A Sustainable Approach for Nickel Nanoparticles Synthesis: An Expeditious Access to *N*-heterocycles under Heterogeneous Condition and its Photo physical studies

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1.0. General considerations

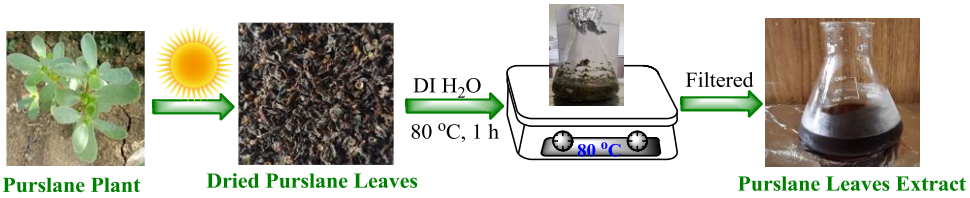
Unless otherwise specified, the presence of phytochemicals in Purslane extract was analysed using GC-MS data which was performed in SHIMADZU GC-MS QP 2010SE system. UV-Visible analysis was carried out with the help of PerkinElmer Lambda 360 UV-Visible spectrophotometer. The crystallographic nature and the phase of the Ni-NPs was examined and confirmed using powder X-ray diffraction spectroscopy (*P*-XRD) noted on a Rigaku X-Ray Diffraction Ultima IV (Rigaku Corporation, Japan) X-ray diffractometer using Ni filtered Cu Kα radiation (λ = 1.5406 Å) with a scan rate of 3º min^{-1} and theta value range of 0- 80° at 30 kV voltage and 15 mA current. The oxidation state and elemental composition of the synthesized Ni-NPs are confirmed by X-ray photoelectron spectroscopy (XPS) noted on AXIS ULTRA DLD, KRATOS System with 200 um spot size. The surface area analysis of Ni-NPs was performed using Brunauer Emmet and Teller (BET) method on Belsorp-Max (M/s. Microtrac BEL, Japan) under N_2 atmosphere at a temperature of -196 ºC. The corresponding pore size distribution of the catalysts was analysed using Barrett Joyner Halenda (BJH) method. The catalyst was degassed at 80 ºC for 2h under vacuum prior to analysis in order to push out absorbed moisture. The thermal degradation of Ni-NPs was determined by a thermal analyser within the temperature window of 26 ºC to 900 ºC under continuous N_2 flow with a heating rate of 10 ºC min^{-1}.The surface morphology of Ni-NPs was investigated using Field Emission Scanning Electron Microscope (JEOL JSM-7100F, Singapore). The carbon tape on the aluminium metal stub was adequately covered with the powdered sample and subjected to sputtering using gold nanoparticles. To know more information about size, shape and surface morphology of Ni-NPs was investigated using HR-TEM analysis. The nickel content in Ni-NPs was estimated through ICP-OES technique. The gas chromatogrphy was performed in GC-7820 A; M/S Agilent, USA equipped with a flame ionization detector (FID) having a capillary column (HP-5, 19091J-413) of 30 m length, 0.32 mm inner diameter and 0.25 mm film thickness. All reactions were carried out in oven dried vials or sealed tubes with magnetic stirring under air atmosphere. All other reagents were directly used as purchased without further purification unless otherwise specified. All experiments were monitored by analytical thin layer chromatography (TLC) on pre-coated silica gel 60 F254 plates. Visualization on TLC was achieved by the use of UV light (254 nm). Column chromatography was undertaken on silica gel (60–120 mesh) using a proper eluent. Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak ($CHCl_3$ in $CDCl_3$: 7.26 ppm). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q),

and multiplet (m). ^{13}C {^{1}H} NMR was recorded on Agilent Technologies DD2 (100 MHz) and was fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the centre of a triplet at 77.0 ppm of $CDCl_3$. All analytical and spectral data are given for newly synthesized products while for reported compounds; the corresponding references are cited.

2. Synthesis of Ni-NPs using Purslane leaves extract

2.1. Preparation of purslane leaves extract

Purslane (*Portulaca oleracea*) is collected from the local area Ballur, Bangalore rural, India and rinsed with distilled water for 3-4 times, cut into small pieces and dried under sunlight. Then, 10 g of the dried leaves was taken in 250 mL Erlenmeyer flask containing 100 mL of distilled water. The mixture was heated at 80 ^{o}C for 1 hour with stirring to extract the phytochemicals present in purslane leaves. Then mixture was cooled, the residues are removed by filtration, centrifuge and stored at 4 ^{o}C.



Scheme 1: Schematic representation for the preparation of Purslane leaves extract

2.2. Gas Chromatography –Mass Spectroscopic (GC-MS) Analysis of Purslane leaves extract:[S1]

Initially, the Purslane (*Portulaca oleracea*) leaves extract was subjected to GC-MS analysis to confirm the presence of phytochemicals (Table 1). This analysis depicts the percentage of phytochemicals present in the plant extract and helps to understand the role of different phytochemicals in the bio-reduction process. The GC-MS chromatogram of ethyl acetate extract of the purslane showed the qualitative presence of compounds having acid groups, OH, NH_2 etc are the major components present in it (**Table 1**) which is directly involved in bio-reduction process.

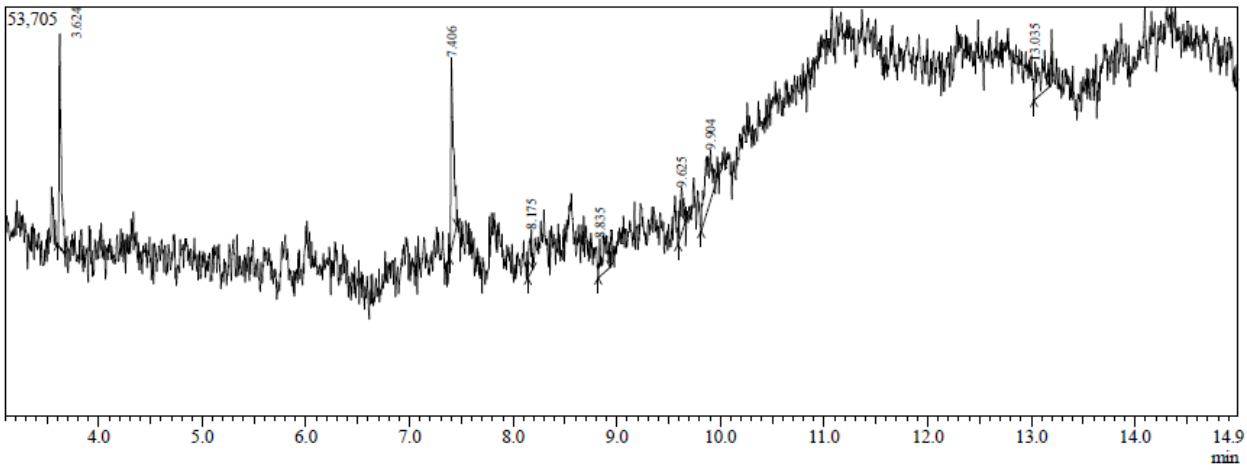
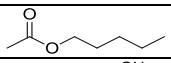
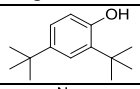
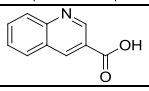
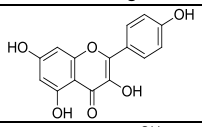
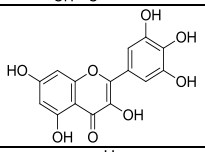
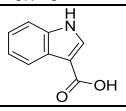
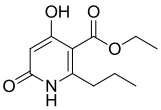
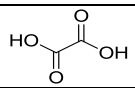
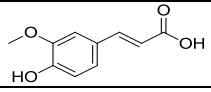


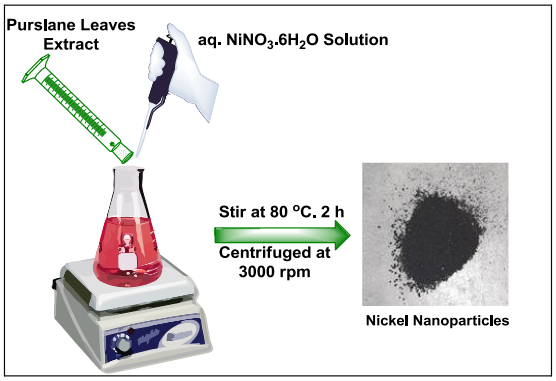
Table-1: Phytochemicals identification using GC–MS

Sl. No.	Retention time	Area percentage (%)	Molecular weight (g/mol)	Name of chemical	Structure
1.	3.624	21.29	130.19	Amyl acetate	
2.	7.406	23.67	206.32	2,4-di-tert-butylphenol	
3.	8.175	5.11	173.05	3-Quinoline carboxylic acid	
4.	8.835	9.80	287.05	Kaempferol	
5.	8.835	9.80	318.04	Myricetin	
6.	9.625	7.49	161.05	Indole-3-carboxylic acid	
7.	9.904	19.31	225.10	1,6-dihydro-4-hydroxy-6-oxo-2-propyl-, ethyl ester, Nicotinic acid	
8.	13.035	13.34	90.00	Oxalic acid	
9.	13.035	13.34	194.06	Ferulic acid	

2.3. Preparation of Ni-NPs using purslane leaves extract

An aqueous solution of 10 mL $Ni(NO_3)_2.6H_2O$ (0.2M) is taken in 100 mL round bottom flask. It is kept for stirring at 80 ^oC and 20 mL of purslane leaves extract were added drop wise. The nanoparticle formation was observed with the change in the colour of solution and precipitate

formation. The mixture was cooled to room temperature and the newly formed nanoparticles was collected through centrifugation at 3500 rpm for 10 minutes. It is then washed with the distilled water and acetone, then dried at 80 ^{o}C for 12 h and characterised by different spectroscopic techniques.

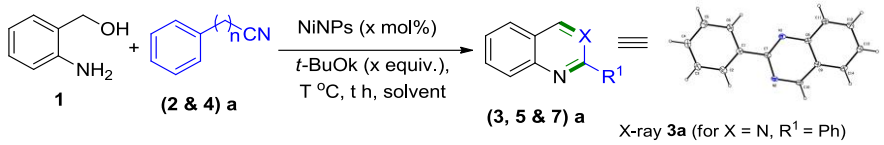


Scheme 2: Schematic representation for synthesis of Ni-NPs

3. General experimental procedure for the synthesis of quinazolines, 2-amino quinolines and *N*-(alkyl amino) quinolines:

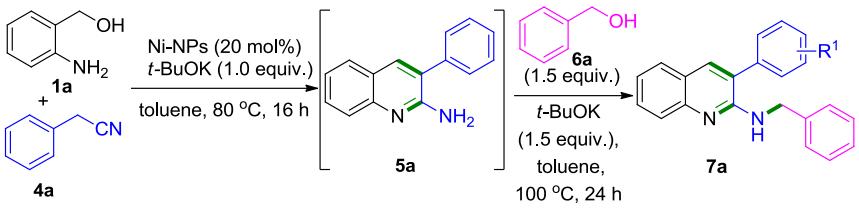
The Ni-NPs (0-20 mol %, Ni content: 45.01% w/w) was added in an oven-dried 15 mL sealed tube containing compound **1** (0.5 mmol, 1.0 equiv.), then the base (0.5 mmol, 1.0 equiv.) and solvent (1.0 mL) is added to the tube. Then, solution (1.0 mL) of compound **2a** (0.65 mmol, 1.3 equiv.) was added slowly. The reaction mixture was stirred at 60-100 ^{o}C for 14-24 h. After complete conversion of starting material (indicated by TLC), ethyl acetate was added to dilute the reaction mixture and filtered using filter paper. Further, the reaction mixture was quenched with water and the organic layer was extracted with EtOAc (10×3) the combined organic layer was dried over anhydrous Na_2SO_4 then the solvent was evaporated under reduced pressure and crude compound was purified by column chromatography (eluent: 3–18% EA/Hexane) to get the compound **3**. The reaction was repeated twice and product was isolated to determine the yield (by average of two run). Similar procedure was followed for the synthesis of 2-amino quinolines and *N*-(alkyl amino) quinolines by changing the solvent from xylene to toluene respectively. The crude compound was purified by column chromatography (eluent: 18-23% and 2-4% EA/Hexane) to get the compounds **5** and **7** respectively. The reaction was repeated twice and product was isolated to determine the yield (by average of two run).

Table 2. Optimization of reaction condition[a]



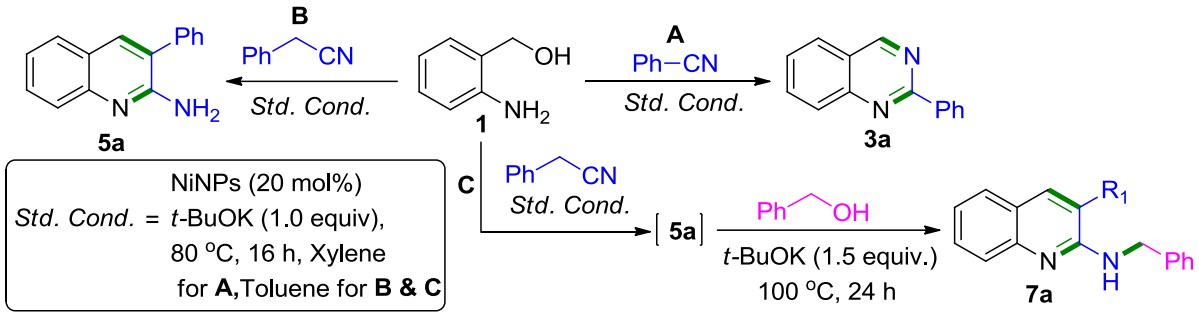
S. N.	(X, R^1,R^2)	Base	Solvent	T (°C) /t (h)	% Yield [f]
1	*n=0, X=N, R^1=Ph*	*t*-BuOK	Toluene	100/24	3a (45)
2	*n=0, X=N, R^1=Ph*	*t*-BuOK	THF	100/24	3a (87)
3	*n=0, X=N, R^1=Ph*	*t*-BuOK	Xylene	100/24	3a (96)
4	*n=0, X=N, R^1=Ph*	*t*-BuOK	DMF	100/24	3a (07)
5	*n=0, X=N, R^1=Ph*	*t*-BuOK	MeCN	100/24	3a (25)
6	*n=0, X=N, R^1=Ph*	*t*-BuOK	1,4-dioxane	100/24	3a (15)
7	*n=0, X=N, R^1=Ph*	*t*-BuOK	Xylene	100/16	3a (96)
8	***n=0, X=N, R^1=Ph***	***t*-BuOK**	**Xylene**	**80/16**	**3a (96)**
9	*n=0, X=N, R^1=Ph*	*t*-BuOK	Xylene	80/14	3a (88)
10	*n=0, X=N, R^1=Ph*	*t*-BuOK	Xylene	60/24	3a (40)
11	*n=0, X=N, R^1=Ph*	KOH	Xylene	80/16	3a (60)
12	*n=0, X=N, R^1=Ph*	Cs_2CO_3	Xylene	80/16	3a (43)
13	*n=0, X=N, R^1=Ph*	KOAc	Xylene	80/16	3a (32)
14 [b]	*n=0, X=N, R^1=Ph*	*t*-BuOK	Xylene	80/16	3a (74)
15 [c]	*n=0, X=N, R^1=Ph*	*t*-BuOK	Xylene	80/16	3a Trace
16 [d]	*n=0, X=N, R^1=Ph*	*t*-BuOK	Xylene	80/24	3a (30)
17 [e]	*n=0, X=N, R^1=Ph*	*t*-BuOK	Xylene	80/16	3a (76)
18	*n=1, X=C-Ph, R^1= NH_2*	*t*-BuOK	Xylene	80/16	5a (77)
19	***n=1, X= C-Ph, R^1= NH_2***	***t*-BuOK**	**Toluene**	**80/16**	**5a (92)**

[a]Reaction conditions: **1a** (0.5 mmol), **2a** & **4a** (0.5-0.65 mmol), base (1.0 equiv.), Ni-NPs (20 mol%, 45.01% w/w), solvent (1 mL), at 80 °C in 14 to 24 h. [b]15 mol% of catalyst. [c]No catalyst. [d]0.5 equiv. Base. [e]1.0 equiv. of compound 2 was used. [f]Yields are reported after purification from silica column (average of two runs).



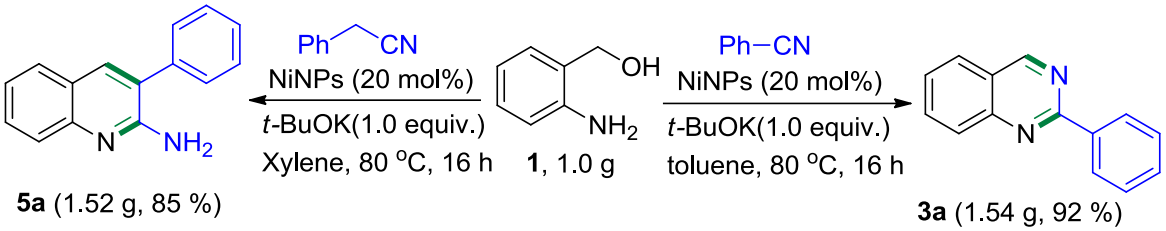
Scheme 3. One pot synthesis of *N*-(alkylamino) quinolines

4. Exact experimental procedure for the synthesis of 2-phenyl quinazoline (3a), 3-phenylquinolin-2-amine (5a) and *N*-benzyl-3-phenylquinolin-2-amine (7a):



The Ni-NPs (59.43 mg, 20 mol %, Ni content: 45.01% w/w) was added in an oven-dried 15 mL sealed tube containing compound **1** (0.5 mmol, 1.0 equiv), then the *t*-BuOK (0.5 mmol, 1.0 equiv.) and xylene (1.0 mL). Then, solution of compound **2a** (0.65 mmol, 1.3 equiv.) in xylene (1.0 mL) was added slowly, the reaction mixture was stirred at 80 °C for 16 h. After complete conversion of starting material (indicated by TLC), ethyl acetate was added to dilute the reaction mixture and filtered using filter paper. Further, the reaction mixture was quenched with water and the organic layer was extracted with EtOAc (10×3) the combined organic layer was dried over anhydrous Na_2SO_4 then the solvent was evaporated under reduced pressure and crude compound was purified by column chromatography (eluent: 4–5% EA/Hexane) to get the compound **3a**. The reaction was repeated twice and product was isolated to determine the yield (by average of two run). Similar procedure was followed for the synthesis of 3-phenylquinolin-2-amine (**5a**) and *N*-benzyl-3-phenylquinolin-2-amine (**7a**) (base 2.5 equiv is used) by changing the solvent from xylene to toluene and the crude compound was purified by column chromatography (eluent: 18-23% and 2-4% EA/Hexane) to get the compounds **5a** and **7a** respectively. The reaction was repeated twice and product was isolated to determine the yield (by average of two run).

5. Representative procedure of gram scale synthesis of 2-phenyl quinazoline (3a) and 3-phenylquinolin-2-amine (5a)



The Ni-NPs (20 mol %, Ni content: 45.01 w/w%) was added in an oven-dried 15 mL sealed tube containing compound **1** (0.5 mmol, 1.0 equiv.), then the *t*-BuOK (0.5 mmol, 1.0 equiv.) and xylene (1.0 mL). Then, the solution of compound **2a** (0.65 mmol, 1.3 equiv.) in xylene (1.0 mL) was added slowly, the reaction mixture was stirred at 80 °C for 16 h. After complete conversion of starting material (indicated by TLC), ethyl acetate was added to dilute the reaction mixture and filtered using filter paper. Further, the reaction mixture was quenched with water and the organic layer was extracted with EtOAc (10×3) the combined organic layer was dried over anhydrous Na_2SO_4 then the solvent was concentrated under reduced pressure and desired 2-phenyl quinazoline (**3a**) was simply purified by recrystallization followed by washing hexane and pentane (1:1) solvents. Similar procedure was followed for the synthesis of 3-phenylquinolin-2-amine (**5a**) by replacing solvent from xylene to toluene.

6. Catalyst recyclability studies for synthesis of Quinazolines:

The recyclability of freshly synthesized the Ni-NPs was examined for quinazoline synthesis under optimized condition. After the completion of reaction, the desired product is purified by column chromatography and yield was determined. However, the heterogeneous Ni-NPs catalyst is separated from reaction mixture by centrifugation, washed with water (3 x 10 mL) followed by ethanol (3 x 10 mL) and dried at 60 °C for 12 hrs. It is then further used for second cycle and so on. As shown in Figure S1, Ni-NPs catalyst used up to five cycle and the yield was determined. The recycled catalyst was further characterised wherein *P*-XRD analysis indicates that, oxidation state is not changed even after five cycles (Fig. S1 b) while FE-SEM images reveals , only slight change in morphology after the five cycles as the activity of Ni-NPs goes on decreasing steadily Fig. S1 (c-e). However, the agglomeration was enhanced as compared to the fresh catalyst.

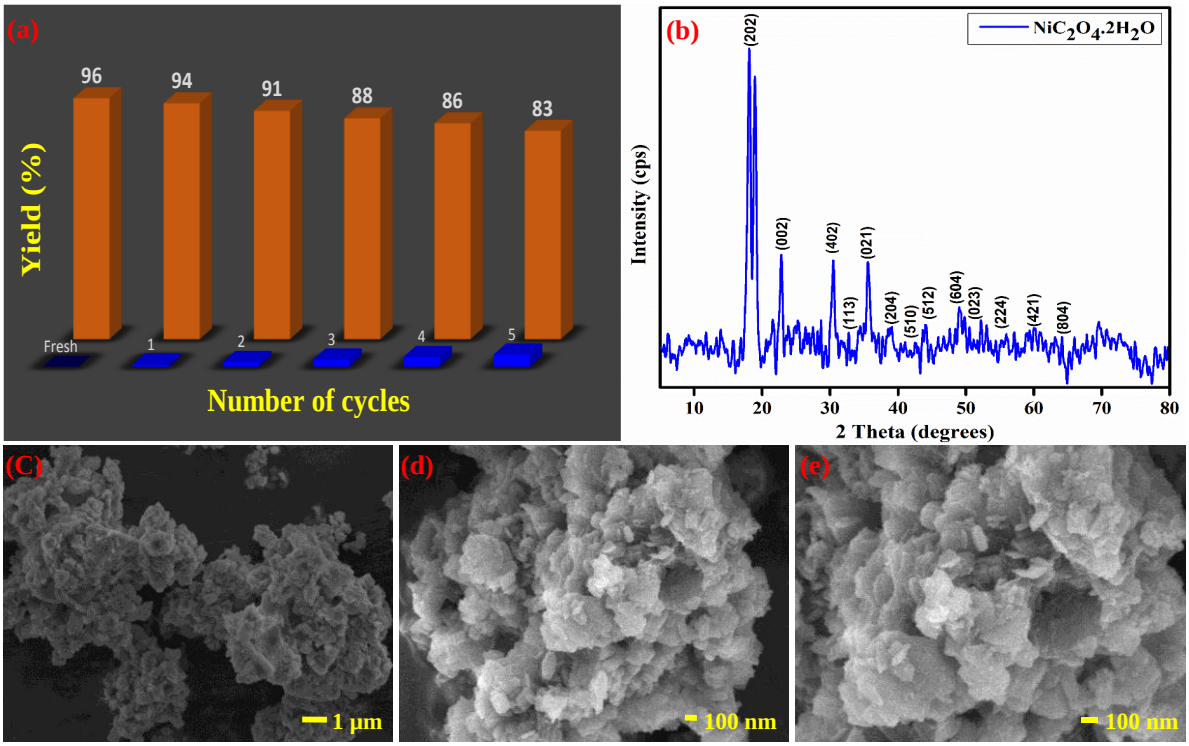
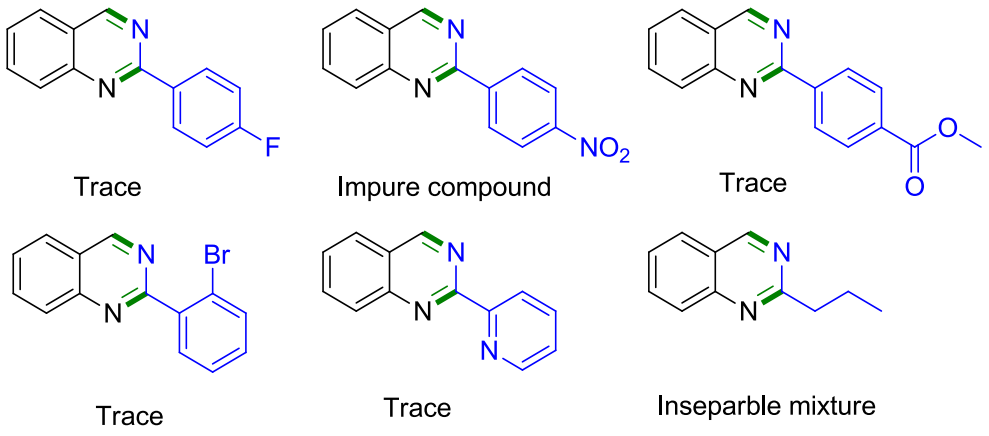


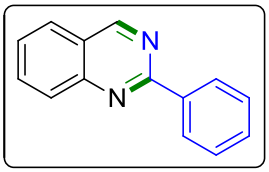
Figure S1. (a) Recycling efficiency of Ni-NPs in quinazolines synthesis, (b) *P*-XRD after 5th cycle (c-e) FE-SEM after 5th cycle.

7. Unsuccessful substrates:



8. Spectroscopic Data of the quinazolines, 2-aminoquinolines and *N*-(alkyl amino) quinolines

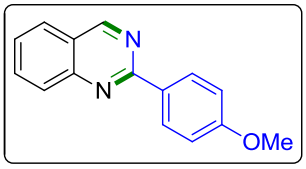
2-phenylquinazoline (3a) [S2]



Purified by column chromatography (5% ethyl acetate in hexane), pale yellow solid (160.77 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (s, 1H), 8.64 (dd, *J* = 7.8, 1.4 Hz, 2H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.95 –7.90

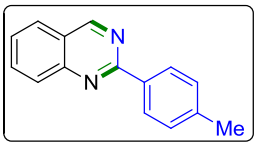
(m, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.59 – 7.53 (m, 3H). ^{13}C NMR(100 MHz, $CDCl_3$) δ 161.0, 160.5, 150.8, 138.0, 134.1, 130.6,128.6, 128.6, 127.2, 127.1, 123.6. HRMS (ESI) calcd. for $C_{14}H_{11}N_2$ $[M+H]^+$: 207.0917; found $[M+H]^+$: 207.0928.[S2]

2-(4-methoxyphenyl)quinazoline (3b) [S3]



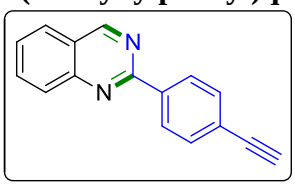
Purified by column chromatography (5% ethyl acetate in hexane), yellow solid (163.07 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (s, 1H), 8.58 (d, *J* =8.8 Hz, 2H), 8.03 (d, *J* = 8.8 Hz, 1H), 7.85 (t, *J* = 7.4 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 9.2 Hz, 2H), 3.88 (s,3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 160.8, 160.3, 150.8, 134.0, 130.7, 130.2, 128.4, 127.1, 126.7, 123.3,114.0, 55.4. HRMS (ESI) calcd. for $C_{15}H_{12}N_2O$ $[M+H]^+$: 237.1020; found $[M+H]^+$: 237.1023. [S3]

2-(*p*-tolyl)quinazoline (3c) [S2]



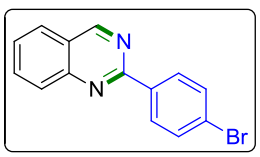
Purified by column chromatography (5% ethyl acetate in hexane), yellow solid (150.23 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.44 (s, 1H), 8.52 (d, *J* = 8 Hz, 2H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.88 (t, *J* = 8 Hz, 2H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 160.4, 150.8, 140.8, 135.3, 134.0, 129.4, 128.5, 127.1, 127.0, 123.5, 21.5. HRMS (ESI) calcd. for $C_{15}H_{12}N_2$ $[M+H]^+$: 221.1073; found $[M+H]^+$: 221.1079. [S2]

2-(4-ethynylphenyl)quinazoline (3d)



Purified by column chromatography (16% ethyl acetate in hexane), pale yellow solid (166.31 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.34 (s, 1H), 8.16 (d, *J* = 6.8 Hz, 1H), 7.90 (d, *J* = 6.4 Hz, 1H),7.81 (s, 3H), 7.80 –7.76 (m, 1H), 7.62 (t, *J* = 6.0 Hz, 1H), 4.50 (s, 1H). ^{13}C NMR(100 MHz, $CDCl_3$) δ 149.1, 147.9, 142.4, 134.0, 133.0, 131.9, 130.3, 129.5, 129.4, 128.2, 128.0, 127.7, 127.5, 70.5, 70.3. HRMS (ESI) calcd. for $C_{16}H_{10}N_2$ $[M+H]^+$: 231.0844.

