Supplementary Information (SI) for Organic & Biomolecular Chemistry.

# Supporting Information

# Molybdenum Catalyzed Acceptorless Dehydrogenative Approach for Quinoline Synthesis Using Amino Alcohol

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## 1. General information

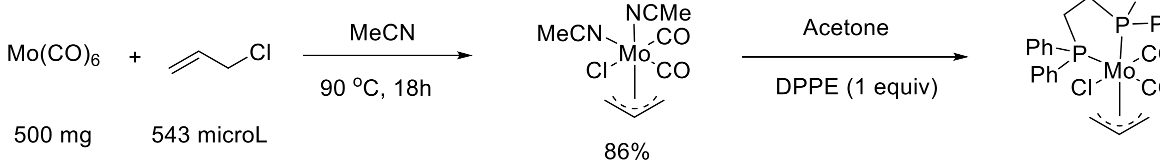
All manipulations were performed under inert nitrogen atmosphere by using standard Schlenk techniques and inside glove box, unless stated otherwise. Standard solvents were heated under reflux over suitable drying agent (sodium/benzophenone for THF, $Et_2O$, hexane; calcium hydride for $CHCl_3$ and kept under freshly dried molecular sieves), distilled, and stored over activated 4Å molecular sieves in the glovebox under nitrogen atmosphere. Deuterated solvents were purged with nitrogen and kept in glovebox. Unless otherwise stated, commercial reagents were used without purification, only acetophenone and 1-phenylethanol were purified via vacuum distillation and 2-aminobenzyl alcohol was purified by crystallization. Molybdenum hexacarbonyl [$Mo(CO)_6$] and phosphine ligands 1,2-Bis(diphenylphosphino)ethane (DPPE), and 1,3-Bis(diphenylphosphino)propane (DPPP) were purchased form Sigma- Aldrich, calcium hydride ($CaH_2$) and all other materials were purchased from Avra, BLDpharma, TCI and Sigma- Aldrich, stored under nitrogen and used as received. Reaction temperature reported is the temperature of the oil bath. All the reaction for ligand synthesis and substrate scope was monitored by TLC and isolated by column chromatography (silica gel 60-120). Then products were condensed with the help of rotary evaporator. Isolated products were characterized by using $^{1}H$ NMR, $^{13}C$ NMR and $^{19}F$ NMR, with the help of Bruker High Perfomance Digital FT-NMR (Model AVANCE III HD, Ascend TM WB, 500 MHz) using $CDCl_3$. All spectra were recorded at room temperature, unless otherwise noted. ATR-IR spectra were recorded on Perkin-Elmer FT-IR spectrometer. Mass spectra were recorded on Agilent spectrometer.

## 2. Experimental Section:

Two homologous diphosphine-based molybdenum-π-allyl complexes **Mo-1** and **Mo-2** were prepared with bidentate phosphine ligands having different bite angles, according to the literature procedures.[1]

### a) Synthesis of $Mo(CO)_2(\eta^3\text{-}C_3H_5)Cl(DPPE)$ (Mo-1)

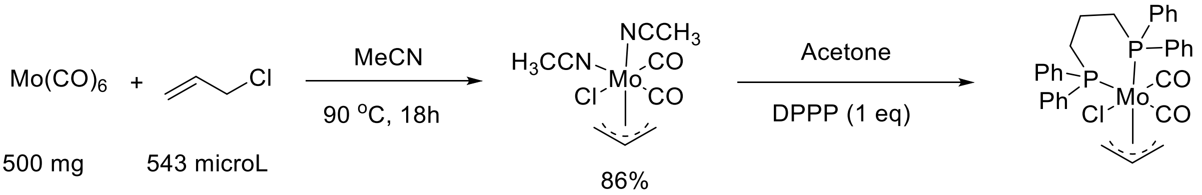
500 mg of $Mo(CO)_6$ (1.894 mmol) was dissolved in dry acetonitrile (10 ml) in an oven dried Schlenk tube. 4 equiv. of allyl chloride (7.6 mmol, 543 microL) was added to this suspension, and the reaction mixture was allowed to heat at 90 °C for 18 h while stirred constantly. After 18 h, a deep yellow solution was obtained, which was cooled and dried in *vacuo* to get $Mo(CO)_2(CH_3CN)_2(\eta^3\text{-}C_3H_5)(Cl)$ (86%, 505 mg). The so obtained $Mo(CO)_2(CH_3CN)_2(\eta^3\text{-}C_3H_5)(Cl)$ was dissolved in 10 ml of dry acetone. To this suspension, 650 mg (1.63 mmol) of DPPE ligand suspension in 10 ml of acetone was added dropwise into a dried Schlenk tube and the resulting reaction mixture was allowed to react at 80 °C for 18 h. The reaction mixture was cooled and dried under *vacuo*. The desired product was obtained after dissolving in dichloromethane and recrystallizing in n-pentane. The orange crystals were dried and then washed with pentane to obtain $Mo(CO)_2(\eta^3\text{-}C_3H_5)Cl(DPPE)$ complex in 76% yield (775 mg). Melting point = 186-188 °C. $^{1}H$ NMR (500 MHz, Chloroform-*d*) δ 7.65 (dt, *J* = 16.7, 8.0 Hz, 4H), 7.45 (q, *J* = 8.2 Hz, 12H), 3.70 (3H, allyl), 2.98 (tdd, *J* = 19.3, 11.7, 7.6 Hz, 2H, DPPE), 2.30 (dp, *J* = 14.0, 4.2 Hz, 2H, DPPE), 1.93 (d, *J* = 9.6 Hz, 2H, allyl) ppm; $^{31}P$ NMR (203 MHz, Chloroform-*d*) δ 47.7 ppm. Selected FT-IR (solid ATR, $cm^{-1}$): ν(CO) = 1932 and 1842 $cm^{-1}$. HRMS: expected m/z = 628.0385, observed = 628.0424, (**Mo-1**), 593.0466 (**Mo-1** - $Cl^-$).



***Scheme S1***: *Synthetic access to* ***Mo-1.***

### b) Synthesis of $Mo(CO)_2(\eta^3\text{-}C_3H_5)Cl(DPPP)$ (Mo-2)

$Mo(CO)_2(CH_3CN)_2(\eta^3\text{-}C_3H_5)(Cl)$ was synthesized following the same procedure as described for **Mo-1**. To 100 mg (0.323 mmol) of $Mo(CO)_2(CH_3CN)_2(\eta^3\text{-}C_3H_5)(Cl)$ dissolved in dry acetone (5 ml), 133 mg (0.323 mmol) of DPPP ligand suspension in 3 ml of acetone was added dropwise into a dried Schlenk tube and the resulting reaction mixture was allowed to react at 80 °C for 18 h. after completion of the reaction, the reaction mixture was cooled and dried under vacuo. The desired product was obtained after dissolving in DCM and recrystallization in n-pentane. The yellow orange crystals were then washed with pentane to obtain Mo(CO)$_2$($\eta^3$-$C_3H_5$)Cl(DPPP) complex in 72% yield (148 mg). Melting point = 183-186 °C.; $^1$H NMR (500 MHz, Benzene-d$_6$) δ 7.72 (ddd, J = 8.7, 5.3, 3.3 Hz, 4H), 7.61 (ddd, J = 7.6, 5.8, 3.5 Hz, 4H), 7.04 (ddt, J = 15.1, 10.0, 4.9 Hz, 12H), 3.66 (dt, J = 6.4, 3.1 Hz, 2H), 3.57 (t, J = 6.5 Hz, 1H), 3.33 – 3.18 (m, 2H), 1.81 (qd, J = 11.7, 9.2, 6.3 Hz, 2H), 1.62 (d, J = 10.0 Hz, 2H), 1.48 – 1.36 (m, 1H), 1.11 (t, J = 7.0 Hz, 1H); $^{31}$P NMR (203 MHz, Benzene-d6) δ 9.08 (d, J = 34.0 Hz). Selected FT-IR (solid ATR, cm$^{-1}$): ν(CO) = 1925, 1840. HRMS: m/z calculated for **Mo-2**= 642.0542, observed m/z = 642.0487.



***Scheme S2**: Synthetic access to **Mo-2**.*

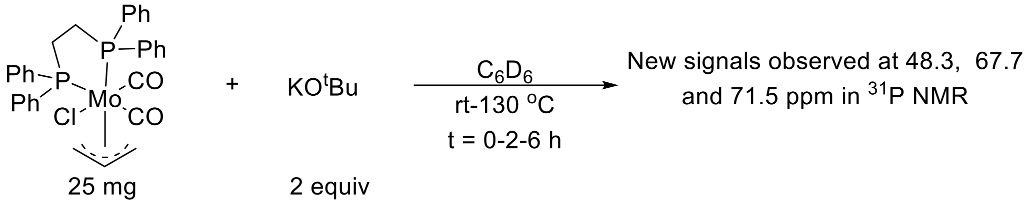
c) **General procedure for optimization of Friedländer quinoline synthesis using 2-aminobenzyl alcohol and acetophenone (Table 1):**
Certain mol% of the **Mo-1** or **Mo-2** complex (according to Table 1) was added to an oven-dried 25 mL Schlenk tube under the nitrogen atmosphere (in glove box) along with $^t$BuOK (X mol%) in 1.5 mL dry solvent (Table 1). Then 0.5 mmol of 2-aminobenzyl alcohol and 0.5 mmol (1 equiv.) of acetophenone were added to the reaction mixture and stirred for 5 min at room temperature. Afterwards the reaction vessel was taken out of the glove box was kept on a pre-heated oil bath at 130 °C (or as per Table 1 entries) for appropriate reaction time as mentioned in Table 1. The yield of the product was determined with the help of $^1$H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

d) **General procedure for Mo-1 catalyzed Friedländer quinoline synthesis using 2-aminobenzyl alcohol and substituted methyl ketones (Scheme 2):**
An oven-dried Schlenk tube (25 mL) under the nitrogen atmosphere was charged with **Mo-1** (3.25 mg, 0.005 mmol, 1 mol% wrt to alcohol), and $^t$BuOK (5.6 mg, 0.05 mmol, 10 mol% relative to alcohol) dissolved in 1.5 mL toluene. Following it, 0.5 mmol of 2-aminobenzyl alcohol and 0.5 mmol (1 equiv.) of various acetophenone derivatives were added to the reaction mixture and stirred for 5 min at room temperature. After the reaction mixture became homogeneous, the reaction vessel was heated at 130 °C for 16 h. After the given time, reaction mixture was cooled to room temperature, and products were analyzed with NMR after detection by TLC and separating through column chromatography.

e) **General procedure for Mo-1 catalyzed Friedländer quinoline synthesis using 2-aminobenzyl alcohol and substituted secondary alcohols (Scheme 3):**
An oven-dried Schlenk tube (25 mL) under the nitrogen atmosphere was charged with **Mo-1** (3.25 mg, 0.005 mmol, 1 mol% wrt to alcohol), and $^t$BuOK (5.6 mg, 0.05 mmol, 10 mol% wrt alcohol) dissolved in 1.5 mL toluene. Afterwards, 0.5 mmol of 2-aminobenzyl alcohol and 0.5 mmol (1 equiv.) of various secondary alcohols were added to the reaction mixture and stirred for 5 min at room temperature. After homogeneous mixing of the reaction mixture, the reaction vessel was heated at 130 °C for 24 h. After the given time, reaction mixture was cooled to room temperature, and products were analyzed by NMR after detection by TLC and separating through column chromatography.

f) **Experimental procedure for the stoichiometric reaction of $^t$BuOK and Mo complex, Mo-1:**
An oven-dried Schlenk tube (25 mL) under the nitrogen atmosphere was charged with **Mo-1** (25 mg, 0.039 mmol), and $^t$BuOK (9 mg, 0.0798 mmol) was added to it in 1.5 mL $C_6D_6$.

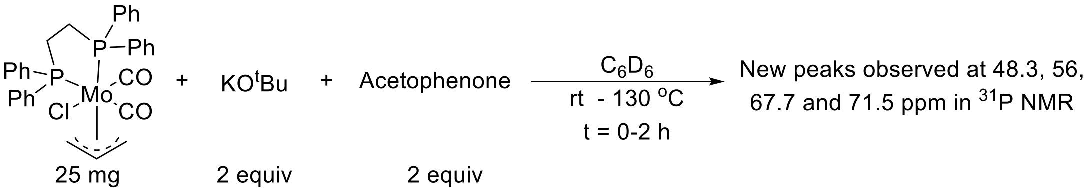
This reaction mixture was stirred for 30 min at room temperature. After 30 min, $^{1}$H NMR and $^{31}$P NMR data were recorded by taking about 0.5 ml of this suspension after filtration. Afterwards the reaction vessel was heated at 130 °C for 2 h. After the given time, reaction mixture was cooled to room temperature and filtered through celite. Then $^{1}$H and $^{31}$P NMR data were recorded again (Scheme S3). The results have been corroborated in Figure S16 and S-17. The observation of new signals in the $^{31}$P NMR indicated formation of new alkoxide species of type **Mo-1a**/**Mo-1a'** (Scheme 6 in the main manuscript).



*Scheme S3: Stoichiometric reaction to study the effect of addition of base to **Mo-1.***

## g) Experimental procedure for the stoichiometric reaction of $^{t}$BuOK, acetophenone and Mo-1:

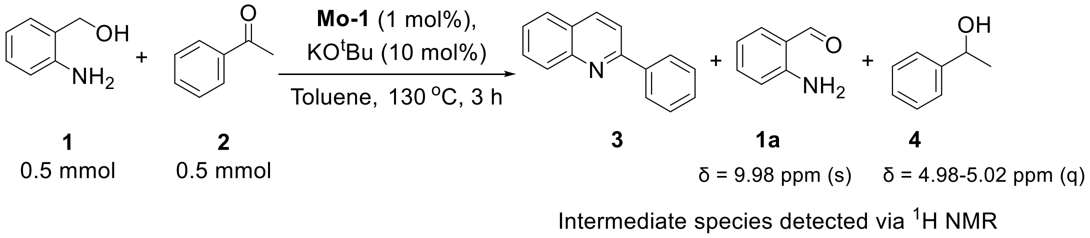
**Mo-1** (25 mg, 0.039 mmol) was added to an oven-dried Schlenk tube (25 mL) under the nitrogen atmosphere and $^{t}$BuOK (9 mg, 0.0798 mmol) was added to it in 2 mL $C_6D_6$, followed by addition of acetophenone (9 µL, 0.0798 mmol). This reaction mixture was stirred for 30 min at room temperature. After completion of the reaction, $^{1}$H NMR and $^{31}$P NMR data were measured by taking about 0.5 ml of this suspension after filtration through celite. The reaction vessel was heated at 130 °C for 2 h. After the given time, the reaction mixture was cooled to room temperature and filtered again to record $^{1}$H and $^{31}$P NMR data (Scheme S4). To elaborate the results after further heating, the reaction mixture was heated upto 6 h and the results have been shown in Figures S16 and S17.



*Scheme S4: Stoichiometric reaction to study the effect of addition of base and acetophenone to **Mo-1**.*

## h) Experimental procedure for detection of reaction intermediates formed during Mo-1 catalyzed Friedländer quinoline synthesis using 2-aminobenzyl alcohol and methyl ketones:

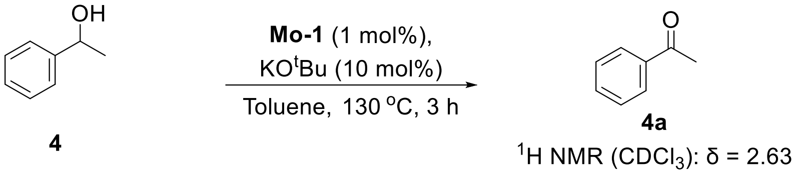
To an oven-dried Schlenk tube (25 mL), 3.25 mg of **Mo-1** (0.005 mmol, 1 mol% relative to alcohol) and 5.6 mg of $^{t}$BuOK (0.05 mmol, 10 mol% wrt alcohol) were dissolved in 1.5 mL toluene under nitrogen atmosphere. Next, 0.5 mmol of 2-aminobenzyl alcohol (62 mg) and 0.5 mmol (59 microL) of acetophenone were added to the reaction mixture and stirred for 5 min at room temperature. After the reaction mixture became homogeneous, the reaction vessel was heated at 130 °C for 3 h. The reaction mixture was cooled to room temperature, and products were analyzed by $^{1}$H NMR and HRMS (Scheme S5; also see Figure S13 and S14).



***Scheme S5:*** Reaction intermediates detected after 3 h of catalytic reaction using **Mo-1**.

### i) Experimental procedure for the dehydrogenation of 1-phenylethanol catalyzed by Mo-1 complex:

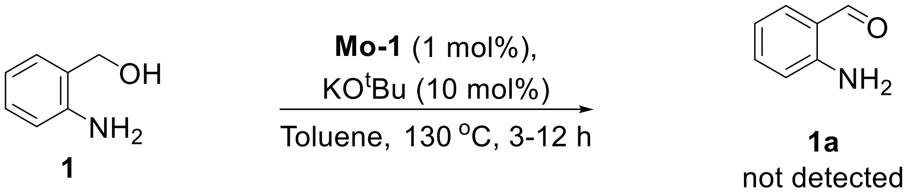
An oven-dried Schlenk tube (25 mL) under the nitrogen atmosphere was charged with 0.005 mmol of **Mo-1** (3.25 mg, 1 mol% wrt to alcohol), and 0.05 mmol of $^t$BuOK(5.6 mg, 10 mol% wrt alcohol) dissolved in 1.5 mL toluene. To this suspension, 0.5 mmol of 1-phenylethanol was added and stirred for 5 min at room temperature. After the reaction mixture became homogeneous, the reaction vessel was heated at 130 °C for 3 h (Scheme S6) After the given time, reaction mixture was cooled to room temperature. The product was analyzed with NMR (Figure S15).



***Scheme S6:*** *Dehydrogenation of 1-phenylethanol using **Mo-1** catalyst.*

### j) Experimental procedure for attempted dehydrogenation of 2-aminobenzyl alcohol catalyzed by Mo-1 complex:

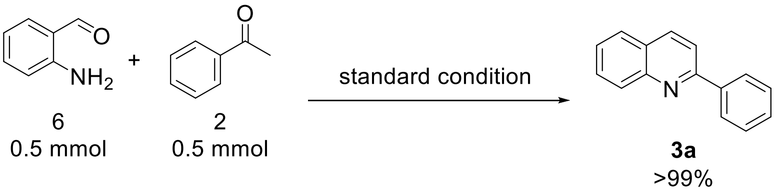
0.5 mmol of 2-aminobenzyl alcohol was added to an oven-dried 25 mL Schlenk tube containing 3.25 mg of **Mo-1** (0.005 mmol, 1 mol% wrt to alcohol) and 5.6 mg of $^t$BuOK ( 0.05 mmol, 10 mol% wrt alcohol) dissolved in 1.5 mL toluene, under the nitrogen atmosphere and stirred for 5 min at room temperature. After the reaction mixture became homogeneous, the reaction vessel was heated at 130 °C for 3 h. This reaction mixture was cooled to room temperature, and products were analyzed by $^1$H NMR (Scheme S7).



***Scheme S7:*** *Attempted reaction for dehydrogenation of 2-aminobenzyl alcohol using **Mo-1** complex.*

### k) Experimental procedure for the reaction of 2-aminobenzaldehyde with acetophenone catalyzed by Mo-1 in presence of $^t$BuOK to form quinoline:

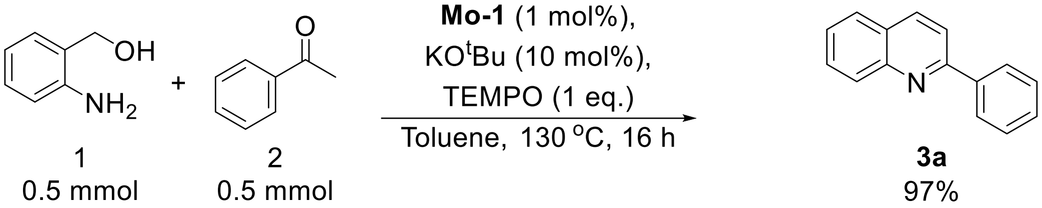
An oven-dried 25 mL Schlenk tube under the nitrogen atmosphere was charged with **Mo-1** (3.25 mg, 0.005 mmol, 1 mol% relative to alcohol), and $^t$BuOK (5.6 mg, 0.05 mmol, 10 mol% wrt alcohol) dissolved in 1.5 mL toluene. Afterwards 0.5 mmol of 2-aminobenzaldehyde and 0.5 mmol (1 equiv.) of acetophenone were added to the reaction mixture and stirred for 5 min at room temperature. Then the reaction vessel was heated at 130 °C for 16 h outside the glovebox. After the reaction was over, the mixture was cooled to room temperature. The product waw analyzed by NMR (Scheme S8).



***Scheme S8:*** *Control experiment using 2-aminobenzaldehyde and acetophenone in the Friedlander Quinoline synthesis catalyzed by **Mo-1.***

### l) Experimental procedure to study the effect of radical scavenger (TEMPO) on the Mo-1 catalyzed Friedländer quinoline synthesis using 2-aminobenzyl alcohol and acetophenone:

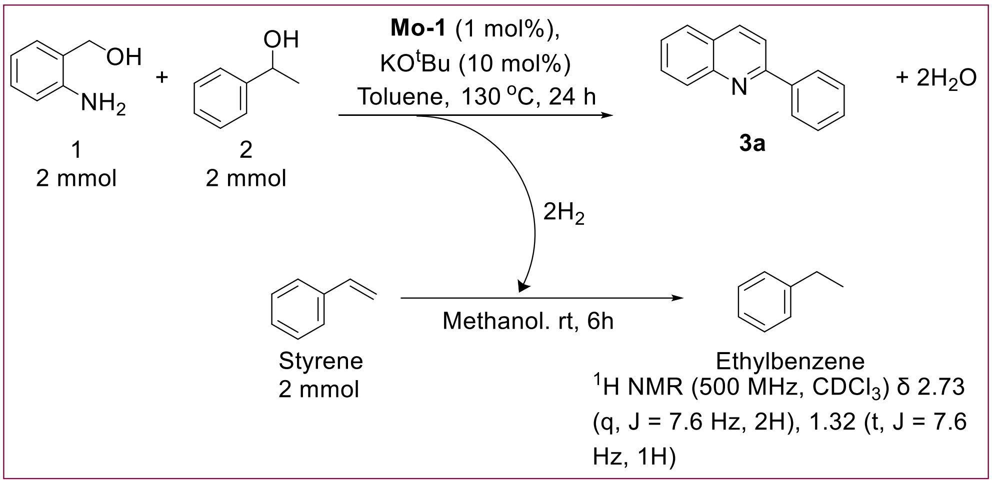
In an oven-dried Schlenk tube (25 mL), **Mo-1** (3.25 mg, 0.005 mmol, 1 mol% relative to alcohol), and $^t$BuOK (5.6 mg, 0.05 mmol, 10 mol% wrt alcohol) were mixed in 1.5 mL toluene under the nitrogen atmosphere. To this suspension, 0.5 mmol of 2-aminobenzyl alcohol and 0.5 mmol (1 equiv.) of acetophenone were added. Then 0.5 mmol of TEMPO was added and stirred for 5 min at room temperature. After the reaction mixture became homogeneous, the reaction mixture was heated at 130 °C for 16 h. The reaction mixture was cooled to room temperature after the reaction was over, and products were analyzed by $^1$H NMR (Scheme S9).



***Scheme S9:*** *Catalytic experiment with the addition of TEMPO under optimized reaction conditions.*

**m) Experimental procedure for hydrogenation of styrene using Pd/C and $H_2$ gas (evolved during formation of quinoline from 2-aminobenzyl alcohol and 1-phenylethanol)**

Inside glovebox, in one chamber of a bridged Schlenk tube was taken 2-aminobenzyl alcohol (2 mmol), 1-phenylethanol (2 mmol), **Mo-1** (1 mol%), $^t$BuOK (10 mol%) and toluene (2 mL), while in the other chamber was added styrene (2 mmol) and Pd/C in methanol (1mL). The first chamber was allowed to stir at 130 °C for 24 h for the quinoline formation. Soon after the completion of the reaction, the Schlenk tube was allowed to cool down and the middle cap was opened slightly, and the generated gas was allowed to pass from the first chamber to second chamber (Figure S1). The second chamber was allowed to stir at room temperature for the next 6 h. The conversion of styrene to ethyl benzene was confirmed via $^1$H NMR: ($^1$H NMR (500 MHz, Chloroform-*d*) δ 2.73 (q, *J* = 7.6 Hz, 2H), 1.32 (t, *J* = 7.6 Hz, 1H) (Scheme S10).



***Scheme S10:*** *Hydrogen detection experiment. Hydrogenation of styrene with the $H_2$ evolved during formation of quinoline from 2-aminobenzyl alcohol and 1-phenylethanol*

***Figure S1:*** *Experimental bridge-shaped Schlenk tube setup for hydrogenation of styrene using Pd/C and generated $H_2$ from annulation of 2-aminobenzyl alcohol with 1-phenylethanol to form quinoline derivatives.*

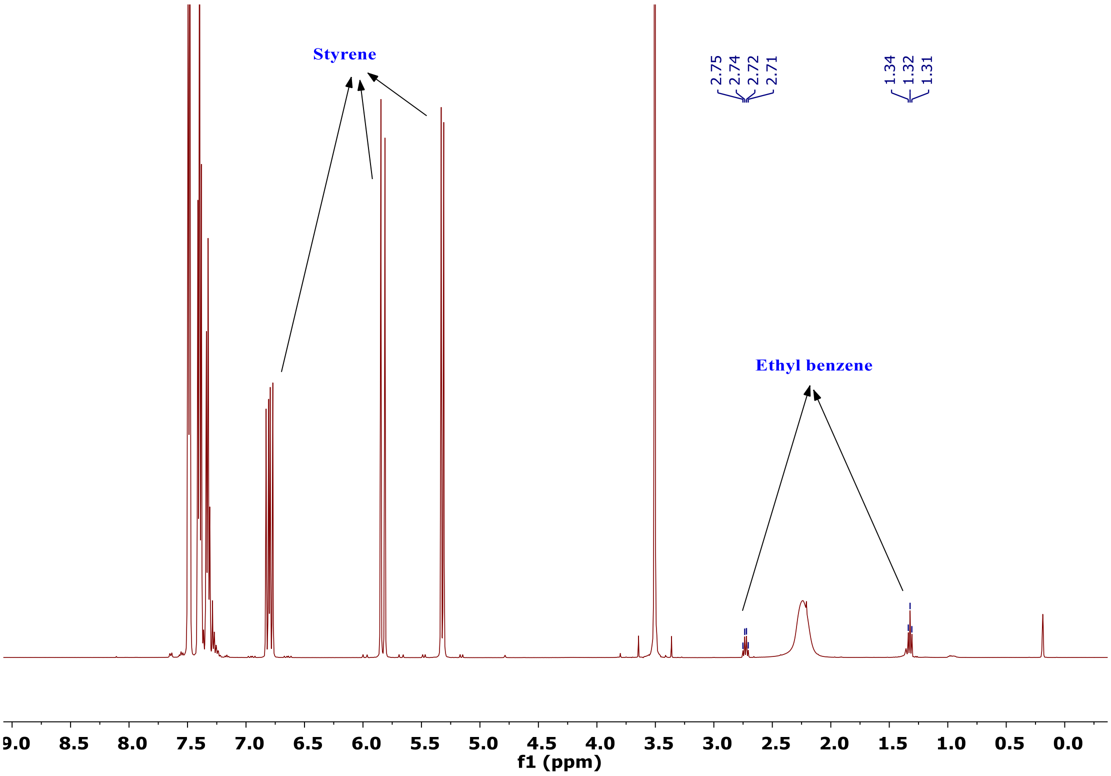


***Figure S2:*** *$^1H$ NMR (500 MHz, 298 K, $CDCl_3$) spectrum of styrene hydrogenation using Pd/C and $H_2$, released from annulation of 2-aminobenzyl alcohol with 1-phenylethanol to form quinoline derivative.*

## 3. X-Ray crystallographic studies

Light yellow crystals of **Mo-1** and **Mo-2** were grown by diffusion of pentane over the solution of metal complexes in DCM. Suitable crystals were selected, and the diffraction data were collected on a Bruker APEX-II CCD diffractometer at 296 K using Mo Kα radiation ($\lambda = 0.71073$ Å). Using Olex2[2], the structures of **Mo-1** and **Mo-2** were solved with the olex2.solve[3] structure solution program using Charge Flipping and refined with the XL[4] refinement package using Least Squares minimisation. The absorption correction was done using the multi-scan method (SADABS). Crystallographic data files **Mo-1** and **Mo-2** have been deposited to the Cambridge Crystallographic Data Centre. CCDC number: **2481402** (**Mo-1**) and **2481403** (**Mo-2**). It is to be noted that the crystallographic data of **Mo-1** was also previously reported, we have reproduced the crystal for establishing the metal connectivity.[1c]

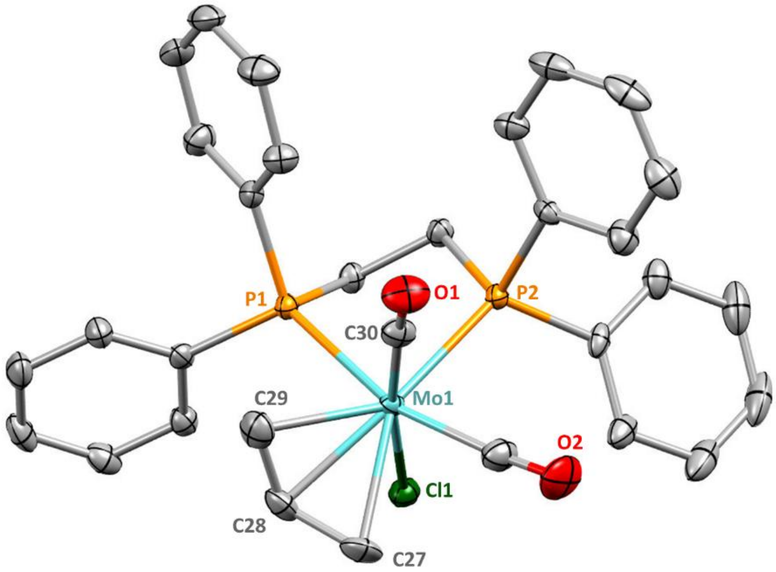


***Figure S3:*** *Molecular structure of **Mo-1**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.*

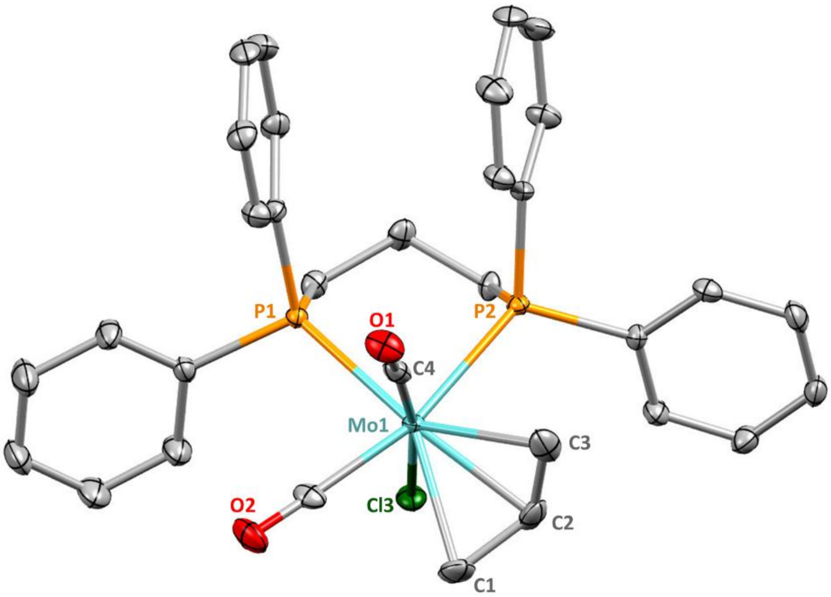


***Figure S4:*** *Molecular structure of **Mo-2**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.*

**Table S1. Crystal data and structure refinement for Mo-1 and Mo-2.**

| | **Mo-1** | **Mo-2** |
|---|---|---|
| Empirical formula | $C_{31}H_{29}ClMoO_2P_2$ | $C_{32}H_{31}ClMoO_2P_2$ |
| Formula weight | 626.87 | 640.90 |

| | | |
|---|---|---|
| Temperature/K | 296.15 | 296.15 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1/n$ | $P2_1/c$ |
| a/Å | 11.314(4) | 16.683(2) |
| b/Å | 17.847(6) | 8.4960(10) |
| c/Å | 14.475(5) | 20.119(2) |
| α/° | 90 | 90 |
| β/° | 106.533(10) | 90.388(4) |
| γ/° | 90 | 90 |
| Volume/Å$^3$ | 2801.9(17) | 2851.5(6) |
| Z | 4 | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.486 | 1.493 |
| μ/mm$^{-1}$ | 0.705 | 0.694 |
| F(000) | 1280.0 | 1312.0 |
| Crystal size/mm$^3$ | 0.58 × 0.28 × 0.22 | 0.7 × 0.4 × 0.3 |
| Radiation | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 3.718 to 55.916 | 4.05 to 55.032 |
| Index ranges | $-14 \leq h \leq 14$, $-23 \leq k \leq 23$, $-19 \leq l \leq 19$ | $-21 \leq h \leq 21$, $-11 \leq k \leq 10$, $-24 \leq l \leq 26$ |
| Reflections collected | 93474 | 38698 |
| Independent reflections | 6720 [$R_{int}$ = 0.0929, $R_{sigma}$ = 0.0356] | 4562 [$R_{int}$ = 0.0641, $R_{sigma}$ = 0.0786] |
| Data/restraints/parameters | 6720/0/334 | 4562/0/351 |
| Goodness-of-fit on F$^2$ | 1.083 | 1.082 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0402, $wR_2$ = 0.0763 | $R_1$ = 0.0526, $wR_2$ = 0.1072 |
| Final R indexes [all data] | $R_1$ = 0.0545, $wR_2$ = 0.0825 | $R_1$ = 0.0954, $wR_2$ = 0.1180 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.52/-0.75 | 0.66/-1.61 |

**Crystallographic Alerts Level A from CheckCIF with the Author Responses**

**Datablock: va-mo_2 (Mo-2)**

PLAT029_ALERT_3_A _diffrn_measured_fraction_theta_full value Low . 0.708 Why?

