Supporting Information

Copper-Catalyzed C(sp)−H Aryl amination Generation Enables Modular Synthesis of Quinolines and 2-Quinolinones

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1. Supplementary Notes

General analytical information:

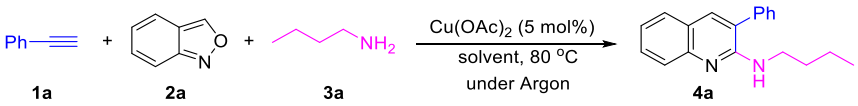
All reactions were performed in oven-dried glassware containing a Teflon-coated stirring bar and dry septum under argon atmosphere. All optimization reactions were monitored by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. NMR spectra were recorded at ambient temperature using chloroform-D ($CDCl_3$) or dimethyl sulfoxide-D6 (DMSO-*D6*) as solvent, with proton, carbon, and fluorine resonances at 400, 100 and 375 MHz, respectively. All NMR data are reported in ppm relative to the solvent signal. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. Column chromatography was performed with 200-300 mesh silica gel plates (GF_{254}), and visualization was effected at 254 nm. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF_{254}). Mass spectral data were acquired on a Varian GC-MS Saturn 2100 T. The ionization was achieved by EI AGC. HRMS analyses were carried out on a Waters GCT Premier CAB163 with a TOF mass analyzer. The MS ionization was achieved by EI^+. Melting points were measured on a Mettler FP 61 and are uncorrected. Parallel heating mantle were used in our experiments.

General reagent information:

All solvents were purified and dried by passage through alumina and Q5 reactant-packed columns on a solvent purification system. Commercial reagents were purchased from Aldrich Chemical, Alfa Aesar, TCI, Acros, Innochem, Adamas-beta, Aladdin, Bide Pharmatech, and were used as received. Anthranils were prepared according to the literature procedure, and were reported in our previous works.[1]

2. Optimization of Reaction Conditions.

Table S1. The screening of solvent.[a]



1a 2a 3a 4a

entry	solvent	Yield of **4a** (%)[b]
1	DMSO	27
2	DMA	20

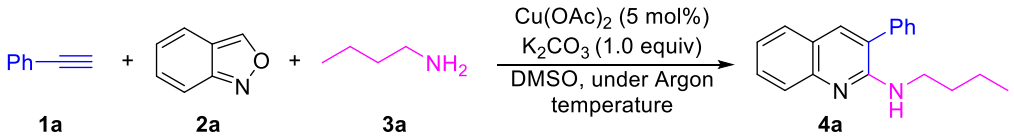
3	DMF	20
4	DMPU	12
5	MeCN	13
6	NMP	10
7	THF	19
8	Toluene	6
9	Cyclohexane	5
10	MeOH	trace

[a]Different solvents were screening with **1a** (0.24 mmol), **2a** (0.2 mmol), **3a** (0.4 mmol), $Cu(OAc)_2$ (5 mol%) in the indicated solvent (1 mL) at 80 °C for 12 h.

[b]Yields were determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard.

DMSO = dimethyl sulfoxide, DMA = N,N-dimethylacetamide, DMF = N,N-dimethylformamide, DMPU = N,N'-dimethylpropyleneurea, NMP = N-methyl pyrrolidone, THF = tetrahydrofuran.

Table S2. The screening of reaction temperature.[a]



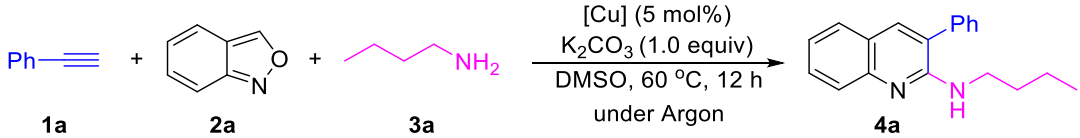
1a **2a** **3a** **4a**

entry	T/°C	Yield of **4a** (%)[b]
1	80	32
2	60	39
3	40	33
4	rt	26

[a]The reaction was conducted with **1a** (0.24 mmol), **2a** (0.2 mmol), **3a** (0.4 mmol), $Cu(OAc)_2$ (5 mol%) and K_2CO_3 (1.0 equiv) in DMSO (1 mL) at indicated temperature for 12 h.

[b]Yields were determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard.

Table S3. The screening of copper catalysts.[a]



1a **2a** **3a** **4a**

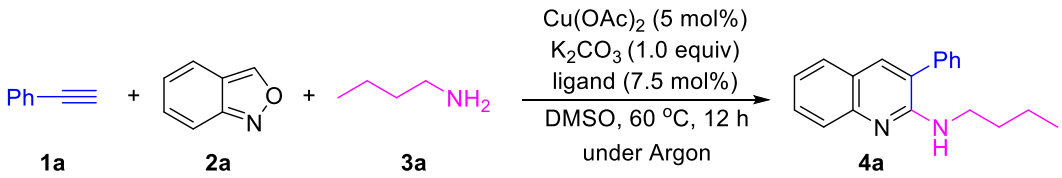
entry	[Cu]	Yield of **4a** (%)[b]

1	$CuCl_2$	35
2	CuCl	30
3	CuBr	38
4	CuI	37
5	Cp^*CuCl_2	trace
6	$Cu(OTf)_2$	28
7	$Cu(OAc)_2$	39

[a]Different copper catalysts were screening with **1a** (0.24 mmol), **2a** (0.2 mmol), **3a** (0.4 mmol), $Cu(OAc)_2$ (5 mol%) in the indicated solvent (1 mL) at 80 °C for 12 h.

[b]Yields were determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard.

Table S4. The screening of ligands.[a]



1a **2a** **3a** **4a**

entry	ligand	Yield of **4a** (%)[b]
1	PPh_3	44
2	PCy_3	50
3	Xantphos	16
4[c]	pyridine	46
5	**L1**	50
6	**L2**	73
7	**L3**	56
8	**L4**	67
9	**L5**	69
10	**L6**	70
11	**L7**	47
12	**L8**	52
13	**L9**	55
14	**L10**	46

15	**L11**	57

[a]The reaction was conducted with **1a** (0.24 mmol), **2a** (0.2 mmol), **3a** (0.4 mmol), $Cu(OAc)_2$ (5 mol%), K_2CO_3 (1.0 equiv) and ligand (7.5 mol%) in DMSO (1 mL) at 60 °C for 12 h.

[b]Yields were determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard.

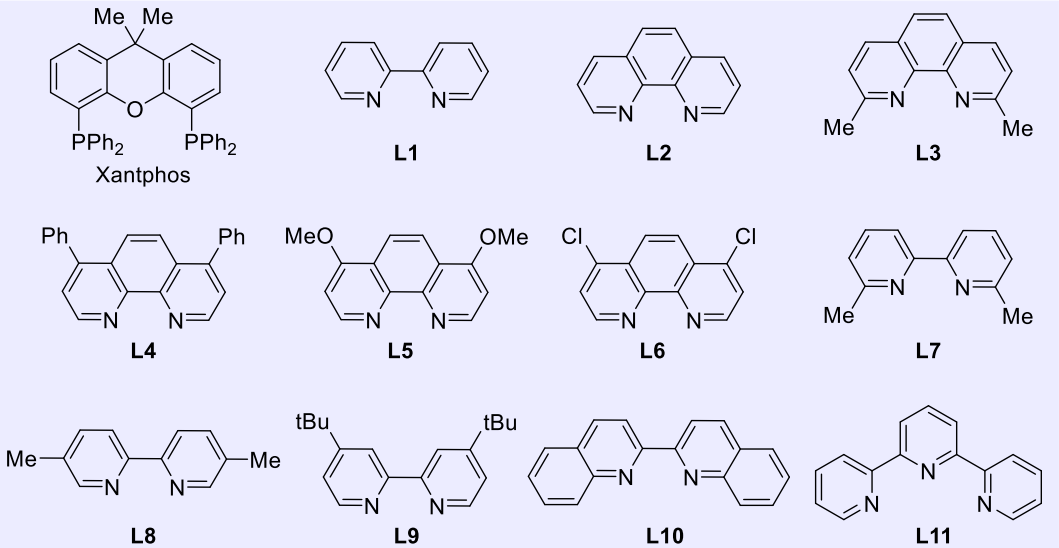
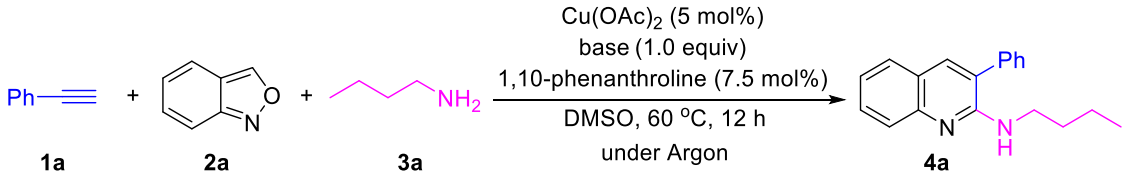


Table S5. The screening of bases.[a]

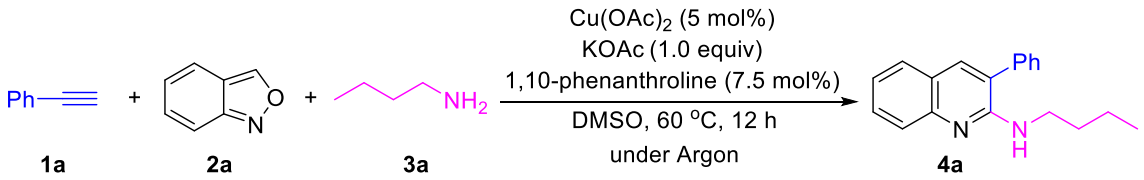


entry	base	Yield of **4a** (%)[b]
1	K_2CO_3	73
2	/	70
3	Cs_2CO_3	10
4	Na_2CO_3	67
5	K_3PO_4	5
6	^{t}BuOK	0
7	KOAc	71

[a]The reaction was conducted with **1a** (0.24 mmol), **2a** (0.2 mmol), **3a** (0.4 mmol), $Cu(OAc)_2$ (5 mol%), base (1.0 equiv) and 1,10-phenanthroline (7.5 mol%) in DMSO (1 mL) at 60 °C for 12 h.

[b]Yields were determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard.

Table S6. The Influence of Reaction Concentration.[a]



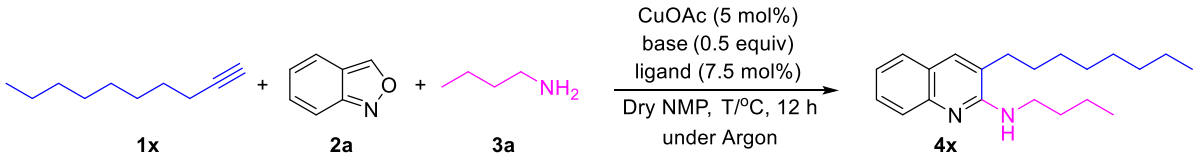
entry	concentration	base	Yield of **4a** (%)[b]
1	0.4 M	KOAc	76
2	0.4 M	/	78
3[c]	0.4 M	/	86
4	0.2 M	KOAc	71
5	0.1 M	KOAc	63

[a]The reaction was conducted with **1a** (0.24 mmol), **2a** (0.2 mmol), **3a** (0.4 mmol), $Cu(OAc)_2$ (5 mol%), K_2CO_3 (1.0 equiv) and ligand (7.5 mol%) in DMSO (0.5 mL) at 60 °C for 12 h.

[b]Yields were determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard.

[c]0.3 mmol **1a** was used.

Table S7. Optimization of the reaction conditions for alkyl alkyne.[a]



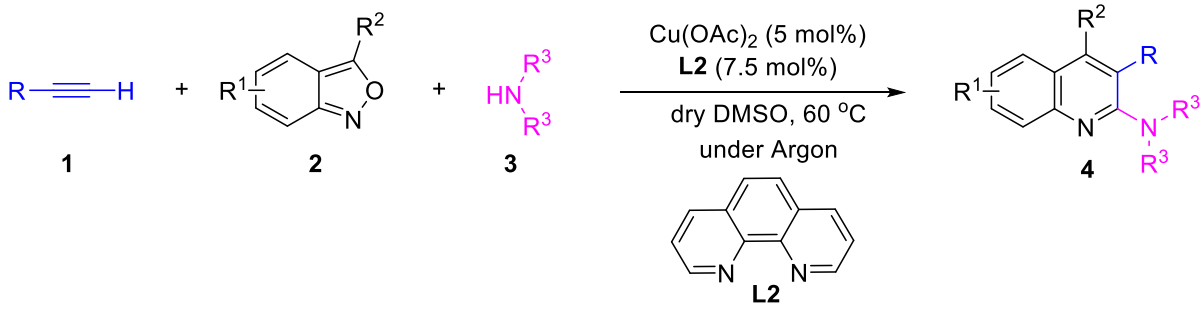
entry	solvent	base	[Cu]	ligand	T/ °C	Yield of **4x** (%)[b]
1	DMSO	/	$Cu(OAc)_2$	L2	60	20
2	DMSO	/	$Cu(OAc)_2$	L2	100	22
3	NMP	/	$Cu(OAc)_2$	L2	100	28
4	NMP	K_2CO_3	$Cu(OAc)_2$	L2	100	30
5	NMP	Cs_2CO_3	$Cu(OAc)_2$	L2	100	22
6	NMP	K_2CO_3	CuOAc	L2	100	31
7	NMP	K_2CO_3	CuOAc	L4	100	52
8	NMP	K_2CO_3	CuOAc	L6	100	25

[a]The reaction was conducted with **1x** (0.2 mmol), **2a** (0.4 mmol), **3a** (0.4 mmol), CuOAc (5 mol%), base (0.5 equiv) and ligand (7.5 mol%) in dry NMP (0.5 mL) at 100 °C for 12 h.

[b]Yields were determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard.

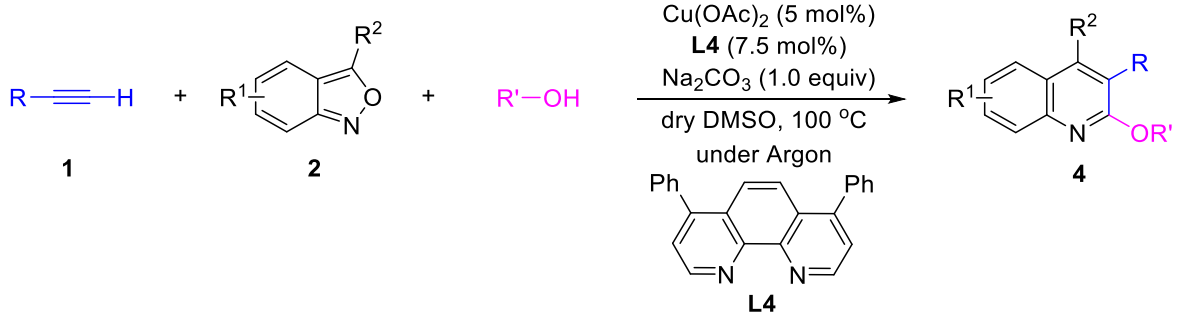
3. Supplementary Methods

General Procedure A for the synthesis of 2-amino quinolines via Cu-catalyzed three-component coupling of alkynes, anthranils and amines.



An oven-dried 20 mL vial was charged with $Cu(OAc)_2$ (5 mol%) and 1,10-phenanthroline (7.5 mol%), and closed with a septum cap. After it was evacuated and back-filled with argon 3 times, DMSO (0.75 mL), anthranil (0.3 mmol, 1.0 equiv), alkyne (0.45 mmol, 1.5 equiv) and amines (0.6 mmol, 2.0 equiv) were successively added via syringe. The reaction mixture was stirred under an argon atmosphere at 60 ℃ for 12 h. After completion of the reaction, the resulting mixture was diluted with 1 M LiCl aqueous solution water (10 mL). Following phase separation, the aqueous layer was extracted 3 times with diethyl ether (5 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous $MgSO_4$, filtered, and the organic phase was evaporated under reduced pressure (rotary evaporator). The residue was purified by column chromatography (SiO_2, ethyl acetate/petroleum ether gradient).

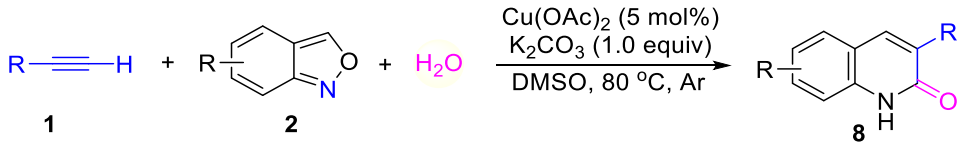
General Procedure B for the synthesis of 2-alkoxy/phenoxyquinolines via Cu-catalyzed three-component coupling of alkynes, anthranils and phenols/alcohols.



An oven-dried 20 mL vial was charged with $Cu(OAc)_2$ (5 mol%), 4,7-diphenyl-1,10-phenanthroline **L4** (7.5 mol%), Na_2CO_3 (1.0 equiv), and phenols (0.36 mmol, 1.2 equiv), and closed with a septum cap. After it was evacuated and back-filled with argon 3 times, DMSO (1.5 mL), anthranil (0.3 mmol, 1.0 equiv), and alkyne (0.45 mmol, 1.5 equiv) were successively added via syringe. The reaction mixture was stirred under an argon atmosphere at 100 ℃ for 12 h.

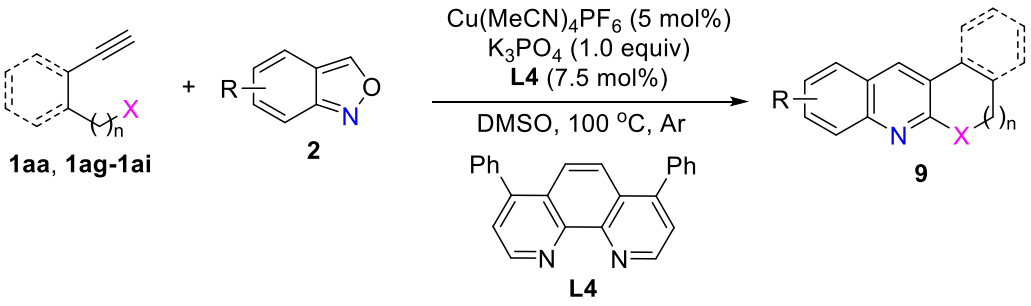
After completion of the reaction, the resulting mixture was diluted with 1 M LiCl aqueous solution water (10 mL). Following phase separation, the aqueous layer was extracted 3 times with diethyl ether (5 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous $MgSO_4$, filtered, and the organic phase was evaporated under reduced pressure (rotary evaporator). The residue was purified by column chromatography (SiO_2, ethyl acetate/petroleum ether gradient).

General Procedure C for the synthesis of 2-quinolinones via Cu-catalyzed three-component coupling of alkynes, anthranils and water.



An oven-dried 20 mL vial was charged with $Cu(OAc)_2$ (5 mol%) and K_2CO_3 (1.0 equiv), and closed with a septum cap. After it was evacuated and back-filled with argon 3 times, DMSO (1.5 mL), anthranil **2a** (0.3 mmol, 1.0 equiv), alkyne (0.45 mmol, 1.5 equiv) and H_2O (1.5 mmol, 5.0 equiv) were successively added via syringe. The reaction mixture was stirred under an argon atmosphere at 80 ℃ for 12 h. After completion of the reaction, the resulting mixture was diluted with 1 M LiCl aqueous solution water (10 mL). Following phase separation, the aqueous layer was extracted 3 times with diethyl ether (5 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous $MgSO_4$, filtered, and the organic phase was evaporated under reduced pressure (rotary evaporator). The residue was purified by column chromatography (SiO_2, ethyl acetate/petroleum ether gradient).

General Procedure D for the synthesis of quinoline-fused heterocycles.

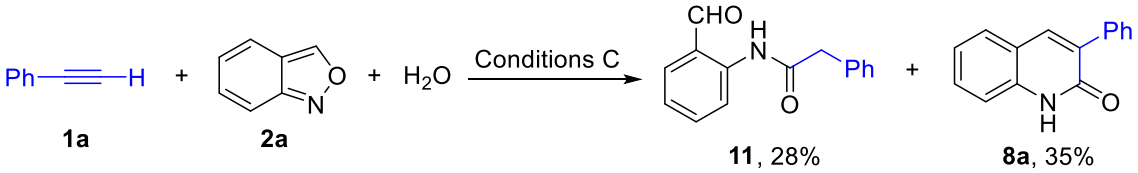


An oven-dried 20 mL vial was charged with $Cu(MeCN)_4PF_6$ (5 mol%), K_3PO_4 (1.0 equiv), and bathophenanthroline (7.5 mol%), and closed with a septum cap. After it was evacuated and back-filled with argon 3 times, DMSO (1.5 mL), anthranil **2a** (0.3 mmol, 1.0 equiv), terminal alkyne (1.2 mmol) were successively added via syringe. The reaction mixture was stirred under an argon atmosphere at 100 ℃ for 12 h. After completion of the reaction, the resulting mixture was diluted with 1 M LiCl aqueous solution water (10 mL). Following phase separation, the aqueous layer was

extracted 3 times with diethyl ether (5 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous $MgSO_4$, filtered, and the organic phase was evaporated under reduced pressure (rotary evaporator). The residue was purified by column chromatography (SiO_2, ethyl acetate/petroleum ether gradient).

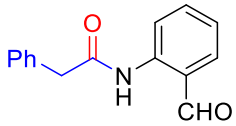
4. Mechanistic study

4.1 Isolation and conversion of amide 11.

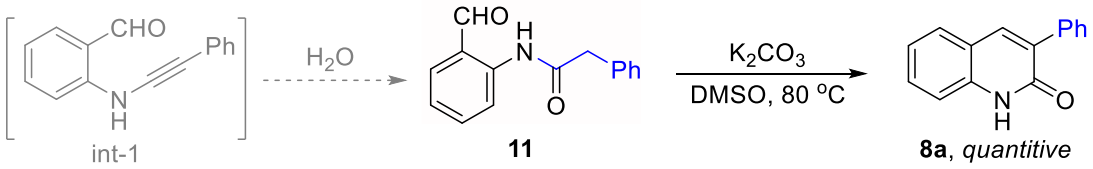


The reaction of phenylacetylene (**1a**) and anthranil **2a** was conducted fellowing the **General Procedure C**, and was quenched with 1 M LiCl aqueous solution (10 mL) in 1 h. After work-up, the residue was purified by column chromatography (SiO_2, ethyl acetate/petroleum ether gradient). Apart from the desired product **8a**, another product was isolated and was identified to be compound **11** accroding to NMR and GC-MS analysis.

N-(2-Formylphenyl)-2-phenylacetamide (11)[2]



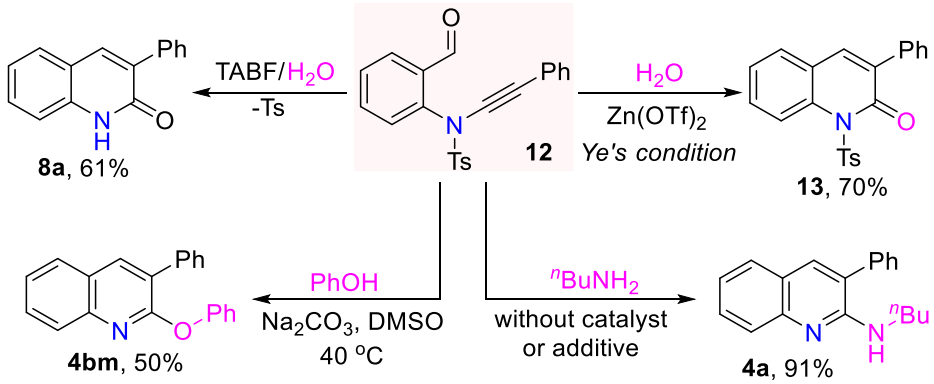
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.09 (s, 1H), 9.82 (s, 1H), 8.75 (d, *J* = 8.4 Hz, 1H), 7.64 – 7.56 (m, 2H), 7.43 – 7.38 (m, 4H), 7.37 – 7.33 (m, 1H), 7.20 (td, *J* = 7.5, 0.9 Hz, 1H), 3.79 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.3, 170.7, 140.8, 136.1, 135.9, 133.9, 129.6, 129.0, 127.5, 123.0, 121.8, 119.8, 45.8. **MS** (EI) m/z (%) 239.0 $[M]^+$, 148.0, 132.0, 121.0, 106.0, 91.0, 77.0. The data match those reported in literature.[2]



The conversion of amide **11** to the desired product **8a** was then investigated. Amide **11** (0.1 mmol) was dissolved in 1 mL DMSO, and K_2CO_3 (0.1 mmol) was added. The reaction mixture was stirred at 80 ℃ for 6 h. After the completion of the reaction, it was found that compound **11** was consumed and converted into **8a** in a quantitive yield. *These results indicate that amide **11** is a possible intermediate in the formation of 2-quinolinone **8a**. Moreover, amide **11** is likely formed via the hydrolysis of secondary N-aryl ynamine **int-1**.*

4.2 Reaction of ynamide 12 with different nucleophlies.

Due to the instability of the proposed secondary N-arylamine intermediate **int-1**, efforts to isolate or identify this intermediate turn out to be unfruitful. Therefore, ynamide **12** bearing a Ts protecting group was prepared from (2-aminophenyl)methanol according to the method reported by Ye's group. The obtained ynamide **12** was then treated with different nucleophlies, including H_2O, PhOH, and $^{n}BuNH_2$.



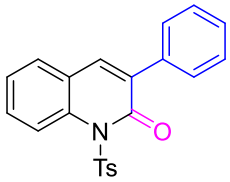
Removing the Ts protecting group from ynamide 12 via the treatment with TABF.xH_2O.

To a solution of ynamide **12** (0.1 mmol) in 1 mL THF, 0.2 mmol TABF.xH_2O was added in one pot. The reaction mixture was strried at 40 ℃ for 3 hours. Upon completion, the reaction mixture was concentrated and the residue was purified by chromatography on silica gel (PE/EA 10:1), and **8a** was obtained in 61% yield.

Procedure for $Zn(OTf)_2$ catalyzed hydrative cyclization of ynamide 12 with H_2O.

The reaction was carried out under the consitions reported by the Ye group,[3] but the reaction time was prolonged. To a mixture solvent (toluene/CH_3CN 3:1, 1 mL), $Zn(OTf)_2$ (0.02 mmol), ynamide **12** (0.1 mmol), and H_2O (0.2 mmol) was added. The reaction mixture was stirred at 80 ℃ for 2 hours. Upon completion, the reaction mixture was concentrated and the residue was purified by chromatography on silica gel (PE/EA 10:1). The main product was identified to be compound **13** accroding to NMR and HRMS analysis.

3-Phenyl-1-tosylquinolin-2(1H)-one (13)[3]



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 9.1 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 2H), 7.68 (s, 1H), 7.59 – 7.52 (m, 2H), 7.50 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.40 – 7.30 (m, 6H), 2.43 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.76, 145.15, 139.02, 137.04, 136.77, 134.87, 133.13, 129.95, 129.47, 128.92, 128.68, 128.67, 128.48, 128.26, 124.52, 121.95, 118.83, 21.68. **HRMS** (ESI) m/z calcd. for $C_{22}H_{18}NO_3S$ $[M+H]^+$ 376.1002, found 376.1006.

Procedure for reaction of phenol and ynamide 12.

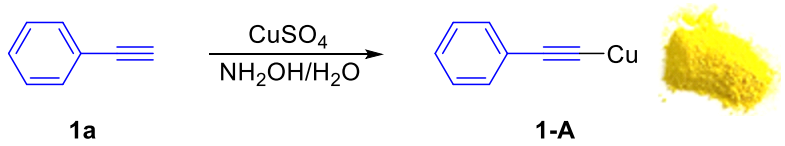
To a solution of ynamide **12** (0.1 mmol) in 1 mL DMSO, Na_2CO_3 (0.1 mmol) and phenol (0.2 mmol) was added. The reaction mixture was strried at 40 ℃ for 12 hours. Upon completion, 0.1 mmol 1,3,5-trimethoxybenzene was added as internal standard. Crude ^{1}H NMR analysis of the obtained mixture indicates that **4bm** was obtained in 50% yield.

Procedure for reaction of *n*-butylamine and ynamide 12.

To a solution of ynamide **12** (0.1 mmol) in 1 mL DMSO, *n*-butylamine (0.2 mmol) was added. The reaction mixture was strried at room temperature for 2 hours. Upon completion, 0.1 mmol 1,3,5-trimethoxybenzene was added as internal standard. Crude ^{1}H NMR analysis of the obtained mixture indicates that **4a** was obtained in 91% yield.

4.3 Exploring the intermediace of (phenylethynyl)copper

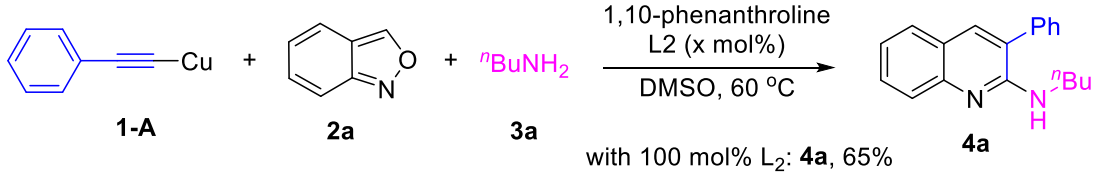
Preparation of (phenylethynyl)copper.[4]



1a **1-A**

To an ice-cooled solution of copper sulfate pentahydrate (1.25g, 5 mmol), 28% aqueous ammonia (5 mL), water (50 mL), and hydroxylamine hydrochloride (0.7 g, 10 mmol) was added a solution of ethynylbenzene (5 mmol) in ethanol (30 mL), and the mixture was stirred for 5 min. The precipitate was filtered, washed with water (15 mL), ethanol (15 mL), and ethyl acetate (2 x 20 mL), dried in vacuo overnight to give the corresponding bright yellow powder of (phenylethynyl)copper (90% yield).

The reactions of (phenylethynyl)copper with anthranl 2a and ^{n}BuNH$_2$.



1-A **2a** **3a** **4a**

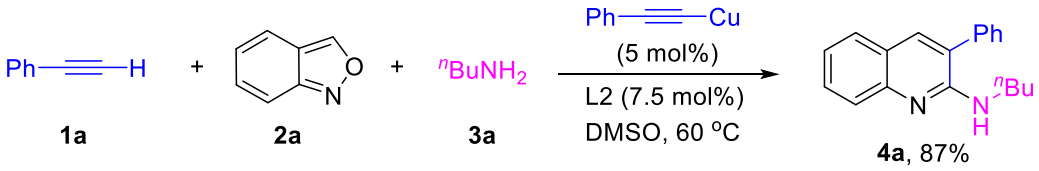
with 100 mol% L_2: **4a**, 65%
with 20 mol% L_2: **4a**, 40%
with 10 mol% L_2: **4a**, 23%
without L_2: **4a**, trace

An oven-dried 20 mL vial was charged with (phenylethynyl)copper **1-A** (0.2 mmol), and different amount of 1,10-phenanthroline (x mol%), and closed with a septum cap. After it was evacuated and back-filled with argon 3 times, DMSO (1.0 mL), anthranil **2a** (0.2 mmol, 1.0 equiv) and amines **3a** (0.4 mmol, 2.0 equiv) were successively added via syringe. The reaction mixture was stirred under an argon atmosphere at 60 ℃ for 12 h. The resulting mixture was quenched with 1 M NH_4Cl aqueous solution water (5 mL), and 0.1 mmol 1,3,5-trimethoxybenzene was added as internal standard. The aqueous layer was extracted 3 times with diethyl ether (5 mL). The combined organic phases

were washed with brine (10 mL), dried over anhydrous $MgSO_4$, filtered, and the organic phase was evaporated under reduced pressure (rotary evaporator). The crude product was analysized by ^{1}H NMR to determine the yield of **4a**.

*To explore the intermediacy of copper alkynyl species in this reaction, copper(I) phenylacetylide was prepared and treated with anthranils and butan-1-amine in DMSO. The reactions were carried out with different amount of 1,10-phenanthroline. When the reaction was conducted without 1,10-phenanthroline, only trace amount of **4a** was detected, which is probably because (phenylethynyl)copper is an inactive polymeric resting state. The additional of 1,10-phenanthroline as ligand can convert (phenylethynyl)copper into a highly active monomeric copper species, thus could facilitate the reaction. **4a** was obtained in 40% yield, when 20 mol% 1,10-phenanthroline was used. When 1,10-phenanthroline was increased to 1 equivalent, **4a** was obtained in 65% yield.*

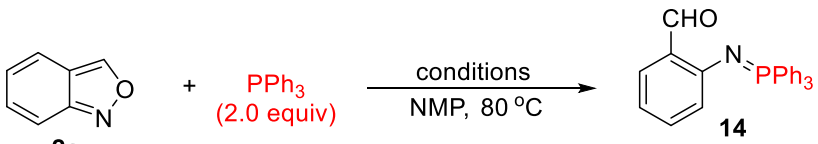
The reaction using (phenylethynyl)copper 1-A as a catalyst.



Fellowing the general procedue A, the reaction of **1a**, **2a** and **3a** was conducted with (phenylethynyl)copper **1-A** as a catalyst. After the reaction, the resulting mixture was quenched with 1 M NH_4Cl aqueous solution water (5 mL), and 0.1 mmol 1,3,5-trimethoxybenzene was added as internal standard. The aqueous layer was extracted 3 times with diethyl ether (5 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous $MgSO_4$, filtered, and the organic phase was evaporated under reduced pressure (rotary evaporator). The crude product was analysized by ^{1}H NMR, and **4a** detected in 87% yield. *This result indicated that (phenylethynyl)copper is an efficient catalyst for the three-component reaction.*

<u>4.4 Inverstigation the role of anthranils by using PPh_3 as a nitrene acceptor.</u>

The reaction of anthranil 2a and PPh_3 under different conditions.

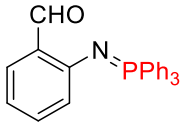


conditions	yield
5 mol% $Cu(OAc)_2$	14%
5 mol% $Cu(OAc)_2$ + 20 mol% K_2CO_3	45%
20 mol% K_2CO_3	trace

The reaction of anthranil **2a** and PPh_3 was carried out under different reaction conditions. First, the corresponding iminophosphorane **14** was detected in 14% NMR yield, when 10 mol% $Cu(OAc)_2$ was used as the catalyst. The yield of iminophosphorane **14** was increased to 45% by using 10 mol% $Cu(OAc)_2$ and 20 mol% K_2CO_3. As a control

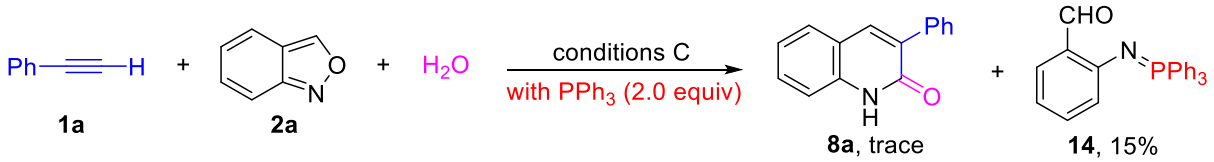
experiment, only a trace amount of iminophosphorane **14** was detected in the absence of copper catalyst. *These results indicates that anthranils may serve as aryl nitrene percusors and Cu(OAc)$_2$ is a reactive catalyst for the nitrene transfer process.*

2-((Triphenyl-l5-phosphanylidene)amino)benzaldehyde (**14**)[5]

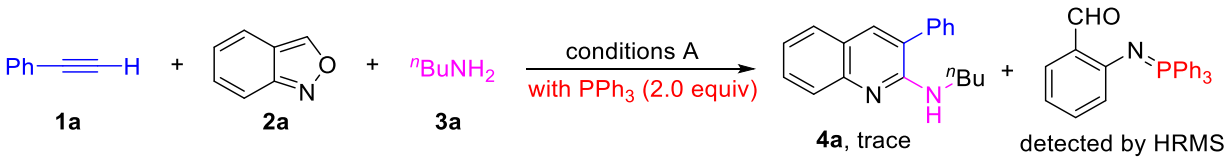


^{1}H NMR (400 MHz, $CDCl_3$) δ 11.11 (s, 1H), 7.78 – 7.66 (m, 6H), 7.69 (dd, *J* = 12.0, 7.2 Hz, 1H), 7.59 – 7.52 (m, 3H), 7.49 – 7.45 (m, 6H), 7.06 – 7.01 (m, 1H), 6.64 (t, *J* = 7.4 Hz, 1H), 6.47 (d, *J* = 8.2 Hz, 1H). **HRMS** (ESI) m/z calcd. for $C_{25}H_{21}NOP$ $[M+H]^+$ 382.1355, found 382.1349.

The influence of PPh_3 on the three-component reaction.



An oven-dried 20 mL vial was charged with $Cu(OAc)_2$ (5 mol%), K_2CO_3 (1.0 equiv) and PPh_3 (0.4 mmol), and closed with a septum cap. After it was evacuated and back-filled with argon 3 times, DMSO (1.0 mL), phenylacetylene (0.3 mmol, 1.5 equiv), anthranil **2a** (0.2 mmol, 1.0 equiv), and H_2O (1.0 mmol, 5.0 equiv) were successively added via syringe. The reaction mixture was stirred under an argon atmosphere at 80 ℃ for 12 h. The resulting mixture was quenched with 1 M LiCl aqueous solution water (5 mL), and 1,3,5-trimethoxybenzene (0.2 mmol) was added as internal standard. The mixture was extracted 3 times with diethyl ether (5 mL). The combined organic phases were dried over anhydrous $MgSO_4$, filtered, and the organic phase was evaporated under reduced pressure (rotary evaporator). The residue was analysized by ^{1}H NMR and GC-MS. Accordingly, the formation of **8a** was almost inhibited, and the corresponding iminophosphorane **14** was detected in 15% NMR yield.

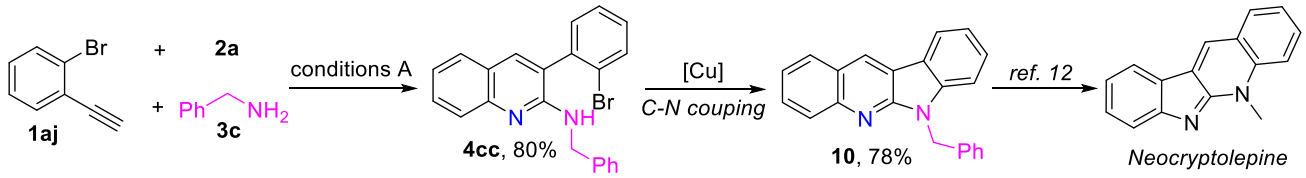


An oven-dried 20 mL vial was charged with $Cu(OAc)_2$ (5 mol%), 1,10-phenanthroline (7.5 mol%) and PPh_3 (0.4 mmol), and closed with a septum cap. After it was evacuated and back-filled with argon 3 times, DMSO (0.5 mL), phenylacetylene (0.3 mmol), anthranil **2a** (0.2 mmol), and *n*-butylamine **3a** (0.4 mmol) were successively added via syringe. The reaction mixture was stirred under an argon atmosphere at 60 ℃ for 12 h. The resulting mixture was

quenched with 1 M LiCl aqueous solution water (5 mL), and the aqueous layer was extracted 3 times with diethyl ether (5 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous $MgSO_4$, filtered, and the organic phase was evaporated under reduced pressure (rotary evaporator). The residue was analysized by ^{1}H NMR, GC-MS, and HRMS. Only trace amount of **4a** was detected. Meanwhile, iminophosphorane **14** was also detected by HRMS.

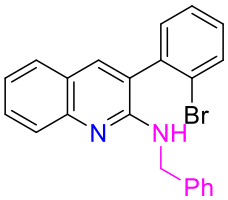
5. Synthetic applications.

5.1 The synthesis of a key intermediate for neocryptolepine



*The synthesis of N-benzyl-3-(2-bromophenyl)quinolin-2-amine (**4cc**)*: Compound **4cc** was prepared following the **general procedure A** from 1-bromo-2-ethynylbenzene **1aj** (1.5 mmol), benzo[*c*]isoxazole **2a** (1.0 mmol) and phenylmethanamine **3c** (2.0 mmol) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a light yellow solid (310.3 mg, 80 %), m.p 83 – 85 ℃.

***N*-Benzyl-3-(2-bromophenyl)quinolin-2-amine (4cc)**

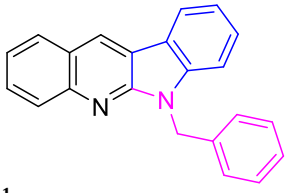


^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (d, *J* = 8.3 Hz, 1H), 9.18 (d, *J* = 8.0 Hz, 1H), 9.15 – 9.07 (m, 3H), 8.93 (d, *J* = 7.4 Hz, 2H), 8.85 – 8.80 (m, 4H), 8.76 (t, *J* = 7.2 Hz, 2H), 8.71 – 8.66 (m, 1H), 6.42 (dd, *J* = 32.4, 5.6 Hz, 2H), 6.25 (t, *J* = 5.6 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.5, 147.7, 139.5, 137.5, 136.6, 133.1, 131.5, 129.8, 129.3, 128.2, 127.9, 127.4, 127.3, 126.7, 126.2, 124.5, 124.0, 123.0, 122.0, 45.1 ppm. **HRMS** (ESI) m/z calcd. for $C_{22}H_{18}BrN$ $[M+H]^+$ 389.0648, found 389.0645.

The C-N coupling was conducted under the reported conditions:[6] An oven-dried 20 mL vial was charged with CuI (30 mol%), Cs_2CO_3 (2.0 equiv), Boc-L-hydroxyproline (30 mol%), and the obtained N-benzyl-3-(2-bromophenyl)quinolin-2-amine (0.5 mmol, 1.0 equiv), and closed with a septum cap. After it was evacuated and back-filled with argon 3 times, toluene (2.0 mL) was added via syringe. The reaction mixture was stirred under an argon atmosphere at 130 ℃ for 24 h. After completion of the reaction, the crude product was filtered through a short pad of

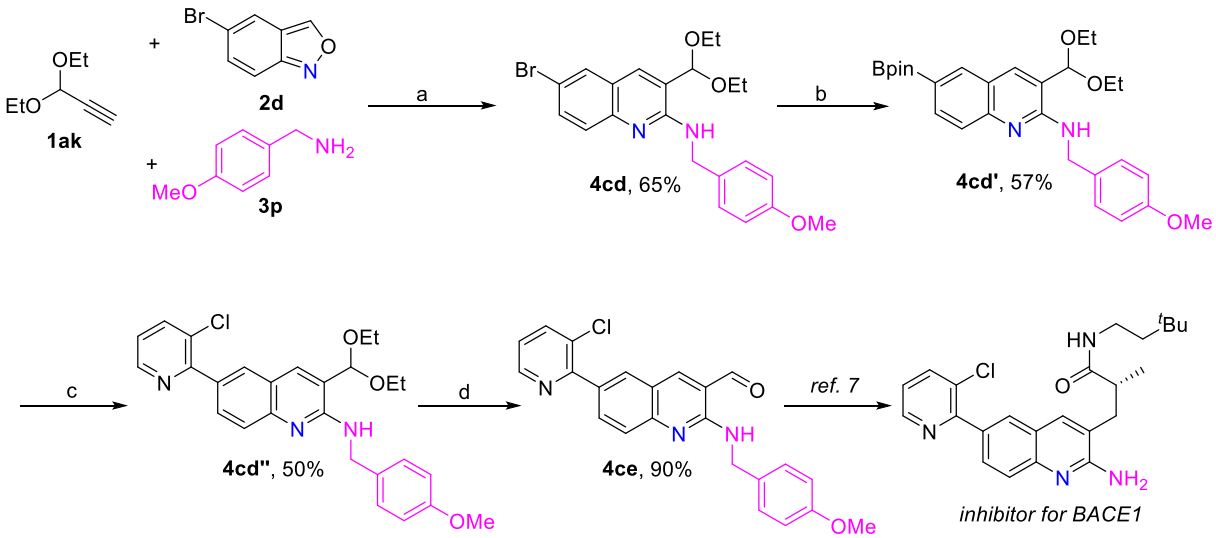
SiO_2 and washed with CH_2Cl_2. The organic phase was evaporated under reduced pressure (rotary evaporator). The residue was purified bycolumn chromatography (SiO_2, PE/EA = 30:1) to give 6-benzyl-6H-indolo[2,3-b]quinoline (87.2 mg, 78%) as a light yellow oil.

6-Benzyl-6H-indolo[2,3-b]quinoline (10)[6]



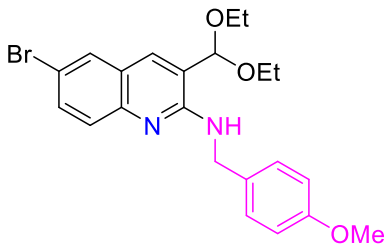
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.11 (d, *J* = 8.0 Hz, 2H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.68 (t, *J* = 8.2 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.33 – 7.26 (m, 3H), 7.23 (dd, *J* = 13.2, 7.4 Hz, 4H), 5.72 (s, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.7, 146.9, 142.1, 137.3, 128.8, 128.6, 128.4, 128.0, 127.7, 127.4, 127.3, 127.2, 124.4, 123.0, 121.4, 120.7, 120.1, 118.1, 109.7, 45.0 ppm. **MS** (EI) m/z (%) 318.0 $[M]^+$, 217.0, 141.0, 91.0. The data match those reported in literature.[6]

5.2 Procedure for the formal synthesis of inhibitor for BACE1.[7]



Step a: The reaction of 3,3-diethoxyprop-1-yne **1ak** (6.0 mmol), 5-bromobenzo[c]isoxazole **2d** (5.0 mmol), and (4-methoxyphenyl)methanamine **3p** (10.0 mmol) was carried out following the **general procedure A**. 6-Bromo-3-(diethoxymethyl)-N-(4-methoxybenzyl)quinolin-2-amine (**4cd**) was purified by column chromatography (SiO_2, PE/EA = 10:1) as a light yellow oil (1.45 g, 65 %).

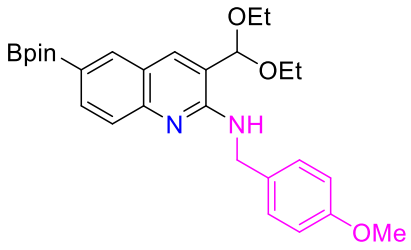
6-Bromo-3-(diethoxymethyl)-N-(4-methoxybenzyl)quinolin-2-amine (4cd)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.73 (d, *J* = 1.9 Hz, 1H), 7.63 – 7.50 (m, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.29 (s, 1H), 5.41 (s, 1H), 4.73 (d, *J* = 5.2 Hz, 2H), 3.77 (s, 3H), 3.63 – 3.45 (m, 4H), 1.19 (t, *J* = 7.1 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.7, 154.3, 146.5, 134.4, 132.5, 131.7, 129.6, 129.1, 127.7, 124.0, 120.8, 114.5, 113.8, 99.4, 61.1, 55.2, 44.6, 15.0 ppm. **HRMS** (ESI) m/z calcd. for $C_{22}H_{26}BrN_2O_3$ $[M+H]^+$ 445.1121, found 445.1132.

Step b: An oven-dried 50 mL vial was charged with dichloro(1,10-bis(diphenylphosphino)ferrocene) palladium (0.15 mmol, 5 mol%), KOAc (6.0 mmol, 2 equiv), $Bpin_2$ (4.5 mmol, 1.5 equiv), and closed with a septum cap. After it was evacuated and back-filled with argon 3 times, a solution of **4cd** (3.0 mmol) in 20 mL toluene was added via syringe. The reaction mixture was stirred under an argon atmosphere at 90 ℃ for 12 h. The reaction was allowed to cool to room temperature before filtering through a pad of silica, and washed with dichloromethane (50 mL). The solvent was evaporated under reduced pressure (rotary evaporator). The residue was purified by column chromatography (SiO_2, PE/EA = 10:1) to give 3-(diethoxymethyl)-N-(4-methoxybenzyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)quinolin-2-amine (**4cd'**) as a yellow oil (0.84 g, 57 %).

3-(Diethoxymethyl)-N-(4-methoxybenzyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)quinolin-2-amine (4cd')

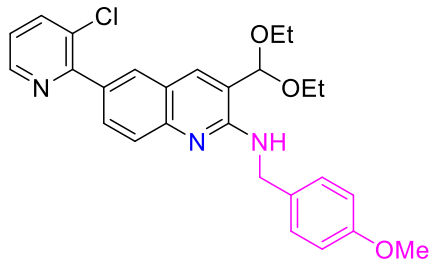


^{1}H NMR (400 MHz, CDCl3) δ 8.14 (s, 1H), 7.97 (s, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.72 (s, 1H), 7.35 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.32 (s, 1H), 5.42 (s, 1H), 4.77 (d, *J* = 5.0 Hz, 2H), 3.80 (s, 3H), 3.64 – 3.47 (m, 4H), 1.37 (s, 12H), 1.19 (t, *J* = 7.1 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, CDCl3) δ 158.7, 154.9, 136.2, 136.0, 134.9, 131.8, 129.2, 125.0, 122.2, 119.9, 113.9, 99.9, 83.7, 61.2, 55.2, 44.8, 29.7, 24.9, 15.0 ppm. **HRMS** (ESI) m/z calcd. for $C_{28}H_{38}BN_2O_5$ $[M+H]^+$ 493.2868, found 493.2884.

Step c: An oven-dried 50 mL vial was charged with bis(4-(di-tert-butylphosphino)-N,N-dimethylbenzenamine) dichloropalladium (5 mol%), KOAc (2 equiv), 2-bromo-3-chloropyridine (1.5 equiv), and closed with a septum cap. After it was evacuated and back-filled with argon 3 times, a solution of **4cd'** (0.738 g, 1.5 mmol) in a mixture solvent of EtOH (30.0 mL) and water (5.0 mL) was added via syringe. The reaction mixture was stirred under an argon atmosphere at 80 ℃ for 5 h. The resulting mixture was quenched with saturate NH_4Cl aqueous solution (20 mL), and the aqueous layer was extracted 3 times with DCM (30 mL). The combined organic phases were dried over anhydrous $MgSO_4$, filtered, and the organic phase was evaporated under reduced pressure (rotary evaporator). The residue was

purified by column chromatography (SiO_2, PE/EA = 10:1) to give 6-(3-chloropyridin-2-yl)-3-(diethoxymethyl)-N-(4-methoxybenzyl)quinolin-2-amine (**4cd''**) as a yellow oil (357.8 mg, 50%).

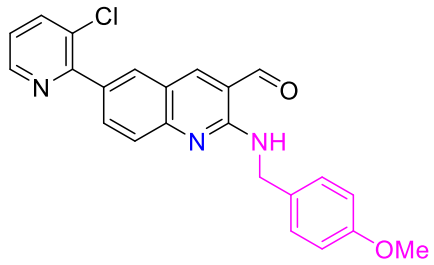
6-(3-Chloropyridin-2-yl)-3-(diethoxymethyl)-N-(4-methoxybenzyl)quinolin-2-amine (4cd'')



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (dd, *J* = 4.6, 1.4 Hz, 1H), 8.07 (d, *J* = 1.9 Hz, 1H), 8.02 (s, 1H), 7.96 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.80 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 7.20 (dd, *J* = 8.0, 4.6 Hz, 1H), 6.88 (d, *J* = 8.6 Hz, 2H), 6.35 (s, 1H), 5.46 (s, 1H), 4.79 (d, *J* = 5.2 Hz, 2H), 3.80 (s, 3H), 3.72 – 3.49 (m, 4H), 1.20 (t, *J* = 7.1 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.7, 156.3, 154.8, 147.6, 138.2, 136.1, 131.8, 131.7, 130.7, 130.1, 129.2, 129.1, 125.5, 122.6, 122.1, 120.3, 113.9, 99.8, 61.2, 55.2, 44.8, 15.0 ppm. **HRMS** (ESI) m/z calcd. for $C_{27}H_{29}ClN_3O_3$ $[M+H]^+$ 478.1892, found 478.1901.

Step d: An oven-dried 20 mL vial was charged with tetrahydrofuran (6.0 mL), and 1 M hydrochloric acid (2 mL), and a solution of **4cd''** (350.0 mg) in 2 mL tetrahydrofuran was added.The reaction mixture was stirred at room temperature for 12 h. The resulting mixture was quenched with saturate $NaHCO_3$ aqueous solution, and the aqueous layer was extracted 3 times with diethyl ether (20 mL). The combined organic phases were washed with brine (30 mL), dried over anhydrous $MgSO_4$, filtered, and the organic phase was evaporated under reduced pressure (rotary evaporator). The residue was purified by column chromatography (SiO_2, PE/EA = 10:1) to give 6-(3-chloropyridin-2-yl)-2-((4-methoxybenzyl)amino)quinoline-3-carbaldehyde (**4ce**) as a yellow oil (266.5 mg, 90 %).

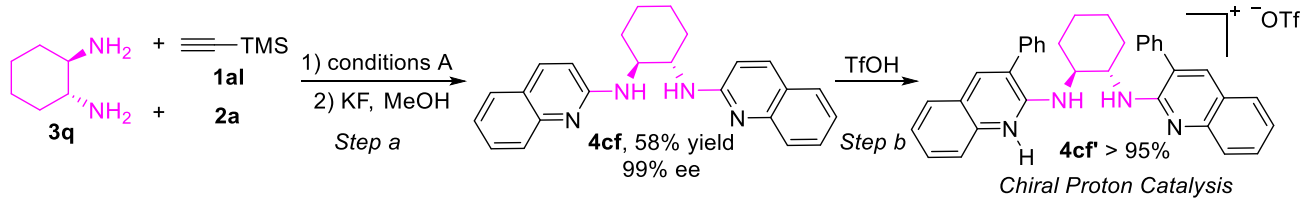
6-(3-Chloropyridin-2-yl)-2-((4-methoxybenzyl)amino)quinoline-3-carbaldehyde (4ce)



^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 8.62 (dd, *J* = 4.6, 1.3 Hz, 1H), 8.37 (t, *J* = 5.0 Hz, 1H), 8.30 (s, 1H), 8.13 (d, *J* = 1.8 Hz, 1H), 8.08 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.24 (dd, *J* = 8.1, 4.6 Hz, 1H), 6.89 (d, *J* = 8.6 Hz, 2H), 4.83 (d, *J* = 5.4 Hz, 2H), 3.80 (s, 3H) ppm. **^{13}C NMR** (100 MHz,

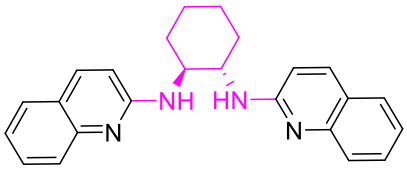
$CDCl_3$) δ 193.0, 158.8, 155.4, 154.9, 149.0, 147.7, 138.3, 134.6, 132.3, 131.1, 130.4, 130.2, 129.2, 126.1, 123.1, 121.4, 117.7, 114.0, 55.3, 44.2, 29.7 ppm. **HRMS** (ESI) m/z calcd. for $C_{23}H_{19}ClN_3O_2$ $[M+H]^+$ 404.1160, found 404.1165.

5.3 Procedure for the synthesis of chiral proton catalyst.



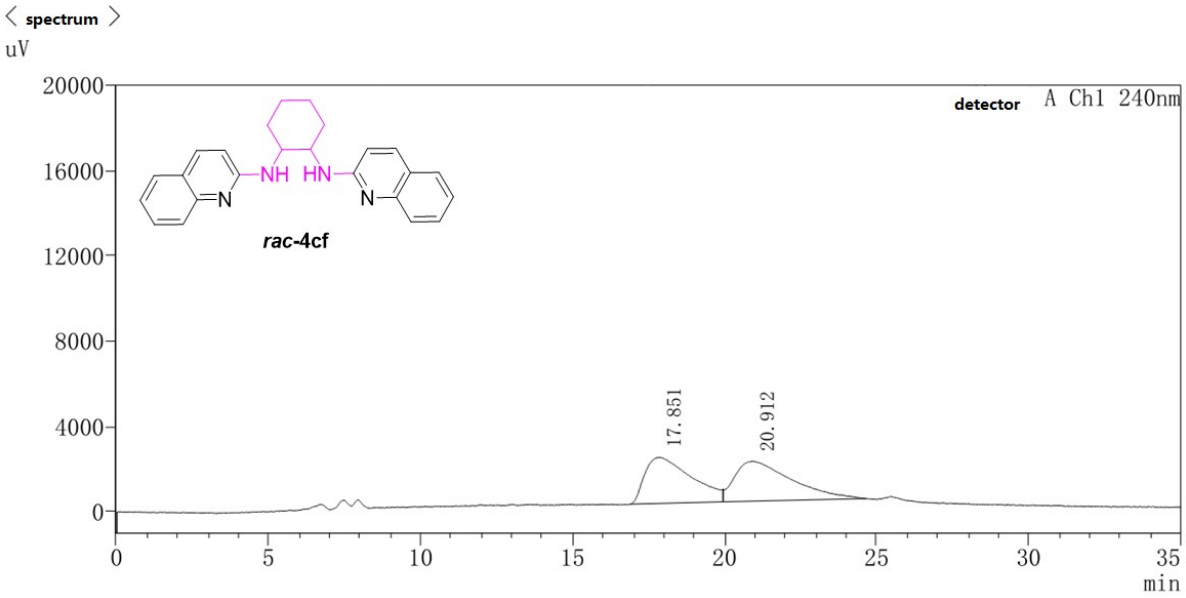
Step a: An oven-dried 20 mL vial was charged with $Cu(OAc)_2$ (5 mol%), 1,10-phenanthroline (7.5 mol%), and $NaHCO_3$ (1.0 mmol, 1.0 equiv), and closed with a septum cap. After it was evacuated and back-filled with argon 3 times, NMP (5.0 mL), anthranil (3.0 mmol, 3.0 equiv), ethynyltriisopropylsilane (8.0 mmol, 8.0 equiv) and (*1R*, *2R*)-cyclohexane-1,2-diamine (1.0 mmol, 1.0 equiv) were successively added via syringe. The reaction mixture was stirred under an argon atmosphere at 60 ℃ for 24 h. After completion of the reaction, the resulting mixture was diluted with 1 M LiCl aqueous solution water (20 mL). Following phase separation, the aqueous layer was extracted 3 times with diethyl ether (10 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous $MgSO_4$, filtered, and the organic phase was evaporated under reduced pressure (rotary evaporator). The residue was dissolved in 3 mL MeOH and 2.0 mmol KF was added. The mixture was stirred at 100 ℃ for 12 h. After completion, the reaction solvent was evaporated under reduced pressure (rotary evaporator). The residue was purified by column chromatography (SiO_2, PE/EA = 2:1) to give **H,Quin-BAM** (**4cf**).

(*1R, 2R*)-*N*^{1},*N*^{2}-Di(quinolin-2-yl)cyclohexane-1,2-diamine (4cf)[8]



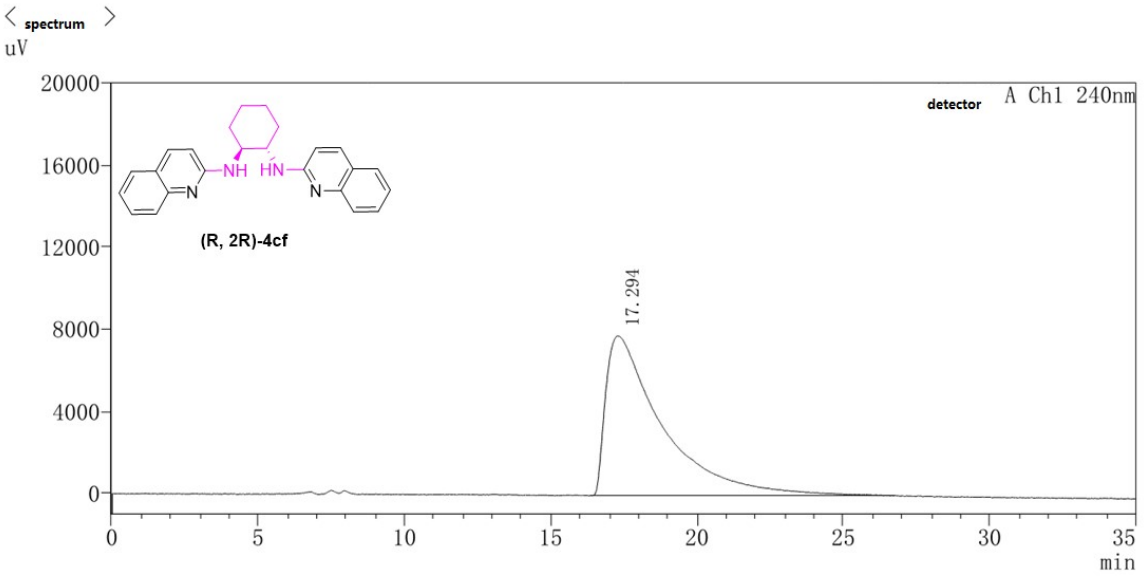
The title compound **4cf** was obtained as a white soild (214.1 mg, 58% yield, 99% ee), m.p 157 – 158 ℃. $[\alpha]_D^{20}$ = +746.4 (*c* 0.1 in $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.9 Hz, 2H), 7.50 (dd, *J* = 8.0, 4.2 Hz, 4H), 7.17 (t, *J* = 7.4 Hz, 2H), 6.30 (d, *J* = 8.8 Hz, 2H), 5.94 (s, 2H), 4.14 (s, 2H), 2.38 (d, *J* = 12.1 Hz, 2H), 1.85 – 1.83 (m, 2H), 1.54 – 1.37 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.0, 147.7, 136.7, 129.4, 127.4, 125.8, 123.2, 121.7, 113.0, 56.1, 32.8, 24.9. **HRMS** (ESI) m/z calcd. for $C_{24}H_{25}N_4$ $[M+H]^+$ 369.2074, found 369.2081. **HPLC analysis**: The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column [Daicel chiracel® IB, 240 nm, *n*-hexane : *i*-PrOH = 95 : 5 as the eluent, flow rate: 0.5 mL/min, temperature 40 ℃, retention time: 17.3 min (major isomer)].

HPLC spectrum



Detector A Ch1 240nm

number	retention time	area	height	concentration	mark	compound
1	17.851	231961	2159	48.875	M	
2	20.912	242640	1869	51.125	V M	
total		474600	4028			



Detector A Ch1 240nm

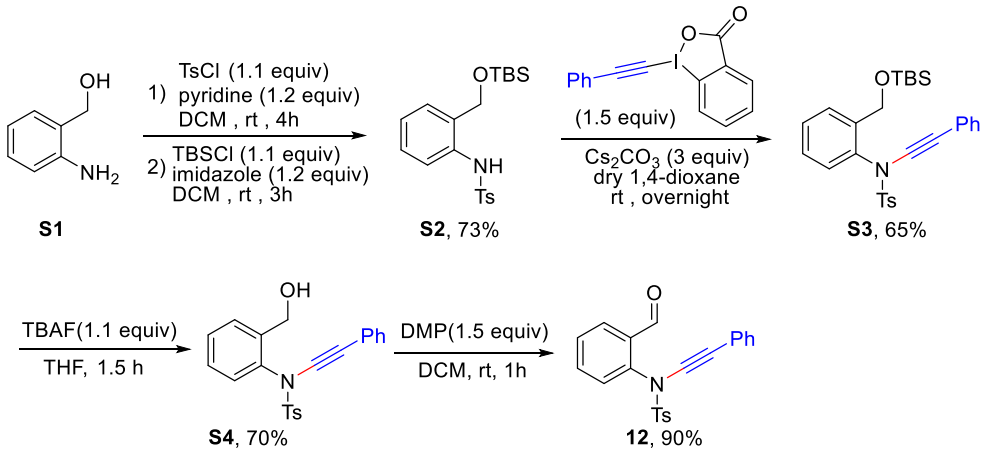
number	retention time	area	height	concentration	mark	compound
1	17.294	1042814	7777	100.000	M	
total		1042814	7777			

Step b: To a solution of **4cf** (0.1 mmol) in DCM was added freshly distilled trifluoromethanesulfonic acid (0.1 mmol, 8 ul) via syringe at 0 ℃ (ice-bath). The reaction was allowed to stir for 2 h and was concentrated to afford **H,Quin-BAM•HOTf (4cf')** as a white solid, mp 135 – 136 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33 (br s, 3H), 7.80 (m, 4H), 7.58 (t, *J* = 7.5 Hz, 2H), 7.54 (d, *J* = 7.9 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 6.83 (br s, 2H), 4.20 (m, 1H), 2.18 (d, *J* = 12.6 Hz, 2H), 1.84 (d, *J* = 8.1 Hz, 2H), 1.74 – 1.71 (d, *J* = 9.3 Hz, 2H), 1.58 – 1.51 (m, 2H). **^{13}C NMR** (100 MHz,

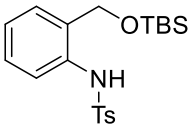
$CDCl_3$) δ 154.1, 140.9, 131.9, 128.0, 124.5, 121.8, 120.5, 118.6, 113.1, 56.4, 31.4, 23.9. **HRMS** (ESI) m/z calcd. for $C_{25}H_{25}F_3N_4O_3S$ $[M]^+$ 369.2074, found 369.2078.

6. Preparation of Substrates

Ynamide 12 was prepared according to the procedure reported by Ye's group.[3]

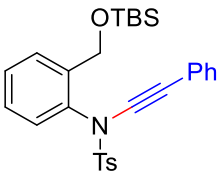


N-(2-(((*tert*-Butyldimethylsilyl)oxy)methyl)phenyl)-4-methylbenzenesulfonamide (S2)



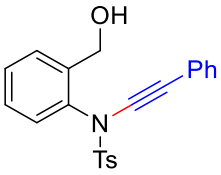
A dried 100mL round bottom flask was charged with N-(2-(hydroxymethyl)phenyl)-4-methylbenzenesulfonamide (19 mmol, 1 equiv, 5.2731 g), TBSCl (20.9 mmol, 1.1 equiv, 3.150 g) and imidazole (22.8 mmol, 1.2 equiv, 1.5522 g) and 40mL dichloromethane.The mixture was stirred at room temperature for 12 h. After completion of the reaction, the resulting mixture was diluted with saturated sodium chloride aqueous solution (20 mL) and DCM (3 x 20 mL) for extraction. Following phase separation, the combined organic phases were washed with brine (10 mL), dried over anhydrous $MgSO_4$, filtered, and the organic phase was evaporated under reduced pressure (rotary evaporator). The residue was purified bycolumn chromatography (SiOg, ethyl acetate/petroleum ether gradient = 20:1) to give the desired product (6.0 g, 80% yeild) as a white solid. **^{1}H NMR** (400 MHz,$CDCl_3$) δ 8.37 (s, 1H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.06 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 1H), 4.38 (s, 2H), 2.41 (s, 3H), 0.95 (s, 9H), 0.10 (s, 6H) ppm. The data match those reported in literature.[3]

N-(2-(((*tert*-Butyldimethylsilyl)oxy)methyl)phenyl)-4-methyl-N-(phenylethynyl)benzenesulfonamide (S3)



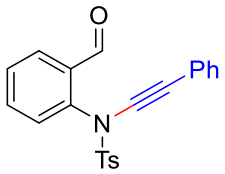
An oven-dried 20 mL vial was charged with dry Cs_2CO_3 (3 equiv, 978 mg), N-(2-(((tert-butyldimethylsilyl)oxy)methyl)phenyl)-4-methylbenzenesulfonamide (1 mmol, 1 equiv, 392 mg) and dry 1-(phenylethynyl)-1,2-benziodoxol-3(1H)-one (1.5 mmol, 1.5 equiv, 566 mg) and closed with a septum cap. After it was evacuated and-back-filled with argon 3 times, dry 1,4-dioxane (5 mL) was added-via syringe. The reaction mixture was stirred under an argon atmosphere at room temperature for overnight. After completion of the reaction, the resulting mixture was diluted with saturated NaCl solution water (10 mL) and DCM (3 x 10 mL) for extraction. The combined organic phases dried over anhydrous $MgSO_4$, and was evaporated under reduced pressure (rotary evaporator). The residue was purified bycolumn chromatography (SiOg, ethyl acetate/petroleum ether gradient = 30:1) to give the desire product (294.6 mg, 60% yield) as a yellow soil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.70 (d, *J* = 6.3 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 8.6 Hz,4H), 7.31 – 7.26 (m, 3H), 7.23 – 7.15 (m, 1H), 6.89 (dd, *J* = 7.9, 1.3 Hz, 1H), 4.91 (s, 2H), 2.48 (s, 3H), 0.96 (s, 9H), 0.12 (s, 6H) ppm. The data match those reported in literature.[3]

N-(2-(Hydroxymethyl)phenyl)-4-methyl-N-(phenylethynyl)benzenesulfonamide (S4)



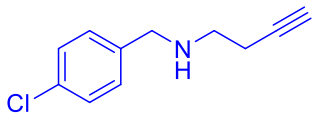
A dried 20 mL pressure-resistant tube was added with N-(2-(((*tert*-butyldimethylsilyl)oxy)methyl)phenyl)-4-methyl-N-(phenylethynyl)benzenesulfonamide (3 mmol, 1 equiv, 1.4735 g), THF (6 mL) and slowly instill TBAF (1.1 equiv). The mixture was stirred at ice water bath to room temperature for 1.5 h. After completion of the reaction, the solvent was removed by distillation under reduced pressure (rotary evaporator). The residue was purified bycolumn chromatography (SiOg, ethyl acetate/petroleum ether gradient = 5:1) to give the pure product N-(2-(hydroxymethyl)phenyl)-4-methyl-N-(phenylethynyl)benzenesulfonamide (791.9 mg, 70% yield) as a yellow soild. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.66 (d, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.39 – 7.33 (m, 4H), 7.28 (dd, *J* = 7.6, 4.4 Hz, 3H), 7.22 (t, *J* = 7.7 Hz, 1H), 6.81 (dd, *J* = 8.0, 1.3 Hz, 1H), 4.84 (s, 2H), 2.63 (s, 1H), 2.49 (s, 3H) ppm. The data match those reported in literature.[3]

N-(2-Formylphenyl)-4-methyl-N-(phenylethynyl)benzenesulfonamide (12)



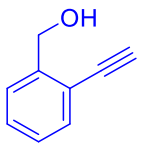
A dried 20 mL pressure-resistant tube was charged with Dess-Martin periodinane (4 mmol, 2 equiv, 1696.6 mg), N-(2-(hydroxymethyl)phenyl)-4-methyl-N-(phenylethynyl)benzenesulfonamide (2 mmol, 1 equiv, 754.19 mg), and DCM (10 mL). The mixture was stirred at ice water bath to room temperature for 1 hour. After completion of the reaction, the resulting mixture was diluted with saturated Na_2CO_3 solution water (10 mL) and DCM (3 x 10 mL) for extraction. The combined organic phases dried over anhydrous $MgSO_4$, and the organic phase was evaporated under reduced pressure (rotary evaporator). The residue was purified bycolumn chromatography (SiOg, ethyl acetate/petroleum ether gradient=10:1) to give the desired product (675.2 mg, 90% yield) as a brown solid. **^{1}H NMR** (400 MHz, $CDCl_3$)δ 10.34 (s, 1H), 8.03 (d, *J* = 9.4 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.58 – 7.48 (m, 2H), 7.39 – 7.35 (m, 3H), 7.33 (s, 1H), 7.32 – 7.29 (m, 3H), 7.09 (d, *J* = 7.3 Hz, 1H), 2.48 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 188.6, 145.8, 140.8, 134.4, 133.6, 132.0, 131.5, 129.8, 129.4, 128.6, 128.5, 128.4, 128.3, 127.8, 122.0, 82.9, 70.8, 21.8 ppm. The data match those reported in literature.[3]

Preparation of N-(4-chlorobenzyl)but-3-yn-1-amine (1ag)[9]



4-Bromobut-1-yne (2 mmol, 1 equiv) was added dropwise to (4-chlorophenyl)methanamine (12 mmol, 6 equiv) and the mixture stirred at room temperature for 15 h. Then, 1 M NaOH (16 mL) and Et_2O (8 mL) were added and the organic layer was separated. The aqueous layer was extracted 3 times with Et_2O, and the combined organic layers were dried over anhydrous magnesium sulfate and concentrated in vacuo (rotary evaporator). The residue was purified by column chromatography (SiOg, ethyl acetate/petroleum ether gradient = 30:1) to afford N-(4-chlorobenzyl)but-3-yn-1-amine **1ag** (216 mg, 56% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 3.8 Hz, 4H), 3.76 (s, 2H), 2.75 (t, *J* = 6.5 Hz, 2H), 2.38 (td, *J* = 6.5, 2.6 Hz, 2H), 1.98 (t, *J* = 2.6 Hz, 1H), 1.66 (s, 1H) ppm. The data match those reported in literature.[9]

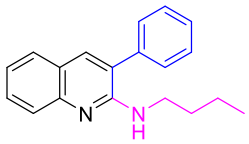
Preparation of (2-ethynylphenyl)methanol (1ah)[10]



To a solution of aryl iodo (2.4 mmol) in triethylamine (2 mL) and DMF (5 mL) were added ethynyltrimethylsilane (282.4 mg, 2.88 mmol) and $Pd(PPh_3)_2Cl_2$ (6 mol%) and CuI (5 mol%) at room temperature. Then the mixture was stirred at 50 ℃ for 12 h under N_2. After the starting material was consumed, the reaction mixture was quenched saturated NH_4Cl solution and extracted with ethyl acetate. The combined organic extracts were washed with water and brine, and dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product obtained in the first step was dissolved in 5 mL MeOH and 2.4 mmol tetrabutylammonium fluoride (TBAF) was added. The reaction mixture was stirred at room temperature for 2 h. After completion, the reaction was quenched saturated NaCl solution and extracted with ethyl acetate. The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel to give **1ah** 282 mg in 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 7.3 Hz, 1H), 7.37 (td, *J* = 7.6, 1.1 Hz, 1H), 7.23 – 7.28 (m, 1H), 4.84 (s, 2H), 3.34 (s, 3H). The data match those reported in literature.[10]

7. Synthesis and Characterization of the Corresponding Products

***N*-Butyl-3-phenylquinolin-2-amine (4a)**[11]



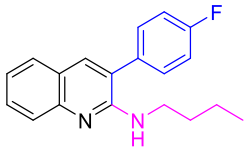
The title compound **4a** was prepared following the **general procedure A** from ethynylbenzene **1a** (0.45 mmol), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow oil (66.3 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.4 Hz, 1H), 7.65 (s, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.57 – 7.53 (m, 1H), 7.53 – 7.42 (m, 5H), 7.21 (t, *J* = 7.4 Hz, 1H), 4.78 (s, 1H), 3.59 (dd, *J* = 12.6, 7.1 Hz, 2H), 1.60 (m, 2H), 1.40 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 147.7, 137.6, 136.0, 129.3, 129.2, 129.0, 128.1, 127.3, 126.0, 125.6, 123.4, 121.9, 41.2, 31.6, 20.3, 13.9 ppm.

MS (EI) m/z (%) 276.0 $[M]^+$, 261.0, 247.0, 233.0, 219.0, 204.0, 77.0. The data match those reported in literature.[11]

***N*-Butyl-3-(4-fluorophenyl)quinolin-2-amine (4b)**



The title compound **4b** was prepared following the **general procedure A** from 1-ethynyl-4-fluorobenzene **1b** (0.45 mmol), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow oil (75 mg, 85%).

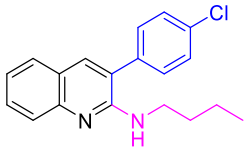
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 1H), 7.59 (s, 1H), 7.57 – 7.49 (m, 2H), 7.44 – 7.38 (m, 2H), 7.21 – 7.13 (m, 3H), 4.63 (t, *J* = 4.6 Hz, 1H), 3.59 – 3.51 (m, 2H), 1.61 – 1.53 (m, 2H), 1.37 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5 (d, *J* = 247.8 Hz), 154.4, 147.7, 136.2, 133.45 (d, *J* = 3.4 Hz), 130.8 (d, *J* = 8.1 Hz), 129.3, 127.3, 126.1, 124.5, 123.2, 122.0, 116.12 (d, *J* = 21.4 Hz), 41.2, 31.6, 20.3, 13.9 ppm.

^{19}F NMR (375 MHz, $CDCl_3$) δ -113.3 ppm.

HRMS (ESI) m/z calcd. for $C_{19}H_{20}FN_2$ $[M+H]^+$ 295.1605, found 295.1603.

***N*-Butyl-3-(4-chlorophenyl)quinolin-2-amine (4c)**



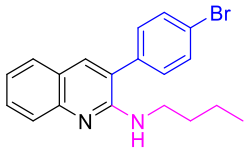
The title compound **4c** was prepared following the **general procedure A** from 1-chloro-4-ethynylbenzene **1c** (0.45 mmol), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow soild (72.6 mg, 78%), m.p 53 – 55 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 1H), 7.62 (s, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.56 – 7.51 (m, 1H), 7.50 – 7.46 (m, 2H), 7.43 – 7.39 (m, 2H), 7.23 – 7.18 (m, 1H), 4.63 (s, 1H), 3.57 (m, 2H), 1.62 – 1.54 (m, 2H), 1.38 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 147.8, 136.3, 136.1, 134.2, 130.4, 129.5, 129.4, 127.4, 126.1, 124.4, 123.2, 122.1, 41.2, 31.6, 20.3, 13.9 ppm.

HRMS (ESI) m/z calcd. for $C_{19}H_{20}ClN_2$ $[M+H]^+$ 311.1310, found 311.1304.

3-(4-Bromophenyl)-*N*-butylquinolin-2-amine (4d)



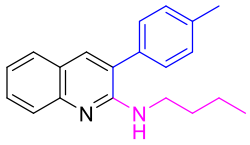
The title compound **4d** was prepared following the **general procedure A** from 1-bromo-4-ethynylbenzene **1d** (0.45 mmol), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow oil (91.4 mg, 86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 1H), 7.65 – 7.62 (m, 2H), 7.61 (s, 1H), 7.59 – 7.53 (m, 2H), 7.37 – 7.32 (m, 2H), 7.24 – 7.19 (m, 1H), 4.66 (t, *J* = 5.0 Hz, 1H), 3.59 (m, 2H), 1.64 – 1.55 (m, 2H), 1.42 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 147.7, 136.5, 136.2, 132.3, 130.7, 129.4, 127.3, 126.1, 124.3, 123.2, 122.3, 122.1, 41.2, 31.6, 20.3, 13.9 ppm.

HRMS (ESI) m/z calcd. for $C_{19}H_{20}BrN_2$ $[M+H]^+$ 355.0804, found 355.0801.

***N*-Butyl-3-(*p*-tolyl)quinolin-2-amine (4e)**



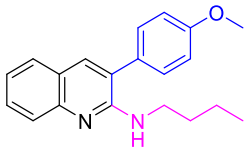
The title compound **4e** was prepared following the **general procedure A** from 1-ethynyl-4-methylbenzene **1e** (0.45 mmol), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow oil (65.3 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 1H), 7.62 (s, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 4.79 (s, 1H), 3.57 (dd, *J* = 12.7, 7.0 Hz, 2H), 2.44 (s, 3H), 1.62 – 1.54 (m, 2H), 1.39 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 147.6, 138.0, 135.9, 134.6, 129.9, 129.1, 128.9, 127.9, 126.0, 125.6, 123.4, 121.8, 41.2, 31.6, 21.2, 20.3, 13.9 ppm.

HRMS (ESI) m/z calcd. for $C_{20}H_{23}N_2$ $[M+H]^+$ 291.1856, found 291.1855.

***N*-Butyl-3-(4-methoxyphenyl)quinolin-2-amine (4f)**



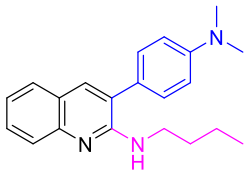
The title compound **4f** was prepared following the **general procedure A** from 1-ethynyl-4-methoxybenzene **1f** (0.45 mmol), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow oil (75.3 mg, 82%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 1H), 7.61 (s, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 8.5 Hz, 2H), 4.78 (s, 1H), 3.88 (s, 3H), 3.57 (dd, *J* = 12.9, 6.7 Hz, 2H), 1.63 – 1.55 (m, 2H), 1.40 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 154.8, 147.5, 135.9, 130.2, 129.7, 129.0, 127.2, 126.0, 125.3, 123.4, 121.8, 114.6, 55.3, 41.2, 31.6, 20.3, 13.9 ppm.

HRMS (ESI) m/z calcd. for $C_{20}H_{23}N_2O$ $[M+H]^+$ 307.1805, found 307.1802.

***N*-Butyl-3-(4-(dimethylamino)phenyl)quinolin-2-amine (4g)**



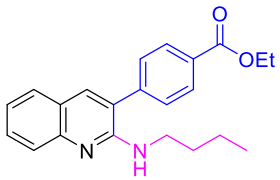
The title compound **4g** was prepared following the **general procedure A** from N,N-dimethyl-4-((trimethylsilyl)ethynyl)aniline **1g** (0.45 mmol), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow oil (54.5 mg, 57%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.3 Hz, 1H), 7.60 (s, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.34 (d, *J* = 8.7 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 6.83 (d, *J* = 8.7 Hz, 2H), 4.92 (s, 1H), 3.57 (dd, *J* = 12.6, 7.0 Hz, 2H), 3.03 (s, 6H), 1.62 – 1.56 (m, 2H), 1.40 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 150.2, 135.5, 129.7, 128.8, 127.2, 126.0, 125.8, 125.7, 124.9, 123.6, 121.8, 112.8, 41.2, 40.4, 31.7, 20.3, 13.9 ppm.

HRMS (ESI) m/z calcd. for $C_{21}H_{26}N_3$ $[M+H]^+$ 320.2121, found 320.2118.

Ethyl 4-(2-(butylamino)quinolin-3-yl)benzoate (4h)



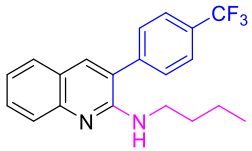
The title compound **4h** was prepared following the **general procedure A** from ethyl 4-ethynylbenzoate **1h** (0.45 mmol), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow oil (79.4 mg, 76%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.14 (m, 2H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.64 (s, 1H), 7.59 – 7.51 (m, 4H), 7.23 – 7.17 (m, 1H), 4.67 (t, *J* = 5.1 Hz, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 3.57 (m, 2H), 1.61 – 1.54 (m, 2H), 1.43 (t, *J* = 7.1 Hz, 3H), 1.36 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 153.9, 147.8, 142.3, 136.3, 130.3, 130.1, 129.5, 129.0, 127.4, 126.0, 124.5, 123.1, 122.0, 61.1, 41.1, 31.5, 20.2, 14.2, 13.8 ppm.

HRMS (ESI) m/z calcd. for $C_{22}H_{25}N_2O_2$ $[M+H]^+$ 349.1911, found 349.1906.

***N*-Butyl-3-(4-(trifluoromethyl)phenyl)quinolin-2-amine (4i)**



The title compound **4i** was prepared following the **general procedure A** from 1-ethynyl-4-(trifluoromethyl)benzene **1i** (0.45 mmol), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow oil (89.8 mg, 87%).

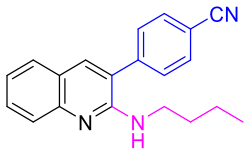
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 3H), 7.65 (s, 1H), 7.58 (m, 4H), 7.23 (t, *J* = 7.4 Hz, 1H), 4.61 (s, 1H), 3.59 (dd, *J* = 12.7, 7.1 Hz, 2H), 1.65 – 1.56 (m, 2H), 1.42 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 147.9, 141.5, 136.6, 130.3 (q, *J* = 32.6 Hz), 129.7, 129.5, 127.4, 126.2, 126.1 (q, *J* = 3.7 Hz), , 124.1, 124.0 (q, *J* = 272.1 Hz), 123.1, 122.2, 41.2, 31.6, 20.3, 13.9 ppm.

^{19}F NMR (375 MHz, $CDCl_3$) δ -62.6 ppm.

HRMS (ESI) m/z calcd. for $C_{20}H_{20}F_3N_2$ $[M+H]^+$ 345.1573, found 345.1571.

4-(2-(Butylamino)quinolin-3-yl)benzonitrile (4j)



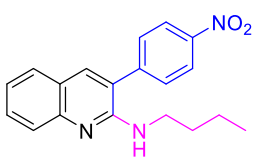
The title compound **4j** was prepared following the **general procedure A** from 4-ethynylbenzonitrile **1j** (0.45 mmol), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (76.8 mg, 85%), m.p 106 – 108 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (m, 3H), 7.63 (s, 1H), 7.58 (m, 4H), 7.22 (t, *J* = 7.4 Hz, 1H), 4.56 (s, 1H), 3.57 (dd, *J* = 13.0, 6.1 Hz, 2H), 1.64 – 1.55 (m, 2H), 1.40 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 147.9, 142.6, 136.6, 132.9, 129.8, 129.8, 127.4, 126.1, 123.6, 122.9, 122.3, 118.4, 111.9, 41.2, 31.5, 20.2, 13.8 ppm.

HRMS (ESI) m/z calcd. for $C_{20}H_{20}N_3$ $[M+H]^+$ 302.1652, found 302.1649.

***N*-Butyl-3-(4-nitrophenyl)quinolin-2-amine (4k)**



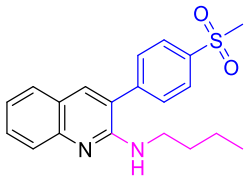
The title compound **4k** was prepared following the **general procedure A** from 1-ethynyl-4-nitrobenzene **1k** (0.45 mmol), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow soild (76.1 mg, 79%), m.p 102 – 104 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.8 Hz, 2H), 7.76 (d, *J* = 8.3 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 3H), 7.62 – 7.54 (m, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 4.57 (s, 1H), 3.59 (dd, *J* = 12.6, 7.1 Hz, 2H), 1.64 – 1.56 (m, 2H), 1.41 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 148.0, 147.5, 144.6, 136.8, 130.0, 127.5, 126.2, 124.4, 123.2, 122.9, 122.4, 41.3, 31.5, 20.3, 13.9 ppm.

HRMS (ESI) m/z calcd. for $C_{19}H_{20}N_3O_2$ $[M+H]^+$ 322.1550, found 322.1547.

***N*-Butyl-3-(4-(methylsulfonyl)phenyl)quinolin-2-amine (4l)**



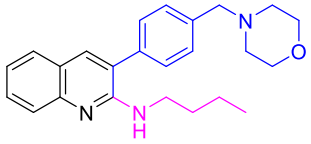
The title compound **4l** was prepared following the **general procedure A** from 1-ethynyl-4-(methylsulfonyl)benzene **1l** (0.45 mmol), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (86 mg, 81%), m.p 147 – 149 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.65 (s, 1H), 7.56 (M, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 4.57 (t, *J* = 4.9 Hz, 1H), 3.57 (dd, *J* = 12.7, 7.0 Hz, 2H), 3.13 (s, 3H), 1.62 – 1.55 (m, 2H), 1.38 (M, 2H), 0.94 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 147.9, 143.6, 140.1, 136.8, 130.0, 129.9, 128.2, 127.4, 126.1, 123.5, 123.0, 122.3, 44.4, 41.2, 31.5, 20.2, 13.8 ppm.

HRMS (ESI) m/z calcd. for $C_{20}H_{23}N_2O_2S$ $[M+H]^+$ 355.1475, found 355.1471.

***N*-Butyl-3-(4-(morpholinomethyl)phenyl)quinolin-2-amine (4m)**



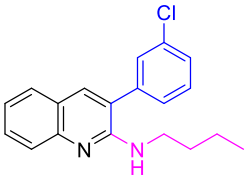
The title compound **4m** was prepared following the **general procedure A** from 4-(4-ethynylbenzyl)morpholine **1m** (0.45 mmol), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (83.3 mg, 74%), m.p 94 – 96 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 1H), 7.63 (s, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.52 (m, 1H), 7.44 (m, 4H), 7.22 – 7.17 (m, 1H), 4.79 (t, *J* = 5.2 Hz, 1H), 3.78 – 3.73 (m, 4H), 3.60 – 3.55 (m, 4H), 2.51 (d, *J* = 4.1 Hz, 4H), 1.63 – 1.55 (m, 2H), 1.39 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 147.6, 137.8, 136.4, 136.0, 129.8, 129.1, 128.8, 127.2, 126.0, 125.3, 123.3, 121.8, 66.9, 63.0, 53.6, 41.1, 31.6, 20.2, 13.9 ppm.

HRMS (ESI) m/z calcd. for $C_{24}H_{30}N_3O$ $[M+H]^+$ 376.2383, found 376.2380.

***N*-Butyl-3-(3-chlorophenyl)quinolin-2-amine (4n)**



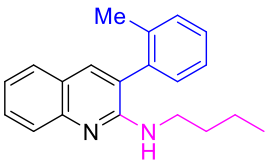
The title compound **4n** was prepared following the **general procedure A** from 1-chloro-3-ethynylbenzene **1n** (0.45 mmol), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow oil (71.6 mg, 77%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 1H), 7.63 (s, 1H), 7.56 (m, 2H), 7.48 (s, 1H), 7.45 – 7.40 (m, 2H), 7.39 – 7.35 (m, 1H), 7.24 – 7.19 (m, 1H), 4.68 (t, *J* = 4.9 Hz, 1H), 3.59 (m, 2H), 1.65 – 1.56 (m, 2H), 1.41 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 147.8, 139.5, 136.3, 135.0, 130.4, 129.5, 129.2, 128.3, 127.4, 127.1, 126.1, 124.1, 123.1, 122.1, 41.2, 31.6, 20.2, 13.9 ppm.

HRMS (ESI) m/z calcd. for $C_{19}H_{20}ClN_2$ $[M+H]^+$ 311.1310, found 311.1306.

***N*-Butyl-3-(o-tolyl)quinolin-2-amine (4o)**



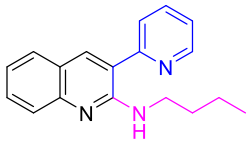
The title compound **4o** was prepared following the **general procedure A** from 1-ethynyl-2-methylbenzene **1o** (0.45 mmol), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow oil (69.6 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.3 Hz, 1H), 7.62 – 7.53 (m, 3H), 7.40 – 7.31 (m, 3H), 7.27 – 7.20 (m, 2H), 4.36 (s, 1H), 3.62 (m, 1H), 3.54 (m, 1H), 2.20 (s, 3H), 1.60 – 1.51 (m, 2H), 1.40 – 1.31 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 147.7, 137.1, 136.4, 135.8, 130.6, 130.1, 129.1, 128.5, 127.2, 126.5, 126.0, 125.3, 123.2, 121.8, 41.0, 31.7, 20.2, 19.6, 13.9 ppm.

HRMS (ESI) m/z calcd. for $C_{20}H_{23}N_2$ $[M+H]^+$ 291.1856, found 291.1853.

***N*-Butyl-3-(pyridin-2-yl)quinolin-2-amine (4p)**



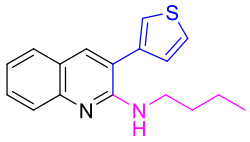
The title compound **4p** was prepared following the **general procedure A** from 2-ethynylpyridine **1p** (0.45 mmol), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (60.7 mg, 73%), m.p 93 – 95 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.65 (d, *J* = 4.9 Hz, 1H), 8.12 (s, 1H), 7.81 (m, 2H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.57 – 7.52 (m, 1H), 7.31 – 7.26 (m, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 3.69 (dd, *J* = 12.2, 7.1 Hz, 2H), 1.74 (m, 2H), 1.50 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 155.2, 148.5, 147.6, 137.2, 136.4, 130.0, 127.8, 125.7, 122.7, 122.6, 121.9, 121.4, 120.2, 40.9, 31.6, 20.5, 14.0 ppm.

HRMS (ESI) m/z calcd. for $C_{18}H_{20}N_3$ $[M+H]^+$ 278.1652, found 278.1651.

***N*-Butyl-3-(thiophen-3-yl)quinolin-2-amine (4q)**



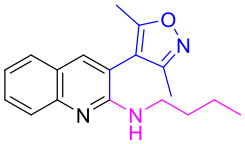
The title compound **4q** was prepared following the **general procedure A** from 3-ethynylthiophene **1q** (0.45 mmol), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow oil (63.5 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 1H), 7.68 (s, 1H), 7.57 – 7.53 (m, 1H), 7.50 (m, 1H), 7.47 (dd, *J* = 4.9, 3.0 Hz, 1H), 7.41 (dd, *J* = 3.0, 1.3 Hz, 1H), 7.24 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.20 – 7.16 (m, 1H), 4.90 (t, *J* = 4.5 Hz, 1H), 3.57 (m, 2H), 1.63 – 1.56 (m, 2H), 1.40 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 147.6, 137.9, 135.9, 129.2, 128.0, 127.2, 127.0, 126.0, 123.7, 123.2, 122.0, 120.5, 41.2, 31.6, 20.3, 13.9 ppm.

HRMS (ESI) m/z calcd. for $C_{17}H_{19}N_2S$ $[M+H]^+$ 283.1264, found 283.1261.

***N*-Butyl-3-(3,5-dimethylisoxazol-4-yl)quinolin-2-amine (4r)**



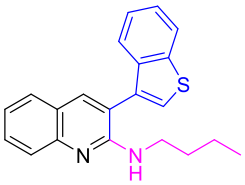
The title compound **4r** was prepared following the **general procedure A** from 3,5-dimethyl-4-((trimethylsilyl)ethynyl)isoxazole **1r** (0.45 mmol), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (58.4 mg, 66%), m.p 130 – 132 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 1H), 7.59 (s, 1H), 7.56 (m, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 4.49 (s, 1H), 3.62 – 3.51 (m, 2H), 2.33 (s, 3H), 2.17 (s, 3H), 1.64 – 1.55 (m, 2H), 1.40 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 159.8, 154.9, 148.1, 138.3, 129.9, 127.3, 126.2, 122.8, 122.2, 113.0, 111.7, 41.1, 31.7, 20.2, 13.8, 11.4, 10.3 ppm.

HRMS (ESI) m/z calcd. for $C_{18}H_{22}N_3O$ $[M+H]^+$ 296.1757, found 296.1754.

3-(Benzo[*b*]thiophen-3-yl)-*N*-butylquinolin-2-amine (4s)



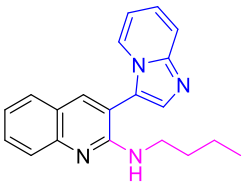
The title compound **4s** was prepared following the **general procedure A** from 3-ethynylbenzo[*b*]thiophene **1s** (0.45 mmol), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow oil (79.7 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.9 Hz, 1H), 7.85 (t, *J* = 9.1 Hz, 1H), 7.79 (s, 1H), 7.63 (m, 1H), 7.59 (m, 2H), 7.54 (s, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.27 – 7.22 (m, 1H), 4.70 (s, 1H), 3.67 – 3.53 (m, 2H), 1.60 – 1.50 (m, 2H), 1.39 – 1.30 (m, 2H), 0.94 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 148.0, 140.4, 137.9, 137.3, 132.8, 129.5, 127.3, 126.1, 125.8, 124.9, 124.5, 123.0, 123.0, 122.9, 121.9, 119.1, 41.0, 31.5, 20.2, 13.8 ppm.

HRMS (ESI) m/z calcd. for $C_{21}H_{21}N_2S$ $[M+H]^+$ 333.1420, found 333.1417.

***N*-Butyl-3-(imidazo[1,2-*a*]pyridin-3-yl)quinolin-2-amine (4t)**



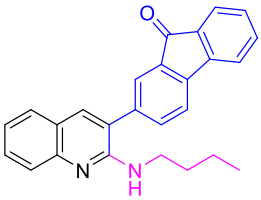
The title compound **4t** was prepared following the **general procedure A** from 3-((trimethylsilyl)ethynyl)imidazo[1,2-a]pyridine **1t** (0.45 mmol), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow oil (56.9 mg, 60%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 6.9 Hz, 1H), 7.85 (s, 1H), 7.78 (m, 3H), 7.58 (m, 2H), 7.29 (dd, *J* = 8.4, 7.4 Hz, 1H), 7.25 – 7.21 (m, 1H), 6.84 (t, *J* = 6.8 Hz, 1H), 4.66 (t, *J* = 5.1 Hz, 1H), 3.54 (td, *J* = 7.1, 5.7 Hz, 2H), 1.56 – 1.48 (m, 2H), 1.32 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 148.4, 146.3, 139.1, 133.5, 130.3, 127.5, 126.3, 125.3, 124.2, 122.6, 122.4, 120.3, 118.0, 112.9, 111.8, 41.1, 31.5, 20.2, 13.8 ppm.

HRMS (ESI) m/z calcd. for $C_{20}H_{21}N_4$ $[M+H]^+$ 317.1761, found 317.1758.

2-(2-(Butylamino)quinolin-3-yl)-9*H*-fluoren-9-one (4u)



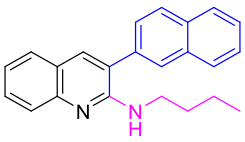
The title compound **4u** was prepared following the **general procedure A** from 2-((trimethylsilyl)ethynyl)-9H-fluoren-9-one **1u** (0.45 mmol), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (88.5 mg, 78%), m.p 151 – 153 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (m, 2H), 7.72 – 7.66 (m, 2H), 7.63 – 7.50 (m, 6H), 7.37 – 7.31 (m, 1H), 7.22 (t, *J* = 7.3 Hz, 1H), 4.71 (s, 1H), 3.59 (dd, *J* = 12.7, 6.9 Hz, 2H), 1.64 – 1.56 (m, 2H), 1.44 – 1.34 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 154.1, 147.7, 144.1, 143.9, 138.7, 136.3, 135.2, 135.0, 134.9, 134.2, 129.6, 129.4, 127.4, 126.1, 125.0, 124.5, 124.4, 123.2, 122.2, 121.0, 120.5, 41.3, 31.6, 20.3, 13.9 ppm.

HRMS (ESI) m/z calcd. for $C_{26}H_{23}N_2O$ $[M+H]^+$ 379.1805, found 379.1801.

***N*-Butyl-3-(naphthalen-2-yl)quinolin-2-amine (4v)**



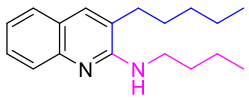
The title compound **4v** was prepared following the **general procedure A** from 2-ethynylnaphthalene **1v** (0.45 mmol), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow oil (78.3 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 1H), 7.92 – 7.85 (m, 3H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.70 (s, 1H), 7.57 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.56 – 7.51 (m, 4H), 7.22 – 7.17 (m, 1H), 4.78 (t, *J* = 5.0 Hz, 1H), 3.57 (m, 2H), 1.58 – 1.50 (m, 2H), 1.37 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 147.8, 136.3, 135.0, 133.6, 132.8, 129.2, 128.8, 128.2, 128.0, 127.8, 127.4, 126.7, 126.6, 126.5, 126.1, 125.5, 123.4, 122.0, 41.2, 31.6, 20.3, 13.9 ppm.

HRMS (ESI) m/z calcd. for $C_{23}H_{23}N_2$ $[M+H]^+$ 327.1856, found 327.1853.

***N*-Butyl-3-pentylquinolin-2-amine (4w)**



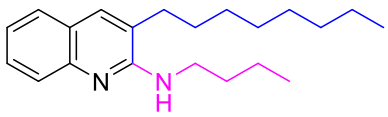
The title compound **4w** was prepared following the **general procedure A** from hept-1-yne **1w** (0.45 mmol), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a yellow oil (38.9 mg, 48%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 1H), 7.57 (s, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 4.54 (s, 1H), 3.64 (dd, *J* = 12.5, 7.0 Hz, 2H), 2.51 (t, *J* = 7.7 Hz, 2H), 1.70 (m, 4H), 1.48 (m, 2H), 1.41 (mz, 4H), 1.00 (t, *J* = 7.3 Hz, 3H), 0.93 (t, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 146.8, 134.1, 128.3, 126.7, 125.9, 123.8, 123.6, 121.7, 41.2, 31.9, 31.7, 30.7, 27.5, 22.5, 20.4, 14.0, 14.0 ppm.

