

SUPPORTING INFORMATION

Solvent-Free Approach for the Synthesis of 2,4-Disubstituted Quinolines Using Zeolites: Evaluation of Biological Activity

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1. Experimental section

All the chemicals were procured from Sigma-Aldrich and used without any further purification. The zeolite β catalyst in ammonia form with a Si/Al ratio of 19 was purchased from Alfa-Aesar. All the samples were systematically characterized using various spectroscopic techniques. ^1H NMR spectra were acquired using Bruker VX NMR FT-300, 400 or 500 MHz spectrometers, while ^{13}C NMR spectra were obtained using Bruker VX NMR FT-101 and 125 MHz spectrometers in CDCl_3 . The chemical shifts (δ) were reported in ppm units downfield from TMS as an internal standard for ^1H NMR and CDCl_3 for ^{13}C NMR spectra. Coupling constants (J) were reported in hertz (Hz), and the following multiplicities were recorded: s (singlet), brs (broad singlet), d (doublet), dd (doublet of doublet), t (triplet), and m (multiplet). The Shimadzu GC-2014 gas chromatograph was used to perform the gas chromatography analysis. It is equipped with an FID detector and a capillary column (EB-5, 30 m in length, 0.25 mm in inner diameter and with a 0.25 mm film). TLC inspections were carried out on Silica Gel 60 F₂₅₄ plates. Column chromatography was performed using silica gel (100-200 mesh). A Micromass Quattro LC mass spectrometer was used to record ESI mass spectra, and ESI-QTOF mass spectrometry was used to obtain high-resolution mass spectra. The XRD patterns of the samples were obtained using a regular Regaku miniflux X-ray Diffractometer with Ni-filtered $\text{CuK}\alpha$ radiation at $2\theta = 2^\circ$ - 80° . The scanning rate was set at 2° min^{-1} , and the beam voltage and current were 30 kV and 15 mA, respectively. FT-IR spectra (Cary 600, Agilent) were recorded in the region of 500 - 4000 cm^{-1} with a resolution of 4 cm^{-1} and 64 scans. The experiments were conducted *in situ* using a specially designed infrared (IR) cell coupled to a conventional vacuum adsorption apparatus. The morphology of the catalyst was examined using a Scanning electron microscopy (SEM) instrument, specifically the JEOL-JSM-7610. Additionally, Transmission electron microscopy (TEM) images were captured using a Tecnai F12 TEM instrument. The Temperature programmed desorption (TPD) of ammonia of H β zeolite samples were determined using the Auto Chem 2910 instrument (Micromeritics, USA). The X-ray photoelectron spectroscopy (XPS) pattern was obtained using a Kratos Axis Ultra Imaging X-ray photoelectron spectrometer equipped with a Mg anode and a multichannel detector. The C 1s peak at 284.8 eV was used as a reference for adjusting the surface charging effects. All the compounds were evaluated *In vitro* for anticancer activity against three cell lines: human prostate carcinoma (PC-3), human breast cancer (MDA-MB-231) and human lung cancer (H460). The biological activities of synthesized compounds were compared to those of standard drugs.

Experimental procedure for large scale reaction

a. 5 mmol scale reaction

2-Aminobenzophenone (5 mmol, 0.986 g) and acetophenone (5 mmol, 0.584 ml) were well mixed in a 15 mL sealed tube. It was then supplemented with 1000 mg (1 g) of H β zeolite and was allowed to stir at 130 °C for 24 h. Later, it was cooled to room temperature and diluted with ethyl acetate. The catalyst was separated through simple filtration, and the crude was obtained by removing the solvent under reduced pressure. The crude was purified by column chromatography using silica gel (100-200 mesh) to obtain the desired product **3a** in 1.306 g (93%).

b. 25 mmol scale reaction

2-Aminobenzophenone (25 mmol, 4.93 g) and acetophenone (25 mmol, 3.4 ml) were well mixed in a 15 mL sealed tube. It was then supplemented with 2000 mg (2 g) of H β zeolite and was allowed to stir at 130 °C for 24 h. Later, it was cooled to room temperature and diluted with ethyl acetate. The catalyst was separated through simple filtration, and the crude was obtained by removing the solvent reduced pressure. The crude was purified by column chromatography using silica gel (100-200 mesh) to obtain the desired product **3a** in 5.996 g (85%).

c. 50 mmol scale reaction

2-Aminobenzophenone (50 mmol, 9.86 g) and acetophenone (50 mmol, 6.8 ml) were well mixed in a 15 mL sealed tube. It was then supplemented with 4000 mg (4 g) of H β zeolite and was allowed to stir at 130 °C for 24 h. Later, it was cooled to room temperature and diluted with ethyl acetate. The catalyst was separated through simple filtration, and the crude was obtained by removing the solvent reduced pressure. The crude was purified by column chromatography using silica gel (100-200 mesh) to obtain the desired product **3a** in 11.710 g (83%).

Biological Studies:

Materials and reagents:

To assess the biological activity of compounds, *in vitro* studies were performed using prostate cancer (PC-3), lung cancer (H460) and breast cancer (MDA-MB-231) cells which were procured from ATCC. Annexin-V binding buffer was procured from Bio Legend, California and RNAase/PI binding buffer was obtained from Invitrogen. Apart from this, phosphate-buffered saline (PBS), Sulforhodamine B dye and other analytical-grade reagents were procured from Sigma-Aldrich (USA).

Methods:**Cell culture:**

MDA-MB-231 cells were maintained using Dulbecco's Modified Eagle's Medium (DMEM), PC-3 cells were cultured in Ham's F12K medium and H460 cells were cultured in RPMI with 10% fetal bovine serum (FBS), and 1X penicillin/streptomycin mixture obtained from Gibco. The grown and sub-cultured cancer cells were maintained at 37°C with a 5% CO₂ atmosphere in the incubator.

***In vitro* cytotoxicity:**

To assess the anti-cancer activity of all compounds, cytotoxicity studies were performed in H460, PC-3 and MDA-MB-231 cell lines using SRB Assay as described earlier.¹ Briefly, cells (3x10³/well) were seeded in 96 well plates, incubated for 16 h and treated at 20 µM and 10 µM concentrations. DMSO was used as a solvent to dissolve all compounds and DMSO was used as a vehicle control in all control wells. After 48 h of treatment, 100 µL cold 10% trichloroacetic acid (TCA) was added to each well, and kept under incubation for 1 h at 4 °C. Later plates were washed under running tap water four times and 100 µl (0.057%) sulphorhodamine B solution to each well of the dry 96-well plates, incubated at room temperature for 30 min in the dark. Plates were quickly washed for four times with 1% acetic acid to remove the sulphorhodamine B solution. After drying, 200 µl of tris base (pH 10.5) buffer was added to each well and kept for shaking for 5 min. The OD values were recorded at wavelength 510 nm using the ELx800 microplate reader (Biotek, USA) described earlier.

IC₅₀ generation:

Based on the initial screening at 20 µM and 10 µM concentrations, a few compounds were selected to assess the half-maximal inhibitory concentration (IC₅₀) using SRB assay. The compounds which showed more than 50 % cell death, those compounds were selected and treated with various concentrations (0.625, 1.25, 2.5, 5, 10 and 20) for 48 h and then subjected to SRB assay. Further IC₅₀ was calculated using GraphPad Prism-5 by the curve-fit method.

Cell Cycle analysis:

To the selected compounds **3m** and **3t** based on their IC₅₀ values, cell cycle analysis was performed using Flow cytometry. To know the various phases of the cell cycle, MDA-MB-231 and PC-3 cells were counted (1x10⁵ cells/well) and seeded in 12 well plates individually. After 16 h of seeding, keeping cisplatin as a standard drug in both cell lines, the MDA-MB-231 cells were treated with compound **3m** at 1 µM, 3 µM and 5 µM and PC-3 cells were treated with compound **3t** at 7 µM, 9 µM and 11 µM for 48 h. Thereafter, cells were

trypsinized and then the cell cycle was performed by flow cytometry (Becton Dickinson FACS Caliber) as described earlier.²

Annexin V-FITC assay:

MDA-MB-231 and PC-3 cells (1×10^5 cells/well) were seeded in individual 12-well plates and incubated overnight. Keeping cisplatin standard with a concentration 50 μ M, MDA-MB-231 cells were treated with compound **3m** at 1 μ M, 3 μ M and 5 μ M; PC-3 cells were treated with compound **3t** at 7 μ M, 9 μ M and 11 μ M. After 48 h of treatment, cells were trypsinized, collected and washed with 1X PBS at 3000 rpm. Later cells were stained with Annexin-V-FITC and propidium iodide using Annexin-V binding buffer. After 20 min of incubation, cells were analysed through flow cytometry (using Becton Dickinson FACS Caliber) as described earlier.³

Statistical Analysis: Statistical analysis were performed using one-way ANOVA followed by Dunnett's post-hoc test. GraphPad Prism 9.0 was used for all evaluations. Data are presented as mean \pm SEM, with $p < 0.05$ considered statistically significant.

Biological evaluation: Anti-cancer Activity

Table S1: IC₅₀ (in μM) values for synthesized compounds on MDAMB-231, PC-3 and H460 cell lines

| Entry | Compound code | MDAMB-231 (μM) | PC-3 (μM) | H460 (μM) | HEK293 (μM) |
|-------|---------------|-----------------------------|------------------------|------------------------|--------------------------|
| 1 | 3a | >20 | >20 | >20 | >20 |
| 2 | 3b | 21.08 \pm 0.9 | 23 \pm 1.44 | 17.02 \pm 1.32 | 20.44 \pm 3.79 |
| 3 | 3c | >20 | 13.63 \pm 2.78 | >20 | 13.81 \pm 1.24 |
| 4 | 3d | 17.54 \pm 0.39 | 12.01 \pm 1.79 | 8.46 \pm 0.31 | 15.60 \pm 1.71 |
| 5 | 3e | 17.19 \pm 1.08 | 16.64 \pm 0.92 | 12.27 \pm 0.93 | 20.25 \pm 1.71 |
| 6 | 3f | 20.06 \pm 2.29 | 11.39 \pm 0.27 | 10.98 \pm 1.57 | 13.25 \pm 1.85 |
| 7 | 3g | >20 | >20 | >20 | 17.78 \pm 4.49 |
| 8 | 3h | >20 | >20 | >20 | 7.9 \pm 1.69 |
| 9 | 3i | 18 \pm 1.24 | >20 | >20 | 11.55 \pm 4.63 |
| 10 | 3j | >20 | >20 | >20 | 16.09 \pm 2.68 |
| 11 | 3k | >20 | >20 | >20 | 16.5 \pm 3.83 |
| 12 | 3l | >20 | >20 | >20 | 17.63 \pm 3.58 |
| 13 | 3m | 3.32 \pm 0.5 | >20 | >20 | 7.9 \pm 1.36 |
| 14 | 3n | >20 | >20 | >20 | >20 |
| 15 | 3o | >20 | >20 | >20 | 10.43 \pm 2.95 |
| 16 | 3p | >20 | >20 | >20 | 8.84 \pm 2.81 |
| 17 | 3q | >20 | 11.13 \pm 2.05 | >20 | 21.53 \pm 0.69 |
| 18 | 3r | >20 | >20 | >20 | 18.99 \pm 3.13 |

| | | | | | |
|----|-------------------------------|------------|------------|------------|------------|
| 19 | 3s | >20 | >20 | >20 | 8.94±0.84 |
| 20 | 3t | >20 | 9.18±0.66 | >20 | 17.85±3.05 |
| 21 | 3u | >20 | >20 | >20 | 7.52±1.47 |
| 22 | 3v | 19.15±1.76 | >20 | >20 | 6.60±0.64 |
| 23 | 3w | >20 | >20 | >20 | 11.8±3.72 |
| 24 | 3x | >20 | >20 | >20 | 1.63±0.69 |
| 25 | 3y | 15.67±2.15 | 14.37±1.87 | >20 | 14.38±2.64 |
| 26 | 3z | >20 | >20 | >20 | >20 |
| 27 | 3aa | 7.46±0.38 | 10.53±0.66 | 6.41±1.03 | 12.43±1.43 |
| 28 | 3ab | >20 | >20 | >20 | 19.99±2.89 |
| 29 | 3ab' | 16.07±1.86 | >20 | >20 | 27.34±6.59 |
| 30 | 3ac | >20 | >20 | >20 | 4.92±0.29 |
| 31 | 3ad | >20 | >20 | 12.94±1.81 | 28.49±3.49 |
| 32 | Doxorubicin (Doxo) | 2.7±0.3 | 2.9±0.57 | 1.8±0.4 | 0.77±0.15 |

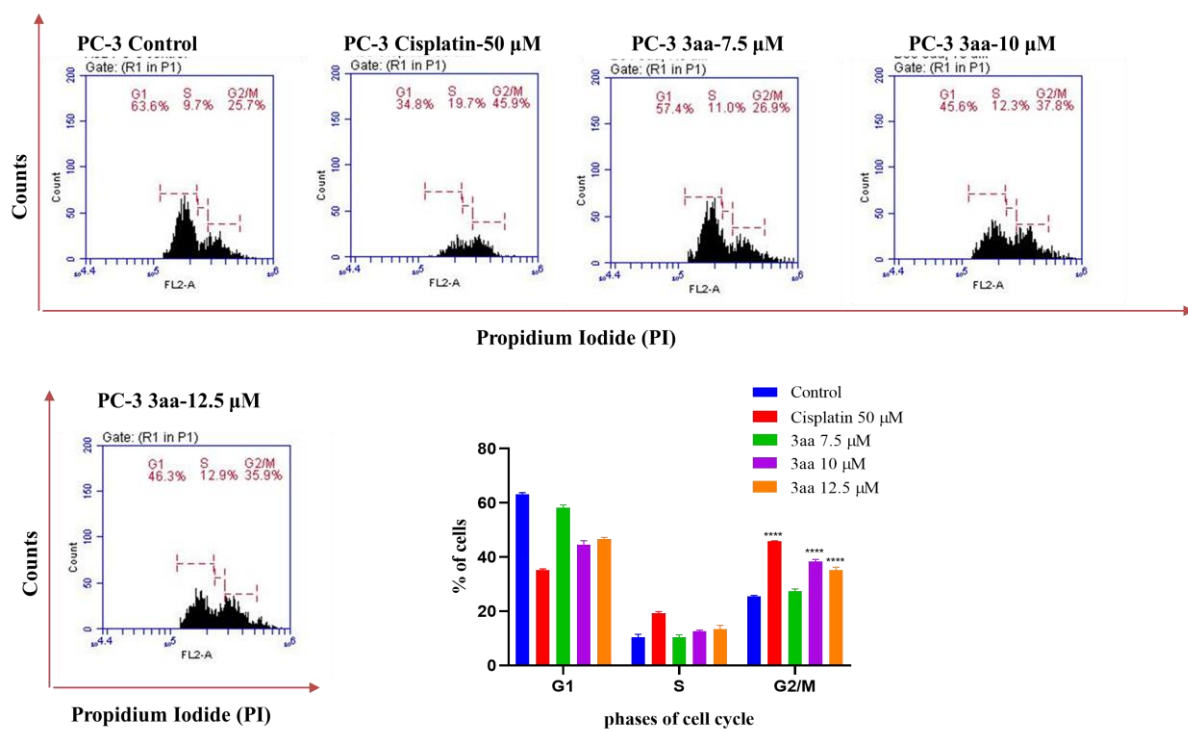
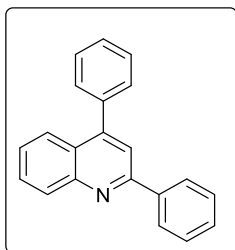


Figure S1. Cell cycle analysis of **3aa** compound

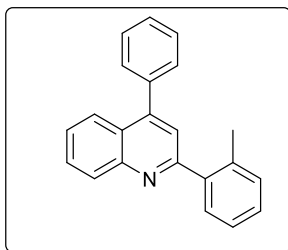
2. Spectroscopic data

2,4-diphenylquinoline (Table 2, 3a)⁴



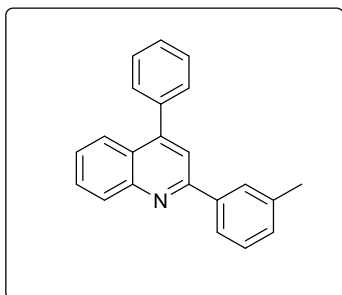
¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.24 (d, J = 8.5 Hz, 1H), 8.18 (d, J = 8.0 Hz, 2H), 7.90 (d, J = 8.4 Hz, 1H), 7.81 (s, 1H), 7.75-7.67 (m, 1H), 7.58-7.40 (m, 9H). ¹³C NMR (126 MHz, CDCl₃): δ (ppm) = 156.94, 149.21, 148.87, 139.71, 138.46, 130.18, 129.62, 129.57, 129.39, 128.89, 128.65, 128.46, 127.64, 126.38, 125.82, 125.69, 119.41. HRMS (ESI): m/z calcd for C₂₁H₁₆N [M+H]⁺ 282.12773 found 282.12842.

4-phenyl-2-(*o*-tolyl)quinoline (Table 2, 3b)⁴



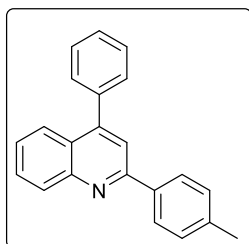
¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.23 (d, J = 8.4 Hz, 1H), 7.96 (dd, J = 8.4, 0.9 Hz, 1H), 7.79-7.70 (m, 1H), 7.60-7.46 (m, 8H), 7.37-7.28 (m, 3H), 2.47 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ (ppm) = 159.88, 148.48, 140.68, 138.20, 136.09, 130.93, 130.05, 129.79, 129.65, 129.50, 129.45, 128.63, 128.56, 128.45, 128.23, 127.55, 126.48, 126.05, 125.67, 125.31, 123.40, 122.62, 120.91, 20.47. HRMS (ESI): m/z calcd for C₂₂H₁₈N [M+H]⁺ 296.14338 found 296.14394.

4-phenyl-2-(*m*-tolyl)quinoline (Table 2, 3c)⁴



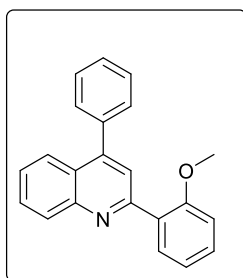
^1H NMR (400 MHz, CDCl_3): δ (ppm) = 8.23 (d, J = 8.4 Hz, 1H), 7.96 (dd, J = 8.2, 1.2 Hz, 1H), 7.80-7.71 (m, 1H), 7.59-7.46 (m, 8H), 7.37-7.27 (m, 3H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ (ppm) = 159.88, 148.48, 140.68, 138.20, 136.09, 130.93, 130.05, 129.79, 129.65, 129.50, 129.45, 128.63, 128.56, 128.45, 128.23, 126.48, 126.05, 125.67, 125.31, 122.62, 20.47. HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{18}\text{N}$ $[\text{M}+\text{H}]^+$ 296.14338 found 296.14398.

4-phenyl-2-(*p*-tolyl)quinoline (Table 2, 3d)⁵



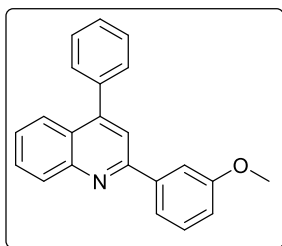
^1H NMR (400 MHz, CDCl_3): δ (ppm) = 8.12 (d, J = 8.5 Hz, 1H), 7.99 (d, J = 8.2 Hz, 2H), 7.77 (d, J = 8.4 Hz, 1H), 7.68 (s, 1H), 7.63-7.55 (m, 1H), 7.47-7.28 (m, 6H), 7.20 (d, J = 8.0 Hz, 2H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ (ppm) = 156.89, 149.08, 148.87, 139.47, 138.54, 136.88, 130.08, 129.61, 129.49, 128.62, 128.40, 127.51, 126.18, 125.74, 125.66, 119.24, 21.39. HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{18}\text{N}$ $[\text{M}+\text{H}]^+$ 296.14338 found 296.14408.

2-(2-methoxyphenyl)-4-phenylquinoline (Table 2, 3e)⁶



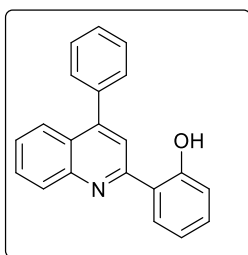
^1H NMR (400 MHz, CDCl_3): δ (ppm) = 8.24 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 7.5 Hz, 1H), 7.87 (dd, J = 7.6, 1.8 Hz, 1H), 7.83 (s, 1H), 7.74-7.68 (m, 1H), 7.60-7.39 (m, 7H), 7.14 (td, J = 7.5, 0.9 Hz, 1H), 7.03 (d, J = 8.3 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ (ppm) = 157.24, 156.74, 148.82, 147.42, 138.58, 131.55, 130.36, 130.06, 129.76, 129.12, 128.53, 128.23, 126.26, 125.57, 123.68, 121.29, 111.46, 55.73. HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{18}\text{ON}$ $[\text{M}+\text{H}]^+$ 312.13829 found 312.13885.

2-(3-methoxyphenyl)-4-phenylquinoline (Table 2, 3f)⁶



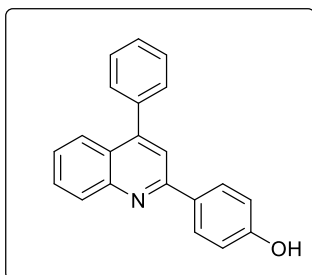
^1H NMR (300 MHz, CDCl_3): δ (ppm) = 8.25 (d, J = 7.9 Hz, 1H), 7.90 (dd, J = 8.4, 0.9 Hz, 1H), 7.83-7.77 (m, 2H), 7.77-7.67 (m, 2H), 7.60-7.29 (m, 7H), 7.05-6.94 (m, 1H), 3.93 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ (ppm) = 160.17, 156.71, 149.19, 148.77, 141.17, 138.41, 130.16, 129.83, 129.60, 129.55, 128.63, 128.45, 126.41, 125.88, 125.66, 121.16, 120.07, 115.50, 112.71, 112.37, 55.47. HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{18}\text{ON}$ $[\text{M}+\text{H}]^+$ 312.13829 found 312.13878.

2-(4-phenylquinolin-2-yl)phenol (Table 2, 3g)⁷



^1H NMR (400 MHz, CDCl_3): δ (ppm) = 8.09 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 5.3 Hz, 2H), 7.88 (dd, J = 8.4, 0.7 Hz, 1H), 7.78-7.68 (m, 1H), 7.60-7.45 (m, 6H), 7.40-7.31 (m, 1H), 7.10 (dd, J = 8.4, 1.1 Hz, 1H), 6.97-6.89 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3): δ (ppm) = 161.17, 157.47, 150.21, 145.28, 137.95, 132.07, 130.34, 129.48, 128.74, 127.99, 126.98, 126.69, 125.87, 125.36, 118.99, 118.74, 118.67, 117.57. HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{15}\text{NO}$ $[\text{M}+\text{H}]^+$ 298.12264 found 298.12331.

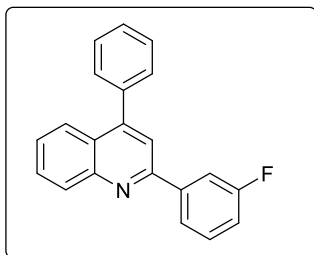
4-(4-phenylquinolin-2-yl)phenol (Table 2, 3h)⁸



^1H NMR (300 MHz, CDCl_3): δ (ppm) = 8.23 (d, J = 8.5 Hz, 1H), 8.08 (t, J = 9.2 Hz, 2H), 7.88 (d, J = 8.4 Hz, 1H), 7.76 (s, 1H), 7.75-7.67 (m, 1H), 7.59-7.49 (m, 5H), 7.44 (d, J = 7.0

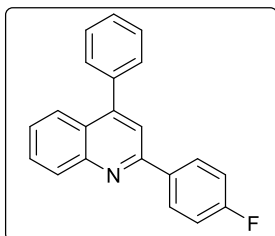
Hz, 1H), 6.93 (d, $J = 8.5$ Hz, 2H), 1.25 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3): δ (ppm) = 157.82, 157.08, 149.51, 148.44, 138.34, 131.48, 129.77, 129.55, 129.33, 129.21, 128.62, 128.47, 126.11, 125.73, 125.56, 119.55, 116.00. HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{15}\text{NO}$ $[\text{M}+\text{H}]^+$ 298.12264 found 298.12351.

2-(3-fluorophenyl)-4-phenylquinoline (Table 2, 3i)⁵



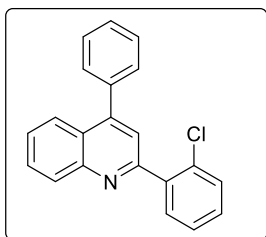
^1H NMR (400 MHz, CDCl_3): δ (ppm) = 8.24 (d, $J = 8.5$ Hz, 1H), 8.00-7.89 (m, 3H), 7.79 (s, 1H), 7.78-7.72 (m, 1H), 7.60-7.43 (m, 7H), 7.21-7.11 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3): δ (ppm) = 163.40 (d, $J_{\text{C-F}} = 245.7$ Hz), 155.41, 149.12 (d, $J_{\text{C-F}} = 71.5$ Hz), 141.99 (d, $J_{\text{C-F}} = 7.4$ Hz), 138.25, 130.36, 130.28, 130.21, 129.75, 129.58, 128.68, 128.55, 126.70, 126.00, 125.72, 123.12 (d, $J = 2.2$ Hz), 119.11, 116.24 (d, $J_{\text{C-F}} = 21.3$ Hz), 114.54 (d, $J_{\text{C-F}} = 22.8$ Hz). HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{15}\text{FN}$ $[\text{M}+\text{H}]^+$ 300.11830 found 300.11909.

2-(4-fluorophenyl)-4-phenylquinoline (Table 2, 3j)⁵



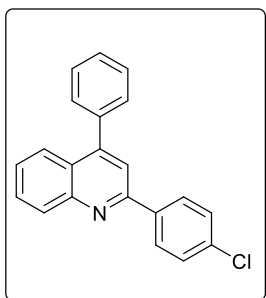
^1H NMR (400 MHz, CDCl_3): δ (ppm) = 8.25-8.15 (m, 3H), 7.95-7.86 (m, 1H), 7.79-7.69 (m, 2H), 7.60-7.44 (m, 6H), 7.29-7.14 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3): δ (ppm) = 163.85 (d, $J_{\text{C-F}} = 249.0$ Hz), 155.77, 149.08 (d, $J_{\text{C-F}} = 70.6$ Hz), 138.35, 135.82 (d, $J_{\text{C-F}} = 3.2$ Hz), 130.07, 129.67, 129.57, 129.48, 129.42, 128.65, 128.50, 126.42, 125.70, 118.99, 115.79 (d, $J_{\text{C-F}} = 21.6$ Hz). HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{15}\text{FN}$ $[\text{M}+\text{H}]^+$ 300.11830 found 300.11913.

2-(2-chlorophenyl)-4-phenylquinoline (Table 2, 3k)⁴



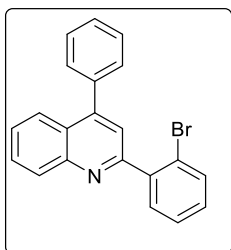
^1H NMR (400 MHz, CDCl_3): δ (ppm) = 8.25 (d, J = 9.0 Hz, 1H), 7.98 (dd, J = 8.6, 1.2 Hz, 1H), 7.78-7.72 (m, 2H), 7.71 (s, 1H), 7.60-7.46 (m, 7H), 7.45-7.34 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3): δ (ppm) = 156.99, 148.67, 148.07, 139.65, 138.08, 132.45, 131.76, 130.14, 129.92, 129.69, 129.55, 128.63, 128.48, 127.22, 126.84, 125.74, 123.04. HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{15}\text{ClN}$ $[\text{M}+\text{H}]^+$ 316.08875 found 316.08918.

2-(4-chlorophenyl)-4-phenylquinoline (Table 2, 3l)⁶



^1H NMR (400 MHz, CDCl_3): δ (ppm) = 8.22 (d, J = 8.0 Hz, 1H), 8.15 (d, J = 8.6 Hz, 2H), 7.92-7.87 (m, 1H), 7.77 (s, 1H), 7.76-7.71 (m, 1H), 7.57-7.45 (m, 8H). ^{13}C NMR (101 MHz, CDCl_3): δ (ppm) = 155.54, 149.44, 148.80, 138.28, 138.06, 135.59, 130.11, 129.72, 129.57, 129.03, 128.85, 128.66, 128.53, 126.57, 125.85, 125.71, 118.92. HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{15}\text{ClN}$ $[\text{M}+\text{H}]^+$ 316.08875 found 316.08965.

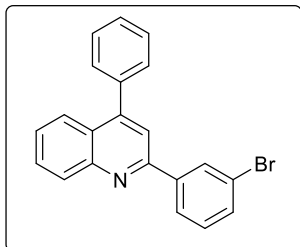
2-(2-bromophenyl)-4-phenylquinoline (Table 2, 3m)⁴



^1H NMR (300 MHz, CDCl_3): δ (ppm) = 8.25 (d, J = 8.0 Hz, 1H), 7.98 (dd, J = 7.9, 1.1 Hz, 1H), 7.78-7.63 (m, 4H), 7.61-7.40 (m, 7H), 7.29 (dd, J = 7.7, 1.9 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3): δ (ppm) = 158.28, 148.55, 148.01, 141.63, 138.06, 133.33, 131.66, 130.13,

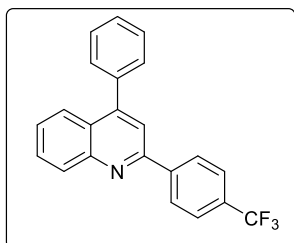
130.05, 129.69, 129.58, 128.64, 128.50, 127.76, 126.87, 125.74, 125.70, 123.03, 121.97.
HRMS (ESI): m/z calcd for $C_{21}H_{15}BrN$ $[M+H]^+$ 360.03824 found 360.03896.

2-(3-bromophenyl)-4-phenylquinoline (Table 2, 3n)⁹



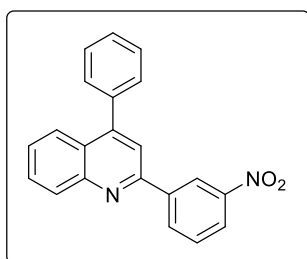
1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.38 (t, J = 1.8 Hz, 1H), 8.24 (d, J = 8.5 Hz, 1H), 8.12 (dt, J = 7.8, 1.3 Hz, 1H), 7.92 (dd, J = 8.4, 0.8 Hz, 1H), 7.78 (s, 1H), 7.76-7.72 (m, 1H), 7.62-7.47 (m, 7H), 7.39 (d, J = 7.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 155.19, 149.53, 148.77, 141.69, 138.21, 132.26, 130.65, 130.34, 130.19, 129.76, 129.56, 128.67, 128.55, 126.72, 126.10, 125.97, 125.71, 123.17, 119.04. HRMS (ESI): m/z calcd for $C_{21}H_{15}BrN$ $[M+H]^+$ 360.03824 found 360.03877.

