Supporting Information

Metal-free alkylation of quinoxalinones with aryl alkyl ketones

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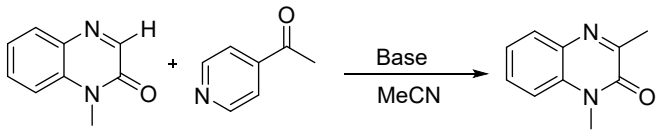
1. General information

All reactions were examined in dry glass reaction tube equipped with a magnetic stir bar under argon atmosphere. Solvents and reagents were purchased from commercial sources and employed as received. Flash column chromatography was performed using silica gel (60-Å pore size, 32-63 μm, standard grade). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Mass spectra and HPLC yields were measured on a LC-MSD-Trap-XCT instrument. NMR spectra were obtained on Bruker AVANCE III systems using $CDCl_3$ as a solvent, $CDCl_3$ as an internal standard substance, at 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR, and 376 MHz for ^{19}F NMR. Melting points were determined with an XT4A microscopic apparatus. The high resolution mass spectrum was received with ESI as ion source. Preparative TLC was performed on silica gel plates and developed with ethyl acetate/petroleum ether.

2. Optimization of the reaction conditions (Table S1-S4)

Table S1. The effect of base on the reaction[a,b]

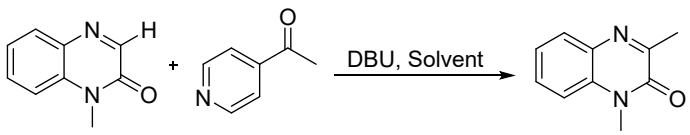


1a **2a** **3a**

Entry	Base	**3a** Yield(%)
1	-	0
1	t-BuOK	0
2	NaOH	0
3	CH_3ONa	0
4	DBU	52
5	Triethylamine	0

[a]Reaction conditions: **1a** (0.5 mmol, 1.0 equiv.), **2a** (1.5 mmol, 3.0 equiv.), Base (1.5 mmol, 3.0 equiv.), MeCN (2.0 mL), 120 °C, Ar, 10 h. [b]The ratio was determined by LC.

Table S2. The effect of solvents on the reactions[a,b]

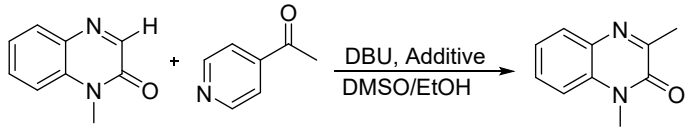


1a **2a** **3a**

Entry	Solvent	**3a** Yield (%)
1	EtOH	35
2	H_2O	22
3	DMF	56
4	DMSO	67
5	DMA	62
6	MeCN	52
7	DMSO+MeCN	60
8	DMSO+EtOH	74
9	DMSO+H_2O	26
10[c]	DMSO+EtOH	70
11[d]	DMSO+EtOH	65

[a]Reaction conditions: **1a** (0.5 mmol, 1.0 equiv.), **2a** (1.5 mmol, 3.0 equiv.), DBU (1.5 mmol, 3.0 equiv.), Solvent (2.0 mL, the ratio of the mixed solvent is 1:1 v/v), 120 ℃, Ar, 10 h. [b]The ratio was determined by LC. [c]DMSO/EtOH (2.0 mL, the ratio of the mixed solvent is 2:1 v/v). [d]DMSO/EtOH (2.0 mL, the ratio of the mixed solvent is 1:2 v/v).

Table S3. The effect of additives on the reactions[a,b]

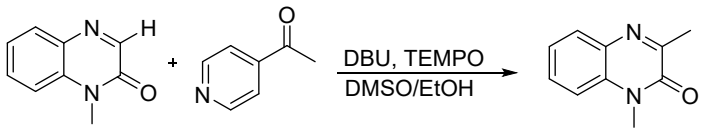


1a **2a** **3a**

Entry	Oxidants	**3a** Yield (%)
1	-	74
2	O_2	81%
3	$(NH_4)_2S_2O_8$	45
4	$K_2S_2O_8$	46
5[c]	TEMPO	88
6[d]	TEMPO	83
7[e]	TEMPO	92(86%)
8[f]	TEMPO	86

[a]Reaction conditions: **1a** (0.5 mmol, 1.0 equiv.), **2a** (1.5 mmol, 3.0 equiv.), DBU (1.5 mmol, 3.0 equiv.), DMSO/EtOH (2.0 mL, 1:1 v/v), Oxidants (1.0 mmol, 2.0 equiv.), 120 ℃, Ar, 10 h. [b]LC yields, **3a** isolated yields are shown in parentheses. [c]The reaction was performed with 2.0 equiv. of TEMPO. [d]The reaction was performed with 3.0 equiv. of TEMPO. [e]The reaction was performed with 1.0 equiv. of TEMPO.[f]The reaction was performed with 0.5 equiv. of TEMPO.

Table S4. The effect of temperature and atmosphere on the reactions[a,b]



1a **2a** **3a**

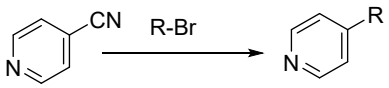
Entry	T	**3a** Yield (%)
1	90 ℃	74
2	100 ℃	84
3	110 ℃	89
4	120 ℃	92
5	130 ℃	91
6[c]	120 ℃	92
7[d]	120 ℃	92

[a]Reaction conditions: **1a** (0.5 mmol, 1.0 equiv.), **2a** (1.5 mmol, 3.0 equiv.), DBU (1.5 mmol, 3.0 equiv.), DMSO/EtOH (2.0 mL, 1:1 v/v), TEMPO (0.5 mmol, 1.0 equiv.), T, air, 10 h. [b] The ratio was determined by LC. [c]The reaction was performed under air. [d]The reaction was performed under oxygen.

3. General experimental procedures

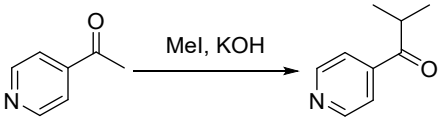
3.1. General procedures for the synthesis of substrates

2-Acylpyridine compounds (**2b**, **2c**, **2d**, **2f**) were synthesized according to reported procedures with some modifications.[1]



Bromo alkanes (1.0 equiv.) were slowly added to a stirred suspension of magnesium (1.0 equiv.) and iodine (1.0 equiv.) in THF (60 mL), then the mixture was heated about 30 min. 4-Cyanopyridine (0.6 equiv.) was dissolved in 30 mL THF, and added to the reaction mixture at 0 ℃ for 30 min. The reaction proceeded at room temperature and stirred for a further 2.5 h. The mixture was added 2 N HCl (60 mL) and stirred at room temperature for 30 min. The reaction was neutralized with 2 N NaOH to pH 8 and diluted with EtOAc. The organic layer was washed with water and brine. The combined organic layers were dried with anhydrous Na_2SO_4, then filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (PE:EA = 10:1) to obtain a yellow oil.

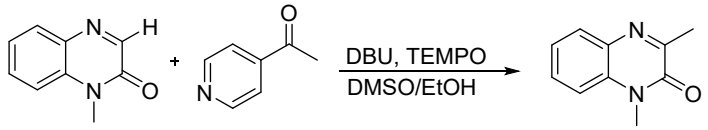
2-Acylpyridine compounds (**2e**) were synthesized according to reported procedures with some modifications.[2]



CH_3I (4.27 g, 30 mmol) was slowly added to a stirred suspension of 4-acetylpyridine (1.21 g, 10 mmol), KOH (5.6 g, 100 mmol) and 18-crown-6 (0.26 g, 0.1 mmol) in toluene (30 mL), then the mixture reacted 4.5 h at room temperature. The reaction

mixture was diluted with EtOAc, then the organic layer was washed with water and brine. The combined organic layers were dried with anhydrous Na_2SO_4, then filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (PE:EA = 6:1) to obtain a yellow oil.

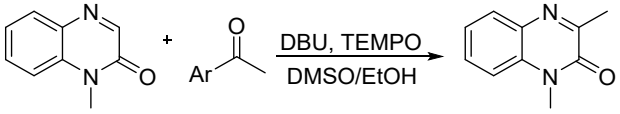
3.2. General procedures for the synthesis of 3-alkylquinoxalin-2(1H)-ones



1a-1t **2a** **3a-3t**

A dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with **1a-1t** (0.5 mmol, 1.0 equiv.), **2a** (1.5 mmol, 3.0 equiv.), DBU (1.5 mmol, 3.0 equiv.), TEMPO (0.5 mmol, 1.0 equiv.), DMSO+EtOH (2.0 mL, 1:1 v/v). Subsequently, the tube was sealed and the mixture was stirred under air at 120 °C for 10 h. The reaction was monitored by TLC. The reaction mixture was concentrated in vacuo, then extracted with ethyl acetate three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography to produce the desired product (purified by flash chromatography PE:EA = 7:1).

3.3. General procedures for the synthesis of 3-alkylquinoxalin-2(1H)-ones (Table 3 and Table 4)



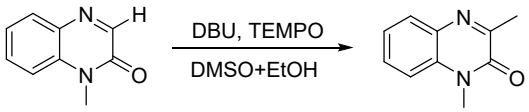
1a **2g-2k** **3a**

A dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with **1a** (0.5 mmol, 1.0 equiv.), **2g-2k** (1.5 mmol, 3.0 equiv.), DBU (1.5 mmol, 3.0 equiv.), TEMPO (0.5 mmol, 1.0 equiv.), DMSO+EtOH (2.0 mL, 1:1 v/v). Subsequently, the tube was sealed and the mixture was stirred under air at 120 °C for 10 h. The reaction was monitored by TLC. The reaction mixture was concentrated in vacuo, then extracted with ethyl acetate three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography to produce the desired product purified by flash chromatography.

3.4. The procedure for a gram-scale experiment.

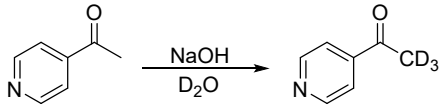
A dried 100 mL round-flask equipped with a magnetic stir bar was charged with **1a** (7 mmol, 1.12 g, 1.0 equiv.), **2a** (21 mmol, 2.54 g, 3.0 equiv.), DBU (21 mmol, 3.19 g, 3.0 equiv.), TEMPO (7 mmol, 1.09 g, 1.0 equiv.), DMSO+EtOH (28.0 mL, 1:1 v/v). Subsequently, the mixture was refluxed in oil bath at 120 °C for 10 h. The reaction was monitored by TLC. The reaction mixture was concentrated in vacuo, then extracted with ethyl acetate three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography to get 0.98 g desired product with 80% yield (purified by flash chromatography PE:EA = 7:1).

3.5. The procedure for control experiment.



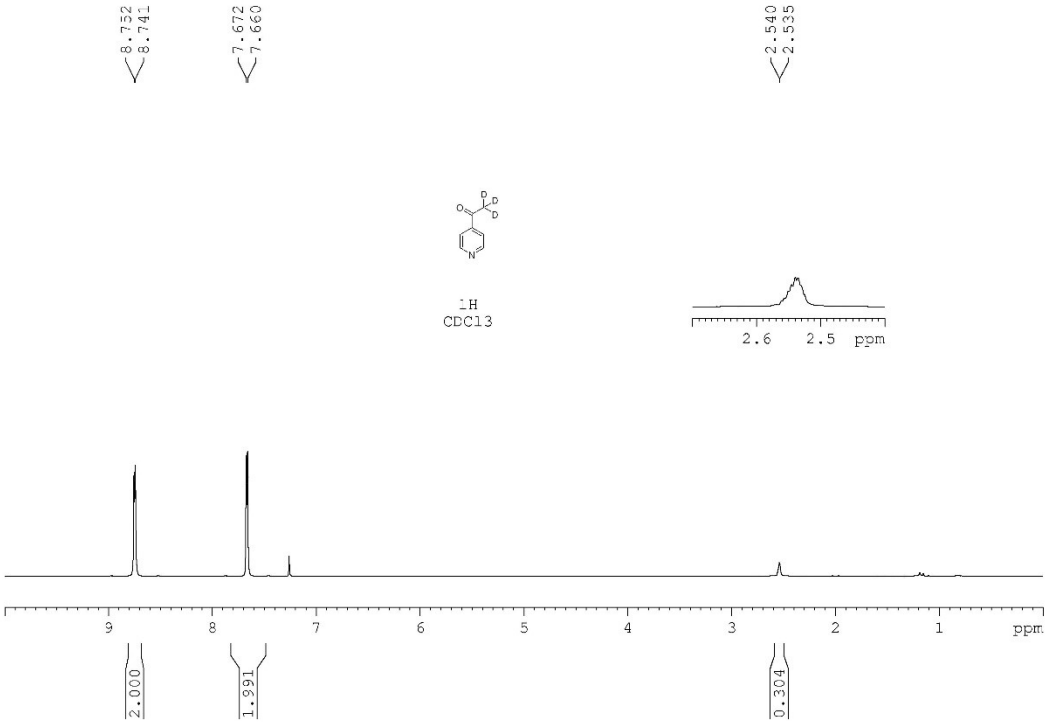
1a **3a,** trace

A dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with **1a** (0.5 mmol, 1.0 equiv.), DBU (1.5 mmol, 3.0 equiv.), TEMPO (0.5 mmol, 1.0 equiv.), DMSO+EtOH (2.0 mL, 1:1 v/v). Subsequently, the tube was sealed and the mixture was stirred under air at 120 °C for 10 h. Only trace amount of the expected product **3a** was obtained (The reaction was monitored by HPLC).



2a **2a'**, 90% D incorporation

A dried 25 mL round-bottomed flask equipped with a magnetic stir bar was charged with 4-acetylpyridine (1.7 g, 14 mmol), NaOH (0.05 g, 1.2 mmol), D_2O (4 mL) under Ar. Subsequently, the mixture was stirred at room temperature for 8 h. Then, the mixture was supplemented with NaOH (0.05 g, 1.2 mmol), D_2O (4 mL) and stirred at room temperature for 8 h. The aqueous layer was extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The unpurified product mixture was subjected to silica gel column chromatography to afford the 1-(pyridin-4-yl)ethan-1-one-2,2,2-d3 **2a'** (90% Deuterium incorporation) as colorless liquid. Deuterium incorporation was detected by ^1H NMR analysis.



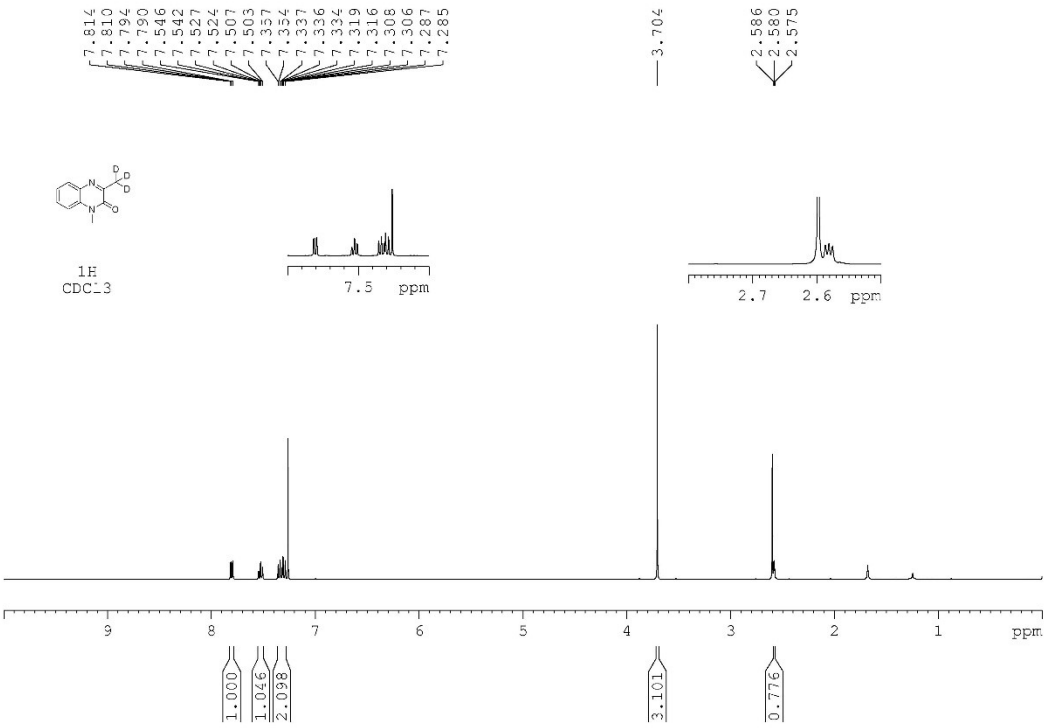
^{1}H NMR of compound **2a'**

1a deuterio-**2a'**, 90% deuterio-**3a',** 74%

To an oven-dried sealed tube charged with **1a** (0.5 mmol) and 1-(pyridin-4-yl)ethan-1-one-2,2,2-d3 **2a**' (1.5 mmol), DBU (1.5 mmol), TEMPO (1.5 mmol) and DMSO (2.0 mL) was added under Ar. The reaction mixture was allowed to stir at 120 ℃ for 10 h, then the mixture was cooled to room temperature and extracted with ethyl acetate (15 mL x 3). The combined organic layer was washed with brine (5 mL x 2), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The unpurified product mixture was subjected to silica gel column chromatography to afford 1-methyl-3-(methyl-d3)-quinoxalin-2(1H)-one **3a**' as white solid. Deuterium incorporation was detected by ^{1}H NMR analysis.

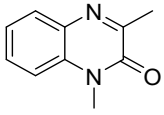
The relatively low deuterium incorporation of the reasons was as follows: First, DBU randomly grab the hydrogen from the methyl group of 4-acetylpyridine in the first step,

causing a mixture of product with one deuterium, two deuterium and three deuterium. Second, the reaction was conducted in DMSO which contain active hydrogen led to the product with low deuterium incorporation.



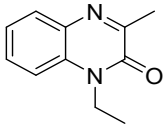
^{1}H NMR of compound **3a'**

4. **Analytical data**



3a

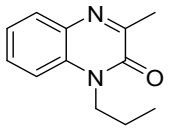
1,3-dimethylquinoxalin-2(1H)-one (**3a**).[3] White solid (69 mg, yield 86%). m.p. 85-87 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.78 (dd, J = 6.6 Hz, 1.4 Hz, 1 H), 7.53-7.48 (m, 1 H), 7.34-7.26 (m, 2 H), 3.68 (s, 3 H), 2.56 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 158.3, 155.1, 133.2, 132.6, 129.5, 129.4, 123.5, 113.5, 29.0, 21.5. MS (ESI) (m/z): 174.1 $[M+H]^+$.



3b

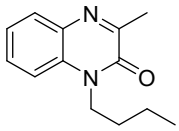
1-ethyl-3-methylquinoxalin-2(1H)-one (**3b**).[4] White solid (72.1 mg, yield 77%). m.p. 77-79 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.81 (dd, J = 6.8 Hz, 1.6 Hz, 1 H),

7.51 (m, 1 H), 7.31 (m, 2 H), 4.32 (q, J = 7.2 Hz, 2 H), 2.59 (s, 3 H), 1.37 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ =158.4, 154.7, 132.9, 132.1, 129.7, 129.5, 123.4, 113.4, 37.2, 21.4, 12.3. MS (ESI) (m/z): 188.1 $[M+H]^+$.



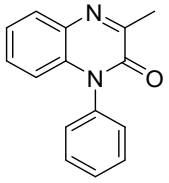
3c

3-methyl-1-propylquinoxalin-2(1H)-one (**3c**).[5] White solid (78.6 mg, yield 78%). m.p. 47-49 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.79 (dd, J = 6.6 Hz, 1.4 Hz, 1 H), 7.48 (m, 1 H), 7.28 (m, 2 H), 4.18 (m, 2 H), 2.57 (s, 3 H), 1.76 (m, 2 H), 1.03 (t, J = 7.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 158.4, 154.9, 132.8, 132.4, 129.6, 129.4, 123.3, 113.6, 43.7, 21.5, 20.6, 11.3. MS (ESI) (m/z): 202.1 $[M+H]^+$.



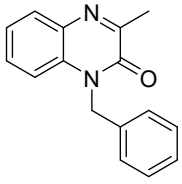
3d

1-butyl-3-methylquinoxalin-2(1H)-one (**3d**).[5] Yellow liquid (86.9 mg, yield 80%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.76 (m, 1 H), 7.48 (m, 1 H), 7.27 (m, 2 H), 4.21 (t, J = 7.7 Hz, 2 H), 2.56 (s, 3 H), 1.70 (m, 2 H), 1.46 (m, 2 H), 0.97 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 158.3, 154.8, 132.9, 132.3, 129.6, 129.4, 123.3, 113.6, 42.0, 29.2, 21.5, 20.2, 13.7. MS (ESI) (m/z): 216.1 $[M+H]^+$.



3e

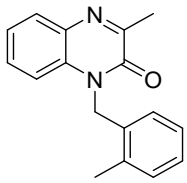
3-methyl-1-phenylquinoxalin-2(1H)-one (**3e**).[4] White solid (69.0 mg, yield 58%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.84 (dd, J = 3.5 Hz, 2.5 Hz, 1 H), 7.58 (m, 3 H), 7.30 (m, 4 H), 6.66 (m, 1 H), 2.64 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 159.2, 154.9, 135.8, 134.1, 132.5, 130.2, 129.4, 129.2, 129.0, 128.2, 123.7, 115.4, 21.4. MS (ESI) (m/z): 236.1 $[M+H]^+$.



3f

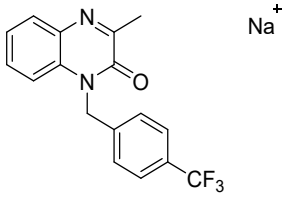
1-benzyl-3-methylquinoxalin-2(1H)-one (**3f**).[4] White solid (108.4 mg, yield 87%). m.p. 90-93 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.81 (dd, J = 6.6 Hz, 1.3 Hz, 1

H), 7.37 (m, 1 H), 7.26 (m, 7 H), 5.48 (s, 2 H), 2.65 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 158.5, 155.2, 135.2, 132.9, 132.5, 129.5 (d), 128.9, 127.7, 126.8, 123.6, 114.4, 45.9, 21.7. MS (ESI) (m/z): 250.1 $[M+H]^+$.



