Electronic Supplementary Material (ESI) for Chemical Communications.

Photoinduced Ligand to Metal Charge Transfer Enabling Cerium Mediated Decarboxylative Alkylation of Quinoxalin-2(1*H*)-ones

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1. General information

Commercial grade reagents, solvents, and starting materials were purchased of pure analytical grades and used as purchased without further purification, unless otherwise stated. Cerium salt is commercially available and used as purchased. Chromatographic purification of products was undertaken on silica gel (230-400 mesh) using a proper eluent system. For thin-layer chromatography (TLC) analysis throughout this work, Merck pre-coated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used and visualized with UV light and developed using ethanol solution of phosphomolybdic acid or basic aqueous potassium permanganate ($KMnO_4$) stain solutions. Organic solutions were concentrated under vacuum pressure using a rotary evaporator. The ^{1}H (400 MHz and 500 MHz) and ^{13}C (101 MHz and 126 MHz) nuclear magnetic resonance spectra were recorded on 400 MHz and 500 MHz spectrometers. Chemical shifts (δ) for ^{1}H and ^{13}C are reported in parts per million (ppm) relative to internal standard tetramethylsilane (tetramethylsilane @ 0 ppm) and residual solvent peak in the NMR solvent (for ^{1}H NMR (DMSO @ 2.50 ppm and $CHCl_3$ @ 7.26 ppm), for ^{13}C NMR (DMSO @ 39.52 ppm and $CHCl_3$ @ 77.16 ppm). Coupling constants are given in Hertz (Hz). The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; q, quartet; p, pentet; sept, septet; m, multiplet; br, broad signal. During the optimization yields were determined by Shimadzu, Nexis GC-2030 gas chromatography (GC) instrument using benzophenone as the internal standard. High-resolution mass spectra (HRMS) were recorded on a Mass Spectrometry Unit using electrospray ionization-time of flight (ESI-TOF) reflectron experiments. UV-Visible spectra were acquired on SHIMADZU-UV-2450 using HPLC grade acetonitrile as solvent. *In-situ* FTIR experiments was conducted using a Mettler-Toledo ReactIR 700 (SN: C049640472) equipped with a TEMCT detector, DiComp (Dimond) probe, with a 9.5mm x 2m AgX fiber interface. *We thank Central Research Facility, IIT Delhi for providing the access to in-situ FTIR facility*.

2. General procedures for the synthesis of starting Materials

The quinoxalin-2(1*H*)-ones derivatives were synthesized according to previously reported literature.[1] In a 100 mL round bottom flask, a mixture of 1,2-phenylenediamine derivatives (12 mmol, 1.0 eq) and ethyl glyoxalate (~50% in toluene, 28.8 mmol, 2.4 eq) in ethanol (40 mL) with a magnetic stirring bead was stirred at 55 °C until the raw material was consumed. Then, the mixture was filtered and washed thrice with distilled water. After that, the solid product was dried under reduced pressure to obtain the quinoxalin-2(1*H*)-one derivative. For the alkylation of quinoxalin-2(1*H*)-ones, a solution of quinoxalin-2(1*H*)-one derivatives (1.0 mmol, 1.0 eq) and potassium carbonate (1.2 eq) in DMSO (0.25 M) was added to a 50 mL round-bottomed flask followed by the addition of the corresponding alkyl halides (1.6 eq). The resultant solution was stirred overnight at room temperature. After the completion, the reaction mixture was extracted three times with saturated brine solution and EtOAc. Then, the organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in rotary evaporation. The resultant residue was purified by column chromatography to achieve the desired *N*-alkylation of quinoxalin-2(1*H*)-ones.

3. Reaction Set-up:

The photochemical reaction setup is shown in Figure S-01. The standard reactions were carried out under blue-violet light irradiation using a light setup (Kessil® PR160-427 nm lamp with a fan) with 100% intensity connected with a compact fan for maintaining ambient temperature. The approximate distance between the glass vial and the Kessel LED was measured to be 4 cm.

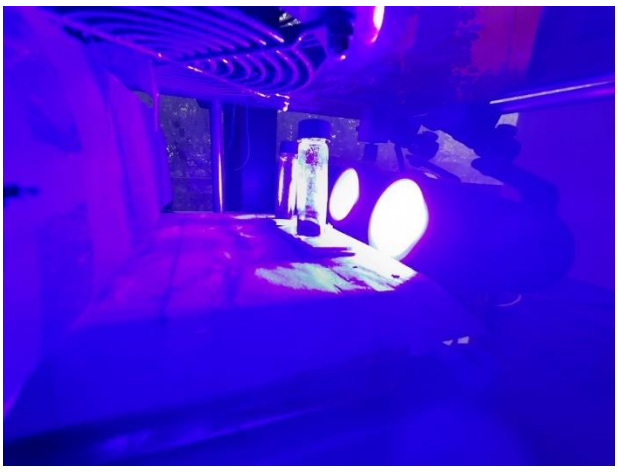
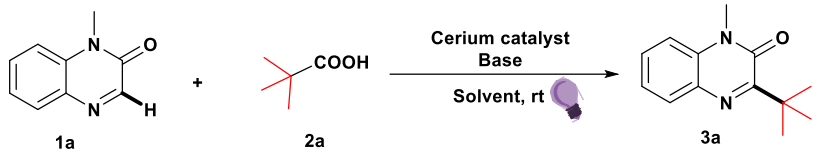


Figure S-01: Kessel light setup.

4. Optimization studies:

Table S1. Optimization of the reaction condition for the decarboxylative alkylation of quinoxalin-2(1*H*)-ones with alkyl carboxylic acids[a]



Entry	Catalyst	Base	Solvent	Yield[b] (%)
1	$CeCl_3$	Cs_2CO_3	CH_3CN	63
2	$CeCl_3$	K_2CO_3	CH_3CN	39
3	$CeCl_3$	K_3PO_4	CH_3CN	24
4	**$CeCl_3$**	**KO^{t}Bu**	**CH_3CN**	**92**
5	$Ce_2(SO_4)_3$	KO^{t}Bu	CH_3CN	trace
6	$Ce(SO_4)_2$	KO^{t}Bu	CH_3CN	trace
7	$(^nBu_4)_2CeCl_6$	KO^{t}Bu	CH_3CN	75
8	$CeCl_3{\cdot}7H_2O$	KO^{t}Bu	CH_3CN	42
9	$Ce(OAc)_3{\cdot}H_2O$	KO^{t}Bu	CH_3CN	24
10	$CeCl_3$	KO^{t}Bu	EtOAc	<10
11	$CeCl_3$	KO^{t}Bu	^{t}BuOH	18
12	$CeCl_3$	KO^{t}Bu	DCE	90
13[c]	$CeCl_3$	KO^{t}Bu	CH_3CN	45
14[d]	$CeCl_3$	KO^{t}Bu	CH_3CN	53
15[e]	-	KO^{t}Bu	CH_3CN	n.r.
16[f]	$CeCl_3$	KO^{t}Bu	CH_3CN	n.r.
17[g]	$CeCl_3$	KO^{t}Bu	CH_3CN	11

[a]Reaction conditions: Unless otherwise specified, quinoxalin-2(1*H*)-one (0.1 mmol), pivalic acid (0.2 mmol), $CeCl_3$ (10 mol%) and base (20 mol%) in 0.6 mL solvent irradiated with blue-violet LED (427 nm) for 24 h under aerobic conditions. [b]yields determined by gas chromatography using benzophenone as the internal standard. [c]5 mol% of $CeCl_3$ was used. [d]10 mol% of KO^{t}Bu was used. [e]In the absence of $CeCl_3$. [f]Reaction was performed under dark conditions. [g]Reaction was performed under nitrogen atmosphere using freeze pump thaw.

5. General procedure for photochemical alkylation:

In a glass vial having septum cap, magnetic stirring bead, $CeCl_3$ (10 mol%), KO^tBu (20 mol%), alkyl carboxylic acid (0.2 mmol) and quinoxalin-2(1*H*)-one (0.1 mmol) was added and then 0.6 mL of CH_3CN solvent was added. The reaction mixtures were irradiated with a Kessil® PR160-427 nm lamp with a cooling fan at a distance of 4 cm and stirred for 24 hours under aerobic conditions. After the completion, the reaction mixture was quenched with saturated $NaHCO_3$ solution and extracted with EtOAc. Then, the organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated in rotary evaporation. The resultant residue was purified by column chromatography using hexane/EtOAc to achieve the desired C-3 alkylation of quinoxalin-2(1*H*)-ones.

6. Characterization data of the synthesized compounds:

3-(*tert*-Butyl)-1-methylquinoxalin-2(1*H*)-one (3a):[2] yield 92% (19.9 mg); White solid, Hexane/EtOAc = 98/2, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.49-7.46 (m, 1H), 7.30-7.27 (m, 1H), 7.23 (d, *J* = 8.4 Hz, 1H) 3.65 (s, 3H), 1.49 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.3, 153.8, 133.4, 132.2, 130.2, 129.5, 123.2, 113.3, 39.5, 28.8, 28.0.

1-Methyl-3-(*tert*-pentyl)quinoxalin-2(1*H*)-one (3b): yield 65% (15.0 mg); Colourless liquid, Hexane/EtOAc = 98/2, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.52-7.48 (m, 1H), 7.33-7.25 (m, 2H), 3.67 (s, 3H), 2.05 (q, *J* = 7.5 Hz, 2H), 1.44 (s, 6H), 0.76 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.9, 153.9, 133.4, 132.4, 130.3, 129.6, 123.2, 113.4, 43.2, 32.5, 28.9, 26.0, 9.6. **HRMS-ESI:** calcd for $C_{14}H_{19}N_2O$ $[M+H]^+$ 231.1492, found 231.1492. **FT-IR** ν (cm^{-1}): 2961,2924, 2852, 1646, 1590, 1454, 1315, 1156, 1080.

1-Methyl-3-(1-methylcyclohexyl)quinoxalin-2(1*H*)-one (3c):[3] yield 75% (19.2 mg); White solid, Hexane/EtOAc = 98/2, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.9 Hz, 1H), 7.51-7.47 (m, 1H), 7.32-7.25 (m, 2H), 3.66 (s, 3H), 2.48-2.42 (m, 2H), 1.67-1.42 (m, 8H), 1.42 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.8, 153.8, 133.2, 132.4, 130.2, 129.6, 123.2, 113.3, 43.1, 35.8, 28.9, 26.7, 24.6, 23.0.

3-(Adamantan-1-yl)-1-methylquinoxalin-2(1*H*)-one (3d):[4] yield 76% (22.4 mg); White solid, Hexane/EtOAc = 98/2, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.51-7.47 (m, 1H), 7.32-7.25 (m, 2H), 3.66 (s, 3H), 2.24 (s, 6H), 2.11 (s, 3H), 1.85-1.77 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.9, 153.8, 133.2, 132.6, 130.2, 129.6, 123.3, 113.4, 42.1, 39.0, 37.1, 28.8, 28.7.

3-Isopropyl-1-methylquinoxalin-2(1*H*)-one (3e):[5] yield 81% (16.4 mg); Yellow solid, Hexane/EtOAc = 98/2, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.53-7.49 (m, 1H), 7.34-7.27 (m, 2H), 3.70 (s, 3H), 3.70-3.60 (m, 1H), 1.32 (d, *J* = 6.8 Hz, 6H). **^{13}C**

NMR (126 MHz, $CDCl_3$) δ 165.1, 154.6, 133.1, 132.9, 129.9, 129.6, 123.5, 113.6, 31.3, 29.1, 20.3.

1-Methyl-3-(pentan-3-yl)quinoxalin-2(1*H*)-one (3f):[3] yield 61% (14.0 mg); Yellow liquid, Hexane/EtOAc = 98/2, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.53-7.49 (m, 1H), 7.34-7.26 (m, 2H), 3.70 (s, 3H), 3.38-3.31 (m, 1H), 1.91-1.82 (m, 2H), 1.75-1.64 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.0, 155.2, 133.0, 132.9, 130.0, 129.6, 123.5, 113.6, 44.8, 29.2, 25.9, 12.1.

1-Methyl-3-(1-phenylpropyl)quinoxalin-2(1*H*)-one (3g): yield 52% (14.5 mg); White solid, Hexane/EtOAc = 98/2, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.44-7.36 (m, 3H), 7.27-7.23 (m, 1H), 7.20-7.14 (m, 3H), 7.11-7.07 (m, 1H), 4.51 (t, *J* = 7.7 Hz, 1H), 3.53 (s, 3H), 2.27-2.20 (m, 1H), 2.05-1.96 (m, 1H), 0.84 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.5, 154.8, 141.7, 133.1, 132.9, 130.2, 129.8, 128.8, 128.4, 126.7, 123.5, 113.6, 49.3, 29.2, 27.2, 12.6. **HRMS-ESI:** calcd for $C_{18}H_{19}N_2O$ $[M+H]^+$ 279.1492, found 279.1504. **m.p:** 120 °C; **FT-IR** ν (cm^{-1}): 2961,2922, 2852, 1645,1595, 1462, 1247, 1180, 1087.

3-Cyclobutyl-1-methylquinoxalin-2(1*H*)-one (3h):[6] yield 44% (9.4 mg); White solid, Hexane/EtOAc = 98/2, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.53-7.49 (m, 1H), 7.35-7.31 (m, 1H), 7.28 (dd, J = 8.5, 1.0 Hz, 1H), 4.11-4.02 (m, 1H), 3.68 (s, 3H), 2.47-2.37 (m, 4H), 2.17-2.08 (m, 1H), 1.95-1.87 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.3, 154.7, 133.1, 133.0, 129.9, 129.5, 123.6, 113.6, 38.4, 29.0, 26.4, 18.3.

3-Cyclopentyl-1-methylquinoxalin-2(*1H*)-one (3i):[3] yield 72% (16.4 mg); White solid, Hexane/EtOAc = 98/2, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.52-7.47 (m, 1H), 7.33-7.26 (m, 2H), 3.76-3.67 (m, 4H), 2.11-2.03 (m, 2H), 1.97-1.88 (m, 2H), 1.86-1.78 (m, 2H), 1.75-1.68 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.8, 155.1, 133.1, 132.9, 129.9, 129.4, 123.5, 113.5, 42.8, 31.0, 29.1, 26.1.

3-Cyclohexyl-1-methylquinoxalin-2(1*H*)-one (3j):[1] yield 85% (20.6 mg); White solid, Hexane/EtOAc = 98/2, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.52-7.48 (m, 1H), 7.32 (td, *J* = 8.2, 1.1 Hz, 1H), 7.28 (d, *J* = 8.3 Hz, 1H), 3.69 (s, 3H), 3.36-3.31 (m, 1H), 1.96-1.94 (m, 2H), 1.88-1.84 (m, 2H), 1.78-1.74 (m, 1H), 1.61-1.53 (m, 2H), 1.51-1.42 (m, 2H), 1.35-1.27 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.4, 154.7, 133.0, 133.0, 129.9, 129.5, 123.5, 113.6, 40.9, 30.6, 29.2, 26.4, 26.3.

3-Cycloheptyl-1-methylquinoxalin-2(1*H*)-one (3k): yield 56% (14.4 mg); White solid, Hexane/EtOAc = 98/2, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 1H), 3.68 (s, 3H), 3.51-3.46 (m, 1H),

1.99-1.95 (m, 2H), 1.86-1.76 (m, 4H), 1.71-1.69 (m, 2H), 1.65-1.59 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.4, 154.5, 132.9, 132.8, 129.8, 129.3, 123.4, 113.5, 42.5, 32.3, 29.1, 28.2, 27.2. **HRMS-ESI:** calcd for $C_{16}H_{21}N_2O$ $[M+H]^+$ 257.1648, found 257.1648. **m.p:** 96 °C; **FT-IR** ν (cm^{-1}): 2915, 2852, 1644, 1595, 1464, 1309, 1185, 1091.

***tert*-Butyl (1-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)ethyl)carbamate (3l):**[6] yield 72% (21.8 mg); White solid, Hexane/EtOAc = 92/8, **^{1}H NMR** (500 MHz, DMSO-d6) δ 7.78 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.64-7.61 (m, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.40-7.36 (m, 1H), 7.08 (d, *J* = 7.7 Hz, 1H), 5.03-4.97 (m, 1H), 3.64 (s, 3H), 1.36 (s, 9H), 1.32 (d, 3H). **^{13}C NMR** (126 MHz, DMSO-d6) δ 160.0, 154.9, 153.2, 133.0, 131.6, 130.1, 128.9, 123.5, 114.7, 77.8, 47.6, 28.8, 28.2, 18.4.

***tert*-Butyl (1-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-2-phenylethyl)carbamate (3m):**[7] yield 65% (24.7 mg); Yellow solid, Hexane/EtOAc = 92/8, **^{1}H NMR** (500 MHz, DMSO-d6) δ 7.77 (d, *J* = 7.7 Hz, 1H), 7.65-7.61 (m, 1H), 7.57 (d, *J* = 8.1 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.31-7.25 (m, 4H), 7.17 (dd, *J* = 17.4, 7.9 Hz, 2H), 5.15 (td, *J* = 9.3, 3.6 Hz, 1H), 3.66 (s, 3H), 3.12 (dd, *J* = 13.6, 3.4 Hz, 1H), 2.79 (dd, *J* = 13.5, 9.8 Hz, 1H), 1.29 (s, 9H). **^{13}C NMR** (126 MHz, DMSO-d6) δ 159.1, 155.3, 153.4, 138.8, 133.1, 131.6, 130.3, 129.2, 128.9, 128.1, 126.2, 123.6, 114.8, 77.9, 54.1, 37.3, 28.9, 28.2.

1-Methyl-3-(tetrahydrofuran-2-yl)quinoxalin-2(1*H*)-one (3n):[1] yield 58% (13.4 mg); Yellow liquid, Hexane/EtOAc = 94/6, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.53 (ddd, *J* = 8.6, 7.4, 1.5 Hz, 1H), 7.35-7.29 (m, 2H), 5.39-5.36 (m, 1H), 4.25-4.19 (m, 1H), 4.03-3.97 (m, 1H), 3.69 (s, 3H), 2.53-2.43 (m, 1H), 2.05-2.01 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.6, 154.2, 133.3, 132.6, 130.6, 130.3, 123.8, 113.6, 77.7, 69.3, 30.6, 28.9, 25.7.

3-Ethyl-1-methylquinoxalin-2(1*H*)-one (3o):[4] yield 42% (7.9 mg); White solid, Hexane/EtOAc = 98/2, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.53-7.49 (m, 1H), 7.35-7.28 (m, 2H), 3.69 (s, 3H), 2.97 (q, *J* = 7.4 Hz, 2H), 1.33 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.1, 155.0, 133.2, 132.9, 129.8, 129.6, 123.6, 113.6, 29.1, 27.6, 10.9.

1-Methyl-3-propylquinoxalin-2(1*H*)-one (3p):[8] yield 45% (9.1 mg); White solid, Hexane/EtOAc = 98/2, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.53-7.49 (m, 1H), 7.35-7.28 (m, 2H), 3.70 (s, 3H), 2.92 (t, *J* = 7.5 Hz, 2H), 1.87-1.78 (m, 2H), 1.05 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.3, 155.1, 133.2, 132.9, 129.8, 129.6, 123.6, 113.7, 36.4, 29.2, 20.4, 14.2.

3-Benzyl-1-methylquinoxalin-2(1*H*)-one (3q):[1] yield 35% (8.8 mg); Yellow solid, Hexane/EtOAc = 98/2, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.52-7.47 (m, 3H), 7.34-7.26 (m, 3H), 7.25-7.19 (m, 2H), 4.27 (s, 2H), 3.65 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.4, 154.8, 137.2, 133.4, 132.8, 130.0, 130.0, 129.6, 128.5, 126.7, 123.7, 113.6, 40.9, 29.2.

1-Methyl-3-phenethylquinoxalin-2(1*H*)-one (3r):[5] yield 52% (13.7 mg); Yellow solid, Hexane/EtOAc = 98/2, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.55-7.51 (m, 1H), 7.37-7.26 (m, 6H), 7.21-7.17 (m, 1H), 3.71 (s, 3H), 3.29-3.25 (m, 2H), 3.15-3.11 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.2, 155.0, 141.8, 133.3, 132.8, 129.8, 129.8, 128.7, 128.5, 126.1, 123.7, 113.7, 36.1, 32.6, 29.2.

3-(5-(2,5-Dimethylphenoxy)-2-methylpentan-2-yl)-1-methylquinoxalin-2(1*H*)-one (3s):[4] yield 45% (14.4 mg); Yellow liquid, Hexane/EtOAc = 97/3, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.50 (ddd, *J* = 8.5, 7.3, 1.5 Hz, 1H), 7.32-7.29 (m, 1H), 7.25-7.23 (m, 1H), 6.96 (d, *J* = 7.4 Hz, 1H), 6.60 (d, *J* = 7.5 Hz, 1H), 6.53 (s, 1H), 3.87 (t, *J* = 6.7 Hz, 2H), 3.63 (s, 3H), 2.24 (s, 3H), 2.20-2.17 (m, 2H), 2.15 (s, 3H), 1.70-1.64 (m, 2H), 1.50 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.5, 157.1, 153.8, 136.5, 133.4, 132.3, 130.3, 129.7, 123.7, 123.3, 120.6, 113.4, 112.0, 68.2, 42.7, 36.1, 28.9, 26.4, 25.5, 21.5, 15.9.

3-(But-3-en-1-yl)-1-methylquinoxalin-2(1*H*)-one (3t):[11] yield 75% (16 mg); Yellow solid, Hexane/EtOAc = 97/3, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.59 – 7.47 (m, 1H), 7.36 – 7.28 (m, 2H), 6.03 – 5.86 (m, 1H), 5.11 (dd, *J* = 17.1, 1.5 Hz, 1H), 4.99 (d, *J* = 10.2 Hz, 1H), 3.70 (s, 3H), 3.11 – 2.98 (m, 2H), 2.57 (dd, *J* = 14.5, 7.5 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.4, 155.0, 137.8, 133.2, 132.8, 129.8, 129.7, 123.7, 115.3, 113.7, 33.6, 30.7, 29.1.

3-(1-(4-*iso*-Butylphenyl)ethyl)-1-methylquinoxalin-2(1*H*)-one (3u):[5] yield 82% (29.9 mg); Yellow liquid, Hexane/EtOAc = 97/3, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.51-7.48 (m, 1H), 7.35-7.32 (m, 3H), 7.25-7.23 (m, 1H), 7.04 (d, *J* = 8.1 Hz, 2H), 4.81 (q, *J* = 7.1 Hz, 1H), 3.62 (s, 3H), 2.40 (d, *J* = 7.2 Hz, 2H), 1.85-1.77 (m, 1H), 1.67 (d, *J* = 7.1 Hz, 3H), 0.87 (d, *J* = 6.6 Hz, 3H), 0.86 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.3, 154.6, 140.4, 140.0, 133.2, 132.9, 130.2, 129.7, 129.2, 128.0, 123.5, 113.6, 45.2, 41.5, 30.3, 29.2, 22.6, 22.6, 19.8.

1-Methyl-3-(2-(4-chlorophenoxy)propan-2-yl)-quinoxalin-2(1*H*)-one (3v): yield 80% (26.3 mg); white solid, Hexane/EtOAc = 97/3, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.62 – 7.55 (m, 1H), 7.38 – 7.30 (m, 2H), 7.11 – 7.06 (m, 2H), 6.84 – 6.79 (m, 2H),

3.69 (s, 3H), 1.87 (s, 6H). **^{13}C NMR** δ 159.8, 154.8, 153.0, 133.9, 131.8, 130.9, 130.8, 128.9, 126.8, 123.6, 121.9, 113.7, 82.7, 29.1, 26.13. **HRMS-ESI:** calcd for $C_{18}H_{17}ClN_2O_2$ $[M+Na]^+$, 351.0864 found 351.0871.

1-Methyl-3-phenylquinoxalin-2(1*H*)-one (3w):[12] yield 38% (8.8 mg); white solid, Hexane/EtOAc = 97/3, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33 – 8.27 (m, 2H), 7.99 – 7.92 (m, 1H), 7.61 – 7.54 (m, 1H), 7.51 – 7.46 (m, 3H), 7.41 – 7.32 (m, 2H), 3.78 (s, 3H). δ **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.8, 154.3, 136.2, 133.5, 133.2, 130.6, 130.4, 129.6, 128.2, 123.8, 113.7, 29.4.

3-(*tert*-Butyl)quinoxalin-2(1*H*)-one (4a):[2] yield 52% (10.5 mg); White solid, Hexane/EtOAc = 98/2, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 12.71 (s, 1H), 7.84 (dd, *J* = 7.3, 1.0 Hz, 1H), 7.50-7.47 (m, 1H), 7.34-7.30 (m, 2H), 1.56 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.9, 156.3, 132.5, 131.5, 129.8, 129.3, 123.9, 115.2, 39.4, 28.0.

3-(*tert*-Butyl)-1-(cyclopropylmethyl)quinoxalin-2(1*H*)-one (4b):[2] yield 86% (22.0 mg); Yellow solid, Hexane/EtOAc = 98/2, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.51-7.47 (m, 1H), 7.38 (d, *J* = 8.3 Hz, 1H), 7.31-7.28 (m, 1H), 4.19 (d, *J* = 7.0 Hz, 2H), 1.48 (s, 9H), 1.29-1.24 (m, 1H), 0.55-0.52 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.6, 153.8, 132.9, 132.6, 130.5, 129.5, 123.1, 113.7, 45.7, 39.6, 28.0, 27.2, 9.8, 4.2.

1-Benzyl-3-(*tert*-butyl)quinoxalin-2(1*H*)-one (4c):[8] yield 98% (28.6 mg); Yellow liquid, Hexane/EtOAc = 98/2, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.9 Hz, 1H), 7.38-7.18 (m, 8H), 5.48 (s, 2H), 1.53 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.6, 153.8, 135.8, 132.8, 132.6, 130.4, 129.6, 129.0, 127.7, 126.9, 123.4, 114.2, 45.7, 39.7, 28.1.

3-(*tert*-Butyl)-1-(2-oxo-2-phenylethyl)quinoxalin-2(1*H*)-one (4d): yield 64% (20.5 mg); White solid, Hexane/EtOAc = 98/2, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05-8.03 (m, 2H), 7.99-7.96 (m, 1H), 7.65-7.62 (m, 2H), 7.55-7.50 (m, 4H), 5.83 (s, 2H), 1.59 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 193.6, 156.1, 154.7, 139.0, 138.6, 135.0, 133.8, 129.0, 129.0, 128.9, 128.0, 126.6, 126.4, 67.6, 38.4, 28.3. **HRMS-ESI:** calcd for $C_{20}H_{21}N_2O_2$ $[M+H]^+$ 321.1598, found 321.1606. **m.p:** 76 °C. **FT-IR** ν (cm^{-1}): 2961, 2923, 1700, 1399, 1323, 1215, 1138, 1090.

Ethyl 2-(3-(*tert*-butyl)-2-oxoquinoxalin-1(2*H*)-yl)acetate (4e):[2] yield 85% (24.5 mg); White solid, Hexane/EtOAc = 98/2, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.48-7.44 (m, 1H), 7.33-7.29 (m, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 4.99 (s, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.48 (s, 9H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.5, 165.3, 153.4, 132.7, 132.4, 130.6, 129.8, 123.6, 112.8, 62.0, 43.4, 39.6, 28.0, 14.2.

1-Allyl-3-(*tert*-butyl)quinoxalin-2(1*H*)-one (4f): yield 82% (19.9 mg); Colourless liquid, Hexane/EtOAc = 98/2, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.9 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.31-7.23 (m, 2H), 5.94 (ddd, *J* = 15.7, 10.2, 5.0 Hz, 1H), 5.25 (d, *J* = 10.4 Hz, 1H), 5.14 (d, *J* = 17.3 Hz, 1H), 4.88 (d, *J* = 4.6 Hz, 2H), 1.49 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.5, 153.3, 132.7, 132.5, 131.2, 130.3, 129.5, 123.3, 117.8, 113.9, 44.3, 39.6, 28.0. **HRMS-ESI:** calcd for $C_{15}H_{19}N_2O$ $[M+H]^+$ 243.1492, found 243.1490. **FT-IR** ν (cm^{-1}): 2955, 2950, 1650, 1597, 1459, 1358, 1309, 1150, 1085.

3-(*tert*-Butyl)-1-(prop-2-yn-1-yl)quinoxalin-2(1*H*)-one (4g):[8] yield 90% (21.6 mg); Colourless liquid, Hexane/EtOAc = 98/2, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.53 (ddd, *J* = 8.6, 7.4, 1.4 Hz, 1H), 7.42-7.41 (m, 1H), 7.35-7.32 (m, 1H), 5.03 (d, *J* = 2.5 Hz, 2H), 2.27 (t, *J* = 2.5 Hz, 1H), 1.48 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.4, 152.7, 132.5, 132.0, 130.4, 129.7, 123.7, 113.9, 77.4, 73.0, 39.7, 31.3, 28.0.

3-(*tert*-Butyl)-6-fluoro-1-methylquinoxalin-2(1*H*)-one (4h):[8] yield 96% (22.5 mg); White solid, Hexane/EtOAc = 98/2, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 8.8, 2.6 Hz, 1H), 7.26-7.21 (m, 2H), 3.67 (s, 3H), 1.48 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.0, 158.7 (d, J_{C-F} = 242.6 Hz), 153.5, 132.9 (d, J_{C-F} = 11.3 Hz), 130.2 (d, J_{C-F} = 1.1 Hz), 117.3 (d, J_{C-F} = 24.1 Hz), 115.6 (d, J_{C-F} = 22.4 Hz), 114.4 (d, J_{C-F} = 8.7 Hz). 39.8, 29.2, 28.0. **HRMS-ESI:** calcd for $C_{13}H_{16}FN_2O$ $[M+H]^+$ 235.1241, found 235.1270. **m.p:** 96 °C; **FT-IR** ν (cm^{-1}): 2919, 2853, 1641, 1591, 1455, 1309, 1268, 1156, 1084.

6-Bromo-3-(*tert*-butyl)-1,8-dimethylquinoxalin-2(1*H*)-one (4i): yield 98% (30.3 mg); White solid, Hexane/EtOAc = 98/2, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 1.1 Hz, 1H), 7.25 (d, *J* = 1.8 Hz, 1H), 3.61 (s, 3H), 2.63 (s, 3H), 1.47 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.9, 153.5, 140.9, 134.5, 129.5, 127.6, 123.2, 114.3, 40.1, 29.1, 27.9, 17.3. **HRMS-ESI:** calcd for $C_{14}H_{18}BrN_2O$ $[M+H]^+$ 309.0597, found 309.0592. **m.p:** 158 °C; **FT-IR** ν (cm^{-1}): 2920, 1643, 1582, 1447, 1306, 1101, 1016.

3-(*tert*-Butyl)-1-isopropyl-6,7-dimethylquinoxalin-2(1*H*)-one (4j): yield 45% (12.2 mg); Colourless liquid, Hexane/EtOAc = 98/2, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.51 (s, 1H), 5.59 (dd, *J* = 12.3, 6.1 Hz, 1H), 2.42 (s, 3H), 2.41 (s, 3H), 1.48 (s, 9H), 1.45 (s, 3H), 1.44 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.4, 155.2, 138.7, 138.2, 136.6, 135.5, 128.3, 125.9, 68.5, 38.2, 28.4, 22.1, 20.3, 19.9. **HRMS-ESI:** calcd for $C_{17}H_{25}N_2O$ $[M+H]^+$ 273.1961, found 273.1967. **FT-IR** ν (cm^{-1}): 2973, 2926, 1570, 1406, 1308, 1262, 1222, 1179, 1095.

3-(*tert*-Butyl)-6,7-dichloro-1-ethylquinoxalin-2(1*H*)-one (4k): yield 85% (24.2 mg); Colourless liquid, Hexane/EtOAc = 98/2, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.85 (s, 1H), 4.55 (q, *J* = 7.1 Hz, 2H), 1.50 (t, *J* = 7.1 Hz, 3H), 1.47 (s, 9H). **^{13}C NMR** (126 MHz,

$CDCl_3$) δ 157.8, 156.6, 138.8, 137.0, 132.9, 129.9, 129.6, 127.2, 62.6, 38.6, 28.2, 14.5. **HRMS-ESI:** calcd for $C_{14}H_{17}Cl_2N_2O$ $[M+H]^+$ 299.0712, found 299.0718. **FT-IR** ν (cm^{-1}): 2972, 2930, 1658, 1576, 1459,1415, 1388, 1311, 1200,1111, 1089.

6,7-Dibromo-3-(*tert*-butyl)-1-methylquinoxalin-2(1*H*)-one (4l): yield 90% (33.7 mg); White solid, Hexane/EtOAc = 98/2, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.52 (s, 1H), 3.61 (s, 3H), 1.45 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.3, 153.2, 134.2, 133.5, 132.1, 125.7, 118.3, 118.0, 39.9, 29.1, 27.9. **HRMS-ESI:** calcd for $C_{13}H_{15}Br_2N_2O$ $[M+H]^+$ 372.9546, found 372.9555. **m.p:** 142 °C; **FT-IR** ν (cm^{-1}): 2966, 2924, 1651, 1582, 1454, 1299, 1151, 1085.

3-(*tert*-Butyl)-1-(2-hydroxyethyl)quinoxalin-2(1*H*)-one (4m): yield 74% (18.2 mg); Colourless liquid, Hexane/EtOAc = 95/5, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.54 – 7.47 (m, 1H), 7.37 – 7.30 (m, 2H), 4.48 (t, *J* = 5.5 Hz, 2H), 4.05 (t, *J* = 5.5 Hz, 2H), 2.63 (s, 1H), 1.48 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.2, 154.9, 132.8, 132.7, 130.6, 129.7, 123.6, 113.4, 61.1, 44.9, 39.5, 28.0. **HRMS-ESI:** calcd for $C_{14}H_{18}N_2O_2$ $[M+Na]^+$, 269.1259 found 269.1260.

3-(*tert*-Butyl)-1-methylquinolin-2(1*H*)-one (4n): yield 48% (10.3 mg); Colourless liquid, Hexane/EtOAc = 98/2, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.54 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.49 (ddd, *J* = 8.6, 7.3, 1.5 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 3.72 (s, 3H), 1.44 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.6, 140.8, 139.1, 133.2, 129.4, 128.6, 121.7, 120.5, 113.6, 35.4, 29.5, 28.9. **HRMS-ESI:** calcd for $C_{14}H_{18}NO$ $[M+H]^+$ 216.1383, found 216.1388. **FT-IR** ν (cm^{-1}): 2953, 1638, 1591, 1456, 1276, 1229, 1074.