**Author Response: Poorly diffracting crystals. Used only to authenticate atom connectivity.**

Alert level B
PLAT911_ALERT_3_B Missing FCF Refl Between Thmin & STh/L= 0.600 1507 Report
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( 1477 More Missing: see the .ckf listing file)
**Author Response: Poorly diffracting crystals. Used only to authenticate atom connectivity.**

**Table S2: Selected bond distances (Å) and bond angles (°) for Mo-1**

| **Atoms** | **Bond distances (Å)** | **Atoms** | **Bond angles (°)** |
|---|---|---|---|
| Mo1-Cl1 | 2.5791(10) | Cl1-Mo1-P1 | 80.76(3) |
| Mo1-P1 | 2.5840(9) | P2-Mo1-Cl1 | 82.62(3) |
| Mo1-P2 | 2.5294(10) | P2-Mo1-P1 | 75.45(3) |
| Mo1-C27 | 2.330(3) | C27-Mo1-Cl1 | 80.58(9) |
| Mo1-C28 | 2.233(3) | C27-Mo1-P1 | 126.29(8) |
| Mo1-C29 | 2.347(3) | C27-Mo1-P2 | 149.31(9) |
| Mo1-C30 | 1.943(3) | C27-Mo1-C29 | 61.51(12) |
| Mo1-C31 | 1.980(3) | C28-Mo1-Cl1 | 82.98(9) |
| O1-C30 | 1.149(4) | C28-Mo1-P1 | 92.14(9) |
| O2-C31 | 1.147(4) | C28-Mo1-P2 | 162.31(8) |
| C27-C28 | 1.404(5) | C28-Mo1-C27 | 35.77(11) |
| C28-C29 | 1.403(5) | C28-Mo1-C29 | 35.56(11) |
|  |  | C29-Mo1-Cl1 | 114.73(9) |
|  |  | C29-Mo1-P1 | 82.19(8) |
|  |  | C29-Mo1-P2 | 149.13(8) |
|  |  | C30-Mo1-Cl1 | 172.19(9) |
|  |  | C30-Mo1-P1 | 101.09(9) |
|  |  | C30-Mo1-P2 | 90.48(9) |
|  |  | C30-Mo1-C27 | 103.96(12) |
|  |  | C30-Mo1-C28 | 104.45(12) |
|  |  | C30-Mo1-C29 | 73.07(12) |
|  |  | C30-Mo1-C31 | 77.48(13) |
|  |  | C31-Mo1-Cl1 | 98.49(10) |
|  |  | C31-Mo1-P1 | 162.92(10) |
|  |  | C31-Mo1-P2 | 87.51(10) |
|  |  | C31-Mo1-C27 | 69.91(12) |
|  |  | C31-Mo1-C28 | 104.75(13) |
|  |  | C31-Mo1-C29 | 113.10(13) |
|  |  | C27-C28-C29 | 116.9(3) |
|  |  | Cl-P1-Mo1 | 106.18(9) |
|  |  | C15-P1-Mo1 | 118.28(9) |
|  |  | C21-P1-Mo1 | 120.91(9) |
|  |  | C2-P2-Mo1 | 112.68(9) |
|  |  | C3-P2-Mo1 | 119.18(10) |
|  |  | C9-P2-Mo1 | 114.02(9) |
|  |  | C28-C27-Mo1 | 68.35(16) |
|  |  | C27-C28-Mo1 | 75.88(17) |
|  |  | C29-C28-Mo1 | 76.65(18) |
|  |  | C28-C29-Mo1 | 67.79(17) |
|  |  | O1-C30-Mo1 | 175.6(3) |

|  |  |  |  |
|---|---|---|---|
|  |  | O2-C31-Mo1 | 173.1(3) |

**Table S3: Selected bond distances (Å) and bond angles (°) for Mo-2**

| **Atoms** | **Bond distances (Å)** | **Atoms** | **Bond angles (°)** |
|---|---|---|---|
| Mo1-Cl3 | 2.5767(9) | Cl3-Mo1-P2 | 83.93(3) |
| Mo1-P1 | 2.5746(10) | P1-Mo1-Cl3 | 82.96(3) |
| Mo1-P2 | 2.6079(9) | P1-Mo1-P2 | 78.48(3) |
| Mo1-C1 | 2.333(4) | C1-Mo1-Cl3 | 79.79(11) |
| Mo1-C2 | 2.240(4) | C1-Mo1-P1 | 148.67(10) |
| Mo1-C3 | 2.360(4) | C1-Mo1-P2 | 124.92(10) |
| Mo1-C4 | 1.930(4) | C1-Mo1-C3 | 61.39(14) |
| Mo1-C32 | 1.991(4) | C2-Mo1-Cl3 | 84.29(11) |
| O1-C4 | 1.165(4) | C2-Mo1-P1 | 163.90(11) |
| O2-C32 | 1.150(4) | C2-Mo1-P2 | 90.44(11) |
| C1-C2 | 1.417(6) | C2-Mo1-C1 | 36.03(14) |
| C2-C3 | 1.407(6) | C2-Mo1-C3 | 35.50(16) |
|  |  | C3-Mo1-Cl3 | 117.00(11) |
|  |  | C3-Mo1-P1 | 149.63(11) |
|  |  | C3-Mo1-P2 | 81.12(10) |
|  |  | C4-Mo1-Cl3 | 171.79(10) |
|  |  | C4-Mo1-P1 | 92.38(11) |
|  |  | C4-Mo1-P2 | 101.83(10) |
|  |  | C4-Mo1-C1 | 101.24(15) |
|  |  | C4-Mo1-C2 | 101.38(15) |
|  |  | C4-Mo1-C3 | 70.06(15) |
|  |  | C4-Mo1-C32 | 79.01(13) |
|  |  | C32-Mo1-Cl3 | 93.96(10) |
|  |  | C32-Mo1-P1 | 87.25(11) |
|  |  | C32-Mo1-P2 | 165.73(11) |
|  |  | C32-Mo1-C1 | 68.20(15) |
|  |  | C32-Mo1-C2 | 103.42(15) |
|  |  | C32-Mo1-C3 | 112.16(14) |

## 4. Characterization data of the Complexes:

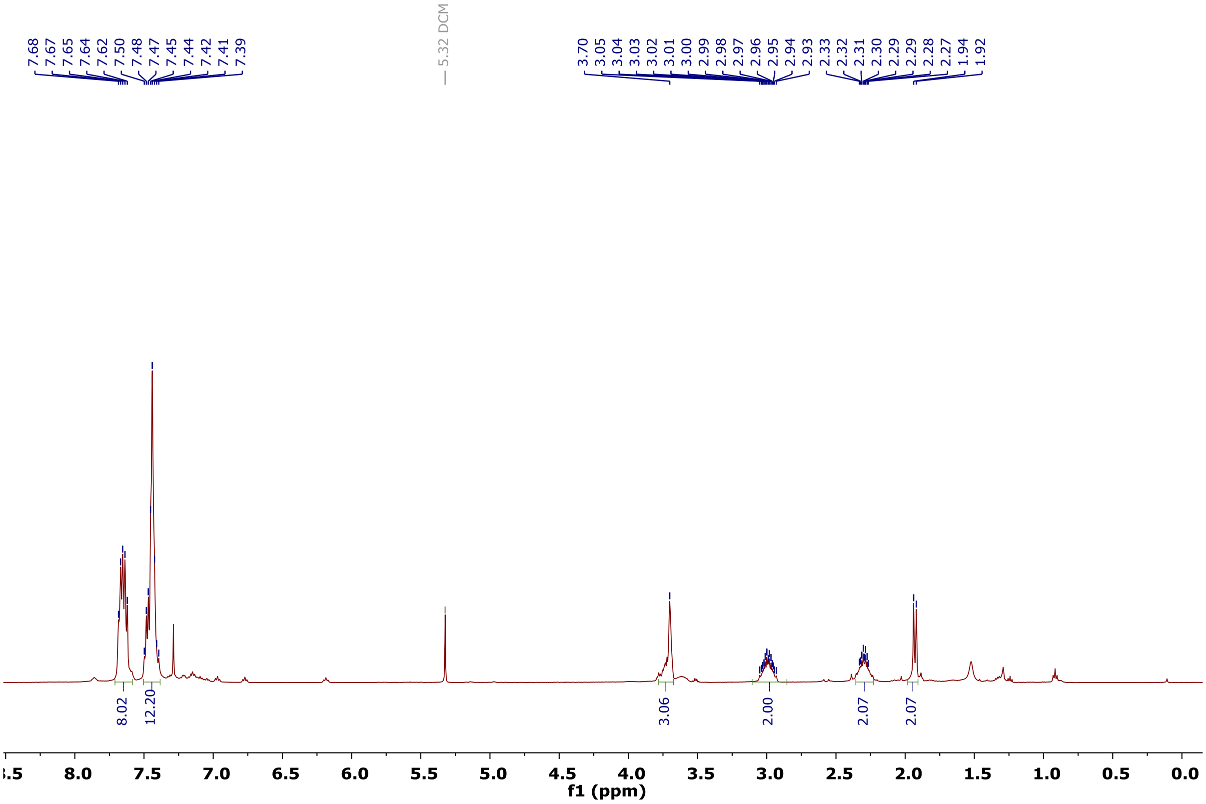


***Figure S5:*** *$^{1}H$ NMR (500 MHz) data recorded for **Mo-1** using $CDCl_3$ solvent at room temperature.*

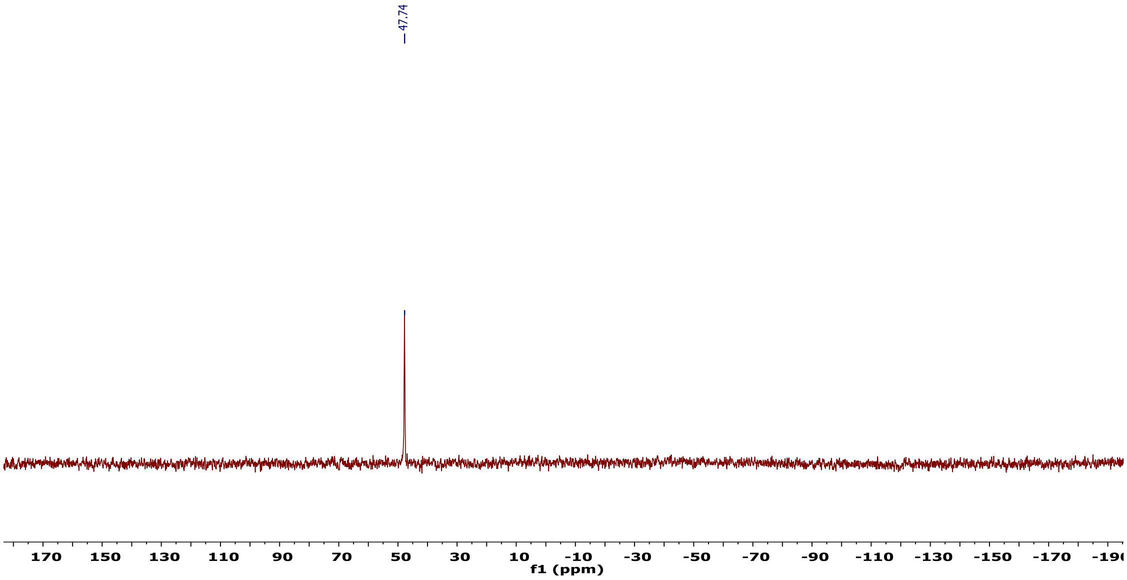


***Figure S6****: $^{31}P$ NMR (203 MHz) data recorded for **Mo-1** using $CDCl_3$ solvent at room temperature.*

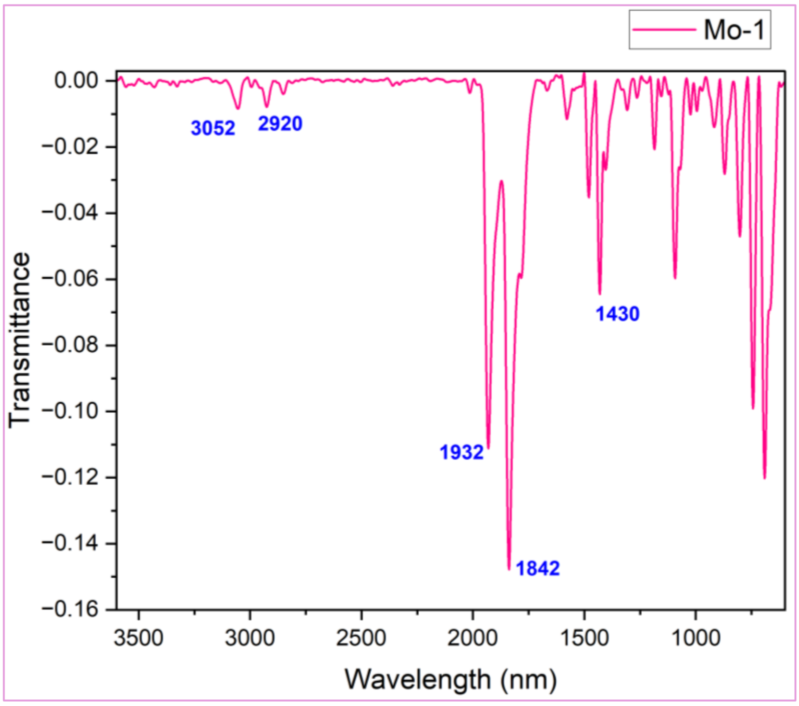


***Figure S7***: *IR data for* ***Mo-1*** *(solid ATR recorded at room temperature).*[1a]

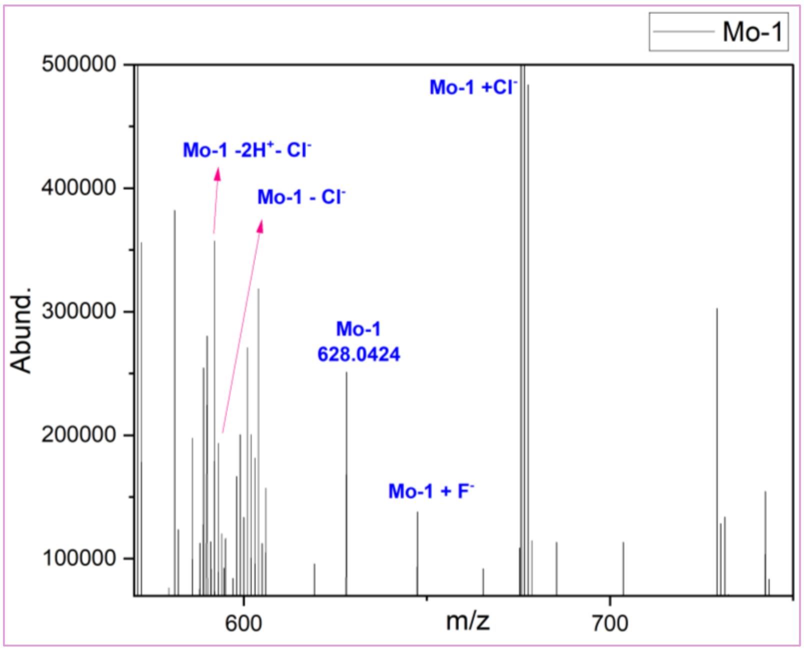


***Figure S8***: *HRMS data for* ***Mo-1*** *(m/z calculated for* ***Mo-1****= 628.0385 , observed m/z = 628.0424).*[1a]

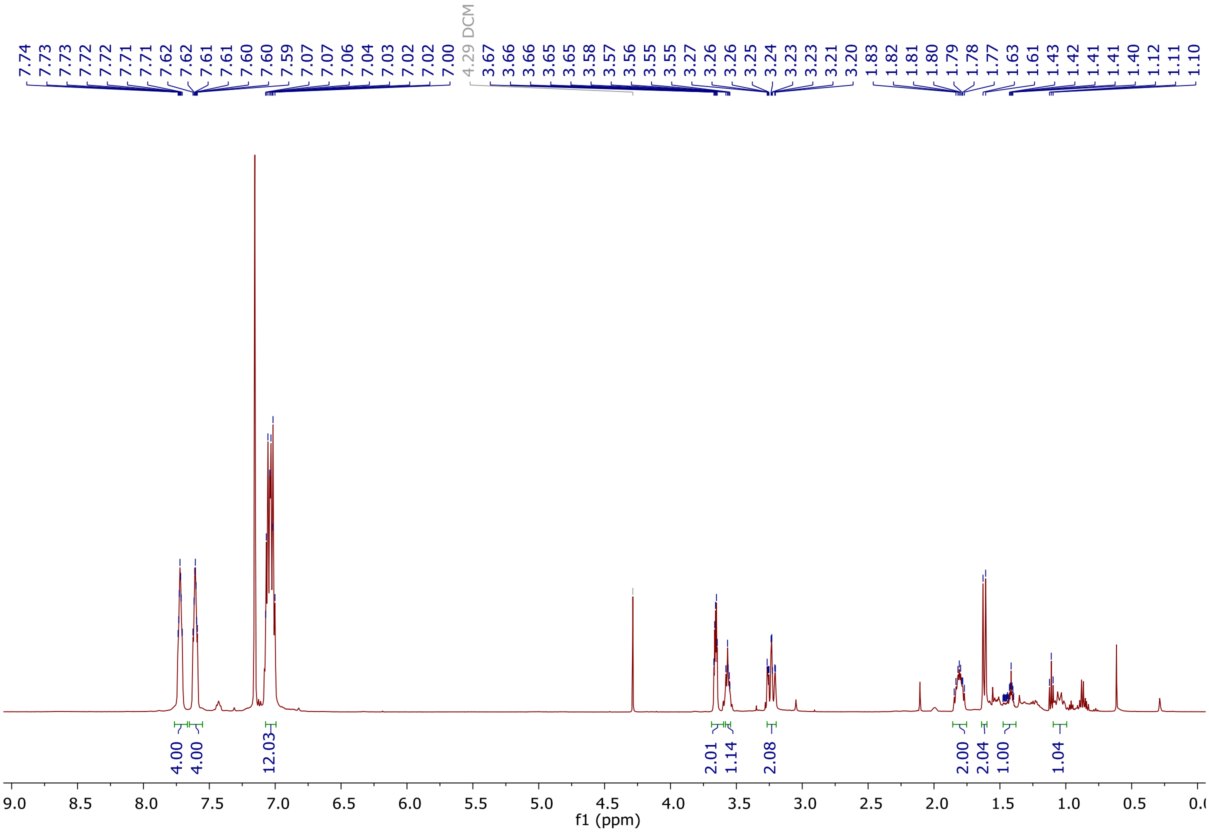


***Figure S9:*** *$^{1}$H NMR (500 MHz) data recorded for **Mo-2** using $C_6D_6$ solvent at room temperature.*

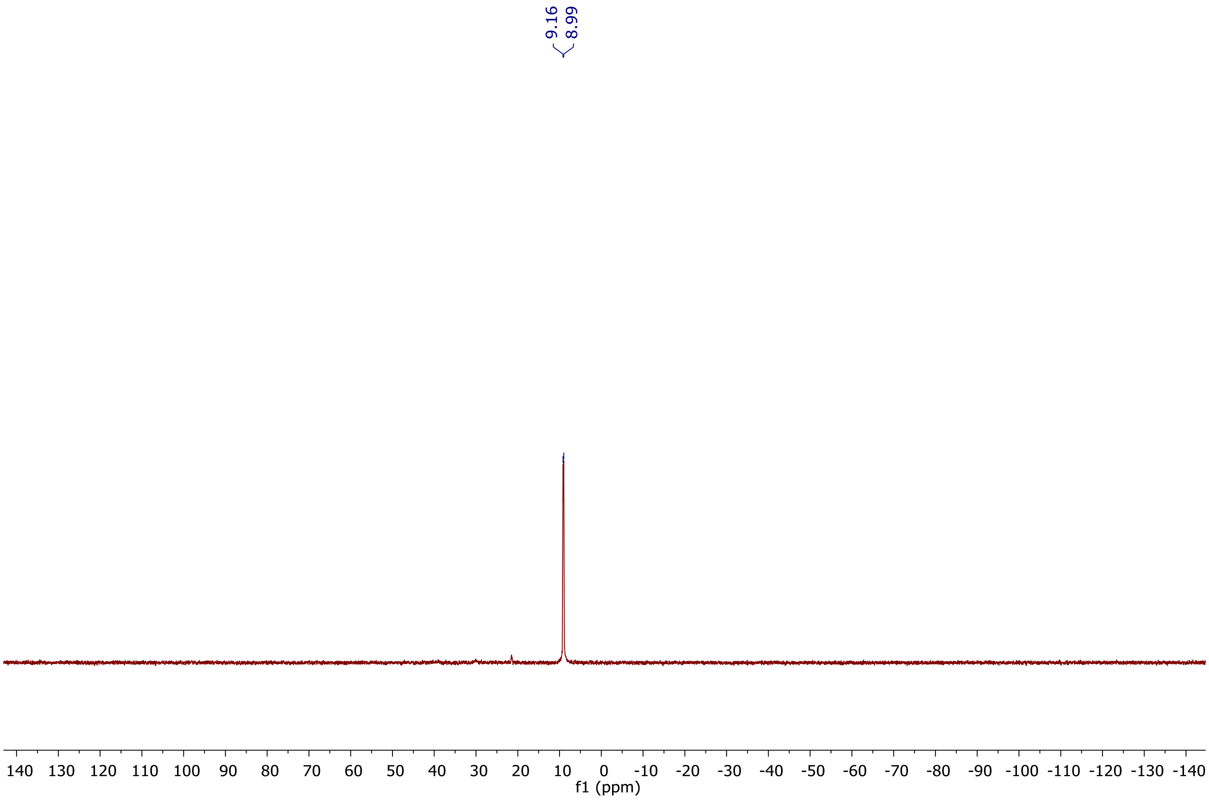


***Figure S10:*** *$^{31}$P NMR (203 MHz) data recorded for **Mo-2** using $C_6D_6$ solvent at room temperature.*

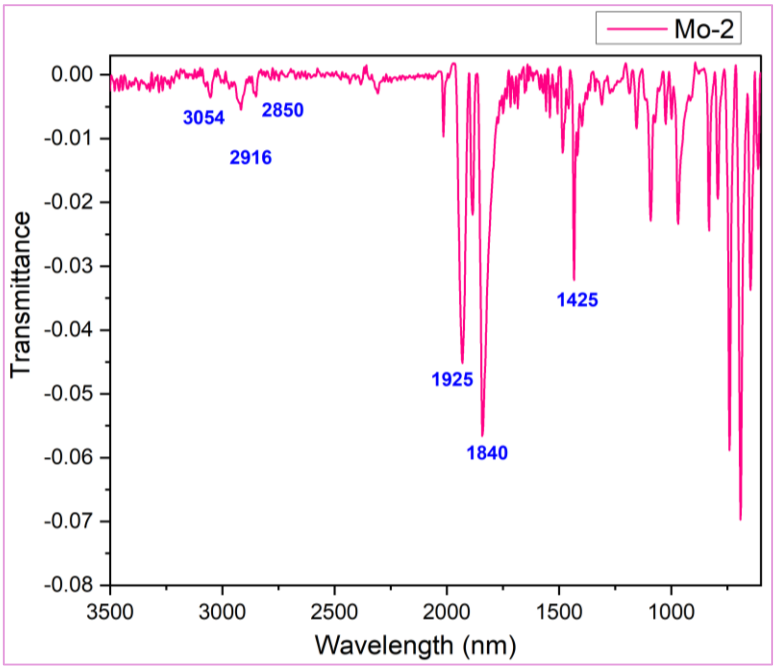


***Figure S11****: IR data for* ***Mo-2*** *(solid ATR recorded at room temperature).*[1a]

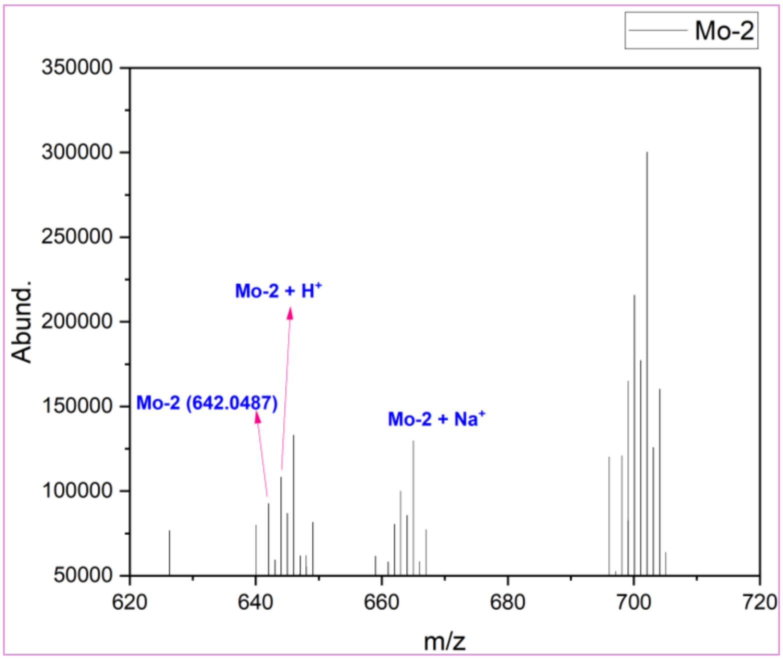


***Figure S12****: HRMS data for* ***Mo-2*** *(m/z calculated for* ***Mo-2****= 642.0542 , observed m/z = 642.0487).*

## 5. Mechanistic studies:

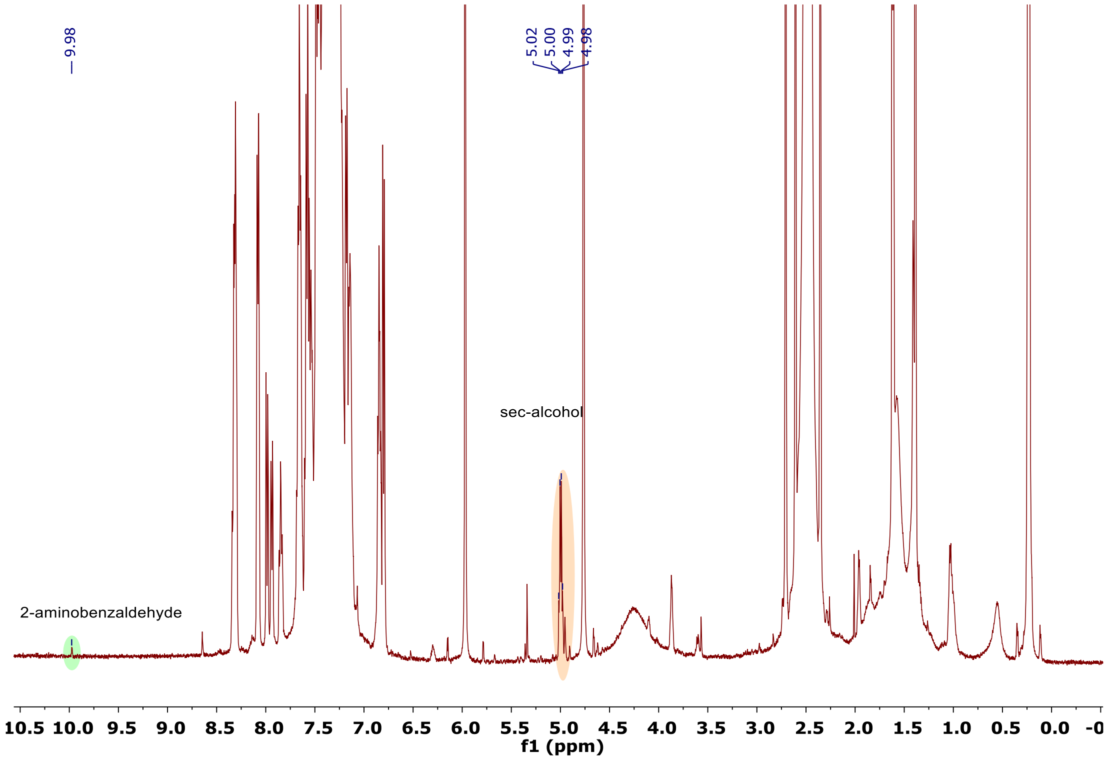


***Figure S13:*** *$^1$H NMR after heating 2-aminobenzyl alcohol (0.5 mmol) and acetophenone (0.5 mmol) with* ***Mo-1*** *(1 mol%) and $^t$BuOK (10%) in toluene for 3 h [ $^1$H NMR (500 MHz, Chloroform-d)].*

