# Electrochemical Ruthenium-Catalyzed C-H Activation of Benzamidine Hydrochlorides with internal alkynes for the Synthesis of 1-Aminoisoquinolines

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# 1. General remarks

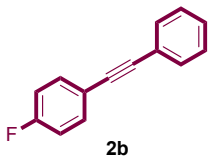
All chemicals and solvents were purchased from commercial suppliers like Spectrochem, Alfa Aesar, and Sigma-Aldrich without further purification. All diphenylacetylene derivatives were synthesized by using reported methods.[1] The conversion of the initial material was monitored using Thin Layer Chromatography (TLC). TLC analyses of the compounds were carried out by using 60F254 silica gel plates with a thickness of 0.25 mm. The product purification were carried out using Silica gel (60-120 mesh) with petroleum ether as the eluent. The $^{1}H$ and $^{13}C$ NMR spectroscopy analyses were performed in Agilent Technologies spectrophotometer ($^{1}H$ NMR at 500 or 400 MHz, $^{13}C$ NMR at 125 or 100 MHz) using TMS as the internal standard. The chemical shift (δ) and the coupling constant (J) were measured in parts per million (ppm) and hertz (Hz) respectively. An undivided cell containing two platinum electrodes of dimensions 0.5 cm x 1.5 cm each were used to carry out the electrochemical reactions. Constant current electrolysis and cyclic voltammetric analysis were carried out using a regulated DC power supply generated by Metrohm Autolab PGSTAT302N and the data were analysed using Nova 2.0 software. The HRMS spectra were recorded using a micromass ESI TOF (time-of-flight) mass spectrometer. The infrared spectra were recorded in the attenuated total reflectance(ATR) mode using a PerkinElmer Spectrum FT-IR spectrometer.

# 2. General procedure and characterization

## 2.1. Preparation of diphenylacetylene derivatives[1]

$Pd(PPh_3)_2Cl_2$ (1 mol%) and CuI (1 mol%) were weighed out to a round bottom flask equipped with a magnetic stir bar and fitted with a rubber septum. The flask was purged with nitrogen, and then THF (3 mL) followed by triethylamine (3 mL) were added via a syringe. Iodobenzene substrates (1 mmol, 1 equiv) followed by phenylacetylene substrate (1 mol, 1 equiv) were added to the above mixture and the reaction was stirred overnight at room temperature. Then the volatiles were evaporated under reduced pressure, and the residue was extracted from ethyl acetate. The organics were dried over $Na_2SO_4$ and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the product.

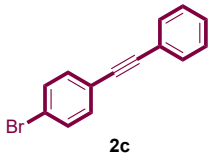
### 2.1.1. Synthesis of diphenylacetylene derivatives



2b

**1-fluoro-4-(phenylethynyl)benzene (2b)**

The procedure was applied to iodobenzene (1 mmol) and 1-ethynyl-4-fluorobenzene (1 mmol). The product **2b** was obtained by silica gel chromatography using petroleum ether as the eluent; **$^{1}$H NMR** (500 MHz, $CDCl_3$)δ 7.51 (dt, 4H),7.40-7.29 (m, 3H), 7.04 (t, 2H).

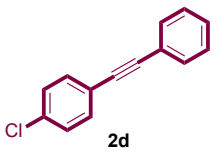


2c

**1-bromo-4-(phenylethynyl)benzene (2c)**

The procedure was applied to 1-iodobenzene (1 mmol) and 1-ethynyl-4-bromobenzene (1 mmol). The product **2c** was obtained by silica gel chromatography using petroleum ether as the eluent; **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.52 (dd, 2H), 7.47 (d, 2H), 7.38 (d, 2H), 7.36 – 7.29 (m, 3H).

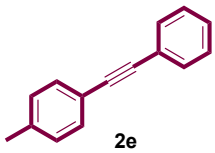
**1-chloro-4-(phenylethynyl)benzene (2d)**



2d

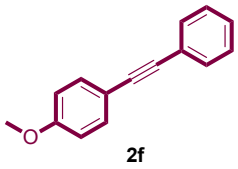
The procedure was applied to 1-iodobenzene (1 mmol) and 1-ethynyl-4-chlorobenzene (1 mmol). The product **2d** was obtained by silica gel chromatography and eluent from petroleum ether; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.52 (dd, 2H), 7.46 (d, 2H), 7.37 – 7.31 (m, 5H).

**1-methyl-4-(phenylethynyl)benzene (2e)**


2e

The procedure was applied to 1-iodobenzene (1 mmol) and 1-ethynyl-4-methylbenzene (1 mmol). The product **2e** was obtained by silica gel chromatography using petroleum ether as the eluent; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.60 (d, 2H), 7.51 (d, 2H), 7.43 – 7.34 (m, 3H), 7.21 (d, 2H), 2.42 (s, 3H).

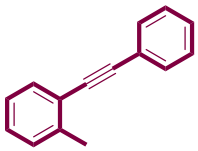
**1-methoxy-4-(phenylethynyl)benzene (2f)**



2f

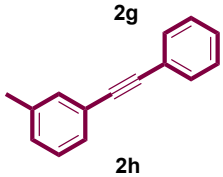
The procedure was applied to 1-iodobenzene (1 mmol) and 1-ethynyl-4-methoxybenzene (1 mmol). The product **2f** was obtained by silica gel chromatography using petroleum ether as the eluent; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.50 (d, 2H), 7.45 (d, 2H), 7.31 – 7.23 (m, 3H), 6.82 (d, 2H), 3.72 (s, 3H).

**1-methyl-2-(phenylethynyl)benzene (2g)**


2g

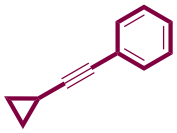
The procedure was applied to 1-iodobenzene (1 mmol) and 1-ethynyl-2-methylbenzene (1 mmol). The product **2g** was obtained by silica gel chromatography using petroleum ether as the eluent; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.63 (dd, 3H), 7.45 – 7.39 (m, 3H), 7.32 (d, 2H), 7.29 – 7.23 (m, 1H), 2.63 (s, 3H).

**1-methyl-3-(phenylethynyl)benzene (2h)**


2h

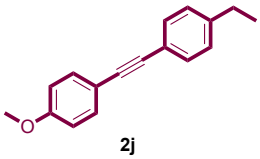
The procedure was applied to 1-iodobenzene (1 mmol) and 1-ethynyl-3-methylbenzene (1 mmol). The product **2h** was obtained by silica gel chromatography using petroleum ether as the eluent; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.52 (dd, 2H), 7.34 (dd, 4H), 7.23 (dd, 2H), 7.14 (d, 1H), 2.35 (s, 3H).

**(cyclopropylethynyl)benzene (2i)**


2i

The procedure was applied to 1-iodobenzene (1 mmol) and ethynylcyclopropane (1 mmol). The product **2i** was obtained by silica gel chromatography using petroleum ether as the eluent; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.41 (dd, 2H), 7.35 – 7.26 (m, 3H), 1.48 (dq, 1H), 0.89 (ddd, 2H), 0.86 – 0.82 (m, 2H).

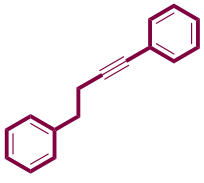
**1-ethyl-4-((4-methoxyphenyl)ethynyl)benzene (2j)**



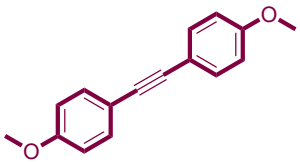
2j

The procedure was applied to 1-ethyl-4-iodobenzene (1 mmol) and 1-ethynyl-4-methoxybenzene (1 mmol). The product **2j** was obtained by silica gel chromatography using petroleum ether as the eluent; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.46 (dd, 4H), 7.18 (d, 2H), 6.88 (d, 2H), 3.83 (s, 3H), 2.67 (dd, 2H), 1.25 (t, 3H).

**But-1-yne-1,4-diyldibenzene (2k)**


2k

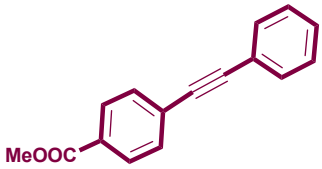
The procedure was applied to 1-iodobenzene (1 mmol) and 3-butynylbenzene (1 mmol). The product **2k** was obtained by silica gel chromatography using petroleum ether as the eluent; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.36 (dd, 2H), 7.32 – 7.09 (m, 8H), 2.89 (t, 2H), 2.66 (t, 2H).



2m

**1,2-bis(4-methoxyphenyl)ethyne (2m)**

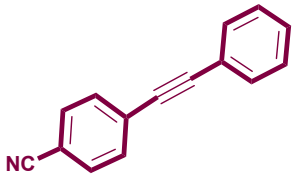
The procedure was applied to 1-iodo-4-methoxybenzene (1 mmol) and 1-ethynyl-4-methoxybenzene (1 mmol). The product **2m** was obtained by silica gel chromatography and eluent from petroleum ether; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.45 (d, 4H), 6.86 (d, 4H), 3.82 (s, 6H).



2n

**Methyl 4-(phenylethynyl)benzoate (2n)**

The procedure was applied to 1-iodobenzene (1 mmol) and methyl 4-(phenylethynyl)benzoate (1 mmol). The product **2n** was obtained by silica gel chromatography and eluent from petroleum ether; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.00 (d, 2H), 7.55 (dd, 4H), 7.37 – 7.29 (m, 3H), 3.88 (s, 3H).

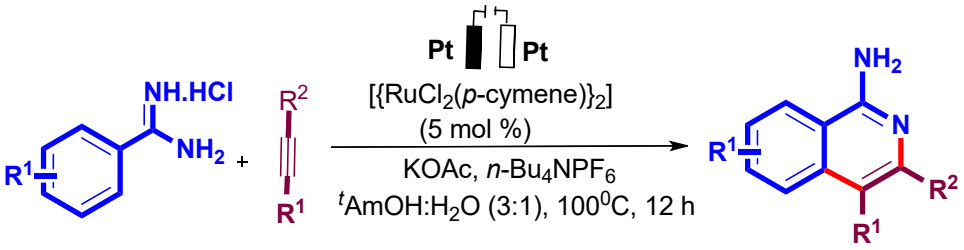


2o

**4-(phenylethynyl)benzonitrile (2o)**

The procedure was applied to 1-iodobenzene (1 mmol) and 4-(phenylethynyl)benzonitrile (1 mmol). The product **2o** was obtained by silica gel chromatography and eluent from petroleum ether; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.60 (q, 4H), 7.55 (dd, 2H), 7.41 – 7.34 (m, 3H).

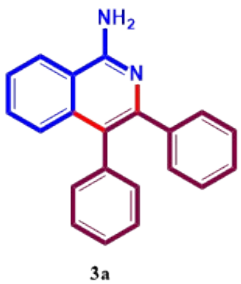
## 2.2. Synthesis of 1-aminoisoquinoline




1 2 3

The electrolysis was performed in an undivided cell with a platinum anode (10 mm × 15 mm) and cathode (10 mm × 15 mm). Benzamidine hydrochloride **1** (0.60 mmol, 2.0 equiv), alkyne **2** (0.30 mmol, 1.0 equiv), *n*-$Bu_4NPF_6$ (0.18 mmol, 0.60 equiv), KOAc (0.60 mmol, 2.0 equiv) and $[RuCl_2(p\text{-cymene})]_2$ (9.2 mg, 5 mol %) were dissolved in *t*-AmOH: $H_2O$ (3:1, 4.0 mL) under a $N_2$ atmosphere and then added to the cell. The reaction mixture was stirred at a constant current of 1.5 mA for 12 h at 100° C. When the reaction was completed, the mixture was diluted with $Et_2O$ and washed with $H_2O$, the organic layer of $Et_2O$ containing the product mixture was separated, evaporated and purified using column chromatography on silica gel using the eluent Pet ether /EtOAc, affording the corresponding products **3**.

### 2.2.1. Synthesis of 1-aminoisoquinoline derivatives

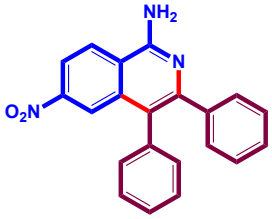


3a

**3,4-diphenylisoquinolin-1-amine (3a)**[2a, 2b, 2c]

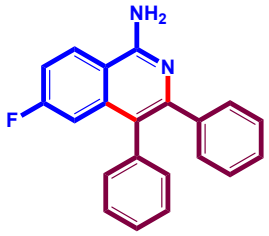
The standard procedure was applied to benzamidine hydrochloride **1a** (0.60 mmol) and diphenylacetylene **2a** (0.30 mmol). The product **3a** was obtained by silica gel chromatography (eluent: petroleum ether/ethyl acetate: 4/1), yielding a dark brown solid (71mg, 80% yield); **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.82 (d, 1H), 7.59 – 7.49 (m, 2H), 7.48 – 7.42 (m, 1H), 7.34 – 7.23 (m, 5H), 7.21 – 7.10 (m, 5H), 5.42 (s, 2H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 155.3, 148.8, 141.1, 138.0,

137.6, 131.9, 130.1, 128.1, 127.5, 126.8, 126.2, 125.7, 122.7, 122.5, 116.5, 77.3, 77.1, 76.8; **IR (ATR)** 3296, 2924, 1630, 1503, 1341, 696 $cm^{-1}$.



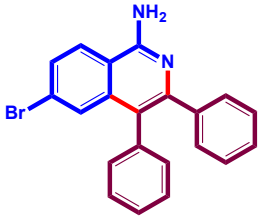
3b

**6-nitro-3,4-diphenylisoquinolin-1-amine (3b)**[2a]
The standard procedure was applied to 4-nitrobenzamidine hydrochloride **1b** (0.60 mmol) and diphenylacetylene **2a** (0.30 mmol). The product **3b** was obtained by silica gel chromatography (eluent: petroleum ether/ethyl acetate: 4/1), yielding a yellow solid (83.8mg, 82% yield). **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 8.47 (d, 1H), 8.20 (dd, 1H), 7.97 (d, 1H), 7.39 – 7.29 (m, 5H), 7.19 (dd, 5H), 5.58 (s, 2H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 155.0, 151.3, 148.6, 140.1, 137.6, 136.4, 131.6, 129.9, 128.6, 127.8– 127.3, 124.7, 123.7, 122.3, 119.0, 118.3, 773, 77.0, 76.8; **IR (ATR)** 3296, 2924, 1633, 1537, 1444, 1338,704 $cm^{-1}$.



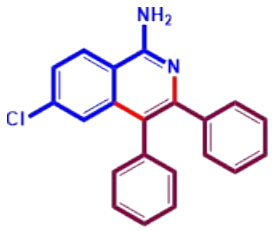
3c

**6-fluoro-3,4-diphenylisoquinoline-1-amine (3c)**[2a]
The standard procedure was applied to 4-fluorobenzamidine hydrochloride **1c** (0.60 mmol) and diphenylacetylene **2a** (0.30 mmol). The product **3c** was obtained by silica gel chromatography (eluent: petroleum ether/ethyl acetate: 4/1), yielding a dark brown solid (81mg, 86% yield). **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.85 (dd, 1H), 7.30 (t, 5H), 7.23 – 7.07 (m, 7H), 5.48 (s, 2H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 164.6, 162.6, 155.1, 149.8, 140.5, 139.8, 137.5, 131.7, 130.0, 128.3, 127.6, 127.1, 125.5, 122.5, 115.6, 115.4, 113.5, 110.3, 110.1, 77.3, 77.1, 76.8; **$^{19}$F NMR** (470 MHz, $CDCl_3$) δ -107.8; **IR (ATR)** 3285, 2919, 1622, 1442, 1269, 694 $cm^{-1}$.



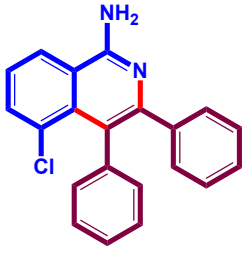
3d

**6-bromo-3,4-diphenylisoquinolin-1-amine (3d)**[2]
The standard procedure was applied to 4- bromobenzamidine hydrochloride **1d** (0.60 mmol) and diphenylacetylene **2a** (0.30 mmol). The product **3d** was obtained by silica gel chromatography (eluent: petroleum ether/ethyl acetate: 4/1), yielding a light yellow solid (61.7 mg, 55% yield). **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.74 (d, 1H), 7.71 (d, 1H), 7.56 (dd, 1H), 7.31 (td, 5H), 7.16 (d, 5H), 5.51 (s, 2H); **$^{13}$C NMR** (126 MHz, cdcl$_3$) δ 155.1, 149.6, 140.3, 139.0, 137.0, 131.7, 129.9, 129.2, 128.4, 127.6, 127.2, 125.5, 124.4, 121.9, 114.9, 77.3, 77.0, 76.8; **IR (ATR)** 3288, 3023, 1633, 1442, 1248, 765 $cm^{-1}$.



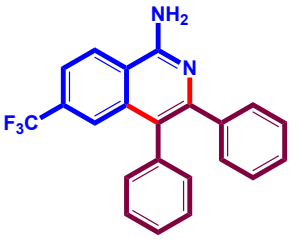
3e

**6-chloro-3,4-diphenylisoquinolin-1-amine(3e)**[2a]
The standard procedure was applied to 4-chlorobenzamidine hydrochloride **1e** (0.60 mmol) and diphenylacetylene **2a** (0.30 mmol). The product **3e** was obtained by silica gel chromatography (eluent: petroleum ether/ethyl acetate: 4/1), yielding a brown solid (84 mg, 85% yield). **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.78 (d, 1H), 7.54 (d, 1H), 7.41 (dd, 1H), 7.38 – 7.27 (m, 5H), 7.23 – 7.12 (m, 5H), 5.44 (s, 2H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 155.0, 150.1, 140.6, 138.8, 137.2, 136.7, 131.7, 130.0, 128.3, 127.6, 127.1, 126.5, 125.2, 124.3, 122.1, 114.7, 77.3, 77.0, 76.8; **IR (ATR)** 3285, 3054, 1630, 1442, 1245,768 $cm^{-1}$.



3f

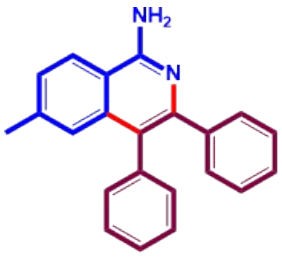
**5-chloro-3,4-diphenylisoquinolin-1-amine (3f)**[2b]
The standard procedure was applied to 5-chlorobenzamidine hydrochloride **1f** (0.60 mmol) and diphenylacetylene **2a** (0.30 mmol). The product **3f** was obtained by silica gel chromatography (eluent: petroleum ether/ethyl acetate: 4/1), yielding a brown solid (81mg, 82% yield). **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.81 (d, 1H), 7.64 (dd, 1H), 7.39 (t, 1H), 7.23 – 6.98 (m, 10H), 5.47 (s, 2H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 155.4, 152.3, 141.2, 139.2, 134.0, 133.8, 132.3, 131.9, 129.7, 127.3, 127.0, 126.7, 126.5, 125.9, 122.0, 121.5, 118.6, 77.3, 77.0, 76.8; **IR (ATR)** 3293, 2922, 1643, 1492, 1256, 768 $cm^{-1}$.




3g

**3,4-diphenyl-6-(trifluoromethyl)isoquinolin-1-amine (3g)**[2a]

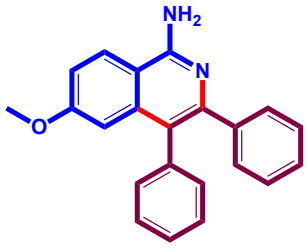
The standard procedure was applied to 4-(trifluoromethyl)benzamidine hydrochloride **1g** (0.60 mmol) and diphenylacetylene **2a** (0.30 mmol). The product **3g** was obtained by silica gel chromatography (eluent: petroleum ether/ethyl acetate: 4/1), yielding a white solid (75.5mg, 69% yield). **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.93 (d, 1H), 7.87 (s, 1H), 7.64 (d, 1H), 7.36 – 7.28 (m, 5H), 7.18 (d, 5H), 5.54 (s, 2H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 155.1, 150.5, 140.5, 137.1, 136.9, 131.9, 131.7, 130.0, 128.4, 127.6, 127.2, 124.9, 123.9 – 123.3, 123.1, 121.4, 117.5, 77.3, 77.0, 76.8; **$^{19}$F NMR** (470 MHz, $CDCl_3$) δ -62.9; **IR (ATR)** 3290, 2924, 1630, 1447, 1261, 696 $cm^{-1}$.




3h

**6-methyl-3,4-diphenylisoquinolin-1-amine(3h)**[2b]

The standard procedure was applied to 4-methylbenzamidine hydrochloride **1h** (0.60 mmol) and diphenylacetylene **2a** (0.30 mmol). The product **3h** was obtained by silica gel chromatography (eluent: petroleum ether/ethyl acetate: 4/1), yielding a dark brown solid (57.9mg, 62% yield). **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.76 (d, 1H), 7.70 – 7.64 (m, 1H), 7.34 – 7.26 (m, 6H), 7.21 – 7.10 (m, 5H), 5.32 (s, 2H), 2.39 (s, 3H);**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 155.0, 148.9, 141.2, 140.5, 138.1, 137.7, 131.9, 130.0, 129.2, 128.1, 127.5, 126.7, 125.3, 122.4, 114.7, 77.3, 77.0, 76.8, 22.0; **IR (ATR)** 3296, 2924,1622, 151, 128 $cm^{-1}$.

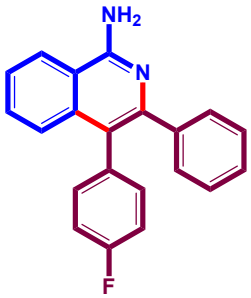



3i

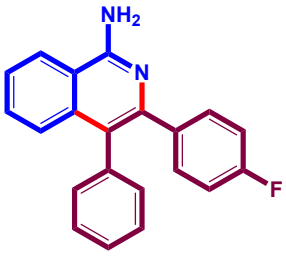
**6-methoxy-3,4-diphenylisoquinolin-1-amine (3i)**[2b]

The standard procedure was applied to 4-methoxybenzamidine hydrochloride **1i** (0.60 mmol) and diphenylacetylene **2a** (0.30 mmol). The product **3i** was obtained by silica gel chromatography (eluent: petroleum ether/ethyl acetate: 4/1), yielding a brown solid (63.8 mg, 65% yield). **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.80 (d, 1H), 7.37 – 7.27 (m, 5H), 7.21 – 7.14 (m, 5H), 7.11 (dd, 1H), 6.86 (d, 1H), 5.50 (s, 2H), 3.71 (s, 3H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 161.0, 155.0, 148.8, 140.5, 139.7, 137.9, 131.7, 130.0, 128.2, 127.5, 127.0, 126.8, 124.6, 122.4, 117.3, 111.6, 105.4, 77.3, 77.0, 76.8, 55.2; **IR (ATR)** 3282, 2919, 1614, 1431, 1221, 773 $cm^{-1}$.

**4-(4-fluorophenyl)-3-phenylisoquinolin-1-amine (3k)** [2c, 2d]
**3-(4-fluorophenyl)-4-phenylisoquinoline-1-amine (3k')**



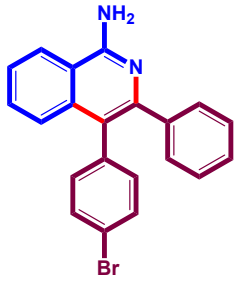

3k




3k'

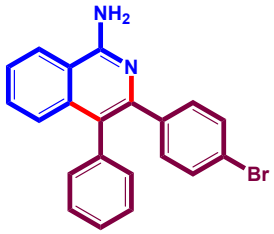
The standard procedure was applied to benzamidine hydrochloride **1a** (0.60 mmol) and 1-fluoro-4-(phenylehtynyl)benzene **2b** (0.30 mmol). The product **3k: 3k' (1:1)** was obtained by silica gel chromatography (eluent: petroleum ether/ethyl acetate: 4/1), yielding a brown solid (56.5 mg, 60% yield); **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.88 (dd, 1H), 7.63 – 7.48 (m, 3H), 7.31 (ddd, 4H), 7.22 – 7.11 (m, 3H), 7.06 – 6.95 (m, 1H), 6.86 (t, 1H), 5.42 (s, 2H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 162.8, 160.9, 155.2, 147.3, 140.6, 137.7, 137.5, 136.8, 133.4, 131.7, 130.4, 130.0, 128.3, 127.7, 127.0, 126.2, 126.0, 122.8, 122.6, 116.5, 115.3, 115.1, 114.5, 114.4, 77.3, 77.0, 76.8; **19F NMR** (470 MHz, $CDCl_3$) δ -115.3, -115.6; **IR (ATR)** 3290, 2922,1635, 1436, 1216, 760 $cm^{-1}$.

**4-(4-bromophenyl)-3-phenylisoquinolin-1-amine (3l)** [2c, 2d]




3l

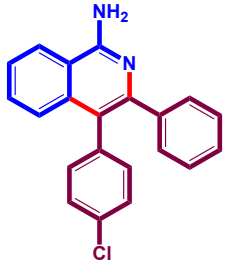
The standard procedure was applied to benzamidine hydrochloride **1a** (0.60 mmol) and 1-bromo-4-(phenylethynyl)benzene **2c** (0.30 mmol). The product **3l** was obtained by silica gel chromatography (eluent: petroleum ether/ethyl acetate: 4/1), yielding a brown solid (57.2 mg, 51% yield); **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.89 (d, 1H), 7.59 – 7.49 (m, 3H), 7.42 – 7.32 (m, 3H), 7.30 (d, 2H), 7.19 (t, 4H), 5.35 (s, 2H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 155.2, 147.1, 139.8, 137.5, 131.7, 130.7, 130.4, 128.4, 127.0, 126.3, 126.1, 122.9, 122.5, 121.3, 116.6, 77.3, 77.0, 76.8; **IR (ATR)** 3296, 2922, 1635, 1436, 1261, 757 $cm^{-1}$.




3l'

**3-(4-bromophenyl)-4-phenylisoquinolin-1-amine (3l')**

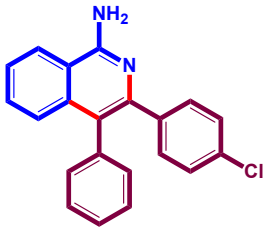
The standard procedure was applied to benzamidine hydrochloride **1a** (0.60 mmol) and 1-bromo-4-(phenylethynyl)benzene **2c** (0.30 mmol). The product **3l'** was obtained by silica gel chromatography (eluent: petroleum ether/ethyl acetate: 4/1), yielding a brown solid (50.0 mg, 45% yield); **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.88 (d, 1H), 7.59 – 7.49 (m, 3H), 7.44 (d, 2H), 7.31 – 7.27 (m, 2H), 7.20 (d, 3H), 7.07 (d,2H), 5.56 (s, 2H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 155.4, 148.6, 140.4, 137.2, 136.9, 133.5, 131.4, 130.5, 130.0, 127.7, 127.1, 126.0, 125.9, 122.6, 121.4, 120.9, 116.5, 77.3, 77.0, 76.8; **IR (ATR)** 3282, 2924, 1614, 1442, 1253, 760 $cm^{-1}$.




3m

**4-(4-chlorophenyl)-3-phenylisoquinolin-1-amine (3m)** [2c, 2d]

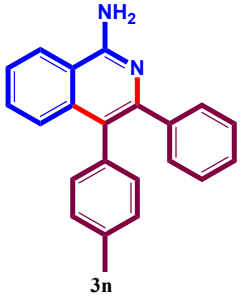
The standard procedure was applied to benzamidine hydrochloride **1a** (0.60 mmol) and 1-chloro-4-(phenylehtynyl)benzene **2d** (0.30 mmol). The product **3m** was obtained by silica gel chromatography (eluent: petroleum ether/ethyl acetate: 4/1), yielding a white solid (53.5 mg, 54% yield);**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.88 (d, 1H), 7.60 – 7.48 (m, 3H), 7.38 – 7.28 (m, 3H), 7.26 (t, 3H), 7.21 – 7.16 (m, 2H), 7.14 (d, 1H), 5.39 (s, 2H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 155.2, 147.2, 139.4, 137.6, 132.9, 131.8, 131.4, 130.3, 128.3, 127.7, 127.0, 126.3, 126.0, 123.0, 122.5, 116.6, 77.3, 77.0, 76.8; **IR (ATR)** 3293, 2922, 1635, 1439, 1264, 760$cm^{-1}$.



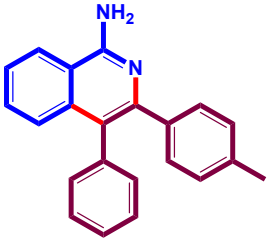

3m'

**3-(4-chlorophenyl)-4-phenylisoquinolin-1-amine (3m')**

The standard procedure was applied to benzamidine hydrochloride **1a** (0.60 mmol) and 1-chloro-4-(phenylehtynyl)benzene **2d** (0.30 mmol). The product **3m'** was obtained by silica gel chromatography (eluent: petroleum ether/ethyl acetate=4/1), yielding a white solid (46.5 mg, 47% yield); **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.88 (d, 1H), 7.54 (tt, 3H), 7.37 – 7.27 (m, 4H), 7.24 – 7.16 (m, 3H), 7.13 (d, 2H), 5.48 (s, 2H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 155.3, 140.5, 137.3, 136.4, 133.2, 132.7, 130.4, 130.0, 128.4, 127.7, 127.1, 125.9, 122.6, 121.4, 116.5, 77.3, 77.0, 76.8; **IR (ATR)** 3288, 2922, 1627, 1439, 1253, 752$cm^{-1}$.