3-Cyclohexyl-1-methylquinolin-2(1*H*)-one (4o):[9] yield 42% (10.1 mg); White solid, Hexane/EtOAc = 98/2, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54-7.48 (m, 2H), 7.47 (s, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 3.75 (s, 3H), 3.01-2.95 (m, 1H), 1.98-1.95 (m, 2H), 1.87-1.83 (m, 2H), 1.79-1.77 (m, 1H), 1.53-1.44 (m, 2H), 1.35-1.22 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.4, 139.2, 138.8, 132.8, 129.4, 128.3, 122.0, 121.0, 113.9, 38.0, 32.7, 29.9, 26.9, 26.5.

2-(*tert*-Butyl)-4,7-dichloroquinoline (4p):[13] yield 52% (13.2 mg); Colourless liquid, Hexane/EtOAc = 98/2, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.11 – 8.06 (m, 2H), 7.58 (s, 1H), 7.51 (dd, *J* = 9.0, 1.8 Hz, 1H), 1.44 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.8, 148.8, 142.4, 136.1, 128.8, 127.7, 125.2, 123.3, 118.7, 38.5 30.0. **HRMS-ESI:** calcd for $C_{13}H_{13}Cl_2N$ $[M+H]^+$ 254.0498, found 254.0496.

1-Cyclohexyl-6-methylisoquinoline (4q):[1] yield 40% (9.1 mg); Yellow oil, Hexane/EtOAc = 98/2, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.43 (d, J = 5.7 Hz, 1H), 8.10 (d, J = 8.7 Hz, 1H), 7.56 (s, 1H), 7.40–7.38 (m, 2H), 3.55–3.49 (m, 1H), 2.52 (s, 3H), 1.98–1.92 (m, 4H), 1.86–1.78 (m, 3H), 1.56–1.48 (m, 2H), 1.43–1.35 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.5, 142.1, 139.8, 136.8, 129.1, 126.6, 124.8, 124.7, 118.6, 41.6, 32.7, 27.0, 26.4, 21.9.

7. Reaction setup and procedure for scale-up reaction:

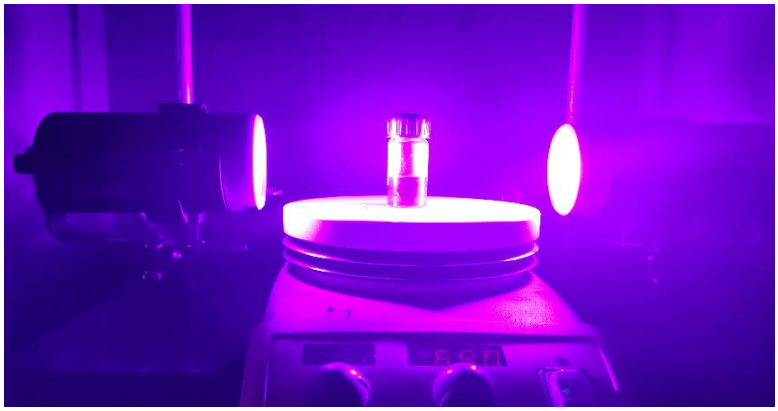


Figure S-02: (a) Kessil lamp setup with equipped fan kit for scale-up reaction.

7.1. Scaled up synthesis of **3a**

In a 20 mL glass vial with a magnetic stirring bead, $CeCl_3$ (10 mol%), KO^{t}Bu (20 mol%), alkyl carboxylic acid (4.0 mmol) and quinoxalin-2(1*H*)-one (2.0 mmol) was added and then 12 mL of CH_3CN solvent was added. The reaction mixtures were irradiated with a two Kessil® PR160-427 nm lamp with a cooling fan at a distance of 4 cm as shown in Figure S-02, and stirred for 24 hours in air. After the completion of reaction, the reaction mixture was quenched with saturated $NaHCO_3$ solution and extracted with EtOAc. Then, the organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated in rotary evaporation. The resultant residue was purified by column chromatography using hexane/EtOAc to achieve the desired C-3 alkylation of quinoxalin-2(1*H*)-ones.

8. Radical inhibition experiments and trapping of radical intermediates

In a septum cap vial with a magnetic stirring bead, $CeCl_3$ (10 mol%), KO^{t}Bu (20 mol%), alkyl carboxylic acid (0.2 mmol), quinoxalin-2(1*H*)-one (0.1 mmol), and TEMPO (3 eq), or BHT (3 eq) was added in 0.6 mL of CH_3CN solvent. The reaction mixtures were irradiated with a Kessil® PR160-427 nm LED and stirred for 24 hours in air. After completion of the reaction, an aliquot portion of the reaction mixture was subjected to GCMS (Figure S-03). We were able to detect *tert*-butyl radical adduct with TEMPO. The GCMS data of TEMPO-adduct of pivalic acid was given below (Figure S-03).

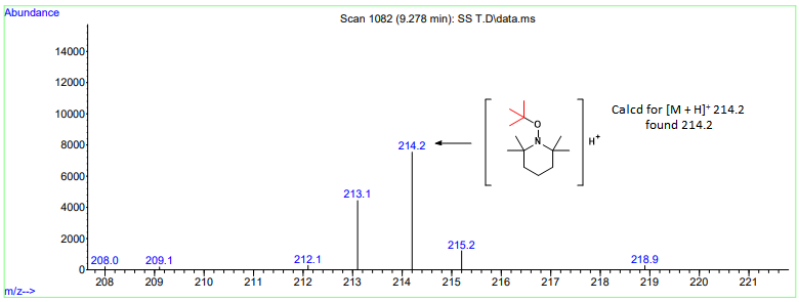
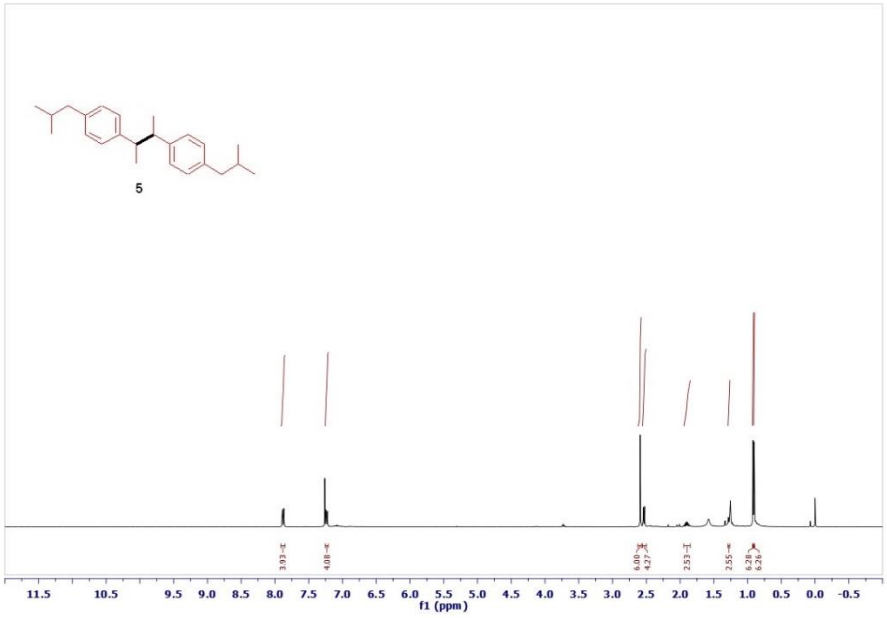


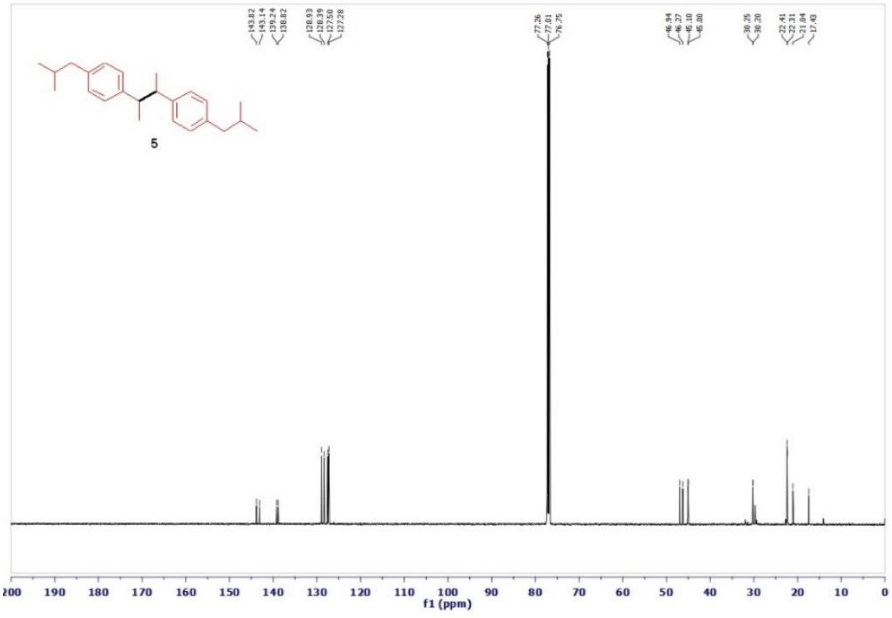
Figure S-03: GCMS data of TEMPO adduct of *tert*-butyl radical

Furthermore, when the reaction was conducted using ibuprofen (0.2 mmol) and quinoxalin-2(1*H*)-one (0.1 mmol) along with product **3u**, the dimer (**5**) was isolated in 20% yield and characterized by ^{1}H and ^{13}C NMR.

^{1}H NMR (400 MHz, $CDCl_3$) of compound **5**



^{13}C NMR (126 MHz, $CDCl_3$) of compound **5**



9. UV-Vis studies

The UV-Vis measurements were carried out using a UV-Vis spectrophotometer (UV-2450, Shimadzu) using a quartz cuvette equipped with a Teflon® septum (1 cm path length). The UV-Vis spectra were collected in the 200-500 nm range. UV-Vis experiments were performed to analyse the involved LMCT process between *Cerium catalyst* and *carboxylic acids* after irradiation of light. In order to verify, a cerium catalyst, $(^{n}Bu_4)_2CeCl_6$ was synthesized following a reported procedure.[10] A stock solution (solution A) was prepared by mixing $(^{n}Bu_4)_2CeCl_6$ (2.2 mg, 2.6 µmol) in 6 mL MeCN solvent. Depending upon the requirement, original stock solution was diluted with dry MeCN.

9.1. UV-Vis absorption spectra of solution A with pivalic acid

In a 3 mL quartz cuvette equipped with a Teflon® septum, 10 µL of 0.44M solution of pivalic acid (**2a**) was mixed with solution A (2 mL, 0.11 mM). UV-Vis spectra were recorded after irradiation the cuvette solution with blue-violet light (427 nm) for 10 second interval initially. Figure S-04 shows a continuous decrease in absorbance of Ce^{IV}, which come around ≈378 nm due to reduction of Ce^{IV} to Ce^{III} after LMCT process with pivalic acid. After increasing the irradiation time interval, fast consumption of Ce^{IV} was observed with appearance of a small peak around ≈330nm of Ce^{III}, which was previously suppressed in Ce^{IV} absorption peak.

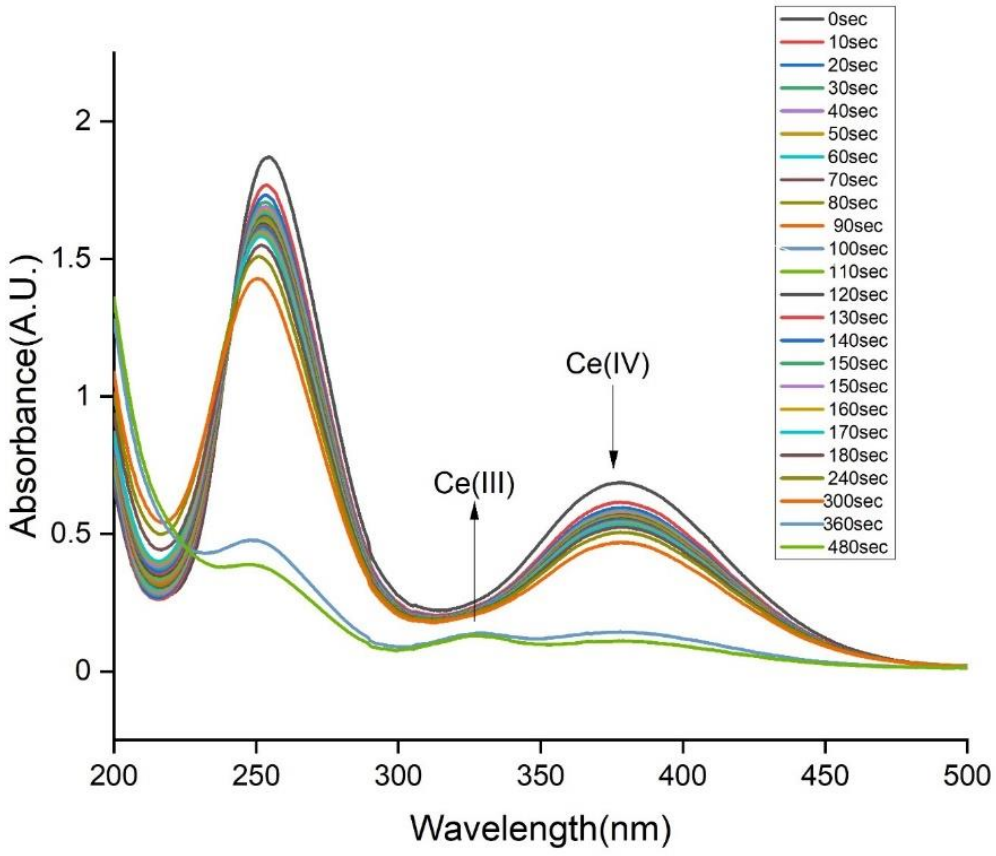


Figure S-04: UV-Vis spectra of a solution of Ce^{IV} complex and **2a** after irradiation with 427 nm

9.2. Normalised UV-Vis spectra for Ce^{IV} LMCT transition at 378 nm

A 2mL (0.11 mM) solution of $(^{n}Bu_4)_2CeCl_6$ was taken in a 3 mL quartz cuvette equipped with a Teflon® septum and UV-Vis spectra were recorded after irradiation the cuvette solution with blue-violet light (427 nm) at 10-120 seconds time duration. Similarly, a solution of $(^{n}Bu_4)_2CeCl_6$ (0.11 mM), ^{t}BuOK (0.22 mM) and pivalic acid (2.2 mM) were taken in cuvette and UV-Vis spectra were recorded after irradiation the cuvette solution with blue-violet light (427 nm) at 10-120 seconds time duration. As shown in figure S-05, with solution of Ce^{IV} complex slight decrease in absorbance of Ce^{IV} was observed after irradiation with light (***Blue line***). However, solution of Ce^{IV} and pivalic acid showed drastic decrease of Ce^{IV} after increasing the duration of light irradiation (***Orange line***). It indicates that carboxylic acid involves in the Ce^{IV}-carboxy complex formation which undergoes LMCT transition forming Ce^{IV} to Ce^{III} species. After addition of base, LMCT process also observed with slower rate than Ce^{IV} and acid solution. We might assume that the base is required for providing the optimal rate of LMCT process in the reaction to generate alkyl radical from carboxylic acid.

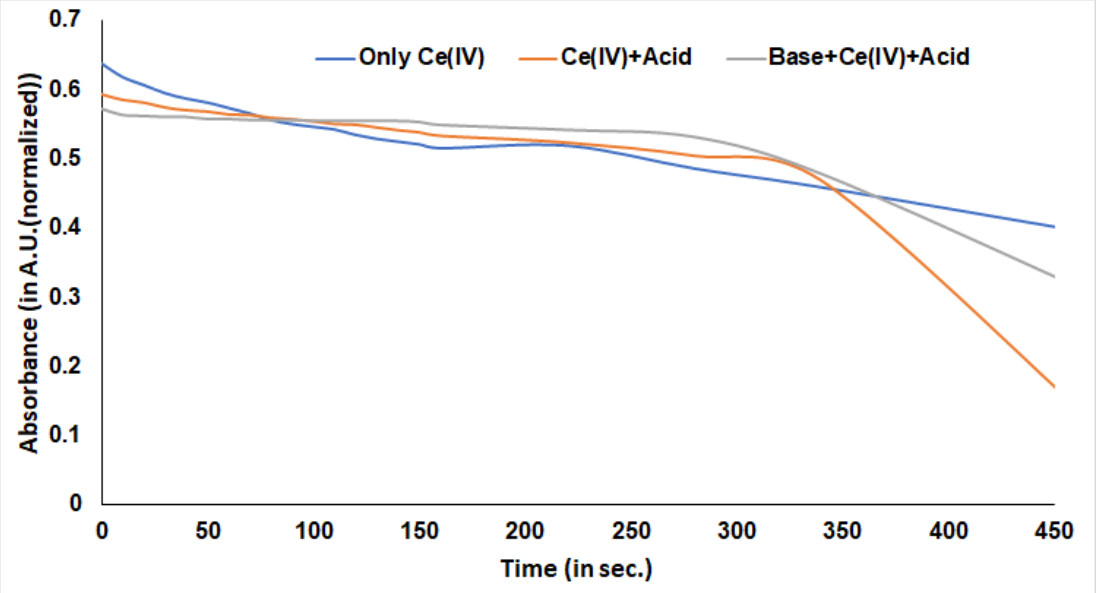


Figure S-05: Normalised UV-Vis spectra recorded at 378 nm of Ce^{IV} complex in different conditions

9.2. UV-Vis spectra for Ce^{IV} LMCT transition after oxygen exposure

In cerium catalytic cycle, it is assume that the oxidation of Ce^{III} to Ce^{IV} species initiated with the help of oxygen. In order to verify the role of oxygen in cerium catalytic cycle, UV-Vis experiments were conducted with the solution of $(^{n}Bu_4)_2CeCl_6$ (2mL, 0.11 mM), ^{t}BuOK (0.22 mM) and pivalic acid (2.2 mM) in quartz cuvette. At first, absorption spectrum was acquired without irradiation (Dotted line, Figure S-06,) then after 3 min irradiation of blue-violet light (427 nm) further absorption spectrum was acquired. It is evident from the spectra that Ce^{IV} was consumed with formation of Ce^{III} (Black line, Figure S-06,). It was observed that after consecutive exposing with oxygen for duration of one minute, the concentration of Ce^{IV} was increased (Red and Blue line, Figure S-06,) which demonstrated the involvement of oxygen for cerium catalytic cycle.

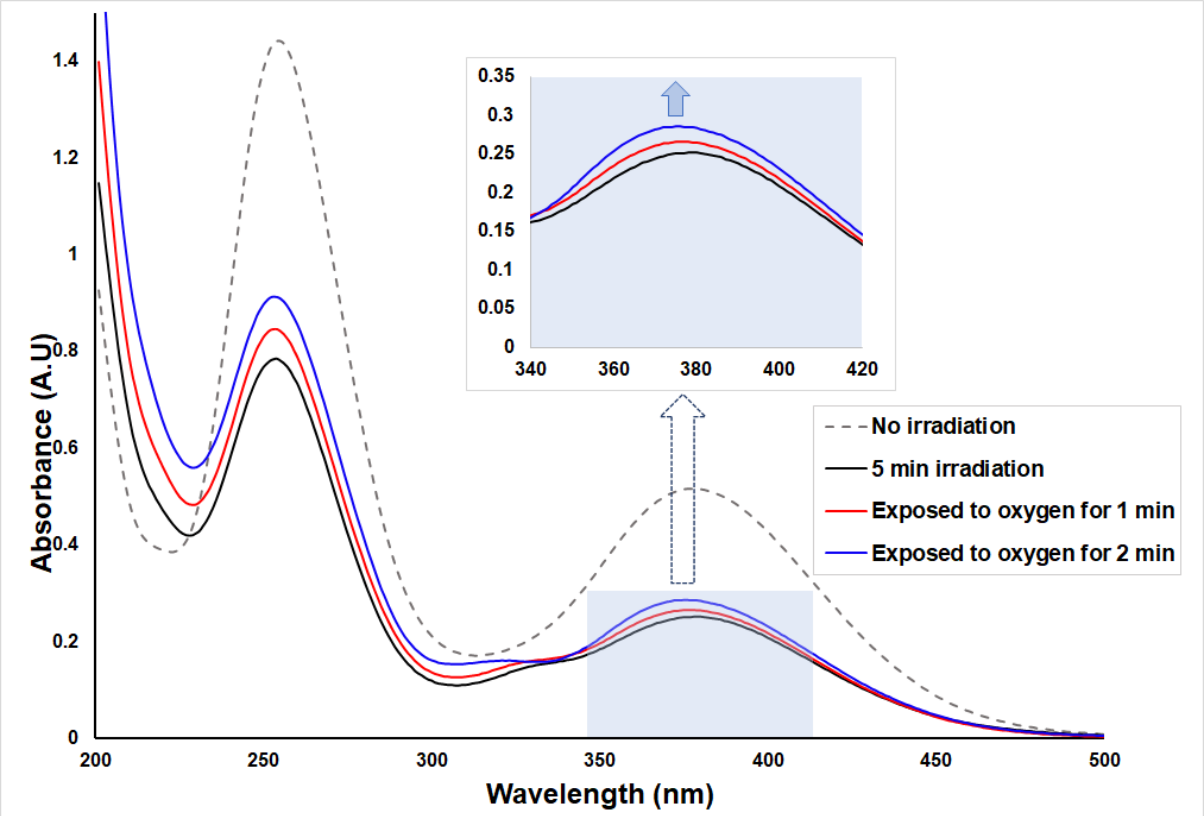


Figure S-06: UV-Vis spectra for the solution of Ce^{IV} complex, pivalic acid and ^{t}BuOK to understand the involvement of oxygen

10. *In-situ* FTIR experiments for detection of CO_2 evolution

For detection of CO_2 evolution in the reaction, *In-situ* FTIR experiments was conducted using a Mettler-Toledo ReactIR 700 (SN: C049640472) equipped with a TEMCT detector, DiComp (Dimond) probe, with a 9.5mm x 2m AgX fiber interface. Data was collected using the spectral window of 2500 to 650 cm^{-1} with 8 cm^{-1} resolution and sampled in 60 second intervals. In a glass vial, $CeCl_3$ (10 mol%), KO^tBu (20 mol%), pivalic acid (0.2 mmol) and quinoxalin-2(1*H*)-one (0.1 mmol) with a magnetic stirring bead was taken and 0.6 mL of CH_3CN solvent was added. Then, diamond probe was inserted in solution containing vial and *in-situ* FTIR spectra were recorded for 6 hr at 60 second intervals. As depicted in figure S-07 (side view and top view), the signal intensity at 2344 cm^{-1} (*corresponding to asymmetric stretching of CO_2*) gradually increases with the progression of the reaction. For the confirmation of CO_2 IR signal, a standard solution of CO_2 gas bubbled in MeCN and then the solution was analysed same way in the *in-situ* FTIR instrument (figure S-07 graph (C).

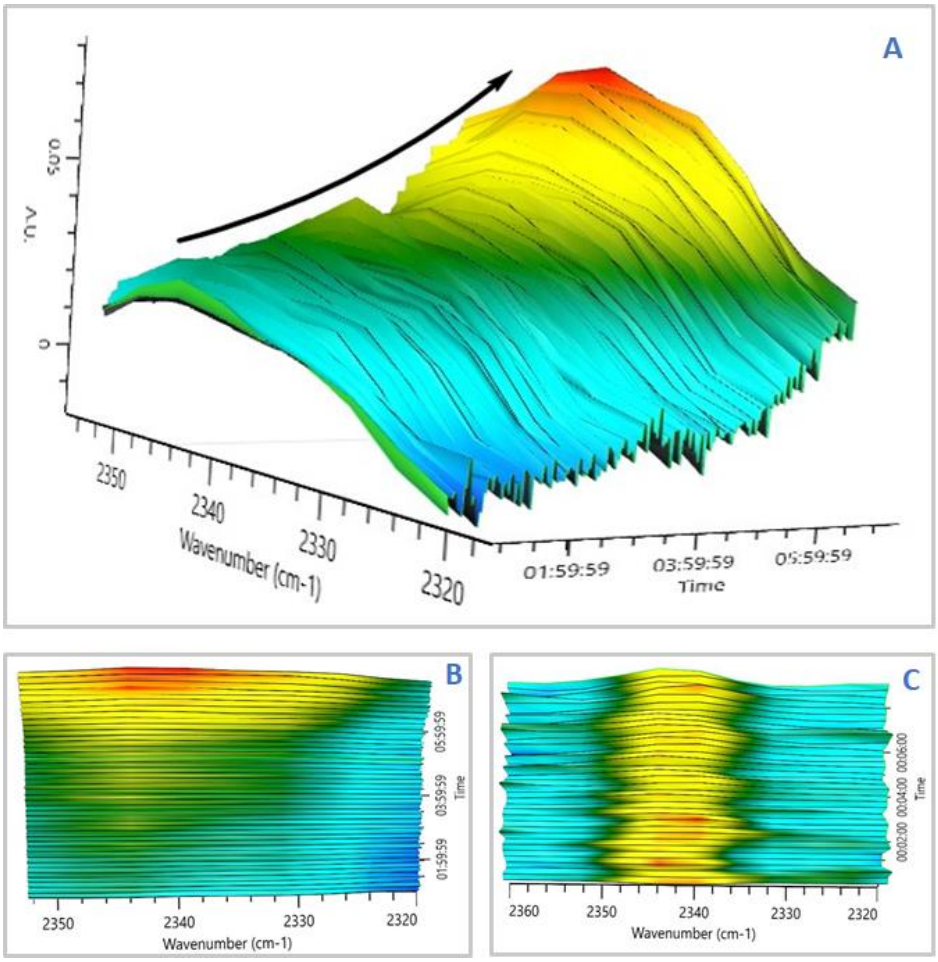


Figure S-07: *In-situ* FTIR graph for CO_2 detection with progress of reaction (A) Side view (B) Top view (C) standard CO_2 bubbled in MeCN.

11. KI/starch test for the detection of hydrogen peroxide (H_2O_2) in the reaction

In photoinduced decarboxylative alkylation, it was anticipated that H_2O_2 can be generated as by-product in the reaction, which was confirmed by KI/starch test. To perform KI/starch test, we have prepared a solution of KI (0.05 M), starch (4 mg/mL), and glacial acetic acid (0.5 M) in 2 mL H_2O (Solution **A**). Reaction mixture was prepared following the optimised reaction procedure (Solution **B**: quinoxalin-2(1*H*)-one (0.1 mmol), pivalic acid (0.2 mmol), $CeCl_3$ (10 mol%) and base (20 mol%) in 0.6 mL solvent irradiated with blue-violet LED (427 nm) for 24 h under aerobic conditions). To validate the formation of H_2O_2, when we have added 100 µL of solution **B** in solution **A**, to our delight the resulting solution turns into dark purple colour (Solution C), which confirms the formation of H_2O_2.

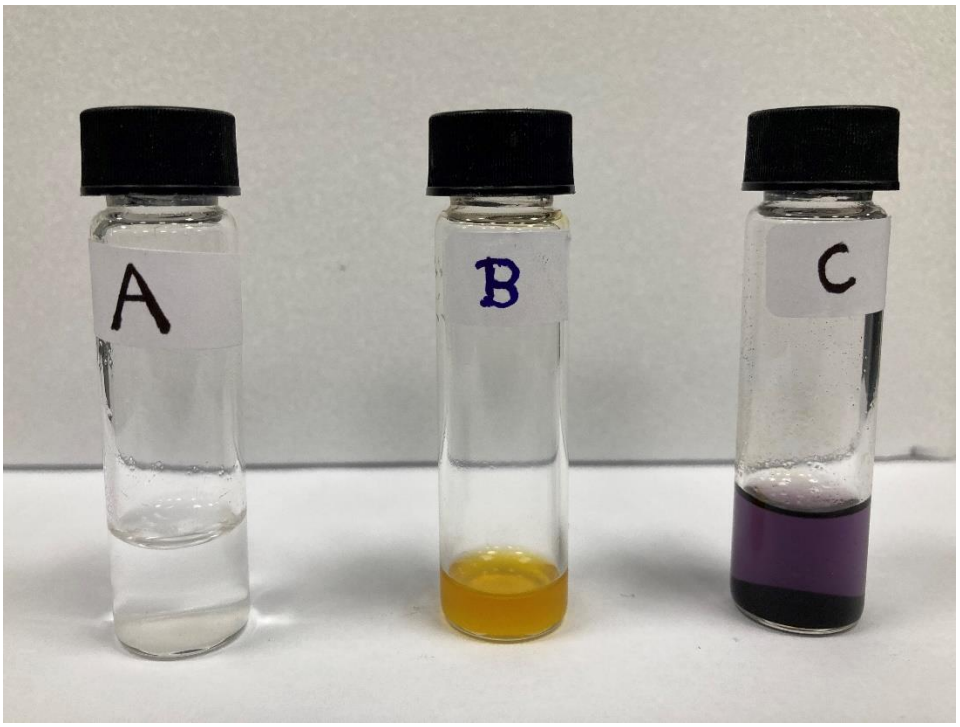
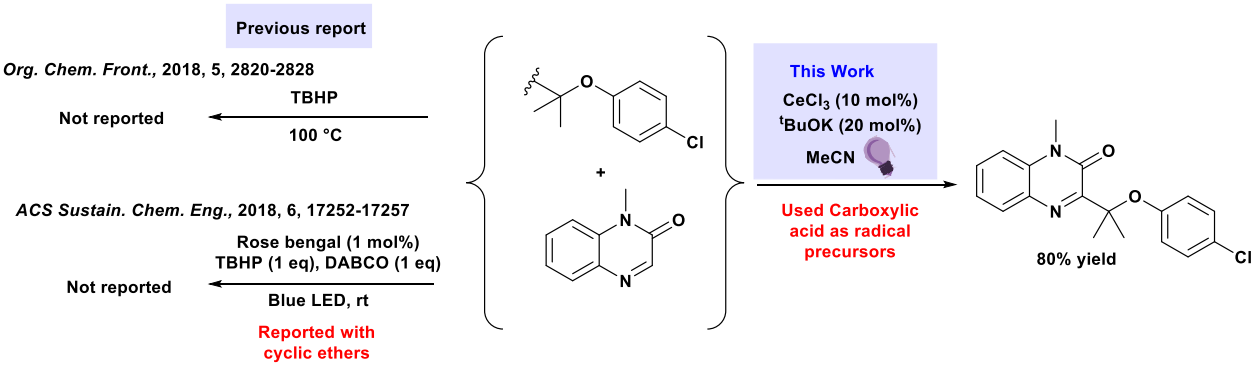


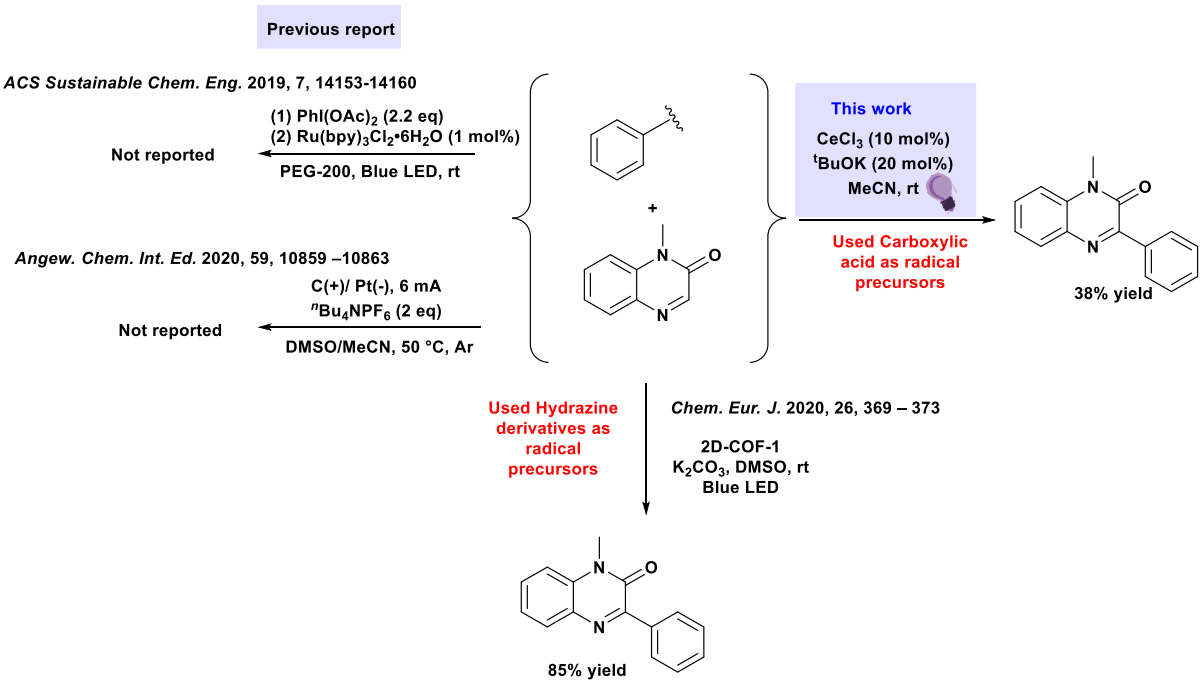
Figure S-08: Detection of hydrogen peroxide (H_2O_2) in the reaction. (**A**) KI and starch in H_2O (**B**) The reaction mixture after completion of reaction (**C**) After addition of 100 µL of solution B in solution A

