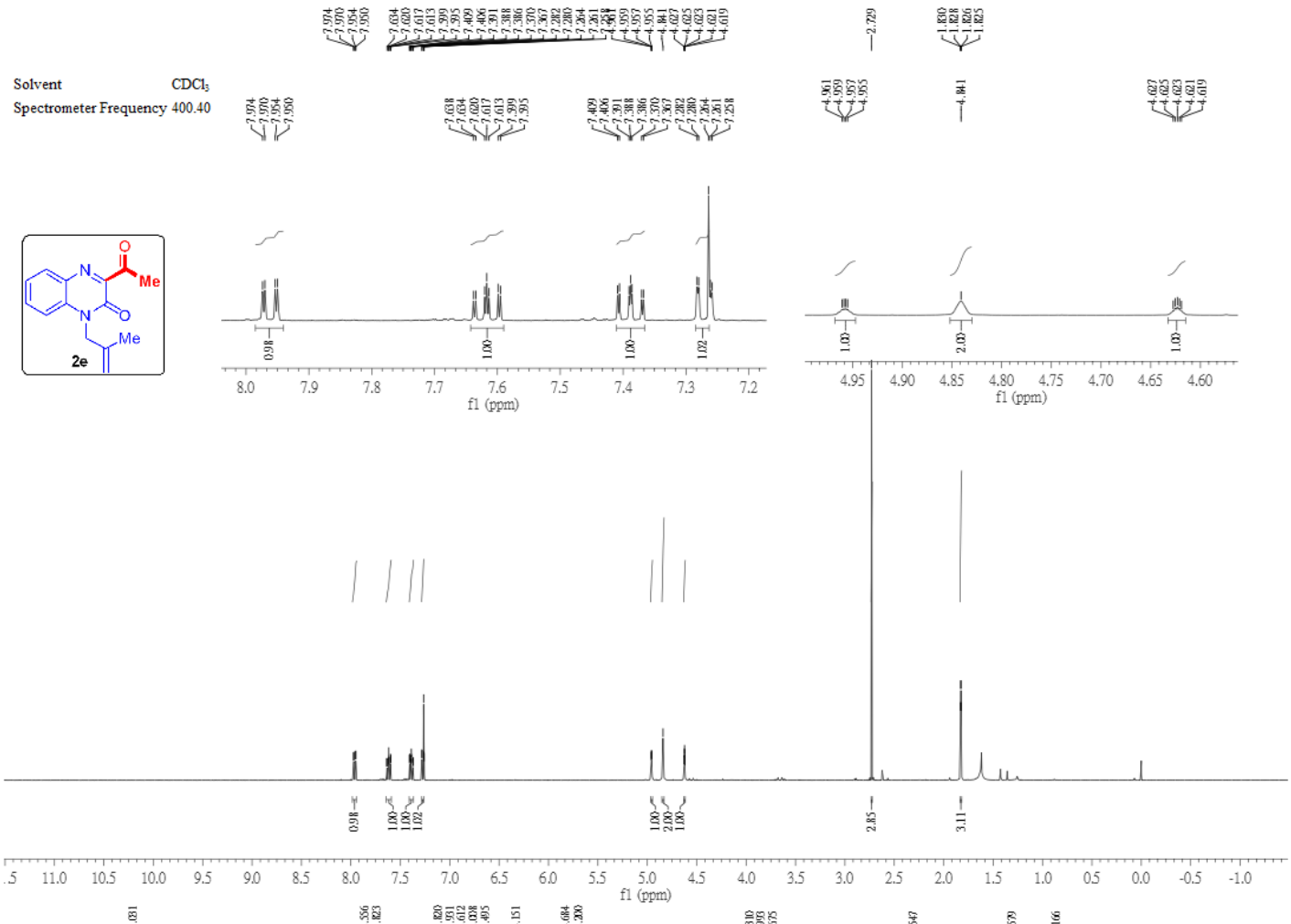
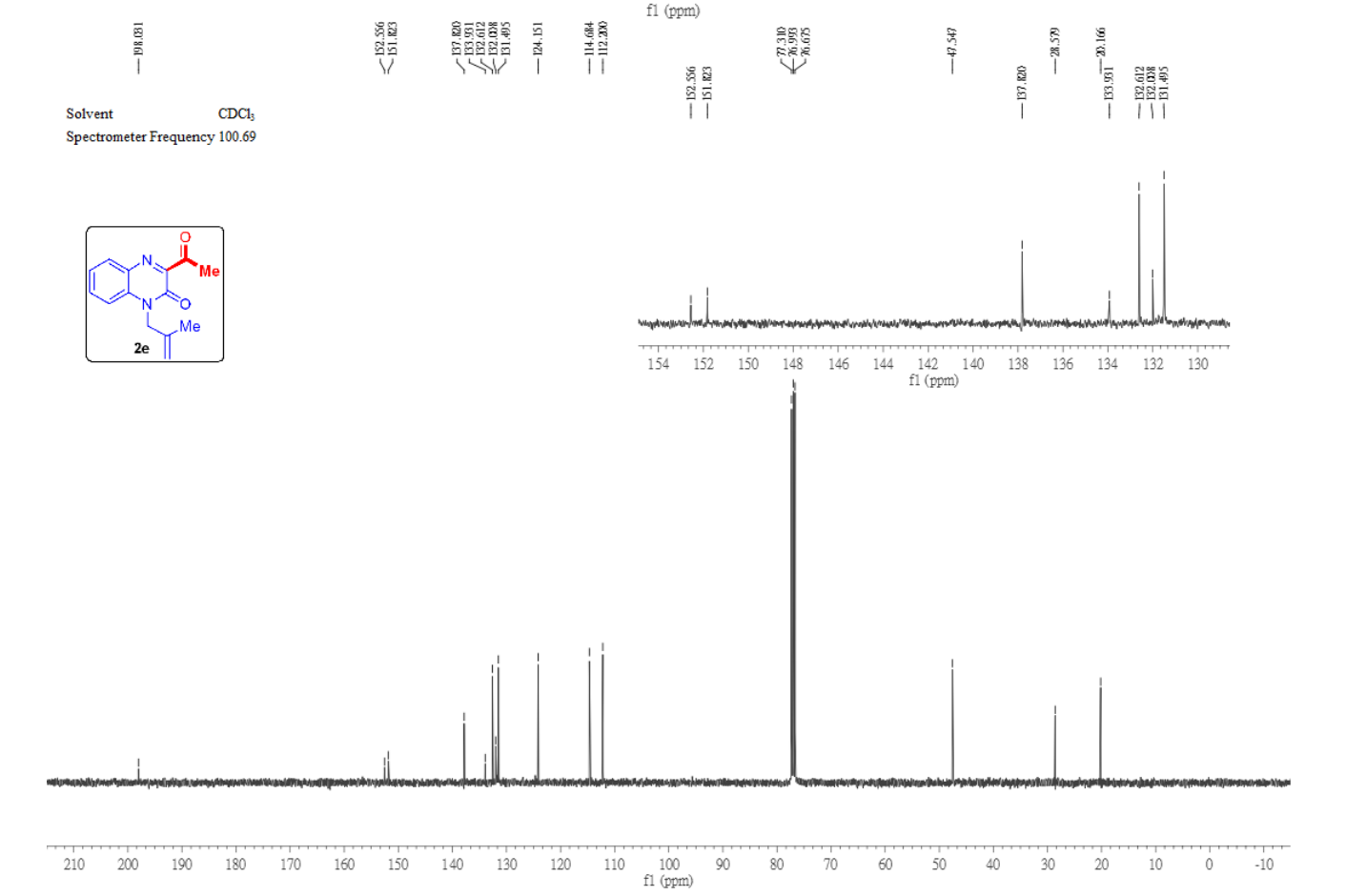
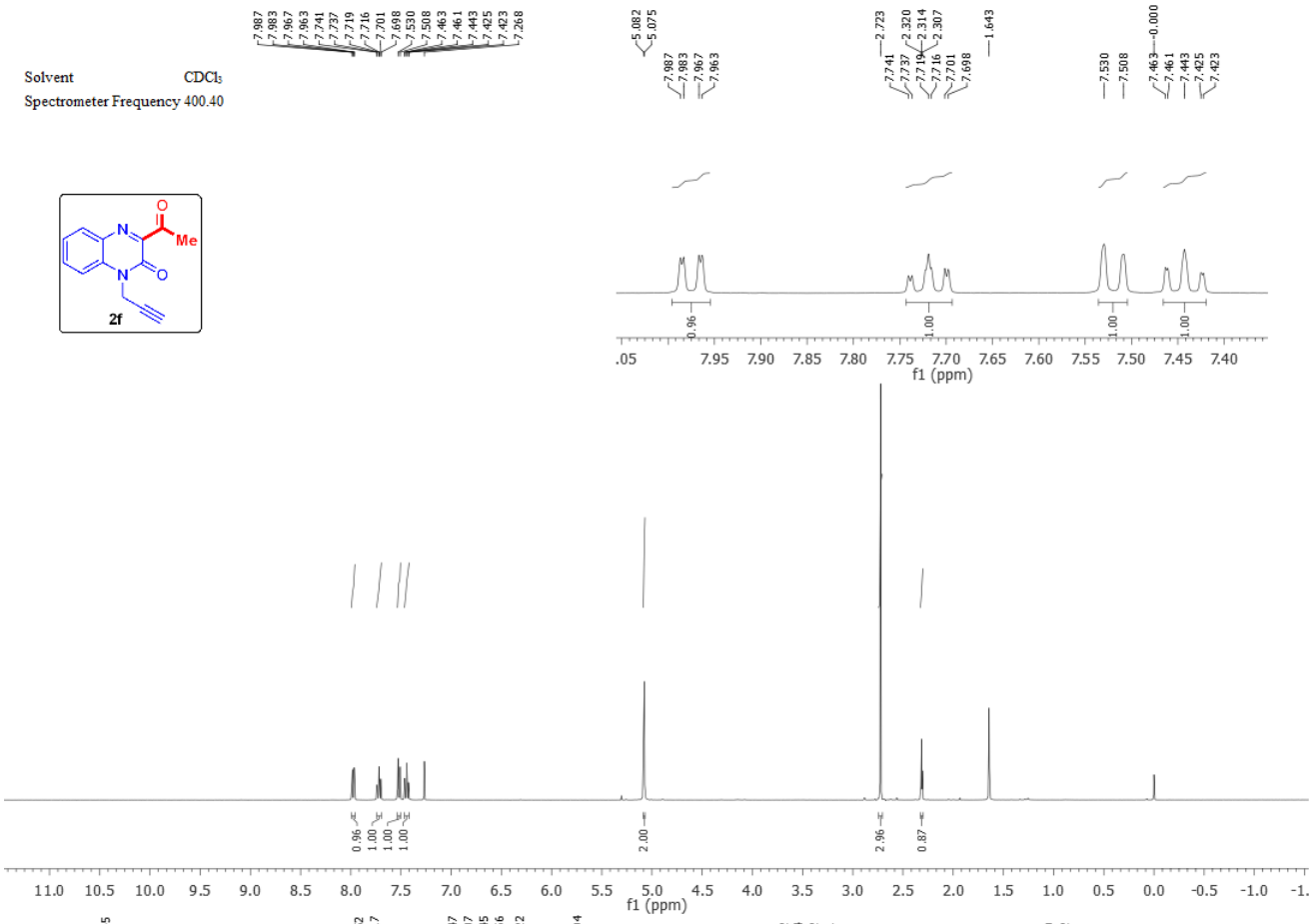
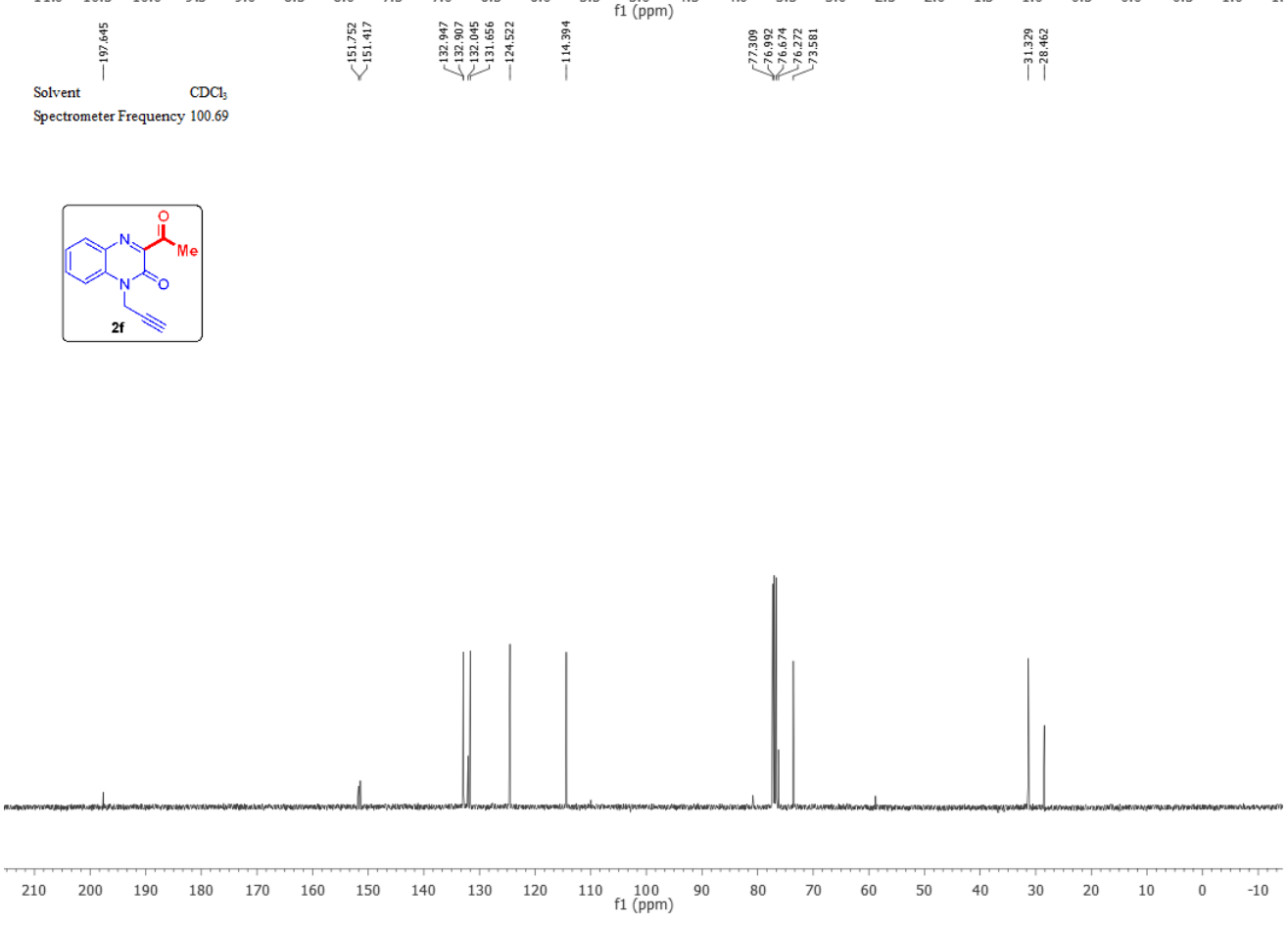
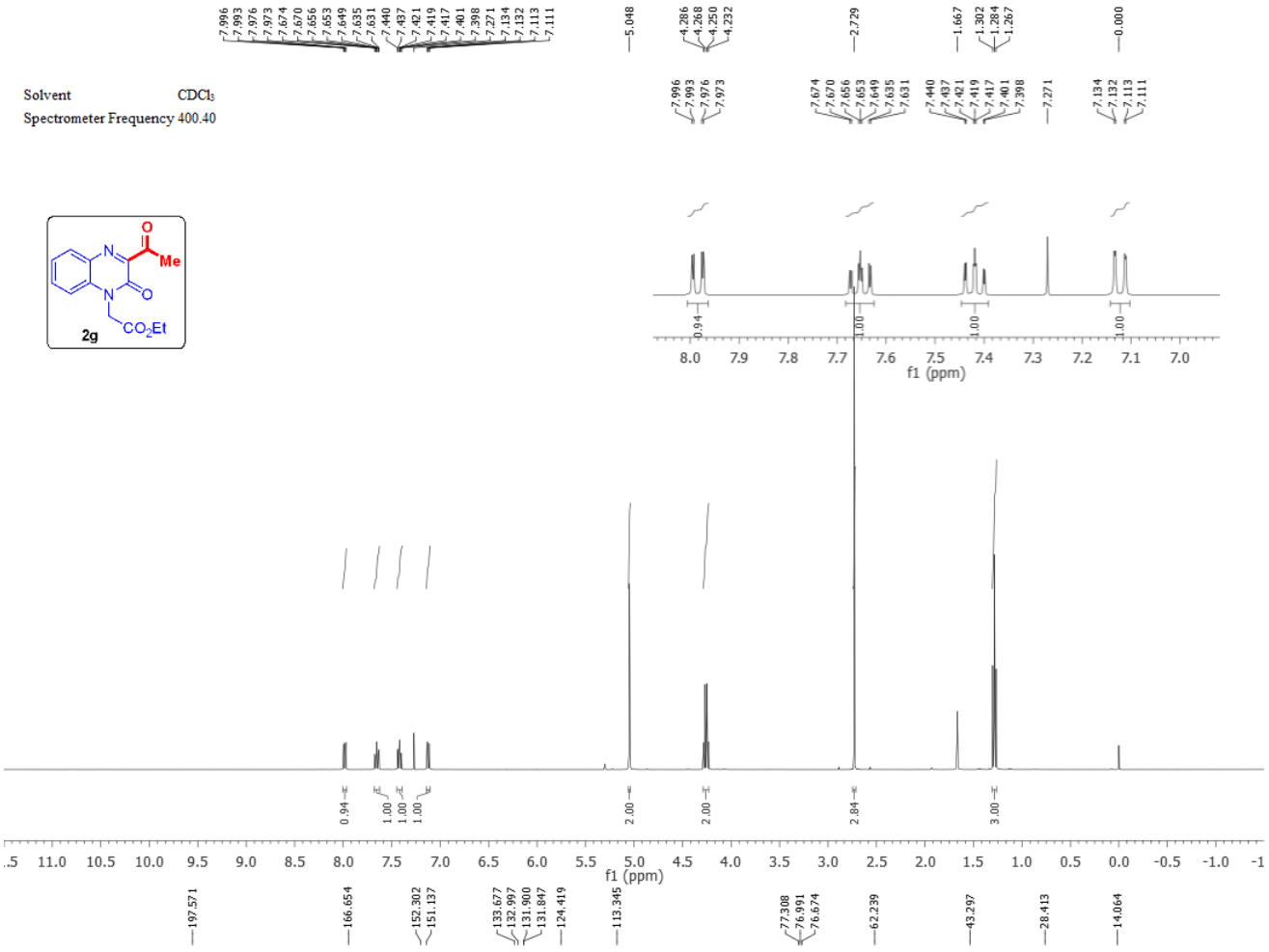
Spectrometer Frequency 400.40
2d
f1 (ppm)
Solvent CDCl3
Spectrometer Frequency 100.69
2d
f1 (ppm)


