Supporting Information

Photoredox Cross Dehydrogenative C(sp^2)–C(sp^3) Coupling of Heteroarenes with Secondary Amines through 1,5-HAT

Vinjamuri Srinivasu[†,a] Swadhin Pattanaik[†,b] Devarajulu Sureshkumar*[a]

[a]Department of Chemical Sciences, Indian Institute of Science Education and Research Kolkata, Mohanpur-741246, West Bengal, India. [b]Department of Chemical Sciences, Indian Institute of Science Education and Research, Berhampur-760010, Odisha.

Department of Chemical Sciences

Indian Institute of Science Education and Research Kolkata

Mohanpur 741246, West Bengal, India.

E-mail: ***suresh@iiserkol.ac.in***

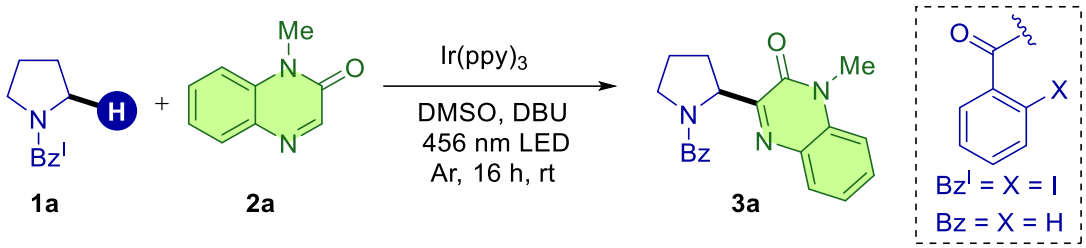
Group webpage: ***https://www.iiserkol.ac.in/~suresh/***

1. General Information:

Commercial reagents were purified prior to use, following the guidelines of L.L Chai and Armarego. All NMR spectra were recorded on a 500 MHz Bruker spectrometer. ^{1}H, ^{13}C, and ^{19}F spectral data are reported as chemical shifts (δ) in parts per million (ppm). Chemical shifts in ppm from tetramethylsilane (TMS) as an internal standard in $CDCl_3$. Chemical shifts (δ) are quoted in parts per million (ppm), and coupling constants (*J*) are measured in hertz (Hz). The following abbreviations are used to describe multiplicities: s=singlet, d=doublet, t=triplet, q=quartet, pent=pentet, b=broad, m=multiplet. NMR spectra were processed in Mestrenova, keeping the $CDCl_3$ residual peaks at 7.26 ppm (^{1}H) and 77.16 ppm (^{13}C). High-resolution mass spectra (HRMS, m/z) were recorded on a Bruker MicroTOF. All fluorescence and UV−vis spectra were recorded in a HORIBA FluoroMax Plus spectrofluorometer and a Hitachi UV−vis spectrophotometer. IUPAC names were obtained using the ChemDraw service. The weighing was performed with a 4-decimal place balance. All reactions were conducted in dried glassware with magnetic stirring under an inert atmosphere unless otherwise noted. All solvents were dried following the guidelines of L.L Chai and Armarego purification of laboratory chemicals. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Flash column chromatography was performed over Merck silica gel (230−400 μm) using the eluent system described for each experiment. TLC was stained with iodine or an ethanolic solution of potassium permanganate ($KMnO_4$) or *p*-anisaldehyde. In a general experiment, 40 W blue LEDs (456 nm) brought from Kessil with a cooling fan were used as a visible light source. The light source was placed at approximately 5.0 cm distance from the reaction tube. The product yields were determined after purification by flash column chromatography using SiO_2, and the purity was determined using ^{1}H NMR spectra.

2. Optimization Studies:

2.1 General Optimization Table:[a]

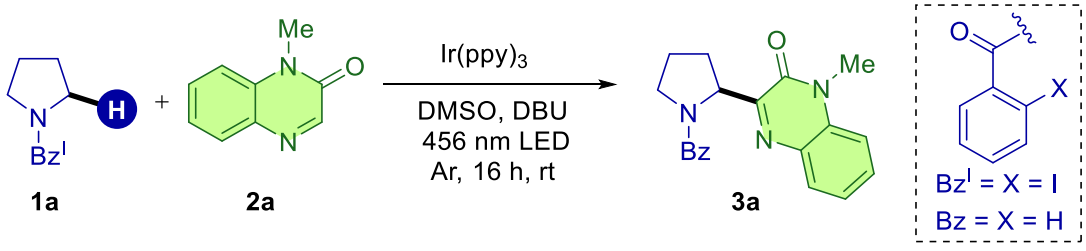


1a 2a 3a

Entry	Solvent	Equiv. (1a : 2a : DBU)	Yield of 3a (%)[b]
1	DMSO (0.1 M)	1 : 1 : 2	78
2	DMSO (0.1 M)	1 : 1.5 : 2	80
3	DMSO (0.1 M)	1.5 : 1 : 2	56
4	DMSO (0.1 M)	1 : 1.5 : 1	40
5	DMSO (0.1 M)	1 : 1.5 : 1.5	62
6	DMSO (0.1 M)	1 : 1.5 : 2.5	90
7	DMSO (0.1 M)	1 : 1.5 : 3	74
8[c]	**DMSO (0.1 M)**	**1 : 1.5 : 2.5**	**95 (90)**[d]
9[e]	DMSO (0.1 M)	1 : 1.5 : 2.5	67, 76
10[f]	DMSO (0.1 M)	1 : 1.5 : 2.5	54, 68
11[g]	Solvent (0.1 M)	1 : 1.5 : 2.5	Trace, 5, 11
12[c]	DMSO (0.2 M)	1 : 1.5 : 2.5	88
13[c]	DMSO (0.067 M)	1 : 1.5 : 2.5	94
14[h]	DMSO (0.1 M)	1 : 1.5 : 2.5	0

[a]Reaction Conditions: Reaction performed in 0.2 mmol scale in DMSO (0.1 M) solvent with $Ir(ppy)_3$ (2.0 mol%) as catalyst under 456 nm LED irradiation at rt for 16 h in Ar atm. [b]^1H NMR yields using 1,1,2,2-tetrachloroethane as an internal standard. [c]With 1.0 mol% of $Ir(ppy)_3$. [d]Isolated Yield. [e]With 0.5 mol% or 3.0 mol% of $Ir(ppy)_3$. [f]With 1.0 mol% of $Ru(bpy)_3Cl_2{\cdot}6H_2O$ or $Ir(dtbbpy)(ppy)_2PF_6$ respectively. [g]With MeCN, EtOAc, or DMF solvents instead of DMSO. [h]Without $Ir(ppy)_3$ or Reaction under dark conditions.

2.2 Equivalents Screening:[a]

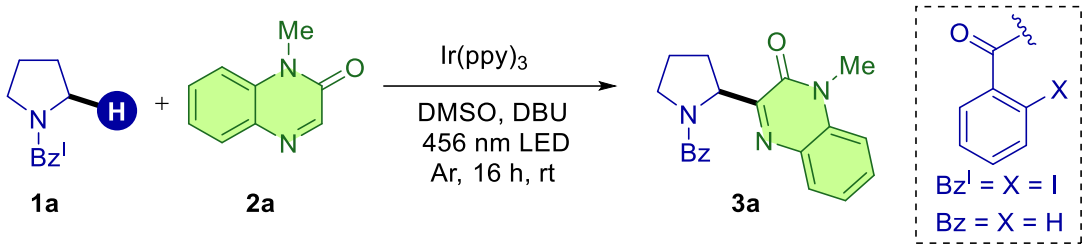


1a 2a 3a

Entry	Equiv. of 1a	Equiv. of 2a	Equiv. of DBU	PC (mol %)	Yield of 3a (%)[b]
1	1	1	2	2.0	78
2.	1	1.5	2	2.0	80
3.	1.5	1	2	2.0	56
4.	1	1.5	1	2.0	40
5.	1	1.5	1.5	2.0	62
6.	1	1.5	2.5	2.0	90
7.	1	1.5	3	2.0	74
8.	1	1.5	2.5	1.0	95
9.	1	1.5	2.5	3.0	76
10.	1	1.5	2.5	0.5	67

[a]Reaction Conditions: Reaction performed in 0.2 mmol scale in DMSO (0.1 M) solvent with $Ir(ppy)_3$ (xx mol%) as catalyst under 456 nm LED irradiation at rt for 16 h in Ar atm. [b]^1H NMR yields using 1,1,2,2-tetrachloroethane as an internal standard.

2.3 Concentration Screening:[a]

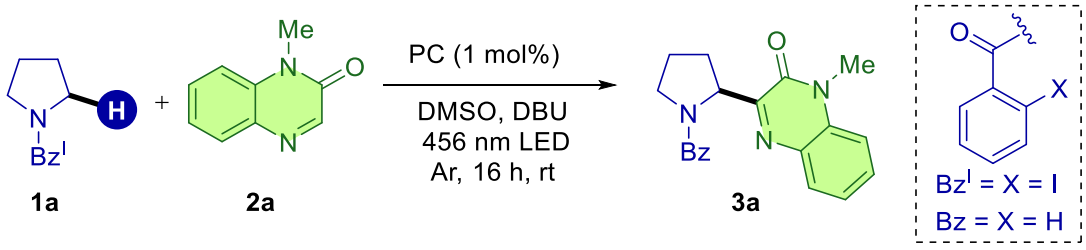


1a 2a 3a

Entry	Concentration	Yield of 3a (%)[b]
1	0.2 M	88
2	**0.1 M**	**95, 93[c]**
3	0.067 M	94

[a]Reaction Conditions: Reaction performed in 0.2 mmol scale in DMSO (0.1 M) solvent with 1 : 1.5 : 2.5 ratio of **1a : 2a : DBU** and $Ir(ppy)_3$ (1.0 mol%) as catalyst under 456 nm LED irradiation at rt for 16 h in Ar atm. [b]^1H NMR yields using 1,1,2,2-tetrachloroethane as an internal standard. [c]repetition of entry 2.

2.4 Photocatalyst Screening:[a]



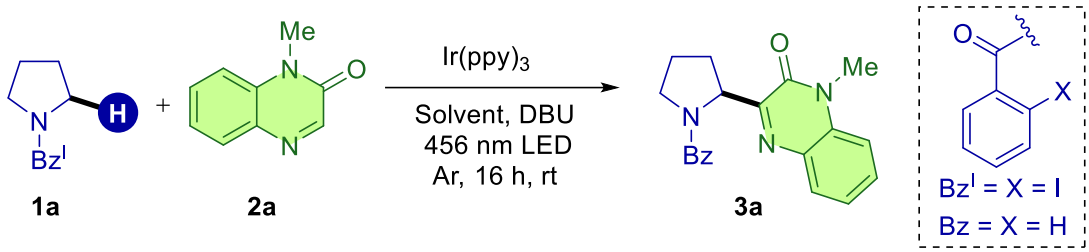
1a 2a 3a

Entry	Photocatalysts	Yield of 3a (%)[b]
1	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	54%

2	$Ir(dtbbpy)(ppy)_2PF_6$	68%
3	EOSIN Y	30%

[a]Reaction Conditions: Reaction performed in 0.2 mmol scale with DMSO (0.1 M) solvent in 1 : 1.5 : 2.5 ratio of **1a : 2a : DBU** and photocatalyst (1.0 mol%) as catalyst under 456 nm LED irradiation at rt for 16 h in Ar atm. [b]^{1}H NMR yields with 1,1,2,2-tetrachloroethane as standard.

2.4 Solvent Screening:[a]

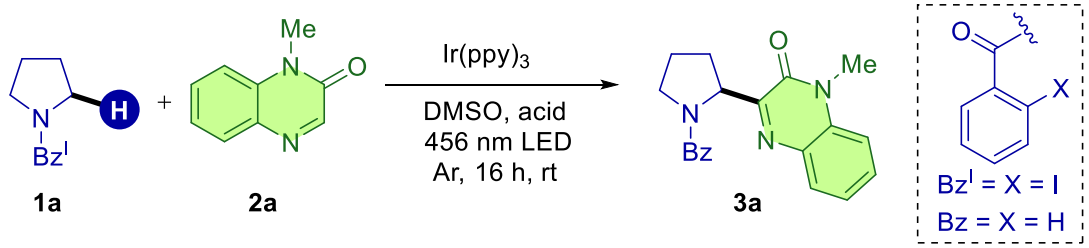


1a 2a 3a

Entry	Solvent	Yield of 3a (%)[b]
1	MeCN	trace
2	EtOAc	< 5%
3	DMF	11%

[a]Reaction Conditions: Reaction performed in 0.2 mmol scale with DMSO (0.1 M) solvent in 1 : 1.5 : 2.5 ratio of **1a : 2a : DBU** and $Ir(ppy)_3$ (1.0 mol%) as catalyst under 456 nm LED irradiation at rt for 16 h in Ar atm. [b]^{1}H NMR yields with 1,1,2,2-tetrachloroethane as standard.

2.5 Acid additive instead of base:

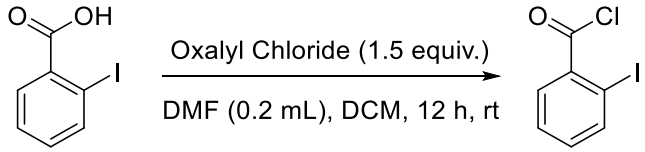


1a 2a 3a

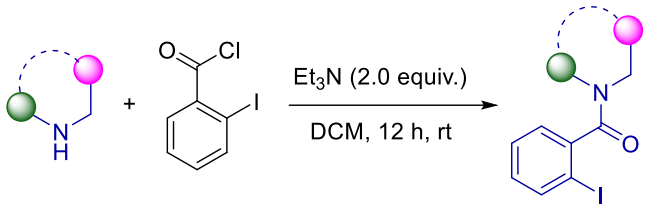
Entry	Acid	Yield of 3a (%)[b]
1	CH_3COOH	0%
2	CF_3COOH	0%
3	PTSA	0%

[a]Reaction Conditions: Reaction performed in 0.2 mmol scale with DMSO (0.1 M) solvent in 1 : 1.5 : 2.5 ratio of **1a : 2a : Acid** and $Ir(ppy)_3$ (1.0 mol%) as catalyst under 456 nm LED irradiation at rt for 16 h in Ar atm. [b]^{1}H NMR yields with 1,1,2,2-tetrachloroethane as standard.

3. Preparation of the substrates 1:[1]



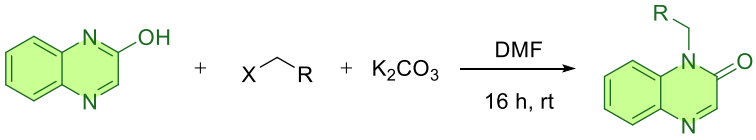
The 2-iodobenzoic acid (0.5 g, 2.0 mmol, 1.0 equiv.) was dissolved in dry CH_2Cl_2 (25 ml) in which catalytic amount of DMF was added followed by oxalyl chloride (5 mmol, 1.5 equiv.) dropwise at 0 °C and the resulting reaction mixture was stirred for 12 h. After the reaction, DCM was evaporated under reduced pressure, and the crude acid chloride was used without further purification.



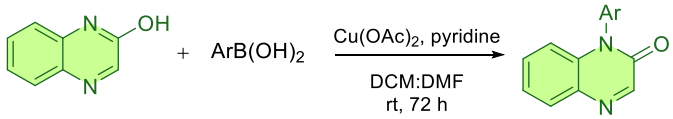
The corresponding amine (1.1 equiv.) and Et_3N (2.1 mL, 15.0 mmol, 3.0 equiv.) were dissolved in CH_2Cl_2 (25 mL) in which 2-iodobenzoyl chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred for 12 h. After the reaction (monitored by TLC), water was added and extracted with CH_2Cl_2 (3 × 30 mL). These combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude amide was purified by column chromatography on silica gel to afford the desired 2-iodobenzoyl-protected amines.

4. General procedure for the synthesis of substrates 2:[2,3,4]

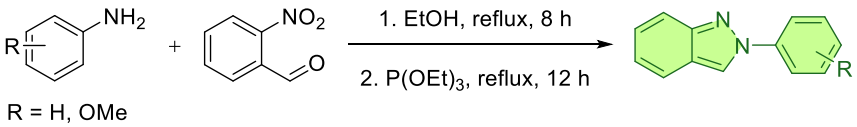
The substrates **2a-2z** were prepared according to previously reported methods, and the NMR data of these compounds was compared with the corresponding reported data.



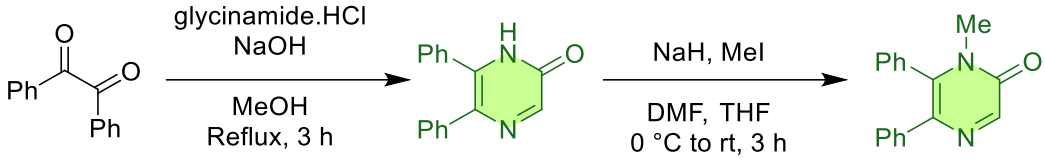
In a 100 mL round bottom flask with a magnetic stirrer, quinoxalin-2(1*H*)-one 6 (1.0 equiv.) was taken and dissolved in DMF. Potassium carbonate (1.2 equiv.) was added to the flask, followed by dropwise (or portion-wise for solids) addition of the haloalkane (1.6 equiv.) while stirring. The reaction was allowed to stir at room temperature for 16 hours in an air atmosphere. It was quenched by adding water (20 mL) and extracted with EtOAc (40 mL). The organic layer was washed with water (2 x 20 mL), a saturated solution of $NaHCO_3$ (20 mL) and brine (20 mL). Then, the organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford the crude product. The crude product is purified by flash column chromatography in EtOAc/n-hexane (15-25%) to obtain corresponding products.



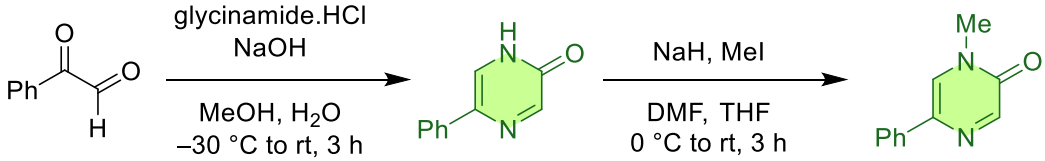
In a dried 100 mL round bottom flask, quinonxalin-2(1*H*)-one (1.0 equiv.), corresponding phenylboronic acid (1.2 equiv.), $Cu(OAc)_2$ (2.0 equiv.), molecular sieves (1.4 g, 4Å), CH_2Cl_2 (13 mL), and DMF (5 mL) were added to pyridine (2.0 equiv.) under air. The reaction mixture was allowed to stir at room temperature for 72 h and then filtered through a Celite pad. The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography EtOAc/n-hexane (15-25%) to afford the corresponding *N*-aryl quinoxalin-2(1*H*)-ones as solids.



In EtOH (0.5 M), a solution of aniline (6 mmol, 1 equiv.) and 2-nitrobenzaldehyde (6 mmol, 1 equiv.) was refluxed for 8 h. The resulting crystalline solid was collected by filtration and dried under reduced pressure. The solid was refluxed in triethyl phosphite (60 mmol, 10 equiv.) for 12 h. The reaction mixture was quenched with water and extracted with CH_2Cl_2. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product is purified by flash column chromatography in EtOAc/n-hexane (15-25%) to obtain corresponding products.

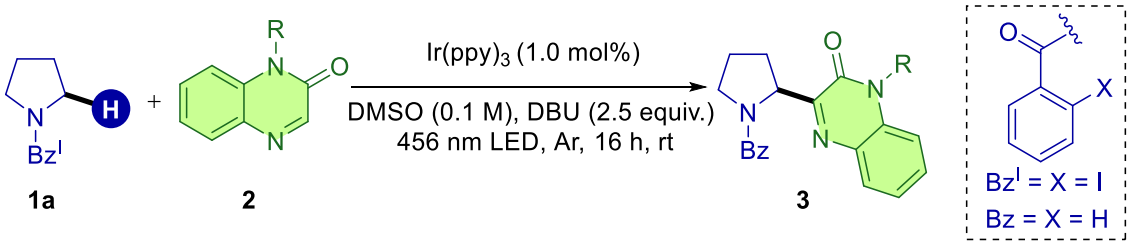


An oven-dried round bottom flask was charged with glycinamide hydrochloride (2.0 g, 18.0 mmol, 1.0 equiv.) and MeOH (18 mL). NaOH (2.4 equiv.) at rt in MeOH (9 mL) was added to the above suspension. Benzil (3.8 g, 18.0 mmol, 1.0 equiv.) was added at rt, and the resulting mixture was refluxed in a silicon oil bath for 3 h. The reaction mixture was cooled in an ice bath and acidified with AcOH. The precipitate separated was collected by filtration and dried to afford 3.1 g of 5,6-diphenylpyrazin-2(1H)-one in 69% yield as a colorless solid. An oven-dried round bottom flask was charged with sodium hydride (210 mg, 5.2 mmol, 1.5 equiv., 60 % dispersion in mineral oil) and DMF (2 mL) under N_2 atmosphere. To the above suspension was added a solution of 5,6-diphenylpyrazin-2(1H)-one (1.0 equiv.) in DMF (2 mL) and THF (2 mL) dropwise at 0 °C. A solution of the corresponding alkyl halide (4.6 mmol, 1.3 equiv) in THF (1 mL) was added dropwise after 15 minutes at 0 °C. The reaction mixture was allowed to stir at room temperature for 3 h. The reaction was quenched by ice water and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography (n-hexanes/EtOAc) to afford the corresponding N-alkyl 5 phenyl pyrazinone.



An oven-dried round bottom flask charged with glycinamide hydrochloride (2.2 g, 20.0 mmol, 1.0 equiv.) and MeOH (18 mL) were added to water (4.4 mL). To the above suspension was added 12.5 M aqueous NaOH solution (2.4 mL, 28.6 mmol, 1.4 equiv.) at –30 °C followed by a solution of NaOH (800 mg, 20.0 mmol, 1.0 equiv.) in MeOH (9 mL). Phenyl glyoxal monohydrate (3.1 g, 20.0 mmol, 1.0 equiv.) was then added at –30 °C, and the resulting mixture was stirred at –30 °C for 2 h. The resulting mixture was further stirred at room temperature for 1 h. The reaction mixture was cooled in an ice bath and acidified with AcOH. The precipitate separated was collected by filtration and dried to afford 2.3 g of 5-phenyl pyrazinone (**2t**) in 70% yield as a pale red solid. An oven-dried round bottom flask was charged with sodium hydride (210 mg, 5.2 mmol, 1.5 equiv., 60 % dispersion in mineral oil) and DMF (2 mL) under N_2 atmosphere. To the above suspension was added a solution of 5-phenylpyrazin-2(1H)-one (602 mg, 3.5 mmol, 1.0 equiv.) in DMF (2 mL) and THF (2 mL) dropwise at 0 °C. A solution of the methyl iodide (4.6 mmol, 1.3 equiv) in THF (1 mL) was added dropwise after 15 minutes at 0 °C. The reaction mixture was allowed to stir at room temperature for 3 h. The reaction was quenched by ice water and extracted with EtOAc. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography (n-hexanes/EtOAc) to afford the corresponding N-methyl 5 phenyl pyrazinone.

5. General procedure for the synthesis of compound 3/4:

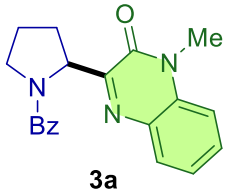


An oven-dried borosilicate test tube equipped with a magnetic stir bar was added 2-iodobenzoyl protected amine **1** (1.0 equiv., 0.2 mmol), quinoxalin-2(1*H*)-one **2** (1.5 equiv., 0.3 mmol), and $Ir(ppy)_3$ (1.0 mol%). The reaction tube was vacuumed and backfilled with argon (3 times), and a septum was placed over the reaction tube. Next, 0.1 M DMSO solvent (2.0 mL) and DBU (54.7 mg, 1.5 equiv., 0.3 mmol) were added through the septum using a syringe, and the

reaction tube was placed approximately 5 cm from the light setup. After the reaction, 10 mL of water was added and extracted with EtOAc (3 × 20 mL). The combined organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was then purified by flash column chromatography on silica gel (mesh 230−400) using hexane and EtOAc as an eluent to afford the corresponding products (**3**/**4**).

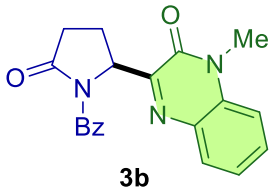
5.1. Characterization and spectral data of the products:

5.1.1 Substrate scope:



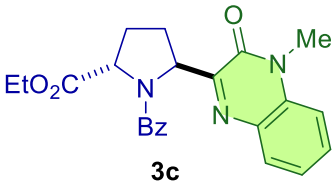
3a

3-(1-Benzoylpyrrolidin-2-yl)-1-methylquinoxalin-2(1H)-one 3a (rr = 1 : 0.5): Synthesised according to the general procedure and after chromatography on SiO_2 (48% to 52% EtOAc in Hexane), the product was isolated as Yellow colour sticky liquid (90%, 60 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 7.9, 1.5 Hz, 0.5H), 7.81 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.64 – 7.58 (m, 2H), 7.52 (dddd, *J* = 20.9, 8.5, 7.3, 1.5 Hz, 1.5H), 7.43 – 7.38 (m, 3H), 7.38 – 7.33 (m, 0.5H), 7.32 – 7.23 (m, 3H), 7.21 – 7.13 (m, 1H), 7.09 (dd, *J* = 8.1, 6.7 Hz, 1H), 5.71 (dd, *J* = 8.2, 5.7 Hz, 1H), 5.43 (dd, *J* = 8.2, 3.0 Hz, 0.5H), 4.02 (ddd, *J* = 12.7, 8.3, 4.6 Hz, 0.5H), 3.89 (ddt, *J* = 21.2, 10.1, 7.3 Hz, 1.5H), 3.68 (s, 3H), 3.60 (ddd, *J* = 10.0, 7.3, 4.6 Hz, 1H), 3.54 (s, 1.5H), 2.53 (ddd, *J* = 13.1, 8.6, 6.1 Hz, 1H), 2.49 – 2.40 (m, 0.5H), 2.10 – 1.99 (m, 3H), 1.98 – 1.89 (m, 1.5H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.9, 169.3, 159.0, 158.9, 154.1, 153.3, 137.8, 137.3, 133.5, 133.1, 132.6, 132.3, 130.5, 130.4, 130.1, 130.1, 129.8, 129.2, 128.3, 128.1, 127.3, 126.3, 123.9, 123.5, 113.7, 60.5, 59.2, 50.5, 47.1, 32.0, 30.4, 29.0, 28.9, 25.4, 22.4. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{20}H_{20}N_3O_2$: 334.1556; found: 334.1552.



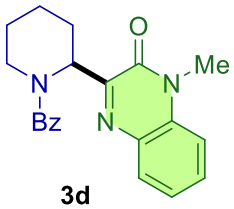
3b

3-(1-Benzoyl-5-oxopyrrolidin-2-yl)-1-methylquinoxalin-2(1H)-one 3b: Synthesised according to the general procedure and after chromatography on SiO_2 (40% to 44% EtOAc in Hexane), the product was isolated as White Colour sticky liquid (64%, 44.4 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (dt, *J* = 8.5, 1.8 Hz, 3H), 7.61 – 7.49 (m, 2H), 7.48 – 7.40 (m, 2H), 7.38 – 7.28 (m, 2H), 6.05 (dd, *J* = 8.6, 3.4 Hz, 1H), 3.73 (s, 3H), 2.81 – 2.73 (m, 1H), 2.73 – 2.67 (m, 1H), 2.66 – 2.59 (m, 1H), 2.20 – 2.12 (m, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 174.8, 170.5, 156.9, 154.0, 134.9, 133.5, 132.4, 131.9, 130.7, 130.4, 129.1, 127.9, 124.0, 113.8, 58.1, 32.0, 29.2, 23.3. HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{20}H_{17}N_3O_3Na$: 370.1168; found: 370.1164.



3c

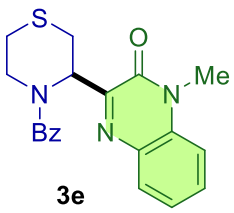
Ethyl 1-benzoyl-5-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)pyrrolidine-2-carboxylate 3c (rr = 1 : 0.6): Synthesised according to the general procedure and after chromatography on SiO_2 (45% to 50% EtOAc in Hexane), the cis product was isolated as yellow sticky liquid **(**76%, 61.4 mg); ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.84 (ddd, *J* = 9.6, 8.0, 1.5 Hz, 1.6H), 7.55 (ddd, *J* = 8.6, 7.3, 1.6 Hz, 1.6H), 7.52 – 7.47 (m, 1.6H), 7.40 – 7.34 (m, 3.2H), 7.34 – 7.28 (m, 1H), 7.25 (dd, *J* = 1.9, 1.2 Hz, 1H), 7.23 (q, *J* = 1.8 Hz, 1.6H), 7.19 – 7.14 (m, 1H), 7.13 – 7.08 (m, 1.8H), 5.97 (dd, *J* = 8.4, 2.3 Hz, 0.6H), 5.64 (dd, *J* = 8.4, 2.0 Hz, 1H), 5.04 (dd, *J* = 9.4, 2.6 Hz, 1H), 4.70 (dd, *J* = 8.6, 2.1 Hz, 0.6H), 4.28 (qd, *J* = 7.1, 2.1 Hz, 2H), 4.08 – 3.88 (m, 1.2H), 3.70 (s, 1.8H), 3.53 (s, 3H), 2.65 (tdd, *J* = 12.3, 8.4, 6.9 Hz, 1H), 2.48 (dtdd, *J* = 24.5, 11.9, 8.7, 5.8 Hz, 1.2H), 2.30 (dddd, *J* = 13.4, 12.3, 9.4, 6.9 Hz, 1H), 2.06 (dddt, *J* = 12.5, 11.0, 6.6, 2.3 Hz, 3.2H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.10 (t, *J* = 7.2 Hz, 1.8H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 172.4, 172.4, 171.1, 170.2, 158.3, 158.1, 154.2, 153.3, 137.4, 137.2, 133.6, 133.1, 132.6, 132.2, 130.7, 130.4, 130.3, 130.2, 129.6, 129.4, 128.4, 128.1, 126.8, 126.4, 124.1, 123.6, 113.7, 113.7, 62.2, 61.4, 61.3, 60.7, 60.2, 59.2, 30.6, 29.8, 29.0, 28.9, 28.4, 27.3, 14.4, 14.1. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{23}H_{24}N_3O_4$: 406.1767; found: 406.1754.



3d

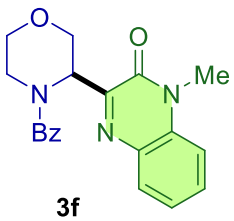
3-(1-Benzoylpiperidin-2-yl)-1-methylquinoxalin-2(1H)-one 3d (rr = 1 : 0.4): Synthesised according to the general procedure and after chromatography on SiO_2 (46% to 49% EtOAc in Hexane), the product was isolated as white solid **(**82%, 56.7 mg); ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.97 – 7.72 (m, 1.5H), 7.45 (ddd, *J* = 44.7, 23.3, 7.2 Hz, 9.5H), 7.27 – 7.04 (m, 2H), 6.18 (s, 1H), 5.35 (s, 0.4H), 4.74 (d, *J* = 13.6 Hz, 0.4H), 4.03 – 3.90 (m, 1H), 3.83 – 3.73 (m, 1.4H), 3.68 – 3.60 (m, 3H), 3.56 (s, 1.2H), 2.49 (d, *J* = 14.4 Hz, 1H), 2.33 (d, *J* = 13.8 Hz, 0.4H), 2.03 (d, *J* = 15.2 Hz, 1.4H), 1.90 (d, *J* = 9.1 Hz, 0.4H), 1.84 – 1.55 (m, 4H), 1.47 – 1.29 (m, 1.4H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 172.2, 171.9, 158.8, 158.3, 153.9, 153.1, 137.1, 133.3, 132.3, 130.5, 130.1, 130.0, 129.2, 128.4, 126.9, 126.0, 123.8, 123.5, 113.7, 56.5, 51.4, 46.5, 40.1, 29.0, 27.7, 26.7, 25.9, 25.4, 20.4. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{21}H_{22}N_3O2$: 348.1712; found: 348.1718.

3-(4-Benzoylthiomorpholin-3-yl)-1-methylquinoxalin-2(1H)-one 3e (rr = 1 : 0.5): Synthesised according to the general procedure and after chromatography on SiO_2 (45% to 55% EtOAc in Hexane), the product was isolated as colorless solid (79%, 57.6 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.9 Hz, 0.5H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.49 (ddd, *J* = 49.8, 25.2, 10.1 Hz, 7H), 7.30 (dd, *J* = 17.5, 8.4 Hz, 4H), 7.22 (t, *J* = 6.4 Hz, 1H), 6.42 (d, *J* = 4.2 Hz, 1H), 5.51 (s, 0.5H), 5.03 (d, *J* = 14.0 Hz, 0.5H), 4.29 (t, *J* = 13.1 Hz, 1H), 4.09 (d, *J* = 12.4 Hz, 0.5H), 3.97 (d, *J* = 14.0 Hz, 1H), 3.83 (d, *J* = 14.5 Hz, 1H), 3.73 – 3.55 (m, 5H), 3.42 – 3.09 (m, 1.5H), 2.85 (d, *J* = 67.9 Hz, 1.5H), 2.68 – 2.42 (m, 1.5H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 172.2, 156.1, 155.8, 153.8, 153.3, 136.4, 133.3, 132.3, 130.8, 130.4, 130.2, 129.6, 128.6, 127.6, 126.9, 126.1, 124.0, 123.6, 113.8, 57.6, 52.0, 46.7, 40.1, 29.9, 29.7, 29.0, 28.4. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{20}H_{20}N_2O_2S$: 366.1276; found: 366.1281.



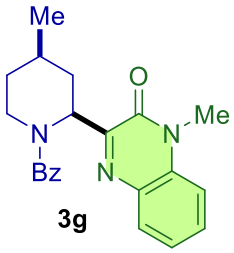
3e

3-(4-Benzoylmorpholin-3-yl)-1-methylquinoxalin-2(1H)-one 3f (rr = 1 : 0.5): Synthesised according to the general procedure and after chromatography on SiO_2 (42% to 47% EtOAc in Hexane), the product was isolated as white sticky liquid (85%, 59.2 mg); ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.01 – 7.90 (m, 0.5H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.62 – 7.49 (m, 3.5H), 7.48 – 7.37 (m, 3.5H), 7.32 (dd, *J* = 22.2, 8.0 Hz, 3.5H), 7.21 (dd, *J* = 15.7, 7.6 Hz, 1.5H), 5.99 (d, *J* = 4.3 Hz, 1H), 5.14 (d, *J* = 4.0 Hz, 0.5H), 4.80 (d, *J* = 12.3 Hz, 1H), 4.62 (d, *J* = 12.1 Hz, 0.5H), 4.53 (d, *J* = 13.6 Hz, 0.5H), 4.26 (td, *J* = 12.9, 3.9 Hz, 1H), 4.01 (td, *J* = 15.3, 7.0 Hz, 2H), 3.93 – 3.73 (m, 1H), 3.67 (d, *J* = 1.8 Hz, 3.5H), 3.59 (d, *J* = 7.5 Hz, 2H), 3.58 – 3.46 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 172.4, 171.9, 155.6, 154.0, 153.4, 136.1, 135.8, 133.4, 133.2, 132.4, 130.8, 130.6, 130.4, 130.2, 129.8, 129.7, 128.6, 128.6, 127.1, 126.2, 124.1, 123.7, 113.8, 67.8, 67.6, 67.4, 67.1, 57.5, 51.9, 46.0, 39.8, 28.0. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{20}H_{20}N_3O_3$: 350.1505; found: 350.1504.



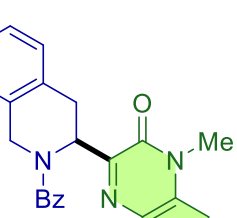
3f

3-(1-Benzoyl-4-methylpiperidin-2-yl)-1-methylquinoxalin-2(1H)-one 3g (rr = 1 : 0.5): Synthesised according to the general procedure and after chromatography on SiO_2 (43% to 46% EtOAc in Hexane), the cis product was isolated as colorless sticky liquid (80%, 57.6 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.9 Hz, 0.5H), 7.80 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.54 (dt, *J* = 22.4, 7.8 Hz, 1.5H), 7.47 (dq, *J* = 4.4, 2.5 Hz, 2H), 7.39 (ddt, *J* = 11.7, 8.0, 3.2 Hz, 3.5H), 7.30 (dt, *J* = 13.4, 7.8 Hz, 3H), 7.27 – 7.21 (m, 1H), 7.18 (d, *J* = 6.9 Hz, 1H), 6.31 (dd, *J* = 7.0, 1.7 Hz, 1H), 5.41 (d, *J* = 5.5 Hz, 0.5H), 4.80 (ddd, *J* = 13.6, 5.1, 2.2 Hz, 0.5H), 4.06 (td, *J* = 13.3, 3.0 Hz, 1H), 3.84 (td, *J* = 13.5, 3.4 Hz, 0.5H), 3.74 (ddd, *J* = 13.2, 4.7, 2.2 Hz, 1H), 3.67 (s, 3H), 3.60 (s, 1.5H), 2.52 (ddt, *J* = 14.0, 3.8, 2.0 Hz, 1H), 2.32 (dt, *J* = 10.9, 2.2 Hz, 0.5H), 1.80 (dd, *J* = 12.6, 3.1 Hz, 0.5H), 1.68 (ddd, *J* = 14.0, 12.5, 7.0 Hz, 1H), 1.63 – 1.51 (m, 3H), 1.22 (dqd, *J* = 37.6, 12.9, 4.6 Hz, 1.5H), 0.90 (d, *J* = 6.4 Hz, 4.5H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 172.1, 171.8, 158.9, 158.4, 153.8, 153.1, 137.2, 137.0, 133.3, 133.2, 132.2, 132.1, 130.6, 130.5, 130.1, 130.0, 129.3, 129.2, 128.5, 128.4, 126.9, 126.0, 123.9, 123.5, 113.8, 113.7, 56.8, 51.3, 46.6, 40.2, 35.8, 34.8, 34.4, 33.9, 29.0, 29.0, 26.8, 26.7, 22.0, 21.9. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{22}H_{24}N_3O_2$: 362.1869; found: 362.1865.



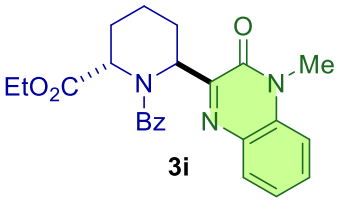
3g

3-(2-Benzoyl-1,2,3,4-tetrahydroisoquinolin-3-yl)-1-methylquinoxalin-2(1H)-one 3h (rr = 1 : 0.8): Synthesised according to the general procedure and after chromatography on SiO_2 (45% to 50% EtOAc in Hexane), the product was isolated as yellow sticky liquid (68%, 53.5 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.69 (m, 1.8H), 7.54 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.51 – 7.41 (m, 5H), 7.36 – 7.26 (m, 5.7H), 7.25 – 7.12 (m, 6.3H), 7.07 (p, *J* = 6.7 Hz, 1.7H), 6.98 (d, *J* = 7.3 Hz, 1H), 6.10 (t, *J* = 6.8 Hz, 1H), 5.66 (dd, *J* = 6.3, 2.7 Hz, 0.8H), 5.36 (d, *J* = 17.4 Hz, 0.8H), 5.08 (d, *J* = 17.4 Hz, 0.8H), 4.97 (d, *J* = 15.2 Hz, 1H), 4.69 (d, *J* = 15.2 Hz, 1H), 3.69 (s, 3H), 3.56 (s, 2.4H), 3.55 – 3.47 (m, 1.8H), 3.46 – 3.37 (m, 1.8H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 172.0, 170.9, 158.7, 157.3, 153.9, 153.2, 136.7, 134.5, 134.0, 133.4, 133.1, 132.5, 132.2, 131.6, 130.6, 130.1, 129.7, 129.5, 128.5, 128.5, 128.3, 128.1, 127.3, 127.1, 126.6, 126.4, 126.3, 126.3, 125.4, 123.8, 123.5, 113.6, 55.8, 52.8, 49.3, 44.7, 32.0, 31.7, 29.0, 28.9. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{25}H_{22}N_3O_2$: 396.1712; found: 396.1707.



3h

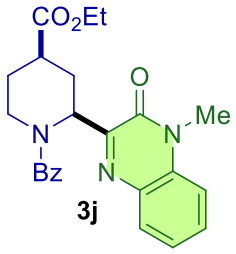
Ethyl 1-benzoyl-6-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)piperidine-2-carboxylate 3i (rr = 1 : 1): Synthesised according to the general procedure and after chromatography on SiO_2 (40% to 44% EtOAc in Hexane), the cis product was isolated as colorless sticky liquid (55%, 45.9 mg); ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.51 – 7.30 (m, 9H), 7.27 (d, *J* = 1.2 Hz, 1H), 7.24 (d, *J* = 1.2 Hz, 1H), 7.15 (d, *J* = 4.2 Hz, 4H), 5.62 (s, 1H), 5.50 (s, 1H), 5.02 (s, 1H), 4.67 (s, 1H), 4.27 (d, *J* = 7.3 Hz, 2H), 4.20 (d, *J* = 6.7 Hz, 2H), 3.69 (s, 3H), 3.51 (s, 3H), 2.37 – 2.07 (m, 8H), 1.91 (s, 1H), 1.64 (d, *J* = 15.2 Hz,



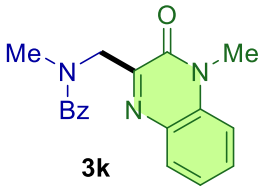
3i

3H), 1.47 – 1.31 (m, 3H), 1.31 – 1.26 (m, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 175.1, 173.2, 172.1, 159.7, 154.2, 152.9, 136.4, 133.2, 132.2, 130.7, 129.9, 129.6, 128.6, 128.3, 127.1, 126.7, 124.0, 123.5, 113.7, 61.8, 61.0, 58.8, 56.4, 55.9, 53.7, 29.2, 29.0, 27.1, 26.9, 26.1, 25.3, 18.1, 17.1, 14.4. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{24}H_{26}N_3O_4$: 420.1923; found:420.1925.

Ethyl 1-benzoyl-2-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)piperidine-4-carboxylate 3j (rr = 1 : 0.5): Synthesised according to the general procedure and after chromatography on SiO_2 (39% to 43% EtOAc in Hexane), the cis product was isolated as colorless sticky liquid (70%, 58.4 mg); ^1H NMR (400 MHz, CHLOROFORM-*D*) δ 7.92 (d, *J* = 8.0 Hz, 0.5H), 7.82 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.61 – 7.53 (m, 1.5H), 7.44 (dq, *J* = 18.6, 3.3 Hz, 5.5H), 7.38 – 7.28 (m, 4H), 7.25 – 7.20 (m, 1H), 6.39 (d, *J* = 6.7 Hz, 1H), 5.52 (d, *J* = 6.3 Hz, 0.5H), 4.86 (d, *J* = 13.7 Hz, 0.5H), 4.10 (q, *J* = 7.1 Hz, 4H), 3.87 – 3.75 (m, 1.5H), 3.71 (s, 3H), 3.62 (s, 1.5H), 2.80 (d, *J* = 14.5 Hz, 1H), 2.65 – 2.47 (m, 2H), 2.21 – 2.07 (m, 2H), 1.90 (d, *J* = 20.0 Hz, 1H), 1.71 (qd, *J* = 13.1, 5.1 Hz, 1.5H), 1.22 (q, *J* = 7.0 Hz, 4.5H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 174.6, 172.3, 171.9, 158.3, 157.7, 153.8, 153.1, 136.7, 133.5, 132.2, 131.0, 130.7, 130.5, 130.2, 129.6, 128.6, 127.0, 126.2, 124.0, 123.7, 113.8, 60.8, 55.5, 50.2, 45.5, 39.3, 37.8, 29.8, 29.2, 28.6, 28.4, 14.3. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{24}H_{26}N_3O_4$: 420.1923; found:420.1921.

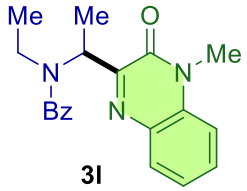


3j



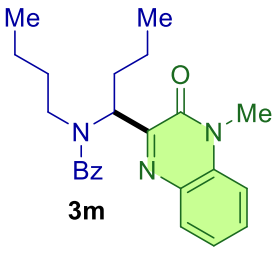
3k

***N*-Methyl-*N*-((4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)methyl)benzamide 3k (rr = 1 : 0.9):** Synthesised according to the general procedure and after chromatography on SiO_2 (38% to 42% EtOAc in Hexane), the product was isolated as white solid (81%, 49.6 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.84 (dd, *J* = 8.0, 1.5 Hz, 0.9H), 7.61 – 7.56 (m, 2.9H), 7.55 – 7.49 (m, 1H), 7.46 – 7.36 (m, 6H), 7.35 – 7.27 (m, 4.5H), 7.25 – 7.22 (m, 1.5H), 4.98 (s, 1.8H), 4.72 (s, 2H), 3.68 (s, 2.7H), 3.63 (s, 3H), 3.16 (s, 3H), 3.09 (s, 2.7H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 173.2, 172.3, 154.5, 154.2, 154.1, 154.1, 136.6, 136.5, 133.1, 133.0, 132.7, 132.6, 130.7, 130.4, 130.2, 130.2, 129.5, 129.5, 128.4, 127.1, 126.6, 124.1, 123.7, 113.8, 113.7, 53.4, 49.7, 38.9, 34.3, 28.9, 28.9. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{18}H_{18}N_3O_2$: 308.1399; found: 308.1391.



3l

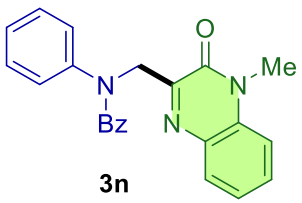
***N*-Ethyl-*N*-(1-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)ethyl)benzamide 3l (rr = 1 : 0.5):** Synthesised according to the general procedure and after chromatography on SiO_2 (38% to 42% EtOAc in Hexane), the product was isolated as white solid (78%, 52.1 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 1.5H), 7.56 (dd, *J* = 31.7, 7.6 Hz, 3.5H), 7.36 (dt, *J* = 28.3, 7.4 Hz, 7H), 7.27 (d, *J* = 8.4 Hz, 1.5H), 5.80 (s, 0.5H), 5.37 (t, *J* = 7.0 Hz, 1H), 3.63 (d, *J* = 10.6 Hz, 4.5H), 3.50 (dq, *J* = 14.1, 7.0 Hz, 1.5H), 3.35 (tt, *J* = 13.3, 6.1 Hz, 1.5H), 2.46 – 2.05 (m, 0.5H), 1.74 (s, 1H), 1.59 (d, *J* = 6.9 Hz, 3H), 1.07 (t, *J* = 7.1 Hz, 4.5H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 172.8, 171.9, 158.9, 157.0, 153.8, 137.6, 133.4, 132.0, 130.8, 130.5, 130.2, 129.2, 128.2, 126.8, 126.4, 123.7, 113.7, 55.0, 52.7, 42.2, 37.0, 29.1, 16.5, 16.0, 14.6. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{22}N_3O_2$: 336.1712; found: 336.1706.



3m

***N*-Butyl-*N*-(1-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butyl)benzamide 3m (rr = 1 : 0.4):** Synthesised according to the general procedure and after chromatography on SiO_2 (41% to 46% EtOAc in Hexane), the product was isolated as a white solid (75%, 58.7 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.0, 1.5 Hz, 1.4H), 7.58 (d, *J* = 7.5 Hz, 3.4H), 7.44 – 7.32 (m, 6H), 7.31 (dd, *J* = 8.4, 1.2 Hz, 1.5H), 5.94 (s, 0.4H), 5.31 (s, 1H), 3.68 (d, *J* = 13.5 Hz, 4.4H), 3.51 – 3.14 (m, 2.8H), 2.42 – 2.31 (m, 1.4H), 2.11 – 1.89 (m, 1H), 1.78 (s, 1H), 1.59 (d, *J* = 44.3 Hz, 2H), 1.40 – 1.27 (m, 2.5H), 1.17 (d, *J* = 56.7 Hz, 2.5H), 1.08 – 0.88 (m, 2H), 0.81 (q, *J* = 8.1 Hz, 6.5H), 0.60 (s, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 173.3, 156.6, 154.2, 150.3, 137.6, 133.4, 132.2, 131.2, 130.9, 130.6, 129.3, 128.2, 127.2, 126.6, 123.9, 123.8, 113.9, 113.8, 58.7, 55.9, 42.8, 33.0, 31.1, 29.8, 29.3, 28.9, 22.8, 20.6, 20.1, 19.7, 13.9. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{24}H_{30}N_3O_2$: 392.2338; found: 392.2343.

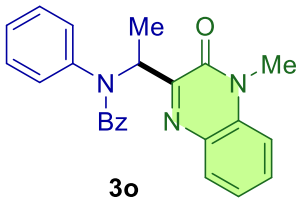
***N*-((4-Methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)methyl)-*N*-phenylbenzamide 3n:** Synthesised according to the general procedure and after chromatography on SiO_2 (36% to 40% EtOAc in Hexane), the product was isolated as colorless sticky liquid (67%, 49.4 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.52 (ddd, *J* = 8.6, 7.3, 1.5 Hz, 1H), 7.46 (dt, *J* = 7.0, 1.4 Hz, 2H), 7.36 – 7.26 (m, 3H), 7.26 – 7.23 (m, 2H), 7.22 – 7.14 (m, 4H), 7.12 – 7.03 (m, 1H), 5.38 (s, 2H), 3.68 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 170.9, 154.3, 144.4, 136.2,



3n

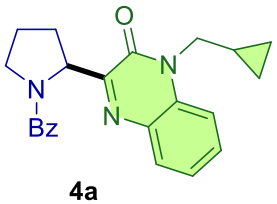
133.2, 132.7, 130.2, 130.1, 129.6, 128.8, 128.7, 128.6, 127.7, 126.5, 123.6, 120.2, 113.6, 52.7, 28.8. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{23}H_{20}N_3O_2$: 370.1556; found: 370.1560.

***N*-(1-(4-Methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)ethyl)-*N*-phenylbenzamide 3o:** Synthesised according to the general procedure and after chromatography on SiO_2 (38% to 42% EtOAc in Hexane), the product was isolated as colorless sticky liquid (64%, 48.9 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.53 (ddd, *J* = 8.6, 7.3, 1.5 Hz, 1H), 7.40 (d, *J* = 7.6 Hz, 2H), 7.37 – 7.28 (m, 4H), 7.20 (td, *J* = 7.4, 1.2 Hz, 2H), 7.18 – 7.05 (m, 4H), 3.72 (s, 3H), 1.52 (d, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.5, 159.7, 154.3, 141.5, 137.0, 133.6, 132.7, 130.6, 130.3, 130.1, 129.1, 128.7, 128.5, 127.6, 127.3, 123.5, 113.7, 55.6, 29.1, 16.4. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{24}H_{21}N_3O_2Na$: 406.1531; found: 406.1544.



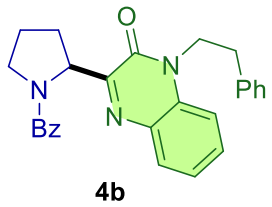
3o

3-(1-Benzoylpyrrolidin-2-yl)-1-(cyclopropylmethyl)quinoxalin-2(1H)-one 4a (rr = 1 : 0.5): Synthesised according to the general procedure and after chromatography on SiO_2 (44% to 48% EtOAc in Hexane), the product was isolated as white solid (86%, 64.2 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.1, 1.5 Hz, 0.5H), 7.81 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.63 – 7.56 (m, 2H), 7.50 (dddd, *J* = 17.4, 8.6, 7.1, 1.6 Hz, 1.5H), 7.38 (dd, *J* = 5.7, 2.5 Hz, 4H), 7.36 – 7.30 (m, 1H), 7.27 (t, *J* = 7.0 Hz, 1H), 7.19 – 7.10 (m, 1.5H), 7.07 (dd, *J* = 8.1, 6.6 Hz, 1H), 5.71 (dd, *J* = 8.3, 5.6 Hz, 1H), 5.41 (dd, *J* = 8.1, 2.7 Hz, 0.5H), 4.17 (d, *J* = 6.9 Hz, 2H), 4.10 – 3.93 (m, 1.5H), 3.87 (ddt, *J* = 28.5, 10.2, 7.3 Hz, 1.5H), 3.57 (ddd, *J* = 10.1, 7.3, 4.8 Hz, 1H), 2.51 (ddt, *J* = 11.9, 7.6, 6.1 Hz, 1H), 2.43 (ddt, *J* = 11.5, 7.7, 3.3 Hz, 0.5H), 2.11 – 1.96 (m, 3.5H), 1.91 (dt, *J* = 12.2, 7.2 Hz, 1H), 1.31 – 1.20 (m, 1H), 1.15 (ddt, *J* = 13.1, 10.0, 4.3 Hz, 0.5H), 0.60 – 0.47 (m, 4.5H), 0.44 (dt, *J* = 8.3, 6.2 Hz, 1H), 0.38 – 0.28 (m, 0.5H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.7, 169.2, 159.2, 159.0, 154.0, 153.3, 137.8, 137.4, 132.9, 132.8, 132.5, 132.4, 130.5, 130.4, 130.3, 129.8, 129.7, 129.1, 128.2, 127.0, 127.2, 126.2, 123.6, 123.2, 113.9, 113.8, 60.3, 59.2, 50.4, 47.1, 46.0, 45.7, 32.0, 30.3 25.2, 22.4, 9.7, 9.59, 4.3, 4.2, 3.9. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{23}H_{24}N_3O_2$: 374.1869; found: 374.1863.



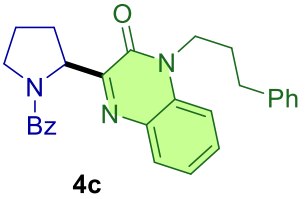
4a

3-(1-Benzoylpyrrolidin-2-yl)-1-phenethylquinoxalin-2(1H)-one 4b (rr = 1 : 0.5): Synthesised according to the general procedure and after chromatography on SiO_2 (46% to 50% EtOAc in Hexane), the product was isolated as colorless sticky liquid (75%, 63.4 mg); ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.83 (dd, *J* = 8.0, 1.5 Hz, 0.5H), 7.79 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.58 (ddd, *J* = 5.4, 3.0, 1.7 Hz, 2H), 7.46 (ddd, *J* = 8.5, 5.5, 1.6 Hz, 1.5H), 7.41 – 7.33 (m, 3H), 7.30 – 7.27 (m, 3.5H), 7.25 – 7.01 (m, 7.5H), 5.70 (dd, *J* = 8.3, 5.2 Hz, 1H), 5.41 (dd, *J* = 8.0, 2.5 Hz, 0.5H), 4.40 (dp, *J* = 8.6, 6.5 Hz, 2H), 4.25 (ddt, *J* = 9.4, 6.4, 3.9 Hz, 0.9H), 4.05 – 3.95 (m, 0.5H), 3.83 (ddt, *J* = 14.3, 10.4, 7.1 Hz, 1.5H), 3.55 (ddd, *J* = 10.2, 7.2, 4.7 Hz, 1H), 3.07 – 2.95 (m, 2H), 2.83 (td, *J* = 7.9, 5.1 Hz, 0.9H), 2.53 – 2.31 (m, 1.5H), 2.05 – 1.91 (m, 3H), 1.95 – 1.84 (m, 1.4H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.8, 169.2, 158.9, 158.9, 153.6, 152.8, 137.9, 137.8, 137.5, 137.4, 132.9, 132.5, 132.4, 132.0, 130.6, 130.5, 130.4, 130.0, 129.8, 129.1, 128.8, 128.8, 128.8, 128.7, 128.2, 128.0, 127.2, 126.9, 126.8, 126.3, 123.8, 123.4, 113.4, 60.2, 59.0, 50.4, 47.1, 43.6, 43.4, 33.4, 33.3, 32.0, 30.3, 25.2, 22.4. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{27}H_{26}N_3O_2$: 424.2025; found: 424.2018.



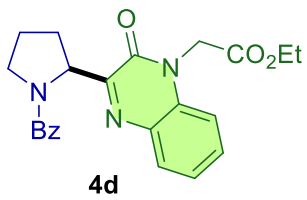
4b

3-(1-Benzoylpyrrolidin-2-yl)-1-(3-phenylpropyl)quinoxalin-2(1H)-one 4c (rr = 1 : 0.5): Synthesised according to the general procedure and after chromatography on SiO_2 (45% to 50% EtOAc in Hexane), the product was isolated as colorless solid (90%, 78.9 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.1, 1.6 Hz, 0.5H), 7.81 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.65 – 7.57 (m, 2H), 7.49 – 7.38 (m, 4.5H), 7.36 – 7.28 (m, 4H), 7.29 – 7.14 (m, 6H), 7.12 – 6.96 (m, 3H), 5.73 (dd, *J* = 8.2, 5.7 Hz, 1H), 5.45 (dd, *J* = 8.2, 2.7 Hz, 0.5H), 4.29 – 4.22 (m, 2H), 4.16 (ddd, *J* = 13.6, 9.4, 6.3 Hz, 0.5H), 4.04 (qd, *J* = 7.7, 4.4 Hz, 1H), 3.88 (ddt, *J* = 24.3, 10.0, 7.2 Hz, 1.5H), 3.60 (ddd, *J* = 10.1, 7.4, 4.7 Hz, 1H), 2.81 (td, *J* = 7.5, 2.5 Hz, 2H), 2.66 (hept, *J* = 7.1 Hz, 1H), 2.59 – 2.47 (m, 1H), 2.46 (td, *J* = 8.4, 4.6 Hz, 0.5H), 2.16 – 1.98 (m, 5.5H), 2.00 – 1.88 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.8, 169.2, 159.1, 158.9, 153.9, 153.1, 140.9, 140.7, 137.9, 137.4, 133.0, 132.6, 132.6, 132.1, 130.7, 130.5, 130.4, 129.9, 129.8, 129.2, 128.7, 128.6, 128.5, 128.4, 128.3, 128.0, 127.3, 126.4, 126.3, 126.3, 123.8, 123.3, 113.5, 113.5, 60.2, 59.2, 50.5, 47.2, 41.8, 41.5, 33.3, 33.1, 32.1, 30.4, 28.6, 25.3, 22.5. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{28}H_{28}N_3O_2$: 438.2182; found: 438.2188.