12. Comparative studies with previous literatures:

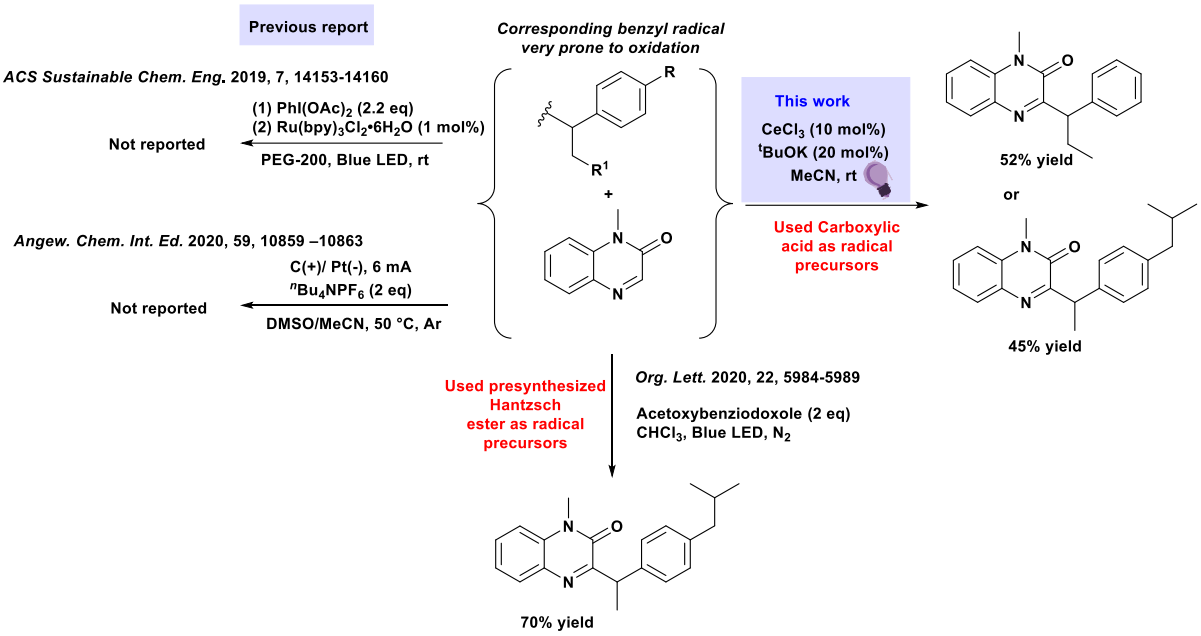
A. Alkylation with tertiary α-oxo radical precursors



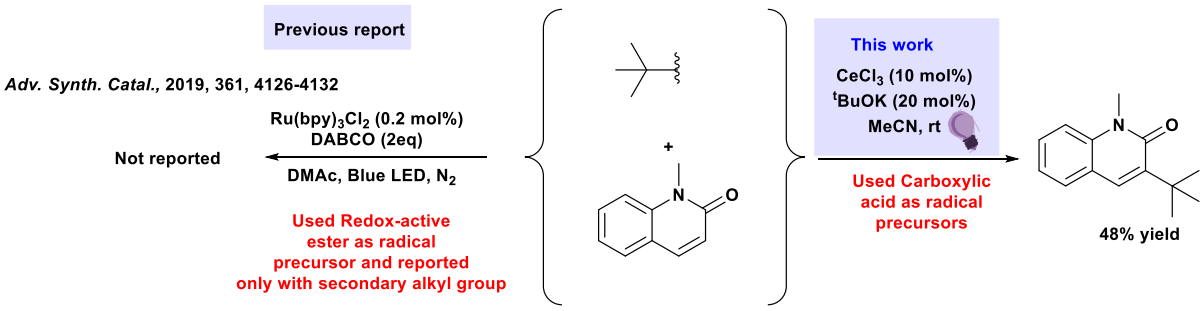
B. Benzoic acid as radical precursors



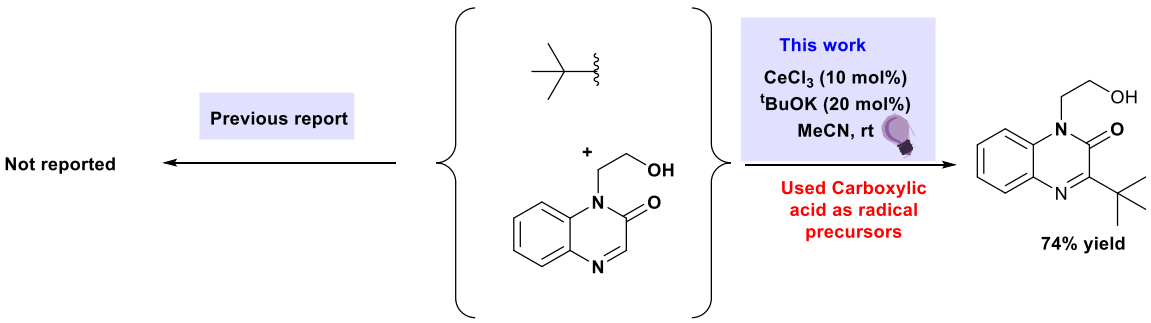
C. Alkylation with secondary benzyl radical precursors



D. Alkylation of quinolinone derivative



E. Hydroxyl group tolerance in decarboxylative alkylation



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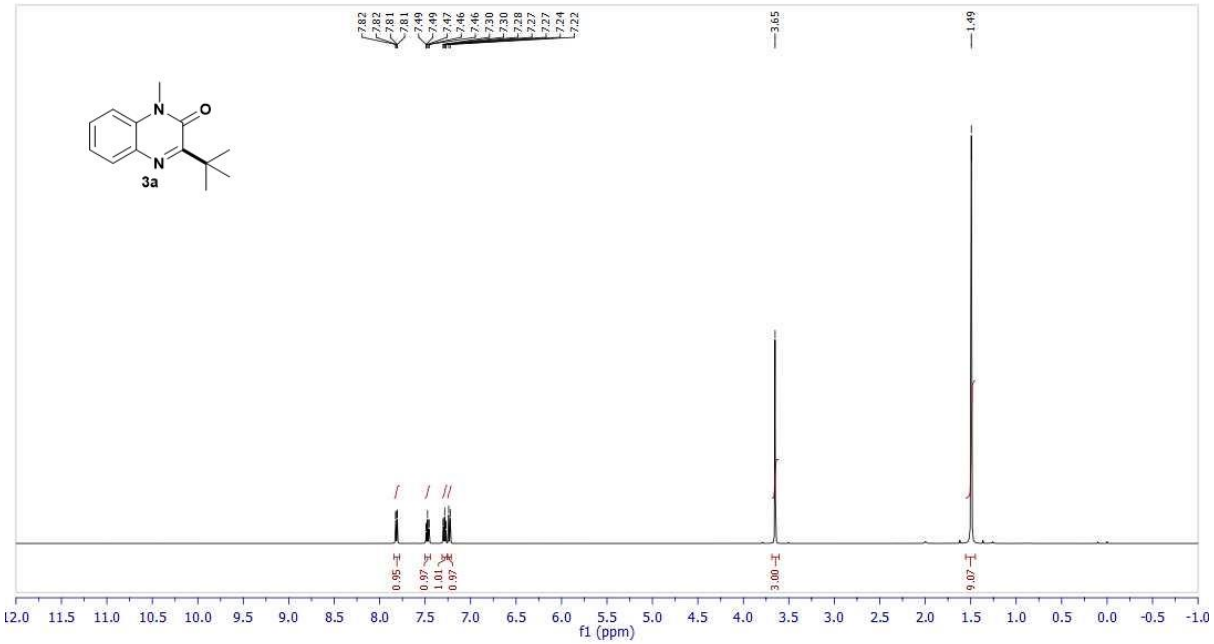
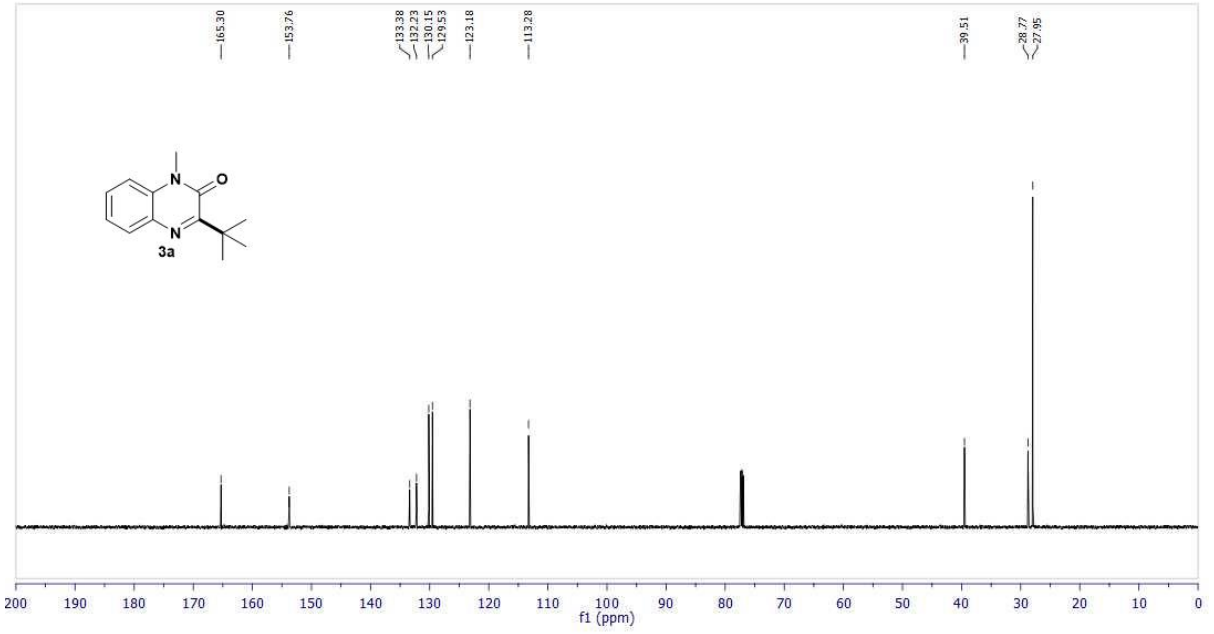
14. ^{1}H and ^{13}C NMR Spectra:

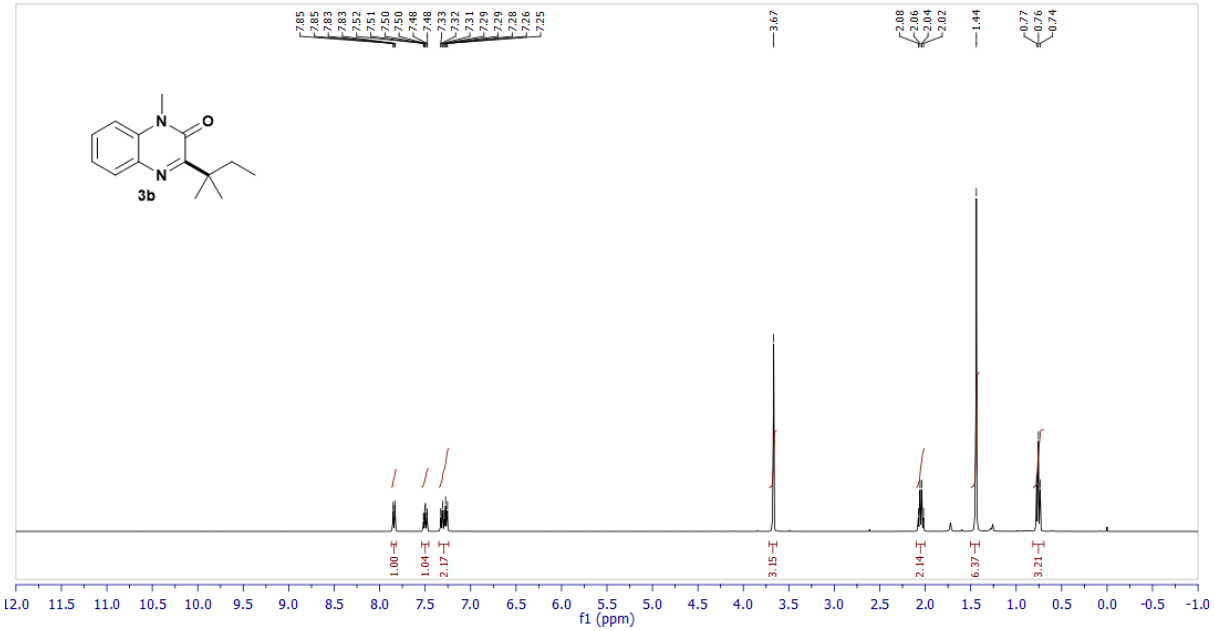
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3a**



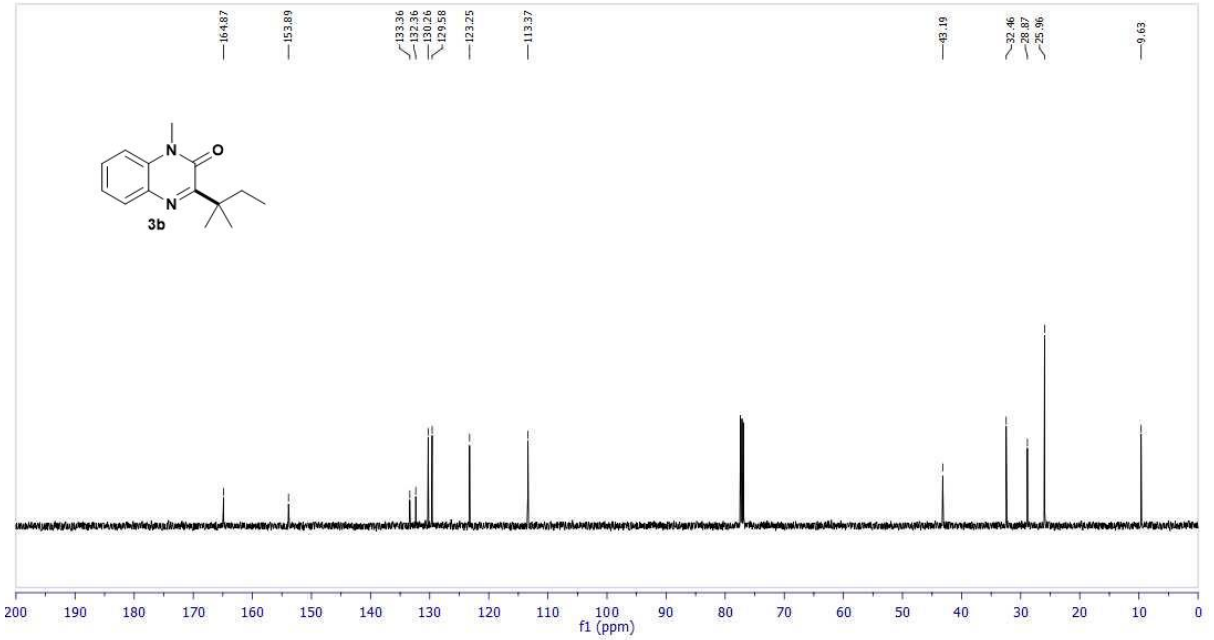
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3a**



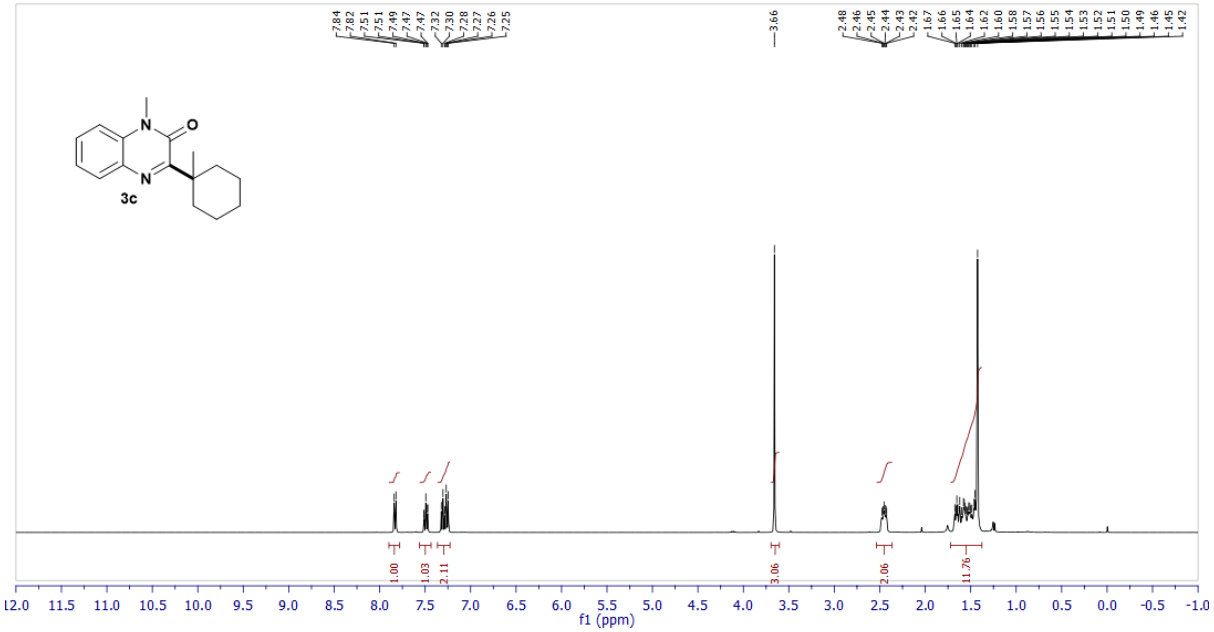
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3b**



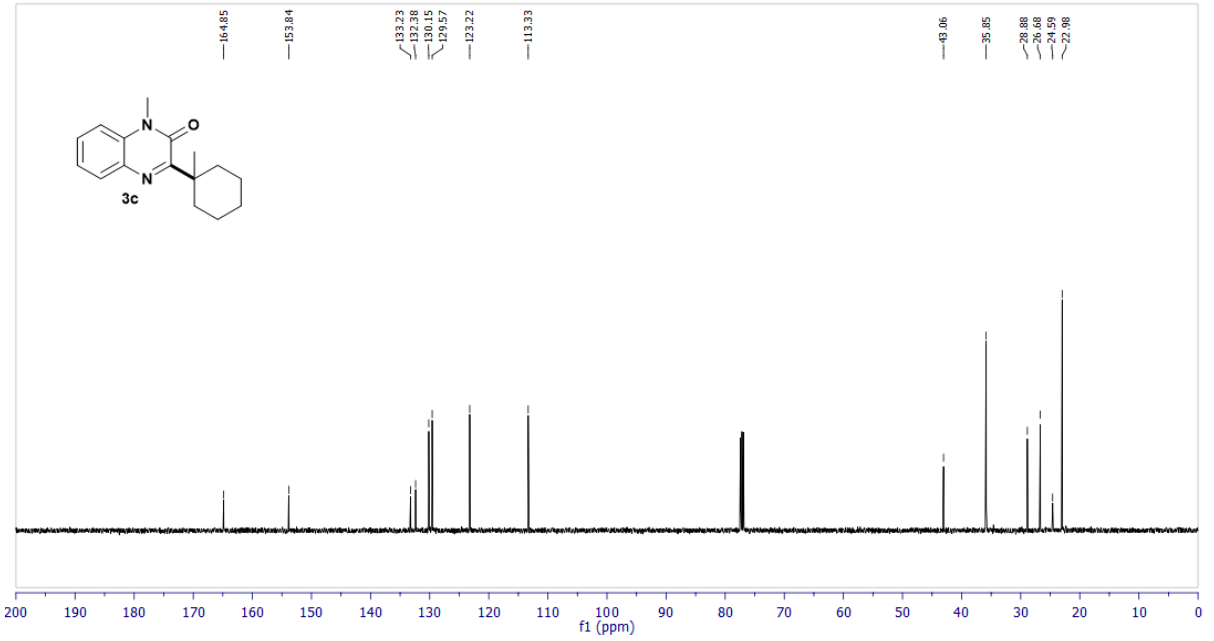
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3b**



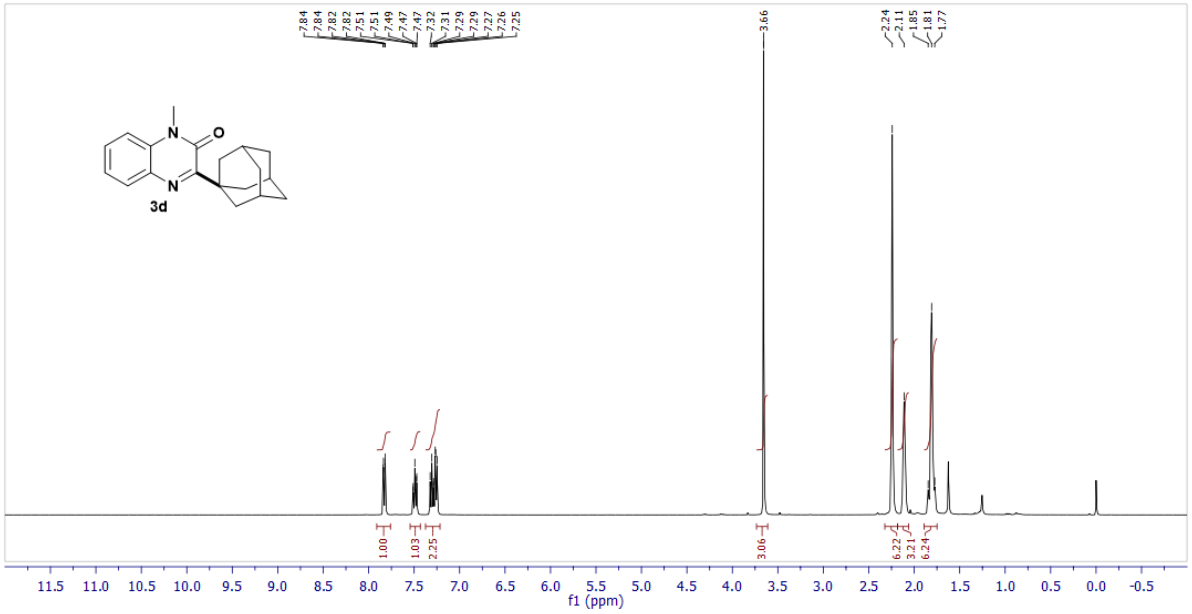
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3c**



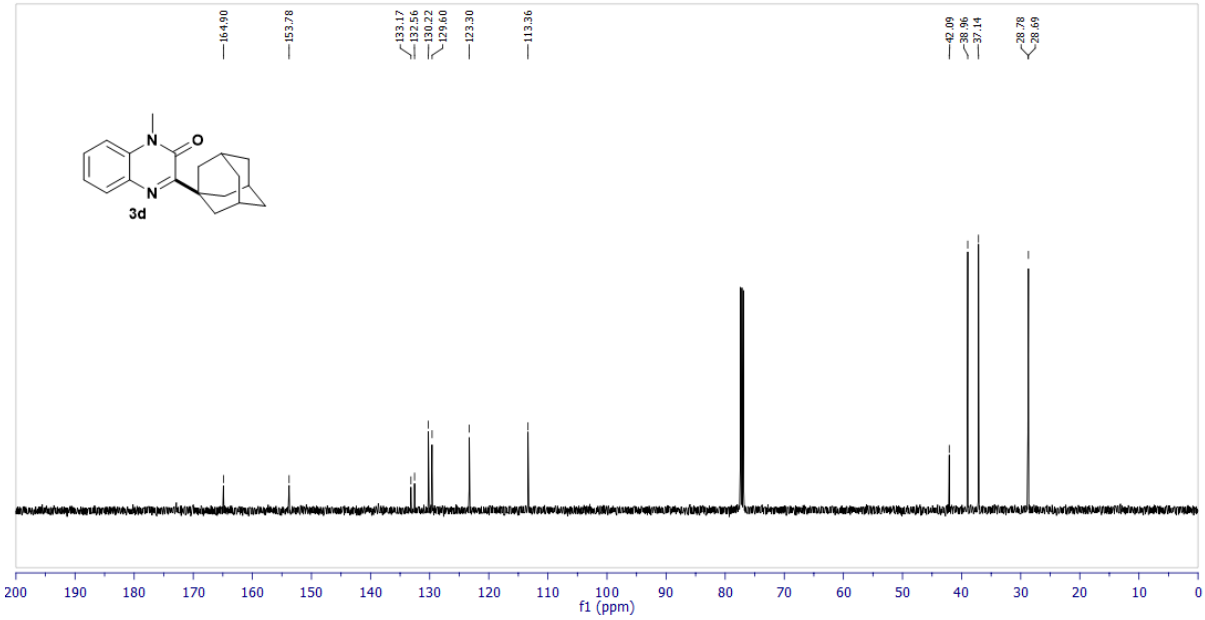
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3c**



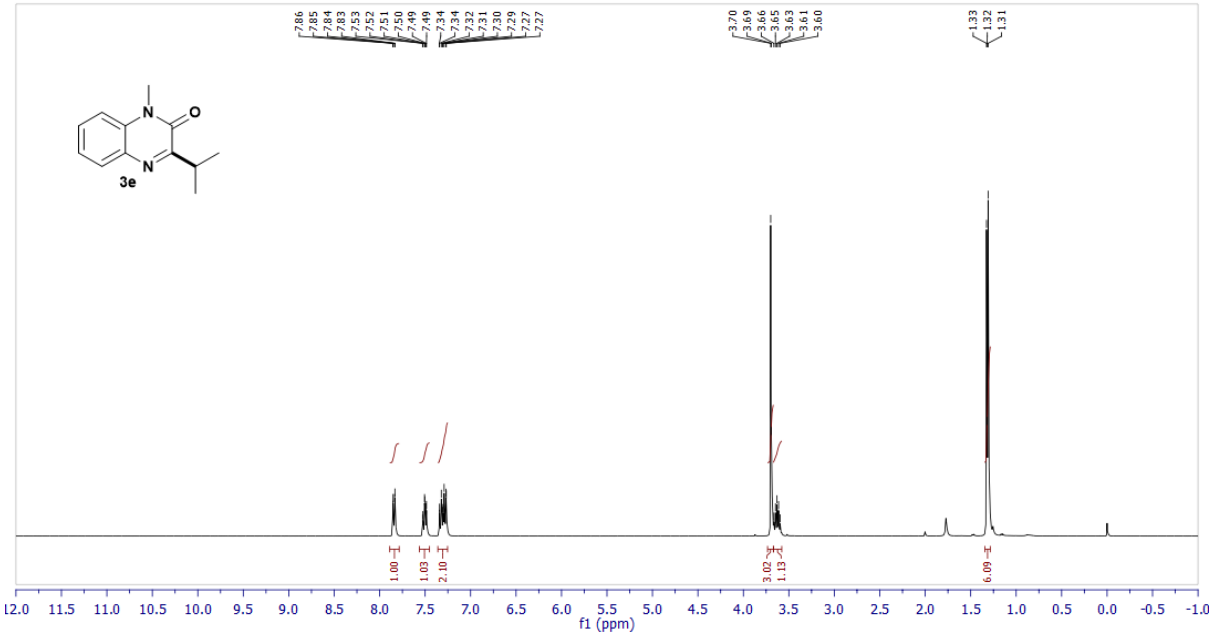
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3d**



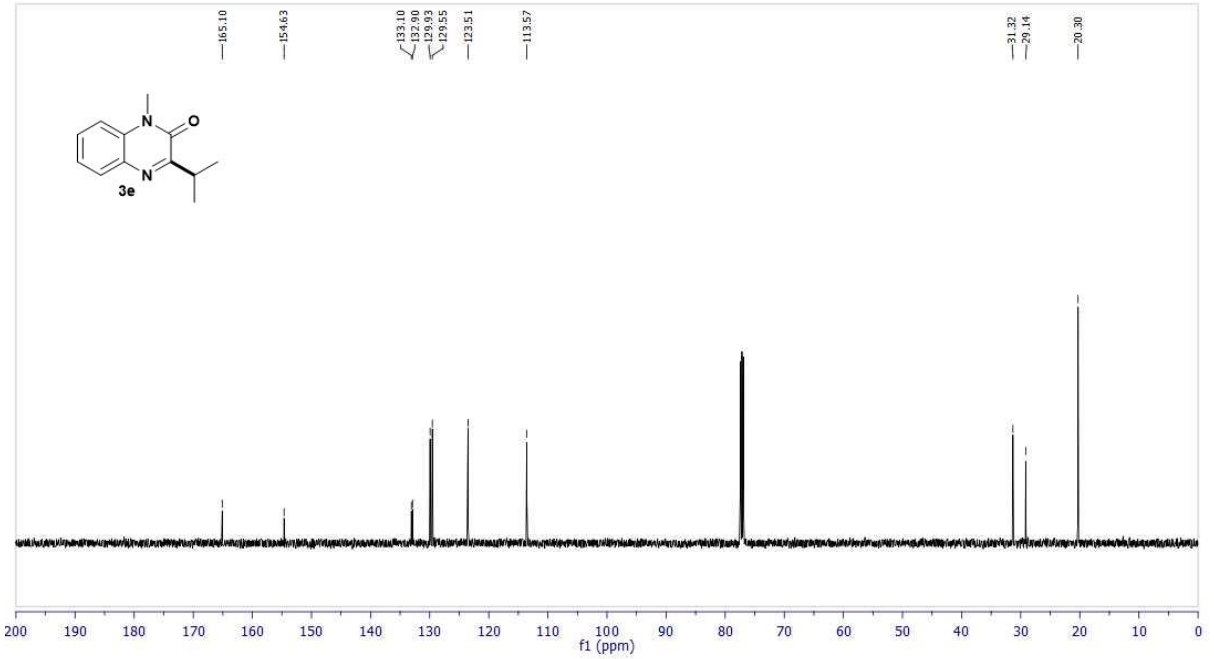
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3d**



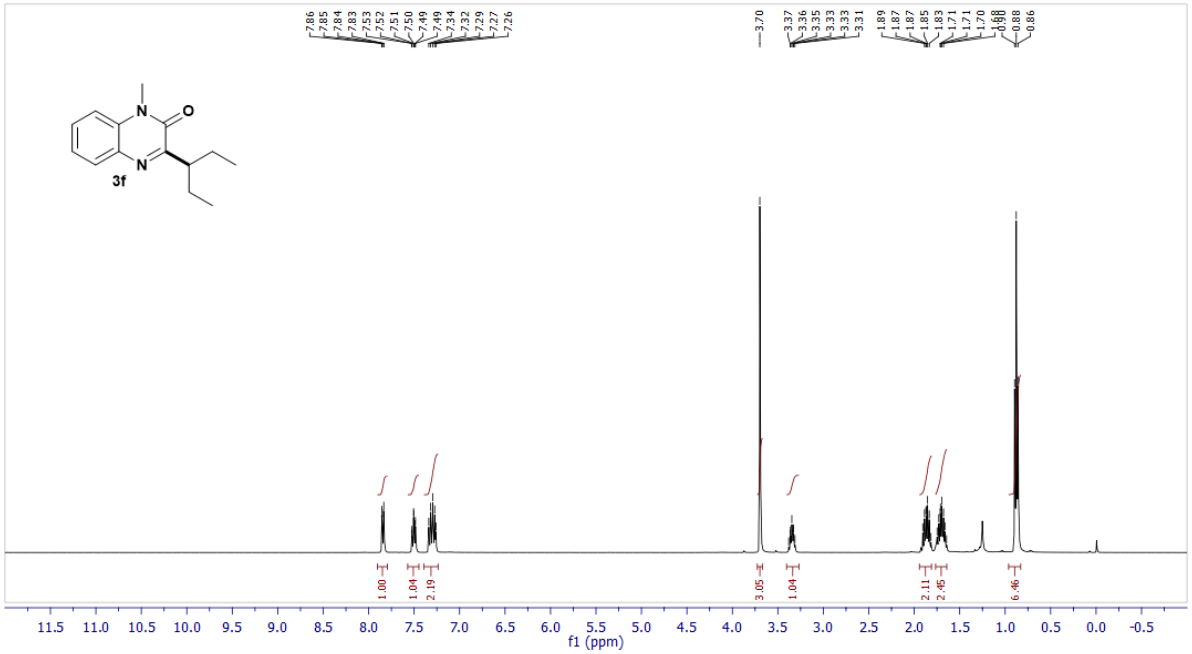
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3e**



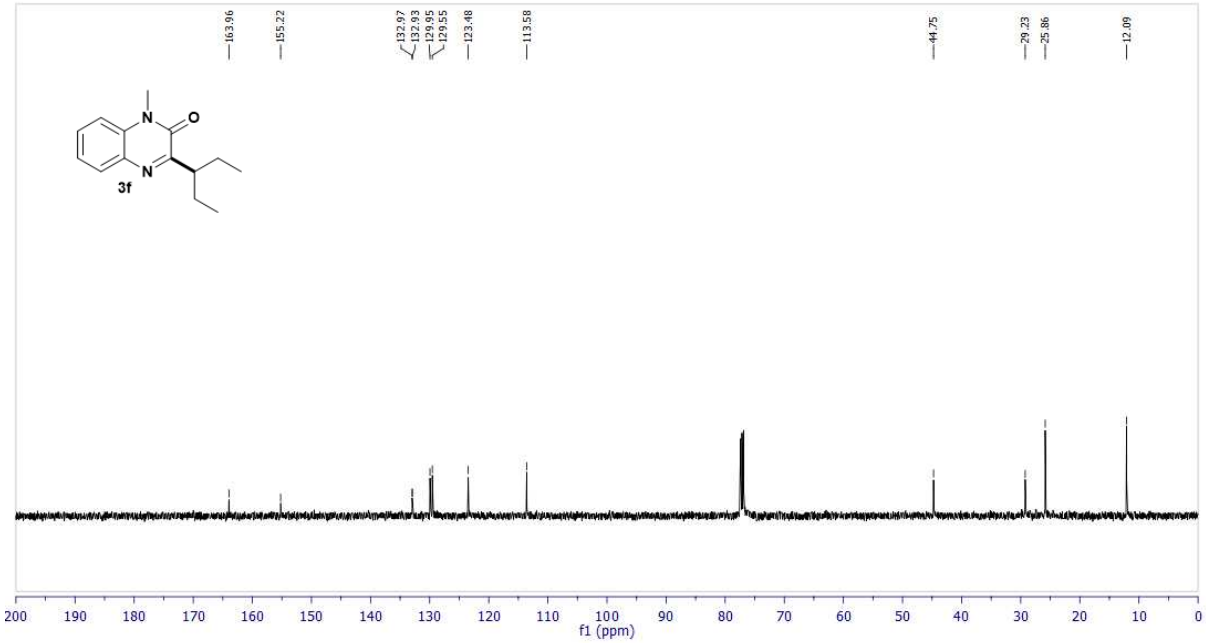
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3e**