HRMS (ESI) m/z calcd. for $C_{18}H_{27}N_2$ $[M+H]^+$ 271.2169, found 271.2166.

***N*-Butyl-3-octylquinolin-2-amine (4x)**



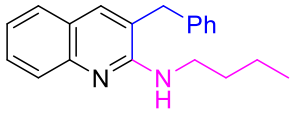
The title compound **4x** was prepared following the **general procedure A1** from dec-1-yne **1x** (0.45 mmol), benzo[c]isoxazole **2a** (0.6 mmol, 66 ul) and n-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a light yellow oil (46.8 mg, 50%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.3 Hz, 1H), 7.57 (s, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.48 (t, J = 8.4 Hz, 1H), 7.18 (t, J = 7.4 Hz, 1H), 4.54 (s, 1H), 3.70 – 3.59 (m, 2H), 2.58 – 2.35 (m, 2H), 1.70 (p, J = 8.0, 7.5 Hz, 4H), 1.55 – 1.42 (m, 4H), 1.30 (s, 8H), 1.00 (t, J = 7.3 Hz, 3H), 0.94 – 0.85 (m, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 146.8, 134.1, 128.3, 126.7, 125.9, 123.7, 123.6, 121.6, 41.2, 31.8, 31.8, 30.7, 29.4, 29.4, 29.2, 27.7, 22.6, 20.3, 14.0, 13.9 ppm.

HRMS (ESI) m/z calcd. for $C_{21}H_{33}N_2$ $[M+H]^+$ 313.2638, found 313.2629.

3-Benzyl-*N*-butylquinolin-2-amine (4y)



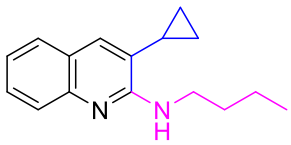
The title compound **4y** was prepared following the **general procedure A1** from prop-2-yn-1-ylbenzene **1y** (0.45 mmol), benzo[c]isoxazole **2a** (0.6 mmol, 66 ul) and n-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a light yellow solid (41.8 mg, 48%), m.p 70 – 72 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.4 Hz, 1H), 7.60 (s, 1H), 7.56 (d, J = 7.9 Hz, 1H), 7.51 (t, J = 7.7 Hz, 1H), 7.32 (q, J = 9.7, 9.3 Hz, 2H), 7.26 (d, J = 3.9 Hz, 1H), 7.21 (d, J = 7.5 Hz, 3H), 4.39 (s, 1H), 3.95 (s, 2H), 3.63 – 3.31 (m, 2H), 1.46 (dd, J = 14.4, 6.9 Hz, 2H), 1.20 (dq, J = 14.6, 7.4 Hz, 2H), 0.86 (t, J = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 147.3, 137.8, 136.4, 128.9, 128.7, 128.5, 127.0, 126.9, 126.0, 123.4, 122.2, 121.8, 41.0, 38.0, 31.4, 20.0, 13.8 ppm.

HRMS (ESI) m/z calcd. for $C_{20}H_{23}N_2$ $[M+H]^+$ 291.1856 , found 291.1853.

***N*-Butyl-3-cyclopropylquinolin-2-amine (4z)**



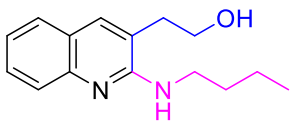
The title compound **4z** was prepared following the **general procedure A** from ethynylcyclopropane **1z** (0.45 mmol), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a yellow oil (40.3 mg, 56%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 1H), 7.56 (s, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 5.21 (s, 1H), 3.67 (dd, *J* = 12.6, 6.9 Hz, 2H), 1.73 (m, 2H), 1.64 (m, 1H), 1.51 (m, 2H), 1.00 (m, 5H), 0.67 (q, *J* = 5.3 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 147.0, 134.0, 128.5, 126.9, 125.8, 124.5, 123.3, 121.6, 41.1, 31.9, 20.3, 14.0, 11.0, 5.1 ppm.

HRMS (ESI) m/z calcd. for $C_{16}H_{21}N_2$ $[M+H]^+$ 241.1699, found 241.1697.

2-(2-(Butylamino)quinolin-3-yl)ethan-1-ol (4aa)



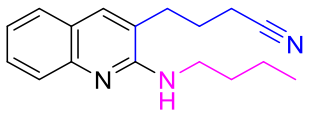
The title compound **4aa** was prepared following the **general procedure A** from but-3-yn-1-ol **1aa** (1.2 mmol), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a light yellow solid (37.4 mg, 51%), m.p 61 – 63 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 1H), 7.56 (s, 1H), 7.51 – 7.45 (m, 2H), 7.19 – 7.15 (m, 1H), 5.18 (s, 1H), 3.95 (t, *J* = 6.0 Hz, 2H), 3.57 (t, *J* = 7.1 Hz, 2H), 2.81 (dd, *J* = 8.2, 3.7 Hz, 2H), 2.15 (s, 1H), 1.69 – 1.61 (m, 2H), 1.45 (dq, *J* = 14.4, 7.3 Hz, 2H), 0.97 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 146.9, 136.2, 128.7, 126.8, 125.6, 123.3, 121.8, 121.8, 62.1, 41.4, 34.6, 31.6, 20.4, 13.9 ppm.

HRMS (ESI) m/z calcd. for $C_{15}H_{21}N_2O$ $[M+H]^+$ 245.1648, found 245.1645.

4-(2-(Butylamino)quinolin-3-yl)butanenitrile (4ab)



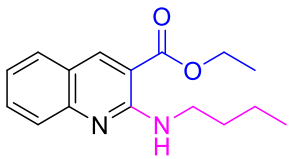
The title compound **4ab** was prepared following the **general procedure A** from hex-5-ynenitrile **1ab** (0.45 mmol), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a white solid (33.7 mg, 42%), m.p 88 – 90 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 1H), 7.59 (s, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.53 – 7.48 (m, 1H), 7.23 – 7.19 (m, 1H), 4.60 (s, 1H), 3.64 (dd, *J* = 12.0, 7.1 Hz, 2H), 2.72 (t, *J* = 7.5 Hz, 2H), 2.43 (t, *J* = 6.9 Hz, 2H), 2.10 – 2.02 (m, 2H), 1.70 (dt, *J* = 14.9, 7.4 Hz, 2H), 1.47 (dq, *J* = 14.6, 7.4 Hz, 2H), 0.99 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 147.1, 135.1, 128.9, 126.8, 126.0, 123.2, 122.1, 120.8, 119.2, 41.4, 31.8, 29.5, 23.7, 20.4, 16.7, 14.0 ppm

HRMS (ESI) m/z calcd. for $C_{17}H_{22}N_3$ $[M+H]^+$ 268.1808, found 268.1803.

Ethyl 2-(butylamino)quinoline-3-carboxylate (4ac)



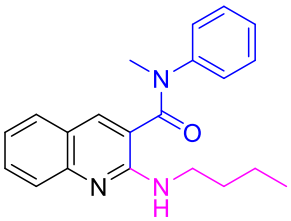
The title compound **4ac** was prepared following the **general procedure A** from ethyl propiolate **1ac** (0.45 mmol), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a yellow oil (30.2 mg, 37%).

^{1}H NMR (400 MHz, DMSO-*D6*) δ 8.73 (s, 1H), 7.92 (t, *J* = 5.2 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.67 – 7.59 (m, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.23 – 7.20 (m, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.53 (dd, *J* = 12.3, 6.9 Hz, 2H), 1.66 – 1.58 (m, 2H), 1.42 – 1.38 (m, 2H), 1.37 (t, *J* = 7.1 Hz, 3H), 0.94 (t, *J* = 7.4 Hz, 3H) ppm..

^{13}C NMR (100 MHz, DMSO-*D6*) δ 167.0, 155.4, 150.4, 142.5, 133.0, 129.9, 126.0, 122.6, 121.7, 110.3, 61.8, 40.6, 31.4, 20.4, 14.6, 14.3 ppm.

HRMS (ESI) m/z calcd. for $C_{16}H_{21}N_2O_2$ $[M+H]^+$ 273.1598, found 273.1601.

2-(Butylamino)-*N*-methyl-*N*-phenylquinoline-3-carboxamide (4ad)



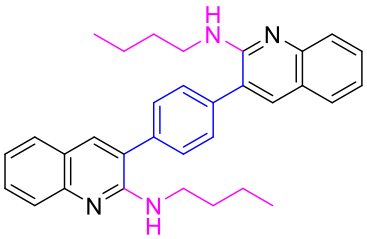
The title compound **4ad** was prepared following the **general procedure A** from *N*-methyl-*N*-phenylpropiolamide **1ad** (0.45 mmol), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow oil (46 mg, 46%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.4 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.32 (s, 1H), 7.20 (m, 3H), 7.10 (m, 3H), 7.05 – 7.00 (m, 1H), 6.38 (s, 1H), 3.60 (dd, *J* = 12.5, 7.0 Hz, 2H), 3.52 (s, 3H), 1.70 (m, 2H), 1.50 (m, 2H), 1.00 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 154.9, 148.0, 144.5, 138.3, 130.6, 129.4, 127.8, 126.9, 126.1, 125.9, 121.9, 121.3, 117.1, 41.1, 38.2, 31.6, 20.4, 14.0 ppm.

HRMS (ESI) m/z calcd. for $C_{21}H_{24}N_3O$ $[M+H]^+$ 334.1914, found 334.1910.

3,3'-(1,4-Phenylene)bis(N-butylquinolin-2-amine) (4ae)



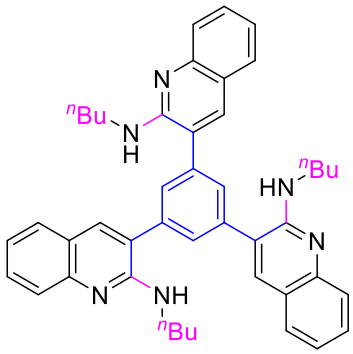
The title compound **4ae** was prepared following the **general procedure A** from 1,4-diethynylbenzene **1ae** (0.3 mmol), benzo[*c*]isoxazole **2a** (0.6 mmol, 66 ul) and *n*-butylamine **3a** (0.9 mmol, 90 ul) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a yellow solid (85.4 mg, 60%), m.p 163 – 165 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.72 (s, 2H), 7.63 – 7.61 (m, 6H), 7.56 (t, *J* = 7.7 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 2H), 4.82 (t, *J* = 4.9 Hz, 2H), 3.62 (dd, *J* = 12.7, 6.9 Hz, 4H), 1.64 (dt, *J* = 14.8, 7.4 Hz, 4H), 1.43 (dq, *J* = 15.0, 7.5 Hz, 4H), 0.97 (t, *J* = 7.4 Hz, 6H) ppm..

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 147.8, 137.6, 136.4, 129.9, 129.5, 127.4, 126.1, 124.9, 123.4, 122.1, 41.3, 31.7, 20.3, 13.9 ppm..

HRMS (ESI) m/z calcd. for $C_{32}H_{35}N_4$ $[M+H]^+$ 475.2856, found 475.2832.

3,3',3''-(Benzene-1,3,5-triyl)tris(N-butylquinolin-2-amine) (4af)



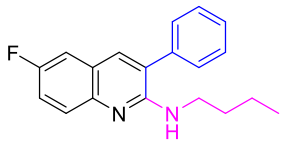
The title compound **4af** was prepared following the **general procedure A** from 1,3,5-triethynylbenzene **1af** (0.3 mmol, 43 mg), benzo[*c*]isoxazole **2a** (0.9 mmol, 99 ul) and *n*-butylamine **3a** (1.2 mmol, 120 ul) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a whtie solid (104.9 mg, 52%), m.p 112 –113 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (t, *J* = 4.1 Hz, 6H), 7.78 (s, 3H), 7.65 (d, *J* = 7.7 Hz, 3H), 7.58 (t, *J* = 7.7 Hz, 3H), 7.26 (d, *J* = 14.6 Hz, 3H), 4.93 (t, *J* = 4.8 Hz, 3H), 3.68 (dd, *J* = 12.6, 7.0 Hz, 6H), 1.73 – 1.63 (m, 6H), 1.47 (dt, *J* = 14.8, 7.4 Hz, 6H), 0.99 (t, *J* = 7.4 Hz, 9H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 147.8, 139.9, 136.6, 129.6, 129.1, 127.3, 126.2, 124.1, 123.2, 122.2, 41.2, 31.6, 20.3, 13.8 ppm.

HRMS (ESI) m/z calcd. for $C_{45}H_{49}N_6$ $[M+H]^+$ 673.4013, found 673.4008.

***N*-Butyl-6-fluoro-3-phenylquinolin-2-amine (4ag)**



The title compound **4ag** was prepared following the **general procedure A** from ethynylbenzene **1a** (0.45 mmol, 52 ul), 5-fluorobenzo[*c*]isoxazole **2b** (0.3 mmol, 41 mg) and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a yellow oil (61.8 mg, 70%).

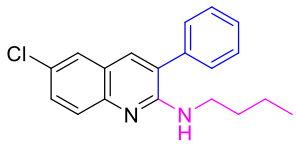
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 9.1, 5.2 Hz, 1H), 7.58 (s, 1H), 7.53 – 7.48 (m, 2H), 7.48 – 7.42 (m, 3H), 7.29 (m, 1H), 7.21 (dd, *J* = 8.9, 2.9 Hz, 1H), 4.72 (s, 1H), 3.54 (td, *J* = 7.1, 5.5 Hz, 2H), 1.62 – 1.53 (m, 2H), 1.37 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9 (d, *J* = 240.7 Hz), 154.1, 144.6, 137.3, 135.3 (d, *J* = 4.4 Hz), 129.2, 129.0, 128.3, 127.9 (d, *J* = 8.4 Hz), 126.6, 123.4 (d, *J* = 9.4 Hz), 118.4 (d, *J* = 24.7 Hz), 110.7 (d, *J* = 21.6 Hz), 41.2, 31.7, 20.3, 13.9 ppm.

^{19}F NMR (375 MHz, $CDCl_3$) δ -120.9 ppm.

HRMS (ESI) m/z calcd. for $C_{19}H_{20}FN_2$ $[M+H]^+$ 295.1605, found 295.1592.

***N*-butyl-6-chloro-3-phenylquinolin-2-amine (4ah)**



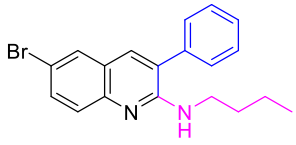
The title compound **4ah** was prepared following the **general procedure A** from ethynylbenzene **1a** (0.45 mmol, 52 ul), 5-chlorobenzo[c]isoxazole **2c** (0.30 mmol, 46 mg), and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a yellow oil (74.4 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.9 Hz, 1H), 7.53 (m, 3H), 7.50 (s, 1H), 7.45 (m, 4H), 4.81 (t, *J* = 4.8 Hz, 1H), 3.56 (m, 2H), 1.58 (m, 2H), 1.43 – 1.35 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 146.2, 137.13 135.0, 129.6, 129.2, 128.9, 128.4, 127.5, 126.8, 126.5, 126.0, 124.0, 41.1, 31.5, 20.2, 13.9 ppm.

HRMS (ESI) m/z calcd. for $C_{19}H_{20}ClN_2$ $[M+H]^+$ 311.1310, found 311.1292.

6-Bromo-N-butyl-3-phenylquinolin-2-amine (4ai)



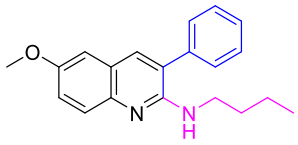
The title compound **4ai** was prepared following the **general procedure A** from ethynylbenzene **1a** (0.45 mmol, 52 ul), 5-bromobenzo[c]isoxazole **2d** (0.30 mmol, 59 mg), and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a yellow solid (88.2 mg, 83%), m.p 78 – 80 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 2.1 Hz, 1H), 7.61 (d, *J* = 8.9 Hz, 1H), 7.57 (m, 1H), 7.52 (s, 1H), 7.50 (m, 2H), 7.47 – 7.42 (m, 3H), 4.81 (t, *J* = 4.9 Hz, 1H), 3.55 (m, 2H), 1.58 (m, 2H), 1.38 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 146.4, 137.1, 134.9, 132.2, 129.3, 129.2, 128.9, 128.4, 127.8, 126.5, 124.6, 114.5, 41.1, 31.5, 20.2, 13.9 ppm.

HRMS (ESI) m/z calcd. for $C_{19}H_{20}BrN_2$ $[M+H]^+$ 355.0804, found 355.0813.

***N*-Butyl-6-methoxy-3-phenylquinolin-2-amine (4aj)**



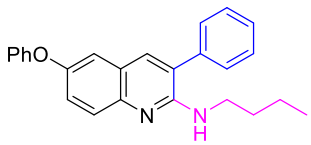
The title compound **4aj** was prepared following the **general procedure A** from ethynylbenzene **1a** (0.45 mmol, 52 ul), 5-methoxybenzo[*c*]isoxazole **2e** (0.30 mmol, 44.7 mg), and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 5:1) as a yellow oil (74.4 mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 9.1 Hz, 1H), 7.58 (s, 1H), 7.52 – 7.42 (m, 5H), 7.22 (m, 1H), 6.96 (s, 1H), 4.62 (s, 1H), 3.87 (s, 3H), 3.54 (m, 2H), 1.62 – 1.52 (m, 2H), 1.44 – 1.34 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 153.4, 143.1, 137.8, 135.3, 129.1, 129.0, 128.0, 127.4, 125.8, 123.6, 120.34, 106.5, 55.4, 41.2, 31.7, 20.3, 13.9 ppm.

HRMS (ESI) m/z calcd. for $C_{20}H_{23}N_2O$ $[M+H]^+$ 307.1805, found 307.1805.

***N*-Butyl-6-phenoxy-3-phenylquinolin-2-amine (4ak)**



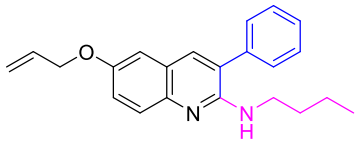
The title compound **4ak** was prepared following the **general procedure A** from ethynylbenzene **1a** (0.45 mmol, 52 ul), 5-phenoxybenzo[c]isoxazole **2f** (0.30 mmol, 63.3 mg), and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow oil (86.2 mg, 78%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 9.0 Hz, 1H), 7.55 (s, 1H), 7.53 – 7.44 (m, 5H), 7.37 – 7.30 (m, 3H), 7.19 (d, *J* = 2.7 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 7.7 Hz, 2H), 4.74 (t, *J* = 5.1 Hz, 1H), 3.58 (m, 2H), 1.64 – 1.56 (m, 2H), 1.41 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 154.2, 151.3, 144.6, 137.5, 135.4, 129.6, 129.2, 128.9, 128.2, 127.7, 126.2, 123.7, 122.9, 122.7, 118.1, 115.4, 41.2, 31.6, 20.3, 13.9 ppm.

HRMS (ESI) m/z calcd. for $C_{25}H_{25}N_2O$ $[M+H]^+$ 369.1961, found 369.1957.

6-(Allyloxy)-*N*-butyl-3-phenylquinolin-2-amine (4al)



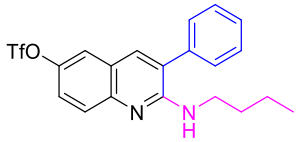
The title compound **4al** was prepared following the **general procedure A** from ethynylbenzene **1a** (0.45 mmol, 52 ul), 5-(allyloxy)benzo[*c*]isoxazole **2g** (0.30 mmol, 52.5 mg), and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow oil (74.7 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 9.1 Hz, 1H), 7.56 (s, 1H), 7.52 – 7.41 (m, 5H), 7.25 (dd, *J* = 9.0, 2.9 Hz, 1H), 6.98 (d, *J* = 2.8 Hz, 1H), 6.11 (m, 1H), 5.46 (ddd, *J* = 17.3, 3.1, 1.6 Hz, 1H), 5.31 (ddd, *J* = 10.5, 2.7, 1.3 Hz, 1H), 4.63 (s, 1H), 4.60 (m, 2H), 3.55 (m, 2H), 1.62 – 1.54 (m, 2H), 1.39 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 153.4, 143.2, 137.8, 135.3, 133.4, 129.1, 129.0, 128.0, 127.4, 125.8, 123.6, 120.8, 117.5, 107.9, 69.1, 41.2, 31.7, 20.3, 13.9 ppm.

HRMS (ESI) m/z calcd. for $C_{22}H_{25}N_2O$ $[M+H]^+$ 333.1961, found 333.1958.

2-(Butylamino)-3-phenylquinolin-6-yl trifluoromethanesulfonate (4am)



The title compound **4am** was prepared following the **general procedure A** from ethynylbenzene **1a** (0.45 mmol, 52 ul), benzo[*c*]isoxazol-5-yl trifluoromethanesulfonate **2h** (0.30 mmol, 80 mg), and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 5:1) as a yellow oil (78.9 mg, 62%).

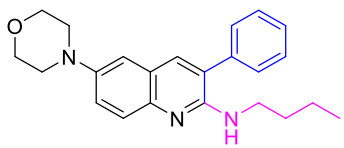
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 9.2 Hz, 1H), 7.62 (s, 1H), 7.53 (m, 2H), 7.49 – 7.43 (m, 4H), 7.39 (dd, *J* = 9.1, 2.8 Hz, 1H), 4.90 (t, *J* = 5.1 Hz, 1H), 3.56 (m, 2H), 1.62 – 1.55 (m, 2H), 1.37 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 146.9, 143.8, 136.7, 135.5, 129.4, 128.8, 128.6, 128.1, 127.2, 123.1, 122.3, 118.9, 118.8 (q, *J* = 321.0 Hz), 41.2, 31.5, 20.2, 13.8 ppm.

^{19}F NMR (375 MHz, $CDCl_3$) δ -72.7 ppm.

HRMS (ESI) m/z calcd. for $C_{20}H_{20}F_3N_2O_3S$ $[M+H]^+$ 425.1141, found 425.1135.

***N*-Butyl-6-morpholino-3-phenylquinolin-2-amine (4an)**



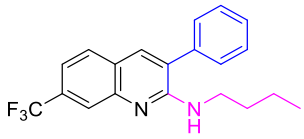
The title compound **4an** was prepared following the **general procedure A** from ethynylbenzene **1a** (0.45 mmol, 52 ul), 5-morpholinobenzo[*c*]isoxazole **2i** (0.30 mmol, 61.3 mg), and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 3:1) as a yellow oil (65 mg, 60%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 9.1 Hz, 1H), 7.56 (s, 1H), 7.51 – 7.40 (m, 5H), 7.31 (dd, *J* = 9.1, 2.7 Hz, 1H), 6.95 (d, *J* = 2.7 Hz, 1H), 4.61 (t, *J* = 4.8 Hz, 1H), 3.93 – 3.87 (m, 4H), 3.53 (dd, *J* = 12.5, 7.0 Hz, 2H), 3.22 – 3.15 (m, 4H), 1.61 – 1.52 (m, 2H), 1.37 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 146.4, 143.2, 137.9, 135.5, 129.1, 129.0, 128.0, 127.0, 125.9, 123.7, 121.8, 111.0, 67.0, 50.5, 41.3, 31.7, 20.3, 13.9 ppm.

HRMS (ESI) m/z calcd. for $C_{23}H_{28}N_3O$ $[M+H]^+$ 362.2227, found 362.2224.

***N*-Butyl-3-phenyl-7-(trifluoromethyl)quinolin-2-amine (4ao)**



The title compound **4ao** was prepared following the **general procedure A** from ethynylbenzene **1a** (0.45 mmol, 52 ul), 6-(trifluoromethyl)benzo[c]isoxazole **2j** (0.30 mmol, 56.1 mg), and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a white solid (73.3 mg, 71%), m.p 55 – 57 ℃.

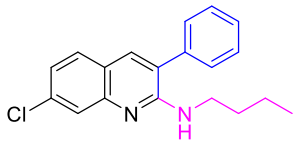
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.66 (m, 2H), 7.53 (m, 2H), 7.47 (m, 3H), 7.37 (dd, *J* = 8.3, 1.1 Hz, 1H), 4.90 (s, 1H), 3.58 (dd, *J* = 12.7, 7.1 Hz, 2H), 1.64 – 1.55 (m, 2H), 1.40 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 147.0, 136.9, 135.5, 130.8 (q, *J* = 32.0 Hz), 129.3, 128.9, 128.6, 128.1, 127.6, 125.1, 124.4 (q, *J* = 272.4 Hz), 123.6 (q, *J* = 4.2 Hz), 117.5 (q, *J* = 3.3 Hz), 41.2, 31.5, 20.2, 13.9 ppm.

^{19}F NMR (375 MHz, $CDCl_3$) δ -62.3 ppm.

HRMS (ESI) m/z calcd. for $C_{20}H_{20}F_3N_2$ $[M+H]^+$ 345.1573, found 345.1558.

***N*-Butyl-7-chloro-3-phenylquinolin-2-amine (4ap)**



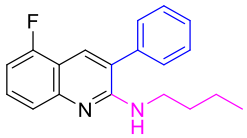
The title compound **4ap** was prepared following the **general procedure A** from ethynylbenzene **1a** (0.45 mmol, 52 ul), 6-chlorobenzo[*c*]isoxazole **2k** (0.30 mmol, 45.9 mg), and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a yellow oil (73.5 mg, 79%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 1.9 Hz, 1H), 7.59 (s, 1H), 7.53 – 7.47 (m, 3H), 7.47 – 7.42 (m, 3H), 7.14 (dd, *J* = 8.5, 2.1 Hz, 1H), 4.85 (t, *J* = 4.8 Hz, 1H), 3.55 (m, 2H), 1.62 – 1.54 (m, 2H), 1.39 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 148.4, 137.2, 135.6, 134.8, 129.2, 128.9, 128.4, 128.3, 125.7, 125.2, 122.5, 121.7, 41.1, 31.5, 20.2, 13.9 ppm.

HRMS (ESI) m/z calcd. for $C_{19}H_{20}ClN_2$ $[M+H]^+$ 311.1310, found 311.1292.

***N*-Butyl-5-fluoro-3-phenylquinolin-2-amine (4aq)**



The title compound **4aq** was prepared following the **general procedure A** from ethynylbenzene **1a** (0.45 mmol, 52 ul), 4-fluorobenzo[*c*]isoxazole **2l** (0.30 mmol, 41.1 mg), and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a yellow oil (67.9 mg, 77%).

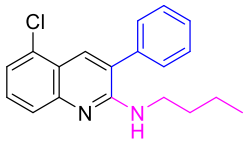
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.54 – 7.49 (m, 3H), 7.47 (m, 3H), 7.44 – 7.39 (m, 1H), 6.89 – 6.83 (m, 1H), 4.87 (s, 1H), 3.57 (m, 2H), 1.62 – 1.54 (m, 2H), 1.38 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6 (d, *J* = 252.0 Hz), 155.0, 148.9 (d, *J* = 3.6 Hz), 137.3, 129.2, 129.0, 128.9 (d, *J* = 4.8 Hz), 128.7 (d, *J* = 9.8 Hz), 128.4, 125.8 (d, *J* = 2.6 Hz), 121.8 (d, *J* = 3.5 Hz), 113.3 (d, *J* = 15.4 Hz), 106.0 (d, *J* = 19.6 Hz), 41.1, 31.5, 20.2, 13.9 ppm.

^{19}F NMR (375 MHz, $CDCl_3$) δ -124.2 ppm.

HRMS (ESI) m/z calcd. for $C_{19}H_{20}FN_2$ $[M+H]^+$ 295.1605, found 295.1596.

***N*-Butyl-5-fluoro-3-phenylquinolin-2-amine (4ar)**



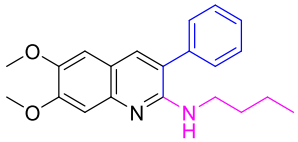
The title compound **4ar** was prepared following the **general procedure A** from ethynylbenzene **1a** (0.45 mmol, 52 ul), 4-chlorobenzo[*c*]isoxazole **2m** (0.30 mmol, 45.9 mg), and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a yellow oil (68.8 mg, 74%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.54 – 7.45 (m, 5H), 7.44 – 7.40 (m, 1H), 7.25 (d, *J* = 6.6 Hz, 1H), 4.86 (s, 1H), 3.57 (m, 2H), 1.59 m, 2H), 1.39 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 148.7, 137.2, 132.6, 131.1, 129.3, 129.0, 128.9, 128.4, 126.5, 125.2, 122.0, 121.2, 41.2, 31.6, 20.2, 13.9 ppm.

HRMS (ESI) m/z calcd. for $C_{19}H_{20}ClN_2$ $[M+H]^+$ 311.1310, found 311.1302.

***N*-Butyl-6,7-dimethoxy-3-phenylquinolin-2-amine (4as)**



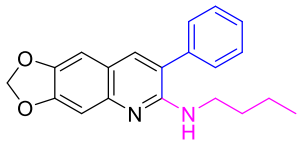
The title compound **4as** was prepared following the **general procedure A** from ethynylbenzene **1a** (0.45 mmol, 52 ul), 5,6-dimethoxybenzo[*c*]isoxazole **2n** (0.30 mmol, 53.7 mg), and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 5:1) as a yellow solid (82.7 mg, 82%), m.p 148 – 150 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.49 – 7.43 (m, 4H), 7.41 – 7.36 (m, 1H), 7.18 (s, 1H), 6.90 (s, 1H), 4.62 (t, *J* = 4.8 Hz, 1H), 4.01 (s, 3H), 3.92 (s, 3H), 3.53 (m, 2H), 1.60 – 1.53 (m, 2H), 1.38 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 151.8, 146.1, 144.0, 138.0, 134.9, 129.0, 127.7, 123.1, 117.3, 106.3, 106.1, 55.9, 55.8, 41.2, 31.6, 20.2, 13.8 ppm.

HRMS (ESI) m/z calcd. for $C_{21}H_{25}N_2O_2$ $[M+H]^+$ 337.1911, found 337.1902.

***N*-Butyl-7-phenyl-[1,3]dioxolo[4,5-*g*]quinolin-6-amine (4at)**



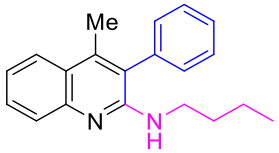
The title compound **4at** was prepared following the **general procedure A** from ethynylbenzene **1a** (0.45 mmol, 52 ul), [1,3]dioxolo[4',5':4,5]benzo[1,2-*c*]isoxazole **2o** (0.30 mmol, 48.9 mg), and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 5:1) as a yellow solid (58.6 mg, 61%), m.p 92 – 94 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.38 (m, 6H), 7.14 (s, 1H), 6.90 (s, 1H), 6.01 (s, 2H), 4.61 (s, 1H), 3.51 (dd, *J* = 12.7, 6.8 Hz, 2H), 1.60 – 1.52 (m, 2H), 1.37 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 150.1, 145.2, 144.2, 137.9, 135.5, 129.1, 129.0, 127.9, 123.0, 118.5, 104.1, 103.4, 101.0, 41.2, 31.8, 20.3, 13.9 ppm.

HRMS (ESI) m/z calcd. for $C_{20}H_{21}N_2O_2$ $[M+H]^+$ 321.1598, found 321.1593.

***N*-Butyl-4-methyl-3-phenylquinolin-2-amine (4au)**



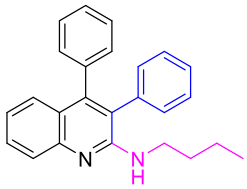
The title compound **4au** was prepared following the **general procedure A** from ethynylbenzene **1a** (0.45 mmol, 52 ul), 3-methylbenzo[*c*]isoxazole **2p** (0.30 mmol, 40 mg), and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow oil (46.1 mg, 53%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.55 – 7.50 (m, 3H), 7.47 – 7.42 (m, 1H), 7.26 – 7.21 (m, 3H), 4.18 (s, 1H), 3.50 (dd, *J* = 12.6, 6.8 Hz, 2H), 2.26 (s, 3H), 1.53 – 1.45 (m, 2H), 1.31 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 147.2, 140.6, 136.7, 130.1, 129.4, 128.9, 128.0, 126.6, 124.5, 123.9, 123.4, 121.7, 41.1, 31.6, 20.2, 15.8, 13.9 ppm.

HRMS (ESI) m/z calcd. for $C_{20}H_{23}N_2$ $[M+H]^+$ 291.1856, found 291.1852.

***N*-Butyl-3,4-diphenylquinolin-2-amine (4av)**



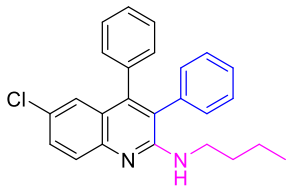
The title compound **4av** was prepared following the **general procedure A** from ethynylbenzene **1a** (0.45mmol, 52 ul), 3-phenylbenzo[*c*]isoxazole **2q** (0.30 mmol, 58.5 mg), and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (57 mg, 54%), m.p 98 – 100 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.3 Hz, 1H), 7.62 – 7.57 (m, 1H), 7.37 – 7.30 (m, 4H), 7.28 (m, 3H), 7.16 (m, 5H), 4.51 (s, 1H), 3.64 (dd, *J* = 12.6, 7.0 Hz, 2H), 1.60 (m, 2H), 1.45 – 1.38 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 147.6, 146.4, 137.1, 136.0, 130.5, 130.0, 129.1, 128.6, 127.6, 127.5, 127.0, 126.5, 126.2, 123.9, 123.1, 121.7, 41.2, 31.6, 20.2, 13.9 ppm.

HRMS (ESI) m/z calcd. for $C_{25}H_{25}N_2$ $[M+H]^+$ 353.2012, found 353.2007.

***N*-Butyl-6-chloro-3,4-diphenylquinolin-2-amine (4aw)**



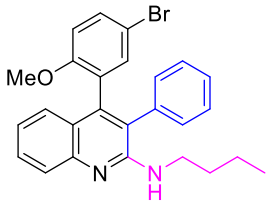
The title compound **4aw** was prepared following the **general procedure A** from ethynylbenzene **1a** (0.45 mmol, 52 ul), 5-chloro-3-phenylbenzo[*c*]isoxazole **2r** (0.30 mmol, 68.7 mg), and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (75.3 mg, 65%), m.p 135 – 137 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.9 Hz, 1H), 7.44 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.21 (m, 7H), 7.10 – 7.03 (m, 4H), 4.47 (t, *J* = 5.1 Hz, 1H), 3.53 (dd, *J* = 12.7, 7.0 Hz, 2H), 1.58 – 1.48 (m, 2H), 1.32 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 146.2, 145.6, 136.4, 135.6, 130.4, 129.8, 129.5, 128.7, 127.8, 127.6, 127.3, 126.8, 125.4, 124.7, 124.0, 41.1, 31.6, 20.2, 13.9 ppm.

HRMS (ESI) m/z calcd. for $C_{25}H_{24}ClN_2$ $[M+H]^+$ 387.1623, found 387.1617.

4-(5-Bromo-2-methoxyphenyl)-N-butyl-3-phenylquinolin-2-amine (4ax)



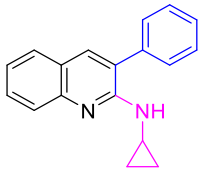
The title compound **4ax** was prepared following the **general procedure A** from ethynylbenzene **1a** (0.45 mmol, 52 ul), 3-(5-bromo-2-methoxyphenyl)benzo[c]isoxazole **2s** (0.30 mmol, 90.9 mg), and *n*-butylamine **3a** (0.6 mmol, 60 ul) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a white solid (85.6 mg, 62%), m.p 90 – 92 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 1H), 7.70 (ddd, *J* = 8.4, 6.8, 1.6 Hz, 1H), 7.50 – 7.40 (m, 4H), 7.38 – 7.33 (m, 2H), 7.31 – 7.26 (m, 3H), 6.81 (d, *J* = 8.8 Hz, 1H), 4.61 (t, *J* = 5.2 Hz, 1H), 3.79 – 3.73 (m, 2H), 3.72 (s, 3H), 1.77 – 1.69 (m, 2H), 1.58 – 1.50 (m, 2H), 1.11 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 154.8, 147.6, 141.8, 135.9, 133.7, 131.6, 130.1, 129.5, 129.0, 128.5, 128.4, 128.29, 127.7, 126.3, 125.8, 124.6, 122.8, 121.7, 112.2, 112.1, 55.4, 41.2, 31.6, 20.2, 13.9 ppm.

HRMS (ESI) m/z calcd. for $C_{26}H_{26}BrN_2O$ $[M+H]^+$ 461.1223, found 461.1219.

***N*-Cyclopropyl-3-phenylquinolin-2-amine (4ay)**



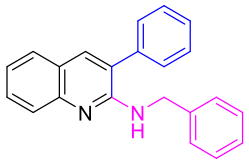
The title compound **4ay** was prepared following the **general procedure A** from ethynylbenzene **1a** (0.45 mmol, 52 ul), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and cyclopropanamine **3b** (0.6 mmol, 42 ul) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a yellow oil (65.6 mg, 84%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 1H), 7.65 (s, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.57 (ddd, *J* = 8.4, 7.1, 1.4 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.43 (m, 3H), 7.26 – 7.21 (m, 1H), 5.02 (s, 1H), 3.01 (m, 1H), 0.86 (m, 2H), 0.53 – 0.47 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 147.6, 137.5, 136.1, 129.2, 129.1, 129.0, 128.1, 127.3, 126.4, 125.4, 123.7, 122.3, 24.4, 7.4 ppm.

HRMS (ESI) m/z calcd. for $C_{18}H_{17}N_2$ $[M+H]^+$ 261.1386, found 261.1386.

***N*-Benzyl-3-phenylquinolin-2-amine (4az)**



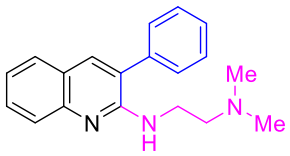
The title compound **4az** was prepared following the **general procedure A** from ethynylbenzene **1a** (0.45 mmol, 52 ul), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and dibenzylamine **3c** (0.6 mmol, 66 ul) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a light yellow oil (80.9 mg, 87%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.4 Hz, 1H), 7.75 (s, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.57 – 7.50 (m, 4H), 7.48 – 7.41 (m, 3H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.33 – 7.27 (m, 2H), 5.20 (t, *J* = 4.9 Hz, 1H), 4.90 (d, *J* = 5.5 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 147.4, 139.7, 137.3, 136.3, 129.2, 129.2, 129.0, 128.4, 128.1, 127.6, 127.3, 126.9, 126.1, 125.5, 123.6, 122.2, 45.3 ppm.

HRMS (ESI) m/z calcd. for $C_{22}H_{19}N_2$ $[M+H]^+$ 311.1543, found 311.1537.

***N*^{1},*N*^{1}-Dimethyl-*N*^{2}-(3-phenylquinolin-2-yl)ethane-1,2-diamine (4ba)**



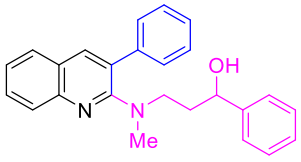
The title compound **4ba** was prepared following the **general procedure A** from ethynylbenzene **1a** (0.45 mmol, 52 ul), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and N^1,N^1-dimethylethane-1,2-diamine **3d** (0.6 mmol, 66 ul) and purified by column chromatography (SiO_2, PE/EA = 5:1) as a light yellow oil (55.9 mg, 64%).

^{1}H NMR (400 MHz, DMSO-*D6*) δ 7.76 (s, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 1H), 7.55 – 7.48 (m, 5H), 7.48 – 7.42 (m, 1H), 7.21 – 7.16 (m, 1H), 5.84 (t, *J* = 5.0 Hz, 1H), 3.53 (t, *J* = 4.1 Hz, 2H), 2.44 (t, *J* = 6.3 Hz, 2H), 2.14 (s, 6H) ppm.

^{13}C NMR (100 MHz, DMSO-*D6*) δ 154.6, 147.7, 137.7, 136.6, 129.8, 129.7, 129.3, 128.7, 128.2, 126.0, 125.9, 123.7, 122.2, 58.1, 45.6, 39.1 ppm.

HRMS (ESI) m/z calcd. for $C_{19}H_{22}N_3$ $[M+H]^+$ 292.1808 , found 292.1803.

3-(Methyl(3-phenylquinolin-2-yl)amino)-1-phenylpropan-1-ol (4bb)



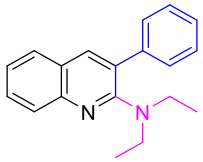
The title compound **4bb** was prepared following the **general procedure A** from ethynylbenzene **1a** (0.45 mmol, 52 ul), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and 3-(methylamino)-1-phenylpropan-1-ol **3e** (0.6 mmol, 99 mg) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a light yellow oil (88.4 mg, 80%).

^{1}H NMR (400 MHz, DMSO-*D6*) δ 7.76 (s, 1H), 7.60 (dd, *J* = 15.5, 8.0 Hz, 2H), 7.48 – 7.41 (m, 1H), 7.38 – 7.29 (m, 4H), 7.24 (t, *J* = 7.1 Hz, 1H), 7.14 (dd, *J* = 12.1, 7.1 Hz, 3H), 7.10 – 7.03 (m, 3H), 5.19 (d, *J* = 4.3 Hz, 1H), 4.28 – 4.20 (m, 1H), 3.36 (s, 3H), 3.19 (dt, *J* = 14.5, 7.4 Hz, 1H), 3.07 (ddd, *J* = 13.8, 8.6, 5.4 Hz, 1H), 1.70 – 1.59 (m, 2H) ppm.

^{13}C NMR (100 MHz, DMSO-*D6*) δ 158.3, 145.9, 145.9, 140.2, 138.9, 129.3, 128.7, 128.0, 127.7, 127.5, 127.6, 127.2, 126.6, 126.2, 125.6, 124.2, 123.1, 70.6, 49.5, 38.7, 36.7 ppm.

HRMS (ESI) m/z calcd. for $C_{25}H_{25}N_2O$ $[M+H]^+$ 369.1961, found 369.1957.

***N,N*-Diethyl-3-phenylquinolin-2-amine (4bc)**



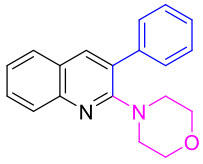
The title compound **4bc** was prepared following the **general procedure A** from ethynylbenzene **1a** (0.45 mmol, 52 ul), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and diethylamine **3f** (0.6 mmol, 62 ul) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a yellow oil (55.5 mg, 67%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.4 Hz, 1H), 7.77 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.56 (m, 3H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.38 – 7.33 (m, 1H), 7.32 – 7.27 (m, 1H), 3.26 (q, *J* = 7.0 Hz, 4H), 1.02 (t, *J* = 7.0 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 146.6, 140.9, 138.8, 129.1, 129.0, 128.6, 128.0, 127.1, 127.1, 126.9, 124.6, 123.2, 44.2, 12.8 ppm.

HRMS (ESI) m/z calcd. for $C_{19}H_{21}N_2$ $[M+H]^+$ 277.1699, found 277.1697.

4-(3-Phenylquinolin-2-yl)morpholine (4bd)



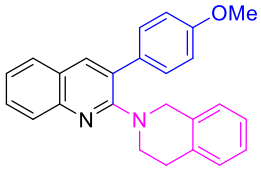
The title compound **4bd** was prepared following the **general procedure A** from ethynylbenzene **1a** (0.45 mmol, 52 ul), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and morpholine **3g** (0.6 mmol, 53 ul) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a yellow solid (67 mg, 77%), m.p 135 – 137 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 1H), 7.86 (s, 1H), 7.72 – 7.66 (m, 3H), 7.64 – 7.58 (m, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.40 – 7.33 (m, 2H), 3.69 – 3.63 (m, 4H), 3.27 – 3.21 (m, 4H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 146.4, 139.9, 138.9, 129.3, 128.8, 128.2, 127.9, 127.6, 127.2, 127.2, 125.2, 124.1, 66.6, 49.4 ppm.

HRMS (ESI) m/z calcd. for $C_{19}H_{19}N_2O$ $[M+H]^+$ 291.1492, found 291.1489.

2-(3,4-Dihydroisoquinolin-2(1H)-yl)-3-(4-methoxyphenyl)quinolone (4be)



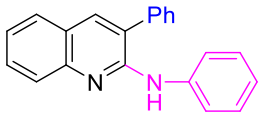
The title compound **4be** was prepared following the **general procedure A** from 1-ethynyl-4-methoxybenzene **1f** (0.45 mmol), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and 1,2,3,4-tetrahydroisoquinoline **3h** (0.6 mmol, 79.9 mg) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a yellow solid (71.4 mg, 65%), m.p 73 – 75 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 1H), 7.84 (s, 1H), 7.69 (d, *J* = 7.4 Hz, 1H), 7.62 – 7.59 (m, 3H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.22 – 7.14 (m, 3H), 7.11 – 7.09 (m, 1H), 6.99 (d, *J* = 8.5 Hz, 2H), 4.64 (s, 2H), 3.89 (s, 3H), 3.38 (t, *J* = 5.7 Hz, 2H), 2.71 (t, *J* = 5.6 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 158.9, 146.3, 138.5, 135.2, 134.7, 132.6, 129.1, 128.7, 128.2, 127.1, 127.1, 126.8, 125.9, 125.7, 125.2, 123.8, 114.2, 55.3, 50.6, 48.0, 28.8 ppm.

HRMS (ESI) m/z calcd. for $C_{25}H_{23}N_2O$ $[M+H]^+$ 367.1805 , found 367.1797.

***N*,3-Diphenylquinolin-2-amine (4bf)**



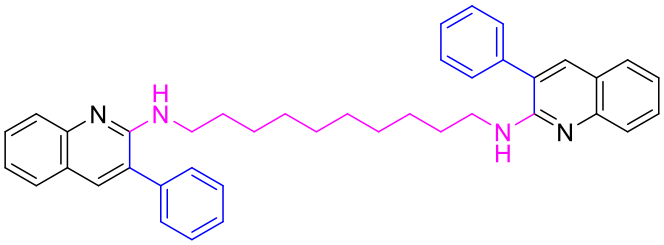
The title compound **4bf** was prepared following the **general procedure A** from ethynylbenzene **1a** (0.45 mmol, 52 ul), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and aniline **3i** (0.6 mmol, 55 ul) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a white solid (44.4 mg, 50%), m.p 94 – 96 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 1H), 7.82 – 7.78 (m, 3H), 7.67 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.61 (ddd, *J* = 8.5, 7.0, 1.5 Hz, 1H), 7.57 – 7.53 (m, 4H), 7.53 – 7.48 (m, 1H), 7.36 – 7.30 (m, 3H), 7.06 – 7.00 (m, 1H), 6.81 (s, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2, 146.8, 140.3, 137.1, 136.9, 129.5, 129.4, 129.3, 128.8, 128.6, 127.2, 126.9, 126.3, 124.1, 123.3, 122.2, 119.1 ppm.

HRMS (ESI) m/z calcd. for $C_{21}H_{17}N_2$ $[M+H]^+$ 297.1386, found 297.1383.

***N*^{1},*N*^{10}-*bis*(3-Phenylquinolin-2-yl)decane-1,10-diamine (4bg)**



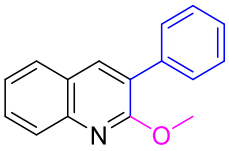
The title compound **4bg** was prepared following the **general procedure A** from ethynylbenzene **1a** (0.9 mmol, 104 ul), benzo[*c*]isoxazole **2a** (0.6 mmol, 66 ul) and decane-1,10-diamine **3j** (0.3 mmol, 61 ul) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a light light yellow oil (111 mg, 64%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.3 Hz, 2H), 7.64 (s, 2H), 7.58 (d, J = 7.9 Hz, 2H), 7.53 (s, 2H), 7.50 (s, 2H), 7.48 (d, J = 3.3 Hz, 5H), 7.46 (s, 3H), 7.20 (t, J = 7.0 Hz, 2H), 4.76 (t, J = 5.1 Hz, 2H), 3.56 (q, J = 7.0 Hz, 4H), 1.59 (p, J = 7.2 Hz, 4H), 1.37 – 1.24 (m, 12H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 147.7, 137.6, 136.0, 129.2, 129.2, 129.0, 128.1, 127.3, 126.0, 125.6, 123.4, 121.9, 41.4, 29.4, 29.4, 29.3, 27.0 ppm.

HRMS (ESI) m/z calcd. for $C_{40}H_{43}N_4$ $[M+H]^+$ 579.3482, found 579.3477.

2-Methoxy-3-phenylquinoline (4bh)



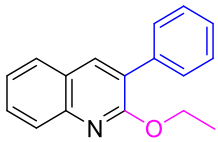
The title compound **4bh** was prepared following the **general procedure B** from ethynylbenzene **1a** (0.45 mmol, 52 ul), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and methanol **5a** (49.4 mmol, 2 ml) and purified by column chromatography (SiO_2, PE/EA = 50:1) as a colourless oil (43.7 mg, 62%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.67 – 7.62 (m, 3H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 4.13 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 145.9, 137.9, 136.8, 129.4, 129.3, 128.2, 127.7, 127.4, 126.9, 126.5, 125.5, 124.2, 53.7 ppm.

HRMS (ESI) m/z calcd. for $C_{16}H_{14}NO$ $[M+H]^+$ 236.1070, found 236.1066.

2-Ethoxy-3-phenylquinoline (4bi)[12]



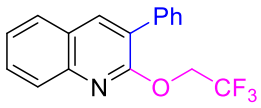
The title compound **4bi** was prepared following the **general procedure B** from ethynylbenzene **1a** (0.45 mmol, 52 ul), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and ethanol **5b** (34.25 mmol, 2 ml) and purified by column chromatography (SiO_2, PE/EA = 50:1) as a colourless oil (47.1 mg, 63%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.69 – 7.66 (m, 2H), 7.65 – 7.60 (m, 1H), 7.47 (dd, *J* = 10.1, 4.7 Hz, 2H), 7.43 – 7.36 (m, 2H), 4.62 (q, *J* = 7.1 Hz, 2H), 1.45 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 145.9, 137.9, 136.9, 129.4, 129.2, 128.1, 127.6, 127.4, 126.8, 126.4, 125.4, 124.0, 62.0, 14.5 ppm.

HRMS (ESI) m/z calcd. for $C_{17}H_{16}NO$ $[M+H]^+$ 250.1226, found 250.1222.

3-Phenyl-2-(2,2,2-trifluoroethoxy)quinolone (4bj)



The title compound **4bj** was prepared following the **general procedure B** from ethynylbenzene **1a** (0.45 mmol, 52 ul), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and 2,2,2-trifluoroethan-1-ol **5c** (0.42 mmol, 31 ul) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a white solid (55.5 mg, 61%), m.p 65 – 66 ℃.

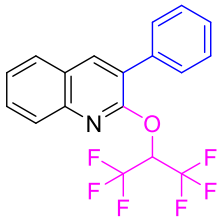
^{1}H NMR (400 MHz, DMSO-*D6*) δ 8.38 (s, 1H), 7.98 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.72 (ddd, *J* = 8.4, 7.0, 1.4 Hz, 1H), 7.66 (dt, *J* = 3.2, 1.8 Hz, 2H), 7.55 – 7.47 (m, 3H), 7.44 – 7.39 (m, 1H), 5.18 (q, *J* = 9.1 Hz, 2H) ppm.

^{13}C NMR (100 MHz, DMSO-*D6*) δ 157.1, 144.9, 139.9, 135.9, 130.7, 129.7, 128.9, 128.6, 128.6, 127.0, 126.4, 125.8, 125.6, 124.7 (q, *J* = 277.8 Hz), 62.1 (q, *J* = 34.7 Hz) ppm.

^{19}F NMR (375 MHz, DMSO-*D6*) δ 3.46 ppm.

HRMS (ESI) m/z calcd. for $C_{17}H_{13}F_3NO$ $[M+H]^+$ 304.0944, found 304.0935.

2-((1,1,1,3,3,3-Hexafluoropropan-2-yl)oxy)-3-phenylquinoline (4bk)



The title compound **4bk** was prepared following the **general procedure B** from ethynylbenzene **1a** (0.45 mmol, 52 ul), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and 1,1,1,3,3,3-hexafluoropropan-2-ol **5d** (0.42 mmol, 45 ul) and purified by column chromatography (SiO_2, PE/EA = 30:1) as a colourless oil (72.4 mg, 65%).

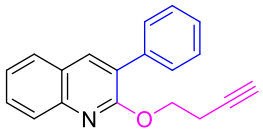
^{1}H NMR (400 MHz, DMSO-*D6*) δ 8.49 (s, 1H), 8.03 (d, *J* = 8.1 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.80 – 7.74 (m, 1H), 7.64 – 7.58 (m, 2H), 7.57 – 7.54 (m, 1H), 7.51 – 7.47 (m, 2H), 7.46 – 7.39 (m, 2H) ppm.

^{13}C NMR (100 MHz, DMSO-*D6*) δ 154.6, 143.6, 140.9, 134.7, 132.4, 130.8, 129.1, 129.0, 128.6, 128.4, 128.2, 126.7, 126.6, 126.2, 124.7, 67.1 (t, *J* = 66.5 Hz) ppm.

^{19}F NMR (375 MHz, DMSO-*D6*) δ -72.24, -72.25 ppm.

HRMS (ESI) m/z calcd. for $C_{18}H_{12}F_6NO$ $[M+H]^+$ 372.0818, found 372.0794.

2-(But-3-yn-1-yloxy)-3-phenylquinoline (4bl)



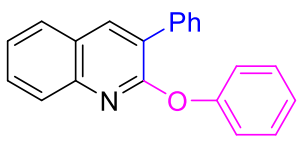
The title compound **4bl** was prepared following the **general procedure B** from ethynylbenzene **1a** (0.45 mmol, 52 ul), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and but-3-yn-1-ol **1aa** (1.2 mmol, 91 ul) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a white solid (35.2 mg, 43%), m.p 72 – 73 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.76 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.72 – 7.69 (m, 2H), 7.63 (ddd, *J* = 8.4, 7.0, 1.5 Hz, 1H), 7.49 – 7.44 (m, 2H), 7.43 – 7.38 (m, 2H), 4.68 (t, *J* = 6.9 Hz, 2H), 2.76 (td, *J* = 6.9, 2.7 Hz, 2H), 2.05 (t, *J* = 2.7 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 145.7, 138.1, 136.5, 129.5, 129.4, 128.1, 127.7, 127.4, 126.9, 126.3, 125.6, 124.3, 81.1, 69.6, 63.9, 19.1 ppm.

HRMS (ESI) m/z calcd. for $C_{19}H_{16}NO$ $[M+H]^+$ 274.1226, found 274.2735.

2-Phenoxy-3-phenylquinoline (4bm)[12]



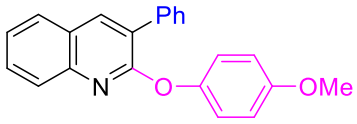
The title compound **4bm** was prepared following the **general procedure B** from ethynylbenzene **1a** (0.45 mmol, 52 ul), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and phenol **5e** (0.36 mmol, 33.9 mg) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a white solid (79.3 mg, 89%), m.p 112 – 114 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.85 – 7.75 (m, 4H), 7.61 (t, J = 7.7 Hz, 1H), 7.51 (t, J = 7.7 Hz, 2H), 7.45 (q, J = 6.7, 6.2 Hz, 4H), 7.31 – 7.25 (m, 2H), 7.23 (d, J = 8.2 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 154.0, 145.5, 139.1, 136.4, 129.5, 129.4, 129.3, 128.3, 127.9, 127.5, 127.3, 126.8, 126.2, 125.0, 124.4, 121.6 ppm.

HRMS (ESI) m/z calcd. for $C_{21}H_{16}NO$ $[M+H]^+$ 298.1226, found 298.1224.

2-(4-Methoxyphenoxy)-3-phenylquinoline (4bn)



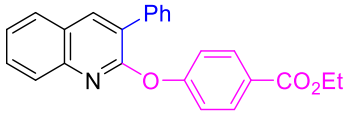
The title compound **4bn** was prepared following the **general procedure B** from ethynylbenzene **1a** (0.45 mmol, 52 ul), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and 4-methoxyphenol **5f** (0.36 mmol, 44.7 mg) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a white solid (68.7 mg, 70%), m.p 149 – 151 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.75 (d, *J* = 8.5 Hz, 3H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.18 (d, *J* = 9.0 Hz, 2H), 6.95 (d, *J* = 9.0 Hz, 2H), 3.84 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 156.4, 147.3, 145.5, 138.9, 136.5, 129.4, 129.4, 128.3, 127.9, 127.5, 127.3, 126.6, 126.1, 124.9, 122.6, 114.3, 55.6 ppm.

HRMS (ESI) m/z calcd. for $C_{22}H_{18}NO_2$ $[M+H]^+$ 328.1332, found 328.1330.

Ethyl 4-((3-phenylquinolin-2-yl)oxy)benzoate (4bo)



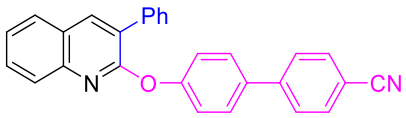
The title compound **4bo** was prepared following the **general procedure B** from ethynylbenzene **1a** (0.45 mmol, 52 ul), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and ethyl 4-hydroxybenzoate **5g** (0.36 mmol, 59.8 mg) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a white solid (94.1 mg, 85%), m.p 100 – 101 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 8.15 – 8.11 (m, 2H), 7.81 (dd, *J* = 11.1, 8.3 Hz, 2H), 7.76 – 7.71 (m, 2H), 7.66 – 7.60 (m, 1H), 7.52 – 7.46 (m, 3H), 7.45 – 7.41 (m, 1H), 7.33 – 7.30 (m, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 158.2, 157.9, 145.3, 139.4, 136.1, 131.1, 129.7, 129.3, 128.4, 128.0, 127.5, 127.3, 126.8, 126.4, 126.4, 125.3, 121.0, 60.8, 14.3 ppm.

HRMS (ESI) m/z calcd. for $C_{24}H_{20}NO_3$ $[M+H]^+$ 370.1438, found 370.1431.

4'-((3-Phenylquinolin-2-yl)oxy)-[1,1'-biphenyl]-4-carbonitrile (4bp)



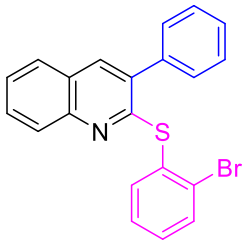
The title compound **4bp** was prepared following the **general procedure B** from ethynylbenzene **1a** (0.45 mmol, 52 ul), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and 4'-hydroxy-[1,1'-biphenyl]-4-carbonitrile **5h** (0.36 mmol, 70.3 mg) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a light yellow solid (84.8 mg, 71%), m.p 114 – 116 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.5 Hz, 1H), 7.76 (d, *J* = 7.7 Hz, 2H), 7.74 – 7.69 (m, 4H), 7.64 – 7.60 (m, 3H), 7.49 (dd, *J* = 15.5, 7.6 Hz, 3H), 7.45 – 7.42 (m, 1H), 7.38 (d, *J* = 8.6 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 154.6, 145.4, 145.1, 139.3, 136.2, 135.2, 132.6, 129.7, 129.4, 128.4, 128.2, 128.0, 127.5, 127.4, 127.4, 126.8, 126.4, 125.3, 122.1, 119.0, 110.6 ppm.

HRMS (ESI) m/z calcd. for $C_{28}H_{19}N_2O$ $[M+H]^+$ 399.1492, found 399.1482.

2-((2-Bromophenyl)thio)-3-phenylquinoline (4bq)



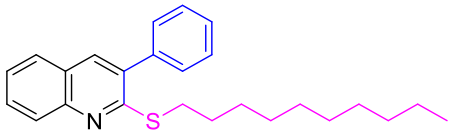
The title compound **4bq** was prepared following the **general procedure A** with addition of Na_2CO_3 (0.3 mmol) from ethynylbenzene **1a** (0.45 mmol, 52 ul), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and 2-bromobenzenethiol **6a** (0.36 mmol, 44 ul) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a light yellow oil (68 mg, 58%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.0 Hz, 1H), 7.59 (dd, J = 12.8, 4.5 Hz, 3H), 7.52 (d, J = 8.0 Hz, 1H), 7.38 – 7.34 (m, 1H), 7.33 – 7.24 (m, 4H), 7.22 – 7.17 (m, 1H), 7.15 (dd, J = 7.9, 1.5 Hz, 1H), 7.09 (dd, J = 11.2, 3.9 Hz, 1H), 6.99 – 6.95 (m, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 136.0, 135.9, 135.7, 133.5, 132.9, 131.8, 130.5, 128.9, 128.7, 128.5, 128.1, 128.0, 127.6, 126.9, 126.6, 125.6, 122.6 ppm.

HRMS (ESI) m/z calcd. for $C_{21}H_{15}BrNS$ $[M+H]^+$ 392.0103, found 392.0103.

2-(Decylthio)-3-phenylquinoline (4br)



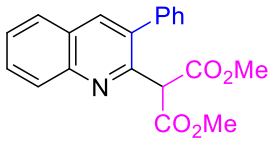
The title compound **4br** was prepared following the **general procedure A** with addition of Na_2CO_3 (0.3 mmol) from ethynylbenzene **1a** (0.45 mmol, 52 ul), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and decane-1-thiol **6b** (0.36 mmol, 77 ul) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow oil (47.5 mg, 42%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.4 Hz, 1H), 7.77 (s, 1H), 7.73 (d, J = 8.1 Hz, 1H), 7.65 (t, J = 7.7 Hz, 1H), 7.51 (d, J = 7.1 Hz, 3H), 7.44 (dd, J = 15.3, 7.7 Hz, 3H), 3.30 (t, J = 7.4 Hz, 2H), 1.74 (dt, J = 14.9, 7.4 Hz, 2H), 1.50 – 1.41 (m, 2H), 1.28 – 1.24 (m, 12H), 0.88 (t, J = 6.6 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 147.4, 138.1, 134.9, 134.8, 129.5, 129.3, 128.3, 128.2, 127.8, 127.5, 125.8, 125.2, 31.9, 30.4, 29.7, 29.6, 29.5, 29.3, 29.2, 29.1, 22.7, 14.1 ppm.

HRMS (ESI) m/z calcd. for $C_{25}H_{32}NS$ $[M+H]^+$ 378.2250, found 378.2240.

Dimethyl-2-(3-phenylquinolin-2-yl)malonate (4bs)



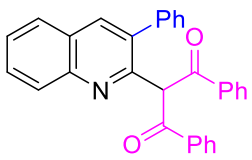
The title compound **4bs** was prepared following the **general procedure A** with addition of K_2CO_3 (0.3 mmol) from ethynylbenzene **1a** (0.45 mmol, 52 ul), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and dimethyl malonate **7a** (0.6 mmol, 69 ul) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a yellow oil (43.2 mg, 43%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.5 Hz, 1H), 8.04 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.72 (t, *J* = 7.7 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.46 (q, *J* = 6.1 Hz, 3H), 7.35 (d, *J* = 7.8 Hz, 2H), 5.20 (s, 1H), 3.73 (s, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 152.0, 147.0, 138.3, 136.8, 135.3, 129.7, 129.5, 129.2, 128.6, 128.2, 127.3, 127.2, 127.2, 58.6, 52.8 ppm.

HRMS (ESI) m/z calcd. for $C_{20}H_{18}NO_4$ $[M+H]^+$ 336.1230, found 336.1223.

1,3-Diphenyl-2-(3-phenylquinolin-2-yl)propane-1,3-dione (4bt)



The title compound **4bt** was prepared following the **general procedure A** with addition of K_2CO_3 (0.3 mmol) from ethynylbenzene **1a** (0.45 mmol, 52 ul), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and 1,3-diphenylpropane-1,3-dione **7b**

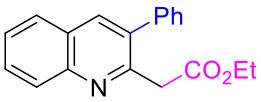
(0.6 mmol, 135 mg) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a yellow solid (64.2 mg, 50%), m.p 150 – 151 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 9.0 Hz, 3H), 7.62 (s, 1H), 7.56 (d, *J* = 4.6 Hz, 4H), 7.51 (d, *J* = 3.5 Hz, 7H), 7.38 (t, *J* = 6.0 Hz, 4H), 7.28 (dd, *J* = 8.1, 3.8 Hz, 1H), 6.11 (s, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 183.8, 154.0, 140.0, 137.5, 137.4, 135.9, 134.4, 130.9, 130.3, 129.1, 128.7, 128.4, 128.2, 127.6, 126.6, 123.8, 123.2, 118.0, 88.8, 29.7 ppm.

HRMS (ESI) m/z calcd. for $C_{30}H_{22}NO_2$ $[M+H]^+$ 428.1645, found 428.1639.

Ethyl 2-(3-phenylquinolin-2-yl)acetate (4bu)



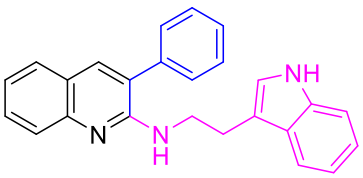
The title compound **4bu** was prepared following the **general procedure A** with addition of K_2CO_3 (0.3 mmol) from ethynylbenzene **1a** (0.45 mmol, 52 ul), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and ethyl 3-oxobutanoate **7c** (0.6 mmol, 76 ul) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a yellow oil (59.4 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.5 Hz, 1H), 8.00 (s, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.69 (s, 1H), 7.51 (s, 1H), 7.43 (dt, *J* = 10.5, 7.6 Hz, 5H), 4.09 (q, *J* = 7.1 Hz, 2H), 4.03 (s, 2H), 1.17 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 153.4, 147.0, 139.0, 136.5, 135.7, 129.3, 129.1, 128.8, 128.4, 127.7,127.3, 127.0, 126.5, 60.7, 42.9, 14.0 ppm.

HRMS (ESI) m/z calcd. for $C_{19}H_{18}NO_2$ $[M+H]^+$ 292.1332, found 292.1328.

***N*-(2-(1H-indol-3-yl)ethyl)-3-phenylquinolin-2-amine (4bv)**



The title compound **4bv** was prepared following the **general procedure A** from ethynylbenzene **1a** (0.45 mmol, 52 ul), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and 2-(1H-indol-3-yl)ethan-1-amine **3k** (0.6 mmol, 96.1 mg) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (89.3 mg, 82%), m.p 129 – 130 ℃.

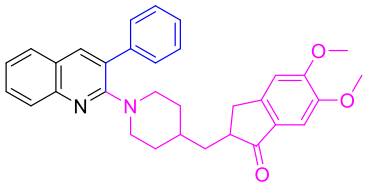
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.50 (s, 1H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.42 (ddd, *J* = 8.4, 7.1, 1.4 Hz, 1H), 7.25 – 7.20 (m, 3H), 7.18 – 7.13 (m, 3H), 7.12 – 7.07 (m, 1H), 7.07

– 7.02 (m, 1H), 6.99 – 6.95 (m, 1H), 6.69 (d, *J* = 1.9 Hz, 1H), 4.83 (t, *J* = 5.3 Hz, 1H), 3.78 (dd, *J* = 12.4, 6.8 Hz, 2H), 2.95 (t, *J* = 6.8 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 147.6, 137.3, 136.3, 136.1, 129.3, 129.0, 128.9, 127.9, 127.4, 125.9, 125.8, 123.4, 122.0, 121.9, 121.9, 119.2, 119.2, 118.9, 113.3, 111.1, 41.7, 24.9 ppm.

HRMS (ESI) m/z calcd. for $C_{25}H_{22}N_3$ $[M+H]^+$ 364.1808, found 364.1803.

5,6-Dimethoxy-2-((1-(3-phenylquinolin-2-yl)piperidin-4-yl)methyl)-2,3-dihydro-1H-inden-1-one (4bw)



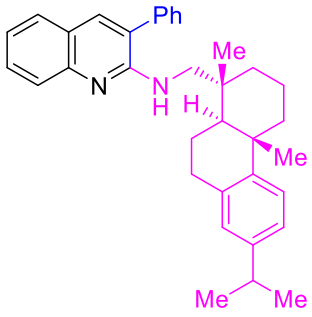
The title compound **4bw** was prepared following the **general procedure A** from ethynylbenzene **1a** (0.45 mmol, 52 ul), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and 5,6-dimethoxy-2-(piperidin-4-ylmethyl)-2,3-dihydro-1H-inden-1-one **3l** (0.6 mmol, 174.6 mg) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a light yellow solid (115.2 mg, 78%), m.p 84 – 85 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 1H), 7.89 (s, 1H), 7.76 – 7.71 (m, 3H), 7.65 (t, *J* = 8.3 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 3H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 1H), 6.93 (s, 1H), 4.03 (s, 3H), 3.98 (s, 3H), 3.83 (d, *J* = 12.5 Hz, 2H), 3.29 (dd, *J* = 17.6, 8.1 Hz, 1H), 2.82 (dd, *J* = 34.5, 13.4 Hz, 4H), 2.00 (s, 1H), 1.76 (d, *J* = 12.8 Hz, 1H), 1.68 (d, *J* = 11.6 Hz, 2H), 1.43 – 1.28 (m, 4H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.7, 159.4, 155.3, 149.3, 148.7, 146.4, 140.2, 138.6, 129.1, 129.0, 128.6, 128.6, 127.8, 127.3, 127.1, 126.9, 125.0, 123.6, 107.3, 104.2, 56.1, 56.0, 49.4, 49.3, 45.4, 38.7, 34.4, 33.0, 32.7, 31.1 ppm.

HRMS (ESI) m/z calcd. for $C_{32}H_{33}N_2O_3$ $[M+H]^+$ 493.2486, found 493.2480.

***N*-((7-Isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)-3-phenylquinolin-2-amine (4bx)**



The title compound **4bx** was prepared following the **general procedure A** from ethynylbenzene **1a** (0.45 mmol, 52 ul), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and ((1R,4aS,10aR)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-

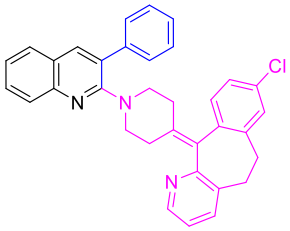
octahydrophenanthren-1-yl)methanamine **3m** (0.6 mmol, 171.3 mg) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a light yellow solid (104 mg, 71%), m.p 75 – 77 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.3 Hz, 1H), 7.49 (s, 1H), 7.45 – 7.38 (m, 2H), 7.30 – 7.21 (m, 5H), 7.05 (dd, *J* = 15.1, 7.4 Hz, 2H), 6.86 (d, *J* = 8.1 Hz, 1H), 6.71 (s, 1H), 4.72 (s, 1H), 3.53 – 3.33 (m, 2H), 2.69 (dd, *J* = 13.7, 6.6 Hz, 2H), 2.52 – 2.39 (m, 1H), 2.15 (d, *J* = 12.6 Hz, 1H), 2.03 – 1.94 (m, 1H), 1.61 (t, *J* = 14.8 Hz, 2H), 1.50 (s, 1H), 1.35 (d, *J* = 11.1 Hz, 1H), 1.28 – 1.16 (m, 3H), 1.11 (d, *J* = 6.7 Hz, 9H), 0.85 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 147.6, 147.2, 145.3, 137.4, 135.9, 134.9, 129.2, 129.1, 128.1, 127.3, 126.8, 125.9, 125.7, 124.1, 123.6, 123.3, 121.8, 51.3, 45.5, 38.7, 37.9, 37.4, 36.4, 33.4, 30.2, 25.3, 24.0, 23.9, 19.1, 18.8, 18.7 ppm.

HRMS (ESI) m/z calcd. for $C_{35}H_{41}N_2$ $[M+H]^+$ 489.3264, found 489.3261.

8-Chloro-11-(1-(3-phenylquinolin-2-yl)piperidin-4-ylidene)-6,11-dihydro-5H-benzo[5,6]cyclohepta[1,2-b]pyridine (4by)



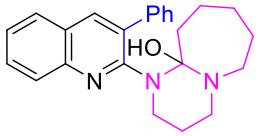
The title compound **4by** was prepared following the **general procedure A** from ethynylbenzene **1a** (0.45 mmol, 52 ul), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and 8-chloro-11-(piperidin-4-ylidene)-6,11-dihydro-5H-benzo[5,6]cyclohepta[1,2-b]pyridine **3n** (0.6 mmol, 186.5 mg) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a yellow solid (100 mg, 65%) m.p 126 – 128 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 6.1 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 2H), 7.67 (t, *J* = 7.4 Hz, 3H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.39 (d, *J* = 7.7 Hz, 1H), 7.33 (dt, *J* = 14.8, 7.6 Hz, 2H), 7.13 (s, 1H), 7.12 (s, 2H), 7.05 (dd, *J* = 7.6, 4.8 Hz, 1H), 3.65 – 3.54 (m, 2H), 3.43 – 3.28 (m, 2H), 2.95 – 2.71 (m, 4H), 2.48 (t, *J* = 10.0 Hz, 1H), 2.40 – 2.26 (m, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 157.4, 146.6, 146.4, 140.2, 139.5, 138.8, 138.7, 137.8, 137.2, 133.3, 133.0, 132.6, 130.7, 129.1, 128.8, 128.7, 128.6, 127.7, 127.4, 127.2, 127.1, 126.0, 125.1, 123.8, 122.0, 50.4, 50.3, 31.7, 31.4, 30.7, 30.4 ppm.

HRMS (ESI) m/z calcd. for $C_{34}H_{29}ClN_3$ $[M+H]^+$ 514.2045, found 514.2040.

1-((3-Phenylquinolin-2-yl)oxy)decahydropyrimido[1,2-*a*]azepine (4bz)



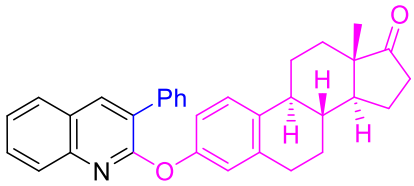
The title compound **4bz** was prepared following the **general procedure A** from ethynylbenzene **1a** (0.45 mmol, 52 ul), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and octahydropyrimido[1,2-a]azepin-10a(6H)-ol **3o** (0.6 mmol, 102 mg) and purified by column chromatography (SiO_2, PE/EA = 1:1) as a white solid (78.4 mg, 70%), m.p 93 – 95 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 1H), 7.64 (s, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.55 – 7.47 (m, 5H), 7.46 – 7.40 (m, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 5.24 (s, 1H), 3.58 (q, *J* = 6.2 Hz, 2H), 3.43 (t, *J* = 6.7 Hz, 2H), 3.32 (d, *J* = 8.0 Hz, 2H), 2.47 (d, *J* = 9.6 Hz, 2H), 1.89 – 1.79 (m, 2H), 1.75 – 1.61 (m, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 154.3, 147.6, 137.4, 136.1, 129.1, 129.1, 129.0, 128.1, 127.3, 125.9, 125.8, 123.4, 121.8, 49.6, 45.9, 38.4, 37.2, 29.9, 28.6, 27.8, 23.4 ppm.

HRMS (ESI) m/z calcd. for $C_{24}H_{28}N_3O$ $[M+H]^+$ 374.2227, found 374.2225.

13-Methyl-3-((3-phenylquinolin-2-yl)oxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (4ca)



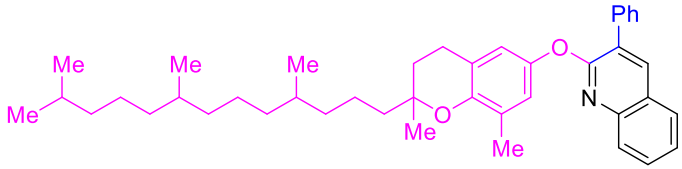
The title compound **4ca** was prepared following the **general procedure B** from ethynylbenzene **1a** (0.45 mmol, 52 ul), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and estrone **5i** (0.36 mmol, 97.3 mg) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a yellow solid (90.9 mg, 64%), m.p 96 – 98 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.81 (dd, *J* = 7.6, 4.6 Hz, 2H), 7.75 (d, *J* = 7.1 Hz, 2H), 7.60 (t, *J* = 8.4 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 1H), 7.07 (d, *J* = 8.5 Hz, 1H), 7.00 (s, 1H), 2.94 (s, 2H), 2.49 (s, 2H), 2.33 (t, *J* = 10.9 Hz, 1H), 2.23 – 2.10 (m, 1H), 2.01 (t, *J* = 11.2 Hz, 3H), 1.71 – 1.58 (m, 3H), 1.57 – 1.44 (m, 3H), 0.94 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 151.7, 145.5, 138.9, 137.7, 136.4, 135.7, 129.3, 128.2, 127.8, 127.4, 127.3, 126.7, 126.1, 126.1, 124.9, 121.3, 118.8, 50.3, 47.9, 44.1, 38.0, 35.8, 31.5, 29.4, 26.4, 25.7, 21.5, 13.8 ppm.

HRMS (ESI) m/z calcd. for $C_{33}H_{32}NO_2$ $[M+H]^+$ 474.2428, found 474.2422.

2-((2,8-Dimethyl-2-(4,8,12-trimethyltridecyl)chroman-6-yl)oxy)-3-phenylquinoline (4cb)



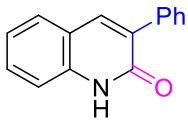
The title compound **4cb** was prepared following the **general procedure B** from ethynylbenzene **1a** (0.45 mmol, 52 ul), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and 2,8-dimethyl-2-(4,8,12-trimethyltridecyl)chroman-6-ol **5j** (0.36 mmol, 144.8 mg) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a light yellow oil (136.2 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.81 (dd, J = 15.9, 8.2 Hz, 2H), 7.76 (d, J = 7.9 Hz, 2H), 7.62 – 7.57 (m, 1H), 7.48 (t, J = 7.4 Hz, 2H), 7.45 – 7.39 (m, 2H), 6.89 (s, 1H), 6.83 (s, 1H), 2.77 (s, 2H), 2.21 (s, 3H), 1.82 (dd, J = 24.3, 6.7 Hz, 2H), 1.66 – 1.59 (m, 2H), 1.54 (dt, J = 13.1, 6.6 Hz, 2H), 1.47 – 1.39 (m, 4H), 1.33 (d, J = 6.4 Hz, 6H), 1.31 – 1.21 (m, 4H), 1.17 (dd, J = 14.8, 8.0 Hz, 4H), 1.13 – 1.07 (m, 2H), 0.93 – 0.86 (m, 12H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 148.8, 145.7, 145.6, 138.8, 136.7, 129.4, 129.2, 128.2, 127.7, 127.6, 127.3, 127.0, 126.8, 126.1, 124.7, 121.4, 120.8, 119.1, 75.9, 40.1, 39.4, 37.5, 37.4, 37.3, 32.8, 32.7, 31.2, 28.0, 24.8, 24.5, 24.3, 22.7, 22.6, 22.6, 21.0, 19.8, 19.7, 16.2 ppm.

HRMS (ESI) m/z calcd. for $C_{42}H_{56}NO_2$ $[M+H]^+$ 606.4306, found 606.4301.

3-Phenylquinolin-2(1H)-one (8a)[13]



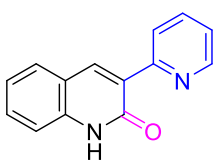
The title compound **8a** was prepared following the **general procedure C** from ethynylbenzene **1a** (0.45 mmol, 52 ul), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and water (1.5 mmol, 27 ul) and purified by column chromatography (SiO_2, PE/EA = 2:1) as a white solid (55 mg, 83%), m.p 218 – 220 ℃.

^{1}H NMR (400 MHz, DMSO-*D6*) δ 11.96 (s, 1H), 8.07 (s, 1H), 7.74 (dd, *J* = 13.1, 7.1 Hz, 3H), 7.49 (t, *J* = 8.3 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.18 (t, *J* = 7.5 Hz, 1H) ppm.

^{13}C NMR (100 MHz, DMSO-*D6*) δ 161.2, 138.4, 137.7, 136.3, 131.6, 130.3, 128.8, 128.2, 128.0, 127.9, 122.0, 119.7, 114.8.ppm.

MS (EI) m/z (%) 221.0 $[M]^+$, 193.0, 165.0, 110.0, 89.0. The data match those reported in literature.[13]

3-(Pyridin-2-yl)quinolin-2(1H)-one (8b)



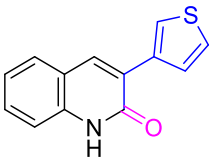
The title compound **8b** was prepared following the **general procedure C** from 2-ethynylpyridine **1p** (0.45 mmol, 47 ul), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and water (1.5 mmol, 27 ul) and purified by column chromatography (SiO_2, PE/EA = 1:1) as a light white solid (41.3 mg, 62%), m.p 234 – 235 ℃.

^{1}H NMR (400 MHz, DMSO-*D6*) δ 12.08 (s, 1H), 8.77 (s, 1H), 8.68 (d, *J* = 3.3 Hz, 1H), 8.52 (d, *J* = 8.0 Hz, 1H), 7.98 – 7.73 (m, 2H), 7.54 (t, *J* = 7.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 7.5 Hz, 1H) ppm.

^{13}C NMR (100 MHz, DMSO-*D6*) δ 161.1, 152.6, 149.2, 139.3, 138.8, 136.2, 131.0, 128.9, 128.8, 123.9, 123.0, 122.1, 119.2, 114.7 ppm.

HRMS (ESI) m/z calcd. for $C_{14}H_{11}N_2O$ $[M+H]^+$ 223.0866 ; found 223.0864.

3-(Thiophen-3-yl)quinolin-2(1H)-one (8c)



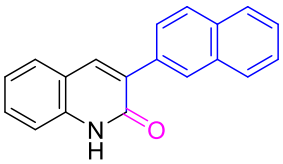
The title compound **8c** was prepared following the **general procedure C** from 3-ethynylthiophene **1q** (0.45 mmol, 45 ul), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and water (1.5 mmol, 27 ul) and purified by column chromatography (SiO2, PE/EA = 2:1) as a light yellow solid (53.1 mg, 78%), m.p 251 – 252 ℃.

^{1}H NMR (400 MHz, DMSO-*D6*) δ 11.99 (s, 1H), 8.38 (d, *J* = 12.6 Hz, 2H), 7.72 (dd, *J* = 15.6, 6.5 Hz, 2H), 7.63 – 7.56 (m, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H). ppm.

^{13}C NMR (100 MHz, DMSO-*D6*) δ 160.8, 137.7, 136.2, 135.5, 130.0, 127.9, 127.1, 125.8, 125.4, 124.9, 122.0, 119.4, 114.7 ppm.

HRMS (ESI) m/z calcd. for $C_{13}H_{10}NOS$ $[M+H]^+$ 228.0478; found 228.0473.

3-(Naphthalen-2-yl)quinolin-2(1H)-one (8d)



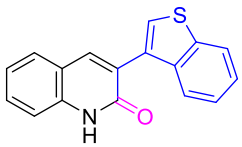
The title compound **8d** was prepared following the **general procedure C** from 2-ethynylnaphthalene **1v** (0.45 mmol, 64 ul), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and water (1.5 mmol, 27 ul) and purified by column chromatography (SiO_2, PE/EA = 2:1) as a white solid (56.9 mg, 70%), m.p 301 – 303 ℃.

^{1}H NMR (400 MHz, DMSO-*D6*) δ 12.03 (s, 1H), 8.37 (s, 1H), 8.26 (s, 1H), 7.94 (m, 4H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.58 – 7.48 (m, 3H), 7.37 (d, *J* = 8.3 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H) ppm.

^{13}C NMR (100 MHz, DMSO-*D6*) δ 161.2, 138.4, 138.1, 133.9, 132.8, 132.4, 131.3, 130.3, 128.2, 127.6, 127.4, 127.1, 126.8, 126.3, 126.2, 122.0, 119.6, 114.7 ppm.

HRMS (ESI) m/z calcd. for $C_{19}H_{14}NO$ $[M+H]^+$ 272.1070; found 272.1061.

3-(Benzo[b]thiophen-3-yl)quinolin-2(1H)-one (8e)



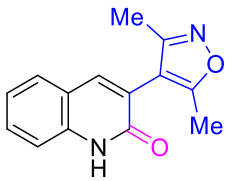
The title compound **8e** was prepared following the **general procedure C** from 3-ethynylbenzo[*b*]thiophene **1s** (0.45 mmol, 71.2 mg), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and water (1.5 mmol, 27 ul) and purified by column chromatography (SiO2, PE/EA = 2:1) as a white solid (62.3 mg, 75%), m.p 242 – 244 ℃.

^{1}H NMR (400 MHz, DMSO-*D6*) δ 12.06 (s, 1H), 8.16 (s, 1H), 8.05 (m, 1H), 7.97 (s, 1H), 7.78 (m, 2H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.46 – 7.35 (m, 3H), 7.22 (s, 1H) ppm.

^{13}C NMR (100 MHz, DMSO-*D6*) δ 160.9, 139.2, 138.7, 138.4, 137.9, 131.8, 130.4, 128.1, 127.1, 127.1, 124.3, 124.3, 123.3, 122.9, 122.0, 119.2, 114.8 ppm.

HRMS (ESI) m/z calcd. for $C_{17}H_{12}NOS$ $[M+H]^+$ 278.0634; found 278.0634.

3-(3,5-Dimethylisoxazol-4-yl)quinolin-2(1H)-one (8f)



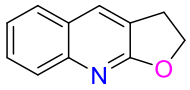
The title compound **8f** was prepared following the **general procedure C** from 3,5-dimethyl-4-((trimethylsilyl)ethynyl)isoxazole **1r** (0.45 mmol, 86.9 mg), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and water (1.5 mmol, 27 ul) and purified by column chromatography (SiO2, PE/EA = 1:1) as a white solid (42.5 mg, 59%), m.p 266 – 268 ℃.

^{1}H NMR (400 MHz, DMSO-*D6*) δ 12.01 (s, 1H), 7.99 (s, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 7.1 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 2.35 (s, 3H), 2.17 (s, 3H) ppm.

^{13}C NMR (100 MHz, DMSO-*D6*) δ 166.6, 160.5, 159.3, 140.2, 138.6, 130.6, 128.0, 122.4, 122.0, 119.1, 115.0, 111.9, 11.6, 10.5 ppm.

HRMS (ESI) m/z calcd. for $C_{14}H_{13}N_2O_2$ $[M+H]^+$ 241.0972; found 241.0971.

2,3-Dihydrofuro[2,3-b]quinolone (9a)



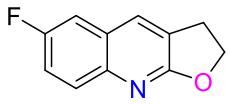
The title compound **9a** was prepared following the **general procedure D** from but-3-yn-1-ol **1aa** (1.2 mmol, 91 ul), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and purified by column chromatography (SiO_2, PE/EA = 3:1) as a white solid (33.4 mg, 65%), m.p 118 – 119 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.4 Hz, 1H), 7.77 (s, 1H), 7.62 (d, *J* = 6.7 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.34 – 7.29 (m, 1H), 4.65 (t, *J* = 8.2 Hz, 2H), 3.31 (td, *J* = 8.3, 1.4 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 146.9, 132.8, 129.1, 127.4, 127.3, 125.4, 124.0, 121.6, 69.1, 27.7 ppm.

HRMS (ESI) m/z calcd. for $C_{11}H_{12}NO$ $[M+H]^+$ 172.0757; found 172.0754.

6-Fluoro-2,3-dihydrofuro[2,3-b]quinoline (9b)



The title compound **9b** was prepared following the **general procedure D** from 3-butyn-1-ol **1aa** (1.2 mmol, 91 ul), 5-fluorobenzo[c]isoxazole **2b** (0.3 mmol, 42 mg) and purified by column chromatography (SiO_2, PE/EA = 3:1) as a white solid (40.9 mg, 72%), m.p 147 – 149 ℃.

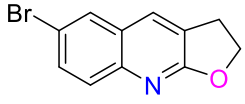
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 9.1, 5.3 Hz, 1H), 7.76 (s, 1H), 7.33 (d, *J* = 8.7 Hz, 1H), 7.30 – 7.25 (m, 1H), 4.69 (t, *J* = 8.2 Hz, 2H), 3.37 (t, *J* = 7.7 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ167.2 (d, *J* = 2.1 Hz), 159.0 (d, *J* = 243.5 Hz), 143.5 (d, *J* = 0.9 Hz), 131.7 (d, *J* = 4.6 Hz), 129.1 (d, *J* = 8.8 Hz), 125.6 (d, *J* = 9.5 Hz), 125.6 (d, *J* = 9.5 Hz), 122.7, 110.8 (d, *J* = 22.1 Hz), 69.0, 27.6 ppm.

^{19}F NMR (365 MHz, $CDCl_3$) δ -118 ppm.

HRMS (ESI) m/z calcd. for $C_{11}H_9FNO$ $[M+H]^+$ 190.0663; found 190.0666.

6-Bromo-2,3-dihydrofuro[2,3-b]quinoline (9c)[14]



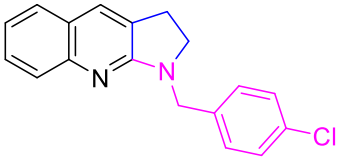
The title compound **9c** was prepared following the **general procedure D** from 3-butyn-1-ol **1aa** (1.2 mmol, 91 ul), 5-bromobenzo[c]isoxazole **2d** (0.3 mmol, 59 mg) and purified by column chromatography (SiO_2, PE/EA = 3:1) as a white solid (52.3 mg, 70%), m.p 174 – 176 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 2.0 Hz, 1H), 7.72 (s, 1H), 7.68 (d, *J* = 8.9 Hz, 1H), 7.62 (s, 1H), 4.70 (t, *J* = 8.2 Hz, 2H), 3.37 (t, *J* = 8.2 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 145.6, 132.2, 131.7, 129.1, 129.0, 126.6, 122.8, 117.2, 69.2, 27.6 ppm.

MS (EI) m/z (%) 248.9 $[M]^+$ 148.0, 118.0, 93.0, 65.0. The data match those reported in literature.[14]

1-(4-Chlorobenzyl)-2,3-dihydro-1H-pyrrolo[2,3-b]quinoline (9d)



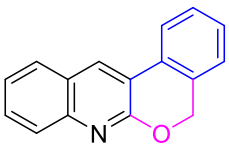
The title compound **9d** was prepared following the **general procedure D** from N-(4-chlorobenzyl)but-3-yn-1-amine **1ag** (1.2 mmol, 232.7 mg), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and purified by column chromatography (SiO_2, PE/EA = 20:1) as a light yellow solid (53.5 mg, 60%), m.p 117 – 119 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 11.4 Hz, 2H), 7.34 – 7.27 (m, 4H), 7.19 (t, *J* = 7.4 Hz, 1H), 4.72 (s, 2H), 3.45 (t, *J* = 7.8 Hz, 2H), 3.05 (t, *J* = 7.8 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 147.7, 136.2, 132.9, 129.7, 129.5, 128.5, 128.3, 127.1, 125.8, 125.7, 124.2, 121.7, 47.9, 25.0 ppm.

HRMS (ESI) m/z calcd. for $C_{18}H_{16}ClN_2$ $[M+H]^+$ 295.0997; found 295.0993.

5*H*-Isochromeno[3,4-b]quinolone (9e)



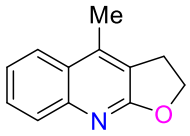
The title compound **9e** was prepared following the **general procedure D** from (2-ethynylphenyl)methanol **1ah** (1.2 mmol, 147 ul), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and purified by column chromatography (SiO_2, PE/EA = 10:1) as a yellow solid (48.8 mg, 69%), m.p 147 – 149 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.87 (dd, *J* = 7.8, 5.5 Hz, 2H), 7.79 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.64 – 7.60 (m, 1H), 7.46 – 7.38 (m, 2H), 7.38 – 7.32 (m, 1H), 7.19 (d, *J* = 0.6 Hz, 1H), 5.43 (s, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 146.8, 131.7, 131.2, 130.0, 128.9, 128.7, 127.6, 127.6, 126.2, 125.0, 124.8, 122.8, 117.7, 68.9 ppm.

HRMS (ESI) m/z calcd. for $C_{16}H_{12}NO$ $[M+H]^+$ 234.0913; found 234.0910.

4-Methyl-2,3-dihydrofuro[2,3-b]quinoline (9f)[14]



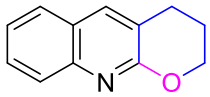
The title compound **9f** was prepared following the **general procedure D** from 3-butyn-1-ol **1aa** (1.2 mmol, 91 ul), 3-methylbenzo[c]isoxazole **2p** (0.3 mmol, 40 mg) and purified by column chromatography (SiO_2, PE/EA = 3:1) as a white solid (34.4 mg, 62%), m.p 119 – 121 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 12.9, 8.3 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 4.65 (t, *J* = 8.2 Hz, 2H), 3.26 (t, *J* = 8.2 Hz, 2H), 2.47 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 146.8, 140.6, 128.7, 127.9, 125.2, 123.6, 123.1, 119.8, 68.8, 27.0, 15.2 ppm.

MS (EI) m/z (%) 185.0 $[M]^+$, 170.0, 155.0, 140.0, 128.0. The data match those reported in literature.[14]

3,4-Dihydro-2H-pyrano[2,3-b]quinolone (9g)



The title compound **9g** was prepared following the **general procedure D** from pent-4-yn-1-ol **1ai** (1.2 mmol, 111 ul), benzo[*c*]isoxazole **2a** (0.3 mmol, 33 ul) and purified by column chromatography (SiO_2, PE/EA = 5:1) as a light yellow solid (41.6 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.5 Hz, 1H), 7.79 (s, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.58 – 7.53 (m, 1H), 7.36 – 7.31 (m, 1H), 4.46 – 4.43 (m, 2H), 2.99 (t, *J* = 6.3 Hz, 2H), 2.07 (tt, *J* = 9.1, 4.6 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 146.2, 137.8, 129.1, 127.2, 126.6, 125.4, 124.0, 119.0, 67.7, 25.7, 22.0 ppm.

HRMS (ESI) m/z calcd. for $C_{12}H_{12}NO$ $[M+H]^+$ 186.0913; found 186.0911.

8. Supplementary References

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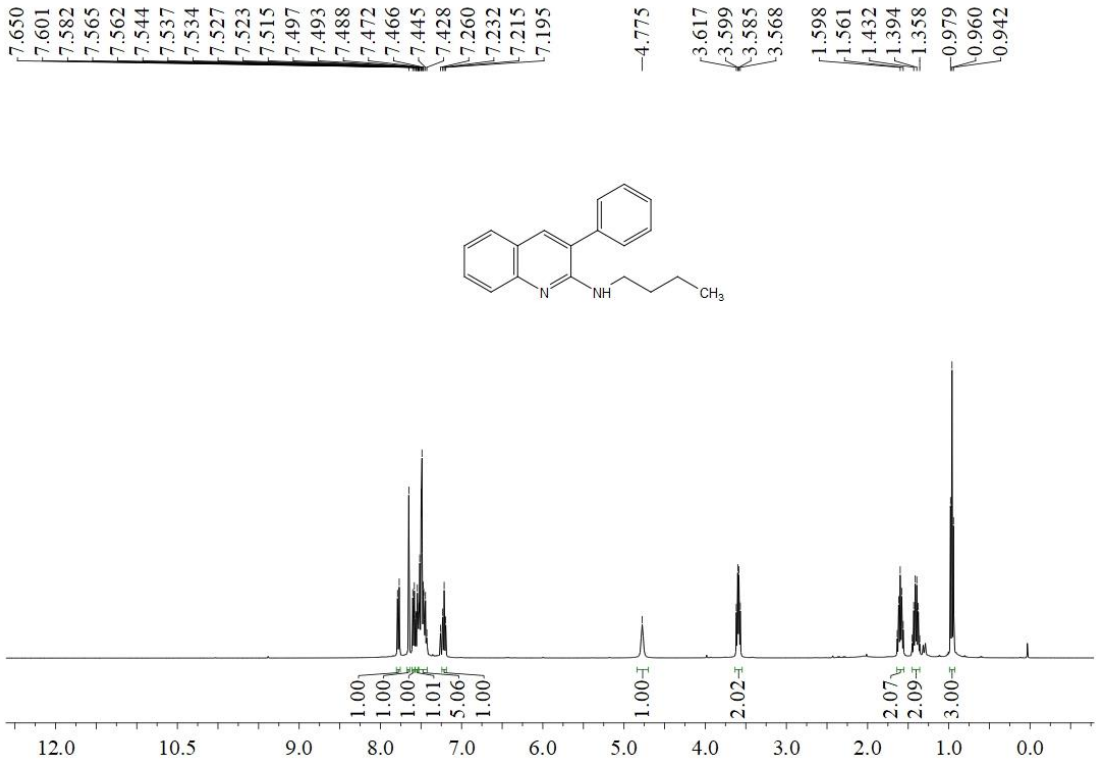
(14) Yu LZ, Hu XB, Xu Q, Shi M. *Chem Commun*, 2016, 52: 2701–2704.