Solvent CDCl3
Spectrometer Frequency 400.40
2e
f1 (ppm)


Solvent CDCl3
Spectrometer Frequency 100.69
2e
f1 (ppm)


Solvent CDCl3
Spectrometer Frequency 400.40
2f
f1 (ppm)


Solvent CDCl3
Spectrometer Frequency 100.69
2f
f1 (ppm)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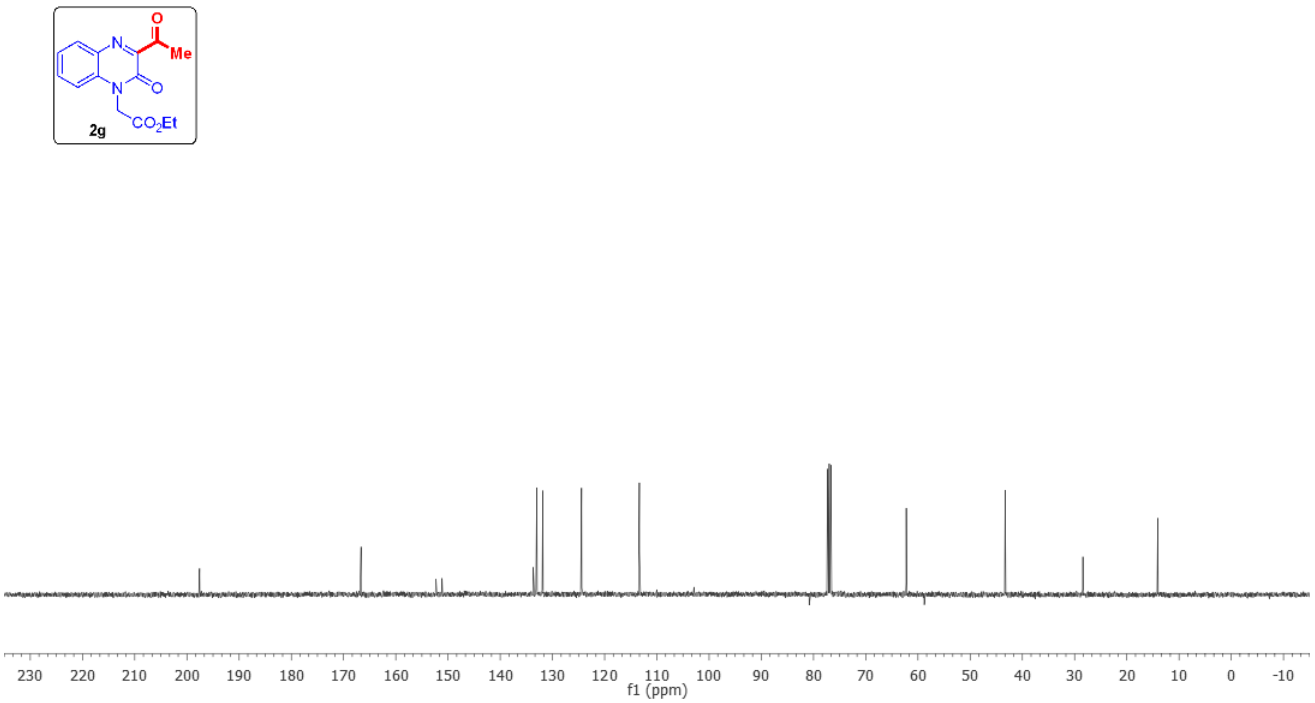
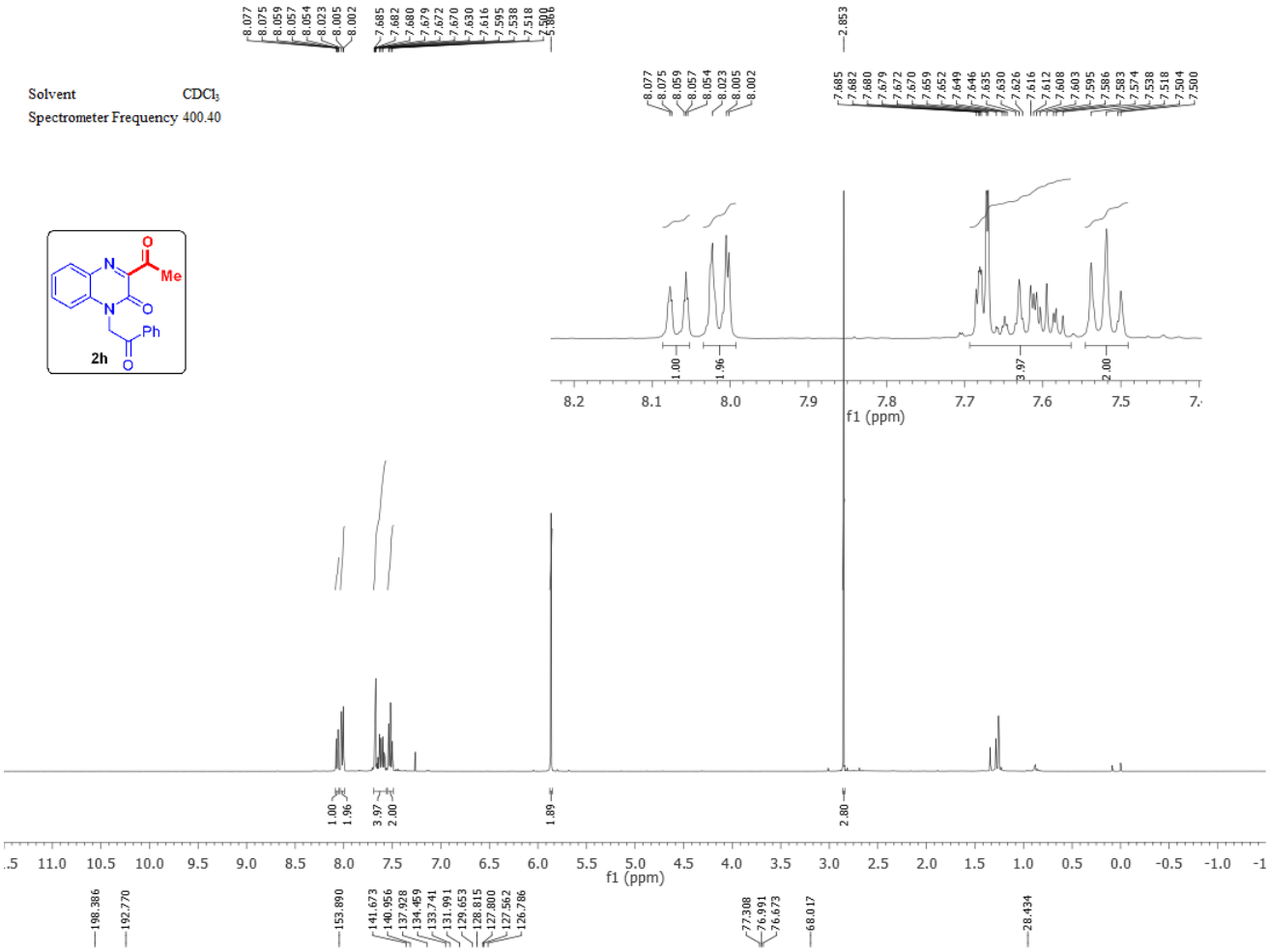
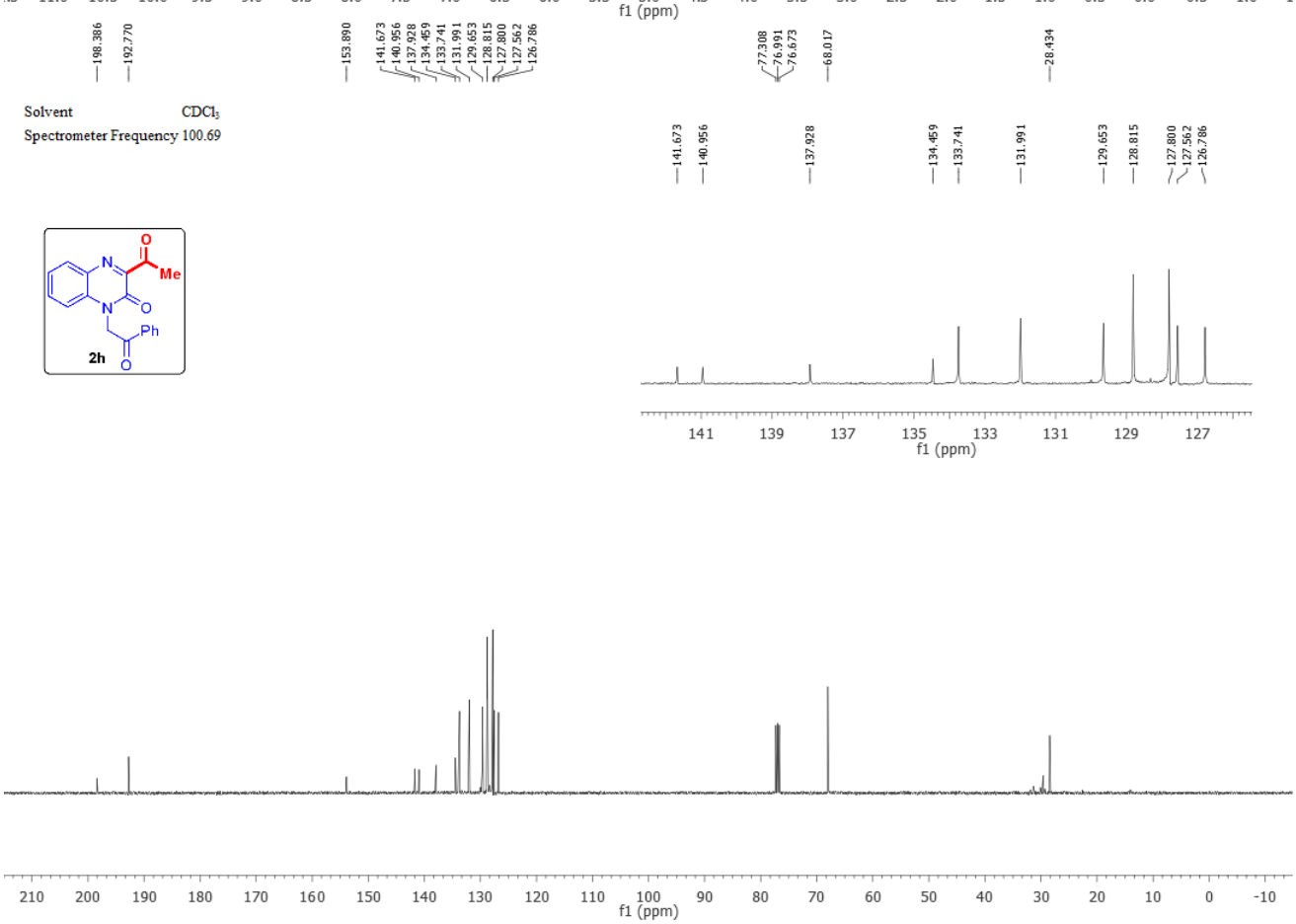
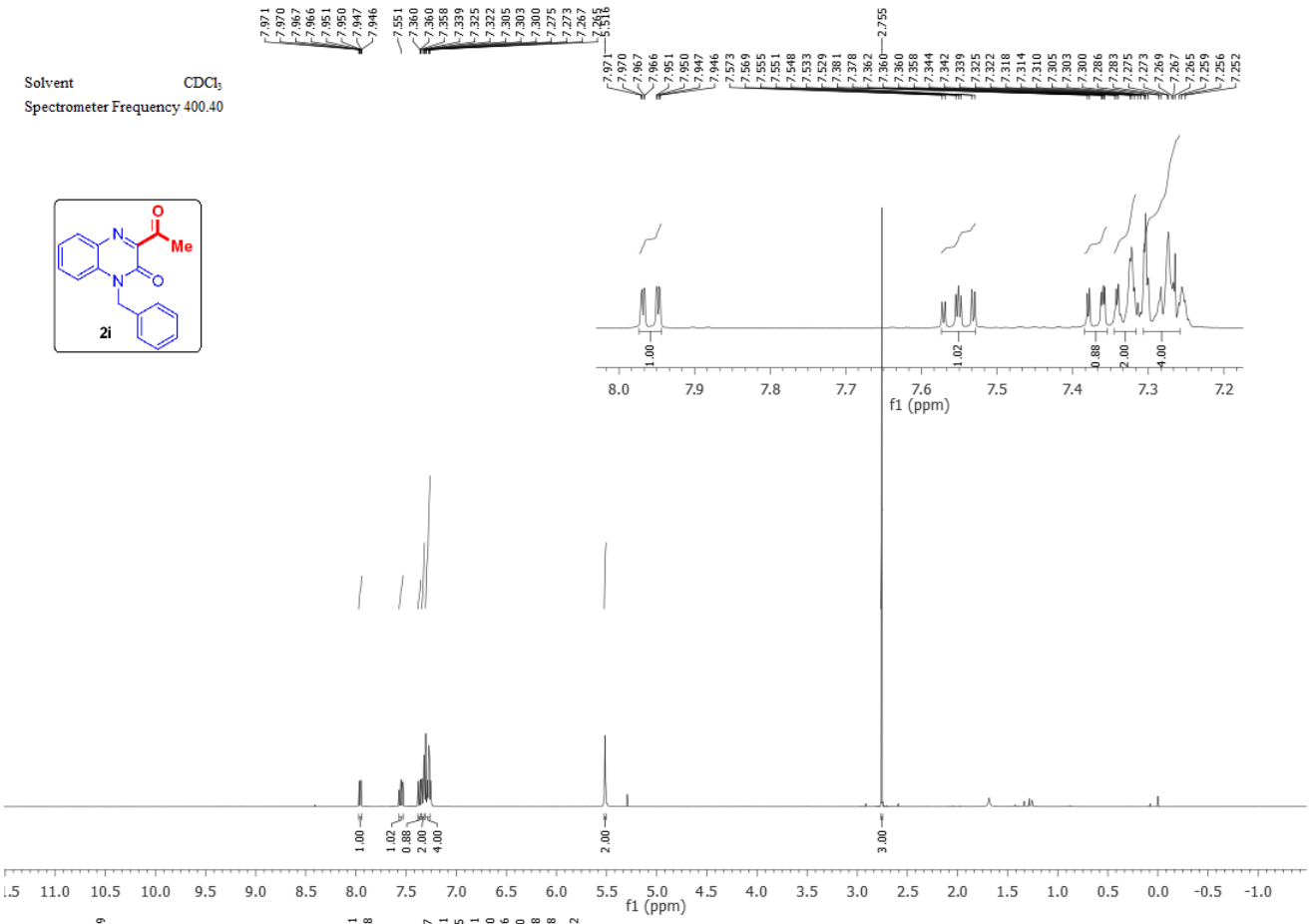
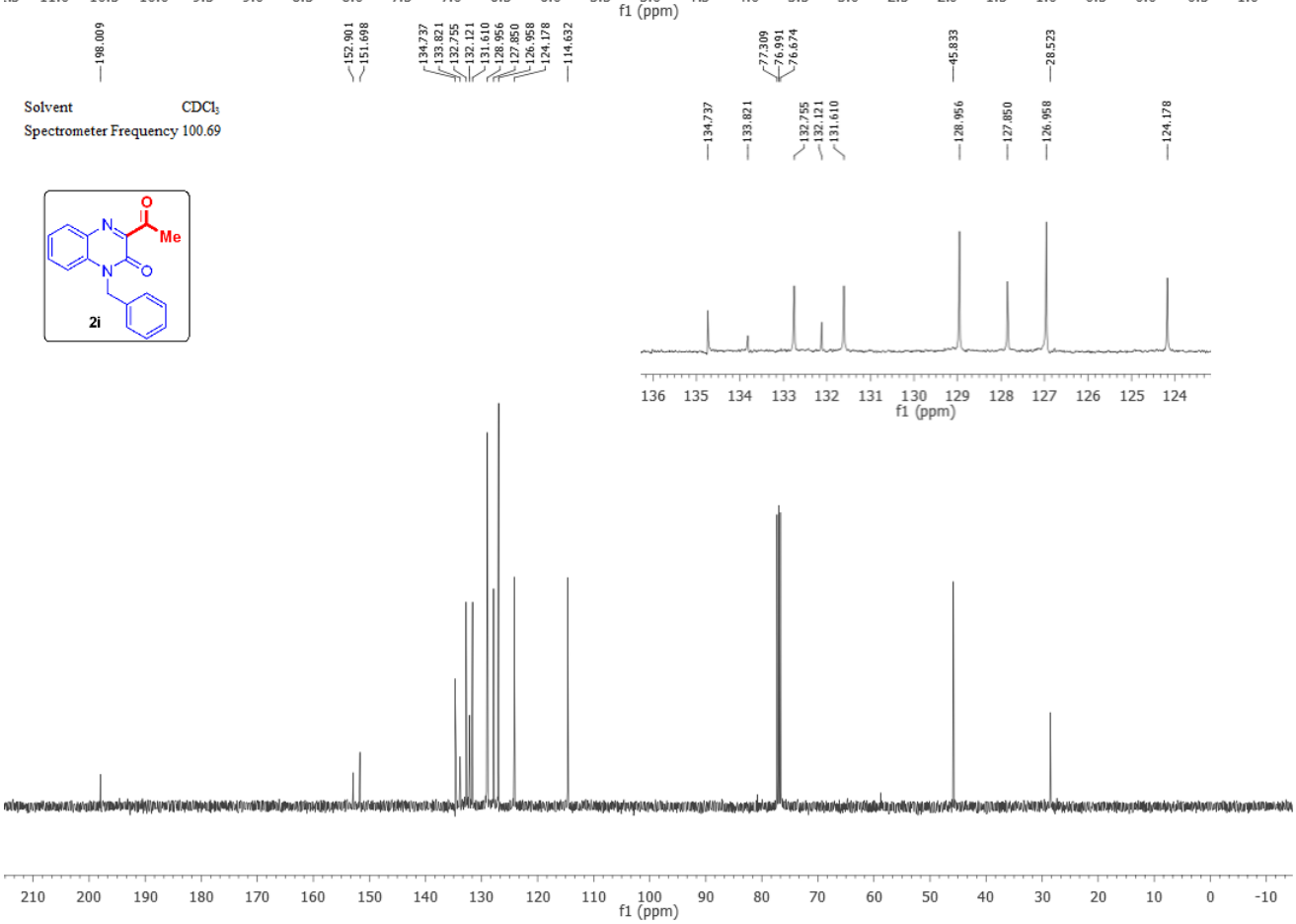
7.993
7.976
7.973
7.674
7.670
7.656
7.653
7.649
7.635
7.631
7.440
7.437
7.421
7.419
7.417
7.401
7.398
7.271
7.134
7.132
7.113
7.111
5.048
4.286
4.268
4.250
4.232
2.729
1.667
1.302
1.284
1.267
0.000
Solvent CDCl3
Spectrometer Frequency 400.40
Me
CO2Et
2g
f1 (ppm)
0.94
1.00
1.00
1.00
2.00
2.00
2.84
3.00
197.571
166.654
152.302
151.137
133.677
132.997
131.900
131.847
124.419
113.345
77.308
76.991
76.674
62.239
43.297
28.413
14.064