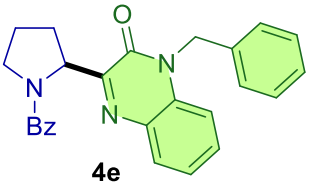
4c

Ethyl 2-(3-(1-benzoylpyrrolidin-2-yl)-2-oxoquinoxalin-1(2H)-yl)acetate 4d (rr = 1 : 0.5): Synthesised according to the general procedure and after chromatography on SiO_2 (47% to 52% EtOAc in Hexane), the product was isolated as yellow sticky liquid (80%, 64.9 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.0, 1.5 Hz, 0.5H), 7.84 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.65 – 7.57 (m, 2H), 7.50 (dddd, *J* = 19.4, 8.5, 7.2, 1.5 Hz, 1.5H), 7.44 – 7.35 (m, 3.5H), 7.31 (td, *J* = 7.6, 1.1 Hz, 1H), 7.22 – 7.09 (m, 2H), 7.05 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.03 – 6.99 (m, 0.5H), 5.70 (dd, *J* = 8.3, 5.8 Hz, 1H), 5.39 (dd, *J* = 8.3, 2.7 Hz, 0.5H), 5.16 (d, *J* = 17.4 Hz, 1H), 4.96 – 4.77 (m, 2H), 4.23 (dq, *J* = 17.7, 7.2 Hz, 3H), 4.03 (dt, *J* = 12.4, 5.8 Hz, 0.5H), 3.97 – 3.82 (m, 1.5H), 3.60 (ddd, *J* = 10.1, 7.3, 4.6 Hz, 1H), 2.64 – 2.46 (m, 1H), 2.48 – 2.38 (m, 0.5H), 2.20 – 2.00 (m, 3.5H), 2.00 – 1.89 (m, 1H), 1.36 – 1.11 (m, 4.5H). ^{13}C{^{1}H} NMR (101 MHz, CHLOROFORM-*D*) δ 169.3, 167.3, 158.9, 153.7, 152.9, 137.3, 132.8, 132.6, 130.8, 130.6, 130.2, 129.9, 129.3, 128.3, 128.2, 127.3, 126.3, 124.3, 123.8, 113.1, 62.1, 60.5, 59.2, 50.5, 47.1, 43.6, 43.3, 31.9, 30.4, 29.8, 25.4, 22.4, 14.2. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{23}H_{25}N_3O_4$: 406.1767; found: 406.1760.



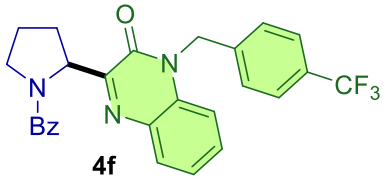
4d

3-(1-Benzoylpyrrolidin-2-yl)-1-benzylquinoxalin-2(1H)-one 4e (rr = 1 : 0.5): Synthesised according to the general procedure and after chromatography on SiO_2 (45% to 50% EtOAc in Hexane), the product was isolated as colorless sticky liquid (78%, 63.7mg); ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.85 (ddd, *J* = 15.9, 7.9, 1.5 Hz, 1.5H), 7.67 – 7.56 (m, 2H), 7.46 – 7.35 (m, 5H), 7.34 – 7.27 (m, 5H), 7.25 – 7.17 (m, 5H), 7.17 (s, 1.5H), 7.03 – 6.96 (m, 1H), 5.78 (dd, *J* = 8.2, 6.0 Hz, 1H), 5.58 – 5.46 (m, 3H), 5.14 (d, *J* = 15.7 Hz, 0.5H), 4.09 (dt, *J* = 12.3, 6.3 Hz, 0.5H), 3.91 (tt, *J* = 9.9, 7.3 Hz, 1.5H), 3.62 (ddd, *J* = 10.0, 7.4, 4.5 Hz, 1H), 2.67 – 2.46 (m, 1.5H), 2.15 (ddd, *J* = 11.4, 7.3, 5.8 Hz, 1H), 2.07 (dd, *J* = 8.2, 3.6 Hz, 2H), 1.97 (qd, *J* = 7.3, 4.4 Hz, 1.5H). ^{13}C{^{1}H} NMR (101 MHz, CHLOROFORM-*D*) δ 170.9, 169.3, 159.3, 159.3, 154.3, 153.5, 138.0, 137.3, 135.4, 135.0, 132.9, 132.8, 132.6, 132.3, 130.5, 130.5, 130.3, 130.0, 129.9, 129.2, 129.1, 129.0, 128.3, 128.1, 127.9, 127.7, 127.3, 127.0, 126.8, 126.4, 124.0, 123.6, 114.5, 60.3, 59.3, 50.6, 47.3, 46.0, 45.5, 32.2, 30.6, 25.5, 22.5. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{26}H_{24}N_3O_2$: 410.1869; found: 410.1865.



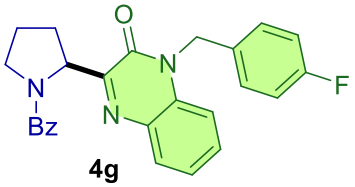
4e

3-(1-Benzoylpyrrolidin-2-yl)-1-(4-(trifluoromethyl)benzyl)quinoxalin-2(1H)-one 4f (rr = 1 : 0.4): Synthesised according to the general procedure and after chromatography on SiO_2 (48% to 53% EtOAc in Hexane), the product was isolated as yellow colour sticky liquid (86%, 82.0 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 7.9, 1.6 Hz, 0.4H), 7.84 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.61 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.55 (t, *J* = 8.6 Hz, 2.8H), 7.46 – 7.31 (m, 6.8H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.25 – 7.15 (m, 1.4H), 7.15 – 7.03 (m, 3H), 5.76 (dd, *J* = 8.2, 6.1 Hz, 1H), 5.55 (dd, *J* = 11.9, 9.0 Hz, 2.8H), 5.18 (d, *J* = 16.0 Hz, 0.4H), 4.15 – 4.05 (m, 0.4H), 3.90 (ddt, *J* = 14.3, 10.0, 7.1 Hz, 1.4H), 3.63 (ddd, *J* = 10.0, 7.4, 4.4 Hz, 1H), 2.55 (dddt, *J* = 17.0, 12.6, 8.7, 4.7 Hz, 1.4H), 2.10 (dddd, *J* = 21.5, 11.3, 7.3, 5.5 Hz, 2.8H), 1.98 (dtd, *J* = 11.8, 7.2, 3.5 Hz, 1.4H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.8, 169.3, 159.4, 159.3, 154.2, 153.3, 139.5, 139.1, 138.0, 137.2, 133.0, 132.6, 132.5, 132.0, 130.7, 130.7, 130.5, 130.2, 130.1, 129.9, 129.9, 129.1, 128.3, 128.1, 127.3, 127.3, 127.1, 126.9, 126.4, 126.0 (m), 126.0, 124.3, 124.1 (d, *J* = 272.1 Hz), 123.9, 114.1, 60.2, 59.2, 50.6, 47.3, 45.5, 45.1, 32.3, 30.6, 25.5, 22.5. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.61, -62.64. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{27}H_{23}F_3N_3O_2$: 478.1742; found: 478.1741.



4f

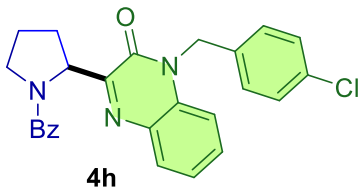
3-(1-Benzoylpyrrolidin-2-yl)-1-(4-fluorobenzyl)quinoxalin-2(1H)-one 4g (rr = 1 : 0.5): Synthesised according to the general procedure and after chromatography on SiO_2 (47% to 52% EtOAc in Hexane), the product was isolated as colorless sticky liquid (76%, 65.1 mg); ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.84 (dd, *J* = 7.9, 1.6 Hz, 0.5H), 7.79 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.58 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.41 – 7.29 (m, 4.6H), 7.28 (t, *J* = 8.0 Hz, 0.5H), 7.27 – 7.07 (m, 6H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.94 (tt, *J* = 5.9, 2.5 Hz, 4H), 5.74 (dd, *J* = 8.1, 5.8 Hz, 1H), 5.50 (dd, *J* = 8.2, 2.7 Hz, 0.5H), 5.43 (d, *J* = 17.9 Hz, 2.5H), 5.06 (d, *J* = 15.6 Hz, 0.5H), 4.06 (dt, *J* = 12.3, 6.2 Hz, 0.5H), 3.95 – 3.76 (m, 1.5H), 3.58 (ddd, *J* = 9.9, 7.4, 4.5 Hz, 1H), 2.59 – 2.42 (m, 1.5H), 2.16 – 1.98 (m, 3.5H), 1.93 (dt, *J* = 11.9, 7.3 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.7, 169.2, 163.2, 163.2, 161.2, 161.2, 159.2, 159.2, 154.1, 153.3, 137.9, 137.2, 132.9, 132.5, 132.5, 132.0, 131.1 (d, *J* = 3.2 Hz), 130.7 (d, *J* = 3.2 Hz), 130.5 (d, *J* = 3.4 Hz), 130.3, 130.0, 129.8, 129.0, 128.8 (d, *J* = 8.2 Hz), 128.6 (d, *J* = 7.9 Hz), 128.2, 128.0, 127.2, 126.3, 124.0, 123.6, 115.9 (d, *J* = 21.6 Hz), 115.8 (d, *J* = 22.1 Hz), 114.2,



4g

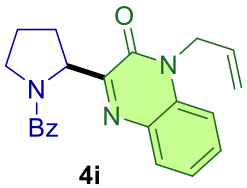
60.1, 59.1, 50.5, 47.2, 45.1, 44.7, 32.2, 30.5, 25.4, 22.4. ^{19}F NMR (376 MHz, CHLOROFORM-*D*) δ -114.06, -114.42. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{26}H_{23}FN_3O2$: 428.1774; found: 428.1773.

3-(1-Benzoylpyrrolidin-2-yl)-1-(4-chlorobenzyl)quinoxalin-2(1H)-one 4h (rr = 1 : 0.5): Synthesised according to the general procedure and after chromatography on SiO_2 (45% to 50% EtOAc in Hexane), the product was isolated as colorless sticky liquid (85%, 75.1 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.0, 1.6 Hz, 0.5H), 7.82 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.65 – 7.56 (m, 2H), 7.42 – 7.34 (m, 4.5H), 7.31 (t, *J* = 7.6 Hz, 0.5H), 7.28 – 7.22 (m, 4H), 7.22 – 7.13 (m, 4.5H), 7.09 (t, *J* = 7.8 Hz, 1.5H), 6.91 (d, *J* = 8.2 Hz, 0.9H), 5.76 (dd, *J* = 8.2, 6.0 Hz, 1H), 5.52 (dd, *J* = 8.2, 2.7 Hz, 0.5H), 5.44 (d, *J* = 10.6 Hz, 2.5H), 5.07 (d, *J* = 15.8 Hz, 0.5H), 4.19 – 4.03 (m, 0.5H), 3.89 (ddt, *J* = 14.3, 10.0, 7.1 Hz, 1.5H), 3.61 (ddd, *J* = 10.0, 7.3, 4.4 Hz, 1H), 2.53 (dddt, *J* = 19.0, 11.2, 7.4, 4.3 Hz, 1.5H), 2.17 – 2.00 (m, 3.5H), 2.01 – 1.91 (m, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.7, 169.2, 159.2, 159.2, 154.1, 153.3, 138.0, 137.2, 133.9, 133.7, 133.5, 133.0, 132.5, 132.5, 132.0, 130.5, 130.5, 130.4, 130.0, 129.8, 129.1, 129.1, 129.0, 128.4, 128.3, 128.2, 128.0, 127.2, 126.3, 124.1, 123.7, 114.2, 60.1, 59.2, 50.5, 47.3, 45.2, 44.8, 32.2, 30.5, 25.4, 22.5. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{26}H_{23}ClN_3O_2$: 444.1479; found: 444.1471.



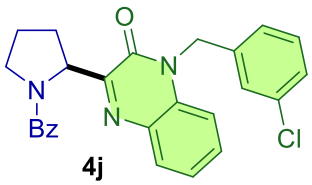
4h

1-Allyl-3-(1-benzoylpyrrolidin-2-yl)quinoxalin-2(1H)-one 4i (rr = 1 : 0.5): Synthesised according to the general procedure and after chromatography on SiO_2 (42% to 47% EtOAc in Hexane), the product was isolated as brown colour solid **(8**7%, 62.5 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.0, 1.6 Hz, 0.5H), 7.81 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.63 – 7.57 (m, 2H), 7.47 (dddd, *J* = 15.7, 8.6, 7.2, 1.6 Hz, 1.5H), 7.43 – 7.36 (m, 3H), 7.37 – 7.30 (m, 0.5H), 7.31 – 7.23 (m, 2.0H), 7.18 (ddd, *J* = 8.4, 6.6, 1.4 Hz, 1.5H), 7.17 – 7.10 (m, 0.5H), 7.07 (dd, *J* = 8.0, 6.6 Hz, 1H), 5.93 (ddt, *J* = 17.3, 10.4, 5.2 Hz, 1H), 5.79 (ddt, *J* = 17.3, 10.2, 5.0 Hz, 0.5H), 5.71 (dd, *J* = 8.2, 5.9 Hz, 1H), 5.45 (dd, *J* = 8.2, 2.7 Hz, 0.5H), 4.94 – 4.85 (m, 2.5H), 4.80 (ddt, *J* = 16.3, 4.9, 1.8 Hz, 0.5H), 4.69 – 4.60 (m, 0.5H), 4.04 (ddd, *J* = 12.4, 7.6, 5.4 Hz, 0.5H), 3.88 (ddt, *J* = 20.8, 10.0, 7.2 Hz, 1.5H), 3.59 (ddd, *J* = 9.9, 7.3, 4.5 Hz, 1H), 2.57 – 2.42 (m, 1.5H), 2.14 – 1.86 (m, 4.5H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.8, 169.2, 159.1, 159.1, 153.7, 152.9, 137.9, 137.4, 132.9, 132.7, 132.5, 132.2, 130.8, 130.4, 130.4, 130.3, 129.9, 129.8, 129.2, 128.3, 128.0, 127.2, 126.3, 123.9, 123.5, 118.2, 117.9, 114.2, 114.2, 60.2, 59.2, 50.5, 47.2, 44.5, 44.1, 32.2, 30.4, 25.4, 22.5. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{22}H_{22}N_3O_2$: 360.1712; found: 360.1716.



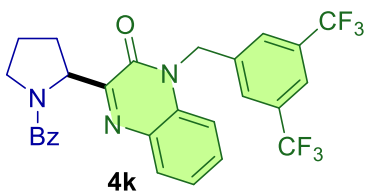
4i

3-(1-Benzoylpyrrolidin-2-yl)-1-(3-chlorobenzyl)quinoxalin-2(1H)-one 4j (rr = 1 : 0.5): Synthesised according to the general procedure and after chromatography on SiO_2 (49% to 53% EtOAc in Hexane), the product was isolated as colorless sticky liquid (76%, 67.2 mg); ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.87 (dd, *J* = 8.0, 1.6 Hz, 0.5H), 7.82 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.61 (ddd, *J* = 5.1, 2.5, 1.5 Hz, 2H), 7.43 – 7.26 (m, 6.5H), 7.25 – 7.18 (m, 4.5H), 7.18 – 7.07 (m, 4H), 7.00 (d, *J* = 2.2 Hz, 0.5H), 6.87 (dt, *J* = 6.3, 2.0 Hz, 0.5H), 5.76 (dd, *J* = 8.2, 6.0 Hz, 1H), 5.62 – 5.30 (m, 3H), 5.06 (d, *J* = 15.8 Hz, 0.5H), 4.08 (dt, *J* = 12.3, 6.7 Hz, 0.5H), 3.89 (ddt, *J* = 14.3, 10.0, 7.2 Hz, 1.5H), 3.67 – 3.54 (m, 1H), 2.53 (qdd, *J* = 15.8, 7.7, 4.5 Hz, 1.5H) 2.13 (ddd, *J* = 10.8, 7.2, 5.6 Hz, 1.5H), 2.08 – 2.02 (m, 2H), 2.00 – 1.90 (m, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.7, 169.2, 159.2, 159.2, 154.1, 153.2, 137.8, 137.4, 137.2, 137.1, 134.9, 134.8, 132.9, 132.5, 132.0, 130.5, 130.4, 130.3, 130.2, 130.0, 129.8, 129.3, 128.2, 128.1, 128.0, 127.9, 127.2, 127.1, 126.8, 126.2, 125.1, 125.0, 124.1, 123.7, 114.1, 114.1, 60.2, 59.2, 50.5, 47.2, 45.4, 45.0, 32.2, 30.5, 25.4, 22.5. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{26}H_{23}ClN_3O_2$: 444.1479; found: 444.1478.



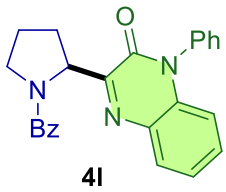
4j

3-(1-Benzoylpyrrolidin-2-yl)-1-(3,5-bis(trifluoromethyl)benzyl)quinoxalin-2(1H)-one 4k (rr = 1 : 0.4): Synthesised according to the general procedure and after chromatography on SiO_2 (45% to 50% EtOAc in Hexane), the product was isolated as yellow colour sticky liquid (73%, 79.3 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.0, 1.5 Hz, 0.4H), 7.87 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.80 (d, *J* = 6.0 Hz, 1.4H), 7.75 (s, 2H), 7.65 – 7.57 (m, 2H), 7.54 (s, 0.8H), 7.52 – 7.37 (m, 4.8H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.23 – 7.18 (m, 0.8H), 7.17 – 7.12 (m, 1.4H), 7.11 – 7.05 (m, 1H), 5.74 (dd, *J* = 8.1, 6.0 Hz, 1H), 5.66 (d, *J* = 16.0 Hz, 1H), 5.58 (d, *J* = 16.0 Hz, 0.4H), 5.52 – 5.42 (m, 1.4H), 5.24 (d, *J* = 16.1 Hz, 0.4H), 4.07 (ddd, *J* = 11.7, 7.6, 4.4 Hz, 0.4H), 3.97 – 3.85 (m, 1.4H), 3.64 (ddd, *J* = 11.0, 7.3, 4.2 Hz, 1H), 2.63 – 2.44 (m, 1.4H), 2.20 – 1.88 (m, 4.2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.9, 169.3, 159.4, 159.3, 154.2, 153.3, 138.3, 138.0, 137.9, 137.2, 133.1, 132.6, 132.4, 132.1, 131.9, 131.1, 130.9, 130.9, 130.4, 130.0, 129.3, 128.3,



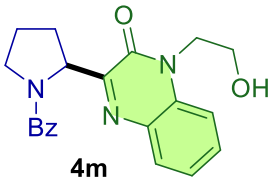
4k

128.1, 127.6, 127.3, 126.3, 124.7, 124.2, 124.2, 122.2, 122.1, 113.5, 60.4, 59.3, 50.6, 47.2, 45.4, 45.1, 32.2, 30.6, 25.6, 22.5. ^{19}F NMR (376 MHz, CHLOROFORM-*D*) δ -62.73. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{28}H_{22}F_6N_3O_2$: 546.1616; found: 546.1613.



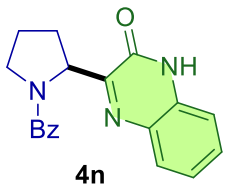
4l

3-(1-Benzoylpyrrolidin-2-yl)-1-phenylquinoxalin-2(1H)-one 4l (rr = 1 : 0.4): Synthesised according to the general procedure and after chromatography on SiO_2 (49% to 54% EtOAc in Hexane), the product was isolated as colorless sticky liquid (75%, 59.0 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 – 7.83 (m, 1.4H), 7.67 – 7.58 (m, 3.8H), 7.54 (ddd, *J* = 12.0, 7.8, 5.7 Hz, 2.8H), 7.41 (dd, *J* = 4.8, 1.9 Hz, 3H), 7.37 – 7.27 (m, 5H), 7.25 – 7.18 (m, 1.4H), 7.14 (t, *J* = 7.4 Hz, 0.8H), 6.99 (d, *J* = 7.4 Hz, 0.4H), 6.69 – 6.62 (m, 1H), 6.60 (dt, *J* = 6.2, 3.7 Hz, 0.4H), 5.70 (dd, *J* = 8.2, 6.4 Hz, 1H), 5.47 (dd, *J* = 8.2, 3.3 Hz, 0.4H), 4.07 (dt, *J* = 12.8, 7.3 Hz, 0.4H), 3.91 (ddt, *J* = 25.0, 10.1, 7.3 Hz, 1.4H), 3.60 (ddd, *J* = 10.2, 7.3, 4.6 Hz, 1H), 2.59 – 2.44 (m, 1.4H), 2.17 (ddt, *J* = 12.8, 7.9, 6.6 Hz, 1H), 2.07 (ddt, *J* = 14.2, 7.3, 3.6 Hz, 1.8H), 1.95 (dq, *J* = 12.3, 7.6 Hz, 1.4H). ^{13}C{^{1}H} NMR (101 MHz, CHLOROFORM-*D*) δ 170.8, 169.4, 160.0, 159.6, 153.8, 153.0, 138.0, 137.4, 135.9, 135.4, 134.3, 133.8, 132.6, 132.2, 130.4, 130.4, 130.3, 130.3, 130.1, 129.9, 129.9, 129.9, 129.7, 129.6, 129.5, 129.2, 128.5, 128.5, 128.4, 128.3, 128.3, 128.2, 128.1, 128.1, 127.3, 127.1, 126.4, 124.1, 123.7, 115.4, 60.1, 59.8, 50.6, 47.3, 32.3, 30.3, 25.4, 22.7. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{25}H_{22}N_3O_2$: 396.1712; found: 396.1714.



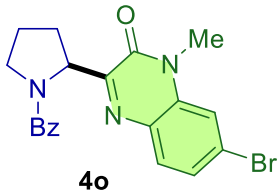
4m

3-(1-Benzoylpyrrolidin-2-yl)-1-(2-hydroxyethyl)quinoxalin-2(1H)-one 4m (rr = 1 : 0.3): Synthesised according to the general procedure and after chromatography on SiO_2 (40% to 50% EtOAc in Hexane), the product was isolated as yellow colour sticky liquid (59%, 42.8 mg); ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.80 (dd, *J* = 7.9, 1.5 Hz, 0.3H), 7.74 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.60 – 7.54 (m, 2H), 7.43 – 7.35 (m, 5.6H), 7.34 – 7.28 (m, 0.6H), 7.21 (dt, *J* = 8.3, 4.2 Hz, 1H), 7.15 – 7.08 (m, 0.9H), 7.08 – 7.00 (m, 0.6H), 5.66 (dd, *J* = 8.2, 5.5 Hz, 1H), 5.38 (dd, *J* = 8.0, 2.8 Hz, 0.3H), 4.37 – 4.21 (m, 2H), 4.12 (t, *J* = 6.0 Hz, 0.6H), 4.02 – 3.94 (m, 0.3H), 3.92 – 3.84 (m, 1H), 3.81 (t, *J* = 6.2 Hz, 2.6H), 3.66 – 3.63 (m, 0.3H), 3.58 (ddd, *J* = 10.3, 7.3, 4.7 Hz, 1H), 2.54 – 2.43 (m, 1H), 2.39 (td, *J* = 8.1, 4.4 Hz, 0.3H), 2.09 – 1.95 (m, 3H), 1.92 (qd, *J* = 7.2, 4.3 Hz, 0.9H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.8, 169.5, 158.7, 158.5, 154.4, 153.6, 137.6, 137.0, 133.1, 132.8, 132.6, 132.5, 130.4, 130.3, 130.1, 130.0, 130.0, 129.2, 128.4, 128.0, 127.1, 126.2, 123.9, 123.5, 114.3, 114.2, 60.2, 59.7, 59.6, 59.1, 50.6, 47.2, 44.7, 44.3, 32.1, 30.4, 25.2, 22.5. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{21}H_{22}N_3O_3$: 364.1661; found: 364.1664.



4n

3-(1-Benzoylpyrrolidin-2-yl)quinoxalin-2(1H)-one 4n (rr = 1 : 0.4): Synthesised according to the general procedure and after chromatography on SiO_2 (10% to 20% EtOAc in Hexane), the product was isolated as colorless oily liquid (58%, 37.8 mg); ^{1}H NMR (400 MHz, DMSO-D_6) δ 12.26 (s, 1H), 7.67 (dd, *J* = 11.7, 8.0 Hz, 1.5H), 7.49 (p, *J* = 3.2 Hz, 2H), 7.41 – 7.31 (m, 5H), 7.24 – 7.11 (m, 3H), 7.10 – 7.03 (m, 1.5H), 5.52 (td, *J* = 8.5, 4.5 Hz, 1H), 5.27 (dd, *J* = 8.1, 3.7 Hz, 0.4H), 3.86 (td, *J* = 8.1, 4.1 Hz, 0.4H), 3.75 (ddt, *J* = 13.6, 10.3, 4.9 Hz, 1H), 3.53 – 3.45 (m, 1.5H), 2.46 – 2.28 (m, 1.4H), 2.00 – 1.91 (m, 3H), 1.90 – 1.83 (m, 1.3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 173.5, 165.0, 164.7, 159.3, 158.5, 142.7, 142.2, 136.9, 136.8, 136.7, 136.5, 134.9, 134.6, 134.5, 134.0, 133.6, 133.5, 133.1, 132.8, 131.8, 130.9, 128.3, 128.0, 120.4, 64.7, 62.9, 55.0, 51.8, 36.5, 35.0, 29.8, 26.9. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{19}H_{18}N_3O_2$: 320.1399; found: 320.1386.

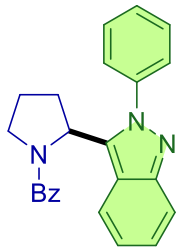


4o

3-(1-Benzoylpyrrolidin-2-yl)-7-bromo-1-methylquinoxalin-2(1H)-one 4o (rr = 1 : 0.4): Synthesised according to the general procedure and after chromatography on SiO_2 (46% to 50% EtOAc in Hexane), the product was isolated as colorless oily liquid (87%, 71.4 mg); ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.71 (d, *J* = 8.5 Hz, 0.4H), 7.65 (dd, *J* = 8.4, 0.7 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.46 (dd, *J* = 8.6, 1.9 Hz, 0.5H), 7.43 (d, *J* = 2.0 Hz, 1H), 7.41 (s, 4.8H), 7.20 – 7.04 (m, 1.5H), 5.66 (dd, *J* = 8.2, 5.7 Hz, 1H), 5.40 (dd, *J* = 8.3, 2.8 Hz, 0.4H), 3.99 (ddd, *J* = 12.4, 8.5, 4.7 Hz, 0.4H), 3.91 – 3.78 (m, 1.5H), 3.65 (d, *J* = 0.8 Hz, 3H), 3.63 – 3.54 (m, 1H), 3.49 (s, 1H), 2.57 – 2.39 (m, 1.4H), 2.09 – 2.03 (m, 1.5H), 2.02 – 1.97 (m, 1.5H), 1.95 – 1.83 (m, 1.4H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 174.3, 169.4, 159.6, 153.9, 137.7, 137.1, 134.6, 132.7, 131.5, 131.5, 131.4, 130.0, 129.3, 128.6, 128.3, 128.2, 127.9, 127.4, 127.1, 126.9, 126.4, 124.7, 124.1, 117.2, 116.8, 60.4, 59.3, 50.6, 47.2, 32.1, 30.4, 29.8, 29.2, 25.5, 20.6. HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{20}H_{18}BrN_3NaO_2$: 434.0480; found: 434.0473.

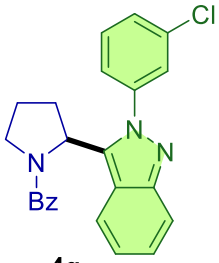
Phenyl(2-(2-phenyl-2H-indazol-3-yl)pyrrolidin-1-yl)methanone 4p (rr = 1 : 0.5): Synthesised according to the general procedure and after chromatography on SiO_2 (35% to 40% EtOAc in Hexane), the product was isolated as colorless sticky liquid (45%, 32.8 mg); ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.76 (dd, *J* = 20.3, 7.8 Hz, 4H), 7.67 (d, *J* = 8.8 Hz, 0.5H),

7.71 – 7.47 (m, 6H), 7.46 – 7.33 (m, 5H), 7.37 – 7.25 (m, 1H), 7.19 – 6.99 (m, 2.5H), 6.82 (dd, *J* = 27.0, 7.5 Hz, 2H), 5.51 (t, *J* = 8.1 Hz, 1H), 5.16 – 5.06 (m, 0.5H), 4.19 – 4.04 (m, 0.5H), 3.92 (td, *J* = 9.9, 5.6 Hz, 1.5H), 3.76 – 3.65 (m, 1H), 2.35 (d, *J* = 11.3 Hz, 1H), 2.28 – 2.16 (m, 1H), 2.16 – 2.01 (m, 2H), 1.87 (dd, *J* = 23.9, 14.2 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 171.1, 170.2, 148.8, 148.6, 140.2, 139.0, 137.2, 136.9, 136.3, 130.5, 129.2, 129.2, 129.1, 128.3, 128.3, 127.5, 127.1, 126.9, 126.7, 126.3, 126.2, 125.7, 122.6, 121.5, 119.9, 119.5, 119.3, 118.8, 118.3, 118.0, 56.6, 54.8, 51.4, 47.9, 35.5, 33.5, 26.3, 23.4. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{24}H_{22}N_3O$: 368.1763; found: 368.1758.



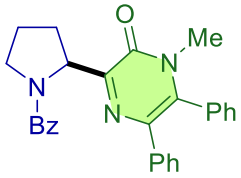
4p

(2-(2-(3-Chlorophenyl)-2H-indazol-3-yl)pyrrolidin-1-yl)(phenyl)methanone 4q (rr = 1 : 0.5): Synthesised according to the general procedure and after chromatography on SiO_2 (38% to 42% EtOAc in Hexane), the product was isolated as colorless sticky liquid (57%, 45.7 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.78 (m, 2H), 7.73 (dd, *J* = 8.6, 3.1 Hz, 2H), 7.66 (d, *J* = 8.8 Hz, 0.5H), 7.59 (d, *J* = 8.6 Hz, 0.5H), 7.52 (t, *J* = 5.7 Hz, 4H), 7.41 (dd, *J* = 12.2, 7.1 Hz, 3.5H), 7.32 (q, *J* = 8.9 Hz, 2.5H), 7.17 (t, *J* = 7.7 Hz, 0.5H), 7.11 (dd, *J* = 15.5, 7.8 Hz, 2H), 6.83 (d, *J* = 7.9 Hz, 0.5H), 6.75 (d, *J* = 7.7 Hz, 1.5H), 5.51 (t, *J* = 8.1 Hz, 1H), 5.11 – 5.05 (m, 0.5H), 4.14 (s,0.5H), 3.95 (td, *J* = 10.2, 6.0 Hz, 1.5H), 3.73 (dd, *J* = 9.9, 6.8 Hz, 1H) 2.40 (s, 1.5H), 2.27 – 2.07 (m, 3.5H), 1.93 (d, *J* = 10.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 170.4, 149.1, 141.2, 137.4, 136.2, 135.0, 130.7, 130.4, 130.0, 129.6, 128.5, 127.6, 127.3, 127.0, 126.8, 125.6, 125.3, 124.3, 123.0, 121.9, 119.5, 119.0, 118.5, 118.1, 56.5, 54.9, 51.5, 48.0, 35.7, 33.6, 26.5, 23.7. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{24}H_{21}ClN_3O$: 402.1373; found: 402.1383.



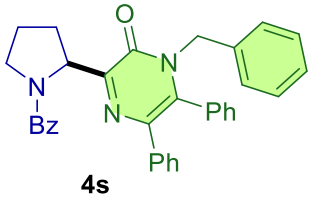
4q

3-(1-Benzoylpyrrolidin-2-yl)-1-methyl-5,6-diphenylpyrazin-2(1H)-one 4r (rr = 1 : 0.3): Synthesised according to the general procedure and after chromatography on SiO_2 (50% to 60% EtOAc in Hexane), the product was isolated as colorless oily liquid (82%, 71.2 mg); ^1H NMR (400 MHz, CHLOROFORM-*D*) δ 7.69 – 7.50 (m, 2H), 7.45 – 7.36 (m, 6.5H), 7.33 – 7.27 (m, 2H), 7.25 – 7.16 (m, 2H), 7.15 – 7.06 (m, 8H), 5.71 (dd, *J* = 8.2, 5.9 Hz, 1H), 5.45 (dd, *J* = 7.8, 4.7 Hz, 0.3H), 4.03 – 3.87 (m, 0.7H), 3.79 (dt, *J* = 10.2, 7.3 Hz, 1H), 3.55 (ddd, *J* = 10.2, 7.3, 5.0 Hz, 1H), 3.31 (s, 3H), 3.09 (s, 1H), 2.66 – 2.41 (m, 1.4H), 2.22 – 2.11 (m, 1.4H), 2.11 – 2.00 (m, 1.4H), 1.99 – 1.87 (m, 1.4H). $^{13}C\{^1H\}$ NMR (101 MHz, CHLOROFORM-*D*) δ 170.6, 169.4, 156.0, 155.6, 154.8, 154.0, 138.2, 138.1, 137.6, 137.4, 137.3, 132.8, 132.5, 132.3, 132.1, 130.3, 130.2, 130.0, 129.8, 129.5, 129.4, 129.2, 129.1, 129.0, 128.4, 128.3, 128.0, 127.9, 127.6, 127.6, 127.3, 127.2, 126.9, 126.6, 60.0, 59.1, 50.5, 47.6, 34.0, 33.8, 32.6, 30.4, 25.4, 23.2. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{28}H_{26}N_3O_2$: 436.2025; found: 436.2029.



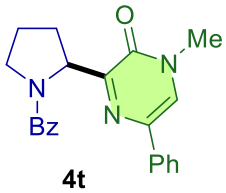
4r

3-(1-Benzoylpyrrolidin-2-yl)-1-benzyl-5,6-diphenylpyrazin-2(1H)-one 4s (rr = 1 : 0.5): Synthesised according to the general procedure and after chromatography on SiO_2 (50% to 60% EtOAc in Hexane), the product was isolated as colorless oily liquid (87%, 89 mg); ^1H NMR (400 MHz, CHLOROFORM-*D*) δ 7.78 – 7.68 (m, 2H), 7.57 – 7.37 (m, 10H), 7.36 – 7.28 (m, 8H), 7.24 – 7.16 (m, 5H), 7.10 – 6.98 (m, 3.5H), 6.93 (d, *J* = 7.6 Hz, 0.5H), 6.83 – 6.72 (m, 1H), 5.91 (dd, *J* = 8.2, 6.0 Hz, 1H), 5.66 (dd, *J* = 8.0, 3.7 Hz, 0.5H), 5.28 (q, *J* = 15.0 Hz, 2.5H), 4.92 (d, *J* = 15.0 Hz, 0.5H), 4.18 (ddd, *J* = 12.9, 7.8, 5.4 Hz, 0.5H), 4.06 (dt, *J* = 11.7, 7.1 Hz, 0.5H), 3.96 (dt, *J* = 10.3, 7.3 Hz, 1H), 3.71 (ddd, *J* = 10.3, 7.3, 4.8 Hz, 1H), 2.81 – 2.59 (m, 1.5H), 2.42 – 2.29 (m, 1.5H), 2.27 – 2.14 (m, 2H), 2.15 – 2.05 (m, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, CHLOROFORM-*D*) δ 170.6, 169.4, 156.8, 156.5, 154.6, 153.7, 138.1, 138.0, 137.6, 137.3, 137.2, 137.2, 136.2, 135.9, 132.5, 132.4, 132.2, 131.9, 130.7, 130.6, 130.4, 129.7, 129.6, 129.5, 129.4, 129.2, 128.8, 128.8, 128.7, 128.5, 128.5, 128.4, 128.3, 128.1, 127.8, 127.5, 127.5, 127.4, 127.2, 127.1, 127.1, 126.8, 126.6, 60.3, 59.3, 50.5, 49.1, 48.7, 47.5, 32.3, 30.4, 25.4, 22.8. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{34}H_{30}N_3O_2$: 512.2338; found: 512.2344.



4s

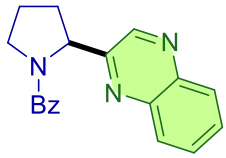
3-(1-Benzoylpyrrolidin-2-yl)-1-methyl-5-phenylpyrazin-2(1H)-one 4t (rr = 1 : 0.5): Synthesised according to the general procedure and after chromatography on SiO_2 (50% to 60% EtOAc in Hexane), the product was isolated as colorless oily liquid (74%, 53.3 mg); ^1H NMR (400 MHz, CHLOROFORM-*D*) δ 7.80 – 7.75 (m, 1H), 7.73 – 7.68 (m, 2H), 7.62 – 7.56 (m, 2H), 7.46 (d, *J* = 12.0 Hz, 2H), 7.43 – 7.37 (m, 4H), 7.35 (dt, *J* = 6.8, 0.8 Hz, 2H), 7.32 – 7.26 (m, 1H), 7.23 – 7.12 (m, 2.5H), 5.69 (dd, *J* = 8.2, 5.1 Hz, 1H), 5.39 (dd, *J* = 8.0, 3.1 Hz, 0.5H), 4.04 (ddd, *J* = 12.5, 8.2, 4.9 Hz, 0.5H), 3.94 – 3.78 (m, 1.5H), 3.64 – 3.59 (m, 1H), 3.59 (s, 3H), 3.44 (s, 1.5H), 2.55 – 2.38 (m, 1.5H), 2.08 – 1.96 (m, 3.5H), 1.92 (qd, *J* = 7.0,



4t

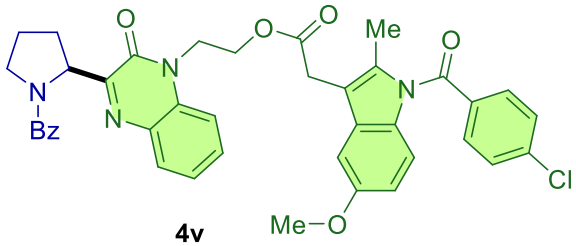
4.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, CHLOROFORM-*D*) δ 170.9, 169.2, 157.3, 154.7, 153.9, 137.9, 137.5, 136.1, 135.2, 132.2, 132.0, 129.8, 129.2, 129.1, 128.8, 128.3, 128.2, 128.1, 127.8, 127.2, 127.2, 126.4, 125.0, 124.9, 124.7, 124.6, 60.1, 58.7, 50.5, 47.1, 37.5, 37.4, 31.9, 30.3, 25.2, 22.5. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{22}H_{22}N_3O_2$: 360.1712; found: 360.1708.

Phenyl(2-(quinoxalin-2-yl)pyrrolidin-1-yl)methanone 4u (rr = 1 : 0.2): Synthesised according to the general procedure and after chromatography on SiO_2 (50% to 60% EtOAc in Hexane), the product was isolated as colorless oily liquid (68%, 41 mg); ^1H NMR (400 MHz, CHLOROFORM-*D*) δ 8.97 (s, 1H), 8.41 (s, 0.2H), 8.13 – 8.01 (m, 2H), 7.97 (d, *J* = 7.8 Hz, 0.4H), 7.81 – 7.66 (m, 2.3H), 7.63 – 7.56 (m, 2H), 7.49 – 7.32 (m, 2.8H), 7.16 (s, 0.2H), 7.07 (s, 1H), 5.57 (dd, *J* = 7.9, 6.5 Hz, 1H), 5.18 (d, *J* = 7.9 Hz, 0.2H), 4.04 (s, 0.5H), 3.89 (dt, *J* = 10.4, 7.4 Hz, 1H), 3.70 (ddd, *J* = 10.7, 7.2, 4.7 Hz, 1H), 2.52 (dq, *J* = 13.3, 6.9 Hz, 1.2H), 2.36 – 2.26 (m, 1.2H), 2.15 (p, *J* = 5.9 Hz, 1.3H), 1.99 (dp, *J* = 12.4, 7.5 Hz, 1.2H). $^{13}C\{^1H\}$ NMR (101 MHz, CHLOROFORM-*D*) δ 170.1, 157.0, 144.6, 142.3, 142.0, 136.4, 130.4, 130.0, 129.4, 129.3, 128.4, 127.5, 61.1, 51.0, 32.5, 25.7. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{19}H_{18}N_3O$: 304.1450; found: 304.1452.



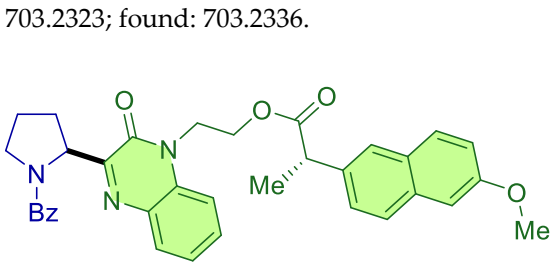
4u

2-(3-(1-Benzoylpyrrolidin-2-yl)-2-oxoquinoxalin-1(2H)-yl)ethyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate 4v (rr = 1 : 0.3): Synthesised according to the general procedure and after chromatography on SiO_2 (48% to 53% EtOAc in Hexane), the product was isolated as colorless sticky liquid (59%, 82.5 mg); ^1H NMR (400 MHz, CHLOROFORM-*D*) δ 7.84 (ddd, *J* = 10.8, 7.9, 1.5 Hz, 1.3H), 7.71 – 7.57 (m, 5H), 7.49 – 7.44 (m, 3H), 7.43 – 7.37 (m, 4H), 7.34 – 7.27 (m, 2.6H), 7.21 – 7.09 (m, 1H), 7.05 (dd, *J* = 8.0, 6.5 Hz, 0.7H), 6.93 (d, *J* = 2.5 Hz, 1H), 6.88 (dd, *J* = 9.0, 0.5 Hz, 1.3H), 6.84 (d, *J* = 9.0 Hz, 0.3H), 6.66 (dt, *J* = 9.0, 2.9 Hz, 1.3H), 5.71 (dd, *J* = 8.2, 5.5 Hz, 1H), 5.42 (dd, *J* = 8.1, 2.7 Hz, 0.3H), 4.64 – 4.45 (m, 4H), 4.41 – 4.29 (m, 1.3H), 4.06 – 3.97 (m, 0.3H), 3.94 – 3.83 (m, 1.3H), 3.81 (d, *J* = 5.8 Hz, 4H), 3.68 – 3.57 (m, 3H), 3.55 (s, 0.6H), 2.60 – 2.38 (m, 1.4H), 2.27 (d, *J* = 6.5 Hz, 4.3H), 2.13 – 2.05 (m, 1.4H), 2.04 – 2.00 (m, 1.3H), 1.98 – 1.84 (m, 1.3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 170.9, 169.2, 168.3, 158.8, 156.1, 154.0, 139.3, 137.2, 136.0, 133.9, 132.8, 131.3, 131.2, 131.1, 130.8, 130.6, 130.5, 130.0, 129.8, 129.2, 129.1, 128.5, 128.2, 128.0, 127.2, 127.0, 126.3, 123.6, 115.0, 113.4, 112.1, 111.7, 111.6, 101.3, 61.3, 61.1, 60.4, 60.0, 58.9, 55.8, 50.4, 42.7, 40.8, 39.4, 38.1, 32.0, 30.4, 30.1, 25.3, 23.2, 13.4, 13.3. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{40}H_{36}ClN_4O_6$: 703.2323; found: 703.2336.



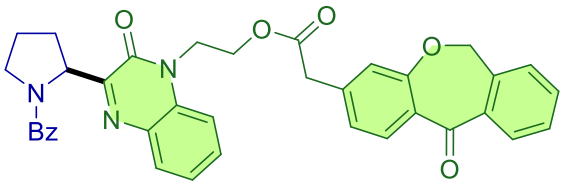
4v

2-(3-(1-Benzoylpyrrolidin-2-yl)-2-oxoquinoxalin-1(2H)-yl)ethyl (2S)-2-(6-methoxynaphthalen-2-yl)propanoate 4w (rr = 1 : 0.4): Synthesised according to the general procedure and after chromatography on SiO_2 (54% to 59% EtOAc in Hexane), the product was isolated as white colour sticky liquid (72%, 82.6 mg); ^1H NMR (400 MHz, CHLOROFORM-*D*) δ 7.82 (ddd, *J* = 7.8, 2.8, 1.7 Hz, 0.4H), 7.78 (dq, *J* = 7.4, 1.2 Hz, 1H), 7.68 – 7.59 (m, 5H), 7.56 (dd, *J* = 5.8, 1.8 Hz, 1H), 7.52 (t, *J* = 2.7 Hz, 0.4H), 7.46 – 7.37 (m, 3H), 7.35 – 7.27 (m, 3H), 7.26 – 7.19 (m, 2.8H), 7.17 – 7.08 (m, 4H), 7.02 (dddd, *J* = 17.8, 8.3, 6.5, 1.4 Hz, 0.8H), 5.69 (ddd, *J* = 8.1, 5.5, 2.0 Hz, 1H), 5.41 (dd, *J* = 7.9, 2.7 Hz, 0.4H), 4.57 – 4.37 (m, 4.4H), 4.37 – 4.19 (m, 1.8H), 4.05 – 3.97 (m, 0.4H), 3.94 – 3.89 (m, 4.5H), 3.84 (ddt, *J* = 10.2, 6.9, 3.6 Hz, 1H), 3.79 – 3.67 (m, 1.4H), 3.60 (ddd, *J* = 14.5, 7.8, 3.4 Hz, 1H), 2.60 – 2.31 (m, 1.4H), 2.10 – 1.89 (m, 4.5H), 1.58 – 1.43 (m, 4.5H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 174.8, 174.7, 174.6, 170.8, 169.3, 167.6, 158.8, 157.9, 157.8, 154.0, 137.8, 137.3, 135.3, 135.3, 135.1, 134.7, 133.9, 133.0, 132.9, 132.8, 132.5, 131.6, 131.4, 130.6, 130.4, 130.4, 130.0, 130.0, 129.9, 129.4, 129.3, 129.2, 129.0, 129.0, 128.6, 128.3, 128.0, 127.4, 127.3, 127.3, 127.1, 126.3, 126.3, 126.2, 126.1, 126.1, 126.0, 126.0, 124.4, 124.0, 123.6, 123.5, 119.2, 119.2, 119.1, 114.1, 113.7, 113.7, 105.7, 105.7, 61.4, 61.4, 61.3, 61.1, 60.0, 59.1, 59.1, 55.4, 50.5, 47.2, 45.4, 45.4, 41.3, 41.0, 41.0, 40.8, 39.4, 38.3, 32.2, 30.4, 25.4, 25.3, 23.3, 22.6, 18.5, 18.5. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{35}H_{34}N_3O_5$: 576.2498; found: 576.2493.



4w

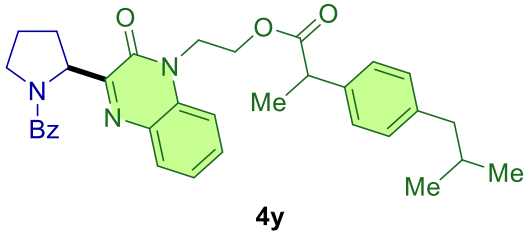
2-(3-(1-Benzoylpyrrolidin-2-yl)-2-oxoquinoxalin-1(2H)-yl)ethyl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-3-yl)acetate 4x (rr = 1 : 0.5): Synthesised according to the general procedure and after chromatography on SiO_2 (50% to 55% EtOAc in Hexane), the product was isolated as colorless sticky liquid (63%, 77.3 mg); ^1H NMR (500



4x

MHz, $CDCl_3$) δ 8.04 (d, *J* = 2.4 Hz, 1H), 8.01 (d, *J* = 2.4 Hz, 0.5H), 7.86 (ddd, *J* = 16.1, 7.9, 1.5 Hz, 2H), 7.80 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.63 – 7.58 (m, 2H), 7.55 (tt, *J* = 7.6, 2.6 Hz, 1.5H), 7.51 – 7.43 (m, 3H), 7.43 – 7.31 (m, 7.5H), 7.30 – 7.21 (m, 1.5H), 7.18 – 7.10 (m, 1.5H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.97 (t, *J* = 8.8 Hz, 1.5H), 5.71 (dd, *J* = 8.1, 5.6 Hz, 1H), 5.43 (dd, *J* = 8.2, 2.7 Hz, 0.5H), 5.16 (d, *J* = 5.1 Hz, 3H), 4.57 – 4.41 (m, 4.5H), 4.41 – 4.26 (m, 1.5H), 4.06 – 3.98 (m, 0.5H), 3.95 – 3.89 (m, 0.5H), 3.85 (dt, *J* = 10.1, 7.1 Hz, 1H), 3.60 (td, *J* = 7.7, 3.9 Hz, 1H), 3.57 (s, 2H), 3.49 (s, 1H), 2.53 (ddd, *J* = 14.2, 8.4, 6.0 Hz, 1.5H), 2.44 (td, *J* = 8.2, 4.4 Hz, 1.5H), 2.13 – 2.04 (m, 1.5H), 2.03 – 1.98 (m, 1.5H), 1.97 – 1.87 (m, 1.5H). $^{13}C\{^1H\}$ NMR (101 MHz, CHLOROFORM-*D*) δ 190.9, 190.9, 171.6, 171.4, 170.8, 169.3, 160.6, 160.6, 159.0, 158.8, 154.0, 153.2, 140.5, 140.4, 137.8, 137.2, 136.5, 136.3, 135.6, 135.6, 133.0, 132.9, 132.8, 132.6, 132.5, 132.5, 130.7, 130.6, 130.5, 130.2, 130.0, 129.6, 129.5, 129.4, 129.4, 129.2, 128.3, 128.1, 128.0, 127.9, 127.3, 127.3, 127.1, 126.3, 125.2, 125.2, 124.1, 123.7, 121.2, 113.6, 113.6, 73.7, 61.4, 61.2, 60.1, 59.1, 50.5, 47.2, 40.9, 40.7, 40.0, 39.9, 32.1, 30.4, 25.3, 22.5. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{18}H_{18}N_3O_2$: 308.1399; found: 308.1391.

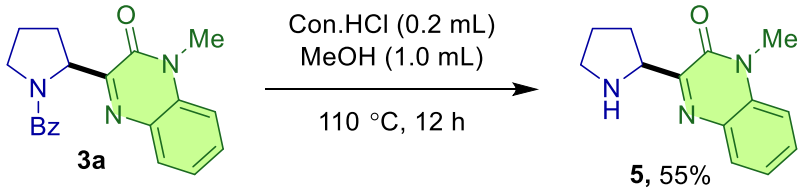
2-(3-(1-Benzoylpyrrolidin-2-yl)-2-oxoquinoxalin-1(2H)-yl)ethyl 2-(4-isobutylphenyl)propanoate 4y (rr = 1 : 0.5): Synthesised according to the general procedure and after chromatography on SiO_2 (52% to 57% EtOAc in Hexane), the product was isolated as colorless sticky liquid (53%, 58.3 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.0, 1.6 Hz, 0.5H), 7.82 (dt, *J* = 8.0, 1.7 Hz, 1H), 7.65 – 7.57 (m, 2H), 7.51 – 7.39 (m, 4.4H), 7.35 (tdd, *J* = 11.8, 6.4, 3.0 Hz, 1.9H), 7.31 – 7.27 (m, 1H), 7.18 – 7.10 (m, 3H), 7.08 – 6.98 (m, 4.8H), 5.70 (dd, *J* = 8.2, 5.6 Hz, 1H), 5.42 (dt, *J* = 8.2, 2.5 Hz, 0.5H), 4.57 – 4.30 (m, 5H), 4.25 (qd, *J* = 7.4, 3.1 Hz, 0.5H), 4.02 (dt, *J* = 12.7, 6.4 Hz, 0.5H), 3.88 (ddt, *J* = 24.4, 10.2, 7.1 Hz, 1.5H), 3.70 – 3.50 (m, 2.8H), 2.58 – 2.46 (m, 1H), 2.43 (t, *J* = 8.1 Hz, 3H), 2.12 – 1.74 (m, 7.5H), 1.49 – 1.33 (m, 4.5H), 0.91 – 0.82 (m, 9H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 174.9, 174.7, 170.8, 169.3, 159.1, 158.8, 158.8, 154.0, 153.1, 140.9, 140.8, 140.8, 139.2, 137.8, 137.4, 137.4, 137.3, 137.2, 137.2, 133.0, 133.0, 132.8, 132.6, 132.5, 130.6, 130.5, 130.4, 130.2, 130.1, 129.9, 129.5, 129.5, 129.2, 128.6, 128.3, 128.0, 127.3, 127.2, 127.2, 127.1, 126.9, 126.3, 126.3, 124.0, 123.6, 113.9, 113.9, 61.2, 61.2, 61.1, 60.0, 60.0, 59.1, 50.5, 48.5, 47.2, 45.7, 45.1, 45.1, 45.1, 40.9, 40.7, 32.2, 30.4, 30.2, 26.1, 25.4, 24.7, 22.6, 22.5, 22.5, 18.5, 18.5, 18.5. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{34}H_{38}N_3O_4$: 552.2862; found: 552.2866.



4y

6. Deprotection of benzoyl group:

1-Methyl-3-(pyrrolidin-2-yl)quinoxalin-2(1H)-one 5:



A solution of **3a** (66.7 mg, 0.2 mmol) in MeOH (1.0 mL) was added to con. HCl (0.2 mL) and stirred overnight at 110 °C in a silicon oil bath. The reaction mixture was neutralized with a saturated sodium bicarbonate solution and extracted with DCM (2 x 20 mL). The organic layer was dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude product was then purified by flash column chromatography on silica gel mesh 230–400 using 5-10% MeOH in DCM as an eluent to afford product **5** (55%, 25 mg). ^1H NMR (400 MHz, CHLOROFORM-*D*) δ 7.92 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.58 (ddd, *J* = 8.6, 7.3, 1.5 Hz, 1H), 7.35 (ddt, *J* = 8.2, 7.3, 1.2 Hz, 1H), 7.29 (dd, *J* = 8.5, 1.2 Hz, 1H), 5.22 (dd, *J* = 8.3, 6.2 Hz, 1H), 3.66 (s, 3H), 3.62 (d, *J* = 6.4 Hz, 1H), 2.71 (ddd, *J* = 13.8, 7.8, 6.0 Hz, 1H), 2.23 – 2.13 (m, 1H), 2.07 (dd, *J* = 13.2, 6.7 Hz, 1H), 2.03 – 1.96 (m, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, CHLOROFORM-*D*) δ 153.5, 153.1, 133.6, 131.6, 131.3, 130.5, 124.6, 113.9, 59.7, 46.5, 30.3, 29.3, 24.6. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{13}H_{16}N_3O$: 230.1293; found: 230.1283.

7. Luminescence quenching studies and Stern-Volmer studies:

To perform luminescence quenching studies, 1 mM $Ir(ppy)_3$, 0.2 M amine (**1a**), *N*-methyl quinoxalin-2(1*H*)-one (**2a**), and DBU in DMSO were prepared as a stock solution, all other solutions with different concentration were prepared by series dilution of the stock solution.

For collection of data, the excitation and emission slit widths were fixed at 3 and 6 nm, respectively. Fluorescence emission spectra of $Ir(ppy)_3$ were recorded from 400 nm to 650 nm with an excitation wavelength of 385 nm. λ_{max}(emission) of $Ir(ppy)_3$ was observed at 520 nm.

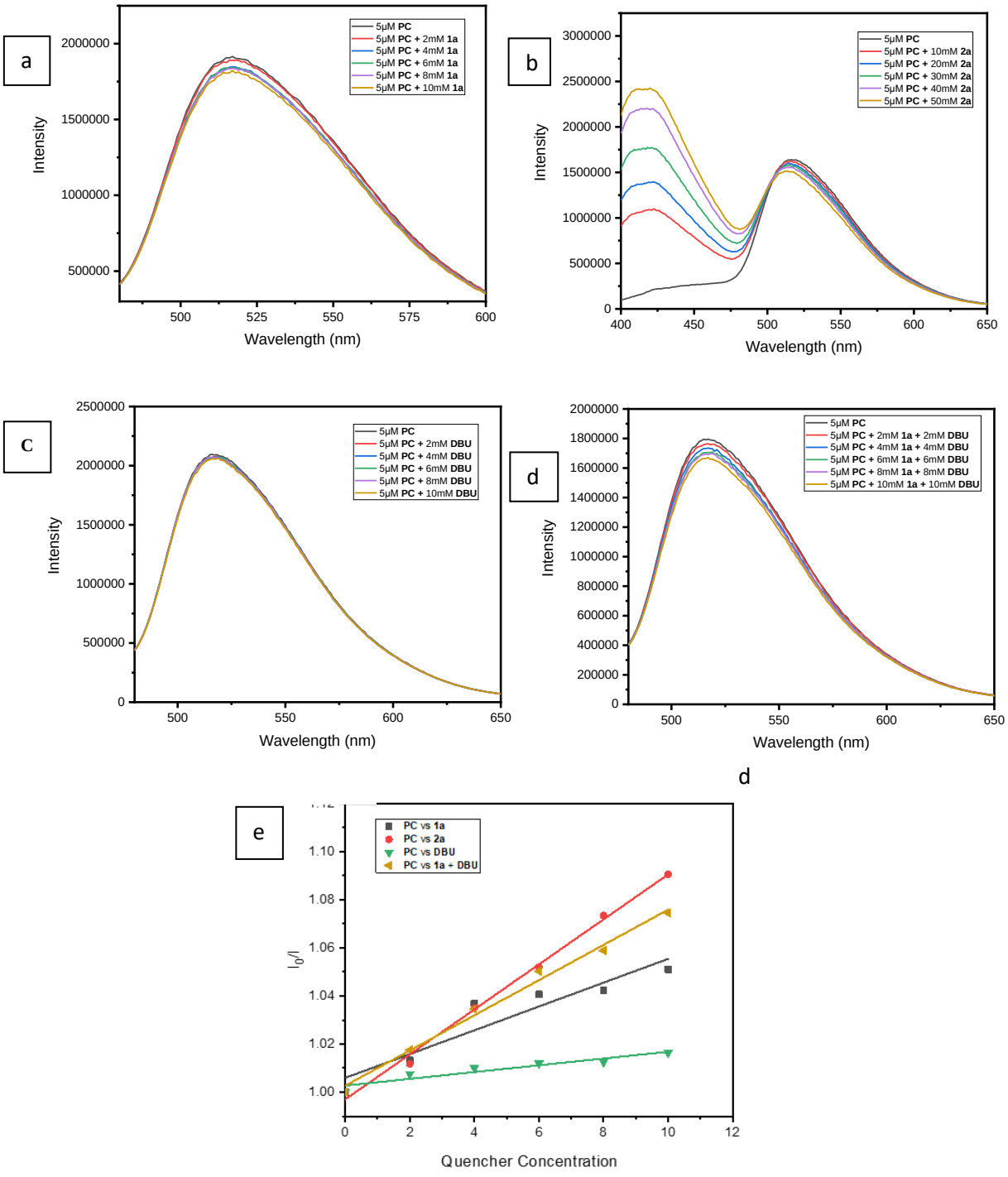
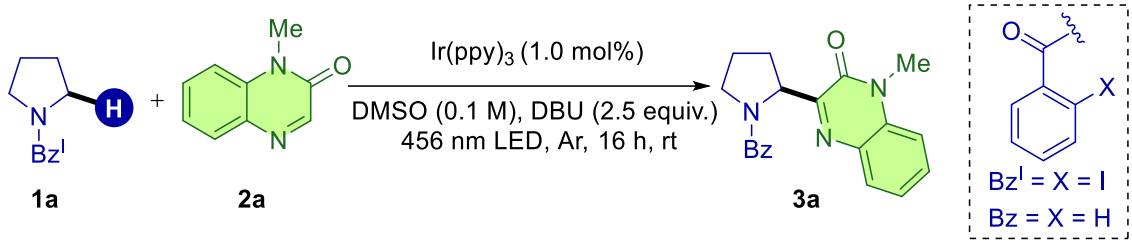


Figure S1. Luminescence quenching spectra of $Ir(ppy)_3$

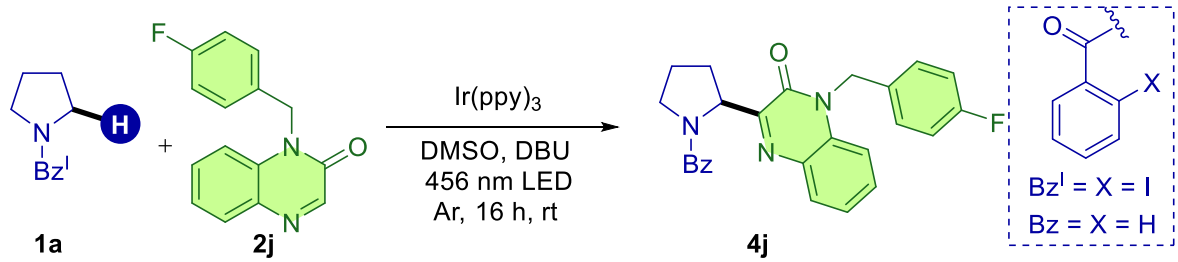
In DMSO Solution: a) 5 μM $Ir(ppy)_3$ *vs.* **1a**; b) 5 μM $Ir(ppy)_3$ *vs.* quinoxalin-2(1*H*)-one (**2a)** c) 5 μM $Ir(ppy)_3$ *vs.* **DBU** ; d) 5 μM $Ir(ppy)_3$ *vs.* **1a** + **DBU**; e) Stern-Volmer plot of Luminescence quenching of 5 μM $Ir(ppy)_3$ *vs.* **1a**, **2a, DBU and 1a** + **DBU**.