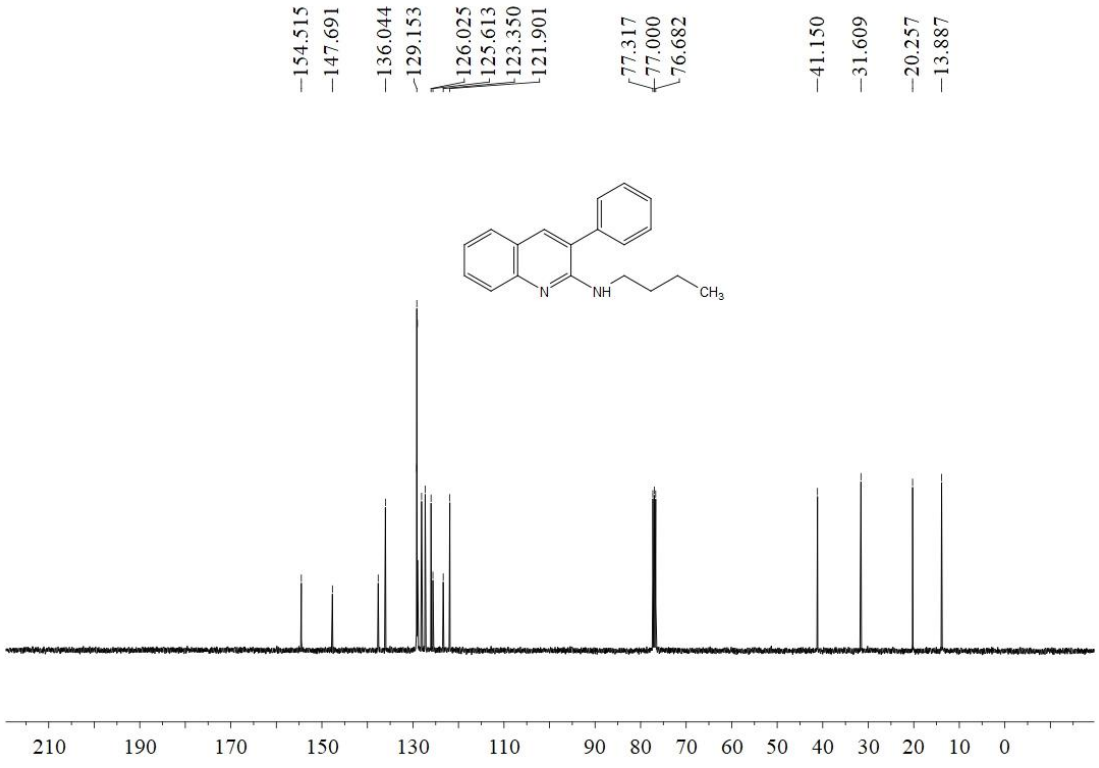
NMR Spectra

N-Butyl-3-phenylquinolin-2-amine (**4a**)

^{1}H NMR (400 MHz, $CDCl_3$)

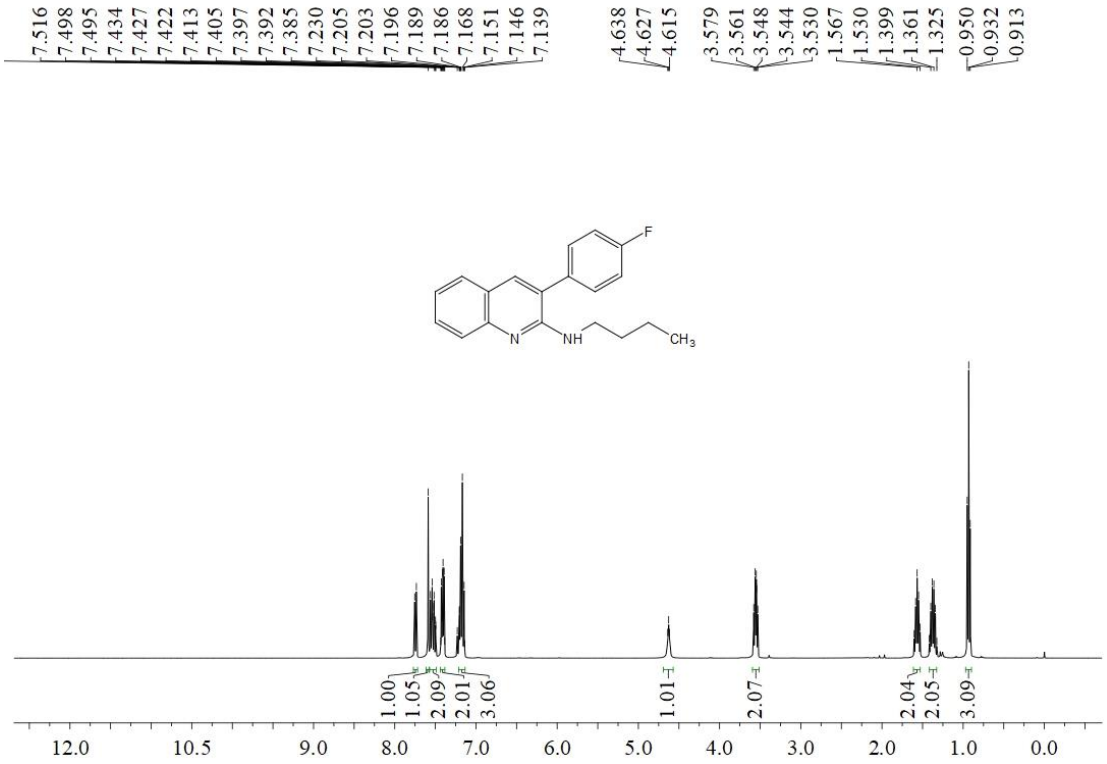


^{13}C NMR (100 MHz, $CDCl_3$)

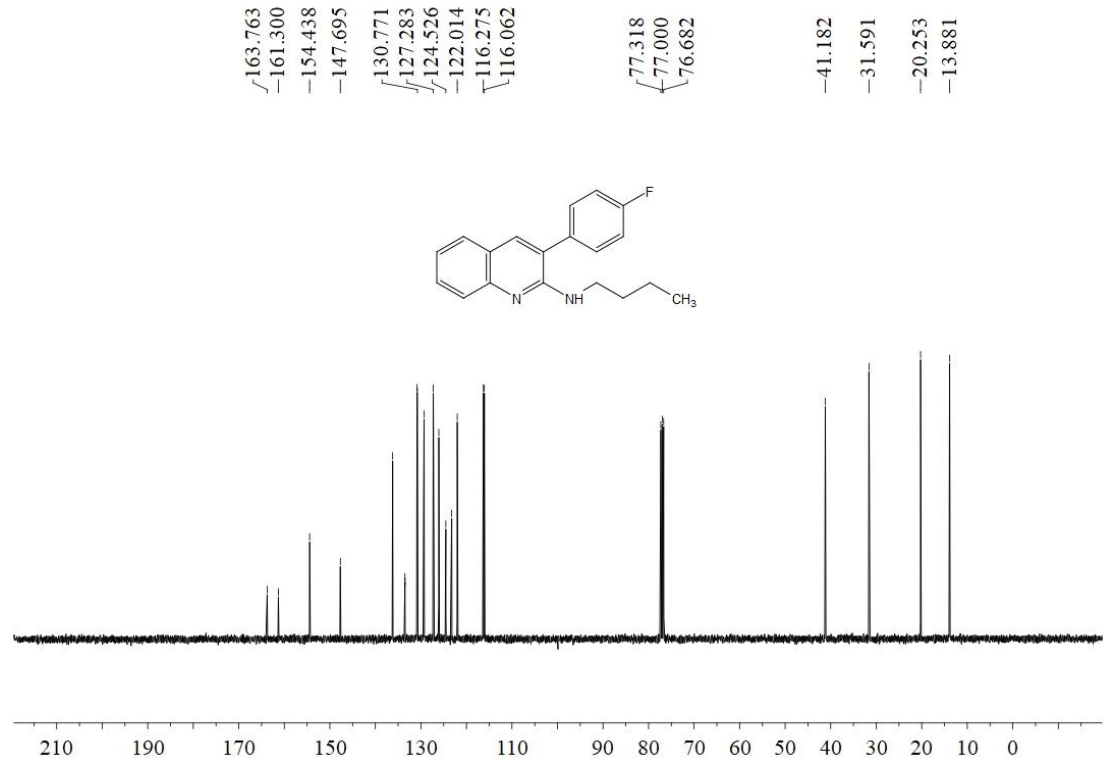


N-Butyl-3-(4-fluorophenyl)quinolin-2-amine (**4b**)

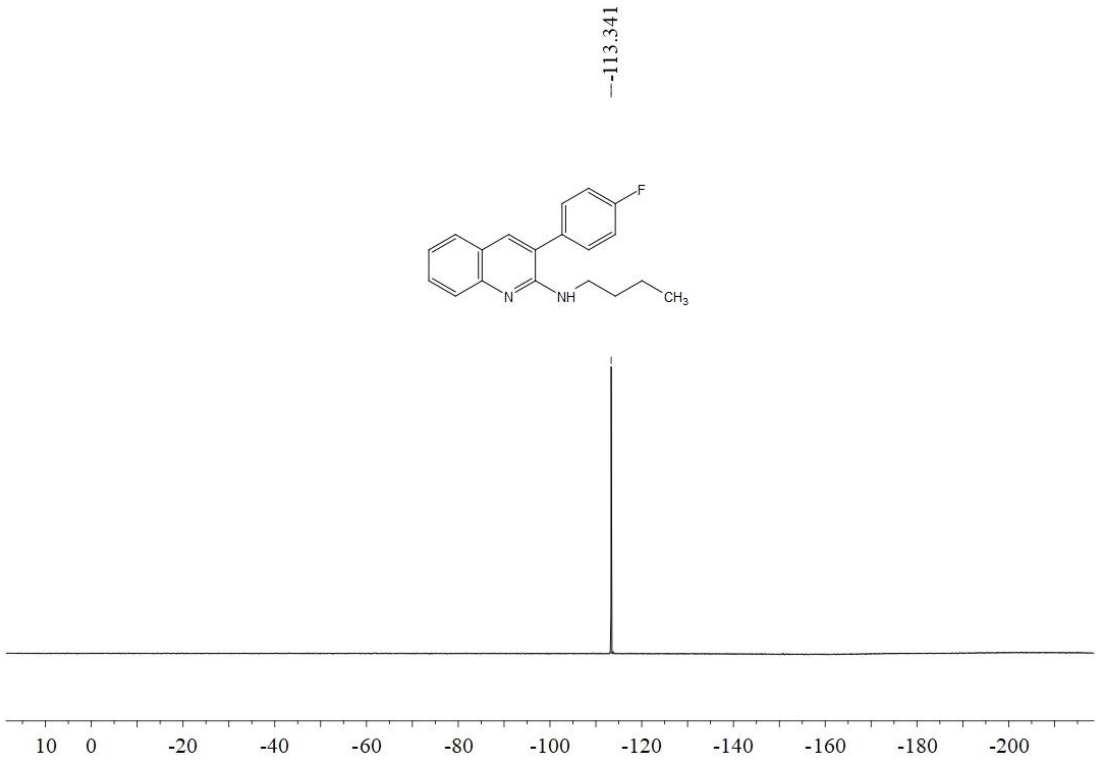
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

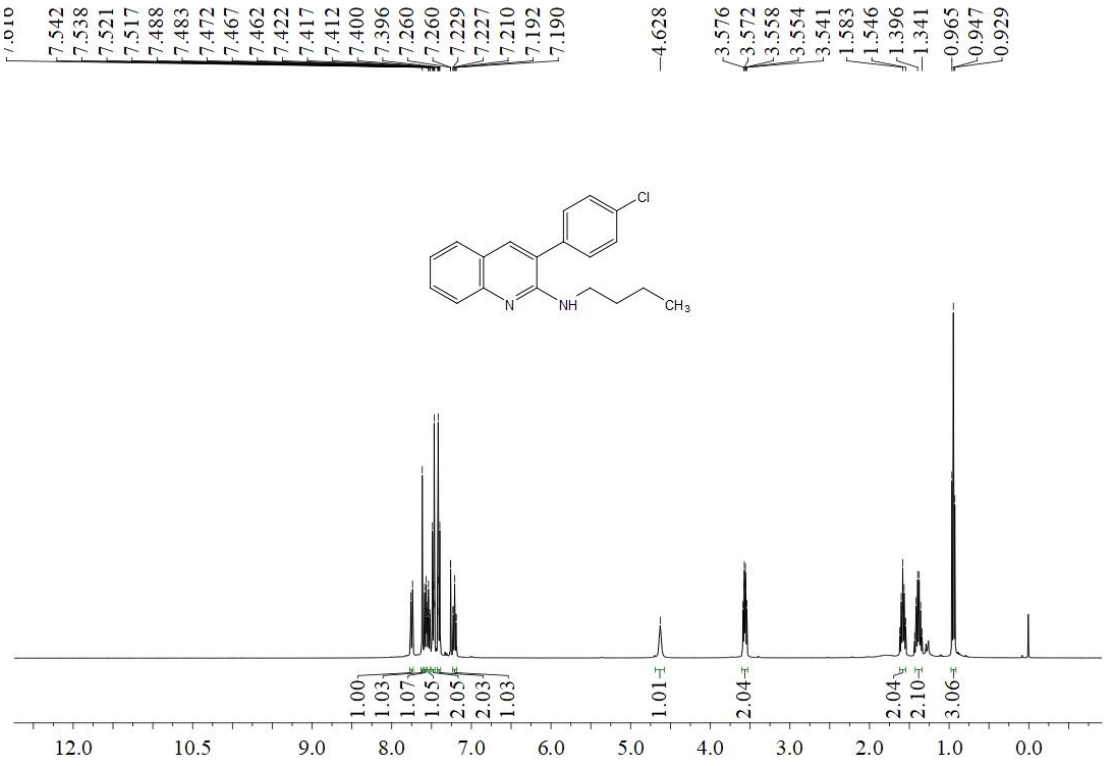


^{19}F NMR (375 MHz, $CDCl_3$)

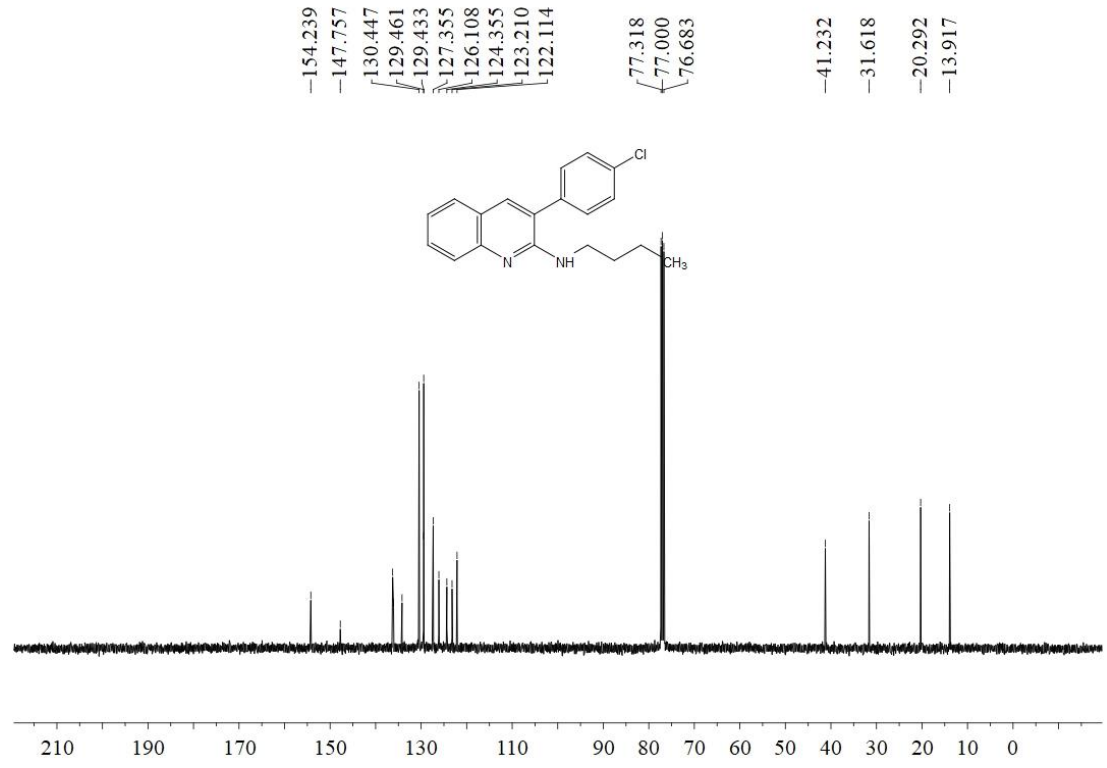


N-Butyl-3-(4-chlorophenyl)quinolin-2-amine (**4c**)

^{1}H NMR (400 MHz, $CDCl_3$)

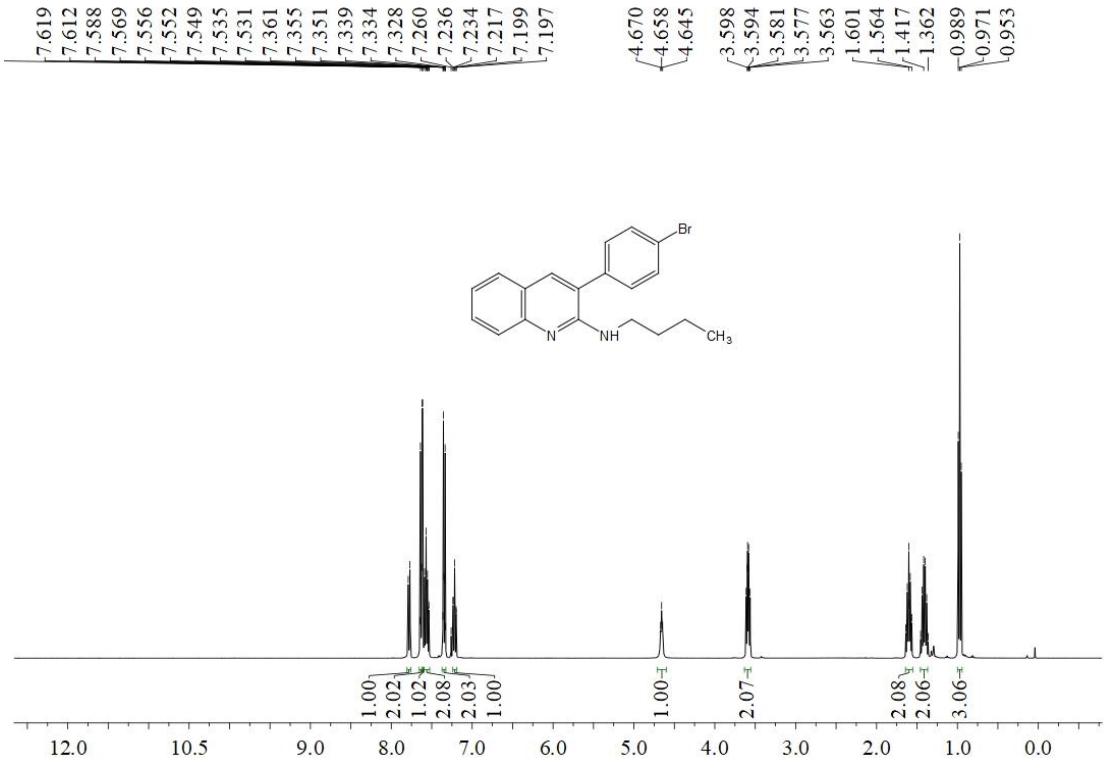


^{13}C NMR (100 MHz, $CDCl_3$)

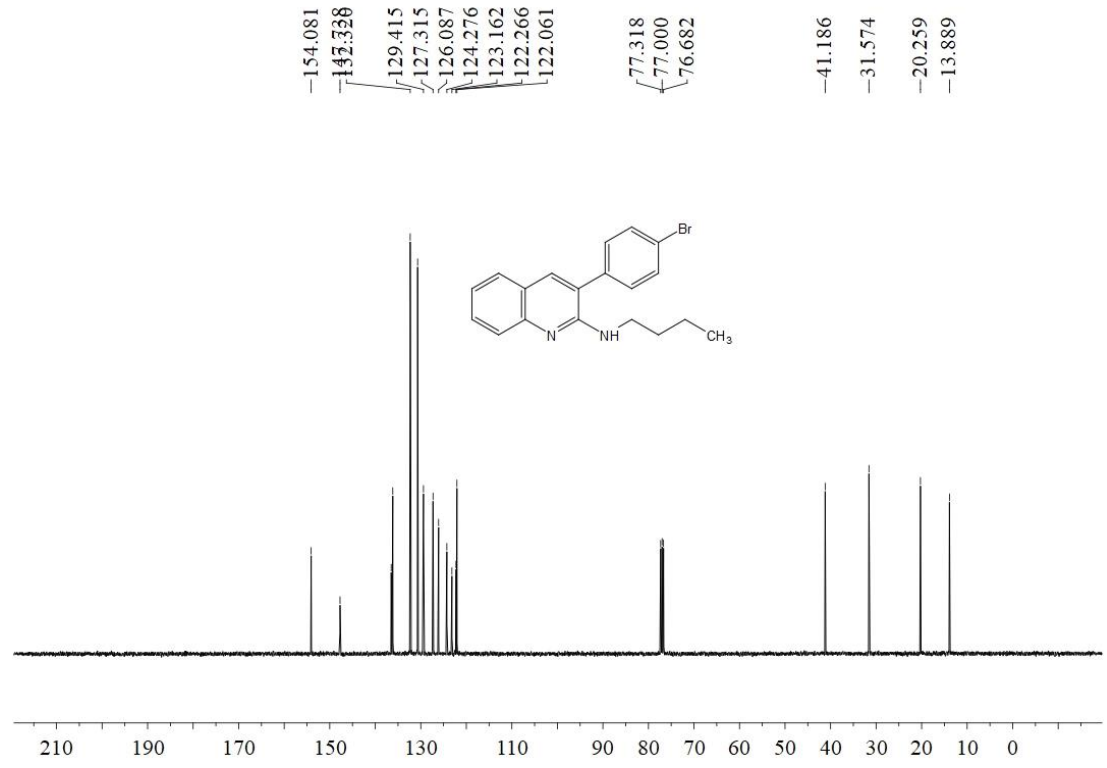


3-(4-Bromophenyl)-*N*-butylquinolin-2-amine (**4d**)

^{1}H NMR (400 MHz, $CDCl_3$)

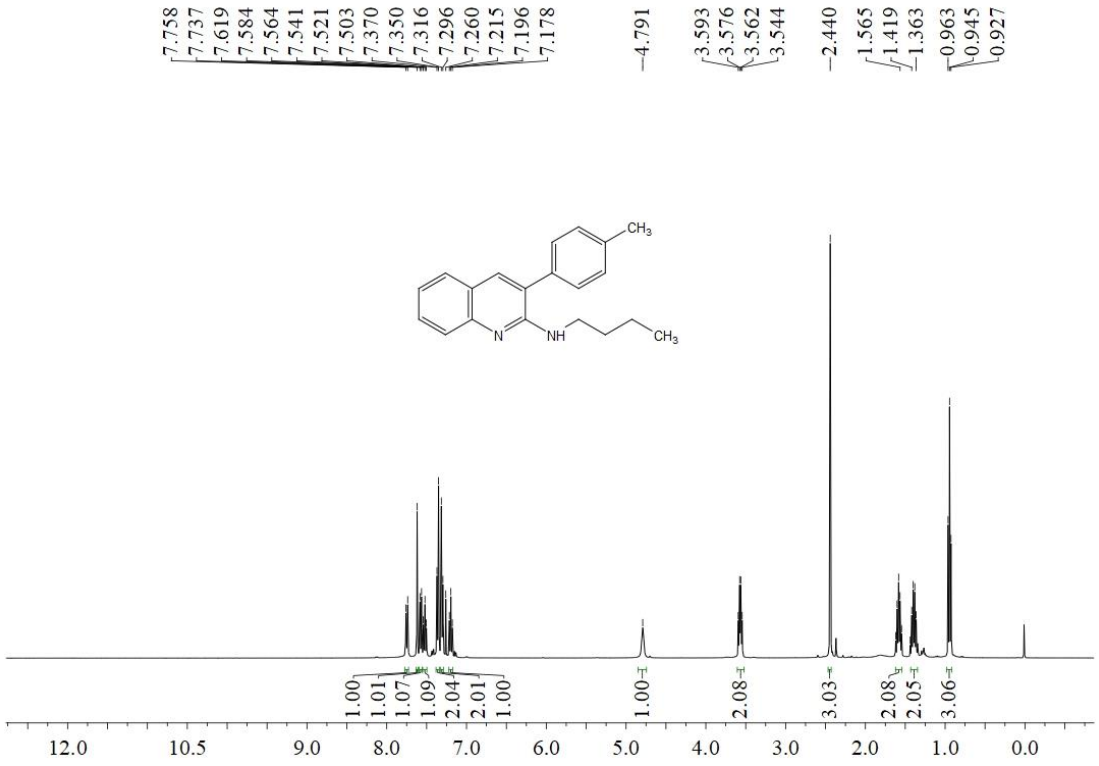


^{13}C NMR (100 MHz, $CDCl_3$)

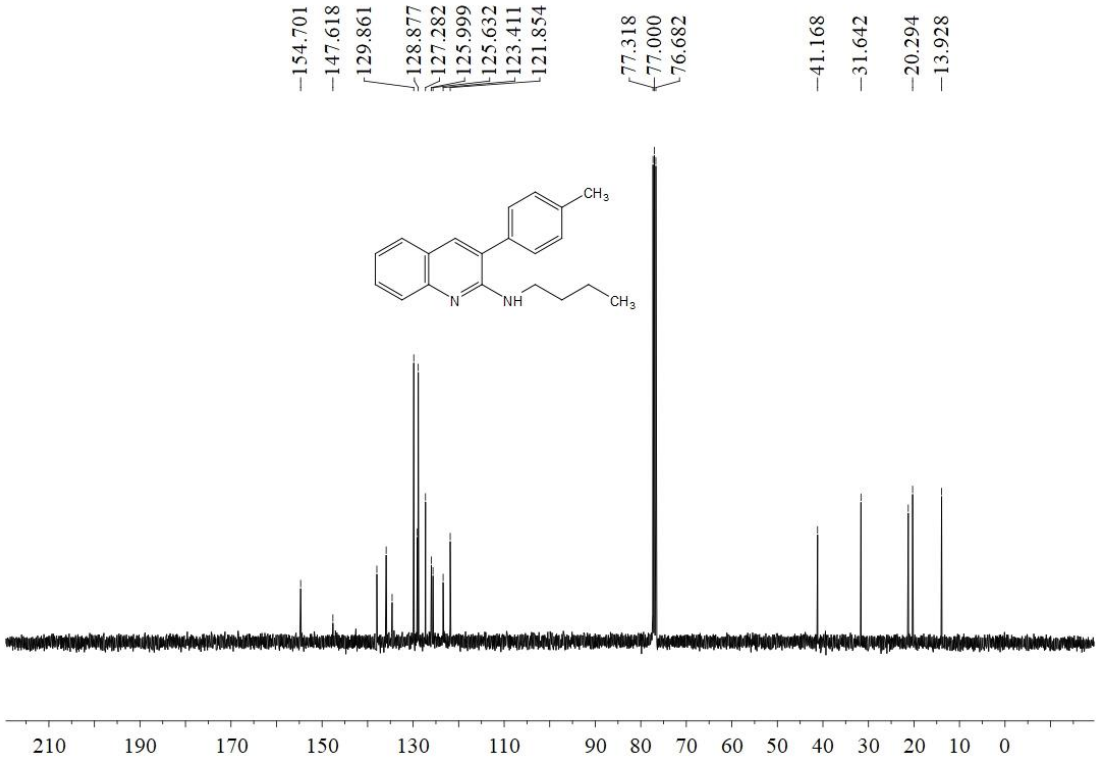


N-Butyl-3-(*p*-tolyl)quinolin-2-amine (**4e**)

^{1}H NMR (400 MHz, $CDCl_3$)

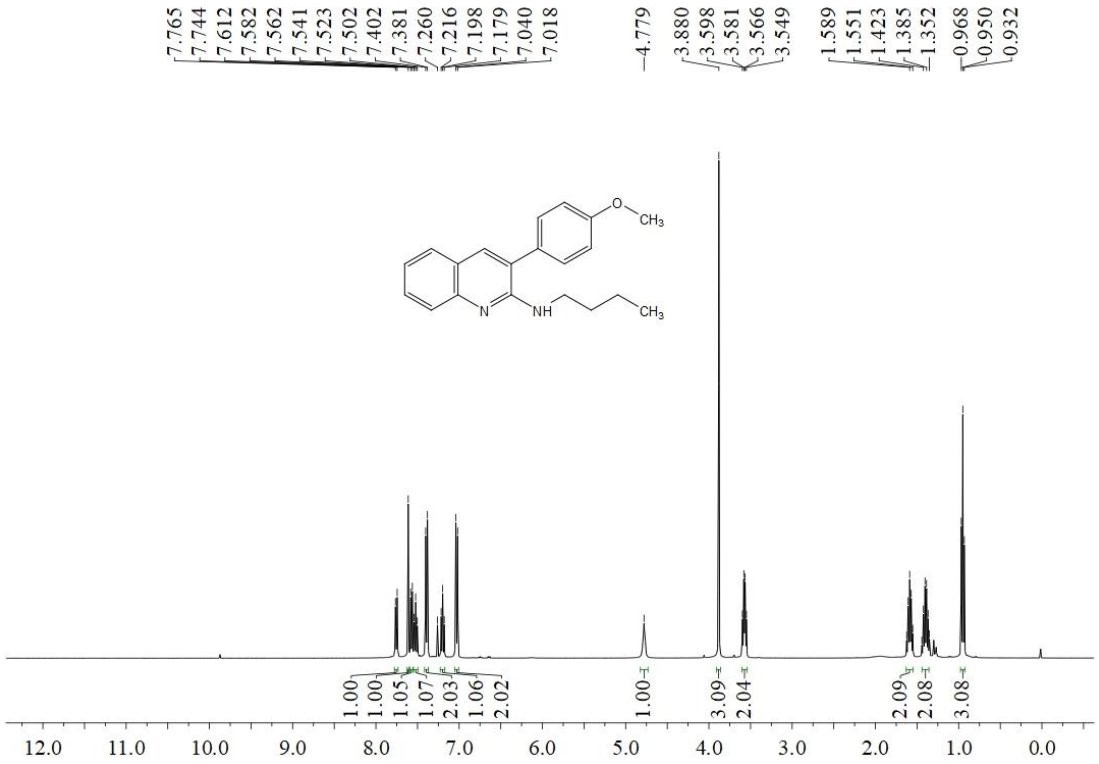


^{13}C NMR (100 MHz, $CDCl_3$)

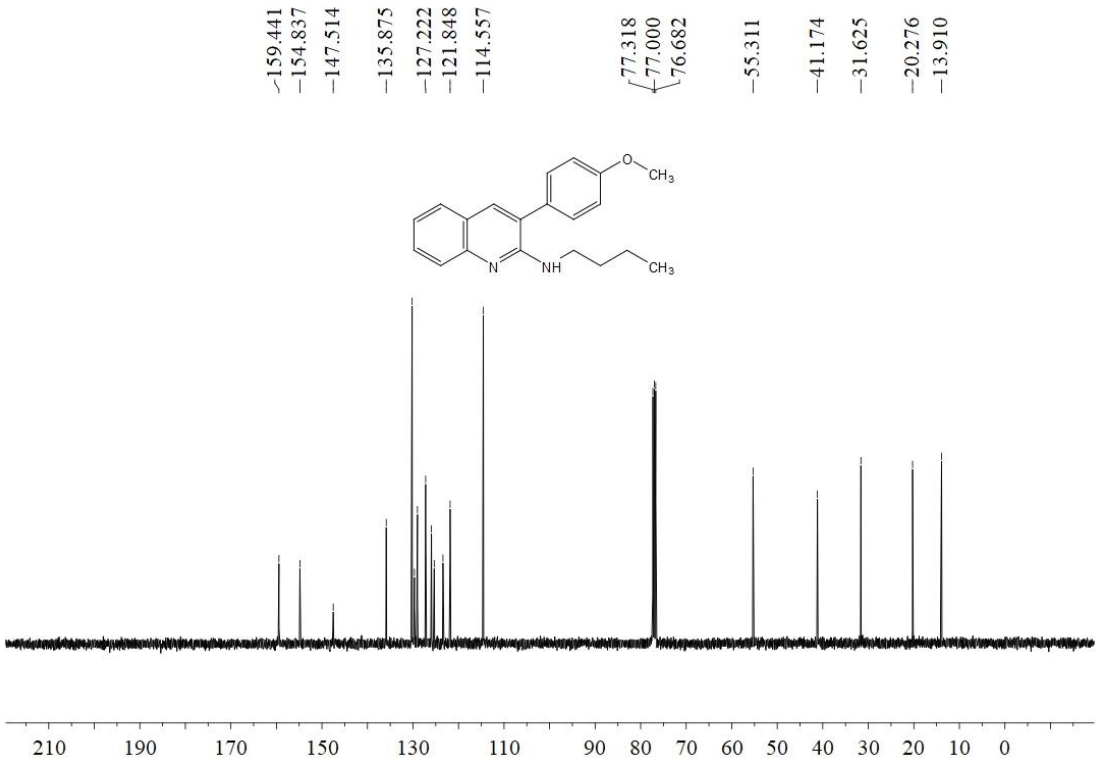


N-Butyl-3-(4-methoxyphenyl)quinolin-2-amine (**4f**)

^{1}H NMR (400 MHz, $CDCl_3$)

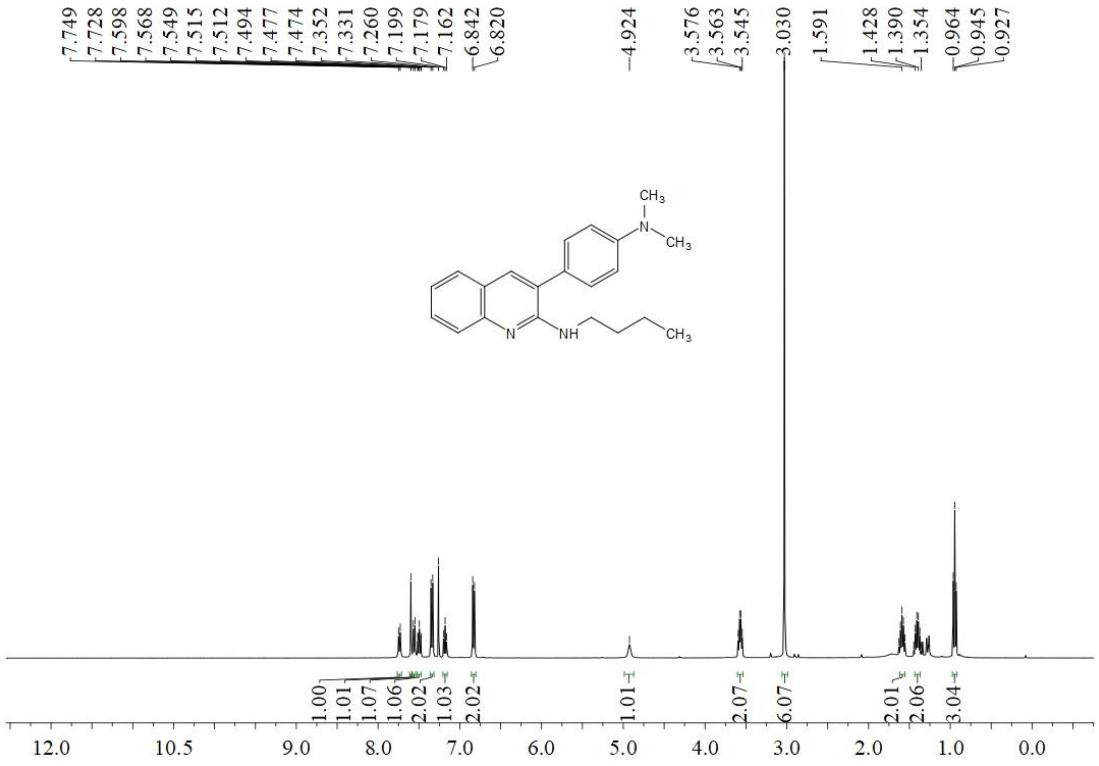


^{13}C NMR (100 MHz, $CDCl_3$)

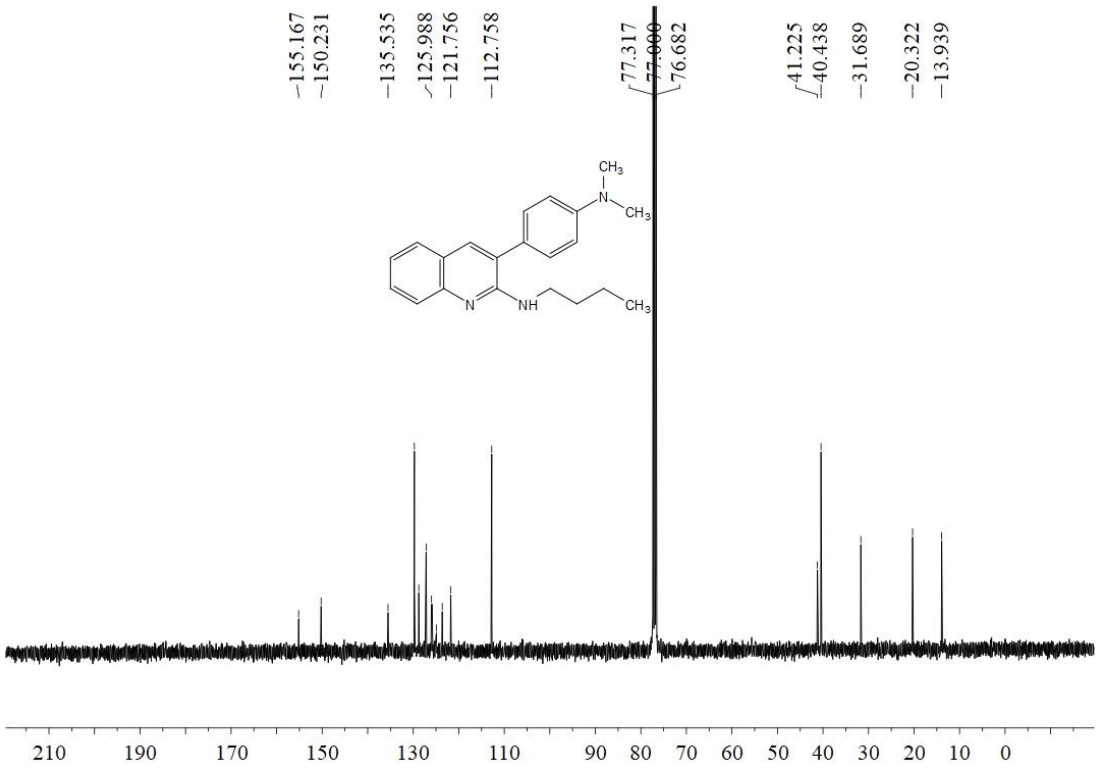


N-Butyl-3-(4-(dimethylamino)phenyl)quinolin-2-amine (**4g**)

^{1}H NMR (400 MHz, $CDCl_3$)

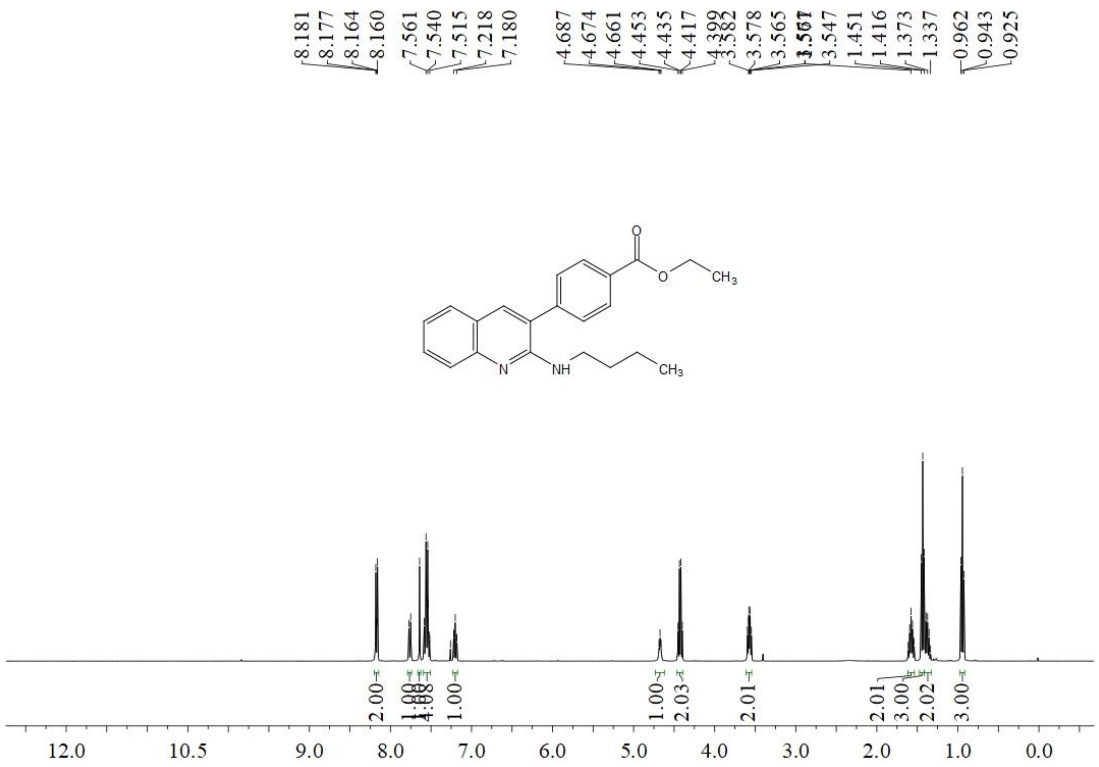


^{13}C NMR (100 MHz, $CDCl_3$)

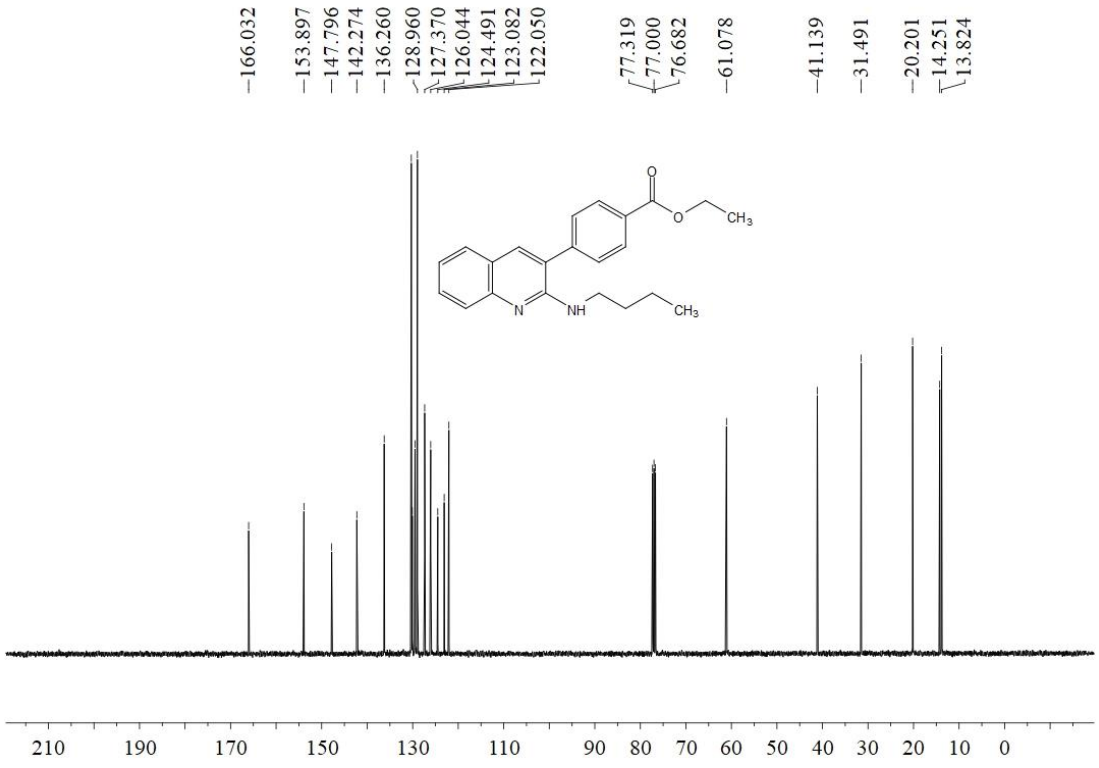


Ethyl 4-(2-(butylamino)quinolin-3-yl)benzoate (**4h**)

^{1}H NMR (400 MHz, $CDCl_3$)

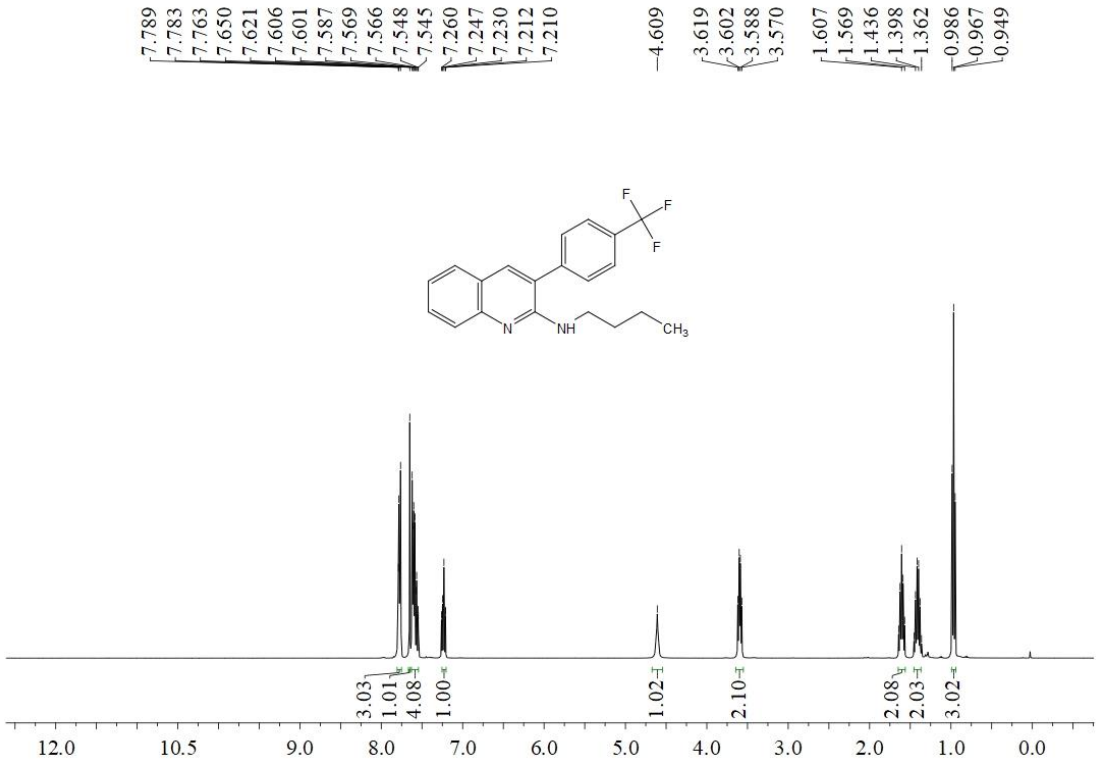


^{13}C NMR (100 MHz, $CDCl_3$)

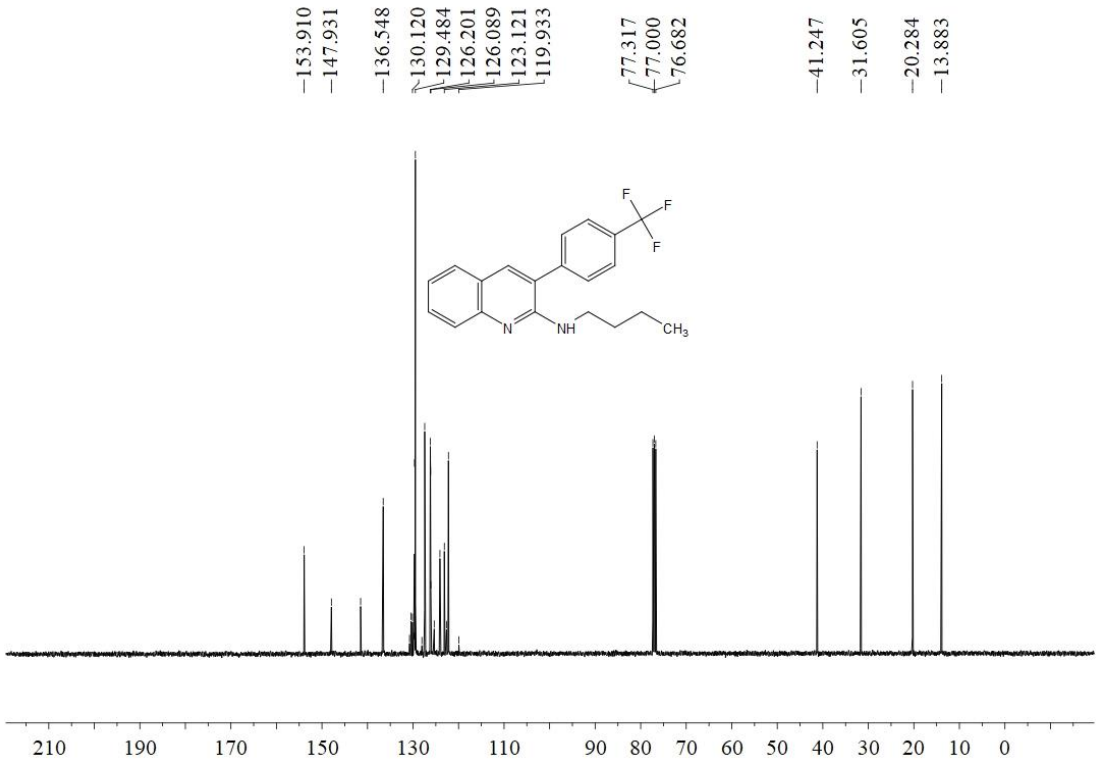


N-Butyl-3-(4-(trifluoromethyl)phenyl)quinolin-2-amine (**4i**)

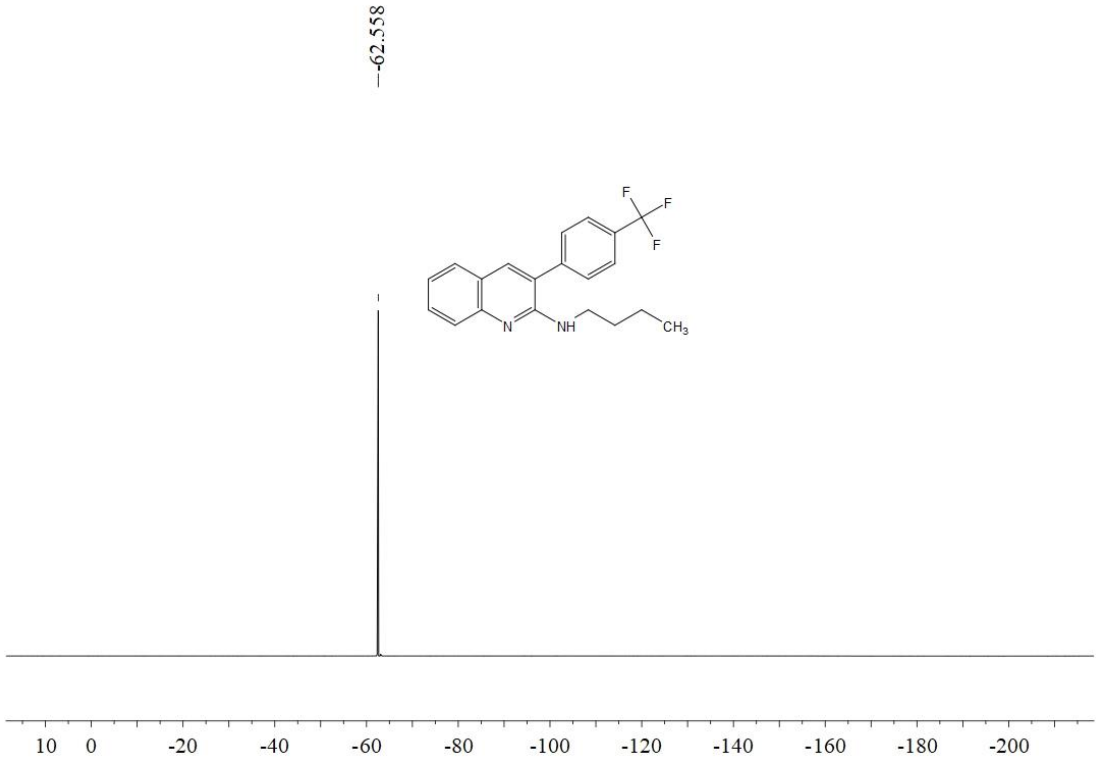
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

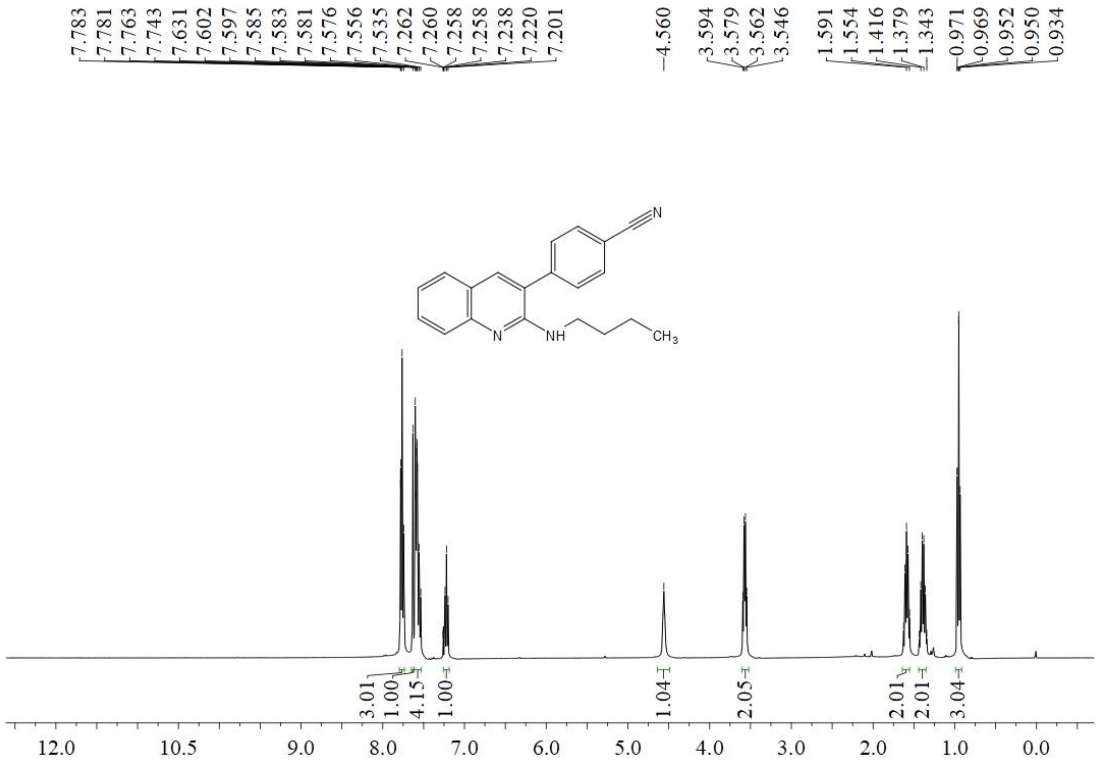


^{19}F NMR (375 MHz, $CDCl_3$)

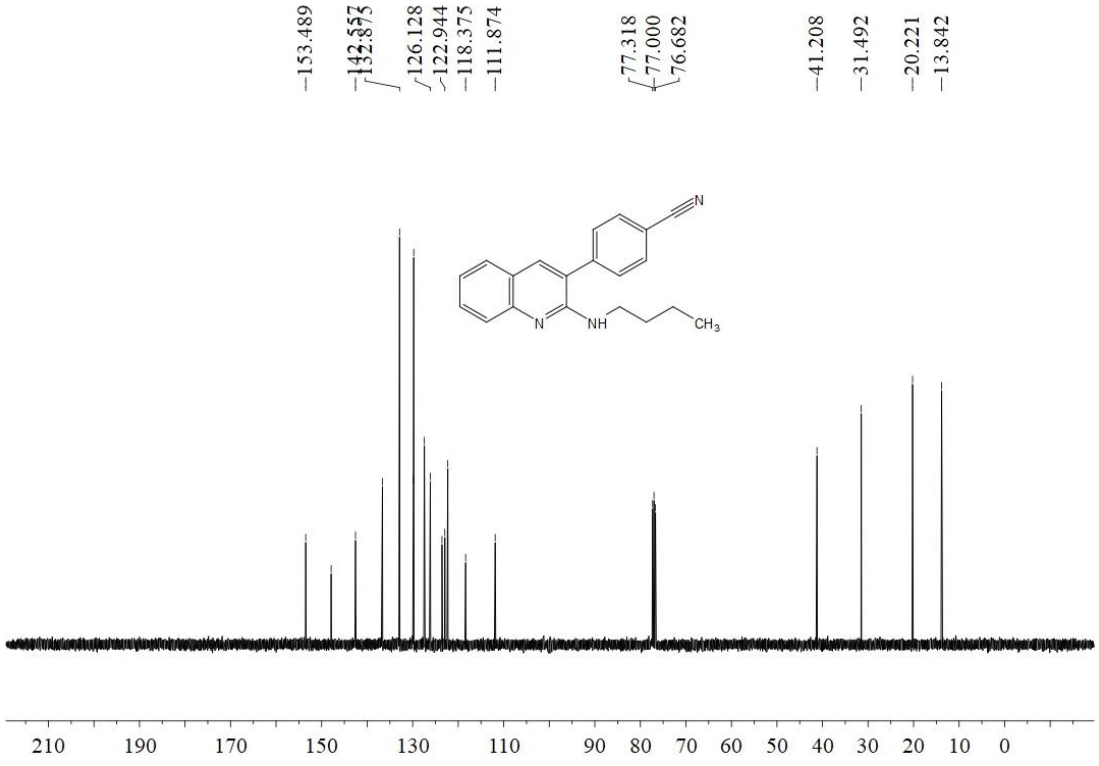


4-(2-(Butylamino)quinolin-3-yl)benzonitrile (**4j**)

^{1}H NMR (400 MHz, $CDCl_3$)

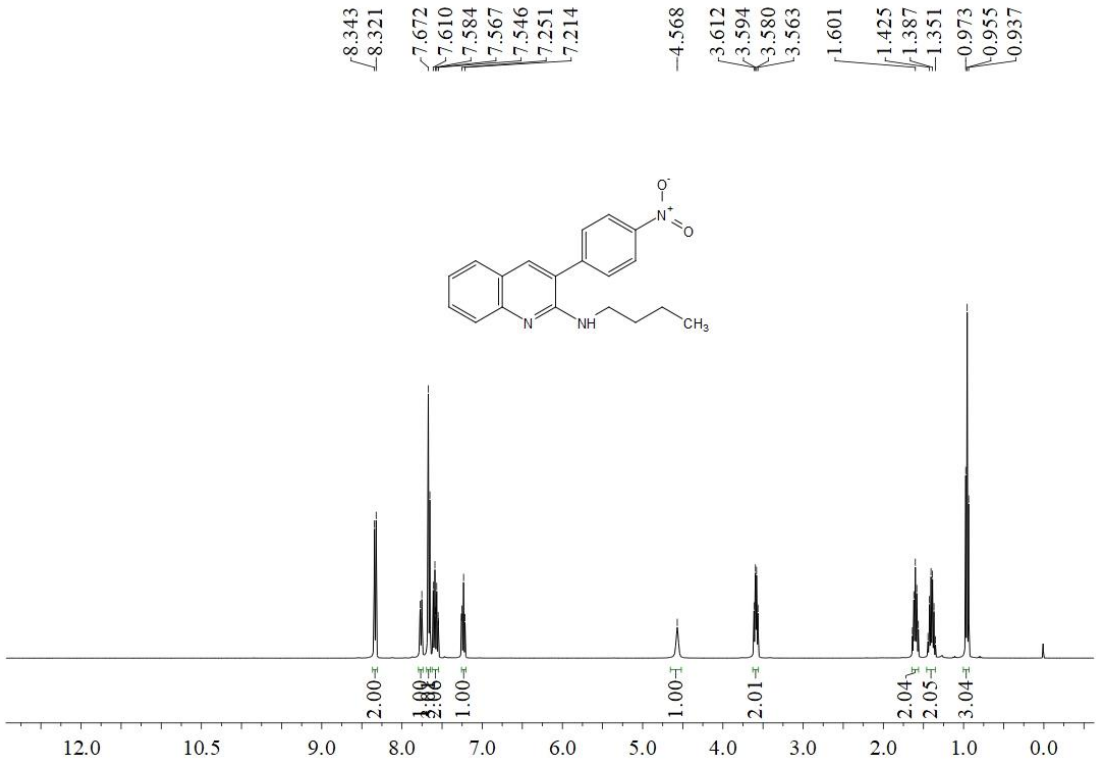


^{13}C NMR (100 MHz, $CDCl_3$)

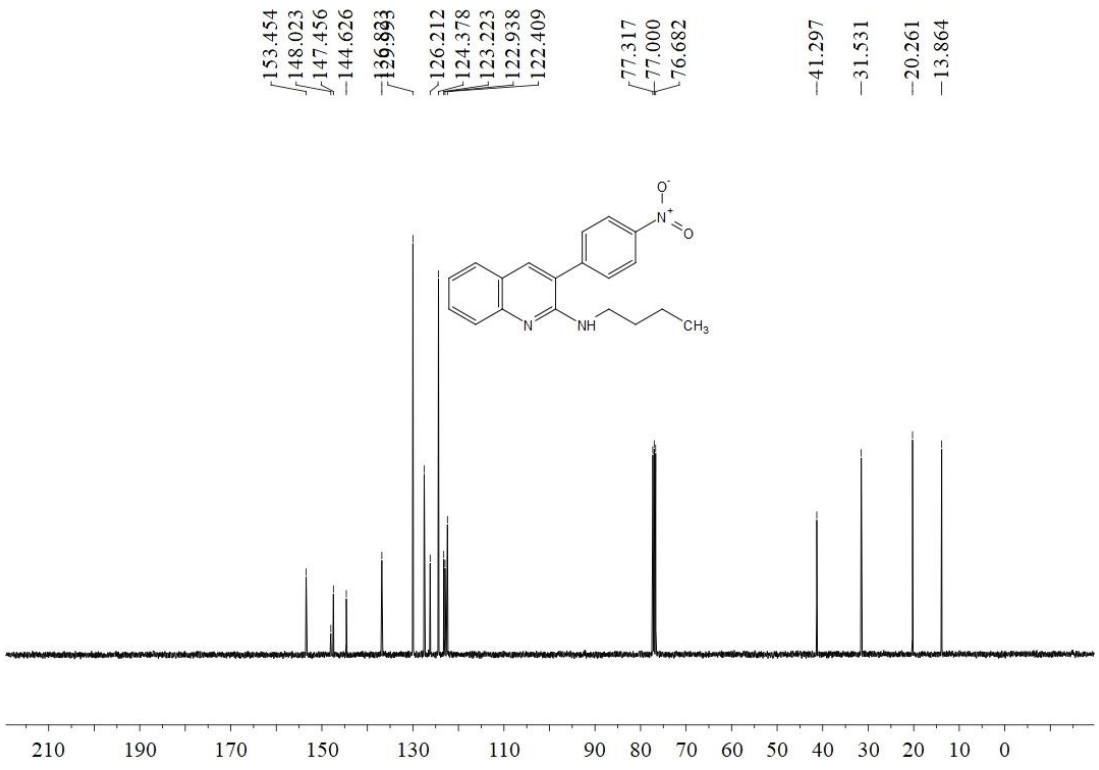


N-Butyl-3-(4-nitrophenyl)quinolin-2-amine (**4k**)

^{1}H NMR (400 MHz, $CDCl_3$)

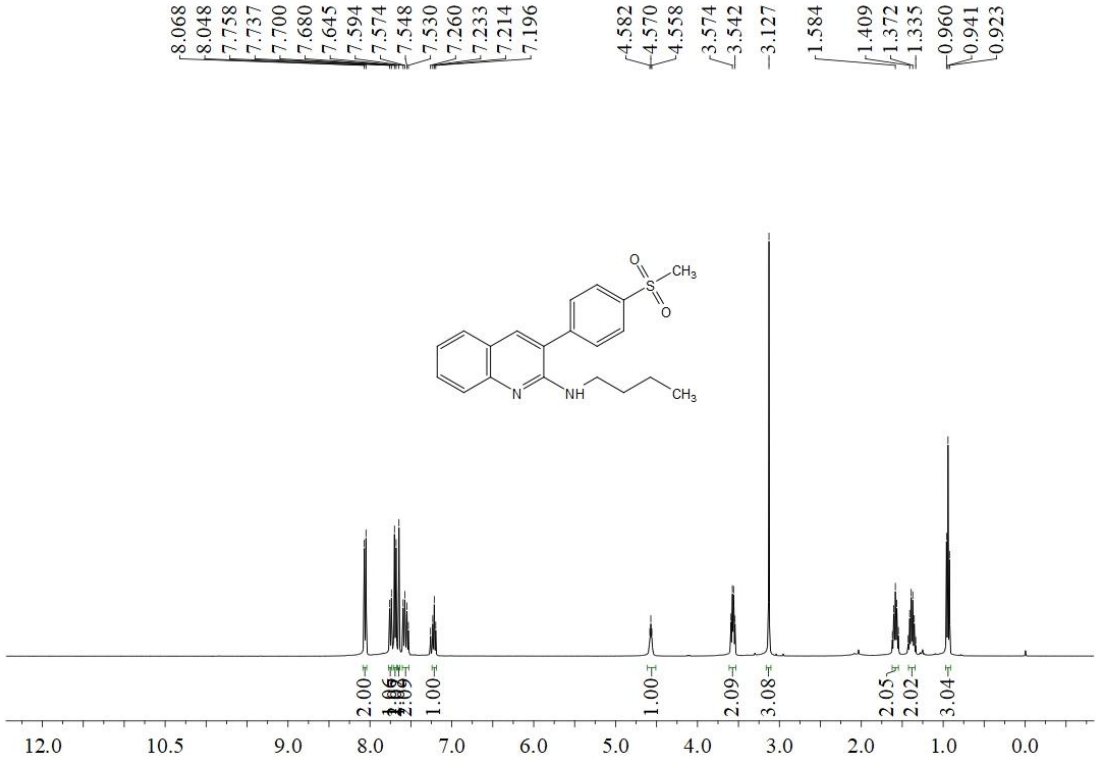


^{13}C NMR (100 MHz, $CDCl_3$)

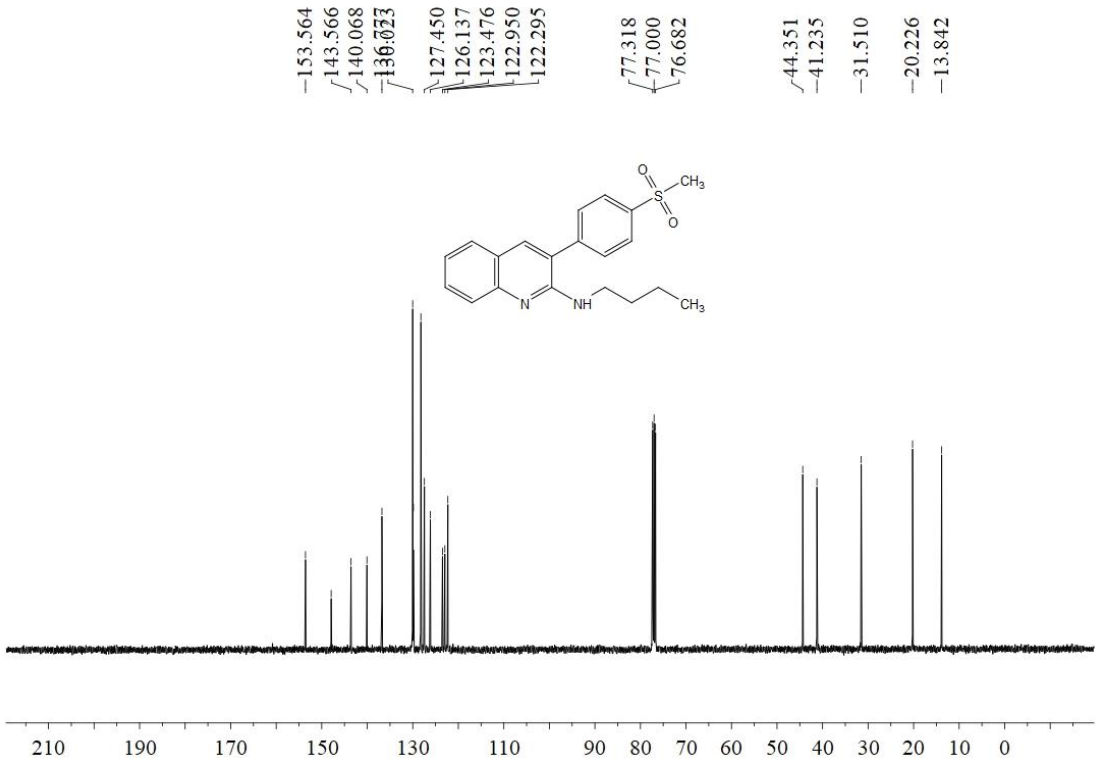


N-Butyl-3-(4-(methylsulfonyl)phenyl)quinolin-2-amine (**4l**)

^{1}H NMR (400 MHz, $CDCl_3$)

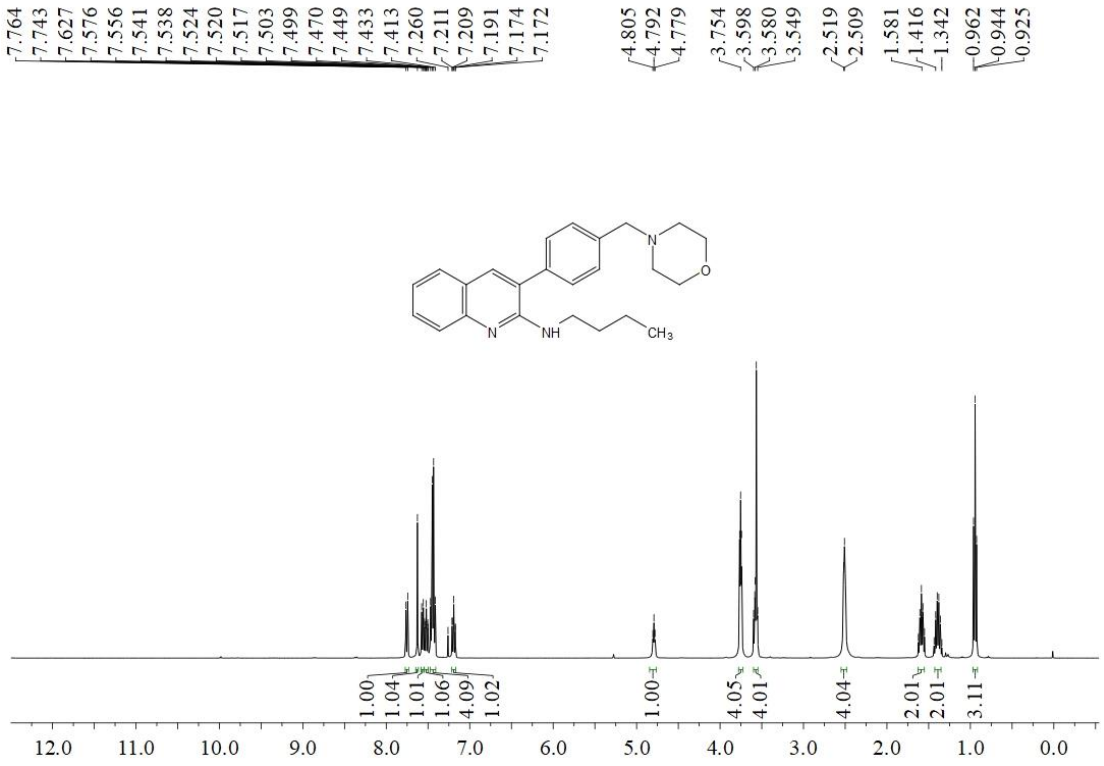


^{13}C NMR (100 MHz, $CDCl_3$)

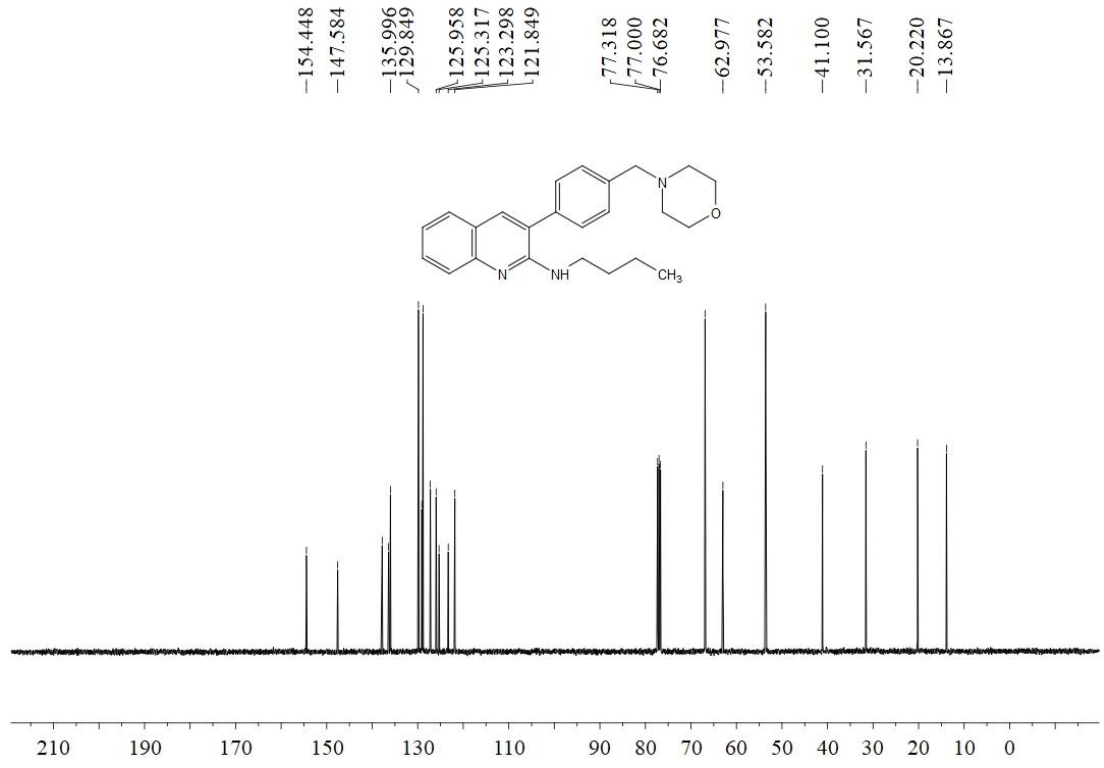


N-Butyl-3-(4-(morpholinomethyl)phenyl)quinolin-2-amine (**4m**)

^{1}H NMR (400 MHz, $CDCl_3$)

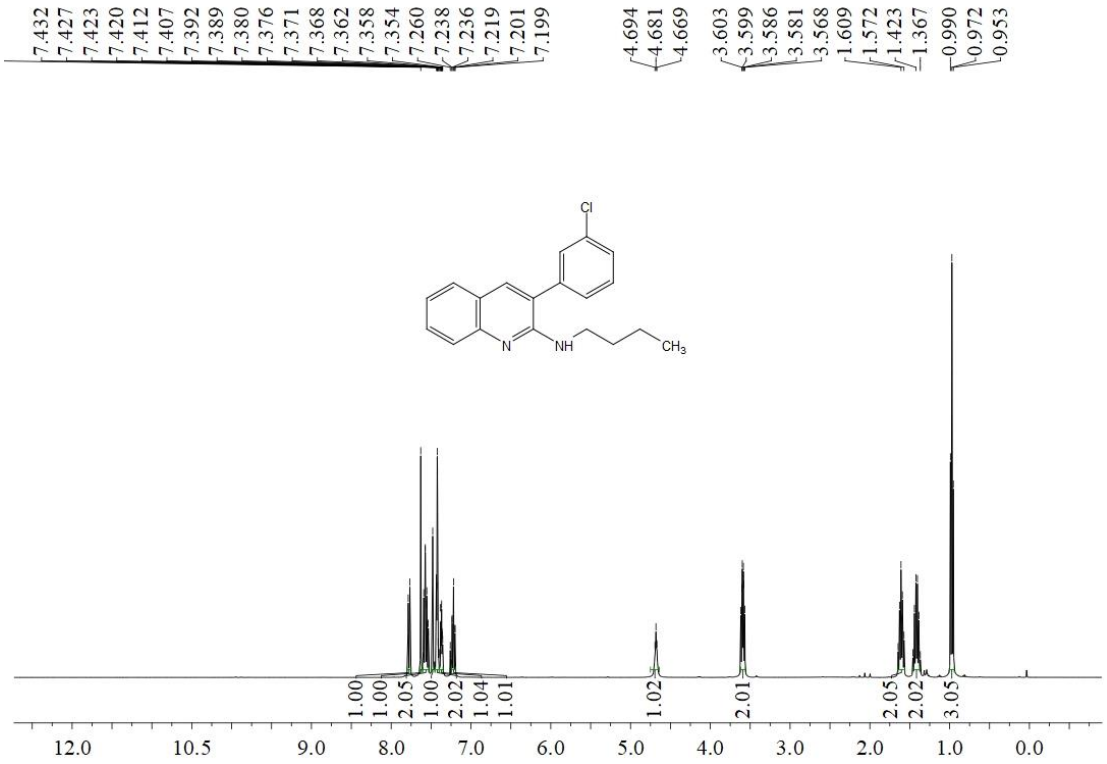


^{13}C NMR (100 MHz, $CDCl_3$)

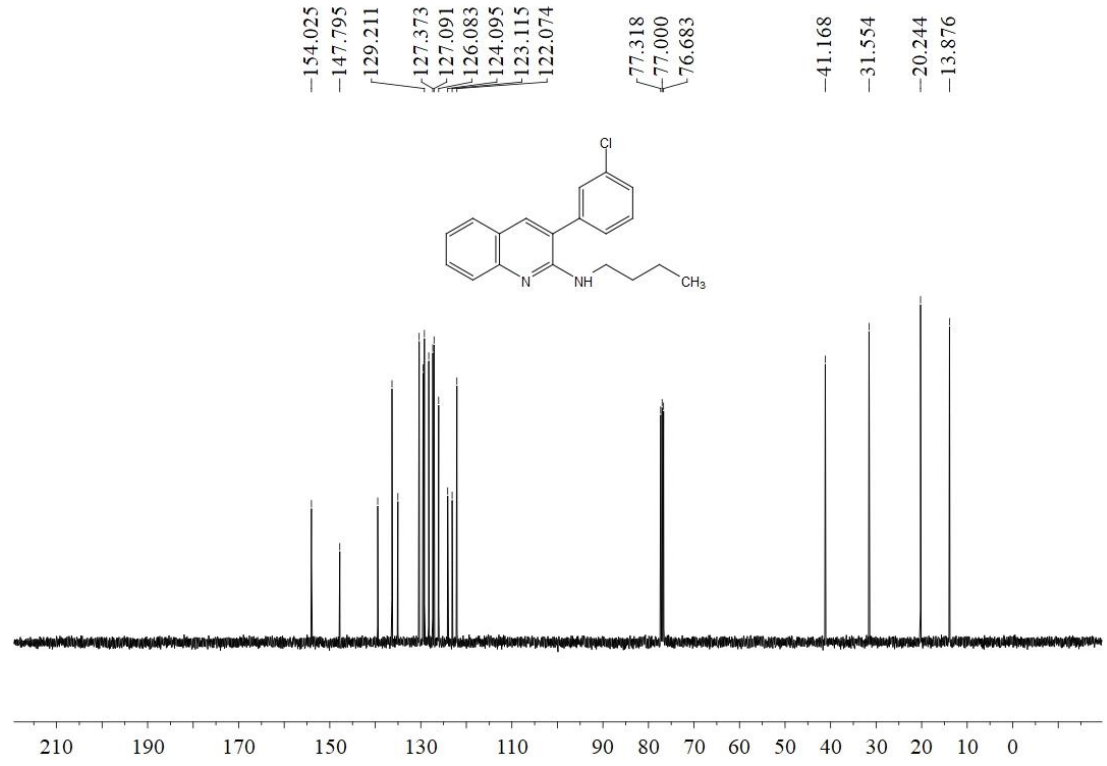


N-Butyl-3-(3-chlorophenyl)quinolin-2-amine (**4n**)

^{1}H NMR (400 MHz, $CDCl_3$)

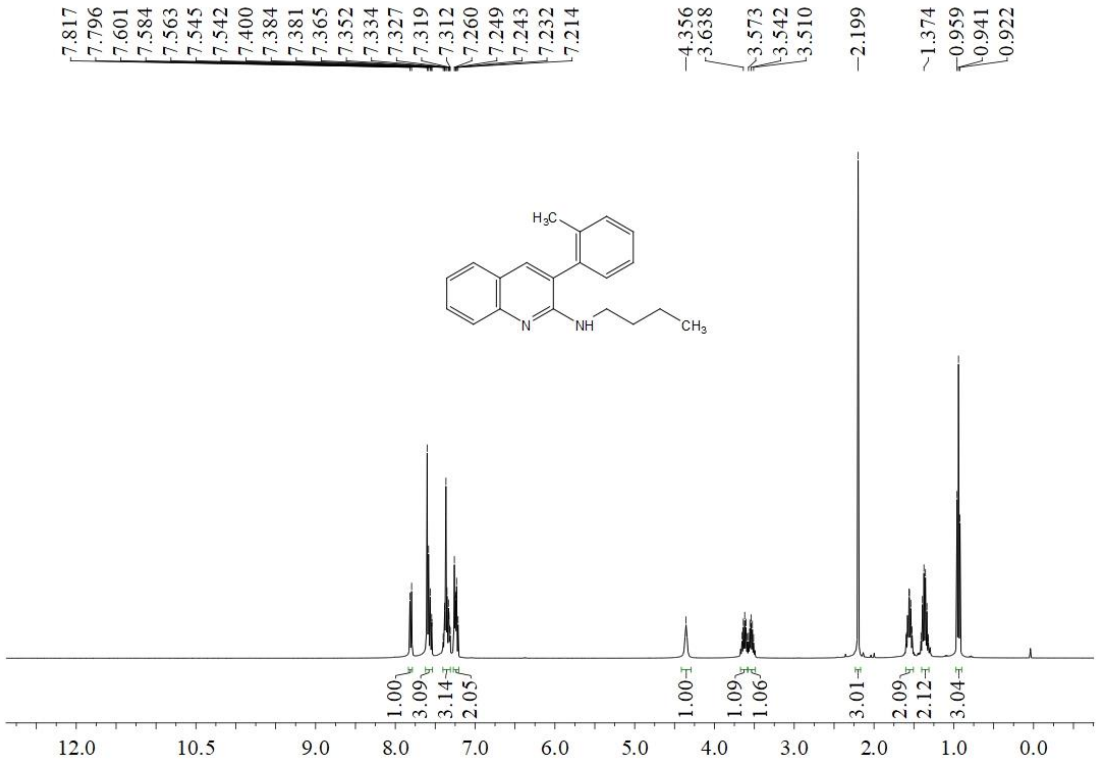


^{13}C NMR (100 MHz, $CDCl_3$)

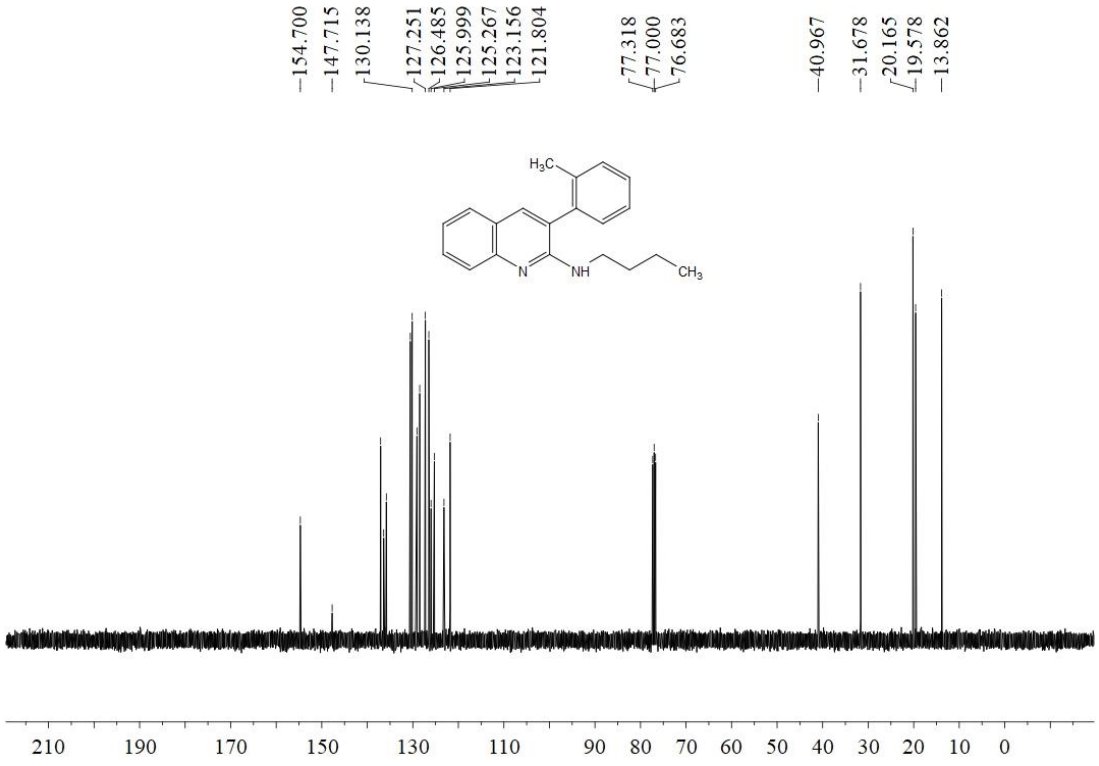


N-Butyl-3-(o-tolyl)quinolin-2-amine (**4o**)

^{1}H NMR (400 MHz, $CDCl_3$)

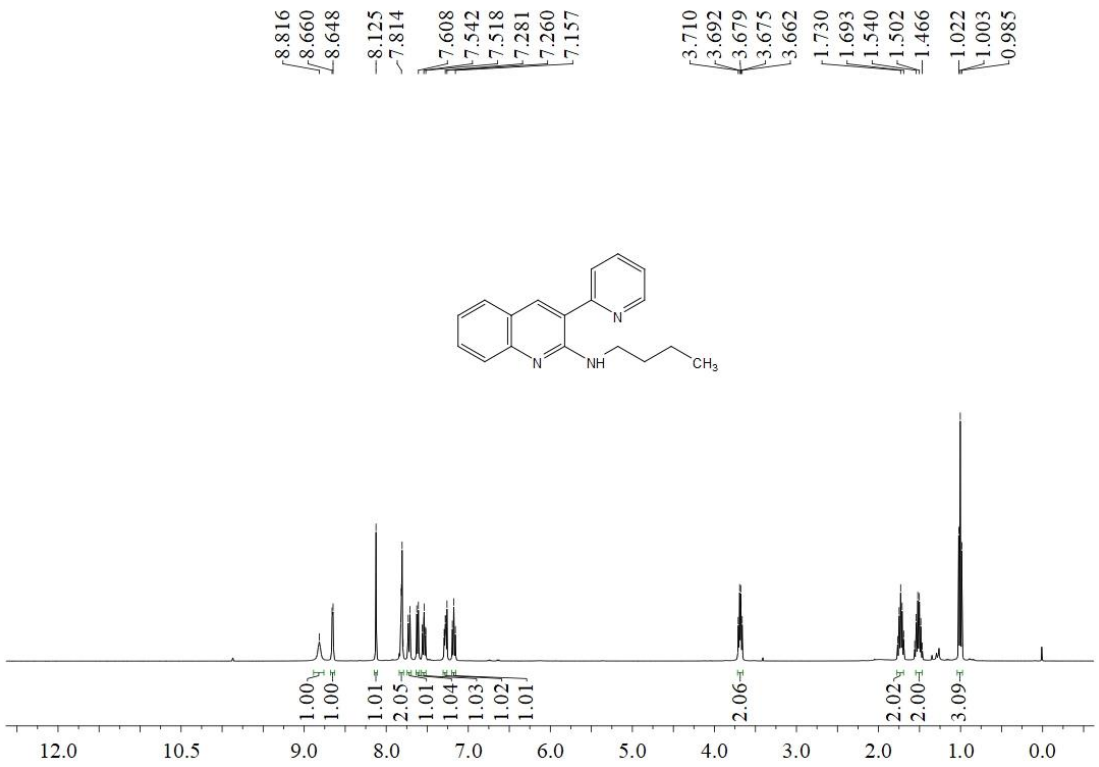


^{13}C NMR (100 MHz, $CDCl_3$)

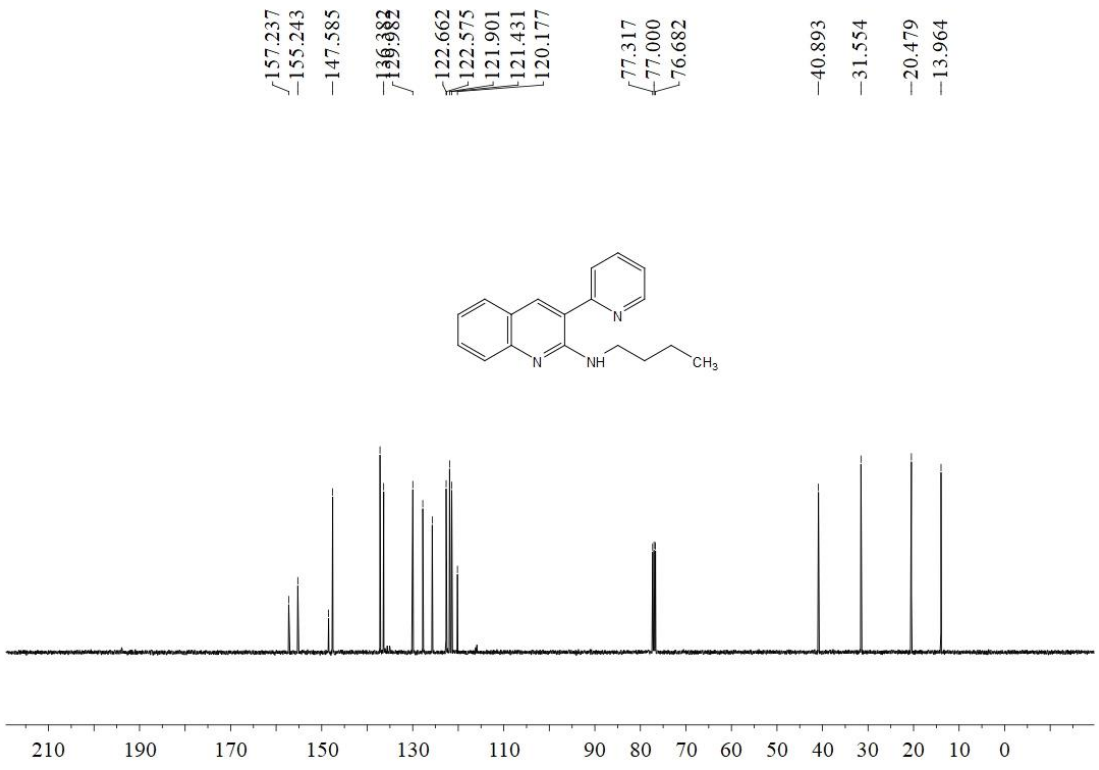


N-Butyl-3-(pyridin-2-yl)quinolin-2-amine (**4p**)

^{1}H NMR (400 MHz, $CDCl_3$)

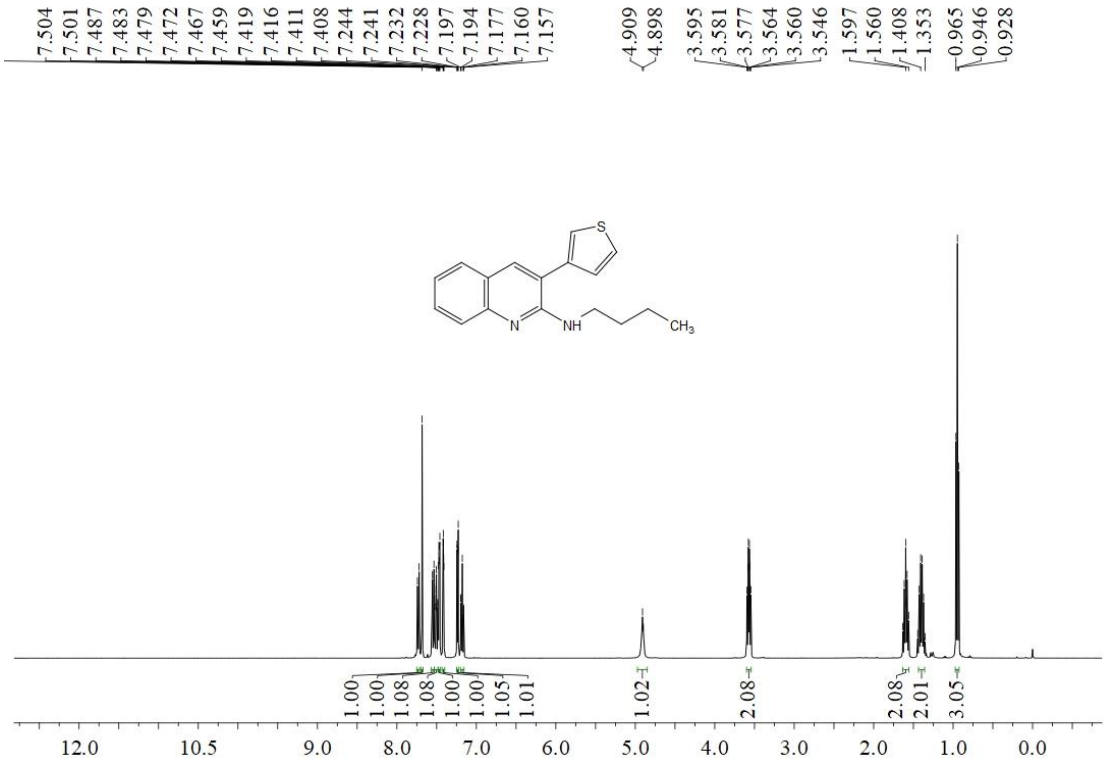


^{13}C NMR (100 MHz, $CDCl_3$)

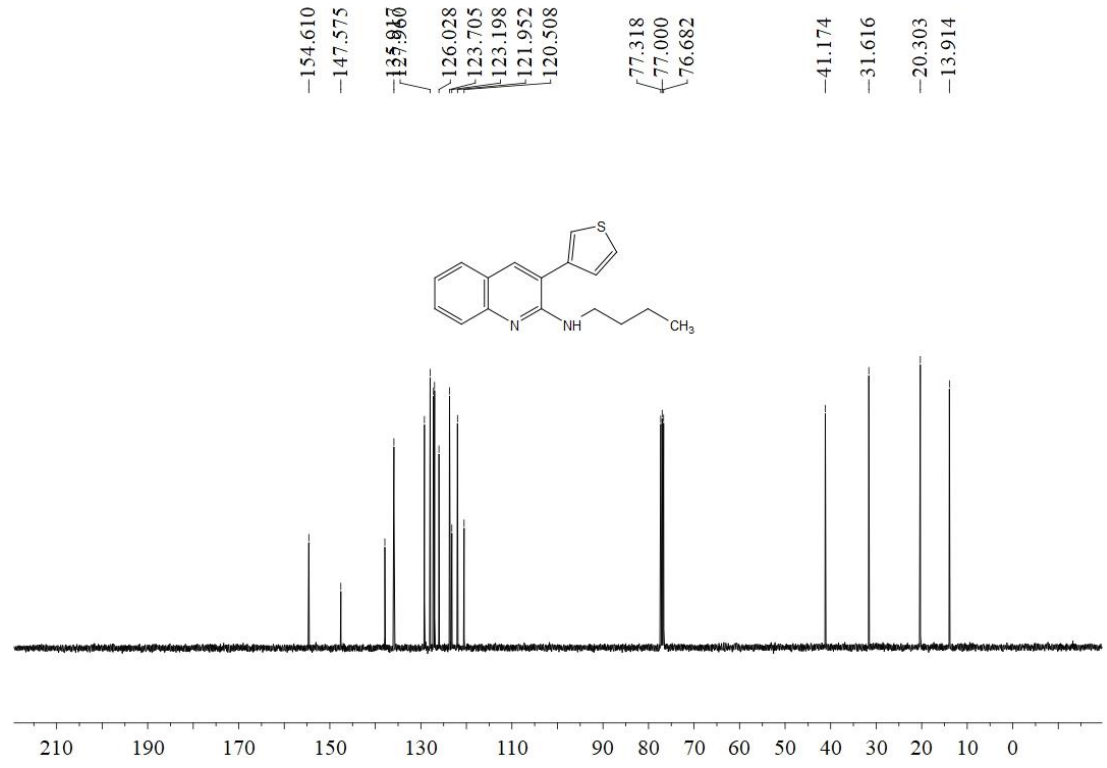


N-Butyl-3-(thiophen-3-yl)quinolin-2-amine (**4q**)

^{1}H NMR (400 MHz, $CDCl_3$)

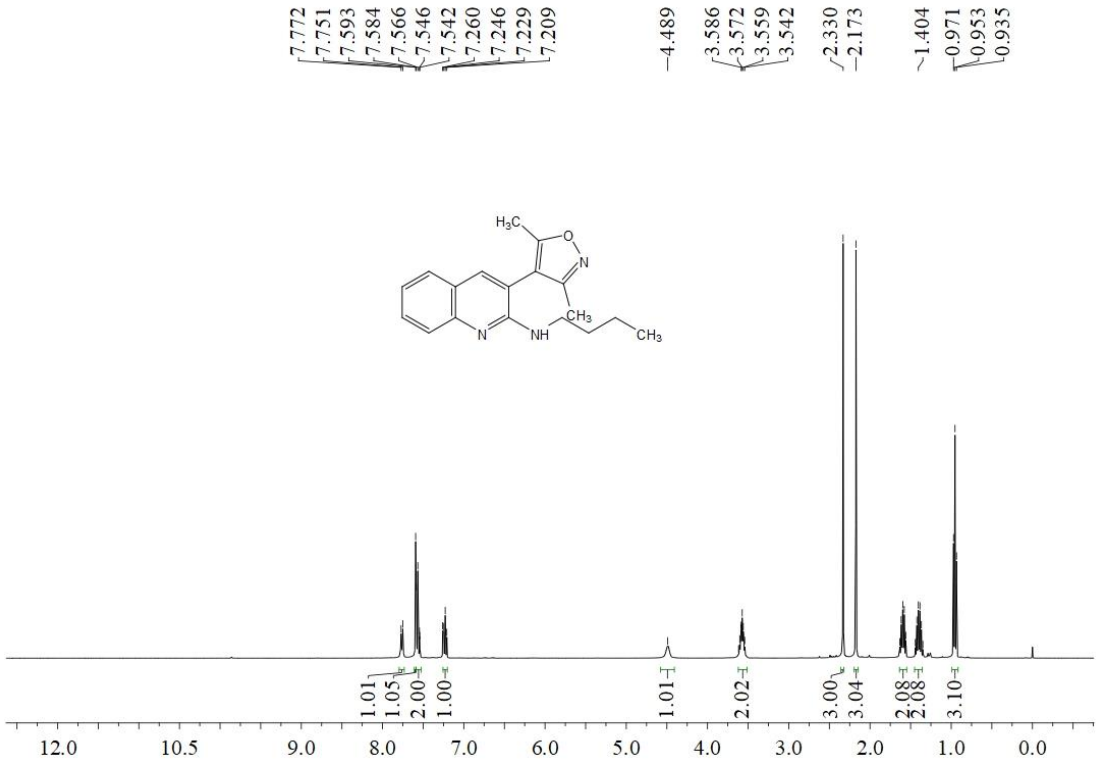


^{13}C NMR (100 MHz, $CDCl_3$)

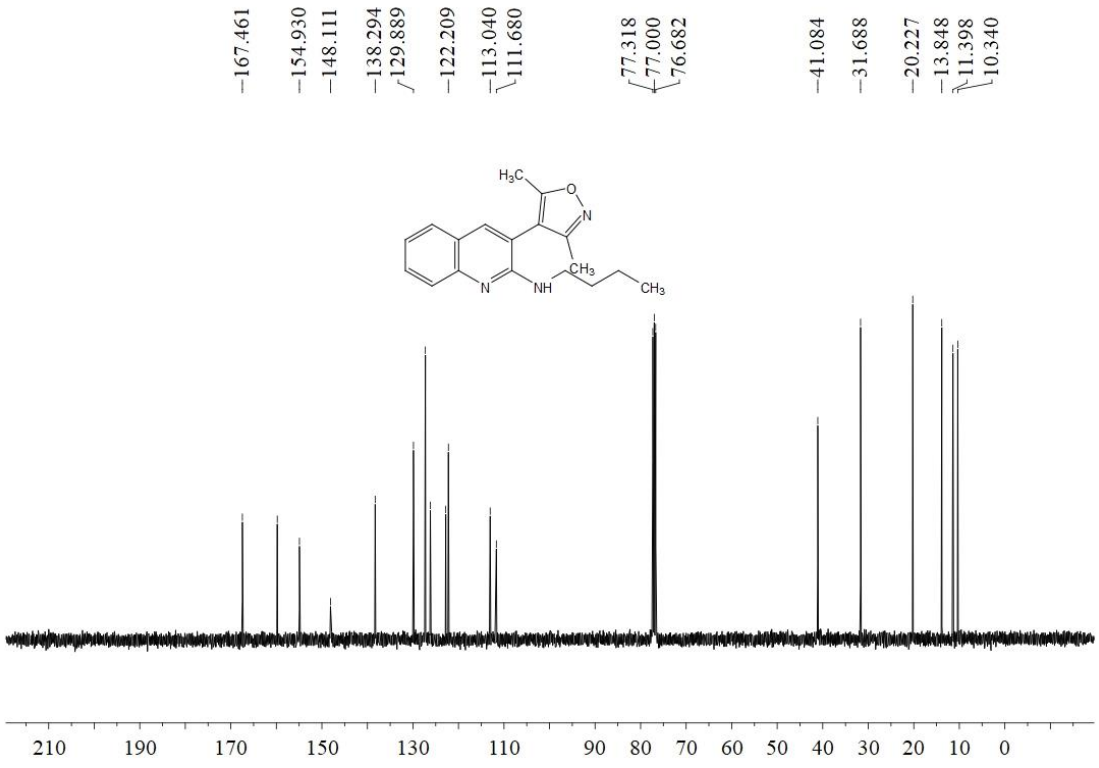


N-Butyl-3-(3,5-dimethylisoxazol-4-yl)quinolin-2-amine (**4r**)