4-phenyl-2-(4-(trifluoromethyl)phenyl)quinoline (Table 2, 3o)⁹



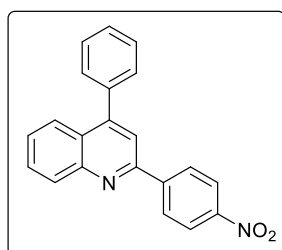
1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.32 (d, J = 8.1 Hz, 2H), 8.26 (d, J = 8.5 Hz, 1H), 7.93 (d, J = 9.4 Hz, 1H), 7.83 (s, 1H), 7.81-7.73 (m, 3H), 7.61-7.45 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 155.24, 149.65, 148.83, 142.97, 138.16, 130.27, 129.85, 129.56, 128.70, 128.61, 127.88, 126.91, 126.07, 125.75, 119.14. HRMS (ESI): m/z calcd for $C_{22}H_{15}F_3N$ $[M+H]^+$ 350.1151 found 350.11567.

2-(3-nitrophenyl)-4-phenylquinoline (Table 2, 3p)⁶



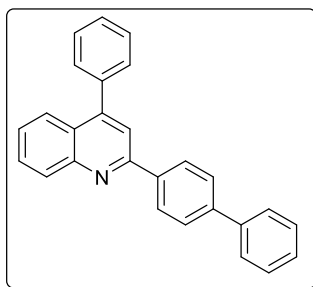
^1H NMR (500 MHz, CDCl_3): δ (ppm) = 9.08 (t, J = 2.0 Hz, 1H), 8.62-8.57 (m, 1H), 8.32 (ddd, J = 8.3, 2.2, 1.0 Hz, 1H), 8.27 (d, J = 8.4 Hz, 1H), 7.94 (dd, J = 8.5, 1.0 Hz, 1H), 7.87 (s, 1H), 7.81-7.76 (m, 1H), 7.71 (t, J = 8.2 Hz, 1H), 7.60-7.51 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ (ppm) = 153.97, 150.01, 148.88, 148.79, 141.32, 137.98, 133.37, 130.27, 130.05, 129.81, 129.55, 128.74, 127.14, 126.17, 125.81, 123.94, 122.46, 118.69. HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{15}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 327.11280 found 327.11368.

2-(4-nitrophenyl)-4-phenylquinoline (Table 2, 3q)⁵



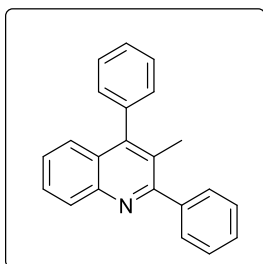
^1H NMR (500 MHz, CDCl_3): δ (ppm) = 8.43-8.34 (m, 4H), 8.26 (d, J = 8.4 Hz, 1H), 7.94 (dd, J = 8.4, 0.9 Hz, 1H), 7.86 (s, 1H), 7.83-7.74 (m, 1H), 7.64-7.49 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3): δ (ppm) = 154.11, 149.92, 148.84, 148.39, 145.50, 137.96, 130.36, 130.09, 129.53, 128.75, 128.36, 127.34, 126.21, 125.81, 124.05, 119.11. HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{15}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 327.11280 found 327.11325.

2-([1,1'-biphenyl]-4-yl)-4-phenylquinoline (Table 2, 3r)⁶



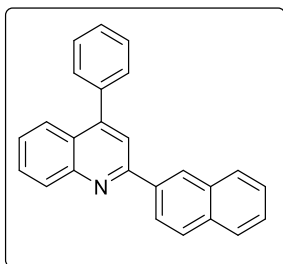
^1H NMR (500 MHz, CDCl_3): δ (ppm) = 8.31-8.27 (m, 2H), 8.26 (d, J = 7.9 Hz, 1H), 7.91 (dd, J = 8.7, 0.9 Hz, 1H), 7.87 (s, 1H), 7.79-7.72 (m, 3H), 7.71-7.66 (m, 2H), 7.60-7.45 (m, 8H), 7.40-7.36 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3): δ (ppm) = 156.44, 149.21, 148.91, 142.12, 140.62, 138.55, 138.46, 130.16, 129.61, 128.87, 128.64, 128.45, 128.00, 127.58, 127.18, 126.36, 125.84, 125.69, 119.25. HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{20}\text{N}$ $[\text{M}+\text{H}]^+$ 358.15903 found 358.15973.

3-methyl-2,4-diphenylquinoline (Table 2, 3s)¹⁰



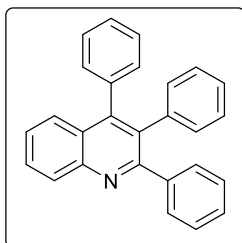
¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.17 (d, *J* = 8.4 Hz, 1H), 7.71-7.59 (m, 3H), 7.58-7.37 (m, 8H), 7.35-7.29 (m, 2H), 2.15 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ (ppm) = 160.86, 147.77, 146.27, 141.56, 137.77, 129.48, 129.35, 128.95, 128.66, 128.53, 128.33, 128.10, 127.84, 127.09, 126.74, 126.25, 125.99, 18.62. HRMS (ESI): *m/z* calcd for C₂₂H₁₈N [M+H]⁺ 296.14338 found 296.14397.

2-(naphthalen-2-yl)-4-phenylquinoline (Table 2, 3t)¹¹



¹H NMR (500 MHz, CDCl₃): δ (ppm) = 8.65 (s, 1H), 8.41 (dd, *J* = 8.4, 1.8 Hz, 1H), 8.29 (d, *J* = 8.5 Hz, 1H), 8.03-7.86 (m, 5H), 7.78-7.72 (m, 1H), 7.62-7.47 (m, 8H). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 156.70, 149.25, 148.94, 138.49, 136.97, 133.92, 133.54, 130.17, 129.63, 128.85, 128.66, 128.47, 127.75, 127.19, 126.74, 126.42, 126.36, 125.72, 125.10, 119.5. HRMS (ESI): *m/z* calcd for C₂₅H₁₈N [M+H]⁺ 332.14338 found 332.14425.

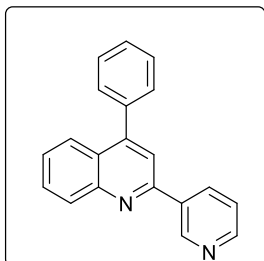
2,3,4-triphenylquinoline (Table 2, 3u)¹²



¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.26 (d, *J* = 8.4 Hz, 1H), 7.77-7.70 (m, 1H), 7.61-7.56 (m, 1H), 7.49-7.43 (m, 1H), 7.40-7.35 (m, 2H), 7.32-7.27 (m, 3H), 7.24-7.19 (m, 3H), 7.16-7.12 (m, 2H), 7.03-6.97 (m, 3H), 6.92-6.86 (m, 2H). ¹³C NMR (75 MHz, CDCl₃): δ

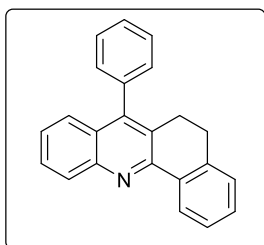
(ppm) = 159.04, 147.70, 147.35, 141.20, 138.37, 136.99, 132.99, 131.40, 130.33, 129.94, 129.73, 129.39, 127.81, 127.69, 127.62, 127.36, 127.30, 126.64, 126.60, 126.34. HRMS (ESI): m/z calcd for $C_{27}H_{20}N$ $[M+H]^+$ 358.1590 found 358.1593.

4-phenyl-2-(pyridin-3-yl)quinoline (Table 2, 3v)¹³



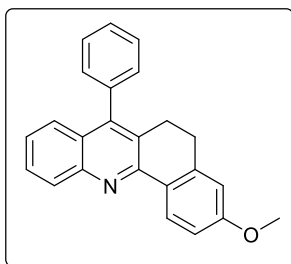
1H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.39 (s, 1H), 8.71 (dd, J = 4.7, 1.3 Hz, 1H), 8.58-8.49 (m, 1H), 8.25 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 9.1 Hz, 1H), 7.82 (s, 1H), 7.80-7.73 (m, 1H), 7.61-7.43 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 154.21, 150.26, 149.70, 148.91, 148.87, 138.08, 135.15, 134.99, 130.17, 129.87, 129.56, 128.71, 128.63, 126.86, 126.00, 125.79, 123.69, 118.87. HRMS (ESI): m/z calcd for $C_{20}H_{15}N_2$ $[M+H]^+$ 283.12370 found 283.12298.

7-phenyl-5,6-dihydrobenzo[c]acridine (Table 2, 3w)¹⁴



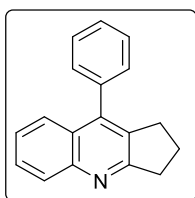
1H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.62 (dd, J = 8.1, 1.1 Hz, 1H), 8.18 (d, J = 8.2 Hz, 1H), 7.68-7.60 (m, 1H), 7.59-7.28 (m, 9H), 7.23 (s, 1H), 2.92-2.80 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 153.15, 147.23, 145.38, 139.33, 136.99, 135.15, 129.64, 129.54, 128.58, 128.48, 128.12, 127.92, 127.70, 127.29, 126.39, 126.05, 125.94, 28.31, 26.53. HRMS (ESI): m/z calcd for $C_{23}H_{18}N$ $[M+H]^+$ 308.14338 found 308.14406.

3-methoxy-7-phenyl-5,6-dihydrobenzo[c]acridine (Table 2, 3x)¹⁵



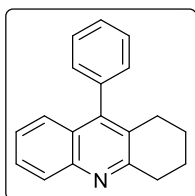
^1H NMR (400 MHz, CDCl_3): δ (ppm) = 8.55 (d, J = 8.7 Hz, 1H), 8.13 (d, J = 8.2 Hz, 1H), 7.61 (ddd, J = 8.4, 6.6, 1.6 Hz, 1H), 7.57-7.46 (m, 3H), 7.41-7.28 (m, 4H), 6.97 (dd, J = 8.8, 2.5 Hz, 1H), 6.76 (d, J = 2.6 Hz, 1H), 3.87 (s, 3H), 2.90-2.74 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3): δ (ppm) = 160.94, 153.15, 147.23, 145.16, 141.16, 137.08, 129.54, 129.34, 128.55, 128.40, 128.20, 128.13, 127.86, 127.50, 127.01, 126.03, 125.50, 113.10, 112.61, 55.36, 28.66, 26.57. HRMS (ESI): m/z calcd for $\text{C}_{24}\text{H}_{20}\text{ON}$ $[\text{M}+\text{H}]^+$ 338.15394 found 338.15456.

9-phenyl-2,3-dihydro-1H-cyclopenta[b]quinoline (Table 2, 3y)¹⁶



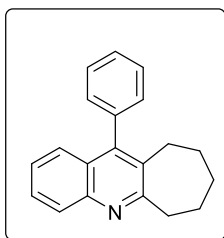
^1H NMR (400 MHz, CDCl_3): δ (ppm) = 8.07 (d, J = 7.9 Hz, 1H), 7.61 (t, J = 7.7 Hz, 2H), 7.55-7.43 (m, 3H), 7.37-7.35 (m, 3H), 3.25-3.21 (m, 2H), 2.90 (t, J = 7.4 Hz, 2H), 2.22-2.09 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3): δ (ppm) = 167.43, 147.98, 142.70, 136.78, 133.64, 129.30, 128.84, 128.51, 128.23, 127.99, 126.23, 125.65, 125.49, 35.22, 30.35, 23.53. HRMS (ESI): m/z calcd for $\text{C}_{18}\text{H}_{16}\text{N}$ $[\text{M}+\text{H}]^+$ 246.1282 found 246.1287.

9-phenyl-1,2,3,4-tetrahydroacridine (Table 2, 3z)¹⁶



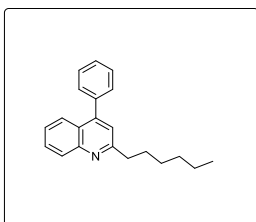
^1H NMR (300 MHz, CDCl_3): δ (ppm) = 8.02 (d, J = 8.4 Hz, 1H), 7.65-7.41 (m, 4H), 7.36-7.28 (m, 2H), 7.27-7.19 (m, 2H), 3.20 (t, J = 6.6 Hz, 2H), 2.61 (t, J = 6.5 Hz, 2H), 2.03-1.91 (m, 2H), 1.85-1.73 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3): δ (ppm) = 159.11, 146.49, 146.34, 139.51, 137.18, 129.13, 128.61, 128.40, 128.35, 127.74, 126.69, 125.80, 125.38, 34.29, 28.07, 23.05, 22.94. HRMS (ESI): m/z calcd for $\text{C}_{19}\text{H}_{18}\text{N}$ $[\text{M}+\text{H}]^+$ 260.1439 found 260.1441.

11-phenyl-7,8,9,10-tetrahydro-6H-cyclohepta[b]quinoline (Table 2, 3aa)¹⁶



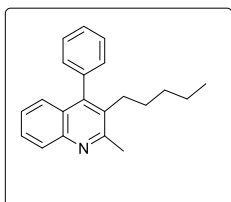
¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.03 (d, *J* = 8.4 Hz, 1H), 7.64-7.55 (m, 1H), 7.54-7.42 (m, 3H), 7.36-7.18 (m, 4H), 3.29 (d, *J* = 4.7 Hz, 2H), 2.76-2.64 (m, 2H), 1.93-1.79 (m, 4H), 1.68-1.52 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ (ppm) = 164.79, 145.85, 145.49, 137.68, 133.84, 129.46, 128.60, 128.44, 128.20, 127.64, 126.96, 126.37, 125.59, 40.19, 31.95, 30.72, 28.53, 27.07. HRMS (ESI): *m/z* calcd for C₂₀H₂₀N [M+H]⁺ 274.1595 found 274.1598.

2-hexyl-4-phenylquinoline (Table 2, 3ab)¹⁷



¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.11 (d, *J* = 8.1 Hz, 1H), 7.89-7.84 (m, 1H), 7.68 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.56-7.39 (m, 6H), 7.24 (s, 1H), 3.03-2.96 (m, 2H), 1.90-1.80 (m, 2H), 1.47-1.36 (m, 2H), 1.34-1.32 (m, 4H), 0.90-0.87 (m, 3H). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 162.68, 148.54, 148.40, 138.35, 129.56, 129.21, 128.53, 128.30, 125.71, 125.64, 125.30, 121.60, 39.43, 31.76, 30.12, 29.33, 22.59, 14.10. HRMS (ESI): *m/z* calcd for C₂₁H₂₄N [M+H]⁺ 290.1908 found 290.1909.

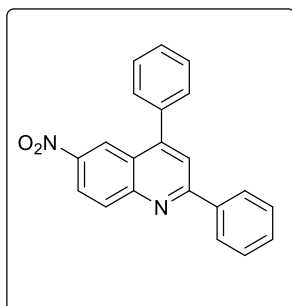
2-methyl-3-pentyl-4-phenylquinoline (Table 2, 3ab¹)



¹H NMR (500 MHz, CDCl₃): δ (ppm) = 8.02 (d, *J* = 8.3 Hz, 1H), 7.62-7.56 (m, 1H), 7.54-7.43 (m, 3H), 7.34-7.28 (m, 1H), 7.27-7.20 (m, 3H), 2.81 (s, 3H), 2.58-2.49 (m, 2H), 1.48-1.38 (m, 2H), 1.24-1.13 (m, 4H), 0.83-0.75 (m, 3H). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) =

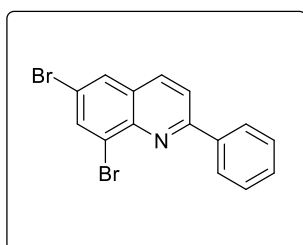
158.61, 146.48, 145.97, 137.45, 132.39, 129.36, 128.32, 128.26, 127.68, 127.17, 126.20, 125.47, 32.08, 30.30, 29.82, 23.82, 22.06, 13.87. HRMS (ESI): m/z calcd for $C_{21}H_{24}N$ $[M+H]^+$ 290.1908 found 290.1909.

6-nitro-2,4-diphenylquinoline (Table 3, 3ac)¹⁸



1H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.86 (d, J = 2.5 Hz, 1H), 8.49 (dd, J = 9.2, 2.5 Hz, 1H), 8.34 (d, J = 9.2 Hz, 1H), 8.25 (dd, J = 8.0, 1.6 Hz, 2H), 7.98 (s, 1H), 7.67-7.48 (m, 8H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 160.06, 151.29, 151.07, 145.42, 138.52, 136.91, 131.79, 130.48, 129.48, 129.35, 129.16, 129.08, 127.86, 124.83, 123.10, 122.95, 120.75. HRMS (ESI): m/z calcd for $C_{21}H_{15}N_2O_2$ $[M+H]^+$ 327.11280 found 327.11359.

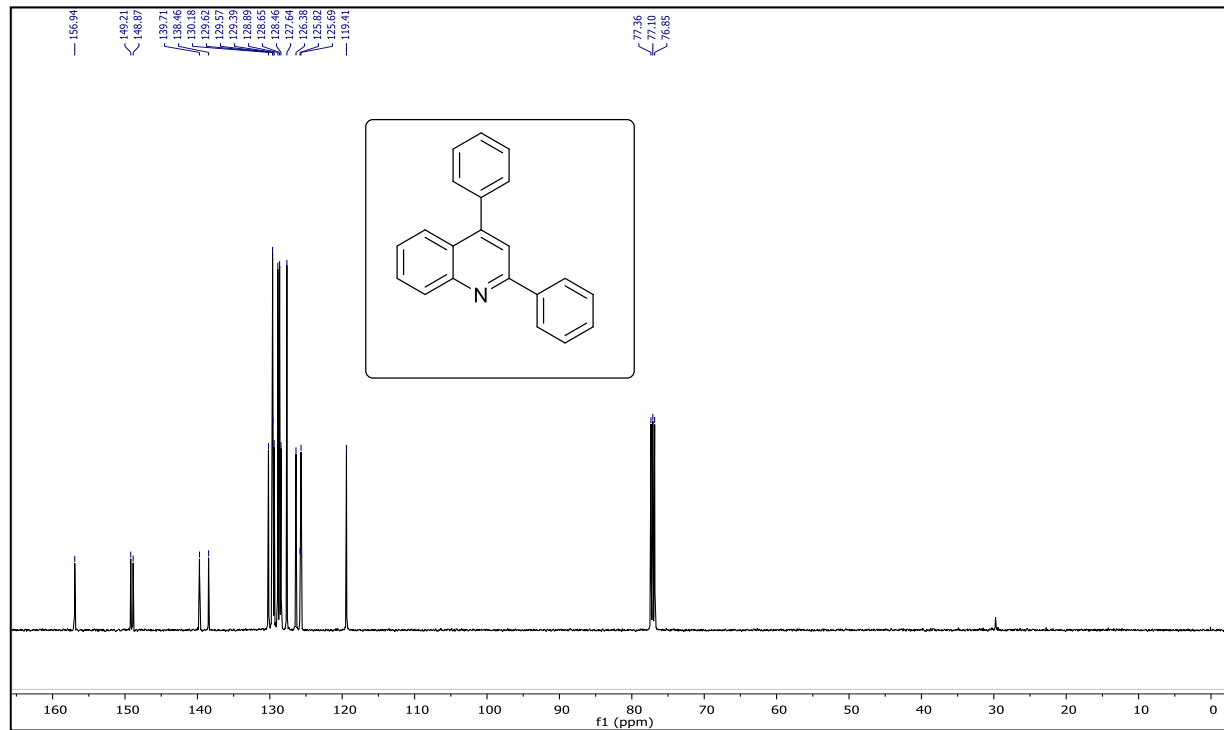
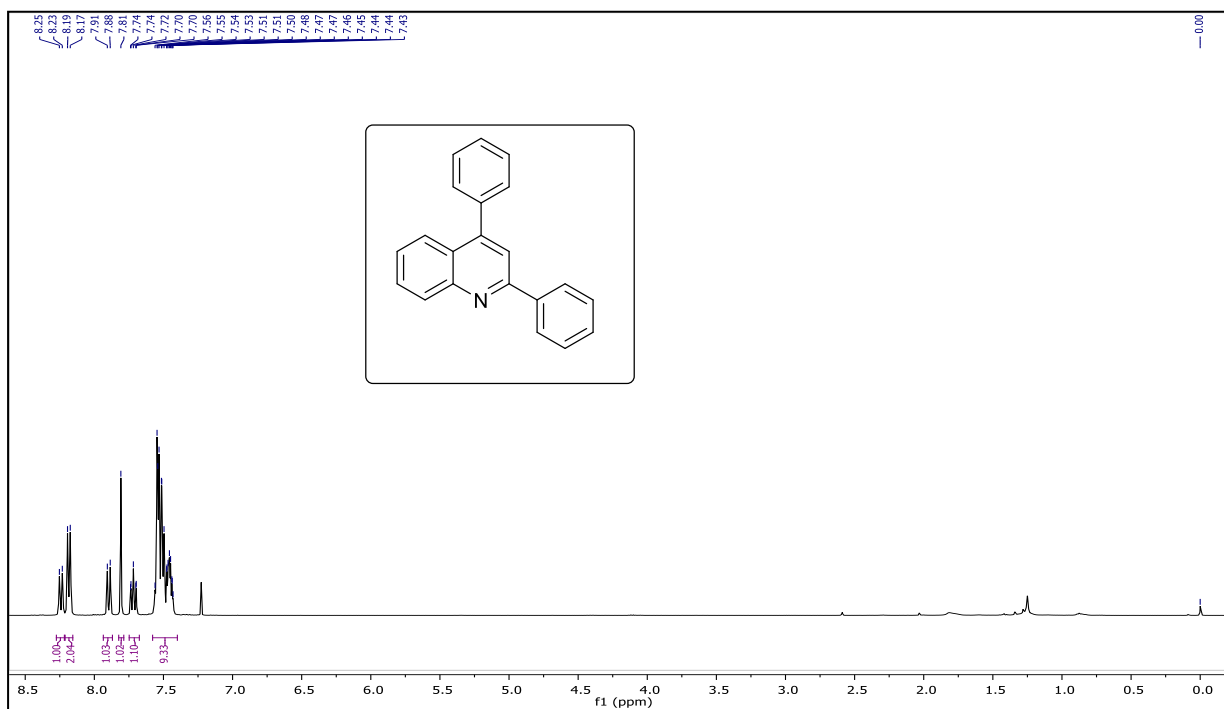
6,8-dibromo-2-phenylquinoline (Table 3, 3ad)¹⁹



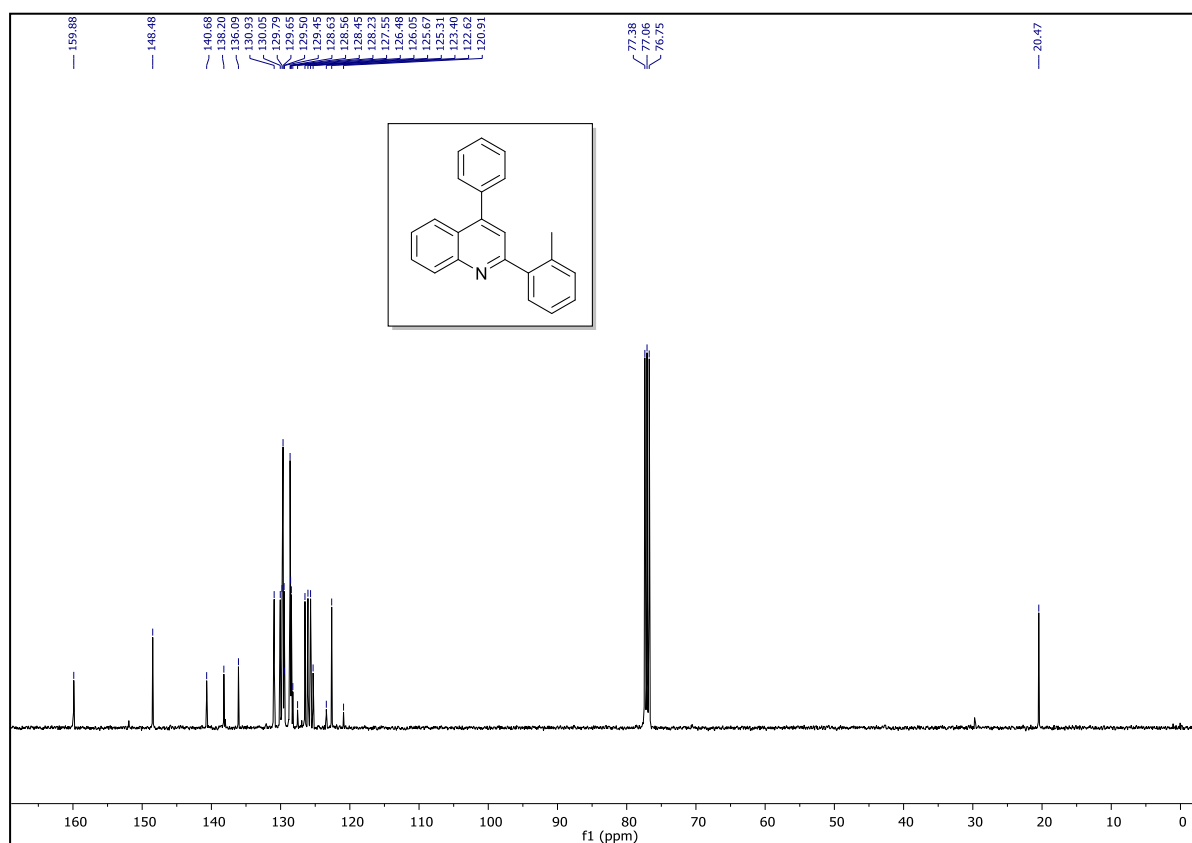
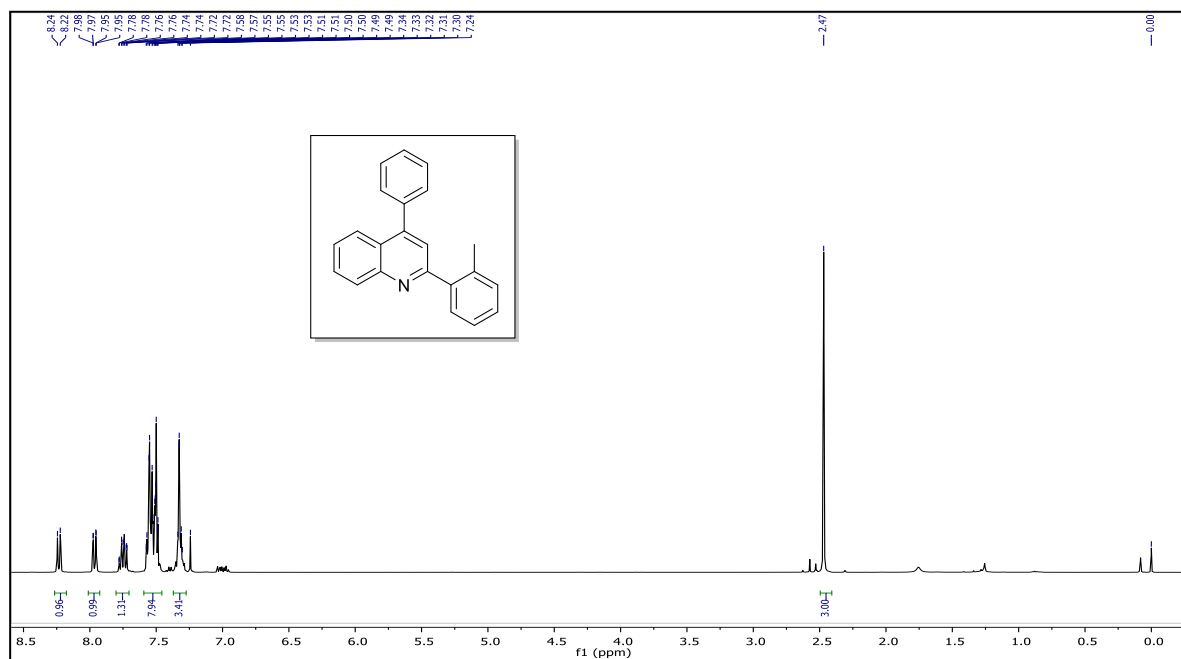
1H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.36-8.18 (m, 2H), 8.17-7.75 (m, 4H), 7.61-7.41 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 157.77, 143.88, 138.44, 136.26, 135.94, 130.10, 129.32, 128.98, 128.87, 127.66, 126.57, 119.96, 119.31. HRMS (ESI): m/z calcd for $C_{15}H_{10}Br_2N$ $[M+H]^+$ 363.05 found 363.914.