3n



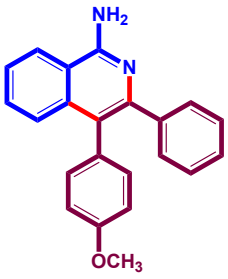

3n'

**3-phenyl-4-(p-tolyl)isoquinolin-1-amine (3n)** [2c, 2d]
**4-phenyl-3-(p-tolyl)isoquinolin-1-amine (3n')**

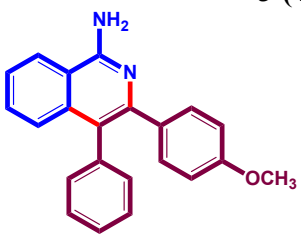
The standard procedure was applied to benzamidine hydrochloride **1a** (0.60 mmol) and 1-methyl-4-(phenylehtynyl)benzene **2e** (0.30 mmol). The product **3n: 3n' (2:3)** was obtained by silica gel chromatography (eluent: petroleum ether/ethyl acetate: 4/1), yielding a brown solid (57 mg, 61% yield);**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.83 (d, 1H), 7.61 – 7.44 (m, 3H), 7.36 – 7.25 (m, 3H), 7.19 (dt, 3H), 7.11

(d, 1H), 7.07 (d, 1H), 6.98 (d, 1H), 5.33 (s, 2H), 2.35 (s, 1.25H), 2.26 (s, 1.75H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 155.1, 148.8, 141.2, 138.2, 137.7, 136.5, 136.2, 134.8, 131.9, 131.7, 130.0, 128.9, 128.2, 127.5, 126.7, 126.2, 125.6, 122.8, 122.6, 122.4, 116.5, 77.3, 77.1, 76.8, 21.2; **IR (ATR)** 3290, 2922, 1638, 1444, 1256, 757 $cm^{-1}$.

**4-(4-methoxyphenyl)-3-phenylisoquinolin-1-amine(3o)**[2c,2d]
**3-(4-methoxyphenyl)-4-phenylisoquinolin-1-amine (3o')**



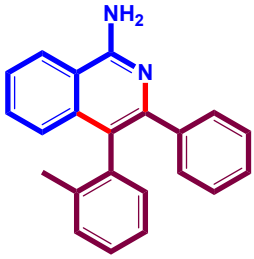
3o



3o'

The standard procedure was applied to benzamidine hydrochloride **1a** (0.60 mmol) and 1-methoxy-4-(phenylehtynyl)benzene **2f** (0.30 mmol). The product **3o: 3o' (1:1)** was obtained by silica gel chromatography (eluent: petroleum ether/ethyl acetate=4/1), yielding a dark brown solid (54.7 mg, 56% yield);**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.86 (d, 1H), 7.61 – 7.45 (m, 3H), 7.32 (dt, 3H), 7.23 – 7.13 (m, 3H), 7.10 (d, 1H), 6.86 (d, 1H), 6.71 (d, 1H), 5.47 (s, 2H), 3.81 (s, 1.45H), 3.74 (s, 1.55H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 158.5, 158.4, 155.1, 148.5, 140.9, 138.1, 137.9, 137.7, 133.1, 132.8, 131.8, 131.3, 130.1, 129.9, 128.2, 127.6, 126.8, 126.3, 126.1, 125.7, 122.5, 116.6, 116.4, 113.6, 113.0, 77.3, 77.0, 76.8, 55.2; **IR (ATR)** 3293, 2924, 1606, 1434, 1240, 1609 $cm^{-1}$.

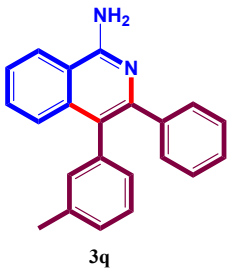
**3-phenyl-4-(o-tolyl)isoquinolin-1-amine (3p)** [2c, 2d]



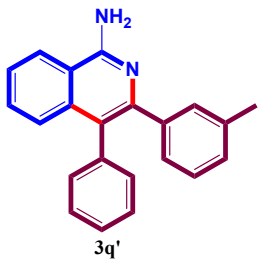
3p

The standard procedure was applied to benzamidine hydrochloride **1a** (0.60 mmol) and 1-methyl-2-(phenylehtynyl)benzene **2g** (0.30 mmol). The product **3p** was obtained by silica gel chromatography (eluent: petroleum ether/ethyl acetate: 4/1), yielding a green solid (38.1 mg, 41% yield);**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.86 (d, 1H), 7.49 (ddd, 2H), 7.37 – 7.26 (m, 3H), 7.17 (ddd, 7H), 5.41 (s, 2H), 1.90 (s, 3H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 155.3, 148.2, 140.9, 137.8, 137.4, 137.2, 132.2, 130.3, 130.0, 129.5, 127.4, 127.0, 126.1, 125.8, 125.6, 122.6, 121.9, 116.6, 77.3, 77.0, 76.8, 20.0; **IR (ATR)** 3293, 2919, 1635, 1436, 1248, 694 $cm^{-1}$.

**3-phenyl-4-(m-tolyl)isoquinolin-1-amine (3q)** [2c]
**4-phenyl-3-(m-tolyl)isoquinolin-1-amine (3q')**

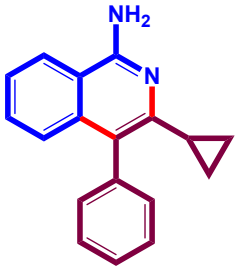


3q



3q'

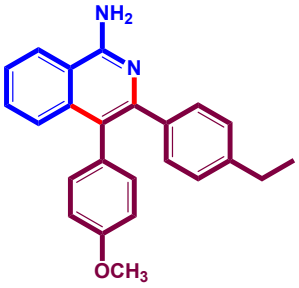
The standard procedure was applied to benzamidine hydrochloride **1a** (0.60 mmol) and 1-methyl-3-(phenylehtynyl)benzene **2h** (0.30 mmol). The product **3q: 3q' (1:2)** was obtained by silica gel chromatography (eluent: petroleum ether/ethyl acetate: 4/1), yielding a brown solid (40.9 mg, 44% yield); **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.86 (d, 1H), 7.53 (tdd, 3H), 7.36 – 7.26 (m, 3H), 7.18 (ddd, 3H), 7.09 (d, 1H), 7.05 – 7.00 (m, 1H), 6.97 (t, 1H), 5.34 (s, 2H), 2.30 (s, 1.18H), 2.24 (s, 1.82H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 155.1, 148.9, 141.1, 140.9, 138.1, 137.8, 137.6, 137.0, 132.5, 131.9, 130.7, 130.0, 128.9, 128.0, 127.5, 127.2, 126.7, 126.3, 125.7, 122.8, 122.4, 116.5, 77.3, 77.0, 76.8, 21.4; **IR (ATR)** 3290, 2924, 1638, 1434, 1264, 696$cm^{-1}$.



3r

**3-cyclopropyl-4-phenylisoquinolin-1-amine (3r)**

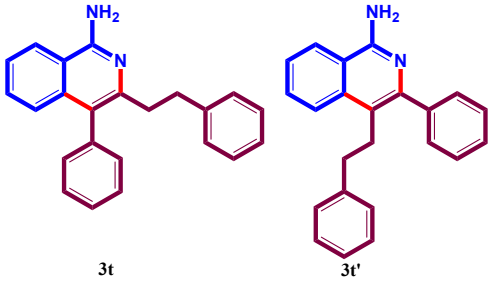
The standard procedure was applied to benzamidine hydrochloride **1a** (0.60 mmol) and (cyclopropylethynyl)benzene **2i** (0.30 mmol). The product **3r** was obtained by silica gel chromatography (eluent: petroleum ether/ethyl acetate: 4/1), yielding a brown solid (35.5 mg, 45% yield); **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 8.45 (d, 1H), 7.84 (d, 1H), 7.71 (t, 1H), 7.67 (d, 2H), 7.50 (t, 1H), 7.42 (t, 2H), 7.35 (t, 1H), 5.44 (s, 2H), 2.08 (ddd, 1H), 0.85 (dt, 2H), 0.14 (q, 2H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 154.4, 150.3, 141.2, 139.2, 130.1, 129.8, 127.6, 127.3, 125.5, 122.9, 120.3, 116.9, 77.3, 77.0, 76.8, 10.6, 9.8; **HRMS(ESI)** m/z found for $C_{18}H_{17}N_2$ [M-H]+, 261.1385, calculated for 260.1313; **IR (ATR)** 3203, 2919, 1617, 1434, 1261, 757cm$^{-1}$.



3s

**3-(4-ethylphenyl)-4-(4-methoxyphenyl)isoquinolin-1-amine (3s)**

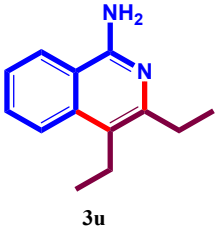
The standard procedure was applied to benzamidine hydrochloride **1a** (0.60 mmol) and1-ethyl-4-((4-methoxyphenyl)ethynyl)benzene **2j** (0.30 mmol). The product **3s** was obtained by silica gel chromatography (eluent: petroleum ether/ethyl acetate=4/1), yielding a brown solid (51 mg, 48% yield; **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.84 (d, 1H), 7.58 (d, 1H), 7.52 (t, 1H), 7.47 (dd, 1H), 7.25 (d, 2H), 7.11 (d, 2H), 7.02 (d, 2H), 6.87 (d, 2H), 5.28 (s, 2H), 3.82 (s, 3H), 2.57 (q, 2H), 1.17 (t, 3H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 158.3, 154.9, 148.9, 142.7, 138.5, 137.9, 132.8, 130.3, 130.0, 127.1, 126.2, 125.5, 122.4, 122.2, 116.5, 113.6, 77.3, 77.0, 76.8, 55.2, 28.5, 15.5; **HRMS(ESI)** m/z found for $C_{24}H_{22}ON_2$ [M-H]+, 355.1800, calculated for 354.1732; **IR (ATR)** 3314, 2927, 1649, 1442, 1242, 768cm$^{-1}$.



3t 3t'

**3-phenethyl-4-phenylisoquinolin-1-amine (3t)**
**4-phenethyl-3-phenylisoquinolin-1-amine (3t')**

The standard procedure was applied to benzamidine hydrochloride **1a** (0.60 mmol) and but-1-yne-1,4-diyldibenzene **2k** (0.30 mmol). The product **3t: 3t' (4:1)** was obtained by silica gel chromatography (eluent: petroleum ether/ethyl acetate: 4/1), yielding a dark brown solid (50.5 mg, 52% yield); **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 8.03 (d, 1H), 7.85 (d, 1H), 7.71 (t, 1H), 7.50 (dd, 1H), 7.44 – 7.35 (m, 4H), 7.25 – 7.19 (m, 2H), 7.19 – 7.13 (m, 1.32H), 7.10 (dd, 0.51H), 7.02 (d, 1.65H), 6.98 (d, 0.35H), 5.36 (s, 2H), 3.11 (dd, 1.67H), 2.93 (dd, 0.38H), 2.85 (dd, 1.61H), 2.79 (dd, 0.4H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 155.4, 154.2, 150.3, 142.01, 141.8, 141.5, 137.7, 136.7, 130.9, 130.4, 128.9, 128.7, 128.3, 127.5, 127.2, 125.9, 125.6, 125.3, 124.0, 123.4, 119.1, 117.4, 77.2, 77.0, 76.8, 37.2, 36.3, 30.4, 29.7; **HRMS(ESI)** m/z found for $C_{23}H_{21}N_2$ [M-H]+, 325.1696, calculated for 324.1626; **IR (ATR)** 3280, 2922, 1627, 1439,1259, 691cm$^{-1}$.



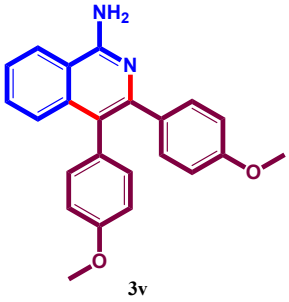
3u

**3,4-diethylisoquinolin-1-amine (3u)**[2b]

The standard procedure was applied to benzamidine hydrochloride **1a** (0.60 mmol) and 3-hexyne **2l** (0.30 mmol). The product **3u** was obtained by silica gel chromatography (eluent: petroleum ether/ethyl acetate: 4/1), yielding a dark brown solid (48.6 mg, 81% yield); **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.88 (d, 1H), 7.83 (d, 1H), 7.64 (t, 1H), 7.43 (t, 1H), 5.45 (s, 2H), 2.92 (q, 2H), 2.80 (q, 2H),

1.30 (t, 3H), 1.24 (t, 3H); **$^{13}$C NMR** (126 MHz, CDCl3) δ 154.1, 150.5, 136.7, 130.2, 124.7, 123.5, 123.2, 120.2, 116.8, 77.2, 77.0, 76.7, 27.7, 20.2, 15.3, 14.5; **IR (ATR)** 3359, 2964, 1614, 1426, 1245, 765 cm$^{-1}$.

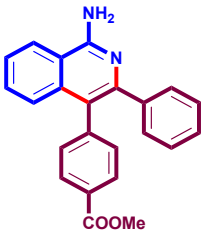
**3,4-bis(4-methoxyphenyl)isoquinolin-1-amine (3v)**[2b, 2e]



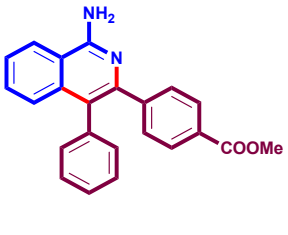
3v

The standard procedure was applied to benzamidine hydrochloride **1a** (0.60 mmol) and 1,2-bis(4-methoxyphenyl)ethyne **2m** (0.30 mmol). The product **3v** was obtained by silica gel chromatography (eluent: petroleum ether/ethyl acetate: 4/1), yielding a brown solid (88.7 mg, 83% yield); **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.84 (d, 1H), 7.58 (d, 1H), 7.54 – 7.50 (m, 1H), 7.48 – 7.44 (m, 1H), 7.32 – 7.26 (m, 2H), 7.13 – 7.08 (m, 2H), 6.90 – 6.86 (m, 2H), 6.74 – 6.70 (m, 2H), 5.29 (s, 2H), 3.83 (s, 3H), 3.76 (s, 3H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 158.4, 154.9, 148.3, 138.0, 133.6, 132.8, 131.3, 130.3, 130.0, 126.2, 125.5, 122.4, 122.0, 116.4, 113.7, 113.0, 77.3, 77.0, 76.8, 55.2; **IR (ATR)** 3322, 2924, 1651, 1511, 1237, 773 cm$^{-1}$.

**Methyl-4-(1-amino-3-phenylisoquinolin-4-yl)benzoate (3x)**
**Methyl-4-(1-amino-4-phenylisoquinolin-3-yl)benzoate(3x')**



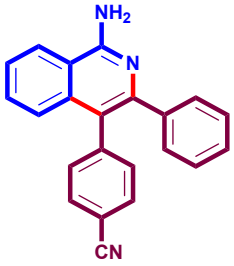
3x



3x'

The standard procedure was applied to benzamidine hydrochloride **1a** (0.60 mmol) and methyl 4-(phenylethynyl)benzoate **2n** (0.30 mmol). The product **3x: 3x' (3.3:2.7)** was obtained by silica gel chromatography (eluent: petroleum ether/ethyl acetate: 4/1), yielding a brown solid (53.1 mg, 50% yield); **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.99 (d, 1H), 7.93 – 7.88 (m, 1H), 7.85 (d, 1H), 7.55 (dq, 3H), 7.40 (d, 1H), 7.30 (dd, 4H), 7.17 (s, 2H), 5.56 (s, 1H), 5.45 (s, 1H), 3.92 (s, 1.65H), 3.87 (s, 1.35H); **13C NMR** (126 MHz, CDCl3) δ 167.1, 155.4, 155.2, 147.3, 145.6, 143.2, 137.4, 137.0, 132.0, 131.8, 130.5, 130.0, 129.4, 128.8, 128.5, 128.3, 127.7, 127.2, 126.5, 126.0, 125.8, 122.7, 122.5, 116.4, 77.3, 77.0, 76.8, 52.1; **HRMS(ESI)** m/z found for $C_{23}H_{18}O_2$ [M-H]+, 355.1407, calculated for 354.1368; **IR (ATR)** 3293, 2924, 1712, 1436, 1285, 763 cm$^{-1}$

**4-(1-amino-3-phenylisoquinolin-4-yl)benzonitrile(3y)**



3y

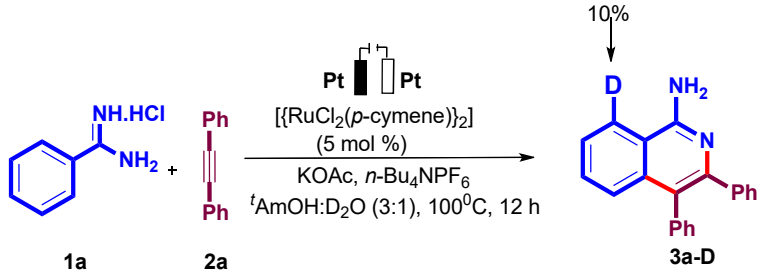
The standard procedure was applied to benzamidine hydrochloride **1a** (0.60 mmol) and 4-(phenylethynyl)benzonitrile **2o** (0.30 mmol). The product **3y** was obtained by silica gel chromatography (eluent: petroleum ether/ethyl acetate: 4/1), yielding a brown solid (41.1 mg, 43% yield); **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.90 (d, 1H), 7.67 – 7.51 (m, 4H), 7.49 – 7.41 (m, 2H), 7.32 (d, 3H), 7.20 (s, 3H), 5.38 (s, 2H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 155.7, 148.9, 143.4, 140.0, 136.7, 132.7, 131.9, 131.5, 130.8, 129.9, 128.5, 127.9, 127.5, 126.3, 125.4, 122.8, 122.5, 119.0, 116.3, 110.6, 77.3), 77.0, 76.8; **HRMS(ESI)** m/z found for $C_{22}H_{15}N_3$ [M-H]+, 322.1307, calculated for 321.1266; **IR (ATR)** 3293, 2224, 1633, 1442, 1255, 760 cm$^{-1}$

# 3. References

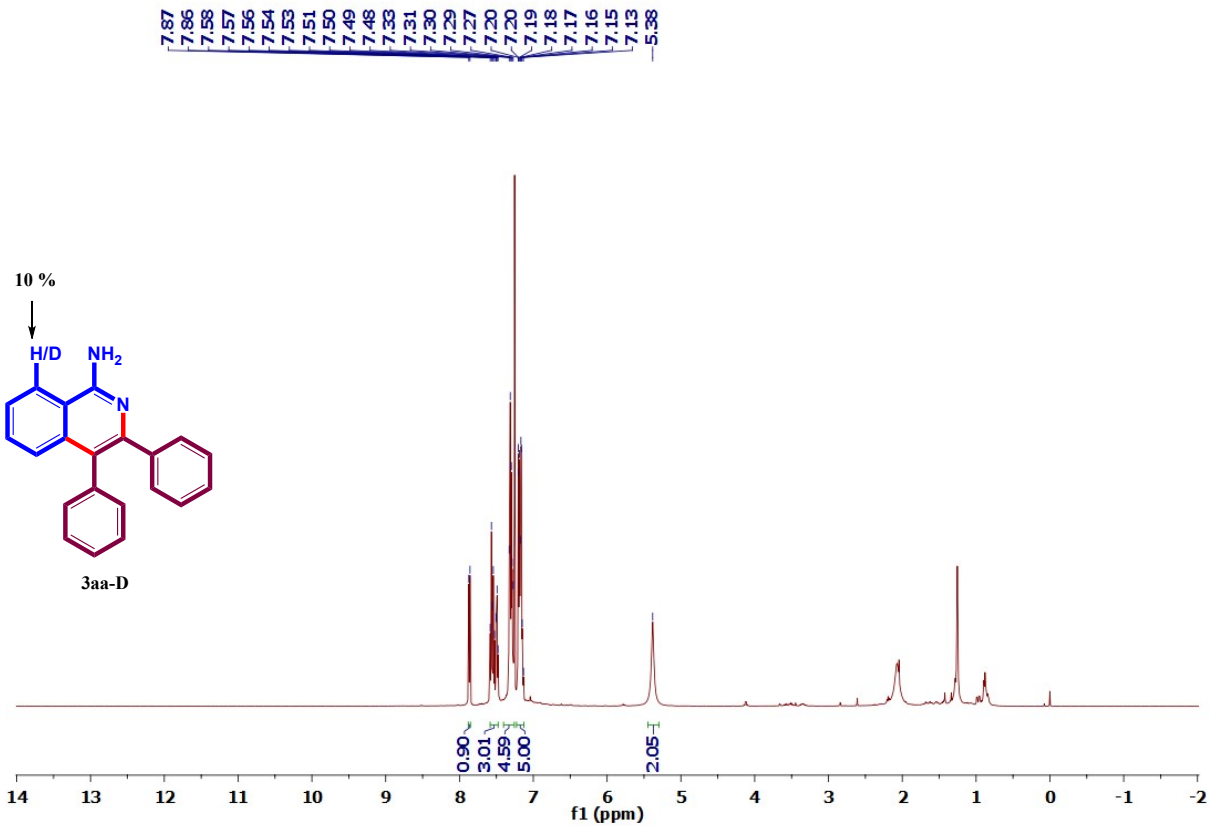
1 (a) Xu, Y.; Zhao, J.; Chen, H.; Wu, W.; Jiang, H. A Convenient Regioselective Synthesis of Cyclopentadienones via Palladium-Catalyzed [2+2+1] Cyclocarbonylation of Alkynes. *Chem. Commun.*2014, ***50***, 2488−2490. (b) D. Stuart, M. laperle. K. M. N. Burgess, K. Fagnour I ndole Synthesis via Rhodium Catalyzed Oxidative Coupling of Acetanilides and Internal Alkynes *J. Am. Chem. Soc.* 2008, 130, **49**, 16474–16475.

2 (a)Xiaolong Yu, Kehao Chen, Fan Yang, Shanke Zha, and Jin Zhu Org. Lett. 2016, **18**, 5412−5415. (b) P. P. Kaishap, a G. Duarah,a D. Chetiab and S. Gogoi; Org. Biomol. Chem., 2017, **15**, 3491–3498. (c) Xicheng Yang, Haihua Yu, Yulong Xu, Liming Shao, J. Org. Chem. 2018, **83**, 9682−9695; (d) Qianqian Zhen, Lepeng Chen, Linjun Qi, Kun Hu, Yinlin Shao, Renhao Li, Jiuxi Chen, *chem.an Asian journal,* 2020, **15,** 106-111; (e) Fan Yang, Jiaojiao Yu, Yun Liu, Jin Zhu, *Org. Lett.* 2017, **19**, 2885−2888.

# 4. H/D exchange experiment[2b]

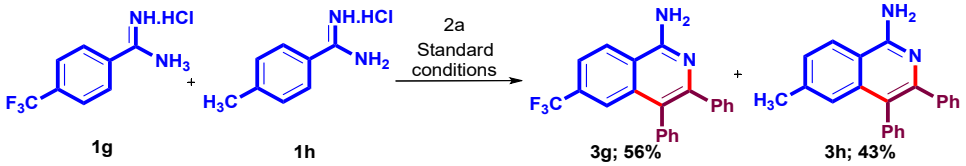



The electrolysis was performed in an undivided cell with a platinum anode (10 mm × 15 mm) and cathode (10 mm × 15 mm). Benzamidine hydrochloride (93.6 mg, 0.60 mmol, 2.0 equiv), alkyne (53.4 mg, 0.30 mmol, 1.0 equiv), *n*-$Bu_4NPF_6$ (69.7 mg, 0.18 mmol, 0.60 equiv), KOAc (58.9 mg, 0.60 mmol, 2.0 equiv) and $[RuCl_2(p\text{-cymene})]_2$ (9.2 mg, 5 mol %) were dissolved in *t*-AmOH: $D_2O$ (3:1, 4.0 mL) under a $N_2$ atmosphere and then added to the cell. The reaction mixture was stirred at a constant current of 1.5 mA for 12 h at 100 $^0$C. When the reaction was completed, the mixture was diluted with $Et_2O$ and washed with $H_2O$, and the product mixture was separated from $Et_2O$ which contained the organic layer. Next, it was evaporated and purified by column chromatography on silica gel (Pet ether /EtOAc: 4/1), affording the corresponding products **3a-D**, yielding a brown solid (70 mg, 79% yield).



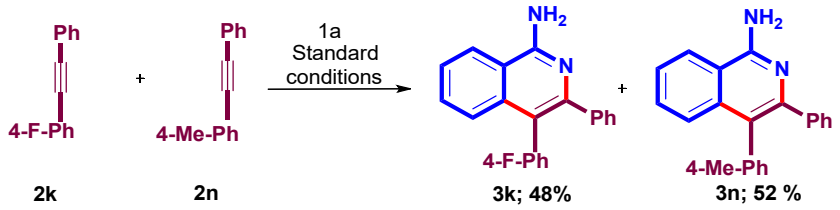

# 5. Competition study

## a. Unsymmetrical benzamidine hydrochloride substrates



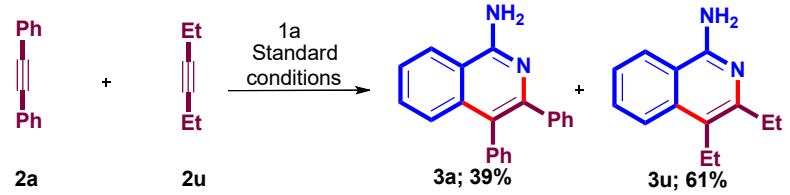

The electrolysis was performed in an undivided cell with a platinum anode (10 mm × 15 mm) and cathode (10 mm × 15 mm). 4-(trifluoromethyl)benzamidine hydrochloride (0.60 mmol, 2.0 equiv), 4-methylbenzamidine hydrochloride(0.60 mmol, 2.0 equiv), diphenyl acetylene (0.30 mmol, 1.0 equiv), *n*-$Bu_4NPF_6$ (0.18 mmol, 0.60 equiv), KOAc (0.60 mmol, 2.0 equiv) and $[RuCl_2(p\text{-cymene})]_2$ (9.2 mg, 5 mol %) were dissolved in *t*-AmOH: $H_2O$ (3:1, 4.0 mL) under a $N_2$ atmosphere and then added to the cell. The reaction mixture was stirred at a constant current of 1.5 mA for 12 h at 100 $^0$C. When the reaction was completed, the mixture was diluted with $Et_2O$ and washed with $H_2O$, and the pure product was separated from $Et_2O$ which contained the organic layer. Next, it was evaporated, affording the products **3g** and **3h** in 56% and 43% yields correspondingly which was confirmed by GCMS analysis.

## b. Unsymmetrical alkyne substrates




The electrolysis was performed in an undivided cell with a platinum anoode (10 mm × 15 mm) and cathode (10 mm × 15 mm). benzamidine hydrochloride (0.60 mmol, 2.0 equiv), 1-fluoro-4-(phenylethynyl)benzene (0.30 mmol, 1.0 equiv), 1-methyl-4-(phenylethynyl)benzene (0.30 mmol, 1.0 equiv), *n*-$Bu_4NPF_6$ (0.18 mmol, 0.60 equiv), KOAc (0.60 mmol, 2.0 equiv) and $[RuCl_2(p\text{-cymene})]_2$ (9.2 mg, 5 mol %) were dissolved in *t*-AmOH: $H_2O$ (3:1, 4.0 mL) under a $N_2$ atmosphere and then added to the cell. The reaction mixture was stirred at a constant current of 1.5 mA for 12 h at 100 $^0$C. When the reaction was completed, the mixture was diluted with $Et_2O$ and washed with $H_2O$, and the product mixture was separated from $Et_2O$ which contained the organic layer. Next, it was evaporated, affording the products **3k** and **3n** in 48% and 52% yields correspondingly which was confirmed by GCMS analysis.