^{1}H NMR (400 MHz, $CDCl_3$)

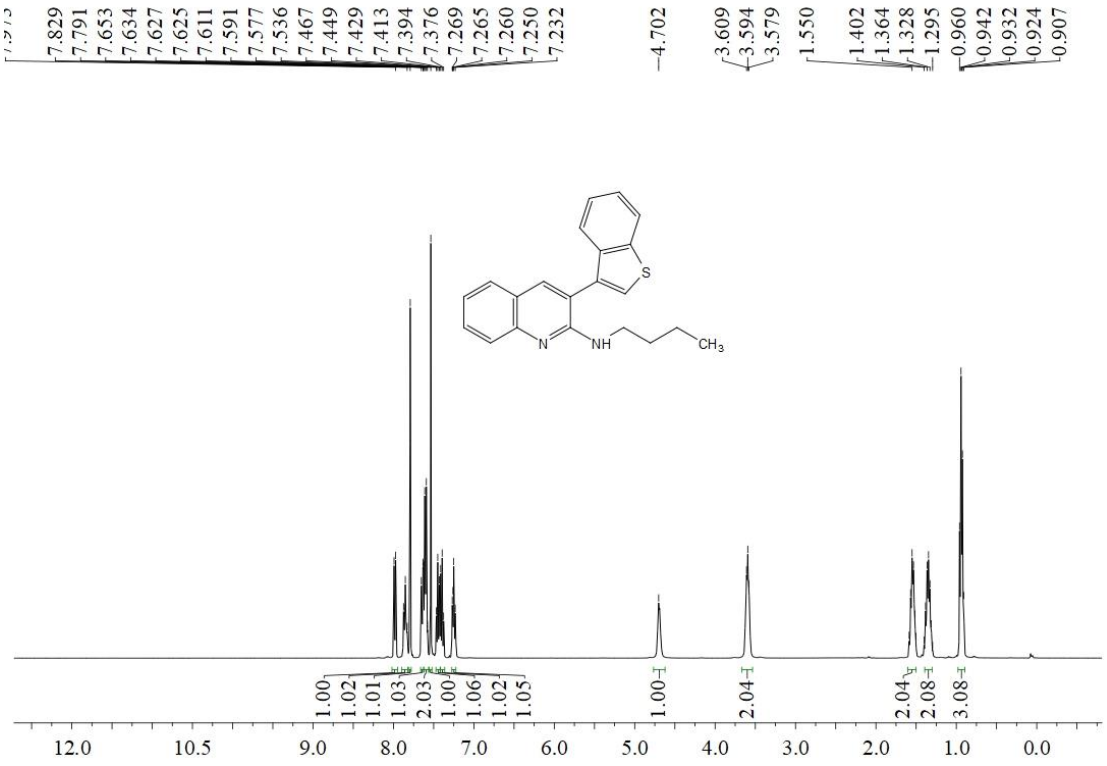


^{13}C NMR (100 MHz, $CDCl_3$)

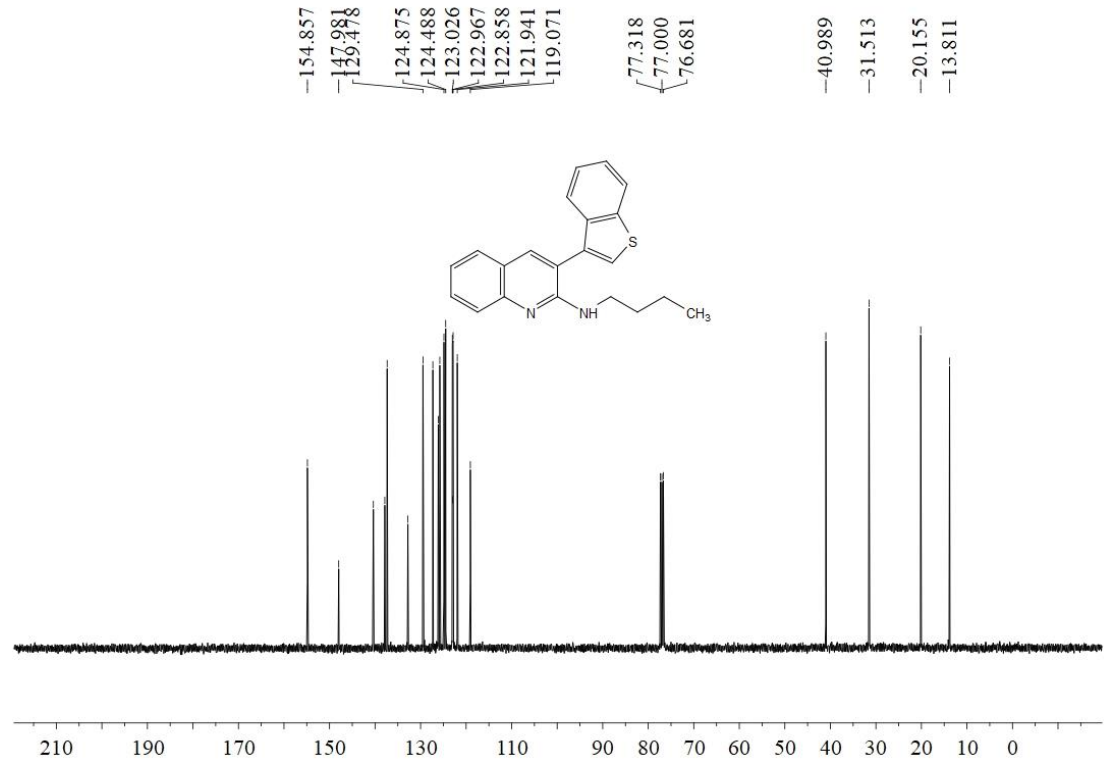


3-(Benzo[*b*]thiophen-3-yl)-*N*-butylquinolin-2-amine (**4s**)

^{1}H NMR (400 MHz, $CDCl_3$)

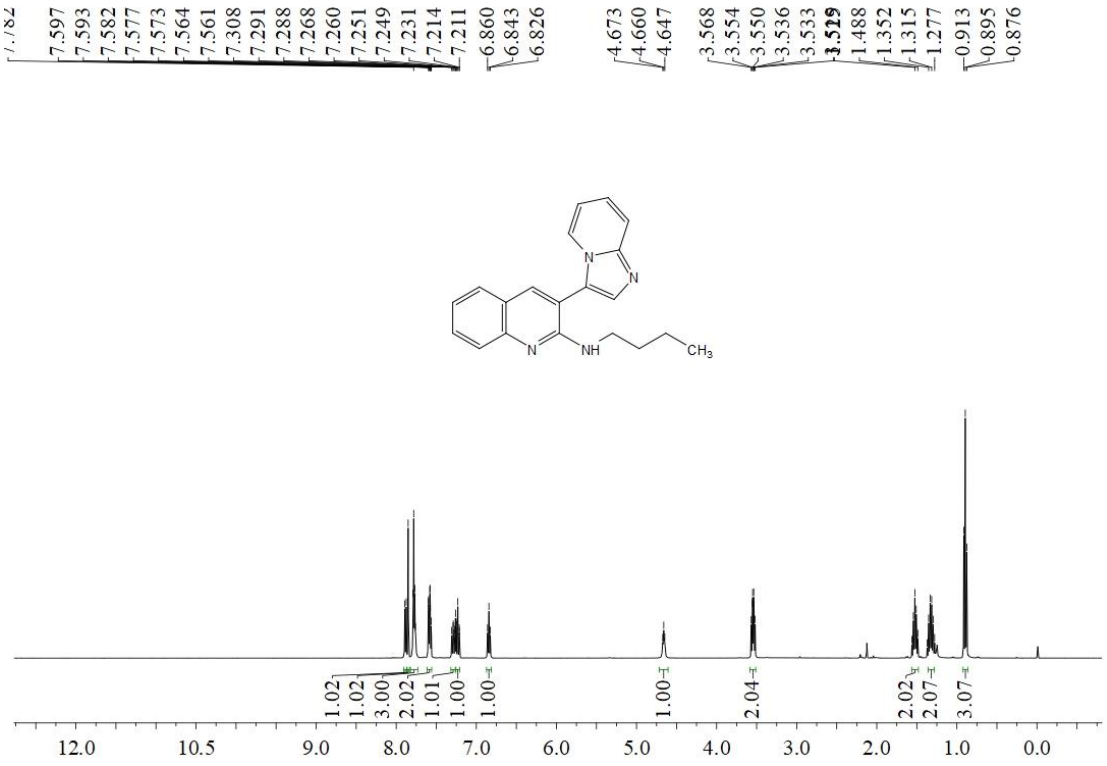


^{13}C NMR (100 MHz, $CDCl_3$)

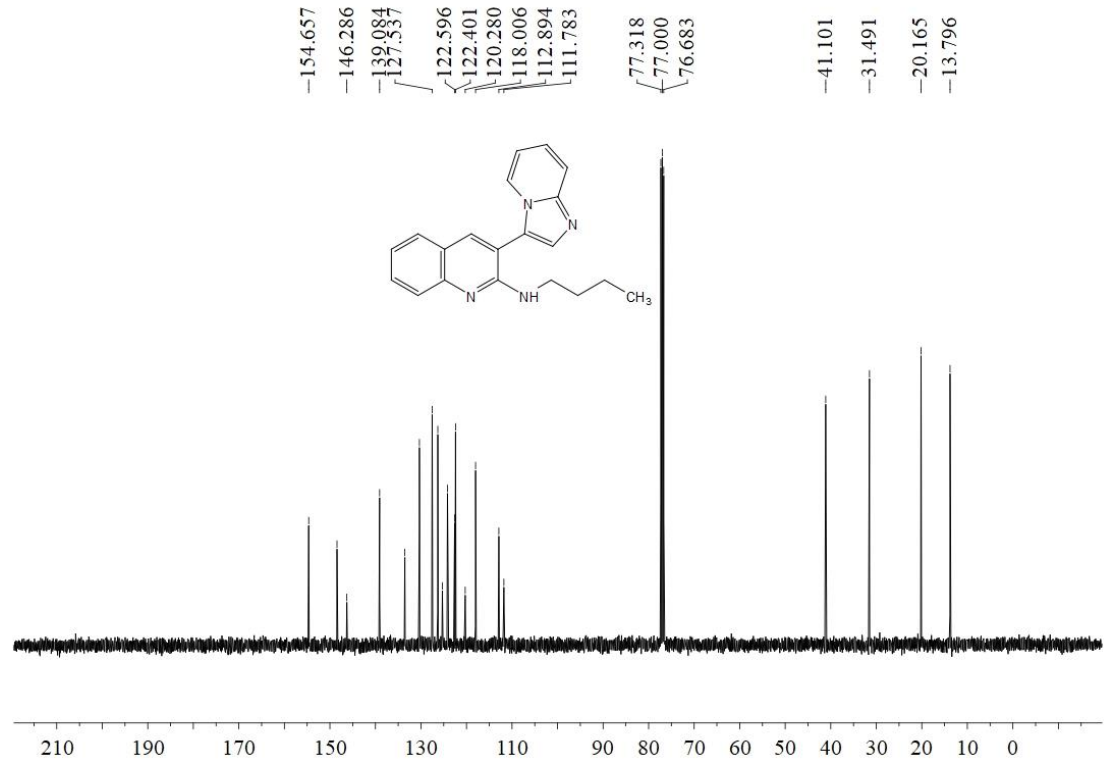


N-Butyl-3-(imidazo[1,2-*a*]pyridin-3-yl)quinolin-2-amine (**4t**)

^{1}H NMR (400 MHz, $CDCl_3$)

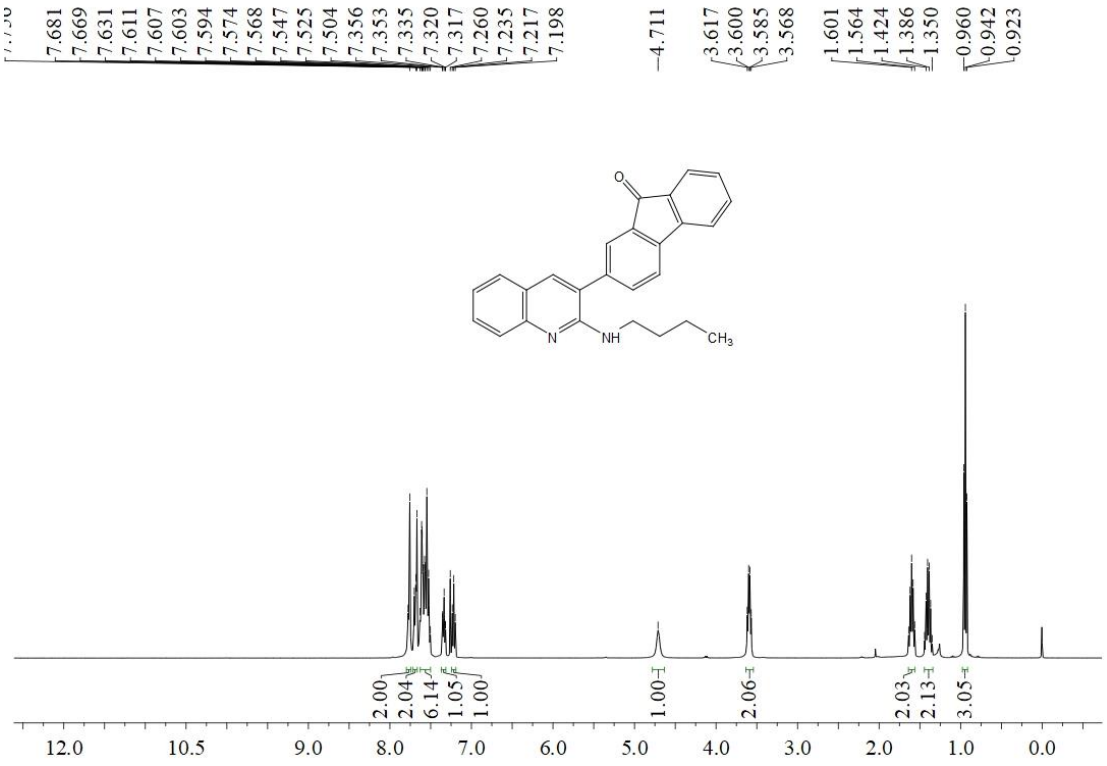


^{13}C NMR (100 MHz, $CDCl_3$)

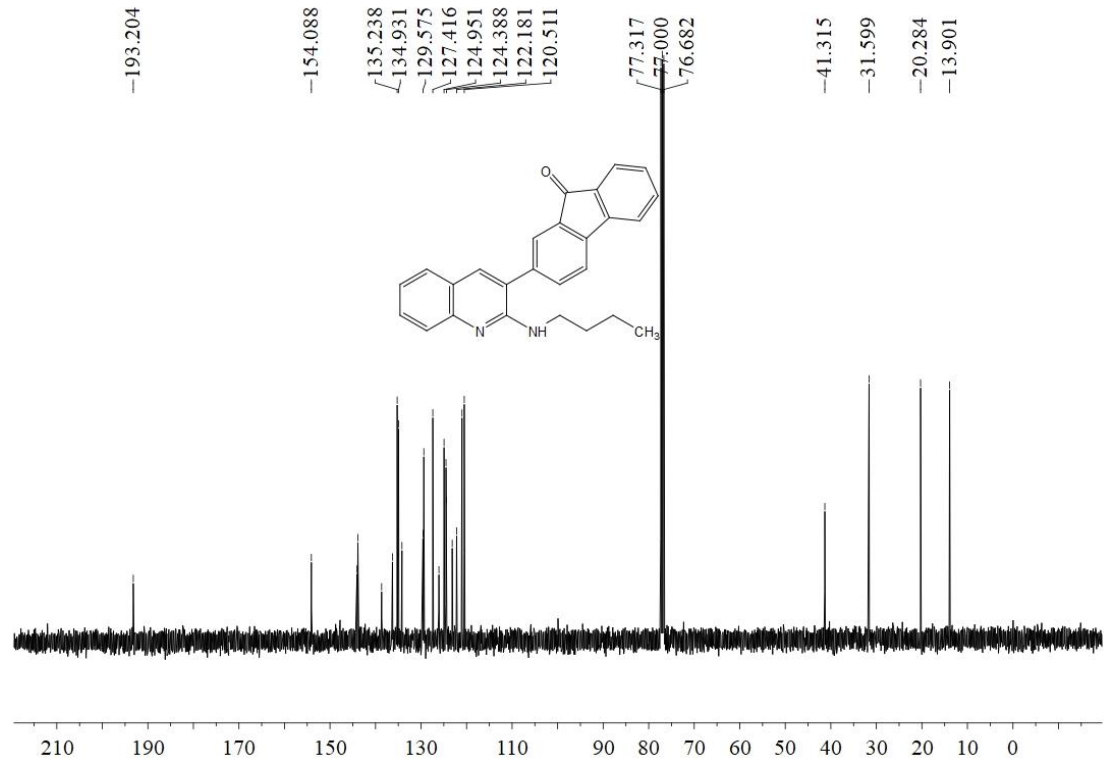


2-(2-(Butylamino)quinolin-3-yl)-9*H*-fluoren-9-one (**4u**)

^{1}H NMR (400 MHz, $CDCl_3$)

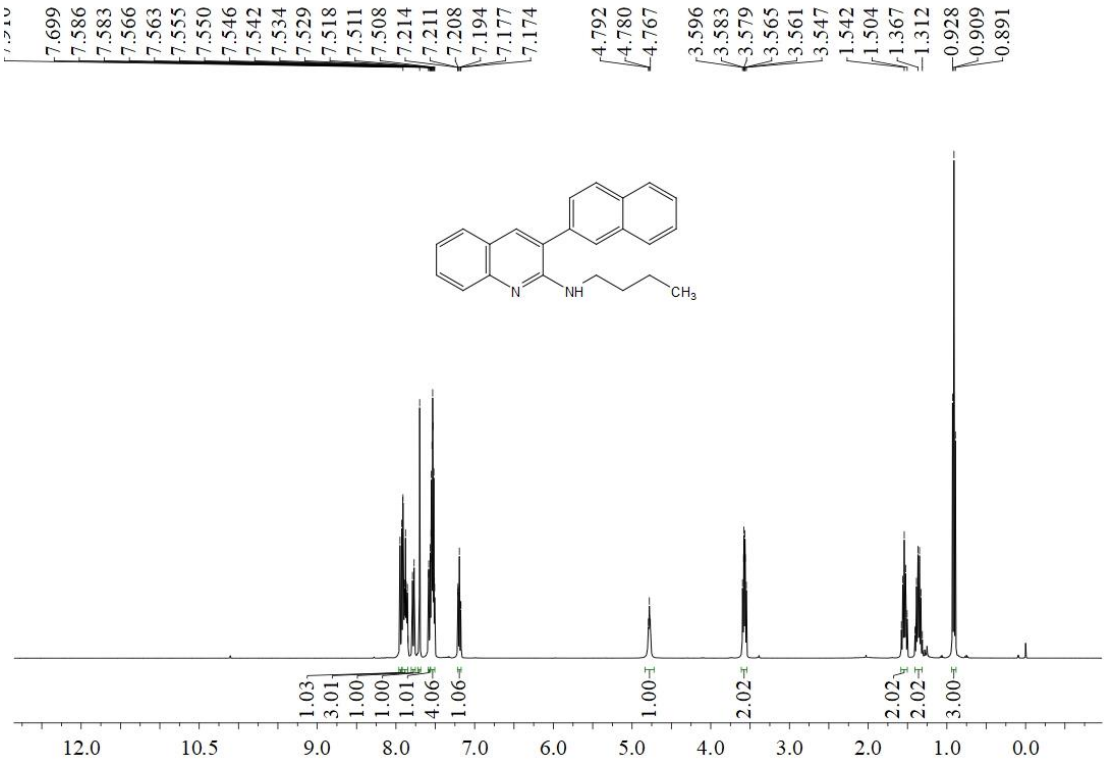


^{13}C NMR (100 MHz, $CDCl_3$)

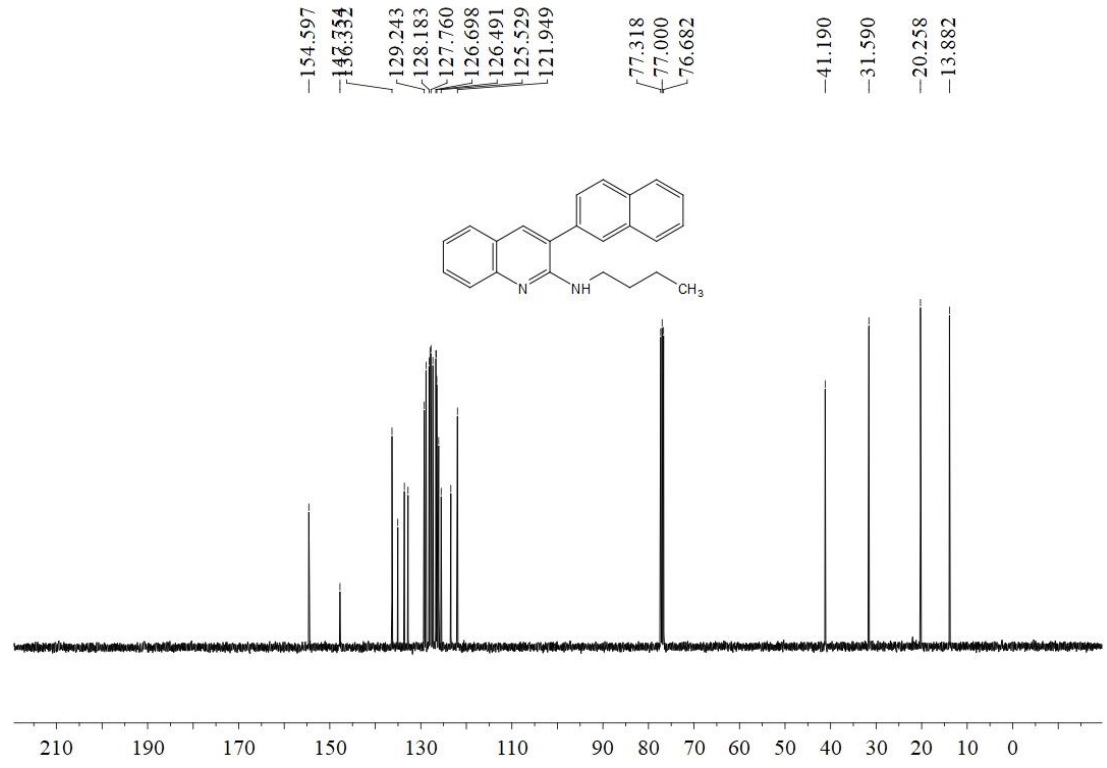


N-Butyl-3-(naphthalen-2-yl)quinolin-2-amine (**4v**)

^{1}H NMR (400 MHz, $CDCl_3$)

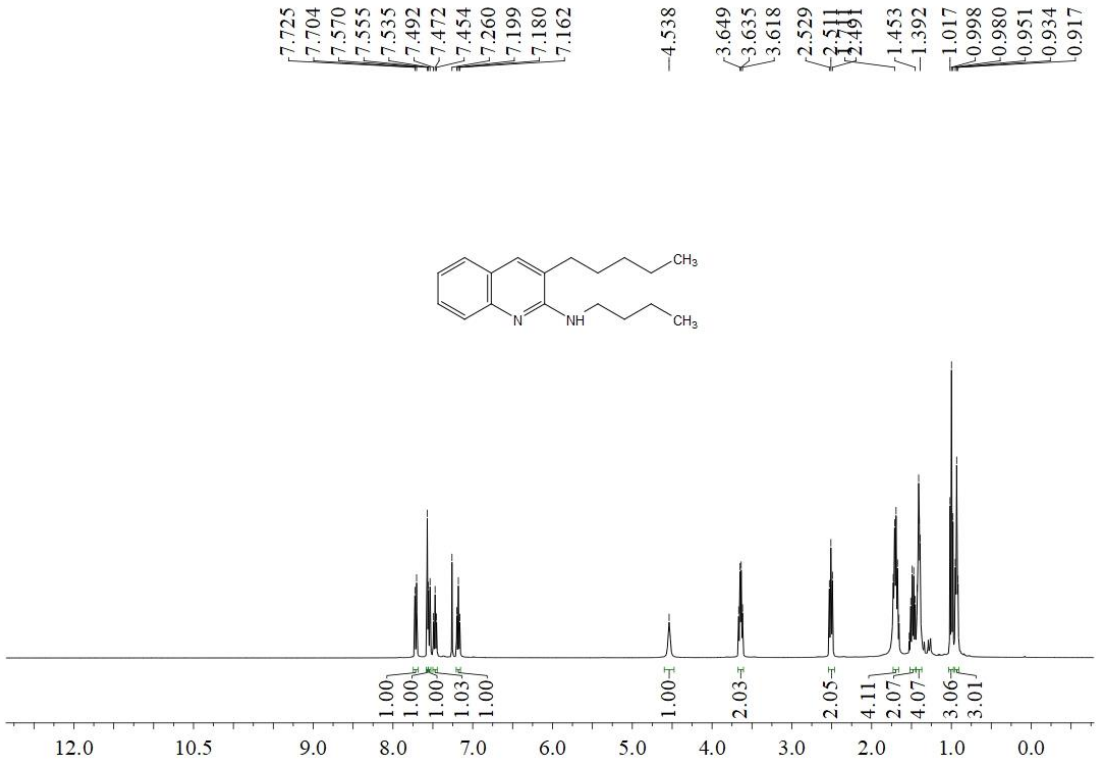


^{13}C NMR (100 MHz, $CDCl_3$)

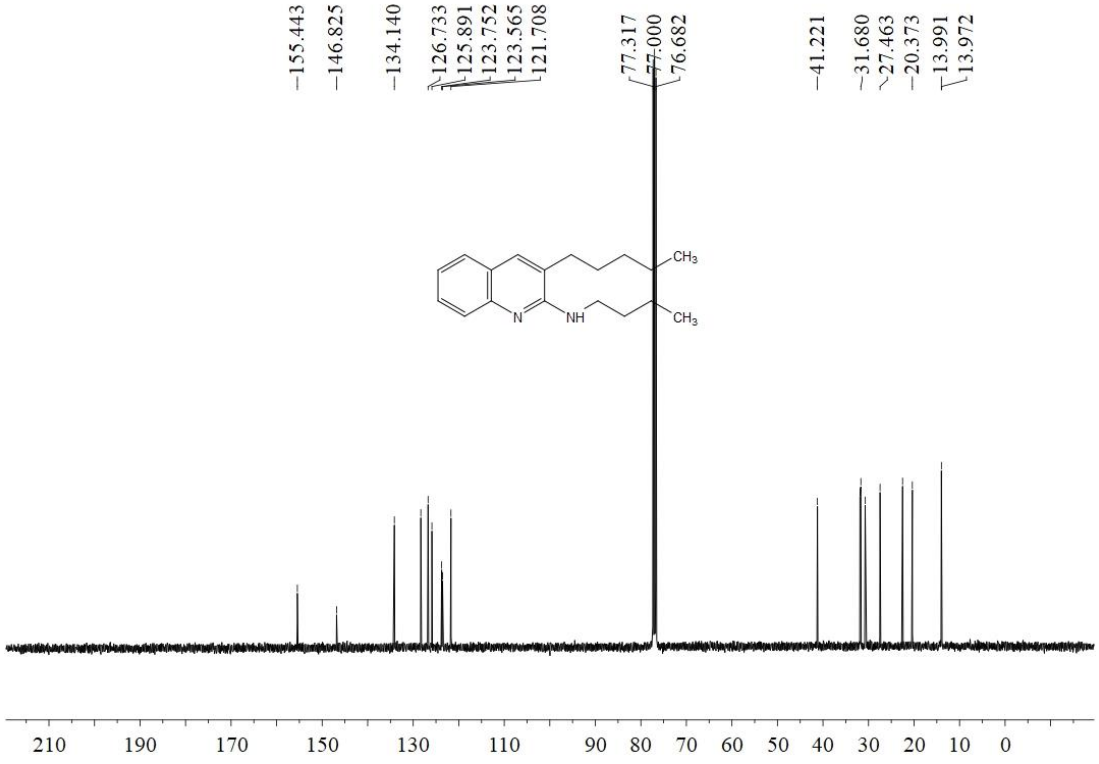


N-Butyl-3-pentylquinolin-2-amine (**4w**)

^{1}H NMR (400 MHz, $CDCl_3$)

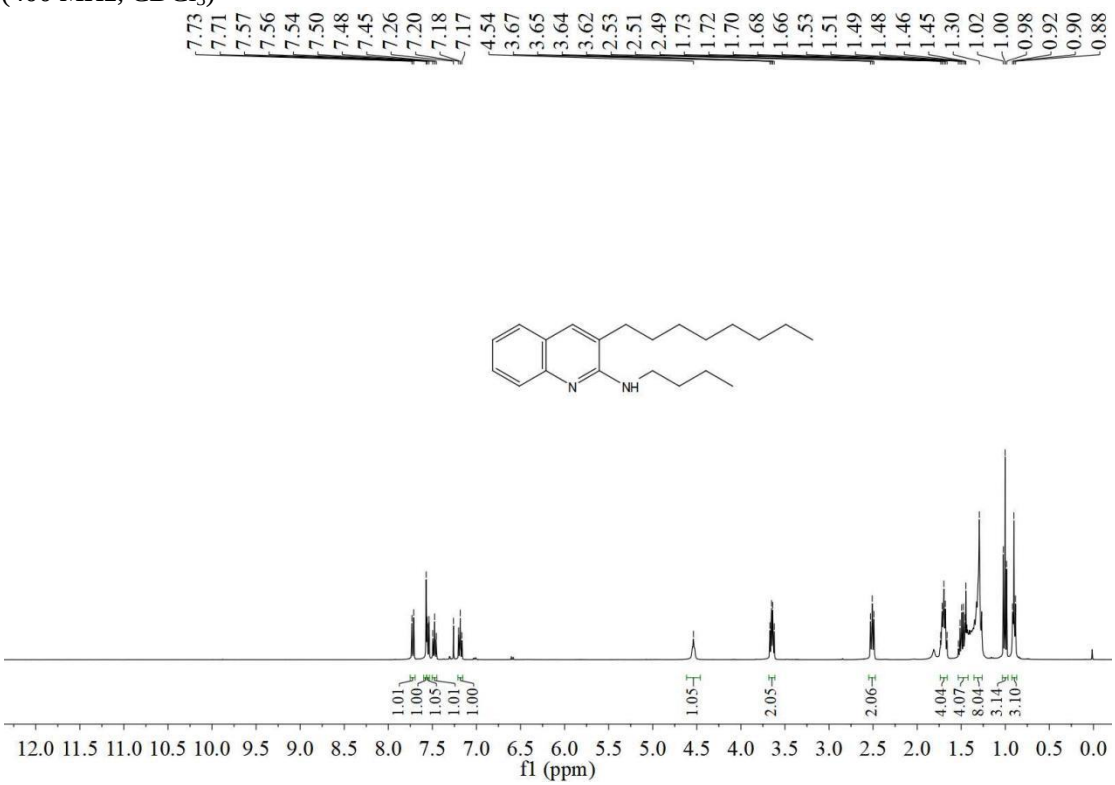


^{13}C NMR (100 MHz, $CDCl_3$)

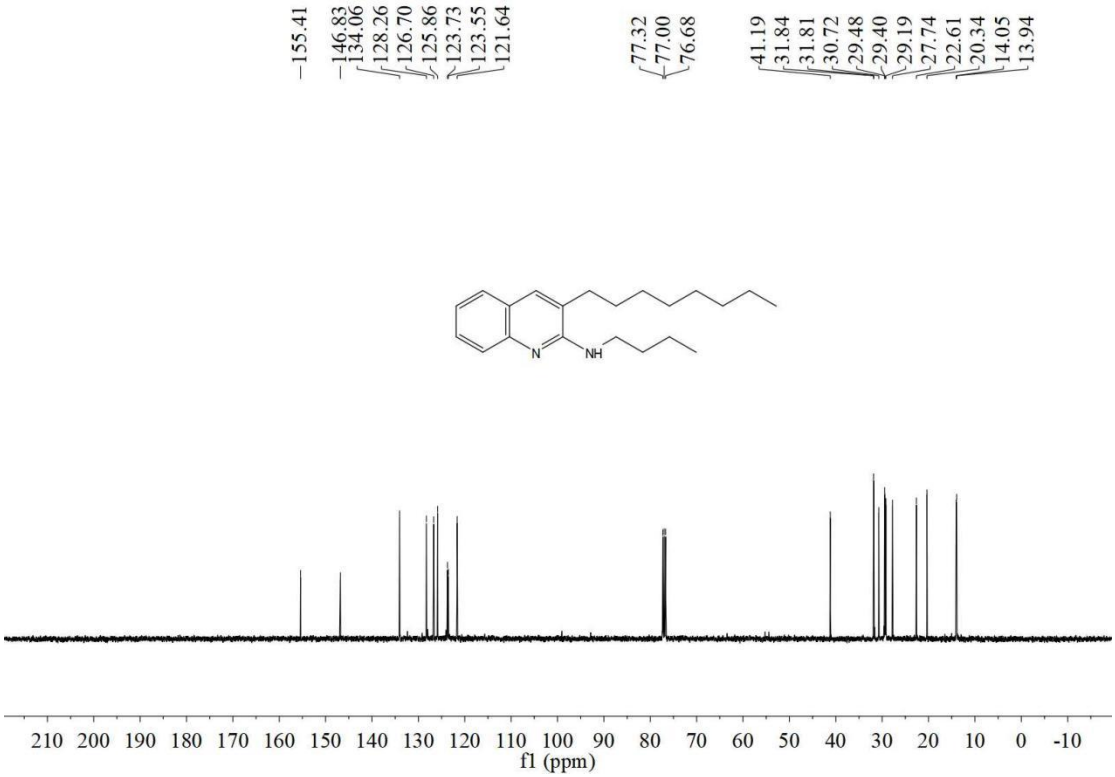


N-Butyl-3-octylquinolin-2-amine (**4x**)

^{1}H NMR (400 MHz, $CDCl_3$)

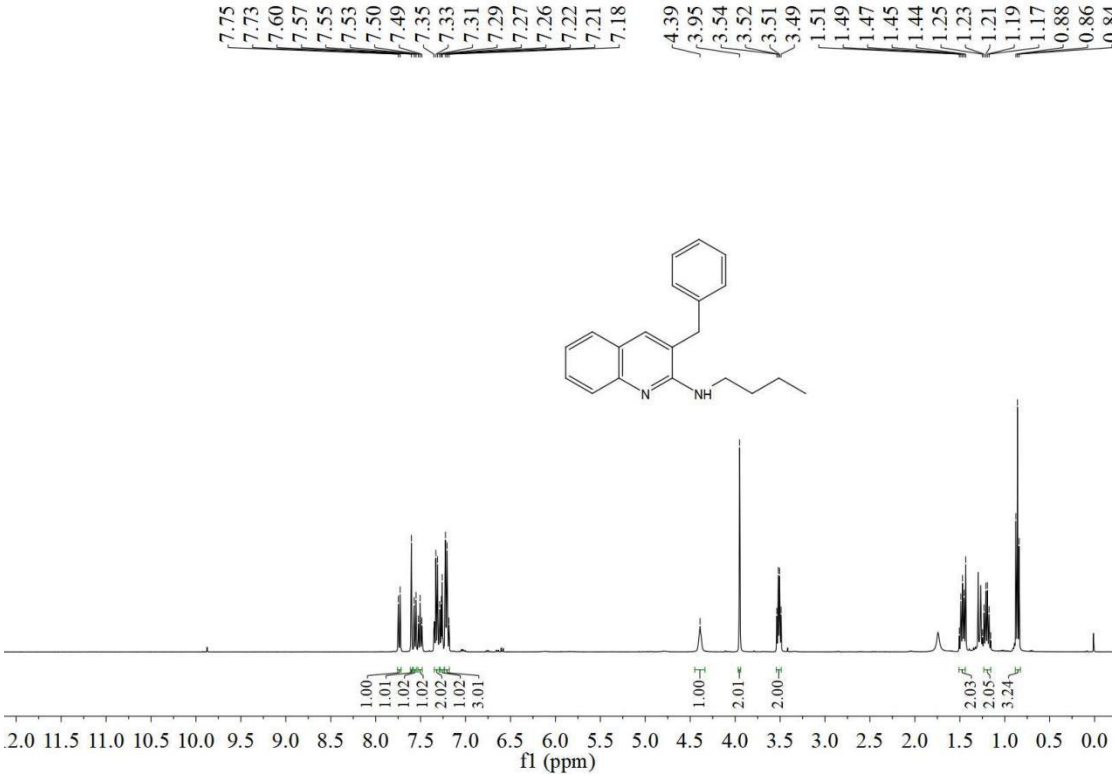


^{13}C NMR (100 MHz, $CDCl_3$)

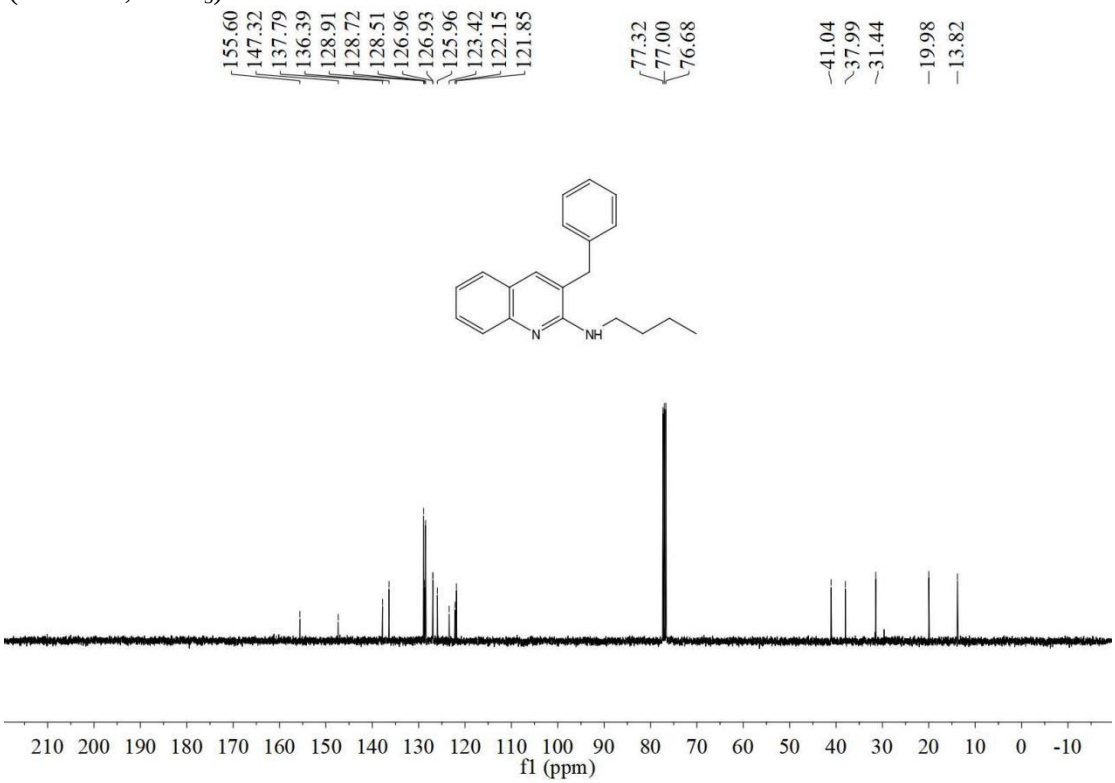


3-Benzyl-*N*-butylquinolin-2-amine (4y)

^{1}H NMR (400 MHz, $CDCl_3$)

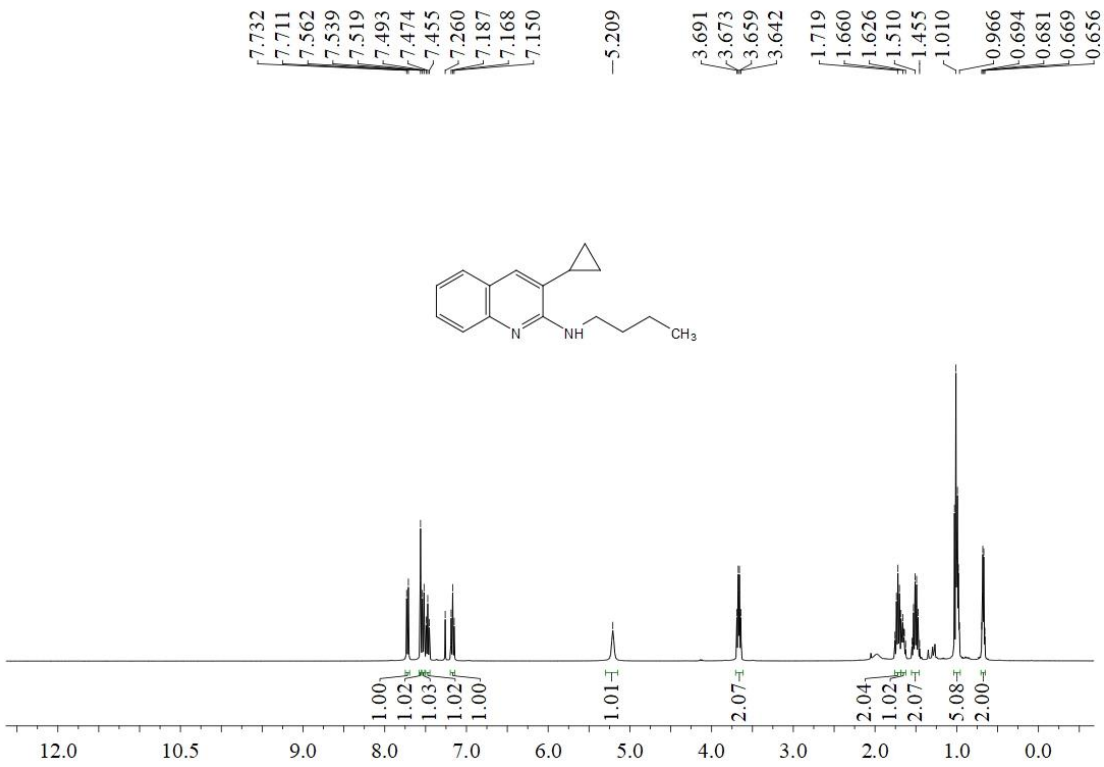


^{13}C NMR (100 MHz, $CDCl_3$)

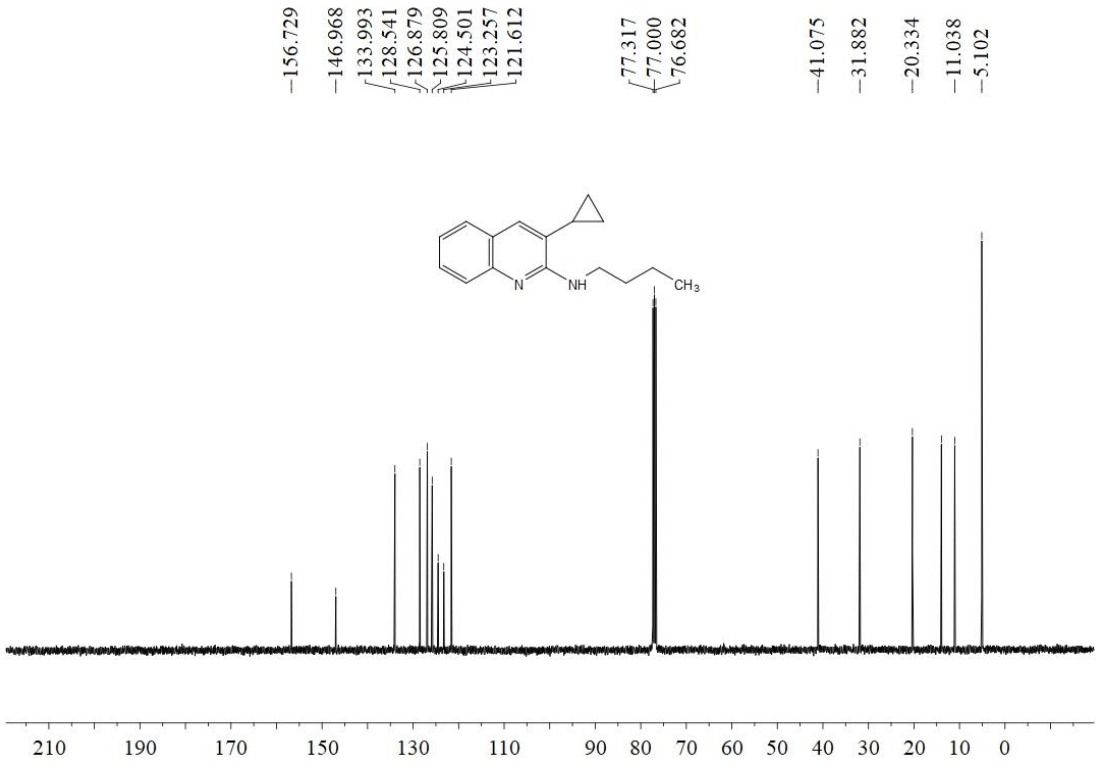


N-Butyl-3-cyclopropylquinolin-2-amine (**4z**)

^{1}H NMR (400 MHz, $CDCl_3$)

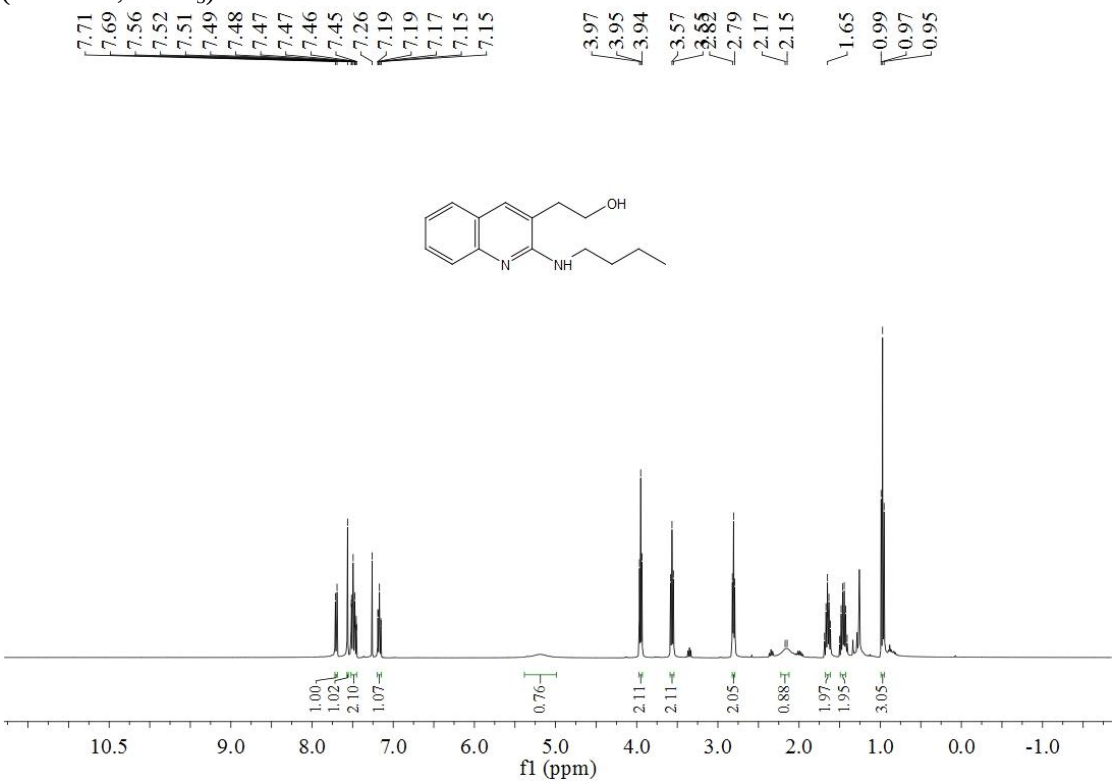


^{13}C NMR (100 MHz, $CDCl_3$)

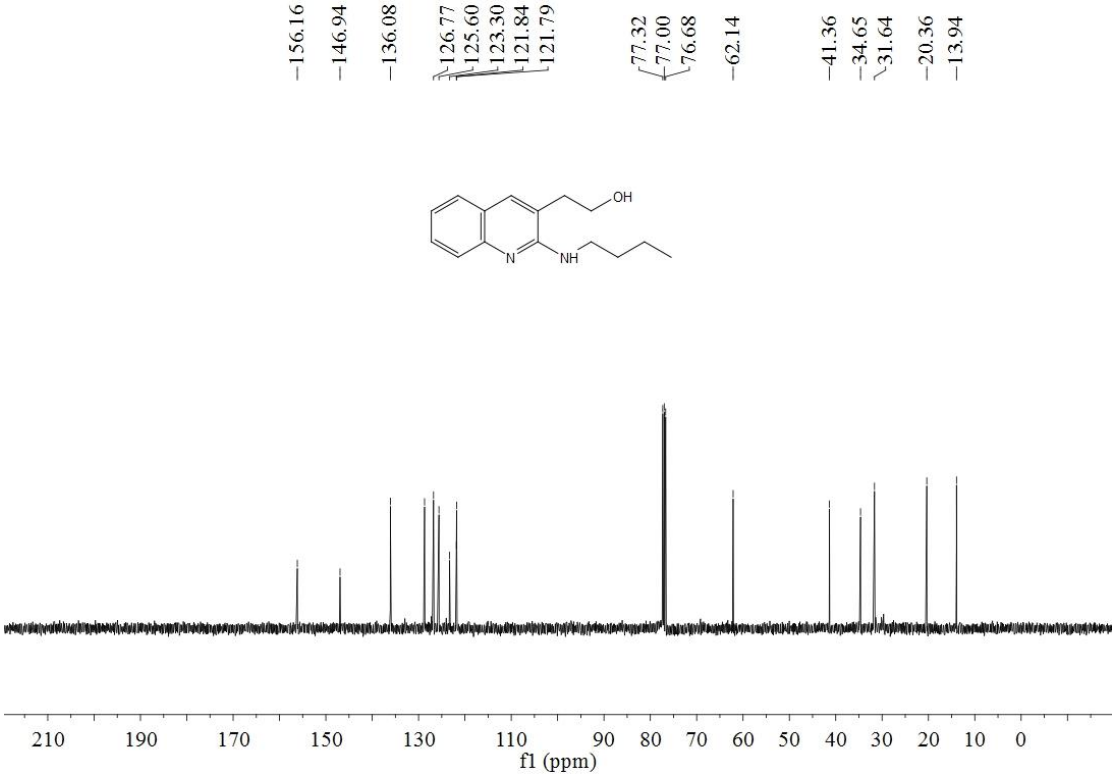


2-(2-(Butylamino)quinolin-3-yl)ethan-1-ol (**4aa**)

^{1}H NMR (400 MHz, $CDCl_3$)

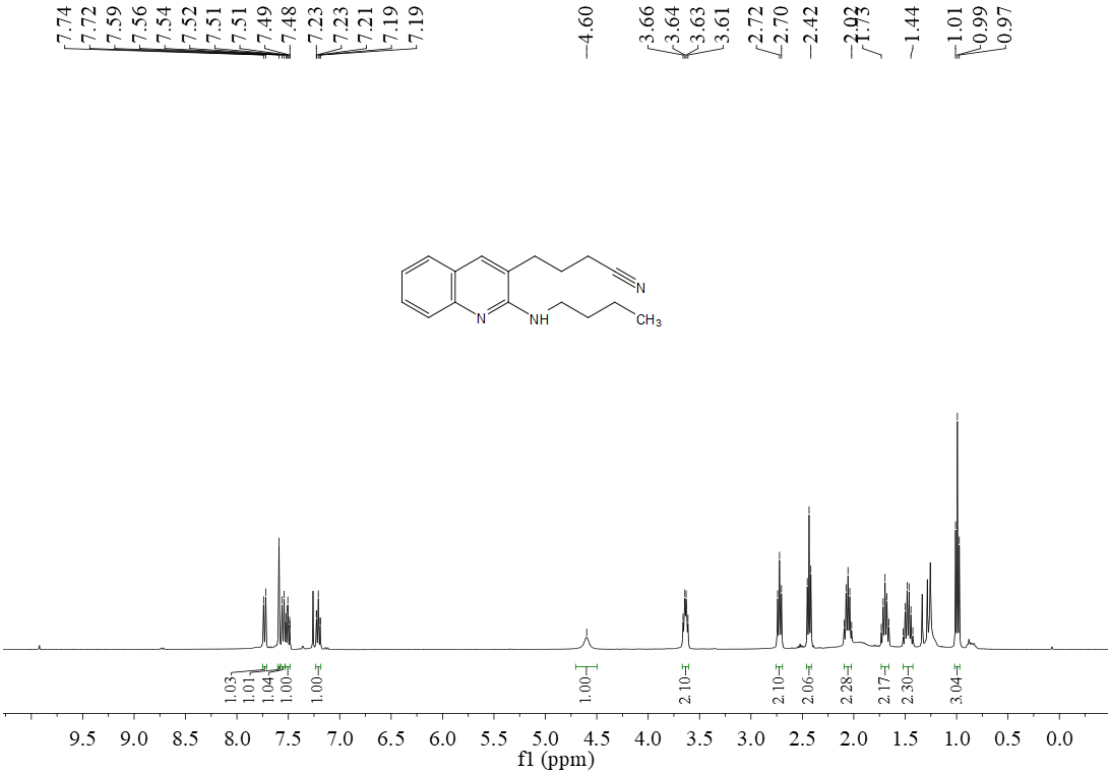


^{13}C NMR (100 MHz, $CDCl_3$)

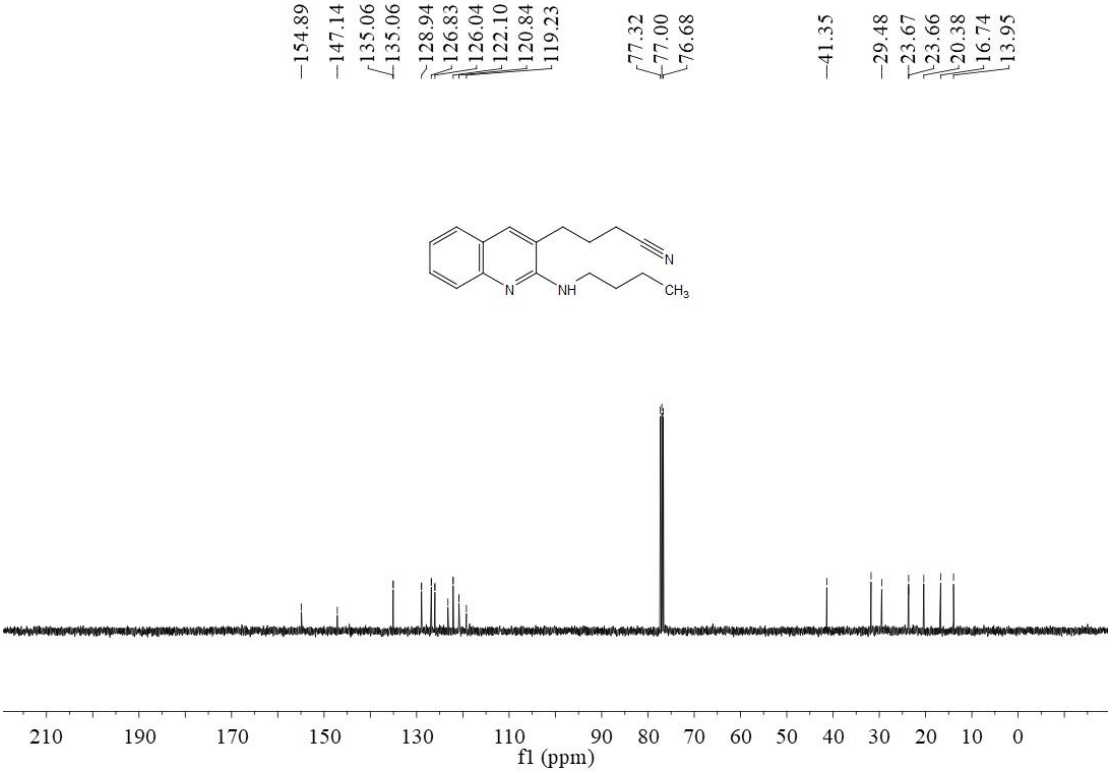


4-(2-(Butylamino)quinolin-3-yl)butanenitrile (**4ab**)

^{1}H NMR (400 MHz, $CDCl_3$)

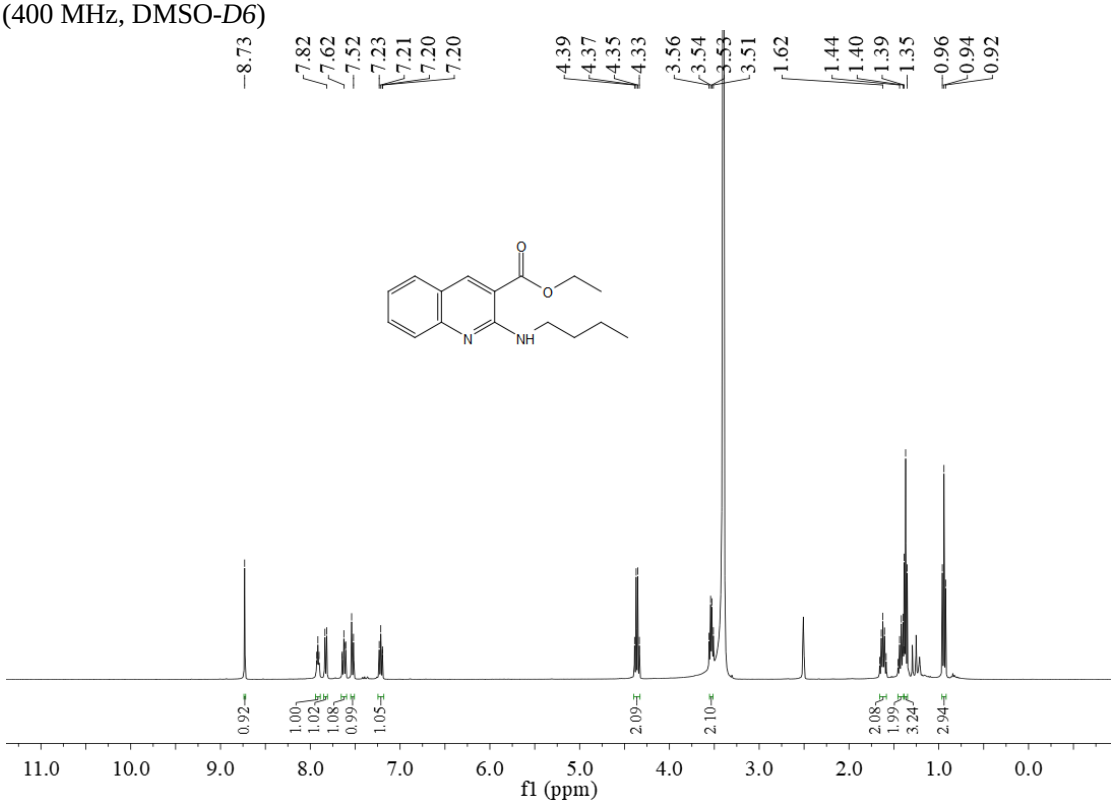


^{13}C NMR (100 MHz, $CDCl_3$)

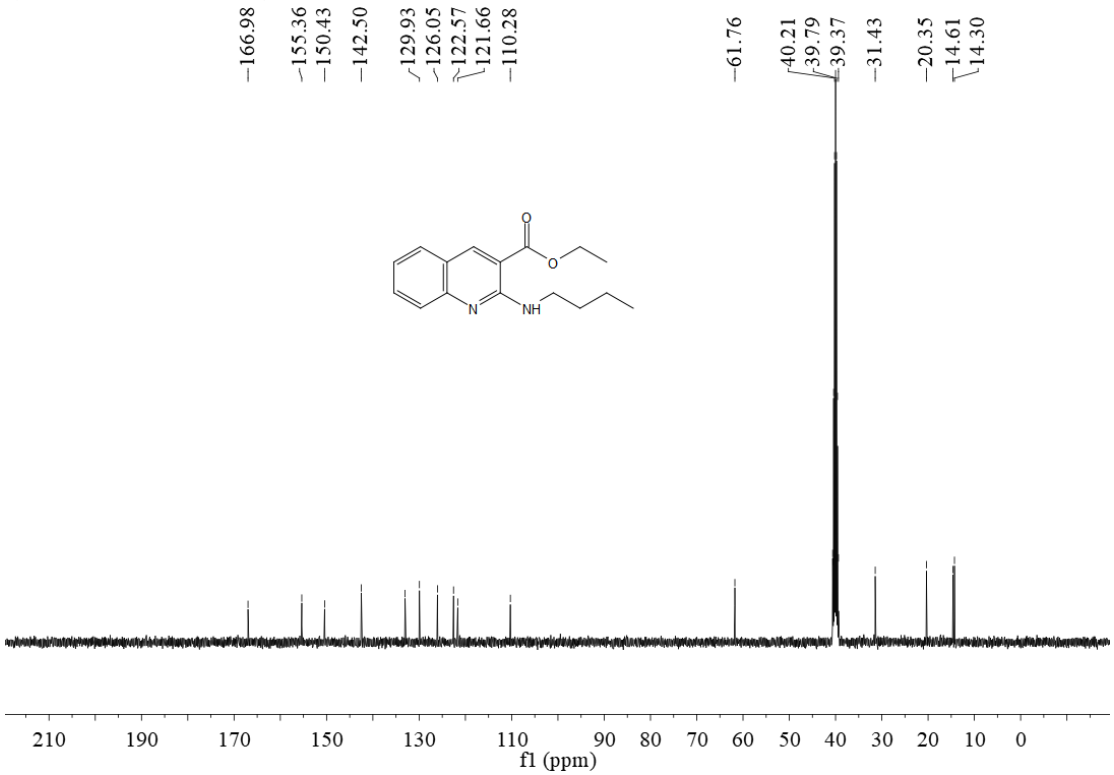


Ethyl 2-(butylamino)quinoline-3-carboxylate (**4ac**)

^{1}H NMR (400 MHz, DMSO-*D6*)

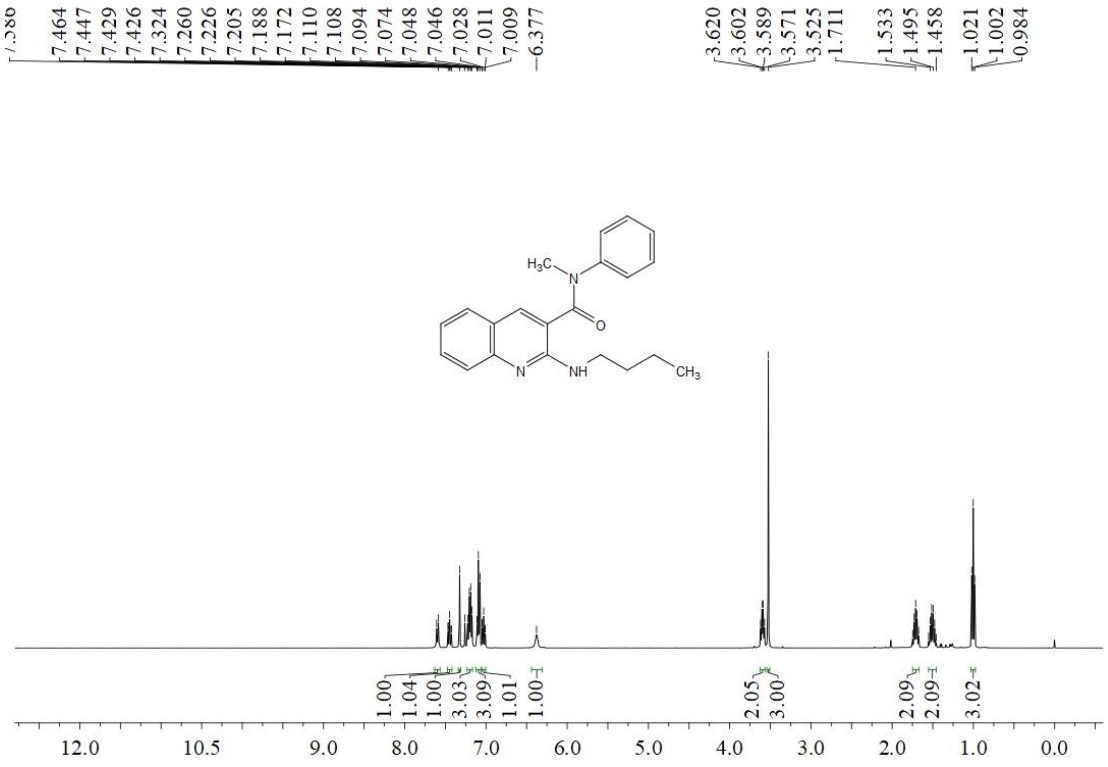


^{13}C NMR (100 MHz, DMSO-*D6*)

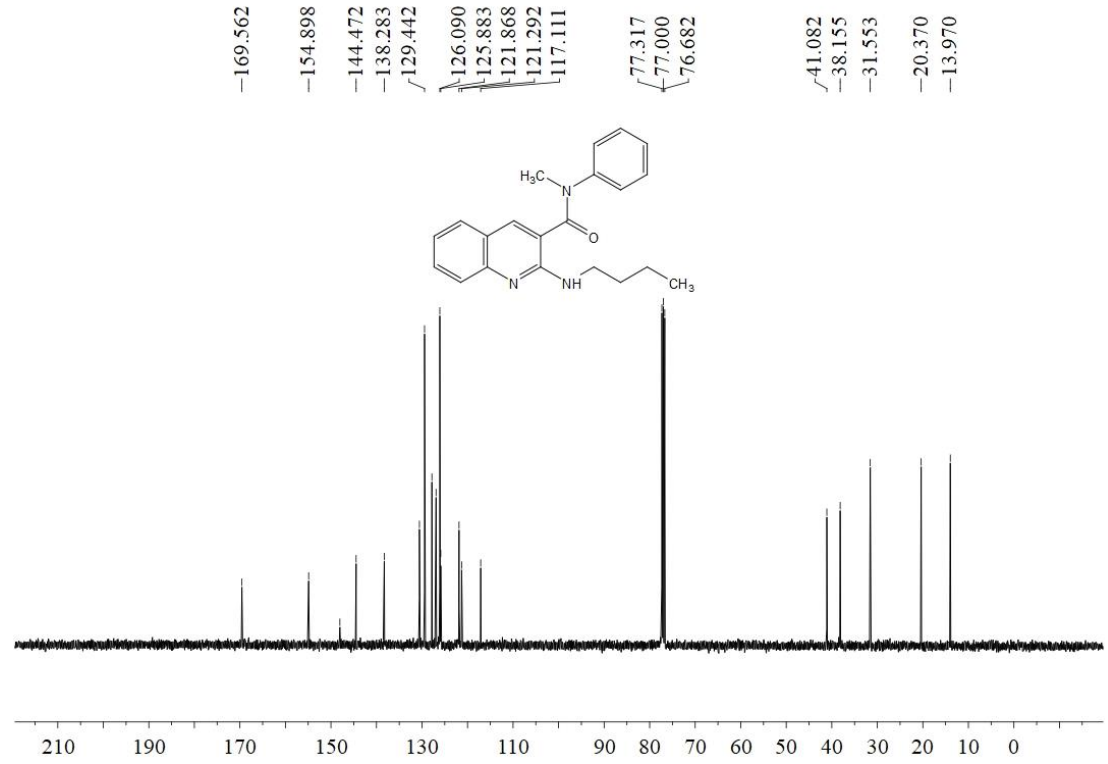


2-(Butylamino)-*N*-methyl-*N*-phenylquinoline-3-carboxamide (**4ad**)

^{1}H NMR (400 MHz, $CDCl_3$)

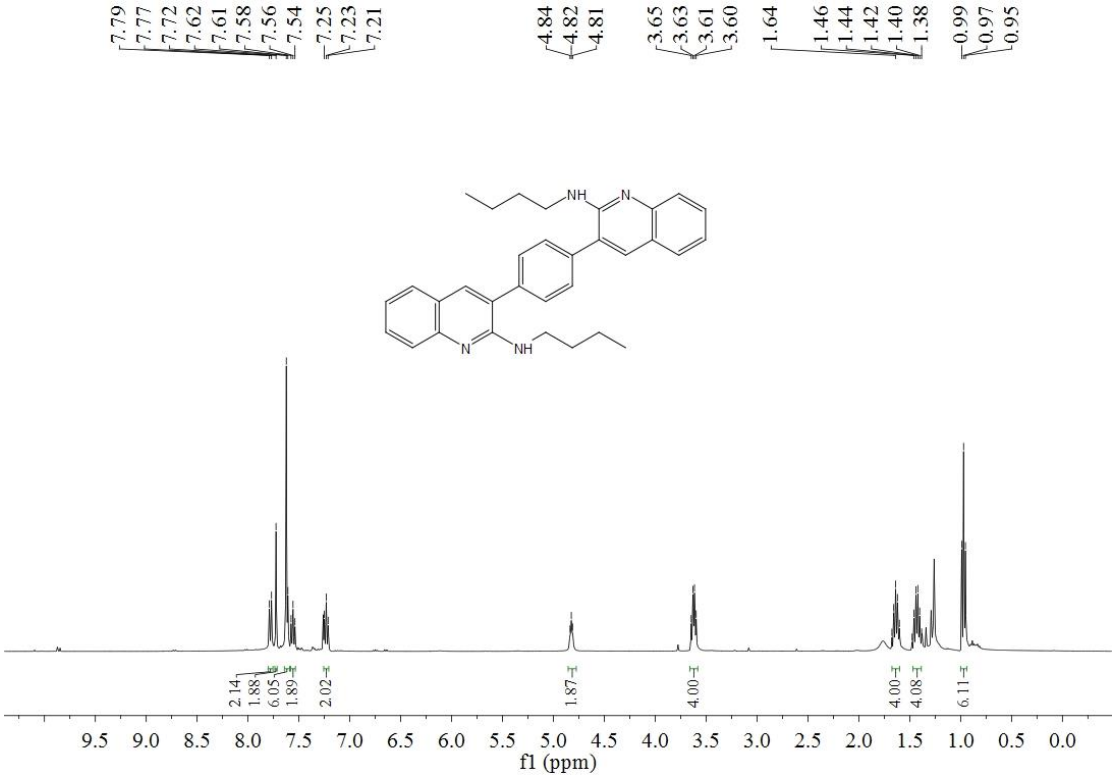


^{13}C NMR (100 MHz, $CDCl_3$)

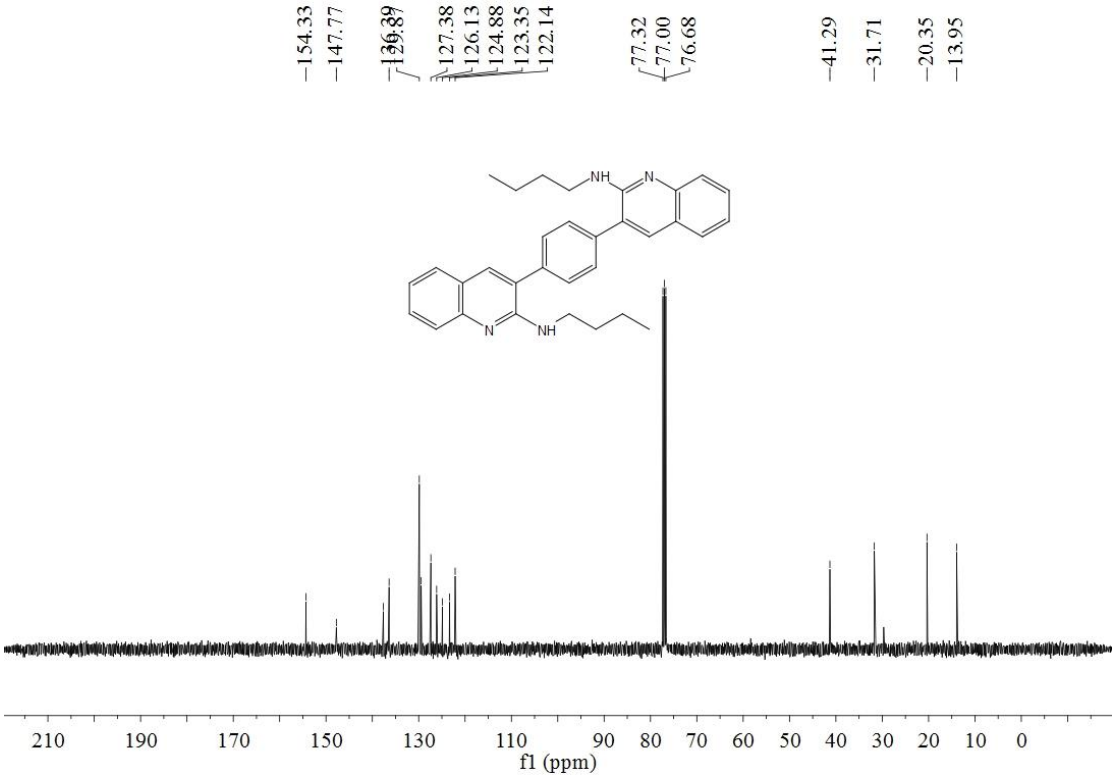


3,3'-(1,4-Phenylene)bis(N-butylquinolin-2-amine) (**4ae**)

^{1}H NMR (400 MHz, $CDCl_3$)

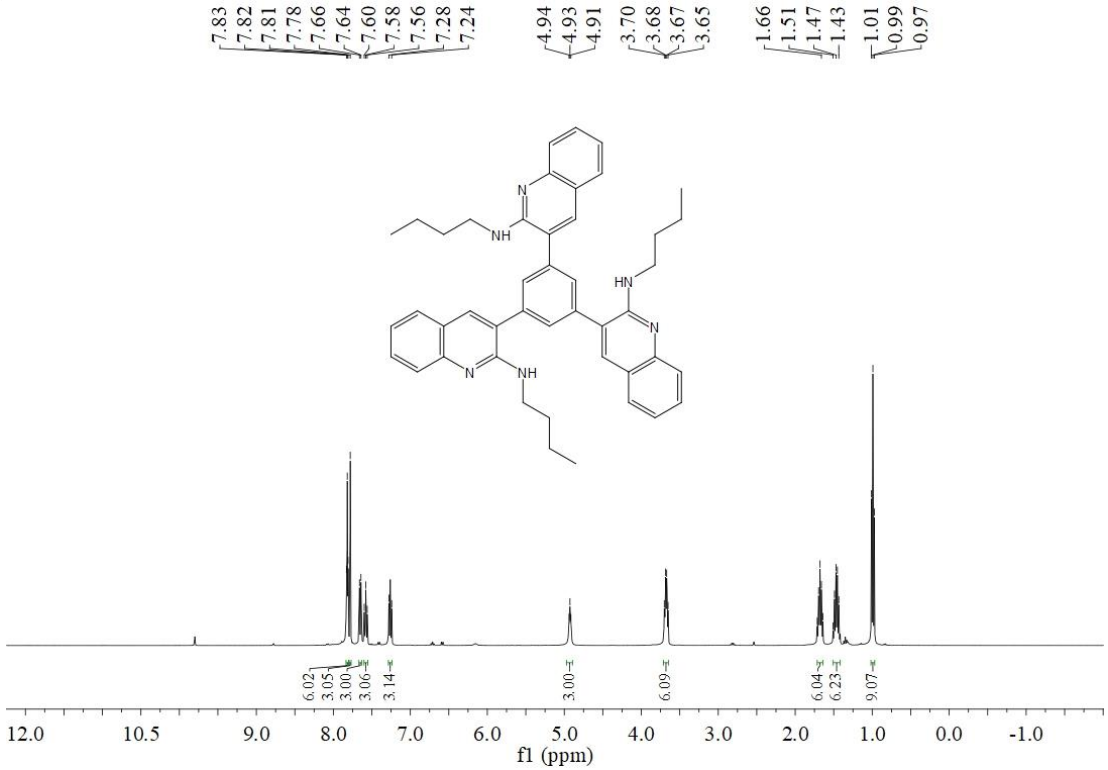


^{13}C NMR (100 MHz, $CDCl_3$)

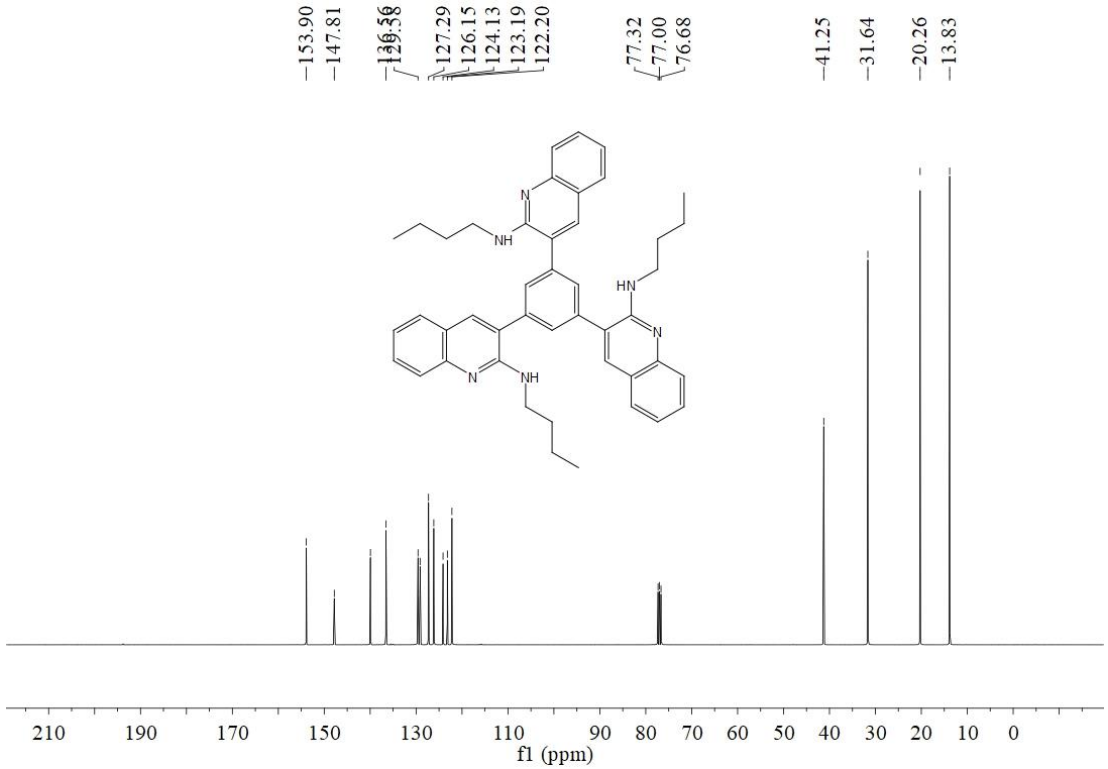


3,3',3"-(Benzene-1,3,5-triyl)tris(N-butylquinolin-2-amine) (**4af**)

^{1}H NMR (400 MHz, $CDCl_3$)

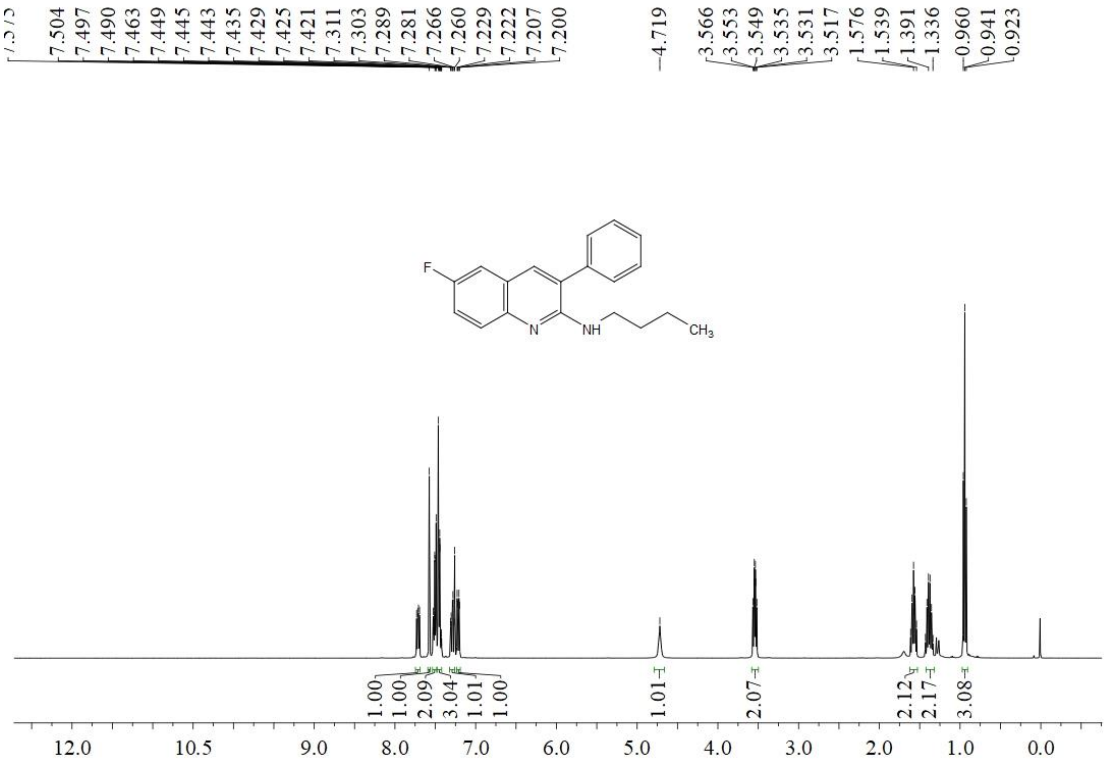


^{13}C NMR (100 MHz, $CDCl_3$)

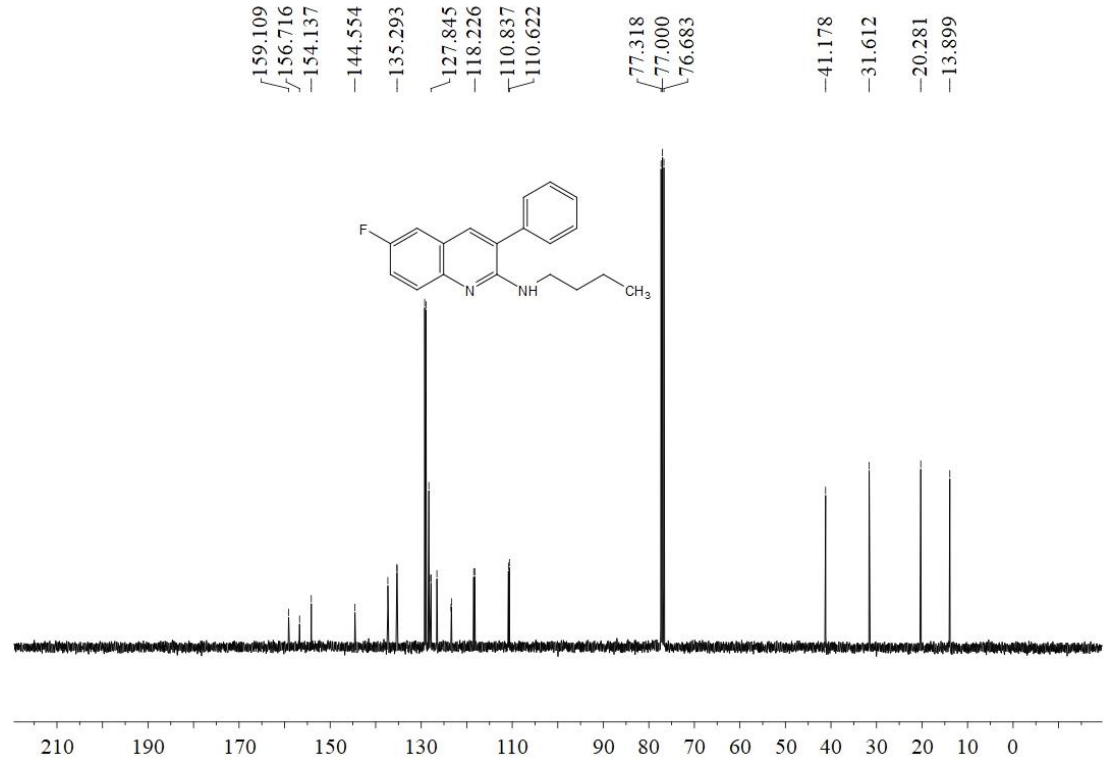


N-Butyl-6-fluoro-3-phenylquinolin-2-amine (**4ag**)

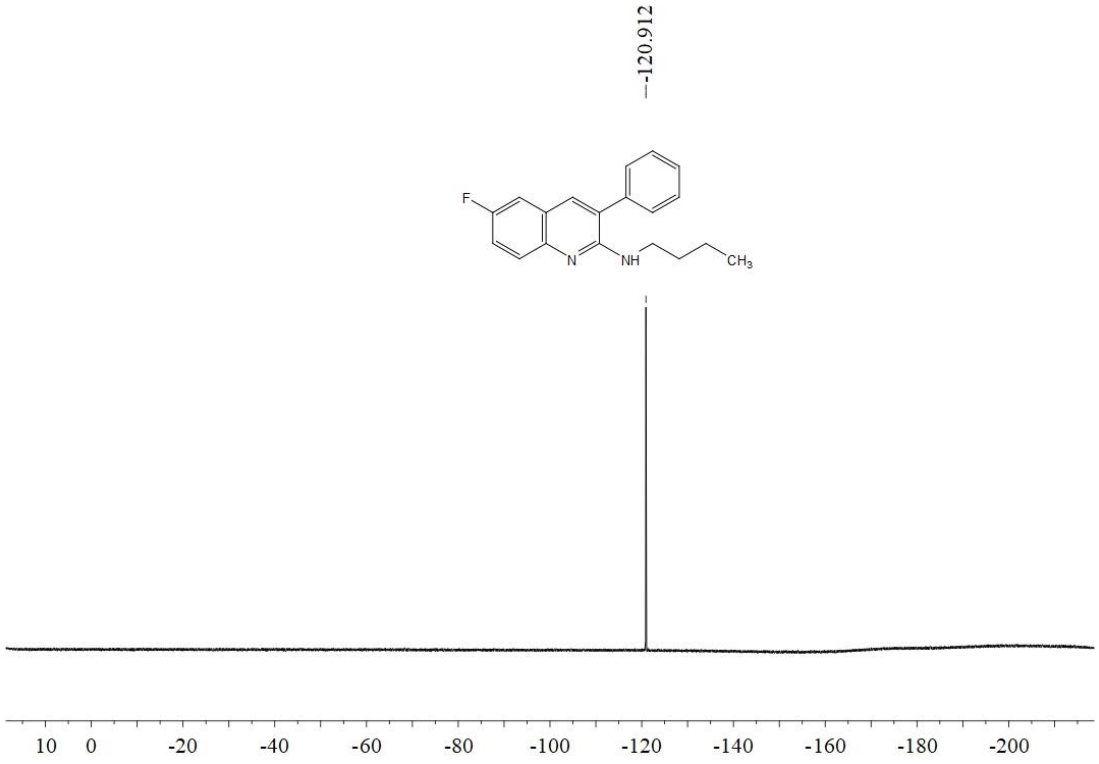
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

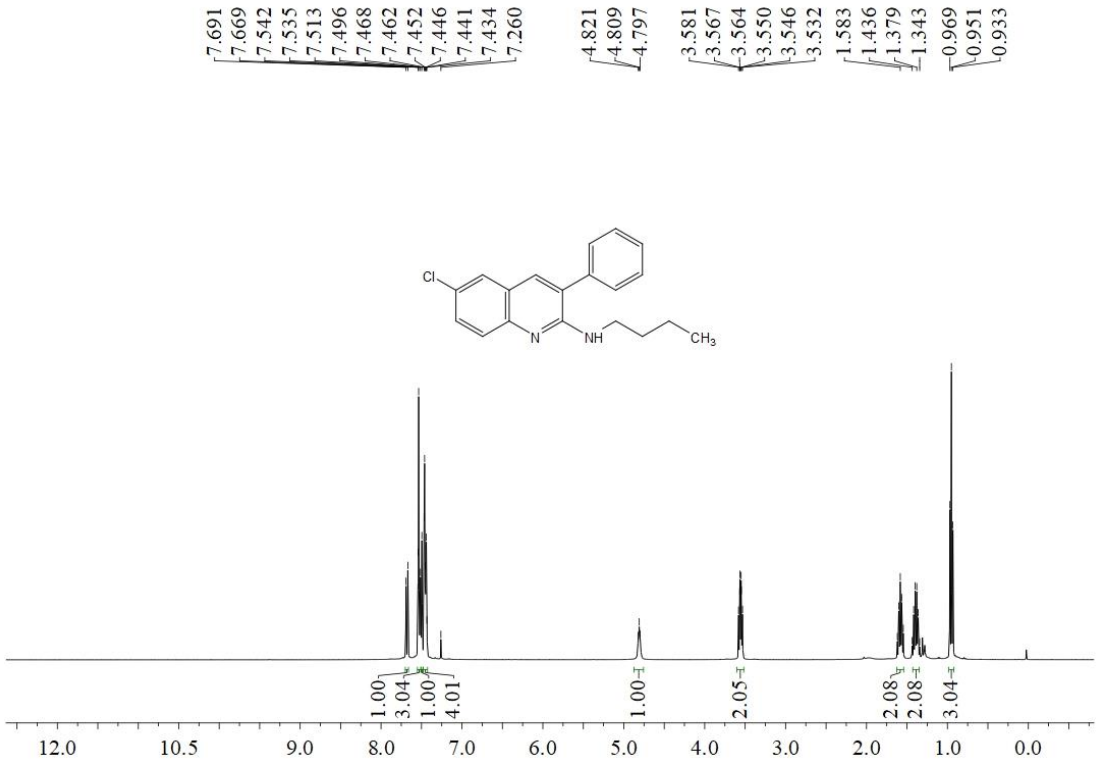


^{19}F NMR (375 MHz, $CDCl_3$)

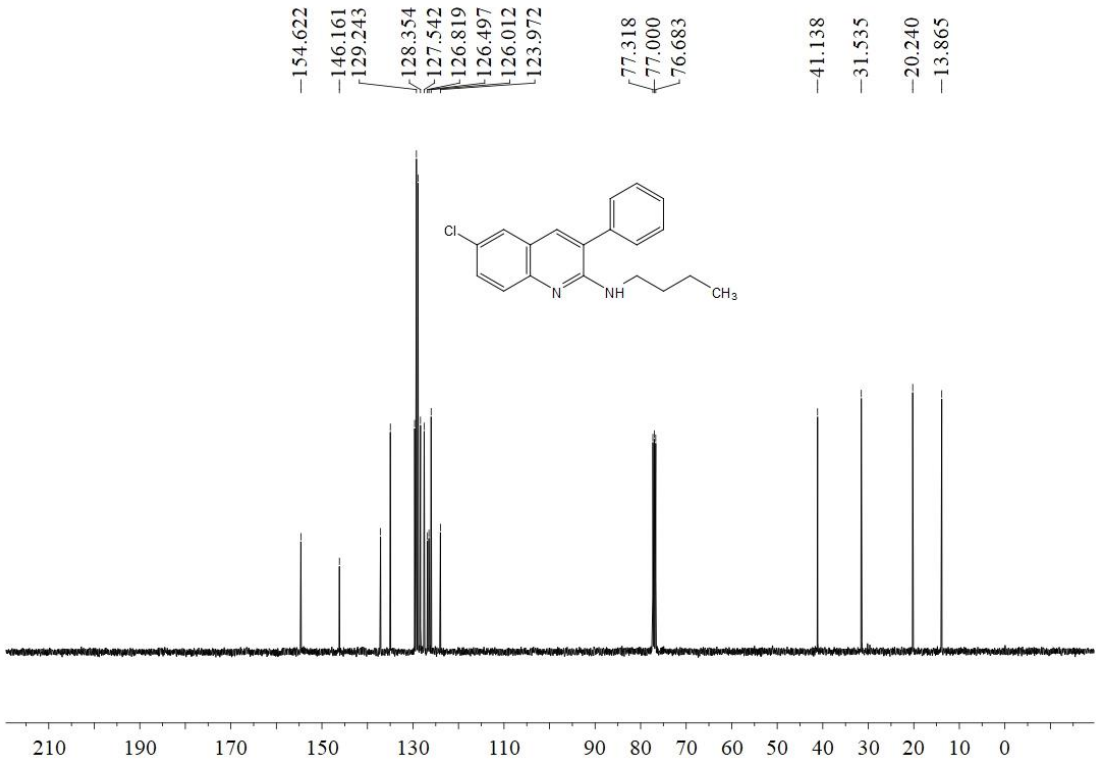


N-Butyl-6-chloro-3-phenylquinolin-2-amine (**4ah**)

^{1}H NMR (400 MHz, $CDCl_3$)

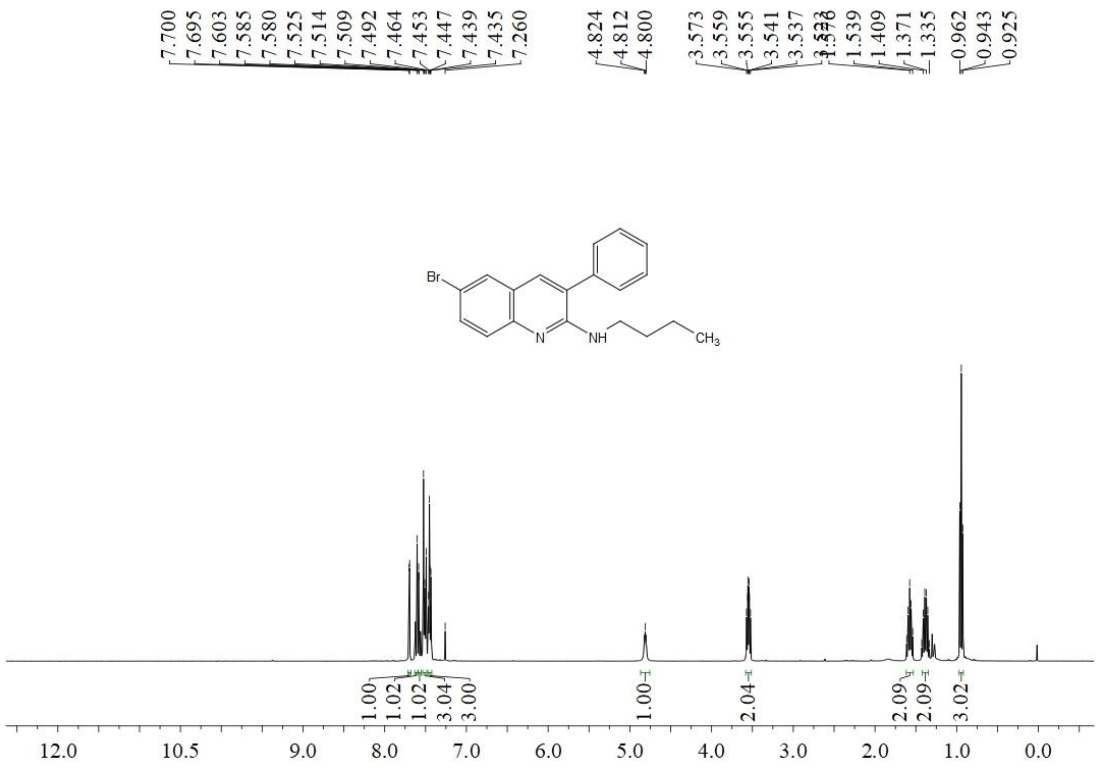


^{13}C NMR (100 MHz, $CDCl_3$)

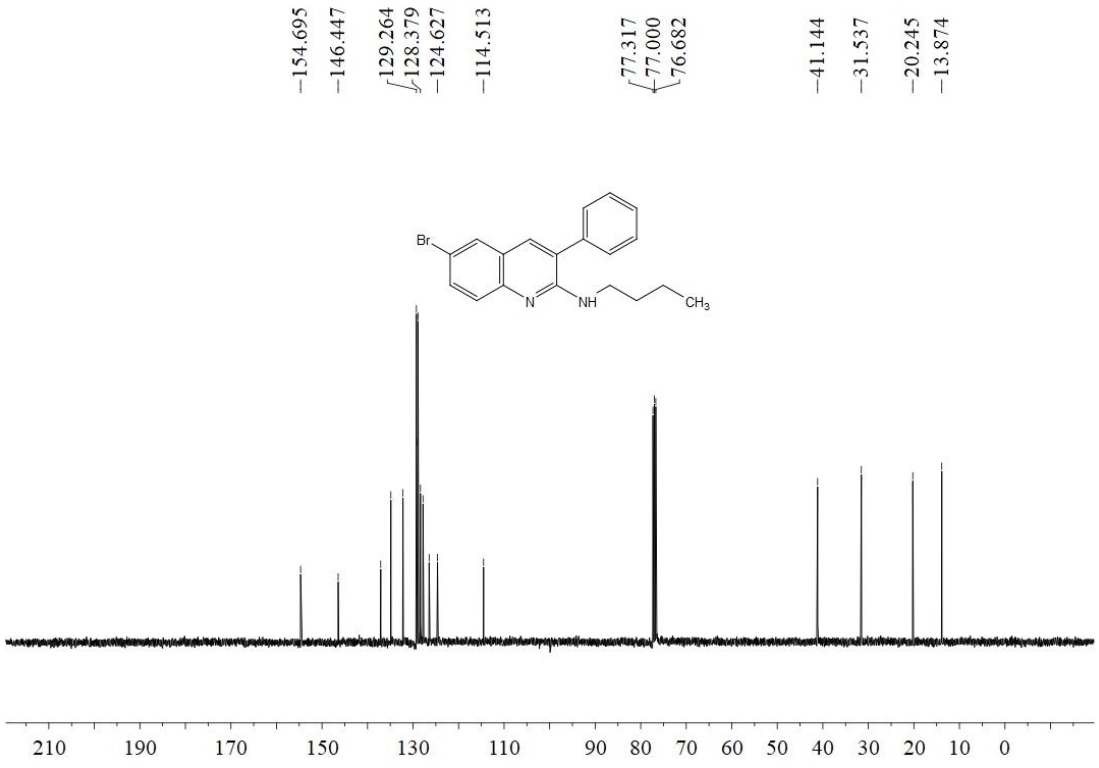


6-Bromo-N-butyl-3-phenylquinolin-2-amine (**4ai**)

^{1}H NMR (400 MHz, $CDCl_3$)

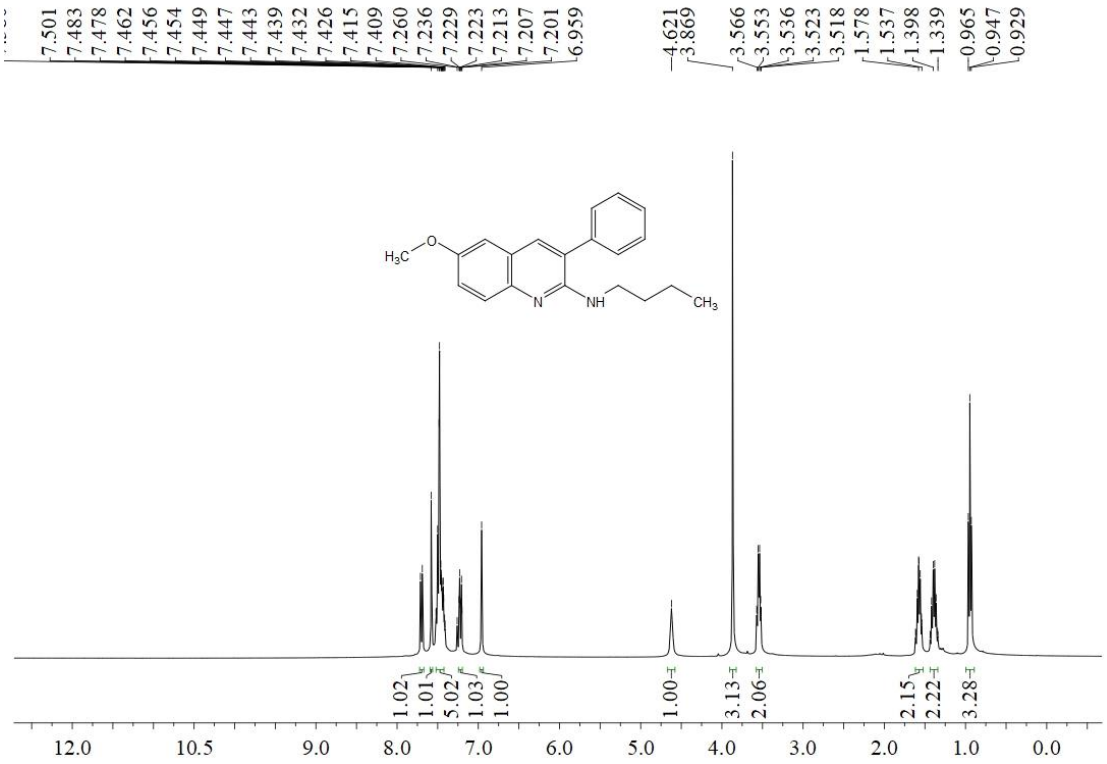


^{13}C NMR (100 MHz, $CDCl_3$)