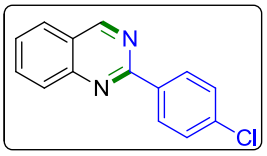
2-(4-bromophenyl)quinazoline (3e) [S2]



Purified by column chromatography (5% ethyl acetate in hexane), pale yellow solid (222.26 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 8.50-8.47 (m, 2H), 8.05 (d, *J* = 9.2 Hz, 1H), 7.91 – 7.87 (m, 2H), 7.66 - 7.59 (m, 3H). 13C NMR (100 MHz, $CDCl_3$) δ 160.5, 160.1, 150.6, 136.9, 134.2, 131.8,

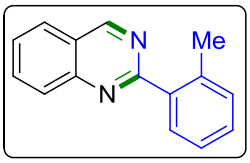
130.1, 128.6, 127.5, 127.1, 125.4, 123.6. HRMS (ESI) calcd. for $C_{14}H_{10}BrN_2$ $[M+H]^+$: 284.9949; found $[M+H]^+$: 284.9985. [S2]

2-(4-chlorophenyl)quinazoline (3f) [S2]



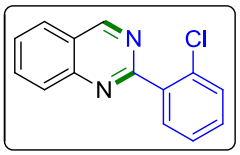
Purified by column chromatography (5% ethyl acetate in hexane), pale yellow solid (185.66 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.41 (s, 1H), 8.56 - 8.54 (m, 2H), 8.05 (d, *J* = 8.8 Hz, 1H), 7.91 – 7.87 (m, 2H), 7.62 - 7.58 (m, 1H), 7.49 - 7.47 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 159.9, 150.6, 136.8, 136.4, 134.2, 129.8, 128.7, 128.5, 127.4, 127.1, 123.5. HRMS (ESI) calcd. for $C_{14}H_{10}ClN_2$ $[M+H]^+$: 241.0527; found $[M+H]^+$: 241.0544. [S2]

2-(o-tolyl)quinazoline (3g) [S2]



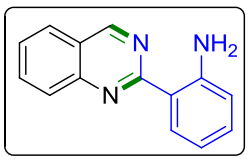
Purified by column chromatography (5% ethyl acetate in hexane), yellow solid (128.77 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.47 (s, 1H), 8.08 (d, *J* = 8.8 Hz, 1H), 7.98 – 7.96 (m, 1H), 7.87 (t, *J* = 7.0 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.38 – 7.35 (m, 3H), 2.65 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 159.8, 150.1, 138.3, 137.2, 133.8, 131.1, 130.5, 129.1, 128.3, 127.2, 126.8,125.7, 122.6, 20.9. HRMS (ESI) calcd. for $C_{15}H_{12}N_2$ $[M+H]^+$: 221.1073; found $[M+H]^+$: 221.1062. [S2]

2-(2-chlorophenyl)quinazoline (3h) [S3]



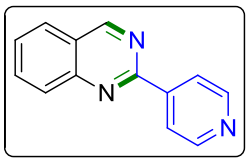
Purified by column chromatography (5% ethyl acetate in hexane), pale yellow solid (140.71 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.55 (s, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 8.02 – 7.96 (m, 2H), 7.85 – 7.82 (m, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.57 - 7.54 (m, 1H), 7.44 – 7.41 (m, 2H). ^{13}C NMR (100 MHz, CDCl3) δ 161.9, 160.2, 150.3, 138.2, 134.4, 132.9, 131.7, 130.5, 130.3, 128.6, 128.1, 127.1, 126.9, 123.3. HRMS (ESI) calcd. for $C_{14}H_{10}ClN_2$ $[M+H]^+$: 241.0527; found $[M+H]^+$: 241.0531. [S3]

2-(quinazolin-2-yl)aniline (3i)



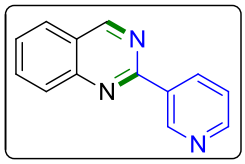
Purified by column chromatography (3% ethyl acetate in hexane), yellow solid (80.85 mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.44 (s, 1H), 8.64 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.90 – 7.87 (m, 2H), 7.59 - 7.53 (m, 1H), 7.28 - 7.24 (m, 1H), 6.85 – 6.78 (m, 2H) 6.56 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 159.7, 149.6, 148.9, 134.0, 131.7, 131.4, 127.9, 127.1, 126.8, 122.5, 119.0, 117.1, 116.9. HRMS (ESI) calcd. for $C_{14}H_{12}N_3$ $[M+H]^+$: 222.0953; found $[M+H]^+$: 222.1022.

2-(pyridin-4-yl)quinazoline (3j) [S3]



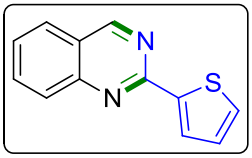
Purified by column chromatography (18% ethyl acetate in hexane), pale brown solid (159.86 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (s, 1H), 8.73 (d, *J* = 6.0 Hz, 2H), 8.38 (dd, *J* = 4.4 Hz, 1.2 Hz, 2H), 8.12 (d, *J* = 8.8 Hz, 1H), 7.88 (t, *J* = 7.8 Hz, 2H), 7. 61 (t, *J* = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 158.9, 150.6, 150.5, 145.3, 134.5, 128.9, 128.3, 127.2, 124.2, 122.4. HRMS (ESI) calcd. for $C_{13}H_{10}N_3$ $[M+H]^+$: 208.0869; found $[M+H]^+$: 208.0860. *S3*

2-(pyridin-3-yl)quinazoline (3k) *S2*



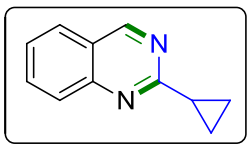
Purified by column chromatography (5% ethyl acetate in hexane), pale brown solid (153.12 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (s, 1H), 9.47 (s, 1H), 8.90 – 8.87 (m, 1H), 7.88 (dd, *J* = 4.6, 1.4 Hz, 1H), 8.10 (d, *J* = 8.8 Hz, 1H), 7.96 – 7.92 (m, 2H), 7.68 – 7.64 (m, 1H), 7.49 – 7.45 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 159.0, 150.8, 150.6, 149.9, 136.0, 134.4, 133.7, 128.6, 127.8, 127.2, 123.8, 123.5. HRMS (ESI) calcd. for $C_{13}H_{10}N_3$ $[M+H]^+$: 208.0869; found $[M+H]^+$: 208.0865. *S2*

2-(thiophen-2-yl)quinazoline (3l) *S2*



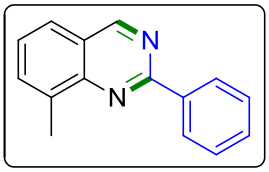
Purified by column chromatography (5% ethyl acetate in hexane), pale yellow solid (160.30 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.35 (s, 1H), 8.15 (dd, *J* = 3.6, 1.2 Hz, 1H), 8.01 (d, *J* = 9.2 Hz, 1H), 7.89 - 7.85 (m, 2H), 7.58 - 7.54 (m, 1H), 7.52 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.20 – 7.18 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 157.8, 150.6, 143.8, 134.3, 129.9, 129.2, 128.4, 128.1, 127.2, 127.0,123.3. HRMS (ESI) calcd. for $C_{12}H_9N_2S$ $[M+H]^+$: 213.0481; found $[M+H]^+$: 213.0455. *S2*

2-cyclopropylquinazoline (3m) *S4*



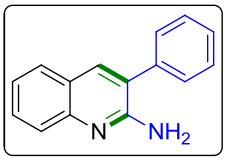
Purified by column chromatography (4% ethyl acetate in hexane), pale yellow solid (129.92 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (s, 1H), 7.87 - 7.85 (m, 1H), 7.81 – 7.77 (m, 2H), 7.47 (ddd, *J* = 7.5, 1.2 Hz, 1H), 2.39 - 2.33 (m, 1H), 1.25 – 1.22 (m, 2H), 1.12 - 1.08 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 160.2, 150.2, 133.9, 127.4, 127.0, 126.2, 123.1, 18.5, 10.6. HRMS (ESI) calcd. for $C_{11}H_{10}N_2$ $[M+H]^+$: 171.0844; found $[M+H]^+$: 171.0878.

8-methyl-2-phenylquinazoline (**3n**)



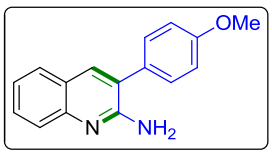
Purified by column chromatography (12% ethyl acetate in hexane), pale yellow solid (166.37 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (s, 1H), 8.66 (d, *J* = 6.4, 2H), 8.12 (t, *J* = 6.0 Hz, 2H), 7.54 –7.47 (m, 4H), 2.85 (s, 3H). ^{13}C NMR(100 MHz, $CDCl_3$) δ 160.5, 159.9, 149.7, 138.3, 137.1, 133.8, 130.4, 128.5, 126.9, 124.8, 123.5, 16.9. HRMS (ESI) calcd. for $C_{15}H_{12}N_2$ $[M+H]^+$: 221.1000.

3-phenylquinolin-2-amine (5a) *S5*



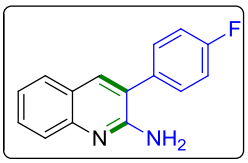
Purified by column chromatography (18% ethyl acetate in hexane), white solid (164.54 mg, 92 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.64 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.58 – 7.54 (m, 1H), 7.51 – 7.42 (m, 5H), 7.28 – 7.26 (m, 1H), 4.99 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 147.2, 137.7, 137.4, 129.8, 129.3, 129.0, 128.3, 127.6, 125.7, 125.1, 124.3, 122.9. HRMS (ESI) calcd. for $C_{15}H_{13}N_2$ $[M+H]^+$: 221.1000; found $[M+H]^+$: 221.1070.

3-(4-methoxyphenyl)quinolin-2-amine (5b) *S5*



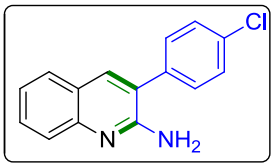
Purified by column chromatography (20% ethyl acetate in hexane), white solid (176.81 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.8 Hz, 2H), 7.63 - 7.56 (m, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 155.6, 142.1, 138.7, 130.7, 130.0, 129.8, 127.6, 127.6, 125.5, 123.6, 122.8, 121.6, 114.8, 55.4. HRMS (ESI) calcd. for $C_{16}H_{15}N_2O$ $[M+H]^+$: 251.1106; found $[M+H]^+$: 251.1176.

3-(4-fluorophenyl)quinolin-2-amine (5c) *S5*



Purified by column chromatography (18% ethyl acetate in hexane), white solid (174.11 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.63 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.59 - 7.54 (m, 1H), 7.50 - 7.47 (m, 2H), 7.29 - 7.27 (m, 1H), 7.20 – 7.15 (m, 2H), 4.98 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (d, J_{C-F} = 246.0 Hz), 155.2, 147.1, 137.6, 133.5, 133.5 130.8 (d, *J* = 8.0 Hz), 129.9, 127.6, 125.6, 124.1(d, *J* = 12.0 Hz), 123.1, 116.3(d, *J* = 22.0 Hz). HRMS (ESI) calcd. for $C_{15}H_{12}FN_2$ $[M+H]^+$: 239.0906; found $[M+H]^+$: 239.0976.

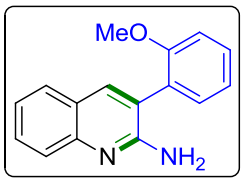
3-(4-chlorophenyl)quinolin-2-amine (5d) *S5*



Purified by column chromatography (18% ethyl acetate in hexane), pale brown solid (188.21 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.69-7.67 (m, 1H), 7.64 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.59 - 7.55 (m,

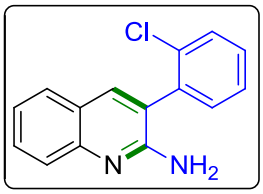
1H), 7.46 (s, 4H), 7.29 - 7.27(m, 1H), 4.90 (s, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 147.3, 137.5, 136.1, 134.4, 130.4, 130.0, 129.5, 127.6, 125.8, 124.2, 123.8, 123.1. HRMS (ESI) calcd. for $C_{15}H_{12}ClN_2$ $[M+H]^+$: 255.0611; found $[M+H]^+$: 255.0680.

3-(2-methoxyphenyl)quinolin-2-amine (5e) *S5*



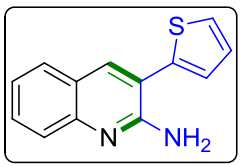
Purified by column chromatography (20% ethyl acetate in hexane), white solid solid (172.75 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.56 - 7.52 (m, 1H), 7.43 - 7.38 (m, 1H), 7.29 (dd, J = 7.6 Hz, 1.6 Hz, 1H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.07 (t, *J* = 7.2 Hz, 1H), 7.01 (d, 8.4 Hz, 1H), 4.97 (s, 2H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 156.0, 147.1, 138.1, 131.6, 130.0, 129.5, 127.5, 126.2, 125.5, 124.0, 122.6, 122.4, 121.3, 111.4, 55.7. HRMS (ESI) calcd. for $C_{16}H_{14}N_2O$ $[M+H]^+$: 251.1106; found $[M+H]^+$: 251.1193.

3-(2-chlorophenyl)quinolin-2-amine (5f) *S5*



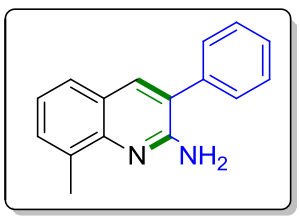
Purified by column chromatography (18% ethyl acetate in hexane), pale brown solid (179.94 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.59 - 7.57 (m, 1H), 7.56 - 7.53 (m, 1H), 7.38 - 7.36 (m, 3H), 7.27 (t, J = 7.2 Hz, 1H), 4.97 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 147.3, 137.9, 135.7, 133.8, 131.6, 130.0, 129.8, 127.5, 127.3, 125.4, 123.4, 122.6, 122.4. HRMS (ESI) calcd. for $C_{15}H_{12}ClN_2$ $[M+H]^+$: 255.0611; found $[M+H]^+$: 255.0681.

3-(2-thiophenyl)quinolin-2-amine (5g) *S5*



Purified by column chromatography (18% ethyl acetate in hexane), off white solid (147.00 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.61 - 7.54 (m, 2H), 7.42 (d, *J* = 4.8 Hz, 1H), 7.27 (t, *J* = 3.6 Hz, 2H), 7.16 - 7.14 (m, 1H), 7.08 - 7.02 (m, 1H), 6.65 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 144.0, 139.2, 137.3, 130.8, 128.1, 127.7, 127.1, 126.9, 123.5, 122.9, 122.8. HRMS (ESI) calcd. for $C_{13}H_{11}N_2S$ $[M+H]^+$: 227.0565; found $[M+H]^+$: 227.0635.

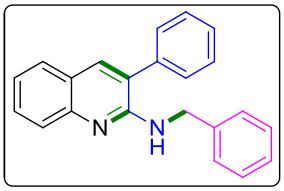
8-methyl-3-phenylquinolin-2-amine(5h)



Purified by column chromatography (14% ethyl acetate in hexane), off white solid (153.00 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.45 – 7.38 (m, 5H), 7.34 (d, *J* = 6.8 Hz, 2H), 7.08 (t, *J* = 7.6 Hz, 1H), 4.86 (s, 2H), 2.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$)

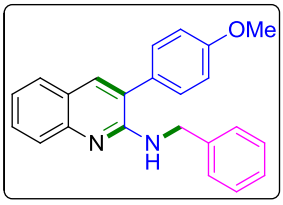
δ154.4, 146.2, 137.9, 137.6, 133.7, 129.9, 129.1, 129.0, 128.1, 125.5, 124.6, 124.1, 122.5, 18.0. HRMS (ESI) calcd. for $C_{16}H_{14}N_2$ $[M+H]^+$: 235.1157.

_N_-benzyl-3phenylquinolin-2-amine (7a) [S5]



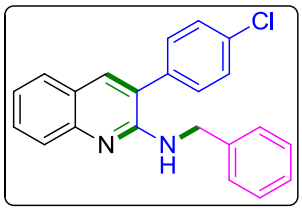
Purified by column chromatography (3% ethyl acetate in hexane), yellow solid (89.17 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 1H), 7.61 (s, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.48 - 7.44 (m, 1H), 7.41 - 7.36 (m, 4H), 7.33 - 7.30 (m, 1H), 7.28 (d, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 2H), 7.17 - 7.15 (m, 2H), 5.03 (t, *J* = 5.0 Hz, 1H), 4.74 (d, *J* = 5.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 147.6, 139.9, 137.5, 136.5, 129.4, 129.3, 129.1, 128.5, 128.3, 127.8, 127.4, 127.1, 126.3, 125.6, 123.7, 122.3, 45.5. HRMS (ESI) calcd. for $C_{22}H_{18}N_2$ $[M+H]^+$: 311.1470; found $[M+H]^+$: 311.1537.

_N_-benzyl-3-(4-methoxyphenyl)quinolin-2-amine (7b)



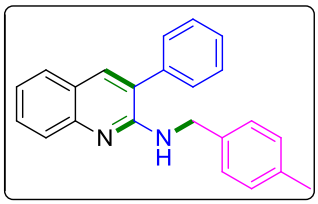
Purified by column chromatography (3% ethyl acetate in hexane), yellow solid (88.75 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 1H), 7.66 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.55 - 7.51 (m, 1H), 7.40 - 7.35 (m, 4H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.25 - 7.12 (m, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 5.11 (s, 1H), 4.81 (d, *J* = 5.2 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 154.6, 147.4, 139.9, 136.3, 130.3, 129.5, 129.2, 128.5, 127.8, 127.3, 127.1, 126.2, 125.3, 123.8, 122.3, 114.7, 55.4, 45.5. HRMS (ESI) calcd. for $C_{23}H_{20}N_2O$ $[M+H]^+$: 341.1576; found $[M+H]^+$: 341.1645.

_N_-benzyl-3-(4-Chlorophenyl)quinolin-2-amine (7c)



Purified by column chromatography (3% ethyl acetate in hexane), yellow solid (84.26 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.4 Hz, 1H), 7.52 (s, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.48 - 7.45 (m, 1H), 7.37 - 7.32 (m, 5H), 7.28 (d, *J* = 6.8 Hz, 2H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.19 - 7.16 (m, 2H), 4.89 (t, *J* = 5.2 Hz, 1H), 4.72 (d, J = 5.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 147.6, 139.7, 136.6, 135.9, 134.3, 130.5, 129.6, 129.5, 128.6, 127.8, 127.4, 127.2, 126.3, 124.3, 123.6, 122.5, 45.6. HRMS (ESI) calcd. for $C_{22}H_{17}ClN_2$ $[M+H]^+$: 345.1080; found $[M+H]^+$: 345.1152.

***N*-(4-methylbenzyl)-3phenylquinolin-2-amine (7d)**



Purified by column chromatography (3% ethyl acetate in hexane), yellow solid (90.24 mg, 61%). 1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.4 Hz, 1H), 7.72 - 7.68 (m, 2H) 7.60 (d, *J* = 7.6 Hz, 1H), 7.53 (dd, *J* = 6.6, 1.0 Hz, 2H), 7.46 (t, *J* = 2.2 Hz, 3H), 7.40 - 7.37 (m, 1H), 7.25 - 7.23 (m, 2H), 7.11 (d, *J* = 7.2 Hz, 2H), 5.06 (s, 1H), 4.76 (d, *J* = 5.2 Hz, 2H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 147.6, 137.5, 136.8, 136.8, 136.5, 129.4, 129.4 129.3, 129.3, 129.2, 128.9, 128.6, 128.3, 127.9, 127.5, 126.3, 125.7, 123.7, 122.3, 45.4, 21.2. HRMS (ESI) calcd. for $C_{23}H_{20}N_2$ $[M+H]^+$: 325.1626; found $[M+H]^+$: 325.1702.

9. Photophysical property:

Table S3: Optical Data of Representative Products

Products	λ_{abs} (nm)[a]	λ_{em} (nm) [a]	ε_{max} (M^{-1} m^{-1}) [b]	Stokes shift (nm)
5a	348	420	29.18 x 10^5	72
5b	347	415	31.46 x 10^5	68
5c	348	417	29.35 x 10^5	69
5d	351	426	29.43 x 10^5	75
5e	353	413	25.12 x 10^5	60
5f	344	415	29.50 x 10^5	71
5g	357	429	21.70 x 10^5	72
5h	351	423	23.16 x 10^5	72
7a	353	422	16.18 x 10^5	69
7b	353	415	35.72 x 10^5	62
7c	349	423	3.80 x 10^5	74
7d	355	422	12.80 x 10^5	67

[a]Wavelength of maximum absorbance (λ_{abs}) or emission intensity (λ_{em}). [b]Molar extinction coefficient in 10^{-5} M N,N-Dimethyl formamide(DMF)

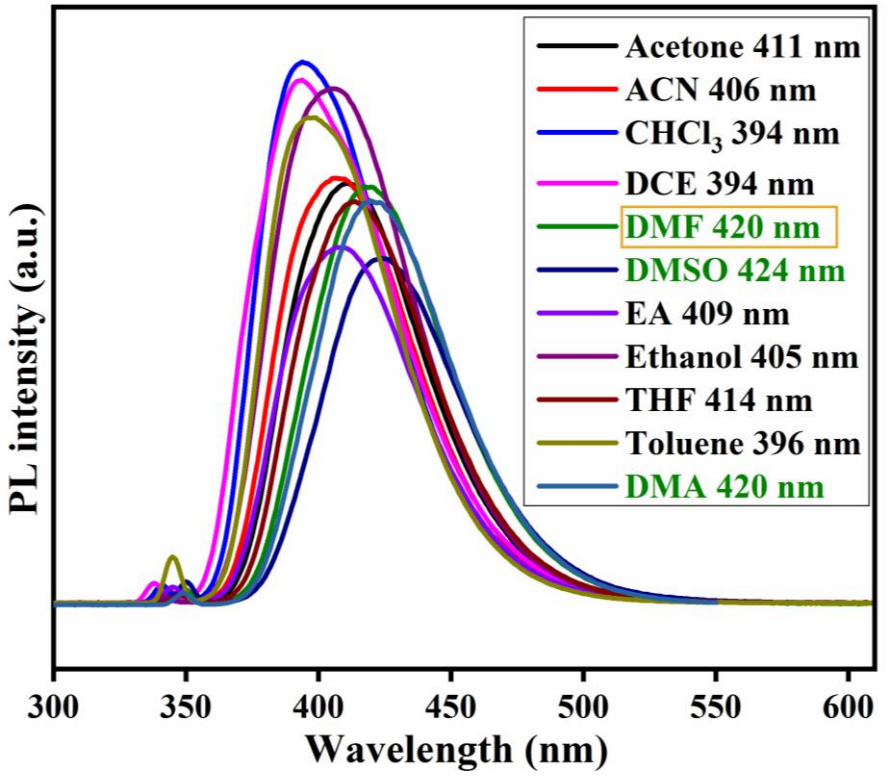


Figure S2. Emission (10^{-5} M in DMF) profiles for solvent study using **5a** compound

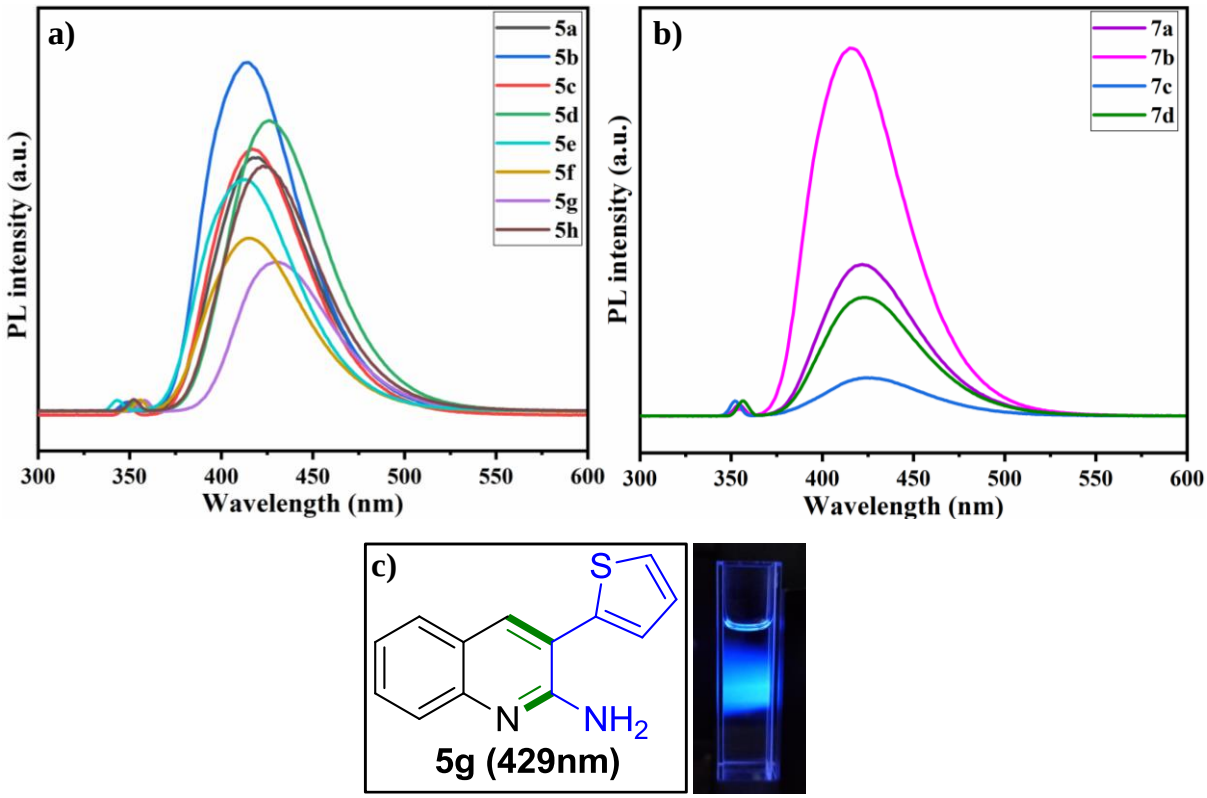


Figure S3. Emission (10^{-5} M in DMF) profiles for newly synthesized heterocycles a) 2-amino quinolines series b) *N*-(alkyl amino) quinolines series c) Photographs of **5g** in DMF solution under 357 nm UV light

References:

S1. Y. X. Zhou, H. L. Xin, K. Rahman, S. J. Wang, C. Peng, H. Zhang, *Biomed Res. Int.*, 2015, https://doi.org/10.1155/2015/925631.

S2. S. Q. Zhang, Y. Cui, B. Guo, D. J. Young, Z. Xu, H. X. Li, *Tetrahedron* 2021, **78**, 131825.

S3. K. Gopalaiah, A. Saini and A. Devi, *Org. Biomol. Chem.* 2017, **15**, 5781-5789.

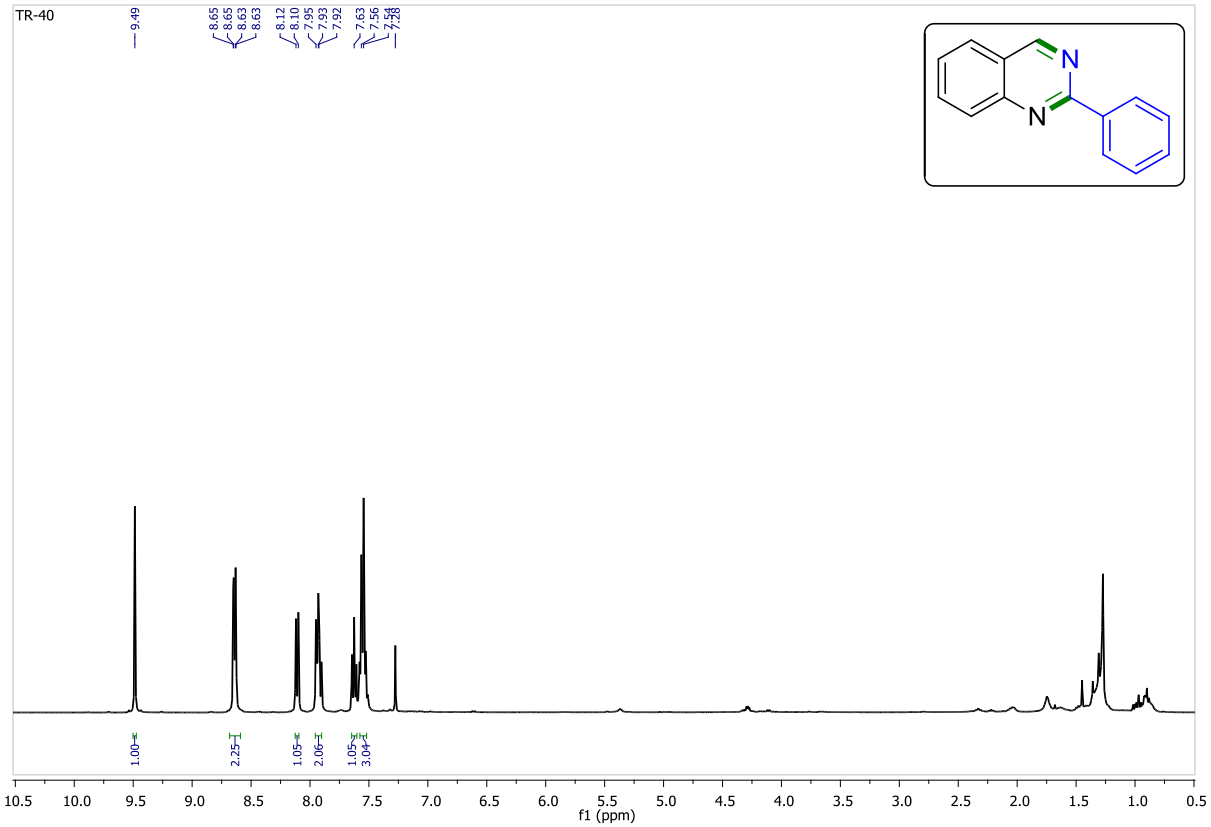
S4. D. Zhao, Q. Shen, Y. R. Zhou, J. X. Li, *Org. Biomol. Chem.*, 2013, **11**, 5908-5912.