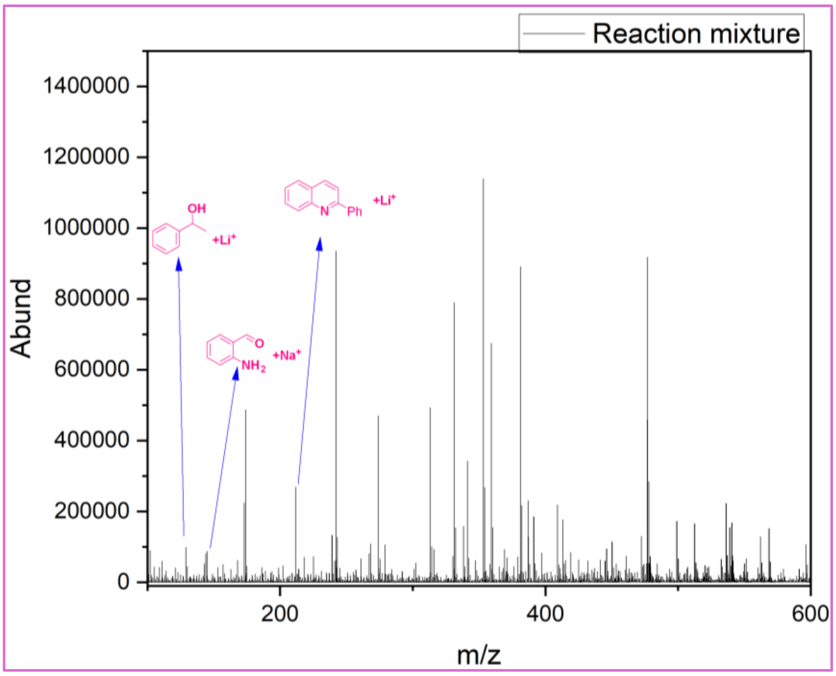


***Figure S14****: HRMS data recorded after heating 2-aminobenzyl alcohol (0.5 mmol) with 1-phenylethanol (0.5 mmol) for 3 h in toluene using* ***Mo-1*** *(1 mol%) catalyst and $^t$BuOK (10 mol%), for detection of reaction intermediates.*

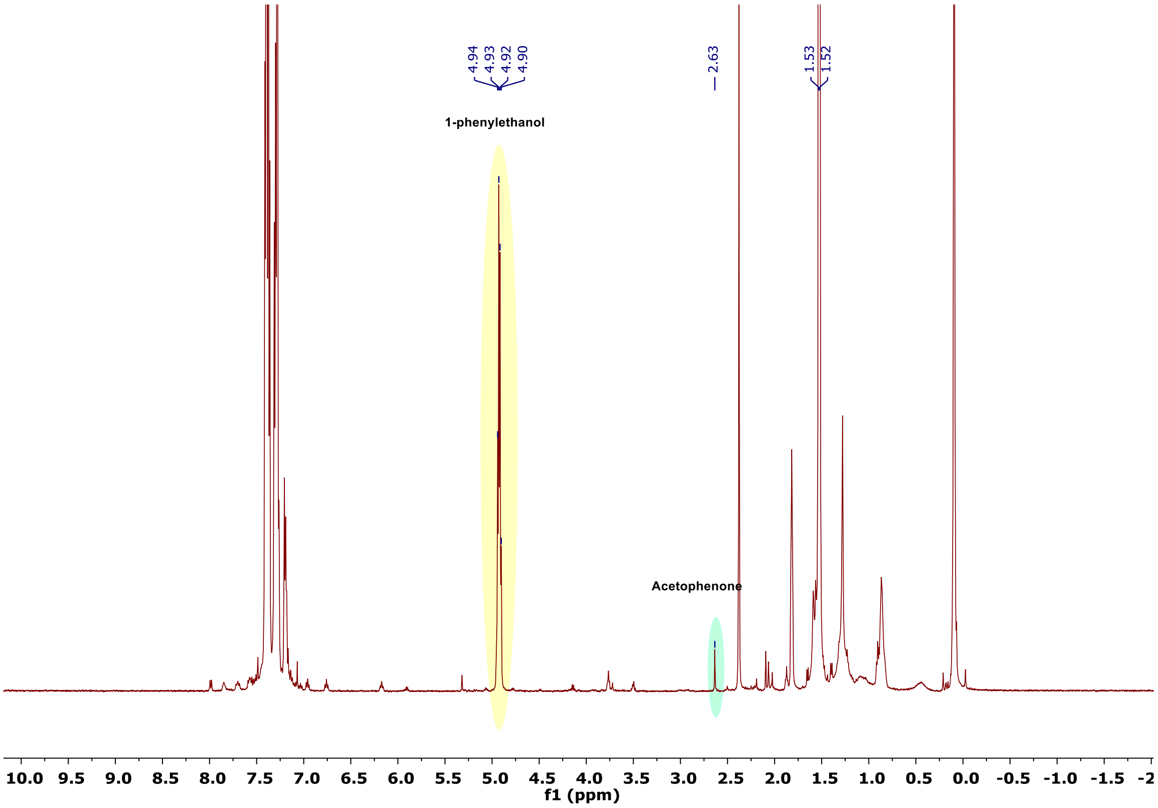


***Figure S15:*** *$^{1}$H NMR after heating 1-phenylethanol (0.5 mmol) with **Mo-1** (1 mol%) and $^{t}$BuOK (10%) in toluene for 3 h [$^{1}$H NMR (500 MHz, Chloroform-d)].*

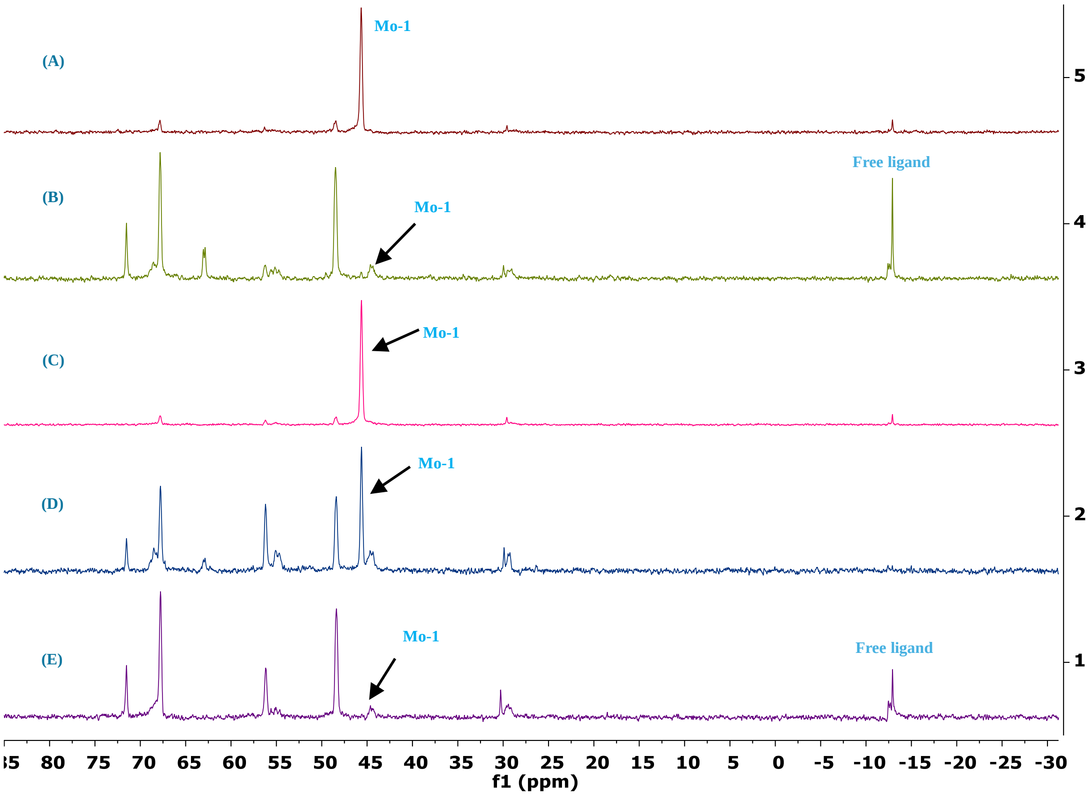


***Figure S16:*** *$^{31}$P NMR study for various reaction conditions for determination of intermediate species using $C_6D_6$. (**A**) Reaction of **Mo-1** with KO$^{t}$Bu at room temperature. (**B**) Reaction of **Mo-1** with $^{t}$BuOK at 130 °C for 2 h. (**C**) Reaction of **Mo-1**, KO$^{t}$Bu and acetophenone at room temperature. (**D**) Reaction of **Mo-1**, KO$^{t}$Bu and acetophenone at 130 °C for 2 h. (**E**) Reaction of **Mo-1**, KO$^{t}$Bu and acetophenone at 130 °C for 6 h.*

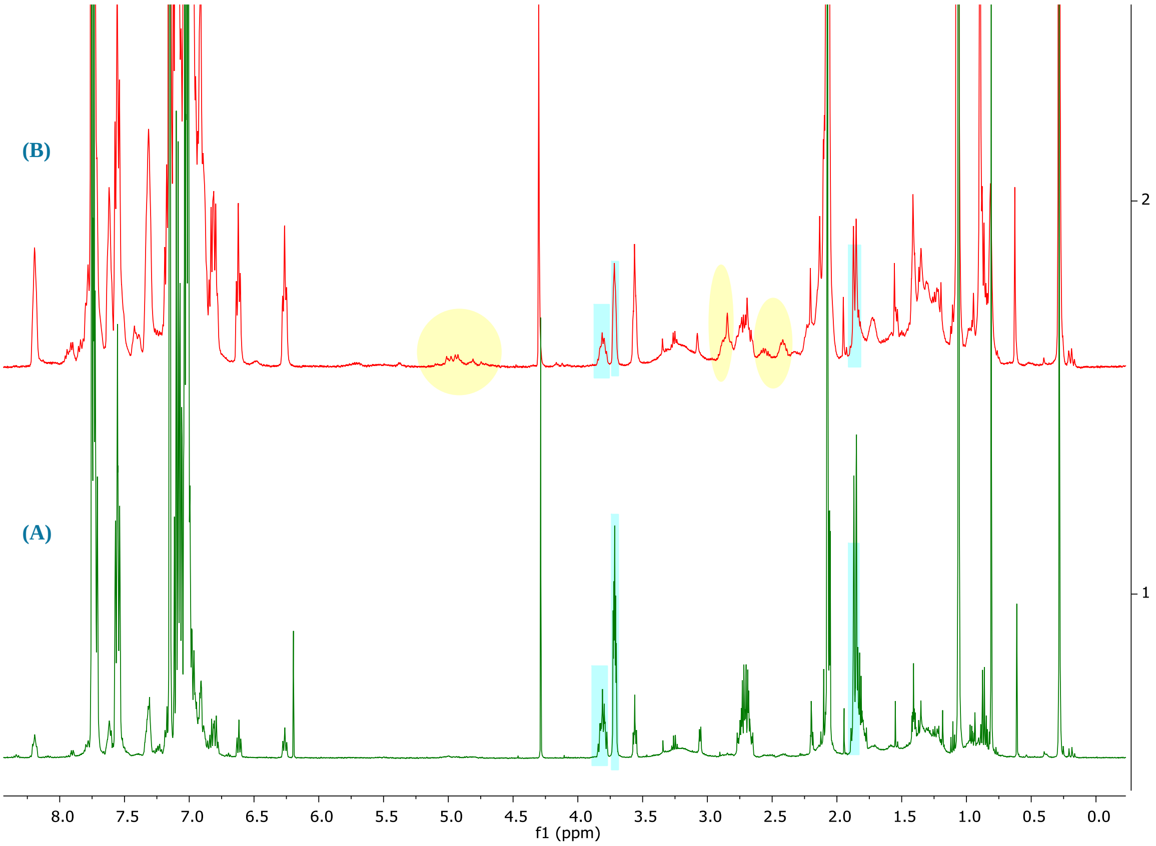
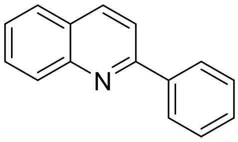


***Figure S17:*** *$^1$H NMR study to identify intermediate species (in $C_6D_6$). (**A**) Bottom spectrum: After adding 2 equiv. of $^t$BuOK and 2 equiv. acetophenone to **Mo-1** (25 mg) at room temperature (**B**) top spectrum: After heating 2 equiv. of $^t$BuOK, 2 equiv. acetophenone and 1 equiv. of **Mo-1** (25 mg) at 130 °C for 2 h. The blue regions highlight the allyl peaks of a catalytically active species generated from **Mo-1** and base. The minor peaks at 5.01 (m), 2.5 (m) and 2.8 (m) ppm (yellow highlight) indicate the formation of 1-Phenyl-pent-4-en-1-one (Tsuji-Trost product).*

## 6. Analytical data of isolated products and NMR spectra

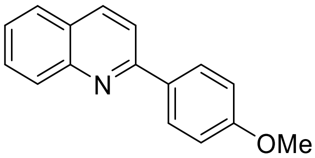
### A. Friedlander Quinoline synthesis using 2-aminobenzyl alcohol and variety of ketones

**1. 2-phenylquinoline (3a)**[5]



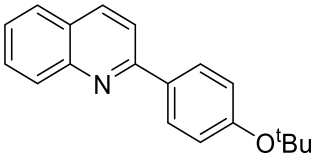
$^1$H NMR (500 MHz, Chloroform-*d*) δ 8.15 – 8.05 (m, 4H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.64 (t, 1H), 7.48 – 7.40 (m, 3H), 7.38 (t, *J* = 7.3 Hz, 1H). $^{13}$C NMR (126 MHz, Chloroform-*d*) δ 157.41, 148.32, 139.73, 136.81, 129.77, 129.69, 129.35, 128.88, 127.61, 127.50, 127.22, 126.32, 119.05. Yield = 86% (88 mg).

**2. 2-(4-methoxyphenyl)quinoline (3b)**[6]



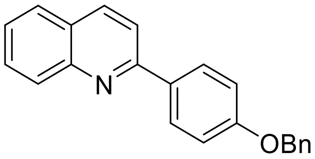
$^1$H NMR (500 MHz, Chloroform-*d*) δ 8.18 (d, *J* = 4.8 Hz, 1H), 8.16 (d, *J* = 4.6 Hz, 2H), 8.14 (s, 1H), 7.82 (d, *J* = 8.6 Hz, 1H), 7.80 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.71 (ddd, *J* = 8.5, 6.8, 1.5 Hz, 1H), 7.50 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.05 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H). $^{13}$C NMR (126 MHz, Chloroform-*d*) δ 160.88, 156.85, 148.13, 136.76, 132.06, 129.65, 129.39, 128.95, 127.43, 126.90, 125.96, 118.56, 114.25, 55.39. Yield = 60% (71 mg).

**3. 2-(4-(tert-butoxy)phenyl)quinoline (3c)**[5]



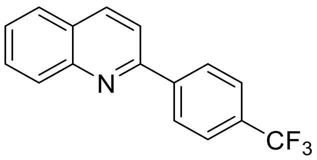
$^1$H NMR (500 MHz, Chloroform-*d*) δ 8.23 (t, 2H), 8.14 (dd, *J* = 8.4, 2.2 Hz, 2H), 7.90 (d, *J* = 8.7 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.75 (t, *J* = 7.7 Hz, 1H), 7.59 (dd, *J* = 8.5, 2.1 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 1.42 (s, 9H). $^{13}$C NMR (126 MHz, Chloroform-*d*) δ 157.37, 152.60, 148.22, 136.73, 129.61, 127.43, 127.32, 127.10, 126.12, 125.83, 118.97, 34.75, 31.29. Yield = 61% (85 mg).

**4. 2-(4-(benzyloxy)phenyl)quinoline (3d)**[5]



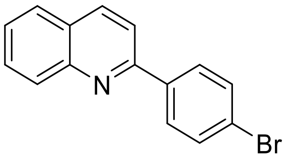
$^1$H NMR (500 MHz, Chloroform-*d*) δ 8.16 (dd, *J* = 11.3, 8.8 Hz, 4H), 7.86 – 7.78 (m, 2H), 7.72 (ddd, *J* = 8.3, 6.9, 1.5 Hz, 1H), 7.50 (dd, *J* = 15.8, 7.3 Hz, 3H), 7.41 (dd, *J* = 8.3, 6.7 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.13 (d, *J* = 8.8 Hz, 2H), 5.16 (s, 2H). $^{13}$C NMR (126 MHz, Chloroform-*d*) δ 160.01, 156.90, 148.33, 136.83, 136.66, 132.54, 129.61, 129.57, 128.94, 128.67, 128.08, 127.53, 127.47, 126.95, 125.96, 118.58, 115.21, 70.10. Yield = 67% (104 mg).

**5. 2-(4-(trifluoromethyl)phenyl)quinoline (3e)**[5]



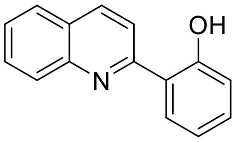
$^{1}$H NMR (500 MHz, Chloroform-*d*) δ 8.47 (s, 1H), 8.36 (d, *J* = 7.8 Hz, 1H), 8.26 (d, *J* = 8.7 Hz, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 7.89 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.85 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.76 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.56 (ddd, *J* = 8.1, 6.8, 1.4 Hz, 1H). $^{13}$C NMR (126 MHz, Chloroform-*d*) δ 156.05, 148.72, 140.84, 137.64, 131.74 (q, *J* = 32.4 Hz), 131.18, 130.37 (d, *J* = 22.1 Hz), 129.78, 127.99, 127.86, 127.25, 126.36 (q, *J* = 3.7 Hz), 124.89 (q, *J* = 3.9 Hz), 119.06. $^{19}$F NMR (471 MHz, Chloroform-*d*) δ -62.50. Yield = 83% (112 mg).

6. **2-(4-bromophenyl)quinoline (3f)**[5]



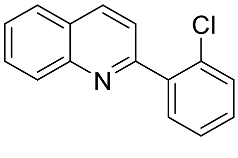
$^{1}$H NMR (500 MHz, Chloroform-*d*) δ 8.21 (d, *J* = 8.6 Hz, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 8.05 (d, *J* = 8.6 Hz, 2H), 7.83 (d, *J* = 8.6 Hz, 2H), 7.74 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.54 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H). $^{13}$C NMR (126 MHz, Chloroform-*d*) δ 156.06, 148.27, 138.52, 137.00, 132.00, 129.81 (d, *J* = 19.3 Hz), 129.12, 127.52, 127.27, 126.55, 123.95, 118.53. Yield = 81% (115 mg).

7. **2-(quinolin-2-yl)phenol (3g)**[5]



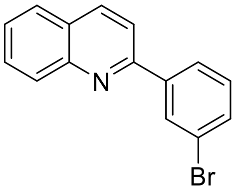
$^{1}$H NMR (500 MHz, Chloroform-*d*) δ 8.25 (t, *J* = 9.3 Hz, 1H), 8.02 (dt, *J* = 8.9, 4.9 Hz, 2H), 7.94 (t, *J* = 6.8 Hz, 1H), 7.81 (t, *J* = 7.5 Hz, 1H), 7.73 (t, *J* = 7.4 Hz, 1H), 7.54 (q, *J* = 7.5, 6.3 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 1H). $^{13}$C NMR (126 MHz, Chloroform-*d*) δ 161.05, 158.00, 144.73, 137.66, 132.09, 130.51, 127.58, 126.97, 126.71, 126.55, 118.99, 118.77, 118.68, 117.25. Yield = 58% (64 mg).

8. **2-(2-chlorophenyl)quinoline (3h)**[7]



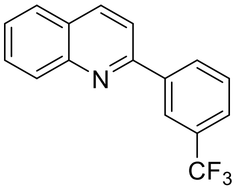
1H NMR (500 MHz, Chloroform-*d*) δ 8.22 (d, *J* = 8.6 Hz, 1H), 8.19 (d, *J* = 8.6 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.71 (d, *J* = 7.4 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.52 (d, *J* = 7.5 Hz, 1H), 7.45 – 7.35 (m, 2H). 13C NMR (126 MHz, Chloroform-*d*) δ 157.65, 148.31, 139.89, 135.88, 132.59, 131.92, 130.31, 130.09, 129.90, 127.78, 127.40, 126.99, 122.99. Yield = 60% (72 mg).

9. **2-(3-bromophenyl)quinoline (3i)**[5]



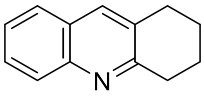
$^{1}$H NMR (500 MHz, Chloroform-*d*) δ 8.37 (d, *J* = 2.3 Hz, 1H), 8.23 (d, *J* = 9.1 Hz, 1H), 8.18 (d, *J* = 8.6 Hz, 1H), 8.08 (d, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 5.8 Hz, 2H), 7.74 (t, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.55 (td, *J* = 7.8, 2.6 Hz, 1H), 7.39 (td, *J* = 8.0, 2.8 Hz, 1H). $^{13}$C NMR (126 MHz, Chloroform-d) δ 156.09, 148.69, 142.15, 137.48, 132.68, 131.11, 130.78, 130.36, 130.26, 127.95, 127.82, 127.13, 126.52, 123.63, 119.13. Yield = 73% (103 mg).

**10. 2-(3-(trifluoromethyl)phenyl)quinoline (3k)[5]**



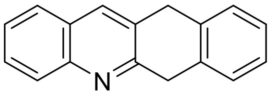
$^{1}$H NMR (500 MHz, Chloroform-*d*) δ 8.28 (t, *J* = 9.9 Hz, 3H), 8.19 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 8.6 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.77 (dd, *J* = 14.3, 7.8 Hz, 3H), 7.57 (t, *J* = 7.6 Hz, 1H). $^{13}$C NMR (126 MHz, Chloroform-d) δ 155.70, 148.30, 142.98, 137.14, 131.11 (q, J = 32.2 Hz), 129.94 (d, J = 14.2 Hz), 127.86, 127.53, 127.46, 126.86, 125.76 (q, J = 3.7 Hz), 125.31, 123.14, 118.79. $^{19}$F NMR (471 MHz, Chloroform-d) δ -62.58. Yield = 78% (106 mg).

**11. 1,2,3,4-tetrahydroacridine (3n)[5]**



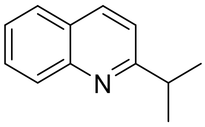
$^{1}$H NMR (500 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.5 Hz, 1H), 7.79 (s, 1H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.60 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 1H), 7.43 (ddd, *J* = 8.0, 6.8, 1.1 Hz, 1H), 3.13 (t, *J* = 6.6 Hz, 2H), 2.98 (t, 2H), 1.99 (ddd, *J* = 9.5, 8.1, 4.6 Hz, 2H), 1.89 (ddd, 2H). $^{13}$C NMR (126 MHz, Chloroform-*d*) δ 159.30, 146.57, 134.98, 130.96, 128.48, 128.24, 127.20, 126.87, 125.52, 33.55, 29.25, 23.22, 22.90. Yield = 46% (42 mg).

**12. 6,11-dihydrobenzo[b]acridine (3o)[5]**



$^{1}$H NMR (500 MHz, Chloroform-*d*) δ 8.57 (d, *J* = 7.7 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.91 (s, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.27 (d, *J* = 7.4 Hz, 1H), 3.12 (t, *J* = 7.0 Hz, 2H), 3.00 (t, 2H). $^{13}$C NMR (126 MHz, Chloroform-d) δ 153.43, 147.66, 139.45, 134.74, 133.73, 130.62, 129.71, 129.44, 128.68, 127.97, 127.36, 126.95, 126.09, 28.87, 28.43. Yield = 45% (52 mg).

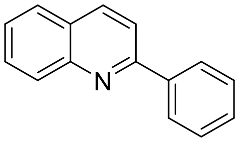
**13. 2-isopropylquinoline[6]**



$^{1}$H NMR (500 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 8.6 Hz, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 7.77 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.68 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 1H), 7.48 (ddd, *J* = 8.0, 6.7, 1.2 Hz, 1H), 7.35 (d, *J* = 8.5 Hz, 1H), 3.27 (hept, *J* = 7.0 Hz, 1H), 1.40 (d, *J* = 6.9 Hz, 6H).$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 167.67, 137.91 – 134.78 (m), 129.22, 128.98, 127.42, 126.92, 125.62, 119.12, 37.32, 22.53. Yield = 52% (45 mg).

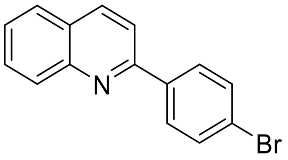
## B. Friedlander Quinoline synthesis using 2-aminobenzyl alcohol and variety of secondary alcohols

### 1. 2-phenylquinoline (5a)[5]



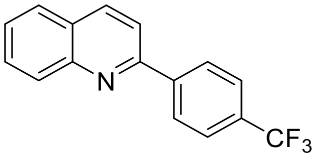
$^1$H NMR (500 MHz, Chloroform-*d*) δ 8.23 (d, *J* = 8.5 Hz, 1H), 8.19 (d, *J* = 8.1 Hz, 3H), 7.86 (d, *J* = 8.6 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.74 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 1H), 7.57 – 7.51 (m, 3H), 7.51 – 7.47 (m, 1H). $^{13}$C NMR (126 MHz, Chloroform-*d*) δ 157.23, 148.16, 139.54, 136.71, 129.62, 129.26, 128.76, 127.50, 127.38, 127.09, 126.20, 118.90. Yield = 84% (86mg).

### 2. 2-(4-bromophenyl)quinoline (5b)[5]



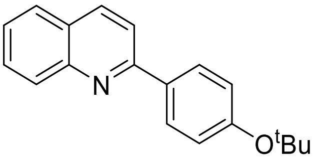
$^1$H NMR (500 MHz, Chloroform-*d*) δ 8.21 (d, *J* = 8.6 Hz, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 8.07 – 8.04 (m, 2H), 7.82 (d, *J* = 8.6 Hz, 2H), 7.74 (t, 1H), 7.67 – 7.64 (m, 2H), 7.54 (t, *J* = 7.6 Hz, 1H). $^{13}$C NMR (126 MHz, Chloroform-*d*) δ 156.04, 148.26, 138.51, 136.99, 131.99, 129.87, 129.73, 129.11, 127.51, 127.27, 126.54, 123.95, 118.51. Yield = 79% (111 mg).

### 3. 2-(4-(trifluoromethyl)phenyl)quinoline (5c)[5]



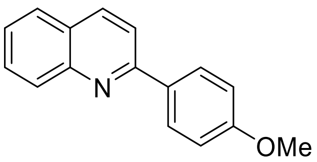
$^1$H NMR (500 MHz, Chloroform-*d*) δ 8.30 (s, 1H), 8.27 (d, *J* = 9.5 Hz, 2H), 8.19 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 8.6 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.79 (d, *J* = 7.9 Hz, 2H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H). $^{13}$C NMR (126 MHz, Chloroform-*d*) δ 155.71, 148.30, 142.98, 137.14, 131.11 (q, *J* = 32.4 Hz), 130.00, 129.89, 127.86, 127.53, 127.46, 126.87, 125.77 (q, *J* = 3.8 Hz), 123.14 (q), 118.80. $^{19}$F NMR (471 MHz, Chloroform-*d*) δ -62.58. Yield = 82% (112 mg).