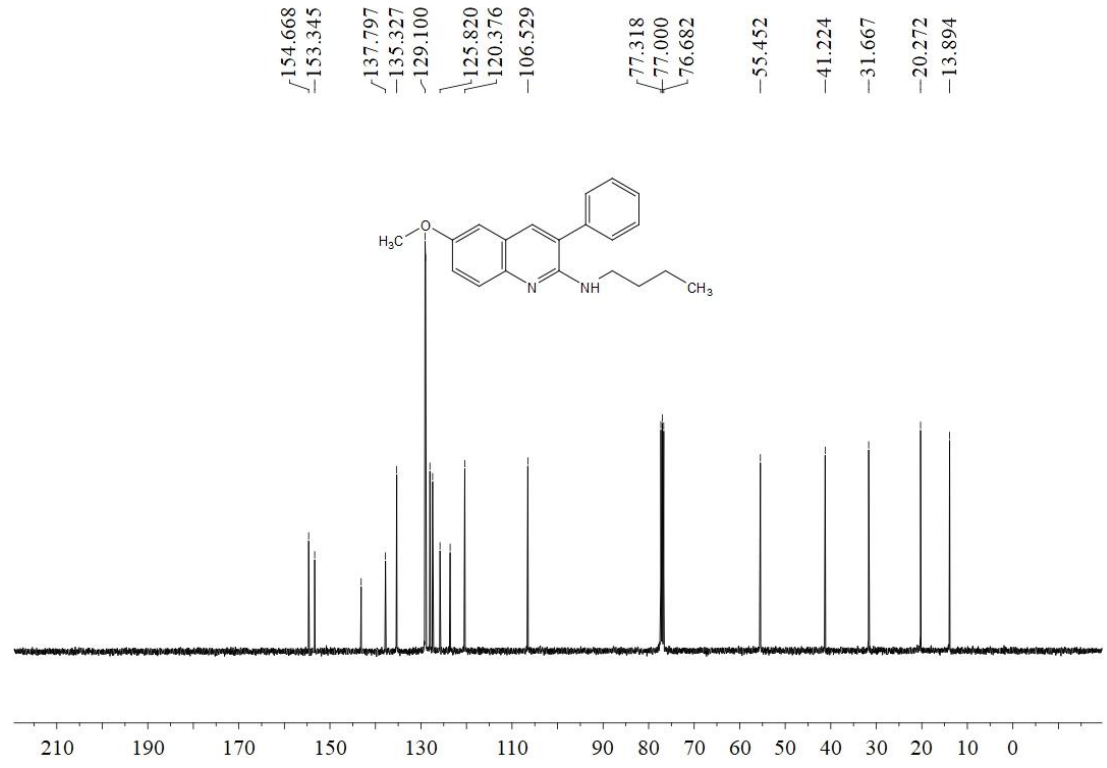


N-Butyl-6-methoxy-3-phenylquinolin-2-amine (**4aj**)

^{1}H NMR (400 MHz, $CDCl_3$)

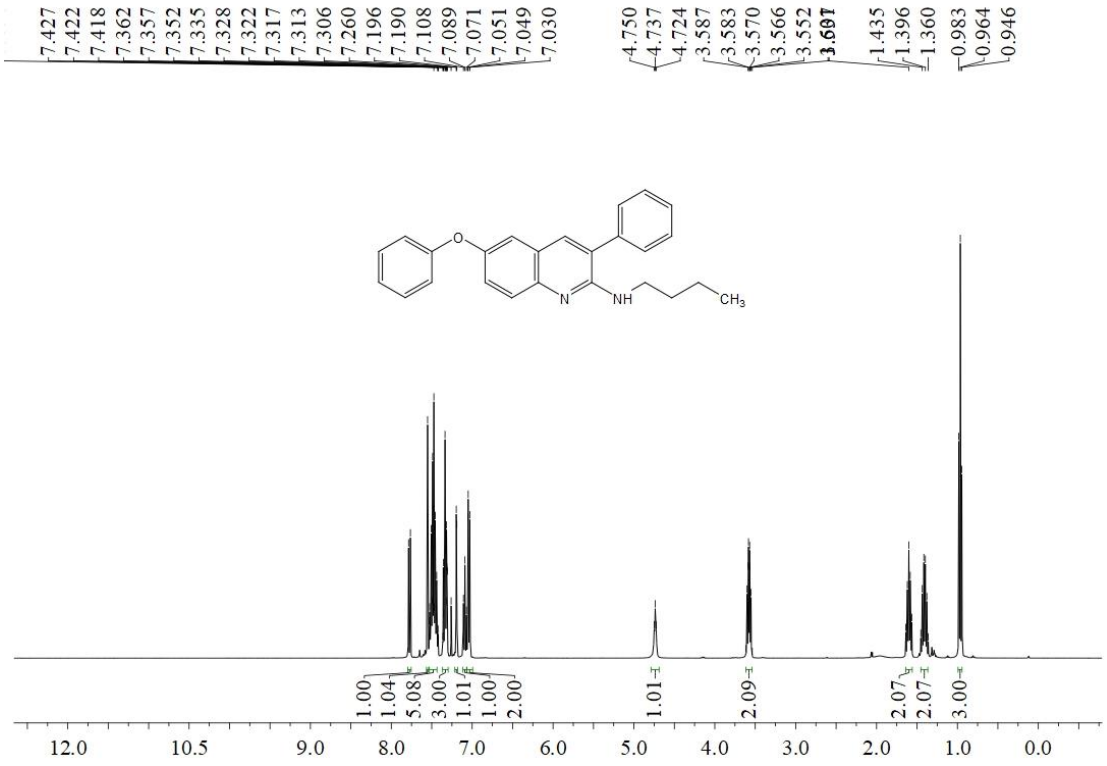


^{13}C NMR (100 MHz, $CDCl_3$)

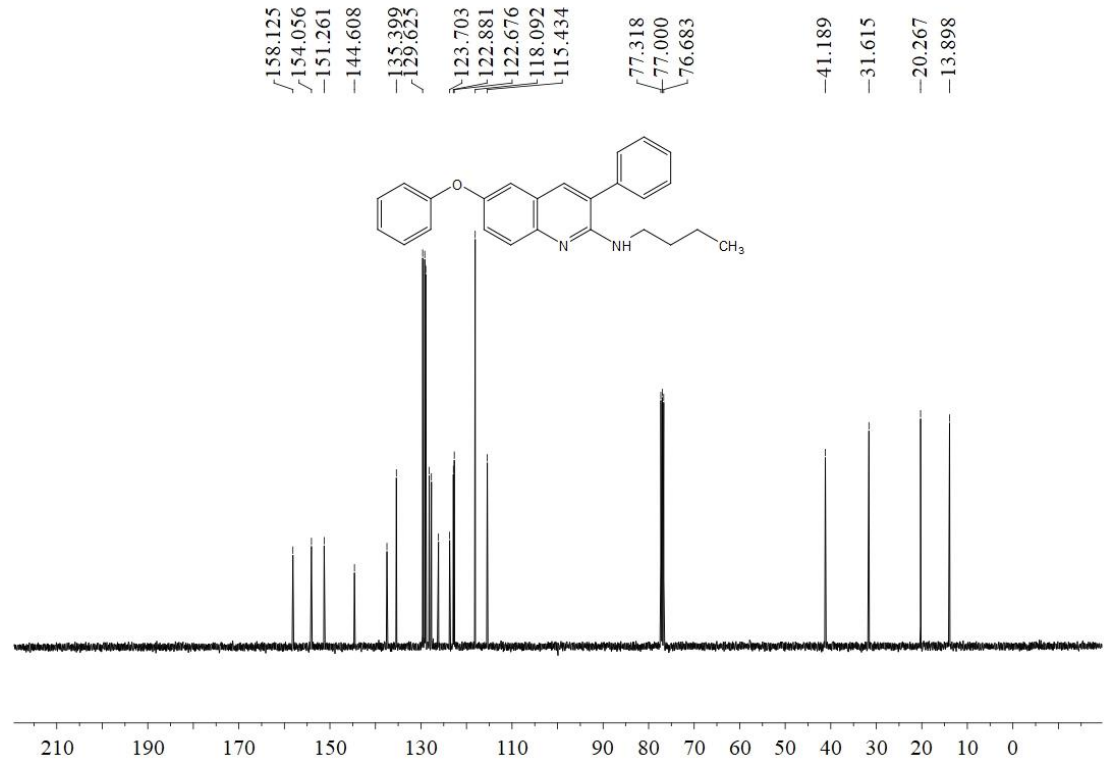


N-Butyl-6-phenoxy-3-phenylquinolin-2-amine (**4ak**)

^{1}H NMR (400 MHz, $CDCl_3$)

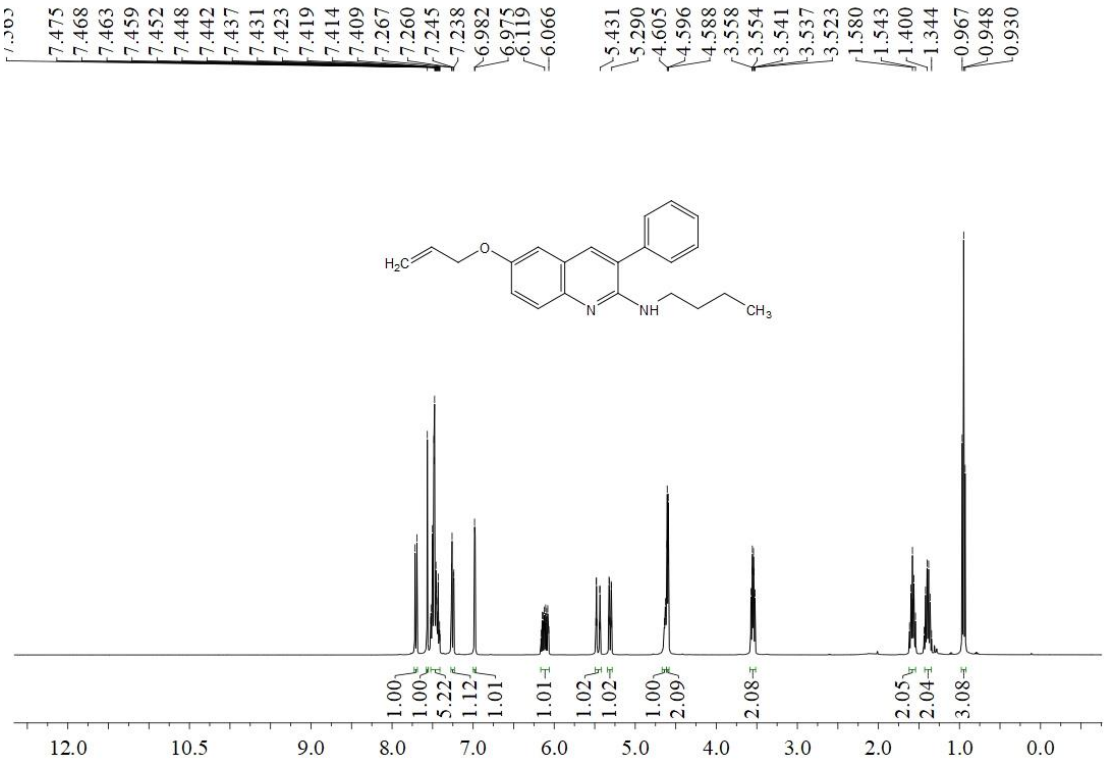


^{13}C NMR (100 MHz, $CDCl_3$)

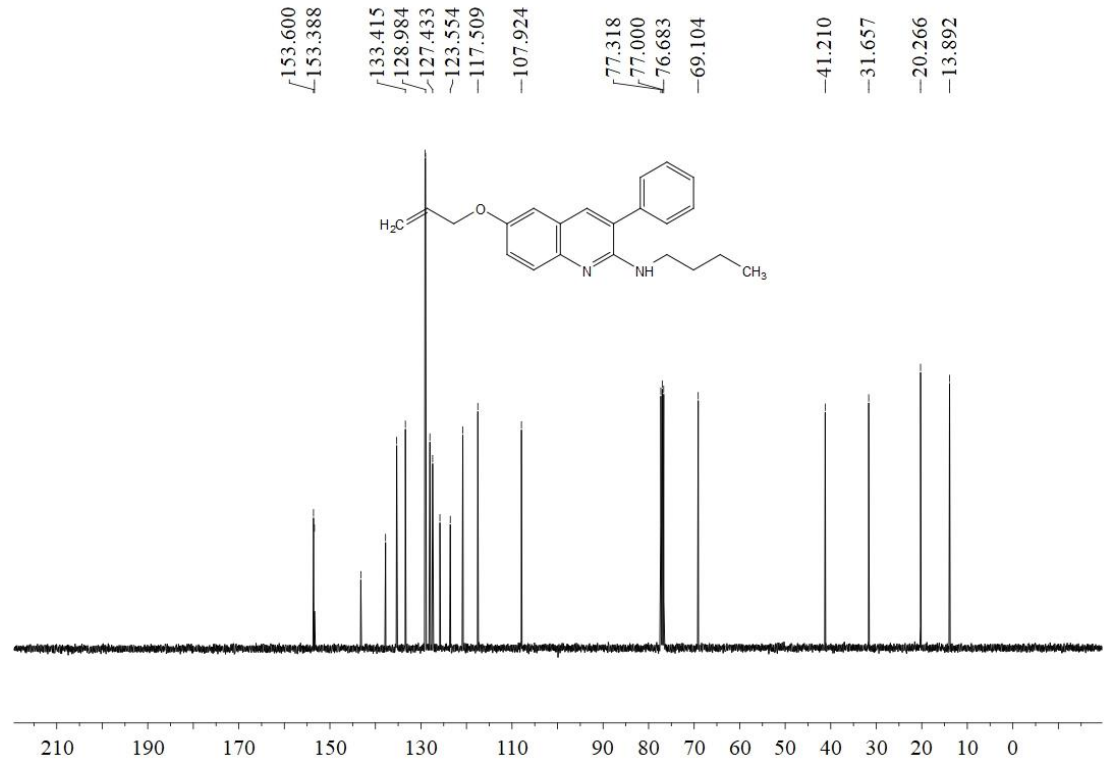


6-(Allyloxy)-*N*-butyl-3-phenylquinolin-2-amine (**4al**)

^{1}H NMR (400 MHz, $CDCl_3$)

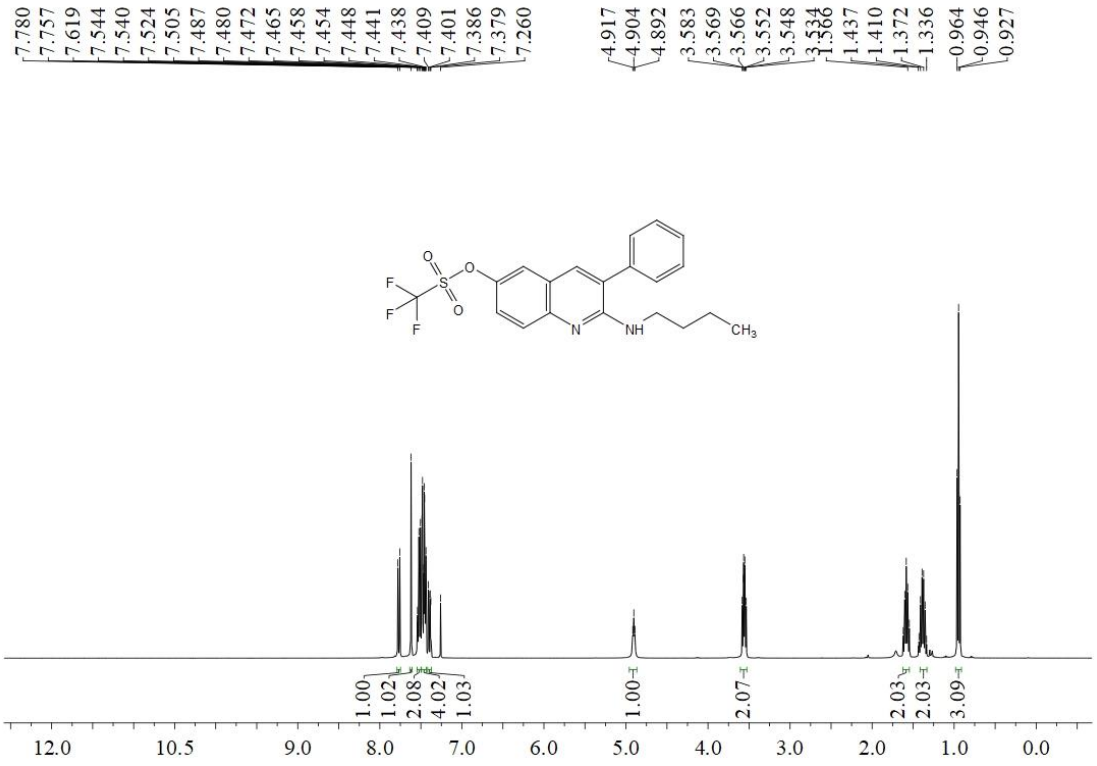


^{13}C NMR (100 MHz, $CDCl_3$)

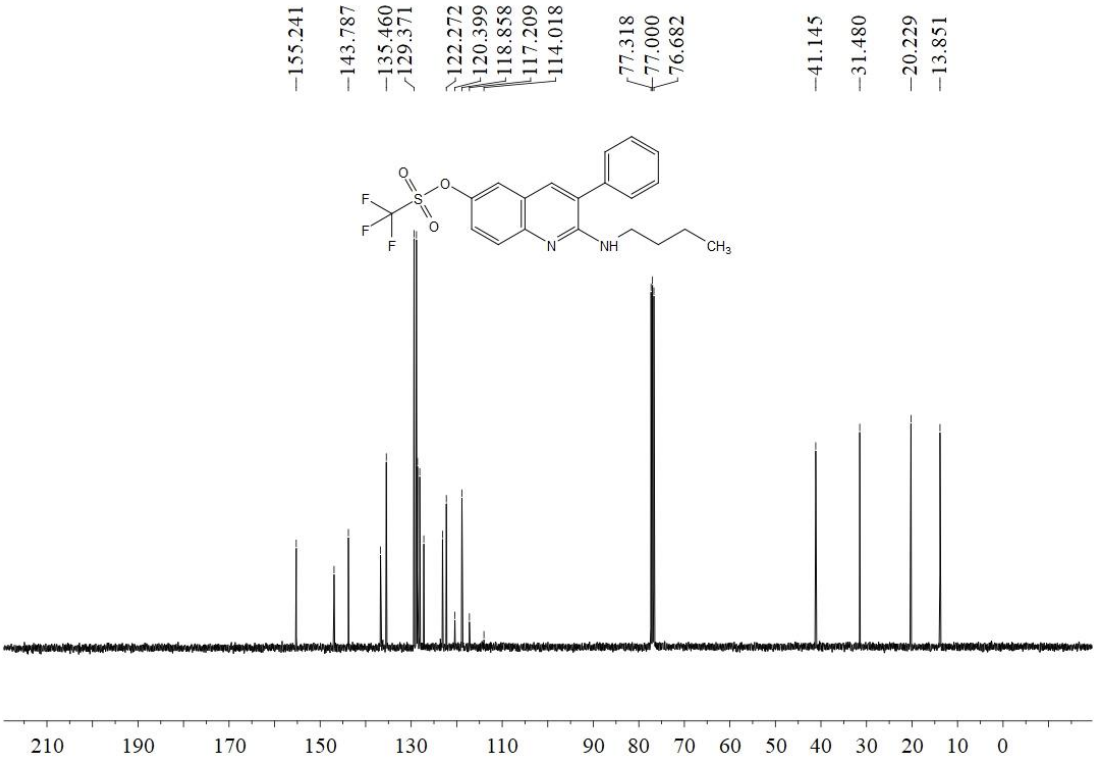


2-(Butylamino)-3-phenylquinolin-6-yl trifluoromethanesulfonate (**4am**)

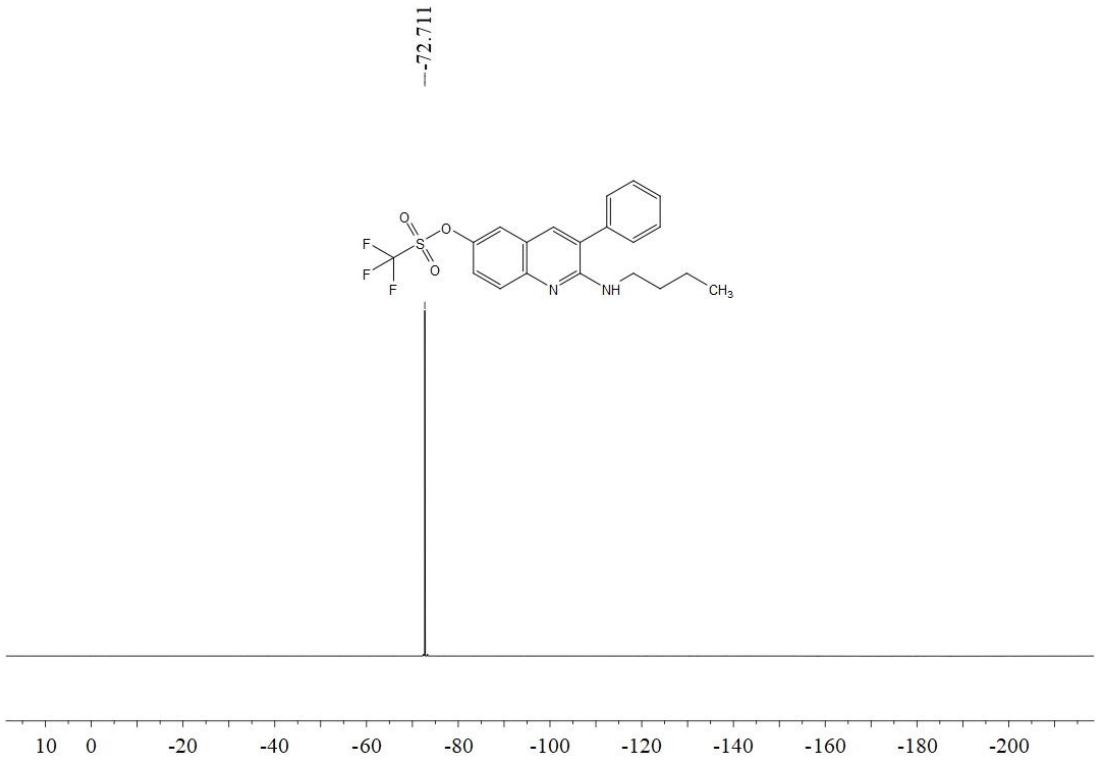
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

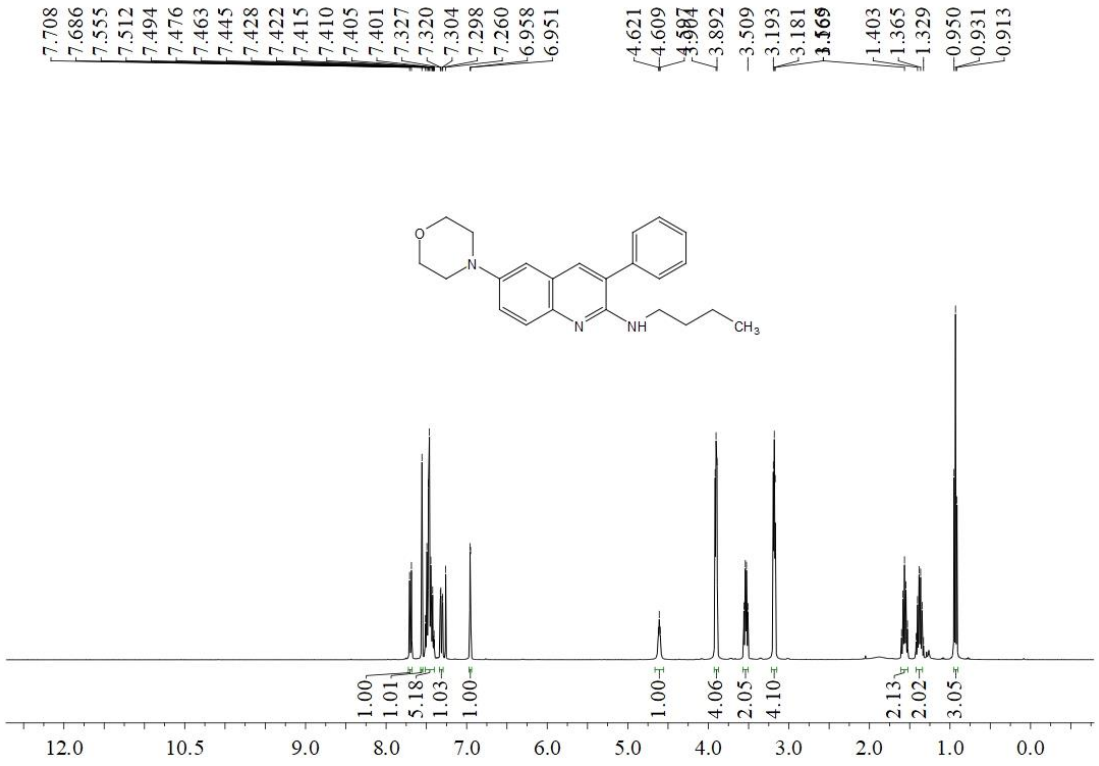


^{19}F NMR (375 MHz, $CDCl_3$)

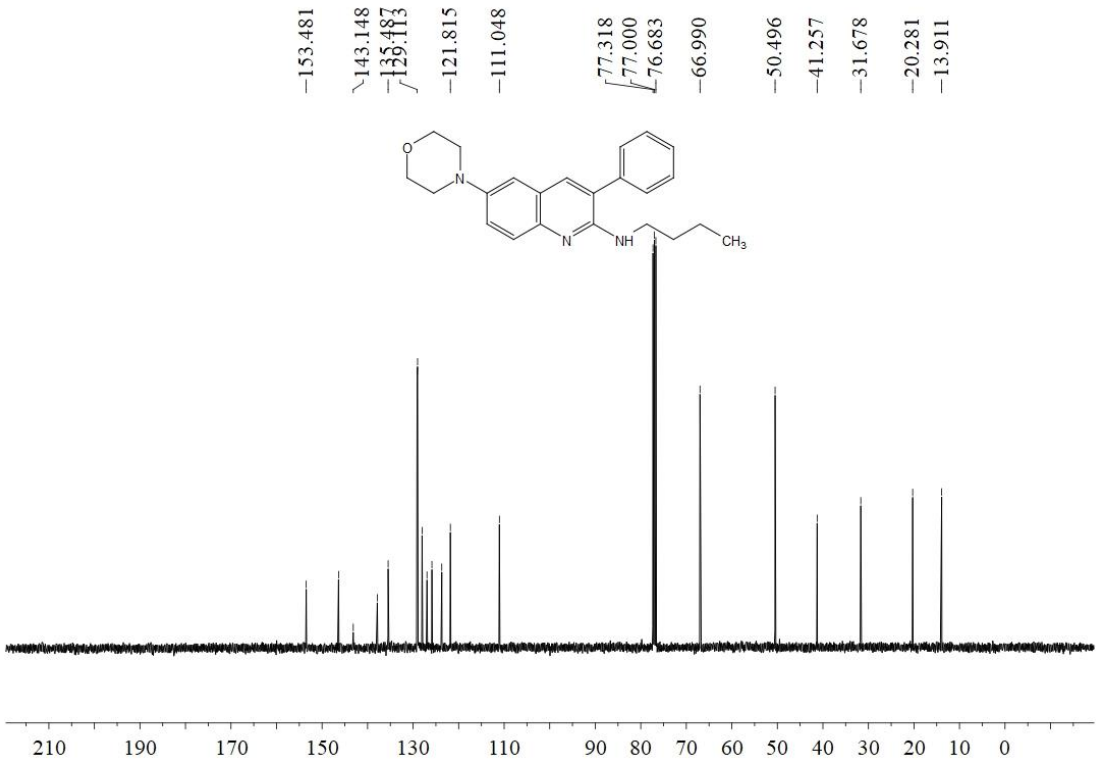


N-Butyl-6-morpholino-3-phenylquinolin-2-amine (**4an**)

^{1}H NMR (400 MHz, $CDCl_3$)

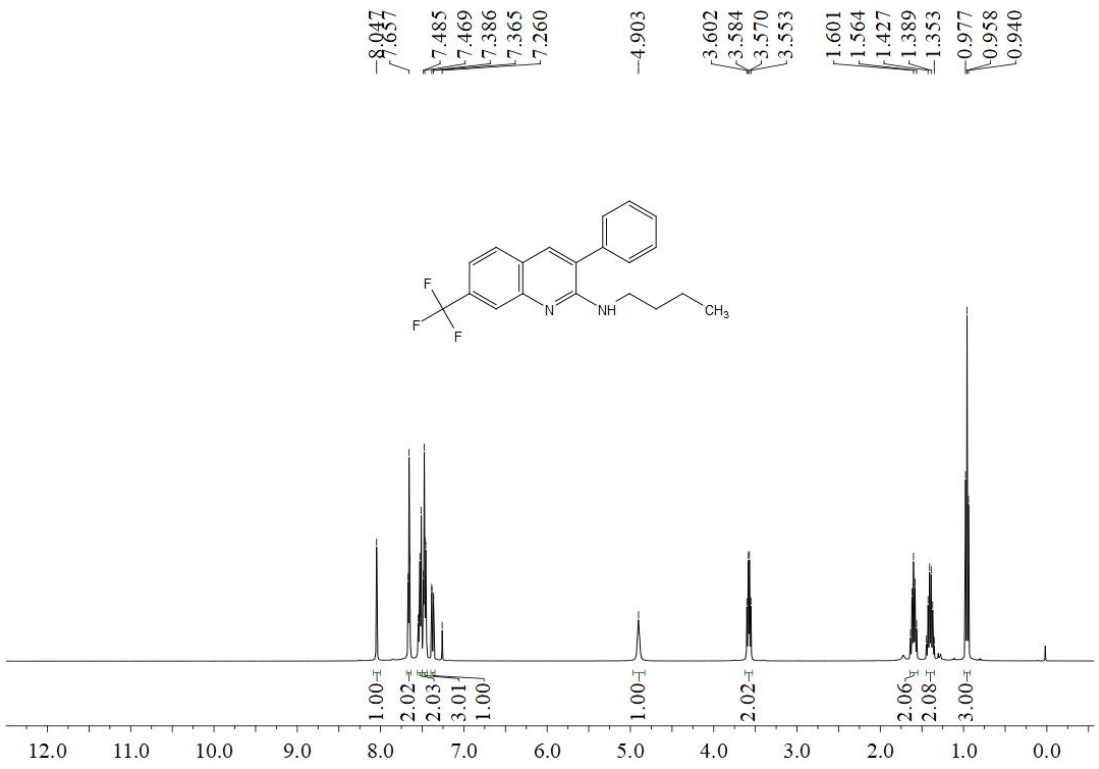


^{13}C NMR (100 MHz, $CDCl_3$)

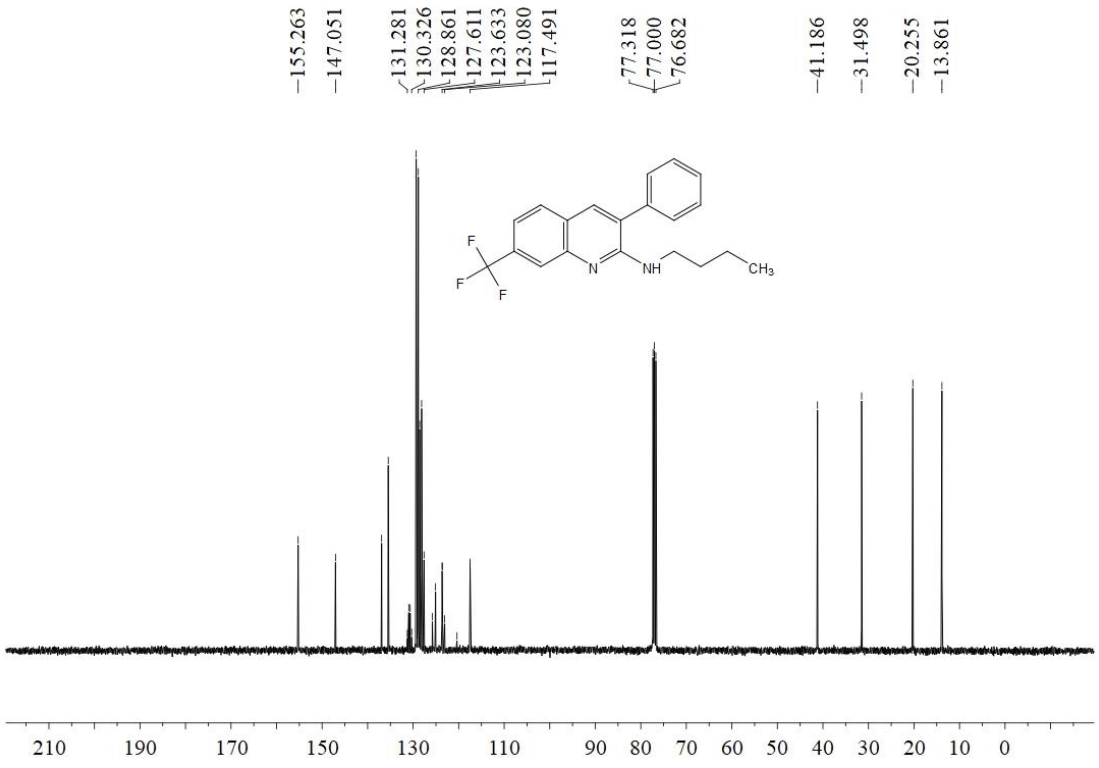


N-Butyl-3-phenyl-7-(trifluoromethyl)quinolin-2-amine (**4ao**)

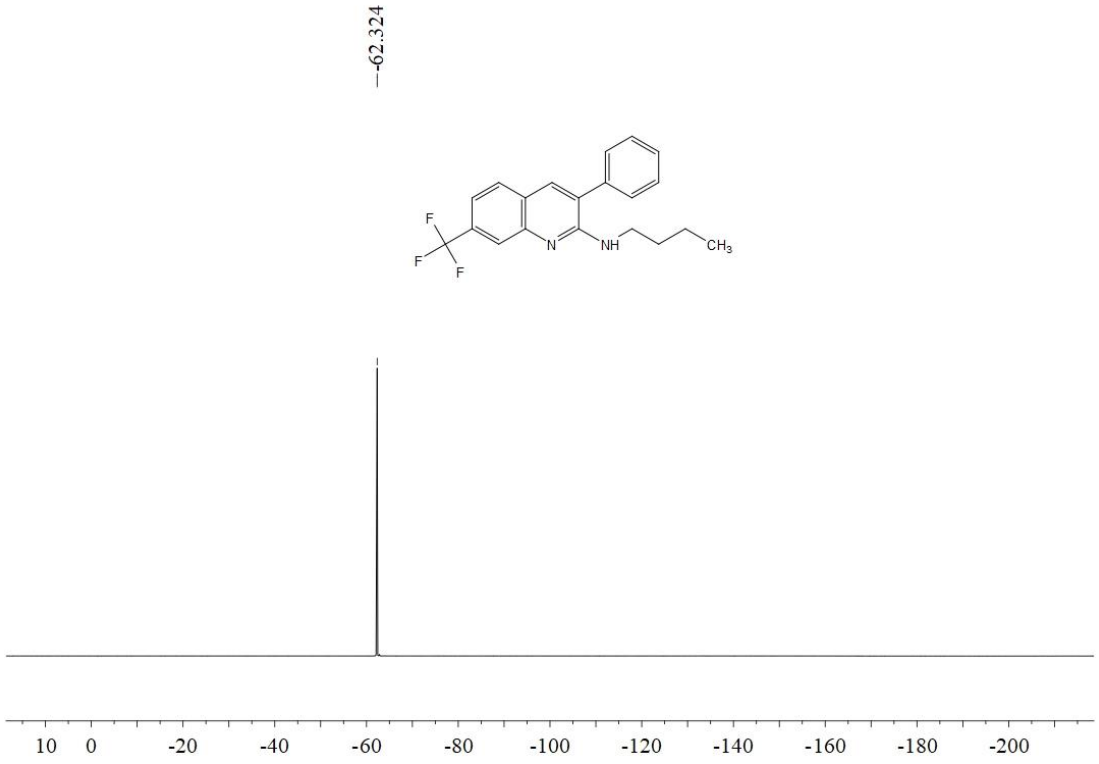
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

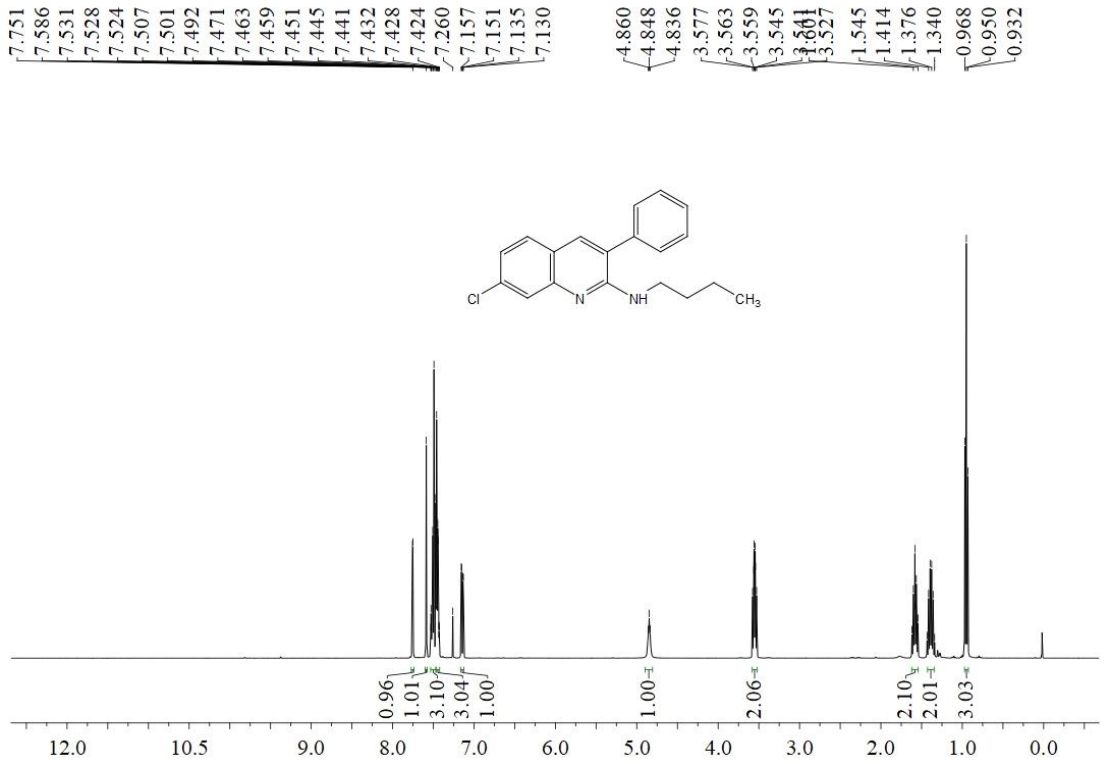


^{19}F NMR (375 MHz, $CDCl_3$)

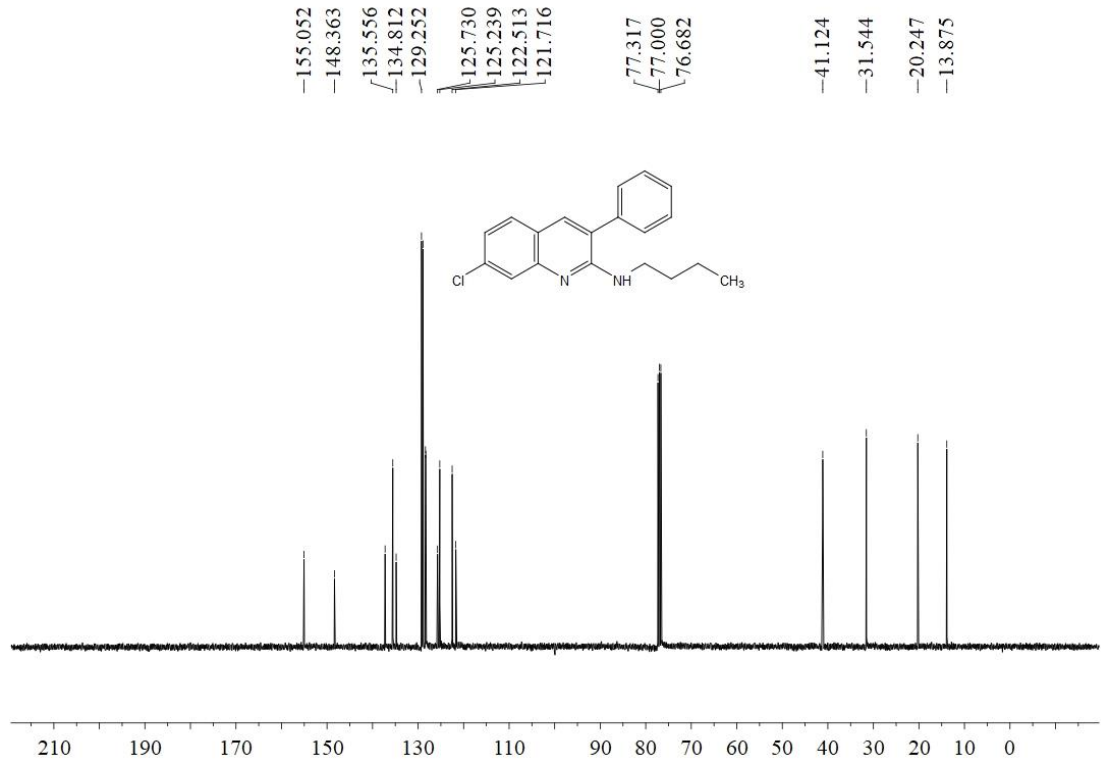


N-Butyl-7-chloro-3-phenylquinolin-2-amine (**4ap**)

^{1}H NMR (400 MHz, $CDCl_3$)

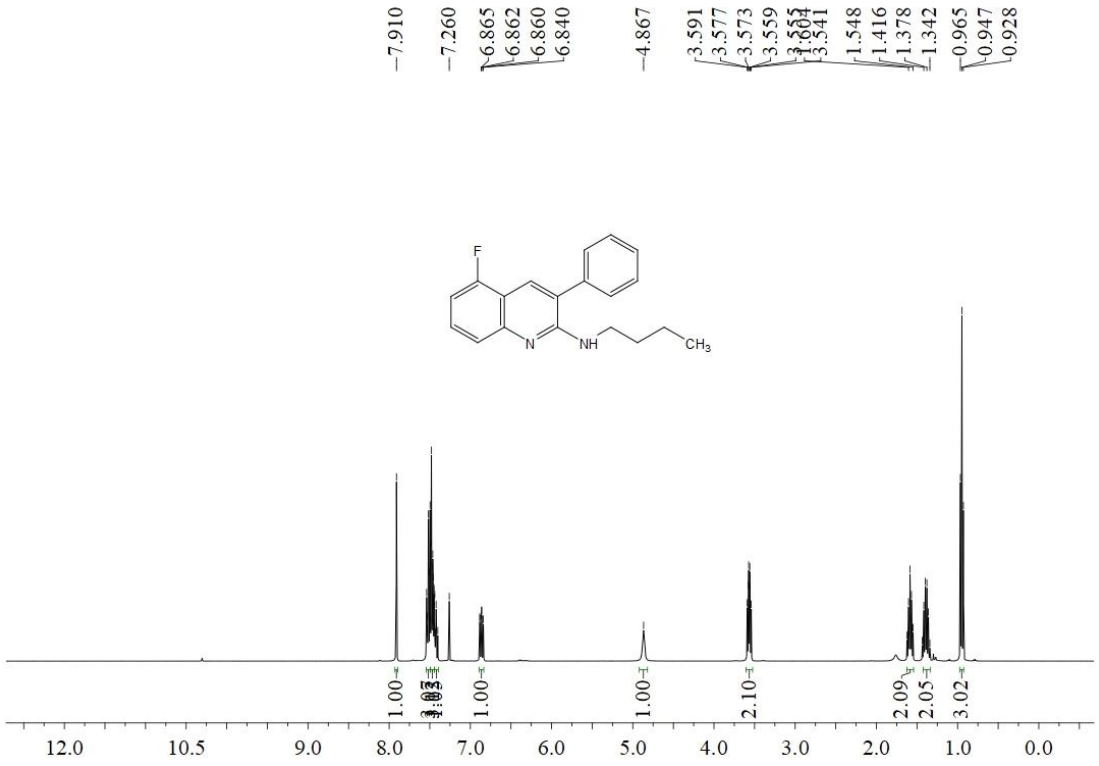


^{13}C NMR (100 MHz, $CDCl_3$)

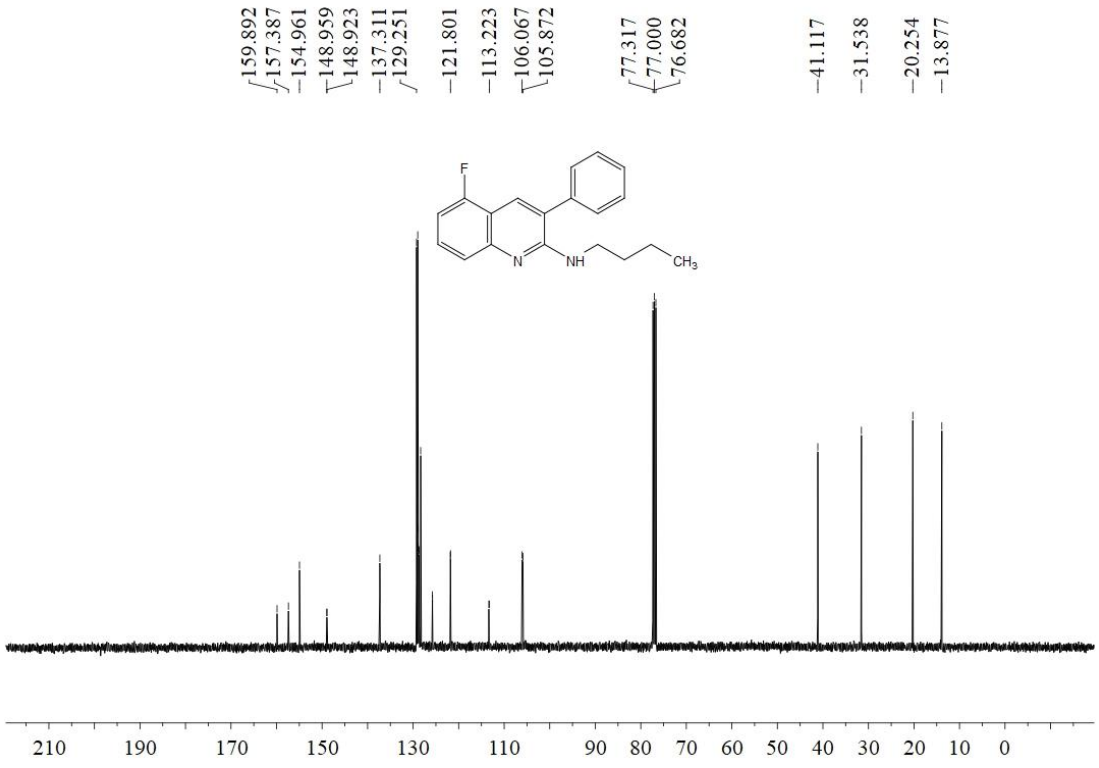


N-Butyl-5-fluoro-3-phenylquinolin-2-amine (**4aq**)

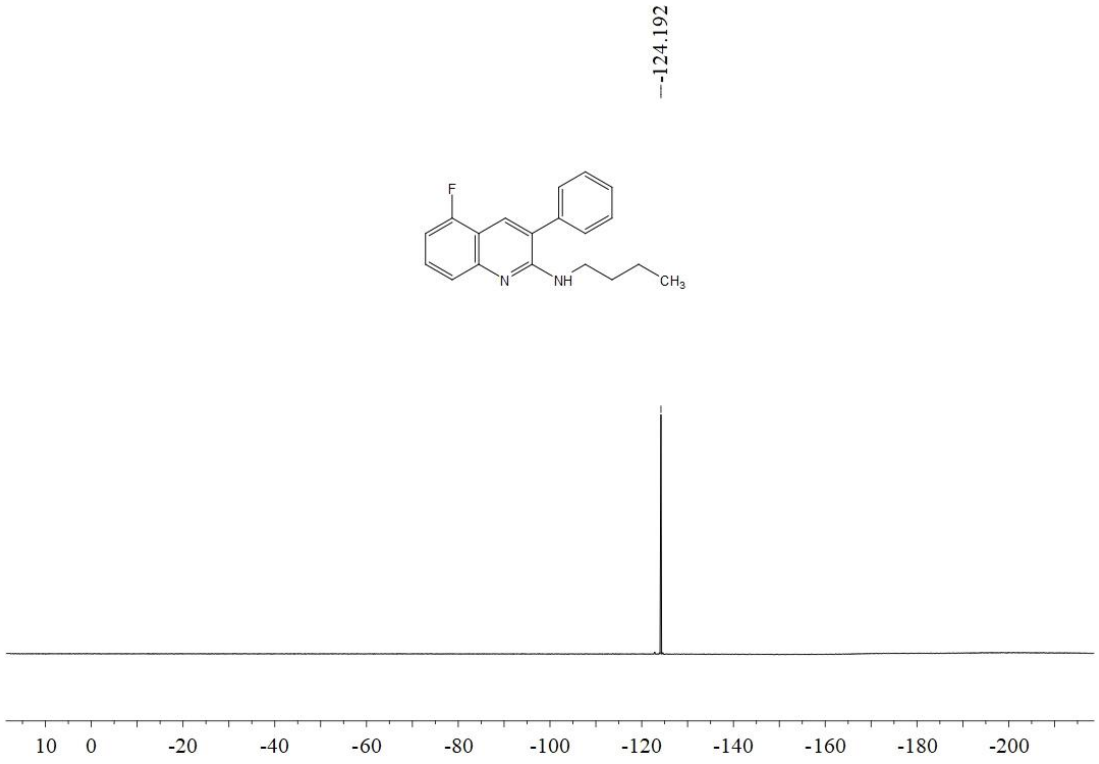
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

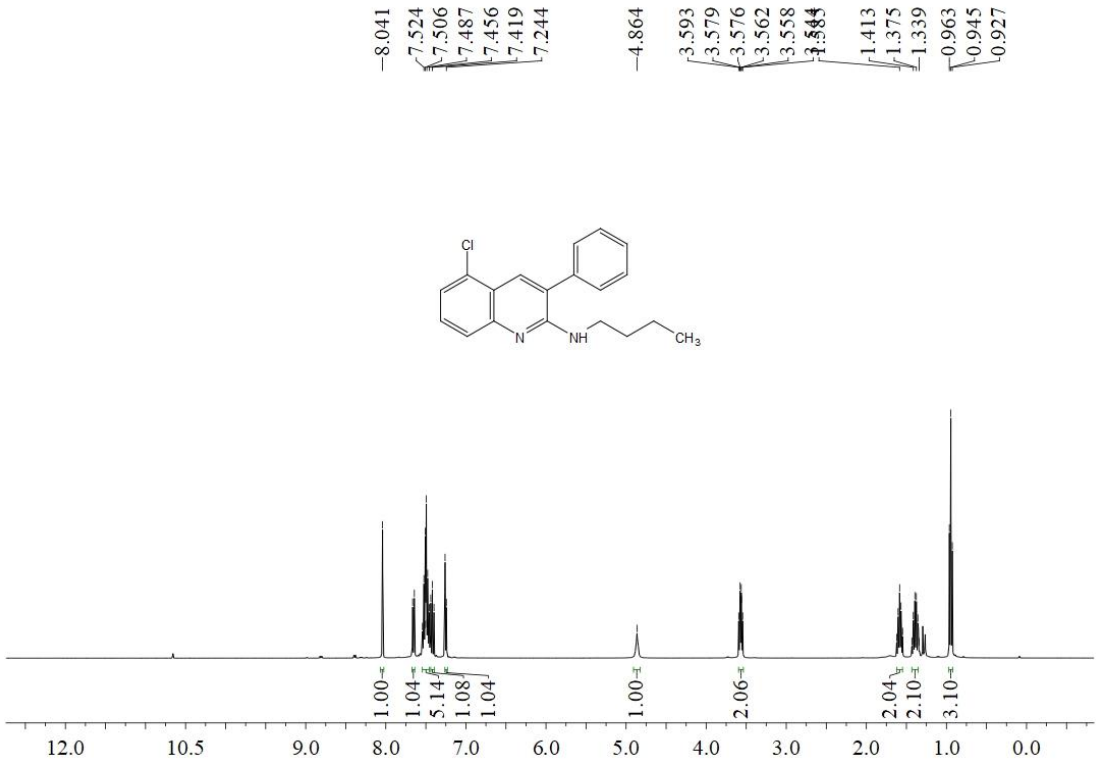


^{19}F NMR (375 MHz, $CDCl_3$)

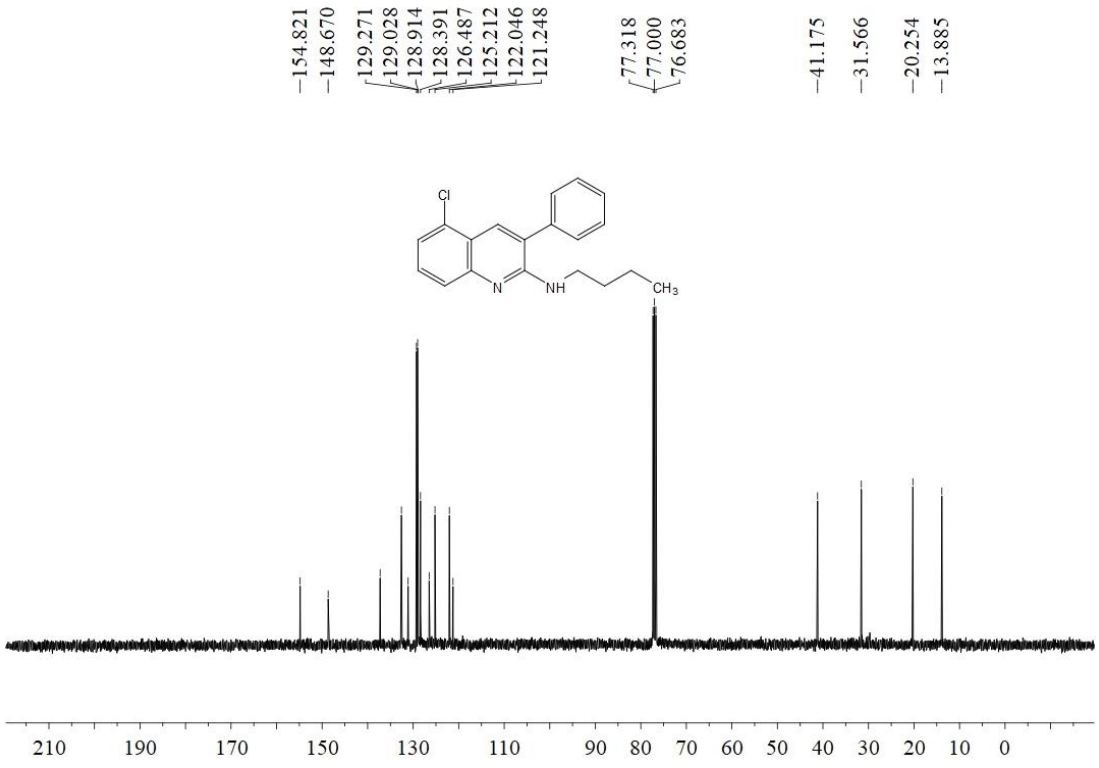


N-Butyl-5-fluoro-3-phenylquinolin-2-amine (**4ar**)

^{1}H NMR (400 MHz, $CDCl_3$)

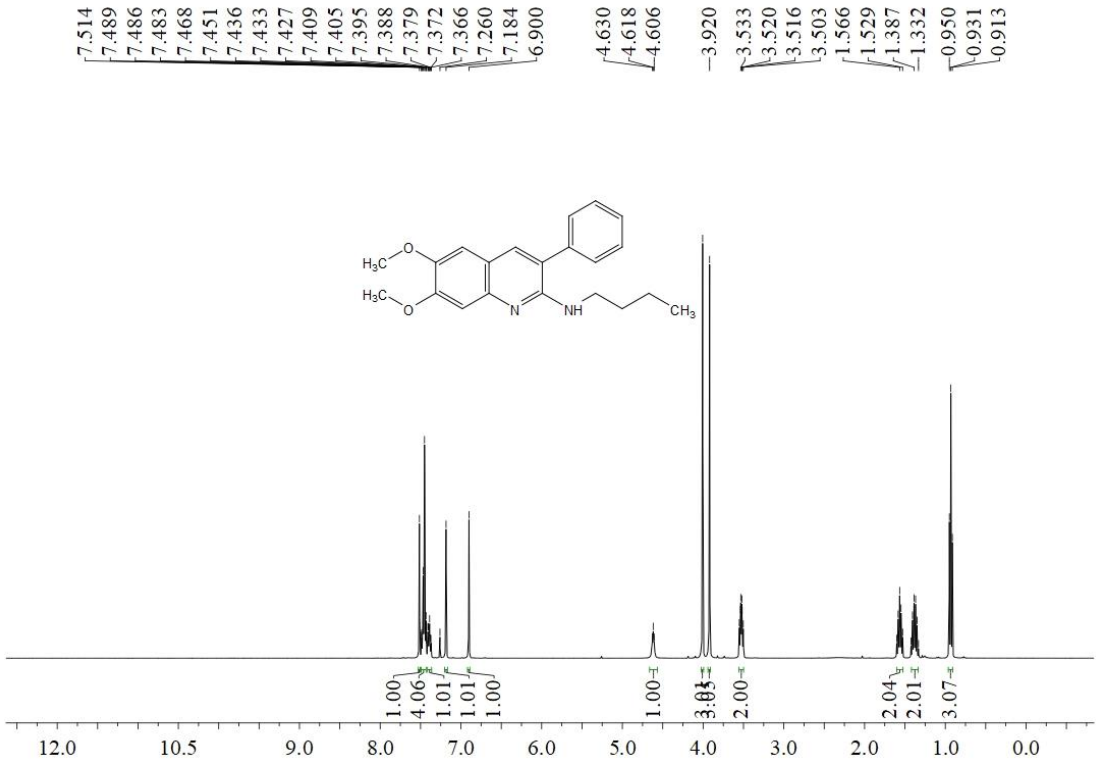


^{13}C NMR (100 MHz, $CDCl_3$)

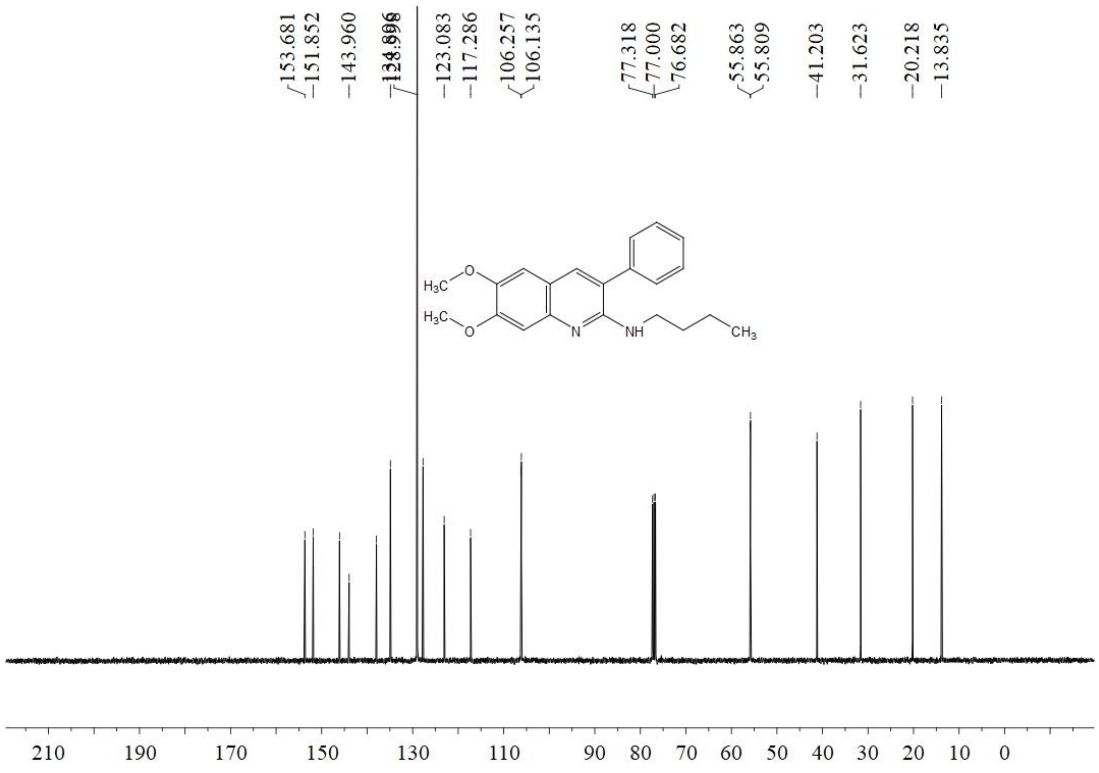


N-Butyl-6,7-dimethoxy-3-phenylquinolin-2-amine (**4as**)

^{1}H NMR (400 MHz, $CDCl_3$)

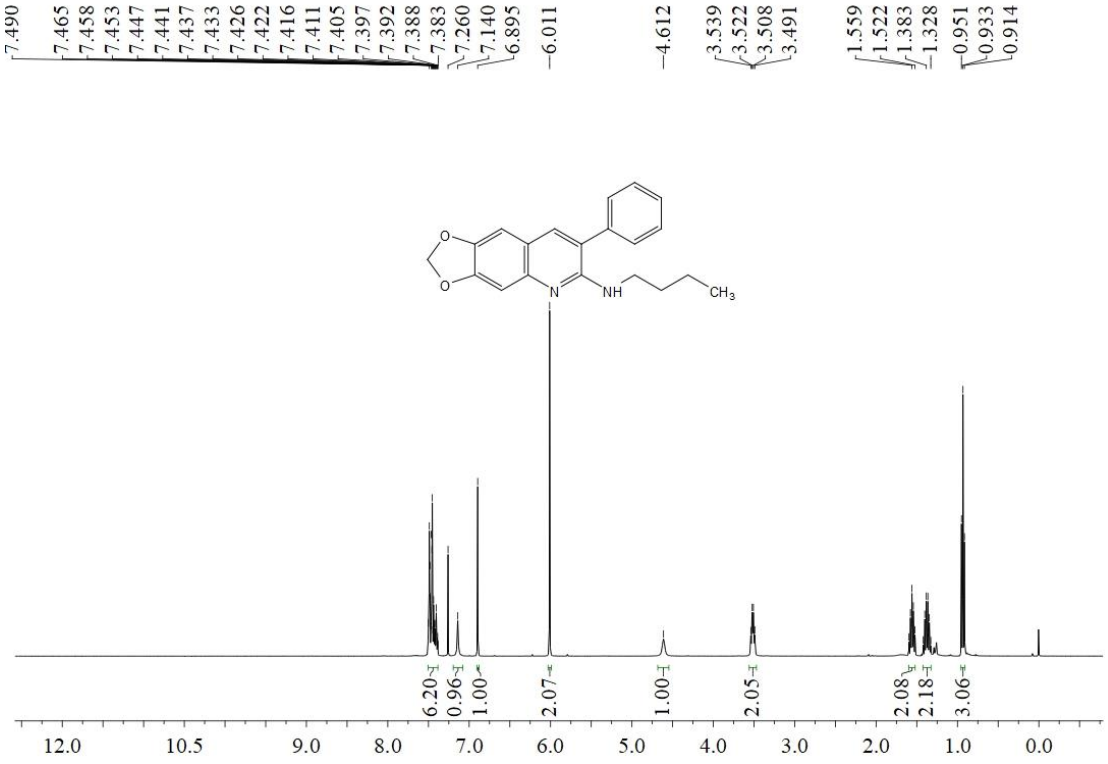


^{13}C NMR (100 MHz, $CDCl_3$)

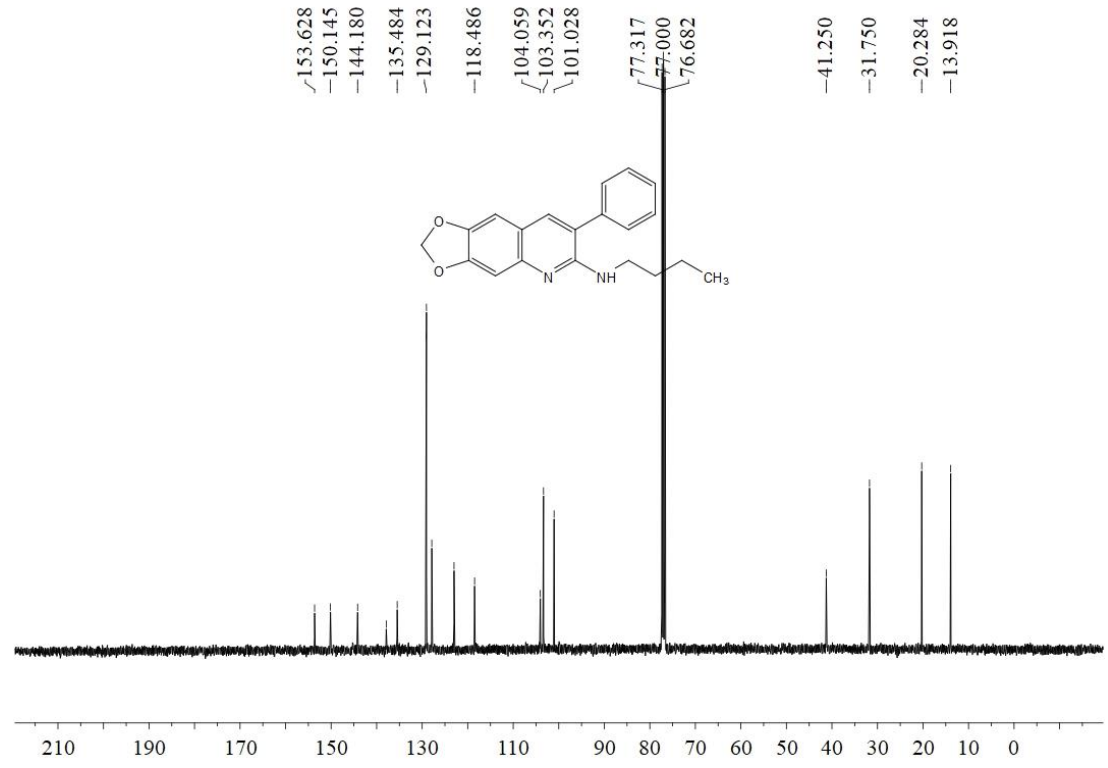


N-Butyl-7-phenyl-[1,3]dioxolo[4,5-*g*]quinolin-6-amine (**4at**)

^{1}H NMR (400 MHz, $CDCl_3$)

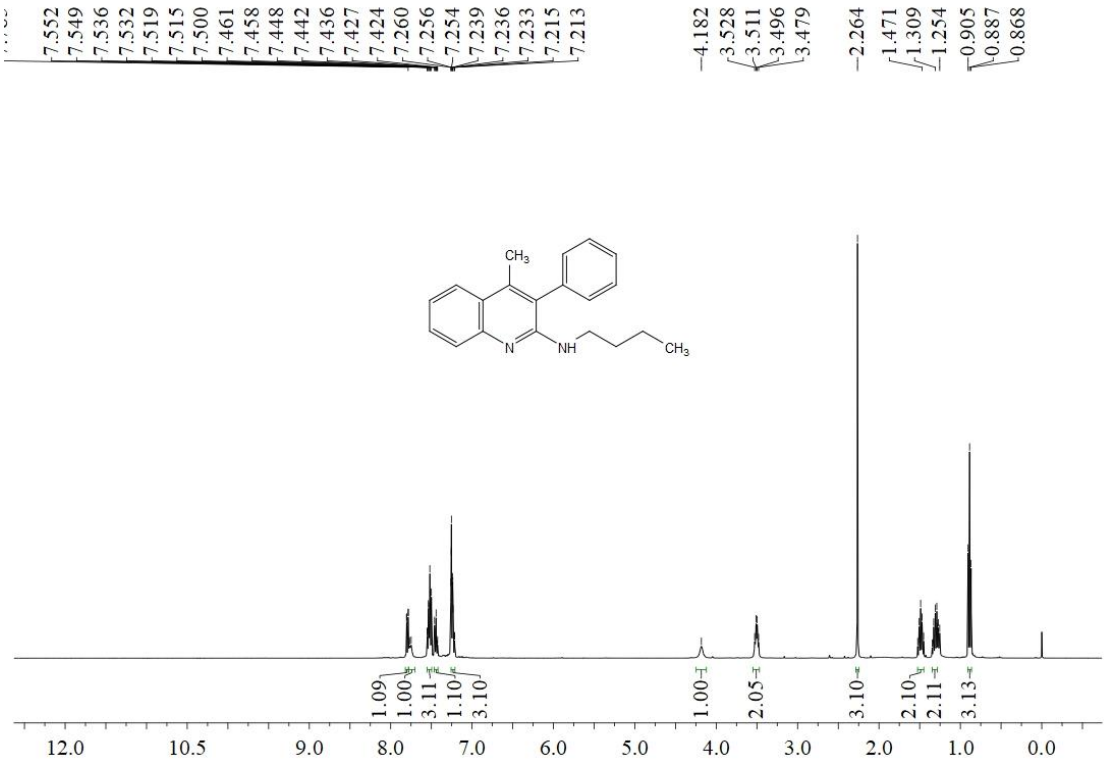


^{13}C NMR (100 MHz, $CDCl_3$)

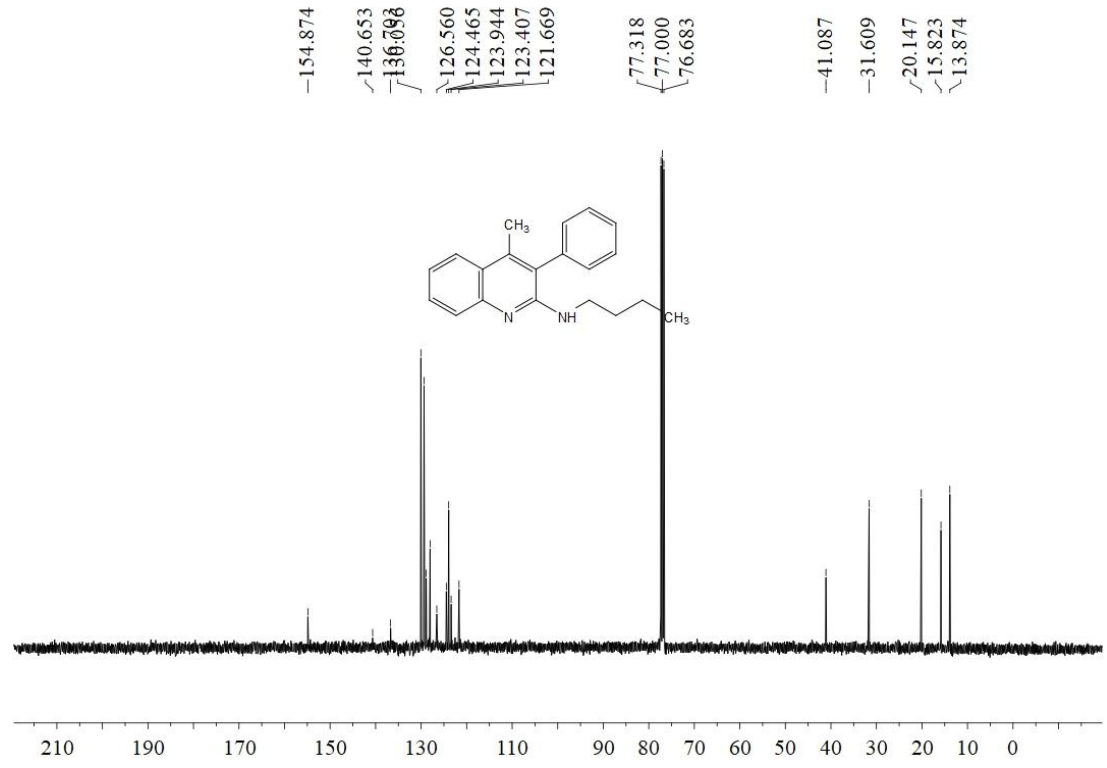


N-Butyl-4-methyl-3-phenylquinolin-2-amine (**4au**)

^{1}H NMR (400 MHz, $CDCl_3$)

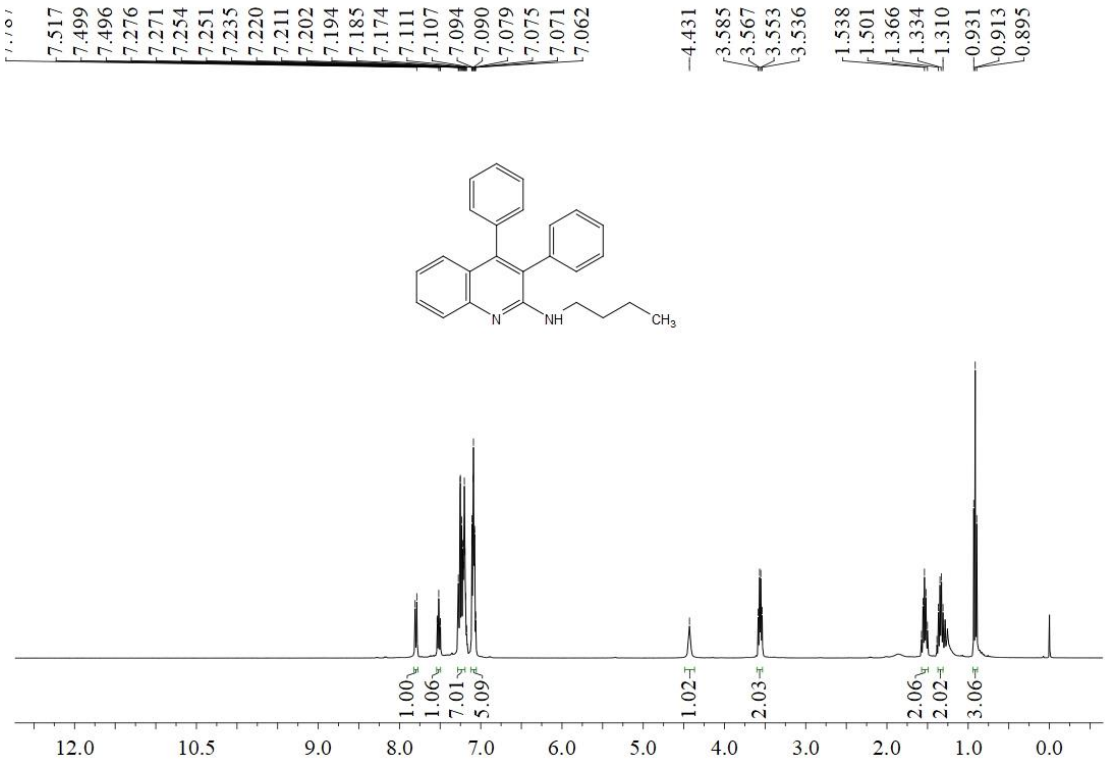


^{13}C NMR (100 MHz, $CDCl_3$)

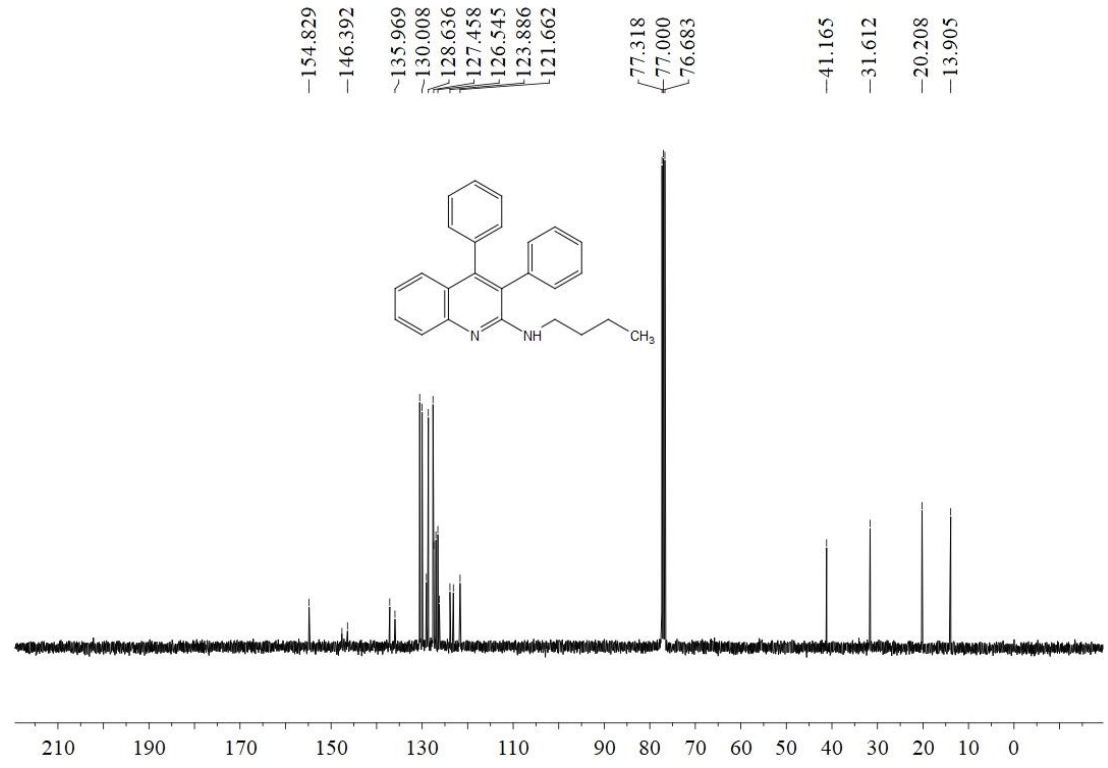


N-Butyl-3,4-diphenylquinolin-2-amine (**4av**)

^{1}H NMR (400 MHz, $CDCl_3$)

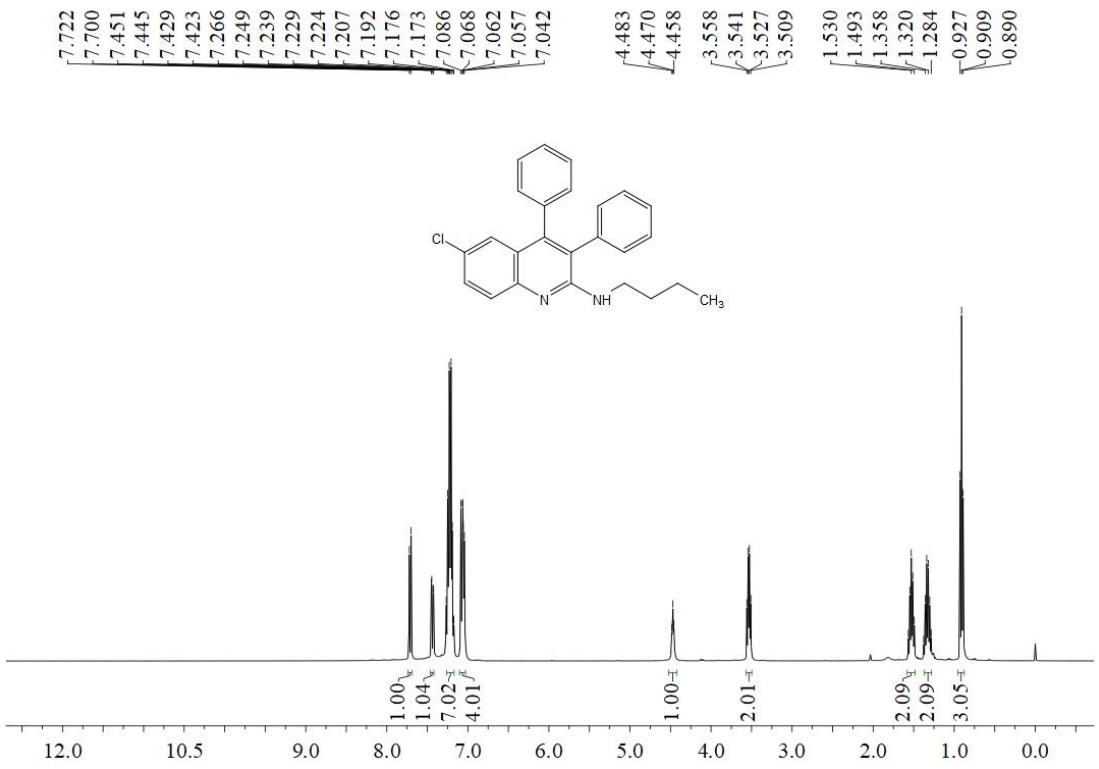


^{13}C NMR (100 MHz, $CDCl_3$)

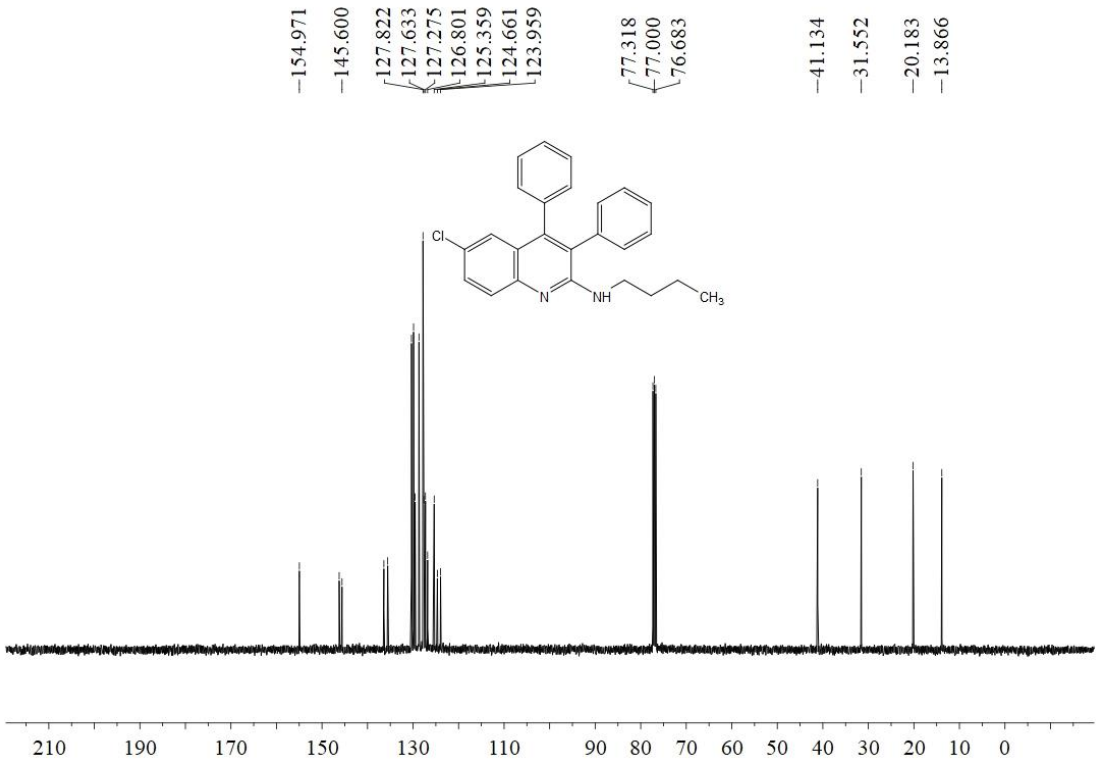


N-Butyl-6-chloro-3,4-diphenylquinolin-2-amine (**4aw**)

^{1}H NMR (400 MHz, $CDCl_3$)

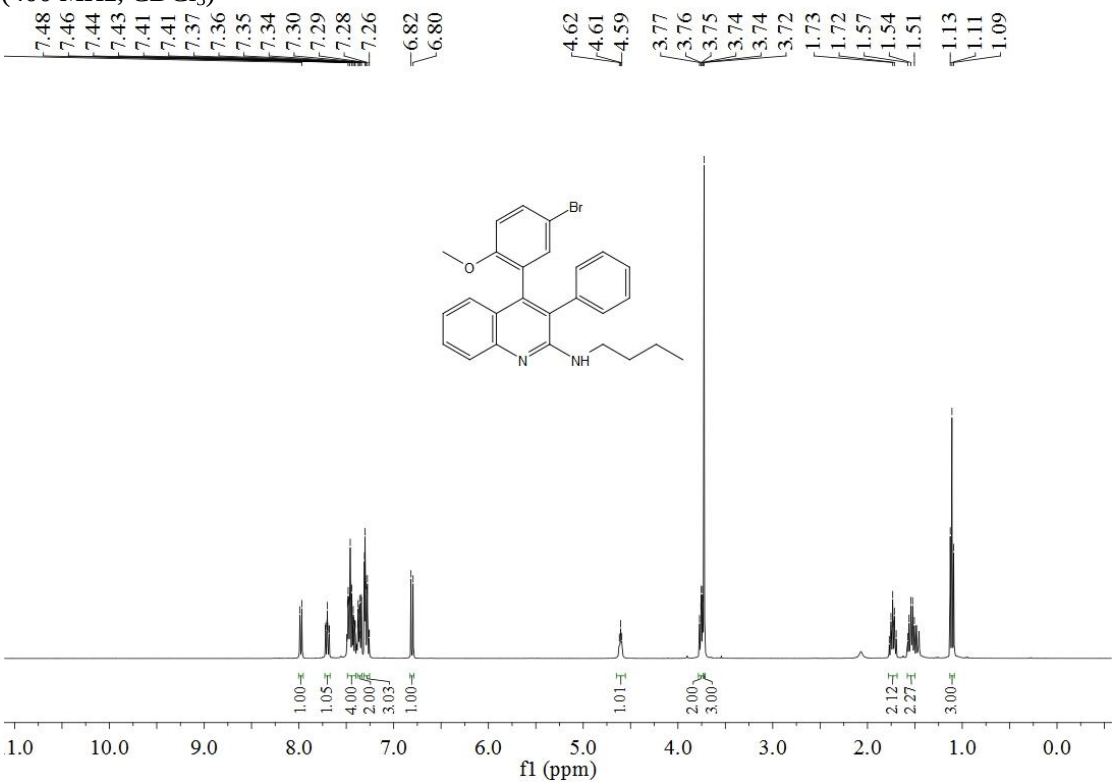


^{13}C NMR (100 MHz, $CDCl_3$)

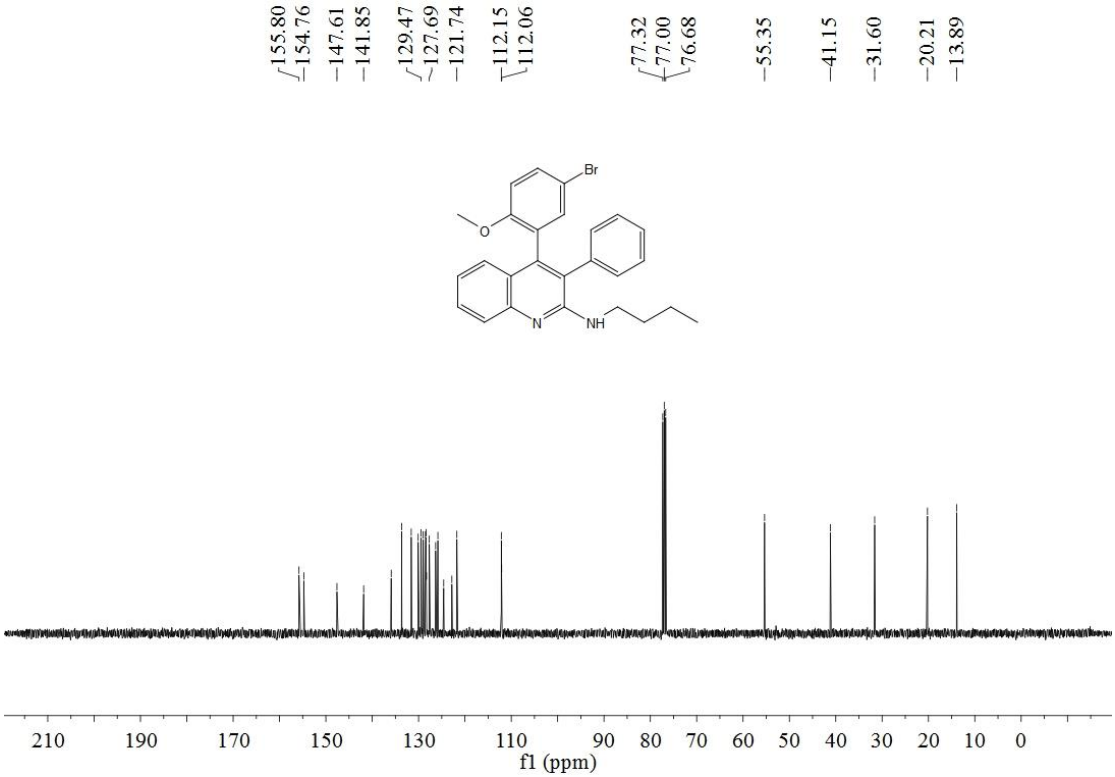


4-(5-Bromo-2-methoxyphenyl)-N-butyl-3-phenylquinolin-2-amine (**4a**x)

^{1}H NMR (400 MHz, $CDCl_3$)

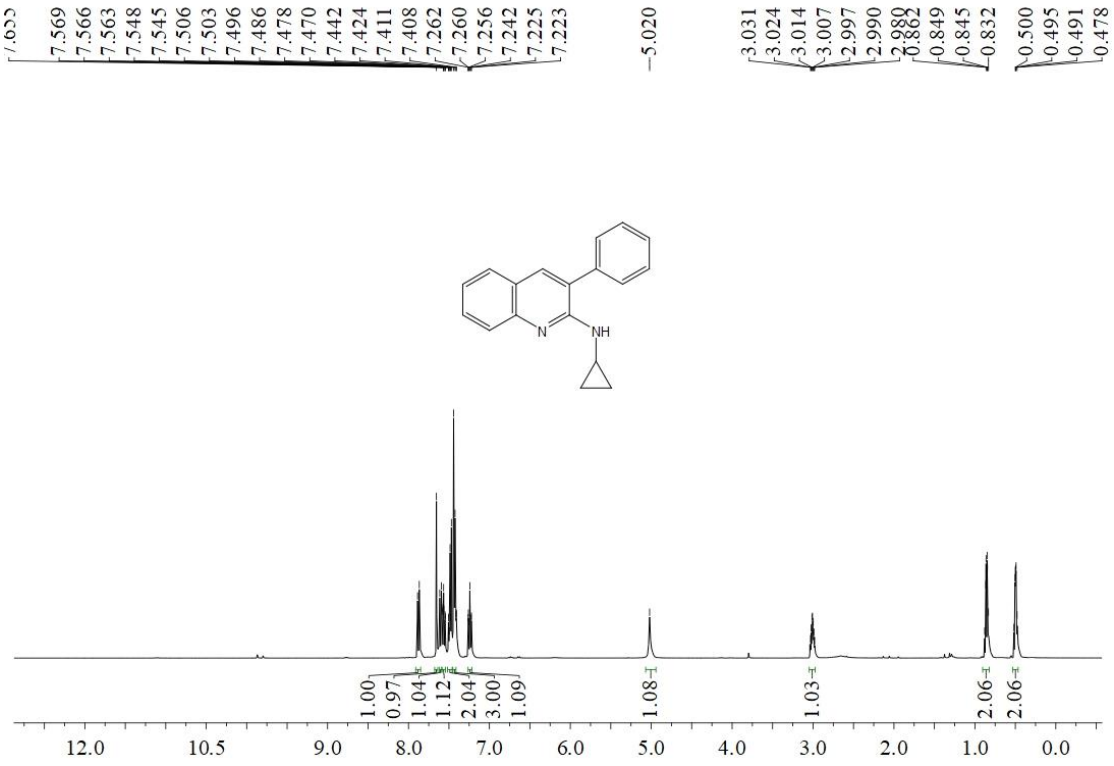


^{13}C NMR (100 MHz, $CDCl_3$)

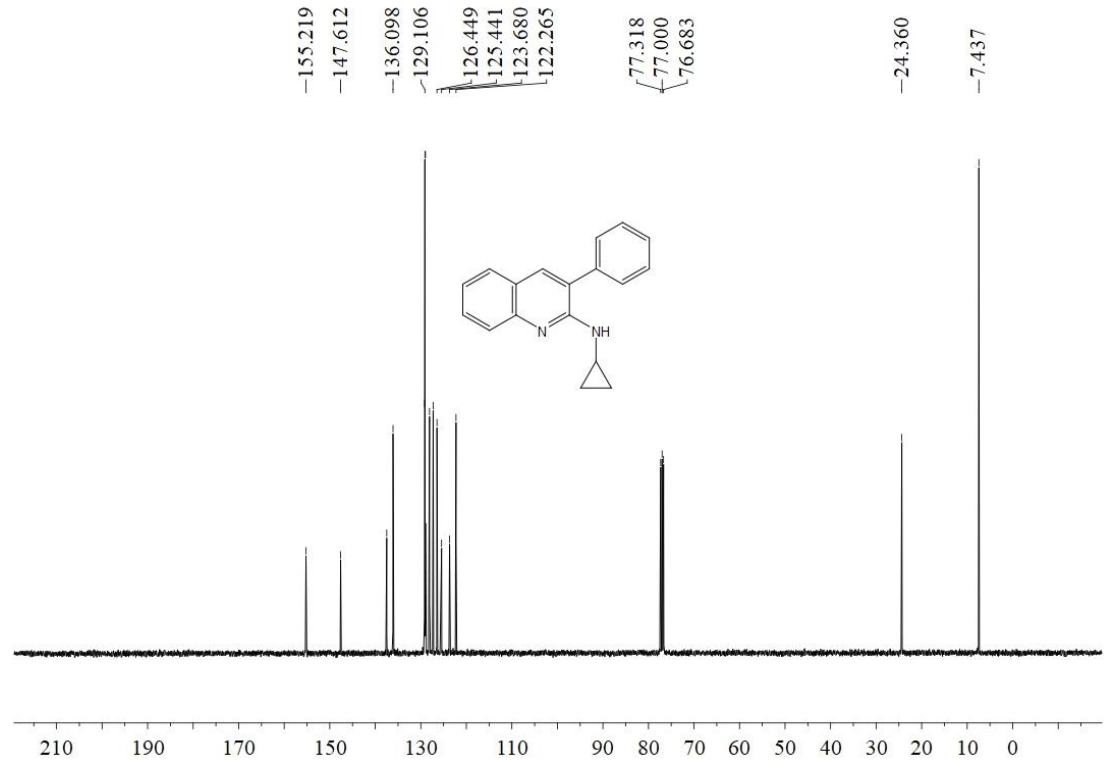


N-Cyclopropyl-3-phenylquinolin-2-amine (**4ay**)

^{1}H NMR (400 MHz, $CDCl_3$)

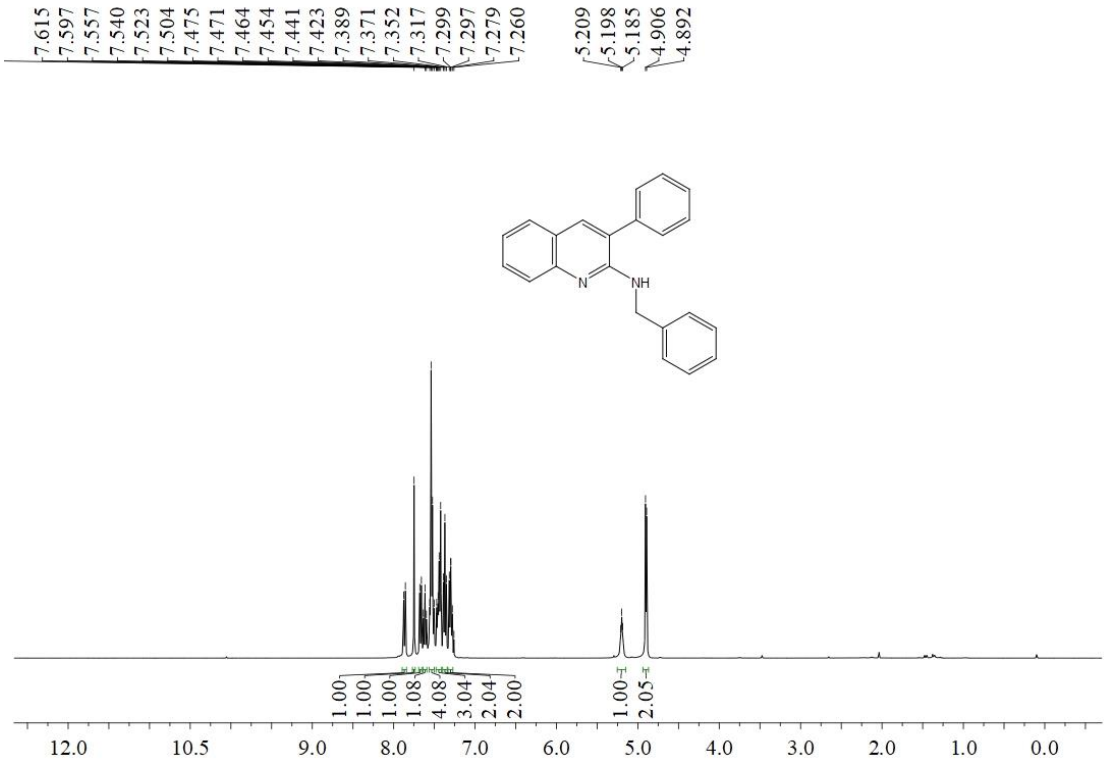


^{13}C NMR (100 MHz, $CDCl_3$)

