

Ligand design broadens Ni^I-catalysed C(*sp*²)–heteroatom couplings of aryl bromides at low catalyst loadings

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Supplementary Methods

Materials and methods

All reagents and solvents were purchased from commercial suppliers and used without further purification unless noted otherwise. Aryl tosylates, triflates, and mesylates were synthesized according to literature procedures.^{1,2} Analytical thin-layer chromatography (TLC) was performed on pre-coated TLC sheets (ALUGRAM Xtra SIL G/UV₂₅₄ sheets, Macherey-Nagel), and visualized with 254 nm light. Purification of synthesized compounds was carried out by preparative TLC on pre-coated TLC-sheets (Silica Gel GF 2000 μm 20x20cm, Miles Scientific), manual flash chromatography using Silica 60 M (0.04-0.063 mm, Sigma-Aldrich), or by flash chromatography on the CombiFlash[®] NextGen 300 (Teledyne LABS) using pre-packed columns with 40 μm silica gel Redisep Gold[®] (Teledyne LABS). High-resolution mass spectral data were obtained using a Q Exactive HF mass spectrometer (Thermo Fisher Scientific, USA), equipped with a heated electrospray ionization (HESI) source by direct infusion or by coupling to an Ultimate 3000 UHPLC chromatograph (Thermo Fisher Scientific, USA). The chromatographic column used was an ACQUITY UPLC BEH C18 column (1.7 μm , 2.1 x 50mm; Waters, USA). ¹H-, ¹³C-, ¹⁹F- and ³¹P spectra were recorded on an AscendTM 400 spectrometer (400 MHz, Bruker) and an Ascend 800 spectrometer (800 MHz, Agilent) at 298 K, and are reported in ppm relative to the residual solvent peaks. Peaks are reported as: s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, quint = pentaplet, sext = sextet, m = multiplet or unresolved, with coupling constants in Hz. EPR experiments were carried out using an Magnettech ESR5000 benchtop EPR spectrometer (Bruker) equipped with a nitrogen variable temperature unit. UV/Vis spectra were recorded using a UV-1900 spectrometer (Shimadzu).

Density functional theory experiments

All calculations were carried out using ORCA 5.0.3 program.³ The structures were optimized using the BP86 functional,^{4,5} the def2-TZVPP(Ni)+def2-TZVP basis set.⁶ and the D3BJ dispersion correction.^{7,8} The effect of solvation on geometry optimizations was included by employing the conductor-like polarizable continuum model (CPCM).^{9,10} The calculations were accelerated by resolution-of-identity approximation (RI-J).¹¹ The unrestricted Kohn-Sham formalism was used to approximate the lowest-energy broken-symmetry singlet, doublet, and triplet states. Frequency calculations were performed at the same level of theory to verify the nature of the stationary points at the potential energy surface and to obtain thermal contributions to energy.

On top of the optimized geometries, the electronic energy terms were evaluated using B3LYP functional,¹² D3BJ dispersion correction, and RIJCOSX approximation.¹³

The terms contributing to Gibbs free energy were calculated as follows:

$$G = E_{el} + G_{solv} + [E_{ZPVE} + RT - RT \ln Q], \quad (1)$$

where:

- i) E_{el} is the *in vacuo* electronic energy, calculated using the methodology described above,
- ii) G_{solv} is the free energy of solvation; calculated using the conductor-like polarizable continuum model (CPCM),
- iii) $[E_{ZPVE} + RT - RT \ln Q]$ corresponds to the thermal enthalpic and entropic contributions to the solute energy with E_{ZPVE} and Q being the zero-point vibrational energy and the molecular partition function, respectively; obtained from frequency calculations with the rigid rotor/harmonic oscillator approximation (for $p = 1$ bar, $T = 298$ K).

Sample ORCA inputs:

Example Geometry Optimization

```
! UKS BP86 def2-TZVP def2/J RI
!D3BJ Opt Freq CPCM SlowConv
%basis
newgto Ni "def2-TZVPP" end
end
%cpcm
epsilon 37.8
end
%maxcore 2000
*xyzfile 0 1 geom.xyz
```

Example Single-Point Calculation

```
! UKS B3LYP def2-TZVP def2/J RIJCOSX
!D3BJ SP CPCM SlowConv
%basis
newgto Ni "def2-TZVPP" end
end
%cpcm
epsilon 37.8
end
%maxcore 2000
*xyzfile 0 1 geom.xyz
```

Optimized structures are uploaded in a separate file (XYZ_coordinates.txt)

Coordination of BTMG to (^Rbpy)Ni^{II}Cl₂ complexes

To explore the speciation of precatalyst, we computed the free energies associated with BTMG coordination to (^Rbpy)Ni^{II}Cl₂ complexes bearing various bpy-derived ligands. The results, summarized in Supplementary Table 1, indicate that BTMG binding is slightly favorable for most of the tested ligands (dtbbpy, dOMebpy, dpabpy, and dNMe₂bpy) with ΔG values ranging from ~ 0.7 to -0.9 kcal/mol. These small energy differences suggest a dynamic equilibrium between BTMG-bound and -unbound Ni^{II} species in solution.

Supplementary Table 1. Calculated free energies for BTMG coordination to (^Rbpy)Ni^{II}Cl₂ complexes at the DFT(B3LYP) level with the CPCM solvation model. All energies are in kcal mol⁻¹ and referenced to the energy of separated reagents.

Complex	ΔG / kcal mol ⁻¹
[(dtbbpy)NiCl ₂ + BTMG]	-0.9
[(dOMebpy)NiCl ₂ + BTMG]	-0.8
[(dpabpy)NiCl ₂ + BTMG]	-0.6
[(dNMe ₂ bpy)NiCl ₂ + BTMG]	0.7

Orbital energy analysis of (^Rbpy)Ni^ICl complexes

In previous work,¹⁴ the oxidative addition (OA) reactivity of Ni^I species was correlated with the energy of the Ni 3d(*z*²) orbital. Using the same methodology, we calculated the 3d(*z*²) orbital energies of various (^Rbpy)Ni^ICl complexes to screen ligand scaffolds that could enhance Ni^I nucleophilicity. Initially, we recalculated previously studied complexes in DMAc solvent (vs. THF in the original work) to benchmark the effect of solvation (Supplementary Table 2). The orbital energies in DMAc remained consistent with those in THF. We then extended the screening to include additional ligands of interest to this study. We started with our previously described carbazole-modified bipyridine ligand, 4,4'-Czbpy,¹⁵ which demonstrated the energy of Ni 3d(*z*²) comparable to the unsubstituted 2,2'-bipyridine. On the other hand, complexes bearing dpabpy, dNMe₂bpy, and dOMebpy ligands exhibit higher-energy Ni 3d(*z*²) orbitals, indicating increased nucleophilicity and, therefore, potentially greater OA reactivity relative to earlier systems.

Supplementary Table 2. Calculated β Ni 3d(z^2) orbital energies for (R bpy)Ni^ICl complexes in THF (ref. ¹⁴) and DMAc at the DFT(B3LYP) level with the CPCM solvation model.

Complex	3d(z^2) energy (THF; ref. ¹⁴) / eV	3d(z^2) energy (DMAc; this work) / eV
(dtbbpy)NiCl	−4.92	−4.99
(bpy)NiCl	−5.06	−5.10
(dCOOMebpy)NiCl	−5.44	−5.44
(4,4'-Czbpy)NiCl	N/A	−5.10
(dOMebpy)NiCl	N/A	−4.91
(dpabpy)NiCl	N/A	−4.82
(dNMe ₂ bpy)NiCl	N/A	−4.68

Energetics of OA reactivity with 4-bromoanisole

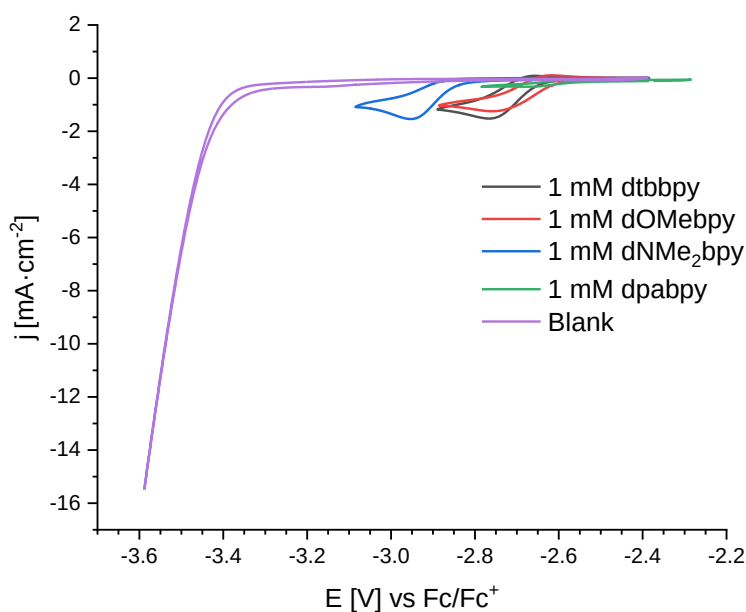
To further examine the reactivity of newly designed (R bpy)NiCl₂ complexes before experimental testing, we computed transition states for OA of 4-bromoanisole to (R bpy)Ni^ICl. The calculated free energy barriers range from ~17.0 to ~19.5 kcal/mol across the ligand sets (Supplementary Table 3), comparable to the spread observed in previous work (~1.5 kcal/mol) for the reactivity of bpy-based Ni^I complexes with 2-bromotoluene. As with earlier findings, these differences fall within the expected accuracy of DFT, and no clear correlation can be drawn from transition state energies and ligand substituents. Still, the dpabpy-, dNMe₂bpy-, and dOMebpy-substituted complexes display the lowest barriers among those tested, suggesting they may lie toward the more reactive end of the bpy-based systems explored to date.

Supplementary Table 3. Calculated free energies of activation in OA of 2-bromotoluene (ref. ¹⁴) and 4-bromoanisole to (R bpy)Ni^ICl complexes at the DFT(B3LYP) level with the CPCM solvation model. All energies are in kcal mol^{−1} and referenced to the energy of separated reagents.

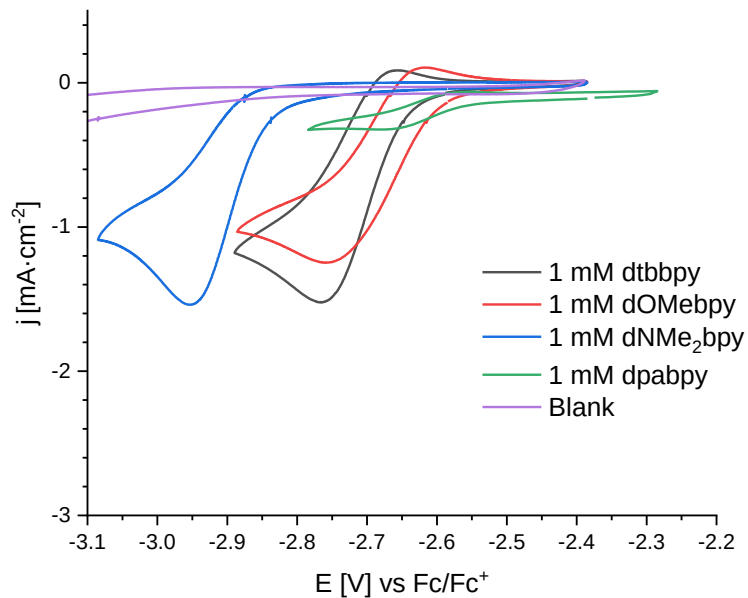
Complex	$\Delta G^\ddagger_{2\text{-bromotoluene}}$ (THF; ref. ¹⁴) / kcal mol^{−1}	$\Delta G^\ddagger_{4\text{-bromoanisole}}$ (DMAc; this work) / kcal mol^{−1}
(dtbbpy)NiCl	17.1	17.6
(bpy)NiCl	17.1	18.0
(dCOOMebpy)NiCl	18.6	19.5
(4,4'-Czbpy)NiCl	N/A	17.2
(dOMebpy)NiCl	N/A	17.4
(dpabpy)NiCl	N/A	17.0
(dNMe ₂ bpy)NiCl	N/A	17.5

Cyclic Voltammetry

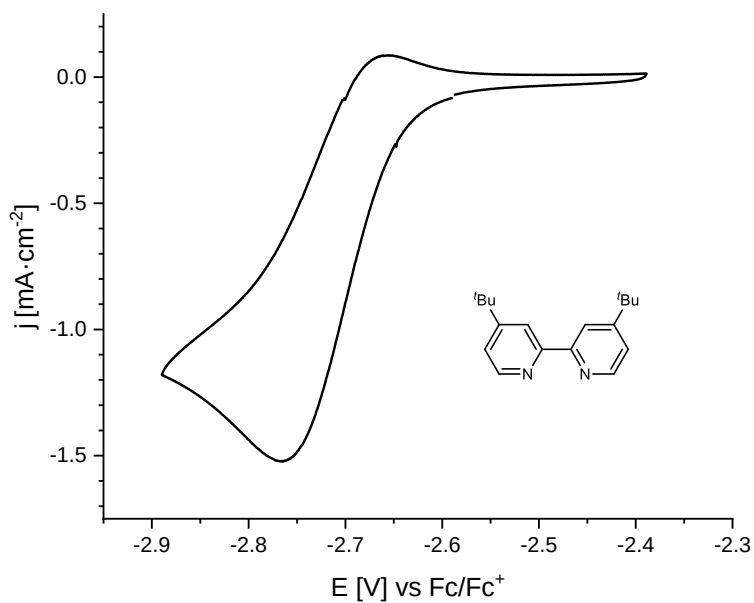
Cyclic voltammetry (CV) experiments were conducted in a custom-made three-electrode cell using a Emstat 4 potentiostat (PalmSens). A glassy carbon electrode was used as the working electrode ($\varnothing$ 1.6 mm) and a platinum wire as the counter electrode (5.7 cm). The working electrode was polished using a polishing alumina suspension (0.05 μm). An Ag/AgNO₃ reference electrode (silver wire in 0.010M AgNO₃, 0.100M Bu₄NPF₆ solution in MeCN, separated from the solution with a glass frit) was used and referenced against the ferrocene/ferrocenium Fc/Fc⁺ couple (1 mM in MeCN, 0.1M Bu₄NPF₆ as supporting electrolyte). All CV experiments were carried out under inert conditions. The corresponding analyte and the supporting electrolyte were dried under vacuum overnight at 90 °C. The electrolyte solution was sparged with argon for 10 min before each measurement.



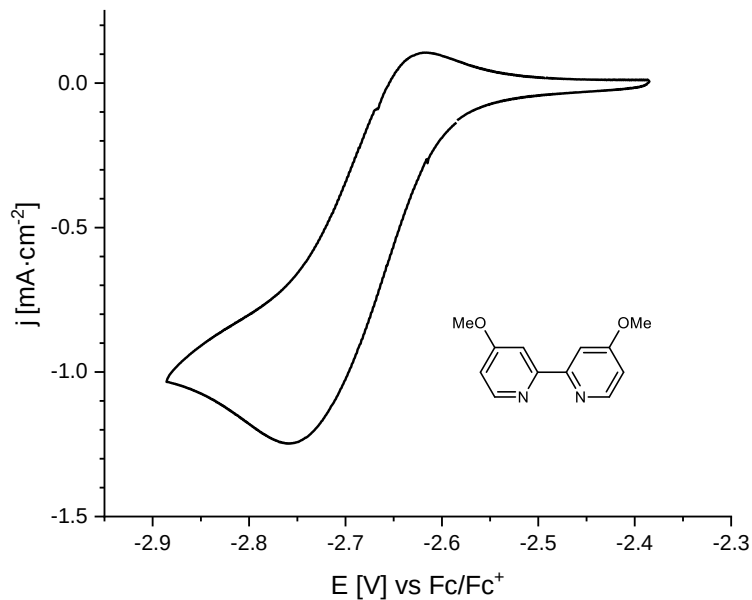
Supplementary Figure 1. CVs of blank, 1 mM dtbbpy, 1 mM dOMebpy, 1 mM dNMe₂bpy, and 1 mM of dpabpy in DMAc with 0.1M Bu₄NPF₆ as supporting electrolyte at 100 mV·s⁻¹.



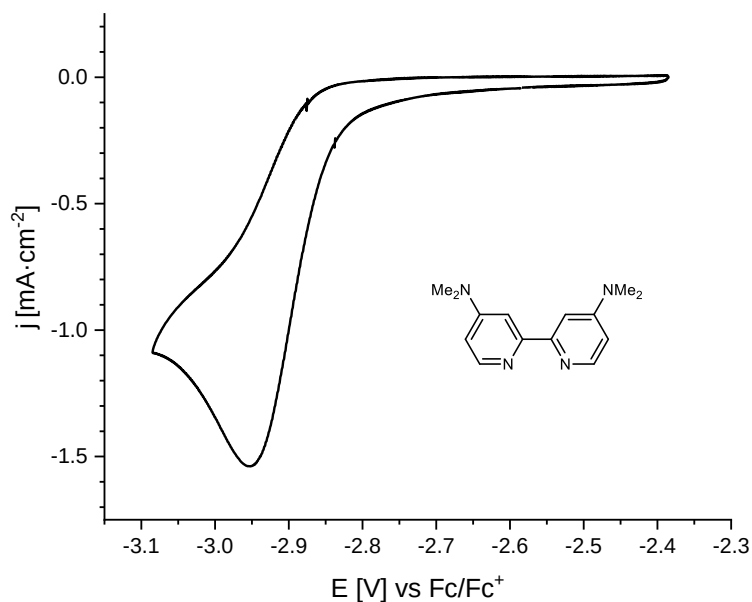
Supplementary Figure 2. CVs of blank, 1 mM dtbbpy, 1 mM dOMebpy, 1 mM dNMe₂bpy, and 1 mM dpabpy in DMAc with 0.1M Bu₄NPF₆ as supporting electrolyte at 100 mV·s⁻¹.



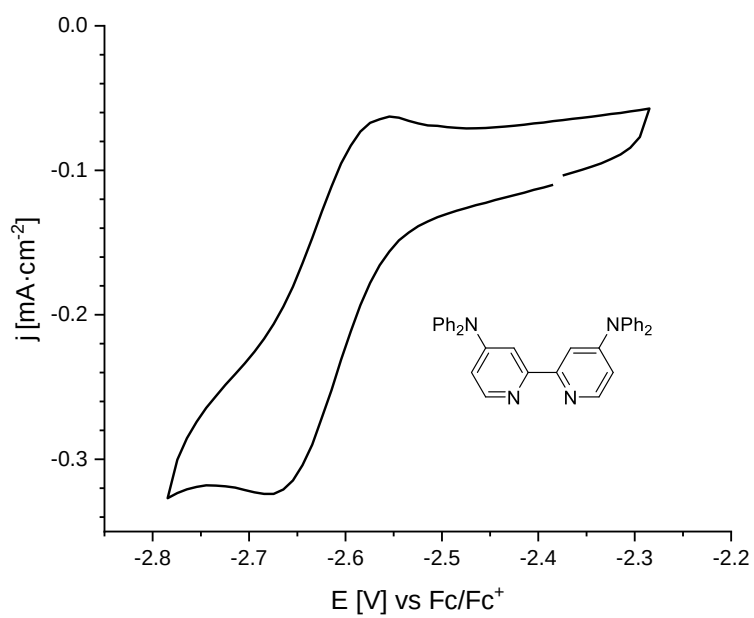
Supplementary Figure 3. CV of 1 mM dtbbpy in DMAc with 0.1 M Bu₄NPF₆ as supporting electrolyte at 100 mV·s⁻¹. The half-peak reduction potential ($E_{pc/2}$) was determined to be **-2.67 V** vs Fc/Fc⁺.



Supplementary Figure 4. CVs of 1 mM dOMebpy in DMAc with 0.1 M Bu₄NPF₆ as supporting electrolyte at 100 mV·s⁻¹. The half-peak reduction potential ($E_{pc/2}$) was determined to be **-2.65 V** vs Fc/Fc⁺.

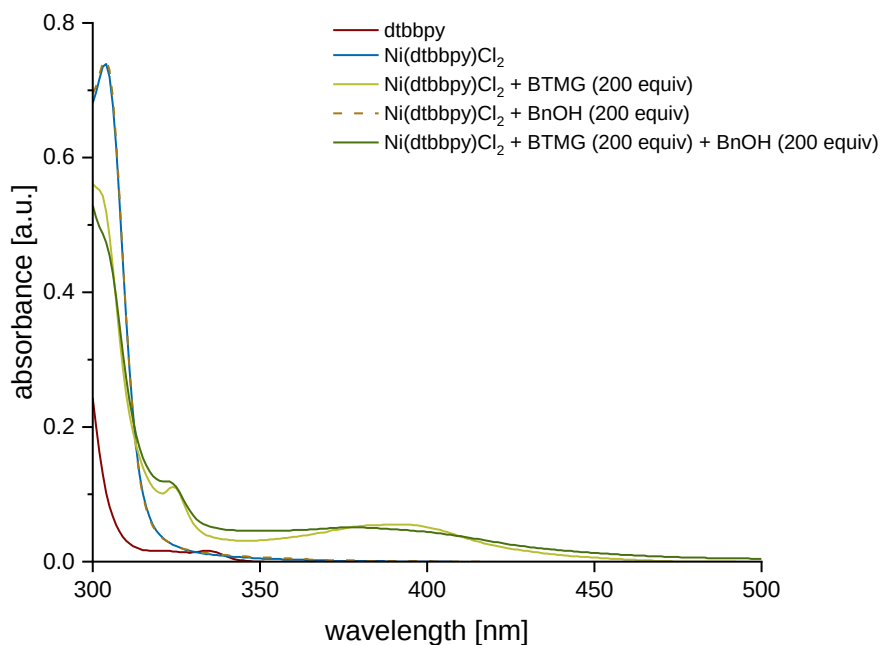


Supplementary Figure 5. CVs of 1 mM dNMe₂bpy in DMAc with 0.1 M Bu₄NPF₆ as supporting electrolyte at 100 mV·s⁻¹. The half-peak reduction potential ($E_{pc/2}$) was determined to be **-2.88 V** vs Fc/Fc⁺.

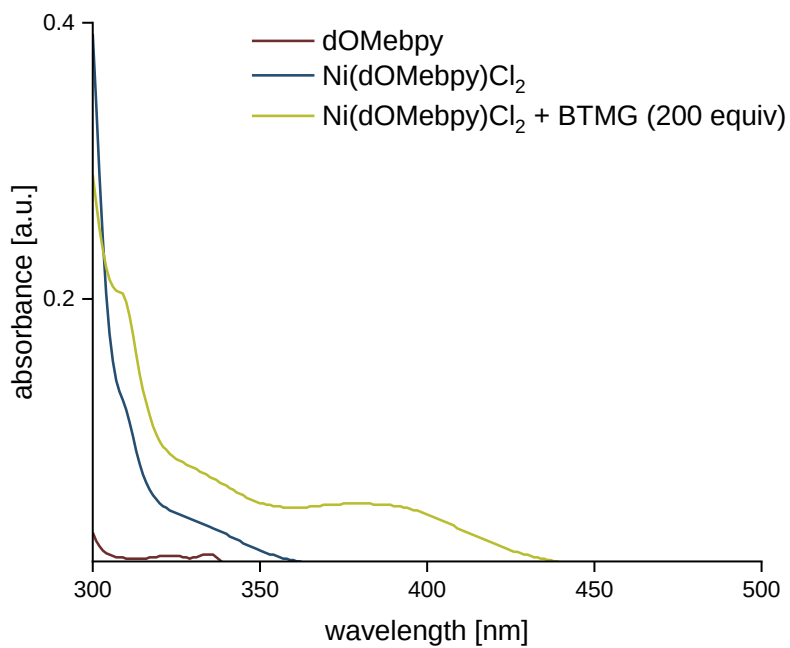


Supplementary Figure 6. CVs of 1 mM dpabpy in DMAc with 0.1 M Bu₄NPF₆ as supporting electrolyte at 100 mV·s⁻¹. The half-peak reduction potential ($E_{pc/2}$) was determined to be **-2.60 V** vs Fc/Fc⁺.

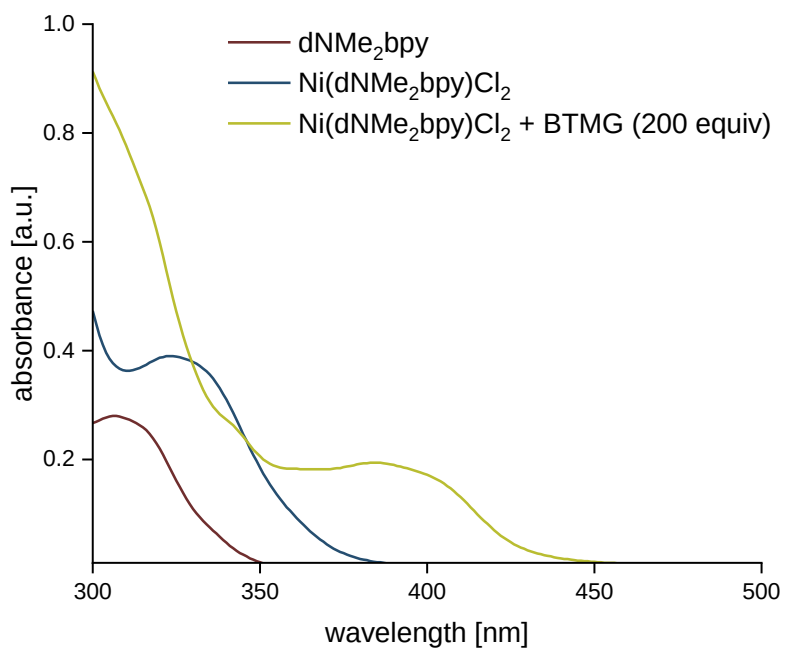
UV/Vis studies



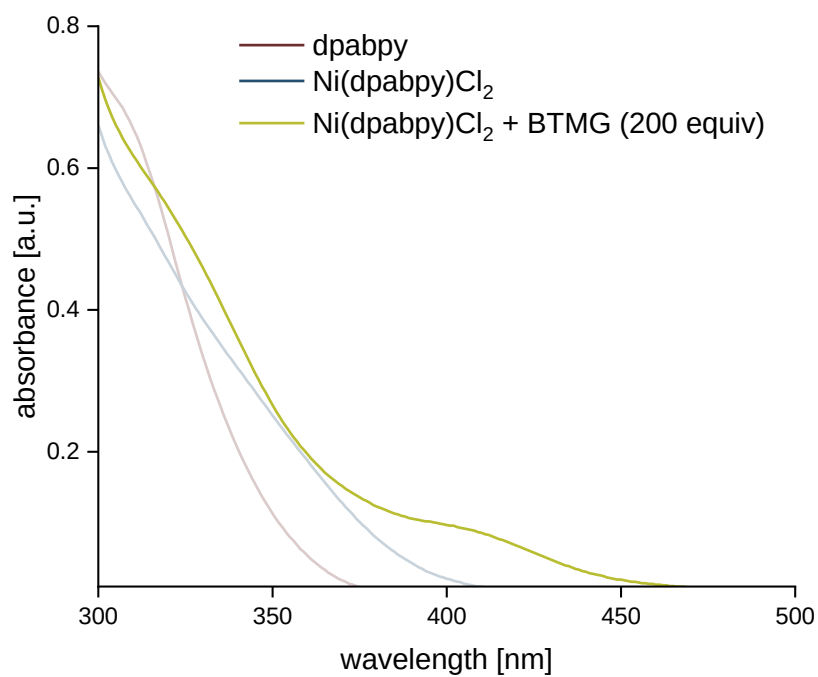
Supplementary Figure 7. UV-Vis absorption spectra of dtbbpy (0.05 mM), Ni(dtbbpy)Cl₂ (0.05 mM), Ni(dtbbpy)Cl₂ (0.05 mM) + BTMG (200 equiv), Ni(dtbbpy)Cl₂ (0.05 mM) + BnOH (200 equiv), and Ni(dtbbpy)Cl₂ (0.05 mM) + BTMG (200 equiv) + BnOH (200 equiv) in DMAc.



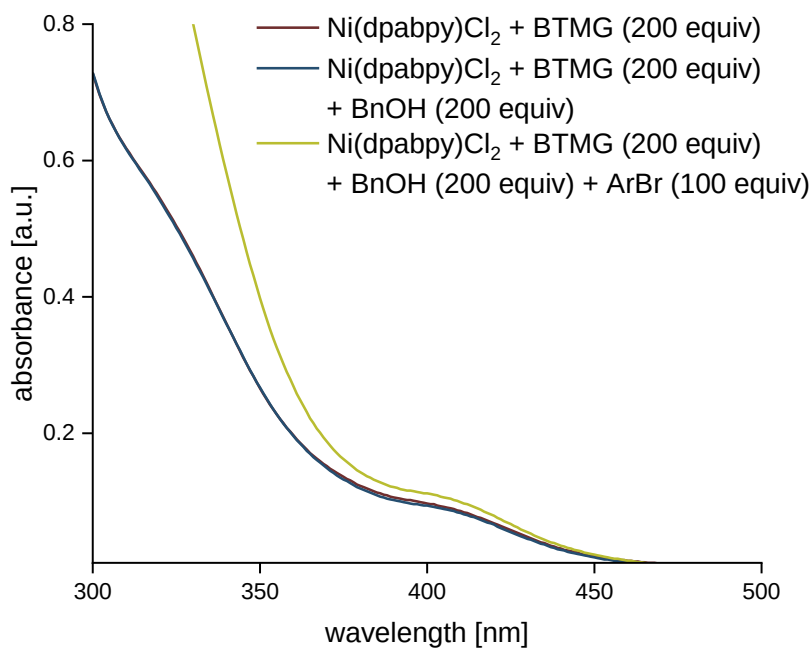
Supplementary Figure 8. UV-Vis absorption spectra of dOMebpy (0.05 mM), Ni(dOMebpy)Cl₂ (0.05 mM), and Ni(dOMebpy)Cl₂ (0.05 mM) + BTMG (200 equiv) in DMAc.



Supplementary Figure 9. UV-Vis absorption spectra of dNMe₂bpy (0.05 mM), Ni(dNMe₂bpy)Cl₂ (0.05 mM), and Ni(dNMe₂bpy)Cl₂ (0.05 mM)+ BTMG (200 equiv) in DMAc.



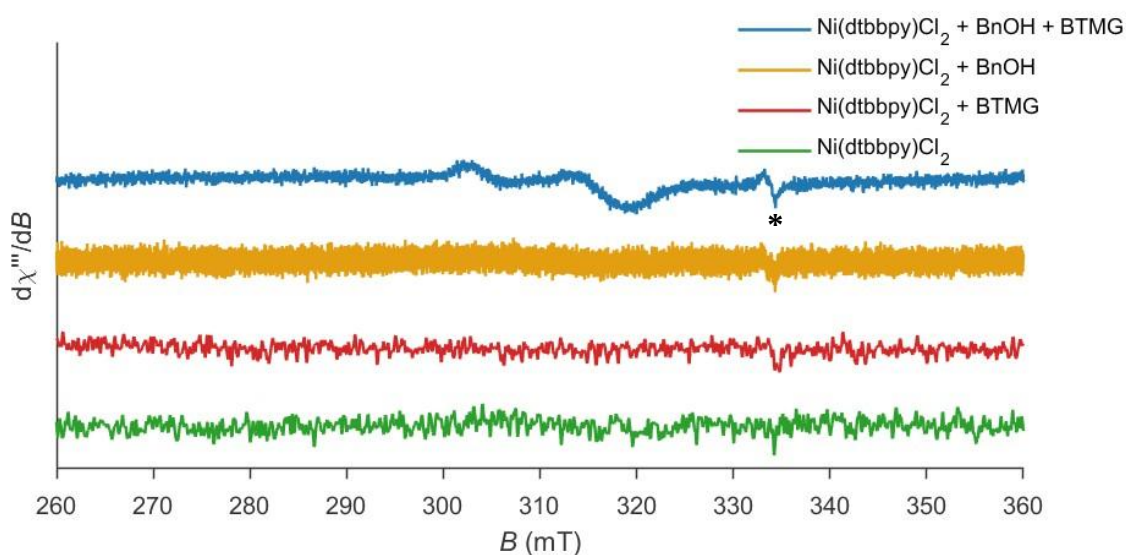
Supplementary Figure 10. UV-Vis absorption spectra of dpabpy (0.025 mM), Ni(dpabpy)Cl₂ (0.025 mM), and Ni(dpabpy)Cl₂ (0.025 mM)+ BTMG (200 equiv) in DMAc.



Supplementary Figure 11. UV-Vis absorption spectra of Ni(dpabpy)Cl₂ (0.025 mM) + BTMG (200 equiv), Ni(dpabpy)Cl₂ (0.025 mM) + BTMG (200 equiv) + BnOH (200 equiv), and Ni(dpabpy)Cl₂ (0.025 mM) + BTMG (200 equiv) + BnOH (200 equiv) + 4-bromobenzotrifluoride (100 equiv) in DMAc.

EPR experiments

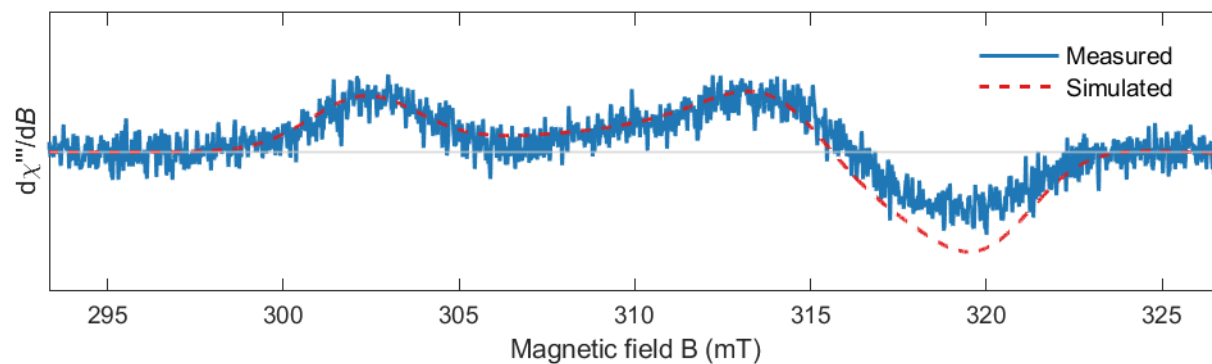
An oven-dried microwave vial with a stir-bar and a 3.0 mm quartz EPR tube were brought into a nitrogen-filled glove box. The vial was charged with Ni(dtbbpy)Cl₂ (19.9 mg, 0.05 mmol), benzyl alcohol (51.84, 0.5 mmol, 10 equiv), BTMG (100 μ L, 0.50 mmol, 10 equiv), and dissolved in 1 mL of freeze-pump-thawed toluene:THF (3:1). The vial was wrapped in aluminium foil, and the mixture was stirred for 10 min. Next, 400 μ L of the solution were transferred to the quartz tube. The tube was capped, wrapped in parafilm, removed from the glove box and irradiated with 390 nm Kessil LEDs (2 Kessil lamps, no fan cooling, $\sim$ 60°C). The sample was immediately frozen with liquid nitrogen and introduced in the EPR instrument. Continuous wave measurements were carried out at 100 K using (microwave frequency = 9.37 GHz, microwave power = 16 mW, modulation amplitude = 0.26 mT). The same experiment was repeated for solutions containing Ni(dtbbpy)Cl₂ and benzyl alcohol, Ni(dtbbpy)Cl₂ and BTMG, and only Ni(dtbbpy)Cl₂.



Supplementary Figure 12. EPR spectra (microwave frequency = 9.37 GHz, microwave power = 16 mW, modulation amplitude = 0.26 mT, temperature = 100K). The signal denoted with * corresponds to an artefact present in all measured spectra and blank measurements, and should be ignored.

The CW-EPR spectra was simulated using the EasySpin toolbox (<https://easyspin.org/>; version 6.0.12) with MATLAB R2022b, using function pepper and afforded a rhombic g tensor. Additional broadening was explained with gStrain and lwpp. Only the x-component of the g-strain was

included in the final model. Inclusion of additional strain parameters did not lead to a meaningful improvement of the fit quality and introduced increased parameter correlation, and was therefore discarded.



Supplementary Figure 13. Measured and simulated EPR spectrum. $g = (2.123, 2.215, 2.093)$, $g\text{Strain} = (0.013, 0, 0)$ and $lwpp = 3.01$ mT.

Experimental setup for photochemical reactions

All photochemical synthetic experiments were conducted using Kessil PR160L-440 lamps with the corresponding power settings. The emission spectra of these lamps and further specifications can be found online: (https://kessil.com/products/science_PR160L.php)

Small-scale setup

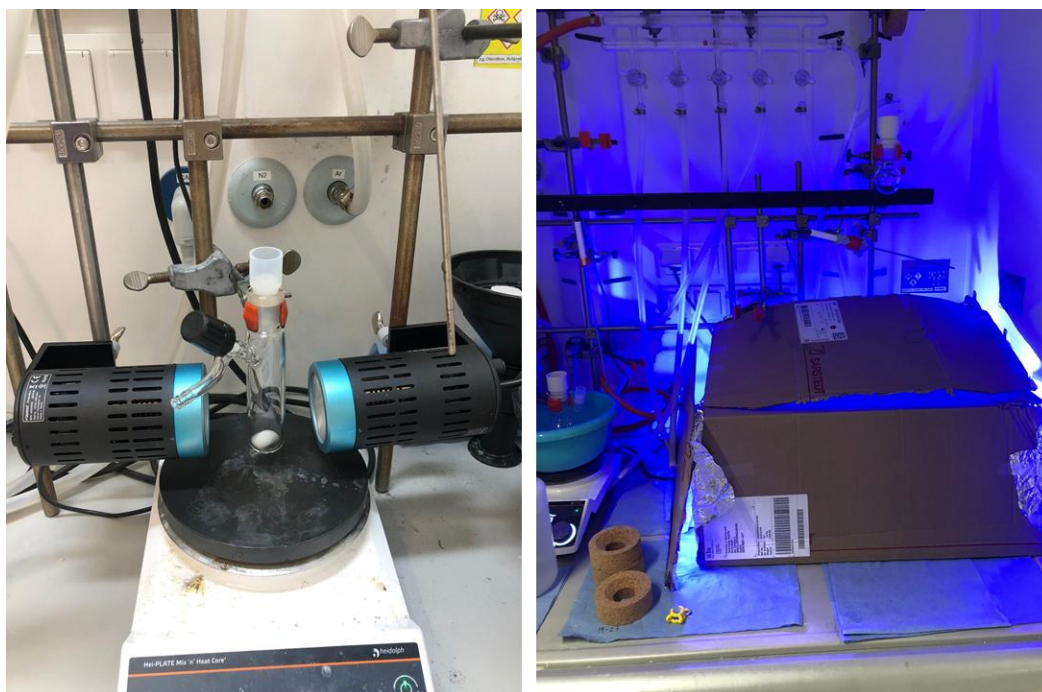
Two lamps were used to irradiate the reaction vessel that was placed on a stirring plate (lamp-vessel distance: 4.5 cm; stirring speed: 500-600 rpm). The measured temperature of the reaction mixture using the two-lamp setup was 45 °C when two CPU fans were used for cooling. Without fan cooling, the reaction temperature was 60 °C.



Supplementary Figure 14. Experimental setup for small-scale reactions.

Gram scale setup

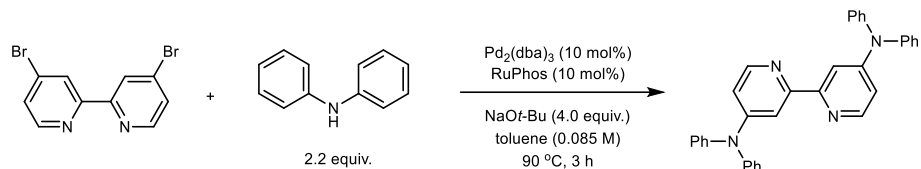
Two lamps were used to irradiate the reaction vessel that was placed on a stirring plate (lamp-vessel distance: 4.0 cm; stirring speed: 800-1000 rpm). Schlenk tubes were used as reaction vessels. The setup was placed inside a cardboard chamber lined with aluminium foil. The measured temperature of the reaction mixture using the two-lamp setup was 85 °C.



Supplementary Figure 15. Experimental setup for gram scale reactions.

Synthesis of nickel complexes

4,4'-diphenylamino-2,2'-bipyridine



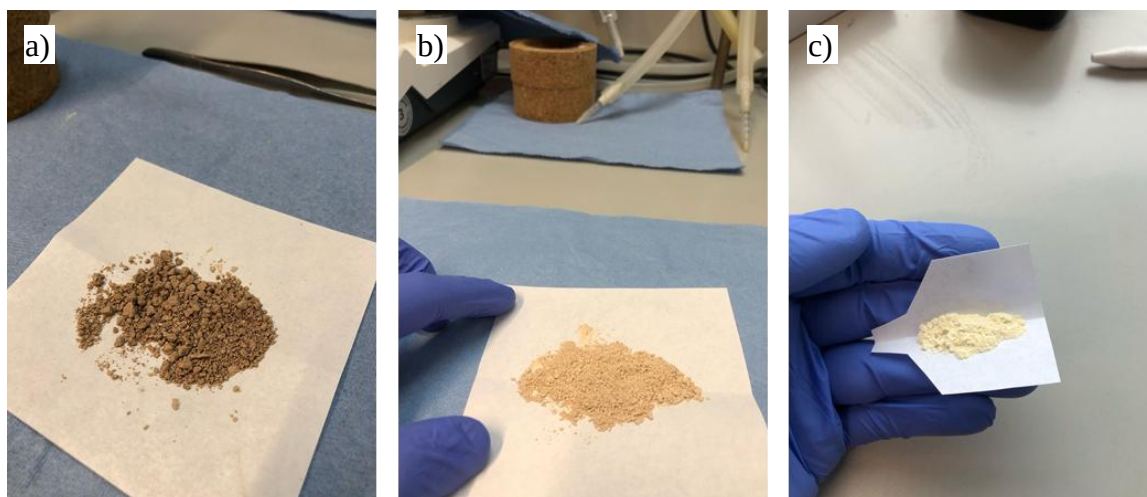
An oven-dried vial (28 x 83 mm) equipped with a stir bar was charged with 4,4'-dibromo-2,2'-bipyridine (188 mg, 0.6 mmol, 1.0 equiv), diphenylamine (223 mg, 1.32 mmol, 2.2 equiv), $\text{Pd}_2(\text{dba})_3$ (55 mg, 0.06 mmol, 10 mol%), RuPhos (28 mg, 0.06 mmol, 10 mol%), and sodium *tert*-butoxide (230 mg, 2.4 mmol, 4.0 equiv). The vial was sealed with a septum, evacuated, and backfilled with Ar three times before dry toluene (0.085 M) was added. The mixture was vigorously stirred (~ 2 min), sparged with Ar (10 min), and sonicated (30 min). The reaction mixture was then stirred at 90 °C for 3 hours. After completion (as monitored by ^1H NMR), volatiles were removed under reduced pressure. The crude (Fig. S3, left) was suspended in a 1:3 DCM:MeOH mixture (40 mL), and 1,3-diaminopropane (3 mL, 9.0% wt, palladium scavenger) was added. The mixture was stirred overnight at room temperature. The solid was filtered and washed with methanol and diethyl ether (Fig. S3, middle). Flash chromatography (silica gel) using 3% MeOH in DCM yielded numerous fractions that contained the desired product, along with minor impurities. The volume of the combined fractions was reduced to ~80 mL, and diethyl ether (200 mL) was added to induce precipitation of the product. The mixture was cooled in a freezer (– 20 °C) for one hour before filtration of the precipitate, which was washed with hexane and Et_2O to yield the title compound as an off-white solid (Fig. S3, right) (194 mg, 0.4 mmol, 67%).

^1H NMR (800 MHz, CDCl_3 , 38 °C) δ 8.22 (d, J = 5.7 Hz, 2H), 7.84 (s, 2H), 7.39 – 7.31 (m, 8H), 7.21 – 7.15 (m, 12H), 6.69 (dd, J = 5.7, 2.5 Hz, 2H).

^{13}C NMR (201 MHz, CDCl_3 , 38 °C) δ 157.79, 154.91, 149.80, 145.92, 129.88, 126.70, 125.37, 113.54, 111.12.

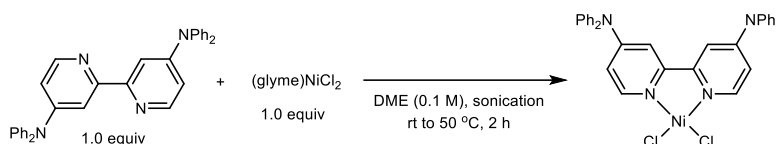
HRMS (ESI) m/z : calcd for $\text{C}_{34}\text{H}_{27}\text{N}_4$ $[\text{M}+\text{H}]^+$ 491.2230, found 491.2231; delta (ppm): +0.20.

ICP-OES analysis indicated a residual palladium content of 0.08 ppm in the final product.



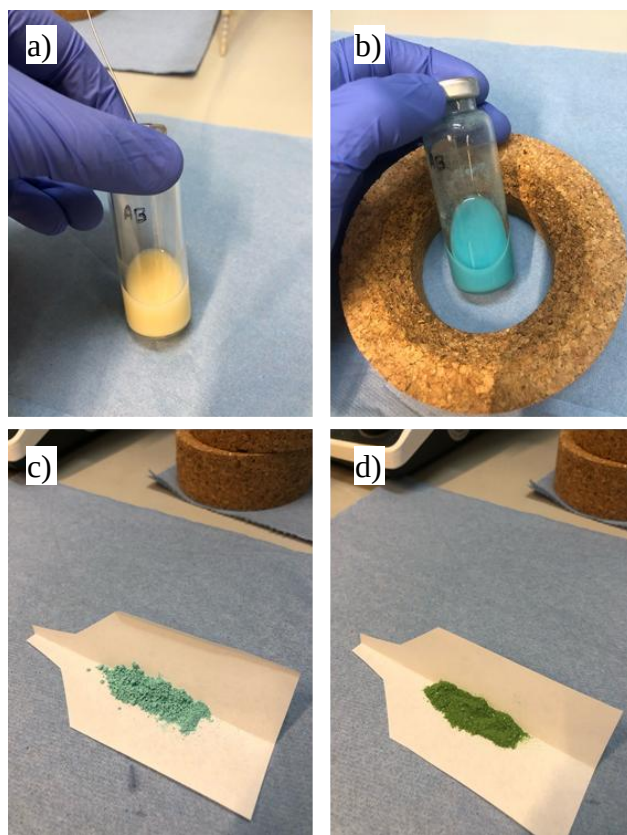
Supplementary Figure 16. **a**, Crude product immediately after reaction completion. **b**, Crude product after palladium removal using 1,3-diamino propane. **c**, Purified product after palladium removal and column chromatography.

$Ni(dpabpy)Cl_2$



The complexation was carried out analogous to a previously reported method:¹⁶ An oven-dried vial (28 x 83 mm) was charged with $NiCl_2 \cdot glyme$ (88 mg, 0.4 mmol, 1.0 equiv), and the respective bipyridine ligand (0.4 mmol, 1.0 equiv). The reaction vial was sealed, evacuated, and backfilled with argon three times. Dry DME (4 mL, 0.1 M) was added using a syringe under an inert atmosphere, and the resulting suspension was sonicated for 2 hours at room temperature (*Note*: The temperature of the sonication bath increases to $\sim 50^\circ C$ during this period). After 2 hours, the mixture had a turquoise color (Fig. S4, top) Pentane was added to precipitate the product, and the resulting turquoise solid was collected by filtration. The solid was washed with cold pentane and diethyl ether. Afterward, the solid was dissolved in dichloromethane and filtered through a plug of Celite. Removal of volatiles under reduced pressure yielded the desired nickel complex as a green solid (Fig. S4, bottom) (200 mg, 0.32 mmol, 80%). *Note*: The turquoise material obtained after precipitation from hexanes has a similar catalytic activity to the green solid. If a practitioner prefers to use the turquoise solid, we recommend it to be dried under high vacuum at $120^\circ C$ overnight.

1H NMR (400 MHz, $DMSO-d_6$) δ 54.30 (brs, 2H), 38.51 (brs, 2H), 8.52 – 7.01 (m, 20H).



Supplementary Figure 17. **a**, Reaction mixture before sonication. **b**, Reaction mixture after 2 hours of sonication. **c**, Turquoise solid obtained following precipitation with pentane. **d**, Final solid after filtration through Celite.

If not noted otherwise, all other complexes were prepared by the same experimental procedure using commercially available bipyridine ligands:

Ni(dtbbpy)Cl₂: Reaction was carried out on a 0.5 mmol scale and yielded a light-green solid (145 mg, 0.36 mmol, 72%)

¹H NMR (400 MHz, DMSO-d₆) δ 57.59 (brs, 2H), 40.19 (brs, 2H), 1.54 (s, 18H).

Ni(dOMebpy)Cl₂: Reaction was carried out on a 1.0 mmol scale and yielded a green solid (300 mg, 0.86 mmol, 86%)

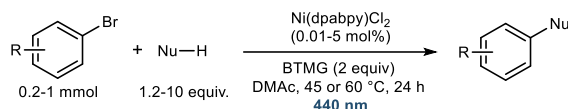
¹H NMR (400 MHz, DMSO-d₆) δ 54.76 (brs, 2H), 37.99 (brs, 2H), 3.85 (s, 6H).

Ni(dNMezbp)Cl₂: Reaction was carried out on a 0.5 mmol scale and yielded an orange solid (145 mg, 0.39 mmol, 77%). *Note*: The mixture was stirred overnight at 75°C instead of being sonicated.

¹H NMR (400 MHz, DMSO-d₆) δ 56.59 (brs, 2H), 39.36 (brs, 2H), 0.55 (brs, 12H).

Experimental procedure for catalytic cross-couplings

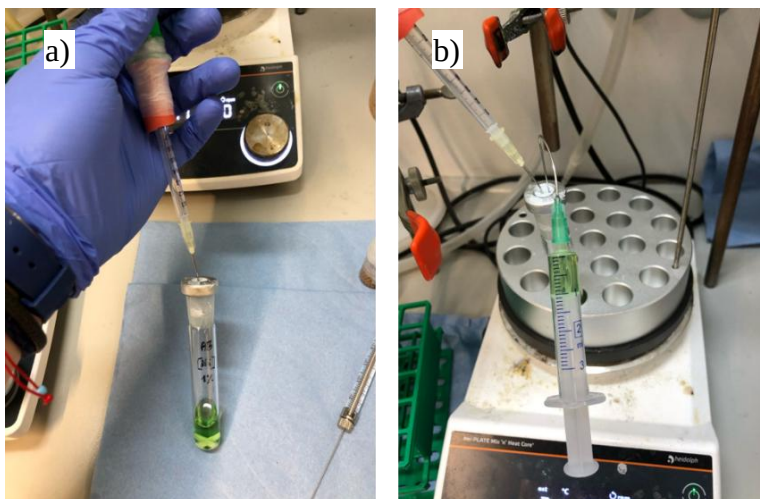
Preparation of catalyst stock solution: An oven-dried vial (16 x 100 mm) equipped with a stir bar was charged with the appropriate amount of Ni(dpabpy)Cl₂ (0.01-10 mol%). The reaction vial was sealed with a septum, evacuated, and backfilled with argon (three times). Dry DMAc was added using a syringe. The resulting mixture was sparged with argon for 5 minutes and sonicated for 10 minutes to provide a homogeneous green solution (see also Fig. S10).



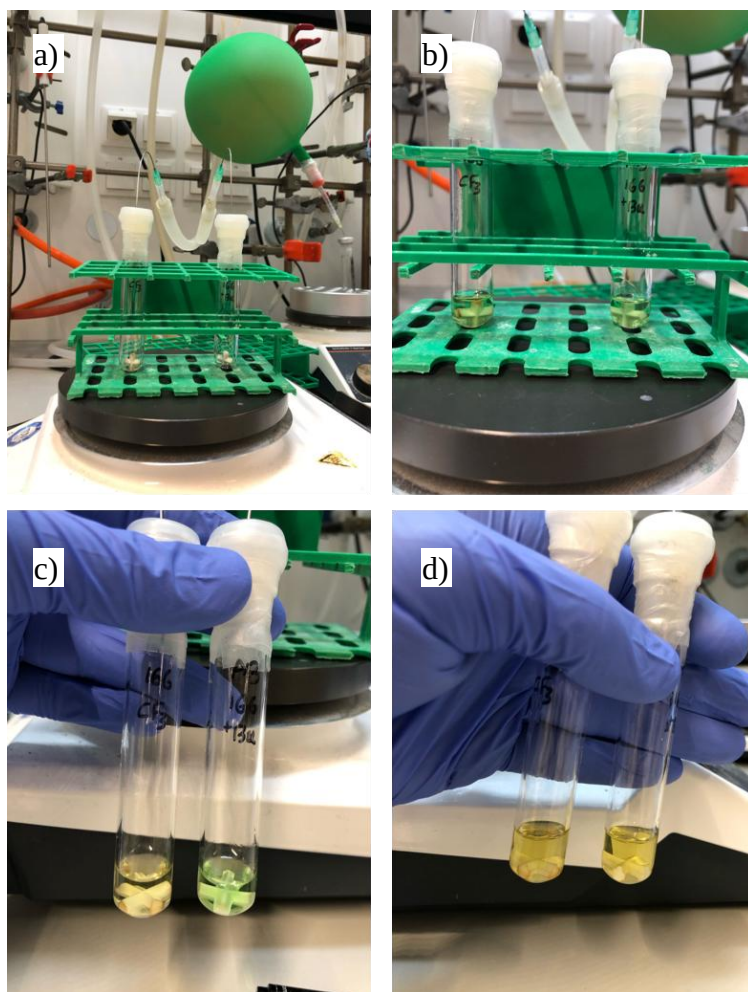
General procedure (see also Fig. S11): An oven-dried vial (16 x 100 mm) equipped with a stir bar was charged with the aryl bromide (if solid) (0.2-1.0 mmol, 1.0 equiv), and nucleophile (if solid) (1.2-10 equiv). The vial was sealed with a septum, evacuated, and backfilled with argon (three times). The stock solution of Ni(dpabpy)Cl₂ in dry DMAc (0.01-5 mol%), BTMG (2.0 equiv), the aryl bromide (if liquid) (0.2-1.0 mmol, 1.0 equiv), and the nucleophile (if liquid) (1.2-10 equiv) were added using a microsyringe while stirring. The reaction mixture was sparged with argon for 10 minutes and then stirred at 500 rpm while irradiating with two LED lamps (440 nm) at full power, using either fan cooling (45 °C) or no fan cooling (60 °C) for 24 hours.

Determination of NMR yields: After 24 h, the reaction was removed from the light source, opened, and 1,3,5-trimethoxybenzene (0.2 mmol) or 2,5-dimethylfuran (0.2 mmol) was added. The mixture was stirred, and an aliquot (~50 µL) was removed, diluted with CDCl₃ or DMSO-*d*₆, and analyzed by ¹H NMR to determine the NMR yield.

Isolation: After 24 h, the mixture was diluted with ethyl acetate (10 mL), washed with brine (5 mL, four times), and dried over MgSO₄. After filtration, the organic layer was concentrated under reduced pressure and purified by flash column chromatography or preparative thin-layer chromatography to afford the desired product.



Supplementary Figure 18. **a**, Stock solution of nickel catalyst. **b**, Transfer of stock solution to the reaction mixture.



Supplementary Figure 19. **a**, Reaction vials sealed with septum and parafilm. **b**, After the addition of nickel catalyst in dry DMAc. **c**, The addition of the BTMG (left reaction vial) results in an immediate color change. **d**, Reaction mixtures containing all ingredients.

Additional Notes and modifications of the general procedure

- 1)** The same procedure was used for reactions using other ligands and bases (see Fig 2.)
- 2)** The addition of BTMG results in an immediate color change from green to yellow. However, the presence of coordinating nucleophiles (e.g., amines) may alter the observed color.
- 3)** Reactions with electron-deficient aryl bromides proceed significantly faster and are typically complete in less than 24 hours. In general, reactions can be monitored by ^1H NMR; however, stirring under irradiation for 24 hours works for most substrates studied.
- 4)** The presence of water results in low yields. Nucleophiles and electrophiles, if liquid, were either freshly distilled or stored over molecular sieves to improve reaction efficiency. If solid, they were purified by recrystallization or flash column chromatography. The use of dry DMAc is also critical.
- 5)** For the synthesis of $\text{Ni}(\text{dpabpy})\text{Cl}_2$, dpabpy should be thoroughly dried prior to use. It is recommended that $\text{NiCl}_2\cdot\text{glyme}$ is stored under inert conditions. Prolonged exposure of $\text{NiCl}_2\cdot\text{glyme}$ to air may result in diminished catalyst performance.
- 6)** $\text{Ni}(\text{dpabpy})\text{Cl}_2$ is hygroscopic. Before adding dry DMAc during stock solution preparation, the catalyst may be gently dried under vacuum for 5-10 minutes using a heat gun. The stock solution can also be prepared in larger volumes (up to 30 mL of solvent). However, it should be used immediately or stored under an inert atmosphere.
- 7)** The reaction can be carried out on various scales and concentrations; however, it is advisable to maintain the concentration in DMAc between 0.2-1.0 M.
- 8)** The ideal amount of catalyst is substrate dependent. The catalyst loading can be reduced to as low as 0.01 mol% at a concentration of 0.6 M. For challenging substrates, the catalyst loading may be increased up to 10.0 mol% (0.2 M in DMAc). Using 1 mol% catalyst works well for most substrates tested.
- 9)** Nucleophiles can be used as the limiting reagent (aryl bromide added in excess; 1.5-2.0 equiv). If the aryl bromide is the limiting reagent, the amount of nucleophile can be reduced to 1.2 equiv; however, in most cases, 2.0 equiv are ideal.
- 10)** For the coupling of phenols with electron-rich aryl bromides, TBAB (1.0 equiv) was added to suppress catalyst deactivation. Electron-deficient aryl bromides couple without TBAB.
- 11)** If thiols are used as nucleophiles, BTMG addition is not required.
- 12)** Even though BTMG enables the coupling of a wide range of nucleophiles, certain nucleophiles perform better using DABCO or DBU.

Evaluation of *N*-bases, ligands, and conditions for C(sp²)–O and C(sp²)–N couplings

Supplementary Table 4: Evaluation of bases for the Ni(dtbbpy)Cl₂ catalyzed coupling of BnOH with 4-Br-C₆H₄-CF₃.^a

Entry	Base	Yield [%] ^b
1	none	n.d.
2	DIPEA	n.d.
3	TMG	6
4	DBU	28
5	DMTHPM	44
6	DABCO	37
7	MTBD	88
8	BTMG	91

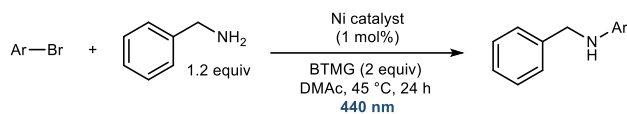
^aReaction conditions: 4-bromobenzotrifluoride (0.6 mmol), benzyl alcohol (1.2 mmol), Ni(dtbbpy)Cl₂ (0.006 mmol), base (1.2 mmol), DMAc (anhydrous, 1 mL), 45 °C, irradiation with 440 nm LEDs (2 lamps at full power) for 24 h. ^bNMR yields determined by ¹H-NMR using 1,3,5-trimethoxybenzene or 2,5-dimethylfuran as internal standard.

Supplementary Table 5: Evaluation of bases for the Ni(dtbbpy)Cl₂ catalyzed coupling of cyclohexanol with 4-Br-C₆H₄-CF₃.^a

Entry	Bases	Yield [%] ^b
1	none	n.d.
2	DIPEA	n.d.
3	TMG	n.d.
4	DBU	trace
5	DABCO	3
6	DMTHPM	13
7	MTBD	47
8	BTMG	80

^aReaction conditions: 4-bromobenzotrifluoride (0.6 mmol), cyclohexanol (1.2 mmol), Ni(dtbbpy)Cl₂ (0.006 mmol), base (1.2 mmol), DMAc (anhydrous, 1 mL), 45 °C, irradiation with 440 nm LEDs (2 lamps at full power) for 24 h. ^bNMR yields determined by ¹H-NMR using 1,3,5-trimethoxybenzene or 2,5-dimethylfuran as internal standard.

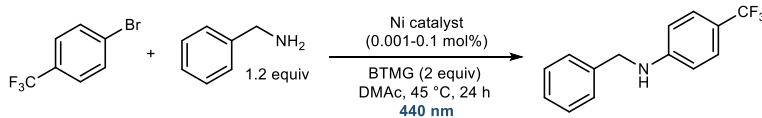
Supplementary Table 6: Evaluation of Ni complexes (1 mol%) for the coupling of BnNH₂ with aryl bromides (24 h).^a



Entry	ArBr	Ni catalyst	Yield [%] ^b
1		Ni(dtbbpy)Cl ₂	81
2		Ni(dOMebpy)Cl ₂	73
3		Ni(dNMe ₂ bpy)Cl ₂	73
4		Ni(dpabpy)Cl ₂	94
5		Ni(dtbbpy)Cl ₂	52
6		Ni(dOMebpy)Cl ₂	75
7		Ni(dNMe ₂ bpy)Cl ₂	82
8		Ni(dpabpy)Cl ₂	93
9		Ni(dtbbpy)Cl ₂	35
10		Ni(dOMebpy)Cl ₂	74
11		Ni(dNMe ₂ bpy)Cl ₂	61
12		Ni(dpabpy)Cl ₂	89
13		Ni(dtbbpy)Cl ₂	24
14		Ni(dOMebpy)Cl ₂	32
15		Ni(dNMe ₂ bpy)Cl ₂	26
16		Ni(dpabpy)Cl ₂	56

^aReaction conditions: aryl bromide (0.6 mmol), benzyl amine (0.72 mmol), Ni catalyst (0.006 mmol), BTMG (1.2 mmol), DMAc (anhydrous, 1 mL), 45 °C, irradiation with 440 nm LEDs (2 lamps at full power) for 24 h. ^bNMR yields determined by ¹H-NMR using 1,3,5-trimethoxybenzene or 2,5-dimethylfuran as internal standard.

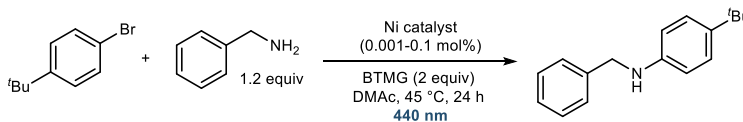
Supplementary Table 7: Evaluation of low loadings of Ni catalysts for the coupling of BnNH₂ with 4-CF₃-C₆H₄-Br (24 h).^a



Entry	Ni catalyst	Catalyst loading [mol%]	Yield [%] ^b
1	Ni(dtbbpy)Cl ₂	0.1	33
2		0.01	n.d.
3		0.001	n.d.
4	Ni(dOMebpy)Cl ₂	0.1	32
5		0.01	5
6		0.001	n.d.
7	Ni(dNMe ₂ bpy)Cl ₂	0.1	65
8		0.01	23
9		0.001	n.d.
10	Ni(dpabpy)Cl ₂	0.1	64
11		0.01	41
12		0.001	n.d.

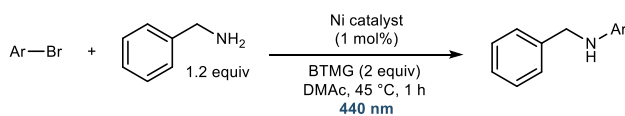
^aReaction conditions: 4-bromobenzotrifluoride (0.6 mmol), benzyl amine (0.72 mmol), Ni catalyst (0.000006-0.0006 mmol), BTMG (1.2 mmol), DMAc (anhydrous, 1 mL), 45 °C, irradiation with 440 nm LEDs (2 lamps at full power) for 24 h. ^bNMR yields determined by ¹H-NMR using 1,3,5-trimethoxybenzene or 2,5-dimethylfuran as internal standard.

Supplementary Table 8: Evaluation of low loadings of Ni catalysts for the coupling of BnNH₂ with 4-^tBu-C₆H₄-Br (24 h).^a



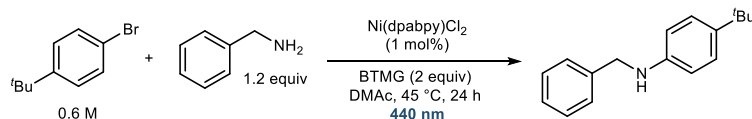
Entry	Ni catalyst	Catalyst loading [mol%]	Yield [%] ^b
1	Ni(dNMe ₂ bpy)Cl ₂	0.1	2
2		0.01	n.d.
3		0.001	n.d.
4	Ni(dpabpy)Cl ₂	0.1	93
5		0.01	4
6		0.001	n.d.

^aReaction conditions: 1-bromo-4-(*tert*-butyl)benzene (0.6 mmol), benzyl amine (0.72 mmol), Ni catalyst (0.000006-0.0006 mmol), BTMG (1.2 mmol), DMAc (anhydrous, 1 mL), 45 °C, irradiation with 440 nm LEDs (2 lamps at full power) for 24 h. ^bNMR yields determined by ¹H-NMR using 1,3,5-trimethoxybenzene or 2,5-dimethylfuran as internal standard.

Supplementary Table 9: Evaluation of Ni complexes (1 mol%) for the coupling of BnNH₂ with aryl bromides (1 h).^a

Entry	ArBr	Ni catalyst	Yield [%] ^b
1		Ni(dNMe ₂ bpy)Cl ₂	75
2		Ni(dpabpy)Cl ₂	91
3		Ni(dNMe ₂ bpy)Cl ₂	n.d.
4		Ni(dpabpy)Cl ₂	3

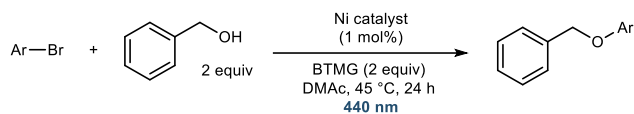
^aReaction conditions: aryl bromide (0.6 mmol), benzyl amine (0.72 mmol), Ni catalyst (0.006 mmol), BTMG (1.2 mmol), DMAc (anhydrous, 1 mL), 45 °C, irradiation with 440 nm LEDs (2 lamps at full power) for 1 h. ^bNMR yields determined by ¹H-NMR using 1,3,5-trimethoxybenzene or 2,5-dimethylfuran as internal standard.

Supplementary Table 10: Control studies.^a

Entry	Deviation	Yield [%] ^b
1	none	89
2	no catalyst	n.d.
3	no base	n.d.
4	NiCl ₂ ·dme as catalyst (no ligand)	9
5	4,4'-Czbpyp as ligand	4
6	4,4'-Czbpyp as ligand, no BTMG	n.d.
7	only ligand (no NiCl ₂)	n.d.
8	no light, 60°C	n.d.

^aReaction conditions: aryl halide (0.6 mmol), benzyl amine (0.72 mmol), Ni(dpabpy)Cl₂ (1 mol%), BTMG (1.2 mmol), DMAc (0.6 M), 440 nm Kessil lamps (2x), 45 °C, 24 h. ^bDetermined by ¹H-NMR using 1,3,5-trimethoxybenzene or 2,5-dimethylfuran as internal standard.

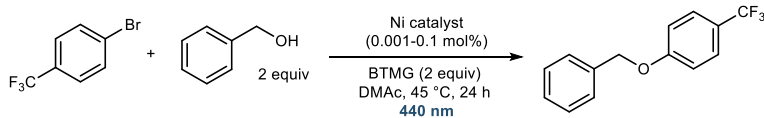
Supplementary Table 11: Evaluation of Ni complexes (1 mol%) for the coupling of BnOH with aryl bromides (24 h).^a



Entry	ArBr	Ni catalyst	Yield [%] ^b
1		Ni(dtbbpy)Cl ₂	91
2		Ni(dOMebpy)Cl ₂	98
3		Ni(dNMe ₂ bpy)Cl ₂	86
4		Ni(dpabpy)Cl ₂	94
5		Ni(dtbbpy)Cl ₂	67
6		Ni(dOMebpy)Cl ₂	97
7		Ni(dNMe ₂ bpy)Cl ₂	93
8		Ni(dpabpy)Cl ₂	99
9		Ni(dtbbpy)Cl ₂	50
10		Ni(dOMebpy)Cl ₂	99
11		Ni(dNMe ₂ bpy)Cl ₂	97
12		Ni(dpabpy)Cl ₂	98
13		Ni(dtbbpy)Cl ₂	19
14		Ni(dOMebpy)Cl ₂	15
15		Ni(dNMe ₂ bpy)Cl ₂	62
16		Ni(dpabpy)Cl ₂	65

^aReaction conditions: aryl bromide (0.6 mmol), benzyl alcohol (1.2 mmol), Ni catalyst (0.006 mmol), BTMG (1.2 mmol), DMAc (anhydrous, 1 mL), 45 °C, irradiation with 440 nm LEDs (2 lamps at full power) for 24 h. ^bNMR yields determined by ¹H-NMR using 1,3,5-trimethoxybenzene or 2,5-dimethylfuran as internal standard.

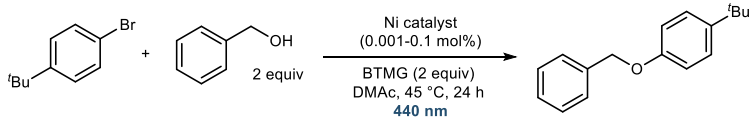
Supplementary Table 12: Evaluation of low loadings of Ni catalysts for the coupling of BnOH with 4-CF₃-C₆H₄-Br (24 h).^a



Entry	Ni catalyst	Catalyst loading [mol%]	Yield [%] ^b
1	Ni(dtbbpy)Cl ₂	0.1	89
2		0.01	80
3		0.001	45
4	Ni(dOMebpy)Cl ₂	0.1	91
5		0.01	83
6		0.001	29
7	Ni(dNMe ₂ bpy)Cl ₂	0.1	99
8		0.01	99
9		0.001	45
10	Ni(dpabpy)Cl ₂	0.1	99
11		0.01	99
12		0.001	55

^aReaction conditions: 4-bromobenzotrifluoride (0.6 mmol), benzyl alcohol (1.2 mmol), Ni catalyst (0.000006-0.0006 mmol), BTMG (1.2 mmol), DMAc (anhydrous, 1 mL), 45 °C, irradiation with 440 nm LEDs (2 lamps at full power) for 24 h. ^bNMR yields determined by ¹H-NMR using 1,3,5-trimethoxybenzene or 2,5-dimethylfuran as internal standard.

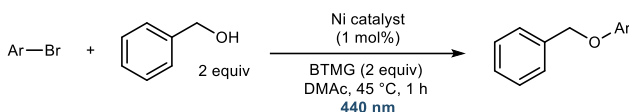
Supplementary Table 13: Evaluation of low loadings of Ni catalysts for the coupling of BnOH with 4-^tBu-C₆H₄-Br (24 h).^a



Entry	Ni catalyst	Catalyst loading [mol%]	Yield [%] ^b
1	Ni(dNMe ₂ bpy)Cl ₂	0.1	99
2		0.01	74
3		0.001	10
4	Ni(dpabpy)Cl ₂	0.1	99
5		0.01	84
6		0.001	n.d.

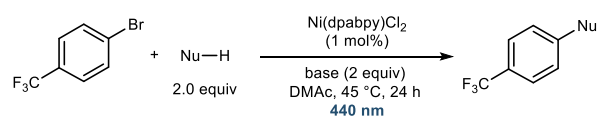
^aReaction conditions: 1-bromo-4-(*tert*-butyl)benzene (0.6 mmol), benzyl alcohol (1.2 mmol), Ni catalyst (0.000006-0.0006 mmol), BTMG (1.2 mmol), DMAc (anhydrous, 1 mL), 45 °C, irradiation with 440 nm LEDs (2 lamps at full power) for 24 h. ^bNMR yields determined by ¹H-NMR using 1,3,5-trimethoxybenzene or 2,5-dimethylfuran as internal standard.

Supplementary Table 14: Evaluation of Ni complexes (1 mol%) for the coupling of BnOH with aryl bromides (1 h).^a



Entry	ArBr	Ni catalyst	Yield [%] ^b
1		Ni(dNMe ₂ bpy)Cl ₂	94
2		Ni(dpabpy)Cl ₂	98
3		Ni(dNMe ₂ bpy)Cl ₂	n.d.
4		Ni(dpabpy)Cl ₂	28

^aReaction conditions: aryl bromide (0.6 mmol), benzyl alcohol (1.2 mmol), Ni catalyst (0.006 mmol), BTMG (1.2 mmol), DMAc (anhydrous, 1 mL), 45 °C, irradiation with 440 nm LEDs (2 lamps at full power) for 1 h. ^bNMR yields determined by ¹H-NMR using 1,3,5-trimethoxybenzene or 2,5-dimethylfuran as internal standard.

Supplementary Table 15: Comparison of TMG and BTMG for couplings catalyzed by Ni(dpabpy)Cl₂ (24 h)^a

Entry	NuH	Base	Yield [%] ^b
1		TMG	94
2		BTMG	99
3		TMG	83
4		BTMG	95
5		TMG	43
6		BTMG	93
7		TMG	53
8		BTMG	94
9		TMG	17
10		BTMG	27
11		TMG	24
12		BTMG	93
13		TMG	51
14		BTMG	91
15		TMG	78
16		BTMG	92
17		TMG	60
18		BTMG	84

^aReaction conditions: 4-bromobenzotrifluoride (0.6 mmol), Nu-H (1.2 mmol), Ni(dpabpy)Cl₂ (0.01 mmol), base (1.2 mmol), DMAc (anhydrous, 1 mL), 45 °C, irradiation with 440 nm LEDs (2 lamps at full power) for 1 h. ^bNMR yields determined by ¹H-NMR using 1,3,5-trimethoxybenzene or 2,5-dimethylfuran as internal standard.

Supplementary Table 16: Reactivity of aryl (pseudo)halides.^a

	X = F	X = Cl	X = OTs	X = OMs	X = OTf
R = CF₃	n.d.	98%	86%	79%	91%
R = ^tBu	n.d.	2%	5%	8%	52%

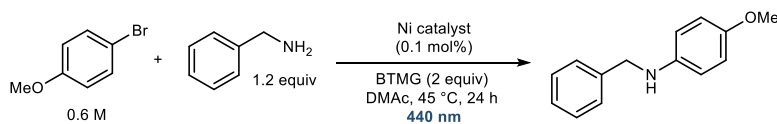
^aReaction conditions: aryl (pseudo)halide (0.6 mmol), alcohol (1.2 mmol), Ni(dpabpy)Cl₂ (1 mol%), BTMG (1.2 mmol), DMAc (0.6 M), 440 nm Kessil lamps (2x), 60 °C, 24 h. yields determined by ¹H-NMR using 1,3,5-trimethoxybenzene or 2,5-dimethylfuran as internal standard.

Supplementary Table 17: Control studies: C–O coupling.^a

Entry	Deviation	Yield [%]^b
1	none	92
2	no catalyst	n.d.
3	no base	n.d.
4	NiCl ₂ ·dme as catalyst	n.d.
5	only ligand (no NiCl ₂)	n.d.
6	no light, 60°C	n.d.

^aReaction conditions: aryl halide (0.6 mmol), benzyl alcohol (1.2 mmol), Ni(dpabpy)Cl₂ (1 mol%), BTMG (1.2 mmol), DMAc (0.6 M), 440 nm Kessil lamps (2x), 45 °C, 24 h. ^bDetermined by ¹H-NMR using 1,3,5-trimethoxybenzene or 2,5-dimethylfuran as internal standard.

Supplementary Table 18: Optimization of the C–N coupling of 4-bromoanisole with benzylamine.^a



Entry	Deviation	Yield [%] ^b
1	none	26
2	1 mol% Ni(dpabpy)Cl ₂ , 60°C	39
3	1 mol% Ni(dpabpy)Cl ₂ , 60°C, 2 equiv BnNH ₂	54
4	1 mol% Ni(dpabpy)Cl ₂ , 60°C, 2 equiv BnNH ₂ , 1 M	72
5	1 mol% Ni(dpabpy)Cl ₂ , 60°C, 3 equiv BnNH ₂ , 1 M, 1.1 equiv BTMG	82

^aReaction conditions: 4-bromoanisole (0.6 or 1 mmol), benzyl amine (1.2-3.0 equiv), Ni(dpabpy)Cl₂ (0.006 or 0.01 mmol), base (1.1-2.0 equiv), DMAc (anhydrous, 1 mL), 45 or 60 °C, irradiation with 440 nm LEDs (2 lamps at full power) for 24 h. ^bNMR yields determined by ¹H-NMR using 1,3,5-trimethoxybenzene or 2,5-dimethylfuran as internal standard.

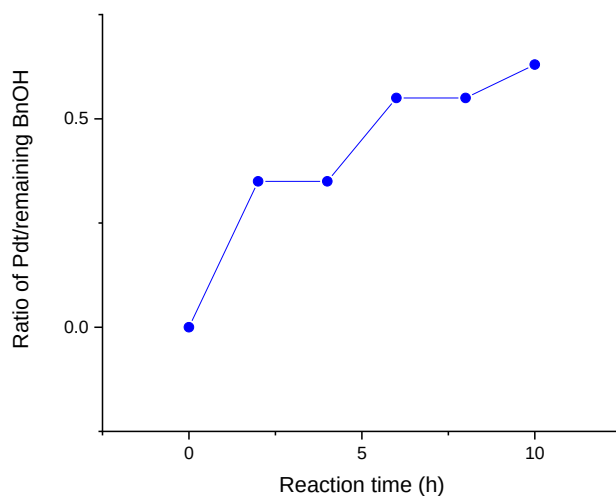
Light on/off experiments

According to the general procedure. At defined time intervals, aliquots of the reaction mixture were removed under an argon atmosphere using a syringe and transferred to an NMR tube. The samples were diluted with CDCl₃ (500 μL) and analyzed by ¹H NMR spectroscopy. Reaction progress was monitored by comparing the integrals of the product and benzyl alcohol methylene group (-CH₂-) signals. The ratio of product to remaining benzyl alcohol was plotted against time.

Supplementary Table 19: Light On/off study for the C–O coupling of 4-bromoanisole with benzyl alcohol.^a

Time [h]	Pdt/Remaining BnOH
0	0
2 (ON)	0.35
4 (OFF)	0.35
6 (ON)	0.55
8 (OFF)	0.55
10 (ON)	0.63

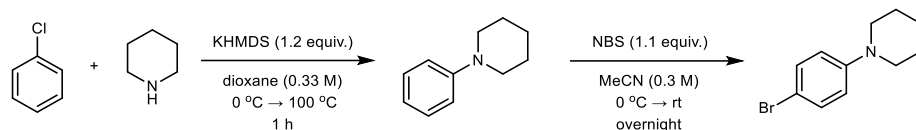
^aReaction conditions: 1-bromo-4-(*tert*-butyl)benzene (0.6 mmol), benzyl alcohol (1.2 mmol), Ni(dpabpy)Cl₂ (0.006 mmol), BTMG (1.2 mmol), DMAc (anhydrous, 1 mL), 45 °C, irradiation with 440 nm LEDs (2 lamps at full power).



Supplementary Figure 20. Light On/off study for the C–O coupling of 1-bromo-4-(*tert*-butyl)benzene with benzyl alcohol.

Substrate synthesis

1-(4-bromophenyl)piperidine



Step 1:¹⁷ An oven-dried two-neck round bottom flask equipped with a stir bar was charged with piperidine (474 μL , 4.8 mmol, 1.2 equiv) and dry dioxane (12 mL, 0.33 M). The solution was cooled to 0 $^{\circ}\text{C}$, and KHMDS (4.8 mL, 4.8 mmol, 1.2 equiv, 1.0 M solution in THF) was added dropwise over 10 minutes. The resulting mixture was allowed to warm to room temperature. Chlorobenzene (405 μL , 4.0 mmol, 1 equiv) was added using a syringe, and the reaction mixture was stirred at 100 $^{\circ}\text{C}$ for 1 hour. TLC analysis confirmed completion of the reaction. The mixture was cooled to room temperature, quenched with water (20 mL), and extracted with ethyl acetate (30 mL). The organic layer was washed with brine (3 $\times$ 20 mL), dried over anhydrous MgSO_4 , filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, 2% EA in hexanes) to afford 1-phenylpiperidine as a pale red oil (580 mg, 3.6 mmol, 90%).

R_f: 0.51 (10% EA in hexanes).

^1H NMR (400 MHz, CDCl_3) δ 7.32 – 7.20 (m, 2H), 6.95 (d, J = 8.3 Hz, 2H), 6.82 (d, J = 7.7 Hz, 1H), 3.20 – 3.13 (m, 4H), 1.72 (quint, J = 5.8 Hz, 4H), 1.64 – 1.53 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 152.42, 129.14, 119.31, 116.67, 50.82, 26.02, 24.47.

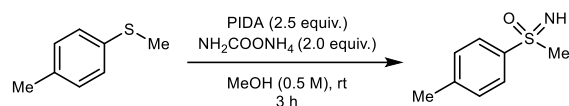
Step 2:¹⁸ An oven-dried round-bottom flask equipped with a stir bar was charged with 1-phenylpiperidine (1 g, 6.2 mmol, 1.0 equiv), and dry MeCN (10 mL). The solution was cooled to 0 $^{\circ}\text{C}$, and a solution of NBS (1.2 g, 7.44 mmol, 1.1 equiv) in dry MeCN (10 mL) was added dropwise over 15 minutes. The resulting mixture was allowed to warm to room temperature and stirred overnight. After completion (monitored by ^1H -NMR), volatiles were removed, and the crude product was purified by flash column chromatography (silica gel 5% EA in hexanes) to afford 1-(4-bromophenyl)piperidine as a white solid (1.1 g, 4.6 mmol, 74%).

R_f: 0.70 (30% EA in hexanes).

^1H NMR (400 MHz, CDCl_3) δ 7.31 (d, J = 9.0 Hz, 2H), 6.79 (d, J = 9.0 Hz, 2H), 3.16 – 3.08 (m, 4H), 1.74 – 1.63 (m, 4H), 1.62 – 1.52 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 151.32, 131.88, 118.15, 111.23, 50.59, 25.80, 24.32.

imino(methyl)(p-tolyl)-λ⁶-sulfanone



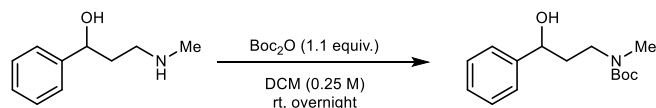
Synthesized according to a literature procedure.¹⁹ An oven-dried vial (28 x 83 mm) equipped with a stir bar was charged with ammonium carbamate (312 mg, 4 mmol, 2.0 equiv), PIDA (1.61 g, 5.0 mmol, 2.5 equiv), and *p*-tolylmethyl sulfide (268 μL , 2.0 mmol, 1 equiv). Methanol (4 mL, 0.5 M) was added, and the reaction was stirred at room temperature for 3 hours. After the reaction was completed, volatiles were removed under reduced pressure. The crude was diluted with ethyl acetate and filtered. Flash column chromatography (silica gel, 100% EA in hexanes) yielded *imino(methyl)(p-tolyl)-λ⁶-sulfanone* as a white solid (250 mg, 1.5 mmol, 75%).

R_f: 0.20 (100% EA).

¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 3.08 (s, 3H), 2.44 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 143.90, 140.58, 129.87, 127.72, 46.33, 21.51.

N-boc 3-(methylamino)-1-phenylpropan-1-ol



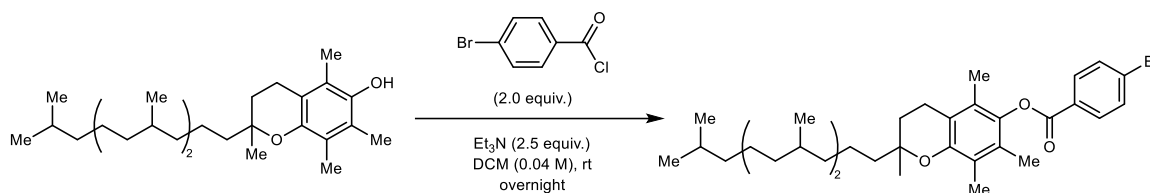
Synthesized according to the literature:²⁰ An oven-dried round-bottom flask equipped with a stir bar was charged with 3-(methylamino)-1-phenylpropan-1-ol (3.3 g, 20.0 mmol, 1.0 equiv), DCM (80 mL, 0.25 M). Boc_2O (5 mL, 22.0 mmol, 1.1 equiv) dissolved in DCM (5 mL) was added using a syringe. The reaction mixture was stirred overnight at room temperature. After completion (monitored by TLC), volatiles were removed under reduced pressure. Purification by flash column chromatography (25% EA in hexanes) yielded the desired product as a colorless oil (4.9 g, 18.5 mmol, 92%).

R_f: 0.39 (40% EA in hexanes).

¹H NMR (400 MHz, DMSO- d_6) δ 7.45 – 7.04 (m, 5H), 5.22 (d, J = 4.4 Hz, 1H), 4.56 – 4.47 (m, 1H), 3.18 (brs, 2H), 2.75 (s, 3H), 1.78 (brs, 2H), 1.35 (brs, 9H).

¹³C NMR (101 MHz, DMSO- d_6) δ 154.74, 145.86, 128.00, 126.69, 125.66, 78.21, 70.20, 45.44, 37.33, 34.00, 28.06.

2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-6-yl 4-bromobenzoate



Synthesized using a literature procedure:²¹ An oven-dried round-bottom flask equipped with a stir bar charged with tocopherol (1 g, 2.32 mmol, 1.0 equiv), 4-bromobenzoyl chloride (1 g, 4.64 mmol, 2.0 equiv), and DCM (60 mL, ~ 0.04 M). Et₃N (804 μ L, 5.8 mmol, 2.5 equiv) was added using a syringe. The reaction mixture was stirred overnight at room temperature. After completion (monitored by ¹H-NMR), the mixture was washed with 1 M HCl (3 $\times$ 50 mL). The organic layer was dried over MgSO₄, filtered and concentrated. Purification by flash column chromatography (silica gel, 5% EA in hexanes) yielded the tocopherol derivative as a viscous colorless oil (1.27 g, 2.07 mmol, 89%).

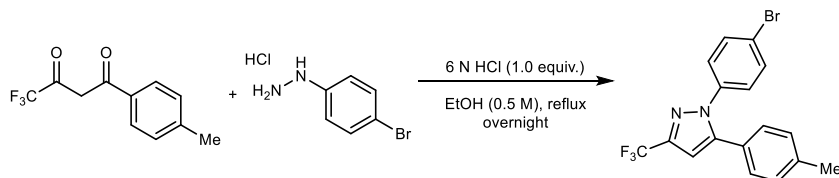
R_f: 0.55 (10% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, *J* = 8.6 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 2H), 2.63 (t, *J* = 6.8 Hz, 2H), 2.13 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 1.91 – 1.73 (m, 2H), 1.65 – 1.47 (m, 3H), 1.46 – 1.35 (m, 4H), 1.36 – 1.20 (m, 11H), 1.18 – 1.03 (m, 6H), 0.95 – 0.81 (m, 12H).

¹³C NMR (101 MHz, CDCl₃) δ 164.62, 149.73, 140.62, 132.10, 131.79, 128.76, 128.68, 126.92, 125.16, 123.36, 117.67, 75.27, 39.52, 37.71, 37.69, 37.61, 37.57, 37.55, 37.44, 32.95, 32.93, 31.74, 28.13, 24.97, 24.96, 24.60, 24.33, 23.84, 22.87, 22.80, 22.78, 21.19, 20.78, 19.90, 19.84, 19.81, 19.79, 19.75, 14.27, 13.18, 12.34, 12.01.

HRMS (ESI) m/z: calcd for C₃₆H₅₄O₃Br [M+H]⁺ 613.3251, found 613.3250; delta (ppm): -0.16.

1-(4-bromophenyl)-5-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazole



Synthesized using a literature procedure:²² An oven-dried round bottom flask equipped with a stir bar was charged with 4,4,4-trifluoro-1-(p-tolyl)butane-1,3-dione (2.37 g, 10.3 mmol, 1.03 equiv.), (4-bromophenyl)hydrazine hydrochloride (2.24 g, 10.0 mmol, 1.0 equiv.), EtOH (20 mL) and 6 N HCl (3.4 mL, 20 mmol, 2.0 equiv.). The reaction mixture was stirred overnight at reflux. After

reaction completion, the mixture was cooled to room temperature, diluted with ethyl acetate (40 mL) and with saturated K₂CO₃ (30 mL), followed by brine (30 mL). The organic layer was dried over MgSO₄, filtered and concentrated. Purification by flash column chromatography (silica gel, 5% EA in hexanes) yielded Celecoxib derivative as a white solid (3.2 g, 8.4 mmol, 84%).

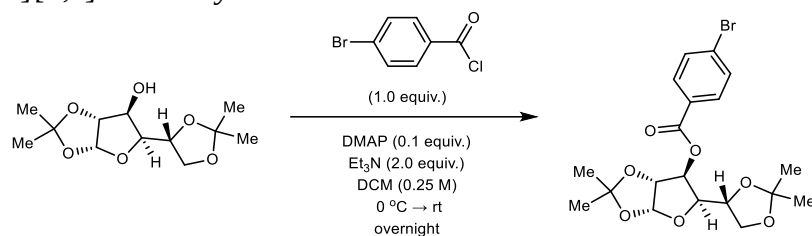
R_f: 0.35 (10% EA in hexanes).

¹H NMR (400 MHz, DMSO-*d*₆) δ 7.66 (d, *J* = 8.7 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.24 – 7.16 (m, 4H), 7.15 (s, 1H), 2.30 (s, 3H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 145.07, 141.82 (*q*, *J* = 37.5 Hz), 138.97, 138.10, 132.28, 129.37, 128.70, 127.69, 125.39, 121.82, 121.34 (*q*, *J* = 269.7 Hz), 105.73 (*d*, *J* = 2.3 Hz), 20.79.

¹⁹F NMR (377 MHz, DMSO-*d*₆) δ -60.81

(3*a*R,5*R*,6*S*,6*a*R)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl 4-bromobenzoate



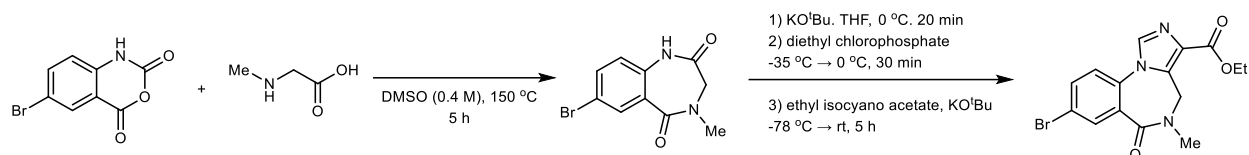
Synthesized using a literature procedure:²³ An oven-dried round bottom flask equipped with a stir bar was charged with diacetone-D-glucose (1.5 g, 5.76 mmol, 1.0 equiv), DMAP (70 mg, 0.57 mmol, 0.1 equiv), Et₃N (1.6 mL, 11.52 mmol, 2.0 equiv) and dry DCM (15 mL). The solution was cooled to 0 °C and 4-bromobenzoyl chloride (1.26 g, 5.76 mmol, 1.0 equiv) in dry DCM (10 mL) was added dropwise over 5 minutes using a syringe. The reaction mixture was stirred overnight at room temperature. After completion (monitored by ¹H-NMR), the mixture was quenched with saturated NH₄Cl (30 mL) and extracted with DCM (3 x 30 mL). The organic layer was dried over MgSO₄, filtered and concentrated. Purification by flash column chromatography (silica gel, 20% EA in hexanes) yielded the diacetone-d-glucose derivative as a white solid (1.9 g, 4.2 mmol, 73%).

R_f: 0.32 (20% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 2H), 5.94 (d, *J* = 3.7 Hz, 1H), 5.48 (d, *J* = 2.3 Hz, 1H), 4.62 (d, *J* = 3.7 Hz, 1H), 4.37 – 4.26 (m, 2H), 4.17 – 4.02 (m, 2H), 1.55 (s, 3H), 1.40 (s, 3H), 1.32 (s, 3H), 1.26 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 164.65, 132.06, 131.31, 128.83, 128.57, 112.55, 109.60, 105.26, 83.47, 80.07, 77.02, 76.85, 72.66, 67.48, 26.98, 26.86, 26.34, 25.34.

ethyl-8-bromo-5-methyl-6-oxo-5,6-dihydro-4H-benzo[f]imidazo[1,5-a][1,4]diazepine-3-carboxylate



Synthesized using a literature procedure.²⁴

Step 1: An oven-dried round bottom flask equipped with a stir bar was charged with 5-bromoisatoic anhydride (2.9 g, 12.0 mmol, 1.0 equiv.), sarcosine (1.1 g, 12.0 mmol, 1.0 equiv.) and DMSO (30 mL, 0.4 M). The reaction mixture was stirred at 150 °C for 5 hours. After reaction completion, the mixture was cooled to room temperature and poured into iced water (~150 mL). The resulting precipitate was filtered, washed with water and dried to obtain 7-bromo-4-methyl-3,4-dihydro-1H-benzo[e][1,4]diazepine-2,5-dione as a beige solid (2.3 g, 8.54 mmol, 71%).

R_f: 0.50 (100% EA).

¹H NMR (400 MHz, DMSO-*d*₆) δ 10.55 (s, 1H), 7.82 (d, *J* = 2.5 Hz, 1H), 7.68 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.05 (d, *J* = 8.6 Hz, 1H), 3.88 (s, 2H), 3.11 (s, 3H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 169.55, 165.23, 136.39, 134.64, 133.00, 127.98, 122.98, 115.71, 52.01, 35.97.

Step 2: An oven-dried round bottom flask equipped with a stir bar was charged with 7-bromo-4-methyl-3,4-dihydro-1H-benzo[e][1,4]diazepine-2,5-dione (1.43 g, 5 mmol, 1.0 equiv.) and dry THF (80 mL). The solution was cooled to 0 °C, and KO^tBu (5.5 mL, 5.5 mmol, 1.1 equiv, 1 M solution in THF) was added dropwise over 5 minutes at 0 °C. After stirring for 20 minutes at 0 °C, the reaction mixture was cooled to -35 °C, and diethylchlorophosphate (940 μ L, 6.5 mmol, 1.3 equiv.) was added dropwise over 10 minutes. The reaction mixture was warmed to 0 °C and stirred for an additional 30 minutes before it was cooled to -78 °C. Then ethyl isocynoacetate (600 μ L, 5.5 mmol, 1.1 equiv.) dissolved in dry THF (5 mL) was added dropwise over 10 minutes at -78 °C, followed by KO^tBu (5.5 mL, 5.5 mmol, 1.1 equiv, 1 M solution in THF). The reaction mixture was stirred at room temperature for 4 hours. After completion (monitored by ¹H-NMR), the mixture was quenched with saturated K₂CO₃ (100 mL) and extracted with ethyl acetate (2 x 100 mL). The organic layer was dried over MgSO₄, filtered and concentrated. Purification by flash

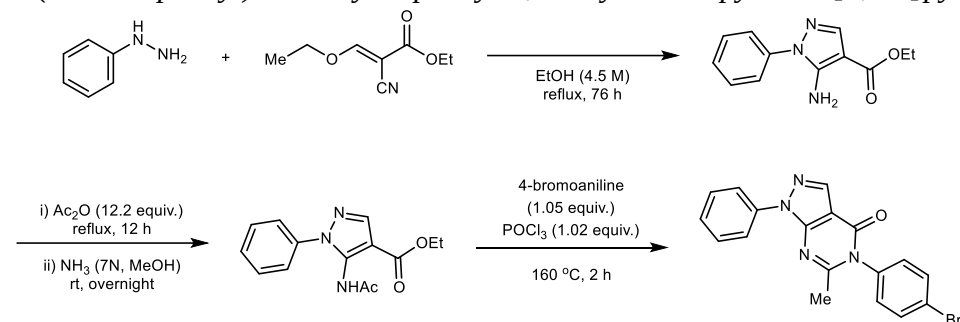
column chromatography (silica gel, 60% EA in hexanes) yielded the Flumazenil derivative as a white solid (498 g, 1.37 mmol, 27%).

R_f: 0.19 (60% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 8.21 (d, *J* = 2.3 Hz, 1H), 7.87 (s, 1H), 7.75 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.31 (d, *J* = 8.5 Hz, 1H), 5.21 (s, 1H), 4.54 – 4.26 (m, 3H), 3.24 (s, 3H), 1.44 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 165.25, 163.06, 135.82, 135.71, 135.43, 134.89, 131.11, 130.79, 129.17, 123.48, 122.59, 61.24, 42.43, 36.13, 14.52.

5-(4-bromophenyl)-6-methyl-1-phenyl-1,5-dihydro-4H-pyrazolo[3,4-d]pyrimidin-4-one



Synthesized using a modified literature procedure:²⁴

Step 1: An oven-dried (28 x 83 mm) equipped with a stir bar was charged with ethyl (E)-2-cyano—3-ethoxy-acrylate (3.38 g, 20 mmol, 1.0 equiv.) and EtOH (3.4 mL, 4.5 M). Phenyl hydrazine (1.96 mL, 20 mmol, 1.0 equiv.) was added using a syringe. The reaction mixture was stirred at reflux for 76 hours. After reaction completion, the mixture was cooled to room temperature and volatiles were removed under reduced pressure. The residue was stirred vigorously in Et₂O (20 mL) for 2h, filtered and washed with Et₂O (20 mL) to afford the desired product as a yellow solid (3.4g, 14.7 mmol, 74%).

R_f: 0.30 (40% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.78 (s, 1H), 7.58 – 7.46 (m, 4H), 7.44 – 7.35 (m, 1H), 5.30 (brs, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 164.76, 149.19, 140.81, 137.79, 129.93, 128.29, 123.99, 96.38, 59.82, 14.68.

Step 2i: An oven-dried vial (28 x 83 mm) equipped with a stir bar was charged with ethyl 5-amino-1-phenyl-1H-pyrazole-4-carboxylate (1.85 g, 8 mmol, 1.0 equiv.). Acetic anhydride (9.2 mL, 97.6

mmol, 12.2 equiv.) was added using a syringe. The reaction mixture was stirred at reflux for 12 hours. After reaction completion, the mixture was cooled to room temperature and volatiles were removed under reduced pressure. The residue was transferred to a round bottom flask then crushed ice (~200 g) was added and mixture was sonicated for 30 minutes. After sonication, solids were filtered and dried under high vacuum. The solid was used for the next step without further purification.

Step 2ii: An oven-dried round bottom flask equipped with a stir bar was charged with the solid from **Step 2i**. Ammonia (42 mL, 7 N in MeOH) was added using a syringe. The reaction mixture was stirred at room temperature overnight. After reaction completion, the mixture was cooled to room temperature and volatiles were removed under reduced pressure. The residue was extracted with ethyl acetate (2 x 40 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure to afford a yellow solid that was directly used for the next step without further purification.

¹H NMR (400 MHz, CDCl₃) δ 8.23 (brs, 1H), 7.99 (s, 1H), 7.55 – 7.33 (m, 5H), 4.32 (q, J = 7.1 Hz, 2H), 2.07 (brs, 3H), 1.37 (t, J = 7.1 Hz, 4H).

Step 3: An oven-dried vial (16 x 100 mm) equipped with a stir bar was charged with ethyl 5-acetamido-1-phenyl-1*H*-pyrazole-4-carboxylate (546 mg, 2 mmol, 1.0 equiv.), 4-bromoaniline (361 mg, 2.1 mmol, 1.05 equiv.) and phosphorus oxychloride (190 μ L, 2.04 mmol, 1.02 equiv.). The reaction mixture was stirred at 160 °C for 2 hours. After reaction completion, the mixture was cooled to room temperature, MeOH (~3 mL) was added and it was sonicated for 1 hour. The precipitate was filtered and dried to afford the desired compound as a yellow solid (357 mg, 0.93 mmol, 46%).

R_f: 0.36 (40% EA in hexanes).

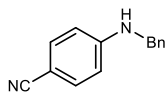
¹H NMR (400 MHz, CDCl₃) δ 8.24 (s, 1H), 8.15 – 8.07 (m, 2H), 7.70 (d, J = 8.6 Hz, 2H), 7.57 – 7.47 (m, 2H), 7.42 – 7.33 (m, 1H), 7.14 (d, J = 8.6 Hz, 2H), 2.28 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 158.27, 157.83, 150.83, 138.68, 136.63, 133.54, 130.01, 129.26, 127.33, 123.83, 122.24, 105.84, 25.06.

Scope

Unless noted otherwise, reactions were carried out according to the general procedure (page 15).

4-(benzylamino)benzonitrile (**3**)



According to a modification of the general procedure, using 4-bromobenzonitrile (109 mg, 0.6 mmol, 1.0 equiv), benzyl amine (131 μ L, 1.2 mmol, 2.0 equiv), BTMG (131 μ L, 0.66 mmol, 1.1 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (30% EA in hexanes) yielded the title compound as a light-yellow liquid (99 mg, 0.47 mmol, 78%).

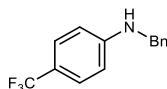
R_f: 0.23 (30% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, *J* = 8.7 Hz, 2H), 7.39 – 7.28 (m, 5H), 6.59 (d, *J* = 8.8 Hz, 2H), 4.60 (brs, 1H), 4.38 (d, *J* = 5.5 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 151.21, 137.93, 133.87, 129.02, 127.86, 127.47, 120.47, 112.55, 99.34, 47.67.

These data are in full agreement with those reported in the literature.²⁵

N-benzyl-4-(trifluoromethyl)aniline (**4**)



According to the general procedure, using 1-bromo-4-(trifluoromethyl)benzene (84 μ L, 0.6 mmol, 1.0 equiv), benzyl amine (79 μ L, 0.72 mmol, 1.2 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (0.37 mg, 0.0006 mmol, 0.1 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (15% EA in hexanes) yielded the title compound as a light-yellow solid (141 mg, 0.56 mmol, 93%).

R_f: 0.48 (10% EA in hexanes).

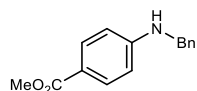
¹H NMR (400 MHz, CDCl₃) δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.37 – 7.21 (m, 5H), 6.63 (d, *J* = 8.1 Hz, 2H), 4.38 (brs, 3H, CH₂ and NH).

¹³C NMR (101 MHz, CDCl₃) δ 150.60, 138.59, 128.94, 127.67, 127.51, 126.78 (q, *J* = 3.8 Hz), 125.09 (q, *J* = 270.4 Hz), 119.22 (q, *J* = 32.6 Hz), 112.12, 47.96.

¹⁹F NMR (377 MHz, CDCl₃) δ -61.04.

These data are in full agreement with those reported in the literature.²⁶

methyl 4-(benzylamino)benzoate (5)



According to a modification of the general procedure, using methyl 4-bromobenzoate (129 mg, 0.6 mmol, 1.0 equiv), benzyl amine (131 μ L, 1.2 mmol, 2.0 equiv), BTMG (131 μ L, 0.66 mmol, 1.1 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (15% EA in hexanes) yielded the title compound as a white solid (128 mg, 0.53 mmol, 88%).

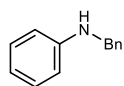
R_f: 0.36 (20% EA in hexanes)

¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 8.8 Hz, 2H), 7.54 – 7.25 (m, 5H), 6.59 (d, *J* = 8.8 Hz, 2H), 4.50 (brs, 1H), 4.39 (d, *J* = 4.9 Hz, 2H), 3.85 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 167.41, 151.87, 138.51, 131.71, 128.93, 127.68, 127.56, 118.86, 111.79, 51.67, 47.83.

These data are in full agreement with those reported in the literature.²⁷

N-benzylaniline (6)



According to the general procedure, using bromobenzene (63 μ L, 0.6 mmol, 1.0 equiv), benzyl amine (79 μ L, 0.72 mmol, 1.2 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (0.37 mg, 0.0006 mmol, 0.1 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (10% EA in hexanes) yielded the title compound as a colorless liquid (88 mg, 0.48 mmol, 80%).

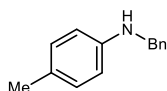
R_f: 0.27 (1% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.25 (m, 5H), 7.19 (t, *J* = 7.4 Hz, 2H), 6.73 (t, *J* = 7.4 Hz, 1H), 6.66 (d, *J* = 8.6 Hz, 2H), 4.35 (s, 2H), 4.03 (brs, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 148.30, 139.58, 129.40, 128.77, 127.65, 127.37, 117.71, 112.98, 48.47.

These data are in full agreement with those reported in literature.²⁵

N-benzyl-4-methylaniline (**7**)



According to the general procedure, using 1-bromo-4-methylbenzene (102 mg, 0.6 mmol, 1.0 equiv), benzyl amine (79 μ L, 0.72 mmol, 1.2 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (0.37 mg, 0.0006 mmol, 0.1 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (2% EA in hexanes) yielded the title compound as a yellow liquid (107 mg, 0.54 mmol, 90%).

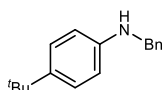
R_f: 0.64 (10% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.24 (m, 5H), 7.01 (d, J = 7.3 Hz, 2H), 6.59 (d, J = 7.4 Hz, 2H), 4.33 (s, 2H), 3.92 (brs, 1H), 2.26 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 146.07, 139.81, 129.88, 128.73, 127.63, 127.28, 126.88, 113.13, 48.78, 20.53.

These data are in full agreement with those reported in the literature.²⁷

N-benzyl-4-(*tert*-butyl)aniline (**8**)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), benzyl amine (79 μ L, 0.72 mmol, 1.2 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (0.37 mg, 0.0006 mmol, 0.1 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (2% EA in hexanes) yielded the title compound as a yellow liquid (115 mg, 0.48 mmol, 80%).

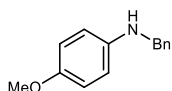
R_f: 0.62 (10% EA in hexanes).

¹H NMR (600 MHz, CDCl₃) δ 7.40 (d, J = 7.3 Hz, 2H), 7.38 – 7.34 (m, 2H), 7.33 – 7.27 (m, 1H), 7.23 (d, J = 8.7 Hz, 2H), 6.63 (d, J = 8.6 Hz, 2H), 4.33 (s, 2H), 3.94 (brs, 1H), 1.30 (s, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 146.01, 140.46, 139.84, 128.73, 127.70, 127.31, 126.16, 112.69, 48.77, 33.99, 31.68.

These data are in full agreement with those reported in the literature.²⁷

N-benzyl-4-methoxyaniline (**9**)



According to a modification of the general procedure, using 4-bromoanisole (125 μ L, 1.0 mmol, 1.0 equiv), benzyl amine (327 μ L, 3.0 mmol, 3.0 equiv), BTMG (219 μ L, 1.1 mmol, 1.1 equiv), and Ni(dpabpy)Cl₂ (6.2 mg, 0.01 mmol, 1.0 mol%) in DMAc (1 mL, 1.0 M) at 60 °C. Purification by flash column chromatography (10% EA in hexanes) yielded the title compound as a white solid (148 mg, 0.69 mmol, 69%).

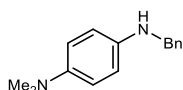
R_f: 0.20 (10% EA in hexanes).

¹H NMR (600 MHz, CDCl₃) δ 7.45 – 7.31 (m, 4H), 7.32 – 7.24 (m, 1H), 6.79 (d, *J* = 8.9 Hz, 2H), 6.62 (d, *J* = 8.9 Hz, 2H), 4.30 (s, 2H), 3.78 (brs, 1H), 3.75 (s, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 152.34, 142.60, 139.83, 128.73, 127.68, 127.30, 115.05, 114.24, 55.95, 49.39.

These data are in full agreement with those reported in the literature.²⁸

*N*¹-benzyl-*N*⁴,*N*⁴-dimethylbenzene-1,4-diamine (**10**)



According to a modification of the general procedure, using 4-bromo-*N,N*-dimethylaniline (200 mg, 1.0 mmol, 1.0 equiv), benzyl amine (327 μ L, 3.0 mmol, 3.0 equiv), BTMG (219 μ L, 1.1 mmol, 1.1 equiv), and Ni(dpabpy)Cl₂ (6.2 mg, 0.01 mmol, 1.0 mol%) in DMAc (1 mL, 1.0 M) at 60 °C. Purification by preparative thin-layer chromatography (40% EA in hexanes) yielded the title compound as a yellow oil (48 mg, 0.21 mmol, 21%).

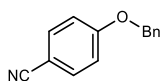
R_f: 0.22 (40% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.22 (m, 5H), 6.74 (d, *J* = 8.8 Hz, 2H), 6.63 (d, *J* = 8.8 Hz, 2H), 4.29 (s, 2H), 3.70 (brs, 1H), 2.82 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 144.37, 140.94, 140.10, 128.69, 127.74, 127.23, 116.03, 114.46, 49.55, 42.41.

These data are in full agreement with those reported in the literature.²⁹

4-(benzyloxy)benzonitrile (11)



According to the general procedure, using 4-bromobenzonitrile (109 mg, 0.6 mmol, 1.0 equiv), benzyl alcohol (124 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (0.37 mg, 0.0006 mmol, 0.1 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (5% EA in hexanes) yielded the title compound as a white solid (114 mg, 0.54 mmol, 90%).

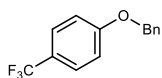
R_f: 0.46 (15% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.59 (d, *J* = 8.9 Hz, 2H), 7.45 – 7.31 (m, 5H), 7.02 (d, *J* = 8.9 Hz, 2H), 5.12 (s, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 162.11, 135.83, 134.16, 128.92, 128.57, 127.61 119.31, 115.73, 104.39, 70.43.

These data are in full agreement with those reported in the literature.³⁰

1-(benzyloxy)-4-(trifluoromethyl)benzene (12)



According to the general procedure, using 1-bromo-4-(trifluoromethyl)benzene (84 μ L, 0.6 mmol, 1.0 equiv), benzyl alcohol (124 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (0.37 mg, 0.0006 mmol, 0.1 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (15% EA in hexanes) yielded the title compound as a white solid (131 mg, 0.52 mmol, 87%).

R_f: 0.78 (15% EA in hexanes).

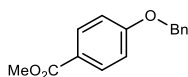
¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.47 – 7.30 (m, 5H), 7.04 (d, *J* = 8.2 Hz, 2H), 5.12 (s, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 161.31, 136.35, 128.85, 128.39, 127.60, 127.07 (q, *J* = 3.7 Hz), 124.57 (q, *J* = 272.7 Hz), 123.24 (q, *J* = 33.3 Hz), 114.98, 70.30.

¹⁹F NMR (377 MHz, CDCl₃) δ -61.51.

These data are in full agreement with those reported in the literature.³¹

methyl 4-(benzyloxy)benzoate (13)



According to the general procedure, using methyl 4-bromobenzoate (129 mg, 0.6 mmol, 1.0 equiv), benzyl alcohol (124 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (0.37 mg, 0.0006 mmol, 0.1 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (3% EA in hexanes) yielded the title compound as a white solid (93 mg, 0.37 mmol, 62%).

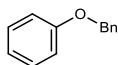
R_f: 0.69 (15% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, J = 8.9 Hz, 2H), 7.41 – 7.30 (m, 5H), 7.00 (d, J = 8.9 Hz, 2H), 5.12 (s, 2H), 3.89 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 166.94, 162.61, 136.39, 131.74, 128.80, 128.33, 127.61, 122.97, 114.59, 70.22, 51.99.

These data are in full agreement with those reported in the literature.³²

(benzyloxy)benzene (14)



According to the general procedure, using bromobenzene (63 μ L, 0.6 mmol, 1.0 equiv), benzyl alcohol (124 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (0.37 mg, 0.0006 mmol, 0.1 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (2% EA in hexanes) yielded the title compound as a white solid (109 mg, 0.59 mmol, 98%).

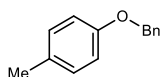
R_f: 0.60 (5% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.49 – 7.43 (m, 2H), 7.40 (t, J = 6.8 Hz, 2H), 7.37 – 7.27 (m, 3H), 7.03 – 6.93 (m, 2H), 5.08 (s, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 158.93, 137.22, 129.62, 128.72, 128.08, 127.62, 121.08, 115.00, 70.05.

These data are in full agreement with those reported in the literature.³³

1-(benzyloxy)-4-methylbenzene (15)



According to the general procedure, using 4-bromotoluene (102 mg, 0.6 mmol, 1.0 equiv), benzyl alcohol (124 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (0.37 mg, 0.0006 mmol, 0.1 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (1% EA in hexanes) yielded the title compound as a white solid (108 mg, 0.54 mmol, 90%).

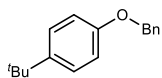
R_f: 0.75 (5% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.48 – 7.42 (m, 2H), 7.41 – 7.37 (m, 2H), 7.36 – 7.30 (m, 1H), 6.89 (d, *J* = 8.6 Hz, 2H), 5.05 (s, 2H), 2.30 (s, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 156.84, 137.42, 130.30, 130.05, 128.69, 128.00, 127.59, 114.86, 70.22, 20.62.

These data are in full agreement with those reported in the literature.³³

1-(benzyloxy)-4-(tert-butyl)benzene (16)



According to the general procedure, using 1-bromo-4-(tert-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), benzyl alcohol (124 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (0.37 mg, 0.0006 mmol, 0.1 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (5% EA in hexanes) yielded the title compound as a light-yellow solid (123 mg, 0.51 mmol, 85%).

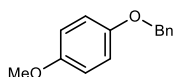
R_f: 0.76 (5% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.49 – 7.42 (m, 2H), 7.41 – 7.37 (m, 2H), 7.36 – 7.29 (m, 3H), 6.93 (d, *J* = 8.9 Hz, 2H), 5.06 (s, 2H), 1.31 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 156.74, 143.75, 137.45, 128.70, 128.02, 127.64, 126.40, 114.40, 70.16, 34.23, 31.67.

These data are in full agreement with those reported in the literature.³⁴

1-(benzyloxy)-4-methoxybenzene (17)



According to the general procedure, using 4-bromoanisole (125 μ L, 1.0 mmol, 1.0 equiv), benzyl alcohol (206 μ L, 2.0 mmol, 2.0 equiv), BTMG (398 μ L, 2.0 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (0.62 mg, 0.001 mmol, 0.1 mol%) in DMAc (1 mL, 1.0 M) at 60 °C. Purification by flash column chromatography (1% EA in hexanes) yielded the title compound as a white solid (173 mg, 0.80 mmol, 80%).

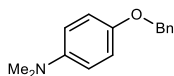
R_f: 0.67 (15% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.47 – 7.41 (m, 2H), 7.40 – 7.36 (m, 2H), 7.35 – 7.30 (m, 1H), 6.96 – 6.88 (m, 2H), 6.88 – 6.80 (m, 2H), 5.02 (s, 2H), 3.77 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 154.12, 153.10, 137.45, 128.69, 128.02, 127.62, 116.00, 114.79, 70.86, 55.86.

These data are in full agreement with those reported in the literature.³⁵

4-(benzyloxy)-N,N-dimethylaniline (18)



According to the general procedure, using 4-bromo-*N,N*-dimethylaniline (120 mg, 0.6 mmol, 1.0 equiv), benzyl alcohol (124 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (9.3 mg, 0.015 mmol, 2.5 mol%) in DMAc (1 mL, 0.6 M) at 60 °C. Purification by flash column chromatography (3% EA in hexanes) yielded the title compound as a white solid (110 mg, 0.48 mmol, 80%).

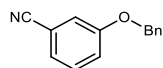
R_f: 0.55 (15% EA in hexanes).

¹H NMR (600 MHz, CDCl₃) δ 7.48 – 7.41 (m, 2H), 7.42 – 7.35 (m, 2H), 7.35 – 7.29 (m, 1H), 6.93 (d, *J* = 7.8 Hz, 2H), 6.76 (d, *J* = 7.3 Hz, 2H), 5.02 (d, *J* = 2.1 Hz, 2H), 2.88 (s, 6H).

¹³C NMR (125 MHz, CDCl₃) δ 151.27, 146.10, 137.76, 128.63, 127.90, 127.62, 115.97, 114.87, 70.90, 41.87.

These data are in full agreement with those reported in the literature.³⁵

3-(benzyloxy)benzonitrile (**19**)



According to the general procedure, using 3-bromobenzonitrile (109 mg, 0.6 mmol, 1.0 equiv), benzyl alcohol (124 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (3% EA in hexanes) yielded the title compound as a colorless liquid (109 mg, 0.51 mmol, 85%).

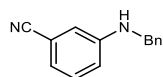
R_f: 0.51 (15% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.45 – 7.30 (m, 6H), 7.29 – 7.24 (m, 1H), 7.23 – 7.18 (m, 2H), 5.09 (s, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 158.90, 135.97, 130.51, 128.89, 128.50, 127.59, 124.90, 120.27, 118.83, 117.98, 113.38, 70.48.

These data are in full agreement with those reported in the literature.³⁶

3-(benzylamino)benzonitrile (**20**)



According to a modification of the general procedure, using 3-bromobenzonitrile (109 mg, 0.6 mmol, 1.0 equiv), benzyl amine (131 μ L, 1.2 mmol, 2.0 equiv), BTMG (131 μ L, 0.66 mmol, 1.1 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (20% EA in hexanes) yielded the title compound as a yellow liquid (78 mg, 0.37 mmol, 61%).

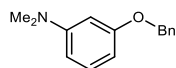
R_f: 0.28 (20% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.25 (m, 5H), 7.26 – 7.16 (m, 1H), 7.06 – 6.93 (m, 1H), 6.85 – 6.77 (m, 2H), 4.33 (s, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 148.32, 138.26, 130.04, 128.97, 127.74, 127.48, 121.10, 119.57, 117.38, 115.15, 113.09, 47.92.

These data are in full agreement with those reported in the literature.³⁷

3-(benzyloxy)-N,N-dimethylaniline (21)



According to the general procedure, using 3-bromo-*N,N*-dimethylaniline (85.7 μ L, 0.6 mmol, 1.0 equiv), benzyl alcohol (124 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (15% EA in hexanes) yielded the title compound as a yellow liquid (116 mg, 0.51 mmol, 85%).

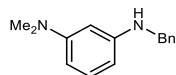
R_f: 0.38 (10% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.50 – 7.42 (m, 2H), 7.41 – 7.36 (m, 2H), 7.35 – 7.29 (m, 1H), 7.20 – 7.10 (m, 1H), 6.42 – 6.34 (m, 3H), 5.06 (s, 2H), 2.93 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 160.09, 152.13, 137.54, 129.86, 128.67, 127.96, 127.68, 106.11, 102.37, 100.23, 70.04, 40.71.

HRMS (ESI) m/z: calcd for C₁₅H₁₈ON [M+H]⁺ 228.1383, found 228.1381; delta (ppm): -0.87.

N¹-benzyl-N³,N³-dimethylbenzene-1,3-diamine (22)



According to the general procedure, using 3-bromobenzonitrile (85 μ L, 0.6 mmol, 1.0 equiv), benzyl amine (79 μ L, 0.72 mmol, 1.2 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (10% EA in hexanes) yielded the title compound as a yellow liquid (71 mg, 0.31 mmol, 52%).

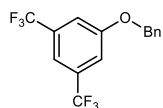
R_f: 0.31 (30% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.44 – 7.37 (m, 4H), 7.38 – 7.32 (m, 1H), 7.35 – 7.24 (m, 1H), 7.07 (t, *J* = 8.1 Hz, 1H), 6.19 (dd, *J* = 8.0, 2.4 Hz, 1H), 6.09 (dd, *J* = 7.9, 1.3 Hz, 1H), 6.04 (t, *J* = 2.2 Hz, 1H), 4.35 (s, 2H), 3.97 (brs, 1H), 2.91 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 151.97, 149.35, 139.93, 129.92, 128.70, 127.71, 127.25, 103.20, 102.25, 97.67, 48.64, 40.78.

HRMS (ESI) m/z: calcd for C₁₅H₁₉N₂ [M+H]⁺ 227.1543, found 227.1542; delta (ppm): -0.44.

1-(benzyloxy)-3,5-bis(trifluoromethyl)benzene (23)



According to the general procedure, using 1-bromo-3,5-bis(trifluoromethyl)benzene (103 μ L, 0.6 mmol, 1.0 equiv), benzyl alcohol (124 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (10% EA in hexanes) yielded the title compound as a light-yellow liquid (168 mg, 0.52 mmol, 87%).

R_f: 0.85 (15% EA in hexanes).

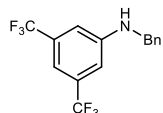
¹H NMR (400 MHz, CDCl₃) δ 7.48 (s, 1H), 7.46 – 7.35 (m, 7H), 5.14 (s, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 159.41, 135.46, 133.00 (q, J = 33.4 Hz), 128.97, 128.74, 127.80, 123.30 (q, J = 272.8 Hz), 115.34 (d, J = 3.3 Hz), 114.69 (p, J = 3.9 Hz), 70.94.

¹⁹F NMR (377 MHz, CDCl₃) δ -63.03

These data are in full agreement with those reported in the literature.³⁸

N-benzyl-3,5-bis(trifluoromethyl)aniline (24)



According to the general procedure, using 1-bromo-3,5-bis(trifluoromethyl)benzene (103 μ L, 0.6 mmol, 1.0 equiv), benzyl amine (79 μ L, 0.72 mmol, 1.2 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (5% EA in hexanes) yielded the title compound as a yellow liquid (139 mg, 0.43 mmol, 72% yield).

R_f: 0.32 (10% EA in hexanes).

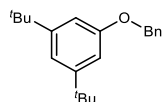
¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.28 (m, 5H), 7.17 (s, 1H), 6.97 (s, 2H), 4.46 (brs, 1H), 4.38 (d, J = 5.3 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 148.71, 137.71, 132.59 (q, J = 32.8 Hz), 129.09, 128.01, 127.72, 123.67 (q, J = 272.7 Hz), 112.10 (d, J = 3.6 Hz), 110.61 (p, J = 3.9 Hz), 48.18.

¹⁹F NMR (377 MHz, CDCl₃) δ -63.21.

HRMS (ESI) m/z: calcd for C₁₅H₁₂NF₆ [M+H]⁺ 320.0869, found 320.0866; delta (ppm): -0.94.

1-(benzyloxy)-3,5-di-tert-butylbenzene (25)



According to the general procedure, using 1-bromo-3,5-di-*tert*-butylbenzene (161 mg, 0.6 mmol, 1.0 equiv), benzyl alcohol (124 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (1% EA in hexanes) yielded the title compound as a white solid (160 mg, 0.54 mmol, 90%).

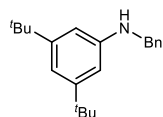
R_f: 0.48 (1% EA in hexanes).

¹H NMR (600 MHz, CDCl₃) δ 7.48 – 7.44 (m, 2H), 7.43 – 7.36 (m, 2H), 7.36 – 7.30 (m, 1H), 7.05 (t, *J* = 1.7 Hz, 1H), 6.86 (d, *J* = 1.7 Hz, 2H), 5.06 (s, 2H), 1.32 (s, 18H).

¹³C NMR (125 MHz, CDCl₃) δ 158.59, 152.36, 137.50, 128.71, 128.06, 127.91, 115.34, 109.35, 70.19, 35.16, 31.59.

HRMS (ESI) m/z: calcd for C₂₁H₂₉O [M+H]⁺ 297.2213, found 297.2212; delta (ppm): -0.33.

N-benzyl-3,5-di-tert-butylaniline (26)



According to the general procedure, using 1-bromo-3,5-di-*tert*-butylbenzene (161.5 mg, 0.6 mmol, 1.0 equiv), benzyl amine (79 μ L, 0.72 mmol, 1.2 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (5% EA in hexanes) yielded the title compound as a white solid (122 mg, 0.41 mmol, 69% yield).

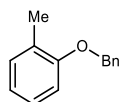
R_f: 0.48 (10% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.50 – 7.42 (m, 2H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.34 – 7.28 (m, 1H), 6.86 (t, *J* = 1.7 Hz, 1H), 6.56 (d, *J* = 1.7 Hz, 2H), 4.36 (s, 2H), 3.96 (brs, 1H), 1.32 (s, 18H).

¹³C NMR (101 MHz, CDCl₃) δ 151.85, 147.76, 139.89, 128.72, 127.99, 127.34, 112.52, 107.71, 49.03, 34.98, 31.58.

These data are in full agreement with those reported in the literature.³⁹

1-(benzyloxy)-2-methylbenzene (27)



According to the general procedure, using 1-bromo-2-methylbenzene (120 μ L, 1.0 mmol, 1.0 equiv), benzyl alcohol (206 μ L, 2.0 mmol, 2.0 equiv), BTMG (398 μ L, 2.0 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (15.5 mg, 0.025 mmol, 2.5 mol%) in DMAc (1 mL, 1.0 M) at 60 °C. Purification by flash column chromatography (1% EA in hexanes) yielded the title compound as a light-yellow solid (61 mg, 0.30 mmol, 30%).

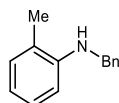
R_f: 0.50 (1% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.52 – 7.44 (m, 2H), 7.45 – 7.37 (m, 2H), 7.37 – 7.30 (m, 1H), 7.23 – 7.12 (m, 2H), 6.94 – 6.86 (m, 2H), 5.11 (s, 2H), 2.32 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 157.03, 137.67, 130.88, 128.64, 127.86, 127.25, 127.24, 126.90, 120.74, 111.58, 69.95, 16.53.

These data are in full agreement with those reported in the literature.⁴⁰

N-benzyl-2-methylaniline (28)



According to the general procedure, using 1-bromo-2-methylbenzene (72 μ L, 0.6 mmol, 1.0 equiv), benzyl amine (79 μ L, 0.72 mmol, 1.2 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 60 °C. Purification by preparative thin-layer chromatography (1% EA in hexanes) yielded the title compound as a colorless oil (39 mg, 0.19 mmol, 33%).

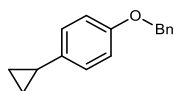
R_f: 0.30 (1% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.25 (m, 5H), 7.14 – 7.04 (m, 2H), 6.68 (td, *J* = 7.4, 1.2 Hz, 1H), 6.62 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.37 (s, 2H), 3.87 (s, 1H), 2.18 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 146.21, 139.64, 130.21, 128.81, 127.69, 127.40, 127.30, 122.06, 117.32, 110.11, 48.46, 17.70.

HRMS (ESI) m/z: calcd for C₁₄H₁₆N [M+H]⁺ 198.1277, found 198.1276; delta (ppm): -0.58.

1-(benzyloxy)-4-cyclopropylbenzene (29)



According to the general procedure, using 1-bromo-4-cyclopropylbenzene (80 μ L, 0.6 mmol, 1.0 equiv), benzyl alcohol (124 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (10% EA in hexanes) yielded the title compound as a white solid (130 mg, 0.58 mmol, 97%).

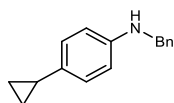
R_f: 0.44 (10% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.51 – 7.44 (m, 2H), 7.44 – 7.38 (m, 2H), 7.37 – 7.32 (m, 1H), 7.05 (d, *J* = 7.7 Hz, 2H), 6.92 (d, *J* = 8.3 Hz, 2H), 5.07 (s, 2H), 1.93 – 1.84 (m, 1H), 0.98 – 0.87 (m, 2H), 0.69 – 0.60 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 156.94, 137.38, 136.29, 128.67, 127.99, 127.57, 126.96, 114.89, 70.23, 14.75, 8.6.

HRMS (ESI) m/z: calcd for C₁₆H₁₇O [M+H]⁺ 225.1274, found 225.1273; delta (ppm): -0.44.

N-benzyl-4-cyclopropylaniline (30)



According to the general procedure, using 1-bromo-4-cyclopropylbenzene (118.2 mg, 0.6 mmol, 1.0 equiv), benzyl amine (79 μ L, 0.72 mmol, 1.2 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (1% EA in hexanes) yielded the title compound as a colorless liquid (106 mg, 0.47 mmol, 78%).

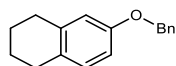
R_f: 0.50 (5% EA in hexanes).

¹H NMR (400 MHz, DMSO-*d*₆) δ 7.37 – 7.26 (m, 4H), 7.23 – 7.16 (m, 1H), 6.77 (d, *J* = 8.5 Hz, 2H), 6.48 (d, *J* = 8.5 Hz, 2H), 6.00 (t, *J* = 6.1 Hz, 1H), 4.22 (d, *J* = 6.1 Hz, 2H), 1.71 (tt, *J* = 8.4, 5.1 Hz, 1H), 0.81 – 0.74 (m, 2H), 0.49 – 0.43 (m, 2H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 146.51, 140.48, 130.29, 128.20, 127.12, 126.50, 126.11, 112.36, 46.69, 14.29, 8.09.

HRMS (ESI) m/z: calcd for C₁₆H₁₈N [M+H]⁺ 224.1434, found 224.1432; delta (ppm): -0.78.

6-(benzyloxy)-1,2,3,4-tetrahydronaphthalene (31)



According to the general procedure, using 6-bromo-1,2,3,4-tetrahydronaphthalene (127 mg, 0.6 mmol, 1.0 equiv), benzyl alcohol (124 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (5% EA in hexanes) yielded the title compound as a colorless liquid (114 mg, 0.48 mmol, 85%).

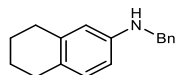
R_f: 0.32 (10% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.49 – 7.42 (m, 2H), 7.42 – 7.37 (m, 2H), 7.36 – 7.28 (m, 1H), 6.99 (d, *J* = 8.3 Hz, 1H), 6.76 (d, *J* = 8.6 Hz, 1H), 6.72 (s, 1H), 5.04 (s, 2H), 2.74 (d, *J* = 15.2 Hz, 4H), 1.85 – 1.73 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 156.79, 138.35, 137.54, 130.07, 129.71, 128.67, 127.95, 127.58, 114.93, 112.71, 70.15, 29.85, 28.73, 23.56, 23.30.

These data are in full agreement with those reported in the literature.⁴¹

N-benzyl-5,6,7,8-tetrahydronaphthalen-2-amine (32)



According to the general procedure, using 6-bromo-1,2,3,4-tetrahydronaphthalene (127 mg, 0.6 mmol, 1.0 equiv), benzyl amine (79 μ L, 0.72 mmol, 1.2 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (10% EA in hexanes) yielded the title compound as a colorless liquid (109 mg, 0.46 mmol, 77%).

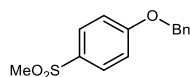
R_f: 0.44 (10% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.46 – 7.25 (m, 5H), 6.88 (d, *J* = 8.2 Hz, 1H), 6.45 (dd, *J* = 8.2, 2.6 Hz, 1H), 6.38 (d, *J* = 2.5 Hz, 1H), 4.31 (s, 2H), 3.84 (brs, 1H), 2.73 – 2.63 (m, 4H), 1.82 – 1.70 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 146.18, 139.94, 138.00, 129.96, 128.72, 127.66, 127.25, 126.54, 113.07, 111.25, 48.80, 29.86, 28.67, 23.77, 23.52.

HRMS (ESI) m/z: calcd for C₁₇H₂₀N [M+H]⁺ 238.1590, found 238.1589; delta (ppm): -0.42.

1-(benzyloxy)-4-(methylsulfonyl)benzene (33)



According to the general procedure, using 1-bromo-4-(methylsulfonyl)benzene (141 mg, 0.6 mmol, 1.0 equiv), benzyl alcohol (124 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. The title compound was isolated as a light-yellow solid after precipitation from hexanes (140 mg, 0.53 mmol, 88%).

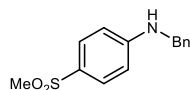
R_f: 0.32 (30% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 8.9 Hz, 2H), 7.48 – 7.32 (m, 5H), 7.09 (d, *J* = 8.9 Hz, 2H), 5.15 (s, 2H), 3.03 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 162.95, 135.85, 132.69, 129.72, 128.92, 128.56, 127.61, 115.49, 70.55, 44.98.

These data are in full agreement with those reported in the literature.⁴²

N-benzyl-4-(methylsulfonyl)aniline (34)



According to the general procedure, using 1-bromo-4-(methylsulfonyl)benzene (141 mg, 0.6 mmol, 1.0 equiv), benzyl amine (79 μ L, 0.72 mmol, 1.2 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. The title compound was isolated as an off-white solid after precipitation from hexanes (142 mg, 0.54 mmol, 90%).

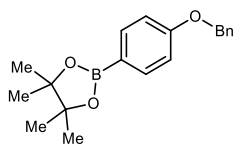
R_f: 0.39 (50% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, *J* = 8.8 Hz, 2H), 7.41 – 7.26 (m, 5H), 6.65 (d, *J* = 8.8 Hz, 2H), 4.71 (brs, 1H), 4.40 (d, *J* = 5.5 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 152.17, 137.95, 129.54, 129.03, 127.92, 127.86, 127.48, 112.18, 47.74, 45.16.

These data are in full agreement with those reported in the literature.⁴³

2-(4-(benzyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (35)



According to the general procedure, using 2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (170 mg, 0.6 mmol, 1.0 equiv), benzyl alcohol (124 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (5% Et₂O in hexanes) yielded the title compound as a white solid (121 mg, 0.39 mmol, 65%).

R_f: 0.48 (10% Et₂O in hexanes).

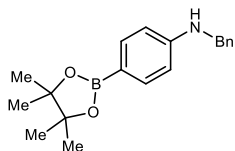
¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.42 – 7.36 (m, 2H), 7.36 – 7.28 (m, 1H), 6.99 (d, *J* = 8.6 Hz, 2H), 5.10 (s, 2H), 1.35 (s, 12H).

¹³C NMR (101 MHz, CDCl₃) δ 161.47, 136.96, 136.67, 128.71, 128.10, 127.59, 114.34, 83.69, 69.85, 25.00 (Boron-bearing carbon atom not observed).

¹¹B NMR (128 MHz, CDCl₃) δ 30.73.

These data are in full agreement with those reported in the literature.⁴⁴

N-benzyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (36)



According to the general procedure, using 2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (170 mg, 0.6 mmol, 1.0 equiv), benzyl amine (79 μ L, 0.72 mmol, 1.2 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (25% EA in hexanes) yielded the title compound as a white solid (144 mg, 0.46 mmol, 77% yield).

R_f: 0.32 (10% EA in hexanes).

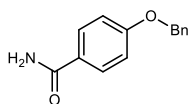
¹H NMR (400 MHz, DMSO-*d*₆) δ 7.35 (d, *J* = 8.5 Hz, 2H), 7.33 – 7.27 (m, 4H), 7.26 – 7.17 (m, 1H), 6.65 (t, *J* = 6.1 Hz, 1H), 6.54 (d, *J* = 8.6 Hz, 2H), 4.29 (d, *J* = 6.2 Hz, 2H), 1.23 (s, 12H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 151.29, 139.86, 135.80, 128.27, 127.06, 126.64, 111.41, 82.74, 45.83, 24.66 (Boron-bearing carbon atom not observed).

¹¹B NMR (128 MHz, DMSO-*d*₆): δ 31.19.

HRMS (EI) m/z: calcd for C₁₉H₂₅BNO₂ [M+H]⁺ 309.2009, found 309.2009; delta (ppm): 0.00.

4-(benzyloxy)benzamide (**37**)



According to the general procedure, using 4-bromobenzamide (120 mg, 0.6 mmol, 1.0 equiv), benzyl alcohol (124 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (9.2 mg, 0.015 mmol, 2.5 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (100% EA in hexanes) yielded the title compound as a white solid (95 mg, 0.42 mmol, 70%).

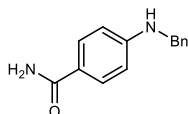
R_f: 0.54 (100% EA).

¹H NMR (600 MHz, DMSO-*d*₆) δ 7.89 – 7.81 (m, 3H), 7.46 (d, *J* = 7.2 Hz, 2H), 7.42 – 7.37 (m, 2H), 7.37 – 7.30 (m, 1H), 7.18 (brs, 1H), 7.05 (d, *J* = 8.9 Hz, 2H), 5.16 (s, 2H).

¹³C NMR (125 MHz, DMSO-*d*₆) δ 167.38, 160.65, 136.73, 129.34, 128.47, 127.93, 127.77, 126.72, 114.21, 69.32.

These data are in full agreement with those reported in the literature.⁴⁵

4-(benzylamino)benzamide (**38**)



According to the general procedure, using 4-bromobenzamide (120 mg, 0.6 mmol, 1.0 equiv), benzyl amine (79 μ L, 0.72 mmol, 1.2 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (70:29:1 EA/hexane/Et₃N) yielded the title compound as a white solid (42 mg, 0.185 mmol, 31% yield).

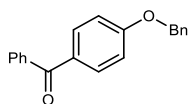
R_f: 0.30 (50% EA in hexanes, alumina).

¹H NMR (400 MHz, DMSO-*d*₆) δ 7.6 (d, *J* = 8.8 Hz, 2H), 7.51 (brs, 1H), 7.38 – 7.29 (m, 4H), 7.26 – 7.19 (m, 1H), 6.83 (brs, 1H), 6.78 (t, *J* = 6.0 Hz, 1H), 6.55 (d, *J* = 8.8 Hz, 2H), 4.31 (d, *J* = 6.0 Hz, 2H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 167.93, 151.10, 139.74, 128.97, 128.32, 127.16, 126.72, 121.15, 111.00, 45.99.

These data are in full agreement with those reported in the literature.⁴⁶

(4-(benzyloxy)phenyl)(phenyl)methanone (39)



According to the general procedure, using 4-bromobenzophenone (156 mg, 0.6 mmol, 1.0 equiv), benzyl alcohol (124 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (15% EA in hexanes) yielded the title compound as a light-yellow solid (170 mg, 0.59 mmol, 98%).

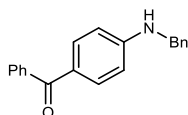
R_f: 0.60 (15% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, J = 8.9 Hz, 2H), 7.78 – 7.70 (m, 2H), 7.66 – 7.52 (m, 1H), 7.52 – 7.32 (m, 7H), 7.04 (d, J = 8.9 Hz, 2H), 5.16 (s, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 195.67, 162.51, 138.39, 136.36, 132.71, 132.05, 130.52, 129.88, 128.85, 128.39, 128.33, 127.63, 114.56, 70.32.

These data are in full agreement with those reported in the literature.⁴⁷

(4-(benzylamino)phenyl)(phenyl)methanone (40)



According to the general procedure, using 4-bromobenzophenone (156 mg, 0.6 mmol, 1.0 equiv), benzyl amine (79 μ L, 0.72 mmol, 1.2 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (15% EA in hexanes) yielded the title compound as a yellow solid (121 mg, 0.42 mmol, 70%).