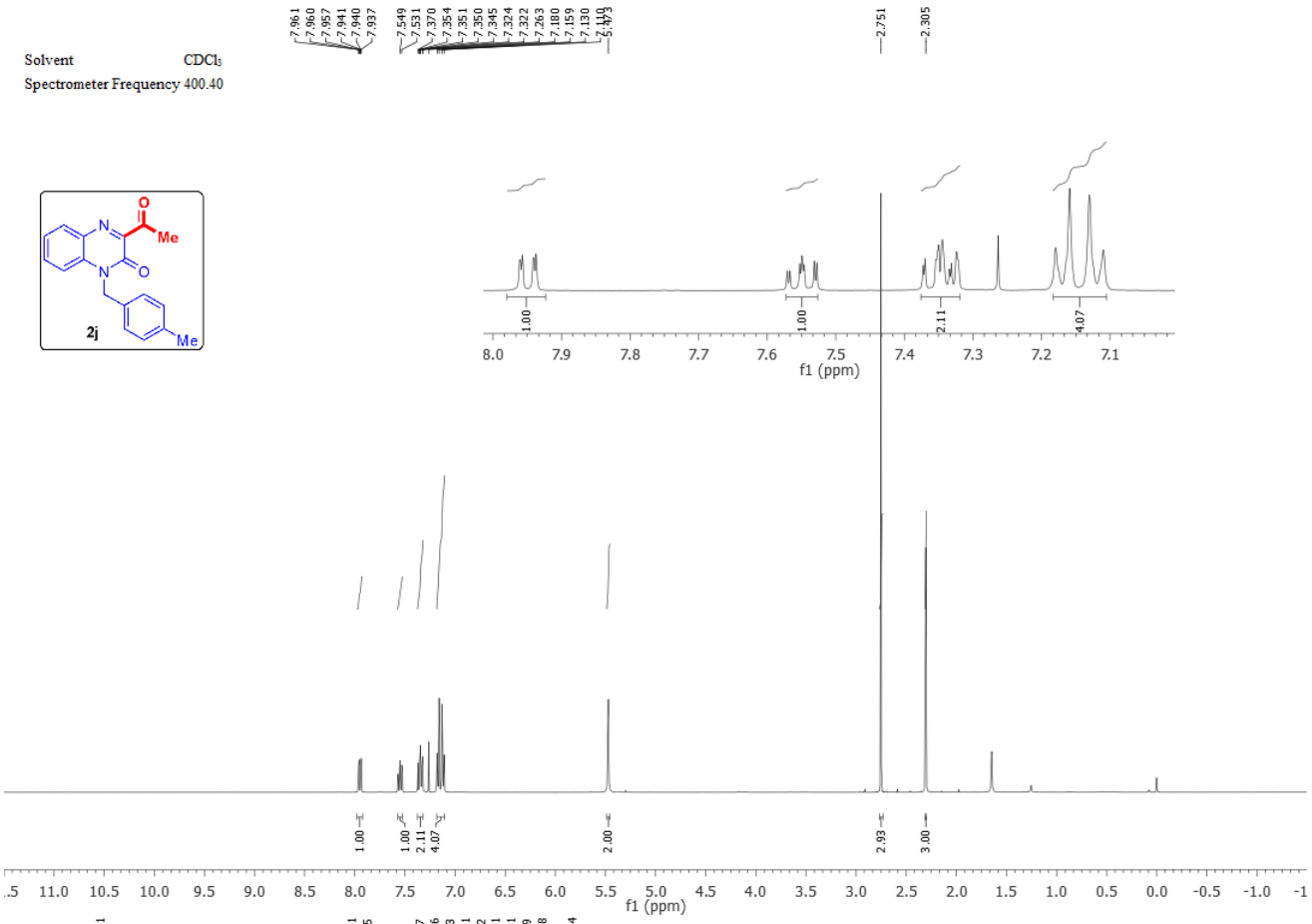

Solvent CDCl3
Spectrometer Frequency 100.69
Me
CO2Et
2g
f1 (ppm)

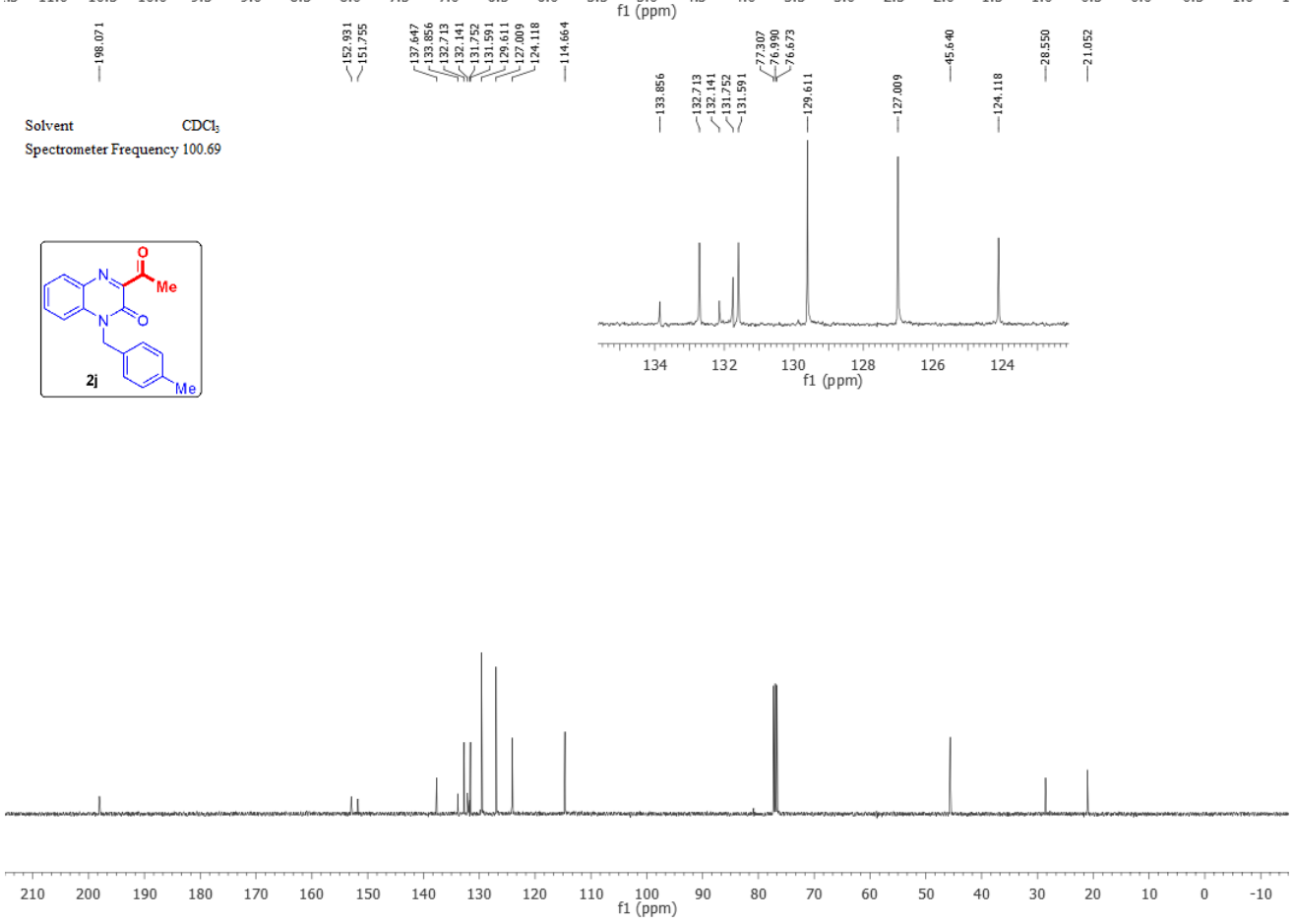

Solvent CDCl3
Spectrometer Frequency 400.40
2h
f1 (ppm)