3. Copies of ^1H , ^{13}C NMR spectra of products

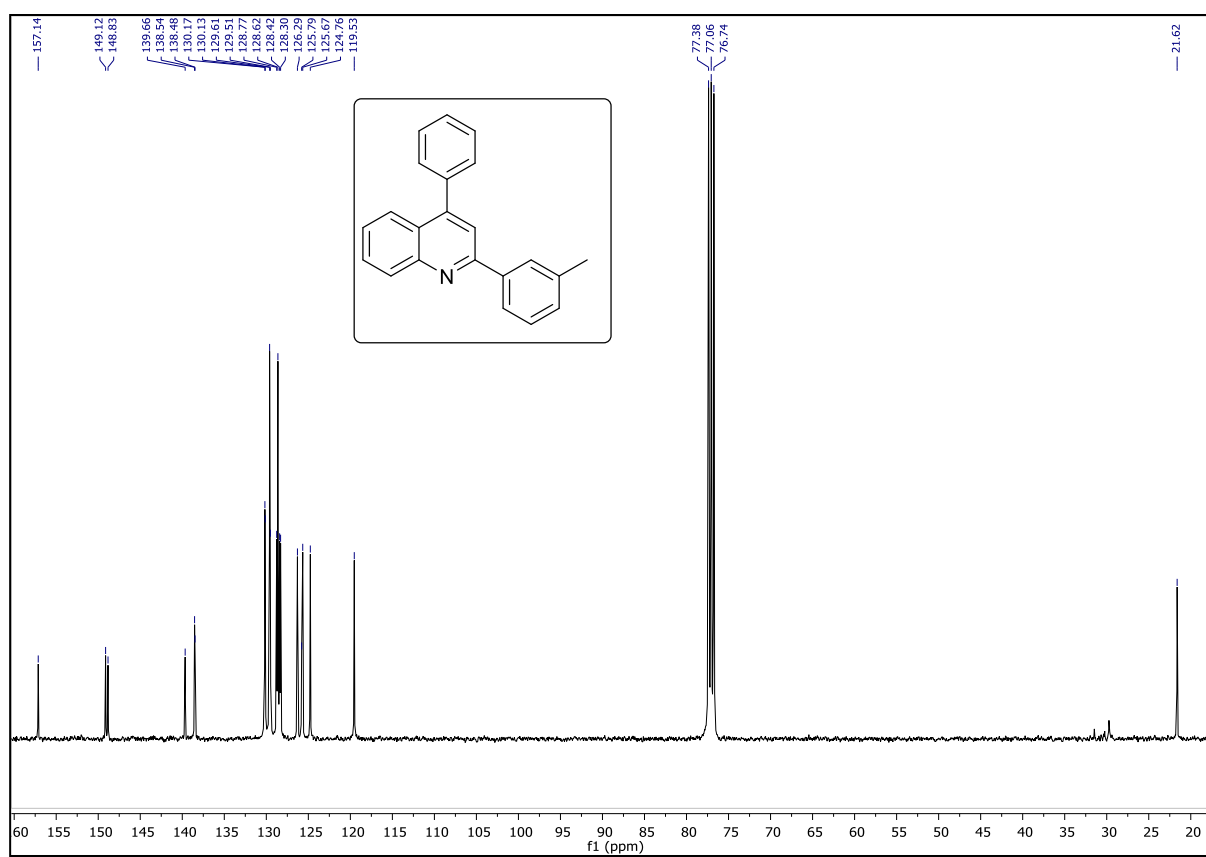
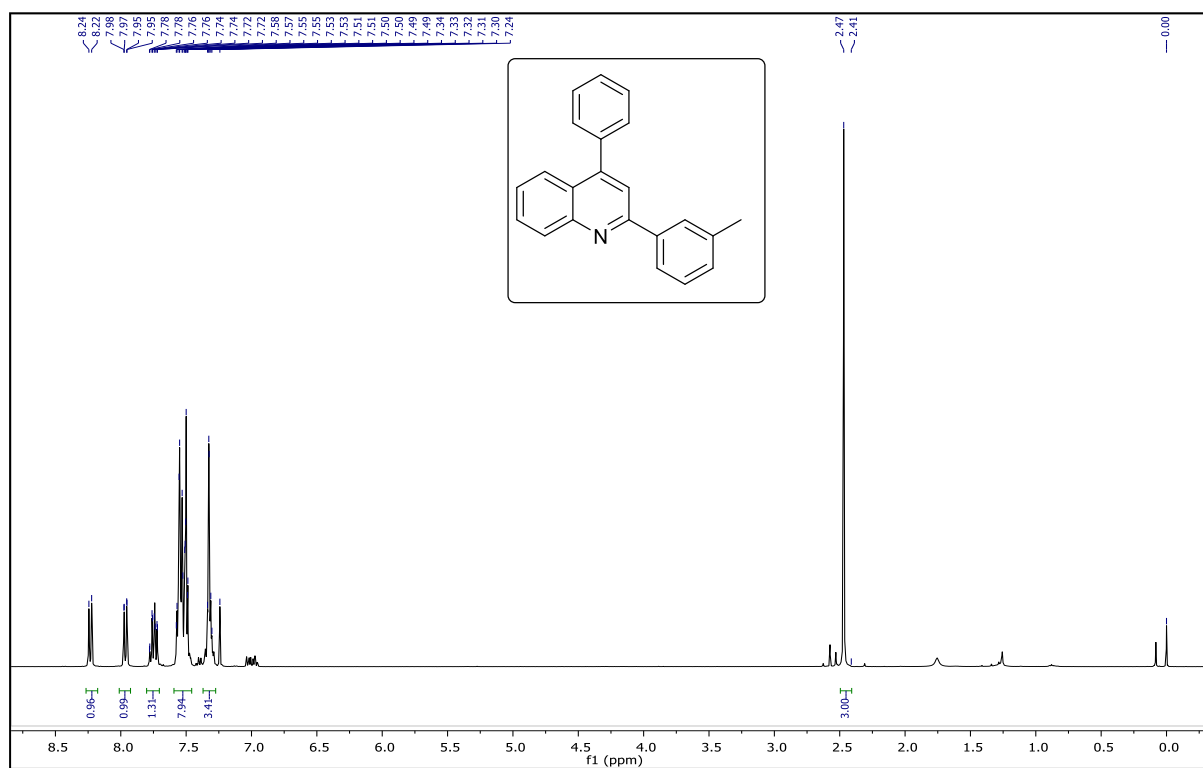
2,4-diphenylquinoline (Table 2, 3a)



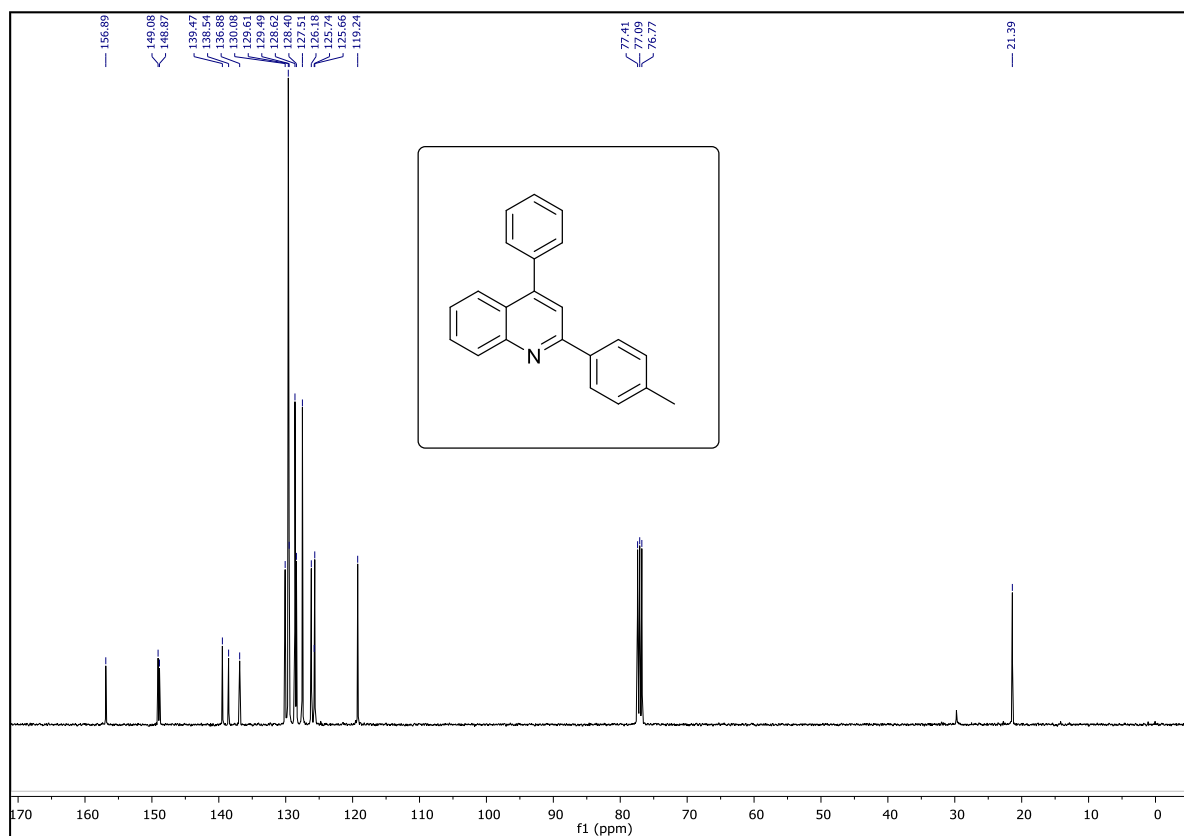
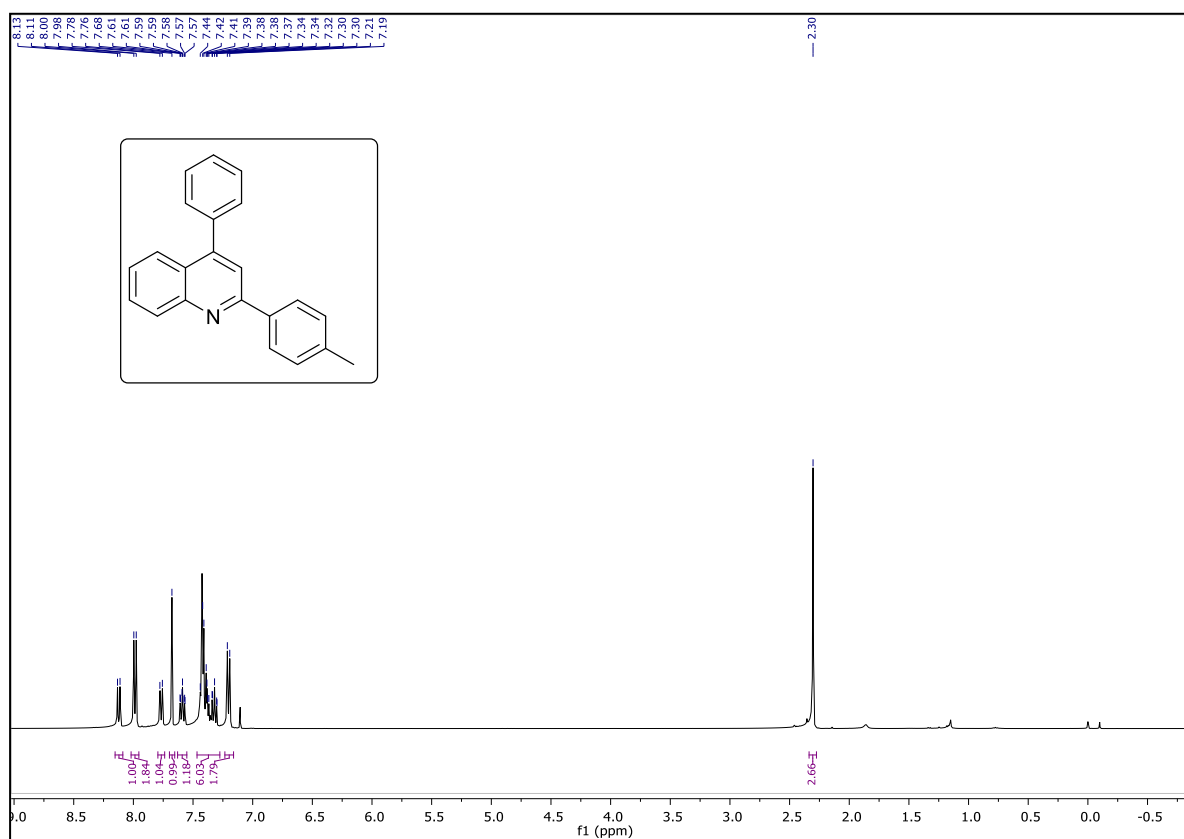
4-phenyl-2-(*o*-tolyl)quinoline (Table 2, 3b)



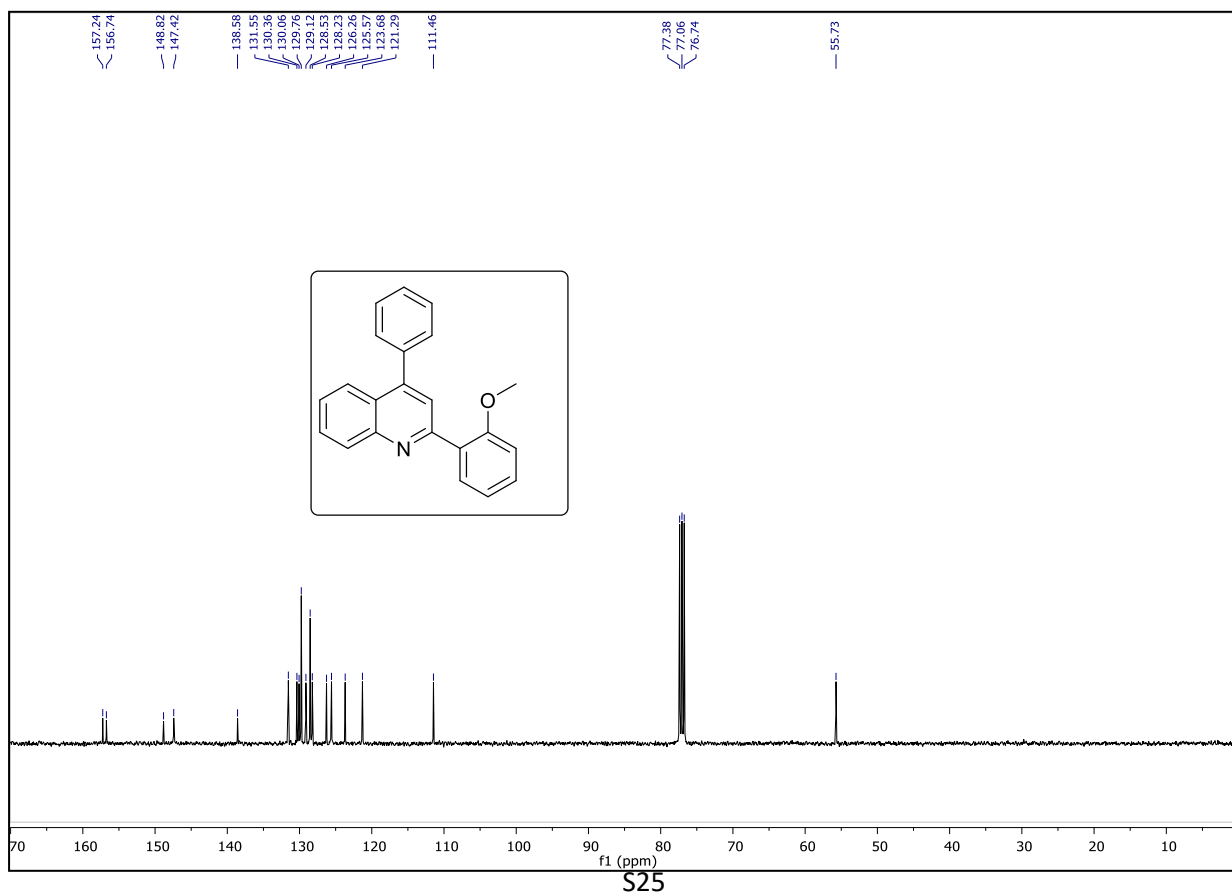
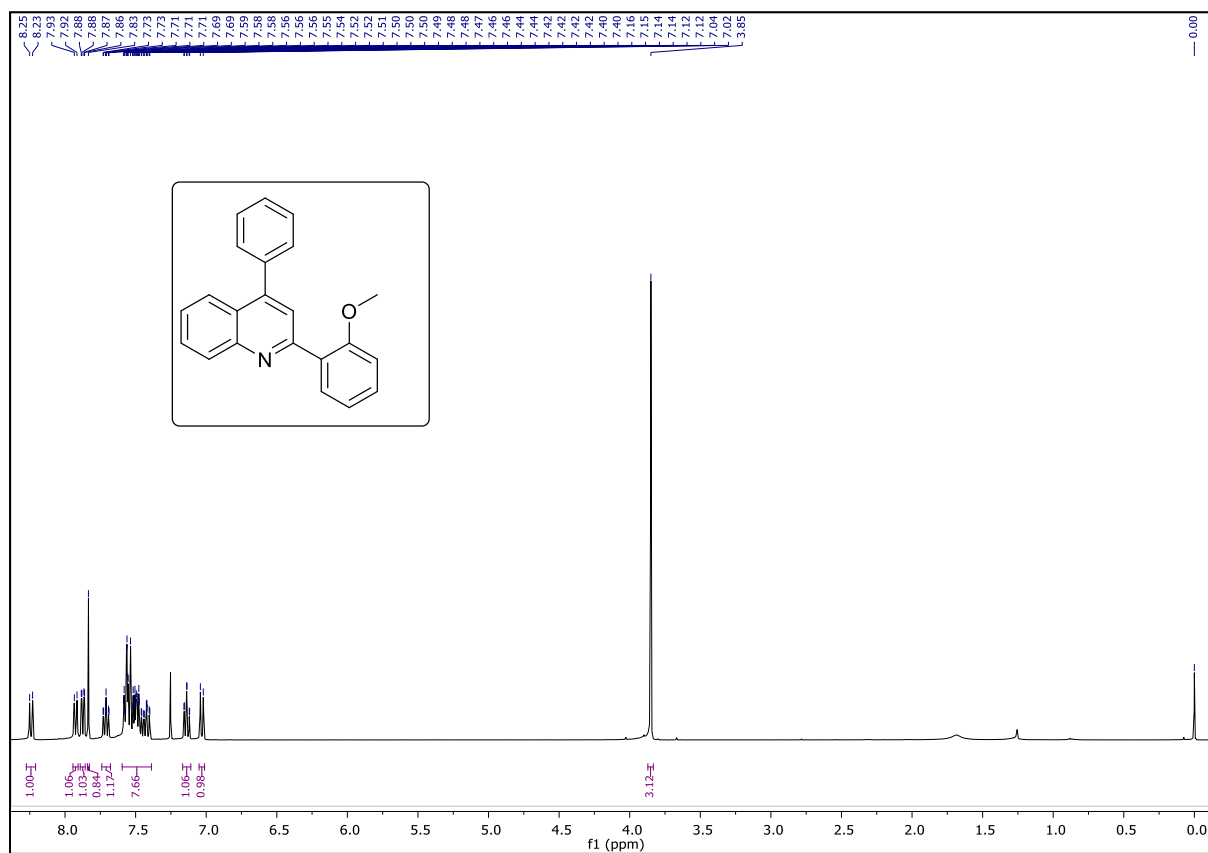
4-phenyl-2-(*m*-tolyl)quinoline (Table 2, 3c)



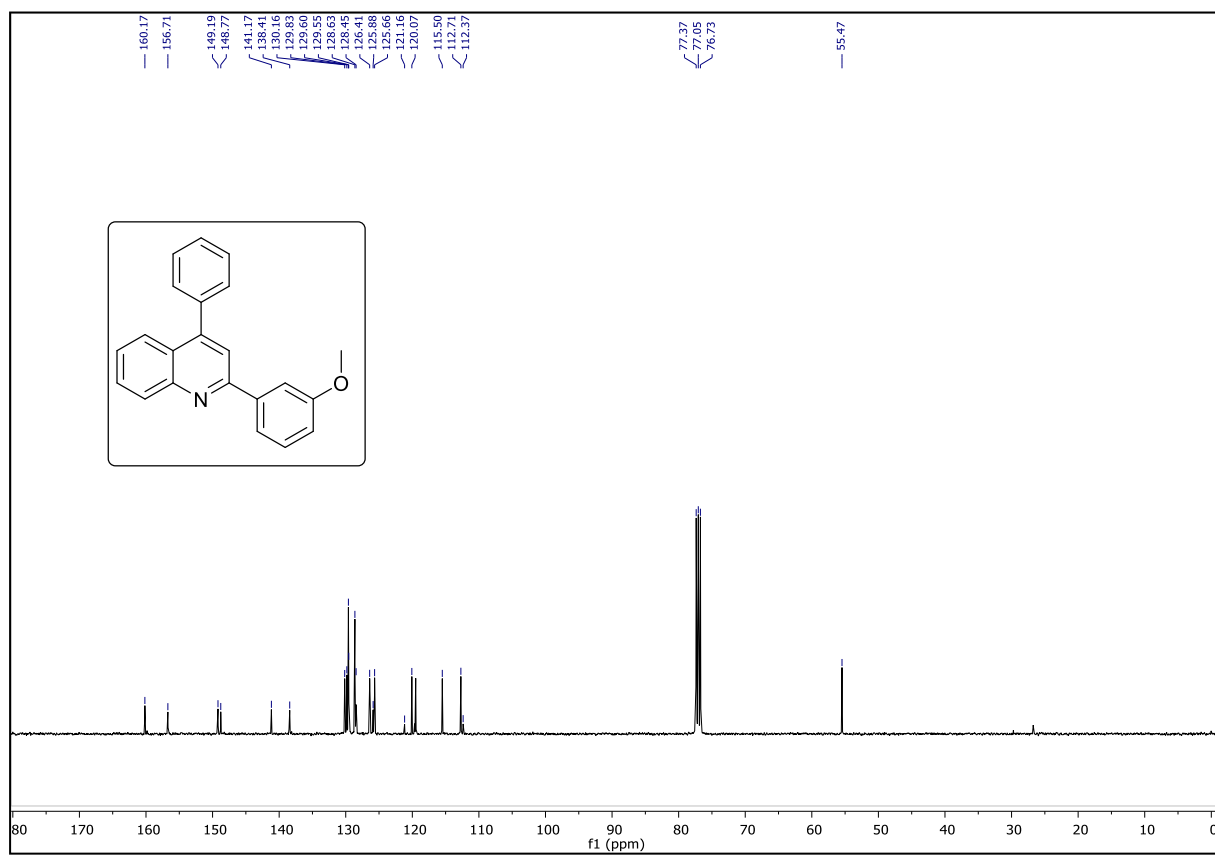
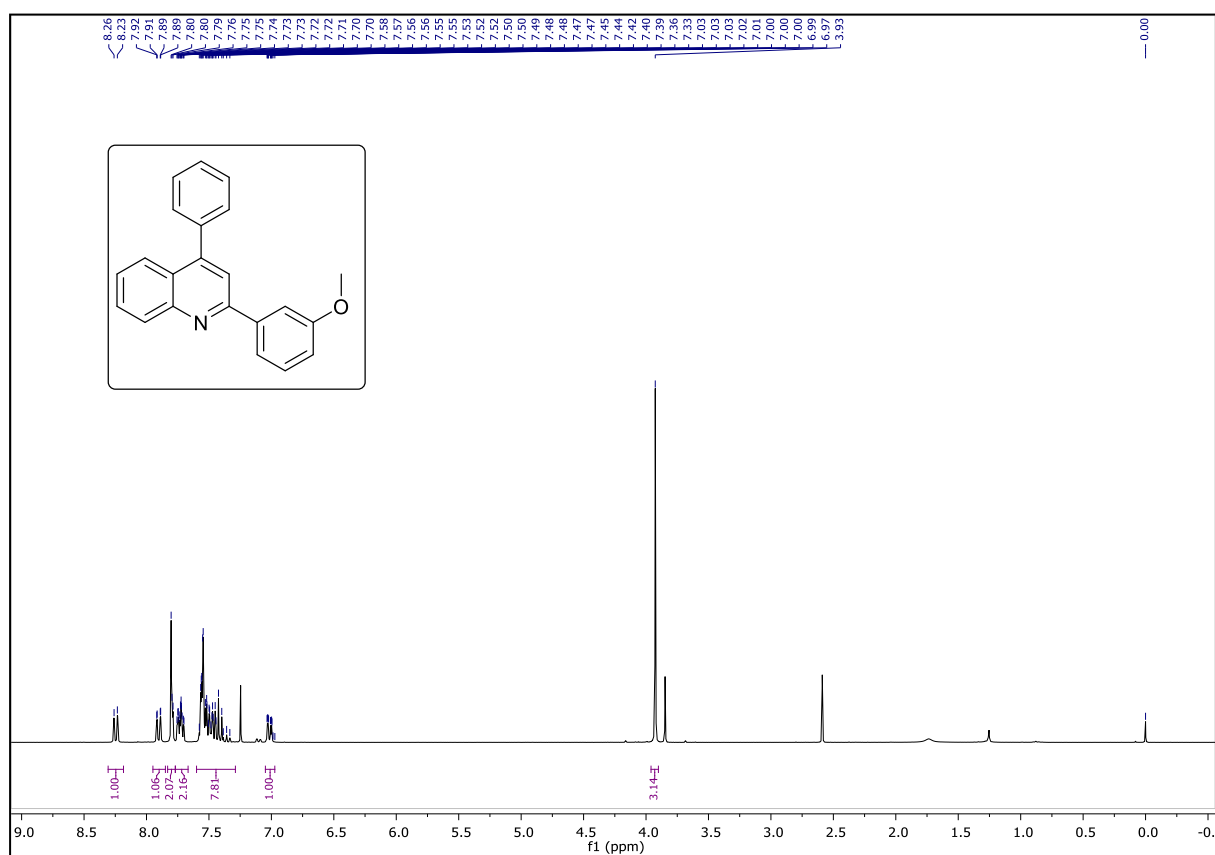
4-phenyl-2-(*p*-tolyl)quinoline (Table 2, 3d)



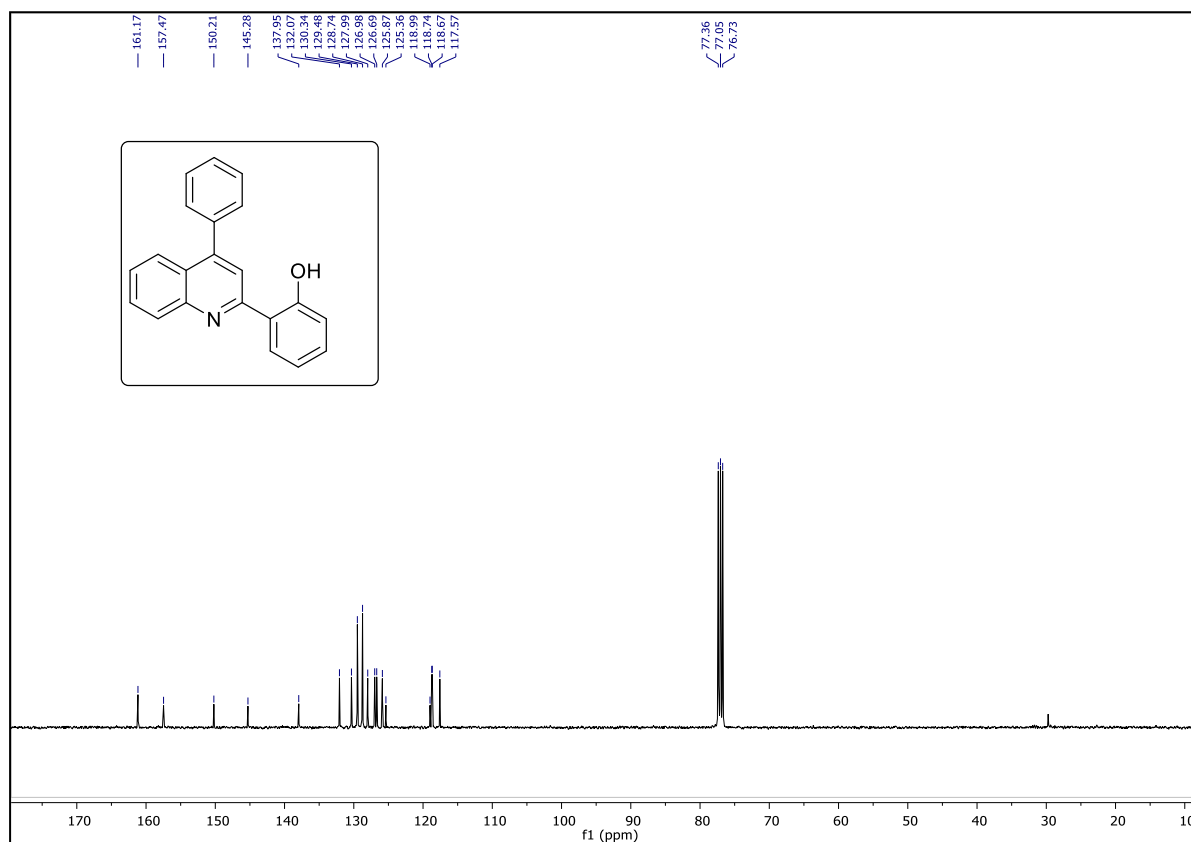
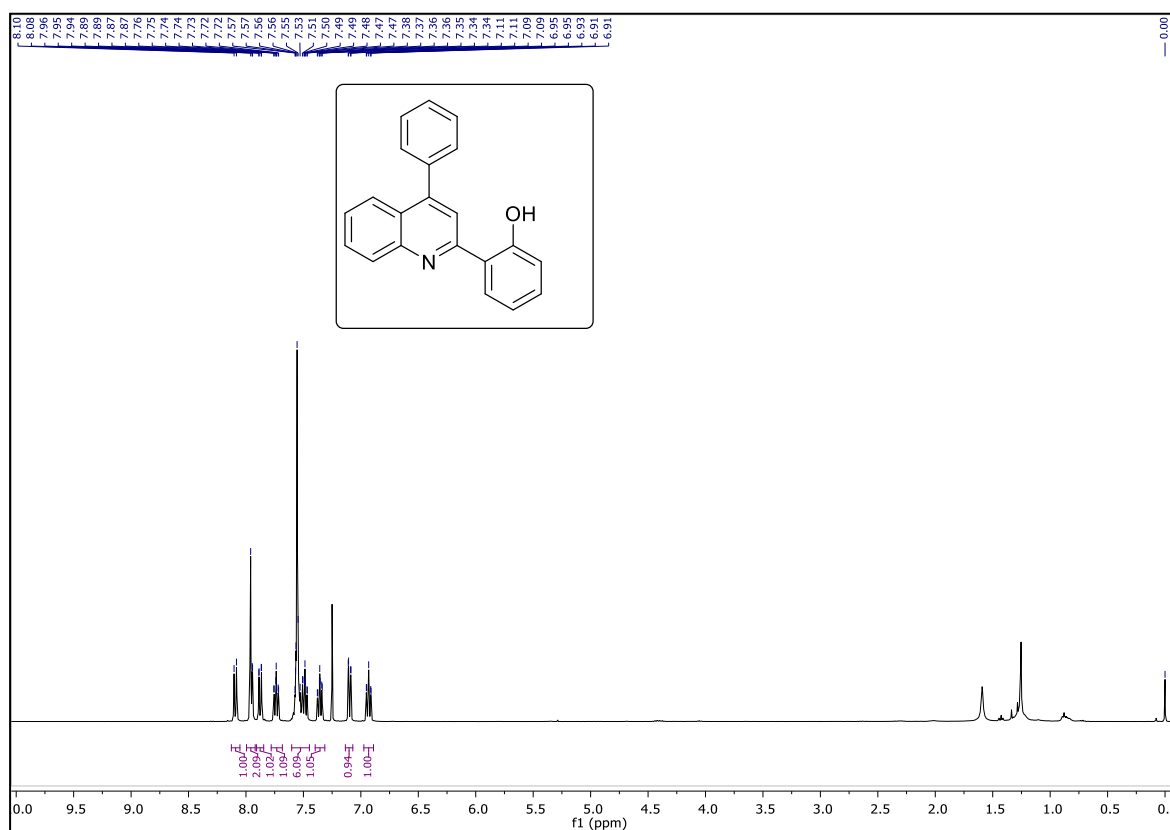
2-(2-methoxyphenyl)-4-phenylquinoline (Table 2, 3e)