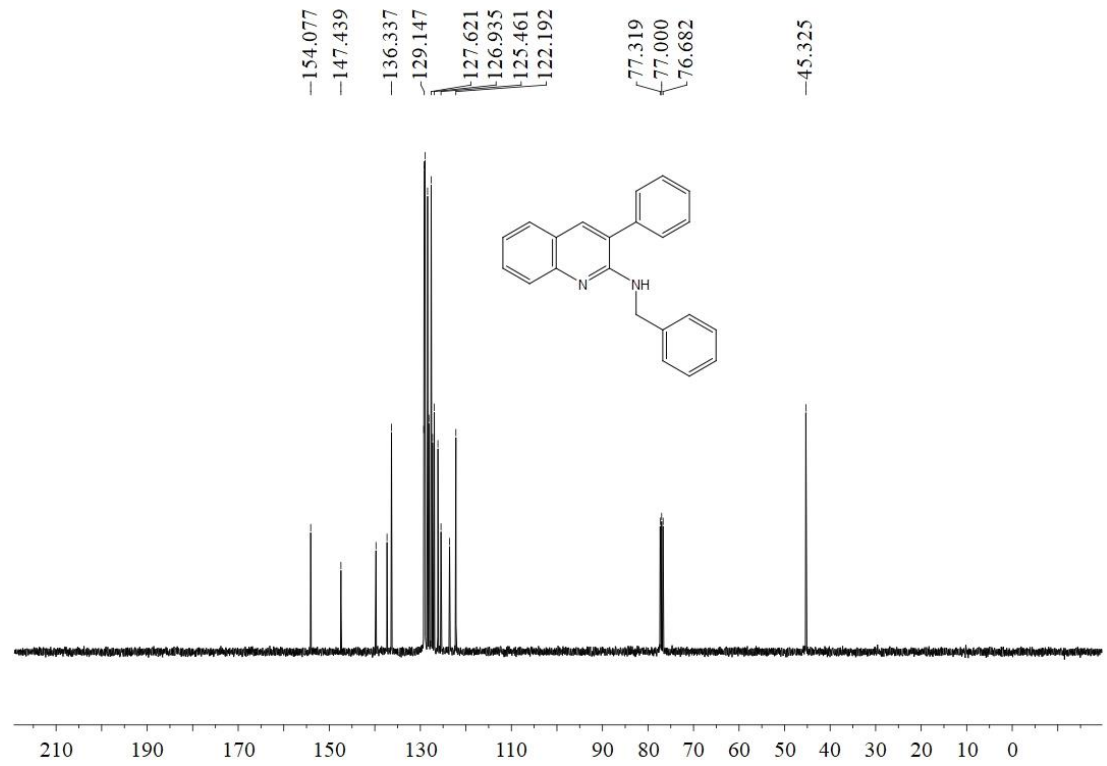


N-Benzyl-3-phenylquinolin-2-amine (**4az**)

^{1}H NMR (400 MHz, $CDCl_3$)

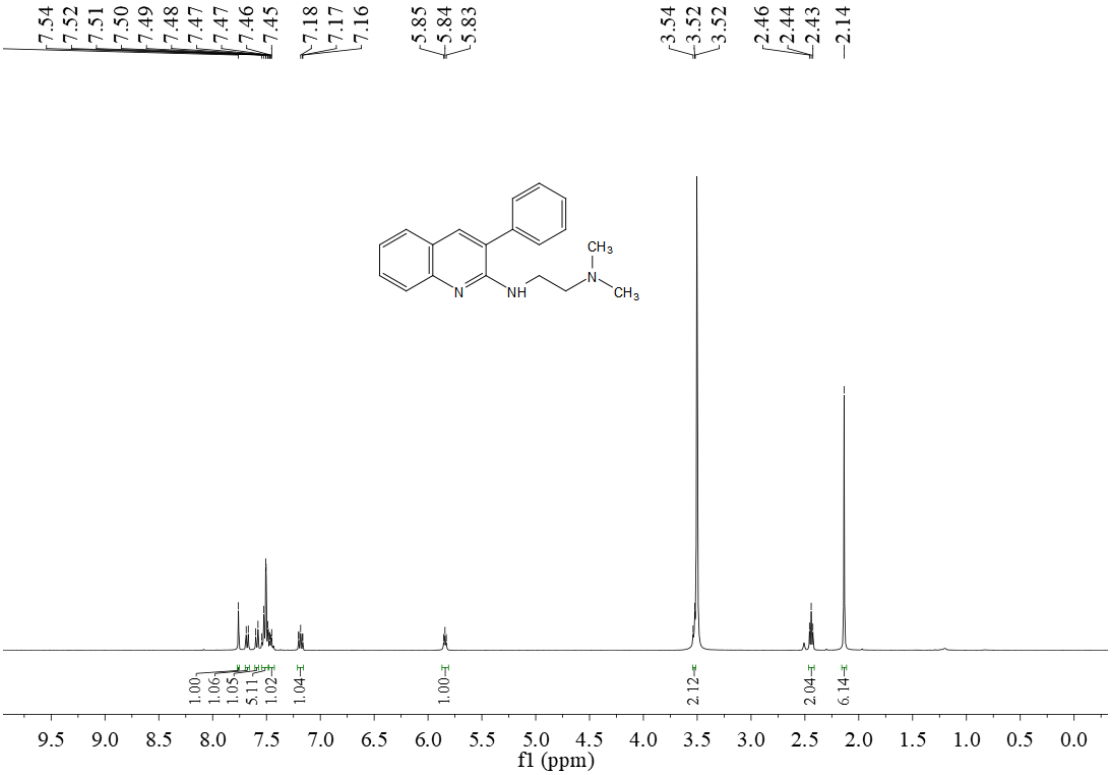


^{13}C NMR (100 MHz, $CDCl_3$)

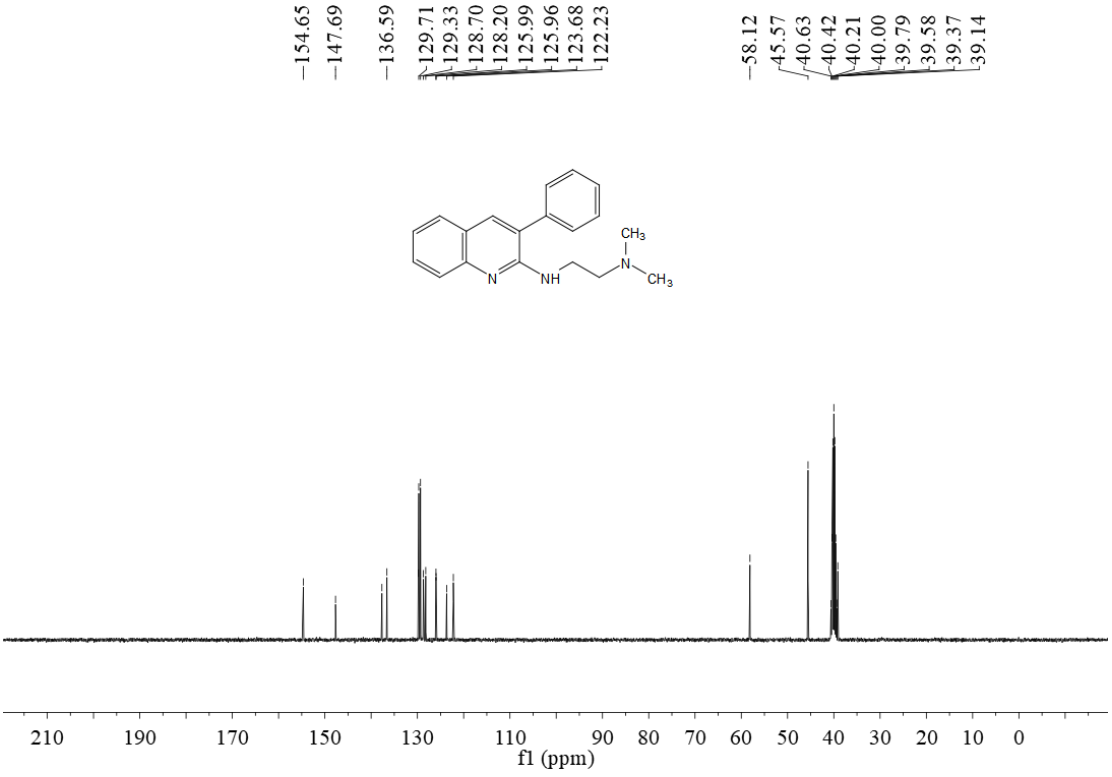


N^1,N^1-Dimethyl-N^2-(3-phenylquinolin-2-yl)ethane-1,2-diamine (**4ba**)

^{1}H NMR (400 MHz, DMSO-*D6*)

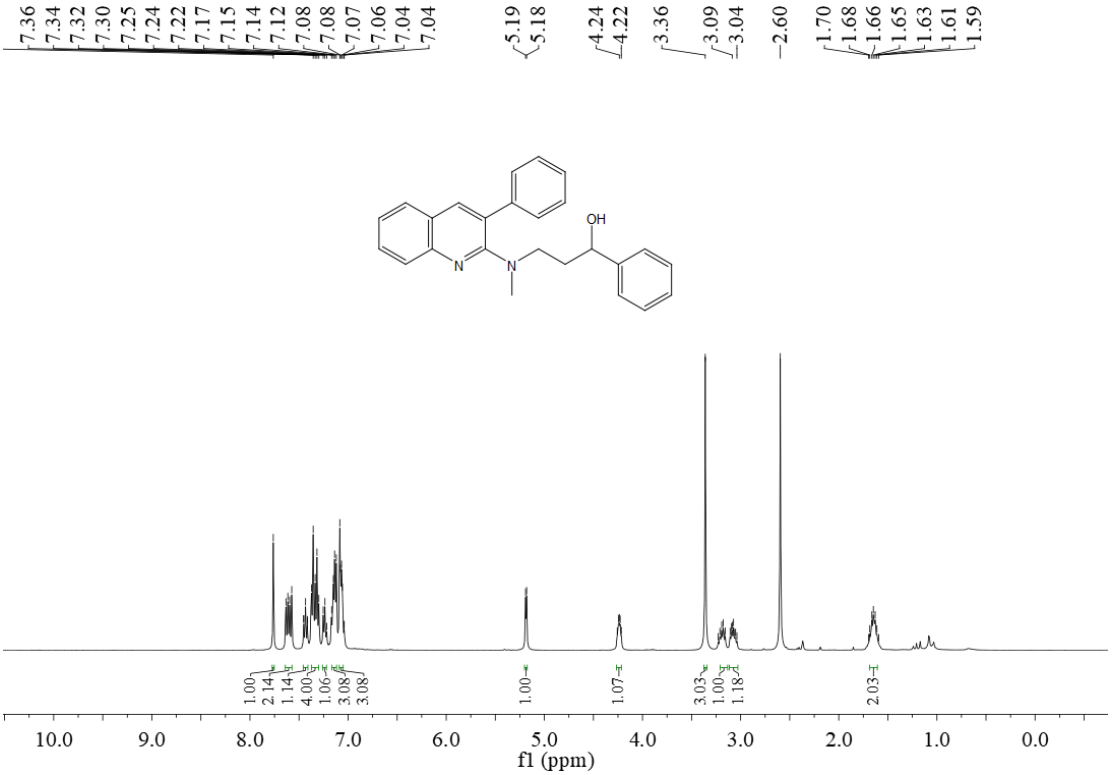


^{13}C NMR (100 MHz, DMSO-*D6*)

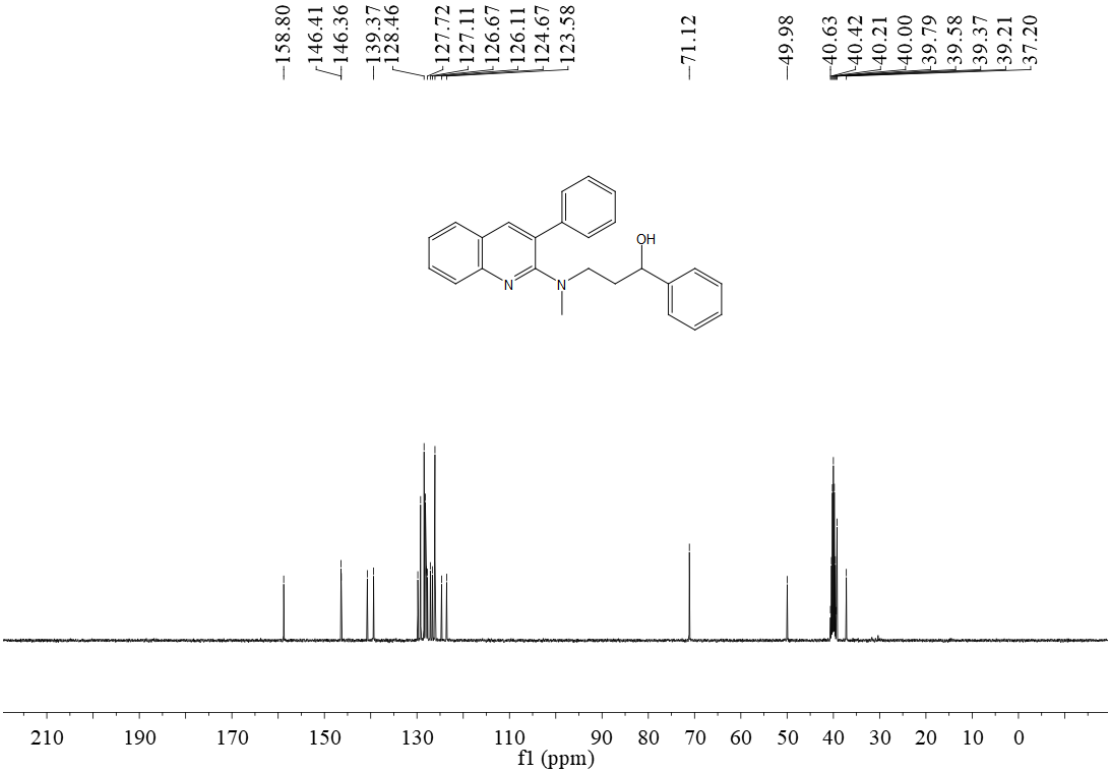


3-(Methyl(3-phenylquinolin-2-yl)amino)-1-phenylpropan-1-ol (**4bb**)

^{1}H NMR (400 MHz, DMSO-*D6*)

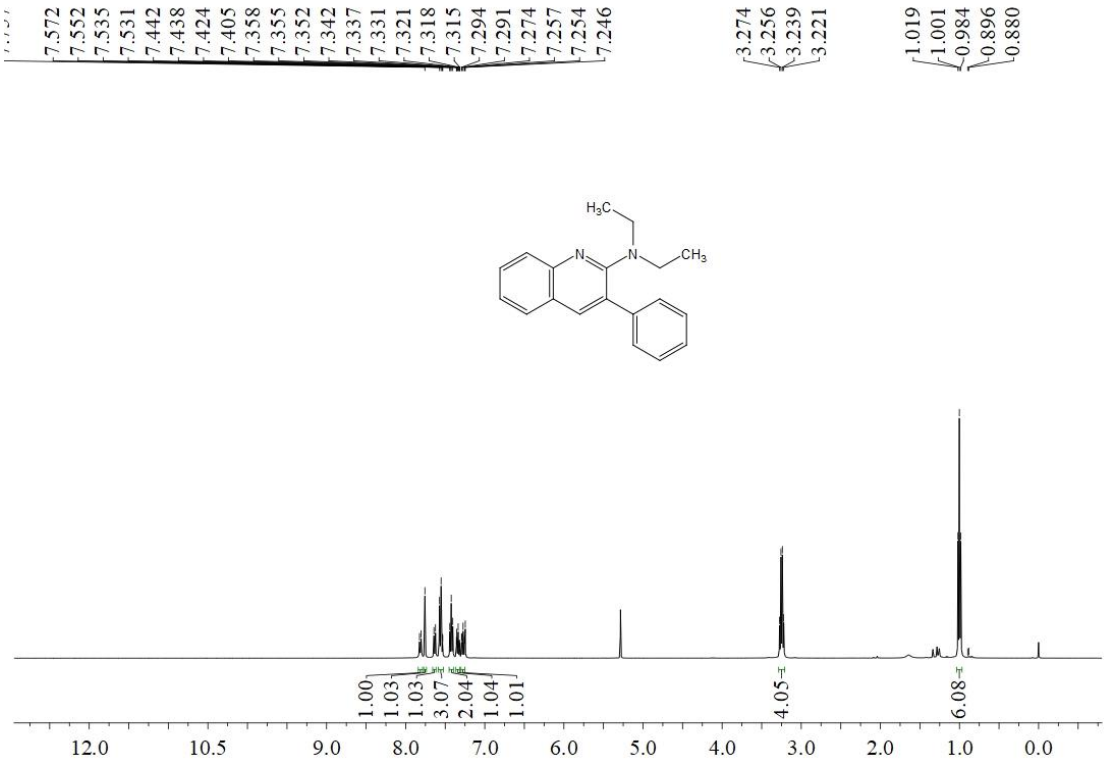


^{13}C NMR (100 MHz, DMSO-*D6*)

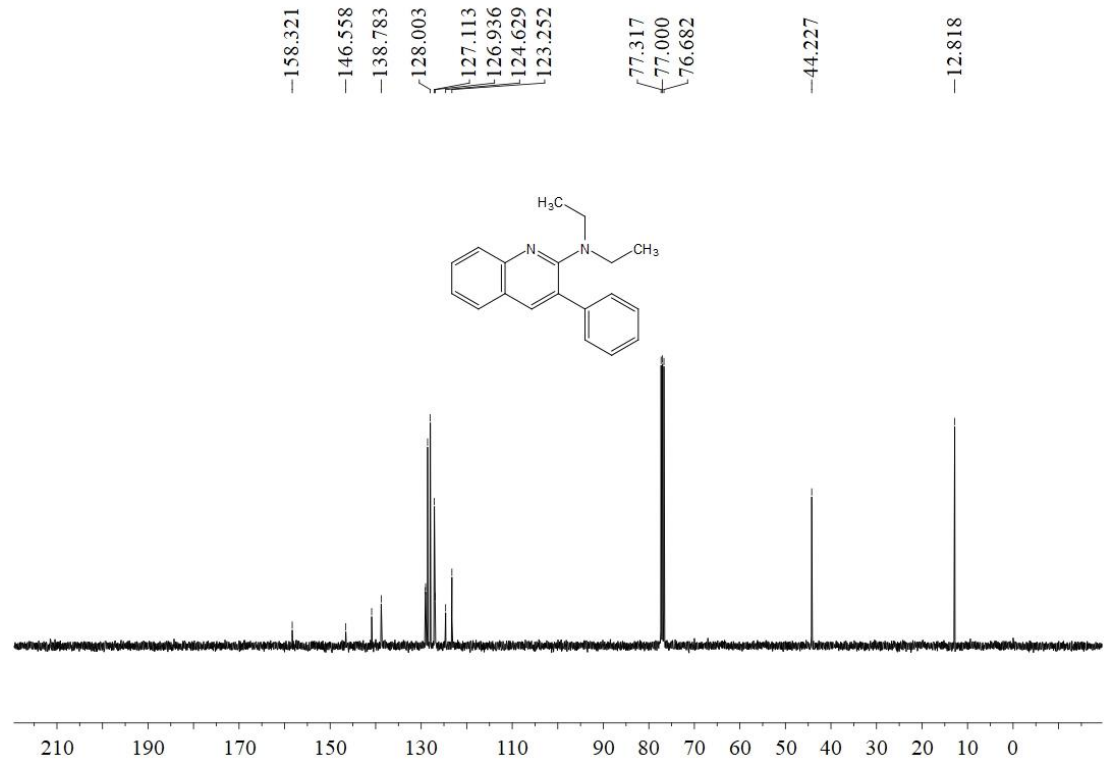


N,*N*-Diethyl-3-phenylquinolin-2-amine (**4bc**)

^{1}H NMR (400 MHz, $CDCl_3$)

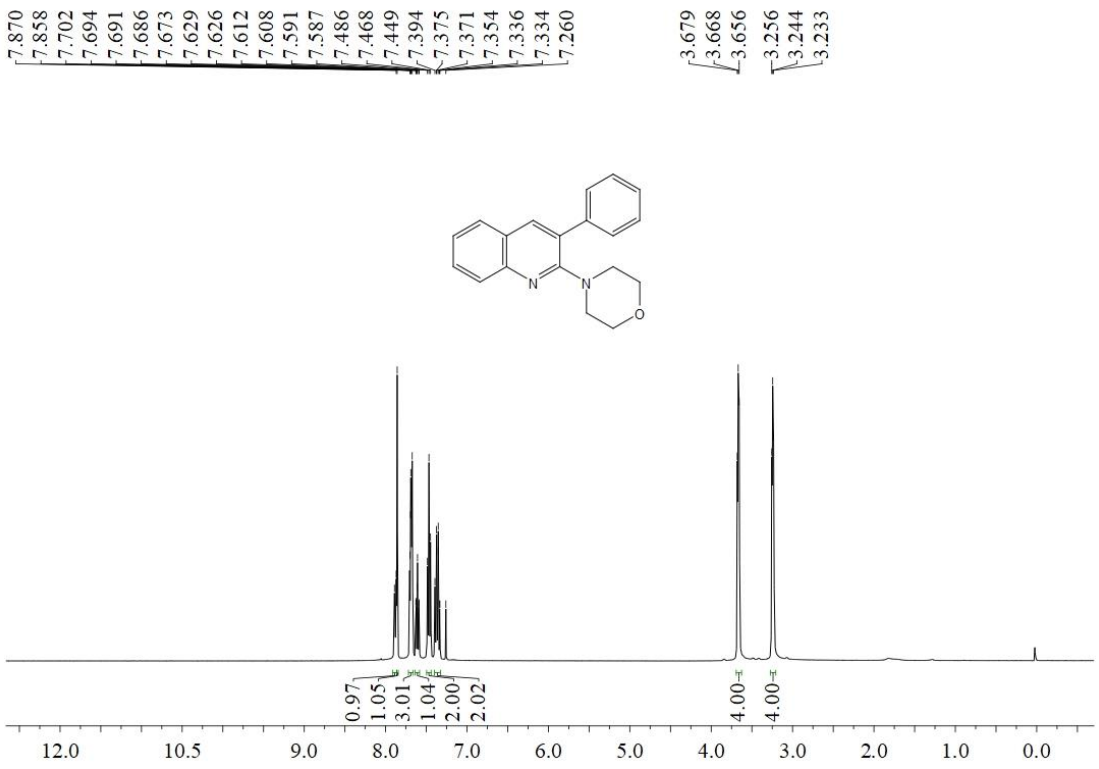


^{13}C NMR (100 MHz, $CDCl_3$)

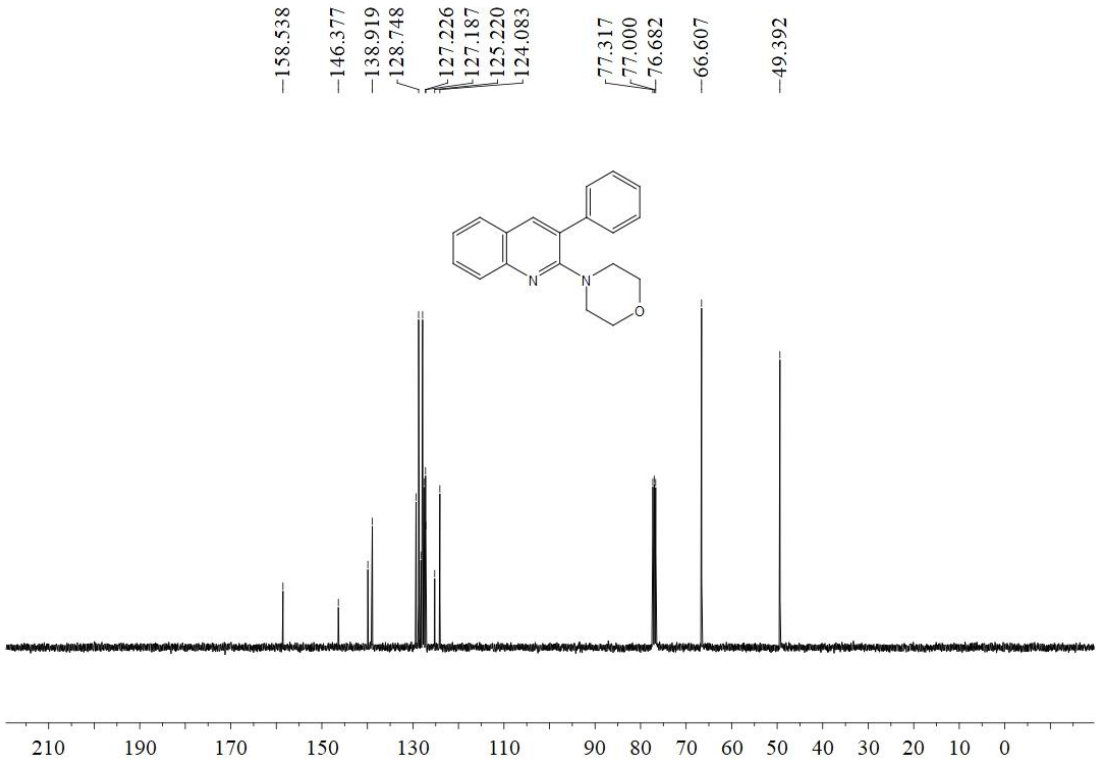


4-(3-Phenylquinolin-2-yl)morpholine (**4bd**)

^{1}H NMR (400 MHz, $CDCl_3$)

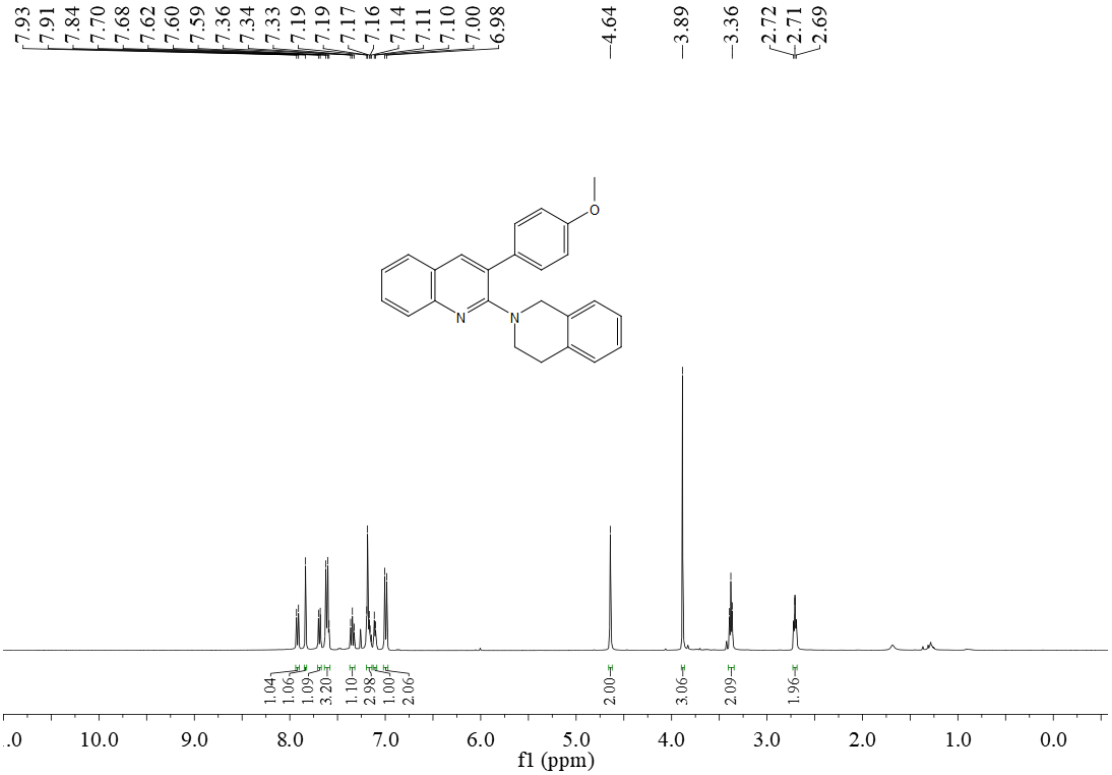


^{13}C NMR (100 MHz, $CDCl_3$)

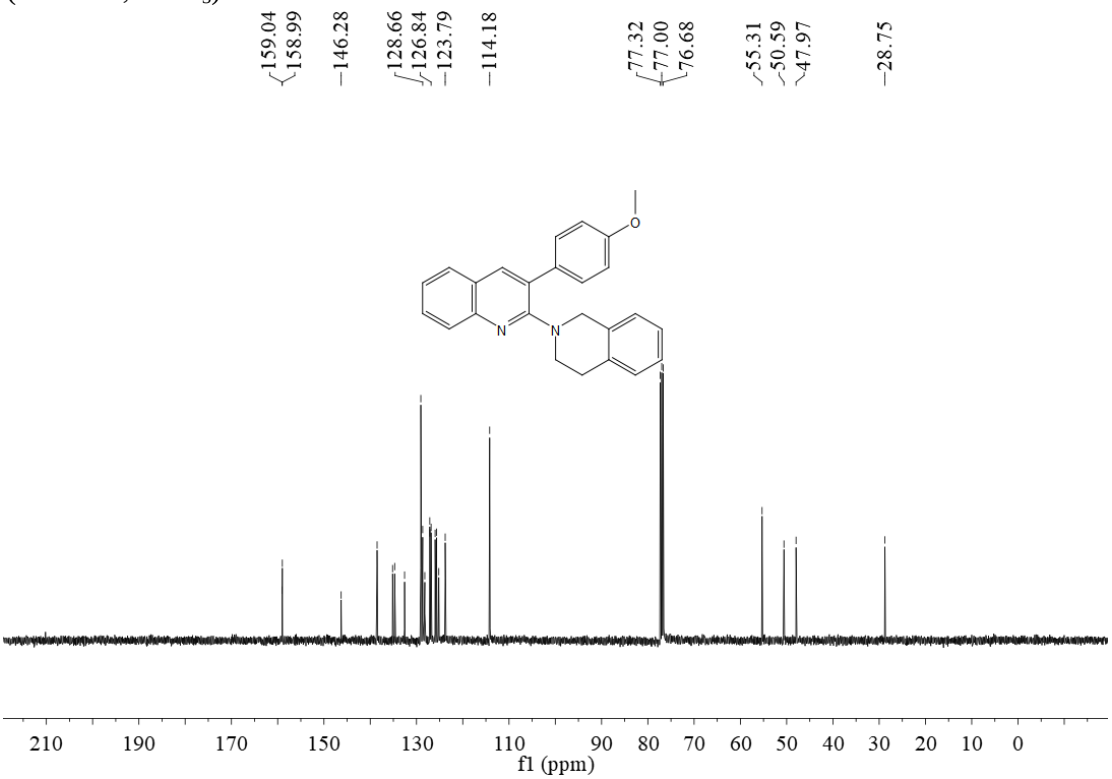


2-(3,4-Dihydroisoquinolin-2(1H)-yl)-3-(4-methoxyphenyl)quinolone (**4be**)

^{1}H NMR (400 MHz, $CDCl_3$)

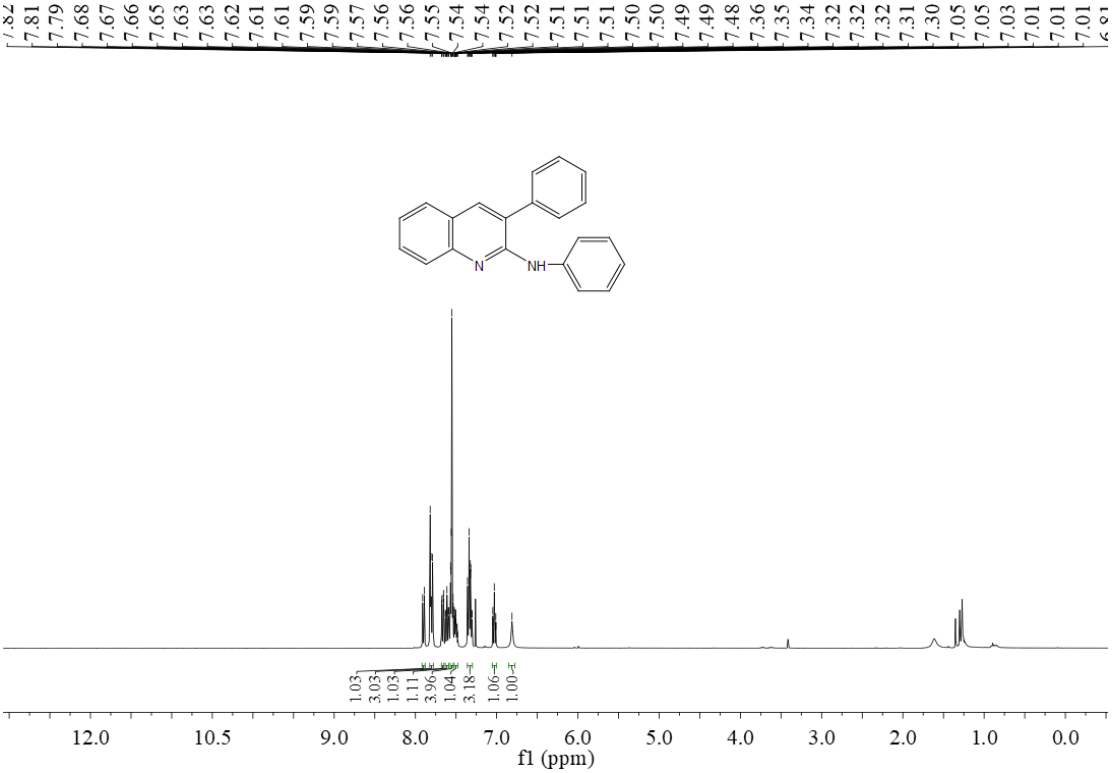


^{13}C NMR (100 MHz, $CDCl_3$)

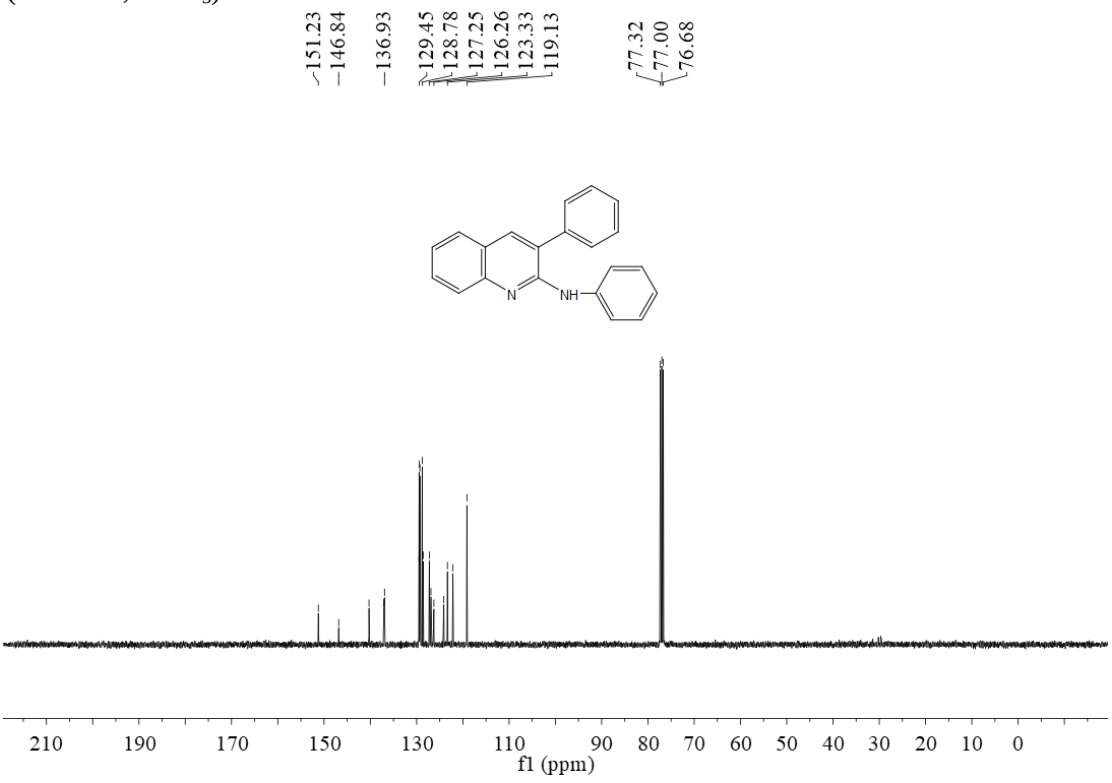


N,3-diphenylquinolin-2-amine (**4bf**)

^{1}H NMR (400 MHz, $CDCl_3$)

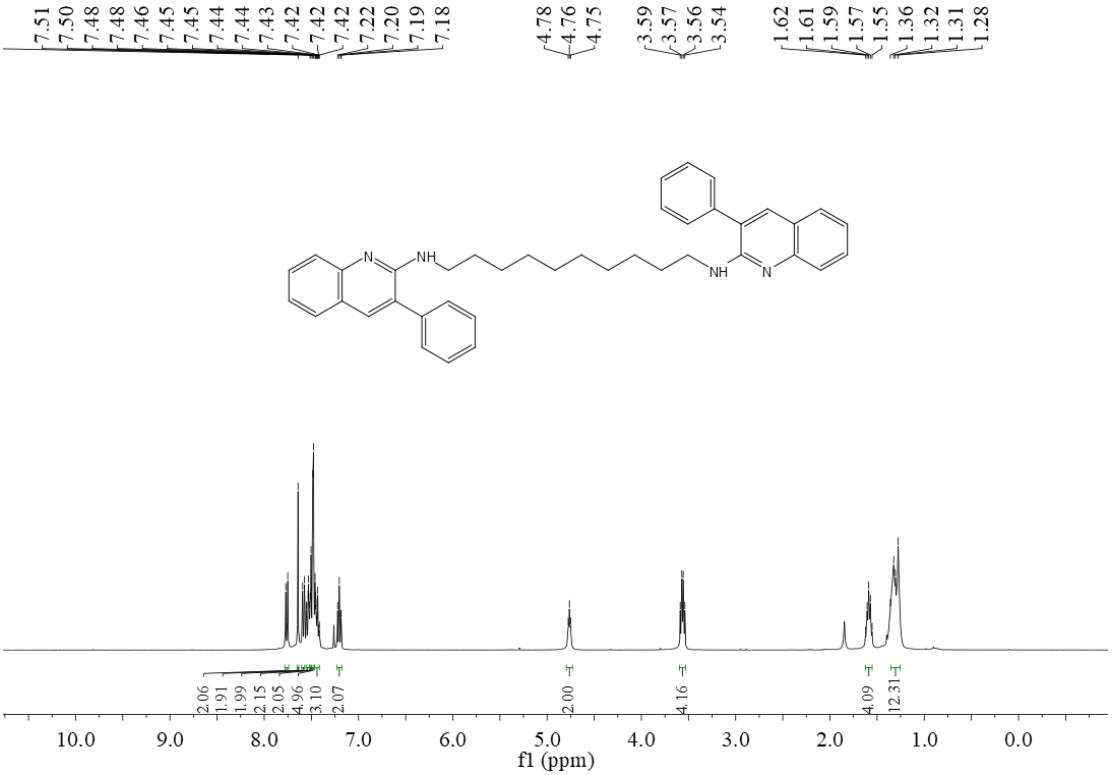


^{13}C NMR (100 MHz, $CDCl_3$)

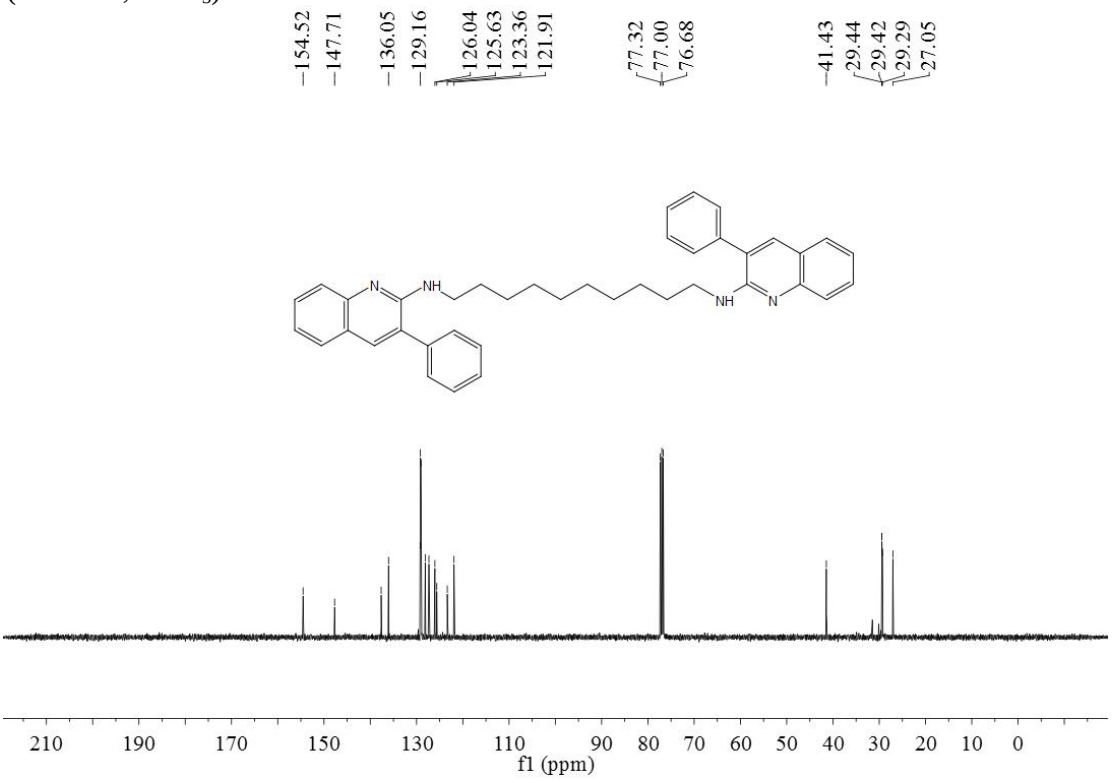


N[1],*N*[10]-*bis*(3-Phenylquinolin-2-yl)decane-1,10-diamine (**4bg**)

^{1}H NMR (400 MHz, $CDCl_3$)

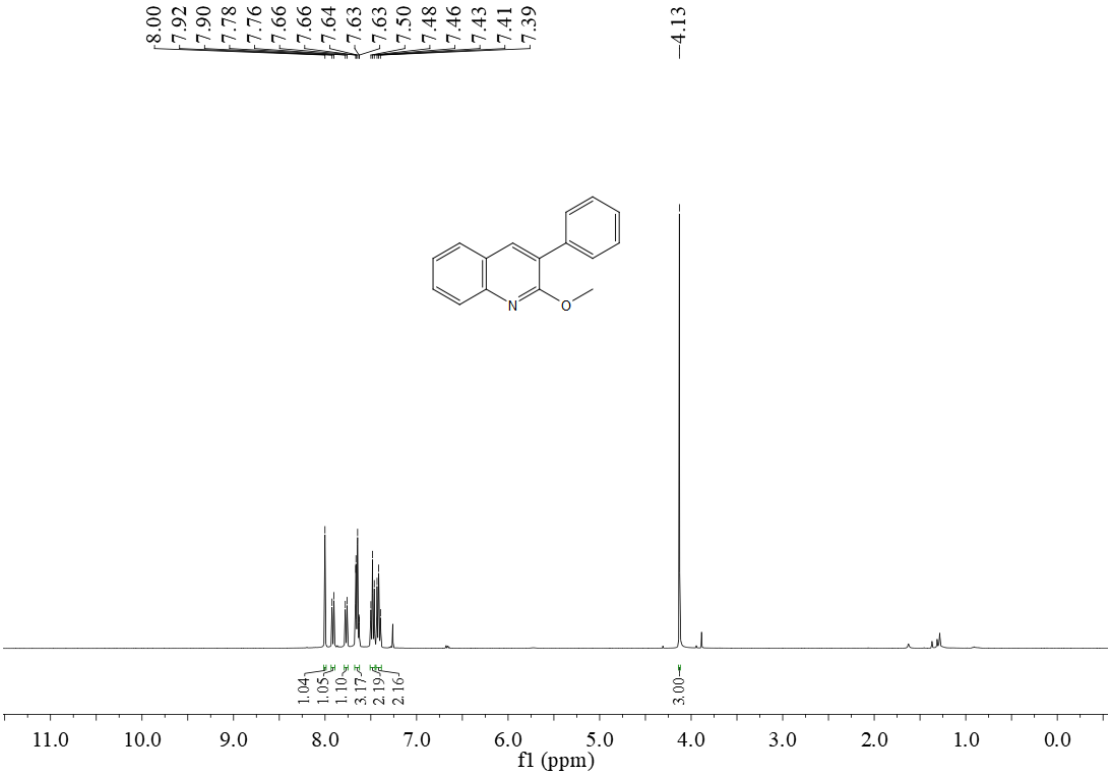


^{13}C NMR (100 MHz, $CDCl_3$)

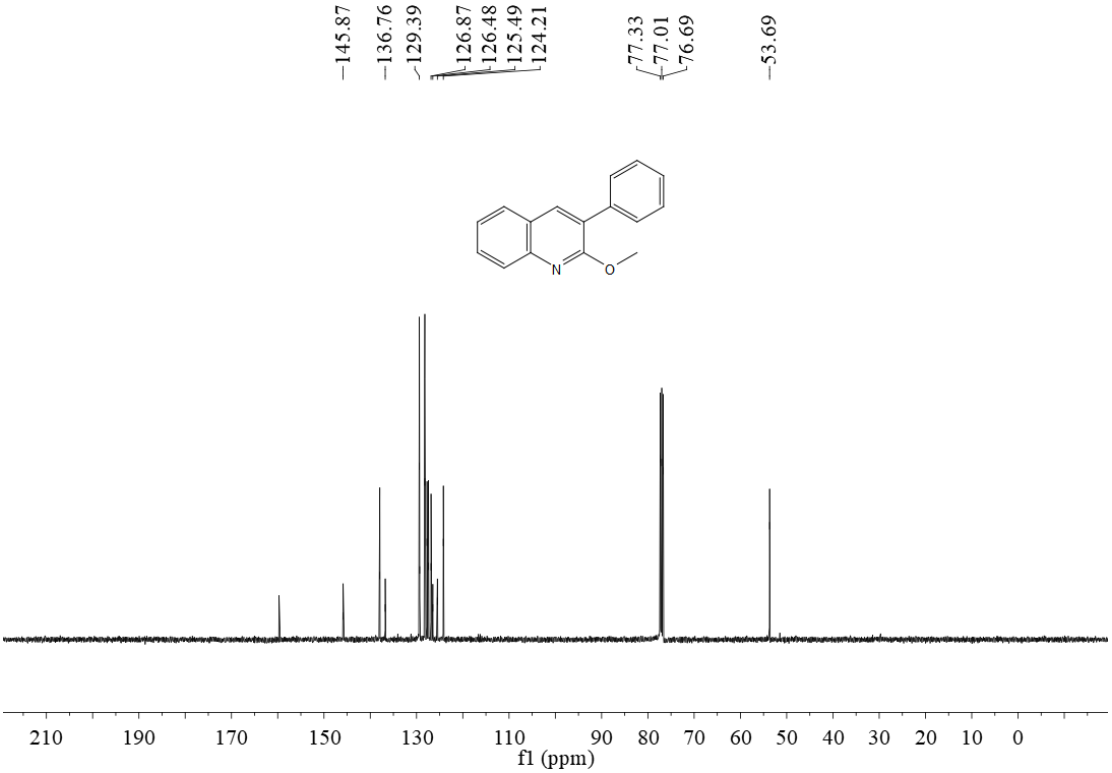


2-Methoxy-3-phenylquinoline (**4bh**)

^{1}H NMR (400 MHz, $CDCl_3$)

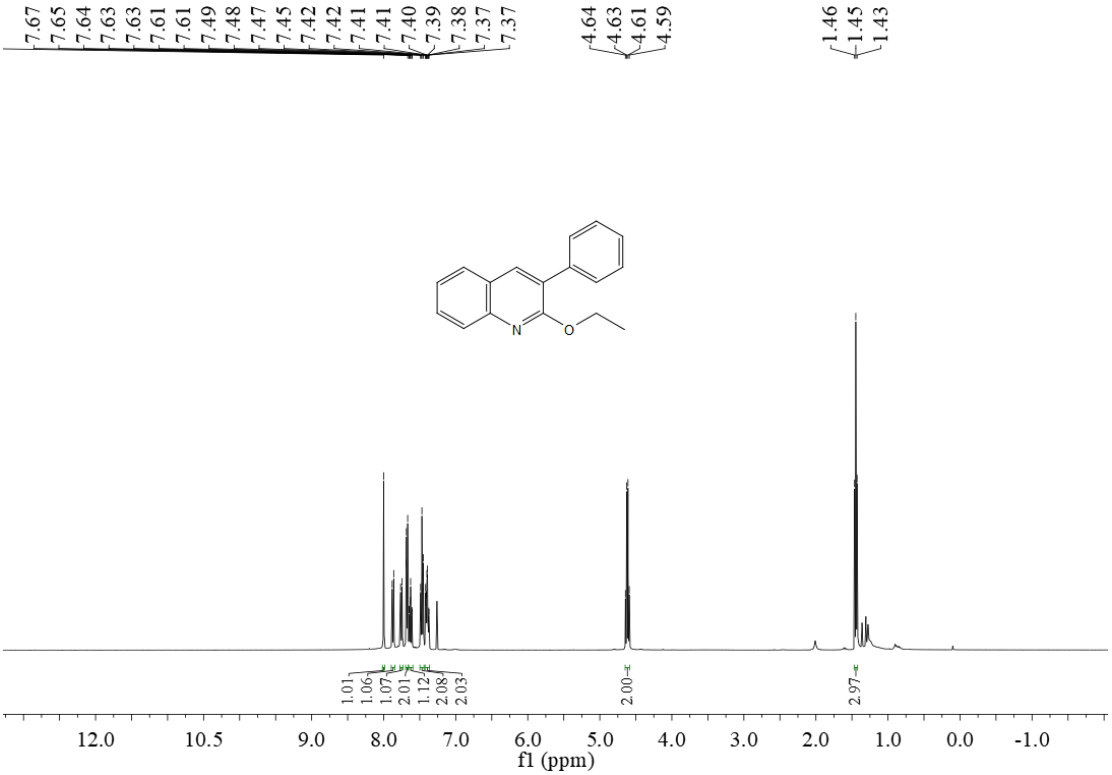


^{13}C NMR (100 MHz, $CDCl_3$)

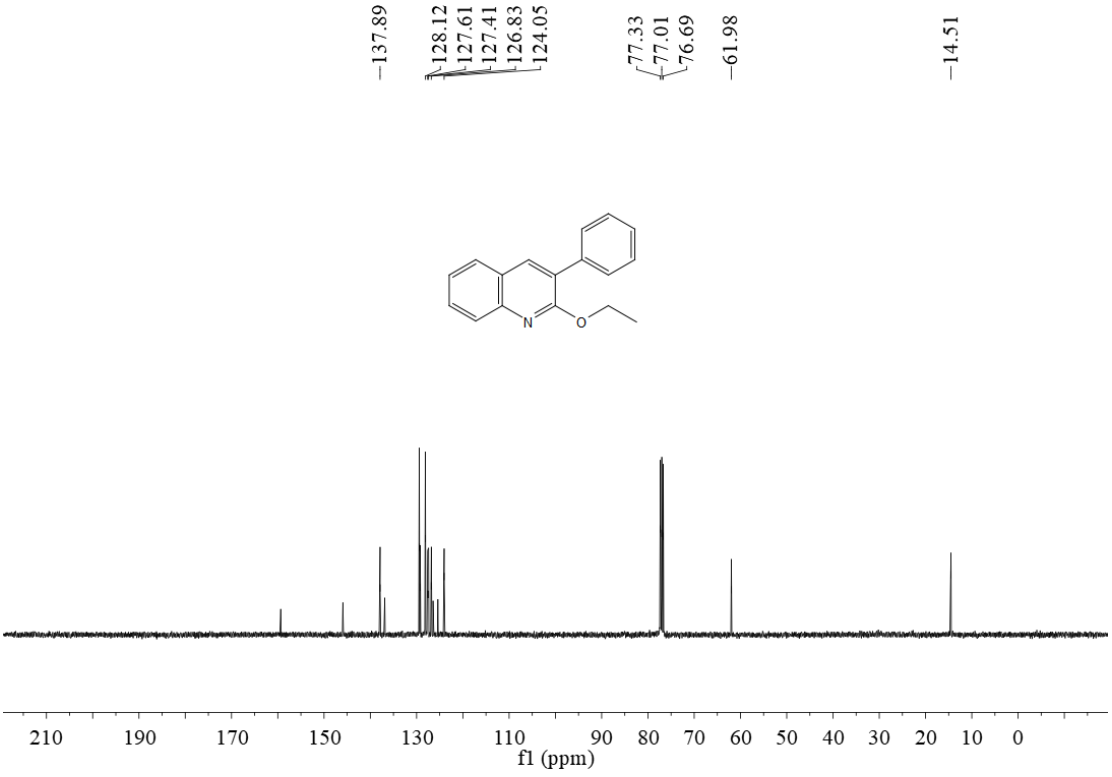


2-Ethoxy-3-phenylquinoline (**4bi**)

^{1}H NMR (400 MHz, $CDCl_3$)

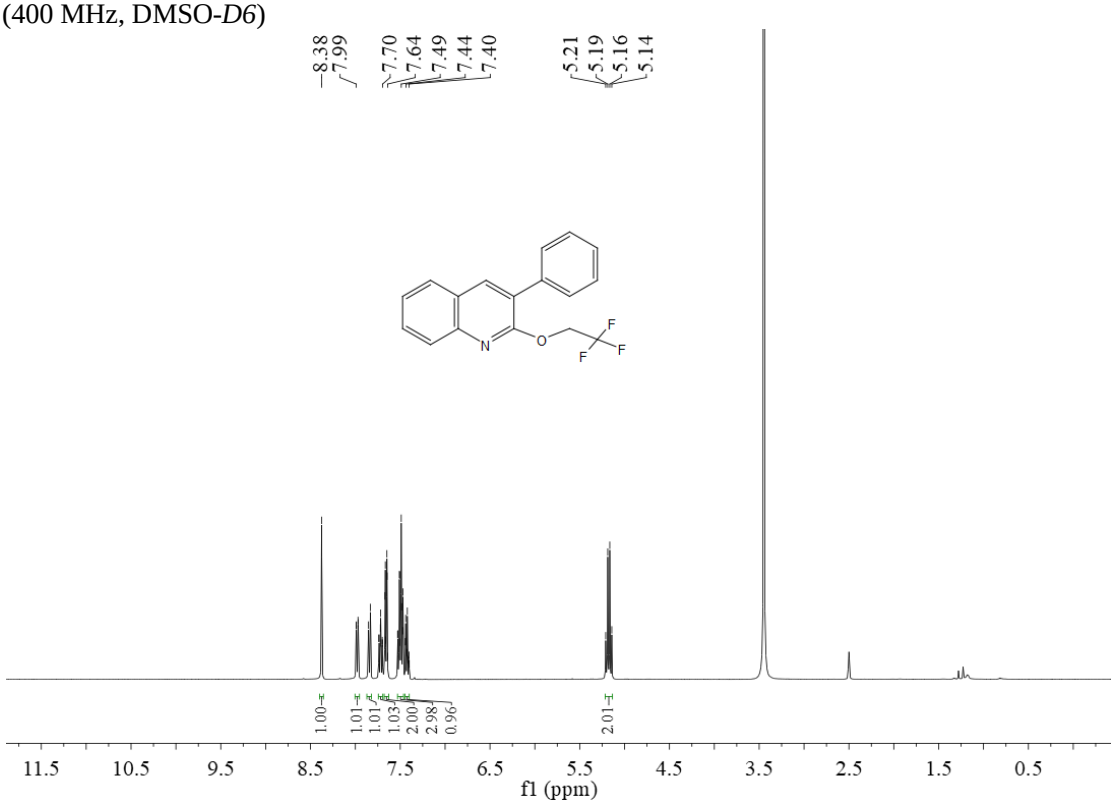


^{13}C NMR (100 MHz, $CDCl_3$)

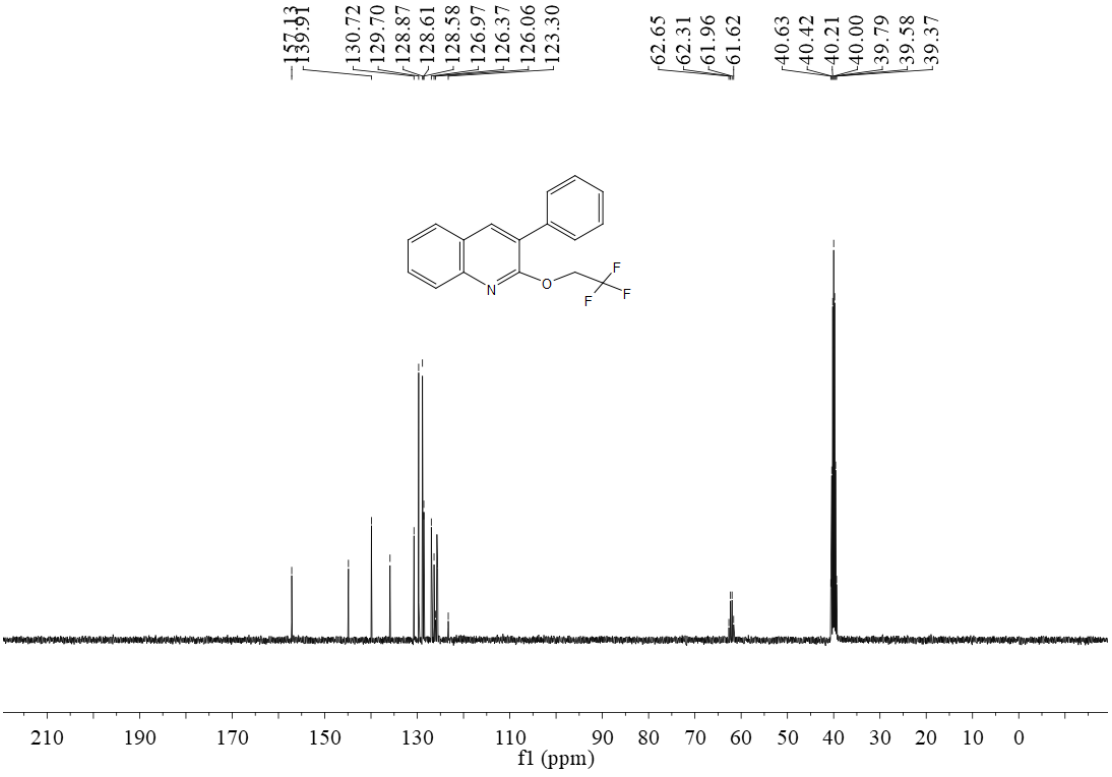


3-phenyl-2-(2,2,2-trifluoroethoxy)quinolone (**4bj**)

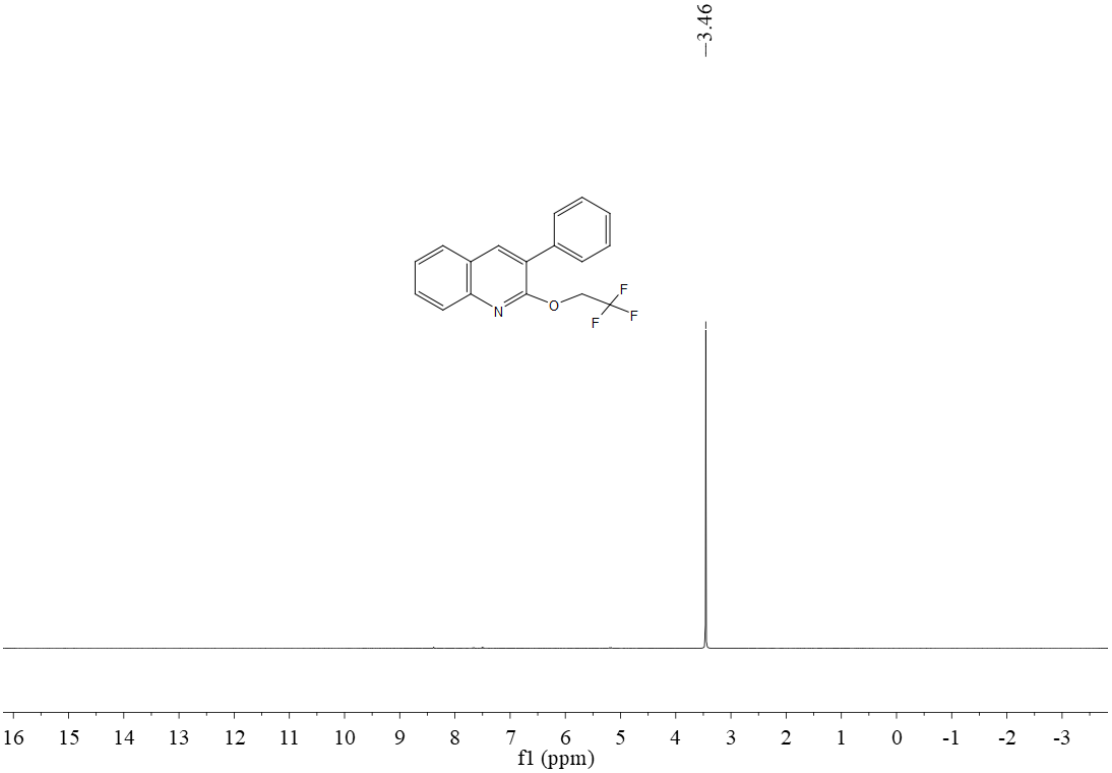
^{1}H NMR (400 MHz, DMSO-*D6*)



^{13}C NMR (101 MHz, DMSO-*D6*)

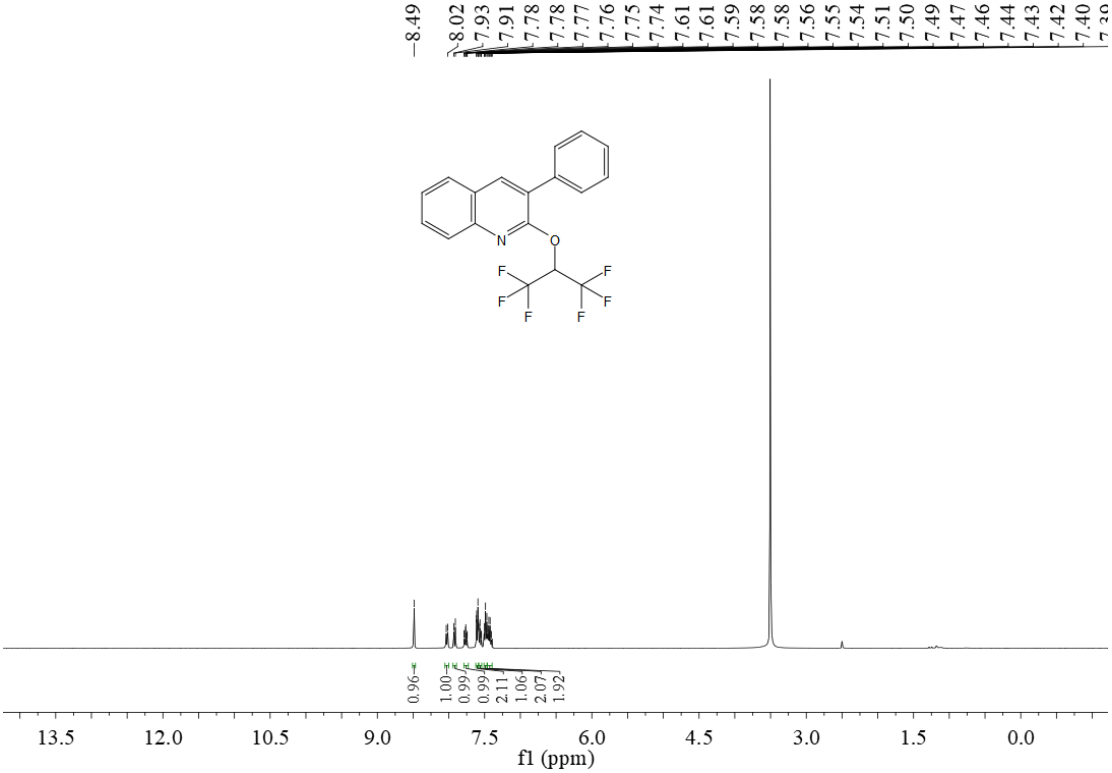


^{19}F NMR (400 MHz, DMSO-*D6*)

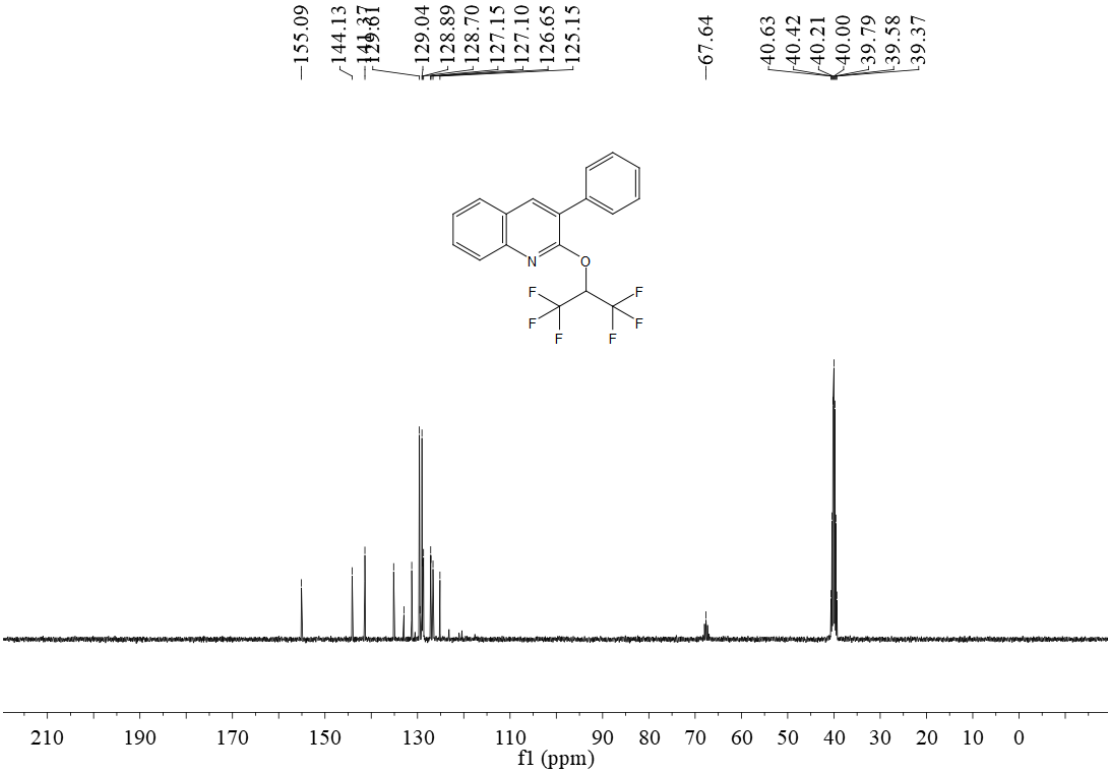


2-((1,1,1,3,3,3-Hexafluoropropan-2-yl)oxy)-3-phenylquinoline (**4bk**)

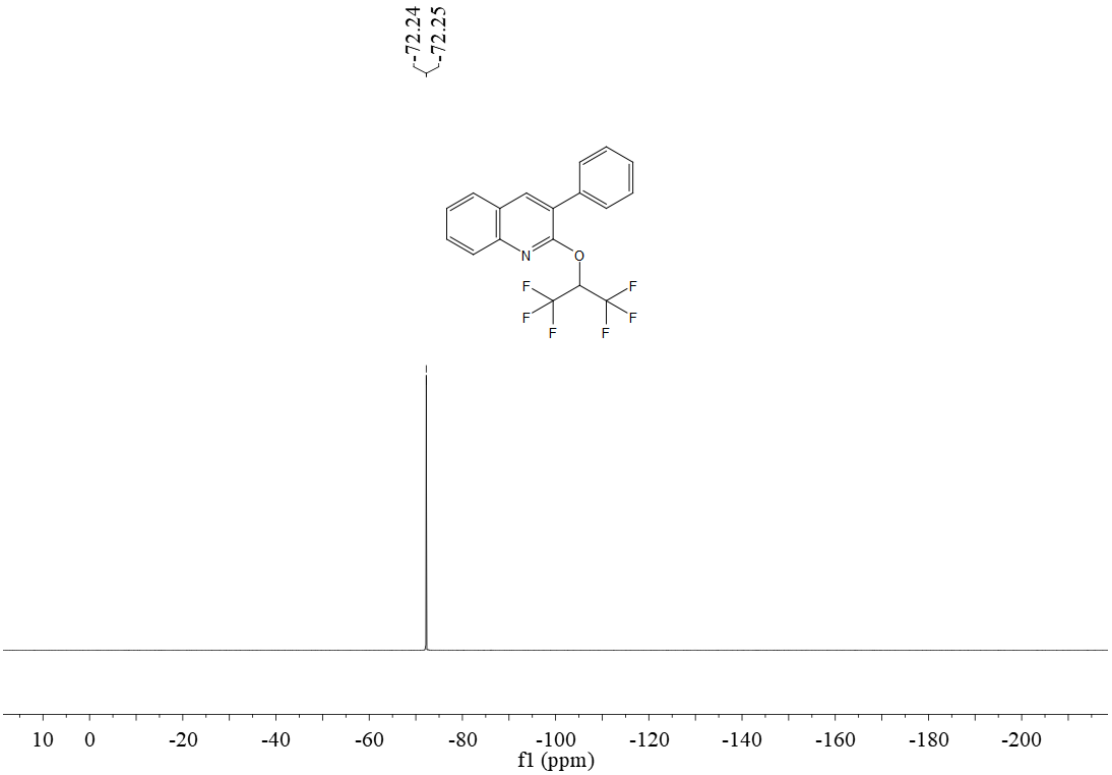
^{1}H NMR (400 MHz, DMSO-*D6*)



^{13}C NMR (100 MHz, DMSO-*D6*)

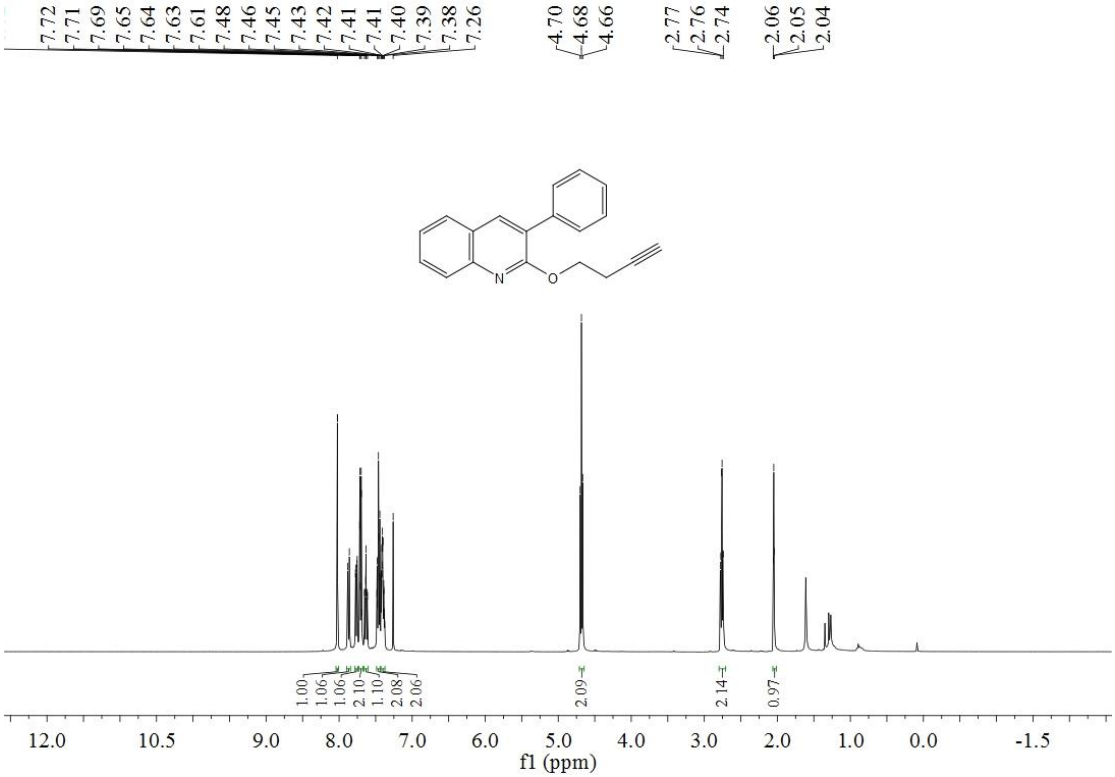


^{19}F NMR (375 MHz, DMSO-*D6*)

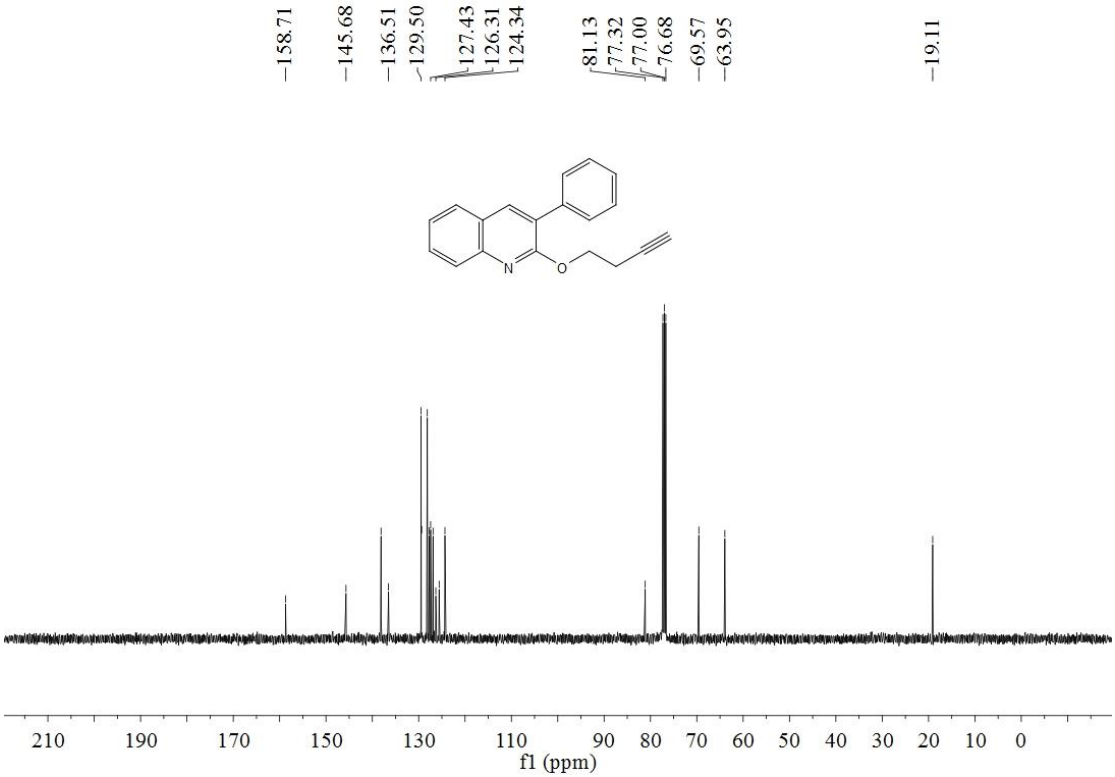


2-(But-3-yn-1-yloxy)-3-phenylquinoline (**4bl**)

^{1}H NMR (400 MHz, $CDCl_3$)

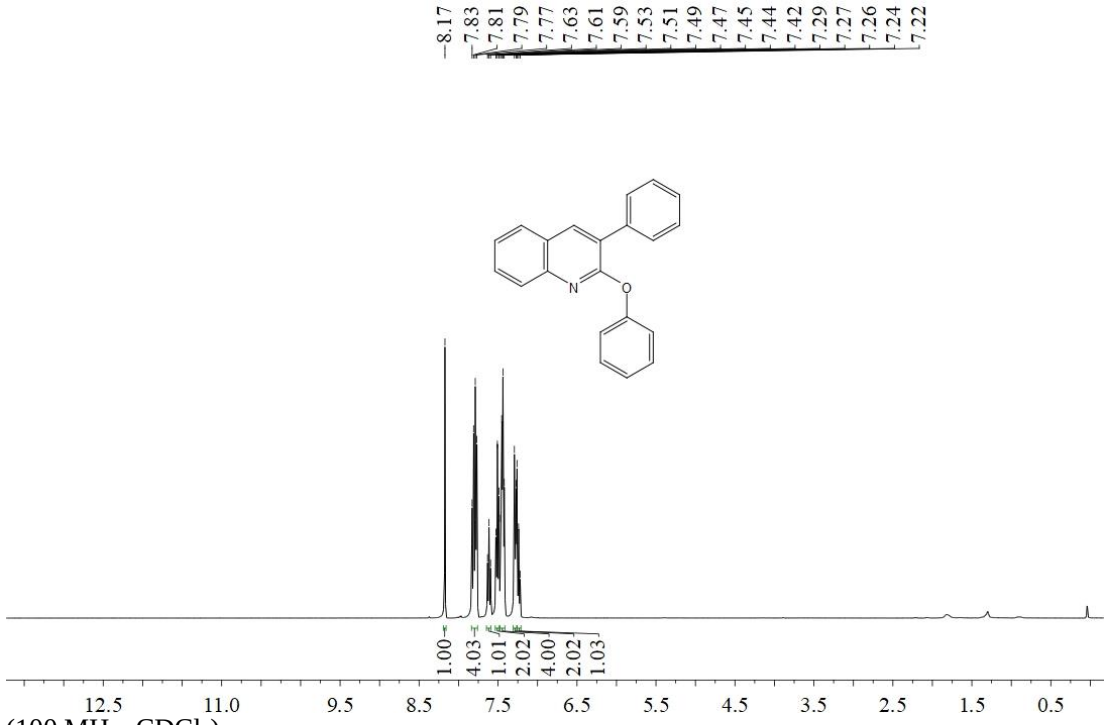


^{13}C NMR (100 MHz, $CDCl_3$)

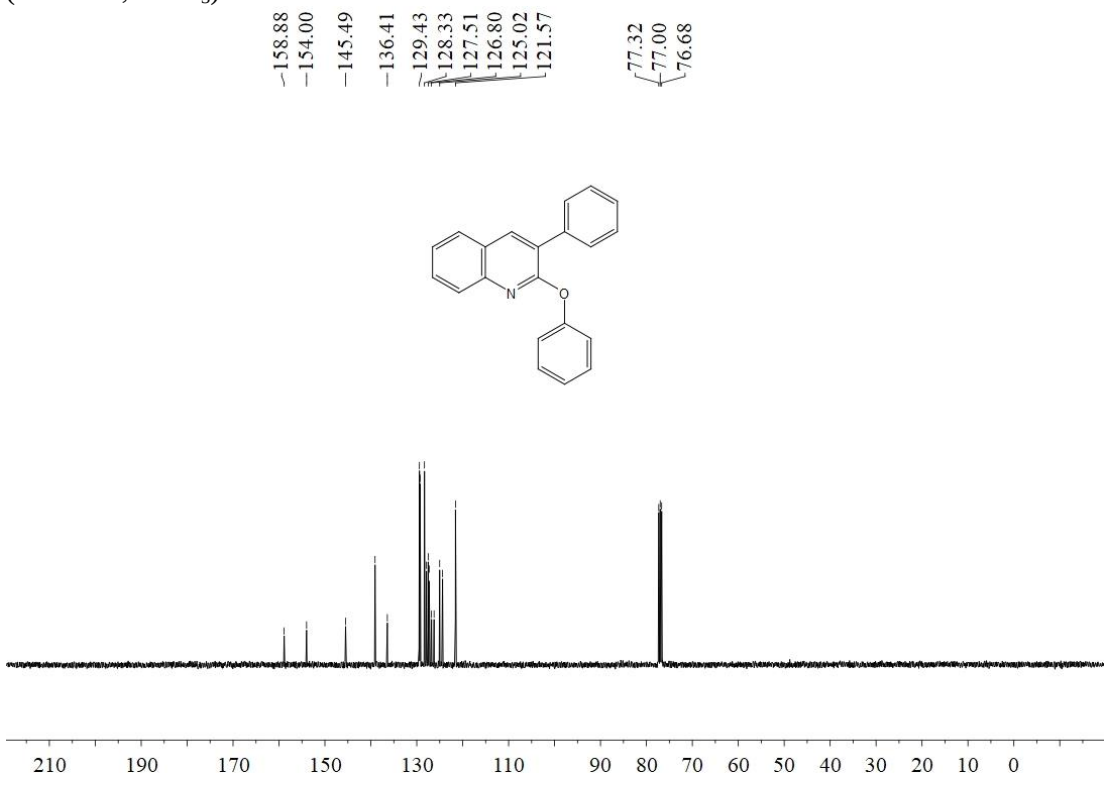


2-Phenoxy-3-phenylquinoline (**4bm**)

^{1}H NMR (400 MHz, $CDCl_3$)

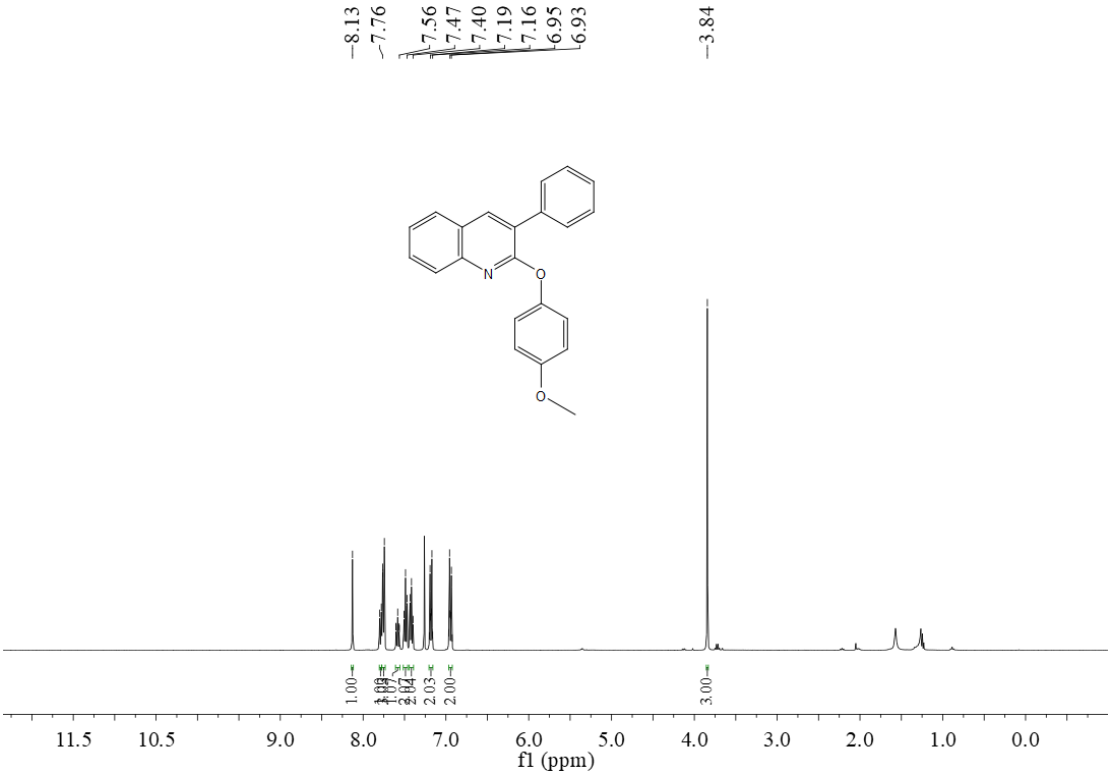


^{13}C NMR (100 MHz, $CDCl_3$)

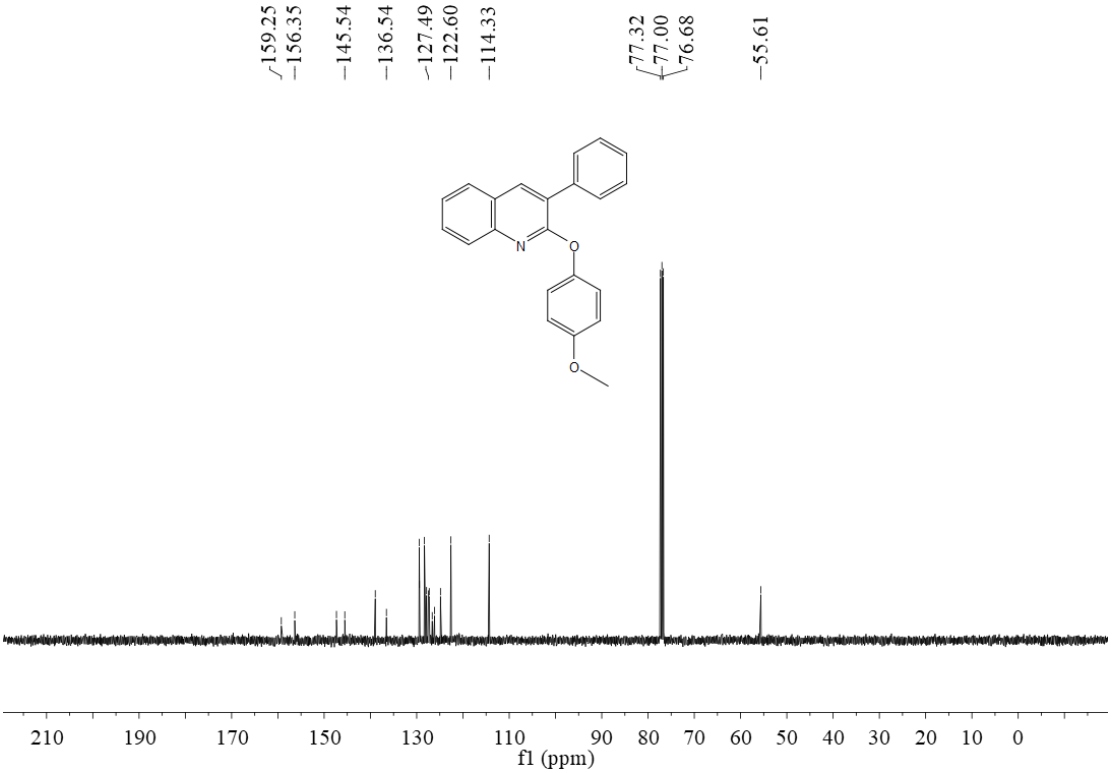


2-(4-Methoxyphenoxy)-3-phenylquinoline (**4bn**)

^{1}H NMR (400 MHz, $CDCl_3$)

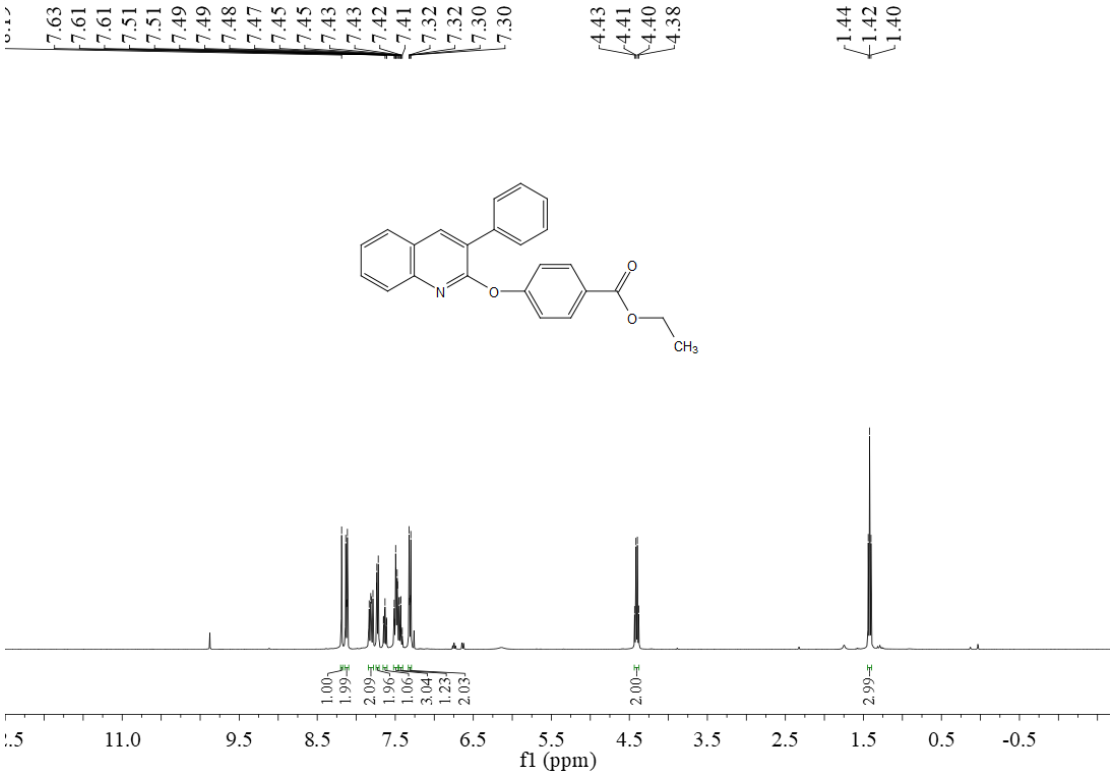


^{13}C NMR (101 MHz, $CDCl_3$)

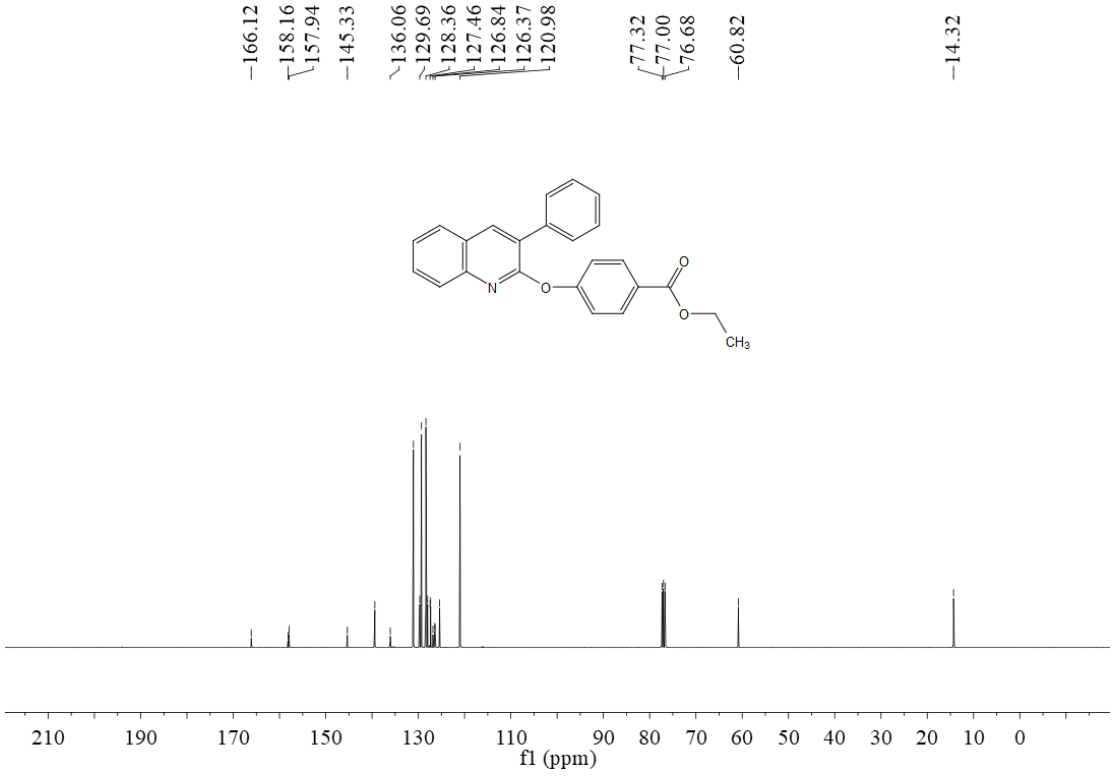


Ethyl 4-((3-phenylquinolin-2-yl)oxy)benzoate (**4bo**)

^{1}H NMR (400 MHz, $CDCl_3$)

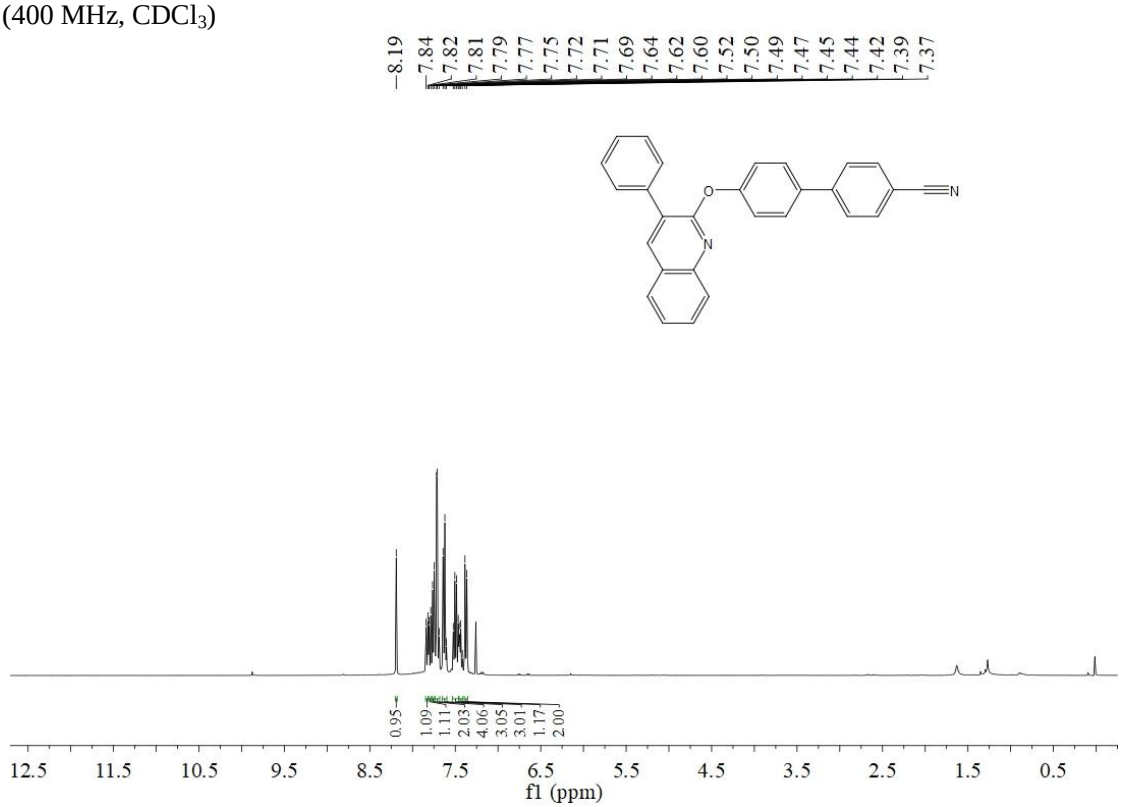


^{13}C NMR (100 MHz, $CDCl_3$)

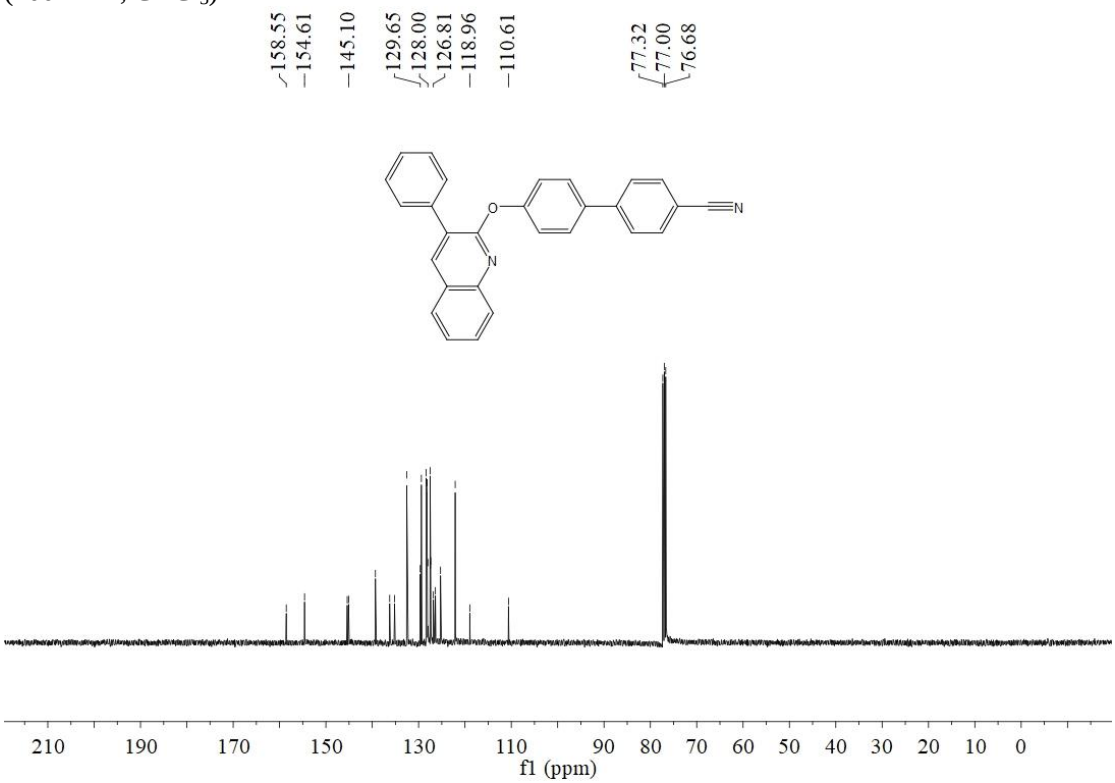


4'-((3-Phenylquinolin-2-yl)oxy)-[1,1'-biphenyl]-4-carbonitrile (**4bp**)

^{1}H NMR (400 MHz, $CDCl_3$)

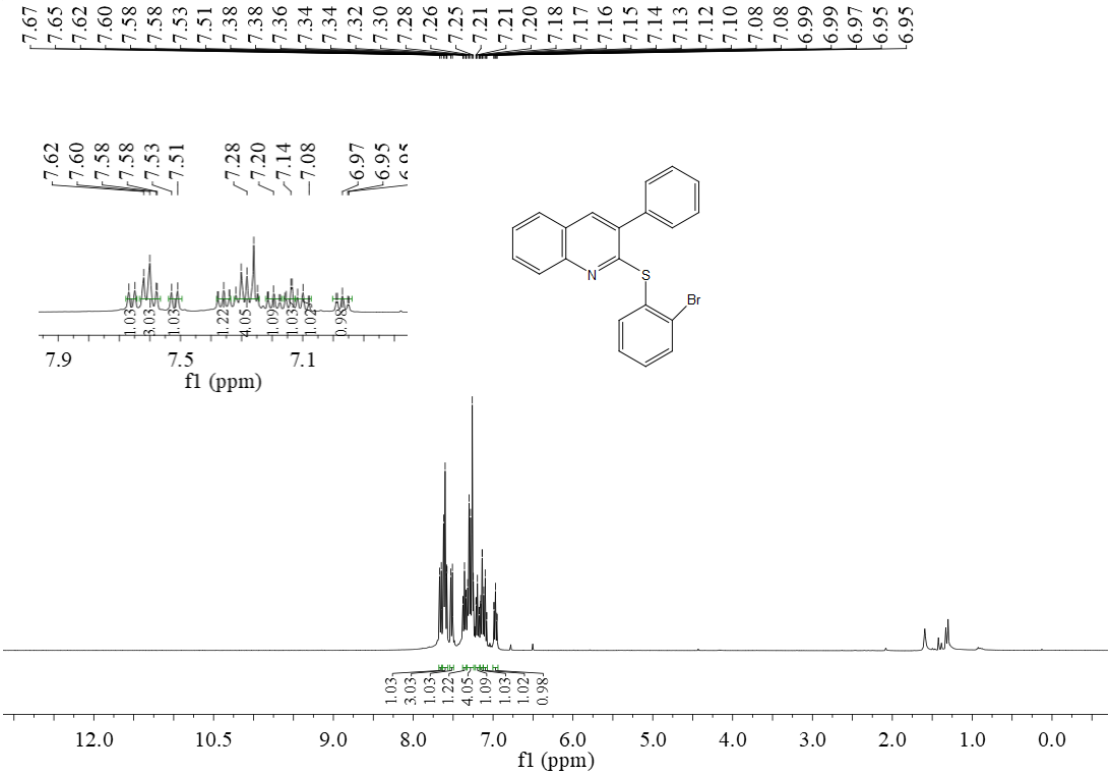


^{13}C NMR (100 MHz, $CDCl_3$)