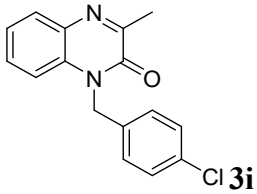
3g

3-methyl-1-(2-methylbenzyl)quinoxalin-2(1H)-one (**3g**). White solid (116.1 mg, yield 88%). m.p. 160-162 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.85 (dd, J = 6.4 Hz, 1.5 Hz, 1 H), 7.37 (m, 1 H), 7.30 (m, 1 H), 7.24 (m, 1H), 7.16 (like t, 1 H), 7.00 (m, 2 H), 6.59 (d, J = 7.7 Hz, 1 H), 5.43 (s, 2 H), 2.66 (s, 3 H), 2.48 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 158.5, 155.2, 134.9, 132.9, 132.7, 132.4, 130.5, 129.6, 129.5, 127.3, 126.4, 124.5, 123.7, 114.5, 43.8, 21.6, 19.2. HRMS (ESI): m/z calcd for $C_{17}H_{16}N_2O$ $[M+Na]^+$: 287.1155, found:287.1152.



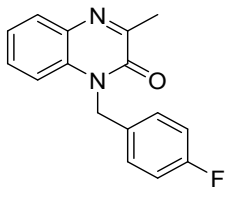
3h

3-methyl-1-(4-(trifluoromethyl)benzyl)quinoxalin-2(1H)-one (**3h**). White solid (119.3 mg, yield 75%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.84 (dd, J = 6.5 Hz, 1.4 Hz, 1 H), 7.57 (d, J = 8.2 Hz, 2 H), 7.41 (m, 1 H), 7.34 (m, 3 H), 7.15 (dd, J = 7.4 Hz, 0.9 Hz, 1 H), 5.54 (s, 2 H), 2.66 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$, ppm): δ = -62.6; ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 158.4, 155.1, 139.3, 132.9, 132.3, 130.1 (q, J = 32 Hz), 129.8, 129.7, 127.1, 125.9 (q, J = 3.9 Hz), 124.0, 123.9 (q, J = 270.5 Hz), 114.0, 45.5, 21.6. HRMS (ESI): m/z calcd for $C_{17}H_{13}F_3N_2O$ $[M+Na]^+$: 341.0872, found:341.0868.



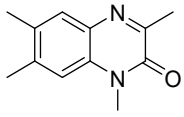
3i

1-(4-chlorobenzyl)-3-methylquinoxalin-2(1H)-one (**3i**).[5] White solid (106.1 mg, yield 75%). m.p. 136-138 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.81 (dd, J = 6.6 Hz, 1.4 Hz, 1 H), 7.41 (m, 1 H), 7.30 (m, 3 H), 7.18 (m, 3 H), 5.45 (s, 2 H), 2.65 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 158.5, 155.2, 133.7, 133.6, 132.9, 132.3, 129.7, 129.6, 129.1, 128.3, 123.8, 114.1, 45.3, 21.6. MS (ESI) (m/z): 384.1 $[M+H]^+$.



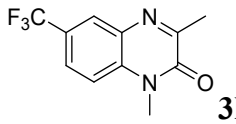
3j

1-(4-fluorobenzyl)-3-methylquinoxalin-2(1H)-one (**3j**).[5] White solid (103.4 mg, yield 77%). m.p. 117-119 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.81 (dd, J = 6.6 Hz, 1.4 Hz, 1 H), 7.41 (m, 1 H), 7.30 (m, 1 H), 7.23 (m, 3 H), 6.99 (m, 2 H), 5.45 (s, 2 H), 2.64 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$, ppm): δ = -114.3; ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 162.2 (d, J = 245 Hz), 158.5, 155.2, 132.9, 132.4, 131.0 (d, J = 3.4 Hz), 129.6 (d, J = 7.3 Hz), 128.7 (d, J = 8.1 Hz), 123.7, 115.9, 115.7, 114.1, 45.2, 21.6. MS (ESI) (m/z): 268.1 $[M+H]^+$.



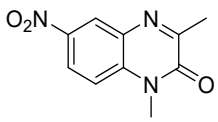
3k

1,3,6,7-tetramethylquinoxalin-2(1H)-one (**3k**).[4] White solid (69.6 mg, yield 69%). m.p. 140-142 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.49 (s, 1 H), 7.00 (s, 1 H), 3.63 (s, 3 H), 2.53 (s, 3 H), 2.37 (s, 3 H), 2.31 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 156.9, 155.2, 139.2, 132.4, 131.1, 131.0, 129.4, 144.1, 28.9, 21.5, 20.4, 19.1. MS (ESI) (m/z): 202.1 $[M+H]^+$.



3l

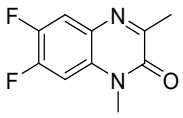
1,3-dimethyl-6-(trifluoromethyl)quinoxalin-2(1H)-one (**3l**).[4] White solid (66.4 mg, yield 55%). m.p. 148-150 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.03 (s, 1 H), 7.70 (dd, J = 7.4Hz, 1.4 Hz, 1 H), 7.35 (like d, 1 H), 3.69 (s, 3 H), 2.57 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$, ppm): δ = -62.0 (s); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 160.1, 154.9, 135.5, 131.9, 126.8 (q, J = 3.8 Hz), 125.9 (q, J = 3.3 Hz), 125.8 (q, J = 33.4 Hz), 123.7 (q, J = 270.2 Hz), 114.2, 29.4, 21.6. MS (ESI) (m/z): 242.1 $[M+H]^+$.



3m

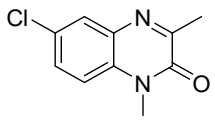
1,3-dimethyl-6-nitroquinoxalin-2(1H)-one (**3m**).[4] Yellow solid (60.1 mg, yield 55%). m.p. 216-218 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.19 (d, J = 2.5 Hz, 1 H), 8.38 (dd, J = 6.6 Hz, 2.5 Hz, 1 H), 7.39 (d, J = 9.2 Hz, 1 H), 3.75 (s, 3 H), 2.63 (s,

3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ =161.1, 154.7, 143.3, 137.9, 131.8, 125.2, 124.1, 114.1, 29.6, 21.7. MS (ESI) (m/z): 219.1 $[M+H]^+$.



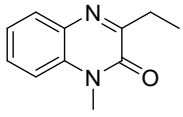
3n

6,7-difluoro-1,3-dimethylquinoxalin-2(1H)-one (**3n**).[4] White solid (60 mg, yield 69%). m.p. 127-129 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.60 (dd, J = 8.3 Hz, 1.9 Hz, 1 H), 7.09 (dd, J = 7.0 Hz, 4.2 Hz, 1 H), 3.65 (s, 3 H), 2.56 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$, ppm): δ = -131.7 (d), -142.1 (d). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 159.0 (d, J = 3.2 Hz), 154.7, 150.9 (dd, J = 236.9 Hz, 14.4 Hz), 146.6 (dd, J = 231.4 Hz, 13.6 Hz), 130.4 (d, J = 8.9 Hz), 128.8 (d, J = 2.9 Hz), 117.1 (d, J = 18.0 Hz), 102.2 (d, J = 22.9 Hz), 29.5, 21.5. MS (ESI) (m/z): 210.1 $[M+H]^+$.



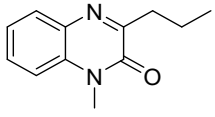
3o

6-chloro-1,3-dimethylquinoxalin-2(1H)-one (**3o**).[6] White solid (60 mg, yield 58%). m.p. 138-141 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.79 (d, J = 2.4 Hz), 7.47 (dd, J = 6.5Hz, 2.4 Hz, 1 H), 7.22 (like d, 1 H), 3.68 (s, 3 H), 2.59 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 159.9, 154.8, 133.2, 131.9, 129.5, 128.8, 114.7, 29.2, 21.7. MS (ESI) (m/z): 208.0 $[M+H]^+$.



3p

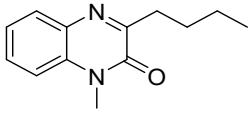
3-ethyl-1-methylquinoxalin-2(1H)-one (**3p**).[3] Yellow solid (71.3 mg, yield 76%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.84 (dd, J = 6.6 Hz, 1.3 Hz, 1 H), 7.52 (m, 1 H), 7.33 (m, 2 H), 3.70 (s, 3 H), 2.97 (q, J = 7.4 Hz, 2 H), 1.33 (t, J = 7.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 161.9, 154.8, 133.0, 132.7, 129.6, 129.4, 123.5, 113.5, 28.9, 27.5, 10.8. MS (ESI) (m/z): 188.1 $[M+H]^+$.



3q

1-methyl-3-propylquinoxalin-2(1H)-one (**3q**).[3] White solid (87.3 mg, yield 86%). m.p. 78-80 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.82 (dd, J = 6.9 Hz, 1.0 Hz, 1 H), 7.51 (m, 1 H), 7.31 (m, 2 H), 3.69 (s, 3 H), 2.92 (t, J = 7.5 Hz, 2 H), 1.82 (m, 2 H)

1.04 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 161.1, 154.9, 133.1, 132.7, 129.6, 129.5, 123.5, 113.5, 36.2, 29.0, 20.2, 14.0. MS (ESI) (m/z): 202.1 $[M+H]^+$.



3r

3-butyl-1-methylquinoxalin-2(1H)-one (**3r**).[3] White solid (62.5 mg, yield 60%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.82 (dd, J = 6.6 Hz, 1.4 Hz, 1 H), 7.51 (m, 1 H), 7.31 (m, 2 H), 3.70 (s, 3 H), 2.94 (t, J = 7.7 Hz, 2 H), 1.77 (m, 2 H), 1.47 (m, 2 H), 0.96 (t, J = 7.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 161.4, 154.9, 133.1, 132.7, 129.6, 129.4, 123.5, 113.5, 34.1, 29.0, 28.9, 13.9. MS (ESI) (m/z): 216.1 $[M+H]^+$.

5. References

[1] (a) H. Huo, C. Wang, K. Harms and E. Meggers, *J. Am. Chem. Soc.* **2015**, *137*, 9551-9554. (b) H. Shimada, T. Tanigawa, K. Matayoshi, K. Katakura, K. Babazono, H. Takayama, T. Murahashi, H. Akita, T. Higuchi, M. Eto and Y. Imamura, *J Enzyme Inhib Med Chem,* **2014**, *29*, 397-400.

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[3] B. Wang, H. Yao, X. Zhong, Z. Yan and S. Lin, *Tetrahedron Lett*. **2021**, *64*, 152720.

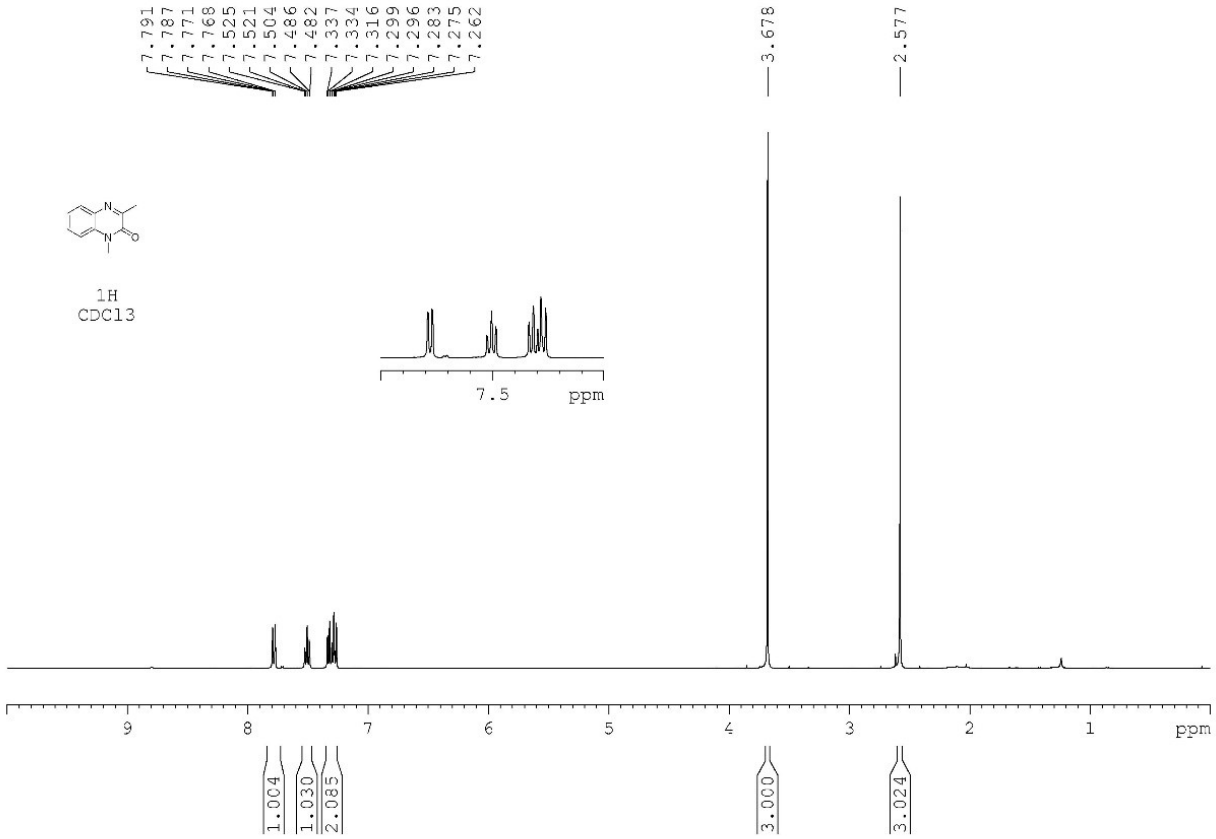
[4] L.-Y. Xie, L.-L. Jiang, J.-X. Tan, Y. Wang, X.-Q. Xu, B. Zhang, Z. Cao and W.-M. He, *ACS Sustainable Chem. Eng.* **2019**, *7*, 14153-14160.

[5] X. Rong, L. Jin, Y. Gu, G. Liang and Q. Xia, *Asian J. Org. Chem.* **2020**, *9*, 185-188.

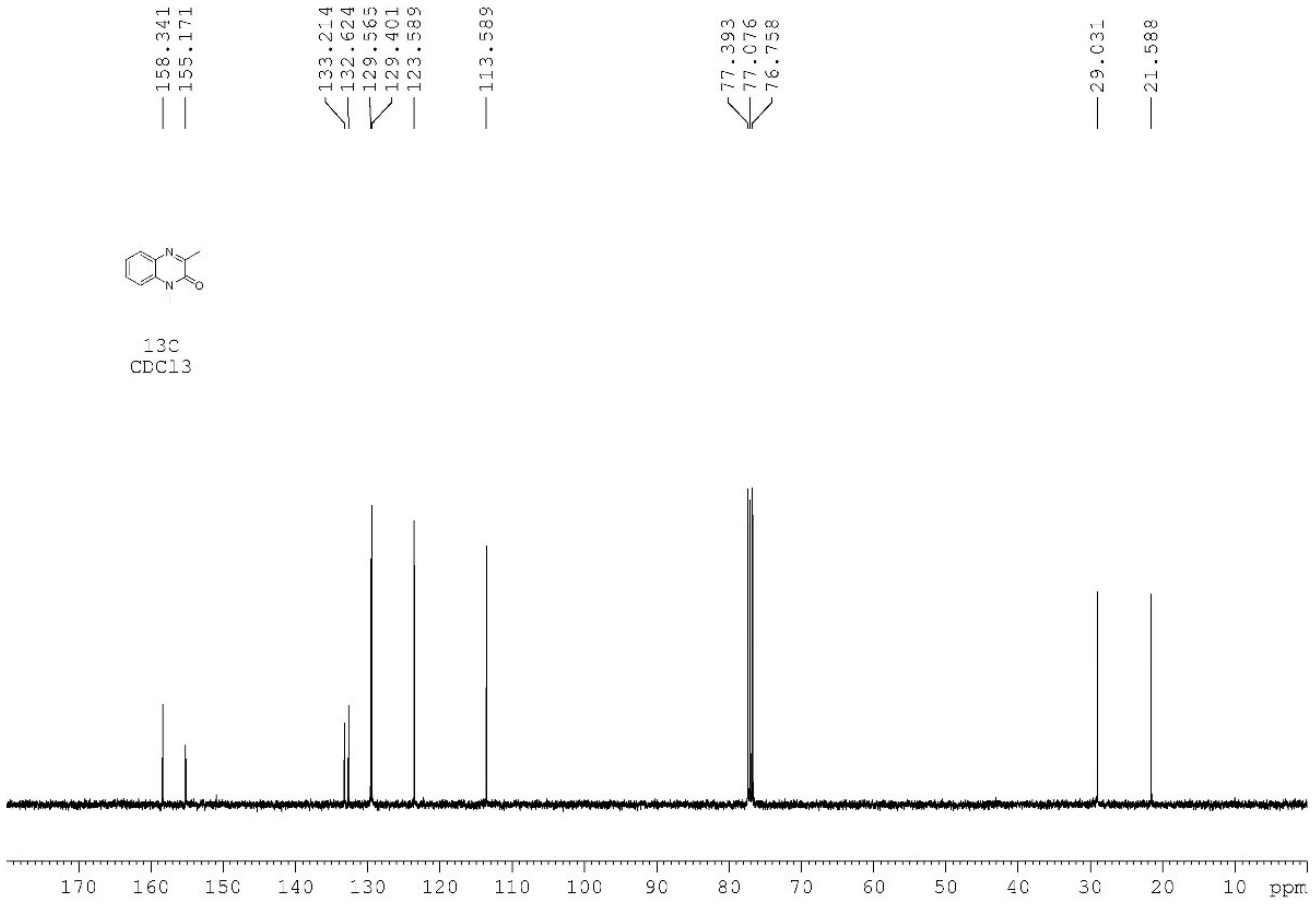
[6] P. Ghosh, N. Y. Kwon, S. Kim, S. Han, S. H. Lee, W. An, N. K. Mishra, S. B. Han and I. S. Kim, *Angew Chem Int Ed.* **2021**, *60*, 191-196.