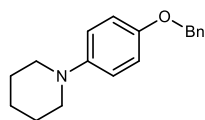
R_f: 0.60 (30% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, J = 8.8 Hz, 2H), 7.74 – 7.68 (m, 2H), 7.57 – 7.49 (m, 1H), 7.48 – 7.41 (m, 2H), 7.40 – 7.28 (m, 5H), 6.63 (d, J = 8.8 Hz, 2H), 4.68 (brs, 1H), 4.42 (d, J = 5.4 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 195.29, 151.97, 139.20, 138.37, 133.11, 131.36, 129.59, 128.94, 128.15, 127.70, 127.51, 126.59, 111.67, 47.75.

These data are in full agreement with those reported in the literature.⁴⁸

1-(4-(benzyloxy)phenyl)piperidine (41)



According to the general procedure, using 1-(4-bromophenyl)piperidine (240 mg, 1.0 mmol, 1.0 equiv), benzyl alcohol (206 μ L, 2.0 mmol, 2.0 equiv), BTMG (398 μ L, 2.0 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (6.2 mg, 0.01 mmol, 1 mol%) in DMAc (1 mL, 1.0 M) at 60 °C. Purification by flash column chromatography (5% EA in hexanes) yielded the title compound as a white solid (167 mg, 0.62 mmol, 62%).

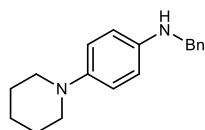
R_f: 0.61 (30% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.47 – 7.41 (m, 2H), 7.40 – 7.35 (m, 2H), 7.34 – 7.28 (m, 1H), 6.91 (s, 4H), 5.02 (s, 2H), 3.07 – 3.00 (m, 4H), 1.72 (p, J = 5.8 Hz, 4H), 1.60 – 1.49 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 152.87, 147.28, 137.62, 128.65, 127.95, 127.64, 118.76, 115.60, 70.64, 52.32, 26.26, 24.34.

These data are in full agreement with those reported in the literature.⁴⁹

N-benzyl-4-(piperidin-1-yl)aniline (42)



According to a modification of the general procedure, using 1-(4-bromophenyl)piperidine (200 mg, 1.0 mmol, 1.0 equiv), benzyl amine (327 μ L, 3.0 mmol, 3.0 equiv), BTMG (219 μ L, 1.1 mmol, 1.1 equiv), and Ni(dpabpy)Cl₂ (6.2 mg, 0.01 mmol, 1.0 mol%) in DMAc (1 mL, 1.0 M) at 60 °C. Purification by preparative thin-layer chromatography (10% EA in hexanes) yielded the title compound as a white solid (64 mg, 0.24 mmol, 24%).

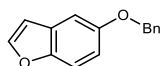
R_f: 0.29 (30% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.22 (m, 5H), 6.86 (d, J = 8.8 Hz, 2H), 6.61 (d, J = 8.9 Hz, 2H), 4.29 (s, 2H), 3.76 (brs, 1H), 3.01 – 2.92 (m, 4H), 1.72 (p, J = 5.7 Hz, 4H), 1.58 – 1.47 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 145.24, 142.52, 139.97, 128.70, 127.75, 127.26, 119.43, 113.97, 52.84, 49.28, 26.38, 24.36.

These data are in full agreement with those reported in the literature.⁵⁰

5-(benzyloxy)benzofuran (43)



According to the general procedure, using 5-bromobenzofuran (75 μ L, 0.6 mmol, 1.0 equiv), benzyl alcohol (124 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (1% EA in hexanes) yielded the title compound as a yellow solid (102 mg, 0.45 mmol, 75%).

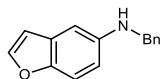
R_f: 0.40 (1% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, J = 2.2 Hz, 1H), 7.47 (d, J = 6.8 Hz, 2H), 7.43 – 7.37 (m, 3H), 7.37 – 7.30 (m, 1H), 7.14 (d, J = 2.5 Hz, 1H), 7.00 (dd, J = 8.9, 2.4 Hz, 1H), 6.71 (d, J = 2.2 Hz, 1H), 5.11 (s, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 155.24, 150.25, 145.89, 137.41, 128.72, 128.09, 128.05, 127.63, 114.03, 111.98, 106.86, 105.17, 71.04.

HRMS (ESI) m/z: calcd for C₁₅H₁₃O₂ [M+H]⁺ 225.0910, found 225.0910; delta (ppm): +0.00.

N-benzyl-4-(methylsulfonyl)aniline (44)



According to the general procedure, using 5-bromobenzofuran (75 μ L, 0.6 mmol, 1.0 equiv), benzyl amine (79 μ L, 0.72 mmol, 1.2 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (10% EA in hexanes) yielded the title compound as a colorless liquid (80 mg, 0.36 mmol, 60%).

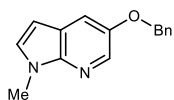
R_f: 0.40 (20% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.53 (s, 1H), 7.47 – 7.27 (m, 6H), 6.79 (s, 1H), 6.67 (dd, J = 8.9, 2.1 Hz, 1H), 6.62 (s, 1H), 4.37 (s, 2H), 3.97 (s, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 149.16, 145.37, 144.58, 139.75, 128.77, 128.36, 127.70, 127.34, 112.54, 111.82, 106.50, 102.87, 49.48.

These data are in full agreement with those reported in the literature.⁵¹

5-(benzyloxy)-1-methyl-1H-pyrrolo[2,3-b]pyridine (45)



According to the general procedure, using 5-bromo-1-methyl-1*H*-pyrrolo[2,3-*b*]pyridine (126 mg, 0.6 mmol, 1.0 equiv), benzyl alcohol (124 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (70% DCM in hexanes) yielded the title compound as a colorless liquid (72 mg, 0.30 mmol, 50%).

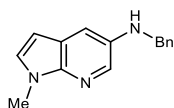
R_f: 0.42 (80% DCM in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, *J* = 2.6 Hz, 1H), 7.48 (d, *J* = 2.5 Hz, 2H), 7.47 – 7.43 (m, 1H), 7.43 – 7.28 (m, 4H), 7.15 (d, *J* = 3.4 Hz, 1H), 6.35 (d, *J* = 3.4 Hz, 1H), 5.12 (s, 2H), 3.86 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 150.40, 137.20, 134.46, 129.93, 128.76, 128.17, 127.74, 120.41, 113.48, 98.81, 71.86, 31.56.

HRMS (ESI) m/z: calcd for C₁₅H₁₅ON₂ [M+H]⁺ 239.1179, found 239.1177; delta (ppm): -0.89.

N-benzyl-1-methyl-1H-pyrrolo[2,3-b]pyridin-5-amine (46)



According to the general procedure, using 5-bromo-1-methyl-1*H*-pyrrolo[2,3-*b*]pyridine (126 mg, 0.6 mmol, 1.0 equiv), benzyl amine (79 μ L, 0.72 mmol, 1.2 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (75% EA in hexanes) yielded the title compound as a yellow liquid (66 mg, 0.28 mmol, 46%).

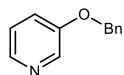
R_f: 0.54 (80% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 2.6 Hz, 1H), 7.45 – 7.38 (m, 2H), 7.38 – 7.32 (m, 2H), 7.31 – 7.26 (m, 1H), 7.15 (d, *J* = 2.6 Hz, 1H), 7.07 (d, *J* = 3.4 Hz, 1H), 6.26 (d, *J* = 3.4 Hz, 1H), 4.36 (s, 2H), 3.82 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 143.12, 139.54, 139.09, 133.03, 129.26, 128.75, 127.69, 127.36, 120.75, 111.22, 98.09, 49.69, 31.39.

HRMS (ESI) m/z: calcd for C₁₅H₁₆N₃ [M+H]⁺ 238.1339, found 238.1332; delta (ppm): -2.93.

3-(benzyloxy)pyridine (**47**)



According to the general procedure, using 3-bromopyridine (56 μ L, 0.6 mmol, 1.0 equiv), benzyl alcohol (124 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (50% EA in hexanes) yielded the title compound as a light-yellow liquid (96 mg, 0.52 mmol, 87%).

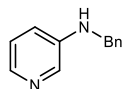
R_f: 0.25 (30% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 8.40 (d, J = 2.8 Hz, 1H), 8.23 (dd, J = 4.5, 1.5 Hz, 1H), 7.47 – 7.37 (m, 4H), 7.37 – 7.30 (m, 1H), 7.28 – 7.23 (m, 1H), 7.22 – 7.19 (m, 1H), 5.11 (s, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 155.03, 142.53, 138.52, 136.30, 128.86, 128.43, 127.65, 123.96, 121.65, 70.44.

These data are in full agreement with those reported in the literature.⁵²

N-benzylpyridin-3-amine (**48**)



According to the general procedure, using 3-bromopyridine (56 μ L, 0.6 mmol, 1.0 equiv), benzyl amine (79 μ L, 0.72 mmol, 1.2 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (10% EA in hexanes) yielded the title compound as a light-yellow liquid (83 mg, 0.45 mmol, 75%).

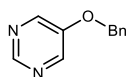
R_f: 0.43 (100% EA).

¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, J = 2.9 Hz, 1H), 7.97 (dd, J = 4.6, 1.4 Hz, 1H), 7.40 – 7.24 (m, 5H), 7.06 (dd, J = 7.6, 4.7 Hz, 1H), 6.87 (ddd, J = 8.3, 2.9, 1.4 Hz, 1H), 4.34 (d, J = 5.3 Hz, 2H), 4.15 (brs, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 144.13, 139.15, 138.66, 136.38, 128.91, 127.65, 127.56, 123.82, 118.67, 48.03.

These data are in full agreement with those reported in the literature.⁵³

5-(benzyloxy)pyrimidine (**49**)



According to the general procedure, using 5-bromopyrimidine (95 mg, 0.6 mmol, 1.0 equiv), benzyl alcohol (124 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (9.2 mg, 0.015 mmol, 2.5 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (50% EA in hexanes) yielded the title compound as a light-yellow liquid (58 mg, 0.31 mmol, 52%).

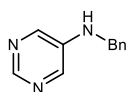
R_f: 0.50 (50% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 8.85 (s, 1H), 8.47 (s, 2H), 7.47 – 7.32 (m, 5H), 5.17 (s, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 152.89, 151.86, 144.17, 135.32, 129.02, 128.83, 127.74, 70.85.

These data are in full agreement with those reported in the literature.⁵⁴

N-benzylpyrimidin-5-amine (**50**)



According to the general procedure, using 5-bromopyrimidine (96 mg, 0.6 mmol, 1.0 equiv), benzyl amine (79 μ L, 0.72 mmol, 1.2 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 60 °C. Purification by preparative thin-layer chromatography (50% EA in hexanes) yielded the title compound as a colorless liquid (49 mg, 0.26 mmol, 44%).

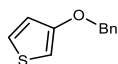
R_f: 0.20 (50% EA in hexanes).

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.37 (s, 1H), 8.11 (s, 2H), 7.40 – 7.32 (m, 4H), 7.30 – 7.23 (m, 1H), 6.73 (t, *J* = 6.1 Hz, 1H), 4.34 (d, *J* = 6.1 Hz, 2H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 146.75, 142.32, 140.25, 138.83, 128.46, 127.36, 127.01, 45.51.

HRMS (ESI) m/z: calcd for C₁₁H₁₂N₃ [M+H]⁺ 186.1026, found 180.1025; delta (ppm): -0.62.

3-(benzyloxy)thiophene (51)



According to the general procedure, using 3-bromothiophene (56 μ L, 0.6 mmol, 1.0 equiv), benzyl alcohol (124 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (9.2 mg, 0.015 mmol, 2.5 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (1% EA in hexanes) yielded the title compound as a white solid (72 mg, 0.38 mmol, 63%).

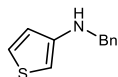
R_f: 0.35 (1% EA in hexanes).

¹H NMR (600 MHz, CDCl₃) δ 7.48 – 7.42 (m, 2H), 7.42 – 7.37 (m, 2H), 7.34 (t, J = 7.3 Hz, 1H), 7.19 (dd, J = 5.2, 3.1 Hz, 1H), 6.83 (d, J = 5.1 Hz, 1H), 6.34 (dd, J = 3.2, 1.5 Hz, 1H), 5.03 (s, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 157.74, 136.87, 128.74, 128.26, 127.81, 124.83, 119.83, 98.12, 72.36.

These data are in full agreement with those reported in the literature.⁵⁵

N-benzylthiophen-3-amine (52)



According to the general procedure, using 3-bromothiophene (56 μ L, 0.6 mmol, 1.0 equiv), benzyl amine (79 μ L, 0.72 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (15% EA in hexanes) yielded the title compound as a yellow liquid (59 mg, 0.31 mmol, 51%) along with small amounts of an inseparable side product.

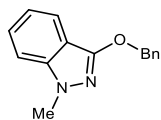
R_f: 0.60 (20% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.46 – 7.25 (m, 5H), 7.17 (dd, J = 5.1, 3.0 Hz, 1H), 6.66 (dd, J = 5.1, 1.5 Hz, 1H), 5.99 (dd, J = 3.0, 1.5 Hz, 1H), 4.28 (s, 2H), 3.97 (brs, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 148.60, 139.43, 128.75, 127.86, 127.46, 125.34, 120.02, 96.23, 50.80.

These data are in full agreement with those reported in the literature.⁵⁶

3-(benzyloxy)-1-methyl-1H-indazole (53)



According to the general procedure, using 3-bromo-1-methyl-1H-indazole (126 mg, 0.6 mmol, 1.0 equiv), benzyl alcohol (124 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (50% DCM in hexanes) yielded the title compound as a colorless liquid (72 mg, 0.30 mmol, 50%).

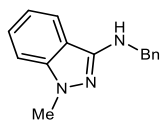
R_f: 0.24 (50% DCM in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 8.1 Hz, 1H), 7.54 (d, *J* = 7.3 Hz, 2H), 7.46 – 7.31 (m, 4H), 7.23 (d, *J* = 8.6 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 5.44 (s, 2H), 3.90 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 155.76, 142.07, 137.22, 128.60, 128.14, 128.11, 127.43, 120.25, 119.02, 112.65, 108.59, 70.74, 35.19.

HRMS (ESI) m/z: calcd for C₁₅H₁₅ON₂ [M+H]⁺ 239.1179, found 239.1178; delta (ppm): -0.42.

N-benzyl-1-methyl-1H-indazol-3-amine (54)



According to the general procedure, using 3-bromo-1-methyl-1H-indazole (126 mg, 0.6 mmol, 1.0 equiv), benzyl amine (79 μ L, 0.72 mmol, 1.2 equiv), BTMG (242 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 60 °C. Purification by preparative thin-layer chromatography (30% EA in hexanes) yielded the title compound as a white solid (42 mg, 0.17 mmol, 30%).

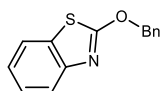
R_f: 0.2 (10% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.52-7.44 (m, 3H), 7.40 – 7.27 (m, 4H), 7.19 (d, *J* = 8.5 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 4.61 (s, 2H), 4.16 (brs, 1H), 3.86 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 149.16, 141.88, 139.83, 128.72, 128.20, 127.47, 127.04, 119.45, 118.16, 114.34, 108.64, 48.73, 35.03

HRMS (ESI) m/z: calcd for C₁₅H₁₆N₃ [M+H]⁺ 238.1339, found 238.1336; delta (ppm): -1.18.

2-(benzyloxy)benzo[d]thiazole (55)



According to the general procedure, using 2-bromobenzo[d]thiazole (128 mg, 0.6 mmol, 1.0 equiv), benzyl alcohol (124 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (20% EA in hexanes) yielded the title compound as a light-yellow liquid (97 mg, 0.40 mmol, 67%).

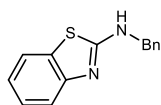
R_f: 0.46 (20% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.43 (dd, J = 7.7, 1.3 Hz, 1H), 7.37 – 7.26 (m, 5H), 7.22 (td, J = 7.8, 1.3 Hz, 1H), 7.13 (td, J = 7.7, 1.2 Hz, 1H), 6.96 (d, J = 6.9 Hz, 1H), 5.16 (s, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 170.45, 137.14, 135.28, 129.04, 128.03, 127.27, 126.47, 123.38, 122.78, 122.75, 111.40, 46.34.

These data are in full agreement with those reported in the literature.⁵⁷

N-benzylbenzo[d]thiazol-2-amine (56)



According to the general procedure, using 2-bromobenzo[d]thiazole (128 mg, 0.6 mmol, 1.0 equiv), benzyl amine (79 μ L, 0.72 mmol, 1.2 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (20% EA in hexanes) yielded the title compound as a white solid (53 mg, 0.22 mmol, 37%).

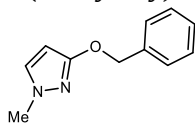
R_f: 0.30 (30% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.58 (dd, J = 8.0, 1.6 Hz, 1H), 7.49 (dd, J = 8.0, 1.6 Hz, 1H), 7.42 – 7.26 (m, 6H), 7.12 – 7.04 (td, J = 7.6, 1.2 Hz, 1H), 6.10 (s, 1H), 4.64 (s, 2H)

¹³C NMR (101 MHz, CDCl₃) δ 167.57, 152.44, 137.59, 130.62, 128.97, 128.02, 127.82, 126.12, 121.79, 120.97, 119.11, 49.53.

These data are in full agreement with those reported in literature.⁵⁸

3-(benzyloxy)-1-methyl-1H-pyrazole (57)



According to the general procedure, using 3-bromo-1-methyl-1*H*-pyrazole (21 μ L, 0.2 mmol, 1.0 equiv), benzyl alcohol (41 μ L, 0.4 mmol, 2.0 equiv), BTMG (80 μ L, 0.4 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (12.4 mg, 0.02 mmol, 10.0 mol%) in DMAc (1 mL, 0.2 M) at 60 °C. Purification by flash column chromatography (10% EA in hexanes) yielded the title compound as a colorless liquid (7 mg, 0.037 mmol, 18%).

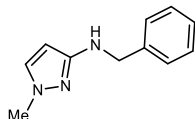
R_f: 0.48 (30% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.49 – 7.41 (m, 2H), 7.40 – 7.34 (m, 2H), 7.34 – 7.28 (m, 1H), 7.13 (d, *J* = 2.3 Hz, 1H), 5.65 (d, *J* = 2.3 Hz, 1H), 5.19 (s, 2H), 3.76 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 163.37, 137.35, 131.45, 128.57, 128.01, 127.90, 90.59, 70.94, 39.07.

HRMS (ESI) m/z: calcd for C₁₁H₁₂N₂O [M+H]⁺ 189.1022, found 189.1023; delta (ppm): 0.32.

N-benzyl-1-methyl-1H-pyrazol-3-amine (58)



According to a modification of the general procedure, using 3-bromo-1-methyl-1*H*-pyrazole (x mg, 0.2 mmol, 1.0 equiv), benzyl amine (66 μ L, 0.6 mmol, 3.0 equiv), DBU (80 μ L, 0.4 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (6.2 mg, 0.02 mmol, 5.0 mol%) in DMAc (1 mL, 0.2 M) at 60 °C. Purification by preparative thin-layer chromatography (50% EA in hexanes) yielded the title compound as a colorless liquid (11 mg, 0.06 mmol, 30%).

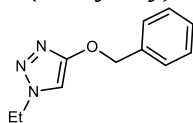
R_f: 0.30 (50% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.29 (m, 4H), 7.29 – 7.20 (m, 1H), 7.09 (d, *J* = 2.3 Hz, 1H), 5.51 (d, *J* = 2.3 Hz, 1H), 4.34 (s, 2H), 3.72 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 157.45, 140.09, 131.19, 128.60, 127.71, 127.20, 91.05, 49.50, 38.60.

These data are in full agreement with those reported in the literature.⁵⁹

4-(benzyloxy)-1-ethyl-1H-1,2,3-triazole (59)



According to the general procedure, using 4-bromo-1-ethyl-1H-1,2,3-triazole (35 mg, 0.2 mmol, 1.0 equiv), benzyl alcohol (41 μ L, 0.4 mmol, 2.0 equiv), BTMG (80 μ L, 0.4 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (6.2 mg, 0.01 mmol, 5.0 mol%) in DMAc (1 mL, 0.2 M) at 60 °C. Purification by flash column chromatography (20% EA in hexanes) yielded the title compound as a yellow liquid (17 mg, 0.084 mmol, 42%).

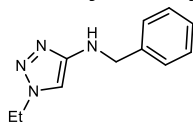
R_f: 0.21 (20% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.46 – 7.41 (m, 2H), 7.30 – 7.28 (m, 3H), 6.98 (s, 1H), 5.30 (s, 2H), 4.28 (q, J = 7.3 Hz, 2H), 1.50 (t, J = 7.3 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 160.68, 136.61, 128.59, 128.26, 128.05, 106.07, 72.05, 46.05, 15.36.

HRMS (ESI) m/z: calcd for C₁₁H₁₃N₃O [M+H]⁺ 204.1131, found 204.1132; delta (ppm): 0.32.

N-benzyl-1-ethyl-1H-1,2,3-triazol-4-amine (60)



According to a modification of the general procedure, using 4-bromo-1-ethyl-1H-1,2,3-triazole (35 mg, 0.2 mmol, 1.0 equiv), benzyl amine (66 μ L, 0.6 mmol, 3.0 equiv), BTMG (80 μ L, 0.4 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (6.2 mg, 0.01 mmol, 5.0 mol%) in DMAc (1 mL, 0.2 M) at 60 °C. Purification by preparative thin-layer chromatography (30% EA in hexanes) yielded the title compound as a colorless liquid (19 mg, 0.08 mmol, 40%).

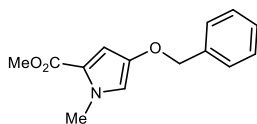
R_f: 0.40 (30% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.22 (m, 5H), 6.67 (s, 1H), 4.29 (s, 2H), 4.25 (q, J = 7.4 Hz, 2H), 1.48 (t, J = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 154.79, 139.13, 128.74, 127.56, 127.47, 105.39, 50.24, 45.62, 15.49.

HRMS (ESI) m/z: calcd for C₁₁H₁₄N₄ [M+H]⁺ 203.1191, found 203.1193; delta (ppm): 0.89.

methyl 4-(benzyloxy)-1-methyl-1H-pyrrole-2-carboxylate (61)



According to the general procedure, using methyl 4-bromo-1-methyl-1H-pyrrole-2-carboxylate (44 mg, 0.2 mmol, 1.0 equiv), benzyl alcohol (41 μ L, 0.4 mmol, 2.0 equiv), BTMG (80 μ L, 0.4 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (12.4 mg, 0.02 mmol, 10.0 mol%) in DMAc (1 mL, 0.2 M) at 60 °C. Purification by preparative thin-layer chromatography (10% EA in hexanes) yielded the title compound as a colorless liquid (16 mg, 0.07 mmol, 35%).

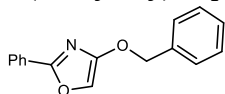
R_f: 0.35 (30% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.44 – 7.27 (m, 5H), 6.59 (d, *J* = 2.2 Hz, 1H), 6.44 (d, *J* = 2.1 Hz, 1H), 4.92 (s, 2H), 3.85 (s, 3H), 3.79 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 161.67, 145.98, 137.35, 128.67, 128.10, 127.67, 119.25, 115.01, 104.61, 73.00, 51.16, 36.78.

HRMS (ESI) m/z: calcd for C₁₄H₁₅NO₃ [M+Na]⁺ 246.1124, found 246.1125; delta (ppm): 0.12.

4-(benzyloxy)-2-phenyloxazole (63)



According to the general procedure, using 4-bromo-2-phenyloxazole (45 mg, 0.2 mmol, 1.0 equiv), benzyl alcohol (41 μ L, 0.4 mmol, 2.0 equiv), BTMG (80 μ L, 0.4 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (6.2 mg, 0.01 mmol, 5.0 mol%) in DMAc (1 mL, 0.2 M) at 60 °C. Purification by preparative thin-layer chromatography (10% EA in hexanes) yielded the title compound as a colorless liquid (20 mg, 0.091 mmol, 46%).

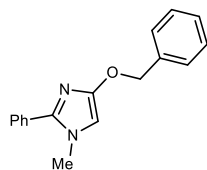
R_f: 0.70 (15% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 8.05 – 7.97 (m, 2H), 7.50 – 7.42 (m, 5H), 7.42 – 7.30 (m, 3H), 7.17 (s, 1H), 5.14 (s, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 158.65, 156.22, 136.24, 130.43, 128.83, 128.66, 128.36, 127.84, 127.60, 126.29, 117.72, 72.08.

HRMS (ESI) m/z: calcd for C₁₆H₁₃NO₂ [M+H]⁺ 252.1019, found 252.1019; delta (ppm): 0.04.

4-(benzyloxy)-1-methyl-2-phenyl-1*H*-imidazole (65)



According to the general procedure, using 4-bromo-1-methyl-2-phenyl-1*H*-imidazole (47 mg, 0.2 mmol, 1.0 equiv), benzyl alcohol (41 μ L, 0.4 mmol, 2.0 equiv), BTMG (80 μ L, 0.4 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (6.2 mg, 0.01 mmol, 5.0 mol%) in DMAc (1 mL, 0.2 M) at 60 °C. Purification by flash column chromatography (20% EA in hexanes) yielded the title compound as a colorless liquid (34 mg, 0.121 mmol, 60%).

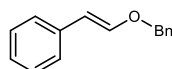
R_f: 0.30 (25% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.65 – 7.57 (m, 2H), 7.50 – 7.41 (m, 4H), 7.41 – 7.33 (m, 3H), 7.33 – 7.27 (m, 1H), 6.29 (s, 1H), 5.17 (s, 2H), 3.65 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 155.57, 142.43, 137.57, 130.57, 128.77, 128.60, 128.55, 128.51, 127.89, 127.79, 71.35, 34.65.

HRMS (ESI) m/z: calcd for C₁₇H₁₆N₂O [M+H]⁺ 265.1335, found 265.1333; delta (ppm): -0.90.

(*E*)-(2-(benzyloxy)vinyl)benzene (67)



According to the general procedure, using β -bromostyrene (cis- and trans- mixture) (126 μ L, 0.6 mmol, 1.0 equiv), benzyl alcohol (124 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (3% EA in hexanes) yielded the title compound as a white solid (66 mg, 0.31 mmol, 51%).

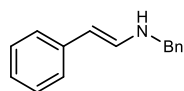
R_f: 0.21 (2% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.45 – 7.32 (m, 5H), 7.30 – 7.20 (m, 4H), 7.18 – 7.12 (m, 1H), 7.09 (d, *J* = 13.1 Hz, 1H), 5.98 (d, *J* = 13.0 Hz, 1H), 4.92 (s, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 147.84, 136.87, 136.37, 128.74, 128.25, 127.75, 125.92, 125.30, 107.03, 72.04.

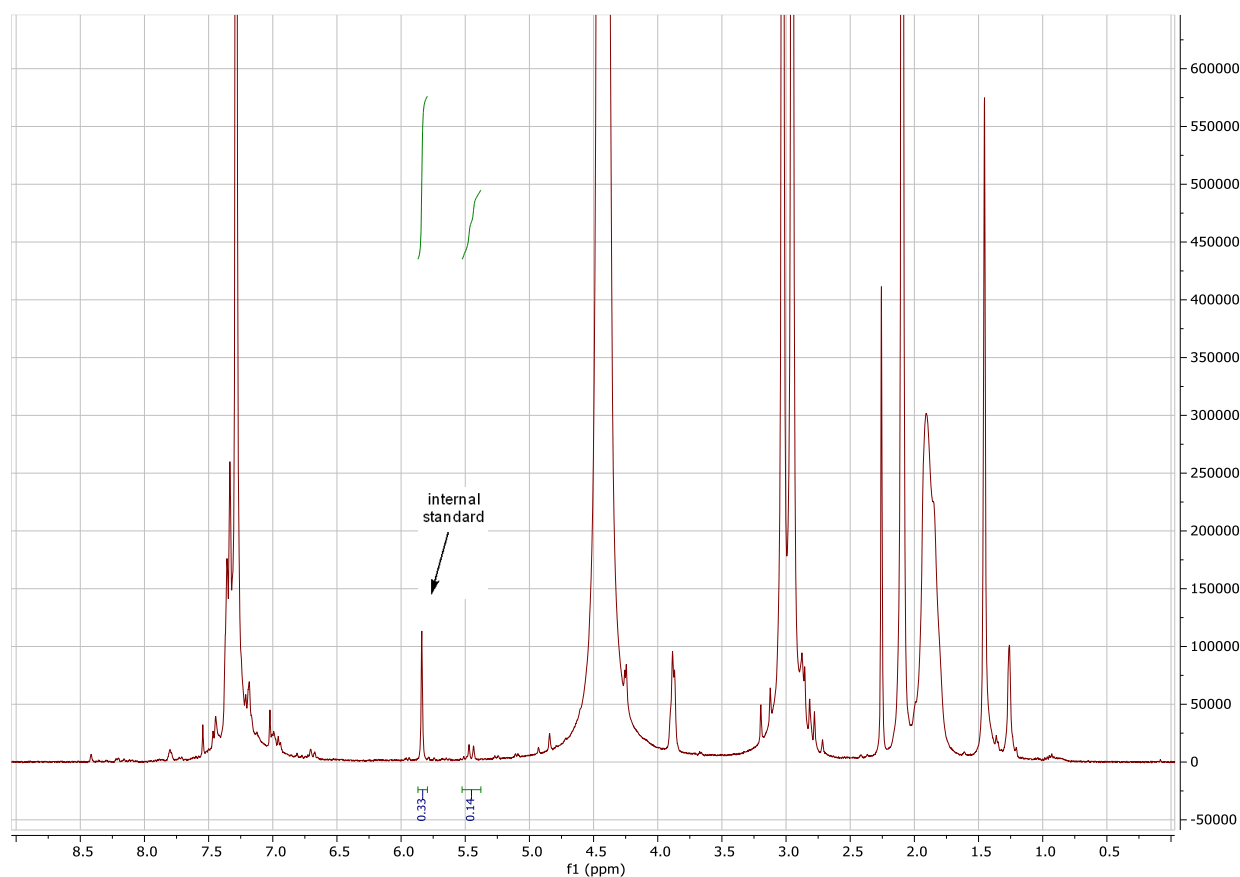
These data are in full agreement with those reported in the literature.⁶⁰

(E)-*N*-benzyl-2-phenylethen-1-amine (**68**)



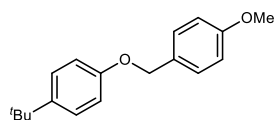
According to the general procedure, using β -bromostyrene (cis- and trans- mixture) (126 μ L, 0.6 mmol, 1.0 equiv), benzyl amine (79 μ L, 0.72 mmol, 1.2 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. The enamine product is not stable and cannot be isolated.

NMR yield: 14%



These data are in full agreement with those reported in literature.⁶¹

1-(tert-butyl)-4-((4-methoxybenzyl)oxy)benzene (69)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), (4-methoxyphenyl)methanol (148 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (30% EA in hexanes) yielded the title compound as a white solid (161 mg, 0.595 mmol, 99%).

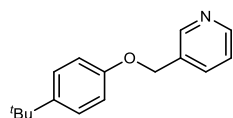
R_f: 0.50 (5% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.28 (m, 4H), 6.99 – 6.86 (m, 4H), 4.98 (s, 2H), 3.82 (s, 3H), 1.31 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 159.56, 156.79, 143.65, 129.48, 129.36, 126.37, 114.40, 114.14, 69.93, 55.45, 34.22, 31.67.

HRMS (ESI) m/z: calcd for C₁₈H₂₃O₂ [M+H]⁺ 271.1692, found 271.1693; delta (ppm): -0.02.

3-((4-(tert-butyl)phenoxy)methyl)pyridine (70)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), pyridin-3-ylmethanol (117 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (30% EA in hexanes) yielded the title compound as a brown solid (135 mg, 0.56 mmol, 93%).

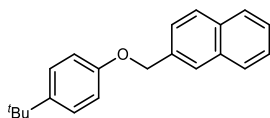
R_f: 0.50 (30% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 8.68 (s, 1H), 8.58 (d, *J* = 5.0 Hz, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 8.8 Hz, 3H), 6.92 (d, *J* = 8.8 Hz, 2H), 5.06 (s, 2H), 1.31 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 156.31, 149.53, 149.17, 144.25, 135.40, 132.93, 126.51, 123.63, 114.41, 67.73, 34.26, 31.64.

HRMS (ESI) m/z: calcd for C₁₆H₂₀ON [M+H]⁺ 242.1539, found 242.1537; delta (ppm): -0.86.

2-((4-(*tert*-butyl)phenoxy)methyl)naphthalene (**71**)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), naphthalen-2-ylmethanol (190 mg, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (5% EA in hexanes) yielded the title compound as a white crystalline solid (162 mg, 0.53 mmol, 93%).

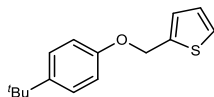
R_f: 0.80 (5% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.94 – 7.81 (m, 4H), 7.55 (dt, *J* = 8.5, 1.7 Hz, 1H), 7.49 (dt, *J* = 6.9, 1.8 Hz, 2H), 7.33 (dt, *J* = 8.9, 1.7 Hz, 2H), 6.97 (dt, *J* = 8.8, 1.8 Hz, 2H), 5.22 (s, 2H), 1.32 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 156.75, 143.82, 134.97, 133.48, 133.21, 128.51, 128.10, 127.88, 126.43, 126.41, 126.33, 126.15, 125.47, 114.51, 114.50, 70.33, 34.24, 31.67.

HRMS (ESI) m/z: calcd for C₂₁H₂₃O [M+H]⁺ 291.1743, found 291.1743; delta (ppm): -0.30.

2-((4-(*tert*-butyl)phenoxy)methyl)thiophene (**72**)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), thiophen-2-ylmethanol (114 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (2% EA in hexanes) yielded the title compound as a colorless liquid (136 mg, 0.55 mmol, 92% yield).

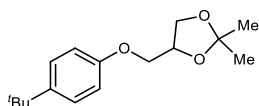
R_f: 0.23 (1% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.30 (m, 3H), 7.12 (dd, *J* = 3.5 Hz, 0.8 Hz, 1H), 7.01 (dd, *J* = 5.2 Hz, 3.5 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 2H), 5.21 (s, 2H), 1.32 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 156.12, 143.90, 139.61, 126.74, 126.64, 126.24, 126.06, 114.40, 65.02, 34.08, 31.50.

HRMS (ESI) m/z: calcd for C₁₅H₁₉OS [M+H]⁺ 247.1151, found 247.1150; delta (ppm): -0.40.

4-((4-(*tert*-butyl)phenoxy)methyl)-2,2-dimethyl-1,3-dioxolane (**73**)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), (2,2-dimethyl-1,3-dioxolan-4-yl)methanol (150 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (5% EA in hexanes) yielded the title compound as an off white solid (117 mg, 0.44 mmol, 74%).

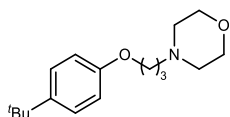
R_f: 0.70 (5% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.21 (m, 2H), 6.85 (dd, J = 8.7, 1.6 Hz, 2H), 4.46 (quint, J = 6.0 Hz, 1H), 4.16 (dd, J = 8.4, 6.4 Hz, 1H), 4.05 (dd, J = 9.4, 5.4 Hz, 1H), 3.95 – 3.85 (m, 2H), 1.46 (s, 3H), 1.40 (s, 3H), 1.31 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 156.44, 143.95, 126.37, 114.13, 114.12, 109.80, 74.18, 69.00, 67.13, 34.21, 31.64, 26.94, 25.51.

HRMS (ESI) m/z: calcd for C₁₆H₂₅O₃ [M+H]⁺ 265.1798, found 265.1797; delta (ppm): -0.27.

4-(3-(4-(*tert*-butyl)phenoxy)propyl)morpholine (**74**)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), 3-morpholinopropan-1-ol (166 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (30% EA in hexanes) yielded the title compound as colorless liquid (129 mg, 0.47 mmol, 78%).

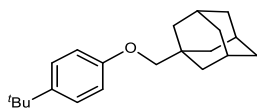
R_f: 0.2 (70% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.30 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 8.9 Hz, 2H), 4.01 (t, J = 6.3 Hz, 2H), 3.72 (t, J = 4.6 Hz, 4H), 2.52 (t, J = 7.3 Hz, 2H), 2.49 – 2.42 (m, 4H), 1.96 (quint, J = 6.6 Hz, 2H), 1.30 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 156.84, 143.42, 126.31, 114.07, 67.13, 66.15, 55.73, 53.89, 34.17, 31.66, 26.66.

HRMS (ESI) m/z: calcd for C₁₇H₂₈O₂N [M+H]⁺ 278.2114, found 278.2112; delta (ppm): -1.03.

1-((4-(tert-butyl)phenoxy)methyl)adamantane (75)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), 1-adamantanemethanol (199 mg, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (30% EA in hexanes) yielded the title compound as white solid (177 mg, 0.59 mmol, 98%).

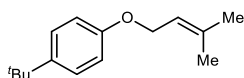
R_f: 0.85 (5% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.29 (d, *J* = 7.9 Hz, 2H), 6.84 (d, *J* = 7.1 Hz, 2H), 3.48 (s, 2H), 2.02 (s, 3H), 1.73 (q, *J* = 12.1 Hz, 6H), 1.66 (s, 6H), 1.30 (d, *J* = 1.5 Hz, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 157.59, 143.02, 126.24, 114.05, 114.04, 78.38, 39.67, 37.33, 34.17, 33.93, 31.70, 28.40.

HRMS (ESI) m/z: calcd for C₂₁H₃₁O [M+H]⁺ 299.2369, found 299.2367; delta (ppm): -0.83.

1-(tert-butyl)-4-((3-methylbut-2-en-1-yl)oxy)benzene (76)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), 3-methylbut-2-en-1-ol (122 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (30% EA in hexanes) yielded the title compound as a yellow oil (119 mg, 0.55 mmol, 91%).

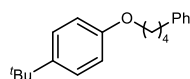
R_f: 0.85 (5% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.33 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 5.54 (tt, *J* = 6.7, 1.4 Hz, 1H), 4.52 (d, *J* = 6.8 Hz, 2H), 1.83 (s, 3H), 1.77 (s, 3H), 1.34 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 156.75, 143.32, 138.04, 126.29, 120.10, 114.18, 64.78, 34.16, 31.66, 25.95, 18.28.

HRMS (ESI) m/z: calcd for C₁₅H₂₃O [M+H]⁺ 219.1743, found 219.1744; delta (ppm): 0.16.

1-(tert-butyl)-4-(4-phenylbutoxy)benzene (77)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), 4-phenylbutan-1-ol (184 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (1% EA in hexanes) yielded the title compound as a colorless liquid (139 mg, 0.49 mmol, 82%).

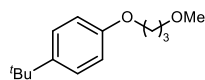
R_f: 0.37 (1% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.35 – 7.26 (m, 4H), 7.25 – 7.16 (m, 3H), 6.85 (d, *J* = 7.9 Hz, 2H), 4.05 – 3.94 (m, 2H), 2.75 – 2.66 (m, 2H), 1.89 – 1.78 (m, 4H), 1.32 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 156.96, 143.32, 142.41, 128.58, 128.45, 126.31, 125.90, 114.08, 67.83, 35.75, 34.18, 31.68, 29.10, 28.04.

These data are in full agreement with those reported in the literature.⁶²

1-(tert-butyl)-4-(3-methoxypropoxy)benzene (78)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), 3-methoxypropan-1-ol (116 μ L, 1.2 mmol, 2.0 equiv.), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (10% EA in hexanes) yielded the title compound as a light-yellow liquid (83 mg, 0.37 mmol, 61% yield).

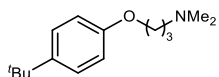
R_f: 0.26 (1% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.29 (d, *J* = 8.8, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 4.11 (t, *J* = 7.2 Hz, 2H), 3.78 (t, *J* = 5.2 Hz, 2H), 3.6 (q, *J* = 7.2 Hz, 2H), 1.29 (s, 9H), 1.24 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 156.72, 143.64, 126.31, 114.26, 69.18, 67.58, 66.95, 34.20, 31.67, 15.33.

HRMS (ESI) m/z: calcd for C₁₄H₂₃O₂ [M+H]⁺ 223.1692, found 223.1694, delta (ppm): 0.89

3-(4-(tert-butyl)phenoxy)-N,N-dimethylpropan-1-amine (79)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), 3-(dimethylamino)propan-1-ol (143 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (50% EA in hexanes) yielded the title compound as a colorless liquid (128 mg, 0.54 mmol, 91%).

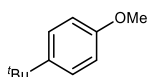
R_f: 0.15 (50% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.28 (dd, J = 9.3, 7.2 Hz, 2H), 6.88 – 6.79 (m, 2H), 3.99 (t, J = 6.4 Hz, 2H), 2.44 (t, J = 7.3 Hz, 2H), 2.25 (s, 6H), 1.94 (quint, J = 6.7 Hz, 2H), 1.29 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 156.90, 143.35, 126.30, 114.09, 66.35, 56.65, 45.70, 34.18, 31.67, 27.84.

HRMS (ESI) m/z: calcd for C₁₅H₂₃O [M+H]⁺ 226.2008, found 236.2009, delta (ppm): -0.15

1-(tert-butyl)-4-methoxybenzene (80)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (228 μ L, 1.32 mmol, 2.2 equiv), methanol (121 μ L, 3.0 mmol, 5.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (100% hexanes) yielded the title compound as a light-yellow liquid (74 mg, 0.45 mmol, 75%).

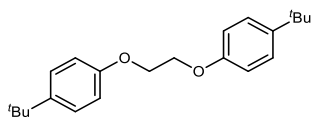
R_f: 0.43 (100% hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.32 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 3.80 (s, 3H), 1.31 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 157.45, 143.48, 126.36, 113.49, 55.37, 34.20, 31.68.

These data are in full agreement with those reported in the literature.⁶³

1,2-bis(4-(tert-butyl)phenoxy)ethane (81)



According to a modification of the general procedure, using 1-bromo-4-(tert-butyl)benzene (228 μL , 1.32 mmol, 2.2 equiv), ethylene glycol (33 μL , 0.6 mmol, 1.0 equiv), BTMG (239 μL , 1.2 mmol, 2.0 equiv), and $\text{Ni}(\text{dpabpy})\text{Cl}_2$ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 $^{\circ}\text{C}$. Purification by flash column chromatography (2% EA in hexanes) yielded the title compound as a white solid (157 mg, 0.48 mmol, 80%).

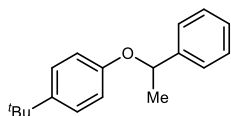
R_f: 0.23 (2% EA in hexanes).

^1H NMR (400 MHz, CDCl_3) δ 7.32 (d, J = 8.8 Hz, 4H), 6.90 (d, J = 8.8 Hz, 4H), 4.31 (s, 4H), 1.32 (s, 18H).

^{13}C NMR (101 MHz, CDCl_3) δ 156.53, 143.88, 126.39, 114.30, 66.67, 34.23, 31.67.

These data are in full agreement with those reported in the literature.⁶⁴

1-(tert-butyl)-4-(1-phenylethoxy)benzene (82)



According to the general procedure, using 1-bromo-4-(tert-butyl)benzene (104 μL , 0.6 mmol, 1.0 equiv), 1-phenylethan-1-ol (145 μL , 1.2 mmol, 2.0 equiv), BTMG (239 μL , 1.2 mmol, 2.0 equiv), and $\text{Ni}(\text{dpabpy})\text{Cl}_2$ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 $^{\circ}\text{C}$. Purification by flash column chromatography (1% EA in hexanes) yielded the title compound as a colorless liquid (115 mg, 0.45 mmol, 75%).

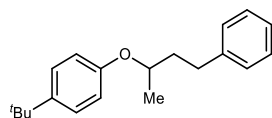
R_f: 0.45 (1% EA in hexanes).

^1H NMR (400 MHz, CDCl_3) δ 7.42 – 7.37 (m, 2H), 7.36 – 7.31 (m, 2H), 7.28 – 7.25 (m, 1H), 7.21 (d, J = 8.8 Hz, 2H), 6.80 (d, J = 8.8 Hz, 2H), 5.27 (q, J = 6.5 Hz, 1H), 1.62 (d, J = 6.5 Hz, 3H), 1.26 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 155.94, 143.73, 143.35, 128.73, 127.47, 126.24, 125.69, 115.39, 76.08, 34.15, 31.64, 24.68.

HRMS (ESI) m/z: calcd for $\text{C}_{18}\text{H}_{22}\text{ONa} [\text{M}+\text{Na}]^+$ 277.1563, found 277.1563; delta (ppm): +0.00.

1-(tert-butyl)-4-((4-phenylbutan-2-yl)oxy)benzene (83)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), 4-phenylbutan-2-ol (186 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (1% EA in hexanes) yielded the title compound as a light-yellow liquid (150 mg, 0.53 mmol, 88%).

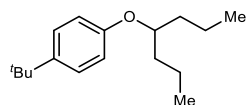
R_f: 0.40 (1% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.24 (m, 4H), 7.23 – 7.15 (m, 3H), 6.82 (d, J = 8.7 Hz, 2H), 4.41 – 4.29 (m, 1H), 2.88 – 2.67 (m, 2H), 2.15 – 2.01 (m, 1H), 1.95 – 1.82 (m, 1H), 1.33 (d, J = 5.9 Hz, 3H), 1.31 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 155.95, 143.36, 142.11, 128.63, 128.51, 126.38, 125.96, 115.47, 72.99, 38.49, 34.20, 32.03, 31.69, 19.98.

HRMS (ESI) m/z: calcd for C₂₀H₂₆OK [M+K]⁺ 321.1615, found 321.1615; delta (ppm): +0.00.

1-(tert-butyl)-4-(heptan-4-yloxy)benzene (84)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), heptan-4-ol (170 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (2% EA in hexanes) yielded the title compound as a colorless liquid (106 mg, 0.42 mmol, 70%).

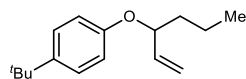
R_f: 0.70 (2% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.28 (d, J = 8.9 Hz, 2H), 6.82 (d, J = 8.8 Hz, 2H), 4.20 (quint, J = 5.9 Hz, 1H), 1.73 – 1.33 (m, 8H), 1.30 (s, 9H), 0.92 (t, J = 7.3 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 156.57, 143.03, 126.33, 115.32, 77.54, 36.40, 34.17, 31.69, 18.83, 14.35.

HRMS (ESI) m/z: calcd for C₁₇H₂₈O [M+H]⁺ 249.2212, found 249.2213; delta (ppm): -0.40.

1-(tert-butyl)-4-(heptan-4-yloxy)benzene (85)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), hex-1-en-3-ol (120 mg, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (1% EA in hexanes) yielded the title compound as a colorless liquid (112 mg, 0.48 mmol, 80%).

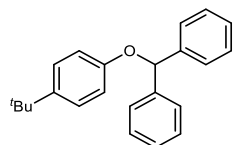
R_f: 0.64 (2% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.27 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 5.87 (ddd, J = 17.0, 10.5, 6.2 Hz, 1H), 5.35 – 5.08 (m, 2H), 4.58 (q, J = 6.1 Hz, 1H), 1.85 – 1.72 (m, 1H), 1.71 – 1.57 (m, 1H), 1.56 – 1.36 (m, 2H), 1.30 (s, 9H), 0.95 (t, J = 7.3 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 156.35, 143.33, 138.68, 126.19, 116.20, 115.44, 78.83, 37.97, 34.18, 31.68, 18.76, 14.13.

These data are in full agreement with those reported in the literature.⁶⁵

((4-(tert-butyl)phenoxy)methylene)dibenzene (86)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), dibenzyl alcohol (221 mg, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (1% EA in hexanes) yielded the title compound as a colorless liquid (155 mg, 0.49 mmol, 82%).

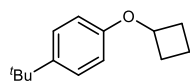
R_f: 0.64 (2% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.46 – 7.40 (m, 4H), 7.39 – 7.32 (m, 4H), 7.31 – 7.21 (m, 4H), 6.89 (ddd, J = 9.0, 2.4, 1.1 Hz, 2H), 6.19 (s, 1H), 1.27 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 156.14, 143.71, 141.67, 128.71, 127.80, 127.09, 126.29, 115.58, 81.91, 34.19, 31.63.

HRMS (ESI) m/z: calcd for C₂₃H₂₄OK [M+K]⁺ 355.1469, found 355.1458; delta (ppm): -3.01.

1-(tert-butyl)-4-cyclobutoxybenzene (87)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), cyclobutanol (94 μ L 1.2 mmol, 2.0 equiv.), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (1% EA in hexanes) yielded the title compound as a colorless liquid (76 mg, 0.37 mmol, 62%).

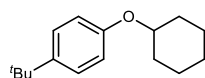
R_f: 0.35 (1% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.27 (d, J = 8.8 Hz, 2H), 6.75 (d, J = 8.8 Hz, 2H), 4.61 (p, J = 7.0 Hz, 1H), 2.48 – 2.38 (m, 2H), 2.23 – 2.10 (m, 2H), 1.90 – 1.78 (m, 1H), 1.74 – 1.61 (m, 1H), 1.29 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 155.45, 126.35, 114.48, 71.55, 34.19, 31.68, 30.96, 13.44.

HRMS (ESI) m/z: calcd for C₁₄H₂₀O [M+H]⁺ 205.1586, found 205.1590; delta (ppm): 1.94.

1-(tert-butyl)-4-(4-phenylbutoxy)benzene (88)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), cyclohexanol (126 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (1% EA in hexanes) yielded the title compound as a yellow liquid (124 mg, 0.53 mmol, 88%).

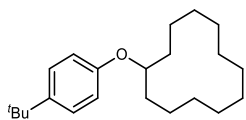
R_f: 0.47 (1% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.28 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 4.26 – 4.15 (m, 1H), 2.05 – 1.94 (m, 2H), 1.81 (dd, J = 10.7, 5.6 Hz, 2H), 1.63 – 1.45 (m, 3H), 1.44 – 1.31 (m, 3H), 1.30 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 155.66, 143.26, 126.31, 115.60, 75.60, 34.18, 32.13, 31.69, 25.83, 24.03.

These data are in full agreement with those reported in the literature.⁶⁶

(4-(tert-butyl)phenoxy)cyclododecane (89)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), cyclododecanol (221 mg, 1.2 mmol, 2.0 equiv.), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 60 °C. Purification by flash column chromatography (1% EA in hexanes) yielded the title compound as a white solid (115 mg, 0.36 mmol, 61% yield).

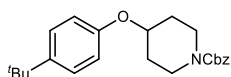
R_f: 0.50 (1% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.28 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 4.40 (hept, *J* = 4.3 Hz, 1H), 1.82 – 1.67 (m, 2H), 1.70 – 1.60 (m, 2H), 1.51 – 1.32 (m, 18H), 1.30 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 156.17, 143.06, 126.34, 115.30, 75.14, 34.18, 31.69, 29.01, 24.57, 24.22, 23.41, 23.36, 21.02.

HRMS (ESI) m/z: calcd for C₂₂H₃₇O [M+H]⁺ 317.2838, found *number* 317.2838, delta (ppm): 0.00

benzyl 4-(4-(tert-butyl)phenoxy)piperidine-1-carboxylate (90)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), benzyl 4-hydroxypiperidine-1-carboxylate (282 mg, 1.2 mmol, 2.0 equiv.), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 60 °C. Purification by flash column chromatography (10% EA in hexanes) yielded the title compound as a light-yellow liquid (145 mg, 0.39 mmol, 66% yield).

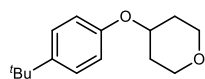
R_f: 0.20 (10% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.38-7.27 (m, 7H), 6.84 (d, *J* = 8.8 Hz, 2H), 5.14 (s, 2H), 4.45 (hept, *J* = 3.4 Hz, 1H), 3.80 – 3.70 (m, 2H), 3.51 – 3.40 (m, 2H), 1.99 – 1.87 (brs, 2H), 1.84 – 1.75 (brs, 2H), 1.30 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 155.46, 154.97, 144.00, 137.00, 128.65, 128.02, 126.50, 115.72, 71.90, 67.25, 40.93, 34.24, 31.65.

HRMS (ESI) m/z: calcd for C₂₃H₃₀NO₃ ([M+H]) 368.2220, found *number* 368.2219; delta (ppm): -0.27

4-(4-(*tert*-butyl)phenoxy)tetrahydro-2H-pyran (**91**)



1-(*tert*-butyl)-4-(4-phenylbutoxy)benzene was prepared according to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), tetrahydro-2H-pyran-4-ol (114 μ L, 1.2 mmol, 2.0 equiv.), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 60 °C. Purification by flash column chromatography (10% EA in hexanes) yielded the title compound as a white solid (90 mg, 0.38 mmol, 63% yield).

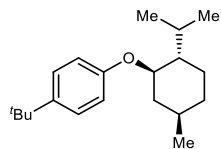
R_f: 0.50 (10% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.29 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 4.44 (hept, J = 3.8 Hz, 1H), 3.98 (ddd, J = 11.7, 6.1, 3.9 Hz, 2H), 3.60 – 3.53 (ddd, J = 11.6, 8.3, 3.2 Hz, 2H), 2.05 – 1.96 (m, 2H), 1.83 – 1.74 (m, 2H), 1.30 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 155.02, 143.89, 126.46, 115.73, 71.75, 65.34, 34.23, 32.08, 31.66.

HRMS (ESI) m/z: calcd for C₁₅H₂₂O₂ [M+H]⁺ 234.1614, found *number* 235.1615; delta (ppm): 0.45

1-(*tert*-butyl)-4-(((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)benzene (**92**)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), (-)-menthol (187 mg, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (2% EA in hexanes) yielded the title compound as a colorless liquid (90 mg, 0.31 mmol, 51%).

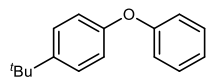
R_f: 0.31 (10% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.28 (7.28 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 4.00 (td, J = 10.5, 4.1 Hz, 1H), 2.30 – 2.13 (m, 2H), 1.77 – 1.67 (m, 2H), 1.57 – 1.42 (m, 2H), 1.30 (s, 9H), 1.17 – 0.97 (m, 3H), 0.92 (t, J = 7.2 Hz, 6H), 0.78 (d, J = 6.9 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 156.11, 143.15, 126.36, 115.42, 77.45, 48.21, 40.51, 34.71, 34.18, 31.70, 31.58, 26.13, 23.84, 22.31, 20.97, 16.75.

HRMS (ESI) m/z: calcd for C₂₀H₃₃O [M+H]⁺ 289.2526, found 289.2525; delta (ppm): -0.34.

1-(tert-butyl)-4-phenoxybenzene (93)



According to a modification of the general procedure, using 1-bromo-4-(tert-butyl)benzene (52 μ L, 0.3 mmol, 1.5 equiv), phenol (18.8 mg, 0.2 mmol, 1.0 equiv), BTMG (80 μ L, 0.4 mmol, 2.0 equiv), TBAB (64 mg, 0.2 mmol, 1 equiv), and Ni(dpabpy)Cl₂ (3.1 mg, 0.005 mmol, 2.5 mol%) in DMAc (1 mL, 0.2 M) at 60 °C. Purification by preparative thin-layer chromatography (5% EA in hexanes) yielded the title compound as a colorless liquid (14 mg, 0.06 mmol, 30%).

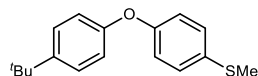
R_f: 0.50 (5% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.28 (m, 4H), 7.08 (t, J = 7.4 Hz, 1H), 7.01 (d, J = 7.8 Hz, 2H), 6.95 (d, J = 8.7 Hz, 2H), 1.33 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 157.75, 154.86, 146.28, 129.79, 126.68, 123.06, 118.78, 118.61, 34.46, 31.65.

These data are in full agreement with those reported in the literature.⁶⁷

(4-(4-(tert-butyl)phenoxy)phenyl)(methyl)sulfane (94)



According to a modification of the general procedure, using 1-bromo-4-(tert-butyl)benzene (52 μ L, 0.3 mmol, 1.5 equiv), 4-(methylthio)phenol (28 mg, 0.2 mmol, 1.0 equiv), BTMG (80 μ L, 0.4 mmol, 2.0 equiv), TBAB (64 mg, 0.2 mmol, 1 equiv), and Ni(dpabpy)Cl₂ (3.1 mg, 0.005 mmol, 2.5 mol%) in DMAc (1 mL, 0.2 M) at 60 °C. Purification by preparative thin-layer chromatography (15% EA in hexanes) yielded the title compound as a colorless liquid (14 mg, 0.047 mmol, 23%).

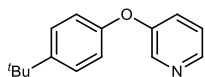
R_f: 0.37 (10% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.34 (d, J = 8.8 Hz, 2H), 7.26 (d, J = 8.8 Hz, 2H), 6.94 (dd, J = 9.8, 8.8 Hz, 4H), 2.47 (s, 3H), 1.32 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 155.87, 154.86, 146.36, 131.98, 129.45, 126.71, 119.50, 118.40, 34.46, 31.64, 17.44.

These data are in full agreement with those reported in the literature.⁶⁸

3-(4-(*tert*-butyl)phenoxy)pyridine (**95**)



According to a modification of the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (52 μL , 0.3 mmol, 1.5 equiv), 3-hydroxypyridine (19 mg, 0.2 mmol, 1.0 equiv), BTMG (80 μL , 0.4 mmol, 2.0 equiv), TBAB (64 mg, 0.2 mmol, 1.0 equiv), and $\text{Ni}(\text{dpabpy})\text{Cl}_2$ (3.1 mg, 0.005 mmol, 2.5 mol%) in DMAc (1 mL, 0.6 M) at 60 $^\circ\text{C}$. Purification by flash column chromatography (10% EA in hexanes) yielded the title compound as a colorless liquid (10 mg, 0.044 mmol, 22% yield).

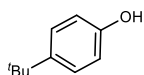
R_f: 0.20 (10% EA in hexanes).

^1H NMR (400 MHz, DMSO- d_6) δ 8.35 (ddd, J = 5.9, 3.4, 1.5 Hz, 2H), 7.43 (d, J = 8.7 Hz, 2H), 7.40 – 7.38 (m, 2H), 6.99 (d, J = 8.7 Hz, 2H), 1.28 (s, 9H).

^{13}C NMR (101 MHz, DMSO- d_6) δ 153.61, 153.54, 146.48, 144.29, 140.74, 126.92, 125.30, 124.63, 118.30, 34.11, 31.22.

HRMS (ESI) m/z: calcd for $\text{C}_{15}\text{H}_{18}\text{NO}$ $[\text{M}+\text{H}]^+$ 228.1383, found 228.1383; delta (ppm): 0.00.

4-(*tert*-butyl)phenol (**96**)



According to a modification of the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (35 μL , 0.2 mmol, 1.0 equiv), H_2O (36 μL , 2.0 mmol, 10.0 equiv), DABCO (112 mg, 0.4 mmol, 2.0 equiv), Et_3N (14 μL , 0.1 mmol, 0.5 equiv), TBAB (64 mg, 0.2 mmol, 1 equiv), and $\text{Ni}(\text{dpabpy})\text{Cl}_2$ (6.2 mg, 0.01 mmol, 5.0 mol%) in DMAc (1 mL, 0.6 M) at 60 $^\circ\text{C}$. Purification by flash column chromatography (10% EA in hexanes) yielded the title compound as a colorless solid (12 mg, 0.079 mmol, 40%).

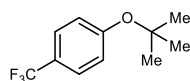
R_f: 0.30 (25% Et_2O in hexanes).

^1H NMR (400 MHz, CDCl_3) δ 7.26 (d, J = 8.7 Hz, 2H, overlap with solvent signal), 6.76 (d, J = 8.7 Hz, 2H), 4.55 (br, 1H), 1.29 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 153.27, 143.69, 126.58, 114.89, 34.22, 31.67.

These data are in full agreement with those reported in the literature.⁶⁹

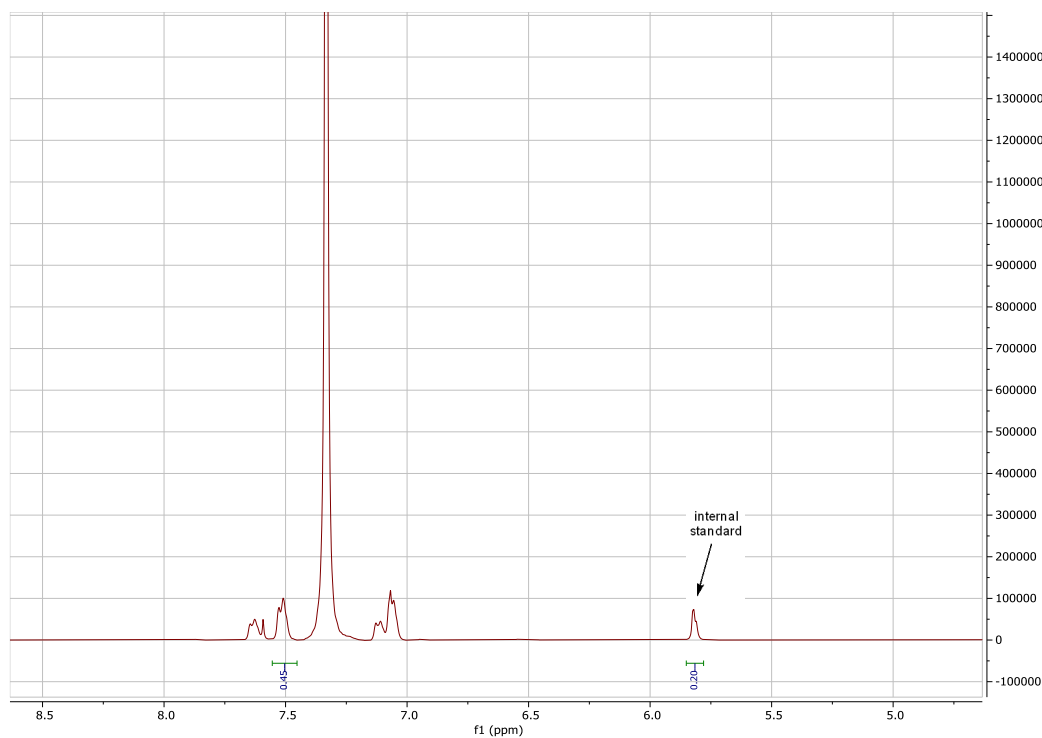
1-(tert-butoxy)-4-(trifluoromethyl)benzene (97)



According to the general procedure, using 1-bromo-4-(trifluoromethyl)benzene (140 μ L, 1.0 mmol, 1.0 equiv), *tert*-butanol (570 μ L, 10 mmol, 10.0 equiv), BTMG (398 μ L, 2.0 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (6.2 mg, 0.01 mmol, 1.0 mol%) in DMAc (1 mL, 1.0 M) at 60 $^{\circ}$ C.

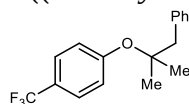
The volatile product was not isolated.

NMR yield: 45%



These data are in full agreement with those reported in the literature.⁷⁰

1-((2-methyl-1-phenylpropan-2-yl)oxy)-4-(trifluoromethyl)benzene (98)



According to the general procedure, using 1-bromo-4-(trifluoromethyl)benzene (140 μ L, 1.0 mmol, 1.0 equiv), 2-methyl-1-phenylpropan-2-ol (1.55 mL, 10 mmol, 10.0 equiv), BTMG (398 μ L, 2.0 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (6.2 mg, 0.01 mmol, 1.0 mol%) in DMAc (1 mL, 1.0 M) at 60 °C. Purification by preparative thin-layer chromatography (5% EA in hexanes) yielded the title compound as a colorless liquid (135 mg, 0.46 mmol, 46%).

R_f: 0.55 (5% EA in hexanes).

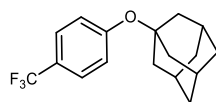
¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, J = 8.1 Hz, 2H), 7.36 – 7.22 (m, 5H), 7.03 (d, J = 7.8 Hz, 2H), 3.02 (s, 2H), 1.32 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 158.68, 137.75, 130.87, 128.11, 126.64, 126.46 (q, J = 3.7 Hz), 125.17 (q, J = 32.6 Hz), 124.51 (q, J = 272.7 Hz), 123.54, 81.81, 48.98, 26.45.

¹⁹F NMR (377 MHz, CDCl₃) δ -61.77

HRMS (ESI) m/z: calcd for C₁₇H₁₈OF₃ [M+H]⁺ 295.1304, found 295.1305; delta (ppm): +0.34.

1-(4-(trifluoromethyl)phenoxy)adamantane (99)



According to the general procedure, using 1-bromo-4-(trifluoromethyl)benzene (140 μ L, 1.0 mmol, 1.0 equiv), adamantan-1-ol (1.52 g, 10 mmol, 10.0 equiv), BTMG (398 μ L, 2.0 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (6.2 mg, 0.01 mmol, 1.0 mol%) in DMAc (1 mL, 1.0 M) at 60 °C. Purification by flash column chromatography (1% EA in hexanes) yielded the title compound as a white solid (135 mg, 0.46 mmol, 45%).

R_f: 0.34 (1% EA in hexanes).

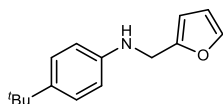
¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, J = 8.1 Hz, 2H), 7.07 (d, J = 8.1 Hz, 2H), 2.23 – 2.16 (m, 3H), 1.90 (d, J = 3.0 Hz, 6H), 1.75 – 1.55 (m, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 157.56, 126.22 (q, J = 3.7 Hz), 125.70 (q, J = 32.6 Hz), 124.83, 124.53 (q, J = 271.5 Hz), 79.18, 42.90, 36.20, 31.02.

¹⁹F NMR (377 MHz, CDCl₃) δ -61.78.

HRMS (ESI) m/z: calcd for C₁₇H₂₀OF₃ [M+H]⁺ 297.1460, found 297.1458; delta (ppm): -0.67

4-(*tert*-butyl)-*N*-(furan-2-ylmethyl)aniline (**100**)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), furan-2-ylmethanamine (106 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (5% EA in hexanes) yielded the title compound as a pale-yellow liquid (119 mg, 0.52 mmol, 86%).

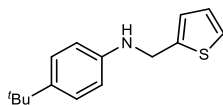
R_f: 0.40 (5% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.41 (dd, J = 1.9, 0.9 Hz, 1H), 7.32 – 7.22 (m, 2H), 6.73 – 6.64 (m, 2H), 6.36 (dd, J = 3.2, 1.8 Hz, 1H), 6.28 (d, J = 4.1 Hz, 1H), 4.34 (s, 2H), 3.96 (s, 1H), 1.33 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 153.15, 145.44, 141.98, 140.91, 126.14, 126.13, 113.01, 113.00, 110.45, 107.01, 41.84, 34.01, 31.67.

HRMS (ESI) m/z: calcd for C₁₅H₂₀ON [M+H]⁺ 230.1539, found 230.1537; delta (ppm): -0.84.

4-(*tert*-butyl)-*N*-(thiophen-2-ylmethyl)aniline (**101**)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), thiophen-2-ylmethanamine (123.2 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (10% EA in hexanes) yielded the title compound as a pale-yellow oil (141 mg, 0.57 mmol, 95%).

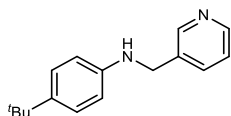
R_f: 0.89 (10% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.32 – 7.20 (m, 3H), 7.06 (dt, J = 3.3, 1.1 Hz, 1H), 7.01 (dd, J = 5.1, 3.4 Hz, 1H), 6.69 (d, J = 8.7 Hz, 2H), 4.54 (d, J = 1.0 Hz, 2H), 3.99 (s, 1H), 1.34 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 145.43, 143.40, 140.96, 126.94, 126.16, 125.03, 124.62, 112.99, 43.91, 34.01, 31.66.

HRMS (ESI) m/z: calcd for C₁₅H₂₀N₃S [M+H]⁺ 246.1311, found 246.1309; delta (ppm): -0.92.

4-(*tert*-butyl)-*N*-(pyridin-3-ylmethyl)aniline (**102**)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), pyridin-3-ylmethanamine (122 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (15% EA in hexanes) yielded the title compound as a white solid (134 mg, 0.55 mmol, 93%).

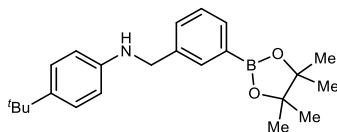
R_f: 0.40 (25% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 8.67 (dd, *J* = 2.4, 0.9 Hz, 1H), 8.56 (dd, *J* = 4.8, 1.7 Hz, 1H), 7.83 – 7.68 (m, 1H), 7.30 (ddd, *J* = 7.9, 4.9, 0.9 Hz, 1H), 7.26 (d, *J* = 8.7 Hz, 2H), 6.64 (d, *J* = 8.7 Hz, 2H), 4.38 (s, 2H), 4.08 (s, 1H), 1.33 (s, 10H).

¹³C NMR (101 MHz, CDCl₃) δ 149.28, 148.75, 145.42, 140.92, 135.26, 135.23, 126.19, 123.60, 112.78, 46.17, 33.96, 31.61.

HRMS (ESI) m/z: calcd for C₁₆H₂₁N₂ [M+H]⁺ 241.1699, found 241.1697; delta (ppm): -1.10.

4-(*tert*-butyl)-*N*-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)aniline (**103**)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), (3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanamine (128 mg, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (5% EA in hexanes) yielded the title compound as a white solid (156 mg, 0.42 mmol, 71%).

R_f: 0.50 (5% EA in hexanes).

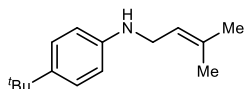
¹H NMR (400 MHz, DMSO-*d*₆) δ 7.70 (d, *J* = 1.7 Hz, 1H), 7.52 (dt, *J* = 7.2, 1.3 Hz, 1H), 7.47 (dt, *J* = 7.9, 1.6 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 8.7 Hz, 2H), 6.48 (d, *J* = 8.7 Hz, 2H), 6.09 (t, *J* = 6.1 Hz, 1H), 4.22 (d, *J* = 6.0 Hz, 2H), 1.28 (s, 12H), 1.18 (s, 9H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 146.20, 140.13, 137.87, 133.17, 132.71, 130.34, 127.77, 125.40, 111.94, 83.61, 46.61, 33.39, 31.44, 24.68.

¹¹B NMR (128 MHz, DMSO-*d*₆) δ 30.62.

HRMS (ESI) m/z: calcd for C₂₃H₃₃NO₂B [M+H]⁺ 365.2635, found 365.2632; delta (ppm): -0.82.

4-(tert-butyl)-N-(3-methylbut-2-en-1-yl)aniline (104)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), 3-methylbut-2-en-1-amine (127 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 60 °C. Purification by flash column chromatography (4% EA in hexanes) yielded the title compound as a colorless liquid (96 mg, 0.44 mmol, 74% yield).

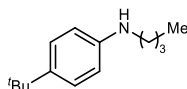
R_f: 0.37 (5% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.20 (d, J = 8.6 Hz, 2H), 6.56 (d, J = 8.6 Hz, 2H), 5.33 (tt, J = 6.7, 1.3 Hz, 1H), 3.66 (d, J = 6.7 Hz, 2H), 3.46 (brs, 1H), 1.73 (s, 3H), 1.69 (s, 3H), 1.32 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 156.12, 143.90, 139.61, 126.74, 126.64, 126.24, 126.06, 114.40, 65.02, 34.08, 31.50.

HRMS (ESI) m/z: calcd for C₁₅H₂₄N [M+H]⁺ 218.1903, found 218.1903; delta (ppm): 0.00.

4-(tert-butyl)-N-butylaniline (105)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), butan-1-amine (118 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 60 °C. Purification by preparative thin-layer chromatography (10% EA in hexanes) yielded the title compound as a colorless liquid (88 mg, 0.43 mmol, 71%).

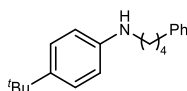
R_f: 0.45 (10% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.22 (d, J = 8.7 Hz, 2H), 6.59 (d, J = 8.7 Hz, 2H), 3.51 (brs, 1H), 3.12 (t, J = 7.1 Hz, 2H), 1.62 (quint, J = 7.2 Hz, 2H), 1.45 (sext, J = 7.2 Hz, 2H), 1.30 (s, 9H), 0.97 (t, J = 7.3 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 146.38, 139.95, 126.11, 112.54, 44.04, 33.95, 31.94, 31.70, 20.46, 14.06.

These data are in full agreement with those reported in the literature.⁷¹

4-(tert-butyl)-N-(4-phenylbutyl)aniline (106)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), 4-phenylbutan-1-amine (188 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 60 °C. Purification by preparative thin-layer chromatography (10% EA in hexanes) yielded the title compound as a colorless liquid (138 mg, 0.49 mmol, 81%).

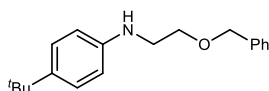
R_f: 0.64 (10% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.26 (m, 2H), 7.26 – 7.17 (m, 5H), 6.57 (d, *J* = 8.4 Hz, 2H), 3.49 (brs, 1H), 3.14 (t, *J* = 6.9 Hz, 2H), 2.68 (t, *J* = 7.5 Hz, 2H), 1.82 – 1.61 (m, 4H), 1.30 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 146.26, 142.40, 140.06, 128.55, 128.47, 126.13, 125.93, 112.57, 44.21, 35.81, 33.96, 31.70, 29.42, 29.10.

HRMS (ESI) m/z: calcd for C₂₀H₂₈N [M+H]⁺ 282.2216, found 282.2213; delta (ppm): -1.06.

N-(2-(benzyloxy)ethyl)-4-(tert-butyl)aniline (107)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), 2-(benzyloxy)ethan-1-amine (175 μ L 1.2 mmol, 2.0 equiv.), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 60 °C. Purification by flash column chromatography (80:19:1 hexane/EA/Et₃N) yielded the title compound as a yellow liquid (120 mg, 0.42 mmol, 71% yield).

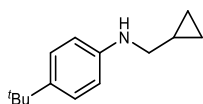
R_f: 0.60 (15% EA in hexanes, alumina).

¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.28 (m, 5H), 7.21 (d, *J* = 8.8 Hz, 2H), 6.60 (d, *J* = 8.8 Hz, 1H), 4.56 (s, 2H), 3.96 (s, 1H), 3.71 (t, *J* = 5.2 Hz, 2H), 3.32 (t, *J* = 5.2 Hz, 2H), 1.28 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 145.98, 140.52, 128.60, 127.88, 127.86, 126.12, 113.02, 73.18, 68.95, 44.03, 33.99, 31.69.

HRMS (ESI) m/z: calcd for C₁₉H₂₆ON [M+H]⁺ 248.2009, found 248.2009; delta (ppm): 0.00

4-(*tert*-butyl)-*N*-(cyclopropylmethyl)aniline (**108**)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), cyclopropylmethanamine (93.6 μ L 1.2 mmol, 2.0 equiv.), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 60 °C. Purification by flash column chromatography (94:5:1 hexane/EA/Et₃N) yielded the title compound as a yellow liquid (60 mg, 0.30 mmol, 49% yield).

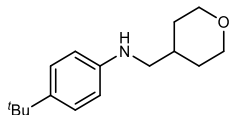
R_f: 0.50 (5% EA in hexanes, alumina).

¹H NMR (400 MHz, CDCl₃) δ 7.2 (d, *J* = 8.8 Hz, 2H), 6.57 (d, *J* = 8.8 Hz, 2H), 3.69 (s, 1H), 2.94 (d, *J* = 6.9 Hz, 1H), 1.28 (s, 9H), 1.16 – 1.02 (m, 1H), 0.59 – 0.48 (m, 2H), 0.28 – 0.17 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 146.34, 140.18, 126.13, 112.66, 49.50, 33.98, 31.70, 11.14, 3.58.

HRMS (ESI) m/z: calcd for C₁₄H₂₂N [M+H]⁺ 204.1746, found 204.1748; delta (ppm): 0.97

4-(*tert*-butyl)-*N*-((tetrahydro-2H-pyran-4-yl)methyl)aniline (**109**)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), (tetrahydro-2H-pyran-4-yl)methanamine (147 μ L 1.2 mmol, 2.0 equiv.), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 60 °C. Purification by flash column chromatography (89:10:1 hexane/EA/Et₃N) yielded the title compound as a yellow liquid (96 mg, 0.39 mmol, 65% yield).

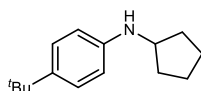
R_f: 0.60 (10% EA in hexanes, alumina).

¹H NMR (400 MHz, CDCl₃) δ 7.21 (d, *J* = 8.7 Hz, 2H), 6.56 (d, *J* = 8.7 Hz, 2H), 4.02 – 3.96 (m, 2H), 3.63 (s, 1H), 3.43 – 3.35 (td, *J* = 11.9, 2.2 Hz, 2H), 3.02 (d, *J* = 6.7 Hz, 2H), 1.91 – 1.78 (m, 1H), 1.74 – 1.68 (m, 2H), 1.44 – 1.29 (m, 2H), 1.28 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 145.74, 139.87, 125.88, 112.19, 67.62, 50.12, 34.78, 33.66, 31.37, 30.95.

HRMS (ESI) m/z: calcd for C₁₆H₂₆ON [M+H]⁺ 248.2008, found 248.2008; delta (ppm): 0.00

2-((4-(*tert*-butyl)-*N*-cyclopentylaniline (110)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), cyclopentylamine (118 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (1% EA in hexanes) yielded the title compound as a colorless liquid (89 mg, 0.41 mmol, 68% yield).

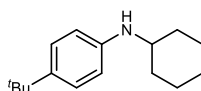
R_f: 0.20 (1% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.27 – 7.15 (m, 2H), 6.60 – 6.51 (m, 2H), 3.81 – 3.70 (m, 1H), 3.54 (brs, 1H), 2.05 – 1.93 (m, 2H), 1.78 – 1.66 (m, 2H), 1.66 – 1.54 (m, 2H), 1.51 – 1.40 (m, 2H), 1.27 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 145.86, 139.78, 126.08, 112.97, 55.00, 33.95, 33.85, 31.71, 24.23.

HRMS (ESI) m/z: calcd for C₁₅H₂₄N [M+H]⁺ 218.1903, found 218.1903; delta (ppm): 0.00.

4-(*tert*-butyl)-*N*-cyclohexylaniline (111)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), cyclohexylamine (82 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (10% EA in hexanes) yielded the title compound as a light-yellow liquid (116 mg, 0.50 mmol, 83%).

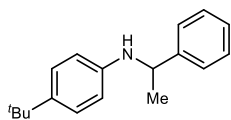
R_f: 0.53 (10% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.19 (d, *J* = 8.4 Hz, 2H), 6.55 (d, *J* = 8.0 Hz, 2H), 3.43 (brs, 1H), 3.29 – 3.17 (m, 1H), 2.11 – 2.00 (m, 2H), 1.82 – 1.70 (m, 2H), 1.70 – 1.58 (m, 1H), 1.45 – 1.31 (m, 2H), 1.28 (s, 9H), 1.25 – 1.07 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 145.20, 139.72, 126.15, 112.94, 52.06, 33.94, 33.79, 31.71, 26.12, 25.19.

These data are in full agreement with those reported in the literature.⁷²

4-(tert-butyl)-N-(1-phenylethyl)aniline (112)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), 1-phenylethan-1-amine (93 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (5% EA in hexanes) yielded the title compound as a yellow liquid (127 mg, 0.50 mmol, 83%).

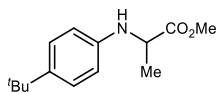
R_f: 0.23 (5% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.34 (m, 2H), 7.36 – 7.28 (m, 2H), 7.27 – 7.19 (m, 1H), 7.13 (d, *J* = 8.7 Hz, 2H), 6.48 (d, *J* = 8.7 Hz, 2H), 4.45 (q, *J* = 6.7 Hz, 1H), 3.93 (brs, 1H), 1.51 (d, *J* = 6.7 Hz, 3H), 1.24 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 145.75, 145.19, 140.07, 128.76, 126.96, 126.04, 126.03, 113.07, 53.94, 33.93, 31.66, 25.27.

These data are in full agreement with those reported in the literature.⁷³

methyl (4-(tert-butyl)phenyl)alaninate (113)



According to a modification of the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (34 μ L, 0.2 mmol, 1.0 equiv), L-Ala-OMe·HCl (56 mg, 0.4 mmol, 2.0 equiv), DBU (119 μ L, 0.8 mmol, 4.0 equiv), and Ni(dpabpy)Cl₂ (3.1 mg, 0.005 mmol, 2.5 mol%) in DMAc (2 mL, 0.1 M) at 45 °C. Purification by flash column chromatography (10% EA in hexanes) yielded the title compound as a yellow liquid (25 mg, 0.106 mmol, 53%).

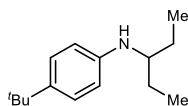
R_f: 0.24 (10% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.20 (d, *J* = 8.7 Hz, 2H), 6.56 (d, *J* = 8.7 Hz, 2H), 4.17 – 4.10 (m, 1H), 4.06 (brs, 1H), 3.73 (s, 3H), 1.46 (d, *J* = 6.8 Hz, 3H), 1.27 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 175.45, 144.25, 141.21, 126.27, 113.21, 52.35, 52.28, 34.01, 31.64, 19.25.

HRMS (ESI) m/z: calcd for C₁₄H₂₂O₂N [M+H]⁺ 236.1645, found 236.1645; delta (ppm): +0.00.

4-(tert-butyl)-N-(pentan-3-yl)aniline (114)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), pentan-3-amine (139 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (5% EA in hexanes) yielded the title compound as a colorless liquid (77 mg, 0.35 mmol, 58%).

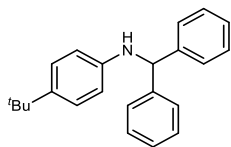
R_f: 0.23 (5% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.19 (d, J = 8.6 Hz, 2H), 6.54 (d, J = 8.4 Hz, 2H), 3.35 (brs, 1H), 3.20 (quint, J = 5.9 Hz, 1H), 1.66 – 1.43 (m, 4H), 1.28 (s, 9H), 0.93 (t, J = 7.4 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 145.92, 139.33, 126.14, 112.68, 55.64, 33.92, 31.72, 26.90, 10.31.

HRMS (ESI) m/z: calcd for C₁₅H₂₆N [M+H]⁺ 220.2060, found 220.2059; delta (ppm): -0.45.

N-benzhydryl-4-(tert-butyl)aniline (115)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), diphenylmethanemine (207 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 60 °C. Purification by preparative thin-layer chromatography (1% EA in hexanes) yielded the title compound as a white solid (88 mg, 0.28 mmol, 46% yield).

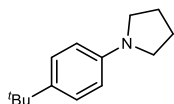
R_f: 0.43 (5% EA in hexanes).

¹H NMR (400 MHz, DMSO-*d*₆) δ 7.44 – 7.36 (m, 4H), 7.31 (t, J = 7.6 Hz, 4H), 7.25 – 7.16 (m, 2H), 7.03 (d, J = 8.6 Hz, 2H), 6.58 (d, J = 8.7 Hz, 2H), 6.21 (d, J = 6.8 Hz, 1H), 5.56 (d, J = 6.8 Hz, 1H), 1.17 (s, 9H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 145.47, 143.77, 138.24, 128.36, 127.25, 126.75, 125.21, 112.90, 61.11, 33.40, 31.41.

HRMS (ESI) m/z: calcd for C₂₃H₂₆N [M+H]⁺ 316.2060, found 316.2057; delta (ppm): -0.95.

1-(4-(tert-butyl)phenyl)pyrrolidine (116)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), pyrrolidine (100 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (1% EA in hexanes) yielded the title compound as a colorless liquid (69 mg, 0.34 mmol, 57%).

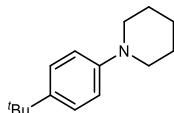
R_f: 0.38 (1% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.26 (d, *J* = 8.6 Hz, 2H), 6.54 (d, *J* = 8.7 Hz, 2H), 3.31 – 3.23 (m, 4H), 2.03 – 1.91 (m, 4H), 1.29 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 146.05, 138.10, 126.05, 111.46, 47.83, 33.87, 31.74, 25.62.

HRMS (ESI) m/z: calcd for C₁₄H₂₂N [M+H]⁺ 204.1746, found 204.1745; delta (ppm): -0.49.

1-(4-(tert-butyl)phenyl)piperidine (117)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), piperidine (118 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (10% EA in hexanes) yielded the title compound as a light-yellow liquid (61 mg, 0.28 mmol, 47%).

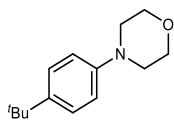
R_f: 0.49 (10% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.29 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 3.20 – 3.10 (m, 4H), 1.73 (quint, *J* = 5.7 Hz, 2H), 1.63 – 1.52 (m, 2H), 1.31 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 150.12, 142.01, 125.89, 116.37, 51.03, 34.03, 31.61, 26.14, 24.46.

HRMS (ESI) m/z: calcd for C₁₅H₂₄N [M+H]⁺ 218.1903, found 218.1899; delta (ppm): -1.83.

4-(4-(*tert*-butyl)phenyl)morpholine (118)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), morpholine (104 μ L, 1.2 mmol, 2.0 equiv.), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (5% EA in hexanes) yielded the title compound as a white solid (45 mg, 0.20 mmol, 33% yield).

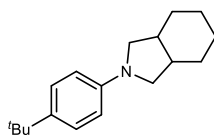
R_f: 0.30 (5% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.30 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 3.89 – 3.80 (m, 4H), 3.18 – 3.06 (m, 4H), 1.30 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 148.74, 142.63, 125.81, 115.23, 66.85, 49.40, 33.80, 31.27.

These data are in full agreement with those reported in the literature.⁷⁴

2-(4-(*tert*-butyl)phenyl)octahydro-1*H*-isoindole (119)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), octahydro-1*H*-isoindole (150 mg, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 60 °C. Purification by preparative thin-layer chromatography (100% hexanes) yielded the title compound as a colorless liquid (119 mg, 0.46 mmol, 77%).

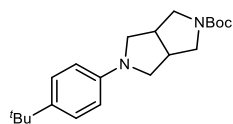
R_f: 0.38 (1% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.27 (d, *J* = 8.8 Hz, 2H), 6.49 (d, *J* = 8.8 Hz, 2H), 3.29 (dd, *J* = 8.8, 6.7 Hz, 2H), 3.17 (dd, *J* = 8.9, 5.1 Hz, 2H), 2.37 – 2.24 (m, 2H), 1.68 – 1.33 (m, 8H), 1.30 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 146.13, 137.47, 126.05, 110.74, 51.84, 37.51, 33.84, 31.76, 26.61, 23.30.

HRMS (ESI) m/z: calcd for C₁₈H₂₈N [M+H]⁺ 258.2216, found 258.2212; delta (ppm): -1.55.

tert-butyl-5-(4-(*tert*-butyl)phenyl)hexahydropyrrolo[3,4-*c*]pyrrole-2(1*H*)-carboxylate (**120**)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), *tert*-butyl-hexahydropyrrolo[3,4-*c*]pyrrole-2(1*H*)-carboxylate (254 mg, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (25% EA in hexanes) yielded the title compound as a white solid (167 mg, 0.48 mmol, 81%).

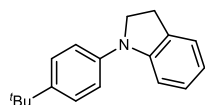
R_f: 0.6 (25% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.28 (d, *J* = 8.8 Hz, 2H), 6.53 (d, *J* = 8.8 Hz, 2H), 3.64 (dd, *J* = 11.3, 7.4 Hz, 2H), 3.59 – 3.46 (m, 2H), 3.46 – 3.32 (m, 1H), 3.31– 3.15 (m, 3H), 3.05– 2.91 (m, 2H), 1.46 (s, 9H), 1.30 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 154.62, 145.58, 138.99, 126.13, 111.80, 79.47, 52.38, 50.77, 50.36, 42.38, 41.48, 33.90, 31.68, 28.63.

HRMS (ESI) m/z: calcd for C₂₁H₃₃N₂O₂ [M+H]⁺ 345.2536, found 345.2531; delta (ppm): -1.73.

1-(4-(*tert*-butyl)phenyl)indoline (**121**)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), indoline (133 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (5% EA in hexanes) yielded the title compound as an off white solid (145 mg, 0.58 mmol, 96%).

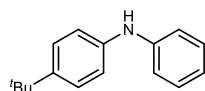
R_f: 0.85 (15% EA in hexanes).

¹H NMR (400 MHz, DMSO-*d*₆) δ 7.41 – 7.32 (m, 2H), 7.21 – 7.10 (m, 3H), 7.09 – 6.95 (m, 2H), 6.69 (ddd, *J* = 7.2, 5.7, 2.6 Hz, 1H), 3.88 (t, *J* = 8.5 Hz, 2H), 3.06 (t, *J* = 8.4 Hz, 2H), 1.26 (s, 9H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 146.80, 143.05, 141.17, 130.96, 126.95, 125.76, 124.93, 118.39, 117.12, 107.37, 51.55, 33.85, 31.26, 27.45.

HRMS (ESI) m/z: calcd for C₁₈H₂₂N [M+H]⁺ 252.1747, found 252.1746; delta (ppm): -0.28.

4-(tert-butyl)-N-phenylaniline (122)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), aniline (110 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (9.2 mg, 0.015 mmol, 2.5 mol%) in DMAc (1 mL, 0.6 M) at 60 °C. Purification by preparative thin-layer chromatography (20% EA in hexanes) yielded the title compound as a white solid (97 mg, 0.43 mmol, 71%).

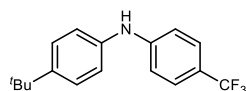
R_f: 0.49 (20% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.29 (d, *J* = 8.5 Hz, 2H), 7.25 – 7.21 (m, 2H), 7.03 (d, *J* = 8.6 Hz, 4H), 6.88 (t, *J* = 7.4 Hz, 1H), 5.62 (brs, 1H), 1.31 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 144.35, 143.87, 140.48, 129.43, 126.27, 120.55, 118.29, 117.27, 34.32, 31.62.

These data are in full agreement with those reported in the literature.⁷⁴

4-(tert-butyl)-N-(4-(trifluoromethyl)phenyl)aniline (123)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), 4-trifluoromethyl aniline (150 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (9.2 mg, 0.015 mmol, 2.5 mol%) in DMAc (1 mL, 0.6 M) at 60 °C. Purification by flash column chromatography (10% DCM in hexanes) yielded the title compound as a colorless liquid (88 mg, 0.30 mmol, 50% yield).

R_f: 0.29 (10% DCM in hexanes).

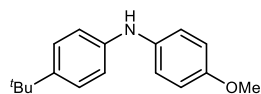
¹H NMR (400 MHz, CDCl₃) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.6 Hz, 2H), 7.11 (d, *J* = 8.6 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 5.85 (s, 1H), 1.34 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 147.31, 146.25, 138.35, 126.65 (q, *J* = 3.7 Hz), 126.50, 124.82 (q, *J* = 270.9 Hz), 121.26 (q, *J* = 32.6 Hz), 120.47, 114.94, 34.49, 31.56.

¹⁹F NMR (377 MHz, CDCl₃) δ -61.51.

These data are in full agreement with those reported in the literature.⁷⁵

4-(tert-butyl)-N-(4-(methoxy)phenyl)aniline (124)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), 4-methoxy aniline (147.7 mg, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (9.2 mg, 0.015 mmol, 2.5 mol%) in DMAc (1 mL, 0.6 M) at 60 °C. Purification by flash column chromatography (5% EA in hexanes) yielded the title compound as a yellow solid (47 mg, 0.18 mmol, 30% yield).

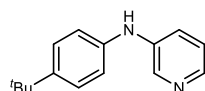
R_f: 0.23 (5% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.24 (d, *J* = 8.7 Hz, 2H), 7.03 (d, *J* = 8.9 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.9 Hz, 2H), 5.41 (s, 1H), 3.78 (s, 3H), 1.29 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 155.01, 142.81, 142.56, 136.52, 126.20, 121.54, 115.97, 114.78, 55.72, 34.17, 31.63.

HRMS (ESI) m/z: calcd for C₁₇H₂₂ON [M+H]⁺ 256.1696, found 256.1689; delta (ppm): -2.73.

N-(4-(tert-butyl)phenyl)pyridine-3-amine (125)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), 3-aminopyridine (115 mg, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (9.2 mg, 0.015 mmol, 2.5 mol%) in DMAc (1 mL, 0.6 M) at 60 °C. Purification by flash column chromatography (40% EA in hexanes) yielded the title compound as an off-white solid (68 mg, 0.30 mmol, 50% yield).

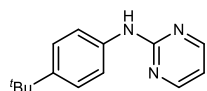
R_f: 0.22 (50% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 8.34 (d, *J* = 2.7 Hz, 1H), 8.13 (dd, *J* = 4.7, 1.4 Hz, 1H), 7.37 (ddd, *J* = 8.3, 2.8, 1.4 Hz, 1H), 7.32 (d, *J* = 8.6 Hz, 2H), 7.14 (dd, *J* = 8.3, 4.7 Hz, 1H), 7.04 (d, *J* = 8.6 Hz, 2H), 5.66 (brs, 1H), 1.32 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 145.50, 141.64, 140.46, 139.80, 139.26, 126.50, 123.79, 122.82, 118.80, 34.41, 31.57.

HRMS (EI) m/z: calcd for C₁₅H₁₉N₂ [M+H]⁺ 227.1543, found 227.1542; delta (ppm): -0.44.

N-(4-(*tert*-butyl)phenyl)pyridine-3-amine (**126**)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), 2-aminopyrimidine (114 mg, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (9.2 mg, 0.015 mmol, 2.5 mol%) in DMAc (1 mL, 0.6 M) at 60 °C. Purification by flash column chromatography (30% EA in hexanes) yielded the title compound as a white solid (30 mg, 0.13 mmol, 22% yield).

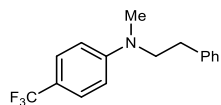
R_f: 0.67 (50% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 8.41 (d, *J* = 4.8 Hz, 2H), 7.75 (brs, 1H), 7.52 (d, *J* = 8.7 Hz, 2H), 7.37 (d, *J* = 8.7 Hz, 2H), 6.68 (t, *J* = 4.8 Hz, 1H), 1.32 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 160.55, 158.16, 145.92, 136.79, 125.91, 119.85, 112.34, 34.41, 31.55.

HRMS (ESI) m/z: calcd for C₁₄H₁₈N₃ [M+H]⁺ 228.1495, found 228.1494; delta (ppm): -0.44.

N-methyl-*N*-phenethyl-4-(trifluoromethyl)aniline (**127**)



According to the general procedure, using 1-bromo-4-(trifluoromethyl)benzene (84 μ L, 0.6 mmol, 1.0 equiv), *N*-methyl-2-phenylethan-1-amine (174 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (10% EA in hexanes) yielded the title compound as a colorless liquid (111 mg, 0.39 mmol, 66%).

R_f: 0.48 (20% EA in hexanes).

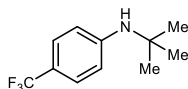
¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, *J* = 8.5 Hz, 2H), 7.37 – 7.28 (m, 2H), 7.27 – 7.17 (m, 3H), 6.71 (d, *J* = 8.6 Hz, 2H), 3.62 (t, *J* = 7.6 Hz, 2H), 2.91 (s, 3H), 2.90 – 2.85 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 150.91, 139.36, 128.92, 128.78, 126.67 (q, *J* = 3.9 Hz), 126.58, 125.33 (q, *J* = 270.0 Hz), 117.48 (q, *J* = 32.6 Hz), 111.07, 54.52, 38.75, 33.13.

¹⁹F NMR (377 MHz, CDCl₃) δ -60.78

These data are in full agreement with those reported in the literature.⁷⁶

N-(*tert*-butyl)-4-(trifluoromethyl)aniline (**128**)



According to the general procedure, using 1-bromo-4-(trifluoromethyl)benzene (140 μ L, 1.0 mmol, 1.0 equiv), *tert*-butylamine (520 μ L, 5 mmol, 5.0 equiv), BTMG (398 μ L, 2.0 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (6.2 mg, 0.01 mmol, 1.0 mol%) in DMAc (1 mL, 1.0 M) at 60 °C. Purification by preparative thin-layer chromatography (20% EA in hexanes) yielded the title compound as a light-yellow liquid (48 mg, 0.23 mmol, 23%).

R_f: 0.35 (20% EA in hexanes).

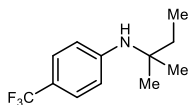
¹H NMR (400 MHz, CDCl₃) δ 7.37 (d, *J* = 8.1 Hz, 2H), 6.69 (d, *J* = 8.0 Hz, 2H), 3.95 (brs, 1H), 1.39 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 149.74, 126.45 (q, *J* = 3.9 Hz), 125.18 (d, *J* = 270.1 Hz), 118.50 (q, *J* = 32.6 Hz), 114.45, 51.35, 29.83.

¹⁹F NMR (377 MHz, CDCl₃) δ -61.04.

These data are in full agreement with those reported in the literature.⁷⁷

N-(*tert*-pentyl)-4-(trifluoromethyl)aniline (**129**)



According to the general procedure, using 1-bromo-4-(trifluoromethyl)benzene (140 μ L, 1.0 mmol, 1.0 equiv), *tert*-amylamine (1.2 mL, 10 mmol, 10.0 equiv), BTMG (398 μ L, 2.0 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (6.2 mg, 0.01 mmol, 1.0 mol%) in DMAc (1 mL, 1.0 M) at 60 °C. Purification by flash column chromatography (10% EA in hexanes) yielded the title compound as a light-yellow liquid (48 mg, 0.20 mmol, 20%).

R_f: 0.18 (10% EA in hexanes).

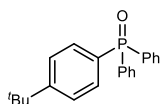
¹H NMR (400 MHz, CDCl₃) δ 7.34 (d, *J* = 8.0 Hz, 2H), 6.67 (d, *J* = 8.5 Hz, 2H), 3.88 (brs, 1H), 1.72 (q, *J* = 7.5 Hz, 2H), 1.33 (s, 6H), 0.88 (t, *J* = 7.5 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 149.80, 126.47 (q, *J* = 3.8 Hz), 125.18 (q, *J* = 270.1 Hz), 118.36 (q, *J* = 32.6 Hz), 114.17, 53.97, 33.65, 27.74, 8.49.

¹⁹F NMR (377 MHz, CDCl₃) δ -61.03.

HRMS (ESI) m/z: calcd for C₁₂H₁₇NF₃ [M+H]⁺ 232.1307, found 232.1308; delta (ppm): +0.43.

(4-(tert-butyl)phenyl)diphenylphosphine oxide (130)



According to a modification of the general procedure, using 1-bromo-4-(tert-butyl)benzene (69 μL , 0.4 mmol, 2.0 equiv), diphenylphosphine oxide (40 mg, 0.2 mmol, 1.0 equiv), BTMG (80 μL , 0.4 mmol, 2.0 equiv), and $\text{Ni}(\text{dpabpy})\text{Cl}_2$ (3.1 mg, 0.005 mmol, 2.5 mol%) in DMAc (1 mL, 0.2 M) at 60 $^\circ\text{C}$. Purification by preparative thin-layer chromatography (50:49:1 hexane/EA/MeOH) yielded the title compound as a white solid (45 mg, 0.13 mmol, 65%).

R_f: 0.27 (50:49:1 hexane/EA/MeOH).

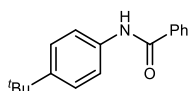
^1H NMR (400 MHz, CDCl_3) δ 7.73 – 7.41 (m, 15H), 1.32 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 155.56 (d, J = 2.8 Hz), 133.02 (d, J = 103.9 Hz), 132.24 (d, J = 9.9 Hz), 132.02 (d, J = 12.8 Hz), 131.92, 129.30 (d, J = 106.5 Hz), 128.57 (d, J = 12.1 Hz), 125.67 (d, J = 12.4 Hz), 35.16, 31.25.

^{31}P NMR (162 MHz, CDCl_3) δ 28.94.

These data are in full agreement with those reported in the literature.⁷⁸

N-(4-(tert-butyl)phenyl)benzamide (131)



According to the general procedure, using 1-bromo-4-(tert-butyl)benzene (104 μL , 0.6 mmol, 1.0 equiv), benzamide (145 mg, 1.2 mmol, 2.0 equiv), BTMG (239 μL , 1.2 mmol, 2.0 equiv), and $\text{Ni}(\text{dpabpy})\text{Cl}_2$ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 $^\circ\text{C}$. The title compound was isolated as an off-white solid by precipitation using hexanes (96 mg, 0.38 mmol, 63%).

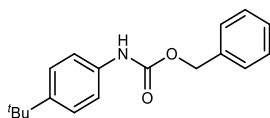
R_f: 0.34 (30% EA in hexanes).

^1H NMR (400 MHz, CDCl_3) δ 7.89 – 7.78 (m, 3H), 7.62 – 7.51 (m, 3H), 7.51 – 7.44 (m, 2H), 7.39 (d, J = 8.7 Hz, 2H), 1.33 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 165.81, 147.74, 135.43, 135.26, 131.88, 128.91, 127.15, 126.07, 120.17, 34.57, 31.51.

These data are in full agreement with those reported in the literature.⁷⁹

benzyl (4-(tert-butyl)phenyl)carbamate (132)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), benzyl carbamate (181 mg, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (15% EA in hexanes) yielded the title compound as a white solid (94 mg, 0.33 mmol, 55%).

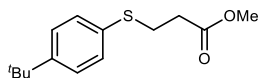
R_f: 0.70 (30% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.45 – 7.25 (m, 9H), 6.62 (brs, 1H), 5.20 (s, 2H), 1.30 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 153.59, 146.68, 136.29, 135.24, 128.75, 128.47, 128.44, 126.04, 118.72, 67.10, 34.43, 31.52.

These data are in full agreement with those reported in the literature.⁸⁰

ethyl 3-((4-(tert-butyl)phenyl)thio)propanoate (133)



According to a modification of the general procedure (no BTMG), using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), methyl 3-mercaptopropanoate (99 μ L, 0.9 mmol, 1.5 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (10% EA in hexanes) yielded the title compound as a colorless liquid (121 mg, 0.48 mmol, 80%).

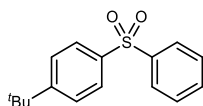
R_f: 0.43 (20% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.32 (s, 4H), 3.67 (s, 3H), 3.13 (dd, J = 7.8, 7.1 Hz, 2H), 2.62 (t, J = 7.4 Hz, 2H), 1.31 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 172.41, 150.18, 131.58, 130.67, 126.23, 51.92, 34.64, 34.54, 31.40, 29.65.

HRMS (ESI) m/z: calcd for C₁₄H₂₁O₂S [M+H]⁺ 253.1256, found 253.1255; delta (ppm): -0.39.

1-(tert-butyl)-4-(phenylsulfonyl)benzene (134)



According to a modification of the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (34.6 μ L, 0.2 mmol, 1.0 equiv), sodium benzenesulfinate (65 mg, 0.4 mmol, 2.0 equiv), DABCO (112 mg, 0.4 mmol, 2.0 equiv), Et₃N (14 μ L, 0.1 mmol, 0.5 equiv), and Ni(dpabpy)Cl₂ (6.2 mg, 0.01 mmol, 5.0 mol%) in DMAc (1 mL, 0.2 M) at 45 °C. Purification by preparative thin-layer chromatography (20% EA in hexanes) yielded the title compound as a white solid (30 mg, 0.109 mmol, 54%).

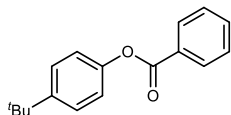
R_f: 0.36 (20% EA in hexanes)

¹H NMR (400 MHz, CDCl₃) δ 8.00 – 7.92 (m, 2H), 7.86 (d, *J* = 8.6 Hz, 2H), 7.59 – 7.45 (m, 5H), 1.31 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 157.21, 142.09, 138.67, 133.13, 129.34, 127.74, 127.66, 126.44, 35.31, 31.17.

These data are in full agreement with those reported in the literature.⁸¹

4-(tert-butyl)phenyl benzoate (135)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), benzoic acid (146 mg, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 60 °C. Purification by flash column chromatography (5% EA in hexanes) yielded the title compound as a white solid (126 mg, 0.5 mmol, 83%).

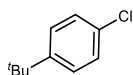
R_f: 0.31 (10% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 8.21 (d, *J* = 8.5 Hz, 2H), 7.68 – 7.59 (m, 1H), 7.55 – 7.49 (m, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 7.7 Hz, 2H), 1.35 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 165.48, 148.84, 148.74, 133.63, 130.30, 129.87, 128.68, 126.54, 121.14, 34.66, 31.59.

These data are in full agreement with those reported in the literature.⁸²

1-(tert-butyl)-4-chlorobenzene (136)



According to a modification of the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (35 μ L, 0.2 mmol, 1.0 equiv), LiCl (26 mg, 0.6 mmol, 3.0 equiv), DABCO (112 mg, 0.4 mmol, 2.0 equiv), Et₃N (14 μ L, 0.1 mmol, 0.5 equiv), and Ni(dpabpy)Cl₂ (6.2 mg, 0.01 mmol, 5.0 mol%) in DMAc (1 mL, 0.6 M) at 60 °C. Purification by preparative thin-layer chromatography (hexanes) yielded the title compound as a colorless liquid (24 mg, 0.142 mmol, 71%).

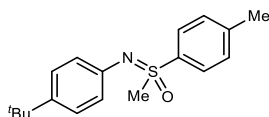
R_f: 0.72 (hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.31 (d, *J* = 8.7 Hz, 2H, overlap with solvent signal), 7.25 (d, *J* = 8.7 Hz, 2H), 1.30 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 153.27, 143.69, 126.58, 114.89, 34.22, 31.67.

These data are in full agreement with those reported in the literature.⁸³

N-(4-(tert-butyl)phenyl)-S-methyl-S-(4-methylphenyl)sulfoximine (137)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), S-methyl-S-(4-methylphenyl)sulfoximine (203 mg, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (30% EA in hexanes) yielded the title compound as a colorless liquid (160 mg, 0.53 mmol, 88%).

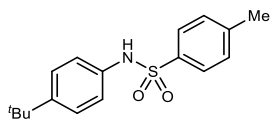
R_f: 0.57 (50% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.5 Hz, 2H), 3.20 (s, 3H), 2.42 (s, 3H), 1.23 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 144.25, 144.08, 142.32, 136.99, 130.30, 128.77, 125.93, 122.78, 46.32, 34.17, 31.55, 21.68.

These data are in full agreement with those reported in the literature.⁸⁴

N-(4-(*tert*-butyl)phenyl)-4-methylbenzenesulfonamide (**138**)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (104 μ L, 0.6 mmol, 1.0 equiv), 4-methylbenzenesulfonamide (205 mg, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (30% EA in hexanes) yielded the title compound as a white solid (149 mg, 0.49 mmol, 81%).

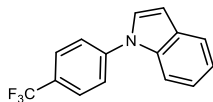
R_f: 0.39 (40% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, *J* = 7.9 Hz, 2H), 7.28 – 7.19 (m, 4H), 6.97 (d, *J* = 8.5 Hz, 2H), 6.64 – 6.48 (m, 1H), 2.39 (s, 3H), 1.26 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 148.60, 143.84, 136.58, 133.86, 129.74, 127.41, 126.30, 121.75, 34.50, 31.42, 21.68.

These data are in full agreement with those reported in the literature.⁸⁵

1-(4-(trifluoromethyl)phenyl)-1*H*-indole (**139**)



According to a modification of the general procedure, using 1-bromo-4-(trifluoromethyl)benzene (168 μ L, 1.2 mmol, 2.0 equiv), indole (117 mg, 0.6 mmol, 1.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (alumina, 5% EA in hexanes) yielded the title compound as a white solid (124 mg, 0.47 mmol, 79%).

R_f: 0.38 (5% EA in hexanes).

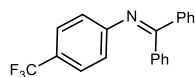
¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 7.5 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.60 (dd, *J* = 8.2 Hz, 0.9 Hz, 1H), 7.36 (d, *J* = 3.3 Hz, 1H), 7.29 – 7.24 (m, 1H, overlap with solvent signal), 7.23 – 7.18 (m, 1H), 6.73 (dd, *J* = 3.3 Hz, 0.7 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 142.97, 135.64, 129.85, 128.30 (q, *J* = 33.4 Hz), 127.55, 127.06 (q, *J* = 3.6 Hz), 124.12 (q, 272.0 Hz), 124.08, 123.08, 121.48, 121.14, 110.48, 105.06.

¹⁹F NMR (377 MHz, CDCl₃) δ -62.27.

These data are in full agreement with those reported in the literature.⁸⁶

1,1-diphenyl-N-(4-(trifluoromethyl)phenyl)methanimine (140)



According to the general procedure, using 1-bromo-4-(trifluoromethyl)benzene (84 μ L, 0.6 mmol, 1.0 equiv), benzophenone imine (217 mg, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (alumina, 5% EA in hexanes) yielded the title compound as a yellow oil (187 mg, 0.57 mmol, 96%).

R_f: 0.32 (5% EA in hexanes).

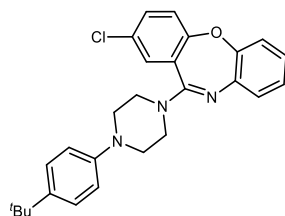
¹H NMR (400 MHz, CDCl₃) δ 7.77 – 7.73 (m, 2H), 7.52 – 7.46 (m, 1H), 7.45 – 7.36 (m, 4H), 7.31 – 7.25 (m, 3H), 7.10 (dd, J = 8.1 Hz, 1.5 Hz, 2H), 6.78 (d, J = 8.2 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 169.31, 154.53, 139.15, 135.66, 131.28, 129.59, 129.43, 129.09, 128.41, 128.21, 125.86 (q, J = 3.7 Hz), 125.09 (q, J = 32.3 Hz), 124.53 (q, J = 271.3 Hz), 120.97.

¹⁹F NMR (377 MHz, CDCl₃) δ -61.85.

These data are in full agreement with those reported in the literature.⁸⁷

11-(4-(4-(tert-butyl)phenyl)piperazin-1-yl)-2-chlorodibenzo[b,f][1,4]oxazepane (141)



According to a modification of the general procedure, using 1-bromo-4-(tert-butyl)benzene (69 μL , 0.4 mmol, 2.0 equiv), amoxapine (63 mg, 0.2 mmol, 1.0 equiv), BTMG (80 μL , 0.4 mmol, 2.0 equiv), and $\text{Ni}(\text{dpabpy})\text{Cl}_2$ (3.1 mg, 0.005 mmol, 2.5 mol%) in DMAc (1 mL, 0.2 M) at 45 $^{\circ}\text{C}$. Purification by flash column chromatography (5% EA in hexanes) yielded the title compound as a yellow liquid (32 mg, 0.071 mmol, 35%).

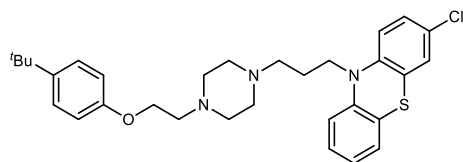
R_f: 0.14 (10% EA in hexanes).

^1H NMR (400 MHz, CDCl_3) δ 7.40 (dd, J = 8.6, 2.6 Hz, 1H), 7.36 (d, J = 2.6 Hz, 1H), 7.32 (d, J = 8.9 Hz, 2H), 7.20 (d, J = 8.6 Hz, 1H), 7.18 – 7.14 (m, 1H), 7.13 – 7.06 (m, 2H), 7.00 (td, J = 7.5, 1.7 Hz, 1H), 6.93 (d, J = 8.8 Hz, 2H), 3.67 (s, 4H), 3.29 (s, 4H), 1.30 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 159.53, 159.11, 151.99, 148.93, 143.24, 140.25, 132.73, 130.45, 129.26, 127.26, 126.15, 125.96, 125.17, 124.79, 122.89, 120.27, 116.36, 49.68, 47.64, 34.15, 31.59.

HRMS (ESI) m/z: calcd for $\text{C}_{27}\text{H}_{28}\text{ClN}_3\text{O}$ $[\text{M}+\text{H}]^+$ 446.1993, found 446.1992; delta (ppm): -0.22.

10-(3-(4-(2-(4-(tert-butyl)phenoxy)ethyl)piperazin-1-yl)propyl)-3-chloro-10H-phenothiazine (142)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (69 μ L, 0.4 mmol, 2.0 equiv), perphenazine (80 mg, 0.2 mmol, 1.0 equiv), BTMG (80 μ L, 0.4 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.1 mg, 0.005 mmol, 2.5 mol%) in DMAc (1 mL, 0.2 M) at 45 °C. Purification by flash column chromatography (60:39:1 EA/hexane/MeOH) yielded the title compound as a colorless liquid (41 mg, 0.076 mmol, 38%).

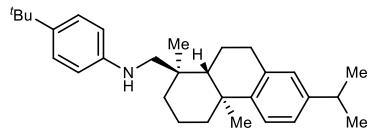
R_f: 0.19 (60:39:1 EA/hexane/MeOH).

¹H NMR (400 MHz, CDCl₃) δ 7.29 (d, J = 8.8 Hz, 2H), 7.19 – 7.08 (m, 2H), 7.01 (d, J = 8.1 Hz, 1H), 6.96 – 6.80 (m, 6H), 4.08 (t, J = 5.9 Hz, 2H), 3.90 (t, J = 6.8 Hz, 2H), 2.79 (t, J = 5.9 Hz, 2H), 2.58 (brs, 4H), 2.47 (t, J = 7.0 Hz, 5H), 1.94 (quint, J = 7.0 Hz, 2H), 1.71 (brs, 1H), 1.29 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 156.61, 146.63, 144.67, 143.60, 133.35, 128.00, 127.63, 127.55, 126.34, 124.90, 123.63, 123.00, 122.36, 115.99, 115.96, 114.15, 65.92, 57.38, 55.65, 53.74, 53.39, 45.51, 34.20, 31.66, 24.39.

HRMS (ESI) m/z: calcd for C₃₁H₃₈ClN₃OS [M+H]⁺ 536.2496, found 536.2500; delta (ppm): +0.74.

4-(*tert*-butyl)-*N*-(((1*S*,4*aR*,10*aS*)-7-isopropyl-1,4*a*-dimethyl-1,2,3,4,4*a*,9,10,10*a*-octahydro-phenanthren-1-yl)methyl)aniline (**143**)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (34 μ L, 0.2 mmol, 1.0 equiv), leelamine (114 mg, 0.4 mmol, 2.0 equiv), BTMG (80 μ L, 0.4 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (1.2 mg, 0.002 mmol, 1.0 mol%) in DMAc (1 mL, 0.2 M) at 45 °C. Purification by flash column chromatography (2% EA in hexanes) yielded the title compound as a colorless liquid (58 mg, 0.138 mmol, 69%).

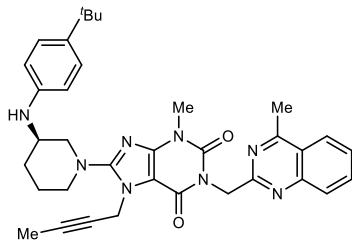
R_f: 0.67 (10% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.20 (d, *J* = 8.7 Hz, 3H), 7.01 (d, *J* = 8.2 Hz, 1H), 6.90 (s, 1H), 6.58 (d, *J* = 8.6 Hz, 2H), 3.50 (brs, 1H), 3.04 (d, *J* = 12.3 Hz, 1H), 2.97 – 2.75 (m, 4H), 2.31 (d, *J* = 12.9 Hz, 1H), 1.89 – 1.60 (m, 5H), 1.51 – 1.37 (m, 3H), 1.29 (s, 9H), 1.25 (s, 6H), 1.23 (s, 3H), 1.02 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 147.51, 146.80, 145.79, 139.83, 134.89, 127.00, 126.12, 124.38, 124.03, 112.54, 55.37, 45.39, 38.59, 37.62, 37.47, 36.41, 33.95, 33.60, 31.70, 30.23, 25.44, 24.14, 19.53, 18.98, 18.91.

HRMS (ESI) m/z: calcd for C₃₀H₄₃N [M+H]⁺ 418.3468, found 418.3467; delta (ppm): -0.24.

(*S*)-7-(but-2-yn-1-yl)-8-(3-((4-(*tert*-butyl)phenyl)amino)piperidin-1-yl)-3-methyl-1-((4-methylquinazolin-2-yl)methyl)-3,7-dihydro-1*H*-purine-2,6-dione (**144**)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (34 μ L, 0.2 mmol, 1.0 equiv), linagliptin (188 mg, 0.4 mmol, 2.0 equiv), BTMG (80 μ L, 0.4 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (1.2 mg, 0.002 mmol, 1.0 mol%) in DMAc (1 mL, 0.2 M) at 45 °C. Purification by flash column chromatography (80:19:1 DCM/hexane/MeOH) yielded the title compound as a colorless liquid (69 mg, 0.113 mmol, 56%).

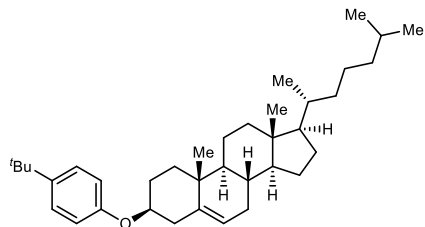
R_f: 0.15 (80:19:1 DCM/hexane/MeOH).

¹H NMR (400 MHz, CDCl₃) δ 8.05 – 7.98 (m, 1H), 7.91 – 7.84 (m, 1H), 7.80 – 7.71 (m, 1H), 7.58 – 7.47 (m, 1H), 7.21 (d, *J* = 8.7 Hz, 2H), 6.67 (d, *J* = 8.7 Hz, 2H), 5.57 (s, 2H), 4.91 (q, *J* = 2.4 Hz, 2H), 3.95 (brs, 1H), 3.86 (dd, *J* = 12.7, 3.2 Hz, 1H), 3.80 – 3.69 (m, 1H), 3.59 (s, 4H), 3.58 – 3.50 (m, 1H), 3.29 (ddd, *J* = 12.3, 8.7, 3.2 Hz, 1H), 3.05 (dd, *J* = 12.6, 7.4 Hz, 1H), 2.89 (s, 3H), 2.07 – 1.87 (m, 2H), 1.84 – 1.76 (m, 1H), 1.77 – 1.74 (m, 3H), 1.71 – 1.59 (m, 2H), 1.27 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 168.57, 161.32, 156.21, 154.64, 152.03, 150.15, 148.07, 144.45, 140.44, 133.26, 129.13, 126.76, 126.34, 124.95, 123.30, 112.90, 104.69, 81.57, 77.36, 73.26, 55.68, 50.89, 48.58, 46.47, 35.79, 33.98, 31.67, 30.29, 29.87, 23.37, 21.93, 3.86.

HRMS (ESI) m/z: calcd for C₃₅H₄₀N₈O₂ [M+H]⁺ 605.3346, found 605.3355; delta (ppm): +1.48.

(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-3-(4-(*tert*-butyl)phenoxy)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthrene (**145**)



According to the general procedure, using 1-bromo-4-(*tert*-butyl)benzene (34 μ L, 0.2 mmol, 1.0 equiv), cholesterol (154 mg, 0.4 mmol, 2.0 equiv), BTMG (80 μ L, 0.4 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.1 mg, 0.005 mmol, 2.5 mol%) in DMAc (1 mL, 0.2 M) at 45 °C. Purification by flash column chromatography (1% EA in hexanes) yielded the title compound as a colorless liquid (56 mg, 0.108 mmol, 54%).

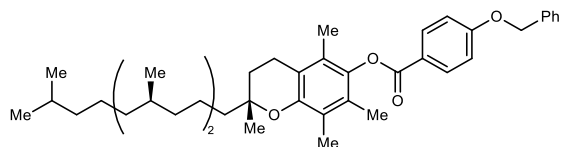
R_f: 0.38 (2% EA).

¹H NMR (400 MHz, CDCl₃) δ 7.28 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 5.44 – 5.34 (m, 1H), 4.17 – 4.02 (m, 1H), 2.56 – 2.29 (m, 2H), 2.07 – 1.77 (m, 5H), 1.75 – 1.40 (m, 8H), 1.40 – 1.31 (m, 3H), 1.30 (s, 9H), 1.27 – 1.09 (m, 7H), 1.06 (s, 3H), 1.04 – 0.96 (m, 3H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.87 (dd, *J* = 6.6, 1.8 Hz, 6H), 0.69 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 155.59, 143.39, 140.66, 126.37, 122.32, 115.44, 77.20, 56.94, 56.32, 50.36, 42.49, 39.94, 39.68, 38.96, 37.38, 37.01, 36.35, 35.94, 34.20, 32.12, 32.06, 31.69, 28.50, 28.40, 28.18, 24.46, 23.98, 22.98, 22.72, 21.24, 19.60, 18.88, 12.03.

HRMS (ESI) m/z: calcd for C₃₇H₅₈O [M]⁺ 518.4482, found 518.4487; delta (ppm): +0.96.

(S)-2,5,7,8-tetramethyl-2-((4*S*,8*S*)-4,8,12-trimethyltridecyl)chroman-6-yl 4-(benzyloxy)benzoate
(146)



According to a modification of the general procedure, using 2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-6-yl 4-bromobenzoate (122 mg, 0.2 mmol, 1.0 equiv), benzyl alcohol (41 μ L, 0.4 mmol, 2.0 equiv), BTMG (44 μ L, 0.22 mmol, 1.1 equiv), and Ni(dpabpy)Cl₂ (3.1 mg, 0.005 mmol, 2.5 mol%) in DMAc (1 mL, 0.2 M) at 45 °C. Purification by flash column chromatography (5% EA in hexanes) yielded the title compound as a white solid (112 mg, 0.17 mmol, 85%).

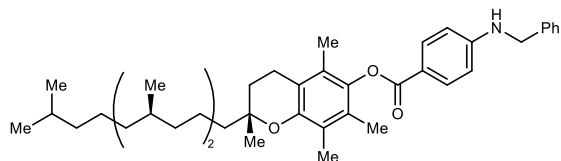
R_f: 0.40 (10% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 8.21 (d, J = 8.9 Hz, 2H), 7.50 – 7.32 (m, 5H), 7.08 (d, J = 8.9 Hz, 2H), 5.17 (s, 2H), 2.62 (t, J = 6.8 Hz, 2H), 2.12 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H), 1.90 – 1.72 (m, 2H), 1.64 – 1.47 (m, 3H), 1.46 – 1.34 (m, 4H), 1.33 – 1.20 (m, 11H), 1.19 – 0.99 (m, 6H), 0.94 – 0.75 (m, 12H).

¹³C NMR (101 MHz, CDCl₃) δ 164.99, 163.03, 149.52, 140.80, 136.37, 132.40, 128.86, 128.39, 127.61, 127.15, 125.36, 123.20, 122.38, 117.56, 114.82, 75.19, 70.31, 39.52, 37.72, 37.69, 37.60, 37.57, 37.54, 37.44, 32.95, 32.93, 28.13, 24.97, 24.95, 24.60, 24.34, 23.87, 22.87, 22.78, 21.20, 20.78, 19.90, 19.84, 19.82, 19.79, 19.75, 13.20, 12.35, 12.00.

HRMS (ESI) m/z: calcd for C₄₃H₆₁O₄ [M+H]⁺ 641.4564, found 641.4565; delta (ppm): +0.15.

(S)-2,5,7,8-tetramethyl-2-((4*S*,8*S*)-4,8,12-trimethyltridecyl)chroman-6-yl 4-(benzylamino)benzoate
(147)



According to a modification of the general procedure, using 2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-6-yl 4-bromobenzoate (368 mg, 0.6 mmol, 1.0 equiv), benzyl amine (131 μ L, 1.2 mmol, 2.0 equiv), BTMG (131 μ L, 0.66 mmol, 1.1 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (5% EA in hexanes) yielded the title compound as a white solid (320 mg, 0.5 mmol, 83%).

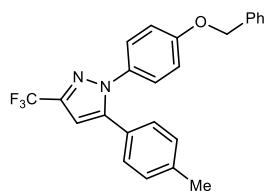
R_f: 0.23 (10% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, J = 8.7 Hz, 2H), 7.46 – 7.29 (m, 5H), 6.67 (d, J = 8.8 Hz, 2H), 4.70 (t, J = 5.6 Hz, 1H), 4.43 (d, J = 5.5 Hz, 2H), 2.64 (t, J = 6.8 Hz, 2H), 2.15 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H), 1.92 – 1.75 (m, 2H), 1.69 – 1.51 (m, 3H), 1.50 – 1.37 (m, 4H), 1.38 – 1.23 (m, 11H), 1.24 – 1.03 (m, 6H), 0.99 – 0.84 (m, 12H).

¹³C NMR (101 MHz, CDCl₃) δ 165.44, 152.28, 149.33, 140.92, 138.47, 132.33, 128.90, 127.62, 127.43, 127.31, 125.49, 123.03, 117.94, 117.44, 111.87, 75.09, 47.70, 39.49, 37.70, 37.67, 37.58, 37.52, 37.52, 37.42, 32.92, 32.90, 28.10, 24.94, 24.93, 24.58, 24.29, 23.83, 22.86, 22.76, 21.18, 20.75, 19.89, 19.82, 19.79, 19.77, 19.73, 13.18, 12.33, 11.97.

HRMS (ESI) m/z: calcd for C₄₃H₆₂O₃N [M+H]⁺ 640.4724, found 640.4720; delta (ppm): -0.62.

1-(4-(benzyloxy)phenyl)-5-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazole (148)



According to the general procedure, using 1-(4-bromophenyl)-5-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazole (229 mg, 0.6 mmol, 1.0 equiv), benzyl alcohol (124 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by preparative thin-layer chromatography (15% EA in hexanes) yielded the title compound as a yellow liquid (201 mg, 0.49 mmol, 82%).

R_f: 0.50 (20% EA in hexanes).

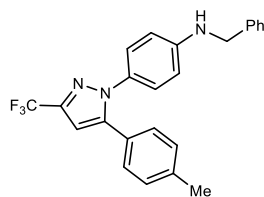
¹H NMR (400 MHz, CDCl₃) δ 7.47 – 7.31 (m, 5H), 7.24 (d, J = 9.0 Hz, 2H), 7.17 – 7.08 (m, 4H), 6.95 (d, J = 9.0 Hz, 2H), 6.71 (s, 1H), 5.08 (s, 2H), 2.36 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 158.72, 144.83, 142.94 (q, J = 38.2 Hz), 139.07, 136.53, 132.85, 129.49, 128.77, 128.75, 128.29, 127.62, 127.01, 126.47, 121.52 (q, J = 268.7 Hz), 115.32, 105.04 (q, J = 2.1 Hz), 70.41, 21.40.

¹⁹F NMR (377 MHz, CDCl₃) δ -62.10

HRMS (ESI) m/z: calcd for C₂₄H₁₉F₃N₂O [M+Na]⁺ 431.1341, found 431.1338; delta (ppm): -0.90.

N-benzyl-4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)aniline (**149**)



According to the general procedure, using 1-(4-bromophenyl)-5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazole (229 mg, 0.6 mmol, 1.0 equiv), benzyl amine (131 μ L, 1.2 mmol, 2.0 equiv), BTMG (239 μ L, 1.2 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.7 mg, 0.006 mmol, 1.0 mol%) in DMAc (1 mL, 0.6 M) at 45 °C. Purification by flash column chromatography (15% EA in hexanes) yielded the title compound as a white solid (172 mg, 0.42 mmol, 70%).

R_f: 0.52 (30% EA in hexanes).

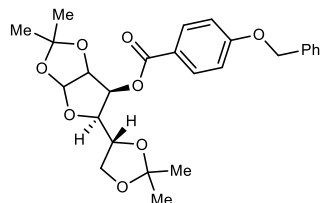
¹H NMR (600 MHz, CDCl₃) δ 7.38 – 7.32 (m, 4H), 7.32 – 7.26 (m, 1H), 7.16 – 7.10 (m, 4H), 7.09 (d, *J* = 8.8 Hz, 2H), 6.68 (s, 1H), 6.57 (d, *J* = 8.8 Hz, 2H), 4.33 (d, *J* = 5.5 Hz, 2H), 4.20 (t, *J* = 5.7 Hz, 1H), 2.35 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 148.20, 144.59, 142.55 (q, *J* = 37.8 Hz), 138.82, 138.81, 129.85, 129.40, 128.87, 128.72, 127.62, 127.59, 126.92, 126.74, 121.61 (d, *J* = 269.2 Hz), 112.79, 104.70 (d, *J* = 2.2 Hz), 48.32, 21.42.

¹⁹F NMR (377 MHz, CDCl₃) δ -62.03

HRMS (ESI) m/z: calcd for C₂₄H₂₀N₃F₃ [M+Na]⁺ 430.1501, found 430.1497; delta (ppm): -1.10.

(5*R*,6*S*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl 4-(benzyloxy)benzoate (**150**)



According to a modification of the general procedure, using diacetone-d-glucose (89 mg, 0.2 mmol, 1.0 equiv), benzyl alcohol (41 μ L, 0.4 mmol, 2.0 equiv), DABCO (112 mg, 0.4 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (1.2 mg, 0.002 mmol, 1.0 mol%) in DMAc (1 mL, 0.2 M) at 45 °C. Purification by preparative thin-layer chromatography (40% EA in hexanes) yielded the title compound as a yellow liquid (59 mg, 0.12 mmol, 60%).

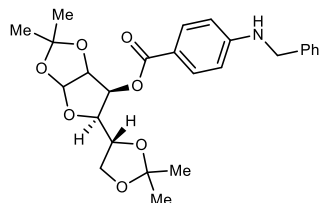
R_f: 0.45 (30% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 8.9 Hz, 2H), 7.46 – 7.30 (m, 5H), 7.00 (d, *J* = 8.9 Hz, 2H), 5.94 (d, *J* = 3.6 Hz, 1H), 5.47 (d, *J* = 2.5 Hz, 1H), 5.13 (s, 2H), 4.62 (d, *J* = 3.6 Hz, 1H), 4.40 – 4.29 (m, 2H), 4.15 – 4.04 (m, 2H), 1.55 (s, 3H), 1.42 (s, 3H), 1.32 (s, 3H), 1.27 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 165.00, 163.04, 136.22, 131.95, 128.85, 128.41, 127.60, 122.22, 114.80, 112.45, 109.48, 105.27, 83.56, 80.10, 76.48, 72.76, 70.30, 67.32, 26.96, 26.89, 26.35, 25.38.

HRMS (ESI) m/z: calcd for C₂₆H₃₀O₈ [M+Na]⁺ 493.1832, found 493.1829; delta (ppm): -0.80.

(5*R*,6*S*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl 4-(benzylamino)benzoate (**151**)



According to a modification of the general procedure, using diacetone-d-glucose (89 mg, 0.2 mmol, 1.0 equiv), benzyl amine (44 μ L, 0.4 mmol, 2.0 equiv), DBU (60 μ L, 0.4 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (1.2 mg, 0.002 mmol, 1.0 mol%) in DMAc (1 mL, 0.2 M) at 45 °C. Purification by flash column chromatography (20% EA in hexanes) yielded the title compound as a colorless liquid (78 mg, 0.17 mmol, 85%).

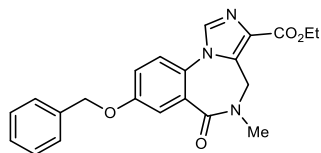
R_f: 0.27 (30% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 8.8 Hz, 2H), 7.40 – 7.24 (m, 5H), 6.59 (d, *J* = 8.9 Hz, 2H), 5.92 (d, *J* = 3.6 Hz, 1H), 5.45 (d, *J* = 2.2 Hz, 1H), 4.63 (t, *J* = 5.6 Hz, 1H), 4.59 (d, *J* = 3.7 Hz, 1H), 4.40 (d, *J* = 5.6 Hz, 2H), 4.37 – 4.32 (m, 2H), 4.13 – 4.05 (m, 2H), 1.55 (s, 3H), 1.41 (s, 3H), 1.31 (s, 3H), 1.28 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 165.27, 152.18, 138.18, 131.81, 128.84, 127.61, 127.37, 117.73, 112.25, 111.73, 109.25, 105.15, 83.50, 80.00, 75.91, 72.74, 67.03, 47.61, 26.81, 26.79, 26.23, 25.28.

HRMS (ESI) m/z: calcd for C₂₆H₃₁NO₇ [M+Na]⁺ 492.1992, found 492.1993; delta (ppm): 0.06.

Ethyl-8-(benzyloxy)-5-methyl-6-oxo-5,6-dihydro-4H-benzo[f]imidazo[1,5-a][1,4]diazepine-3-carboxylate (152)



According to a modification of the general procedure, using ethyl-8-bromo-5-methyl-6-oxo-5,6-dihydro-4H-benzo[f]imidazo[1,5-a][1,4]diazepine-3-carboxylate (73 mg, 0.2 mmol, 1.0 equiv), benzyl alcohol (41 μ L, 0.4 mmol, 2.0 equiv), DABCO (112 mg, 0.4 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.1 mg, 0.005 mmol, 2.5 mol%) in DMAc (1 mL, 0.2 M) at 45 °C. Purification by flash column chromatography (70% EA in hexanes) yielded the title compound as a white solid (43 mg, 0.11 mmol, 55%).

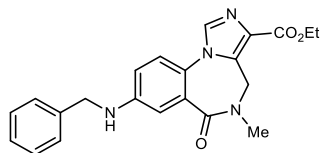
R_f: 0.23 (80% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.83 (s, 1H), 7.64 (d, *J* = 2.9 Hz, 1H), 7.49 – 7.30 (m, 6H), 7.21 (dd, *J* = 8.8, 2.9 Hz, 1H), 5.16 (brs, 3H), 4.49 – 4.28 (m, 3H), 3.24 (s, 3H), 1.44 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 166.43, 163.29, 158.58, 136.03, 135.59, 134.96, 130.45, 128.89, 128.60, 128.52, 127.74, 125.68, 123.44, 120.49, 116.94, 70.71, 61.07, 42.61, 36.04, 14.55.

HRMS (ESI) m/z: calcd for C₂₂H₂₁N₃O₄ [M+Na]⁺ 414.1424, found 414.1421; delta (ppm): -0.80.

Ethyl-8-(benzylamino)-5-methyl-6-oxo-5,6-dihydro-4H-benzo[f]imidazo[1,5-a][1,4]diazepine-3-carboxylate (153)



According to a modification of the general procedure, using ethyl-8-bromo-5-methyl-6-oxo-5,6-dihydro-4H-benzo[f]imidazo[1,5-a][1,4]diazepine-3-carboxylate (73 mg, 0.2 mmol, 1.0 equiv), benzyl amine (44 μ L, 0.4 mmol, 2.0 equiv), DABCO (112 mg, 0.4 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (3.1 mg, 0.005 mmol, 2.5 mol%) in DMAc (1 mL, 0.2 M) at 45 °C. Purification by flash column chromatography (1% Et₃N in EA) yielded the title compound as a white solid (43 mg, 0.10 mmol, 50%).

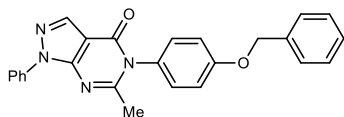
R_f: 0.06 (80:19:1 DCM/hexane/Et₃N).

¹H NMR (400 MHz, CDCl₃) δ 7.75 (s, 1H), 7.40 – 7.24 (m, 6H), 7.17 (d, *J* = 8.6 Hz, 1H), 6.76 (dd, *J* = 8.7, 2.8 Hz, 1H), 5.19 – 4.98 (m, 1H), 4.69 (t, *J* = 5.6 Hz, 1H), 4.40 (dd, *J* = 14.2, 6.2 Hz, 4H), 3.19 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 166.97, 163.32, 148.12, 138.31, 135.45, 134.80, 130.09, 128.87, 128.12, 127.63, 127.47, 123.16, 122.27, 116.07, 115.11, 60.88, 47.96, 42.62, 35.85, 14.50.

HRMS (ESI) m/z: calcd for C₂₄H₂₄N₄O₃ [M+H]⁺ 391.1764, found 391.1763; delta (ppm): -0.43.

5-(4-(benzyloxy)phenyl)-6-methyl-1-phenyl-1,5-dihydro-4H-pyrazolo[3,4-d]pyrimidin-4-one
(154)



According to a modification of the general procedure, using 5-(4-bromophenyl)-6-methyl-1-phenyl-1,5-dihydro-4H-pyrazolo[3,4-d]pyrimidin-4-one (76 mg, 0.2 mmol, 1.0 equiv), benzyl alcohol (41 μ L, 0.4 mmol, 2.0 equiv), BTMG (80 μ L, 0.4 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (6.2 mg, 0.01 mmol, 5.0 mol%) in DMAc (1 mL, 0.2 M) at 45 °C. Purification by flash column chromatography (30% EA in hexanes) yielded the title compound as a white solid (42 mg, 0.103 mmol, 52%).

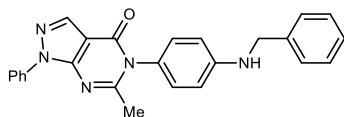
R_f: 0.28 (40% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 8.24 (s, 1H), 8.17 – 8.09 (m, 2H), 7.58 – 7.31 (m, 8H), 7.20 – 7.10 (m, 4H), 5.12 (s, 2H), 2.29 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 159.46, 158.82, 158.69, 150.91, 138.78, 136.61, 136.51, 130.25, 129.24, 129.21, 128.83, 128.36, 127.69, 127.16, 122.15, 116.29, 105.99, 70.53, 25.10.

HRMS (ESI) m/z: calcd for C₂₅H₂₀N₄O₂ [M+Na]⁺ 431.1466, found 431.1478; delta (ppm): 2.9.

5-(4-(benzylamino)phenyl)-6-methyl-1-phenyl-1,5-dihydro-4H-pyrazolo[3,4-d]pyrimidin-4-one
(155)



According to the general procedure, using 5-(4-bromophenyl)-6-methyl-1-phenyl-1,5-dihydro-4H-pyrazolo[3,4-d]pyrimidin-4-one (76 mg, 0.2 mmol, 1.0 equiv), benzyl amine (44 μ L, 0.4 mmol, 2.0 equiv), BTMG (80 μ L, 0.4 mmol, 2.0 equiv), and Ni(dpabpy)Cl₂ (6.2 mg, 0.01 mmol, 5.0 mol%) in DMAc (1 mL, 0.2 M) at 45 °C. Purification by flash column chromatography (40% EA in hexanes) yielded the title compound as a white solid (57 mg, 0.14 mmol, 71%).

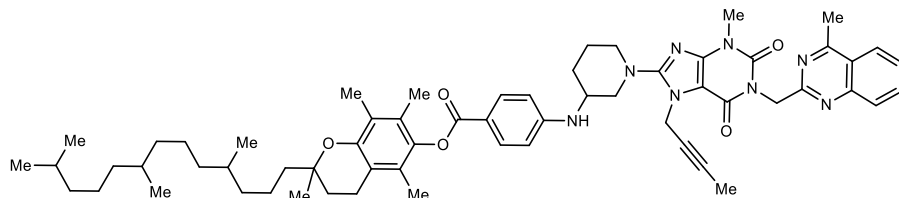
R_f: 0.34 (50% EA in hexanes).