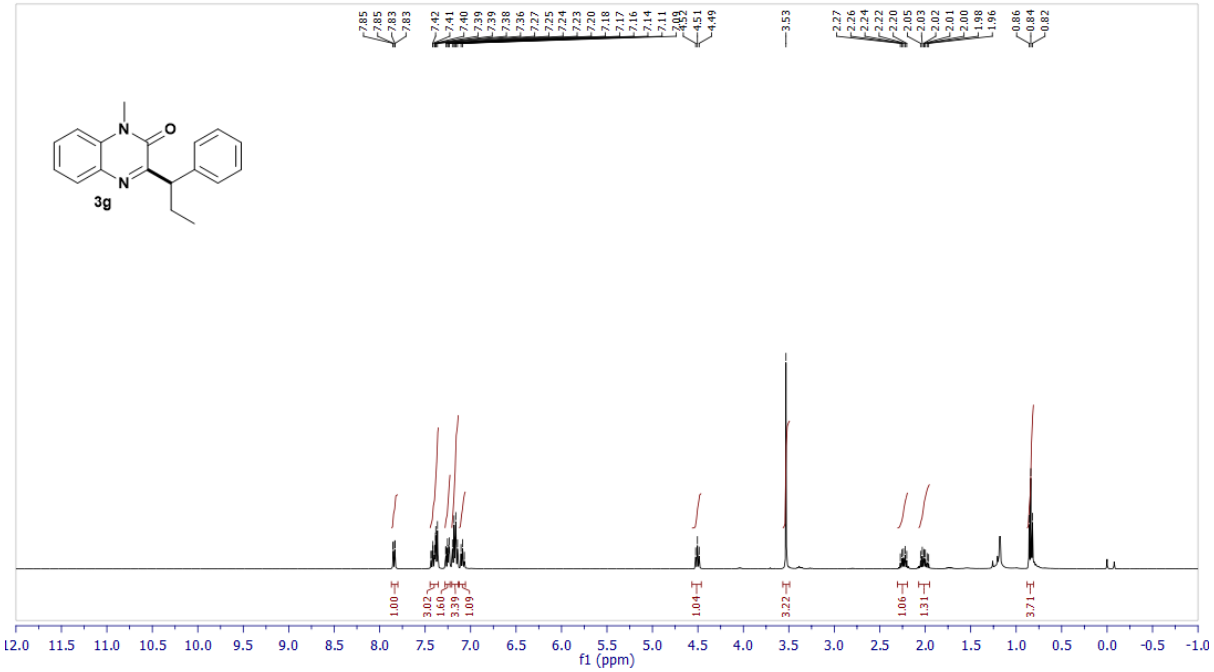
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3f**



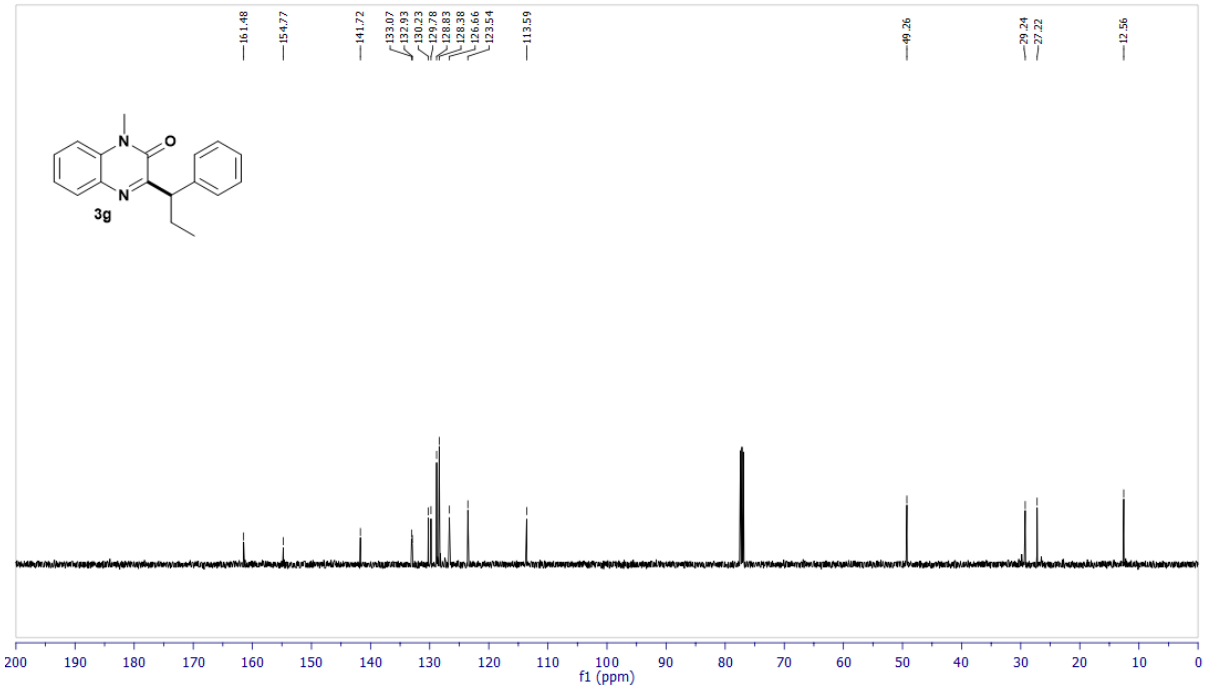
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3f**



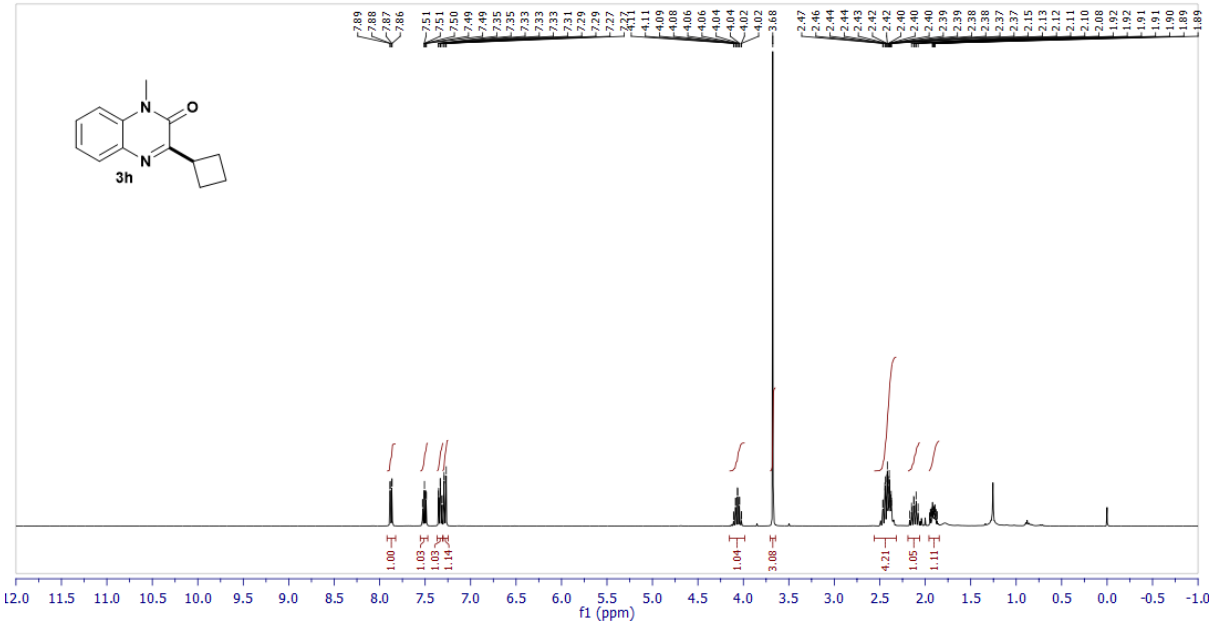
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3g**



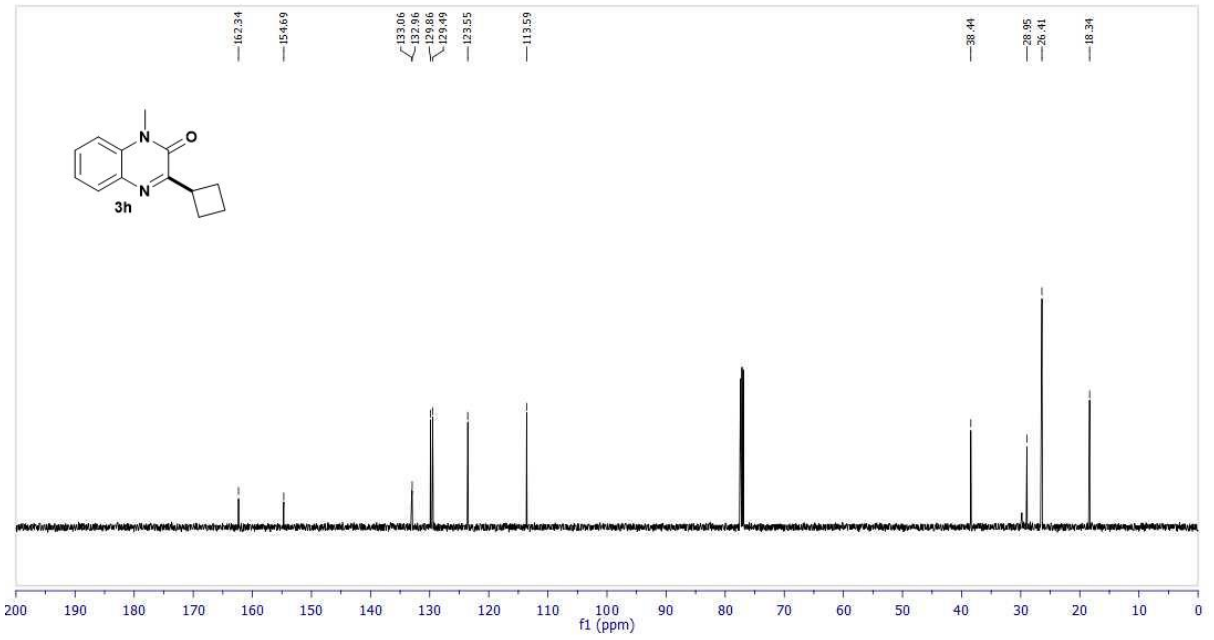
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3g**



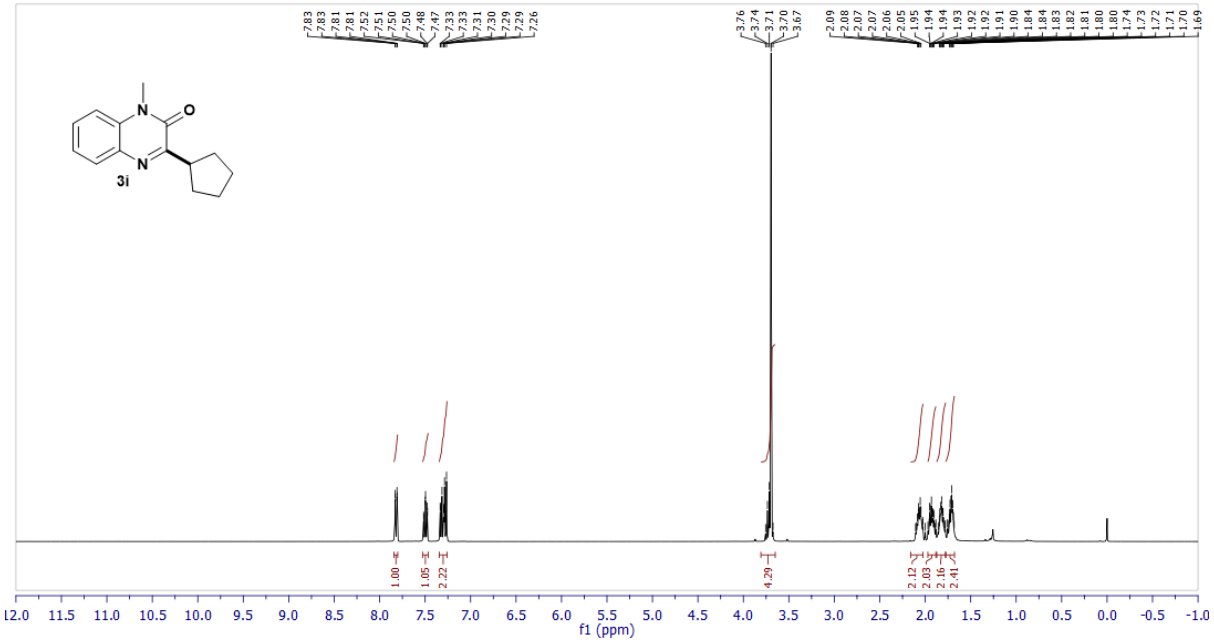
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3h**



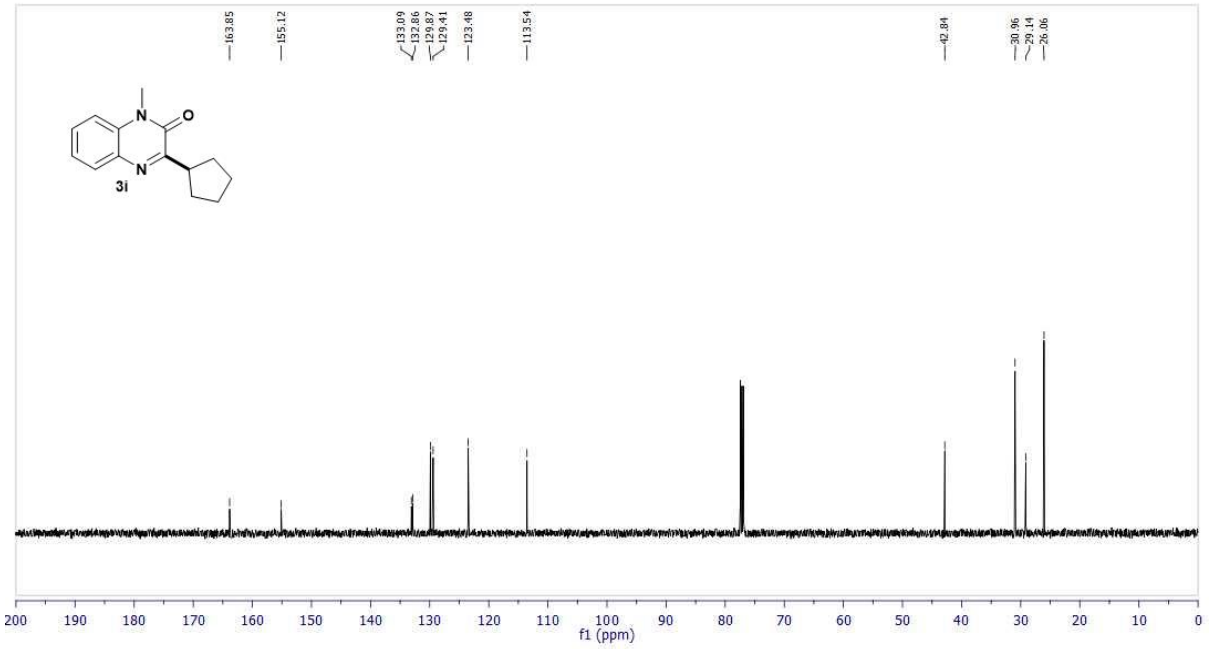
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3h**



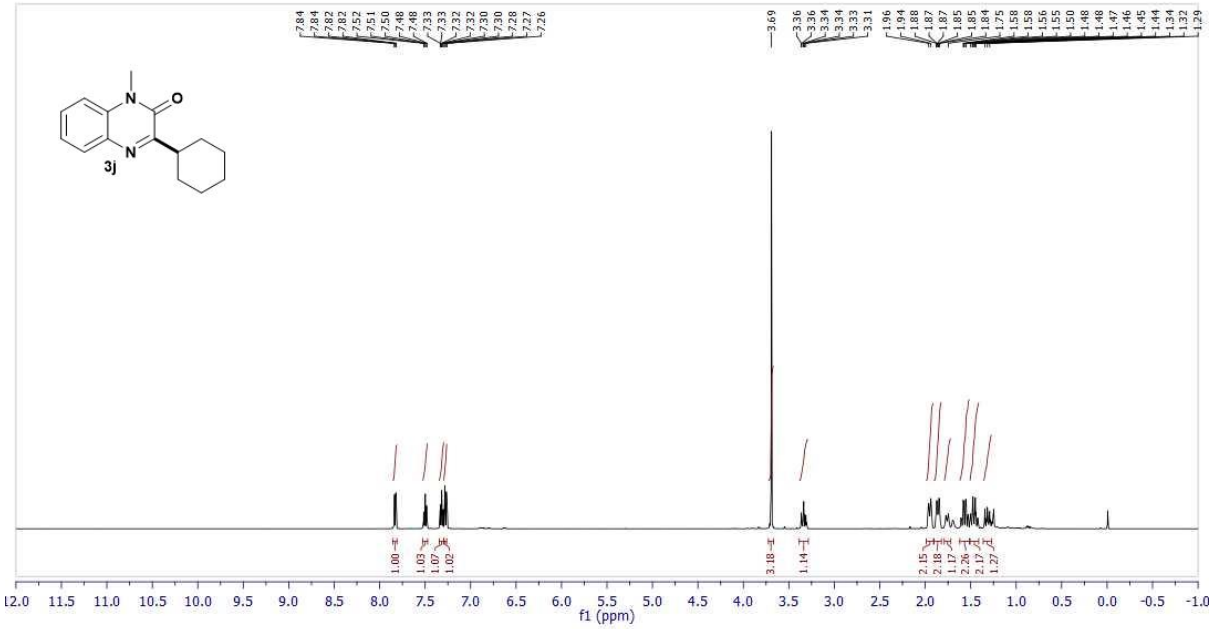
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3i**



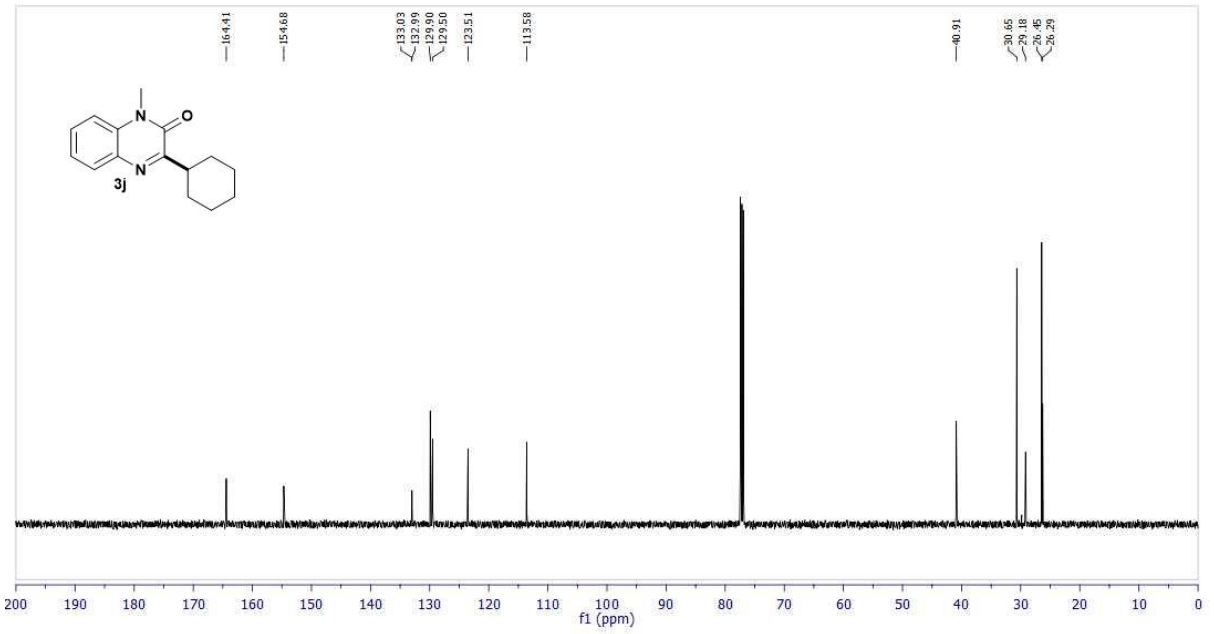
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3i**



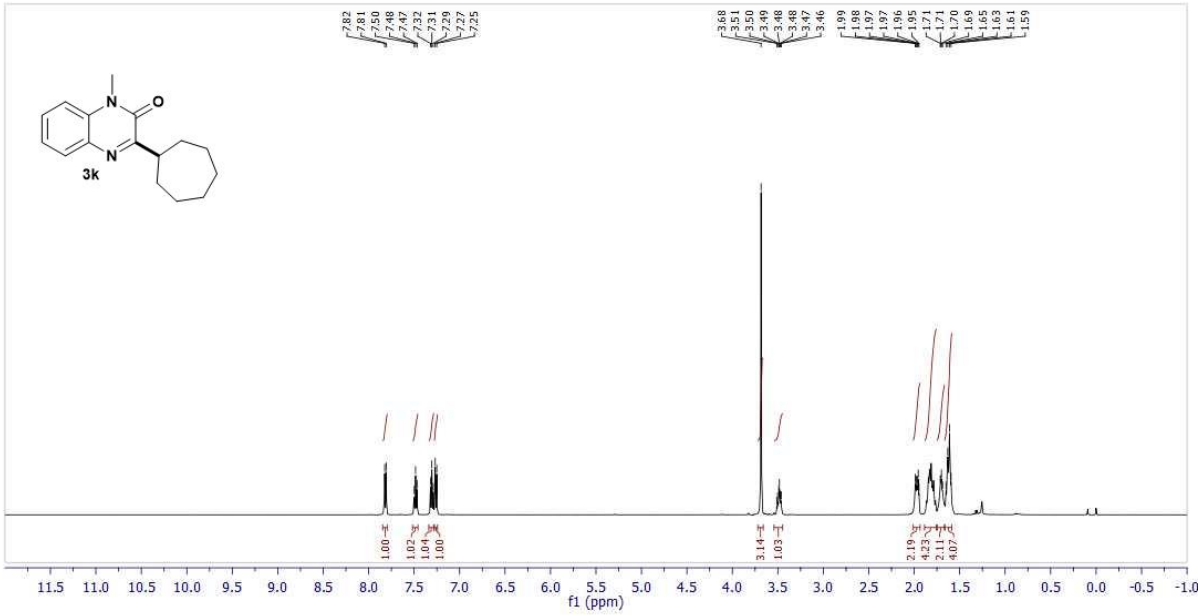
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3j**



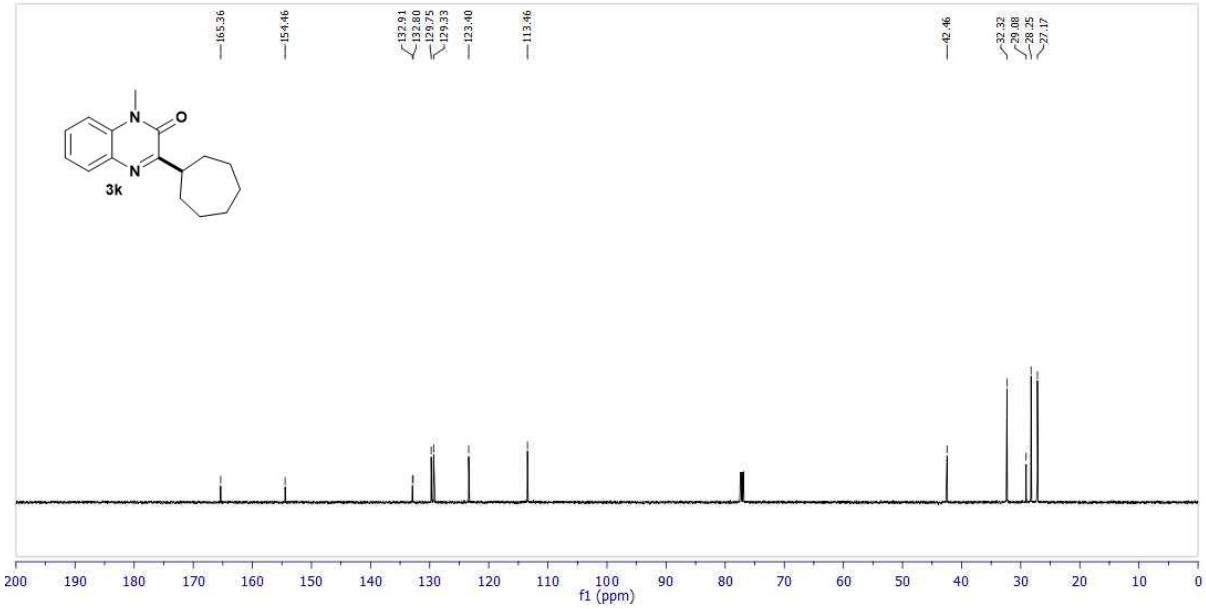
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3j**



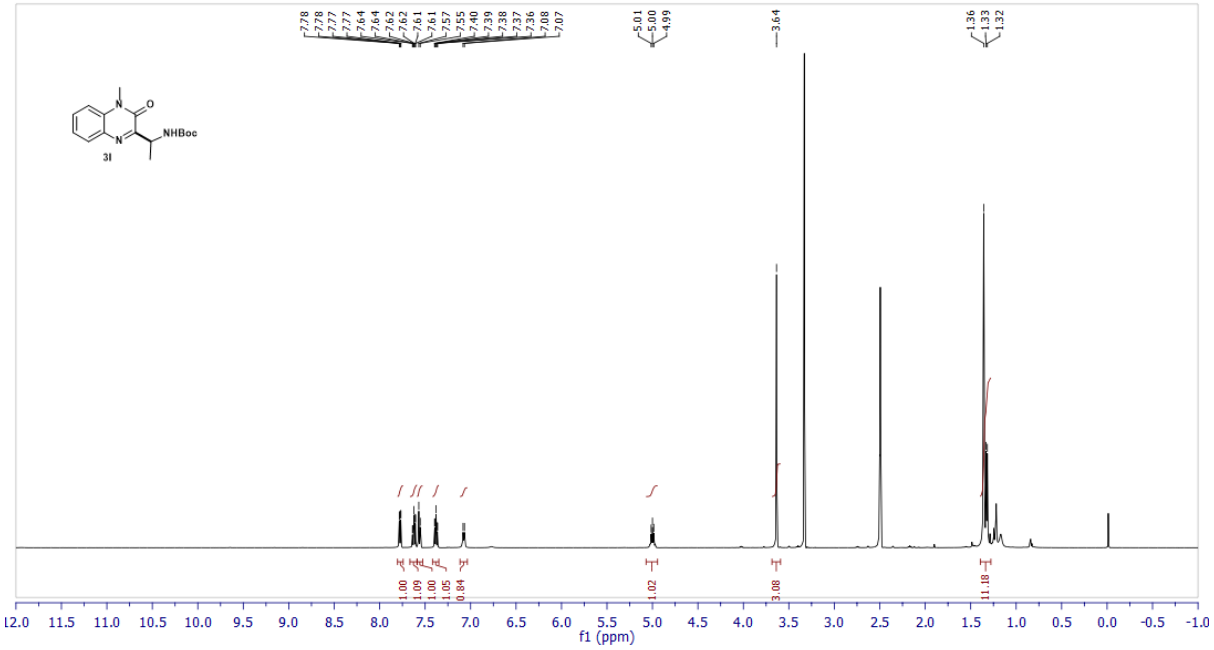
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3k**



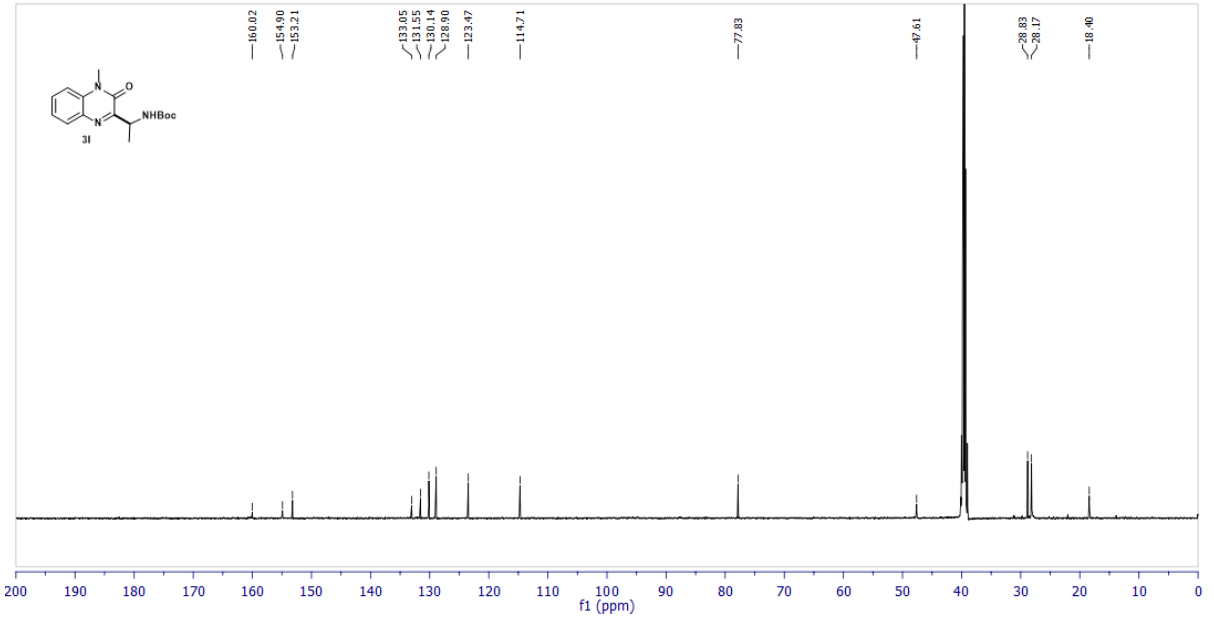
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3k**



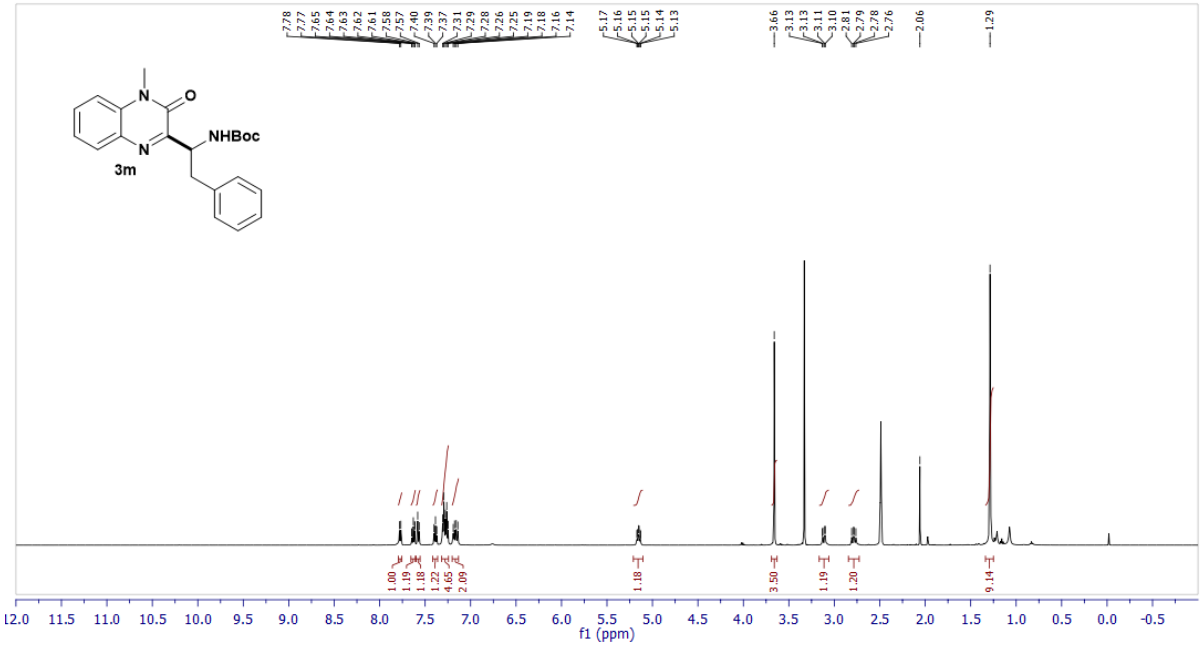
^{1}H NMR (500 MHz, DMSO) of compound **3l**



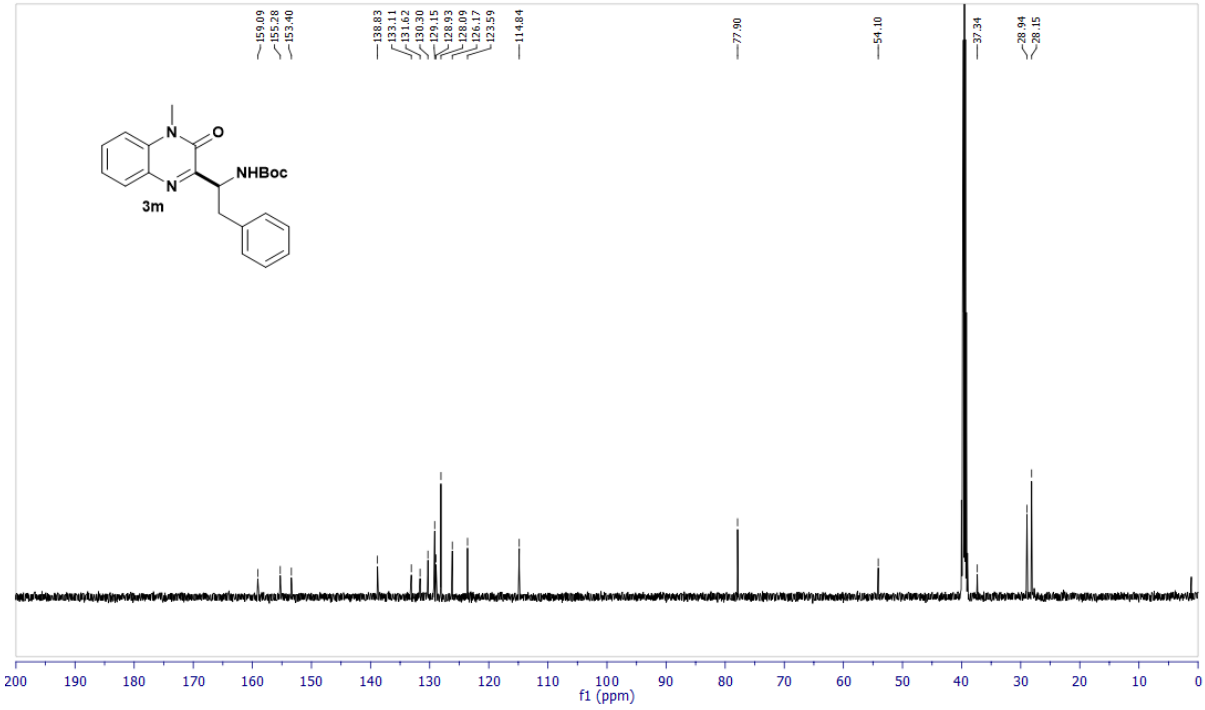
^{13}C NMR (126 MHz, DMSO) of compound **3l**