6. Copies of NMR spectra

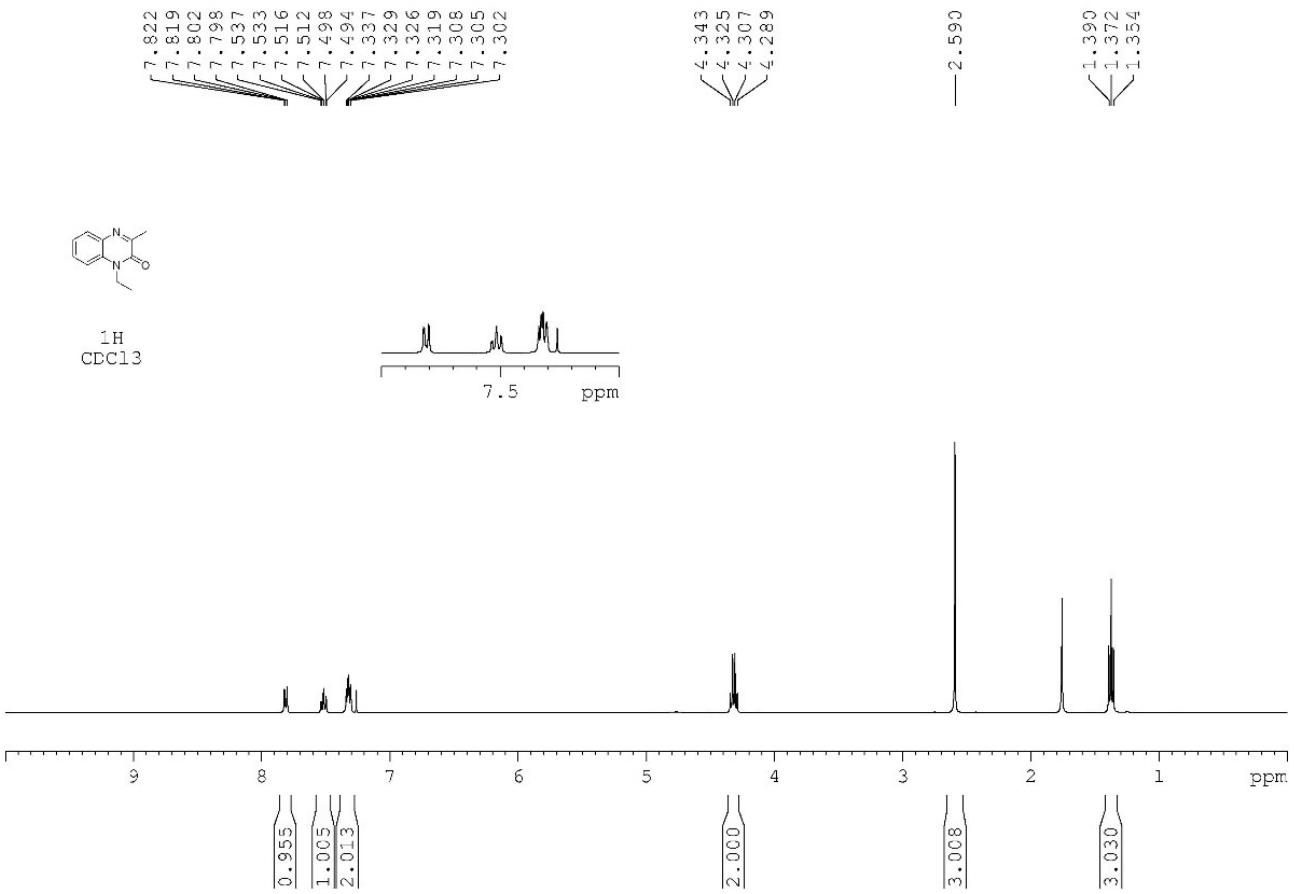
^{1}H NMR of compound **3a**



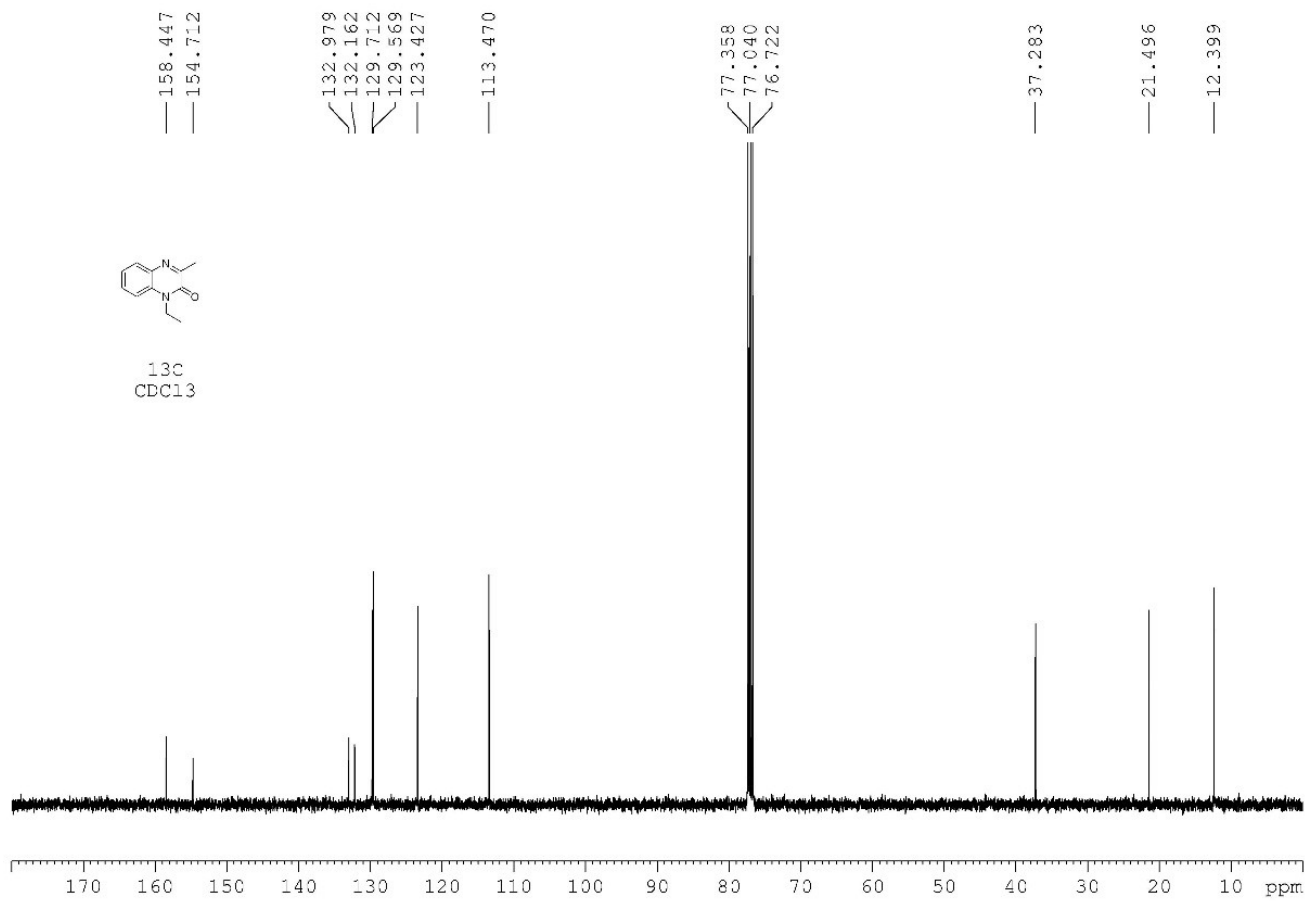
^{13}C NMR of compound **3a**



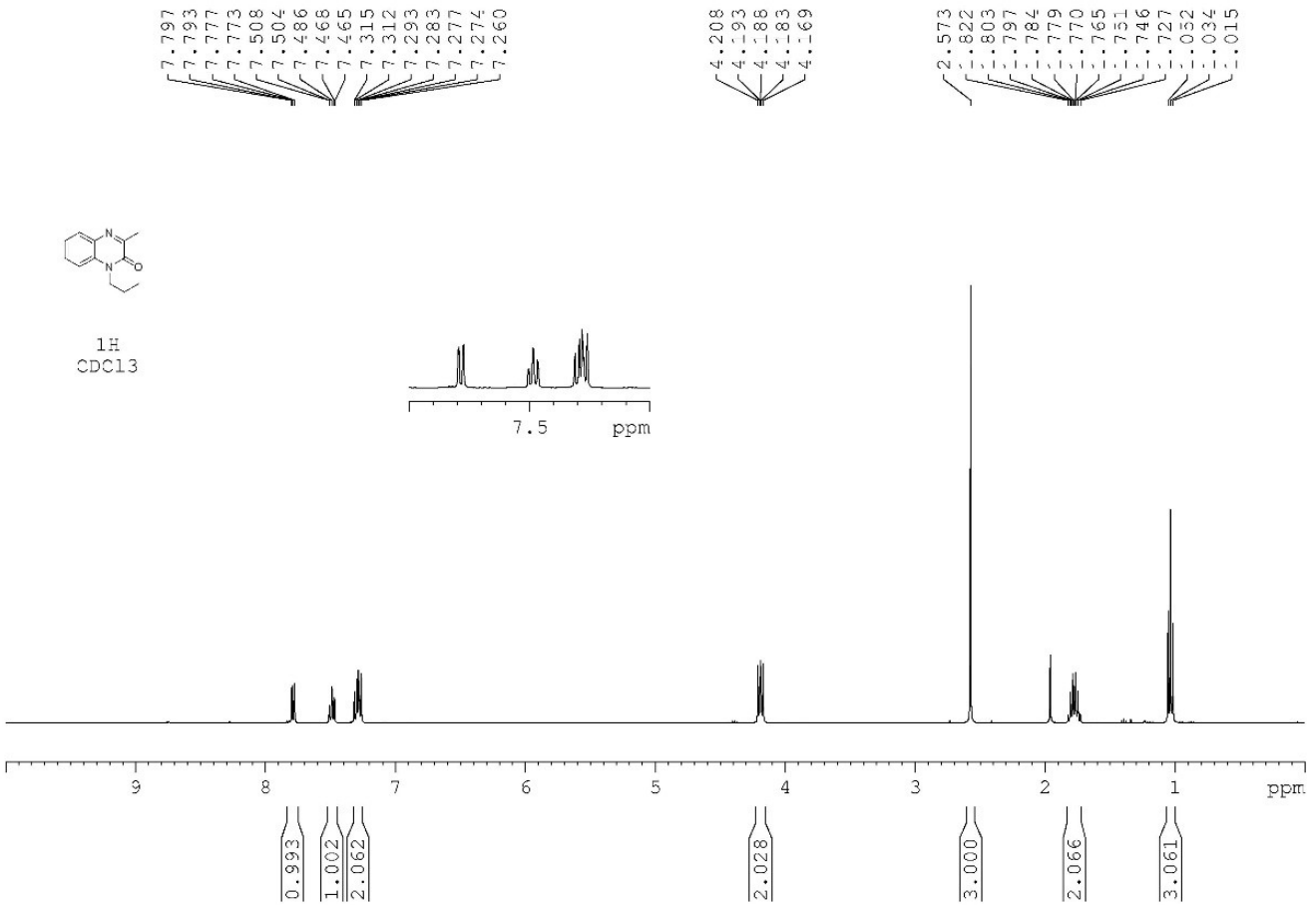
^{1}H NMR of compound **3b**



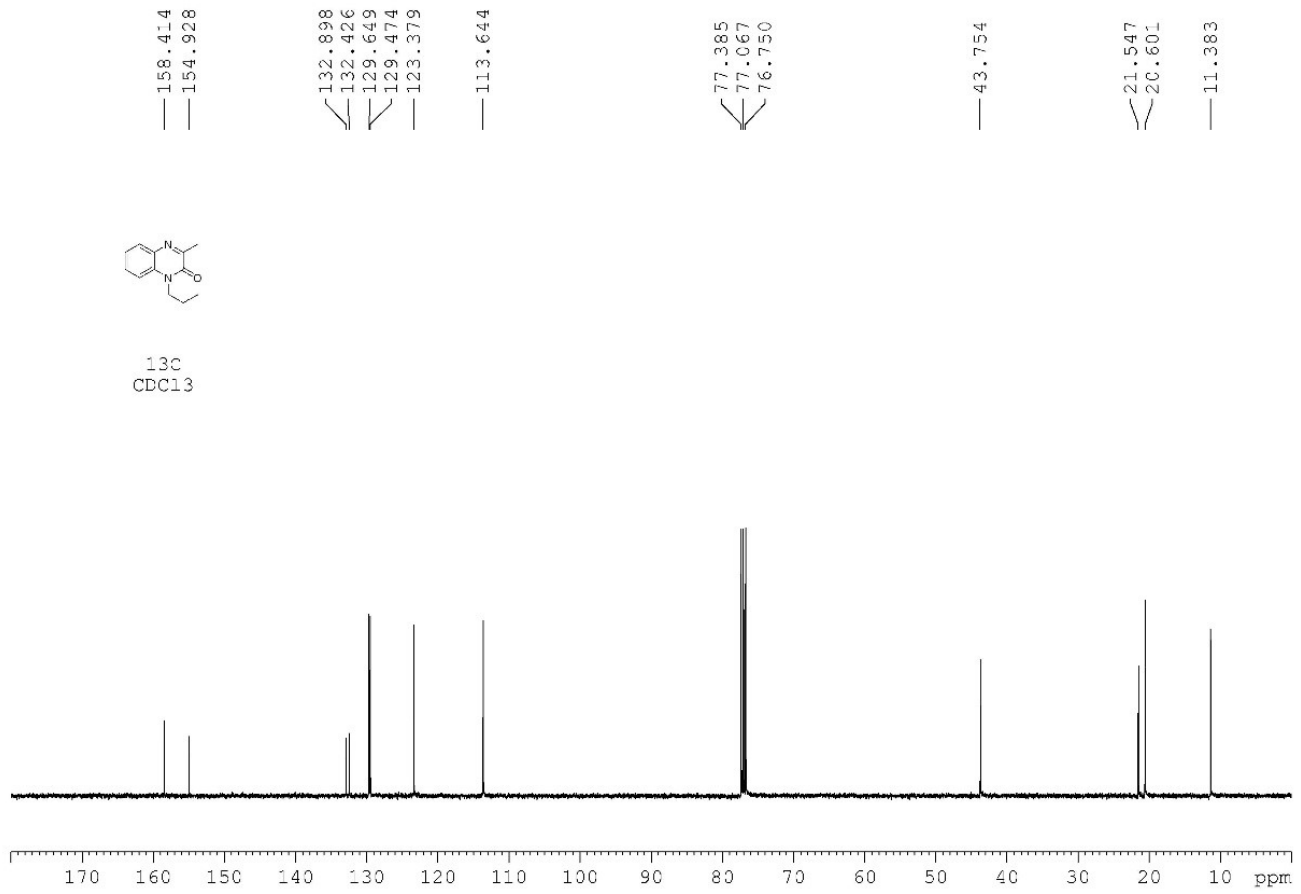
^{13}C NMR of compound **3b**



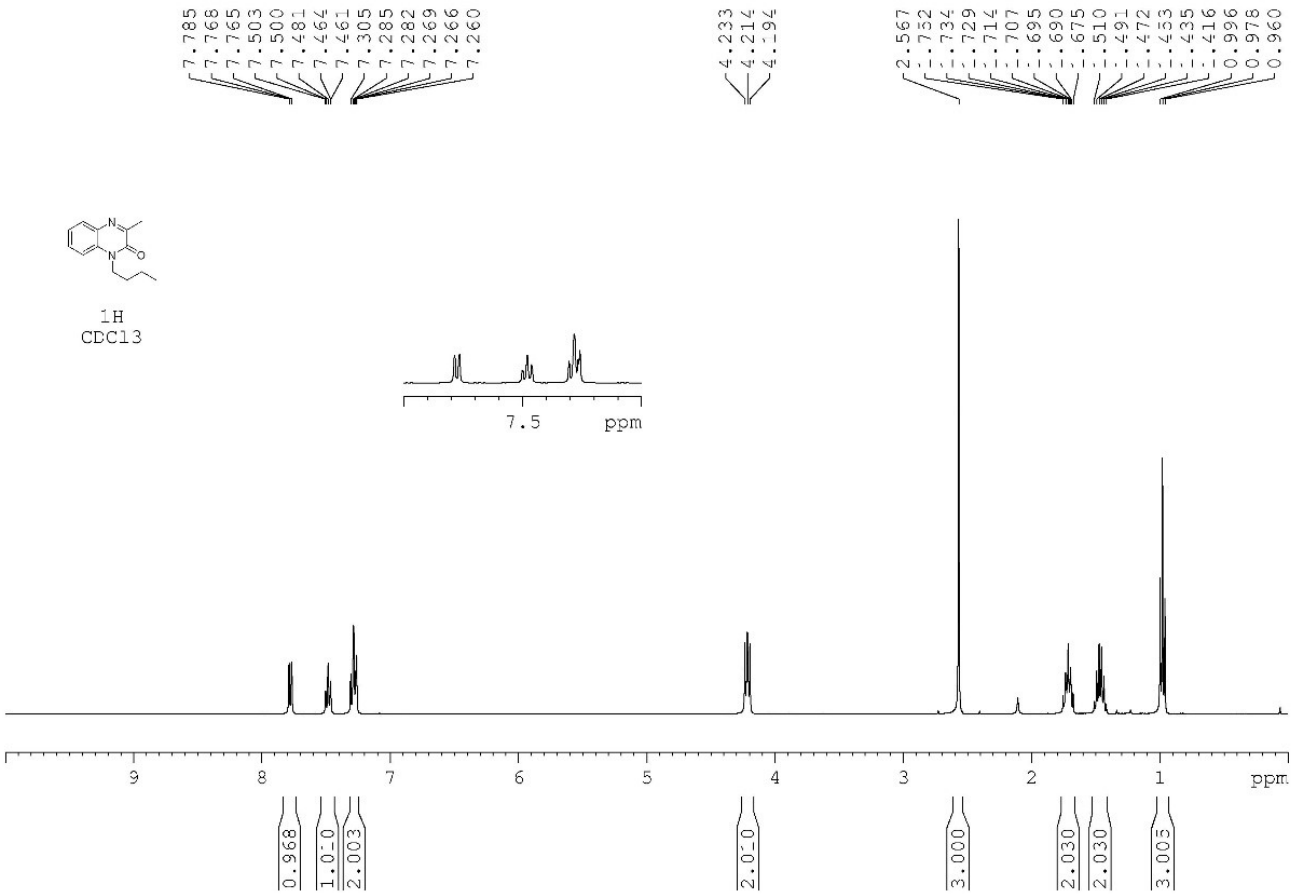
^{1}H NMR of compound **3c**