### 4. 2-(4-(tert-butoxy)phenyl)quinoline (5d)[5]



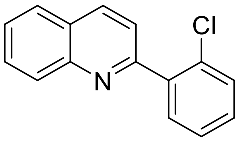
$^1$H NMR (500 MHz, Chloroform-*d*) δ 8.19 (dd, *J* = 12.5, 8.6 Hz, 2H), 8.10 (d, *J* = 8.3 Hz, 2H), 7.87 (d, *J* = 8.6 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.72 (ddd, *J* = 8.5, 5.1, 1.6 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.52 (ddd, *J* = 8.2, 6.8, 1.5 Hz, 1H), 1.39 (s, 9H). $^{13}$C NMR (126 MHz, Chloroform-*d*) δ 157.43, 152.58, 148.33, 136.69, 129.71, 129.60, 127.47, 127.32, 127.12, 126.12, 125.86, 119.00, 68.01, 34.77, 31.33. Yield = 65% (90 mg).

### 5. 2-(4-methoxyphenyl)quinoline (5e)[7]



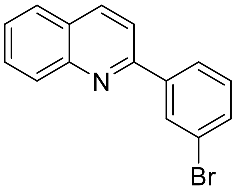
$^{1}$H NMR (500 MHz, Chloroform-*d*) δ 8.21 – 8.16 (m, 4H), 7.86 (d, *J* = 8.6 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.73 (ddd, 1H), 7.57 – 7.48 (m, 1H), 7.08 (d, *J* = 8.9 Hz, 2H), 3.91 (s, 3H). $^{13}$C NMR (126 MHz, Chloroform-*d*) δ 160.81, 156.91, 148.30, 136.61, 132.27, 129.56, 129.52, 128.88, 127.43, 126.91, 125.90, 118.54, 114.22, 55.39. Yield = 55% (64 mg).

### 6. 2-(2-chlorophenyl)quinoline (5f)[8]



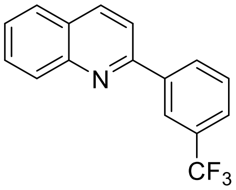
$^{1}$H NMR (500 MHz, Chloroform-*d*) δ 8.28 (d, *J* = 8.1 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.79 (dd, *J* = 7.7, 4.1 Hz, 2H), 7.75 (d, *J* = 7.3 Hz, 1H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.55 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.44 (dtd, *J* = 14.7, 7.3, 1.6 Hz, 2H). $^{13}$C NMR (126 MHz, Chloroform-*d*) δ 157.65, 148.30, 139.88, 135.88, 132.59, 131.92, 130.31, 130.09, 129.90, 127.77, 127.38, 126.99, 122.99. Yield = 64% (76 mg).

### 7. 2-(3-bromophenyl)quinoline (5g)[5]



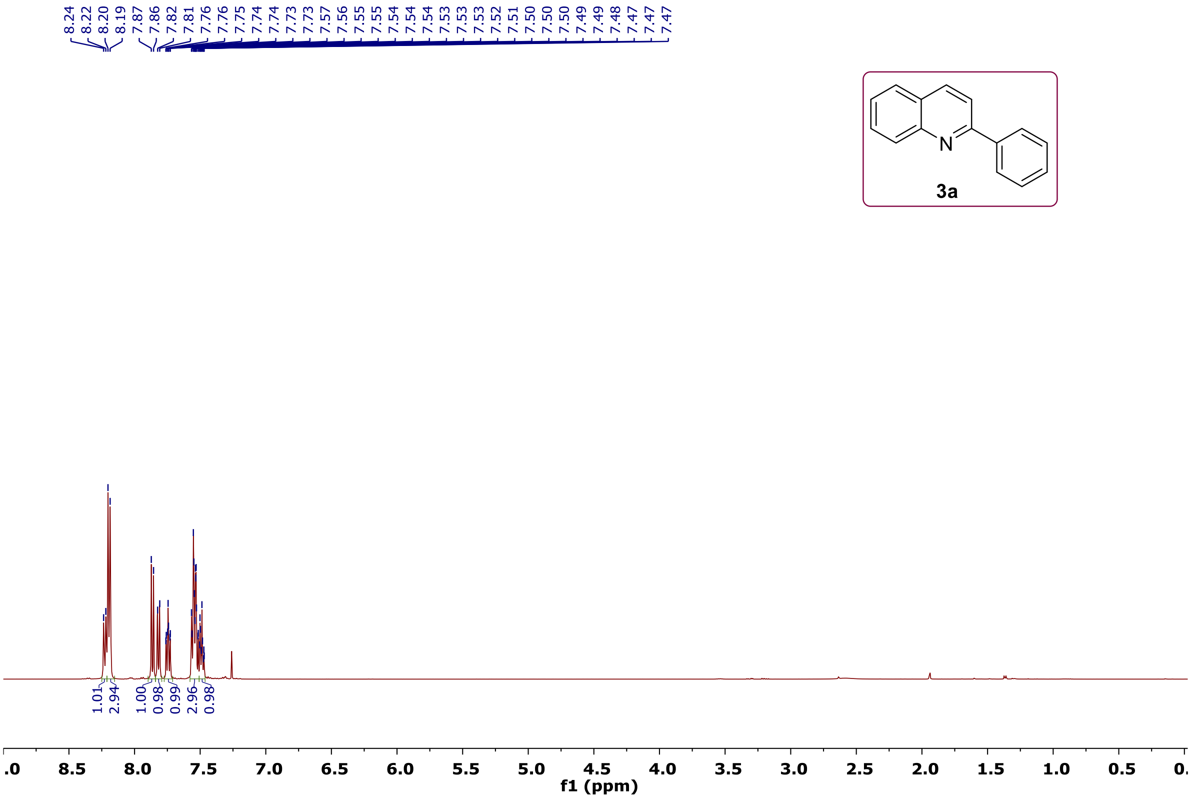
$^{1}$H NMR (500 MHz, Chloroform-*d*) δ 8.36 (s, 1H), 8.22 (d, *J* = 8.6 Hz, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 8.08 (d, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.75 (t, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.9 Hz, 1H). $^{13}$C NMR (126 MHz, Chloroform-*d*) δ 155.63, 148.24, 141.70, 137.03, 132.23, 130.65, 130.33, 129.90, 129.82, 127.50, 127.37, 126.67, 126.07, 123.18, 118.68. Yield = 72% (102 mg).

### 8. 2-(3-(trifluoromethyl)phenyl)quinoline (5h)[5]

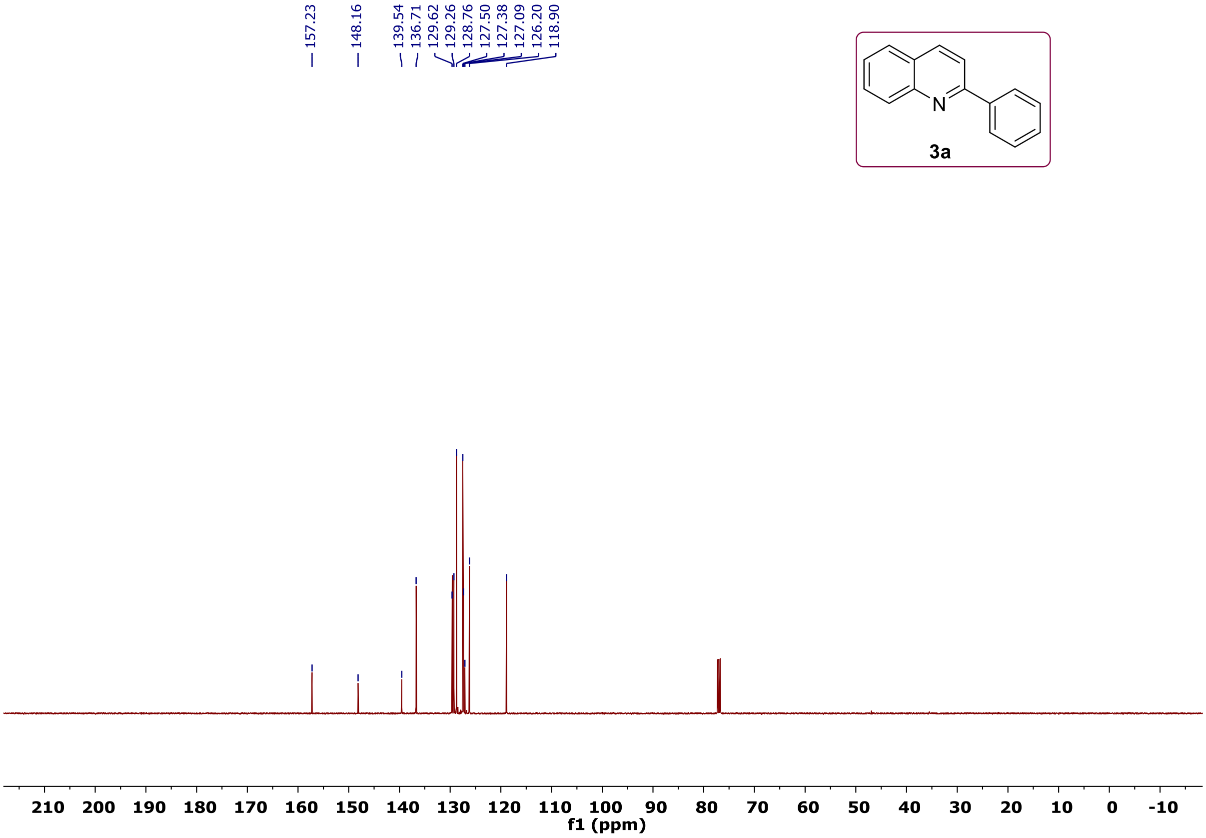


$^{1}$H NMR (500 MHz, Chloroform-*d*) δ 8.47 (s, 1H), 8.36 (d, *J* = 7.8 Hz, 1H), 8.27 (d, *J* = 8.6 Hz, 1H), 8.19 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.76 (dd, *J* = 8.8, 7.1 Hz, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H). $^{13}$C NMR (126 MHz, Chloroform-*d*) δ 155.62, 148.27, 140.39, 137.19, 131.29 (q, *J* = 32.4 Hz), 130.73, 130.01, 129.83, 129.33, 127.54, 127.40, 126.80, 125.90 (q, *J* = 3.7 Hz), 125.30, 124.44 (q, *J* = 3.9 Hz), 118.62. $^{19}$F NMR (471 MHz, Chloroform-*d*) δ -62.52. Yield = 75% (102 mg).

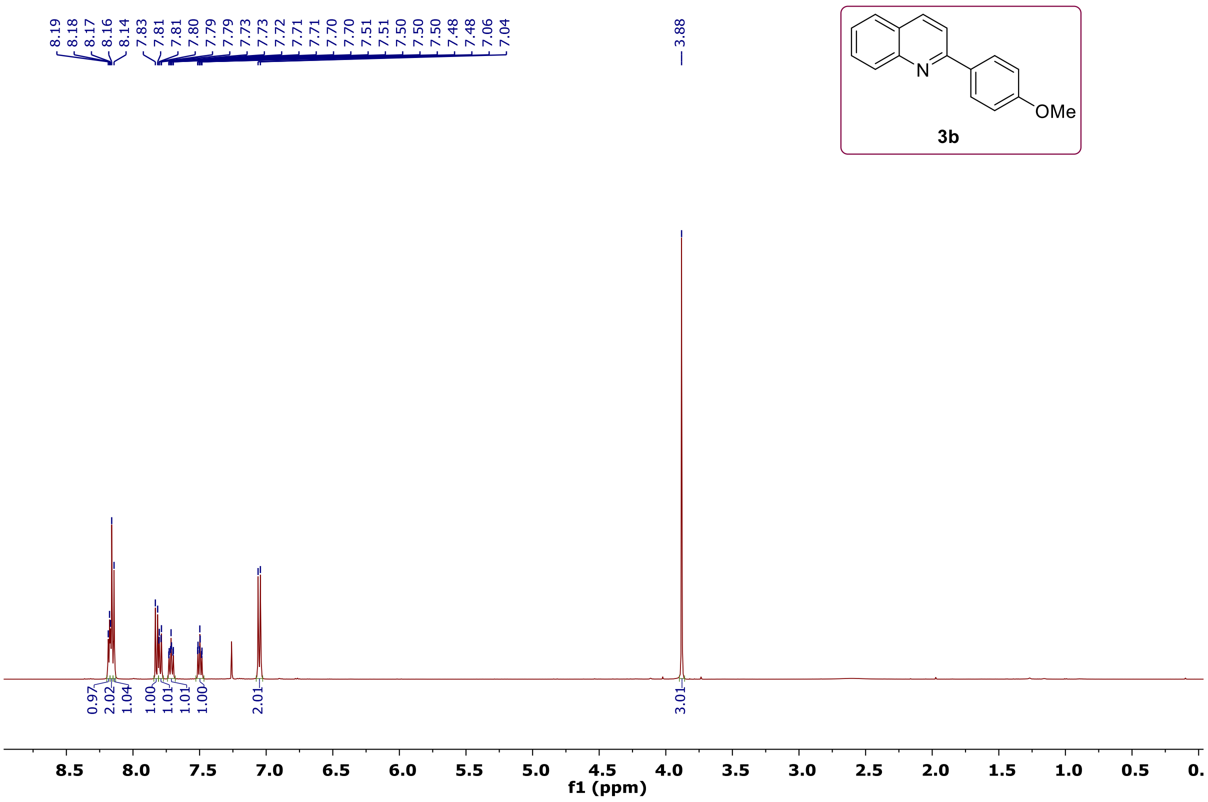
## 7. $^{1}$H (500 MHz), $^{13}$C (126 MHz) and $^{19}$F (471 MHz) NMR spectra recorded for various substrates in CDCl$_3$ solvent at room temperature.



**3a**



**3a**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7.51
7.50
7.50
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7.48
7.06
7.04
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OMe
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1.04
1.00
1.01
1.01
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2.01
3.01
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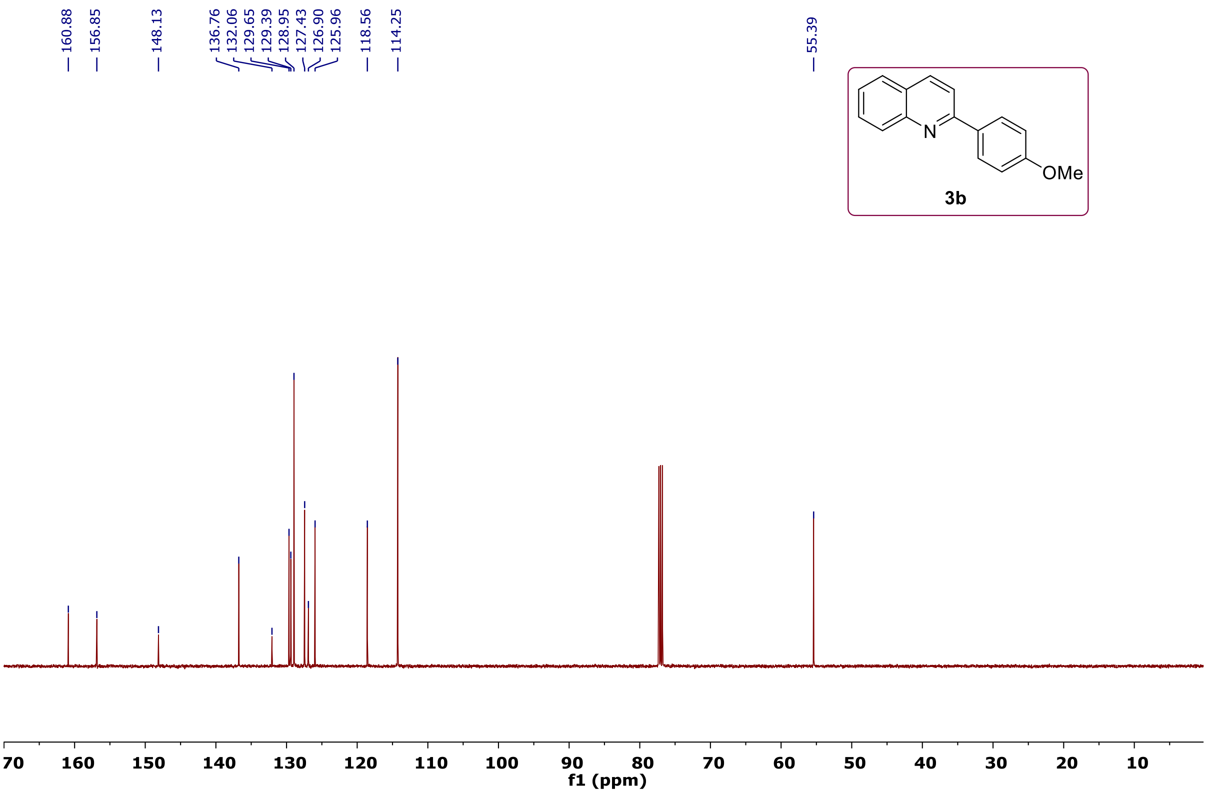
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OMe
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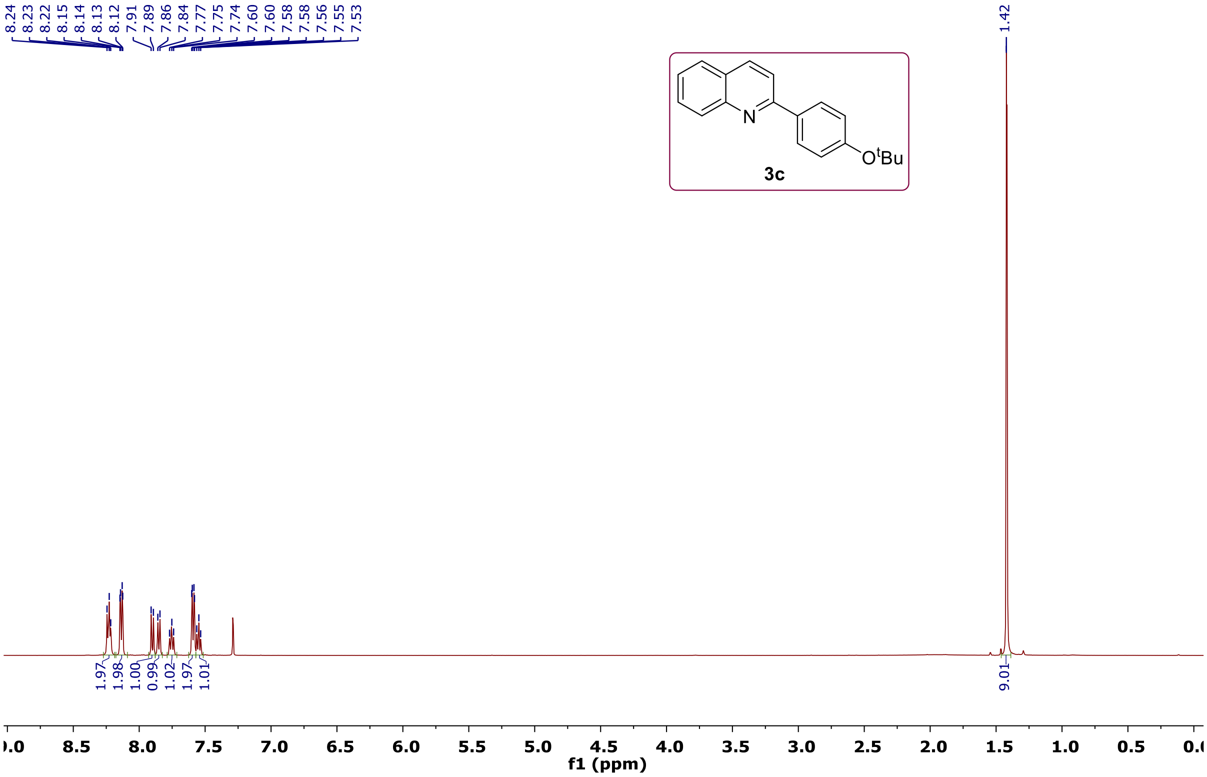
f1 (ppm)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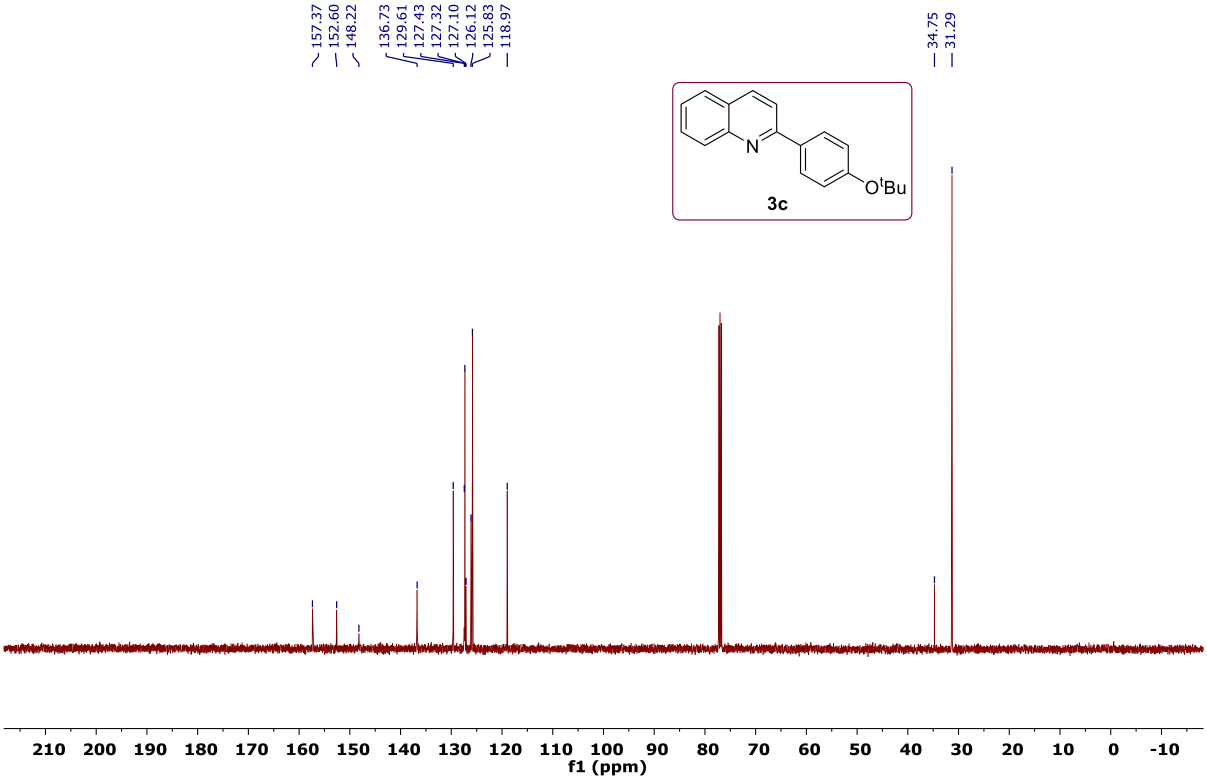
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O<sup>t</sup>Bu
3c
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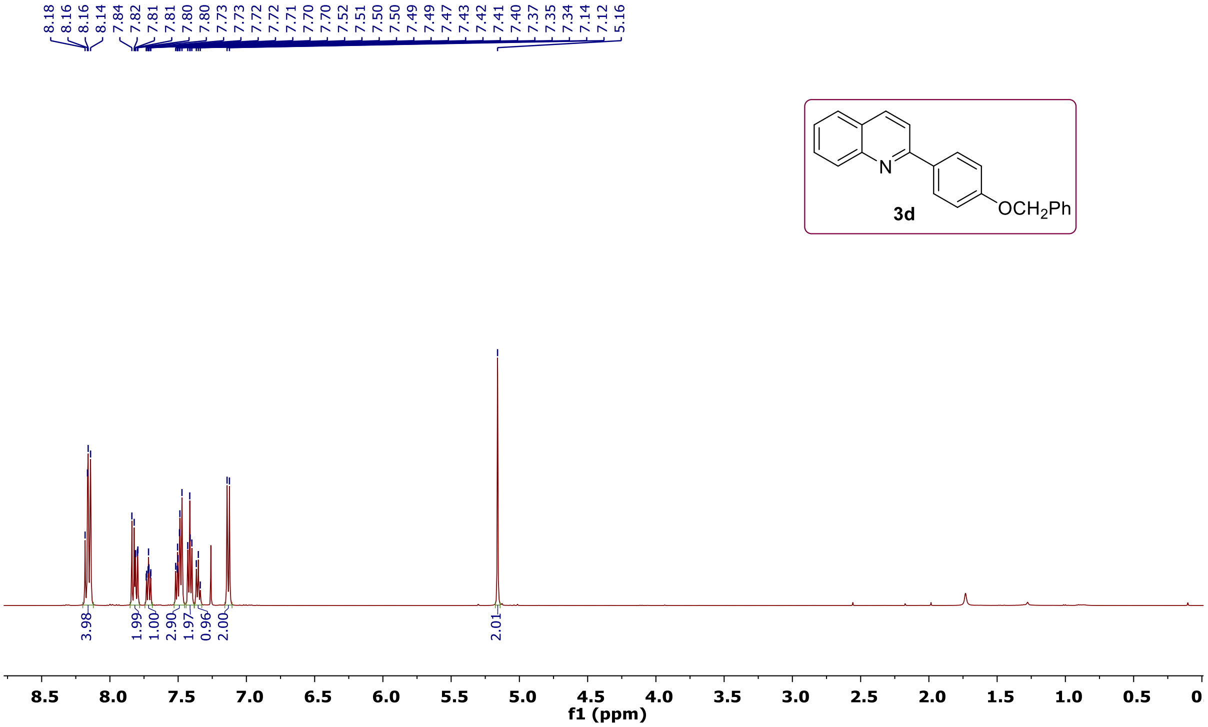
f1 (ppm)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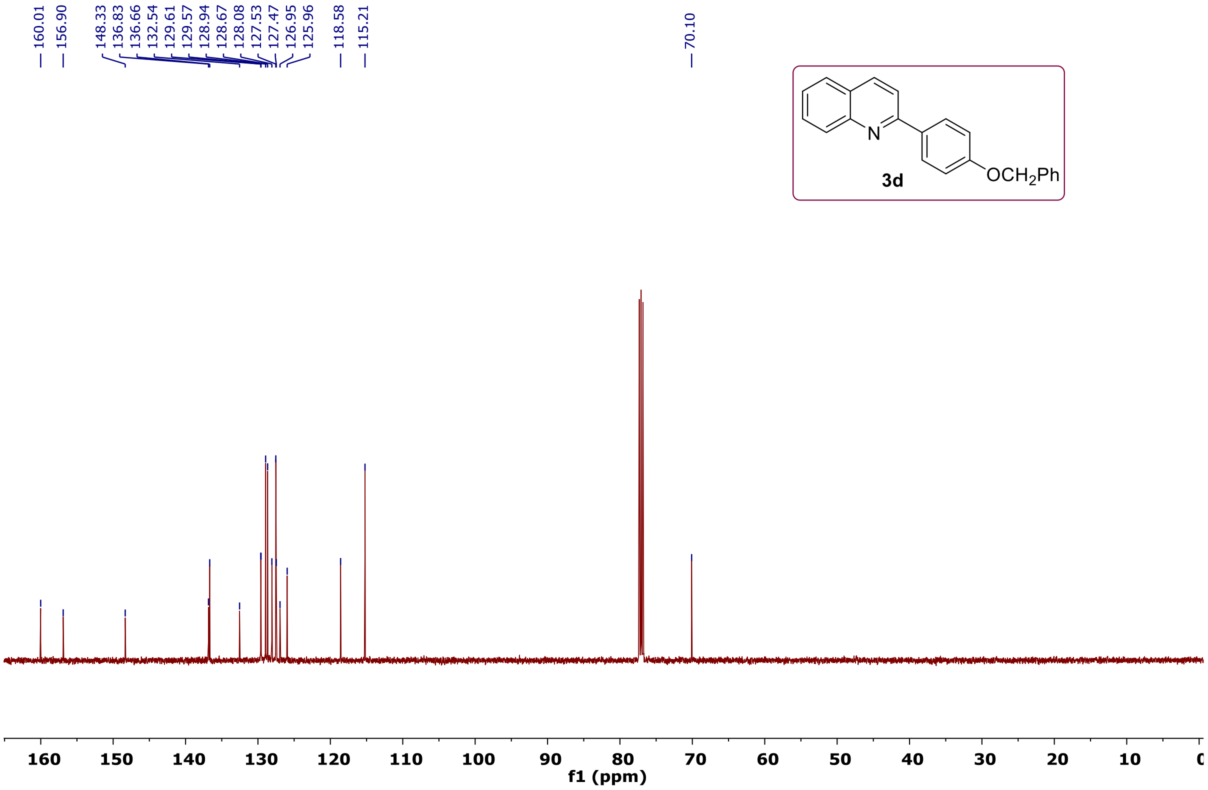
f1 (ppm)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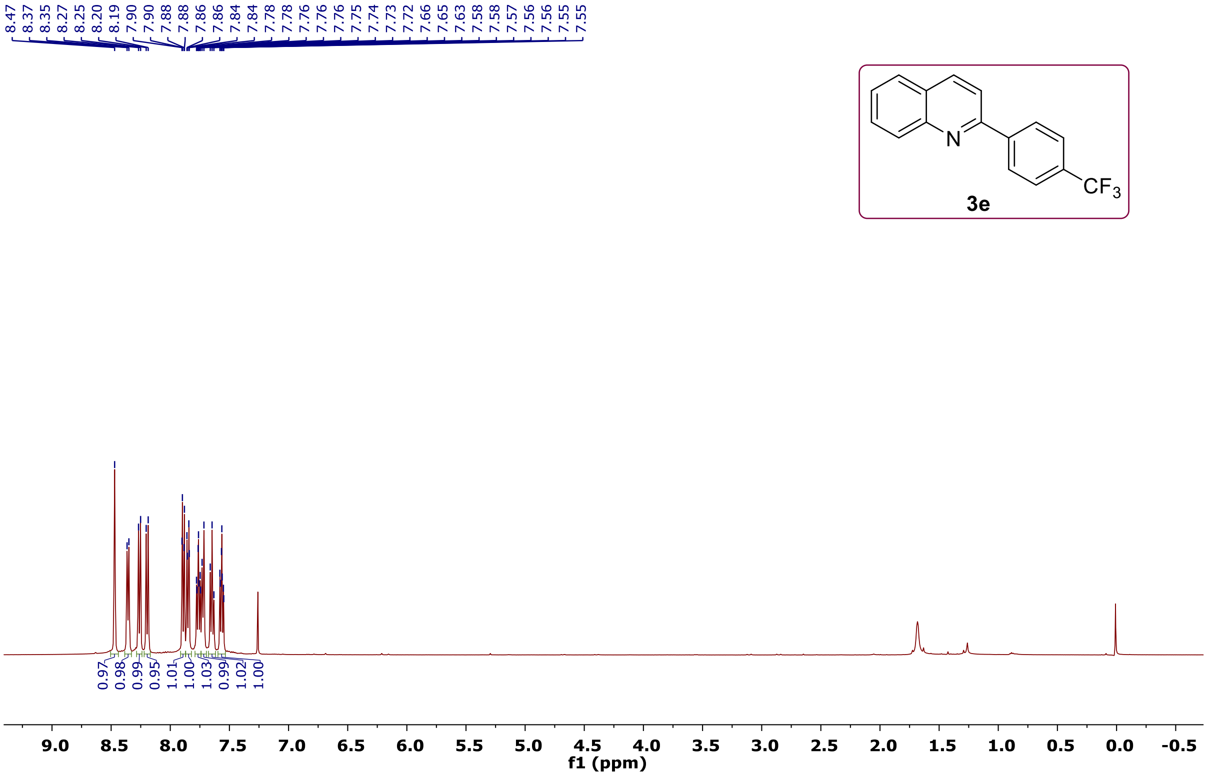
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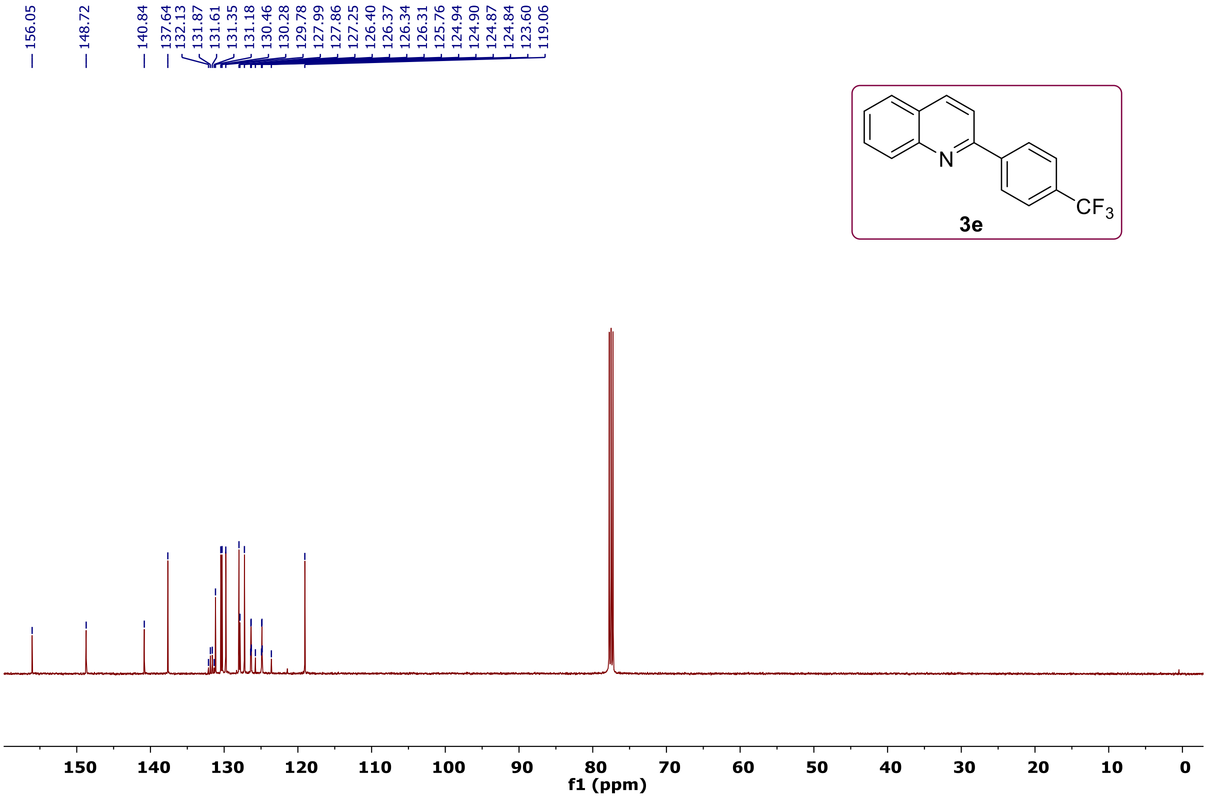
f1 (ppm)