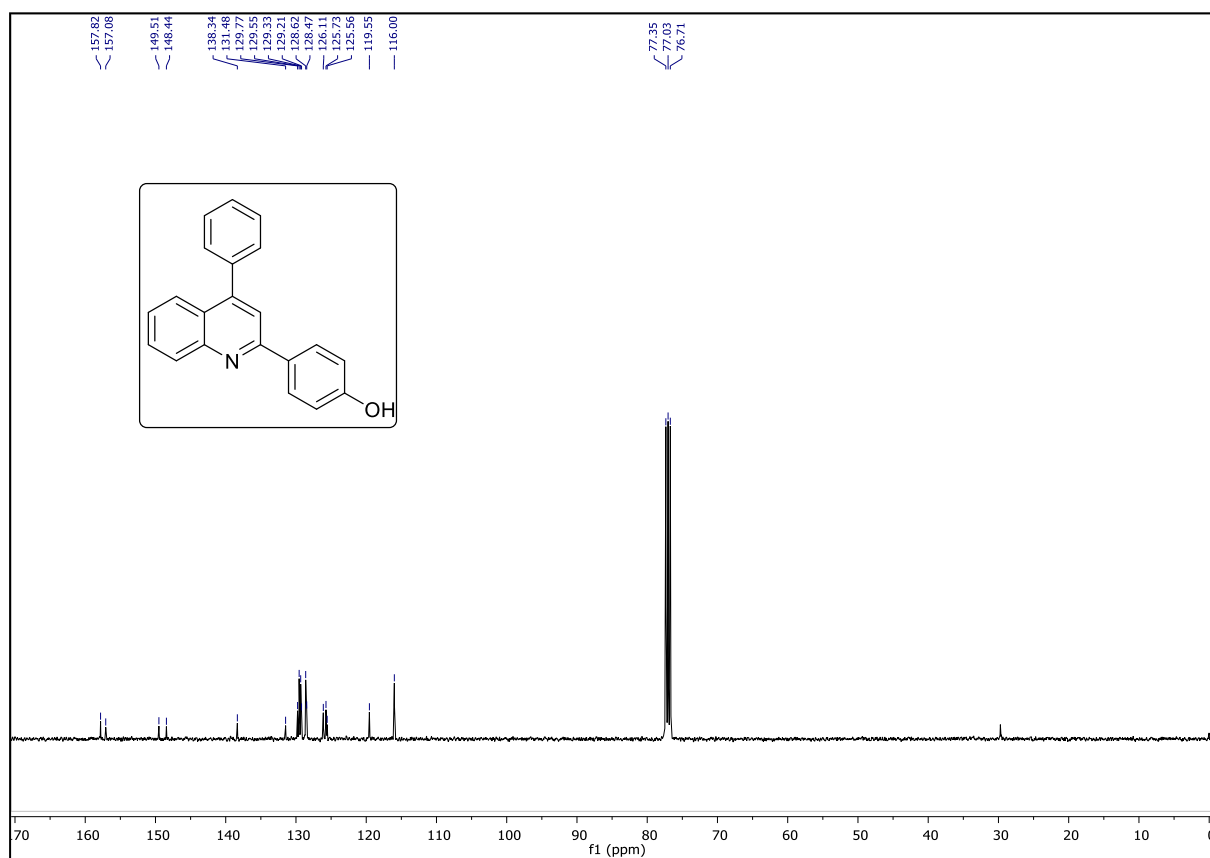
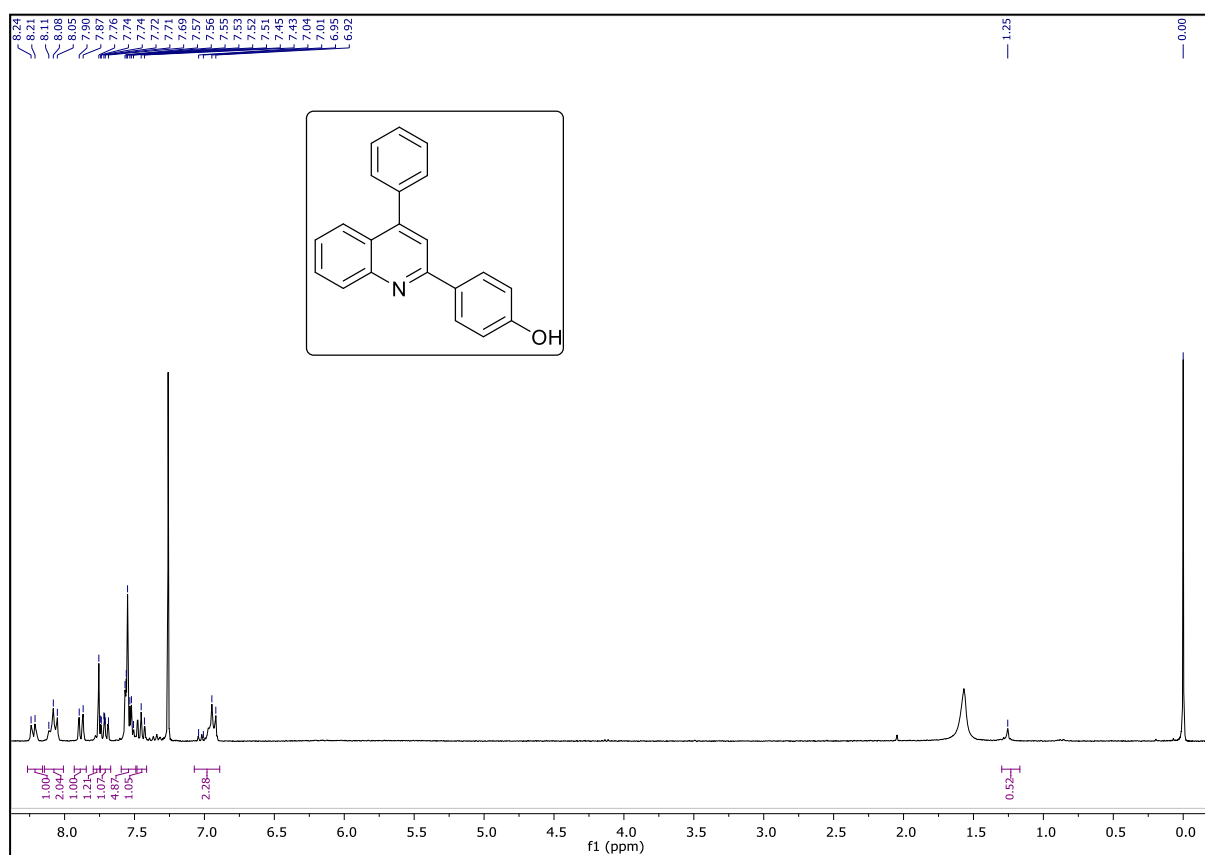
2-(3-methoxyphenyl)-4-phenylquinoline (Table 2, 3f)



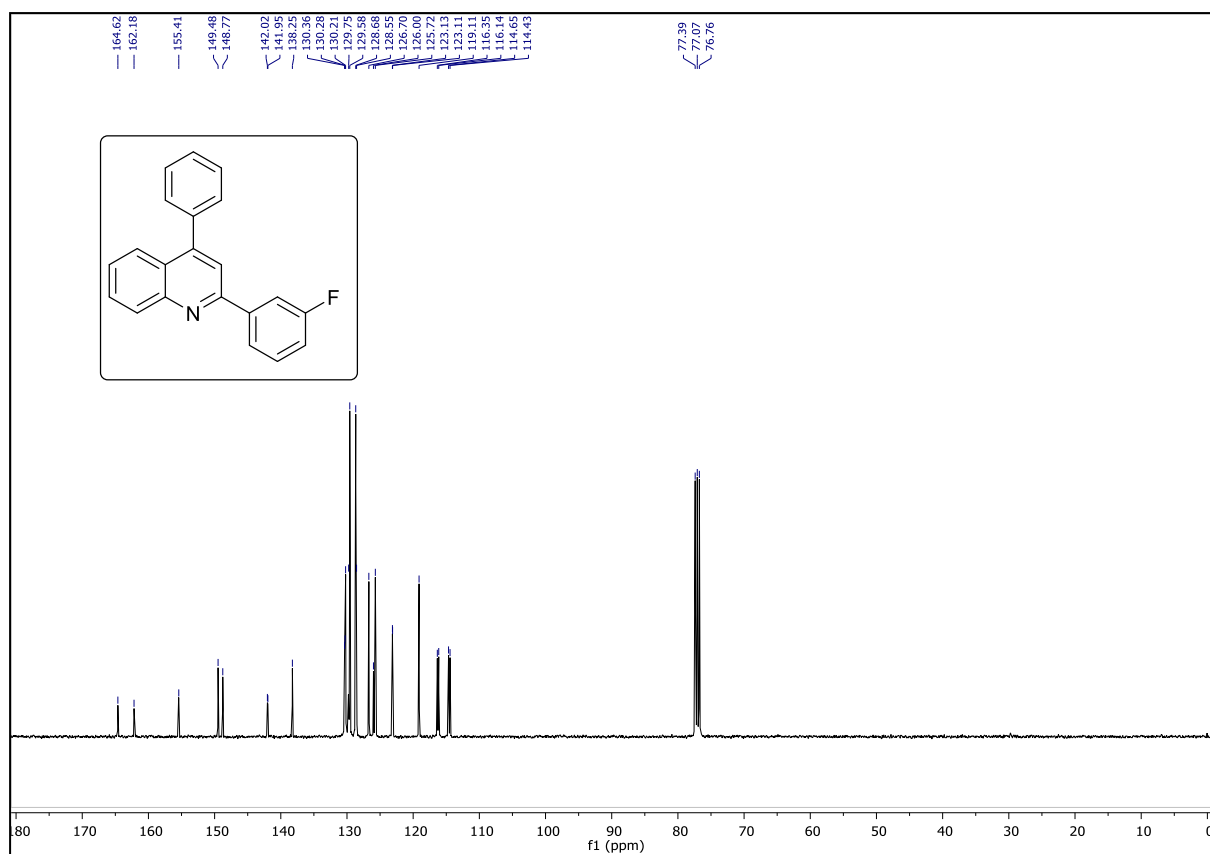
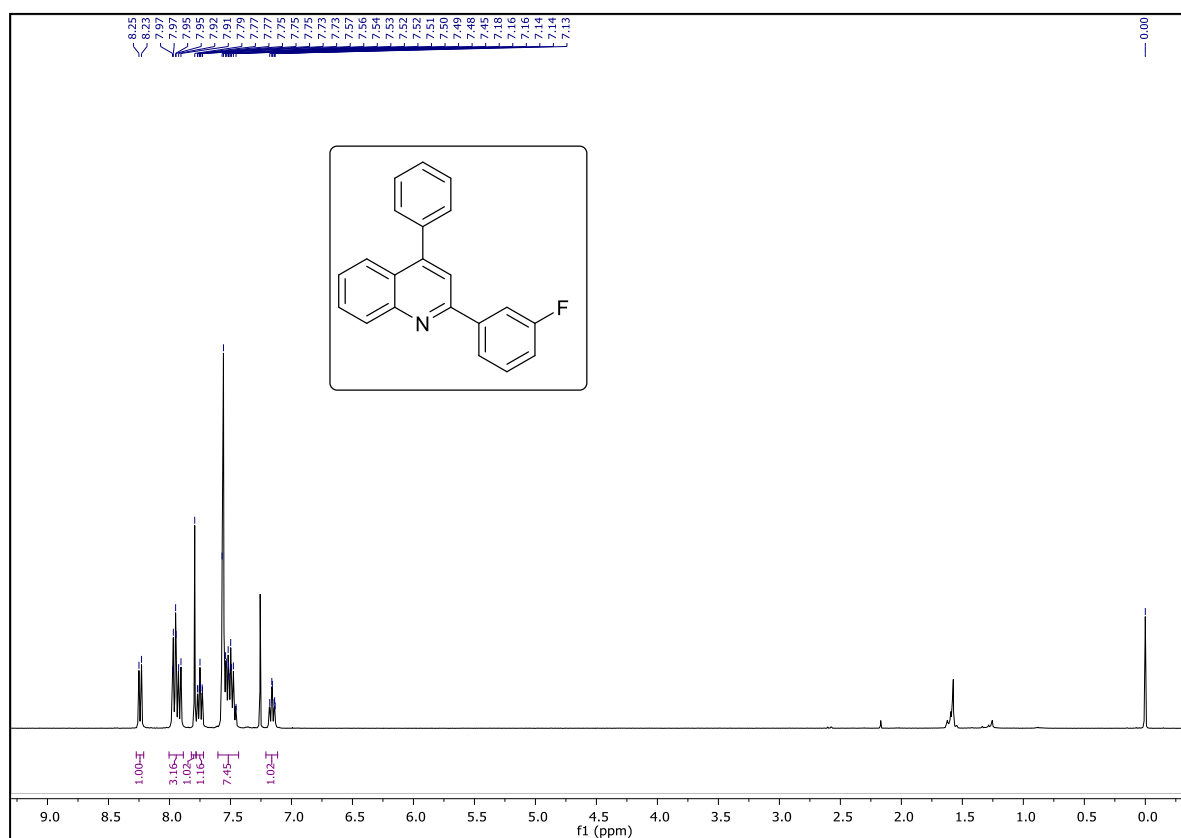
2-(4-phenylquinolin-2-yl)phenol (Table 2, 3g)



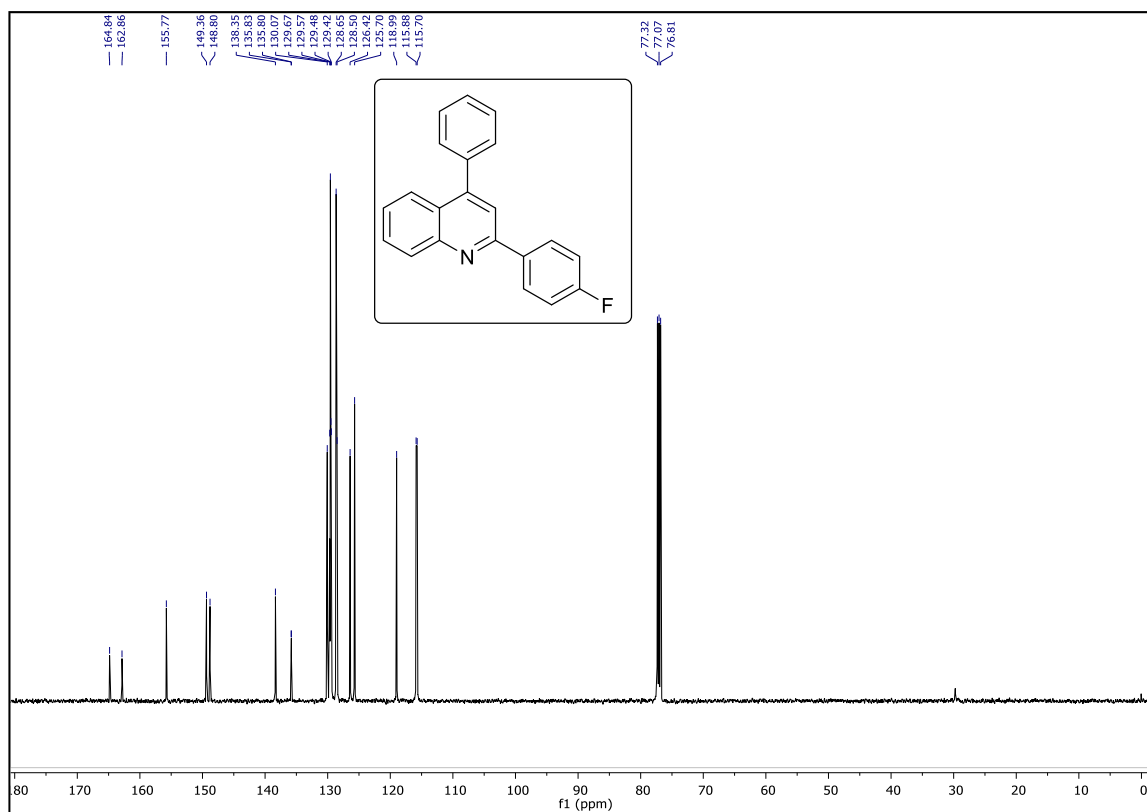
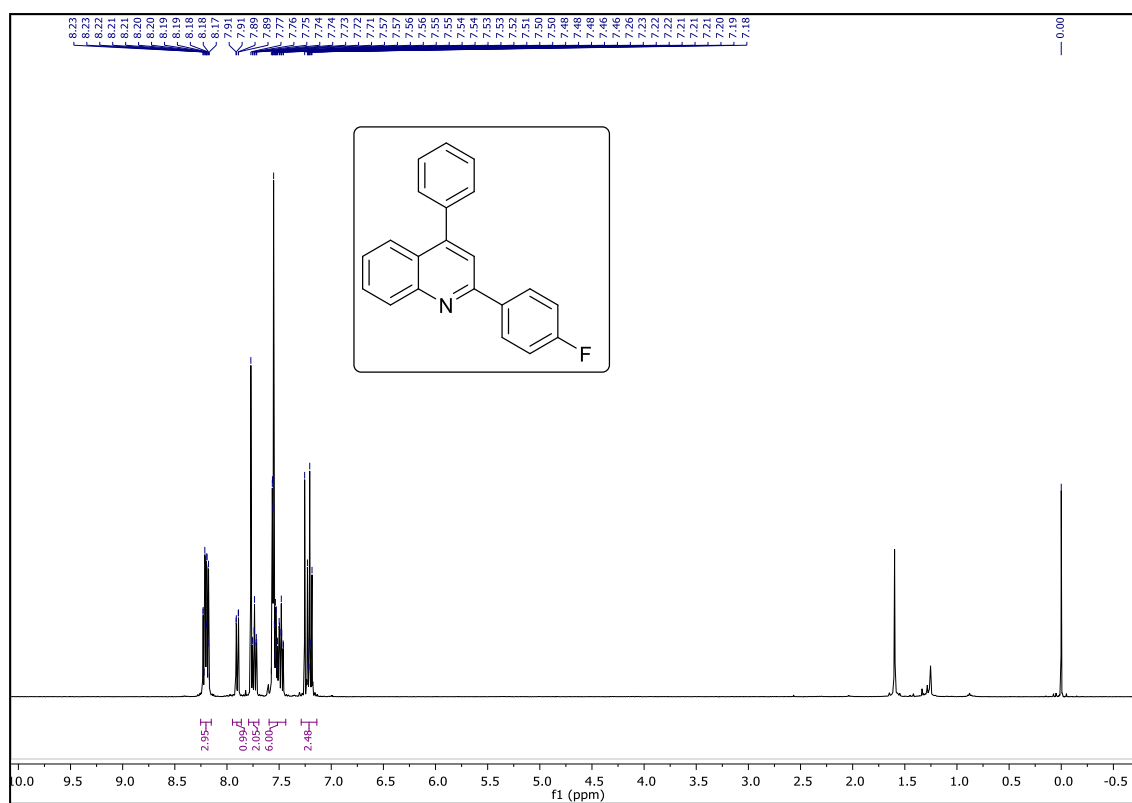
4-(4-phenylquinolin-2-yl)phenol (Table 2, 3h)



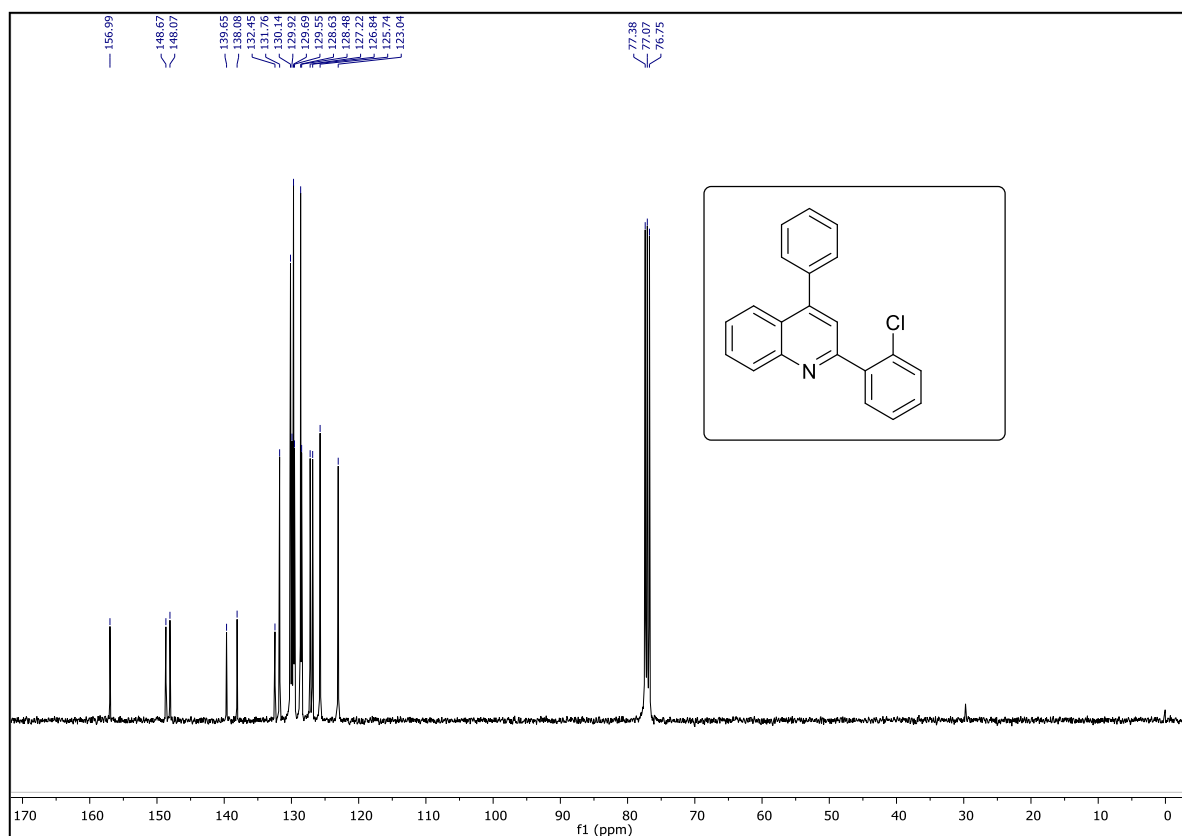
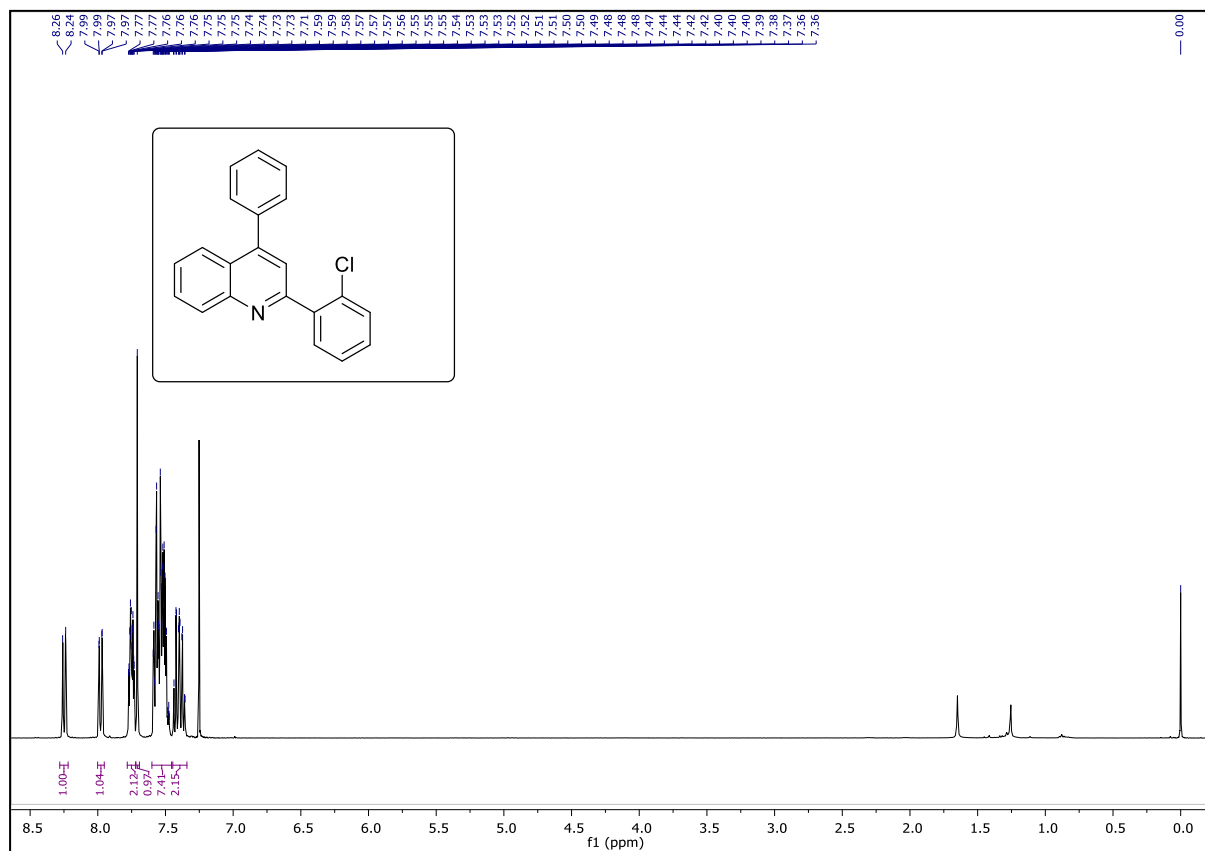
(3-fluorophenyl)-4-phenylquinoline (Table 2, 3i)



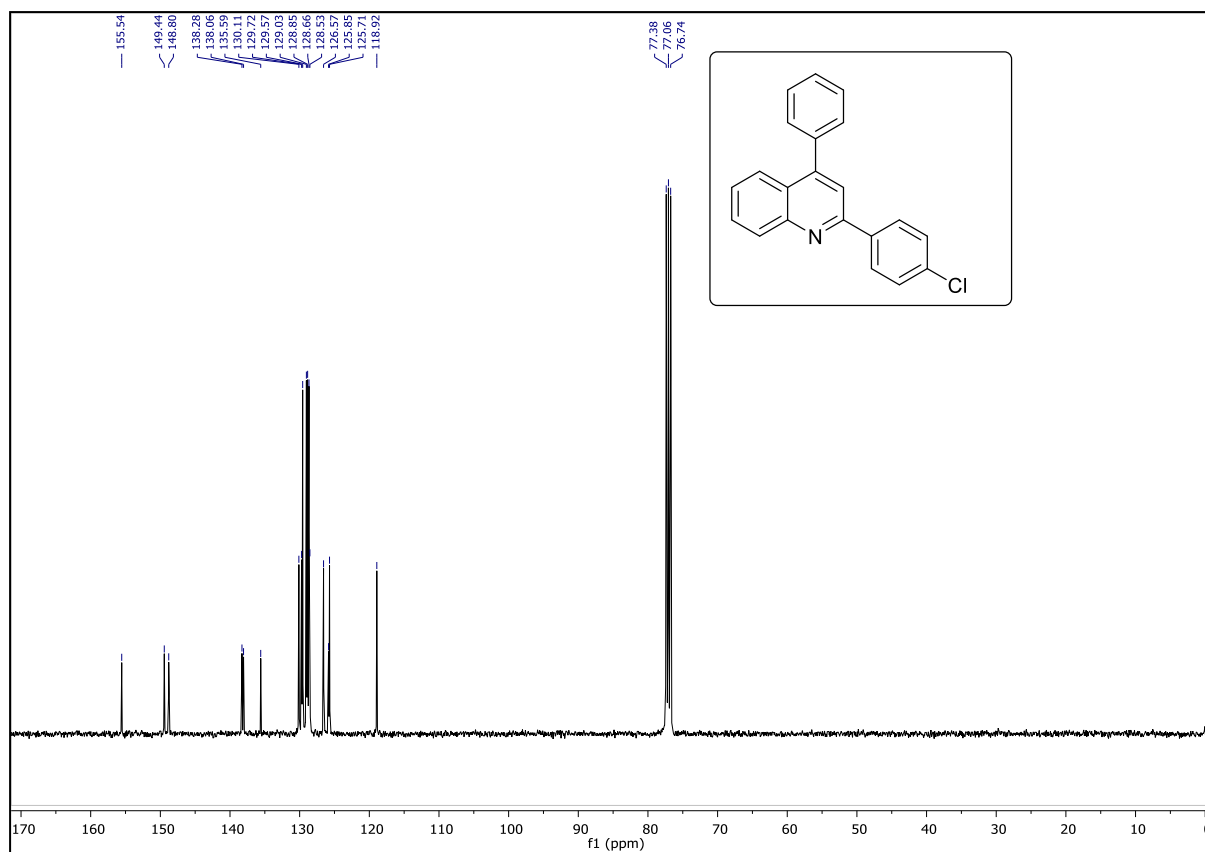
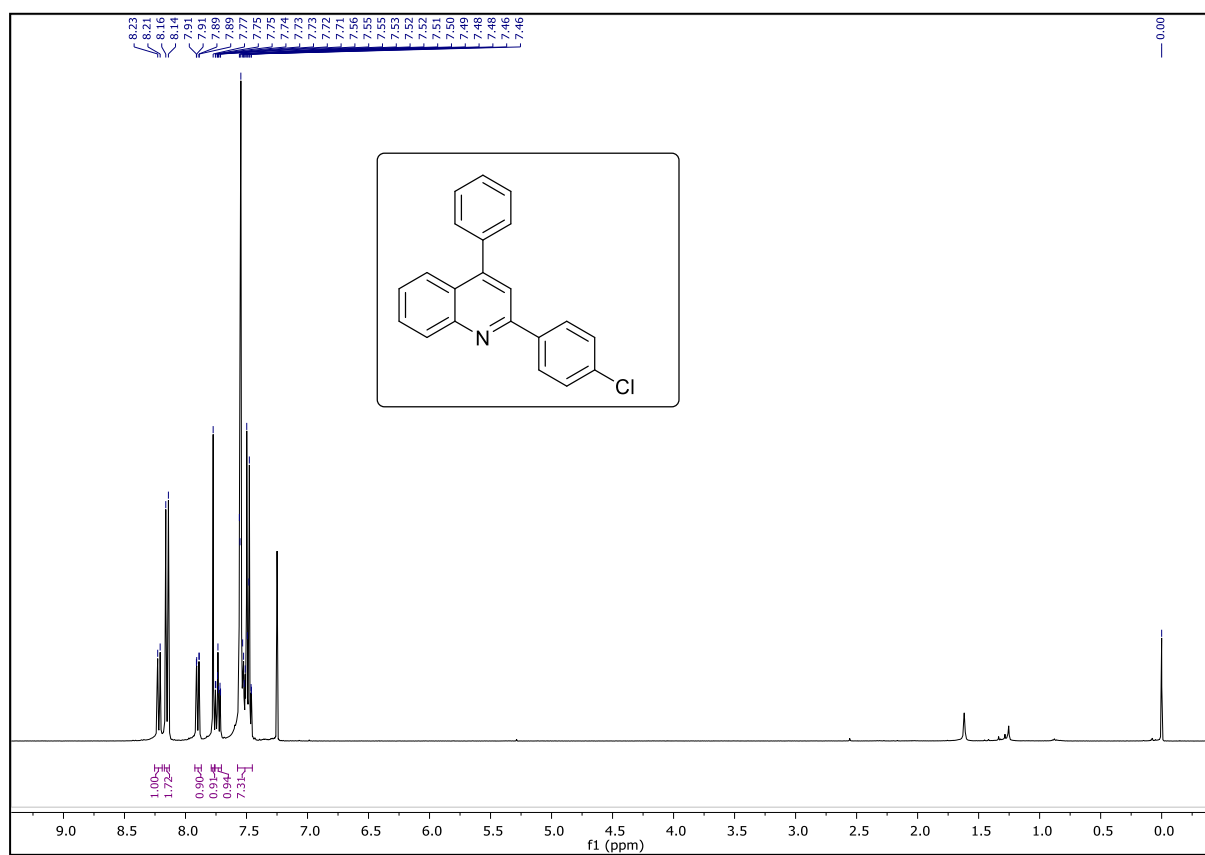
2-(4-fluorophenyl)-4-phenylquinoline (Table 2, 3j)