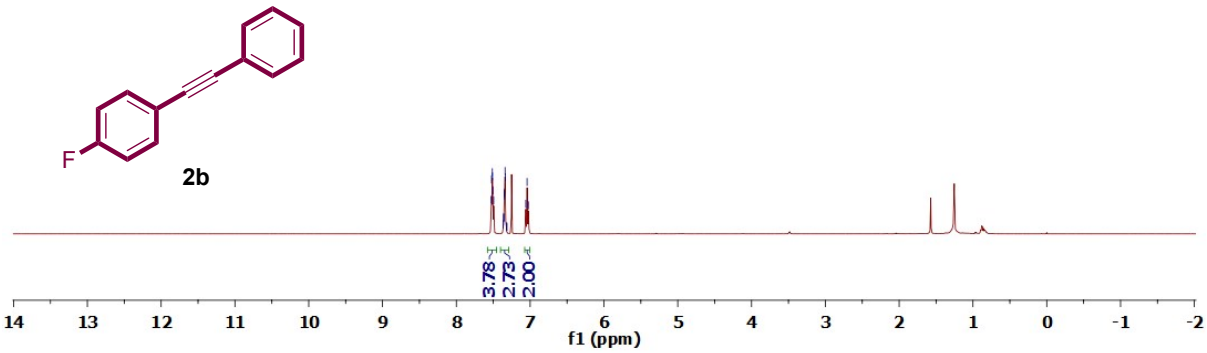
### c. Symmetrical diaryl and dialkyl substrate



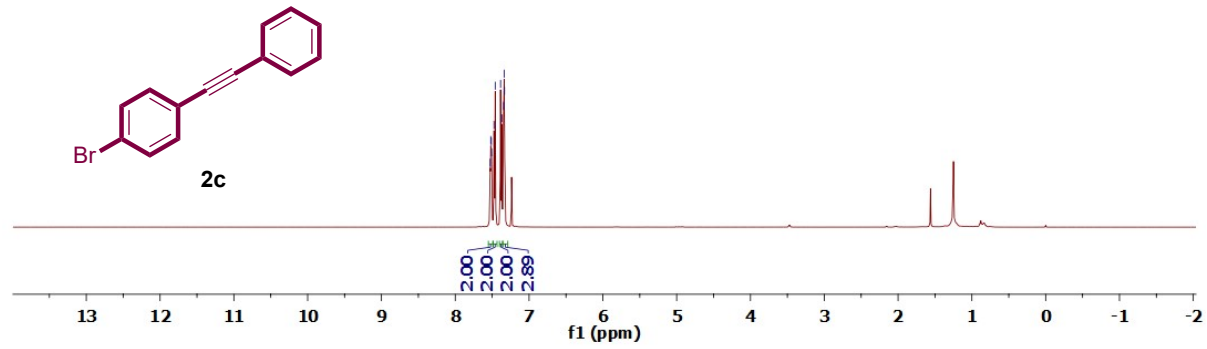

The electrolysis was performed in an undivided cell with a platinum anode (10 mm × 15 mm) and cathode (10 mm × 15 mm). Benzamidine hydrochloride (0.60 mmol, 2.0 equiv), diphenyl acetylene (0.30 mmol, 1.0 equiv), hexyne (0.30 mmol, 1.0 equiv), *n*-$Bu_4NPF_6$ (0.18 mmol, 0.60 equiv), KOAc (0.60 mmol, 2.0 equiv) and $[RuCl_2(p\text{-cymene})]_2$ (9.2 mg, 5 mol %) were dissolved in *t*-AmOH: $H_2O$ (3:1, 4.0 mL) under a $N_2$ atmosphere and then added to the cell. The reaction mixture was stirred at a constant current of 1.5 mA for 12 h at 100 $^0$C. When the reaction was completed, the mixture was diluted with $Et_2O$ and washed with $H_2O$, and the product mixture was separated from $Et_2O$ which contained the organic layer. Next, it was evaporated, affording the corresponding products **3a** and **3u** in 39% and 61% yields correspondingly which was confirmed by GCMS analysis.

# 6. NMR spectra

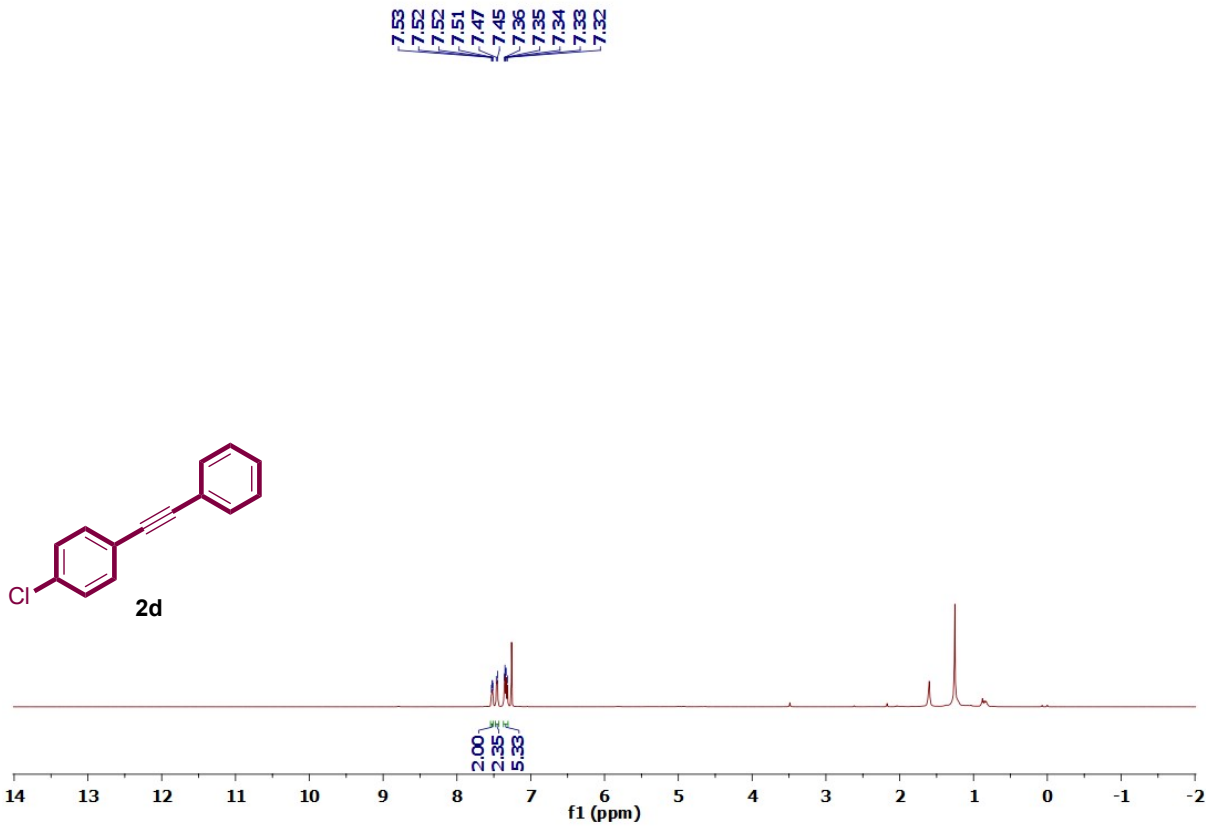
**1-fluoro-4-(phenylethynyl)benzene (2b)**