**3e**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123.60
119.06
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CF3
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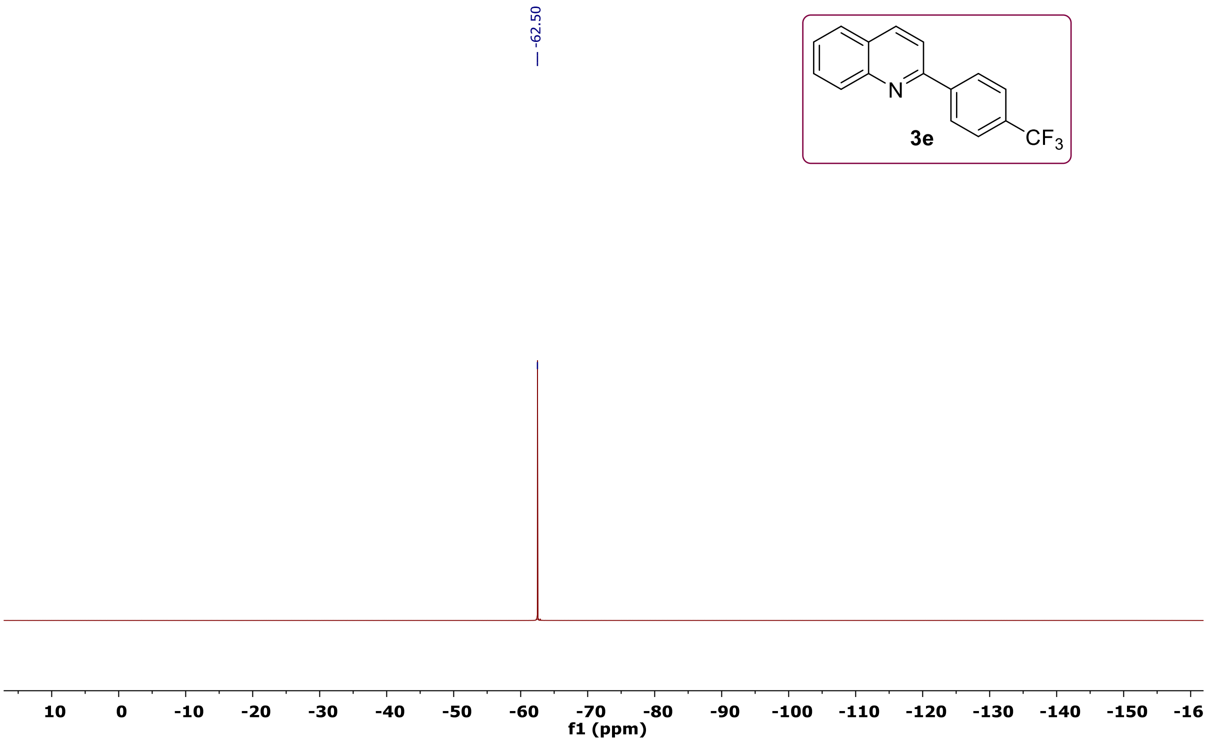
f1 (ppm)

**3e**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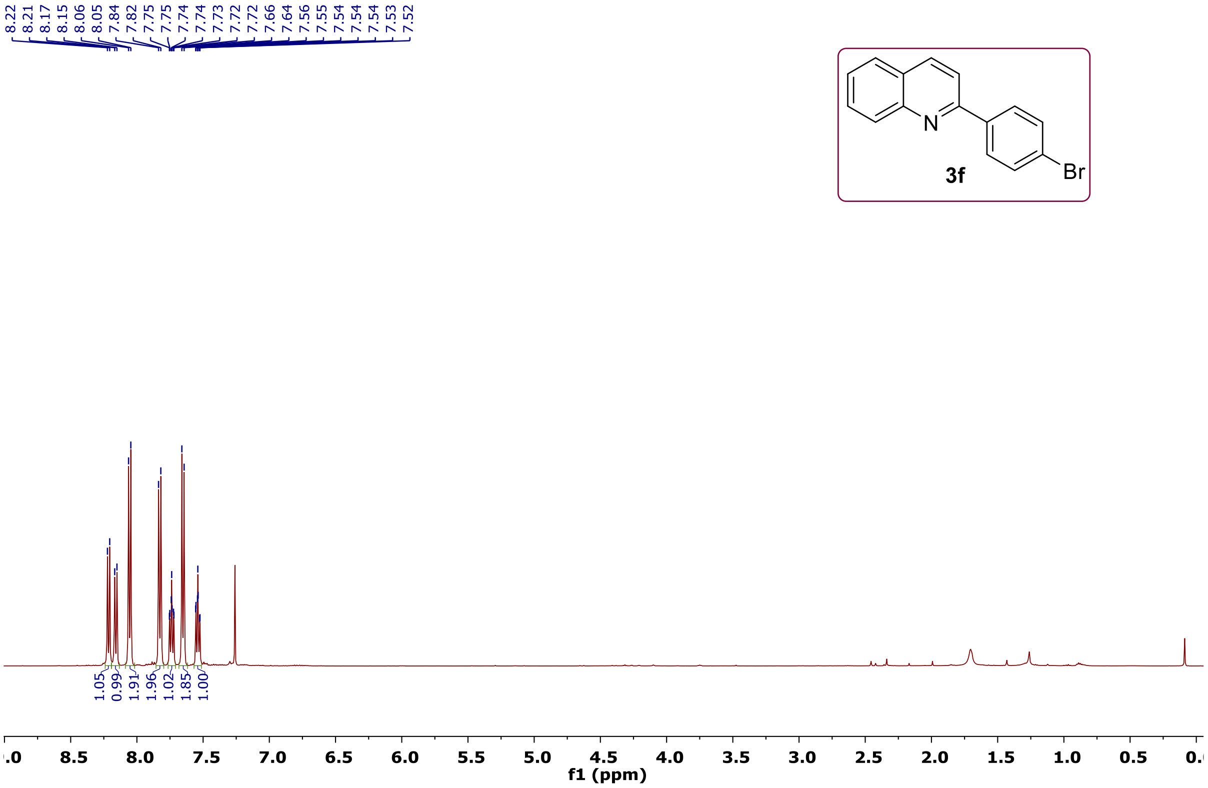
f1 (ppm)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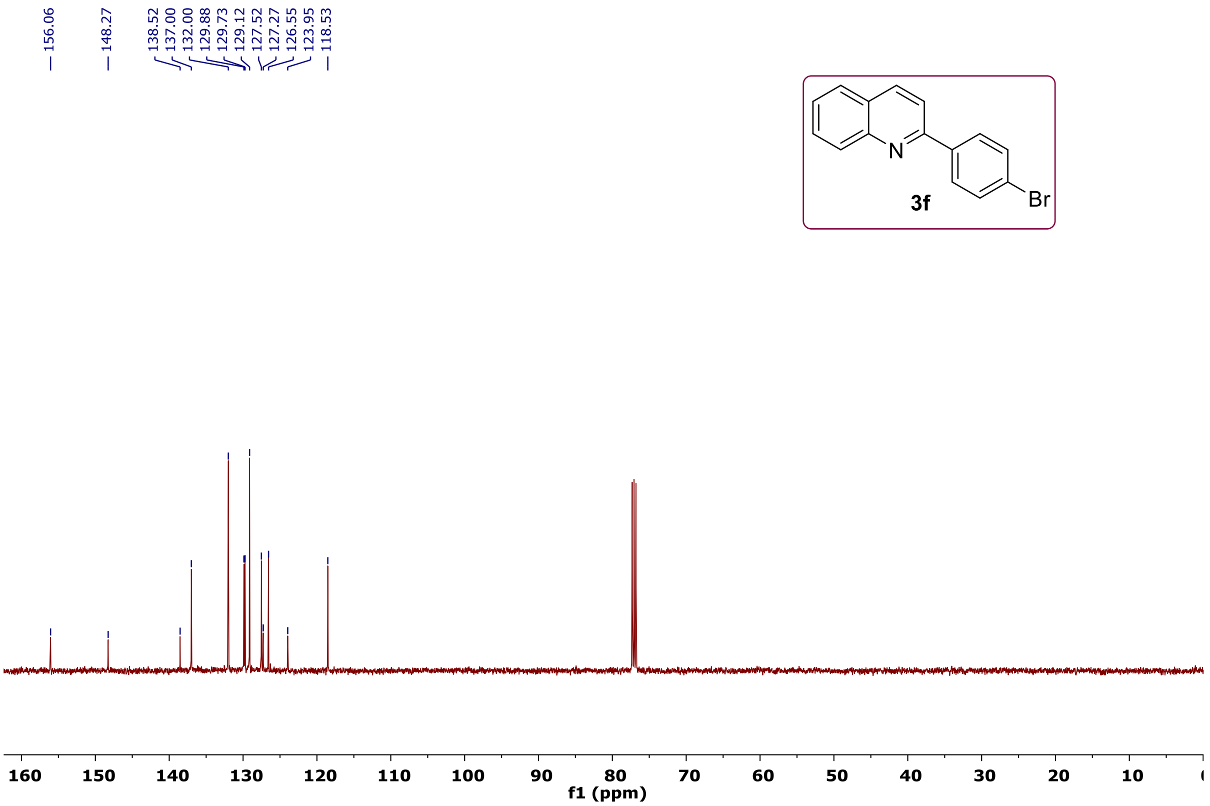
f1 (ppm)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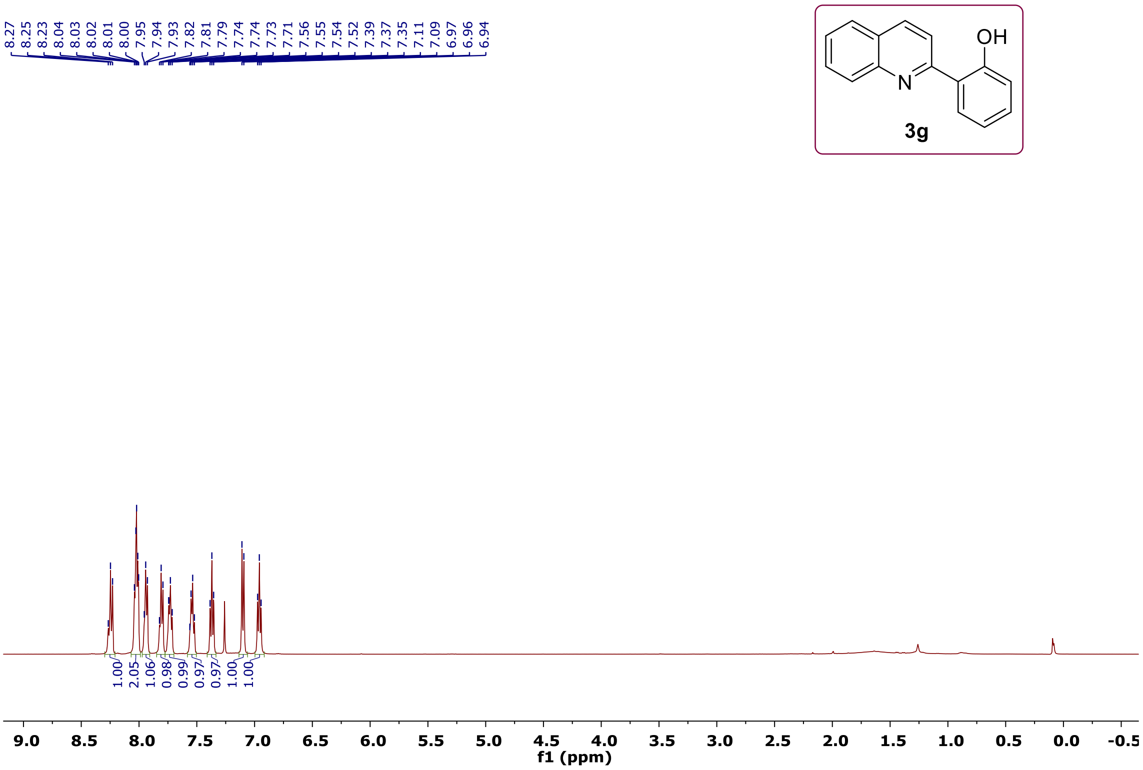
f1 (ppm)

**3f**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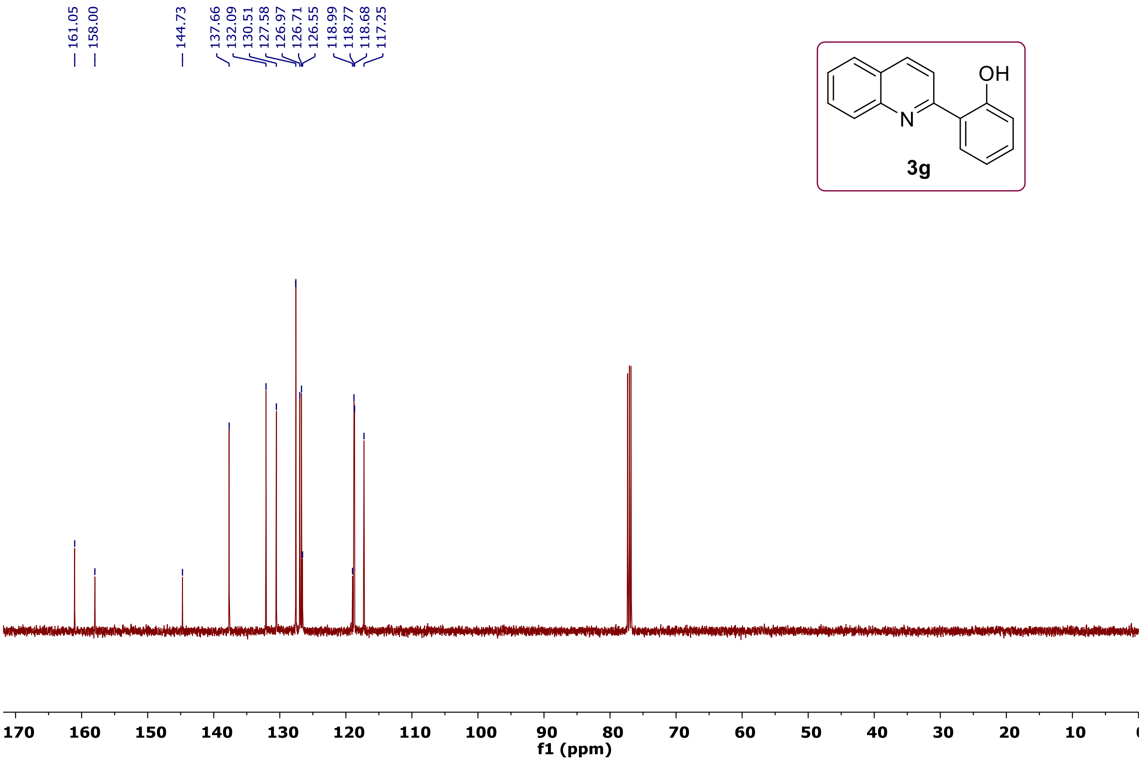
f1 (ppm)

**3g**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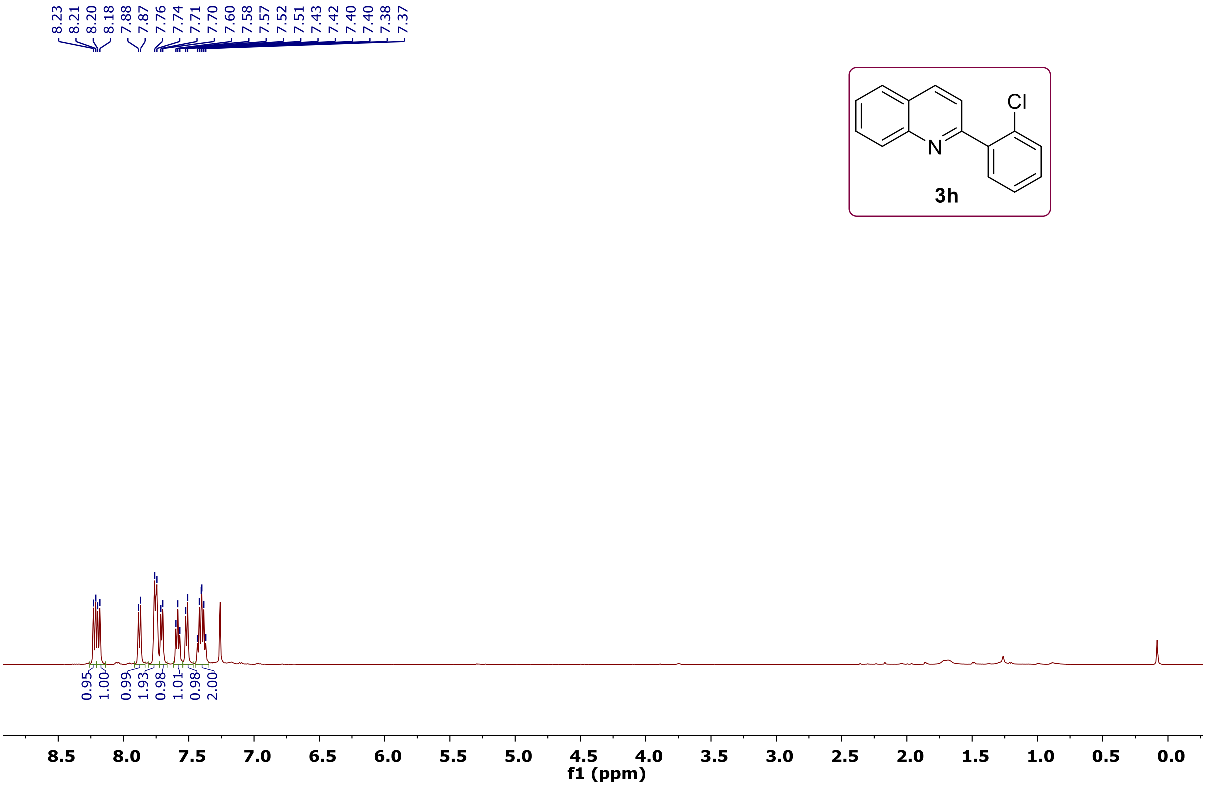
118.77
118.68
117.25
OH
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

**3g**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8.20
8.18
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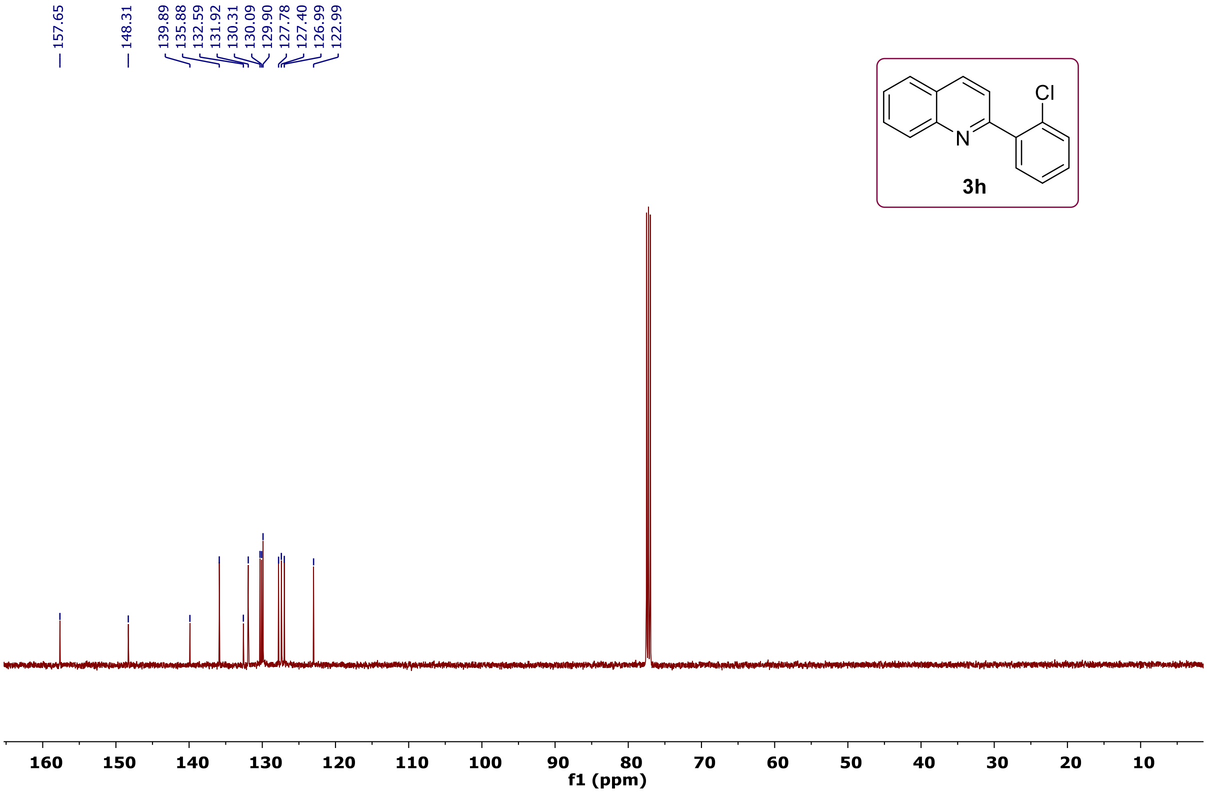
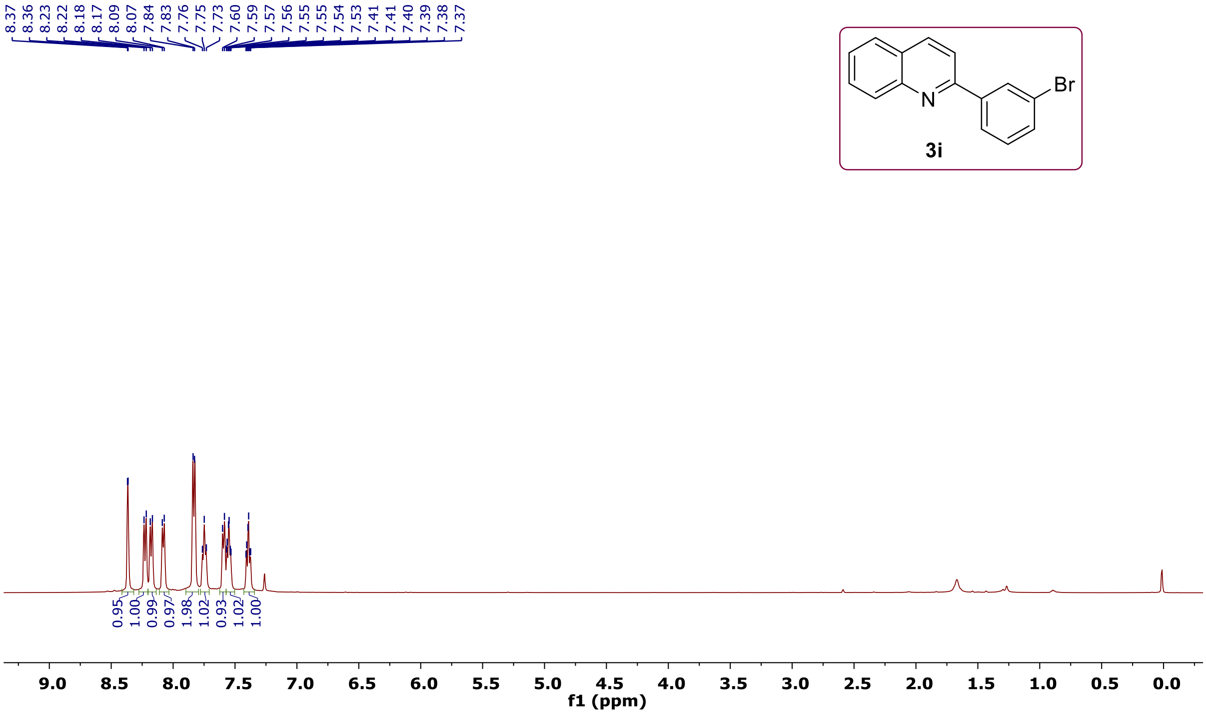
7.87
7.76
7.74
7.71
7.70
7.60
7.58
7.57
7.52
7.51
7.43
7.42
7.40
7.38
7.37
Cl
N
0.95
1.00
0.99
1.93
0.98
1.01
0.98
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

**3h**


157.65
148.31
139.89
135.88
132.59
131.92
130.31
130.09
129.90
127.78
127.40
126.99
122.99
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Cl
N