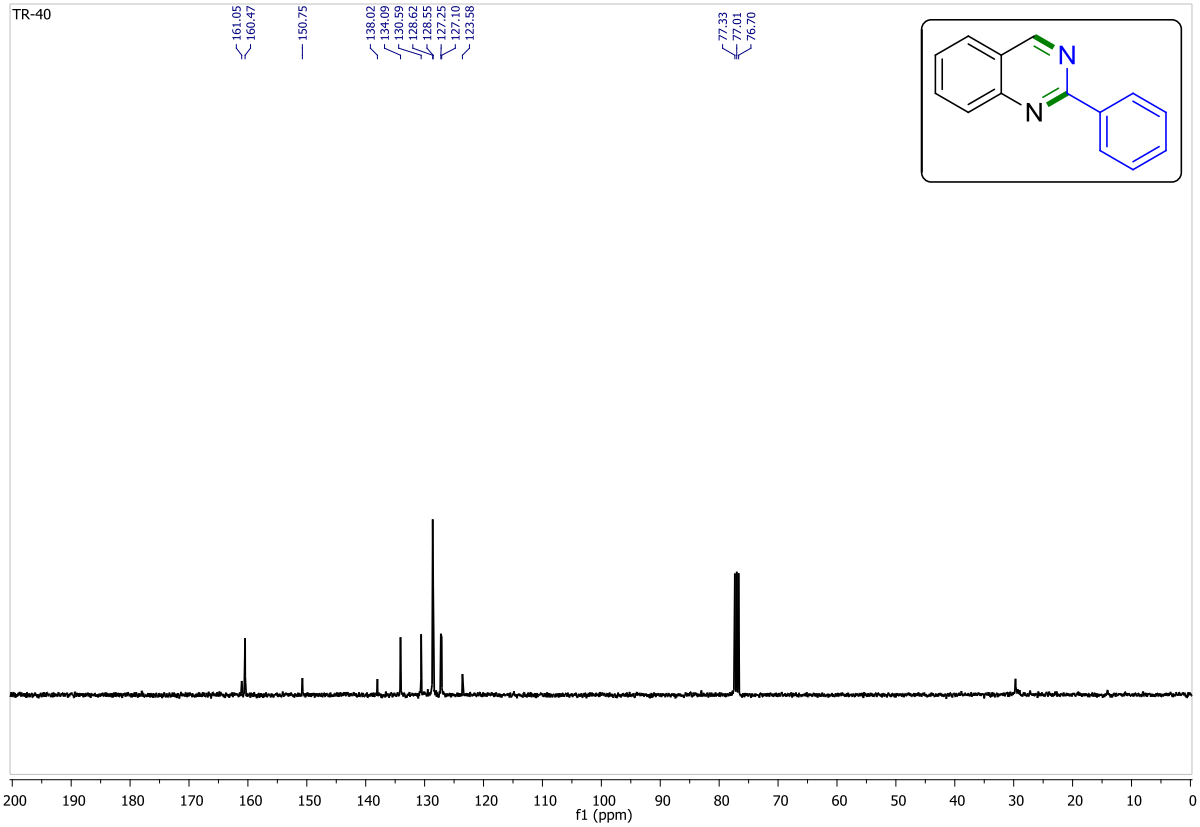
S5. K. Das, A. Mondal, D. Pal, D. Srimani, *Organic letters*, 2019, **21**, 3223-3227.

Appendix-I

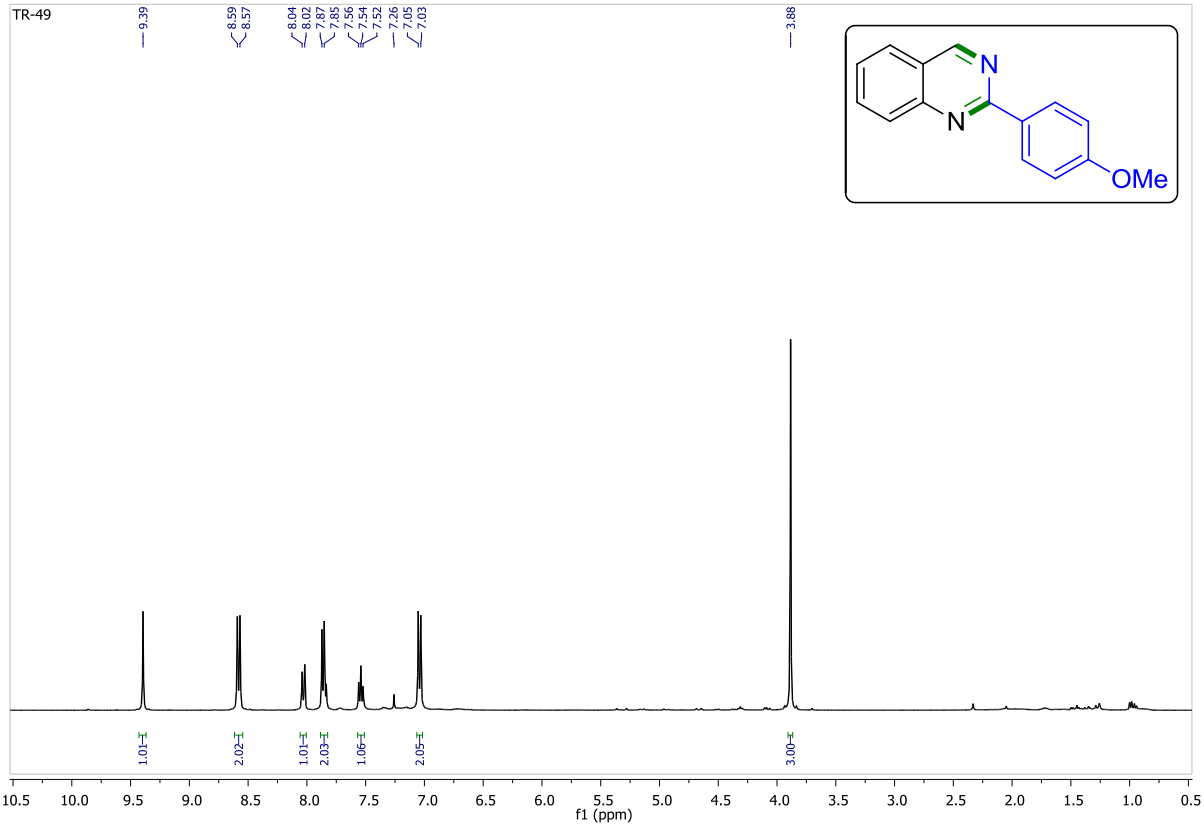
Spectral copies of ^{1}H and ^{13}C NMR of compounds

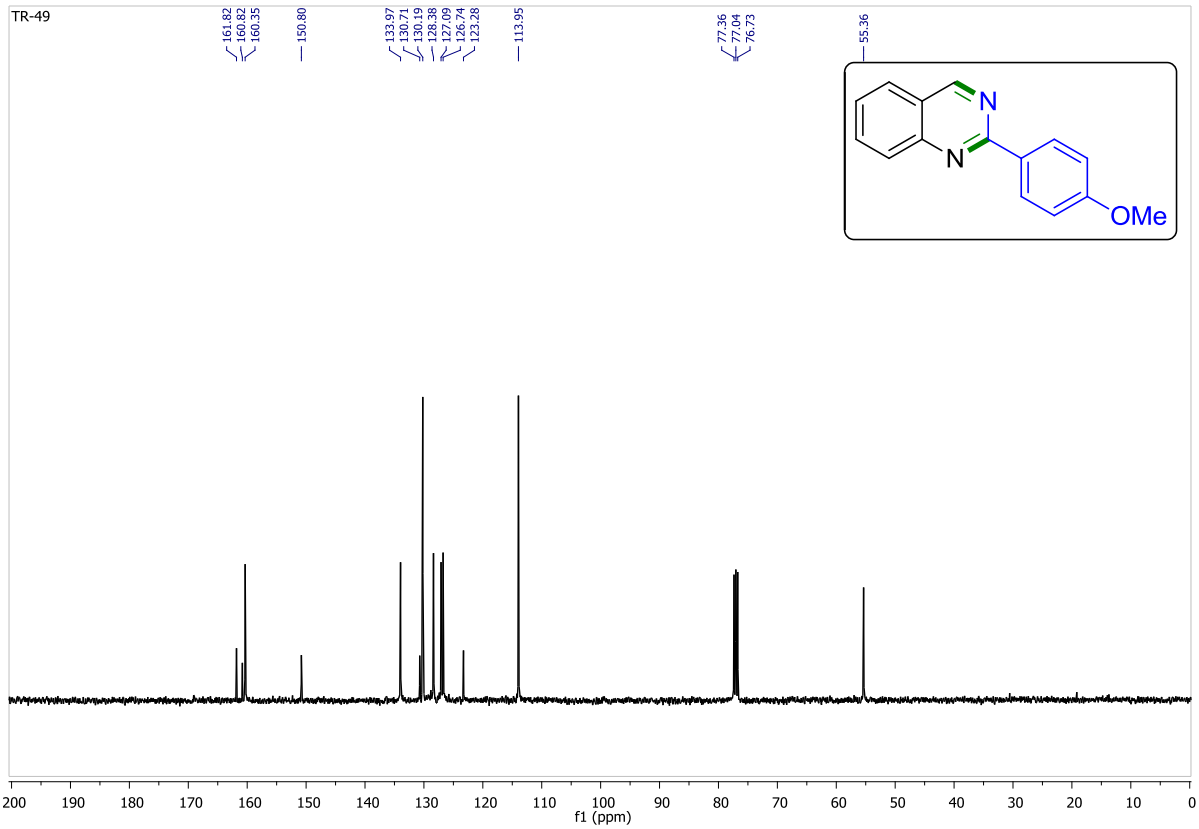
2-phenylquinazoline (3a)



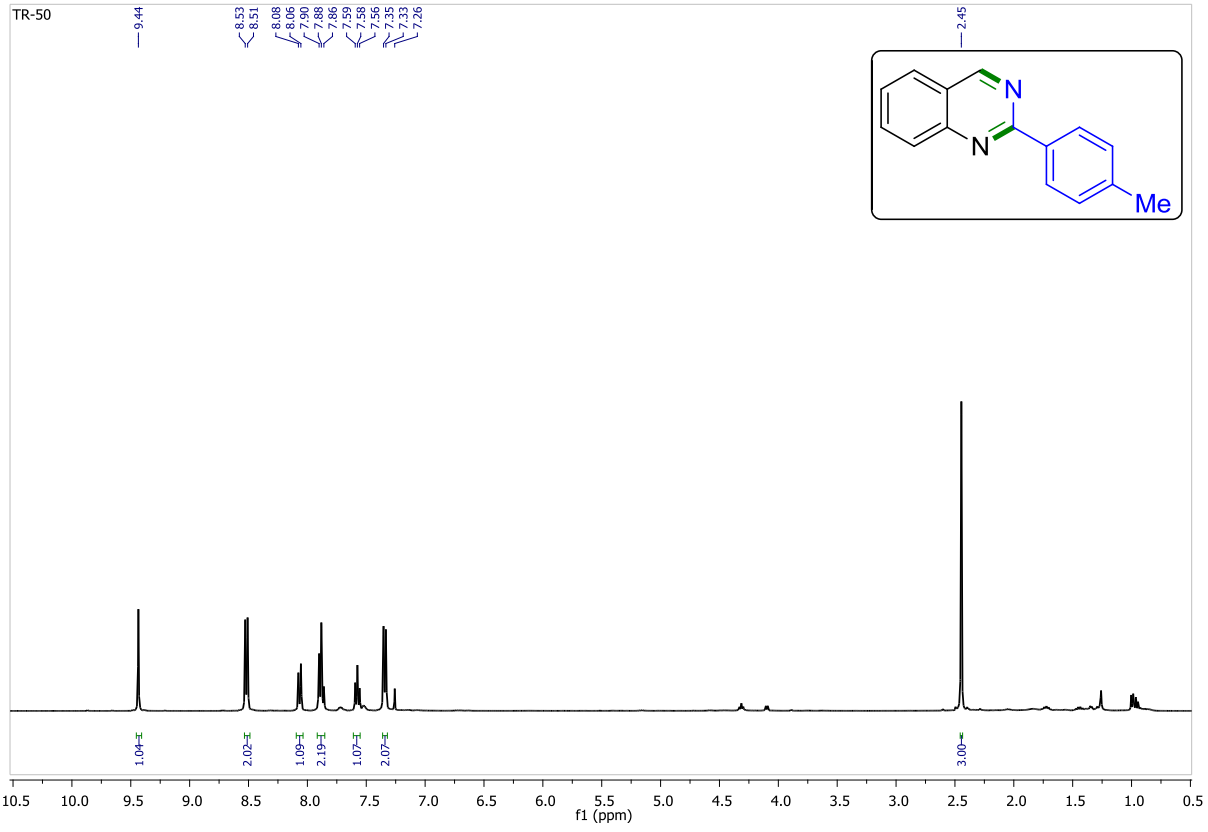


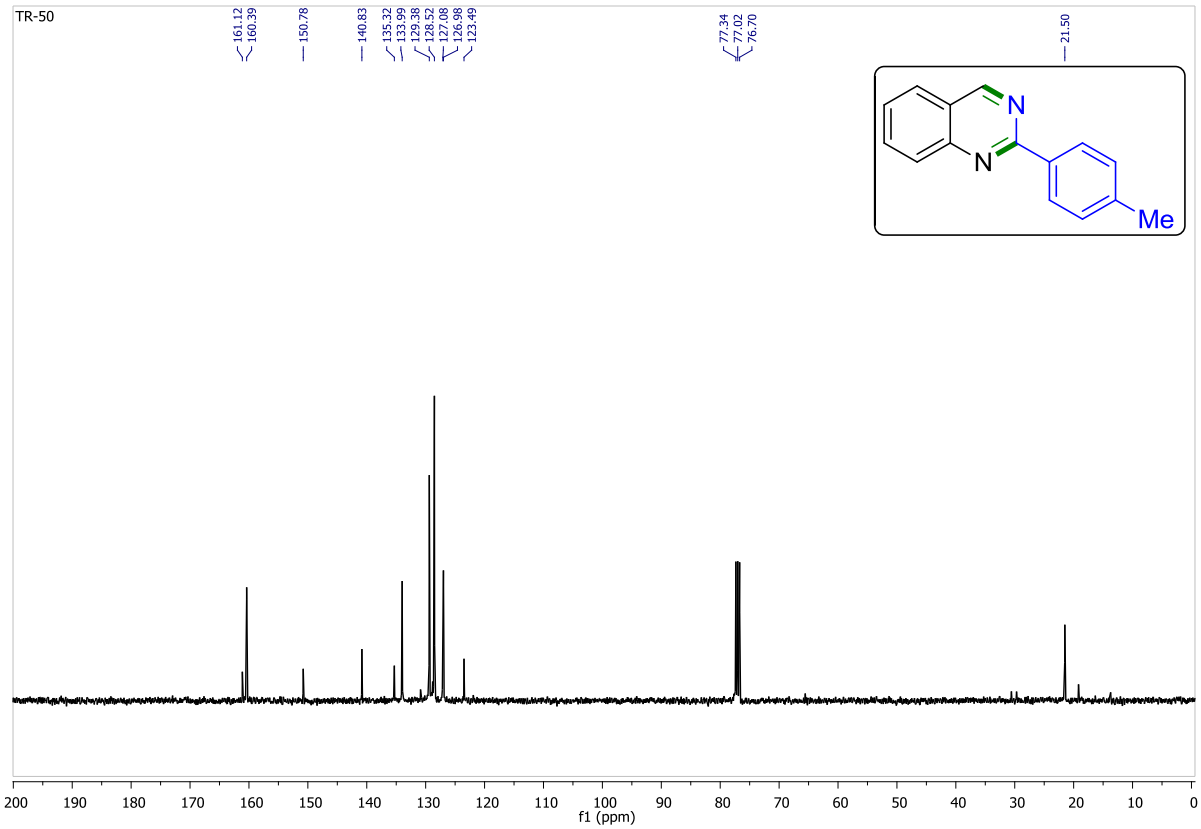
2-(4-methoxyphenyl)quinazoline (3b)



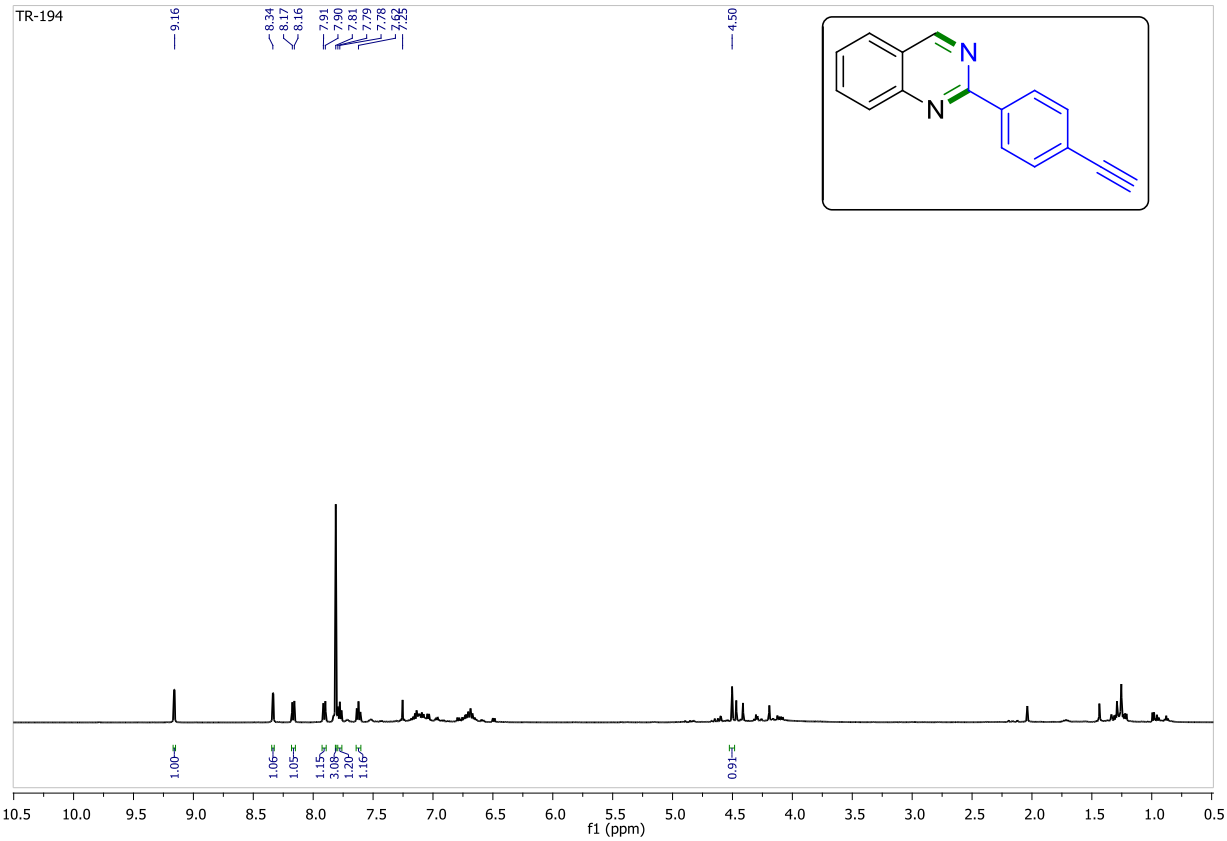


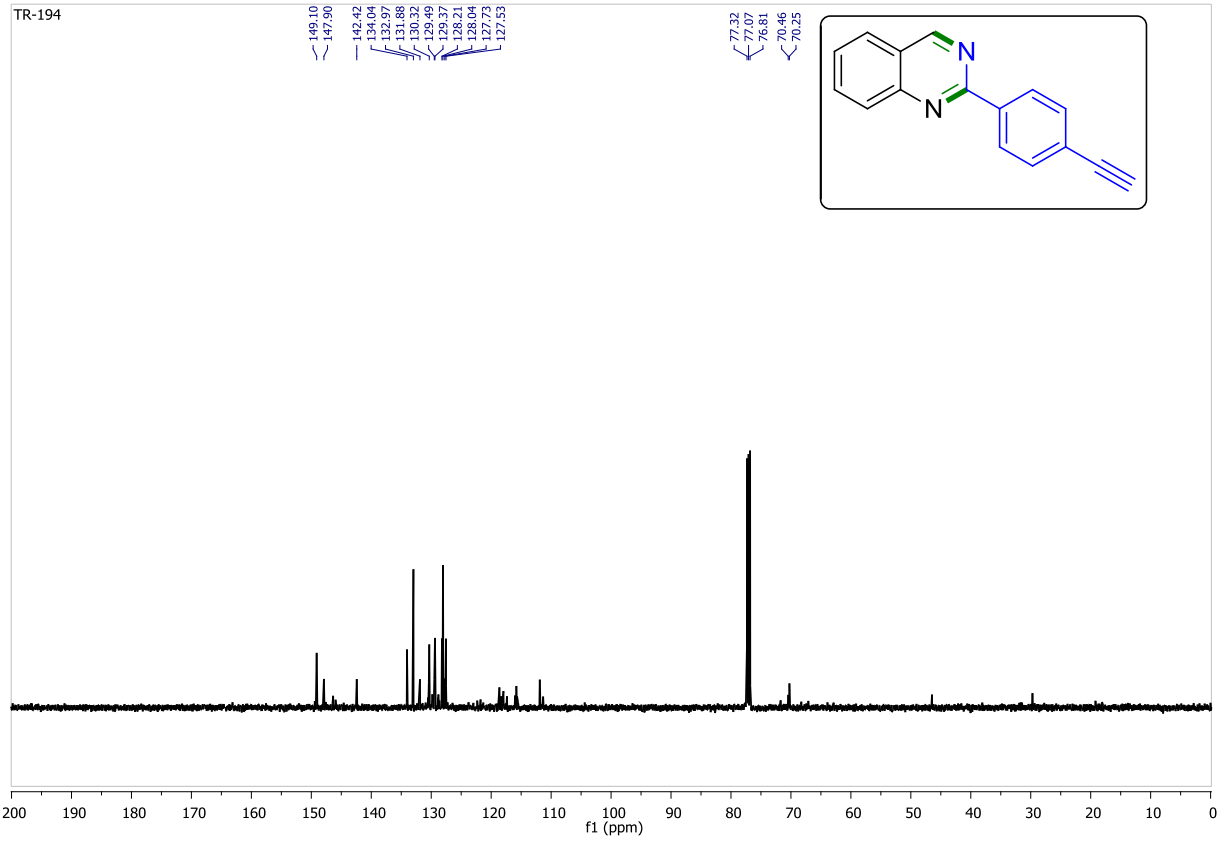
2-(p-tolyl)quinazoline (3c)



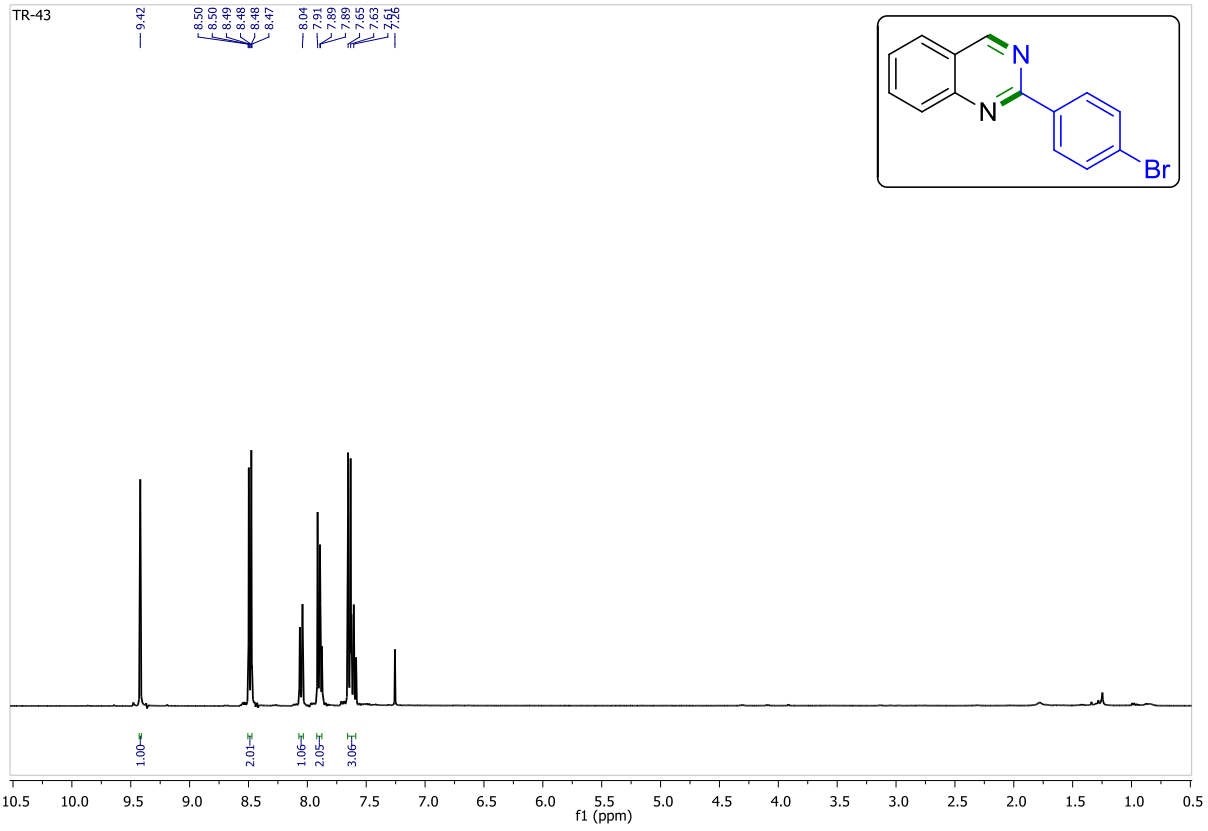


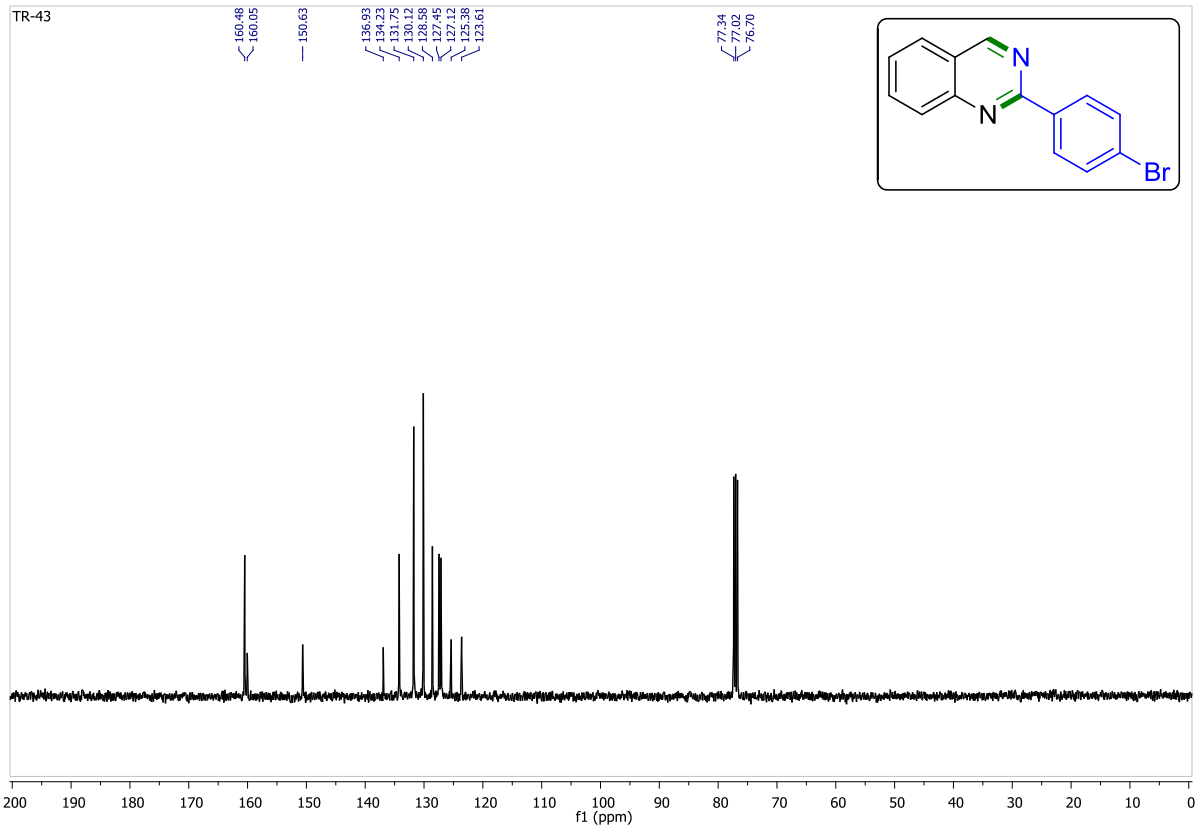
2-(4-ethynylphenyl)quinazoline (3d)