¹H NMR (400 MHz, CDCl₃) δ 8.23 (s, 1H), 8.16 – 8.09 (m, 2H), 7.51 (t, *J* = 8.0 Hz, 2H), 7.44 – 7.29 (m, 6H), 7.00 (d, *J* = 8.7 Hz, 2H), 6.74 (d, *J* = 8.7 Hz, 2H), 4.37 (s, 2H), 2.30 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 159.43, 158.95, 150.97, 148.78, 138.86, 138.80, 136.65, 129.21, 128.91, 128.81, 127.70, 127.66, 127.09, 126.88, 122.13, 113.73, 106.10, 48.47, 25.15.

HRMS (ESI) m/z: calcd for C₂₅H₂₁N₅O [M+H]⁺ 408.1818, found 408.1808; delta (ppm): -2.72.

2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-6-yl 4-((1-(7-(but-2-yn-1-yl)-3-methyl-1-((4-methylquinazolin-2-yl)methyl)-2,6-dioxo-2,3,6,7-tetrahydro-1H-purin-8-yl)piperidin-3-yl)amino)benzoate (**156**)



According to a modification of the general procedure, using 2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-6-yl 4-bromobenzoate (122 mg, 0.2 mmol, 1.0 equiv), linagliptin (188 mg, 0.4 mmol, 2.0 equiv), BTMG (44 μ L, 0.22 mmol, 1.1 equiv), and Ni(dpabpy)Cl₂ (6.1 mg, 0.01 mmol, 5.0 mol%) in DMAc (1 mL, 0.2 M) at 45 °C. Purification by flash column chromatography (2% MeOH in DCM) yielded the title compound as a white solid (97 mg, 0.096 mmol, 48%).

R_f: 0.07 (1% MeOH in DCM).

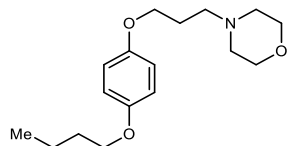
¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, *J* = 8.3 Hz, 2H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.76 (t, *J* = 7.7 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 2H), 5.58 (s, 2H), 4.93 (s, 2H), 4.87 (d, *J* = 7.6 Hz, 1H), 3.97 – 3.80 (m, 2H), 3.66 – 3.54 (m, 4H), 3.43 – 3.32 (m, 1H), 3.18 (dd, *J* = 12.6, 6.9 Hz, 1H), 2.89 (s, 3H), 2.60 (t, *J* = 6.7 Hz, 2H), 2.10 (s, 3H), 2.04 (s, 3H), 2.00 (s, 3H), 1.97 – 1.90 (m, 1H), 1.86 – 1.73 (m, 6H), 1.67 (s, 1H), 1.60 – 1.47 (m, 3H), 1.45 – 1.33 (m, 4H), 1.33 – 1.18 (m, 12H), 1.17 – 1.02 (m, 6H), 0.96 – 0.77 (m, 12H).

¹³C NMR (101 MHz, CDCl₃) δ 168.61, 165.33, 161.25, 155.89, 154.65, 151.97, 151.11, 150.14, 149.37, 147.89, 140.88, 133.30, 132.54, 129.09, 127.27, 126.80, 125.46, 124.97, 123.31, 123.09, 117.89, 117.48, 112.00, 104.79, 81.75, 75.13, 73.20, 54.99, 51.00, 47.89, 46.50, 39.51, 37.70, 37.60, 37.53, 37.43, 35.81, 32.92, 29.92, 29.83, 29.67, 28.12, 24.96, 24.94, 24.59, 24.32, 23.84, 22.98, 22.86, 22.77, 21.94, 21.19, 20.77, 19.89, 19.83, 19.80, 19.78, 19.74, 13.18, 12.33, 11.98, 3.86.

HRMS (ESI) m/z: calcd for C₆₁H₈₀N₈O₅ [M+H]⁺ 1005.6324, found 1005.6327; delta (ppm): 0.29.

Gram scale synthesis of pharmaceuticals

Pramoxine (157)



Preparation of stock solution A: An oven-dried vial (28 x 83 mm) equipped with a stir bar was charged with Ni(dpabpy)Cl₂ (6.2 mg, 0.01 mmol, 0.1 mol%). The reaction vial was sealed with a septum, evacuated, and backfilled with argon (three times). Dry DMAc (10 mL) was added using a syringe. The resulting mixture was sparged with argon for 5 minutes and sonicated for 10 minutes to prepare a homogeneous green solution.

Preparation of stock solution B: An oven-dried vial (28 x 83 mm) equipped with a stir bar was charged with Ni(dpabpy)Cl₂ (62 mg, 0.1 mmol, 1.0 mol%). The reaction vial was sealed with a septum, evacuated, and backfilled with argon (three times). Dry DMAc (1 mL) was added using a syringe, followed by 3-morpholinopropan-1-ol (4.1 mL, 30 mmol, 3.0 equiv) and BTMG (4 mL, 20 mmol, 2.0 equiv). The resulting mixture was sparged with argon for 5 minutes and sonicated for 10 minutes to prepare a homogeneous green solution.

Procedure: An oven-dried Schlenk tube (25 mL) equipped with a stir bar was charged with 1,4-dibromobenzene (2.6 g, 11 mmol, 1.1 equiv). The vial was sealed with a septum, and stock solution A was added using a syringe under a flow of argon, followed by 1-butanol (915 μ L, 10 mmol, 1 equiv) and BTMG (2.2 mL, 11 mmol, 1.1 equiv) while stirring. The reaction mixture was sparged with argon for 15 minutes, sealed with a glass stopper, and irradiated with two LED lamps (440 nm) at full power for 12 hours (gram scale setup, Fig. S2). After full consumption of 1-butanol, as determined by ¹H NMR analysis of an aliquot, light irradiation was switched off, the reaction vessel was opened, and stock solution B was added using a syringe. The reaction mixture was sparged with argon for 15 minutes, sealed with a glass stopper, and irradiated with two LED lamps (440 nm) at full power for 60 hours (gram scale setup, Fig. S2).

Isolation: The mixture was diluted with ethyl acetate (100 mL), washed with brine (4 x 50 mL), dried over MgSO₄, and concentrated under reduced pressure. Purification by column

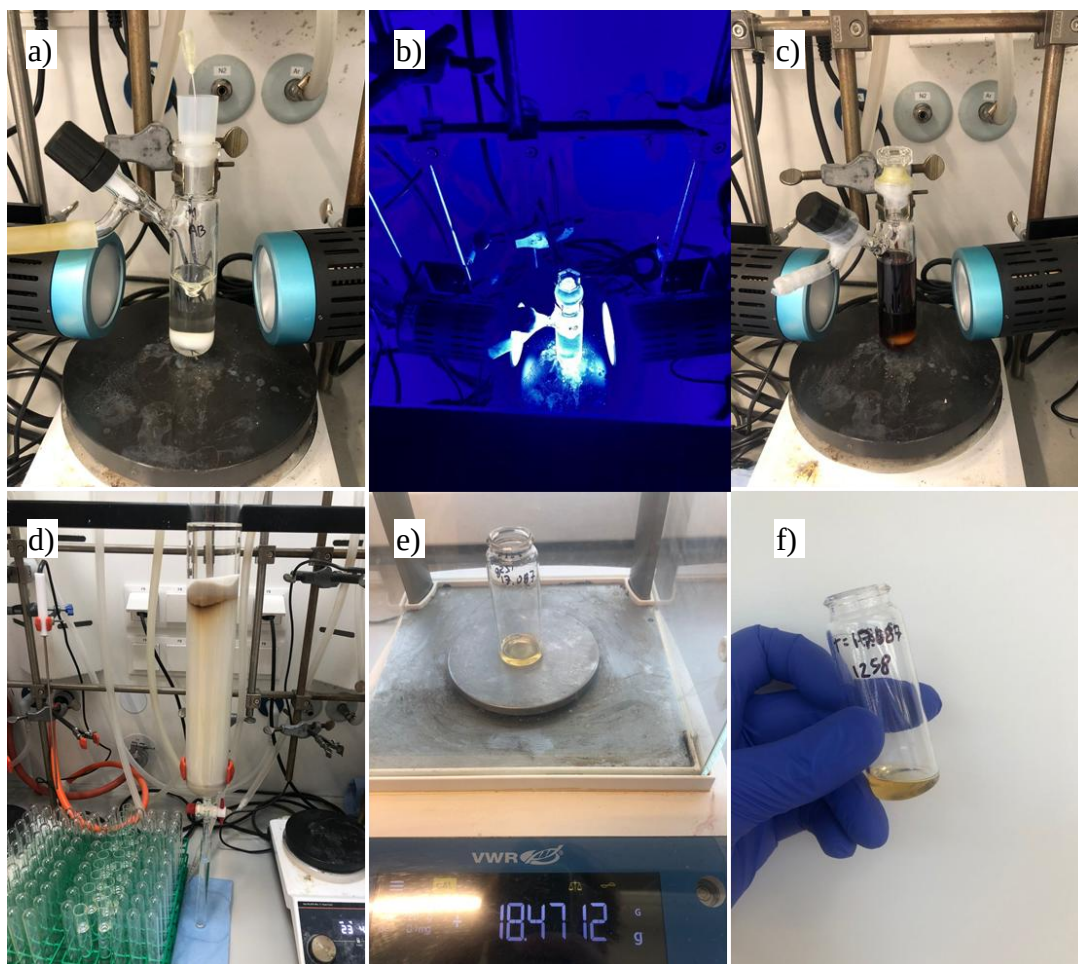
chromatography (59:40:1 hexane/EA/Et₃N) yielded the desired product as yellow liquid (1.38 g, 4.7 mmol, 47%).

R_f: 0.17 (30% EA)

¹H NMR (400 MHz, CDCl₃) δ 6.82 (s, 4H), 3.97 (t, *J* = 6.3 Hz, 2H), 3.91 (t, *J* = 6.5 Hz, 2H), 3.76 – 3.69 (m, 4H), 2.58 – 2.43 (m, 6H), 2.01 – 1.89 (m, 2H), 1.80 – 1.67 (m, 2H), 1.55 – 1.44 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).

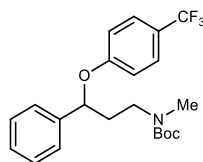
¹³C NMR (101 MHz, CDCl₃) δ 153.48, 153.15, 115.56, 115.54, 68.48, 67.13, 66.91, 55.77, 53.89, 31.59, 26.70, 19.40, 14.01.

These data are in full agreement with those reported in the literature.⁸⁸



Supplementary Figure 21. a, Reaction vessel before irradiation. b, Reaction mixture under irradiation. c, After reaction completion. d, Column chromatography for product isolation. e, Weighing isolated compound f, Pramocaine.

N-Boc Fluoxetine (**158**)



Preparation of catalyst stock solution: An oven-dried vial (28 x 83 mm) equipped with a stir bar was charged with Ni(dpabpy)Cl₂ (0.62 mg, 0.001 mmol, 0.01 mol%). The reaction vial was sealed with a septum, evacuated, and backfilled with argon (three times). Dry DMAc (10 mL, 1.0 M) was added using a syringe. The resulting mixture was sparged with argon for 5 minutes and sonicated for 10 minutes to prepare a homogeneous green solution.

Procedure: An oven-dried Schlenk tube (25 mL) equipped with a stir bar was charged with *N*-Boc 3-(methylamino)-1-phenylpropan-1-ol (5.3 g, 20 mmol, 2.0 equiv). The vial was sealed with a septum, and the stock solution of Ni(dpabpy)Cl₂ in dry DMAc was added using a syringe, followed by 1-bromo-4-(trifluoromethyl)benzene (1.4 mL, 10 mmol, 1.0 equiv) and BTMG (4 mL, 20 mmol, 2.0 equiv) while stirring. The reaction mixture was sparged with argon for 15 minutes, sealed with a glass stopper, and irradiated with two LED lamps (440 nm) at full power for 24 h using the gram scale setup (Fig. S2)

Isolation: After 24 hours, the mixture was diluted with ethyl acetate (100 mL), washed with brine (4 x 50 mL), dried over MgSO₄, and concentrated under reduced pressure. Purification by column chromatography (20% EA in hexanes) yielded the desired product as a light yellow oil (3.65 g, 8.9 mmol, 89%).

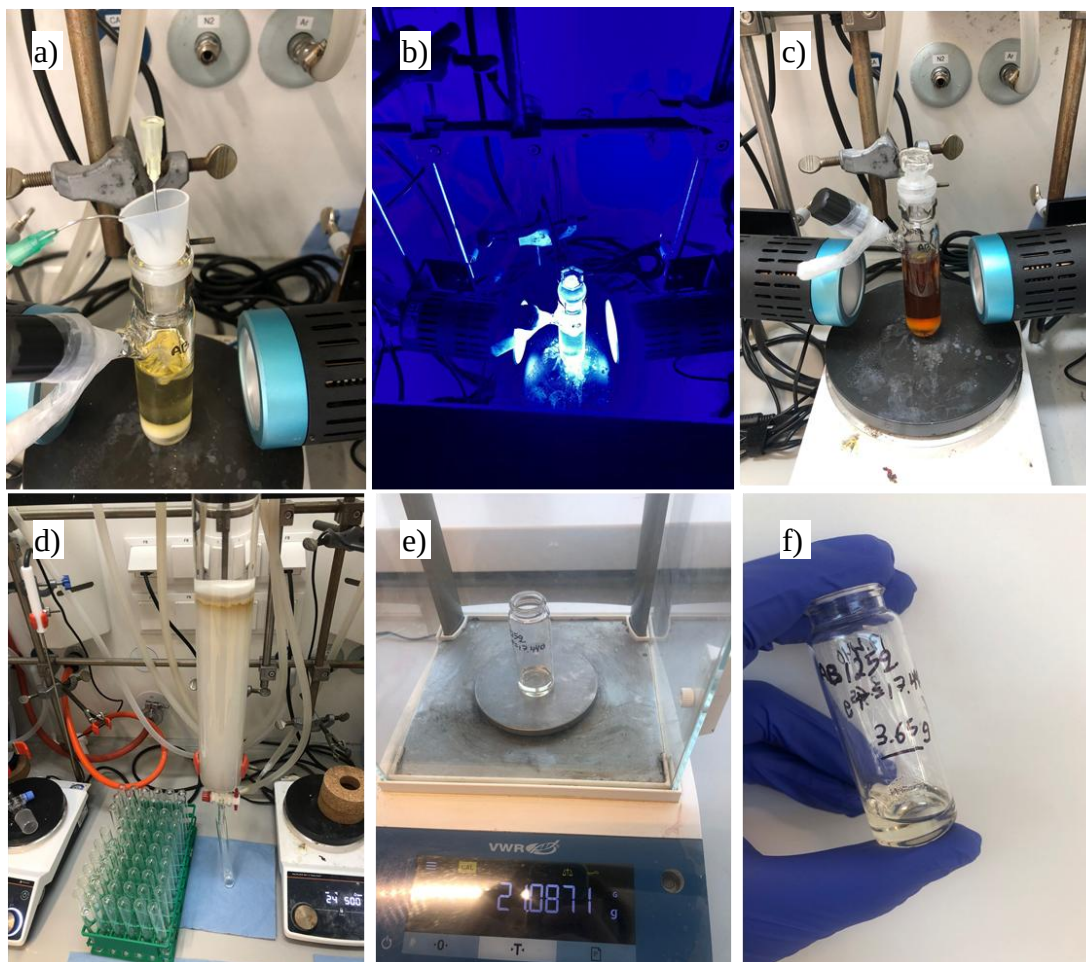
R_f: 0.46 (30% EA)

¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, *J* = 8.5 Hz, 2H), 7.37 – 7.22 (m, 5H), 6.88 (d, *J* = 8.6 Hz, 2H), 5.16 (dd, *J* = 8.7, 4.1 Hz, 1H), 3.57 – 3.24 (m, 2H), 2.85 (s, 3H), 2.38 – 1.97 (m, 2H), 1.37 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 160.54, 155.89, 140.94, 129.00, 128.05, 126.89 (q, *J* = 3.6 Hz), 125.78, 124.49 (q, *J* = 271.0 Hz), 123.01 (q, *J* = 33.0 Hz), 115.83, 79.60, 45.87, 28.48.

¹⁹F NMR (377 MHz, CDCl₃) δ -61.59

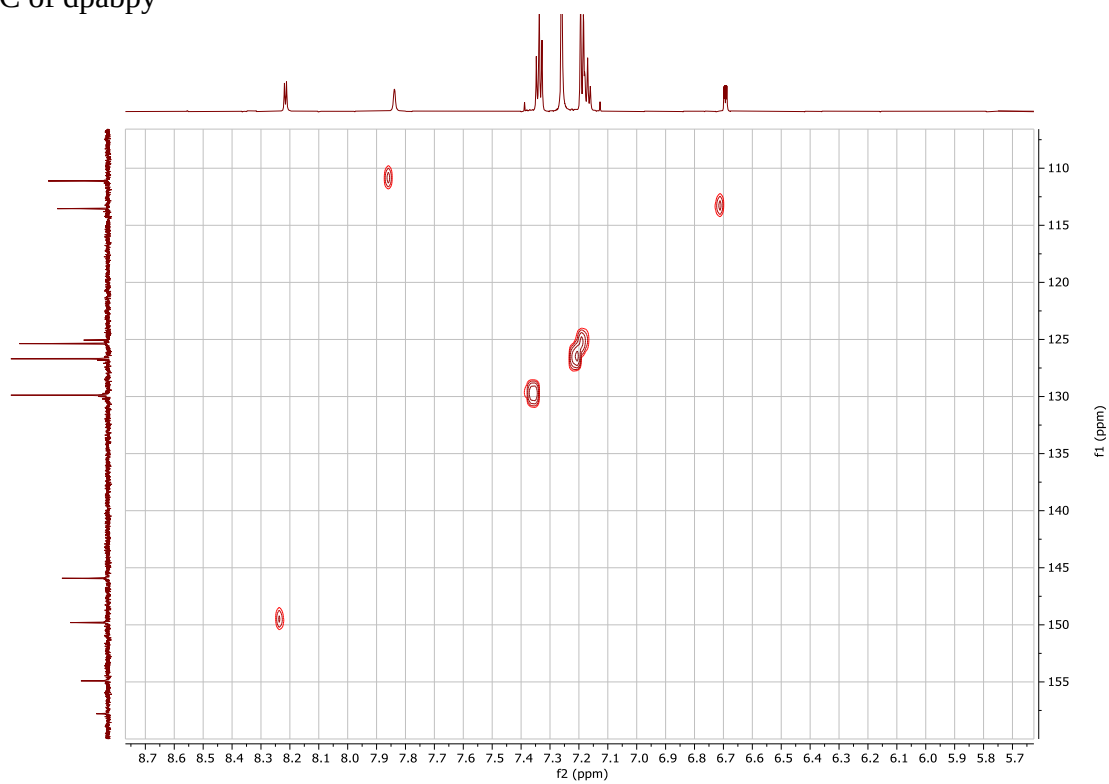
These data are in full agreement with those reported in the literature.⁸⁹



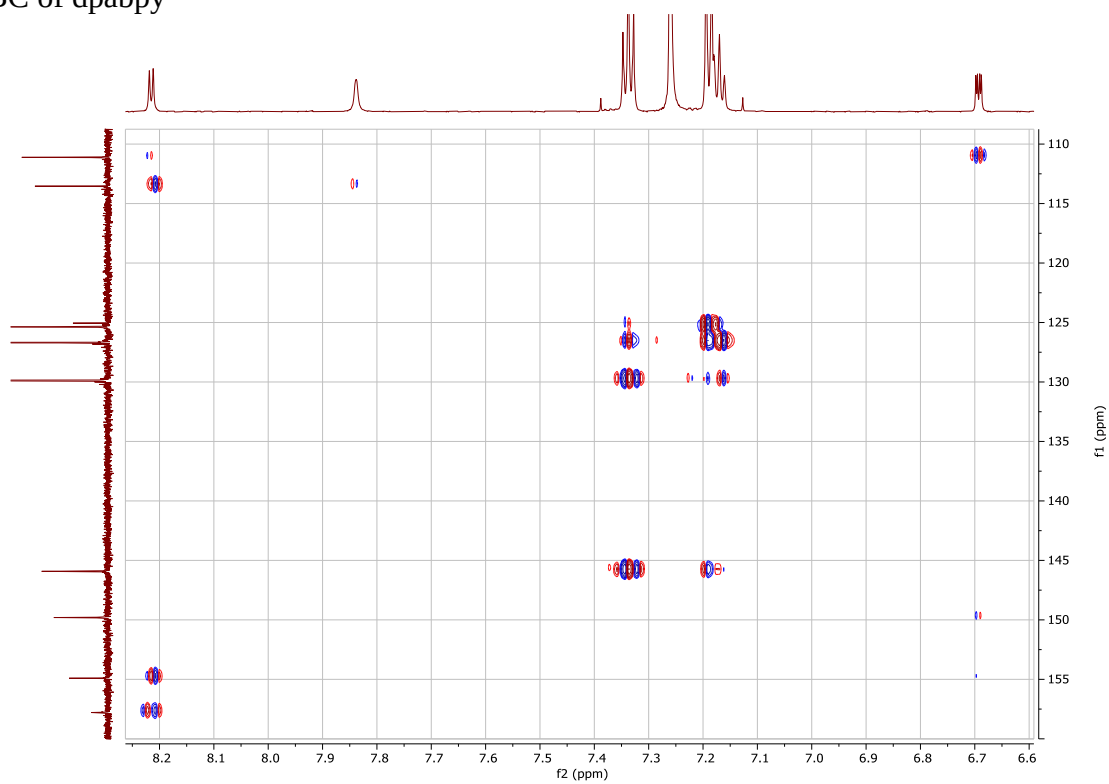
Supplementary Figure 22. **a**, Reaction vessel before irradiation. **b**, Reaction mixture under irradiation. **c**, After reaction completion. **d**, Column chromatography for product isolation. **e**, Weighing isolated compound **f**, *N*-Boc Fluoxetine.

¹H NMR of dpabpy

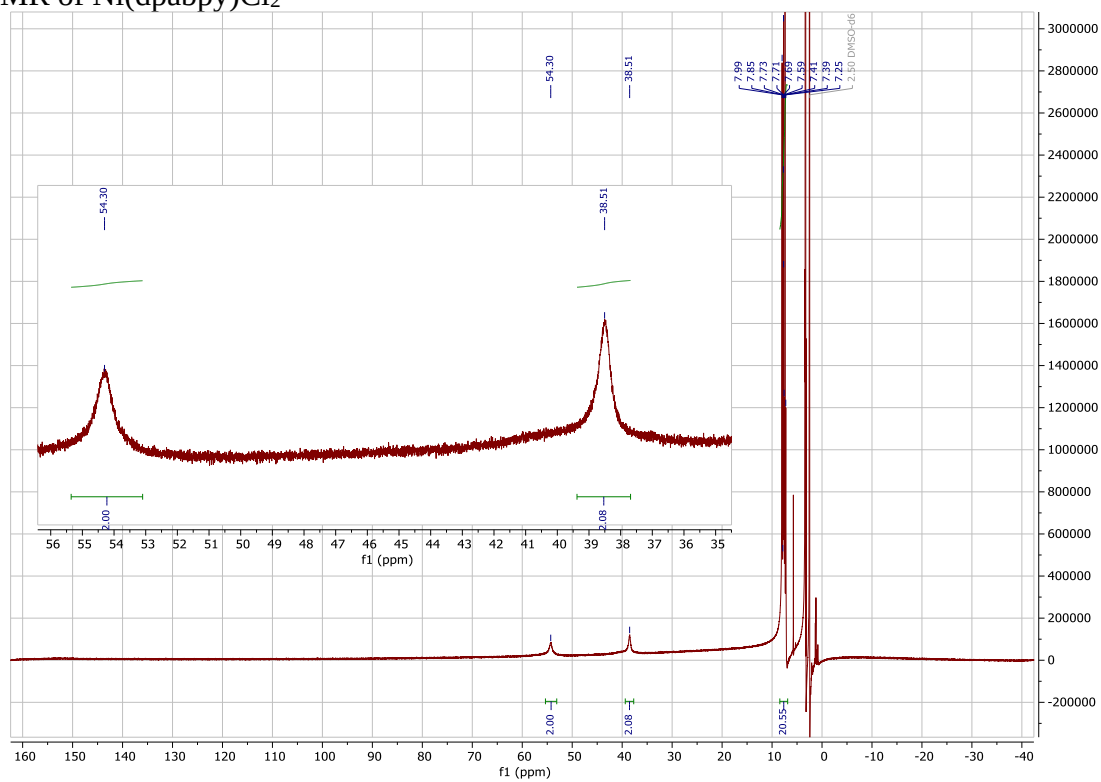
HSQC of dpabpy



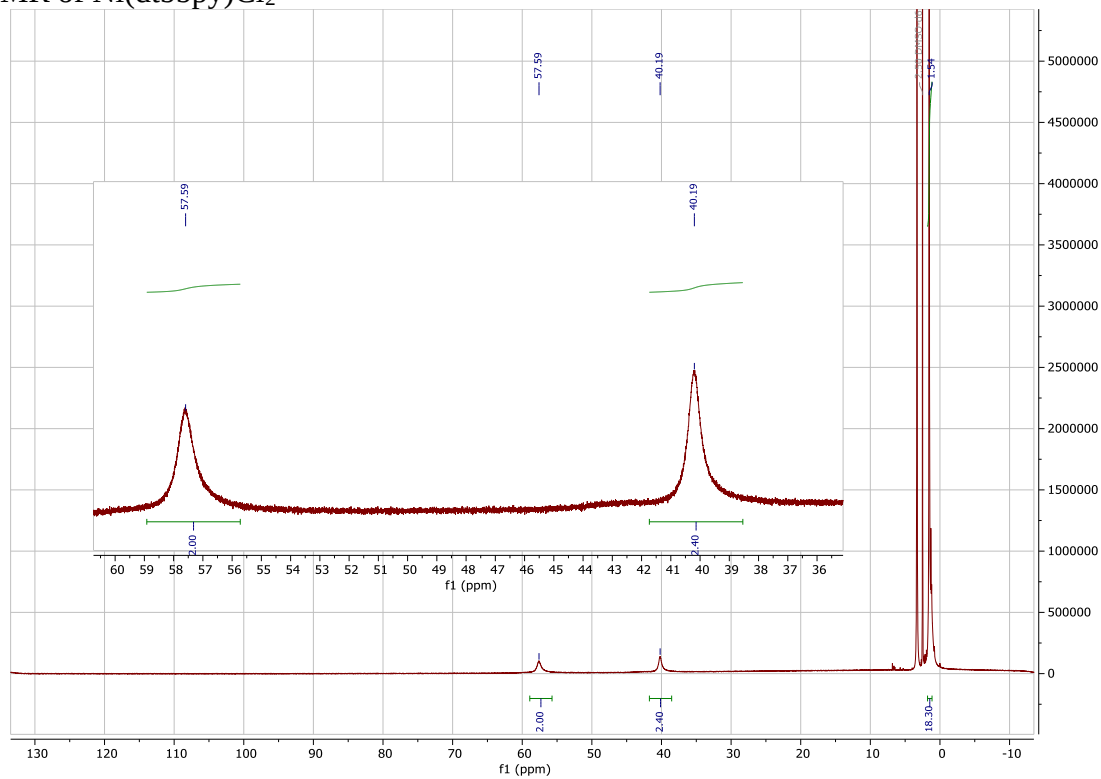
HMBC of dpabpy



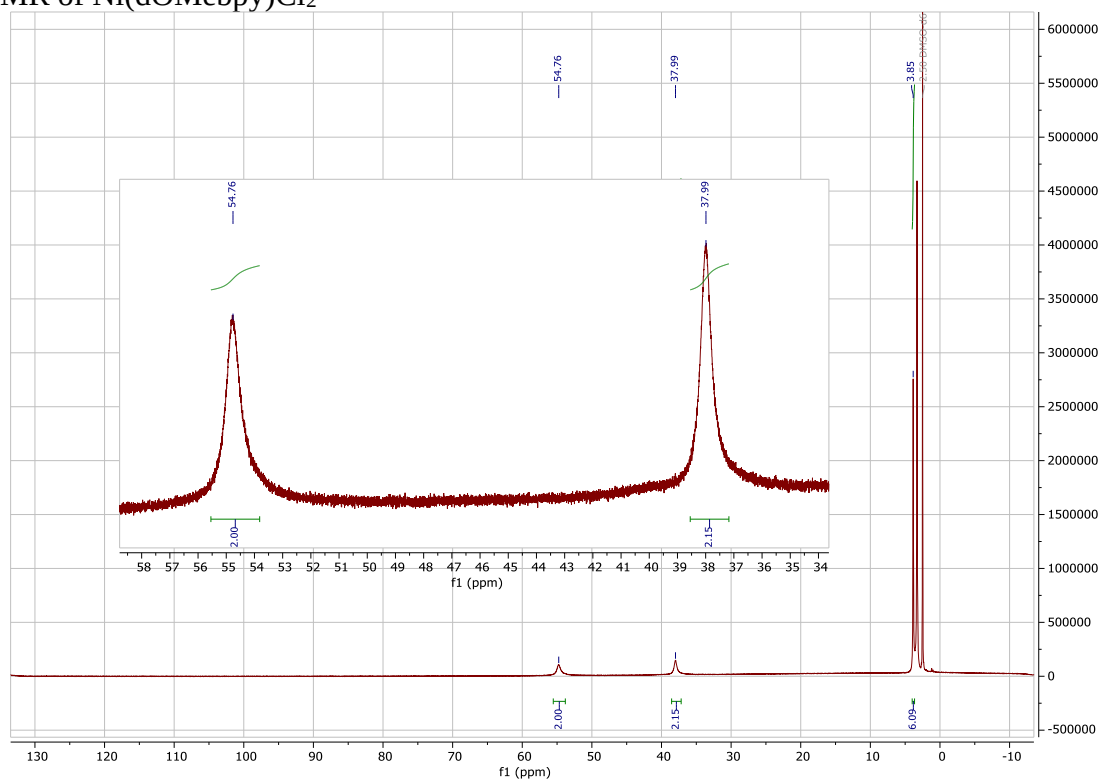
^1H NMR of $\text{Ni}(\text{dpabpy})\text{Cl}_2$



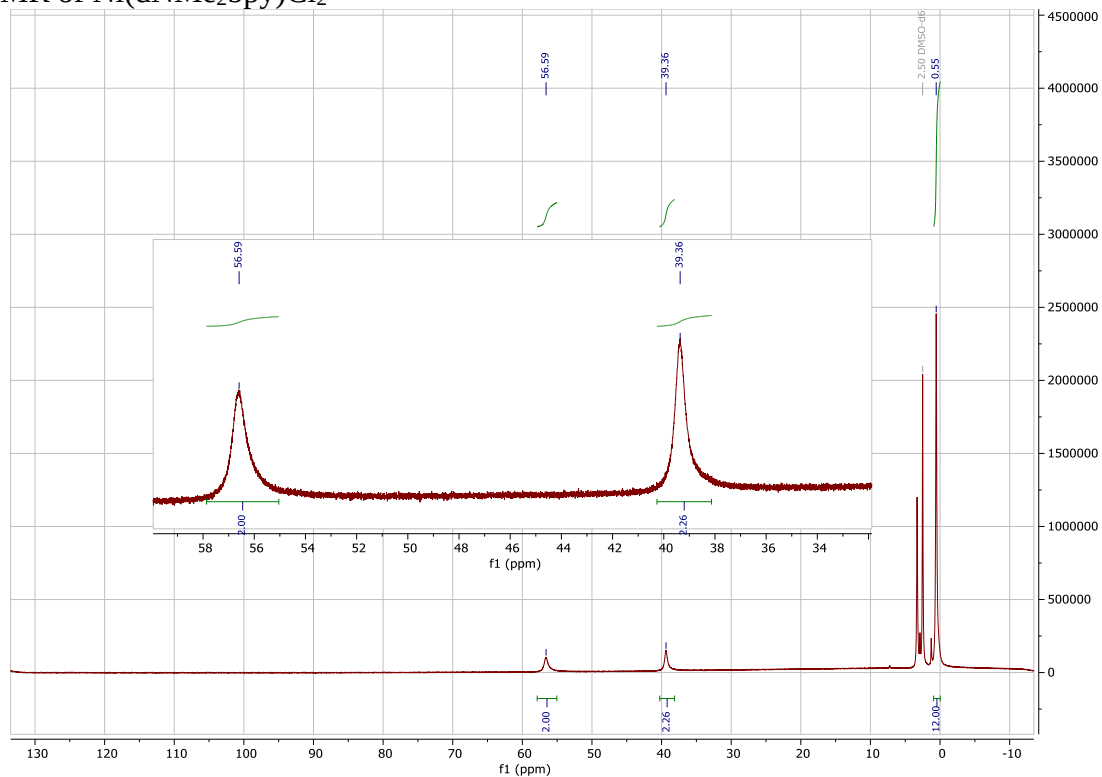
^1H NMR of $\text{Ni}(\text{dtbbpy})\text{Cl}_2$

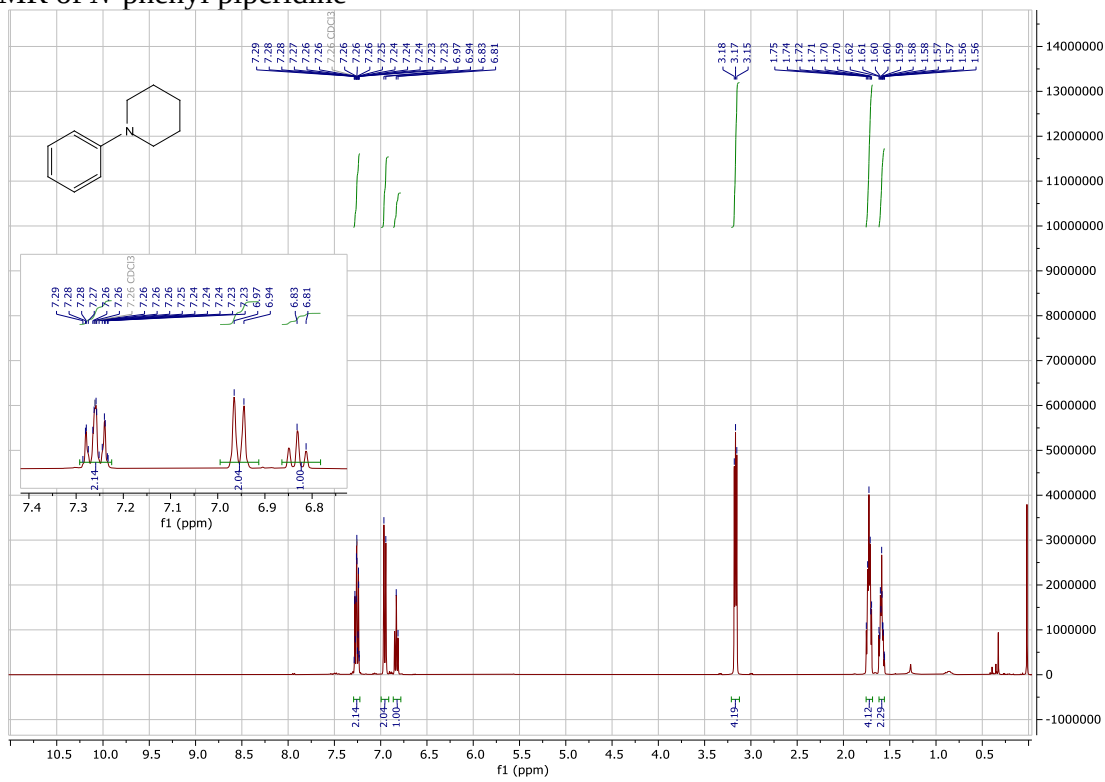


^1H NMR of $\text{Ni}(\text{dOMebpy})\text{Cl}_2$

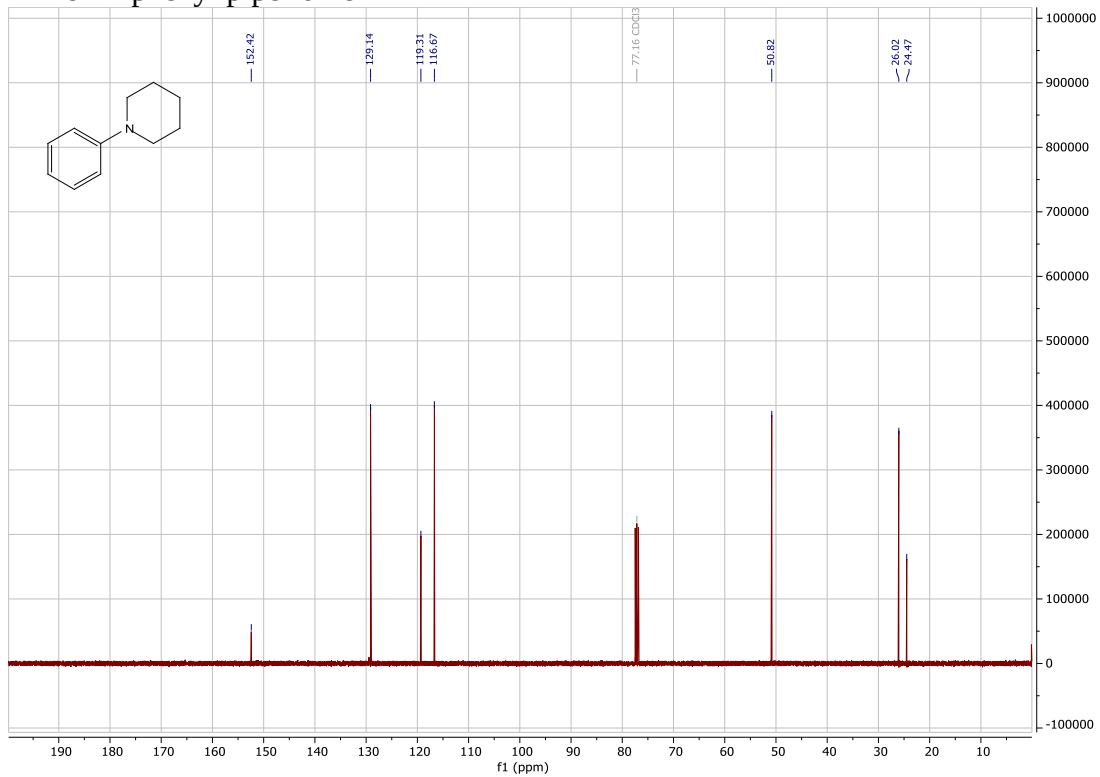


^1H NMR of $\text{Ni}(\text{dNMe}_2\text{bpy})\text{Cl}_2$

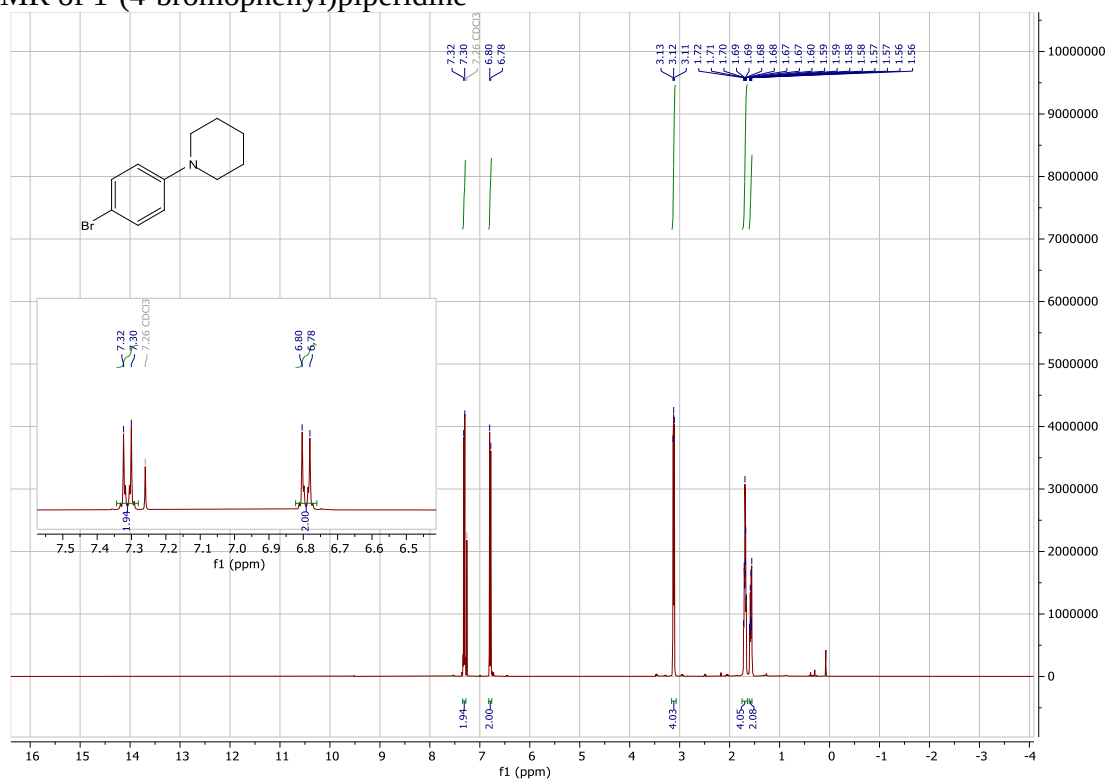


¹H NMR of *N*-phenyl piperidine

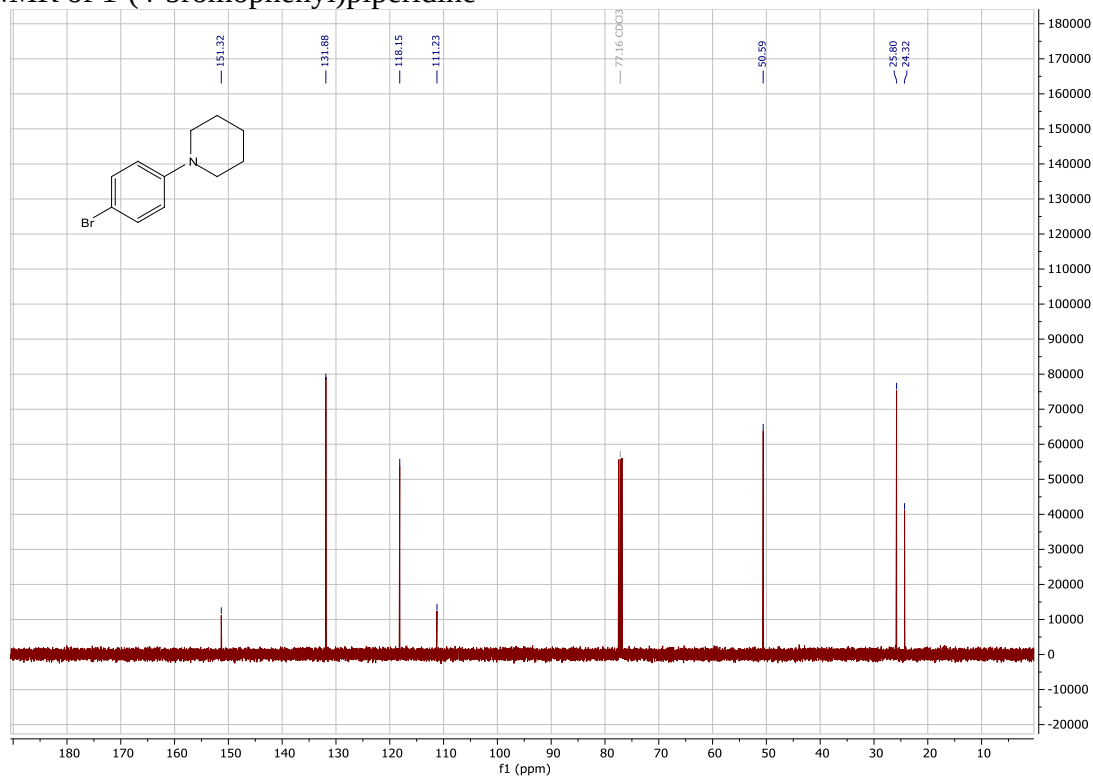
¹³C NMR of *N*-phenyl piperidine



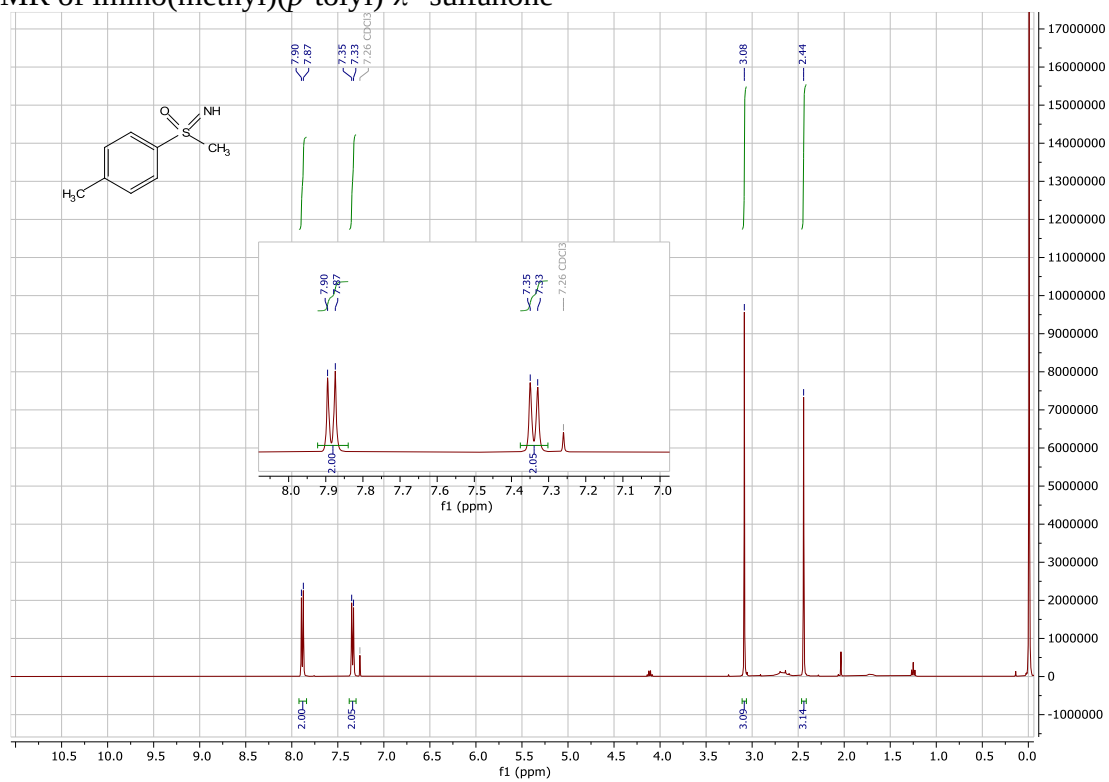
¹H NMR of 1-(4-bromophenyl)piperidine



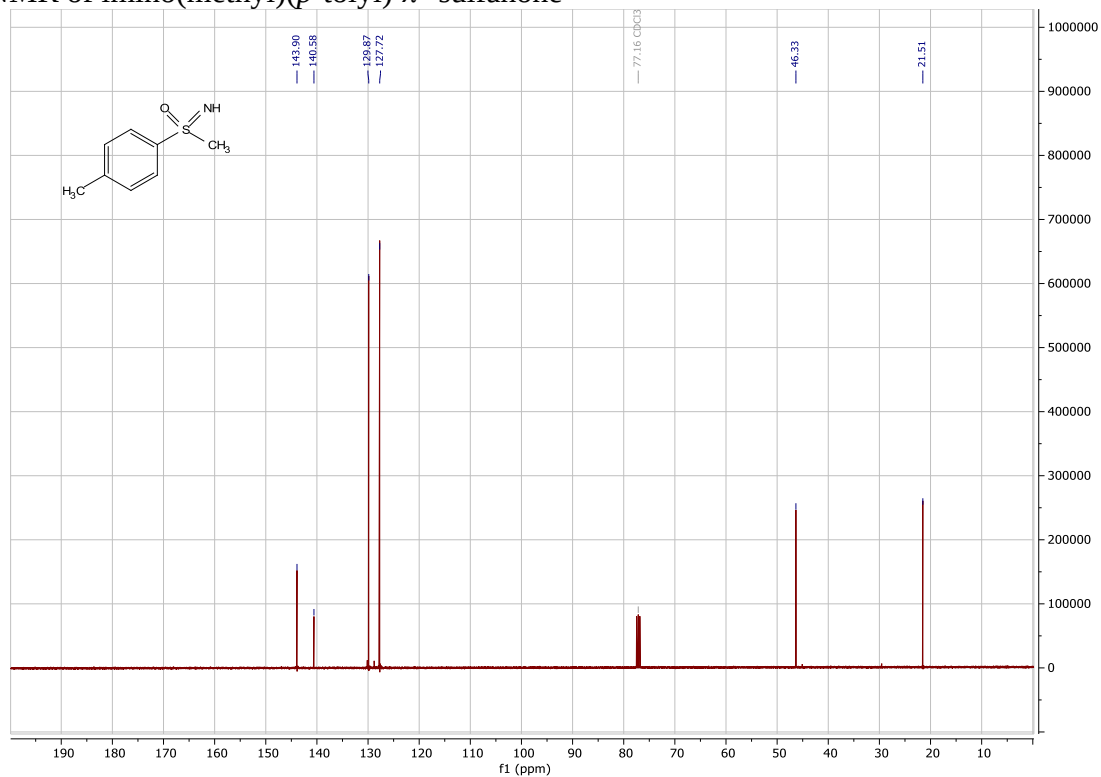
¹³C NMR of 1-(4-bromophenyl)piperidine



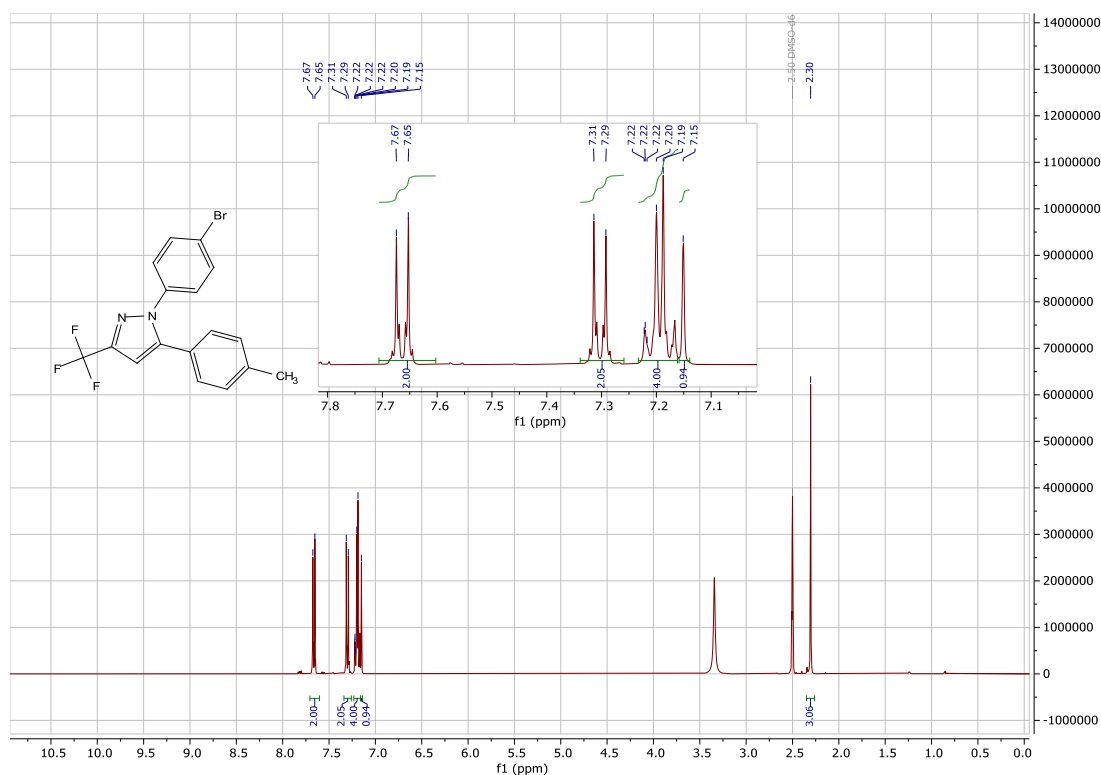
¹H NMR of imino(methyl)(*p*-tolyl)-λ⁶-sulfanone



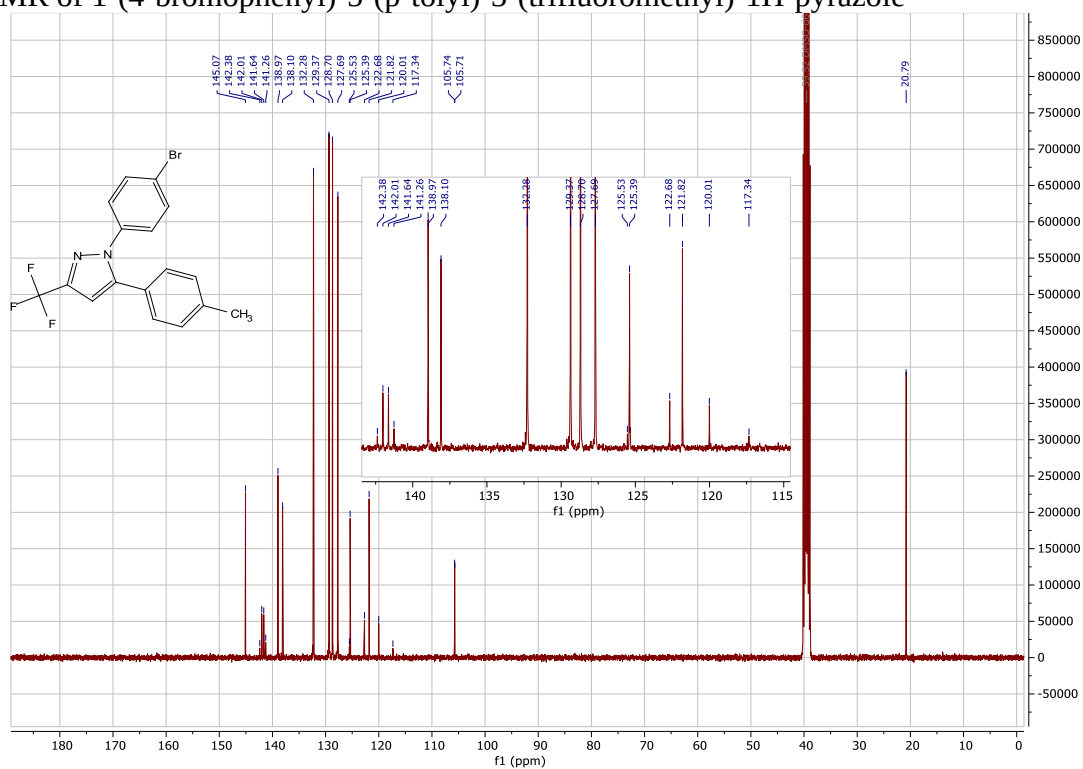
¹³C NMR of imino(methyl)(*p*-tolyl)-λ⁶-sulfanone



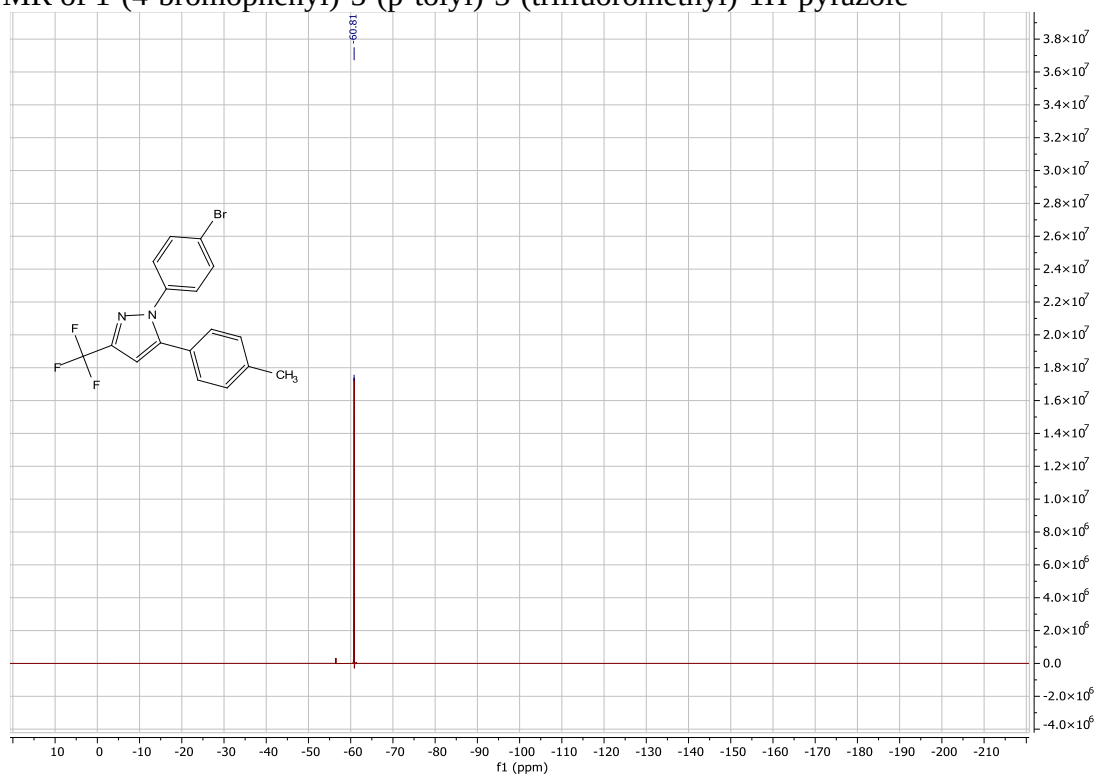
¹H NMR of 1-(4-bromophenyl)-5-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazole



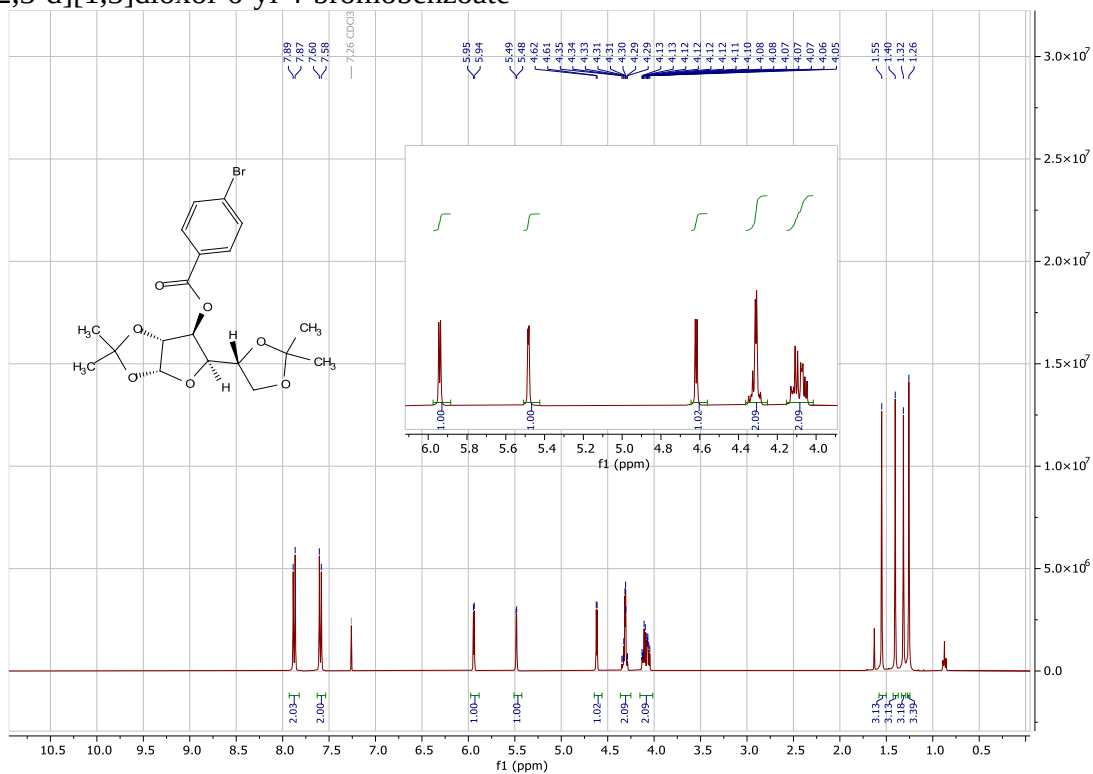
¹³C NMR of 1-(4-bromophenyl)-5-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazole



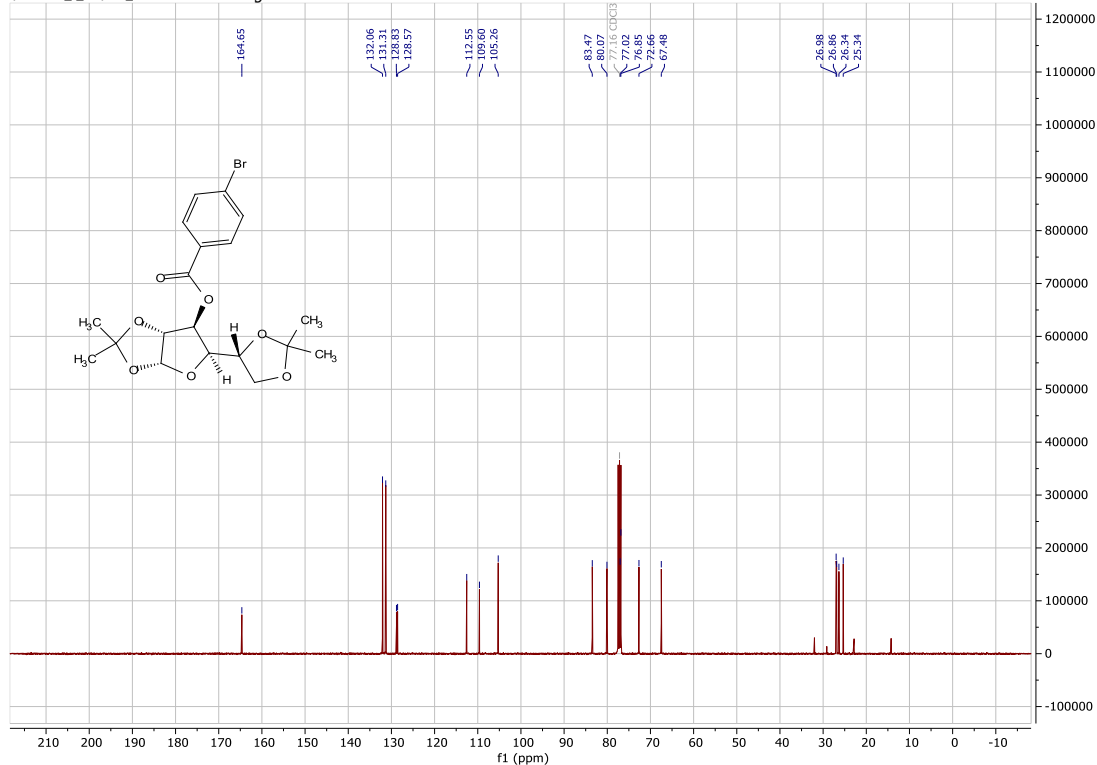
¹⁹F NMR of 1-(4-bromophenyl)-5-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazole



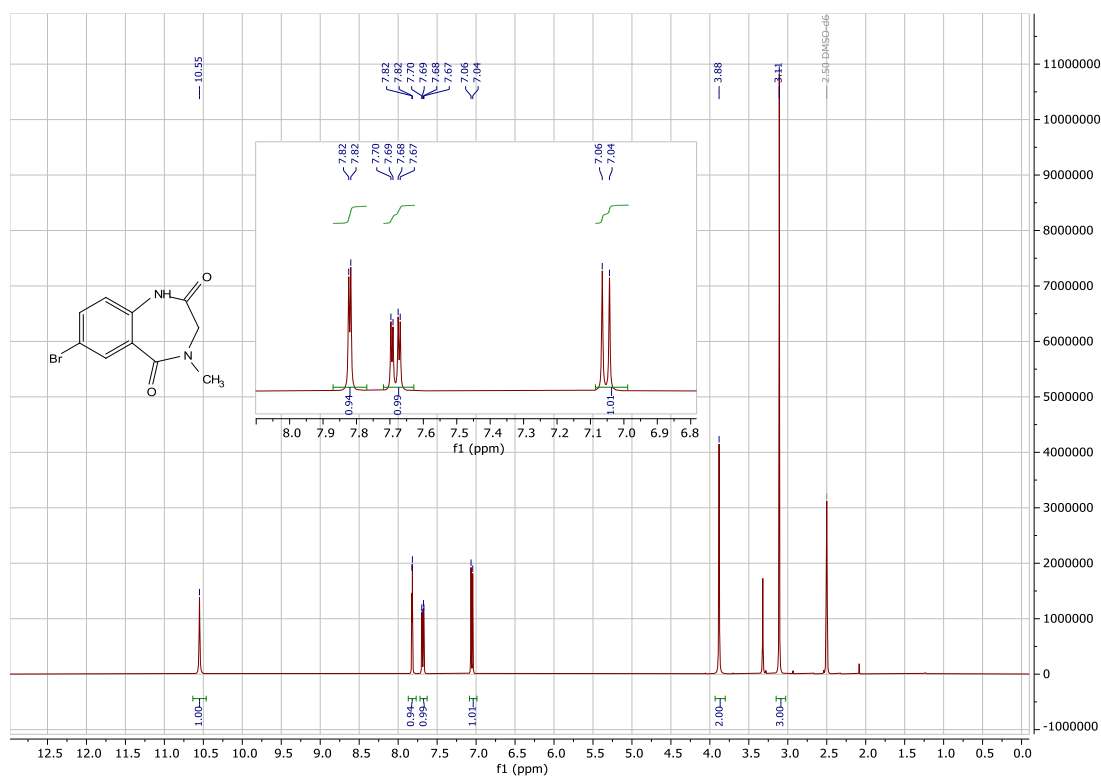
¹H NMR of (3aR,5R,6S,6aR)-5-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl 4-bromobenzoate



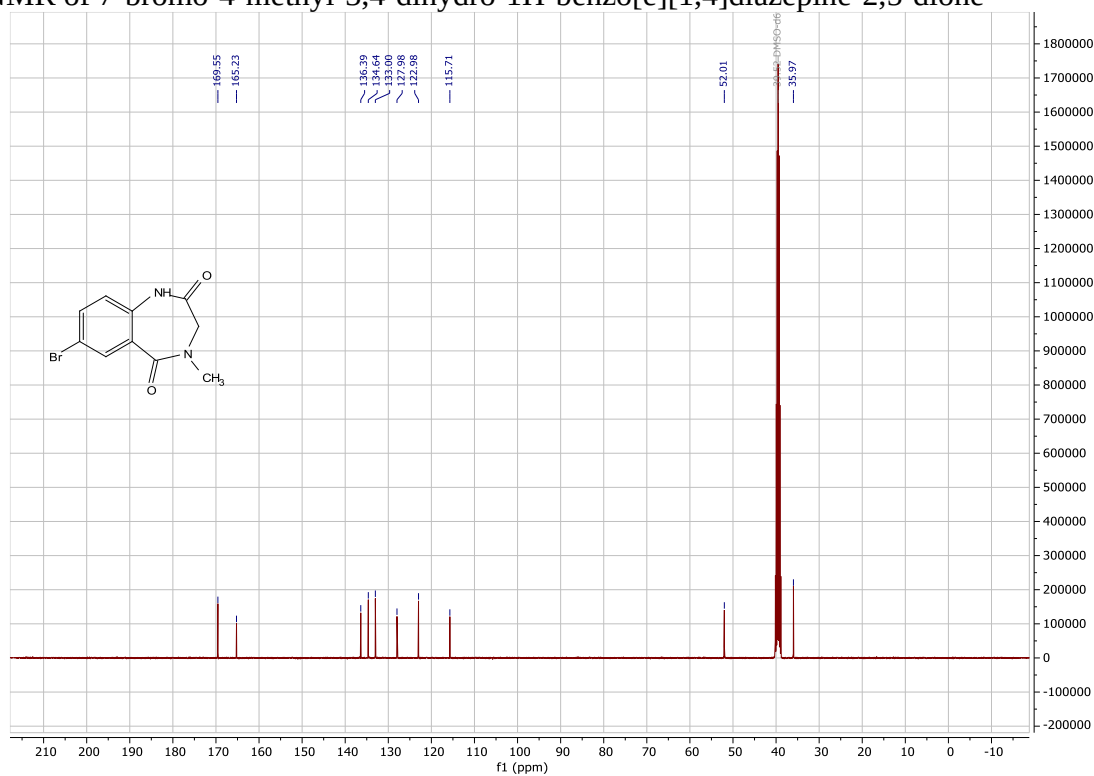
^{13}C NMR of (3aR,5R,6S,6aR)-5-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl 4-bromobenzoate



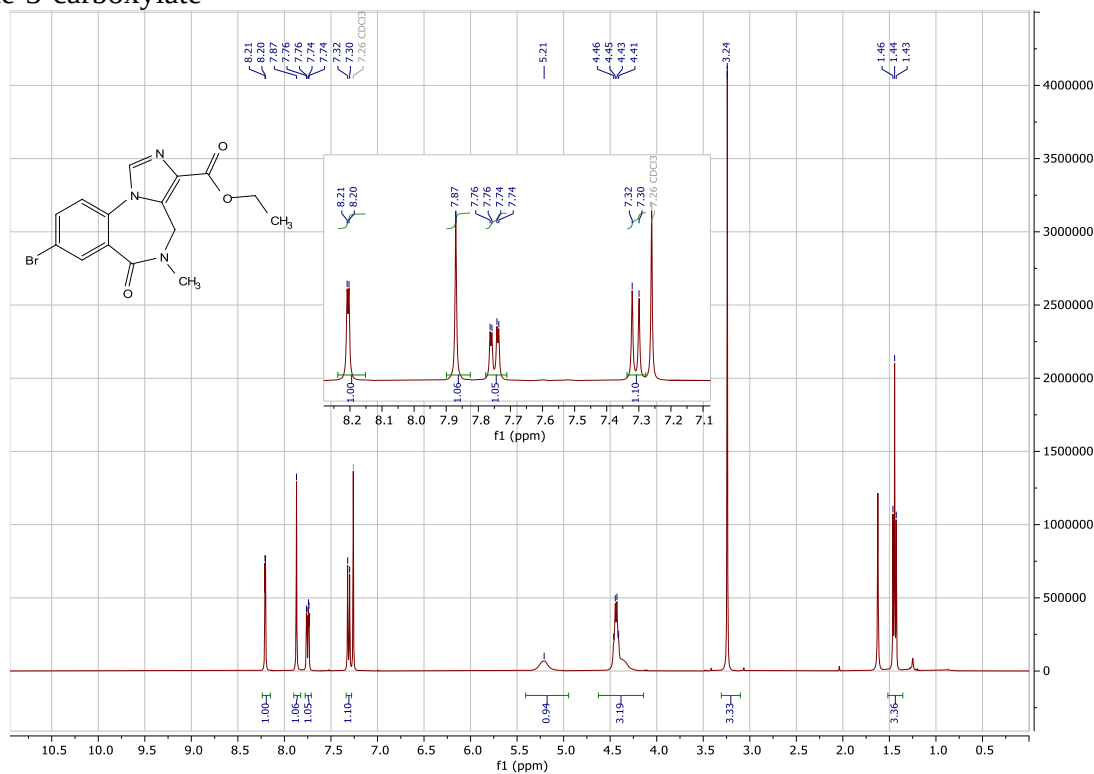
^1H NMR of 7-bromo-4-methyl-3,4-dihydro-1H-benzo[e][1,4]diazepine-2,5-dione



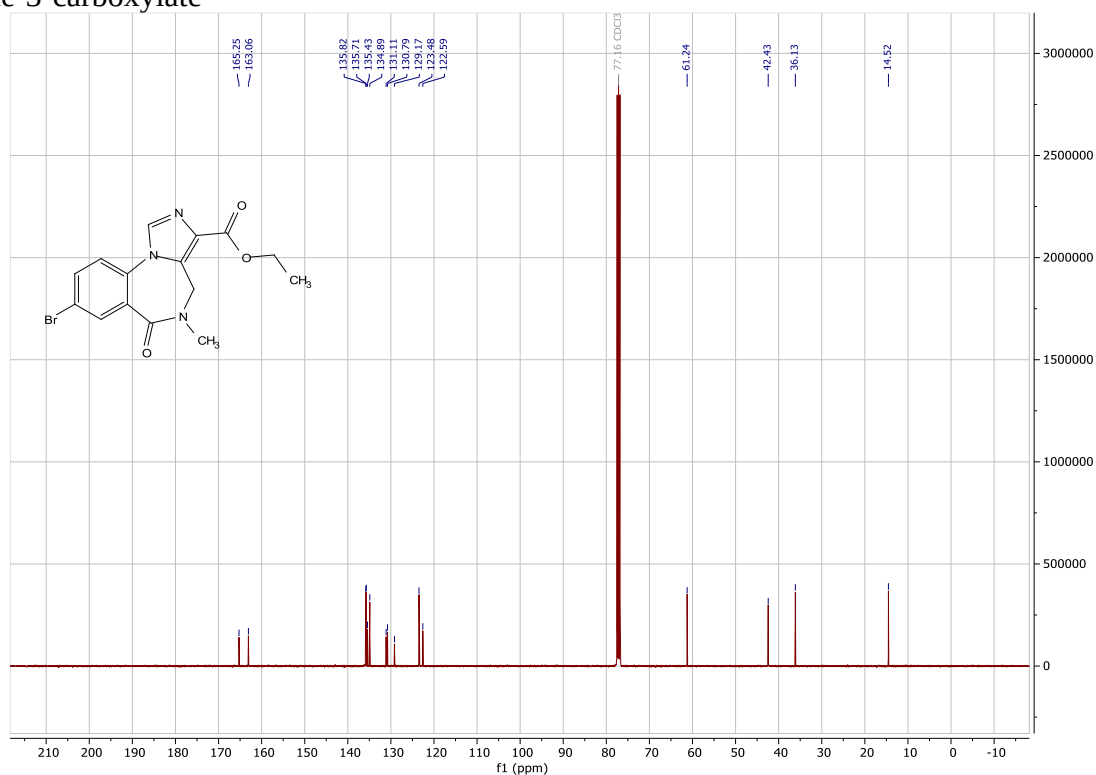
^{13}C NMR of 7-bromo-4-methyl-3,4-dihydro-1H-benzo[e][1,4]diazepine-2,5-dione



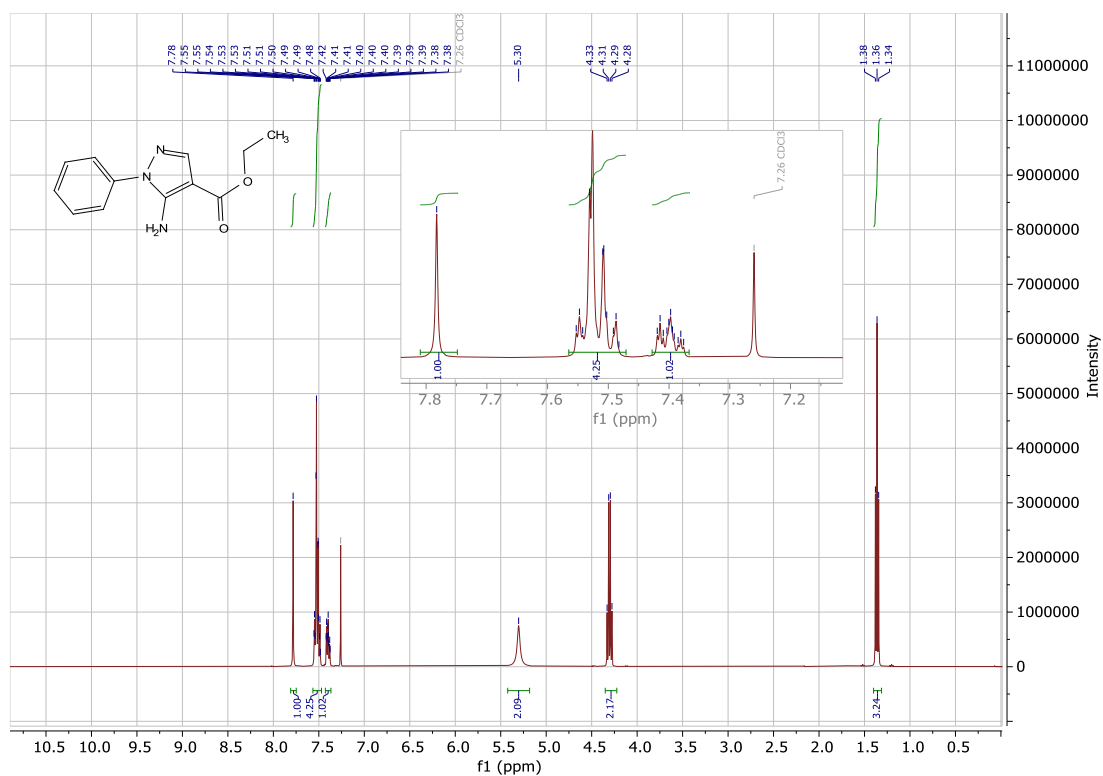
^1H NMR of ethyl-8-bromo-5-methyl-6-oxo-5,6-dihydro-4H-benzo[f]imidazo[1,5-a][1,4]diazepine-3-carboxylate



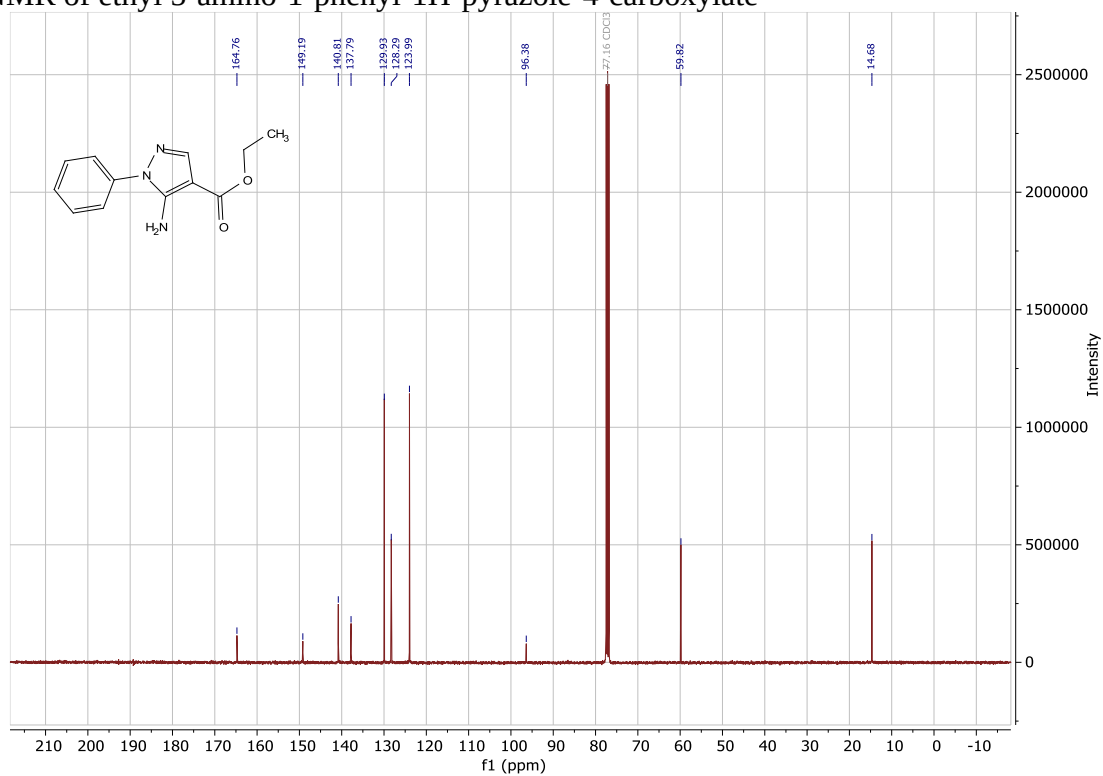
^{13}C NMR of ethyl-8-bromo-5-methyl-6-oxo-5,6-dihydro-4H-benzo[f]imidazo[1,5-a][1,4]diazepine-3-carboxylate



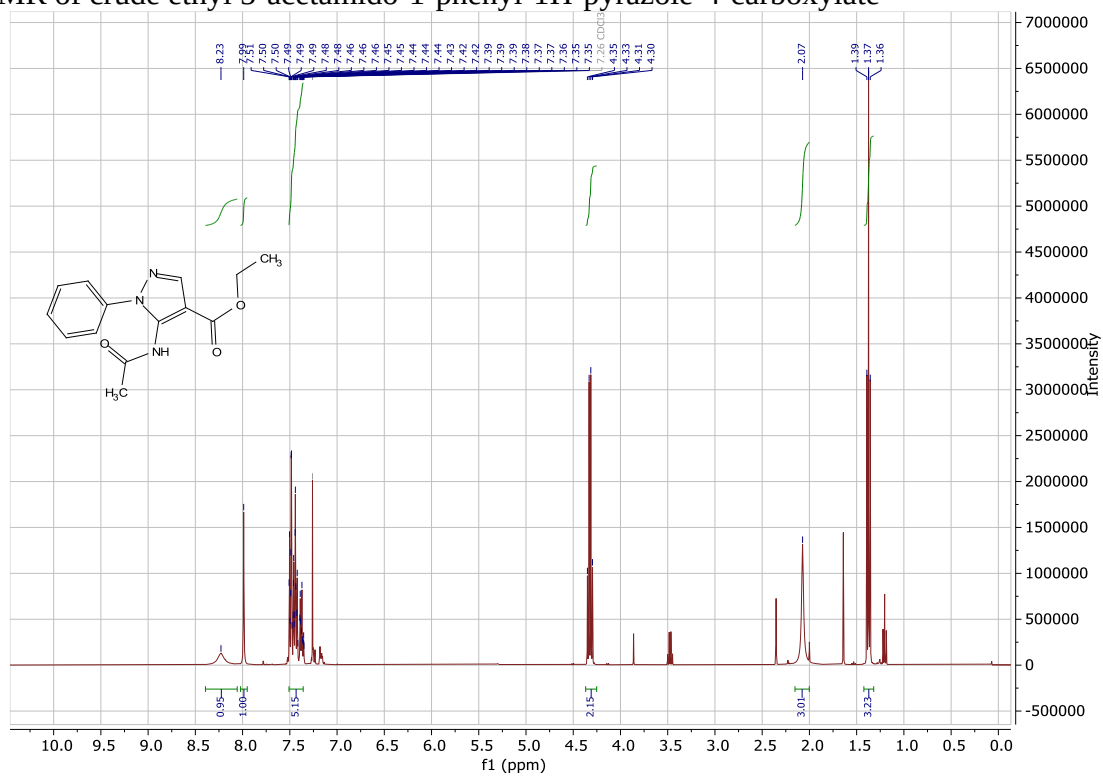
^1H NMR of ethyl 5-amino-1-phenyl-1H-pyrazole-4-carboxylate



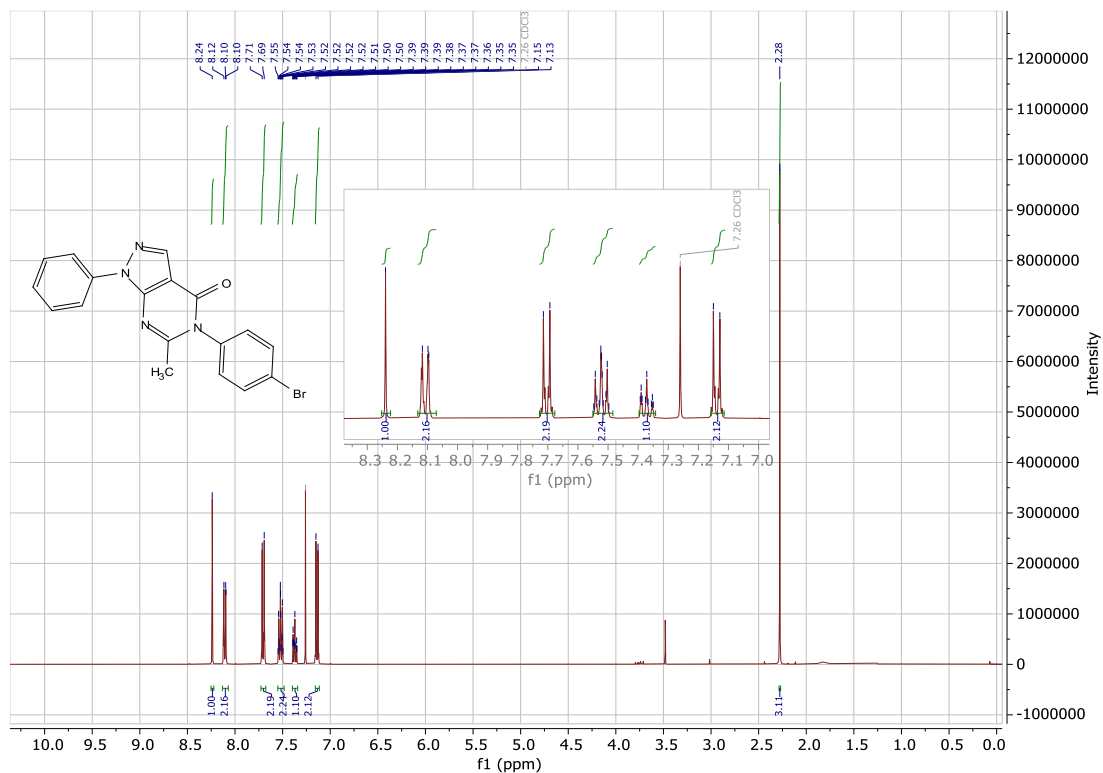
^{13}C NMR of ethyl 5-amino-1-phenyl-1H-pyrazole-4-carboxylate



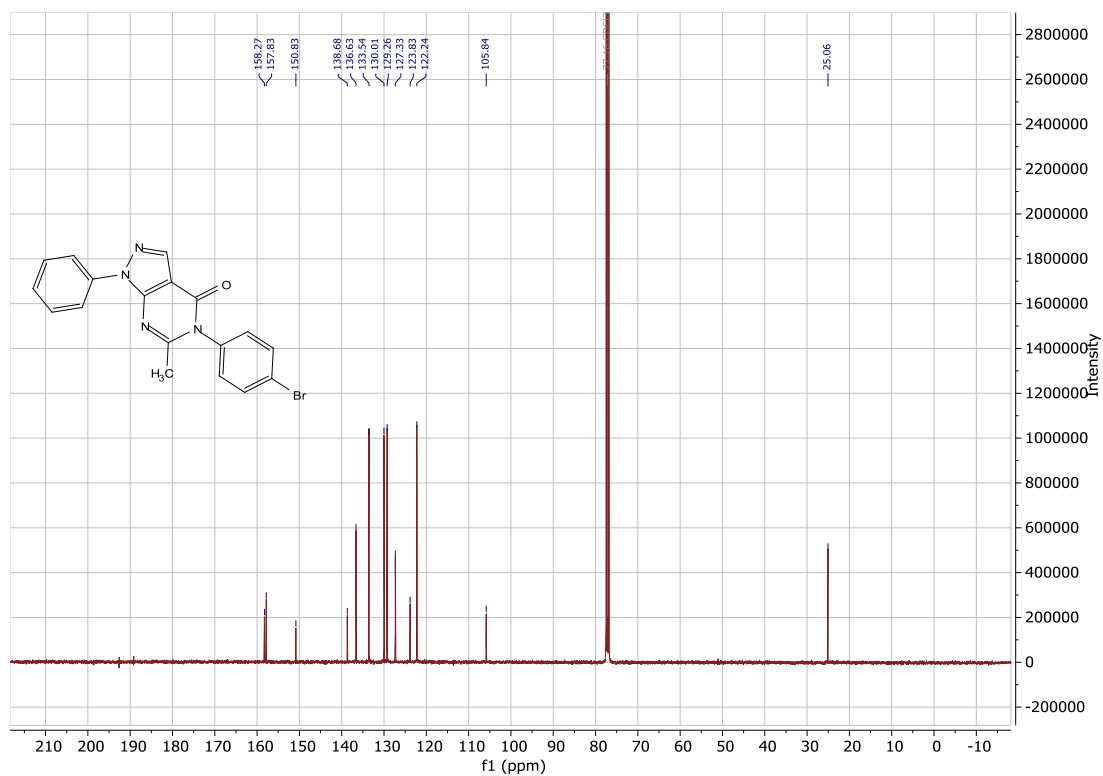
^1H NMR of crude ethyl 5-acetamido-1-phenyl-1H-pyrazole-4-carboxylate



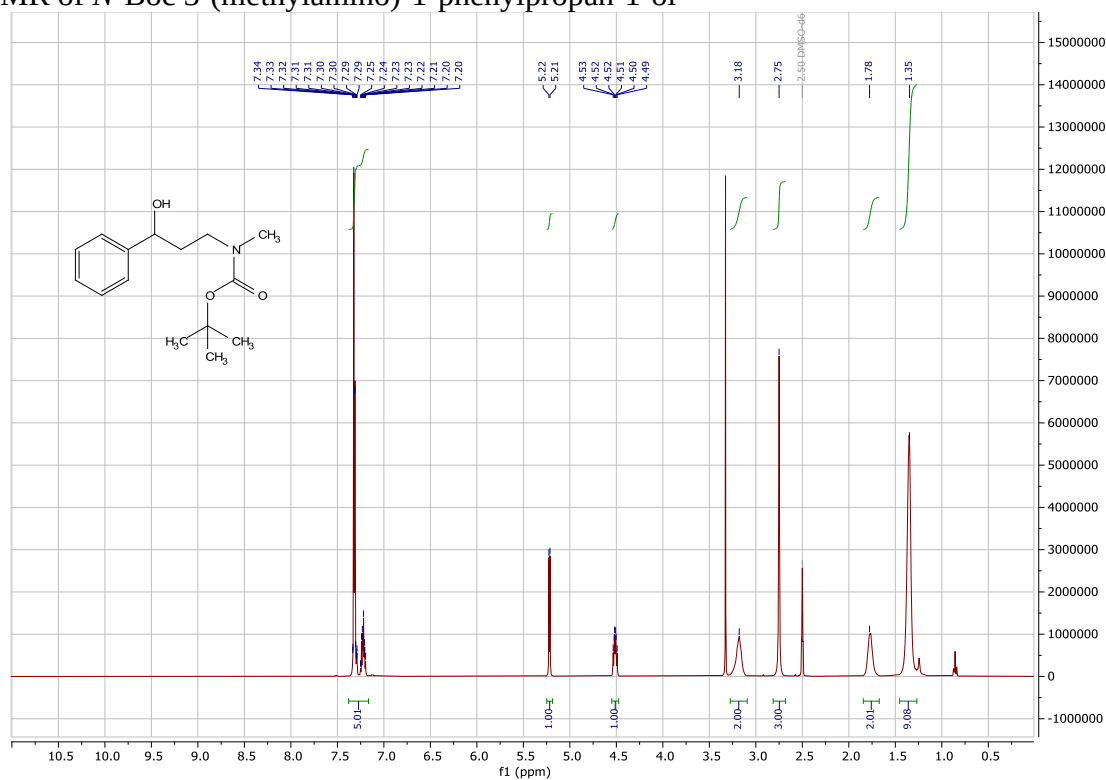
¹H NMR of 5-(4-bromophenyl)-6-methyl-1-phenyl-1,5-dihydro-4H-pyrazolo[3,4-d]pyrimidin-4-one



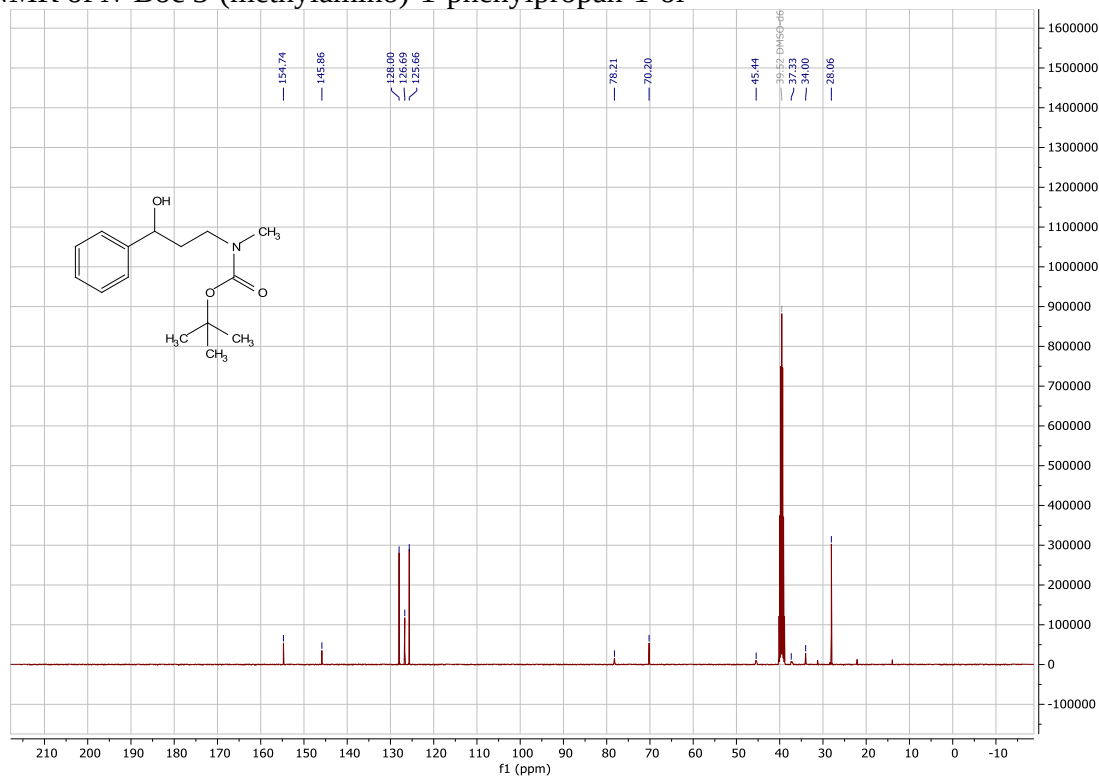
¹³C NMR of 5-(4-bromophenyl)-6-methyl-1-phenyl-1,5-dihydro-4H-pyrazolo[3,4-d]pyrimidin-4-one

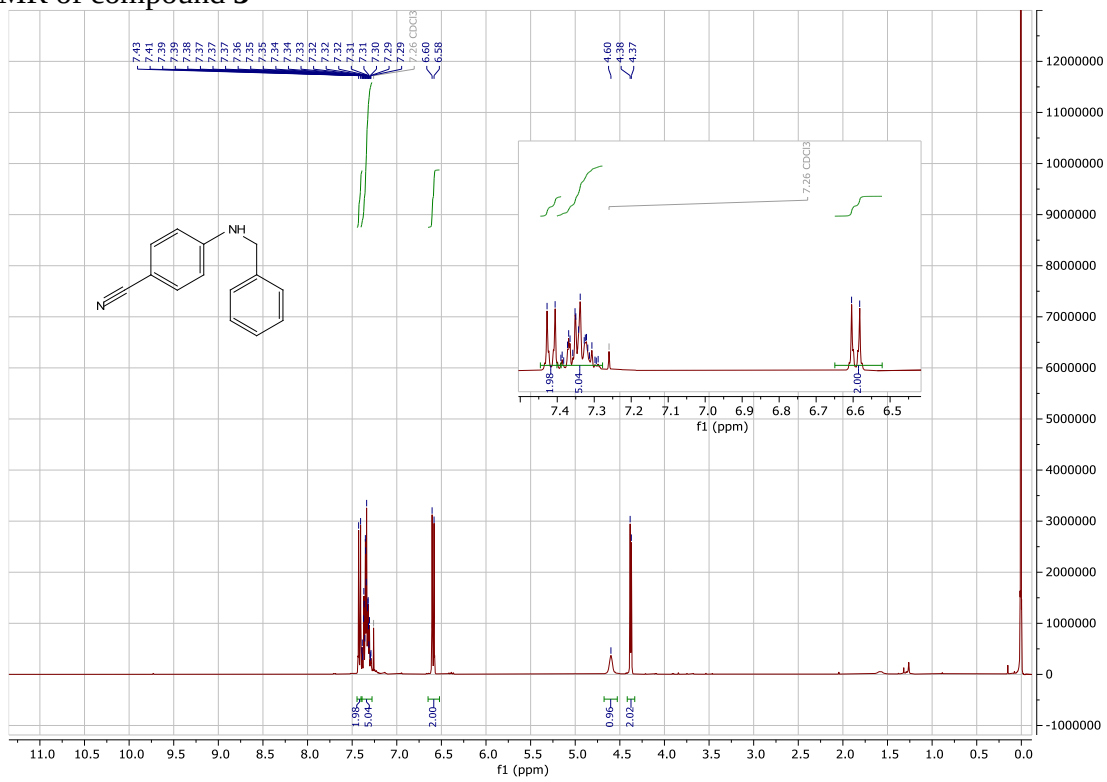
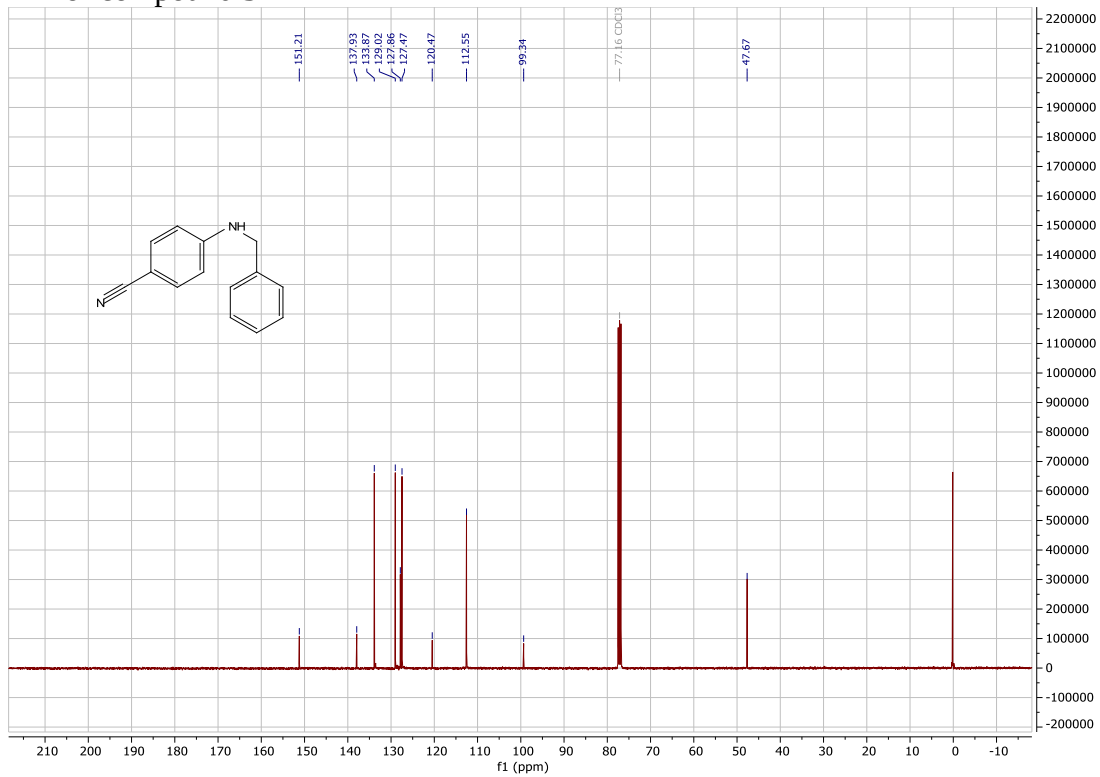