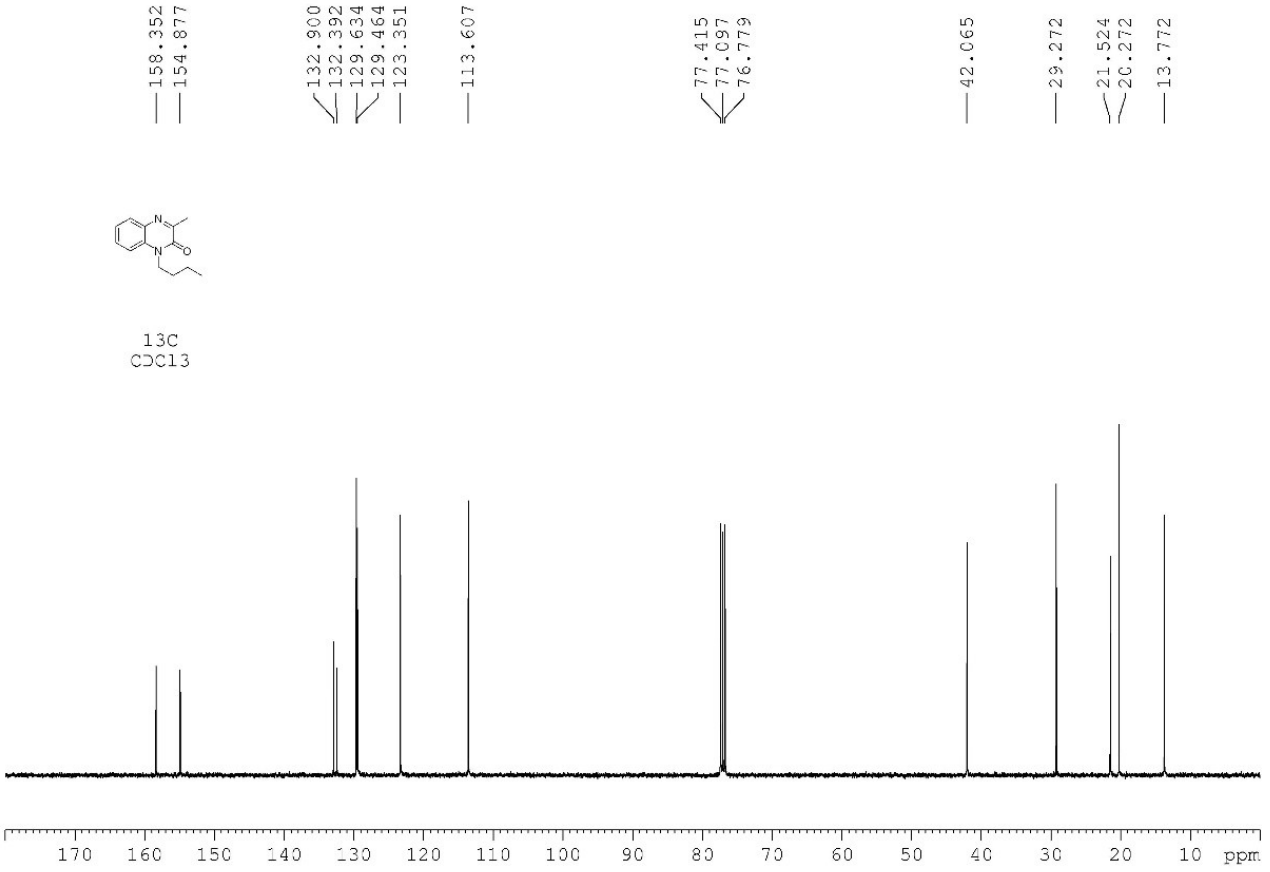
^{13}C NMR of compound **3c**



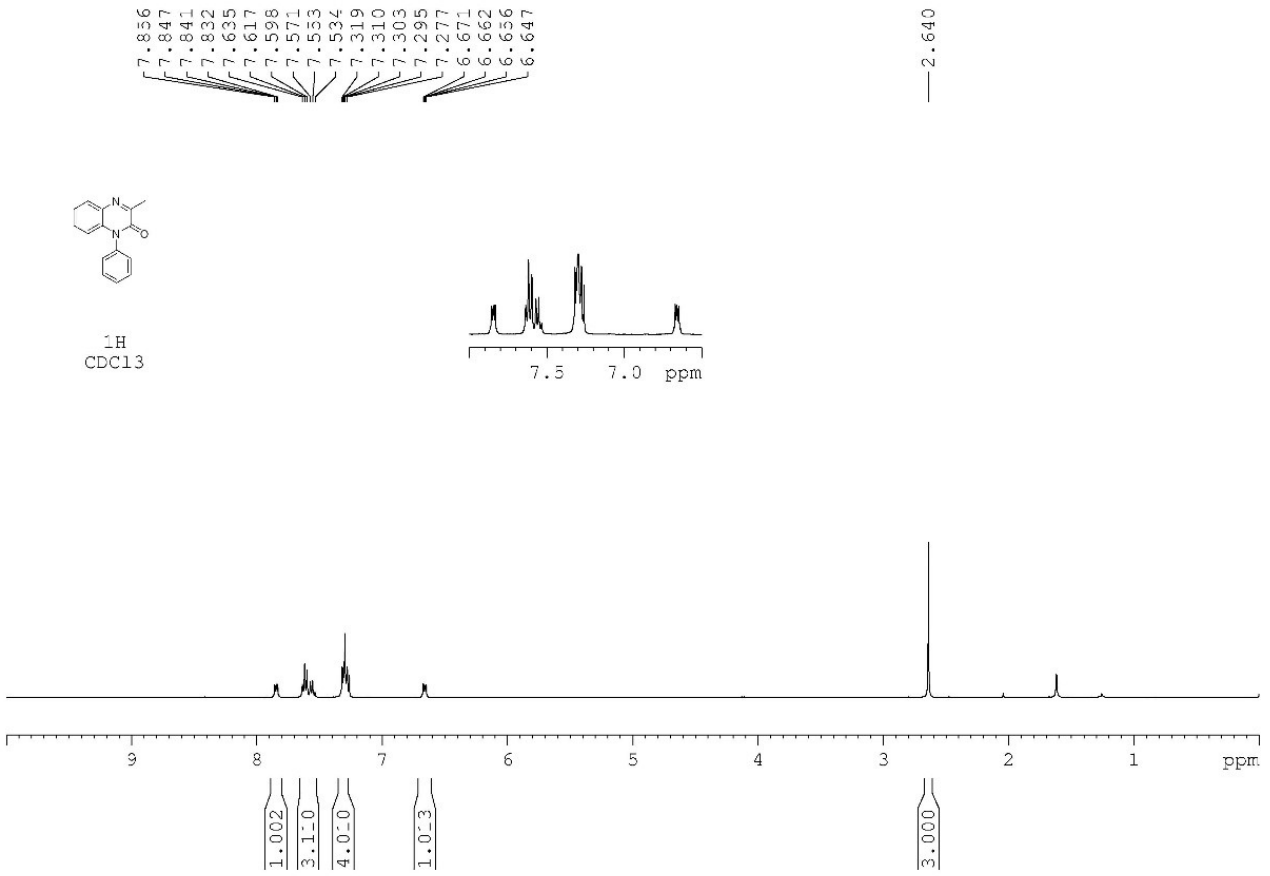
[1]H NMR of compound **3d**



^{13}C NMR of compound **3d**



^{1}H NMR of compound **3e**



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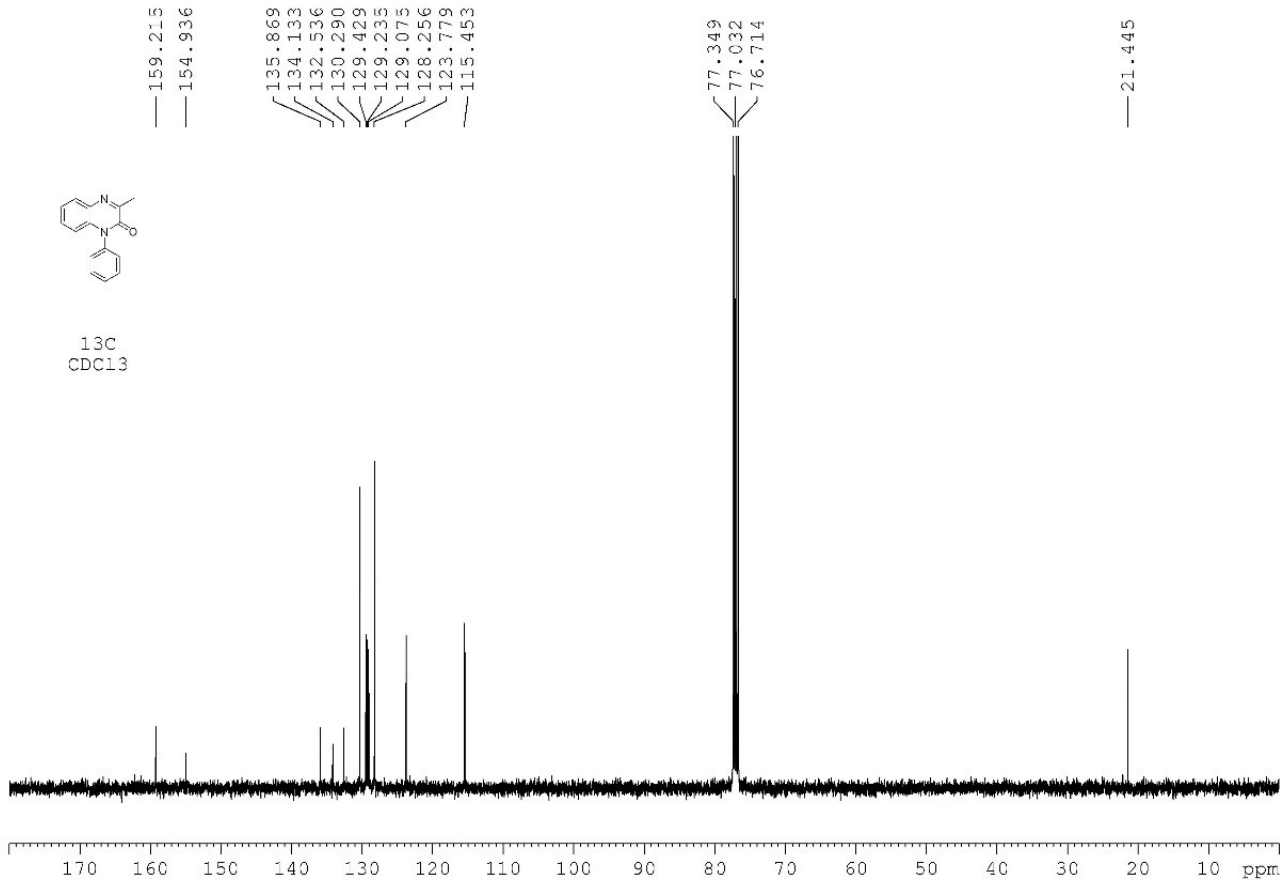
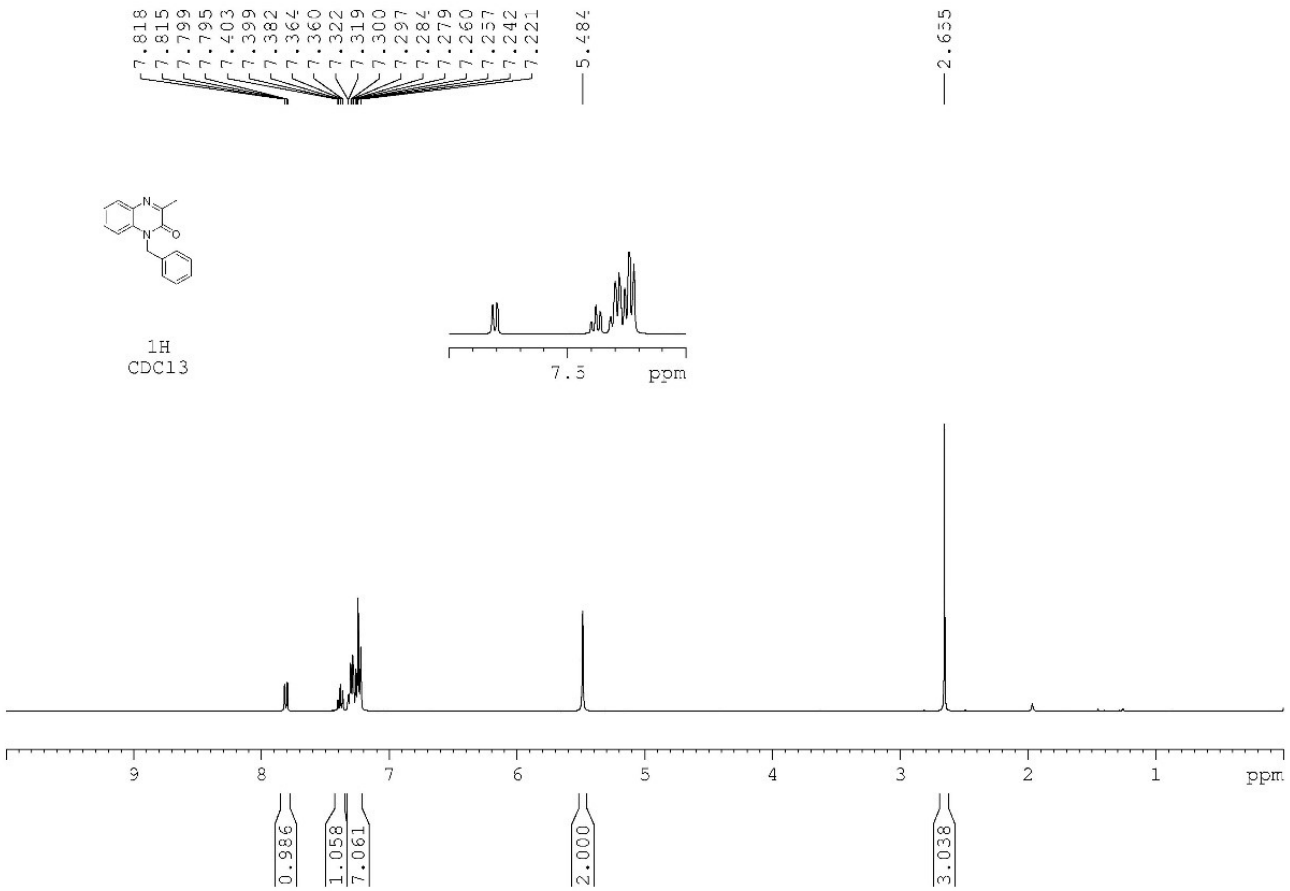
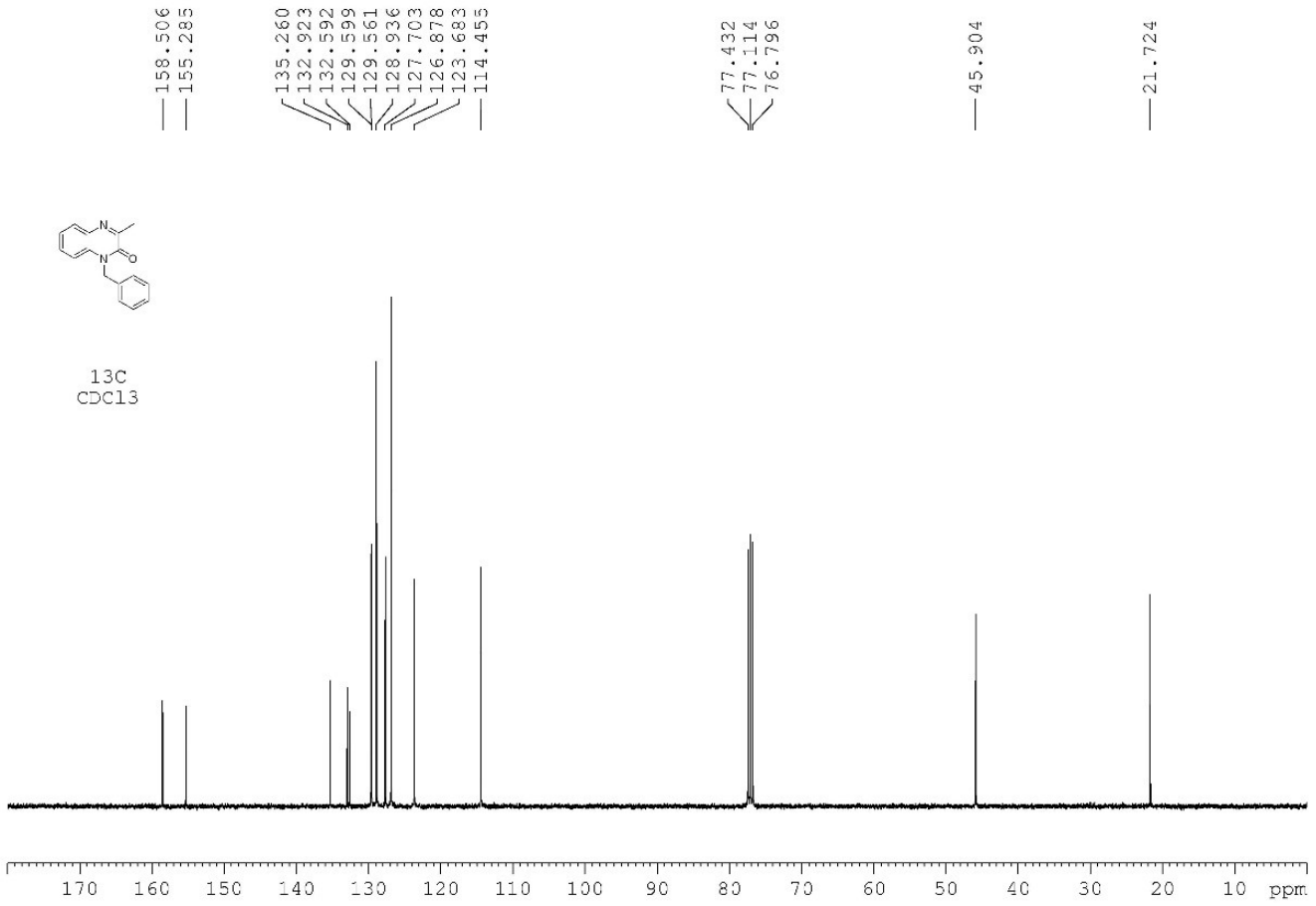