**3h**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8.36
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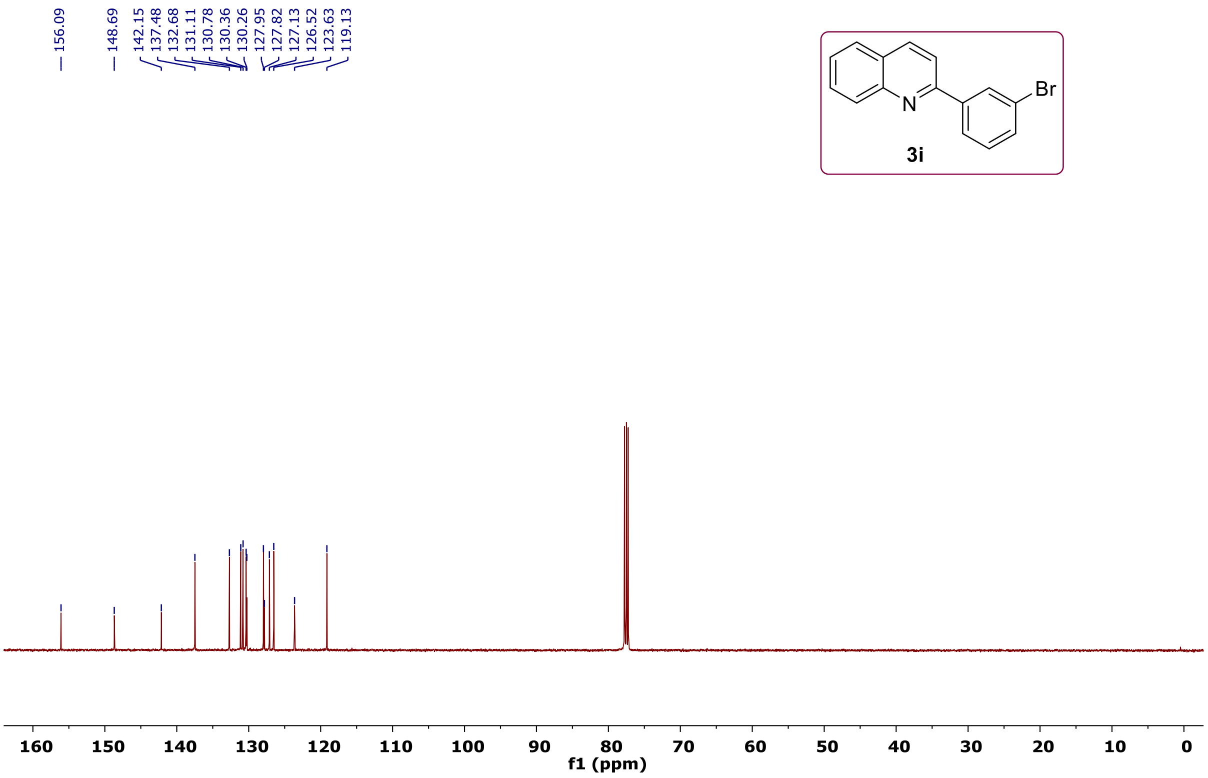
8.18
8.17
8.09
8.07
7.84
7.83
7.76
7.75
7.73
7.60
7.59
7.57
7.56
7.55
7.55
7.54
7.53
7.41
7.40
7.39
7.38
7.37
0.95
1.00
0.99
0.97
1.98
1.02
0.93
1.02
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

Br
N

**3i**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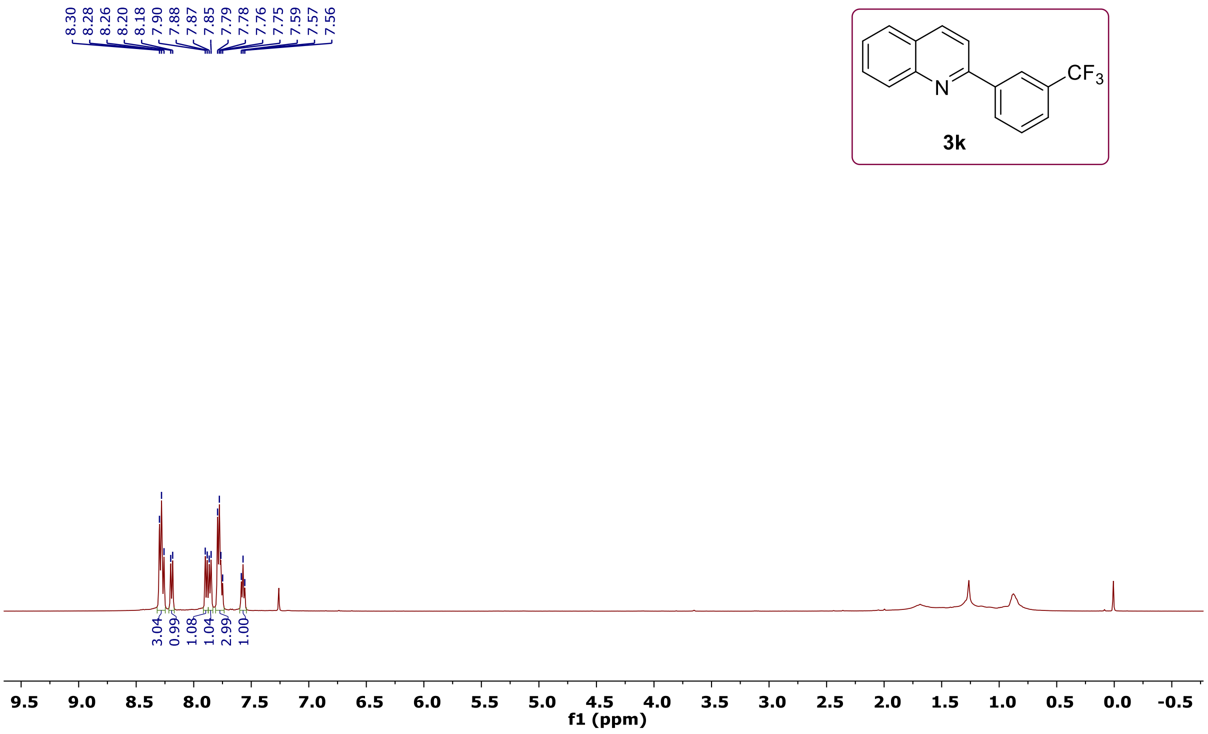
142.15
137.48
132.68
131.11
130.78
130.36
130.26
127.95
127.82
127.13
126.52
123.63
119.13
Br
N
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

**3i**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8.18
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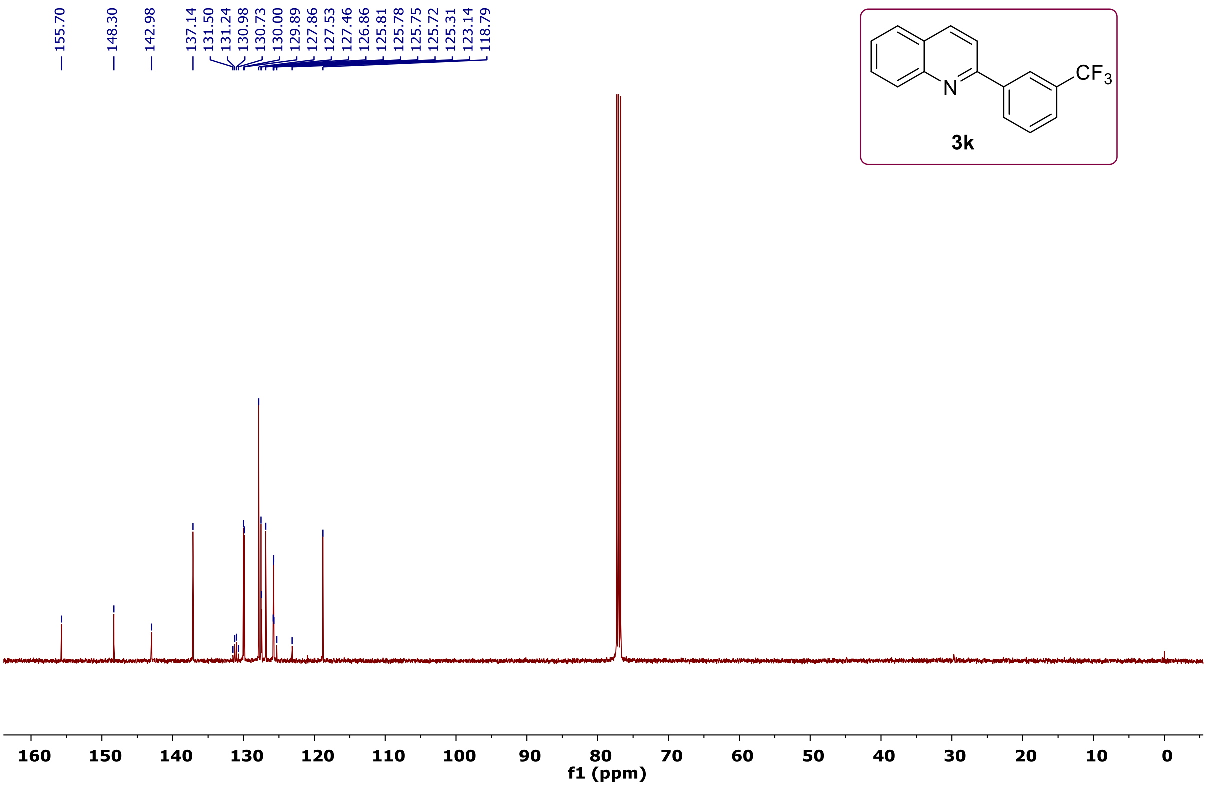
7.88
7.87
7.85
7.79
7.78
7.76
7.75
7.59
7.57
7.56
$CF_3$
N
3.04
0.99
1.08
1.04
2.99
1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

**3k**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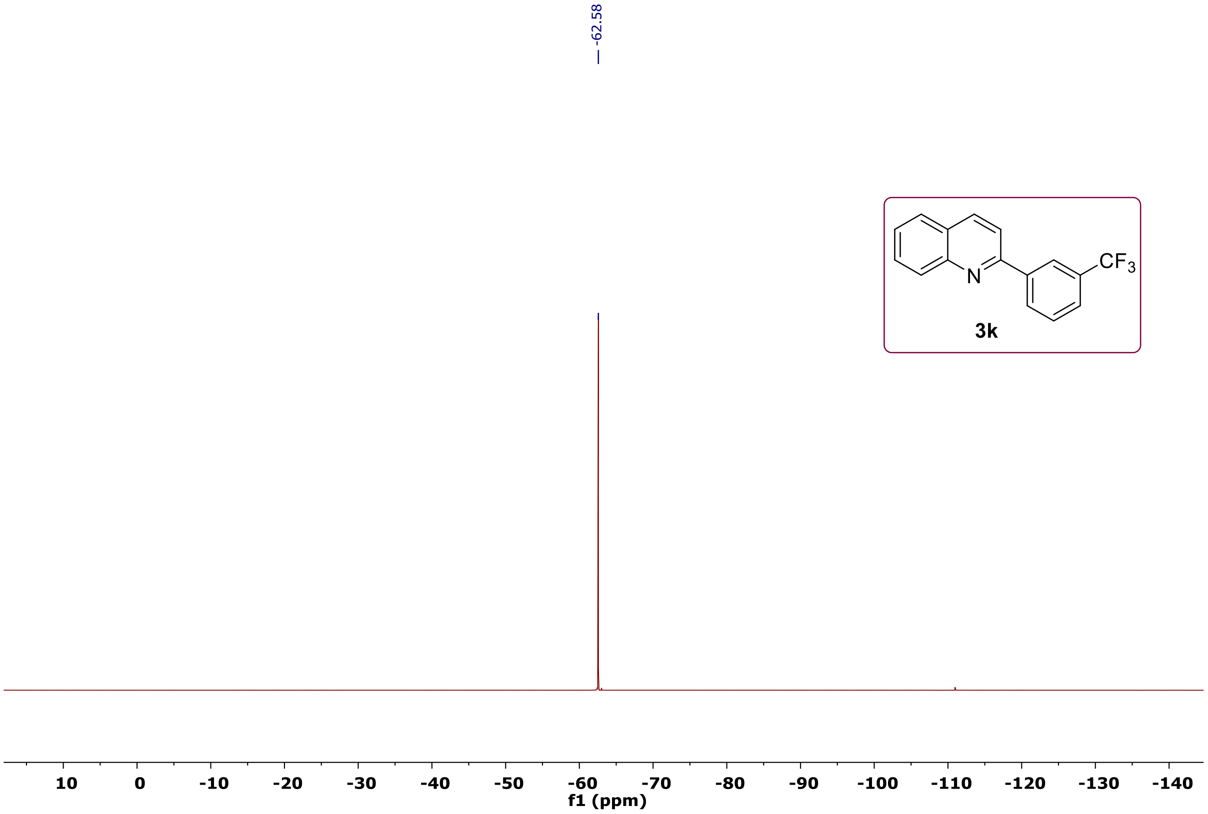
131.50
131.24
130.98
130.73
130.00
129.89
127.86
127.53
127.46
126.86
125.81
125.78
125.75
125.72
125.31
123.14
118.79
N
CF3
3k
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-62.58
N
CF3
3k
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
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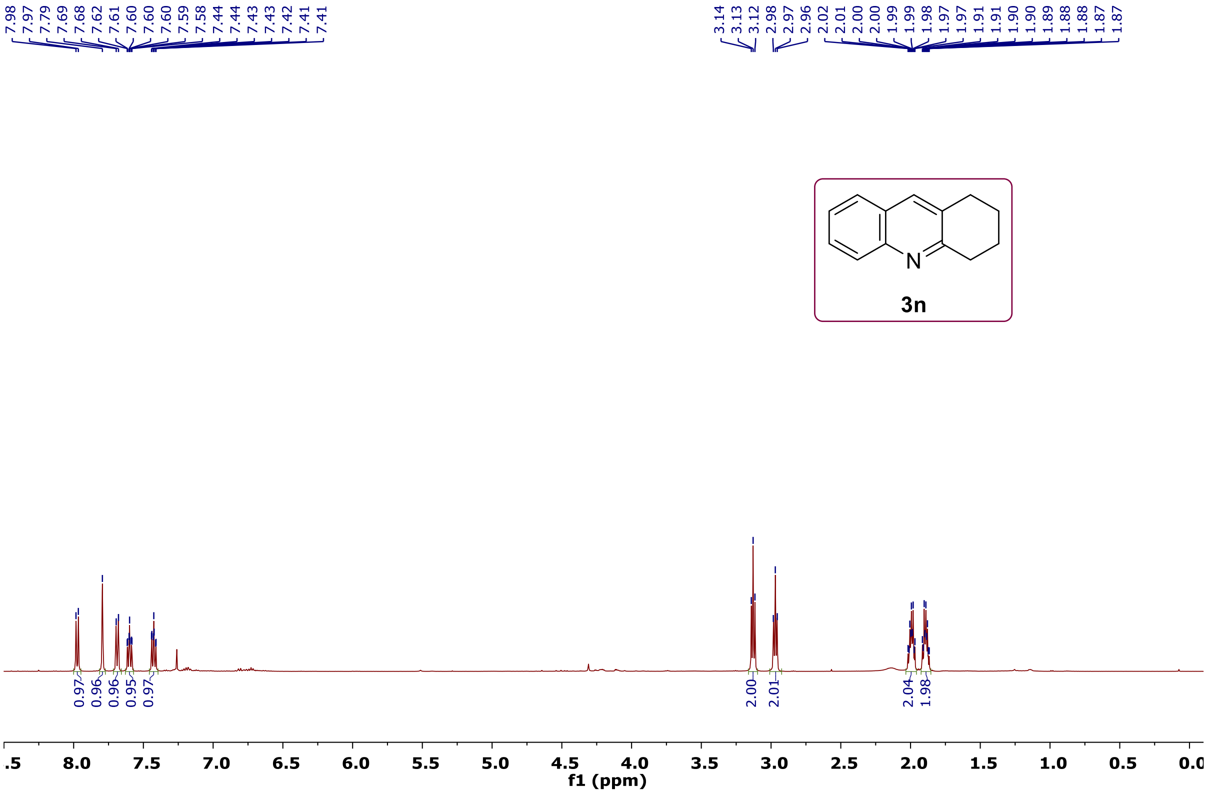
-120
-130
-140
f1 (ppm)


7.98
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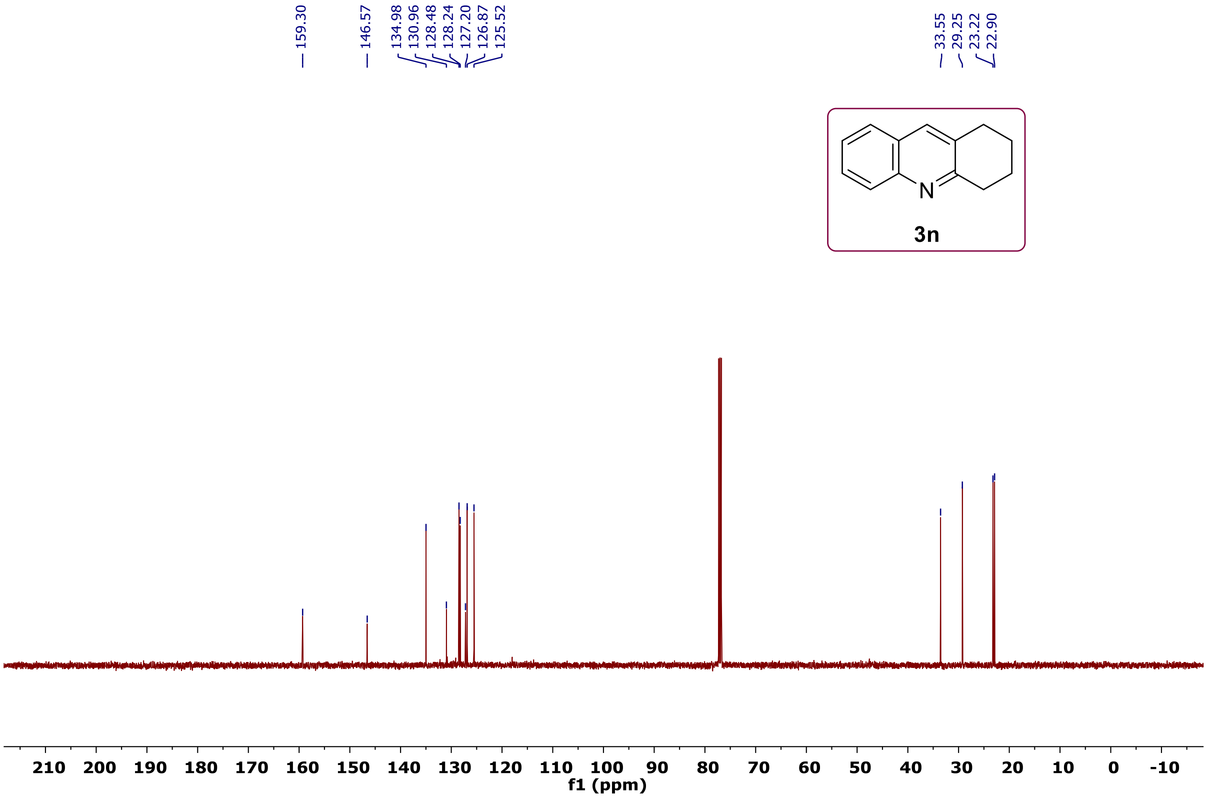
7.62
7.61
7.60
7.60
7.59
7.58
7.44
7.44
7.43
7.43
7.42
7.41
7.41
3.14
3.13
3.12
2.98
2.97
2.96
2.02
2.01
2.00
1.99
1.99
1.98
1.97
1.97
1.91
1.91
1.90
1.90
1.89
1.88
1.88
1.87
1.87
N
3n
0.97
0.96
0.96
0.95
0.97
2.00
2.01
2.04
1.98
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


159.30
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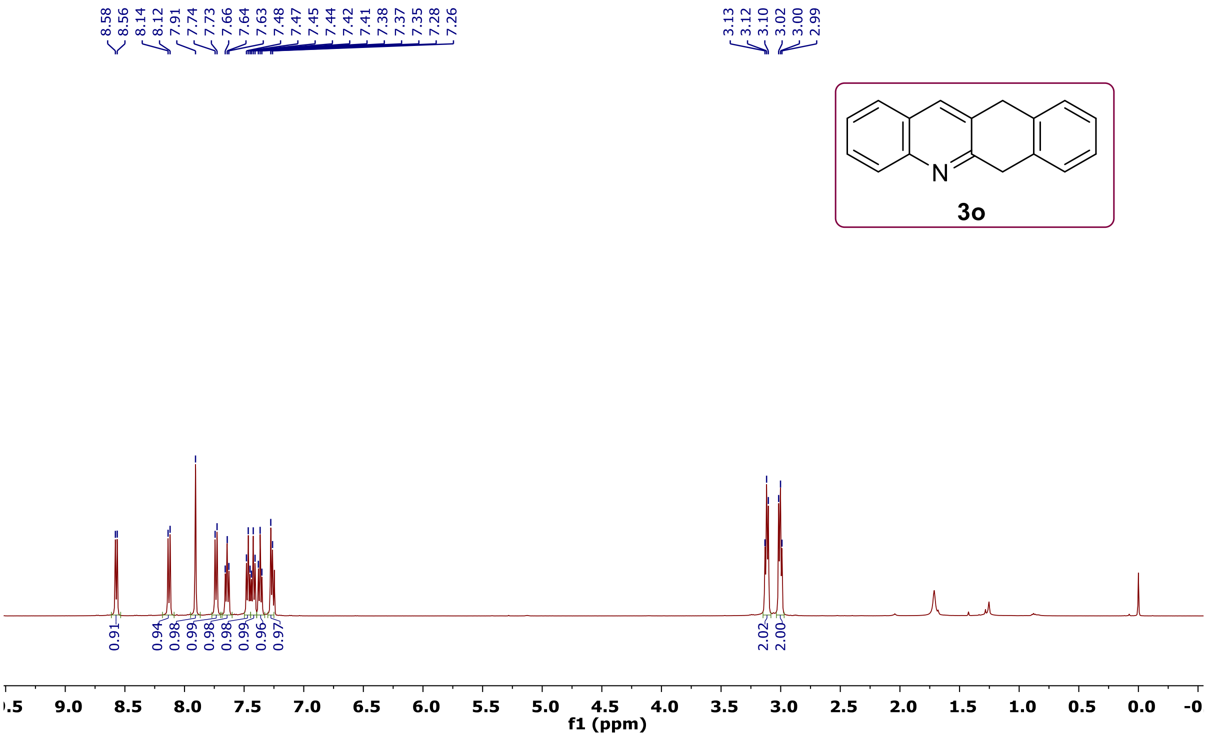
128.48
128.24
127.20
126.87
125.52
33.55
29.25
23.22
22.90
N
3n
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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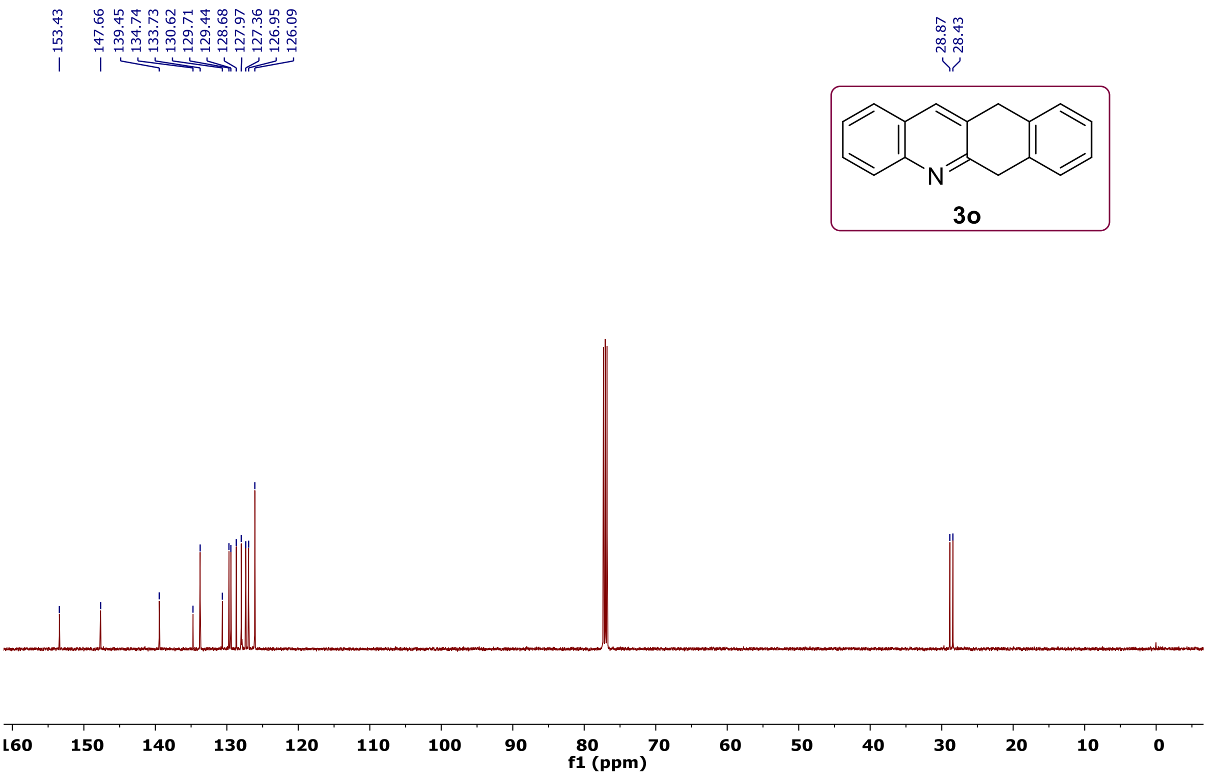
7.74
7.73
7.66
7.64
7.63
7.48
7.47
7.45
7.44
7.42
7.41
7.38
7.37
7.35
7.28
7.26
3.13
3.12
3.10
3.02
3.00
2.99
N
3o
0.91
0.94
0.98
0.99
0.98
0.98
0.99
0.96
0.97
2.02
2.00
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)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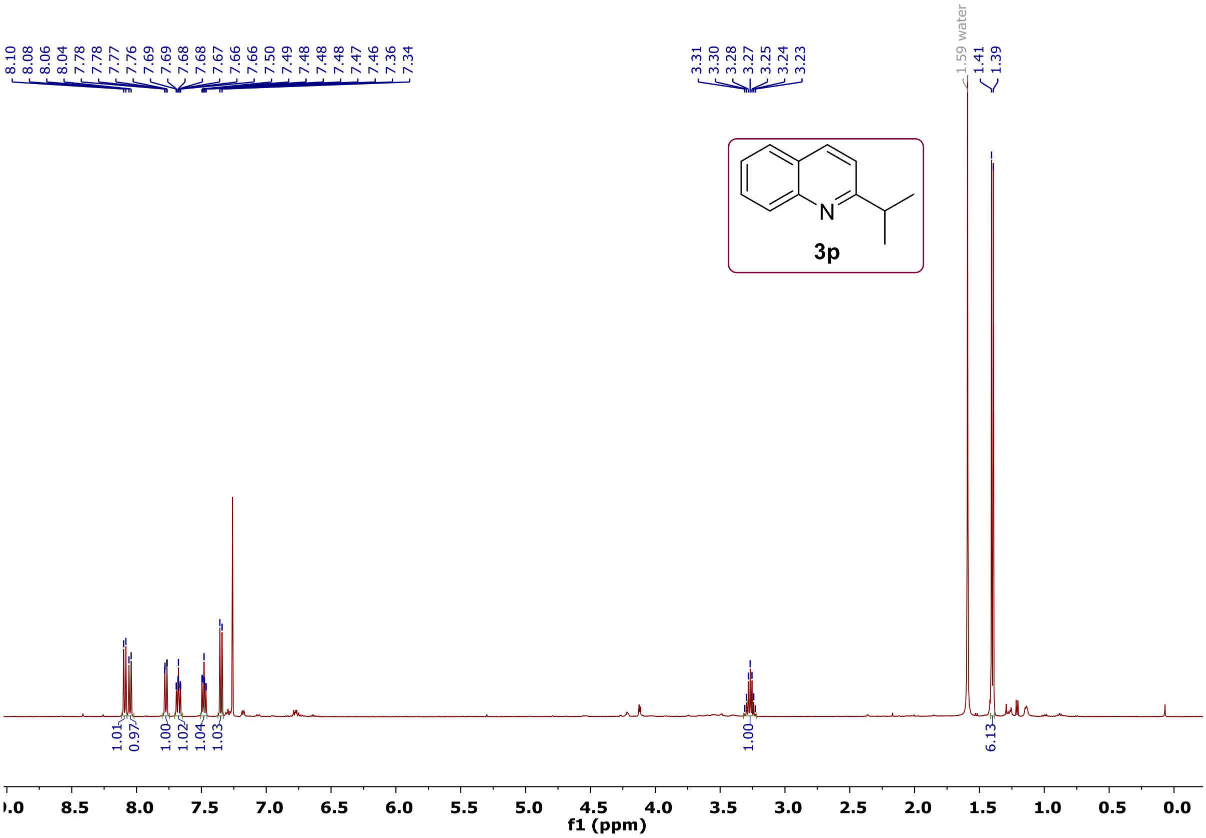
139.45
134.74
133.73
130.62
129.71
129.44
128.68
127.97
127.36
126.95
126.09
28.87
28.43
N
3o
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.06
8.04
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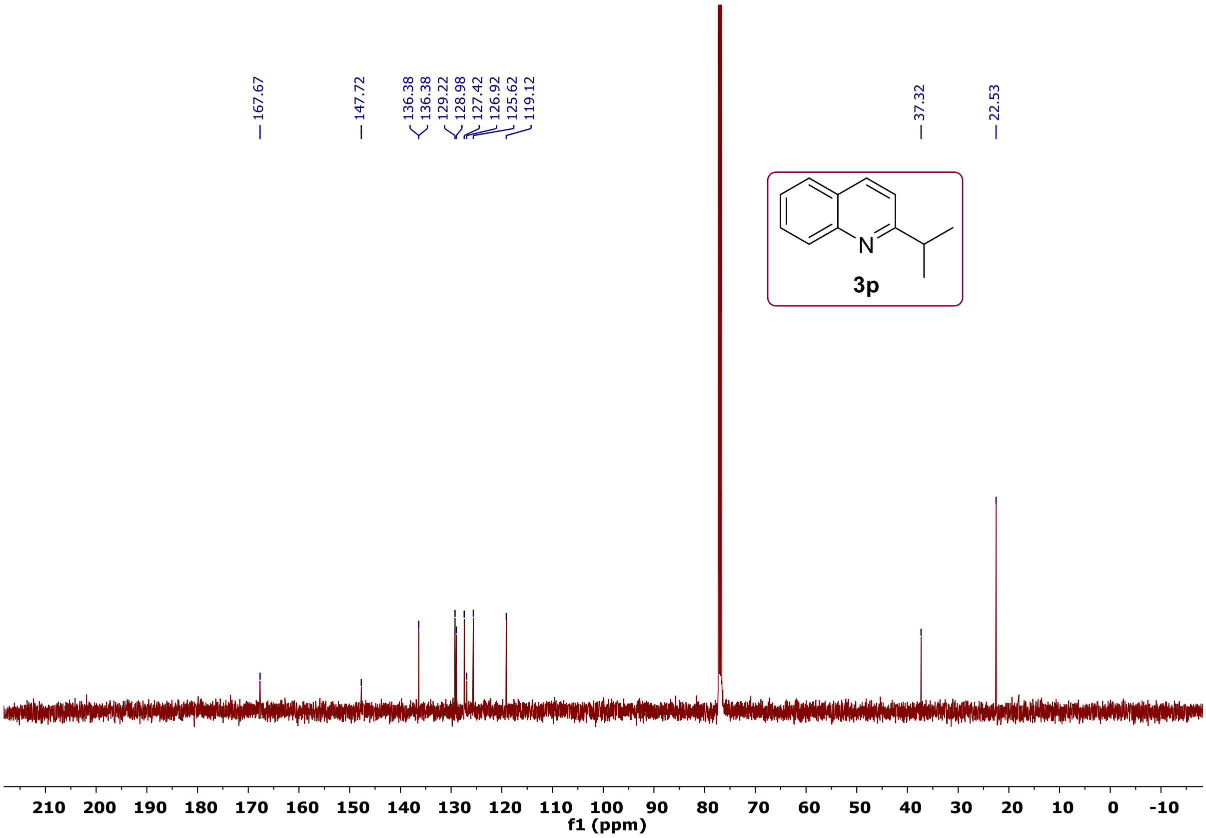
7.78
7.77
7.76
7.69
7.69
7.68
7.68
7.67
7.66
7.66
7.50
7.49
7.48
7.48
7.48
7.47
7.46
7.36
7.34
3.31
3.30
3.28
3.27
3.25
3.24
3.23
1.59 water
1.41
1.39
N
3p
1.01
0.97
1.00
1.02
1.04
1.03
1.00
6.13
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