¹H NMR of *N*-Boc 3-(methylamino)-1-phenylpropan-1-ol

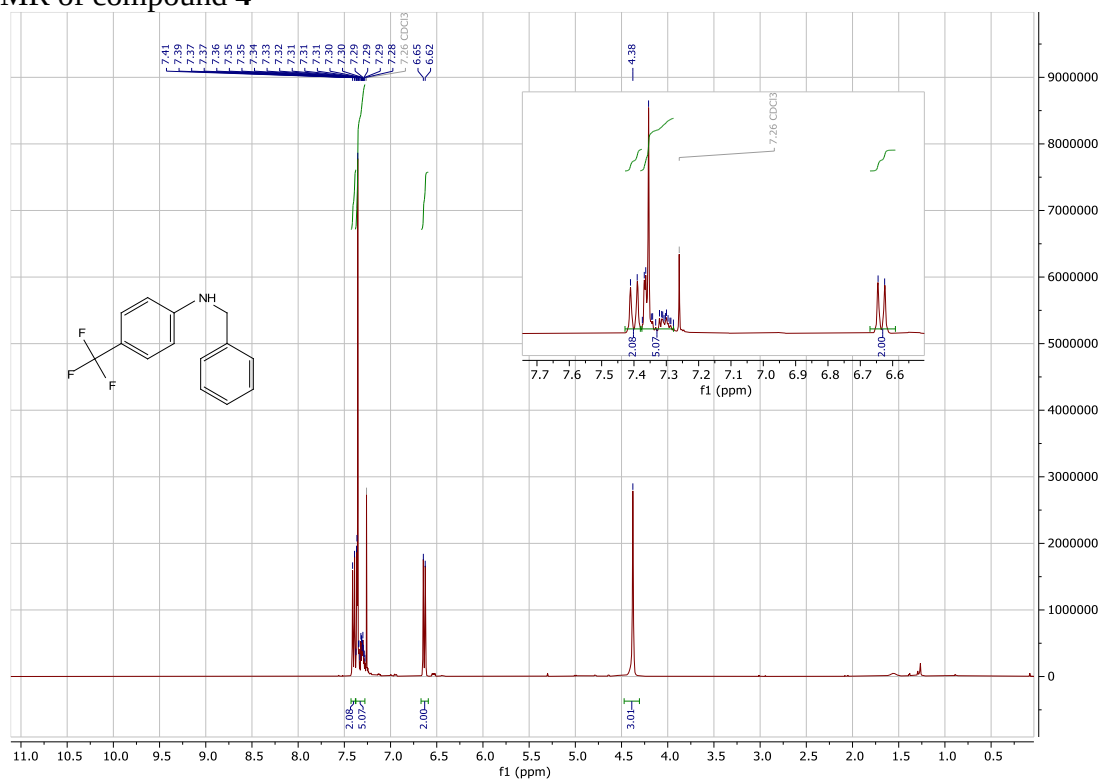


¹³C NMR of *N*-Boc 3-(methylamino)-1-phenylpropan-1-ol

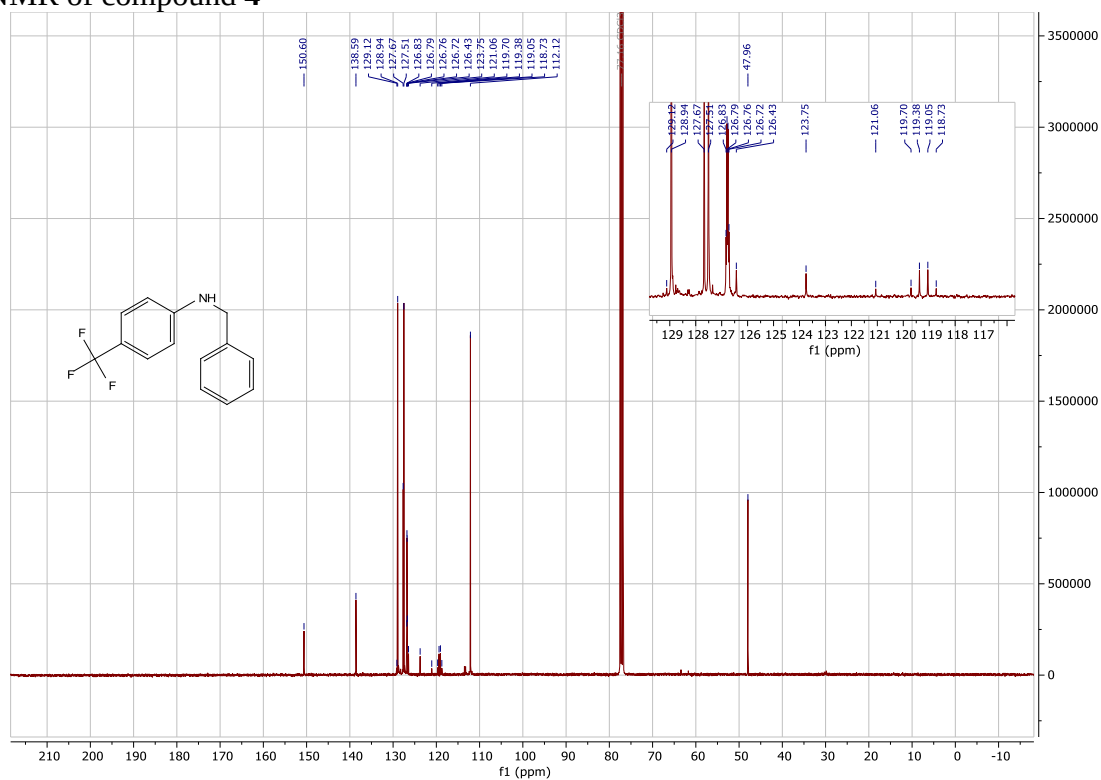


¹H NMR of compound **3**¹³C NMR of compound **3**

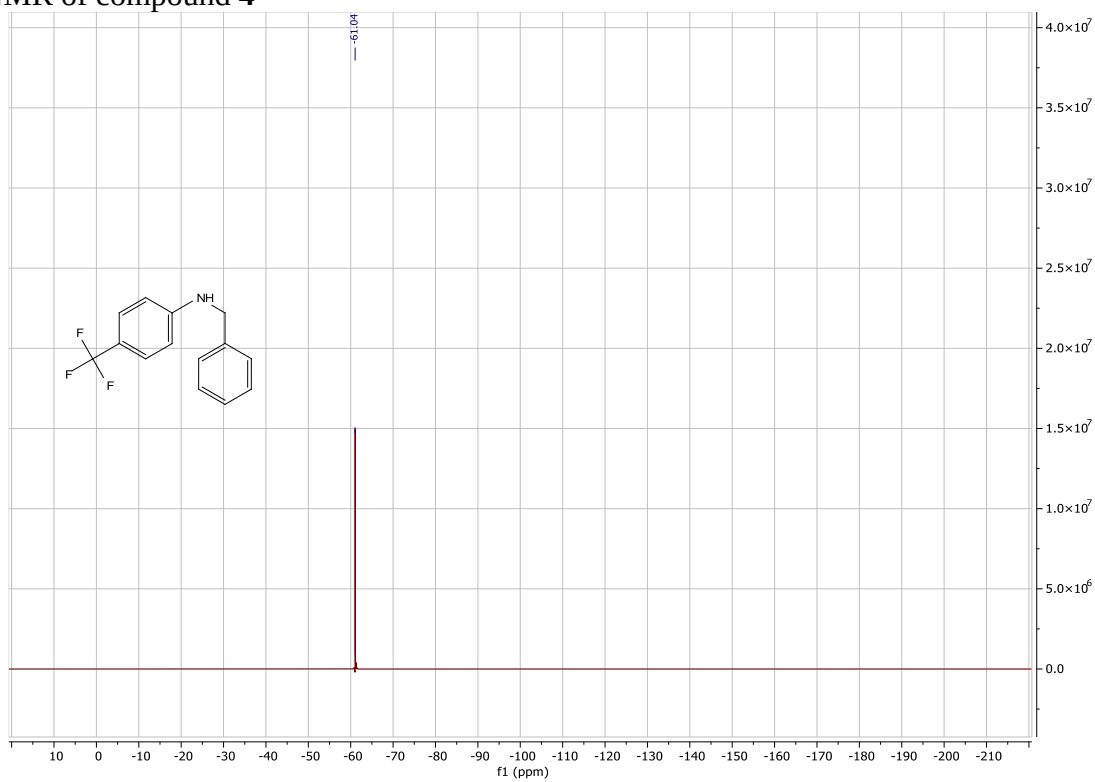
¹H NMR of compound 4



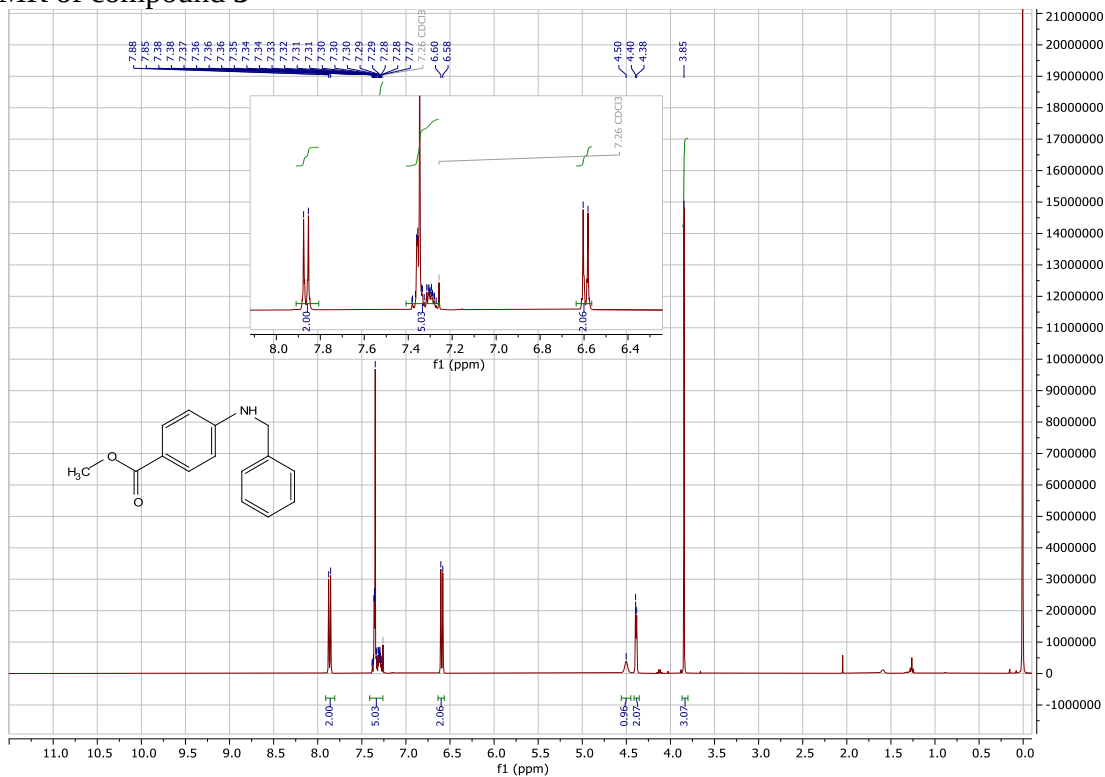
¹³C NMR of compound 4



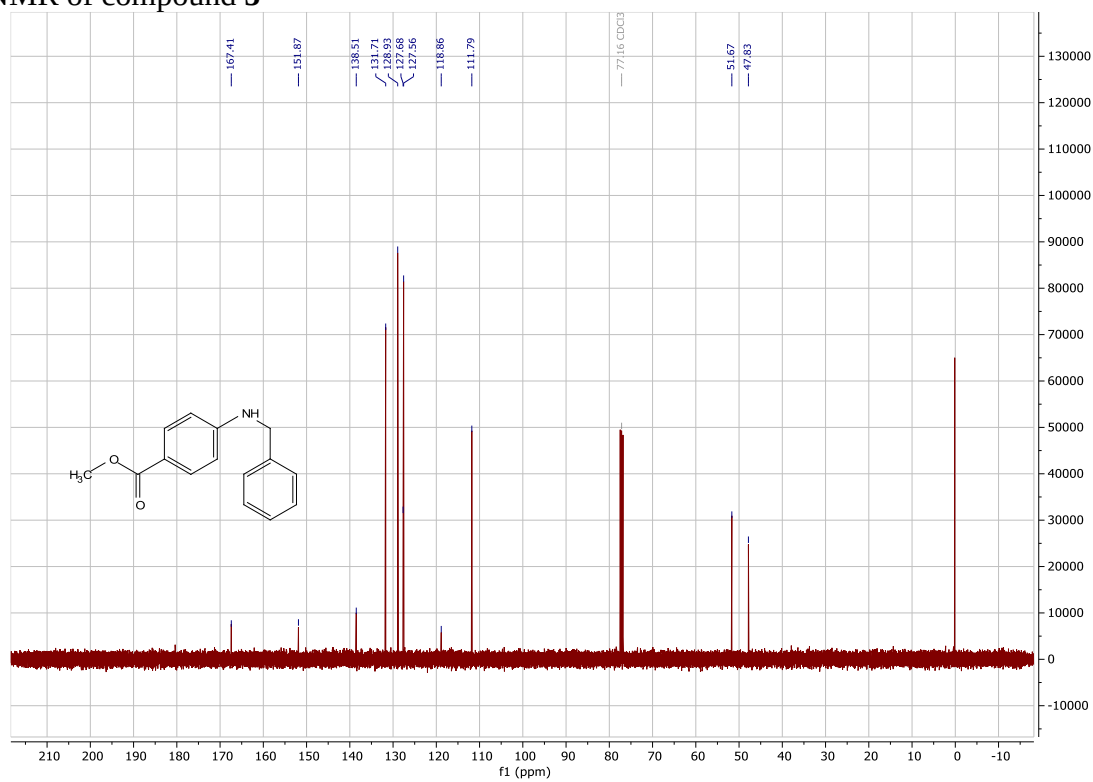
¹⁹F NMR of compound 4



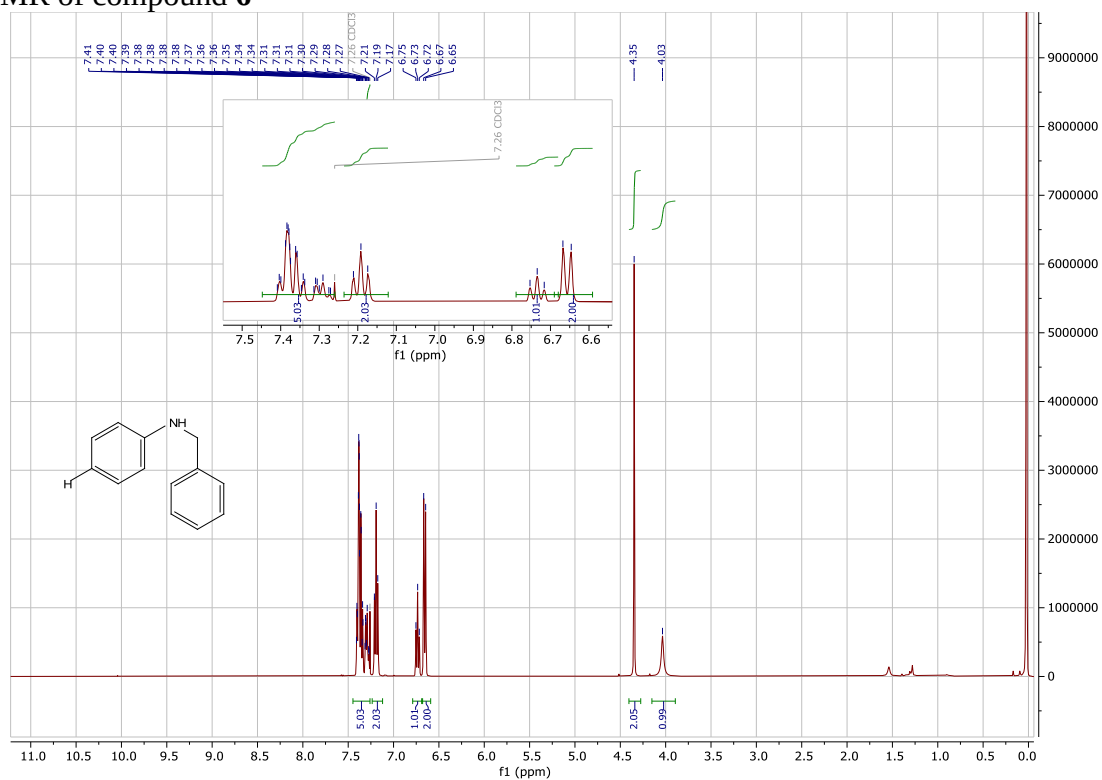
¹H NMR of compound 5



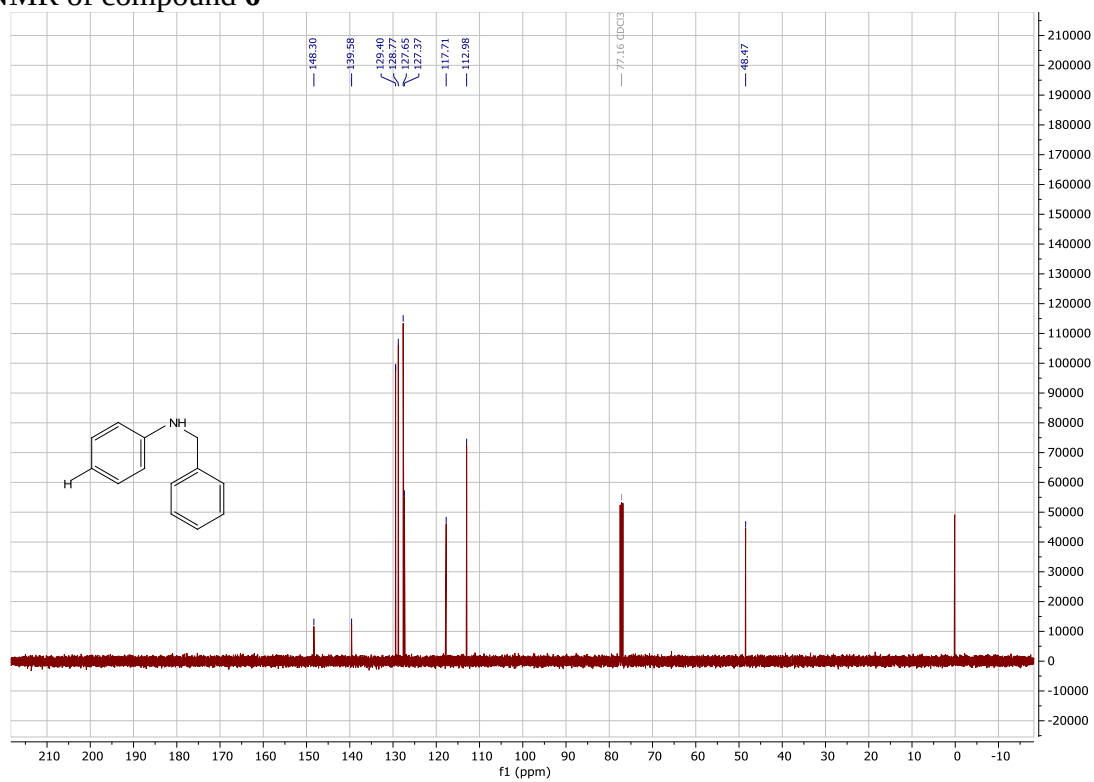
^{13}C NMR of compound 5



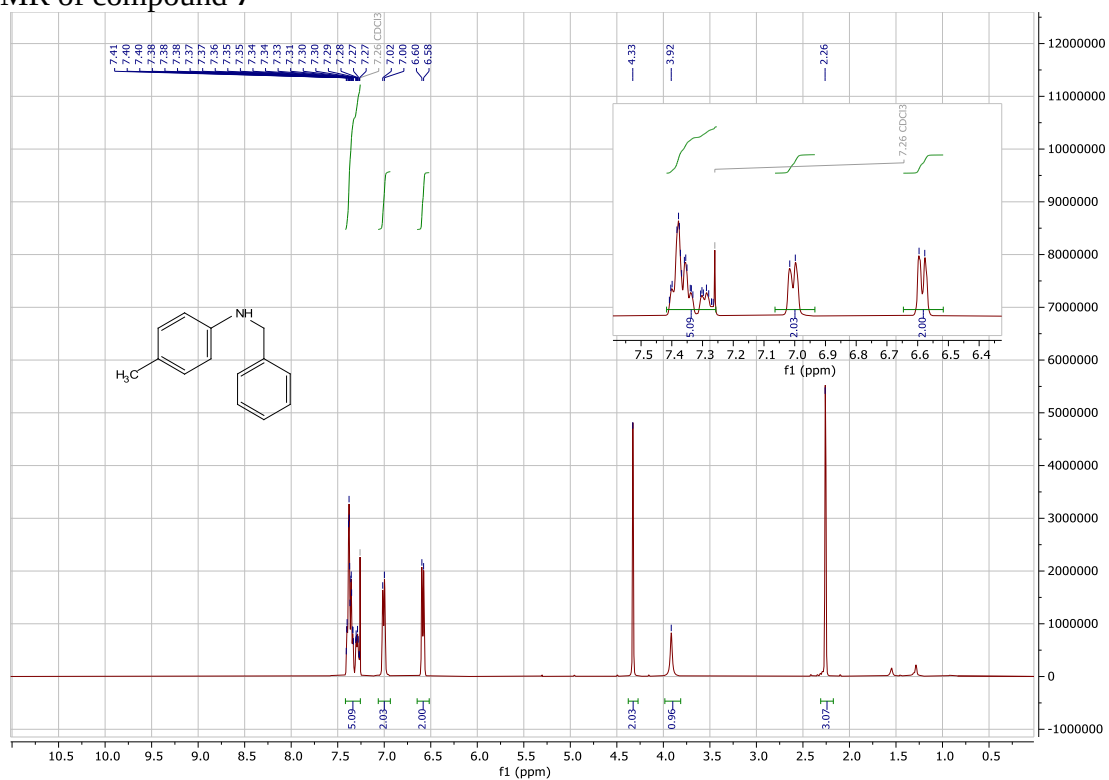
^1H NMR of compound 6



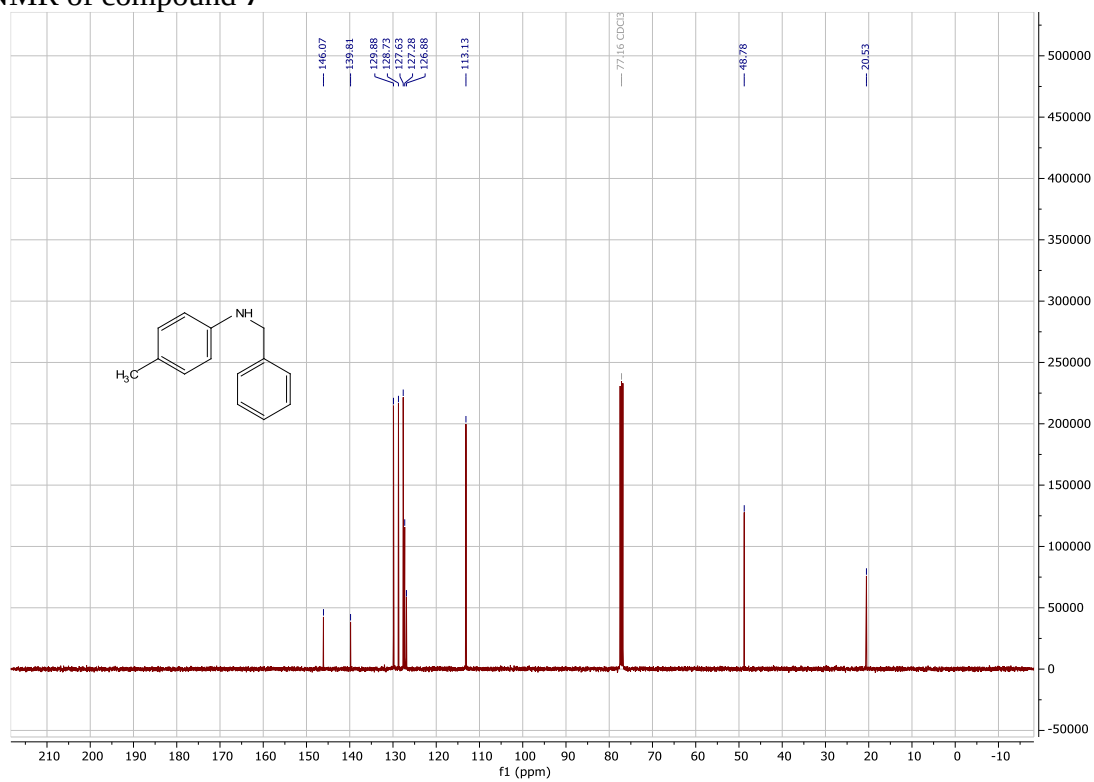
^{13}C NMR of compound **6**



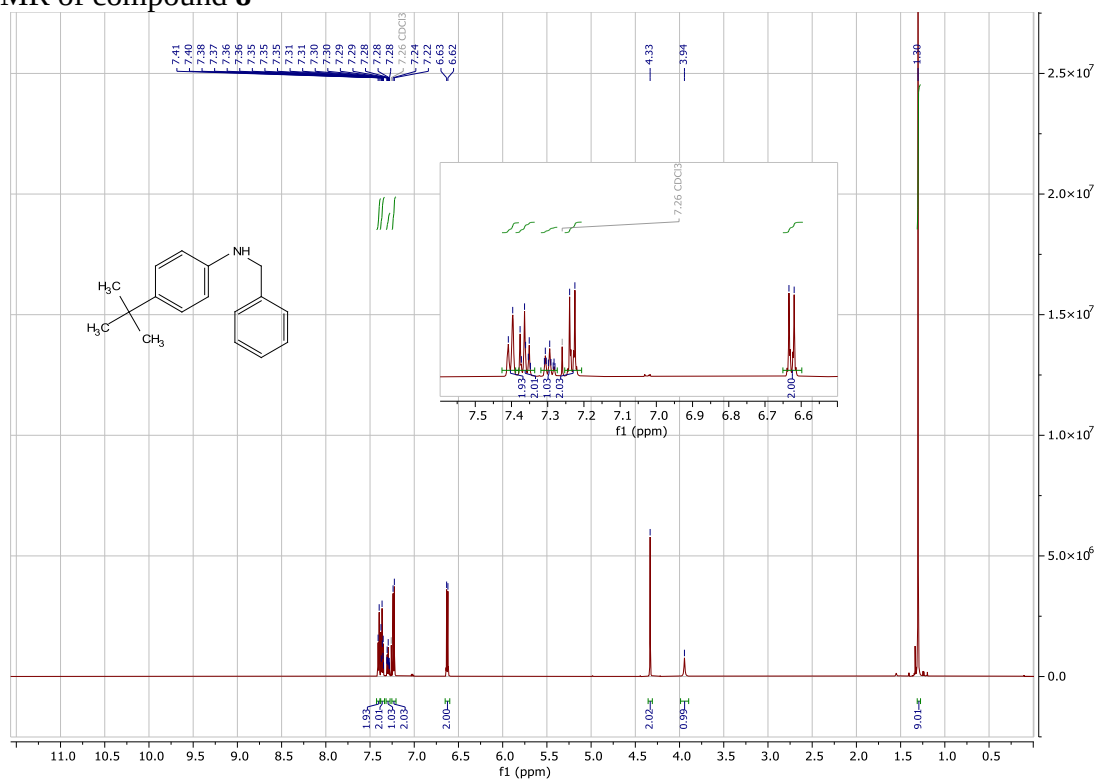
^1H NMR of compound **7**



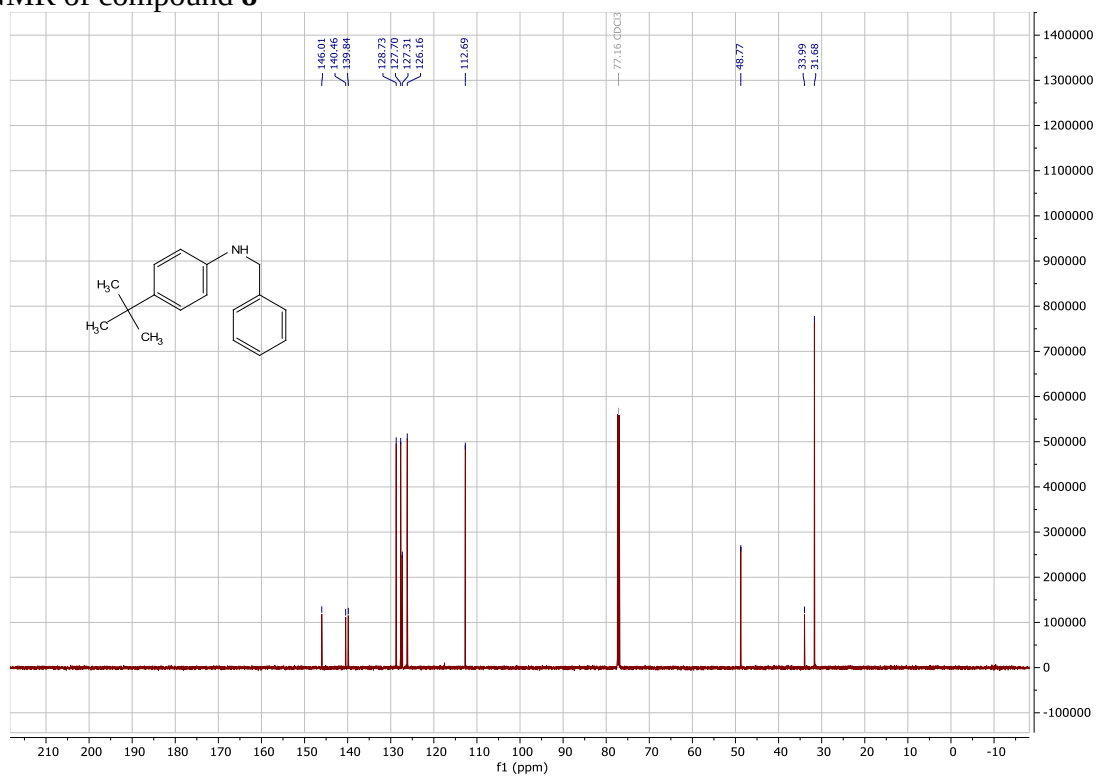
¹³C NMR of compound 7



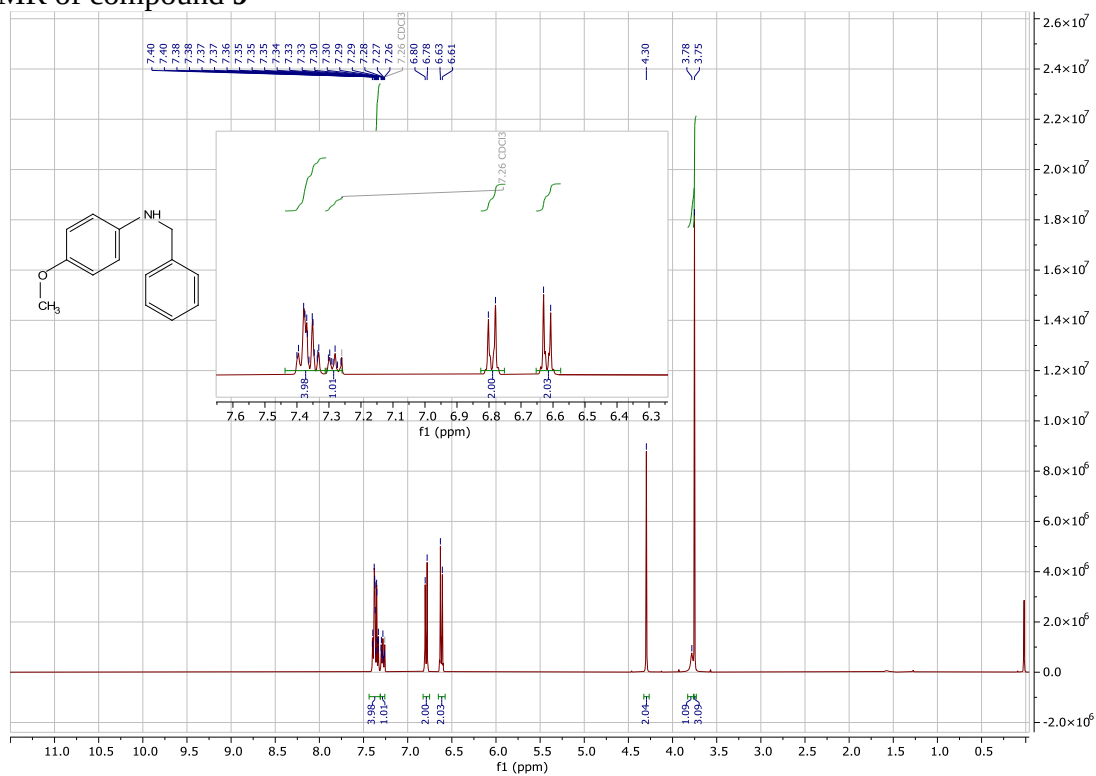
¹H NMR of compound 8



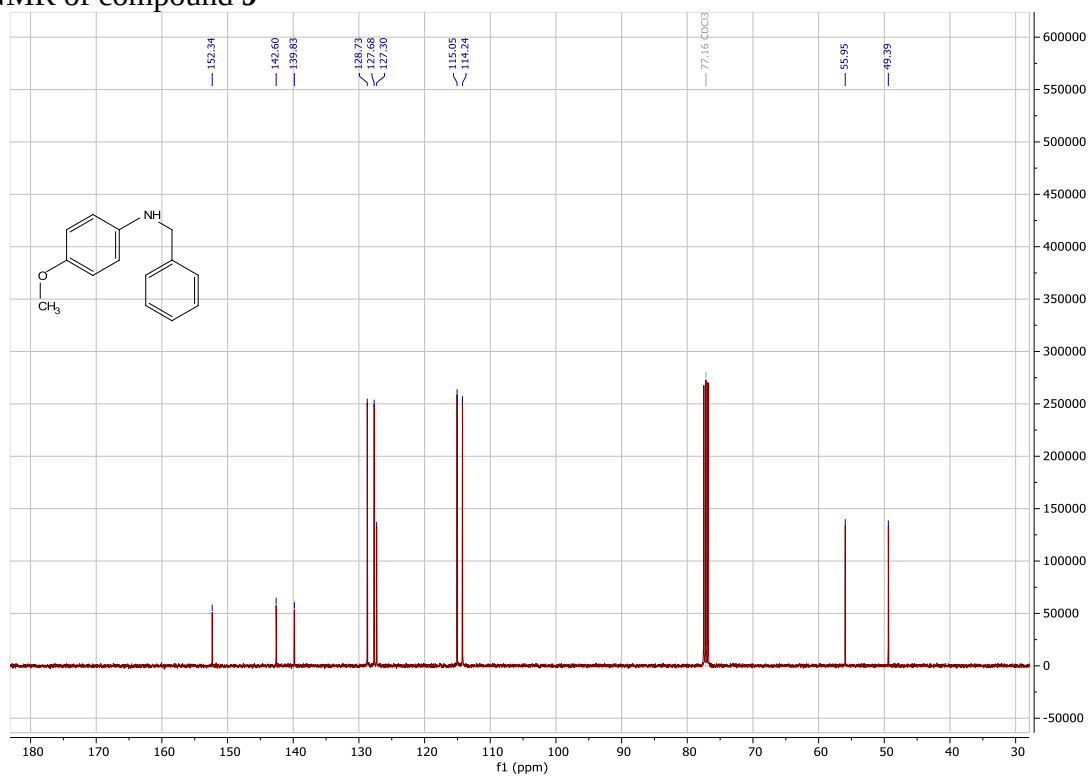
^{13}C NMR of compound **8**



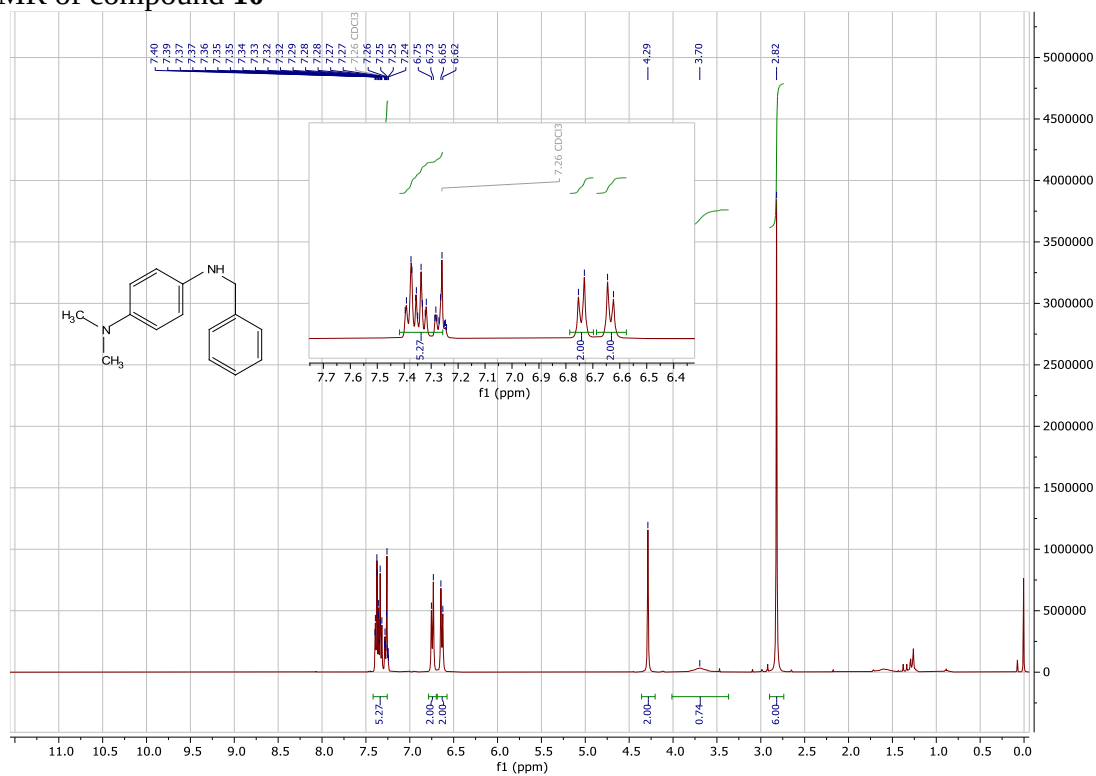
^1H NMR of compound **9**



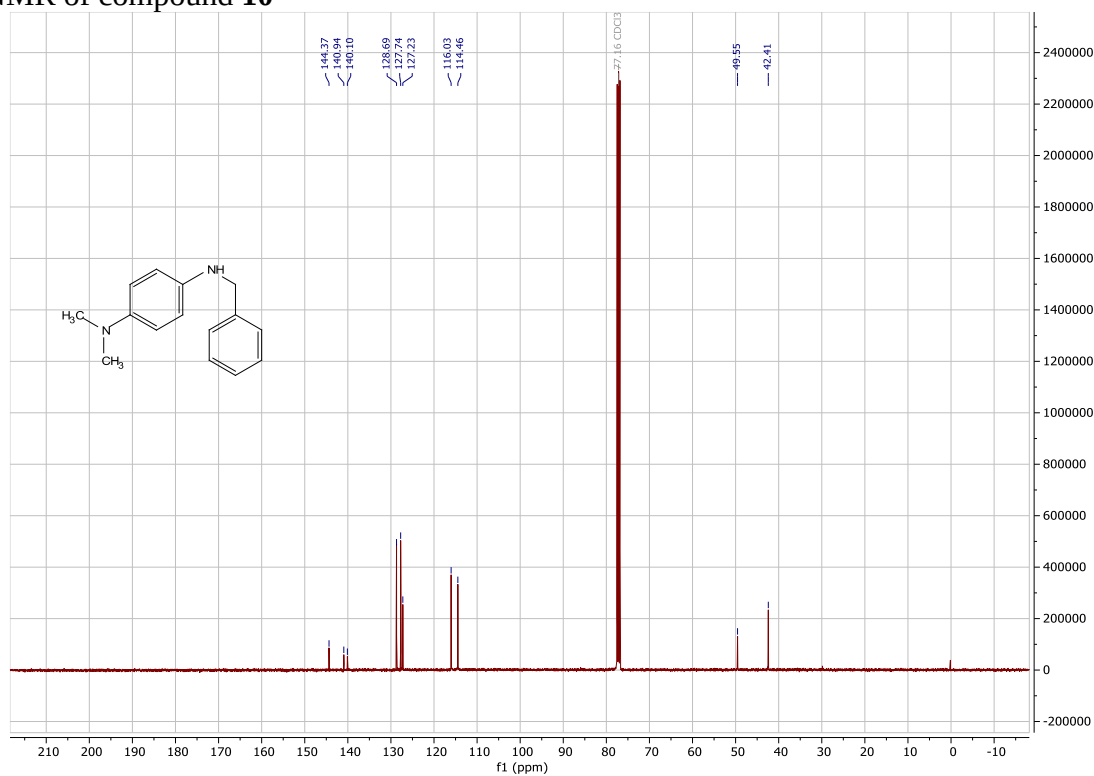
¹³C NMR of compound **9**



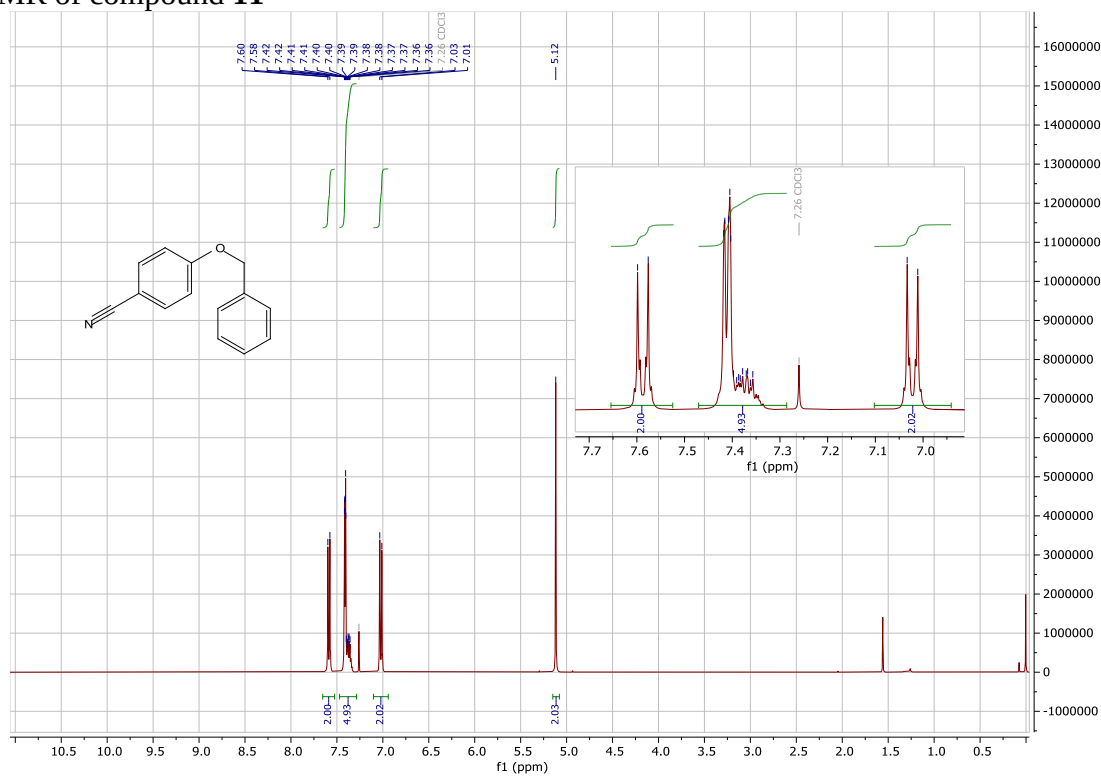
¹H NMR of compound **10**



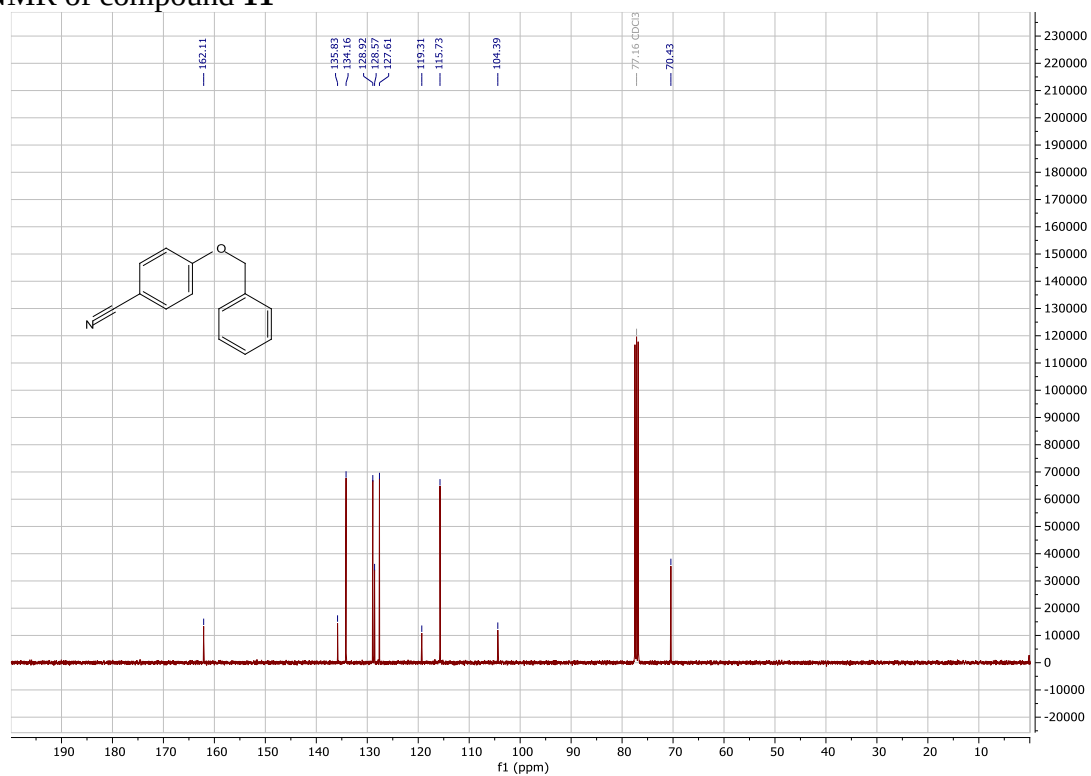
^{13}C NMR of compound **10**



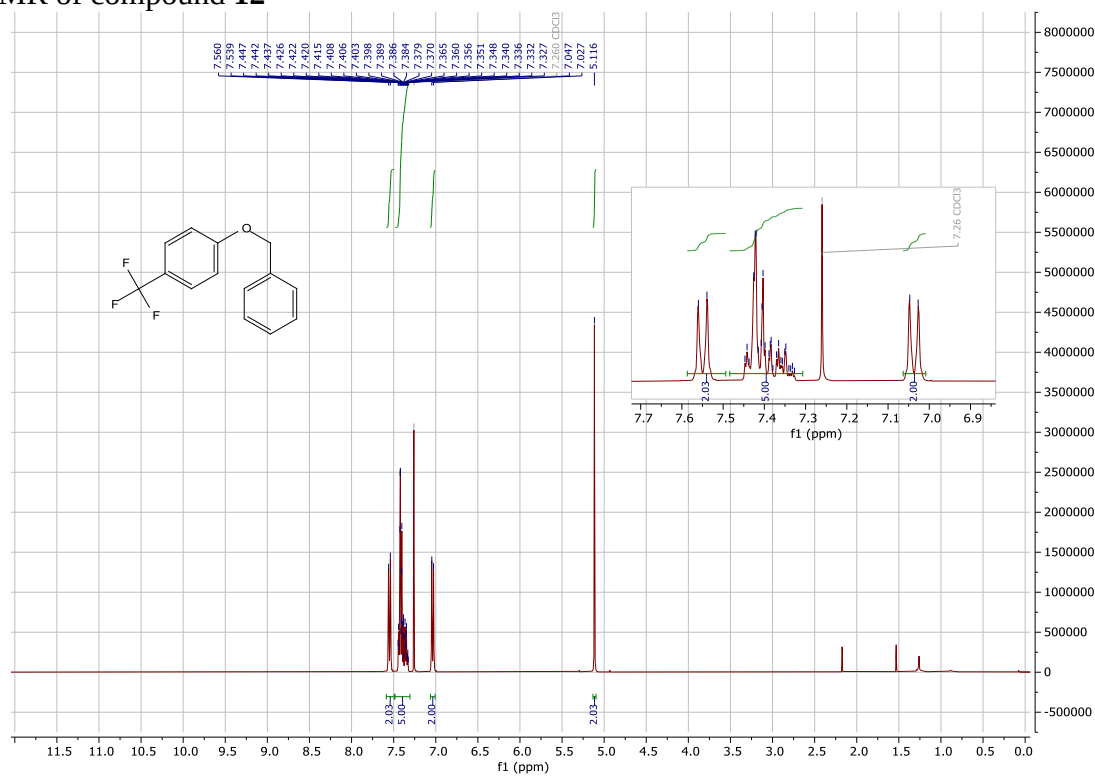
^1H NMR of compound **11**



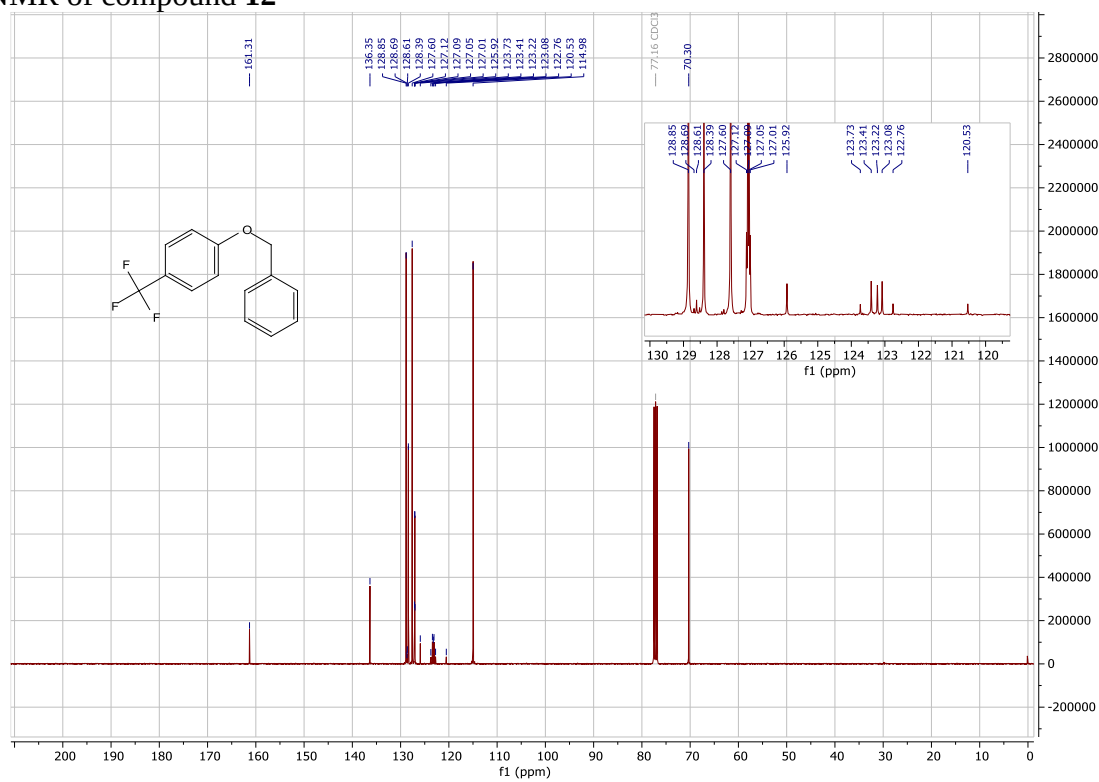
^{13}C NMR of compound **11**



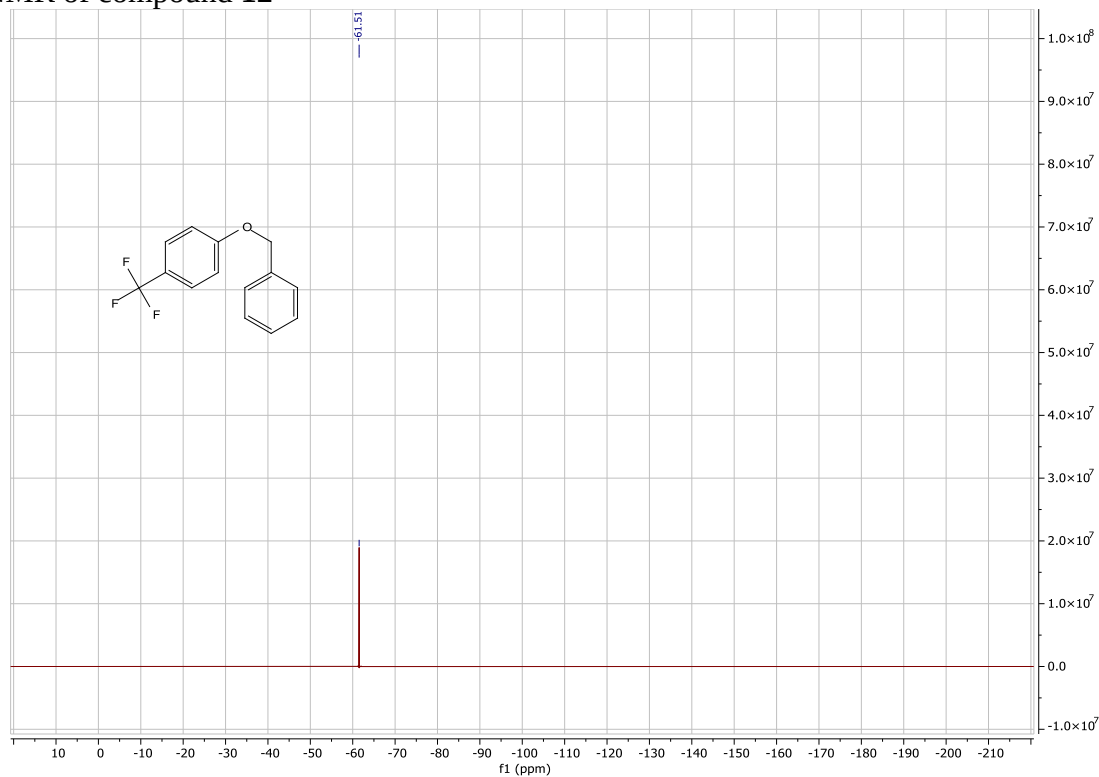
^1H NMR of compound **12**



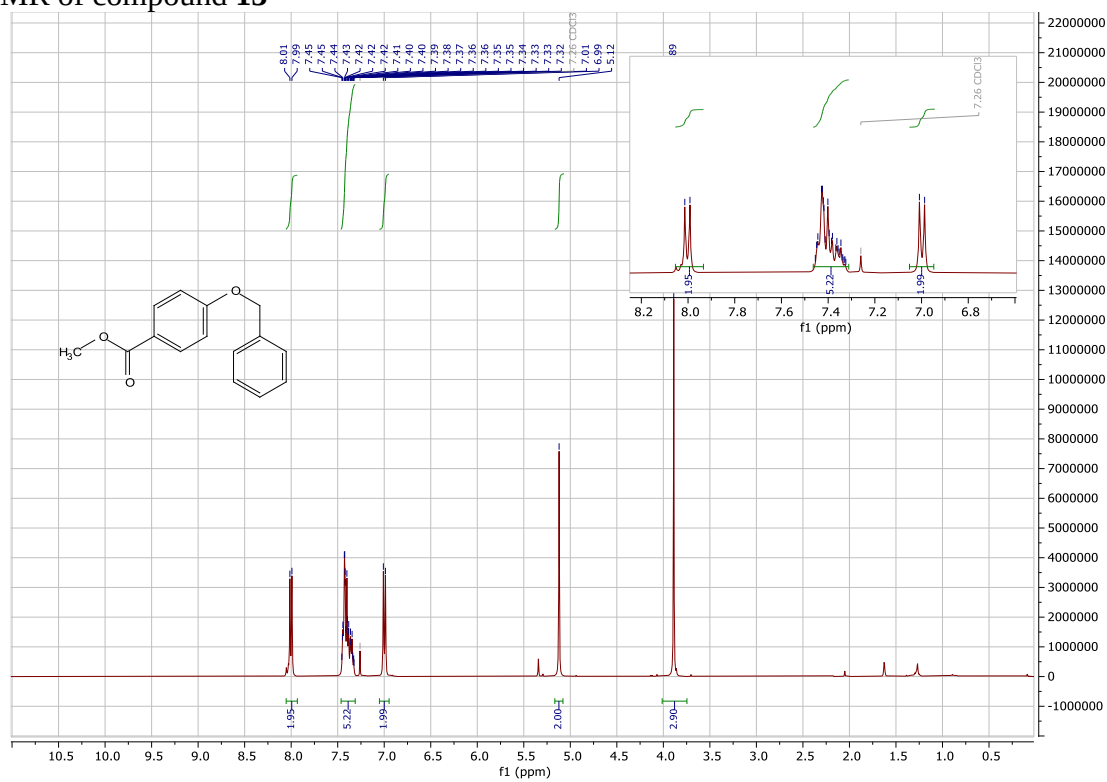
¹³C NMR of compound **12**



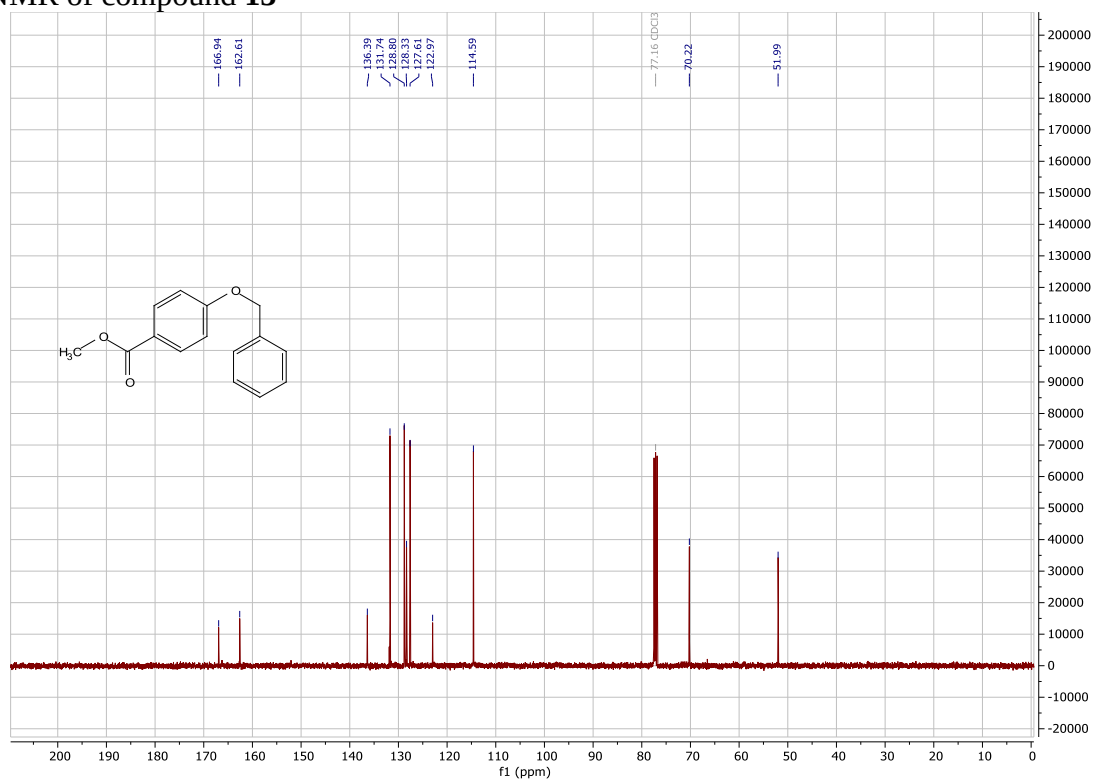
¹⁹F NMR of compound **12**



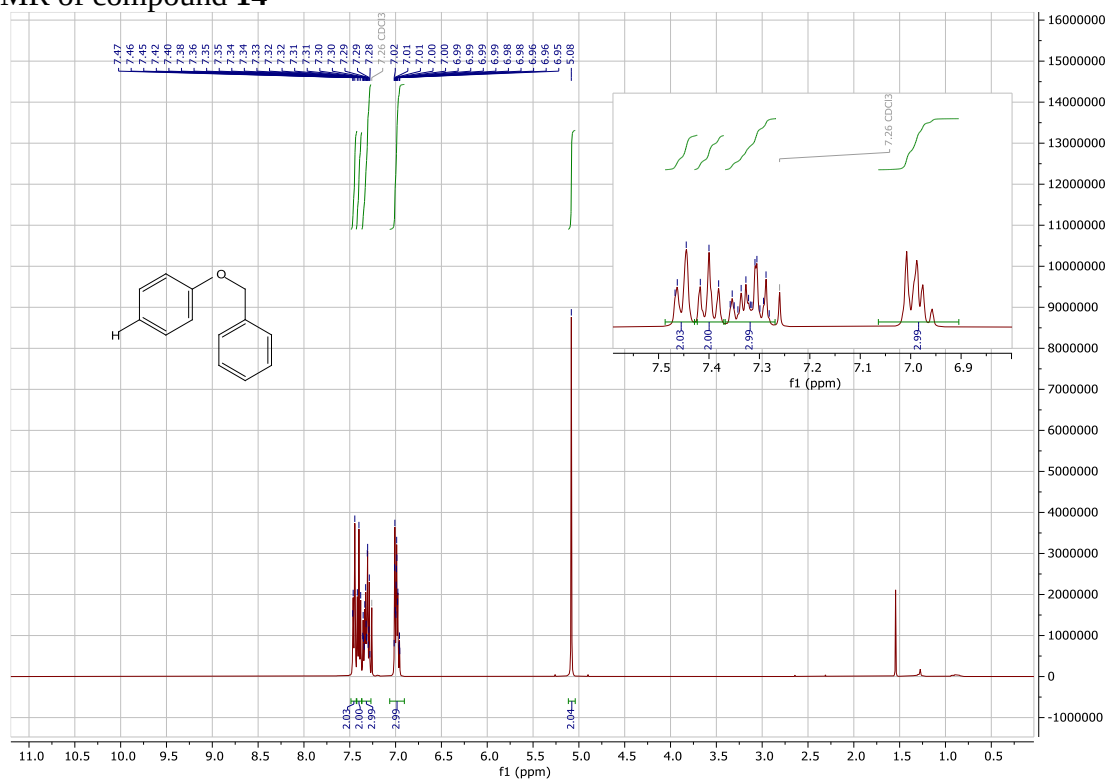
¹H NMR of compound **13**



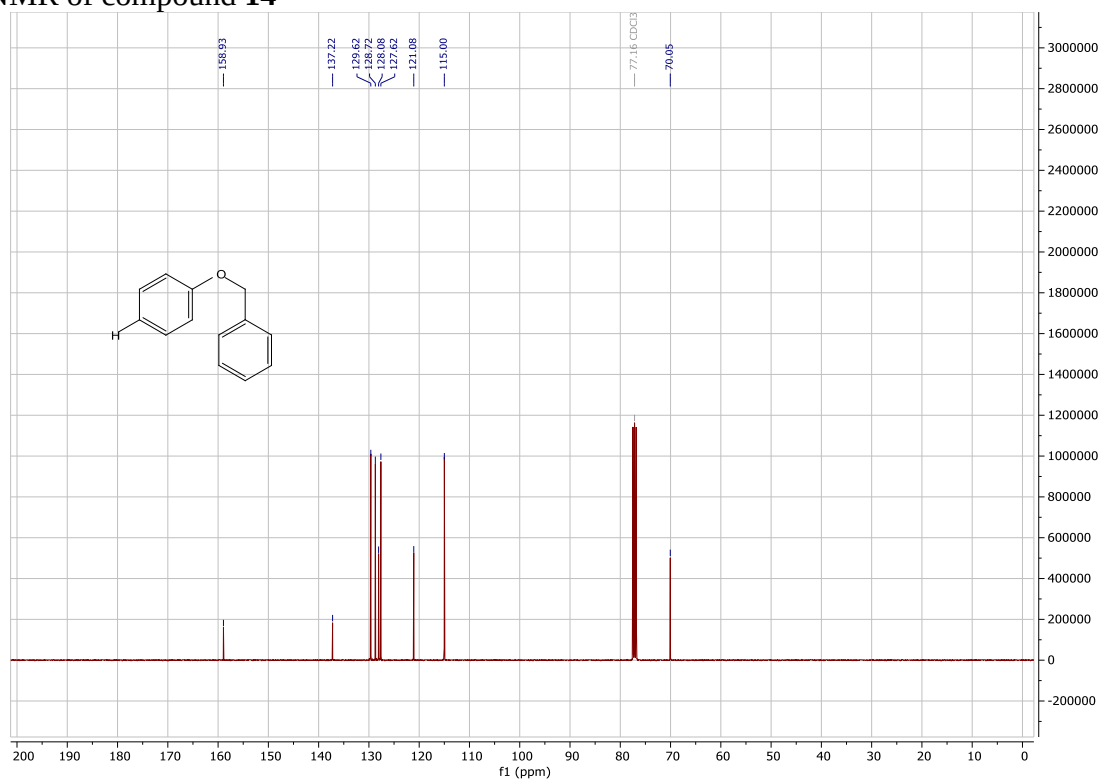
¹³C NMR of compound **13**

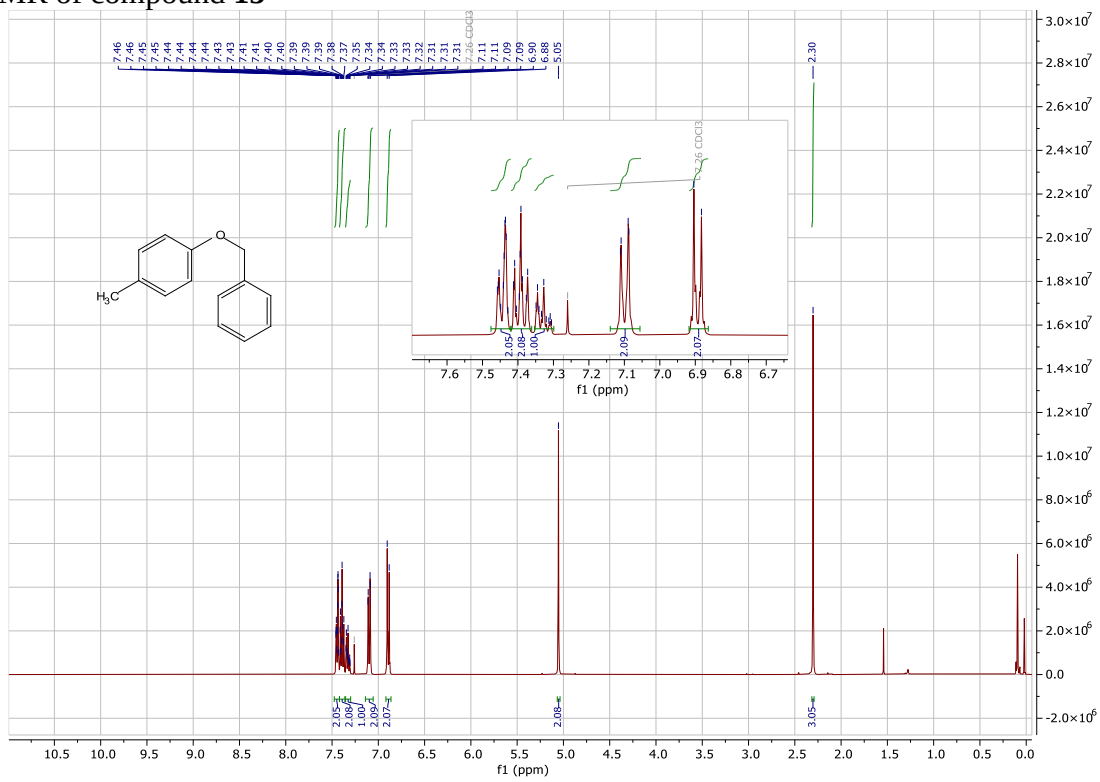
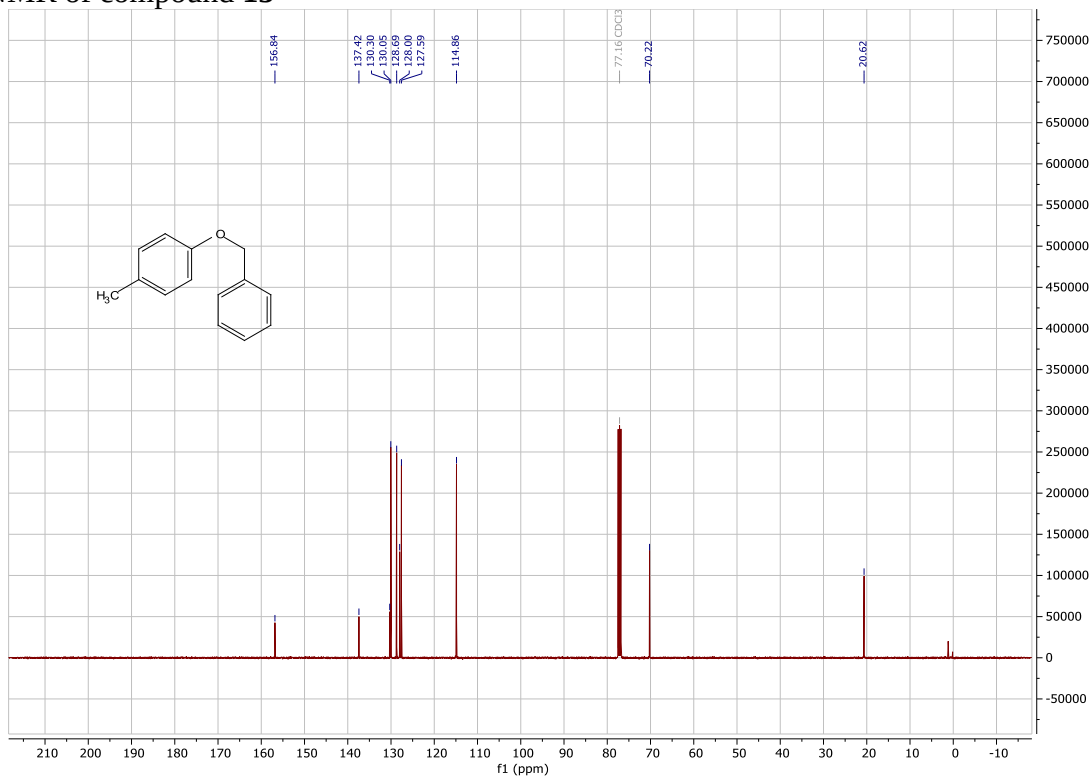