2-(4-bromophenyl)quinazoline (3e)





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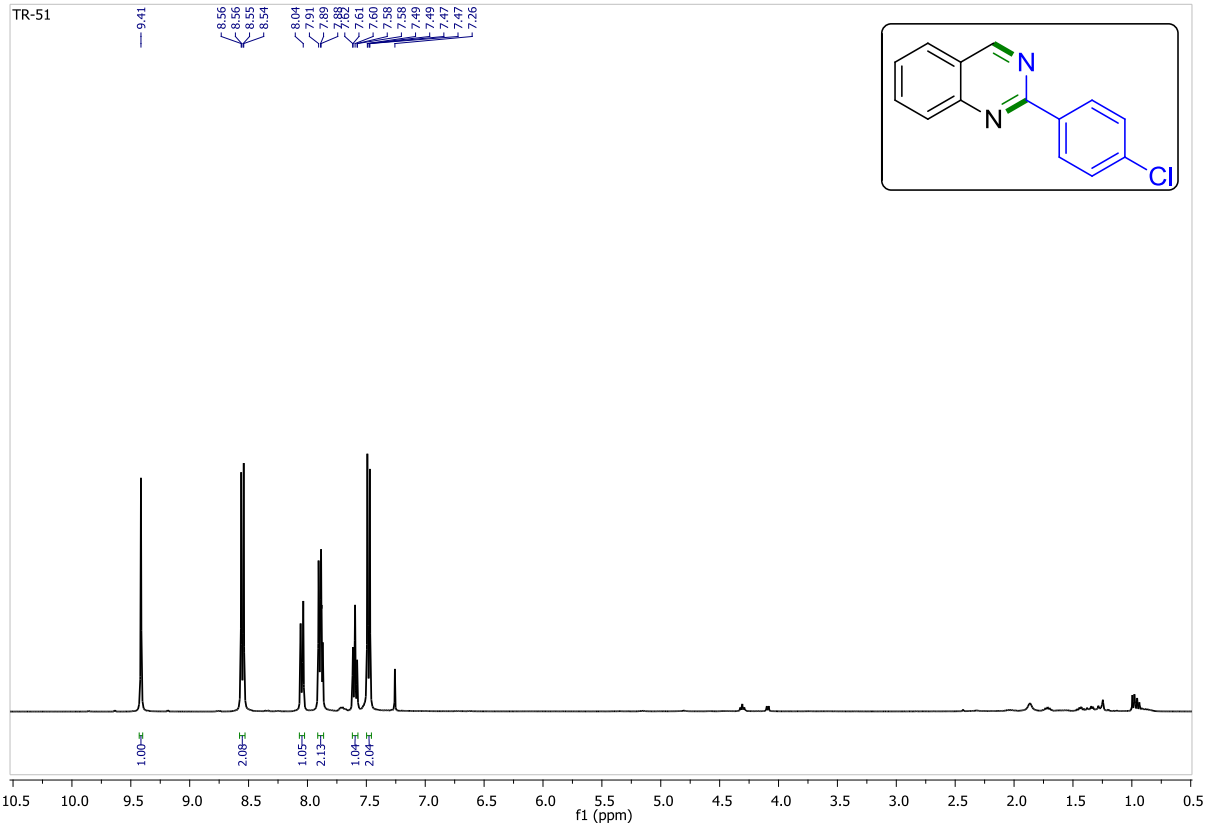
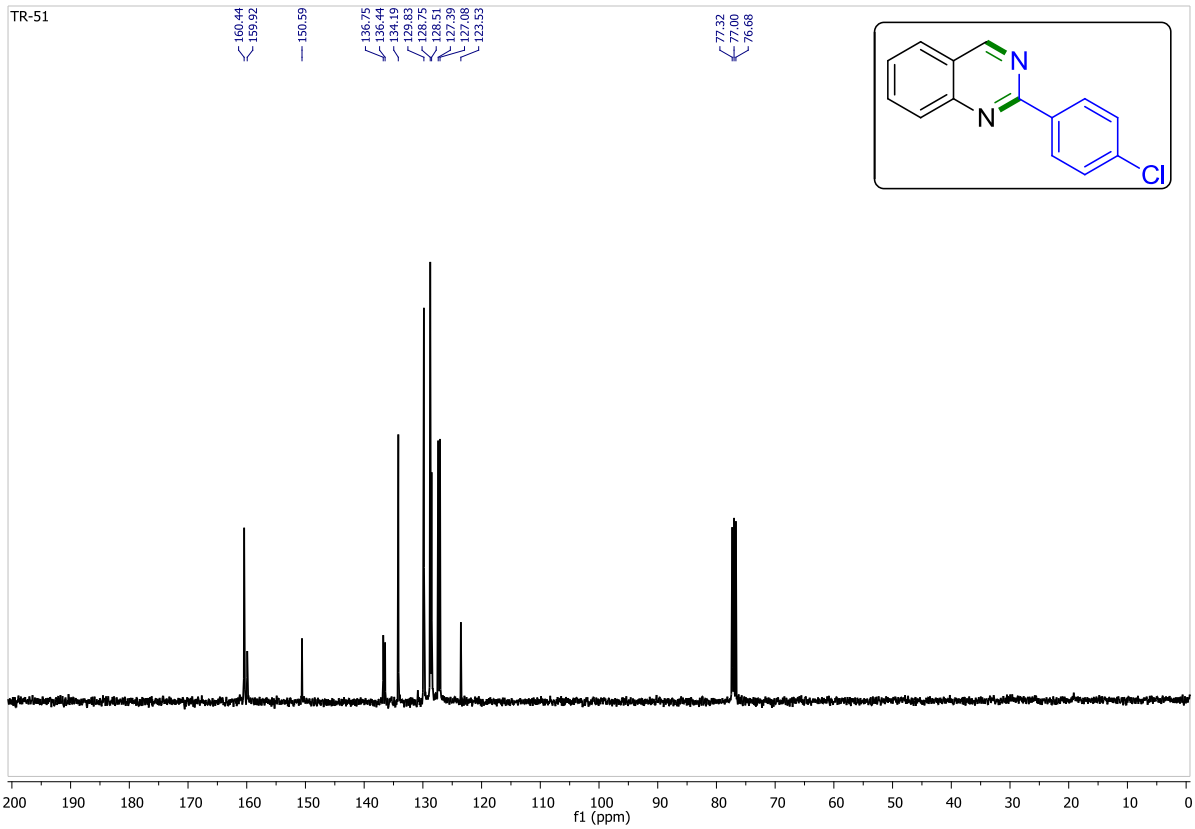
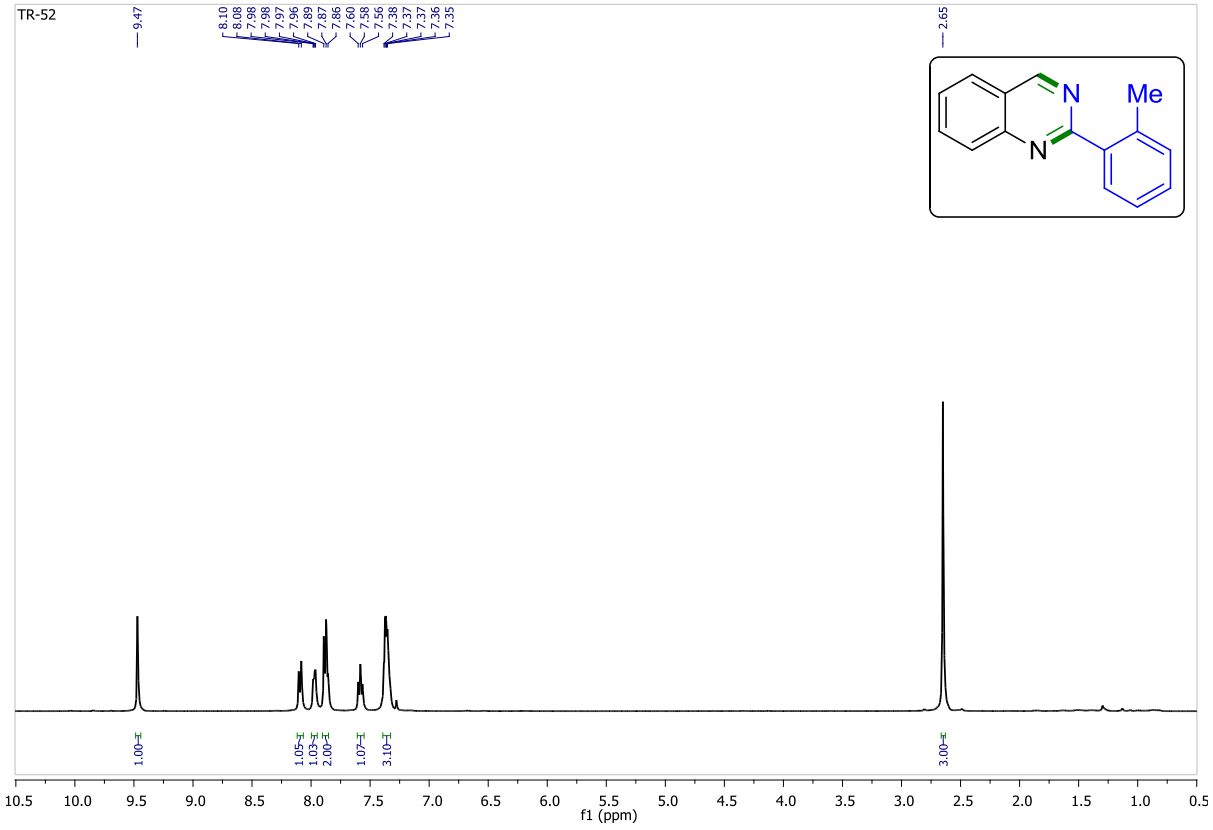
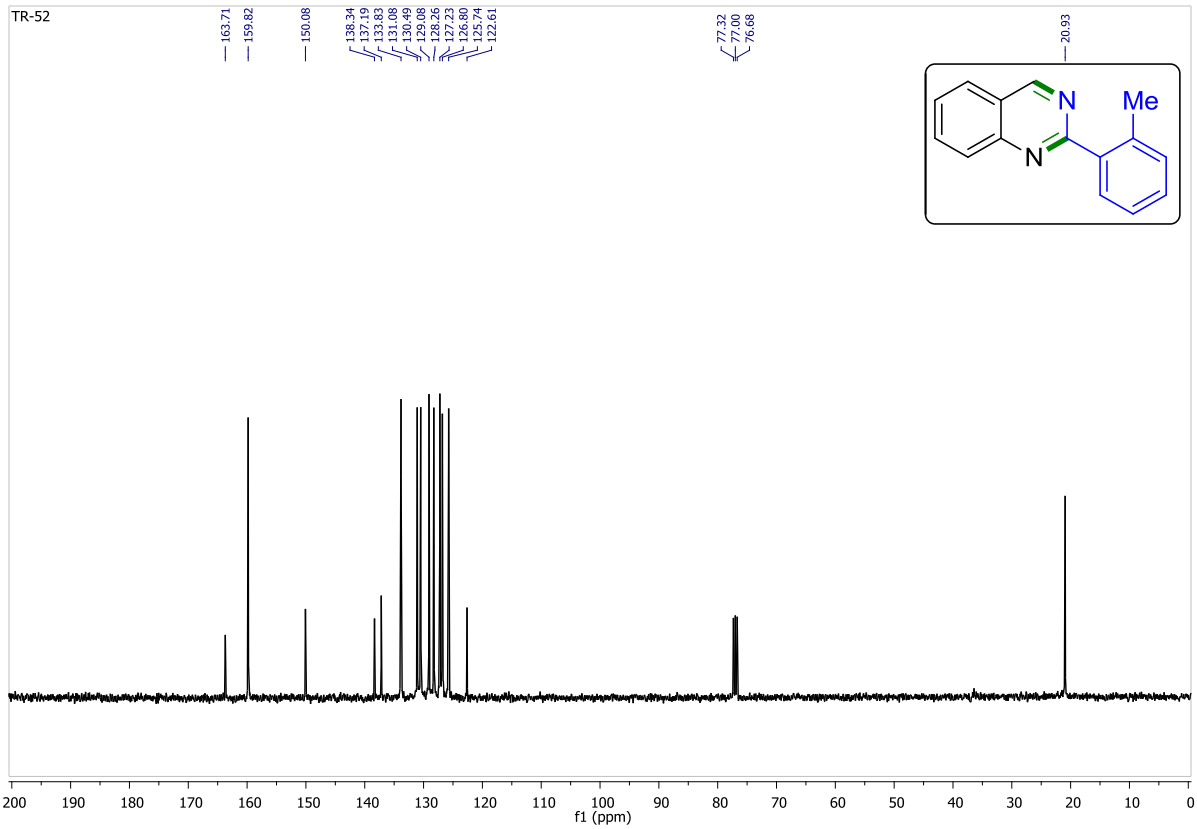


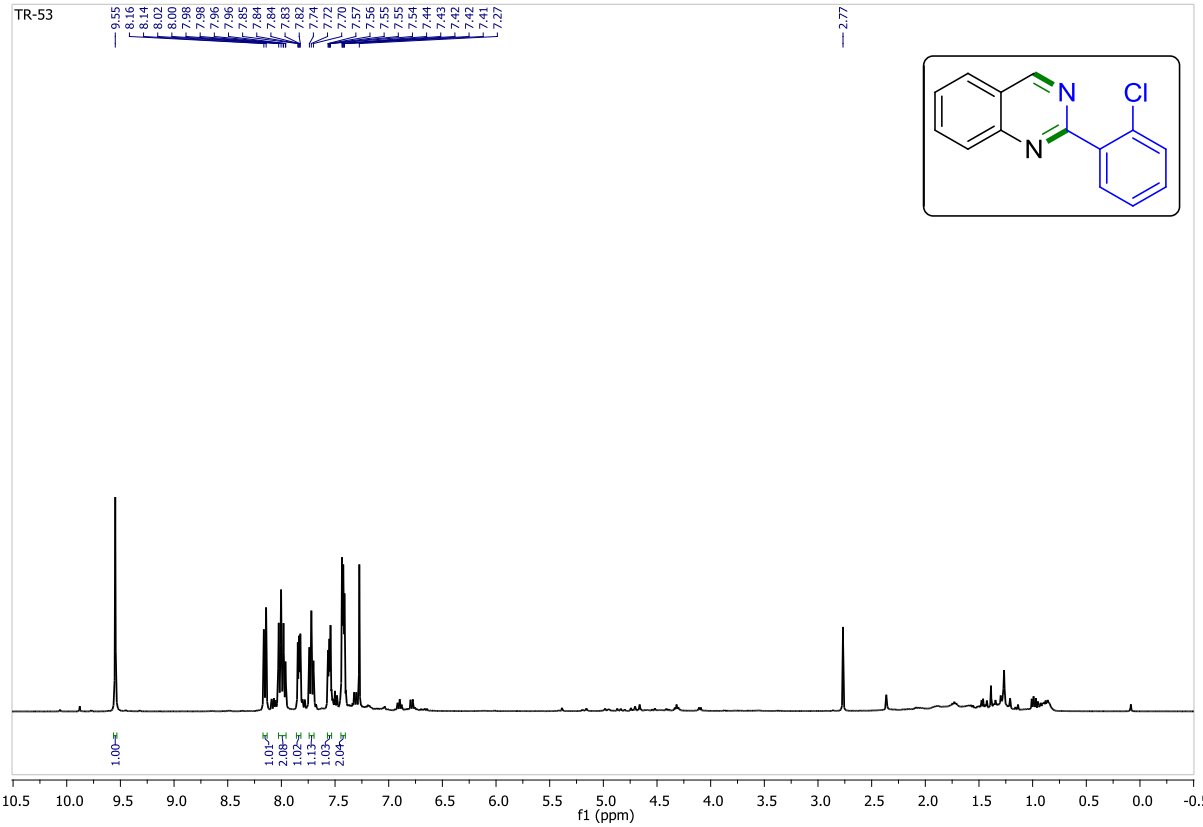


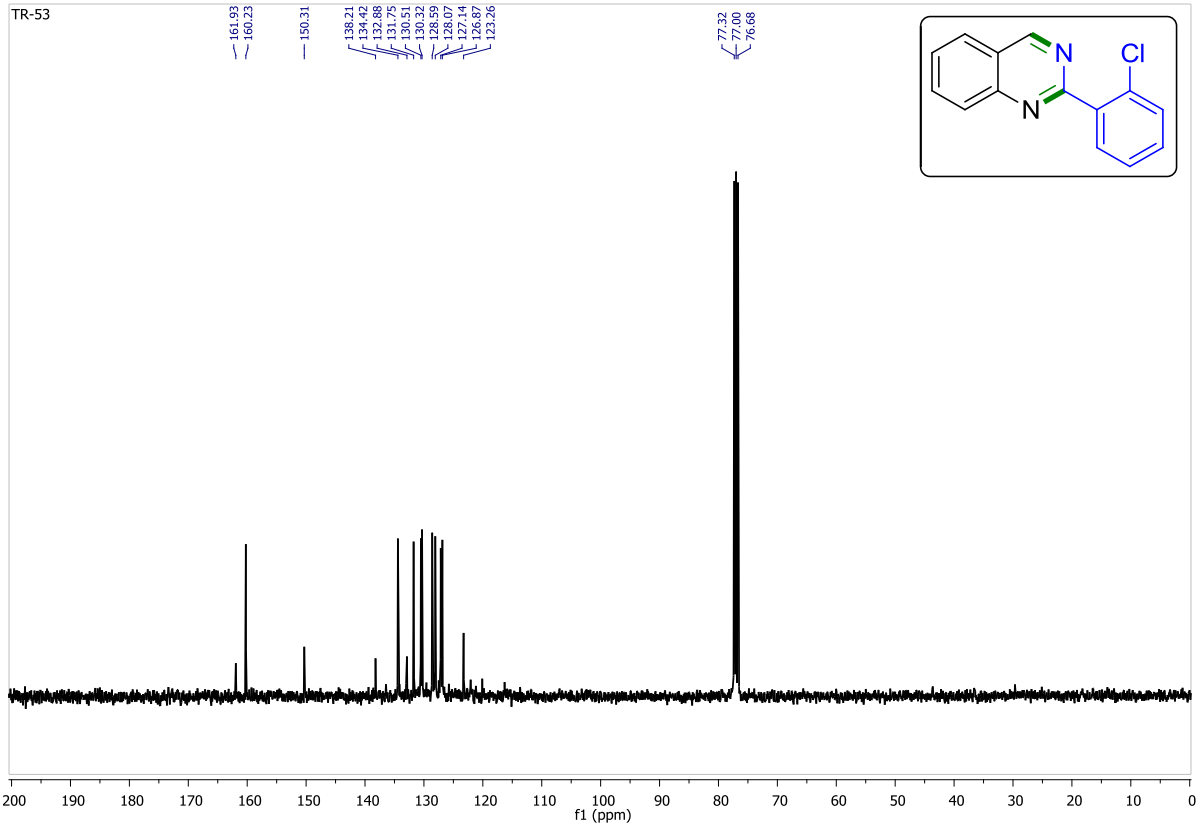
2-(o-tolyl)quinazoline (3g)



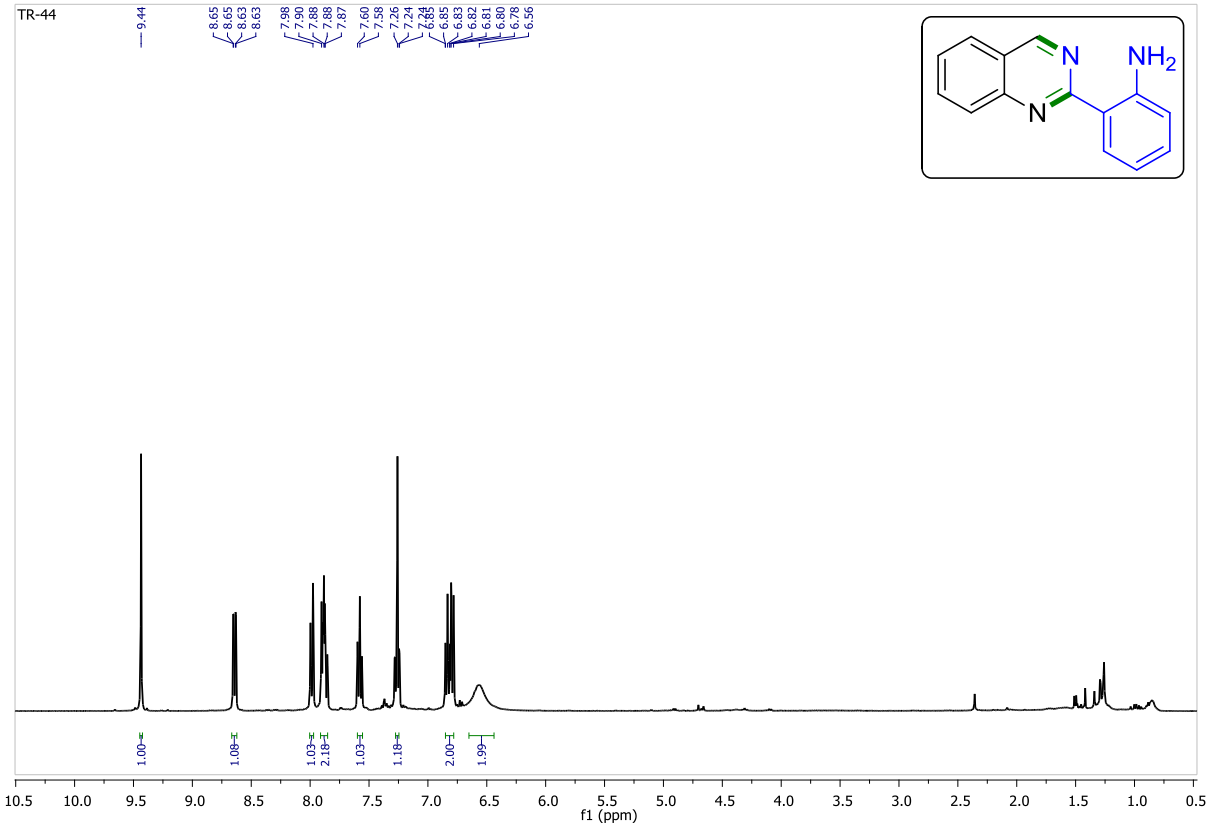


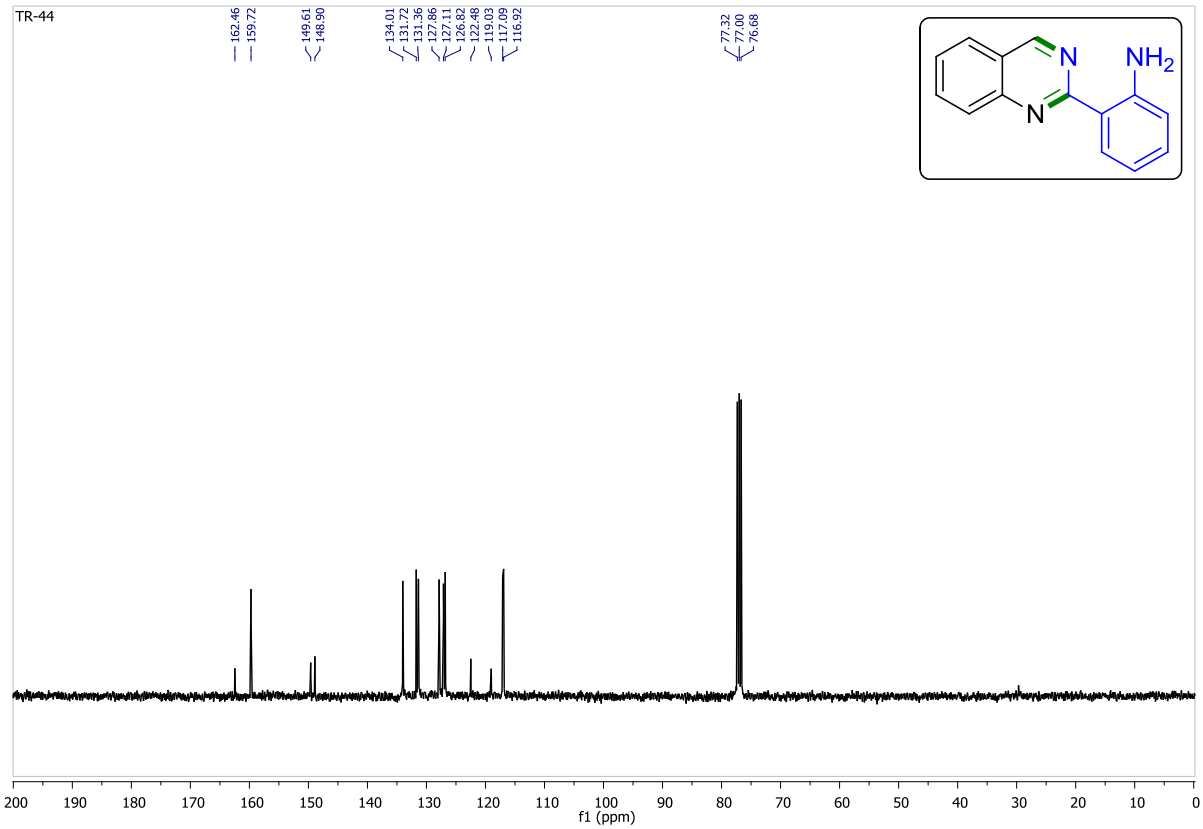
2-(2-chlorophenyl)quinazoline (3h)