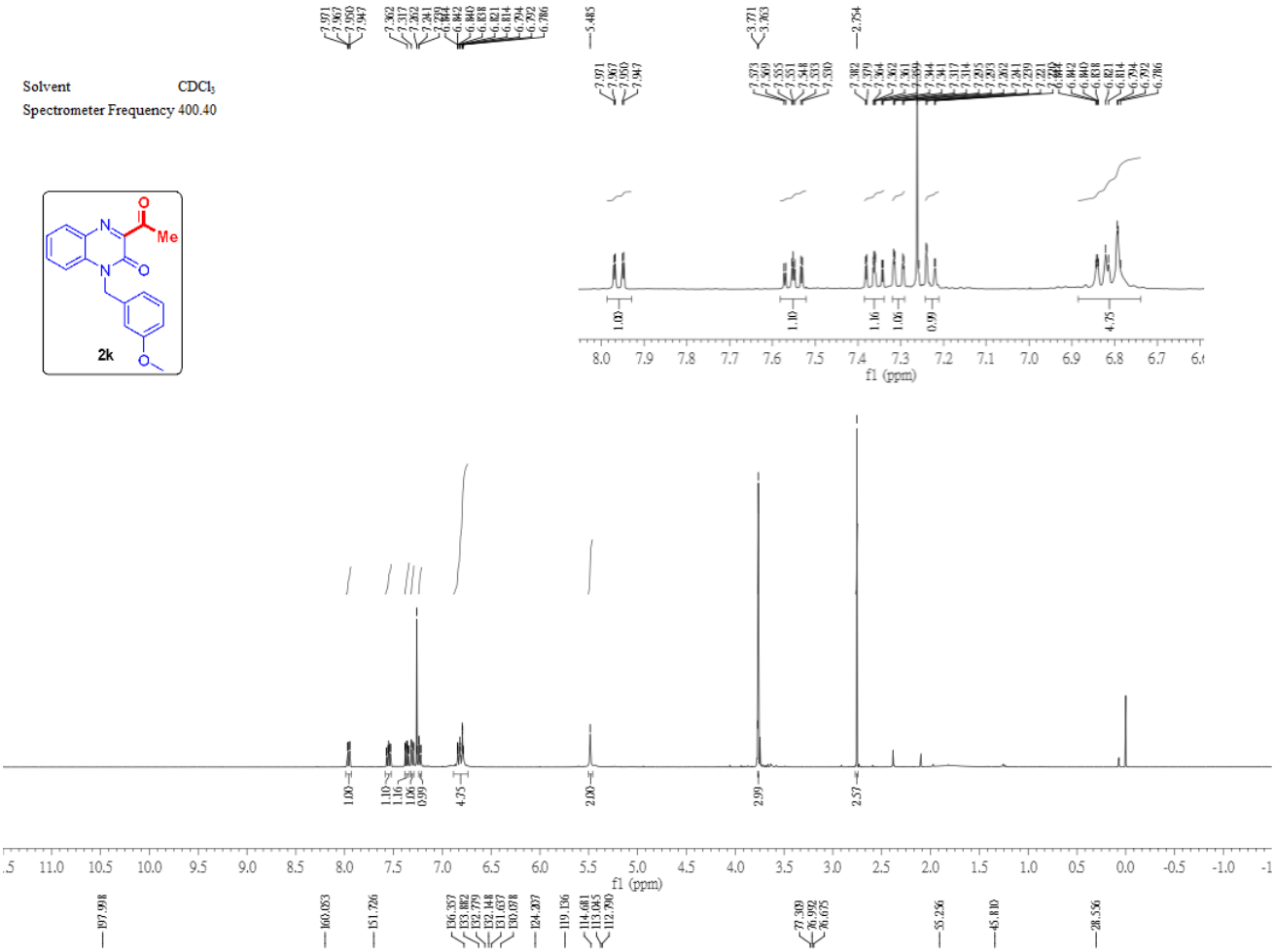

Solvent CDCl3
Spectrometer Frequency 100.69
2h
f1 (ppm)

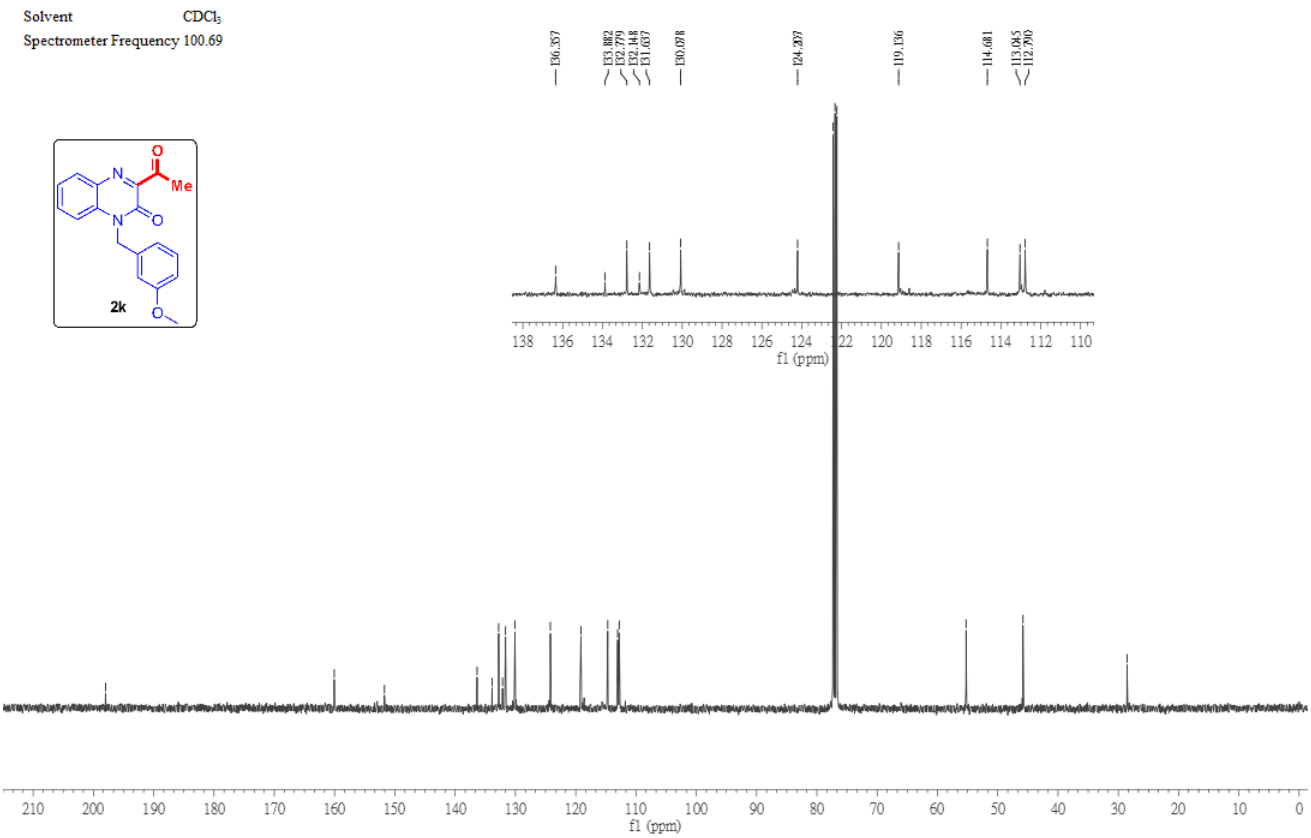

Solvent CDCl3
Spectrometer Frequency 400.40
Me
2i
f1 (ppm)

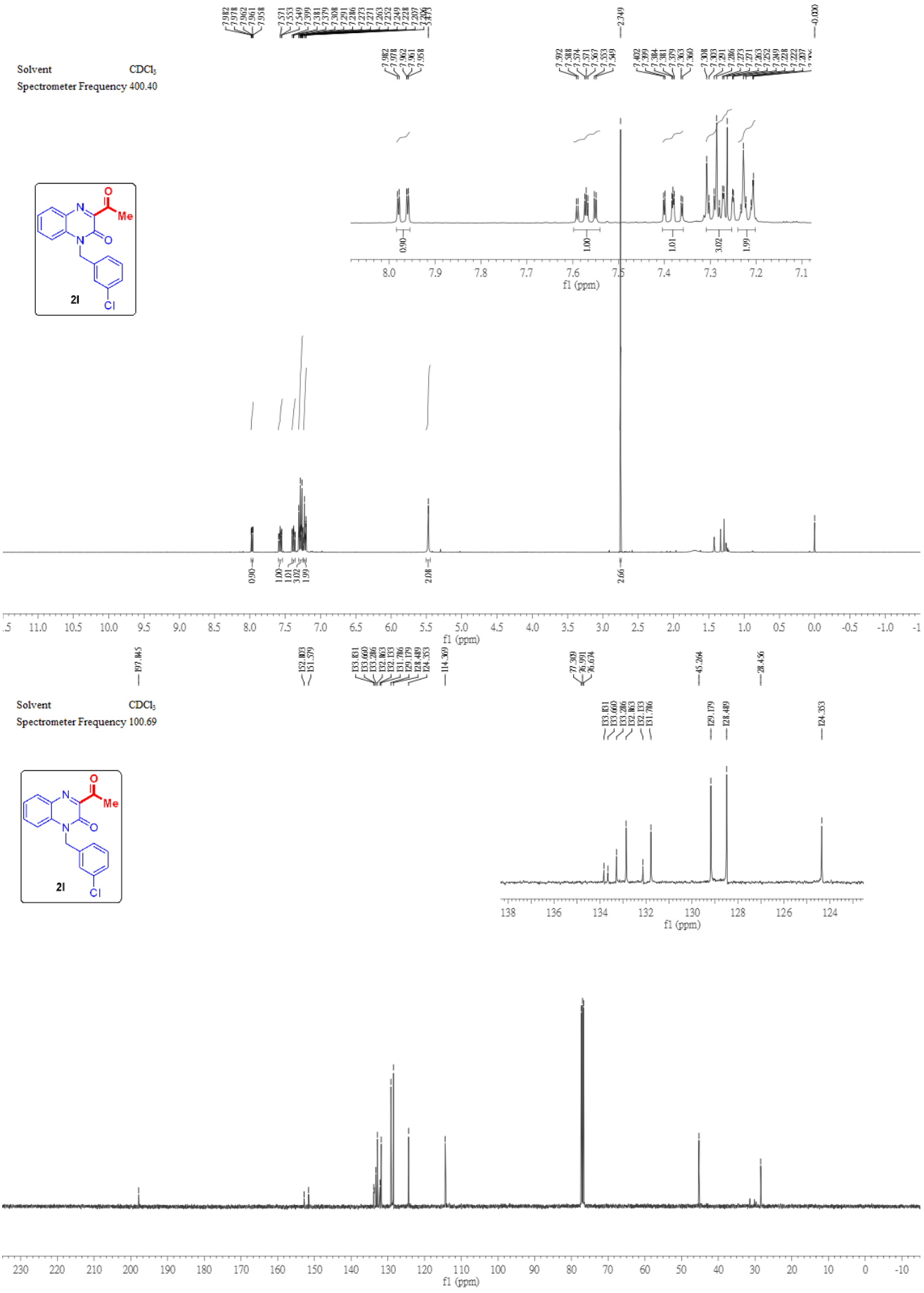

Solvent CDCl3
Spectrometer Frequency 100.69
Me
2i
f1 (ppm)

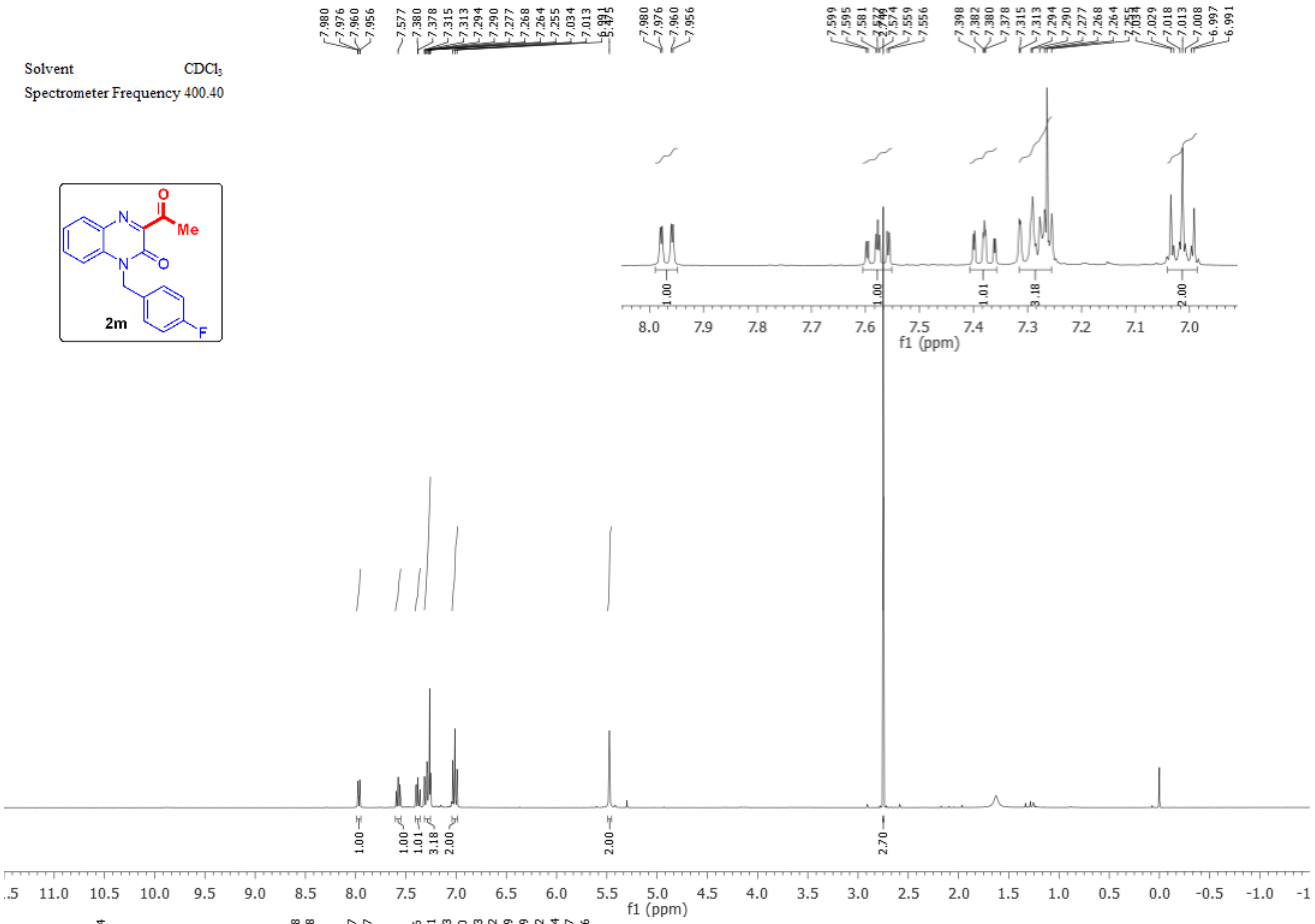

Solvent CDCl3
Spectrometer Frequency 400.40
2j
f1 (ppm)