8. Large-scale synthesis of compound 3a:



An oven-dried borosilicate 2 necked round bottom flask equipped with a magnetic stir bar was added 2-iodobenzoyl protected amine **1a** (600 mg, 1.0 equiv., 2 mmol), quinoxalin-2(1*H*)-one **2a** (480 mg, 1.5 equiv., 3 mmol), and Ir(ppy)$_3$ (1.0 mol%). The reaction tube was vacuumed and backfilled with argon (3 times), and a septum was placed over the reaction tube. Next, 0.1 M DMSO solvent (20 mL) and DBU (547 mg, 1.5 equiv., 3 mmol) were added through the septum using a syringe, and the reaction tube was placed approximately 5 cm from the light setup. After the reaction, 30 mL of water was added and extracted with EtOAc (3 × 30 mL). The combined organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was then purified by flash column chromatography on silica gel (mesh 230–400) using hexane and EtOAc as an eluent to afford the corresponding products **3**a in 76% yield (505 mg).

9. Light on/off experiment over time:



An oven-dried borosilicate test tube equipped with a magnetic stir bar was added 2-iodobenzoyl protected amine **1** (1.0 equiv., 0.2 mmol), quinoxalin-2(1*H*)-one **2j** (1.5 equiv., 0.3 mmol), and Ir(ppy)$_3$ (1.0 mol%). The reaction tube was vacuumed and backfilled with argon (3 times), and a septum was placed over the reaction tube. Next, 0.1 M DMSO solvent (2.0 mL) and DBU (54.7 mg, 1.5 equiv., 0.3 mmol) were added through the septum using a syringe, and the reaction tube was placed approximately 5 cm from the light setup. The light on/off experiment was performed by altering light-dark conditions (light : dark; 2 : 2 h) for up to 12 h. At the end of each light/dark session, the reaction progress was monitored by measuring the yield based on ^{19}F NMR using $PhCF_3$ as an internal standard. Figure S2 shows the essential role of light as the reaction progressed in the presence of light and stopped in the dark. From the experiment, we conclude that a continuous light supply is needed for the reaction and confirm that the reaction does not proceed through a chain propagation mechanism.

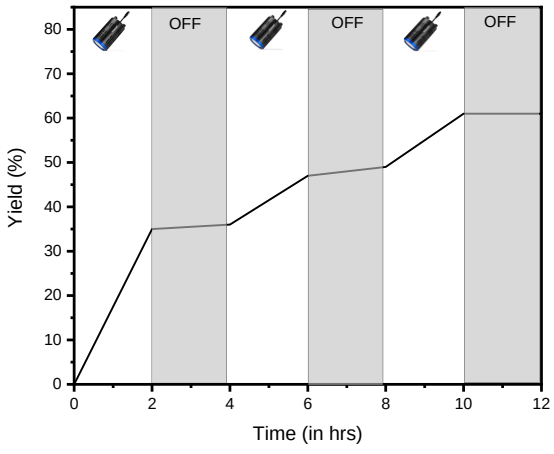
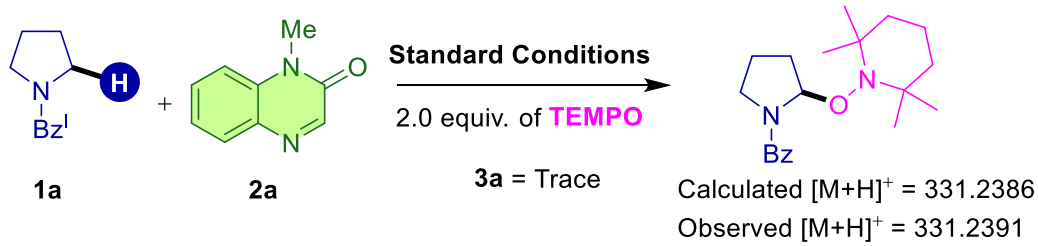


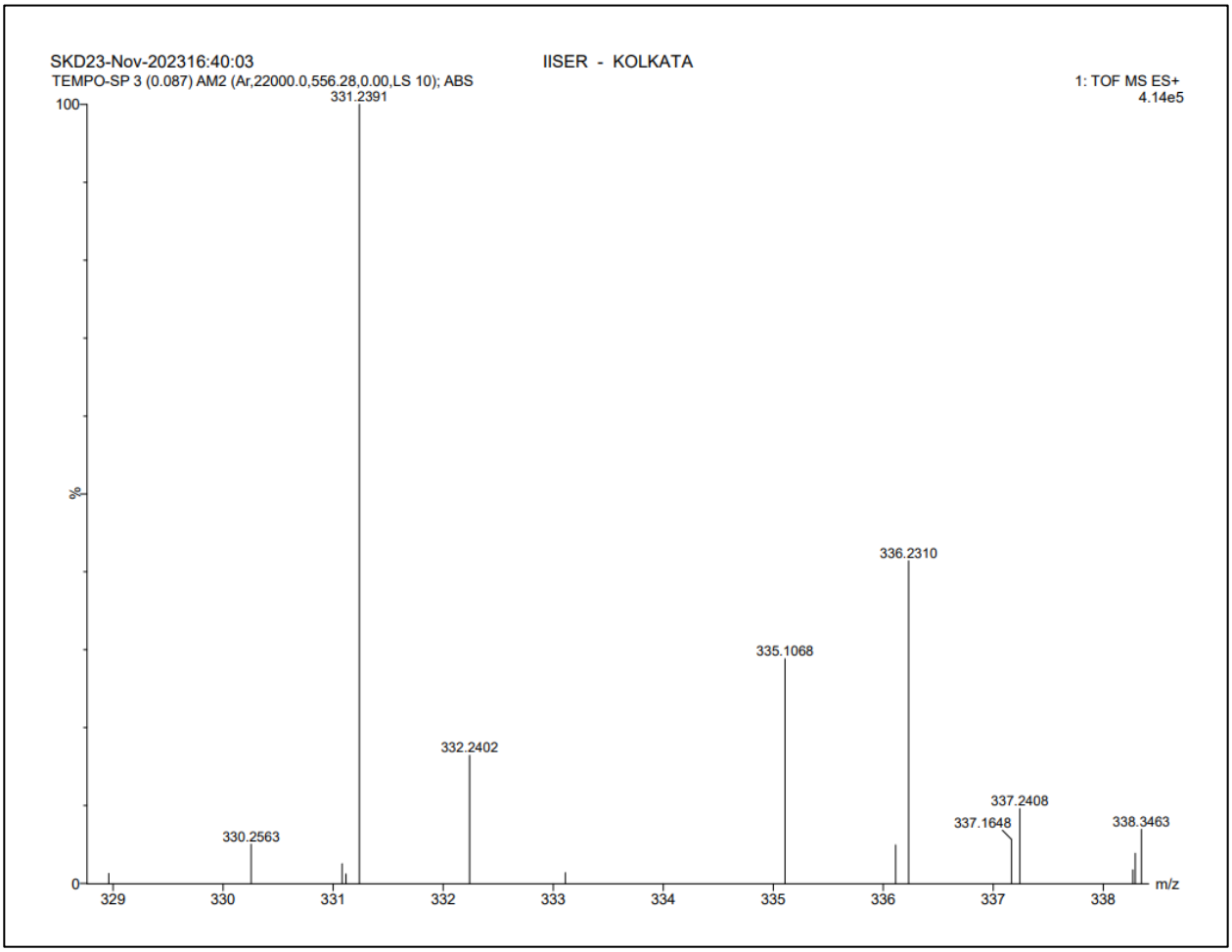
Figure S2: Light on/off experiments

10. Control Experiments:

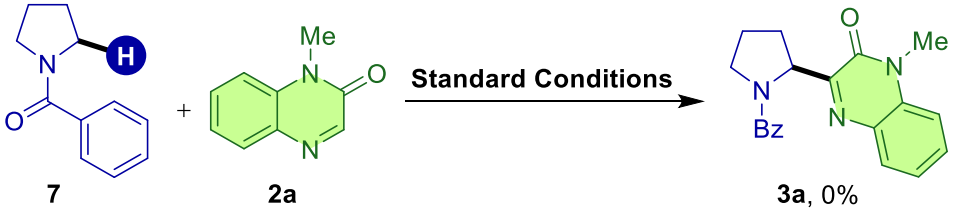
10.1 Radical inhibition experiment with TEMPO:



The compounds 2-iodobenzoyl protected amine **1** (1.0 equiv., 0.2 mmol), quinoxalin-2(1*H*)-one **2a** (1.5 equiv., 0.3 mmol), $Ir(ppy)_3$ (1.0 mol%), and TEMPO (3.0 equiv.) were taken in the pre-dried reaction tube. It was evacuated and backfilled with argon (3 times), and the reaction tube was sealed with a septum. Next, 0.1 M DMSO solvent (2.0 mL) and DBU (54.7 mg, 1.5 equiv., 0.3 mmol) were added using a syringe through the septum and irradiated for 16 h with the help of light, which was arranged at a distance of approximately 5 cm from the reaction tube. After the completion of the reaction time, water and EtOAc were added, and the organic layer was separated and washed with water (2 × 10 mL). The organic layer was dried with the help of Na_2SO_4, and the solvent was removed under vacuum. The product **3a** was not observed. Instead, TEMPO adduct **10** was observed in HRMS, which dictates that our reaction proceeds through the radical process.



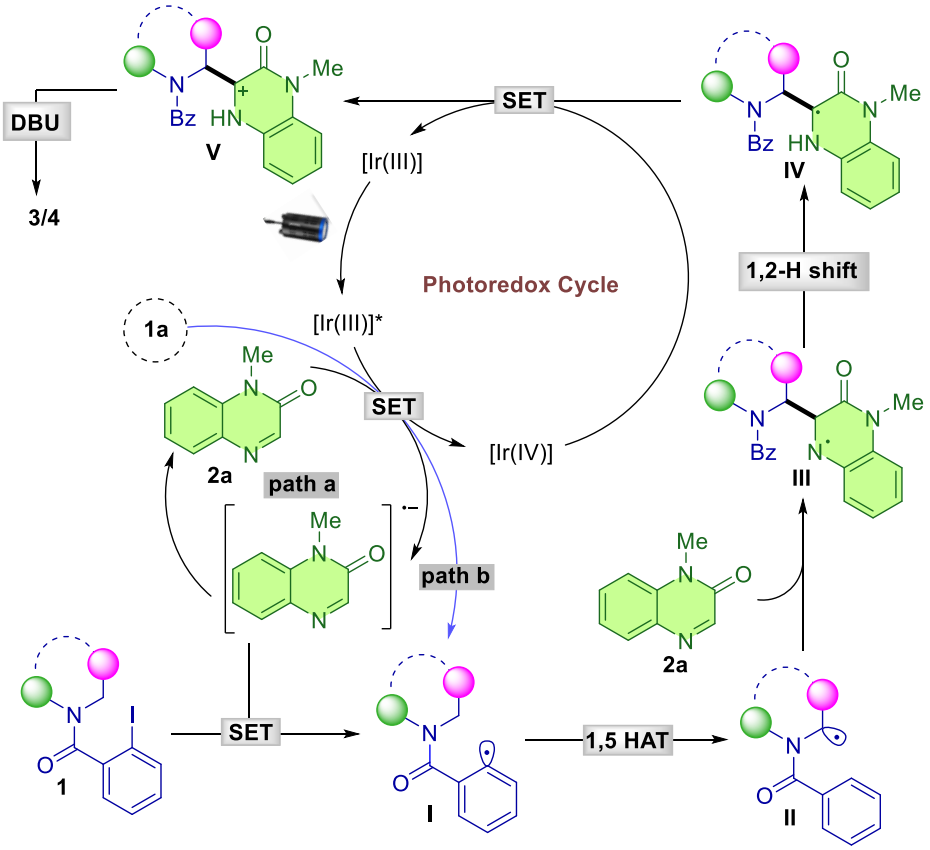
10.2 Reaction with *N*-benzoyl-protected pyrrolidine:



The compounds 2-iodobenzoyl protected amine **1** (1.0 equiv., 0.2 mmol), quinoxalin-2(1*H*)-one **2a** (1.5 equiv., 0.3 mmol), $Ir(ppy)_3$ (1.0 mol%) were taken in the pre-dried reaction tube. It was evacuated and backfilled with argon (3 times), and the reaction tube was sealed with a septum. Next, 0.1 M DMSO solvent (2.0 mL) and DBU (54.7 mg, 1.5 equiv., 0.3 mmol) were added using a syringe through the septum and irradiated for 16 h with the help of light, which was arranged at a distance of approximately 5 cm from the reaction tube. After the completion of the reaction time, water and EtOAc were added, and the organic layer was separated and washed with water (2 × 10 mL). The organic layer was dried with the help of Na_2SO_4, and the solvent was removed under vacuum. The product **3a** was not observed, indicating the necessity of iodo substitution at the ortho position of the benzene ring, which directs the 1,5-H shift.

11. Plausible Mechanism:

The excited state of $Ir(ppy)_3$ undergoes SET with **2a** to give the reduced **2a,** which upon SET with **1** furnishes aryl radical intermediate **I**. The other possibility where substrate **1** directly undergoes SET with excited state PC to generate **I** cannot be ruled out. The aryl radical **I** is electrophilic, which abstracts hydrogen next to the nitrogen atom through 1,5-HAT to give radical intermediate **II**. The radical addition of intermediate **II** with **2a** followed by 1,2-H shift to generate intermediate **IV**. Finally, this intermediate **IV** undergoes single electron oxidation with the photocatalyst producing cationic intermediate **V** and regenerated photocatalyst, which will further be involved in the catalytic cycle. The intermediate **V** upon deprotonation with DBU afforded the final cross-coupled product **3/4**.



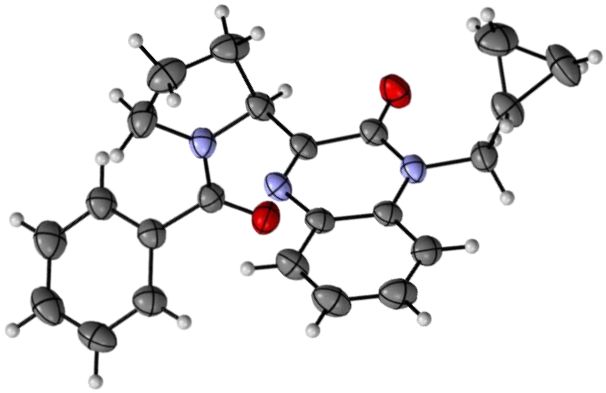
12. X-Ray data:

Sample preparation:

The pure sample of **4a** was dissolved in a minimum amount of DCM, and the large excess of hexane was added and stored in a –20 °C freezer for two days to obtain suitable crystals of compound **4a**.

X-ray crystallographic data of **4a** with 50% ellipsoid contour probability:

Table 1 Crystal data and structure refinement for 4a.

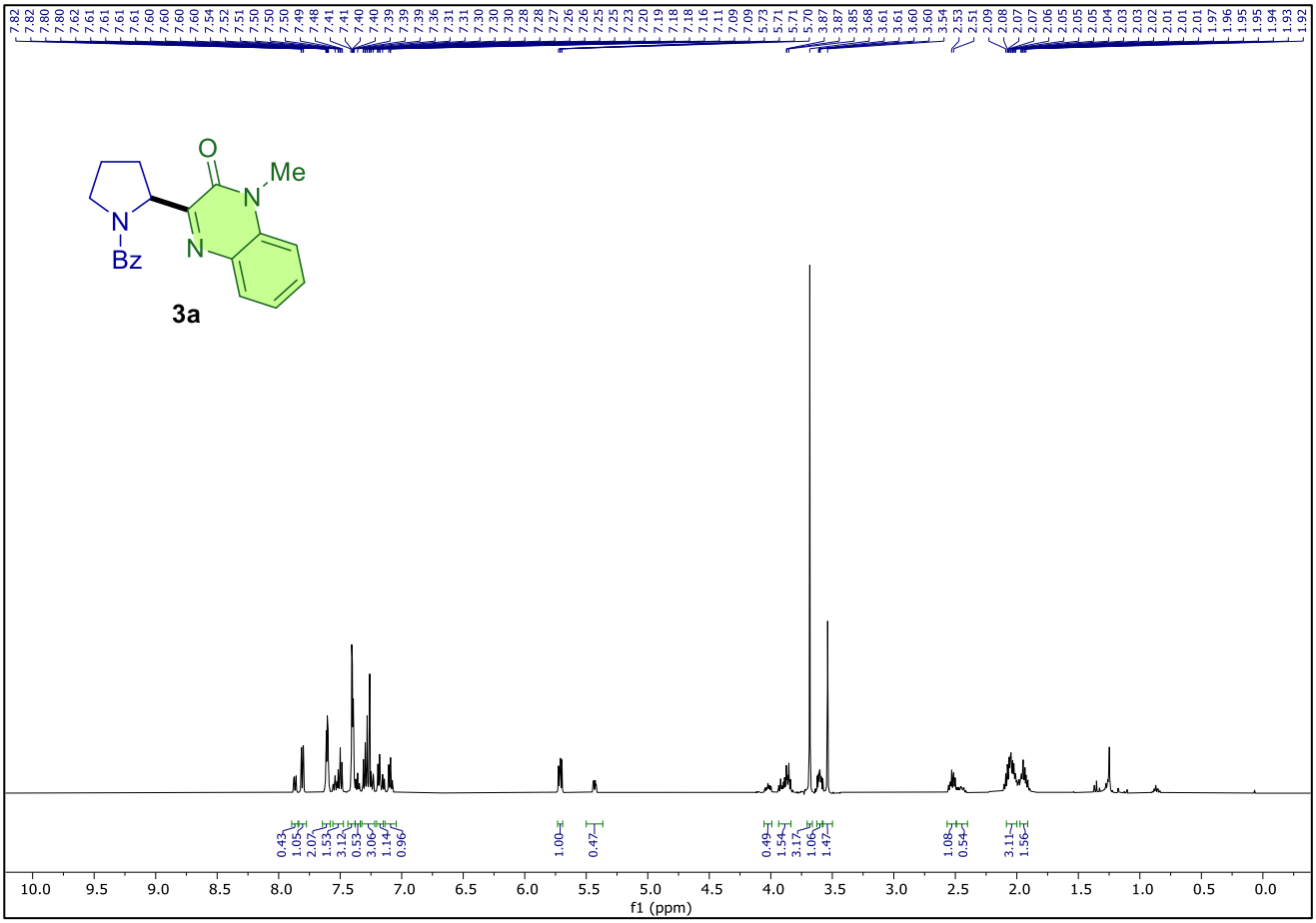


Identification code	4a
CCDC number	2357318
Empirical formula	$C_{23}H_{23}N_3O_2$
Formula weight	373.44
Temperature/K	273.15
Crystal system	triclinic
Space group	P-1
a/Å	9.4621(13)
b/Å	9.9741(14)
c/Å	11.4369(15)
α/°	71.120(4)
β/°	86.589(4)
γ/°	79.453(4)
Volume/Å^3	1004.0(2)
Z	2
ϱ_{calc}g/cm^3	1.235
μ/mm^{-1}	0.080
F(000)	396.0
Crystal size/mm^3	0.33 × 0.25 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.782 to 57.006
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -15 ≤ l ≤ 15
Reflections collected	38081
Independent reflections	5092 [R_{int} = 0.1064, R_{sigma} = 0.0730]
Data/restraints/parameters	5092/0/254
Goodness-of-fit on F^2	1.009
Final R indexes [I>=2σ (I)]	R_1 = 0.0714, wR_2 = 0.1695
Final R indexes [all data]	R_1 = 0.1610, wR_2 = 0.2216
Largest diff. peak/hole / e Å^{-3}	0.31/-0.24

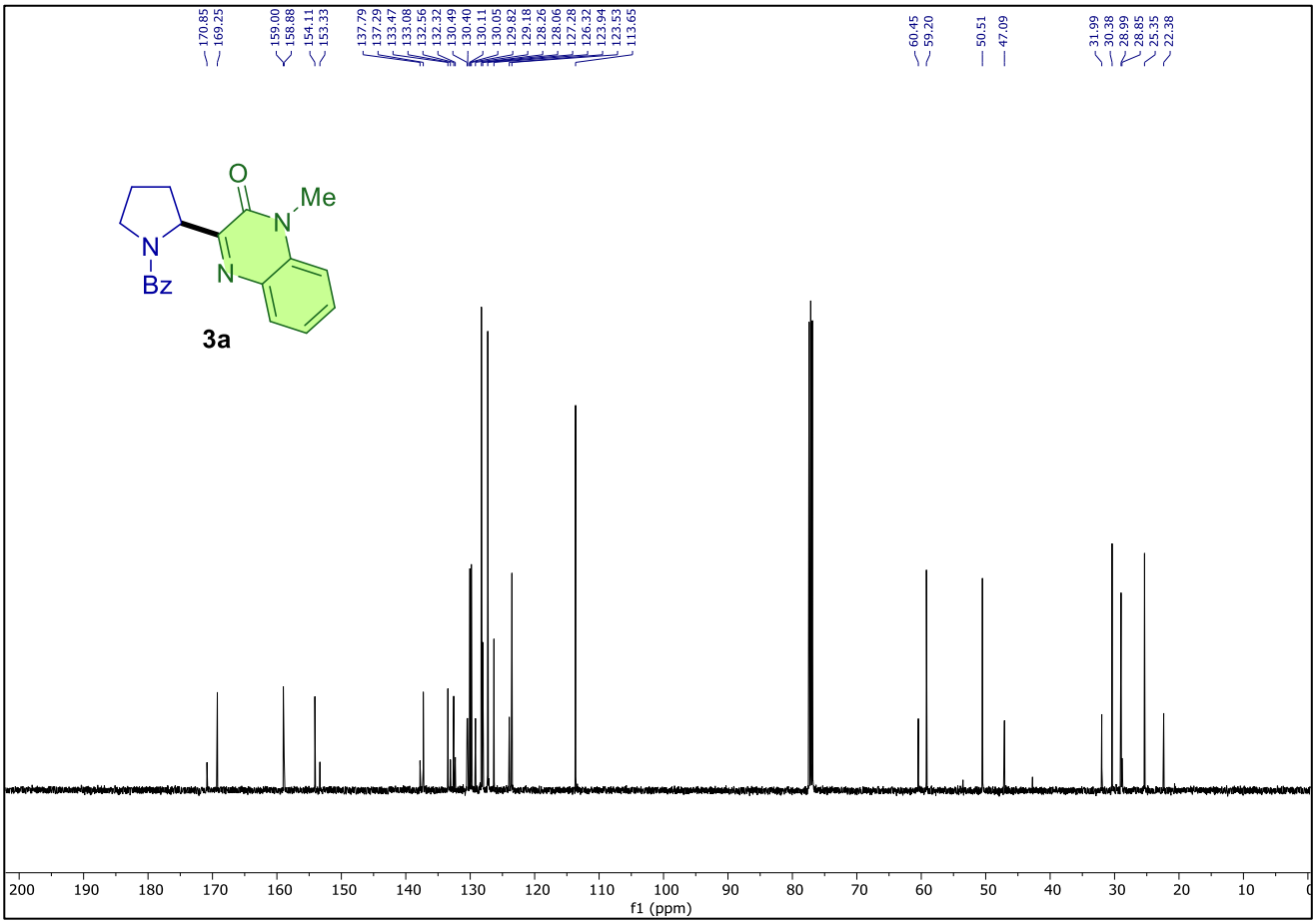
References:

1. Z. Lei, W. Zhang and J. Wu, *ACS Catal*., 2023, **13**, 16105–16113.
2. 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.
3. A. F. Garrido-Castro, A. Gini, M. C. Maestro and J. Alemán, *Chem. Commun*., 2020, **56**, 3769–3772.
4. Z.-G. Niu, H.-B. Han, M. Li, Z. Zhao, G.-Y. Chen, Y.-X. Zheng, G.-N. Li and J.-L. Zuo, *Organometallics*, 2018, **37**, 3154–3164.

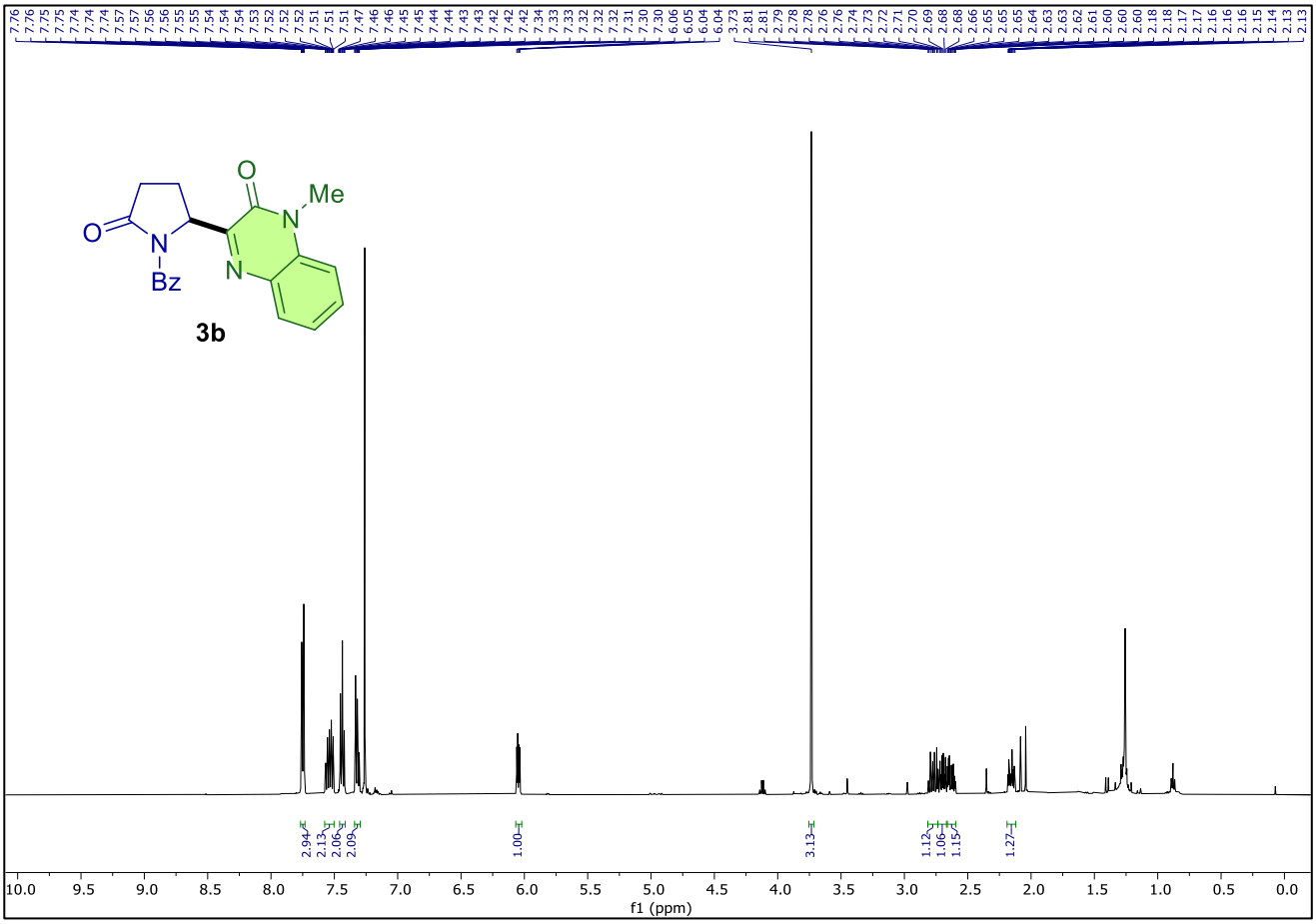
13. NMR spectral data:



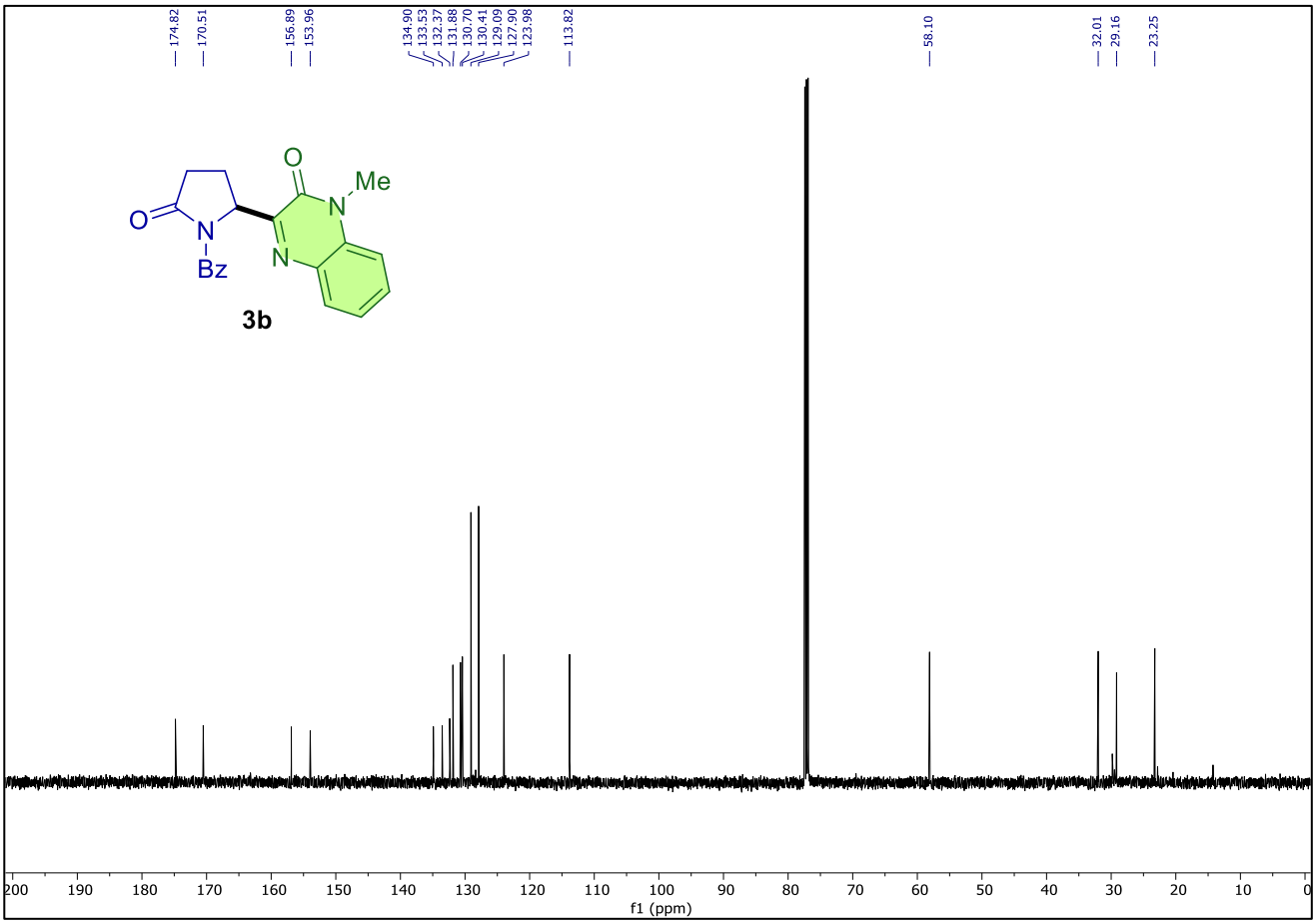
^{1}H NMR of compound **3a** (500 MHz, $CDCl_3$)



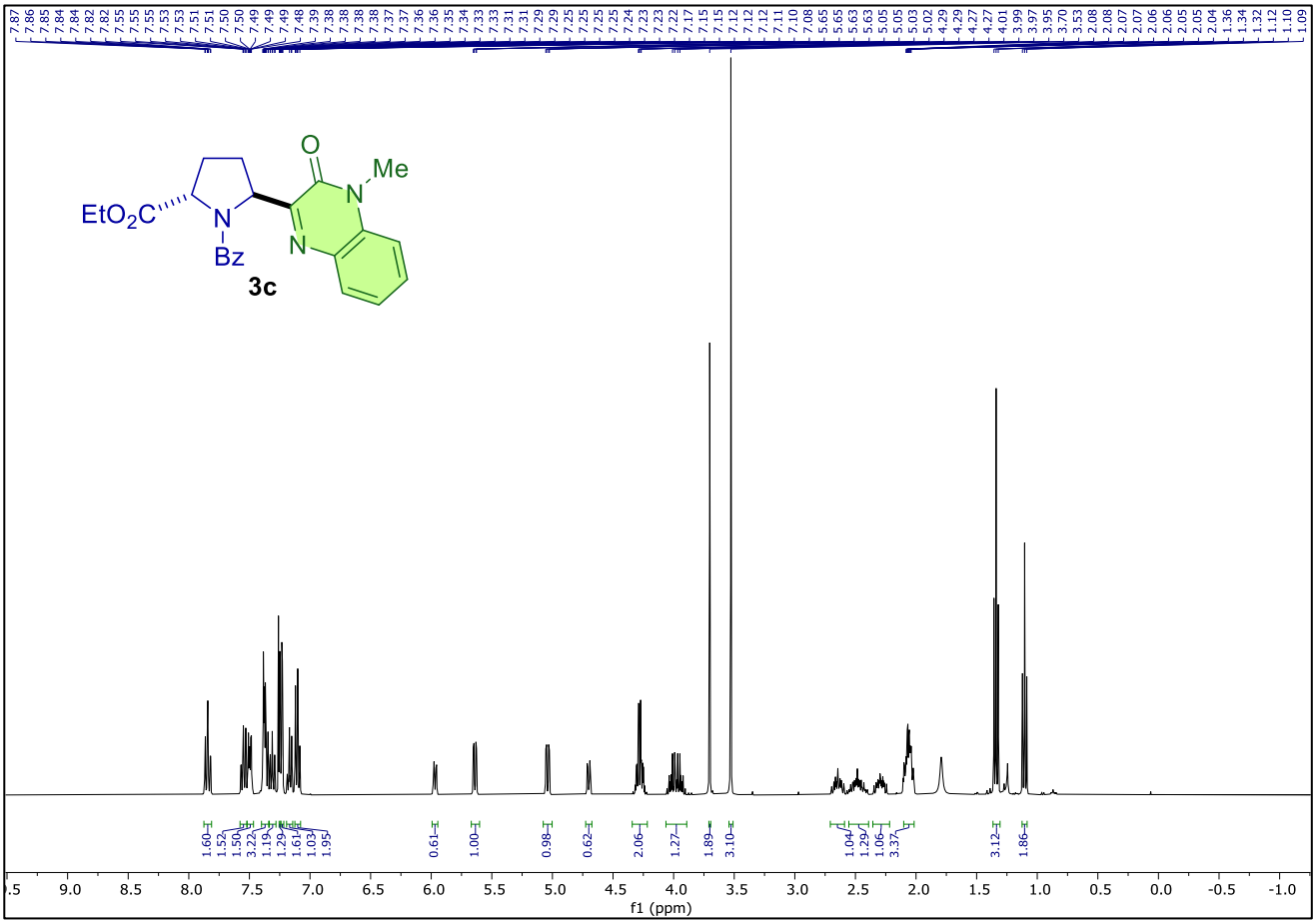
^{13}C{^{1}H} NMR of compound **3a** (126 MHz, $CDCl_3$)



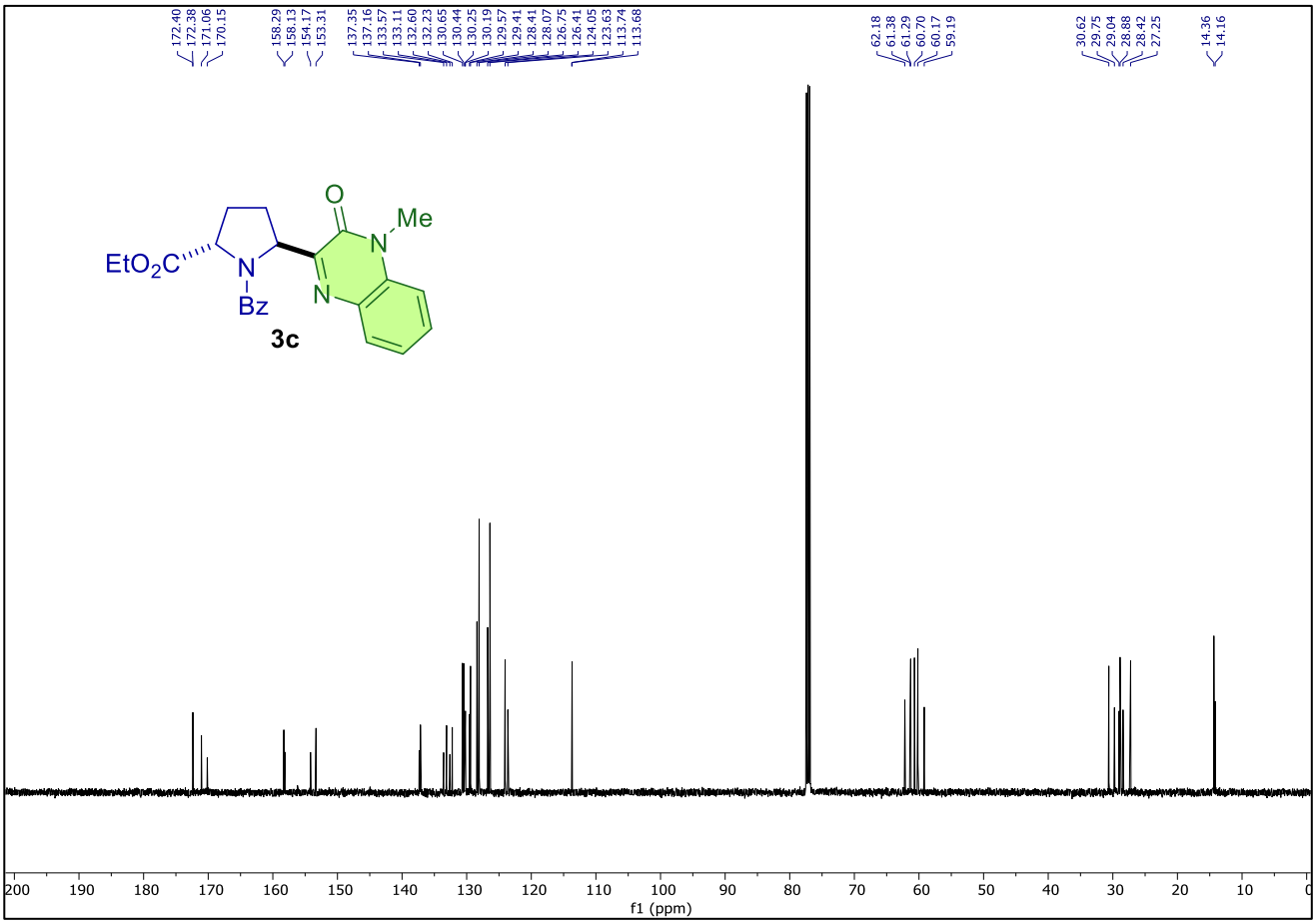
^{1}H NMR of compound **3b** (500 MHz, $CDCl_3$)



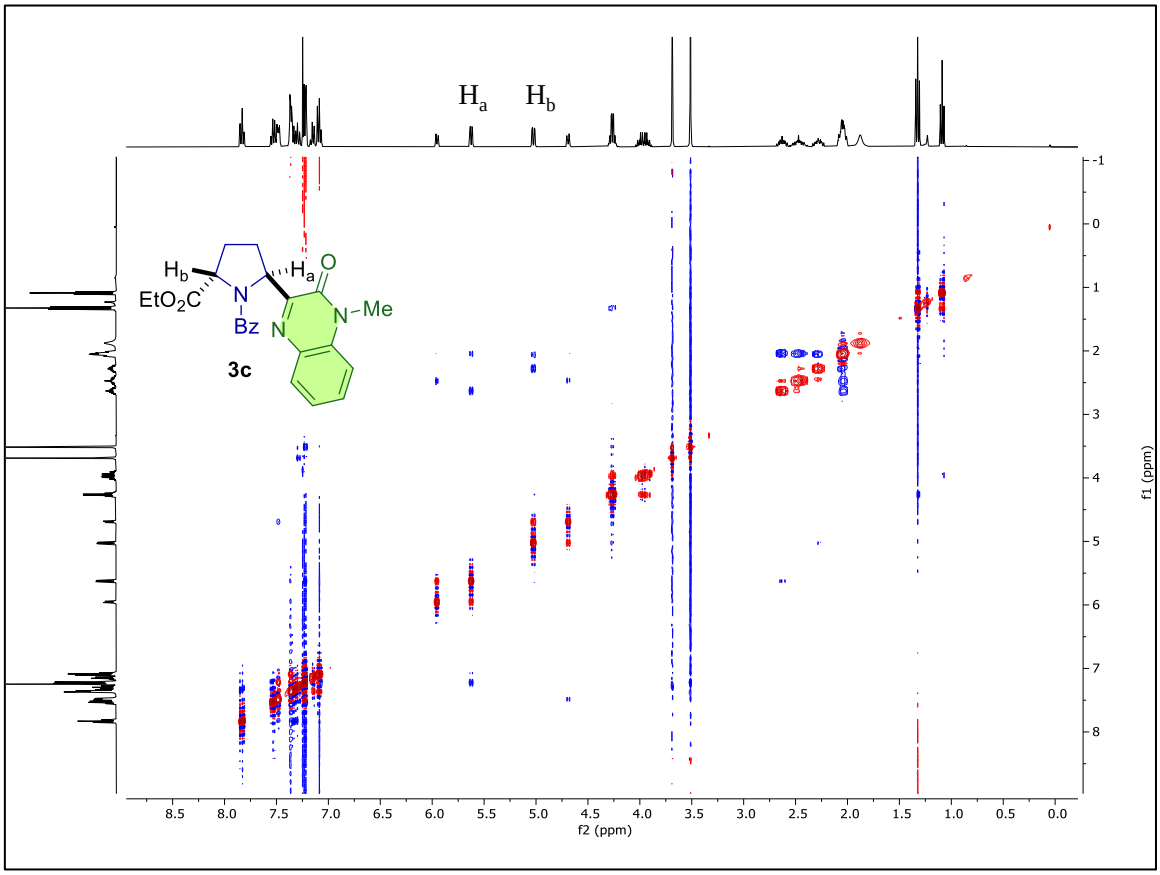
^{13}C{^{1}H} NMR of compound **3b** (126 MHz, $CDCl_3$)



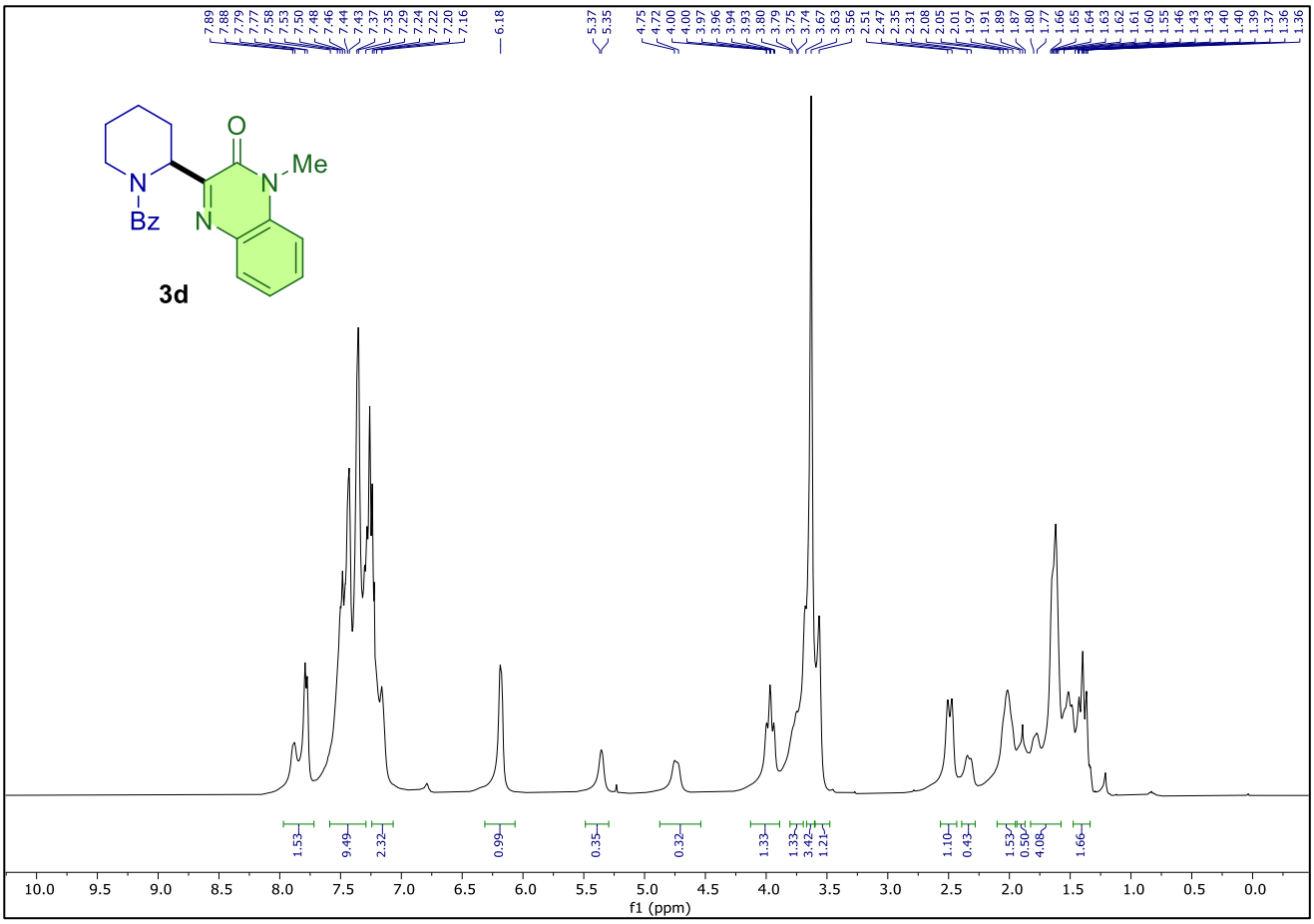
^{1}H NMR of compound **3c** (400 MHz, $CDCl_3$)



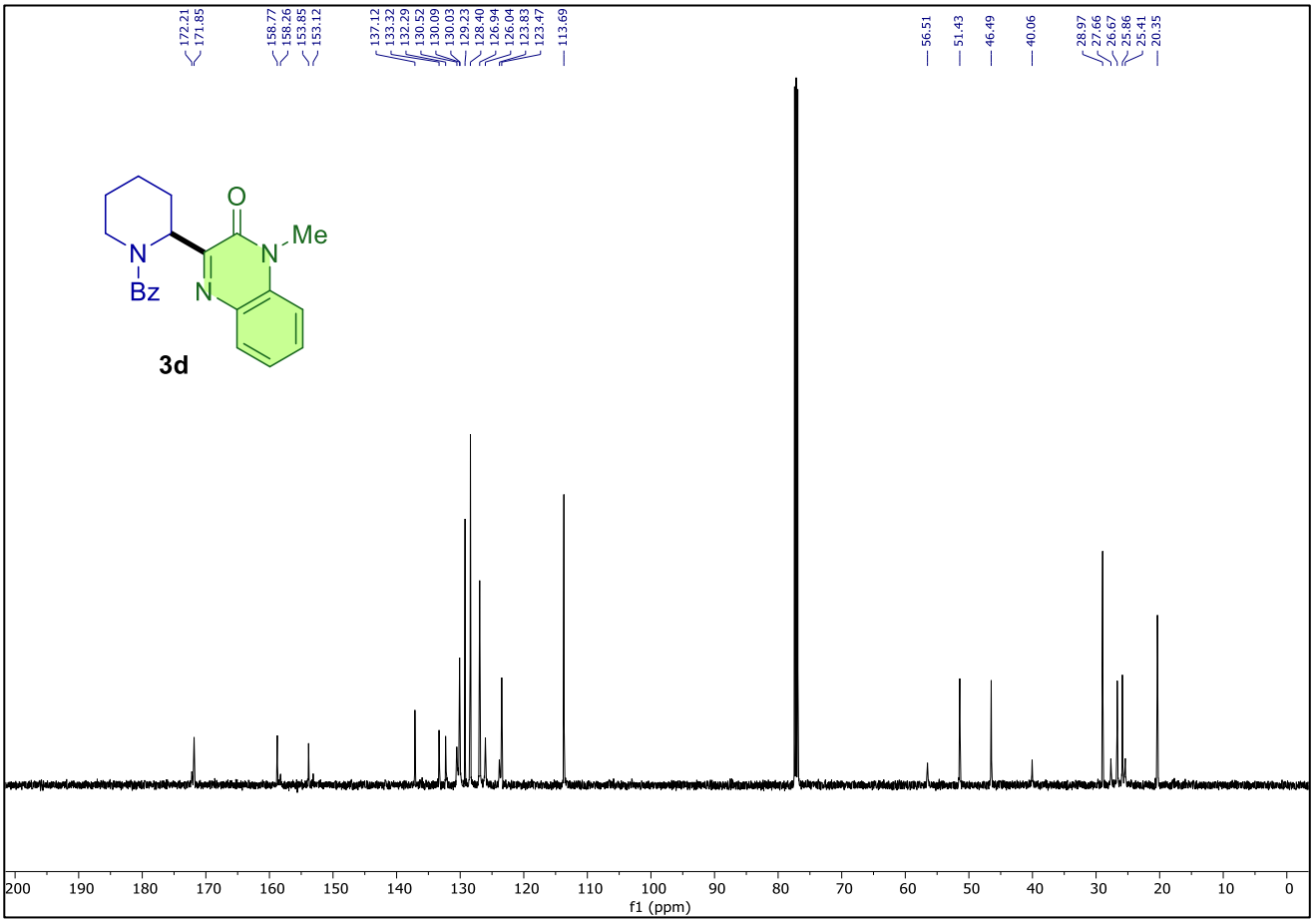
^{13}C{^{1}H} NMR of compound **3c** (126 MHz, $CDCl_3$)



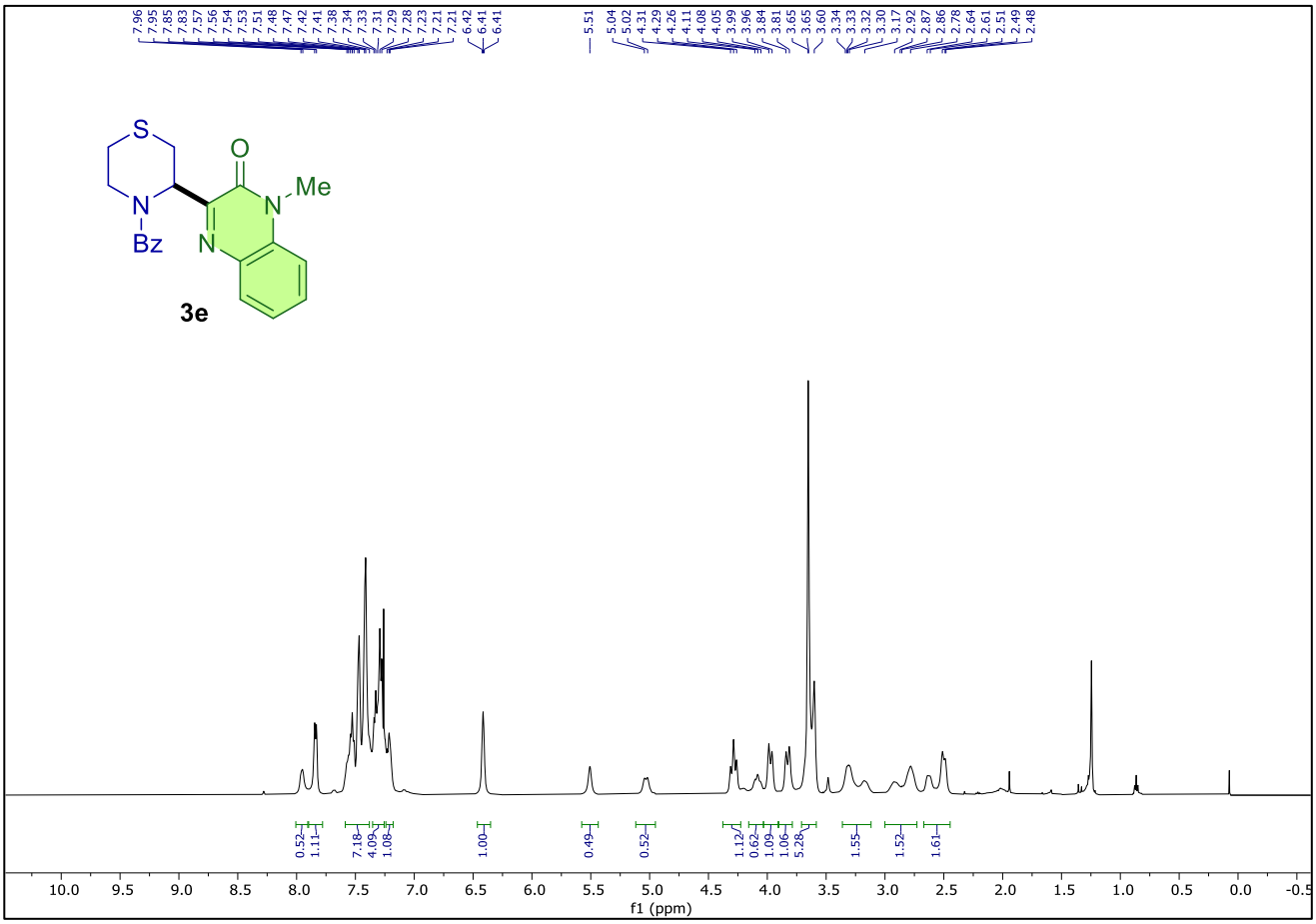
NOESY of compound **3c** (400 MHz, $CDCl_3$)



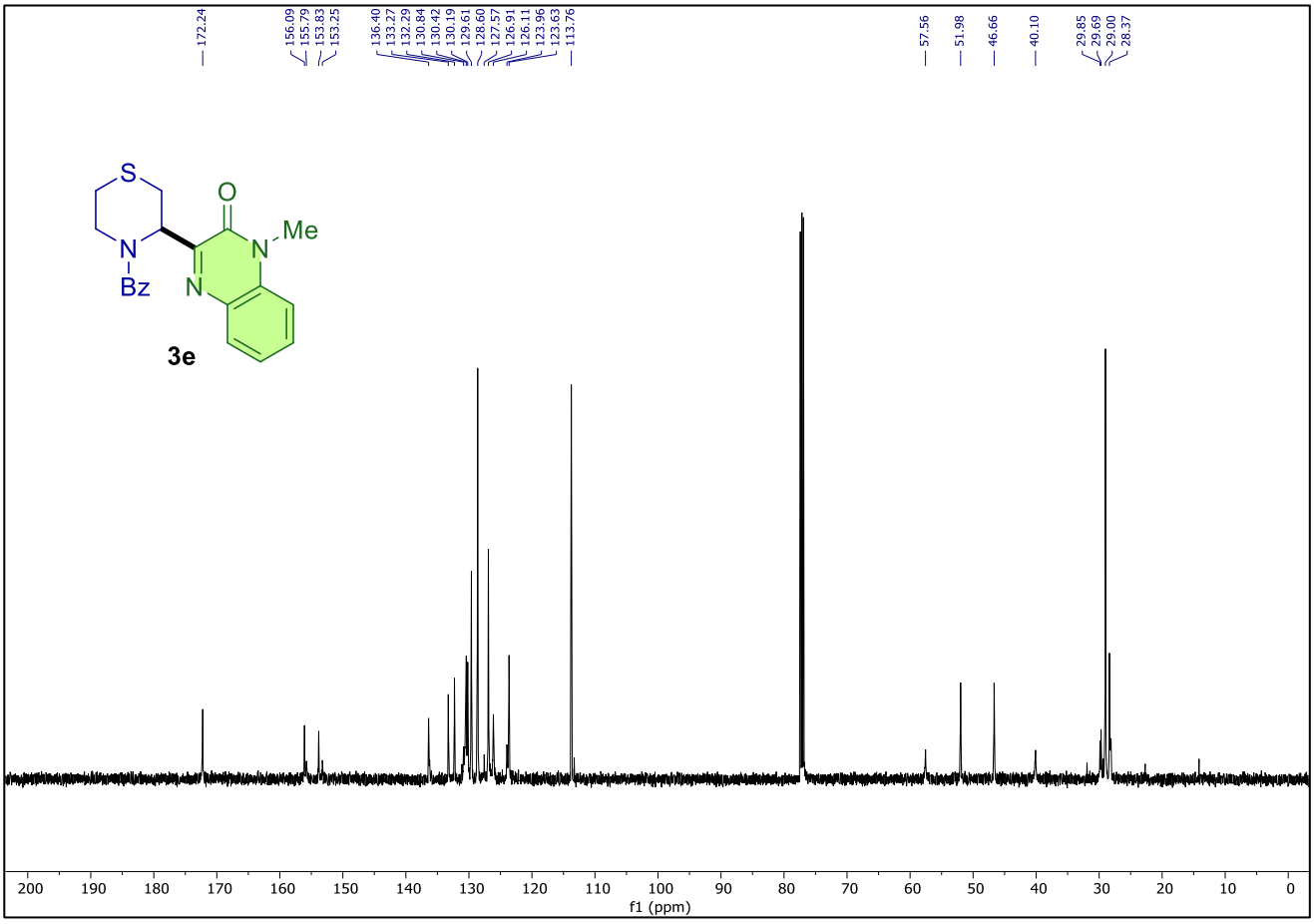
^{1}H NMR of compound **3d** (400 MHz, $CDCl_3$)