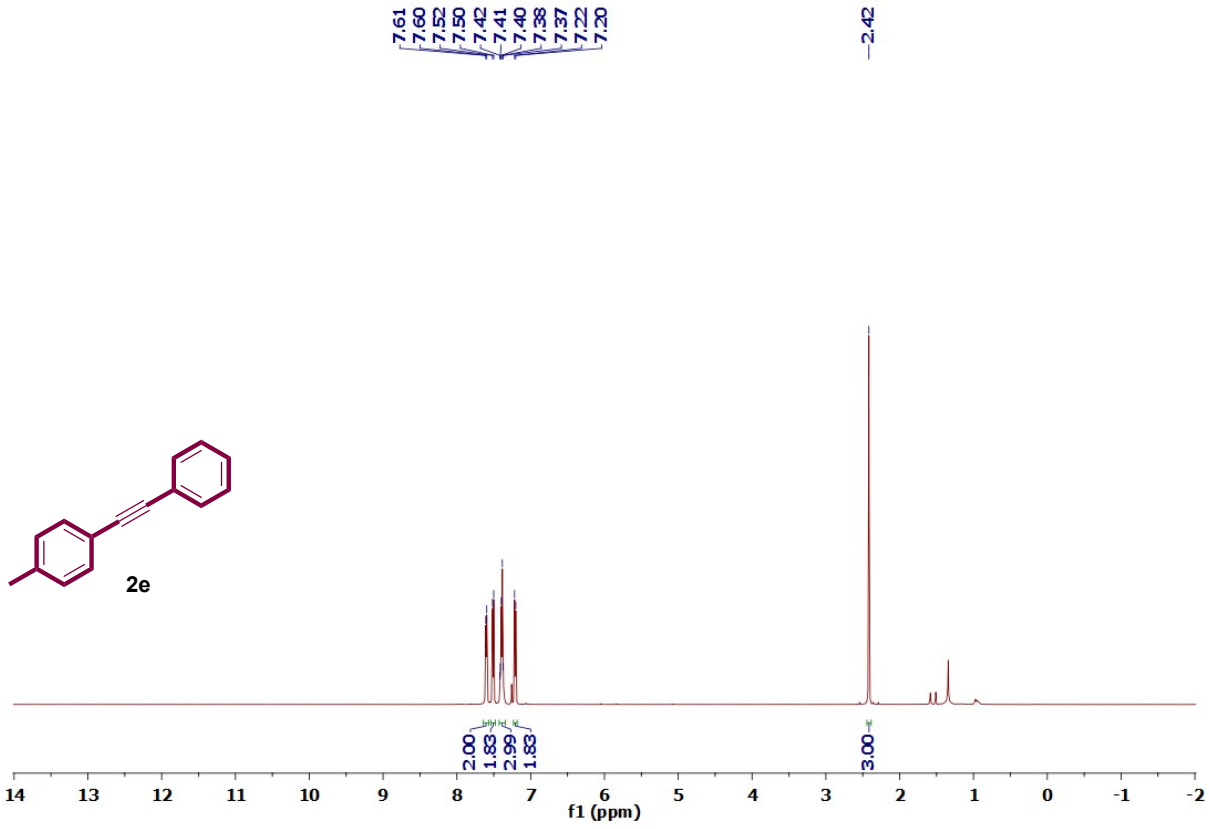

**1-bromo-4-(phenylethynyl)benzene (2c)**

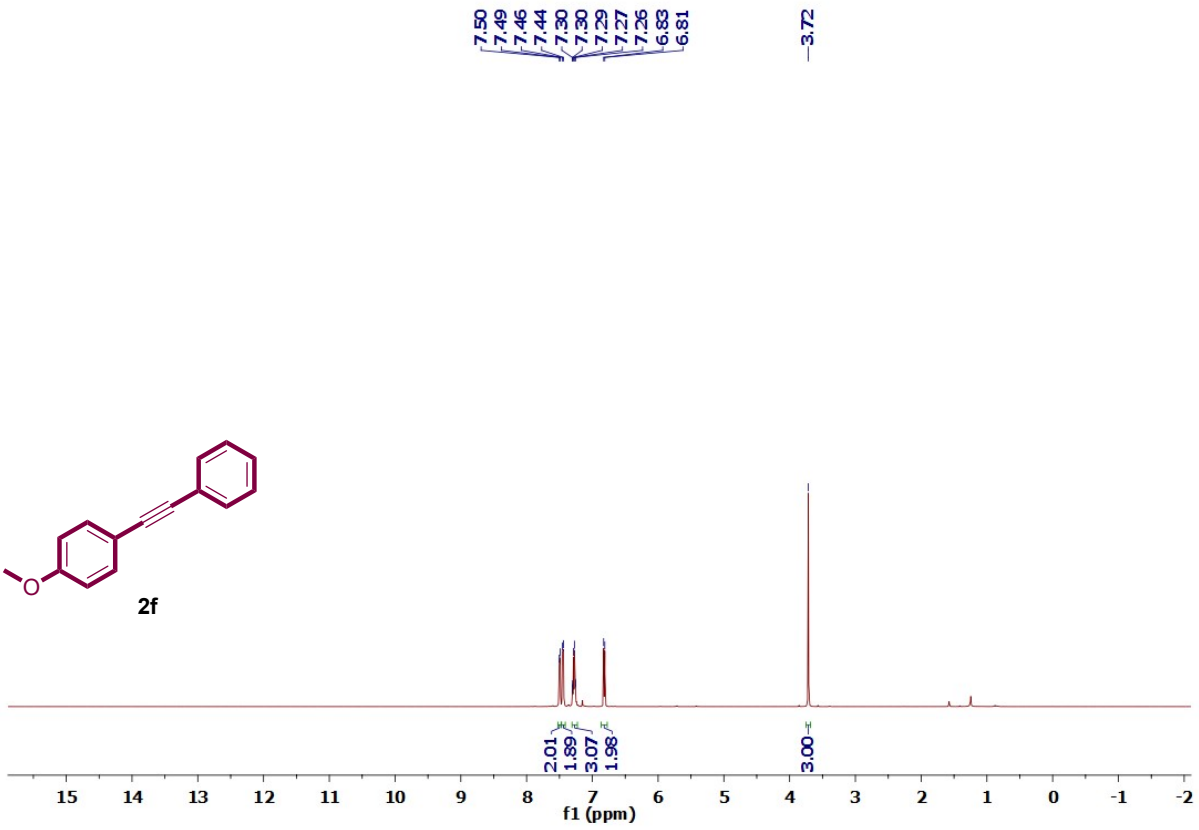

**1-chloro-4-(phenylethynyl)benzene (2d)**



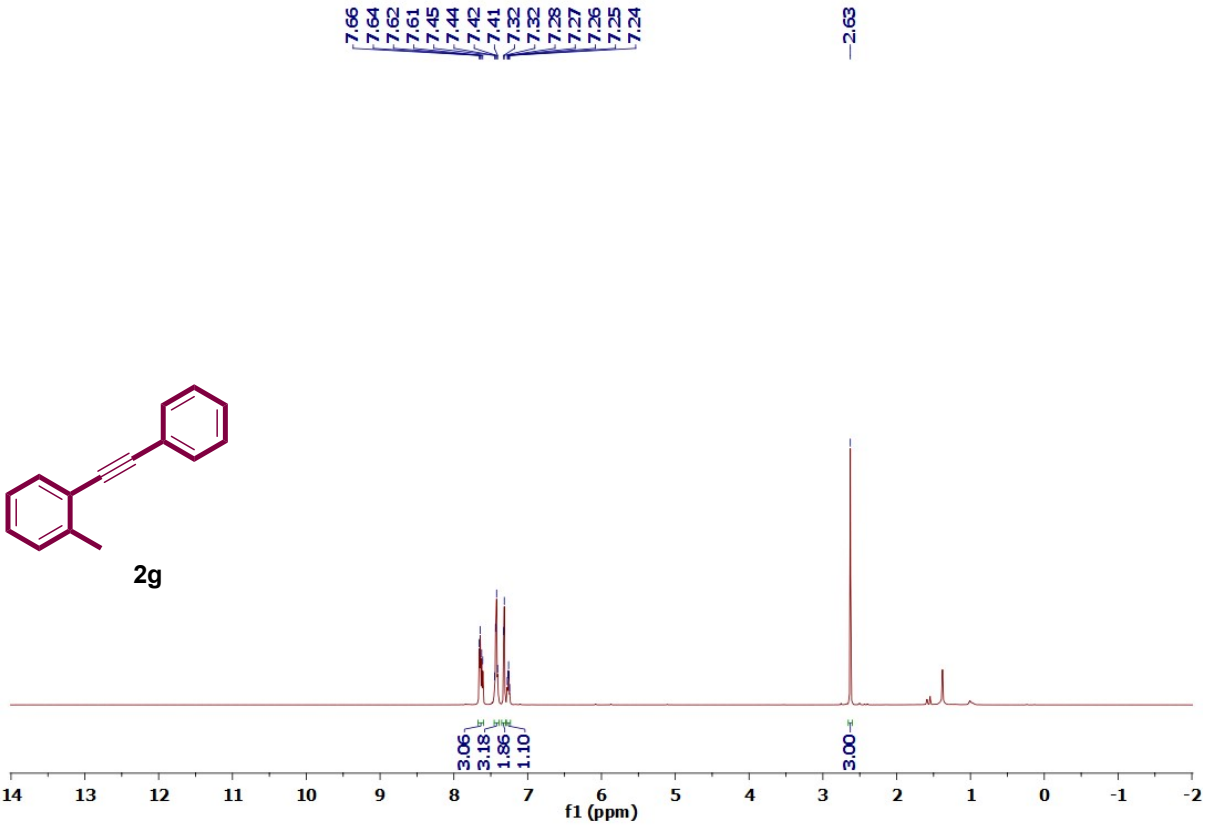

**1-methyl-4-(phenylethynyl)benzene (2e)**



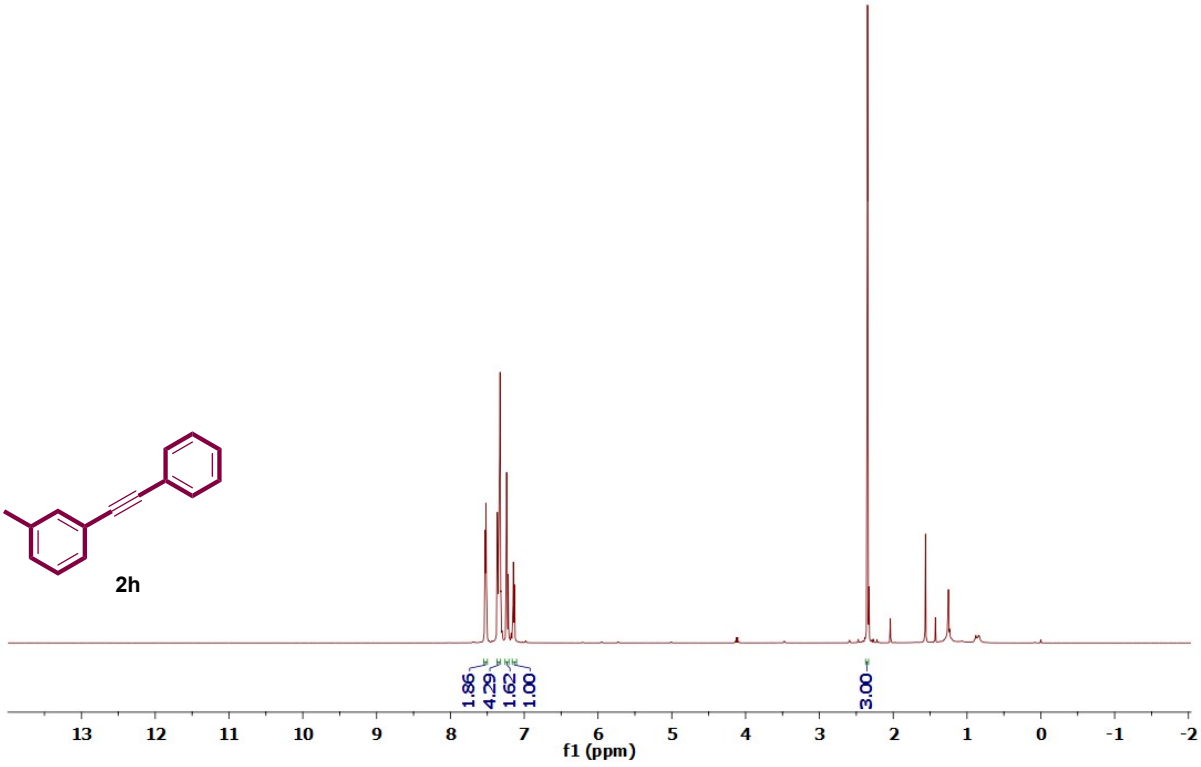

**1-methoxy-4-(phenylethynyl)benzene (2f)**



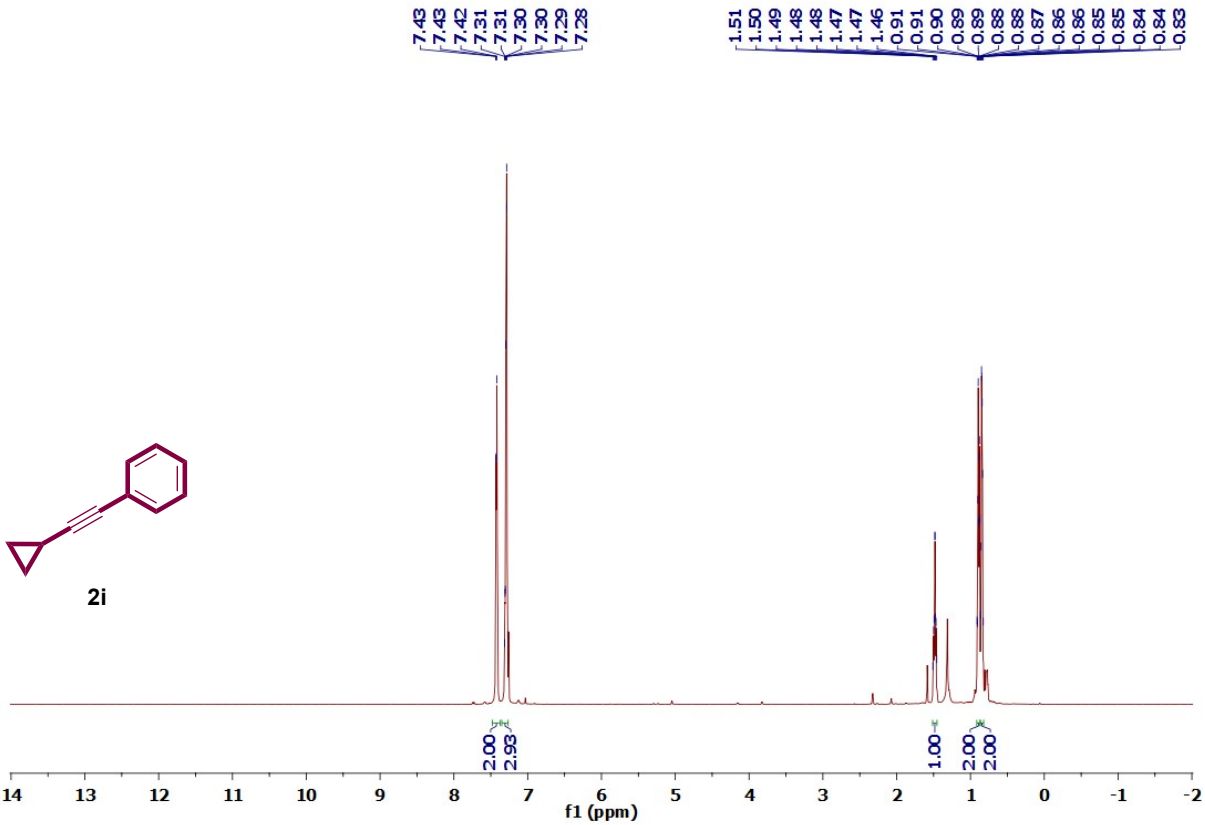

**1-methyl-2-(phenylethynyl)benzene (2g)**



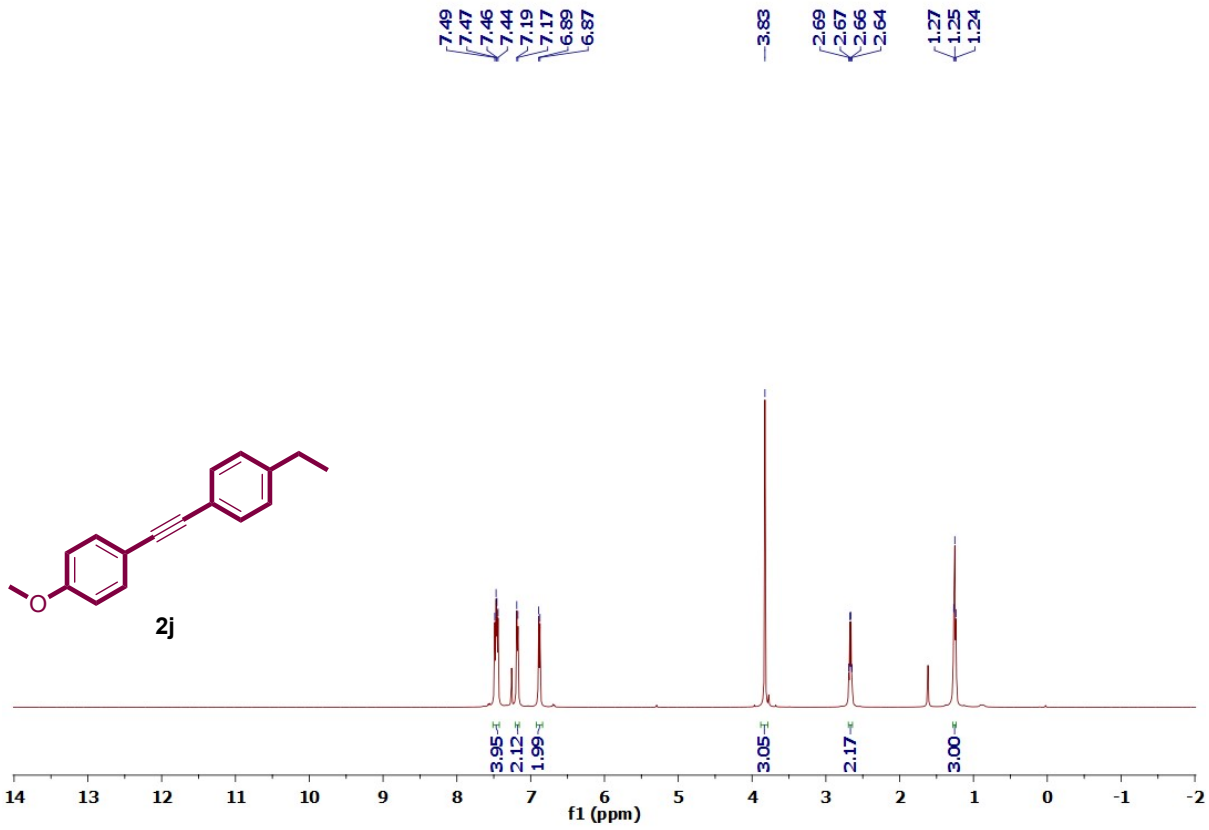

**1-methyl-3-(phenylethynyl)benzene (2h)**



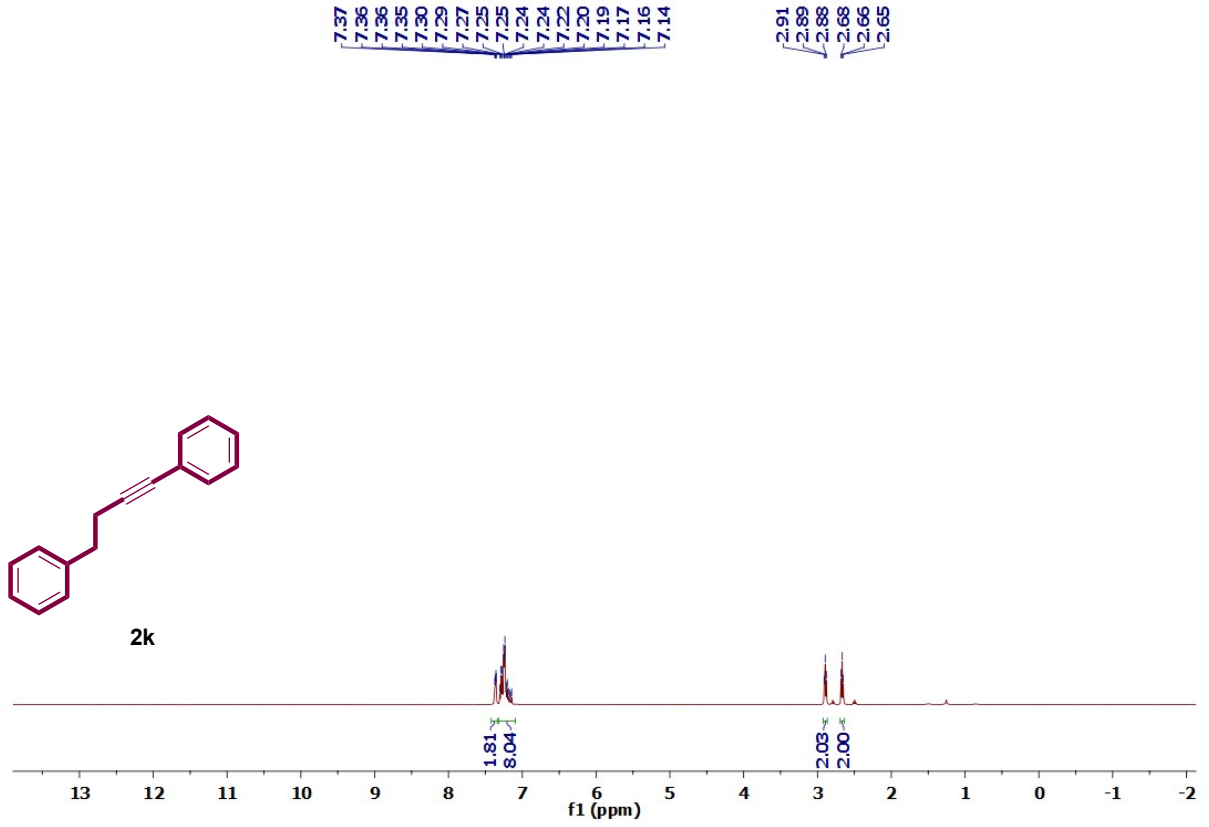

**(cyclopropylethynyl)benzene (2i)**



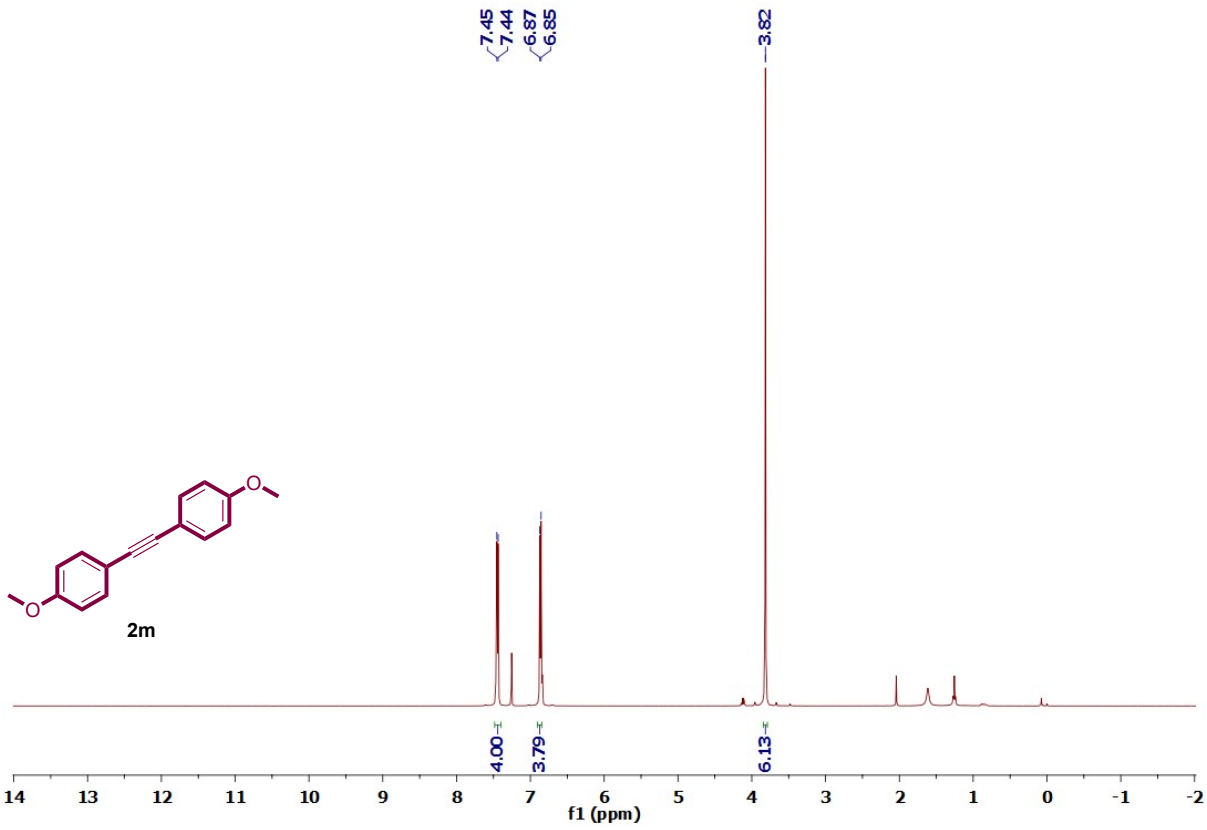

**1-ethyl-4-((4-methoxyphenyl)ethynyl)benzene (2j)**



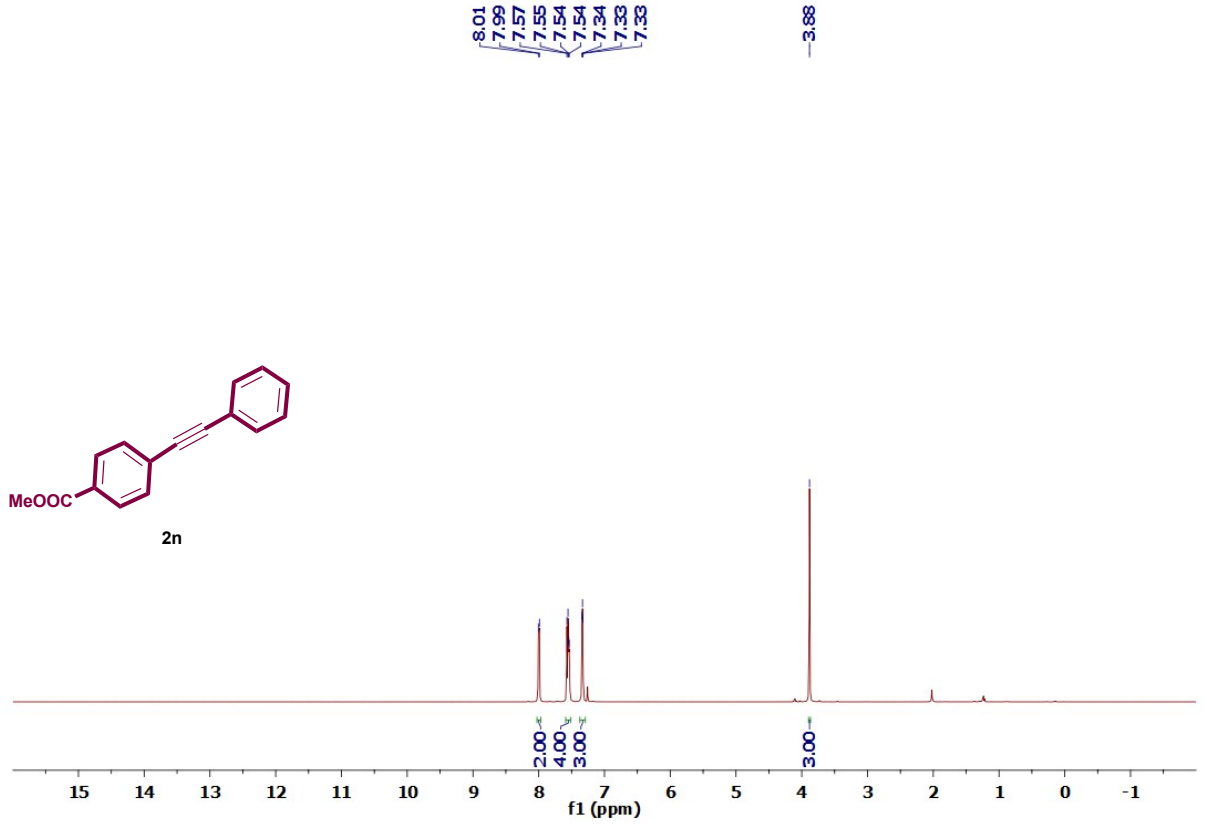

**But-1-yne-1,4-diyldibenzene (2k)**



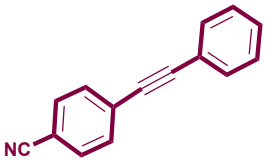

**1,2-bis(4-methoxyphenyl)ethyne (2m)**



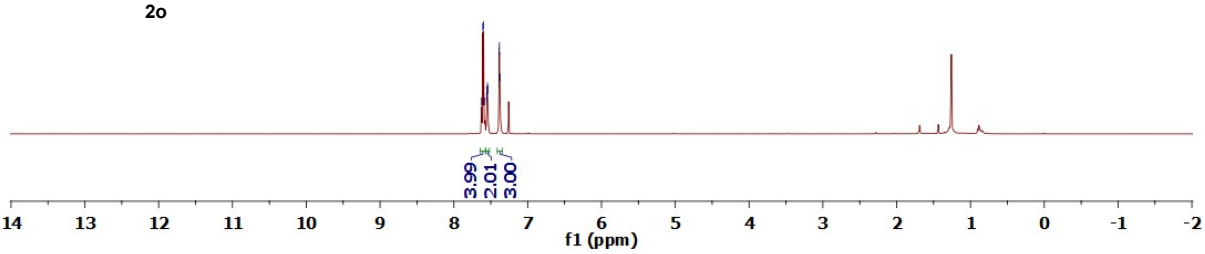

**Methyl 4-(phenylethynyl)benzoate (2n)**



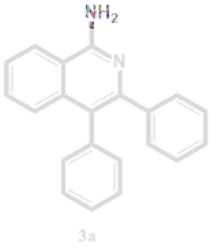
**4-(phenylethynyl)benzonitrile (2o)**

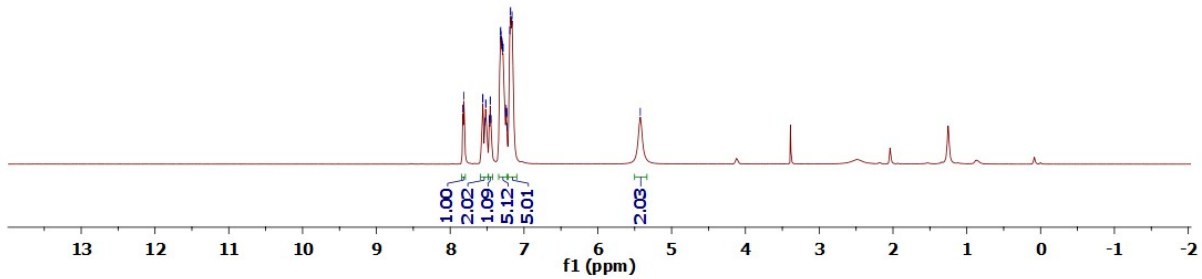

2o




**3,4-diphenylisoquinolin-1-amine (3a)**[2a, 2b, 2c]

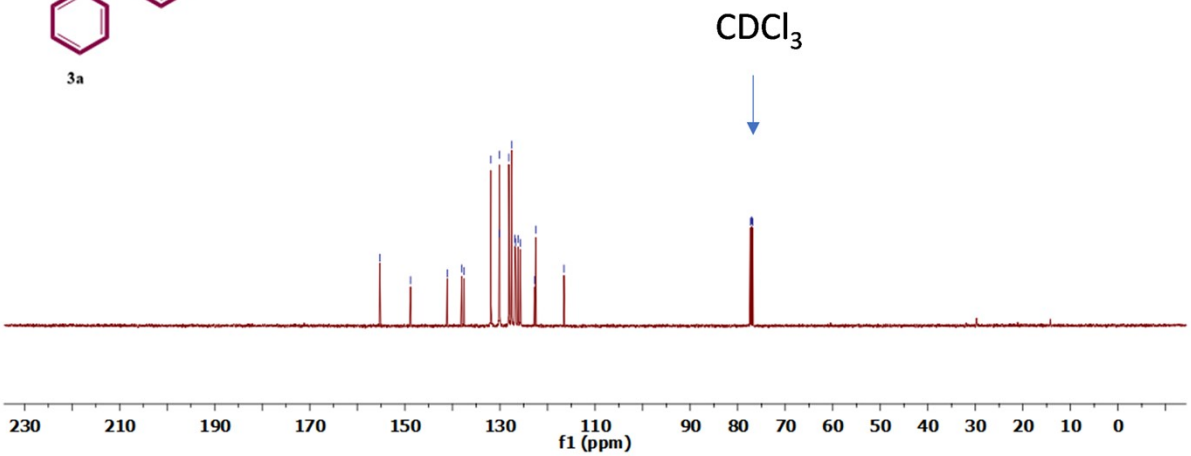




3a

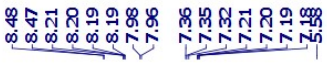


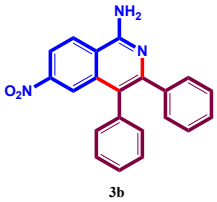


3a

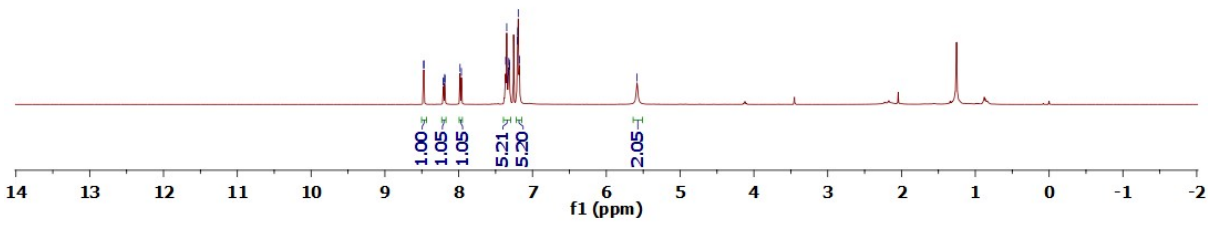


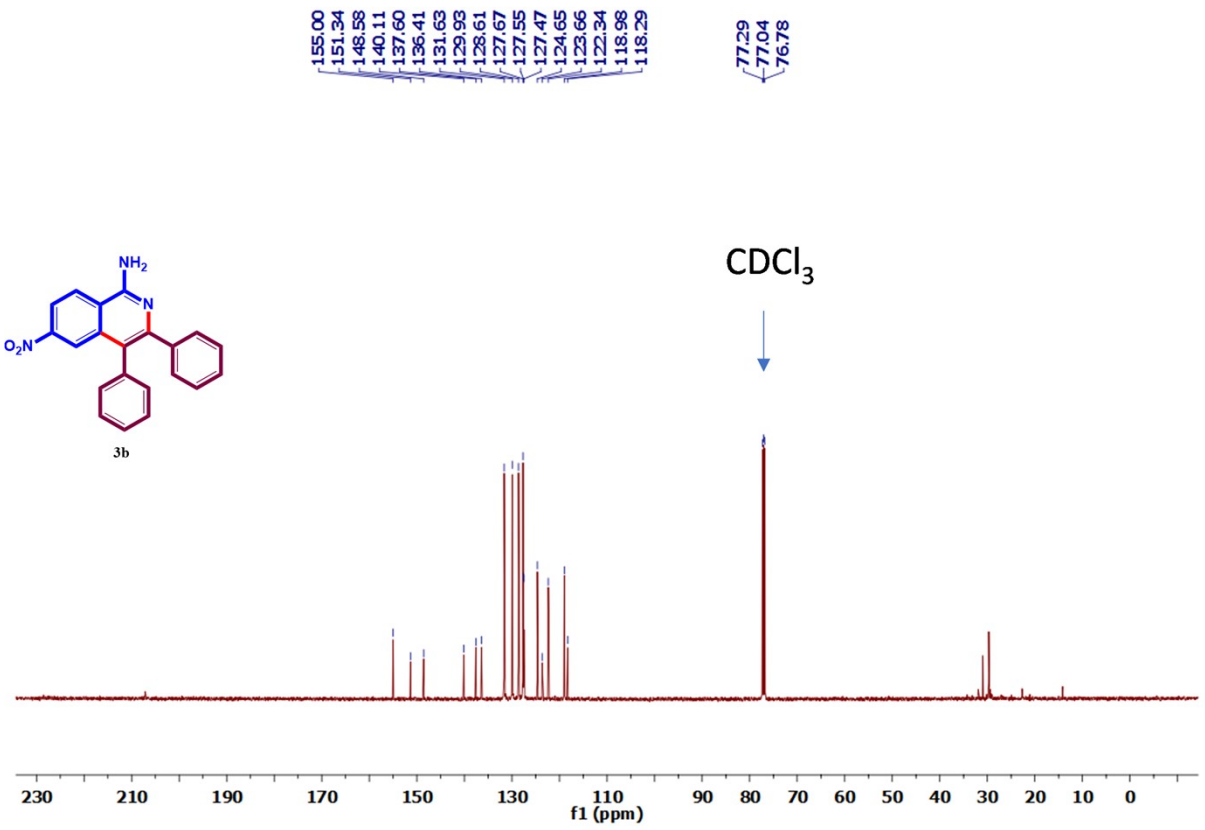

**6-nitro-3,4-diphenylisoquinolin-1-amine (3b)**[2a]



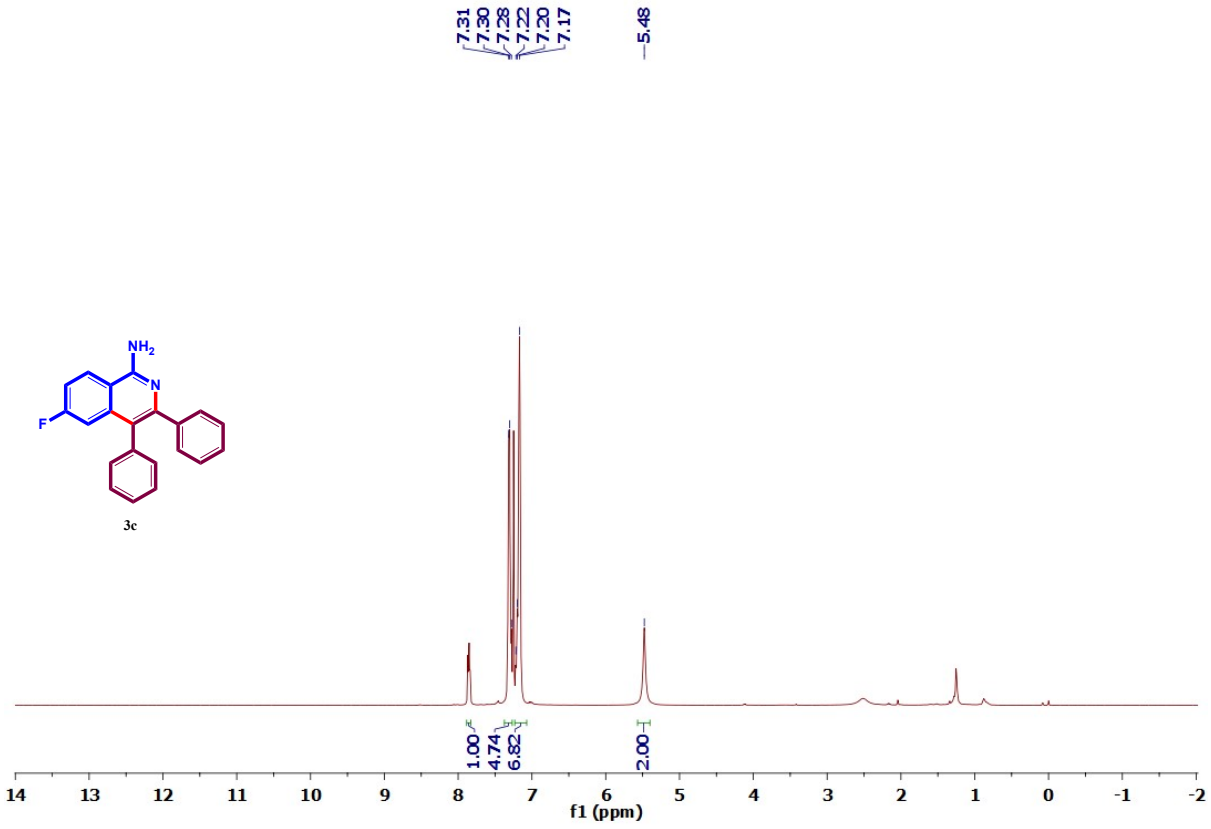



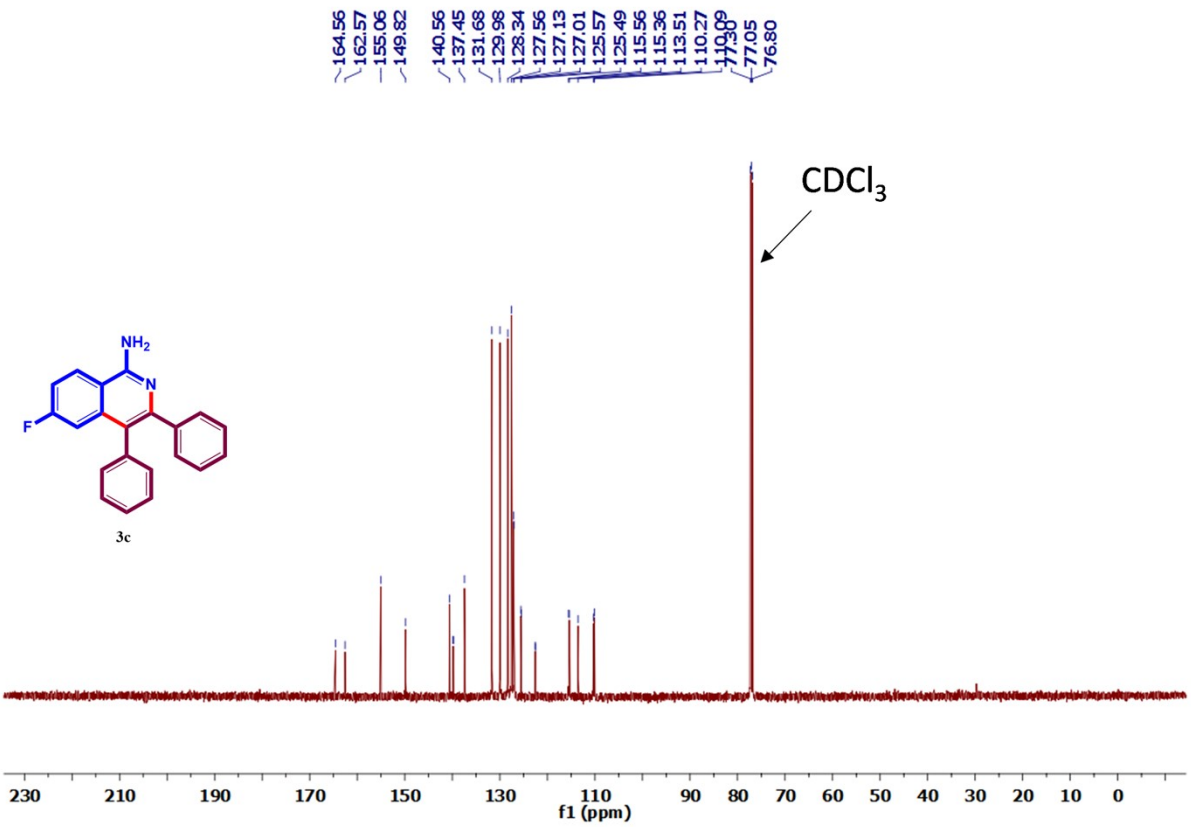

3b






**6-fluoro-3,4-diphenylisoquinolin-1-amine (3c)**[2a]

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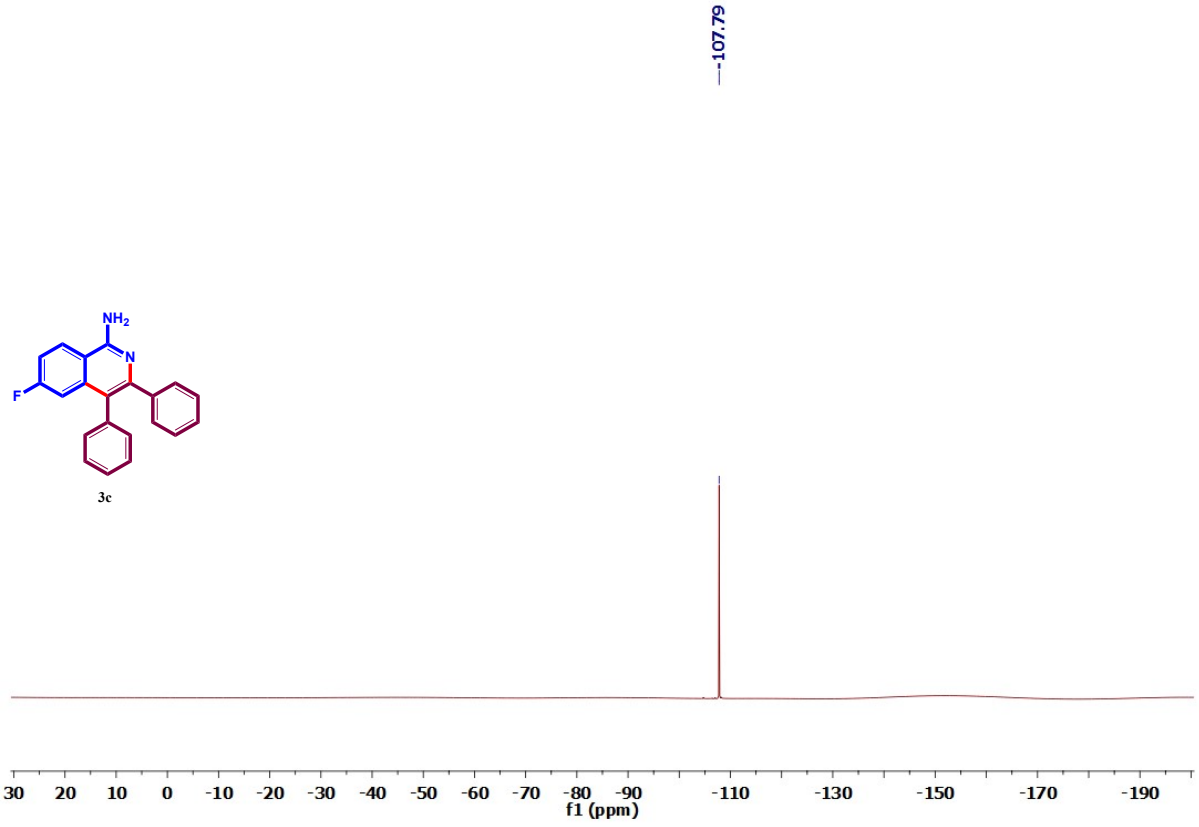
f1 (ppm)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-90
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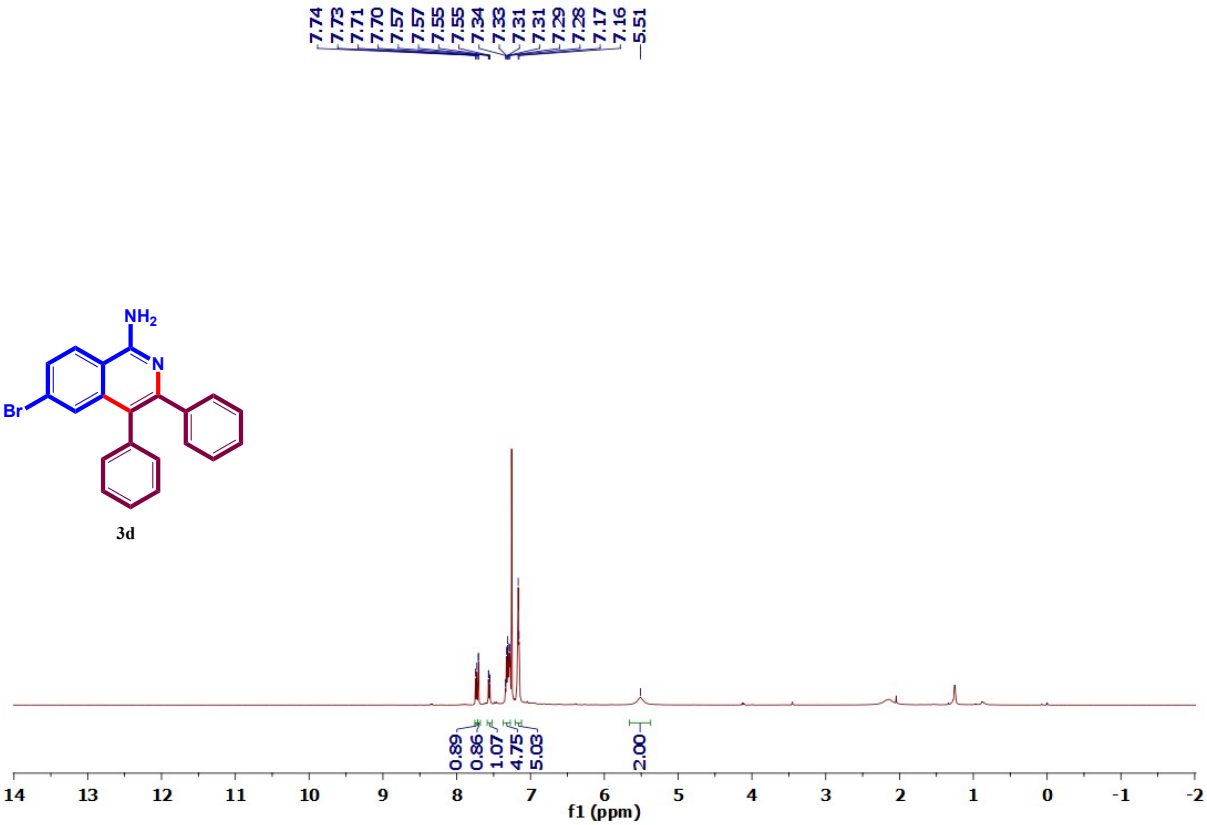
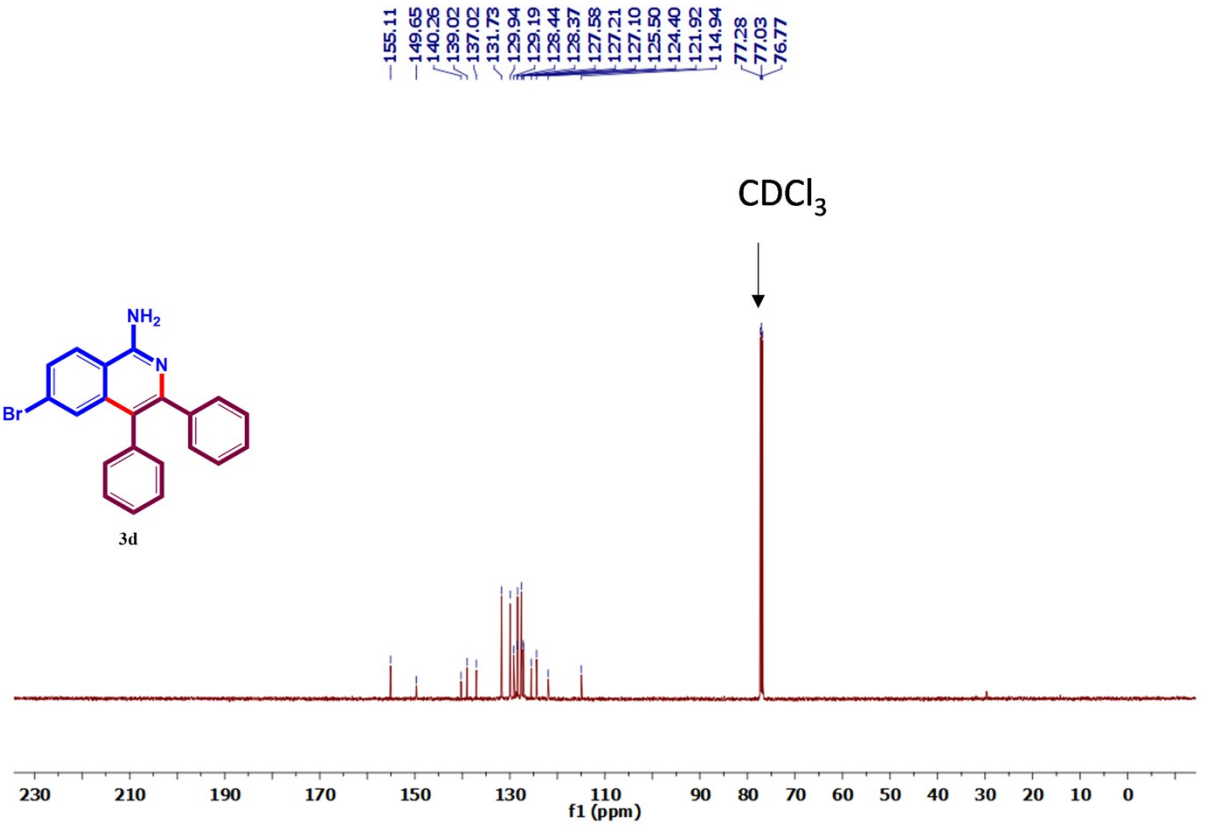
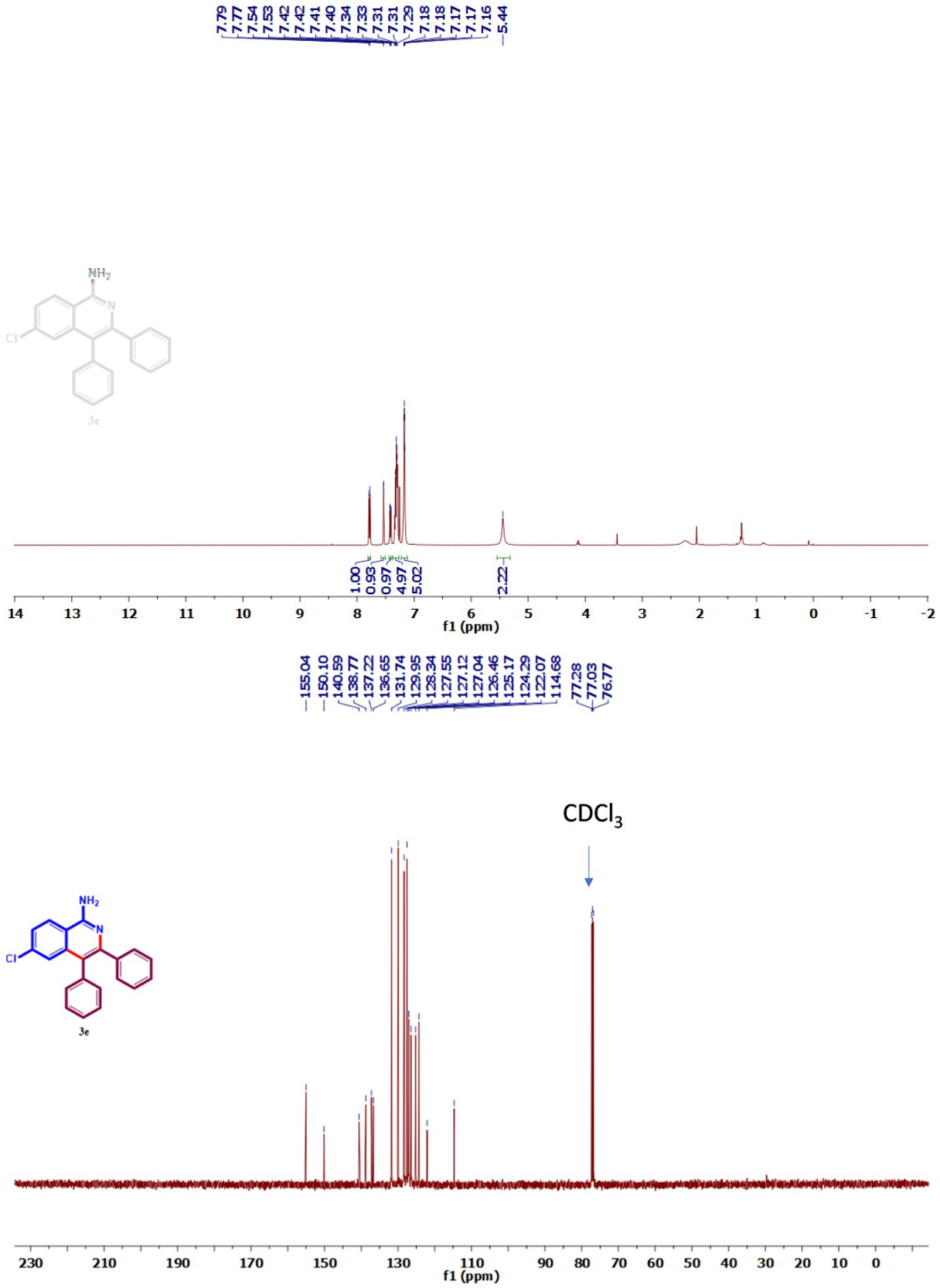
-190
f1 (ppm)