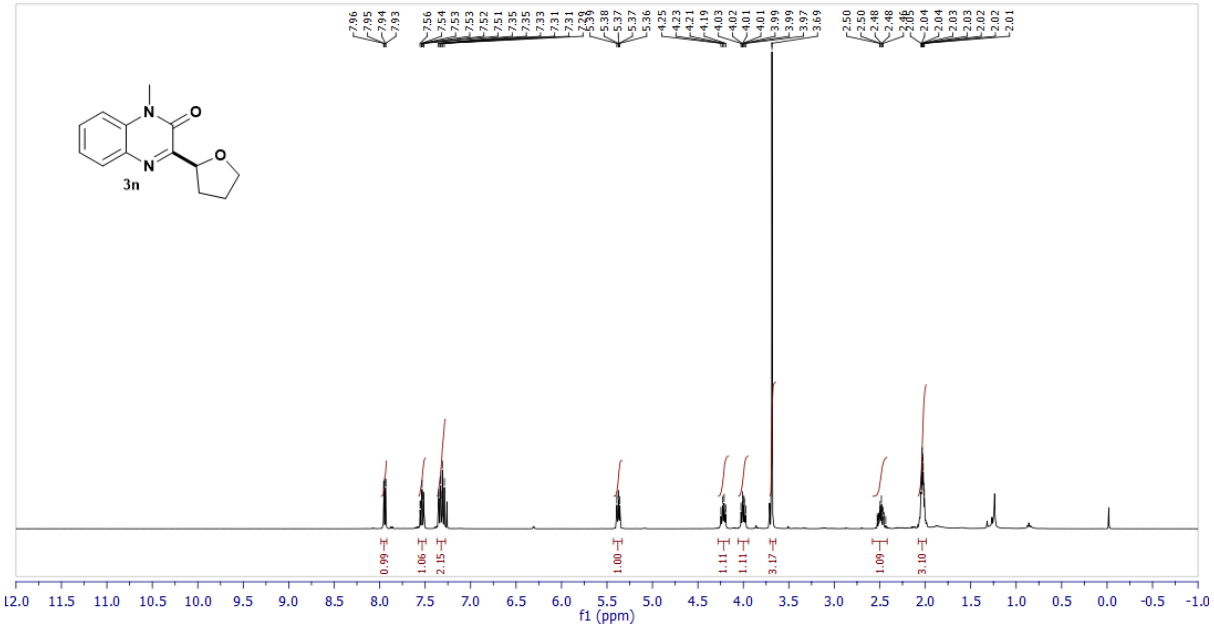
^{1}H NMR (500 MHz, DMSO) of compound **3m**



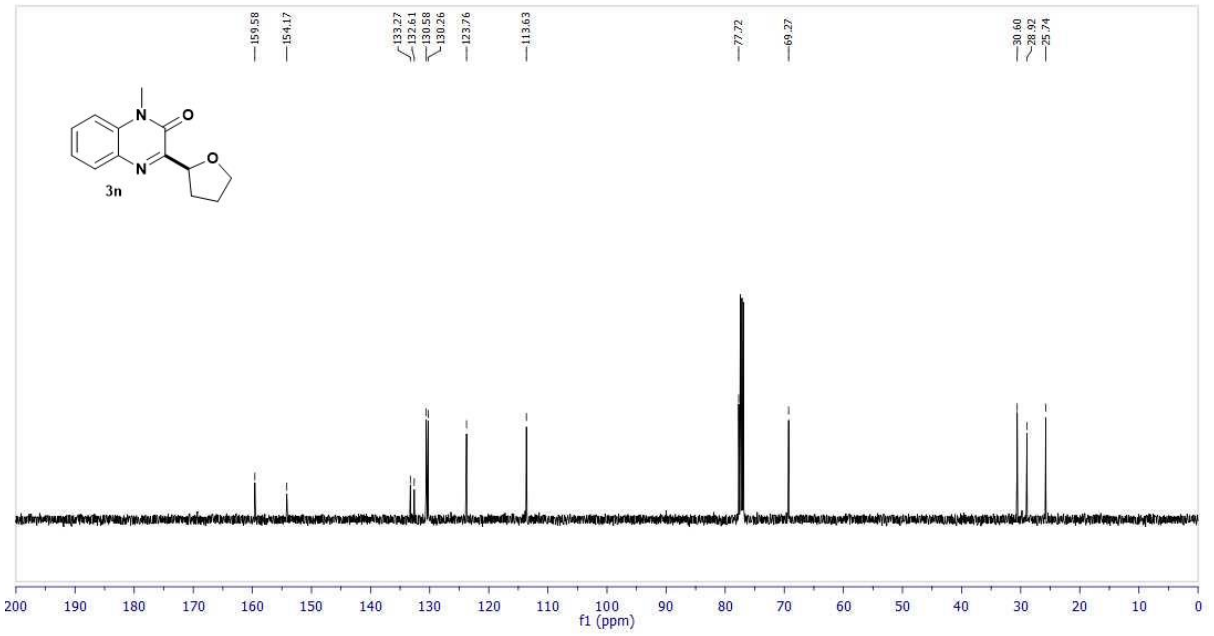
^{13}C NMR (126 MHz, DMSO) of compound **3m**



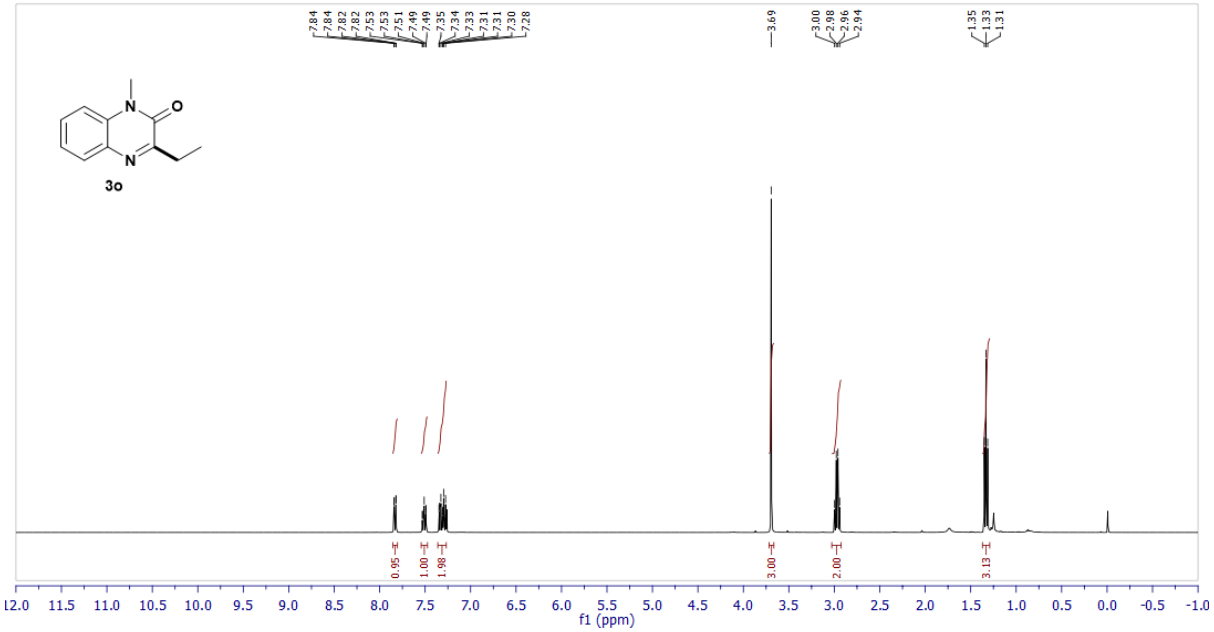
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3n**



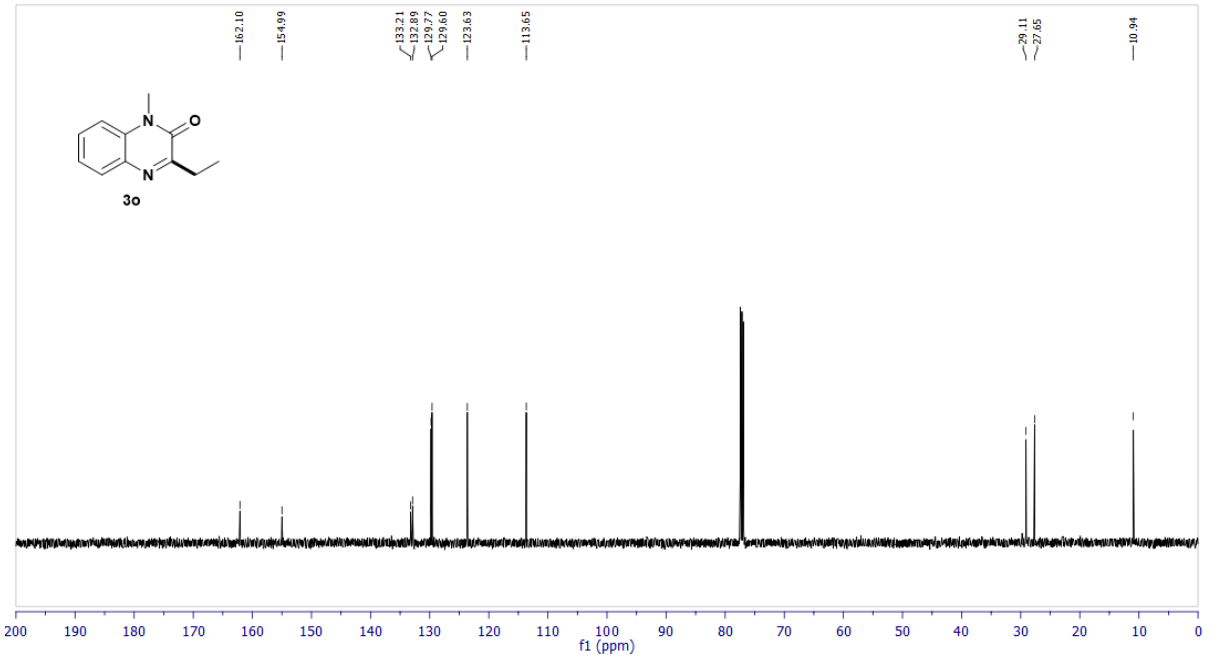
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3n**



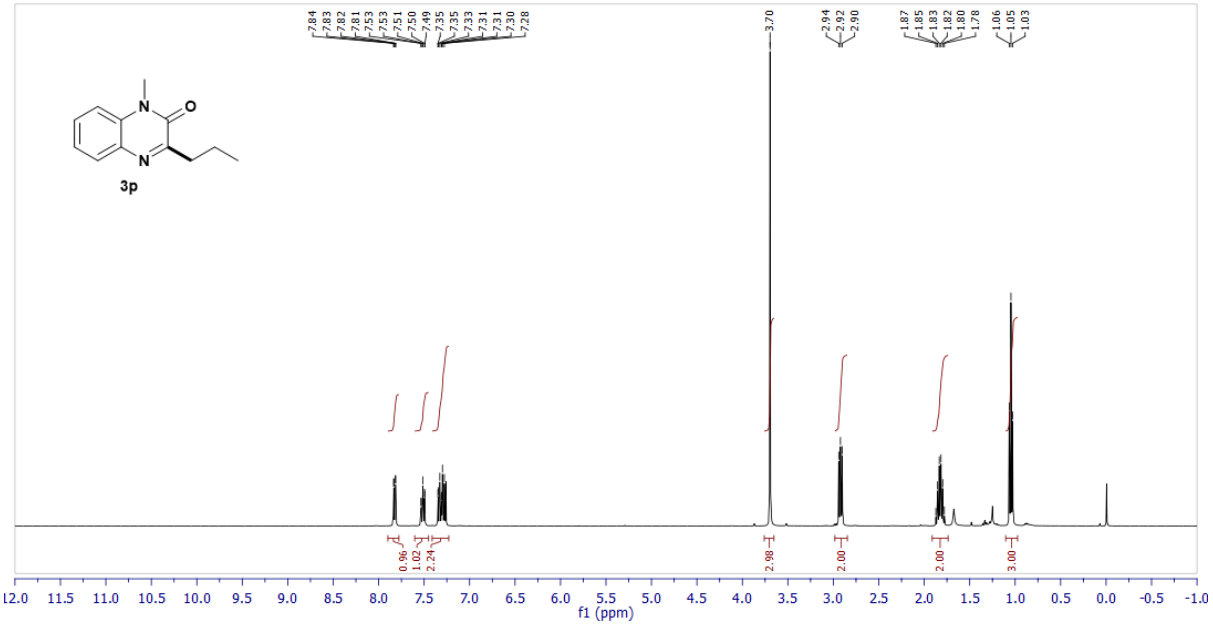
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3o**



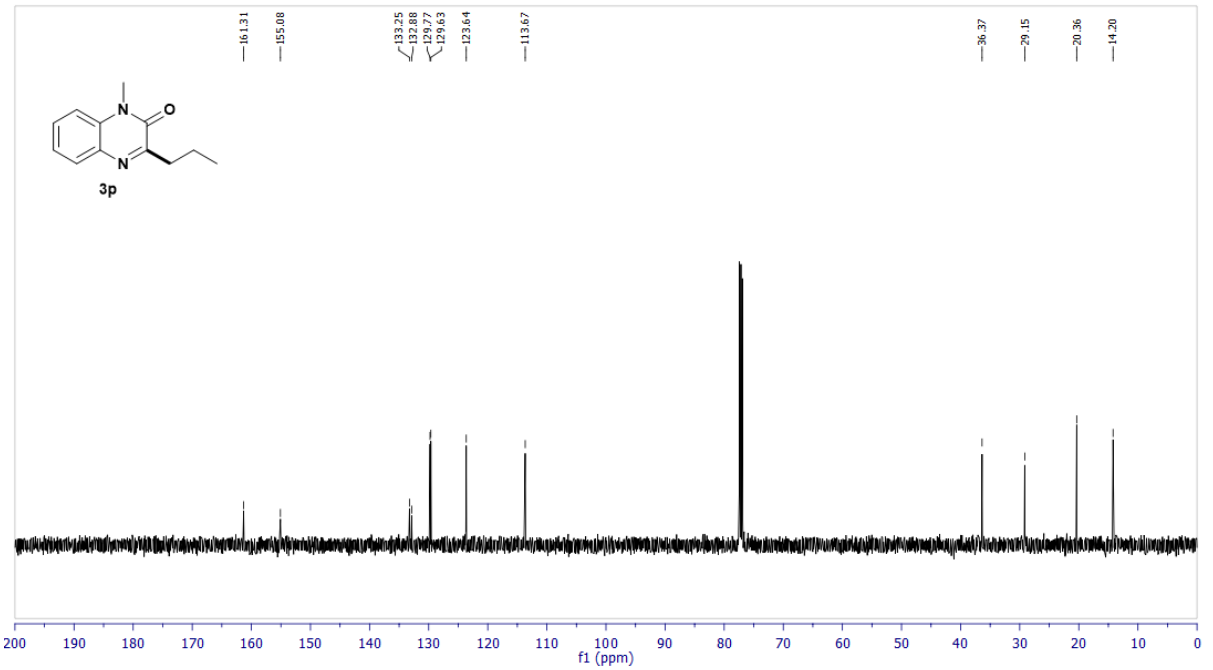
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3o**



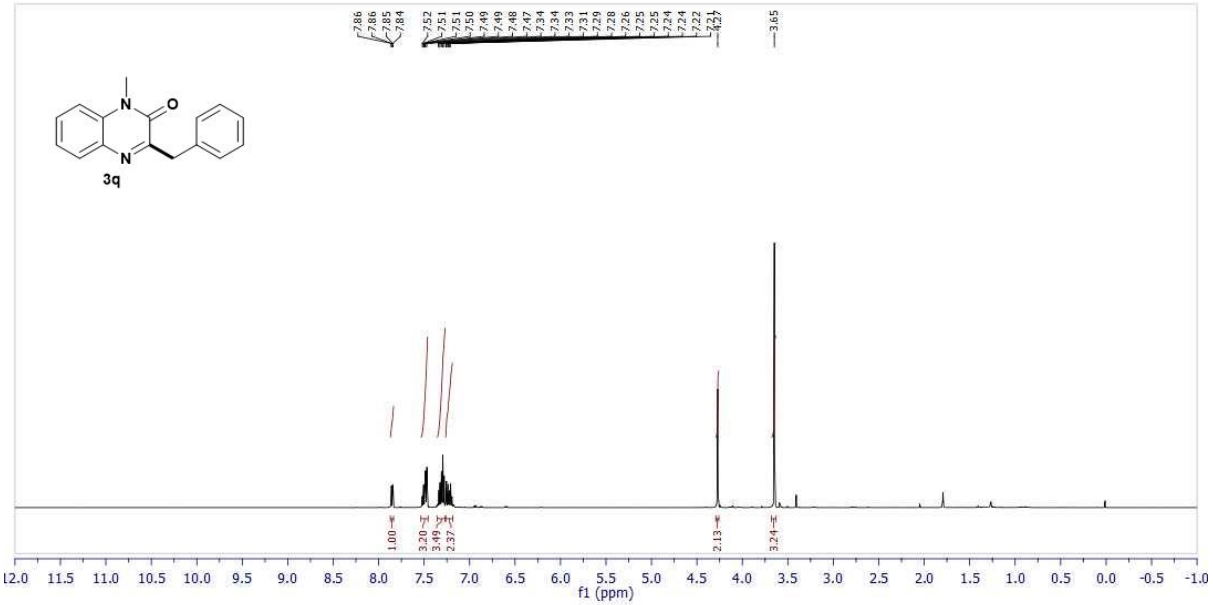
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3p**



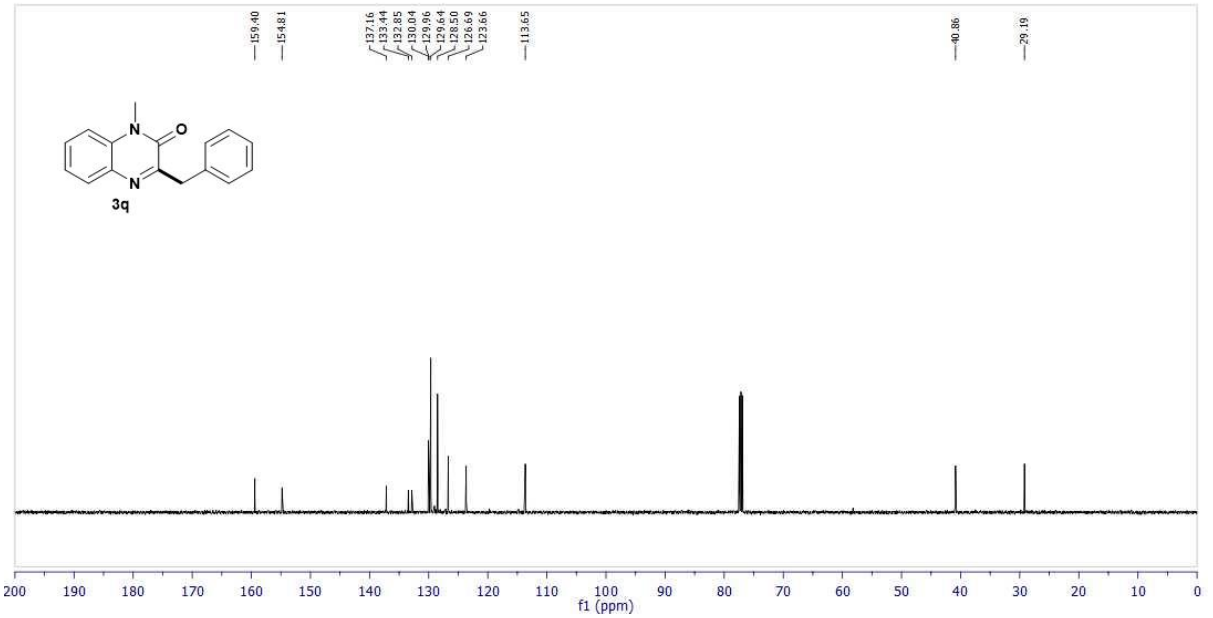
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3p**



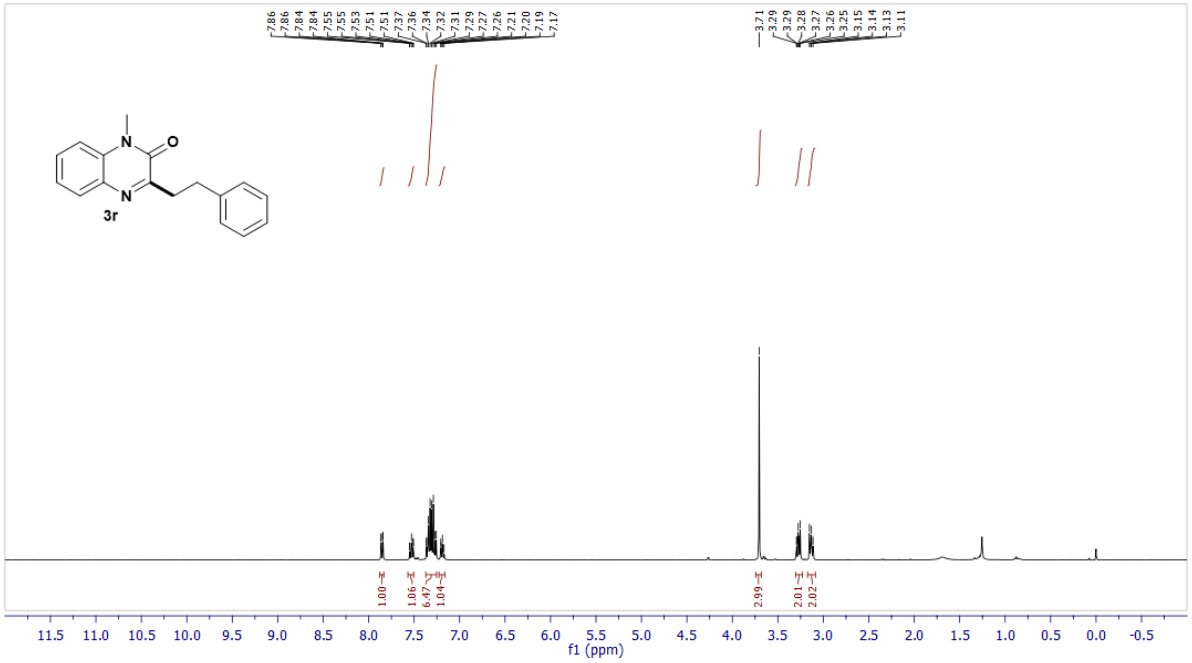
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3q**



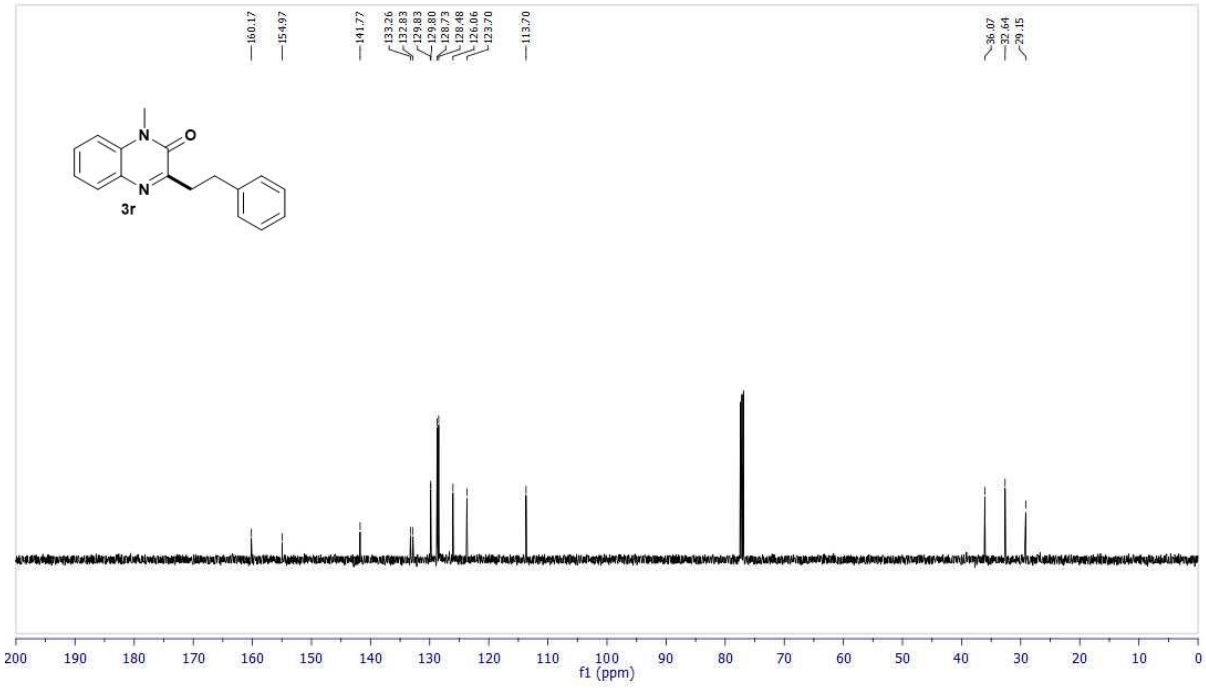
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3q**



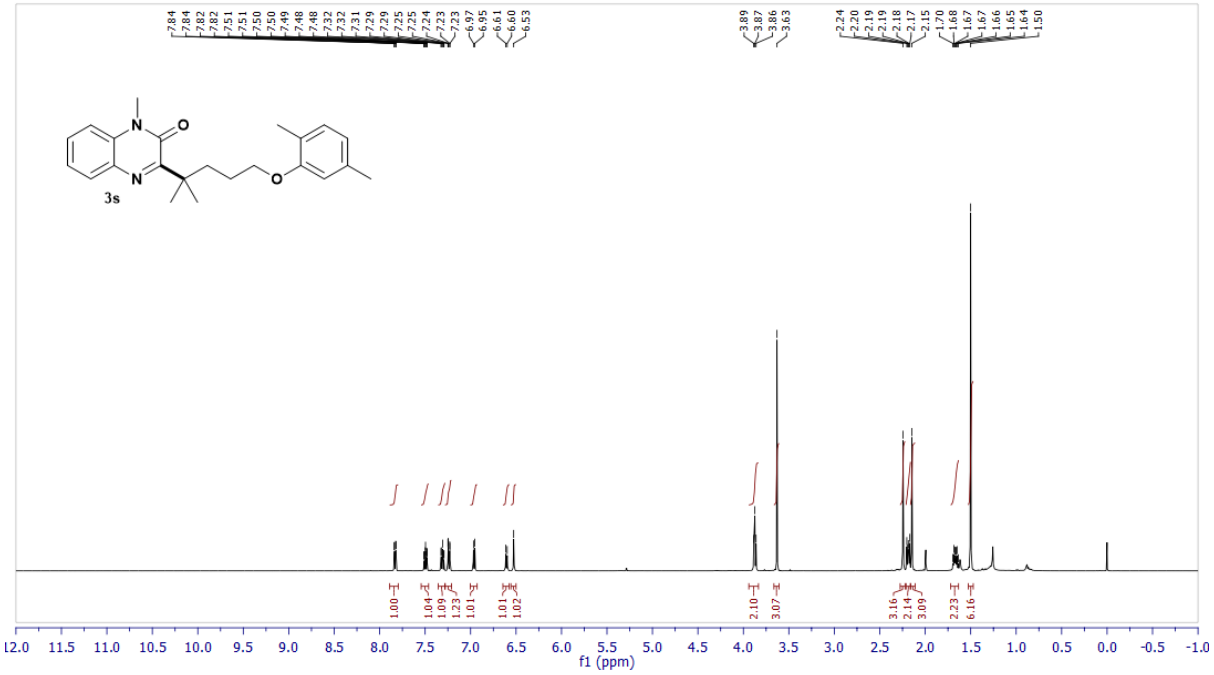
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3r**



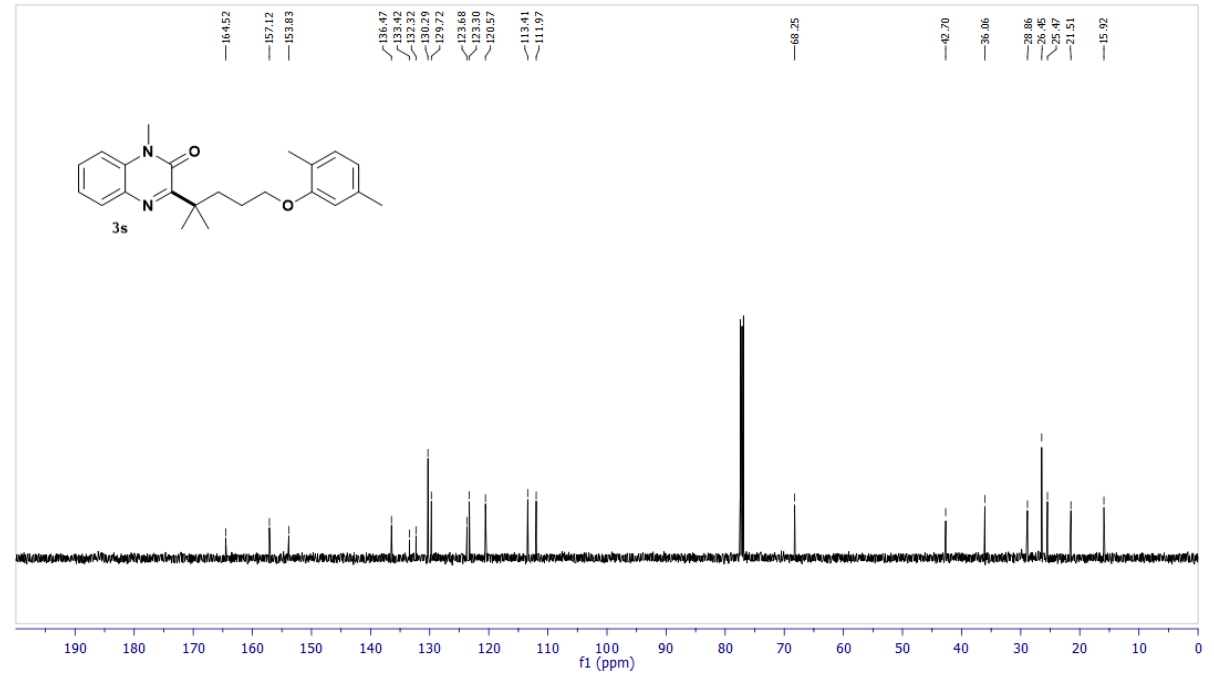
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3r**



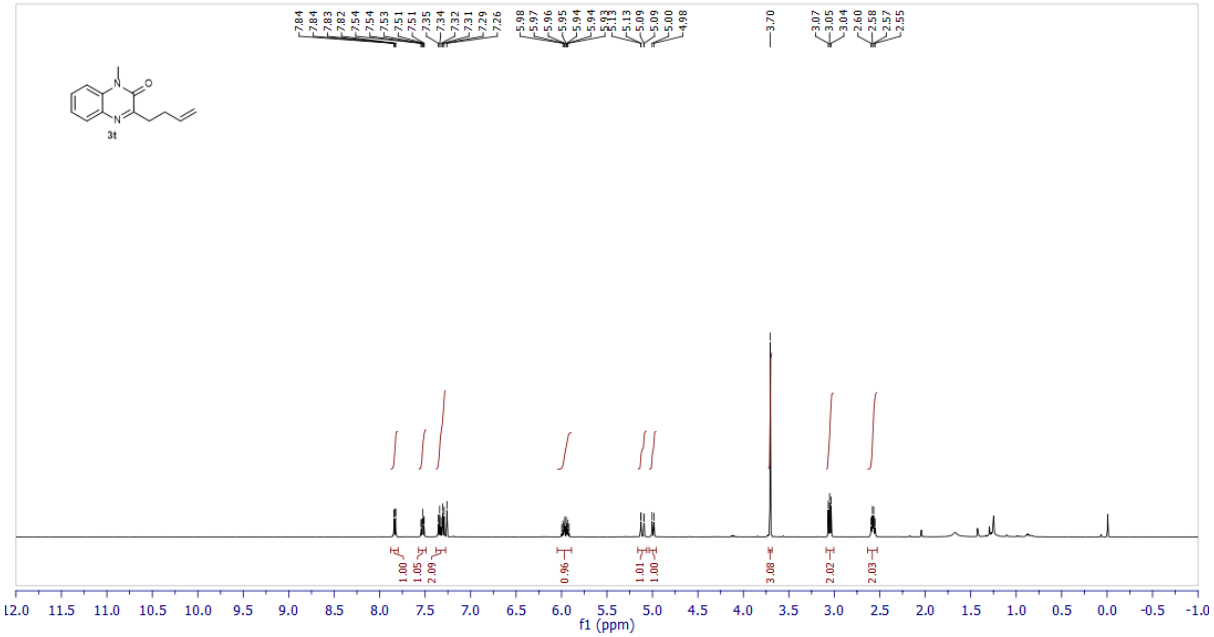
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3s**