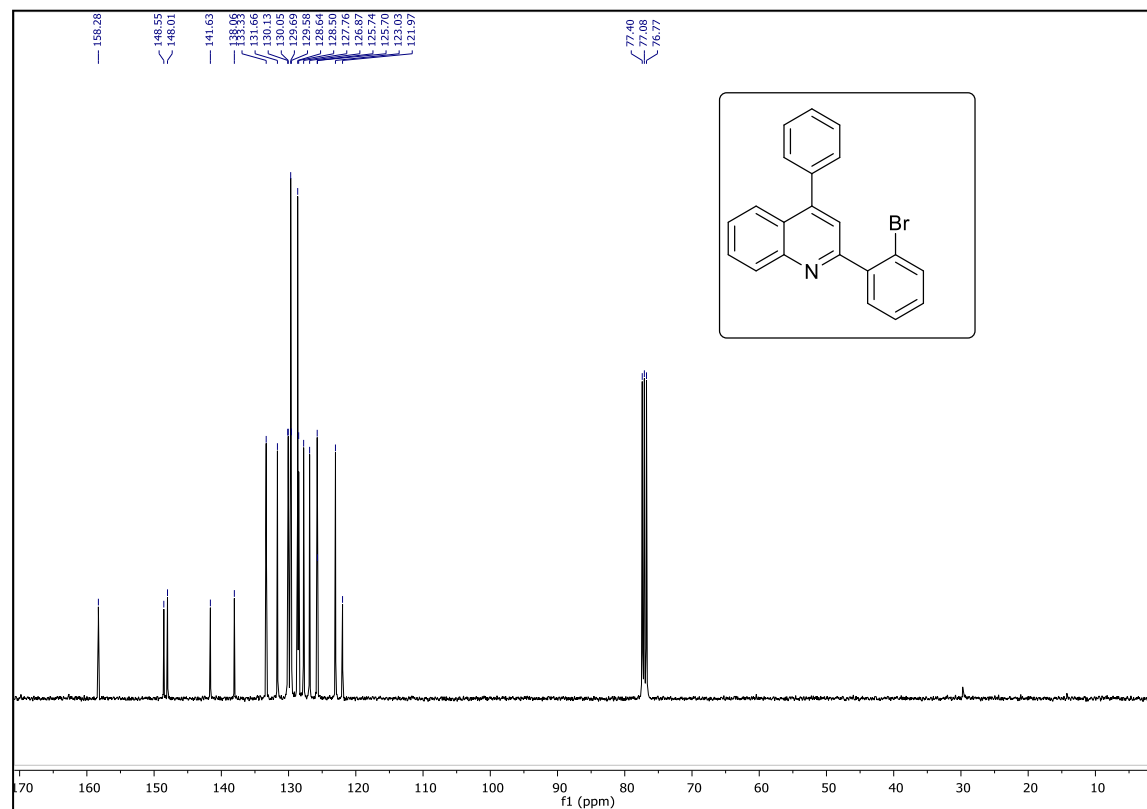
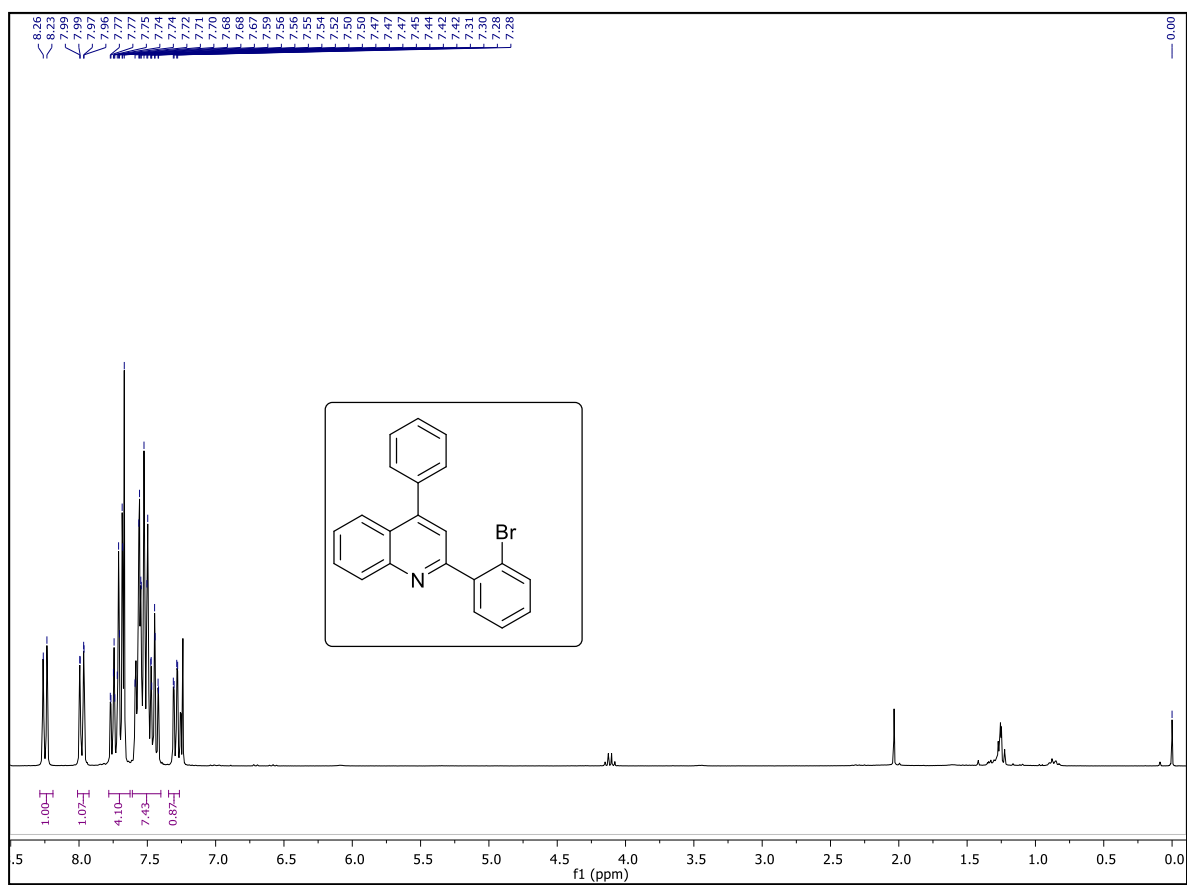
2-(2-chlorophenyl)-4-phenylquinoline (Table 2, 3k)



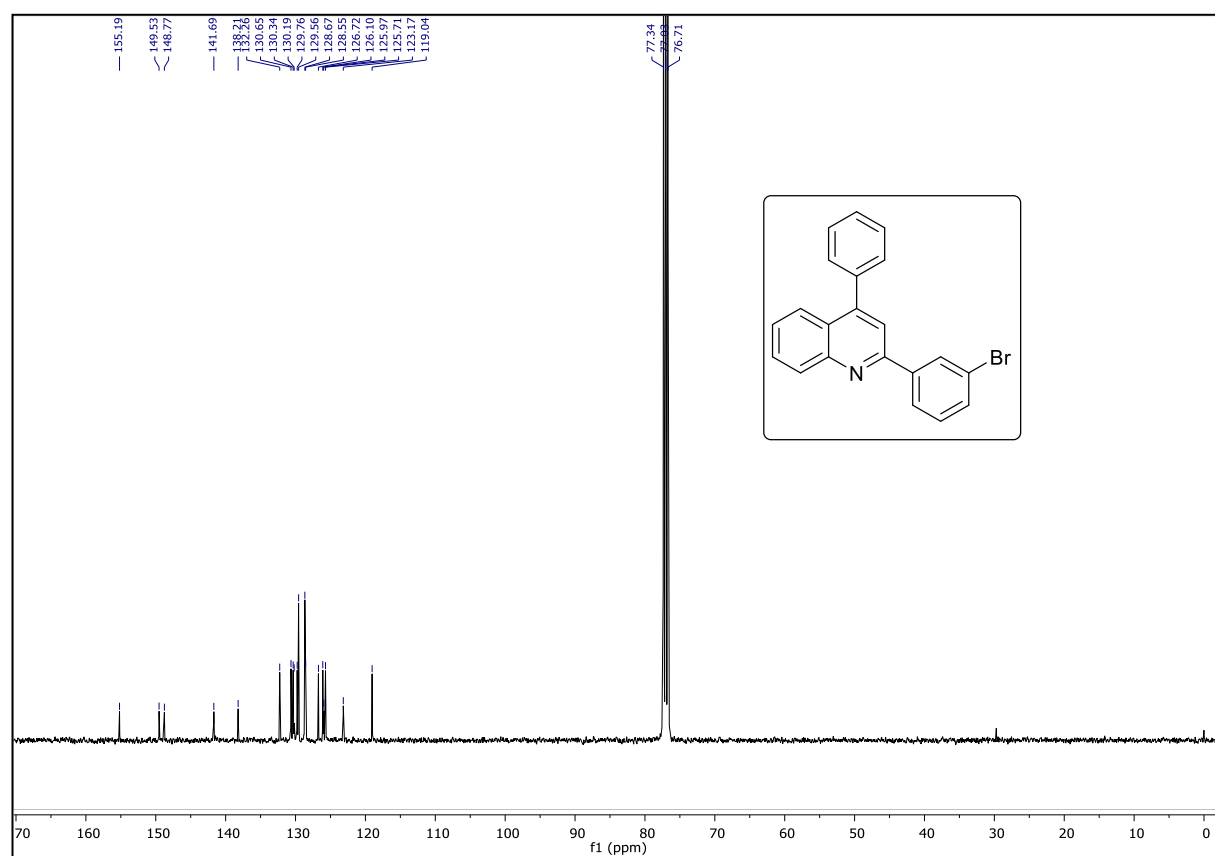
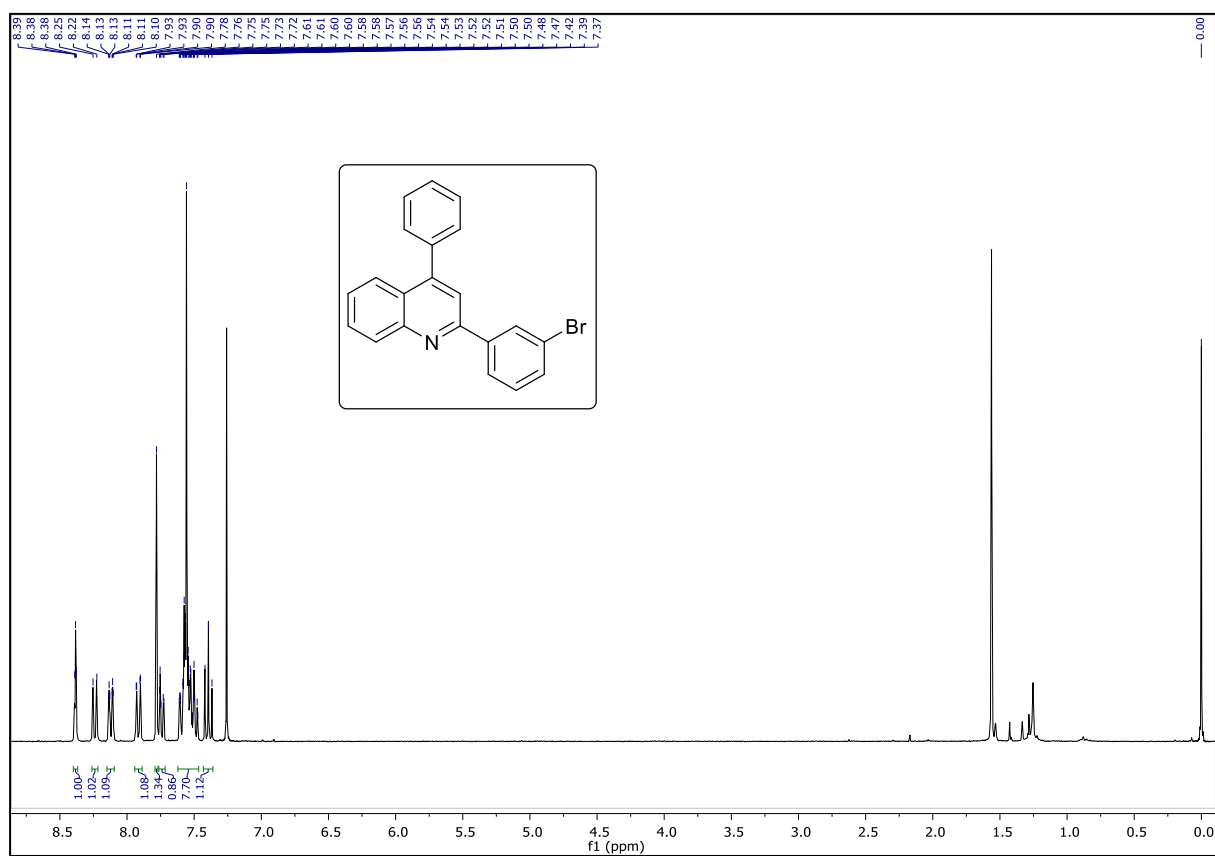
2-(4-chlorophenyl)-4-phenylquinoline (Table 2, 3I)



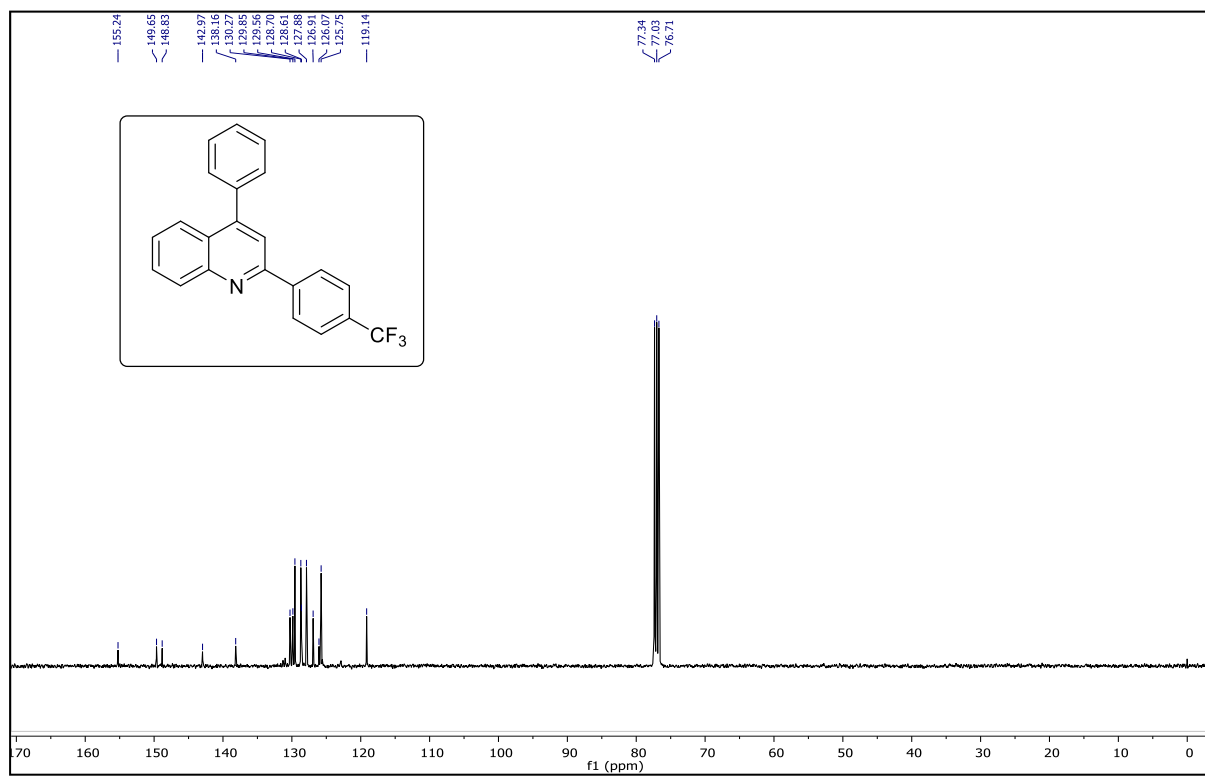
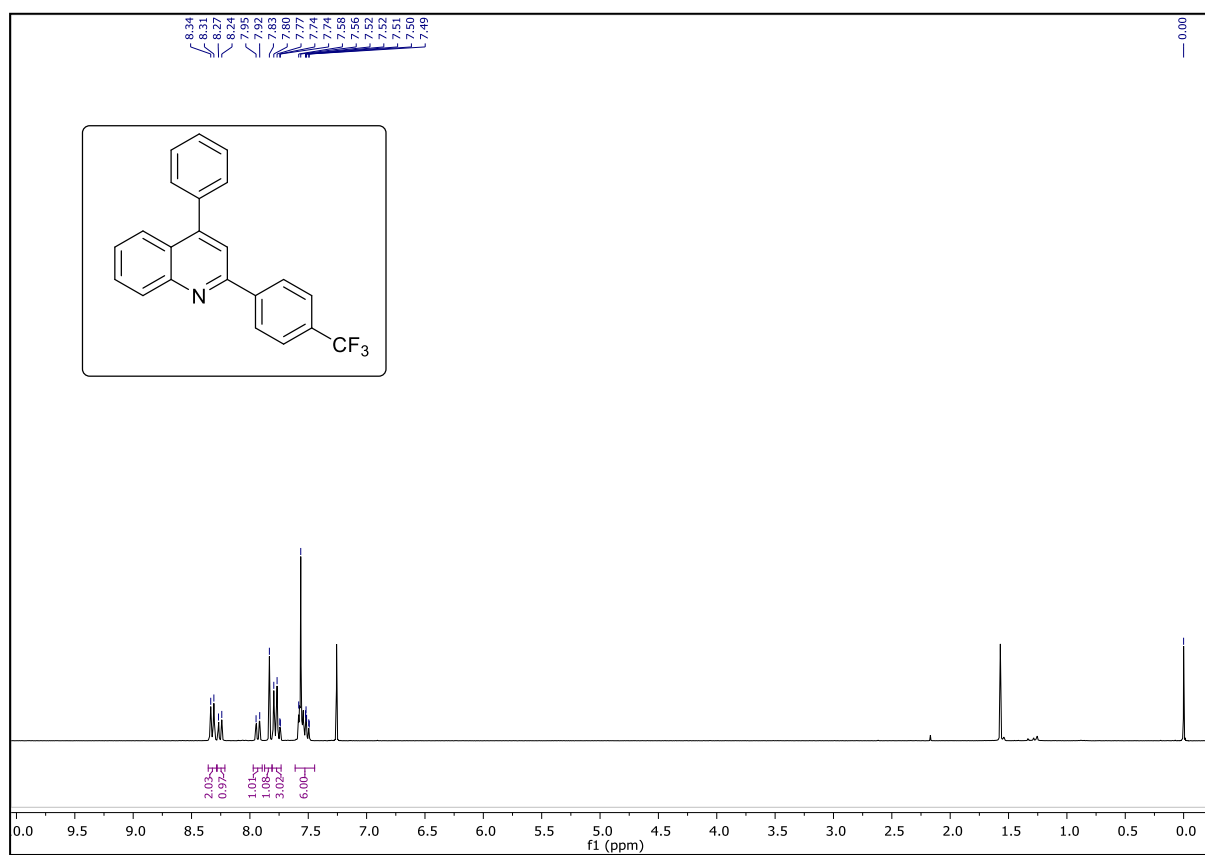
2-(2-bromophenyl)-4-phenylquinoline (Table 2, 3m)



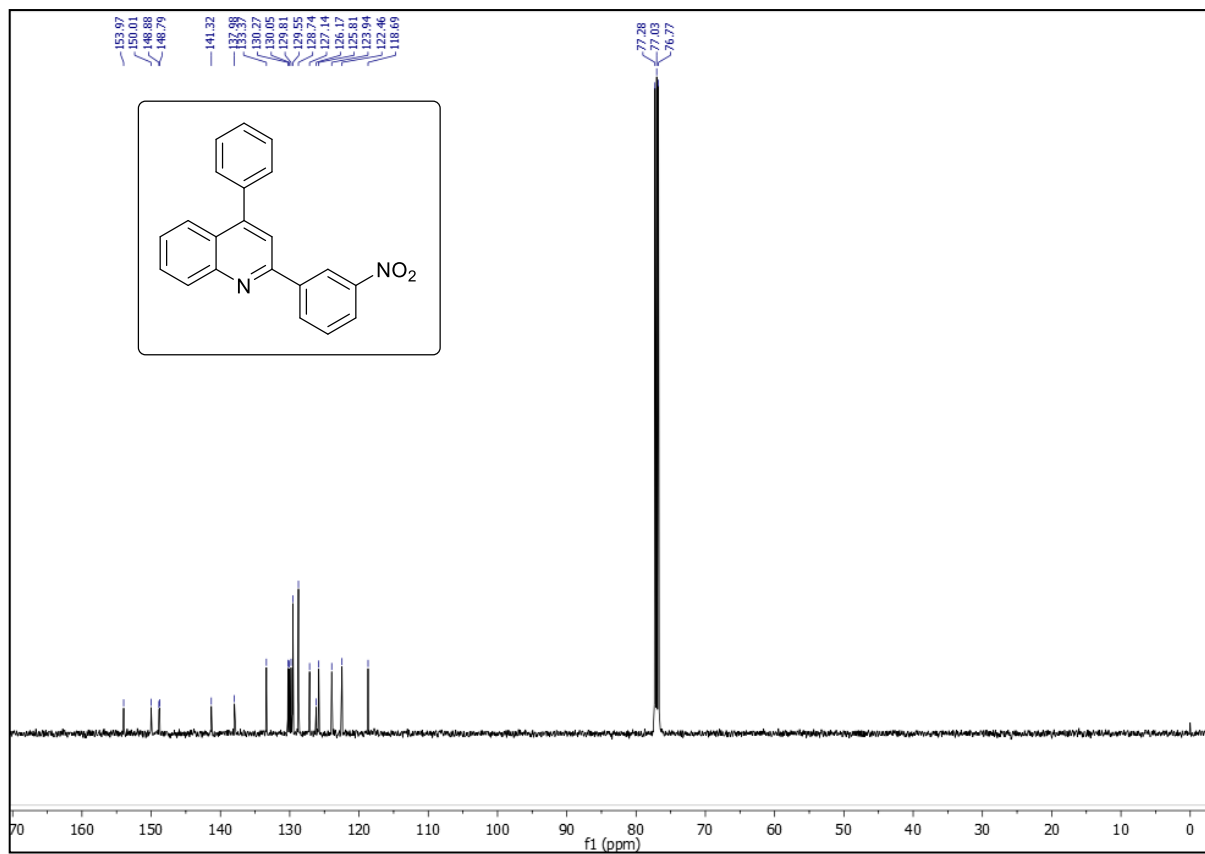
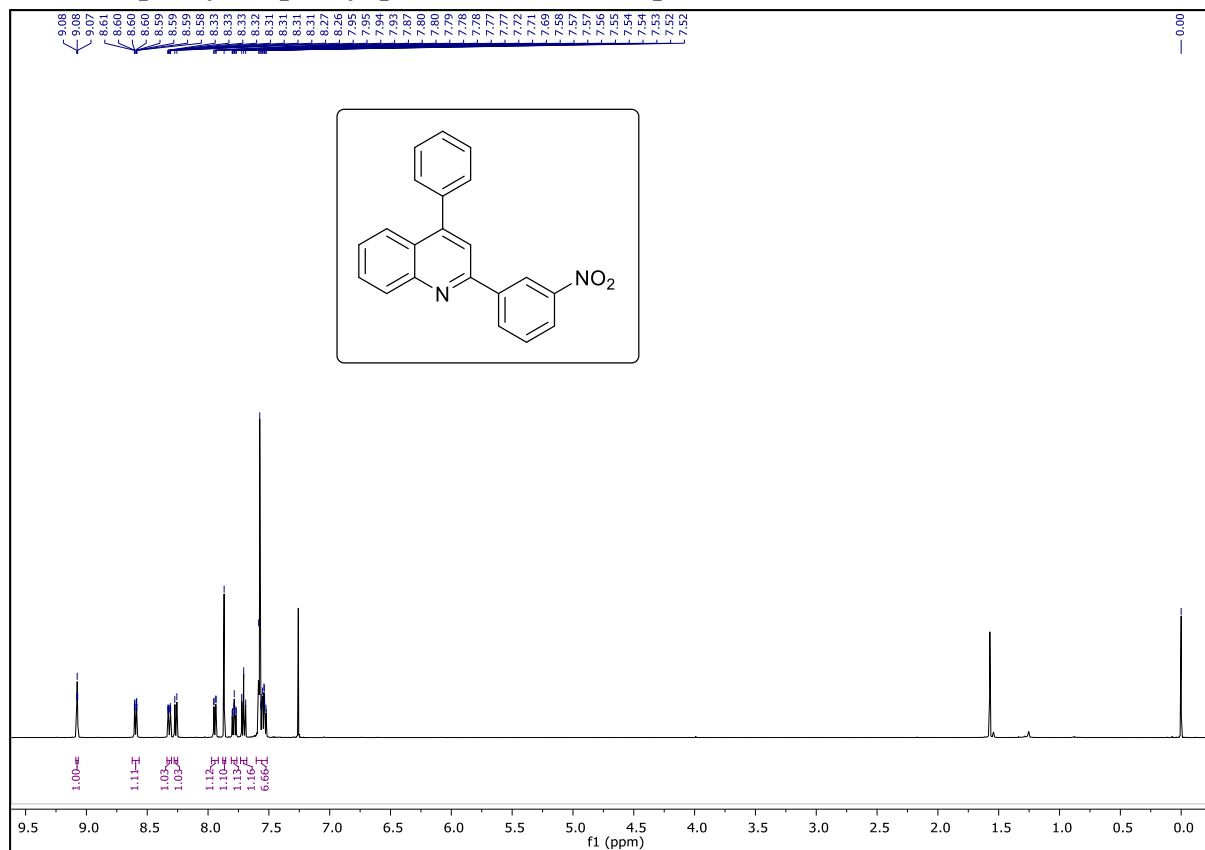
2-(3-bromophenyl)-4-phenylquinoline (Table 2, 3n)