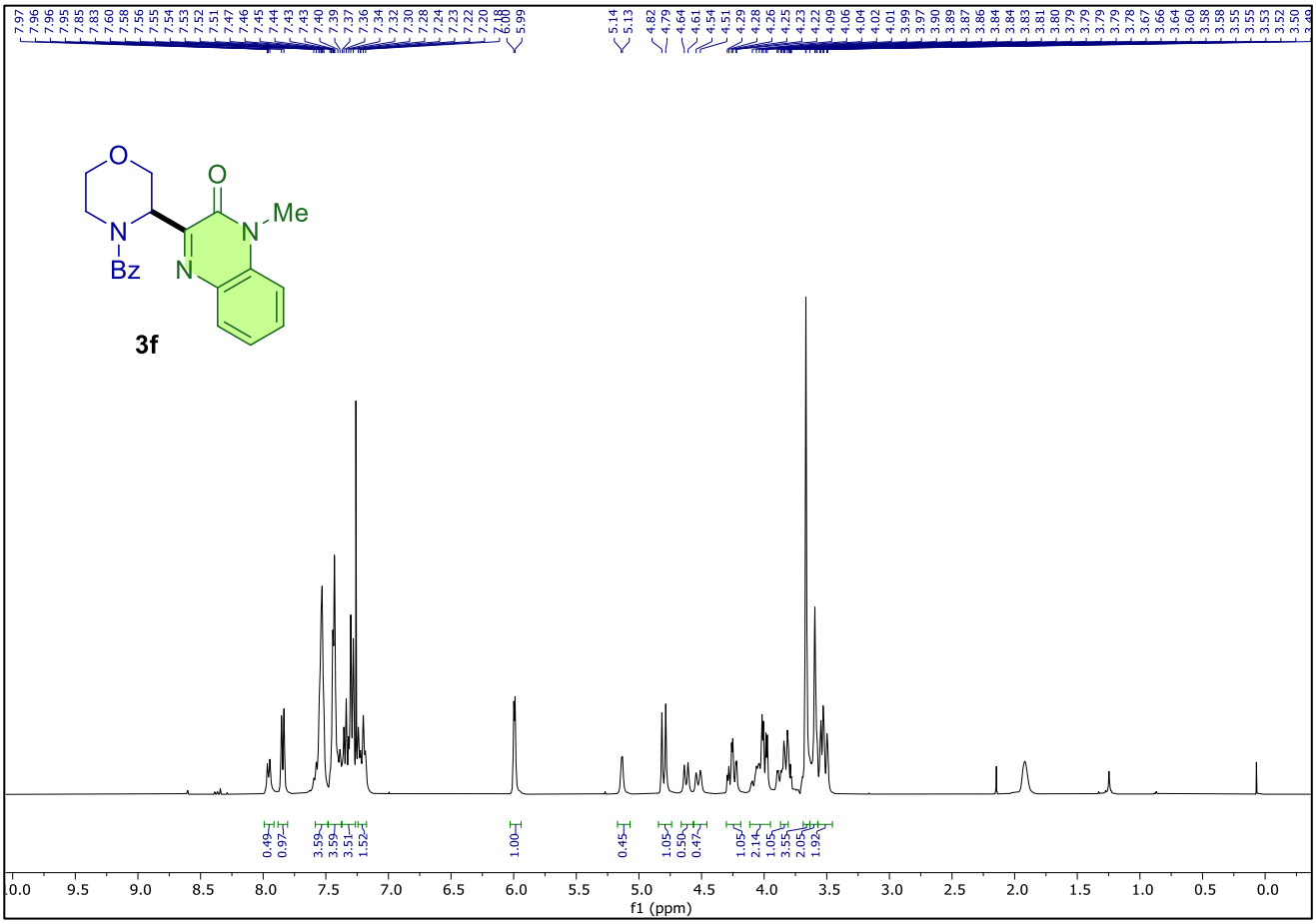
$^{13}C\{^{1}H\}$ NMR of compound **3d** (126 MHz, $CDCl_3$)



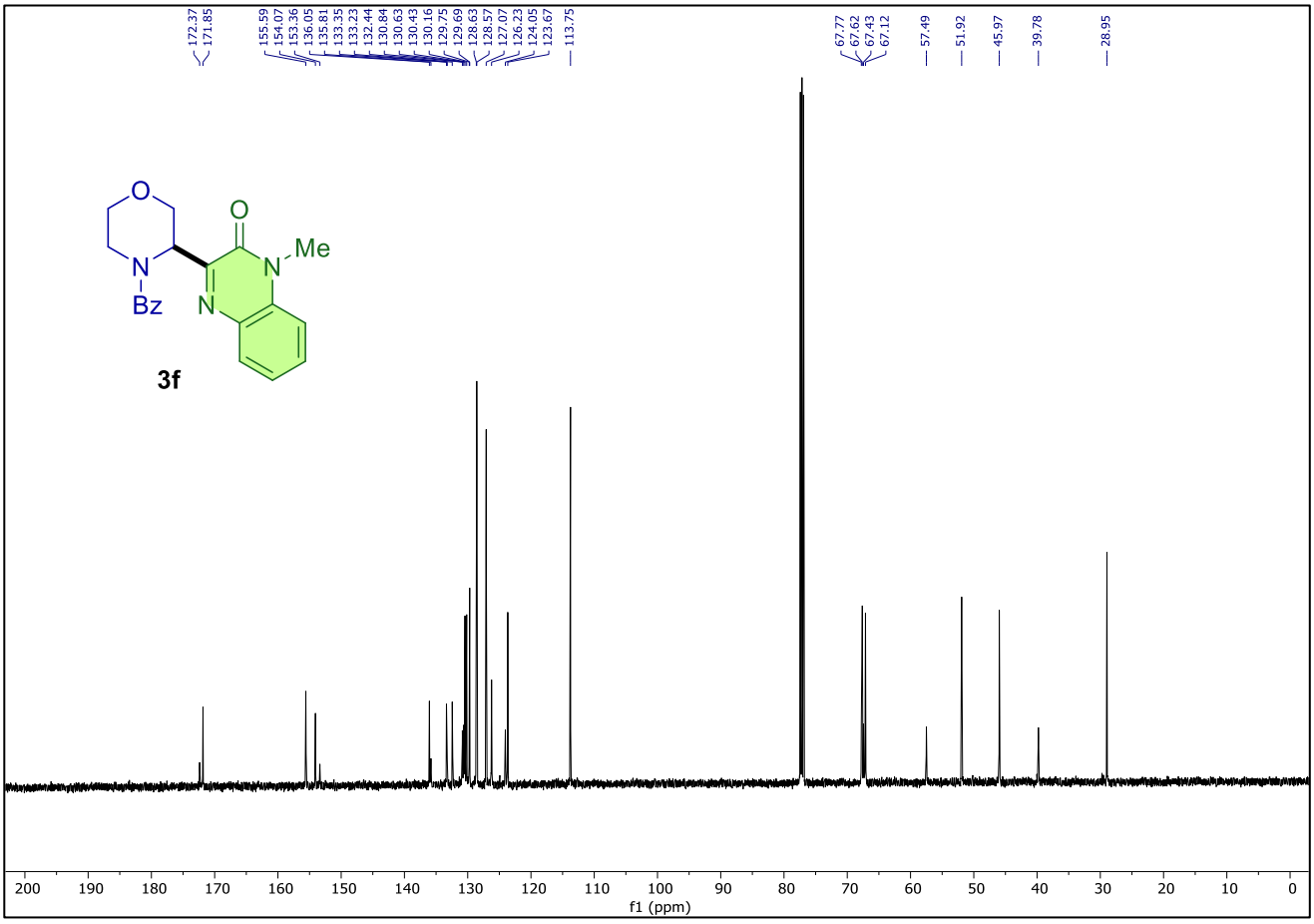
^{1}H NMR of compound **3e** (500 MHz, $CDCl_3$)



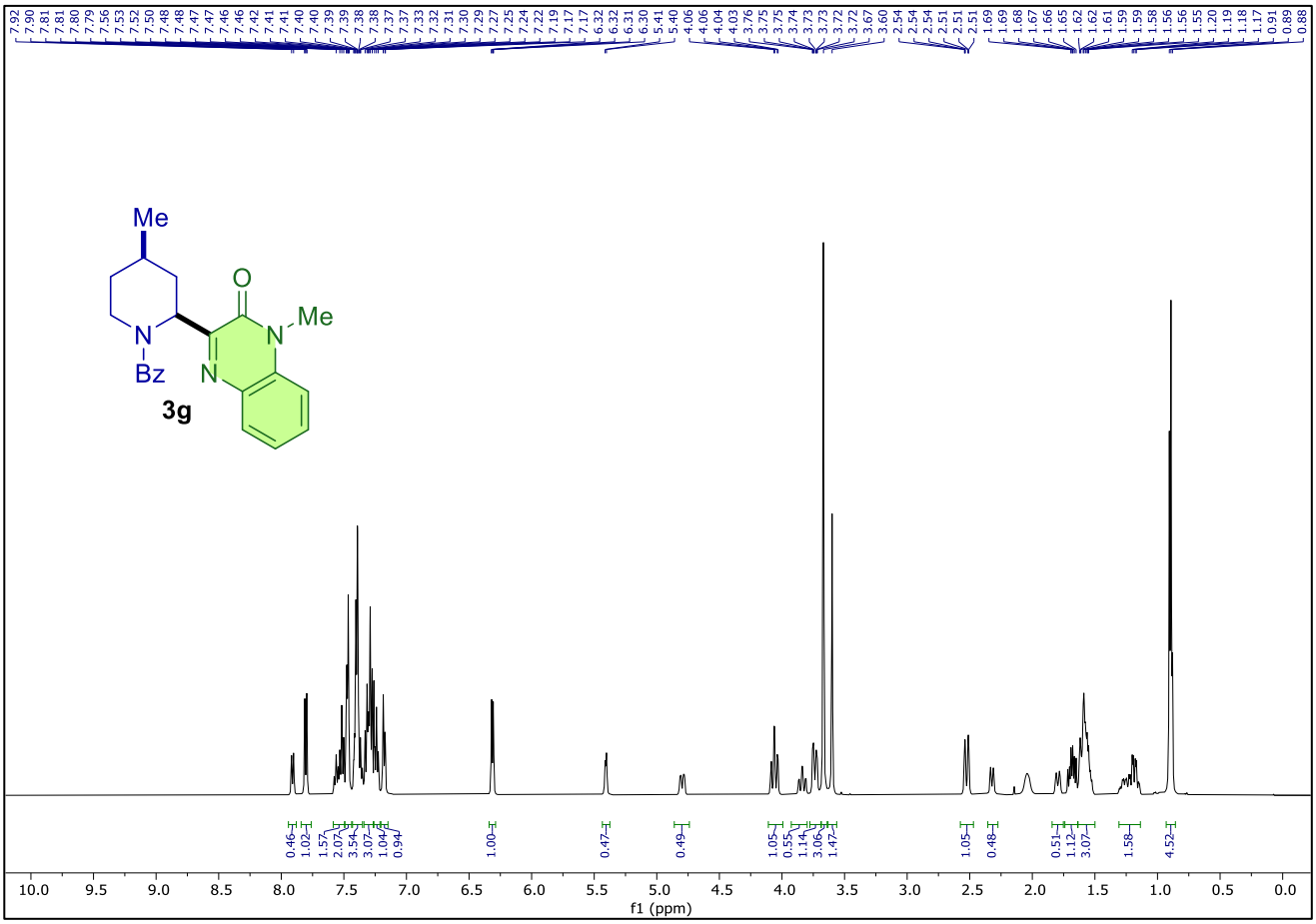
$^{13}C\{^{1}H\}$ NMR of compound **3e** (126 MHz, $CDCl_3$)



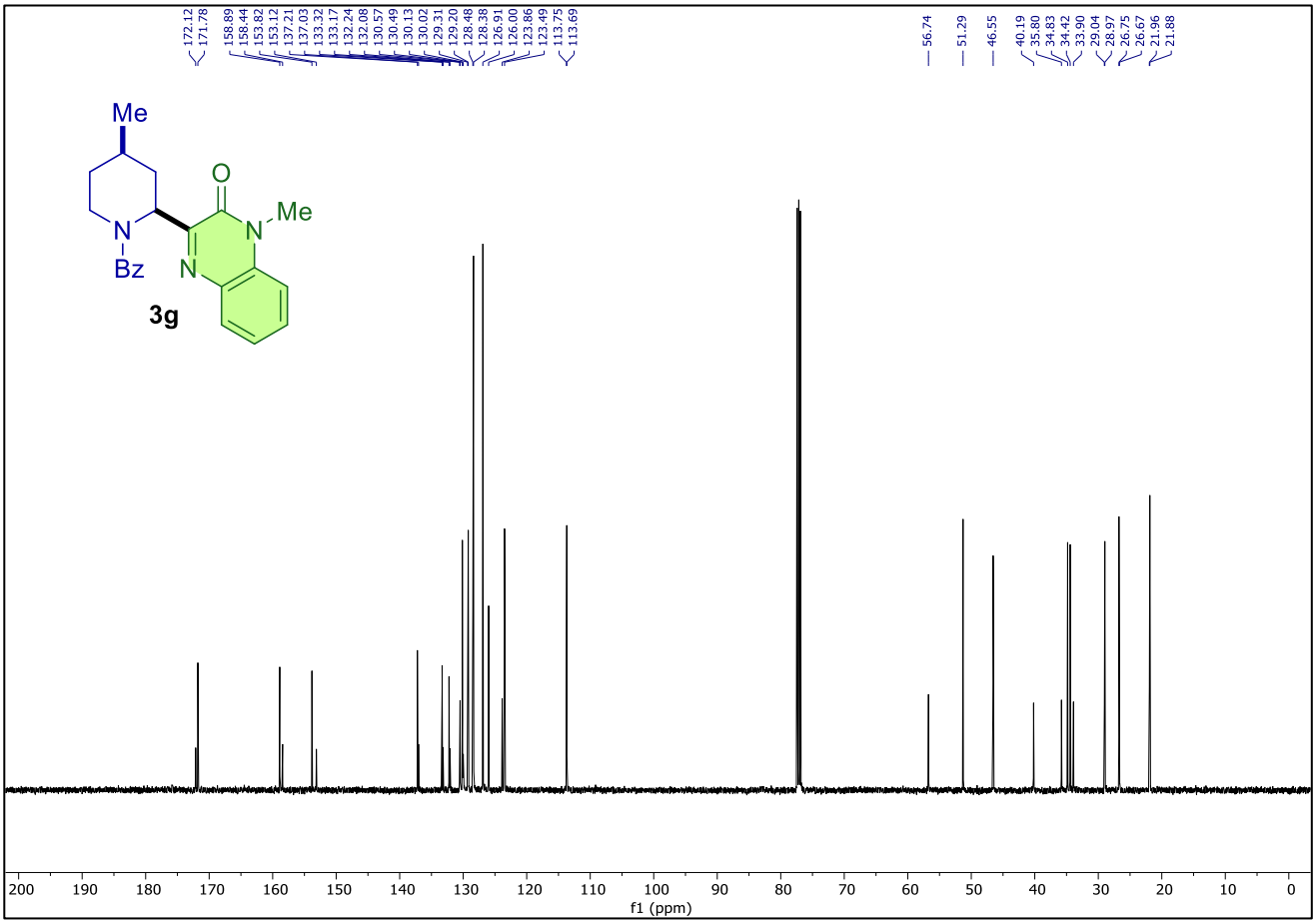
^{1}H NMR of compound **3f** (400 MHz, $CDCl_3$)



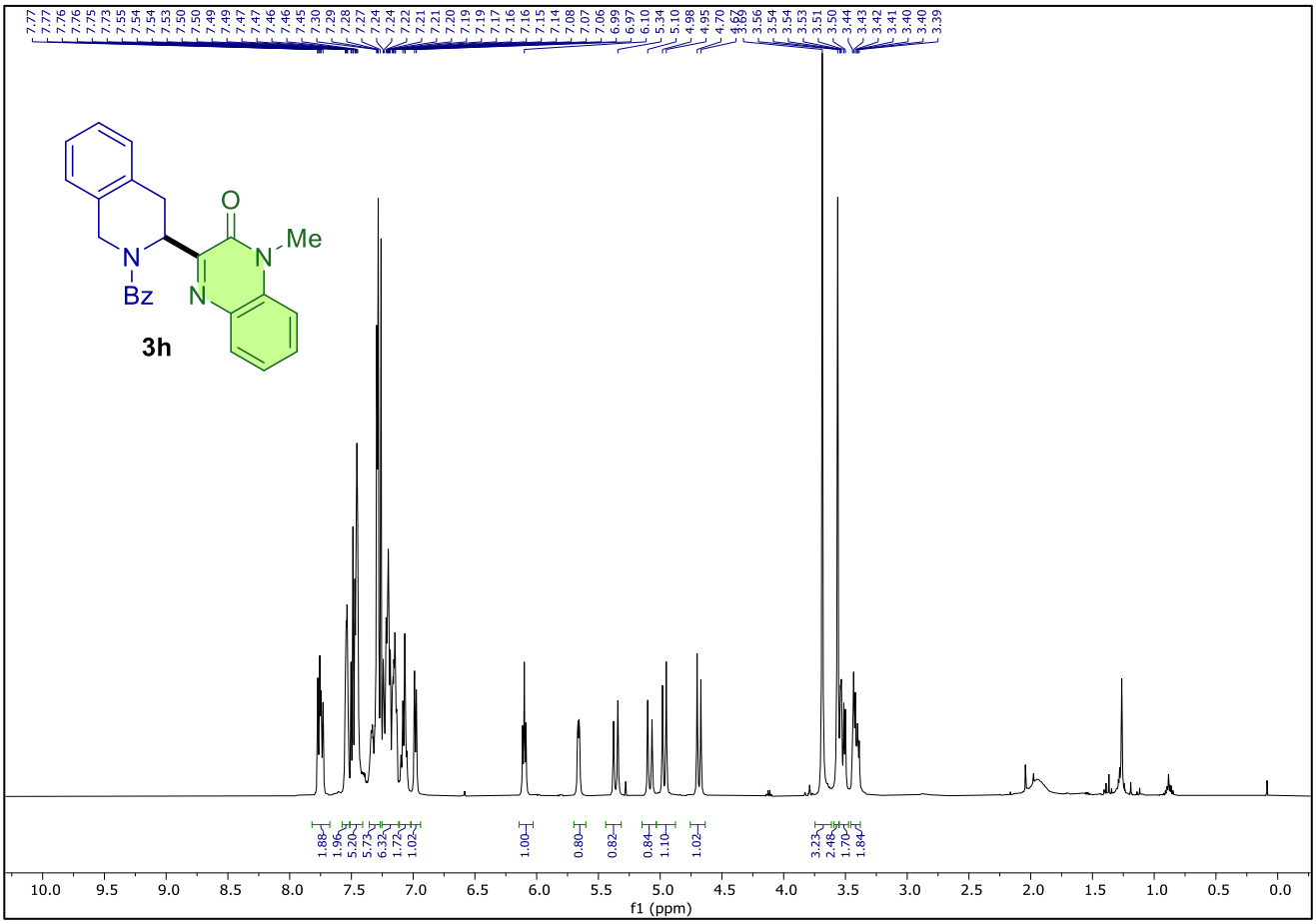
$^{13}C\{^{1}H\}$ NMR of compound **3f** (126 MHz, $CDCl_3$)



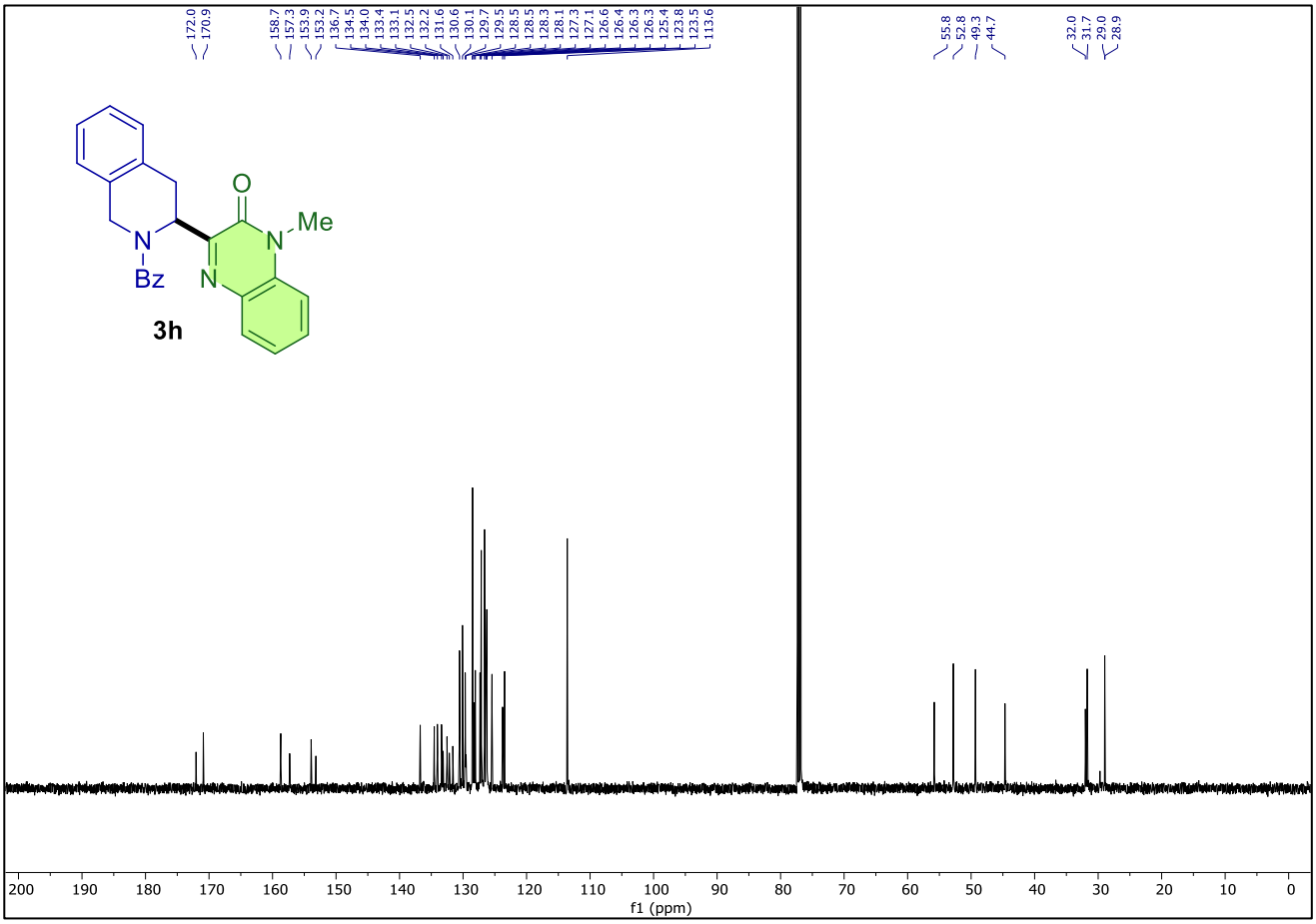
^{1}H NMR of compound **3g** (500 MHz, $CDCl_3$)



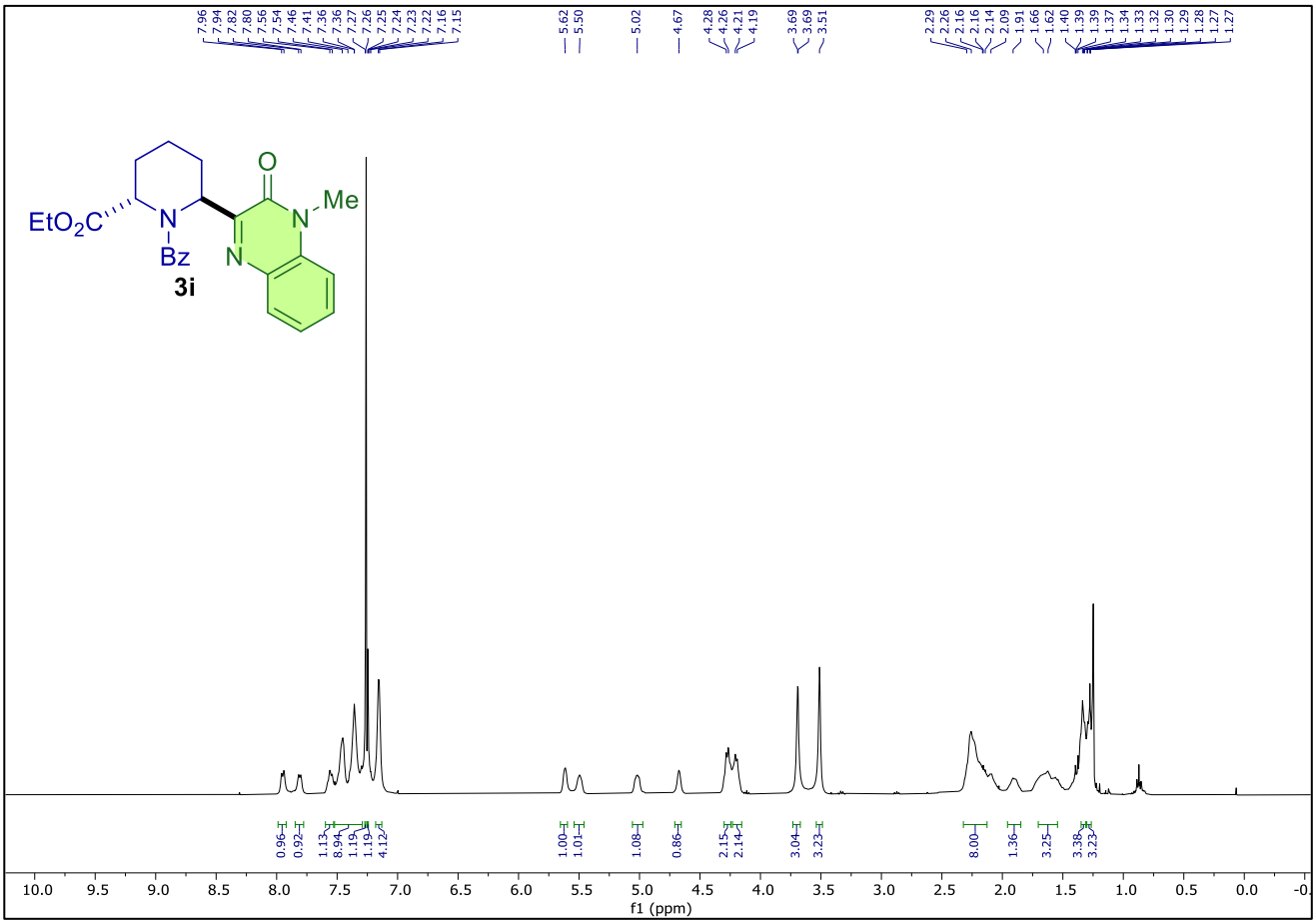
$^{13}C\{^{1}H\}$ NMR of compound **3g** (126 MHz, $CDCl_3$)



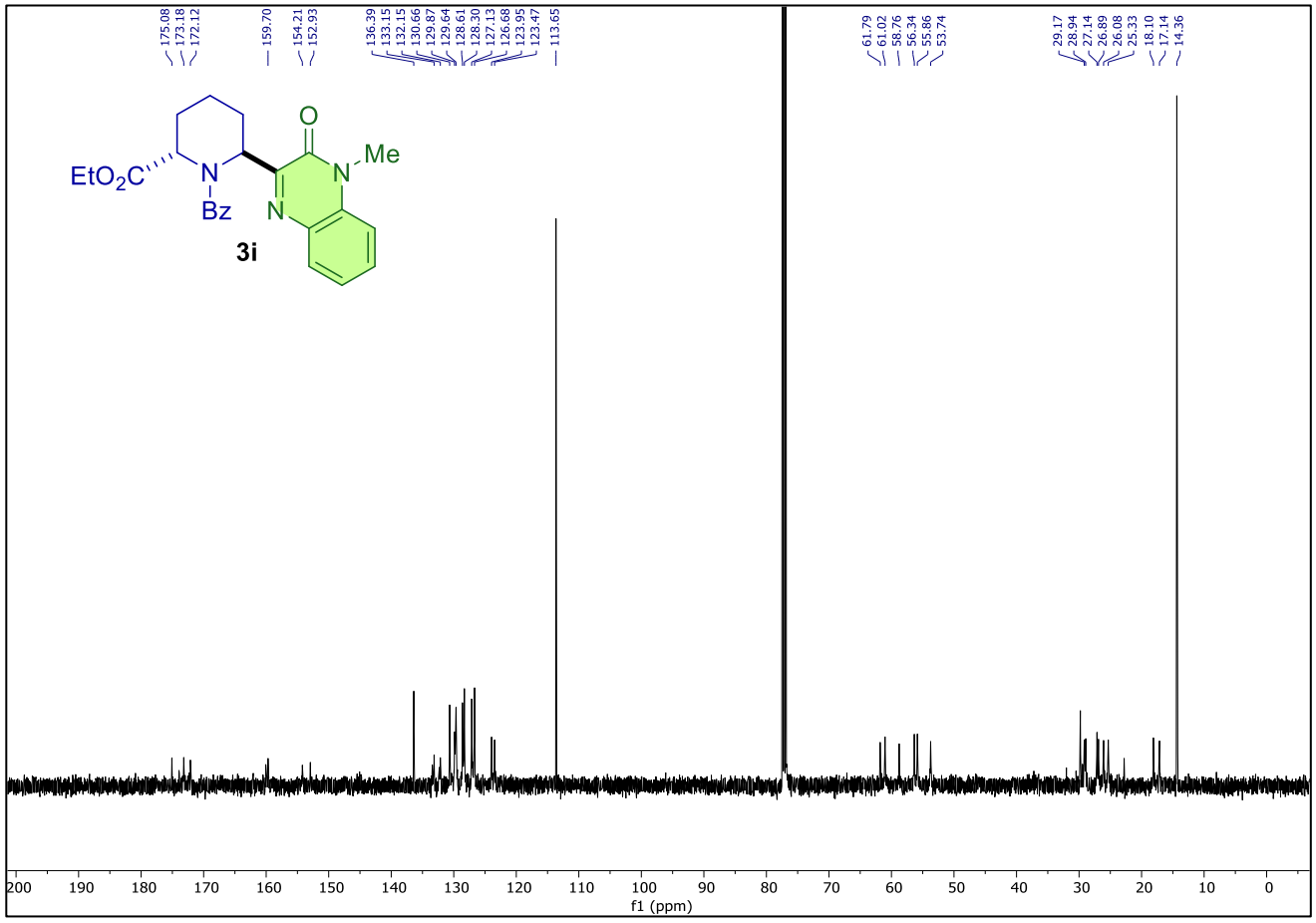
^{1}H NMR of compound **3h** (500 MHz, $CDCl_3$)



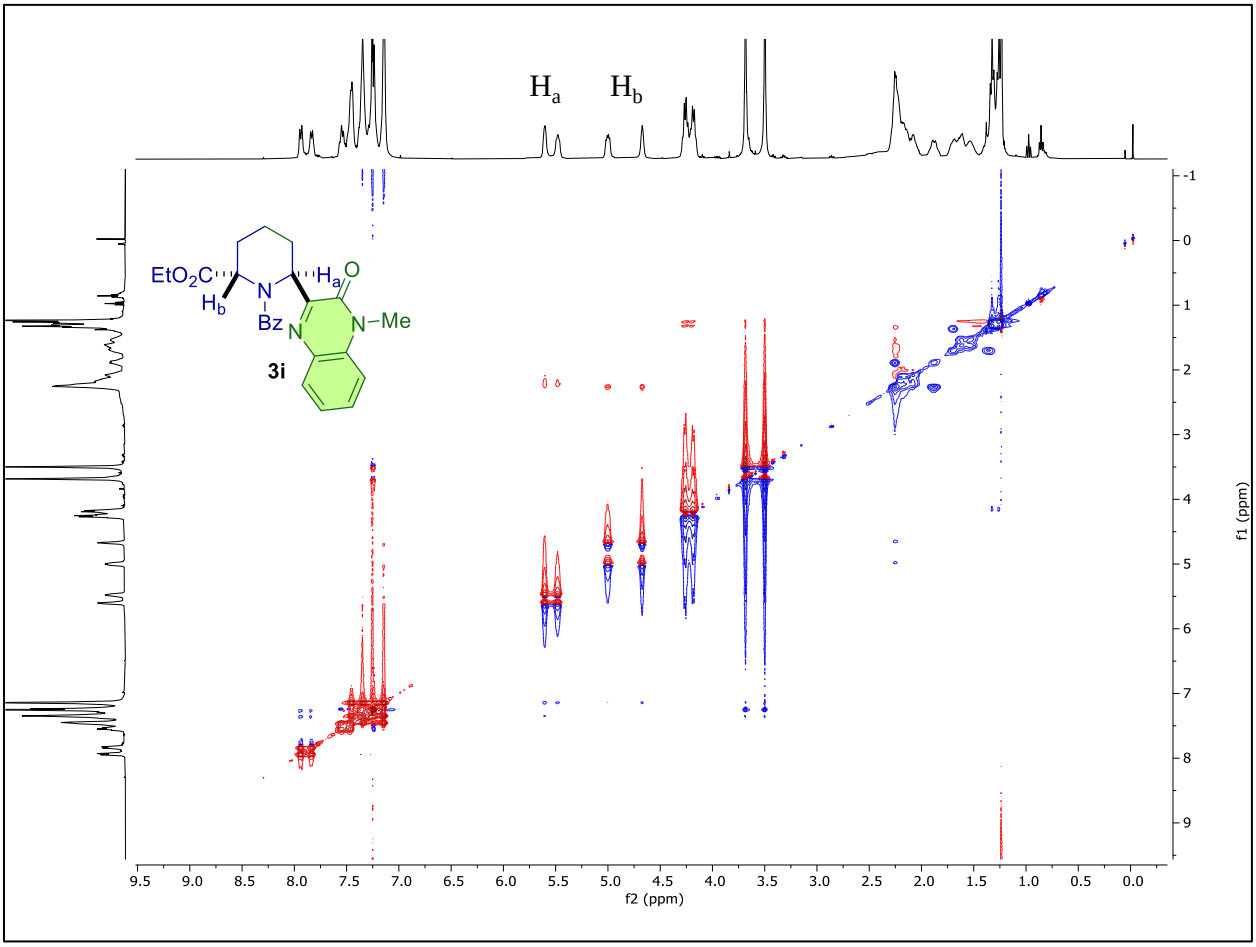
$^{13}C\{^{1}H\}$ NMR of compound **3h** (126 MHz, $CDCl_3$)



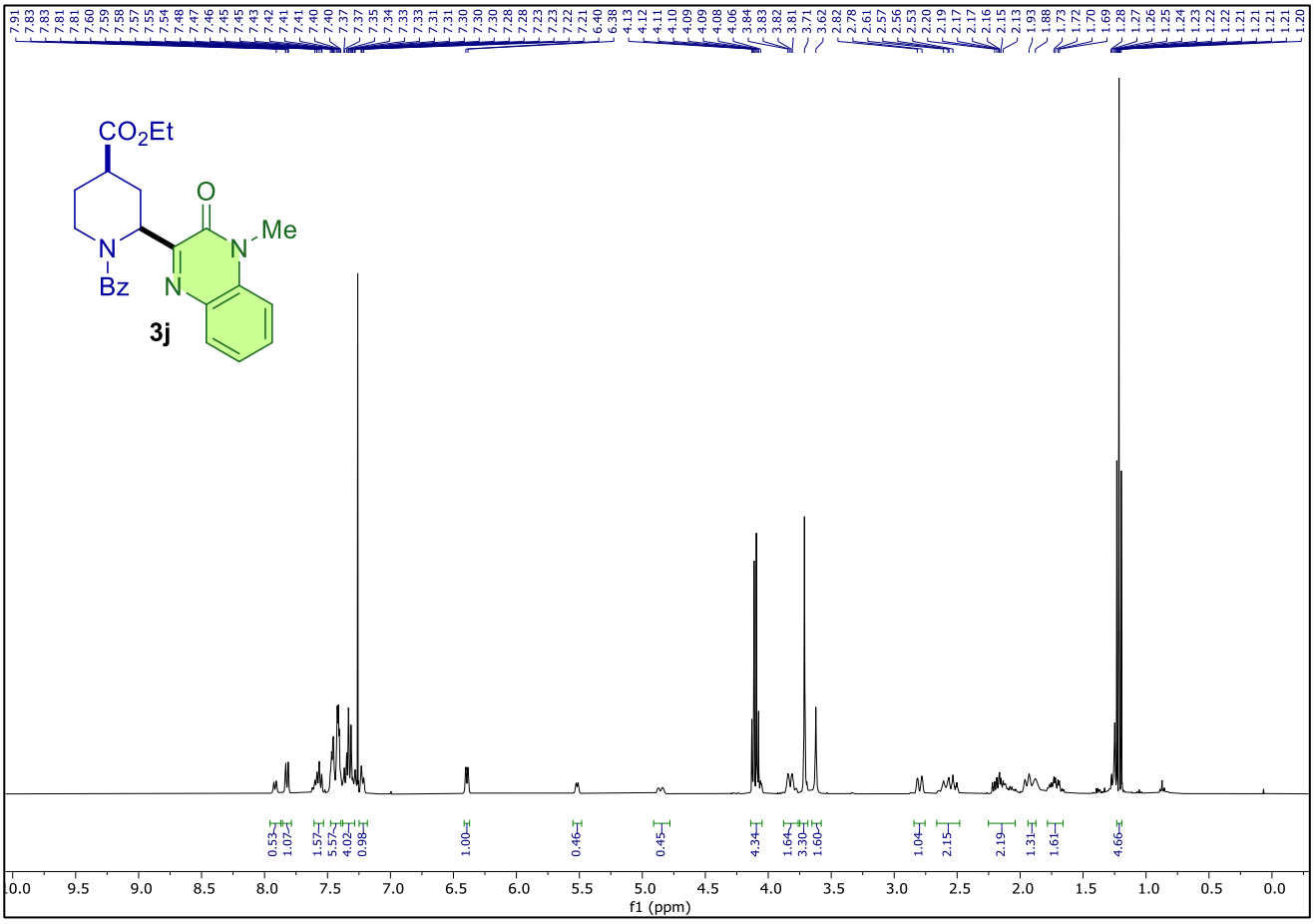
^{1}H NMR of compound **3i** (400 MHz, $CDCl_3$)



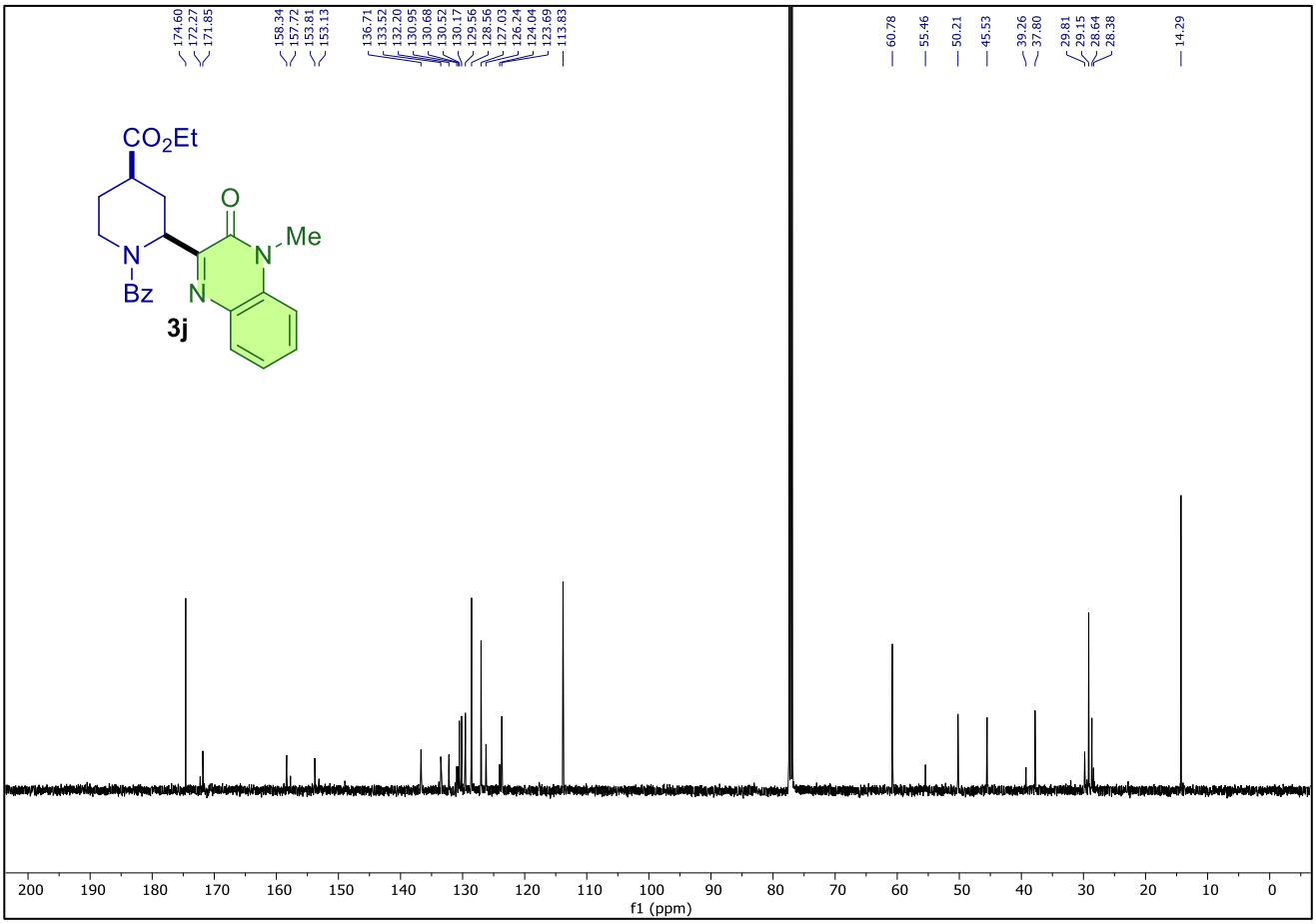
$^{13}C\{^{1}H\}$ NMR of compound **3i** (126 MHz, $CDCl_3$)



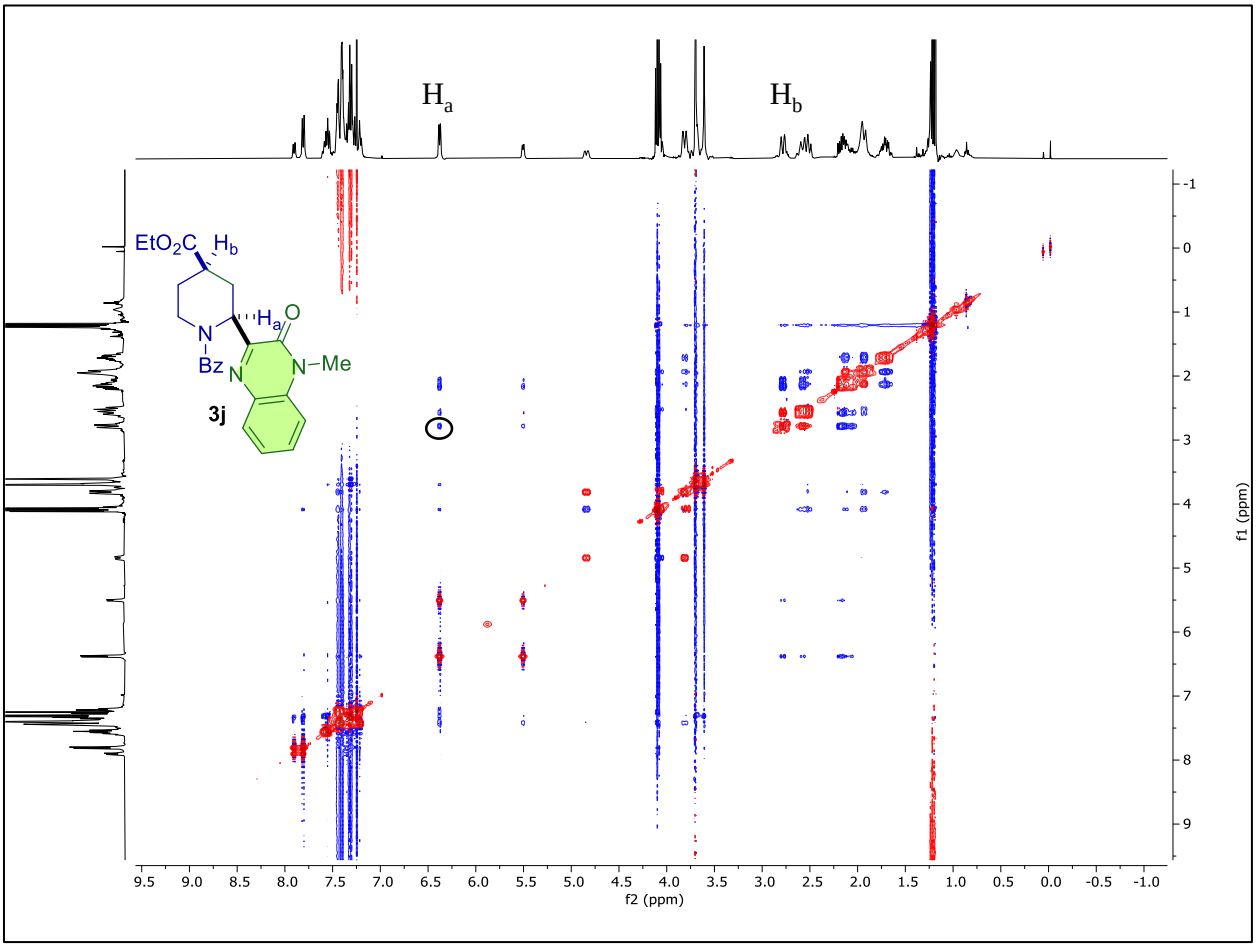
NOESY of compound **3i** (400 MHz, $CDCl_3$)



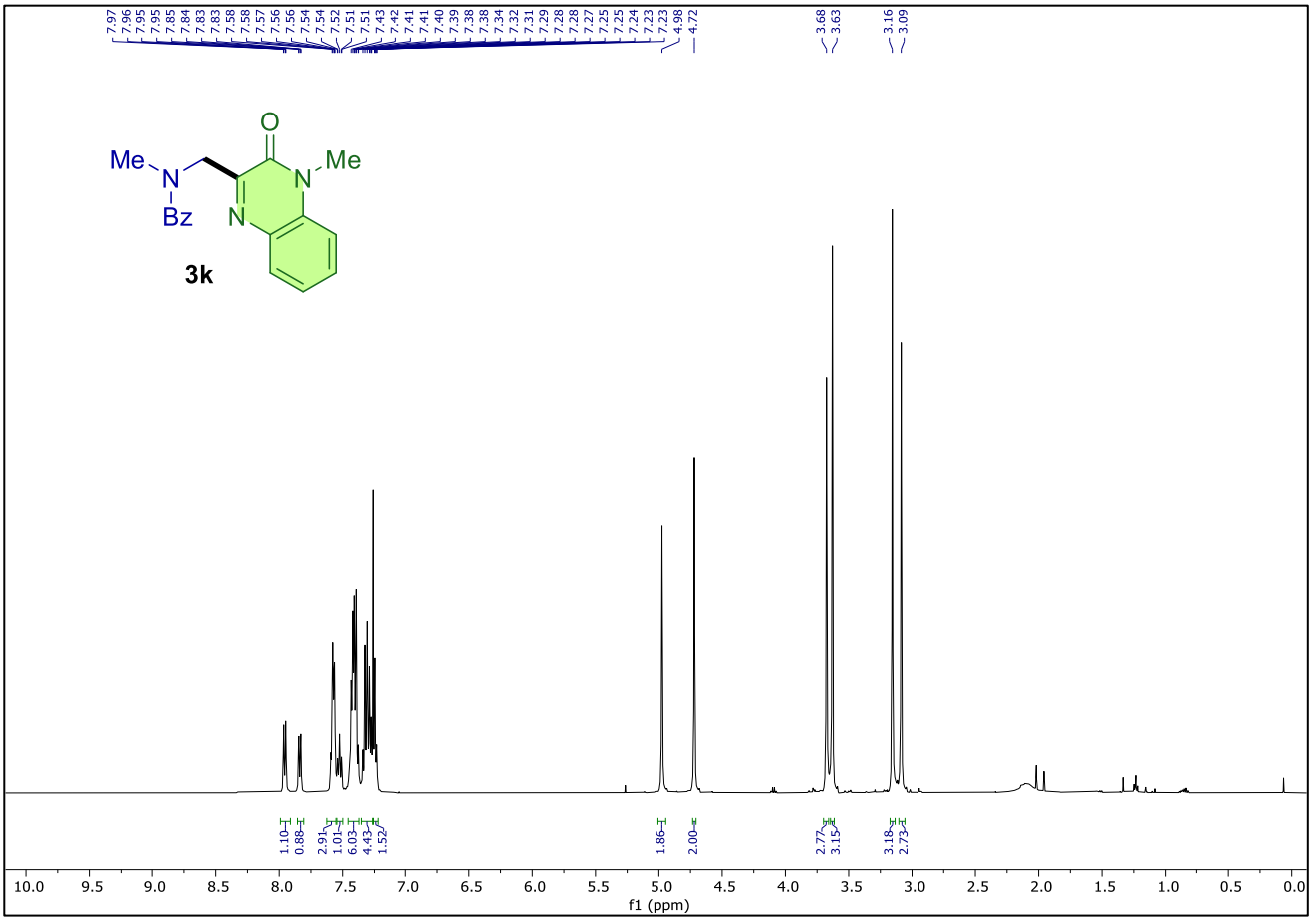
^{1}H NMR of compound **3j** (400 MHz, $CDCl_3$)



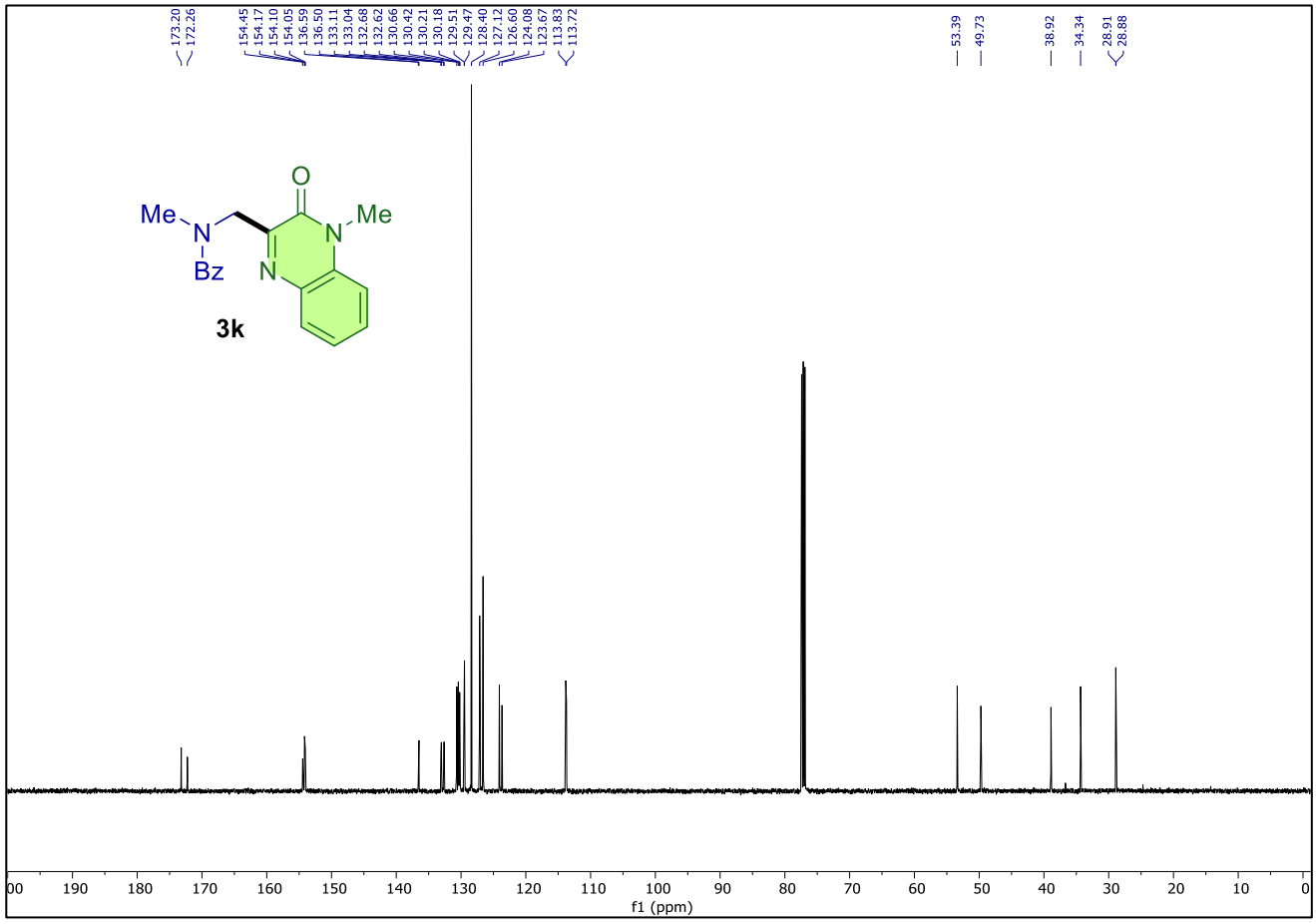
^{13}C{^{1}H} NMR of compound **3j** (126 MHz, $CDCl_3$)



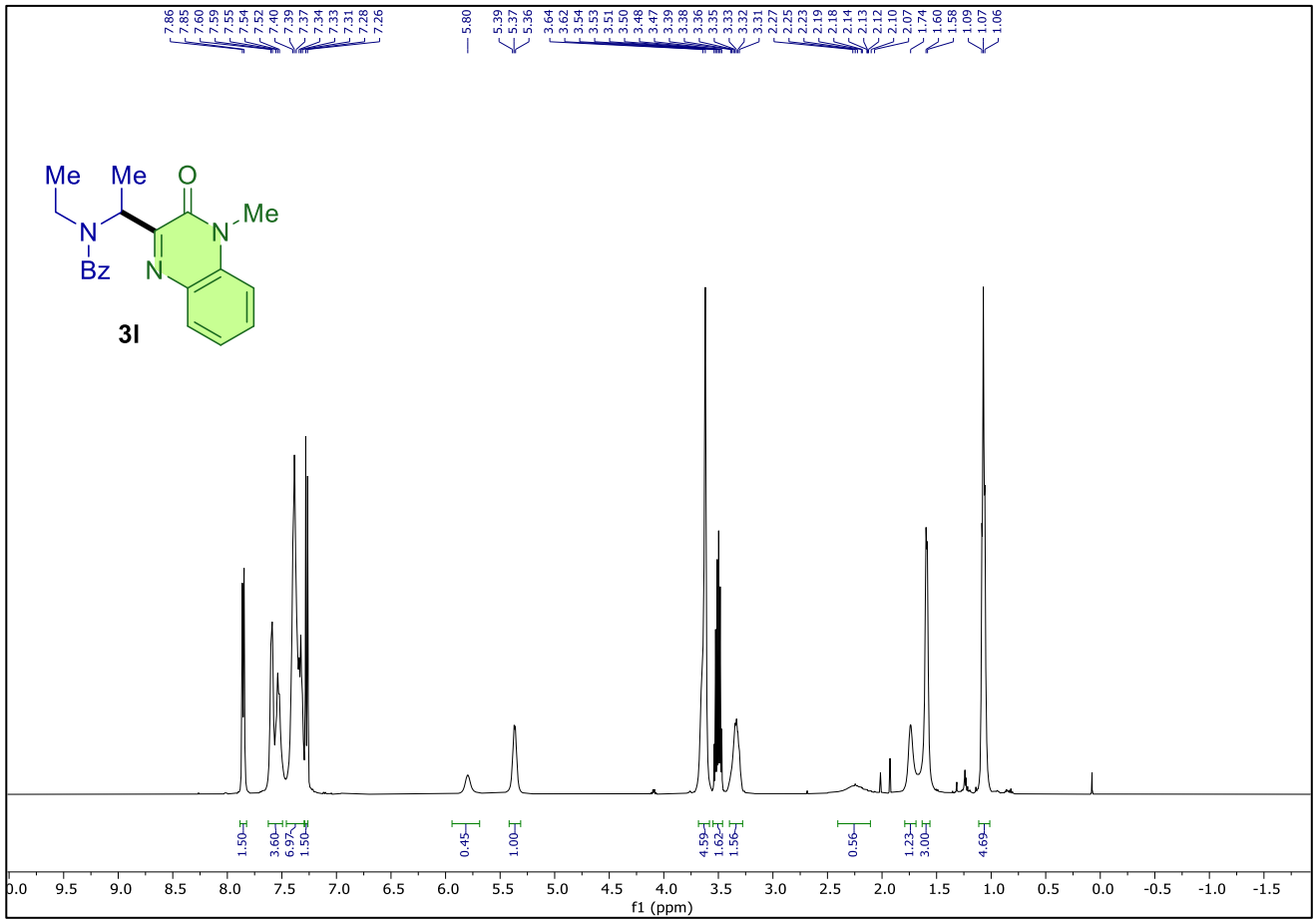
NOESY of compound **3j** (400 MHz, $CDCl_3$)