167.67
147.72
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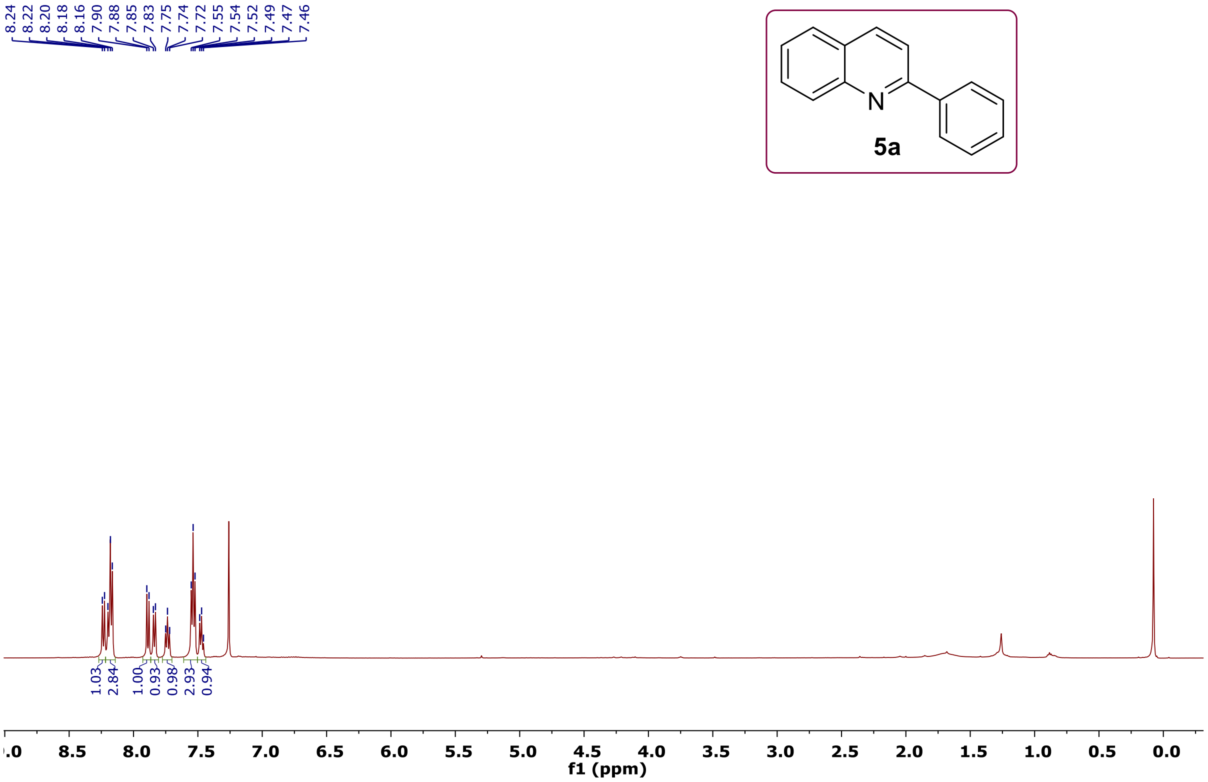
136.38
129.22
128.98
127.42
126.92
125.62
119.12
37.32
22.53
N
3p
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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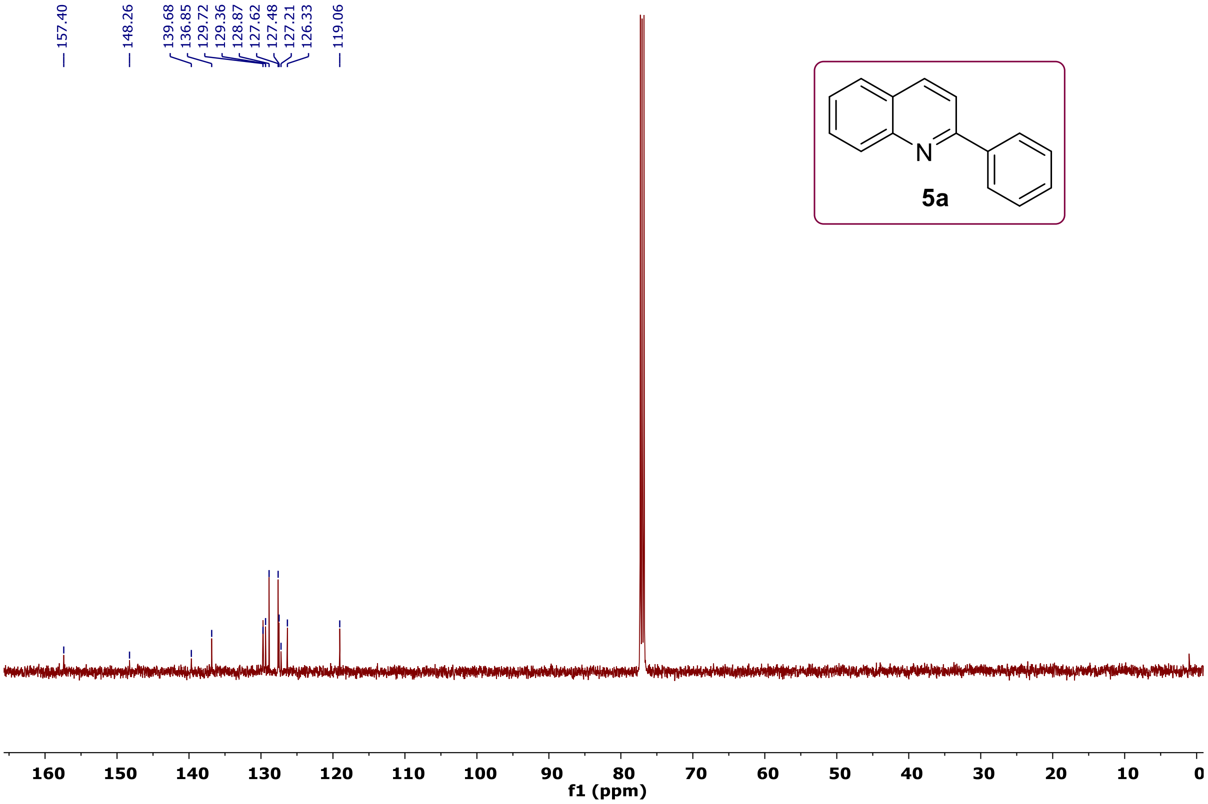
8.16
7.90
7.88
7.85
7.83
7.75
7.74
7.72
7.55
7.54
7.52
7.49
7.47
7.46
N
5a
1.03
2.84
1.00
0.93
0.98
2.93
0.94
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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129.36
128.87
127.62
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127.21
126.33
119.06
N
5a
160
150
140
130
120
110
100
90
80
70
60
50
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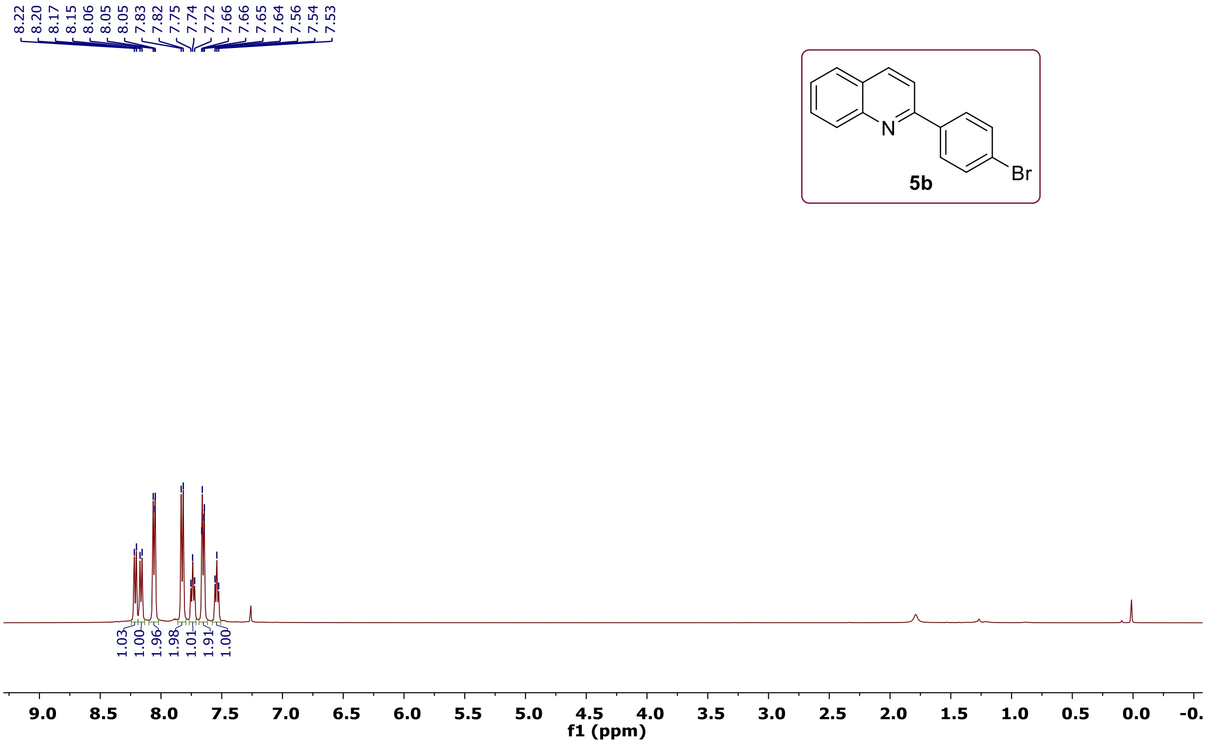
30
20
10
0
f1 (ppm)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8.06
8.05
8.05
7.83
7.82
7.75
7.74
7.72
7.66
7.66
7.65
7.64
7.56
7.54
7.53
N
Br
5b
1.03
1.00
1.96
1.98
1.01
1.91
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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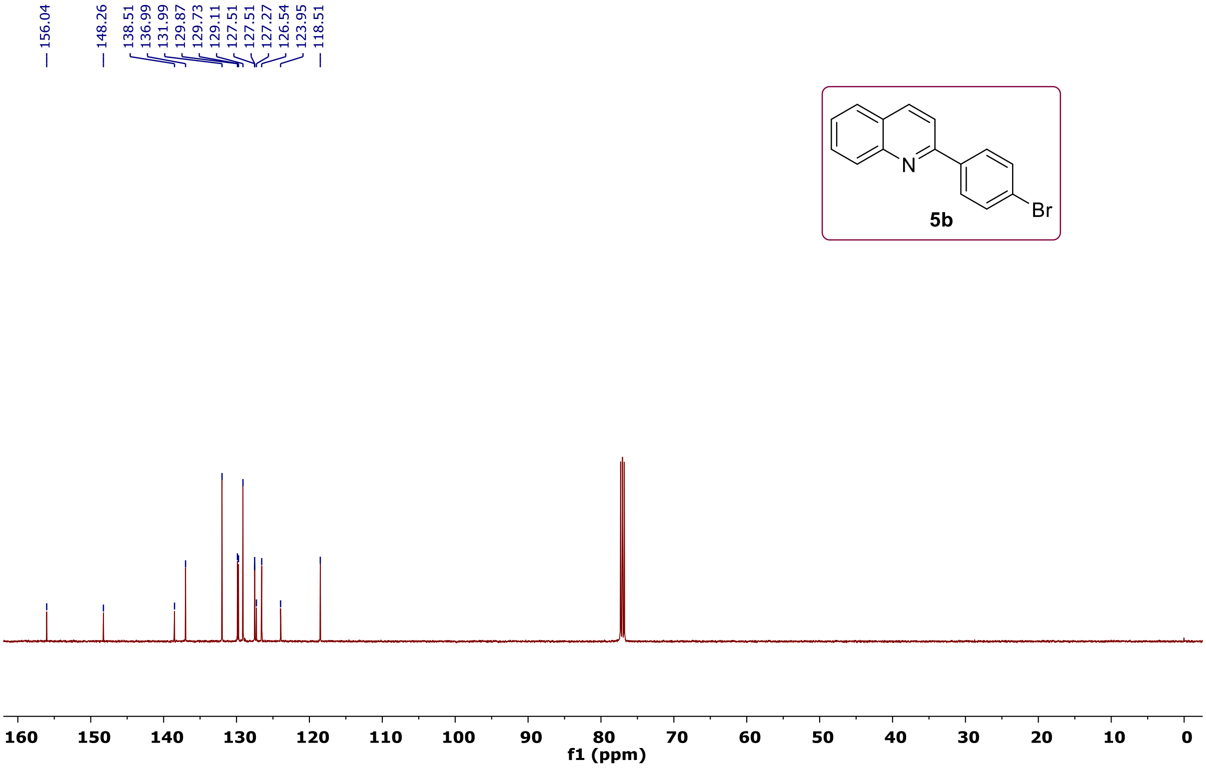
-0.
f1 (ppm)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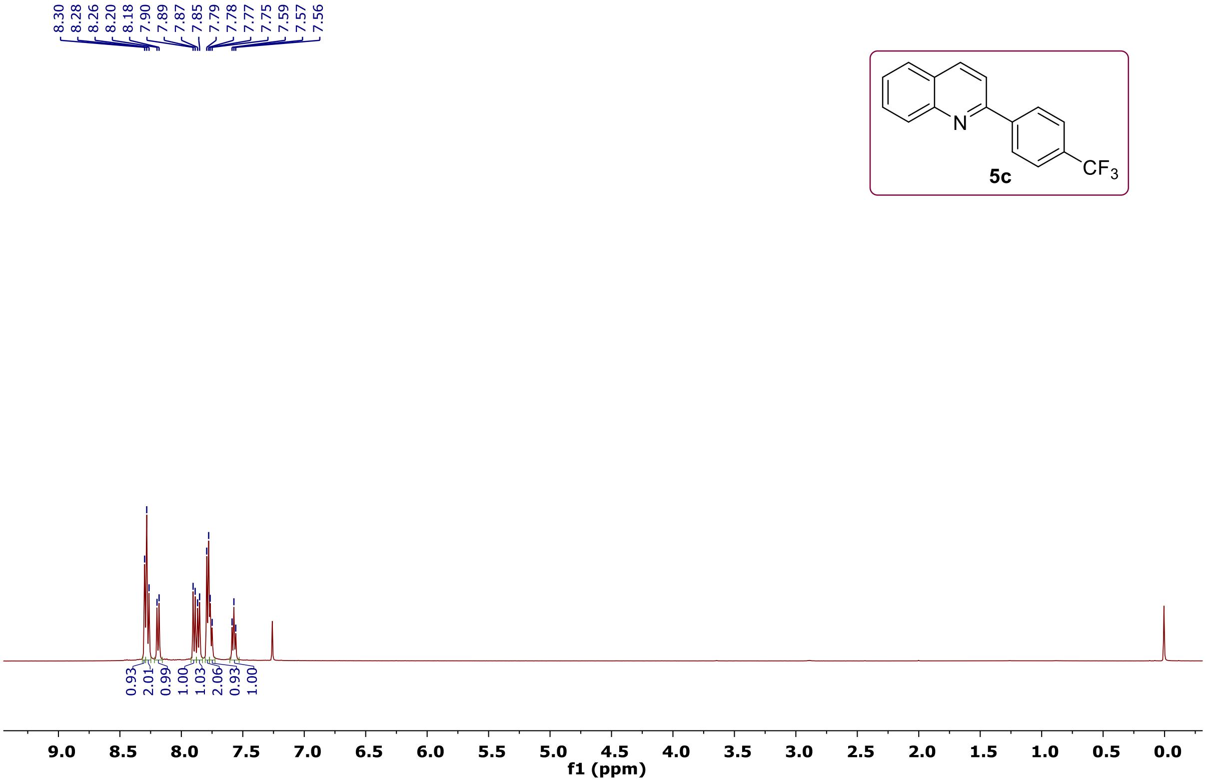
129.11
127.51
127.51
127.27
126.54
123.95
118.51
N
Br
5b
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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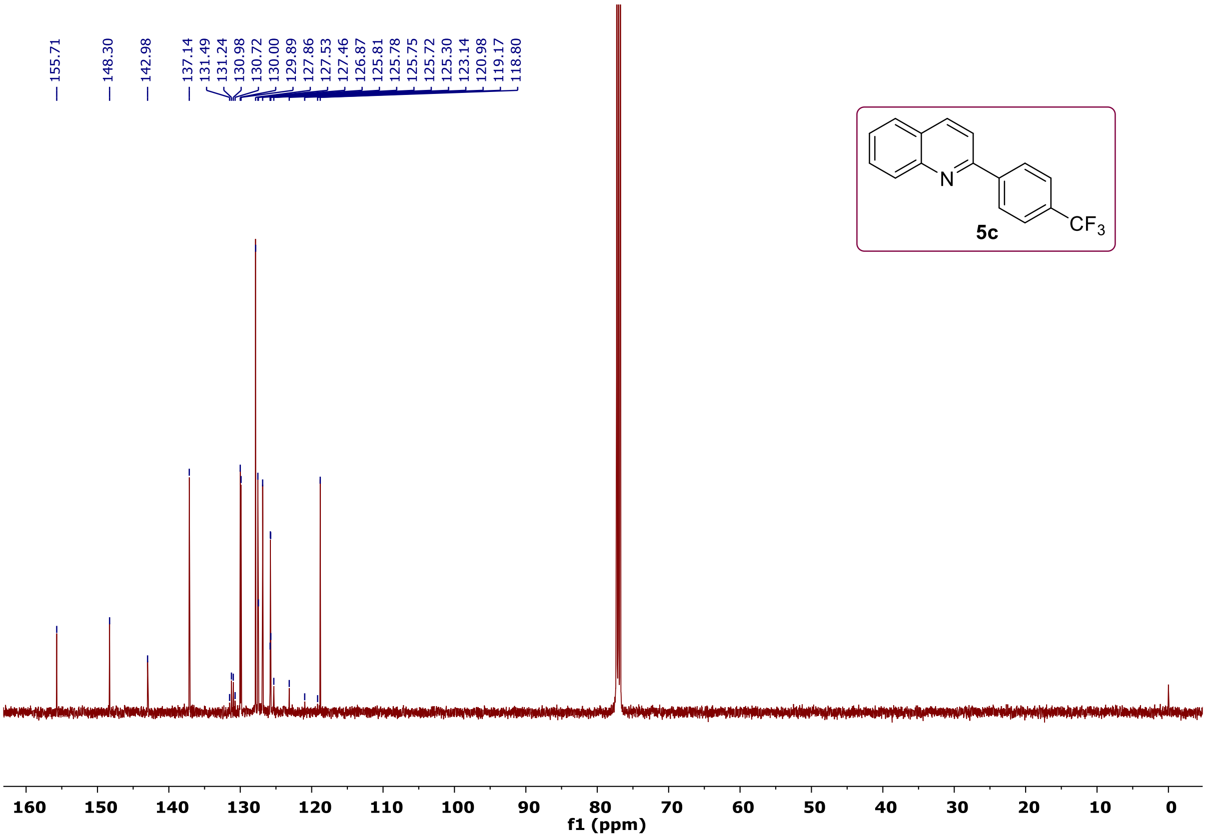
7.75
7.59
7.57
7.56
N
CF3
5c
0.93
2.01
0.99
1.00
1.03
2.06
0.93
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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127.86
127.53
127.46
126.87
125.81
125.78
125.75
125.72
125.30
123.14
120.98
119.17
118.80
N
CF3
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150
140
130
120
110
100
90
80
70
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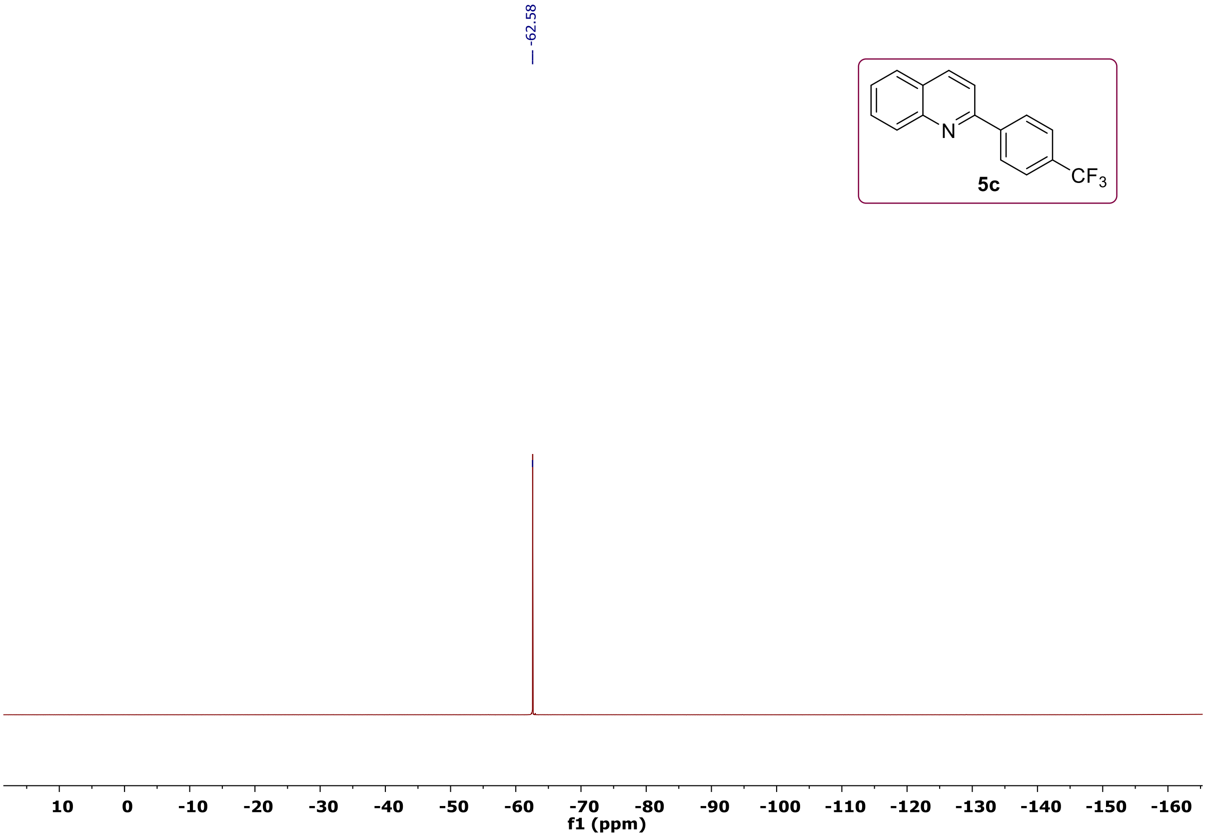
50
40
30
20
10
0
f1 (ppm)