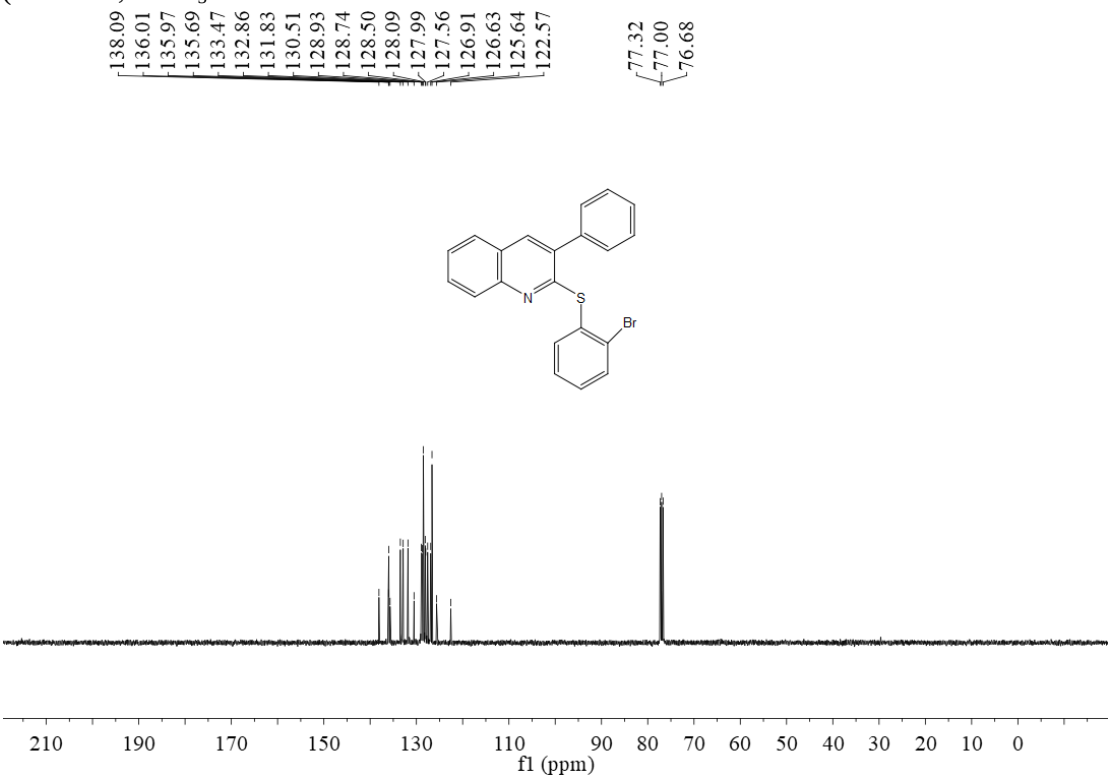


2-((2-Bromophenyl)thio)-3-phenylquinoline (**4bq**)

^{1}H NMR (400 MHz, $CDCl_3$)

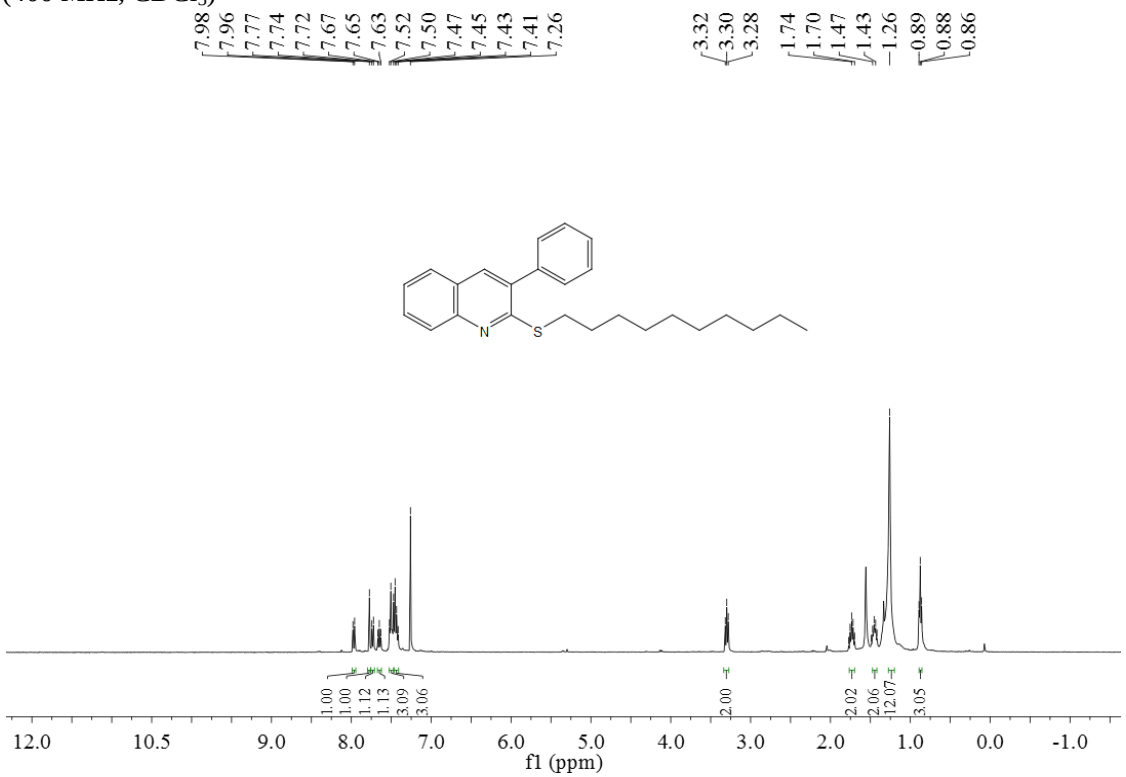


^{13}C NMR (100 MHz, $CDCl_3$

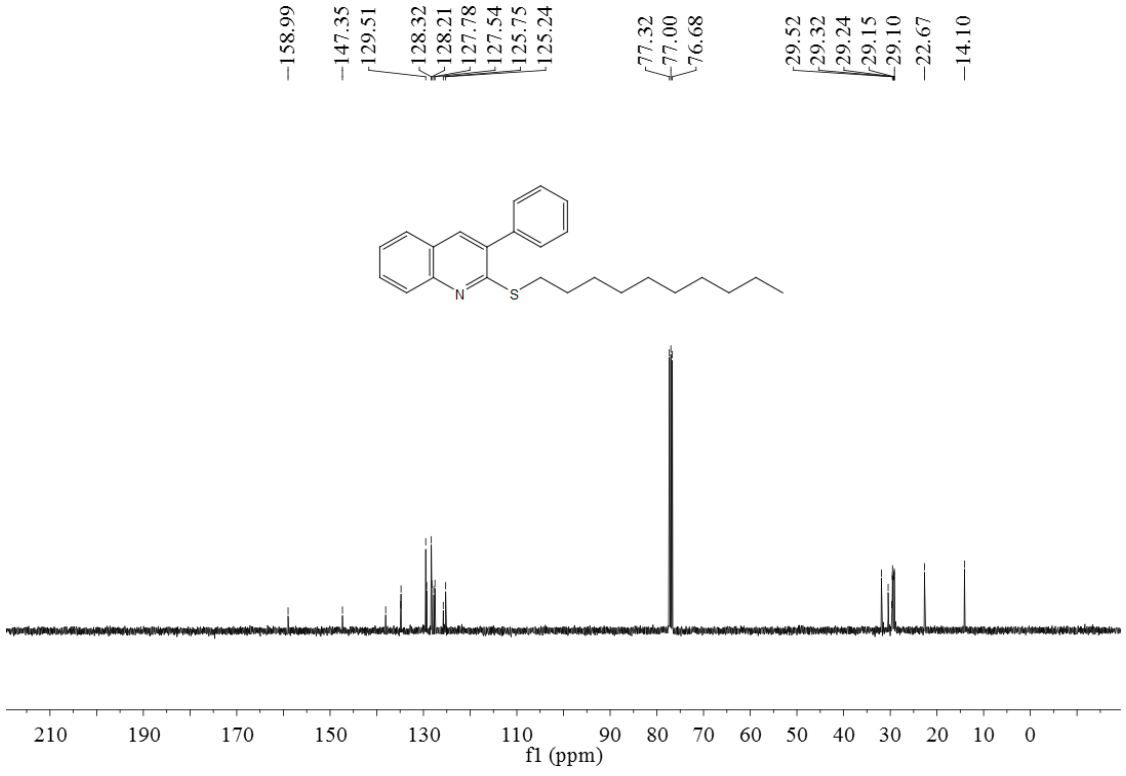


2-(Decylthio)-3-phenylquinoline (**4br**)

^{1}H NMR (400 MHz, $CDCl_3$)

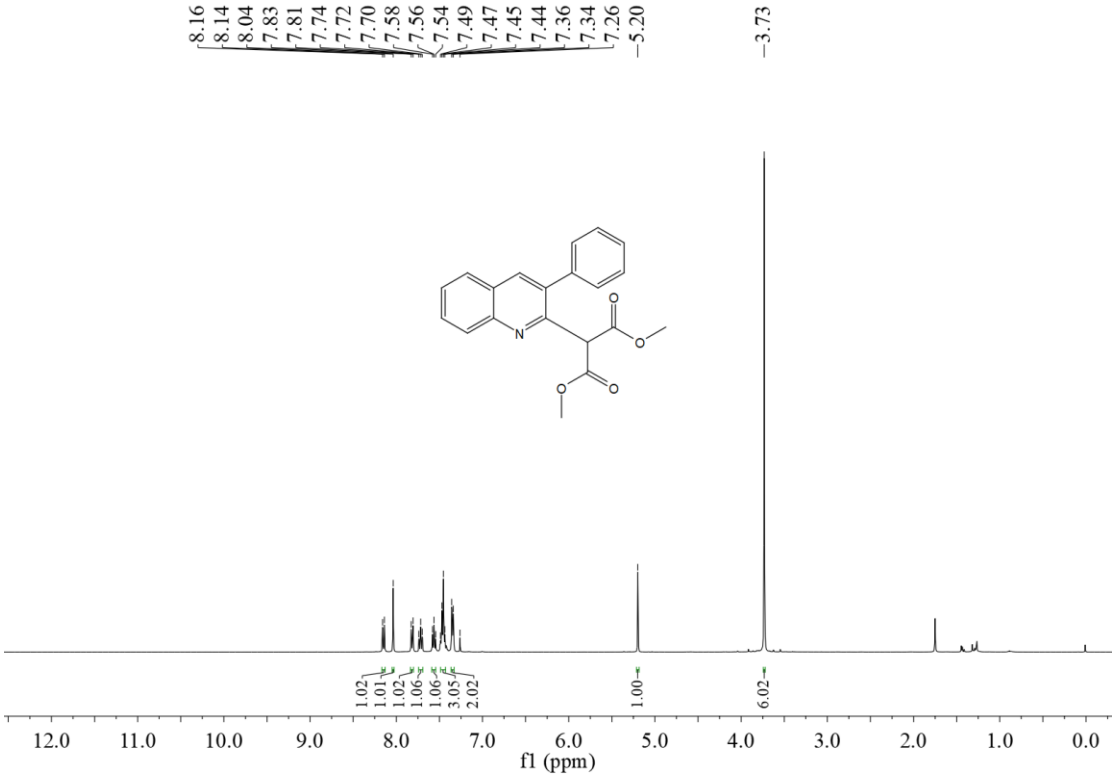


^{13}C NMR (100 MHz, $CDCl_3$)

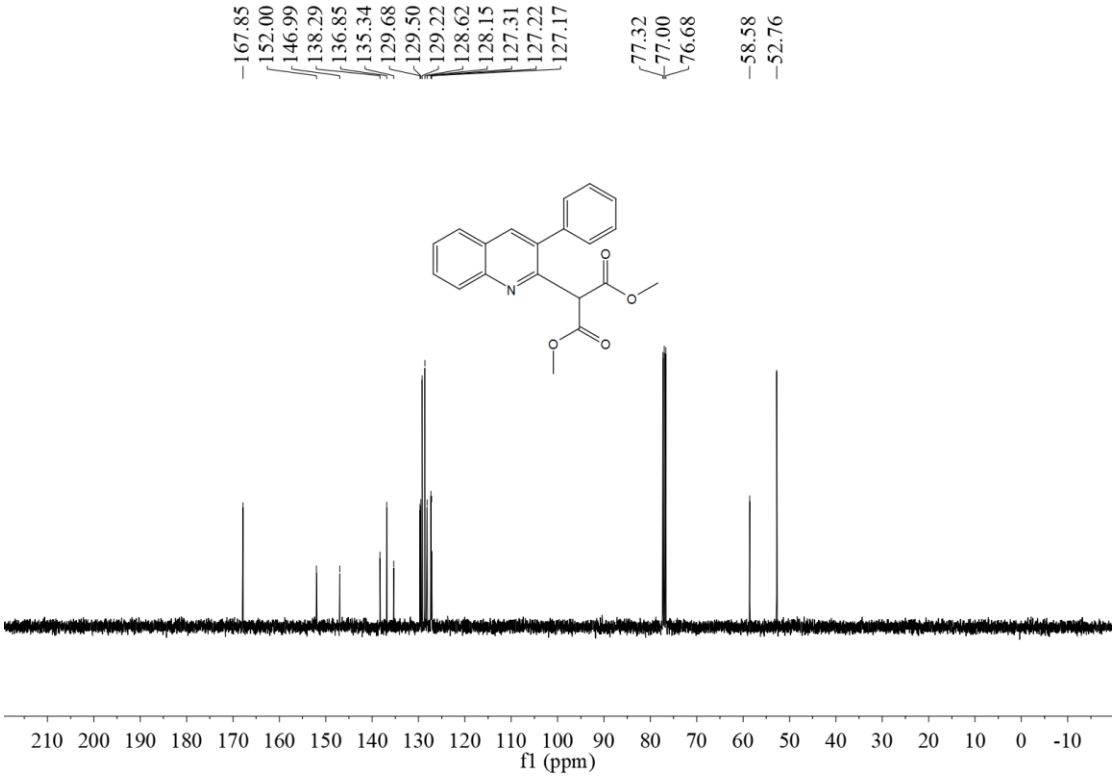


Dimethyl-2-(3-phenylquinolin-2-yl)malonate (**4bs**)

^{1}H NMR (400 MHz, $CDCl_3$)

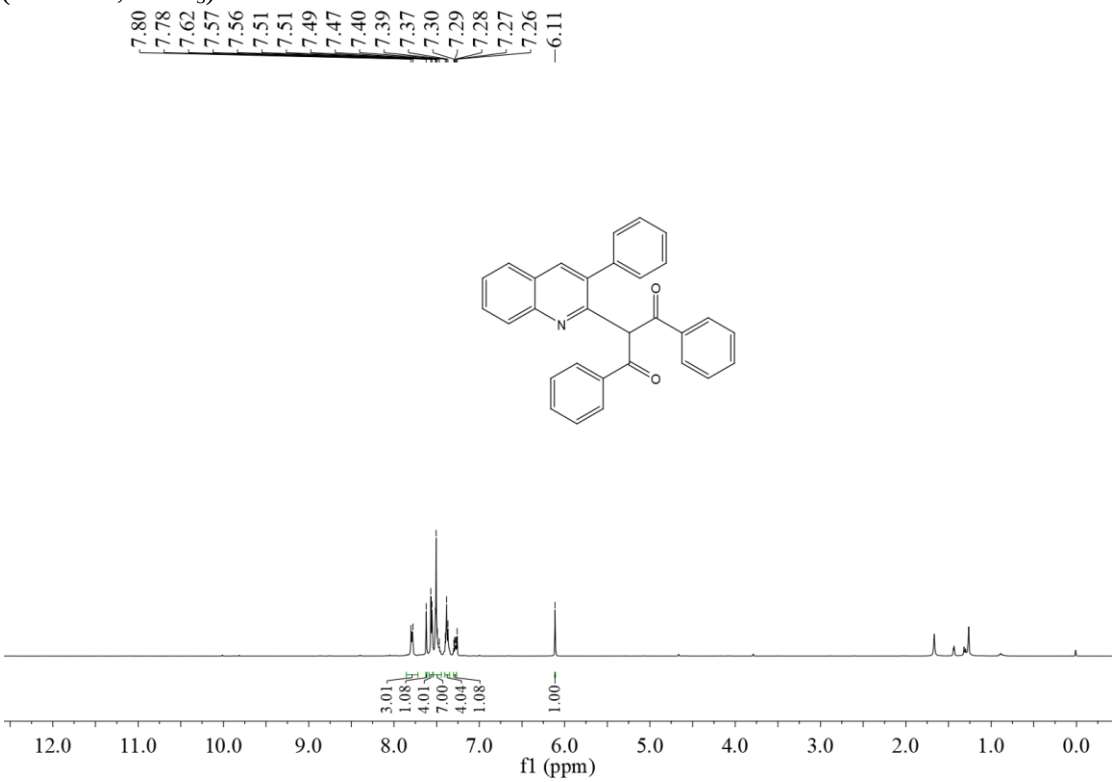


^{13}C NMR (100 MHz, $CDCl_3$)

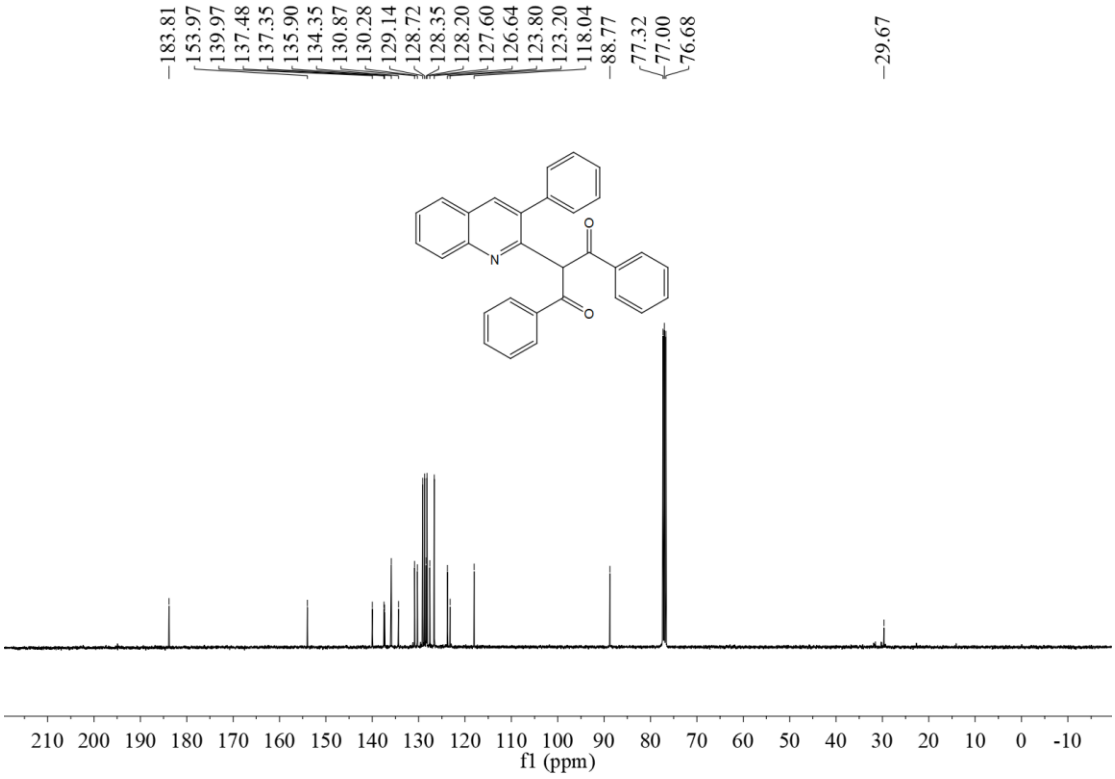


1,3-Diphenyl-2-(3-phenylquinolin-2-yl)propane-1,3-dione (**4bt**)

^{1}H NMR (400 MHz, $CDCl_3$)

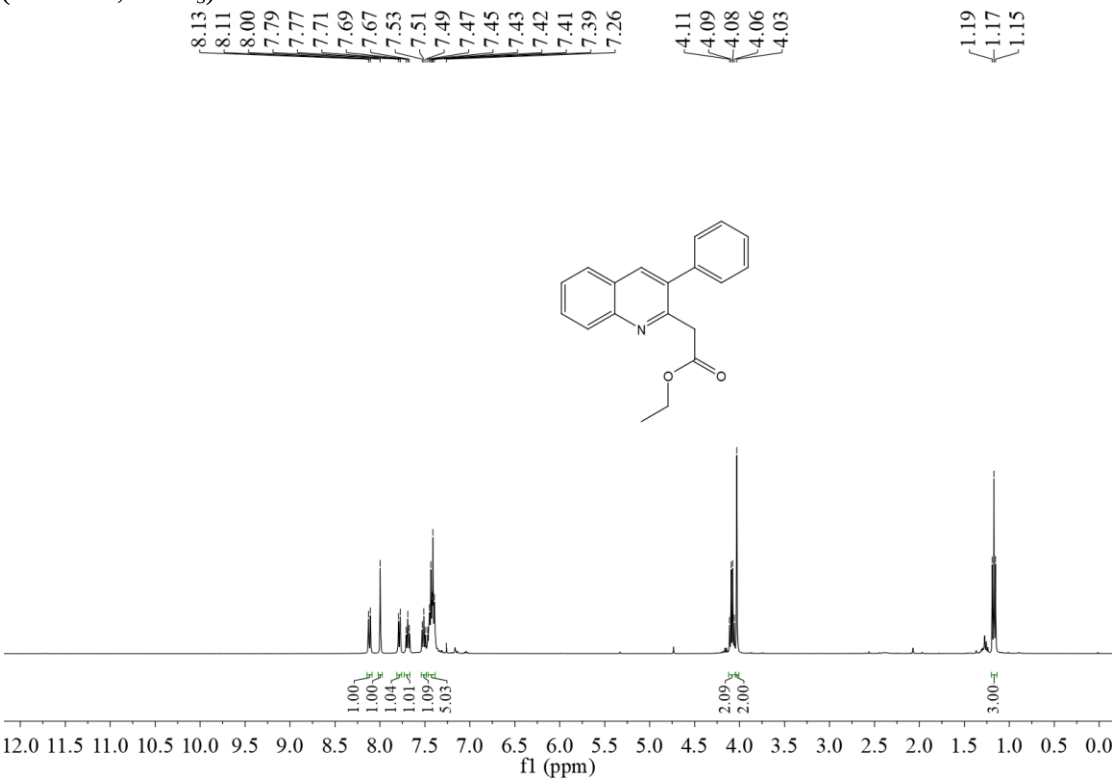


^{13}C NMR (100 MHz, $CDCl_3$)

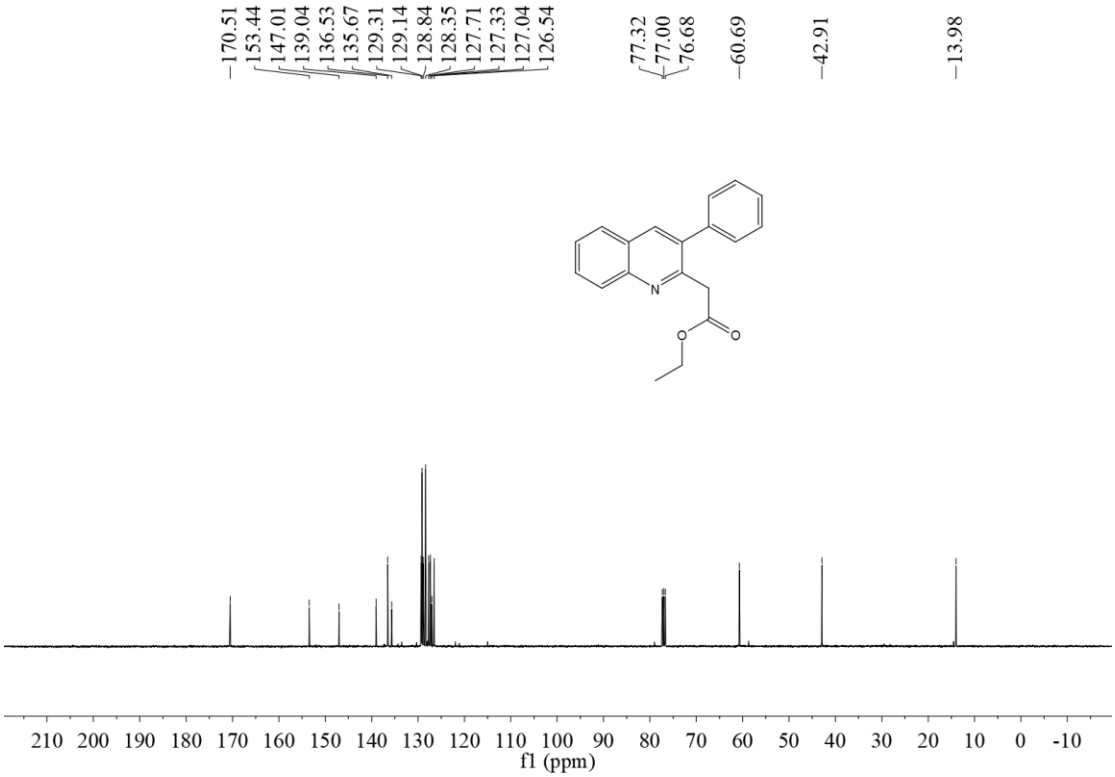


Ethyl 2-(3-phenylquinolin-2-yl)acetate (**4bu**)

^{1}H NMR (400 MHz, $CDCl_3$)

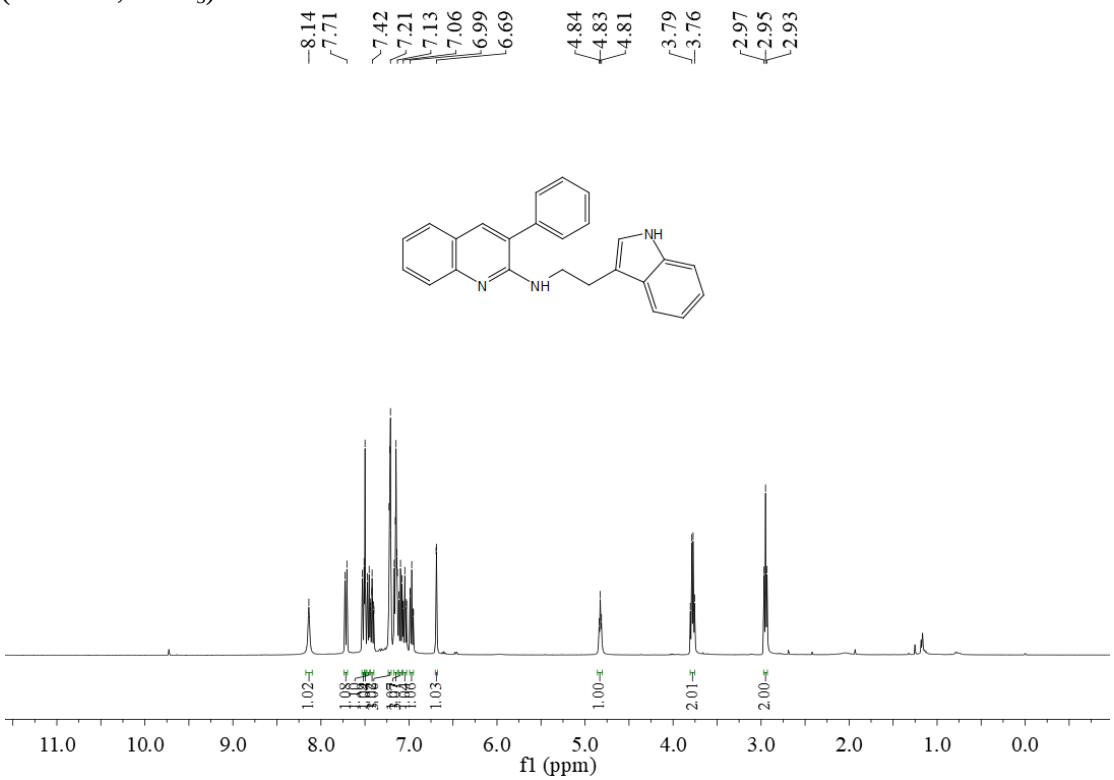


^{13}C NMR (100 MHz, $CDCl_3$)

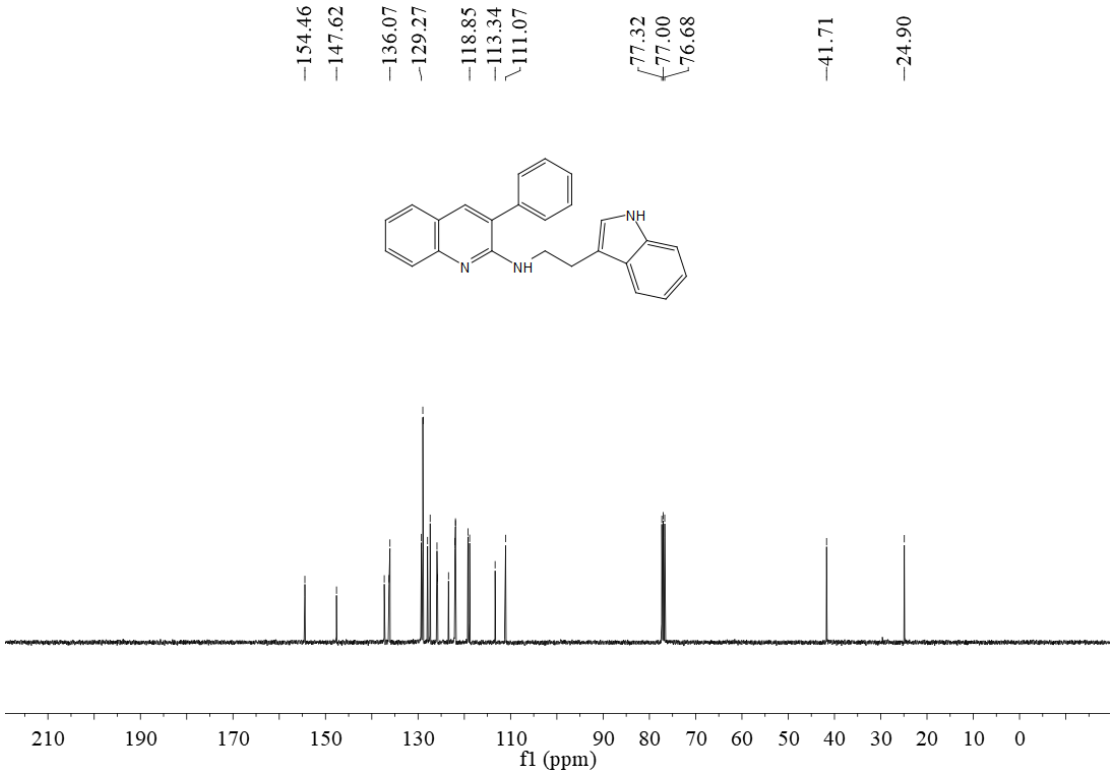


N-(2-(1H-indol-3-yl)ethyl)-3-phenylquinolin-2-amine (**4bv**)

^{1}H NMR (400 MHz, $CDCl_3$)

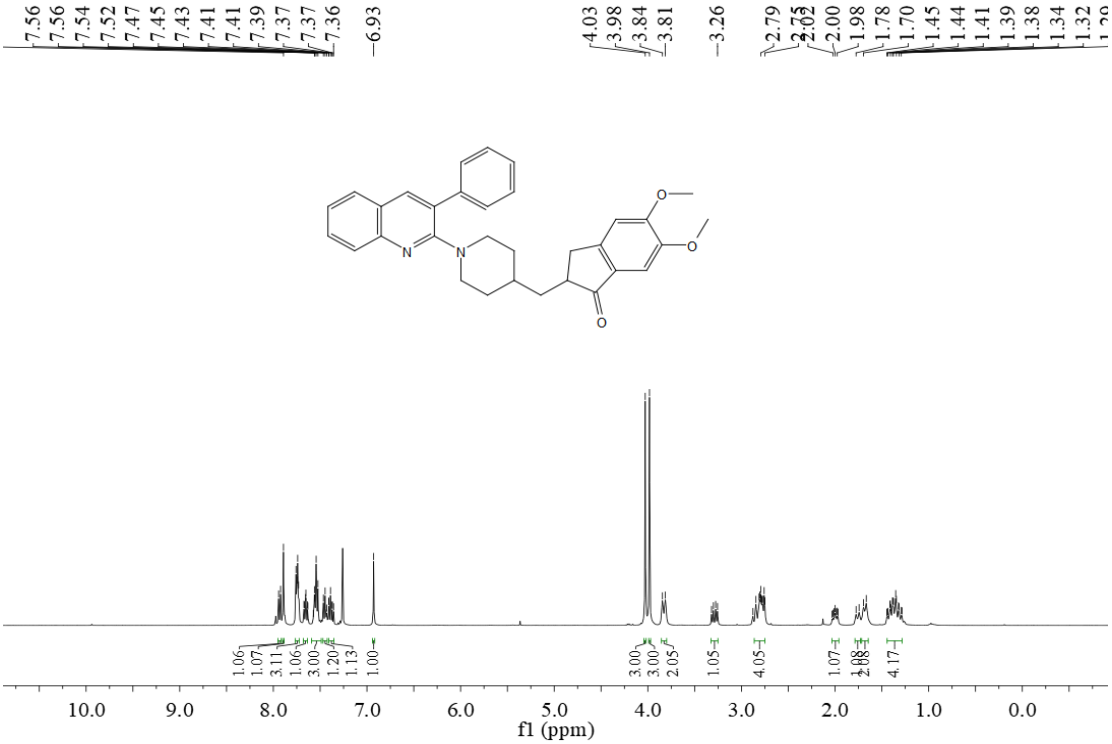


^{13}C NMR (100 MHz, $CDCl_3$)

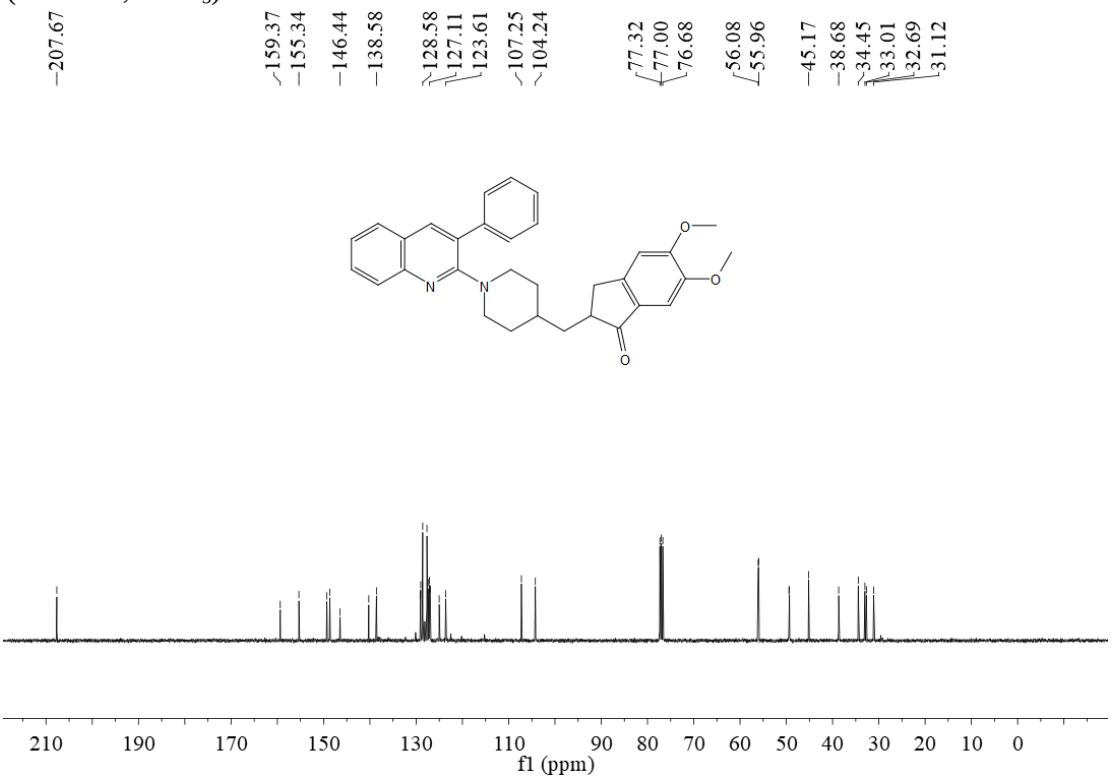


5,6-Dimethoxy-2-((1-(3-phenylquinolin-2-yl)piperidin-4-yl)methyl)-2,3-dihydro-1H-inden-1-one (**4bw**)

^{1}H NMR (400 MHz, $CDCl_3$)

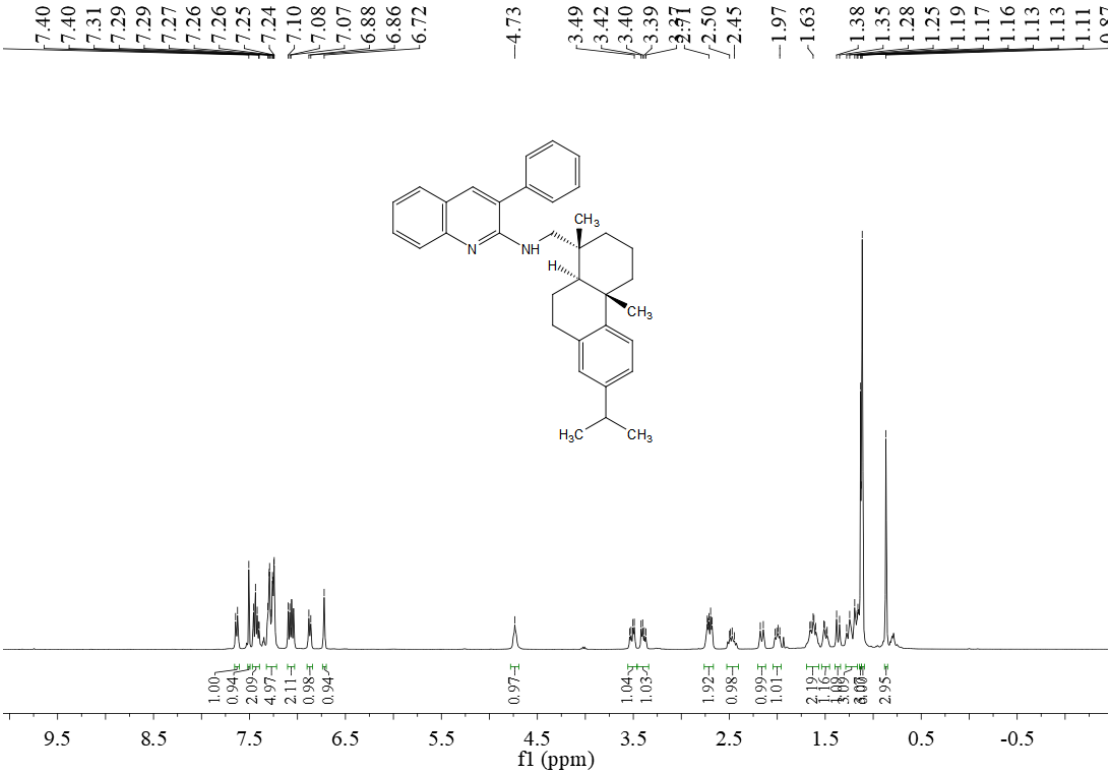


^{13}C NMR (100 MHz, $CDCl_3$)

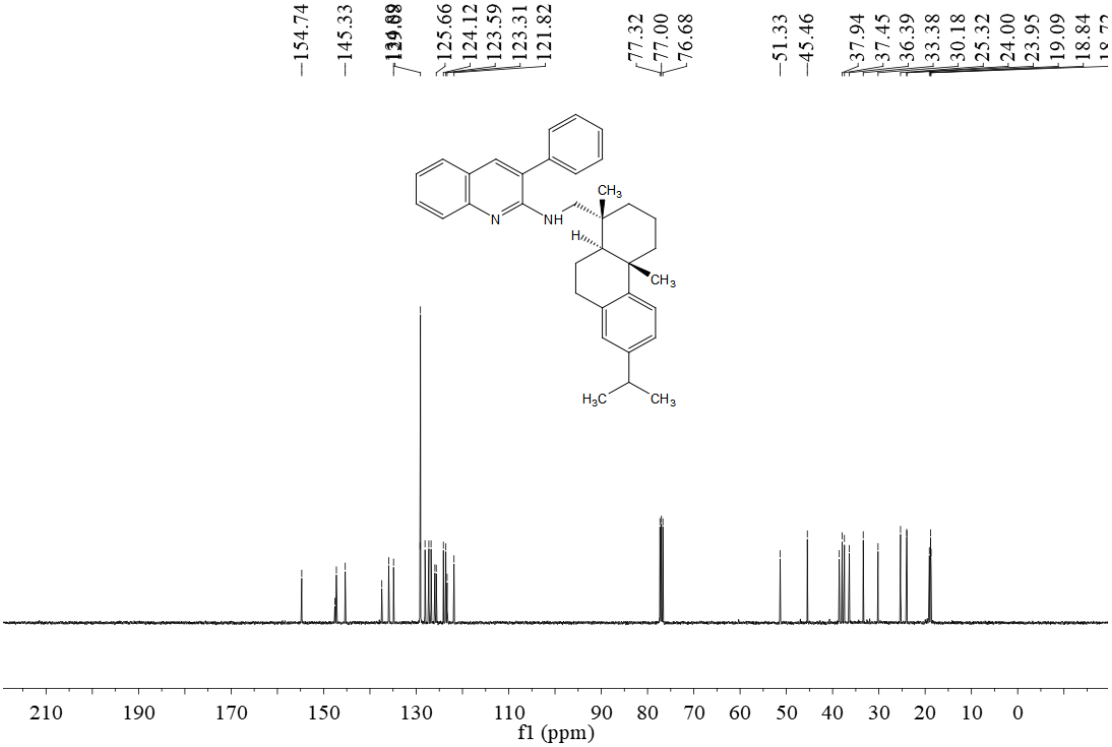


N-((7-Isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)-3-phenylquinolin-2-amine (**4bx**)

^{1}H NMR (400 MHz, $CDCl_3$)

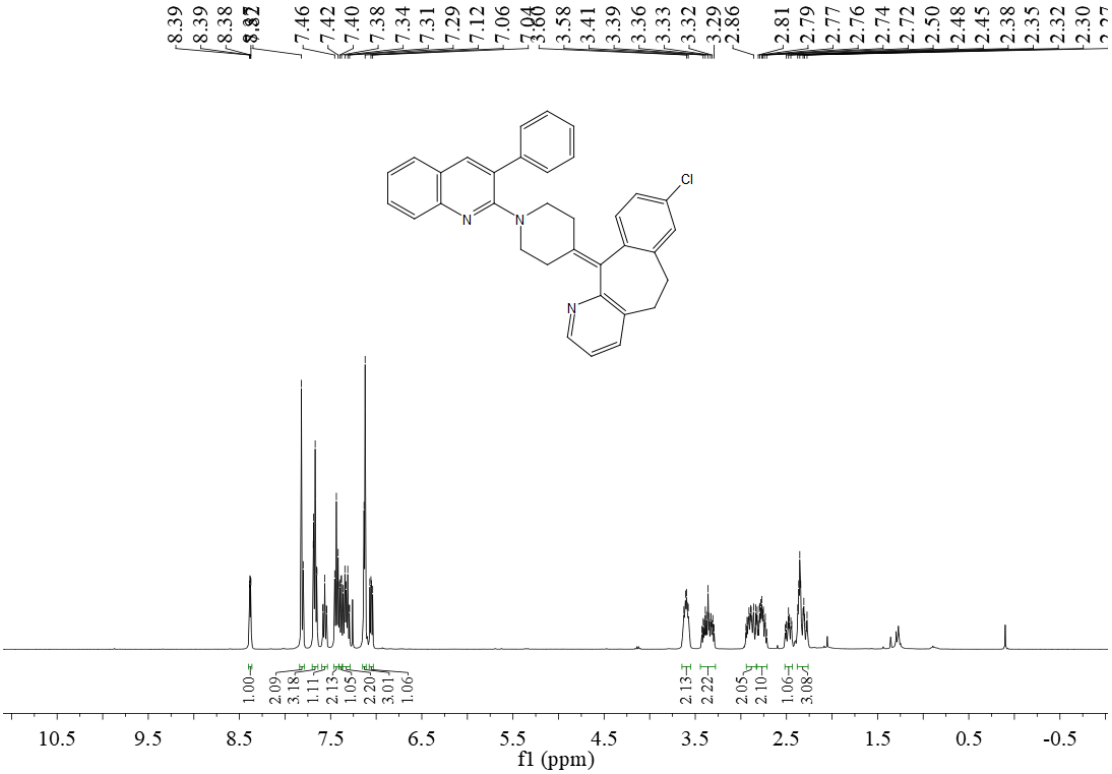


^{13}C NMR (100 MHz, $CDCl_3$)

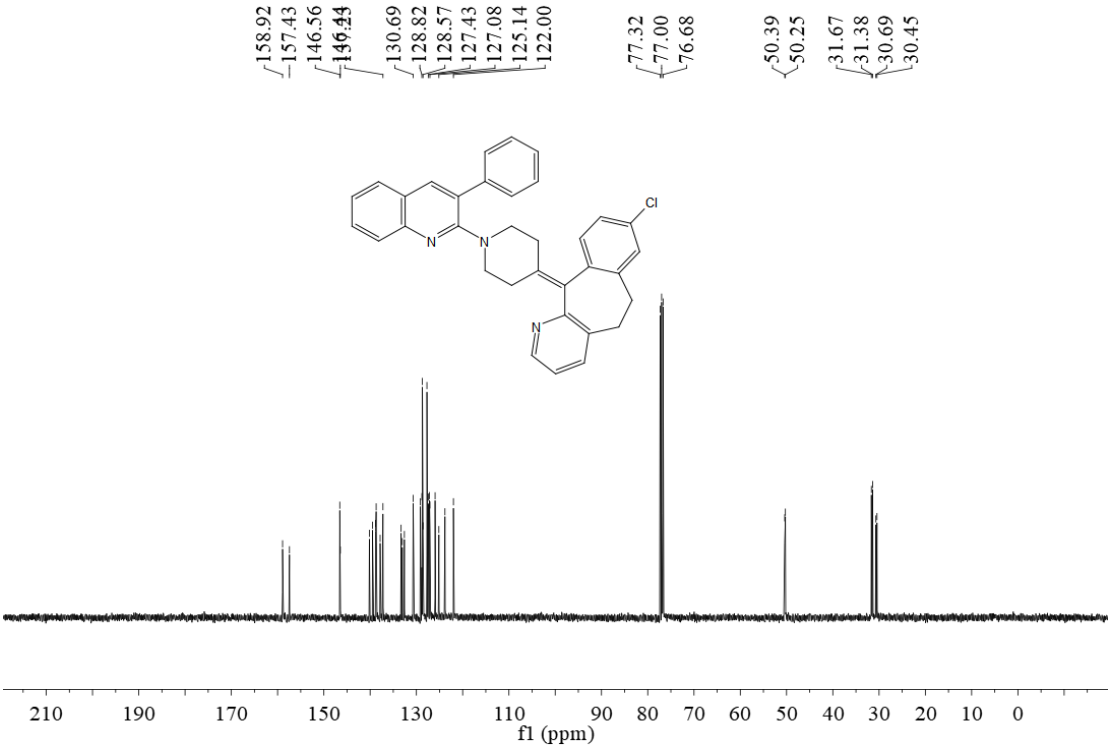


8-Chloro-11-(1-(3-phenylquinolin-2-yl)piperidin-4-ylidene)-6,11-dihydro-5H-benzo[5,6]cyclohepta[1,2-b]pyridine (**4by**)

^{1}H NMR (400 MHz, $CDCl_3$)

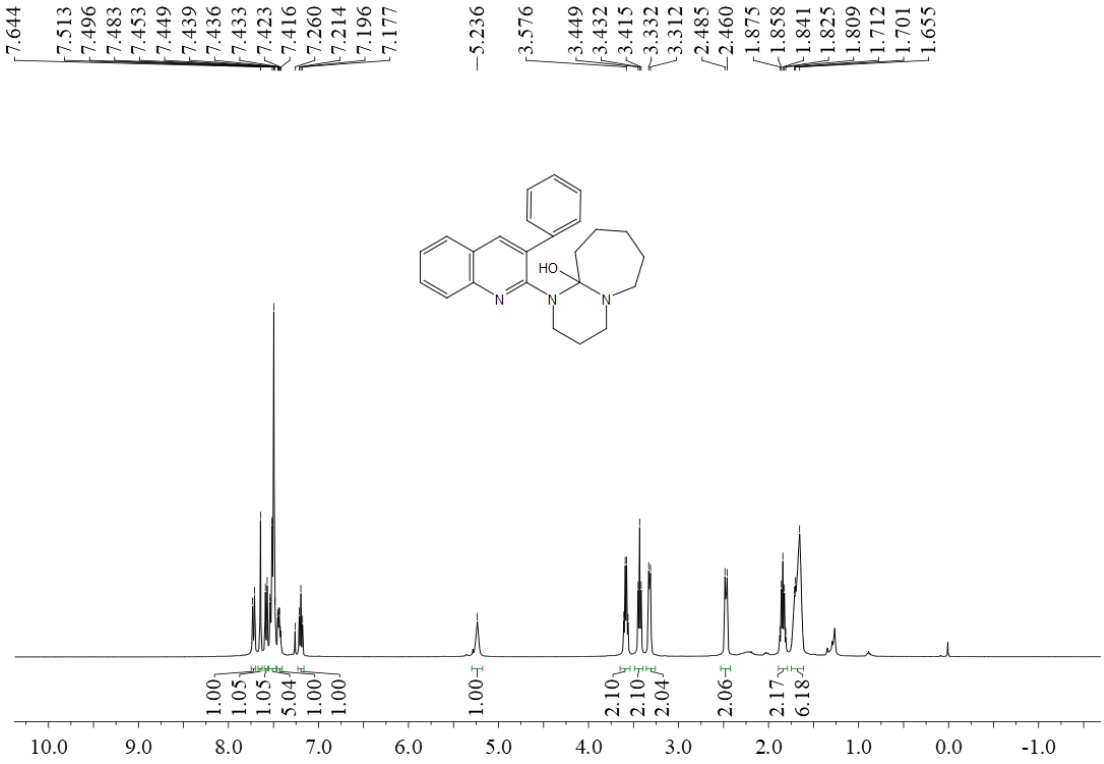


^{13}C NMR (100 MHz, $CDCl_3$)

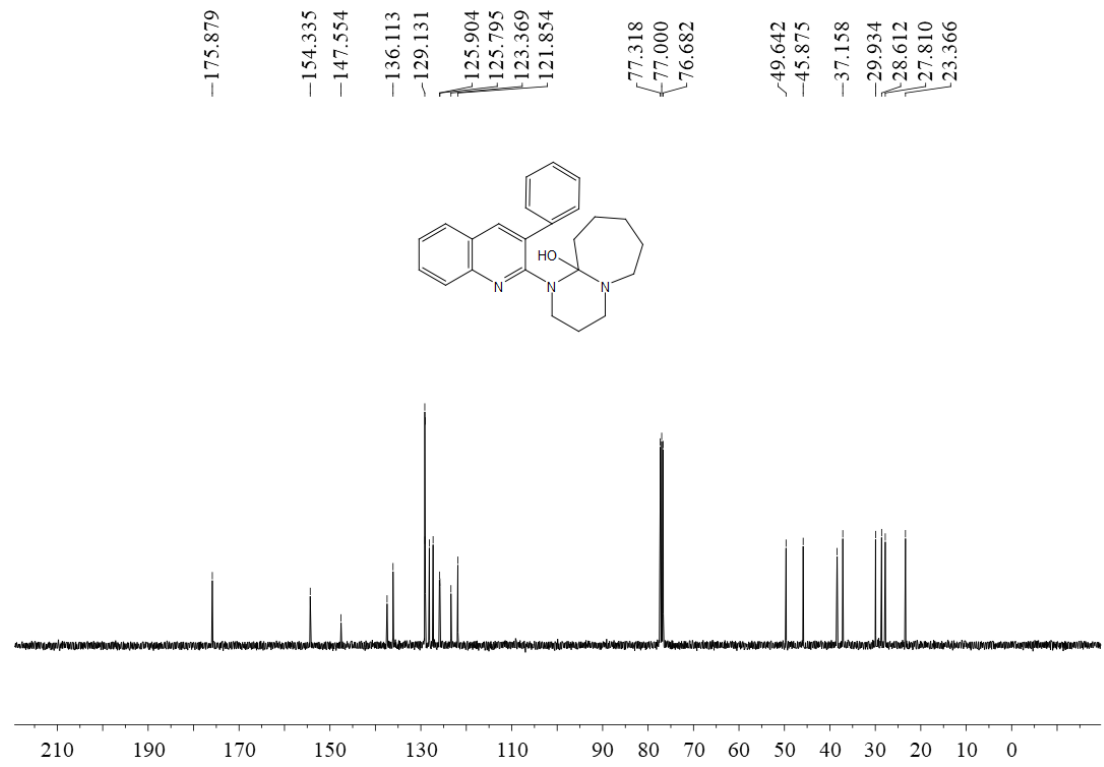


1-((3-Phenylquinolin-2-yl)oxy)decahydropyrimido[1,2-*a*]azepine (**4bz**)

^{1}H NMR (400 MHz, $CDCl_3$)

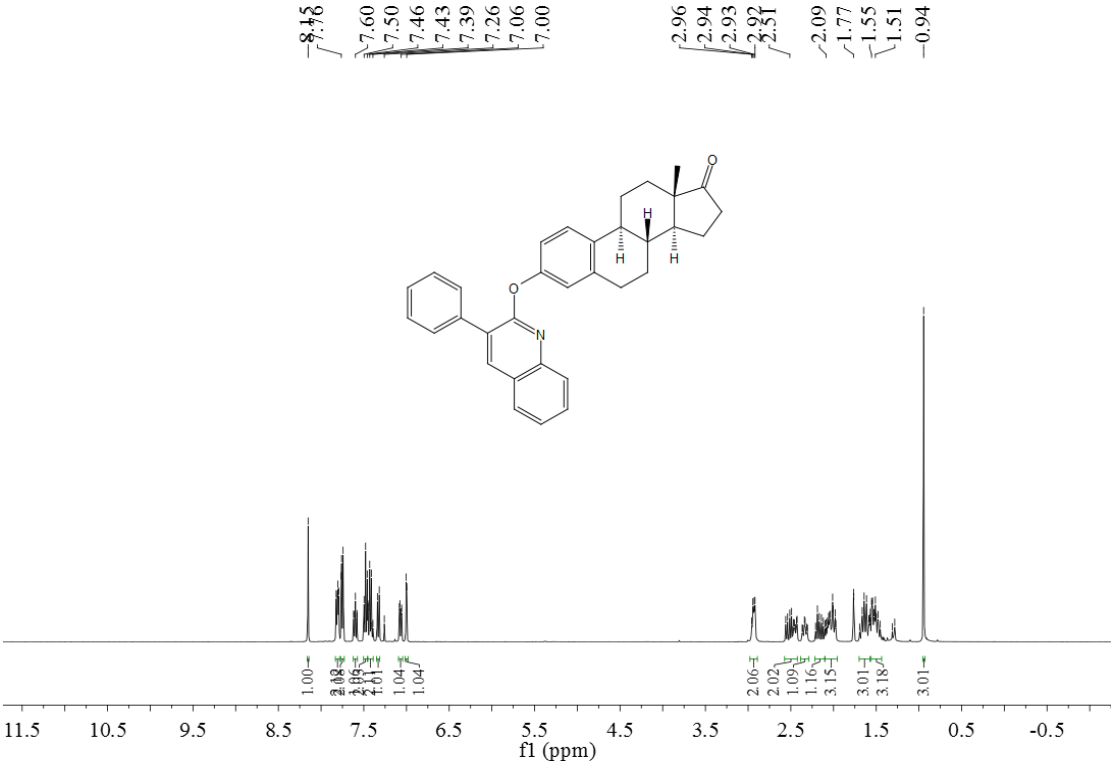


^{13}C NMR (100 MHz, $CDCl_3$)

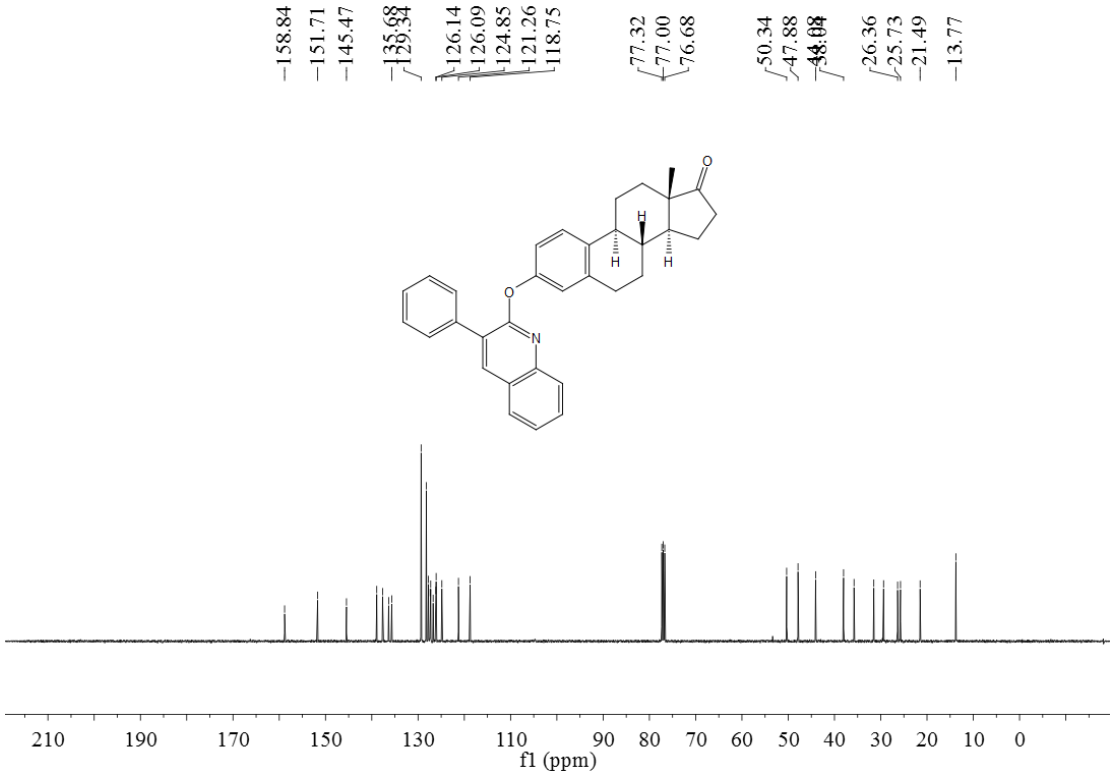


13-Methyl-3-((3-phenylquinolin-2-yl)oxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (**4ca**)

^{1}H NMR (400 MHz, $CDCl_3$)

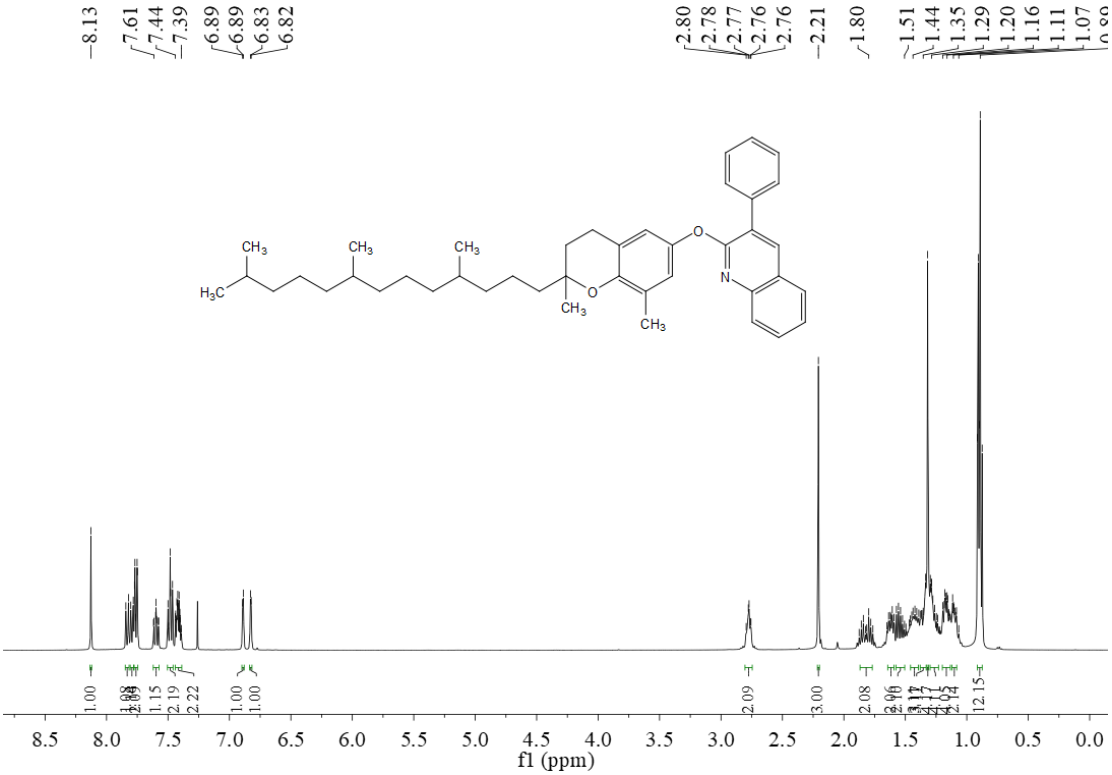


^{13}C NMR (100 MHz, $CDCl_3$)

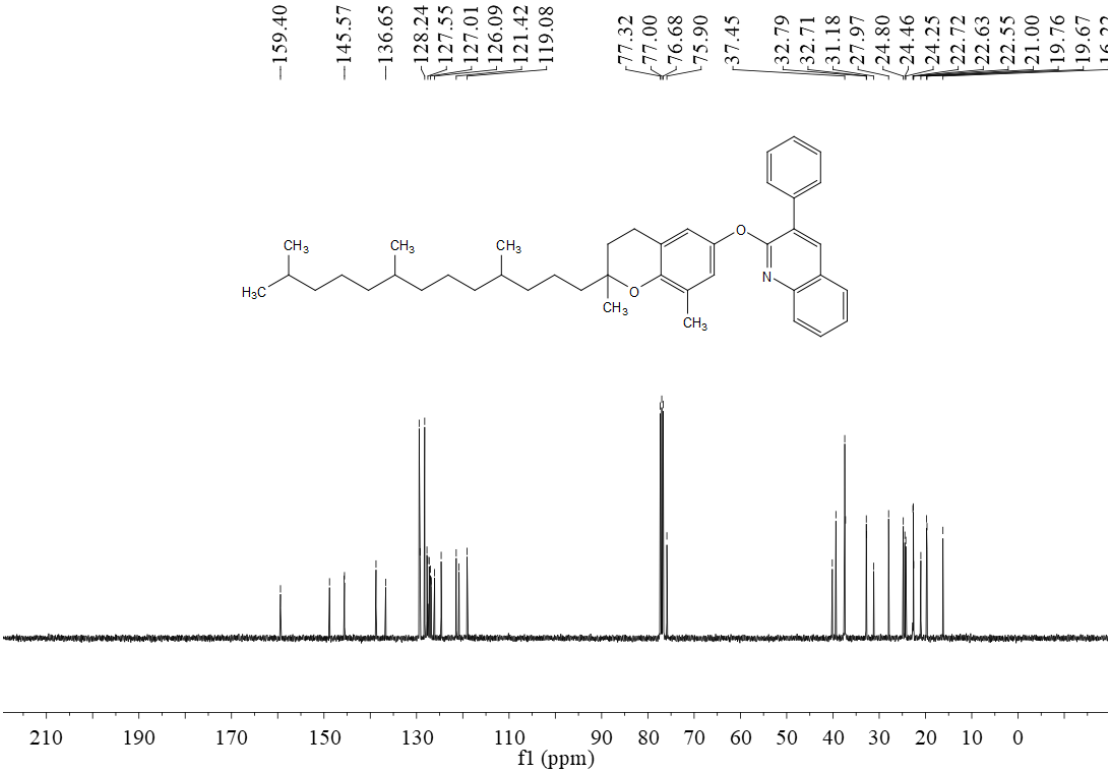


2-((2,8-Dimethyl-2-(4,8,12-trimethyltridecyl)chroman-6-yl)oxy)-3-phenylquinoline (**4cb**)

^{1}H NMR (400 MHz, $CDCl_3$)

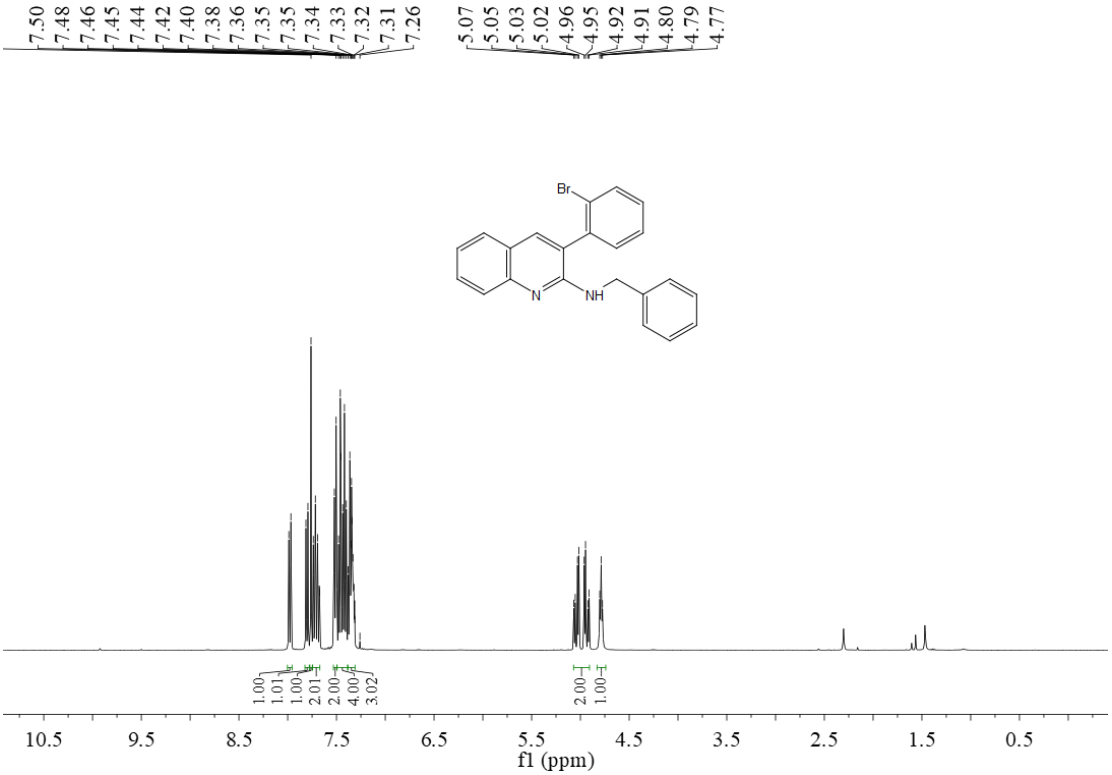


^{13}C NMR (100 MHz, $CDCl_3$)

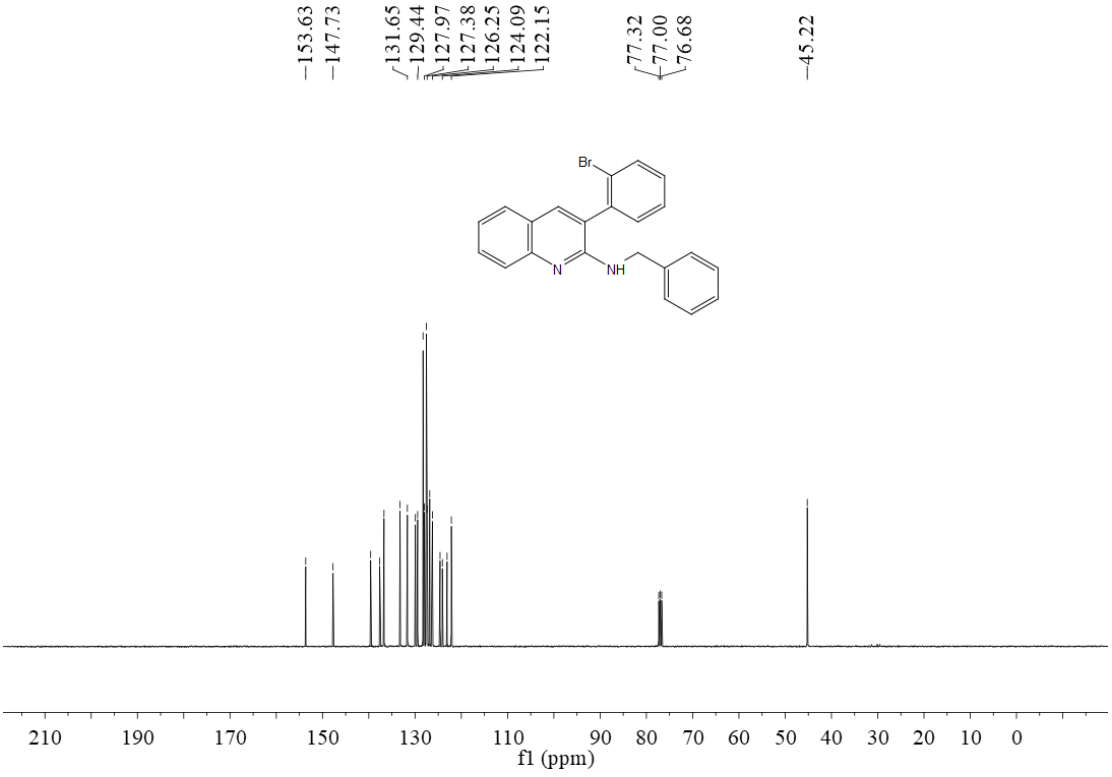


N-Benzyl-3-(2-bromophenyl)quinolin-2-amine (**4cc**)

^{1}H NMR (400 MHz, $CDCl_3$)

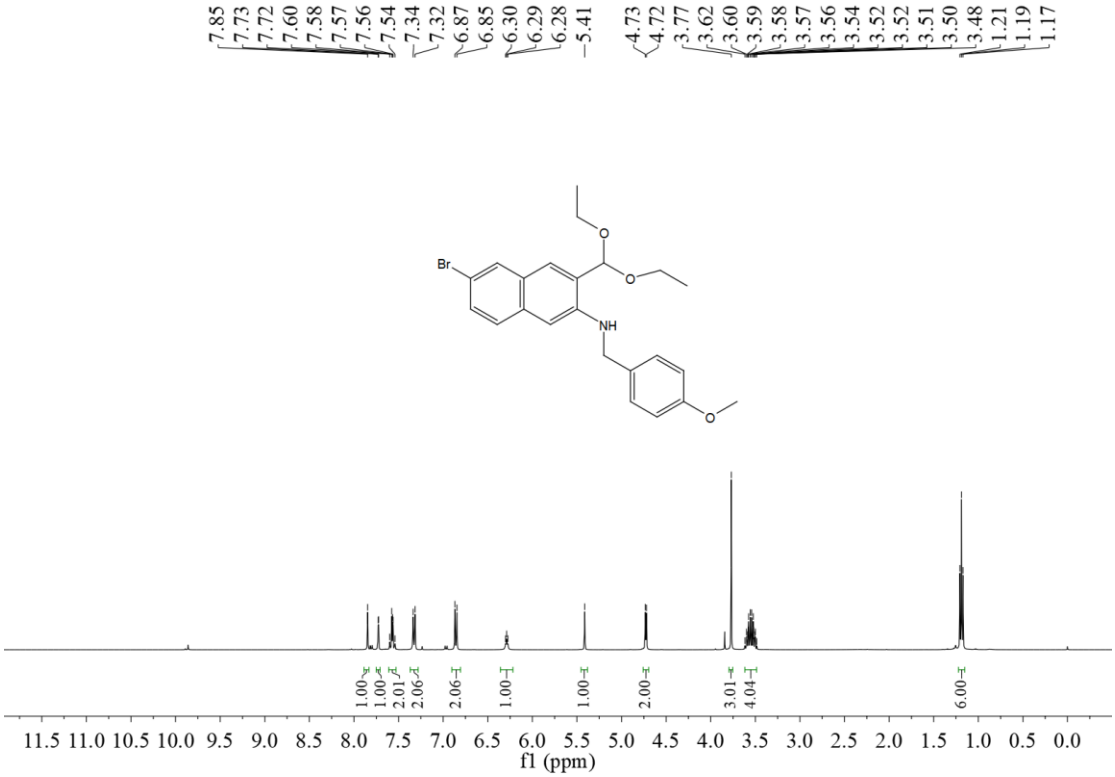


^{13}C NMR (100 MHz, $CDCl_3$)

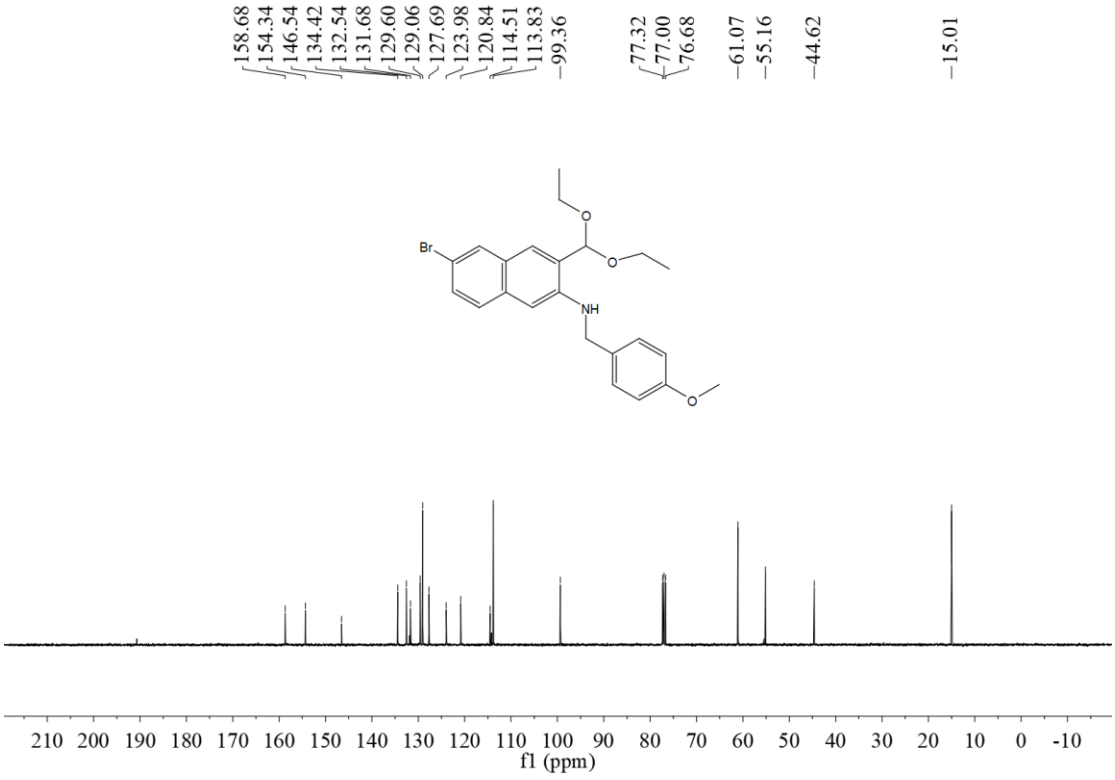


6-Bromo-3-(diethoxymethyl)-N-(4-methoxybenzyl)quinolin-2-amine (**4cd**)

^{1}H NMR (400 MHz, $CDCl_3$)

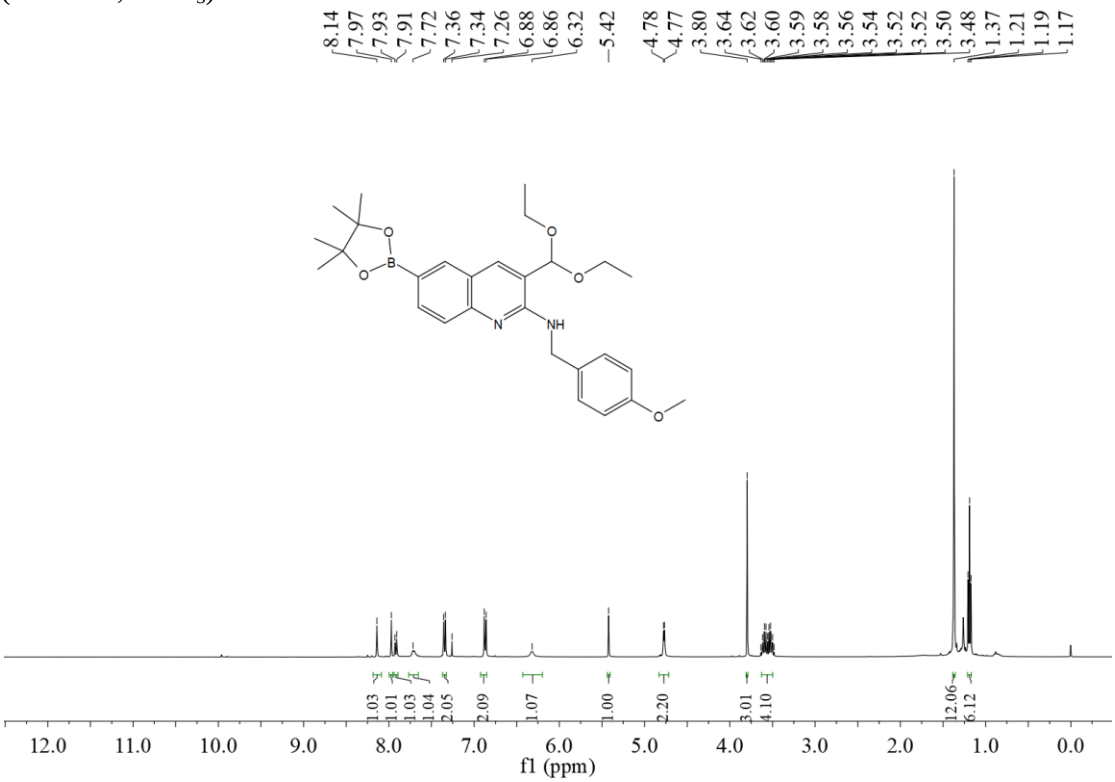


^{13}C NMR (100 MHz, $CDCl_3$)

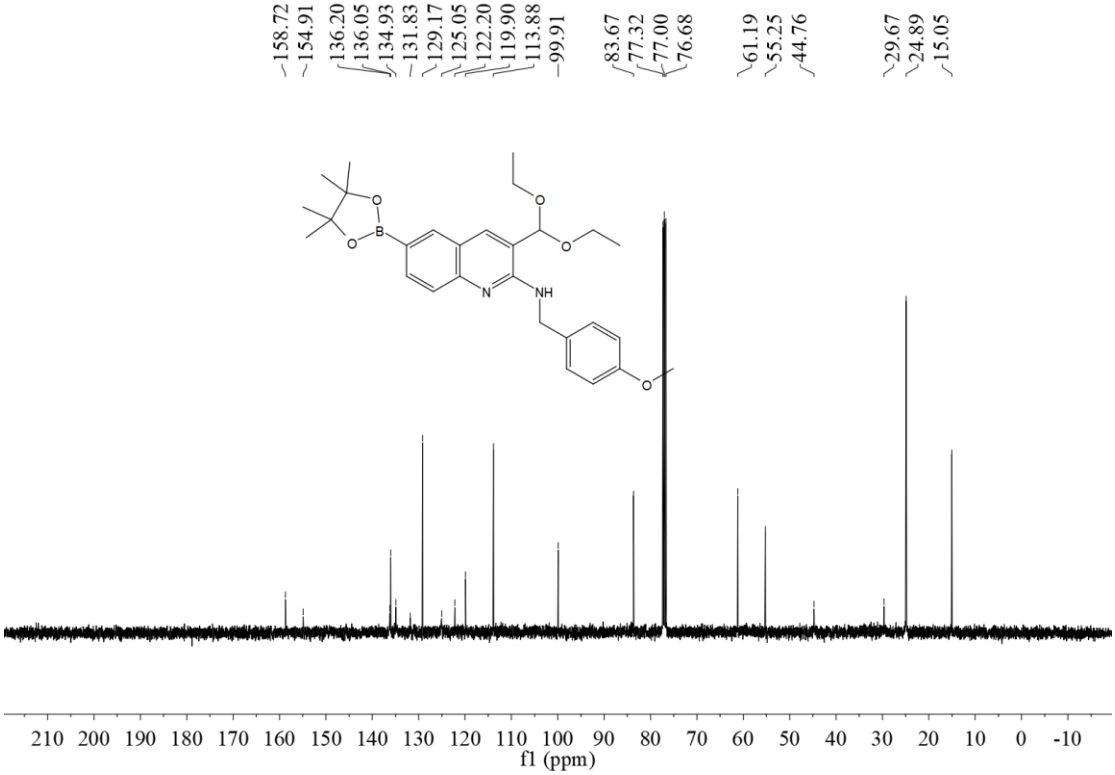


3-(Diethoxymethyl)-N-(4-methoxybenzyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)quinolin-2-amine (**4cd'**)

^{1}H NMR (400 MHz, $CDCl_3$)

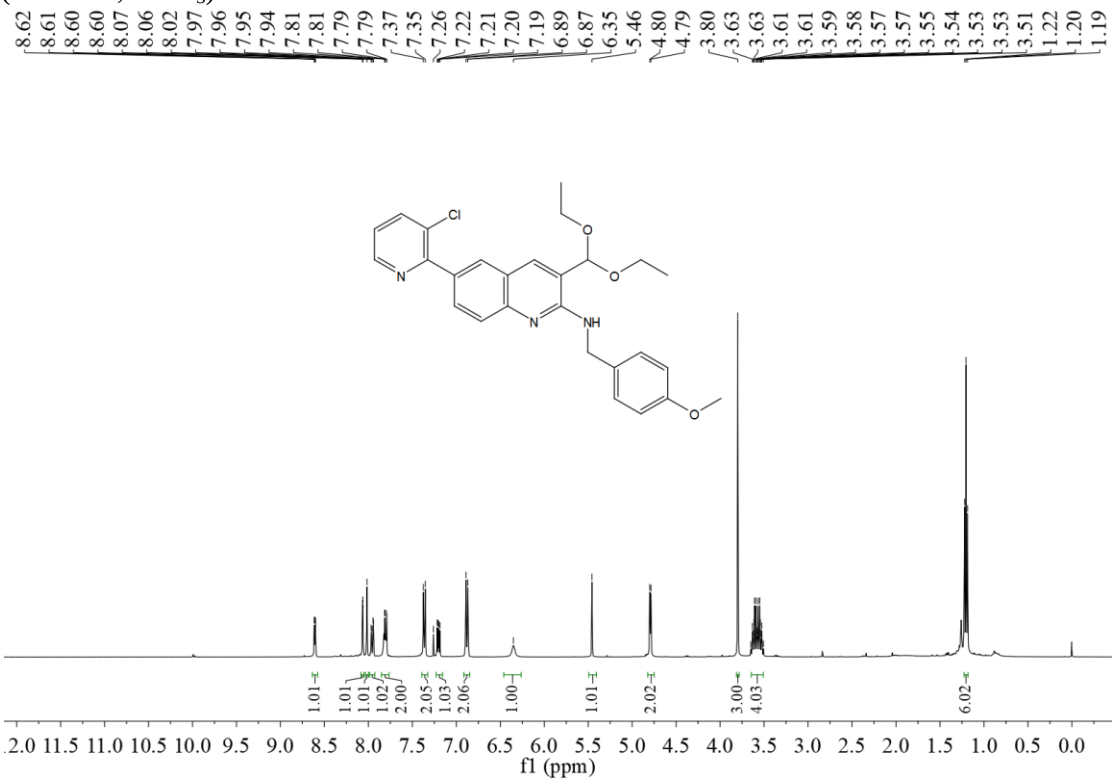


^{13}C NMR (100 MHz, $CDCl_3$)

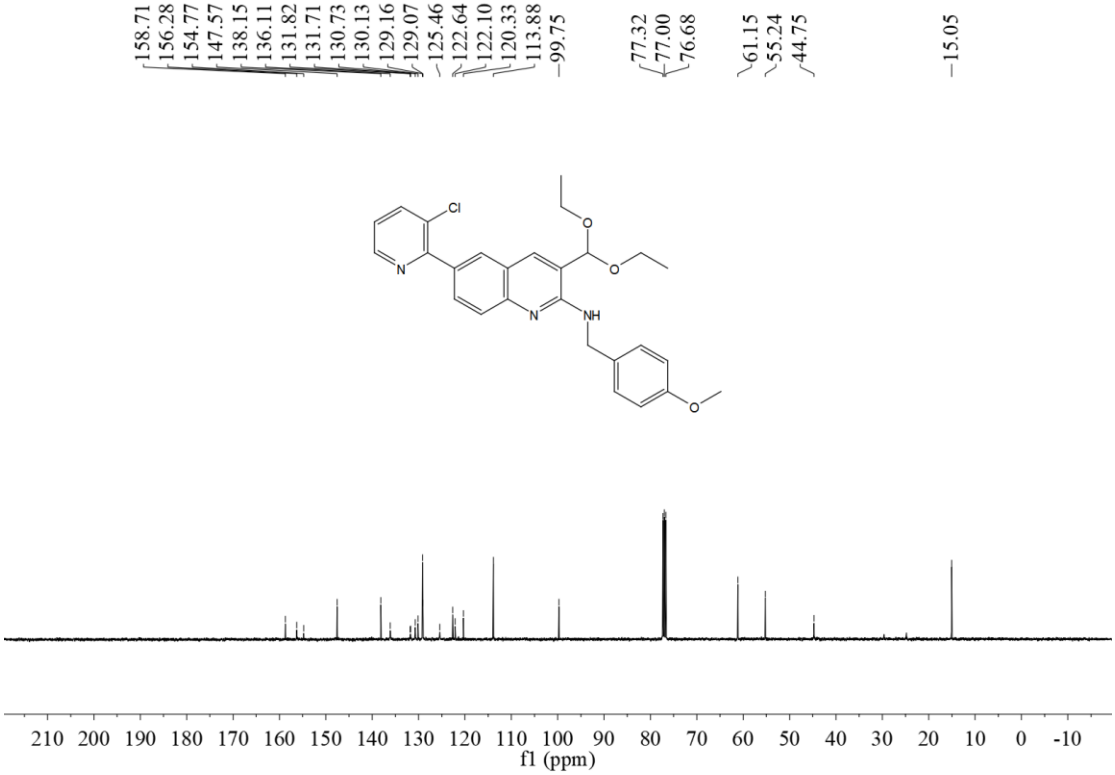


6-(3-Chloropyridin-2-yl)-3-(diethoxymethyl)-N-(4-methoxybenzyl)quinolin-2-amine (**4cd''**)

^{1}H NMR (400 MHz, $CDCl_3$)

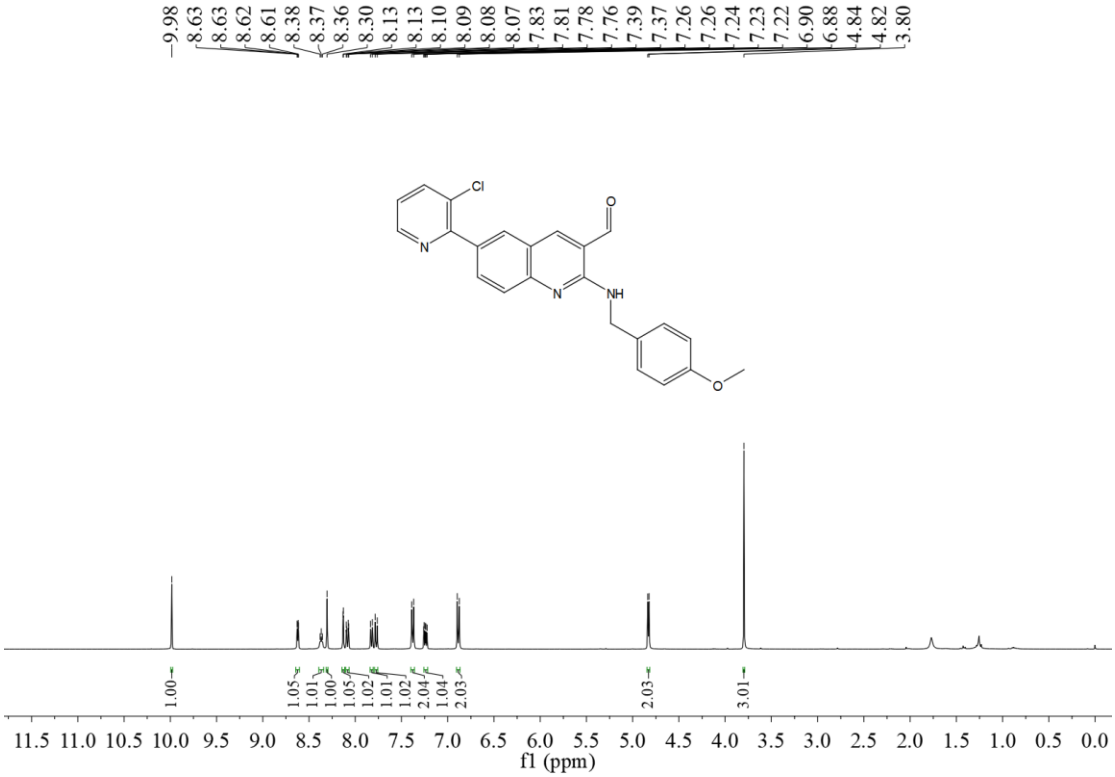


^{13}C NMR (100 MHz, $CDCl_3$)

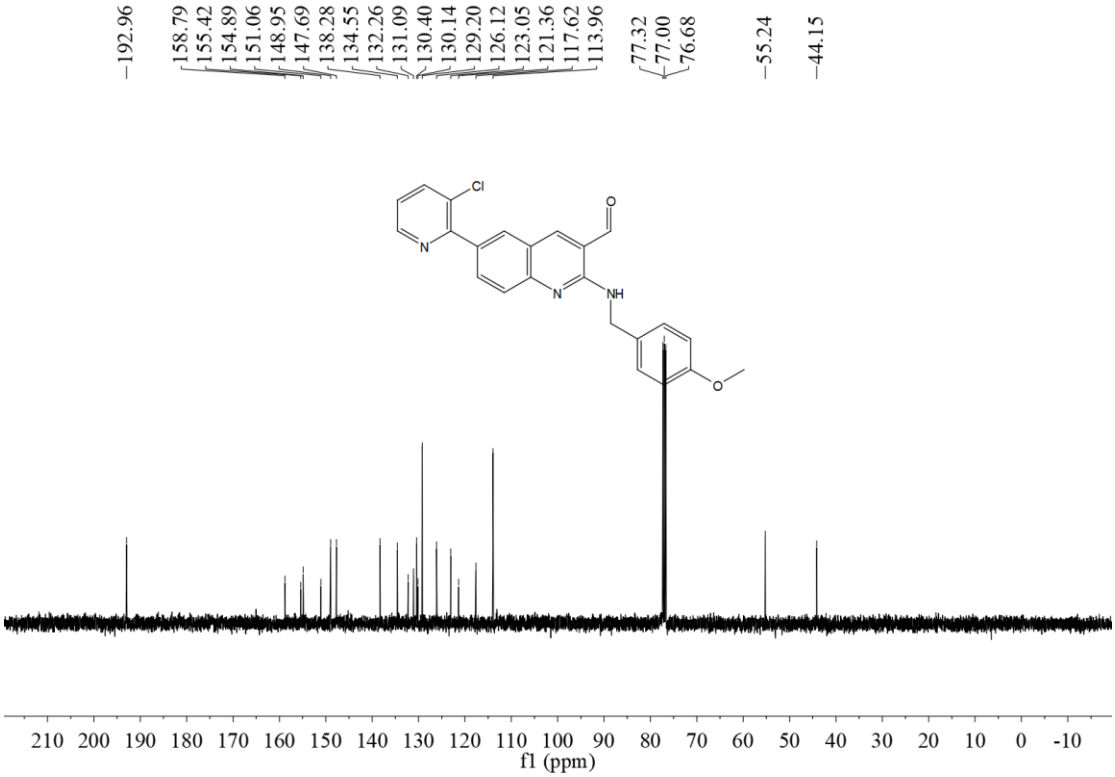


6-(3-Chloropyridin-2-yl)-2-((4-methoxybenzyl)amino)quinoline-3-carbaldehyde (**4ce**)

^{1}H NMR (400 MHz, $CDCl_3$)

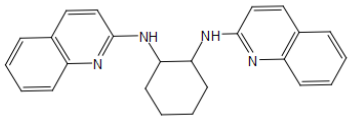


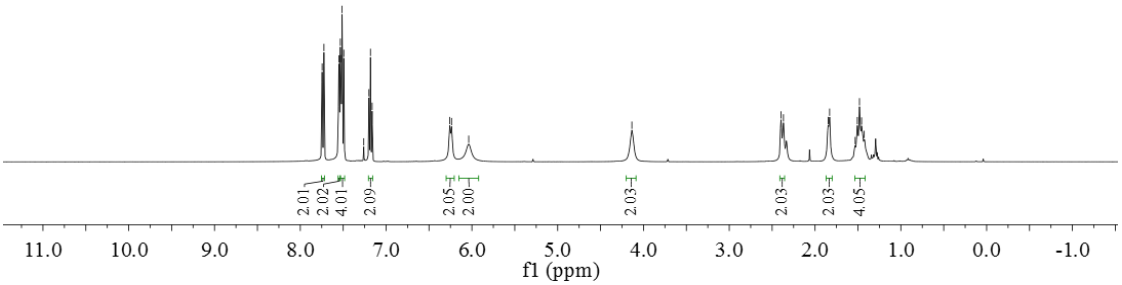
^{13}C NMR (100 MHz, $CDCl_3$)



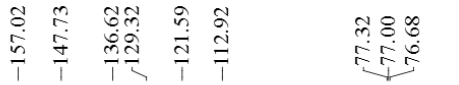
(*1R, 2R*)-N^1,N^2-Di(quinolin-2-yl)cyclohexane-1,2-diamine (**4cf**)

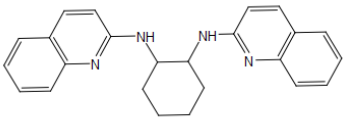
^{1}H NMR (400 MHz, $CDCl_3$)

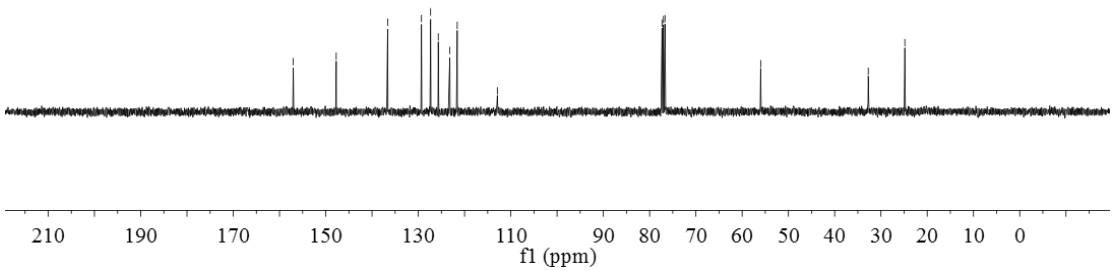




^{13}C NMR (100 MHz, $CDCl_3$)

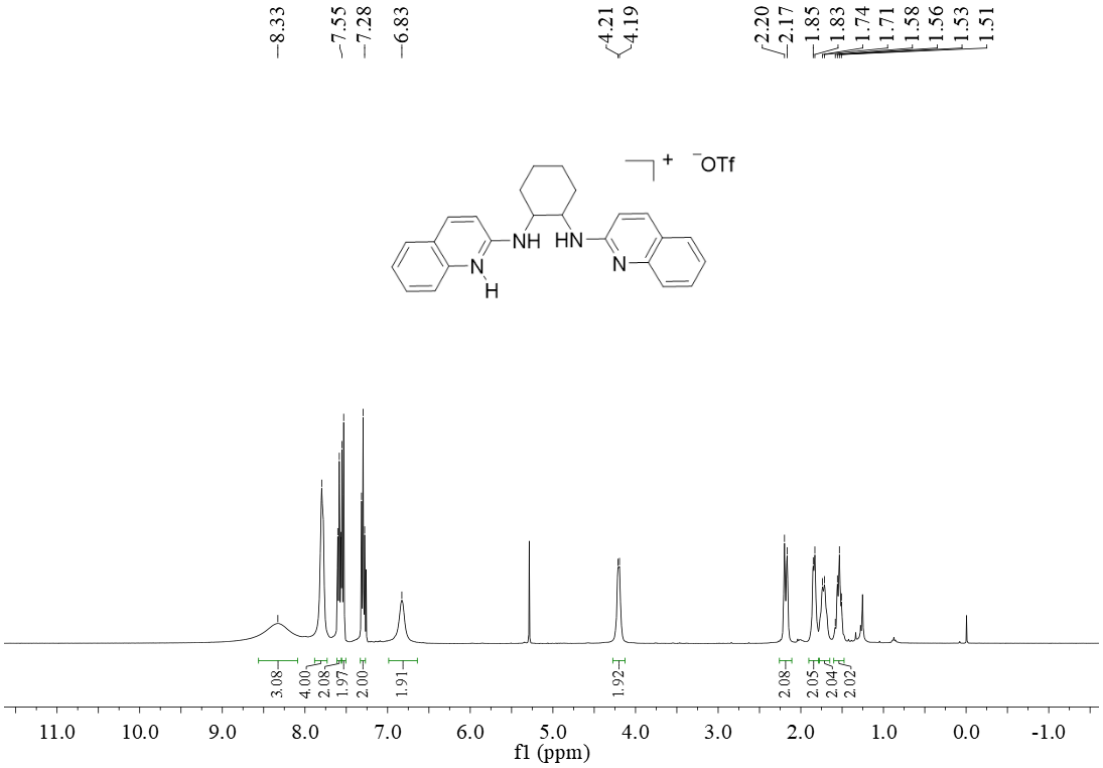




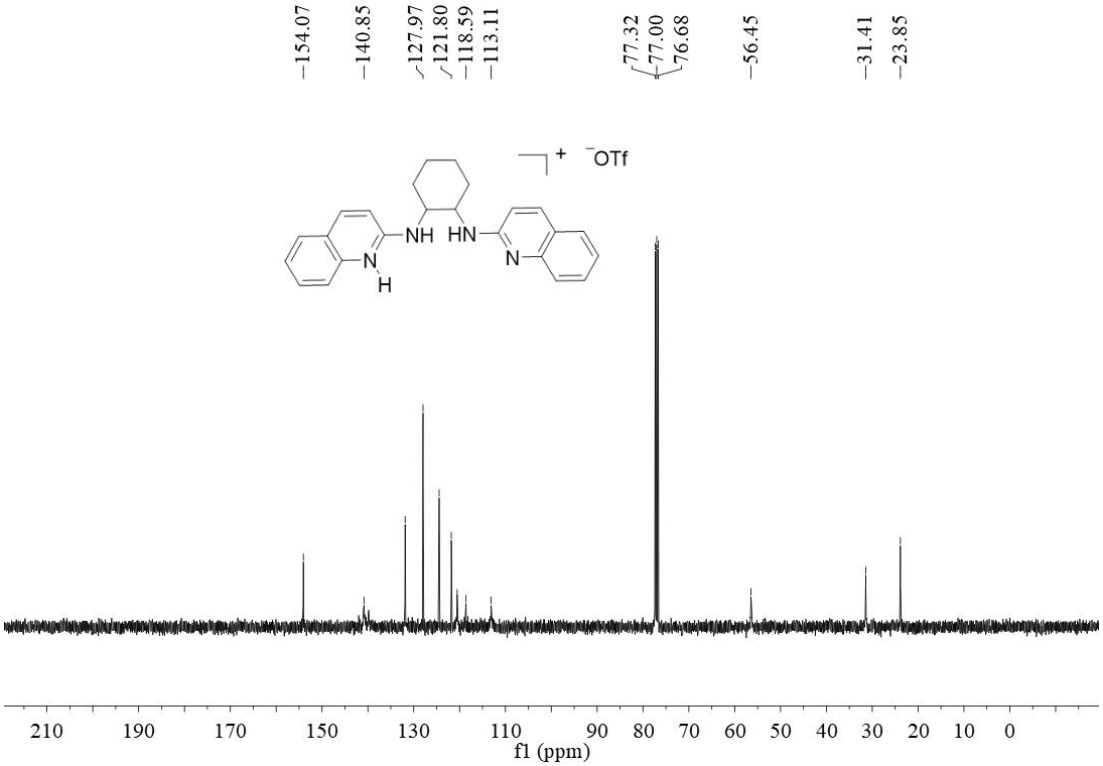


H,Quin-BAM•HOTf (**4cf'**)