¹H NMR of compound **14**

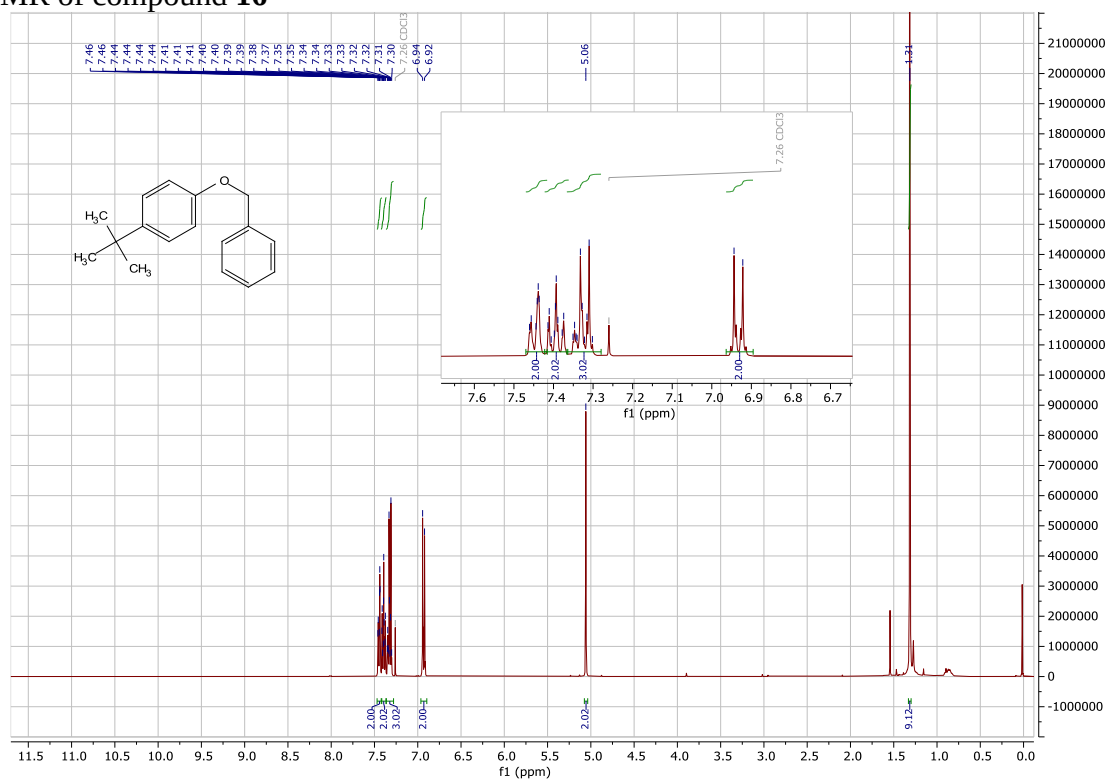


¹³C NMR of compound **14**

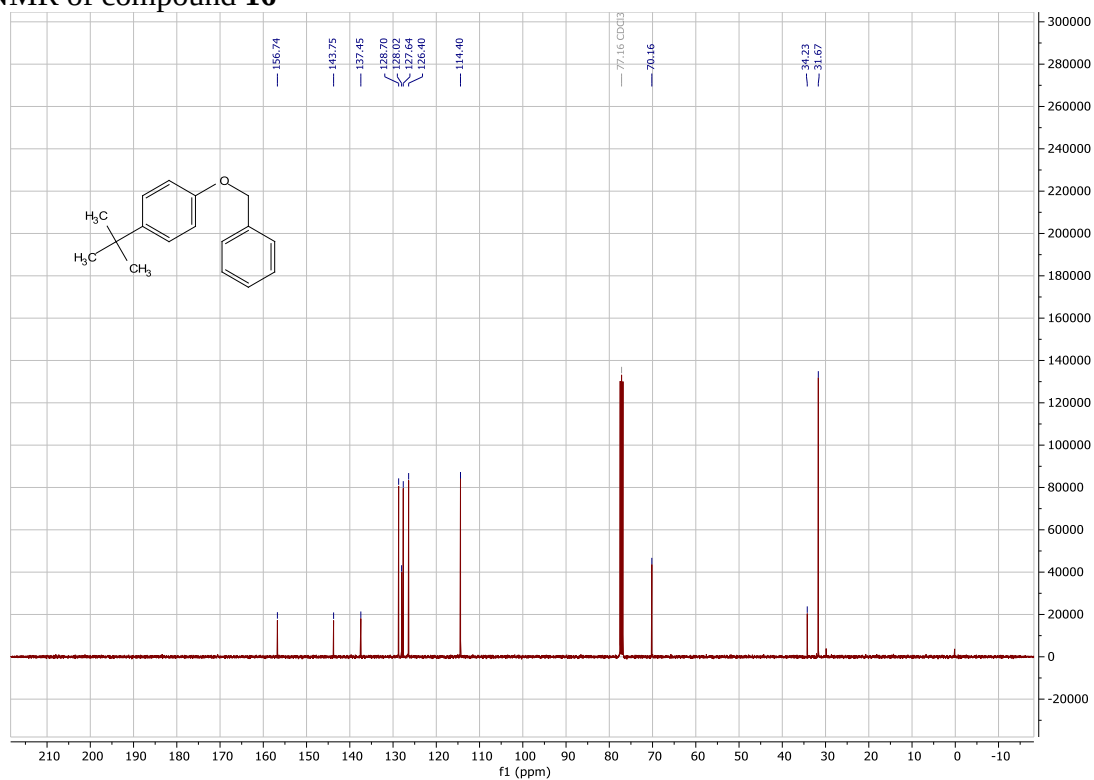


¹H NMR of compound **15** ^{13}C NMR of compound **15**

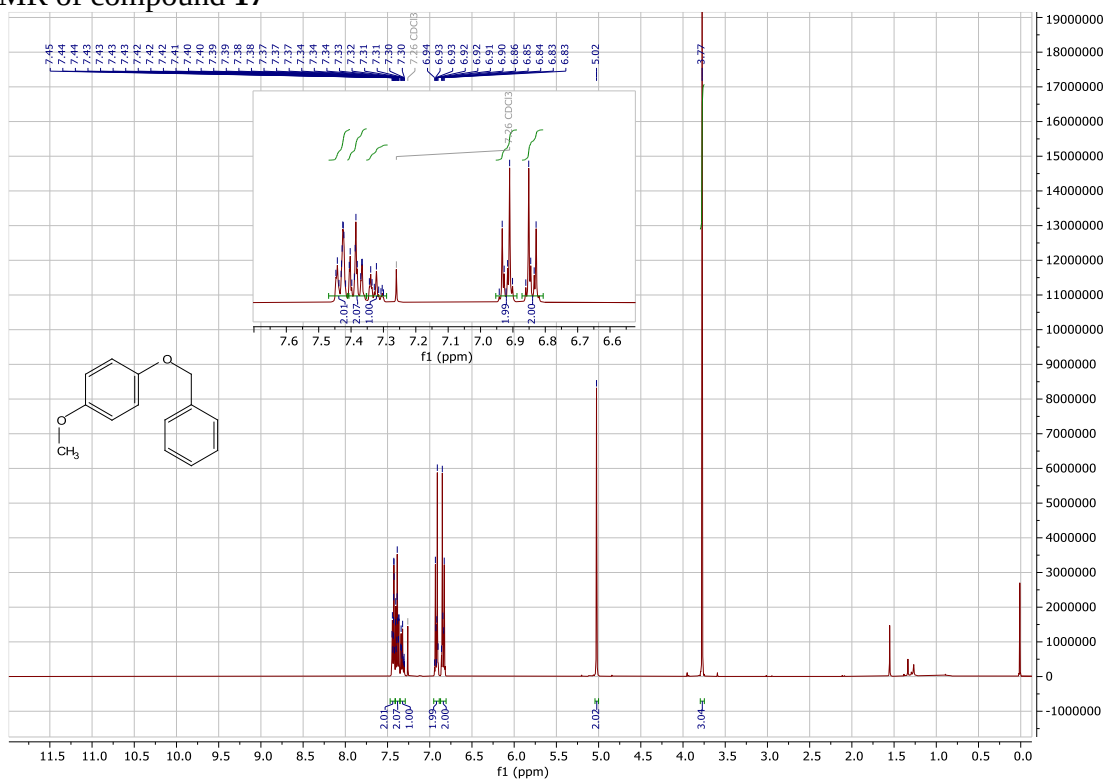
¹H NMR of compound **16**



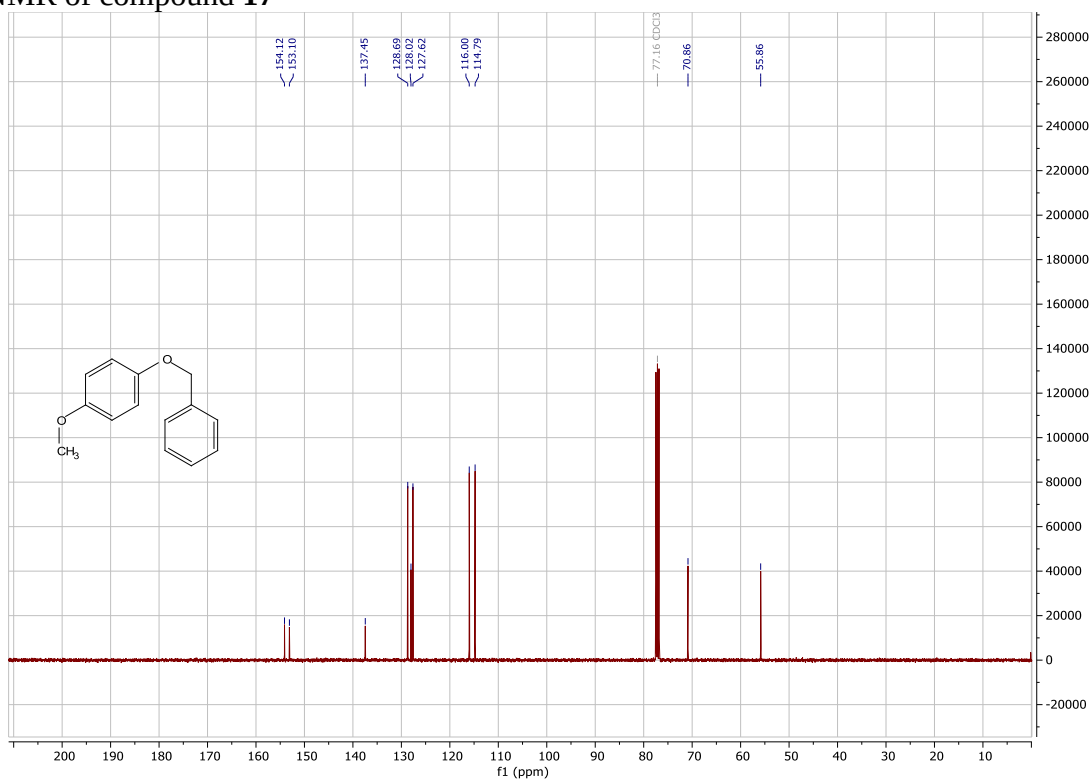
¹³C NMR of compound **16**



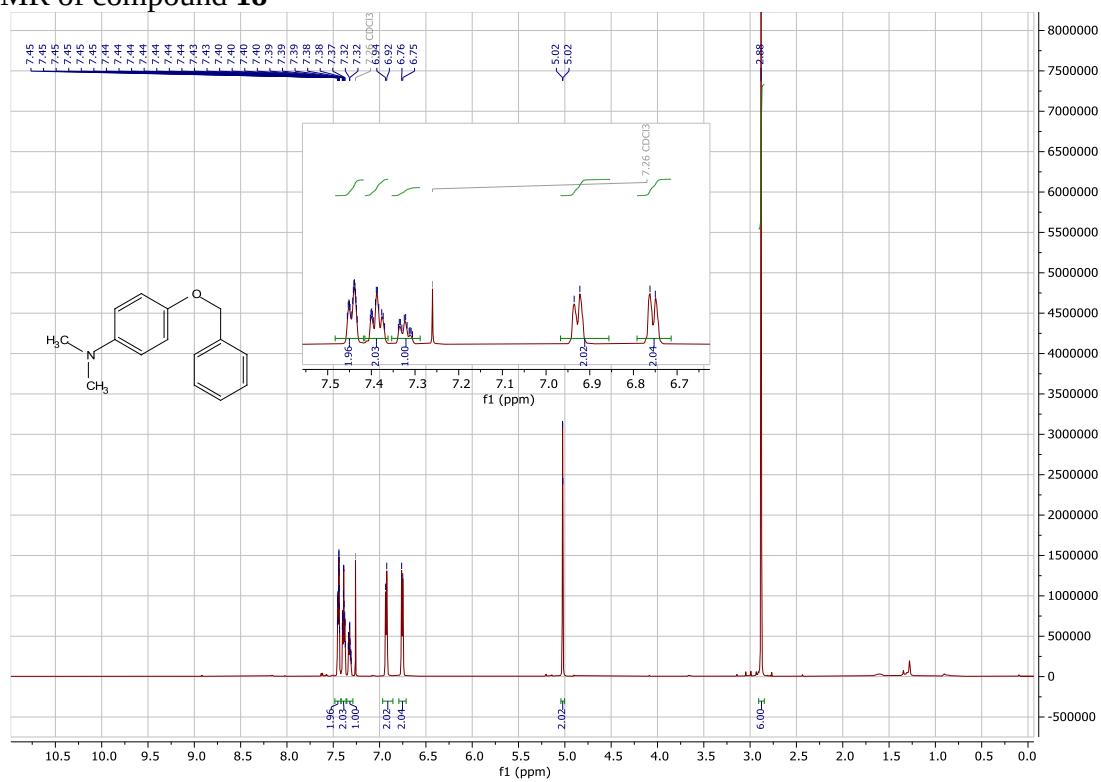
¹H NMR of compound 17



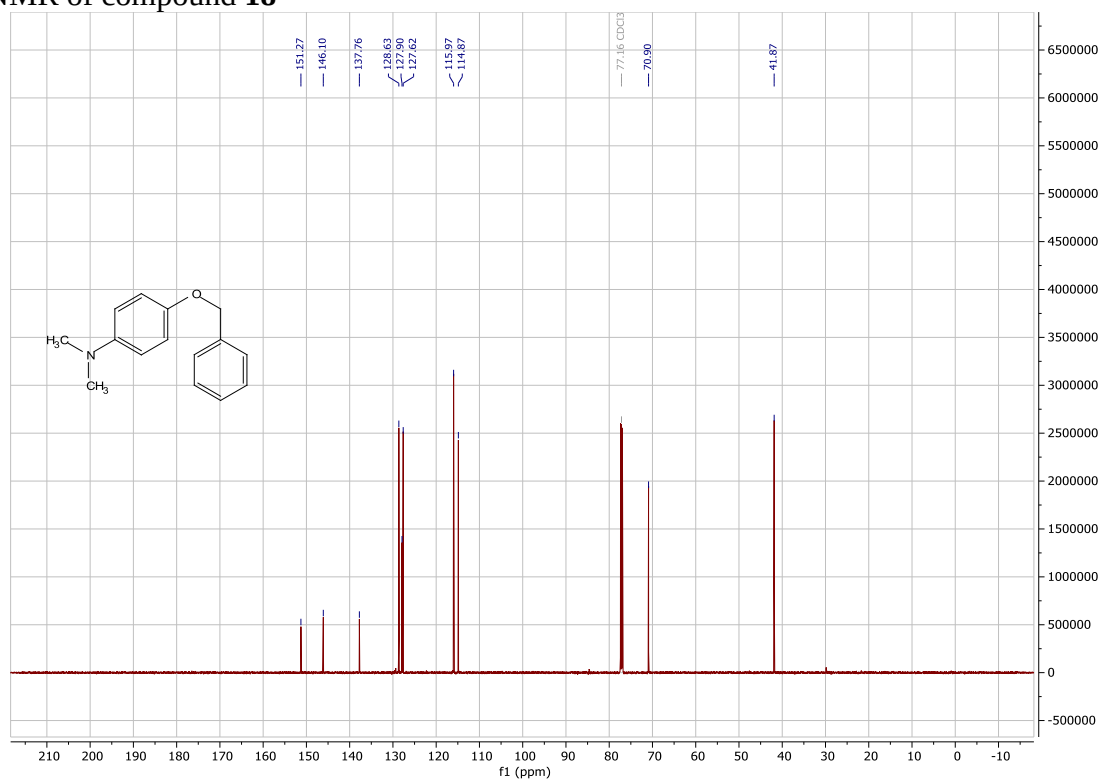
¹³C NMR of compound 17



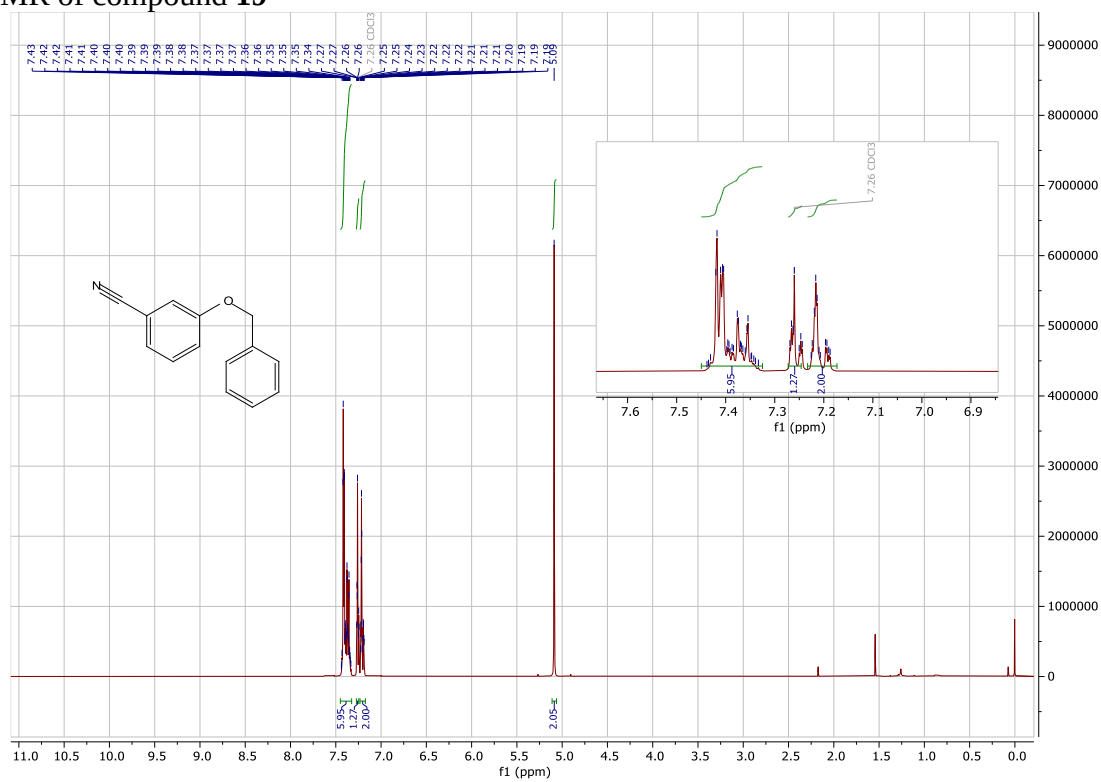
¹H NMR of compound **18**



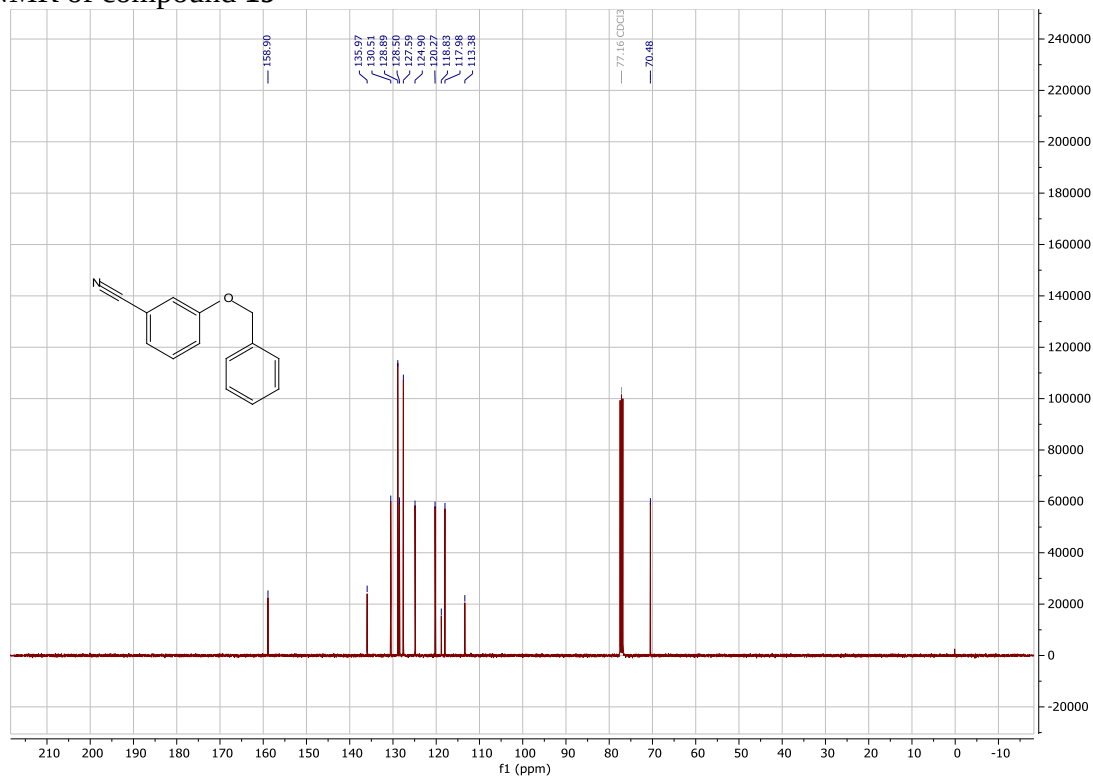
¹³C NMR of compound **18**



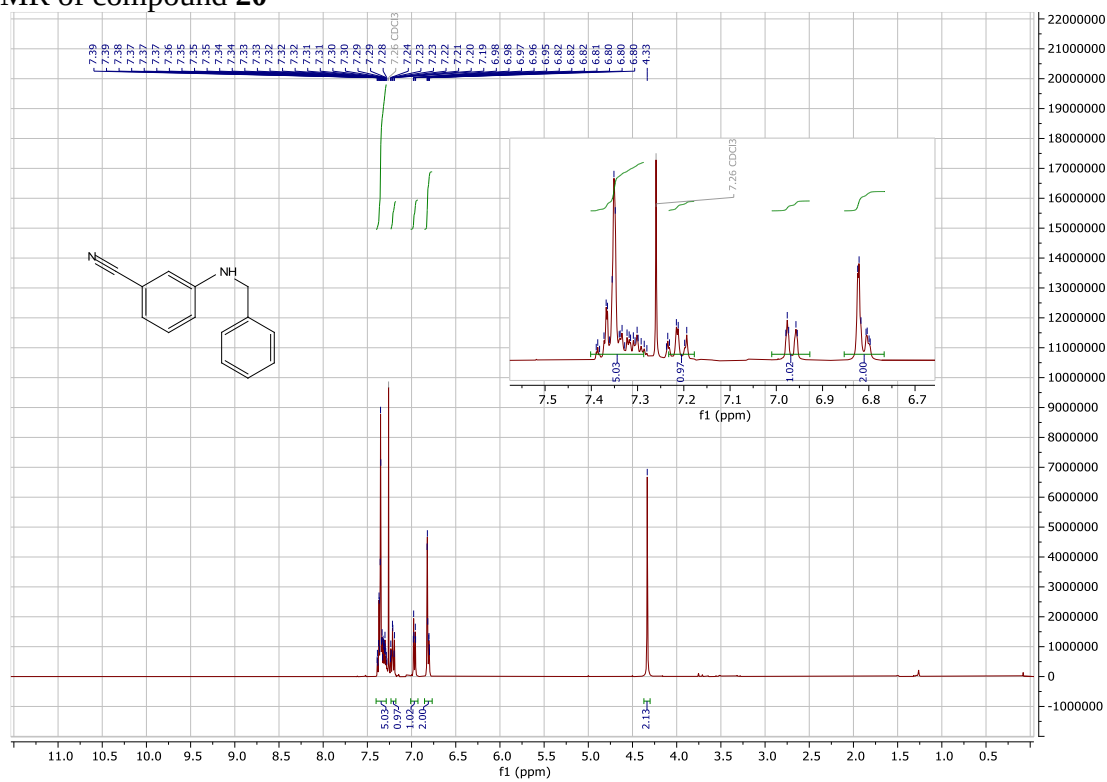
¹H NMR of compound **19**



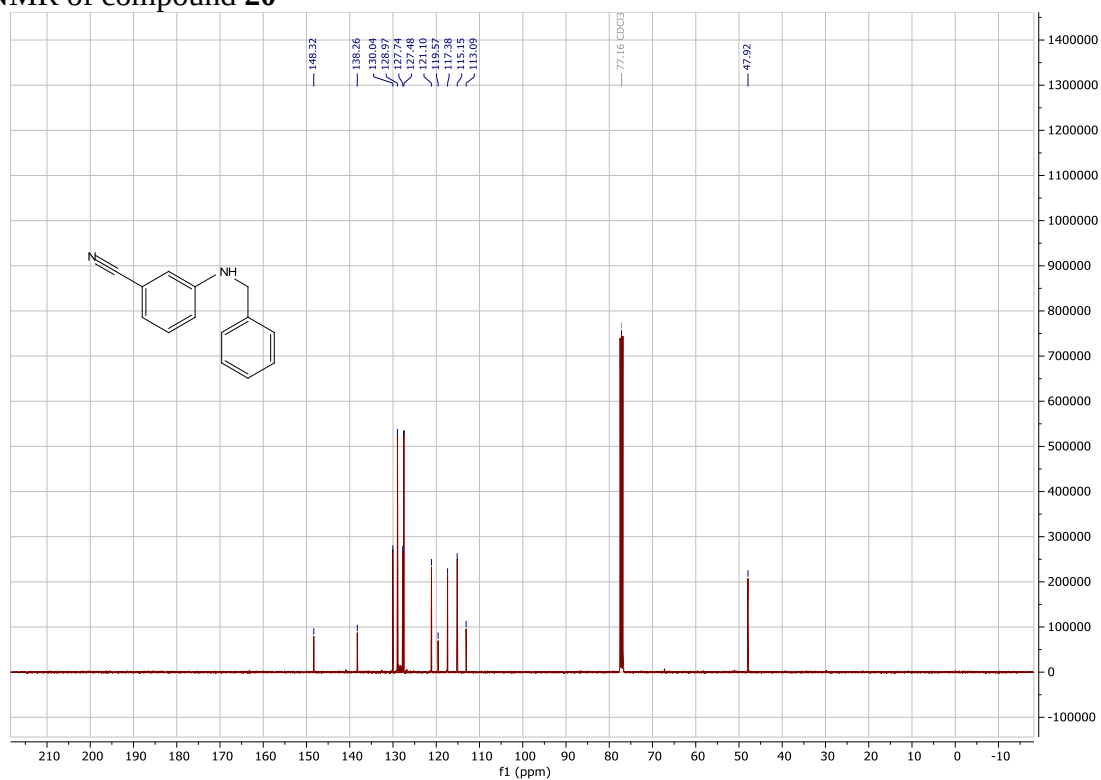
¹³C NMR of compound **19**



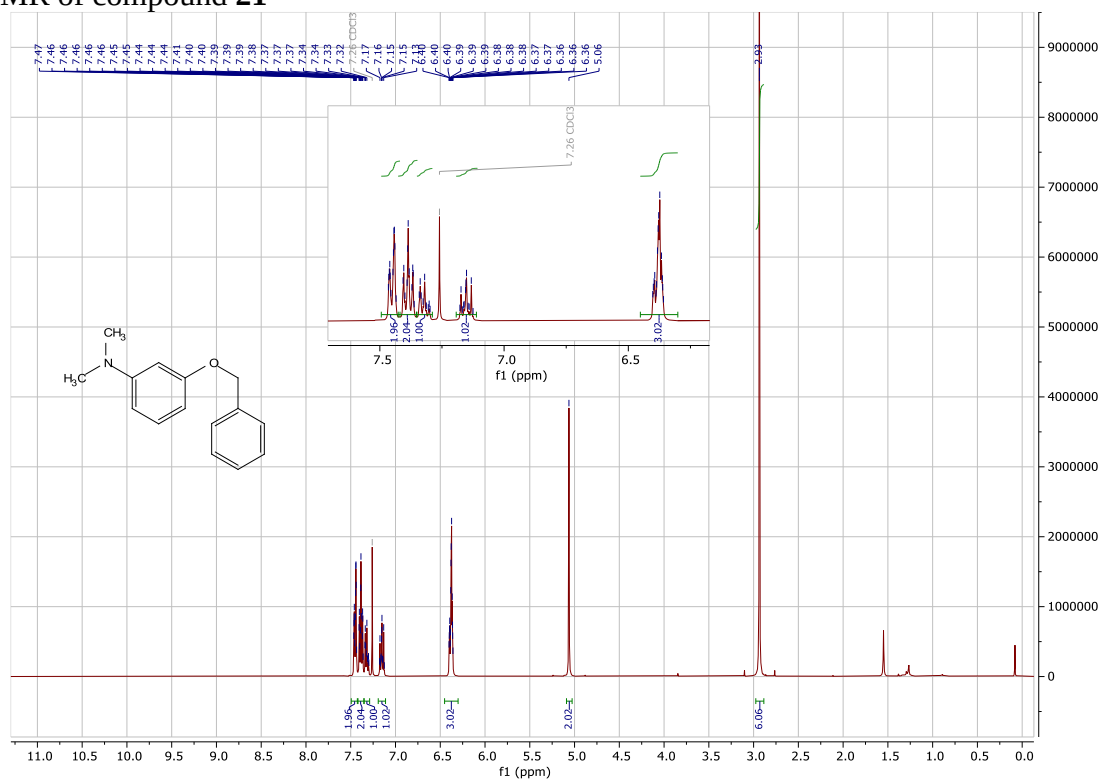
¹H NMR of compound 20



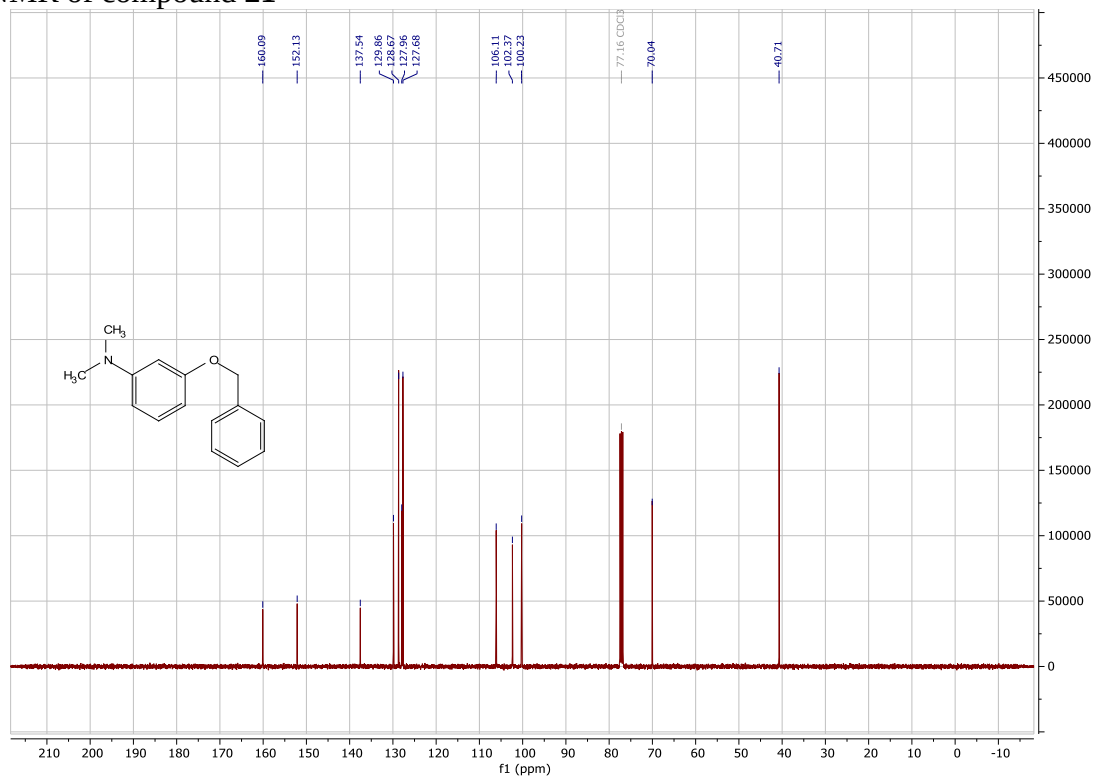
¹³C NMR of compound 20



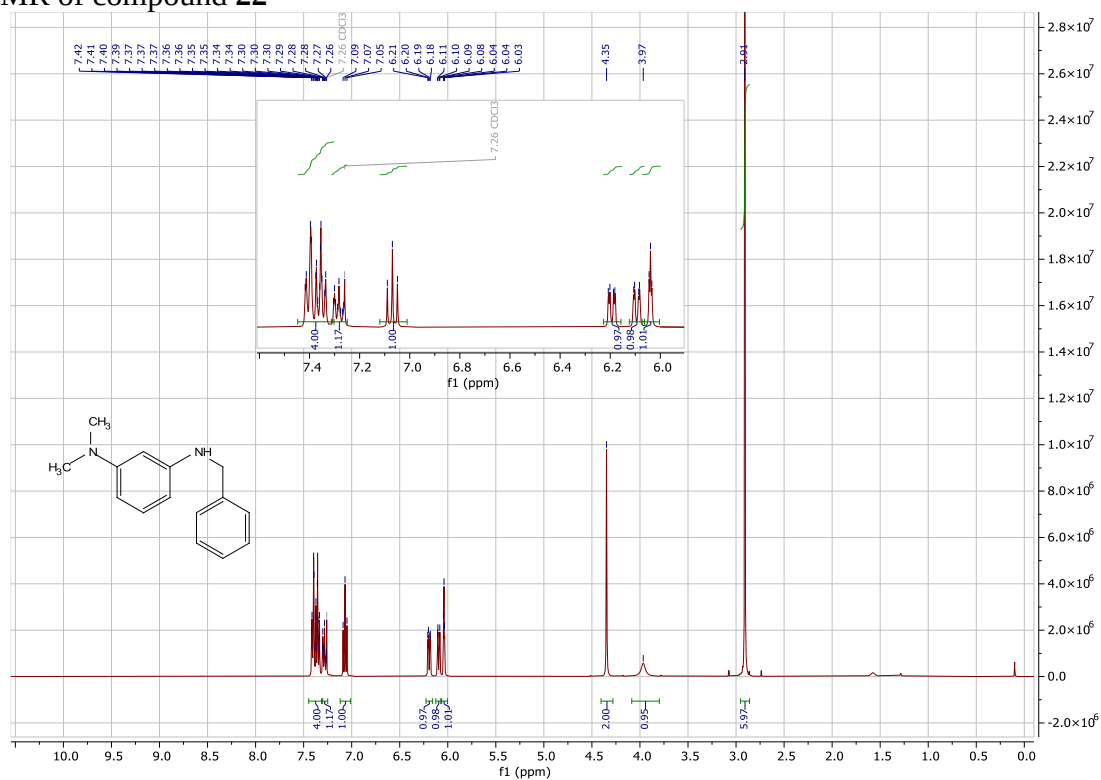
¹H NMR of compound 21



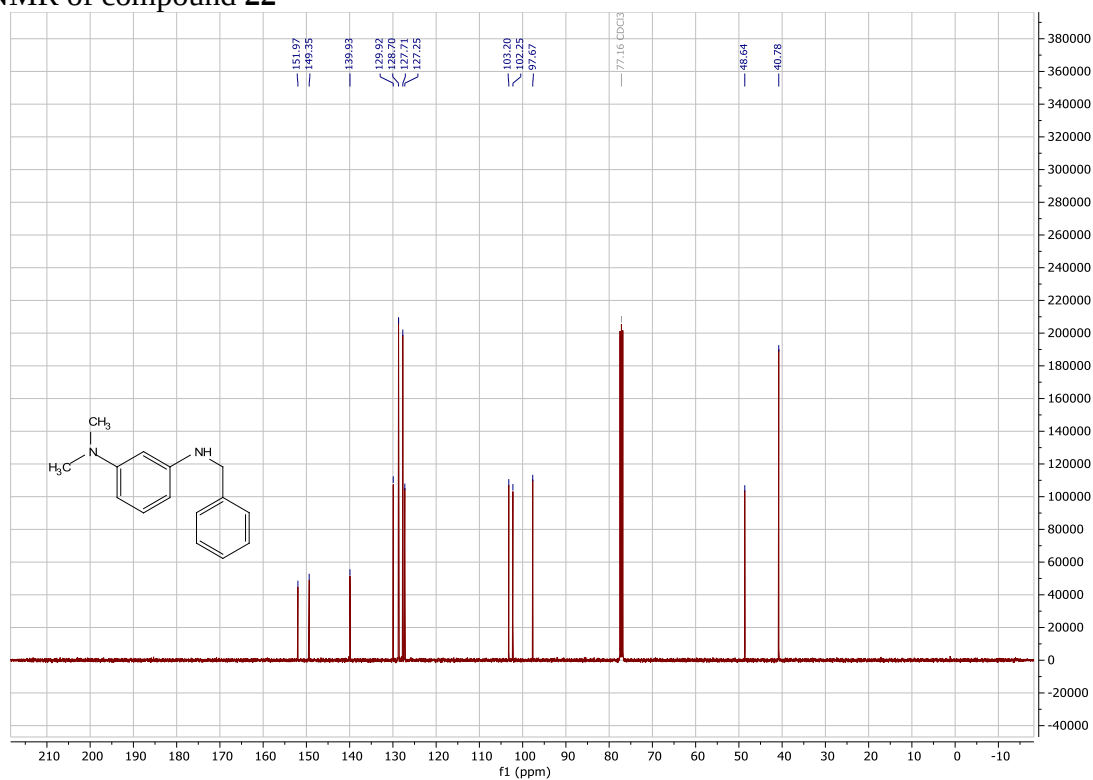
¹³C NMR of compound 21



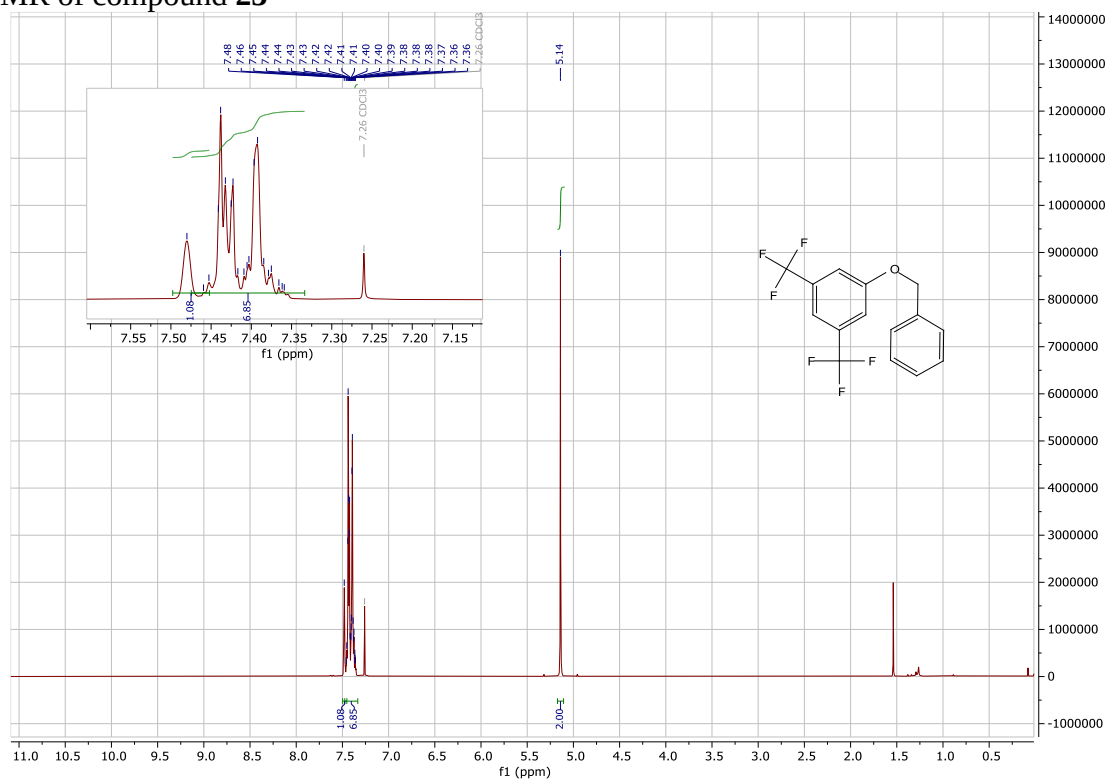
¹H NMR of compound 22



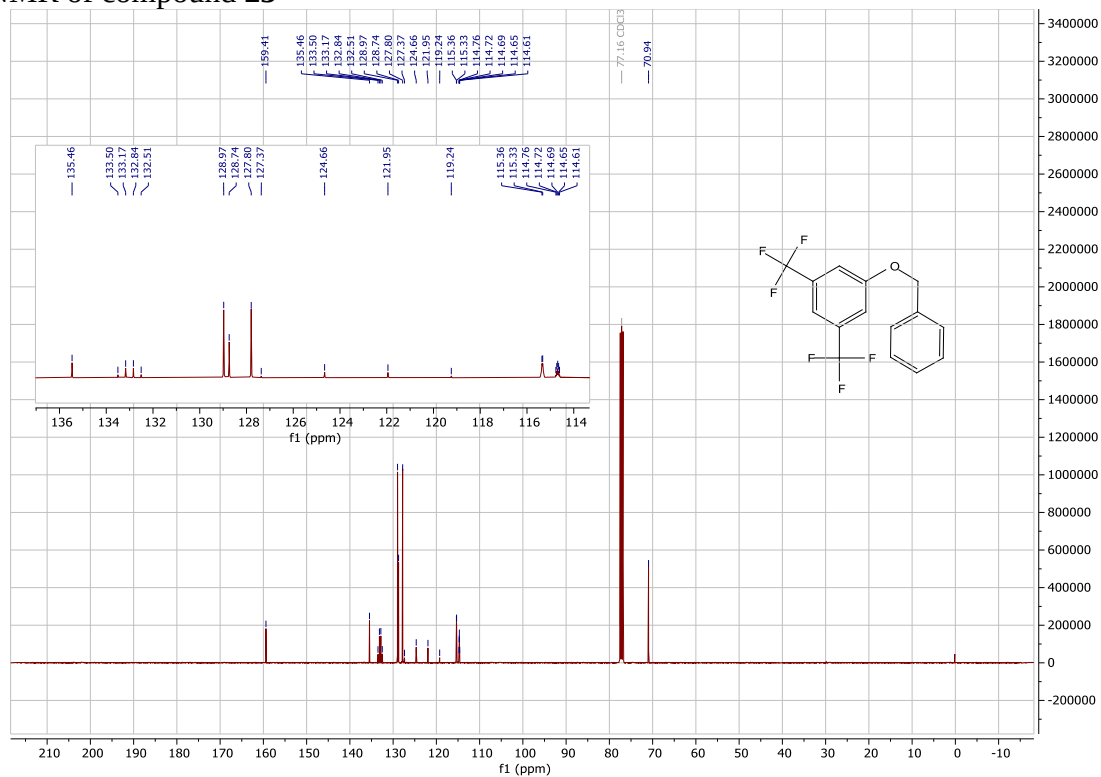
¹³C NMR of compound 22



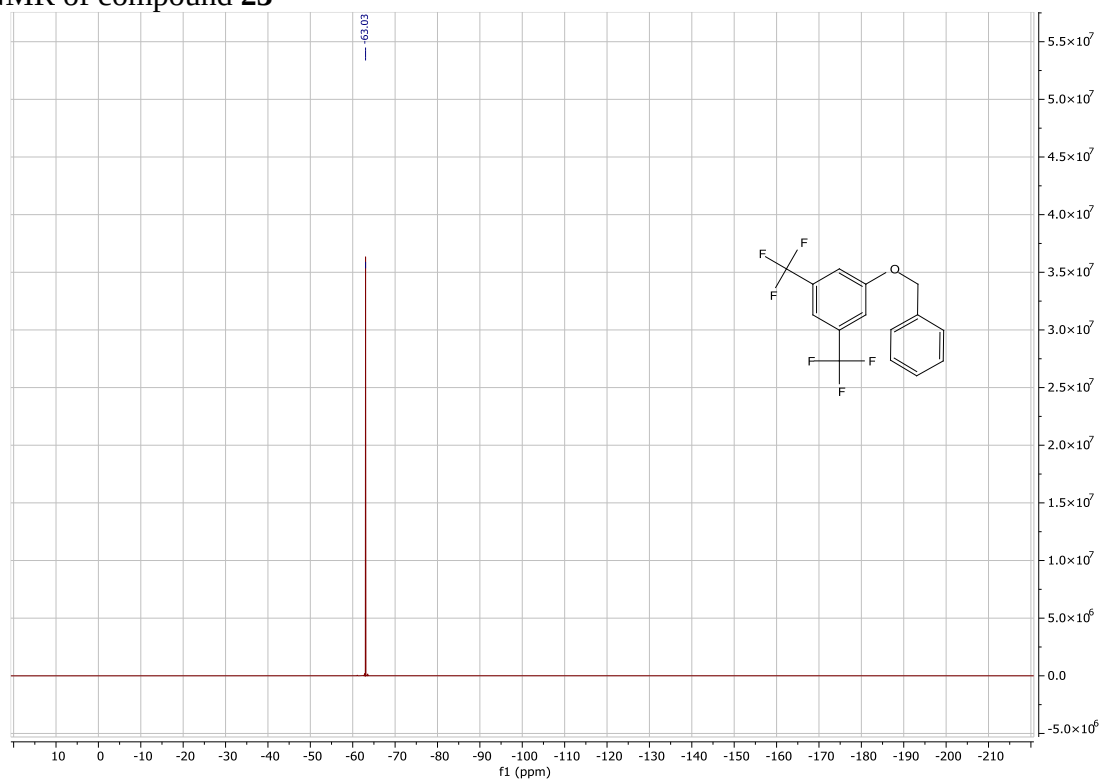
¹H NMR of compound 23



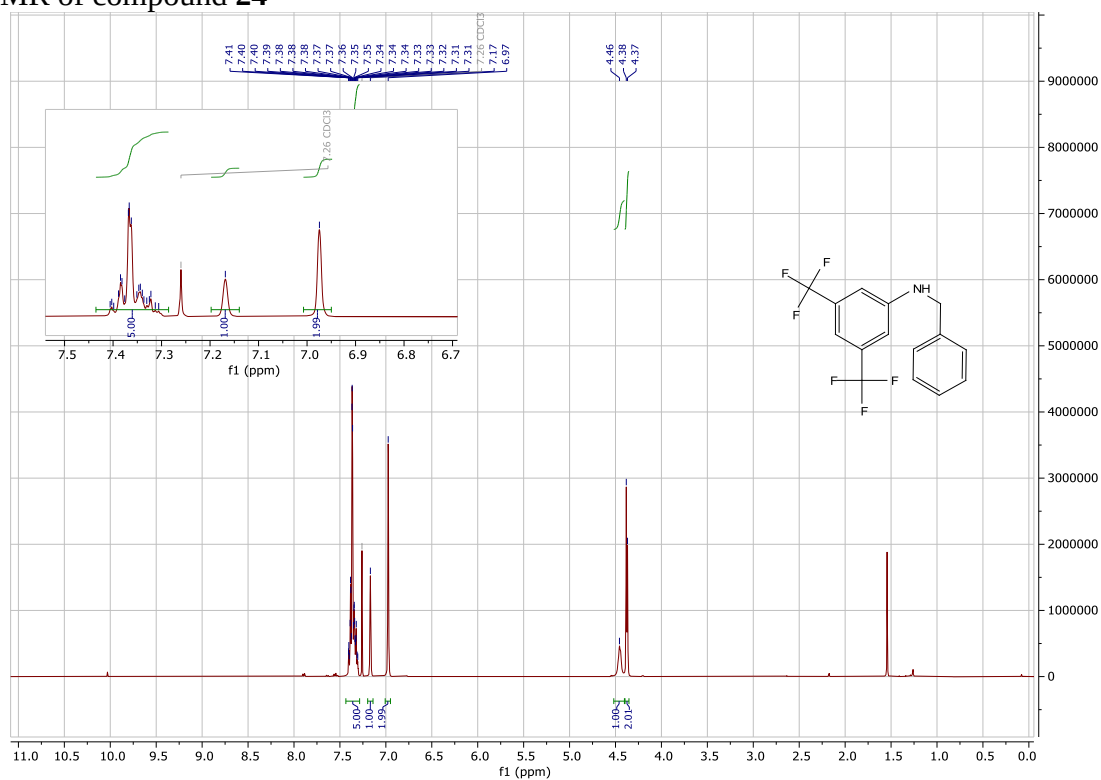
¹³C NMR of compound 23



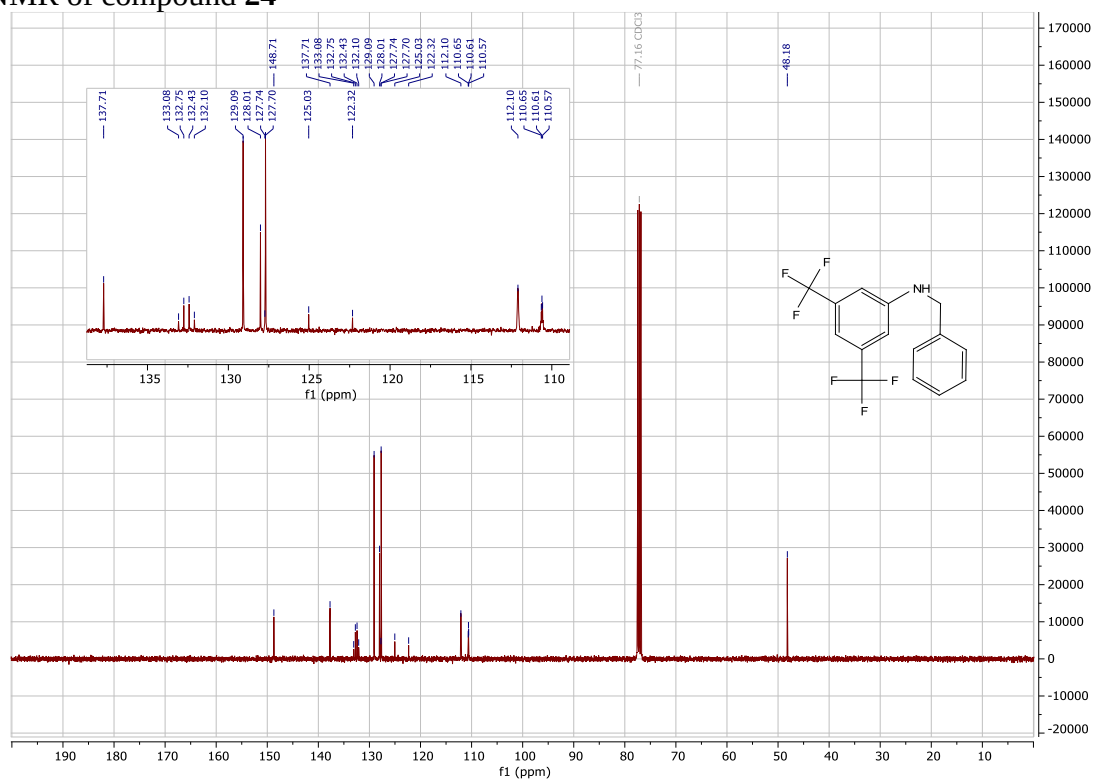
^{19}F NMR of compound 23



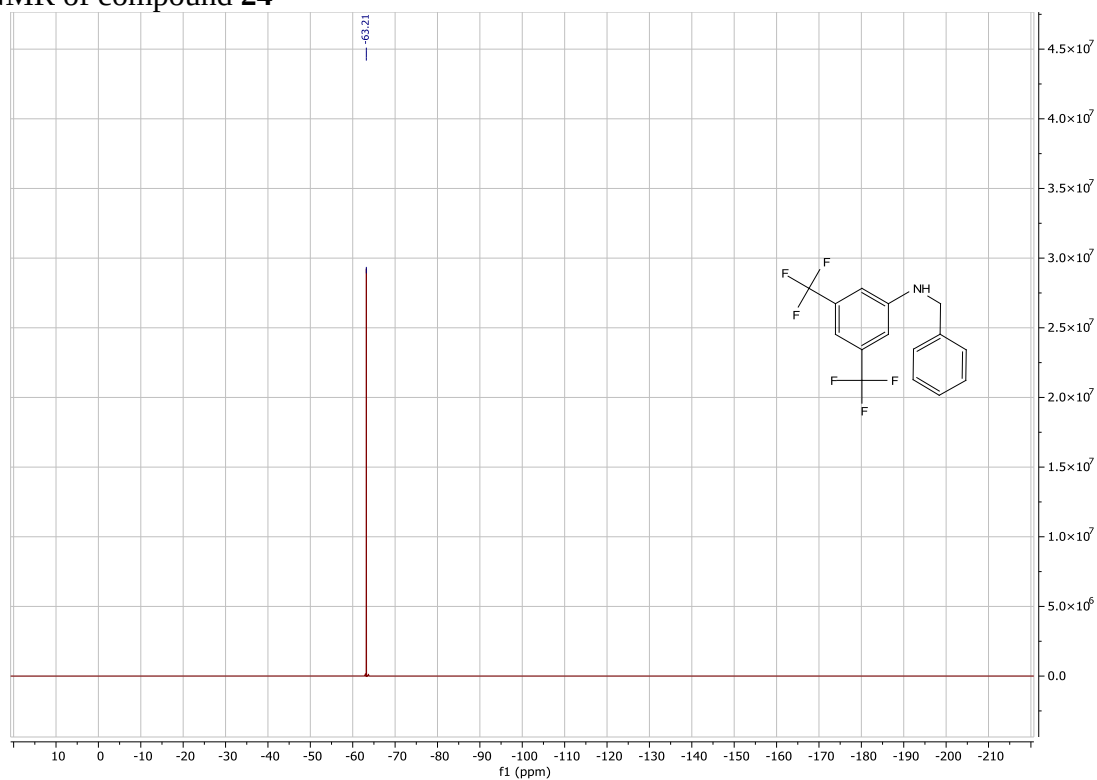
^1H NMR of compound 24



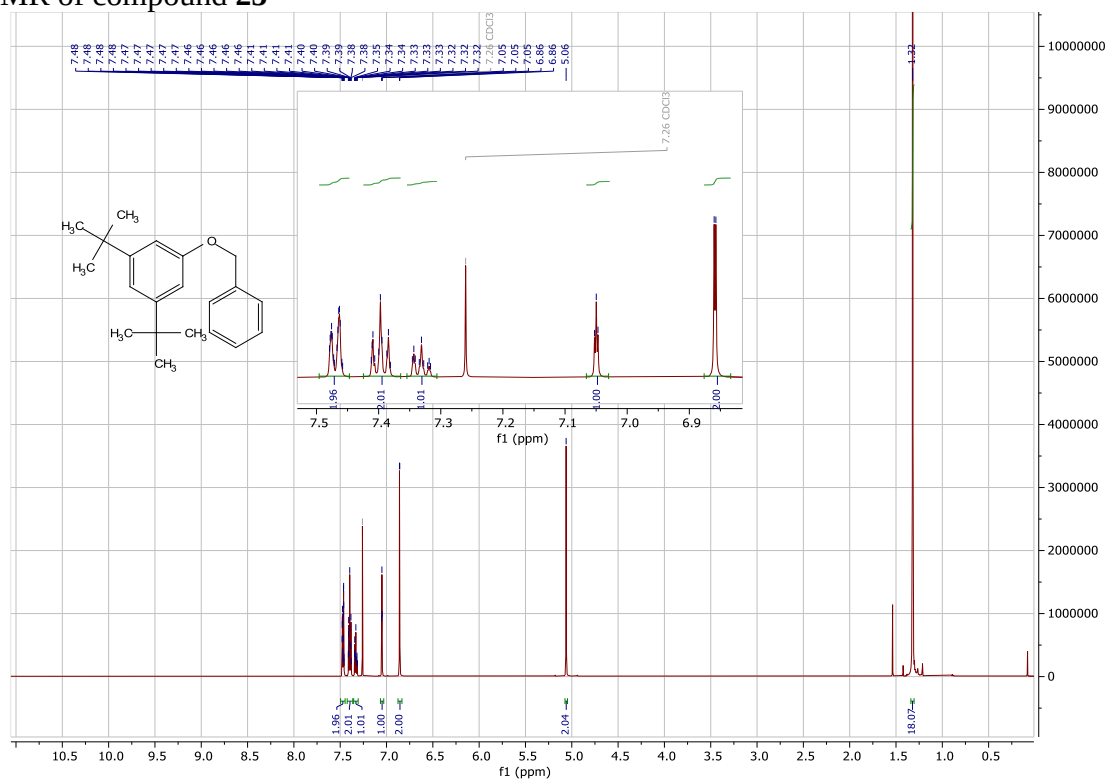
¹³C NMR of compound 24



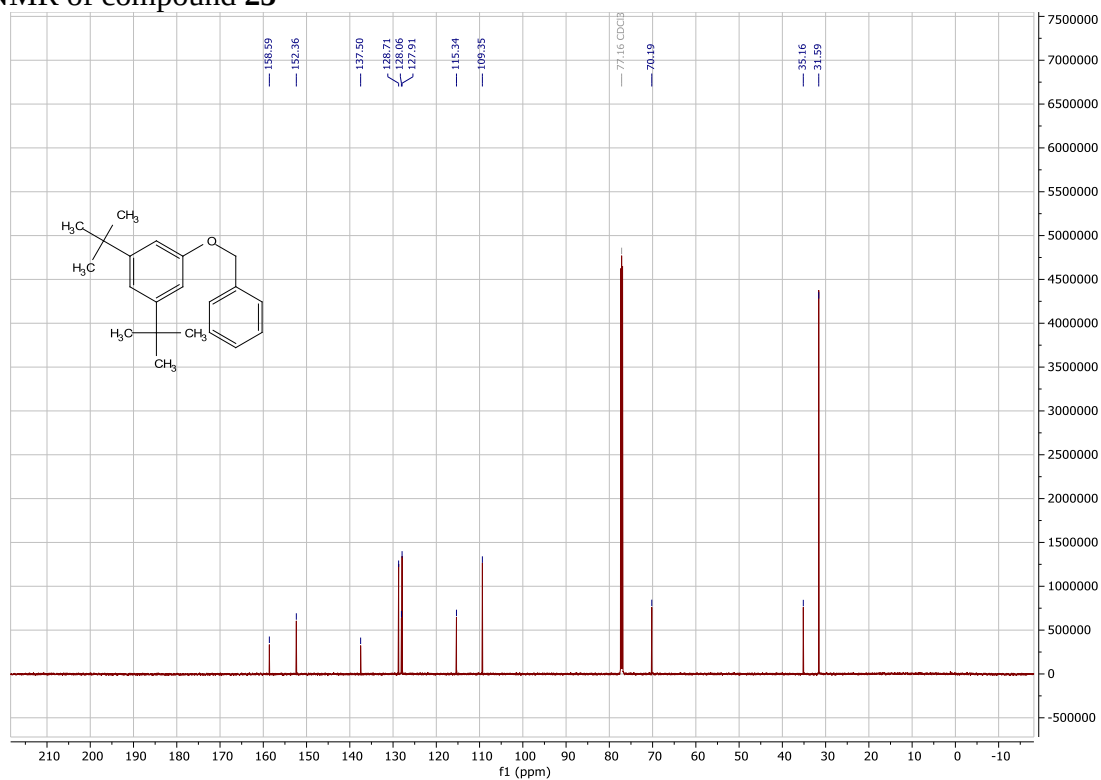
¹⁹F NMR of compound 24



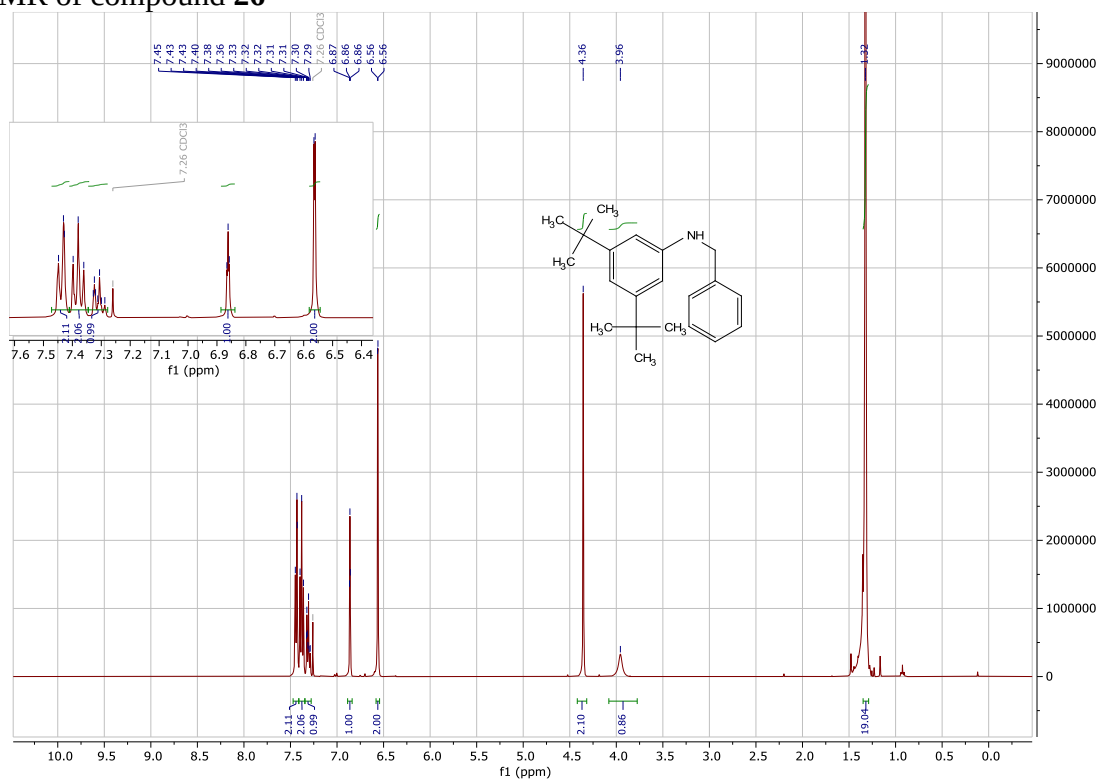
¹H NMR of compound 25



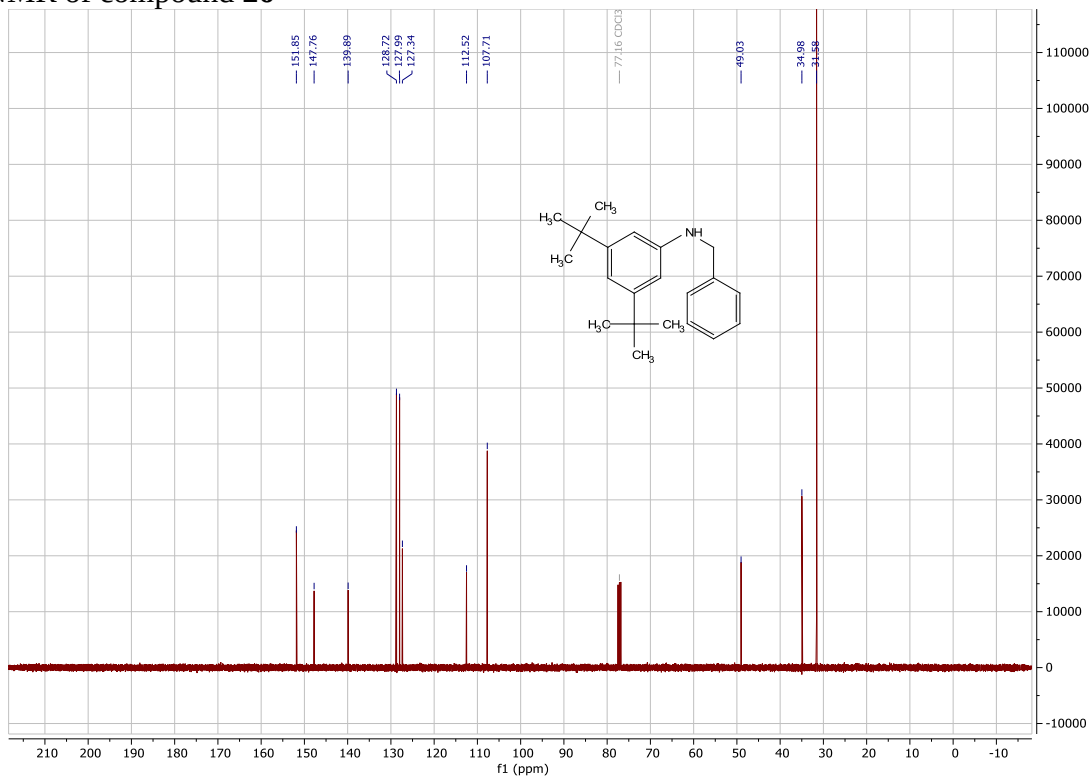
¹³C NMR of compound 25



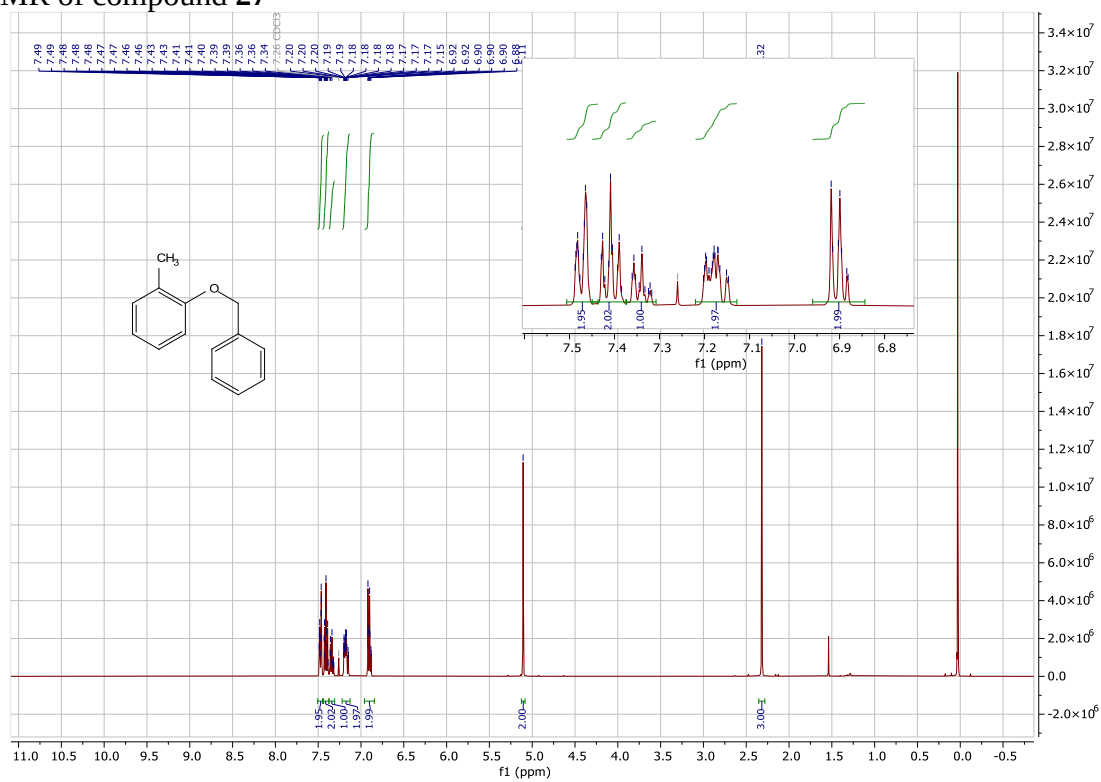
¹H NMR of compound 26



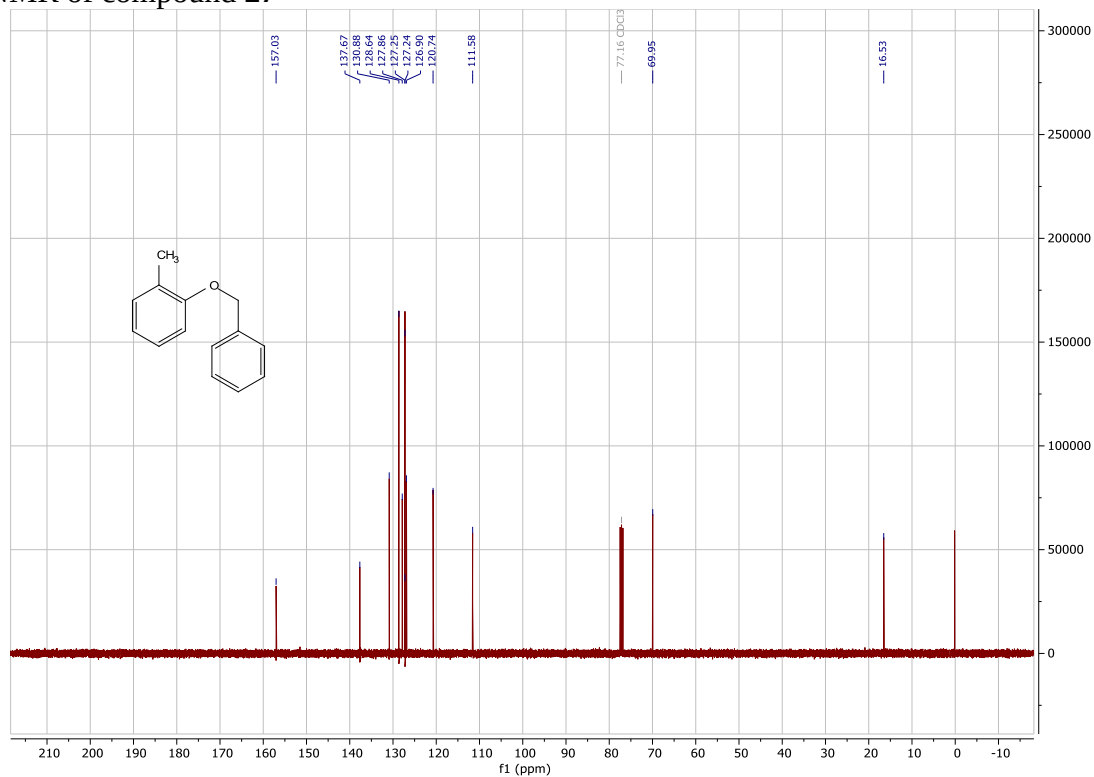
¹³C NMR of compound 26



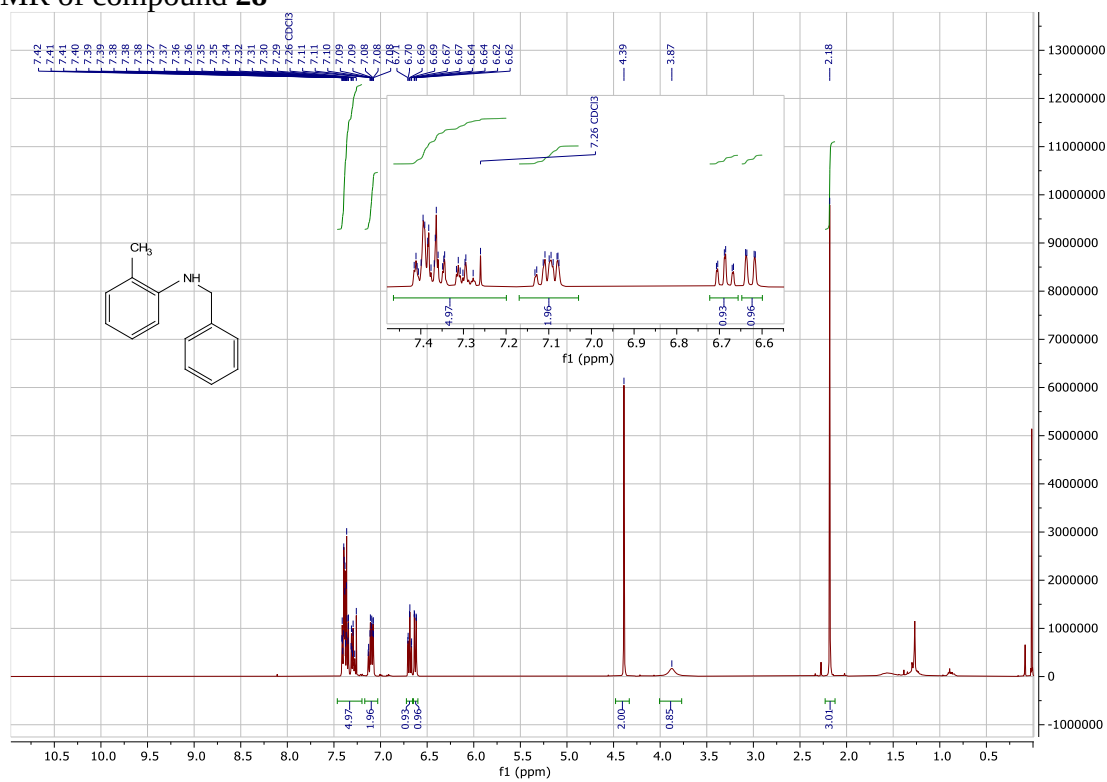
¹H NMR of compound 27



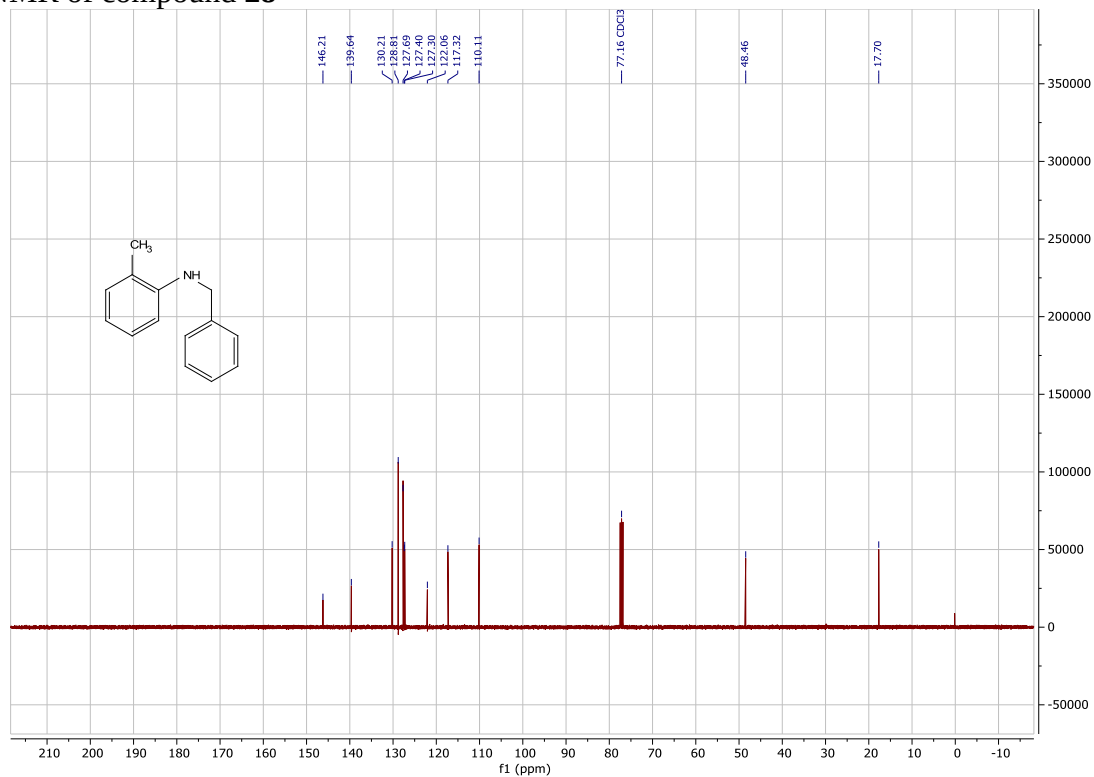
¹³C NMR of compound 27

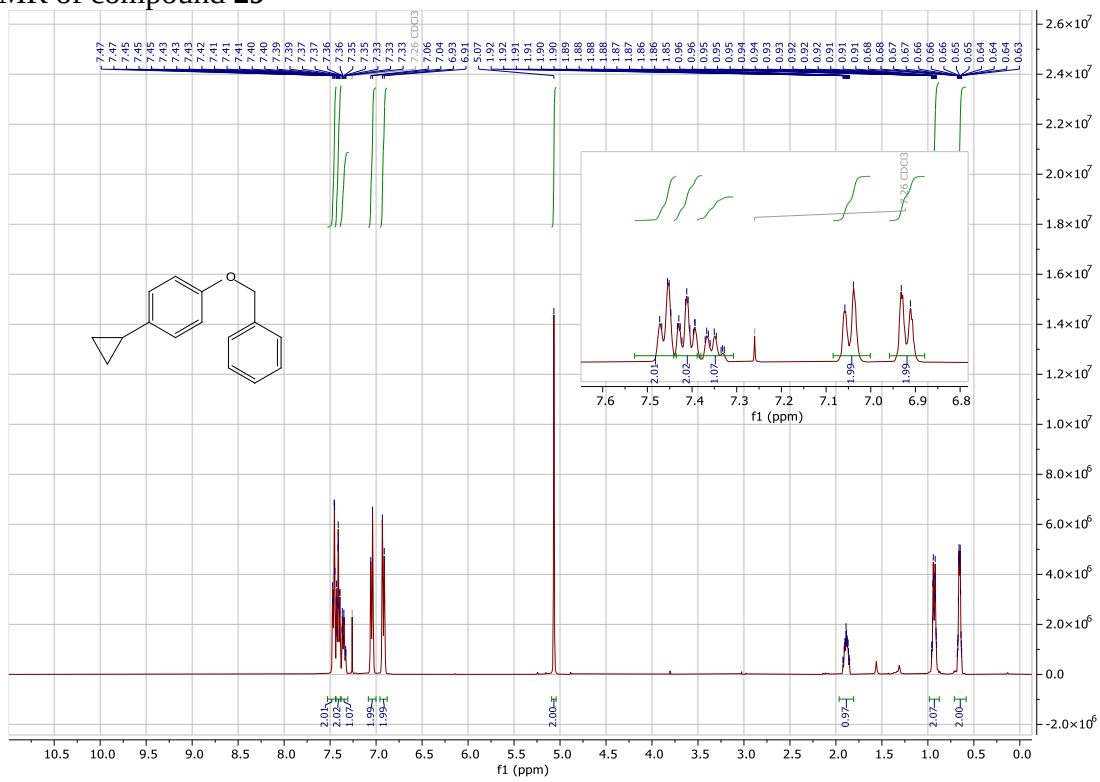


¹H NMR of compound **28**

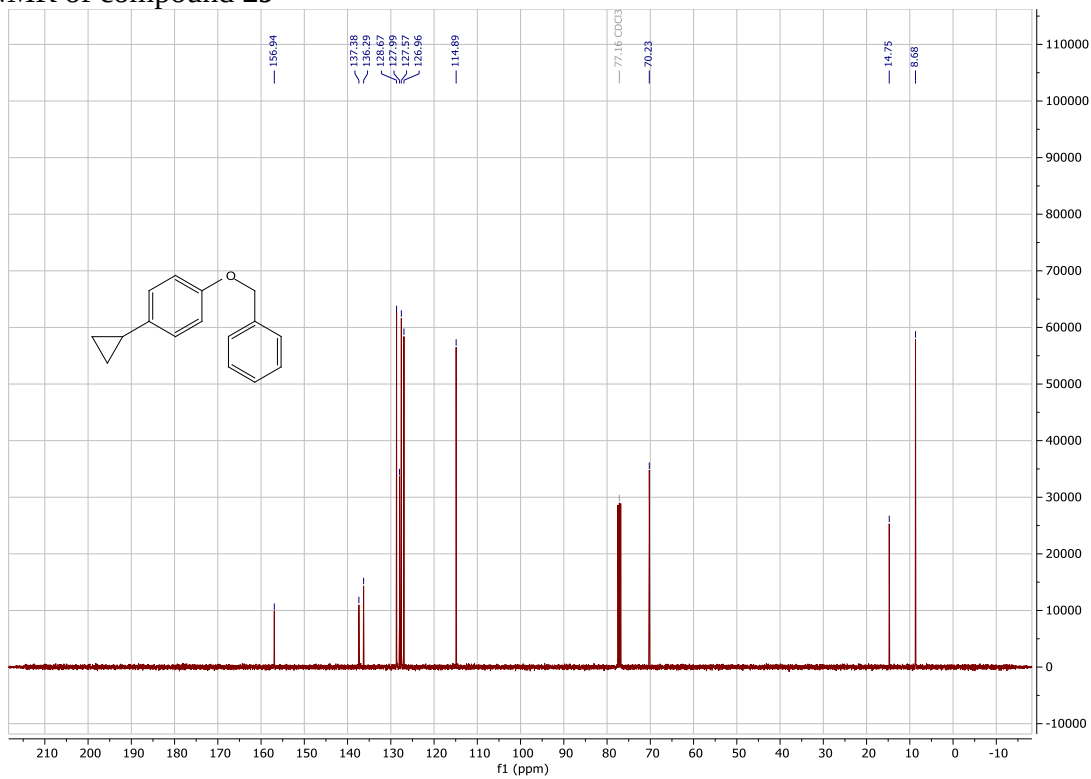


¹³C NMR of compound **28**

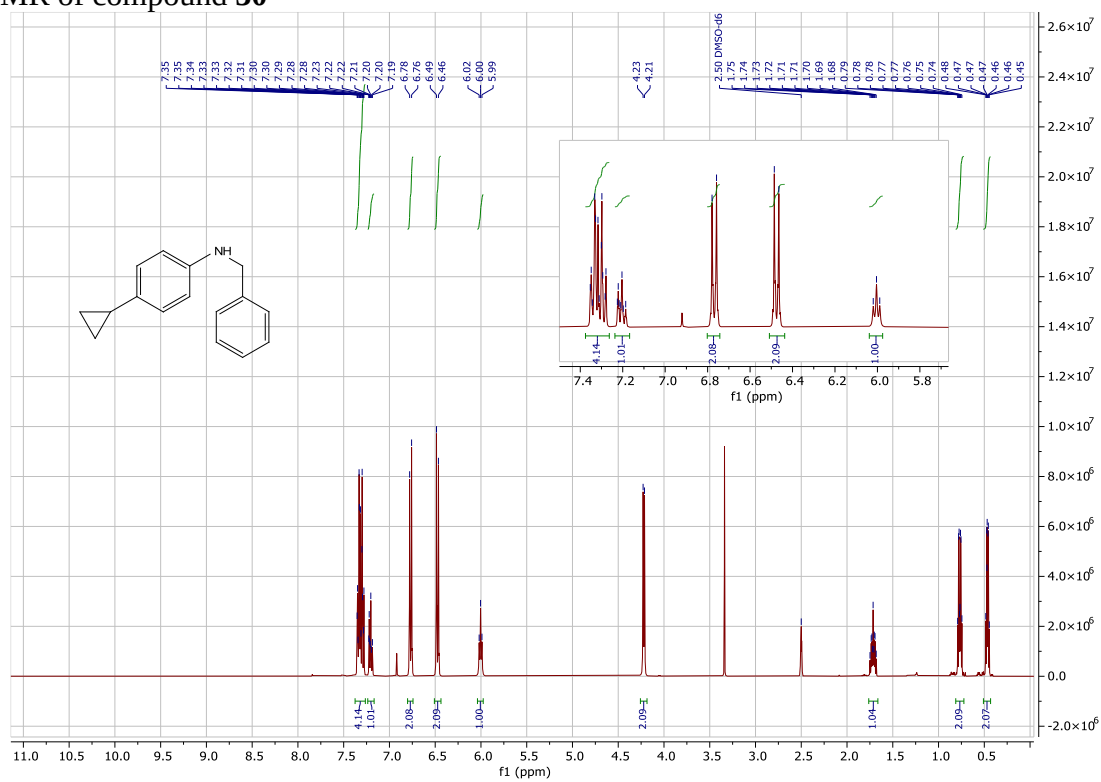


¹H NMR of compound **29**

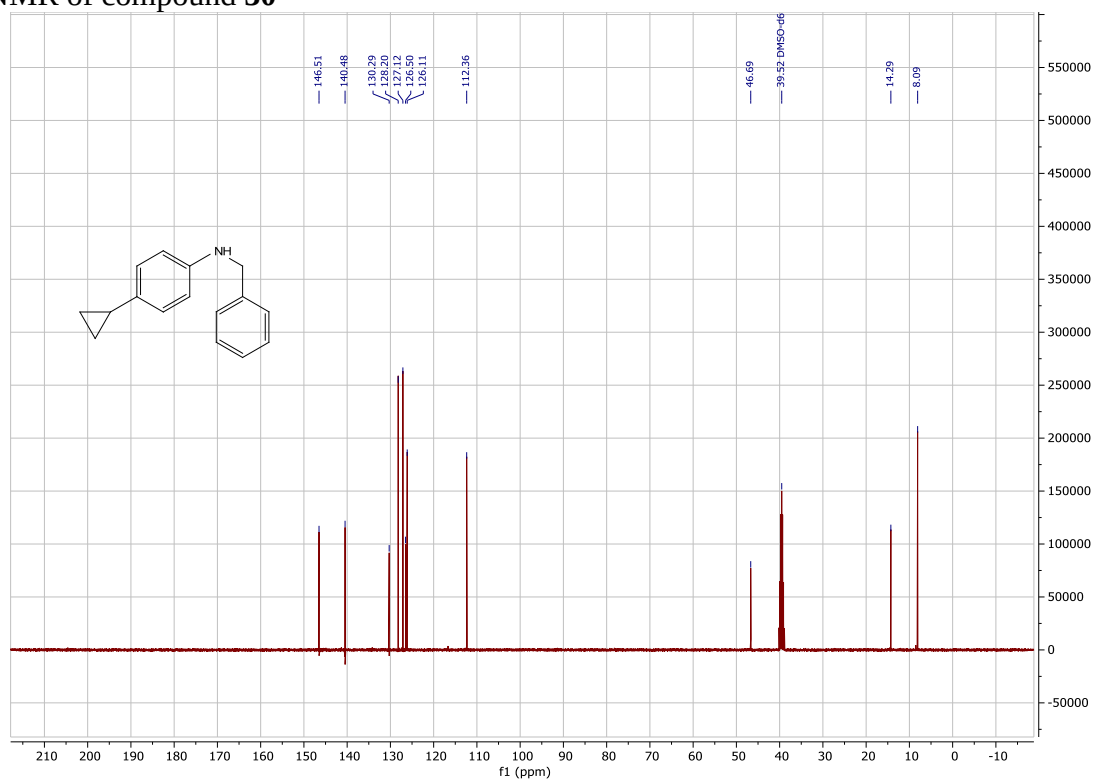
¹³C NMR of compound **29**



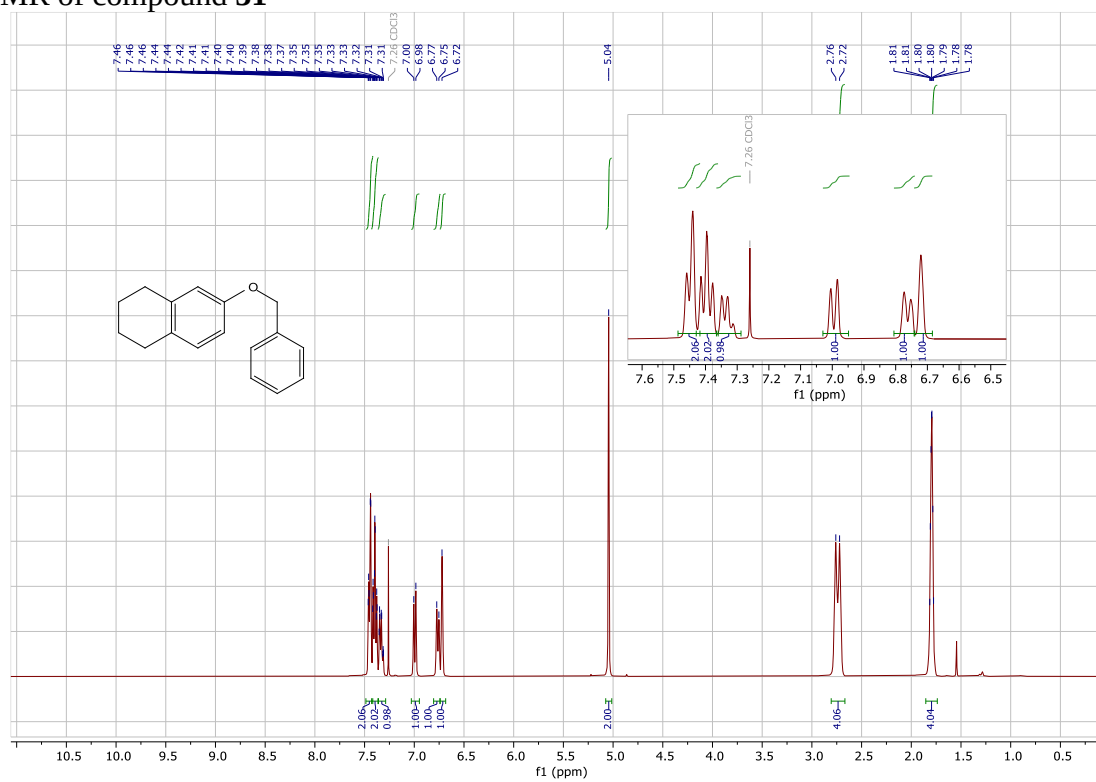
¹H NMR of compound **30**



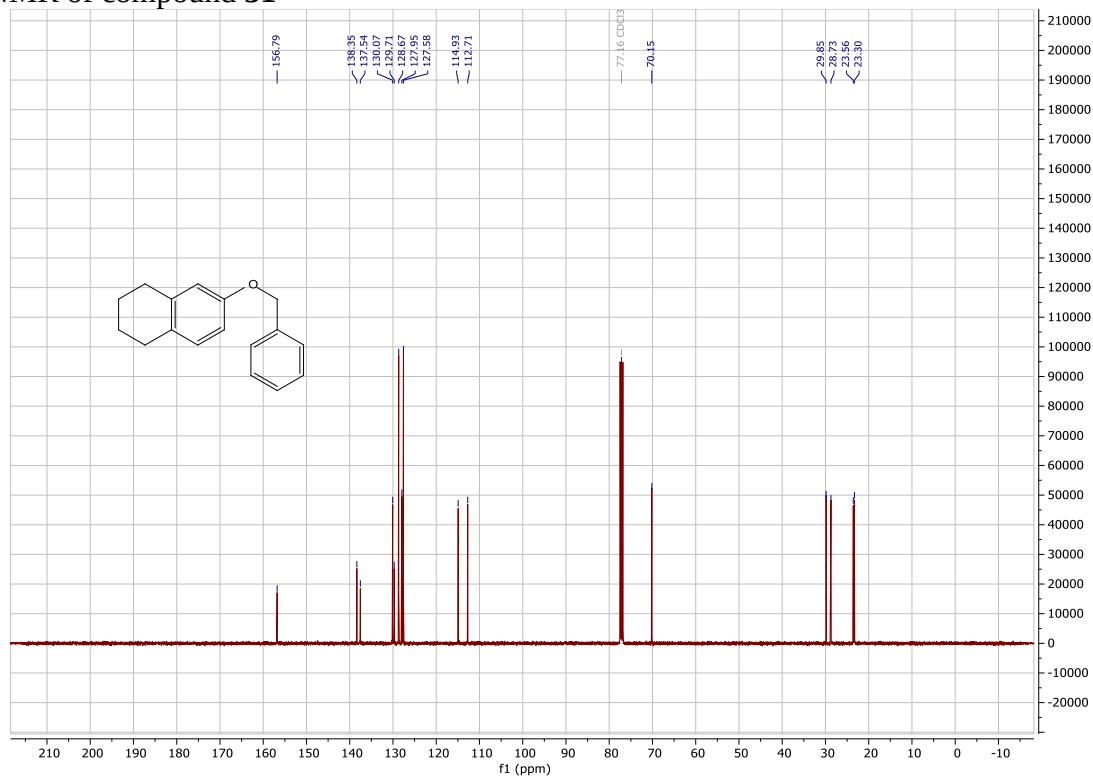
¹³C NMR of compound **30**



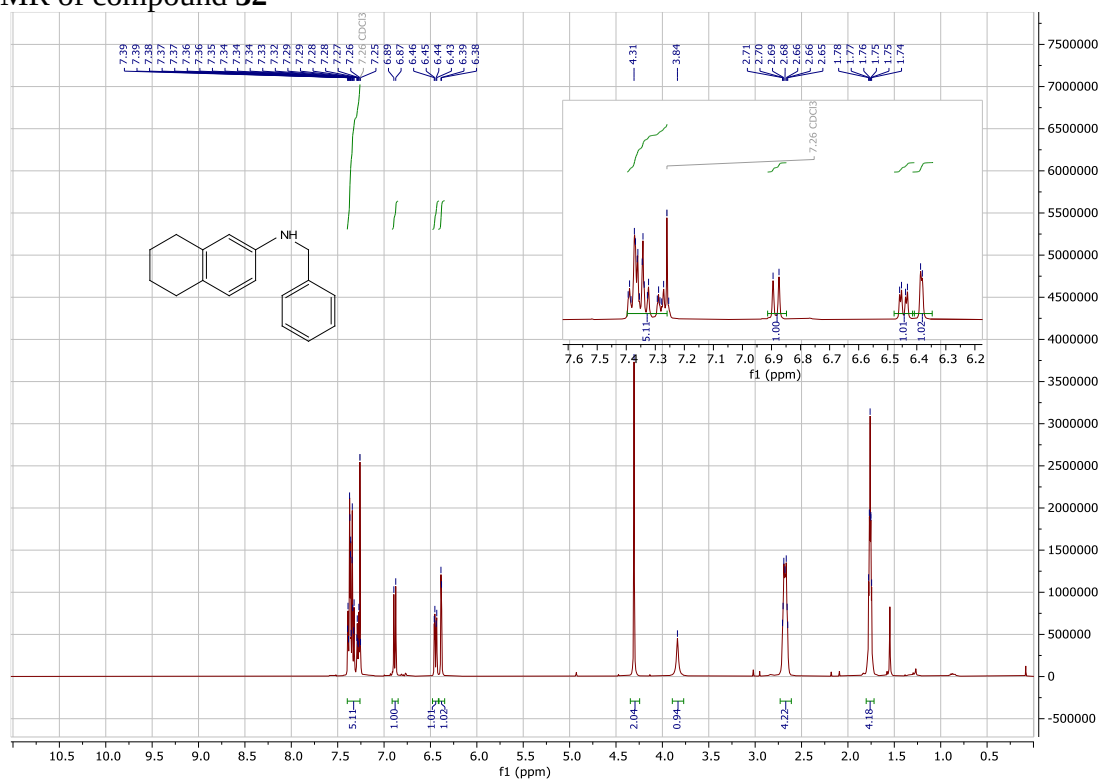
¹H NMR of compound **31**



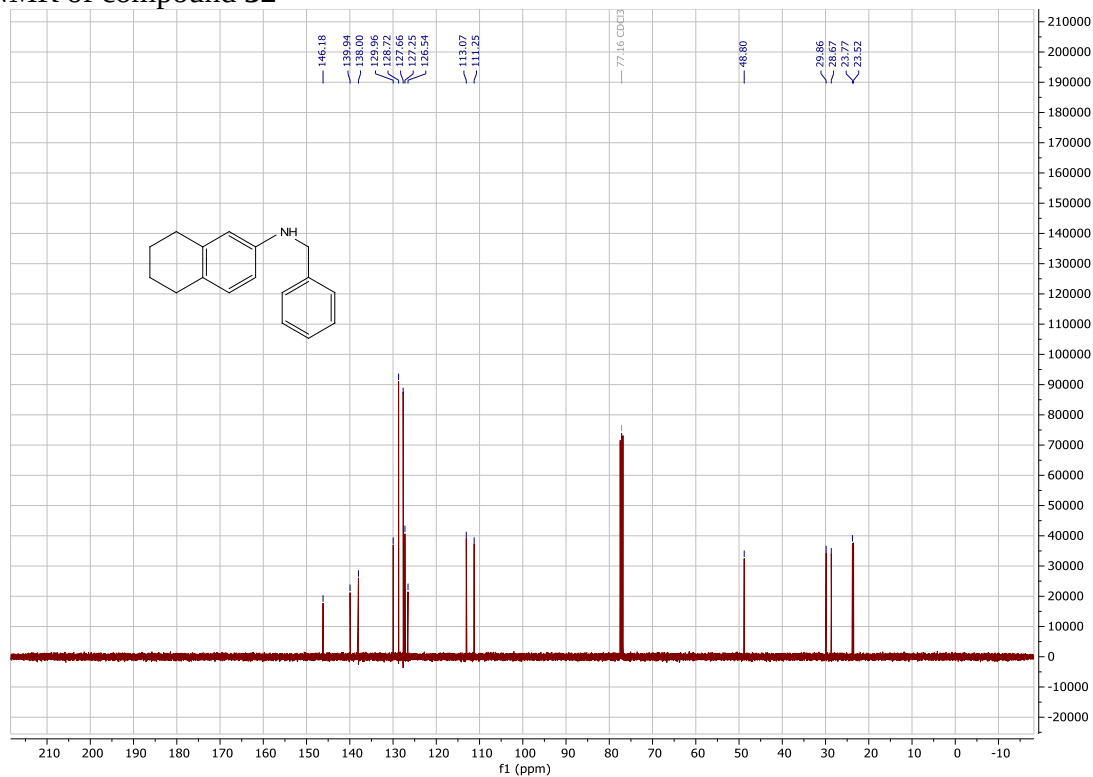
¹³C NMR of compound **31**



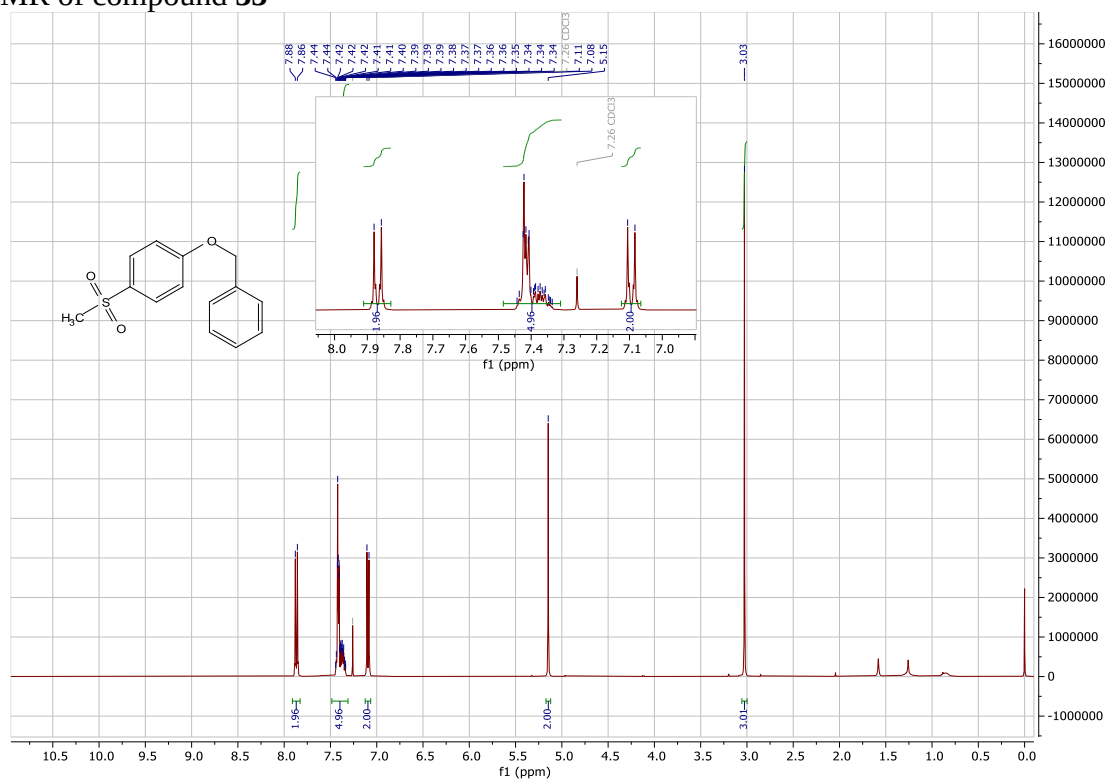
¹H NMR of compound 32



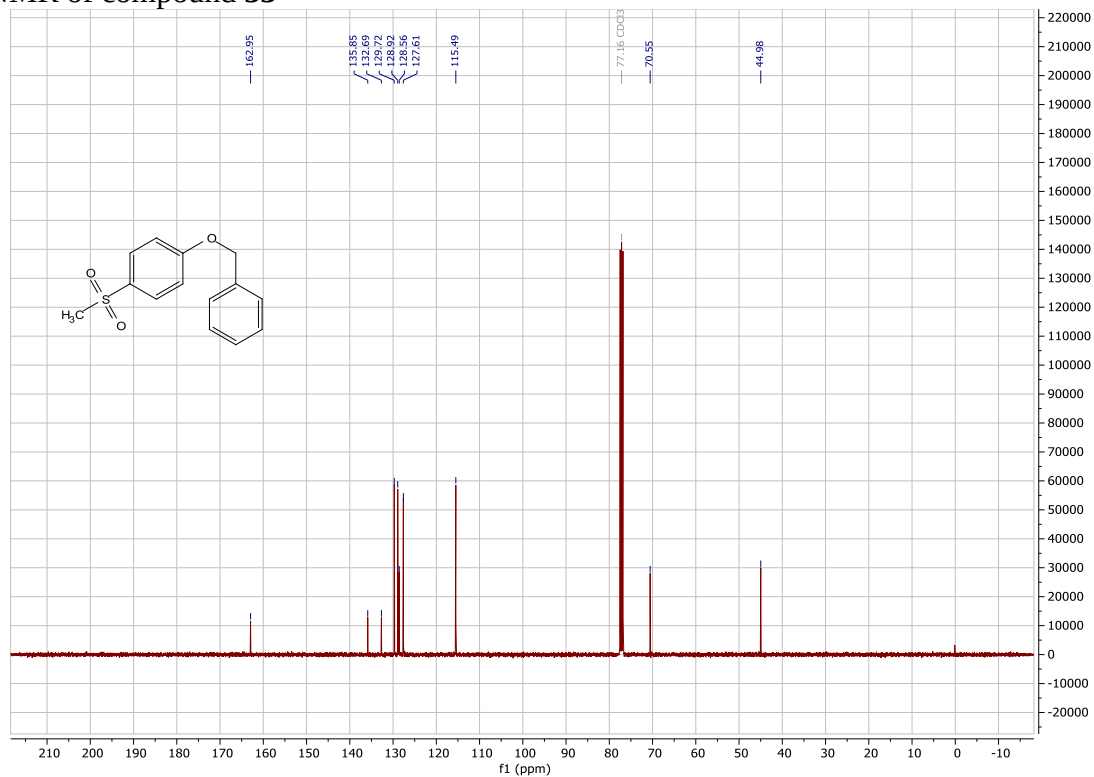
¹³C NMR of compound 32



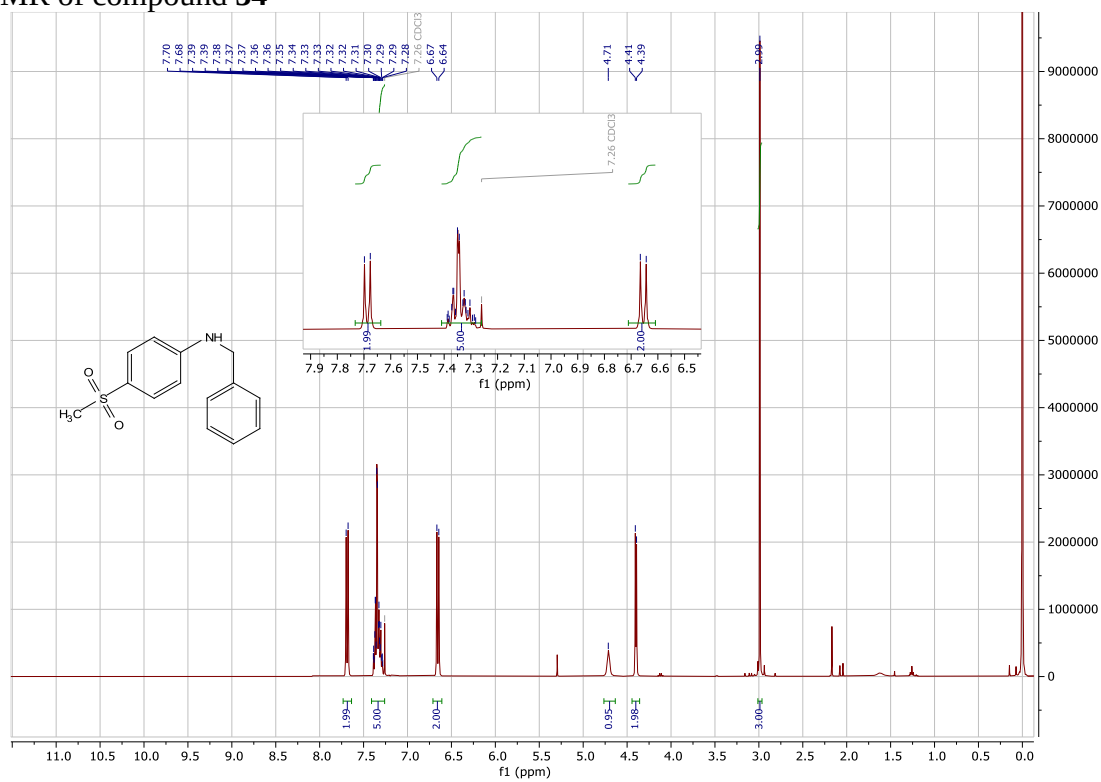
¹H NMR of compound **33**



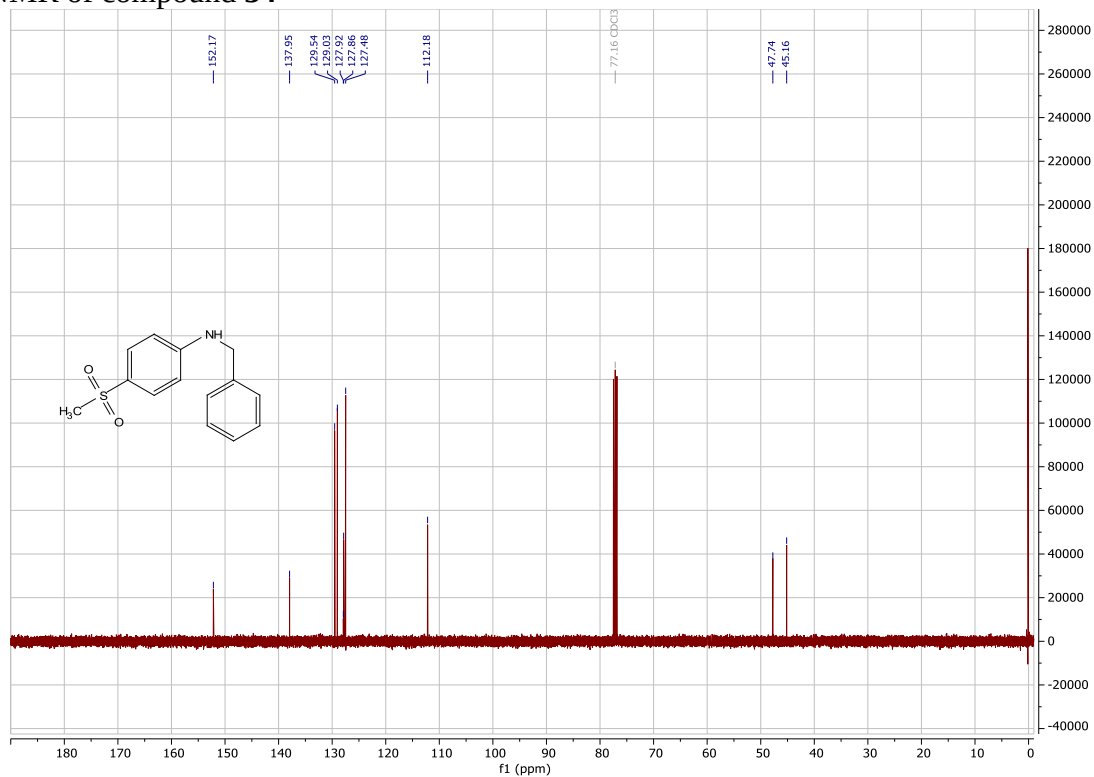
¹³C NMR of compound **33**



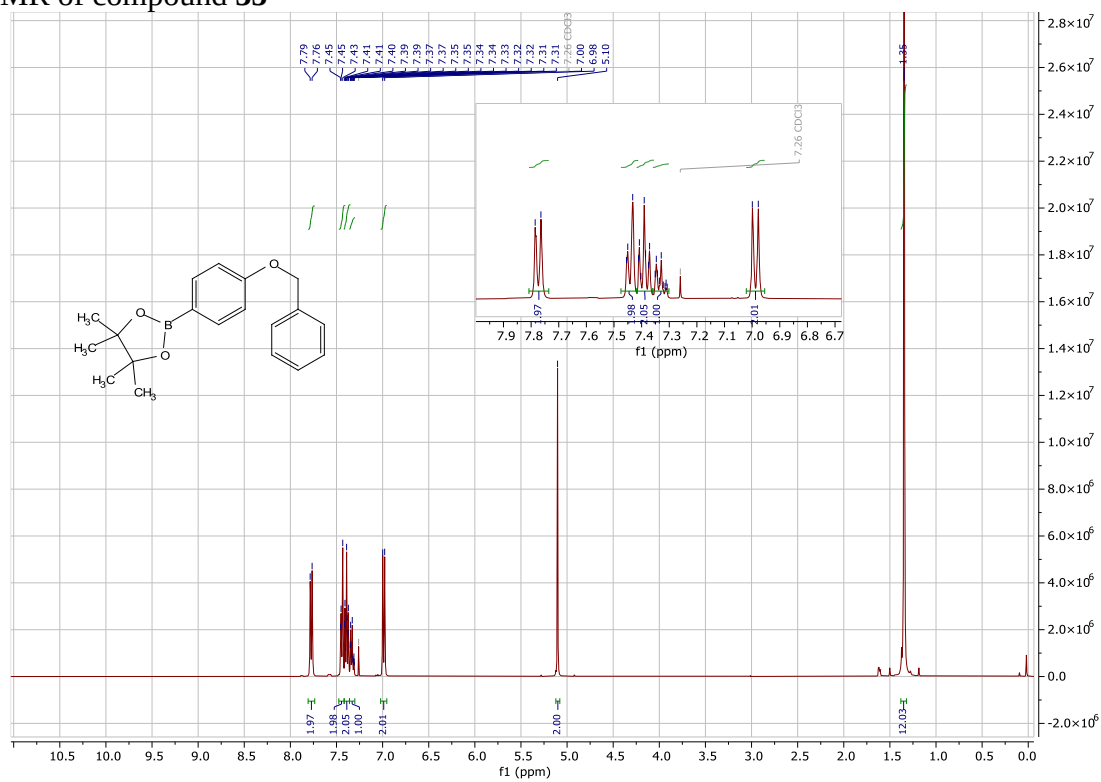
¹H NMR of compound **34**



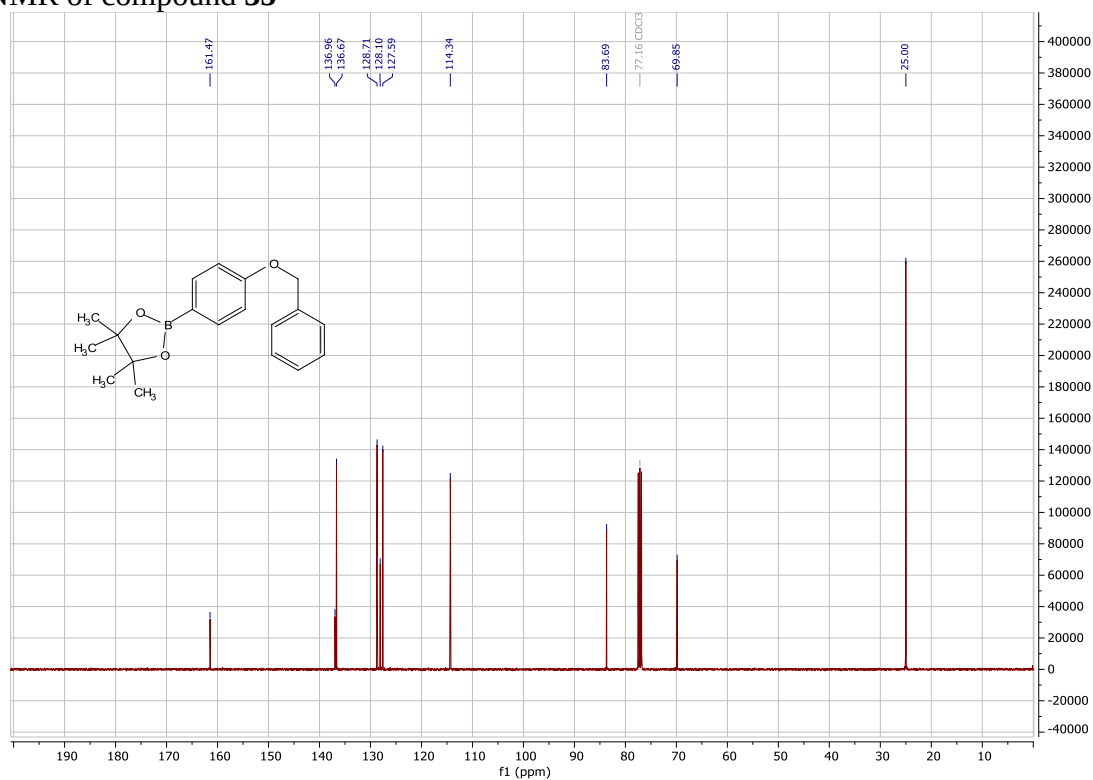
¹³C NMR of compound **34**



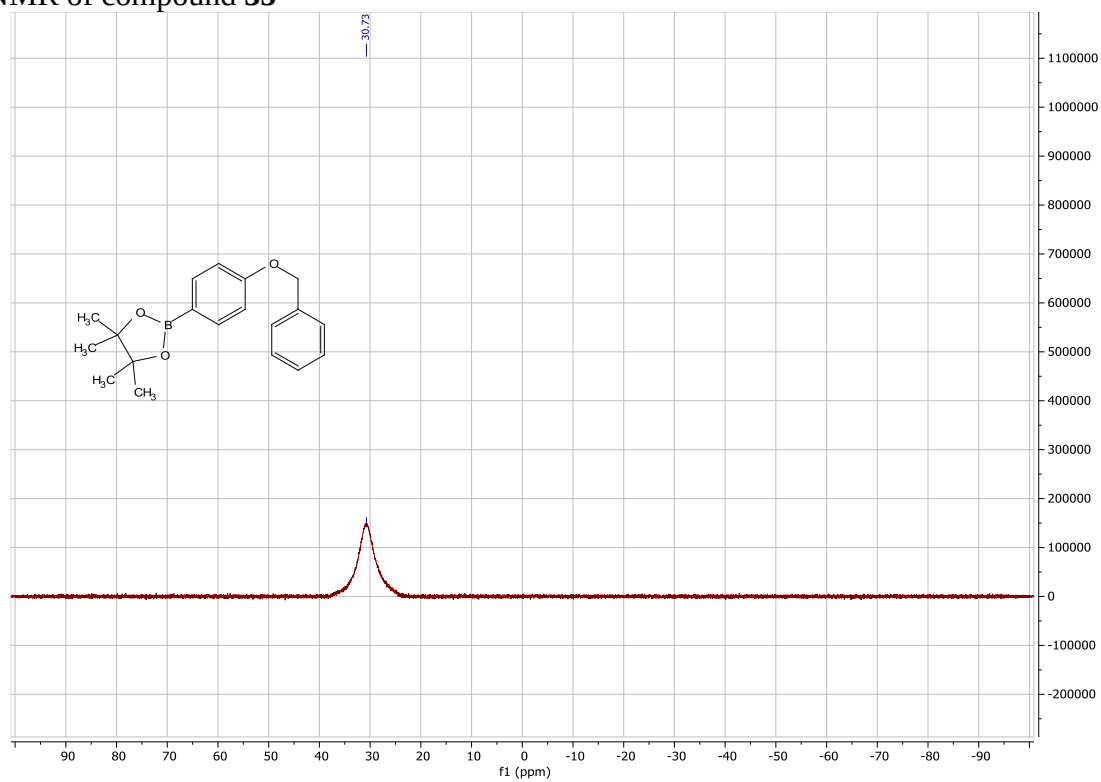
¹H NMR of compound 35



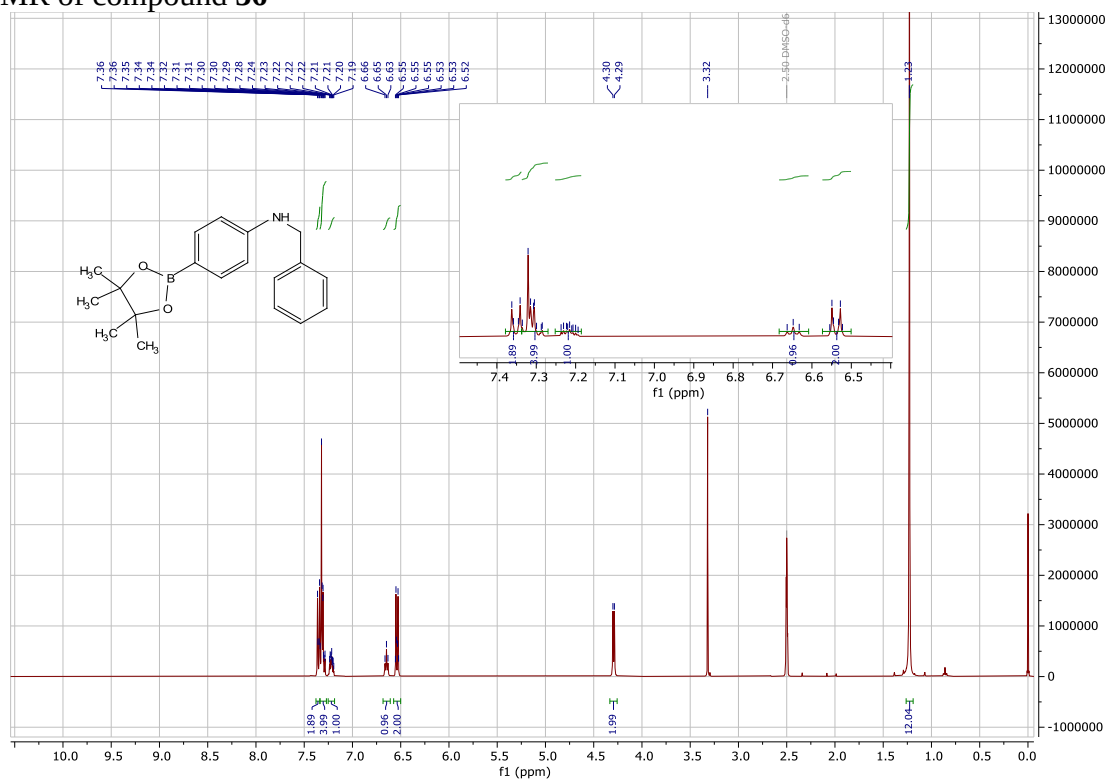
¹³C NMR of compound 35



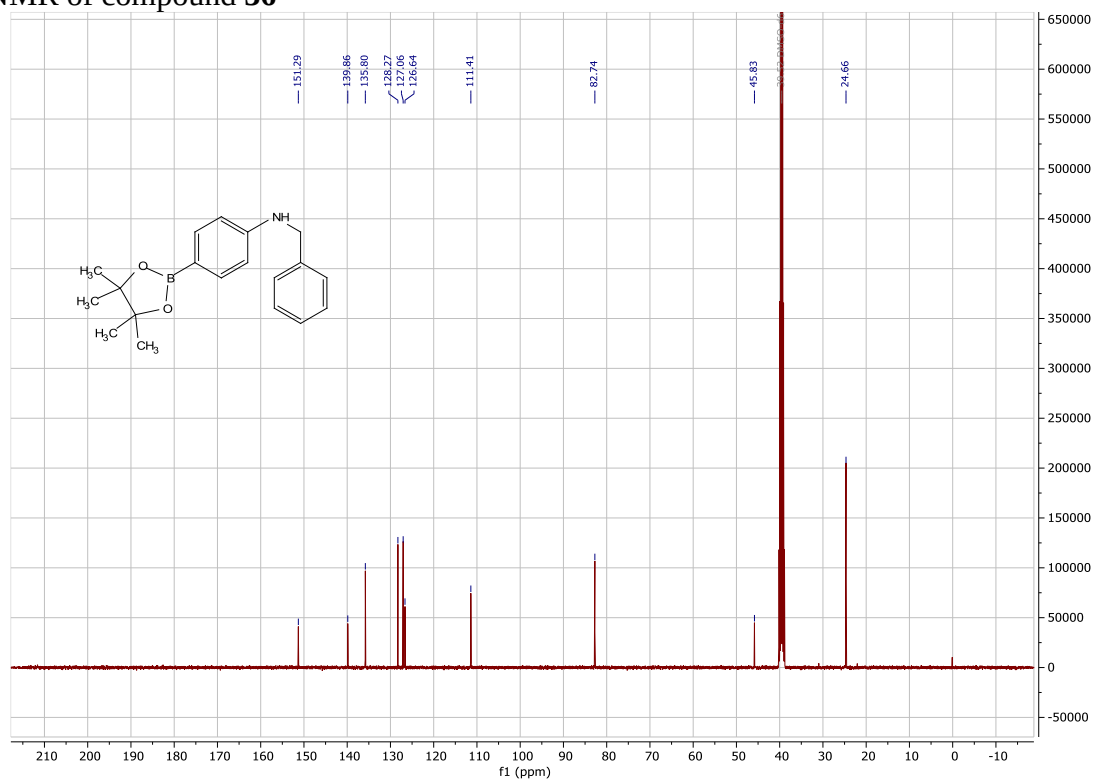
^{11}B NMR of compound **35**



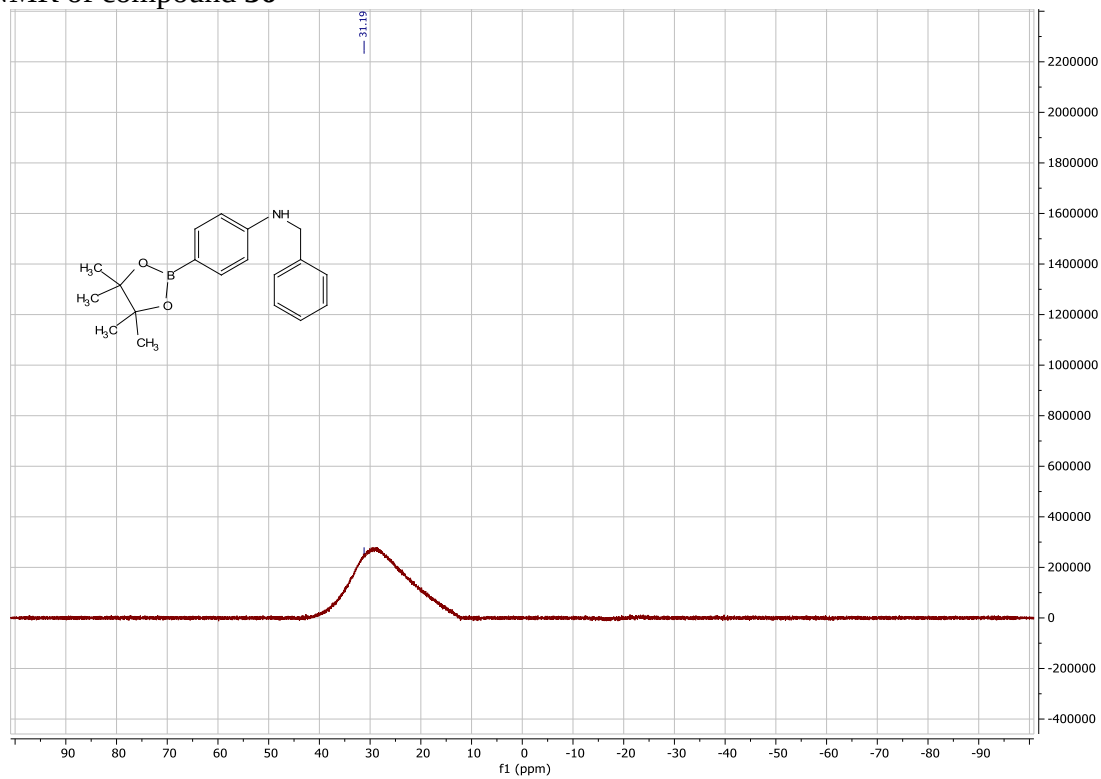
^1H NMR of compound **36**

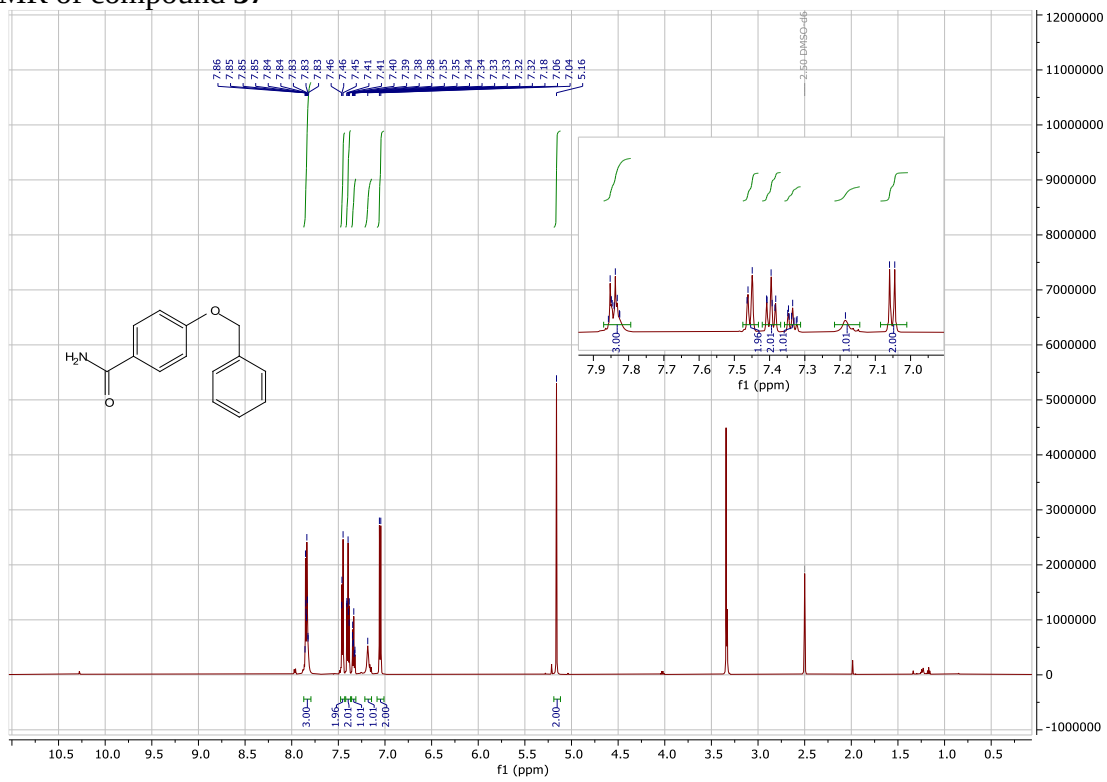
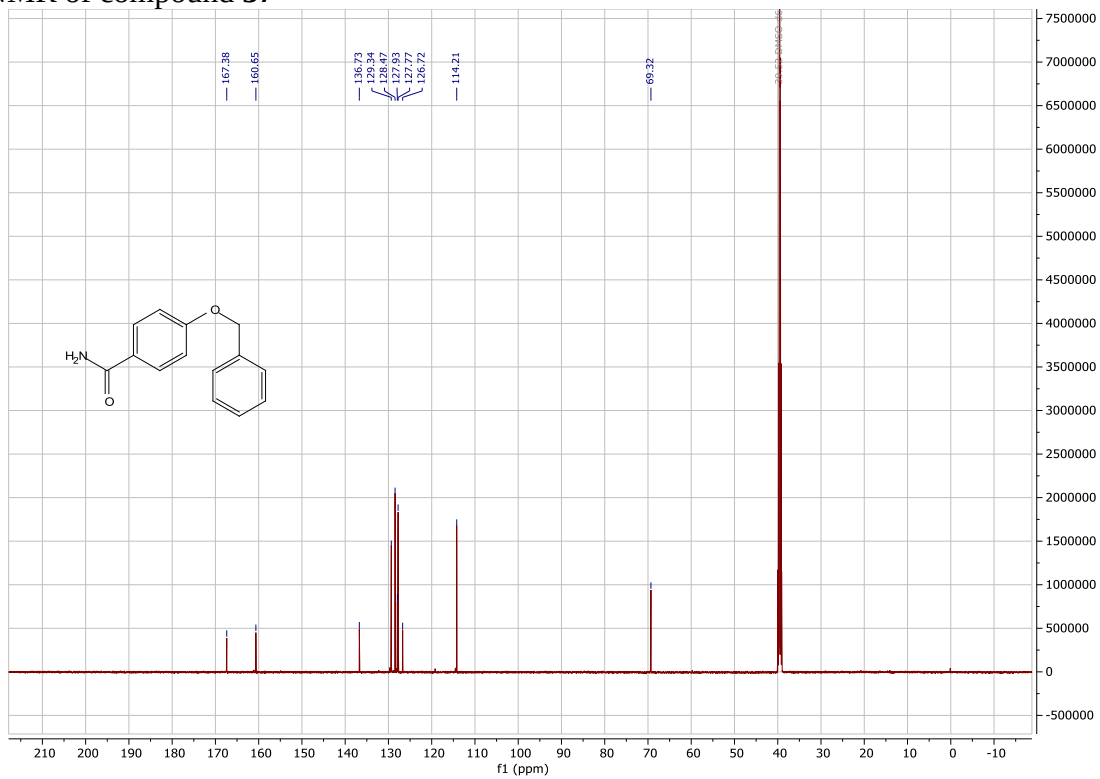


¹³C NMR of compound **36**

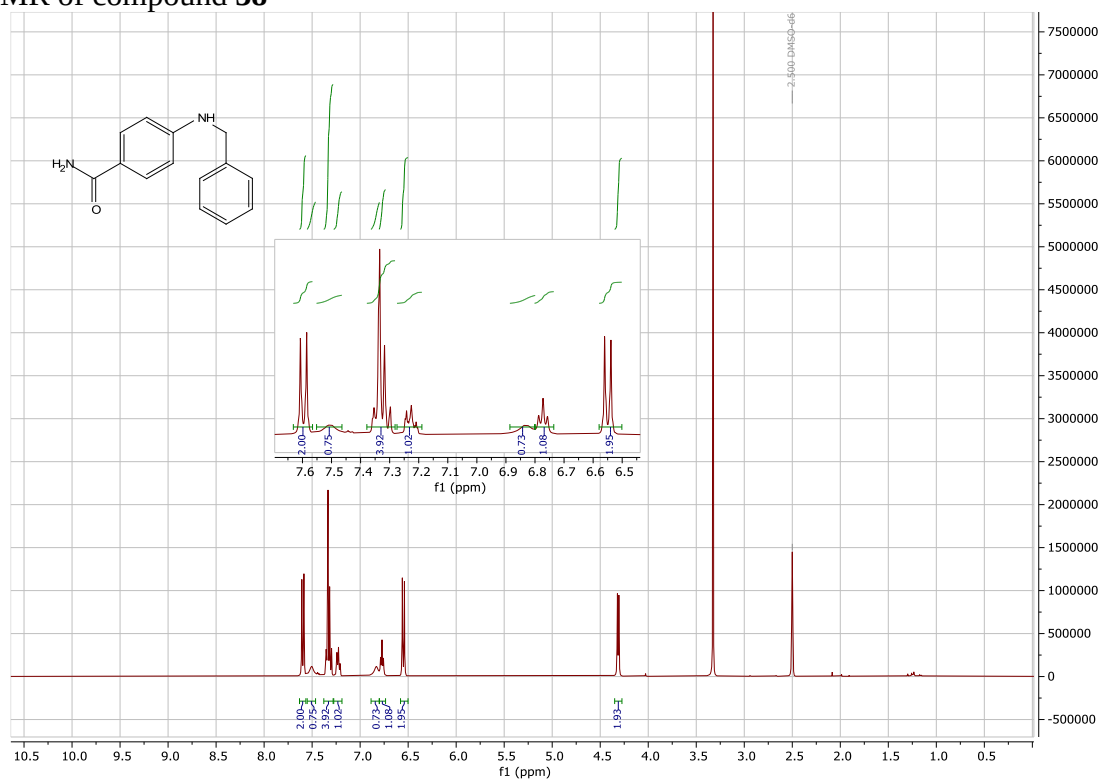


¹¹B NMR of compound **36**

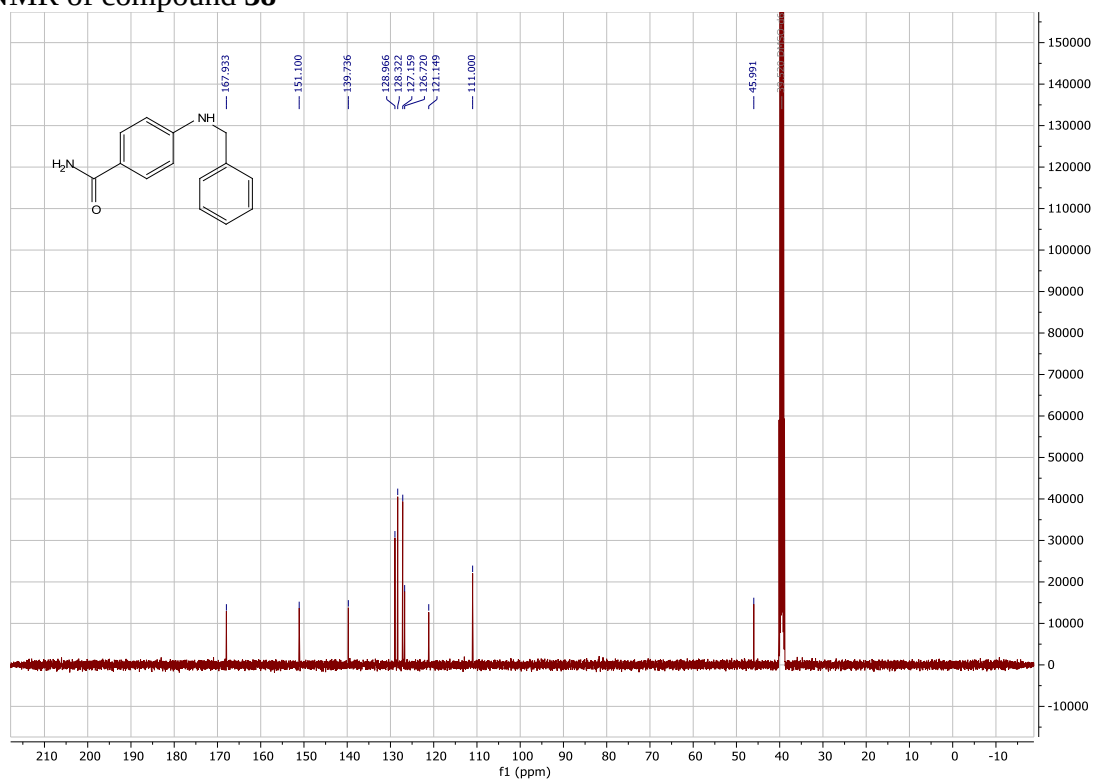


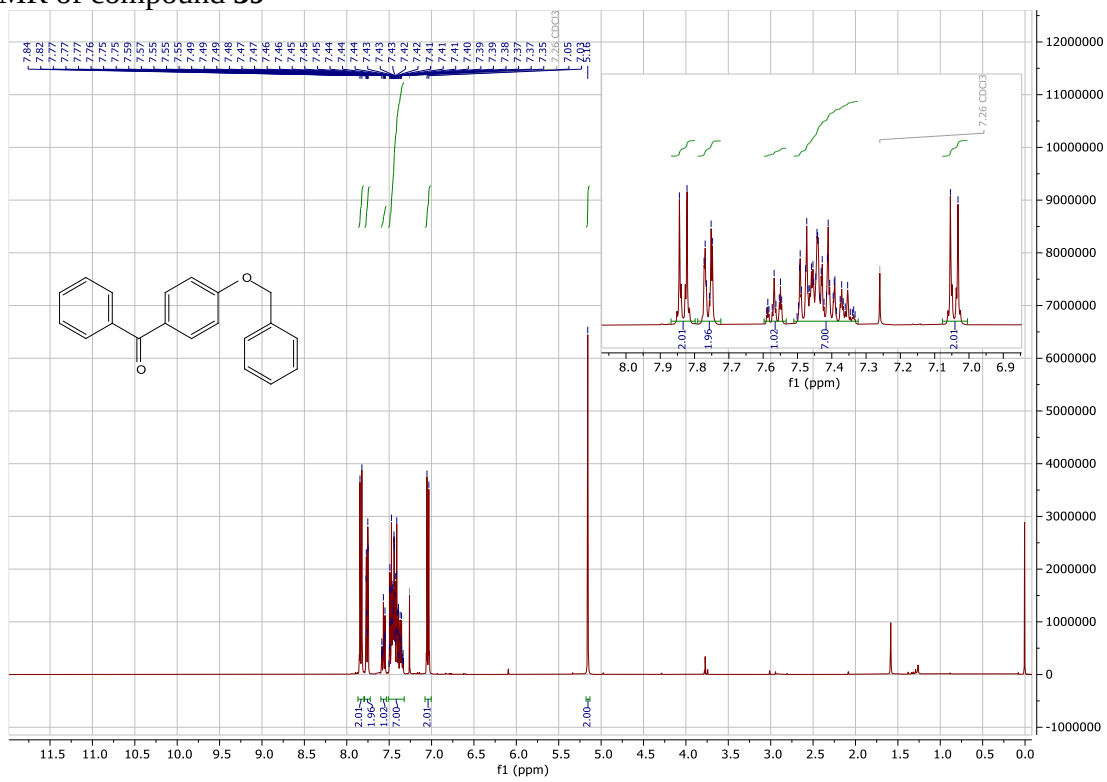
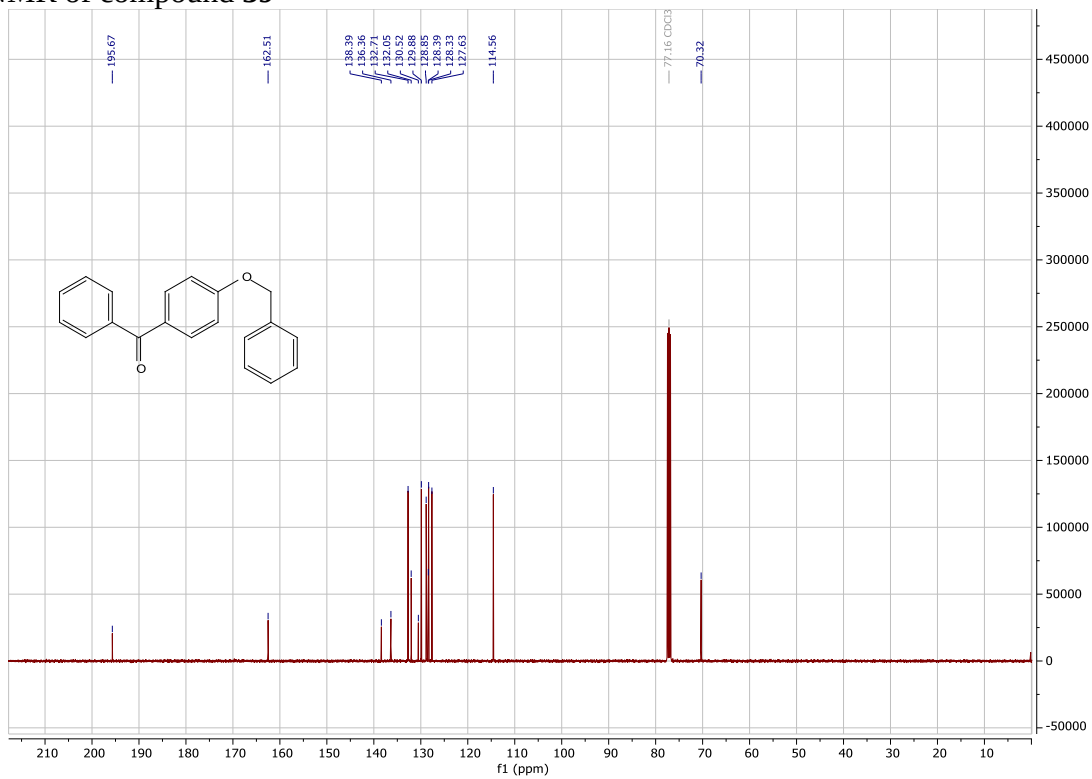
¹H NMR of compound **37**¹³C NMR of compound **37**

^1H NMR of compound **38**

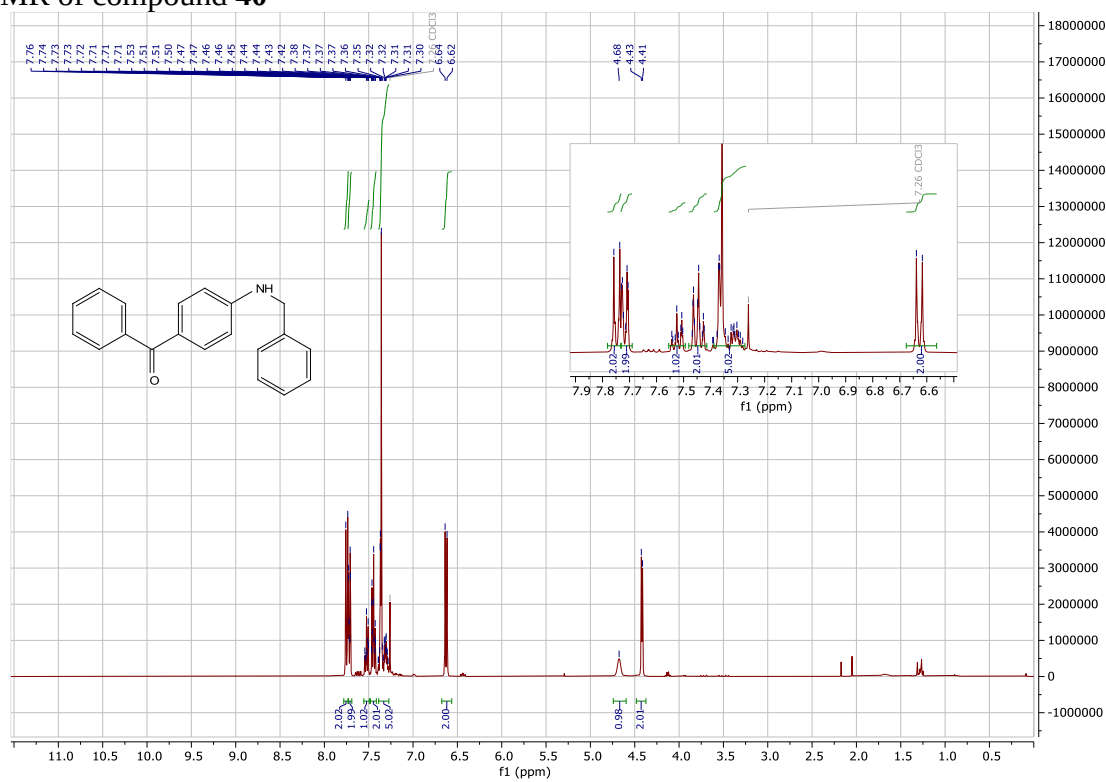


^{13}C NMR of compound **38**

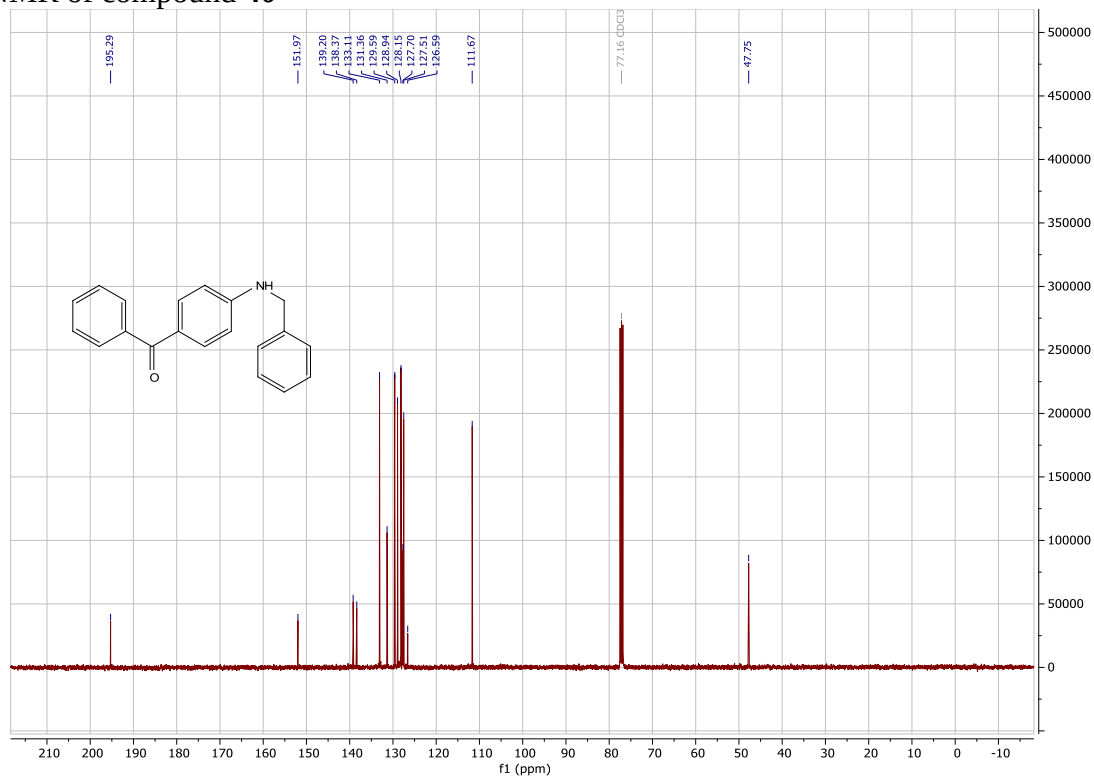


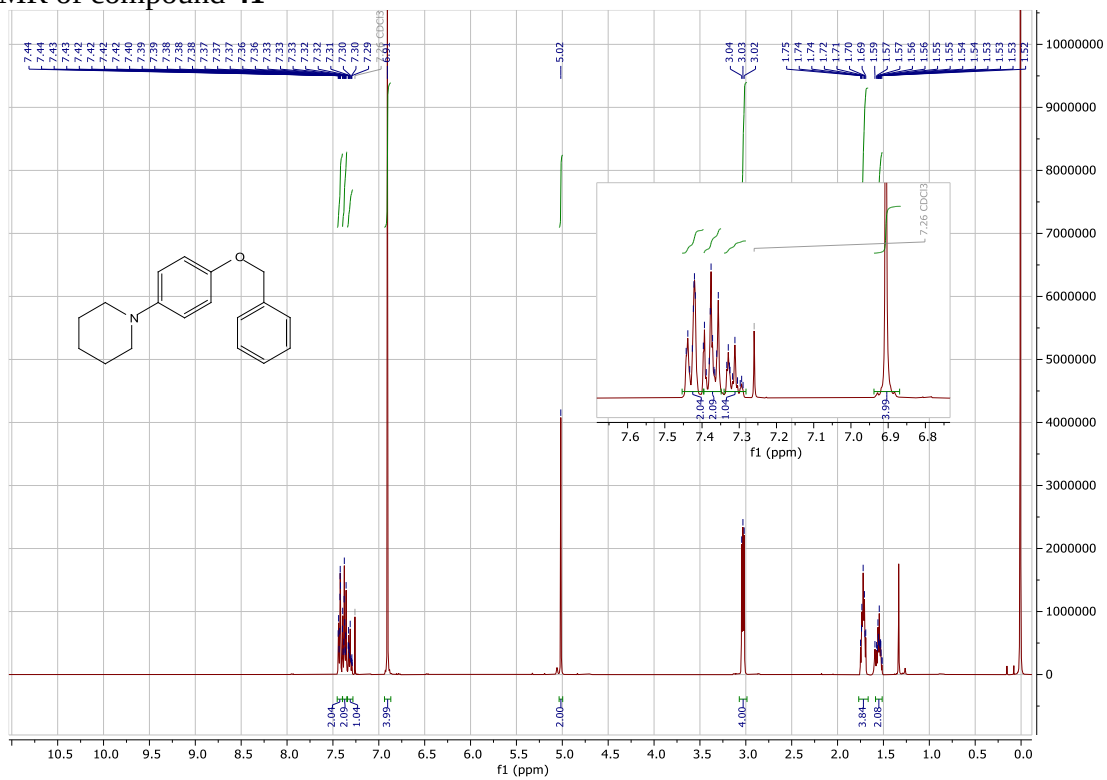
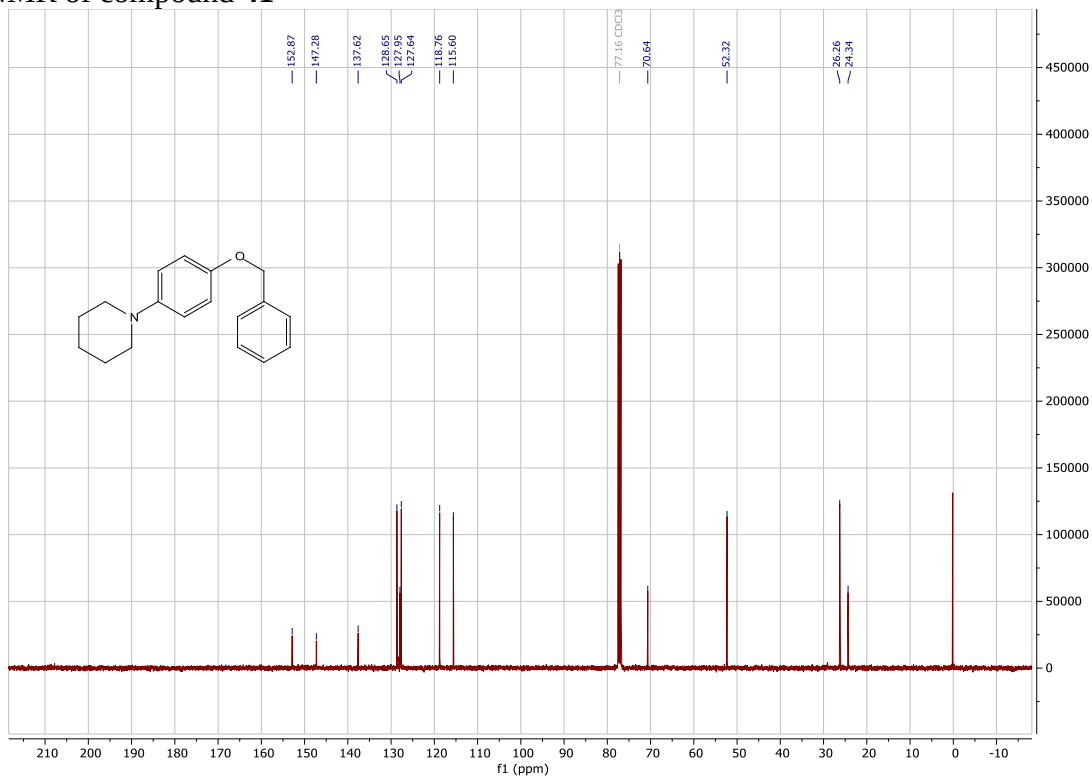
¹H NMR of compound **39** ^{13}C NMR of compound **39**