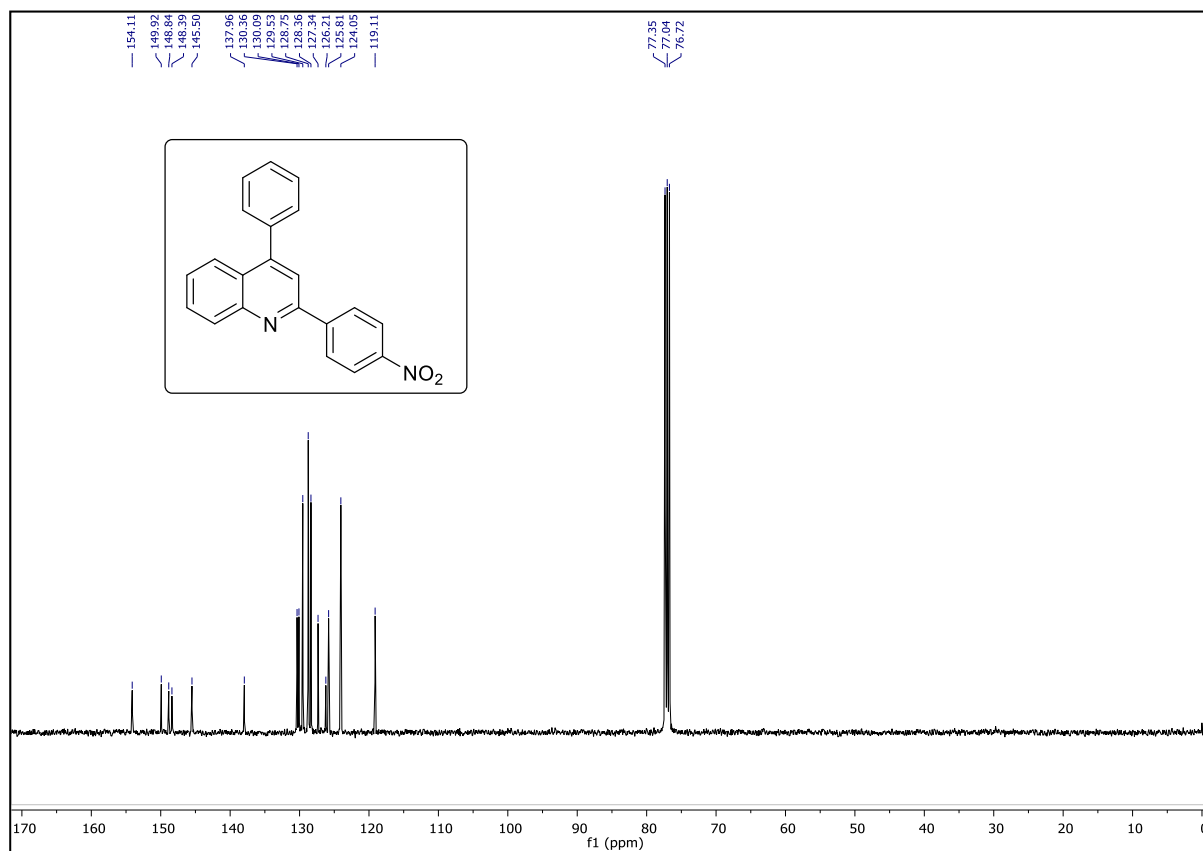
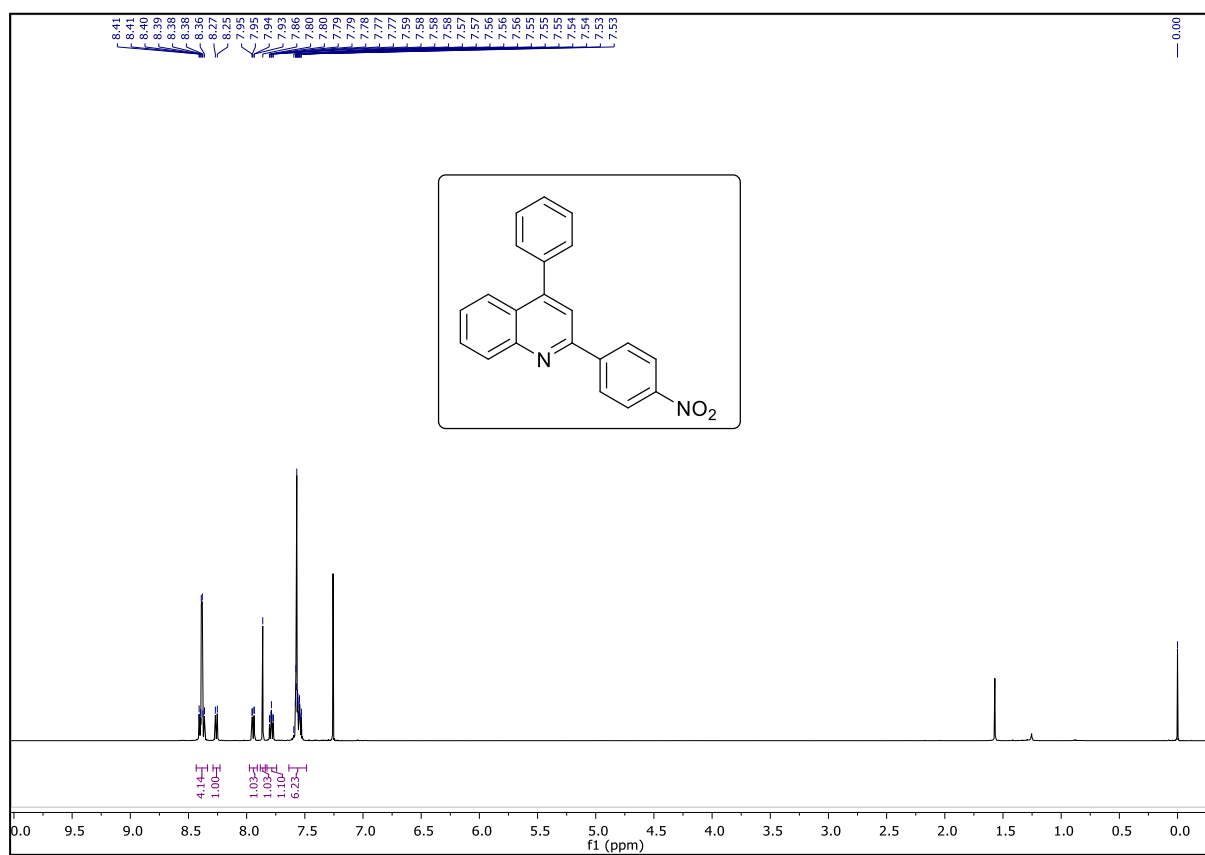
4-phenyl-2-(4-(trifluoromethyl)phenyl)quinoline (Table 2, 3o)



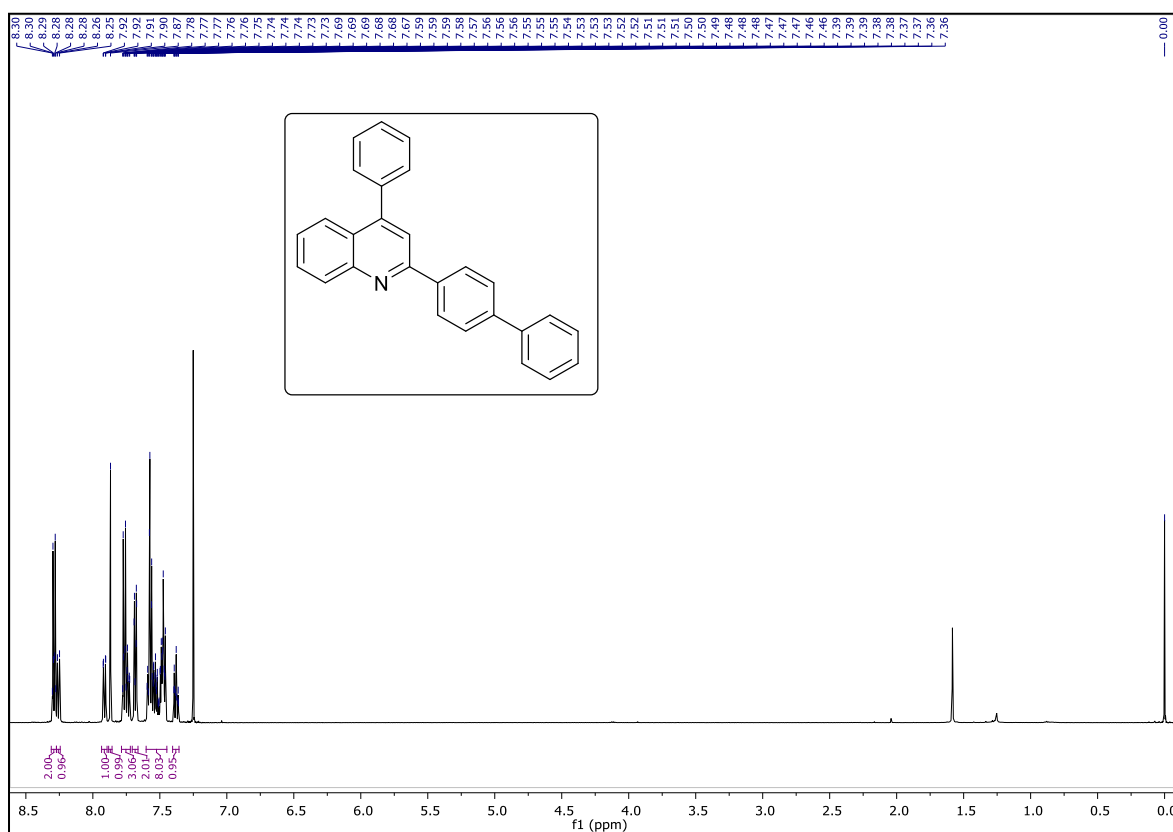
2-(3-nitrophenyl)-4-phenylquinoline (Table 2, 3p)



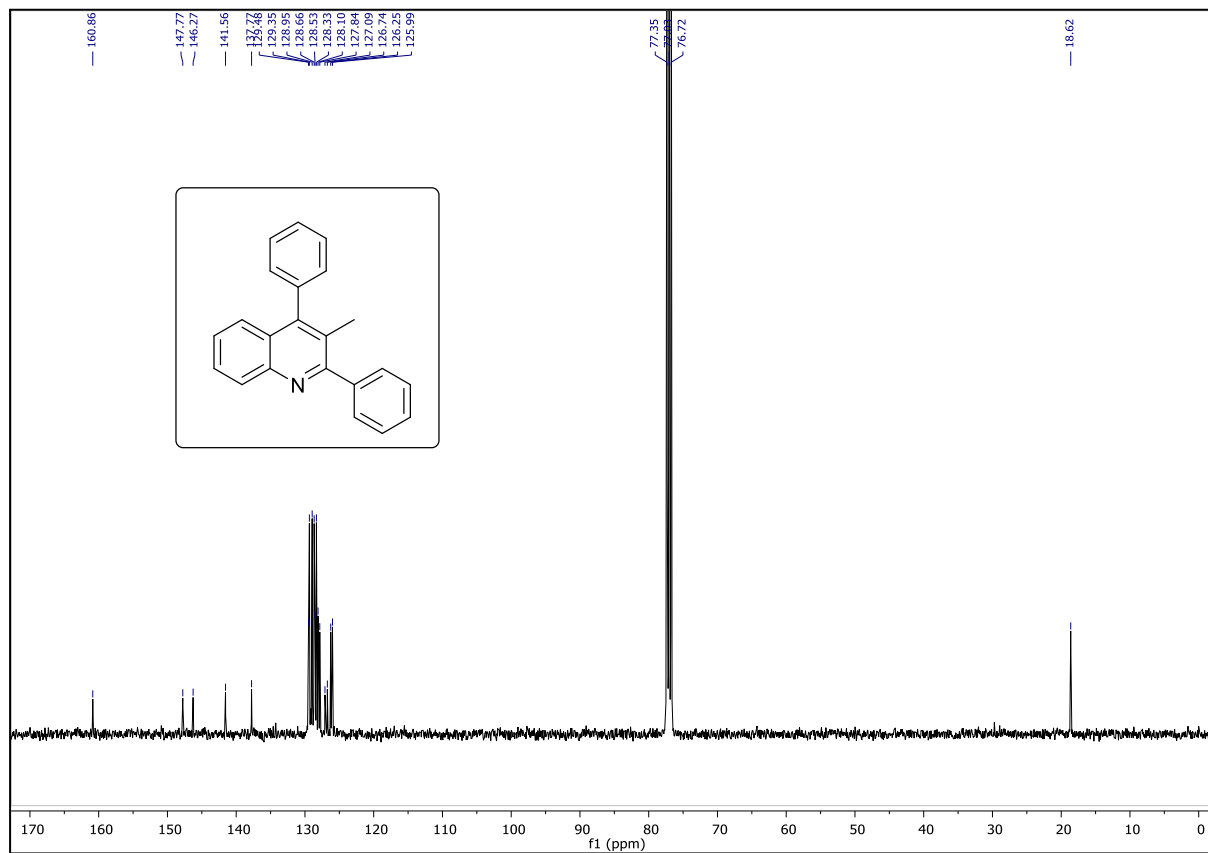
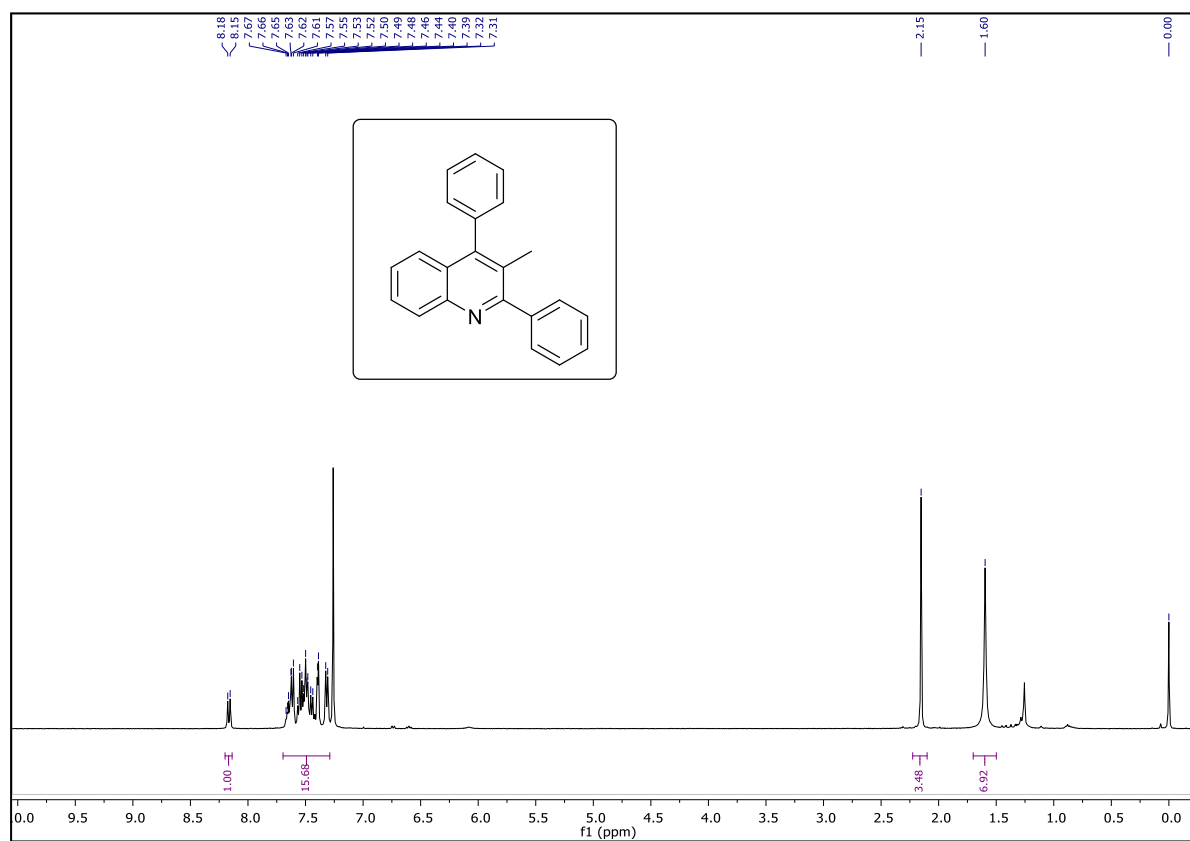
2-(4-nitrophenyl)-4-phenylquinoline (Table 2, 3q)



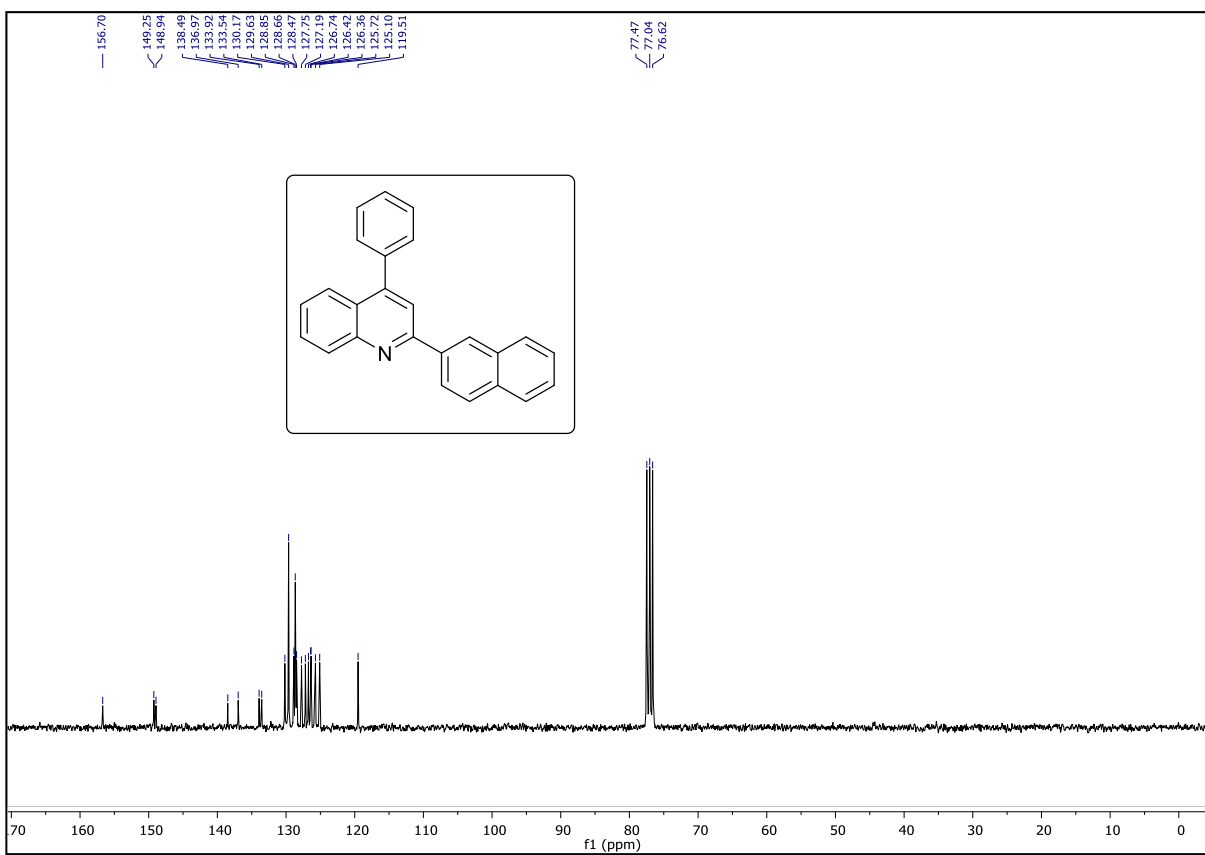
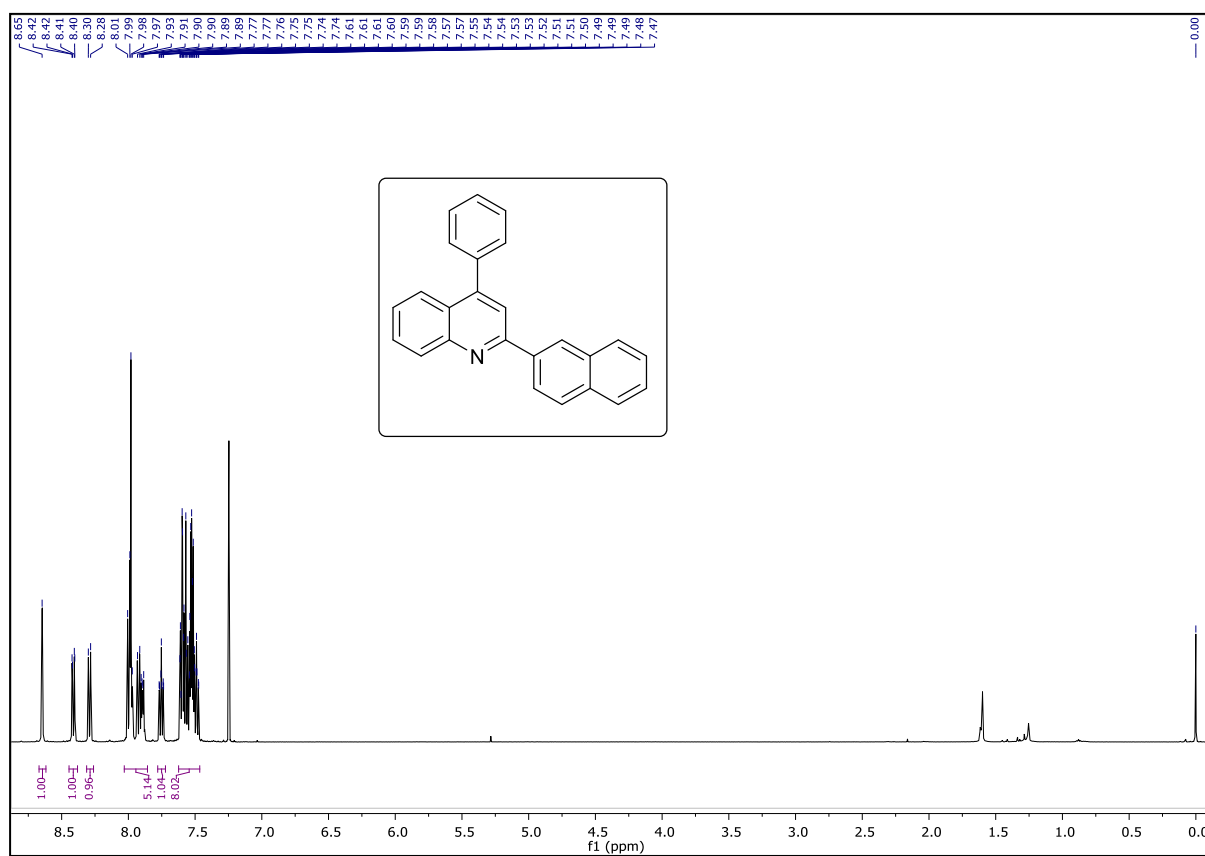
2-([1,1-biphenyl]-4-yl)-4-phenylquinoline (Table 2, 3r)



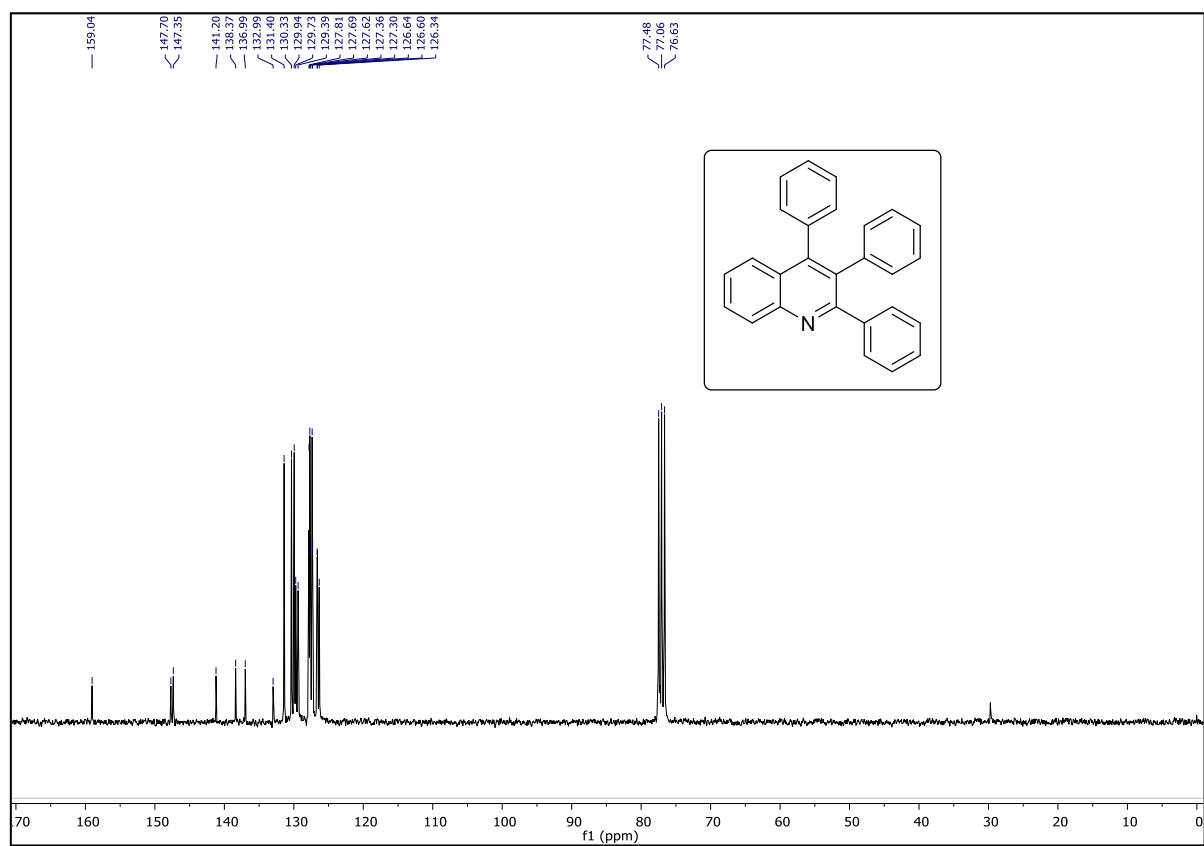
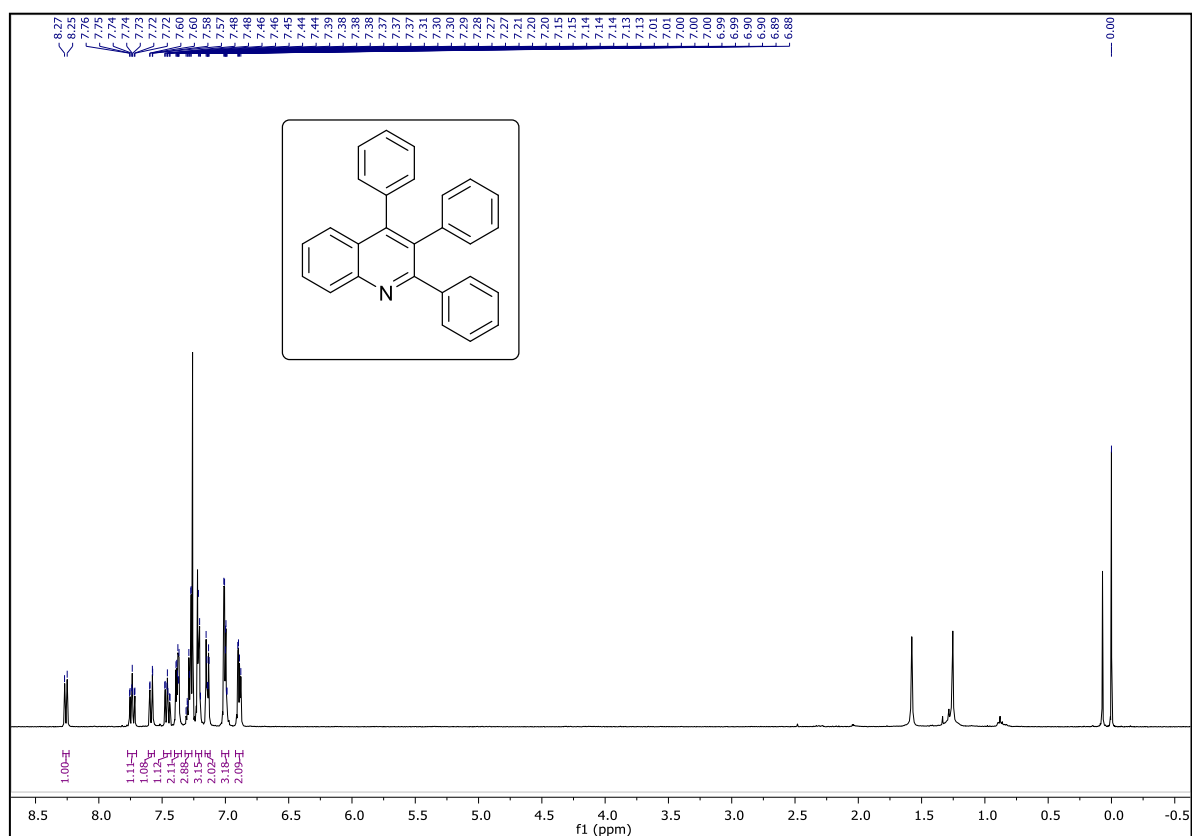
3-methyl-2,4-diphenylquinoline (Table 2, 3s)



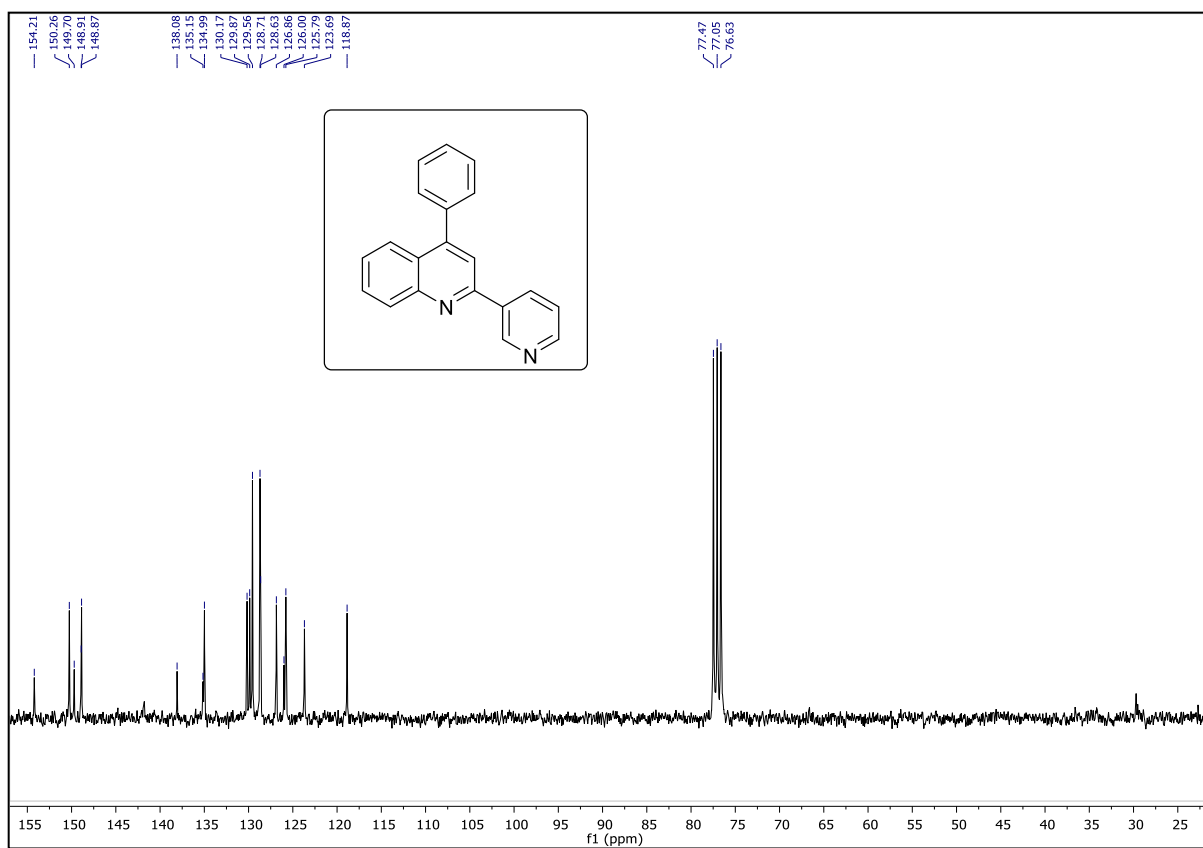
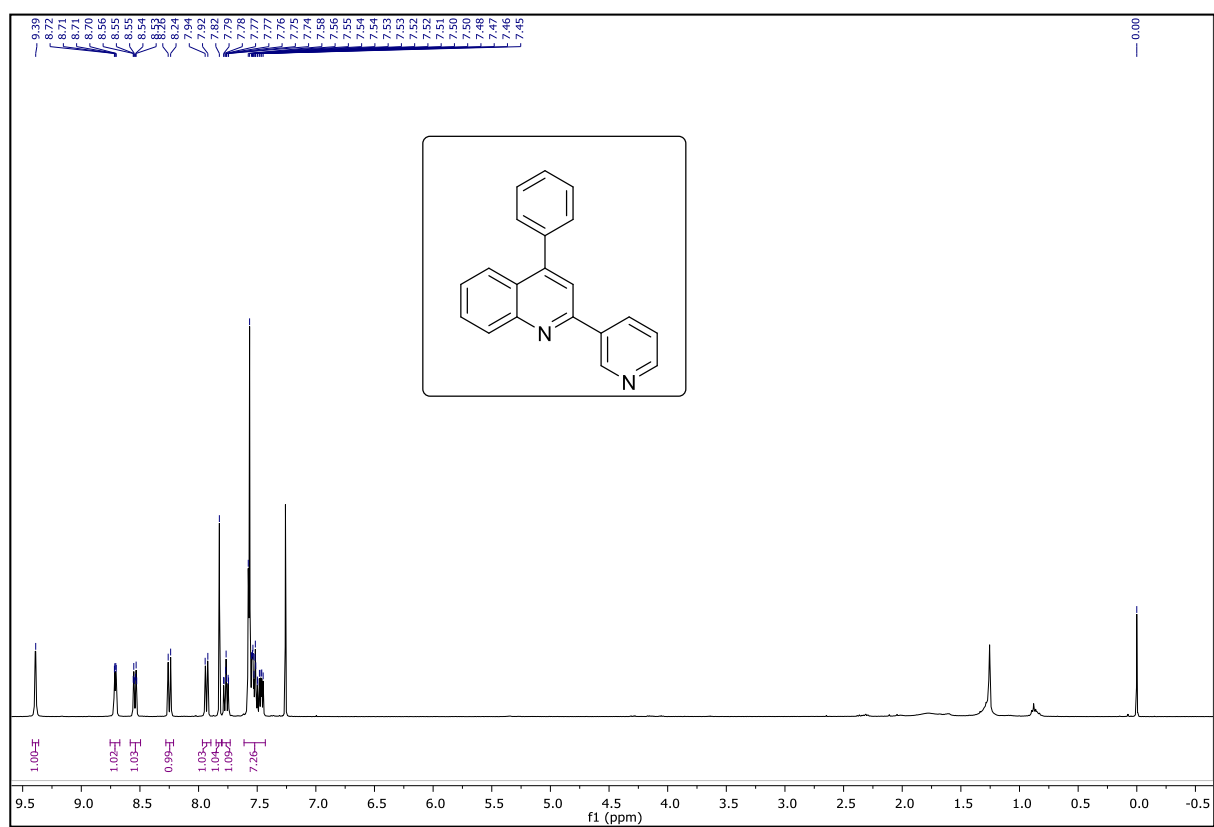
2-(naphthalen-2-yl)-4-phenylquinoline (Table 2, 3t)