^{1}H NMR (400 MHz, $CDCl_3$)

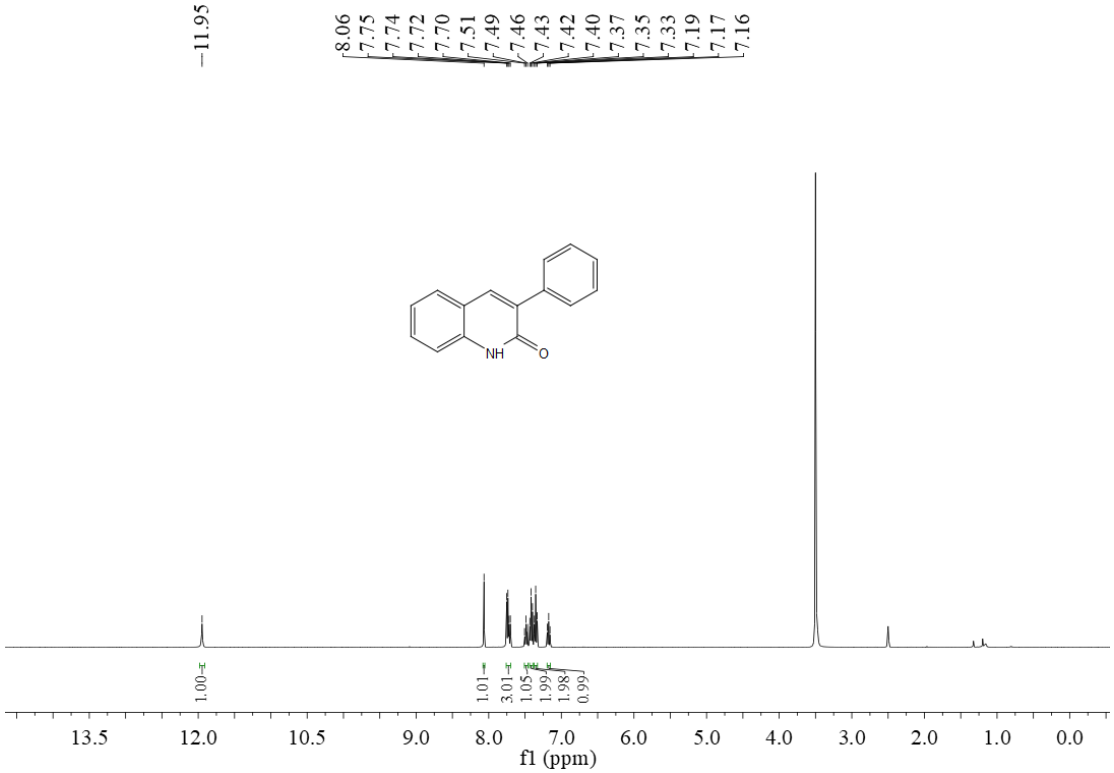


^{13}C NMR (100 MHz, $CDCl_3$)

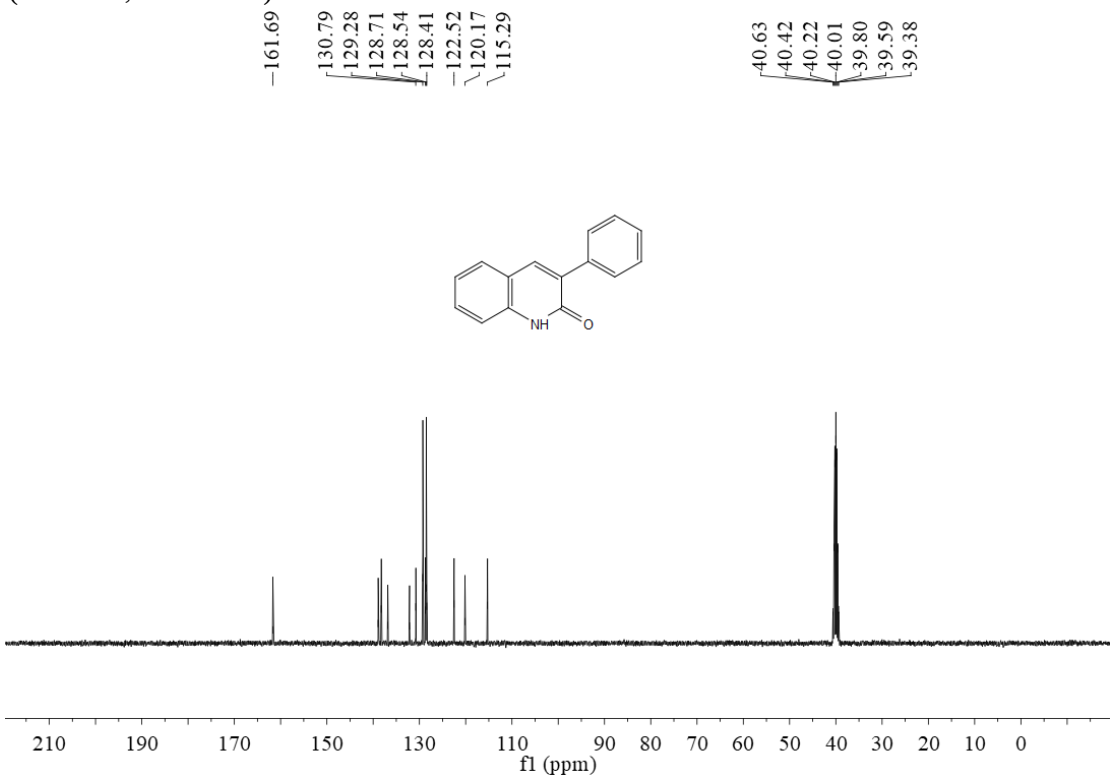


3-Phenylquinolin-2(1H)-one **(8a)**

^{1}H NMR (400 MHz, DMSO-*D6*)

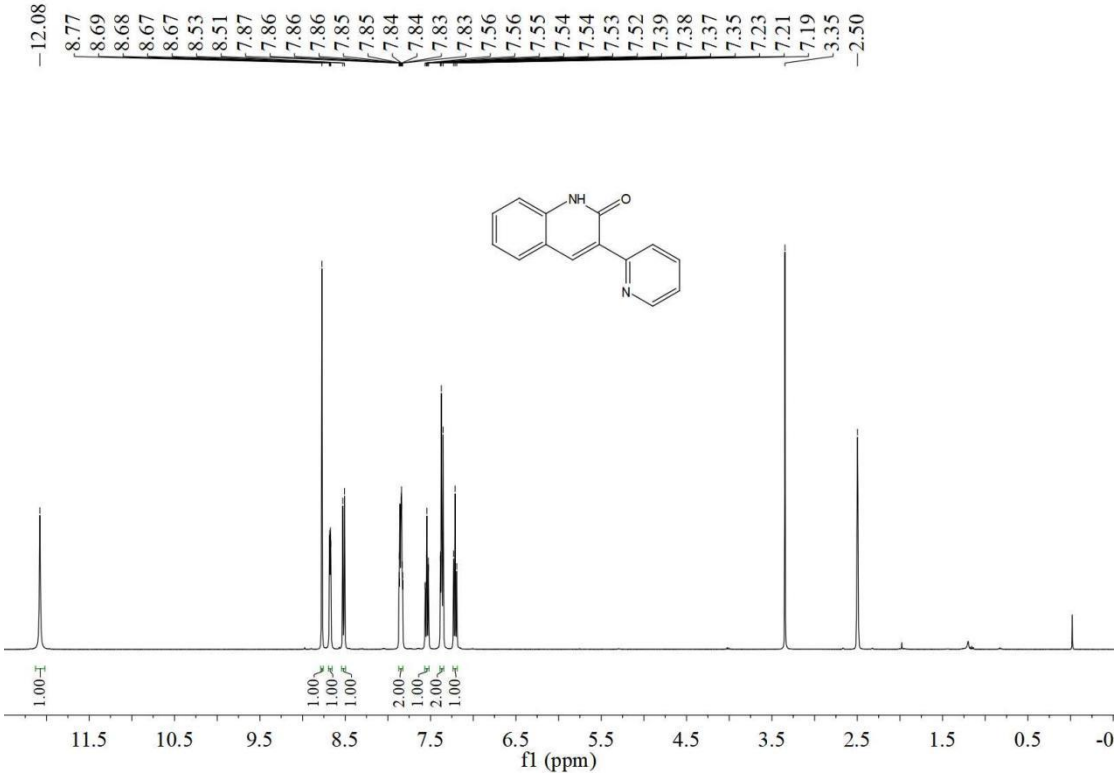


^{13}C NMR (100 MHz, DMSO-*D6*)

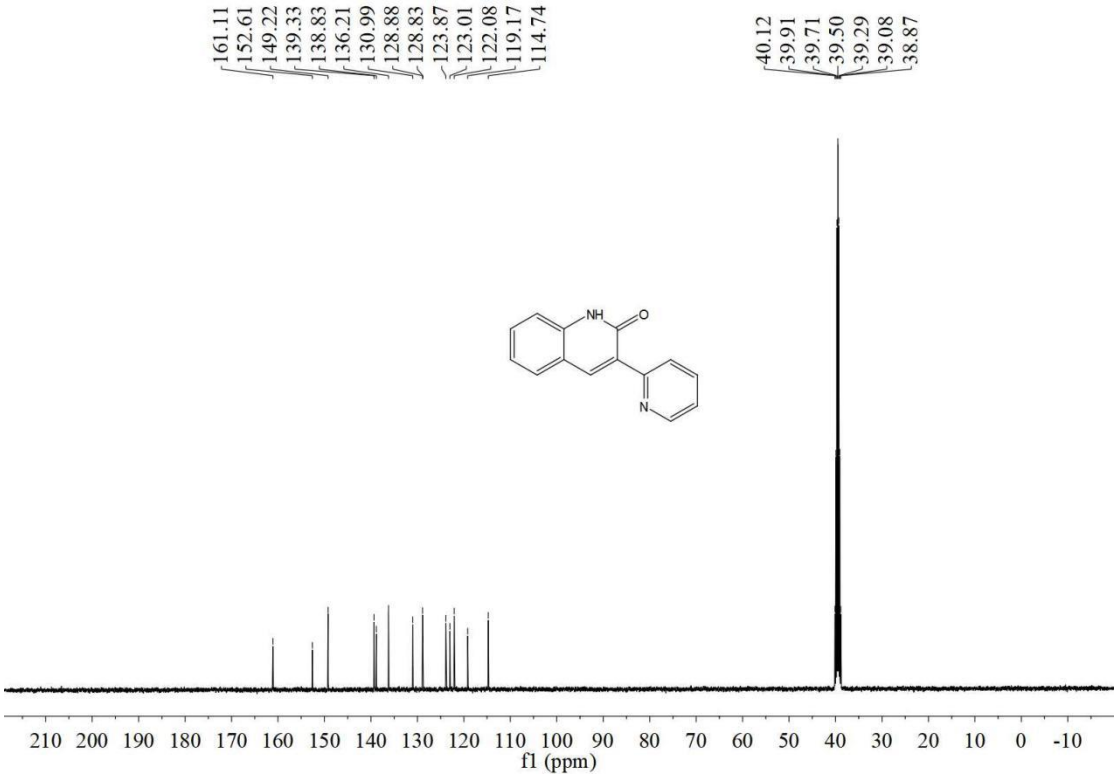


3-(*P*yridin-2-yl)quinolin-2(1H)-one **(8b)**

^{1}H NMR (400 MHz, DMSO-*D6*)

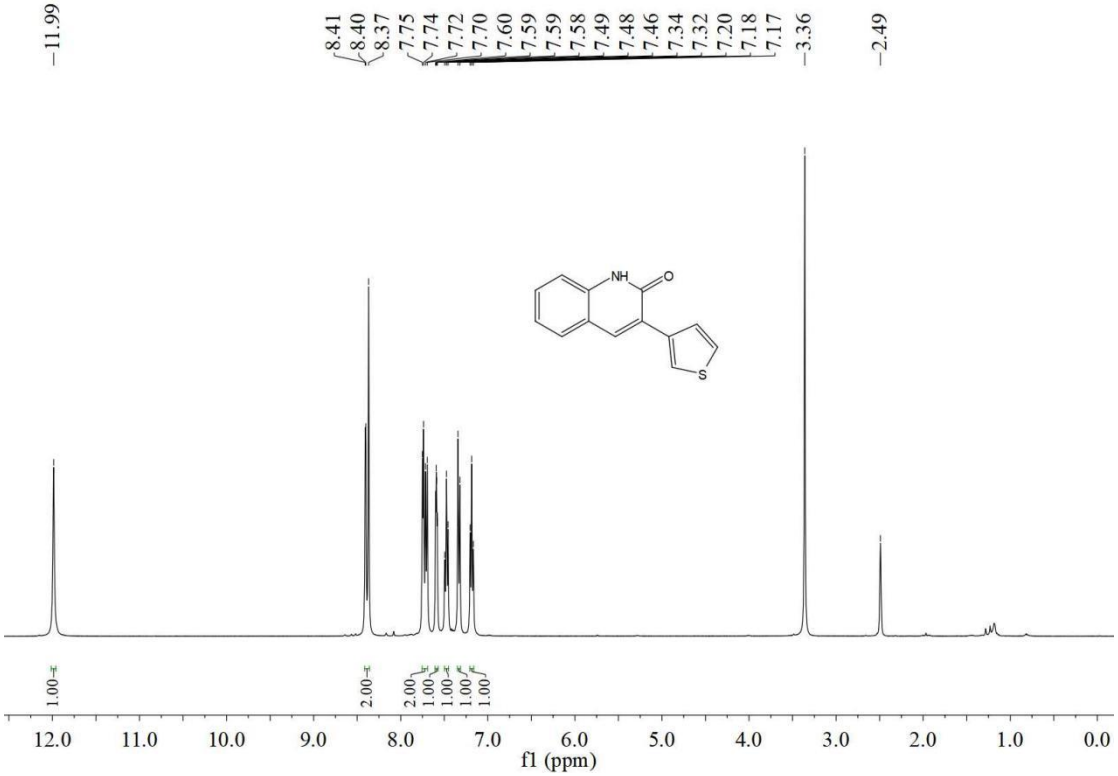


^{13}C NMR (100 MHz, DMSO-*D6*)

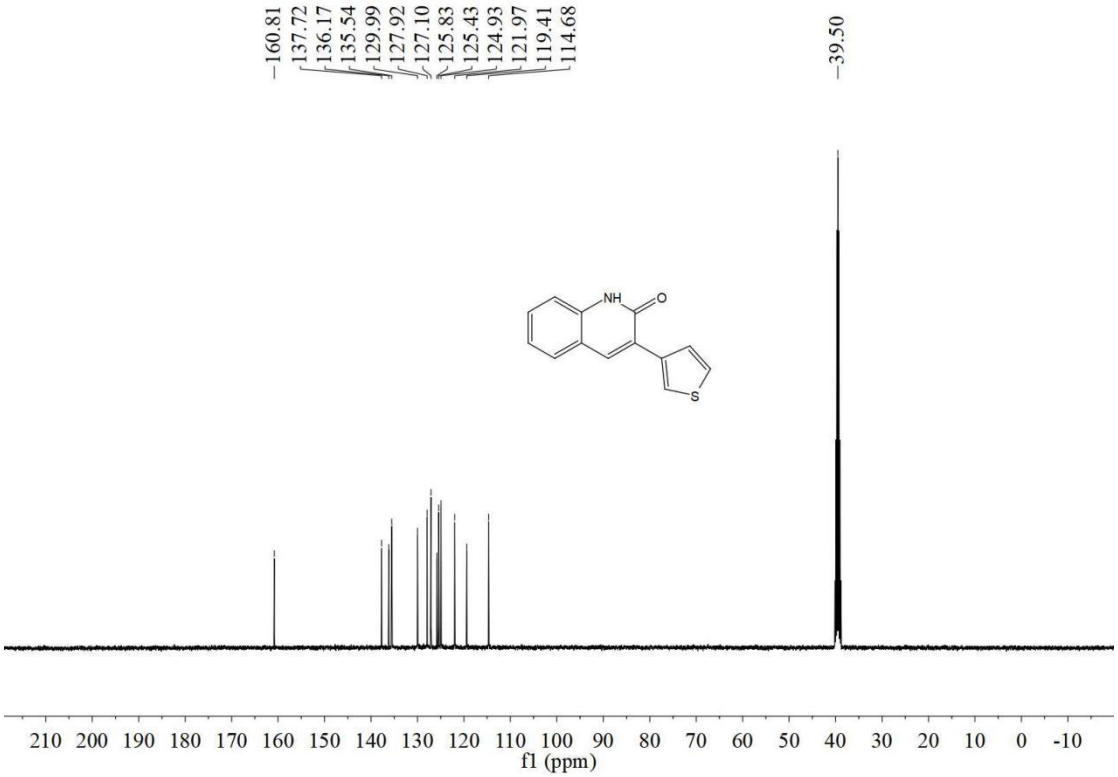


3-(Thiophen-3-yl)quinolin-2(1H)-one **(8c)**

^{1}H NMR (400 MHz, DMSO-*D6*)

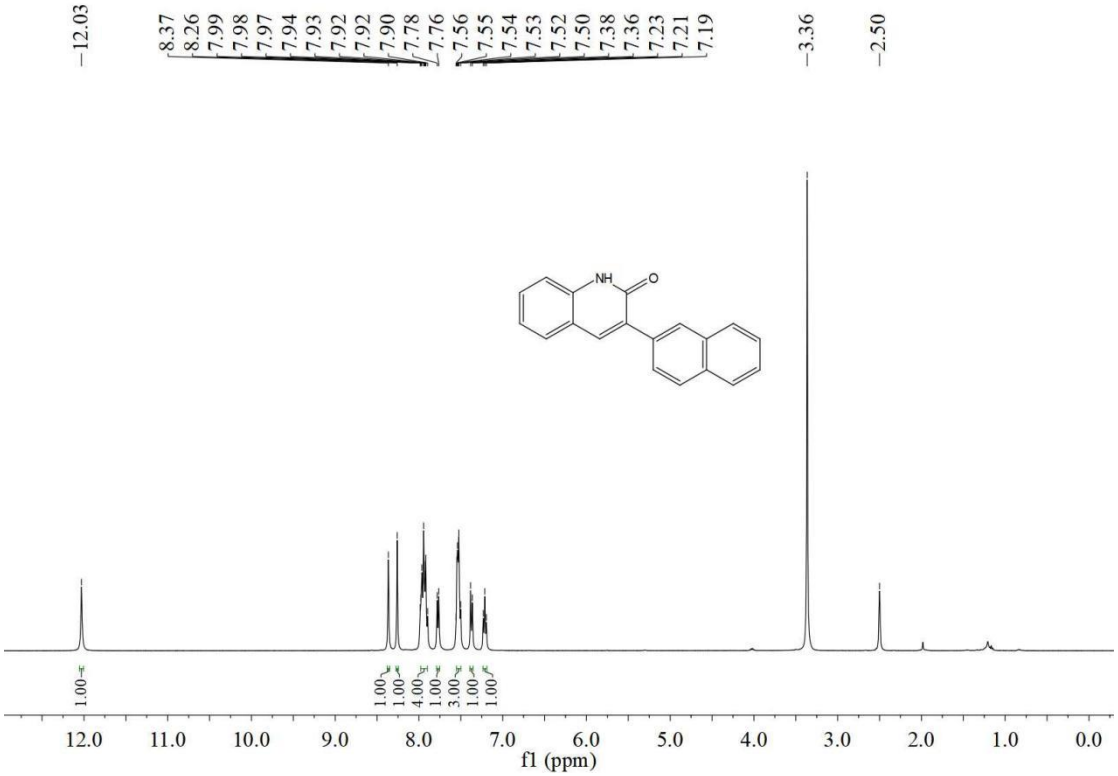


^{13}C NMR (100 MHz, DMSO-*D6*)

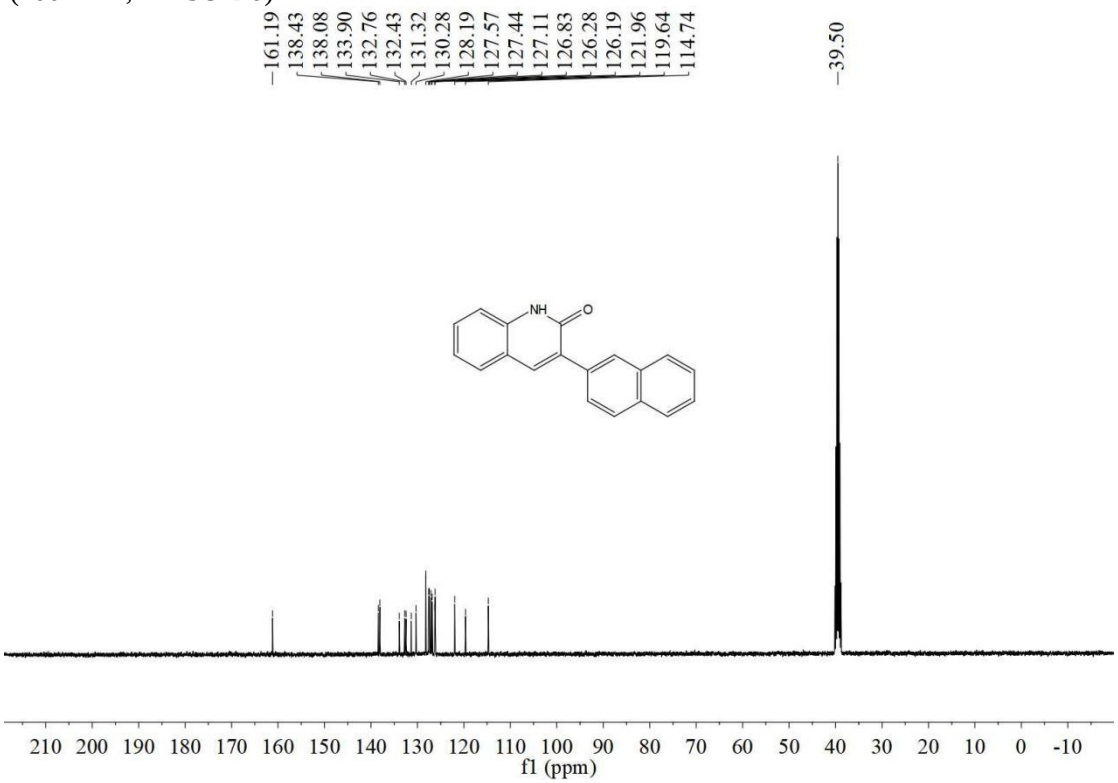


3-(Naphthalen-2-yl)quinolin-2(1H)-one **(8d)**

^{1}H NMR (400 MHz, DMSO-*D6*)

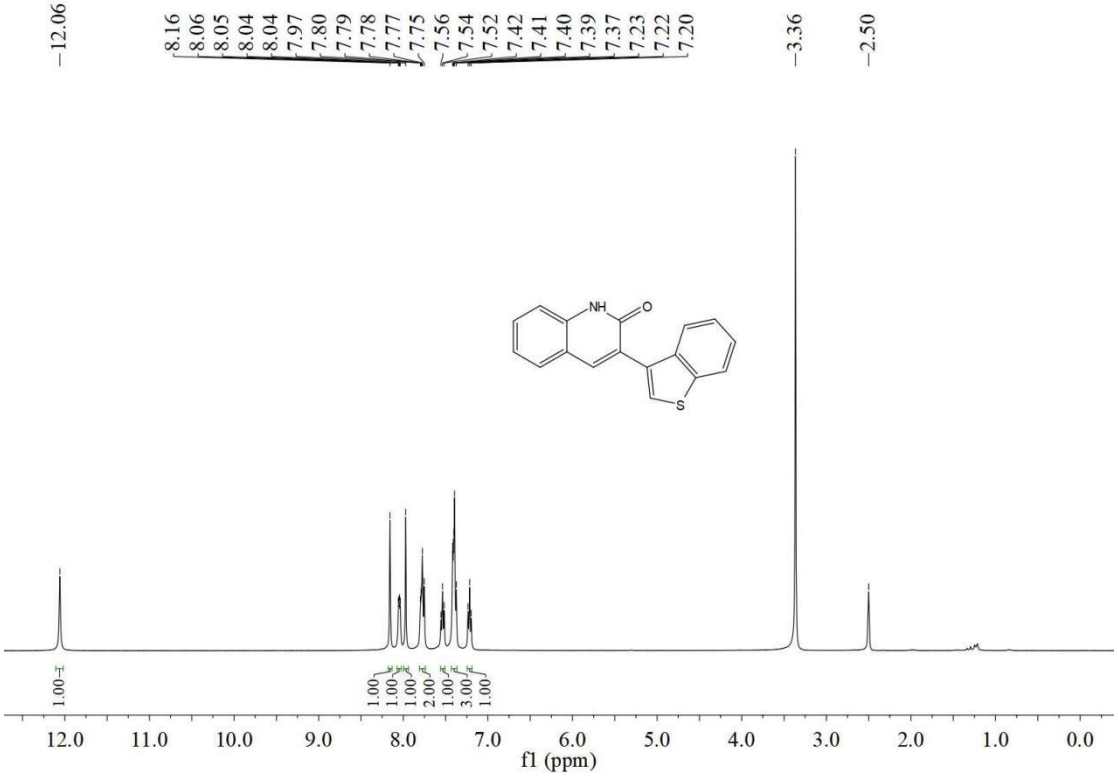


^{13}C NMR (100 MHz, DMSO-*D6*)

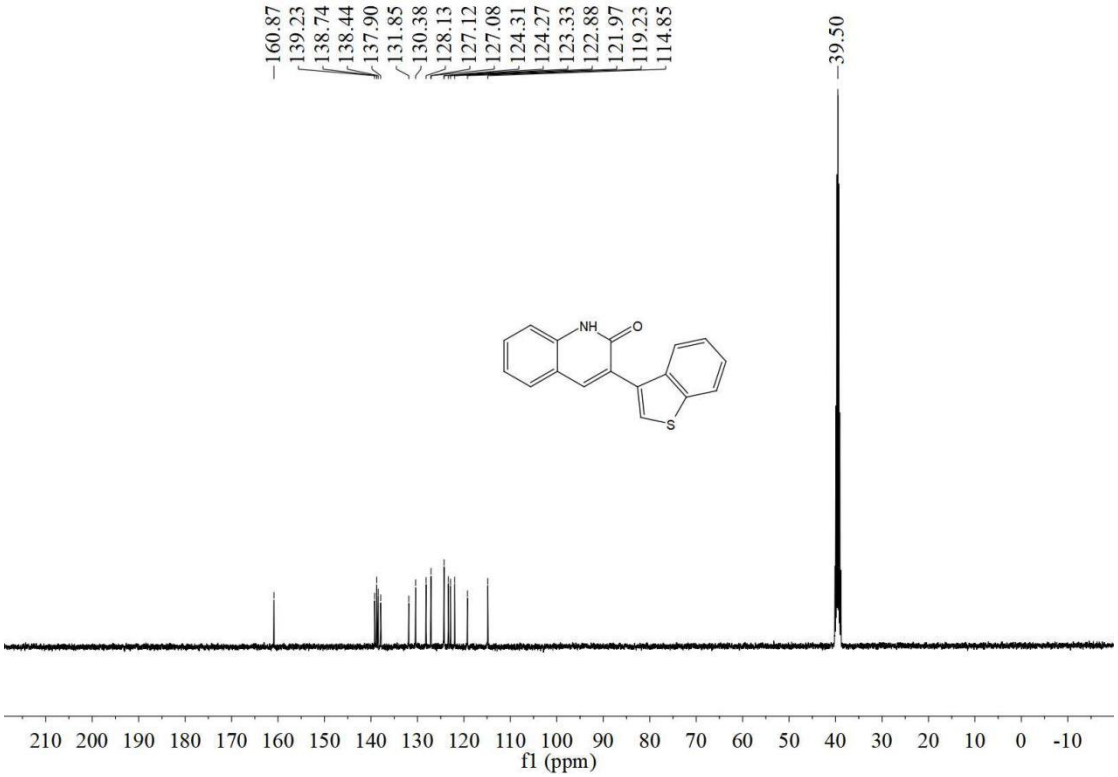


3-(Benzo[b]thiophen-3-yl)quinolin-2(1H)-one **(8e)**

^{1}H NMR (400 MHz, DMSO-*D6*)

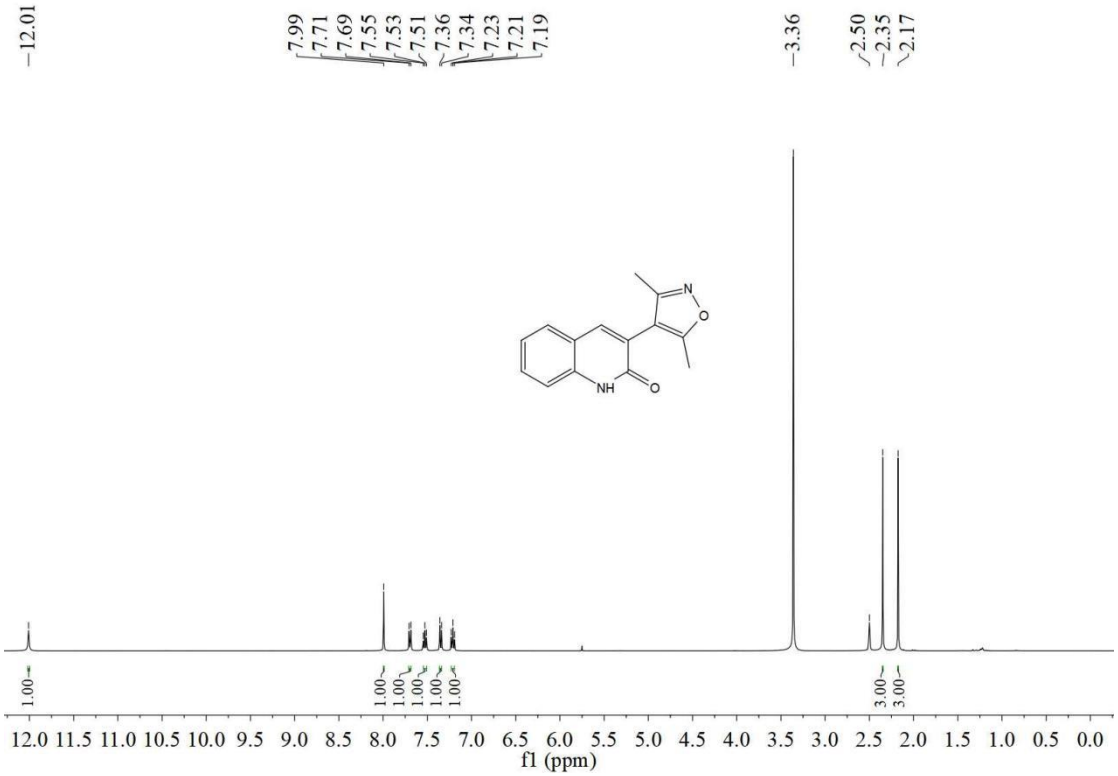


^{13}C NMR (100 MHz, DMSO-*D6*)

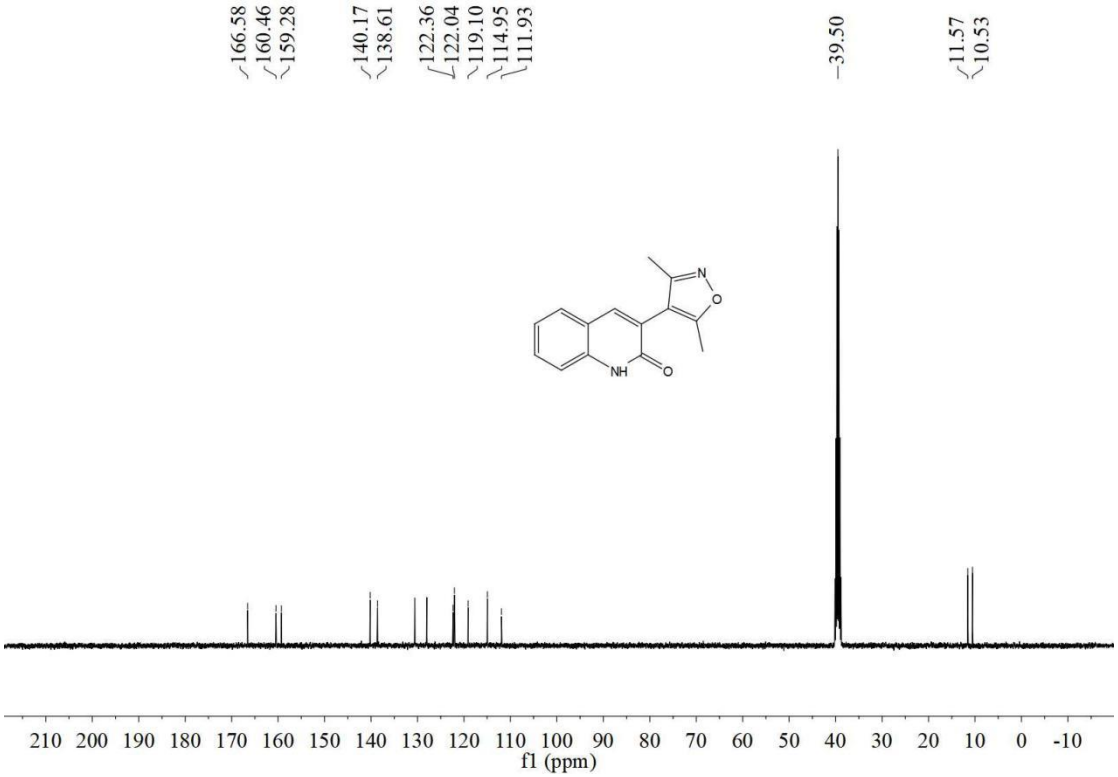


3-(3,5-Dimethylisoxazol-4-yl)quinolin-2(1H)-one **(8f)**

^{1}H NMR (400 MHz, DMSO-*D6*)

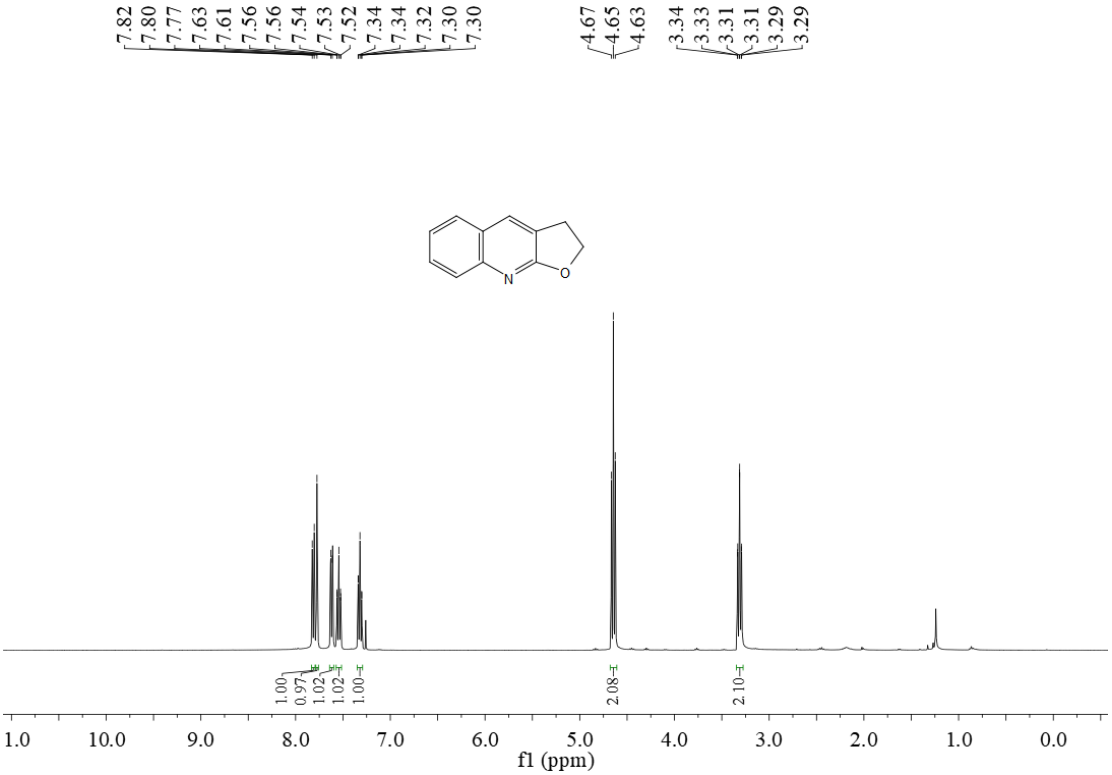


^{13}C NMR (100 MHz, DMSO-*D6*)

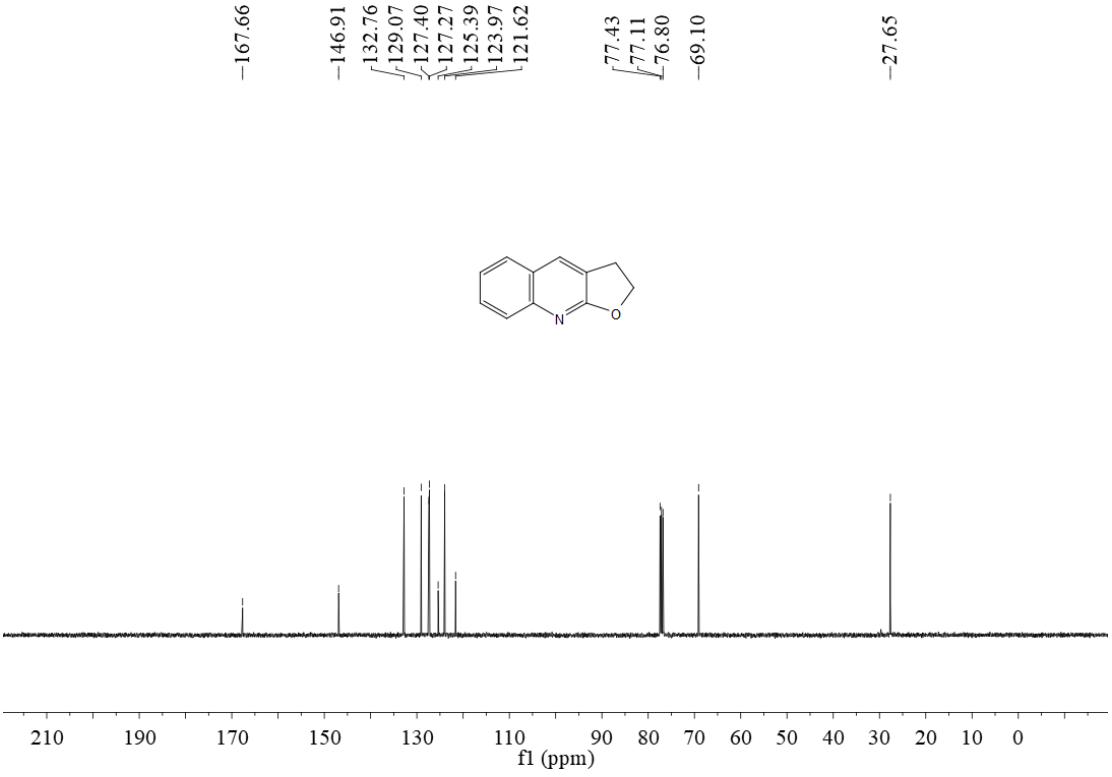


2,3-Dihydrofuro[2,3-b]quinolone **(9a)**

^{1}H NMR (400 MHz, $CDCl_3$)

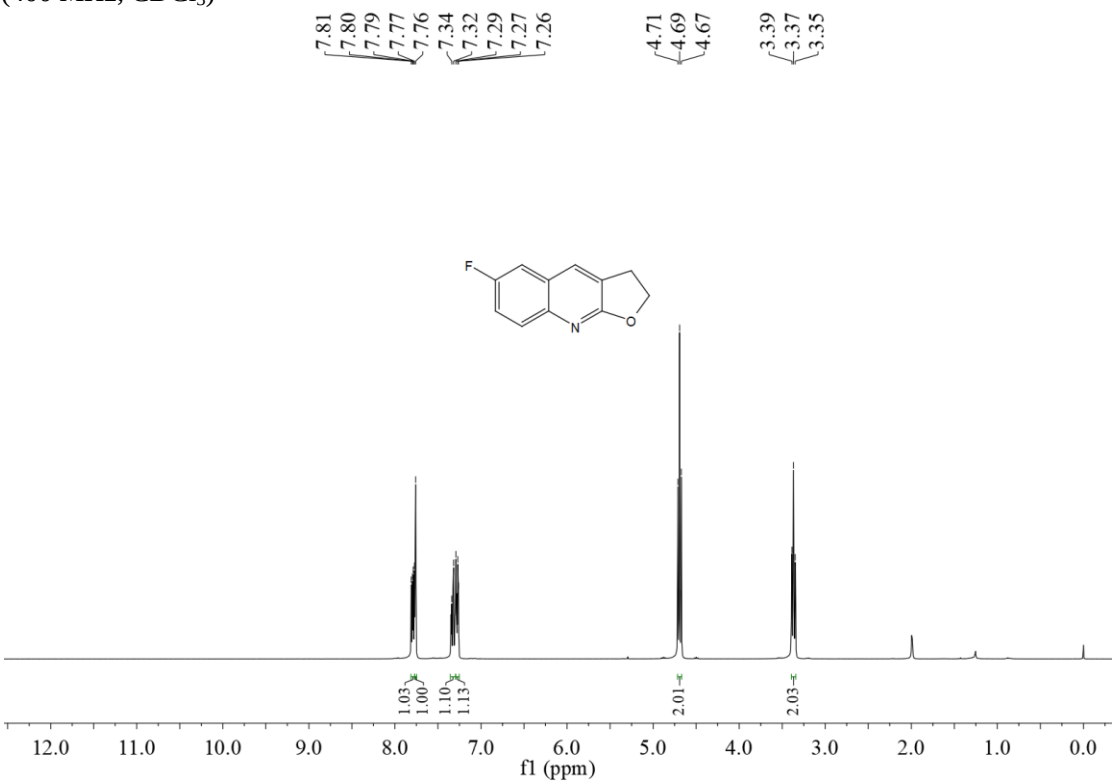


^{13}C NMR (100 MHz, $CDCl_3$)

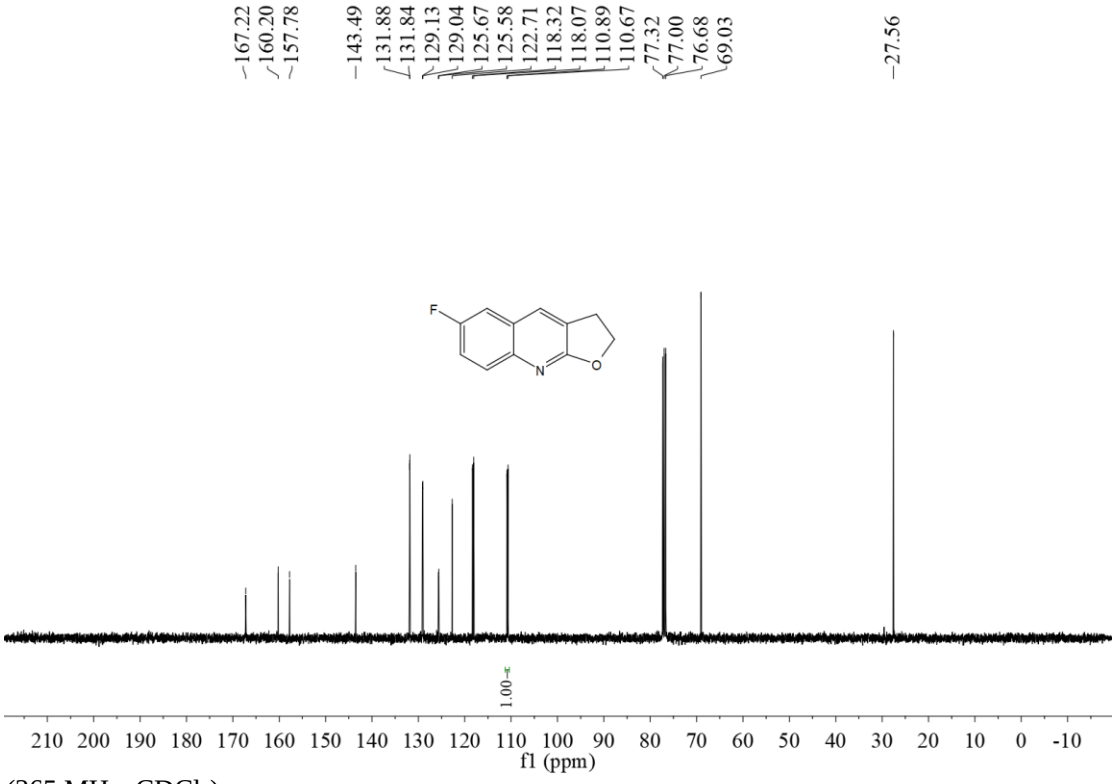


6-Fluoro-2,3-dihydrofuro[2,3-b]quinoline (**9b**)

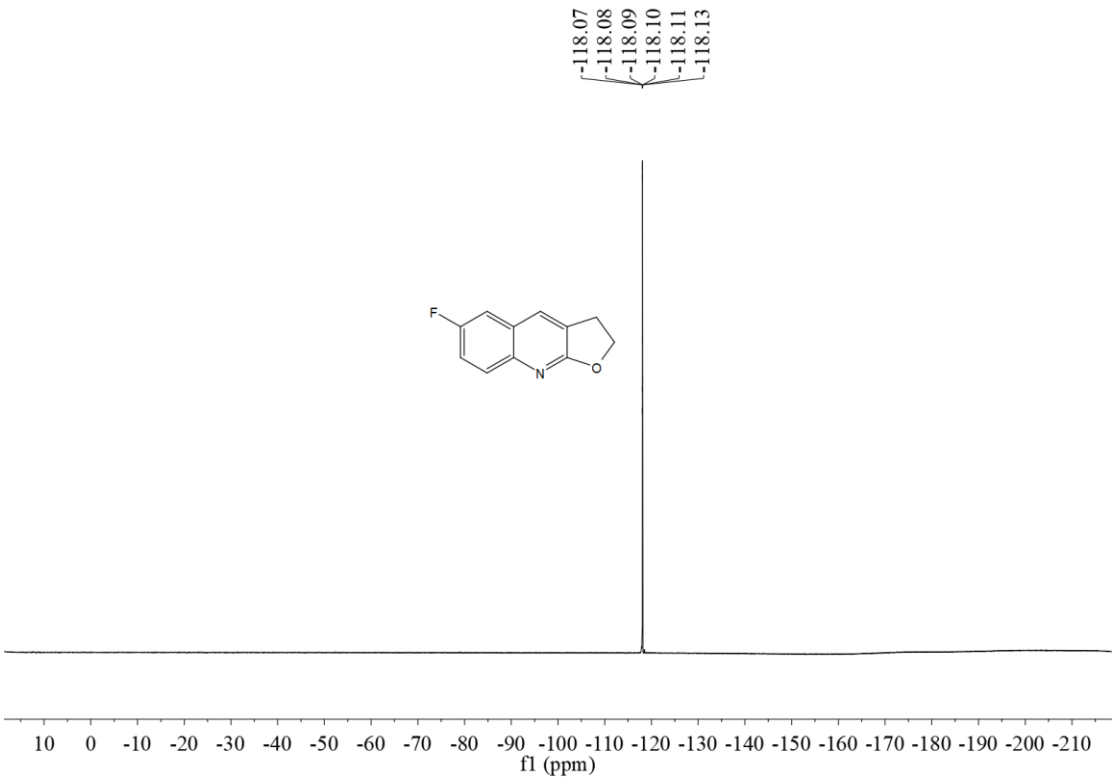
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

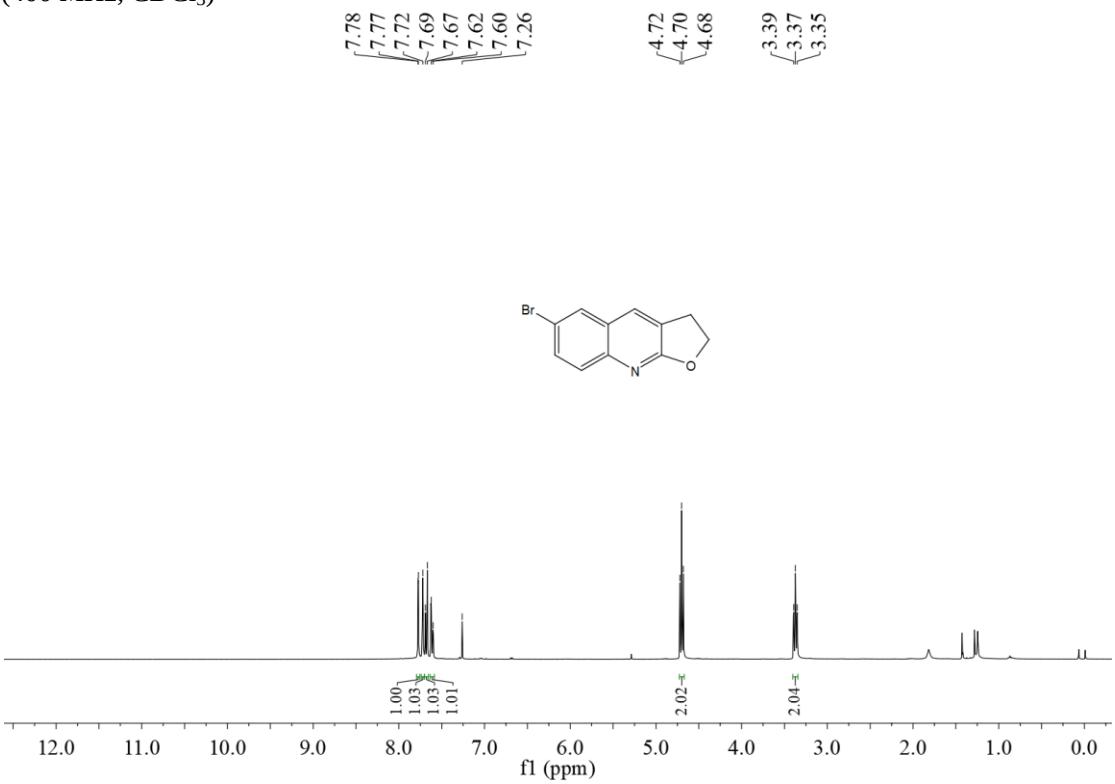


^{19}F NMR (365 MHz, $CDCl_3$)

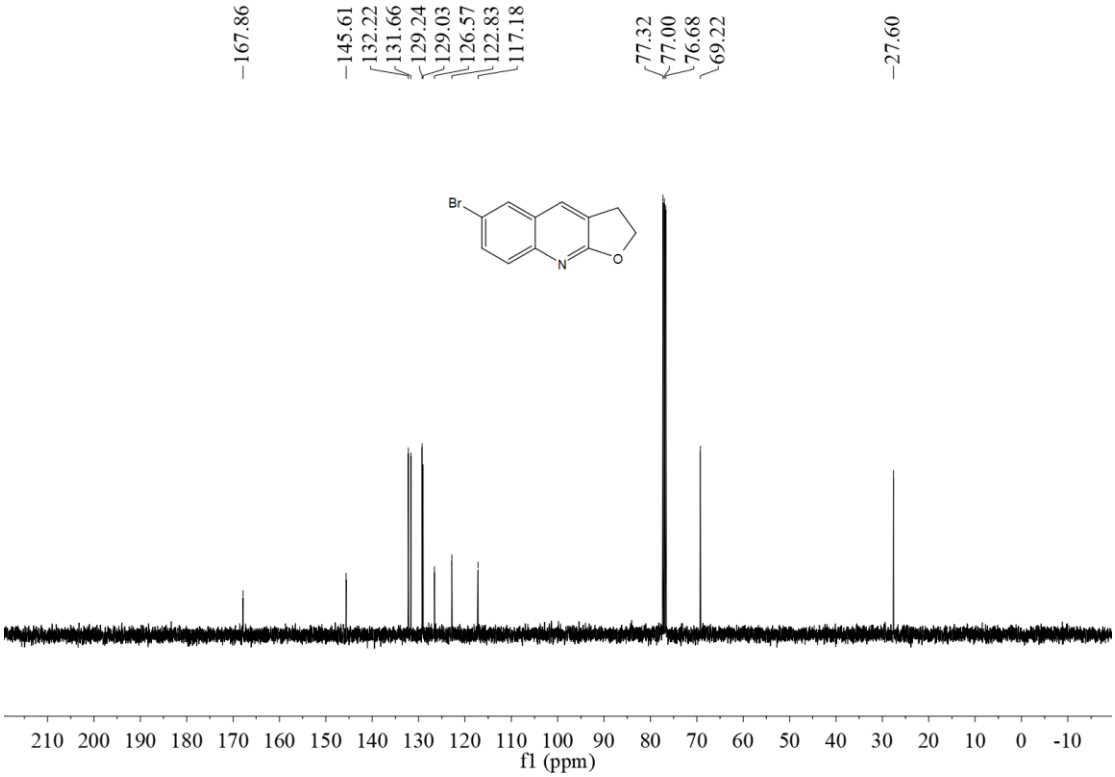

-118.07
-118.08
-118.09
-118.10
-118.11
-118.13
F
N
O
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

6-Bromo-2,3-dihydrofuro[2,3-b]quinoline (**9c**)

^{1}H NMR (400 MHz, $CDCl_3$)

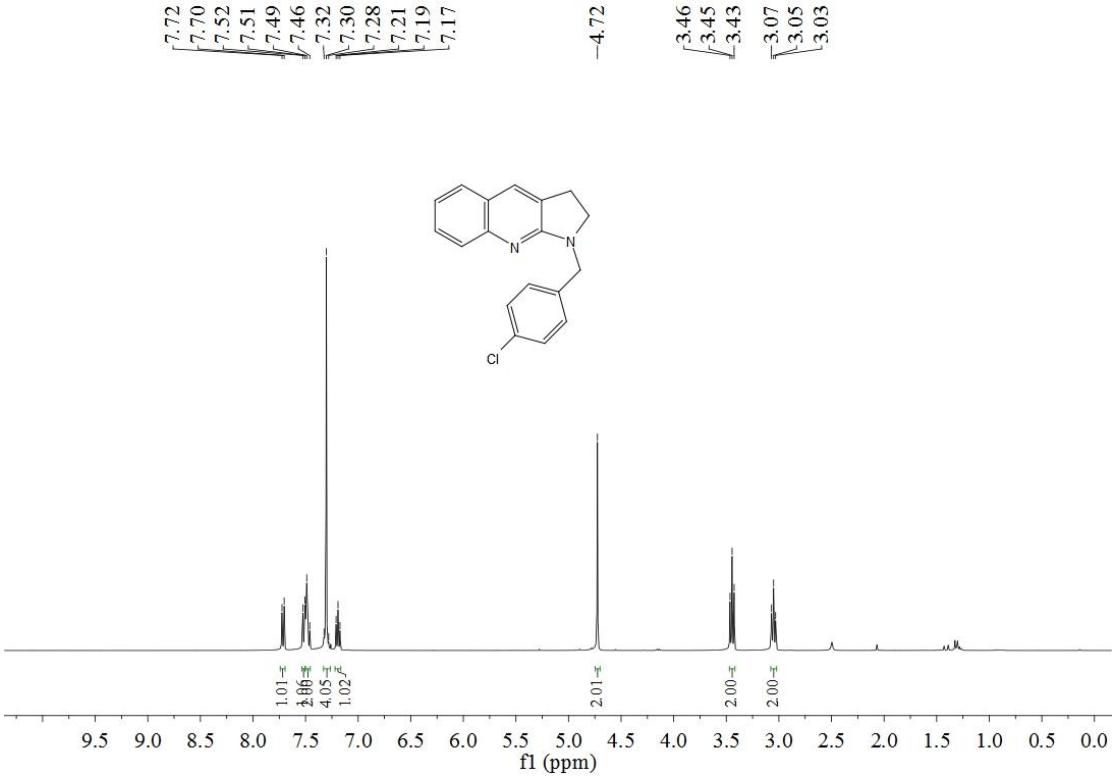


^{13}C NMR (100 MHz, $CDCl_3$)

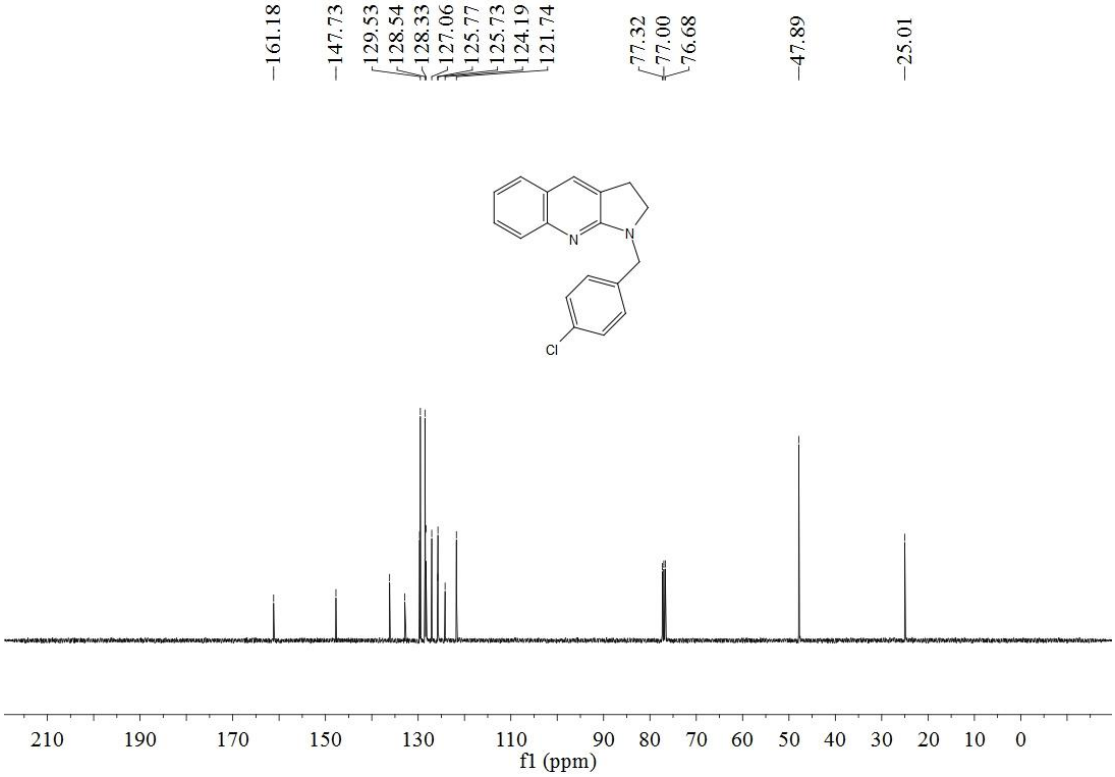


1-(4-Chlorobenzyl)-2,3-dihydro-1H-pyrrolo[2,3-b]quinoline (**9d**)

^{1}H NMR (400 MHz, $CDCl_3$)

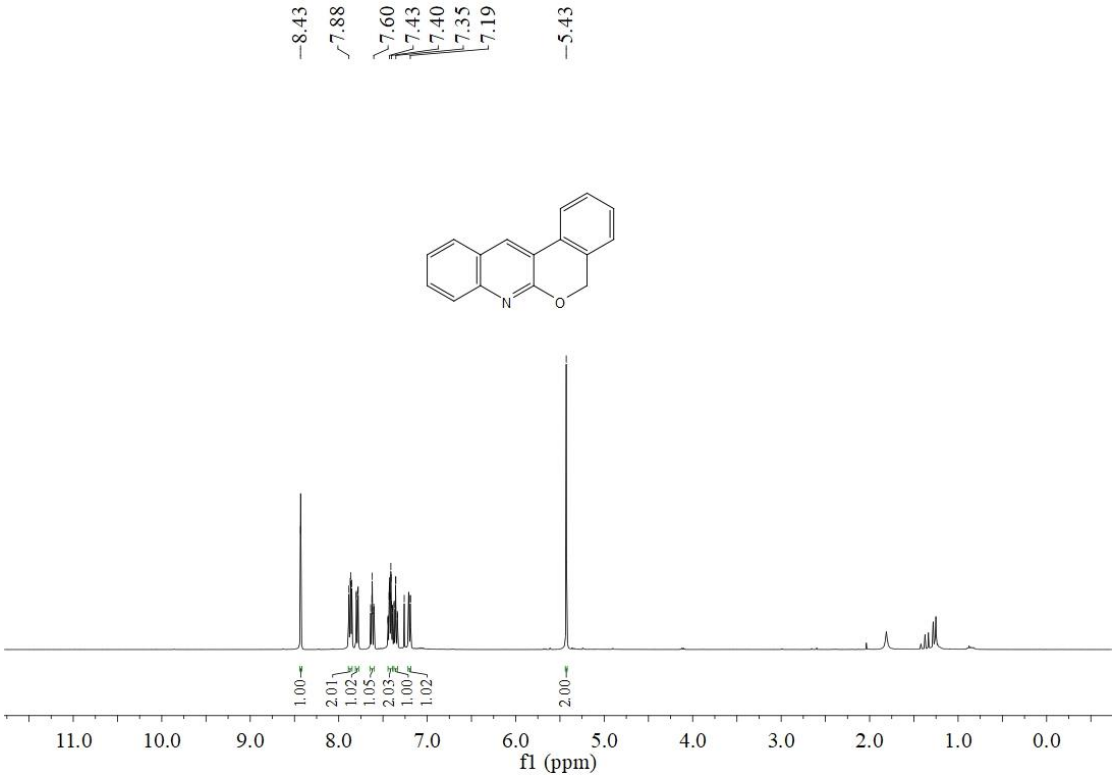


^{13}C NMR (100 MHz, $CDCl_3$)

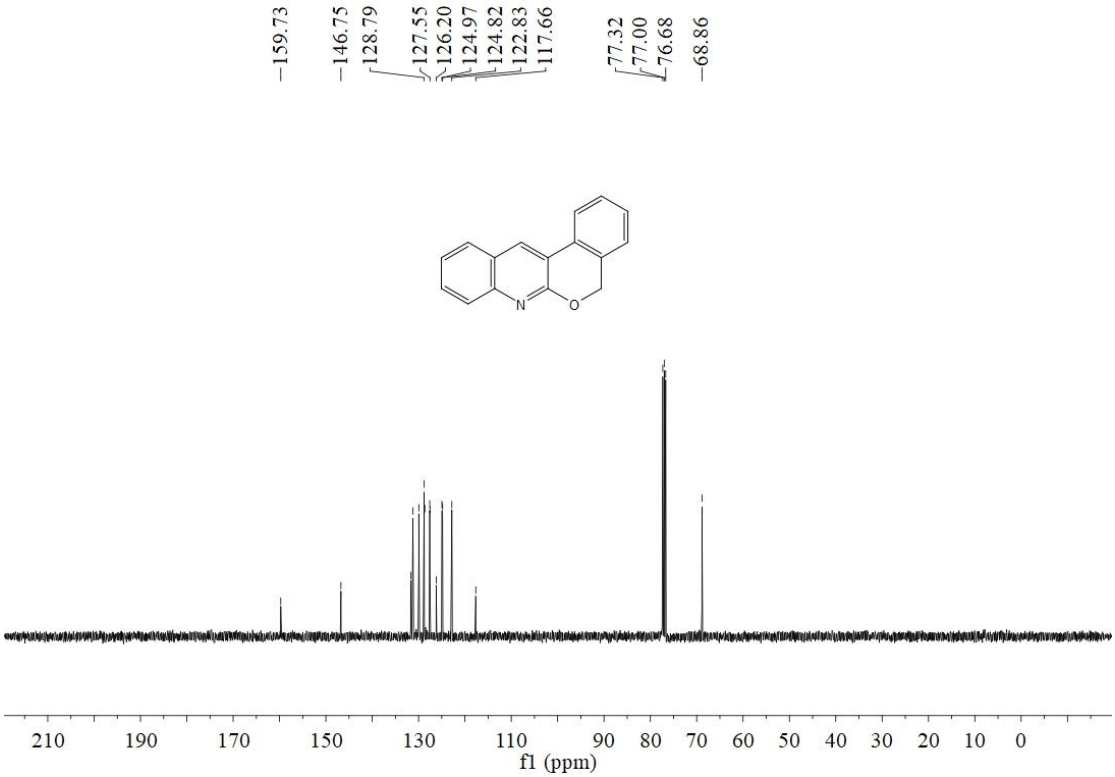


5*H*-Isochromeno[3,4-b]quinolone (**9e**)

^{1}H NMR (400 MHz, $CDCl_3$)

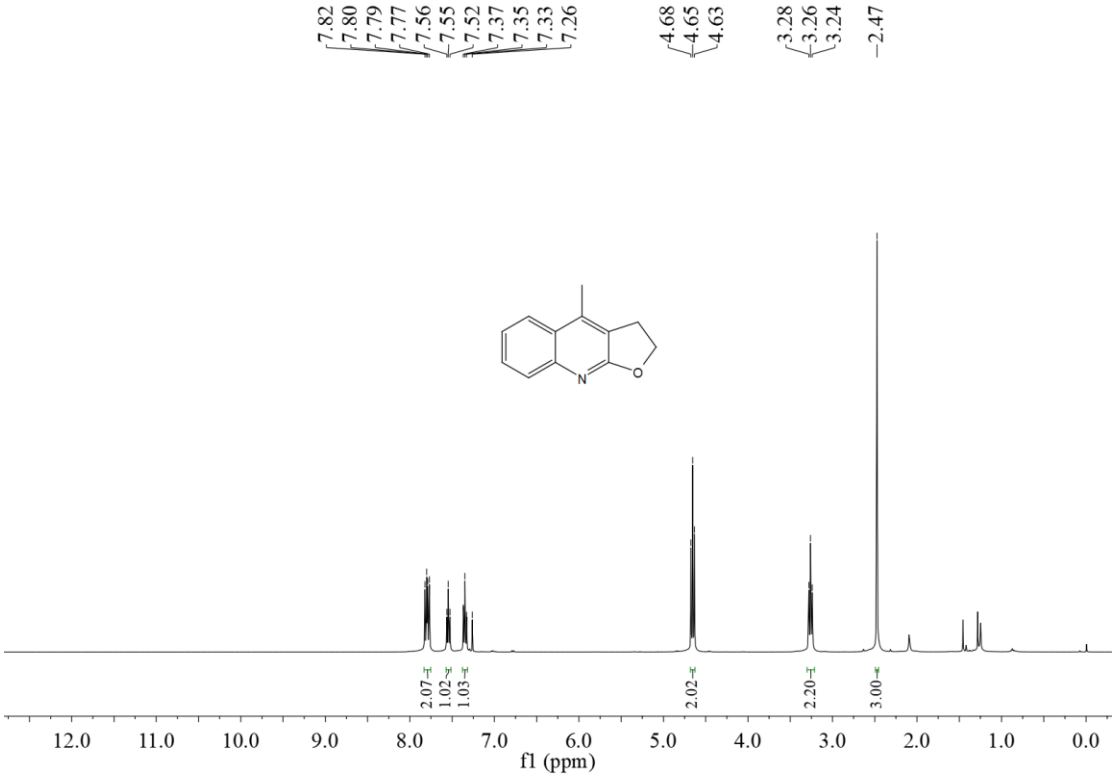


^{13}C NMR (100 MHz, $CDCl_3$)

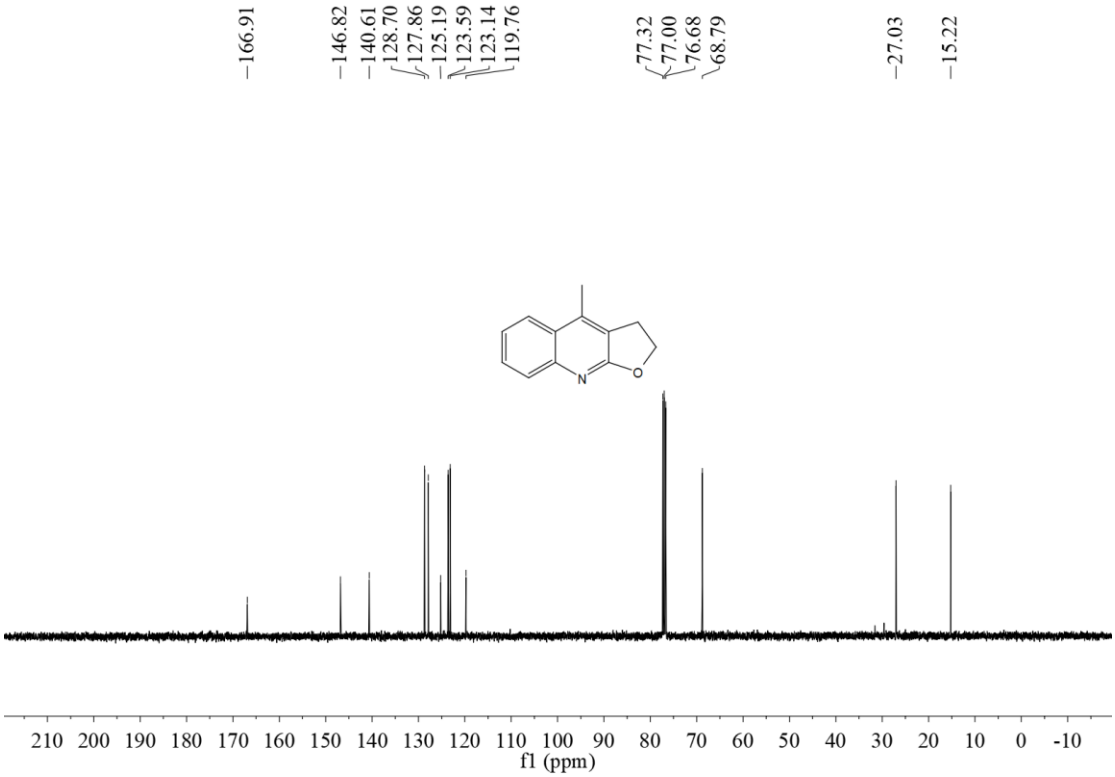


4-Methyl-2,3-dihydrofuro[2,3-b]quinoline (**9f**)

^{1}H NMR (400 MHz, $CDCl_3$)

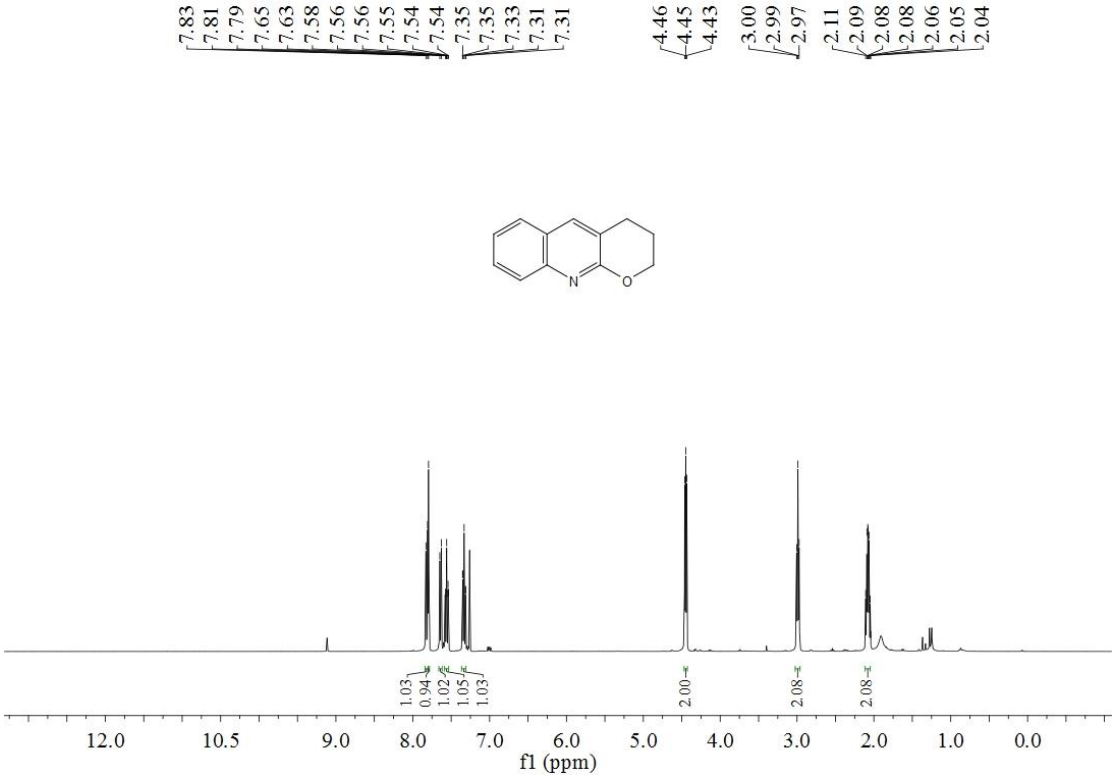


^{13}C NMR (100 MHz, $CDCl_3$)

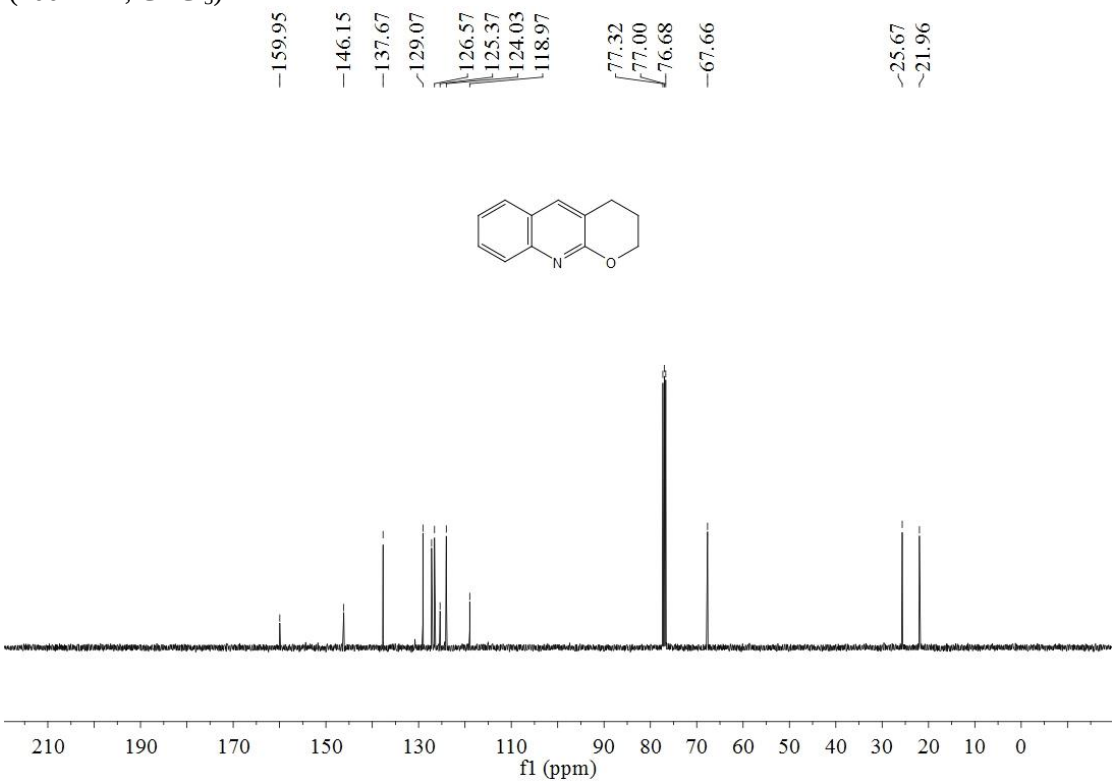


3,4-Dihydro-2H-pyrano[2,3-b]quinolone (**9g**)

^{1}H NMR (400 MHz, $CDCl_3$)

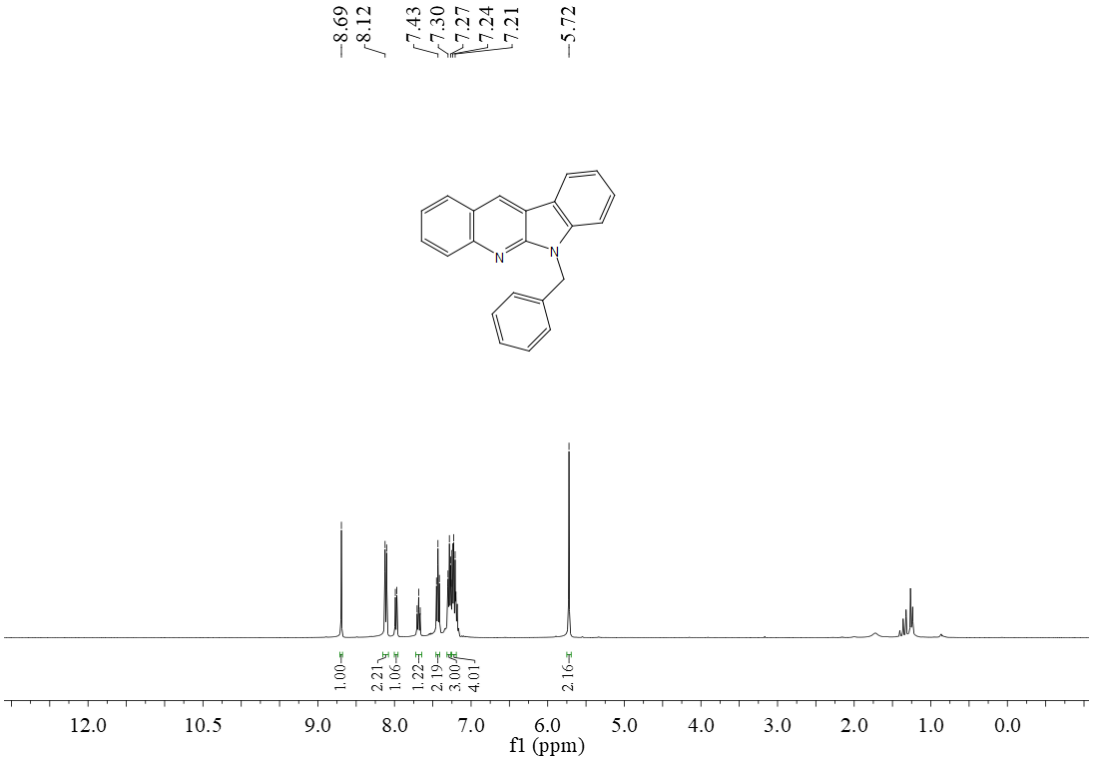


^{13}C NMR (100 MHz, $CDCl_3$)

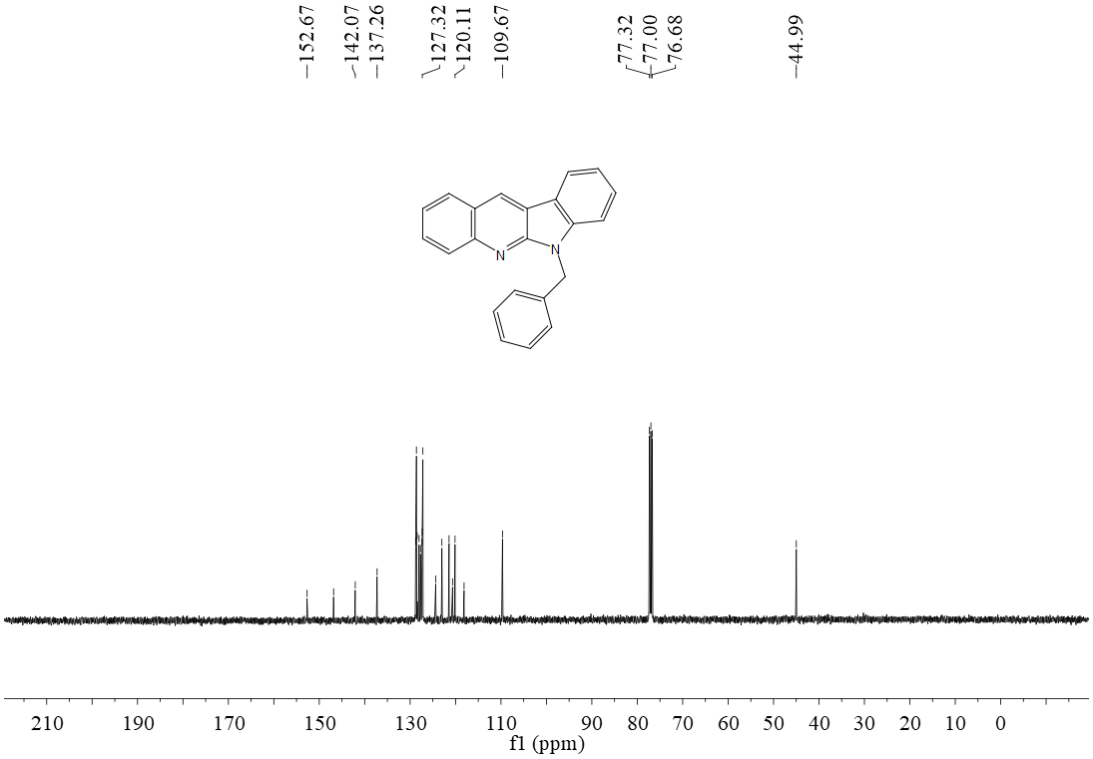


6-Benzyl-6H-indolo[2,3-b]quinoline (**10**)

^{1}H NMR (400 MHz, $CDCl_3$)

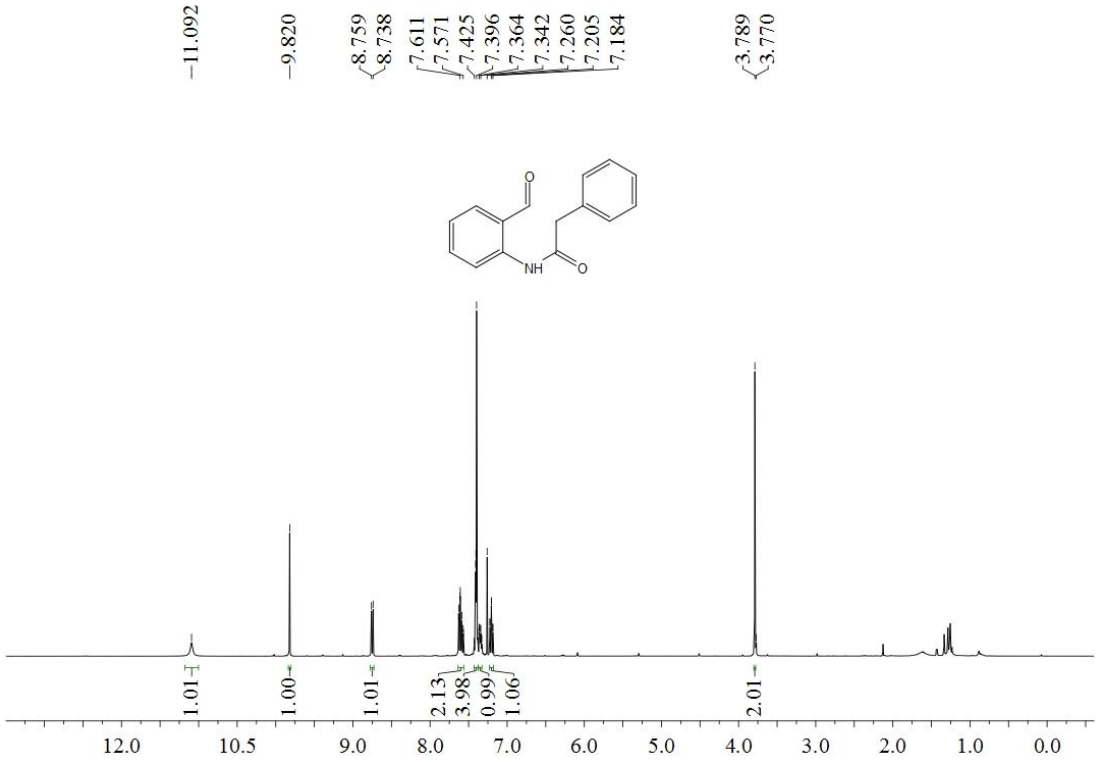


^{13}C NMR (100 MHz, $CDCl_3$)

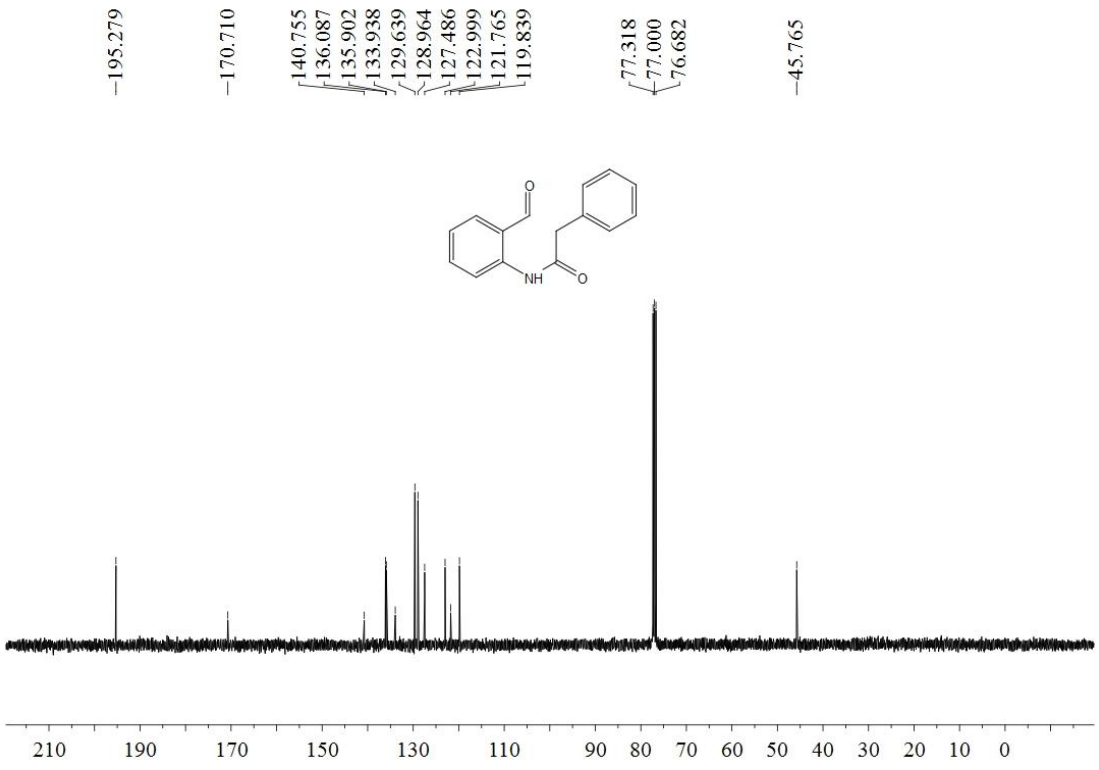


N-(2-formylphenyl)-2-phenylacetamide (**11**)

^{1}H NMR (400 MHz, $CDCl_3$)

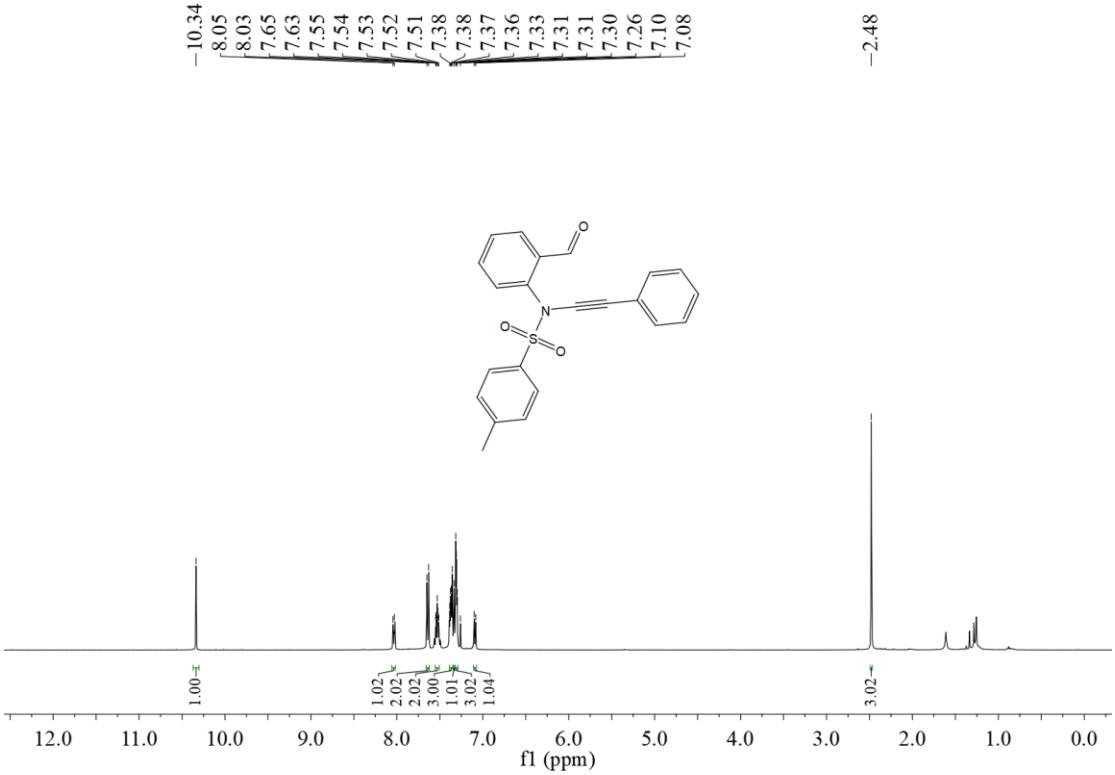


^{13}C NMR (100 MHz, $CDCl_3$)

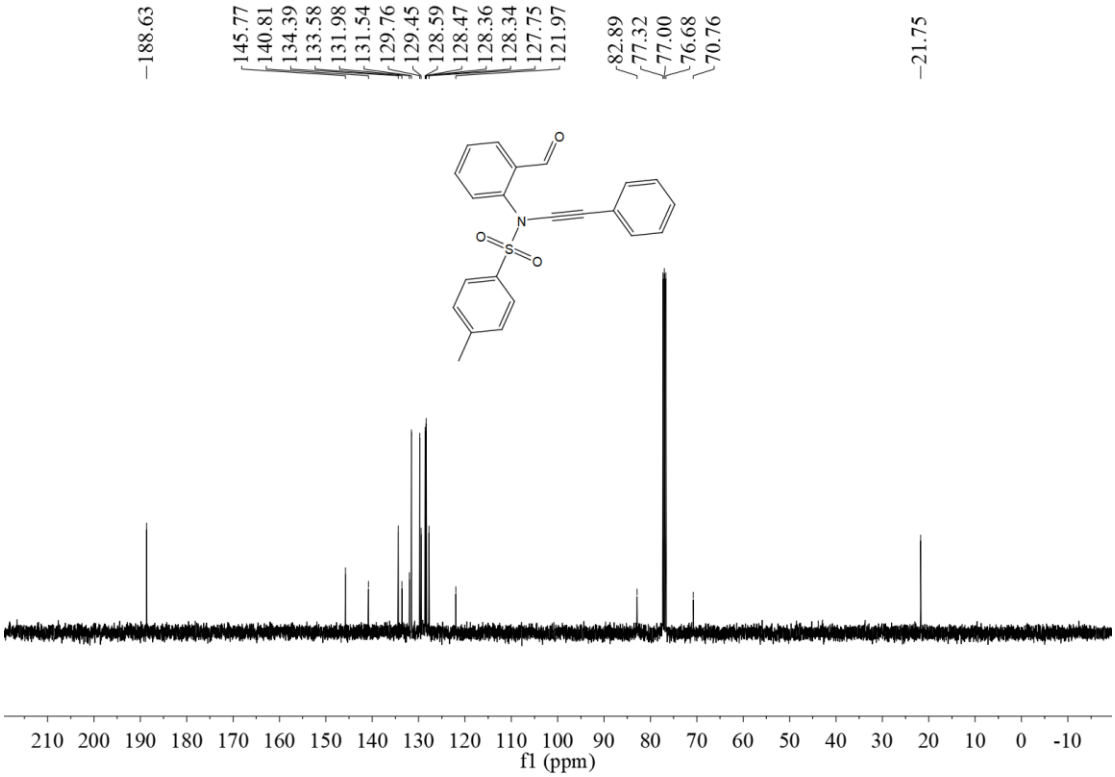


N-(2-Formylphenyl)-4-methyl-N-(phenylethynyl)benzenesulfonamide (**12**)

^{1}H NMR (400 MHz, $CDCl_3$)

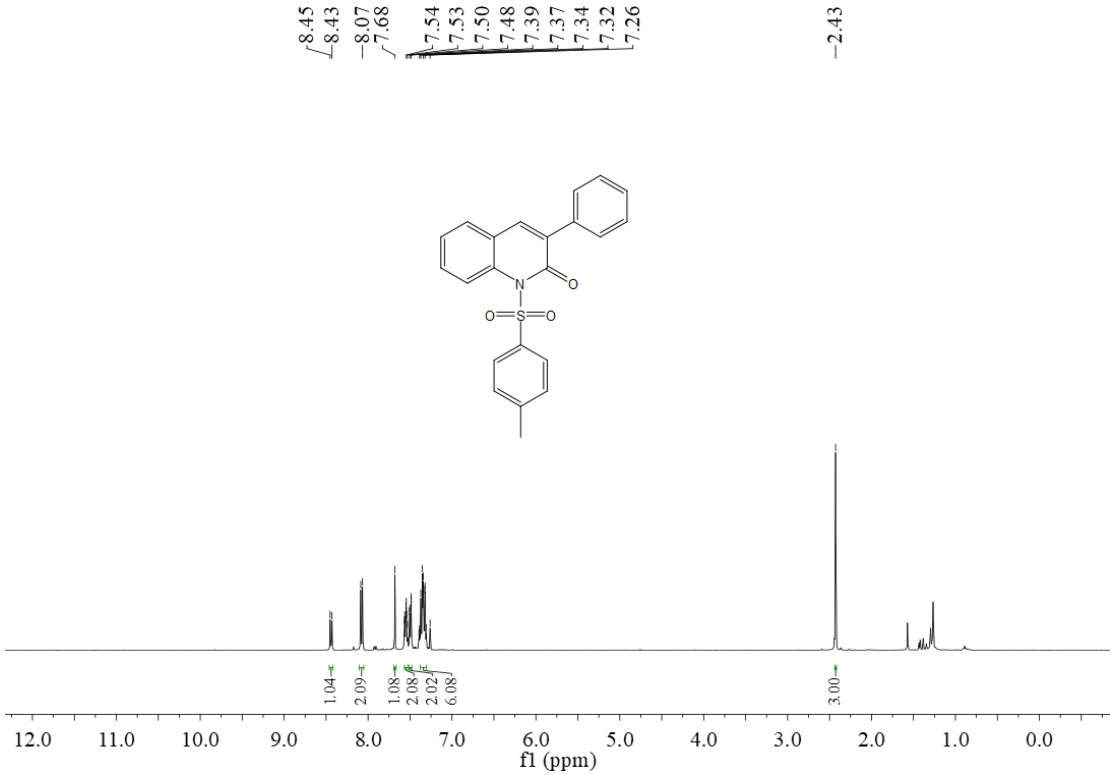


^{13}C NMR (100 MHz, $CDCl_3$)

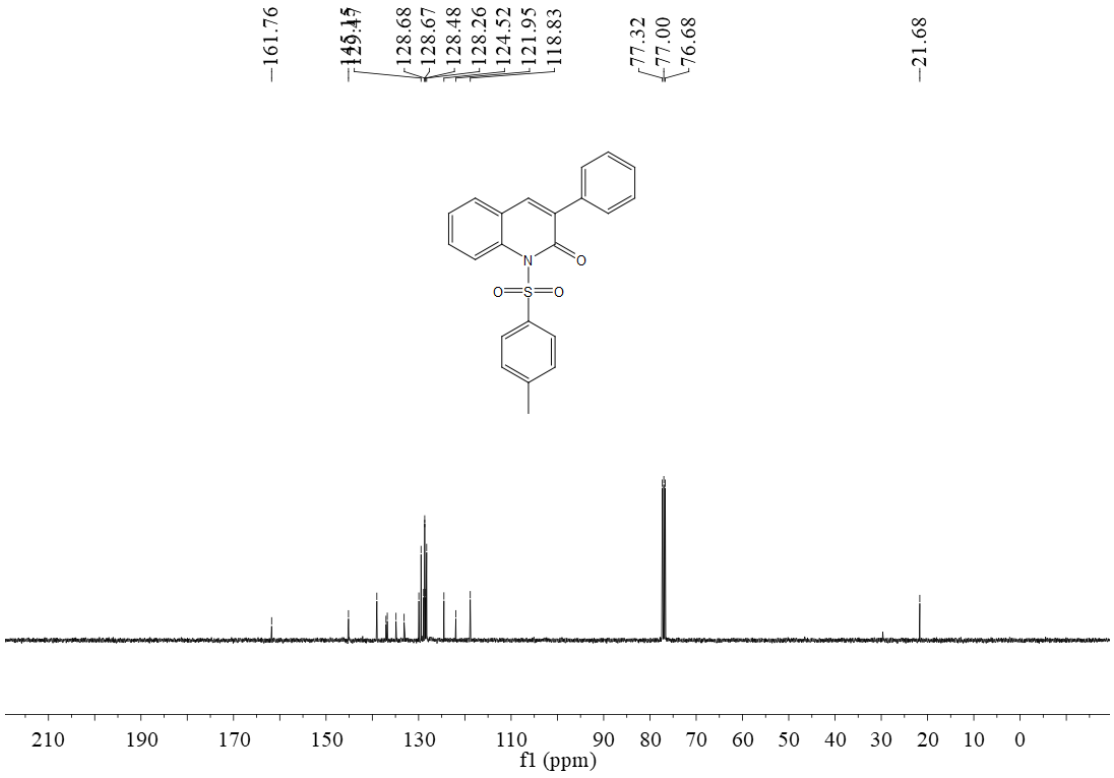


3-Phenyl-1-tosylquinolin-2(1H)-one (**13**)

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



2-((Triphenyl-λ^5-phosphanylidene)amino)benzaldehyde (**14**)

^{1}H NMR (400 MHz, $CDCl_3$)