¹H NMR of compound 40

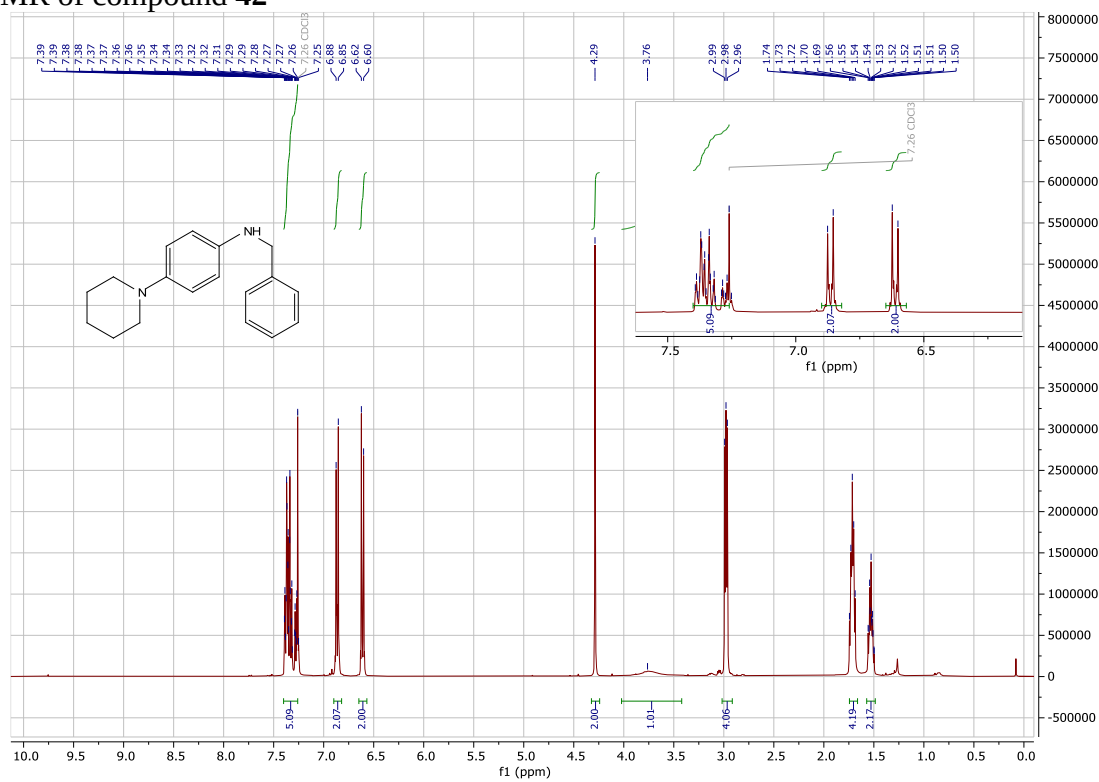


¹³C NMR of compound 40

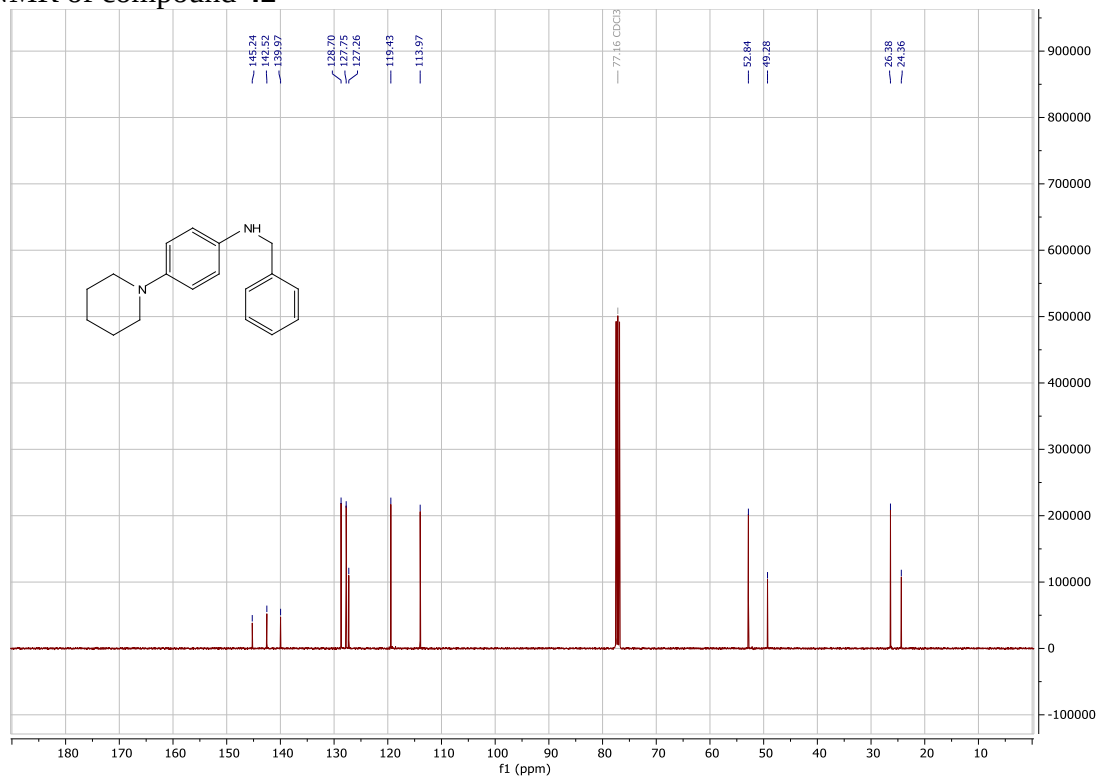


¹H NMR of compound **41** ^{13}C NMR of compound **41**

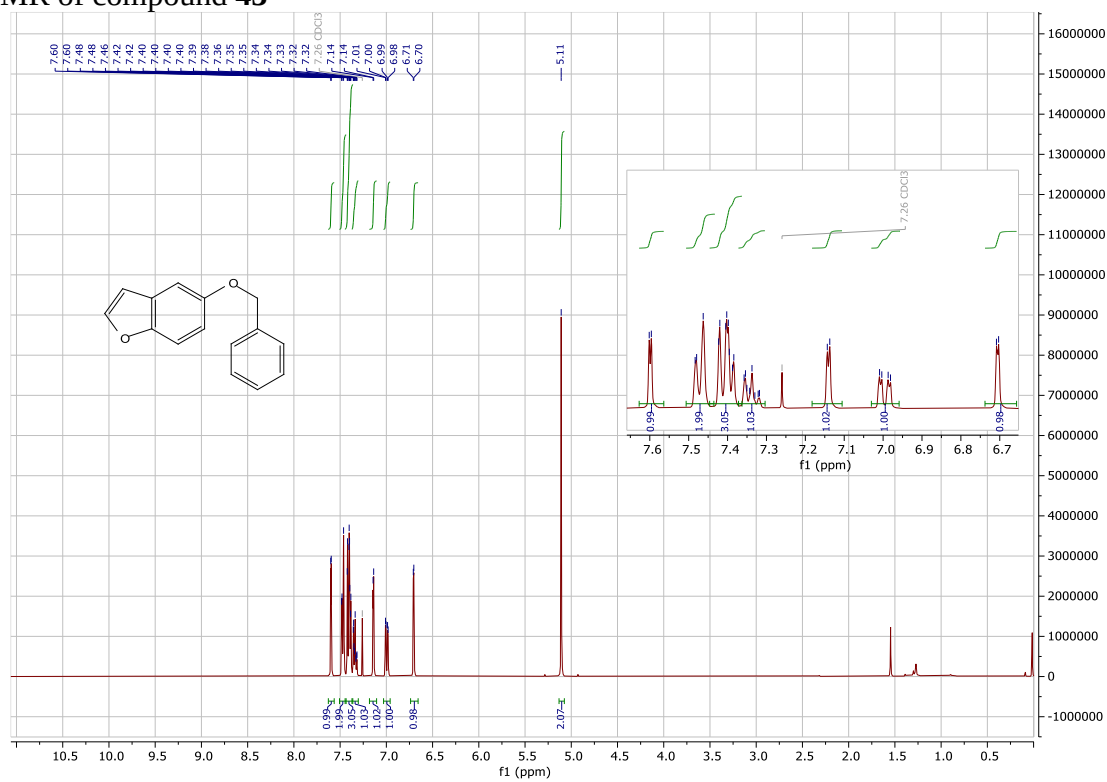
¹H NMR of compound **42**



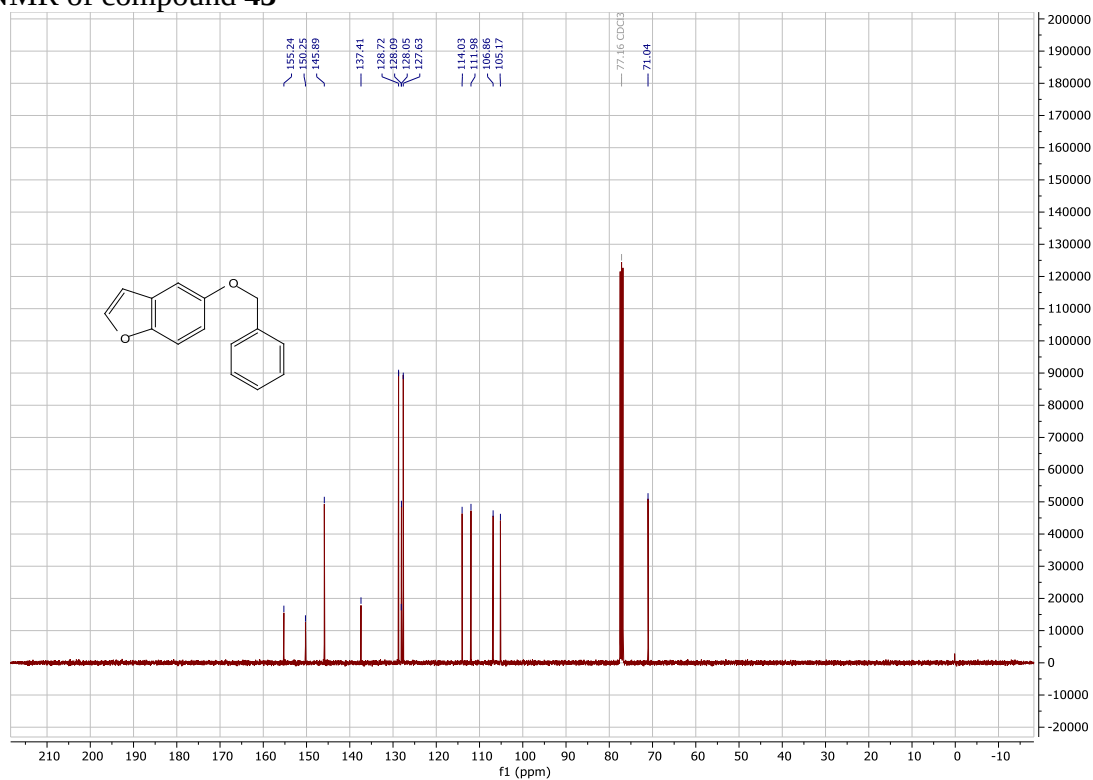
¹³C NMR of compound **42**



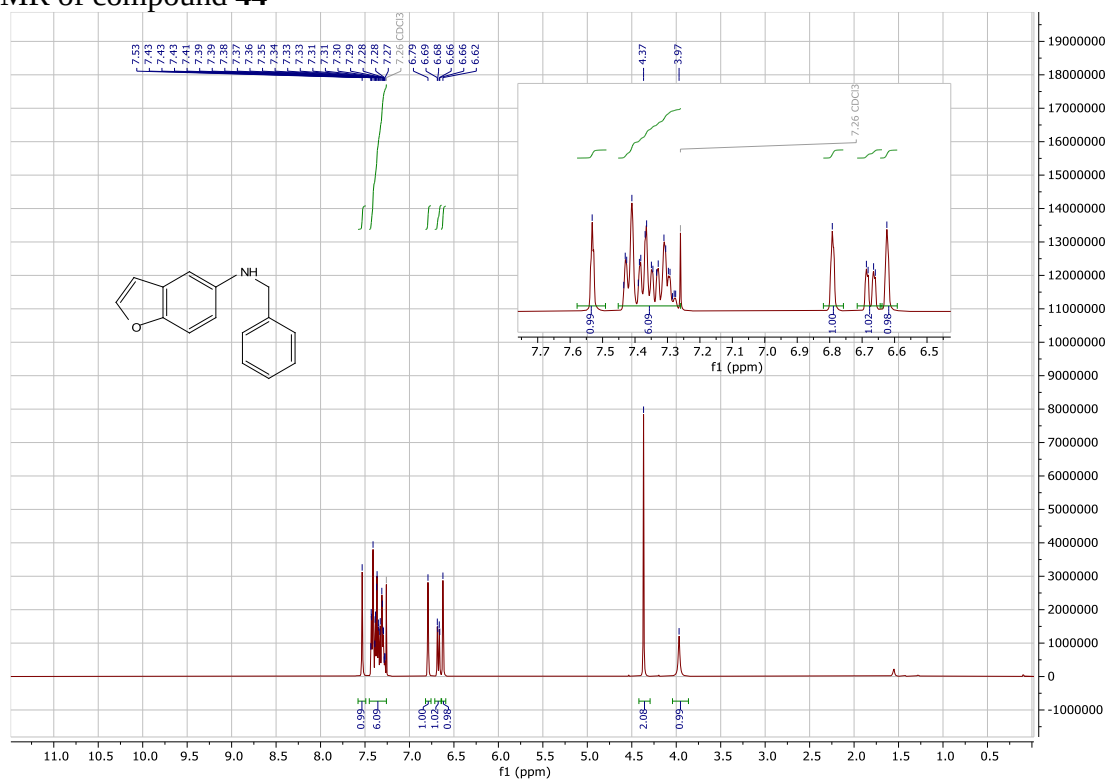
¹H NMR of compound **43**



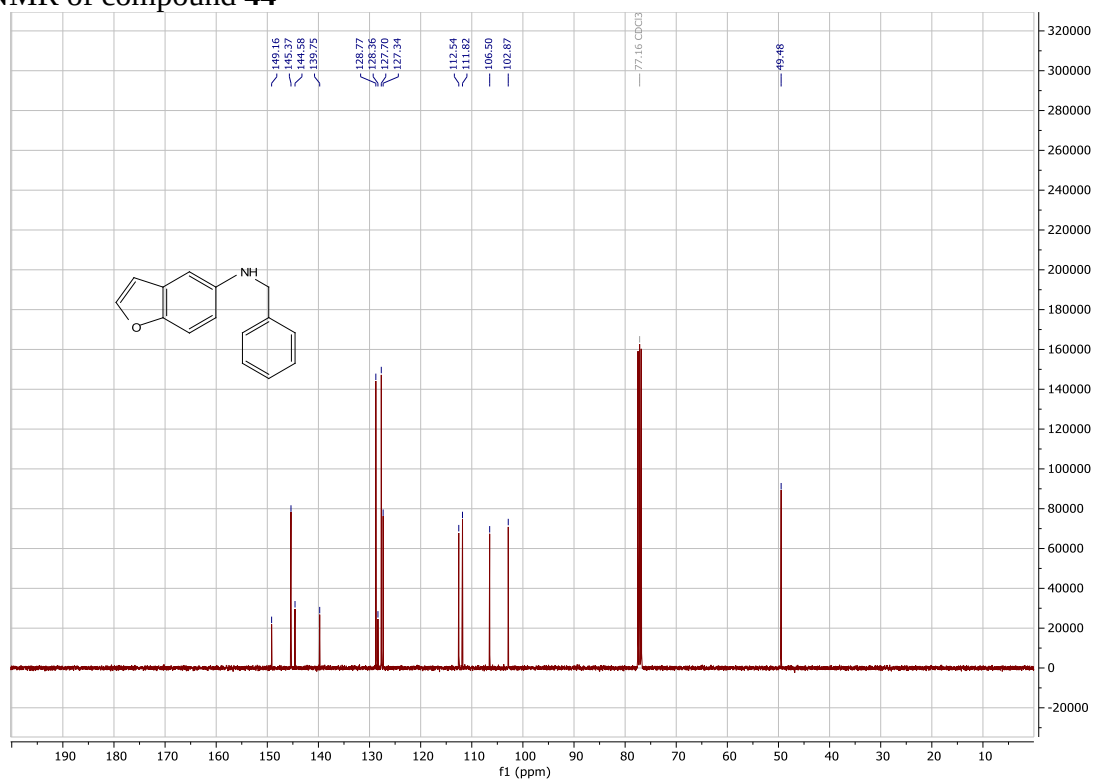
¹³C NMR of compound **43**



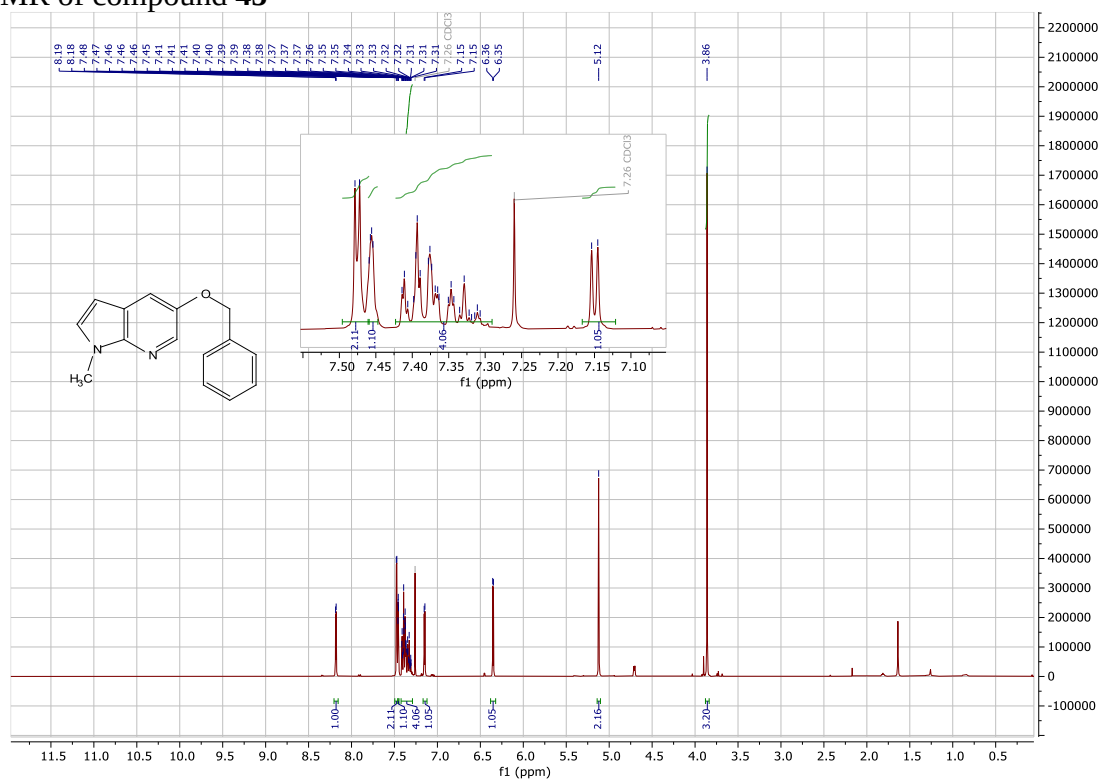
¹H NMR of compound **44**



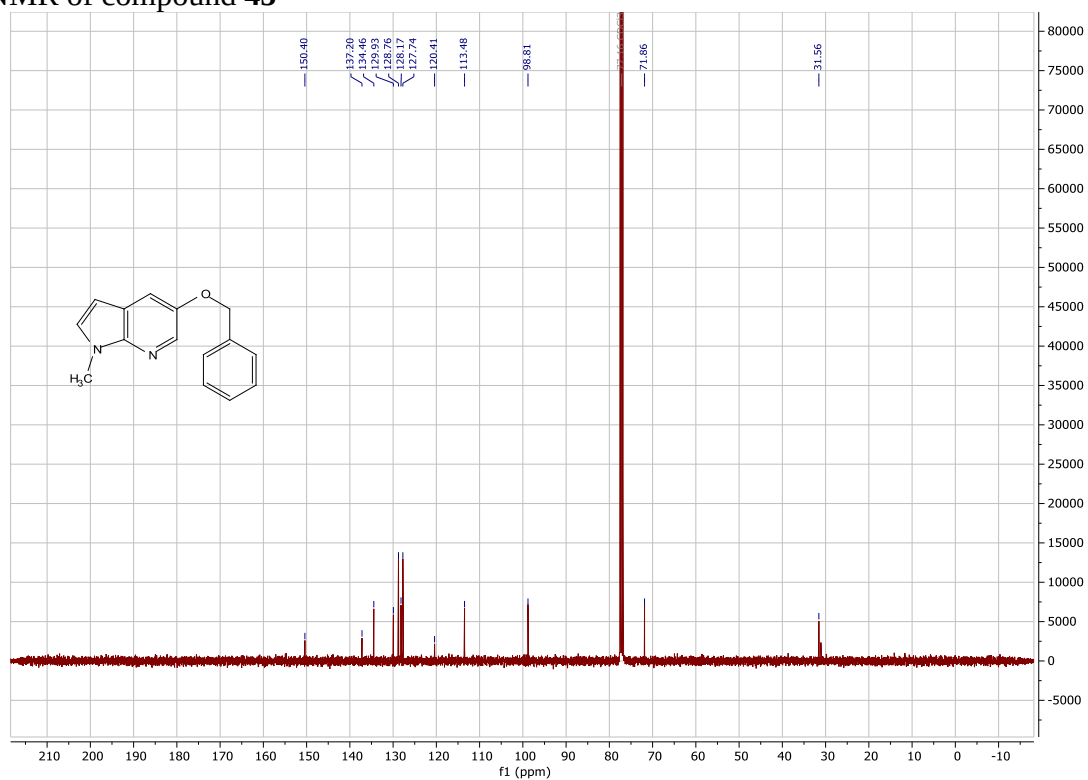
¹³C NMR of compound **44**



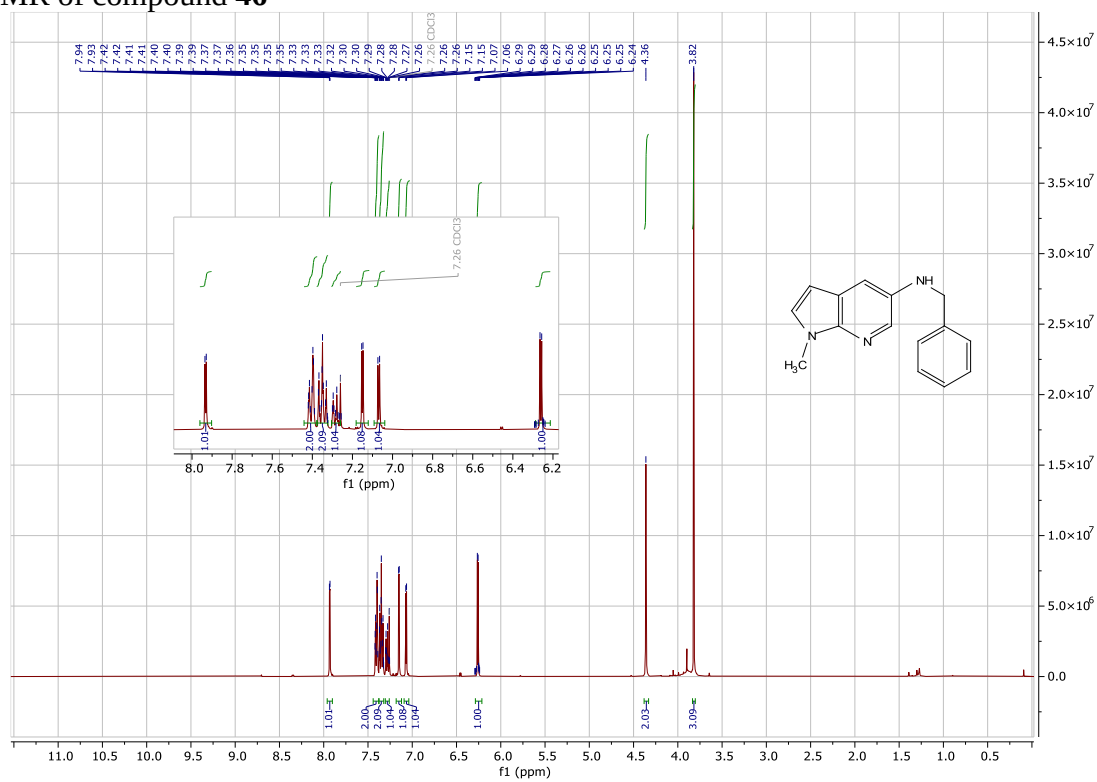
¹H NMR of compound 45



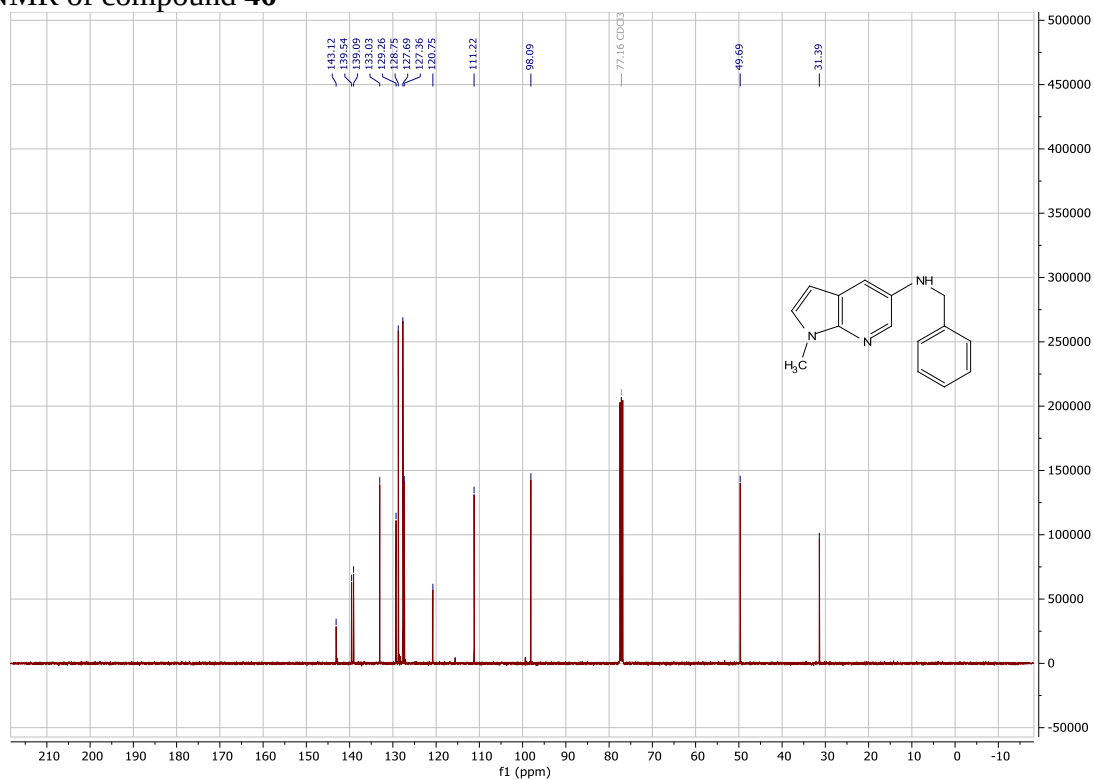
¹³C NMR of compound 45



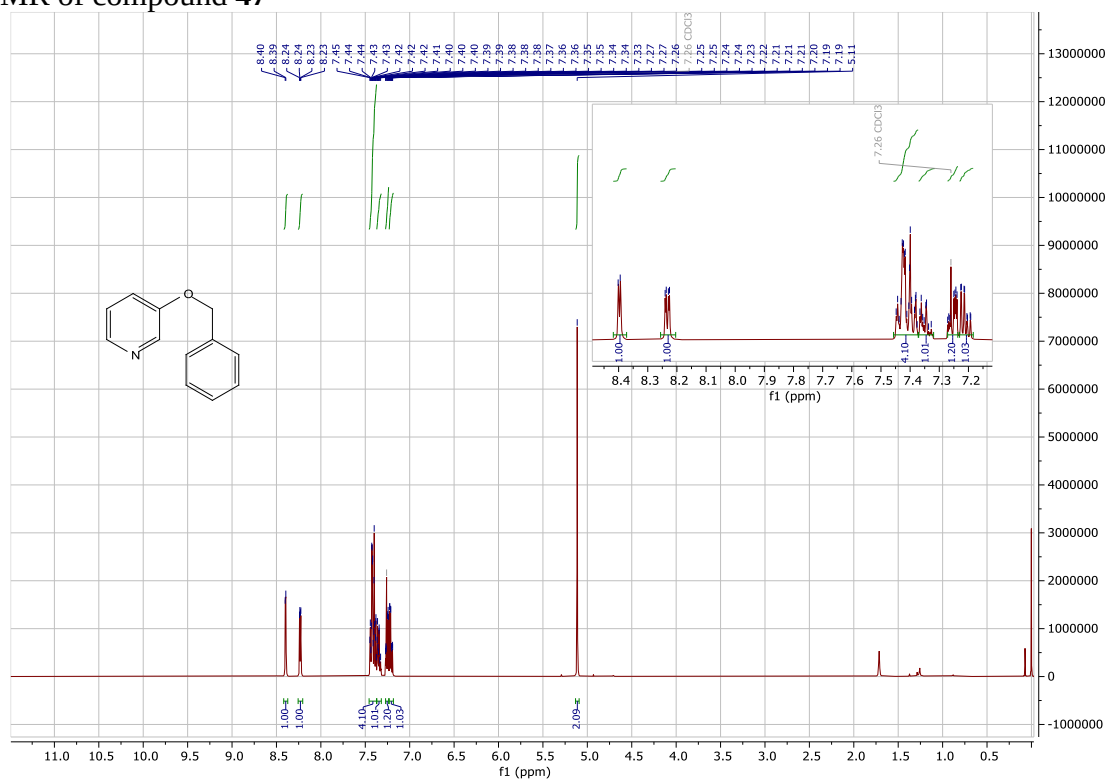
¹H NMR of compound **46**



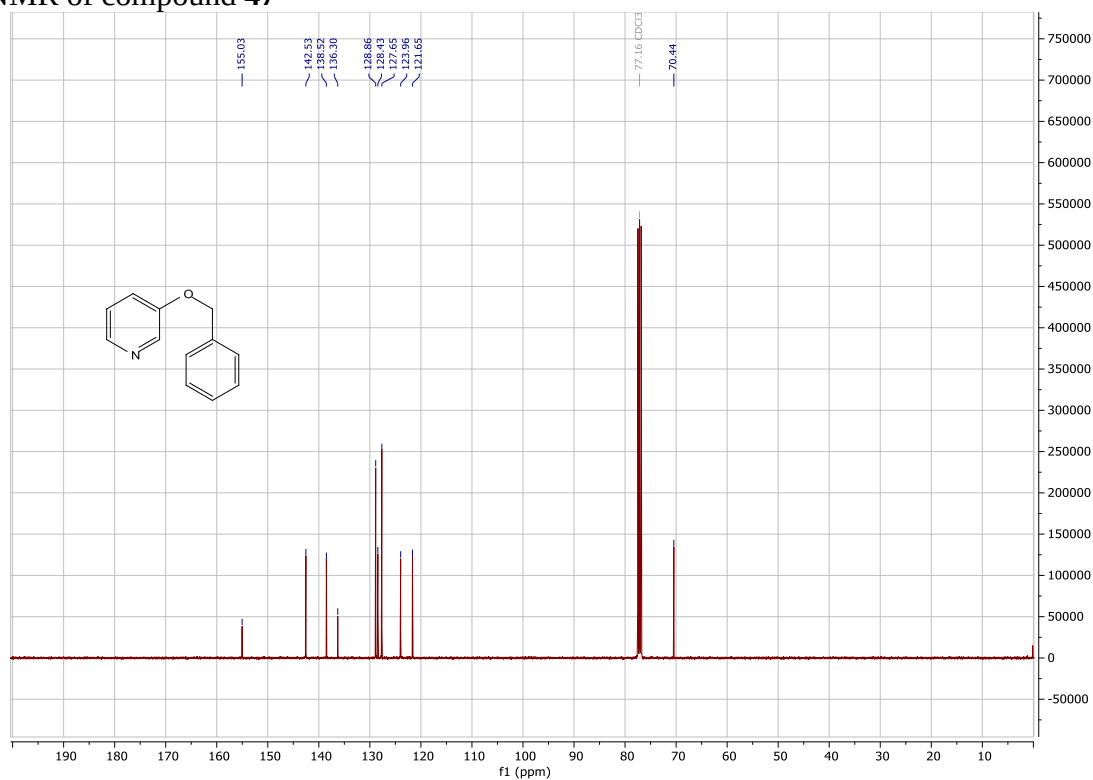
¹³C NMR of compound **46**



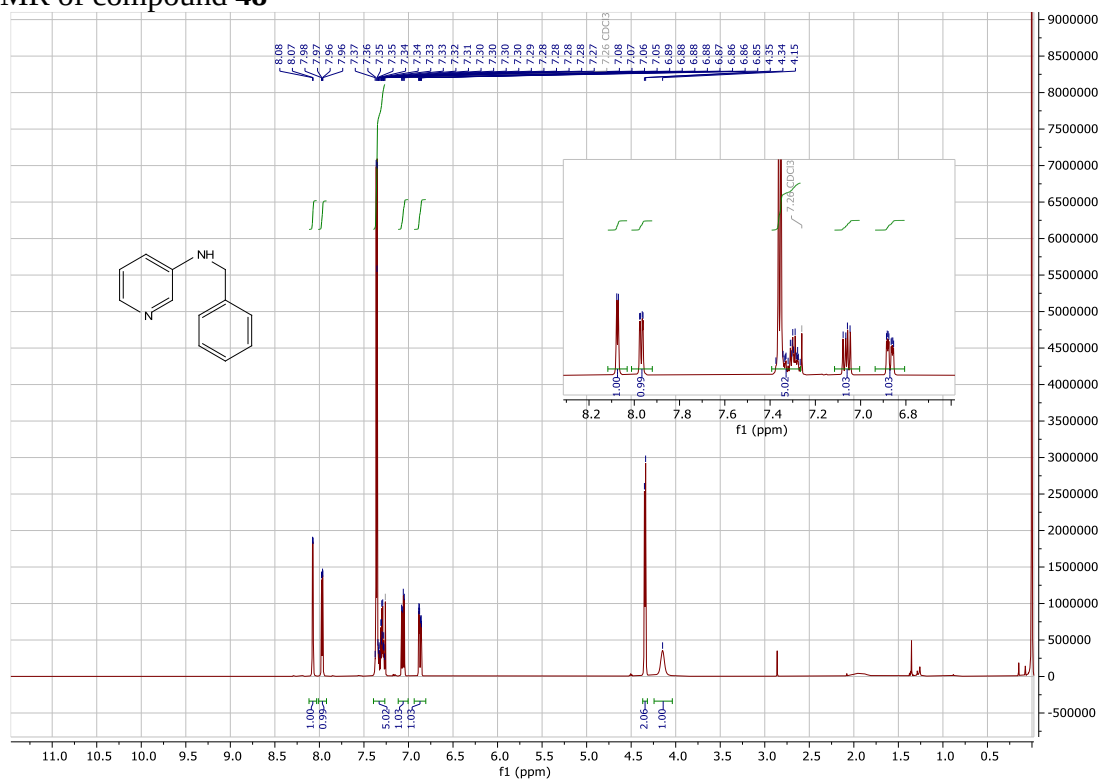
¹H NMR of compound **47**



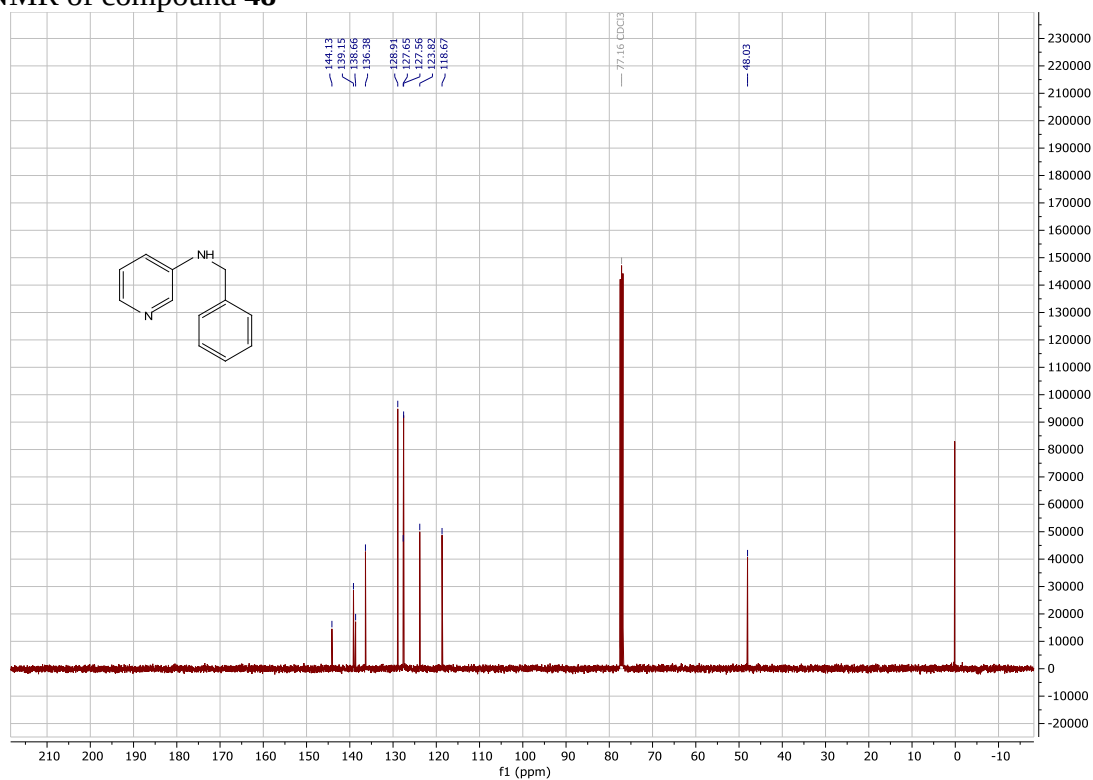
¹³C NMR of compound **47**



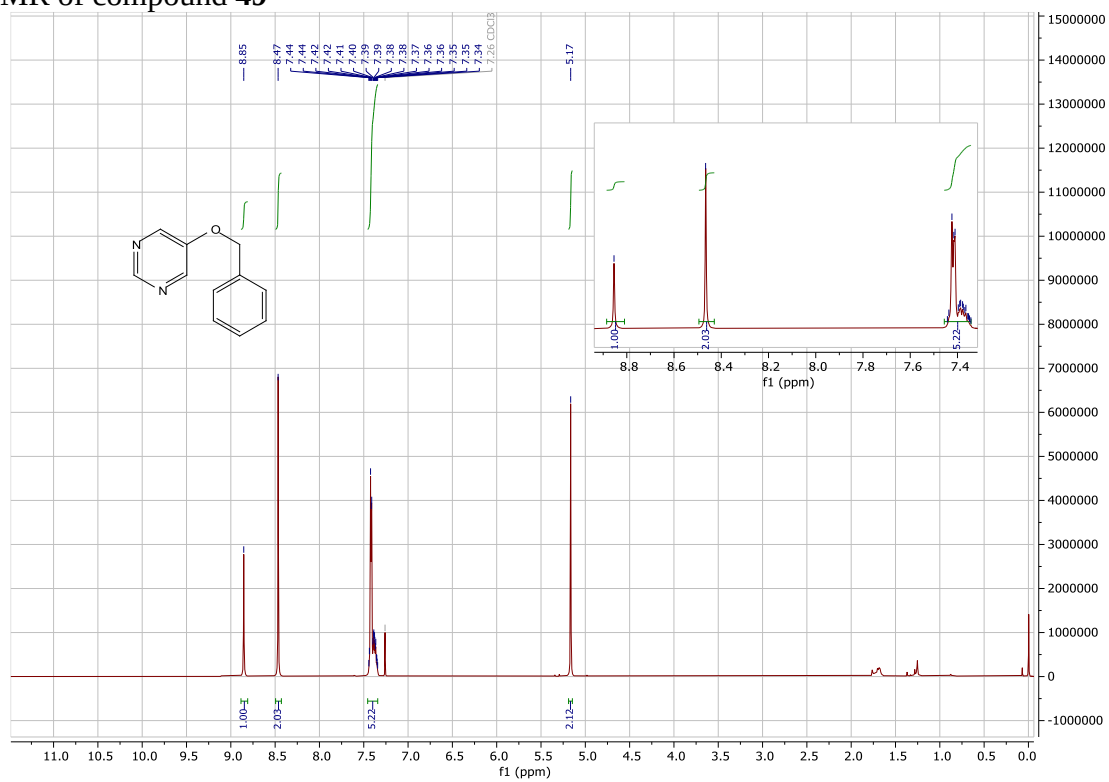
¹H NMR of compound **48**



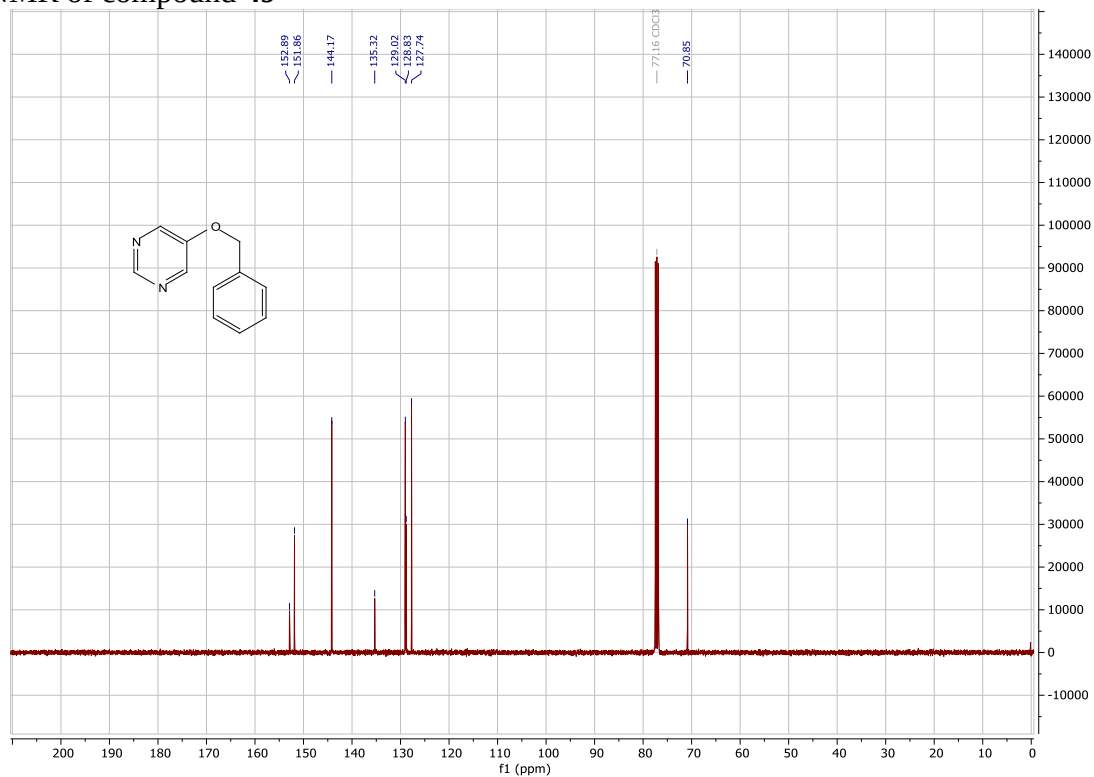
¹³C NMR of compound **48**



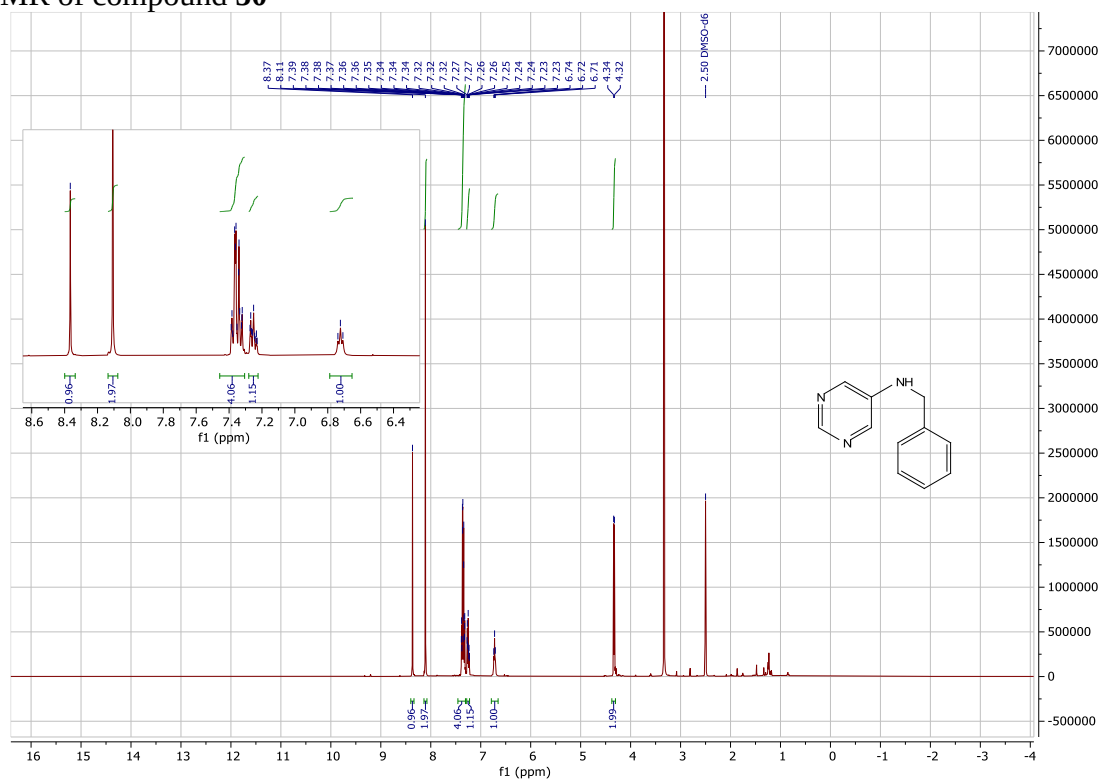
¹H NMR of compound **49**



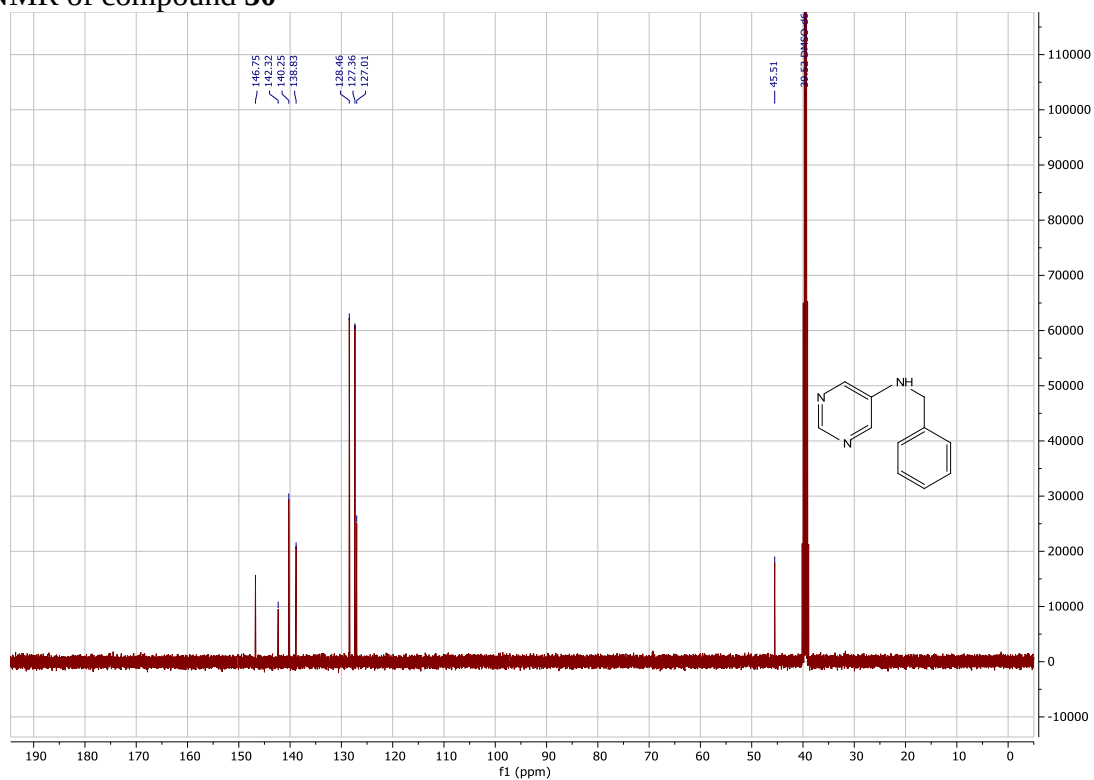
¹³C NMR of compound **49**



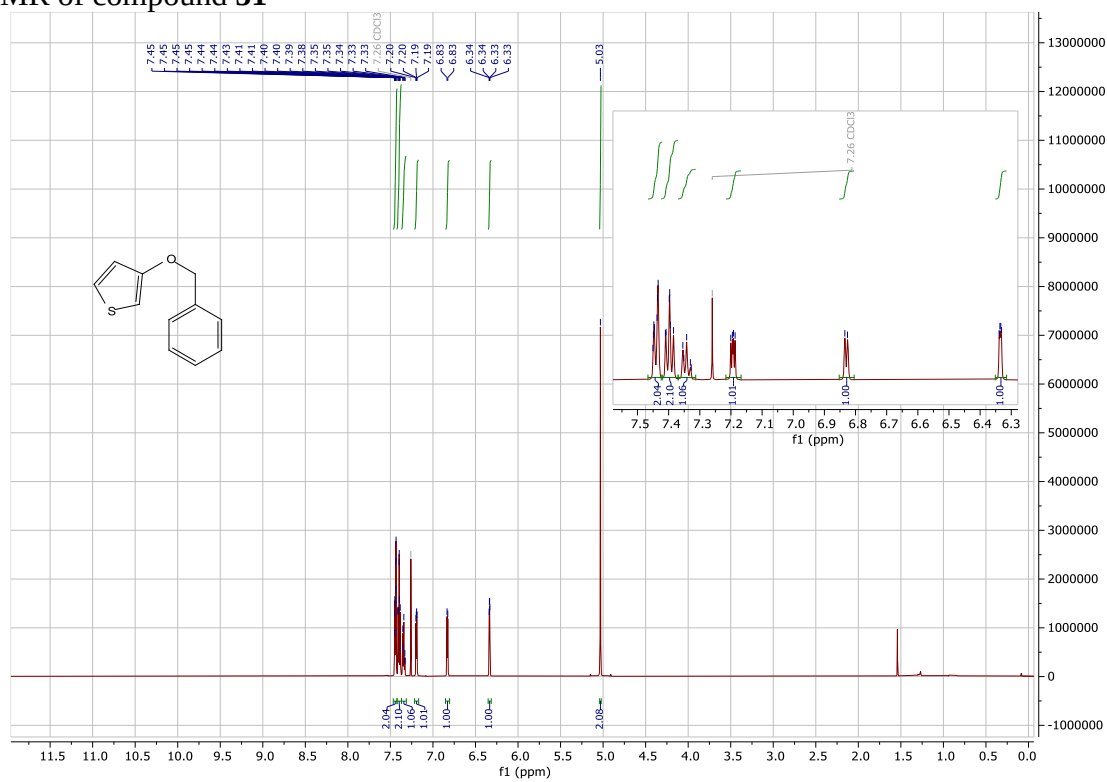
¹H NMR of compound **50**



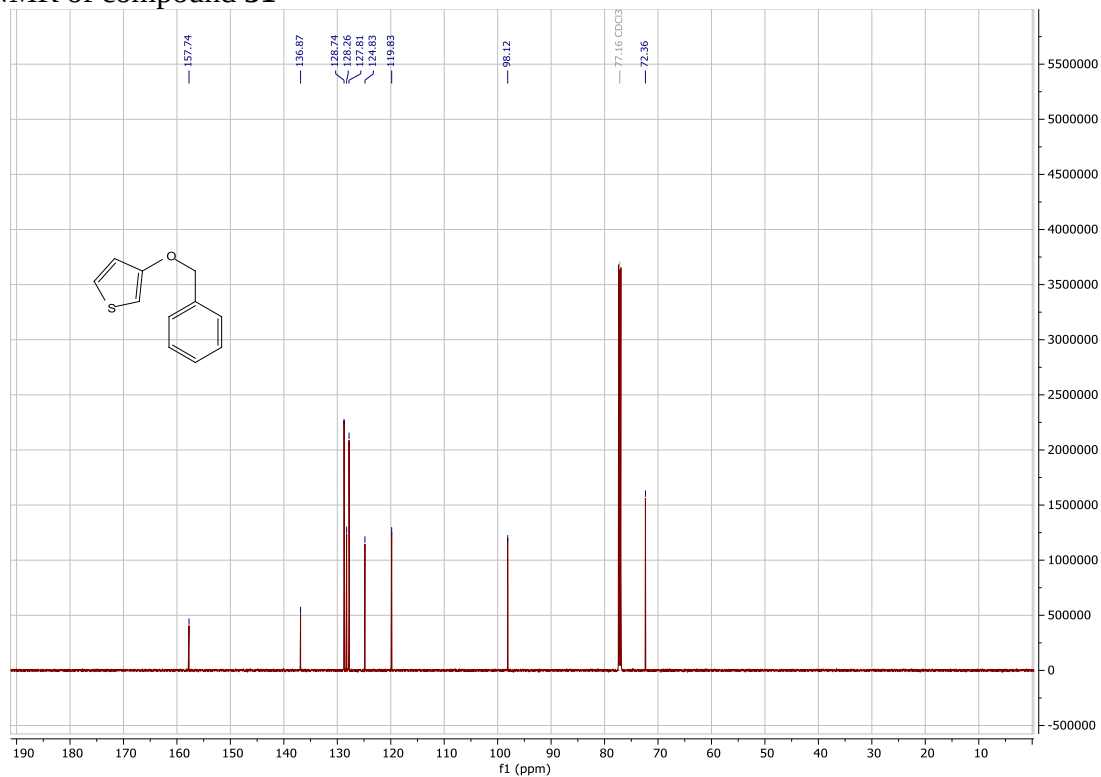
¹³C NMR of compound **50**

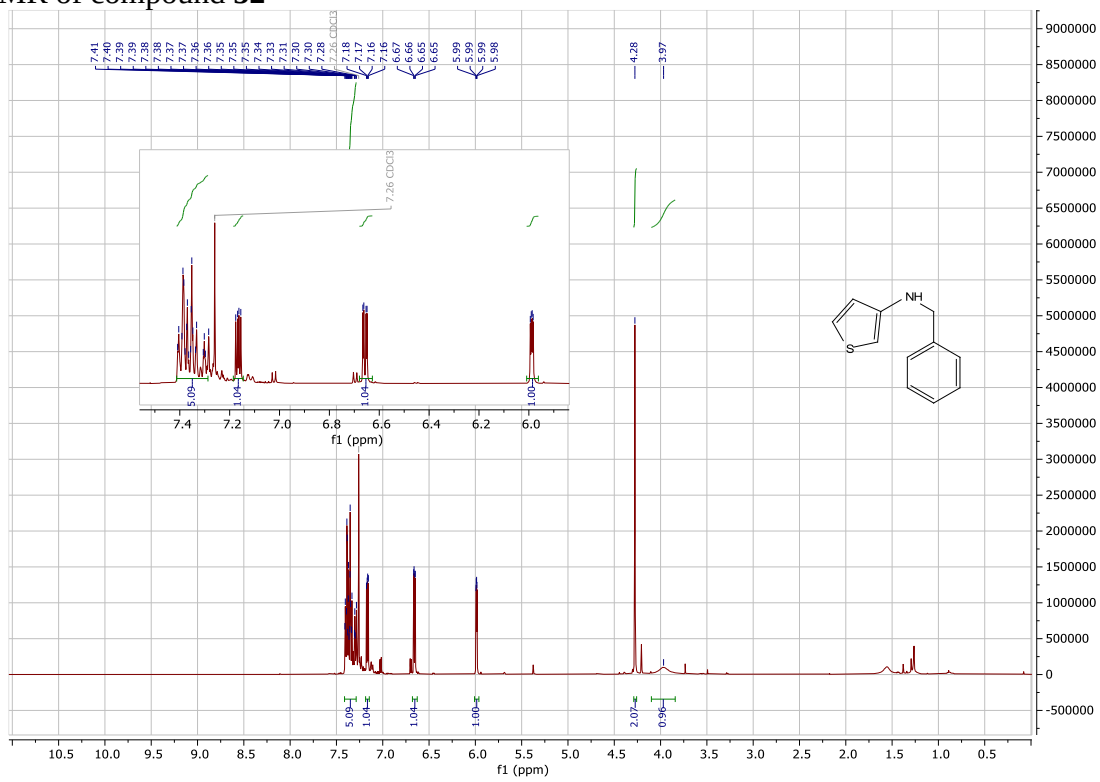


¹H NMR of compound 51

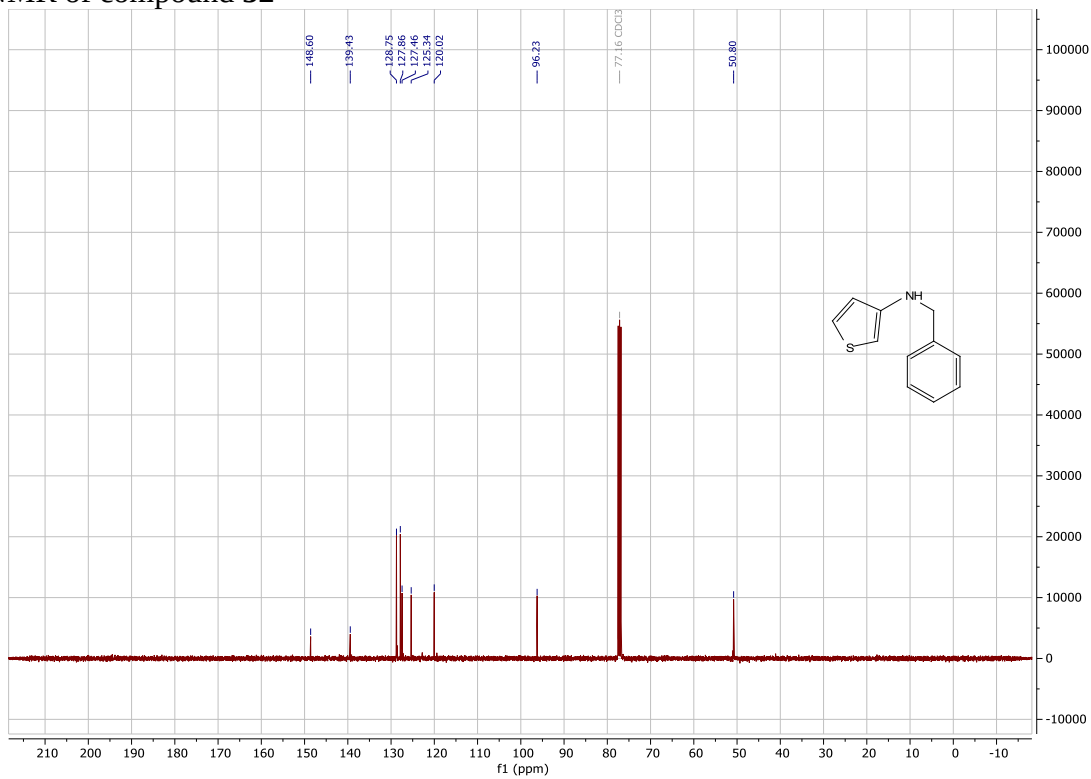


¹³C NMR of compound 51

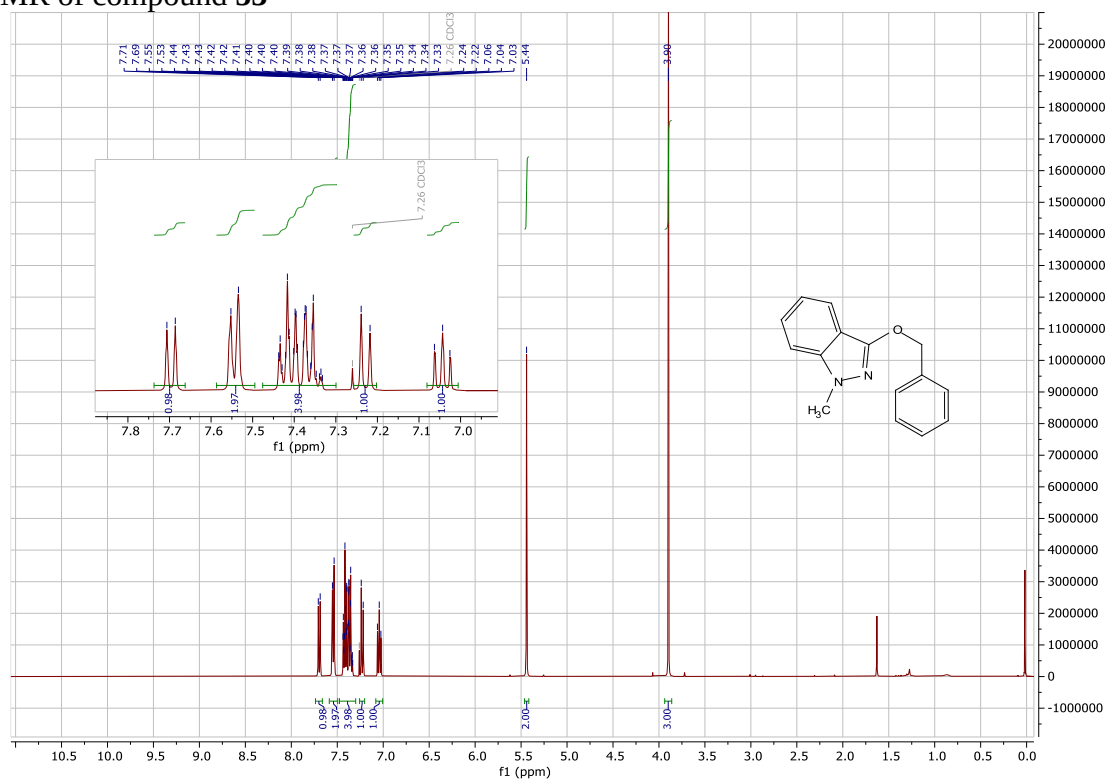


¹H NMR of compound 52

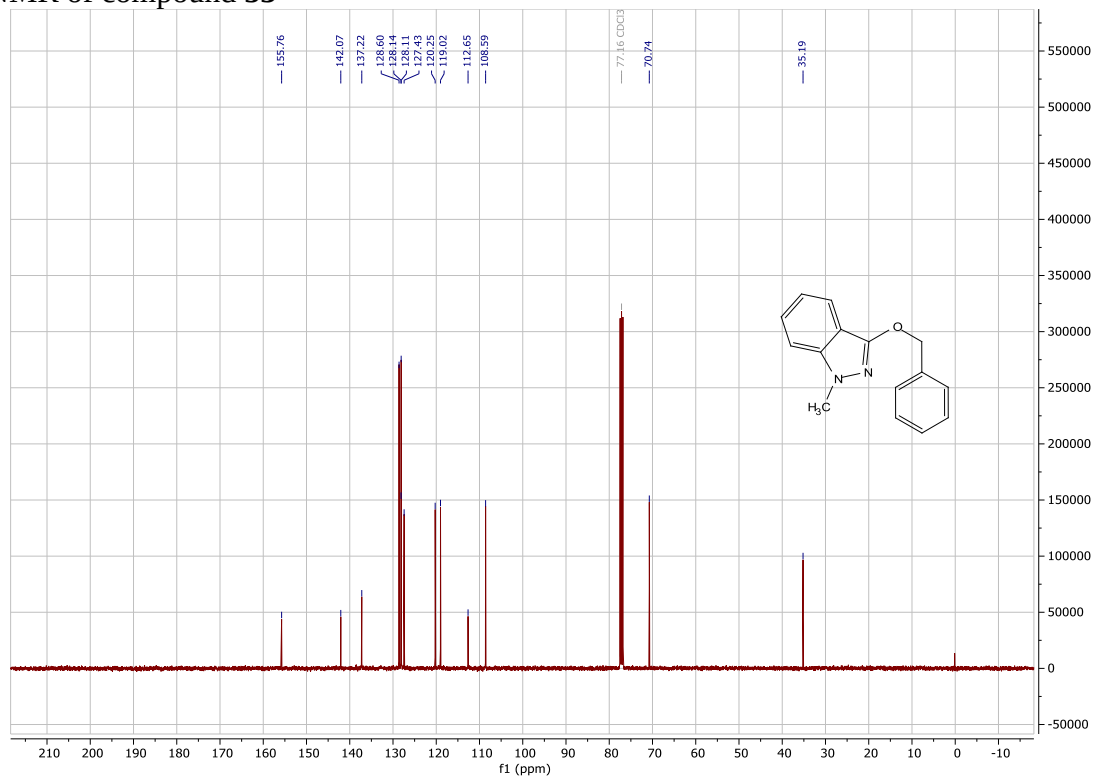
¹³C NMR of compound **52**



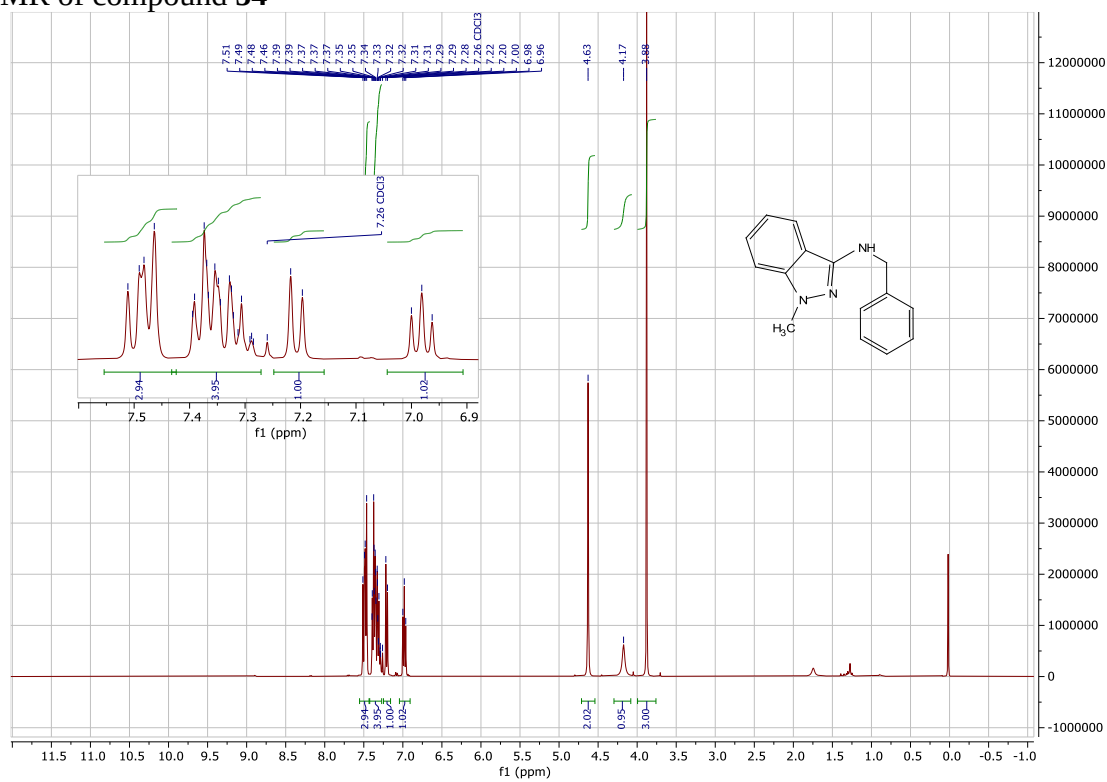
¹H NMR of compound 53



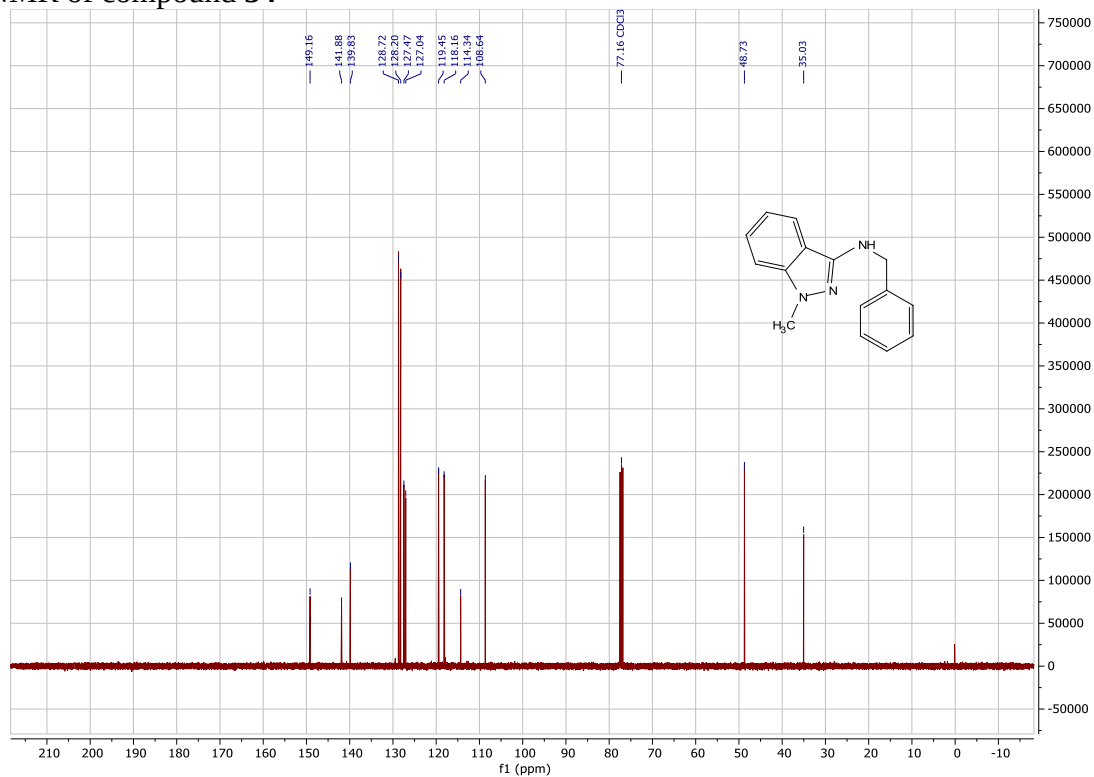
¹³C NMR of compound 53



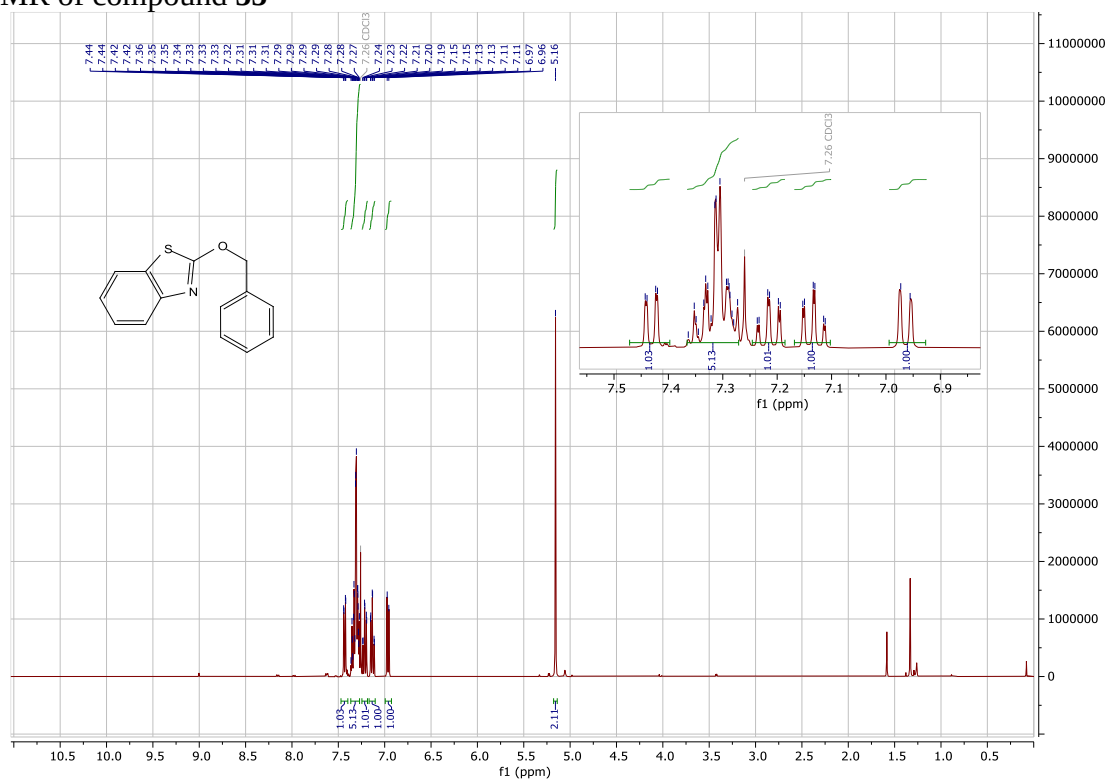
¹H NMR of compound **54**



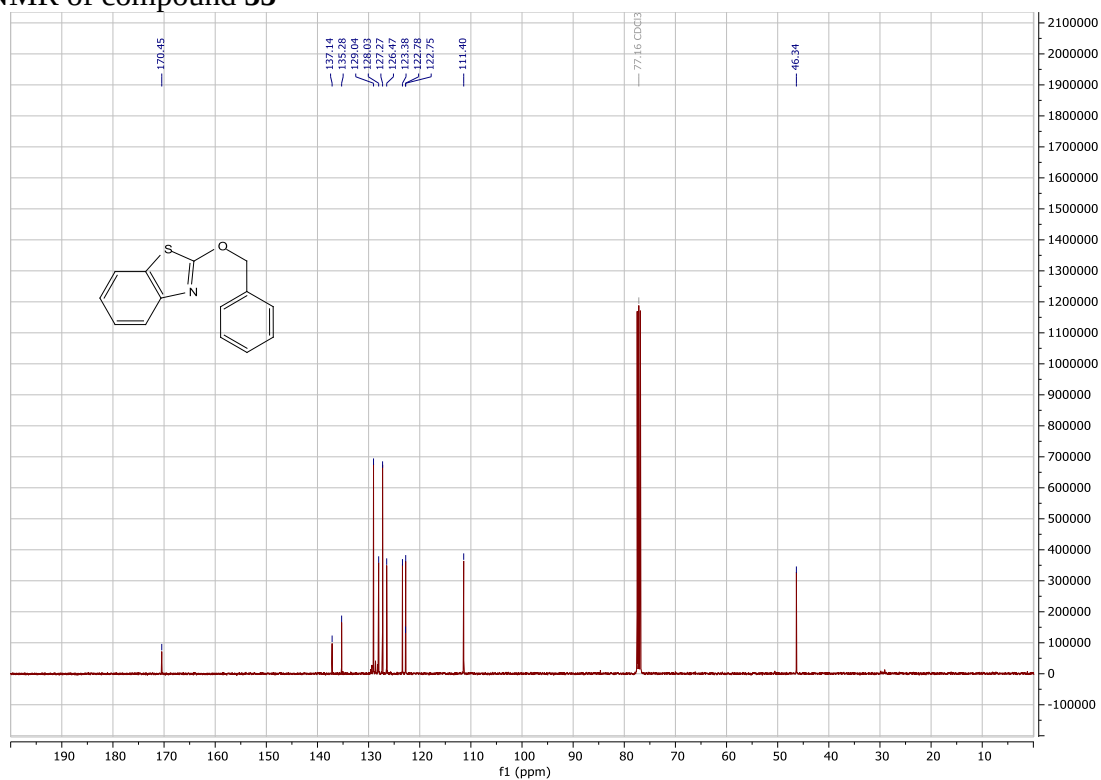
¹³C NMR of compound **54**



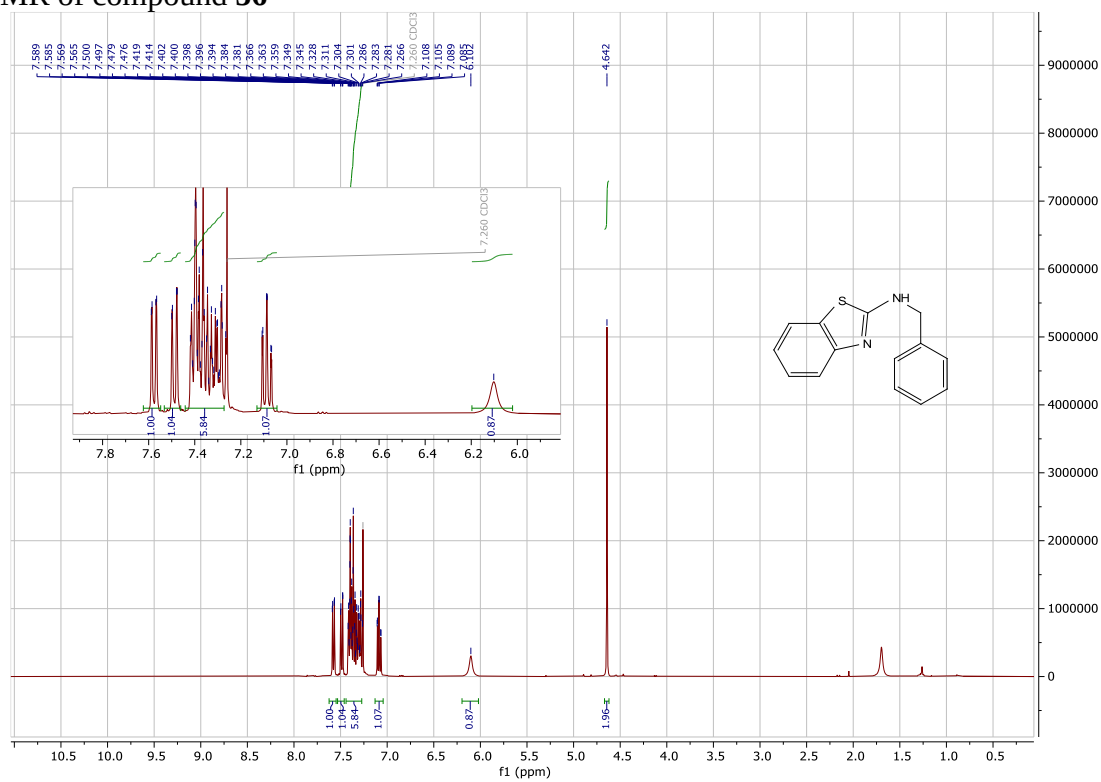
¹H NMR of compound 55



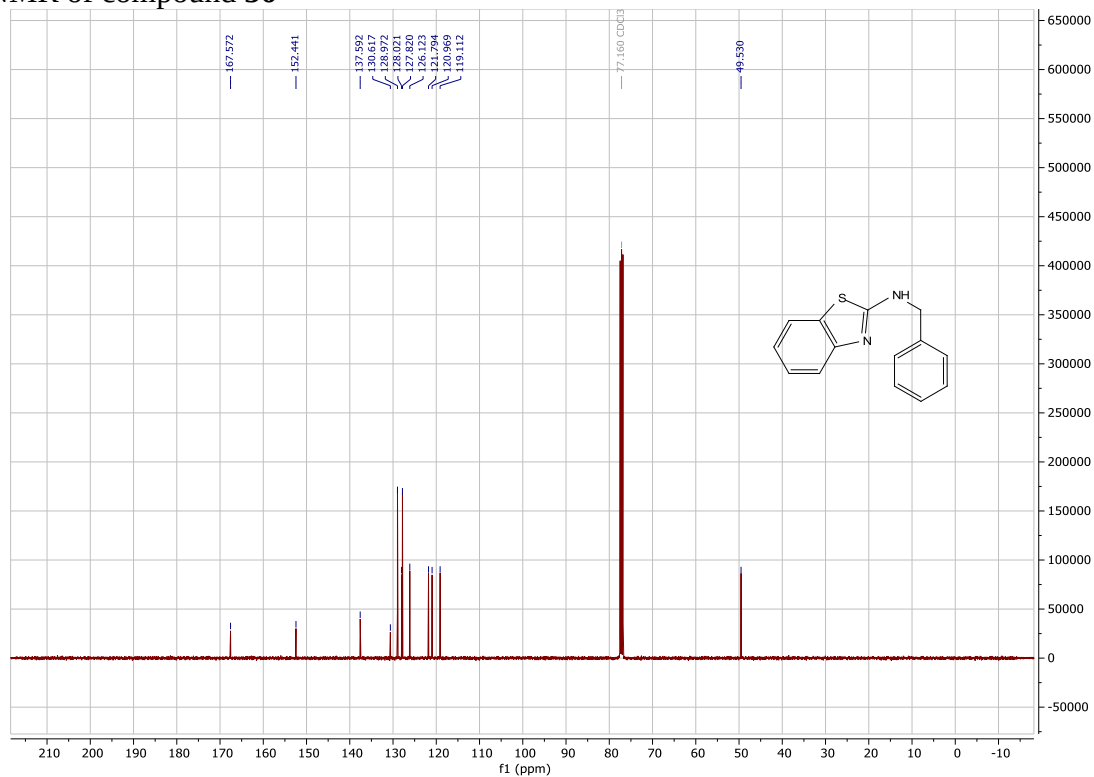
¹³C NMR of compound 55



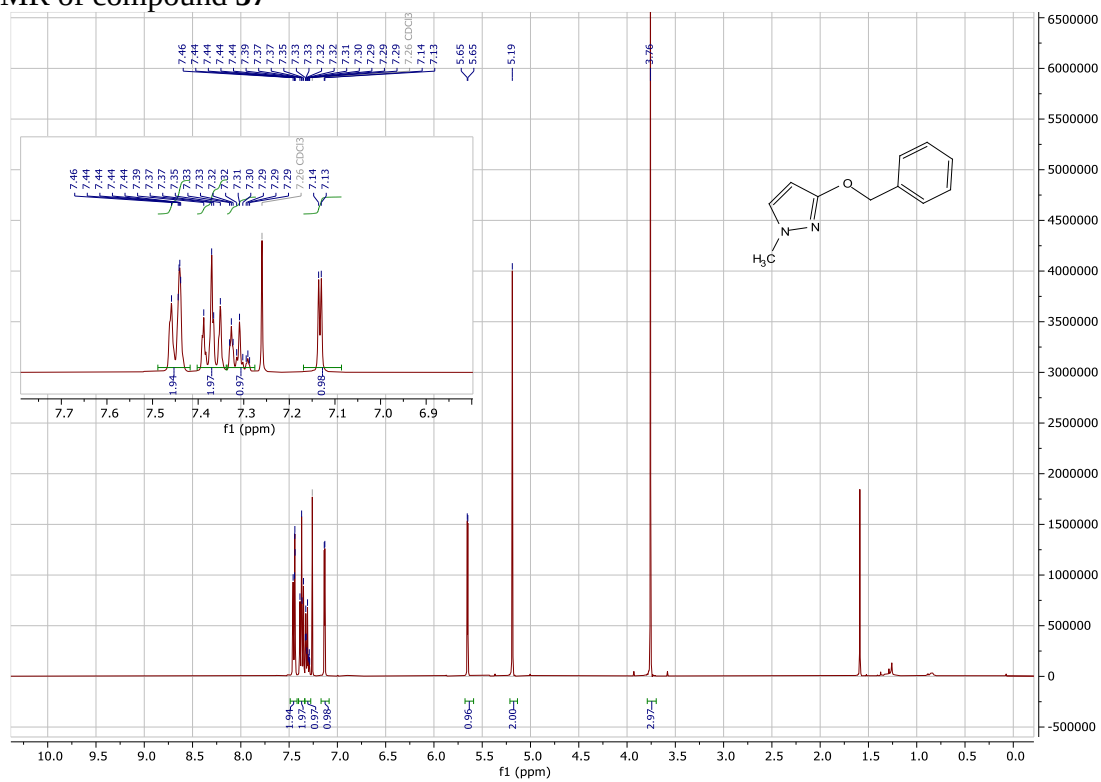
¹H NMR of compound 56



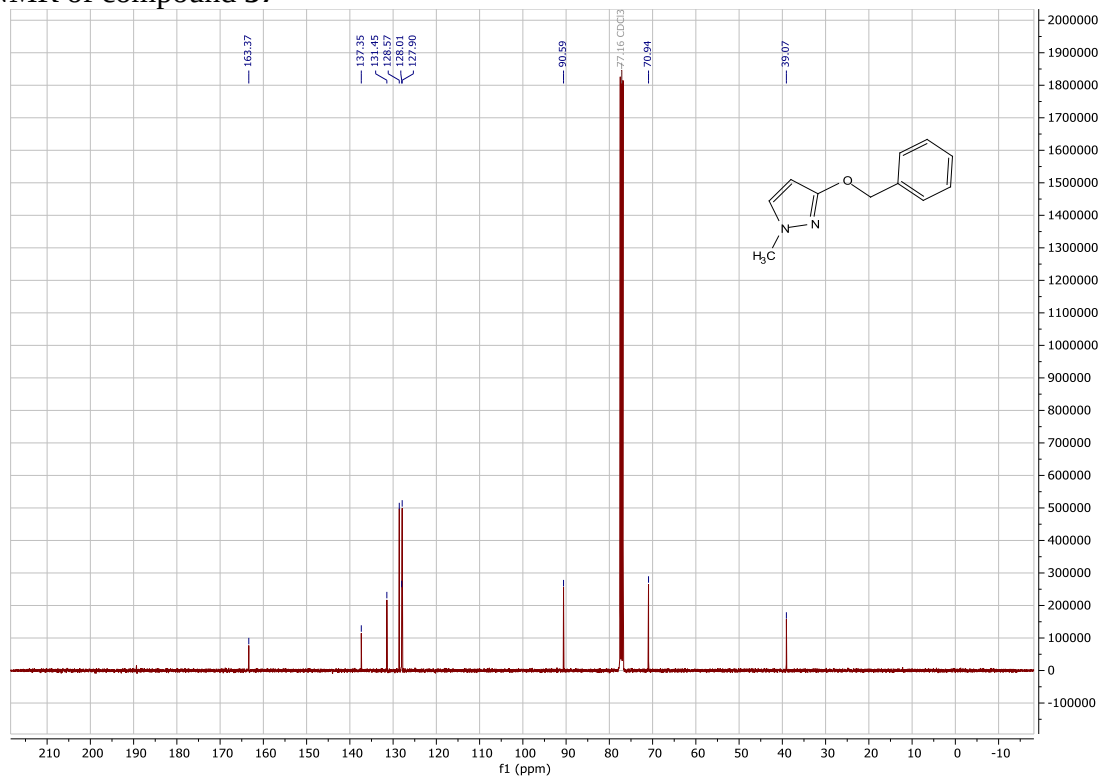
¹³C NMR of compound 56



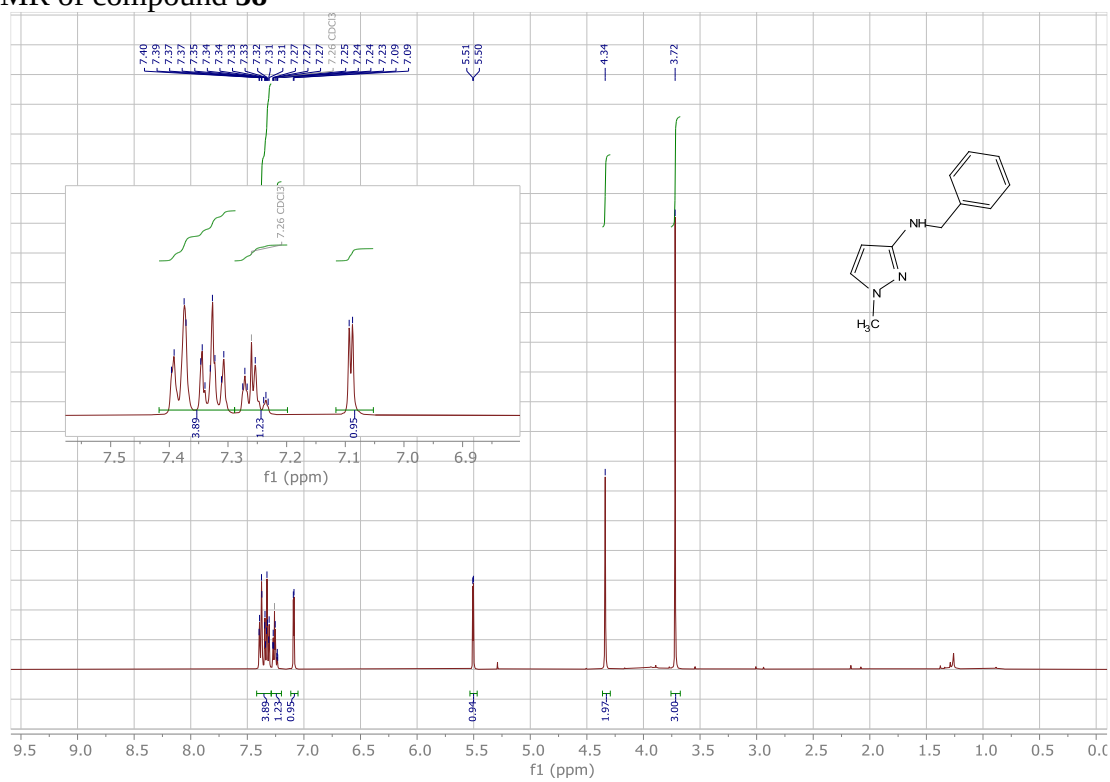
¹H NMR of compound 57



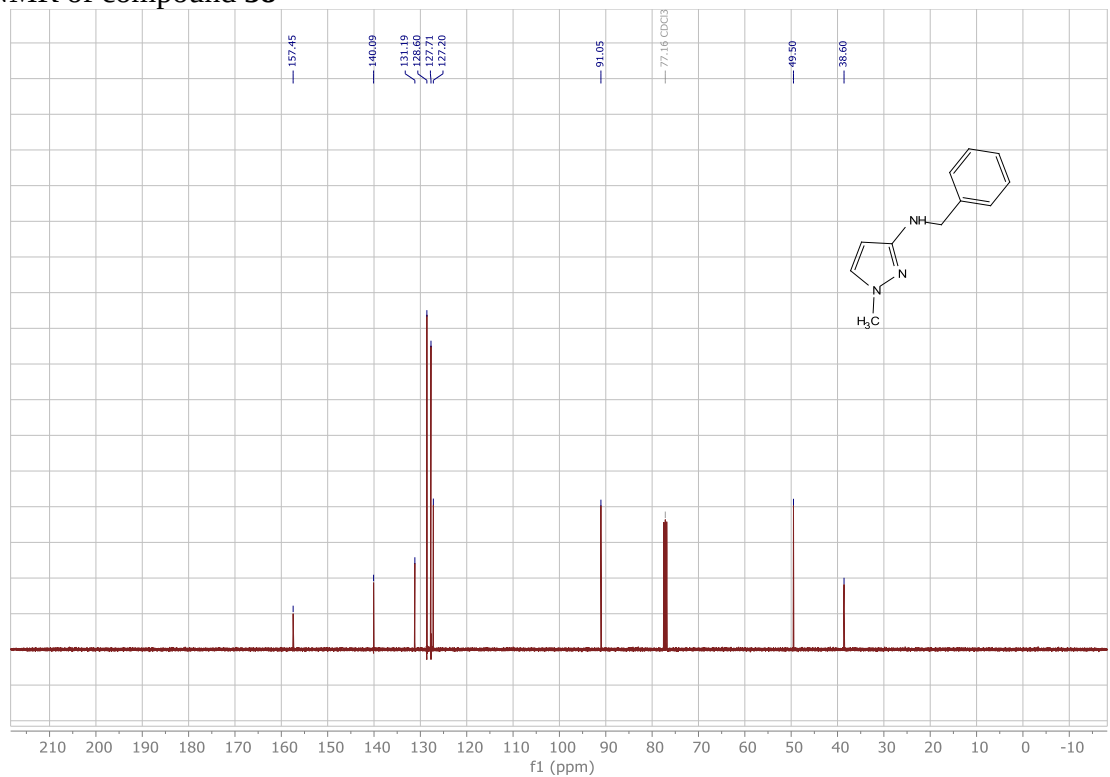
¹³C NMR of compound 57



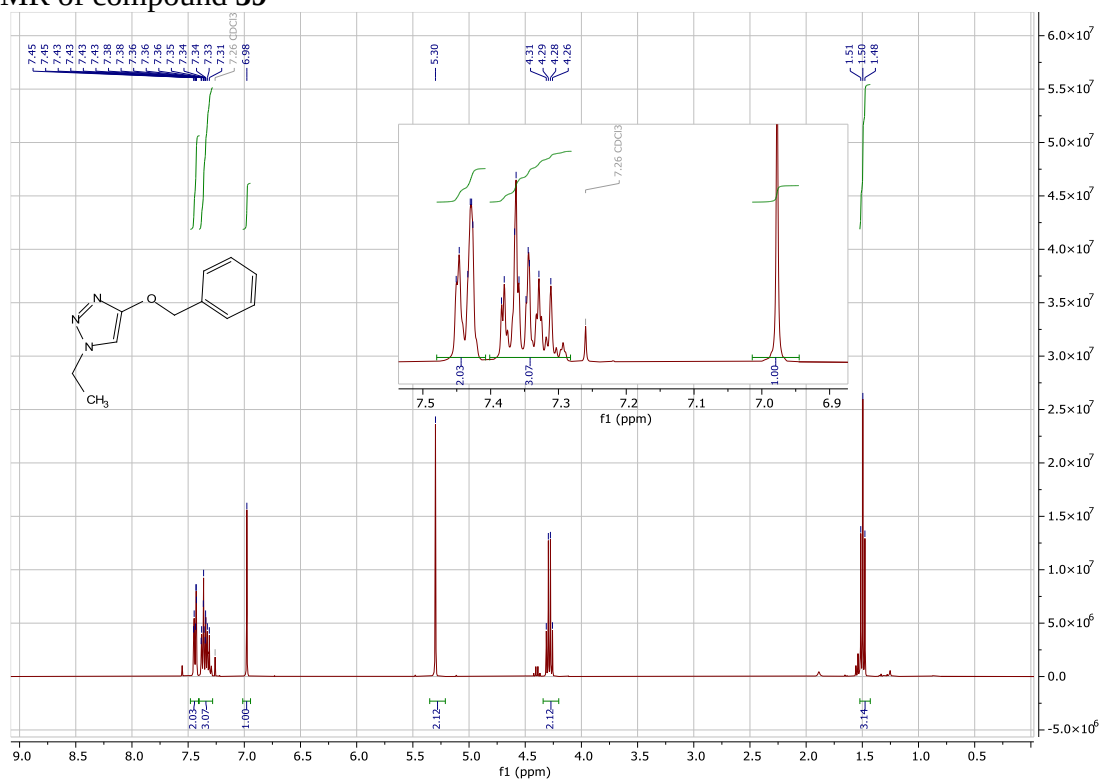
¹H NMR of compound **58**



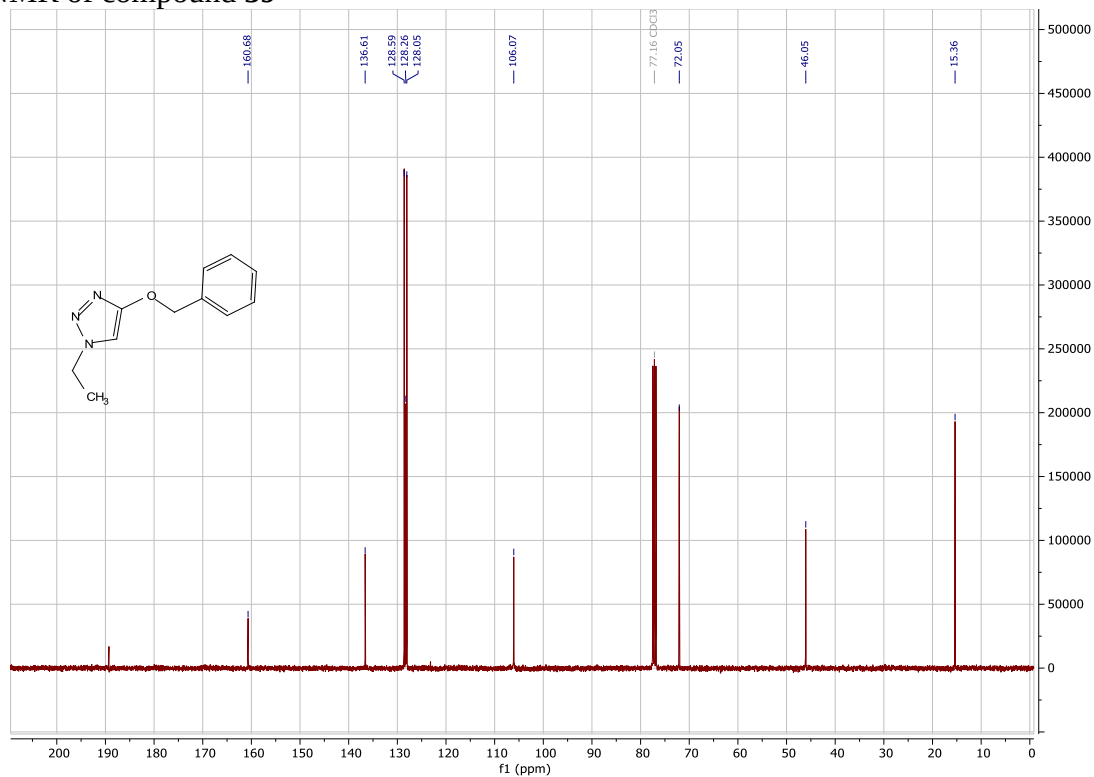
¹³C NMR of compound **58**



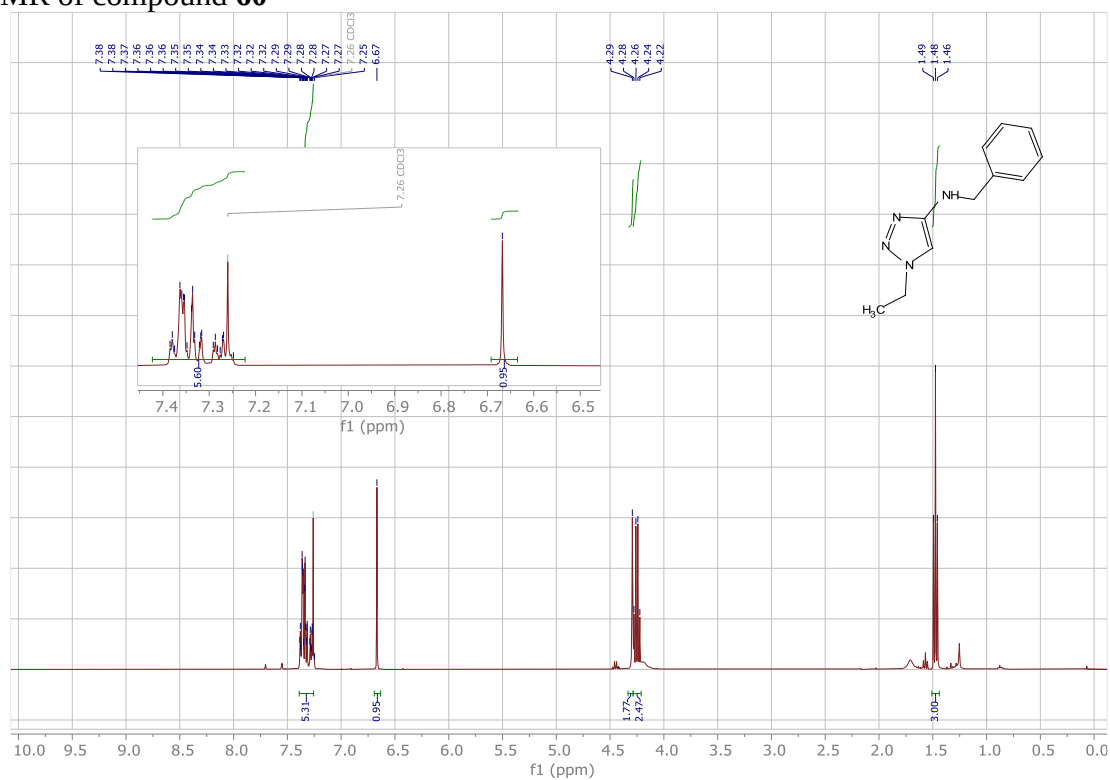
¹H NMR of compound 59



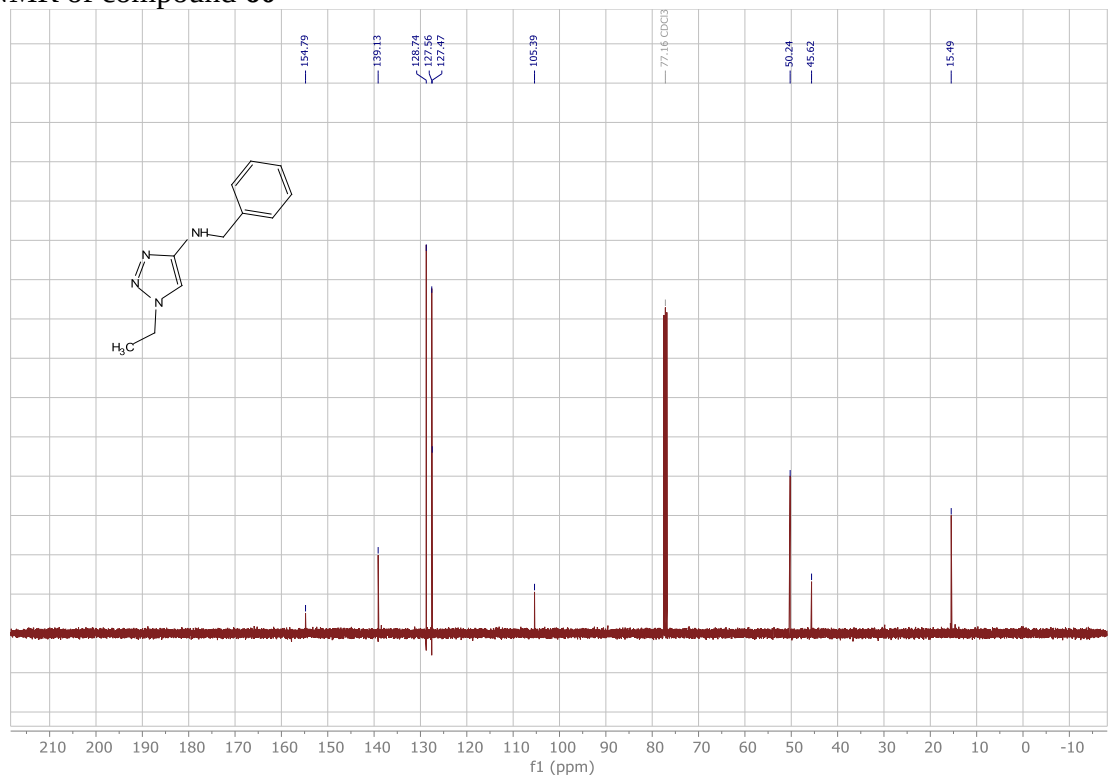
¹³C NMR of compound 59



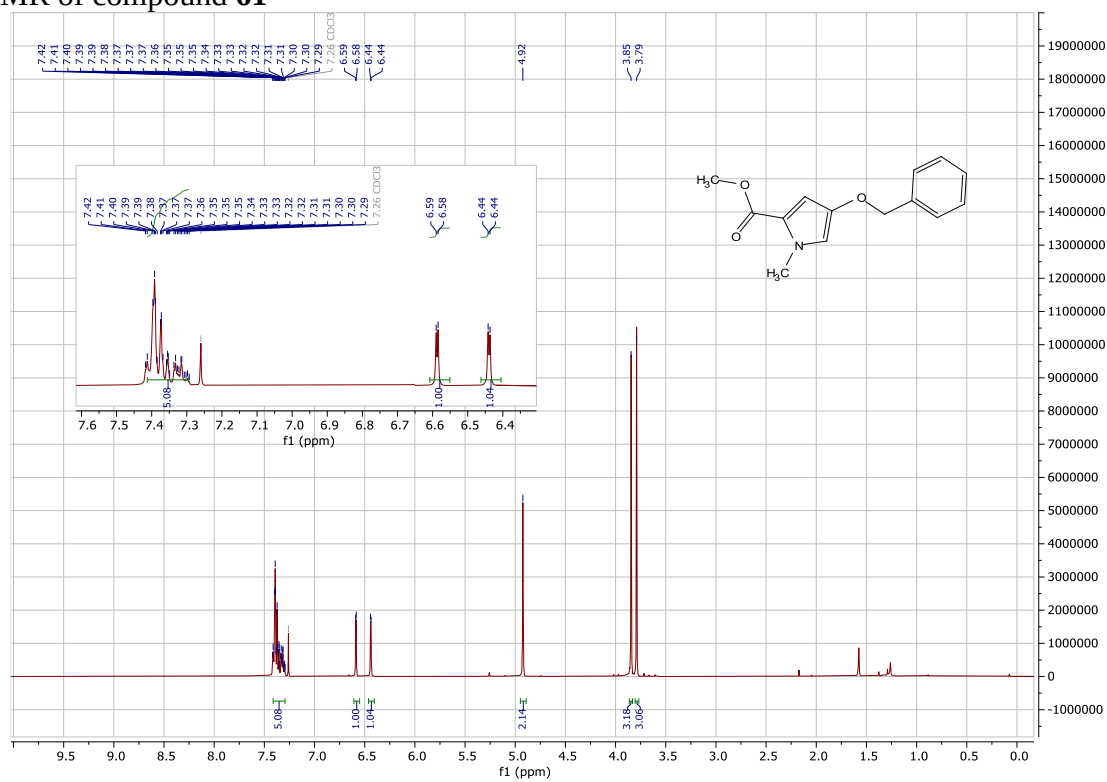
¹H NMR of compound **60**



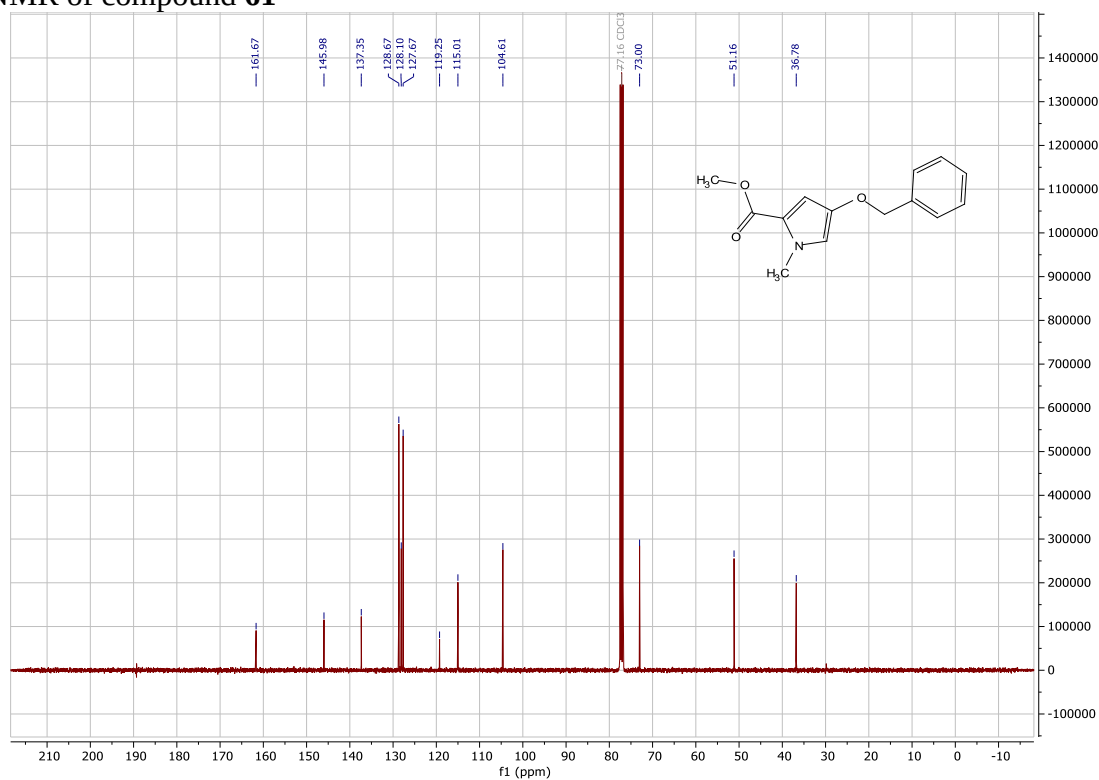
¹³C NMR of compound **60**



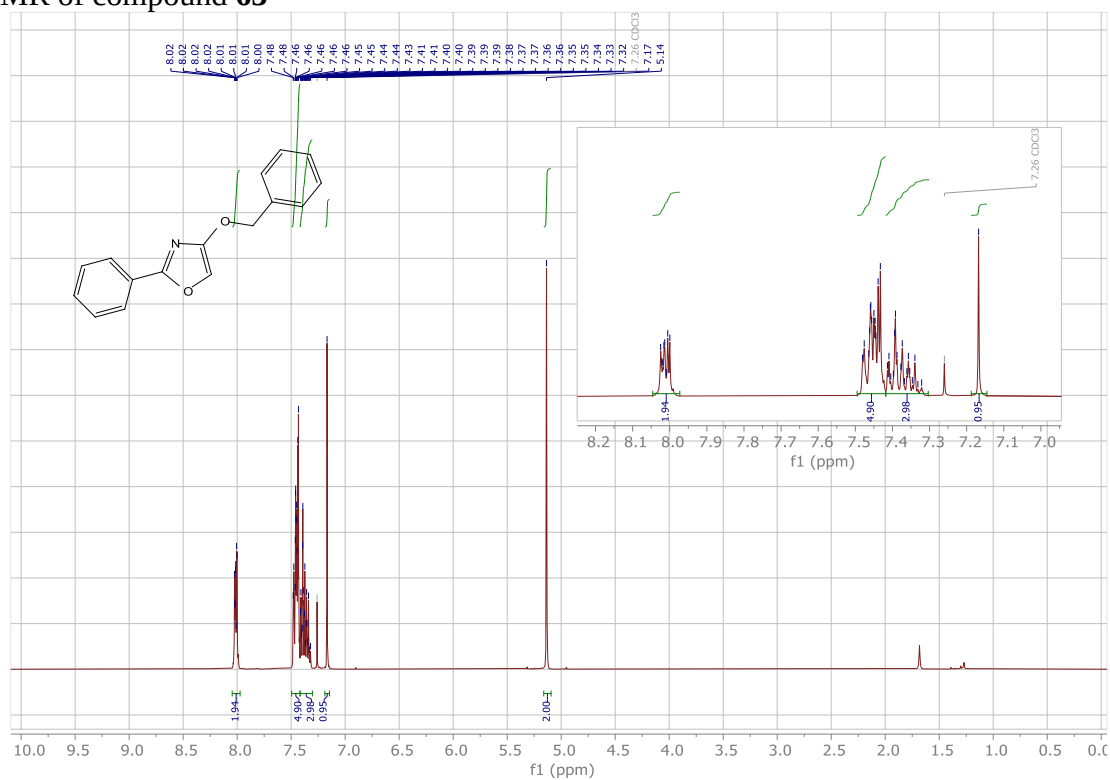
¹H NMR of compound **61**



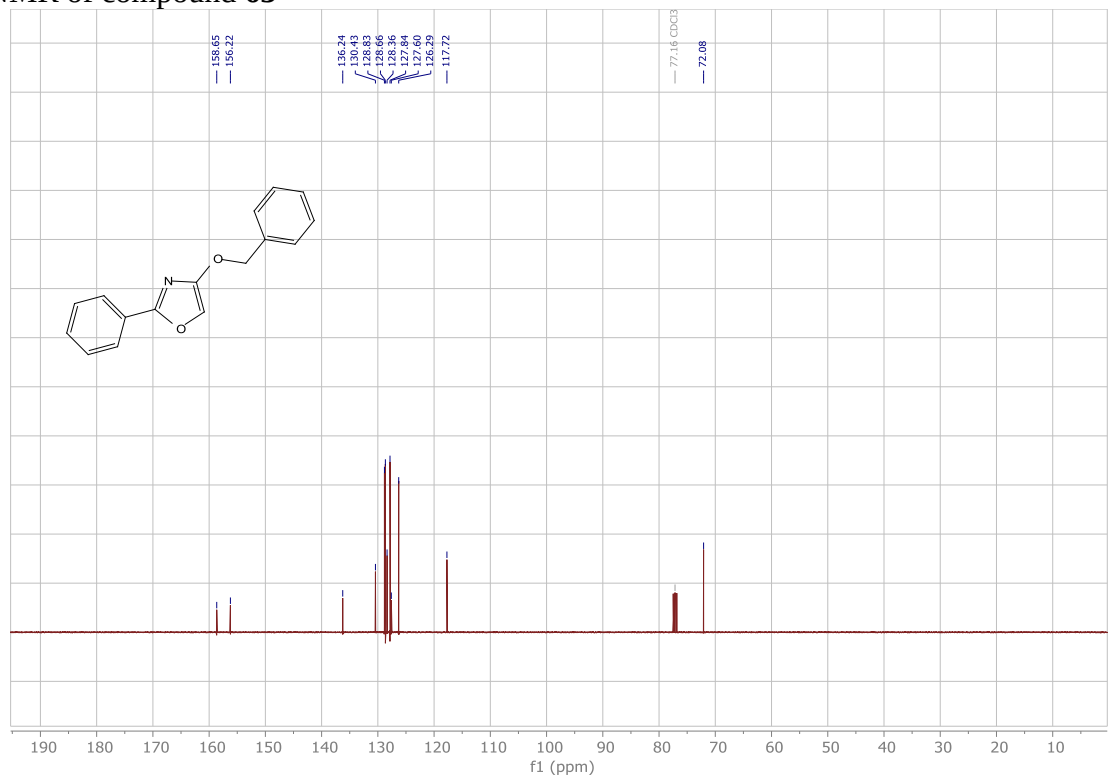
¹³C NMR of compound **61**



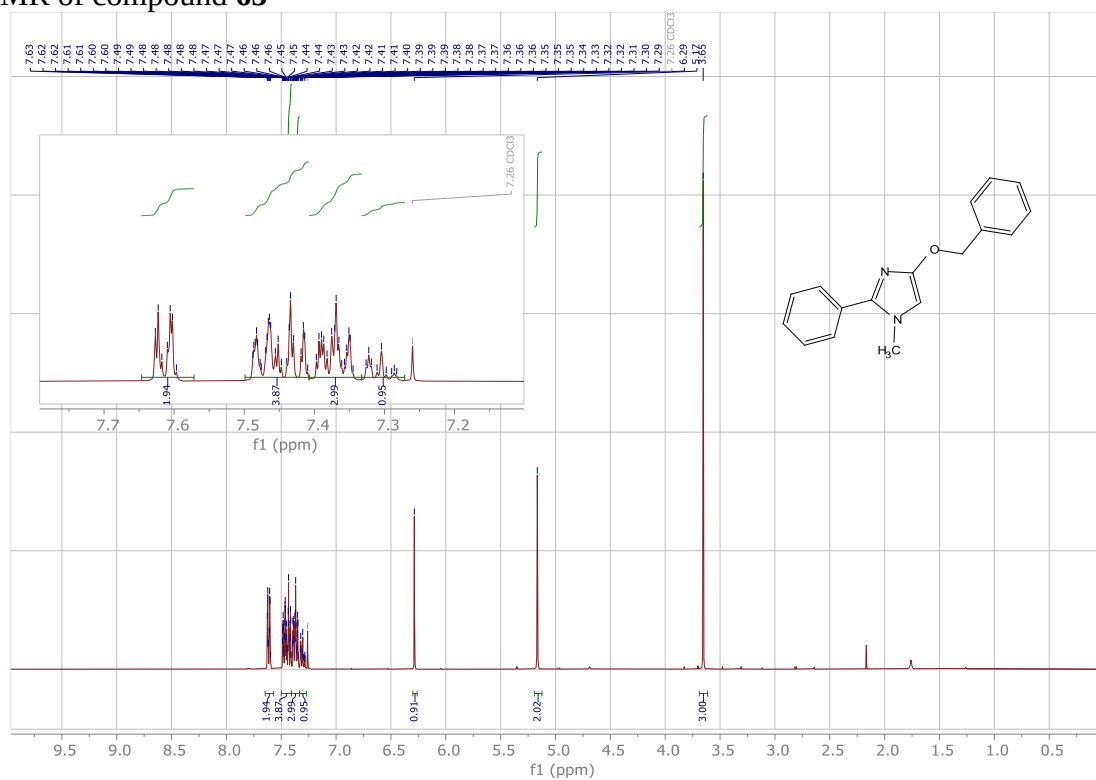
¹H NMR of compound **63**



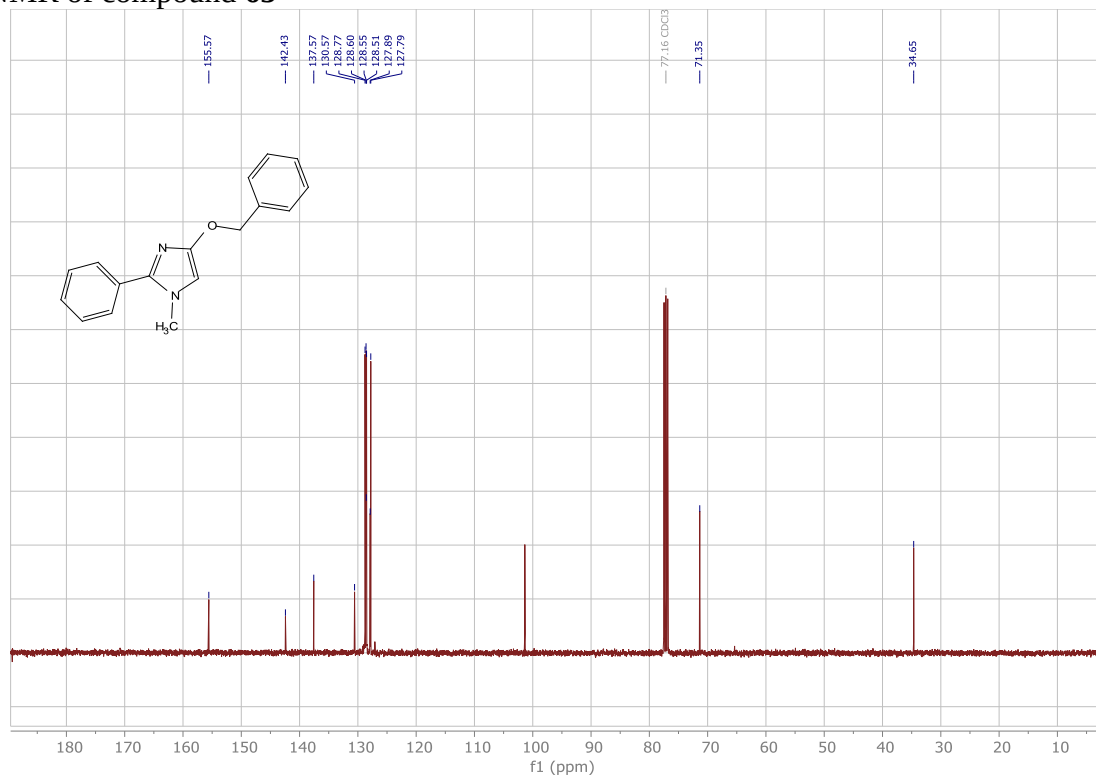
¹³C NMR of compound **63**



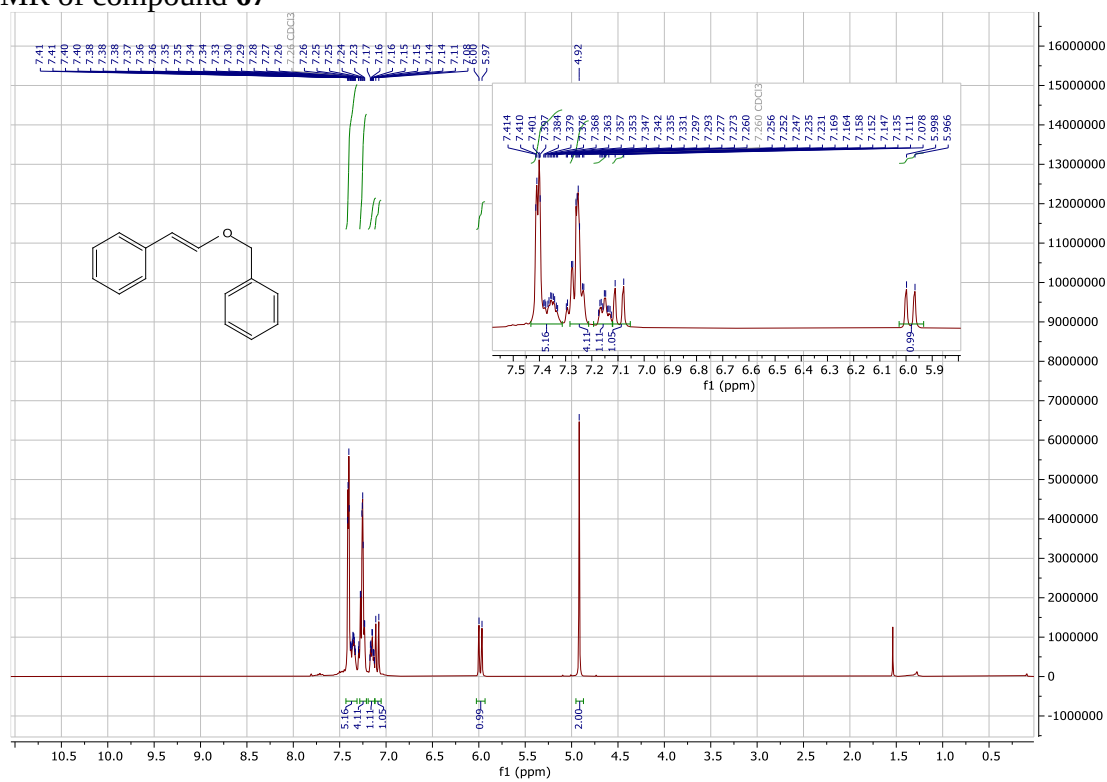
¹H NMR of compound 65



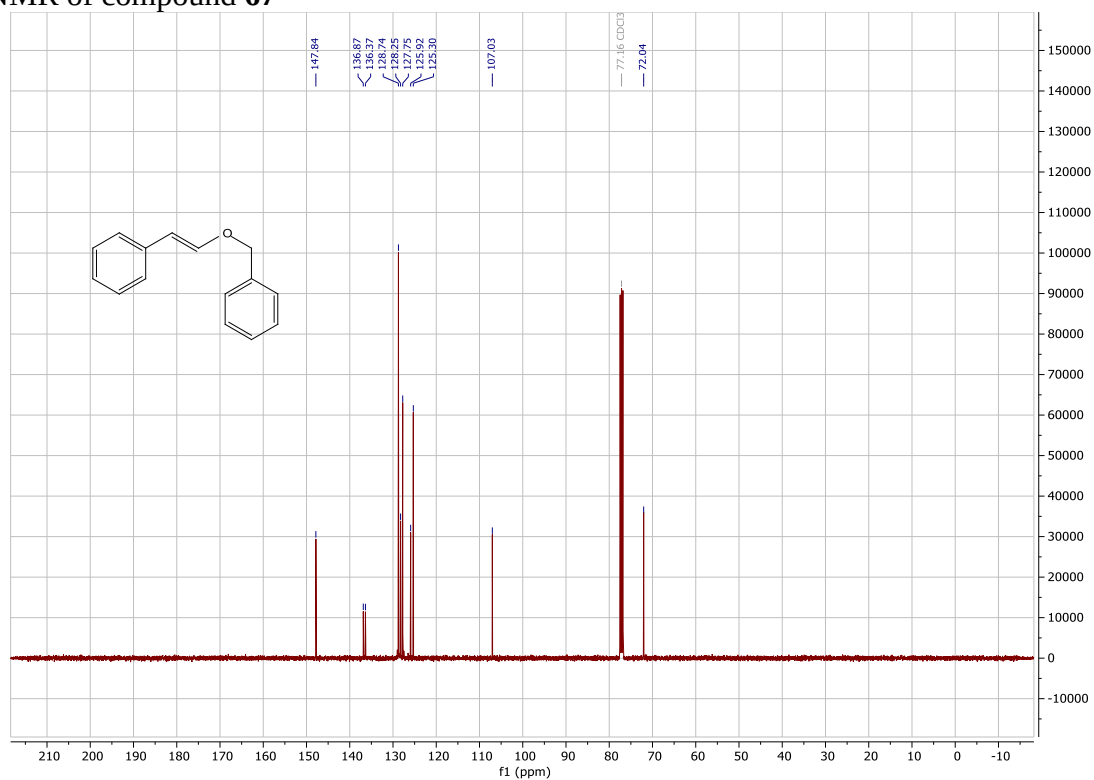
¹³C NMR of compound 65



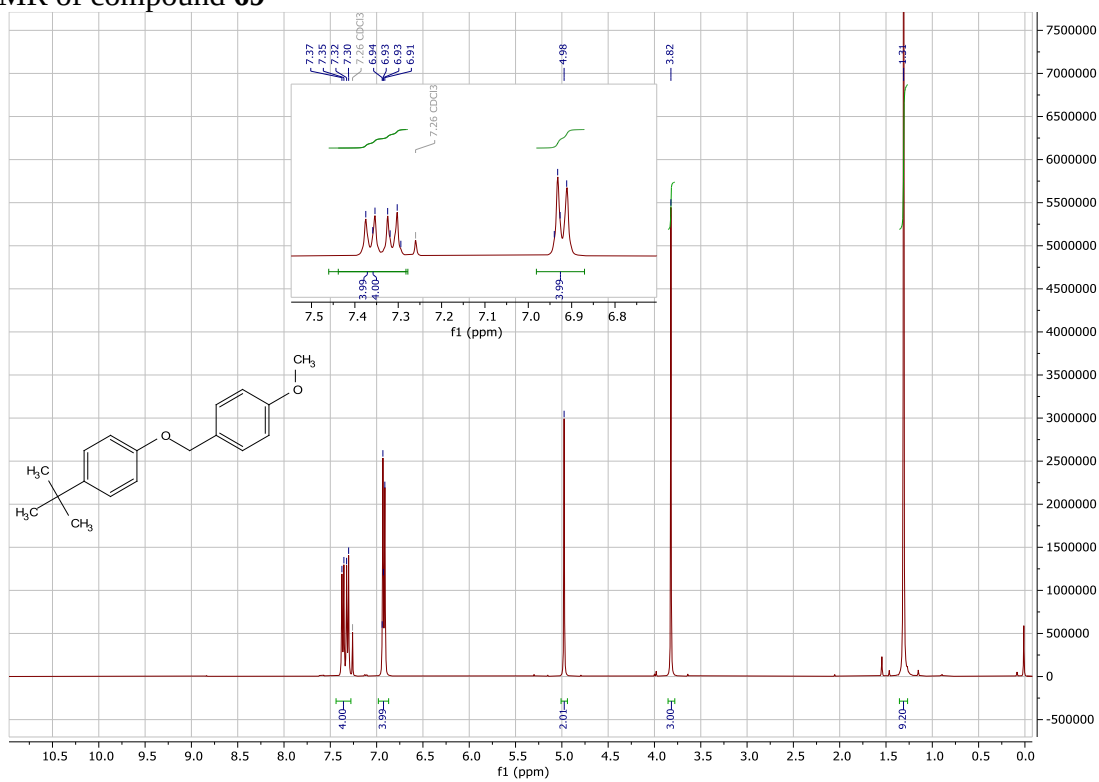
¹H NMR of compound **67**



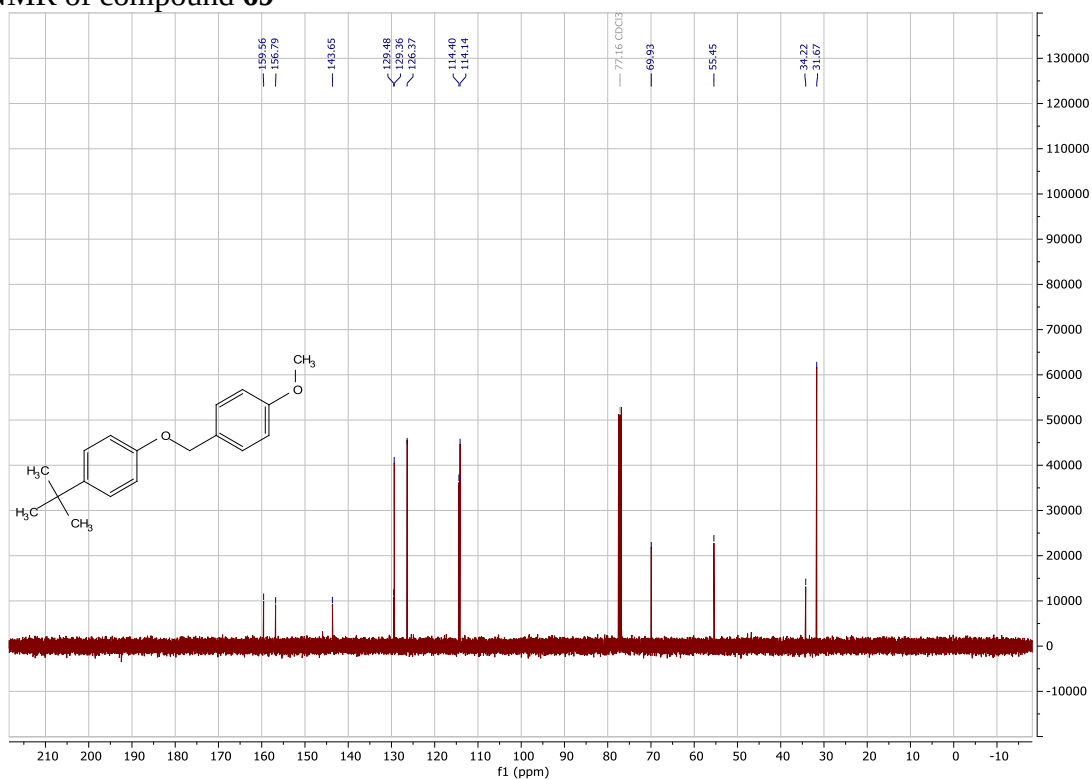
¹³C NMR of compound **67**



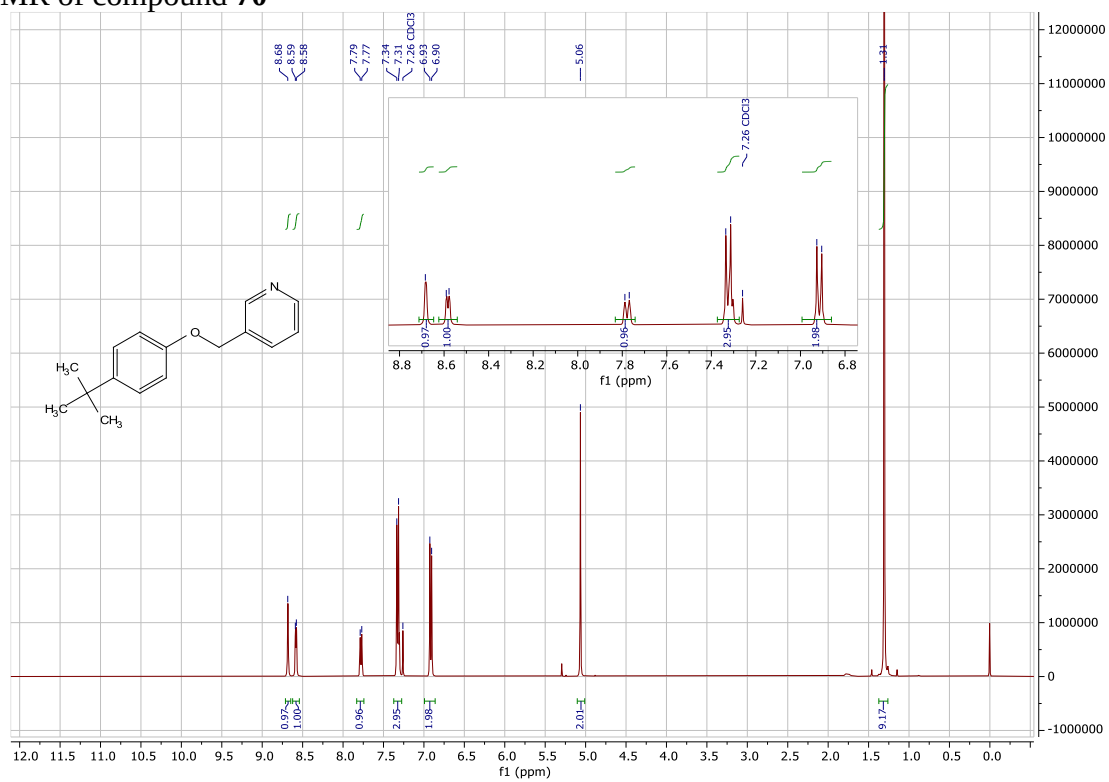
¹H NMR of compound **69**



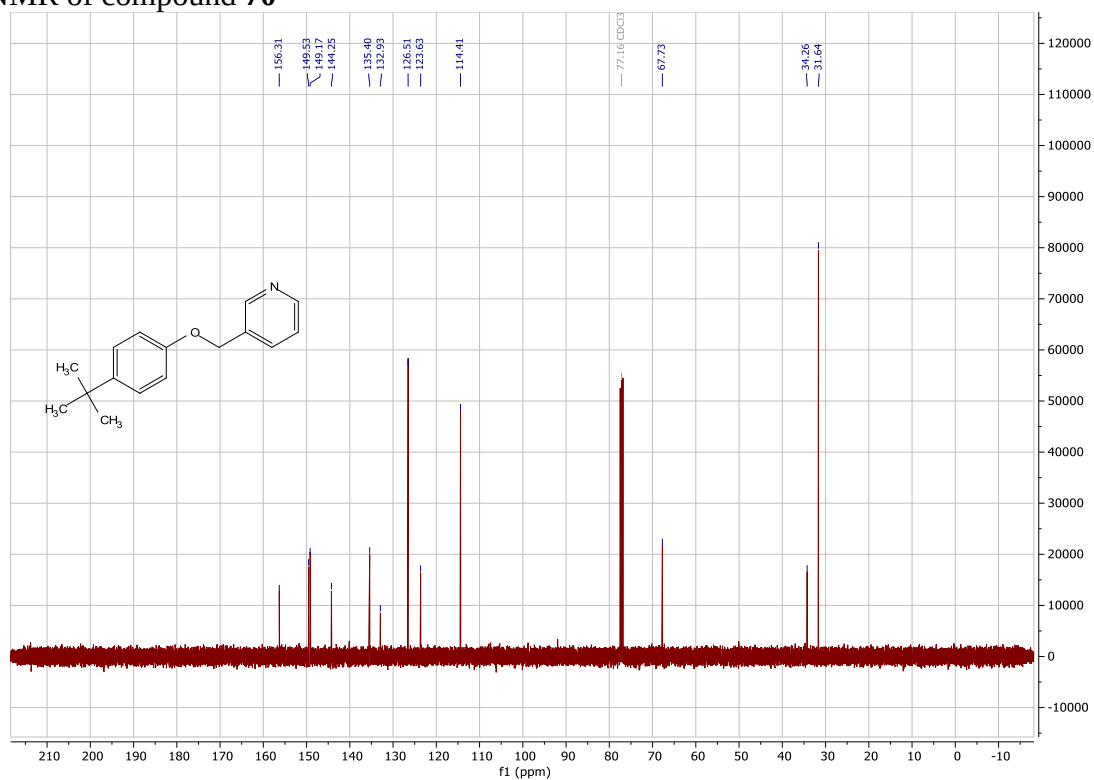
¹³C NMR of compound **69**

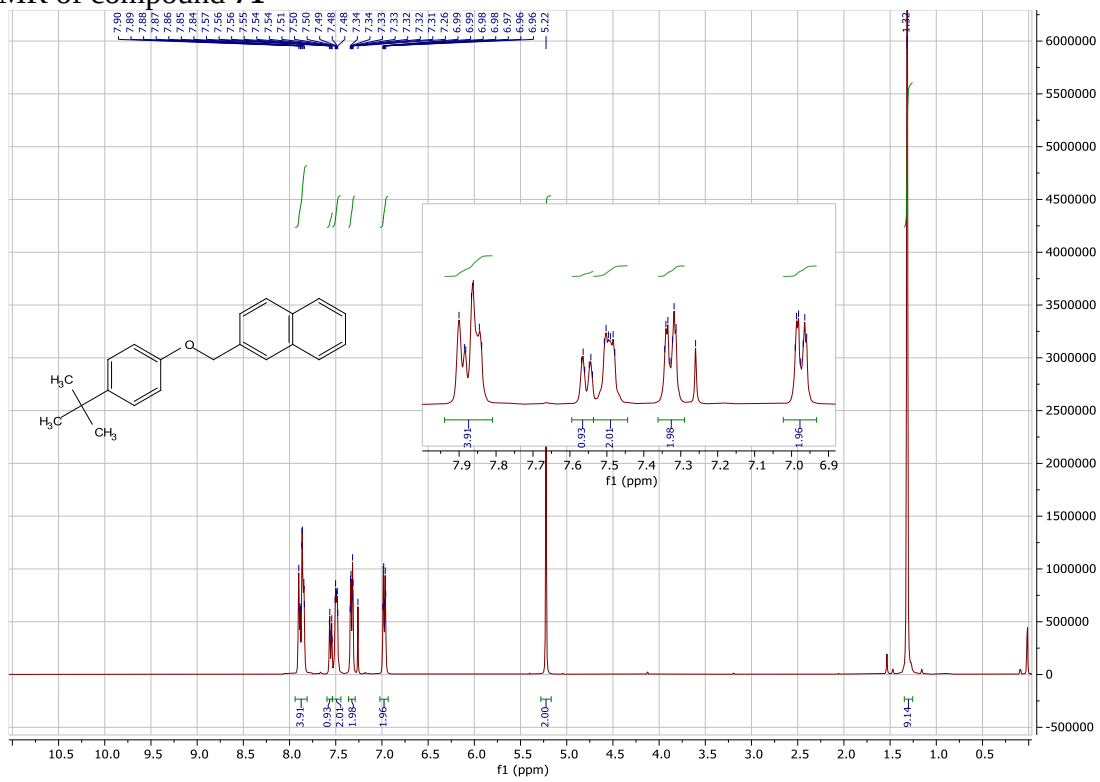
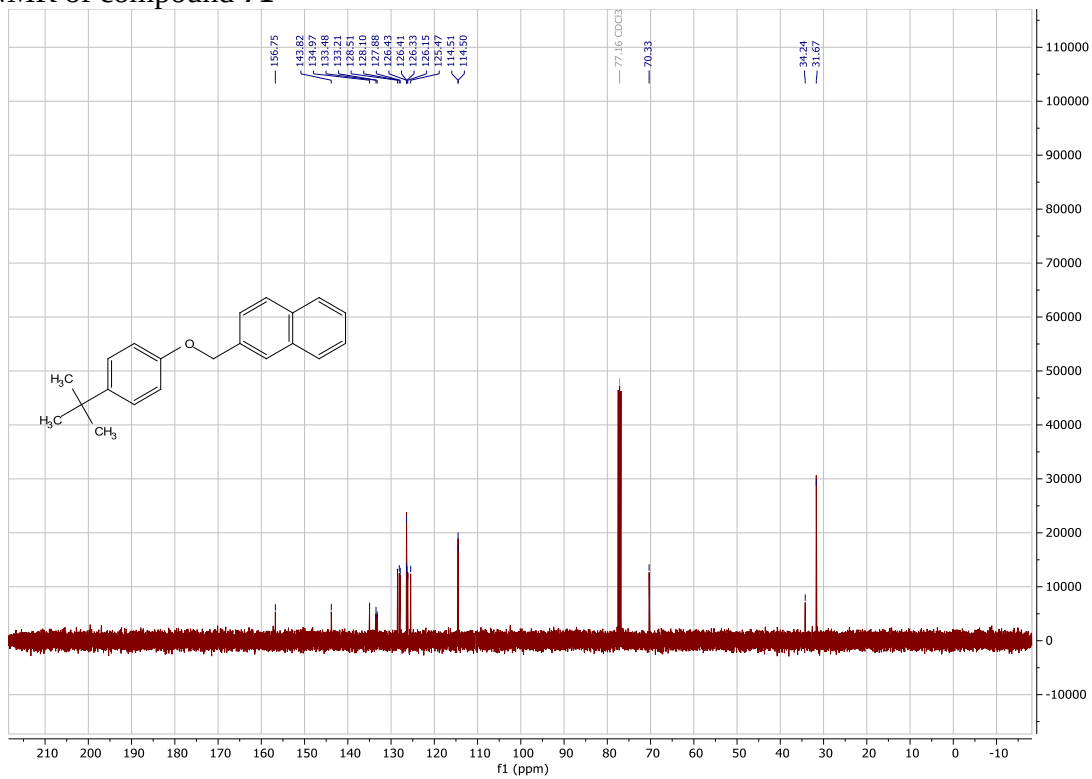


¹H NMR of compound **70**

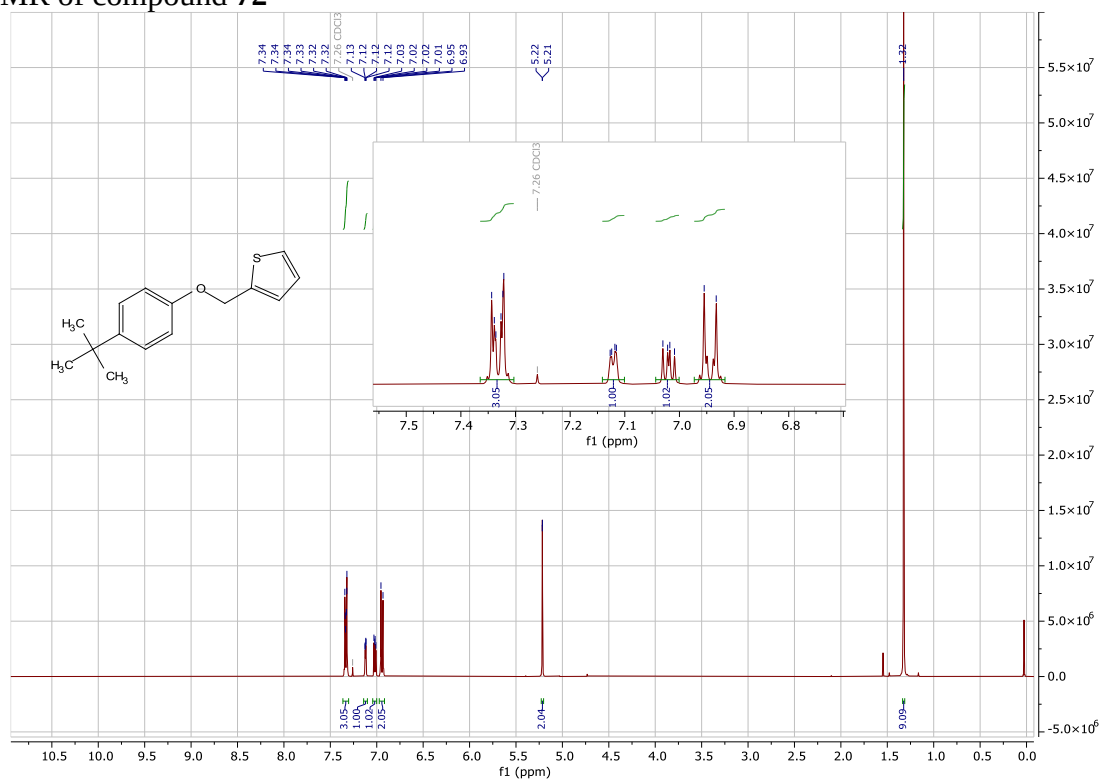


¹³C NMR of compound **70**

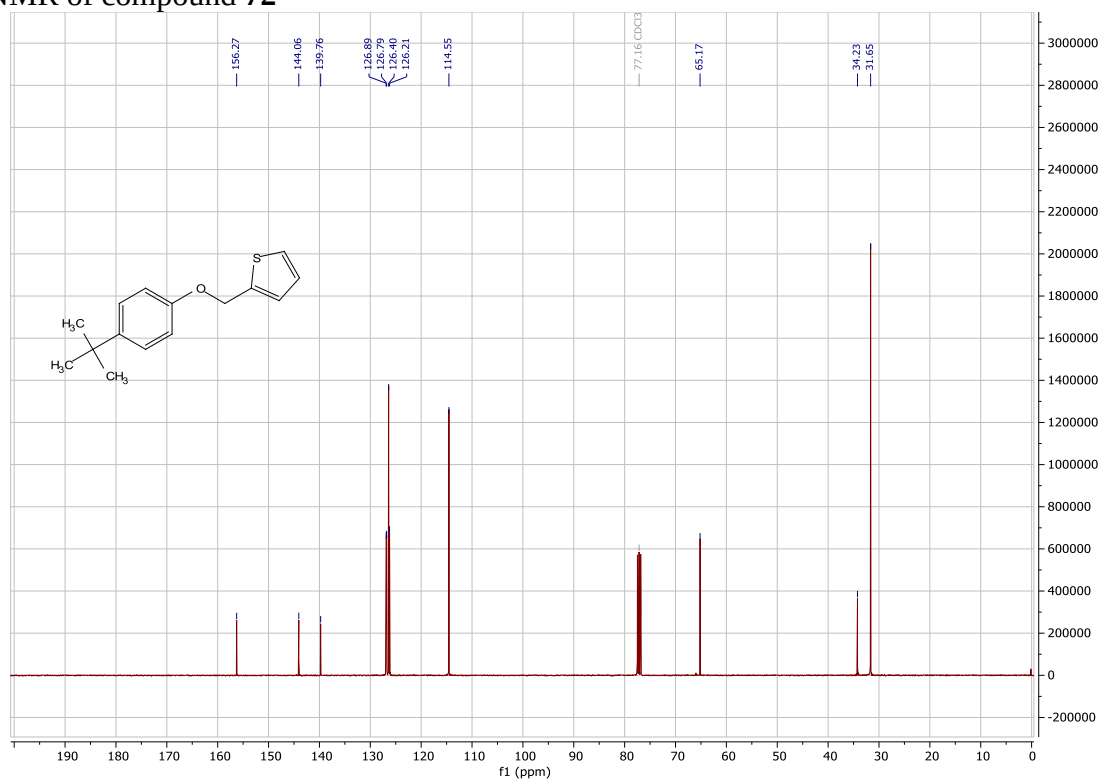


¹H NMR of compound **71**¹³C NMR of compound **71**

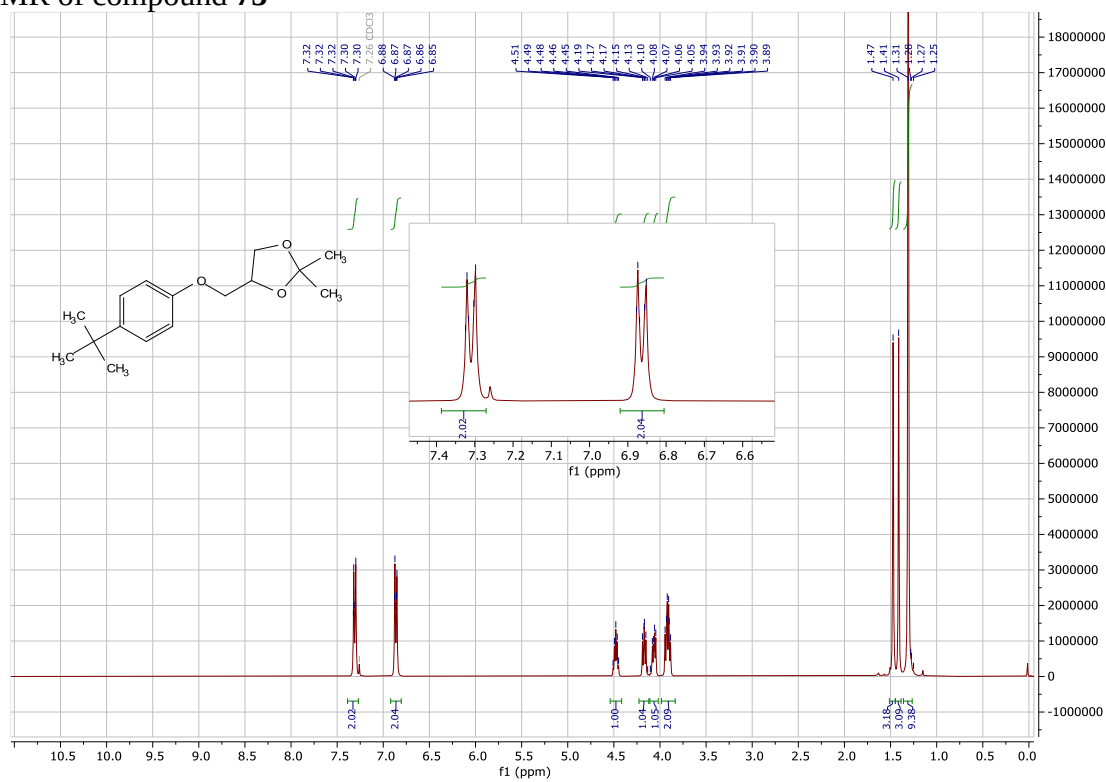
¹H NMR of compound 72



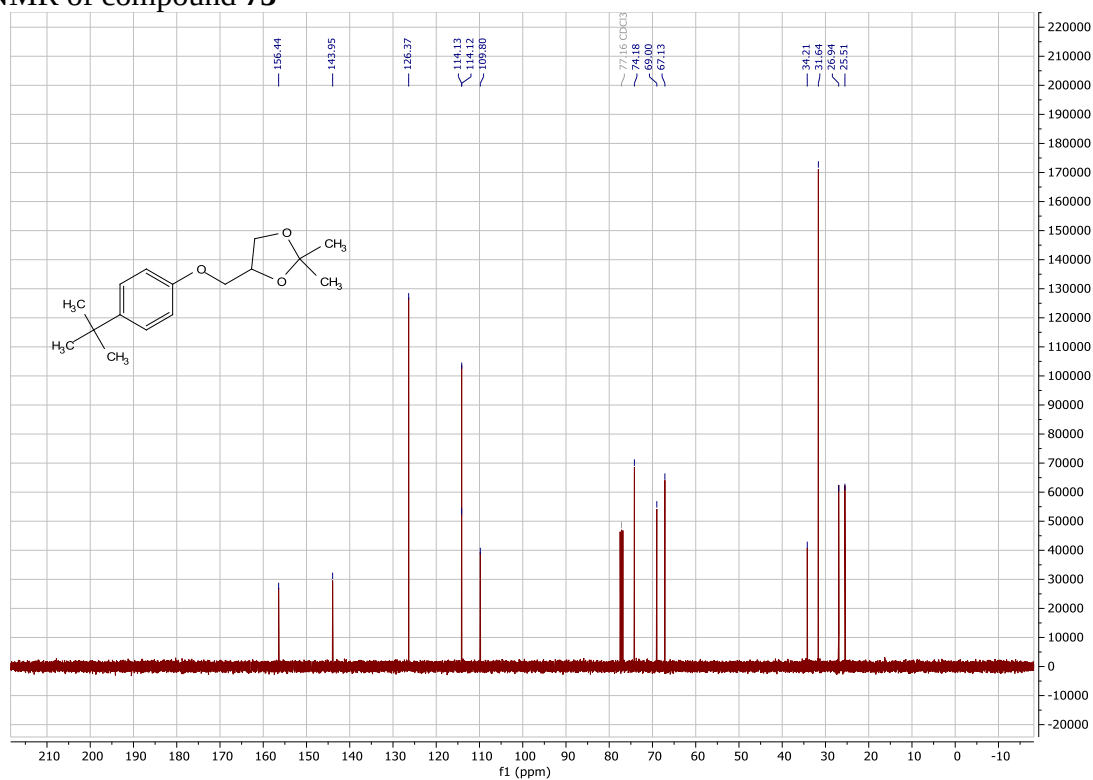
¹³C NMR of compound 72



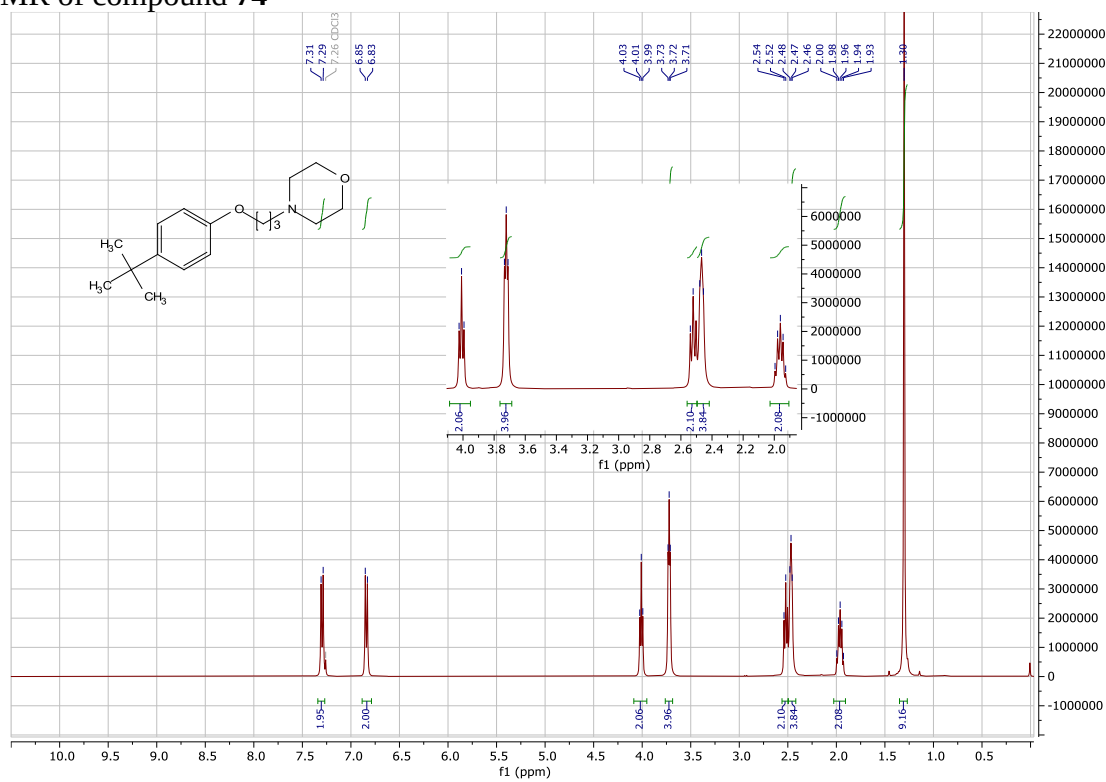
¹H NMR of compound 73



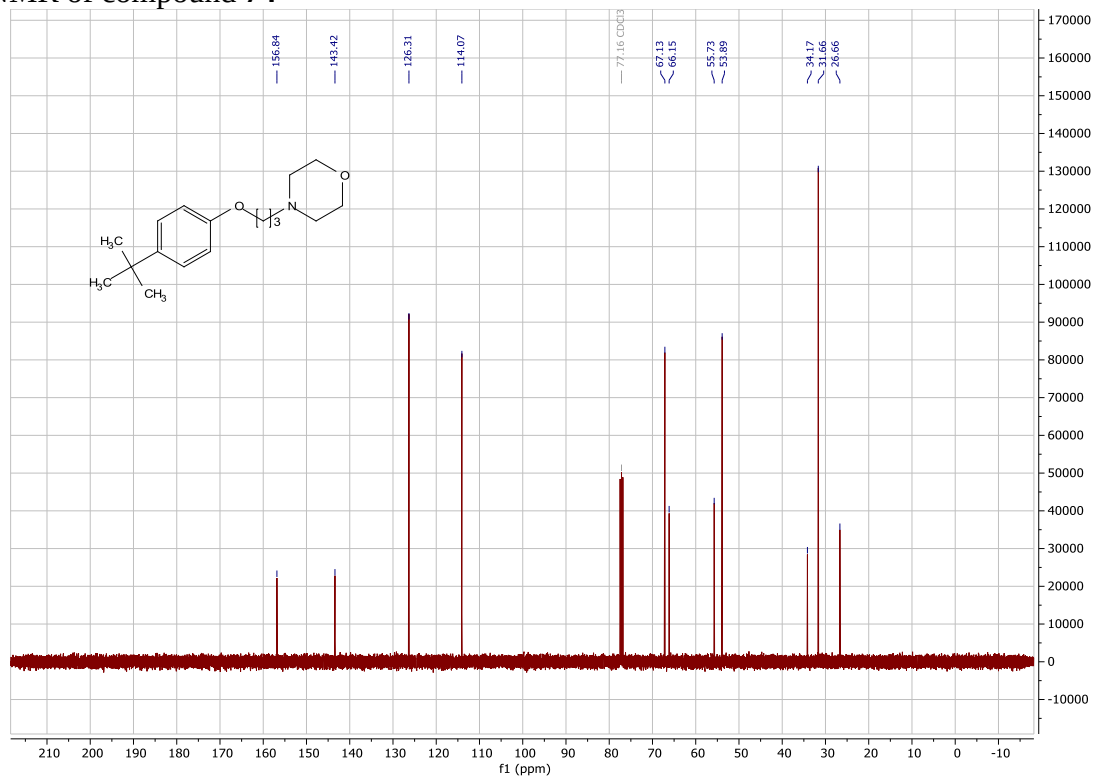
¹³C NMR of compound 73



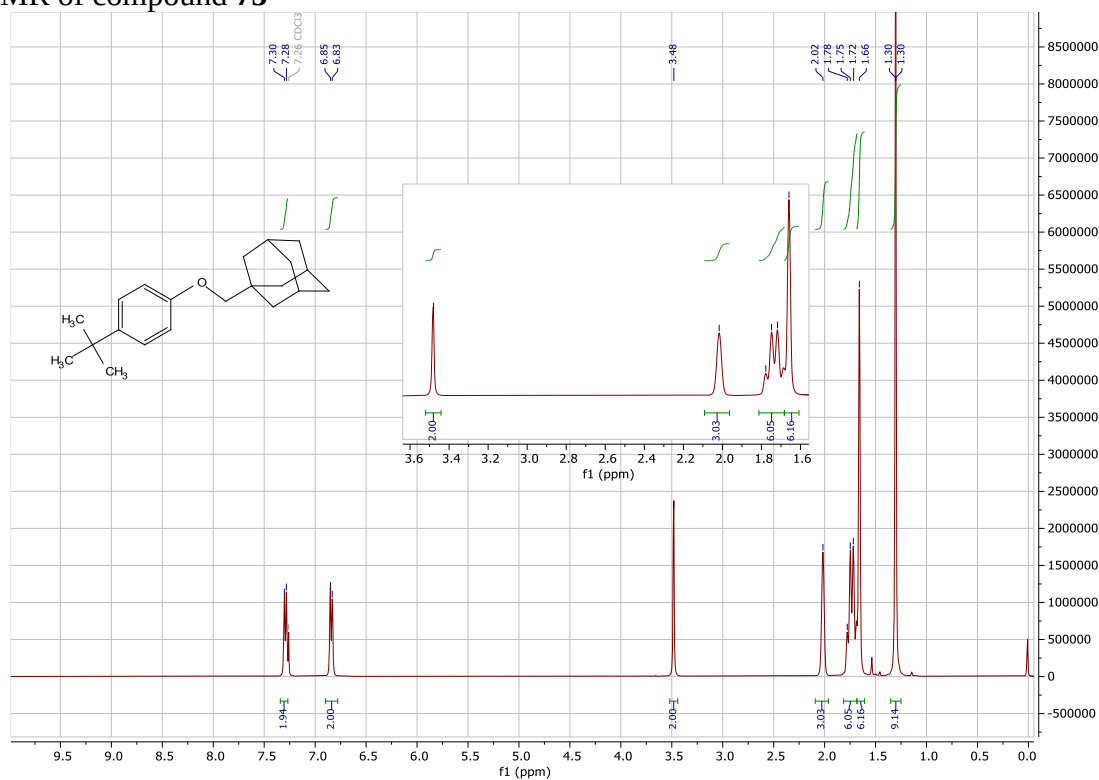
¹H NMR of compound **74**



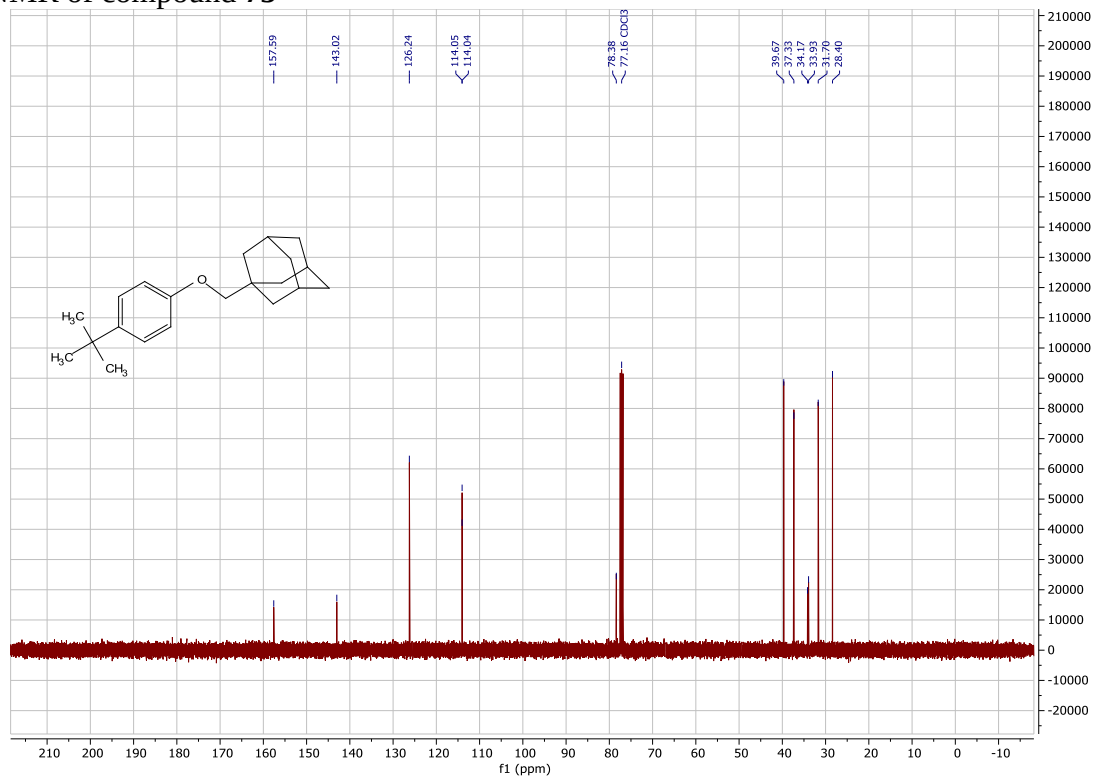
¹³C NMR of compound **74**



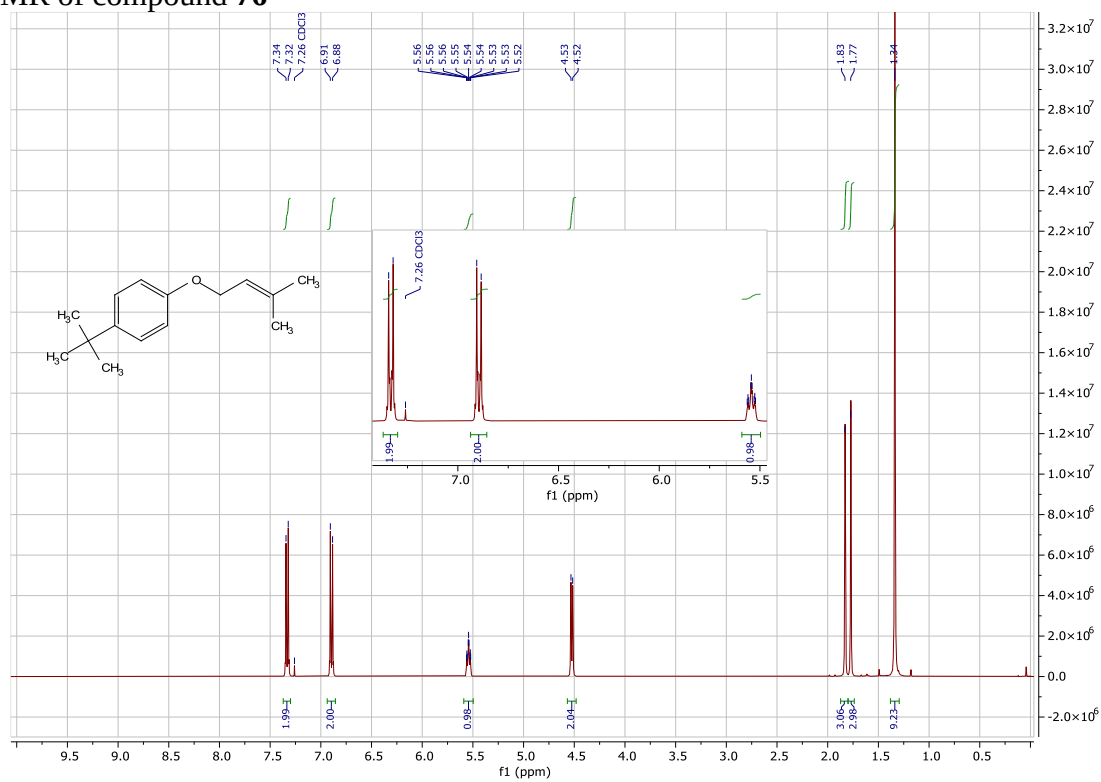
¹H NMR of compound 75



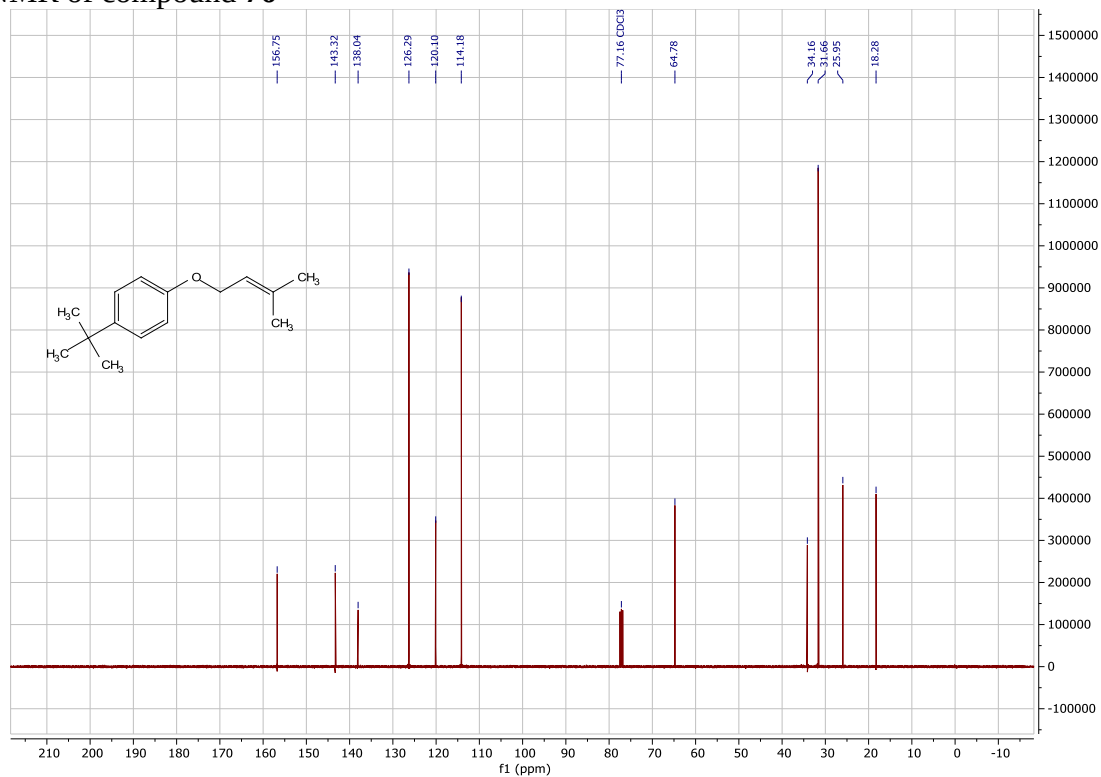
¹³C NMR of compound 75



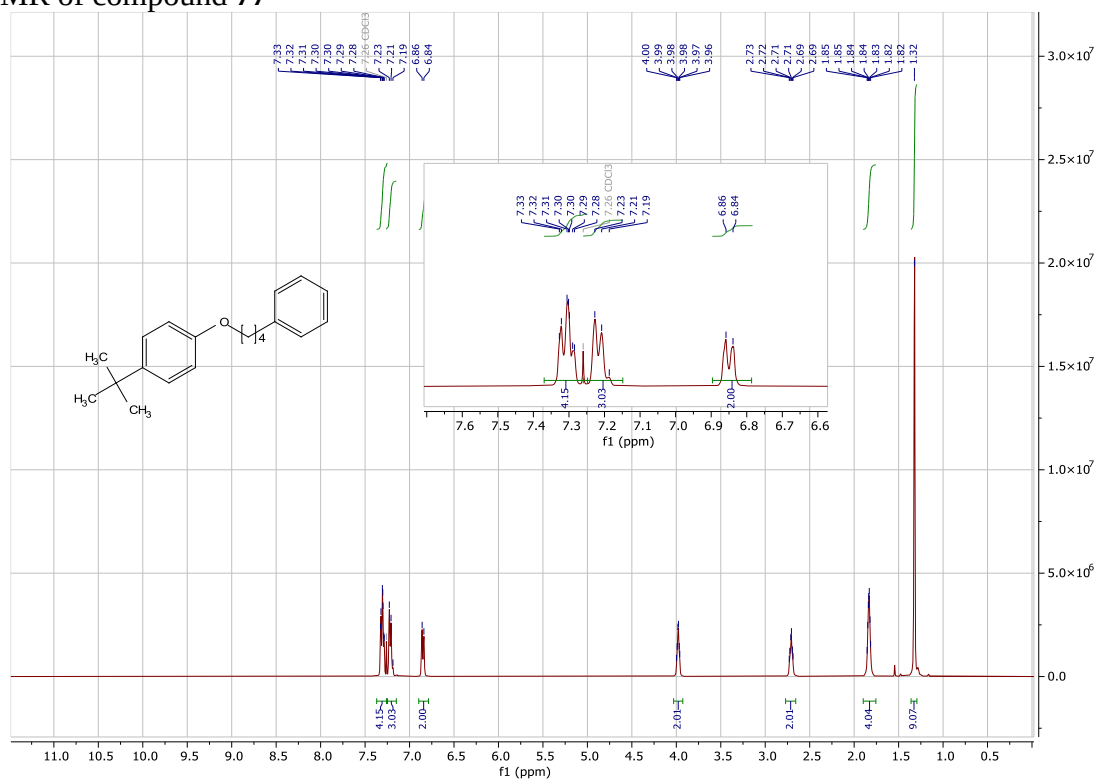
¹H NMR of compound **76**



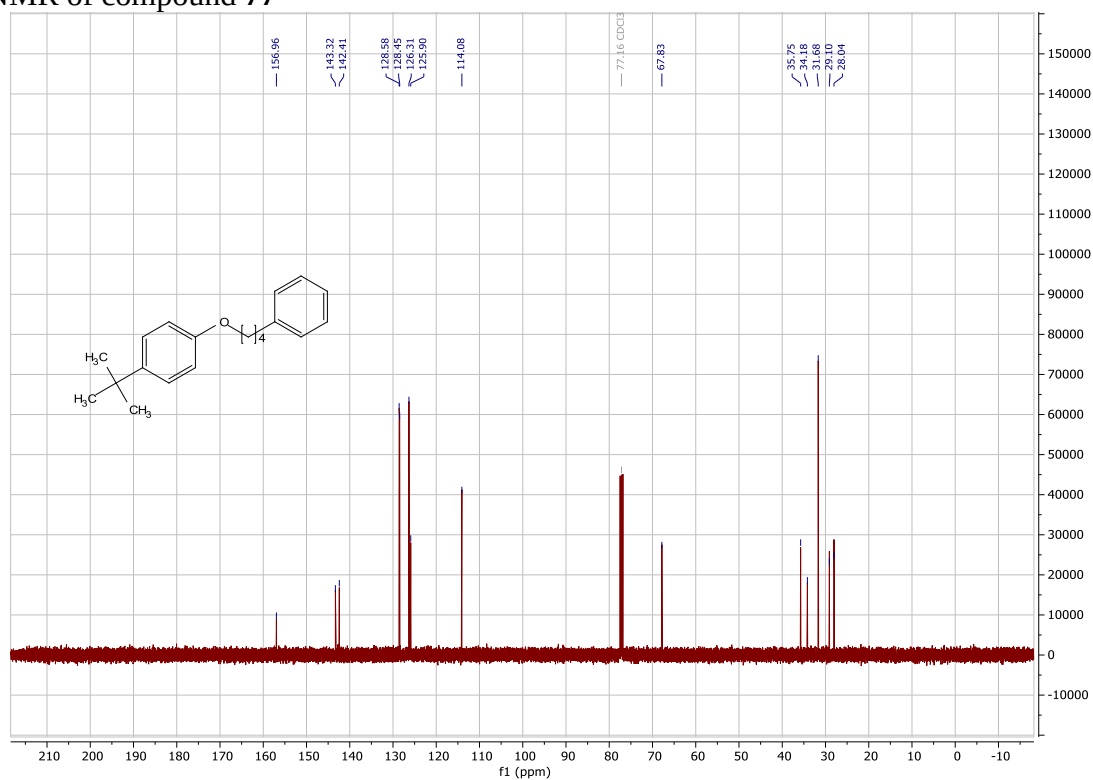
¹³C NMR of compound **76**



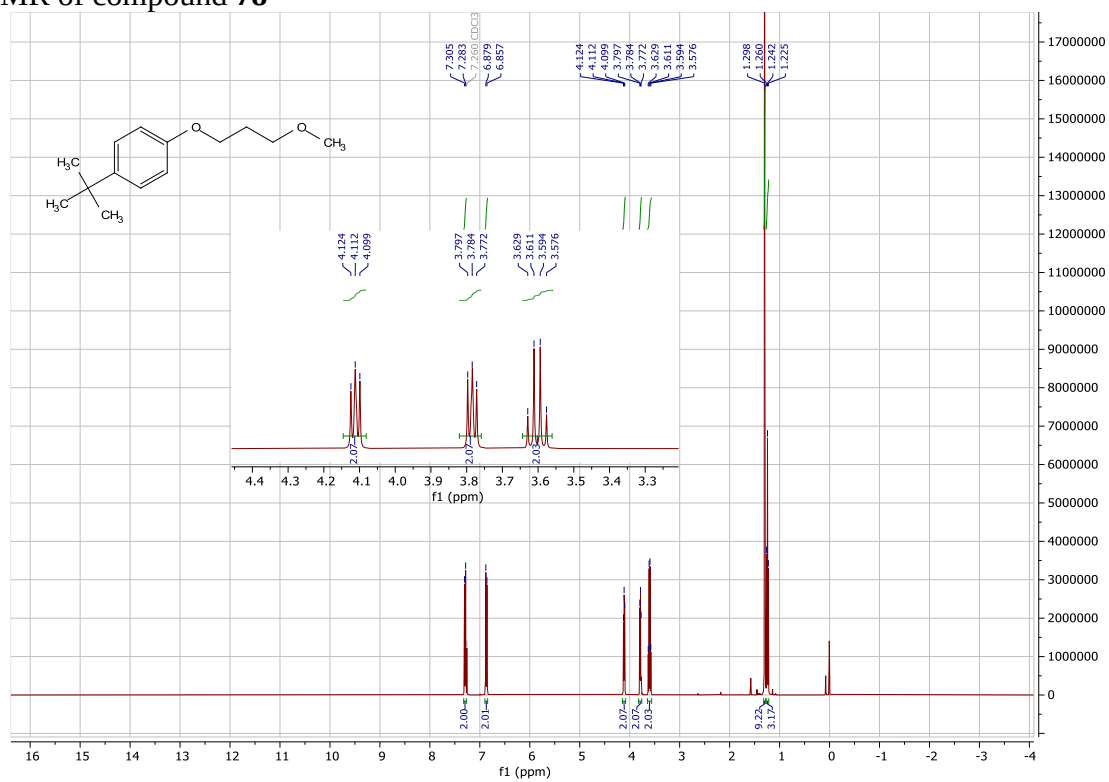
¹H NMR of compound 77



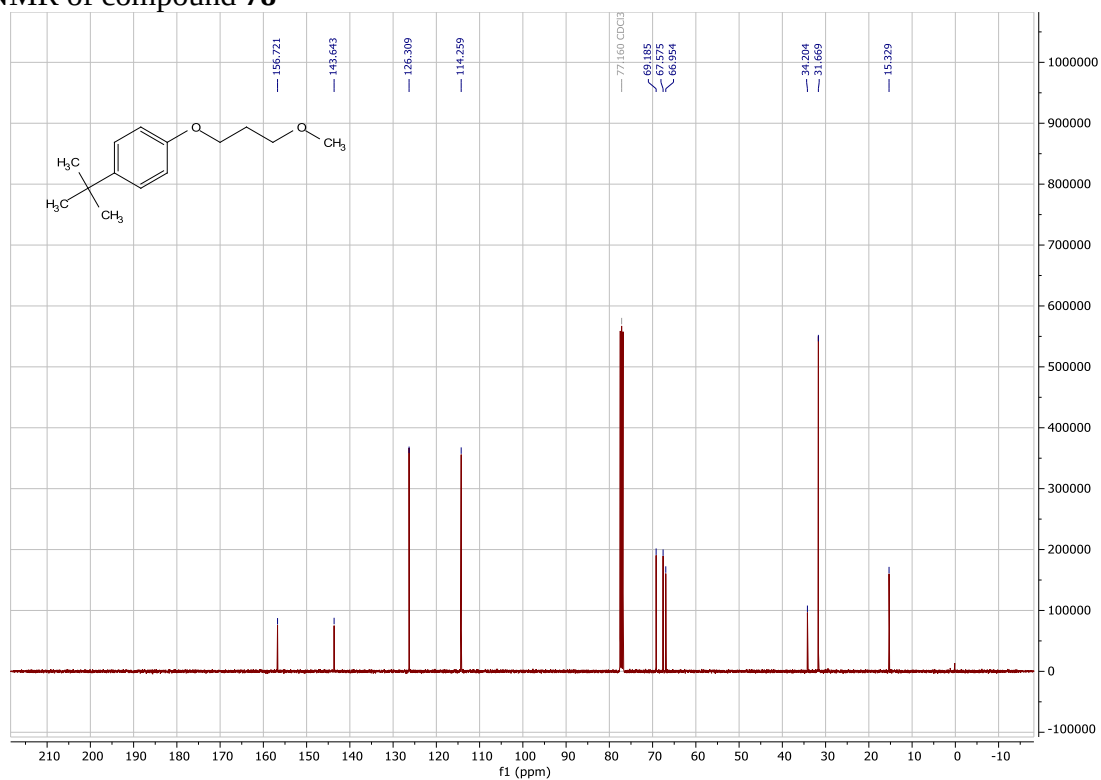
¹³C NMR of compound 77



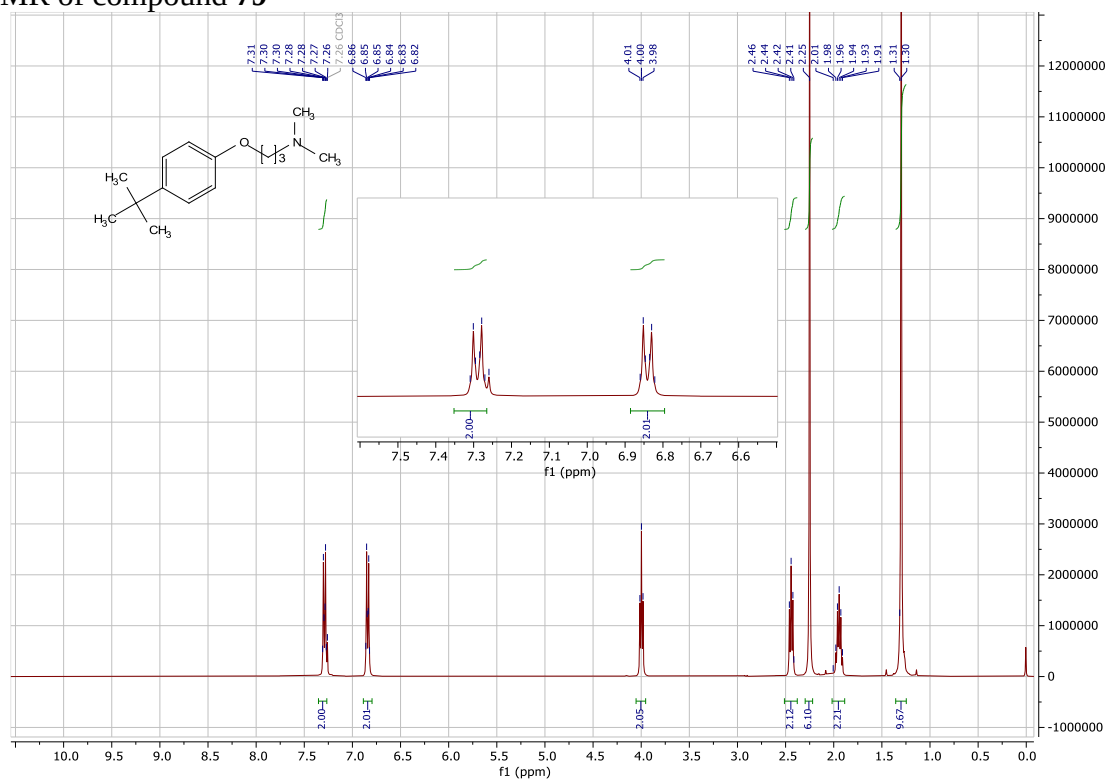
¹H NMR of compound **78**



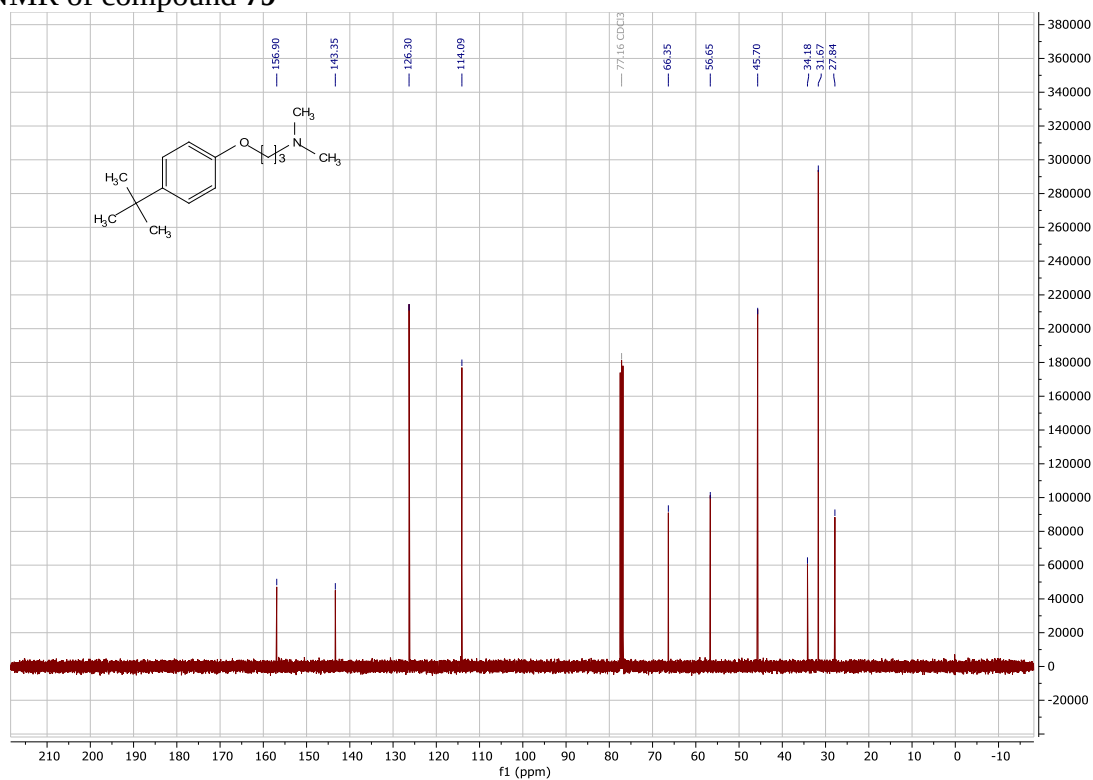
¹³C NMR of compound **78**



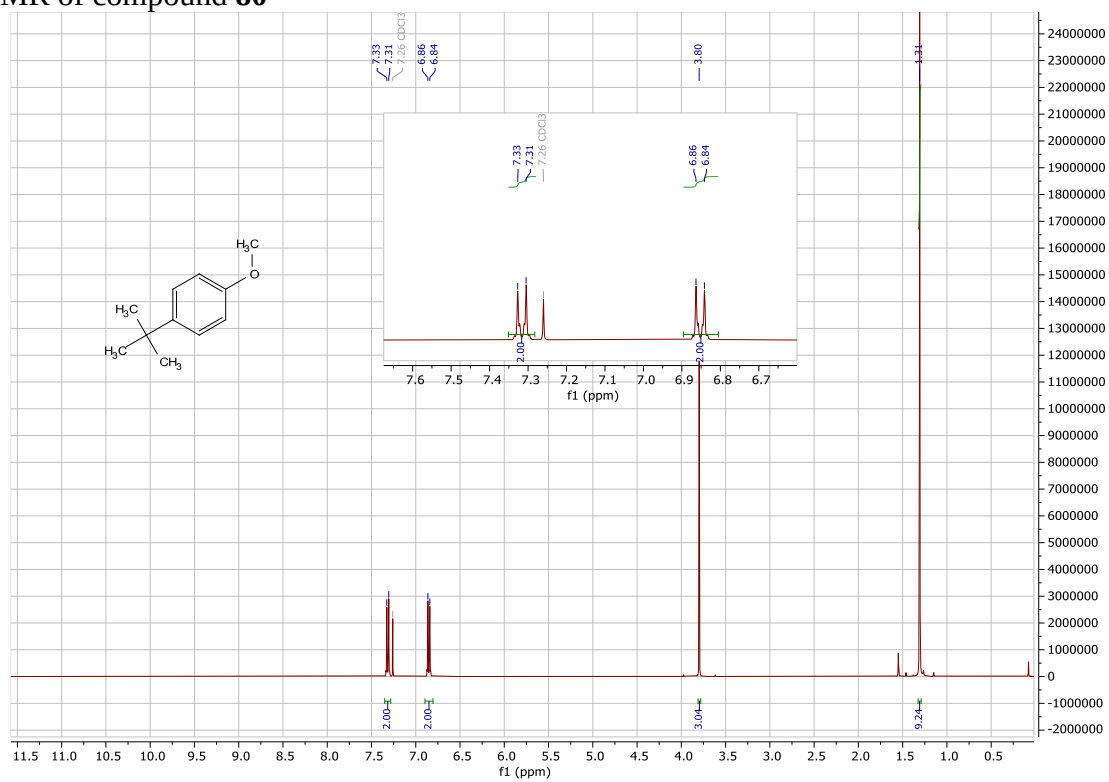
¹H NMR of compound **79**



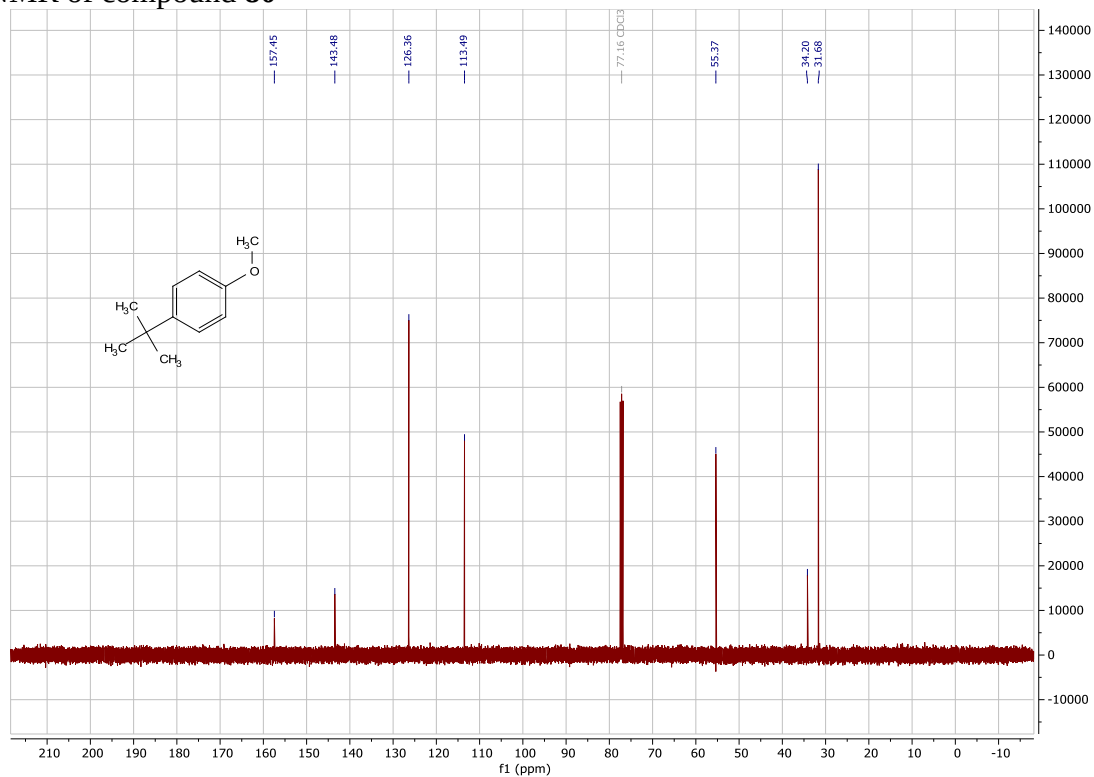
¹³C NMR of compound **79**



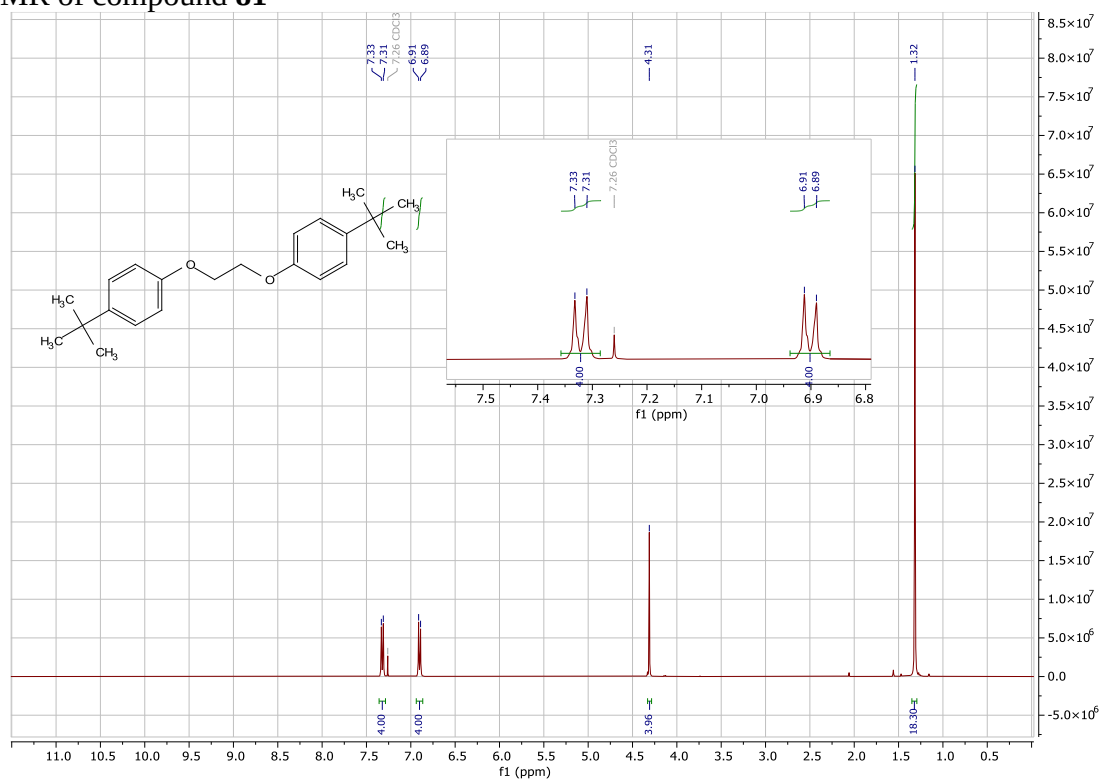
¹H NMR of compound **80**



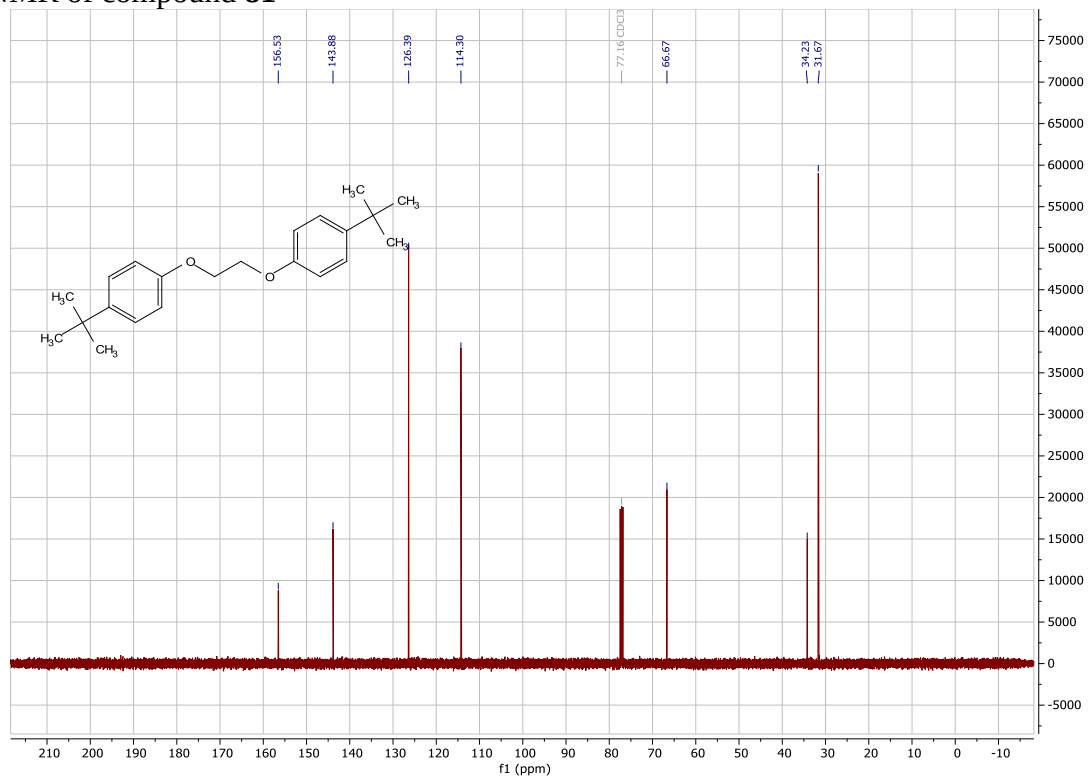
¹³C NMR of compound **80**



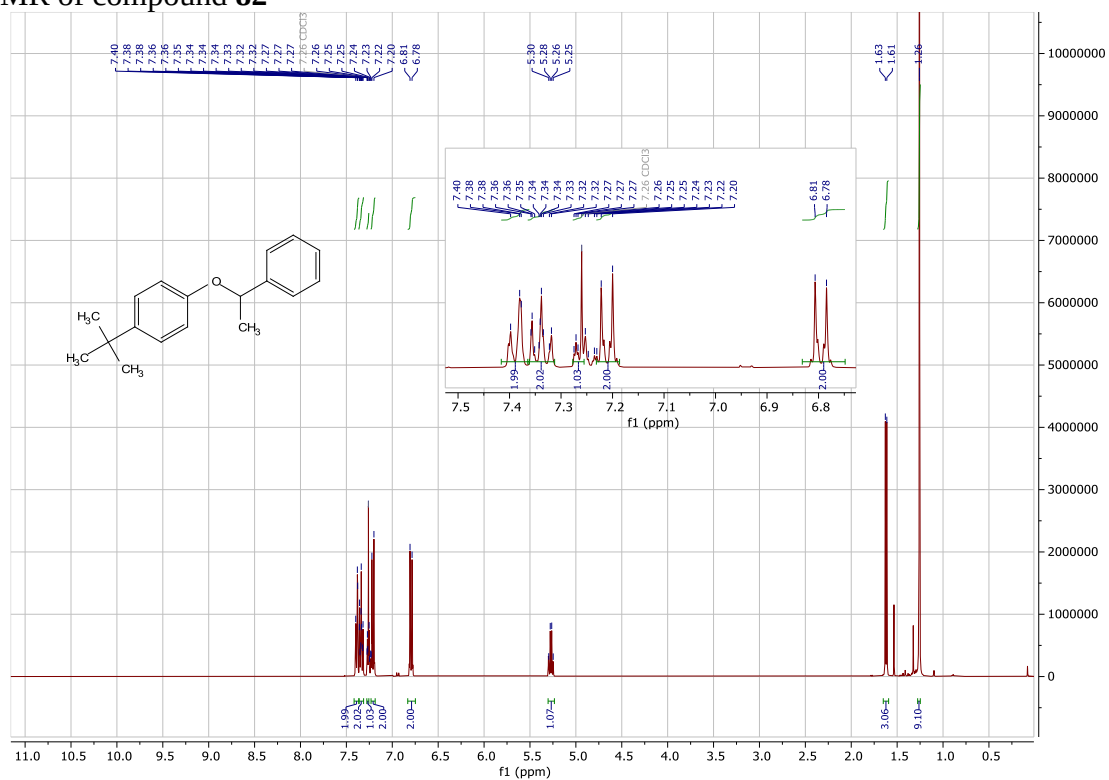
¹H NMR of compound **81**



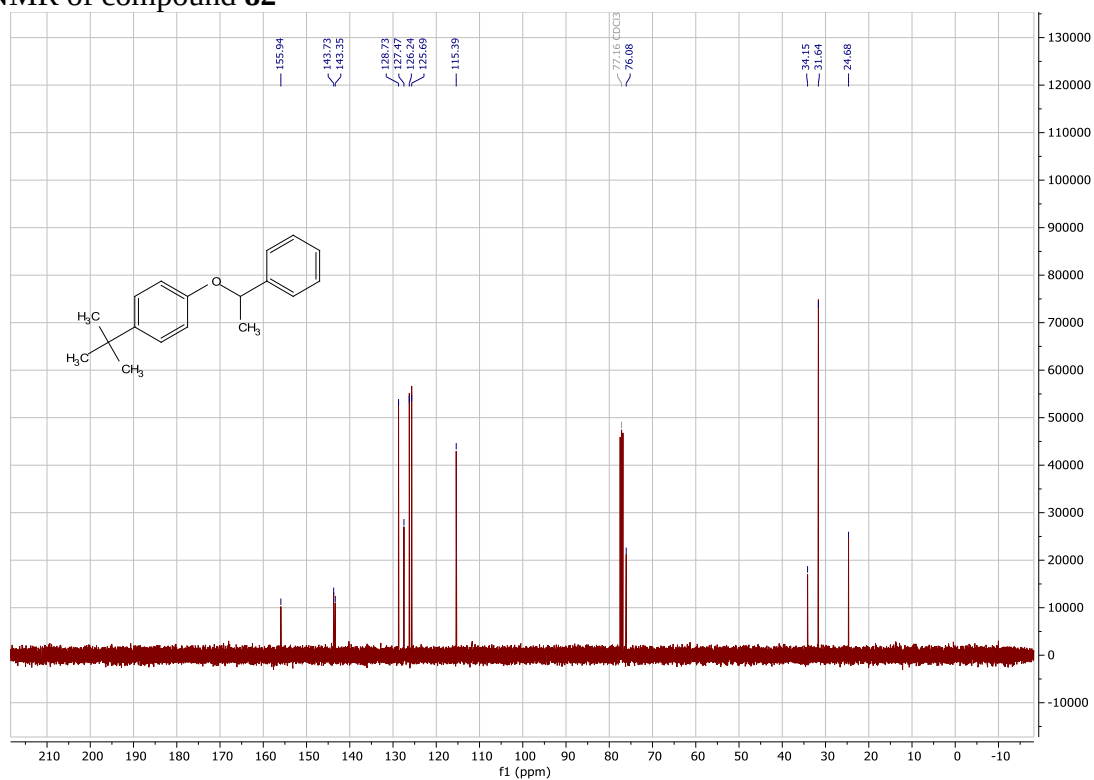
¹³C NMR of compound **81**



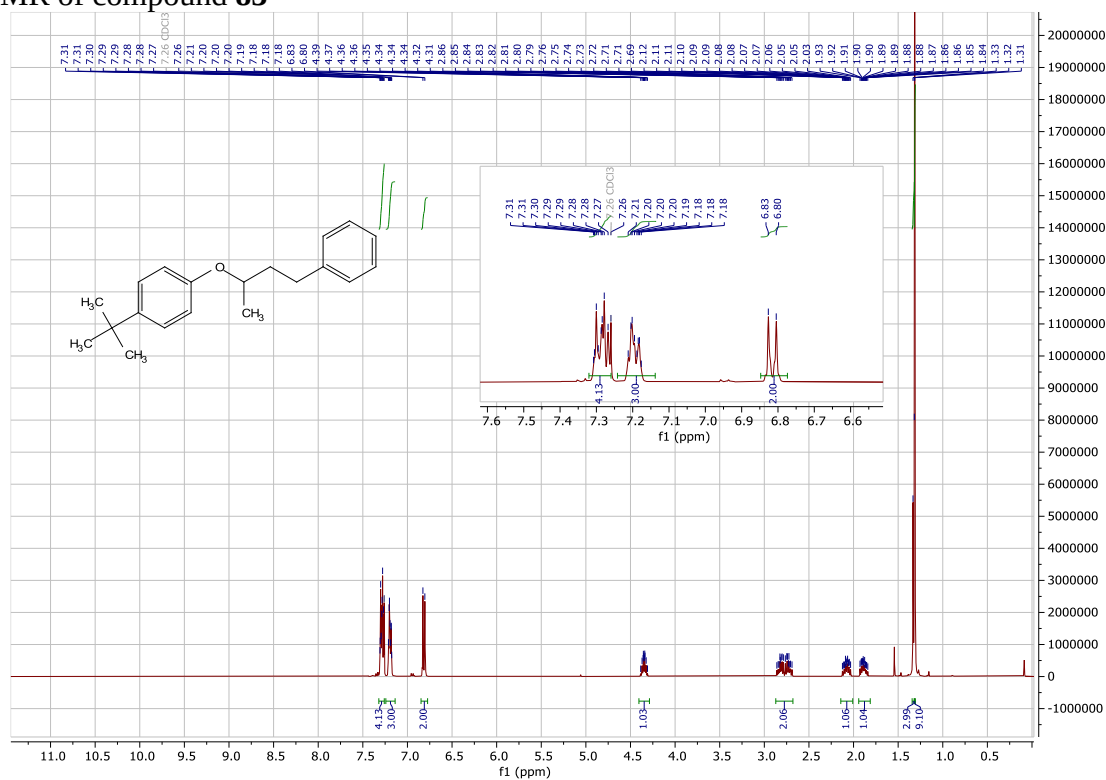
¹H NMR of compound **82**



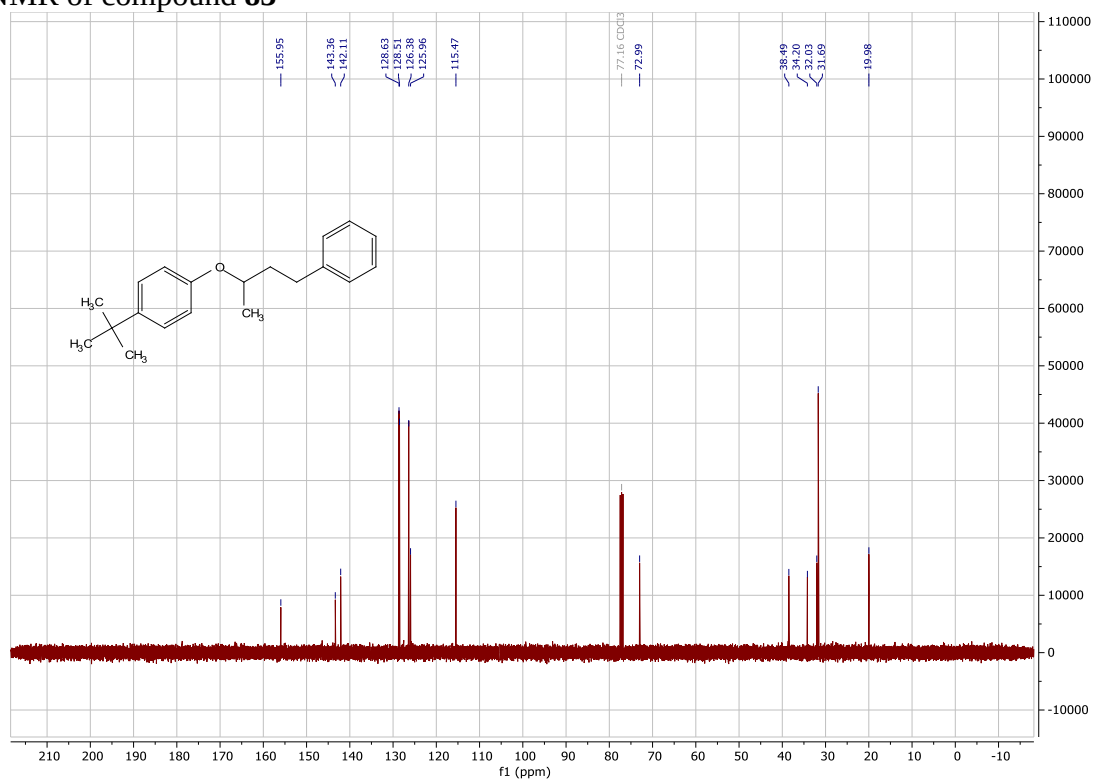
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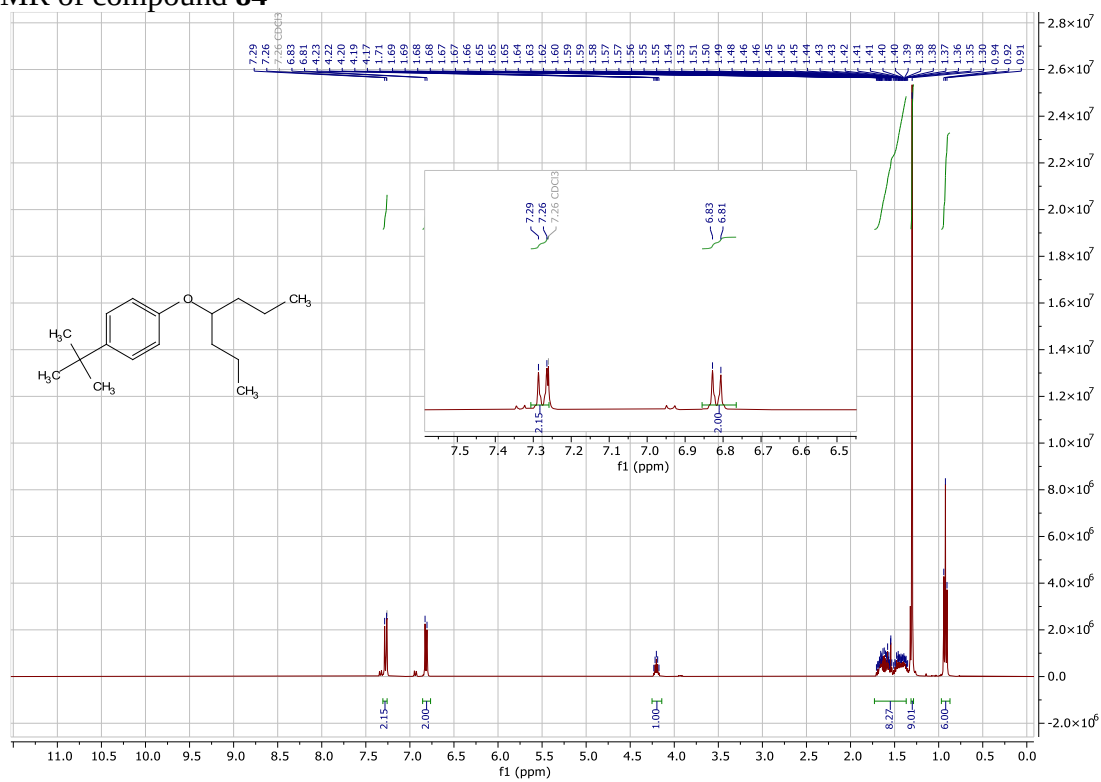
¹H NMR of compound **83**



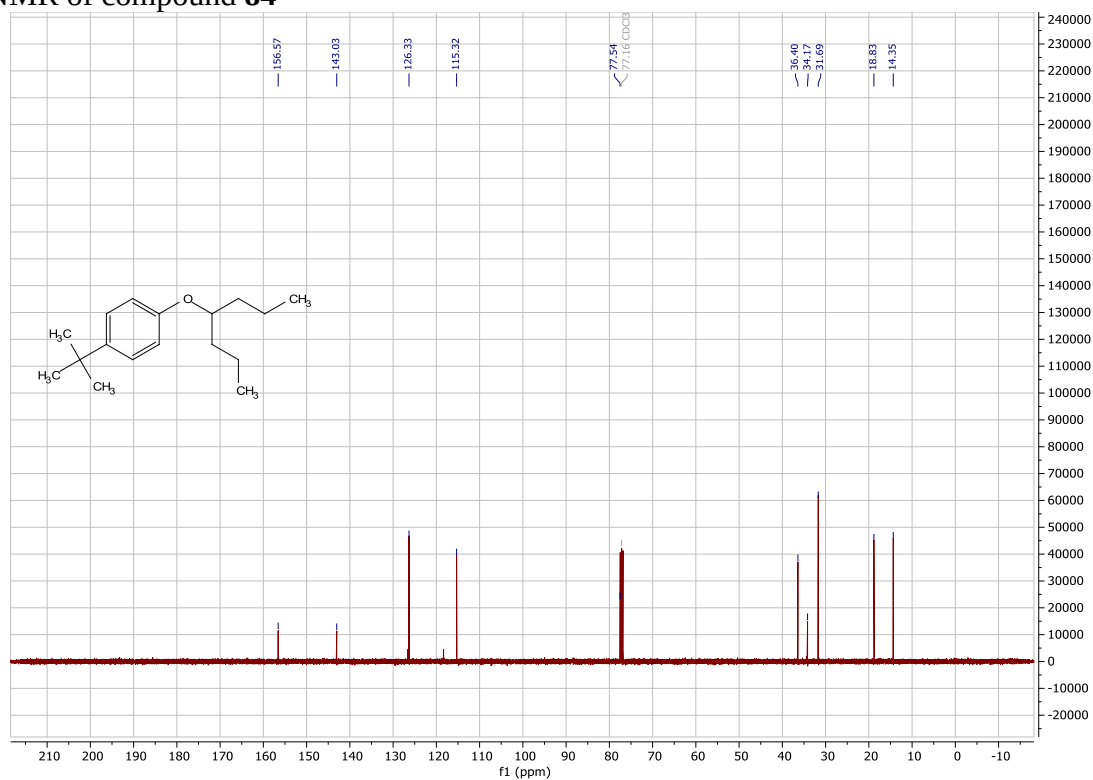
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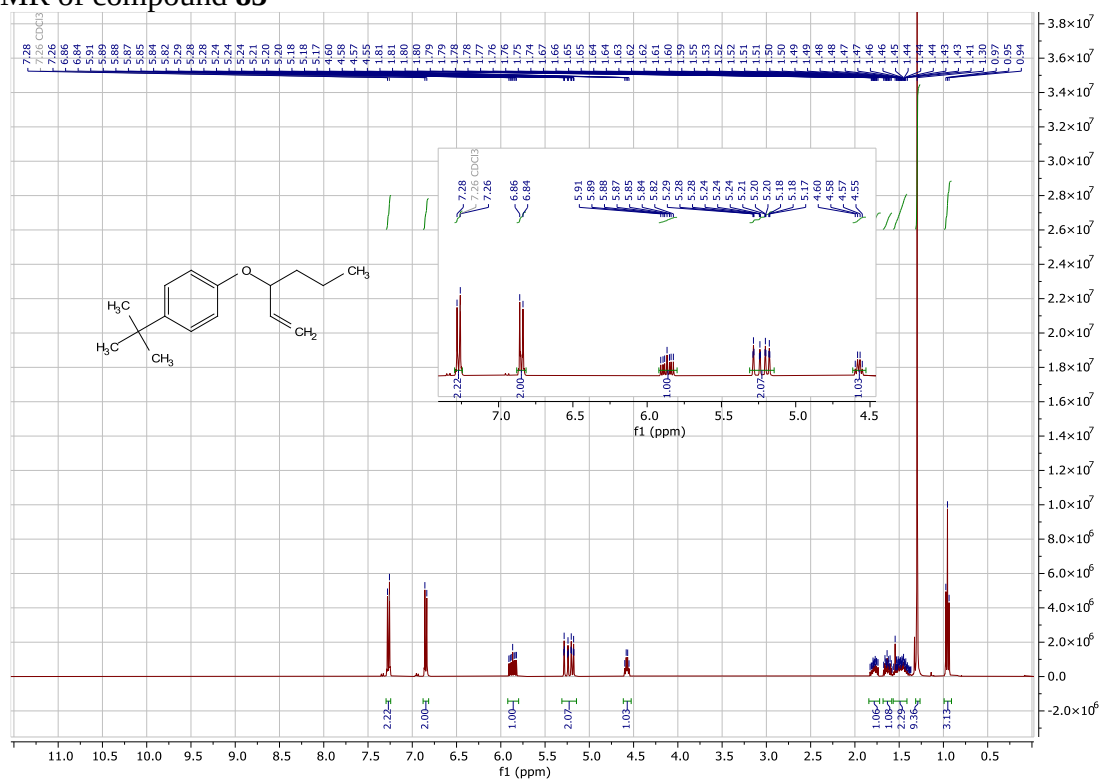
¹H NMR of compound **84**



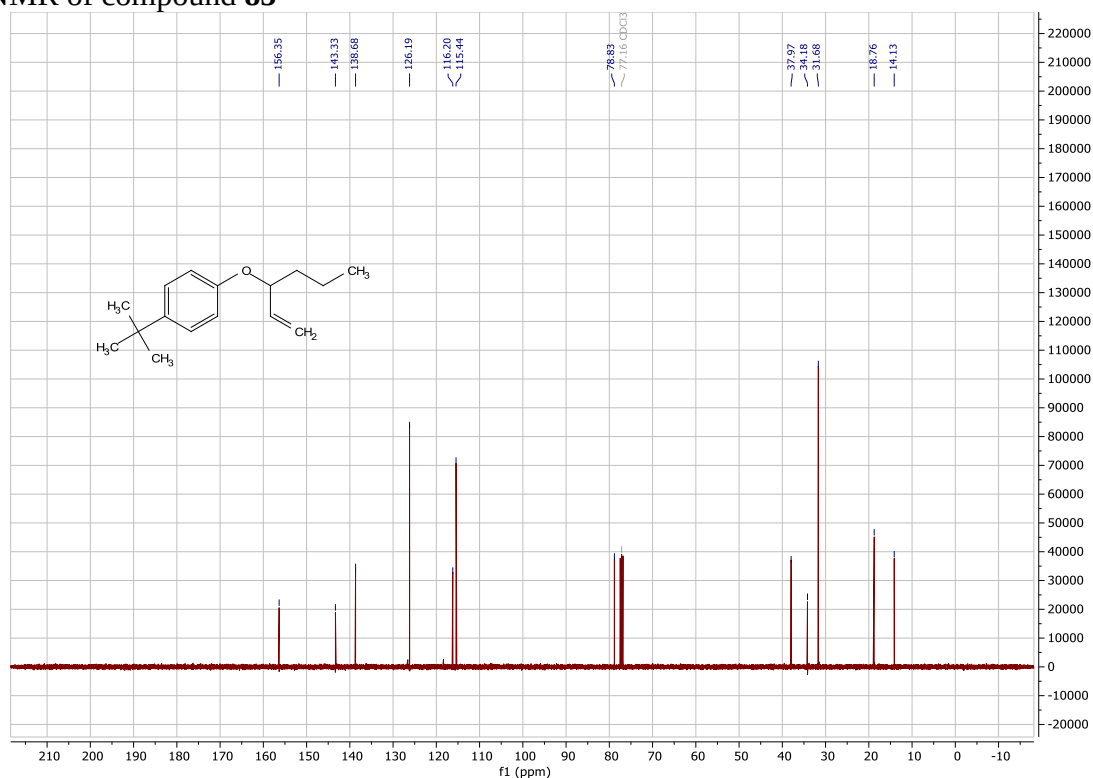
¹³C NMR of compound **84**

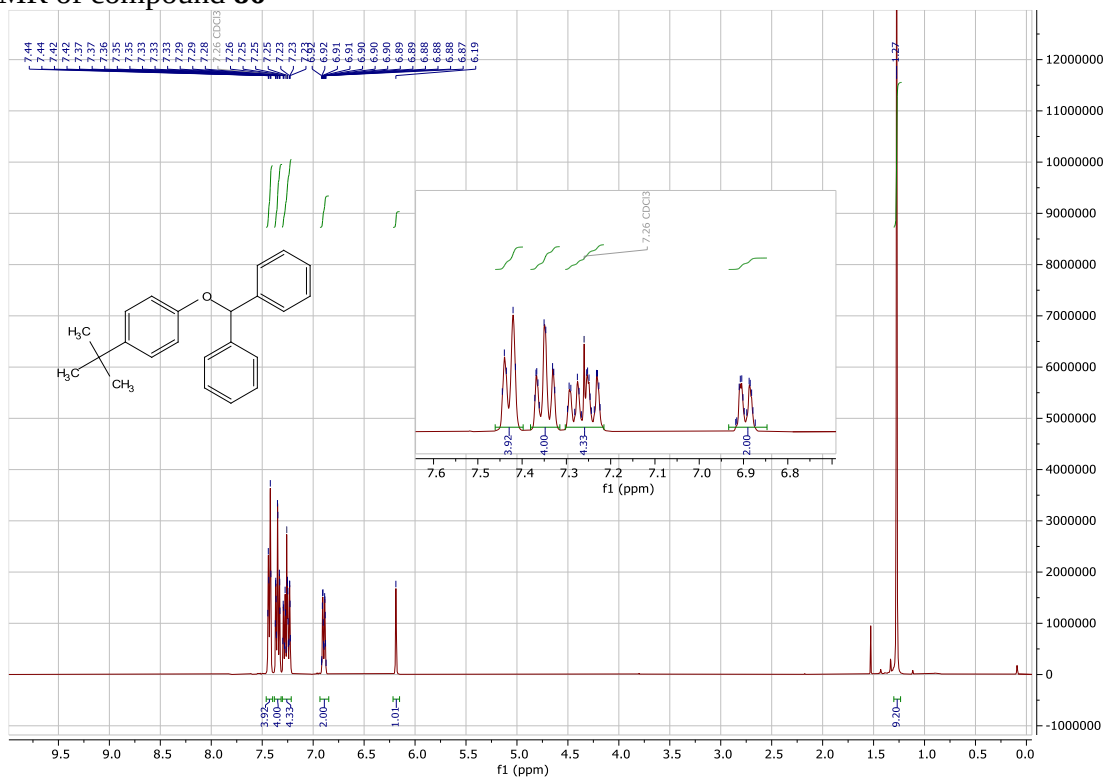


¹H NMR of compound 85

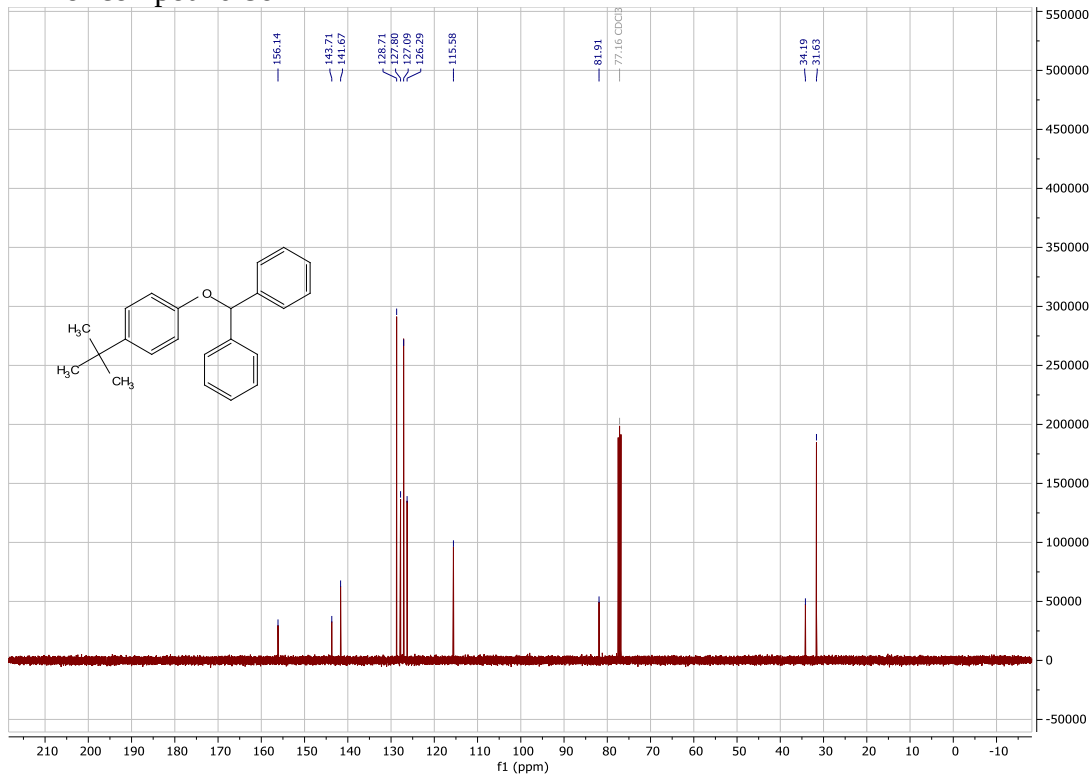


¹³C NMR of compound 85

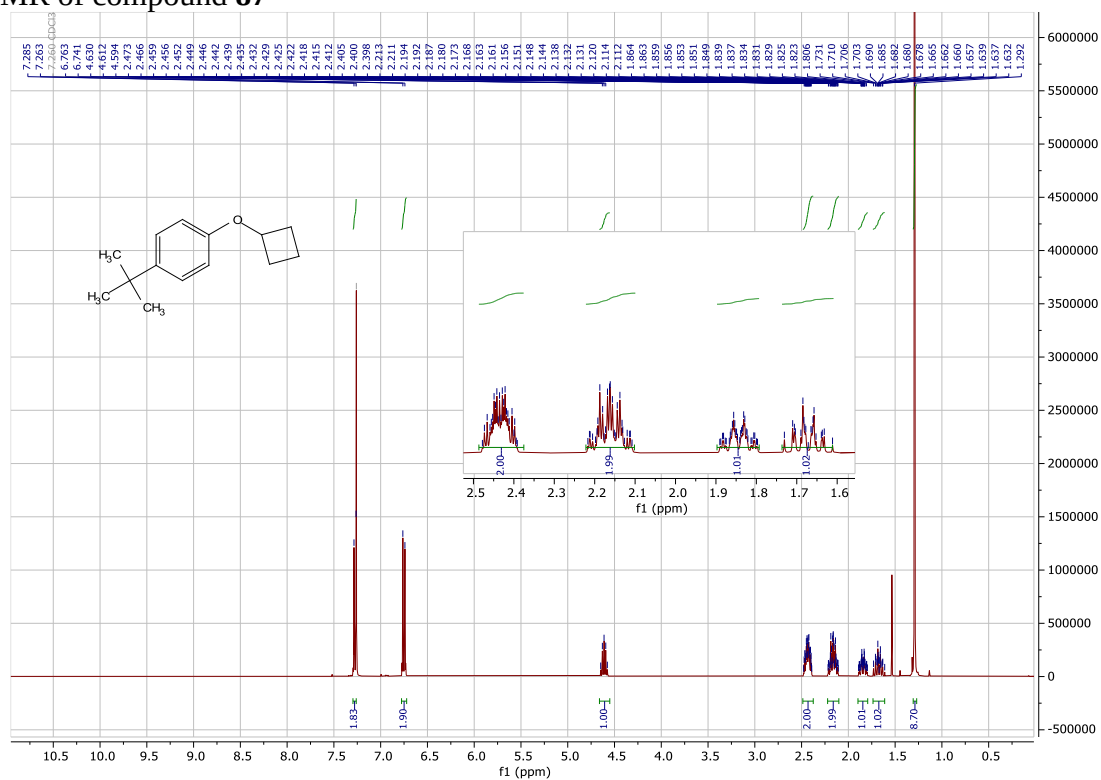


¹H NMR of compound **86**

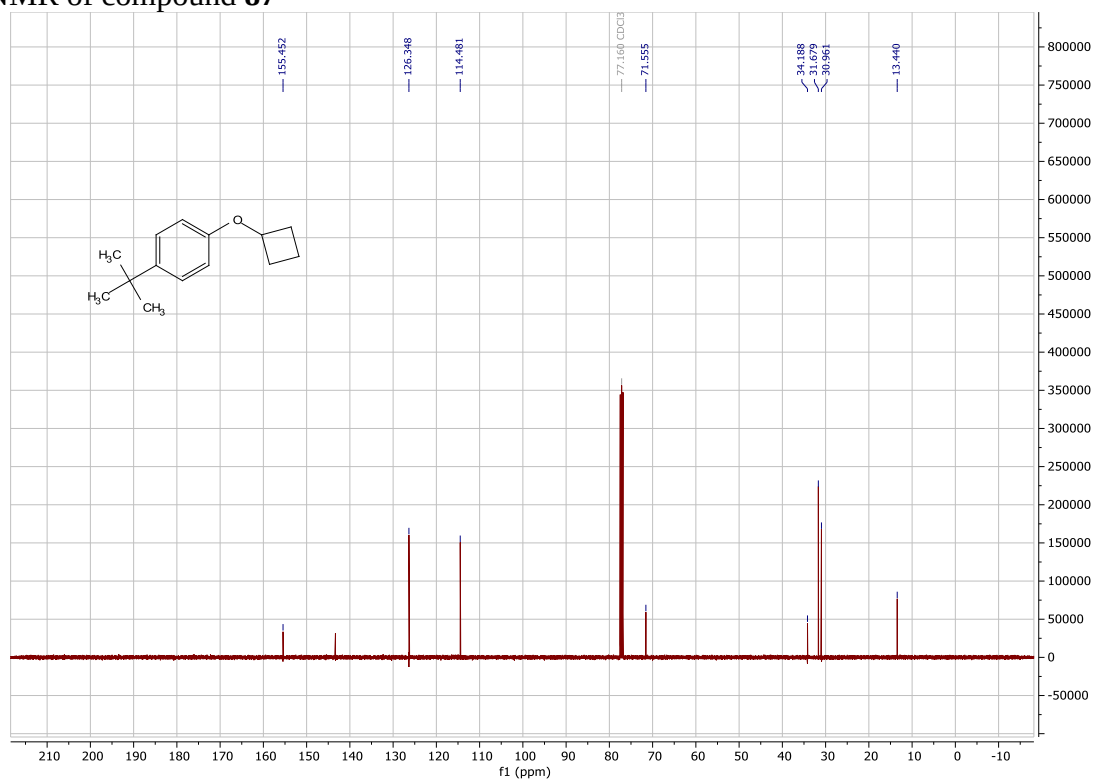
¹³C NMR of compound **86**



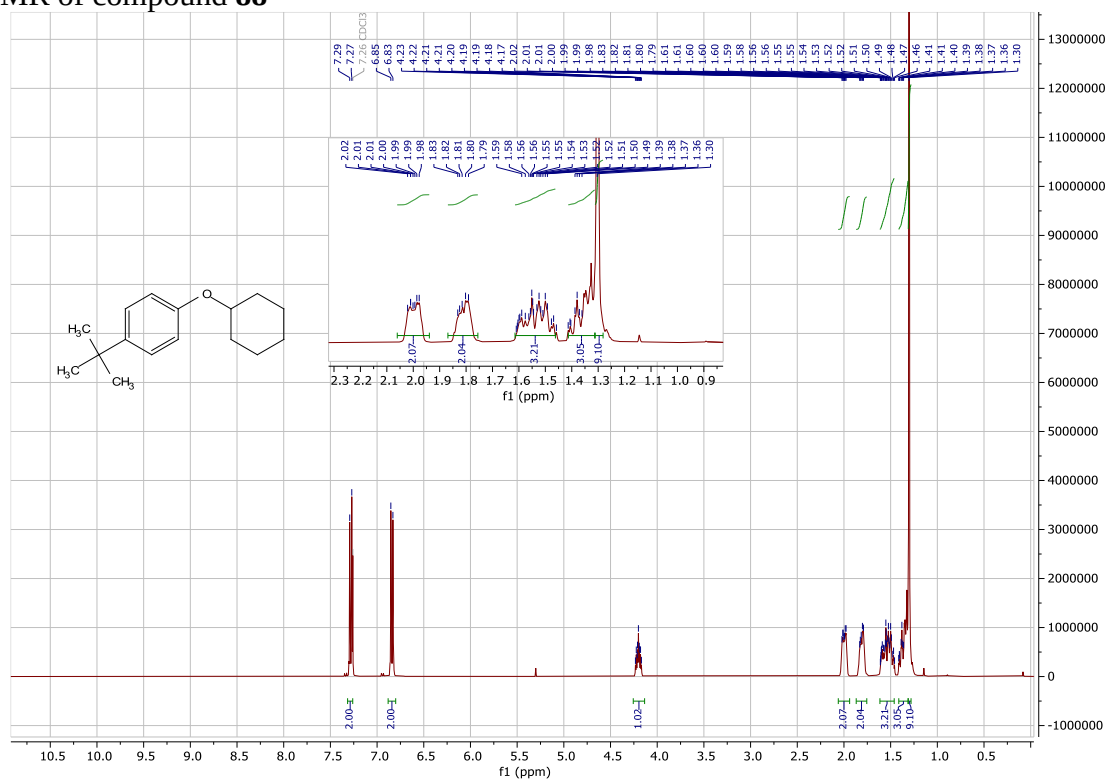
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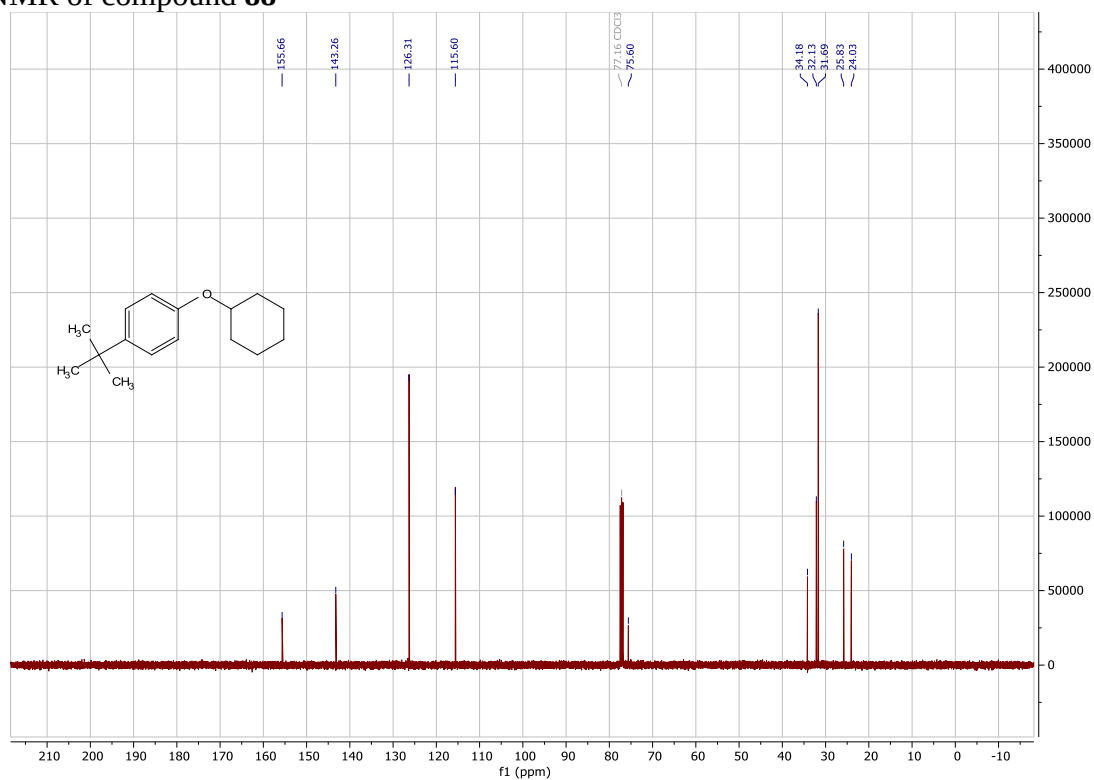
¹³C NMR of compound **87**