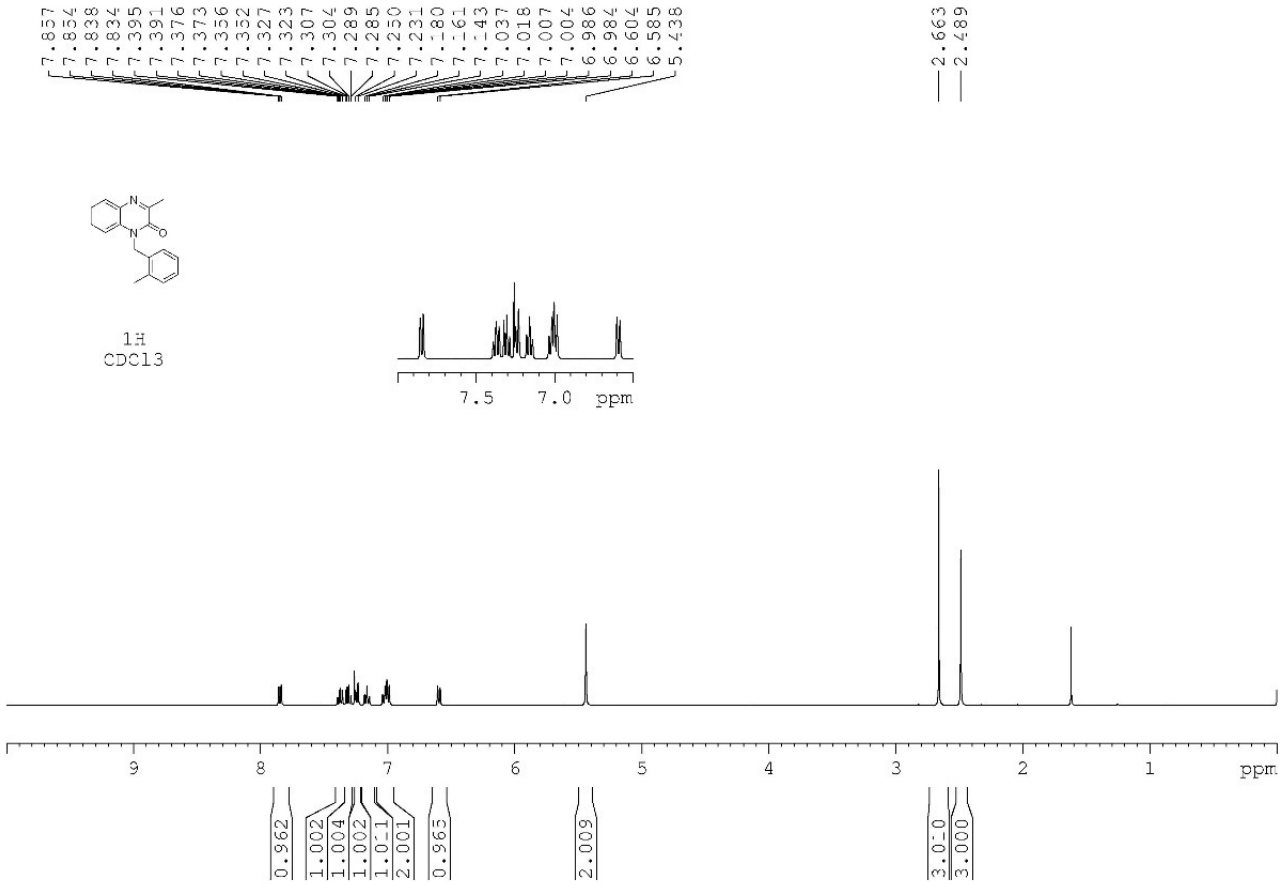
[1]H NMR of compound **3f**



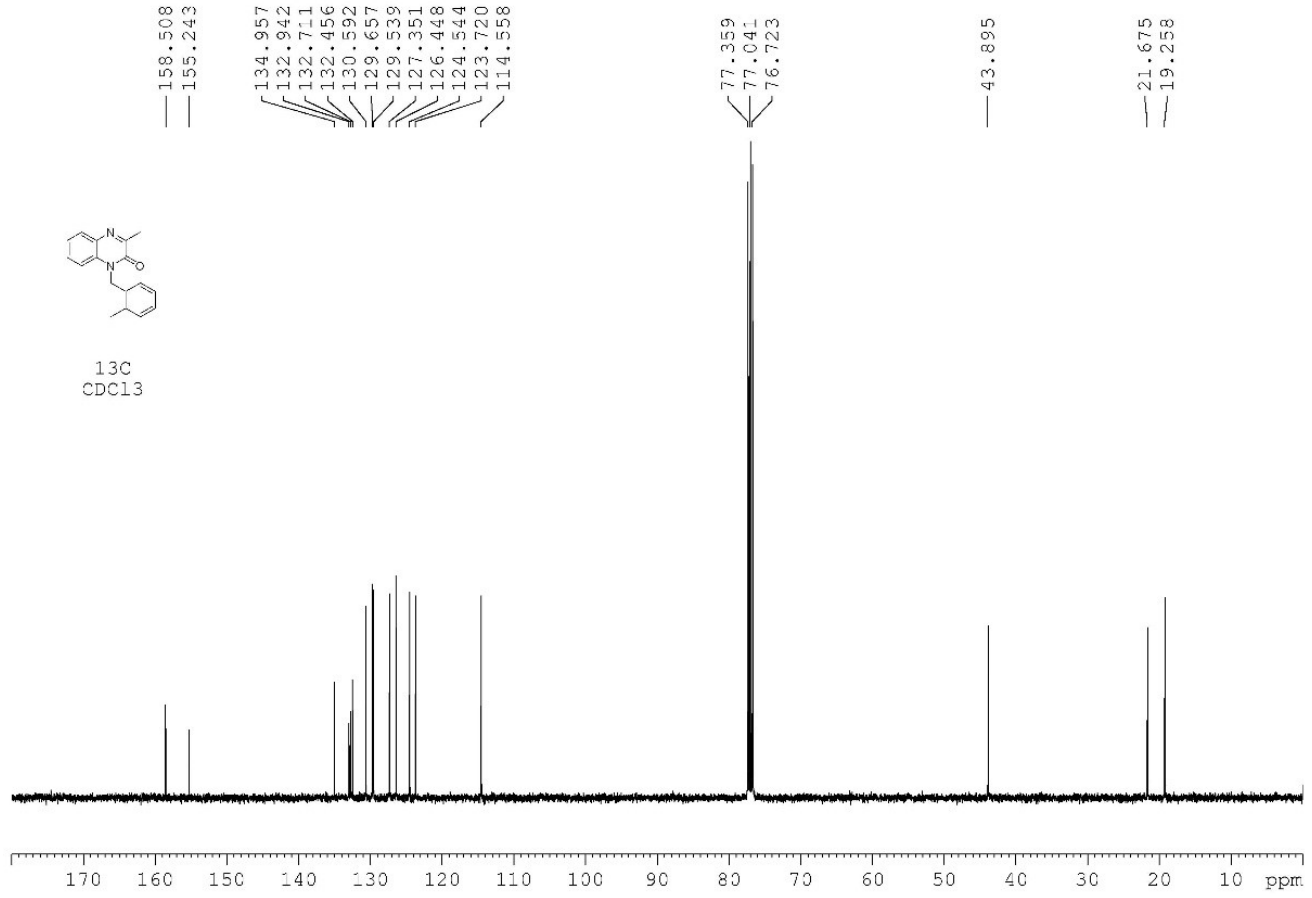
^{13}C NMR of compound **3f**



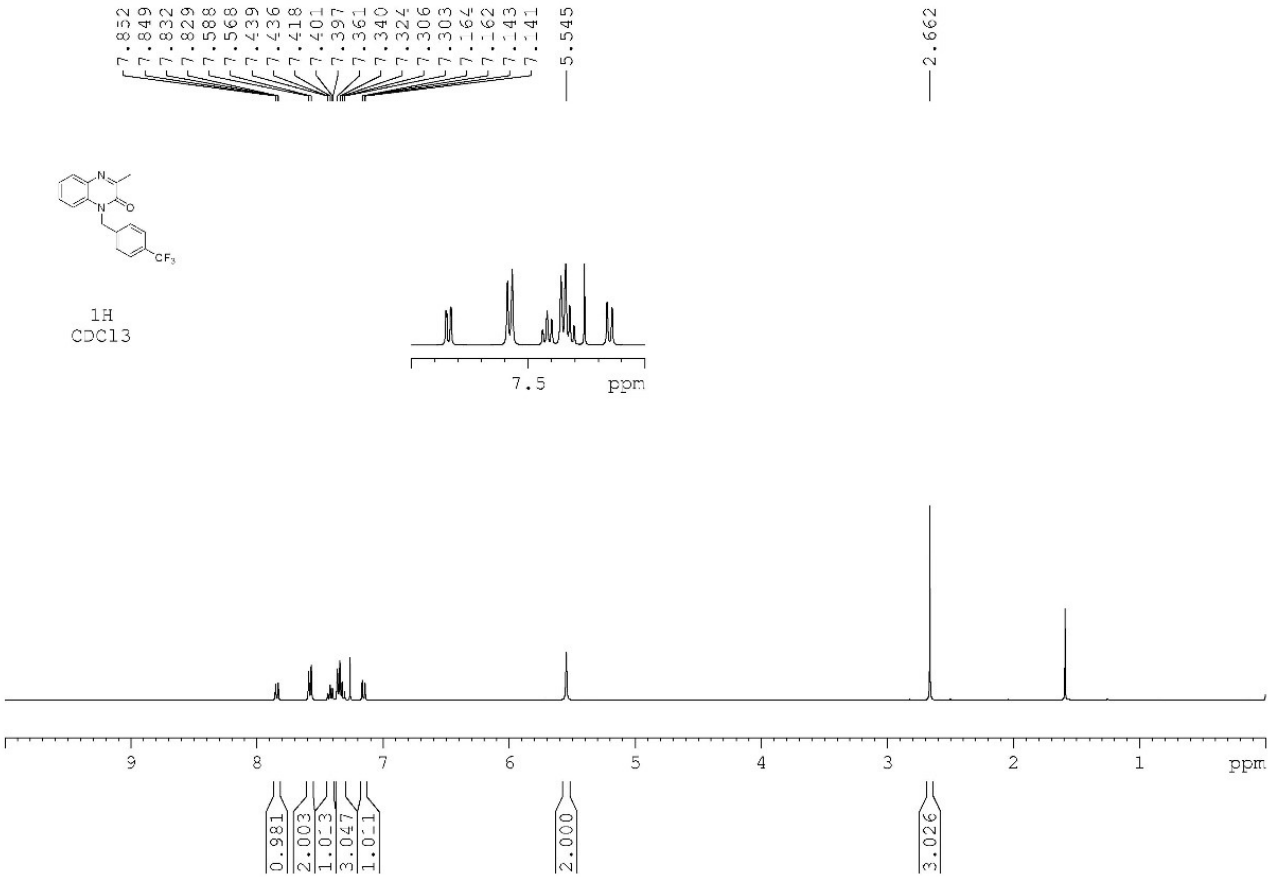
[1]H NMR of compound **3g**



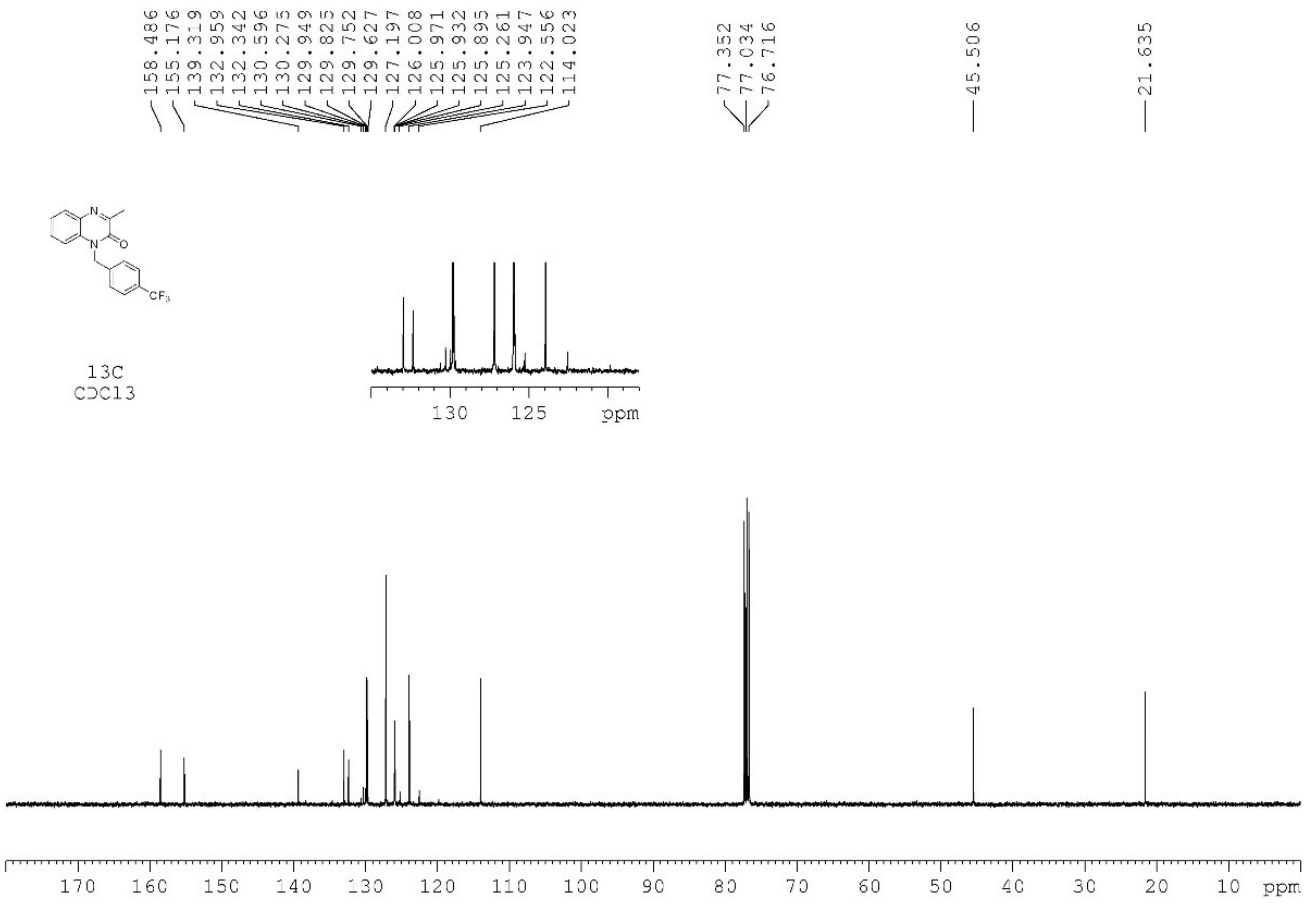
^{13}C NMR of compound **3g**



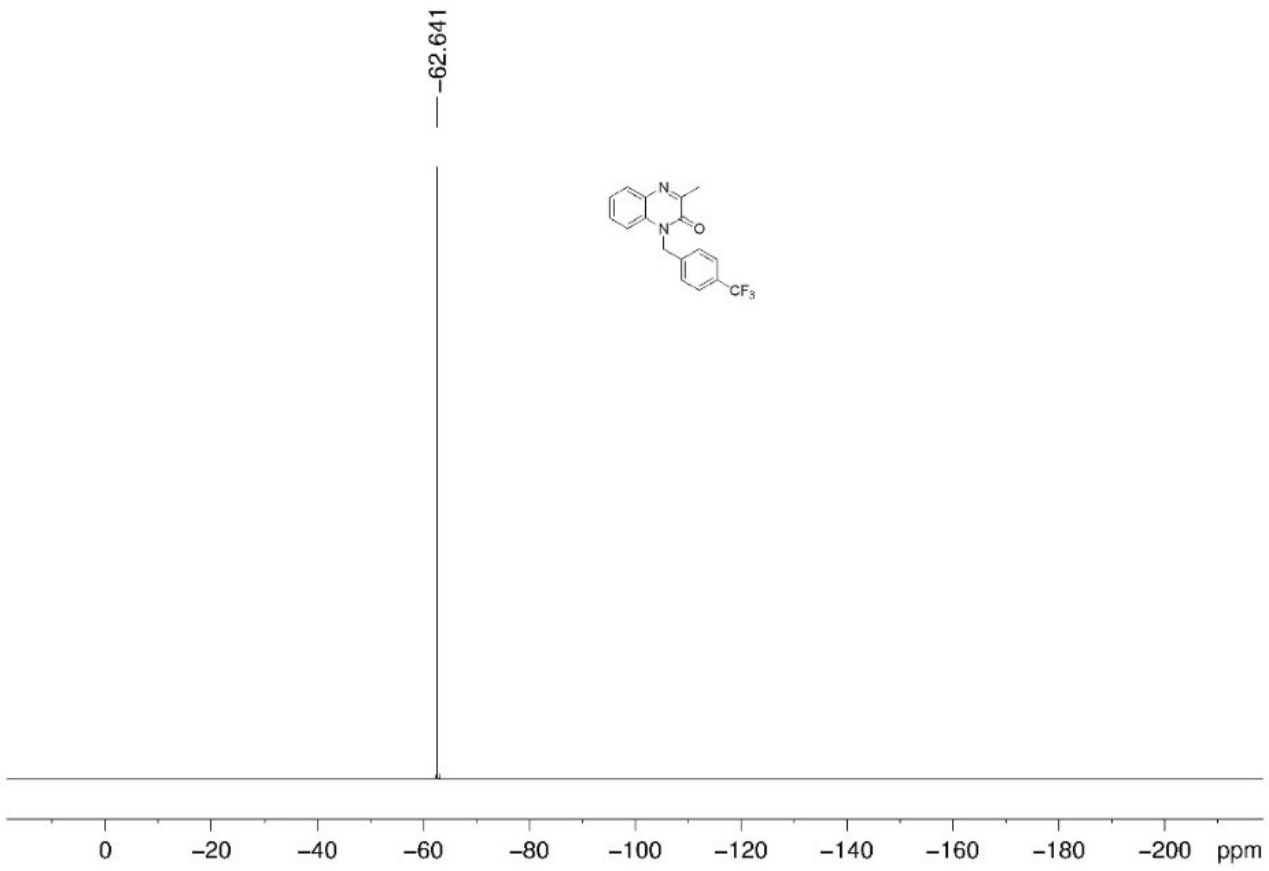
[1]H NMR of compound **3h**



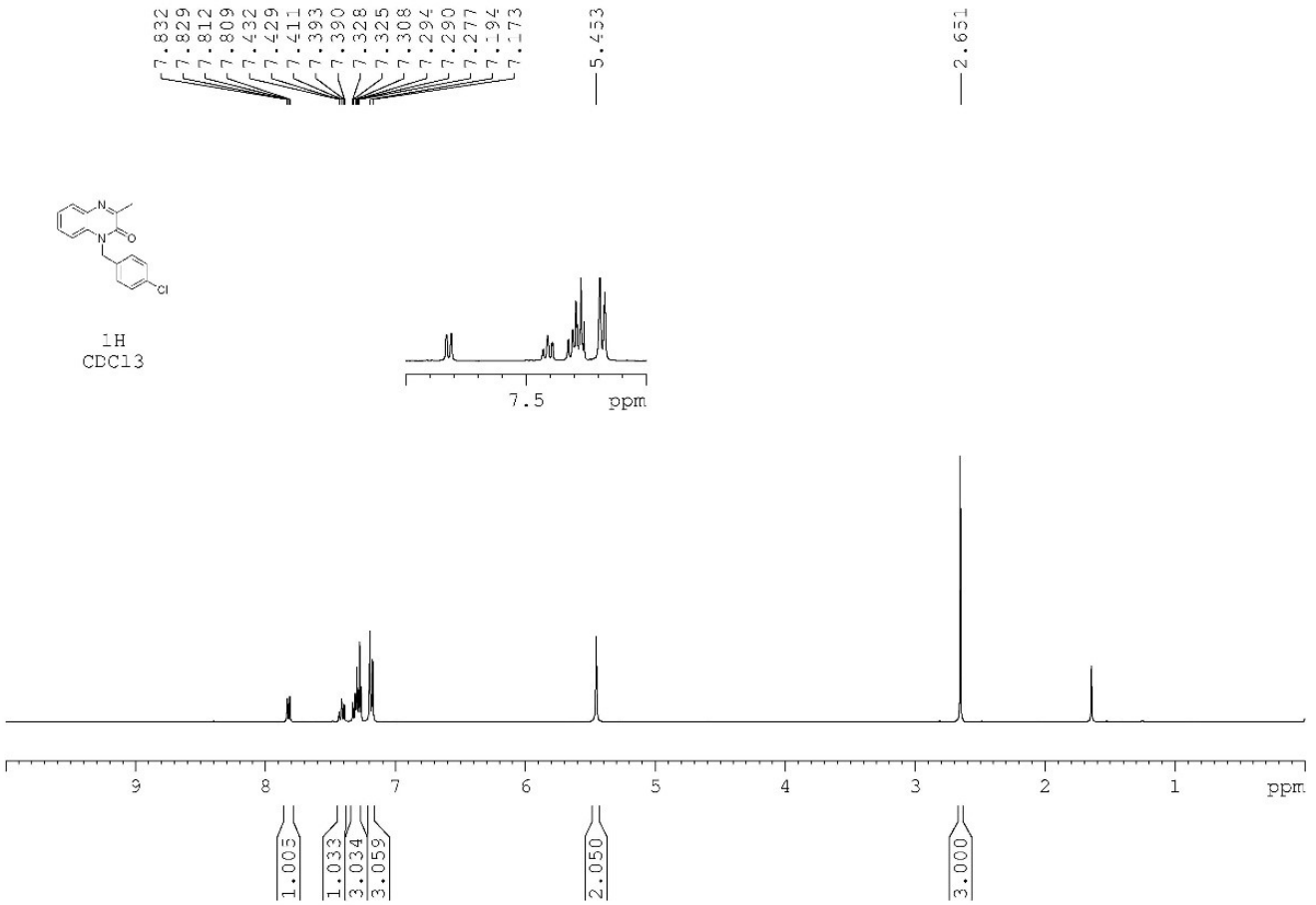
^{13}C NMR of compound **3h**



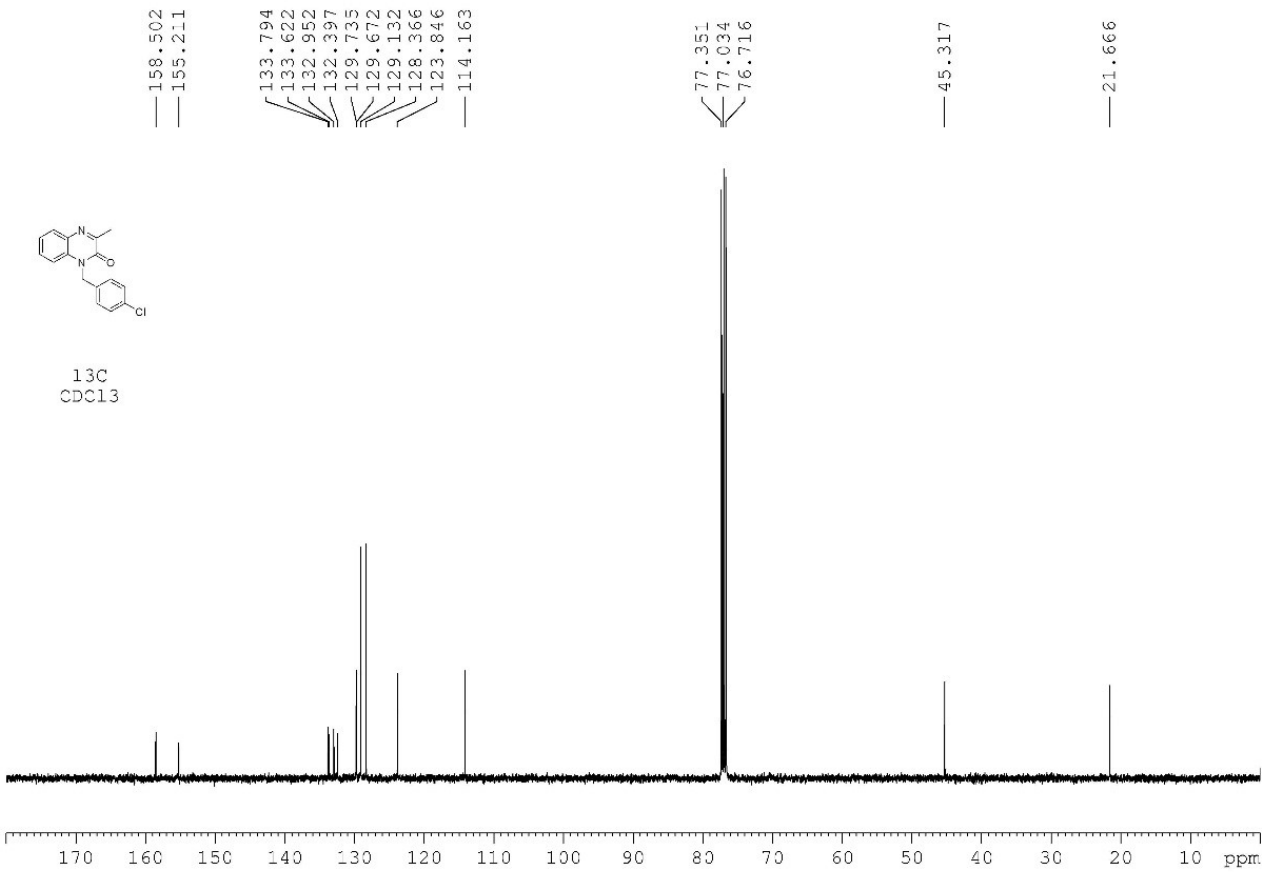
^{19}F NMR of compound **3h**