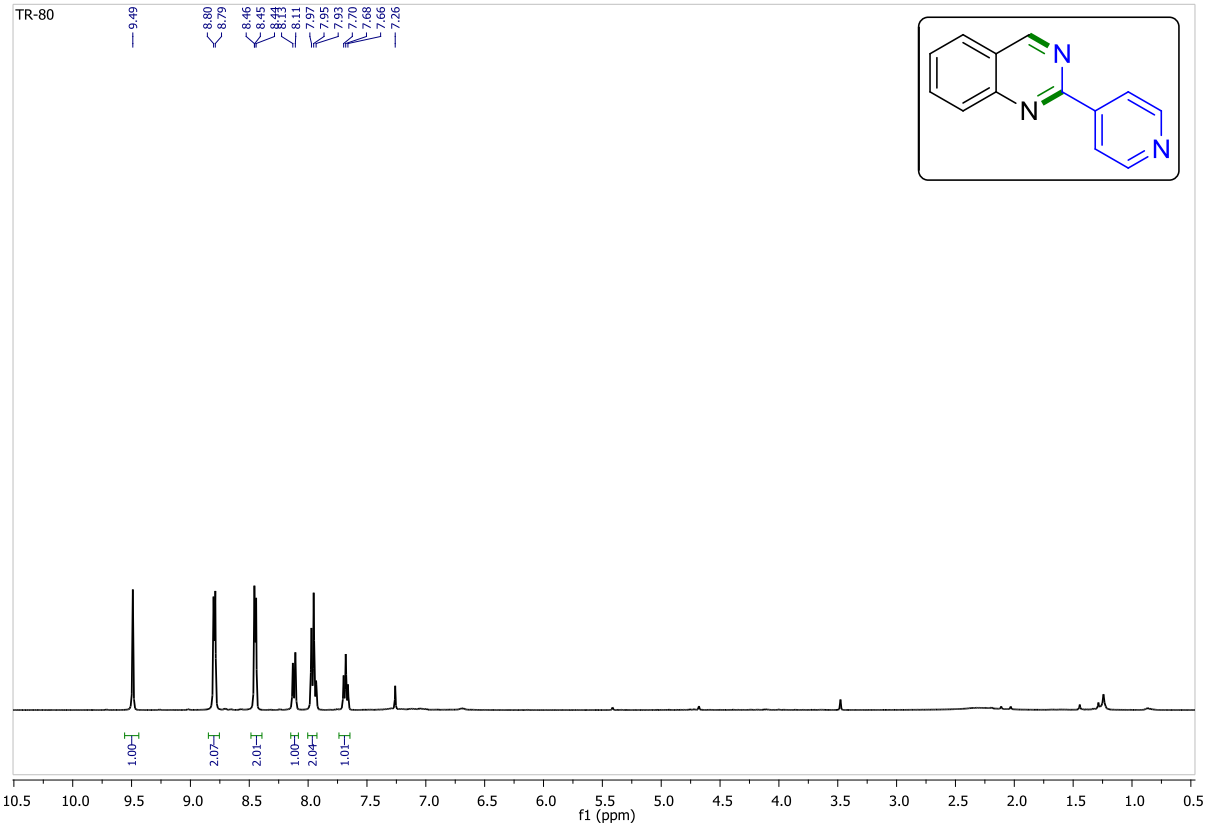


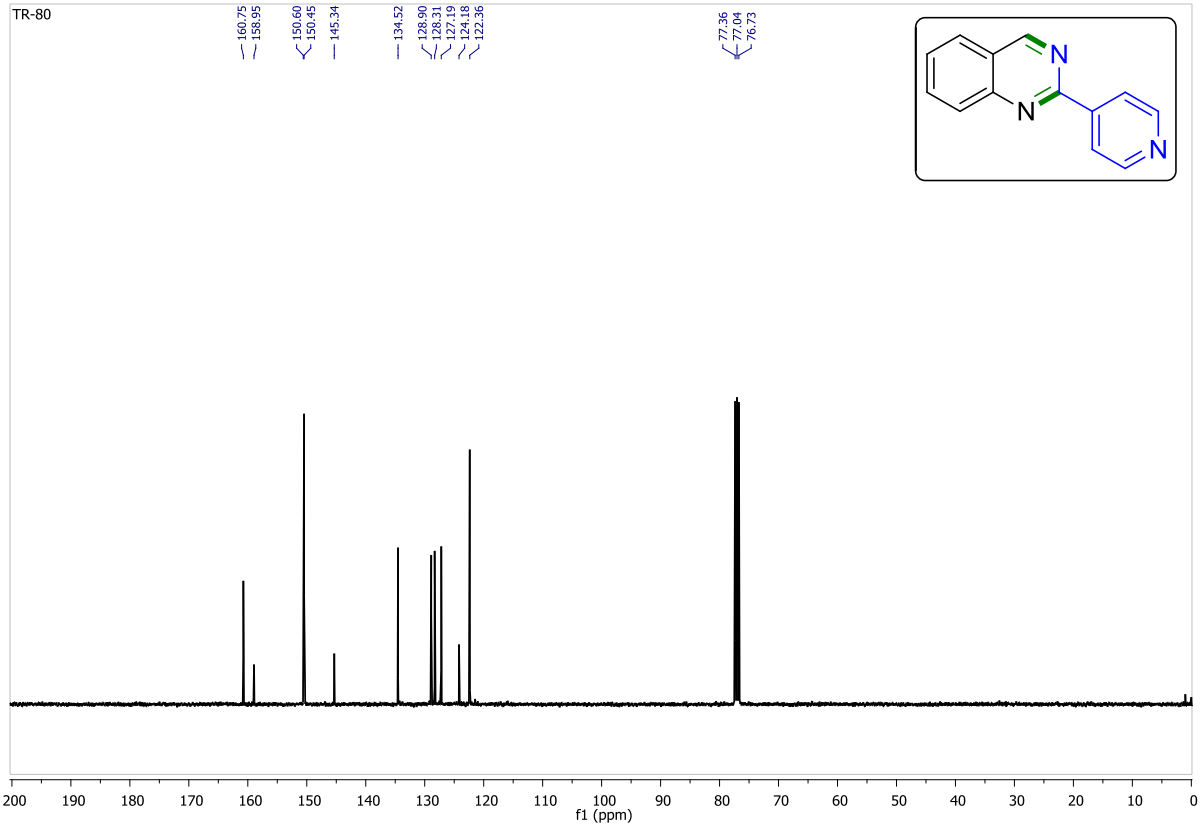
2-(quinazolin-2-yl)aniline (3i)



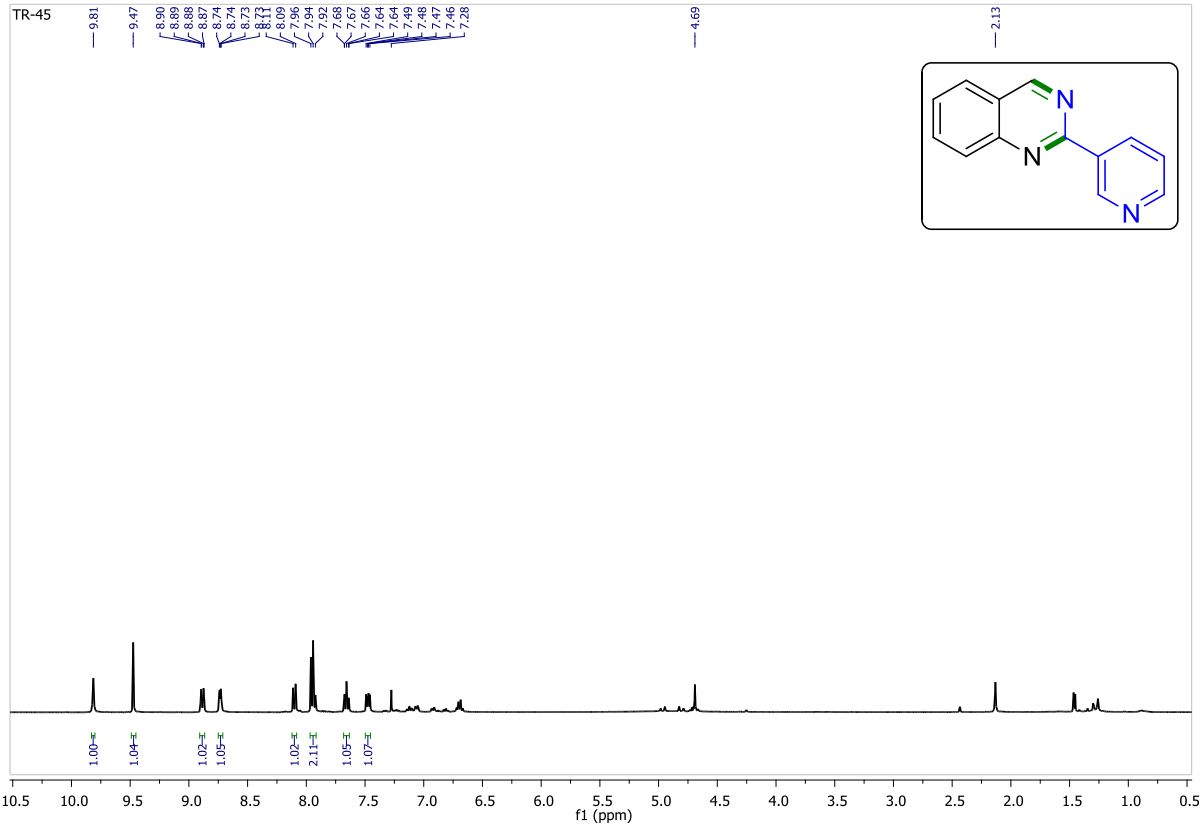


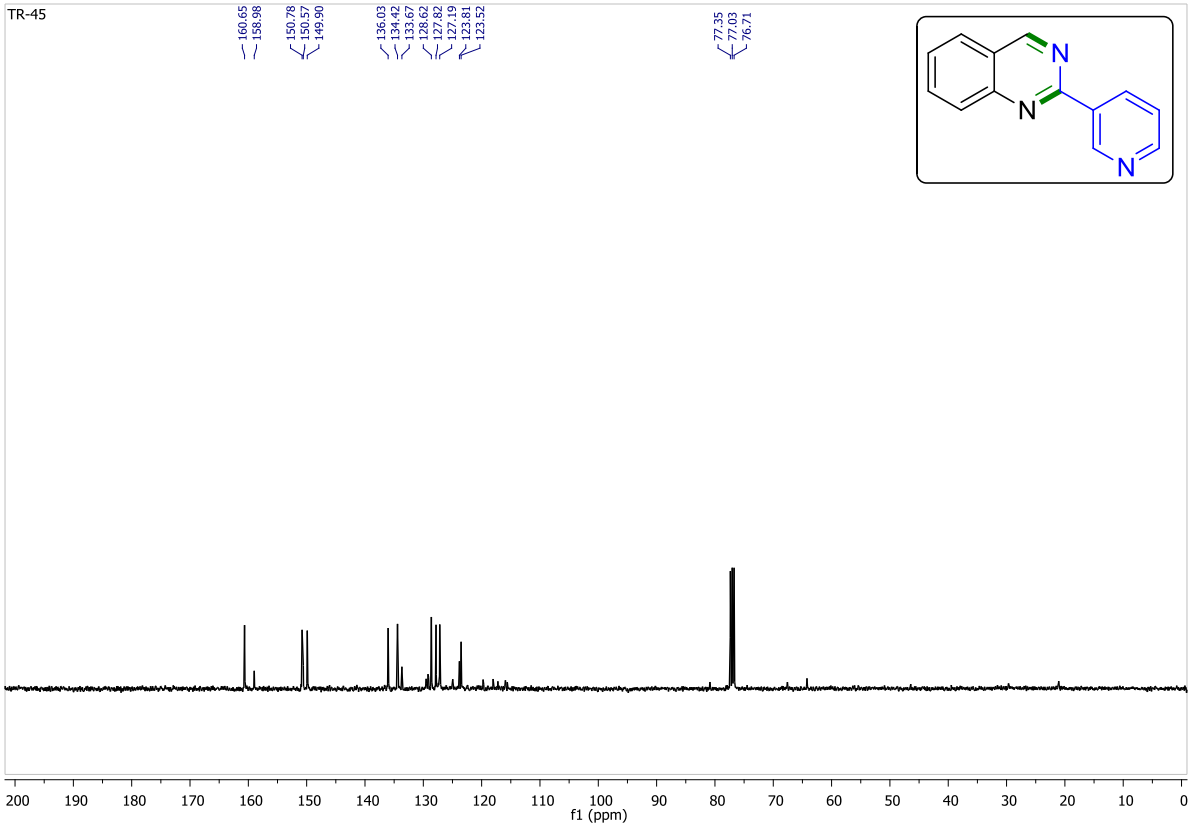
2-(pyridin-4-yl)quinazoline (3j)



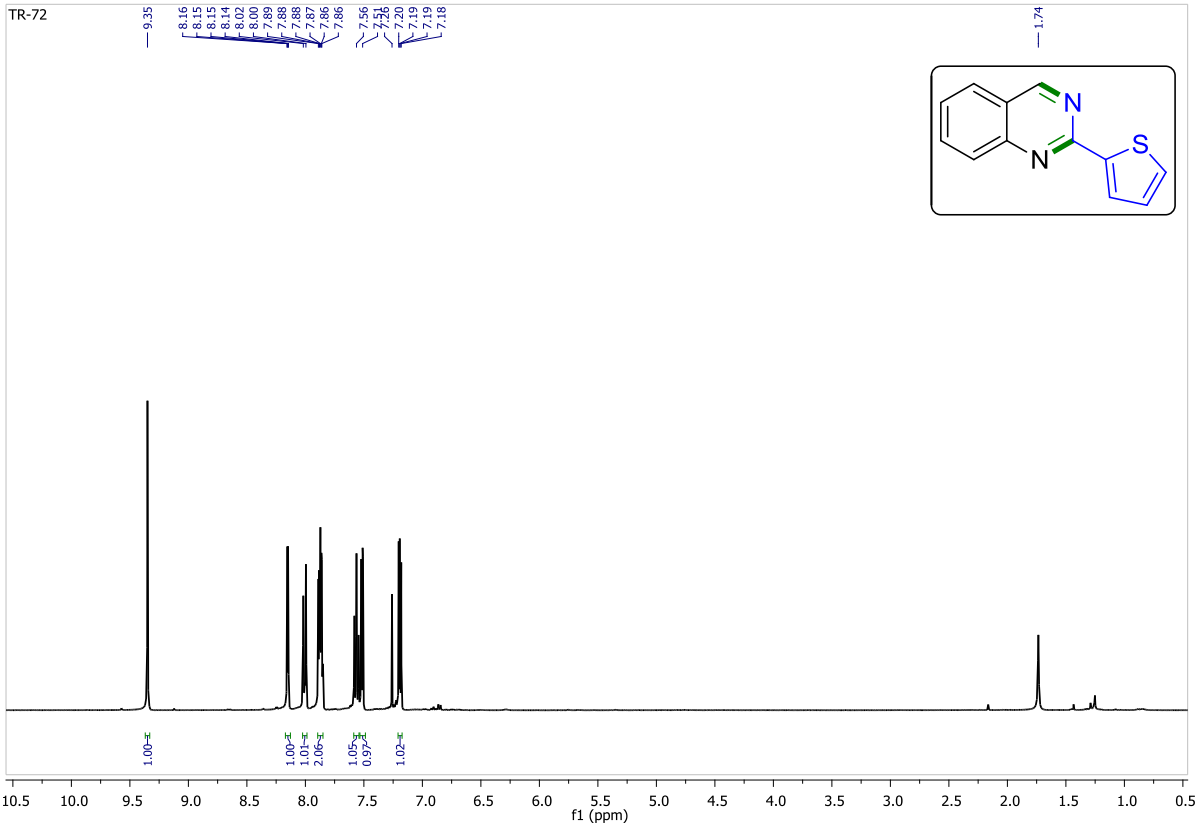


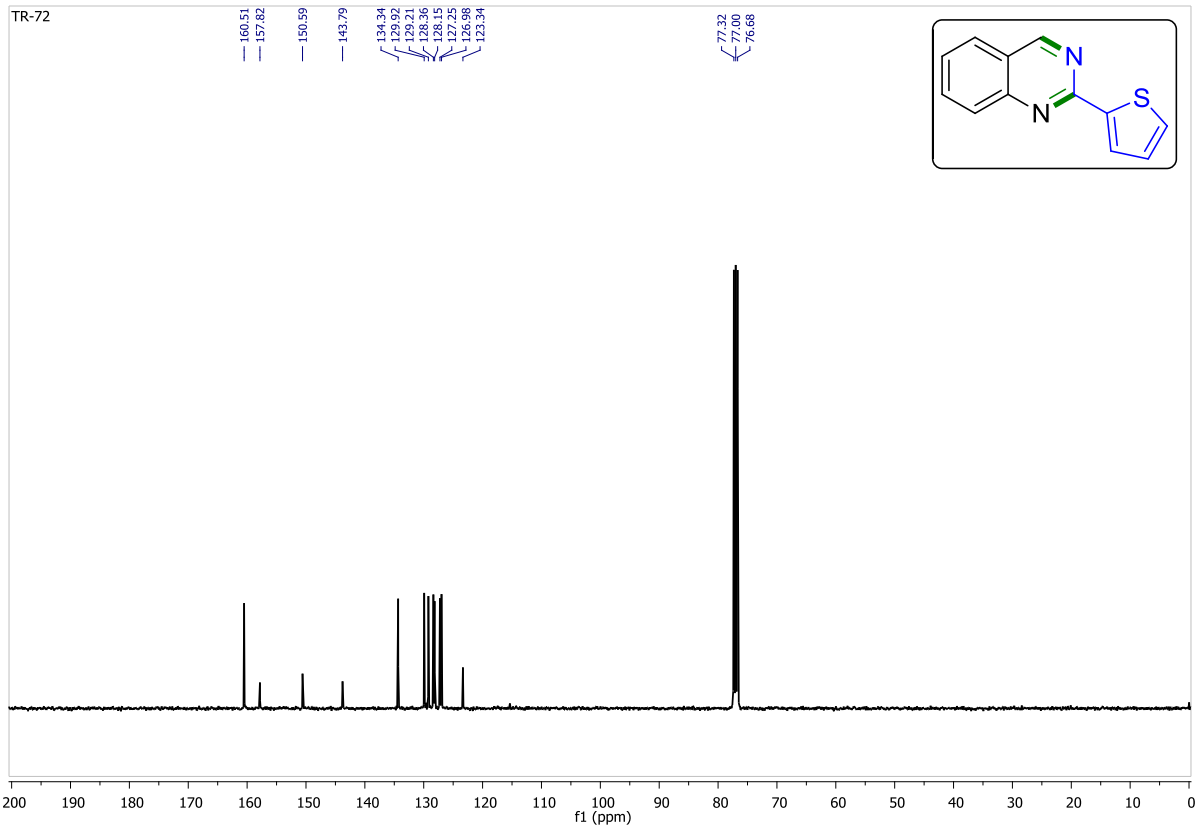
2-(pyridin-3-yl)quinazoline (3k)



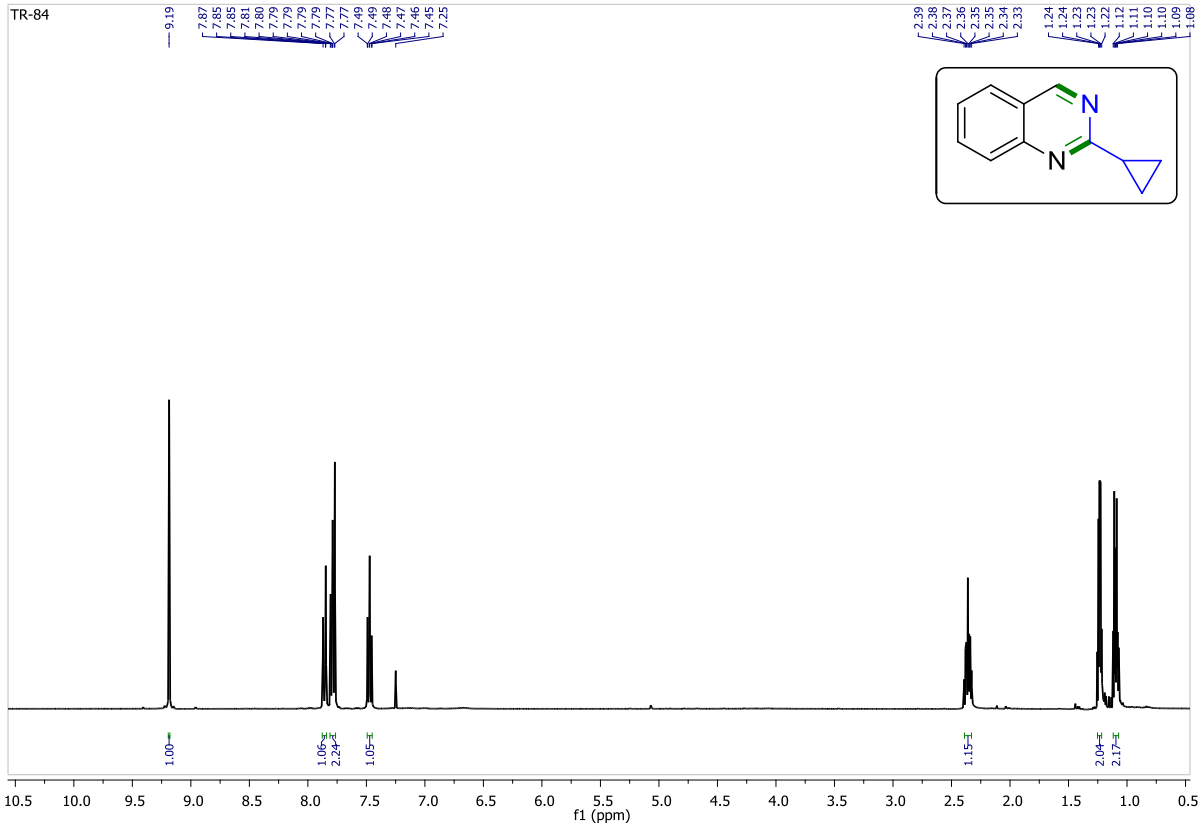


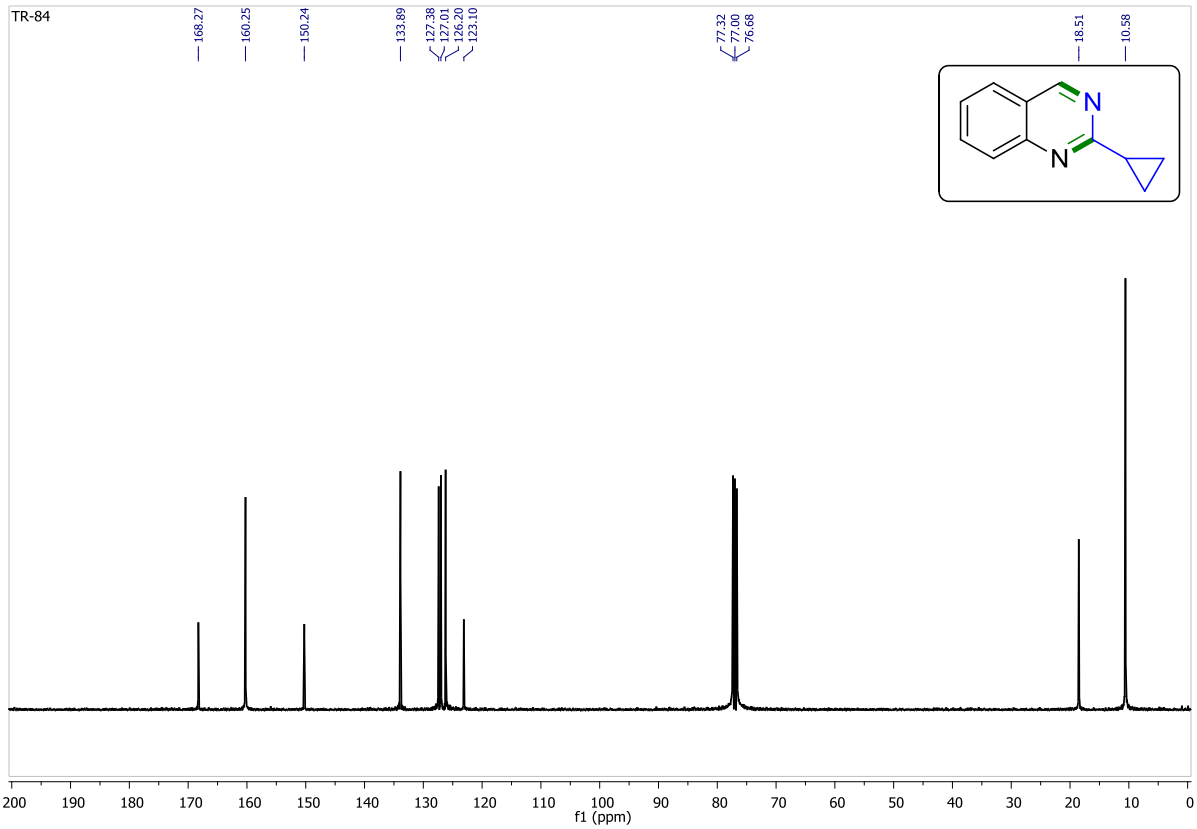
2-(thiophen-2-yl)quinazoline (3l)



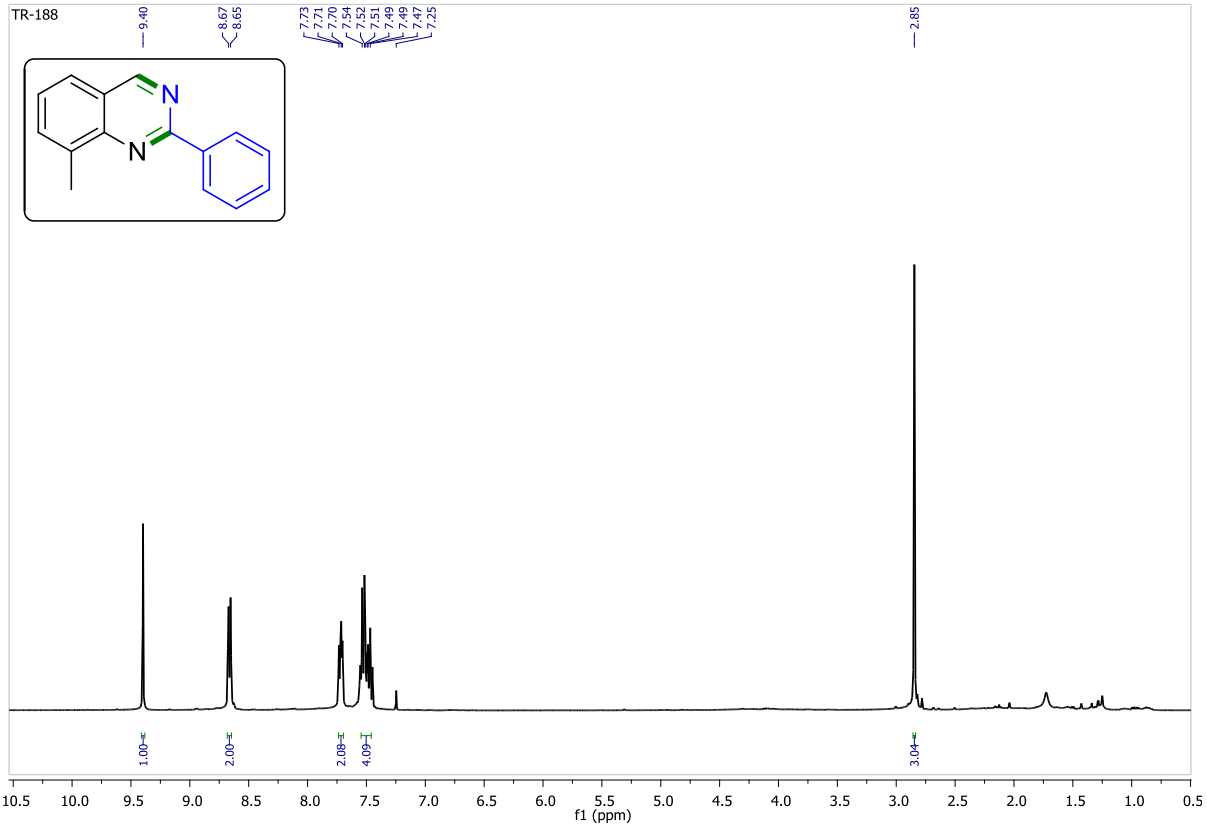


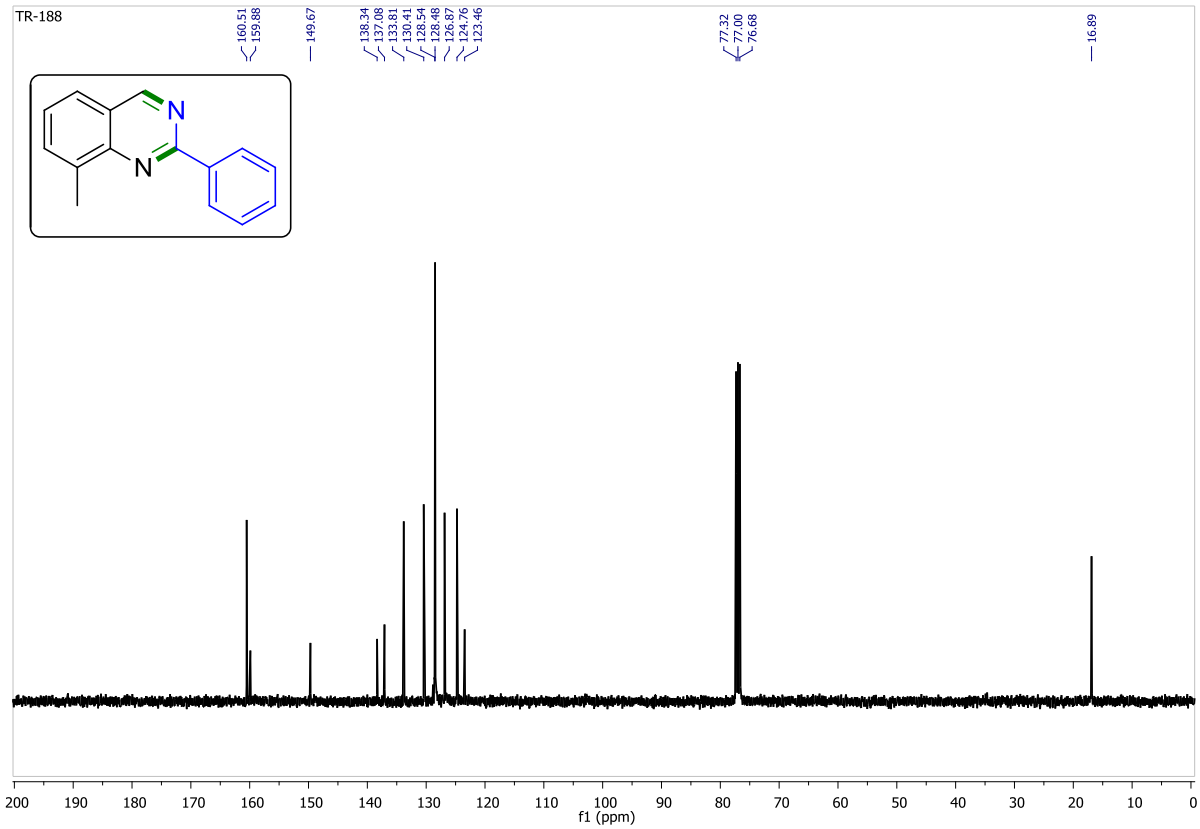
2-cyclopropylquinazoline (3m)