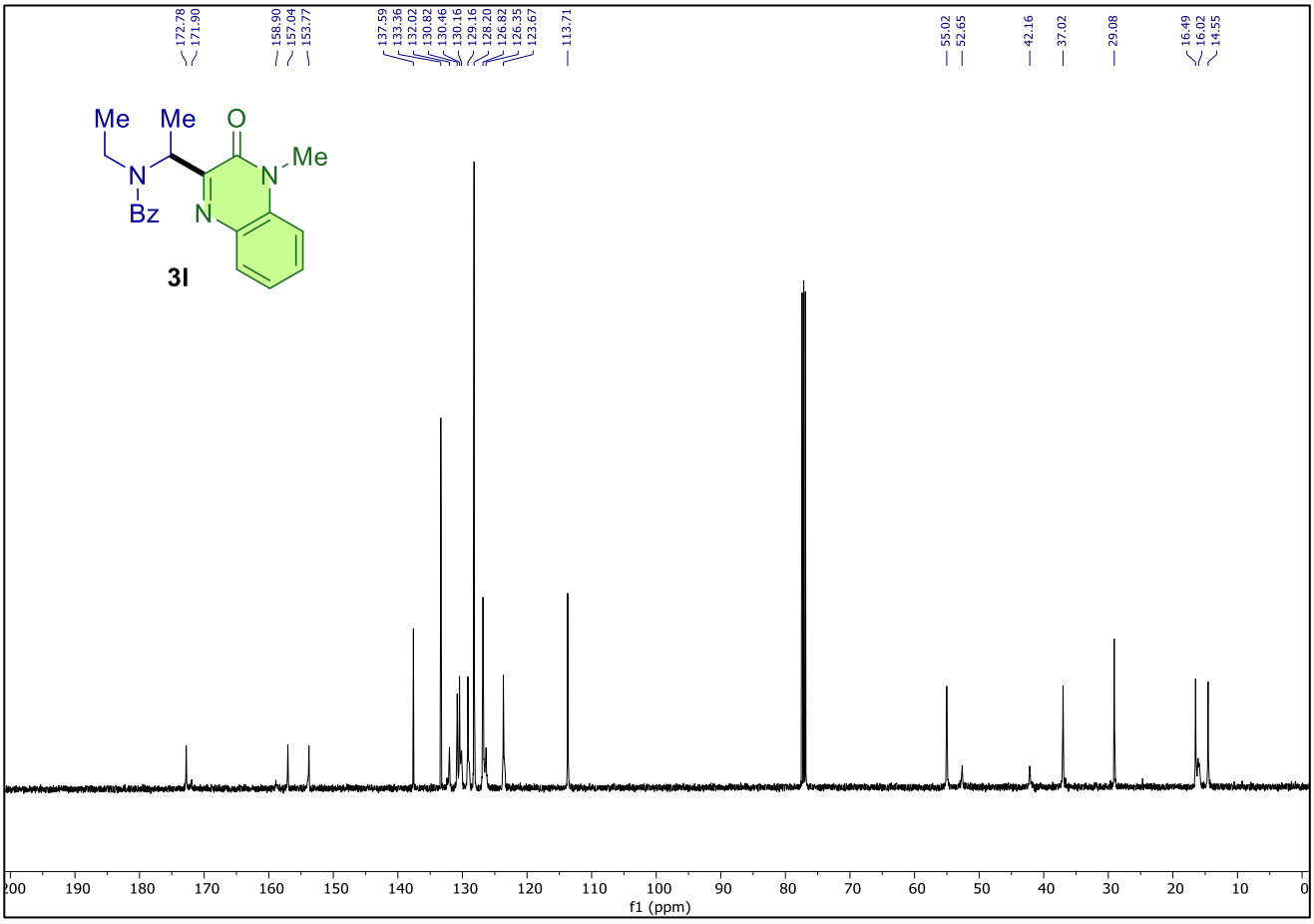
^{1}H NMR of compound **3k** (500 MHz, $CDCl_3$)



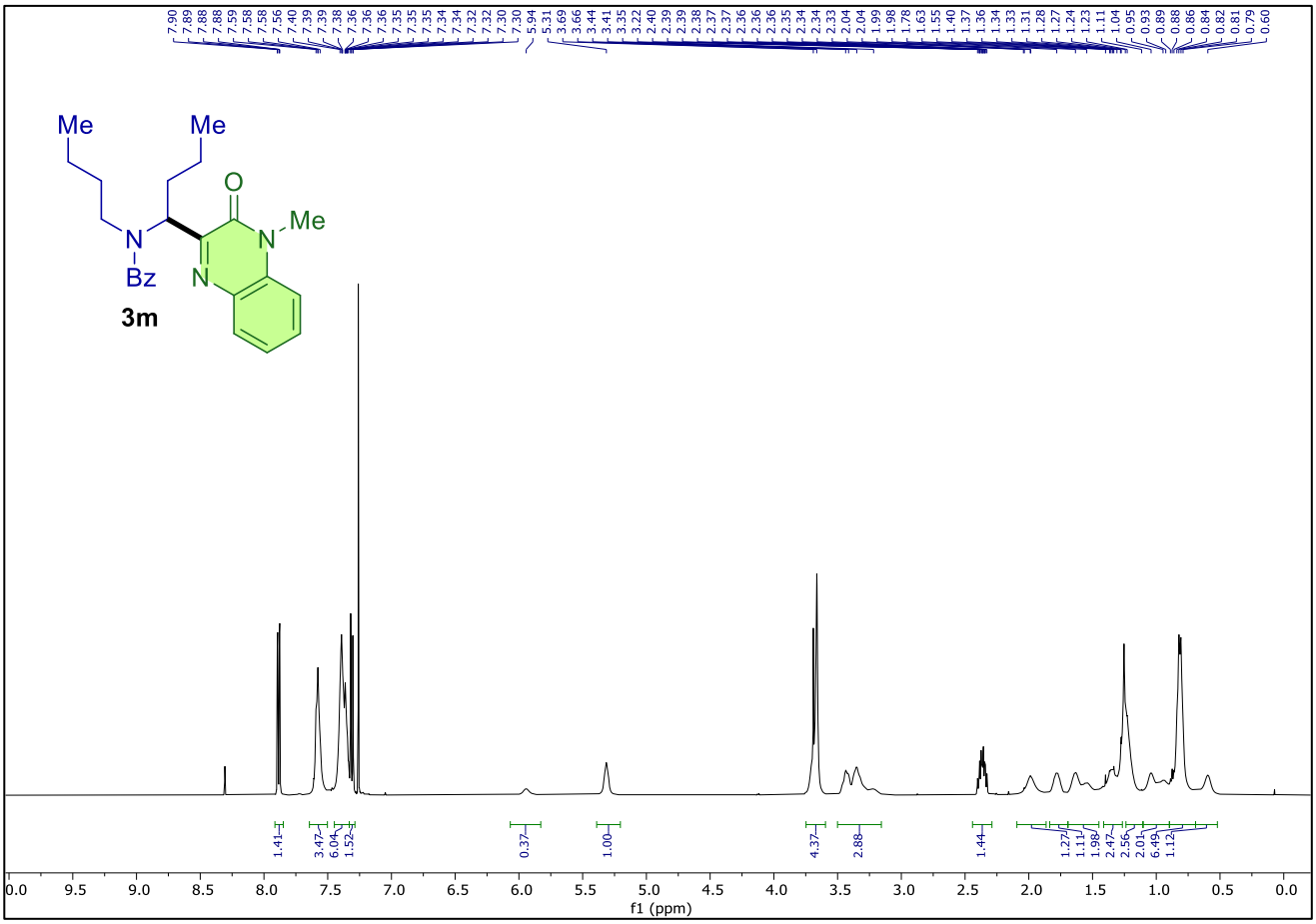
$^{13}C\{^{1}H\}$ NMR of compound **3k** (126 MHz, $CDCl_3$)



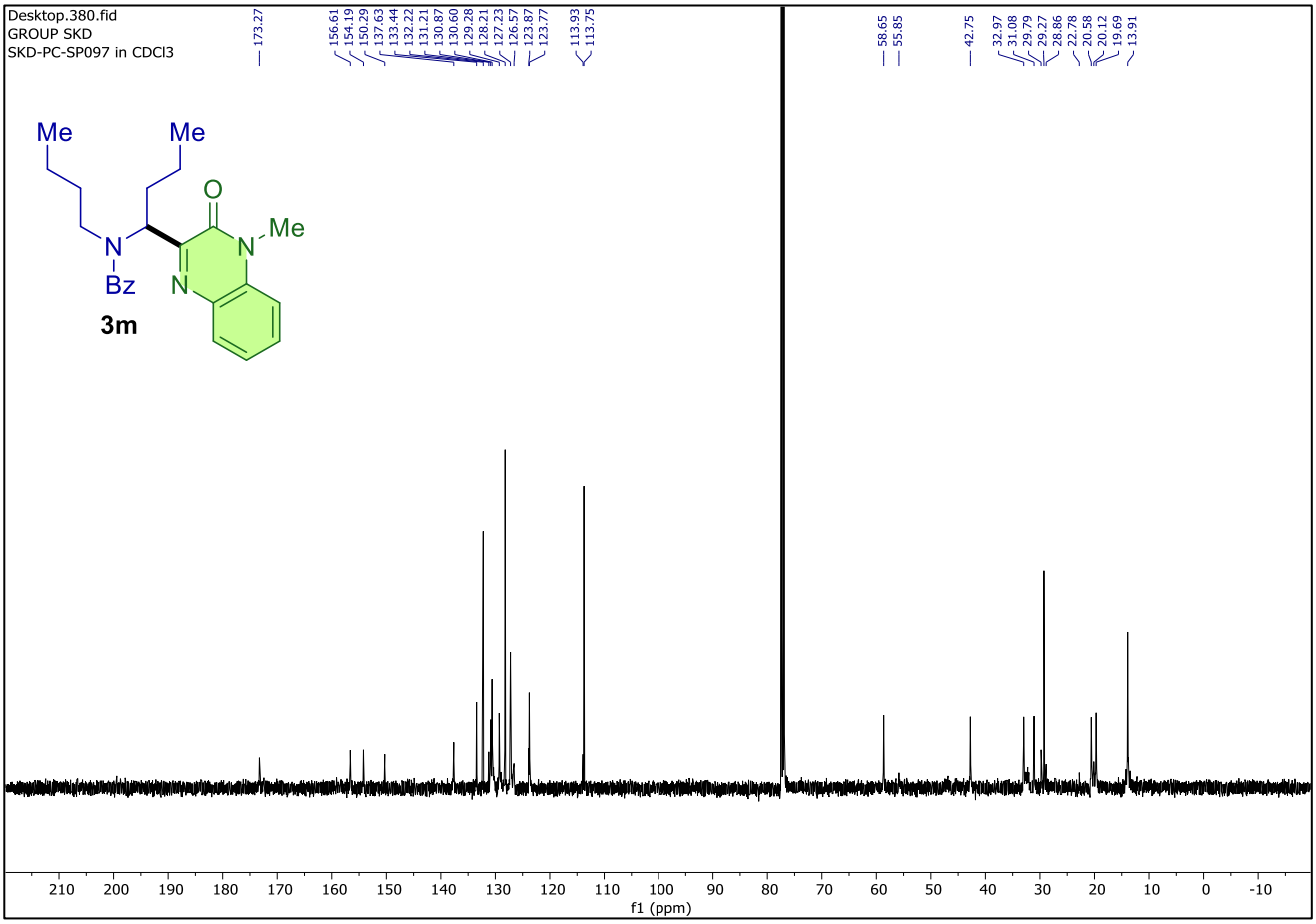
^{1}H NMR of compound **3l** (500 MHz, $CDCl_3$)



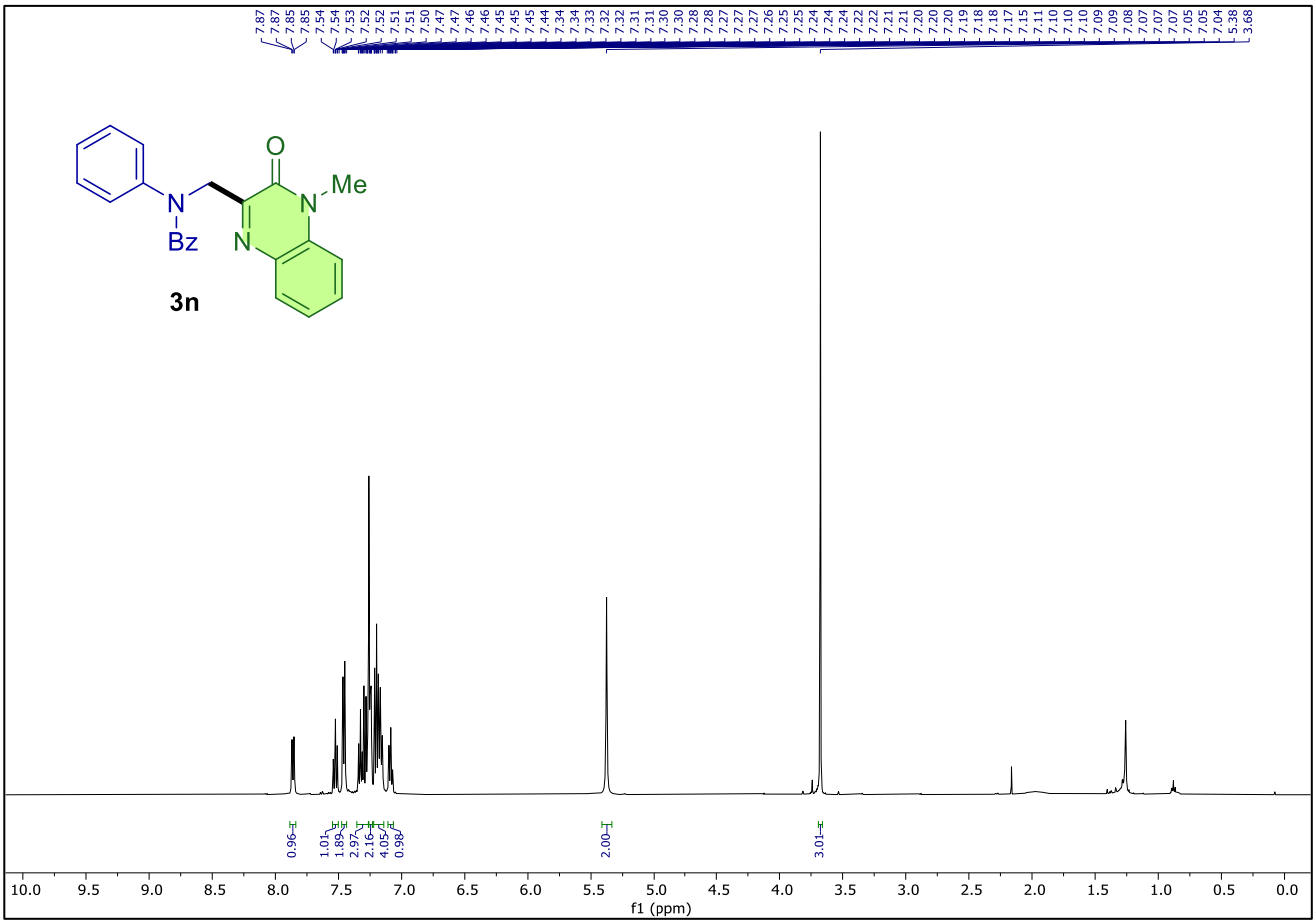
$^{13}C\{^{1}H\}$ NMR of compound **3l** (126 MHz, $CDCl_3$)



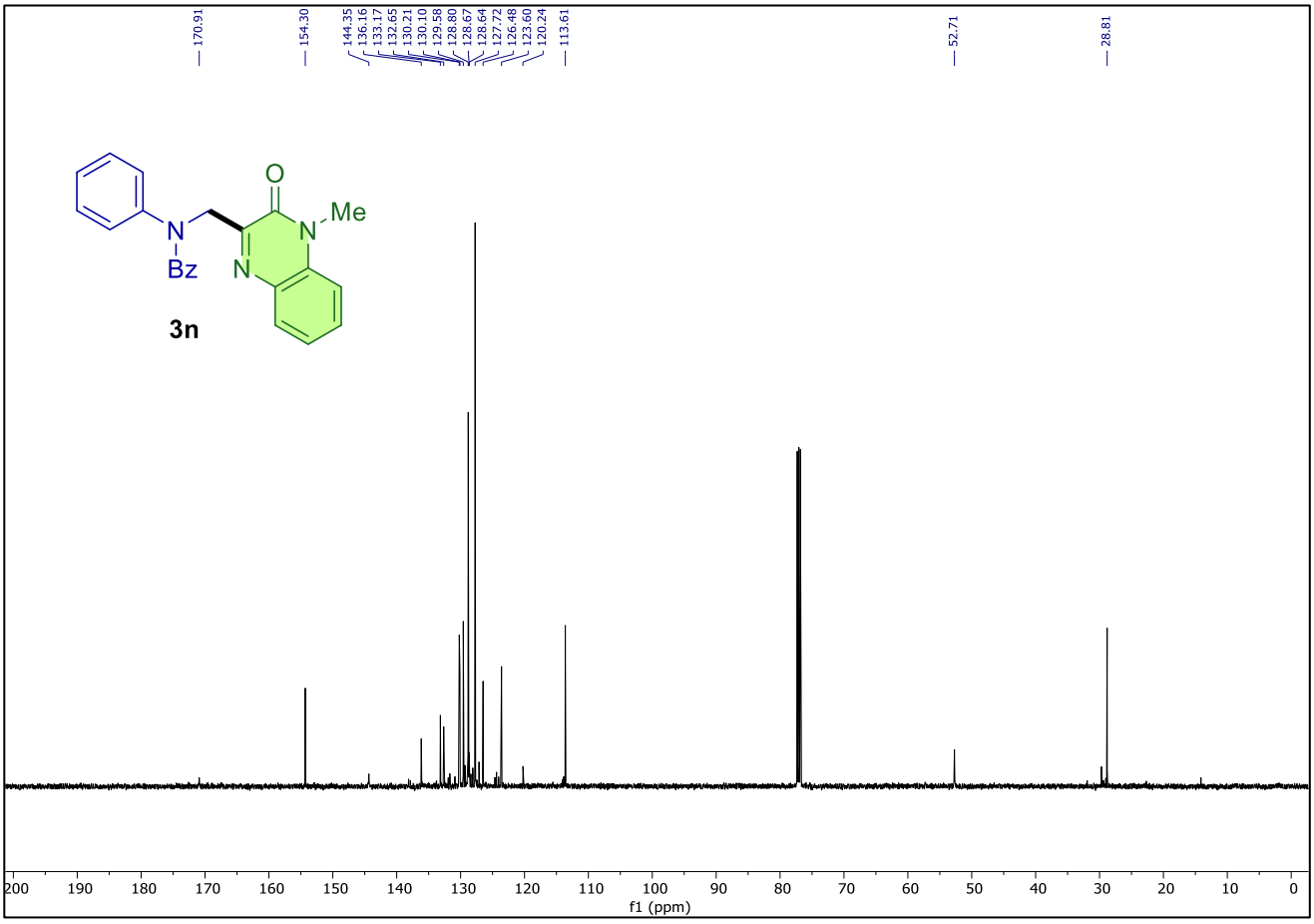
^{1}H NMR of compound **3m** (500 MHz, $CDCl_3$)



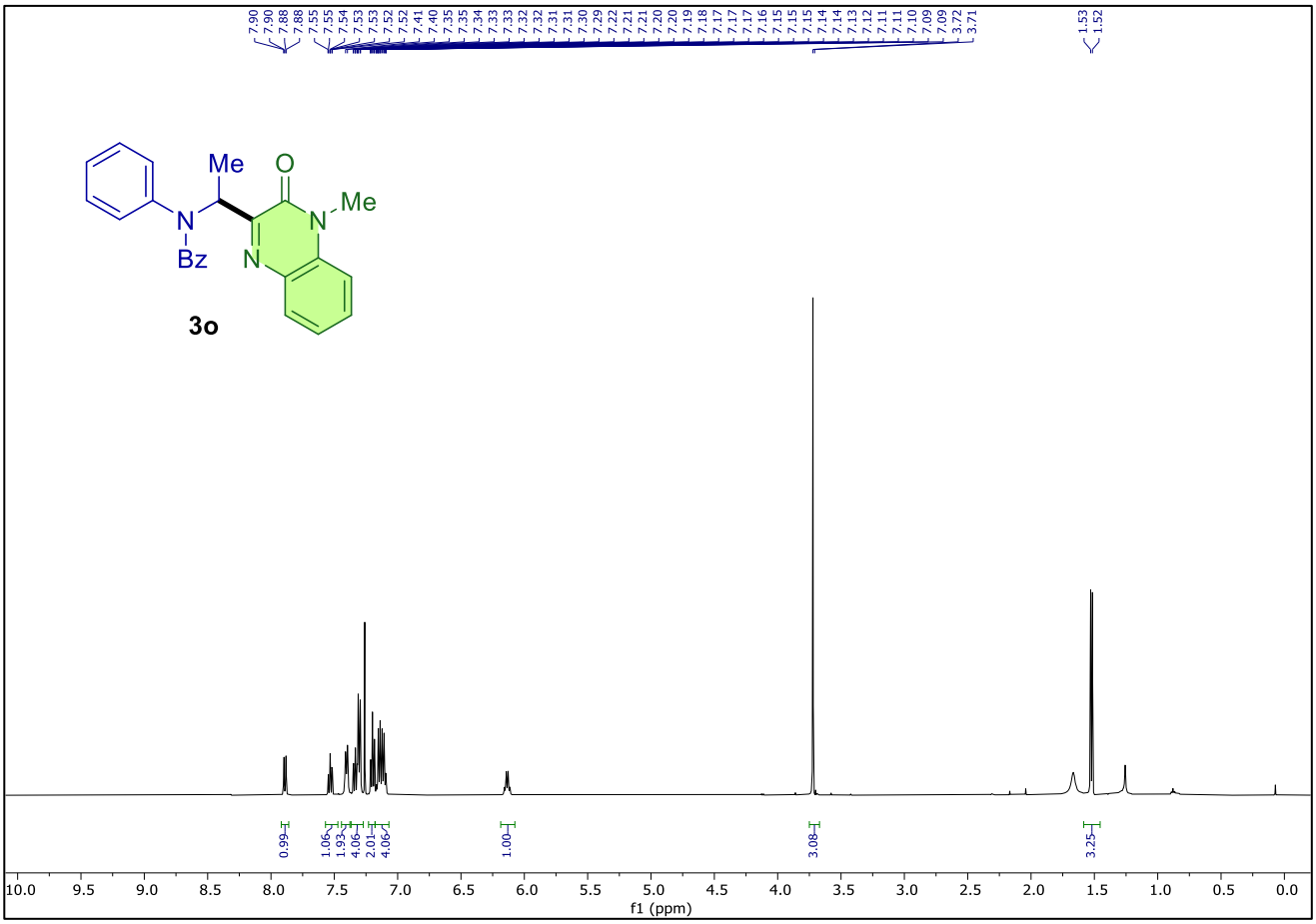
$^{13}C\{^{1}H\}$ NMR of compound **3m** (126 MHz, $CDCl_3$)



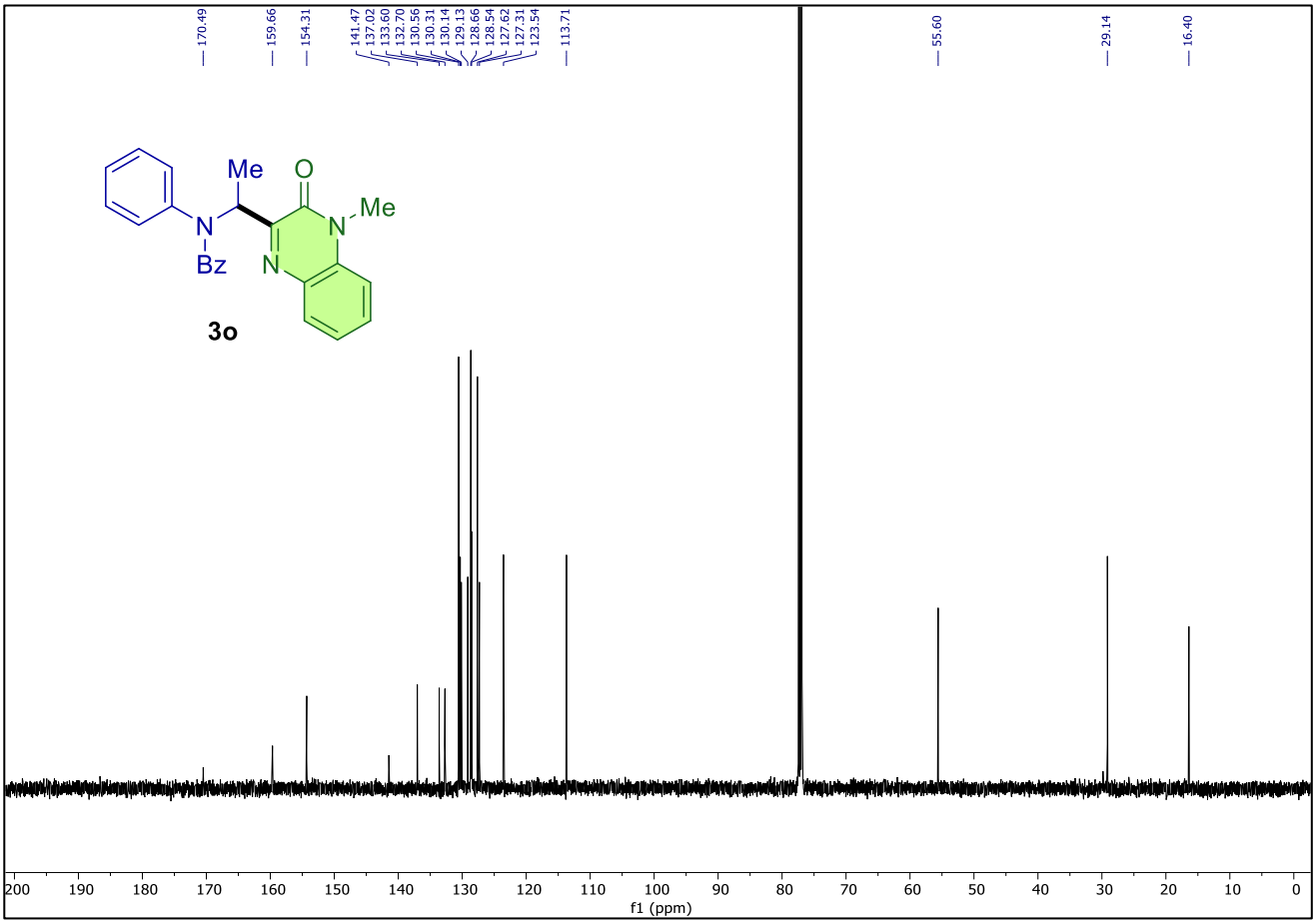
^{1}H NMR of compound **3n** (500 MHz, $CDCl_3$)



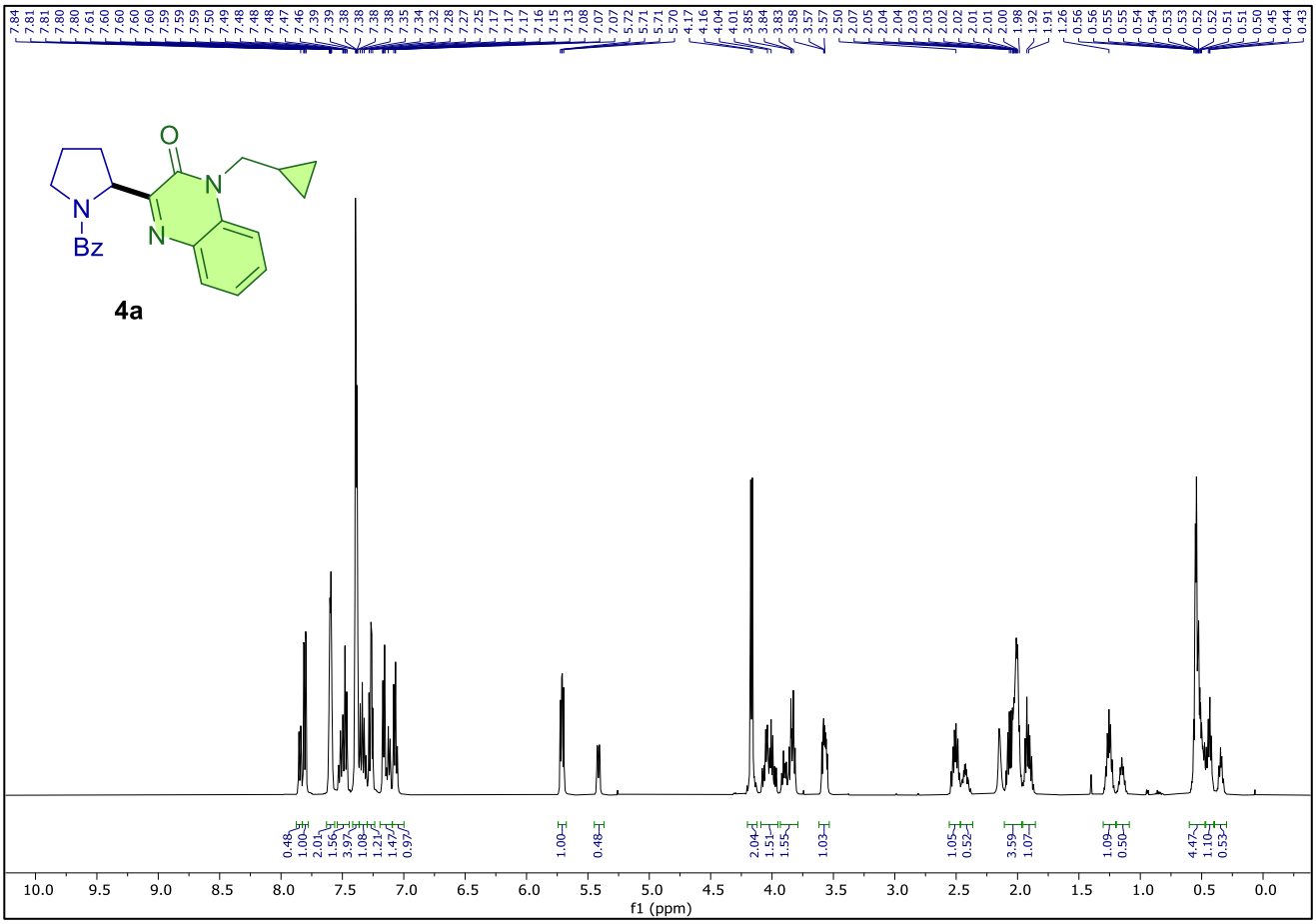
$^{13}C\{^{1}H\}$ NMR of compound **3n** (126 MHz, $CDCl_3$)



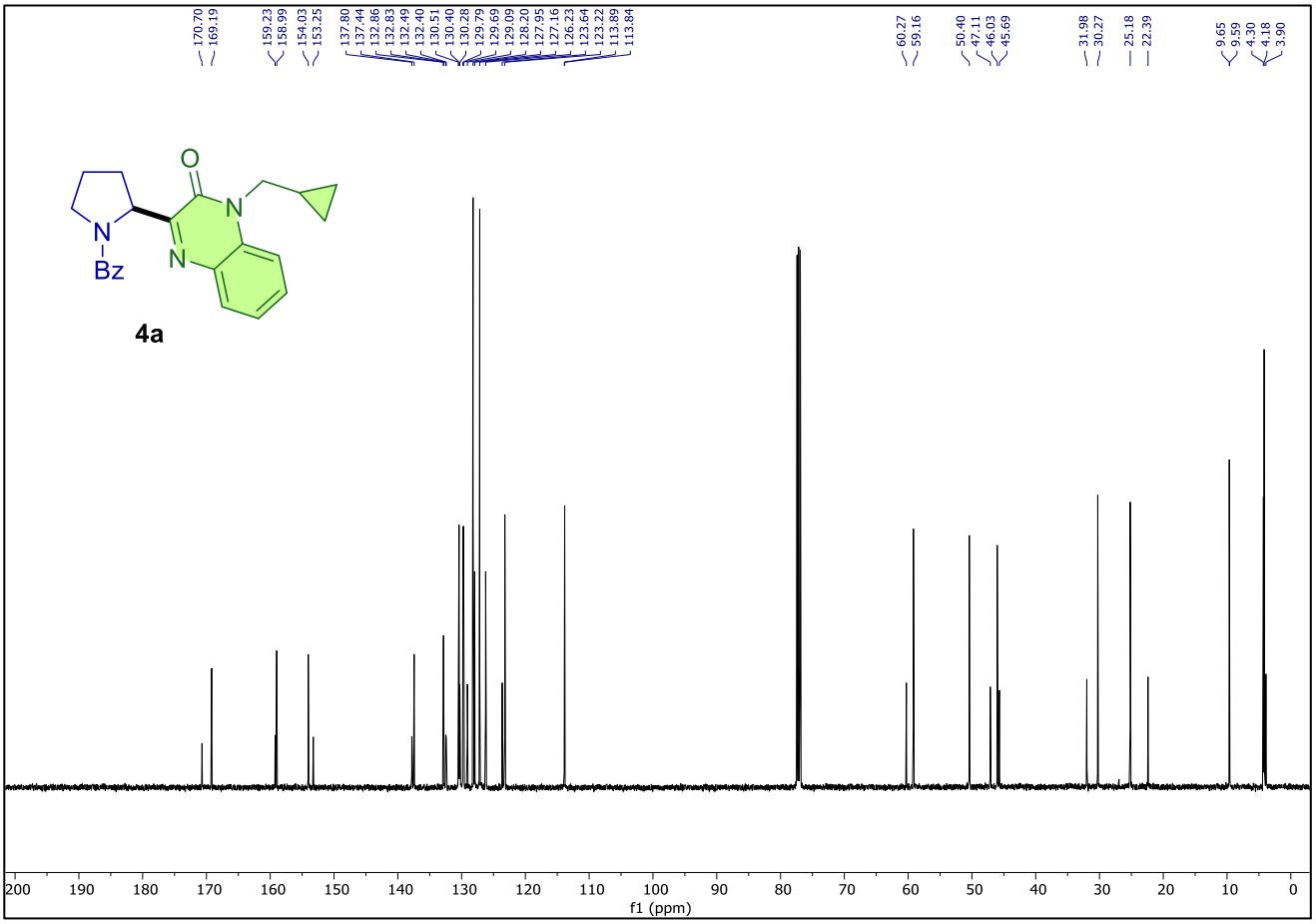
^{1}H NMR of compound **3o** (500 MHz, $CDCl_3$)



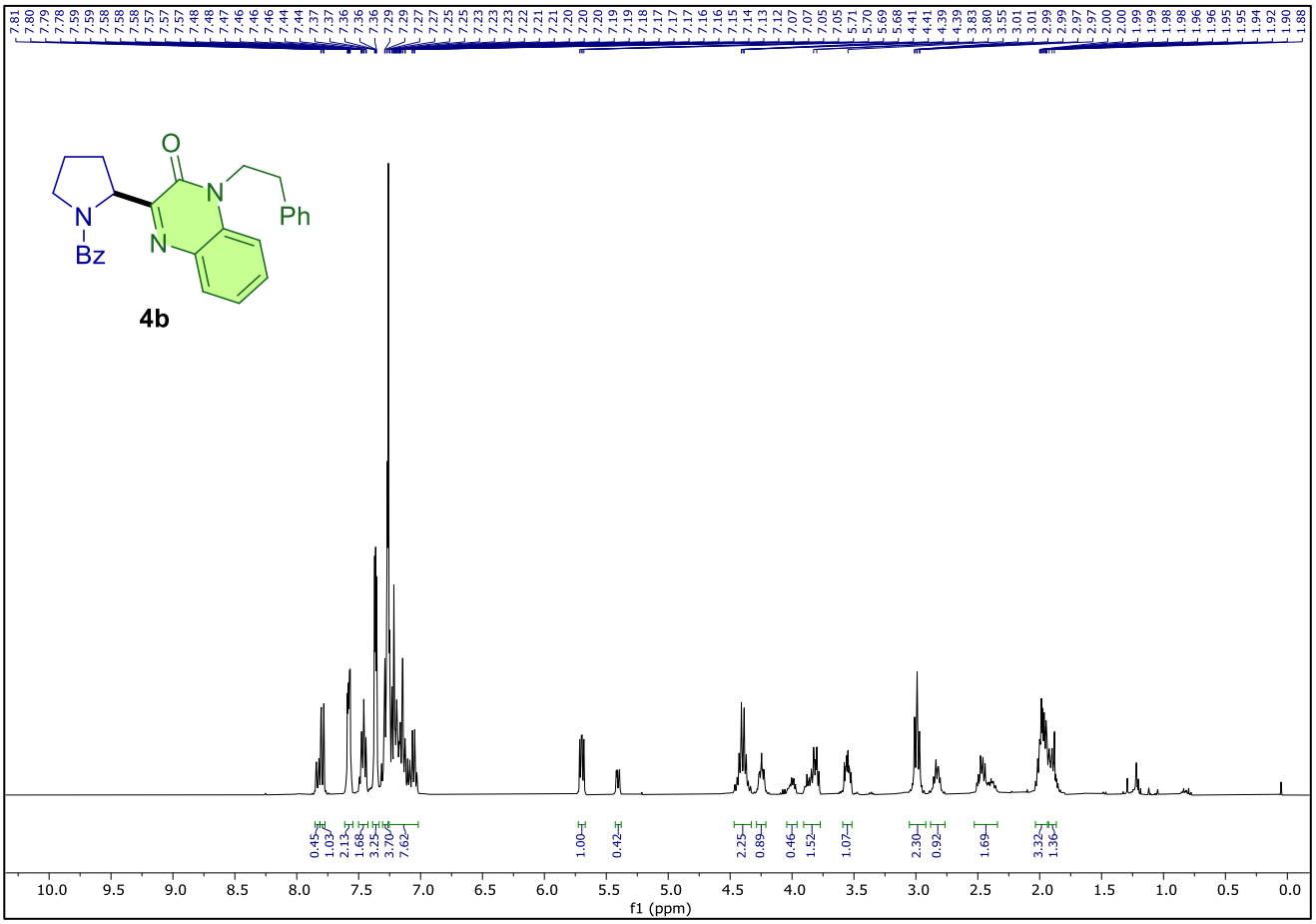
$^{13}C\{^{1}H\}$ NMR of compound **3o** (126 MHz, $CDCl_3$)



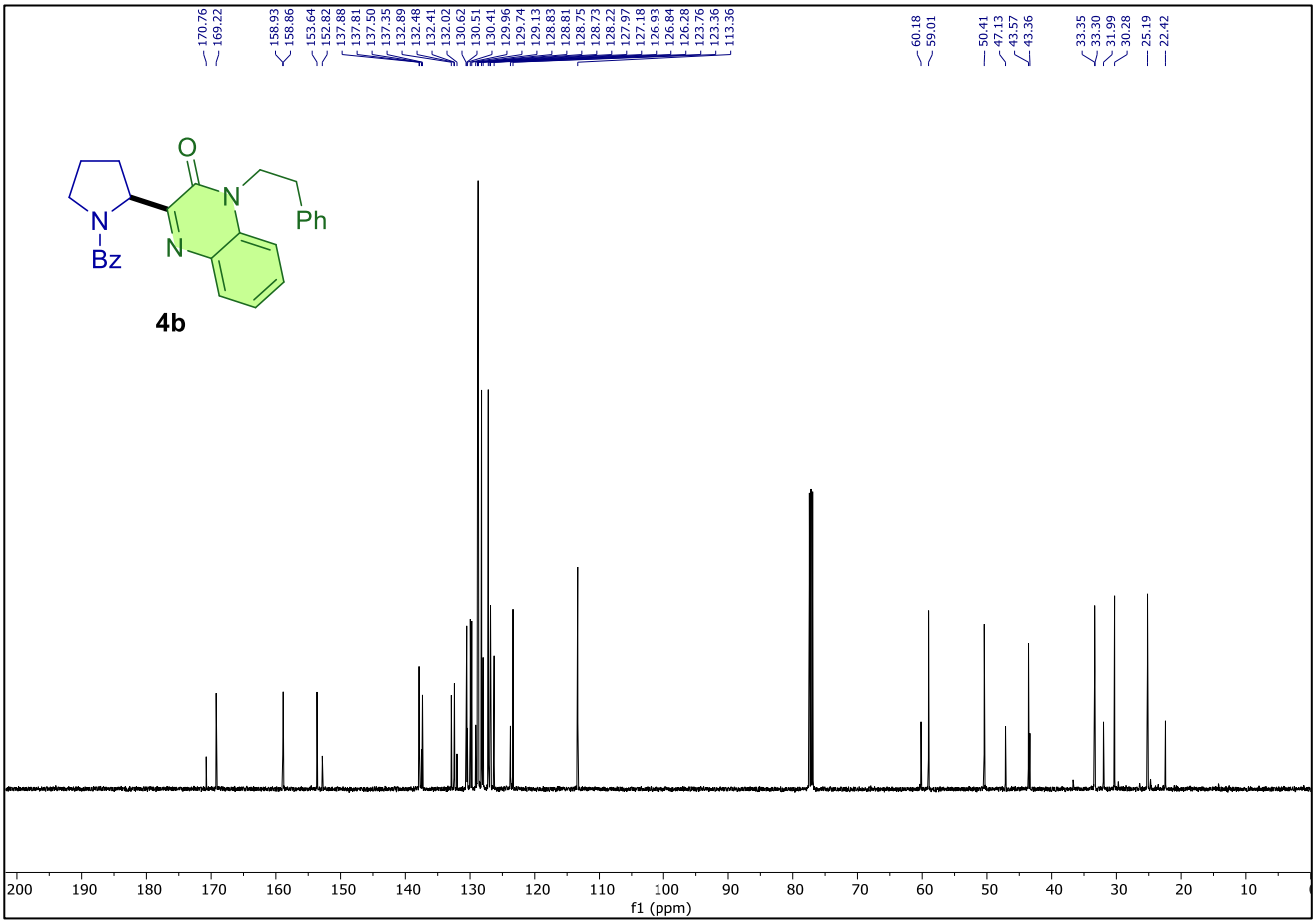
^{1}H NMR of compound **4a** (500 MHz, $CDCl_3$)



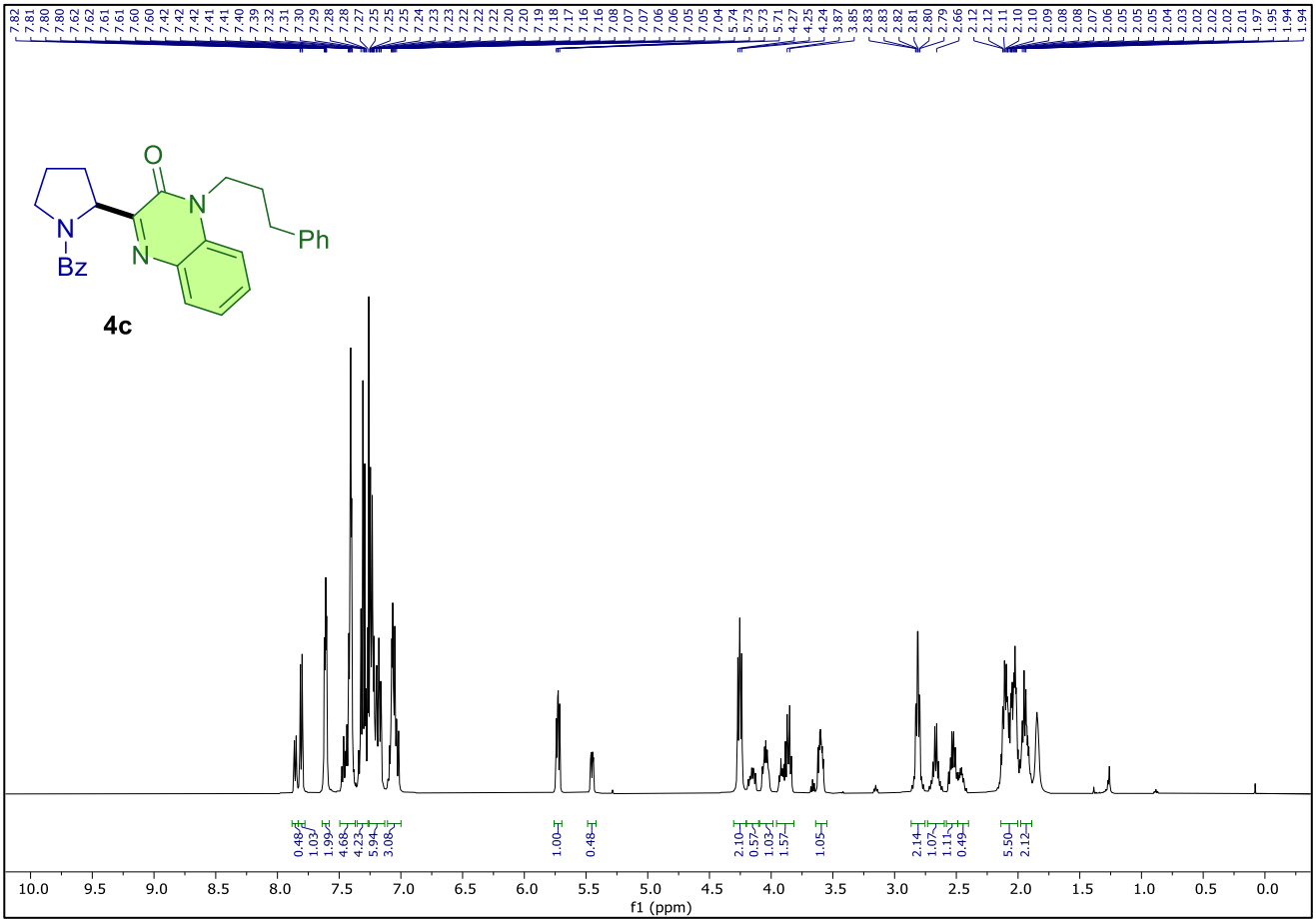
$^{13}C\{^{1}H\}$ NMR of compound **4a** (126 MHz, $CDCl_3$)



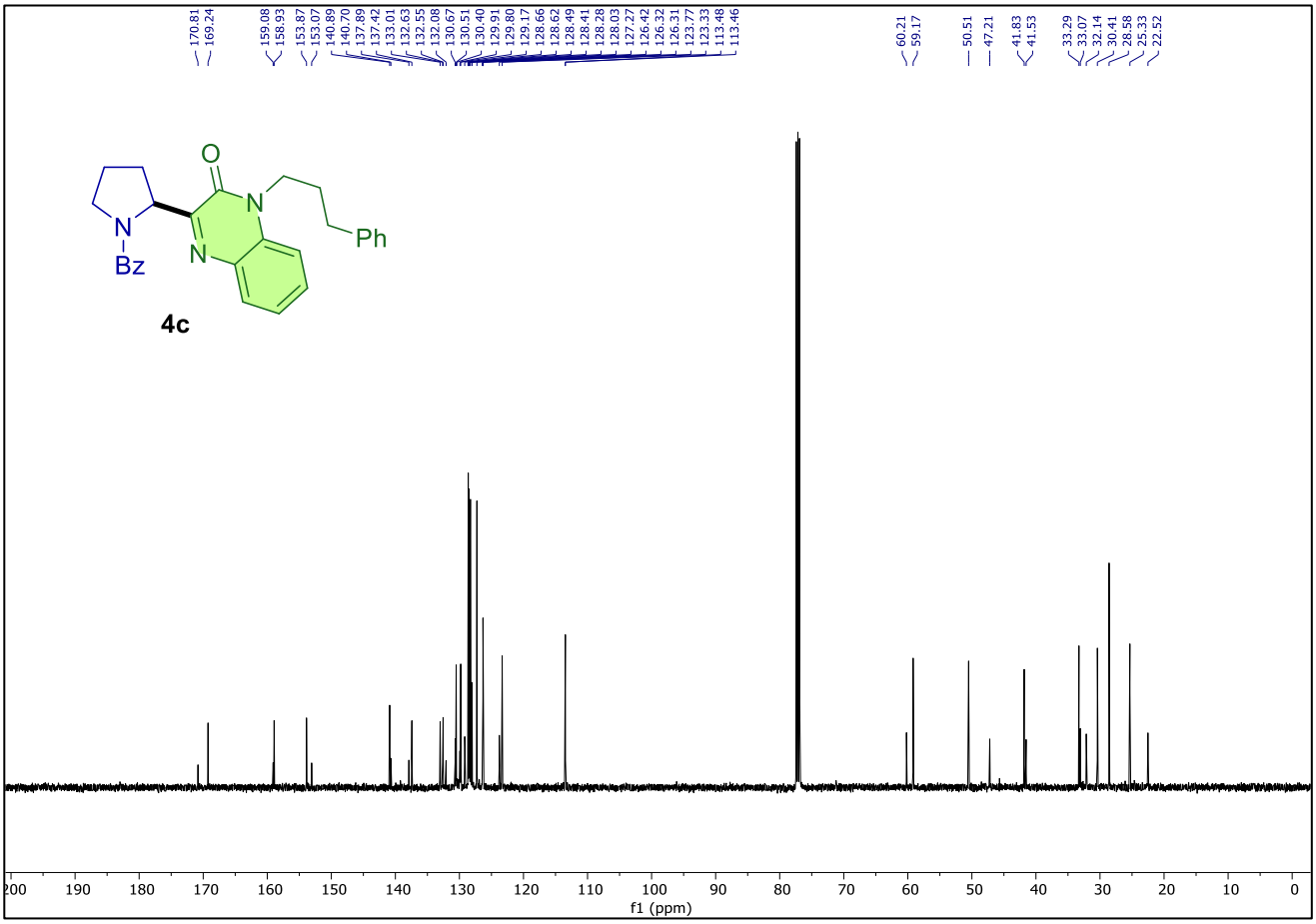
^{1}H NMR of compound **4b** (400 MHz, $CDCl_3$)



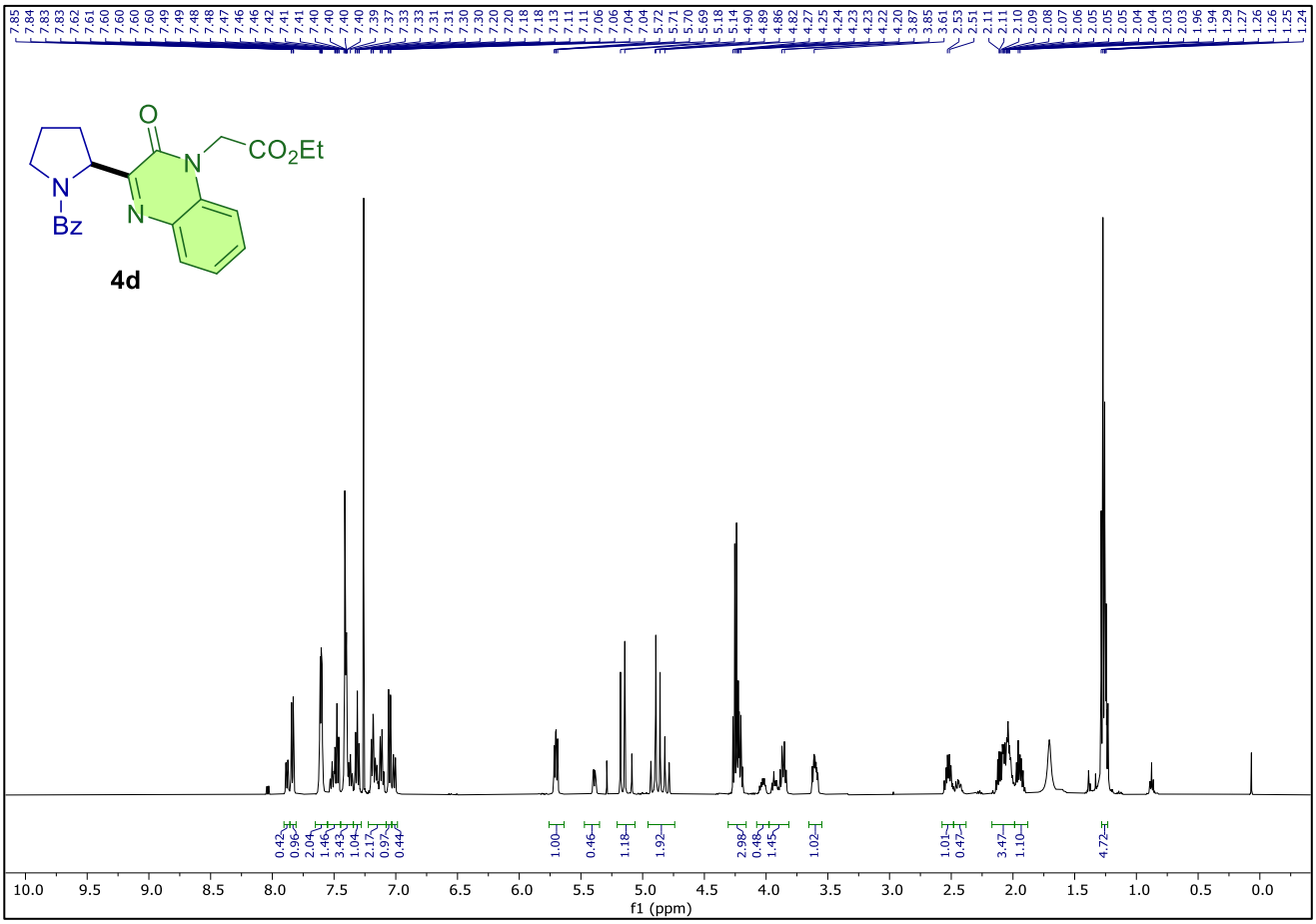
$^{13}C\{^{1}H\}$ NMR of compound **4b** (126 MHz, $CDCl_3$)



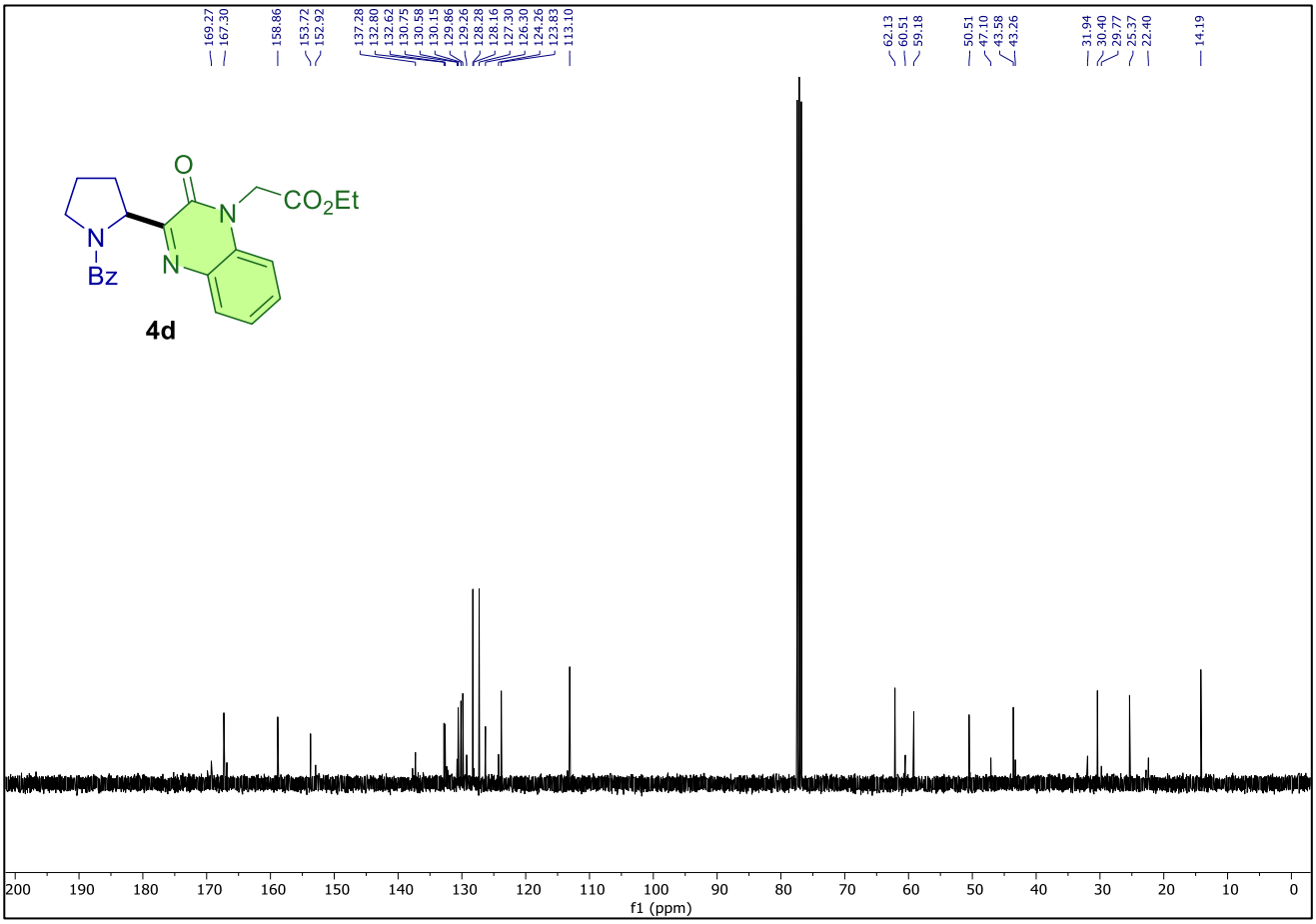
^{1}H NMR of compound **4c** (500 MHz, $CDCl_3$)



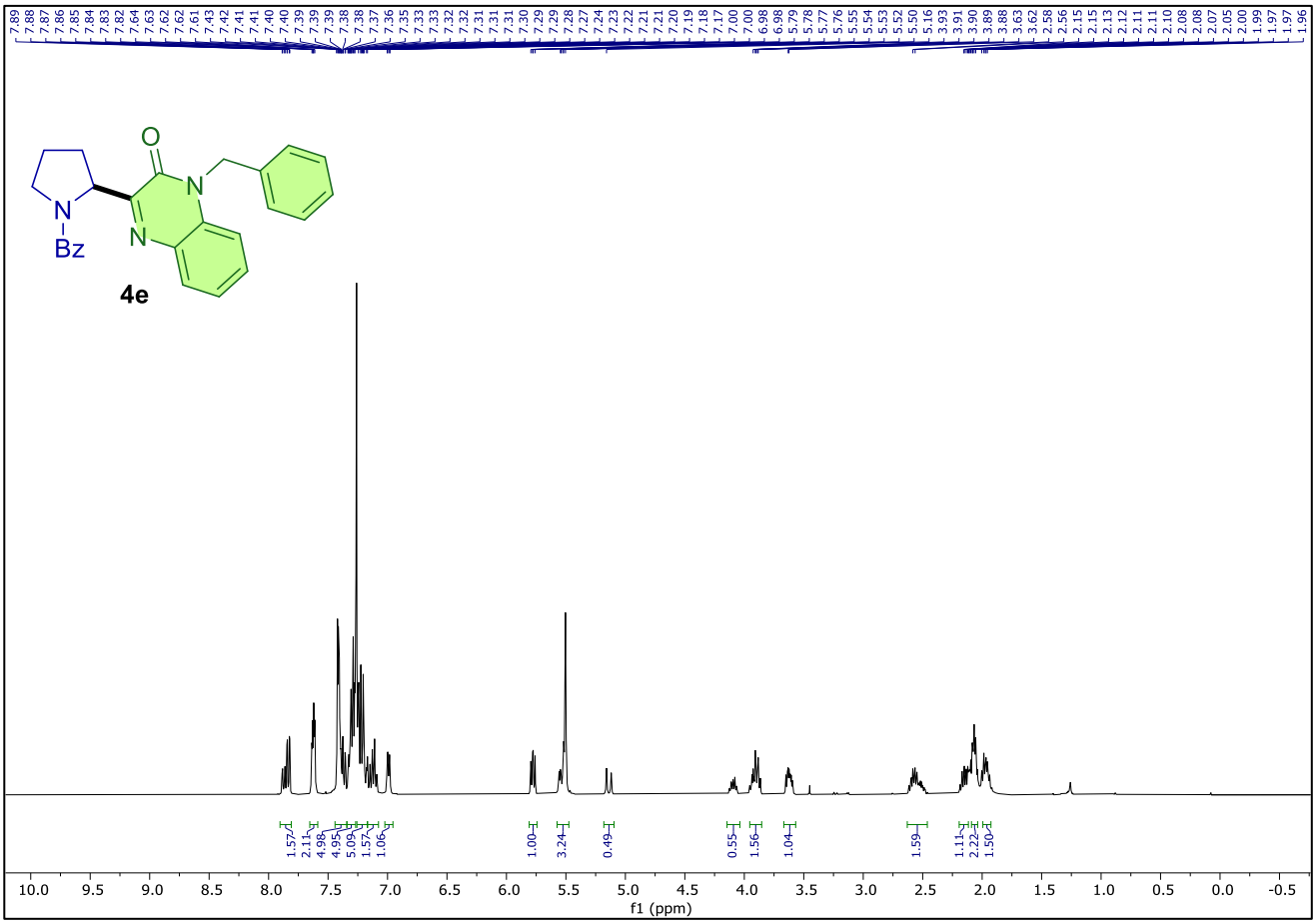
$^{13}C\{^{1}H\}$ NMR of compound **4c** (126 MHz, $CDCl_3$)