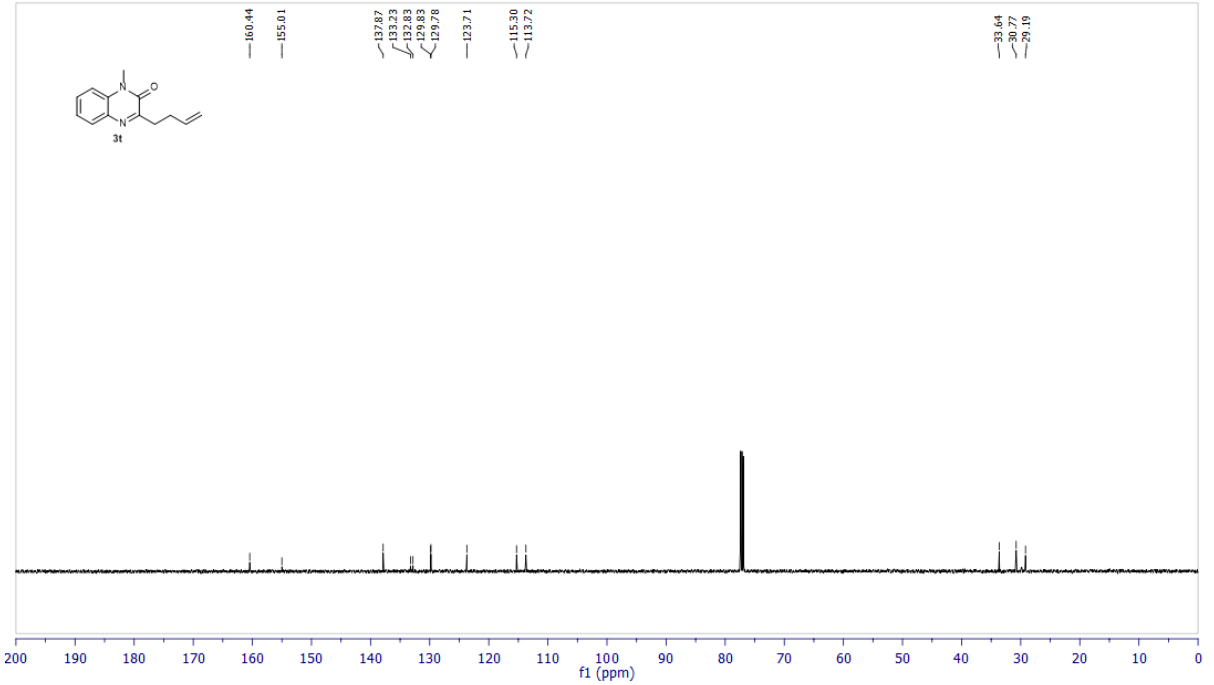
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3s**



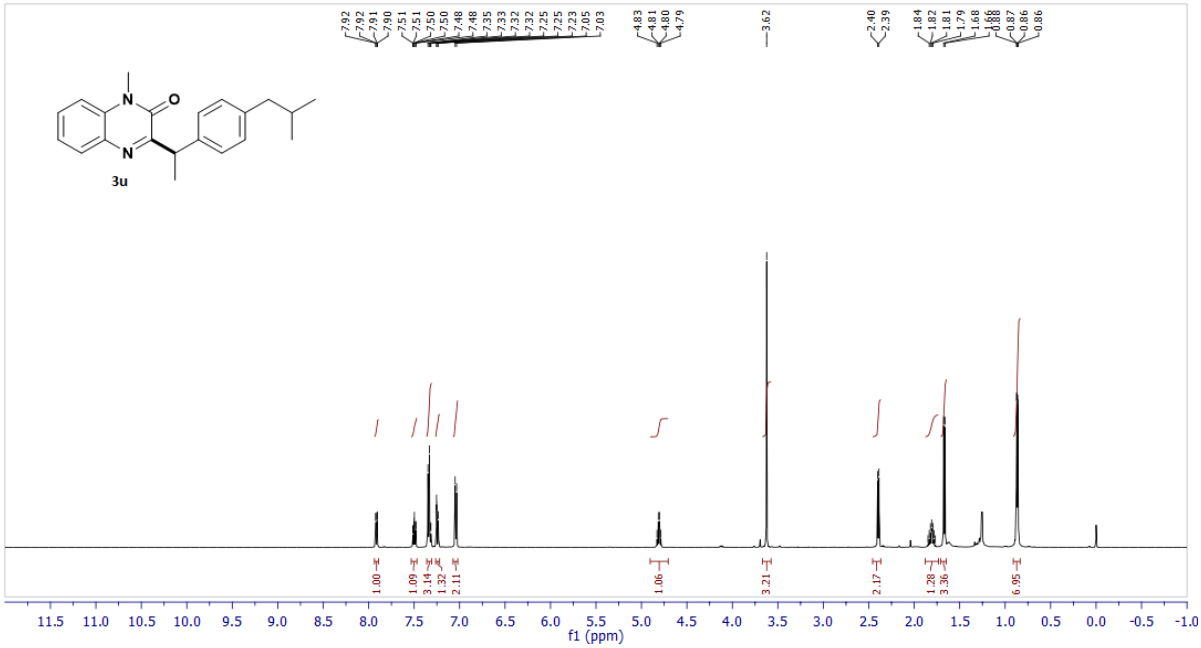
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3t**



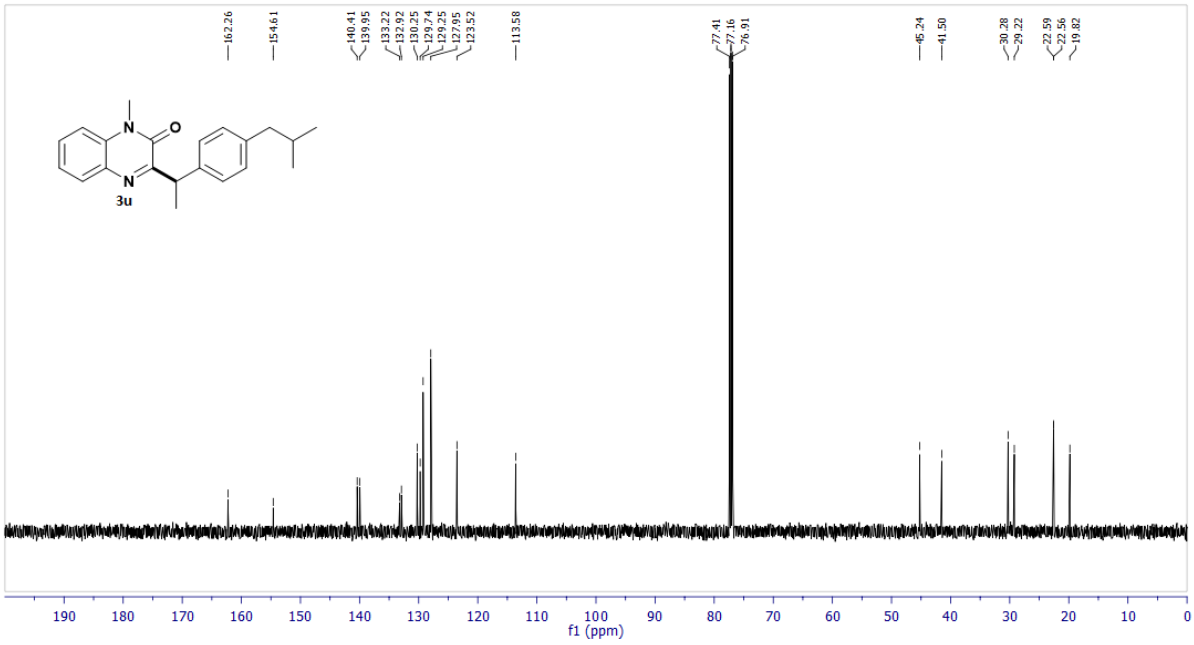
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3t**



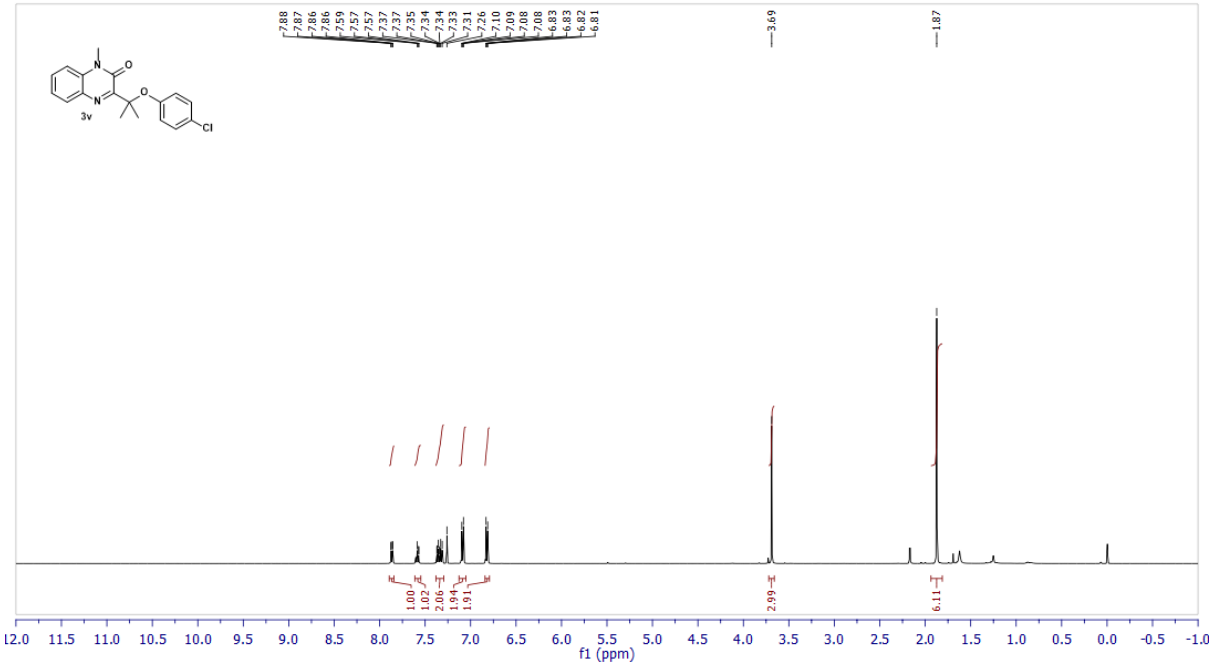
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3u**



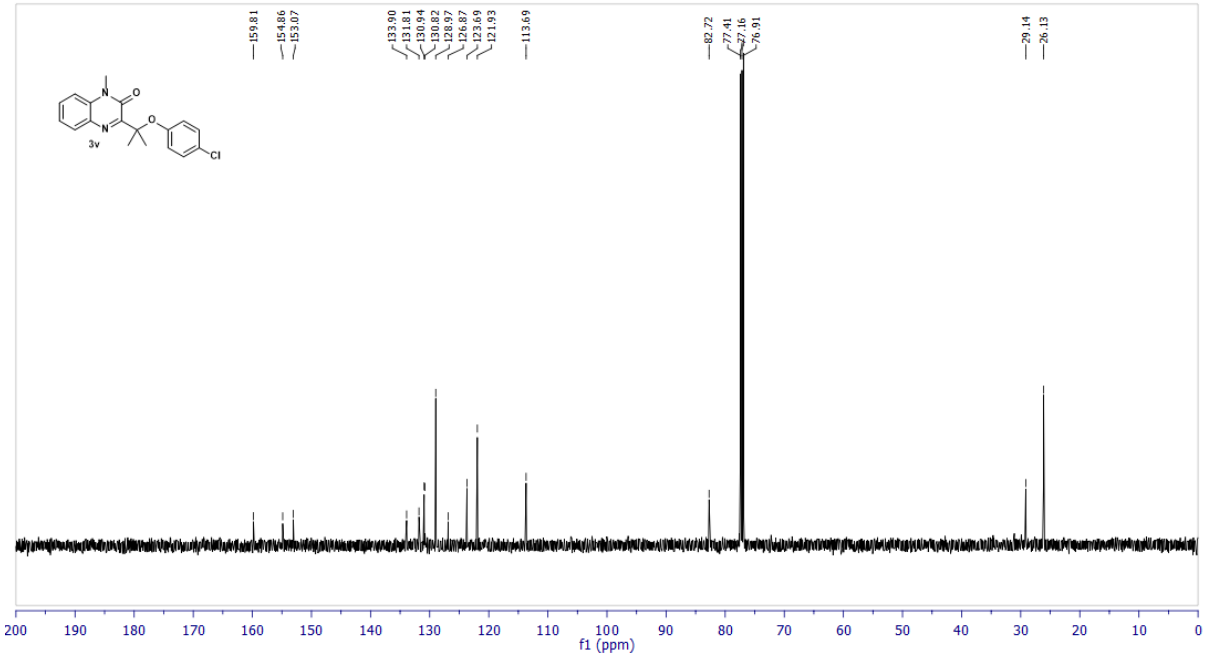
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3u**



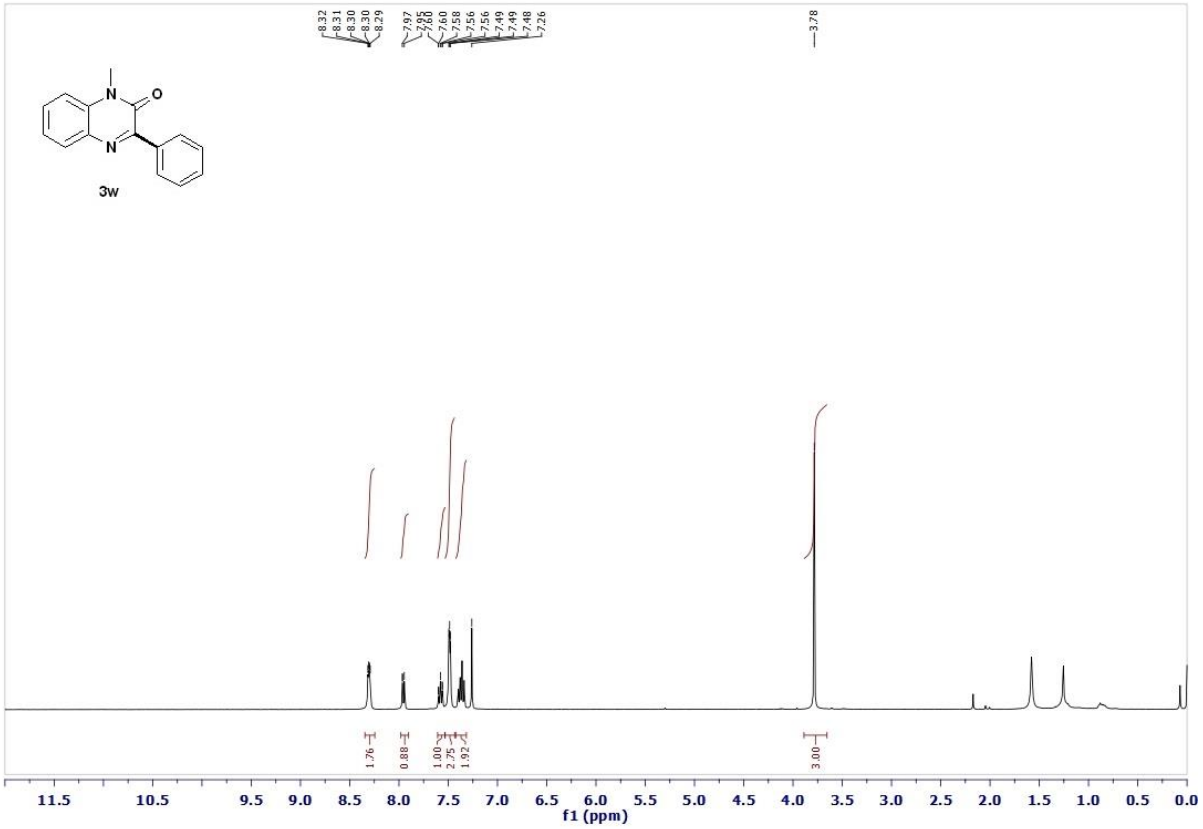
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3v**



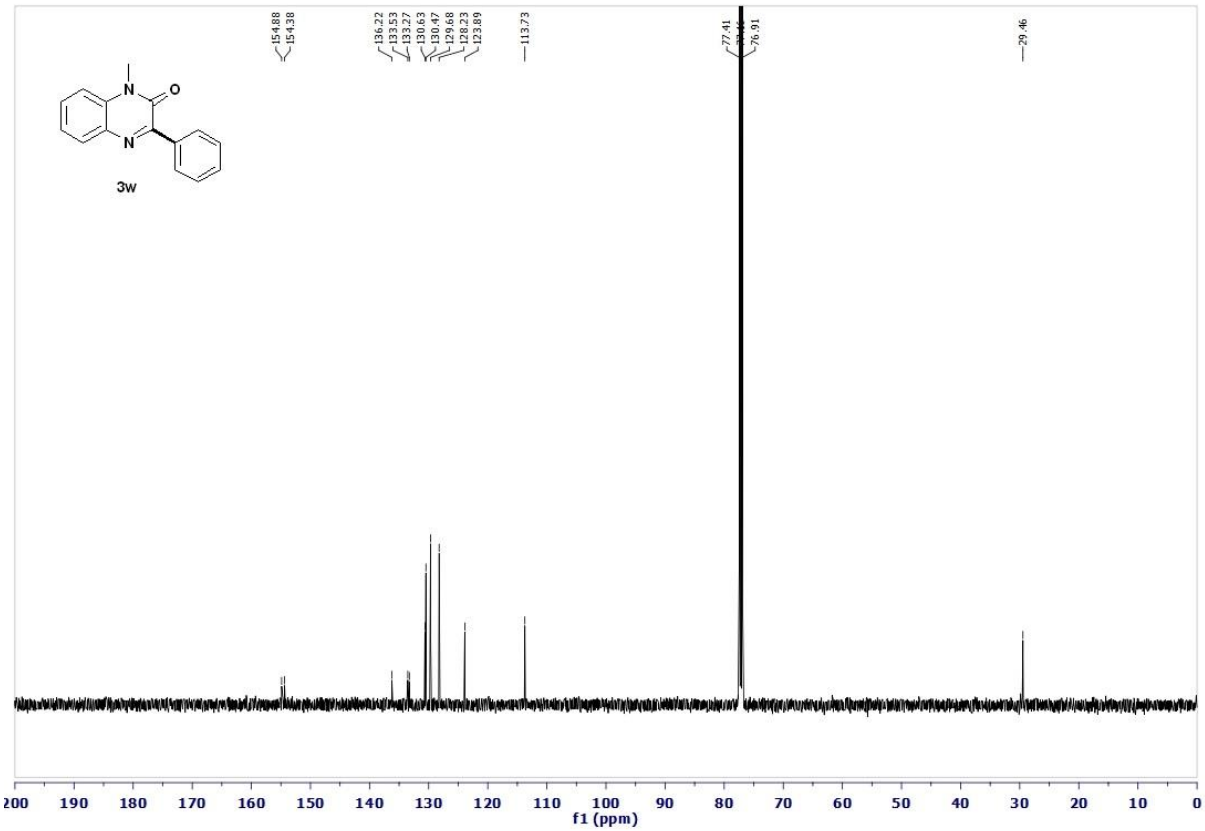
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3v**



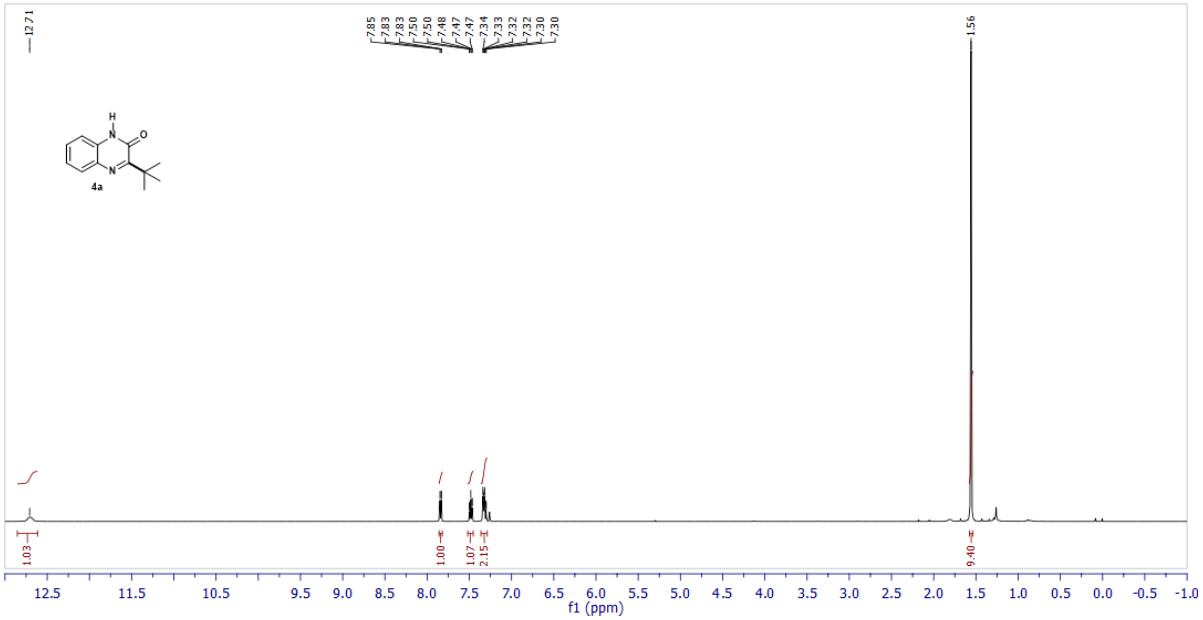
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3w**



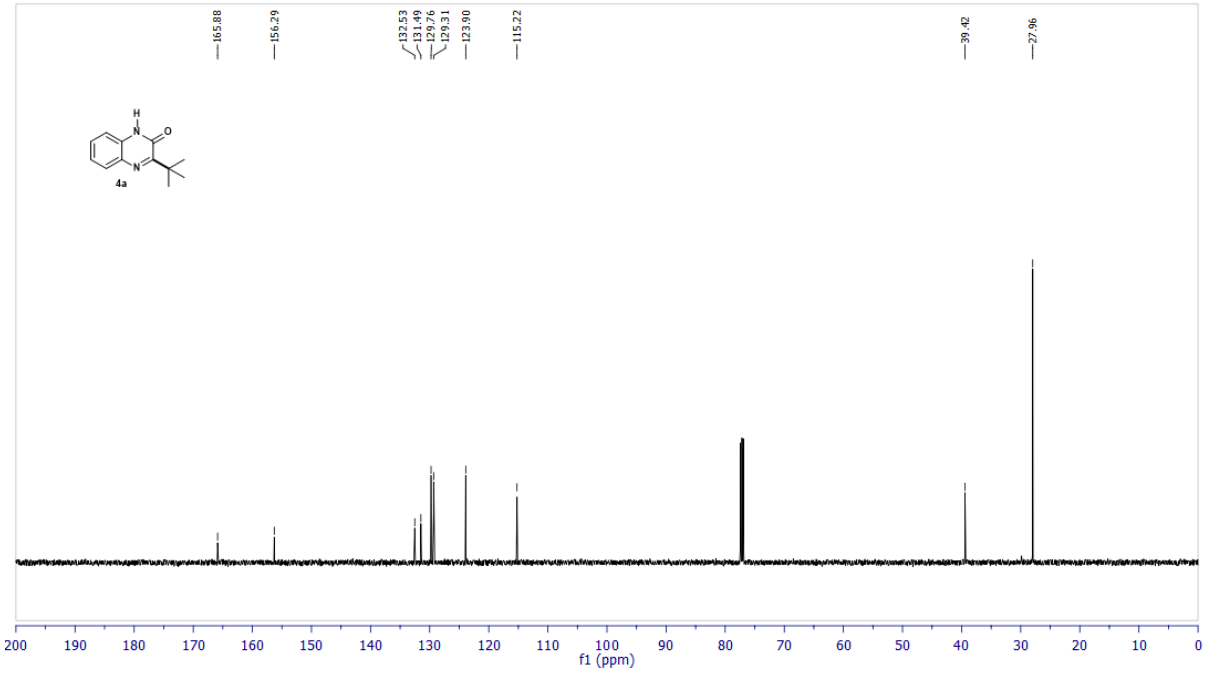
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3w**



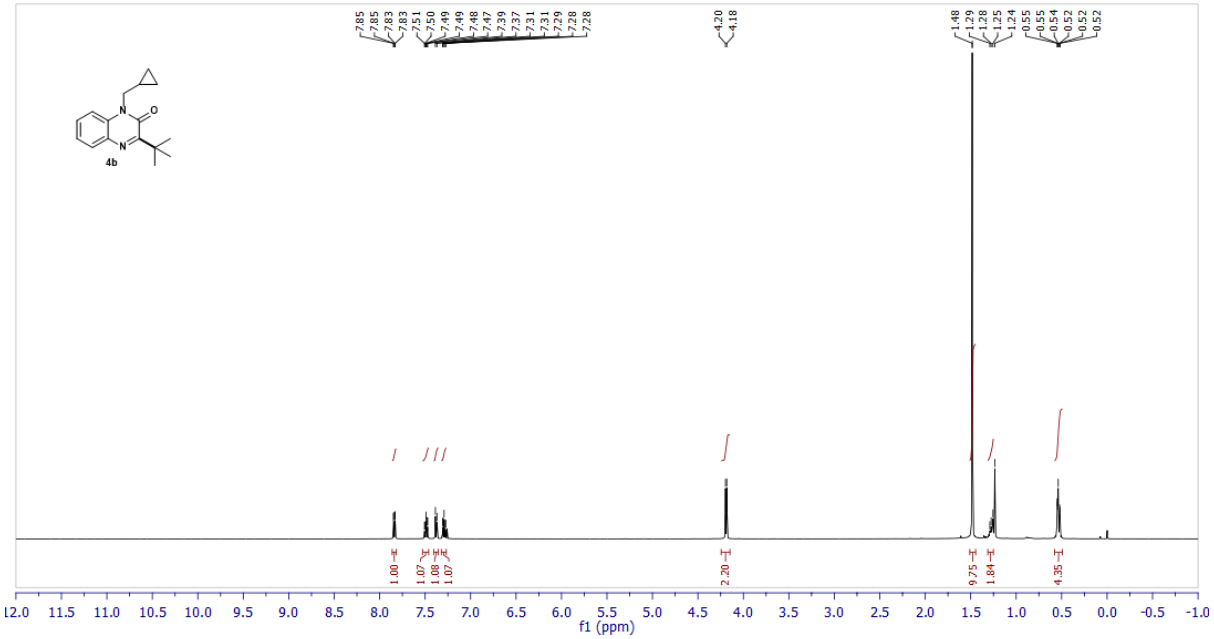
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4a**



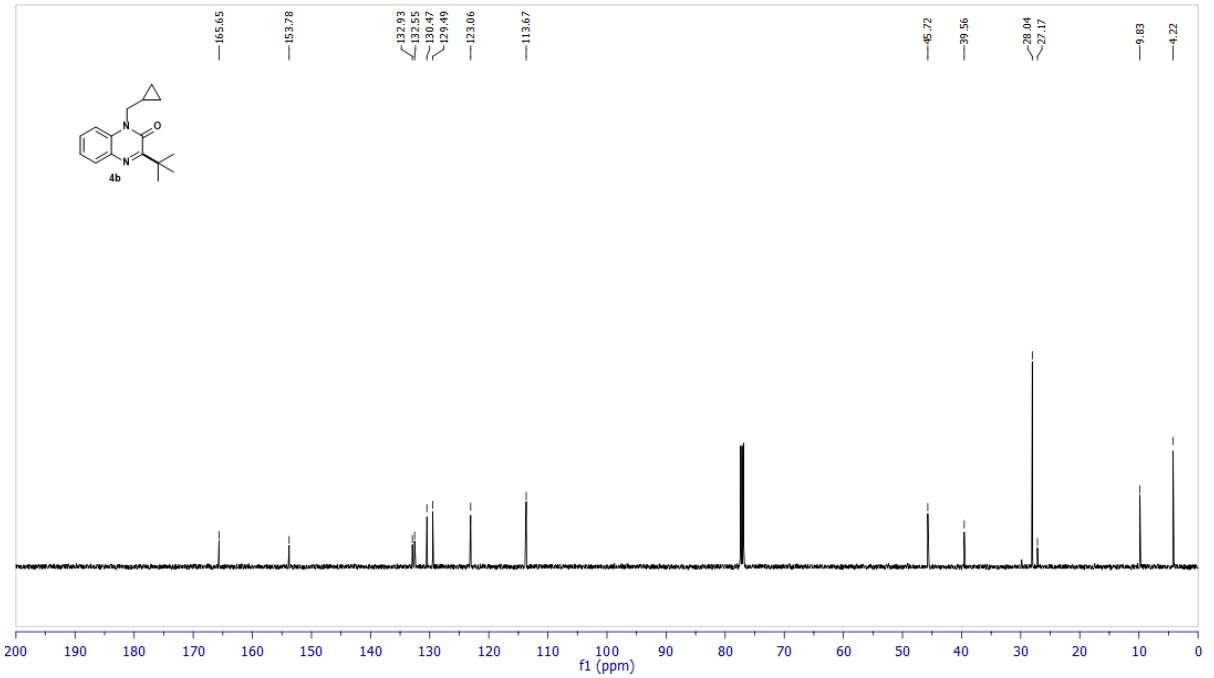
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4a**



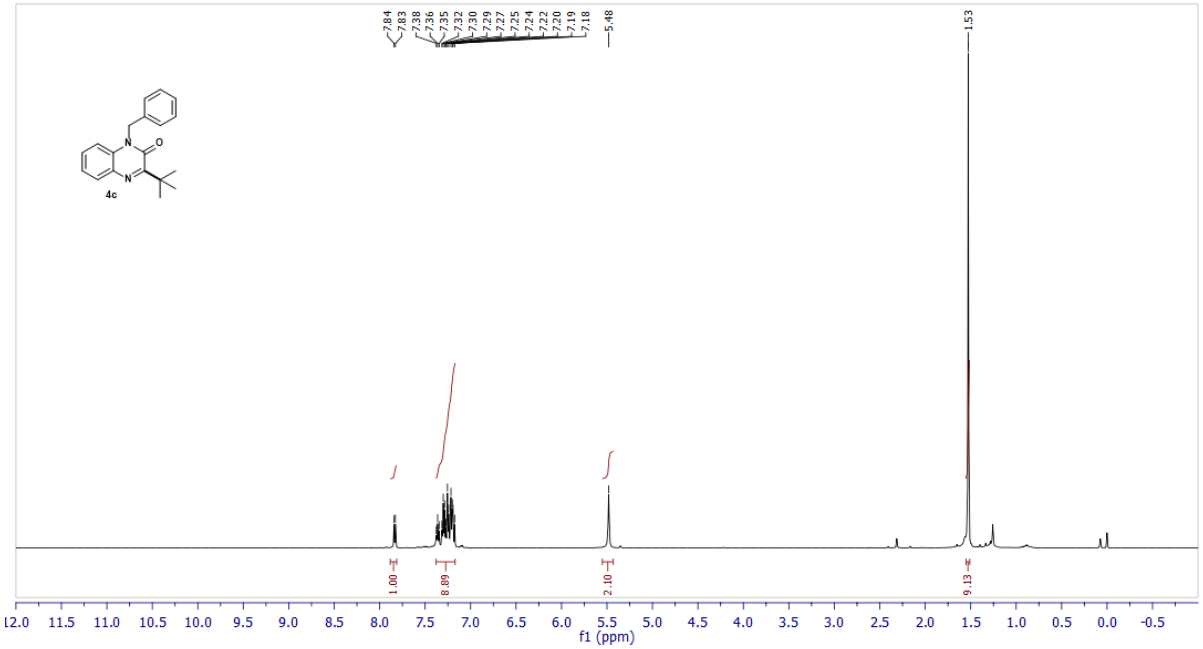
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4b**



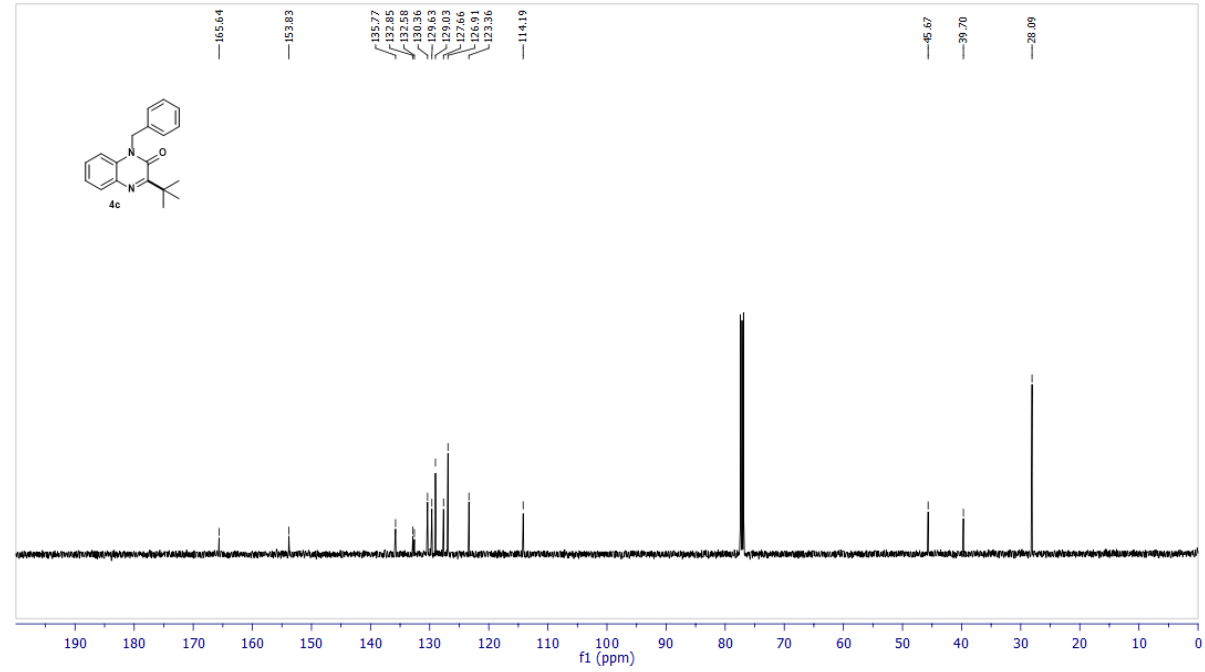
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4b**