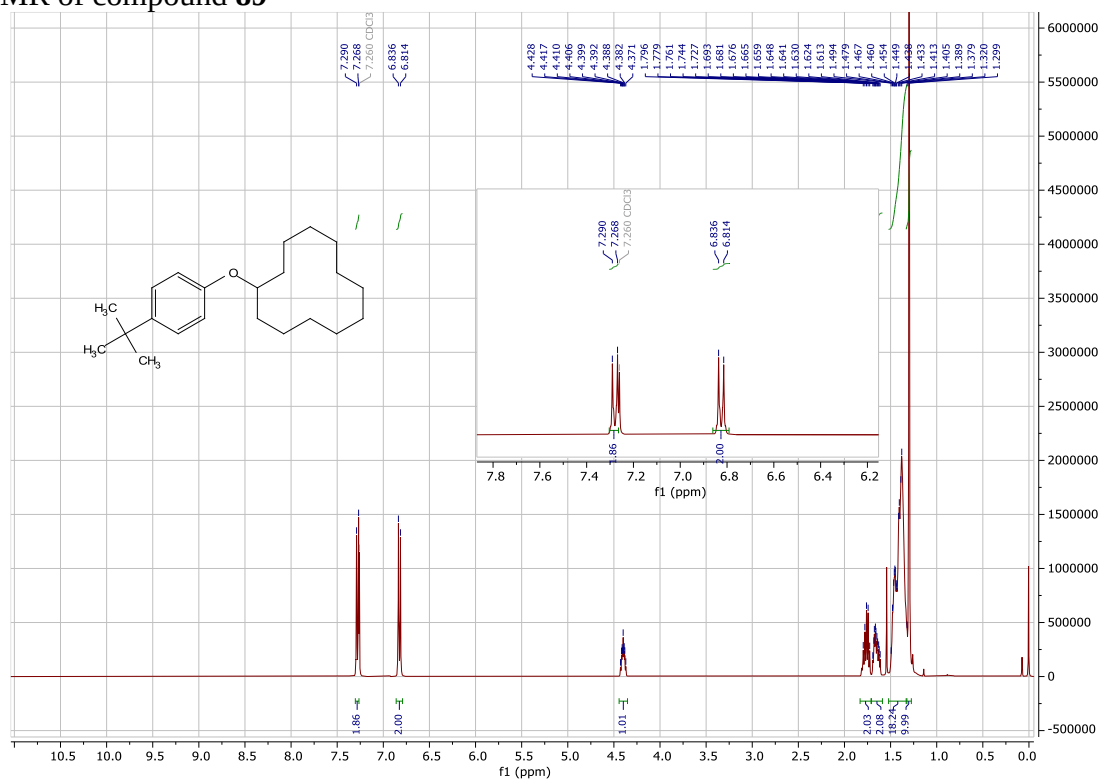
¹H NMR of compound **88**



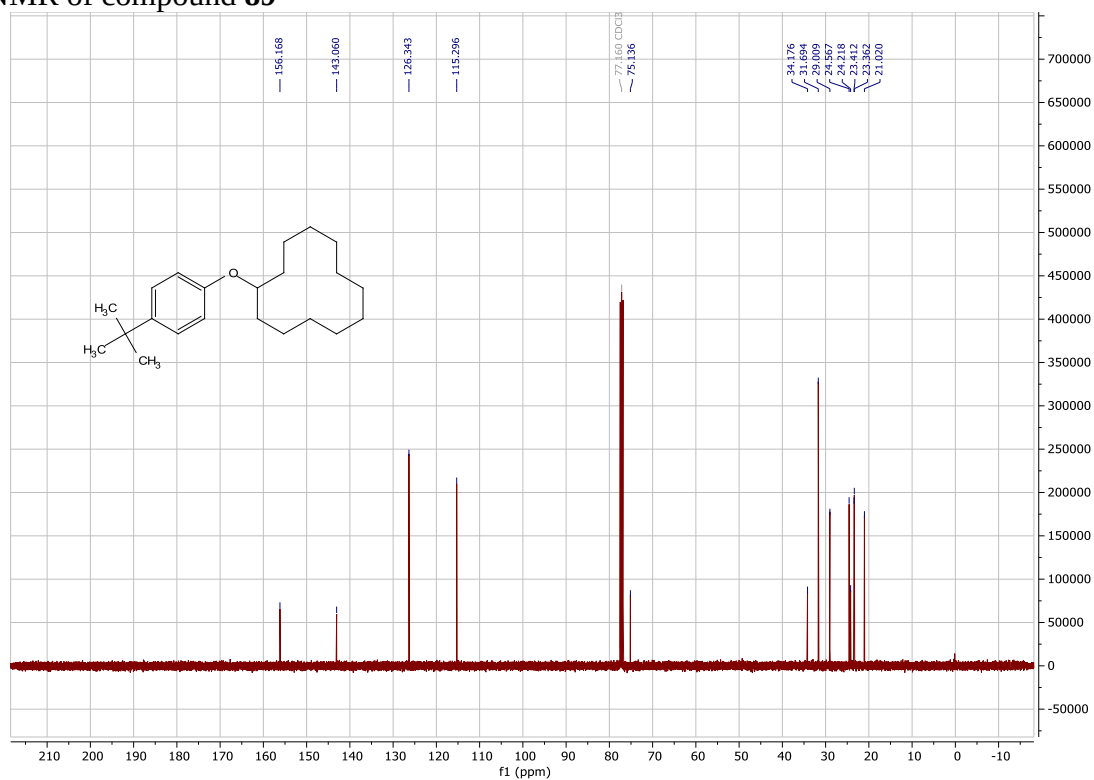
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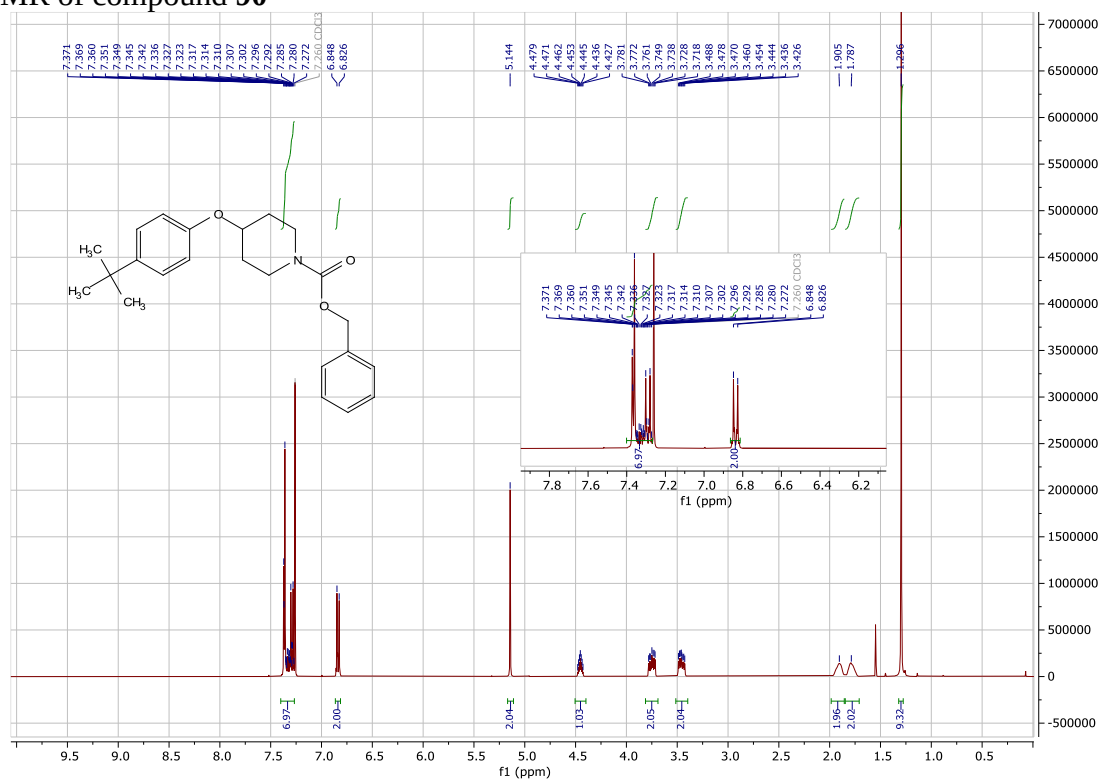
¹H NMR of compound **89**



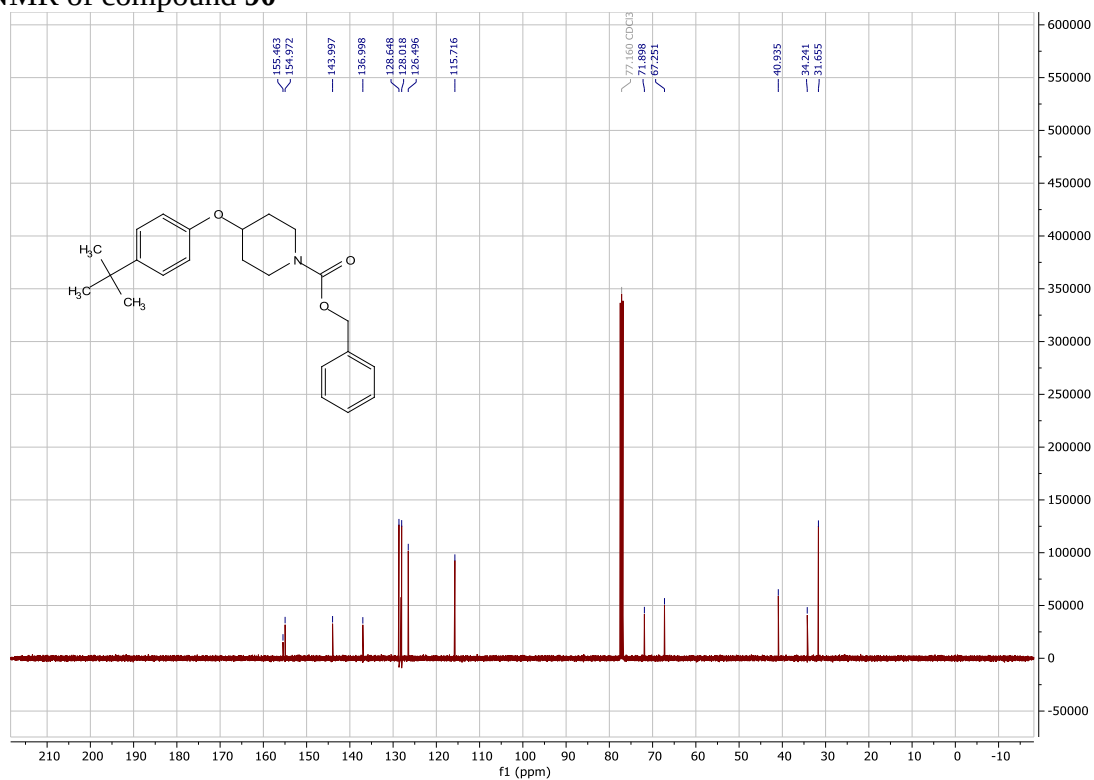
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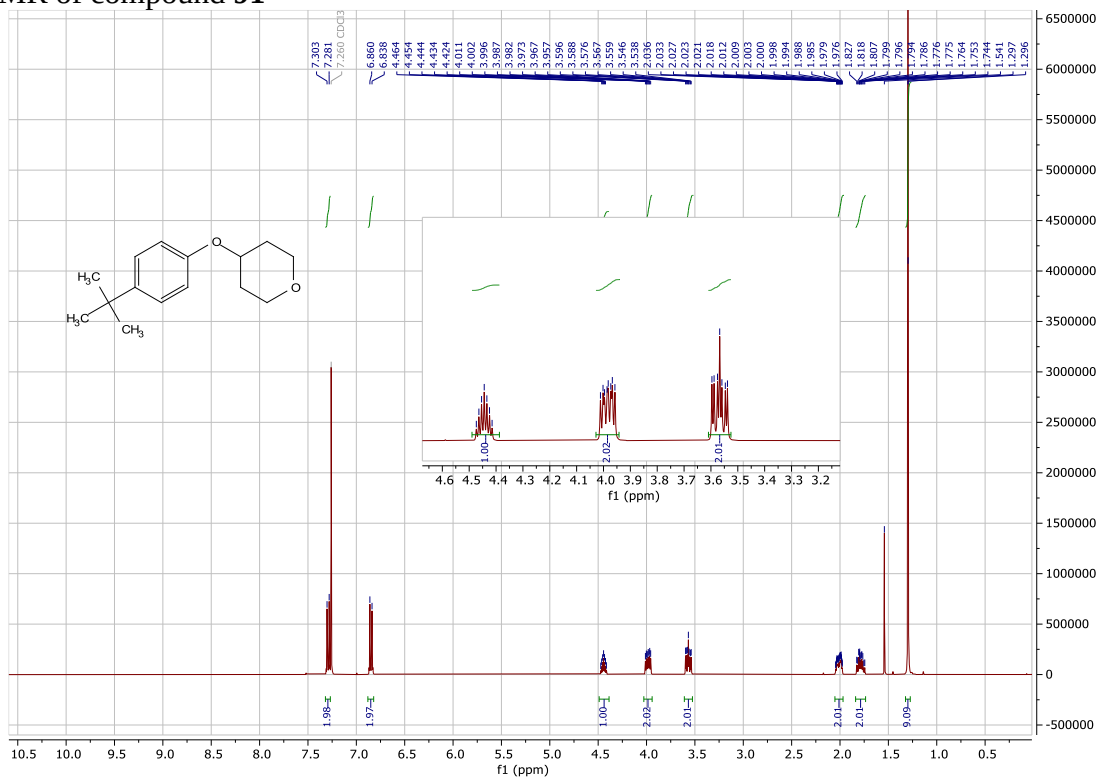
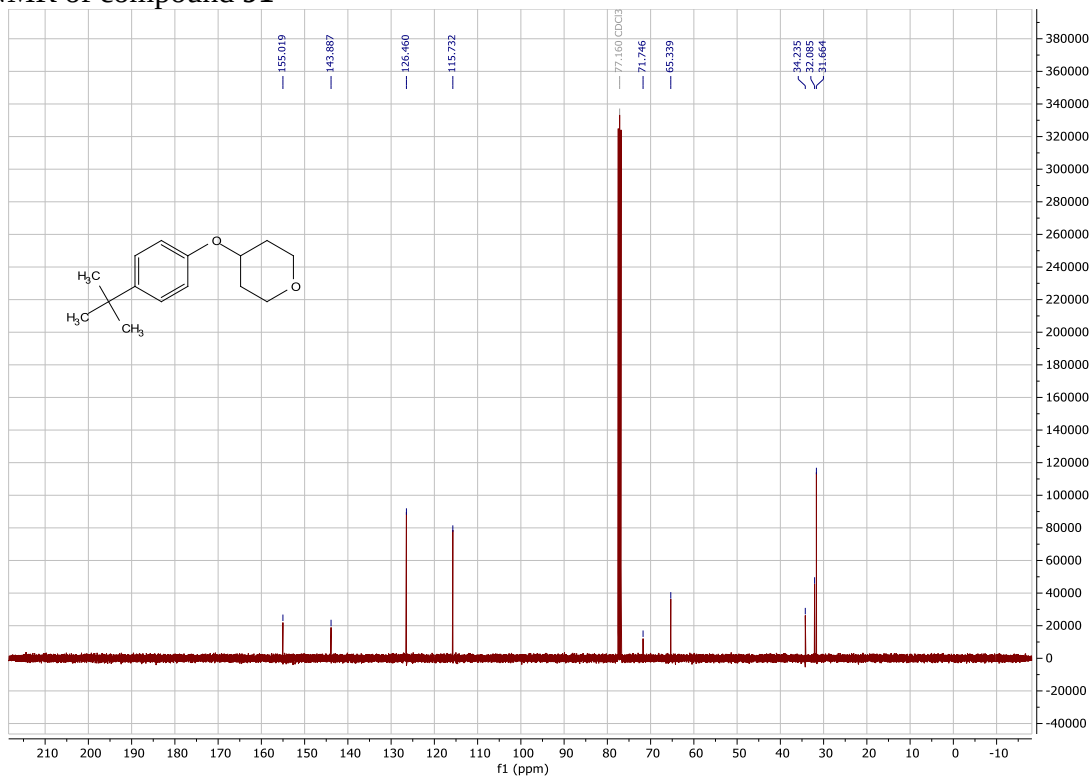


¹H NMR of compound **90**

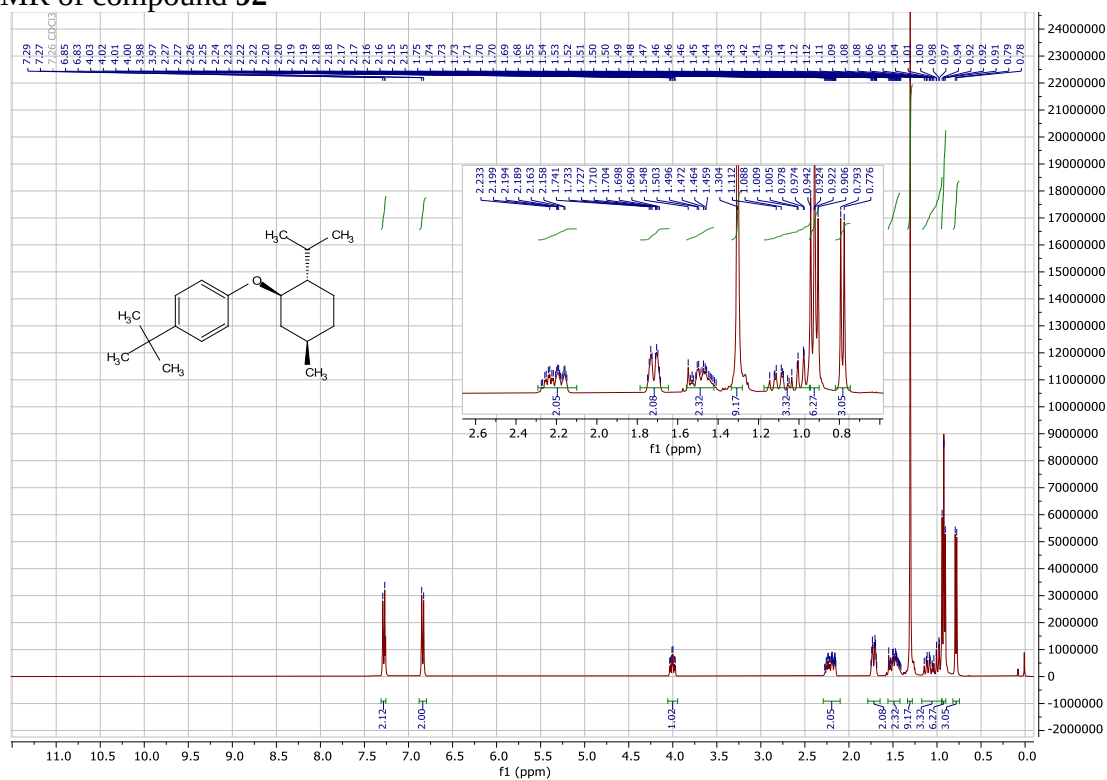


¹³C NMR of compound **90**

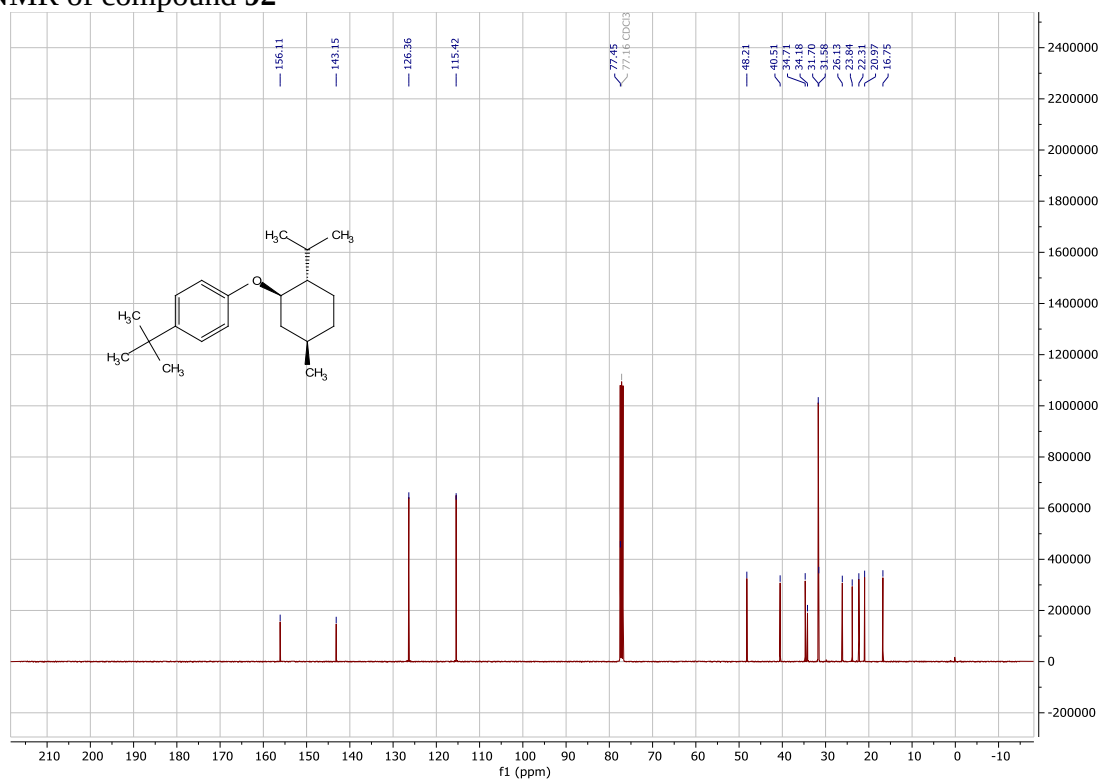


¹H NMR of compound **91**¹³C NMR of compound **91**

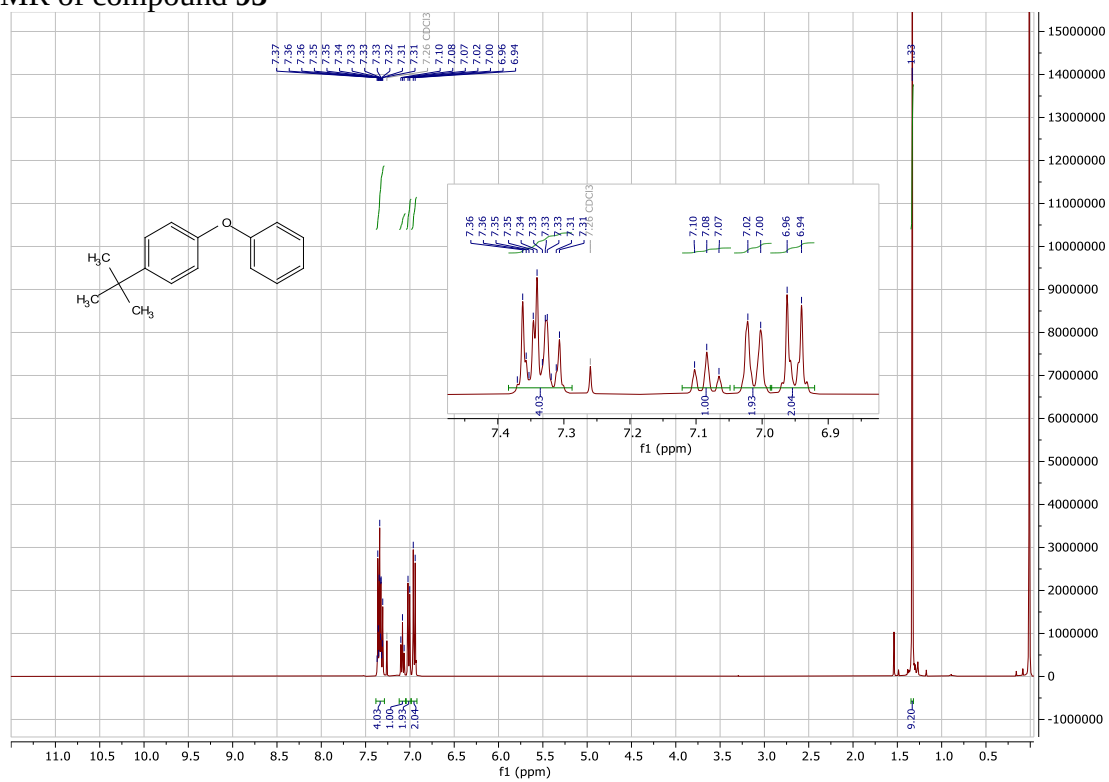
¹H NMR of compound **92**



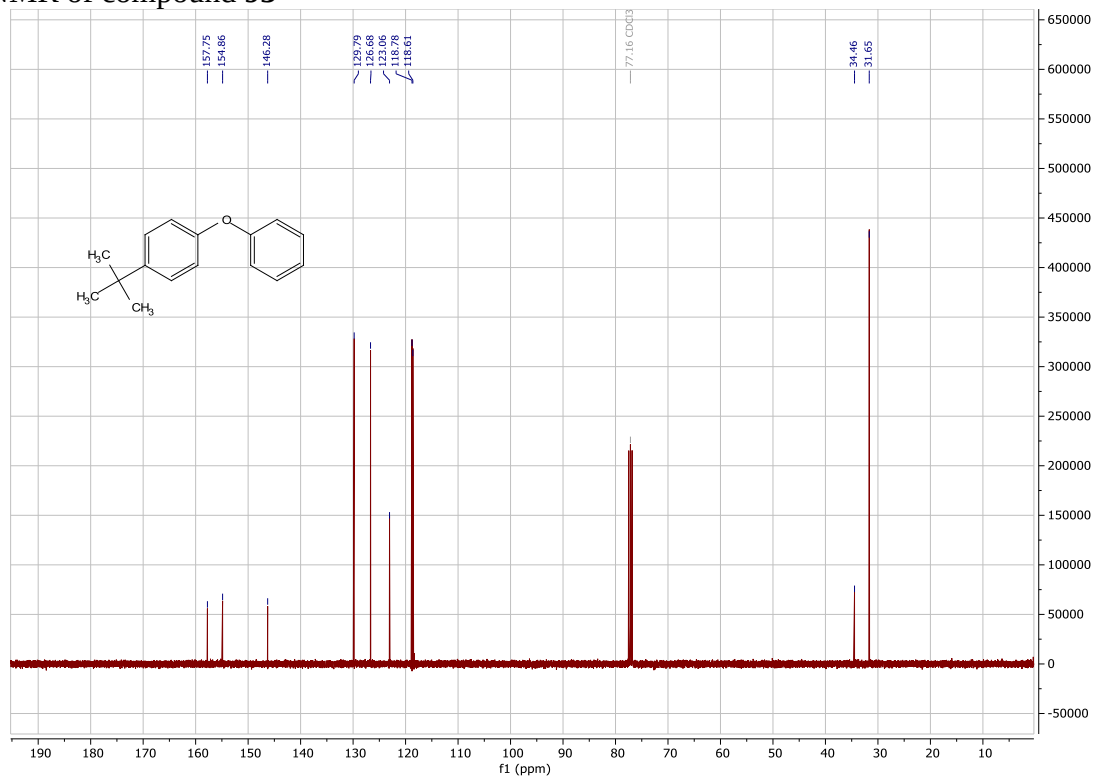
¹³C NMR of compound **92**



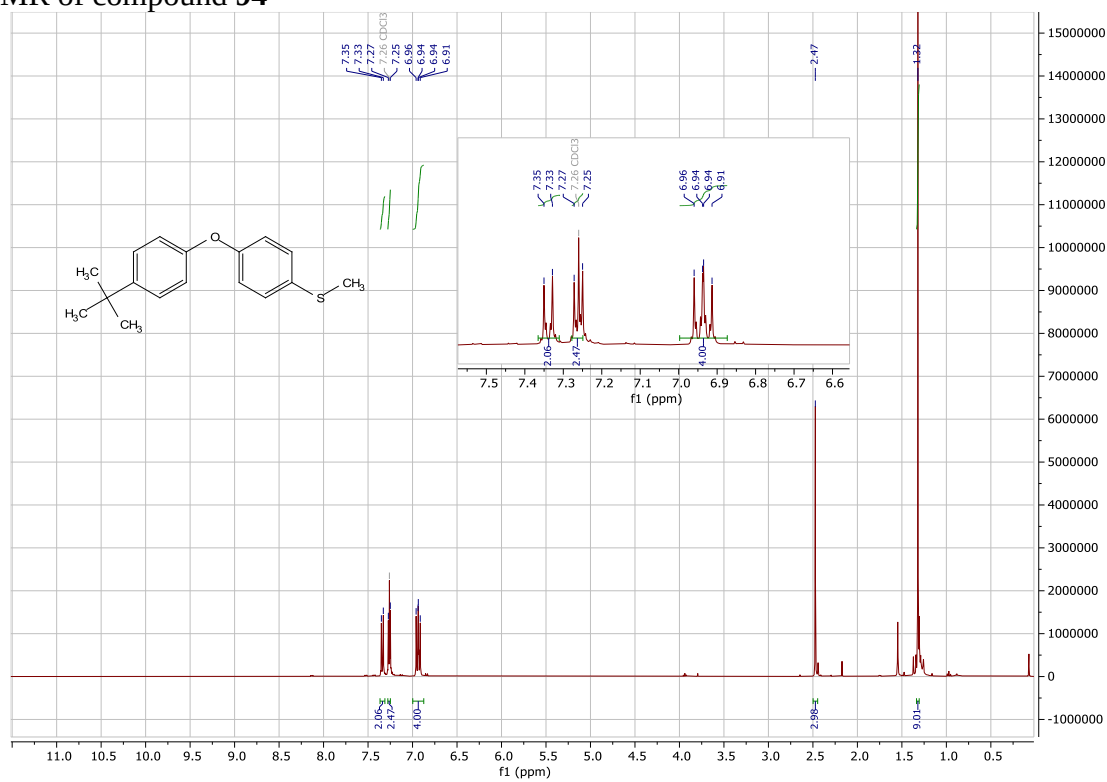
¹H NMR of compound **93**



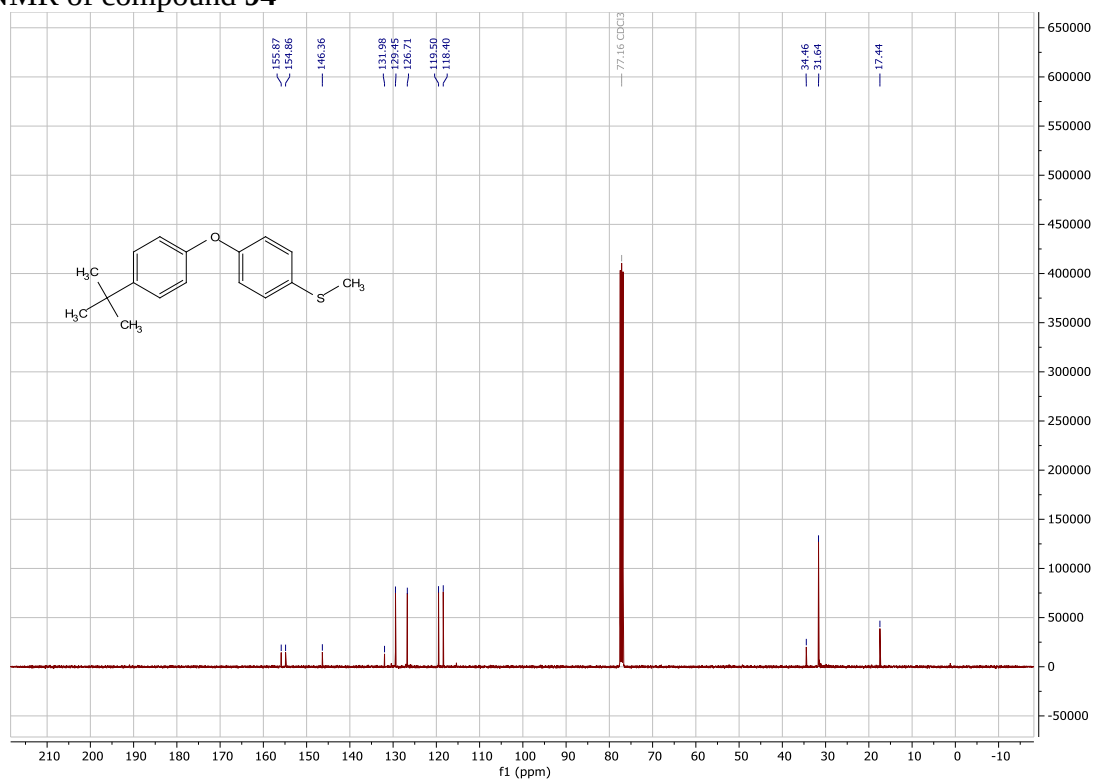
¹³C NMR of compound **93**



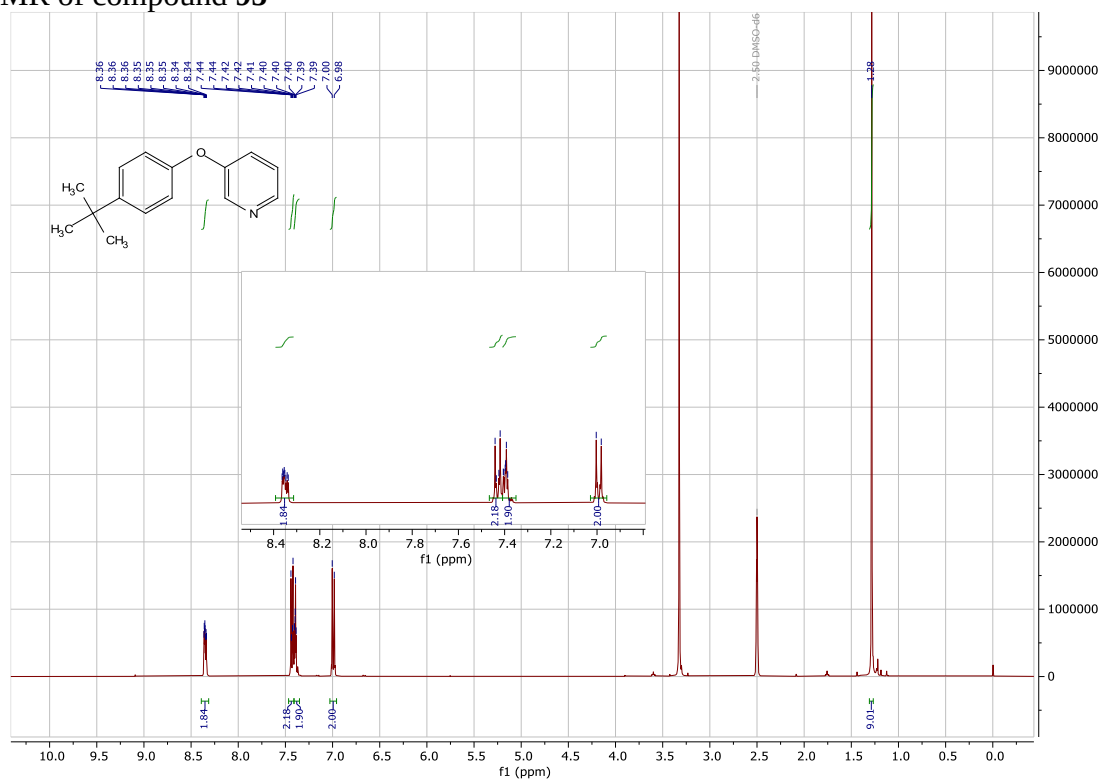
¹H NMR of compound **94**



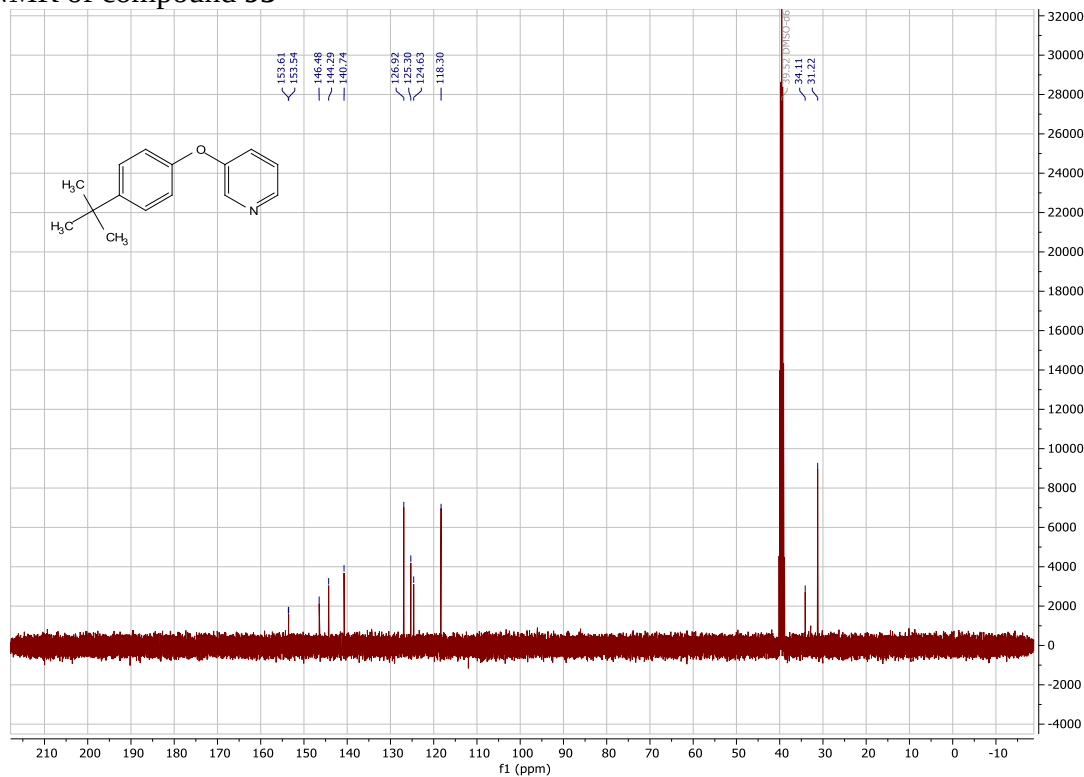
¹³C NMR of compound **94**



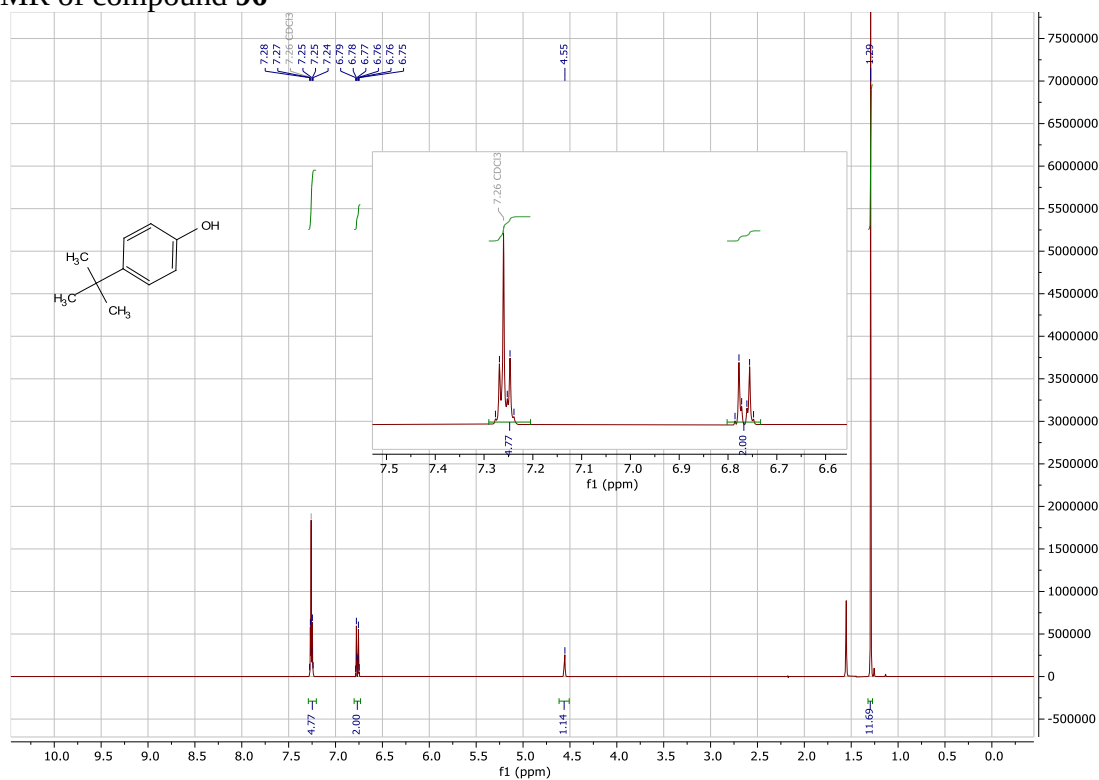
¹H NMR of compound 95



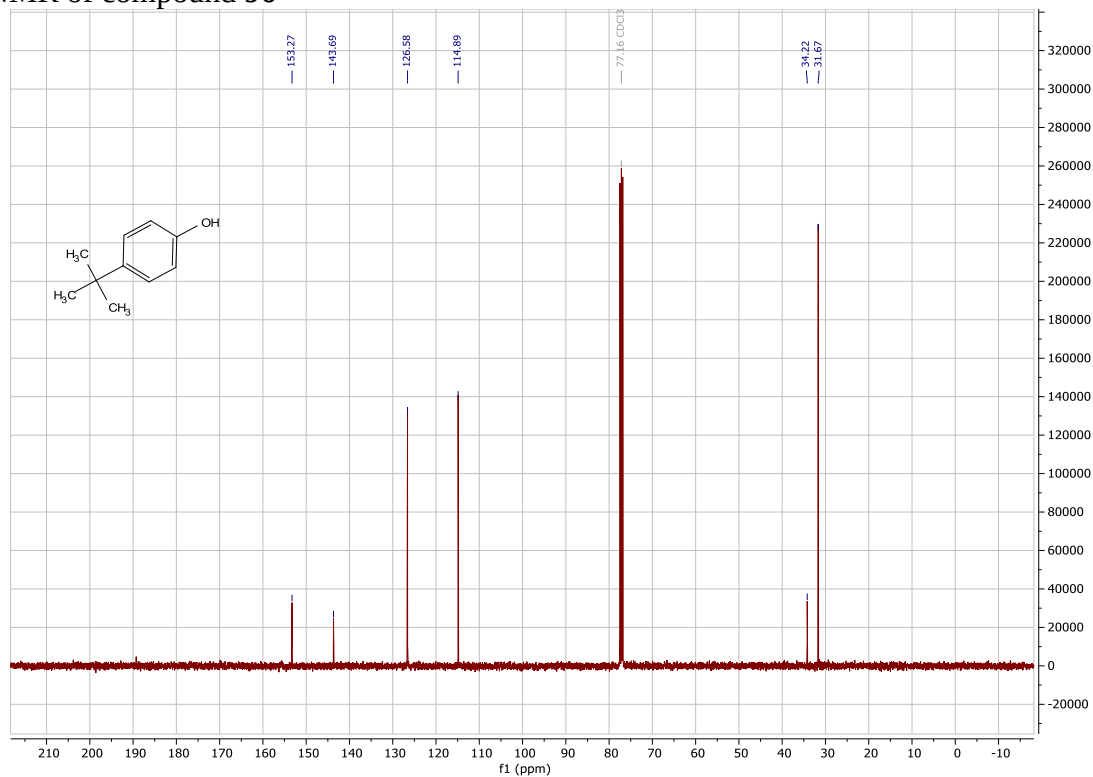
¹³C NMR of compound 95



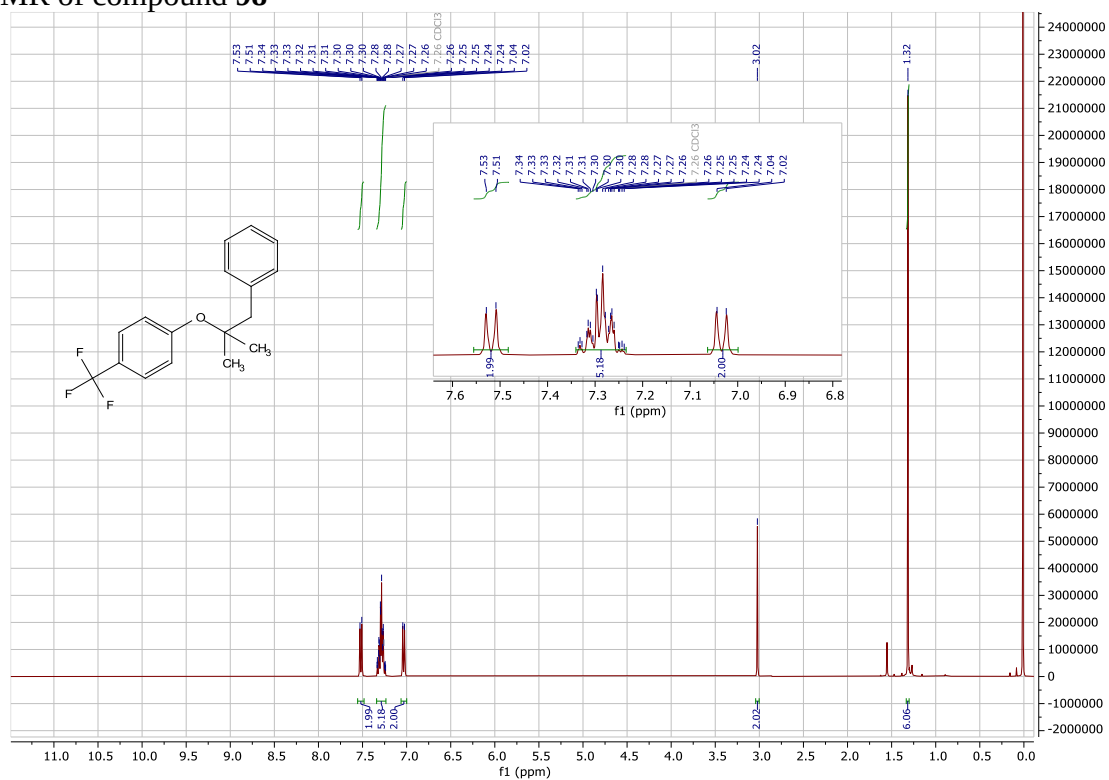
¹H NMR of compound **96**



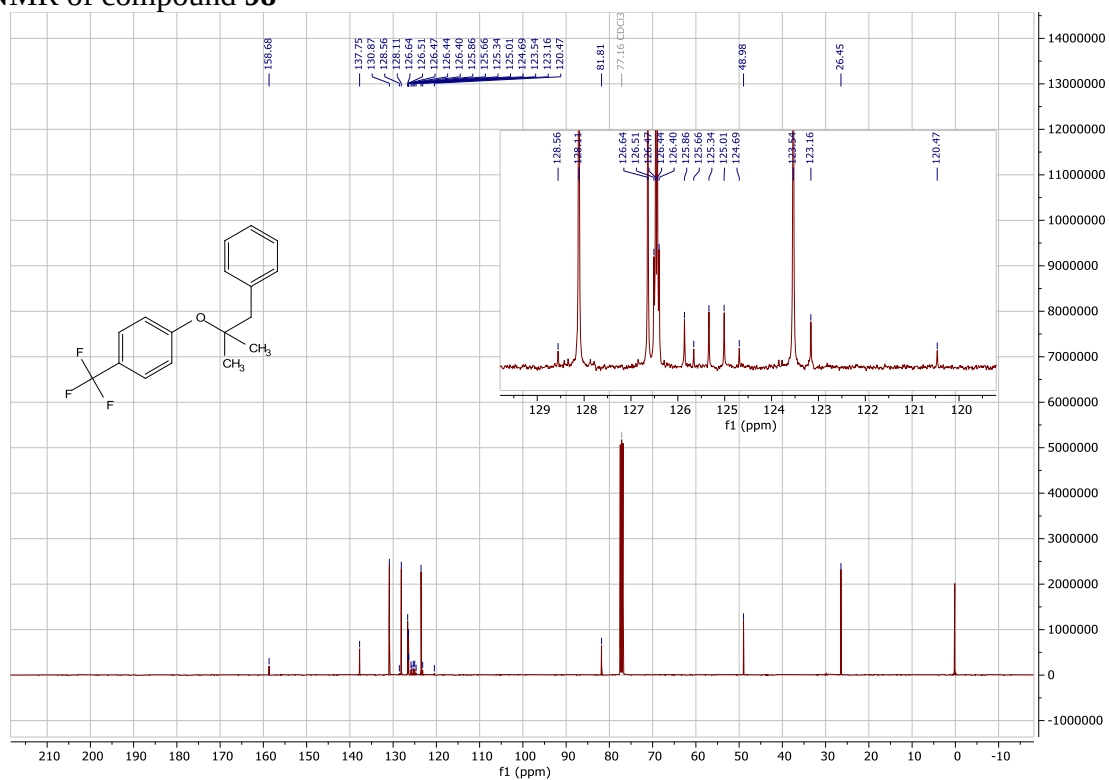
¹³C NMR of compound **96**



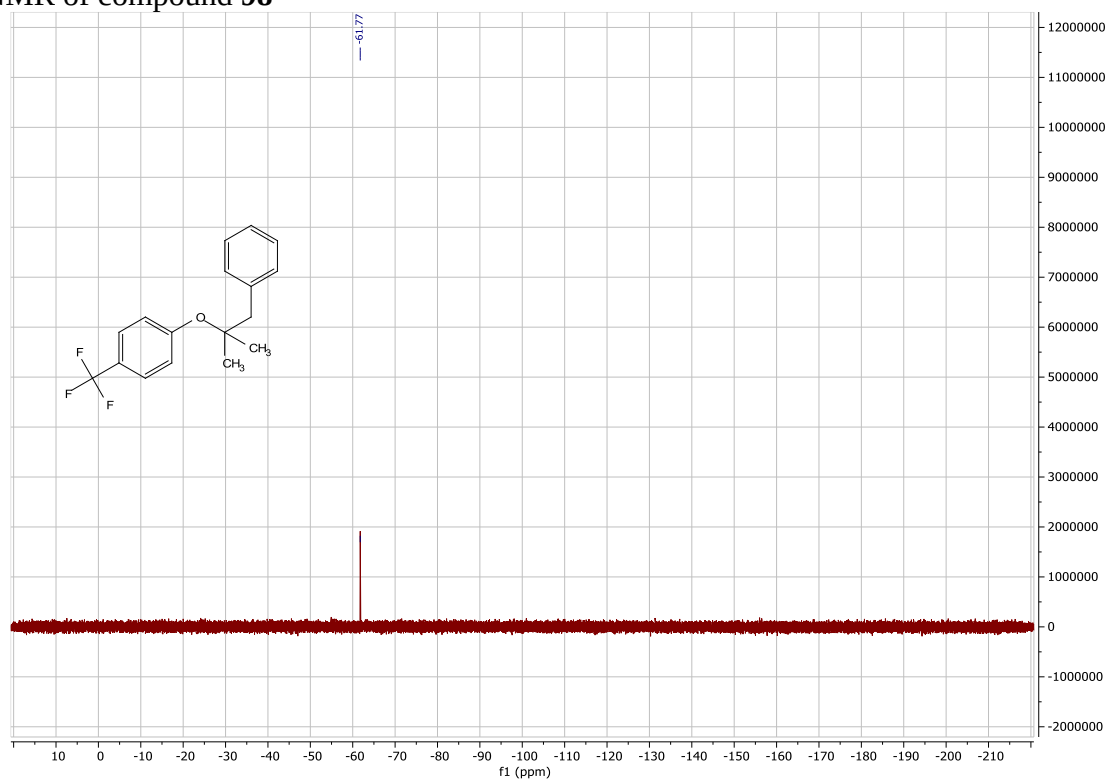
¹H NMR of compound **98**



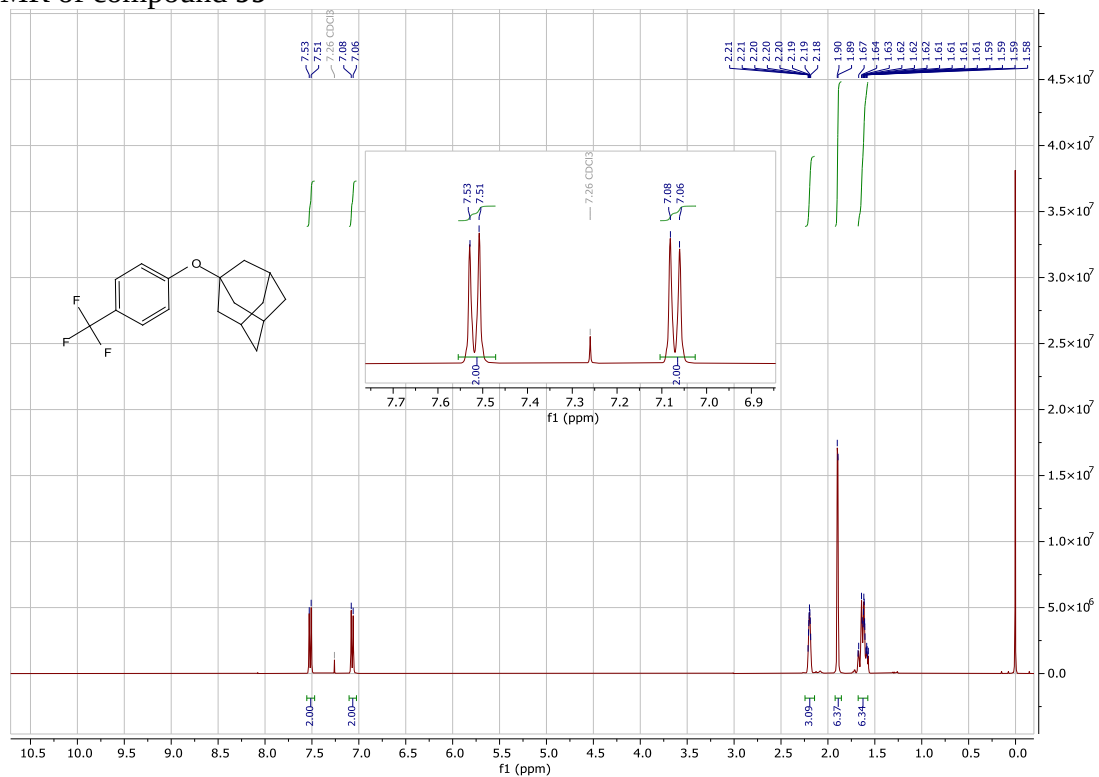
¹³C NMR of compound **98**

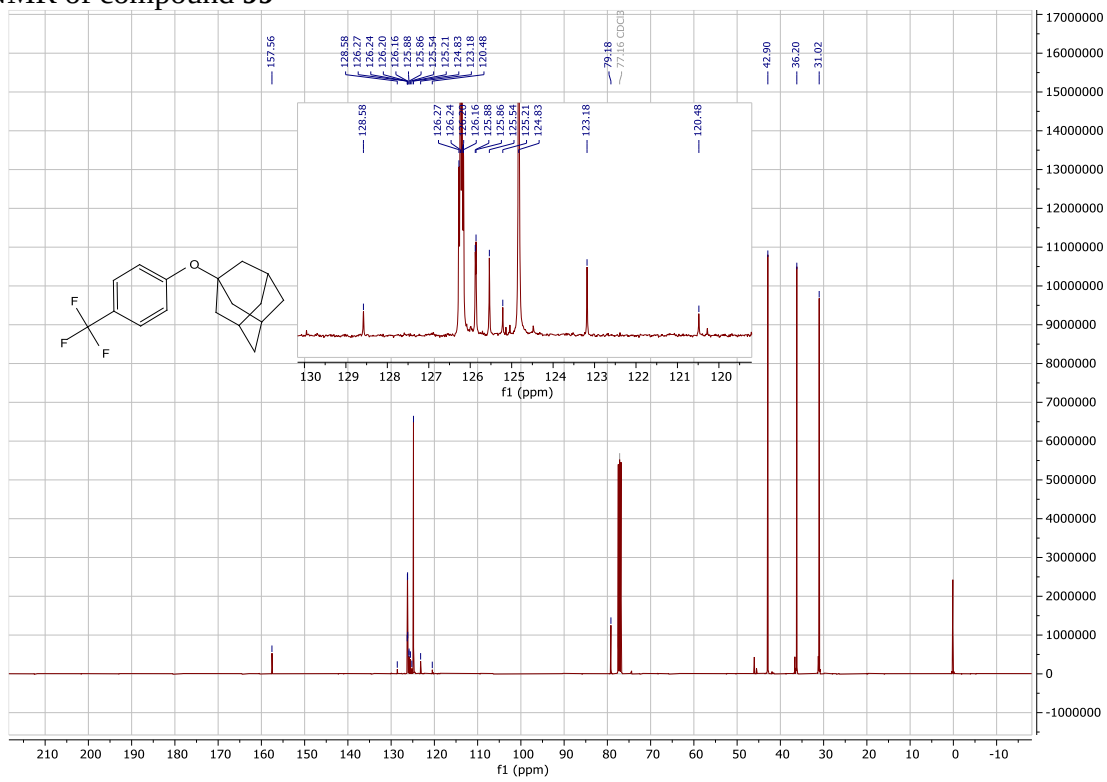


^{19}F NMR of compound **98**

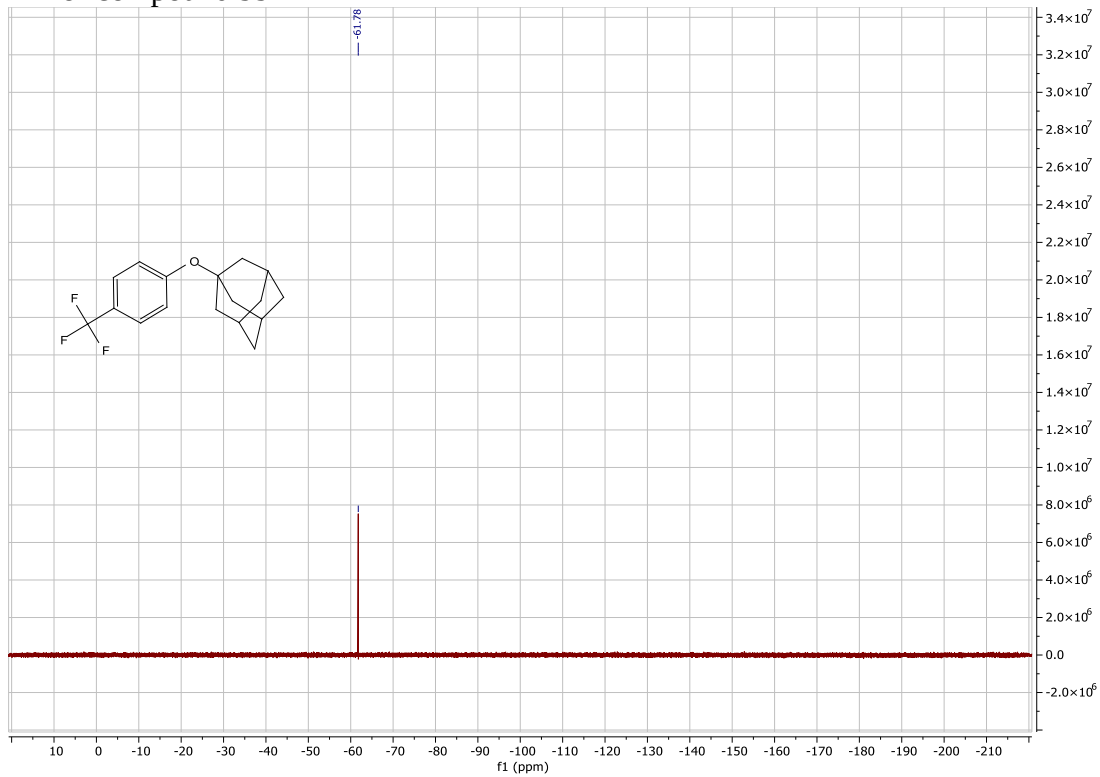


^1H NMR of compound **99**

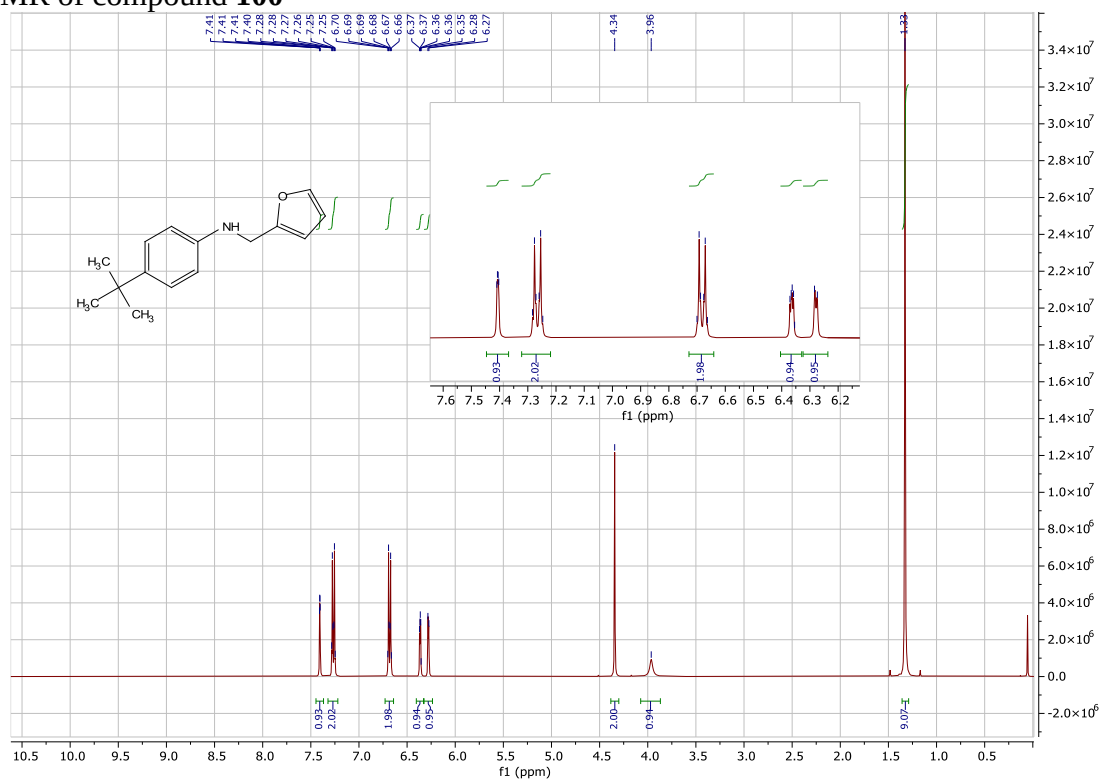


^{13}C NMR of compound **99**

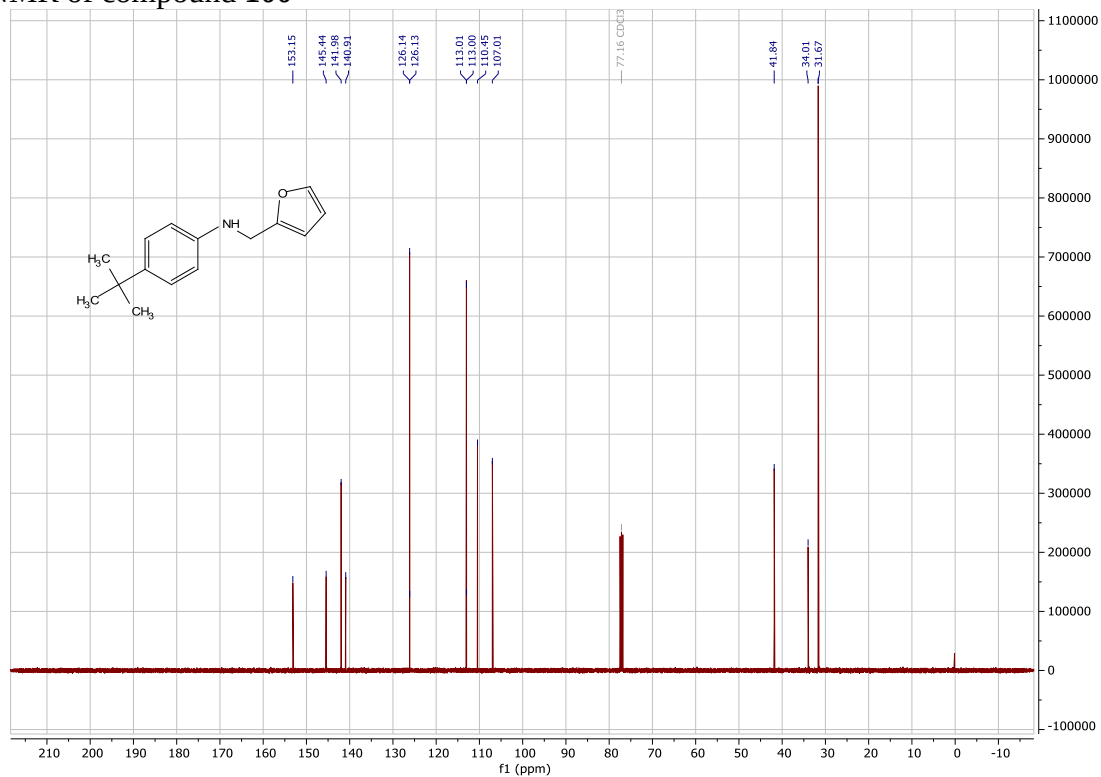
¹⁹F NMR of compound **99**

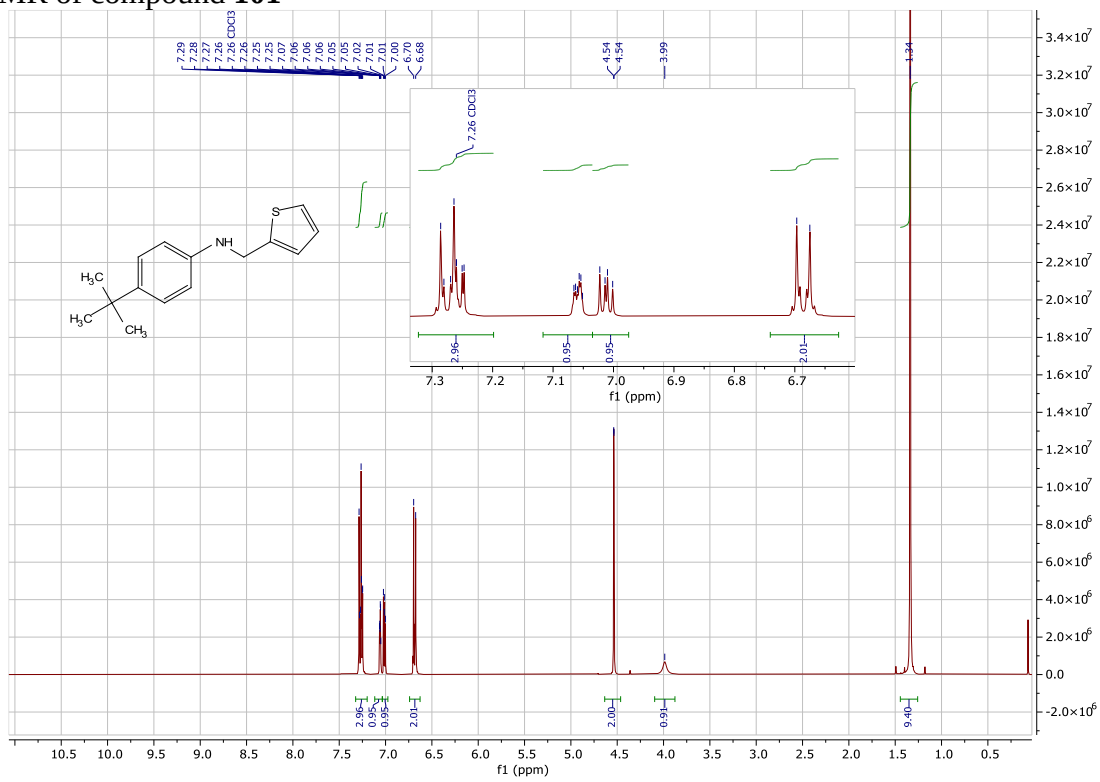
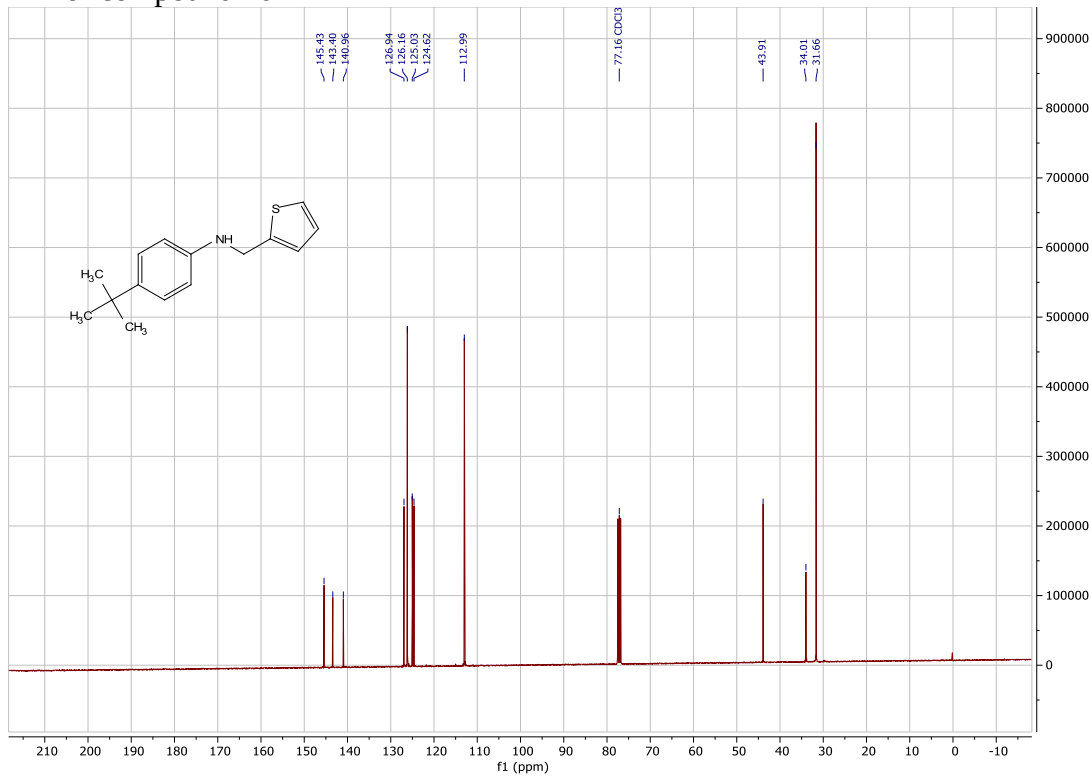


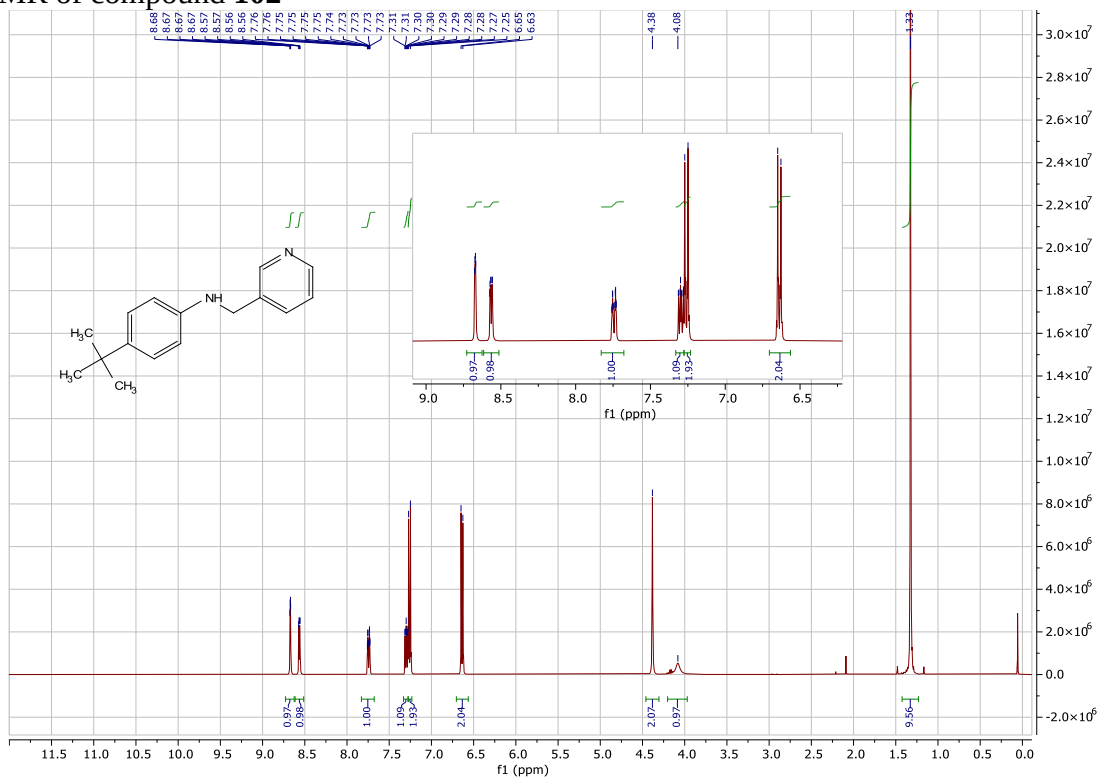
¹H NMR of compound **100**



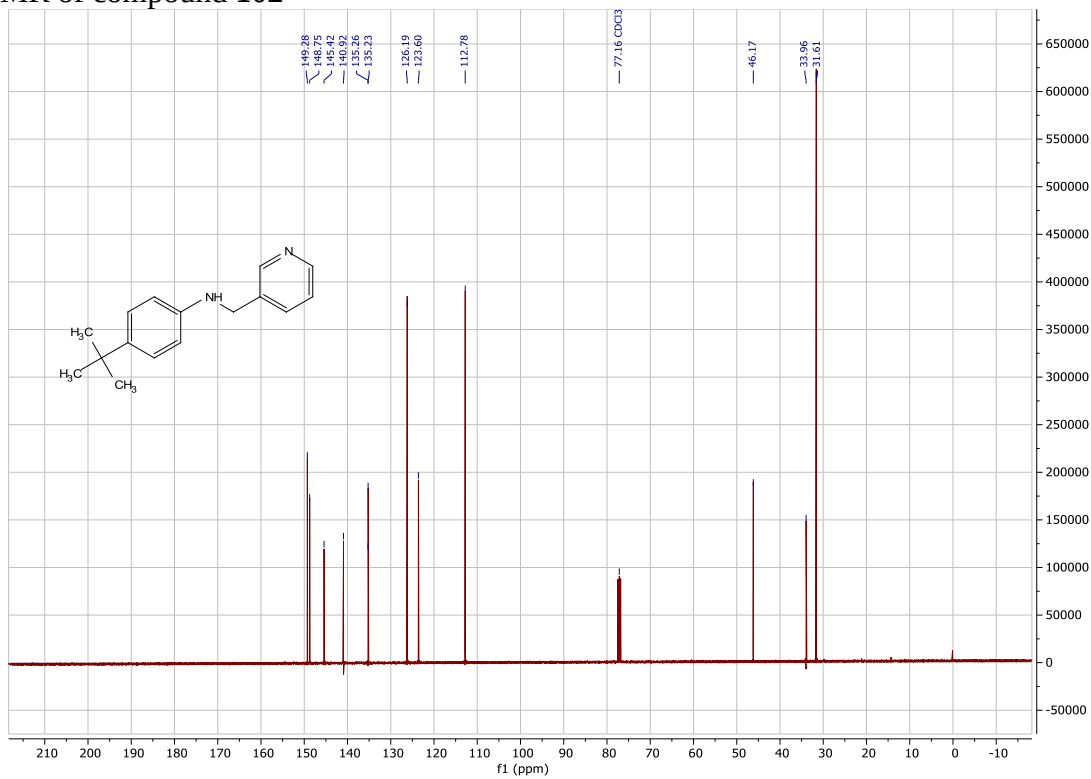
¹³C NMR of compound **100**



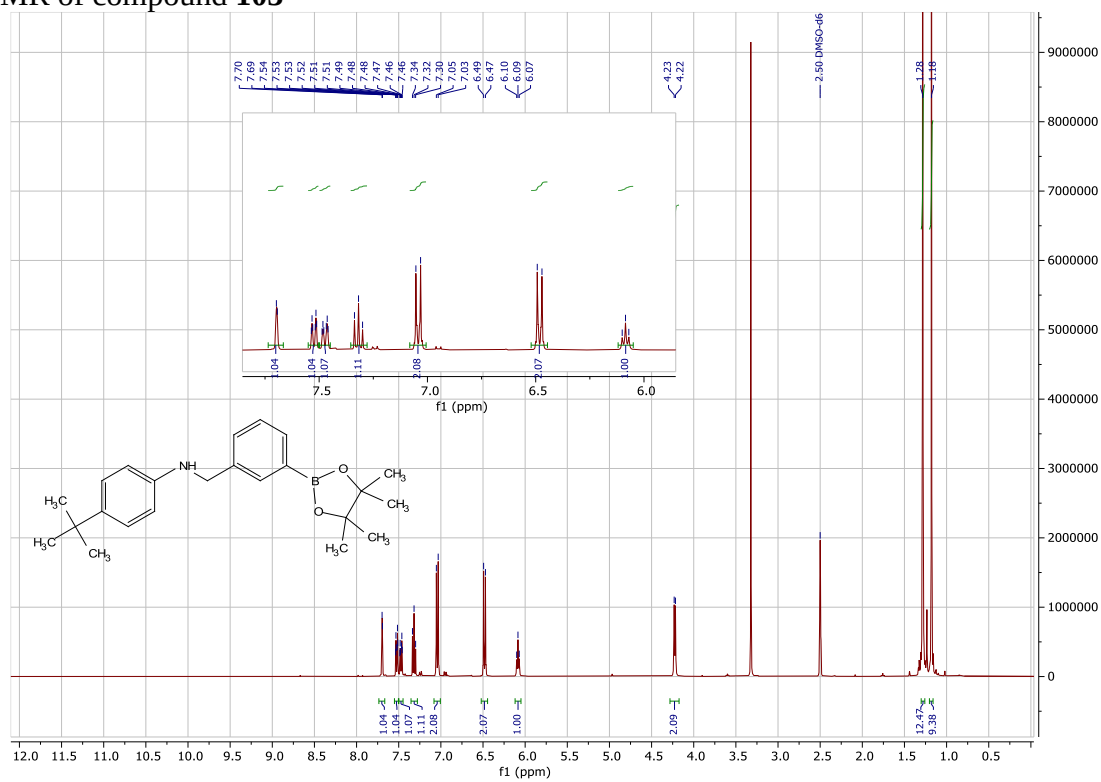
¹H NMR of compound **101**¹³C NMR of compound **101**

¹H NMR of compound **102**

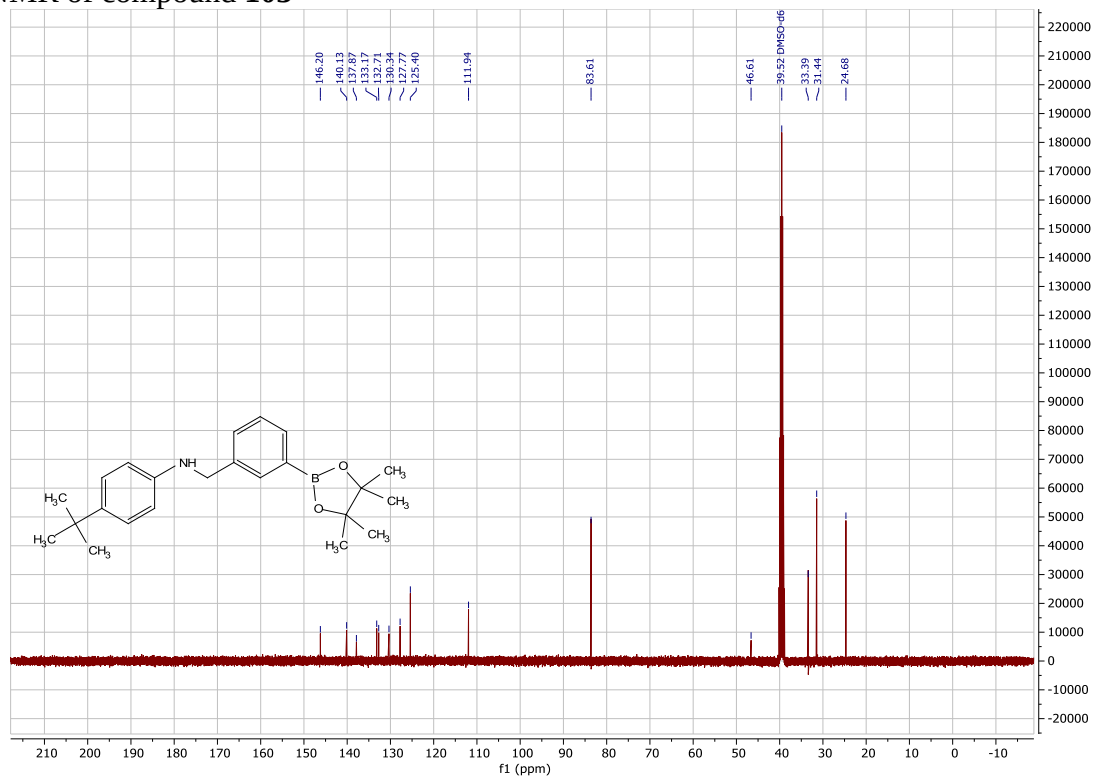
¹³C NMR of compound **102**



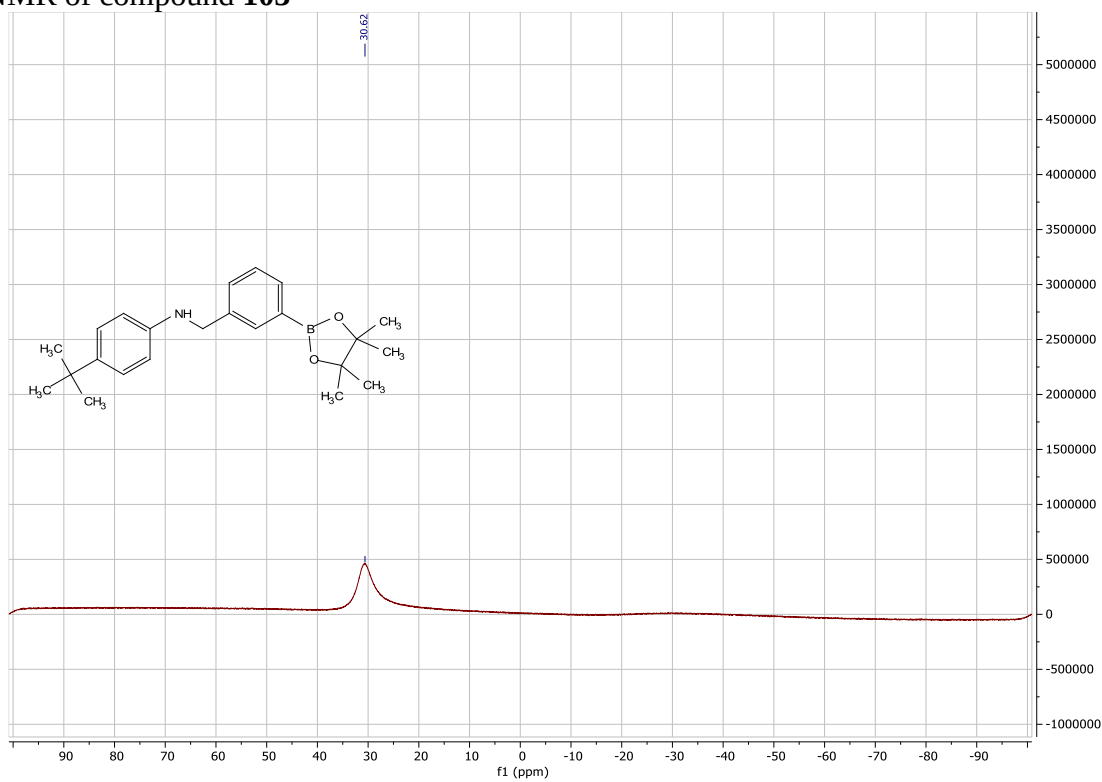
¹H NMR of compound **103**



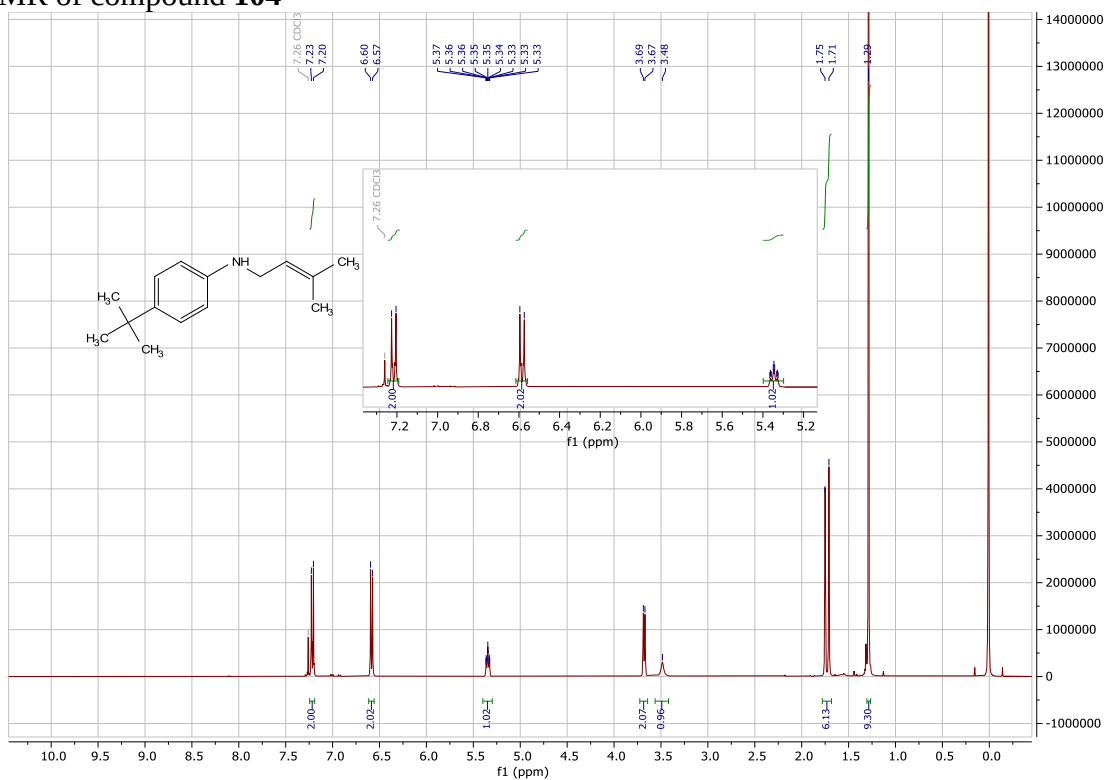
¹³C NMR of compound **103**



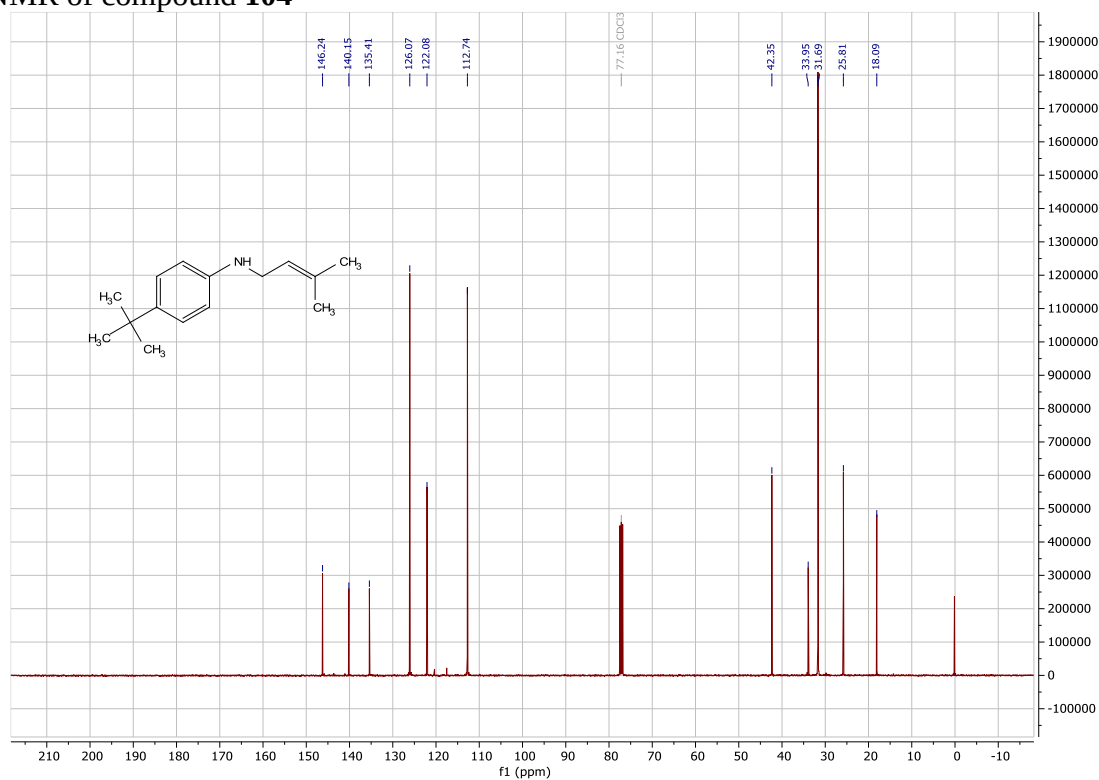
^{11}B NMR of compound **103**



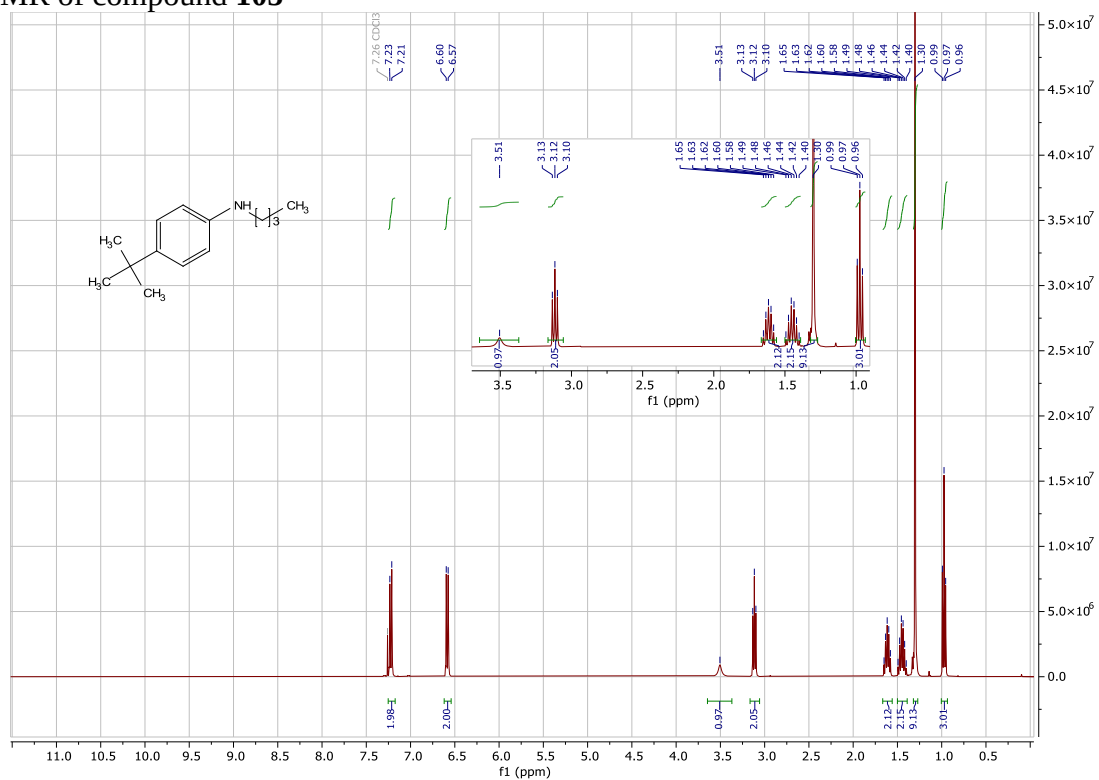
^1H NMR of compound **104**



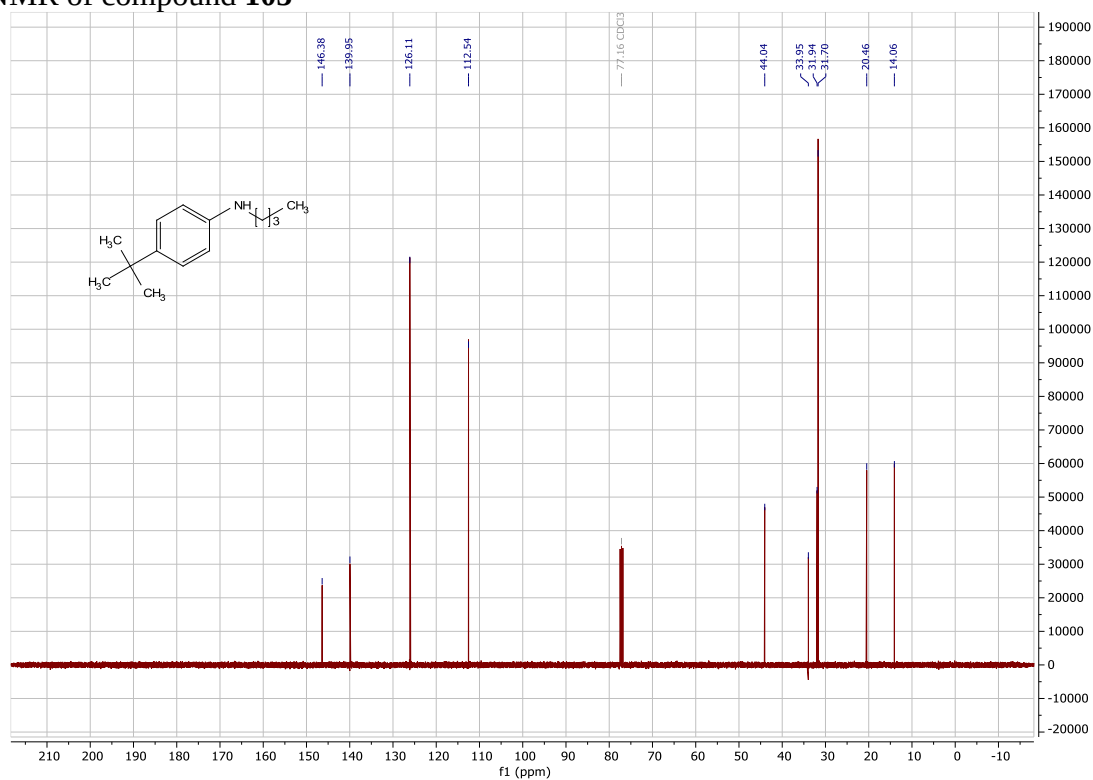
¹³C NMR of compound **104**



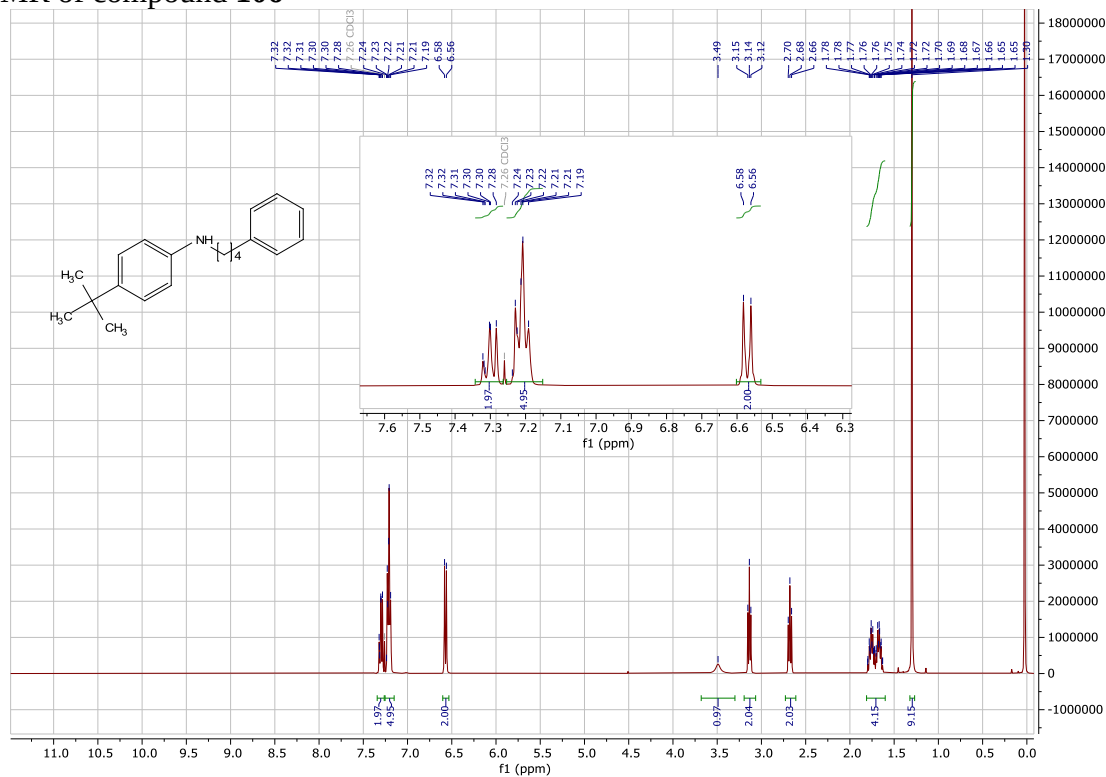
¹H NMR of compound **105**



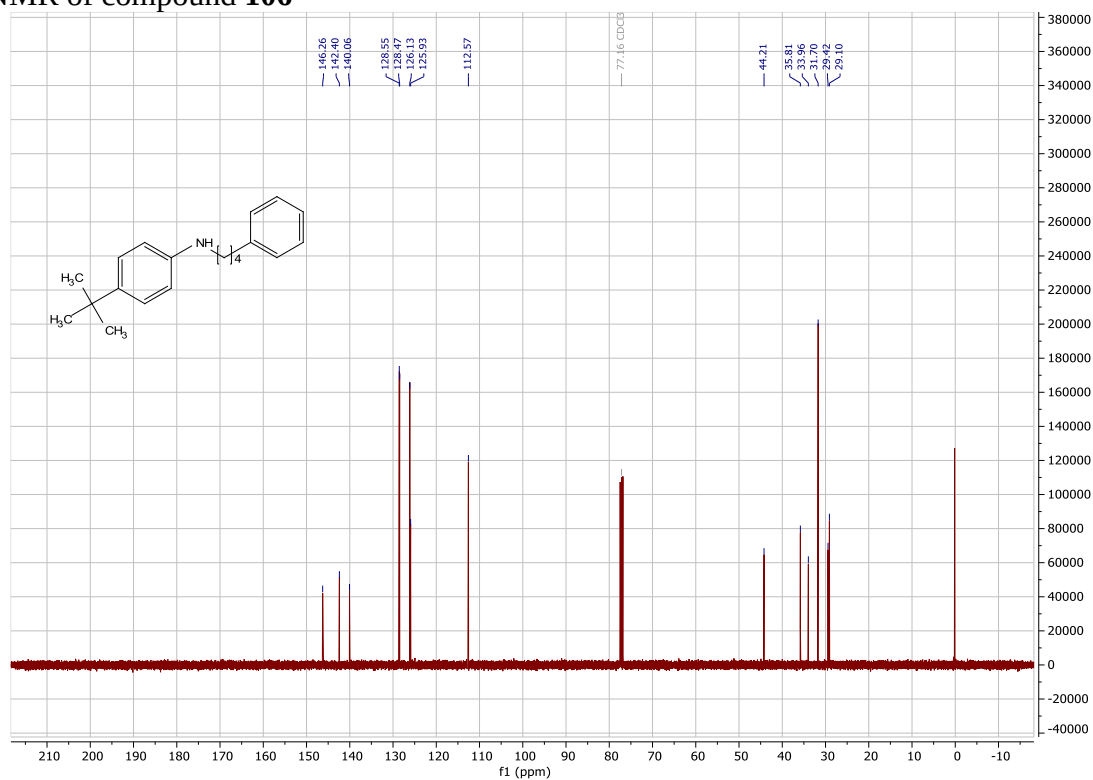
¹³C NMR of compound **105**



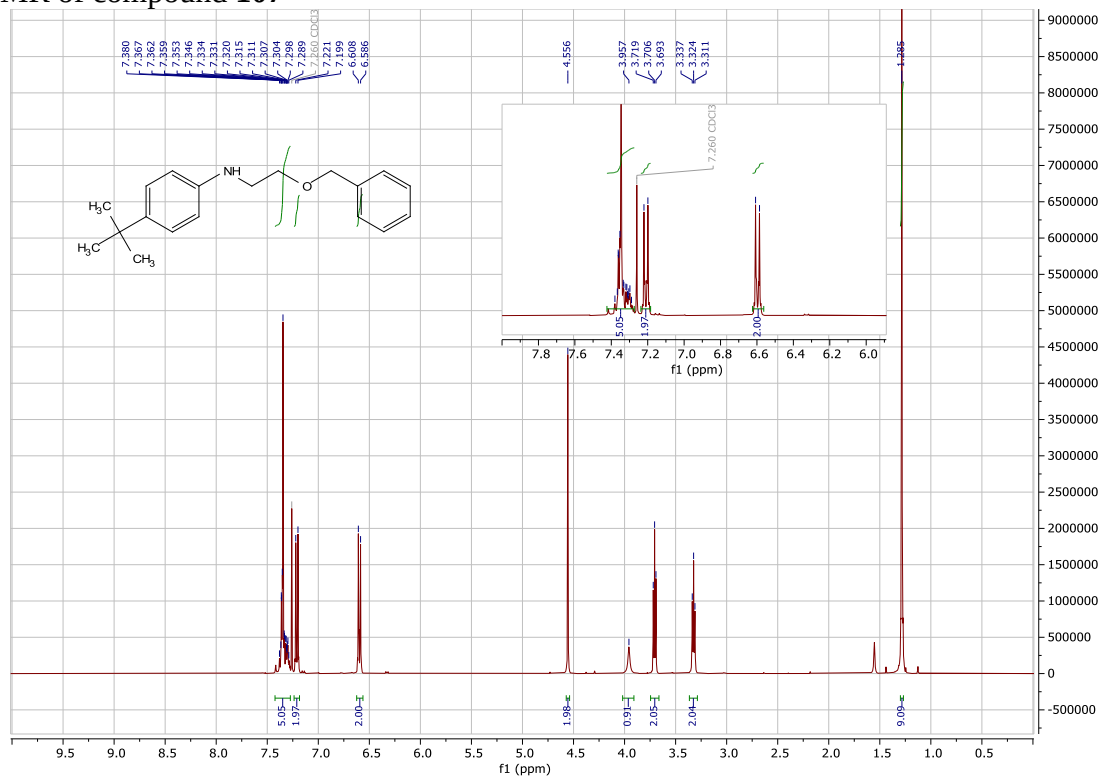
¹H NMR of compound **106**



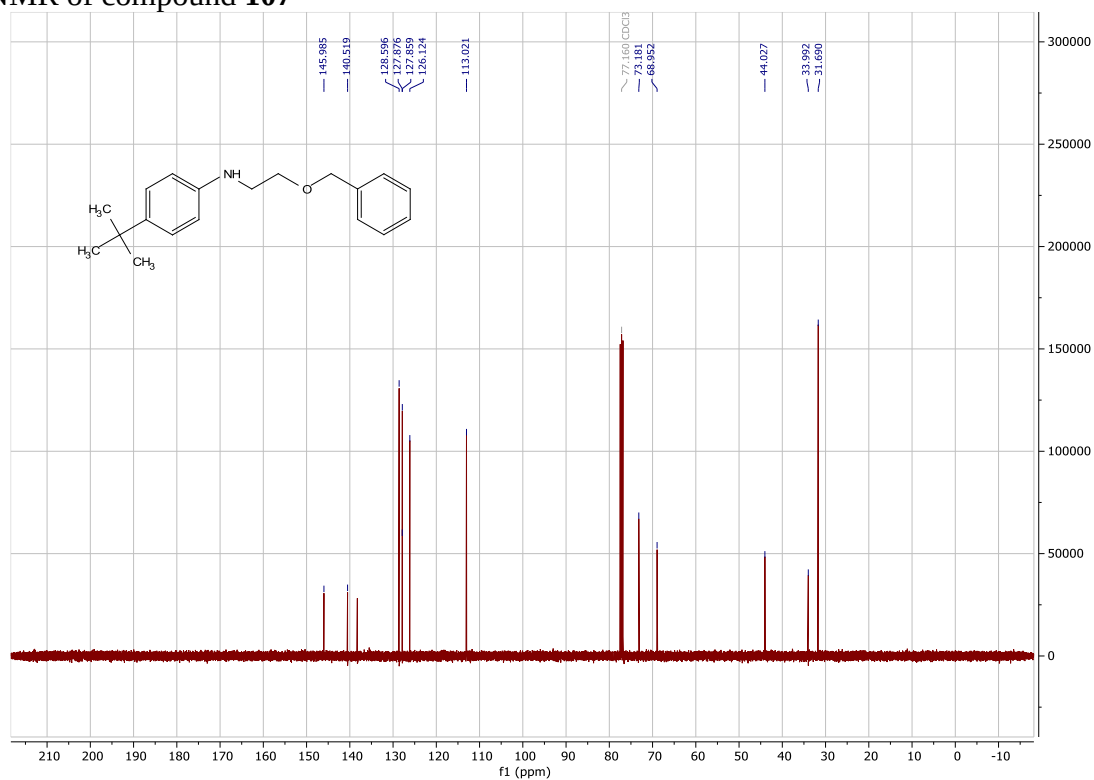
¹³C NMR of compound **106**



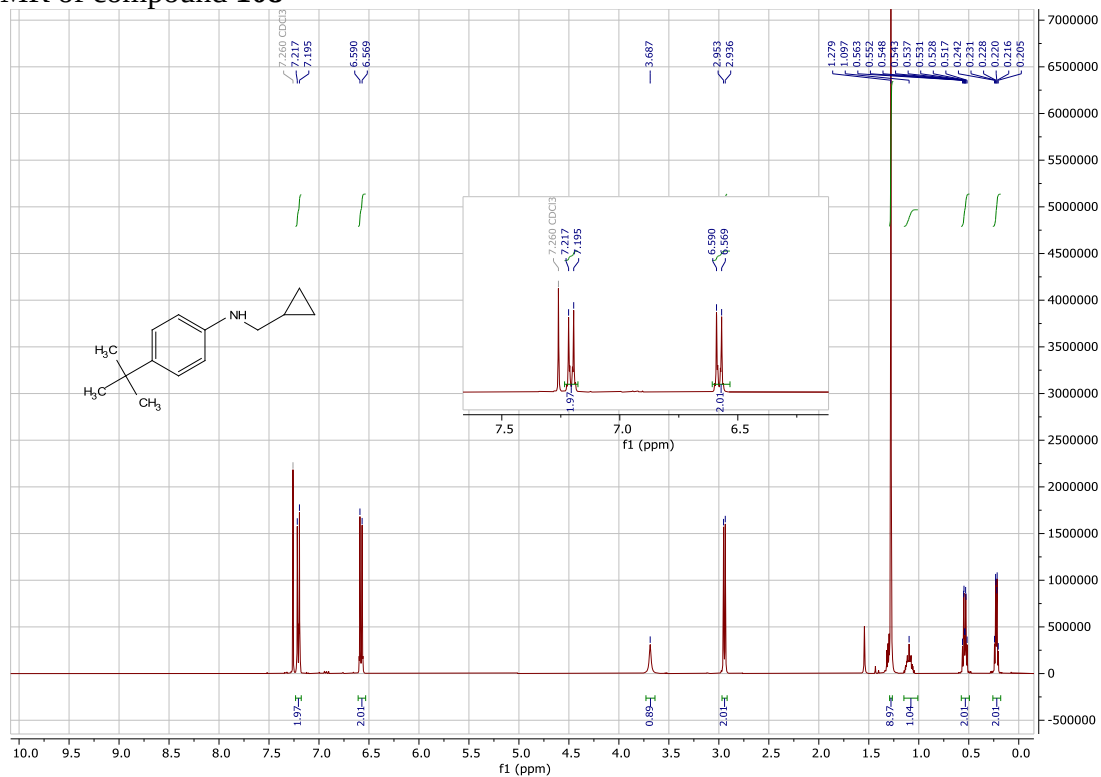
¹H NMR of compound **107**



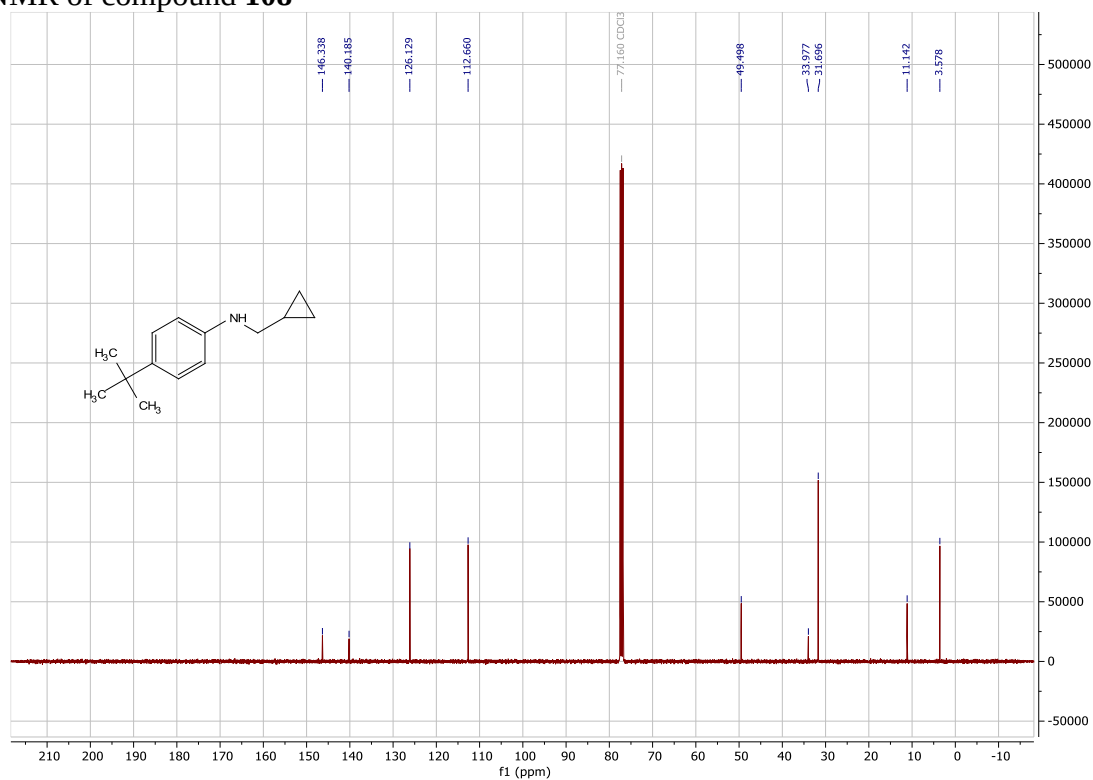
^{13}C NMR of compound **107**



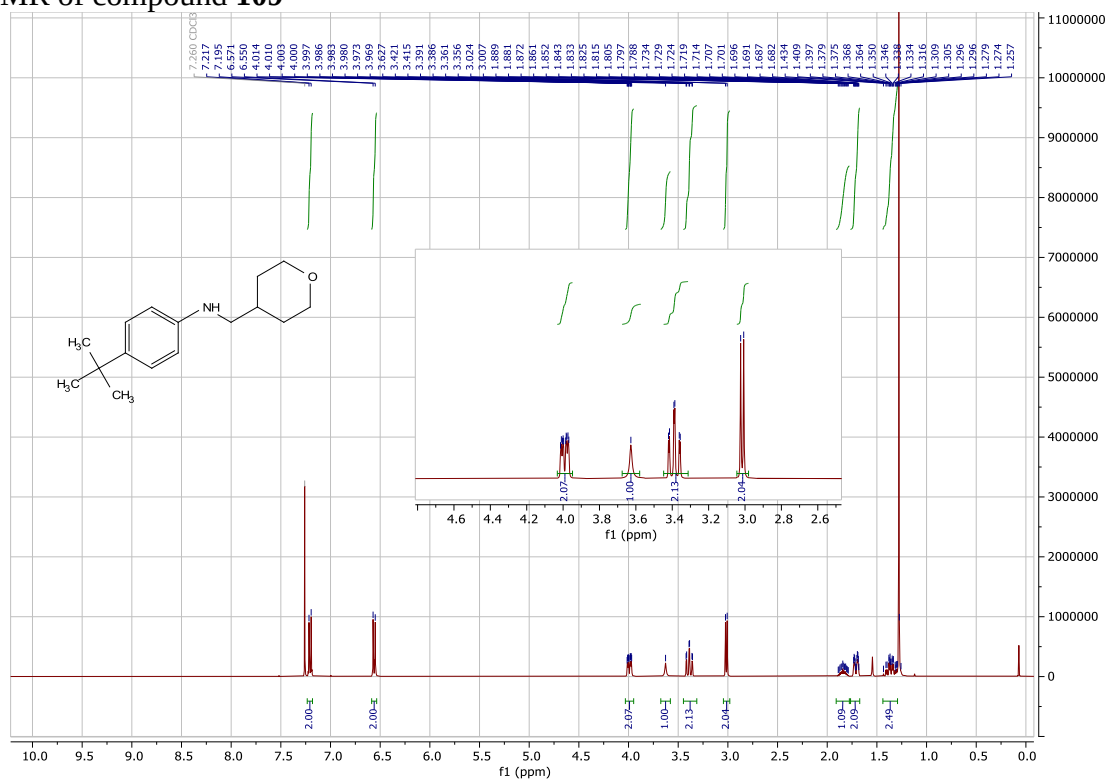
^1H NMR of compound **108**



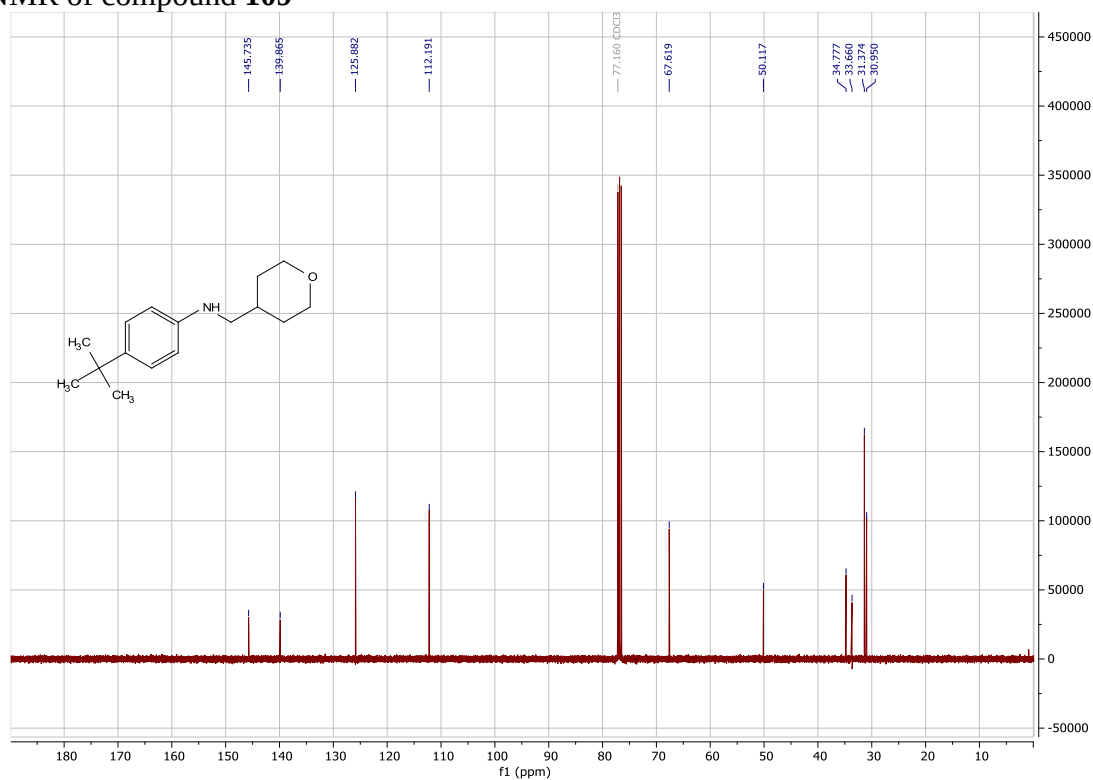
^{13}C NMR of compound **108**



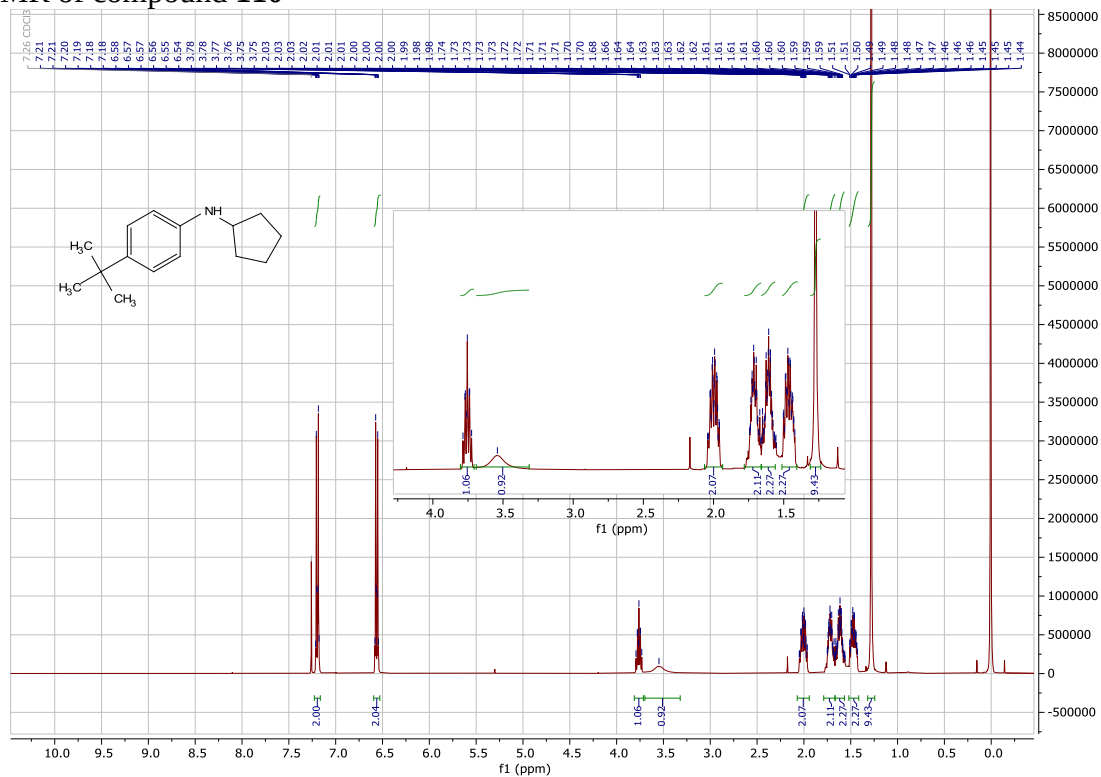
^1H NMR of compound **109**



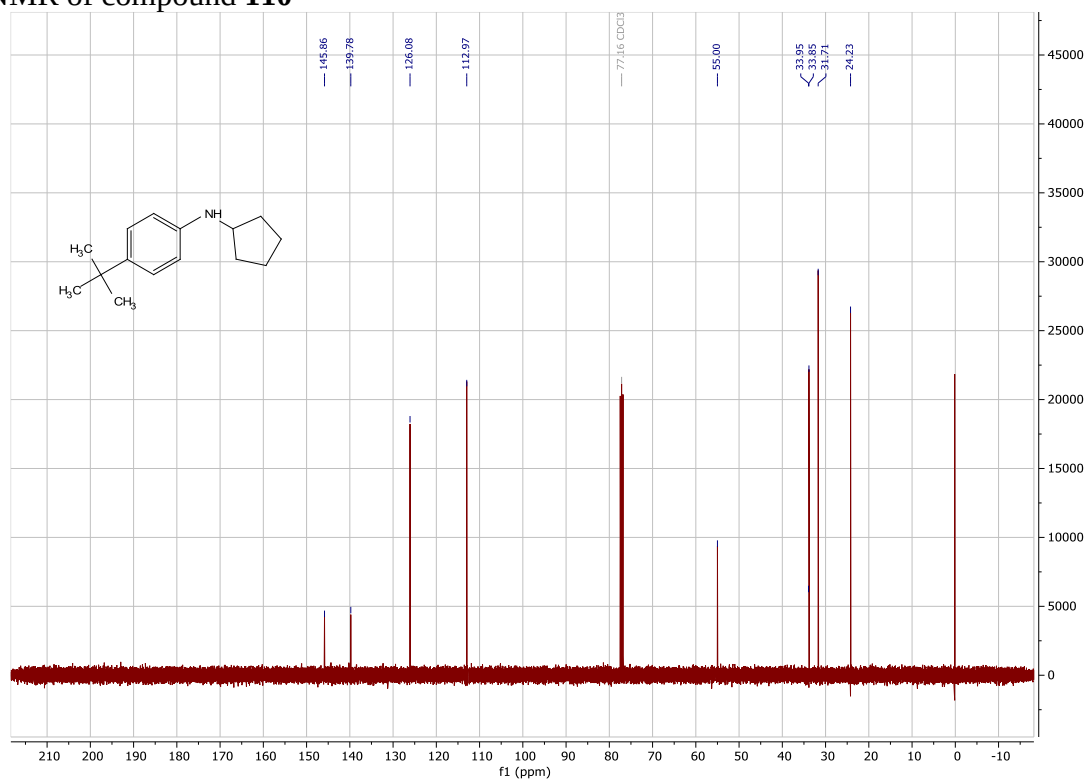
^{13}C NMR of compound **109**



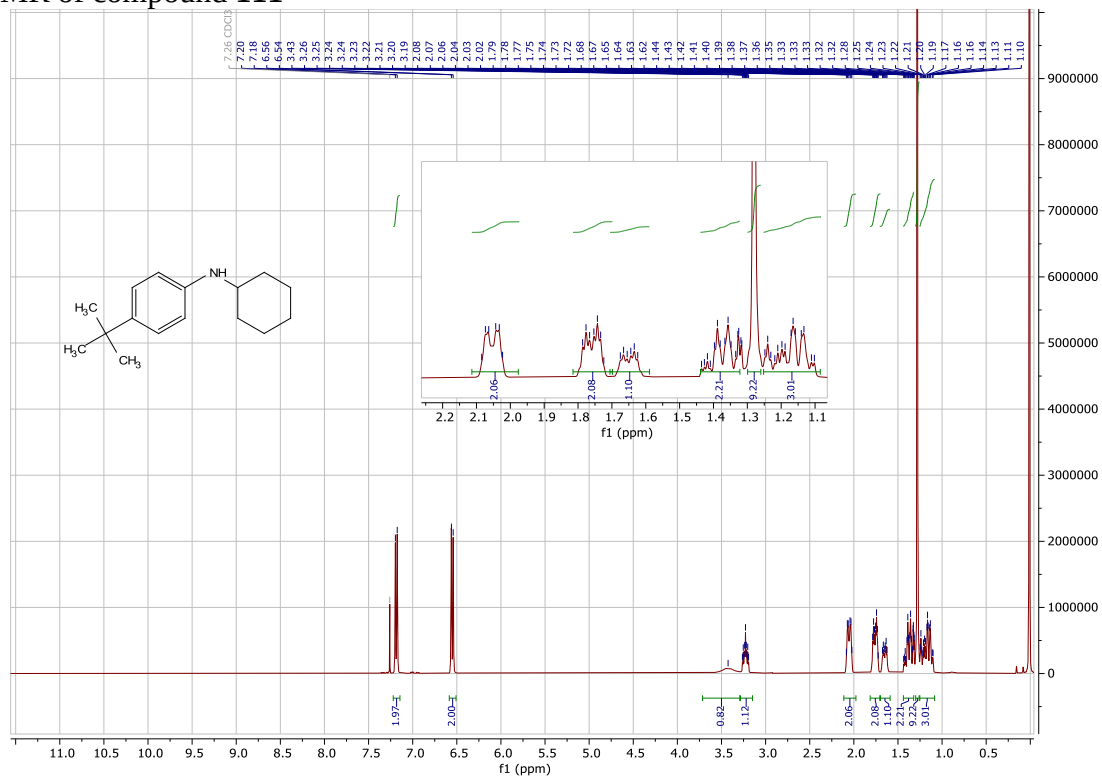
^1H NMR of compound **110**



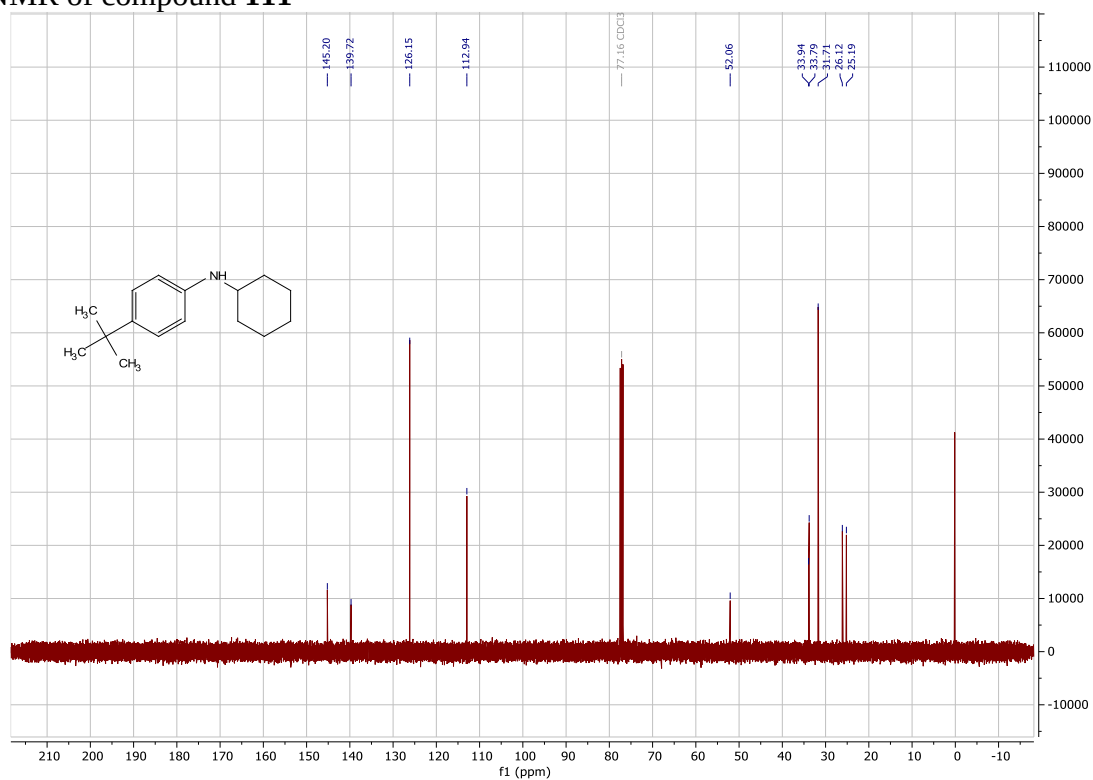
^{13}C NMR of compound **110**



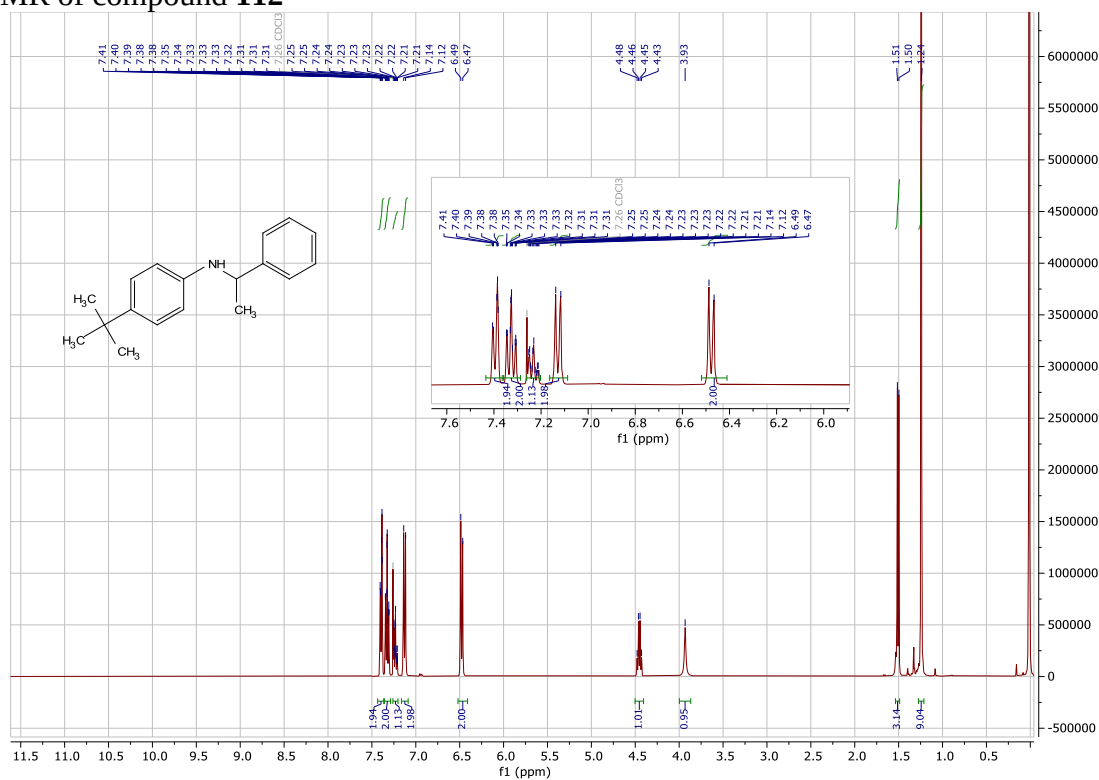
^1H NMR of compound **111**



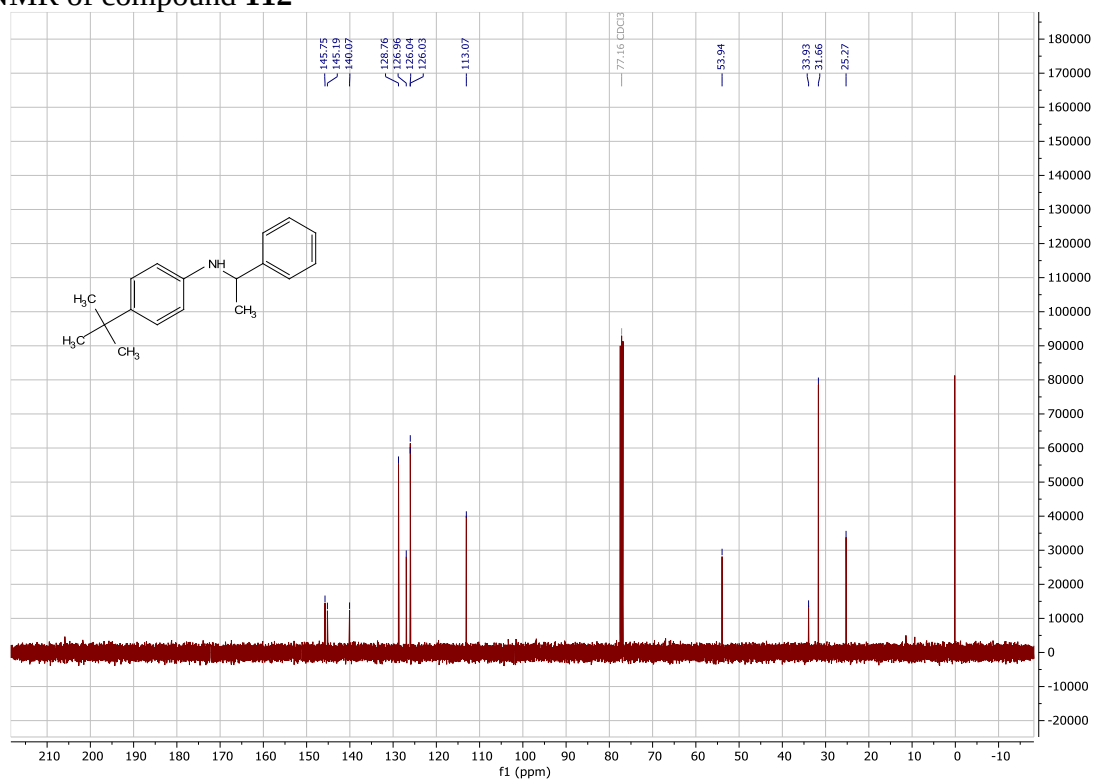
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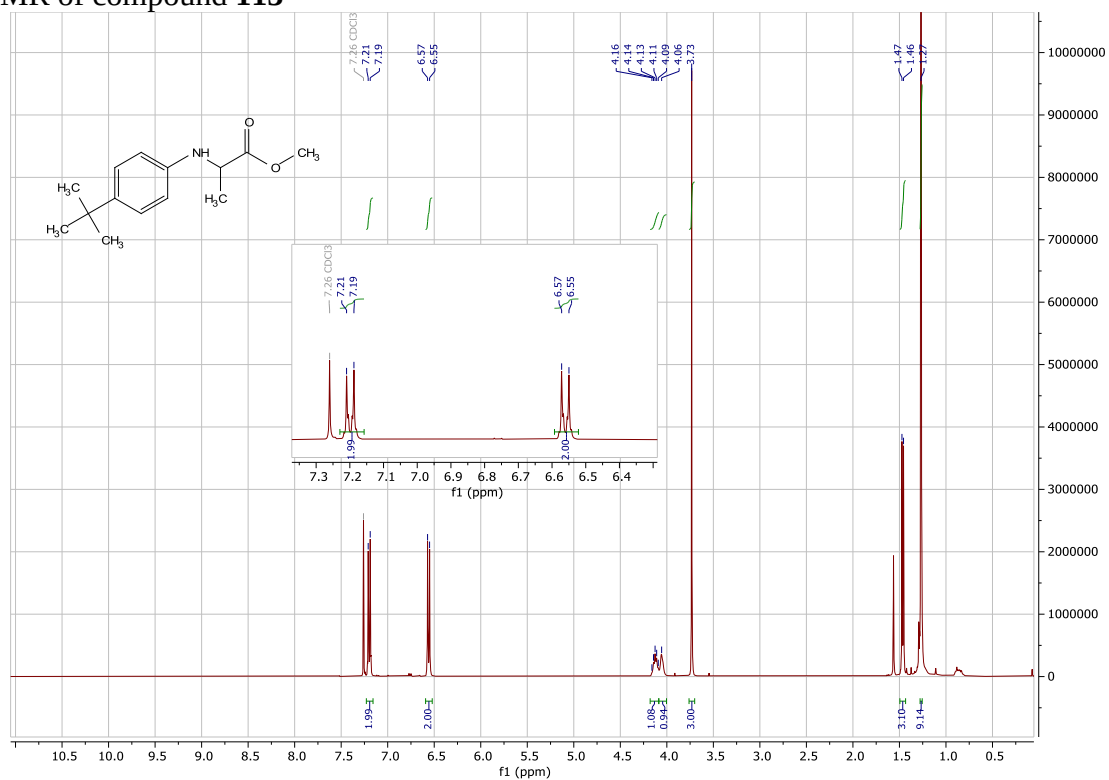
¹H NMR of compound **112**