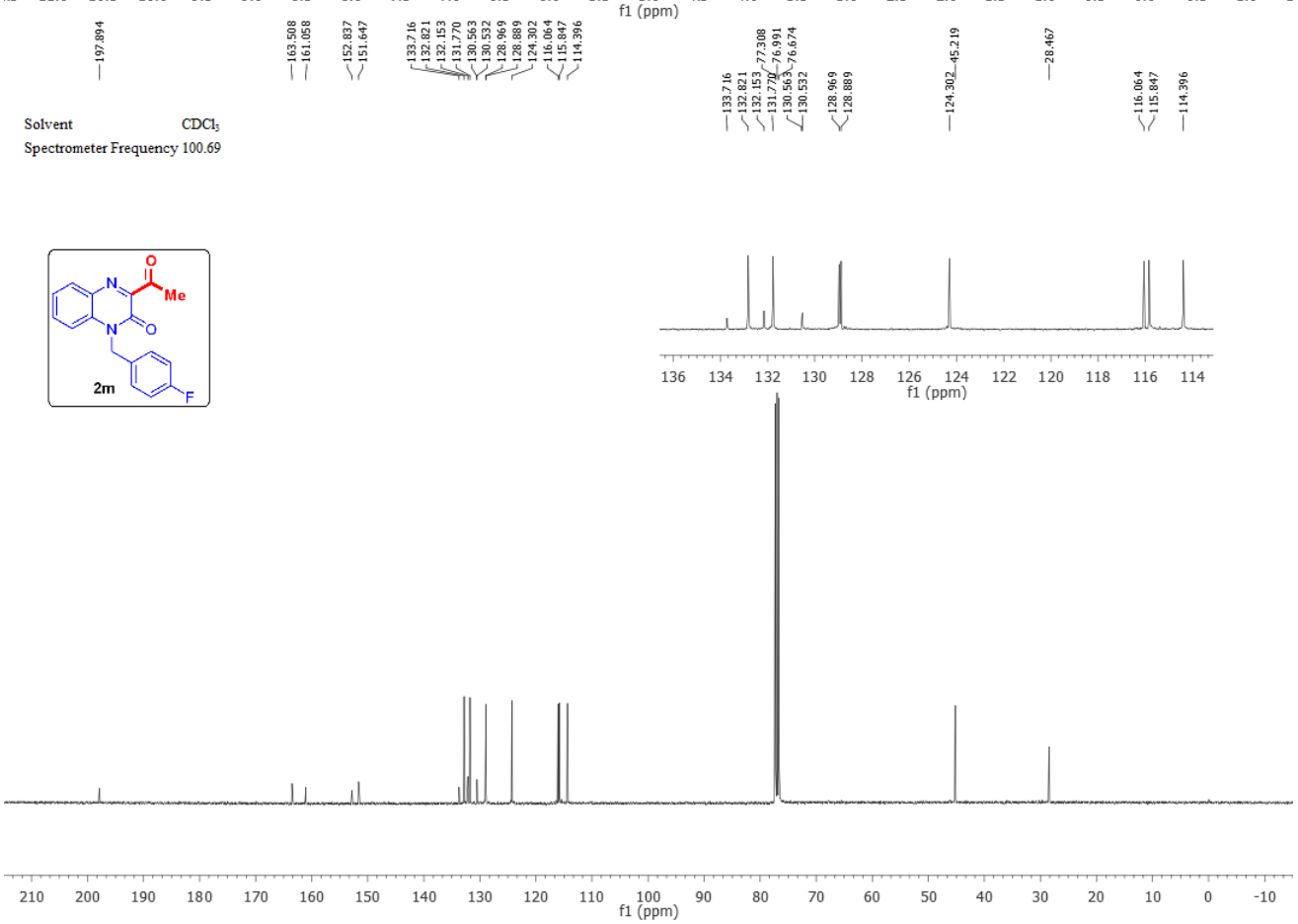

Solvent CDCl3
Spectrometer Frequency 100.69
2j
f1 (ppm)


Solvent CDCl3
Spectrometer Frequency 400.40
2k
f1 (ppm)


Solvent CDCl3
Spectrometer Frequency 100.69
2k
f1 (ppm)

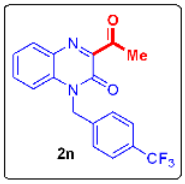

Solvent CDCl3
Spectrometer Frequency 400.40
2l
Cl
f1 (ppm)
Solvent CDCl3
Spectrometer Frequency 100.69
2l
Cl
f1 (ppm)
f1 (ppm)


Solvent CDCl3
Spectrometer Frequency 400.40
2m
f1 (ppm)


Solvent CDCl3
Spectrometer Frequency 100.69
2m
f1 (ppm)