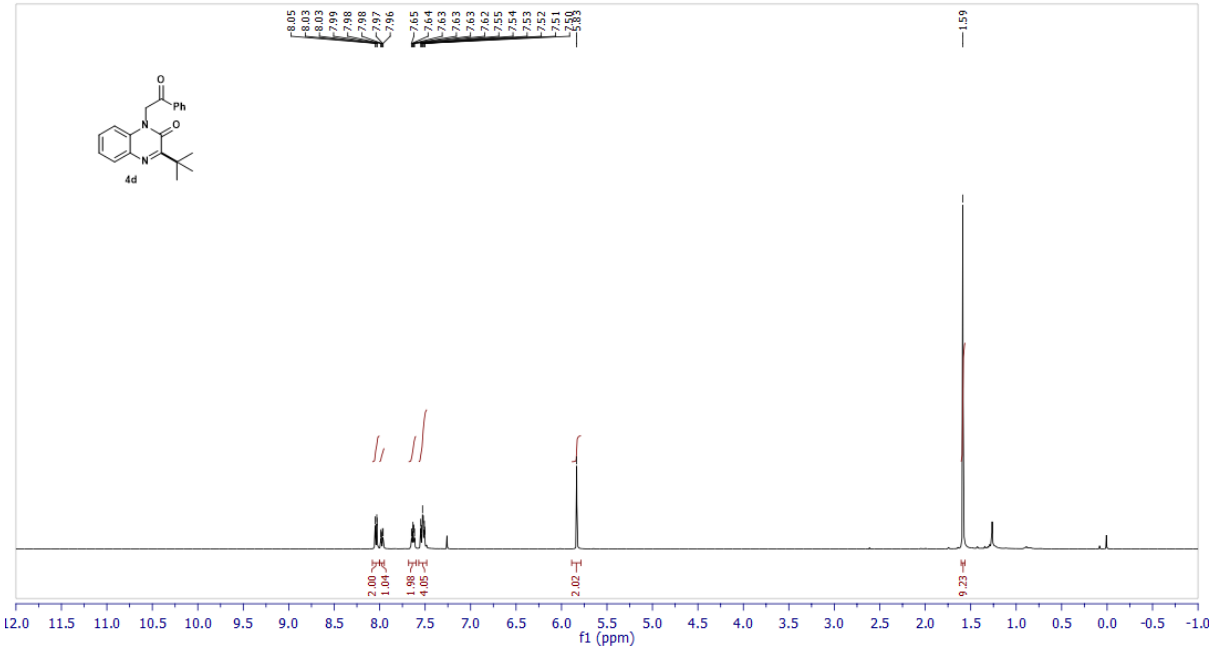
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4c**



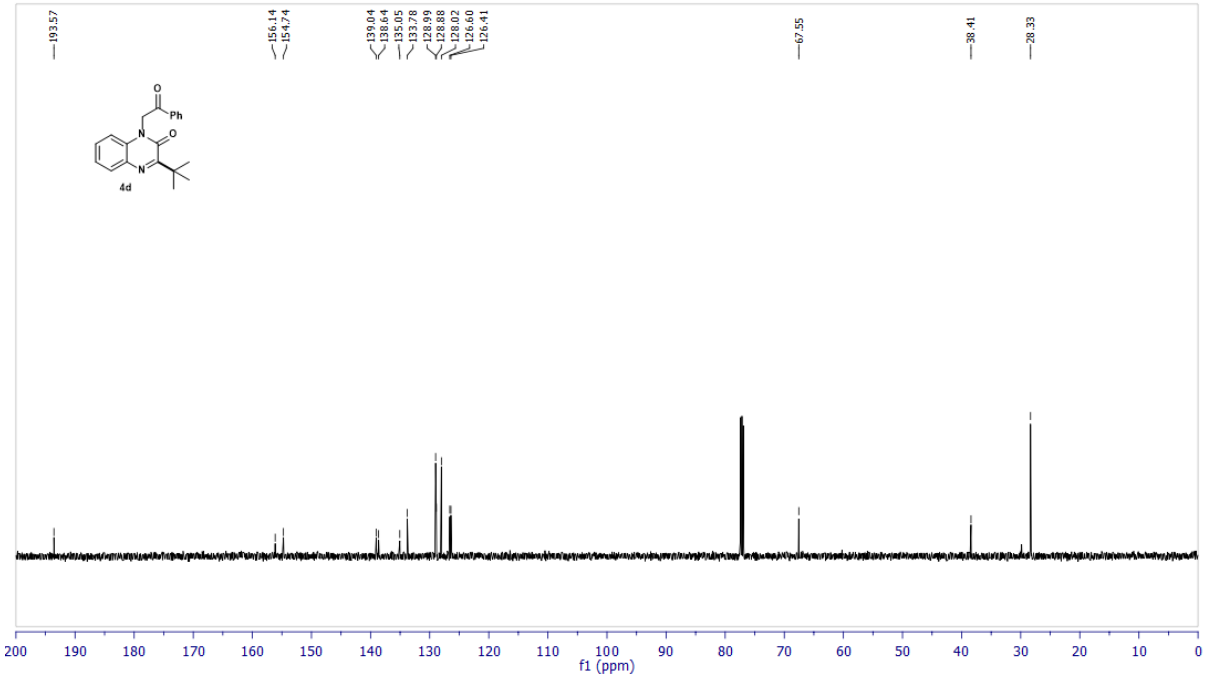
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4c**



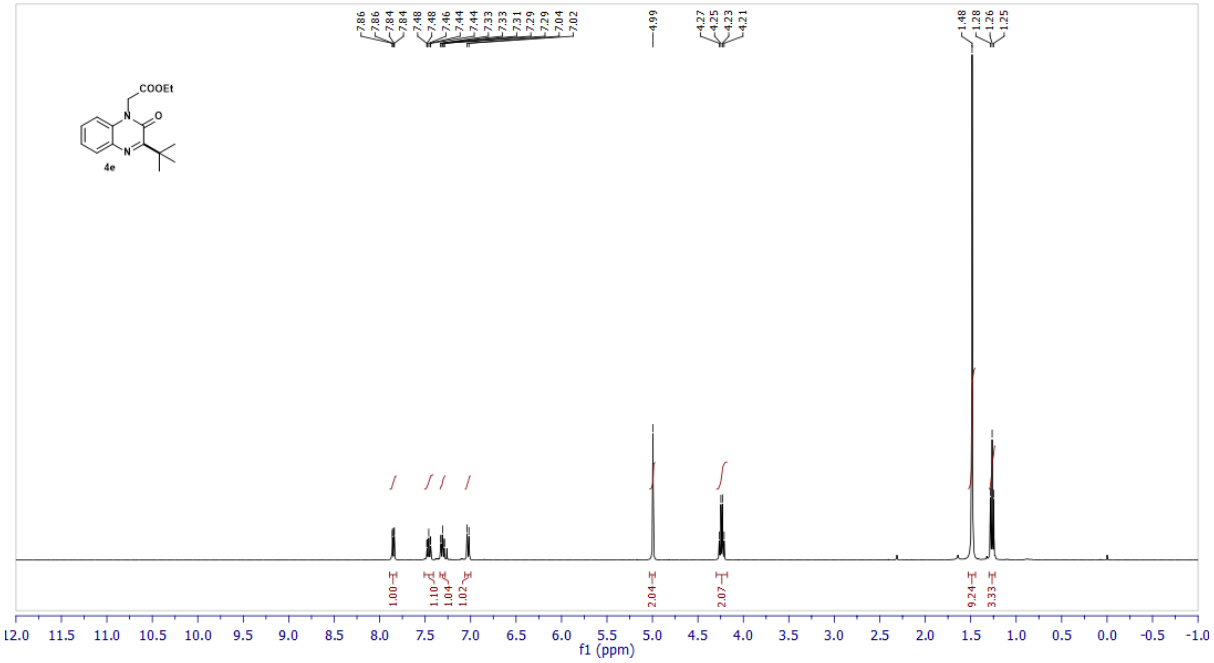
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4d**



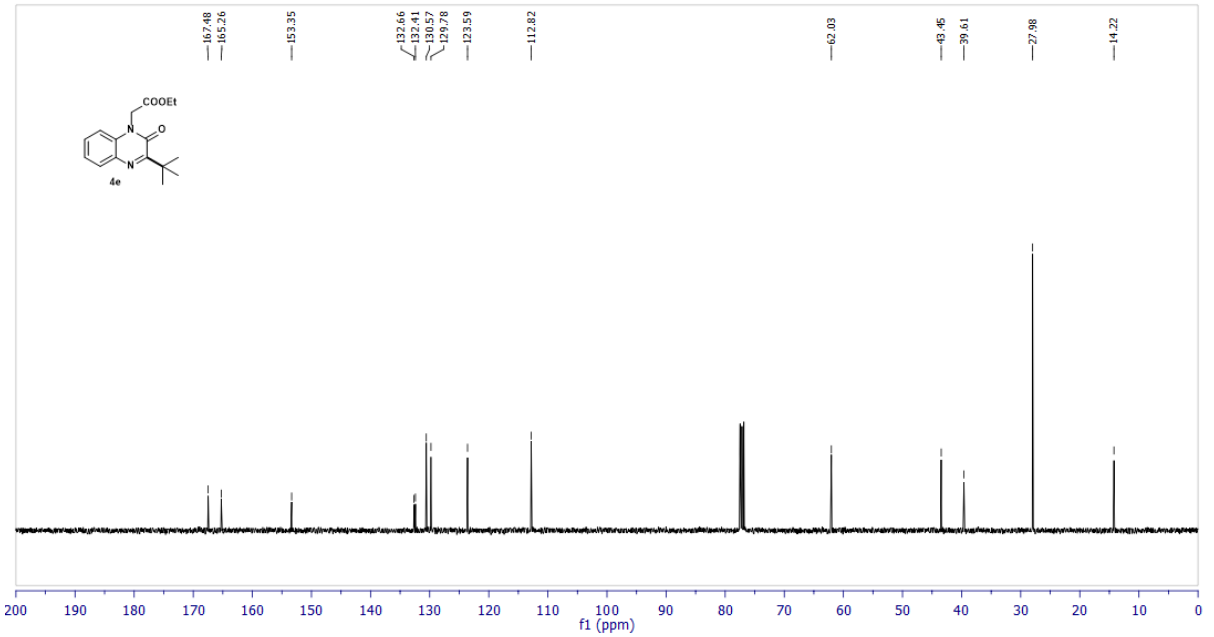
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4d**



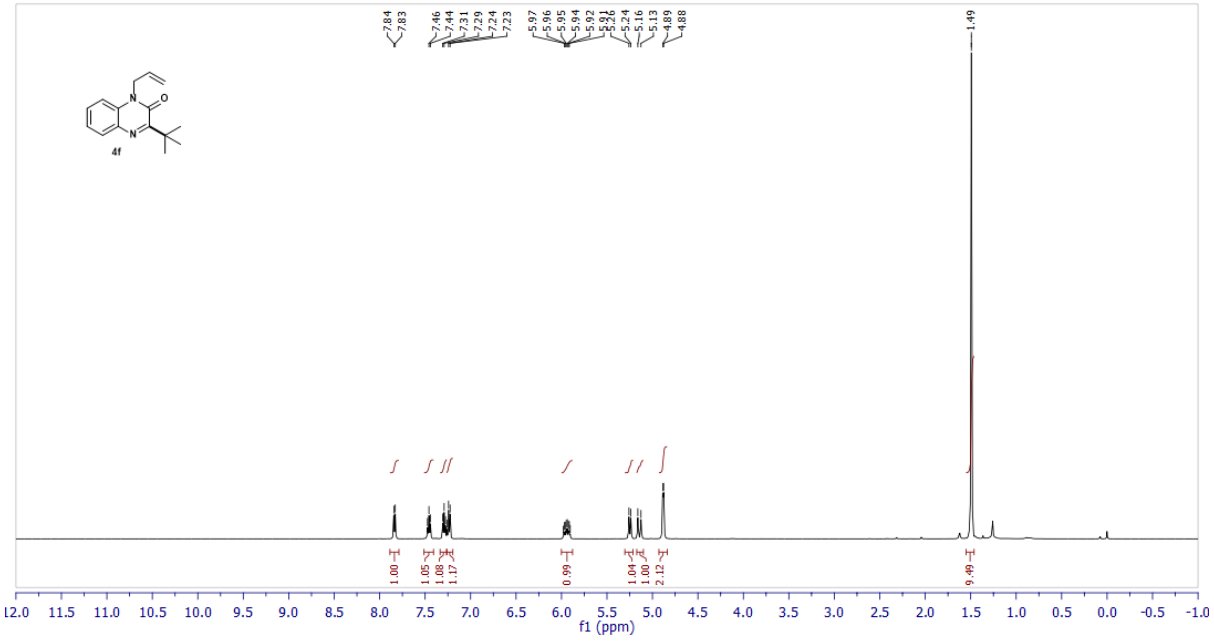
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4e**



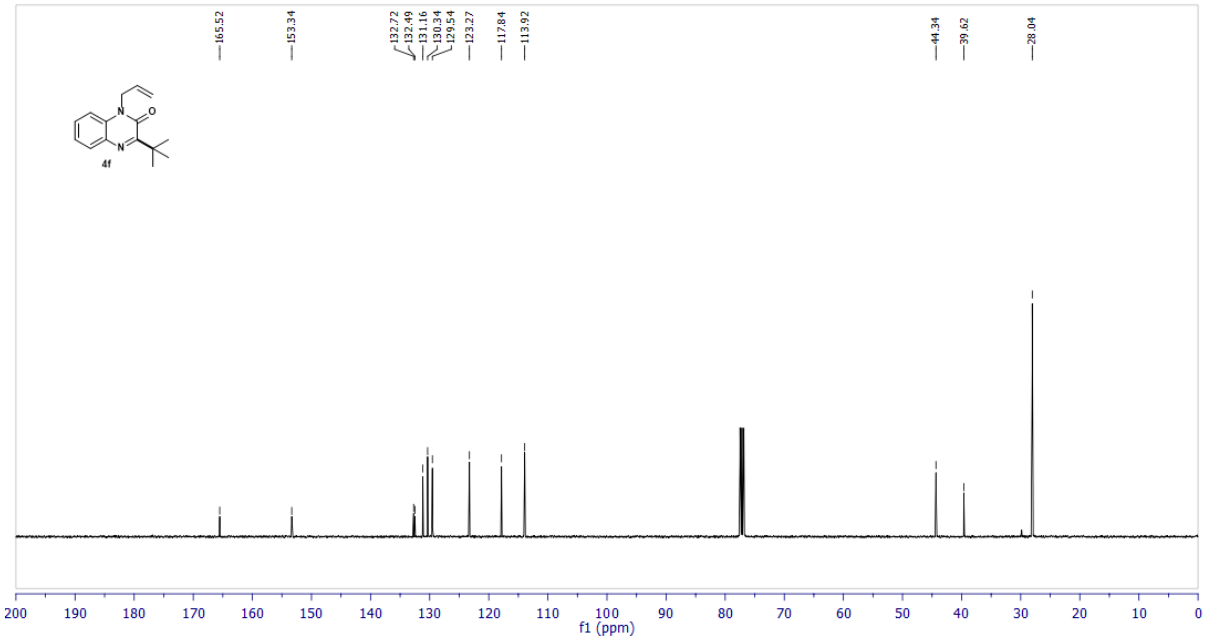
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4e**



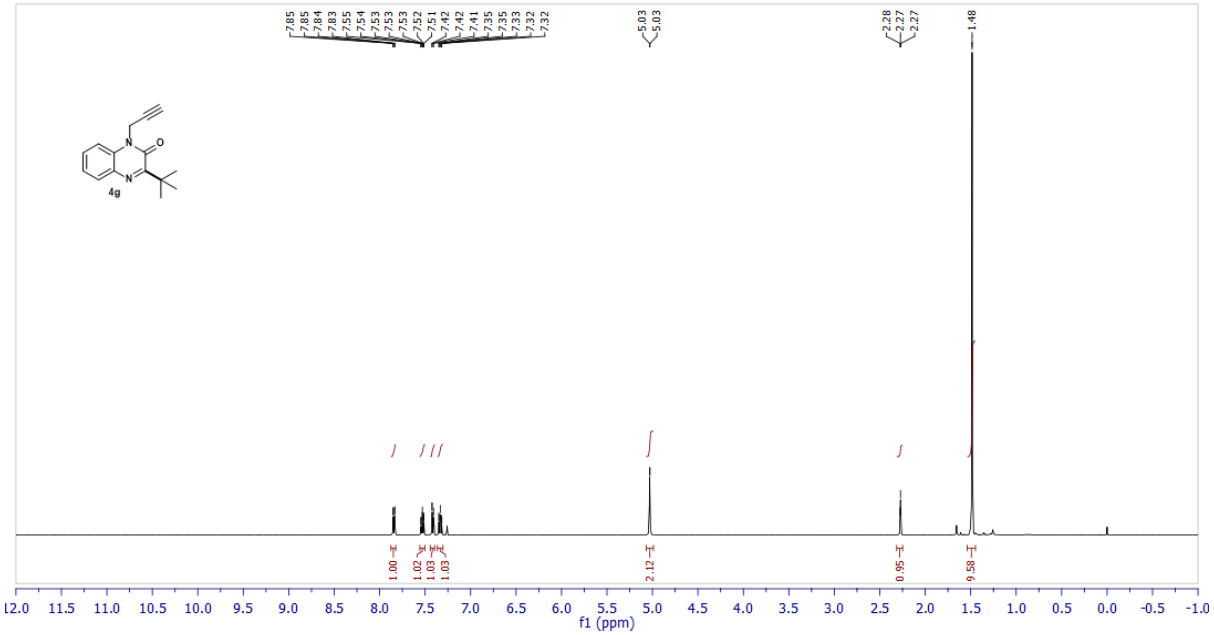
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4f**



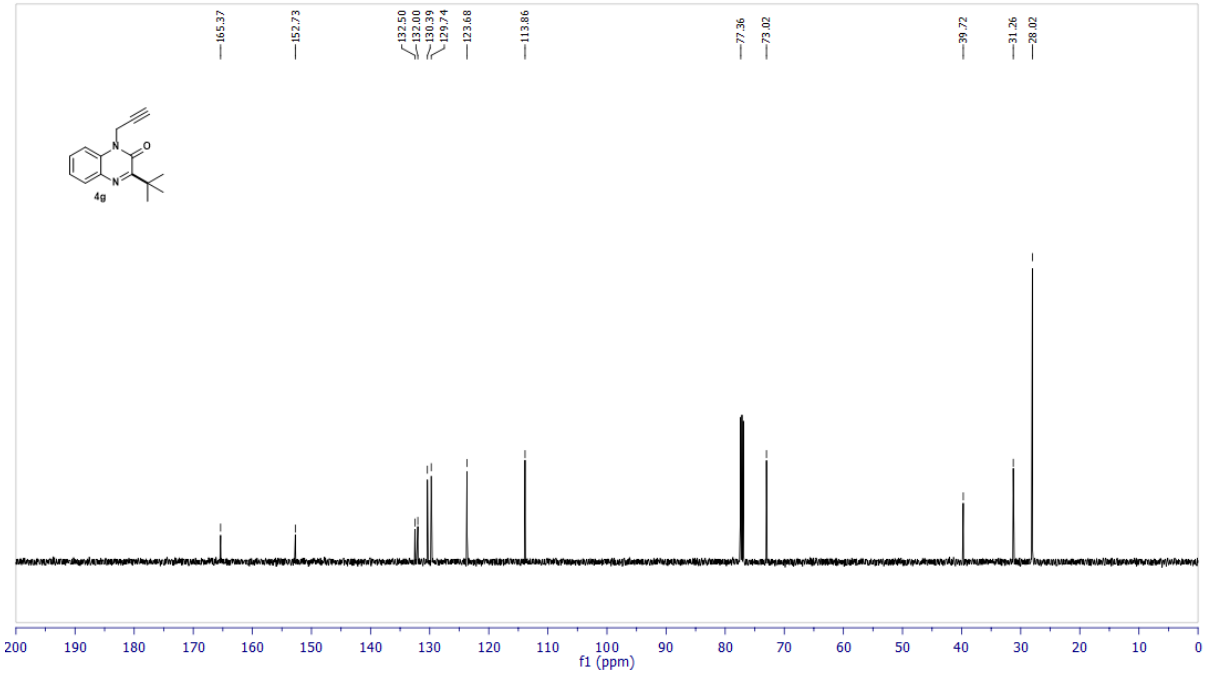
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4f**



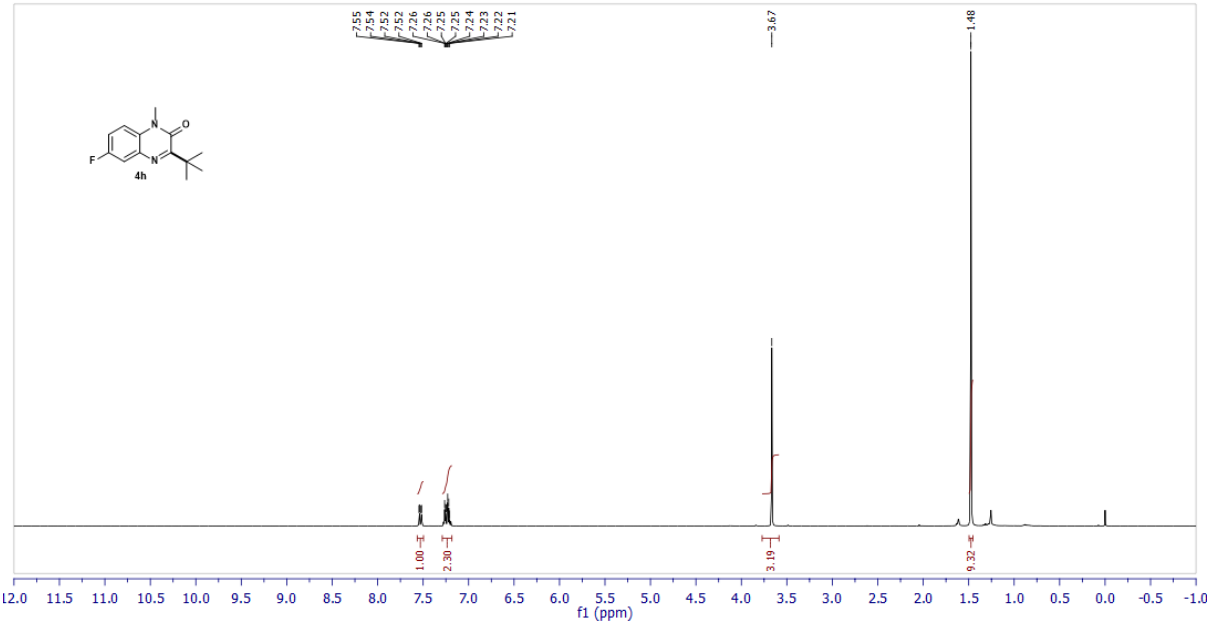
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4g**



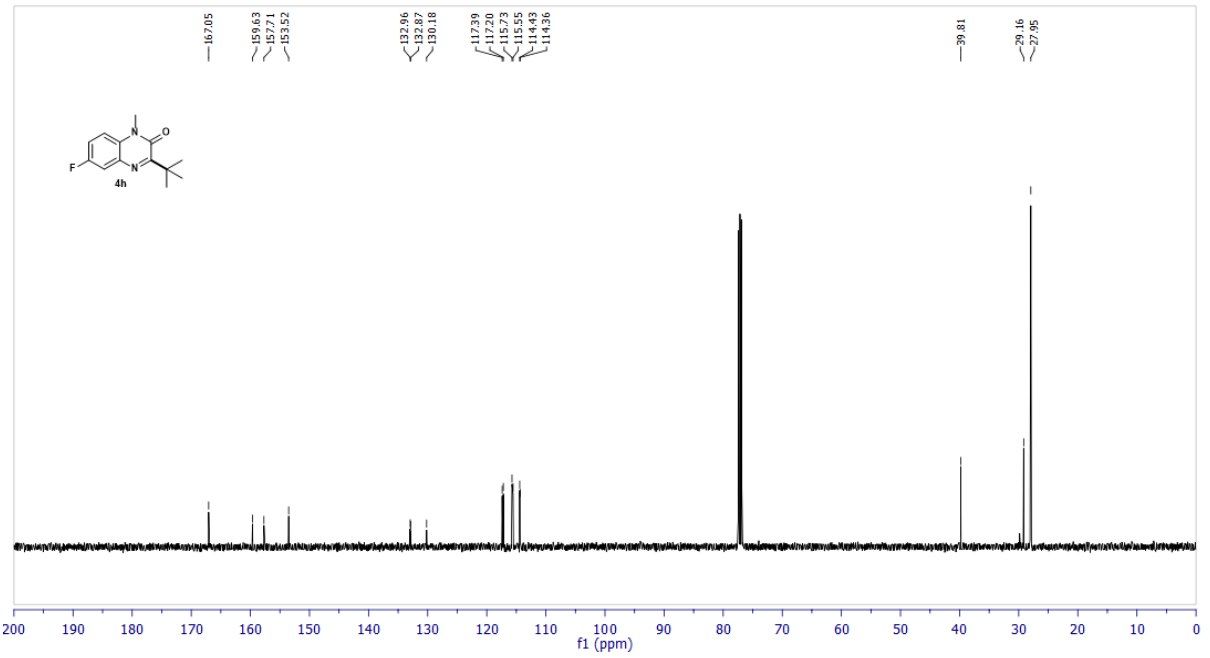
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **4g**



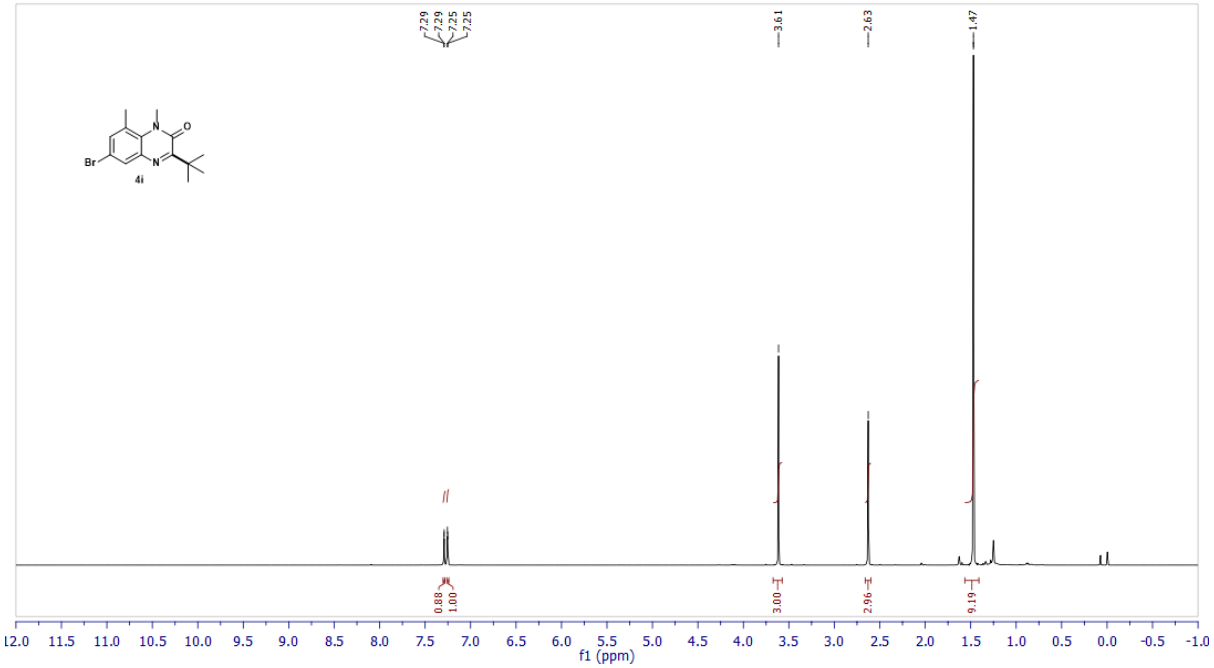
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4h**



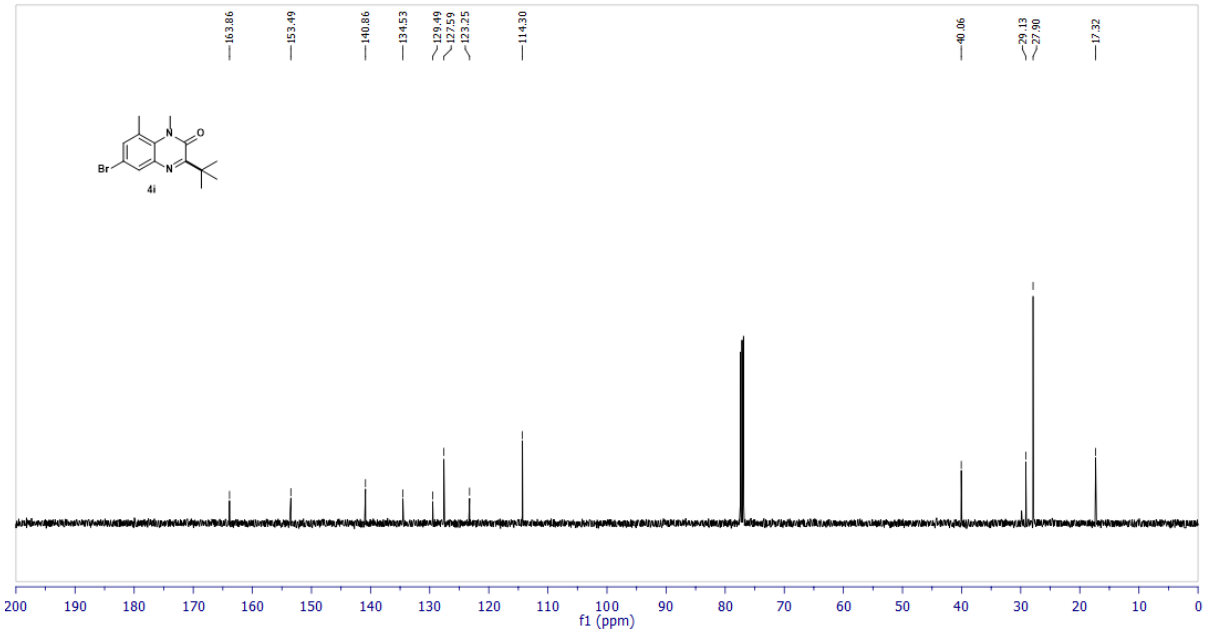
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4h**



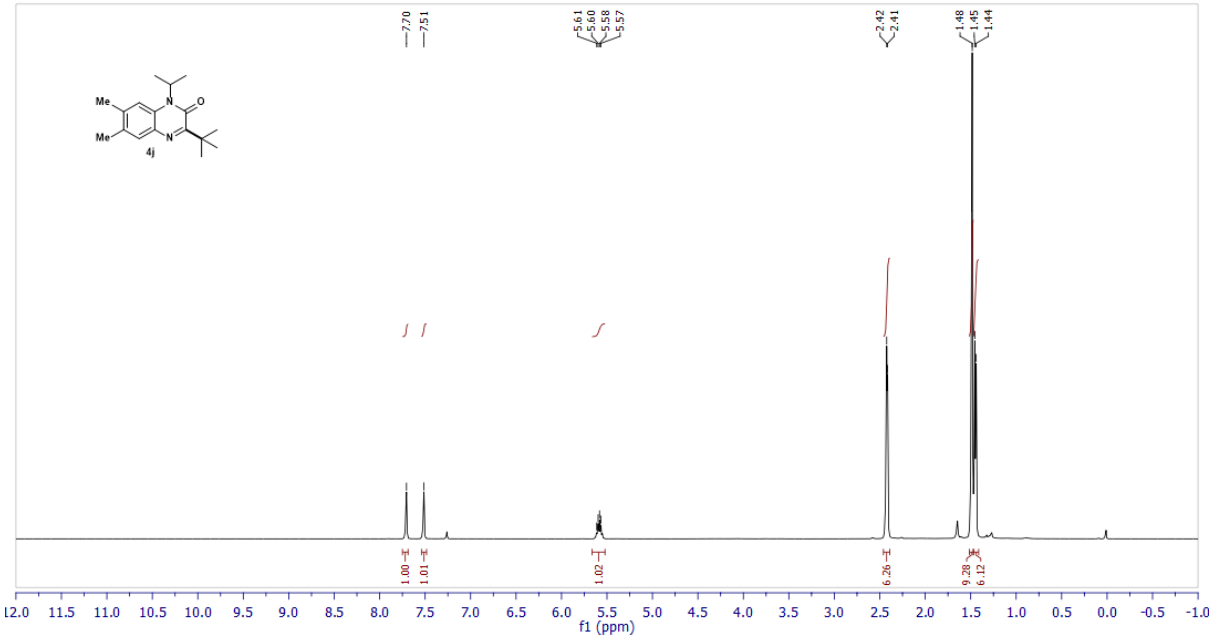
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4i**



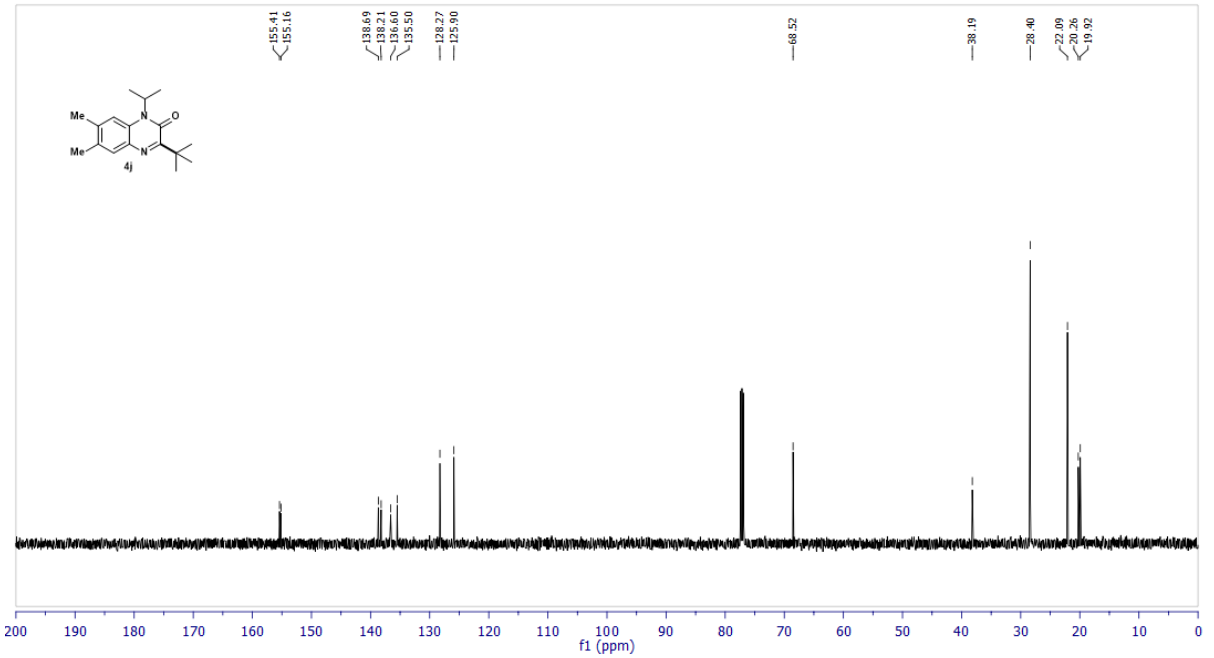
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4i**