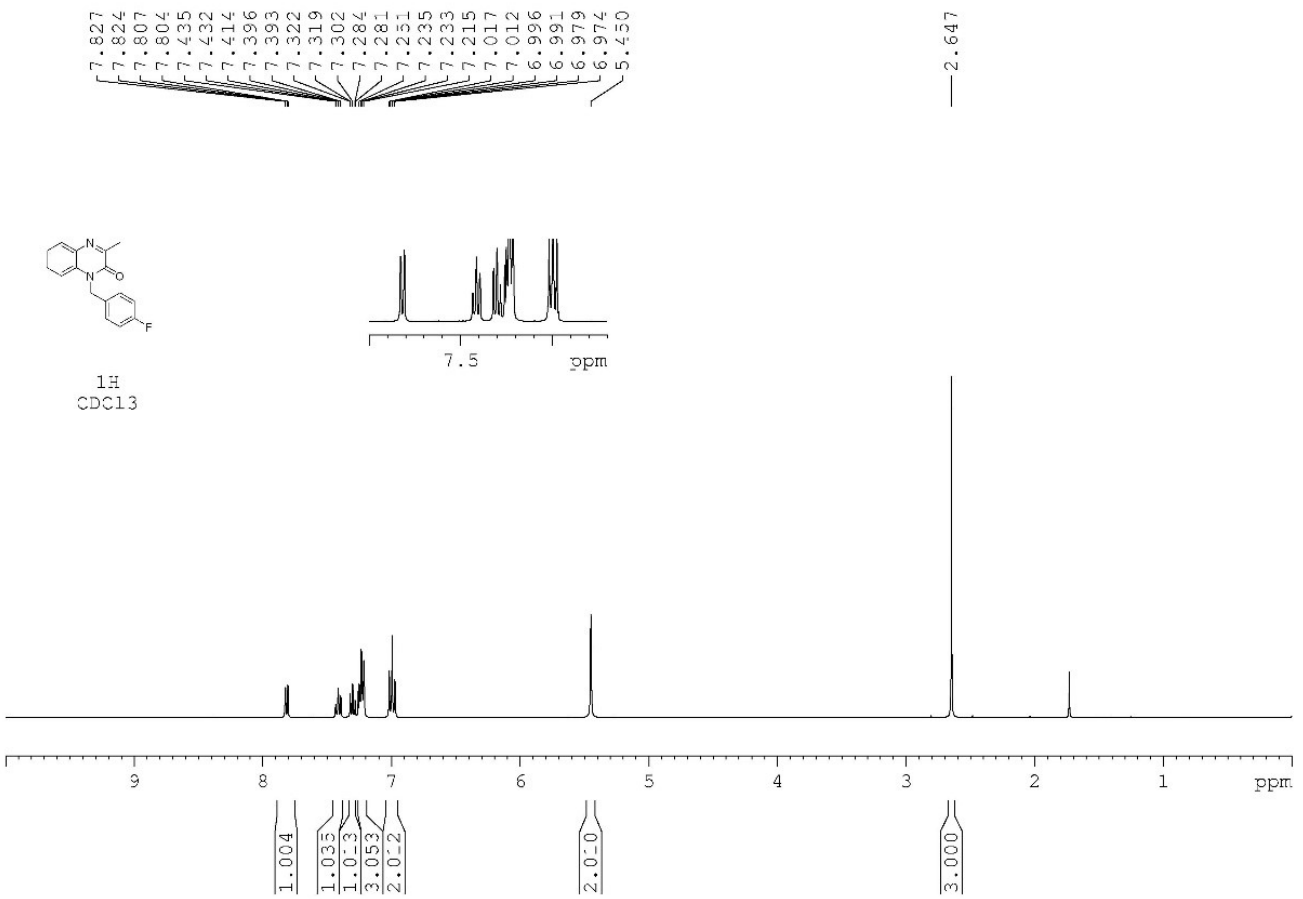
^{1}H NMR of compound **3i**



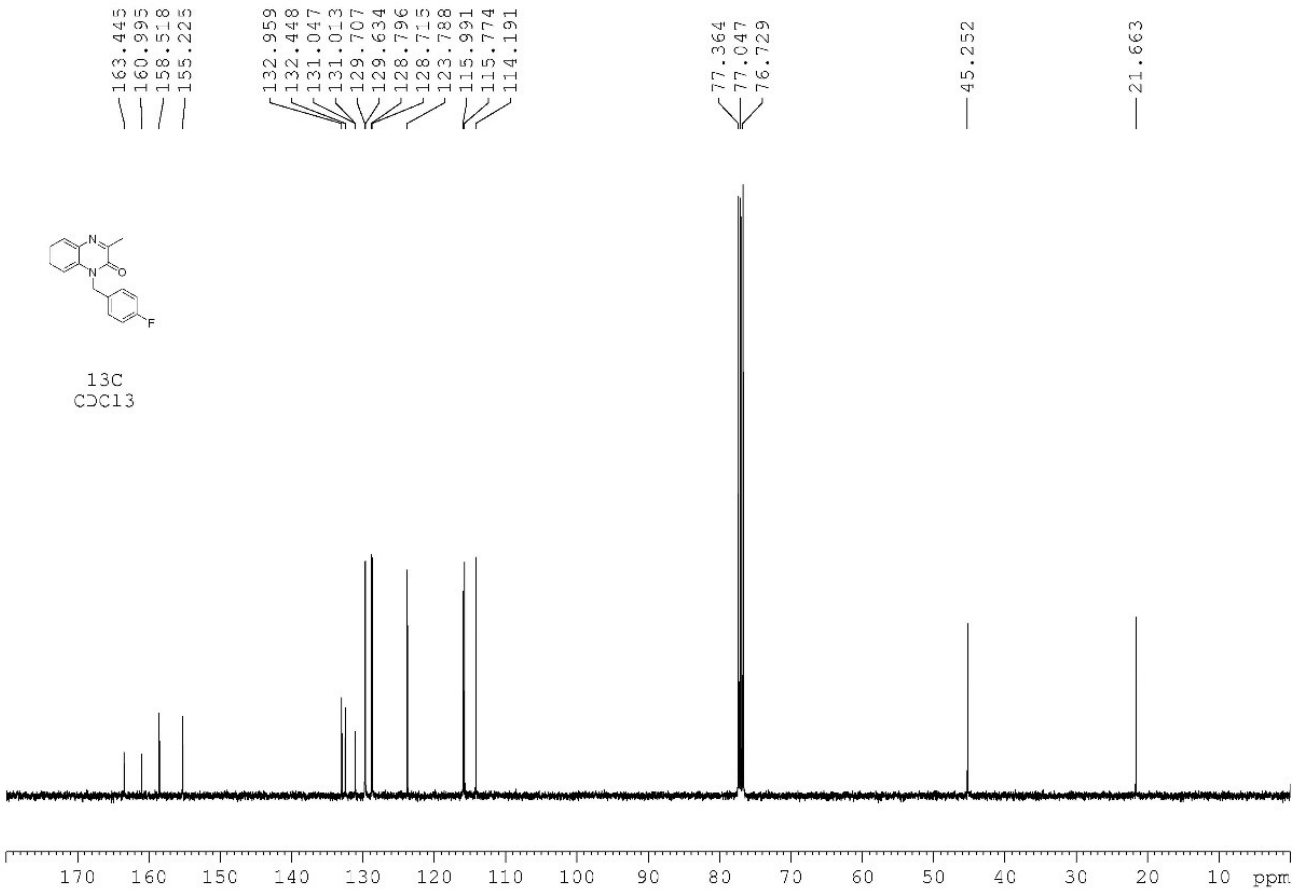
^{13}C NMR of compound **3i**



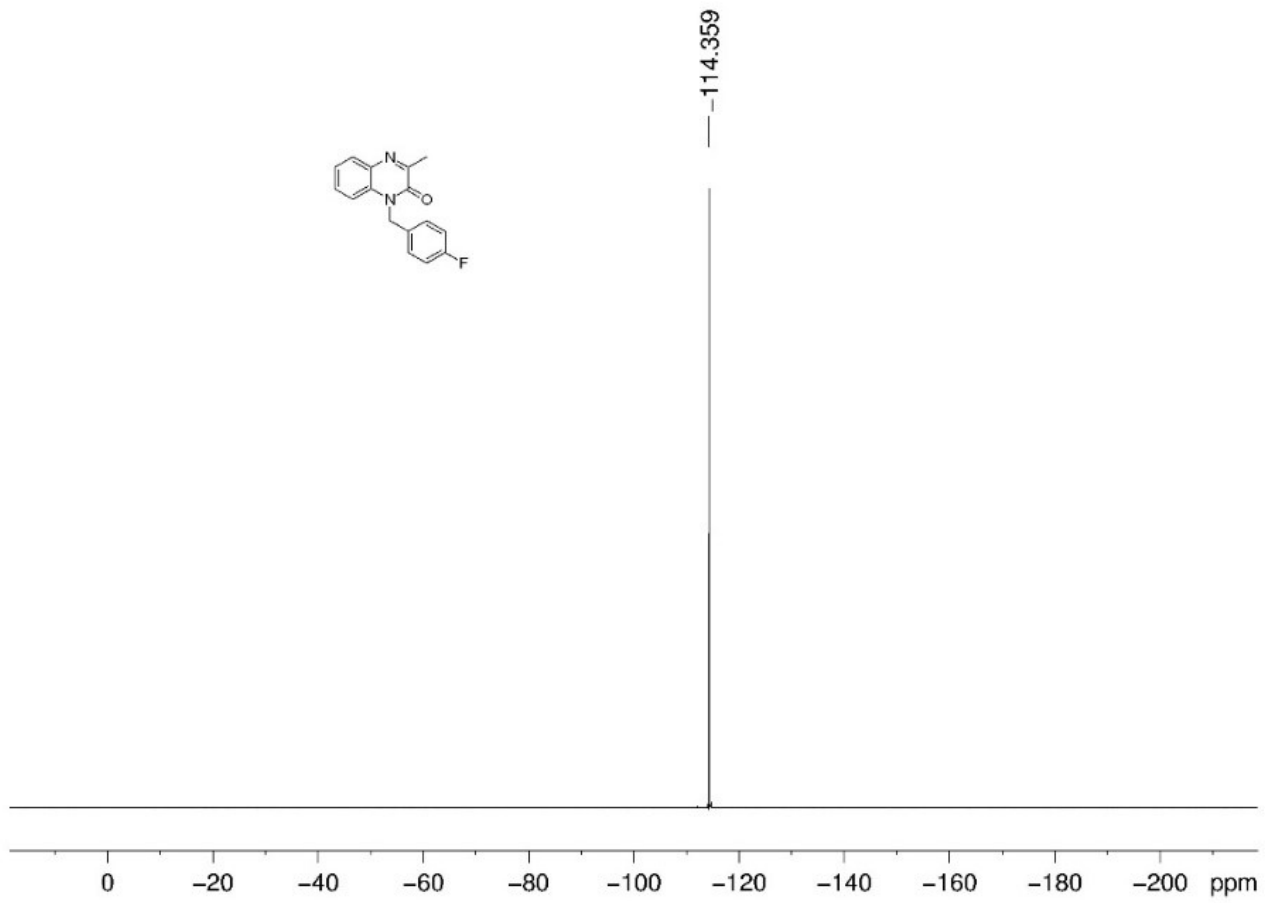
^{1}H NMR of compound **3j**



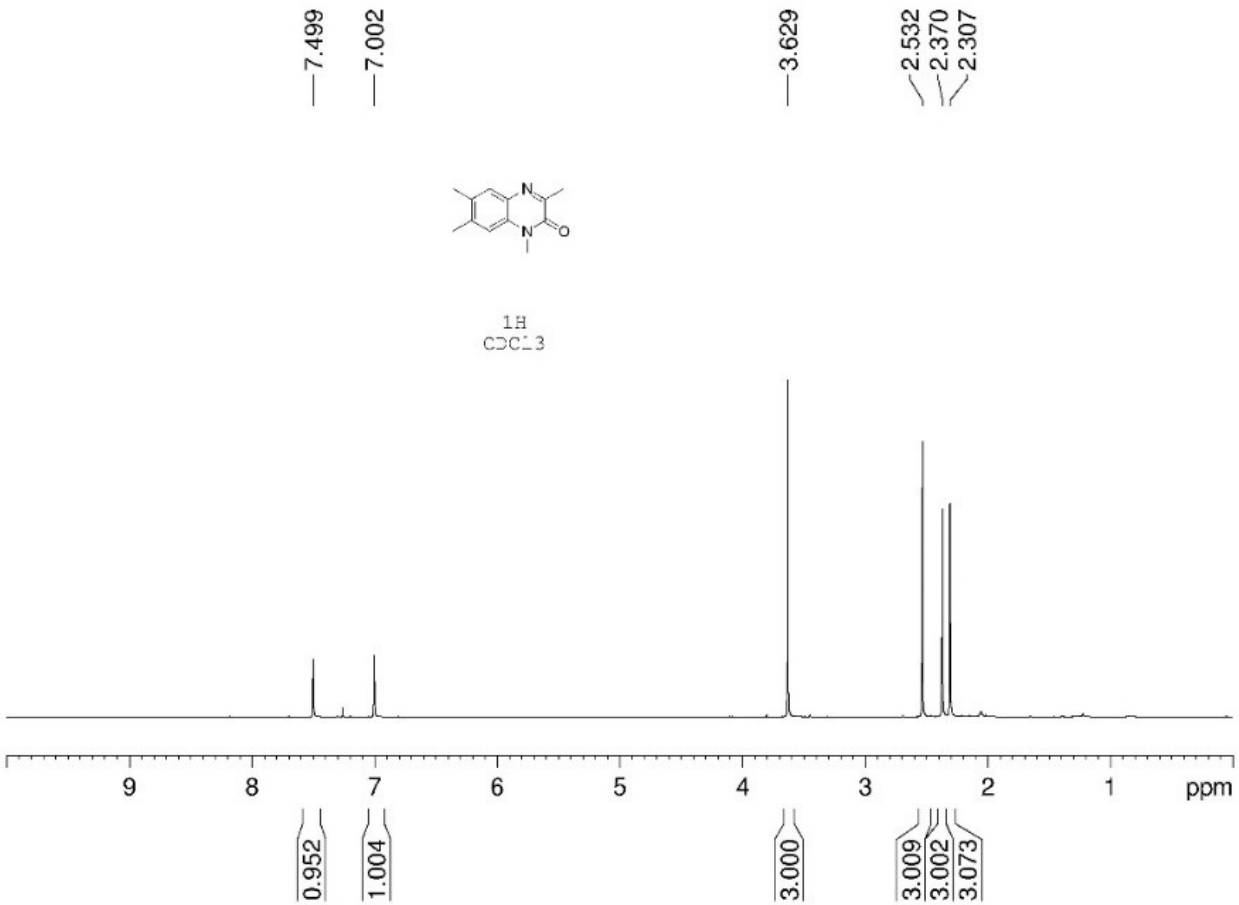
^{13}C NMR of compound **3j**



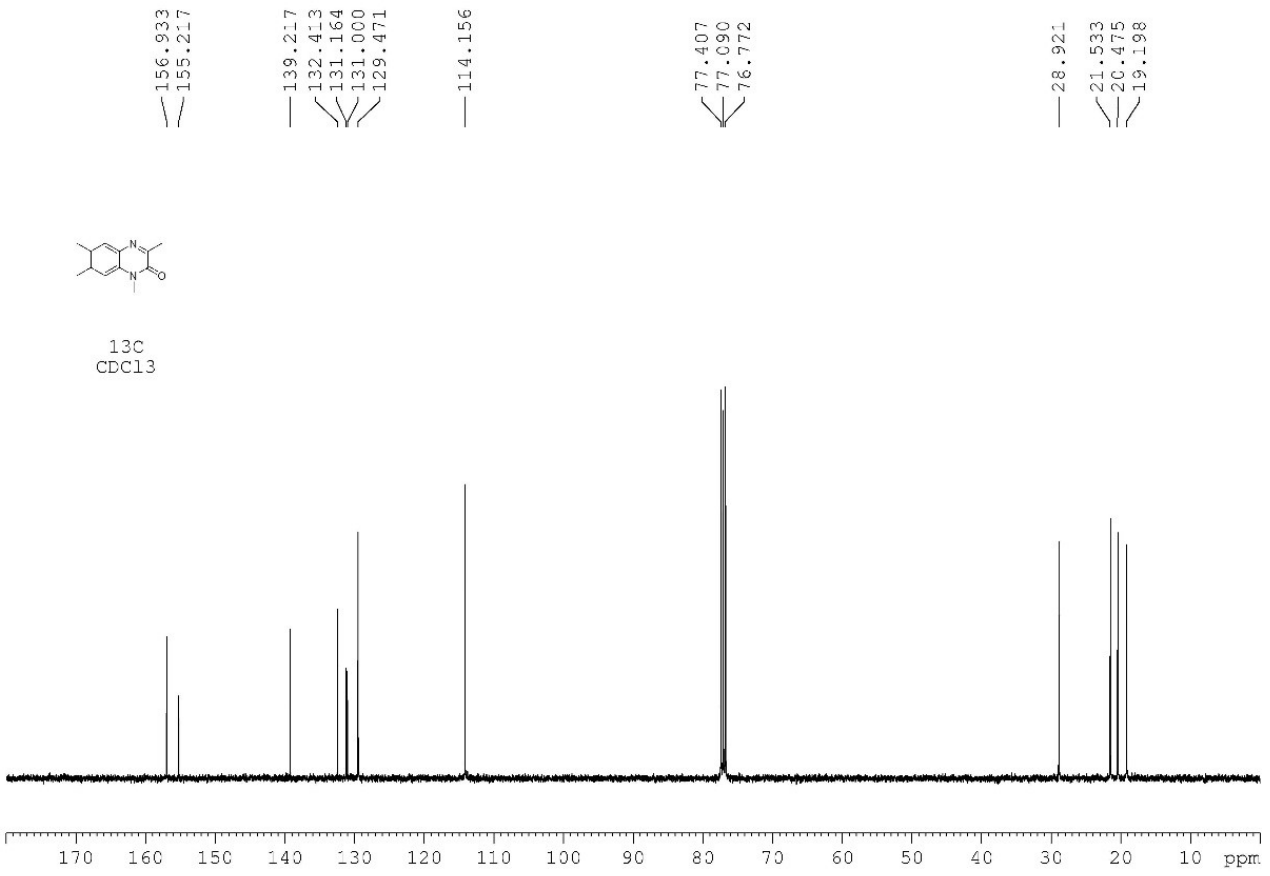
^{19}F NMR of compound **3j**



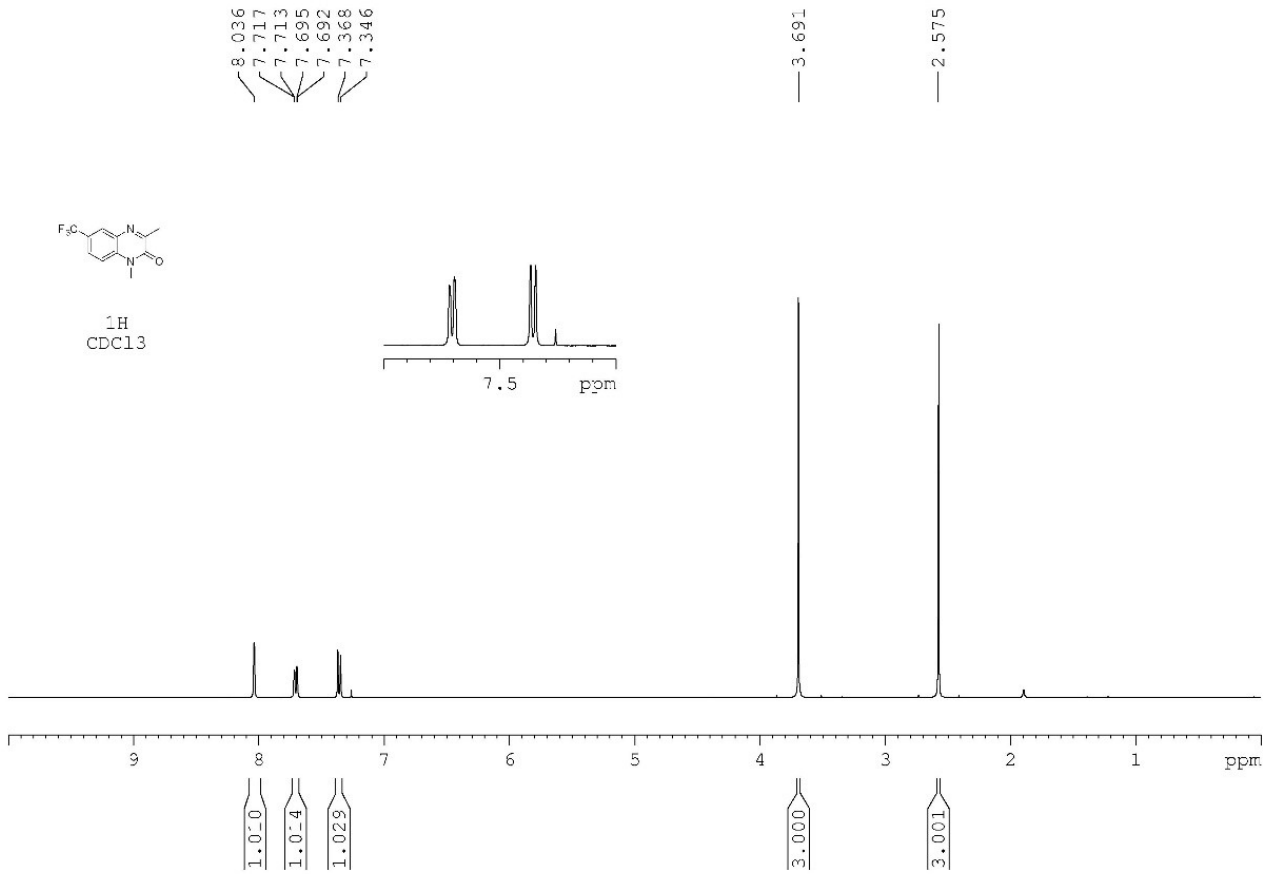
^{1}H NMR of compound **3k**



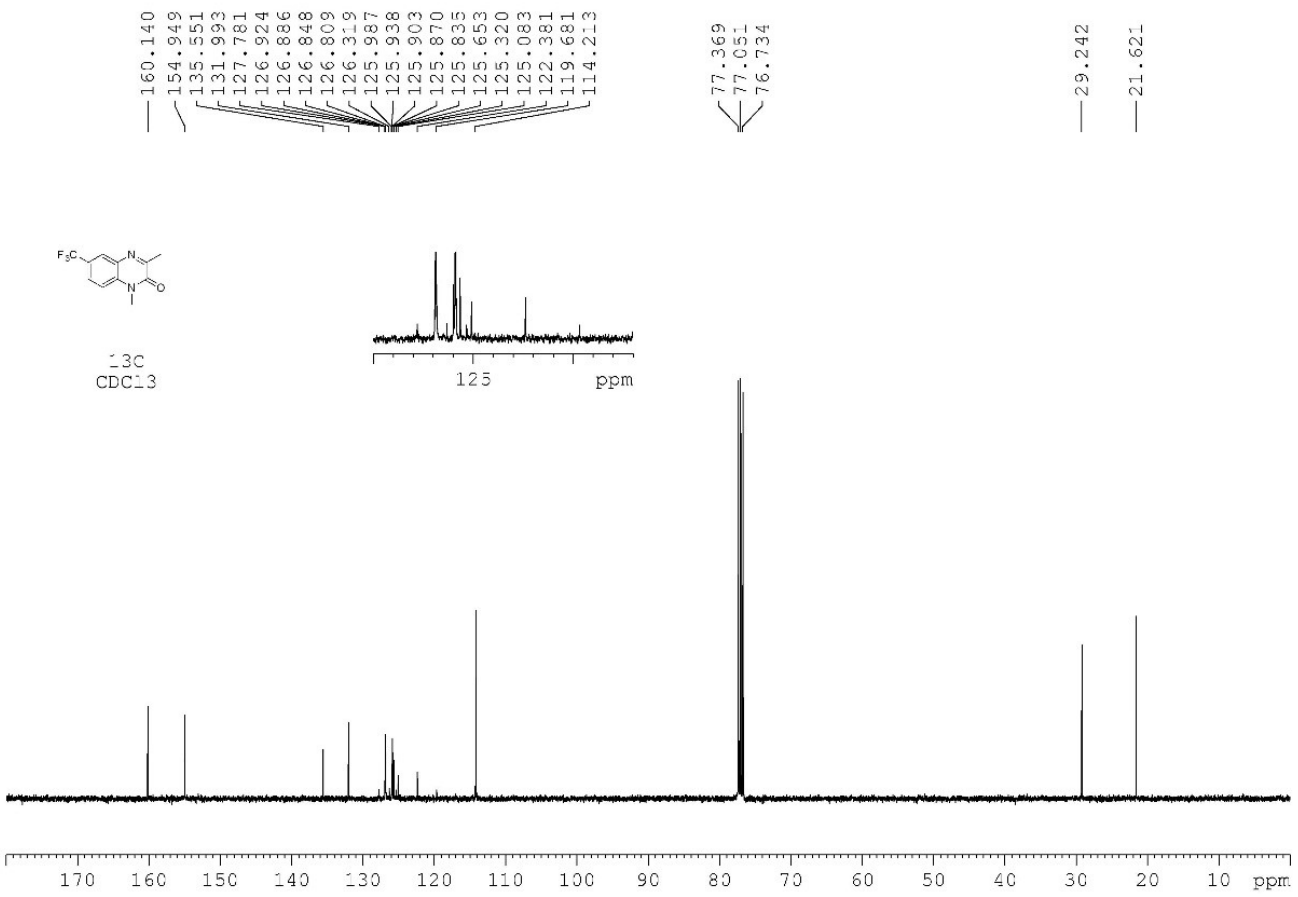
^{13}C NMR of compound **3k**