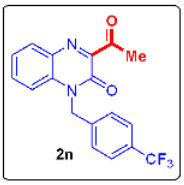
Solvent $CDCl_3$

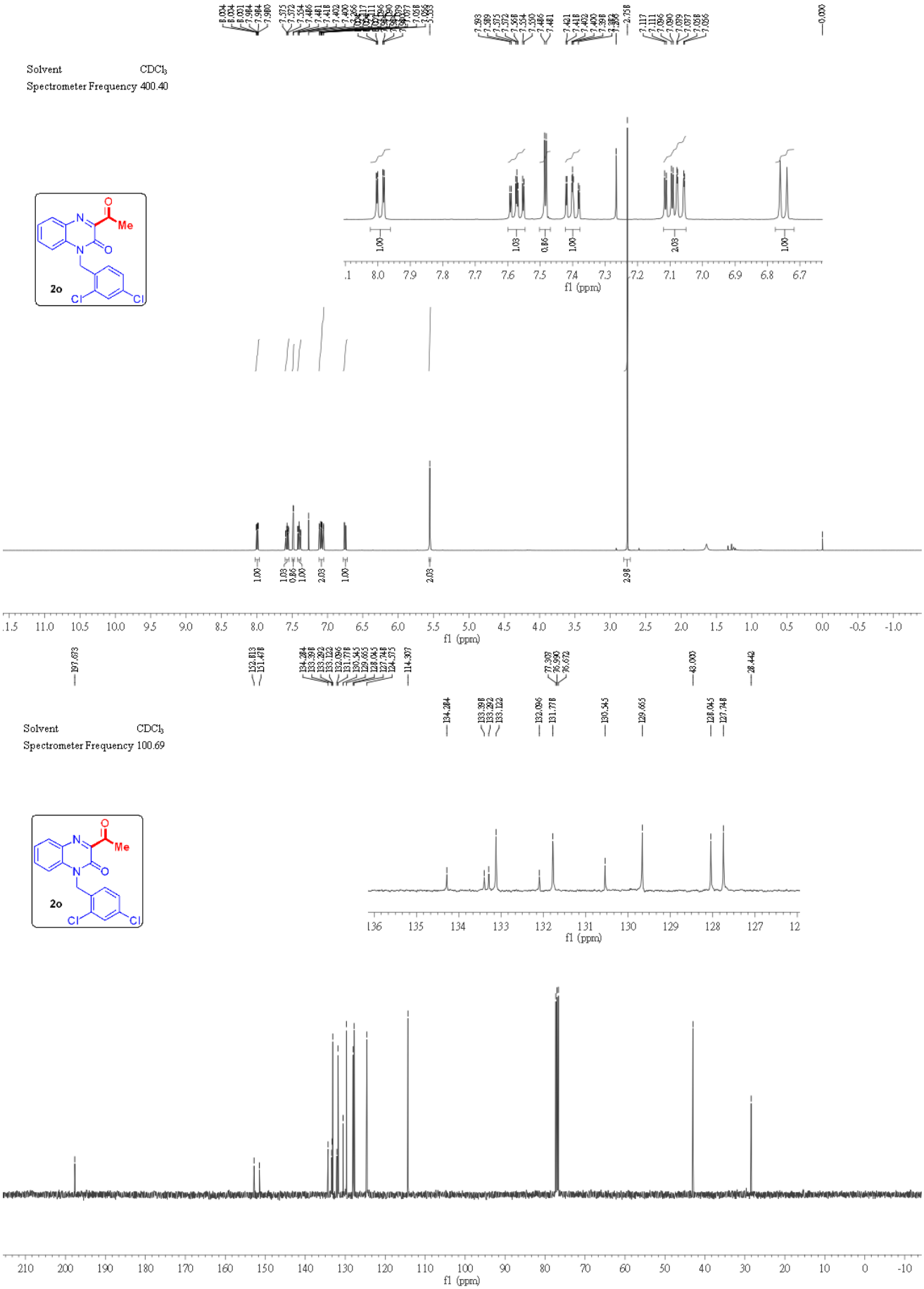
Spectrometer Frequency 400.40

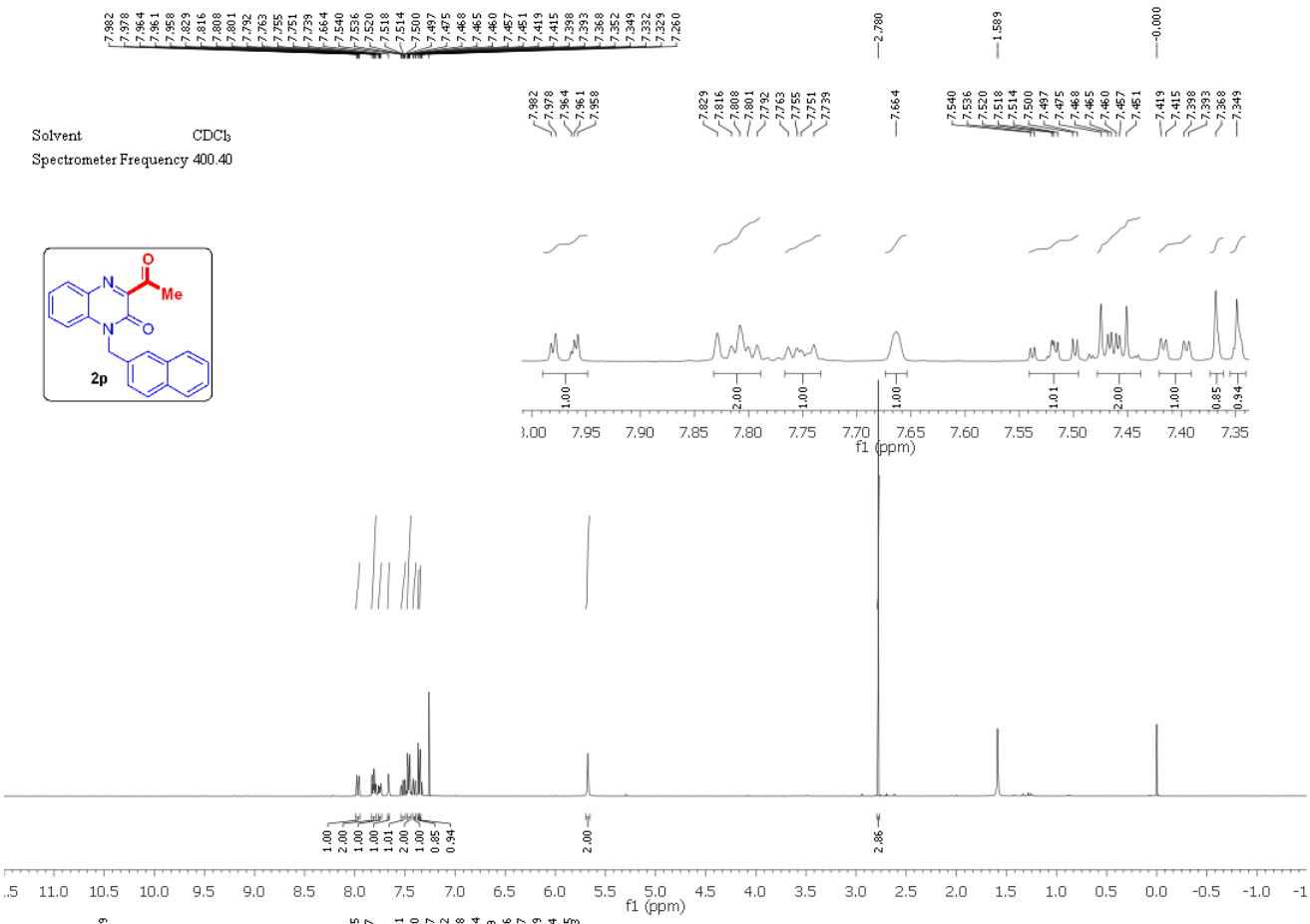


Solvent $CDCl_3$

Spectrometer Frequency 100.69




Solvent CDCl3
Spectrometer Frequency 400.40
2o
f1 (ppm)
Solvent CDCl3
Spectrometer Frequency 100.69
2o
f1 (ppm)
f1 (ppm)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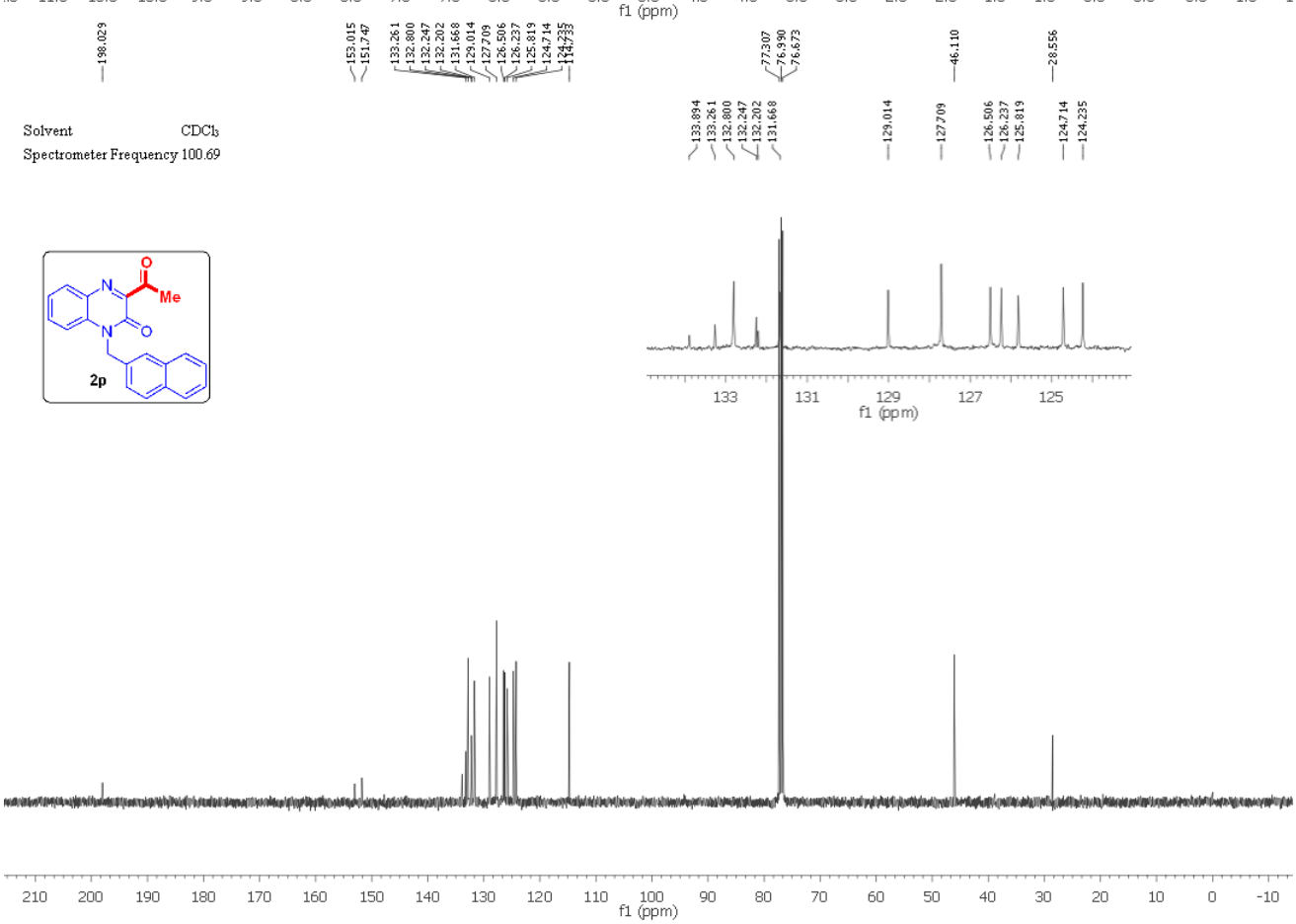
2p
f1 (ppm)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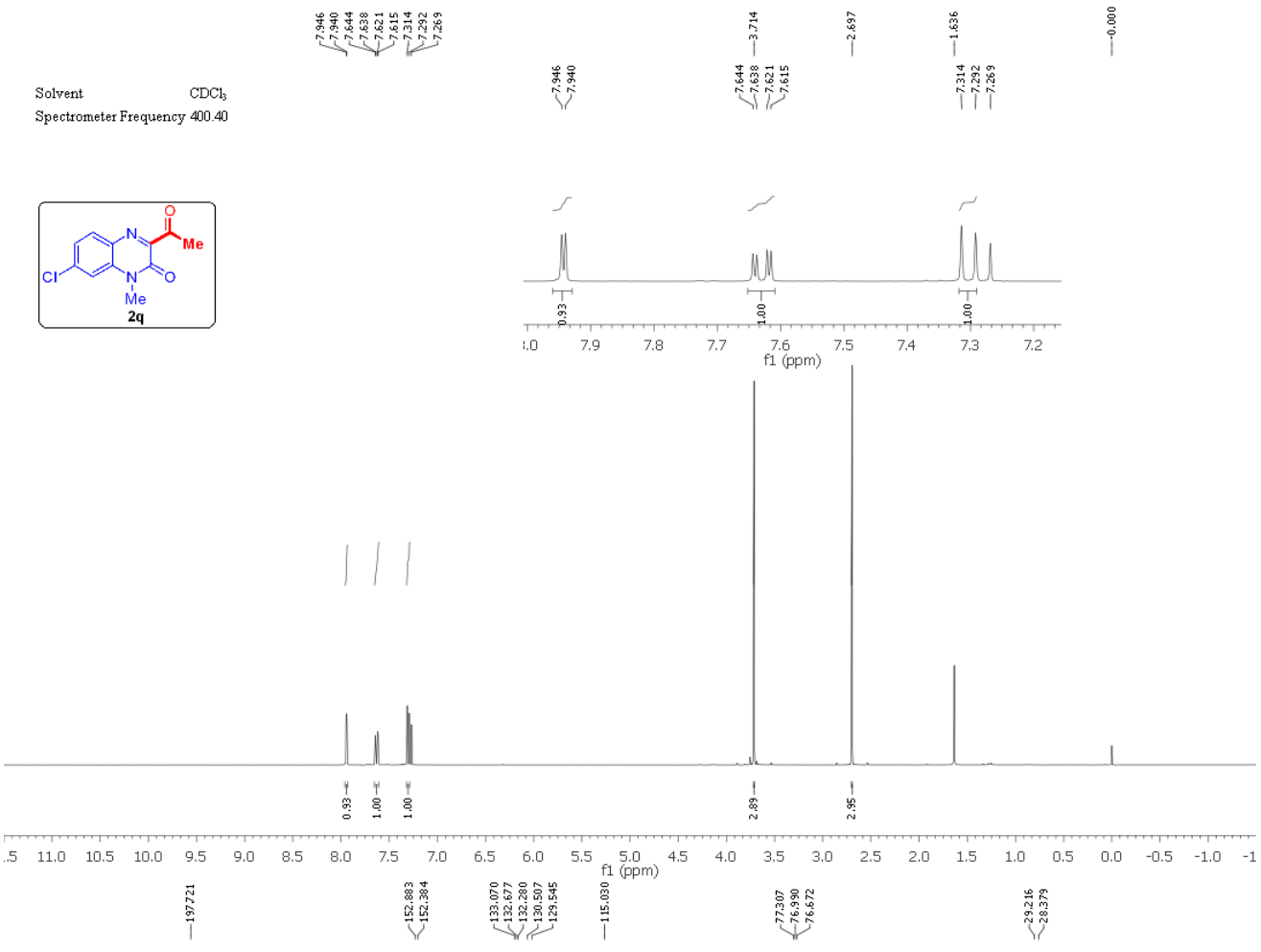
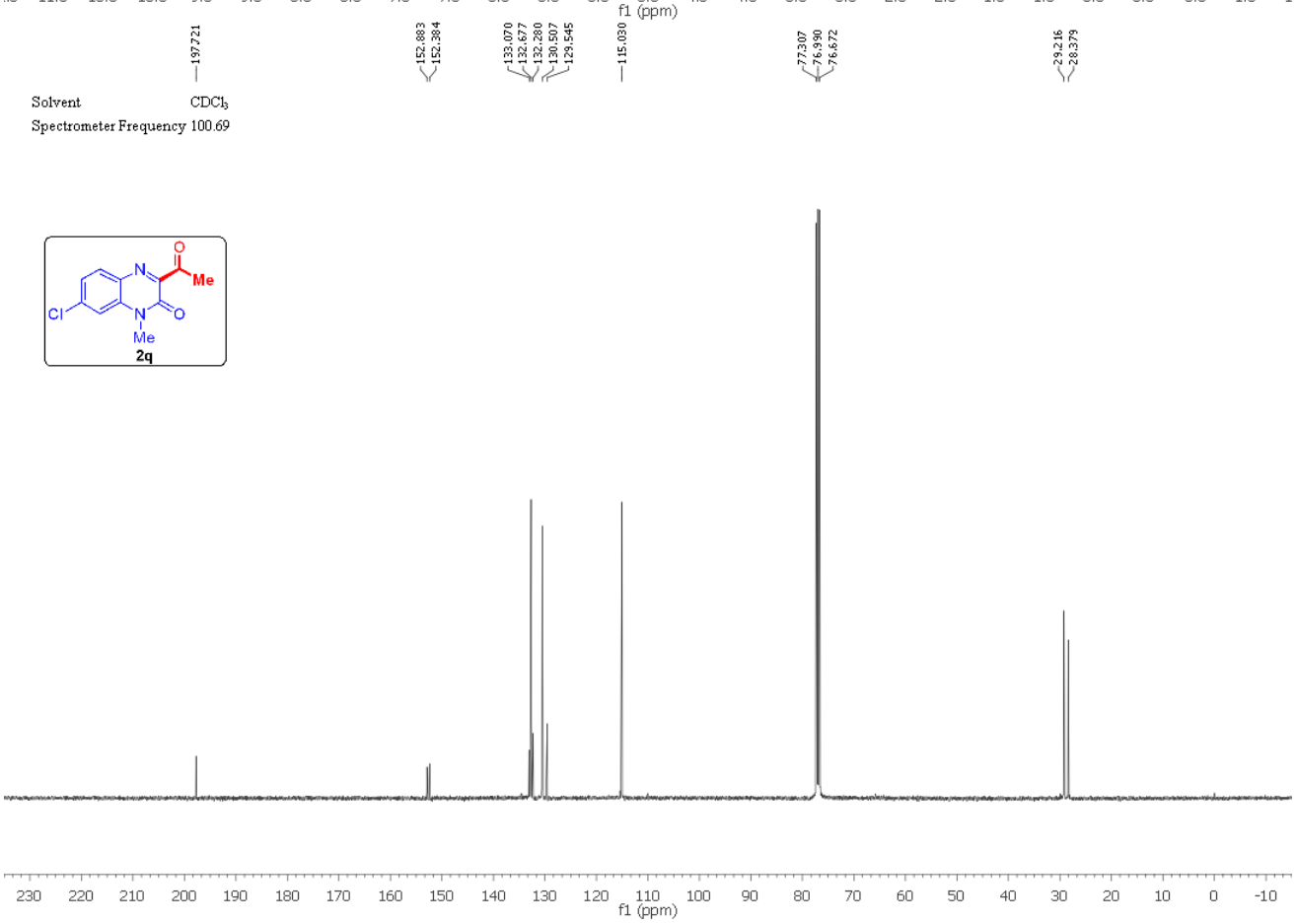
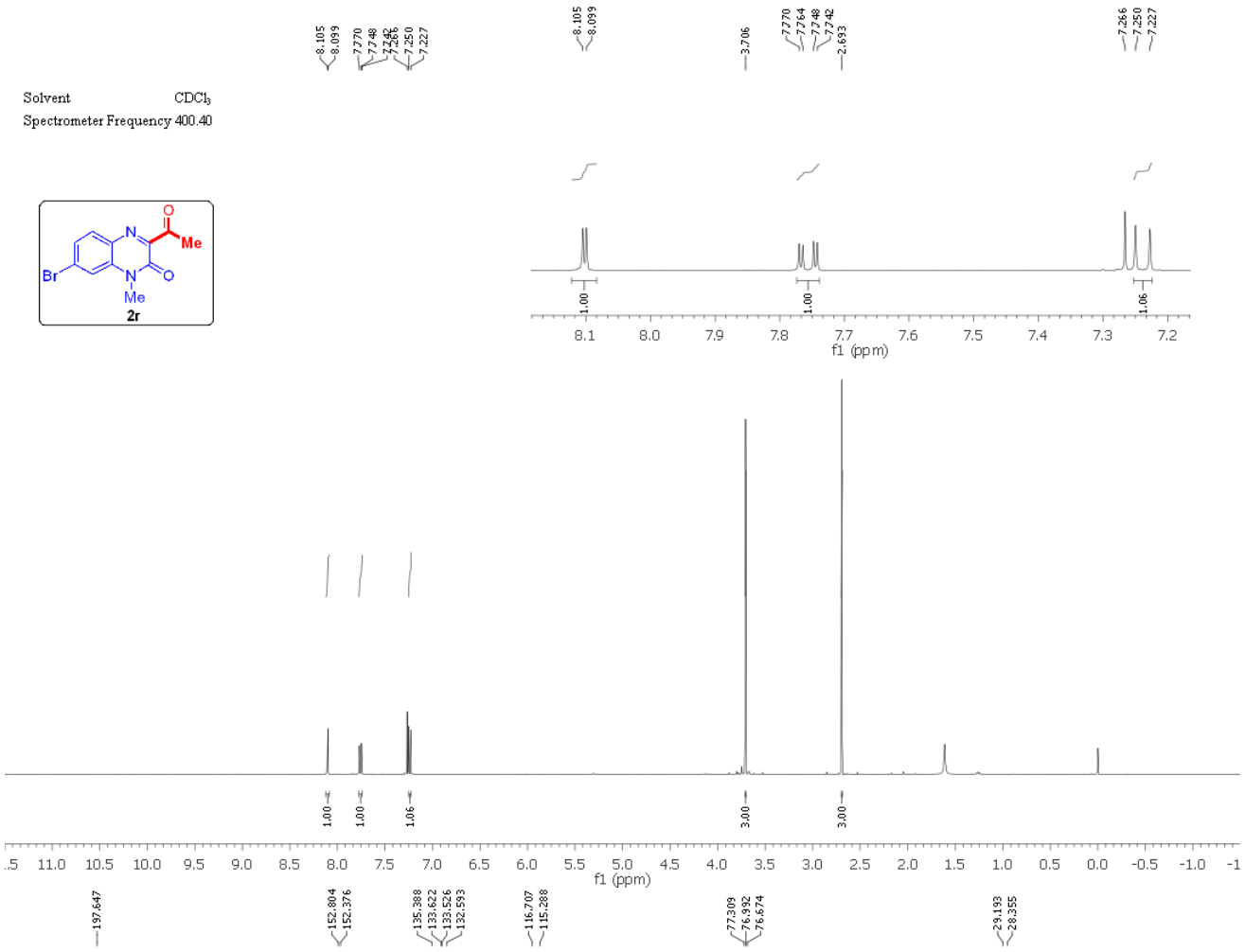
Spectrometer Frequency 100.69
2p
f1 (ppm)


Solvent CDCl3
Spectrometer Frequency 400.40
2q
f1 (ppm)