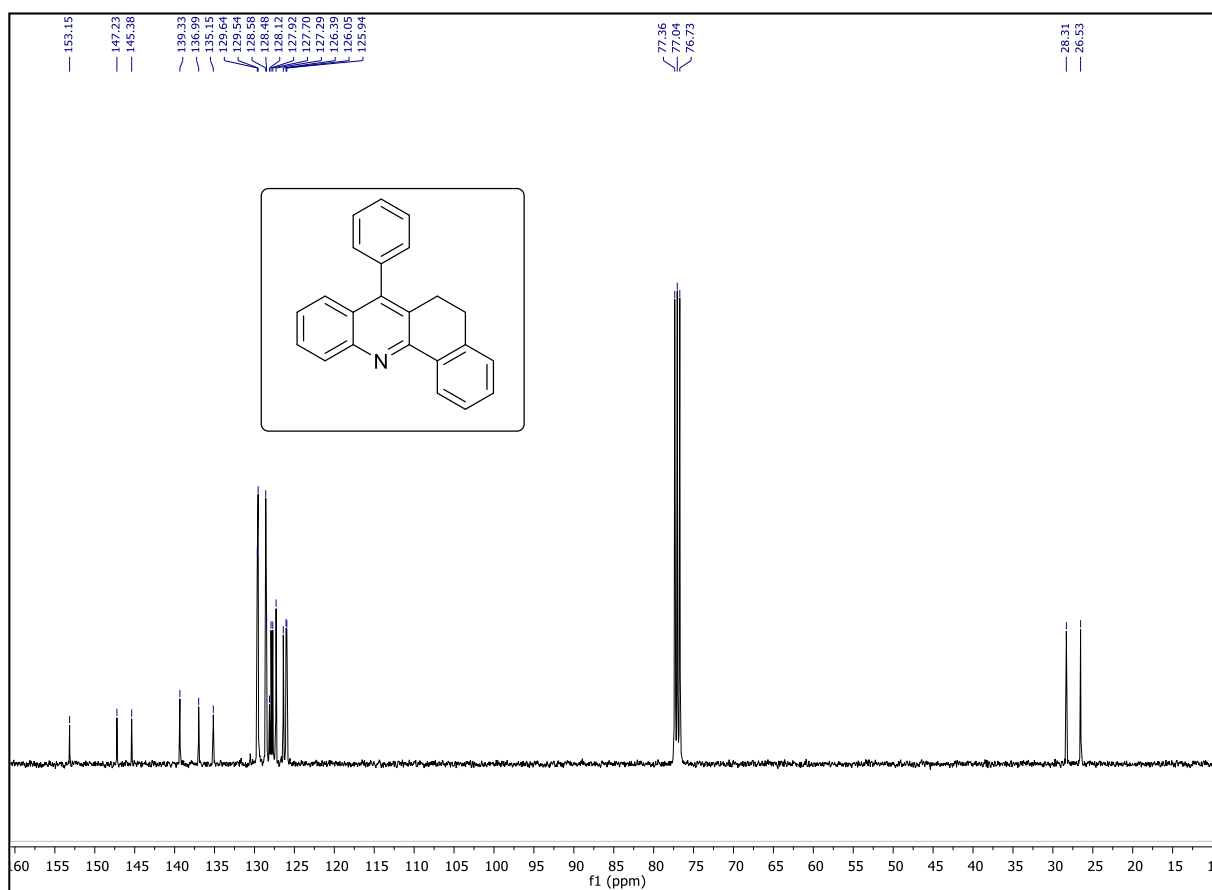
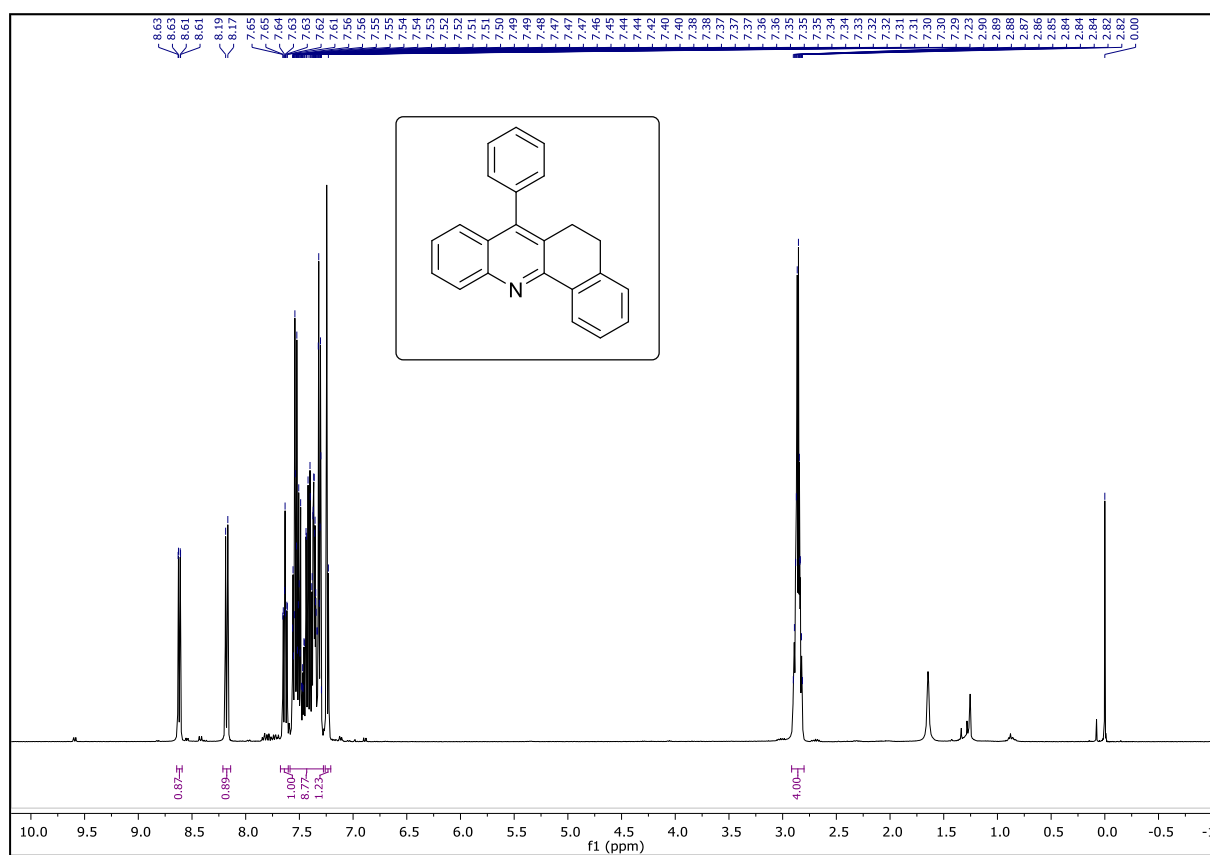
2,3,4-triphenylquinoline (Table 2, 3u)



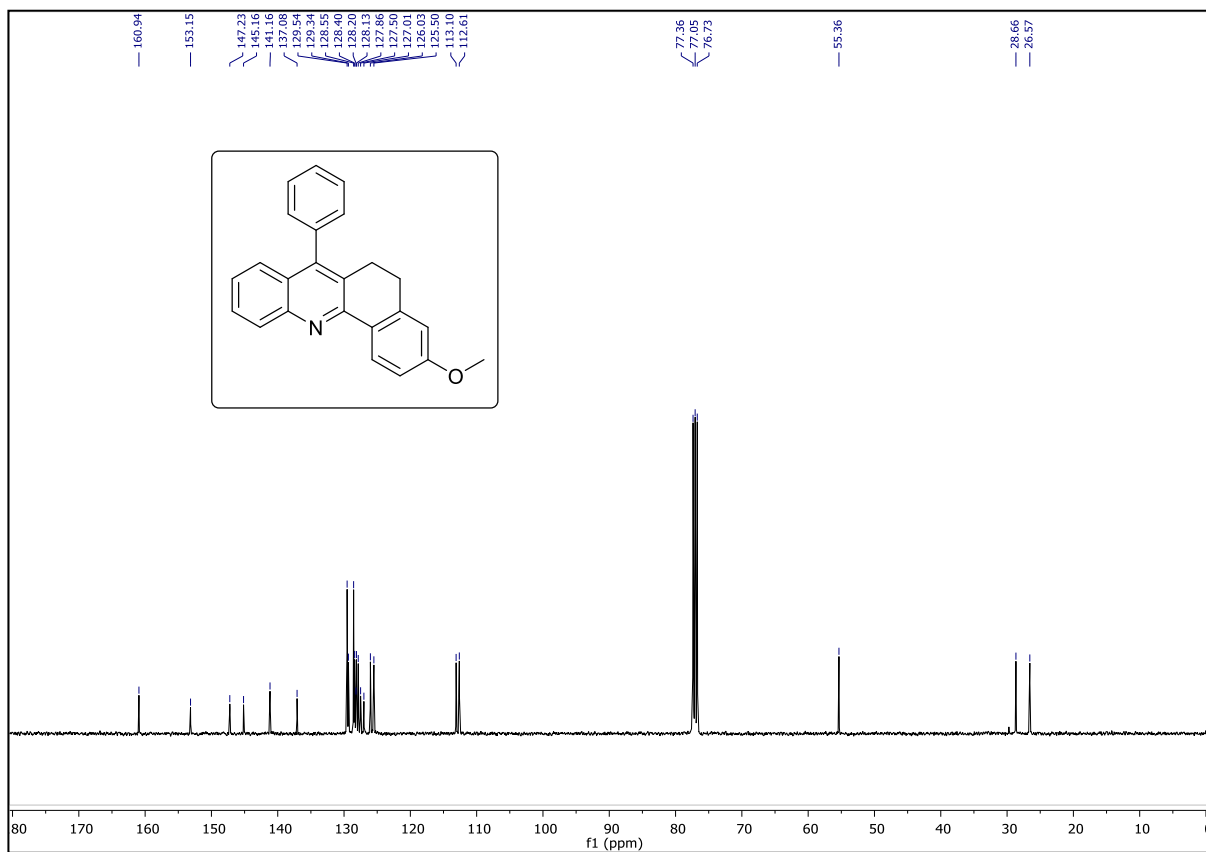
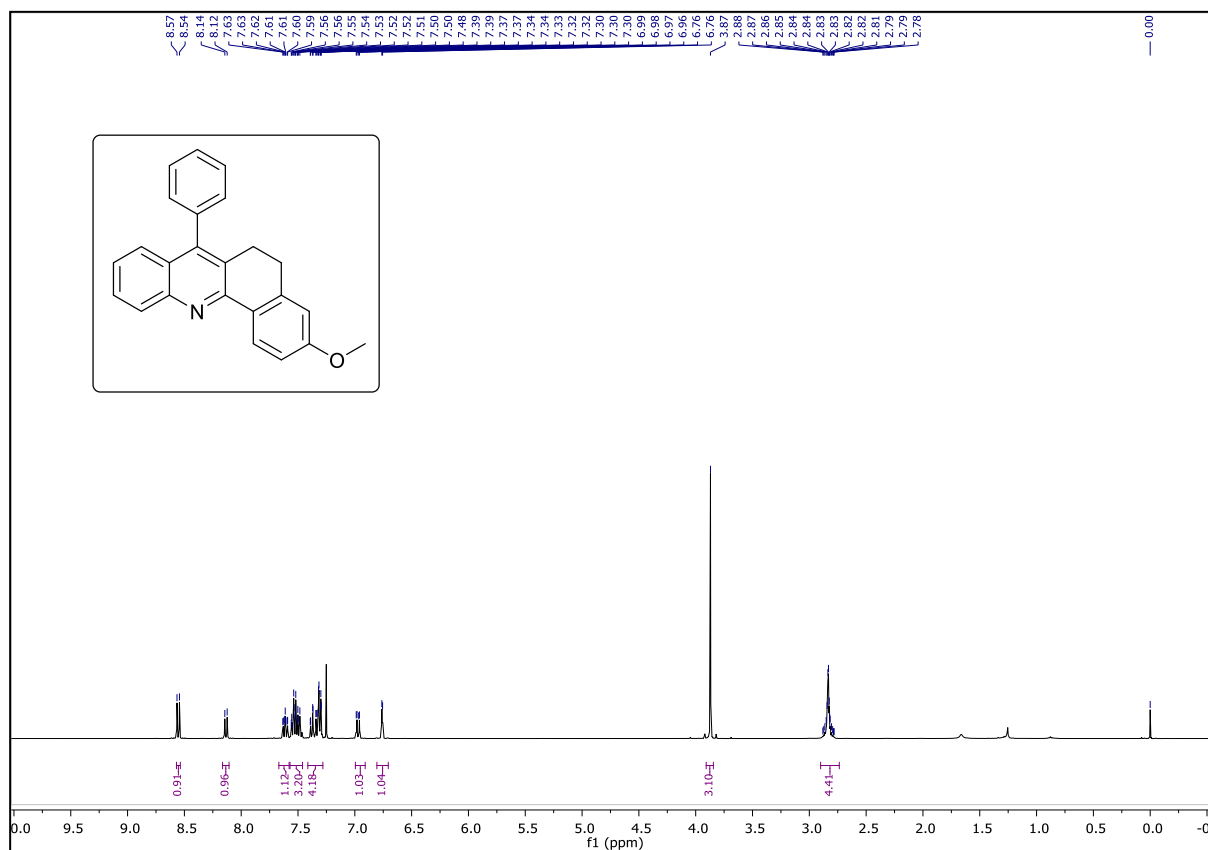
4-phenyl-2-(pyridin-3-yl)quinoline (Table 2, 3v)



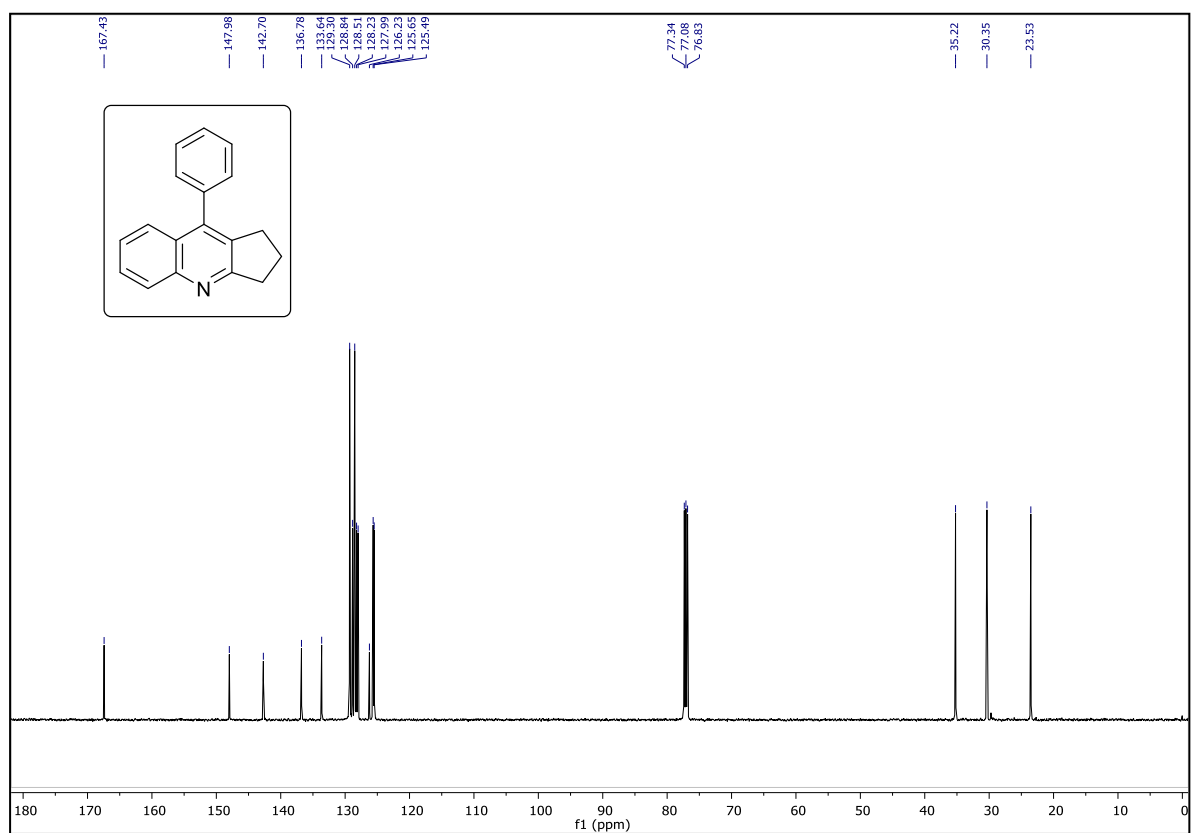
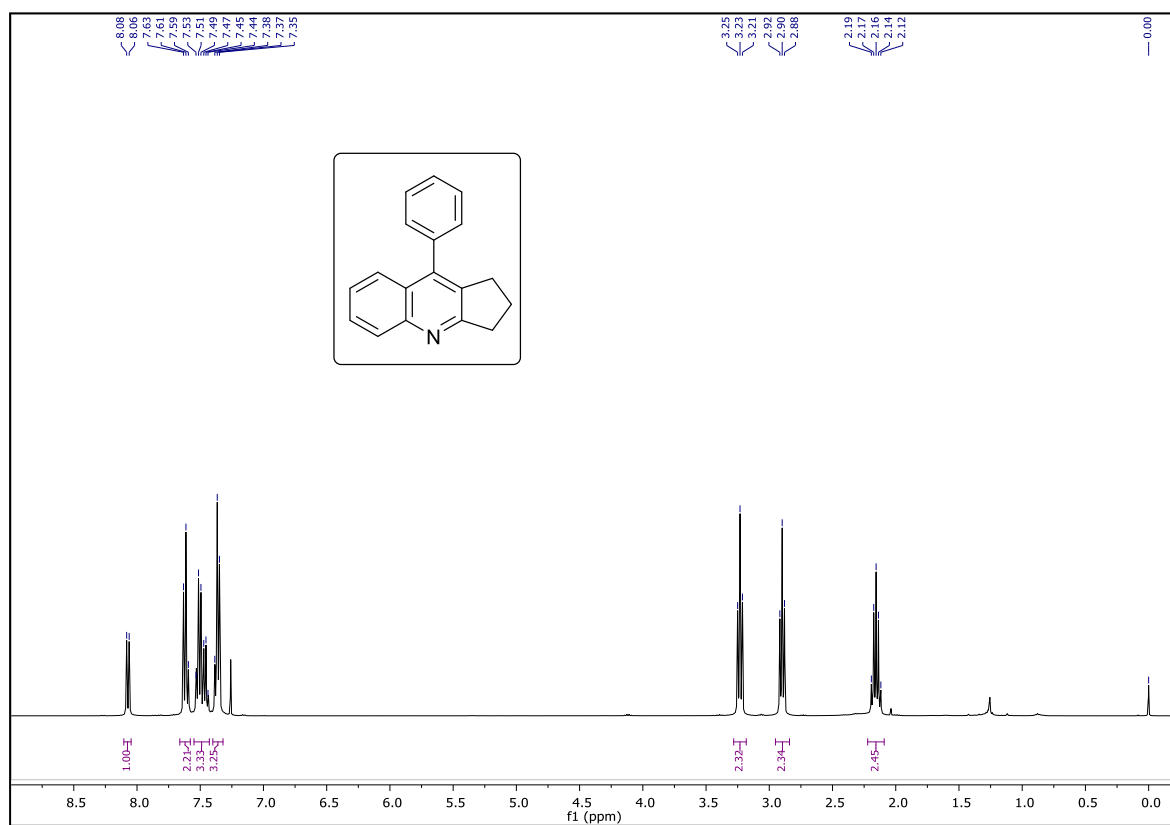
7-phenyl-5,6-dihydrobenzo[c]acridine (Table 2, 3w)



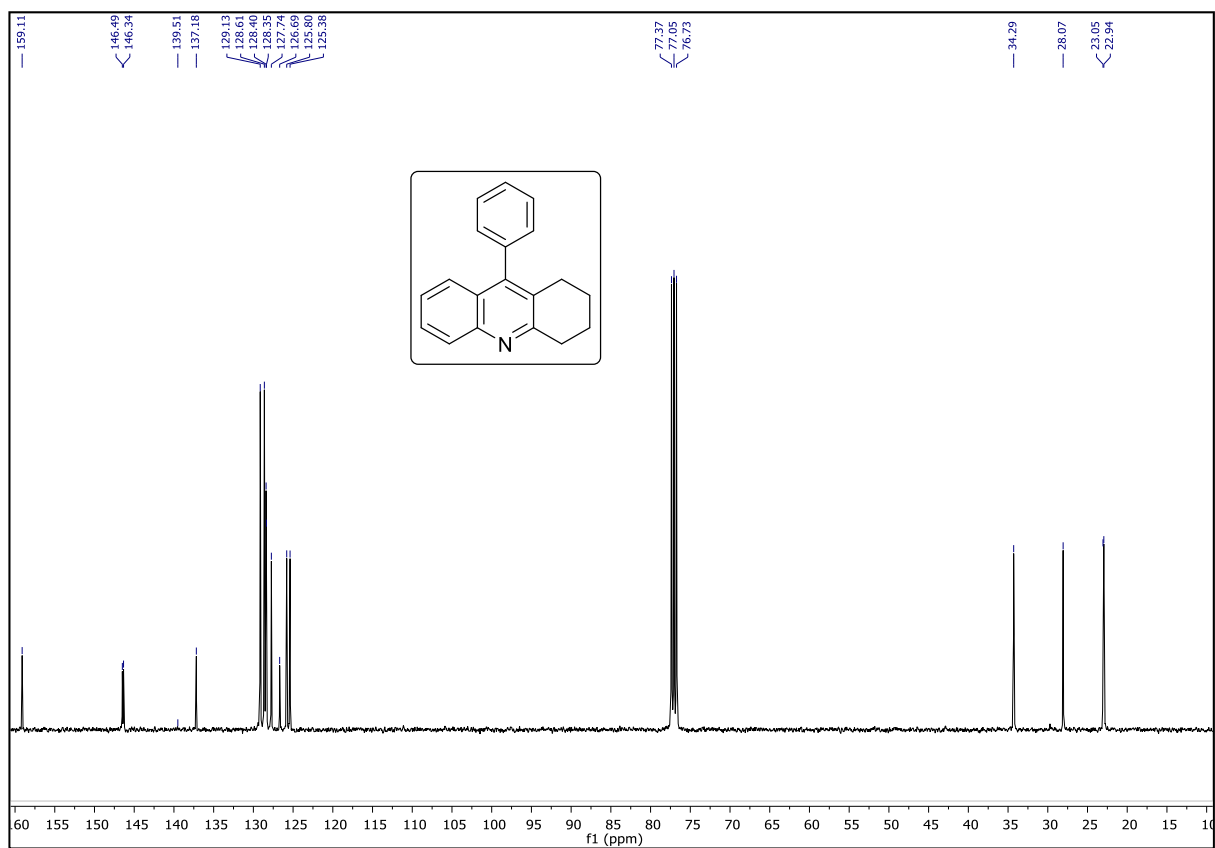
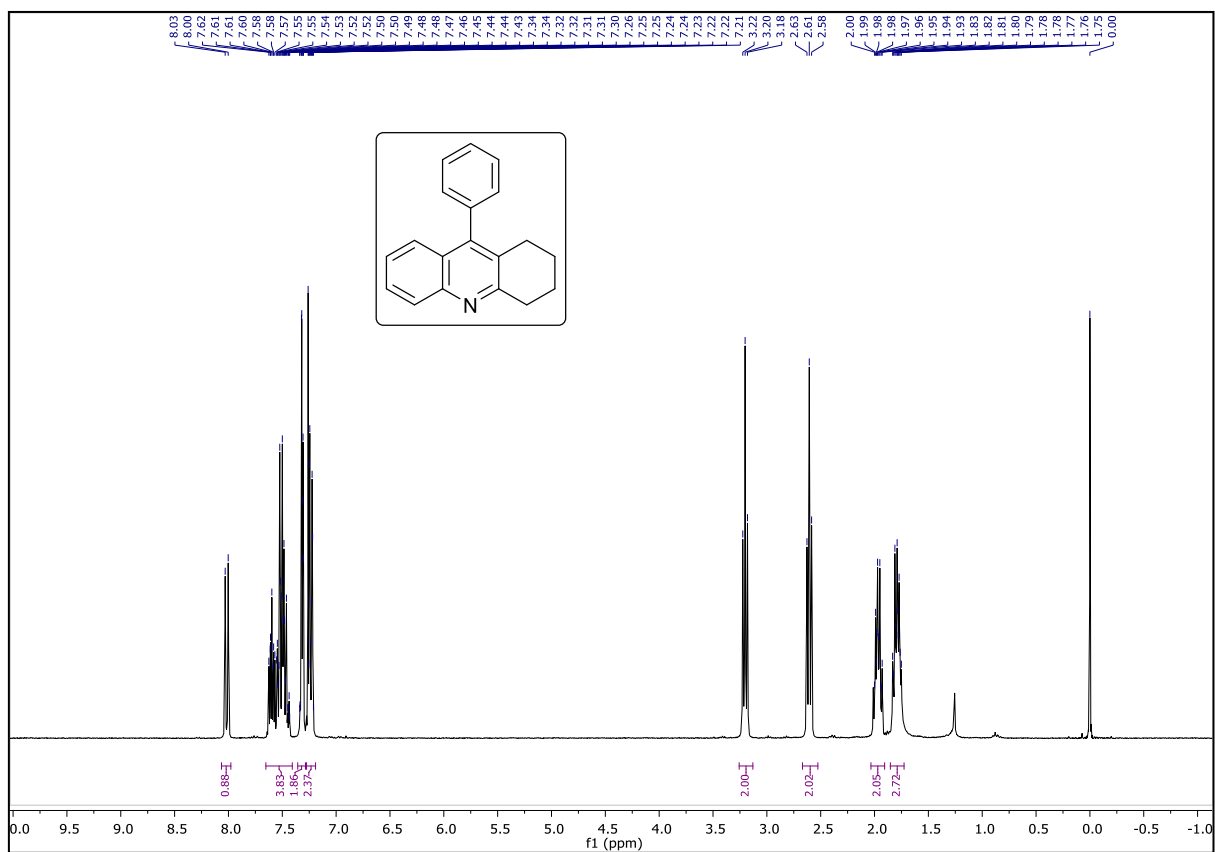
3-methoxy-7-phenyl-5,6-dihydrobenzo[c]acridine (Table 2, 3x)