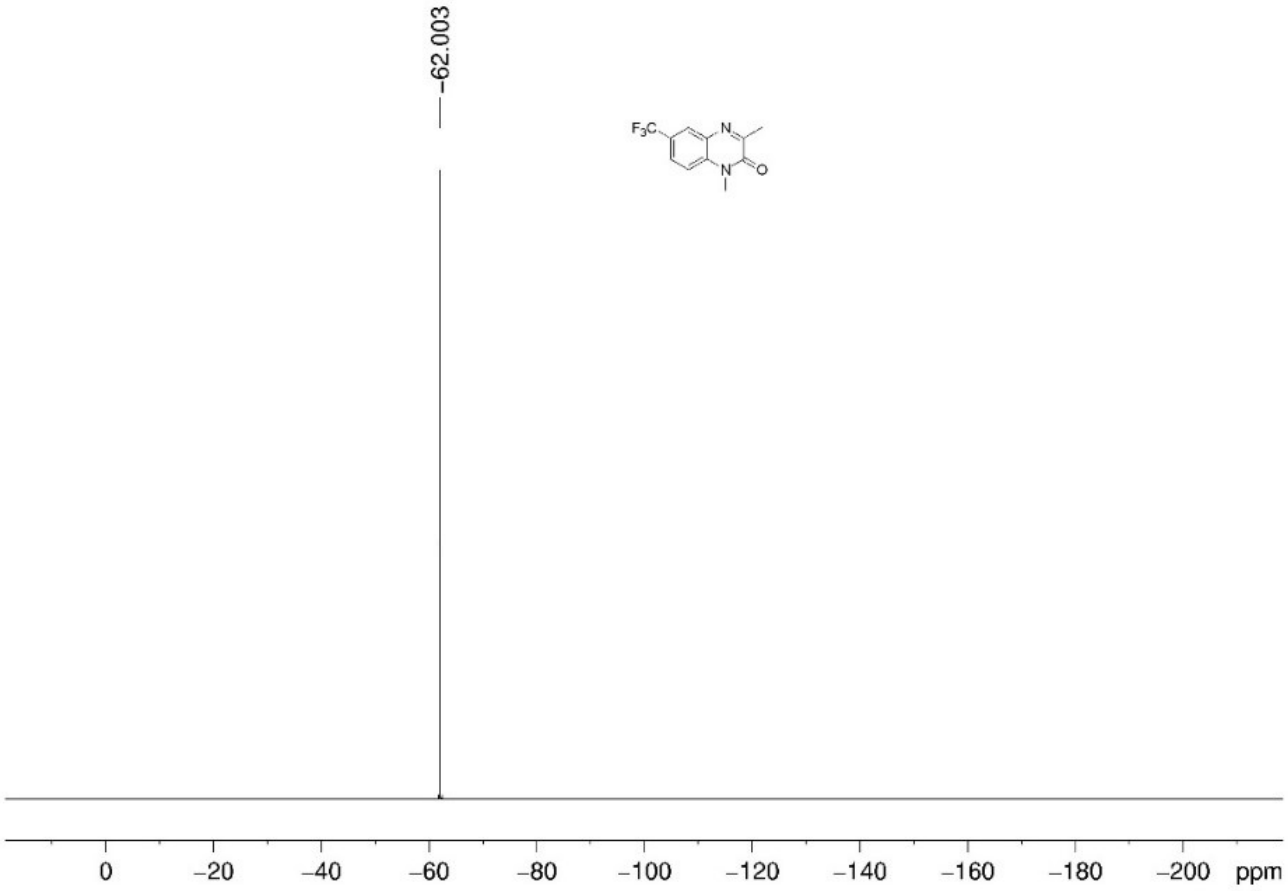
^{1}H NMR of compound **31**



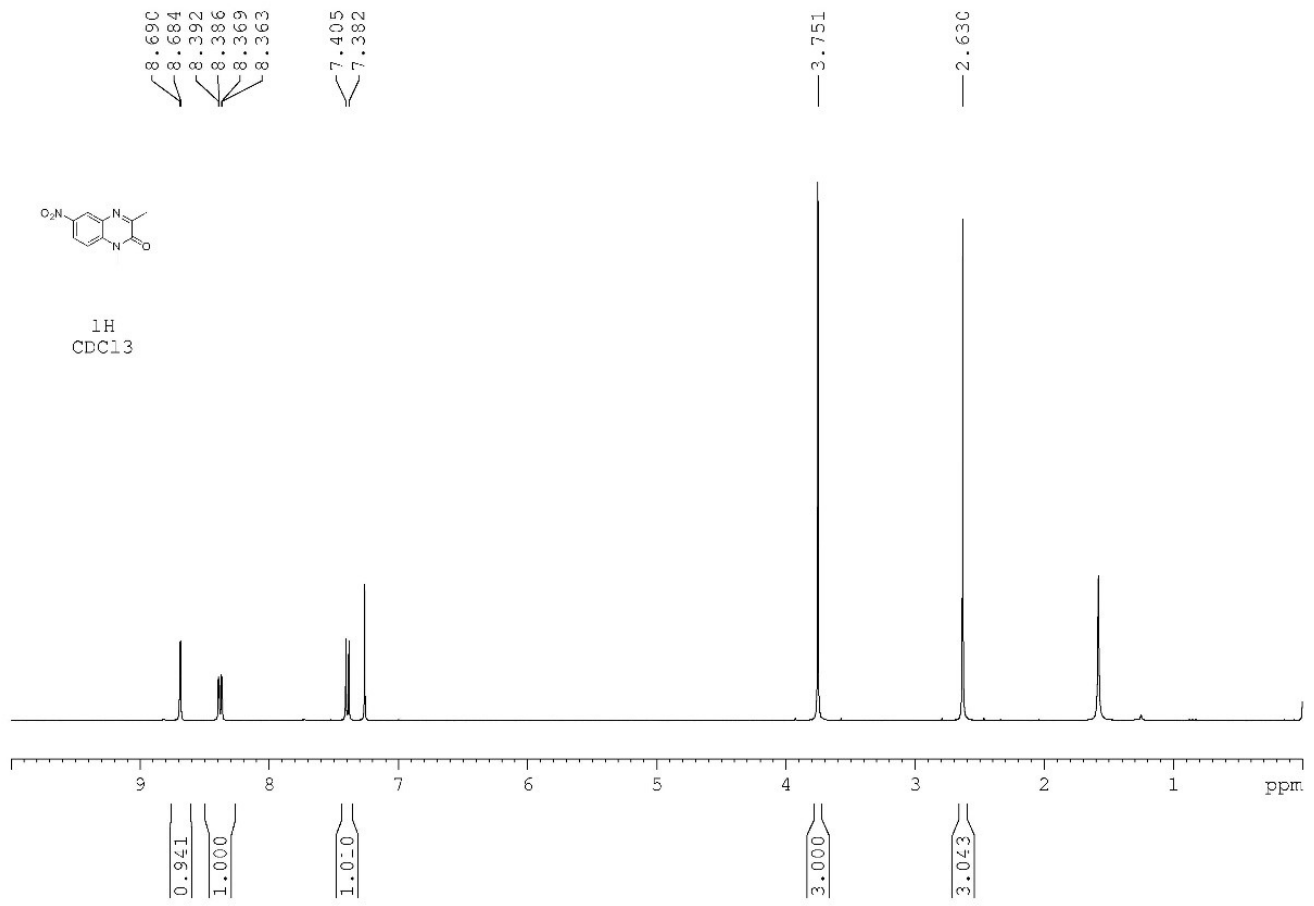
^{13}C NMR of compound **3l**



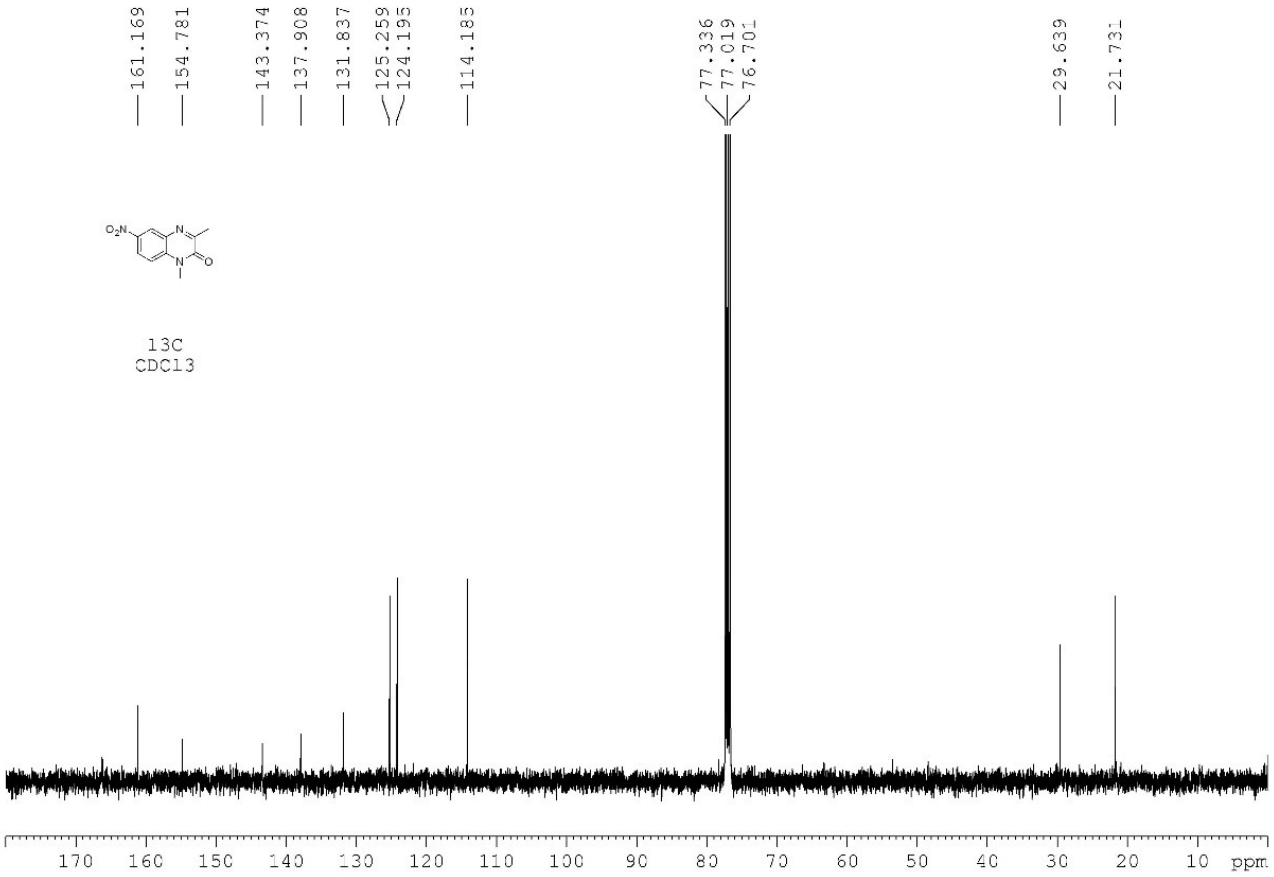
^{19}F NMR of compound **3l**



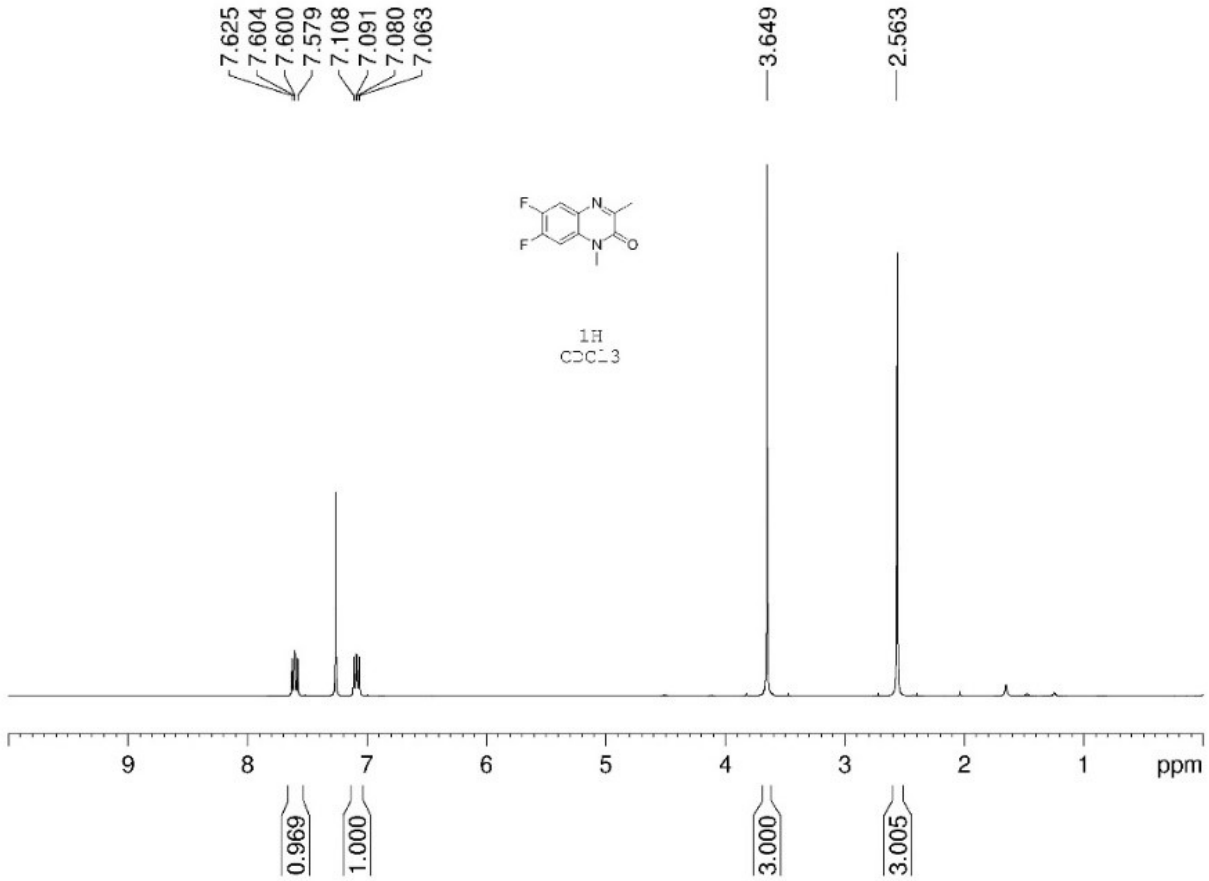
^{1}H NMR of compound **3m**



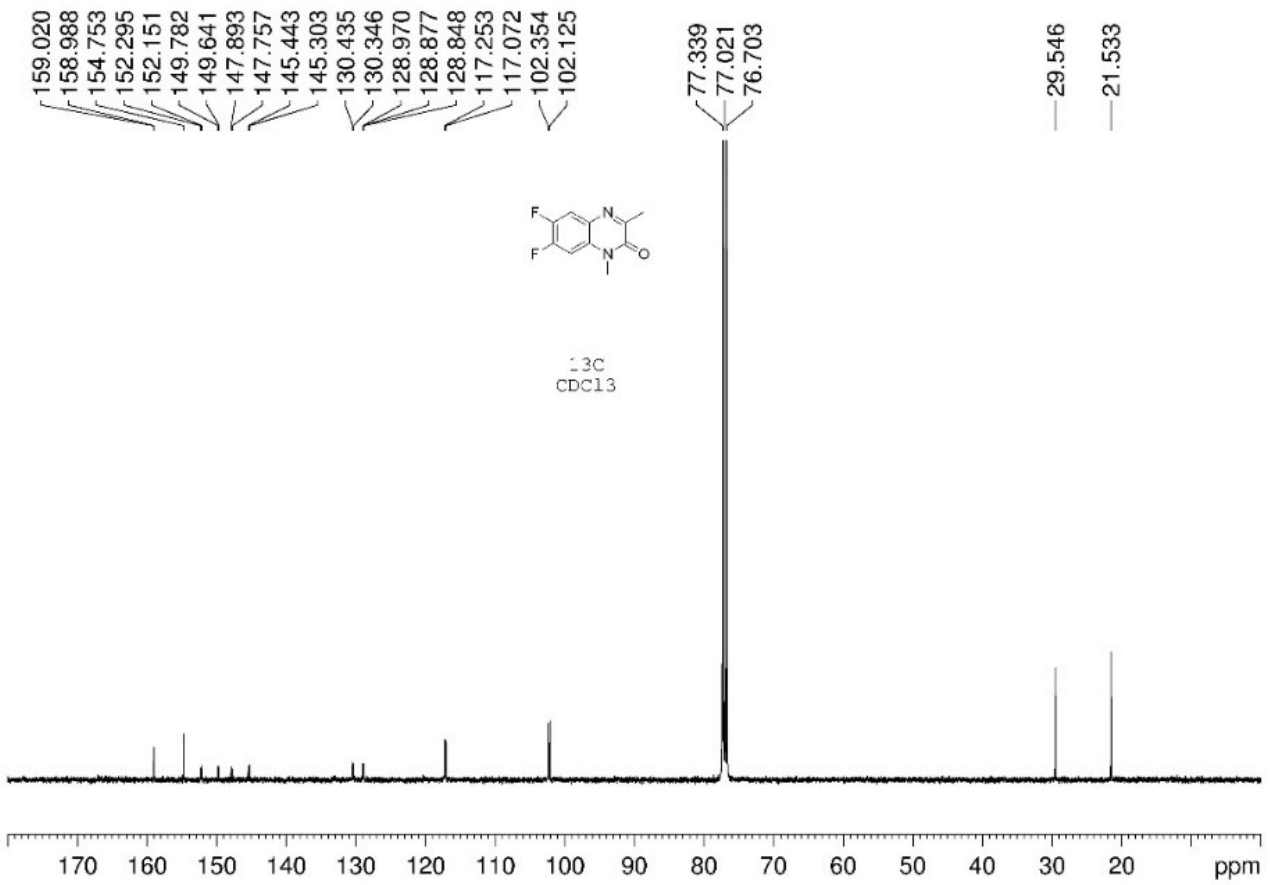
^{13}C NMR of compound **3m**



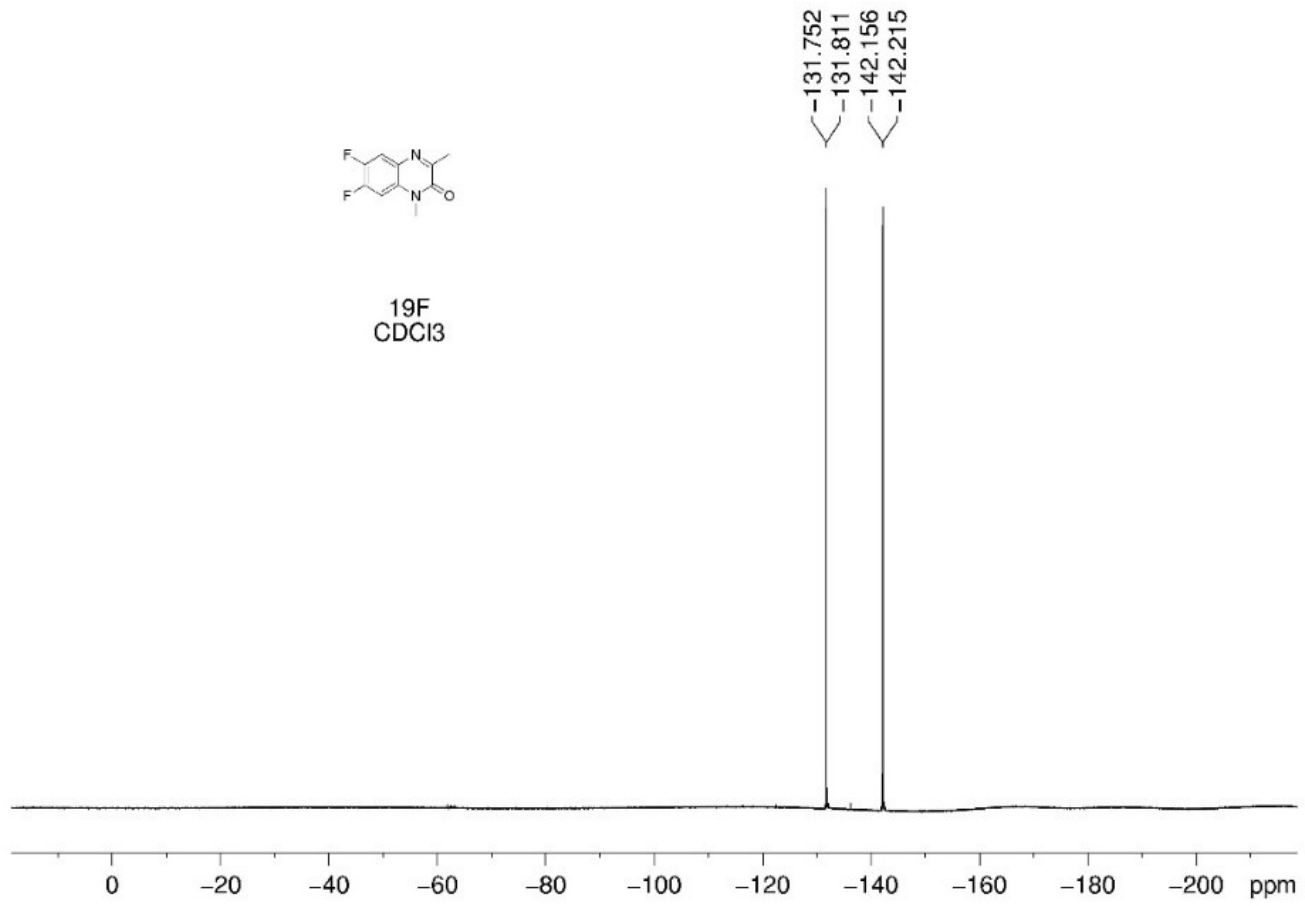
^{1}H NMR of compound **3n**



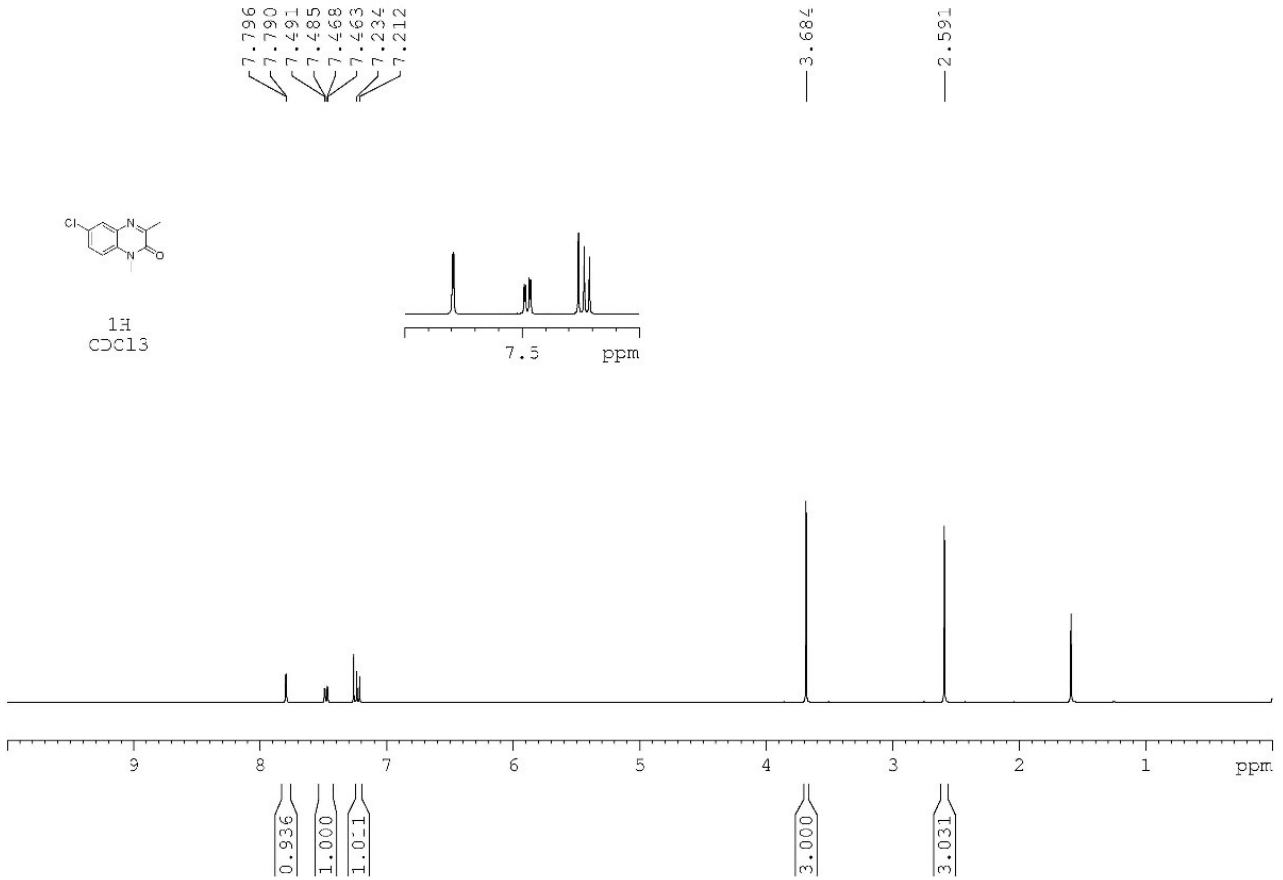
^{13}C NMR of compound **3n**