Solvent CDCl3
Spectrometer Frequency 100.69
2q
f1 (ppm)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8.099
7.770
7.748
7.742
7.266
7.250
7.227
3.706
7.770
7.764
7.748
7.742
2.693
7.266
7.250
7.227
Solvent CDCl3
Spectrometer Frequency 400.40
Br
N
O
Me
N
Me
O
2r
1.00
1.00
1.06
f1 (ppm)
1.00
1.00
1.06
3.00
3.00
f1 (ppm)
197.647
152.804
152.376
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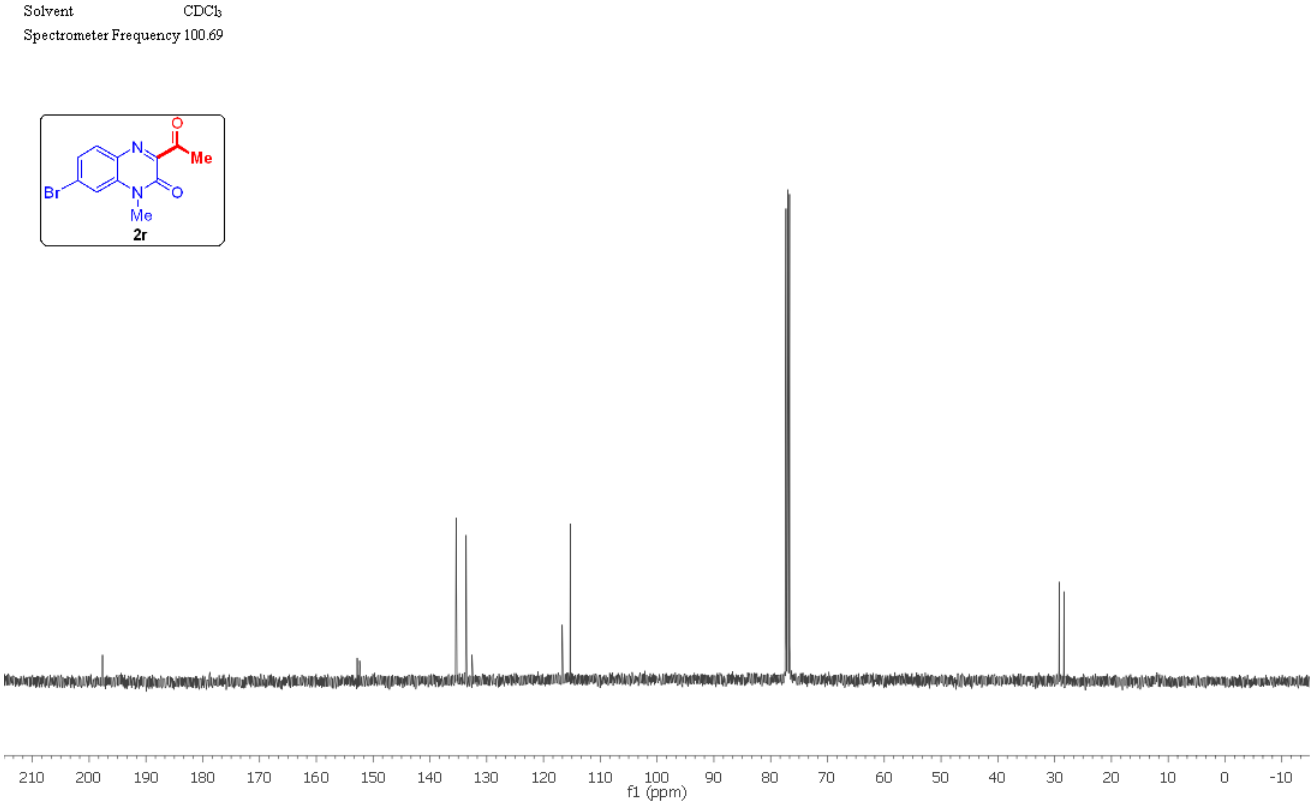
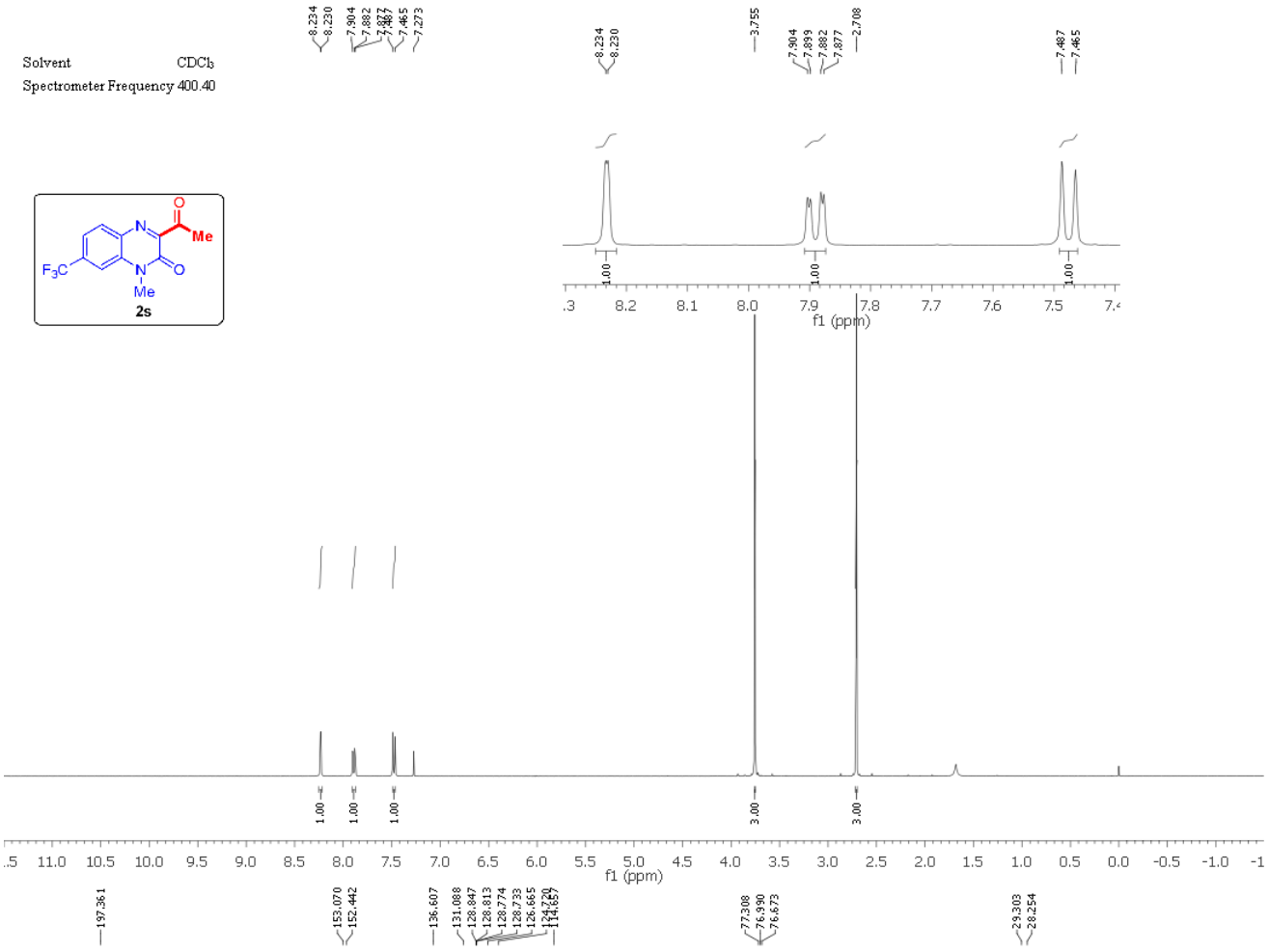
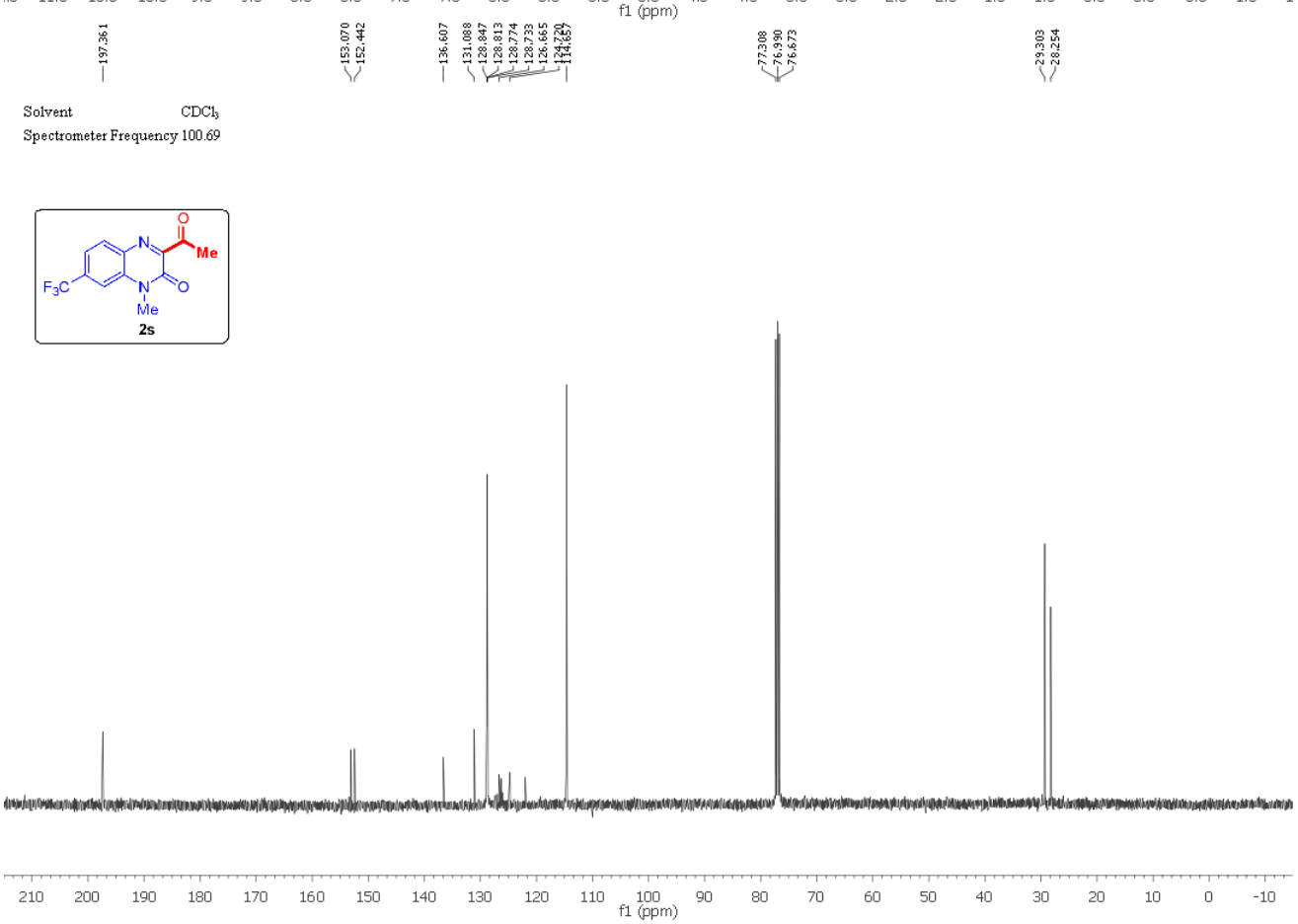

Solvent CDCl3
Spectrometer Frequency 100.69
Br
N
O
Me
N
Me
O
2r
f1 (ppm)


Solvent CDCl3
Spectrometer Frequency 400.40
2s
f1 (ppm)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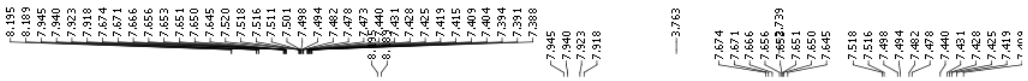
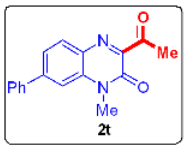
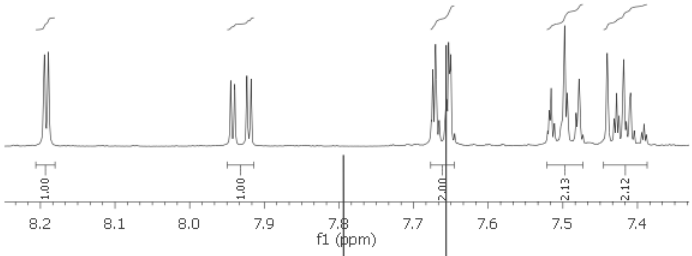
Spectrometer Frequency 100.69
2s
f1 (ppm)

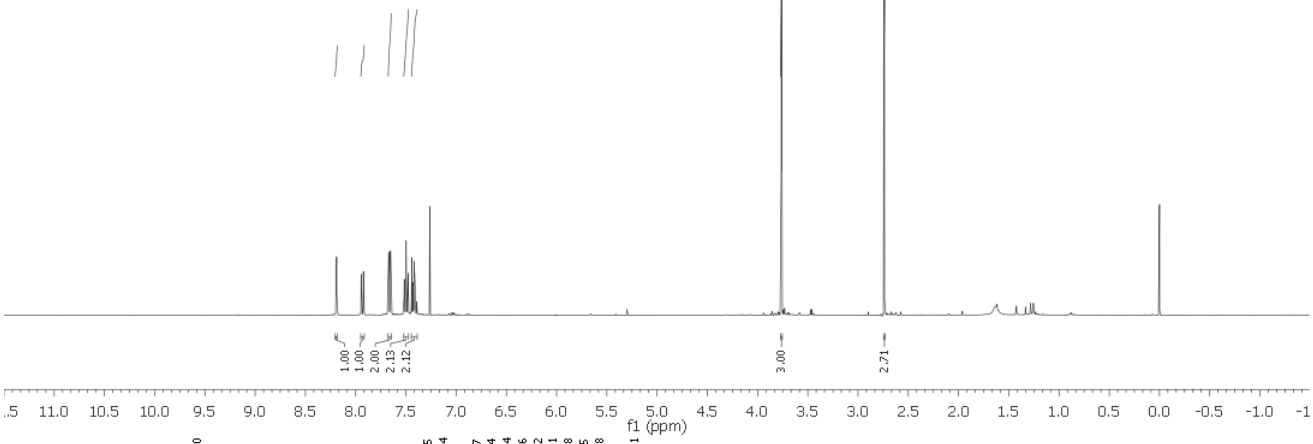


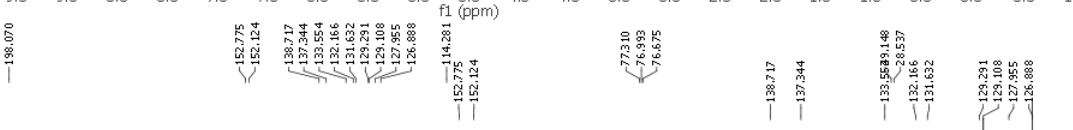
Solvent CDCl3
Spectrometer Frequency 400.40