**6-bromo-3,4-diphenylisoquinolin-1-amine (3d)**[2]

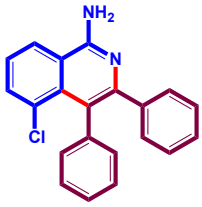


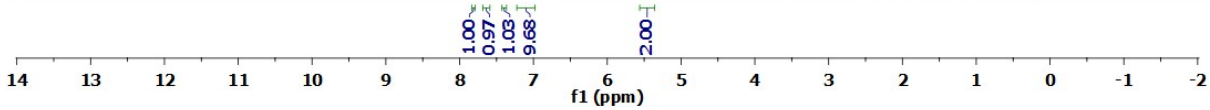
**6-chloro-3,4-diphenylisoquinolin-1-amine (3e)**[2a]



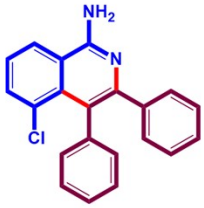
**5-chloro-3,4-diphenylisoquinolin-1-amine (3f)**[2b]


3f

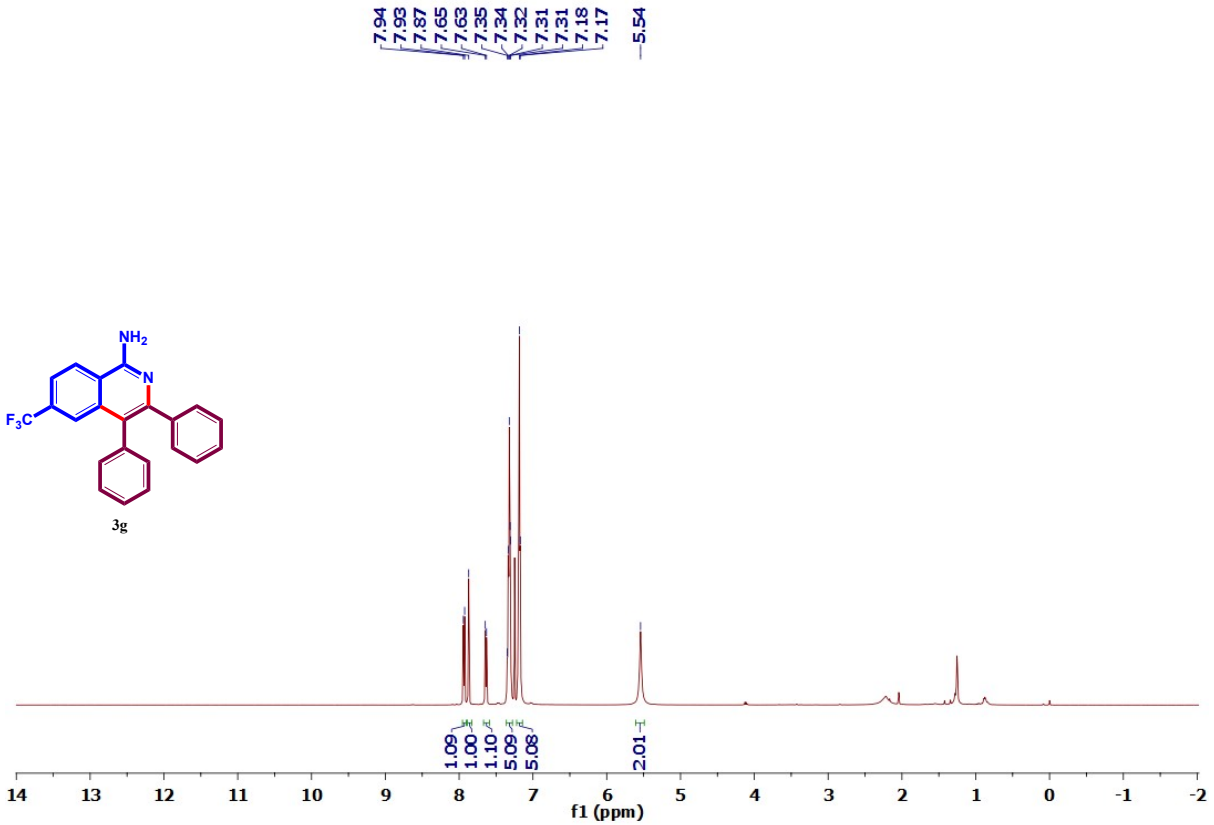


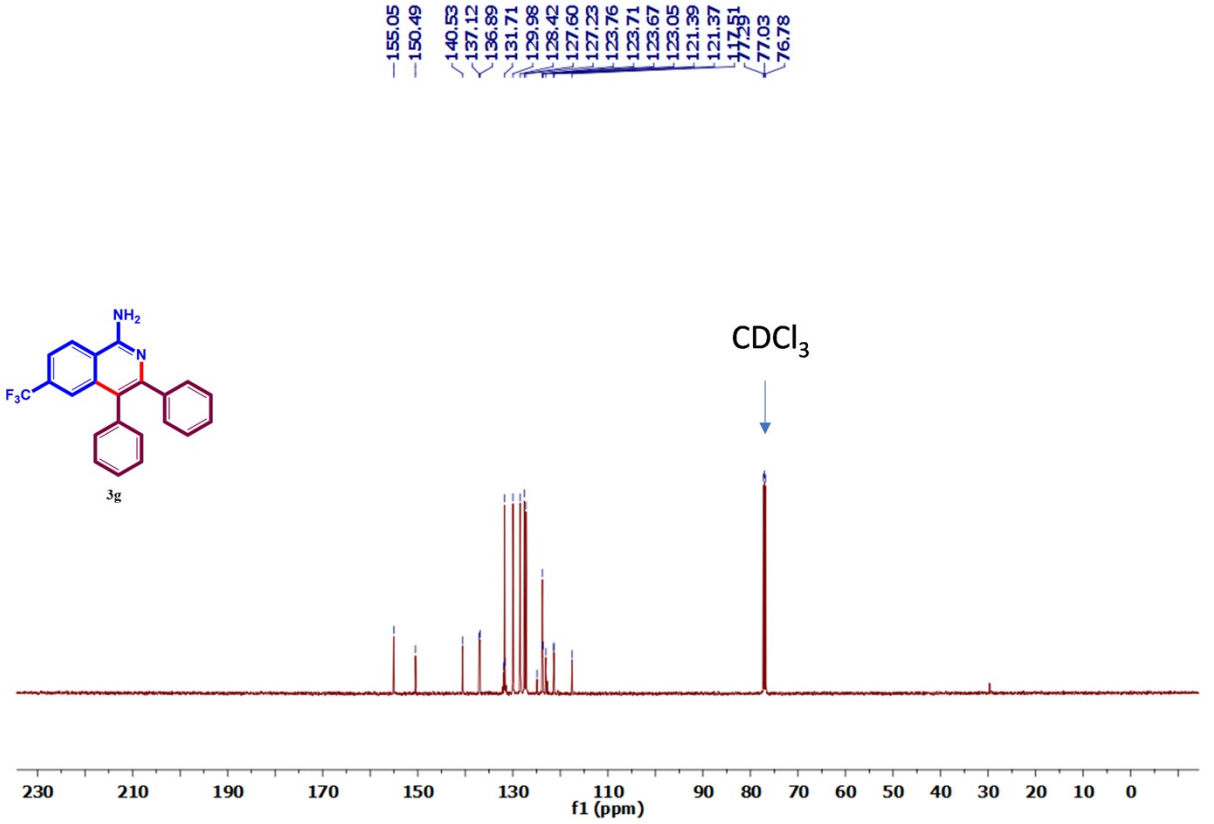


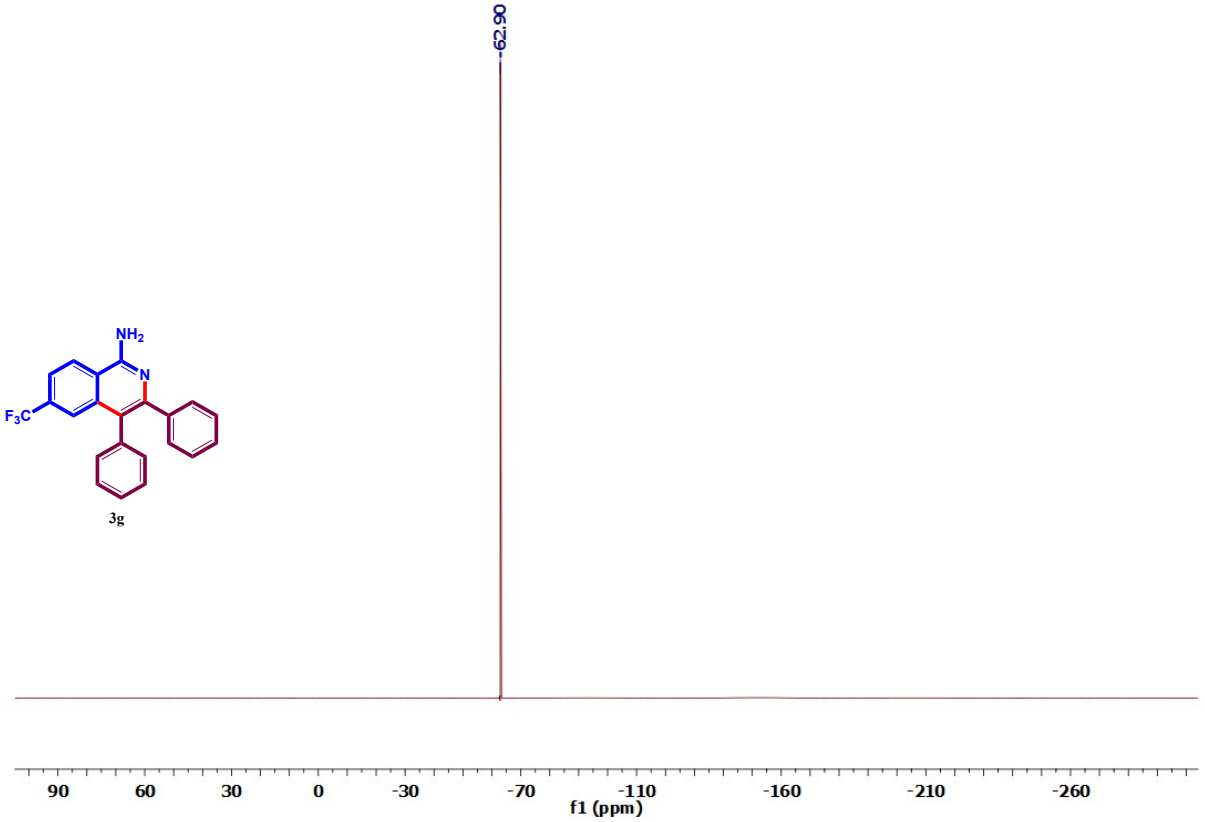



3f

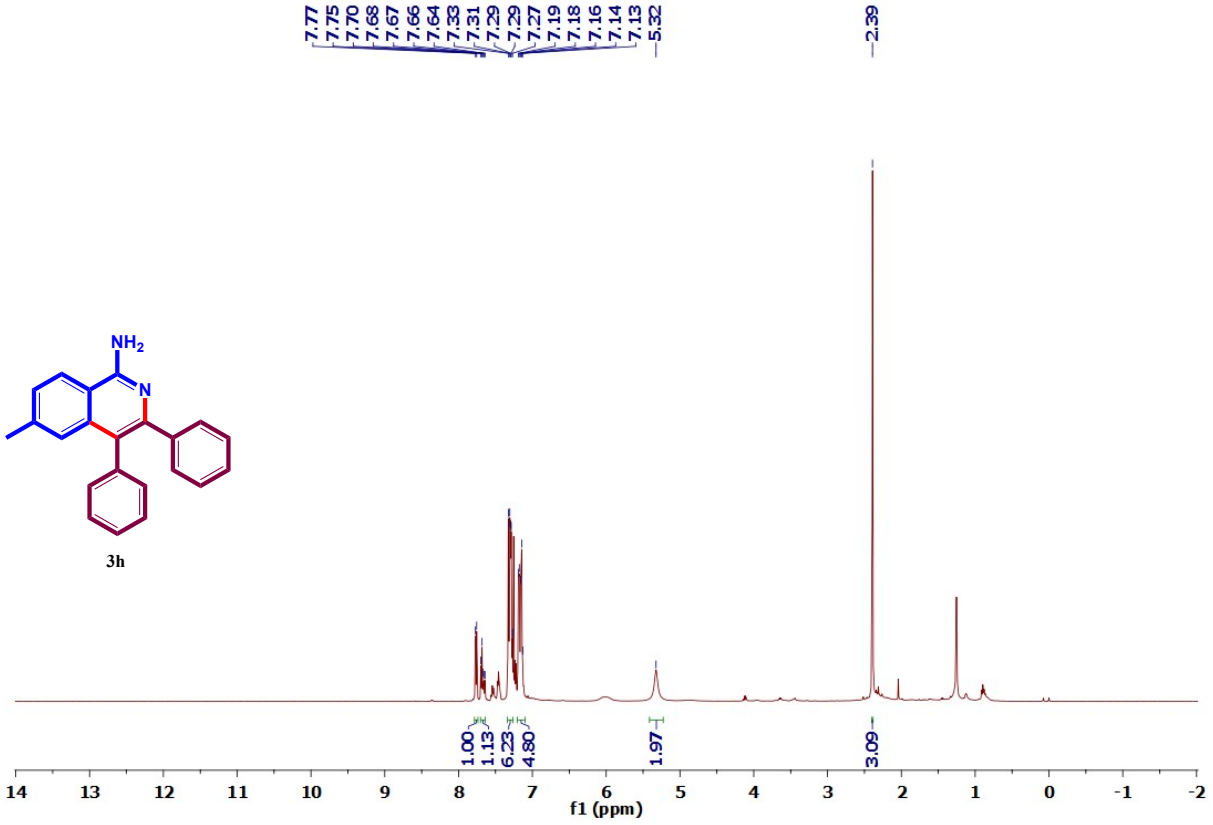
**3,4-diphenyl-6-(trifluoromethyl)isoquinolin-1-amine (3g)**[2a]