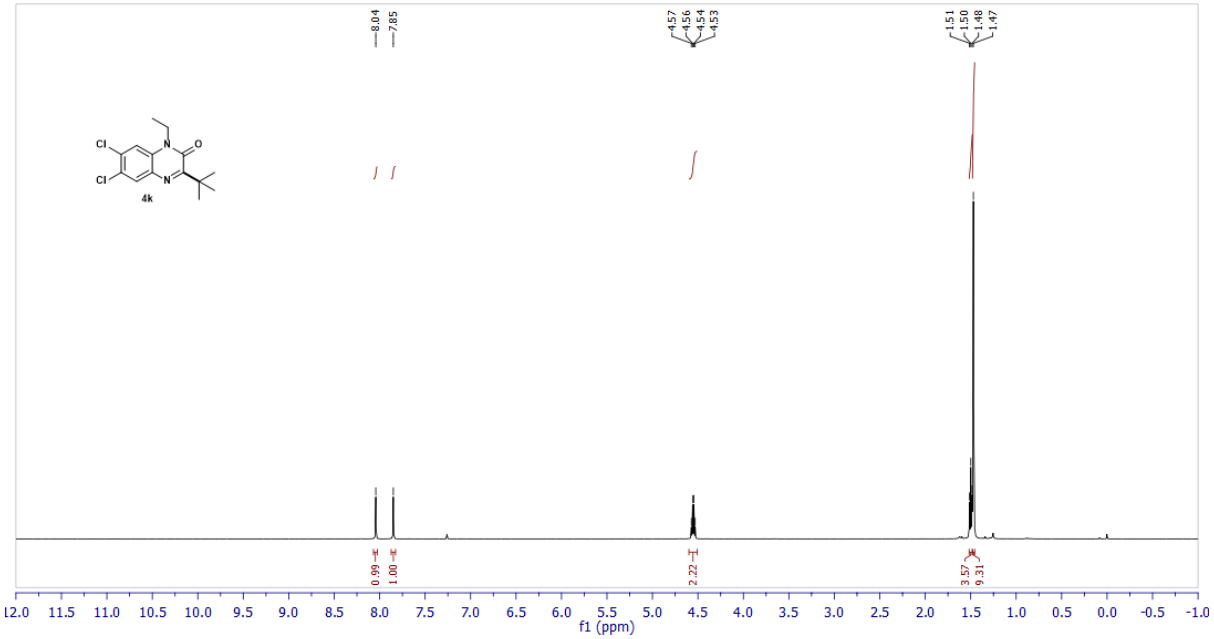
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4j**



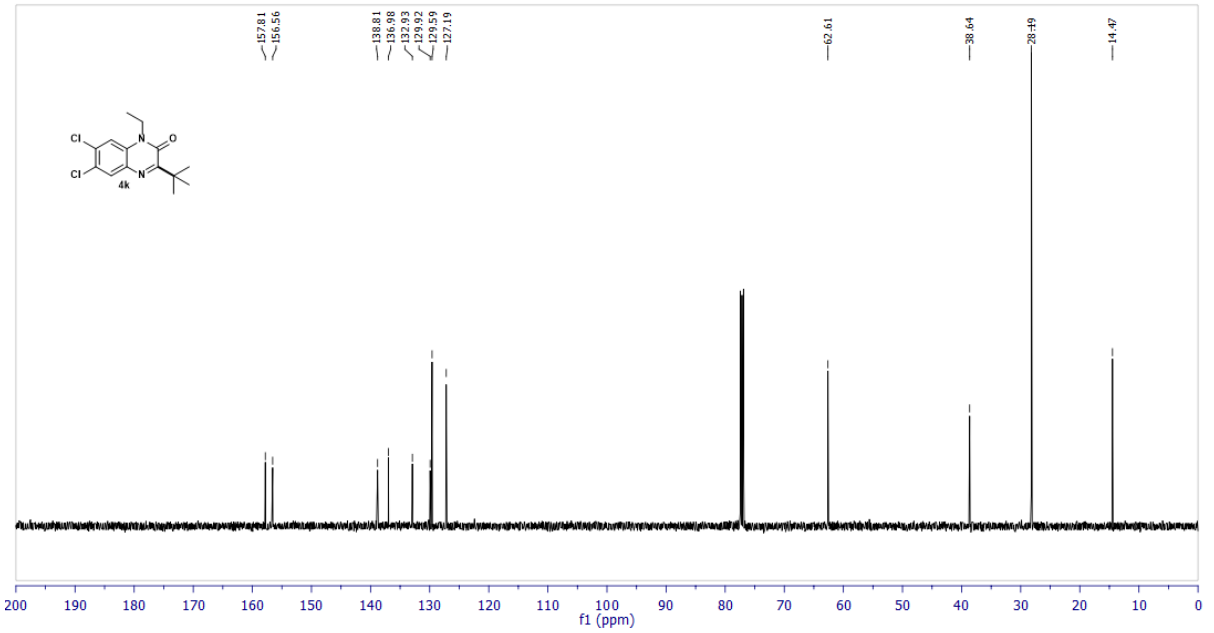
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4j**



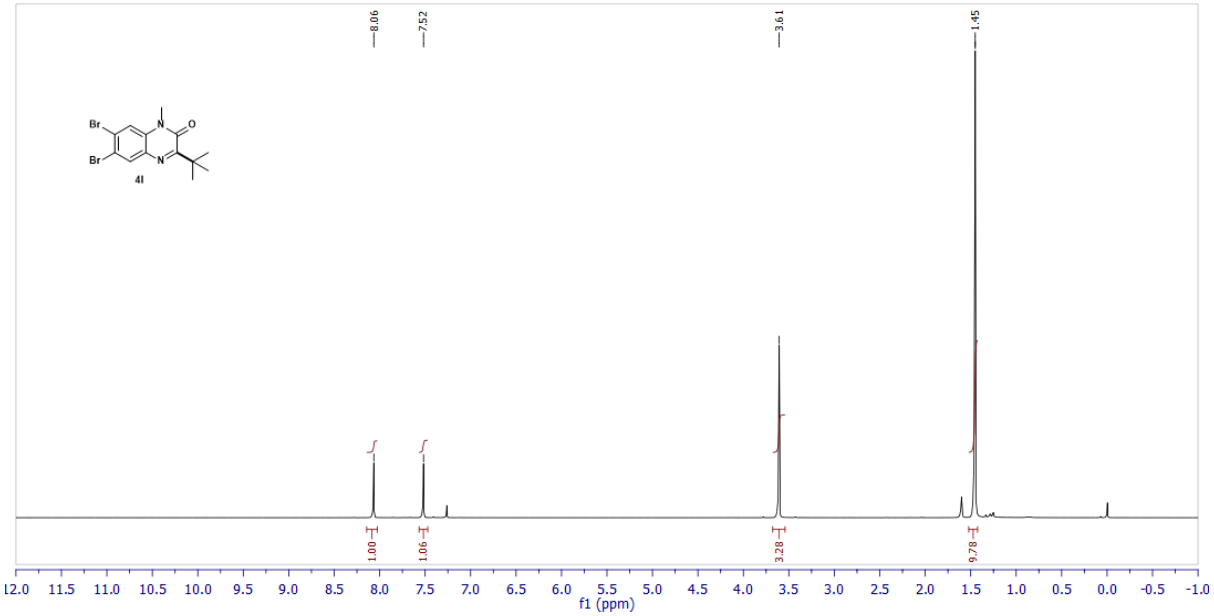
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4k**



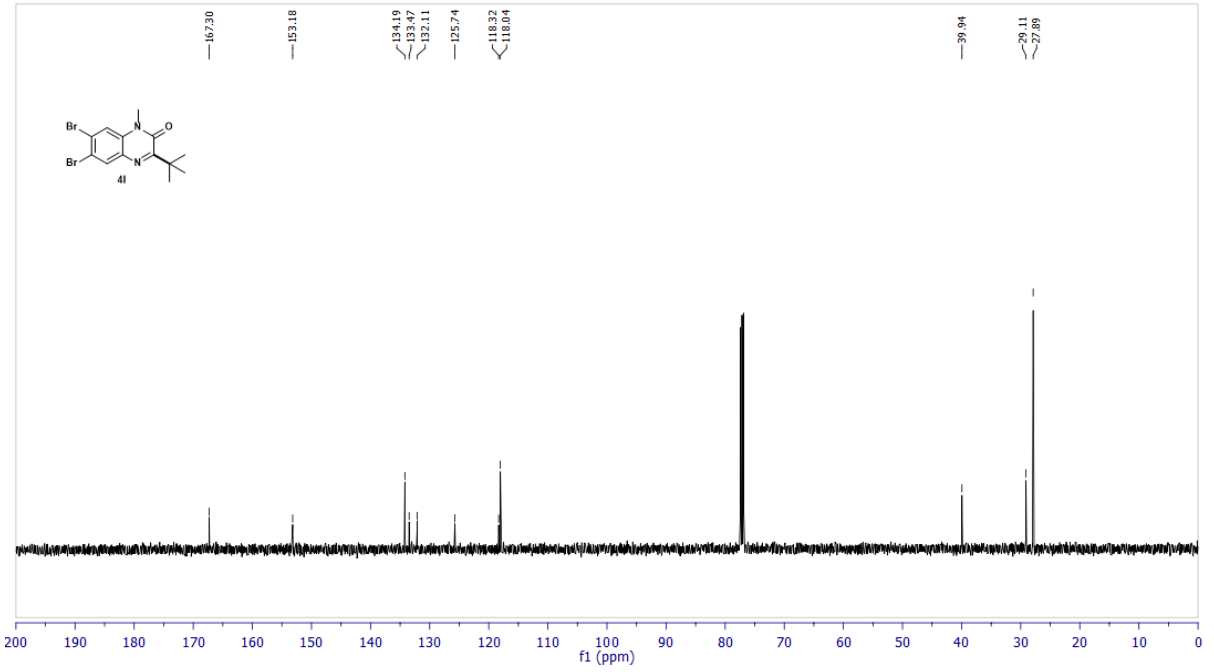
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4k**



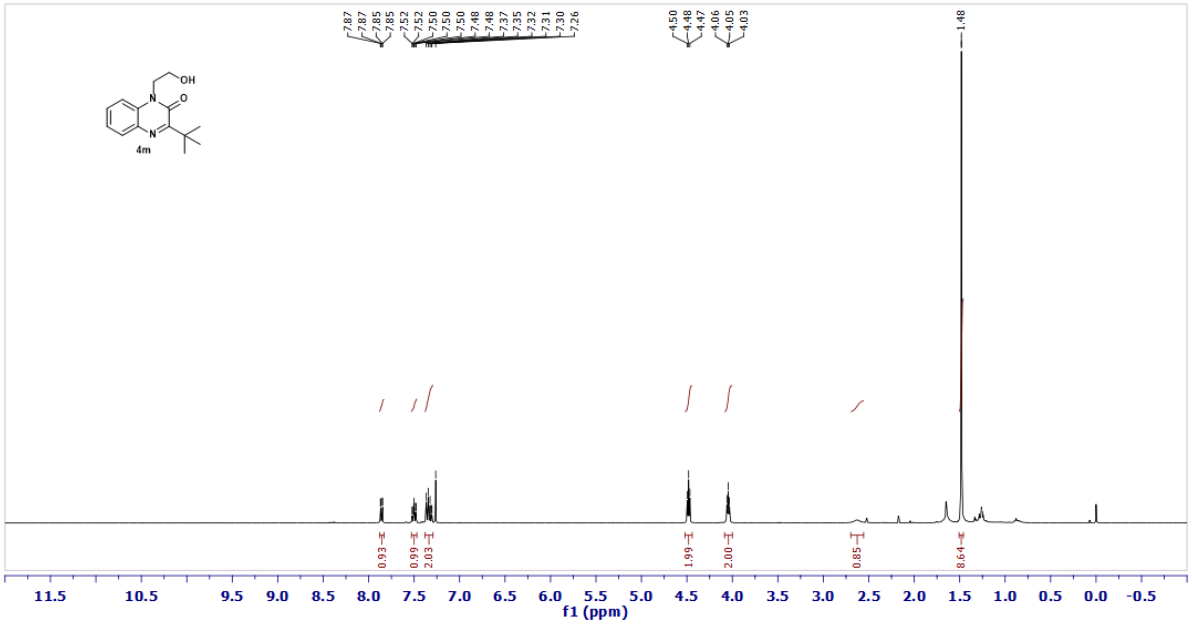
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4l**



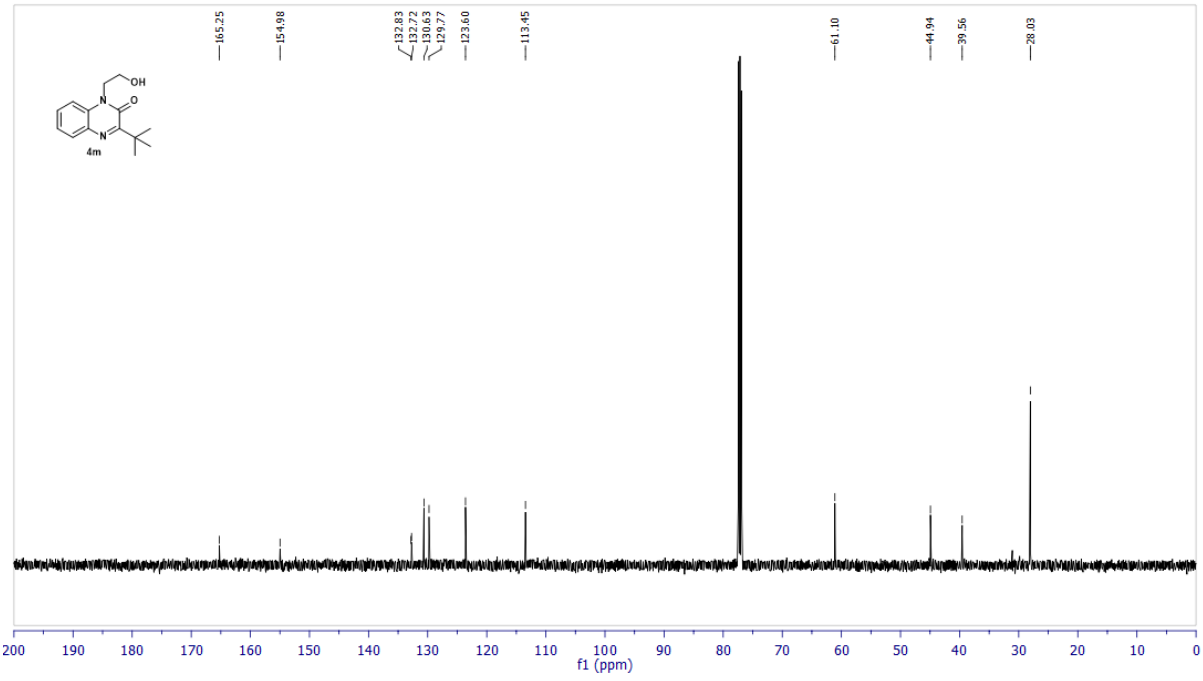
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4l**



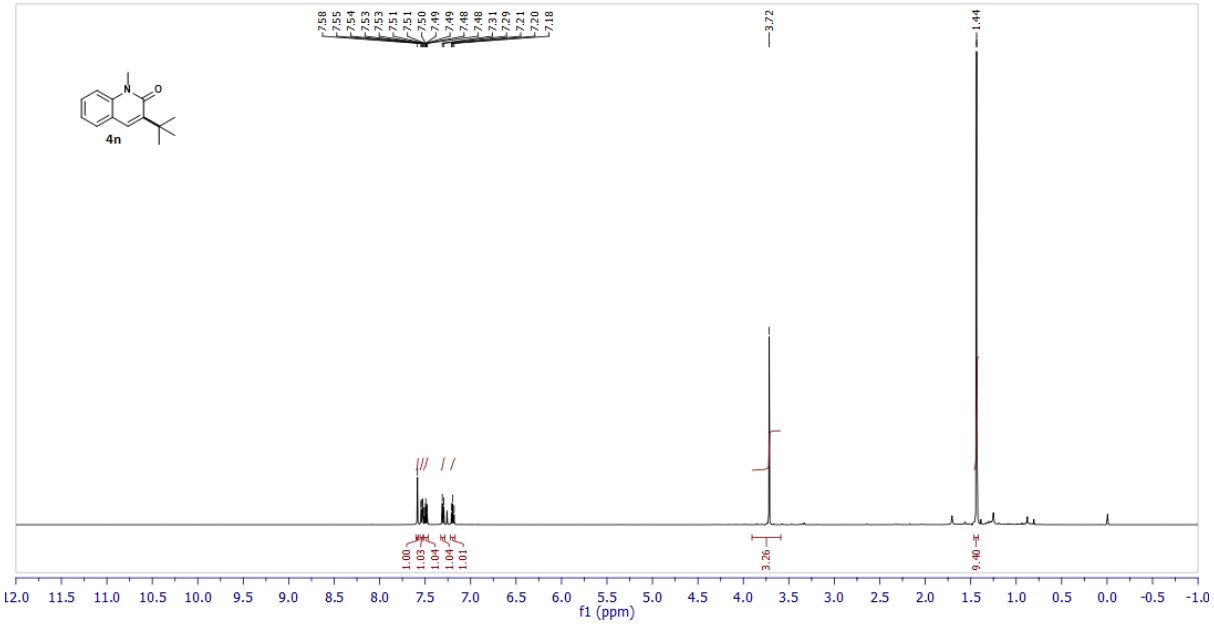
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4m**



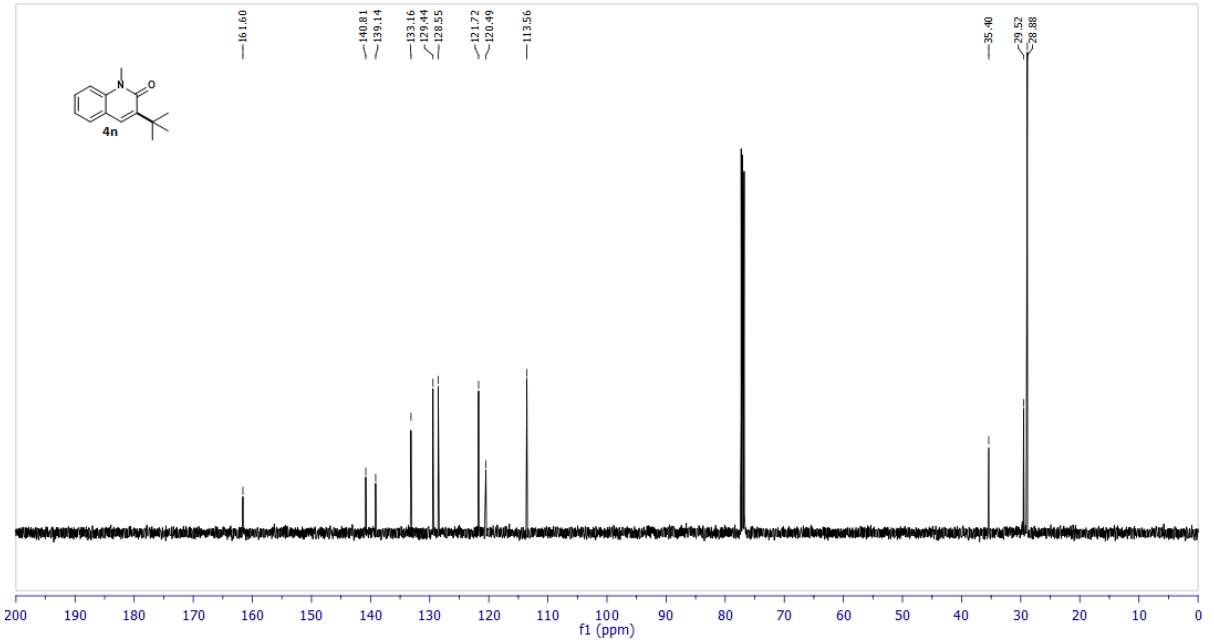
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4m**



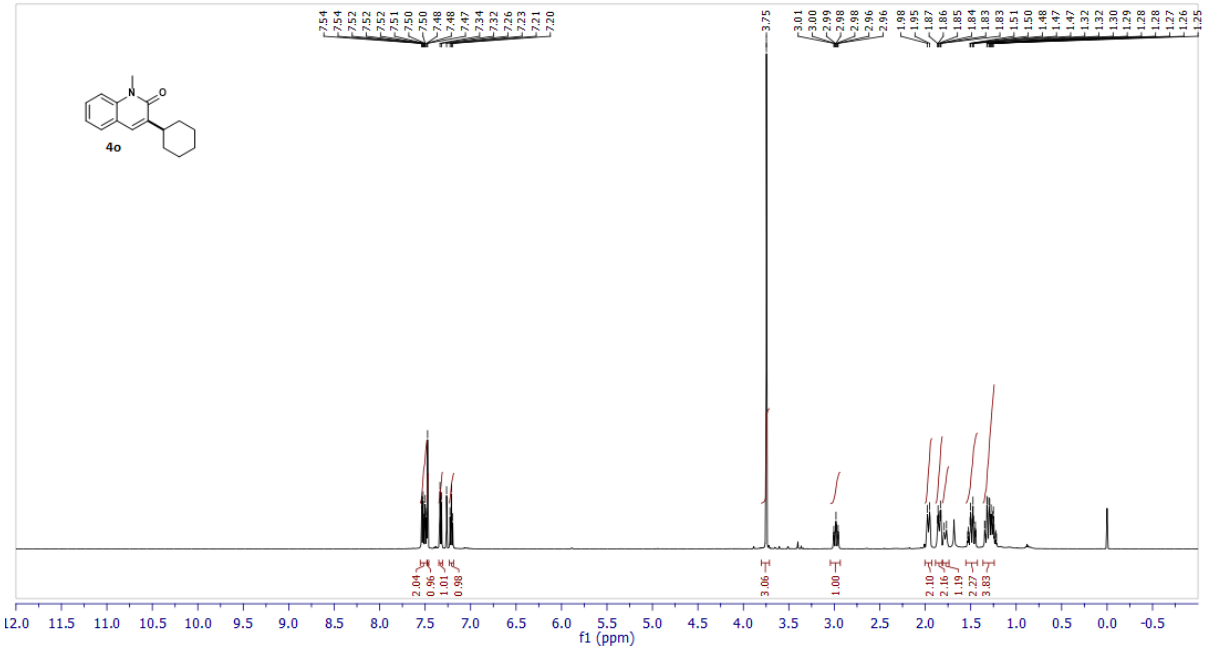
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4n**



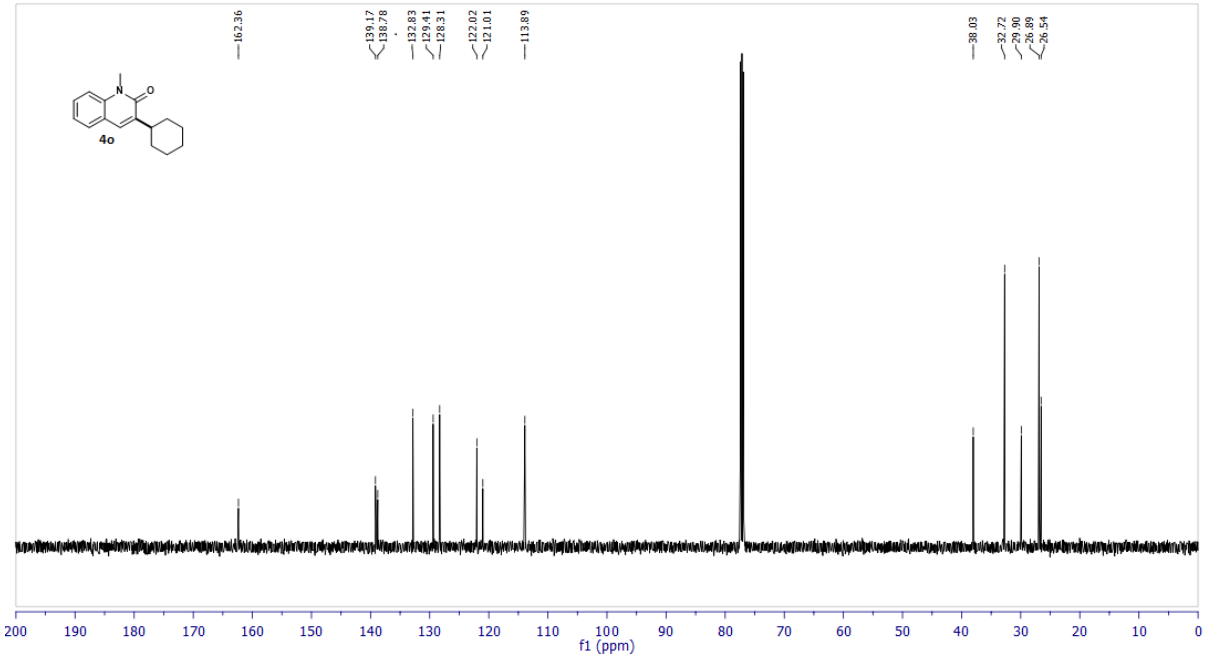
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **4n**



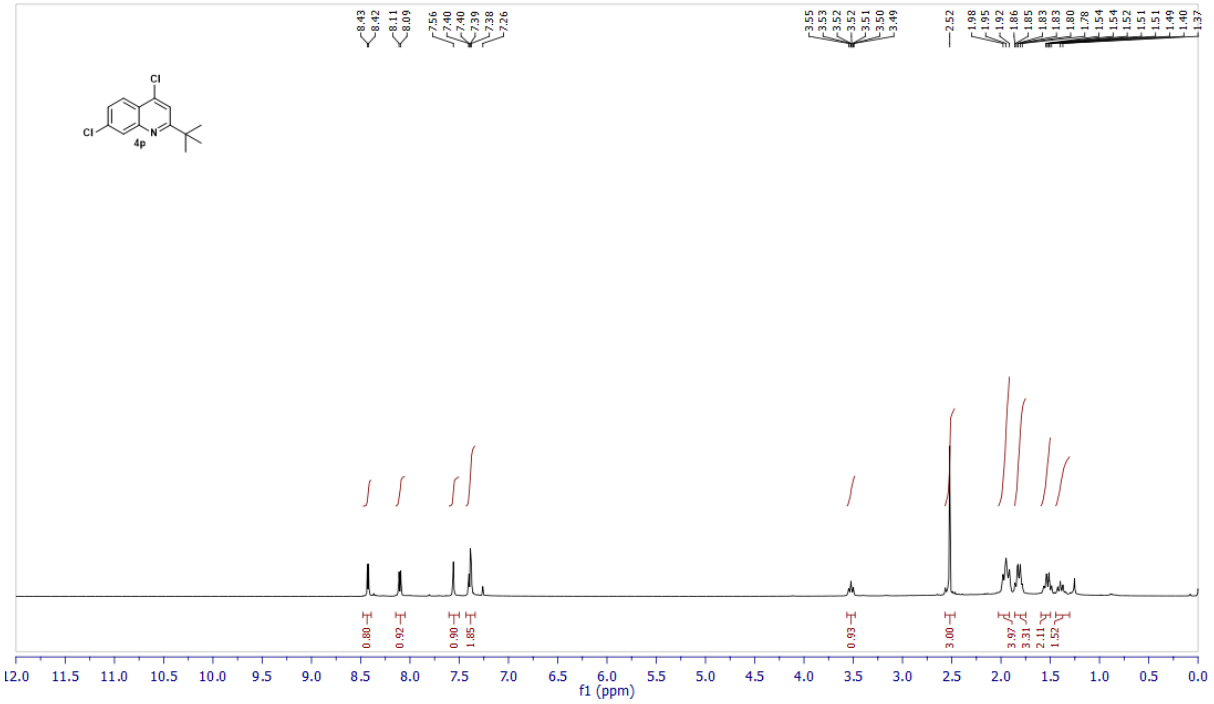
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4o**



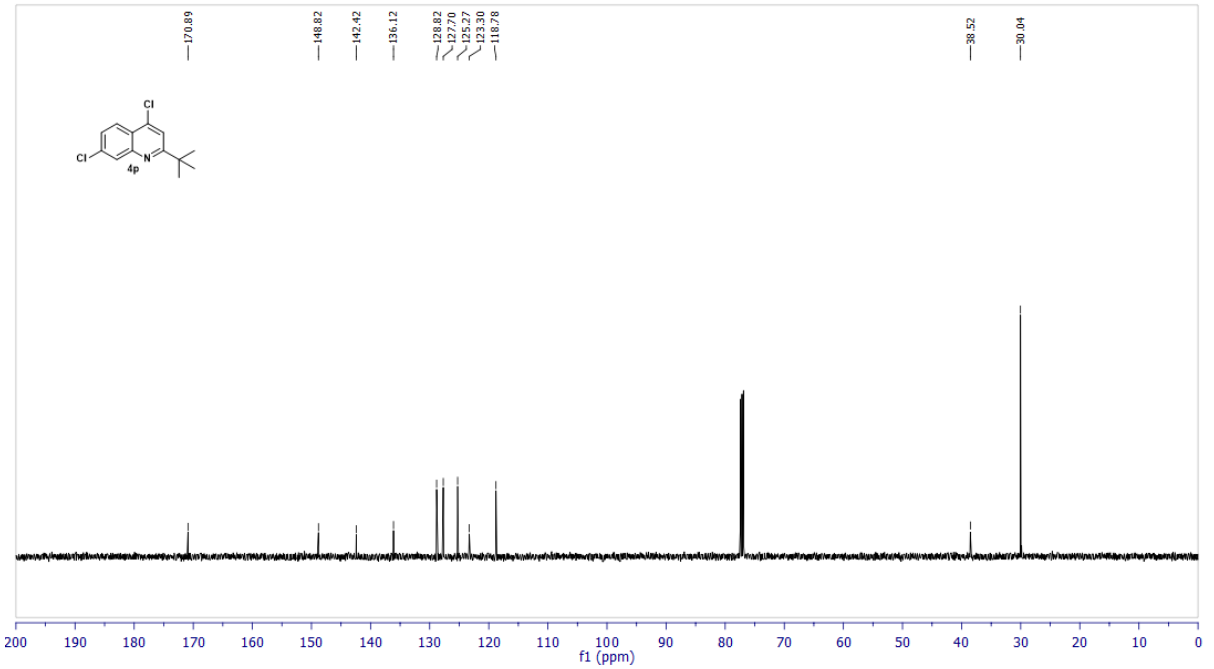
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4o**



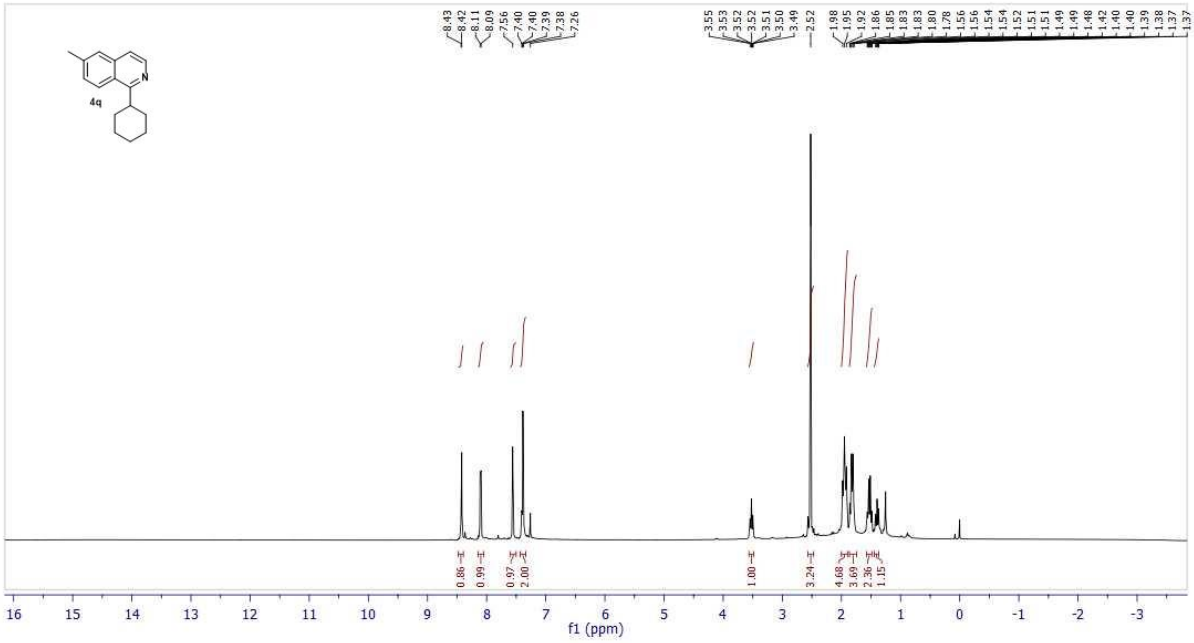
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4p**



^{13}C NMR (126 MHz, $CDCl_3$) of compound **4p**



^{1}H NMR (500 MHz, $CDCl_3$) of compound **4q**



^{13}C NMR (126 MHz, $CDCl_3$) of compound **4q**