-62.58
N
CF3
5c
10
0
-10
-20
-30
-40
-50
-60
-70
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-90
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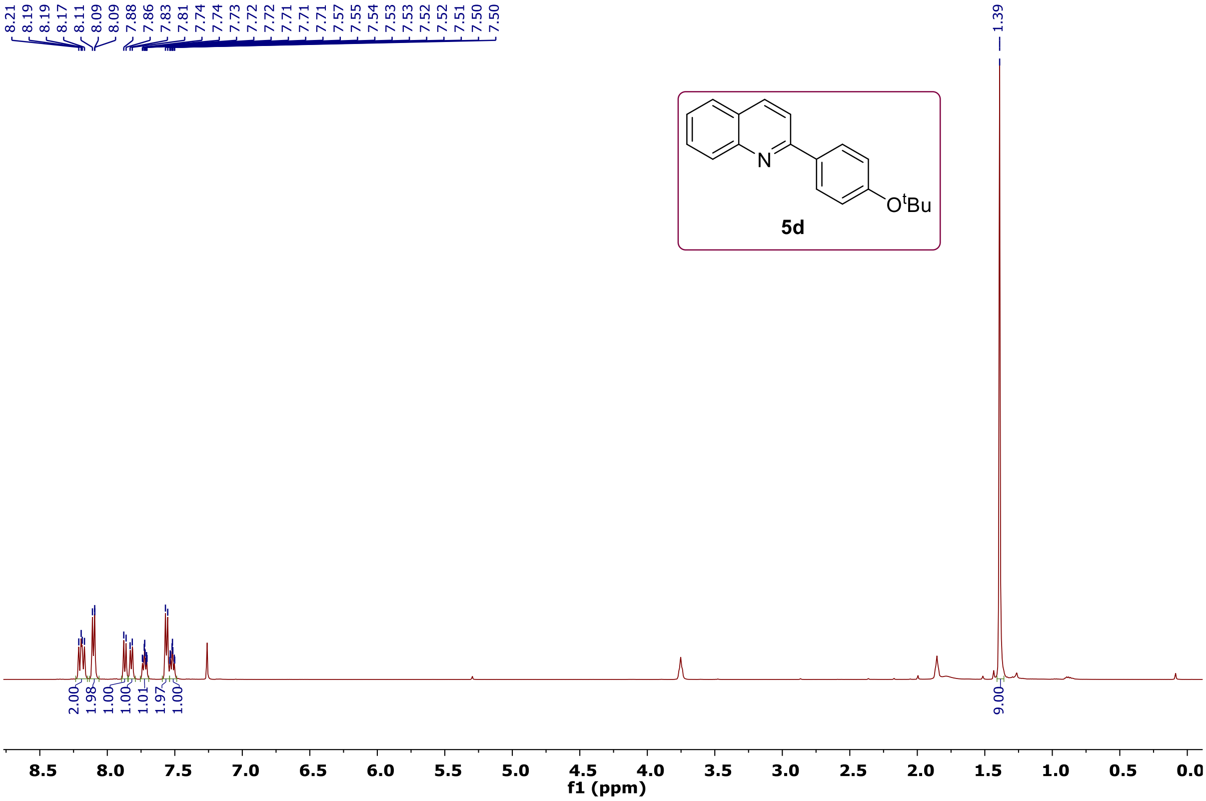
-140
-150
-160
f1 (ppm)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7.83
7.81
7.74
7.74
7.73
7.72
7.72
7.71
7.71
7.71
7.57
7.55
7.54
7.53
7.53
7.52
7.52
7.51
7.50
7.50
1.39
N
O^tBu
5d
2.00
1.98
1.00
1.00
1.01
1.97
1.00
9.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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3.5
3.0
2.5
2.0
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1.0
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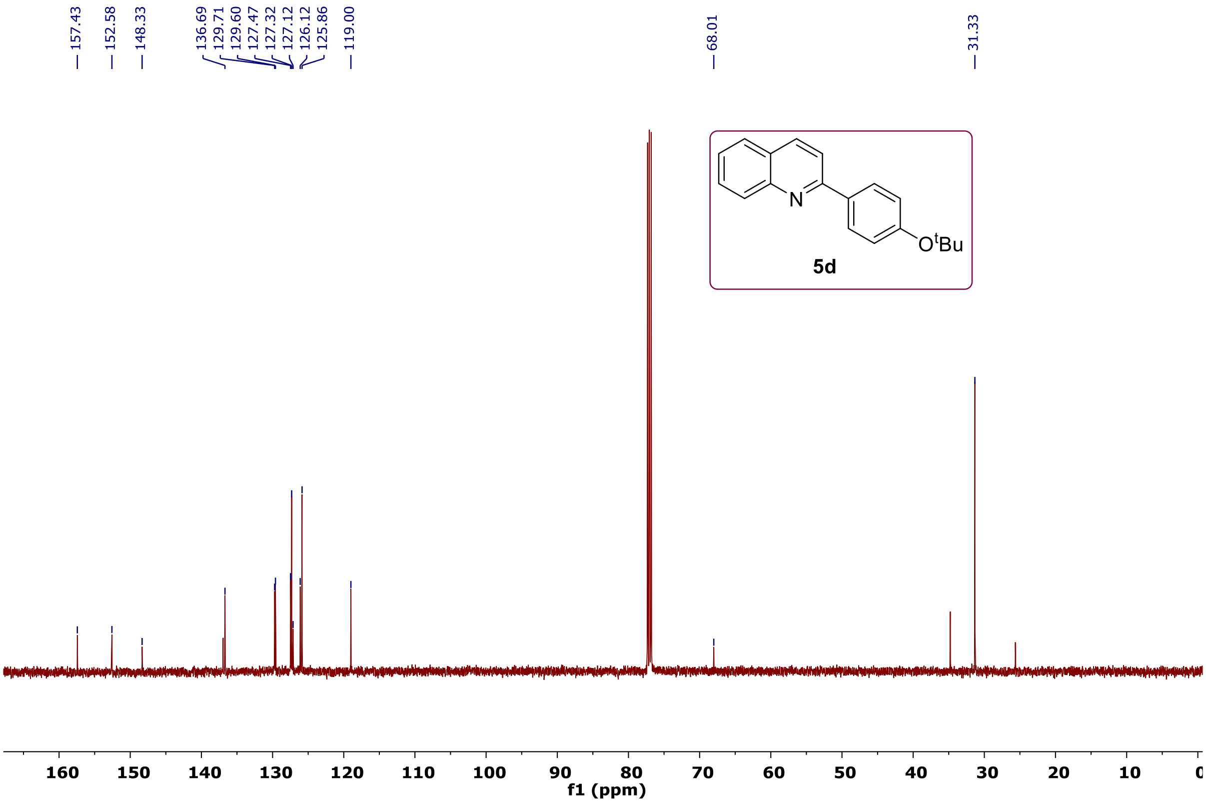
0.0
f1 (ppm)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126.12
125.86
119.00
68.01
31.33
N
O$^t$Bu
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110
100
90
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70
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50
40
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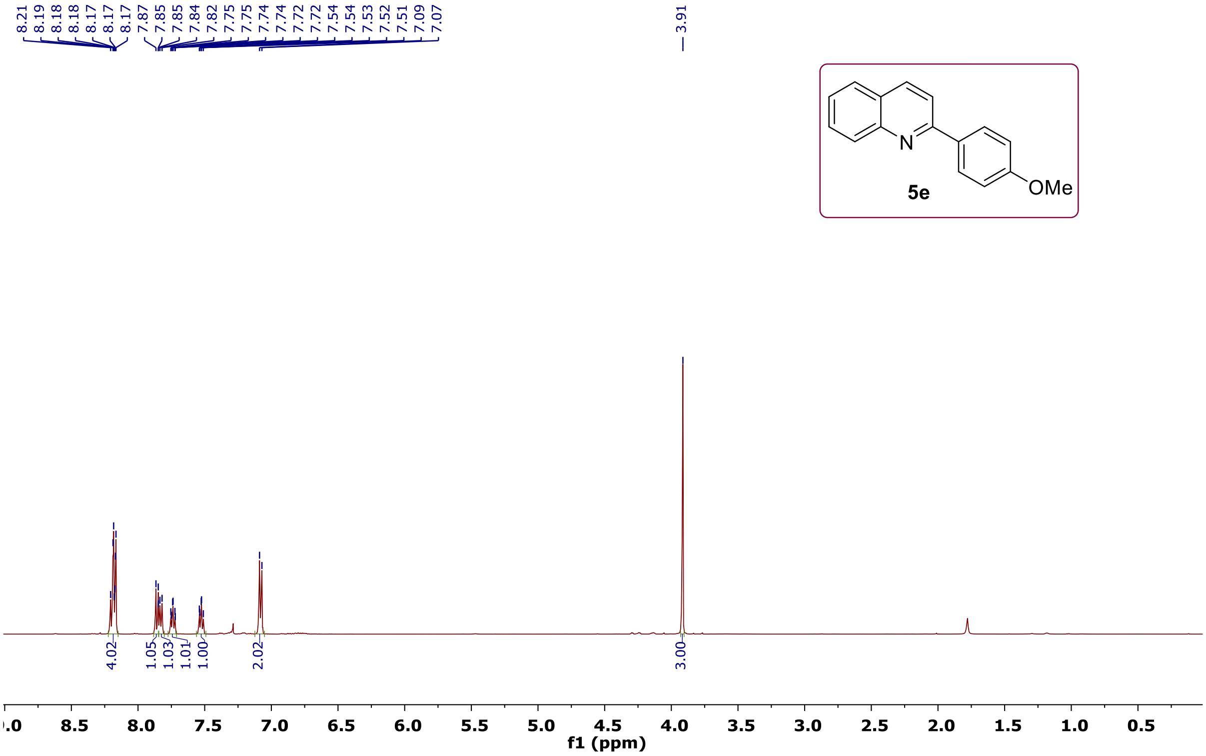
10
0
f1 (ppm)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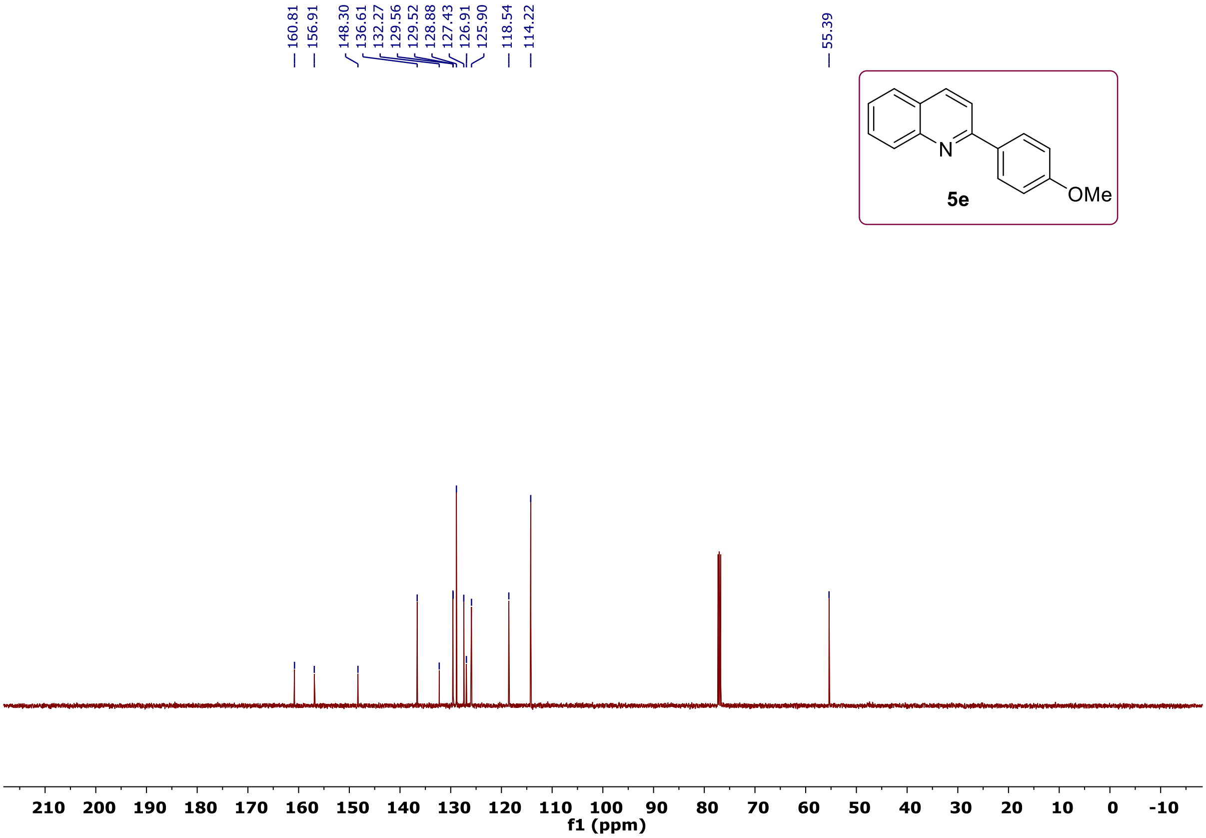
7.75
7.74
7.74
7.72
7.72
7.54
7.54
7.53
7.52
7.51
7.09
7.07
3.91
N
OMe
5e
4.02
1.05
1.03
1.01
1.00
2.02
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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128.88
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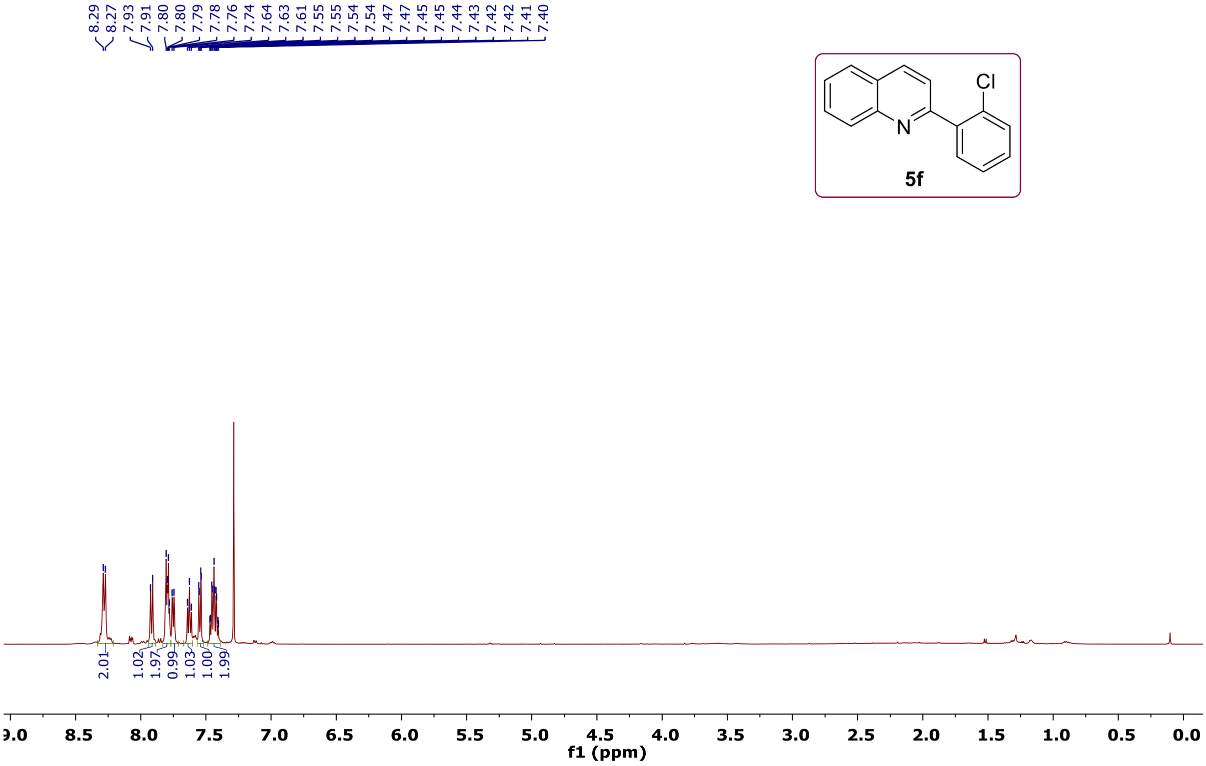
126.91
125.90
118.54
114.22
55.39
N
OMe
5e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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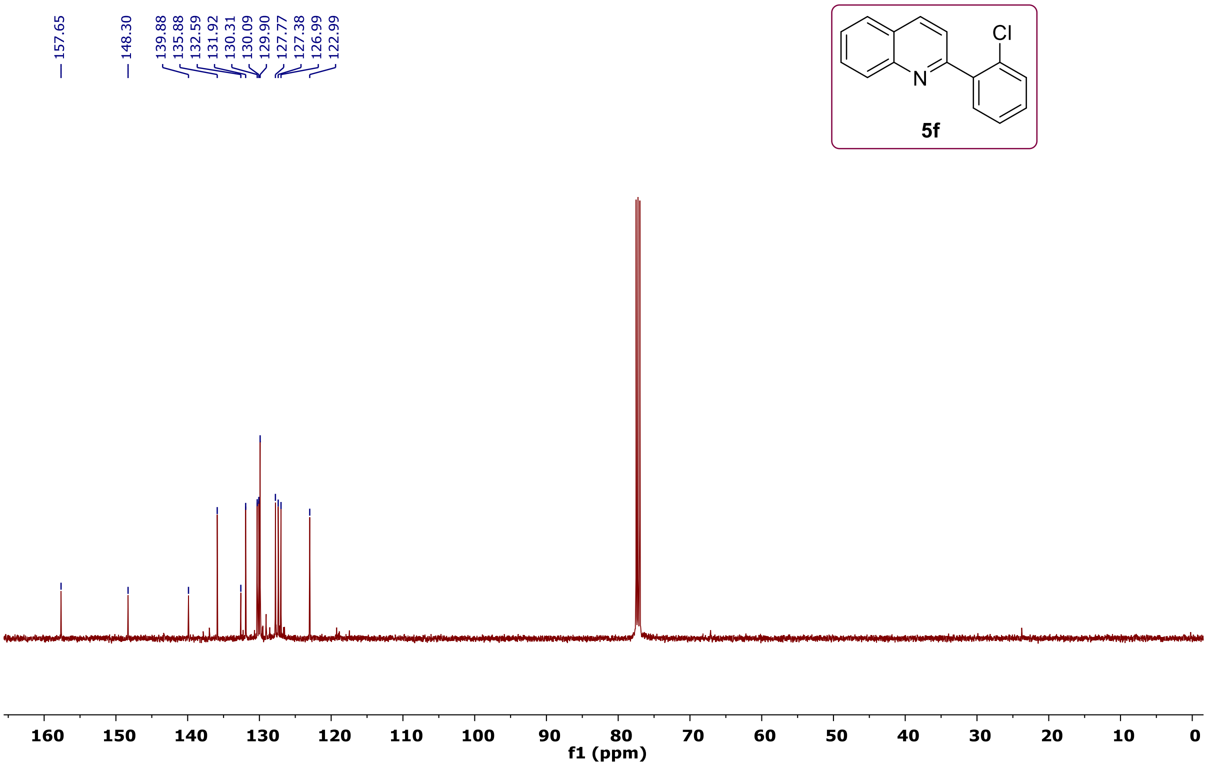
7.78
7.76
7.74
7.64
7.63
7.61
7.55
7.55
7.54
7.47
7.45
7.45
7.44
7.43
7.42
7.41
7.40
N
Cl
5f
2.01
1.02
1.97
0.99
1.03
1.00
1.99
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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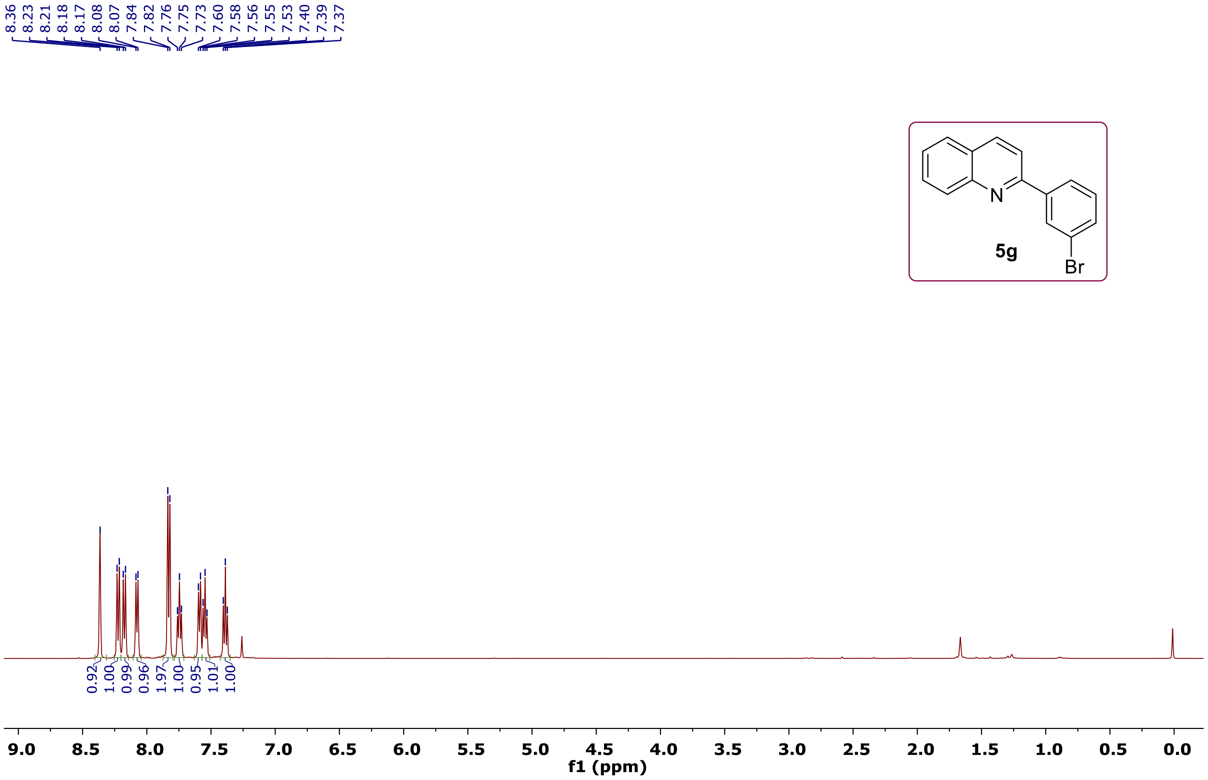
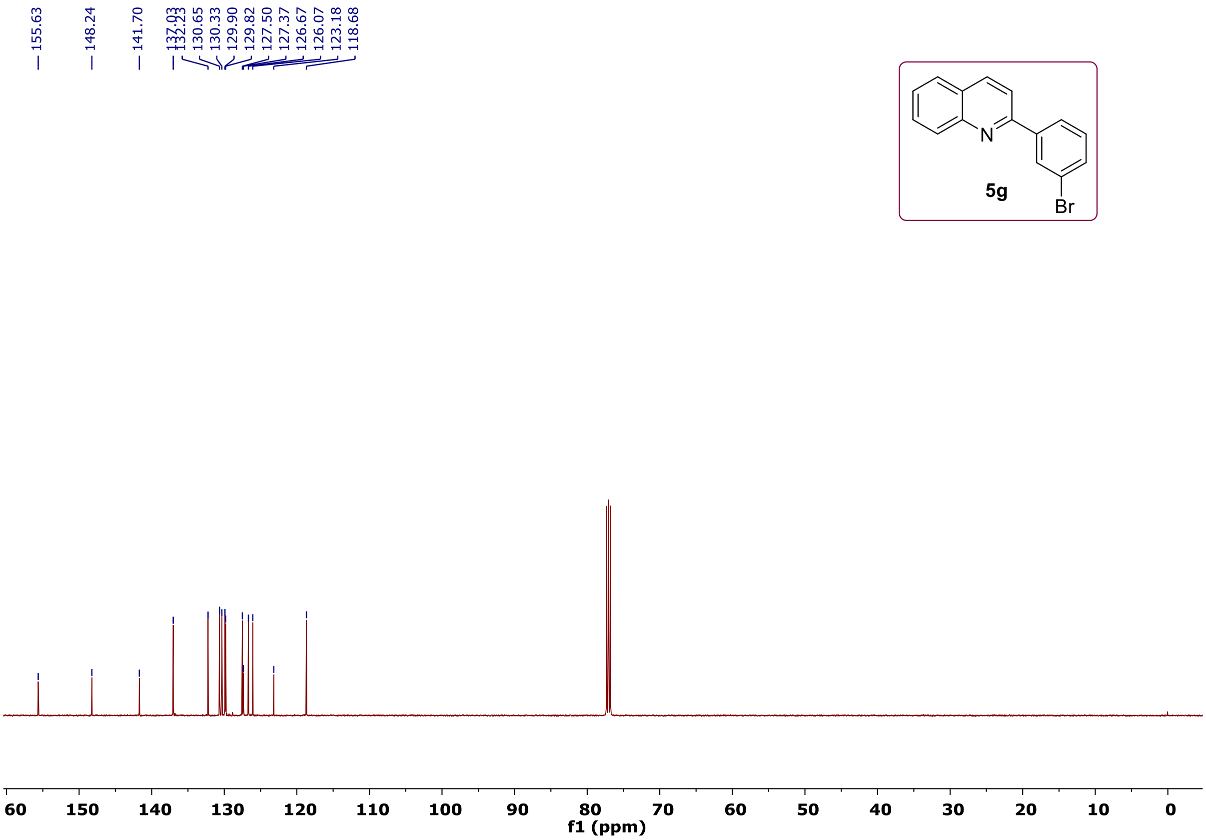
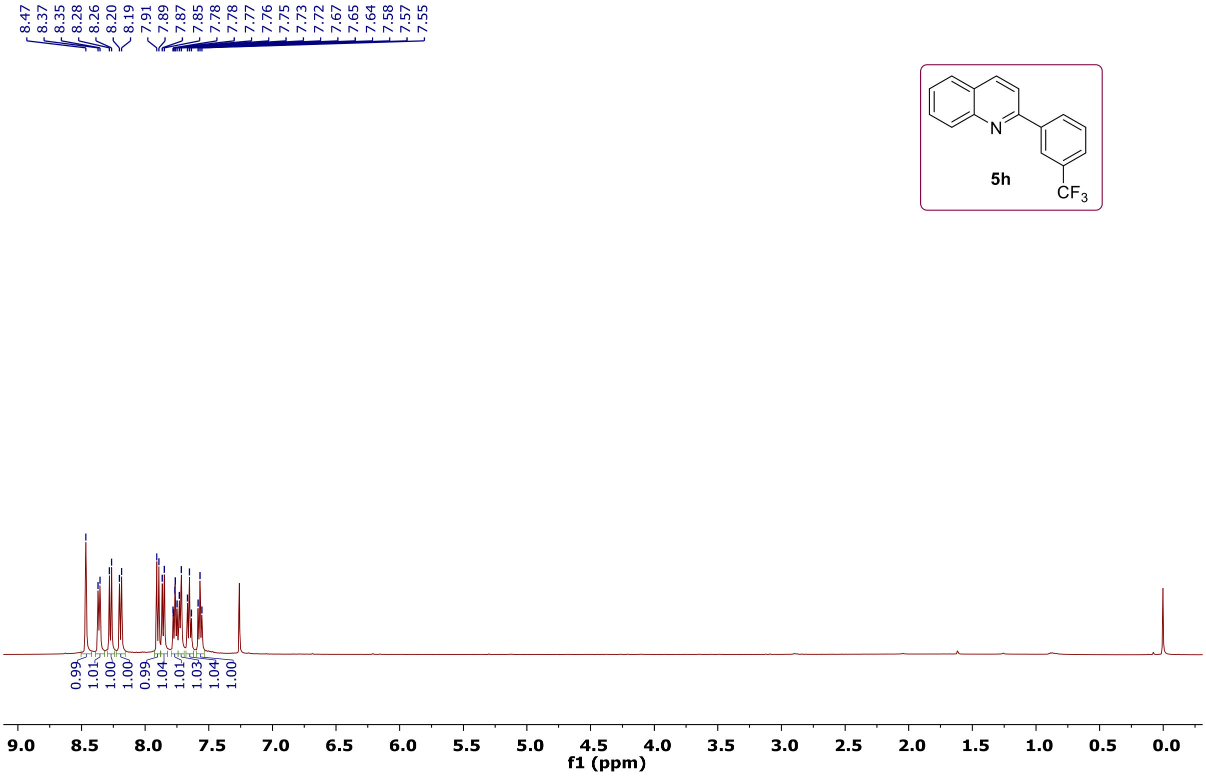
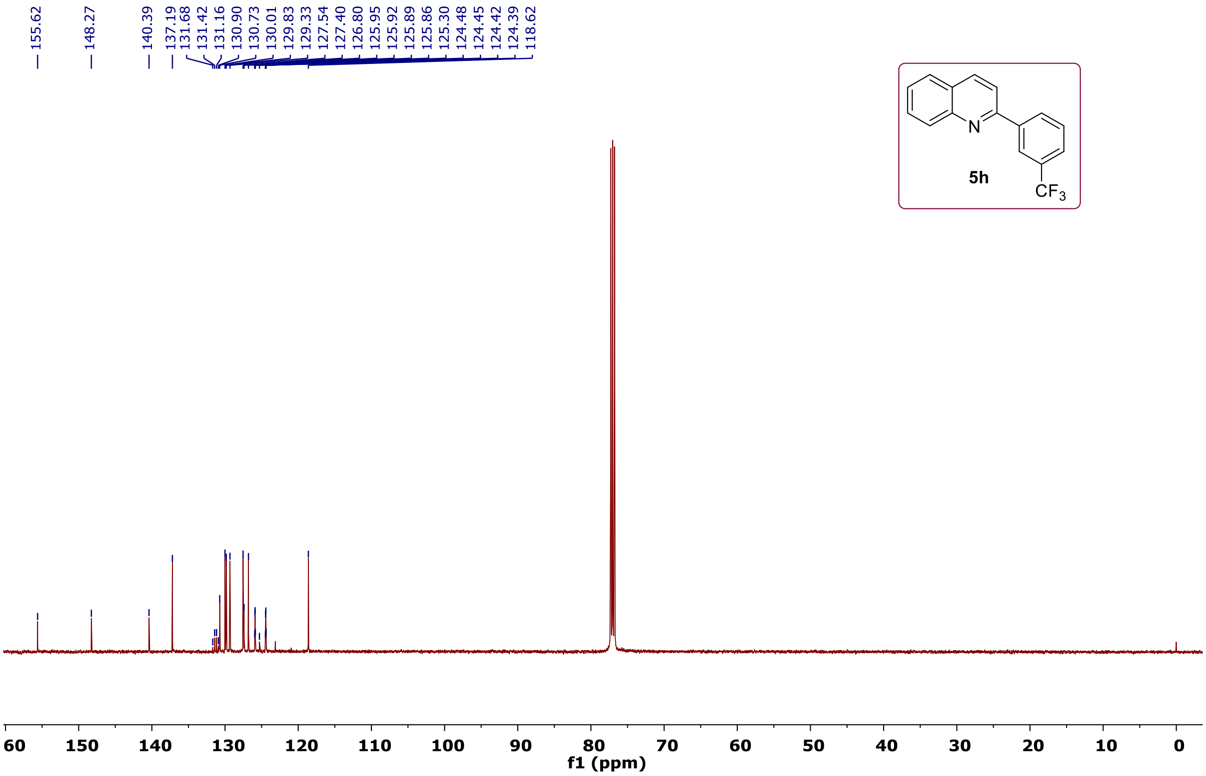
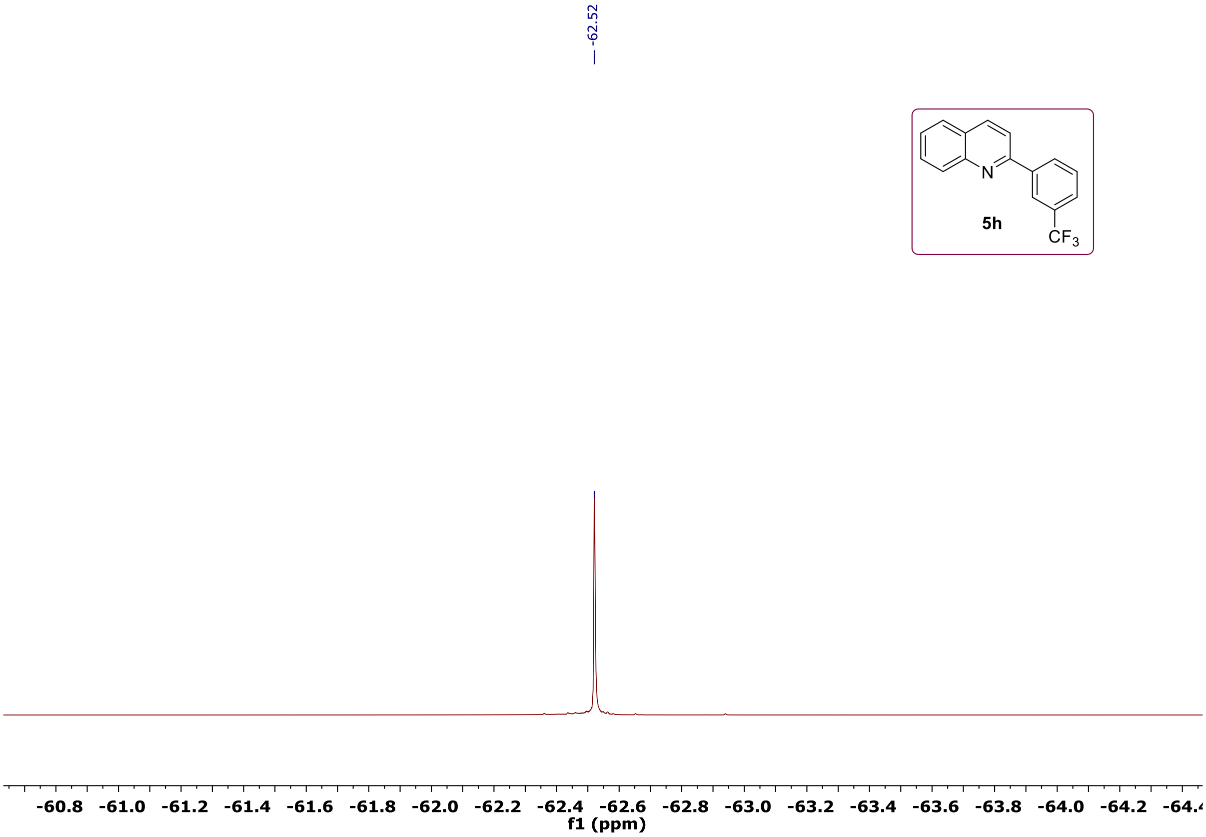
135.88
132.59
131.92
130.31
130.09
129.90
127.77
127.38
126.99
122.99
Cl
N
5f
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.36
8.23
8.21
8.18
8.17
8.08
8.07
7.84
7.82
7.76
7.75
7.73
7.60
7.58
7.56
7.55
7.53
7.40
7.39
7.37
N
5g
Br
0.92
1.00
0.99
0.96
1.97
1.00
0.95
1.01
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


155.63
148.24
141.70
137.03
132.23
130.65
130.33
129.90
129.82
127.50
127.37
126.67
126.07
123.18
118.68
N
5g
Br
60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.47
8.37
8.35
8.28
8.26
8.20
8.19
7.91
7.89
7.87
7.85
7.78
7.78
7.77
7.76
7.75
7.73
7.72
7.67
7.65
7.64
7.58
7.57
7.55
N
5h
CF3
0.99
1.01
1.00
1.00
0.99
1.04
1.01
1.03
1.04
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


155.62
148.27
140.39
137.19
131.68
131.42
131.16
130.90
130.73
130.01
129.83
129.33
127.54
127.40
126.80
125.95
125.92
125.89
125.86
125.30
124.48
124.45
124.42
124.39
118.62
N
5h
CF3
60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-62.52
N
5h
CF3
-60.8
-61.0
-61.2
-61.4
-61.6
-61.8
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-62.2
-62.4
-62.6
-62.8
-63.0
-63.2
-63.4
-63.6
-63.8
-64.0
-64.2
-64.
f1 (ppm)

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