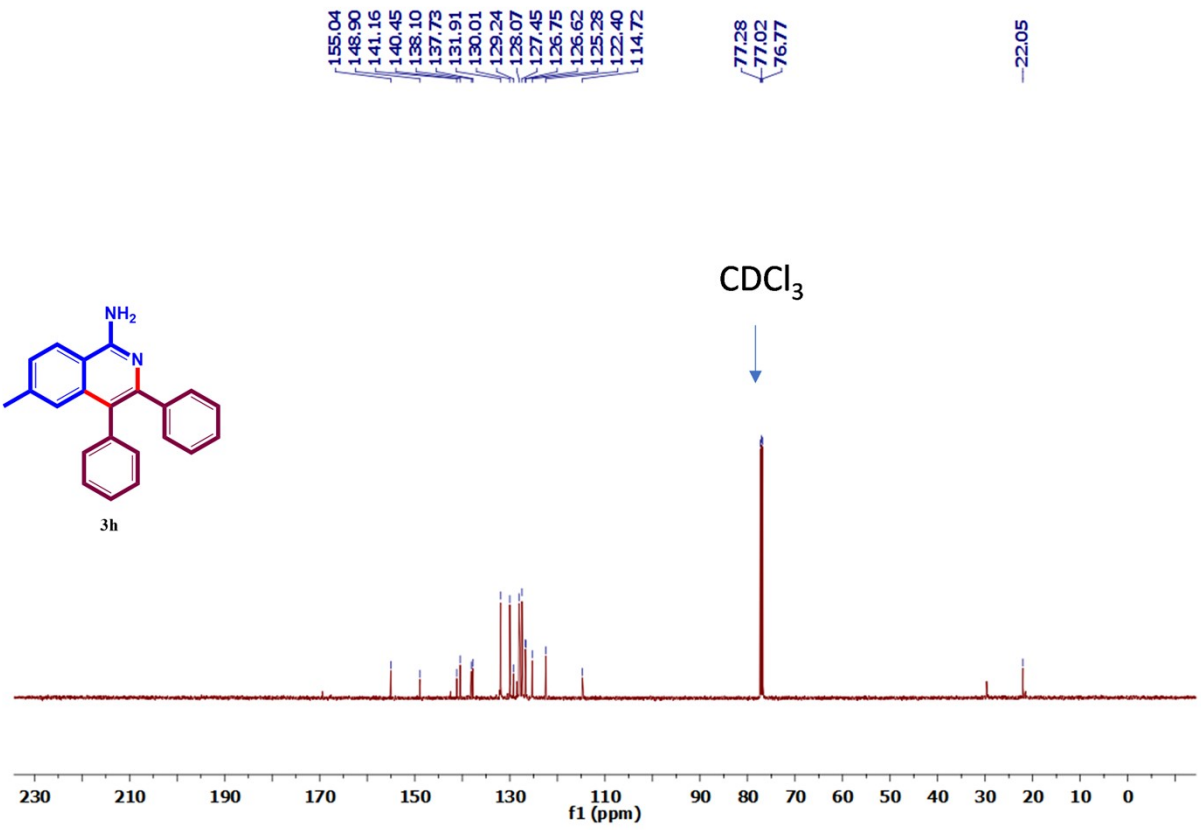


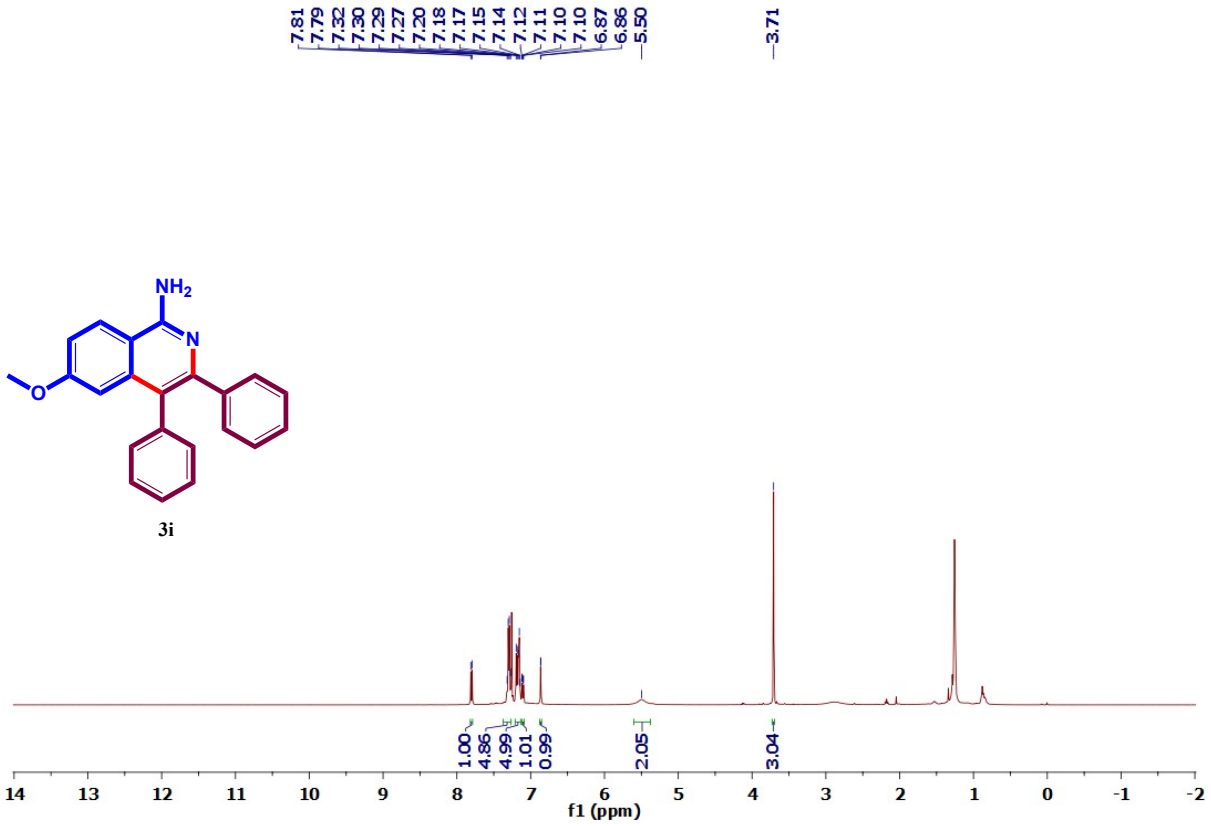


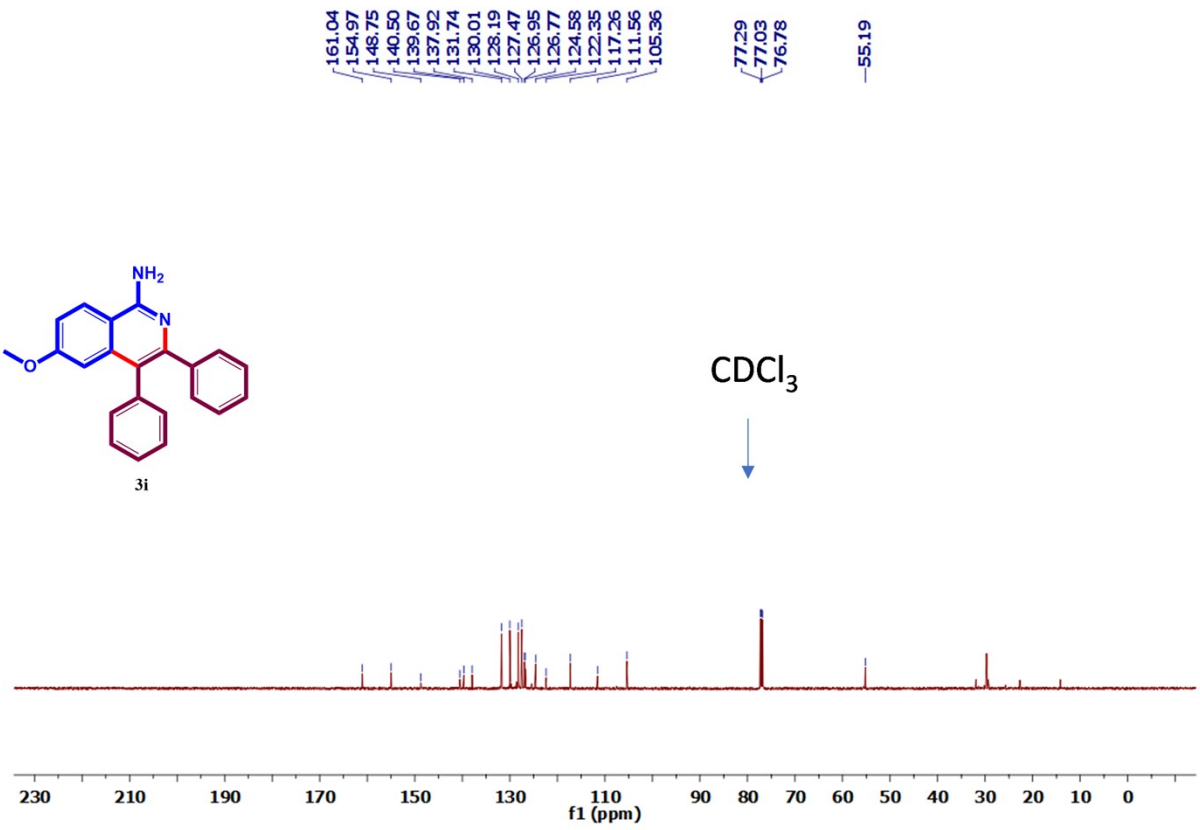

**6-methyl-3,4-diphenylisoquinolin-1-amine (3h)**[2b]



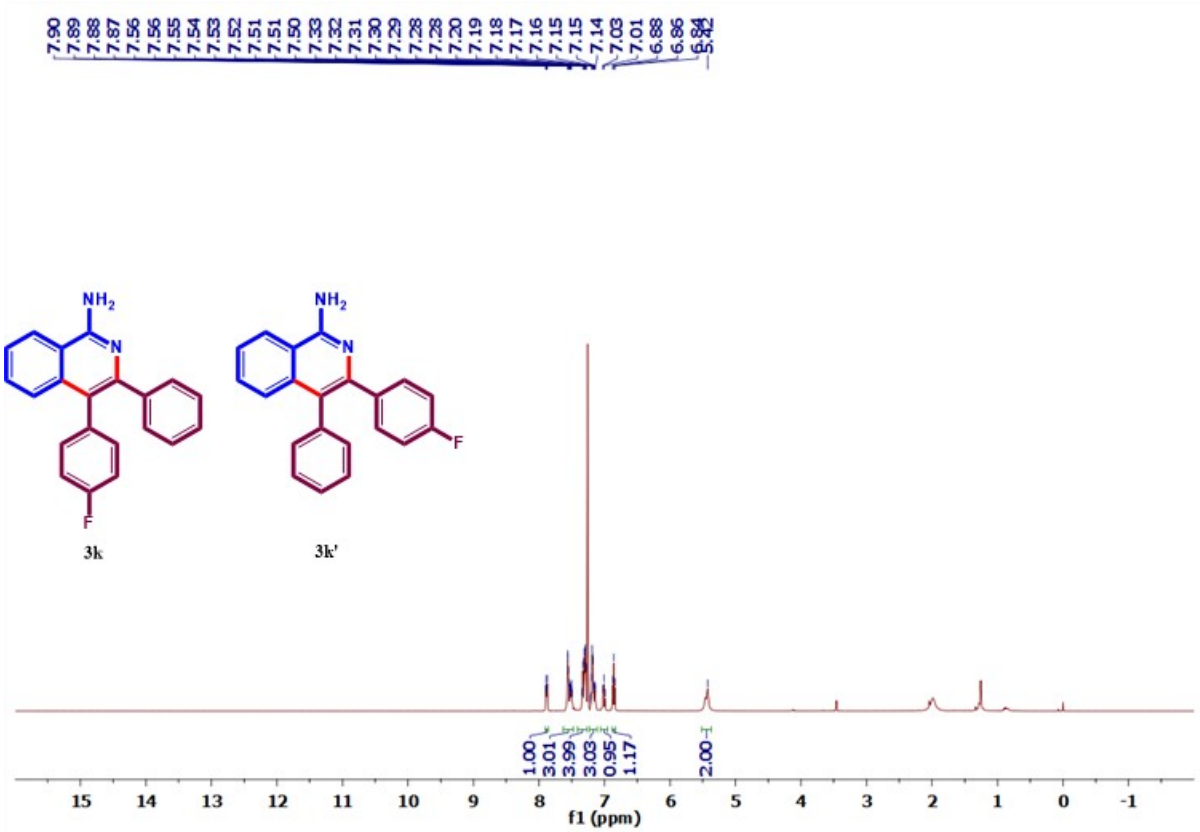


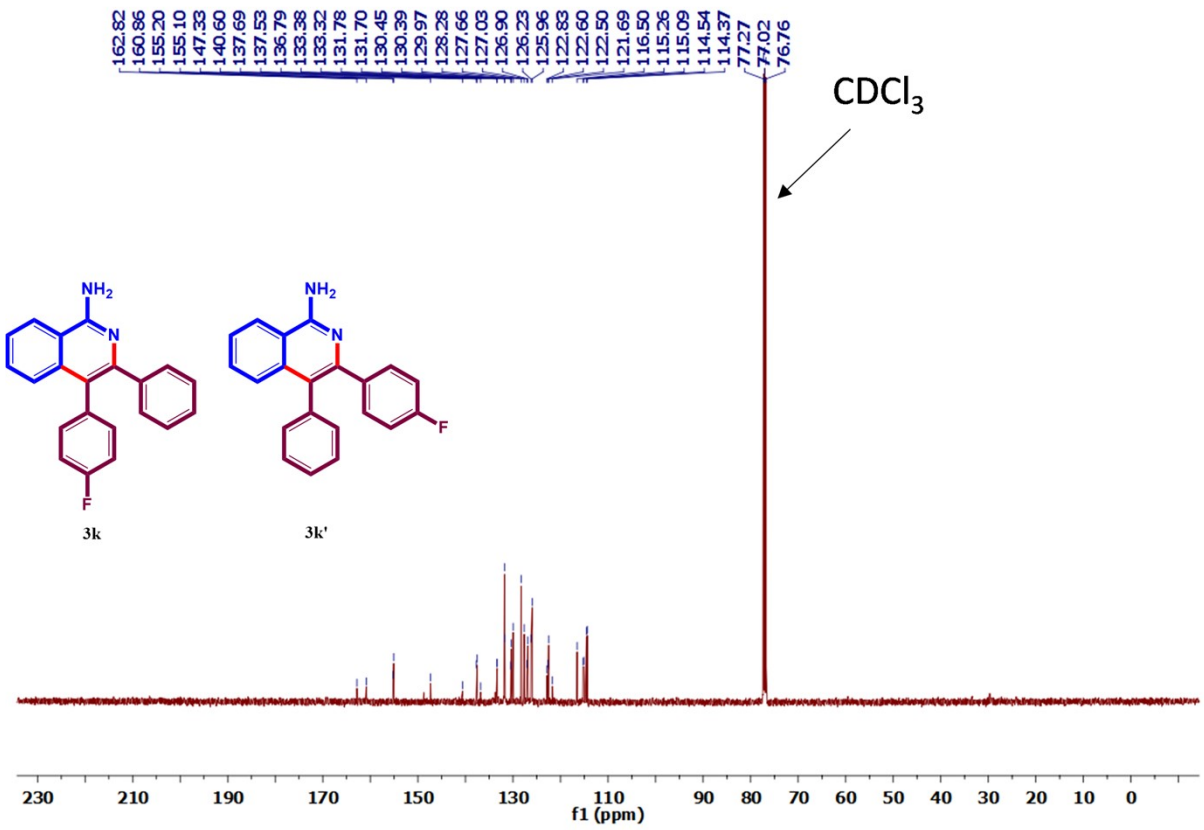

**6-methoxy-3,4-diphenylisoquinolin-1-amine (3i)**[2b]

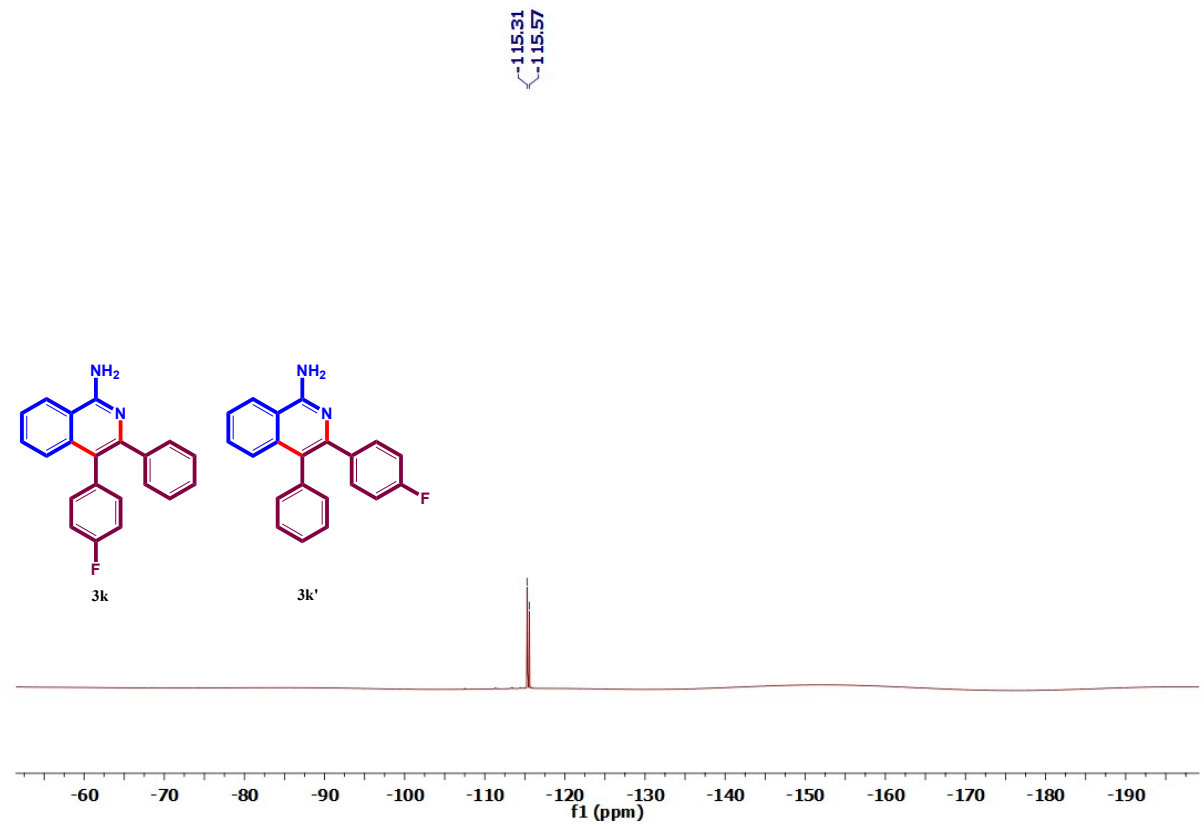




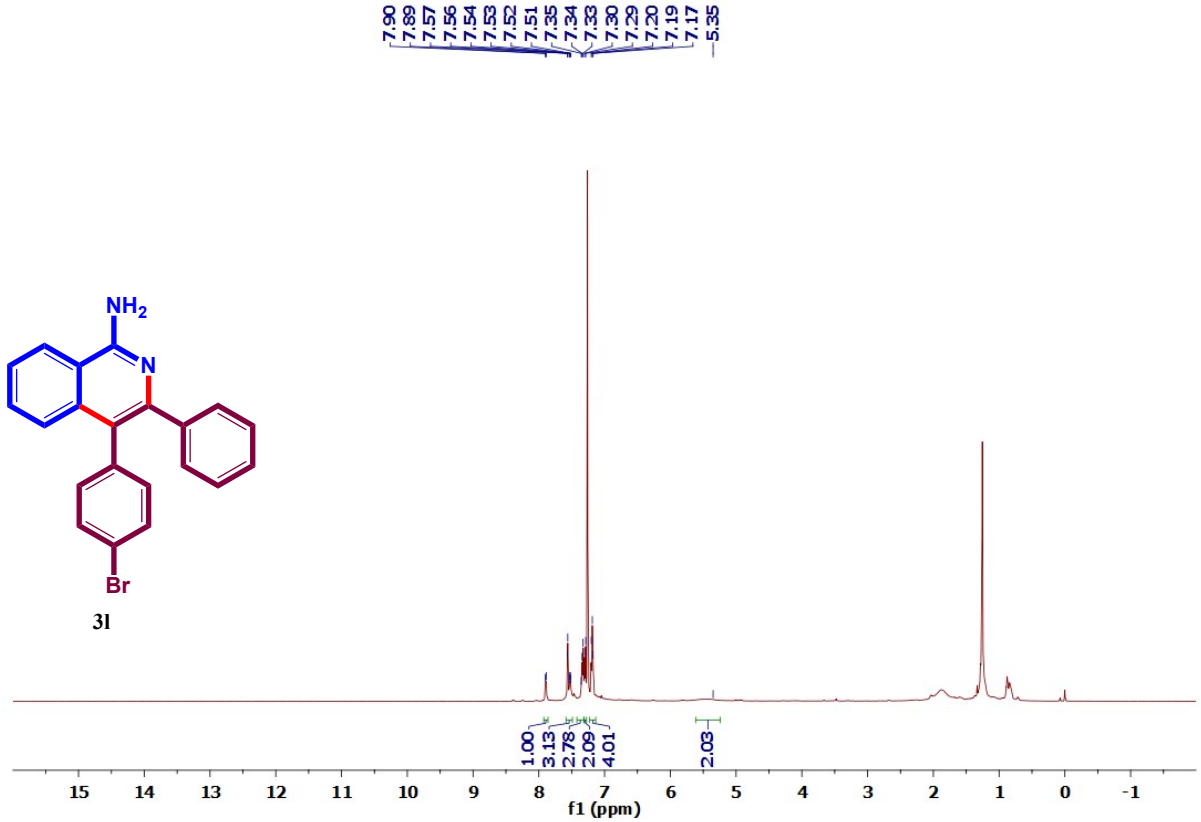

**4-(4-fluorophenyl)-3-phenylisoquinolin-1-amine (3k)** [2c, 2d]
**3-(4-fluorophenyl)-4-phenylisoquinolin-1-amine (3k')**

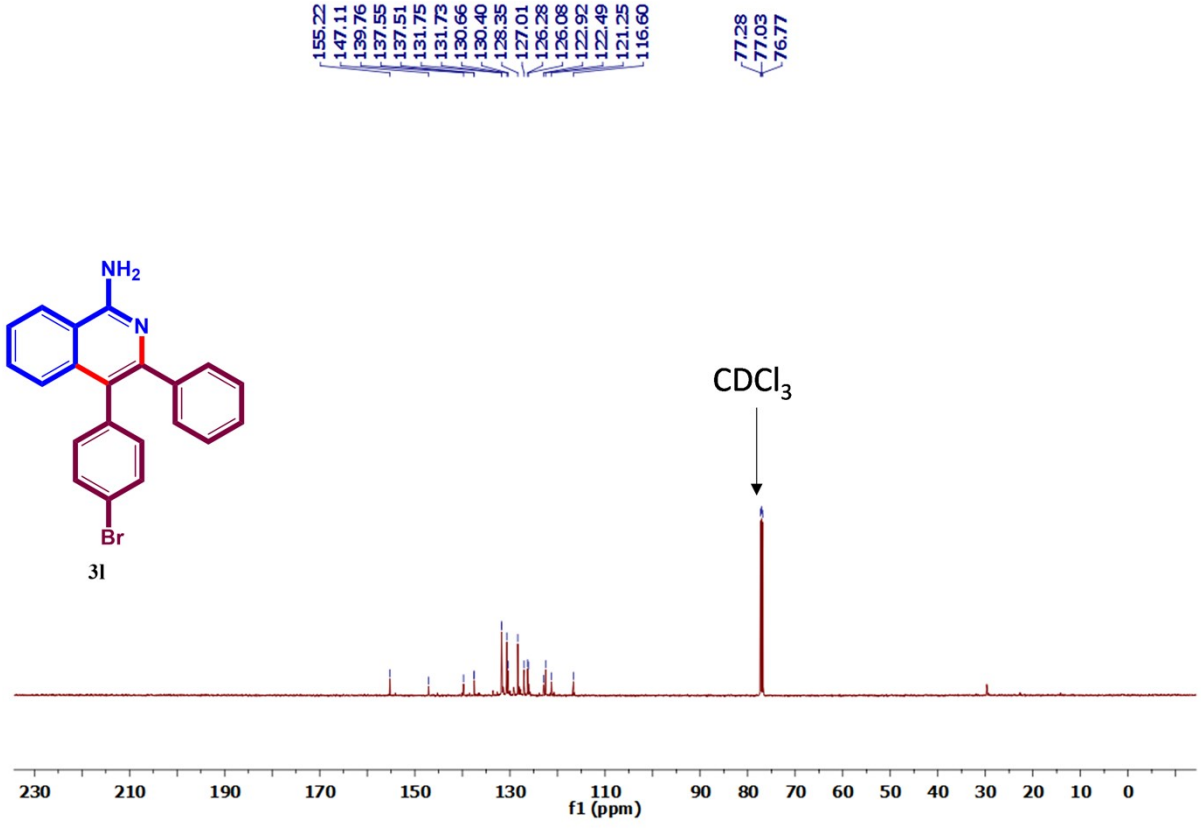



162.82
160.86
155.20
155.10
147.33
140.60
137.69
137.53
136.79
133.38
133.32
131.78
131.70
130.45
130.39
129.97
128.28
127.66
127.03
126.90
126.23
125.96
122.83
122.60
122.50
121.69
116.50
115.26
115.09
114.54
114.37
77.27
77.02
76.76
CDCl3
NH2
N
F
3k
3k'
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

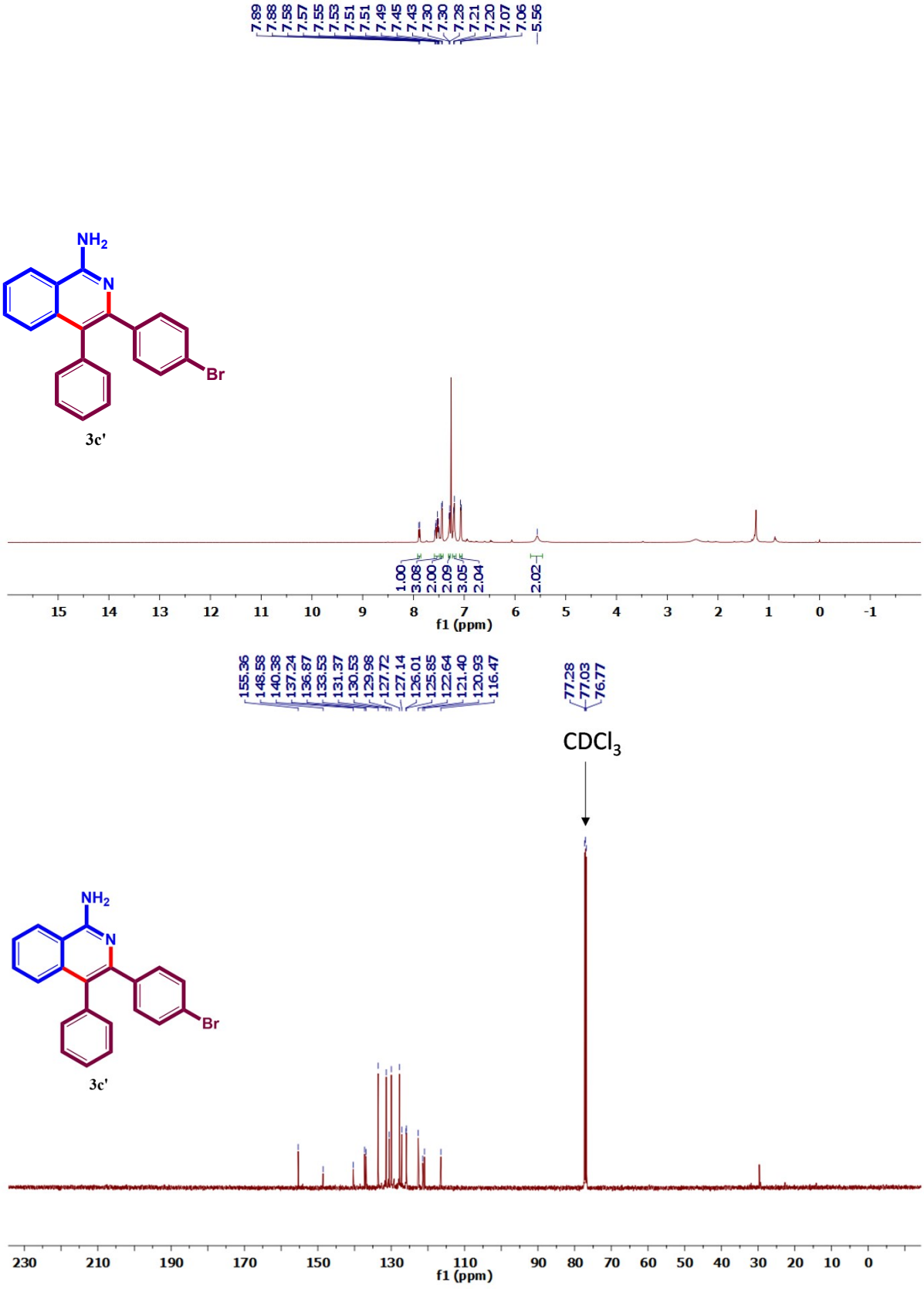

-115.31
-115.57
NH2
N
F
3k
3k'
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

**4-(4-bromophenyl)-3-phenylisoquinolin-1-amine (3l)**[2c, 2d]

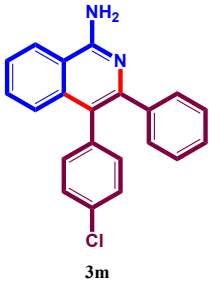


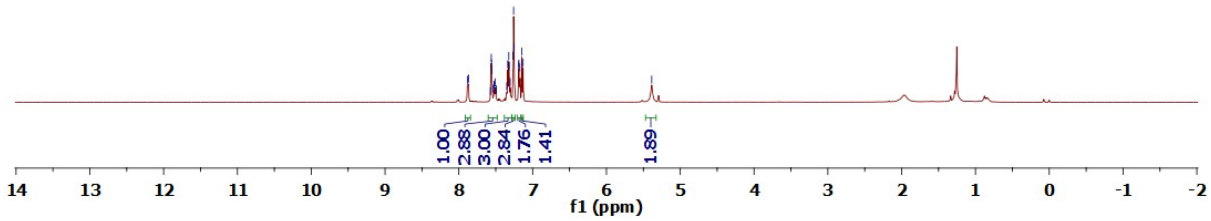
**3-(4-bromophenyl)-4-phenylisoquinolin-1-amine (3l')**



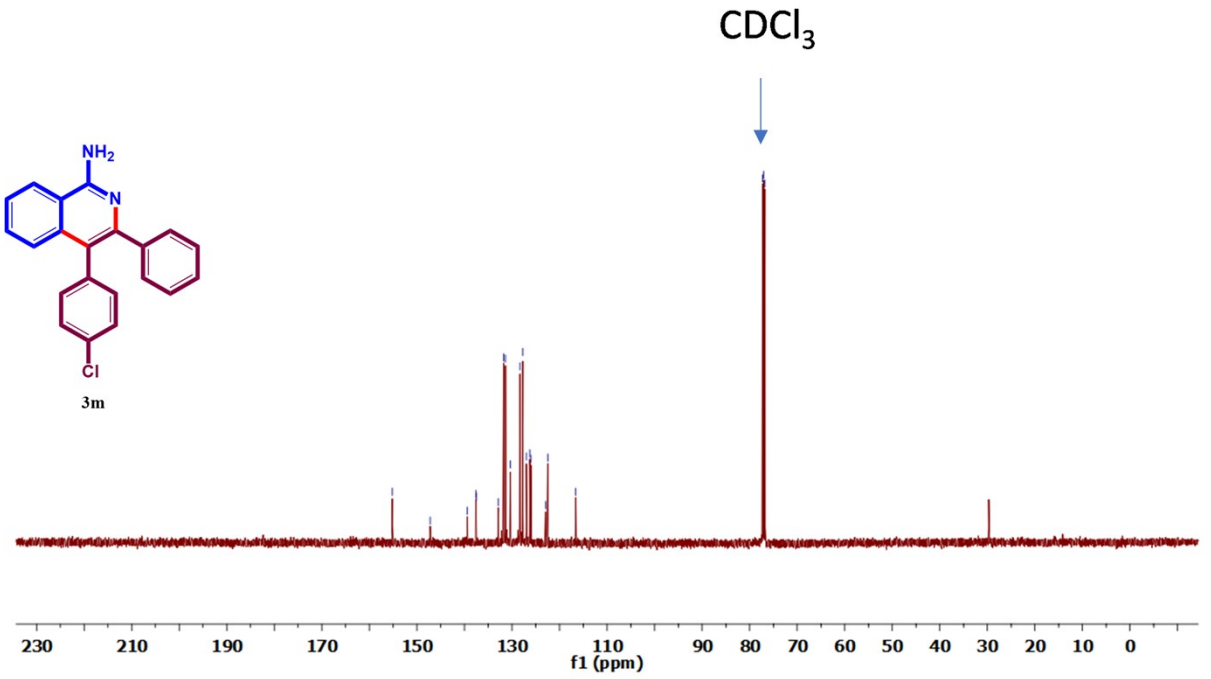
**4-(4-chlorophenyl)-3-phenylisoquinolin-1-amine (3m)** [2c, 2d]