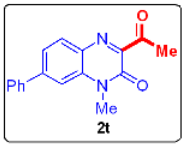
2t



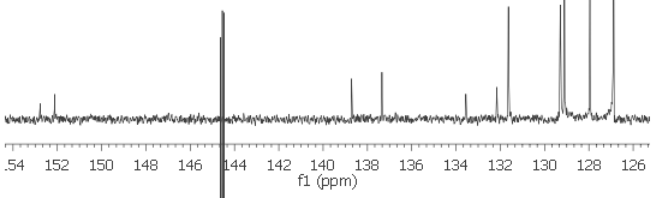


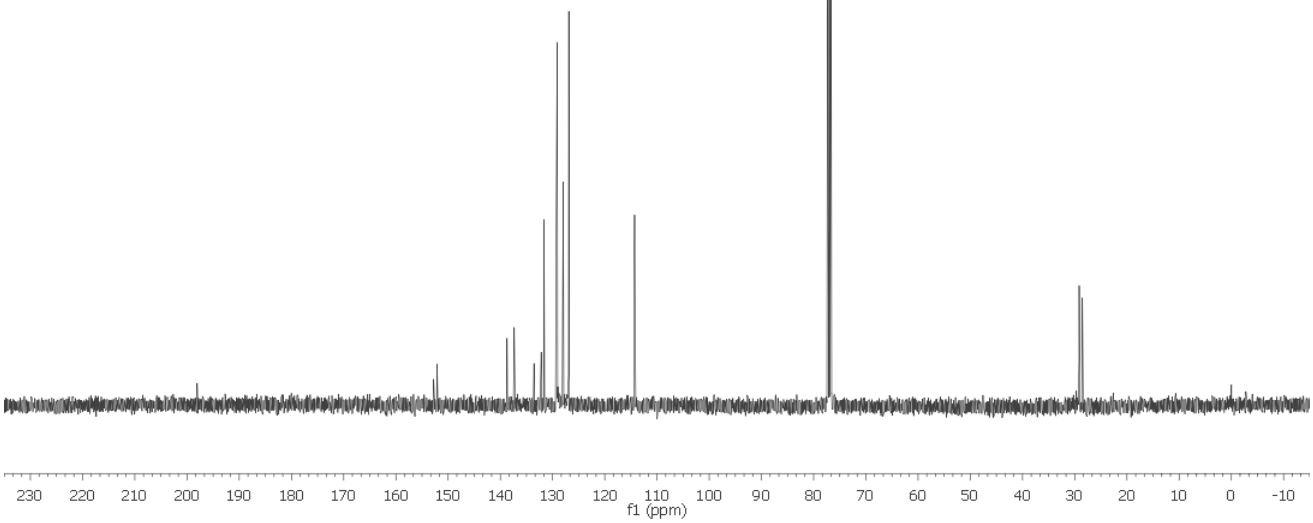


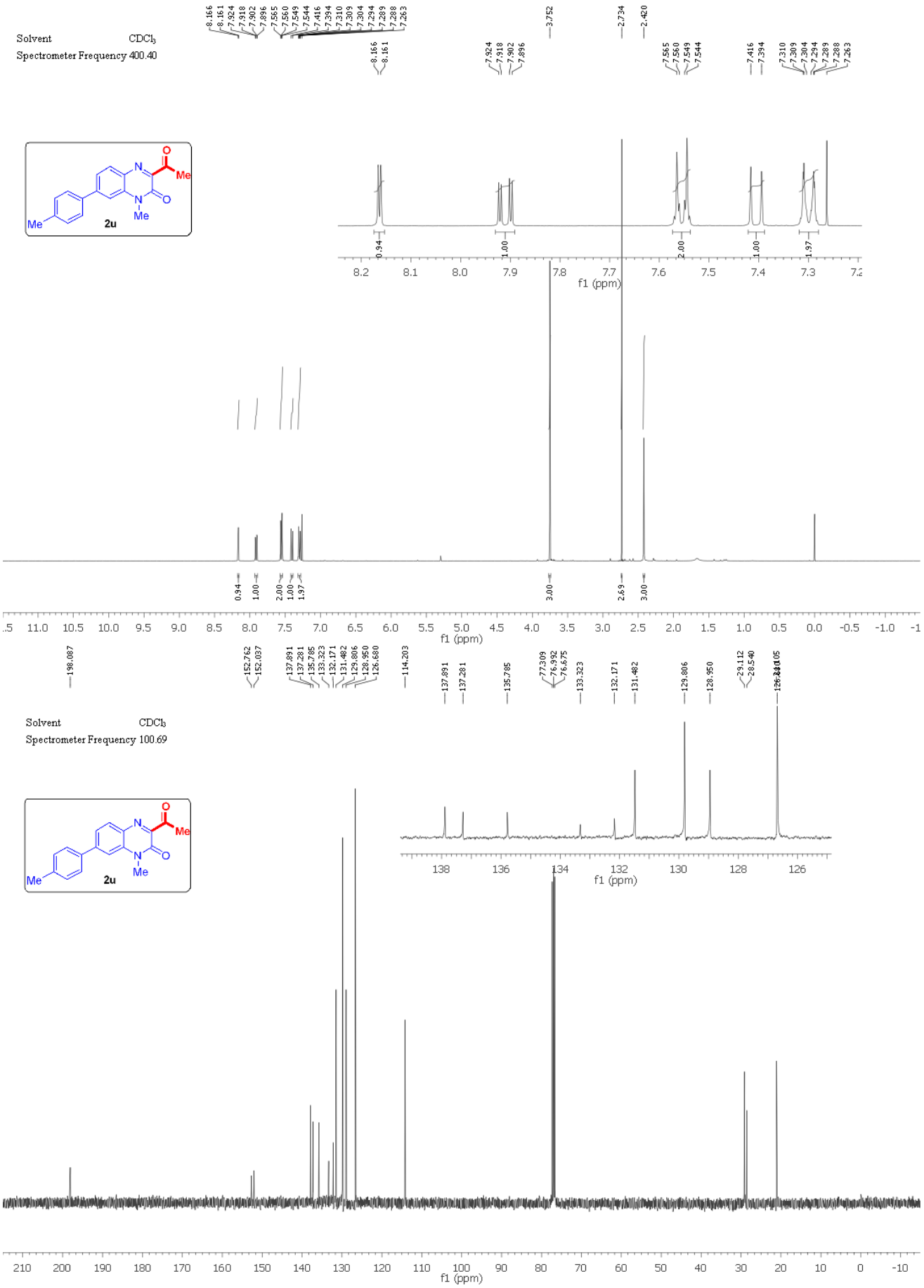
Solvent CDCl3
Spectrometer Frequency 100.69



2t






Solvent CDCl3
Spectrometer Frequency 400.40
2u
f1 (ppm)
Solvent CDCl3
Spectrometer Frequency 100.69
2u
f1 (ppm)

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) I

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

No syntax errors found. CIF dictionary Interpreting this report

Datablock: I

Bond precision: C-C = 0.0021 A Wavelength=0.71073

Cell: a=4.6921(1) b=21.3139(7) c=14.5759(4)
alpha=90 beta=97.032(3) gamma=90
Temperature: 113 K

	Calculated	Reported
Volume	1446.73(7)	1446.73(7)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C18 H16 N2 O2	C18 H16 N2 O2
Sum formula	C18 H16 N2 O2	C18 H16 N2 O2
Mr	292.33	292.33
Dx,g cm-3	1.342	1.342
Z	4	4
Mu (mm-1)	0.089	0.089
F000	616.0	616.0
F000'	616.26	
h,k,lmax	5,25,17	5,25,17
Nref	2555	2512
Tmin,Tmax	0.978,0.982	0.832,1.000
Tmin'	0.978	

Correction method= # Reported T Limits: Tmin=0.832 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.983 Theta(max)= 24.997

R(reflections)= 0.0404(2068) wR2(reflections)= 0.1052(2512)

S = 1.094 Npar= 201

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.595         43 Report
PLAT918_ALERT_3_C Reflection(s) with I(obs) much Smaller I(calc) .          1 Check
```

Alert level G

```
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still        65% Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...          3 Note
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ...........        3.8 Low
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          5 Info
```

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
2 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
4 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
2 ALERT type 2 Indicator that the structure model may be wrong or deficient
4 ALERT type 3 Indicator that the structure quality may be low
0 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

checkCIF publication errors

Alert level A

```
PUBL004_ALERT_1_A  The contact author's name and address are missing,
            _publ_contact_author_name and _publ_contact_author_address.
PUBL005_ALERT_1_A  _publ_contact_author_email, _publ_contact_author_fax and
            _publ_contact_author_phone are all missing.
            At least one of these should be present.
PUBL006_ALERT_1_A  _publ_requested_journal is missing
            e.g. 'Acta Crystallographica Section C'
PUBL008_ALERT_1_A  _publ_section_title is missing. Title of paper.
PUBL009_ALERT_1_A  _publ_author_name is missing. List of author(s) name(s).
PUBL010_ALERT_1_A  _publ_author_address is missing. Author(s) address(es).
PUBL012_ALERT_1_A  _publ_section_abstract is missing.
            Abstract of paper in English.
```

7 **ALERT level A** = Data missing that is essential or data in wrong format
0 **ALERT level G** = General alerts. Data that may be required is missing

Publication of your CIF

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

If level A alerts remain, which you believe to be justified deviations, and you intend to submit this CIF for publication in a journal, you should additionally insert an explanation in your CIF using the Validation Reply Form (VRF) below. This will allow your explanation to be considered as part of the review process.

Validation response form

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

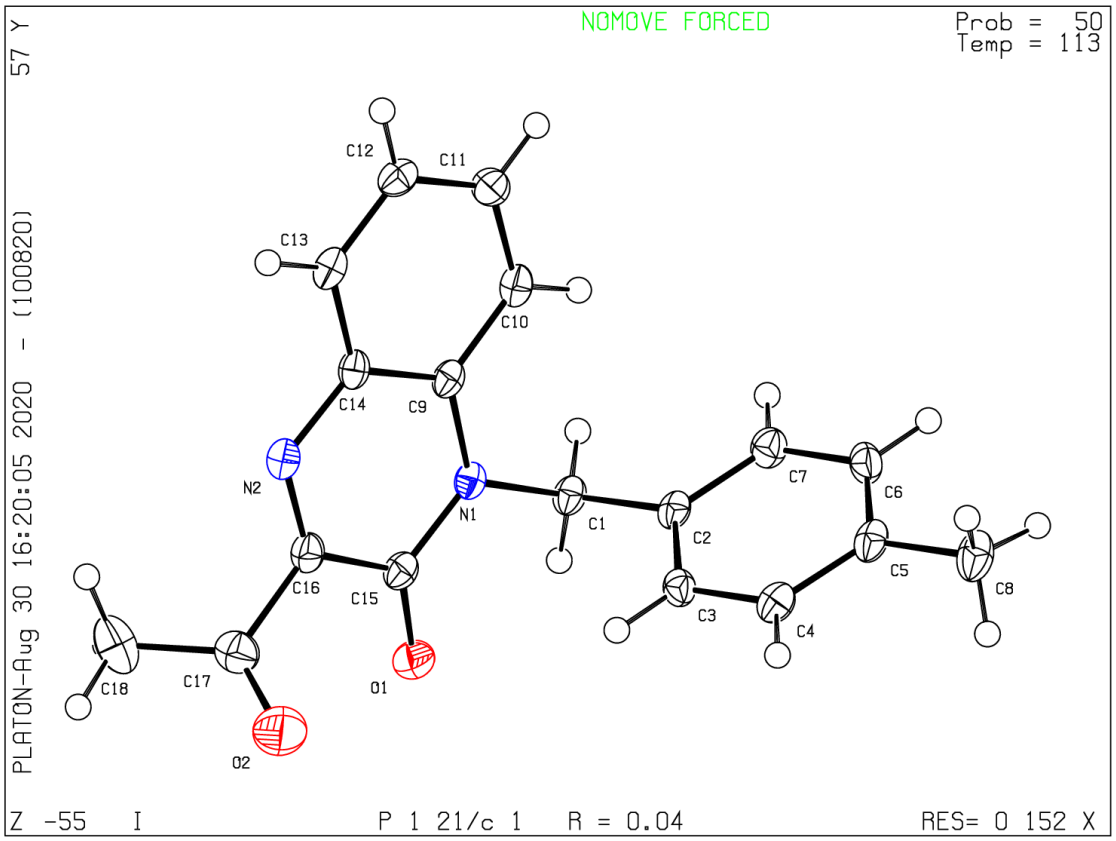
```
# start Validation Reply Form
_vrf_PUBL004_GLOBAL
;
PROBLEM: The contact author’s name and address are missing,
RESPONSE: ...
;
_vrf_PUBL005_GLOBAL
;
PROBLEM: _publ_contact_author_email, _publ_contact_author_fax and
RESPONSE: ...
;
_vrf_PUBL006_GLOBAL
;
PROBLEM: _publ_requested_journal is missing
RESPONSE: ...
;
_vrf_PUBL008_GLOBAL
;
PROBLEM: _publ_section_title is missing. Title of paper.
RESPONSE: ...
;
_vrf_PUBL009_GLOBAL
;
PROBLEM: _publ_author_name is missing. List of author(s) name(s).
RESPONSE: ...
;
_vrf_PUBL010_GLOBAL
;
PROBLEM: _publ_author_address is missing. Author(s) address(es).
RESPONSE: ...
;
_vrf_PUBL012_GLOBAL
;
```

```
PROBLEM: _publ_section_abstract is missing.
RESPONSE: ...
;
# end Validation Reply Form
```

If you wish to submit your CIF for publication in Acta Crystallographica Section C or E, you should upload your CIF via the web. If you wish to submit your CIF for publication in IUCrData you should upload your CIF via the web. If your CIF is to form part of a submission to another IUCr journal, you will be asked, either during electronic submission or by the Co-editor handling your paper, to upload your CIF via our web site.

PLATON version of 10/08/2020; check.def file version of 06/08/2020

Datablock I - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) I

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

No syntax errors found. CIF dictionary Interpreting this report

Datablock: I

Bond precision: C-C = 0.0020 A Wavelength=0.71073

Cell: a=7.7070(1) b=17.6134(2) c=22.5179(2)
alpha=90 beta=93.088(1) gamma=90
Temperature: 113 K

	Calculated	Reported
Volume	3052.29(6)	3052.29(6)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C17 H12 Cl2 N2 O2	2(C17 H12 Cl2 N2 O2)
Sum formula	C17 H12 Cl2 N2 O2	C34 H24 Cl4 N4 O4
Mr	347.19	694.37
Dx,g cm-3	1.511	1.511
Z	8	4
Mu (mm-1)	0.436	0.436
F000	1424.0	1424.0
F000'	1426.89	
h,k,lmax	9,22,28	9,22,28
Nref	6693	6459
Tmin,Tmax	0.877,0.897	0.638,1.000
Tmin'	0.877	

Correction method= # Reported T Limits: Tmin=0.638 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.965 Theta(max)= 27.039

R(reflections)= 0.0305(5716) wR2(reflections)= 0.0777(6459)

S = 1.059 Npar= 417

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600          5 Report
```

Alert level G

```
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ     Please Check
PLAT045_ALERT_1_G Calculated and Reported Z Differ by a Factor ...       2.00 Check
PLAT143_ALERT_4_G s.u. on c - Axis Small or Missing ..............    0.00020 Ang.
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety .....        C17 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact  O1       ..C32             2.98 Ang.
                                                    x,y,z  =      1_555 Check
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          2 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600        227 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...          3 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.         15 Info
```

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2 ALERT type 3 Indicator that the structure quality may be low
3 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

checkCIF publication errors

Alert level A

```
PUBL004_ALERT_1_A  The contact author's name and address are missing,
           _publ_contact_author_name and _publ_contact_author_address.
PUBL005_ALERT_1_A  _publ_contact_author_email, _publ_contact_author_fax and
           _publ_contact_author_phone are all missing.
           At least one of these should be present.
PUBL006_ALERT_1_A  _publ_requested_journal is missing
           e.g. 'Acta Crystallographica Section C'
PUBL008_ALERT_1_A  _publ_section_title is missing. Title of paper.
PUBL009_ALERT_1_A  _publ_author_name is missing. List of author(s) name(s).
PUBL010_ALERT_1_A  _publ_author_address is missing. Author(s) address(es).
PUBL012_ALERT_1_A  _publ_section_abstract is missing.
           Abstract of paper in English.
```

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;
PROBLEM: The contact author’s name and address are missing,
RESPONSE: ...
;
_vrf_PUBL005_GLOBAL
;
PROBLEM: _publ_contact_author_email, _publ_contact_author_fax and
RESPONSE: ...
;
_vrf_PUBL006_GLOBAL
;
PROBLEM: _publ_requested_journal is missing
RESPONSE: ...
;
_vrf_PUBL008_GLOBAL
;
PROBLEM: _publ_section_title is missing. Title of paper.
RESPONSE: ...
;
_vrf_PUBL009_GLOBAL
;
PROBLEM: _publ_author_name is missing. List of author(s) name(s).
RESPONSE: ...
;
_vrf_PUBL010_GLOBAL
;
PROBLEM: _publ_author_address is missing. Author(s) address(es).
RESPONSE: ...
;
_vrf_PUBL012_GLOBAL
;
```

```
PROBLEM: _publ_section_abstract is missing.
RESPONSE: ...
;
# end Validation Reply Form
```

If you wish to submit your CIF for publication in Acta Crystallographica Section C or E, you should upload your CIF via the web. If you wish to submit your CIF for publication in IUCrData you should upload your CIF via the web. If your CIF is to form part of a submission to another IUCr journal, you will be asked, either during electronic submission or by the Co-editor handling your paper, to upload your CIF via our web site.

PLATON version of 22/04/2020; check.def file version of 09/03/2020

Datablock I - ellipsoid plot