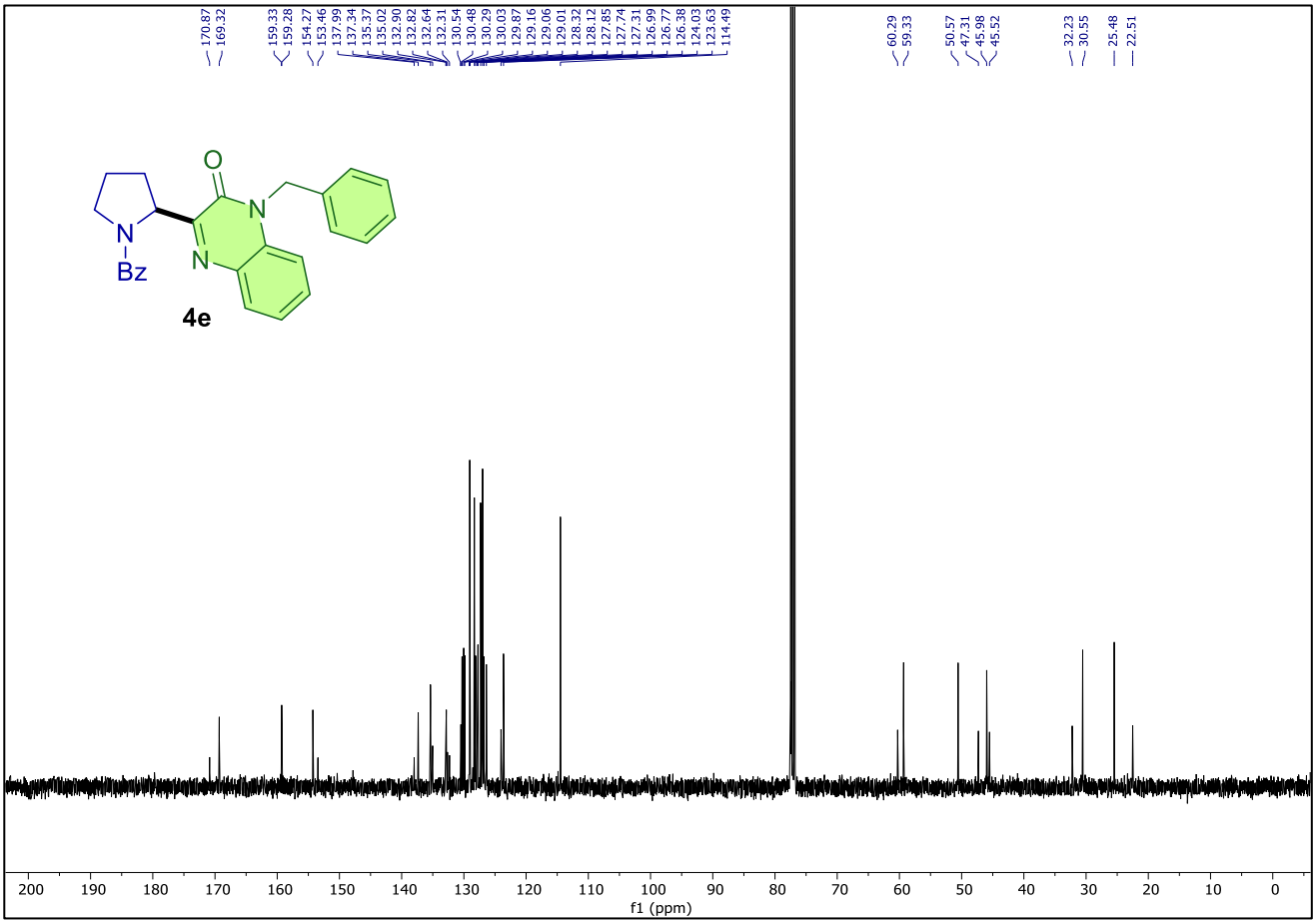
^{1}H NMR of compound **4d** (500 MHz, $CDCl_3$)



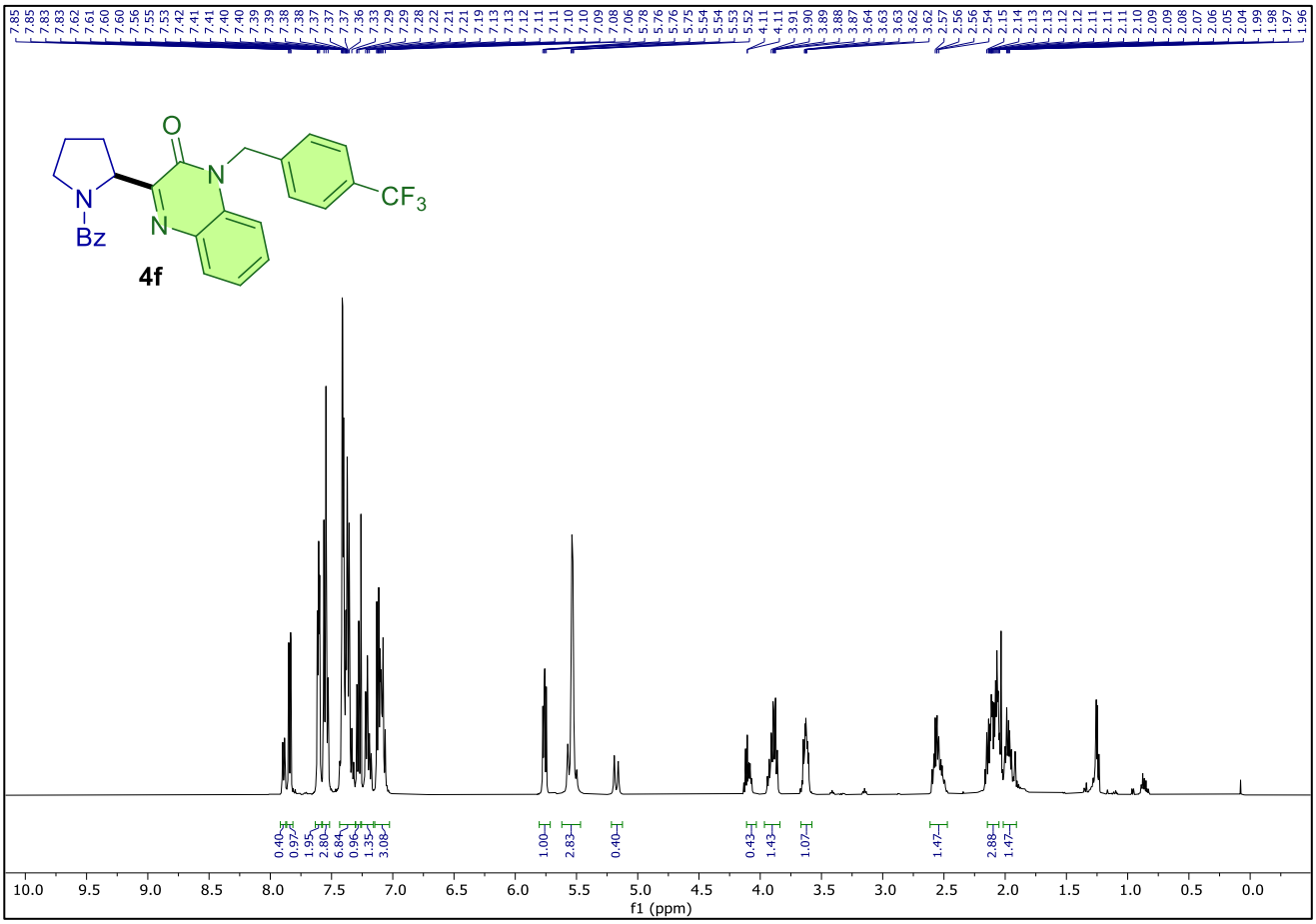
$^{13}C\{^{1}H\}$ NMR of compound **4d** (101 MHz, $CDCl_3$)



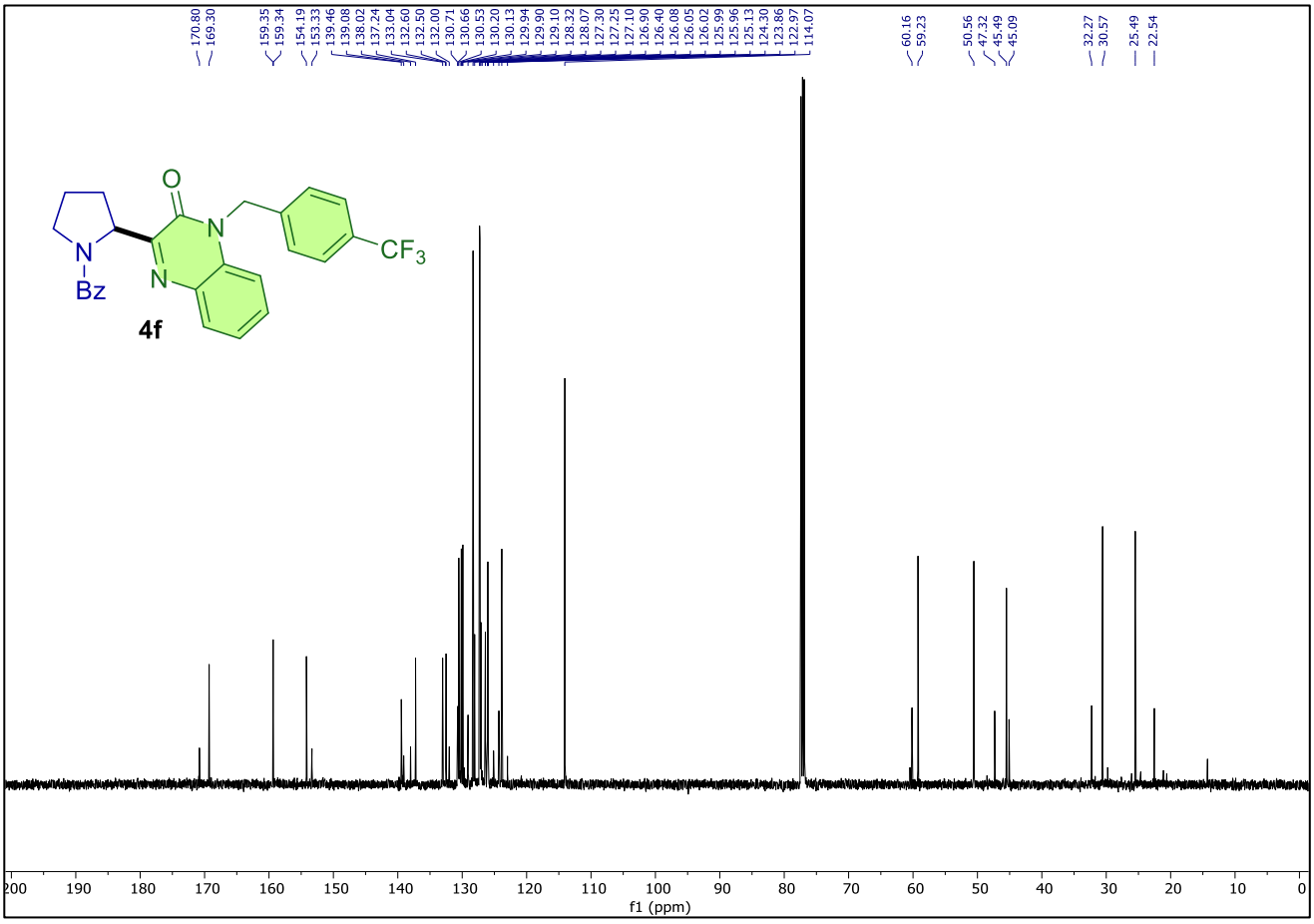
^{1}H NMR of compound **4e** (400 MHz, $CDCl_3$)



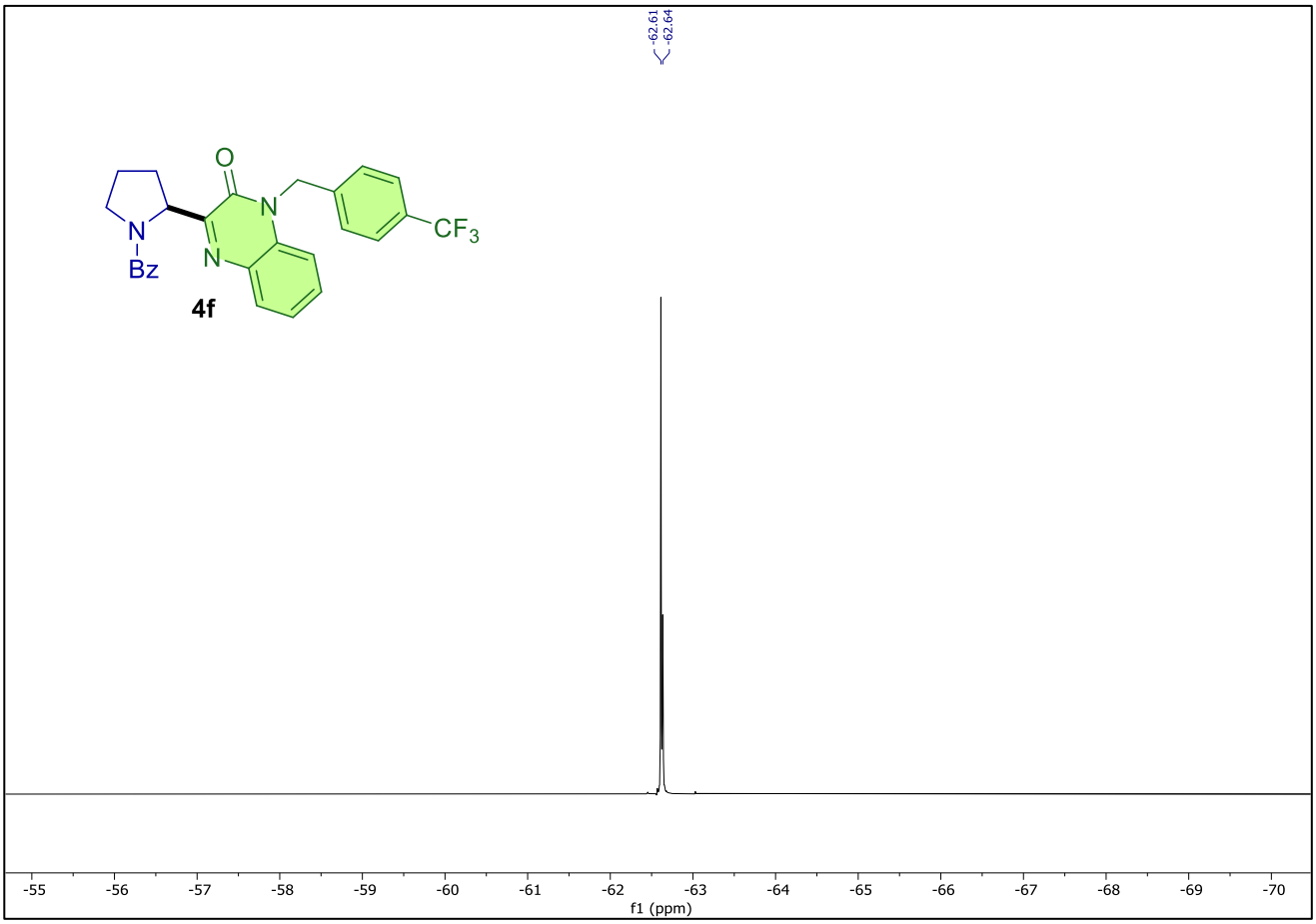
$^{13}C\{^{1}H\}$ NMR of compound **4e** (101 MHz, $CDCl_3$)



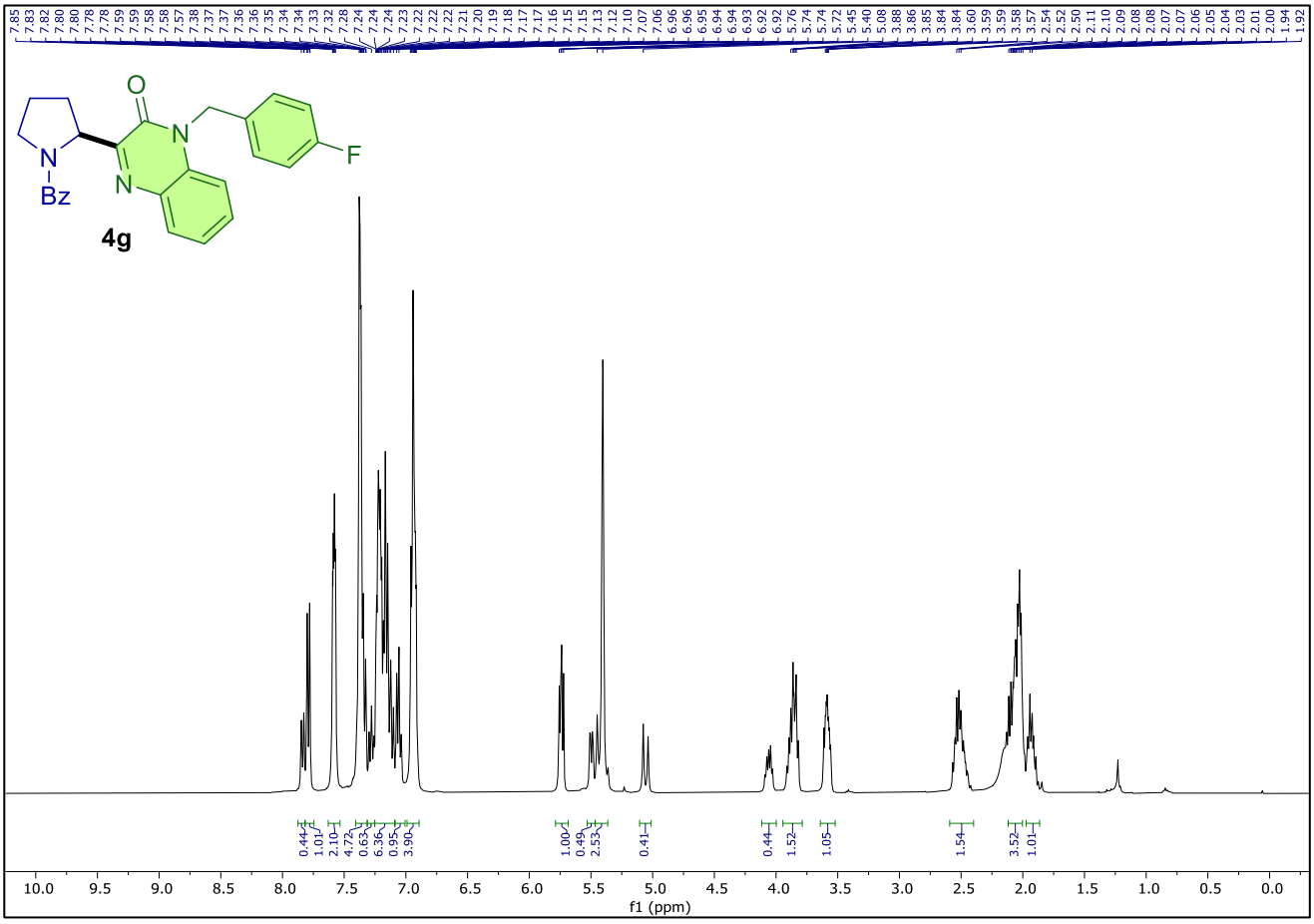
^{1}H NMR of compound **4f** (500 MHz, $CDCl_3$)



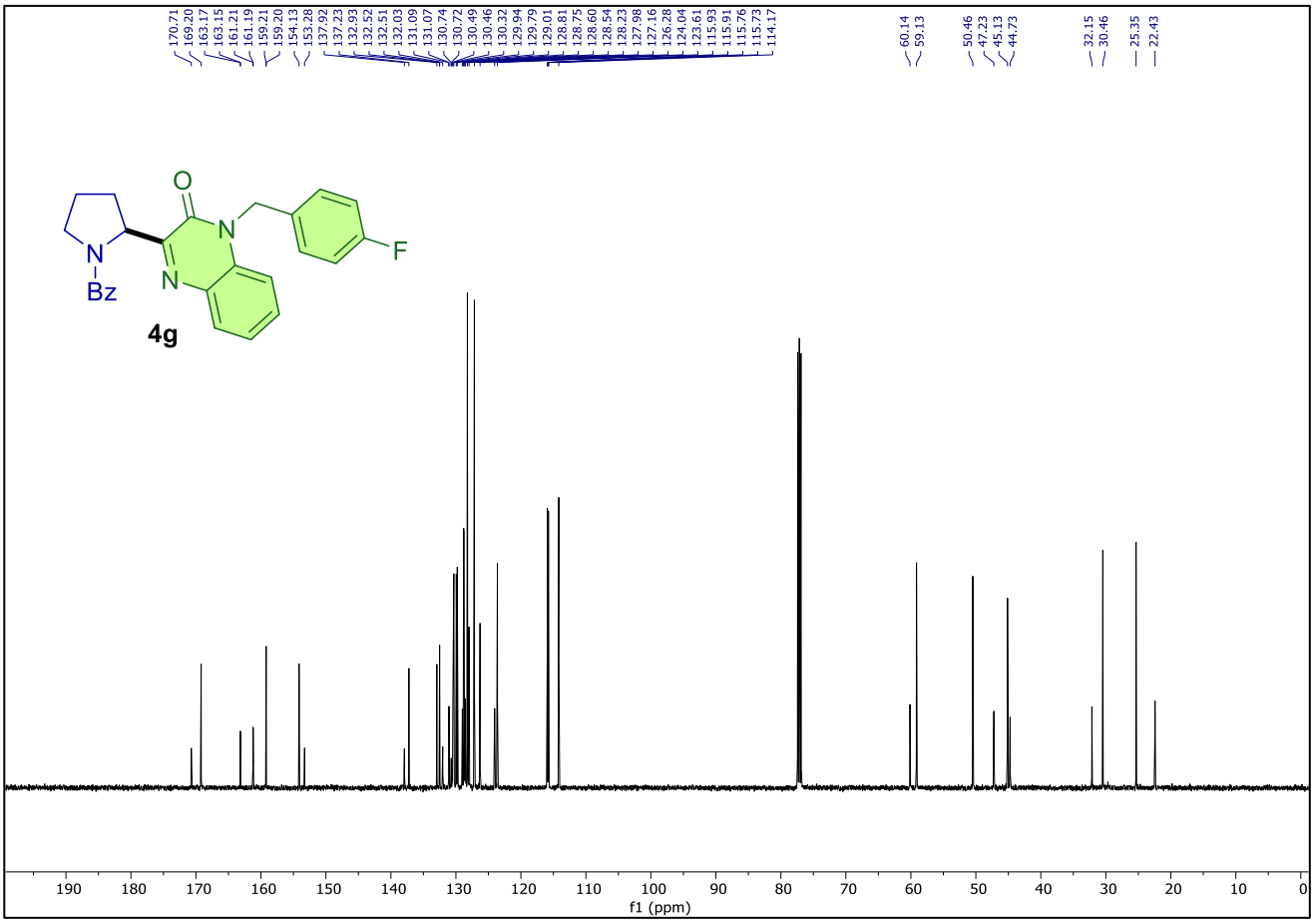
$^{13}C\{^{1}H\}$ NMR of compound **4f** (126 MHz, $CDCl_3$)



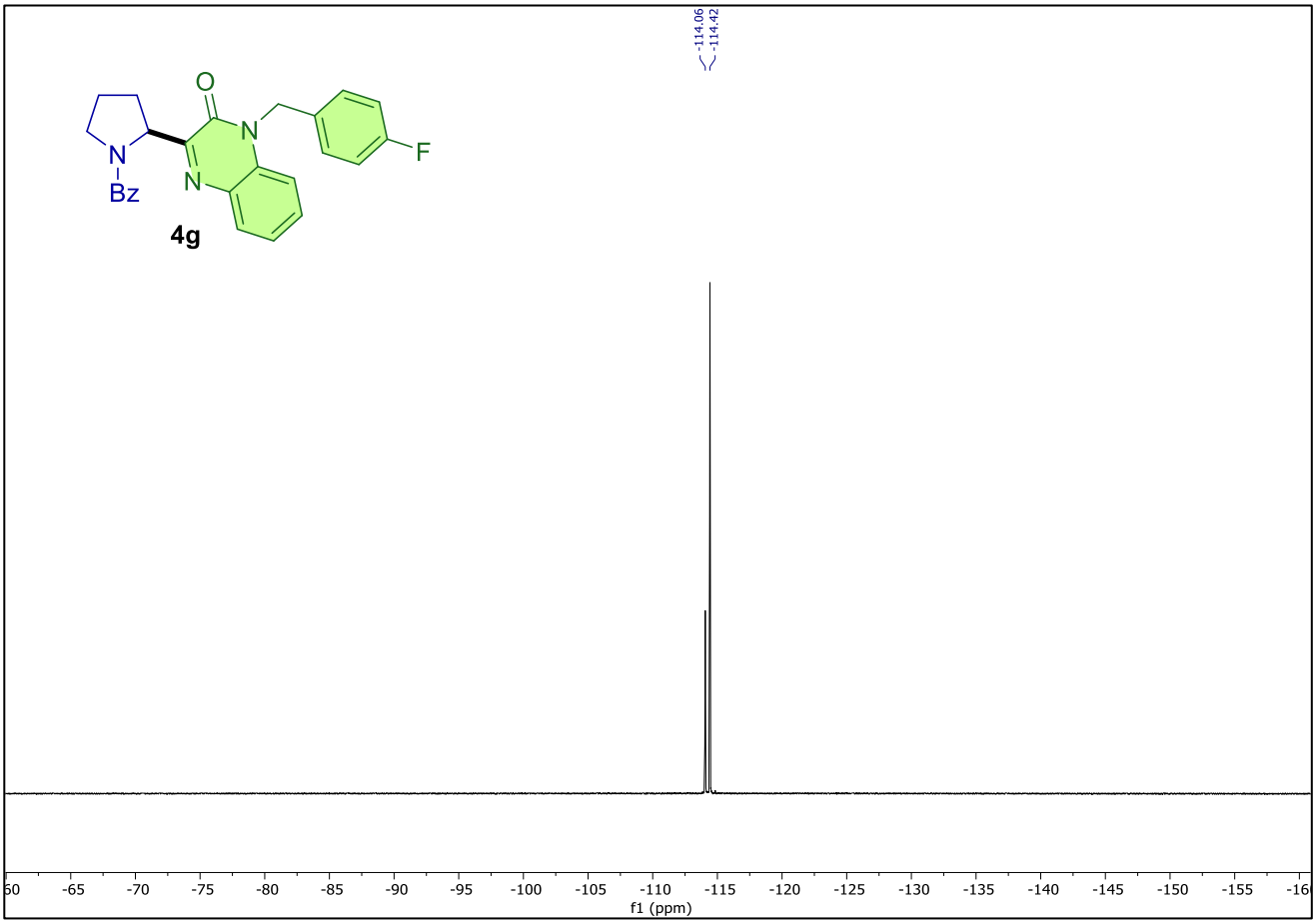
^{19}F NMR of compound **4f** (471 MHz, $CDCl_3$)



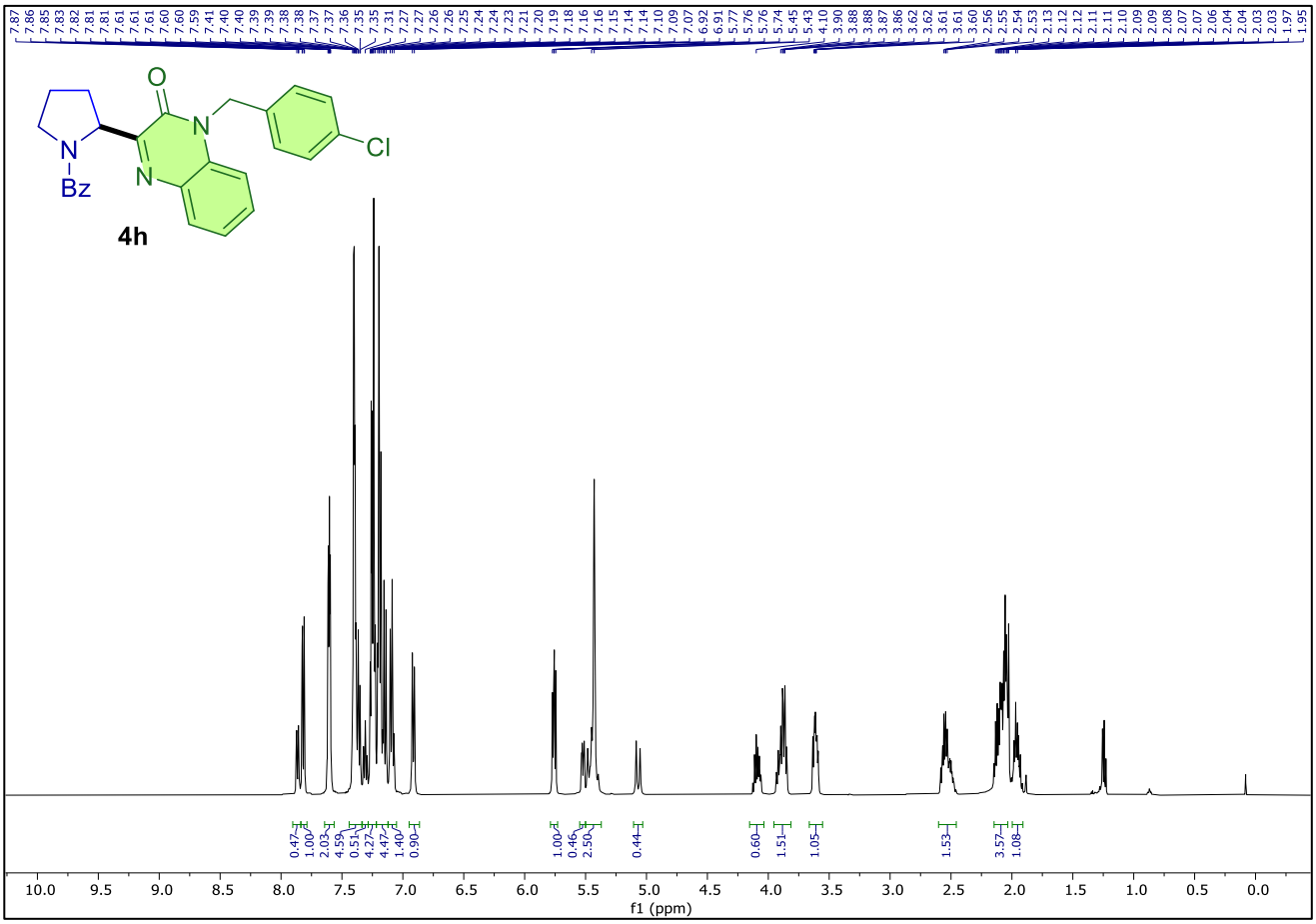
^{1}H NMR of compound **4g** (400 MHz, $CDCl_3$)



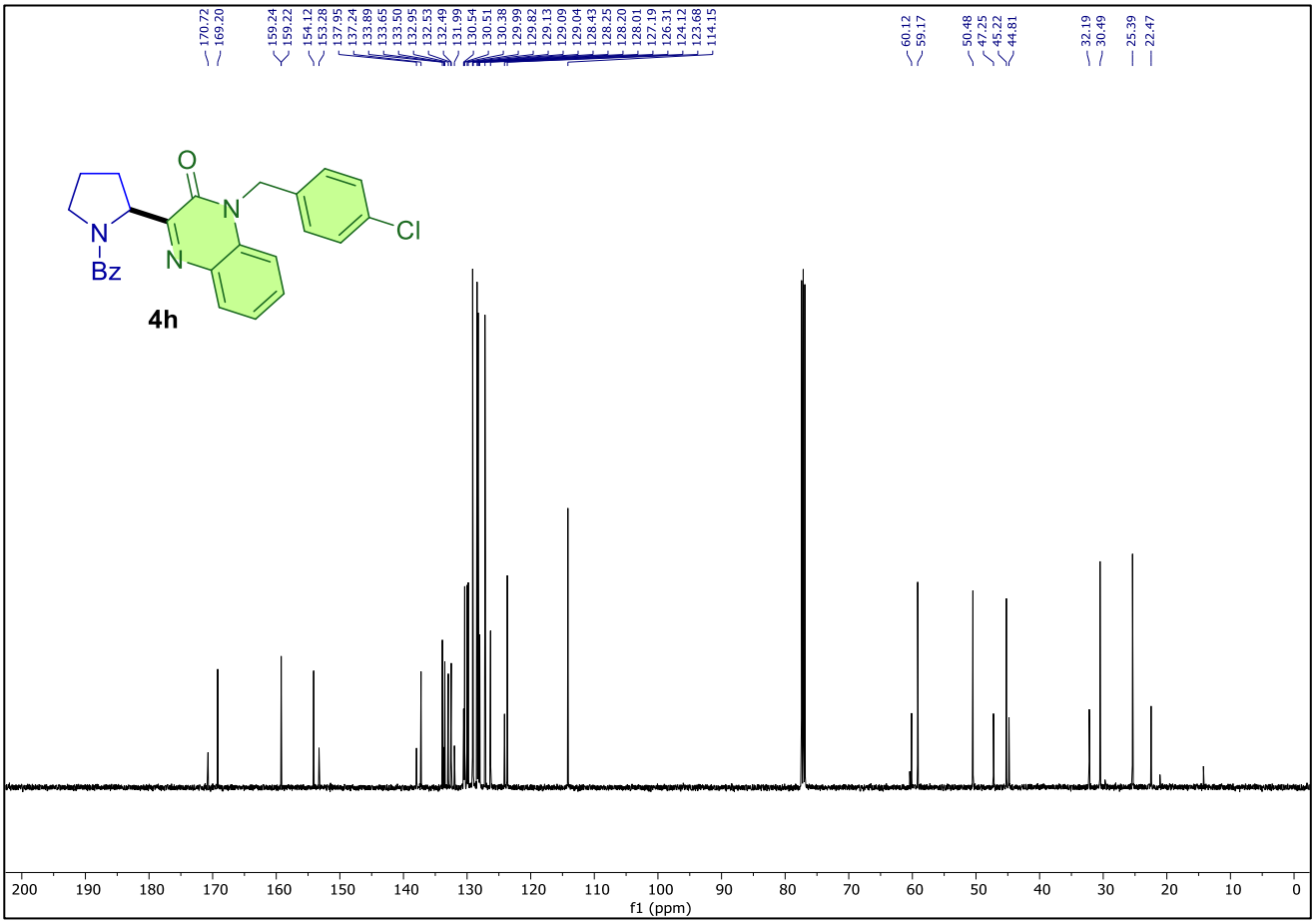
^{13}C{^{1}H} NMR of compound **4g** (126 MHz, $CDCl_3$)



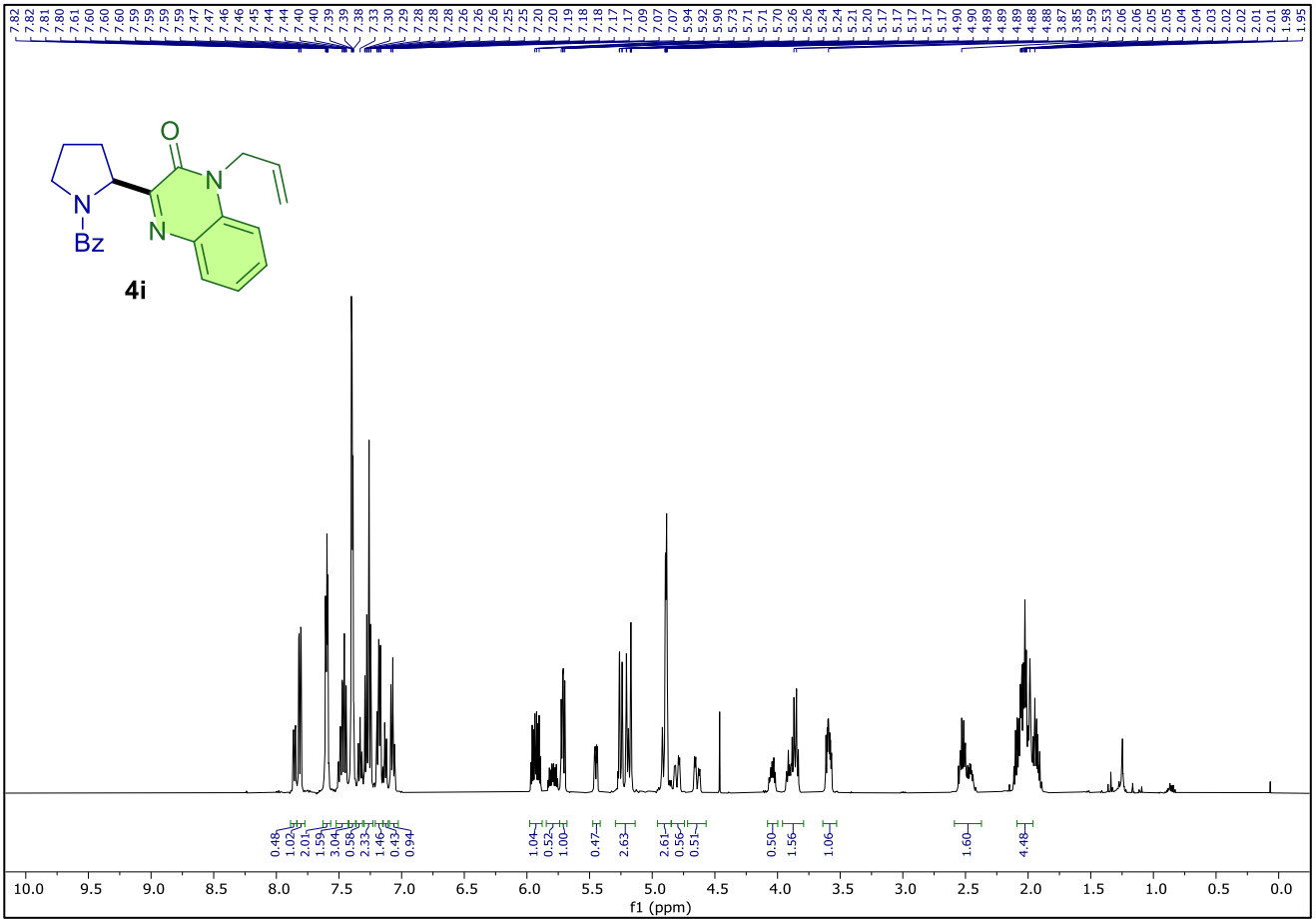
^{19}F NMR of compound **4g** (376 MHz, $CDCl_3$)



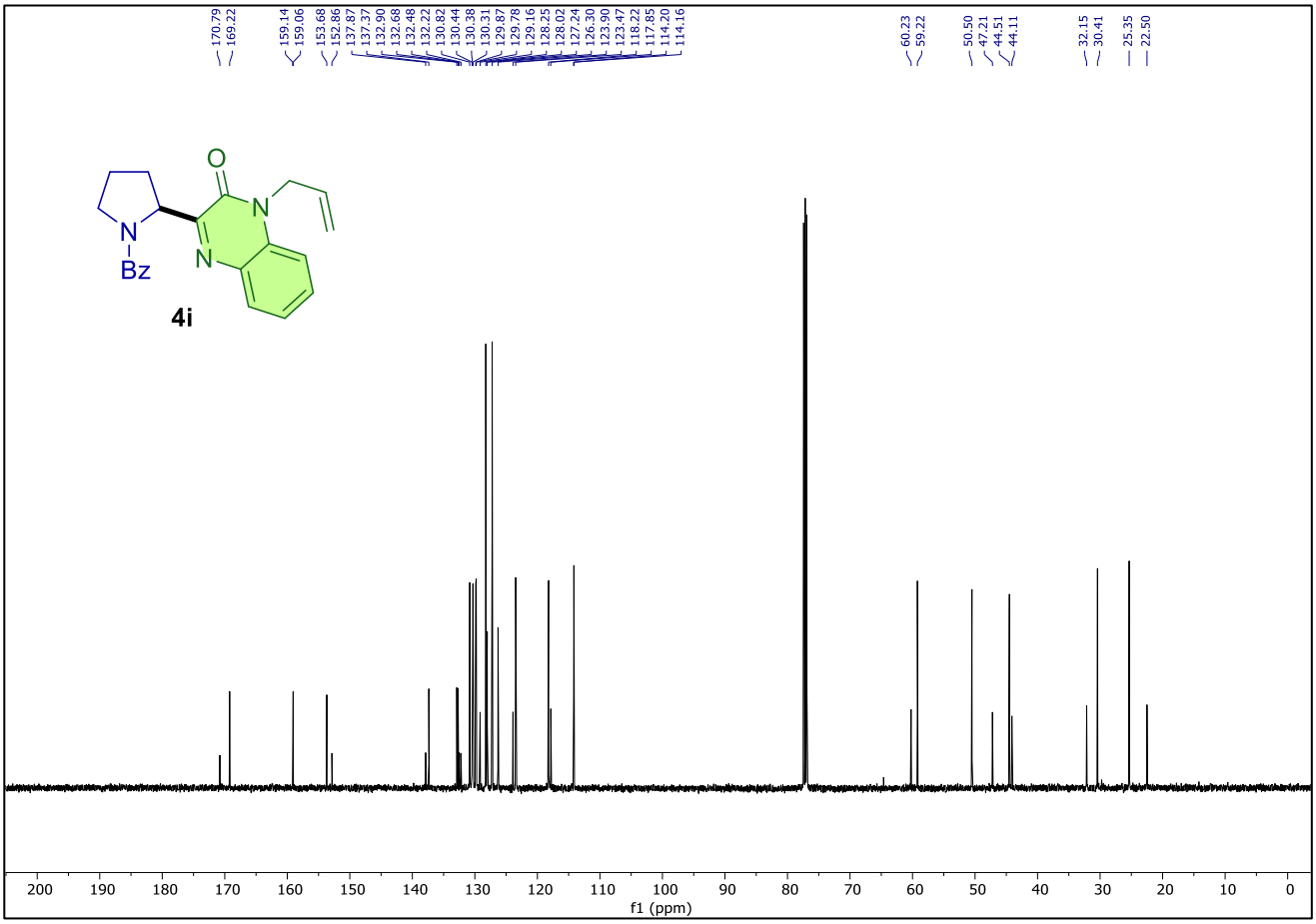
^{1}H NMR of compound **4h** (500 MHz, $CDCl_3$)



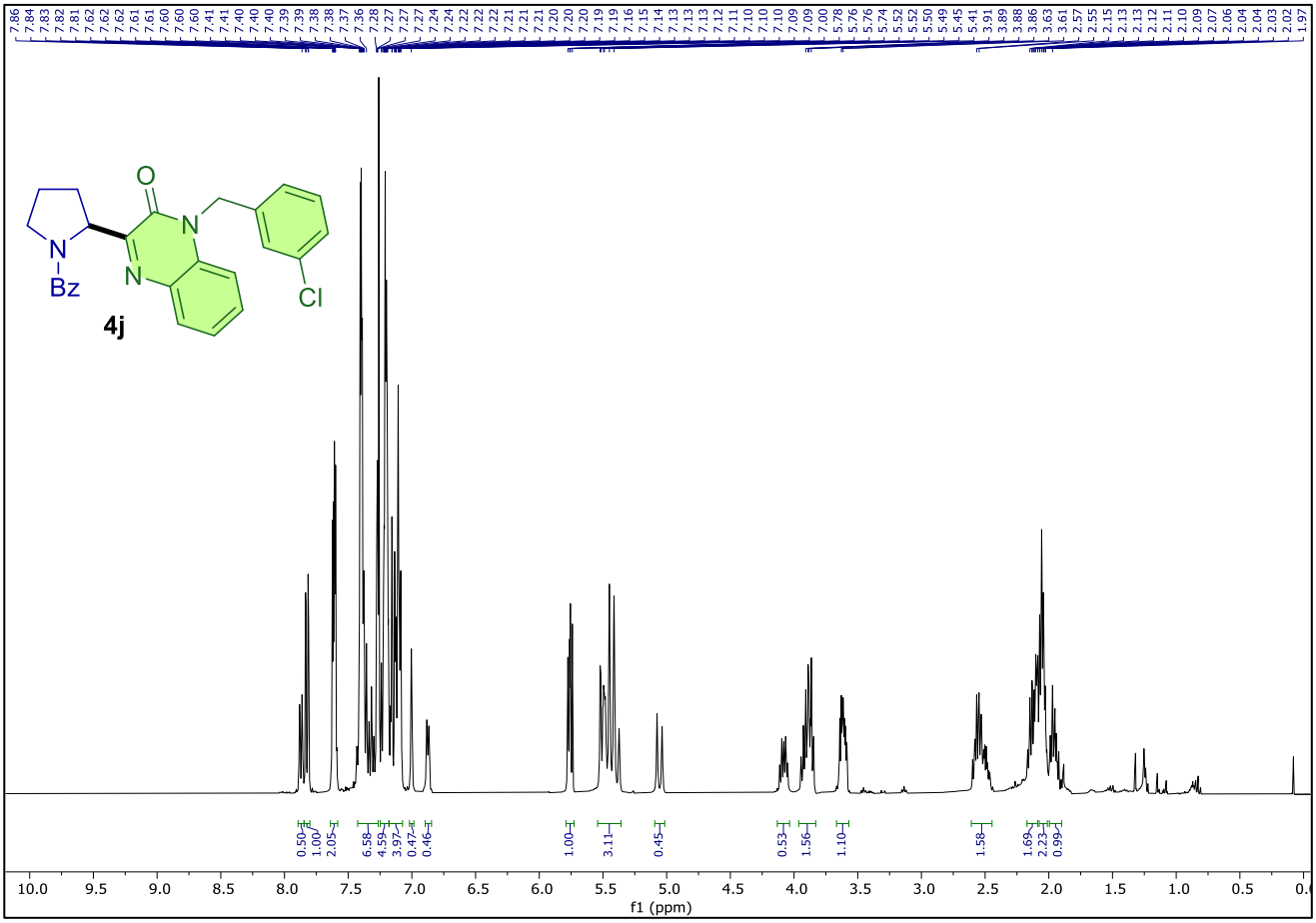
$^{13}C\{^{1}H\}$ NMR of compound **4h** (126 MHz, $CDCl_3$)



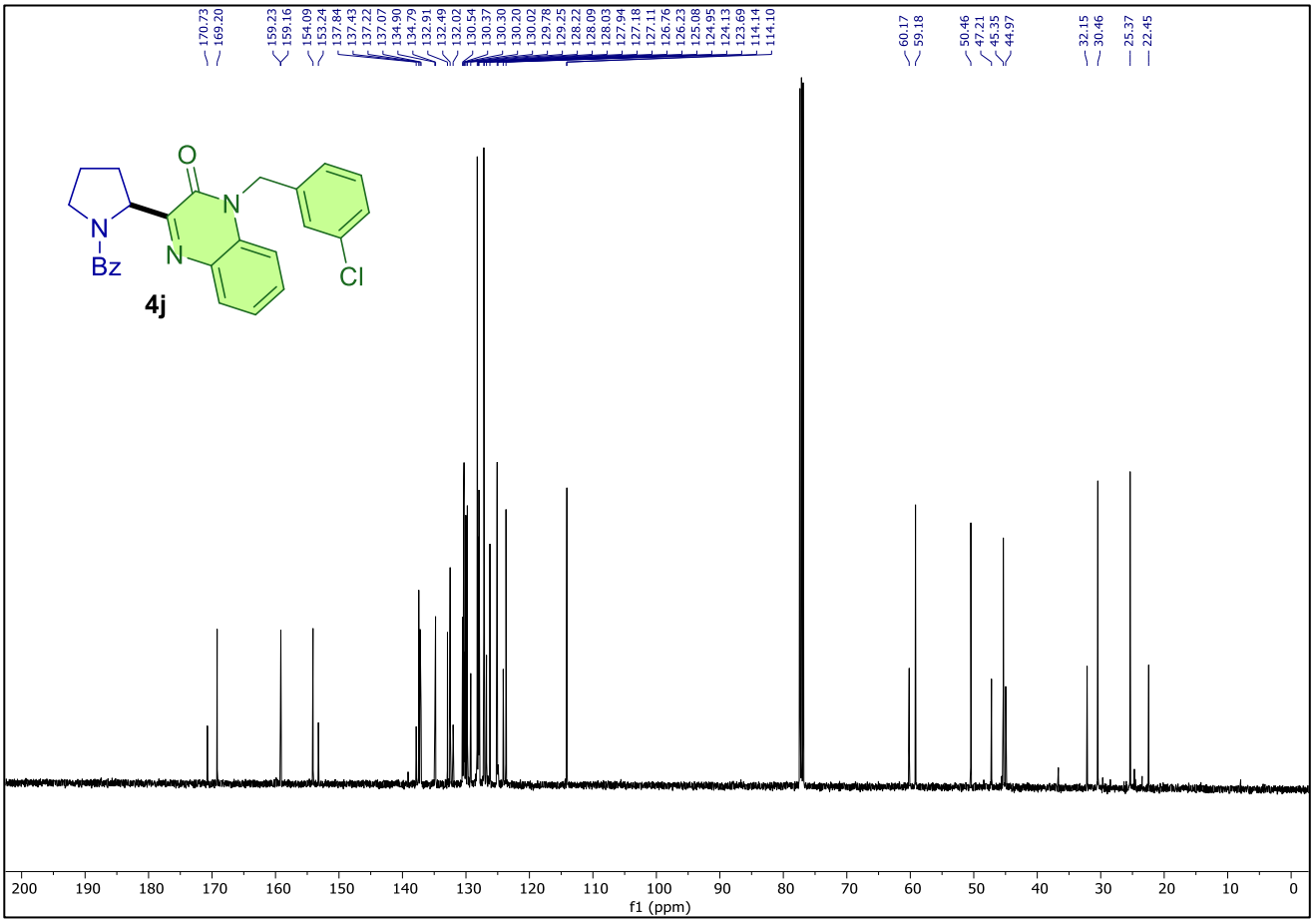
^{1}H NMR of compound **4i** (500 MHz, $CDCl_3$)



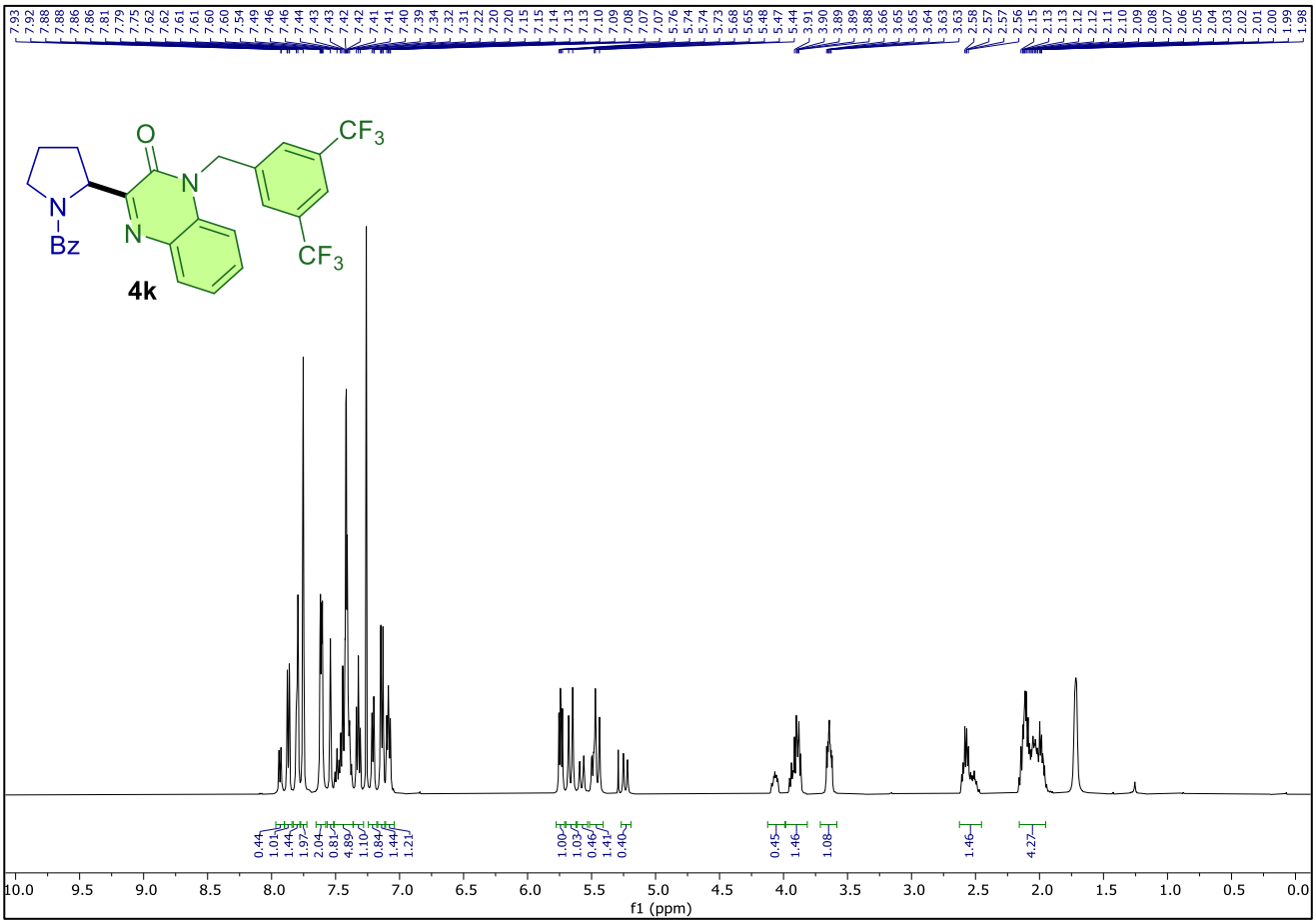
$^{13}C\{^{1}H\}$ NMR of compound **4i** (126 MHz, $CDCl_3$)



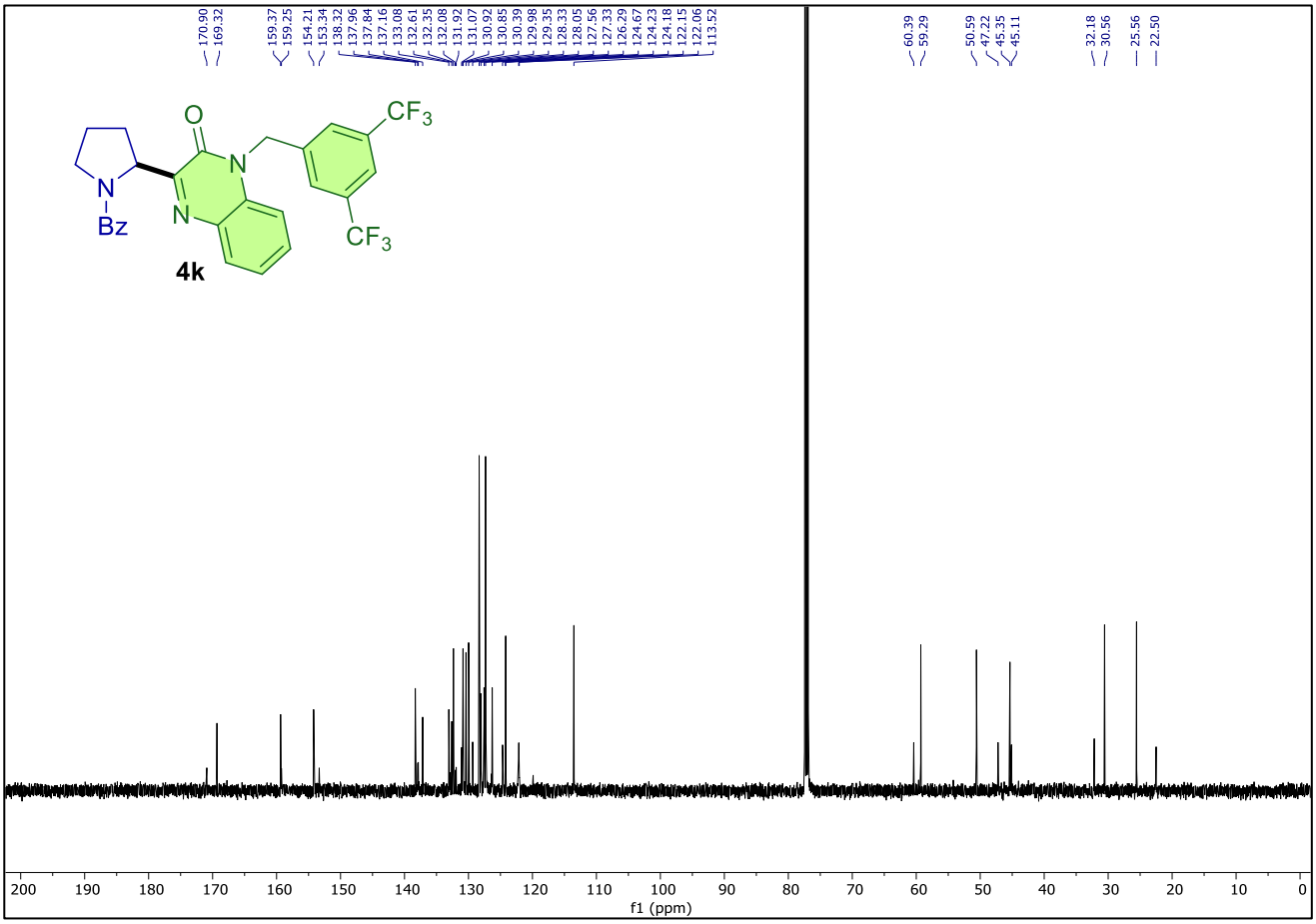
^{1}H NMR of compound **4j** (400 MHz, $CDCl_3$)