3m

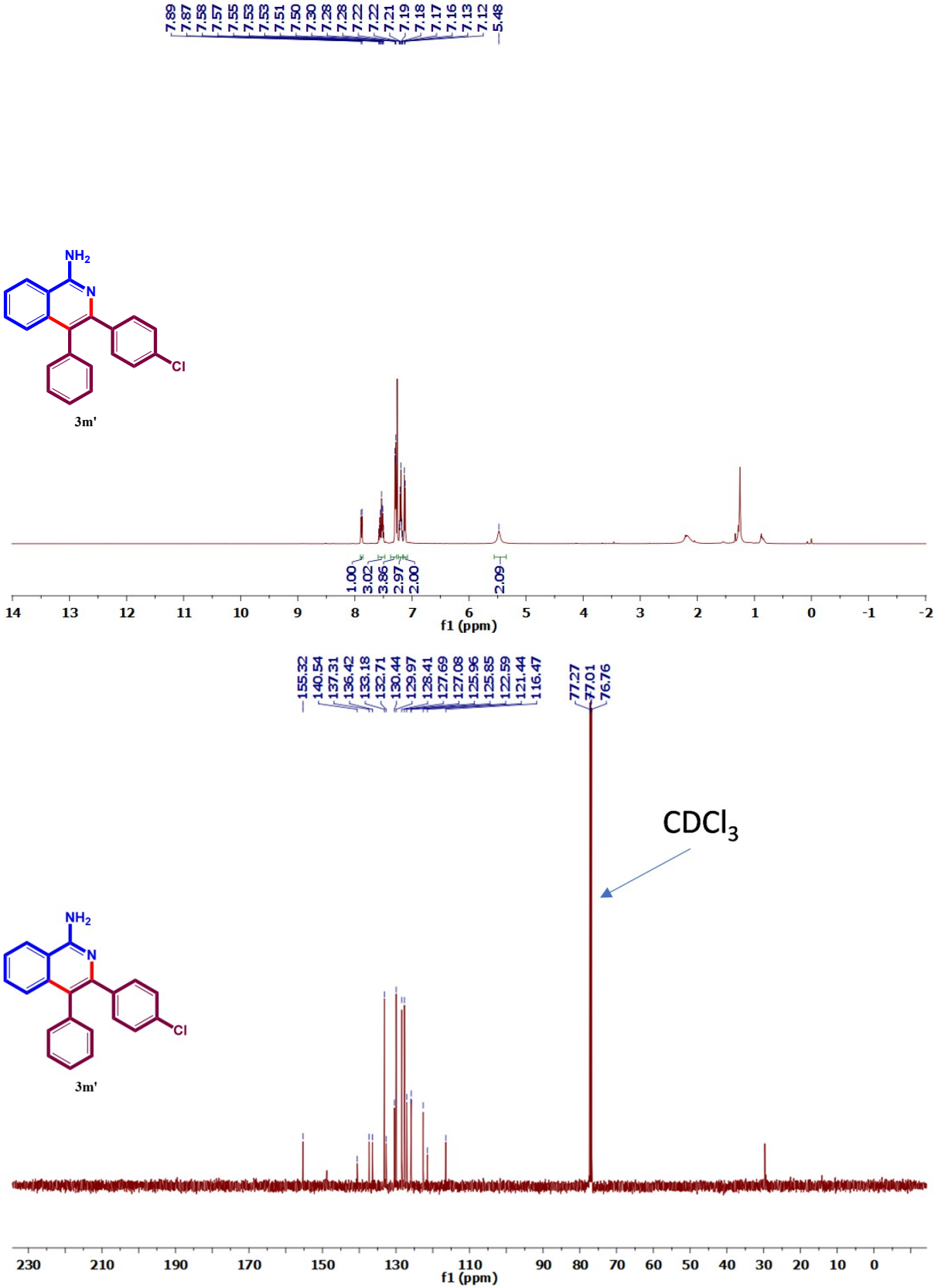




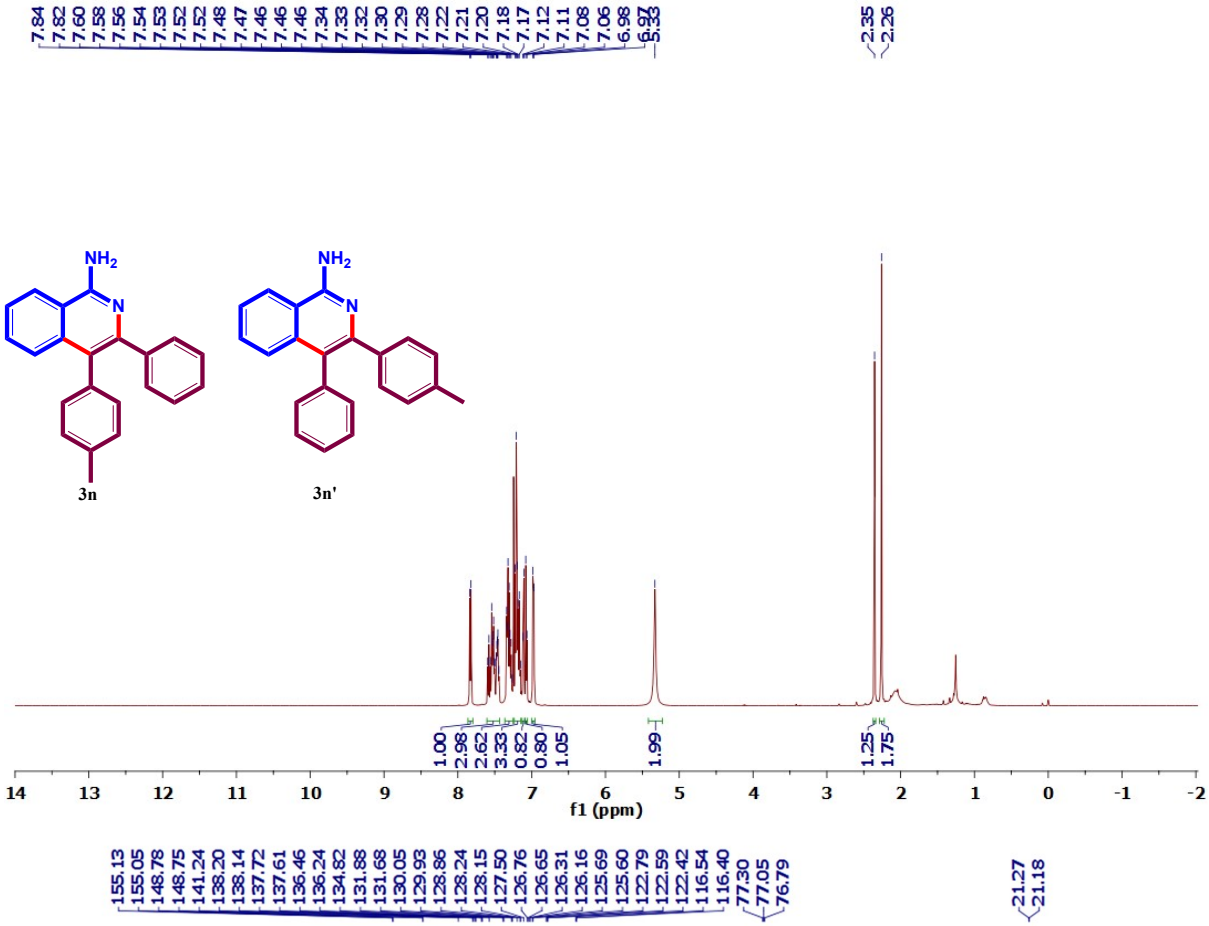


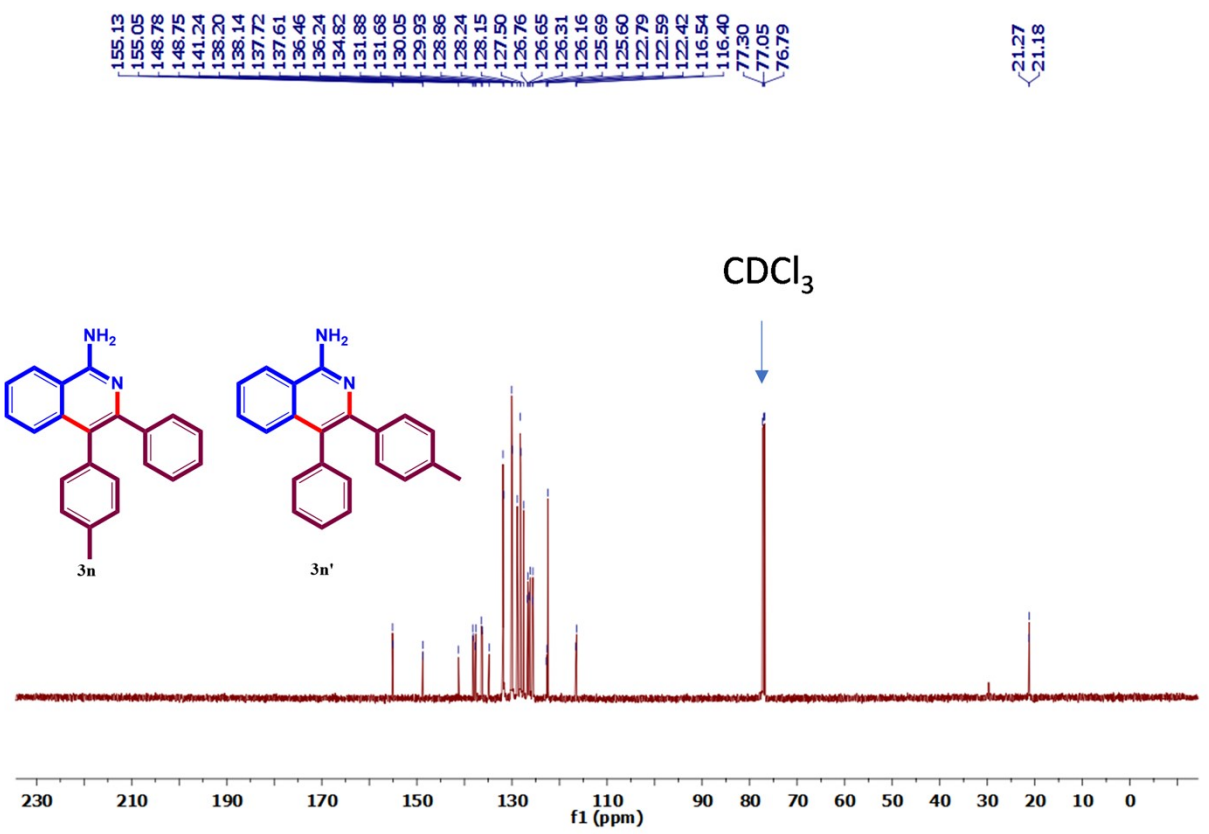

3m

**3-(4-chlorophenyl)-4-phenylisoquinolin-1-amine (3m')**

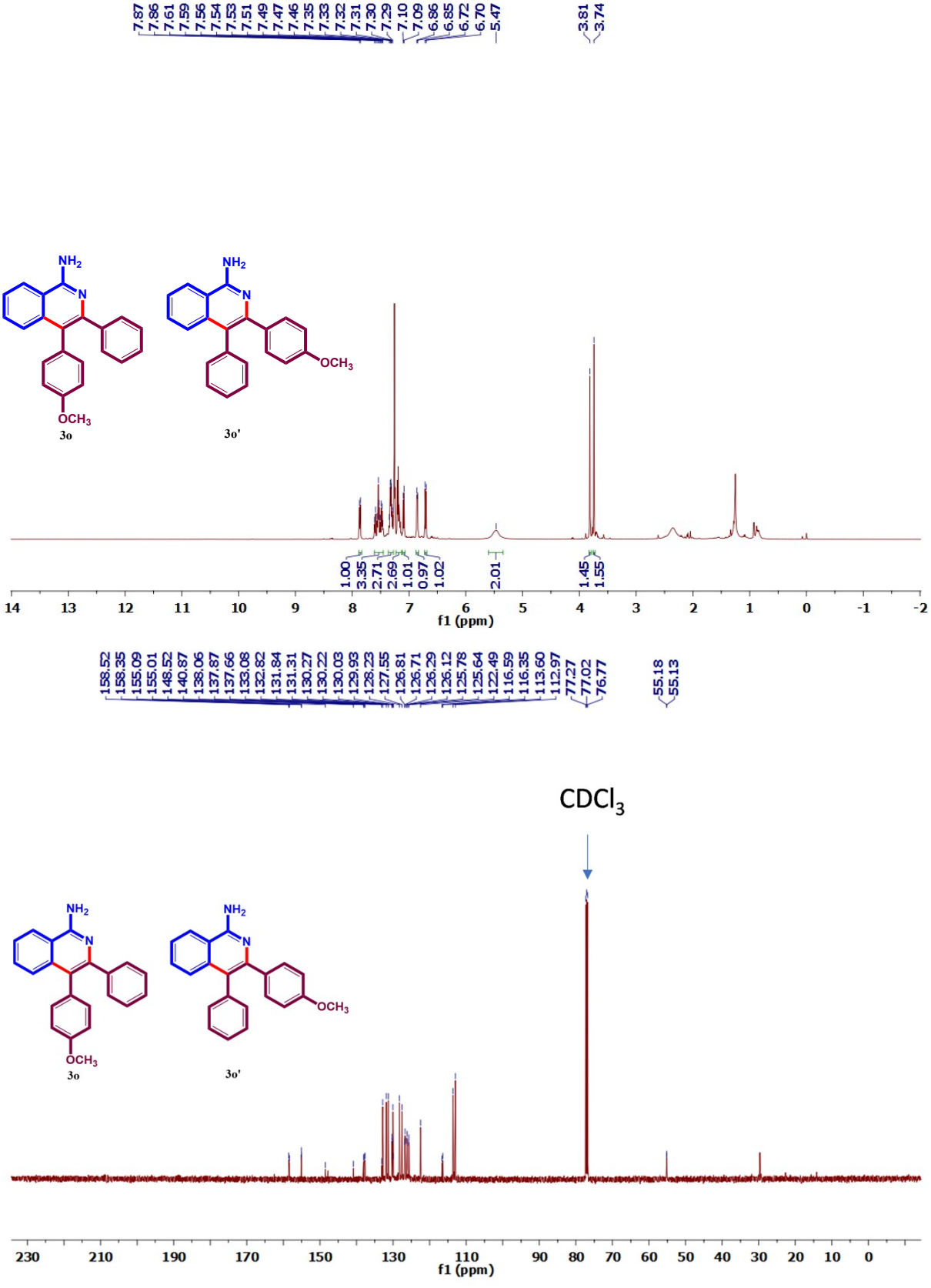


**3-phenyl-4-(p-tolyl)isoquinolin-1-amine (3n)** [2c, 2d]
**4-phenyl-3-(p-tolyl)isoquinolin-1-amine (3n')**

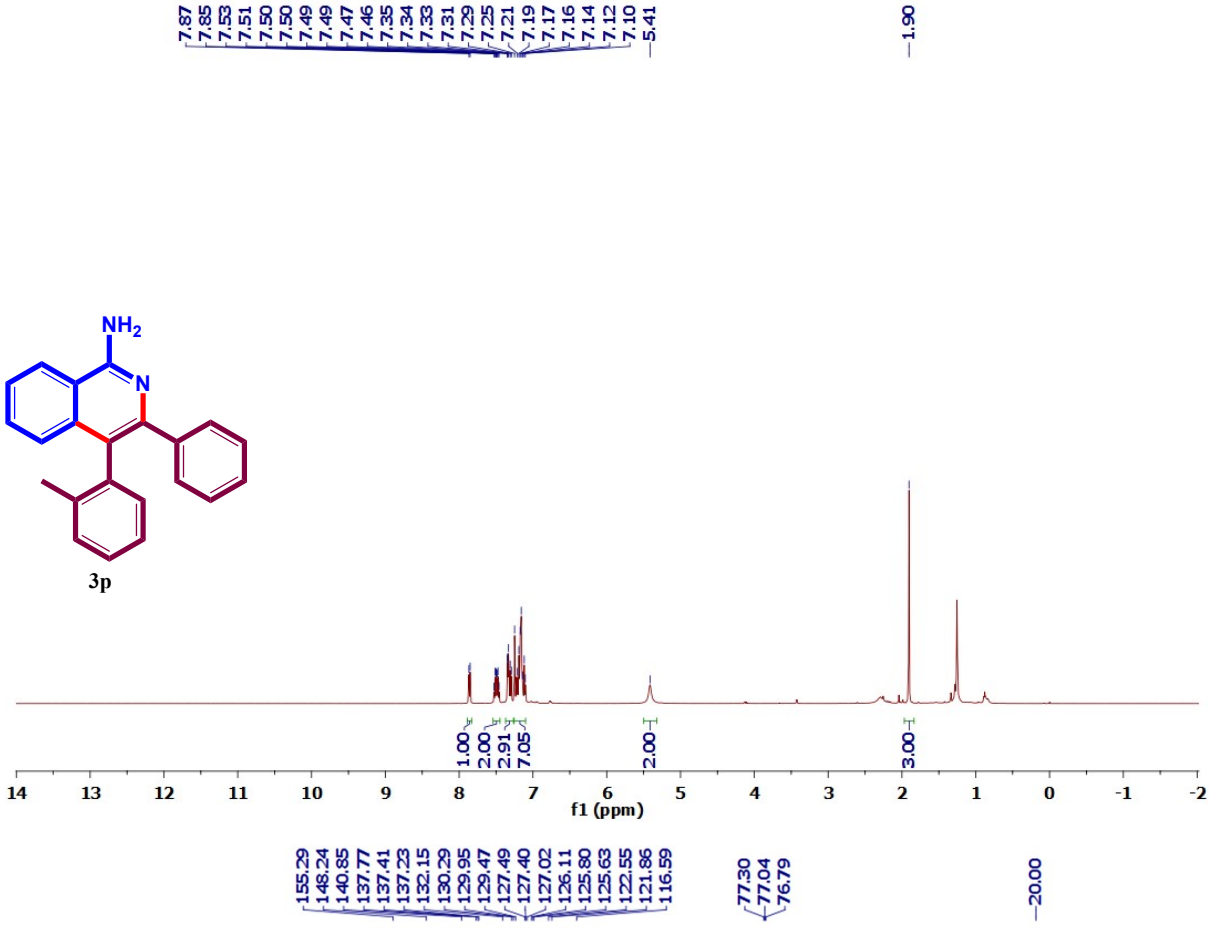


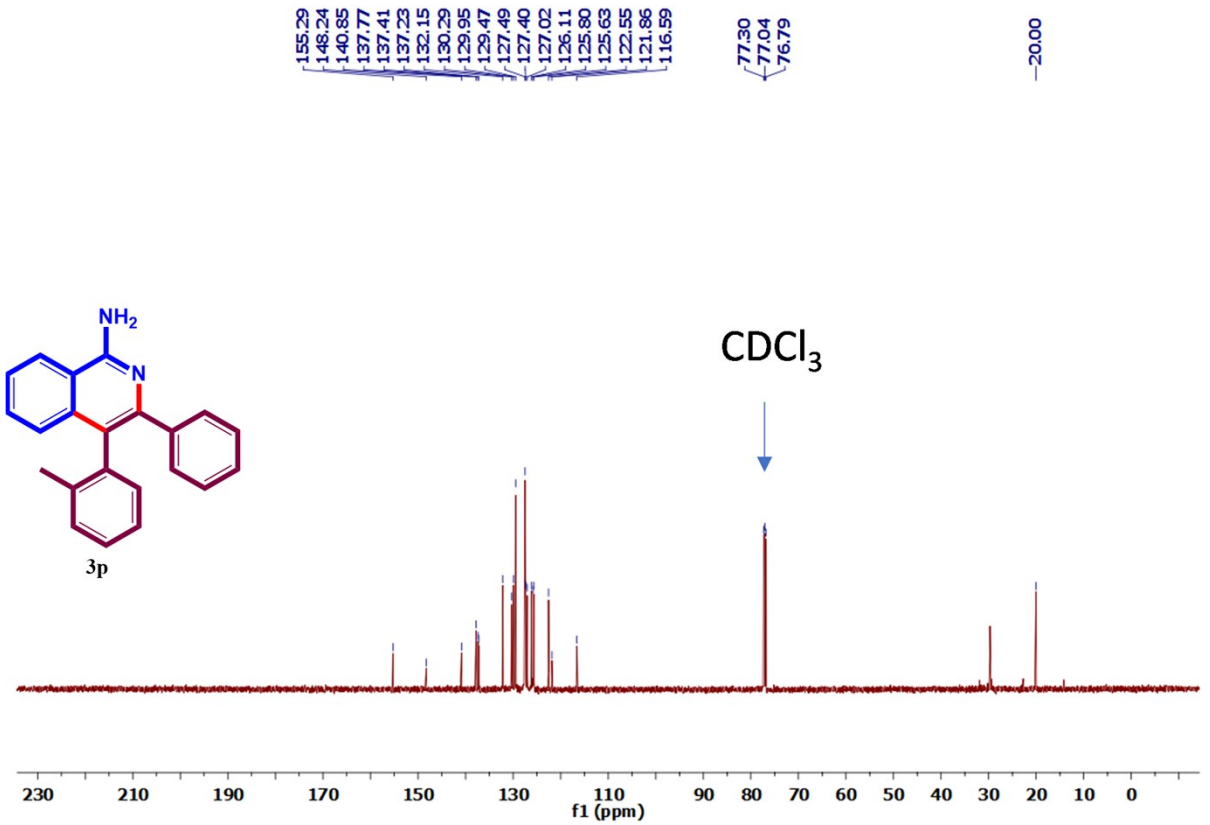



**4-(4-methoxyphenyl)-3-phenylisoquinolin-1-amine (3o)** [2c, 2d]
**3-(4-methoxyphenyl)-4-phenylisoquinolin-1-amine (3o')**

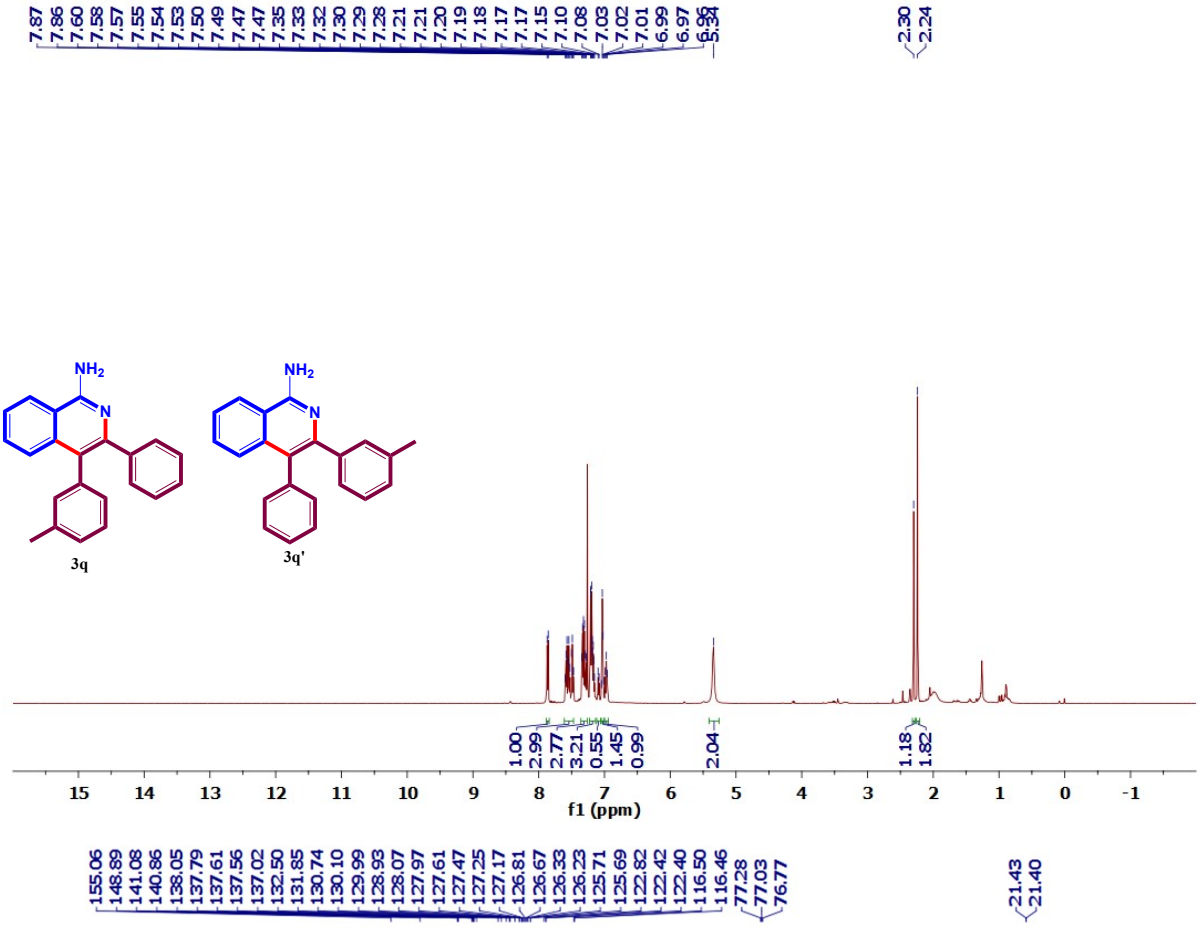


**3-phenyl-4-(o-tolyl)isoquinolin-1-amine (3p)** [2c, 2d]

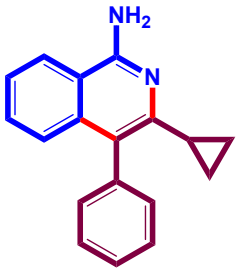


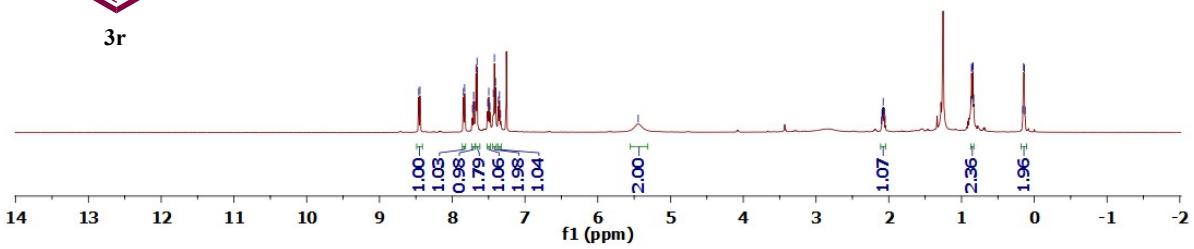
**3-phenyl-4-(m-tolyl)isoquinolin-1-amine (3q)** [2c]
**4-phenyl-3-(m-tolyl)isoquinolin-1-amine (3q')**



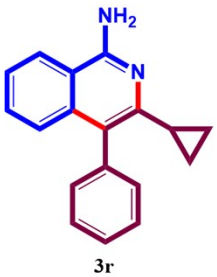
**3-cyclopropyl-4-phenylisoquinolin-1-amine (3r)**


3r

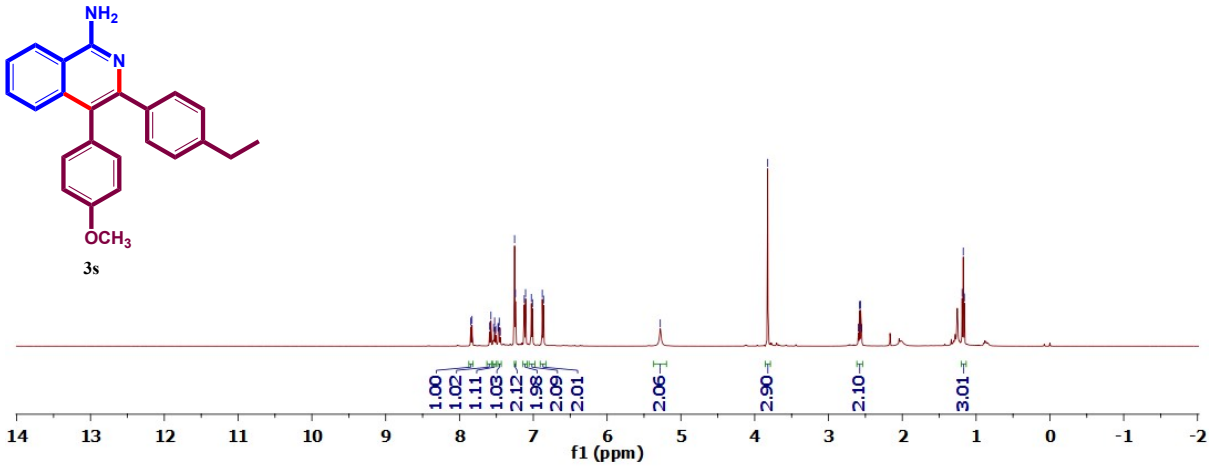




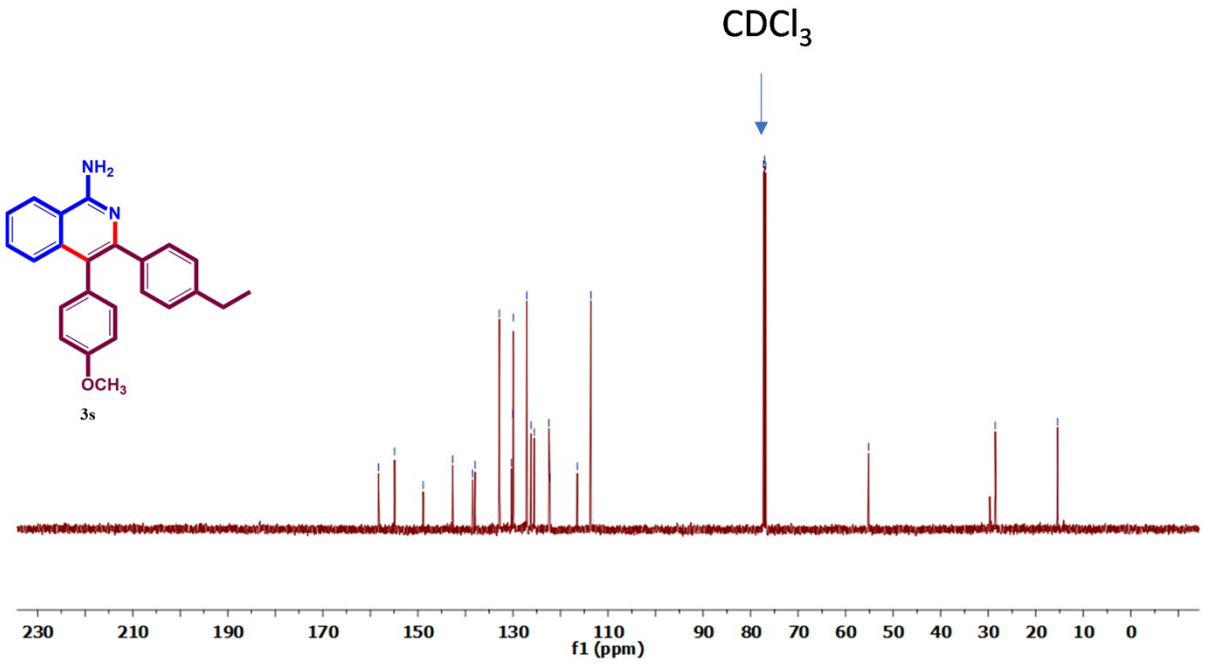



3r

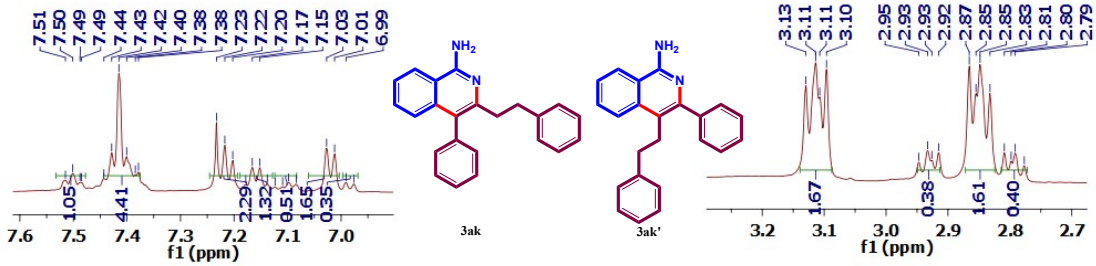
**3-(4-ethylphenyl)-4-(4-methoxyphenyl)isoquinolin-1-amine (3s)**

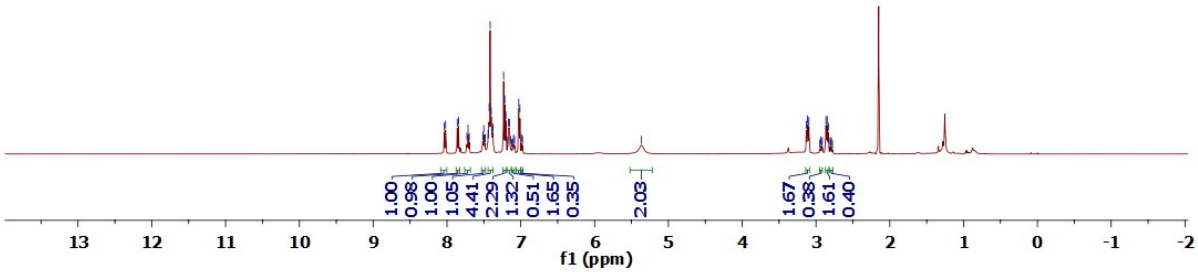



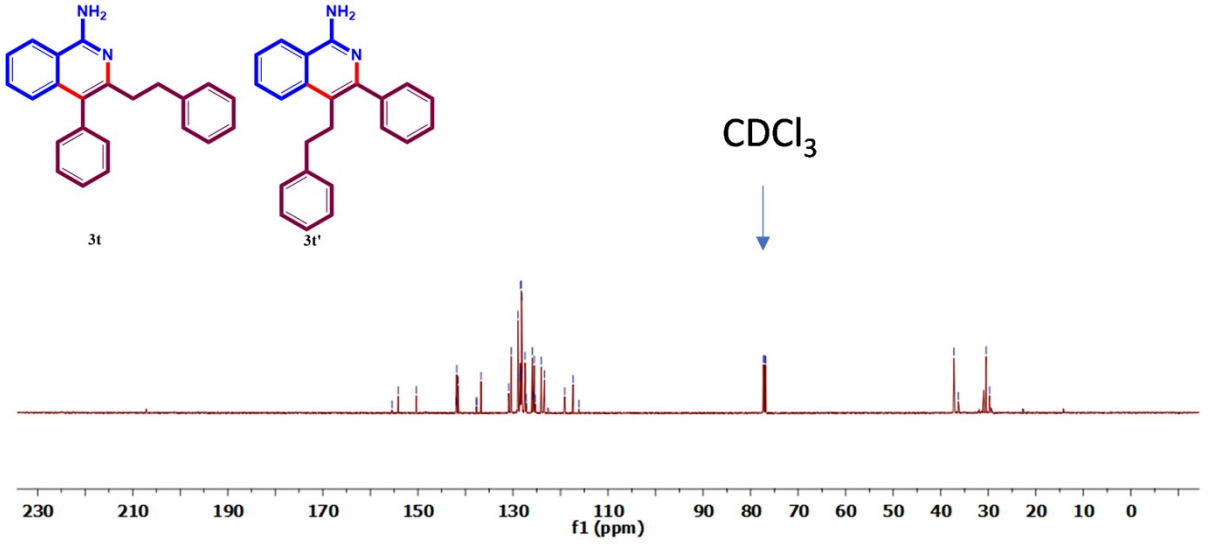




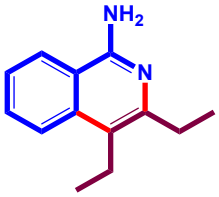
**3-phenethyl-4-phenylisoquinolin-1-amine (3t)**
**4-phenethyl-3-phenylisoquinolin-1-amine (3t')**