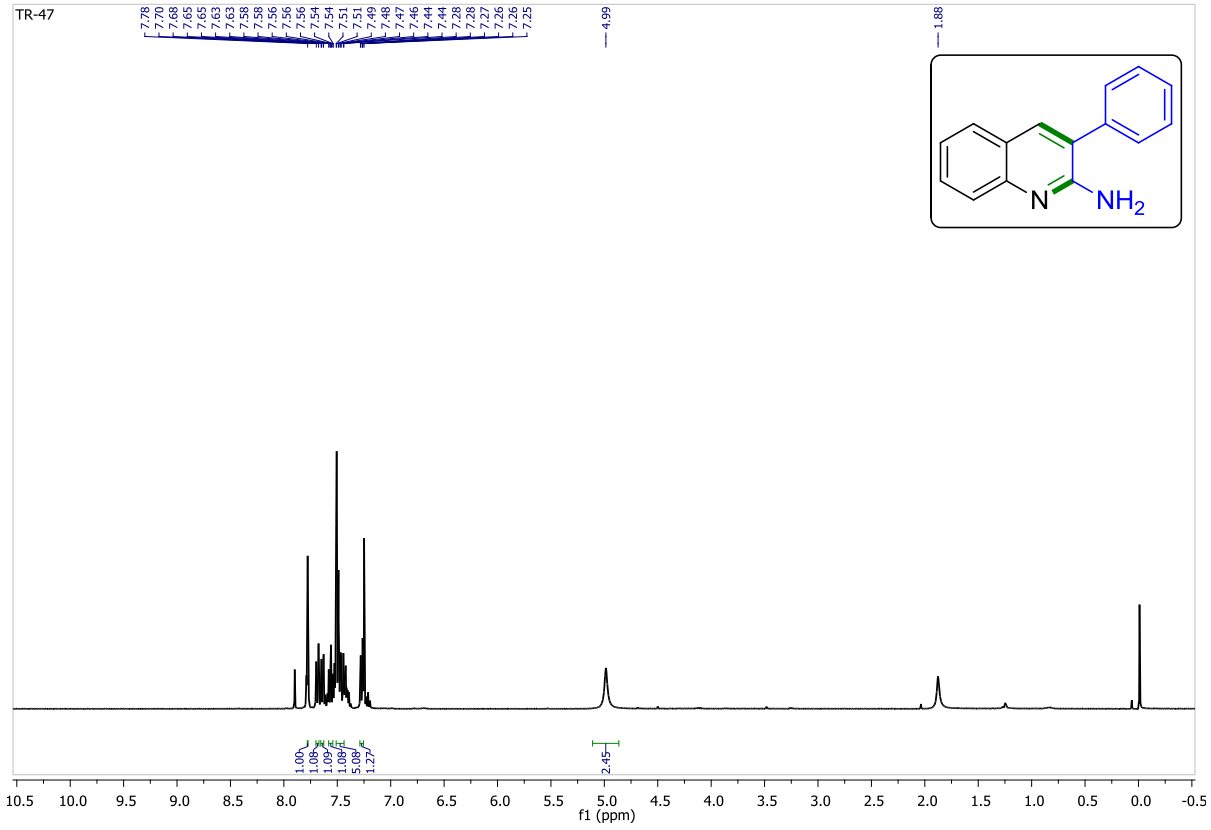


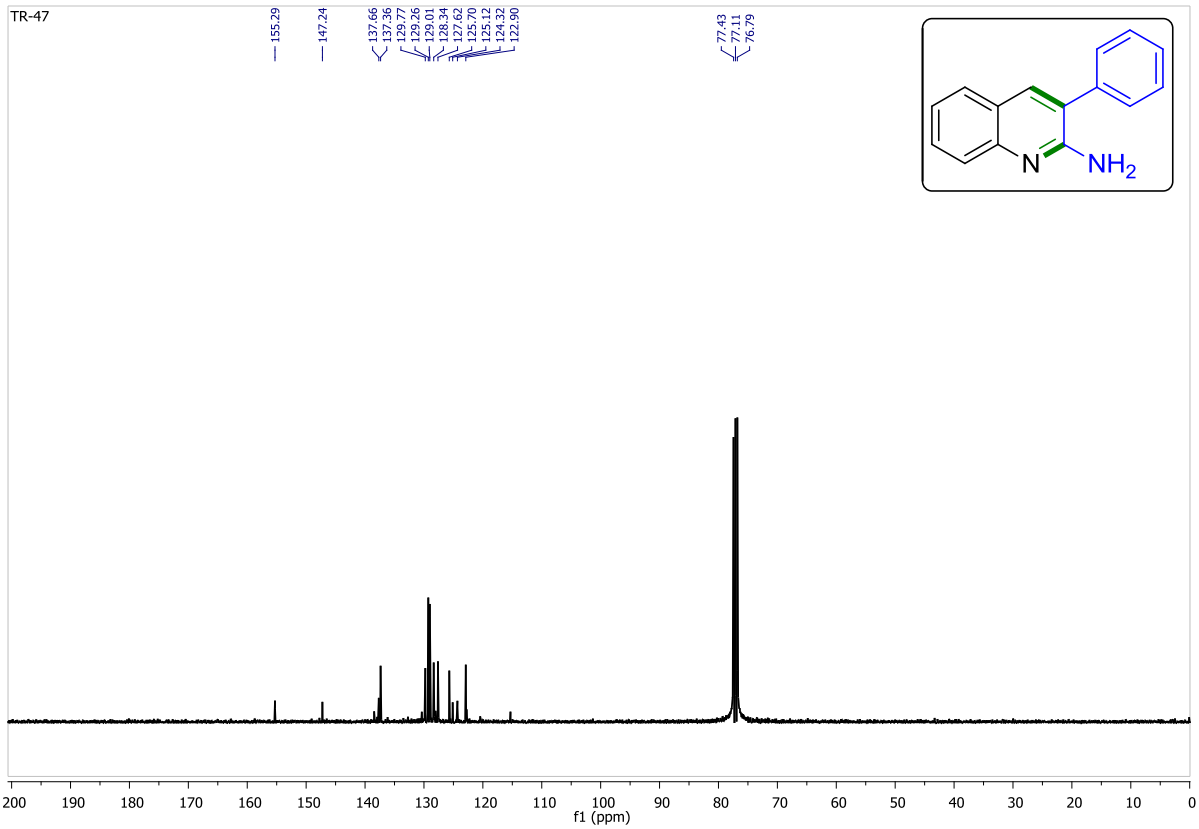
8-methyl-2-phenylquinazoline (3n)



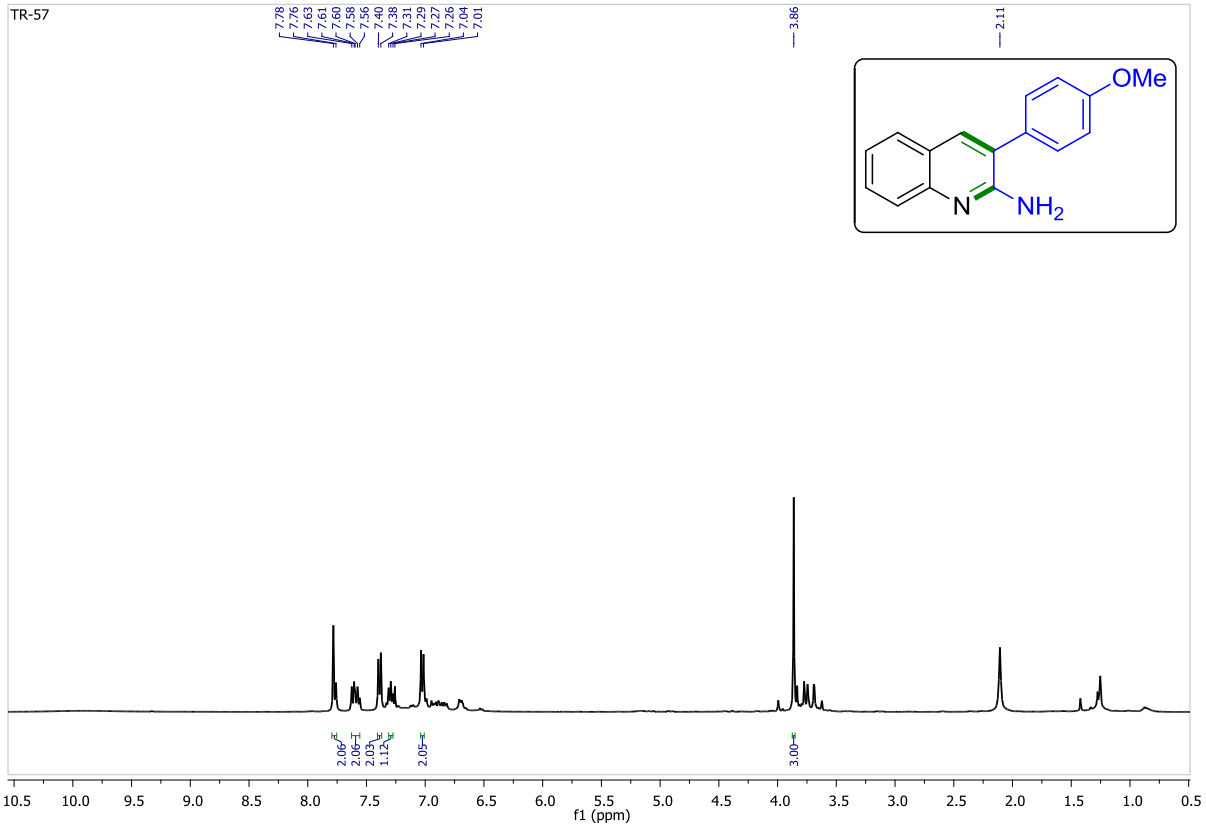


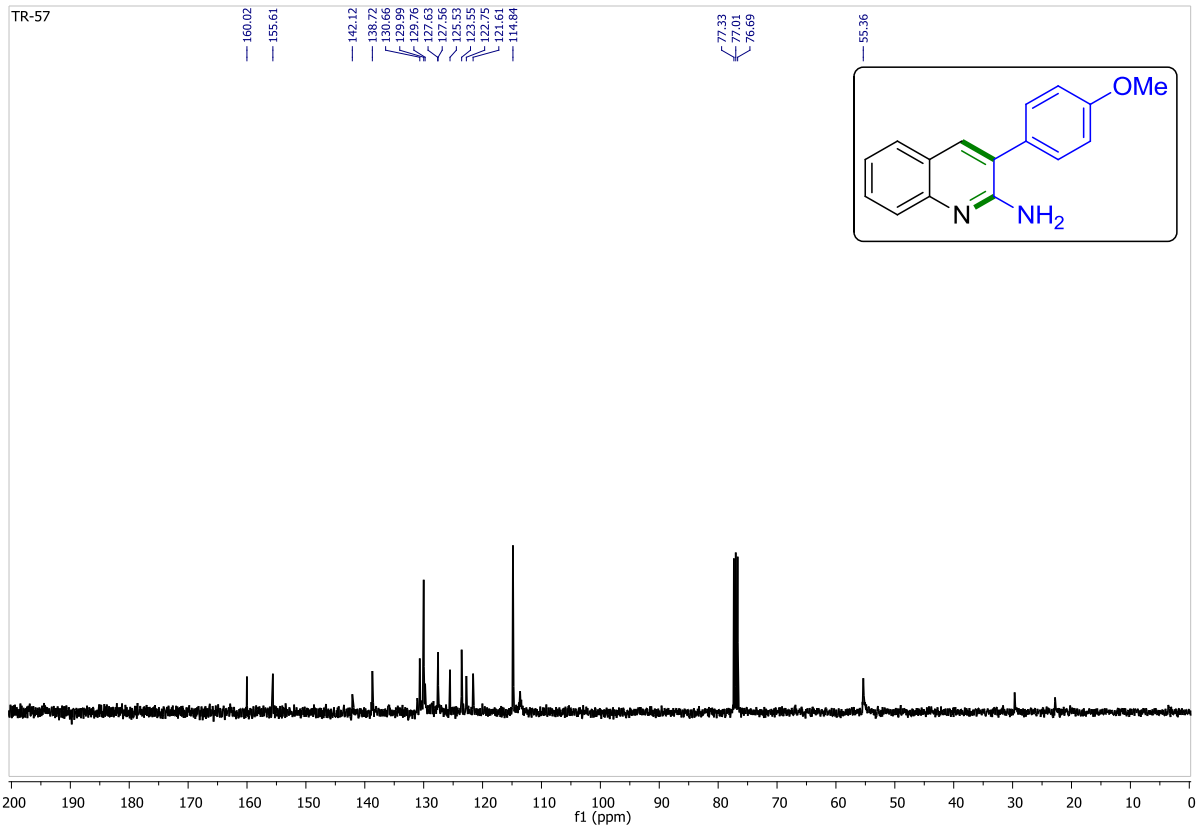
3-phenylquinolin-2-amine (5a)



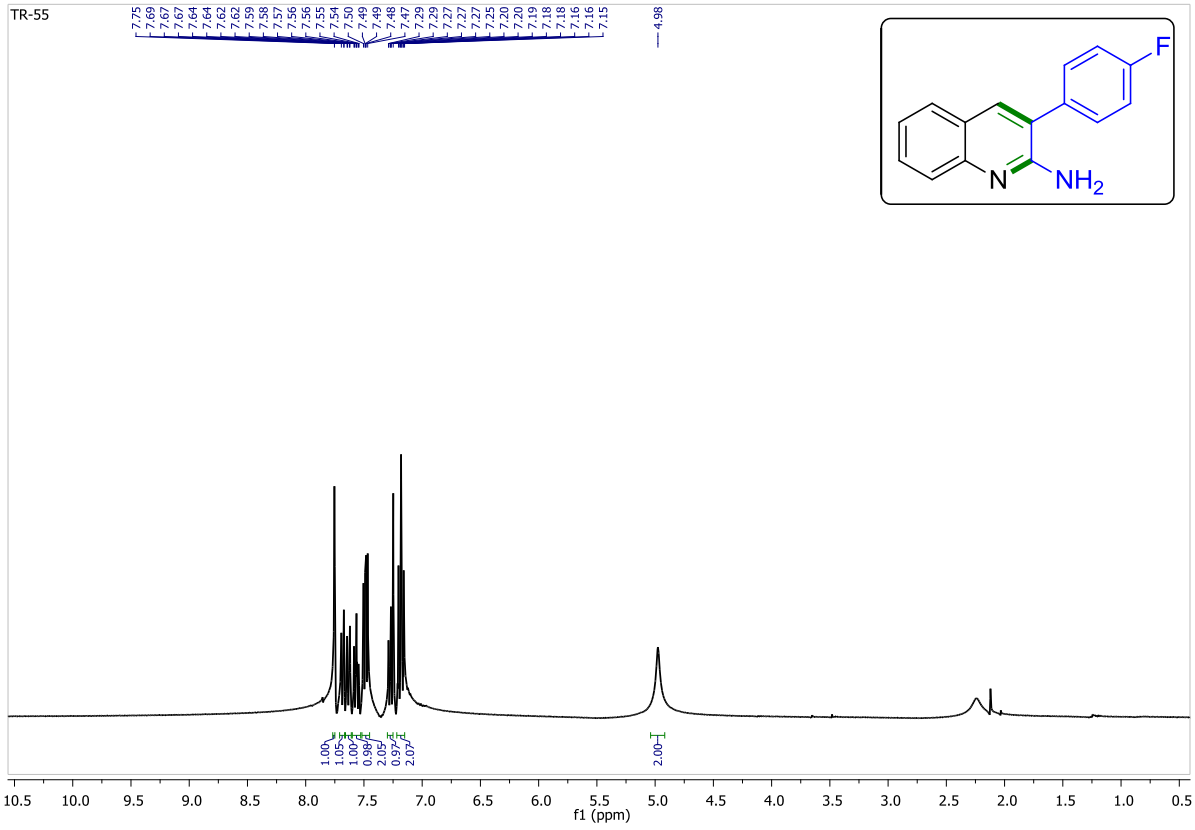


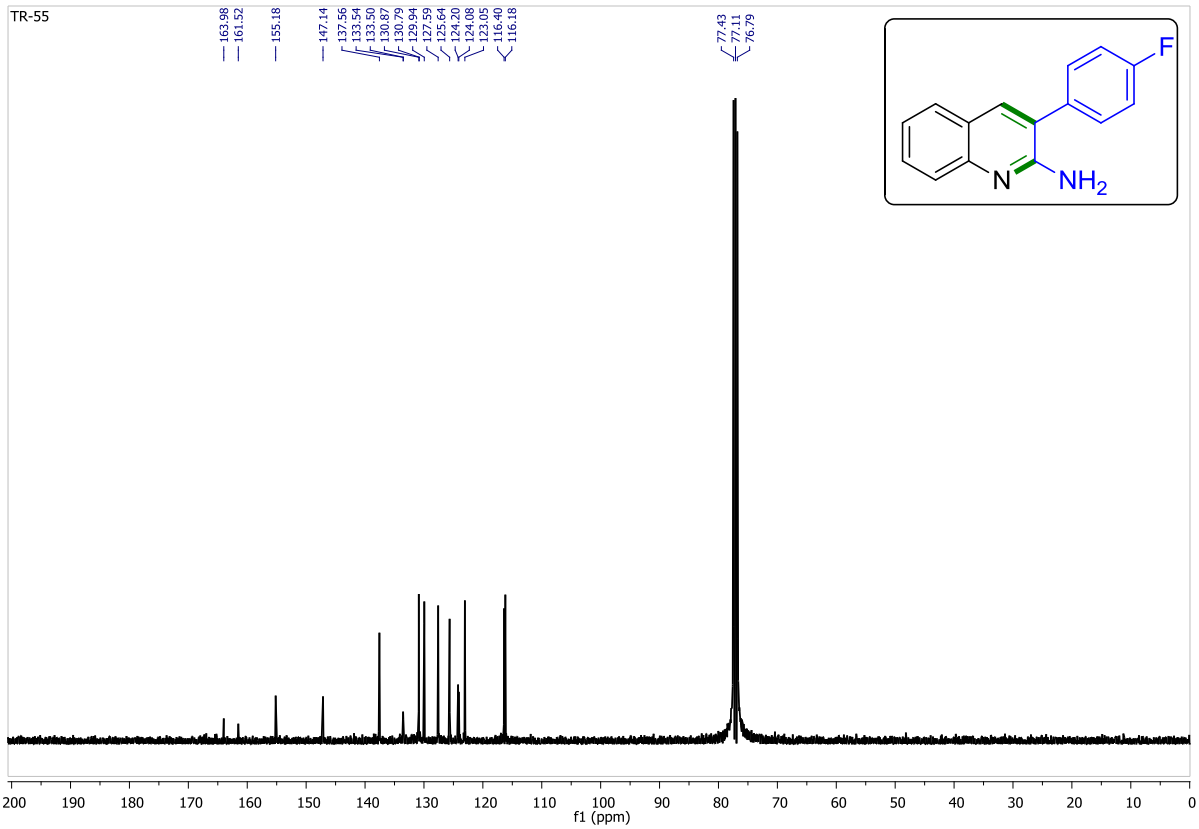
3-(4-methoxyphenyl)quinolin-2-amine (5b)



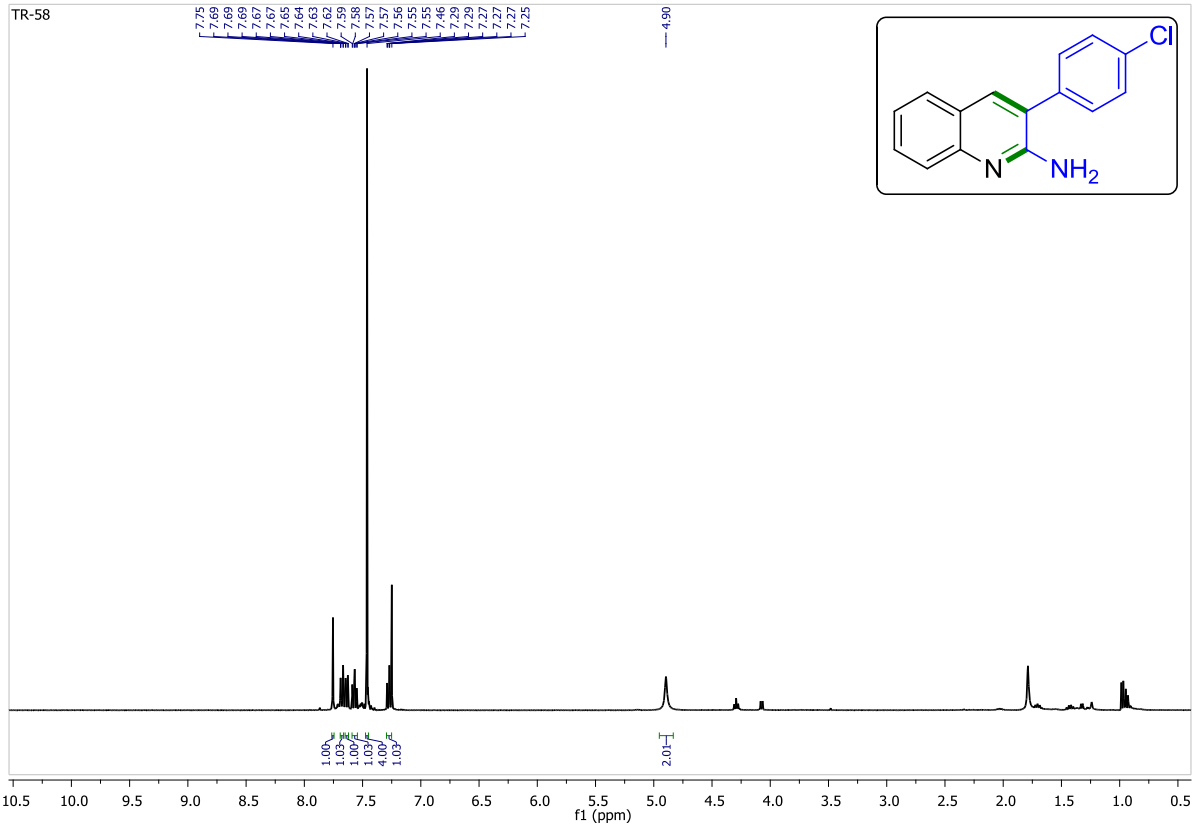


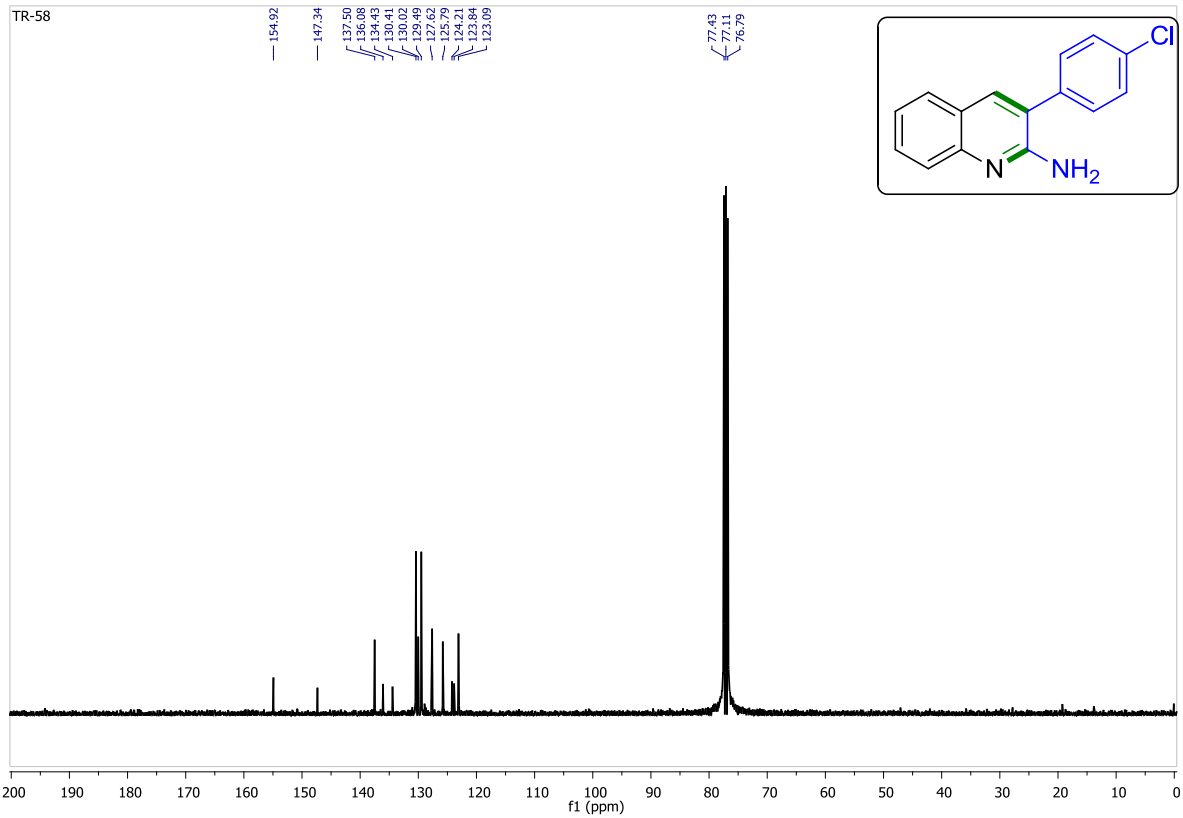
3-(4-fluorophenyl)quinolin-2-amine (5c)



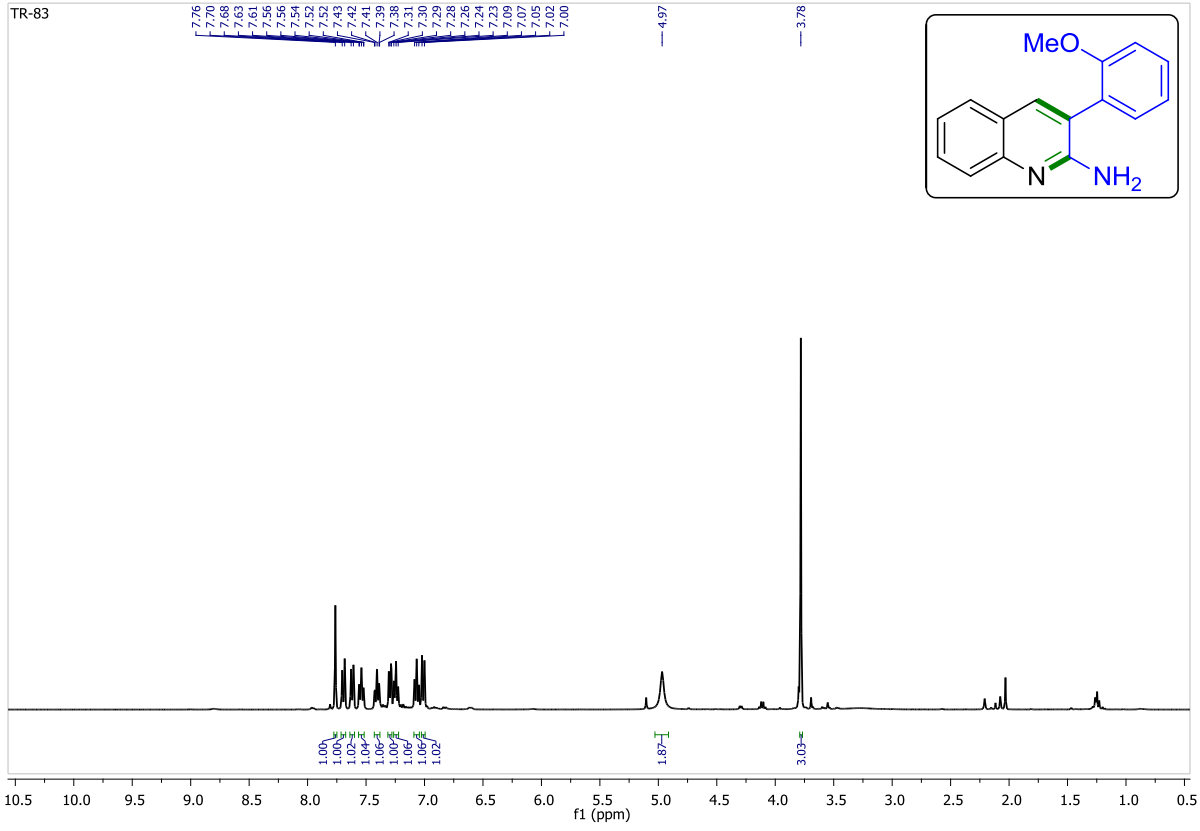


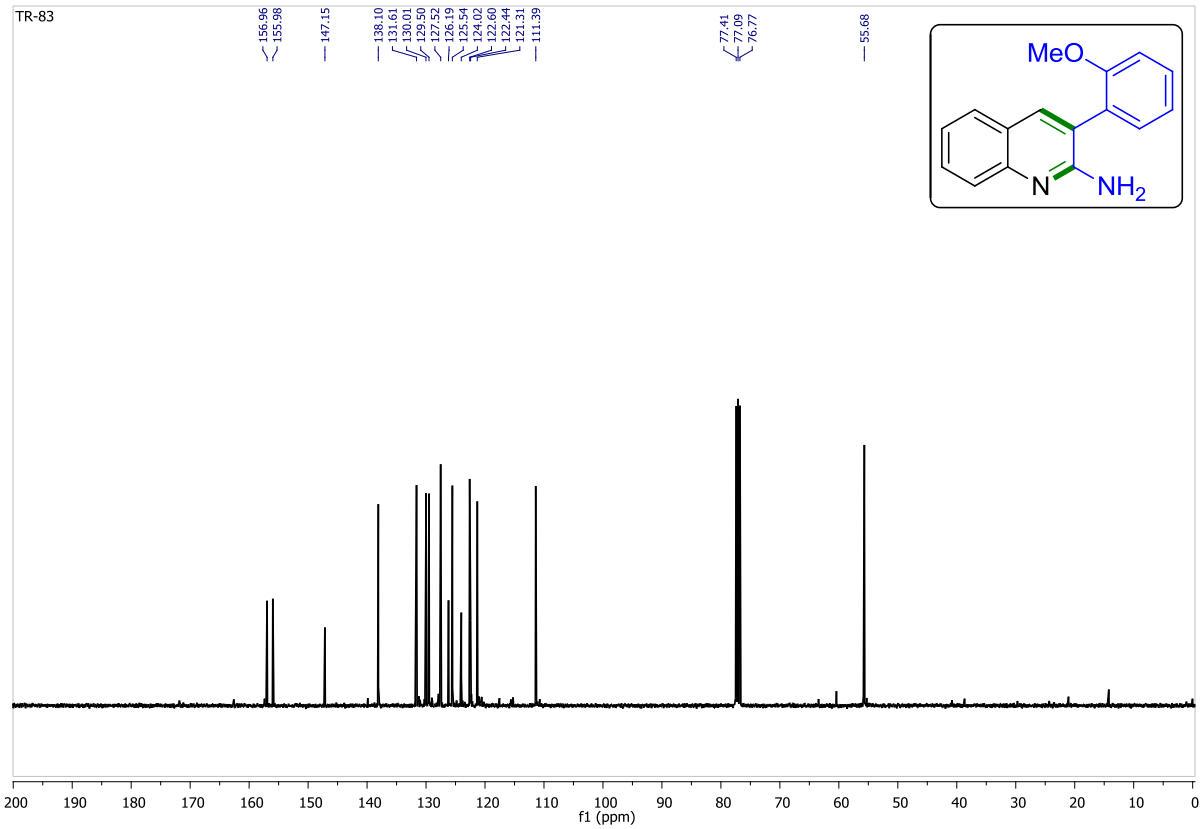
3-(4-chlorophenyl)quinolin-2-amine (5d)