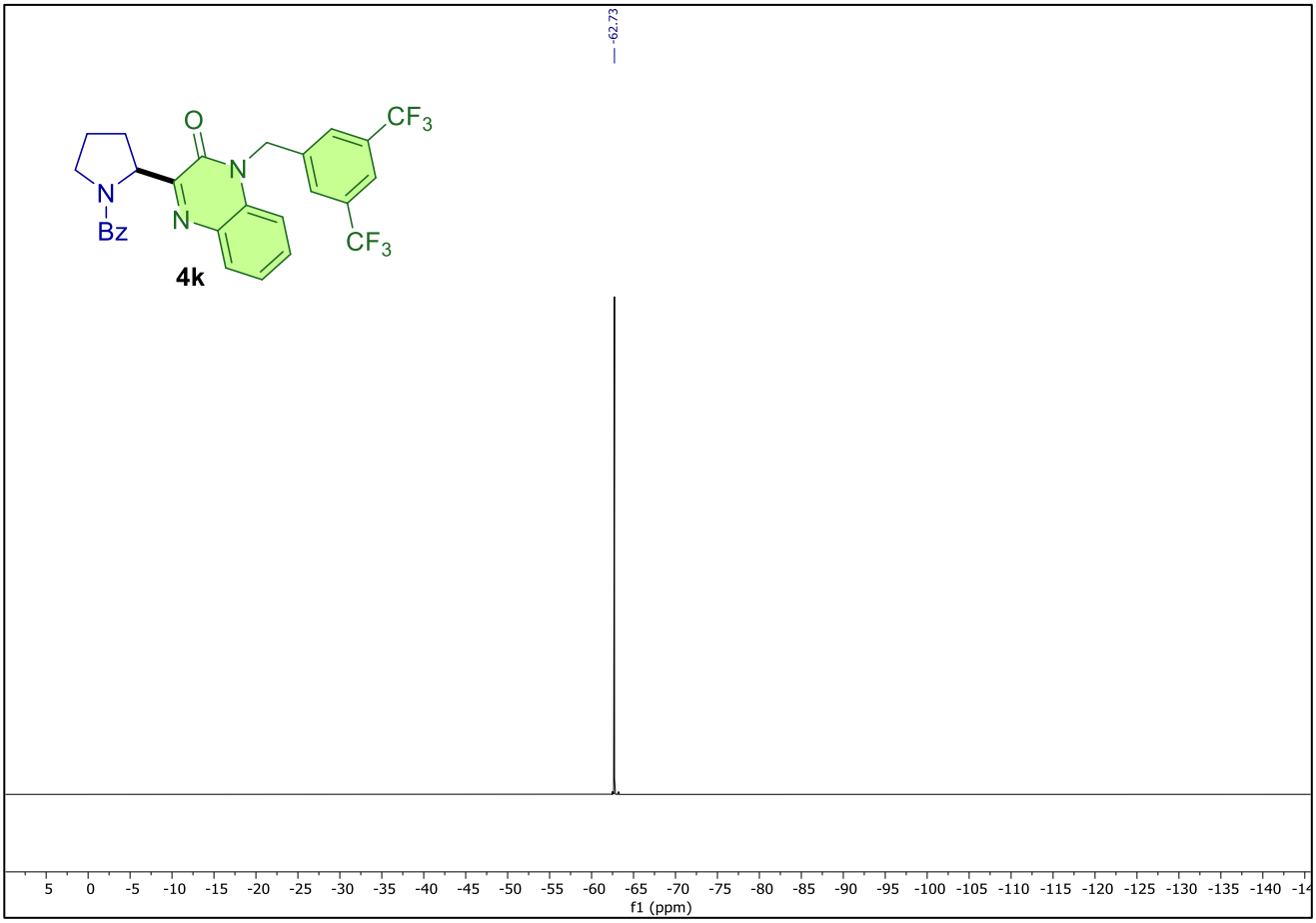
$^{13}C\{^{1}H\}$ NMR of compound **4j** (126 MHz, $CDCl_3$)



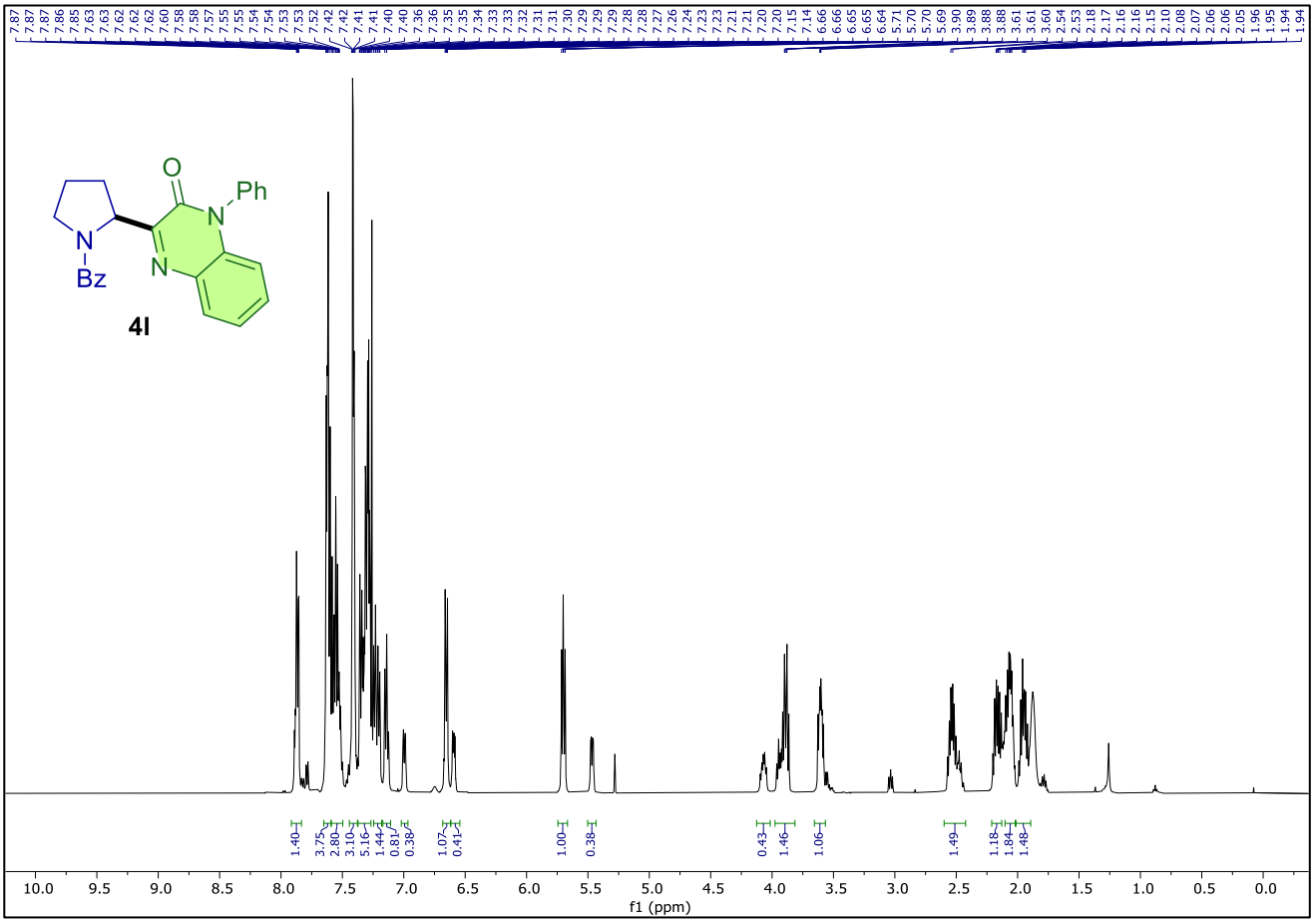
^{1}H NMR of compound **4k** (500 MHz, $CDCl_3$)



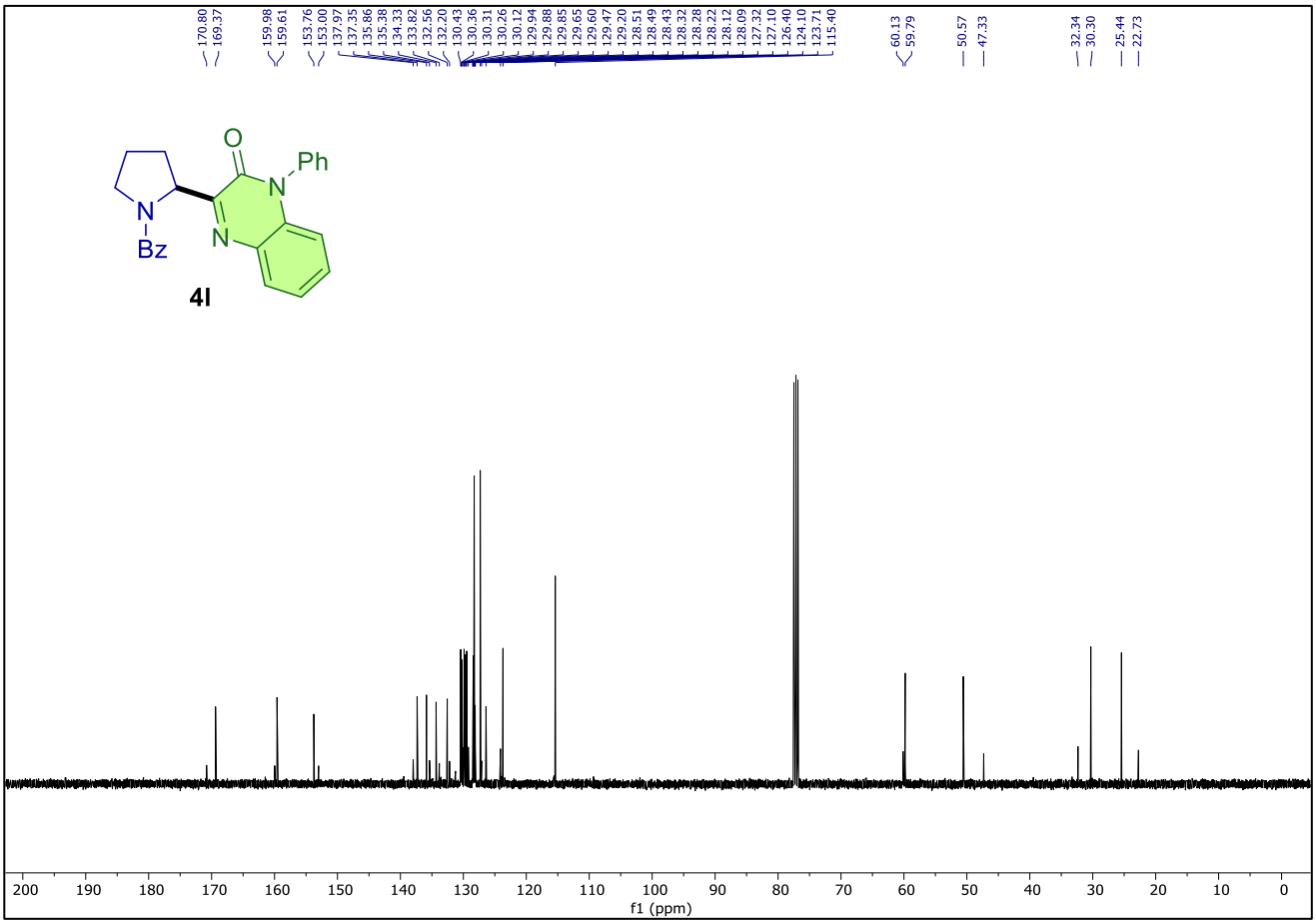
$^{13}C\{^{1}H\}$ NMR of compound **4k** (126 MHz, $CDCl_3$)



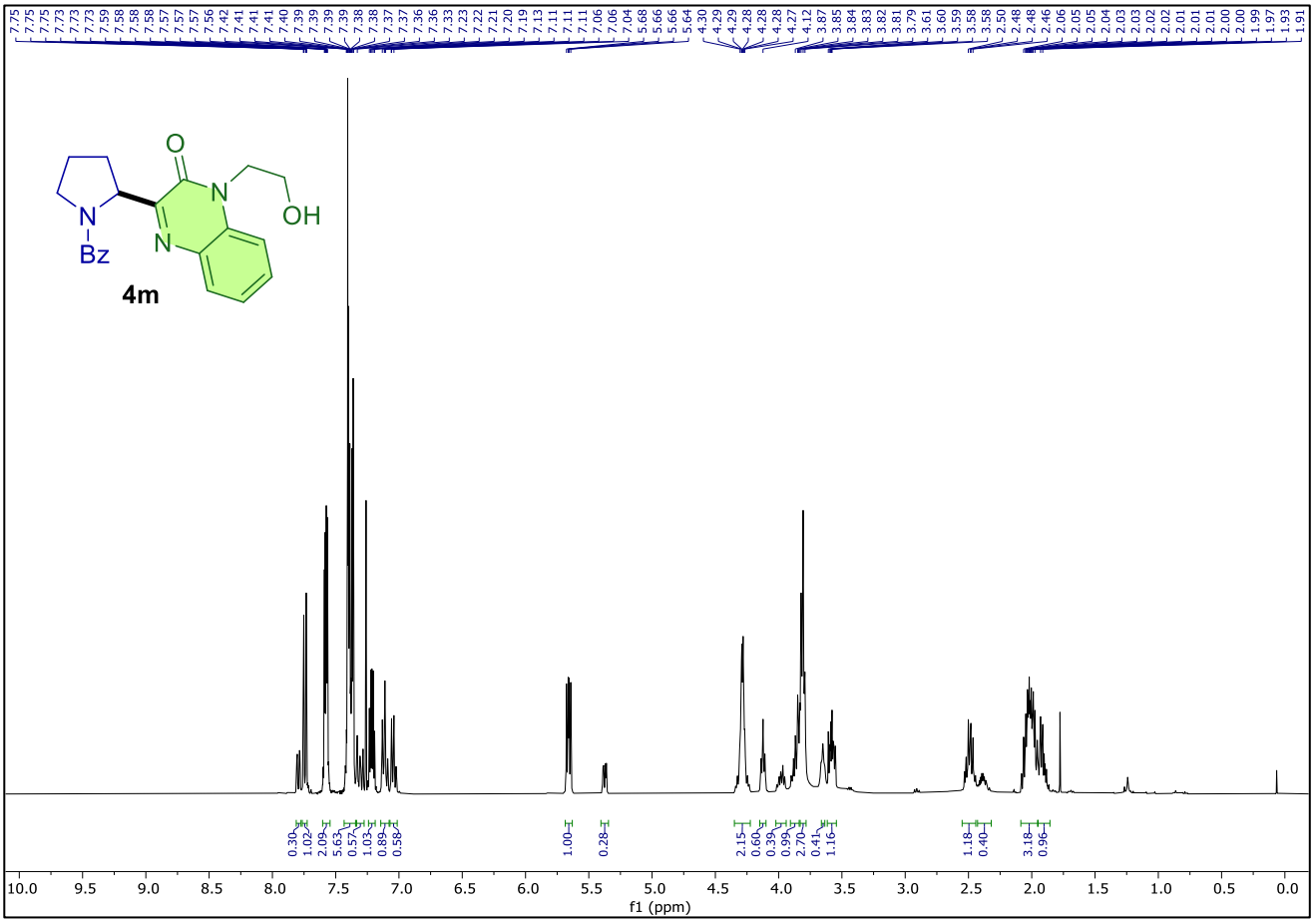
^{19}F NMR of compound **4k** (376 MHz, $CDCl_3$)



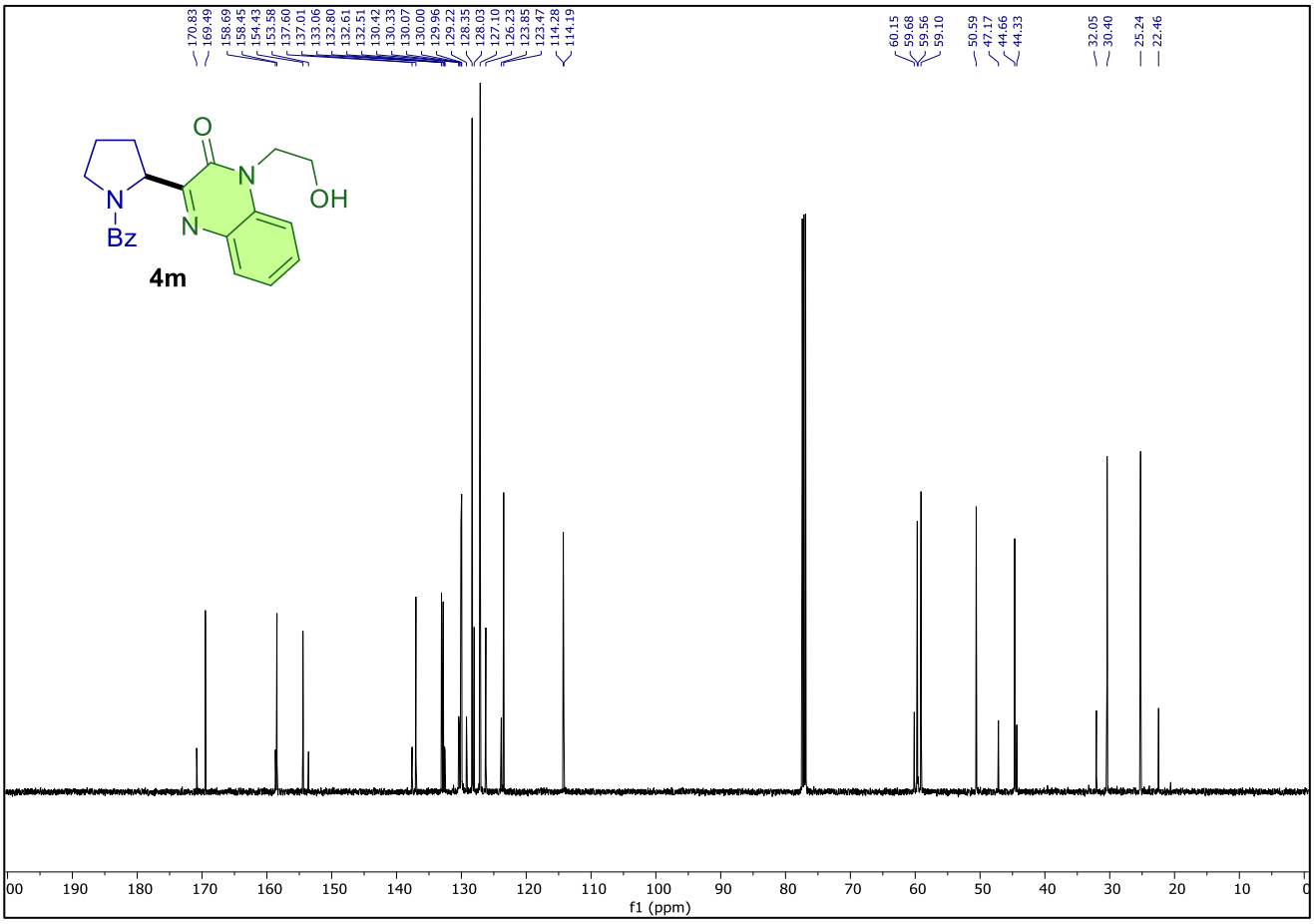
^{1}H NMR of compound **4l** (500 MHz, $CDCl_3$)



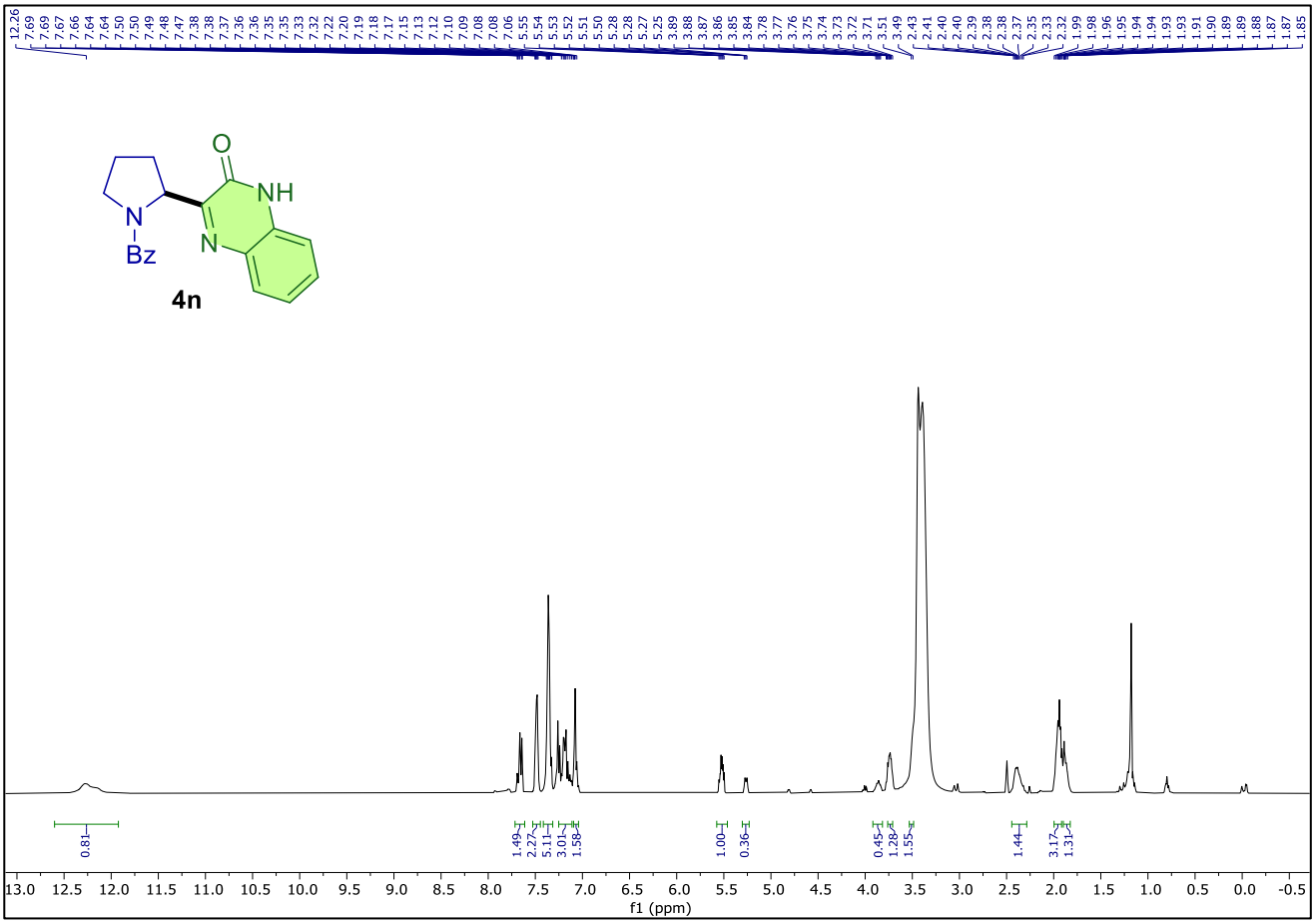
^{13}C{^{1}H} NMR of compound **4l** (101 MHz, $CDCl_3$)



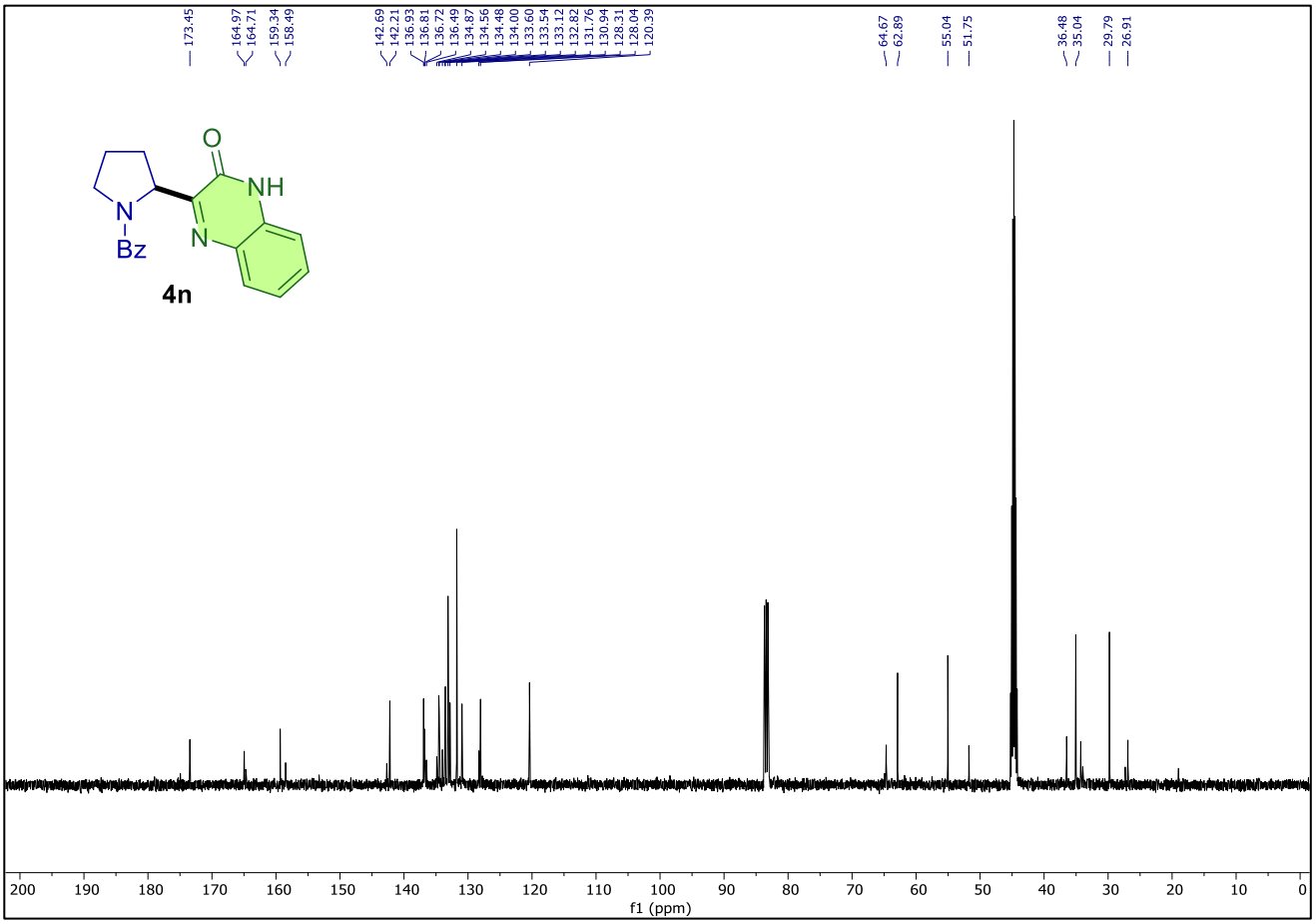
^{1}H NMR of compound **4m** (400 MHz, $CDCl_3$)



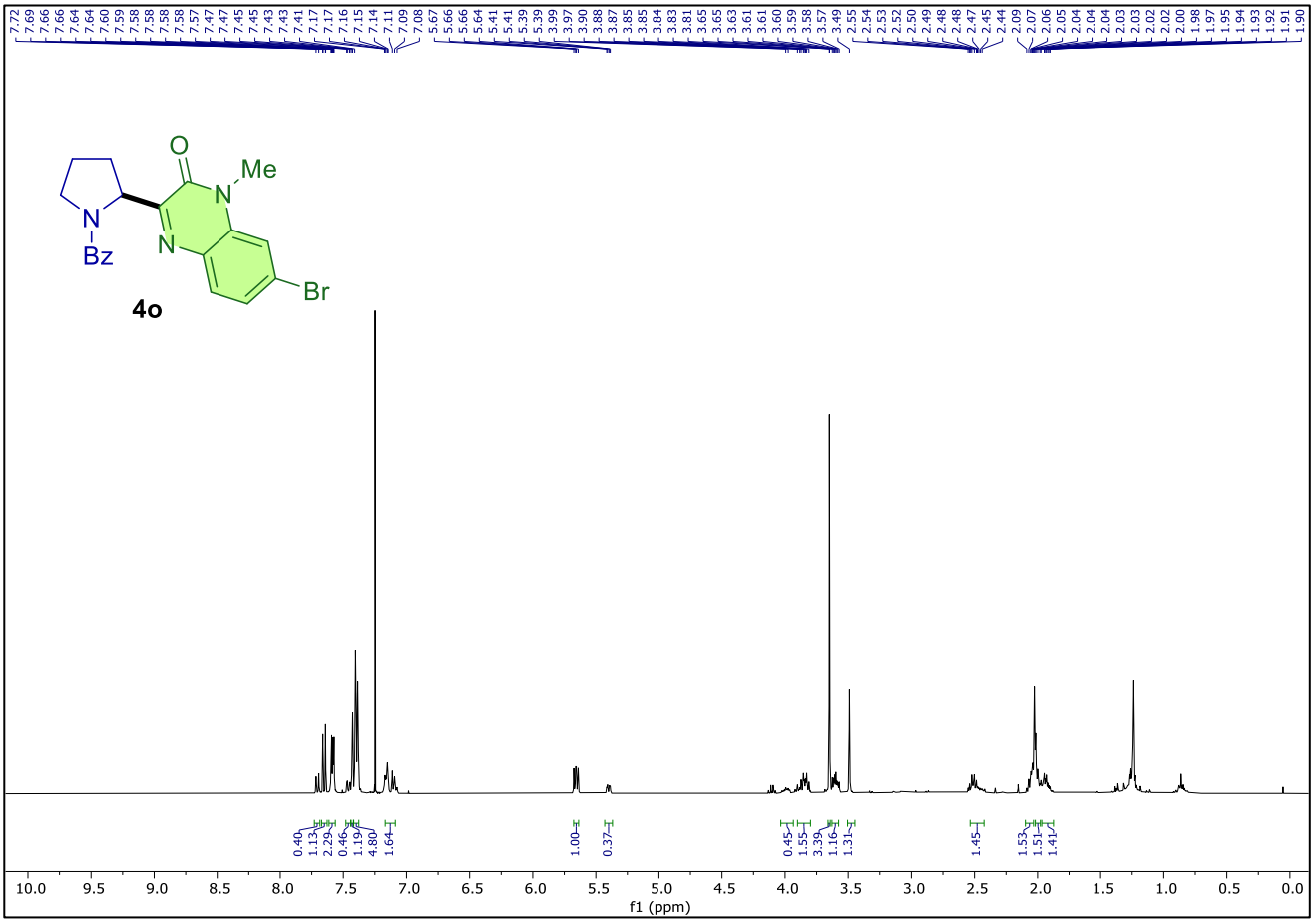
^{13}C{^{1}H} NMR of compound **4m** (126 MHz, $CDCl_3$)



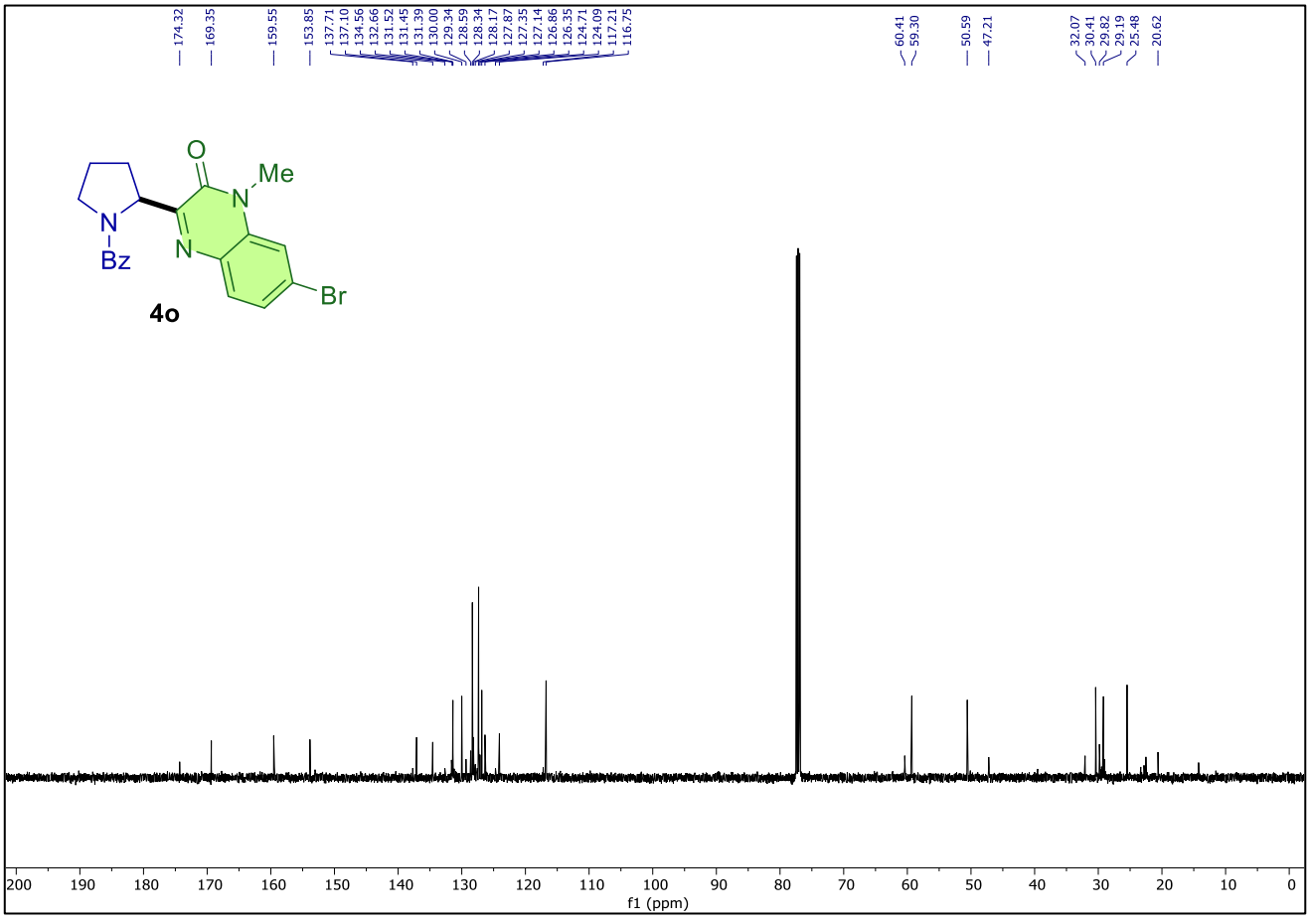
^{1}H NMR of compound **4n** (400 MHz, $CDCl_3$)



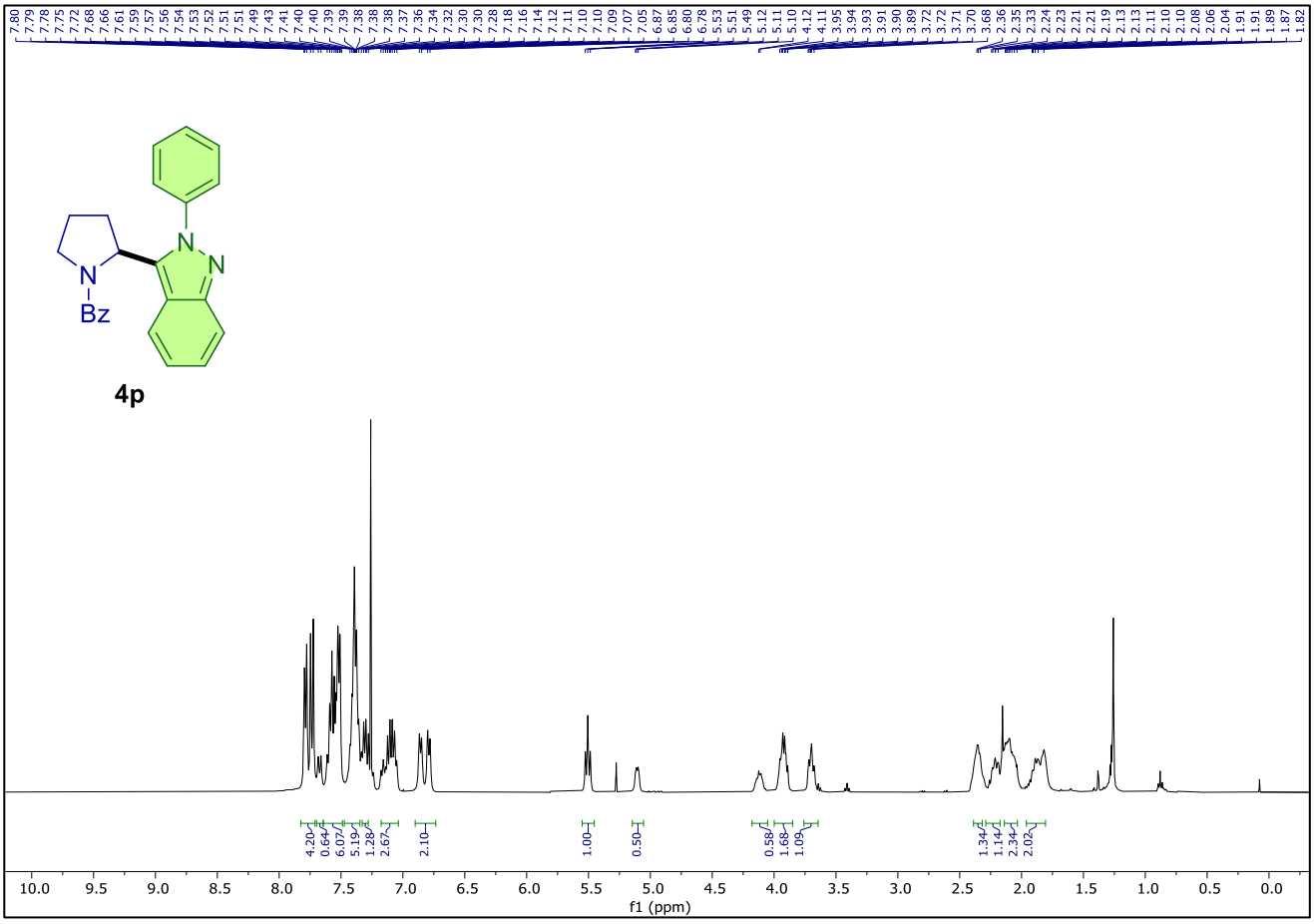
^{13}C{^{1}H} NMR of compound **4n** (126 MHz, $CDCl_3$)



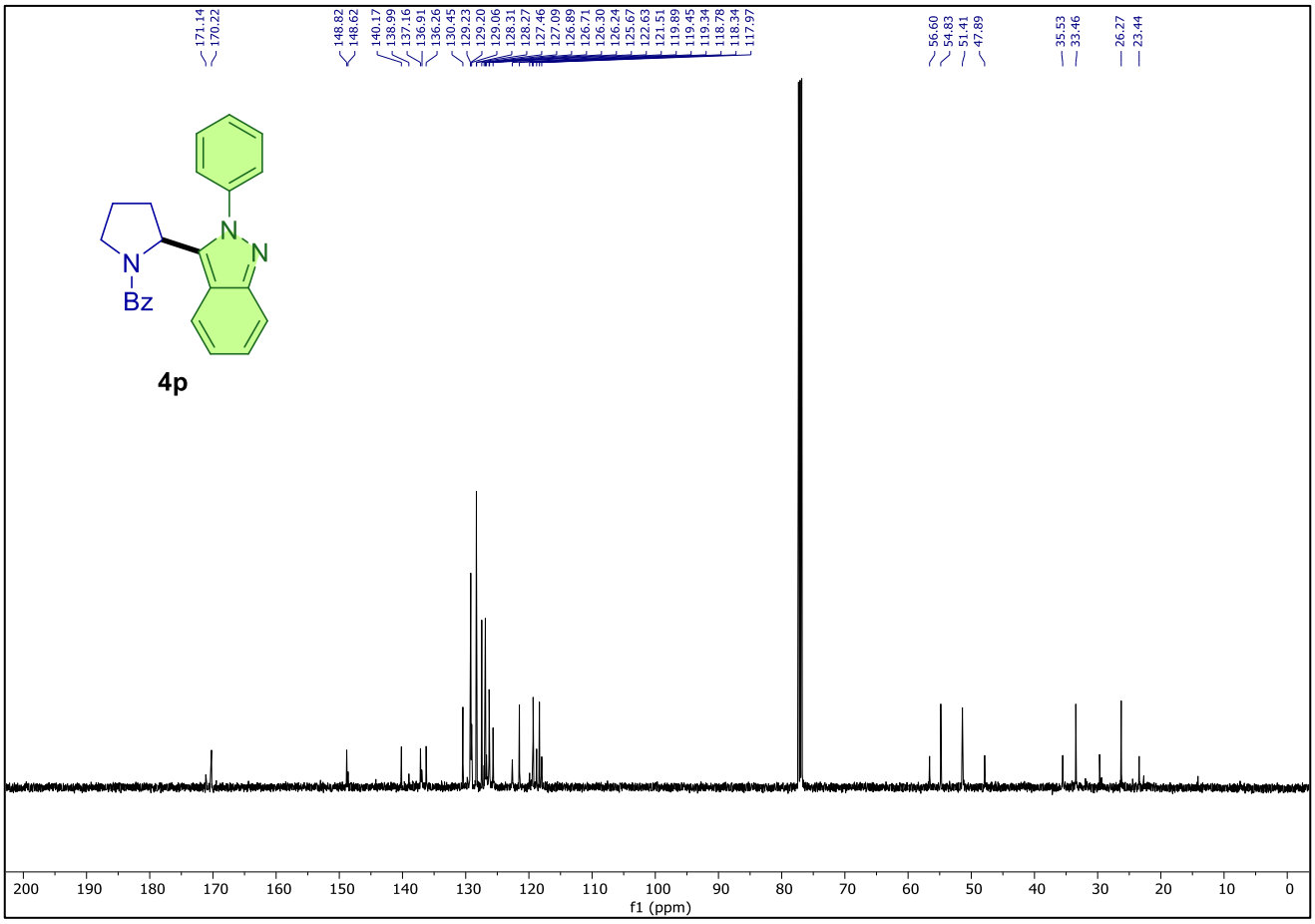
^{1}H NMR of compound **4o** (400 MHz, $CDCl_3$)



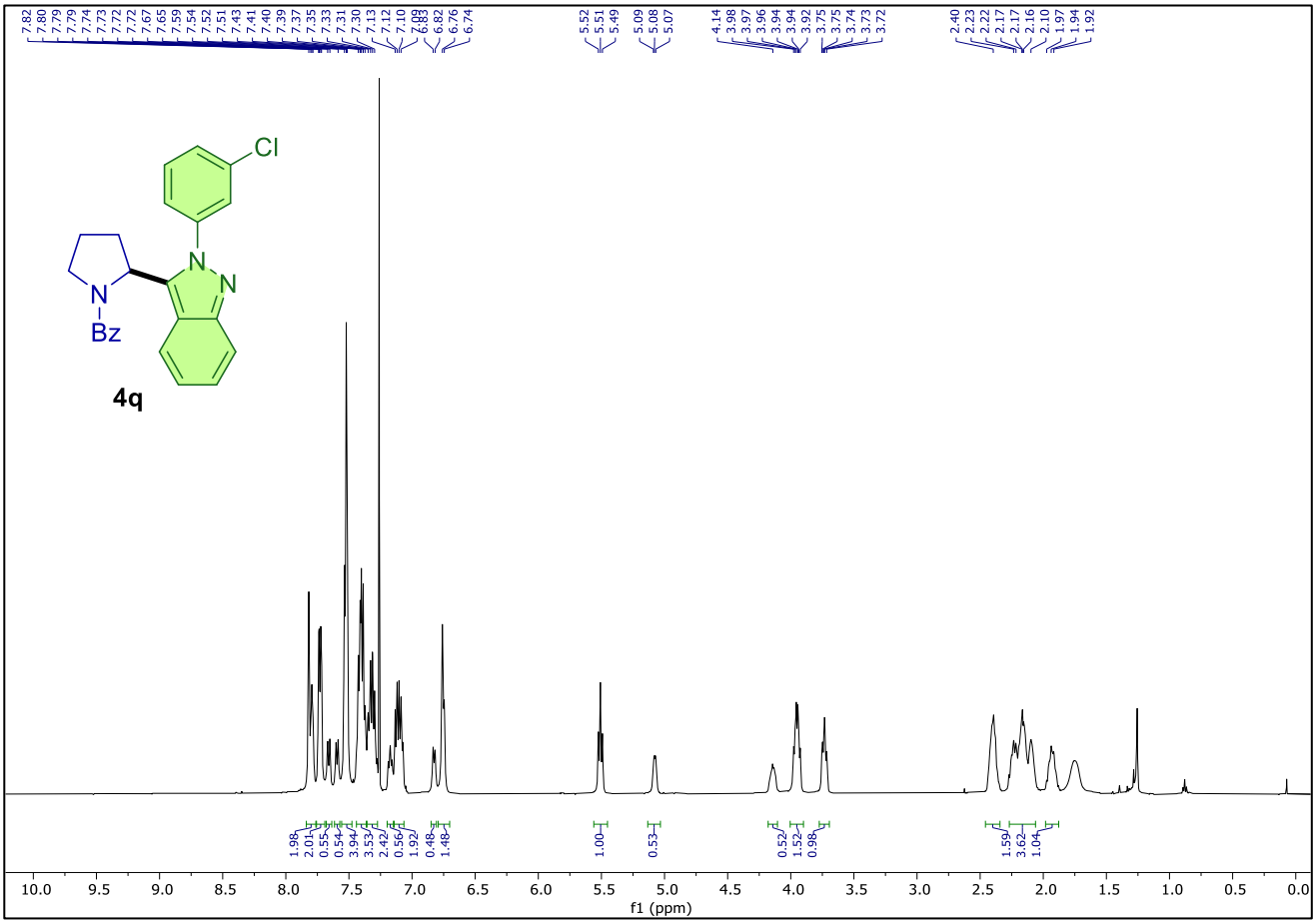
^{13}C{^{1}H} NMR of compound **4o** (126 MHz, $CDCl_3$)



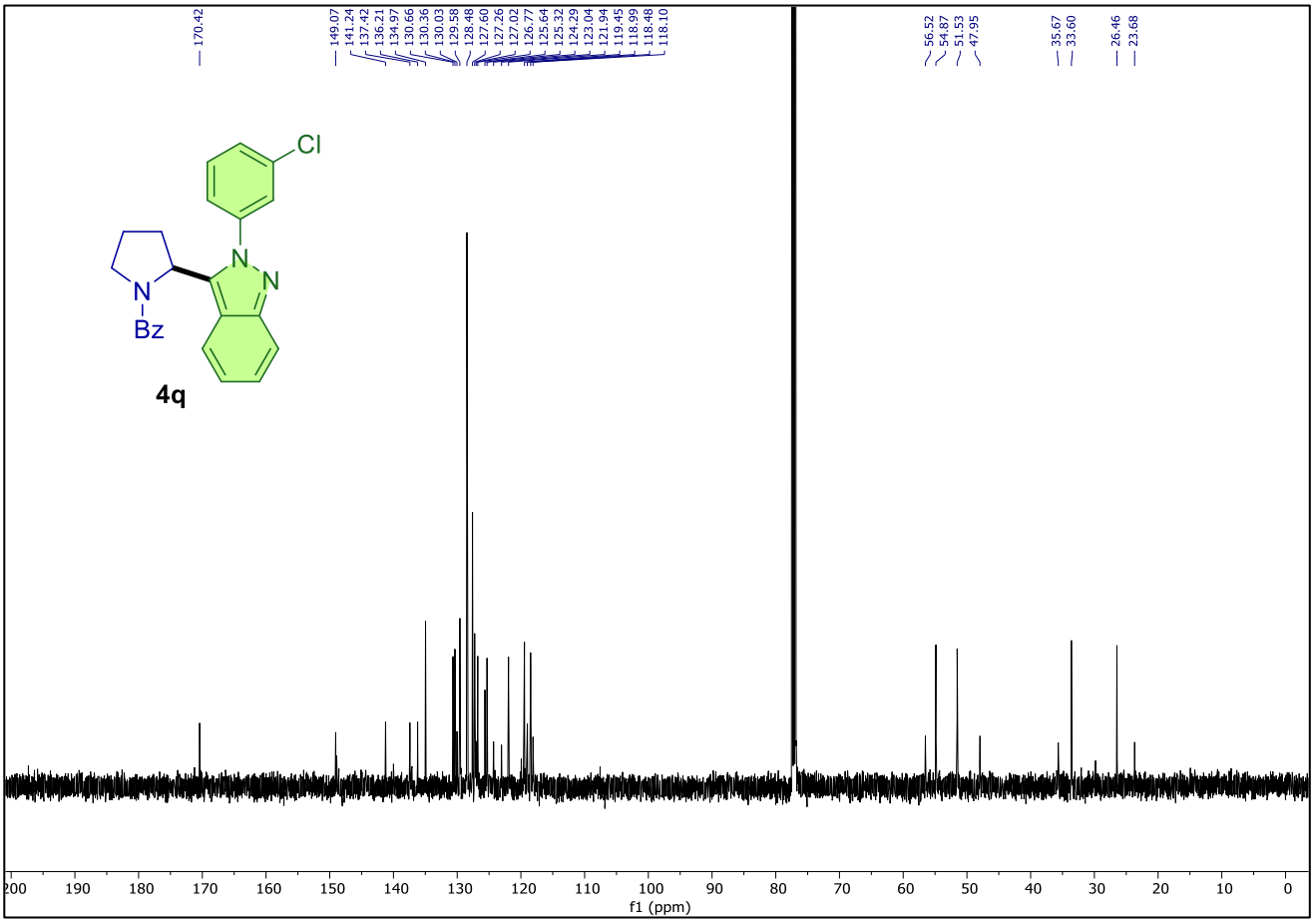
^{1}H NMR of compound **4p** (400 MHz, $CDCl_3$)



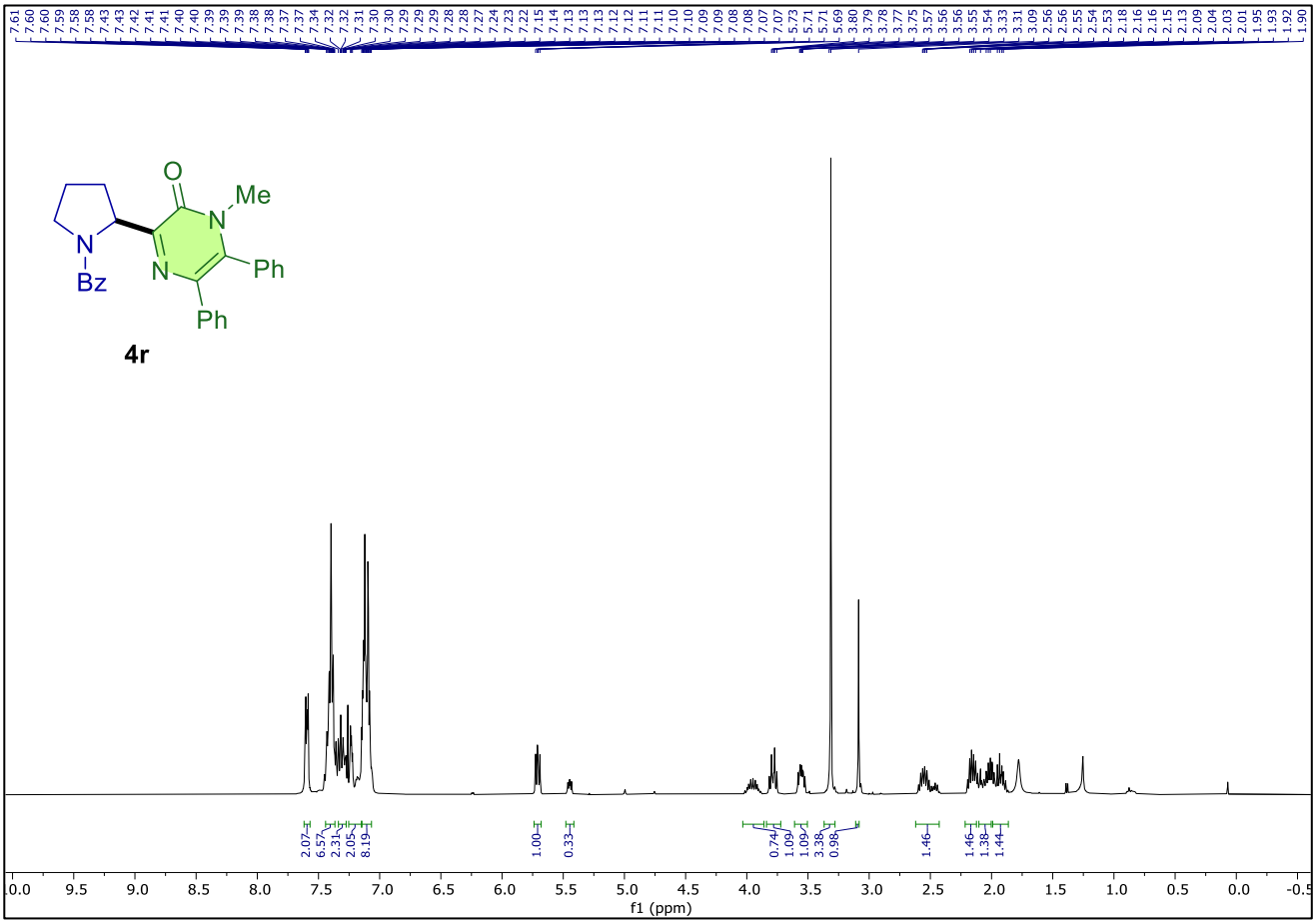
^{13}C{^{1}H} NMR of compound **4p** (126 MHz, $CDCl_3$)



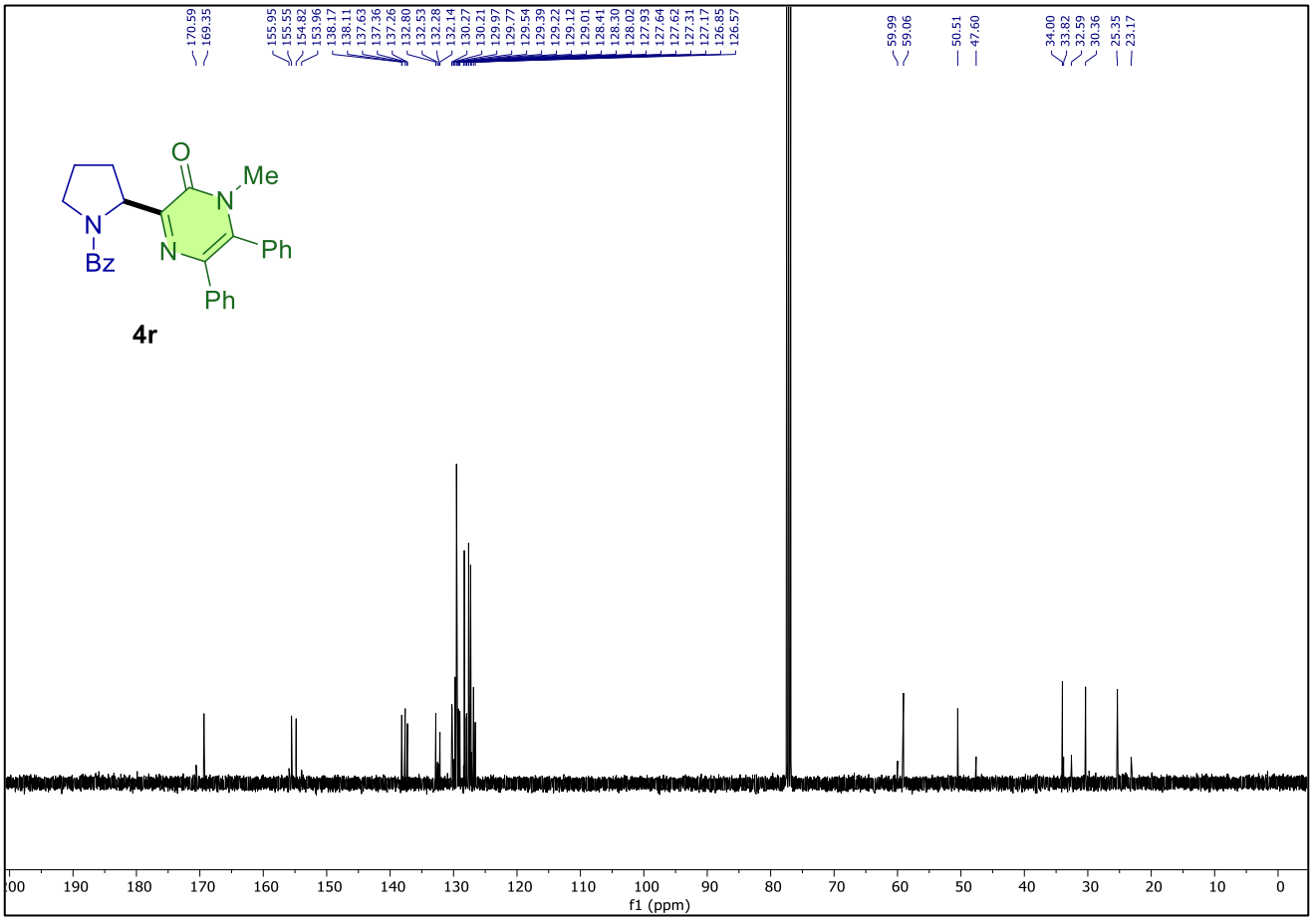
^{1}H NMR of compound **4q** (500 MHz, $CDCl_3$)



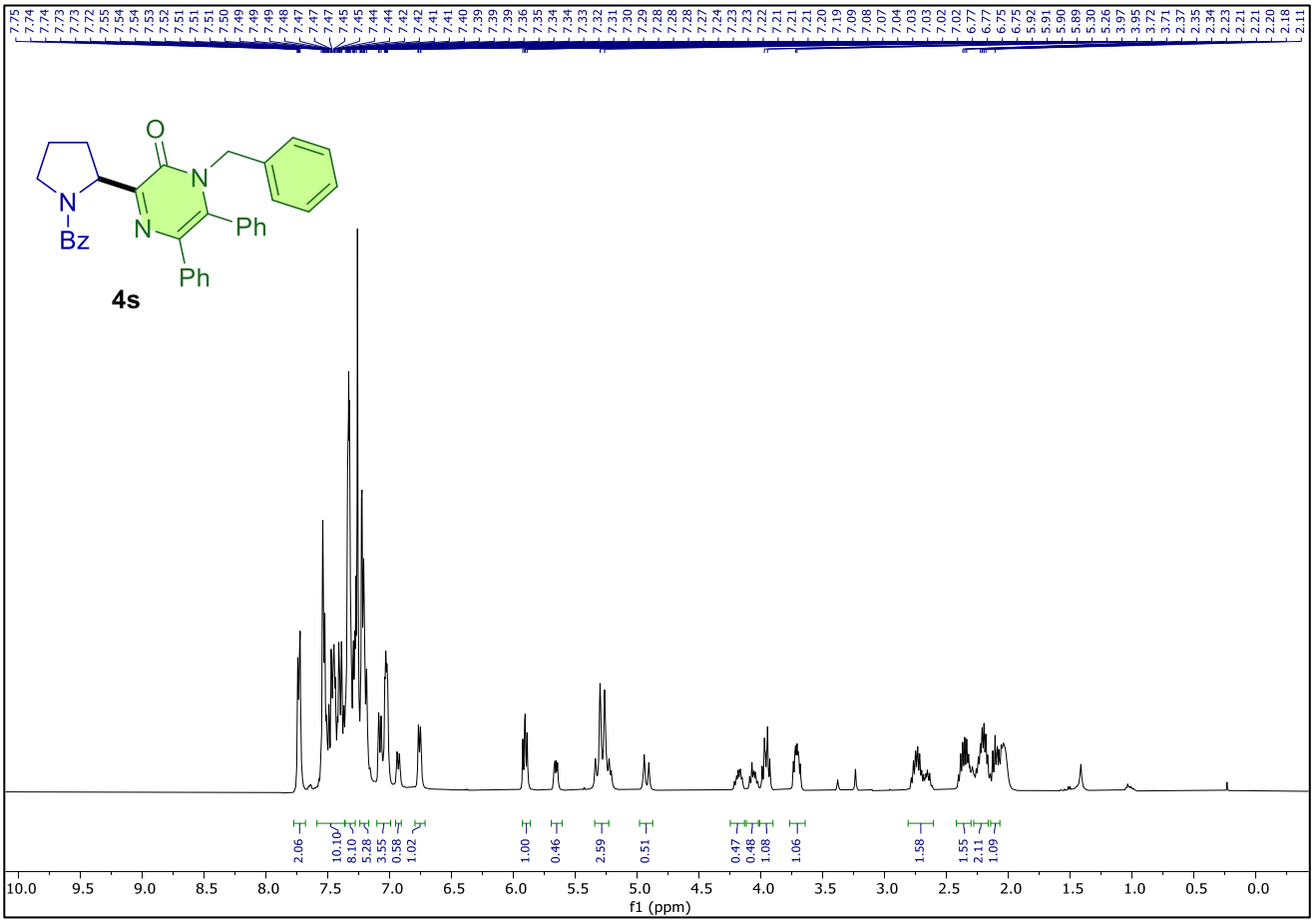
^{13}C{^{1}H} NMR of compound **4q** (126 MHz, $CDCl_3$)