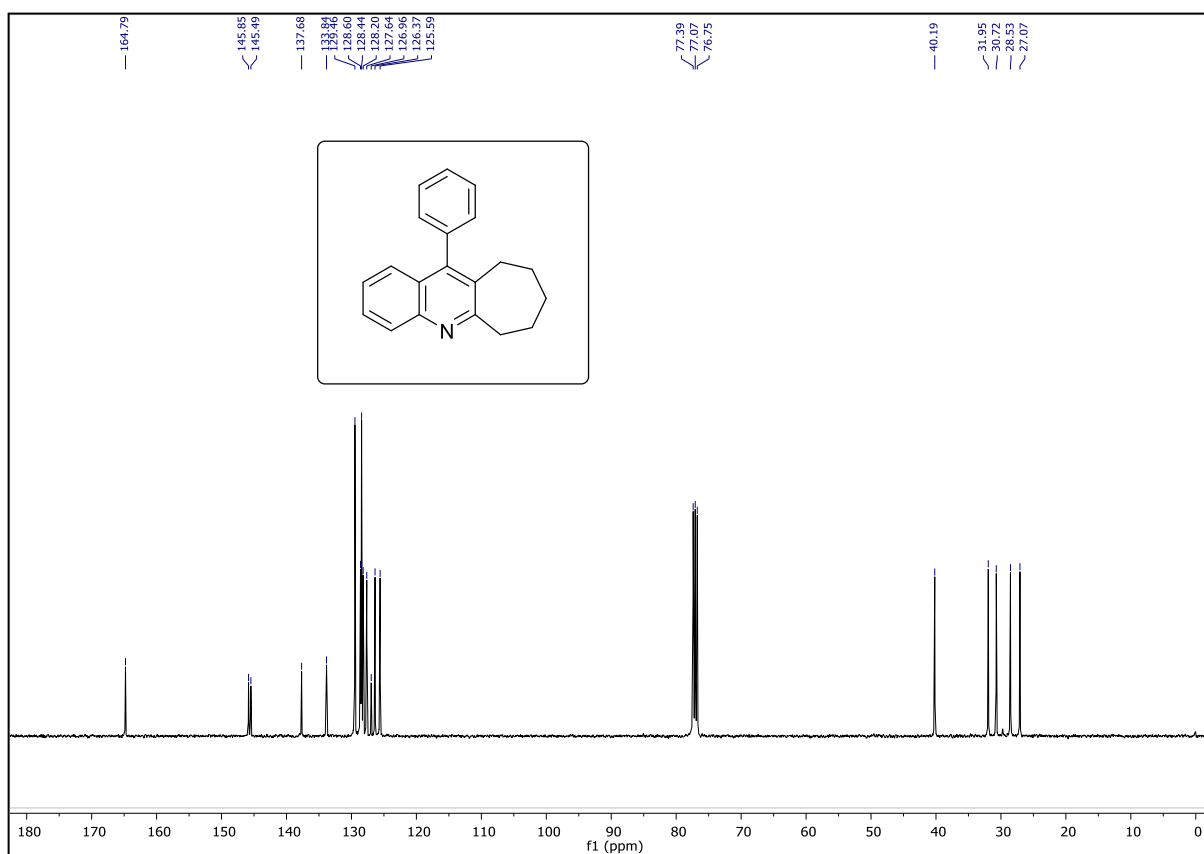
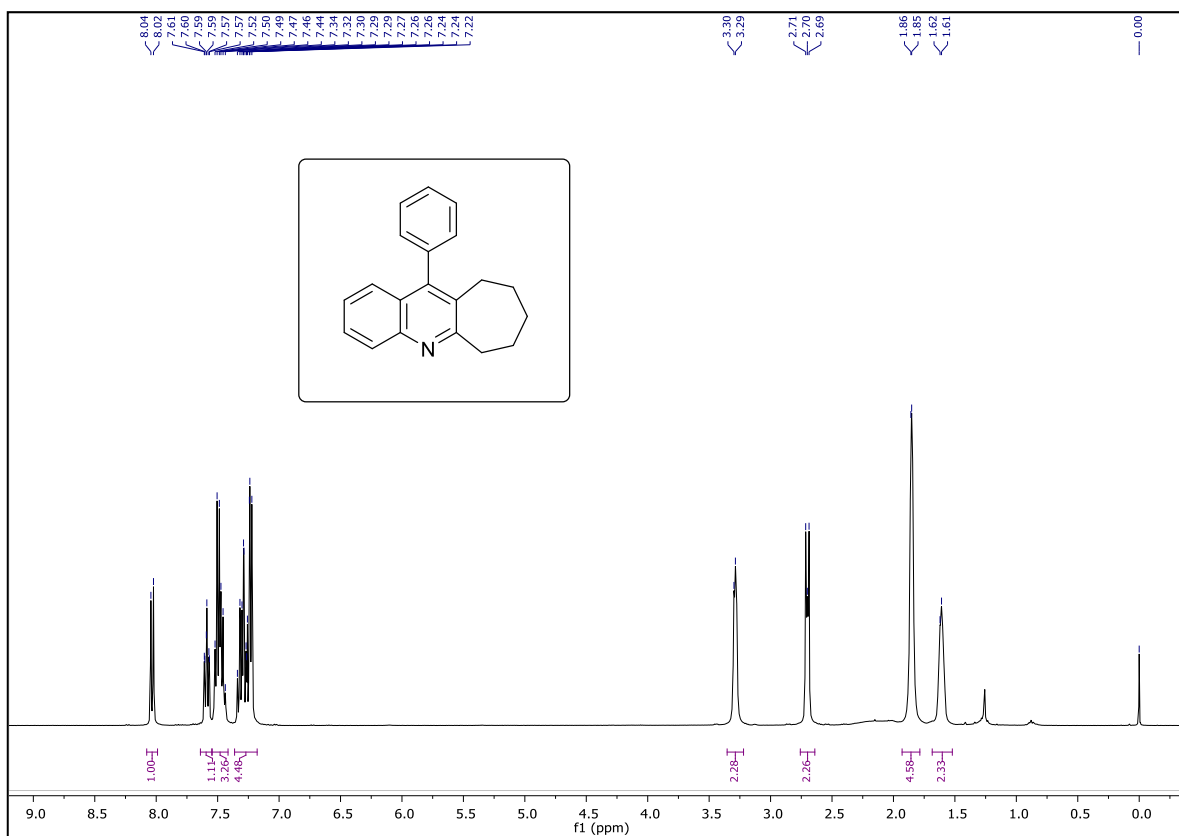
9-phenyl-2,3-dihydro-1H-cyclopenta[b]quinoline (Table 2, 3y)



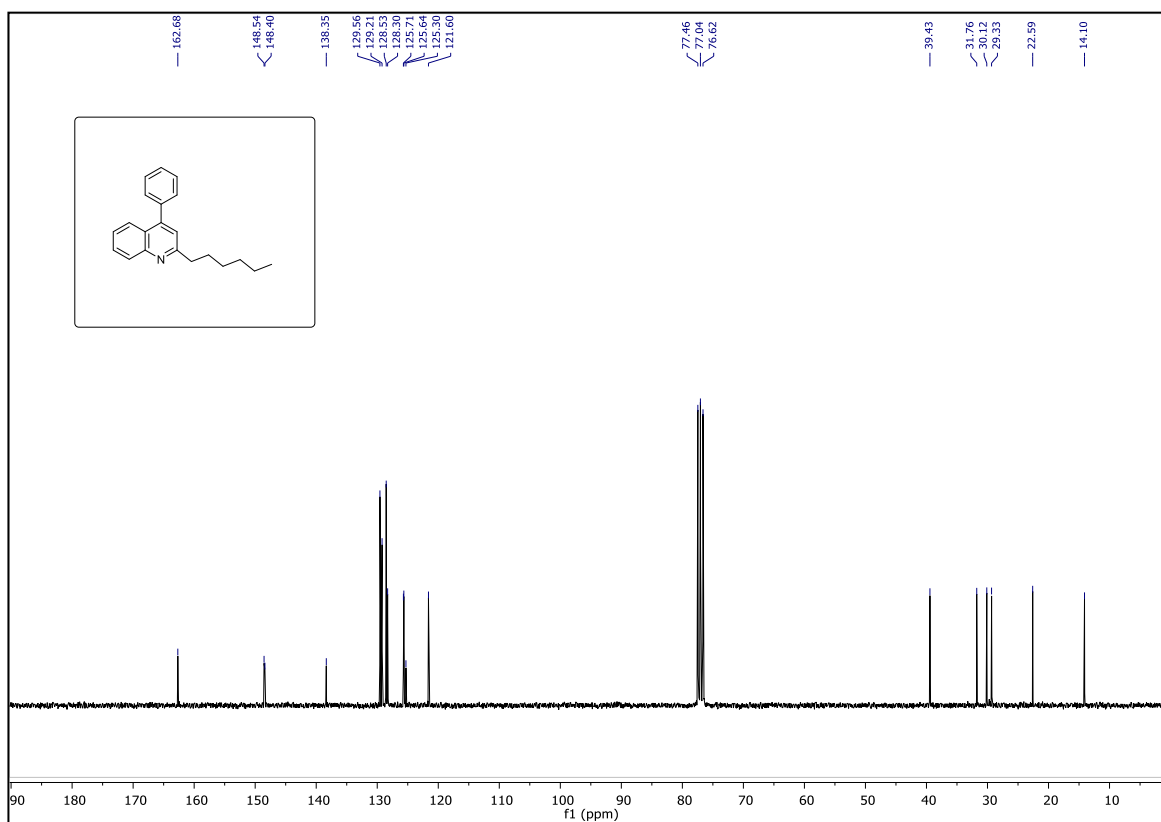
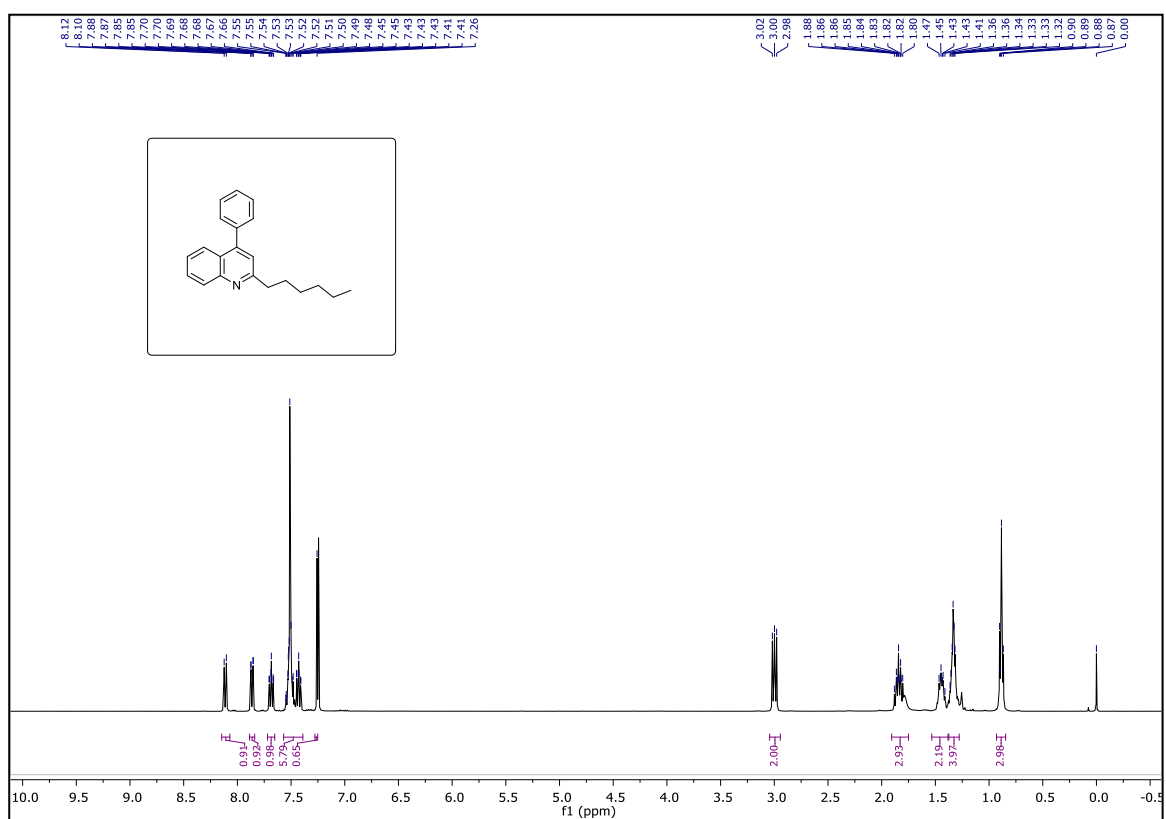
9-phenyl-1,2,3,4-tetrahydroacridine (Table 2, 3z)



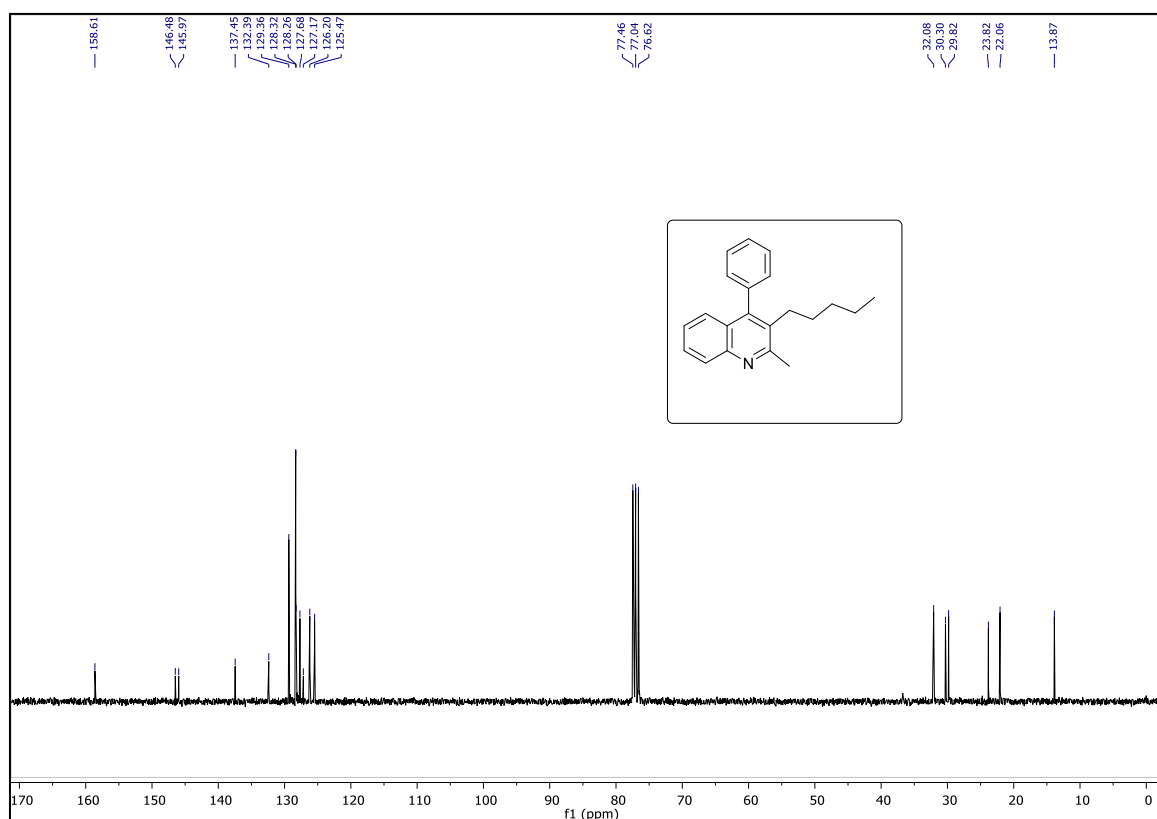
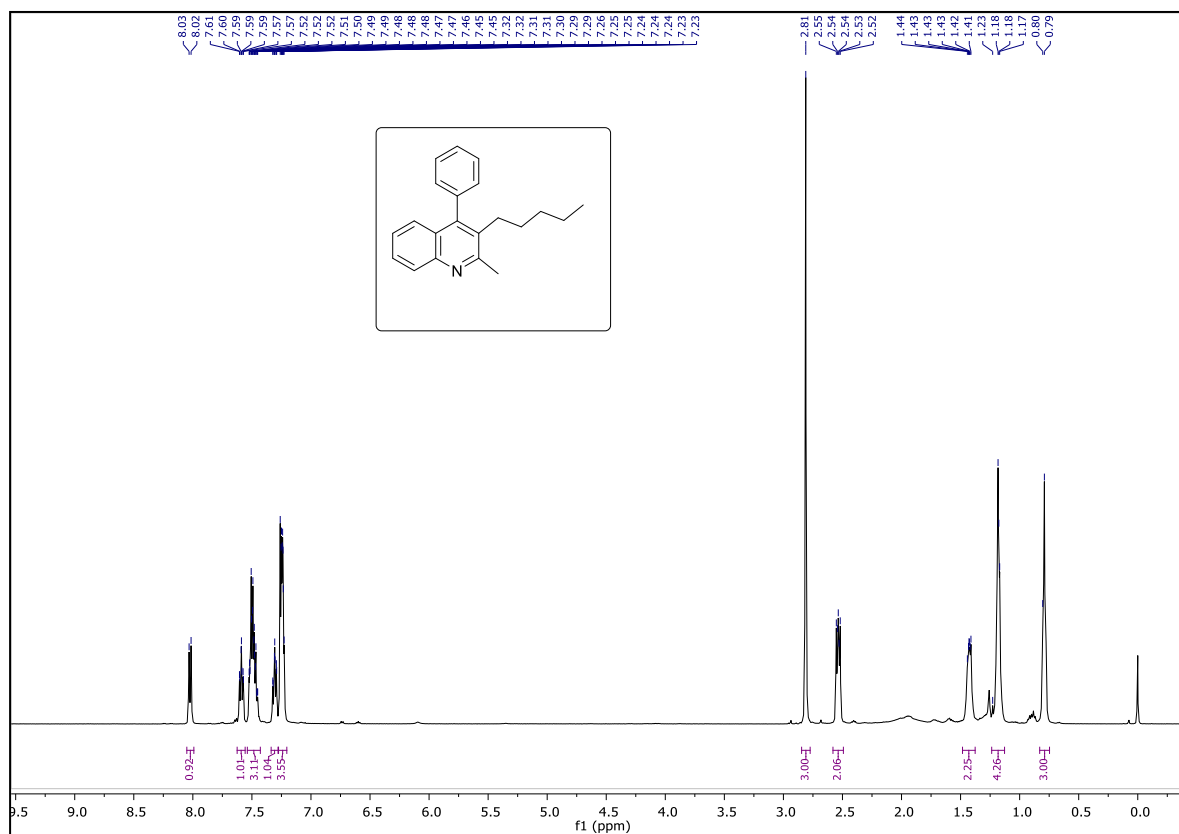
11-phenyl-7,8,9,10-tetrahydro-6H-cyclohepta[b]quinoline (Table 2, 3aa)



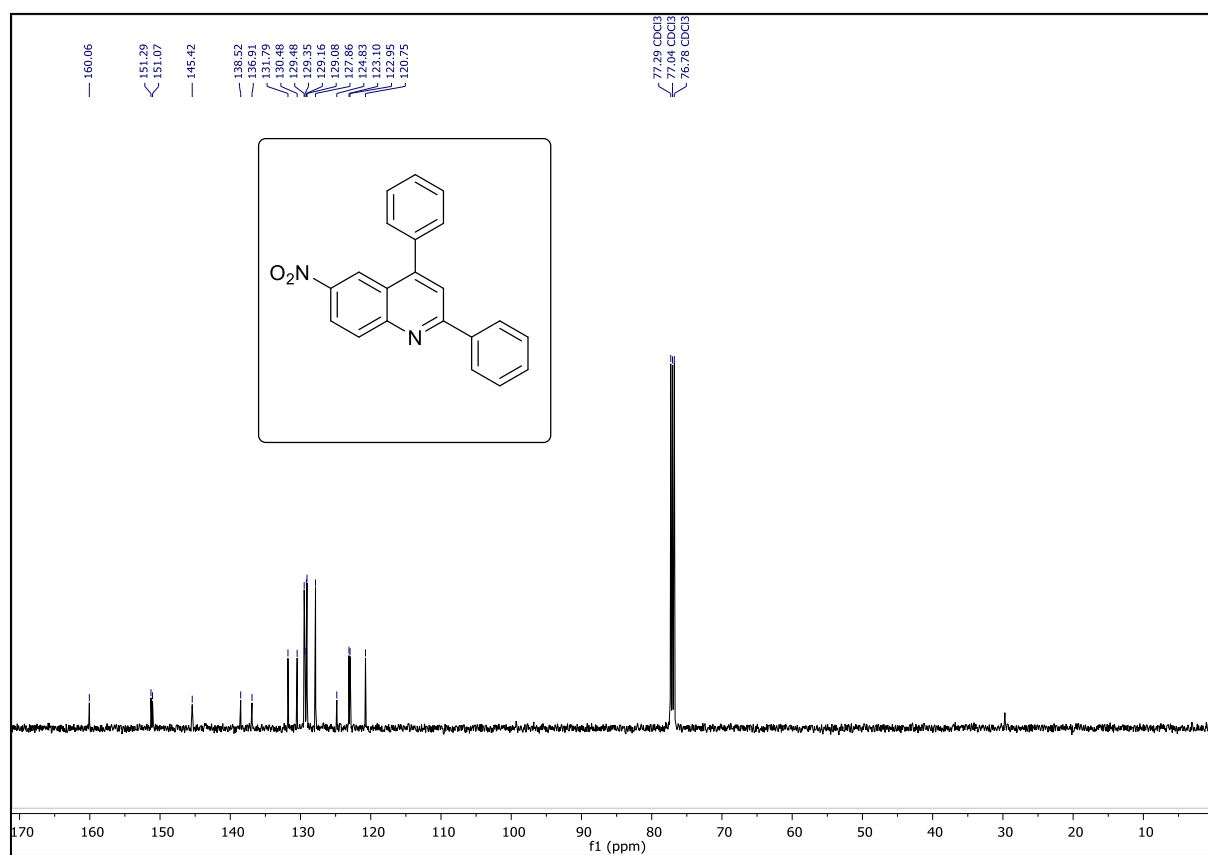
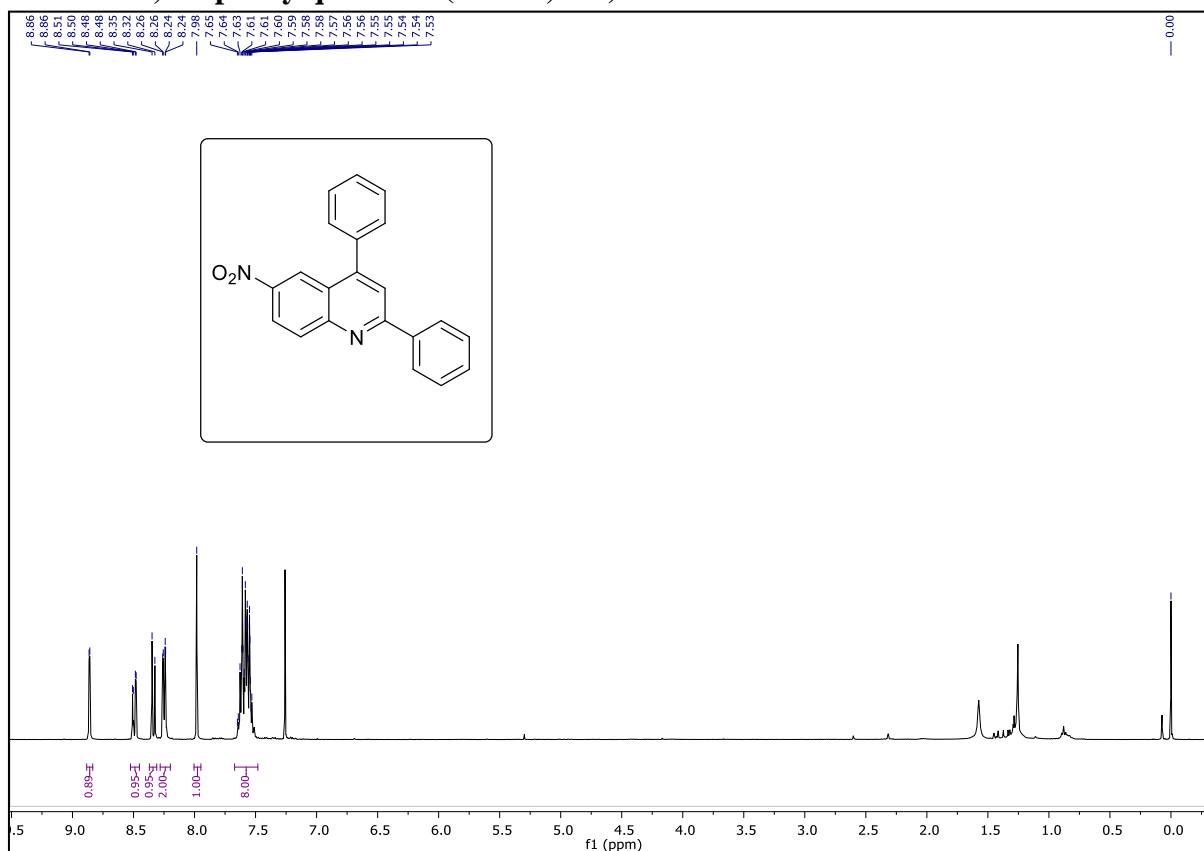
2-hexyl-4-phenylquinoline (Table 2, 3ab)



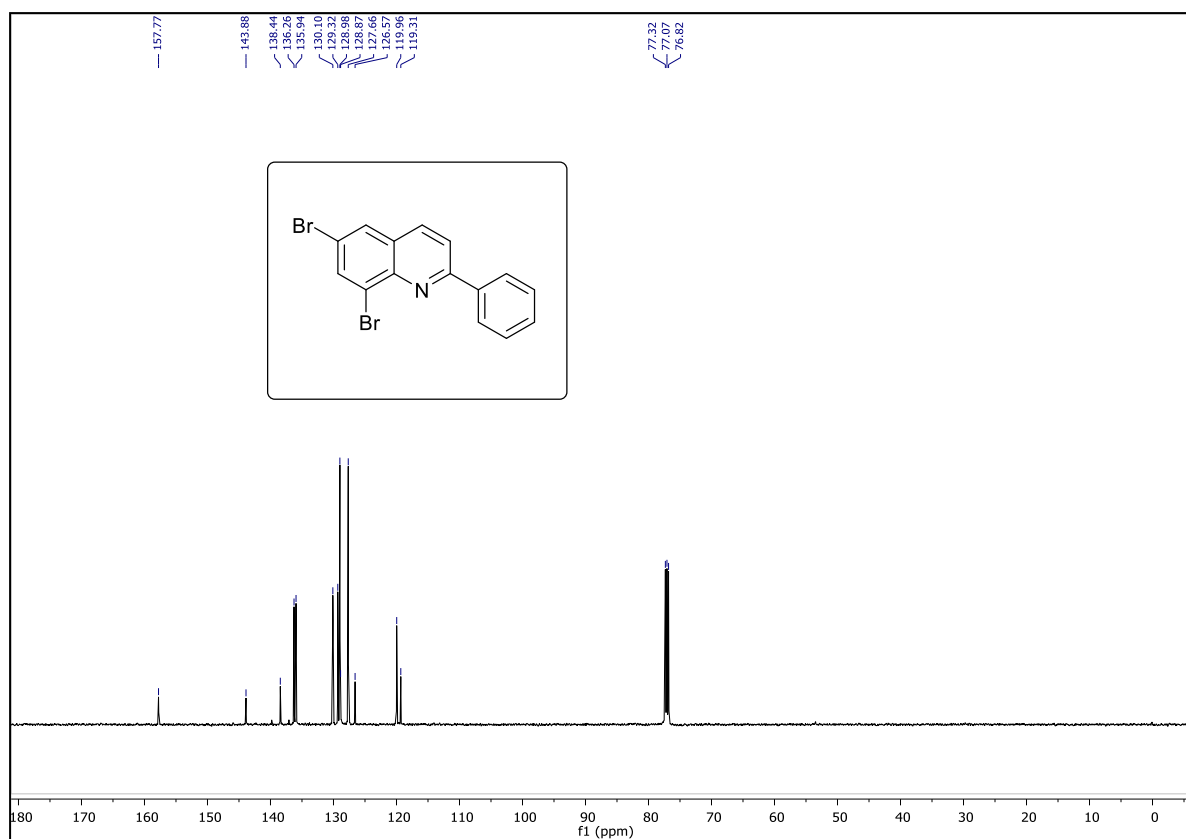
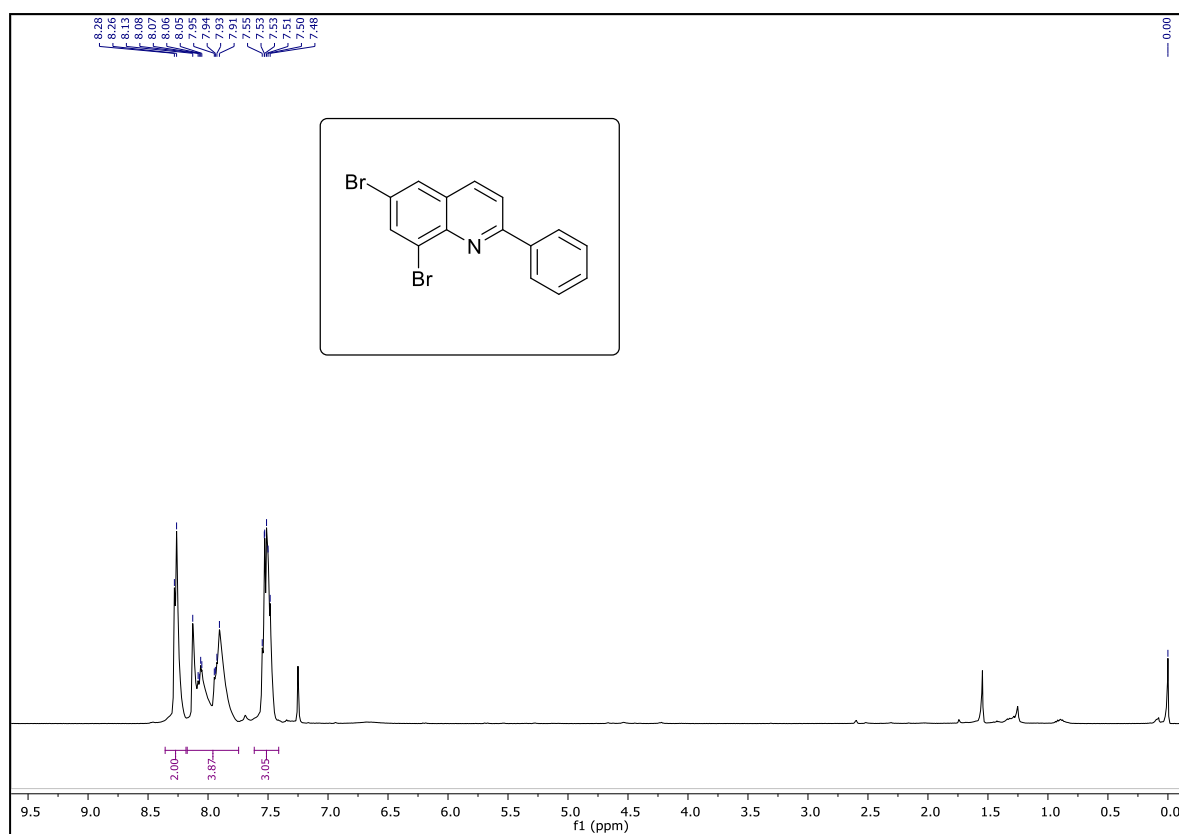
2-methyl-3-pentyl-4-phenylquinoline (Table 2, 3ab¹)



6-nitro-2,4-diphenylquinoline (table 3, 3ac)



6,8-dibromo-2-phenylquinoline (table 3, 3ad)



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