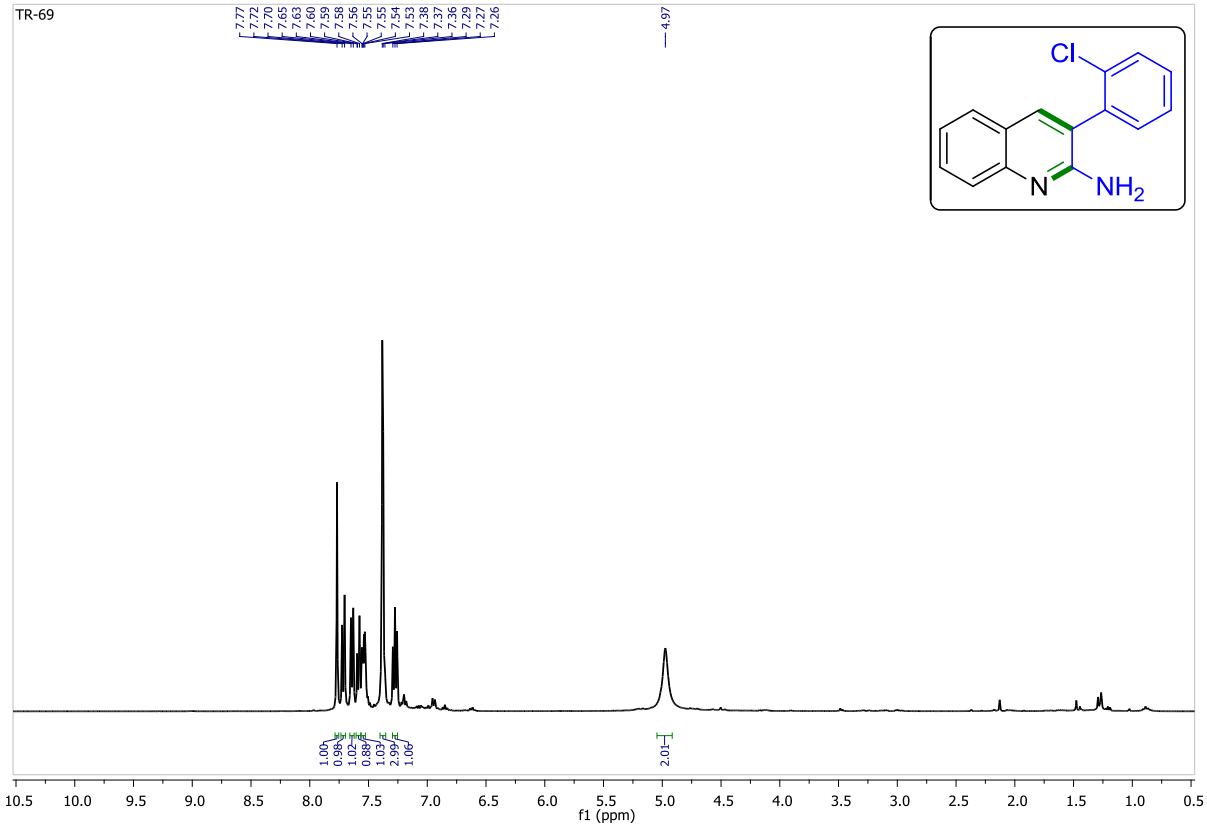


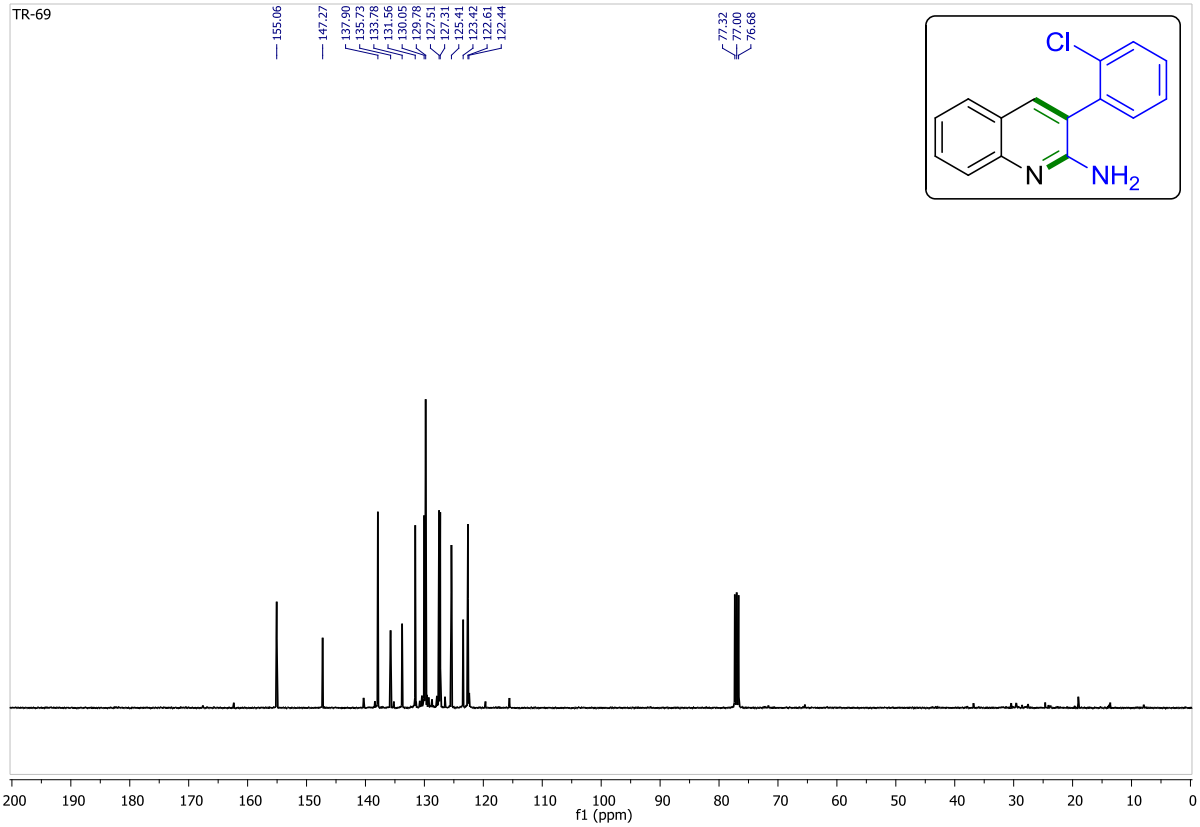
3-(2-methoxyphenyl)quinolin-2-amine (5e)



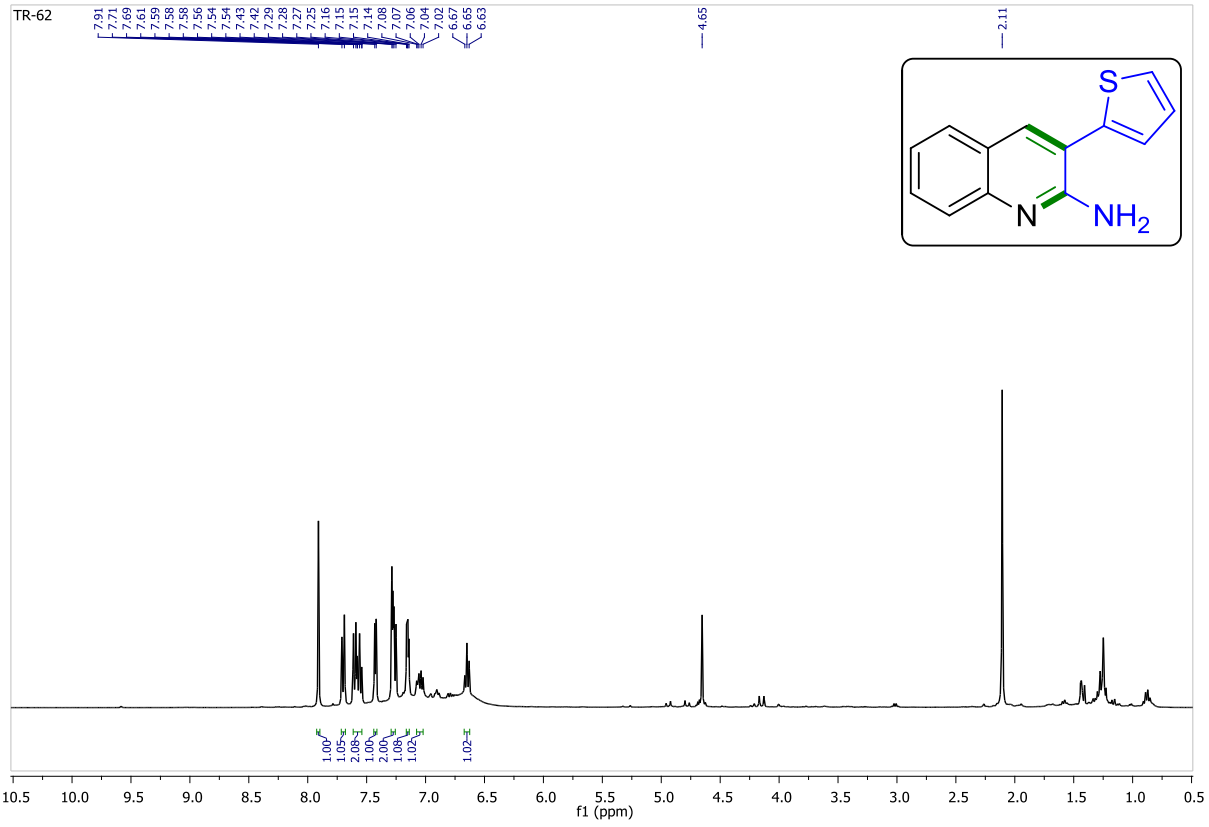


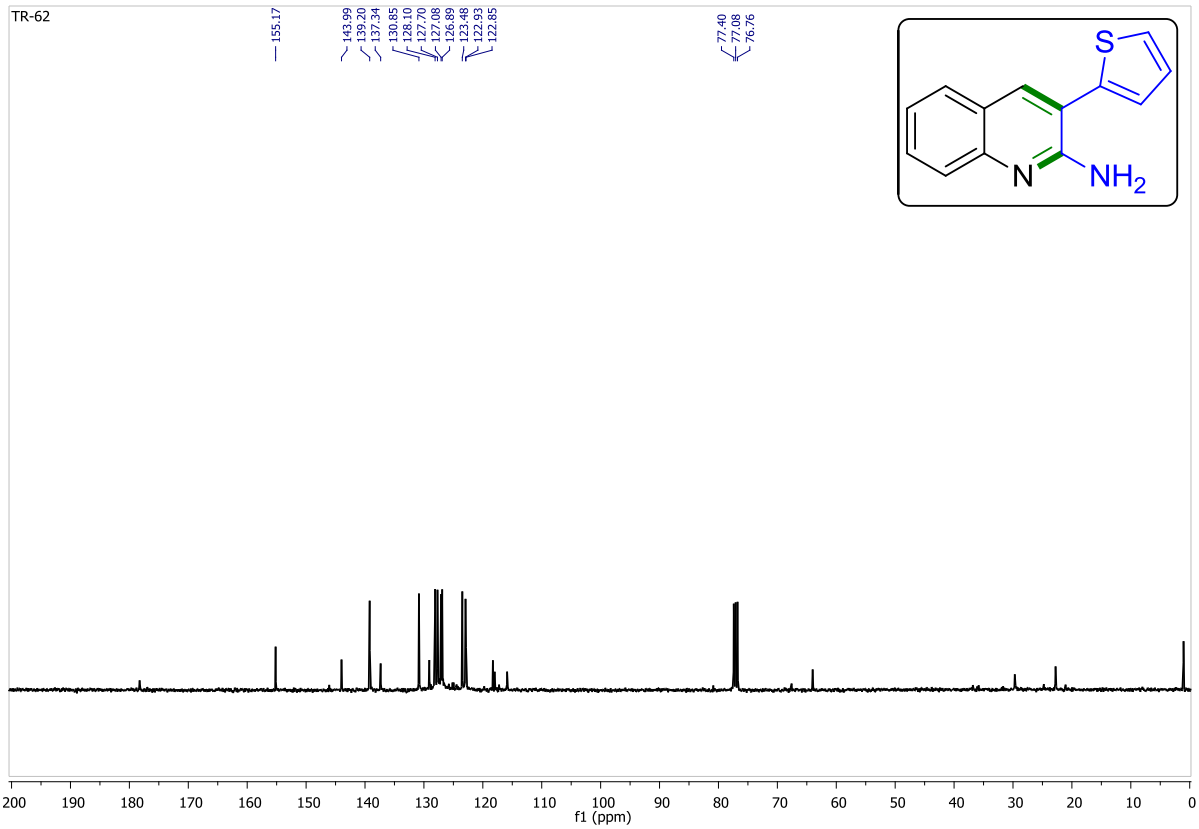
3-(2-chlorophenyl)quinolin-2-amine (5f)



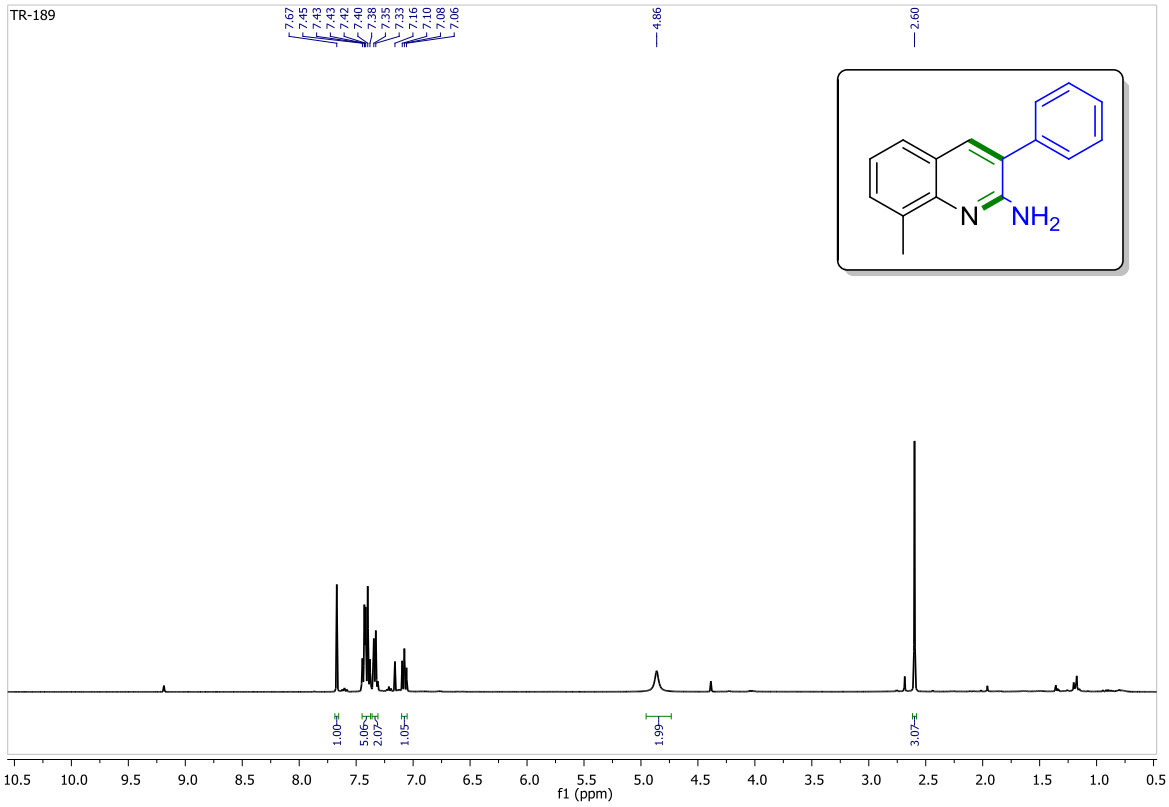


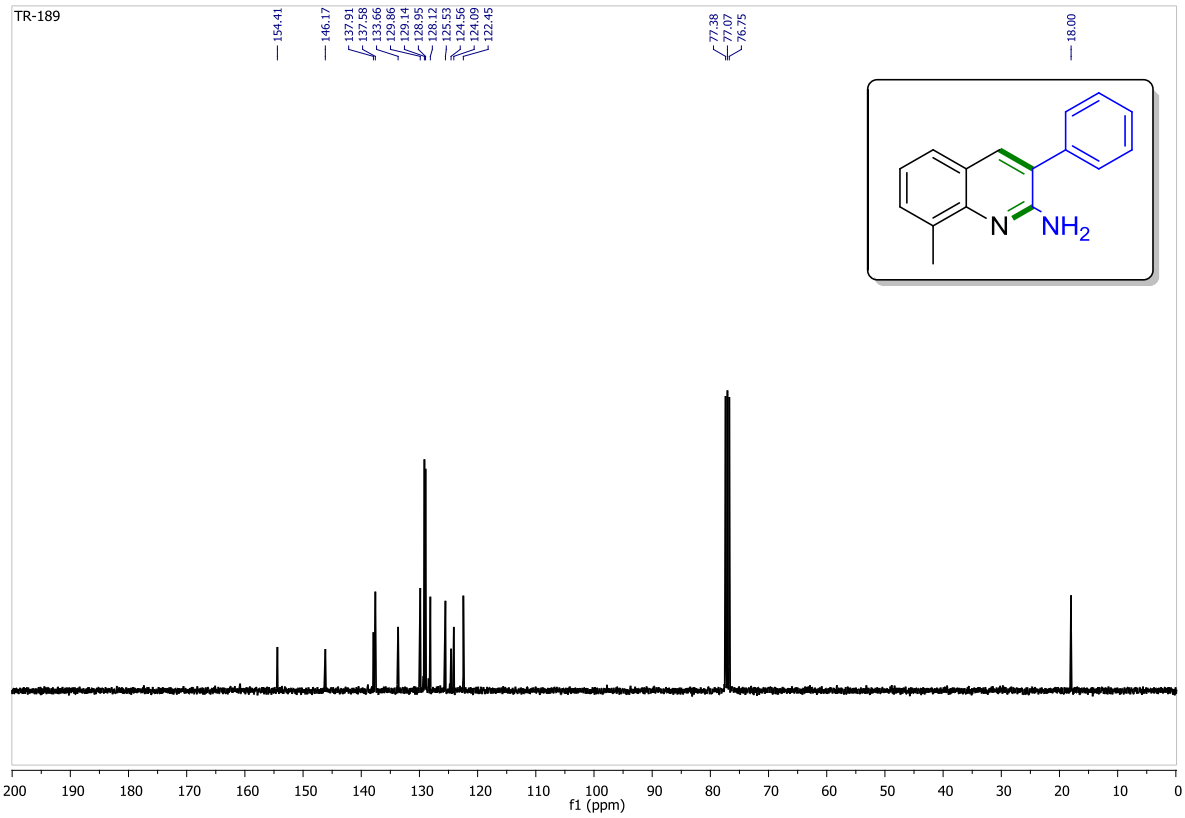
3-(2-thiophenyl)quinolin-2-amine (5g)



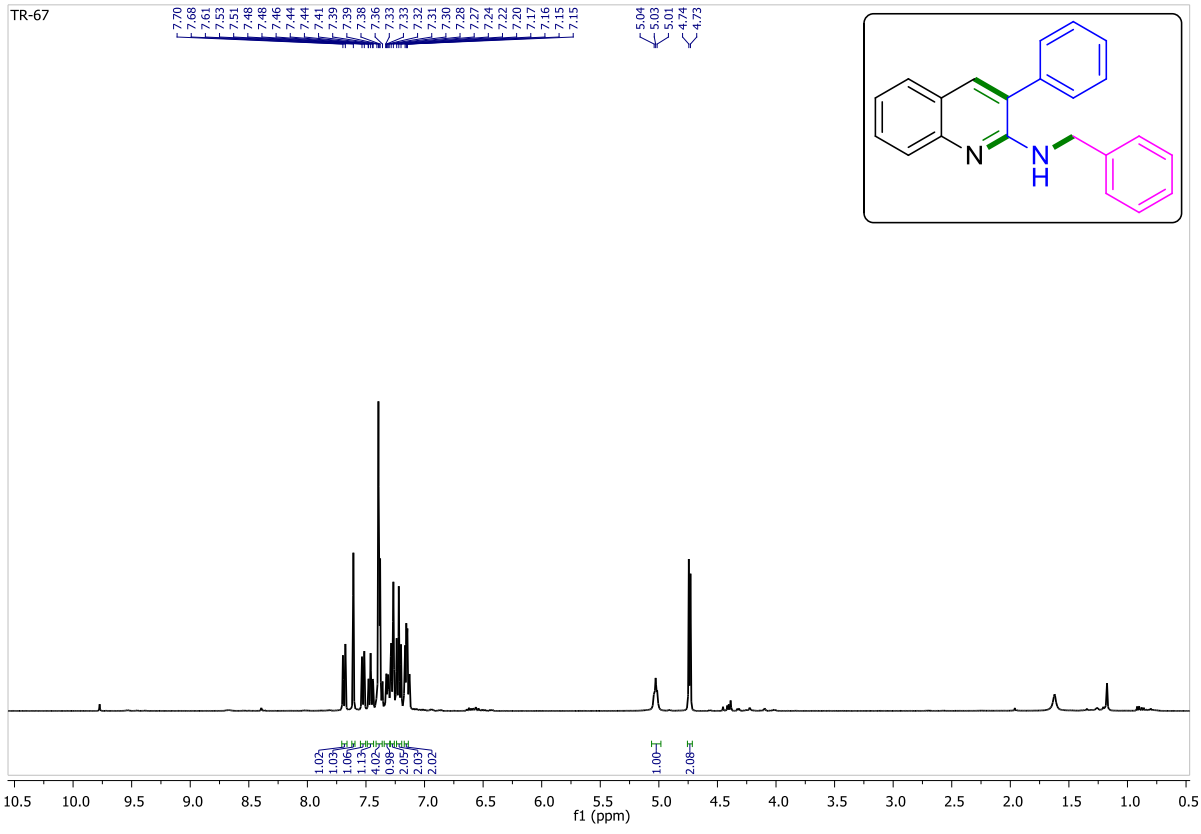


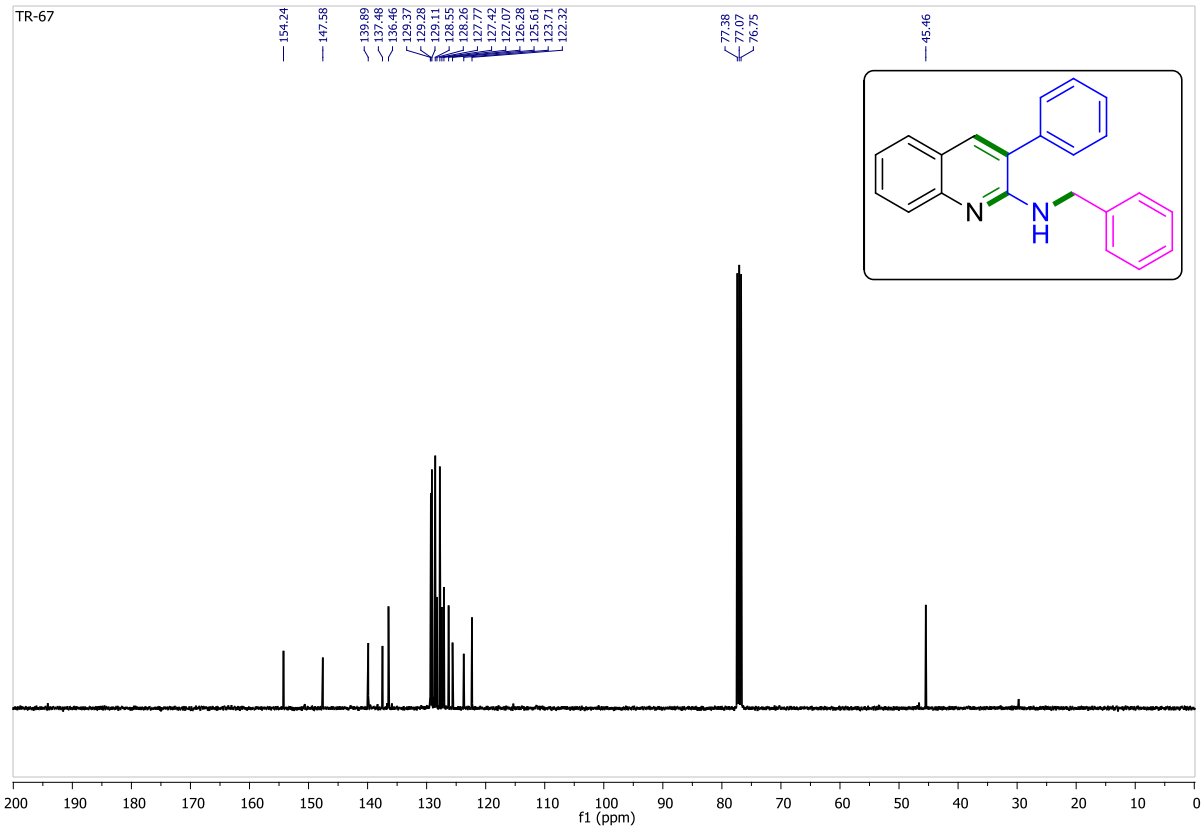
8-methyl-3-phenylquinolin-2-amine (5h)