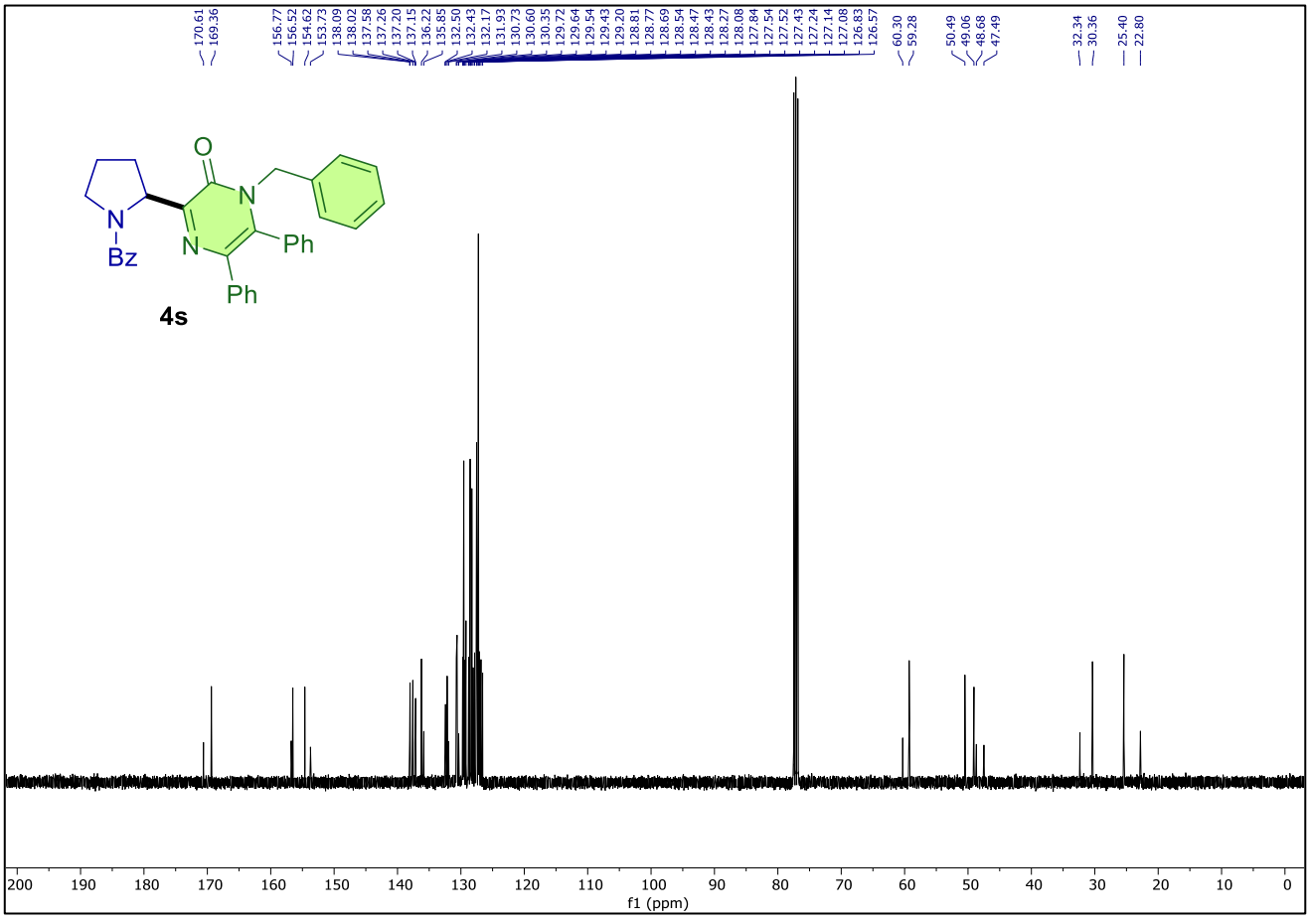
^{1}H NMR of compound **4r** (400 MHz, $CDCl_3$)



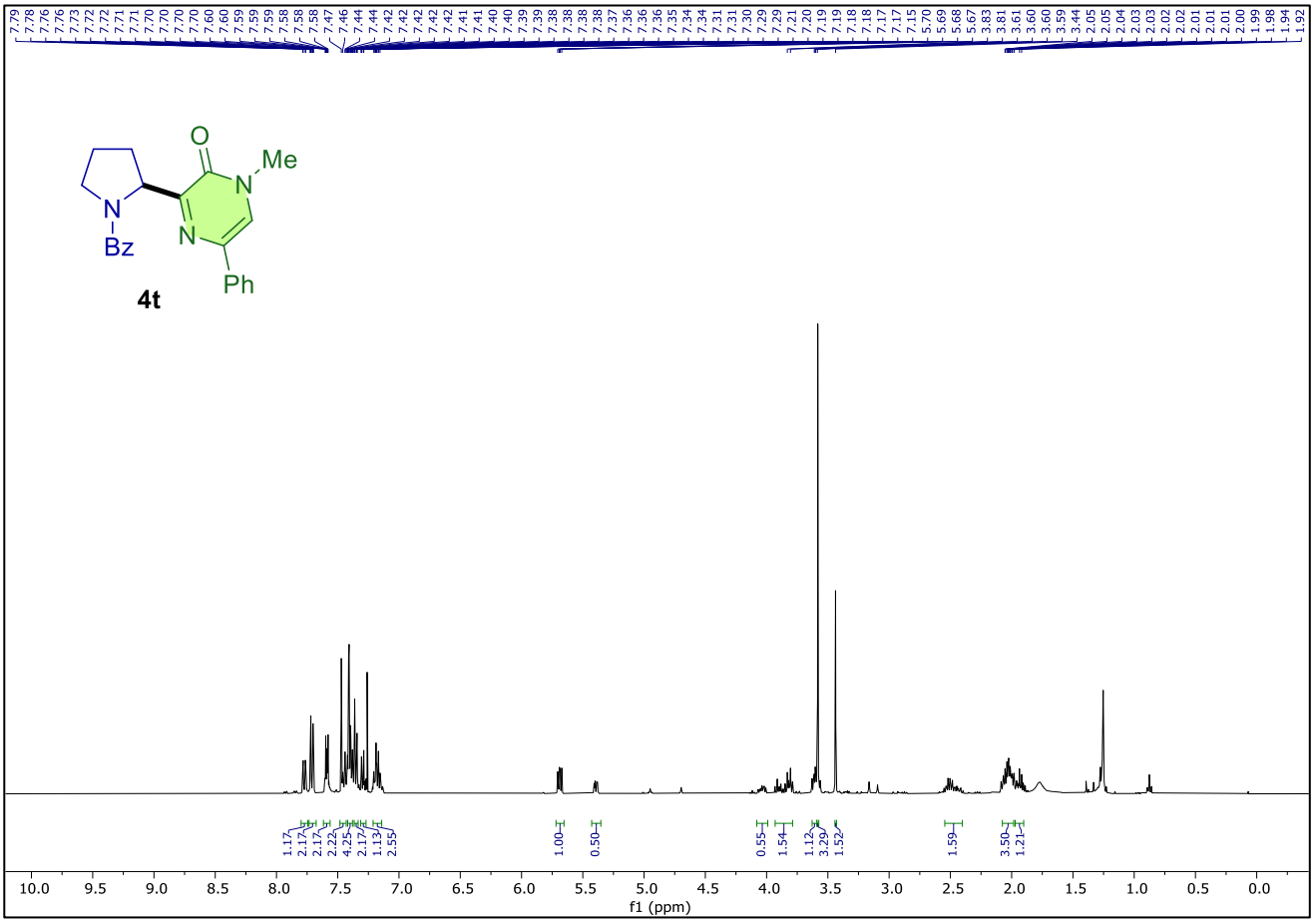
^{13}C{^{1}H} NMR of compound **4r** (101 MHz, $CDCl_3$)



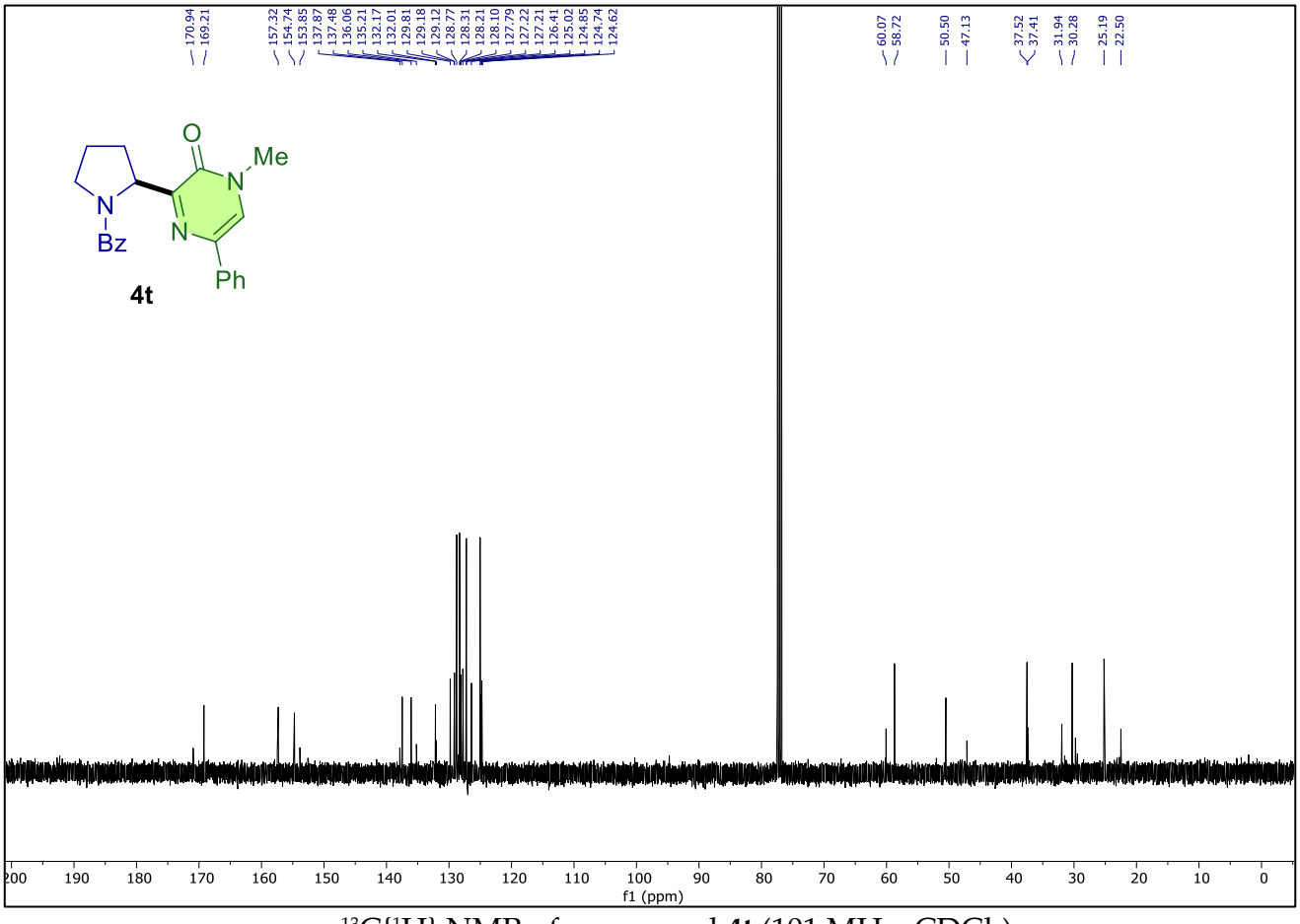
^{1}H NMR of compound **4s** (400 MHz, $CDCl_3$)



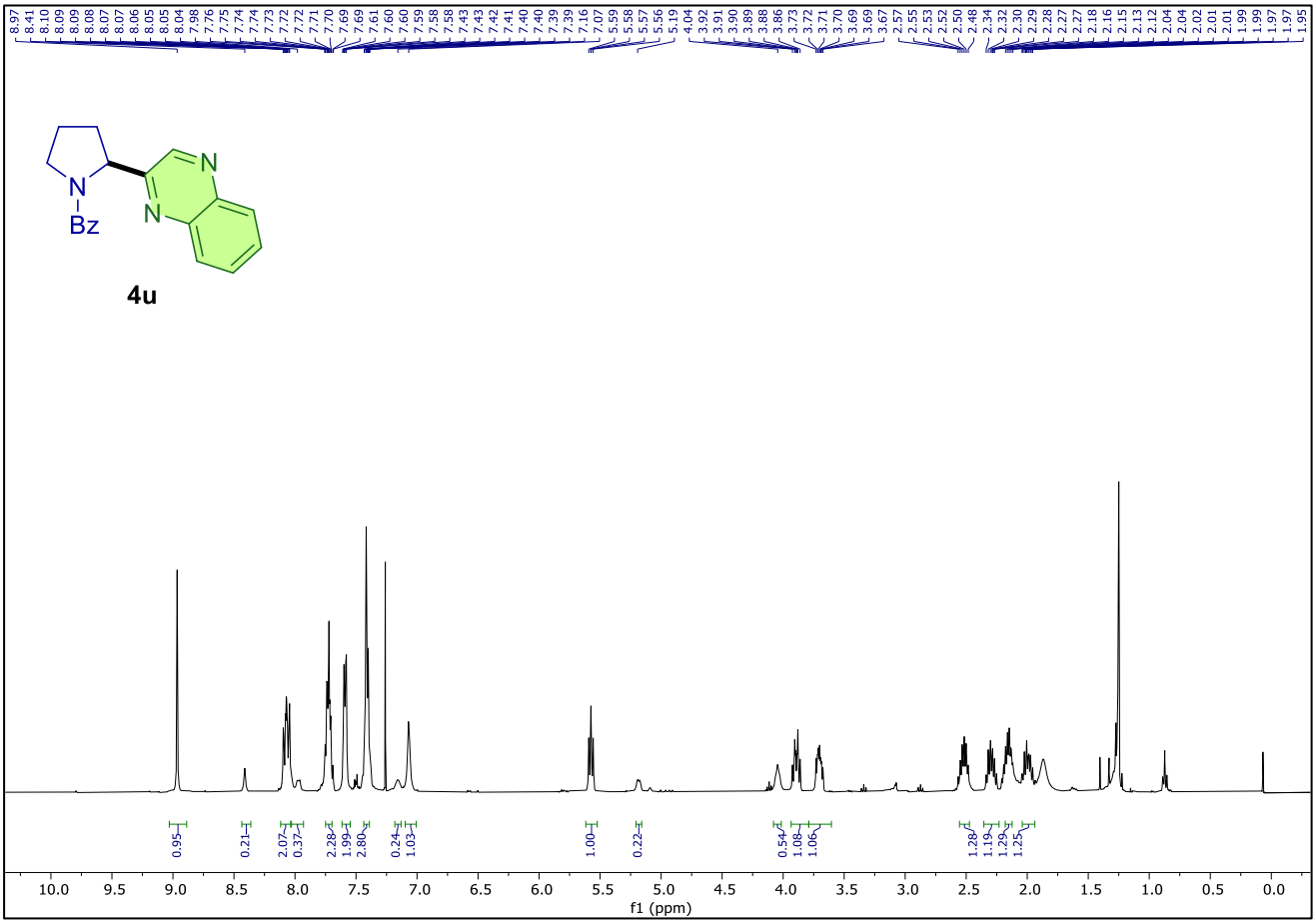
^{13}C{^{1}H} NMR of compound **4s** (101 MHz, $CDCl_3$)



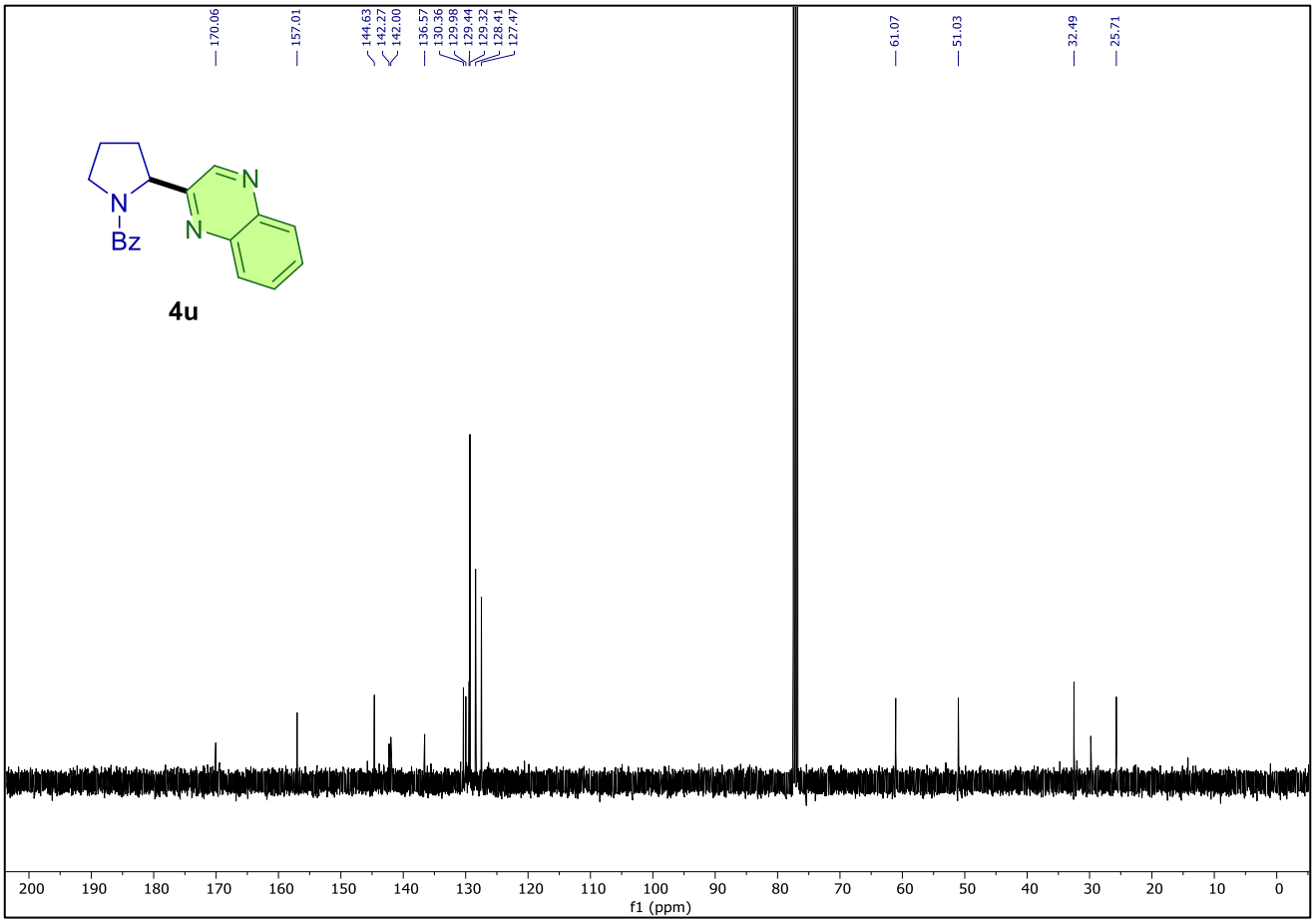
^{1}H NMR of compound **4t** (400 MHz, $CDCl_3$)



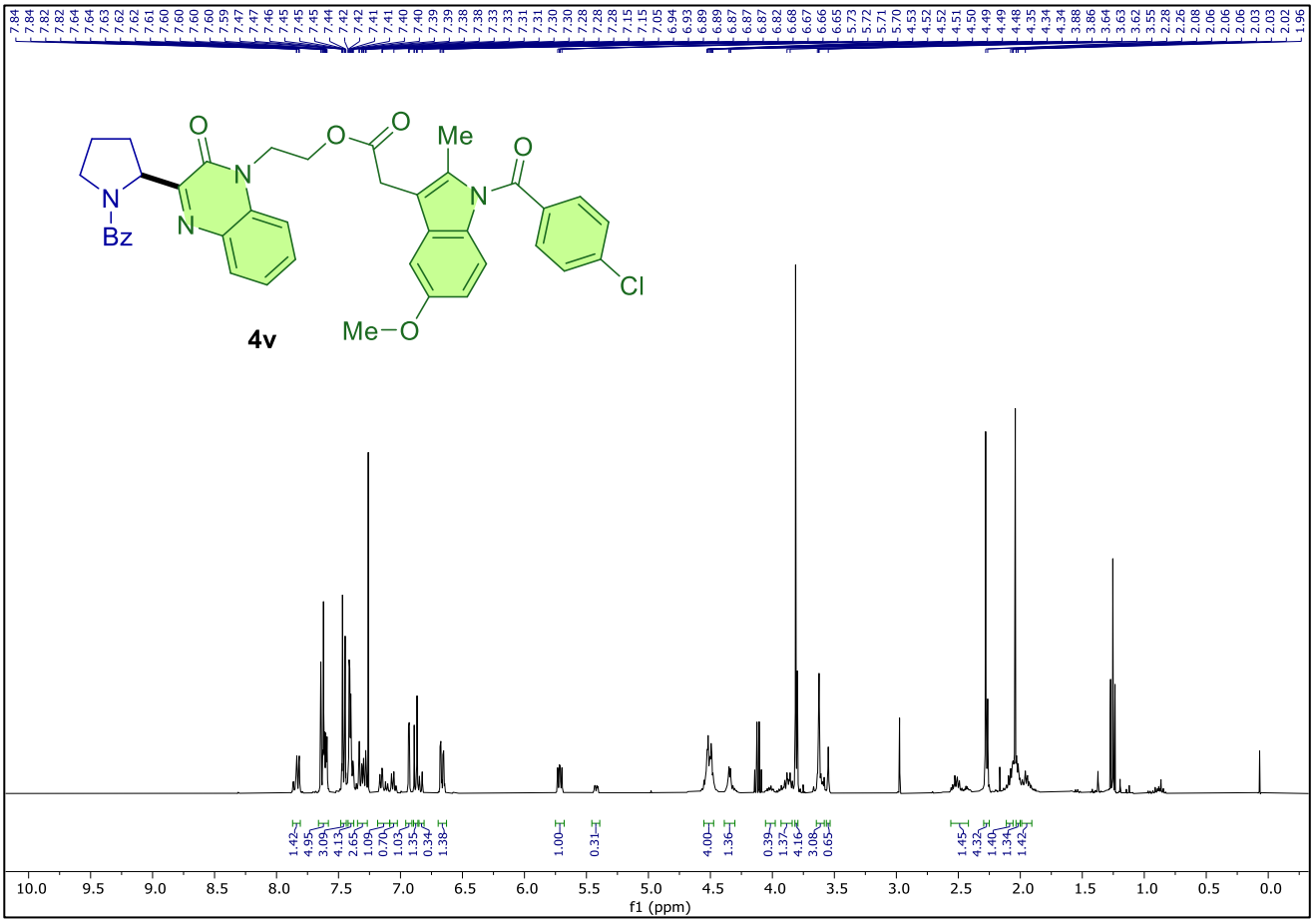
^{13}C{^{1}H} NMR of compound **4t** (101 MHz, $CDCl_3$)



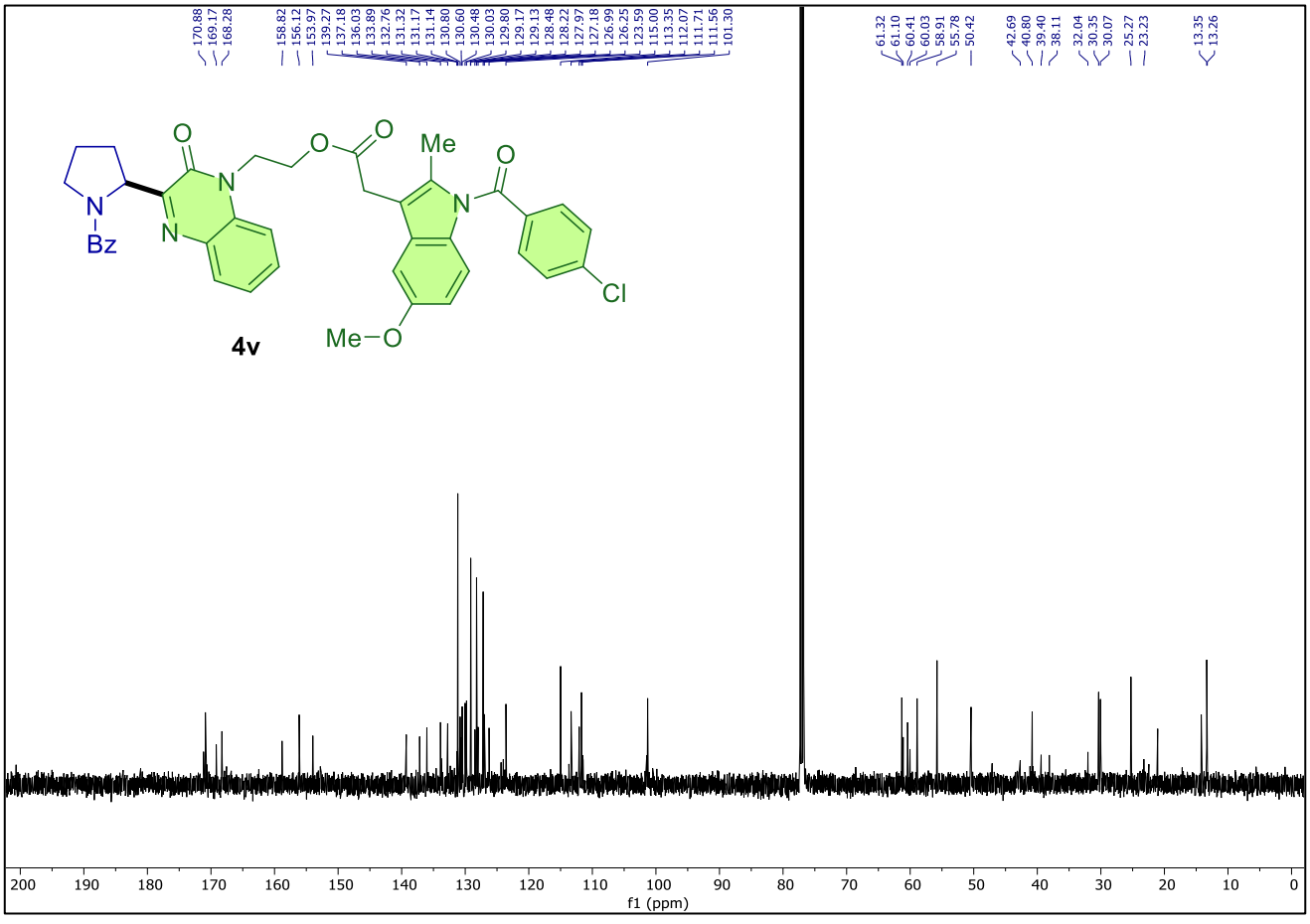
^{1}H NMR of compound **4u** (400 MHz, $CDCl_3$)



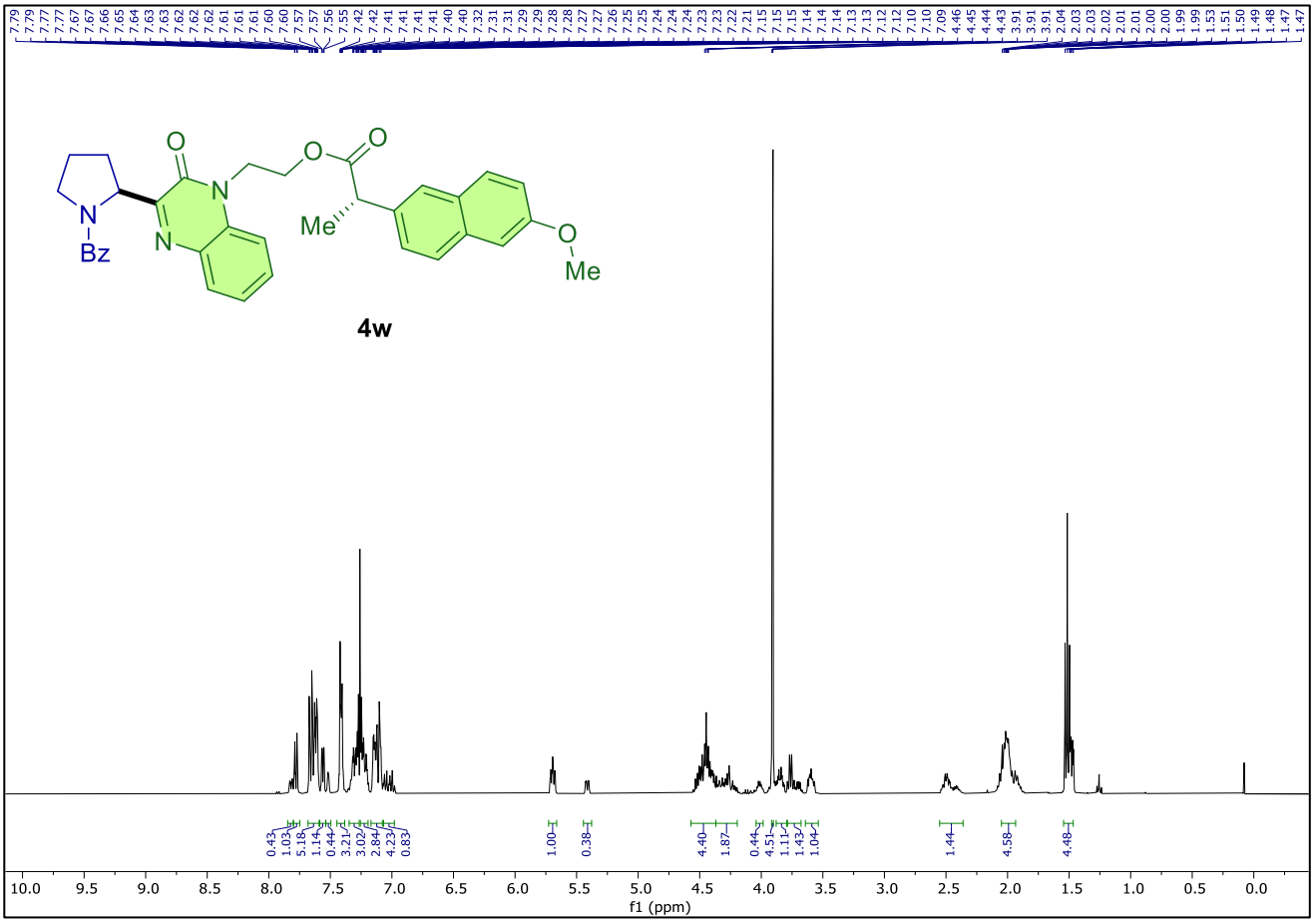
^{13}C{^{1}H} NMR of compound **4u** (101 MHz, $CDCl_3$)



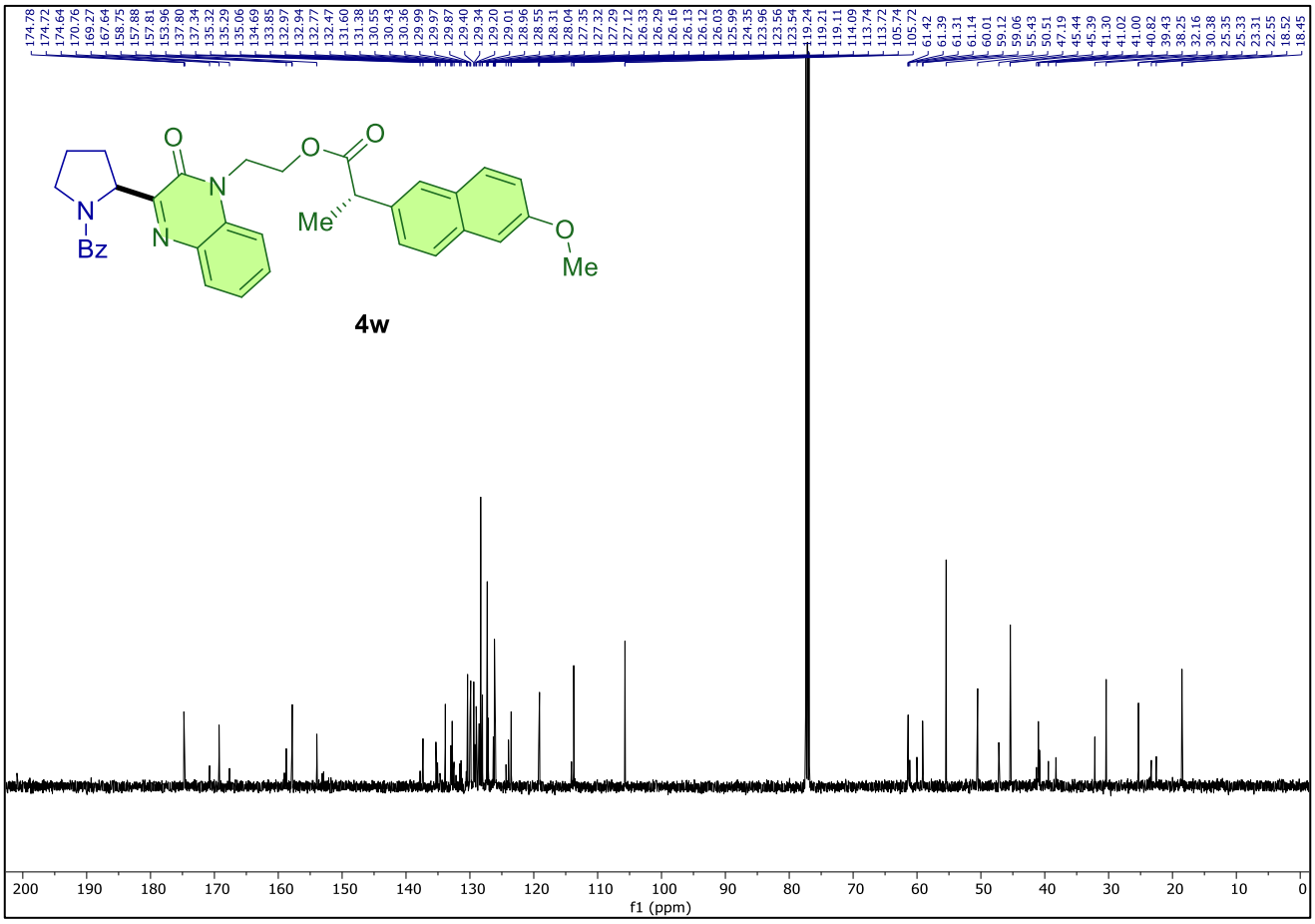
^{1}H NMR of compound **4v** (400 MHz, $CDCl_3$)



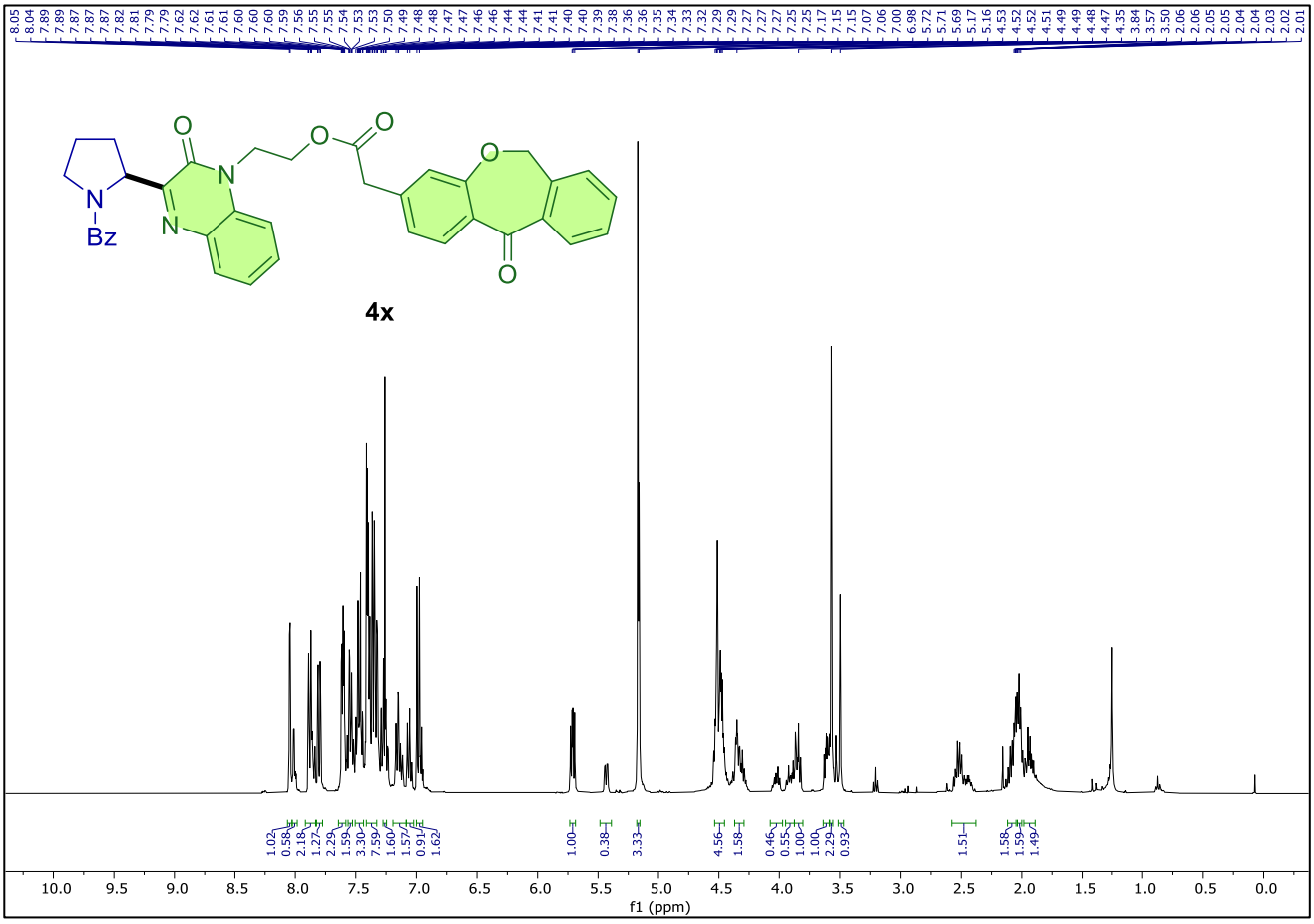
^{13}C{^{1}H} NMR of compound **4v** (126 MHz, $CDCl_3$)



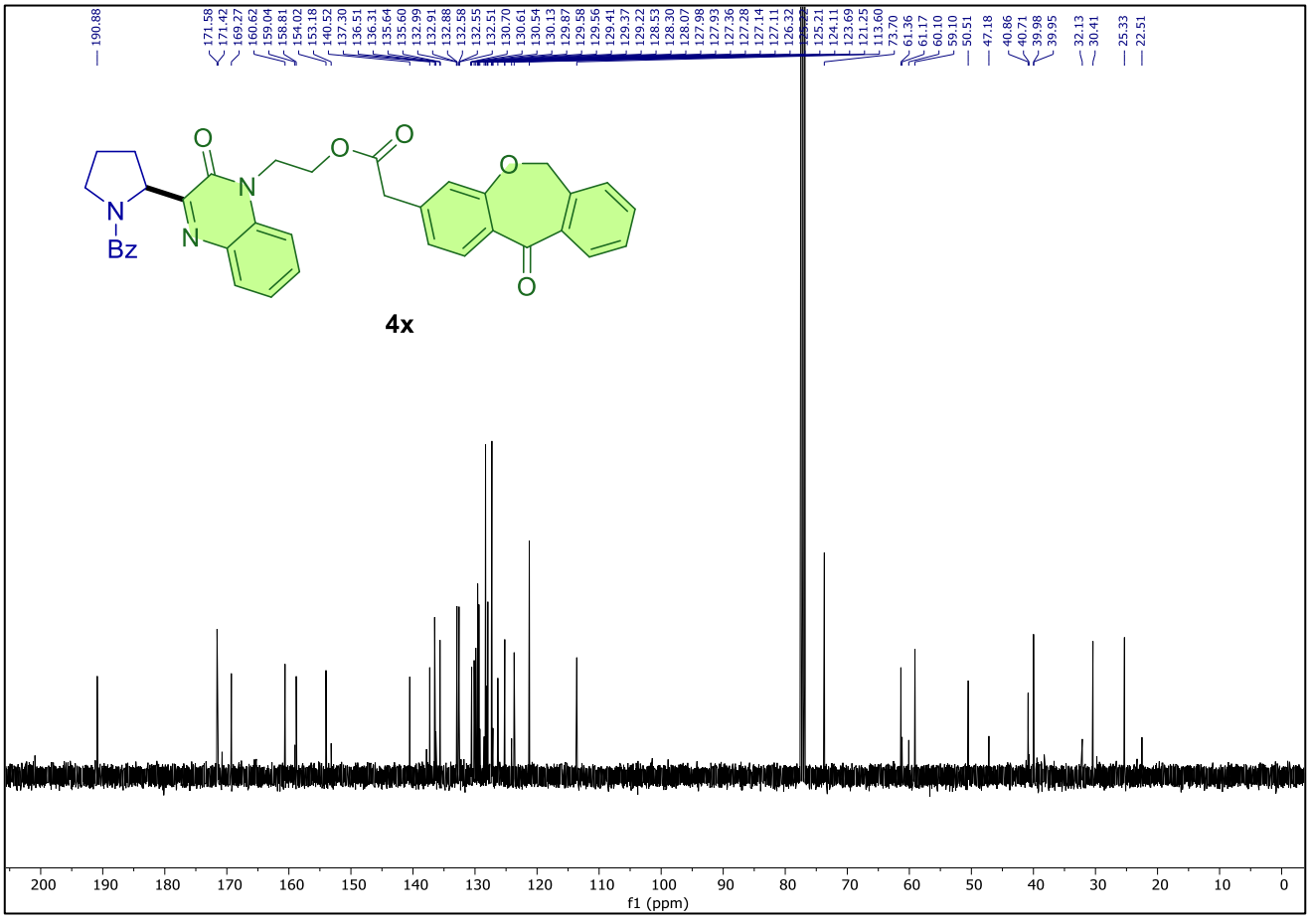
^{1}H NMR of compound **4w** (400 MHz, $CDCl_3$)



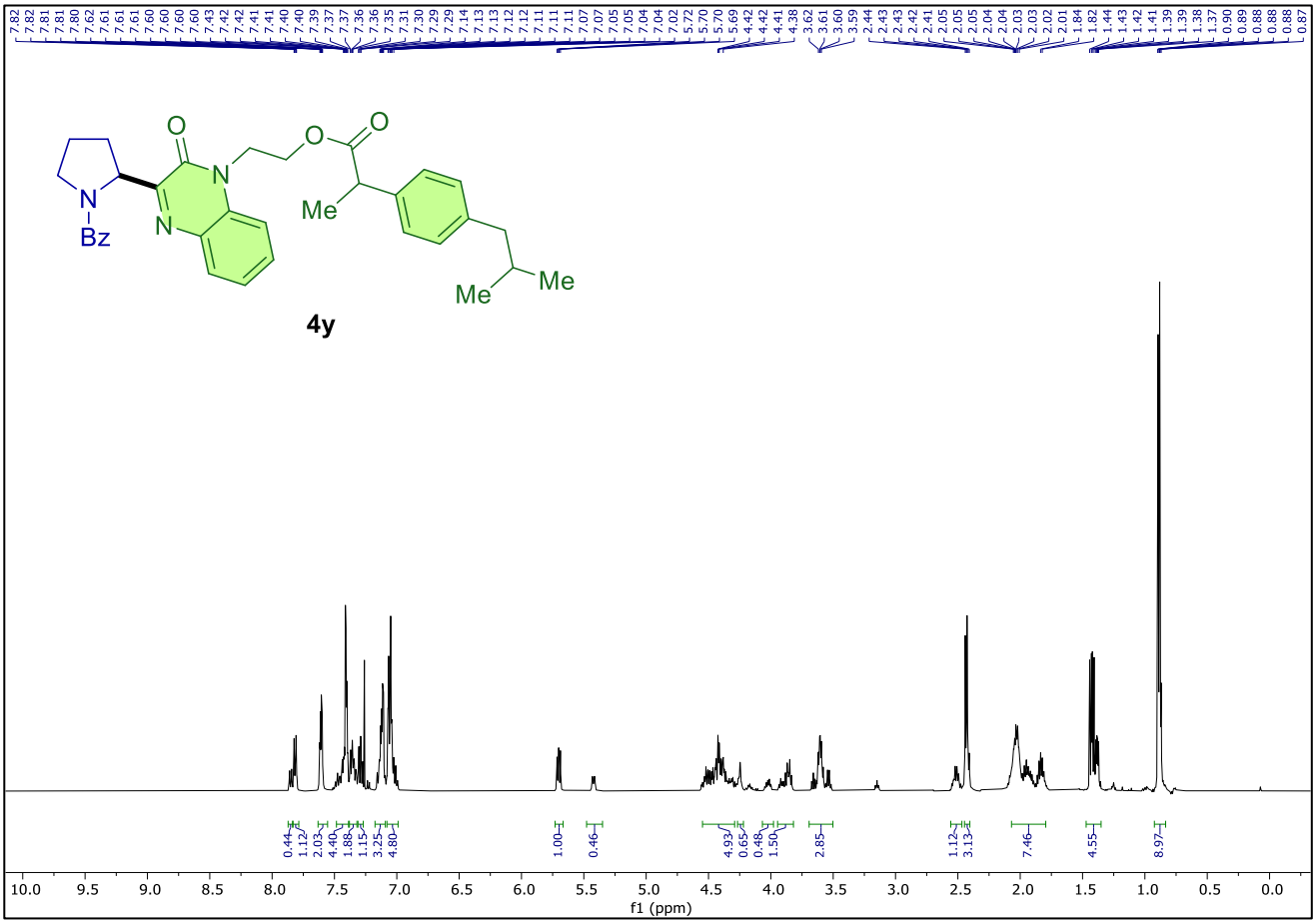
^{13}C{^{1}H} NMR of compound **4w** (126 MHz, $CDCl_3$)



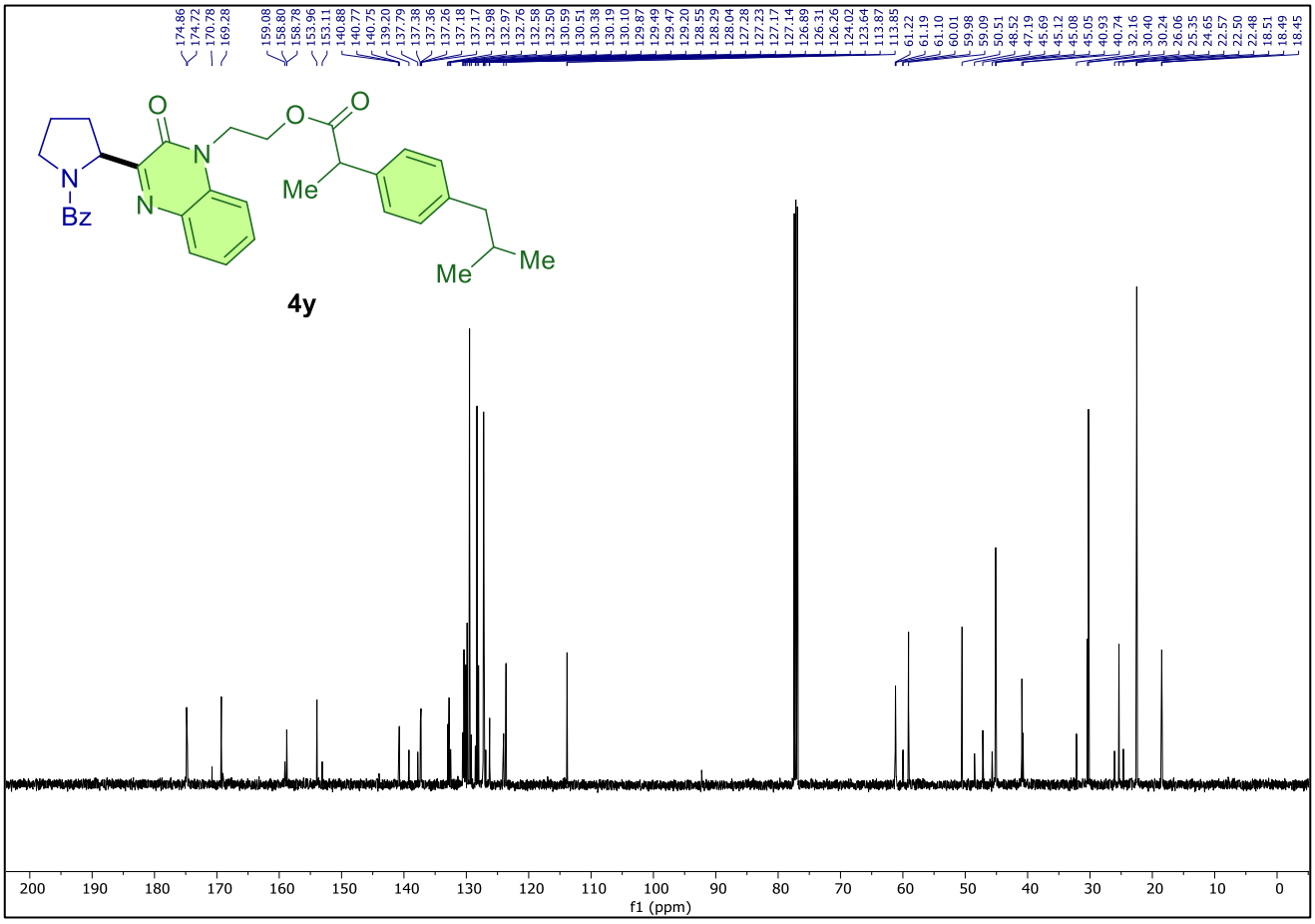
^{1}H NMR of compound **4x** (500 MHz, $CDCl_3$)



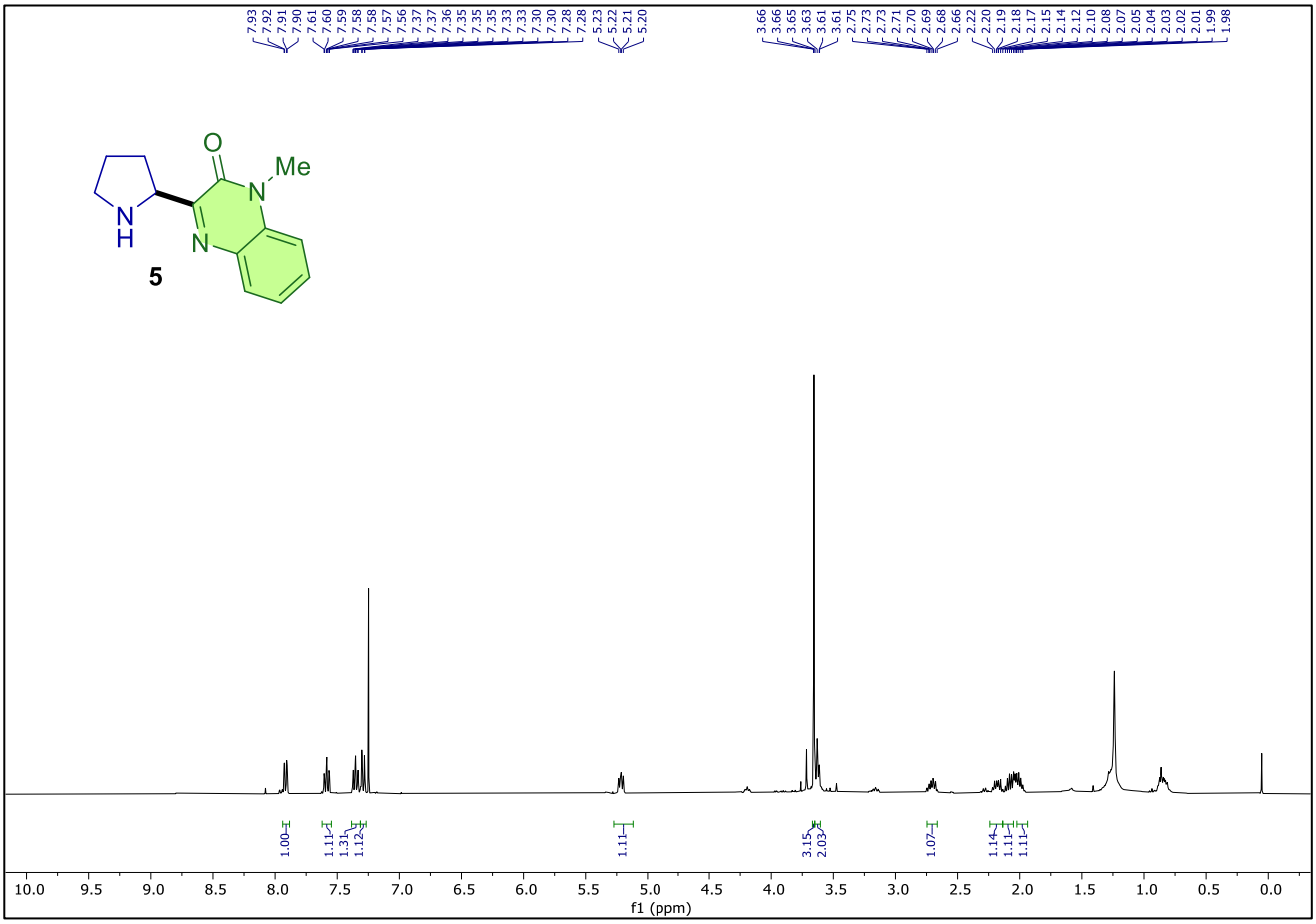
^{13}C{^{1}H} NMR of compound **4x** (101 MHz, $CDCl_3$)



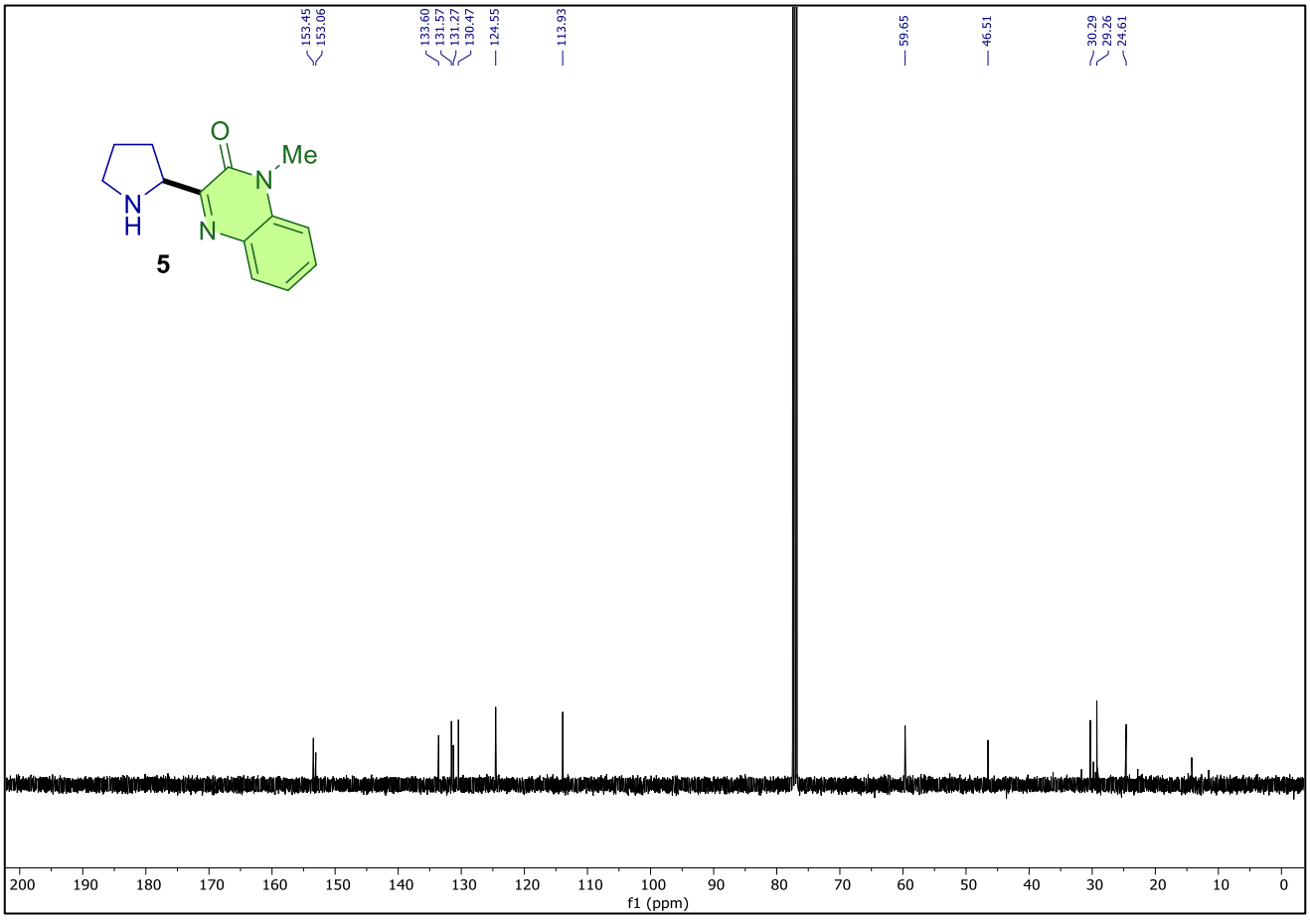
^{1}H NMR of compound **4y** (500 MHz, $CDCl_3$)



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



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



^{13}C{^{1}H} NMR of compound **5** (101 MHz, $CDCl_3$)