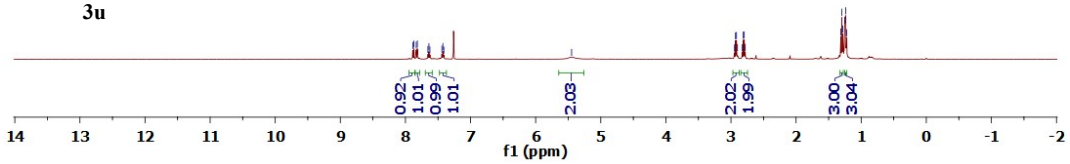



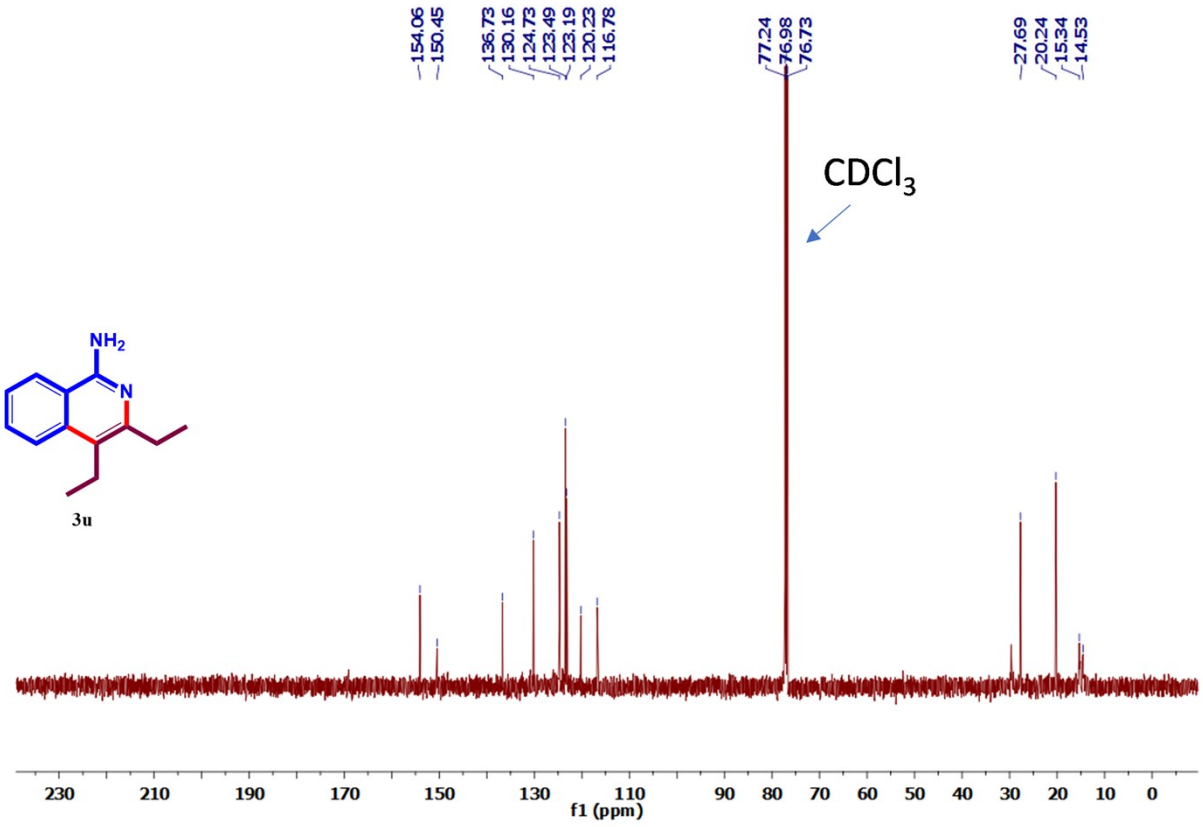



**3,4-diethylisoquinolin-1-amine (3u)** [2b]

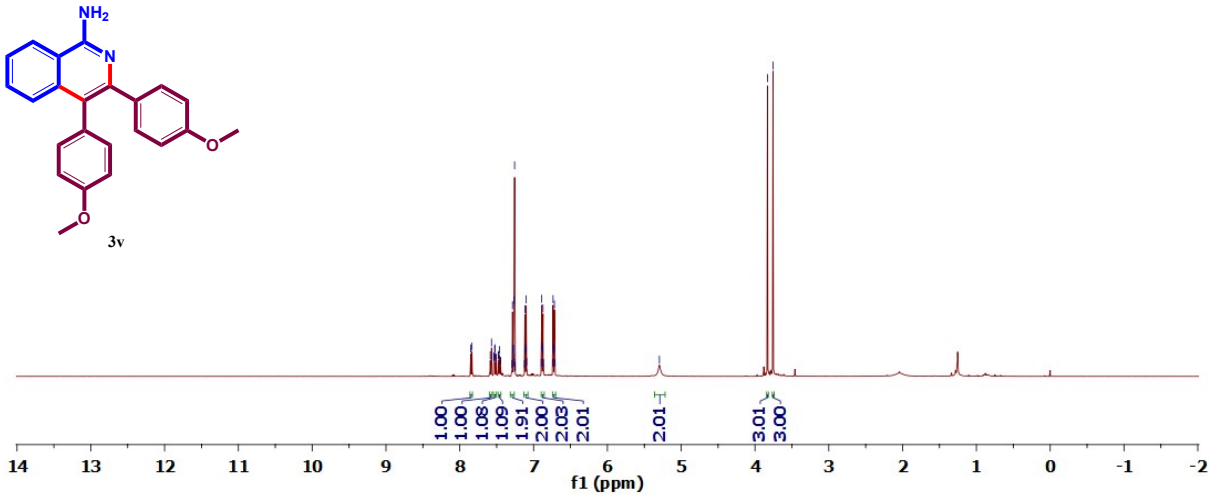

3u



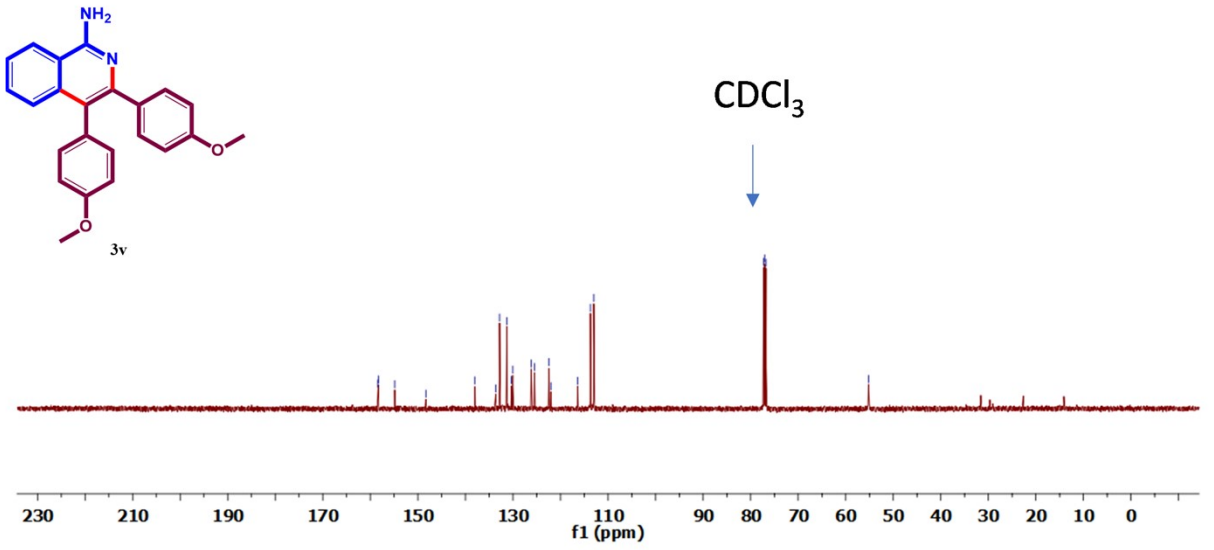




3u

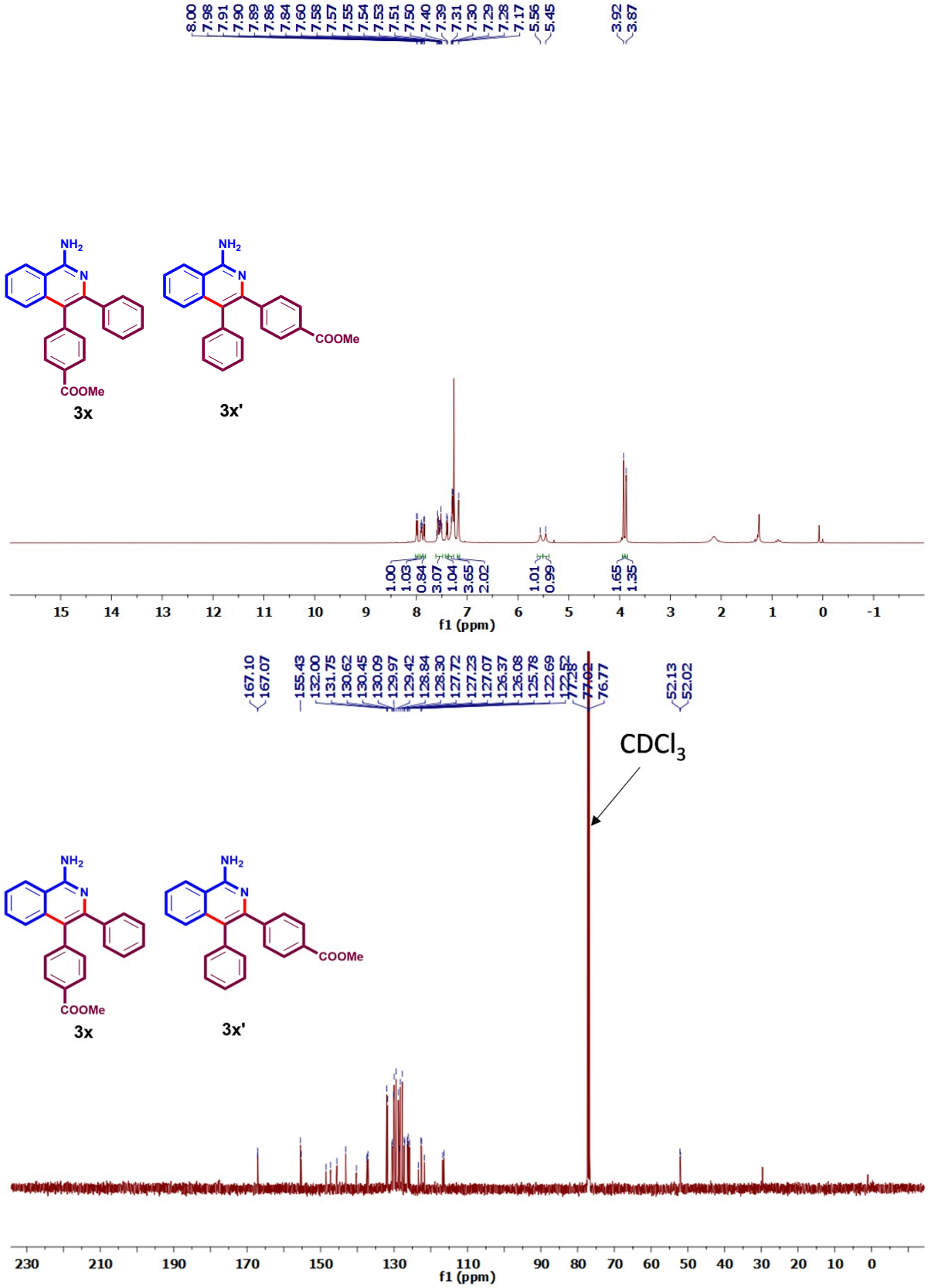
**3,4-bis(4-methoxyphenyl)isoquinolin-1-amine (3v)** [2b]

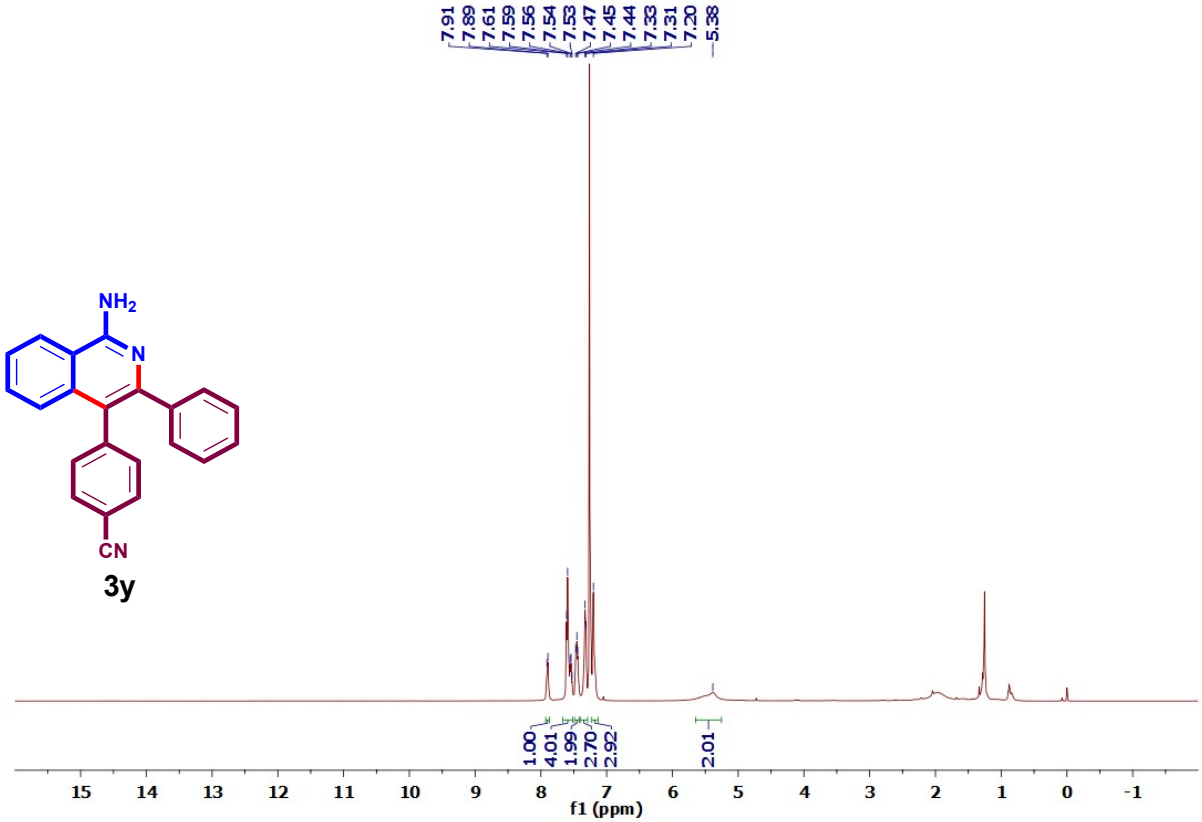


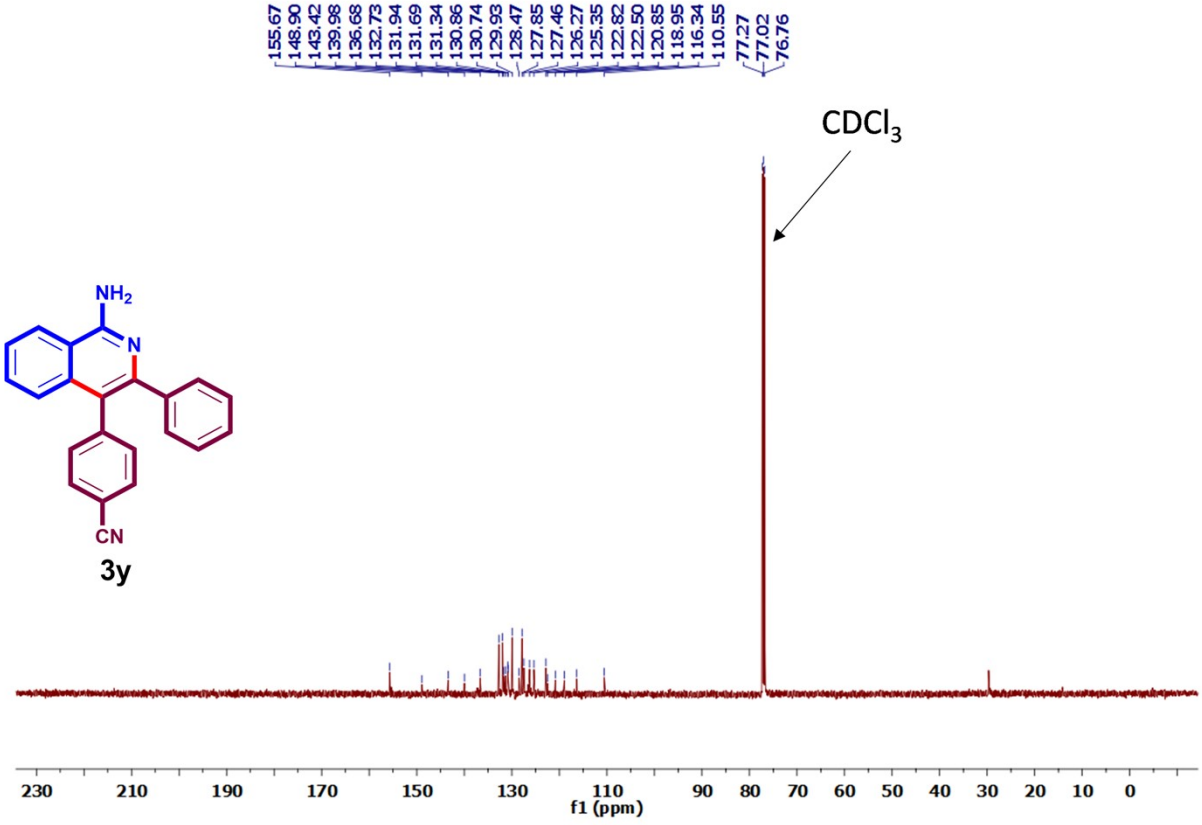


**Methyl-4-(1-amino-3-phenylisoquinolin-4-yl)benzoate(3x)**
**Methyl-4-(1-amino-4-phenylisoquinolin-3-yl)benzoate(3x')**



**4-(1-amino-3-phenylisoquinolin-4-yl)benzonitrile(3y)**

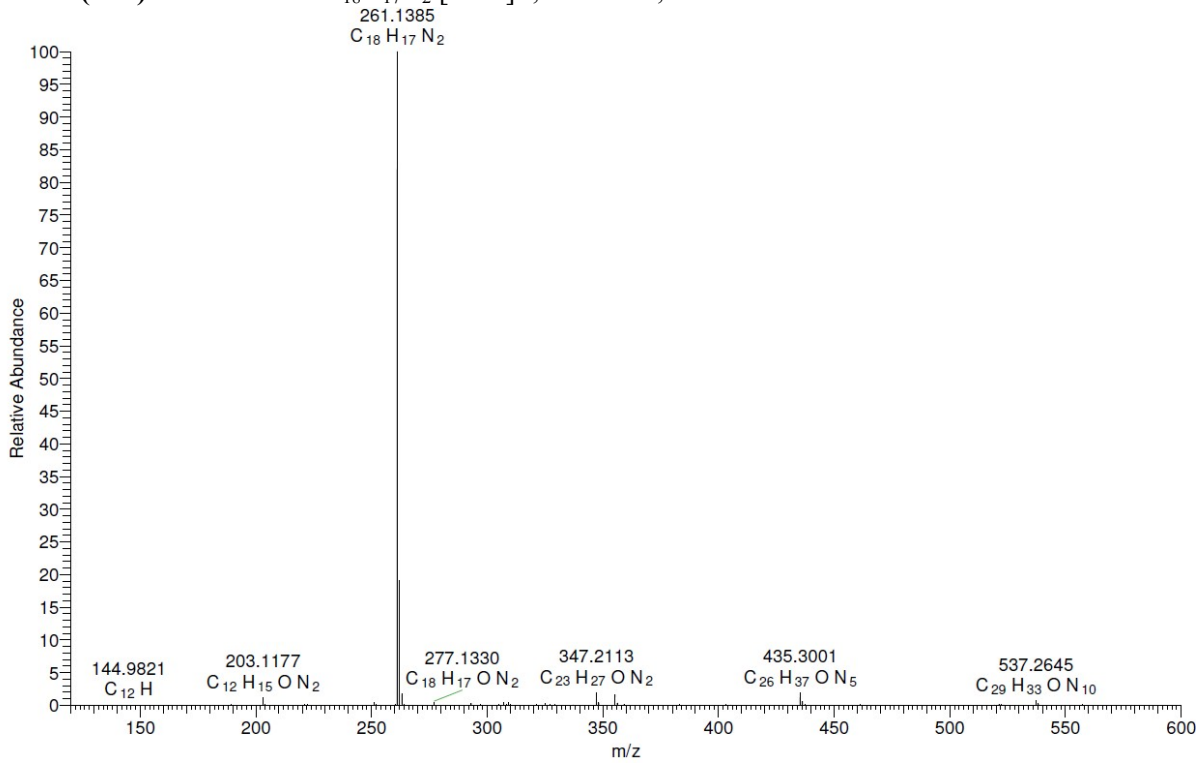


# 7: HRMS

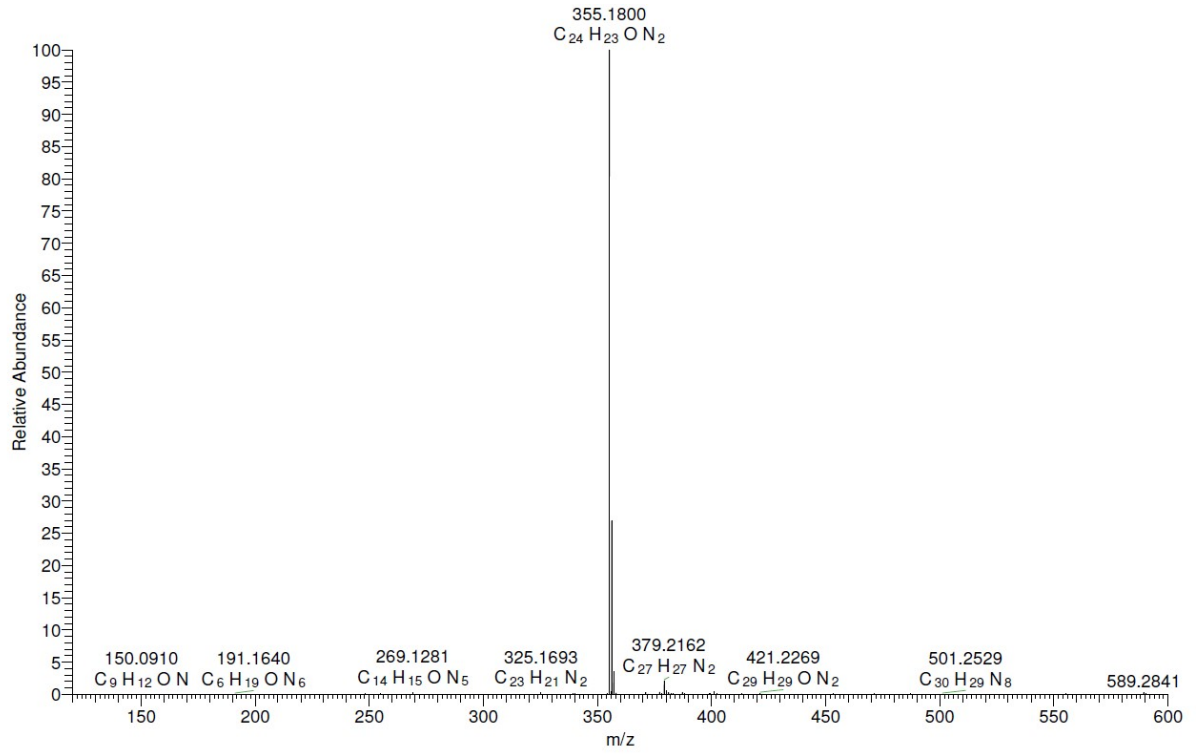
**3-cyclopropyl-4-phenylisoquinolin-1-amine (3r)**

**HRMS(ESI)** m/z found for $C_{18}H_{17}N_2$ [M-H]+, 261.1385, calculated for 260.1313

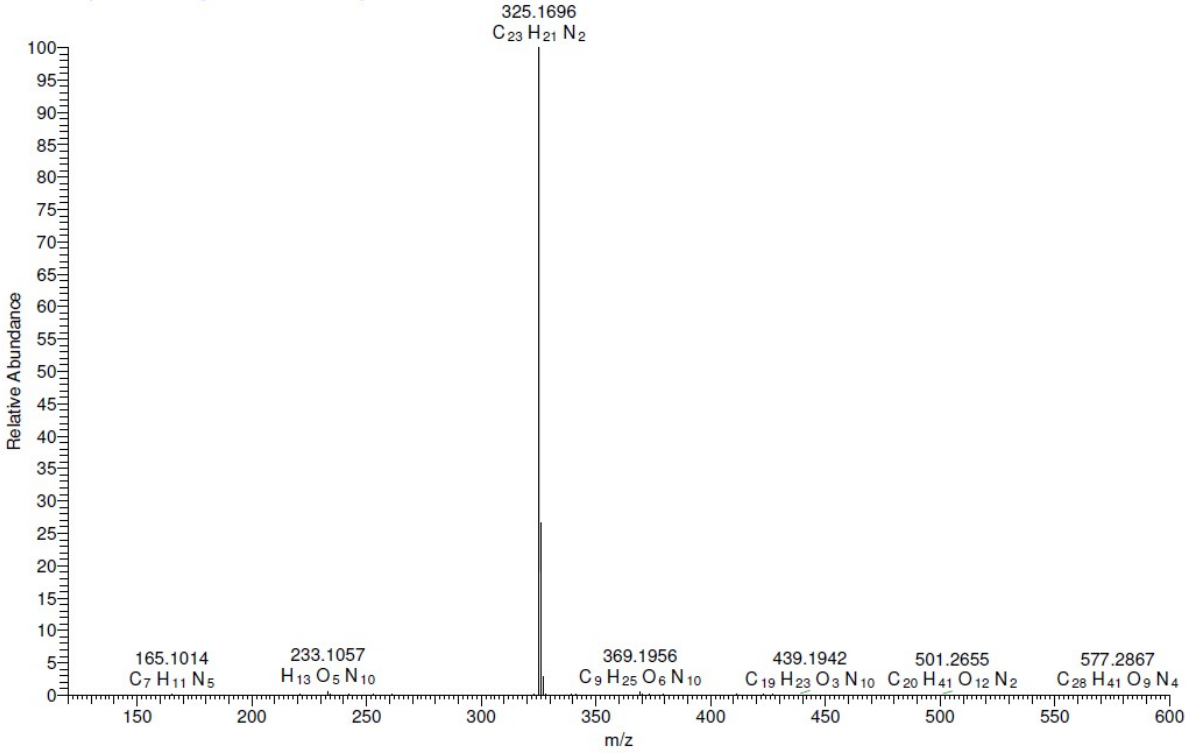



**3-(4-ethylphenyl)-4-(4-methoxyphenyl)isoquinolin-1-amine (3s)**

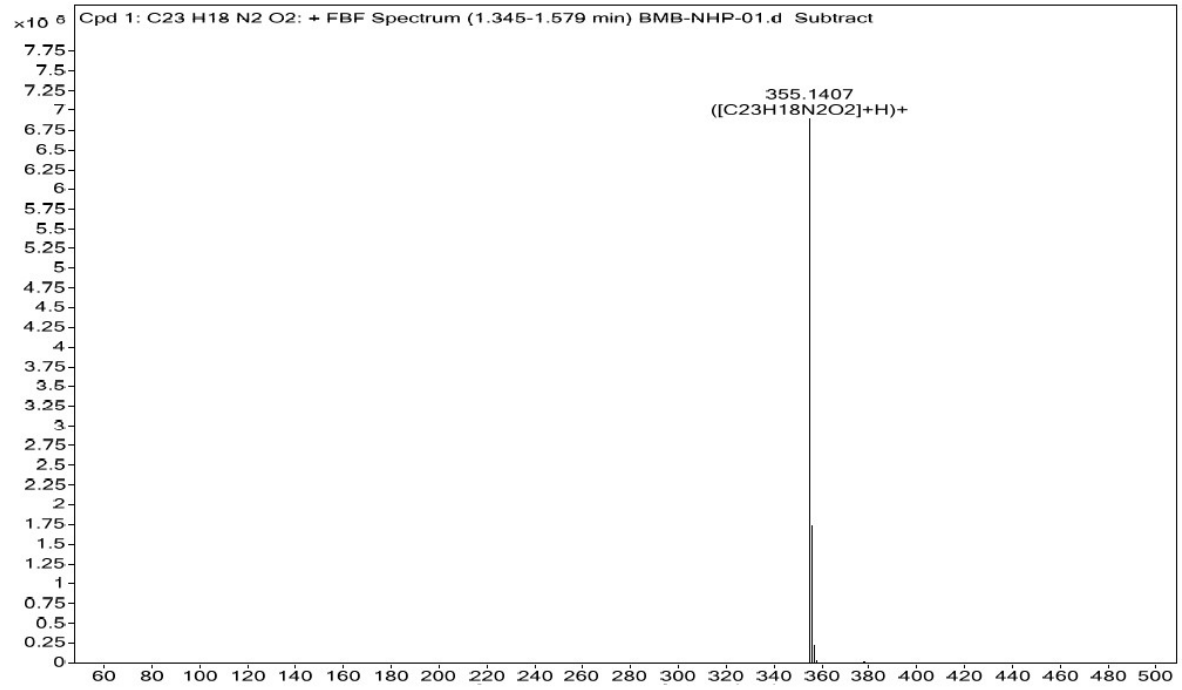
**HRMS(ESI)** m/z found for $C_{24}H_{23}ON_2$ [M-H]+, 355.1800, calculated for 354.1732



**3-phenethyl-4-phenylisoquinolin-1-amine (3t)**
**4-phenethyl-3-phenylisoquinolin-1-amine (3t')**
**HRMS(ESI)** m/z found for $C_{23}H_{21}N_2$ [M-H]+, 325.1696, calculated for 324.1626




**Methyl-4-(1-amino-3-phenylisoquinolin-4-yl)benzoate (3x)**
**Methyl-4-(1-amino-4-phenylisoquinolin-3-yl)benzoate(3x')**
**HRMS(ESI)** m/z found for $C_{23}H_{18}O_2$ [M-H]+, 355.1407, calculated for 354.1368



**4-(1-amino-3-phenylisoquinolin-4-yl)benzonitrile(3y)**

**HRMS(ESI)** m/z found for $C_{22}H_{15}N_3$ [M-H]+, 322.1307, calculated for 321.1266