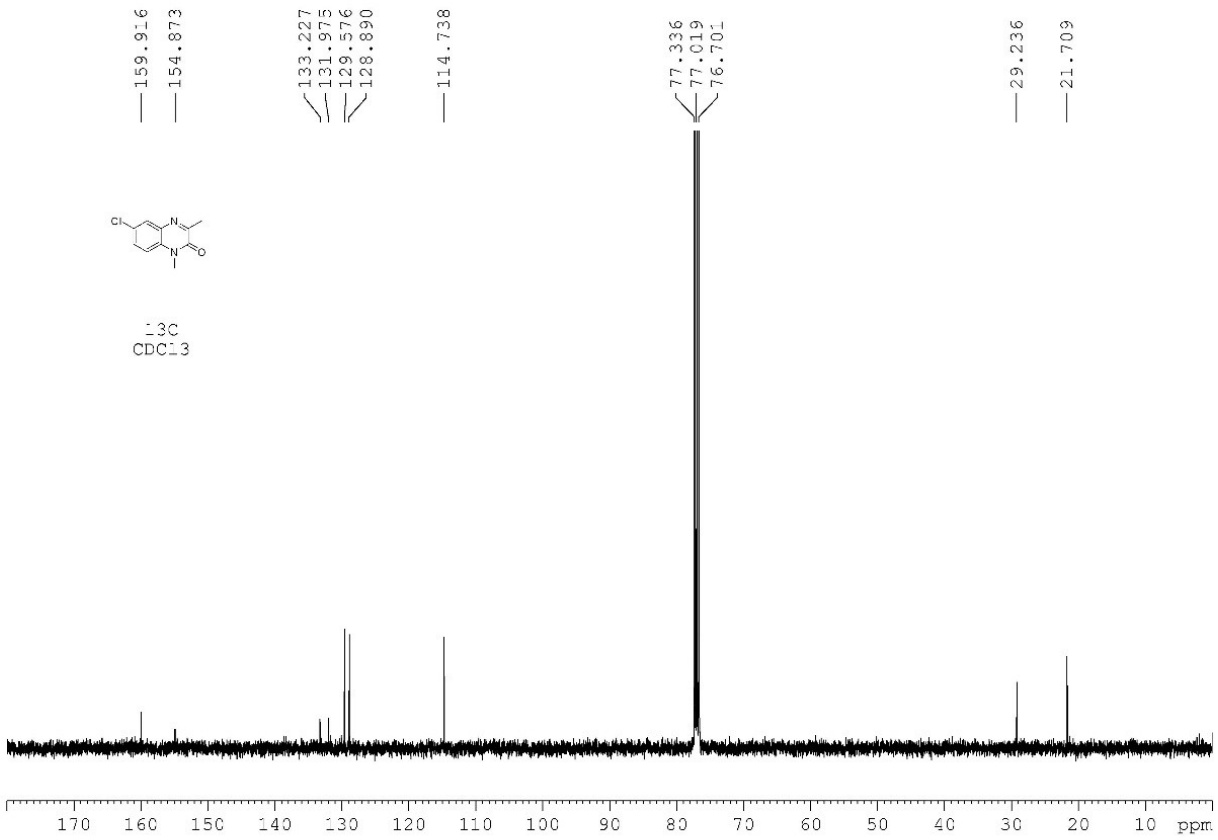
^{19}F NMR of compound **3n**



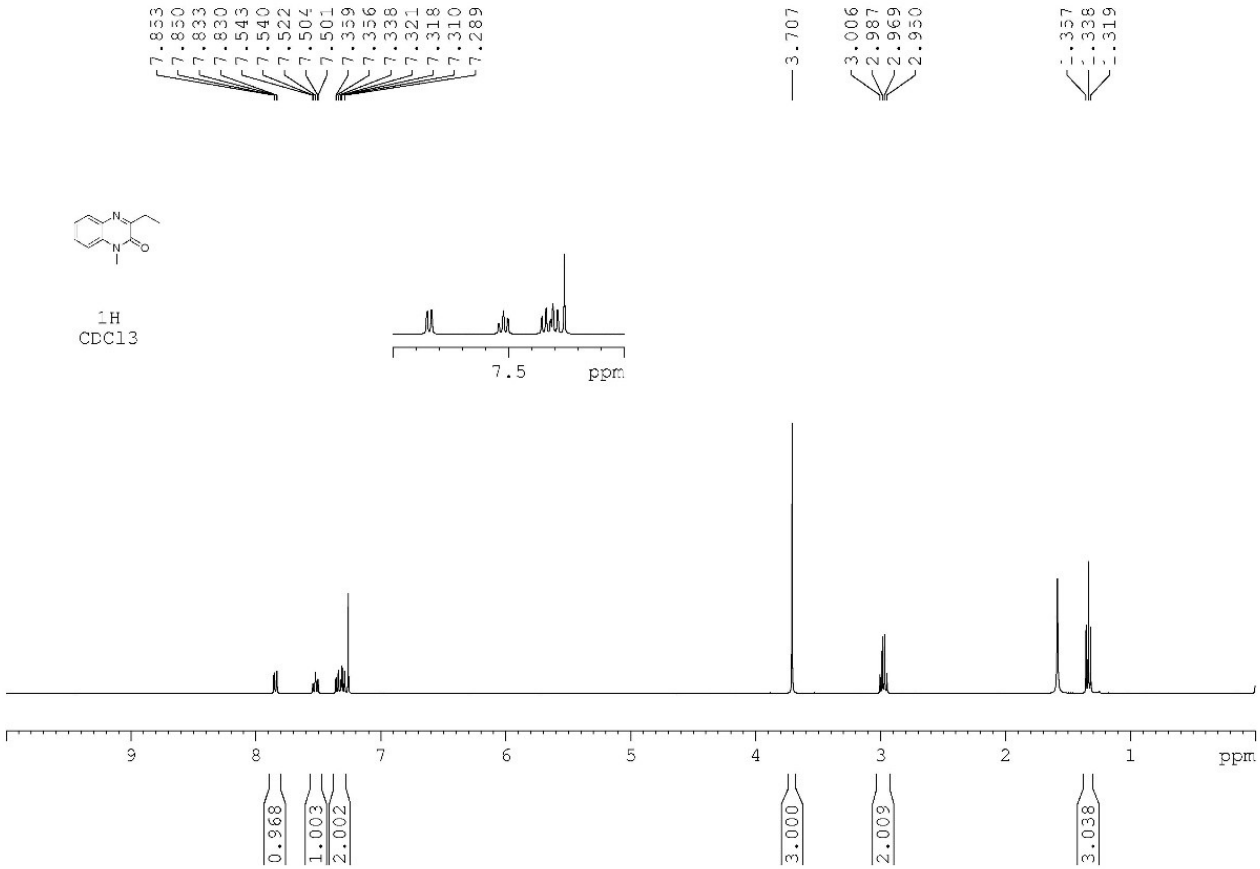
^{1}H NMR of compound **3o**



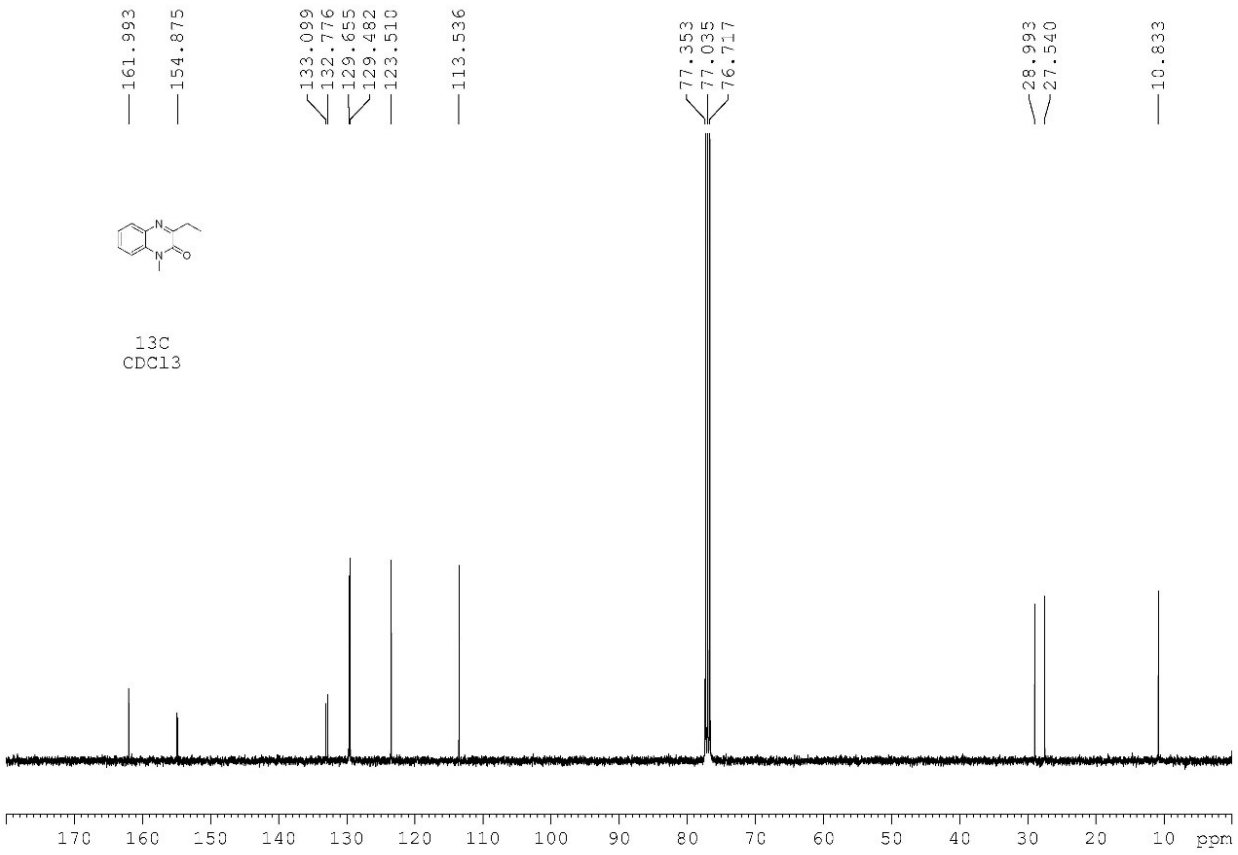
^{13}C NMR of compound **3o**



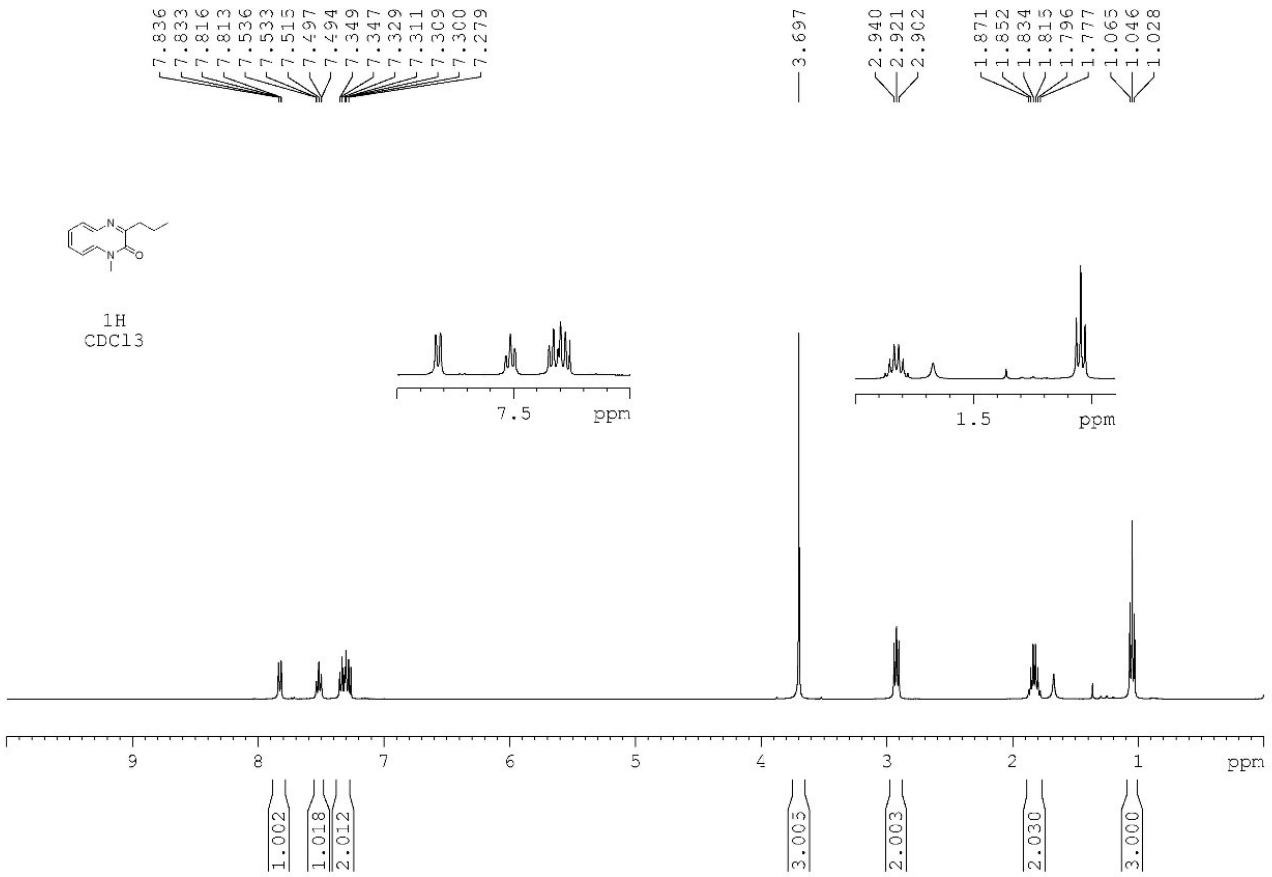
^{1}H NMR of compound **3p**



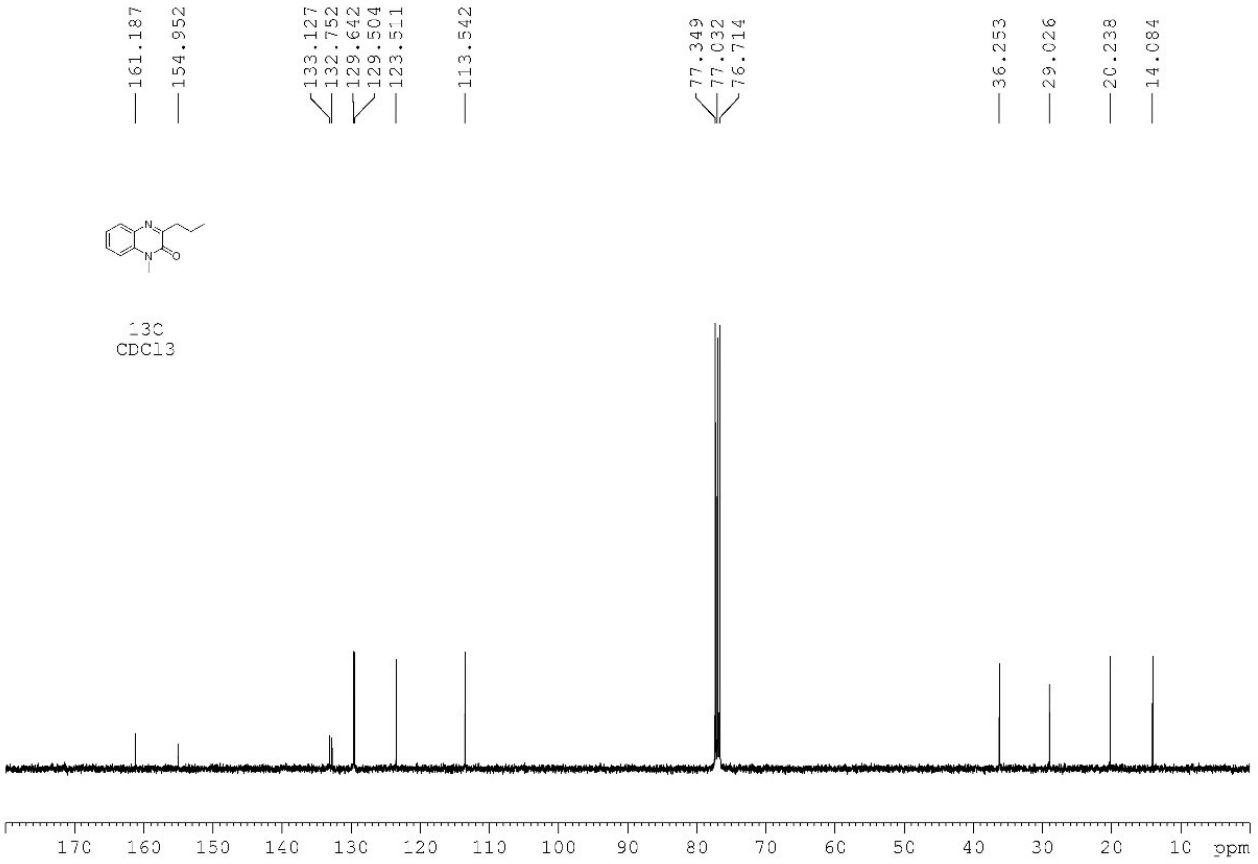
^{13}C NMR of compound **3p**



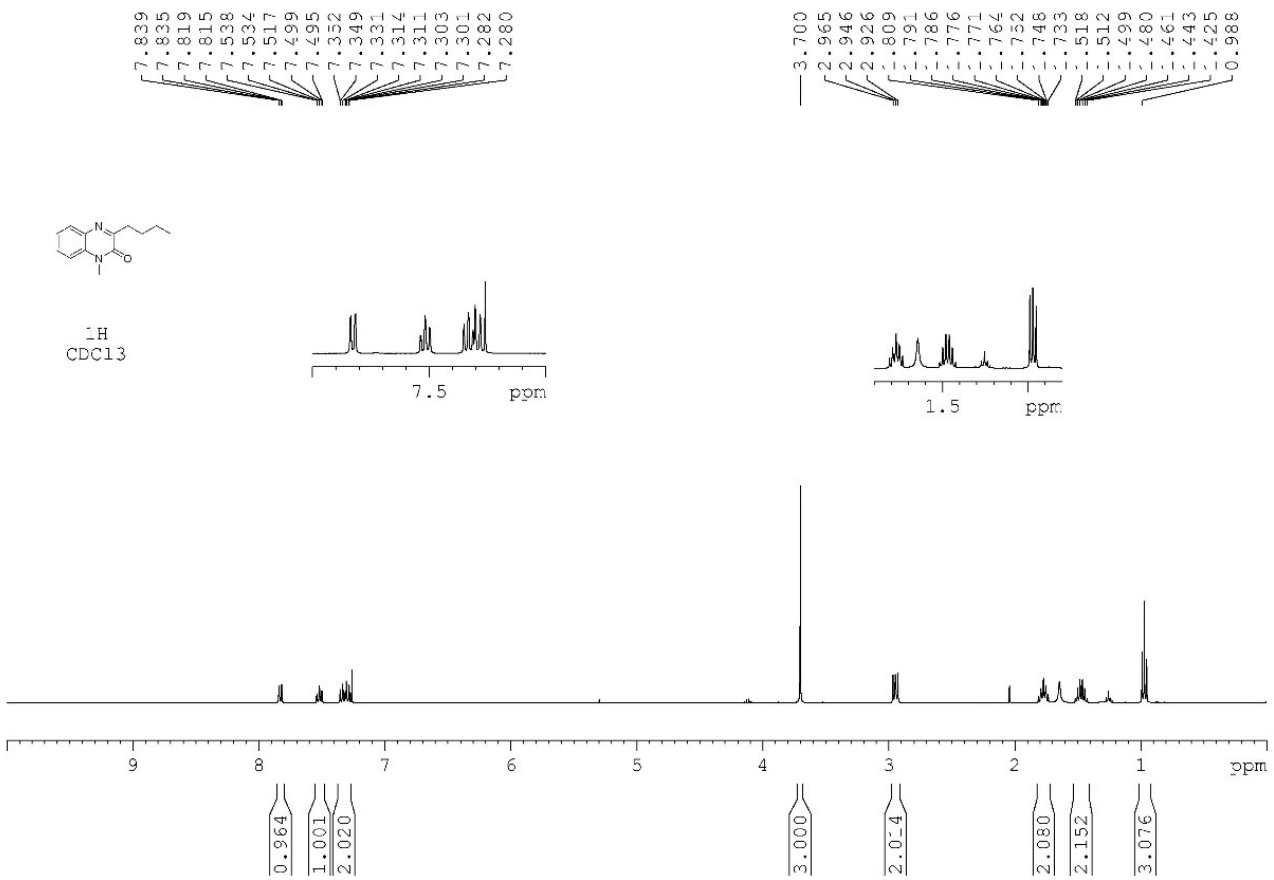
[1]H NMR of compound **3q**



^{13}C NMR of compound **3q**



^{1}H NMR of compound **3r**



^{13}C NMR of compound **3r**