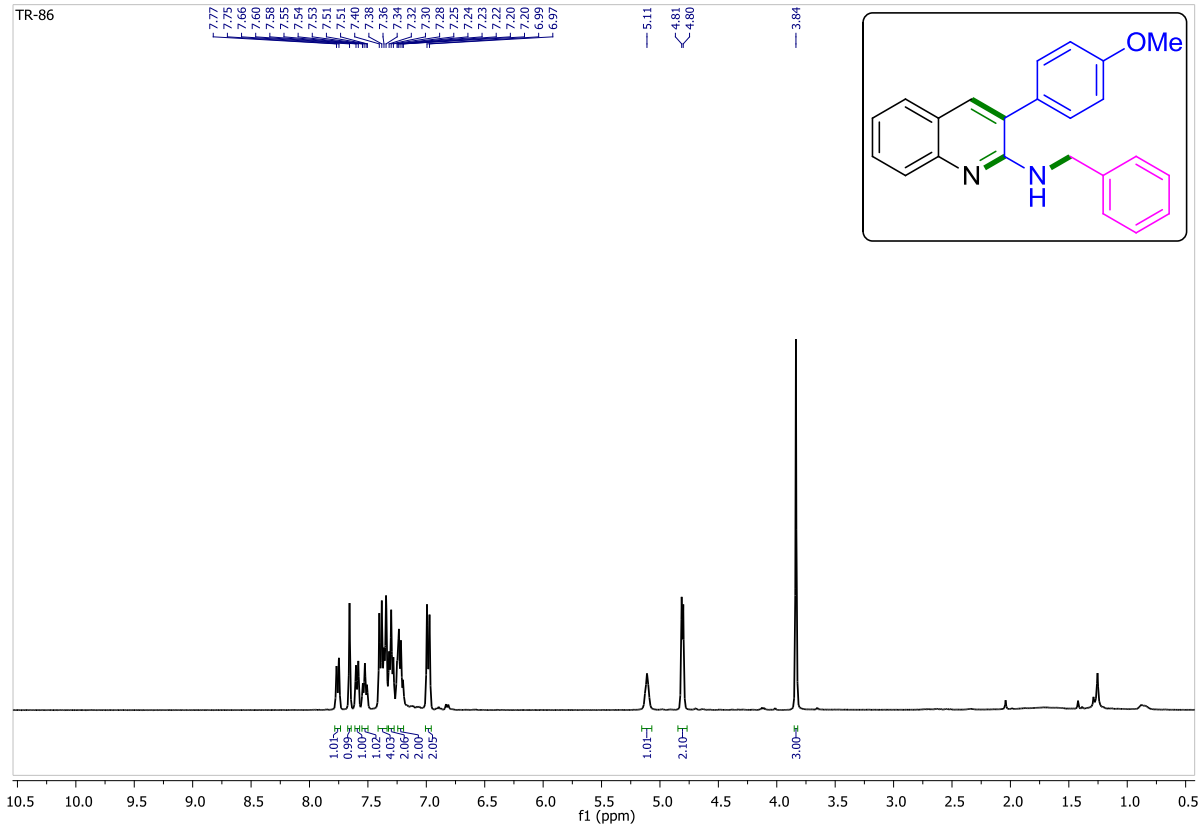


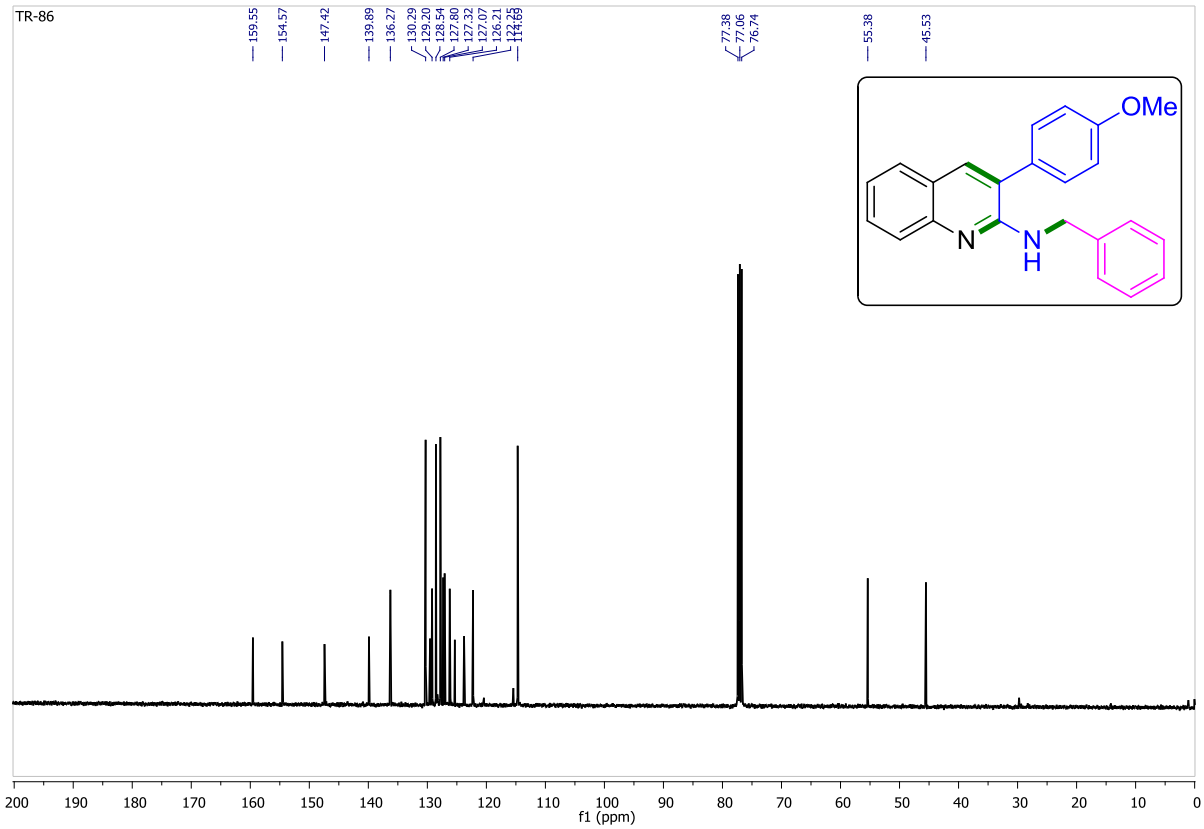
N-benzyl-3phenylquinolin-2-amine (7a)



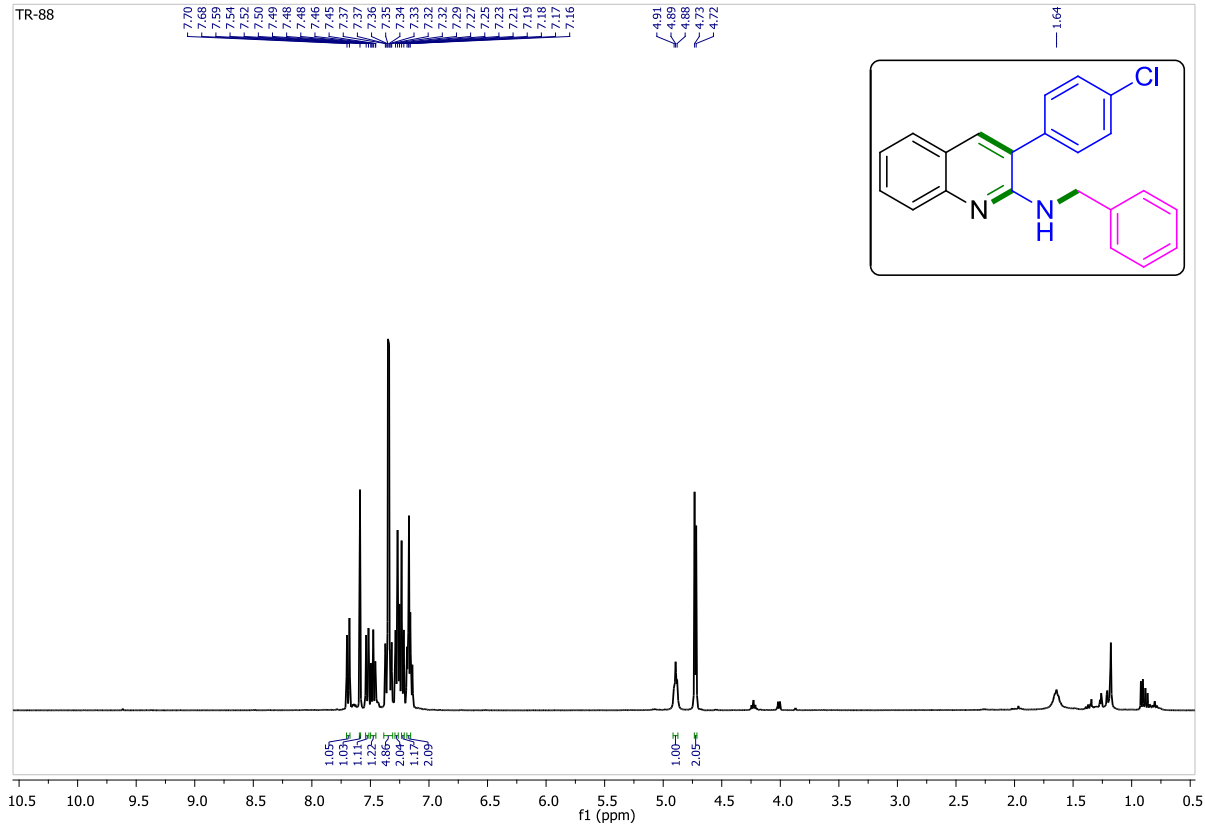


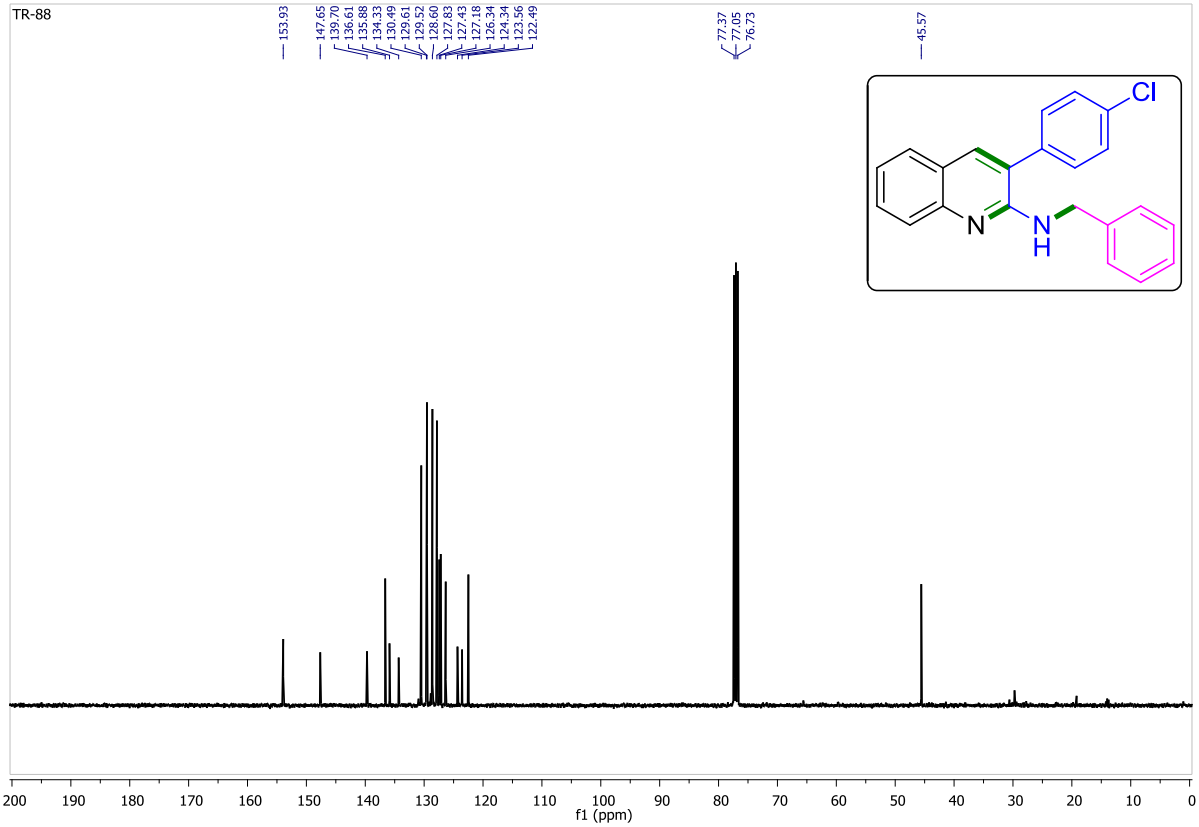
N-benzyl-3-(4-methoxyphenyl)quinolin-2-amine (7b)



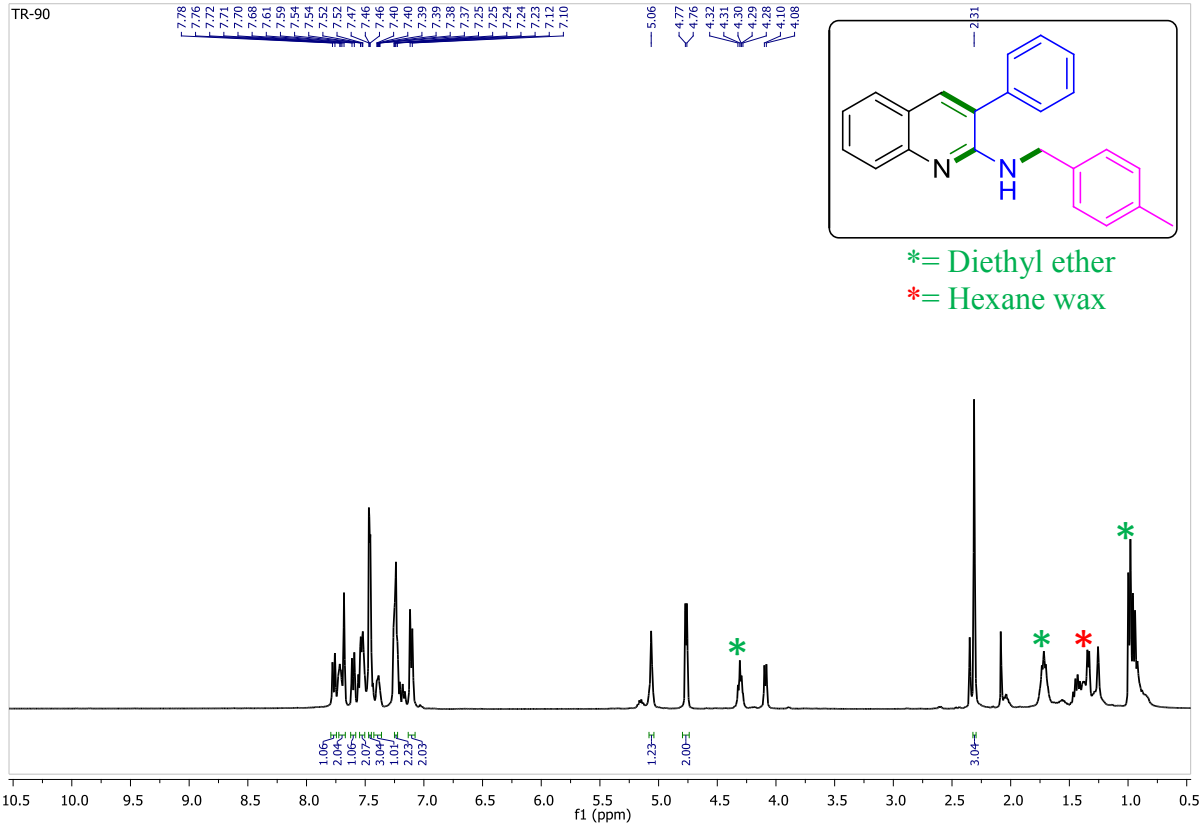


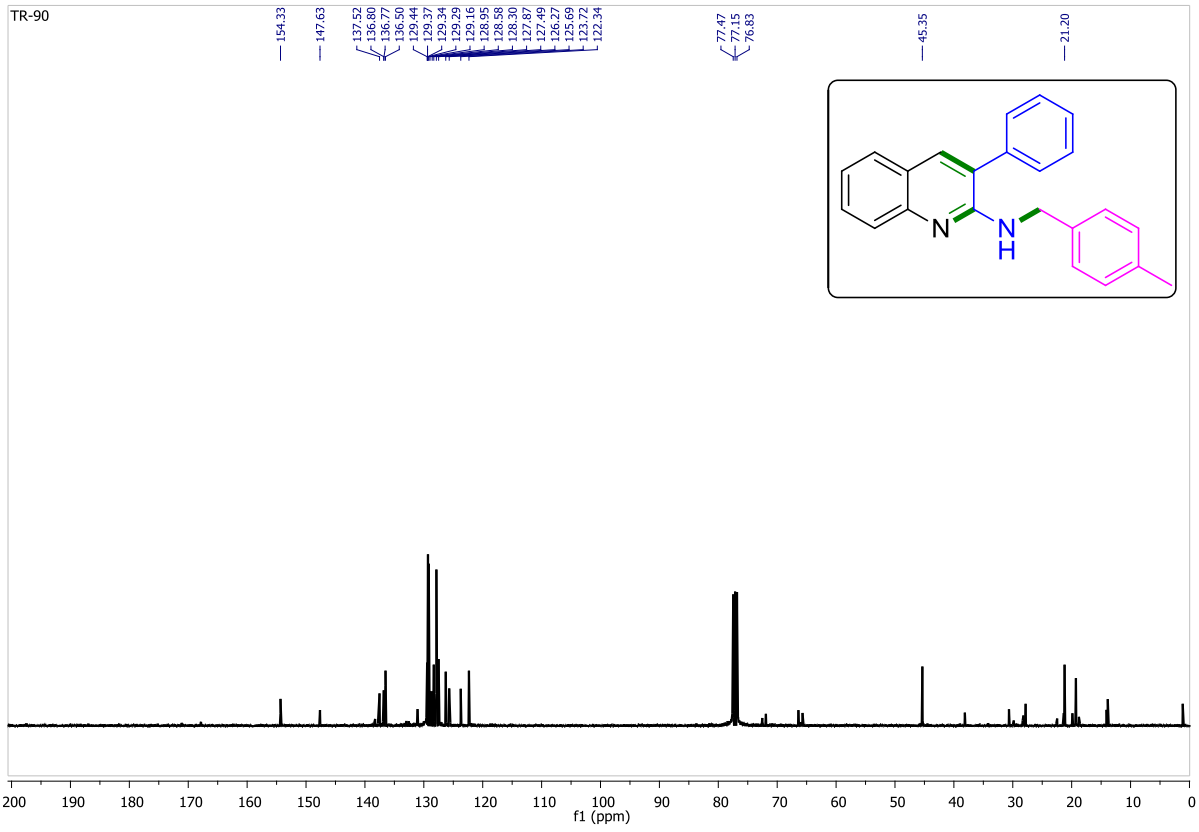
N-benzyl-3-(4-Chlorophenyl)quinolin-2-amine (7c)



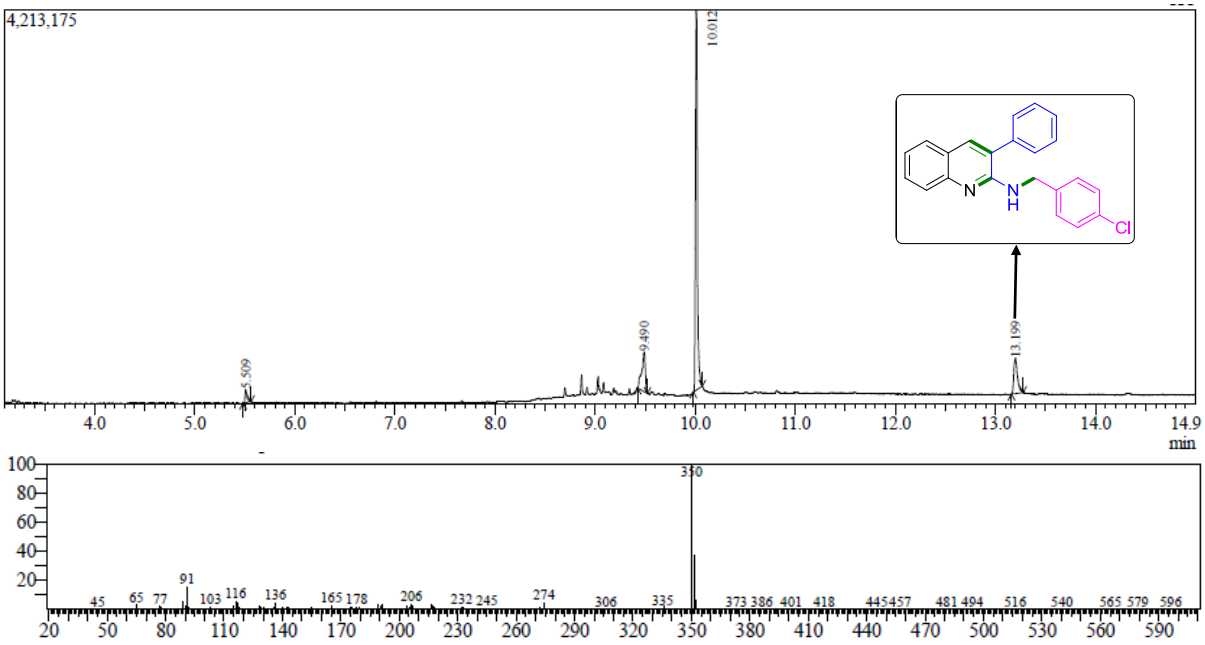


_N_-(4-methylbenzyl)-3phenylquinolin-2-amine (7d)

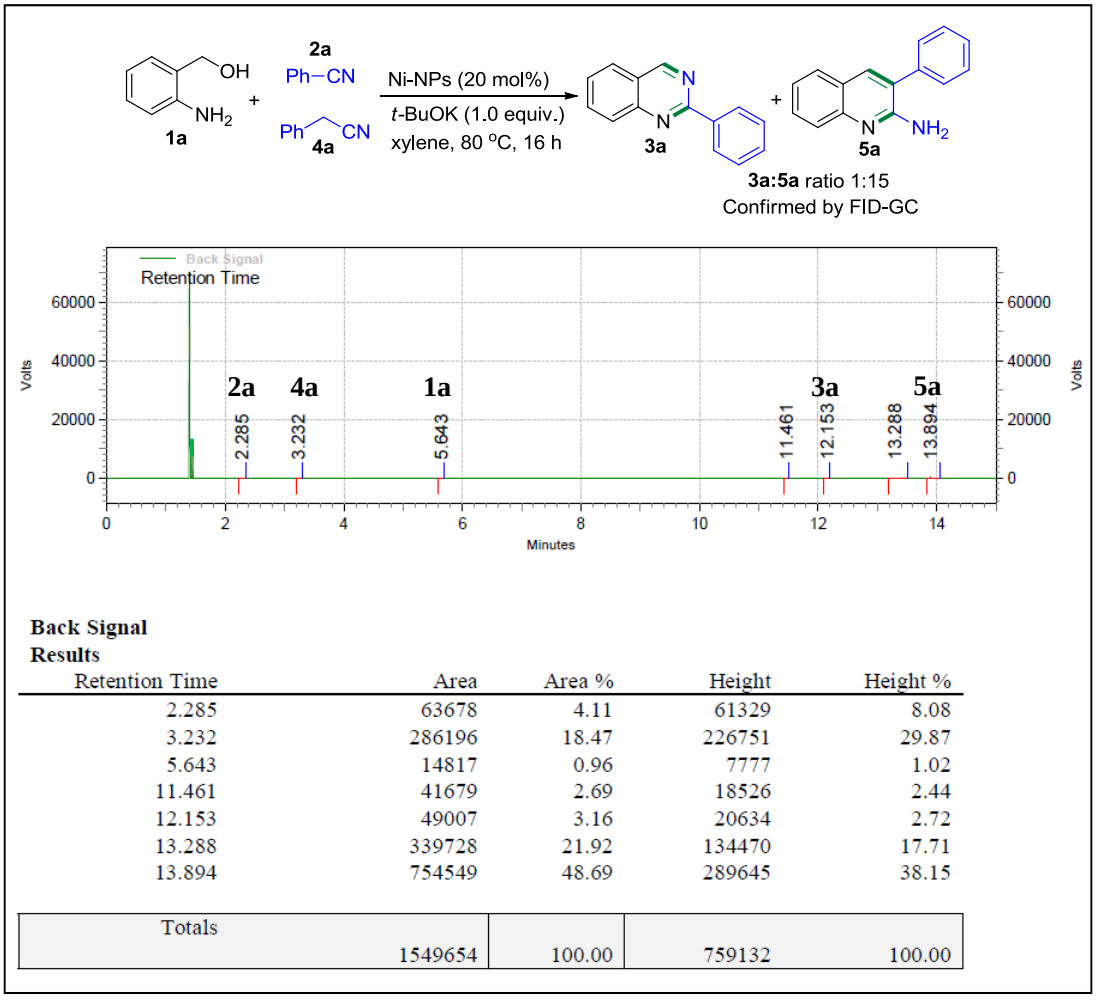




GCMS spectra of *N*-(4-chlorobenzyl)-3-phenylquinolin-2-amine (7d)



FID-GC spectra of reaction scheme 4d



Back Signal
Results

Retention Time	Area	Area %	Height	Height %
2.285	63678	4.11	61329	8.08
3.232	286196	18.47	226751	29.87
5.643	14817	0.96	7777	1.02
11.461	41679	2.69	18526	2.44
12.153	49007	3.16	20634	2.72
13.288	339728	21.92	134470	17.71
13.894	754549	48.69	289645	38.15
Totals	1549654	100.00	759132	100.00

Appendix-II

Crystallographic data of compound 3a

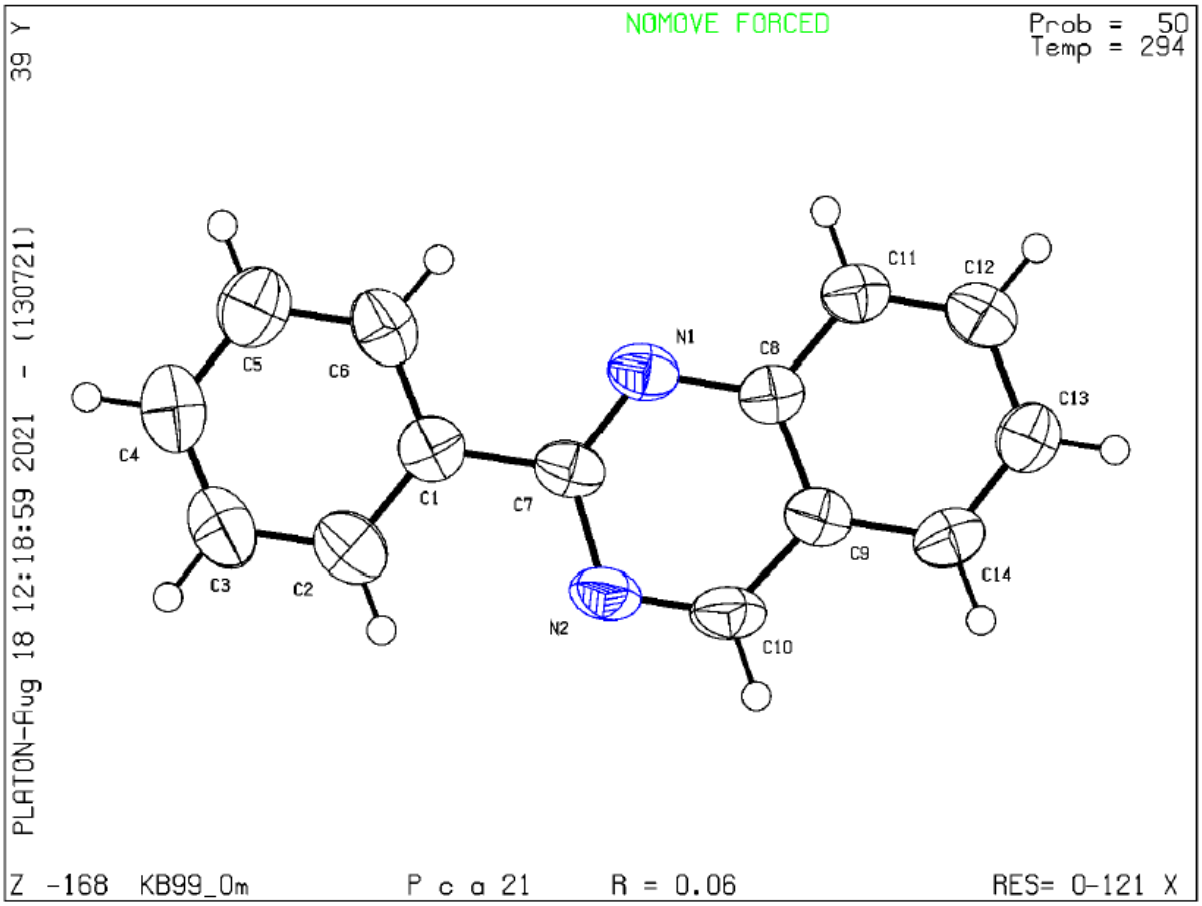


Fig.1. A view of **3a**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary radii.

X-ray data for the compound **3a** was collected on a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 A) and a PHOTON-III detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs [1]. The structure was solved using intrinsic phasing method [2] and further refined with the SHELXL [2] program and expanded using Fourier techniques. Anisotropic displacement parameters were included for all non-hydrogen atoms. All C bound H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and Uiso(H) = 1.5Ueq(C) for methyl H or 1.2Ueq(C) for other H atoms].

Crystal sample preparation of 3a

Crystal of **3a** was prepared using Pentane and Dichloromethane as solvent, the solution was evaporated at room temperature for about five days, and single crystals were formed.

Crystal structure determination of 3a

Crystal Data for $C_{14}H_{10}N_2$ (M =206.24 g/mol): orthorhombic, space group Pca21 (no. 29), a = 18.564(10) Å, b = 5.046(2) Å, c = 11.181(5) Å, V = 1047.3(9) Å3, Z = 4, T = 294.15 K, μ(MoKα) = 0.079 mm-1, Dcalc = 1.308 g/cm3, 16279 reflections measured (5.704° ≤ 2Θ ≤ 56.536°), 2564 unique (Rint = 0.0714, Rsigma = 0.0739) which were used in all calculations. The final R1 was 0.0608 (I > 2σ(I)) and wR2 was 0.1598 (all data). CCDC 2211562 contains supplementary Crystallographic data for the structure. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk].

1. Bruker (2016). APEX3, SAINT and SADABS. Bruker AXS, Inc., Madison, Wisconsin, USA.

2. Sheldrick G. M. (2015) Acta Crystallogr C71: 3-8.