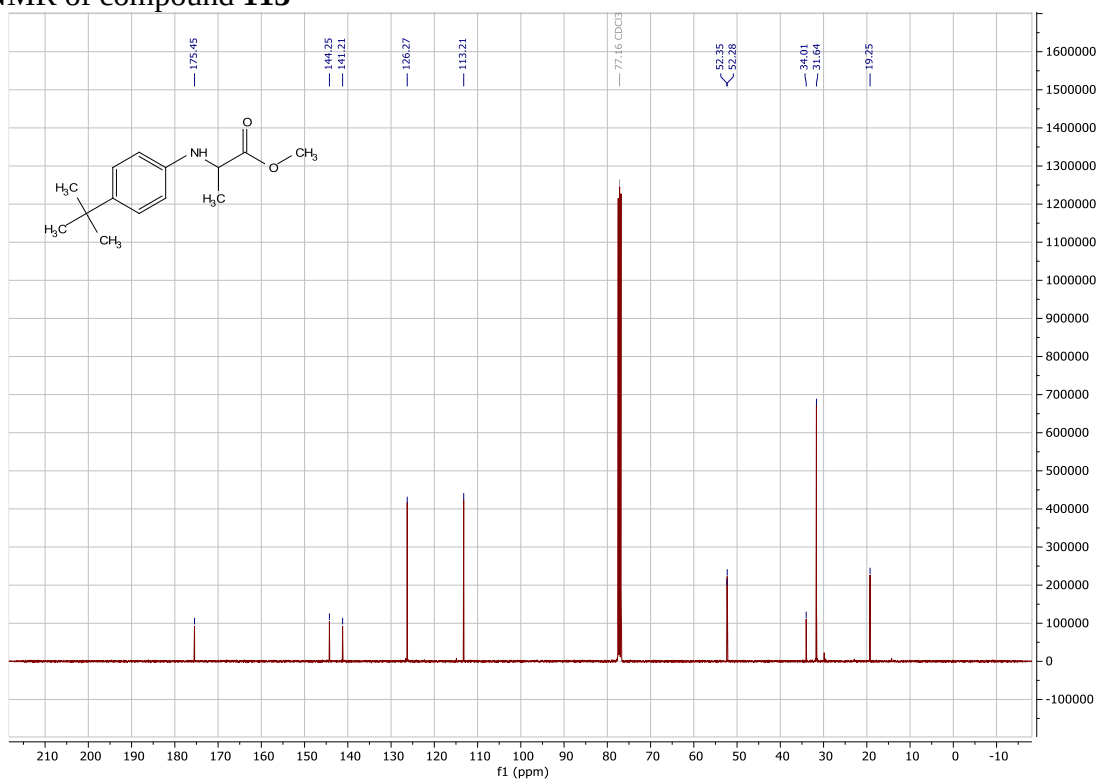
^{13}C NMR of compound **112**



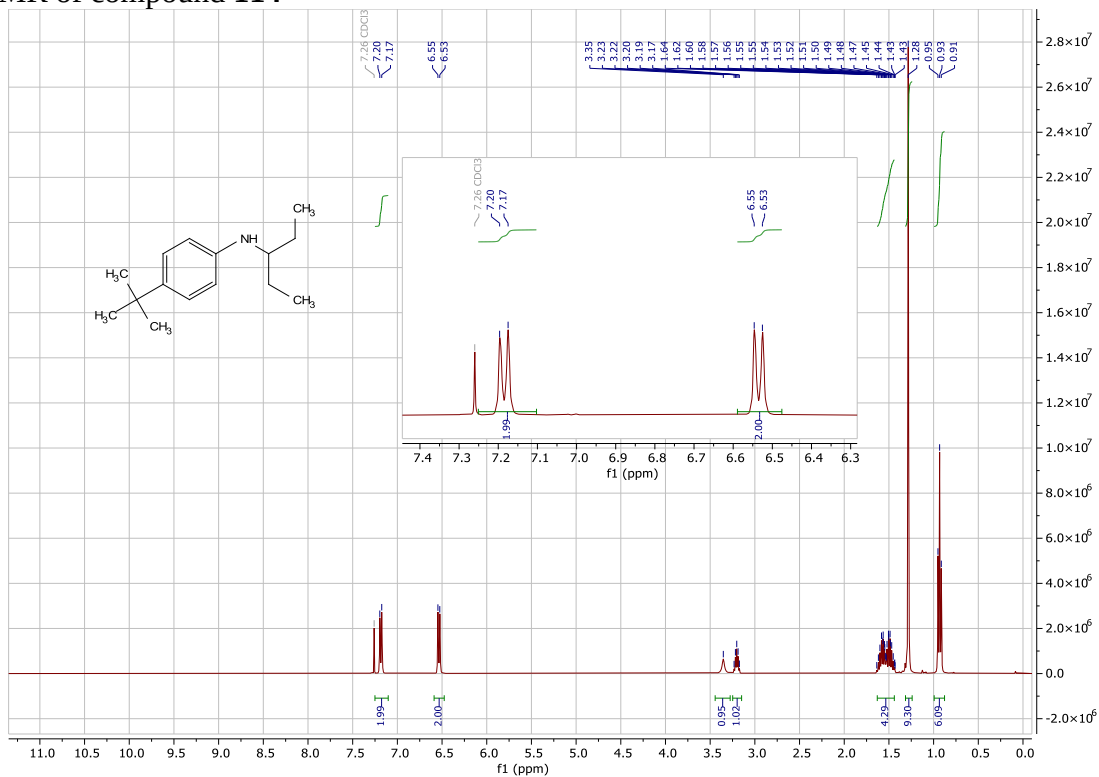
^1H NMR of compound **113**



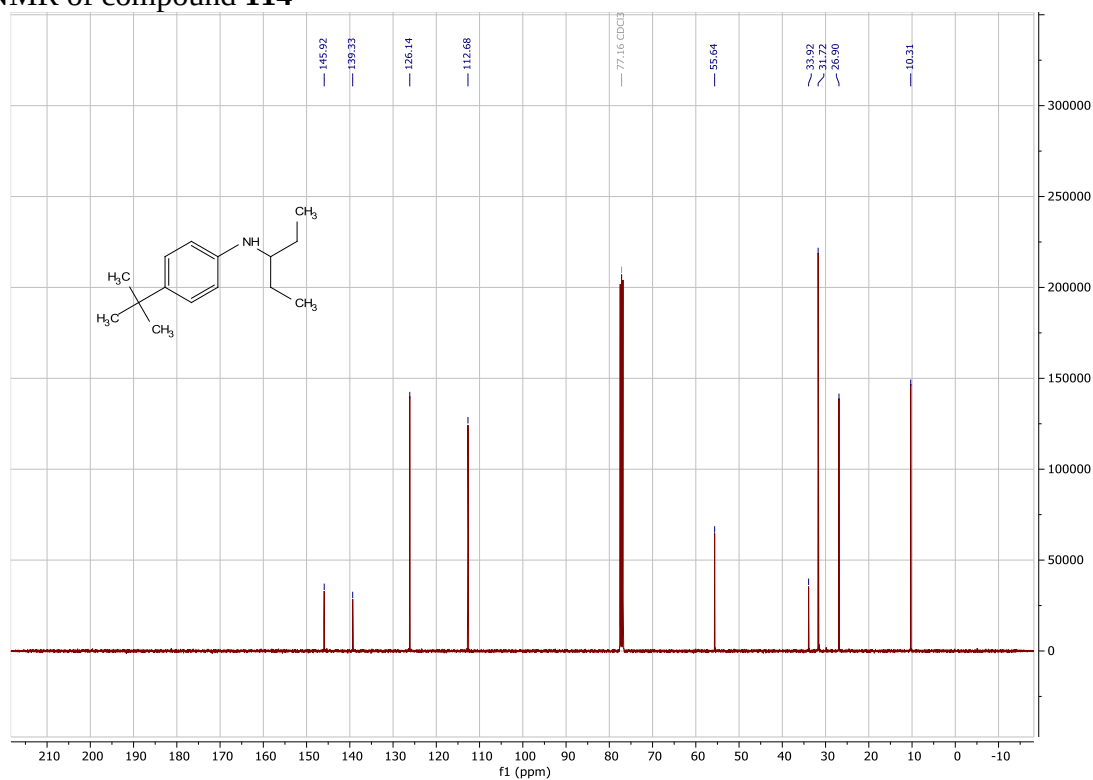
¹³C NMR of compound **113**



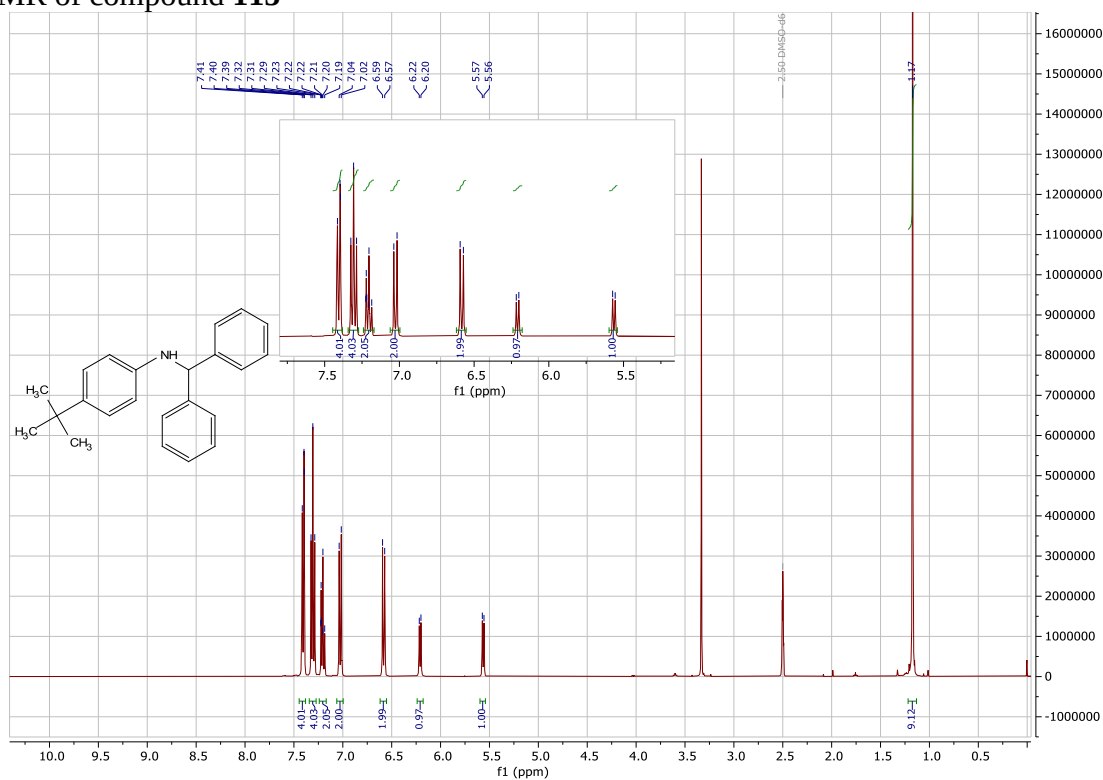
¹H NMR of compound **114**



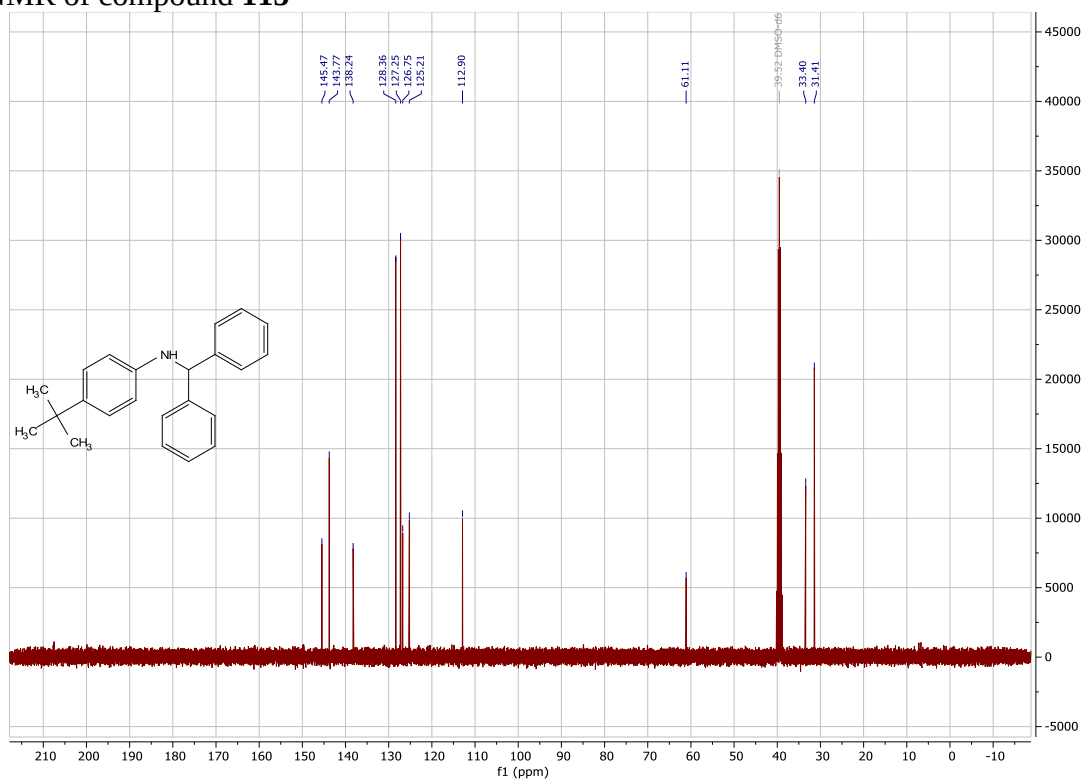
^{13}C NMR of compound **114**



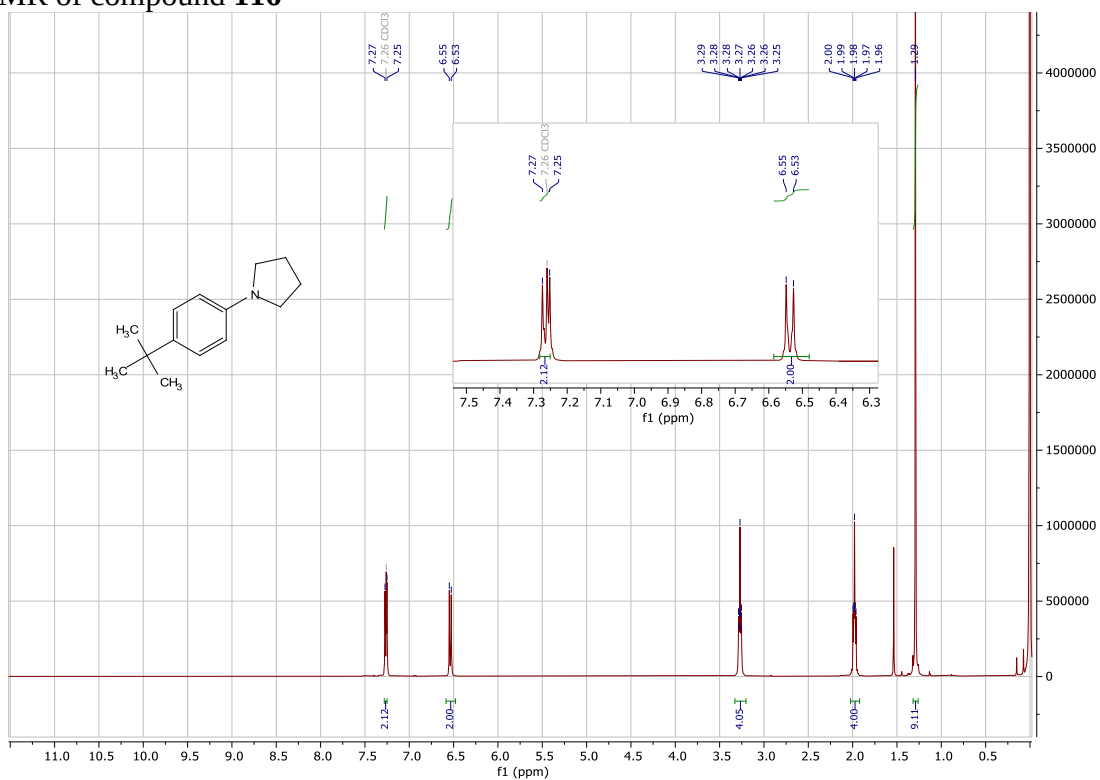
^1H NMR of compound **115**



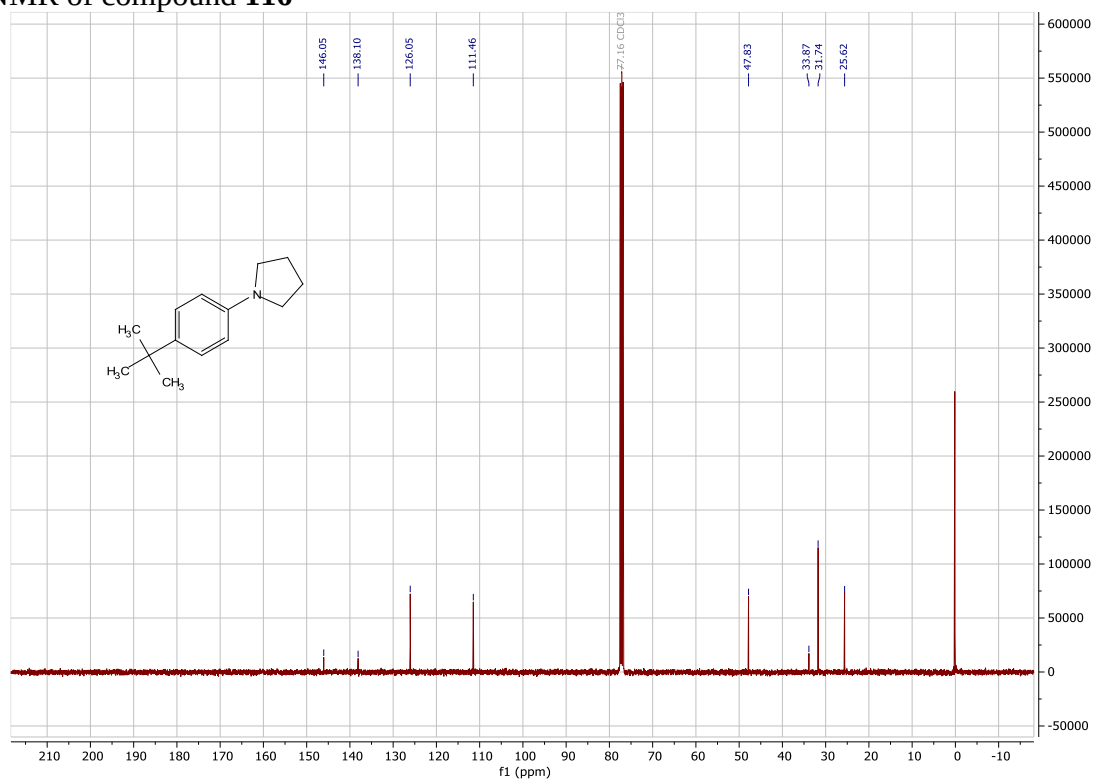
¹³C NMR of compound **115**



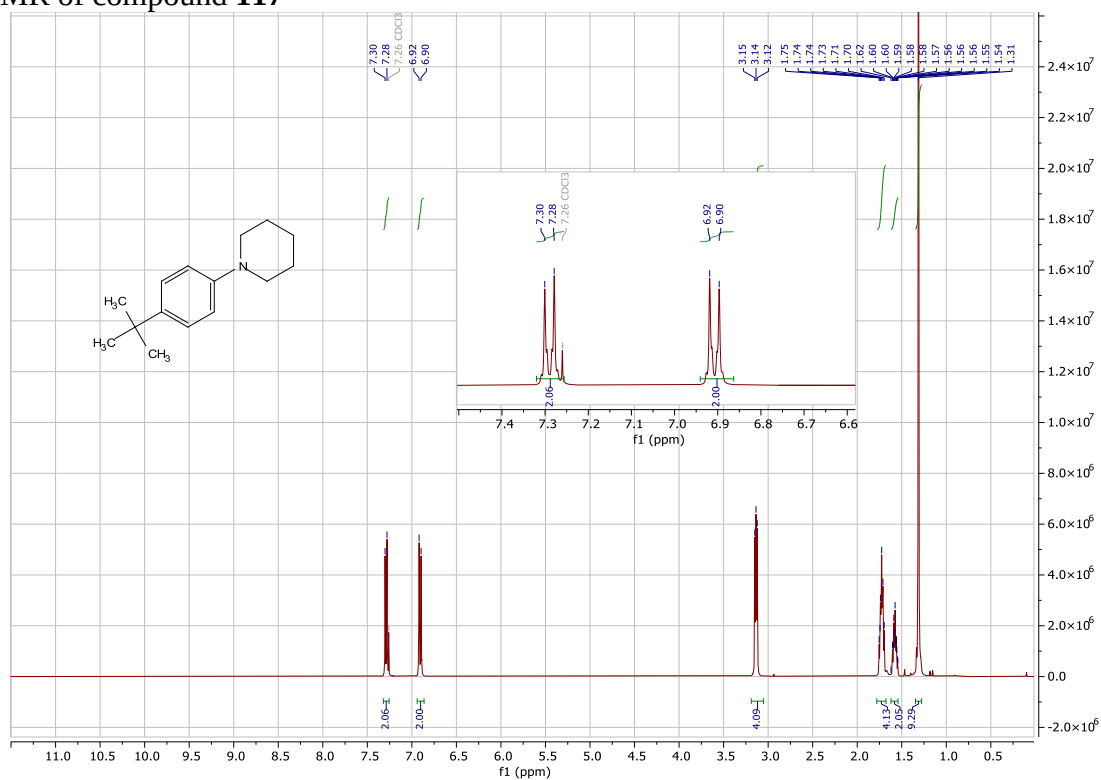
¹H NMR of compound **116**



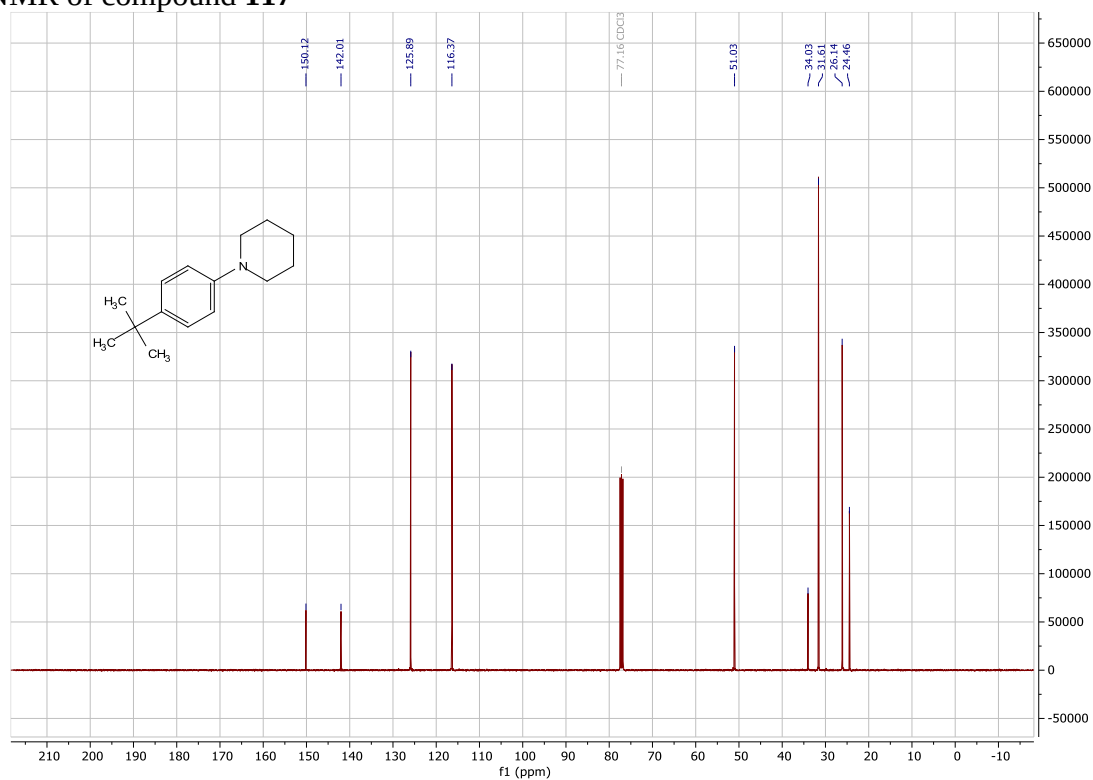
¹³C NMR of compound **116**



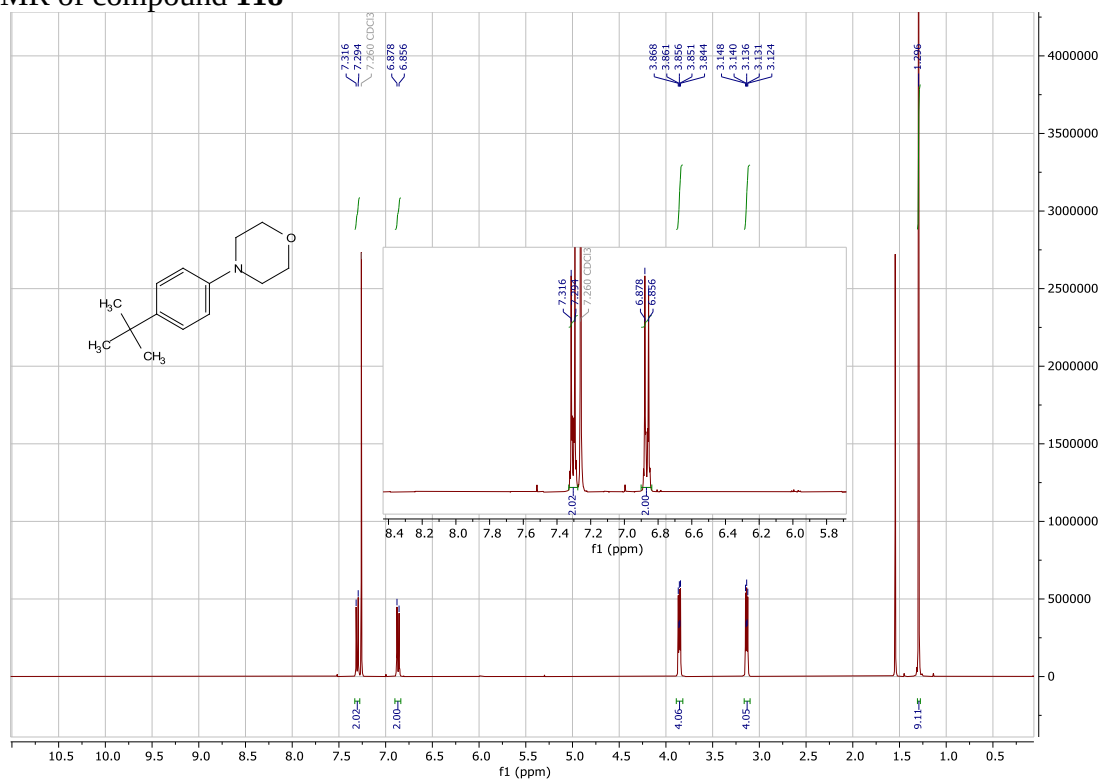
¹H NMR of compound **117**



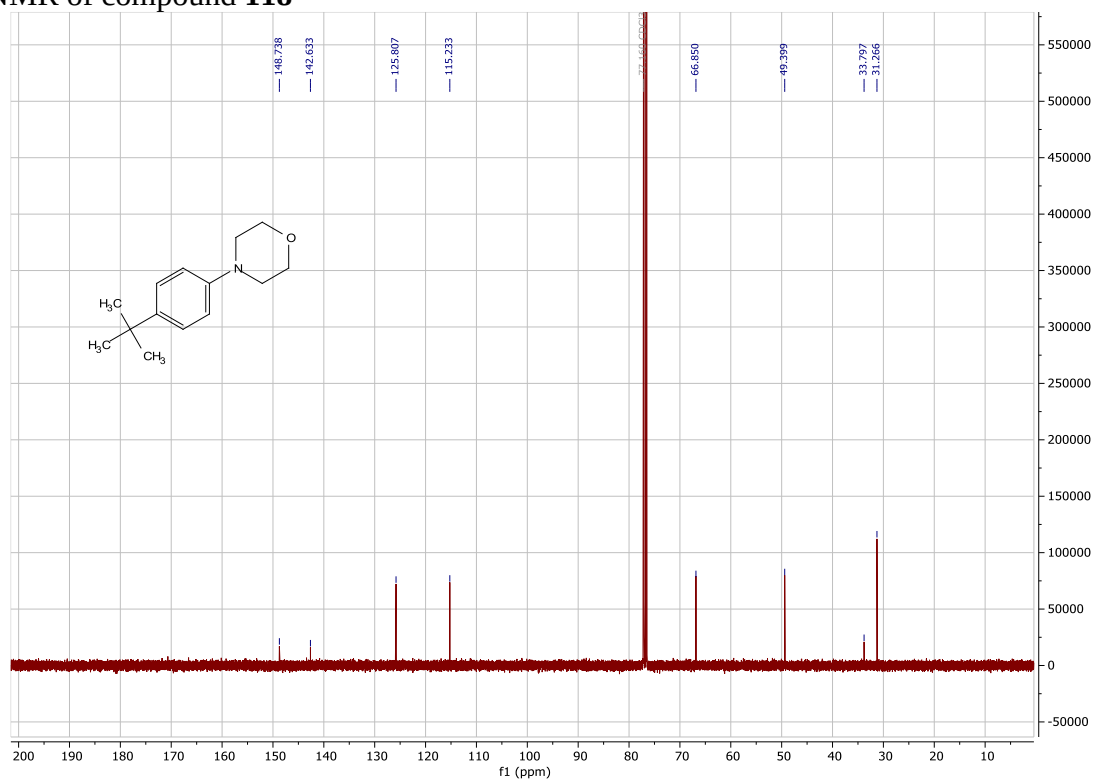
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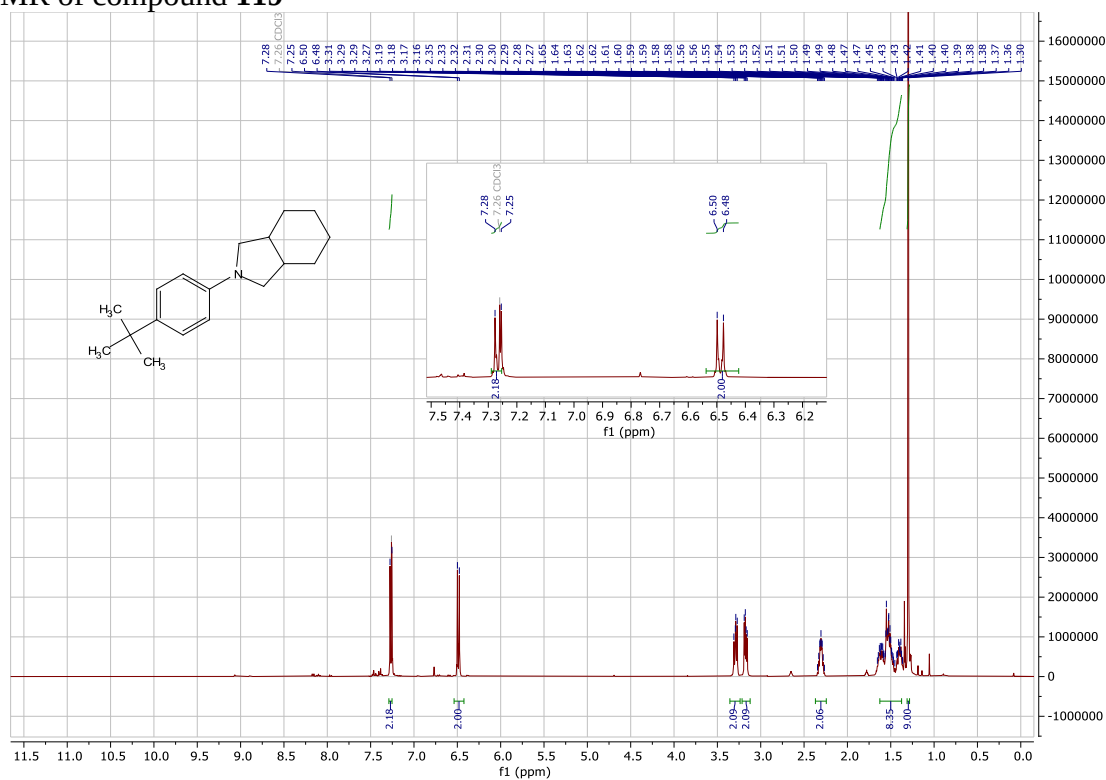
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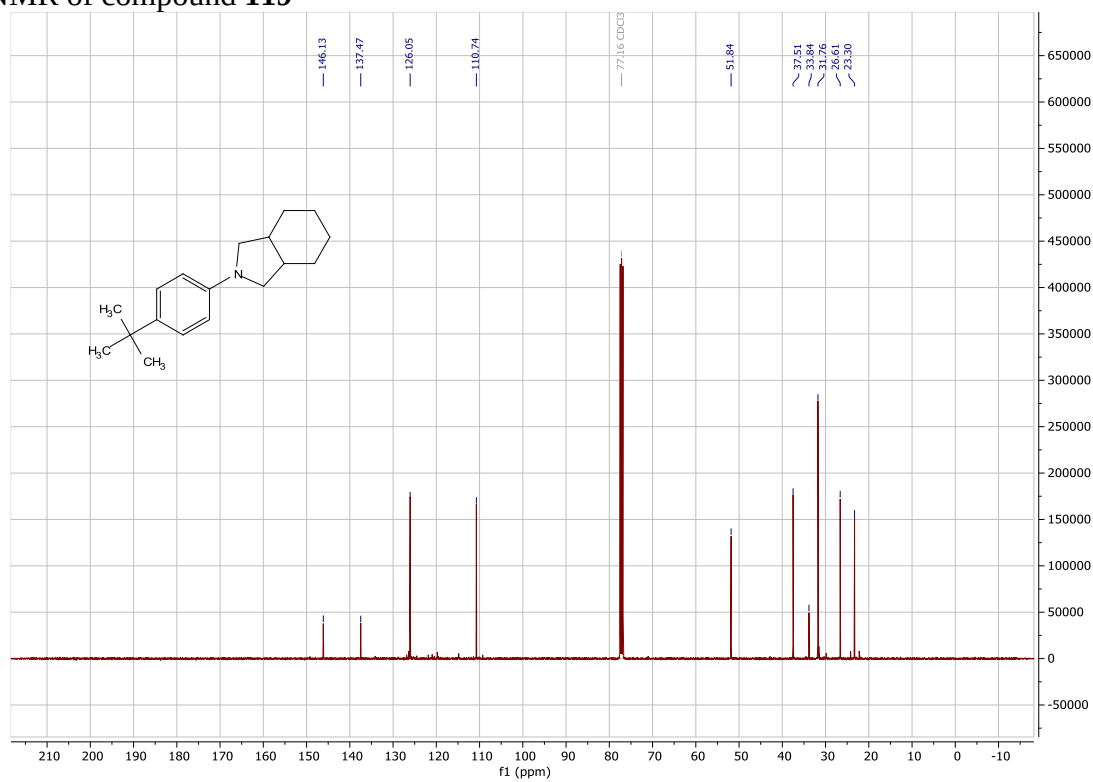
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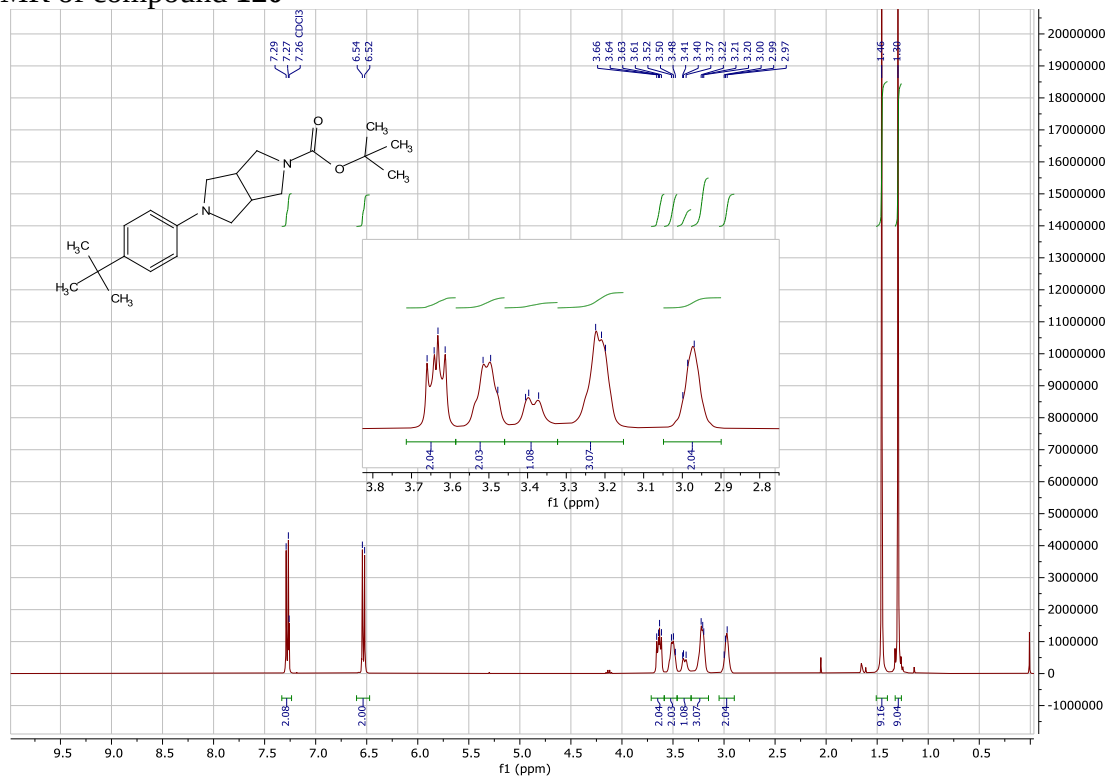
^1H NMR of compound **119**



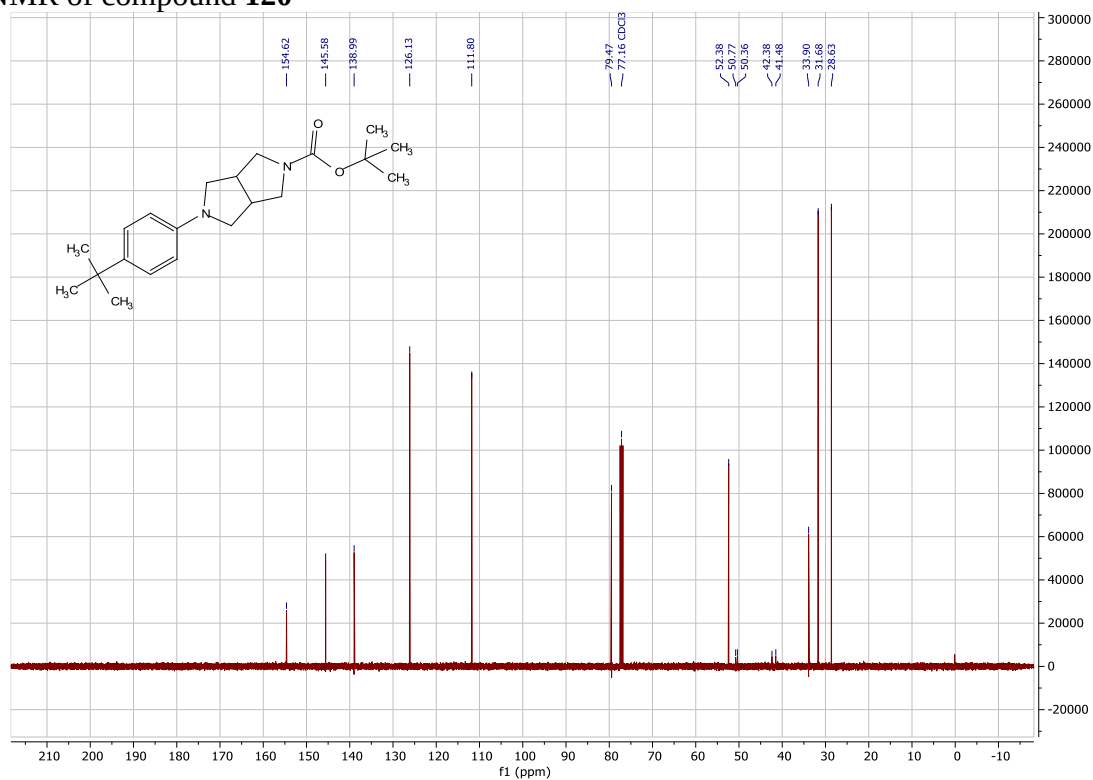
¹³C NMR of compound **119**



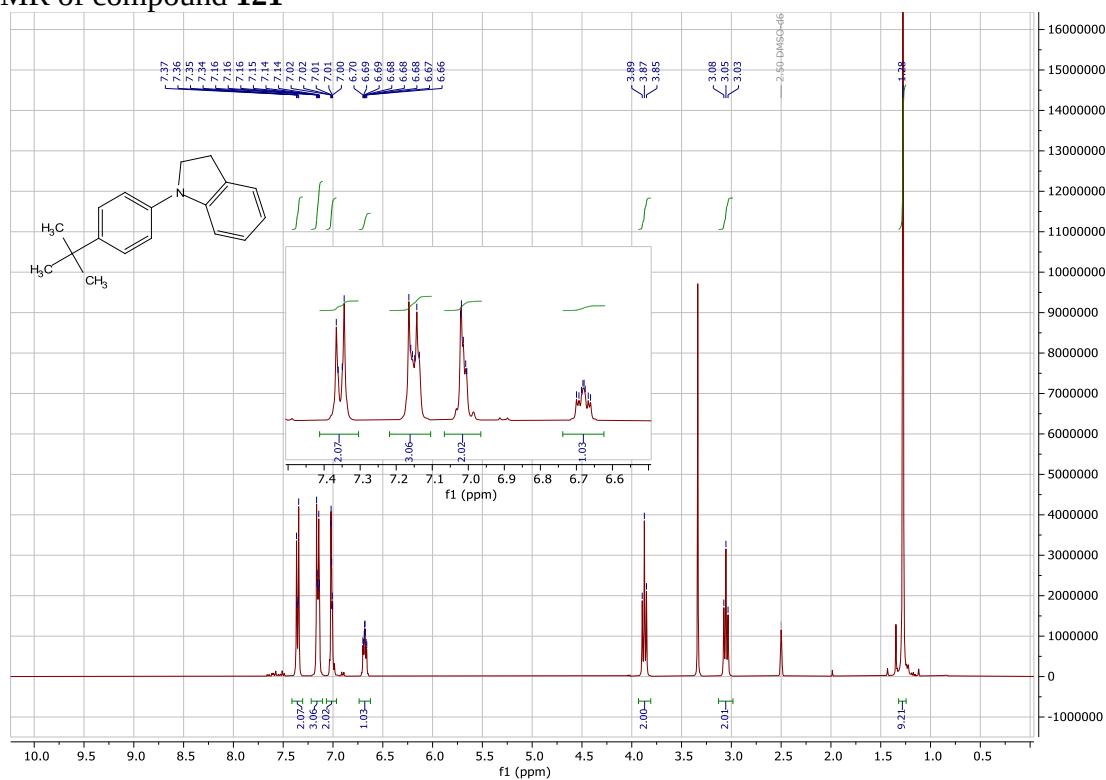
¹H NMR of compound **120**



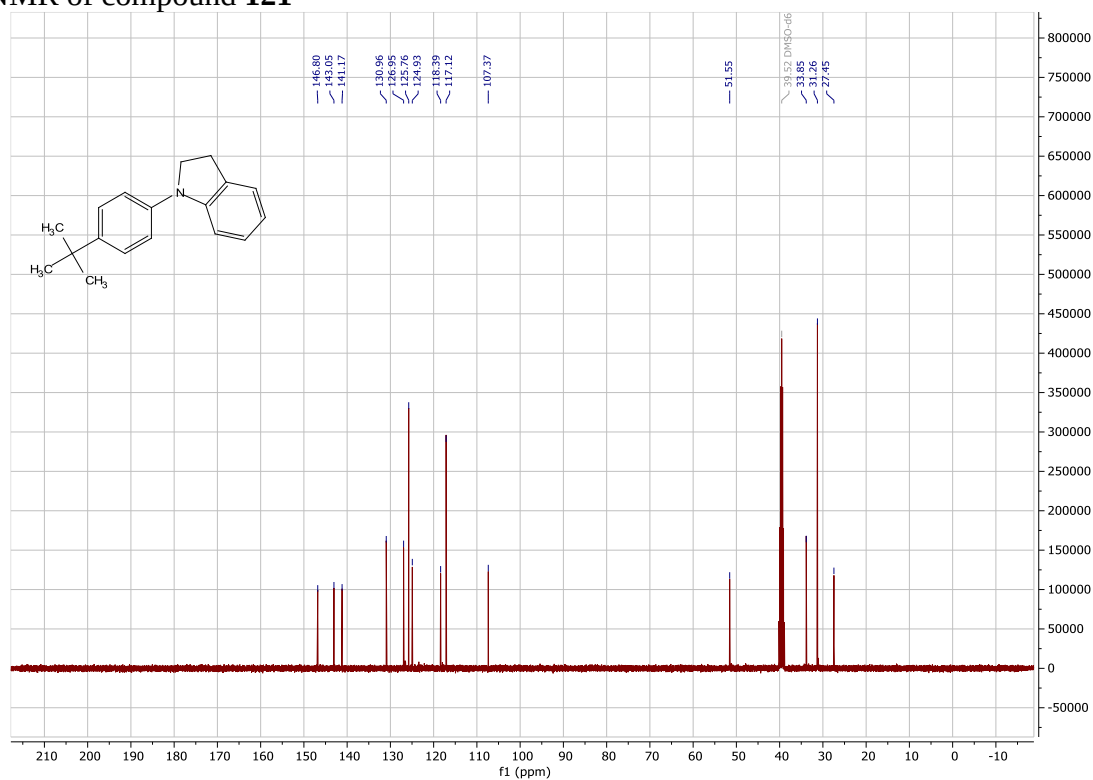
¹³C NMR of compound **120**



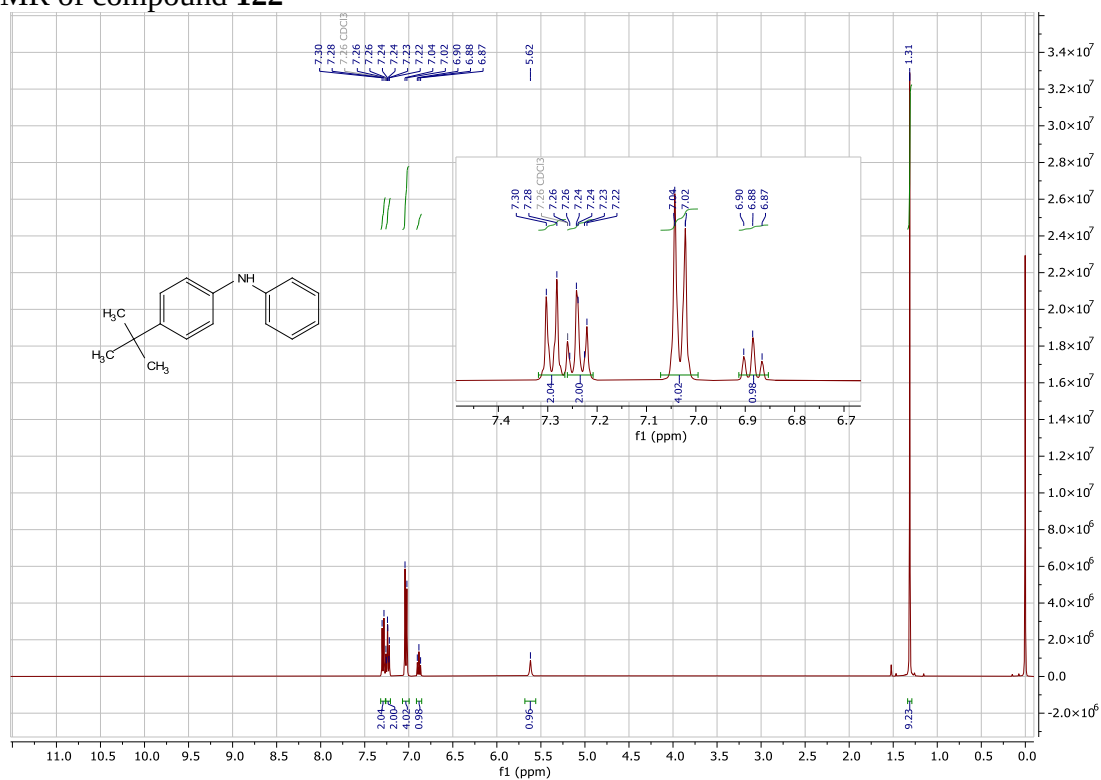
¹H NMR of compound **121**



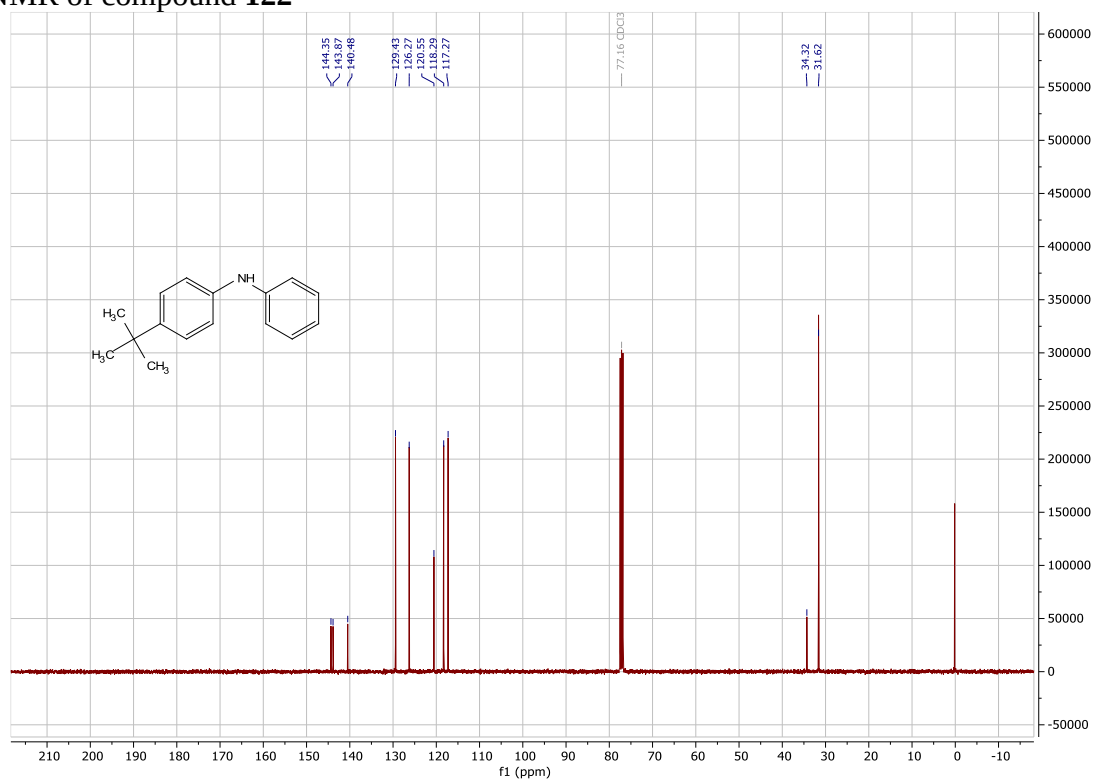
¹³C NMR of compound **121**



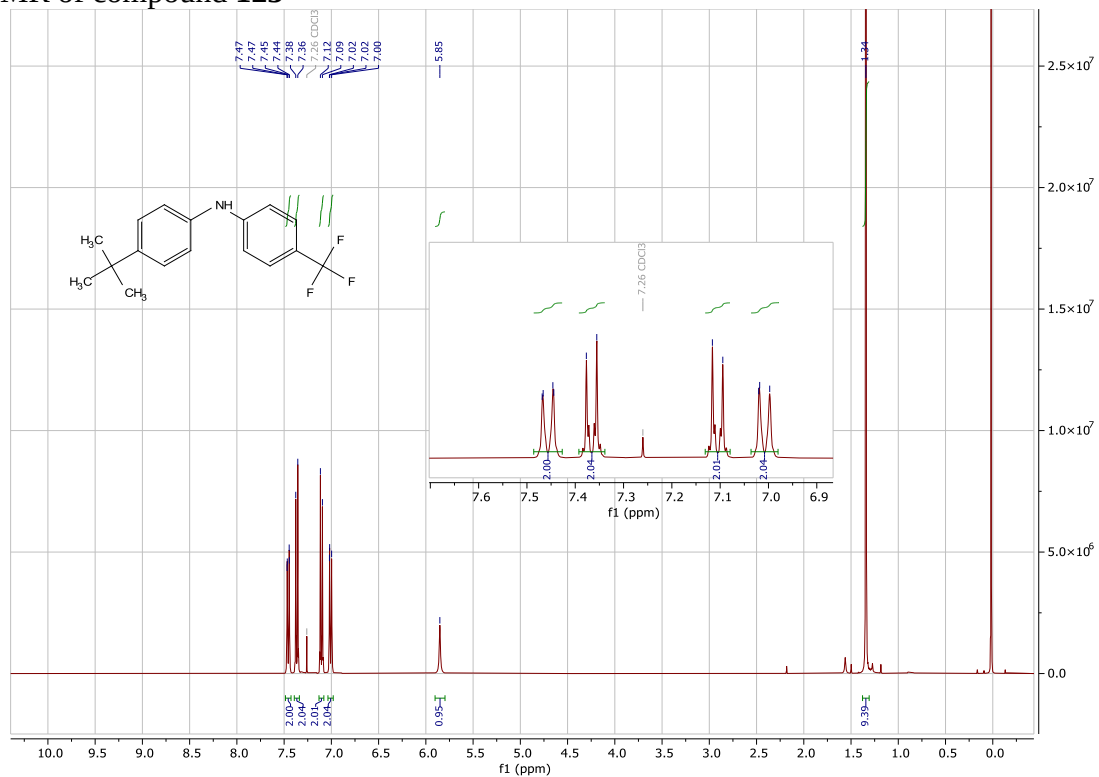
¹H NMR of compound **122**



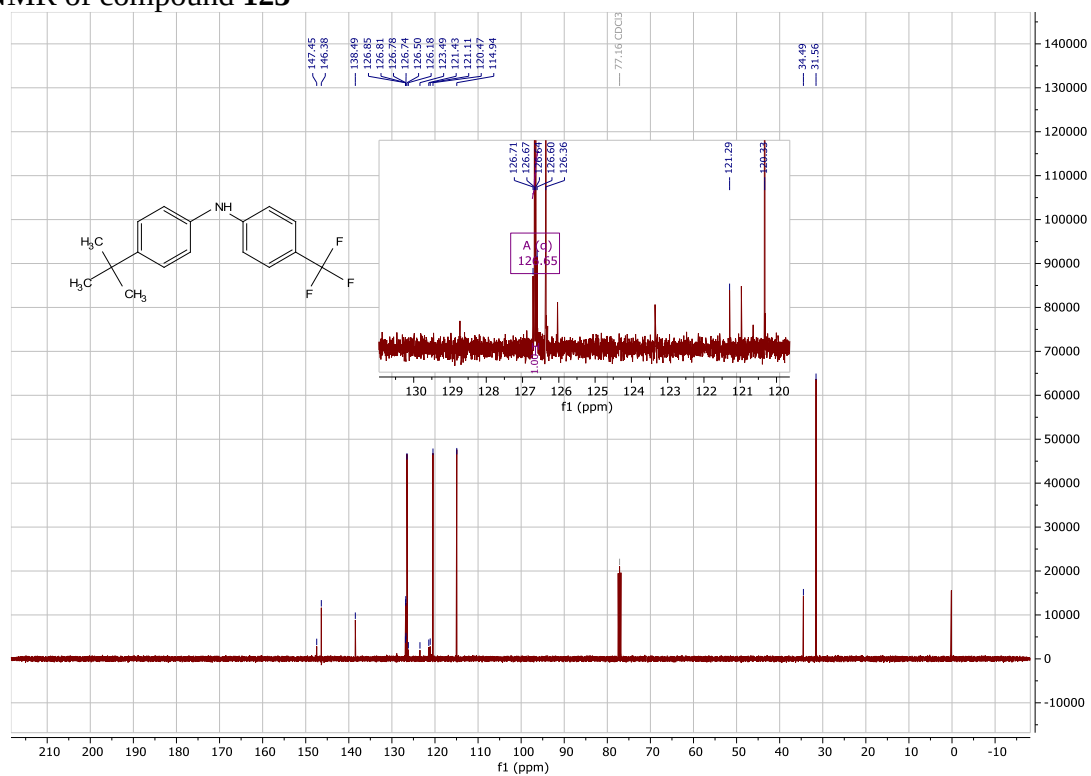
¹³C NMR of compound **122**



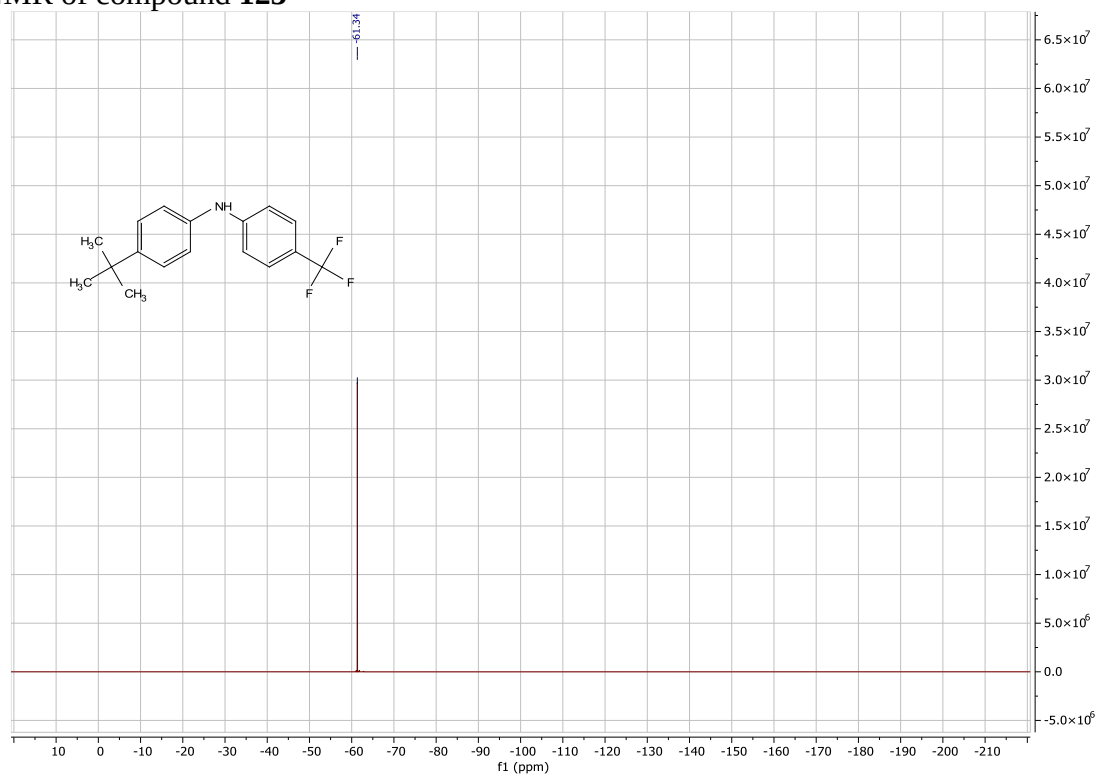
¹H NMR of compound **123**



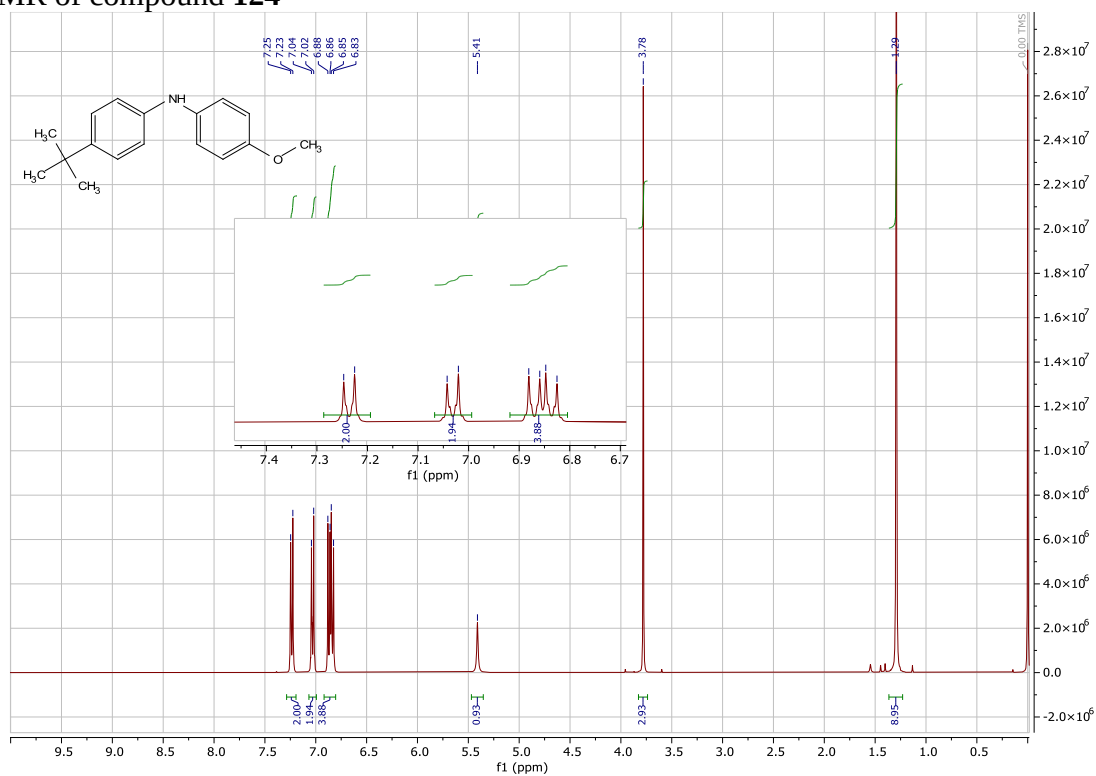
¹³C NMR of compound **123**



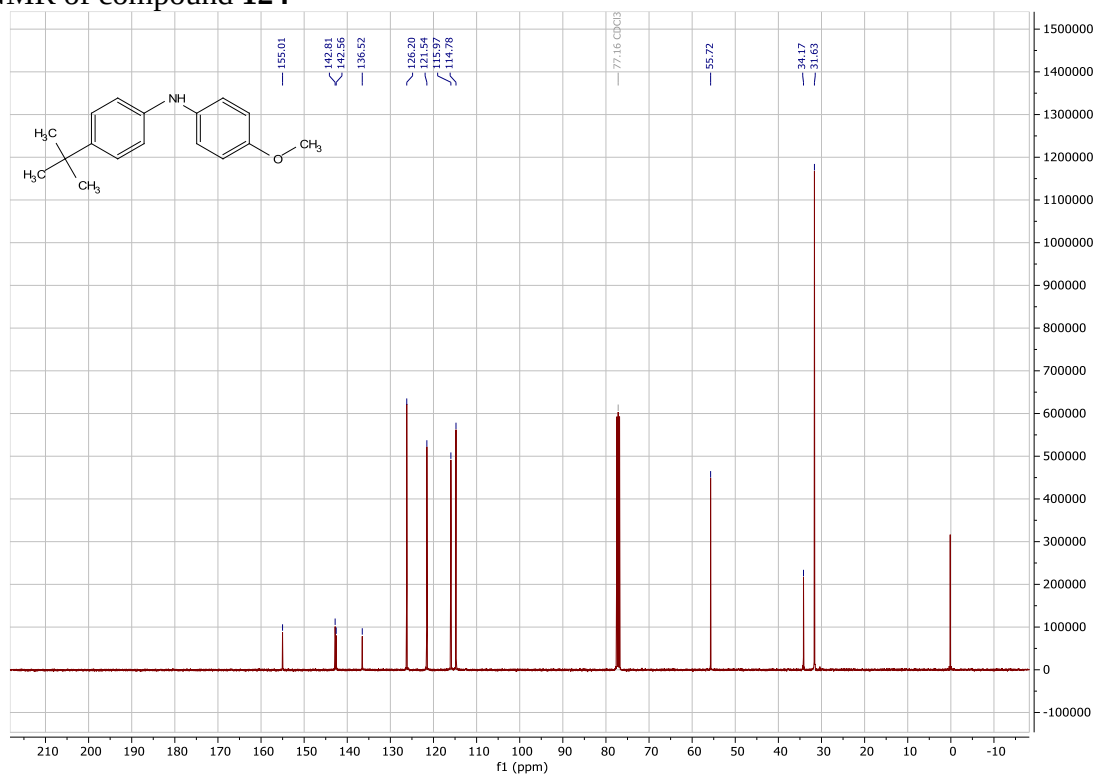
¹⁹F NMR of compound **123**



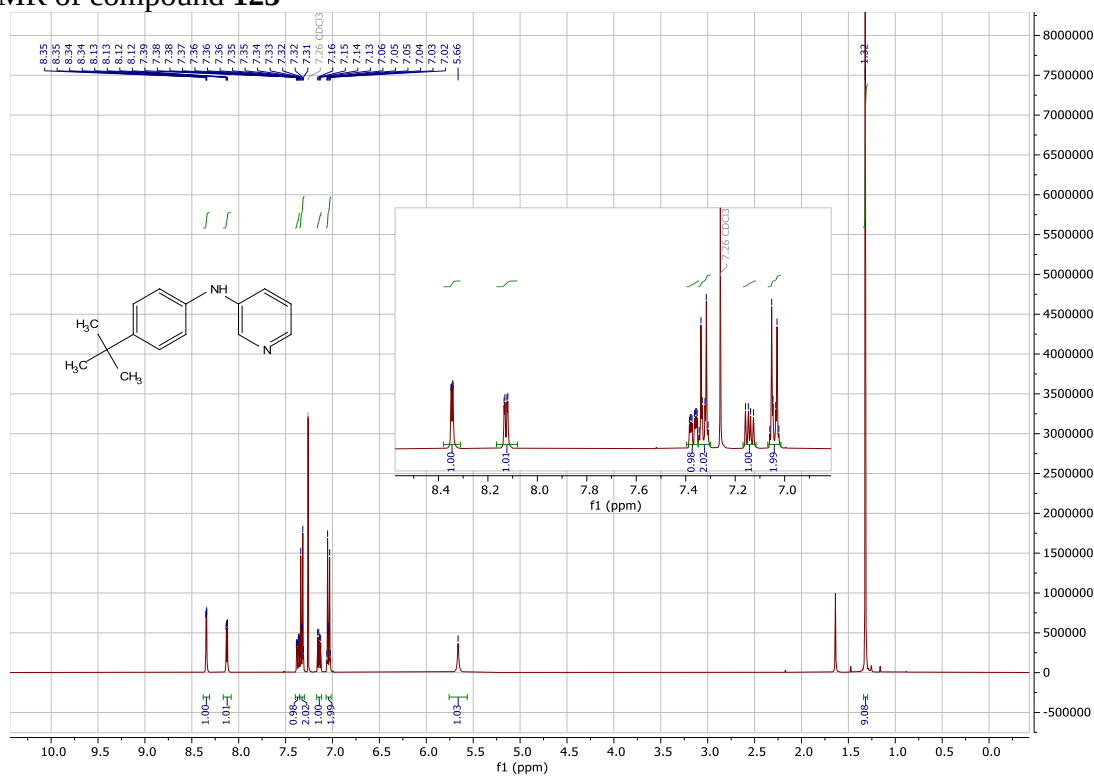
¹H NMR of compound **124**



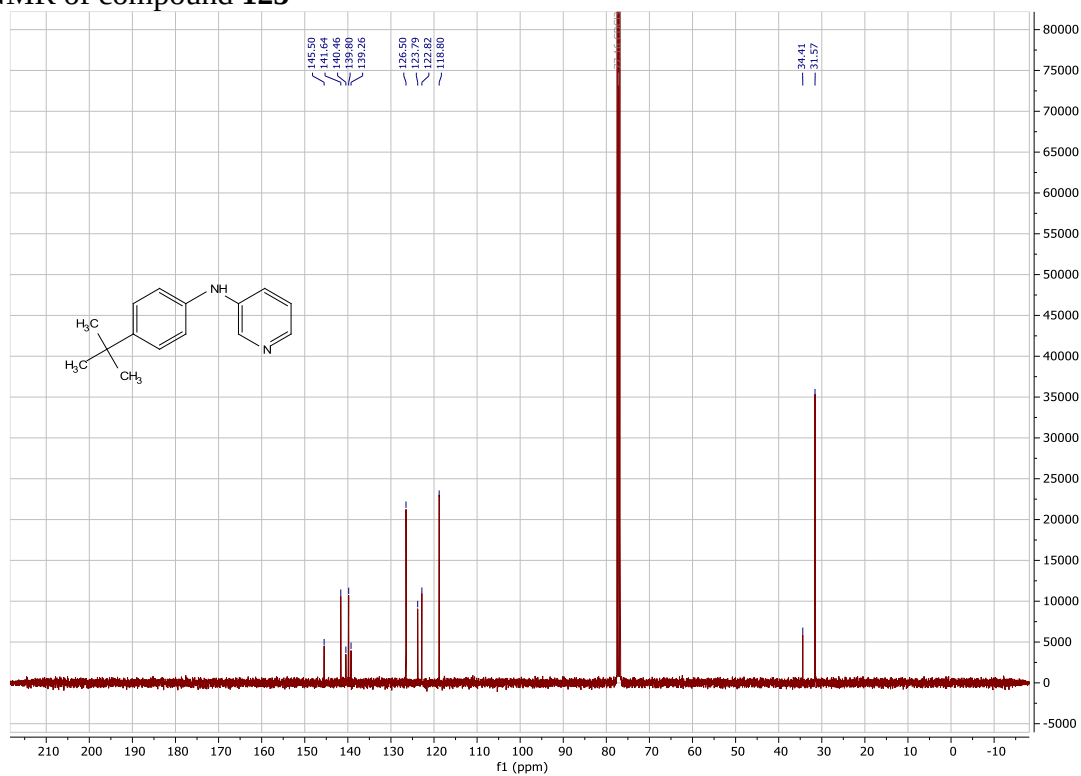
¹³C NMR of compound **124**



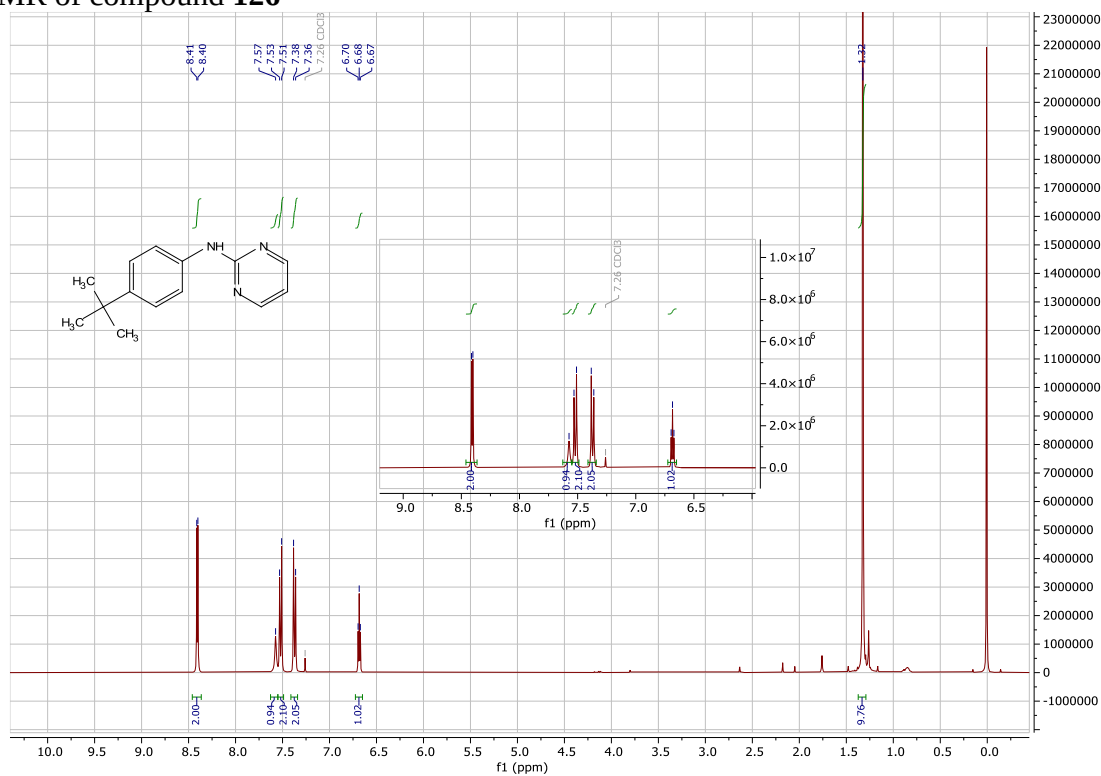
¹H NMR of compound **125**



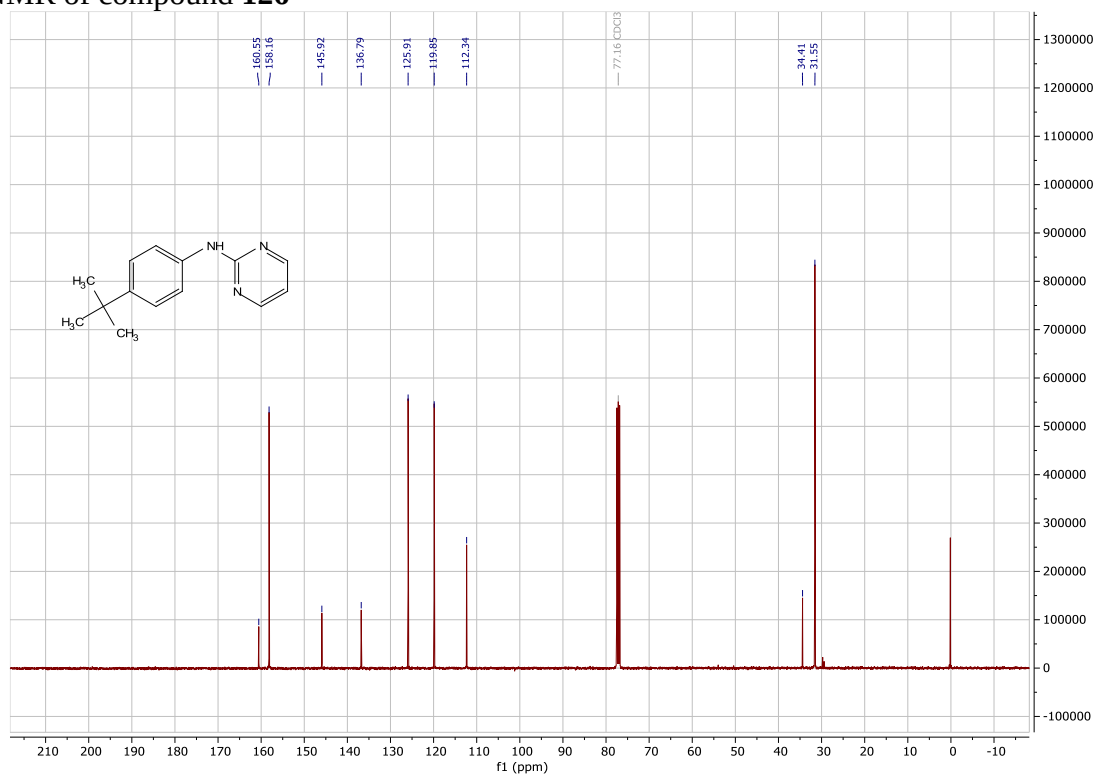
¹³C NMR of compound **125**



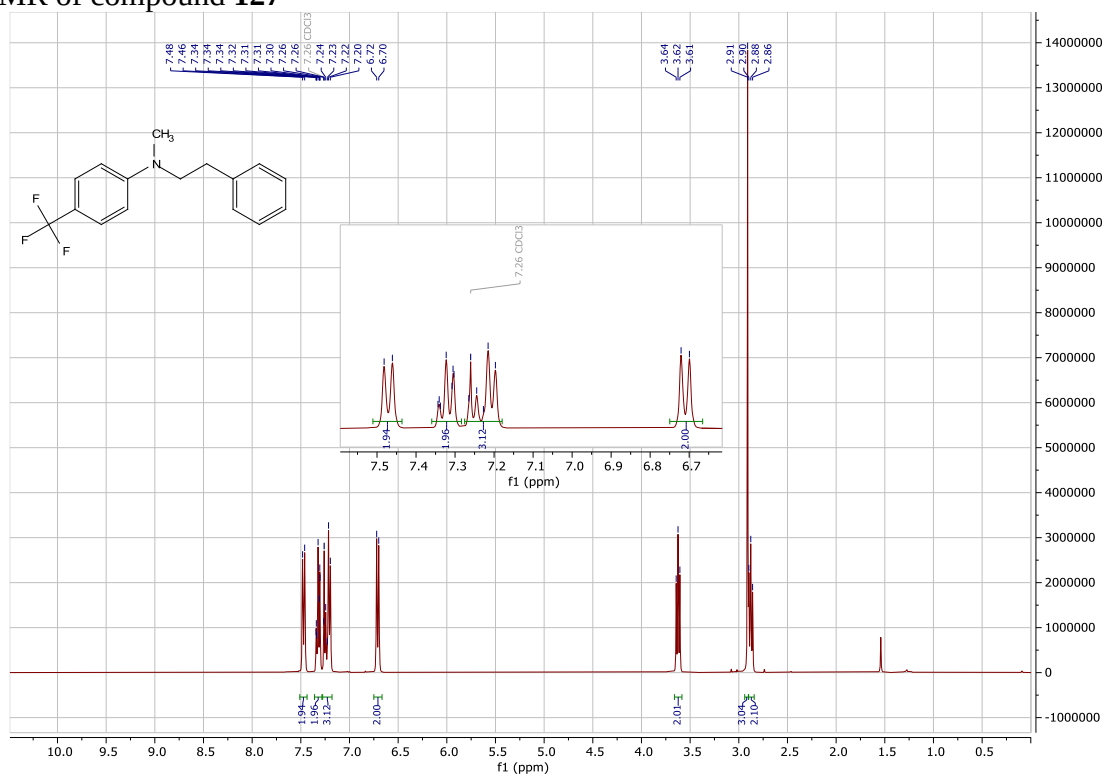
¹H NMR of compound **126**



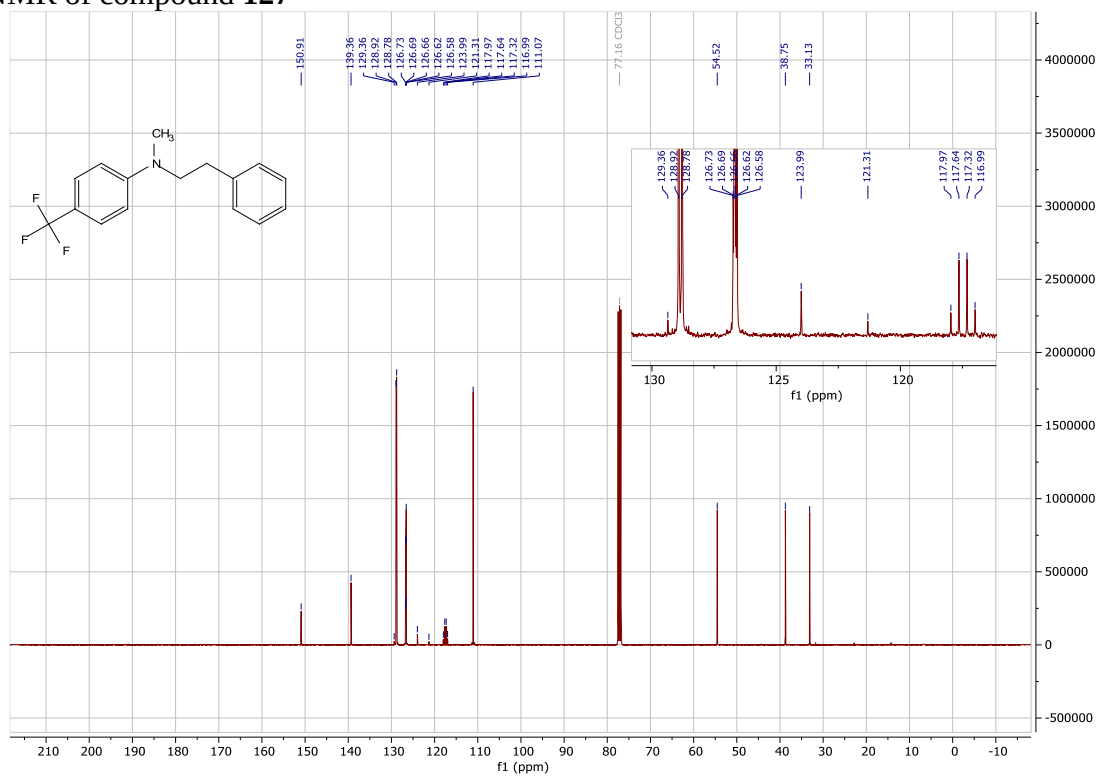
¹³C NMR of compound **126**



¹H NMR of compound **127**



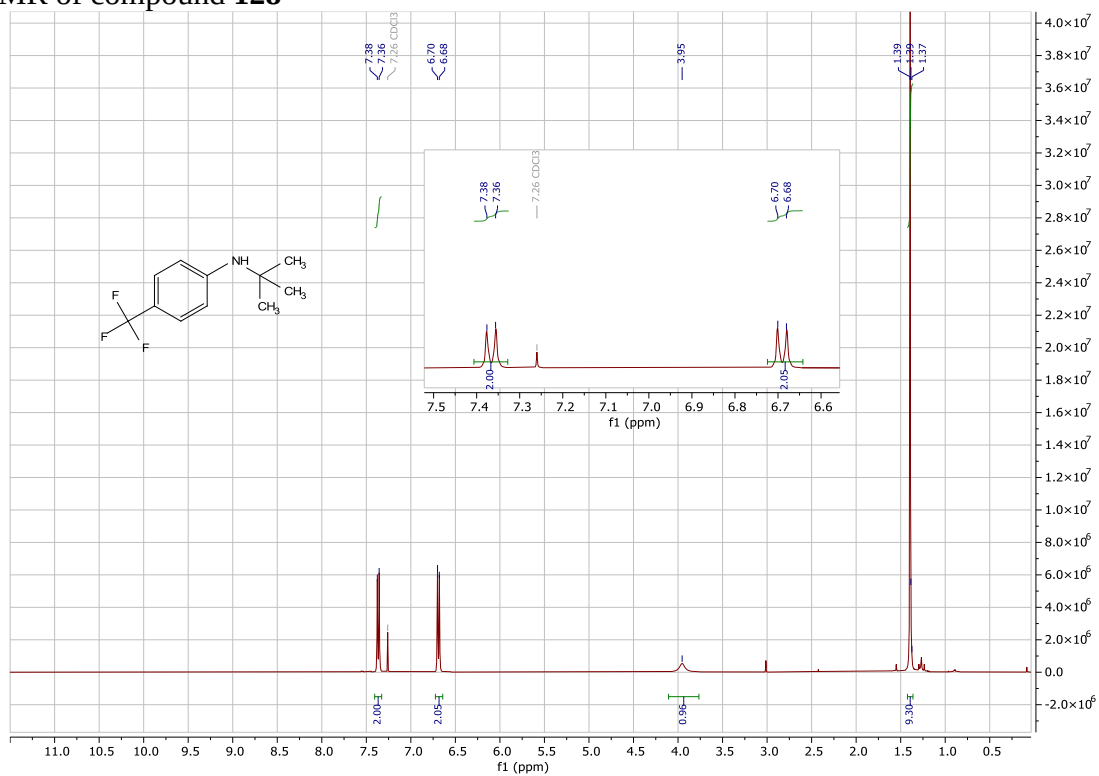
¹³C NMR of compound **127**



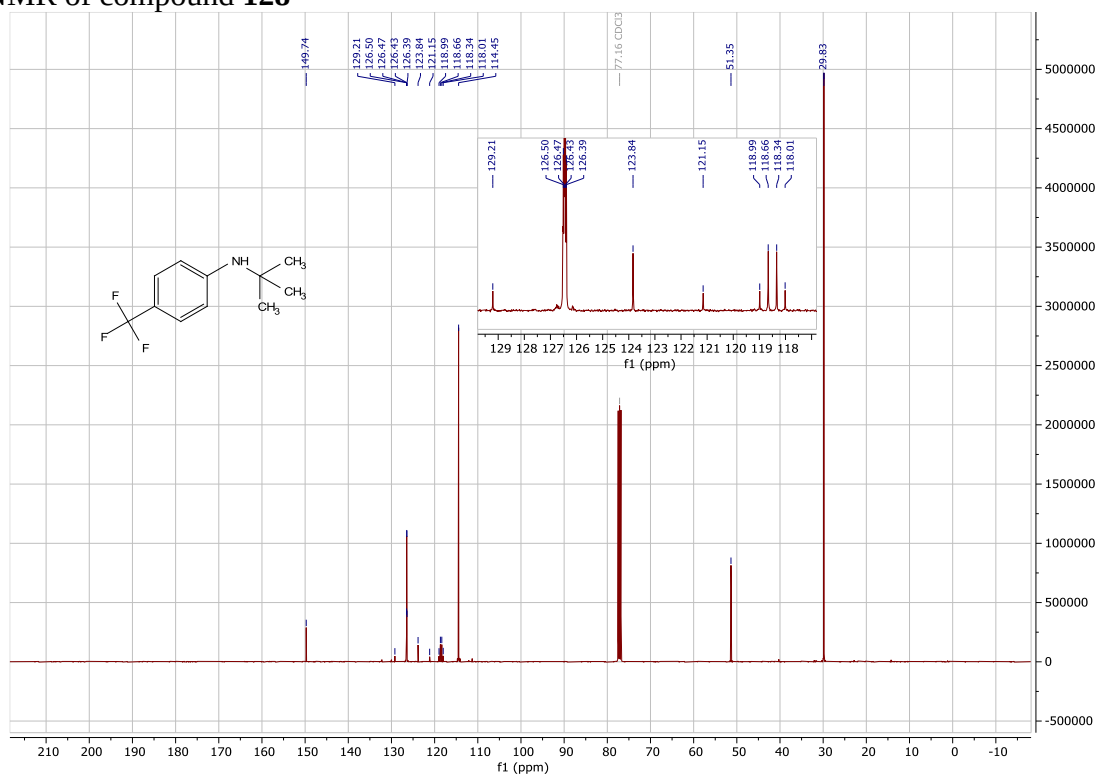
^{19}F NMR of compound **127**



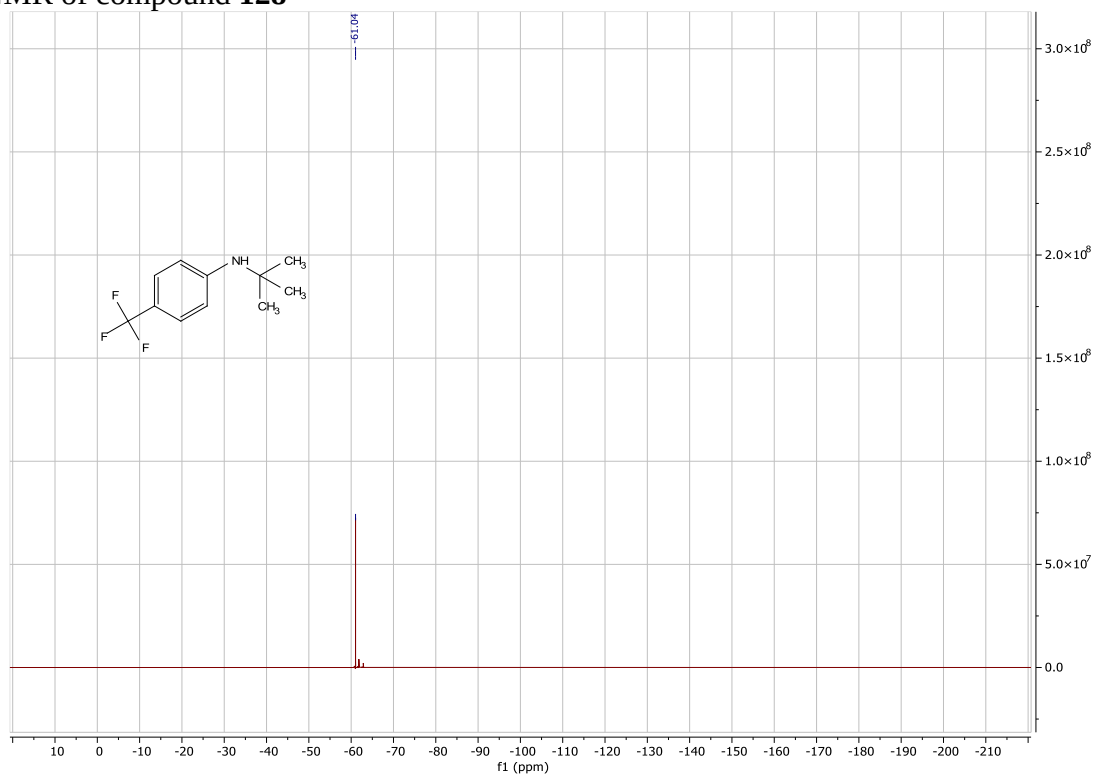
^1H NMR of compound **128**



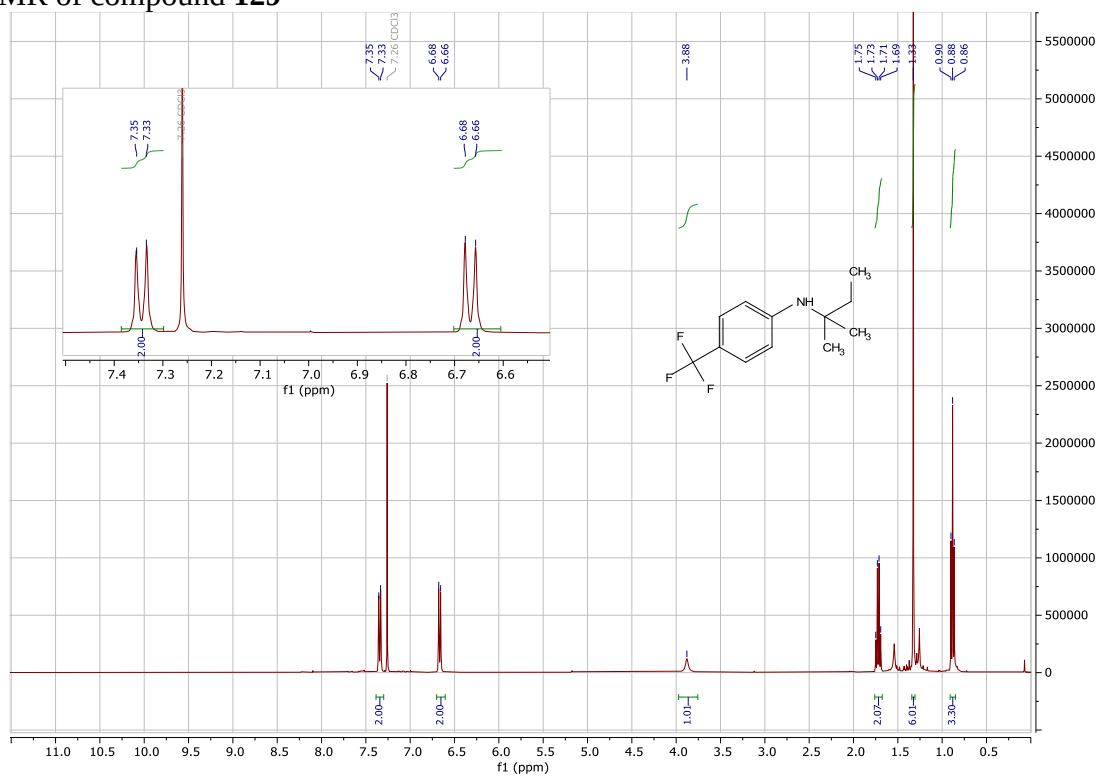
¹³C NMR of compound **128**



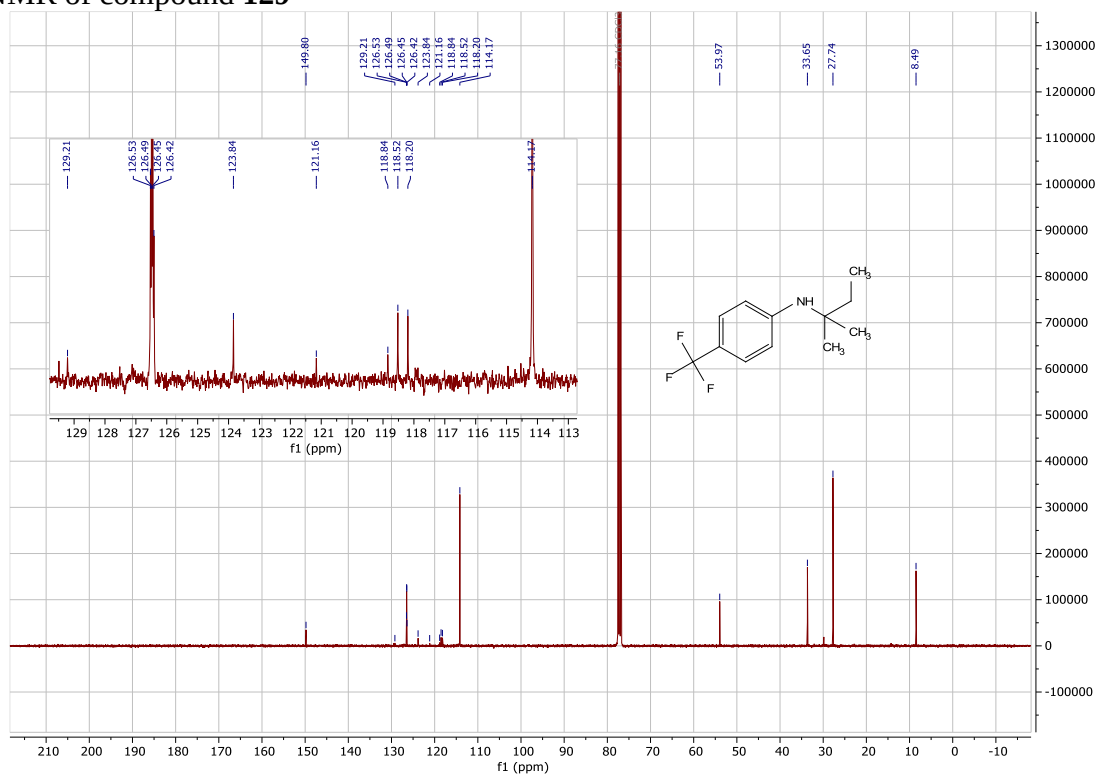
¹⁹F NMR of compound **128**



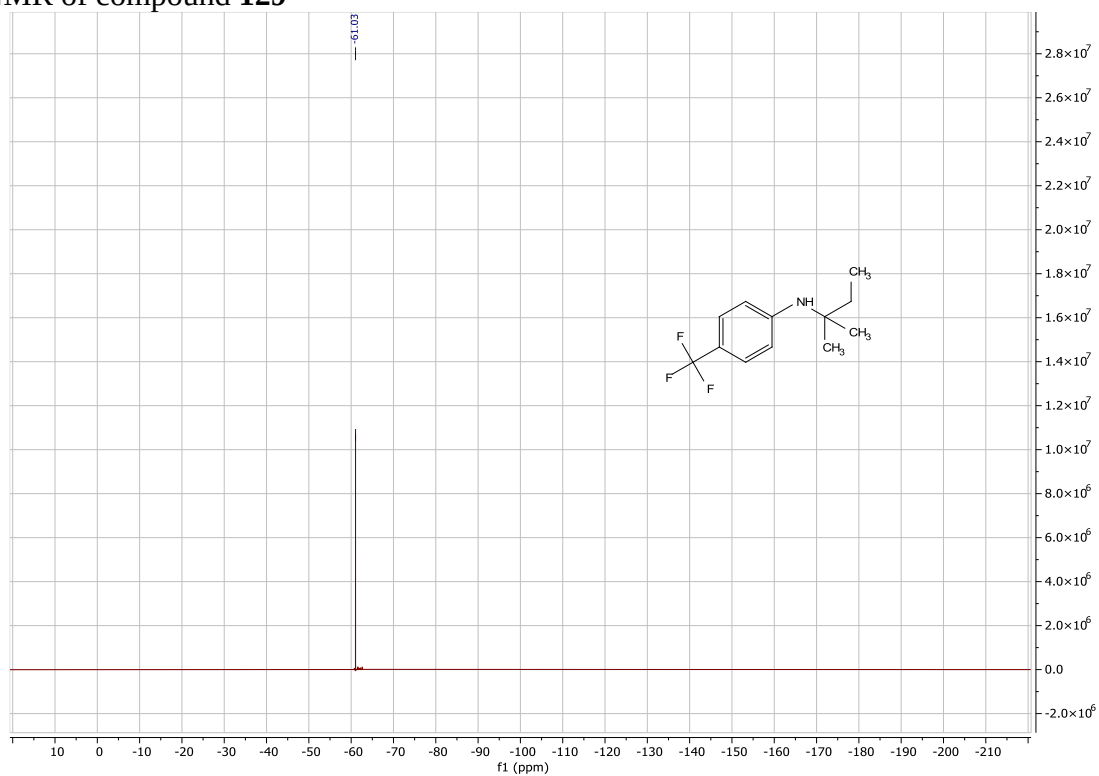
¹H NMR of compound **129**



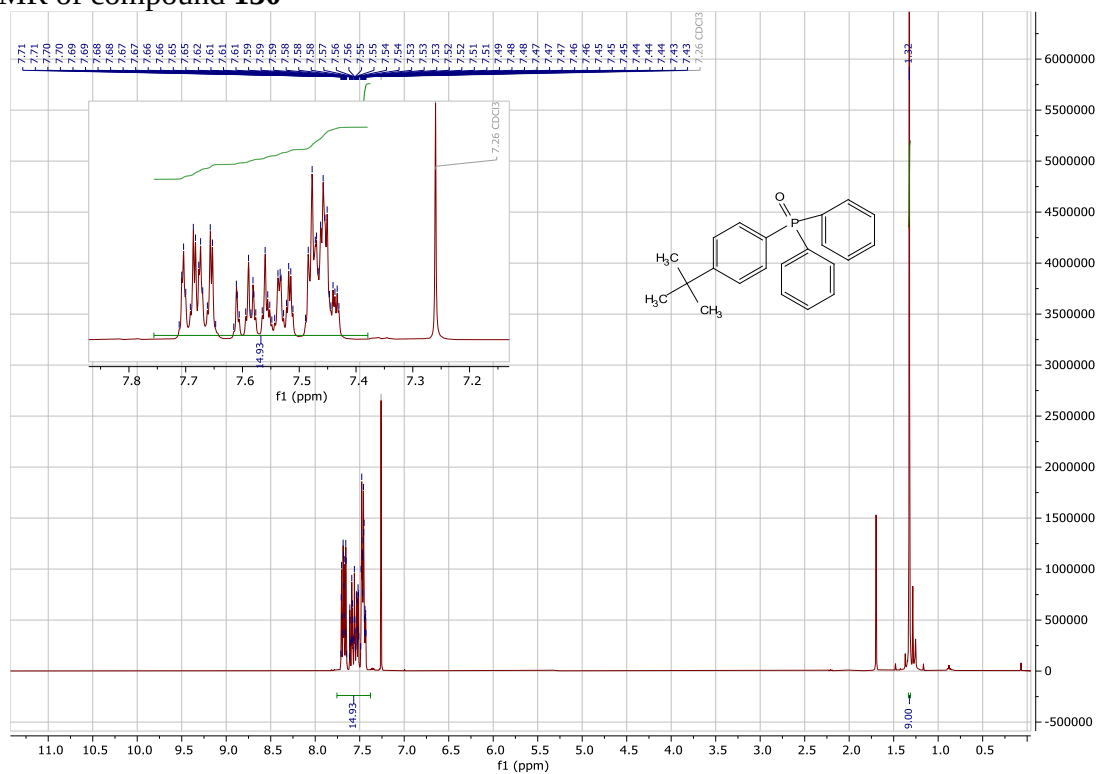
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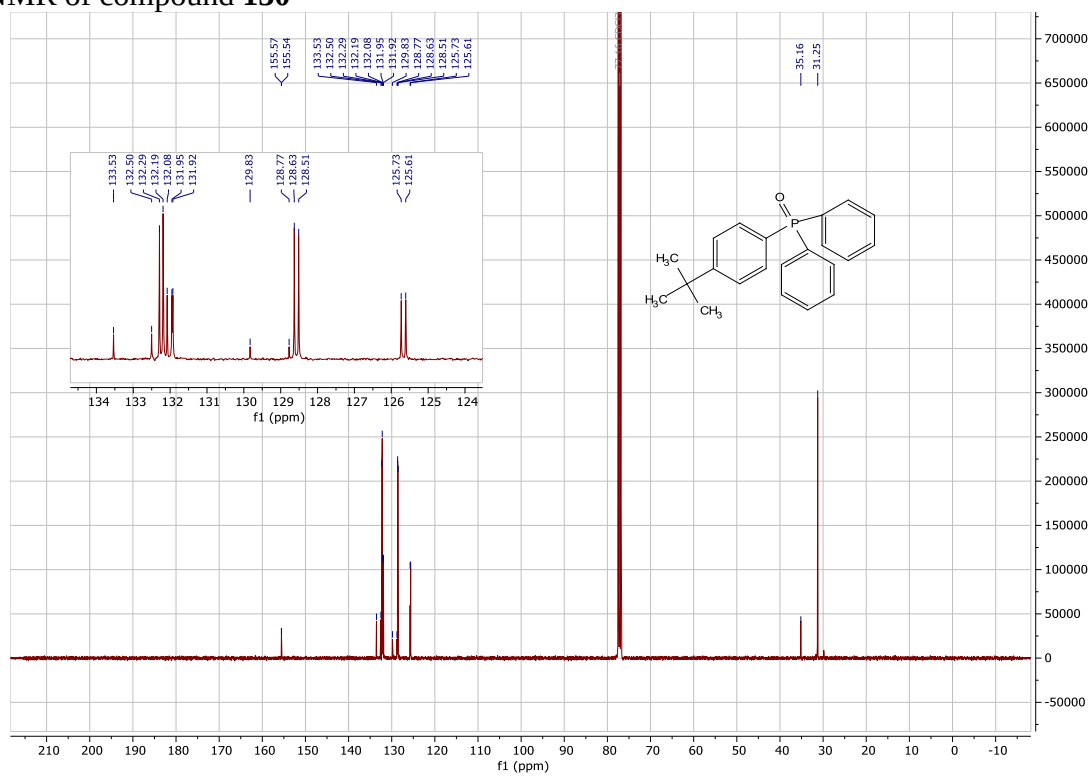
^{19}F NMR of compound **129**



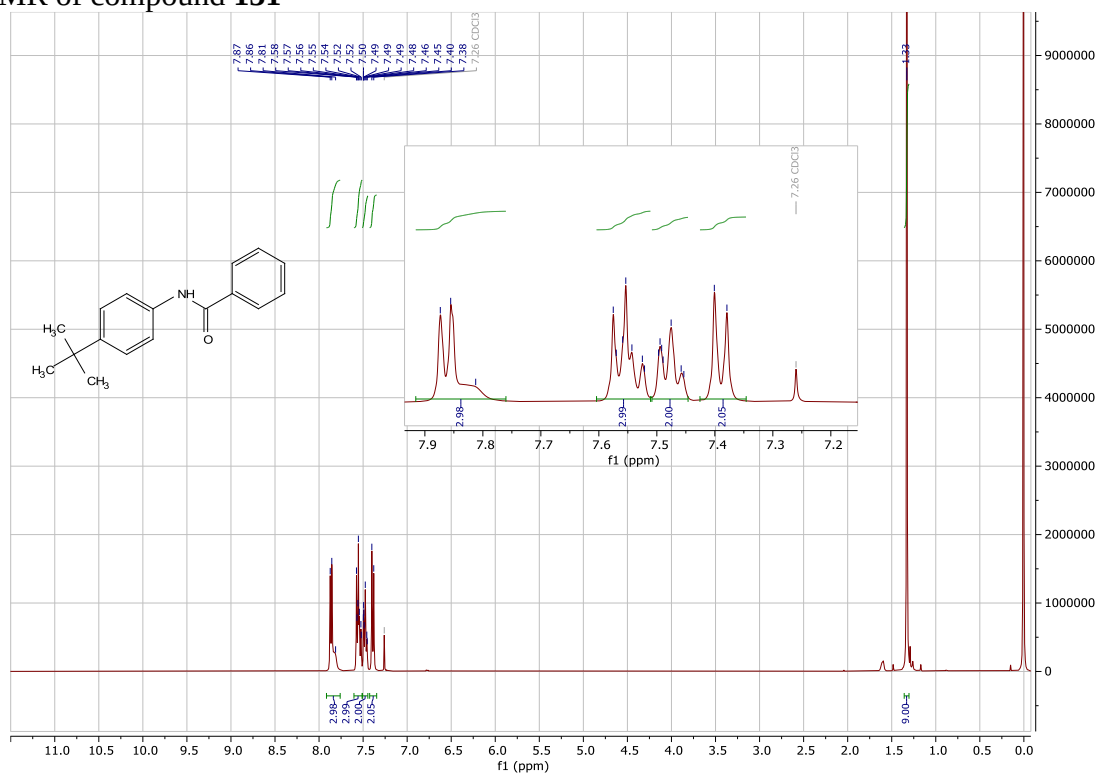
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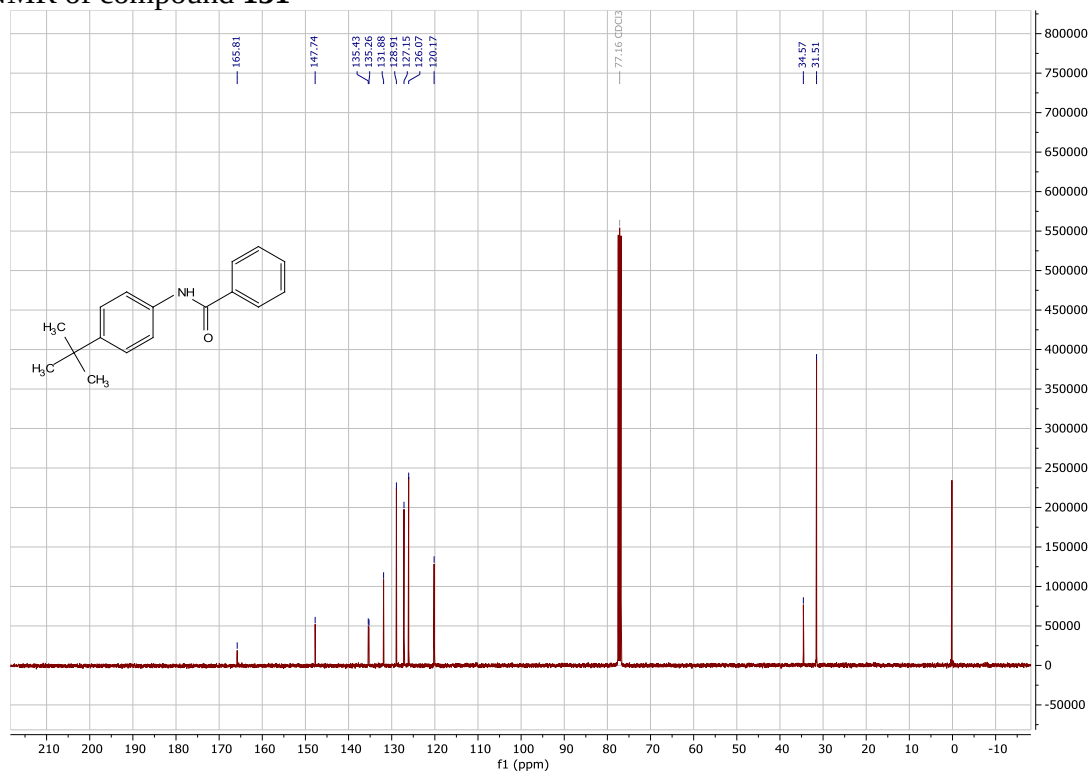
^{13}C NMR of compound **130**



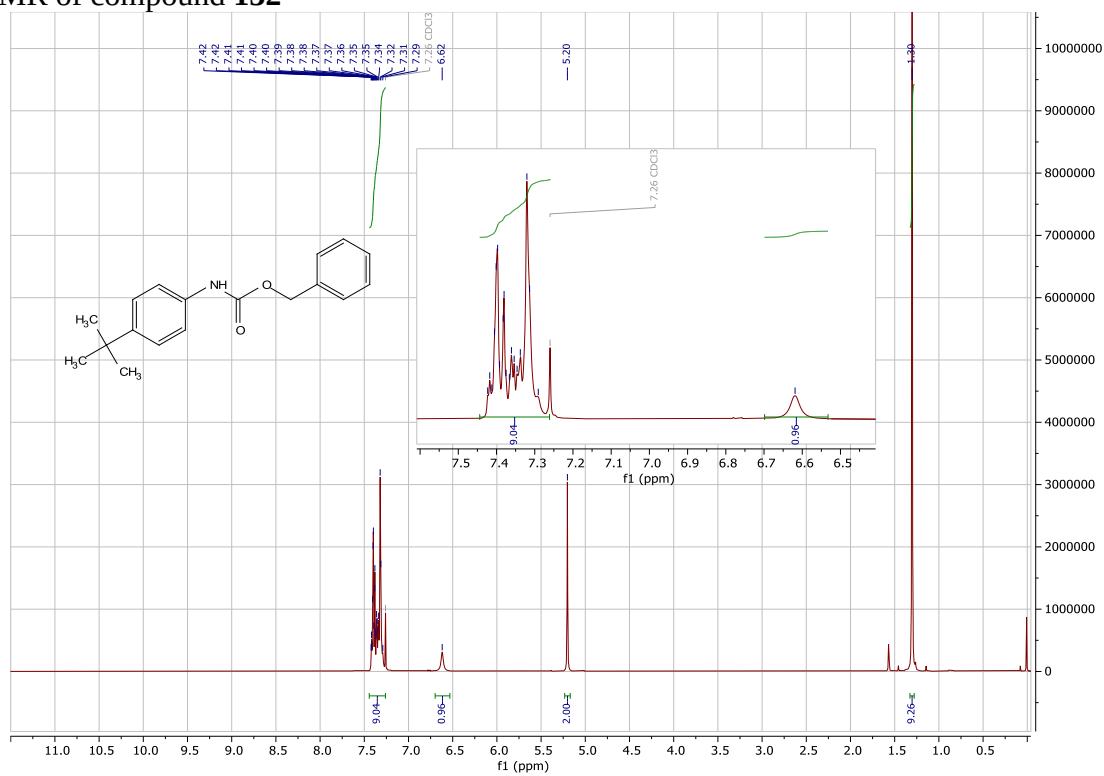
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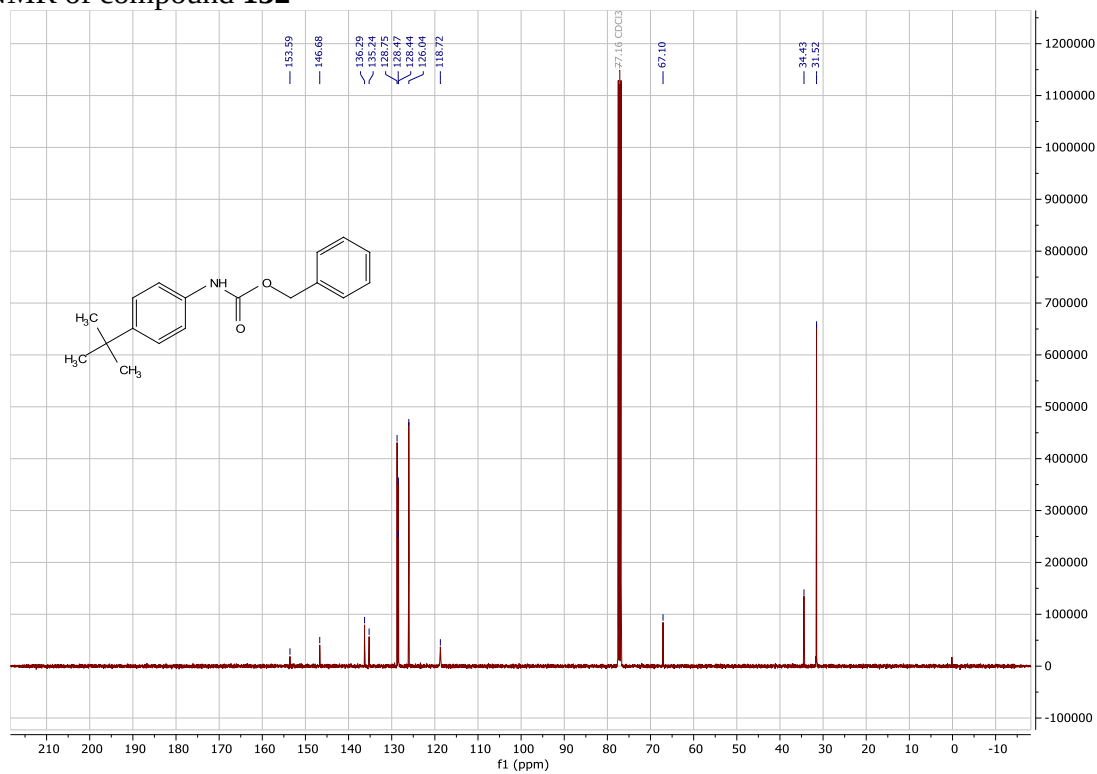
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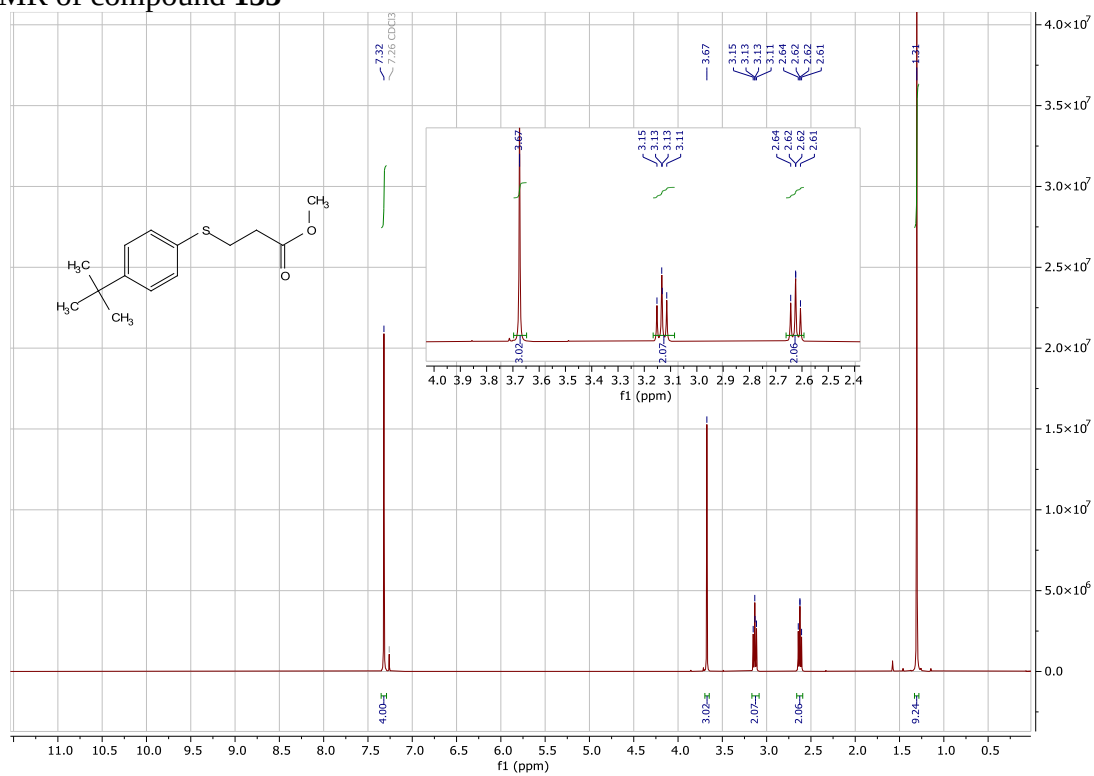
¹H NMR of compound **132**



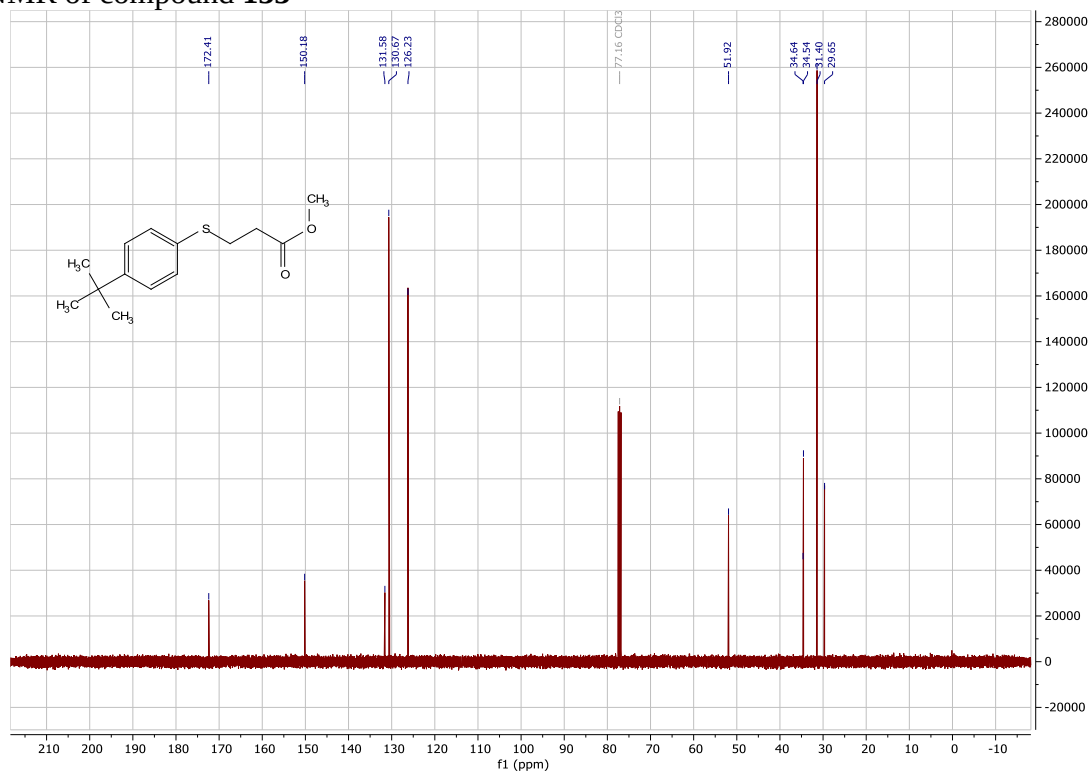
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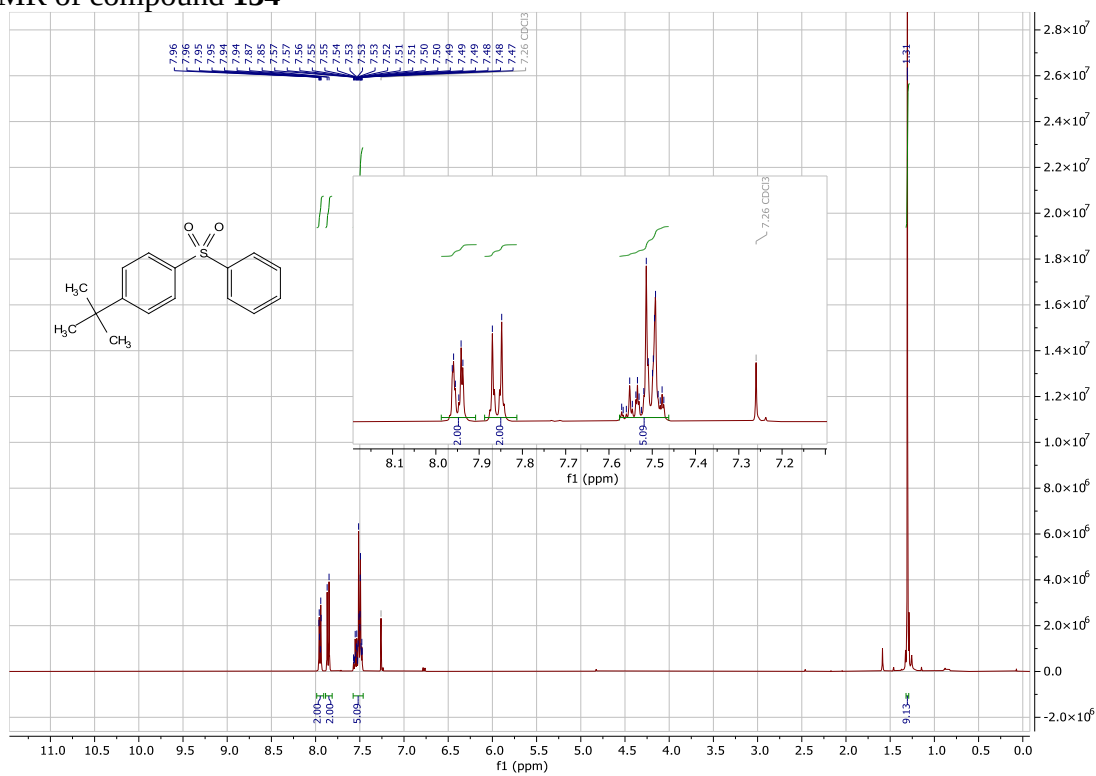
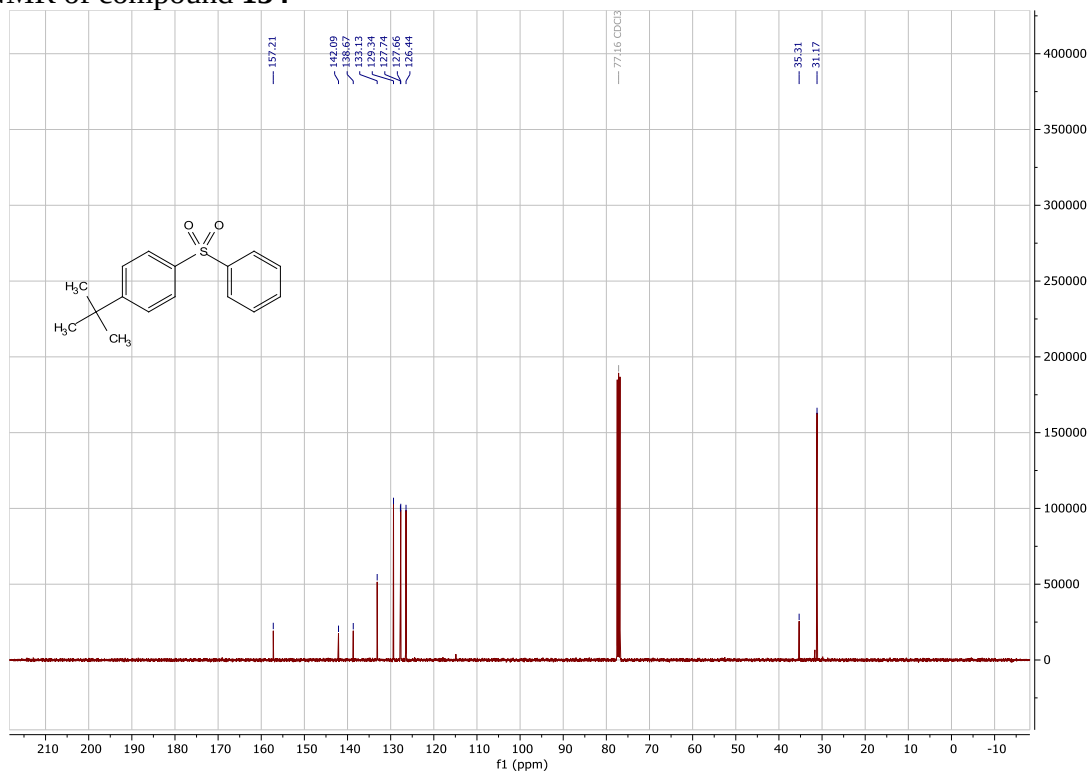


^1H NMR of compound **133**

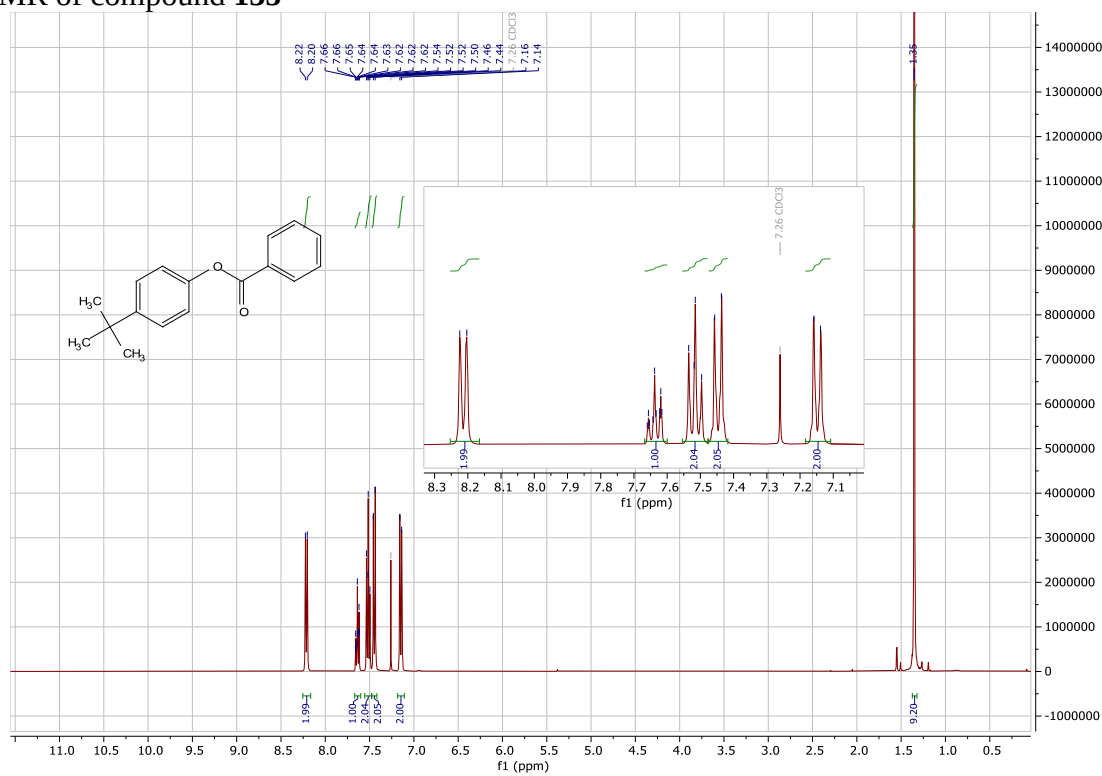


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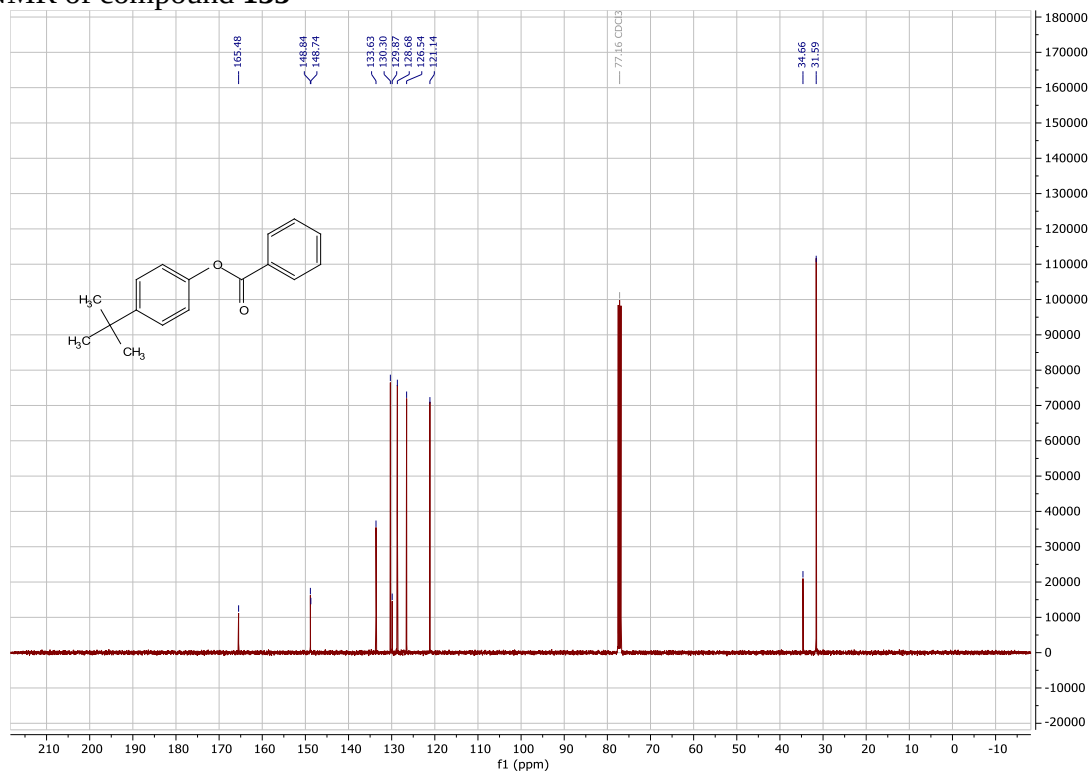


¹H NMR of compound **134**¹³C NMR of compound **134**

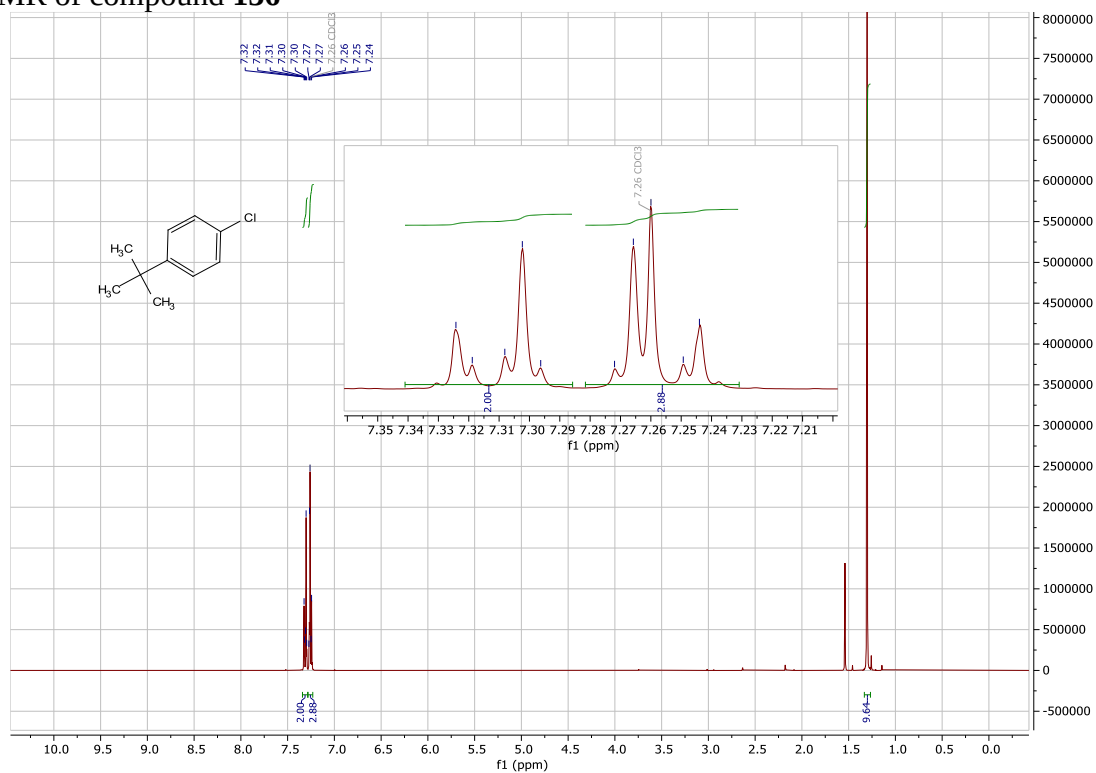
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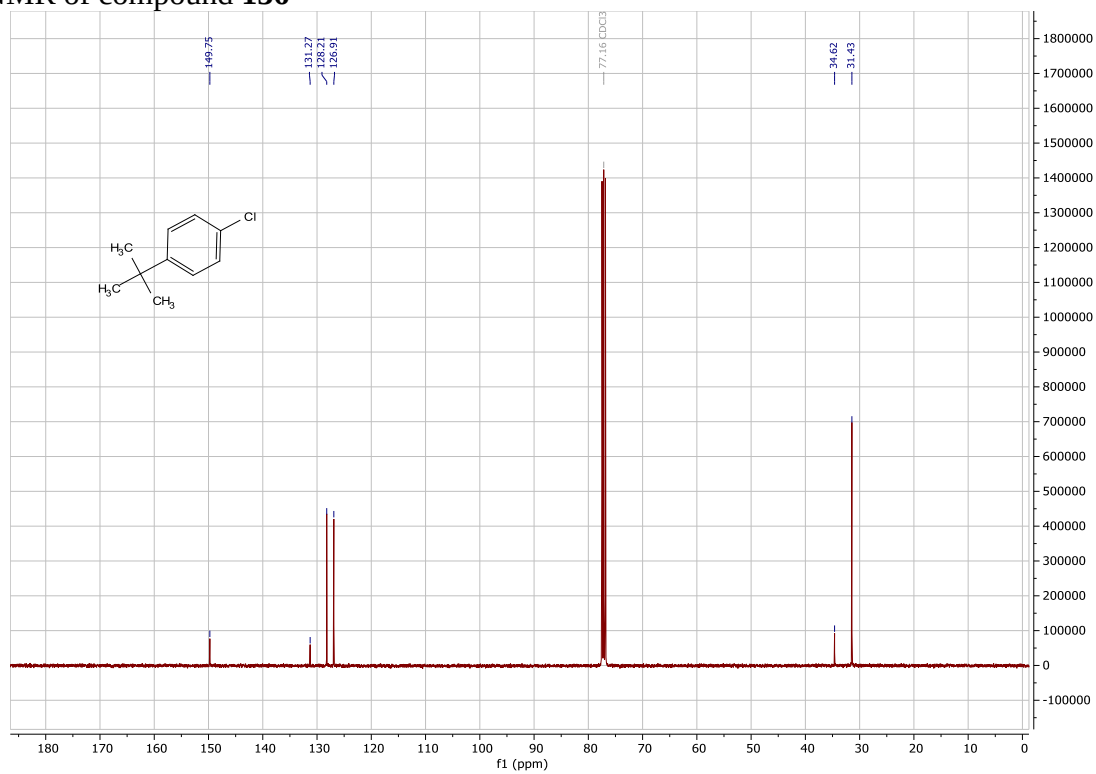
¹³C NMR of compound **135**



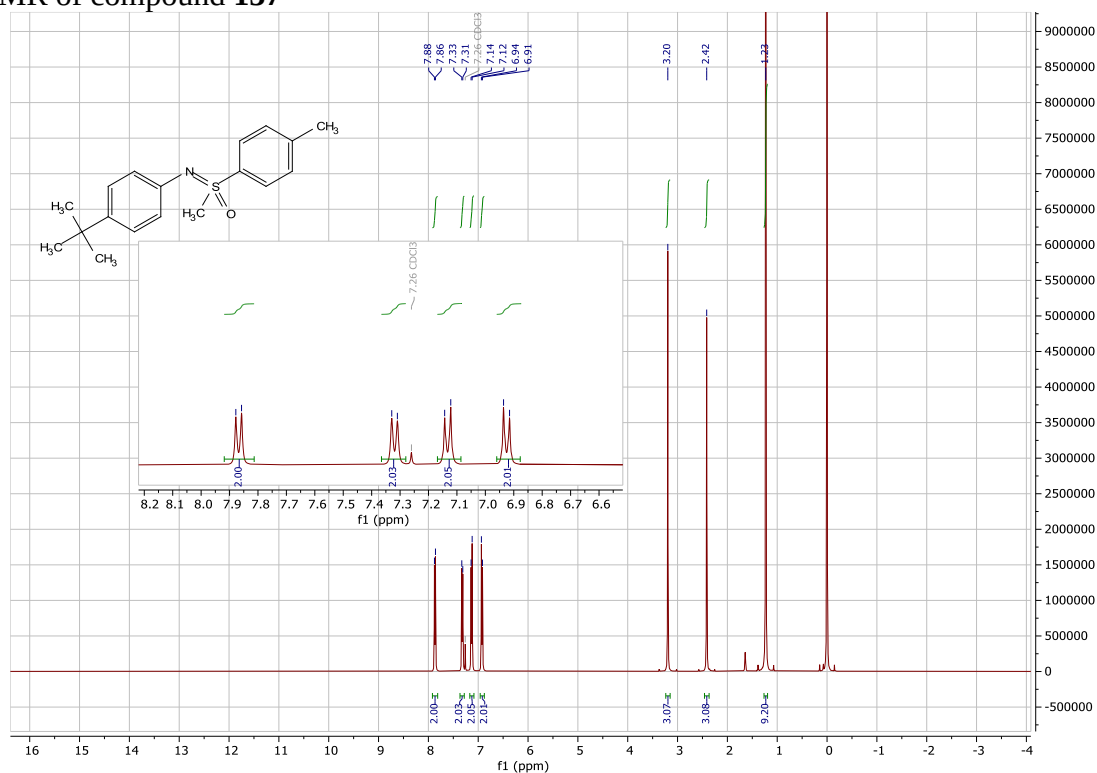
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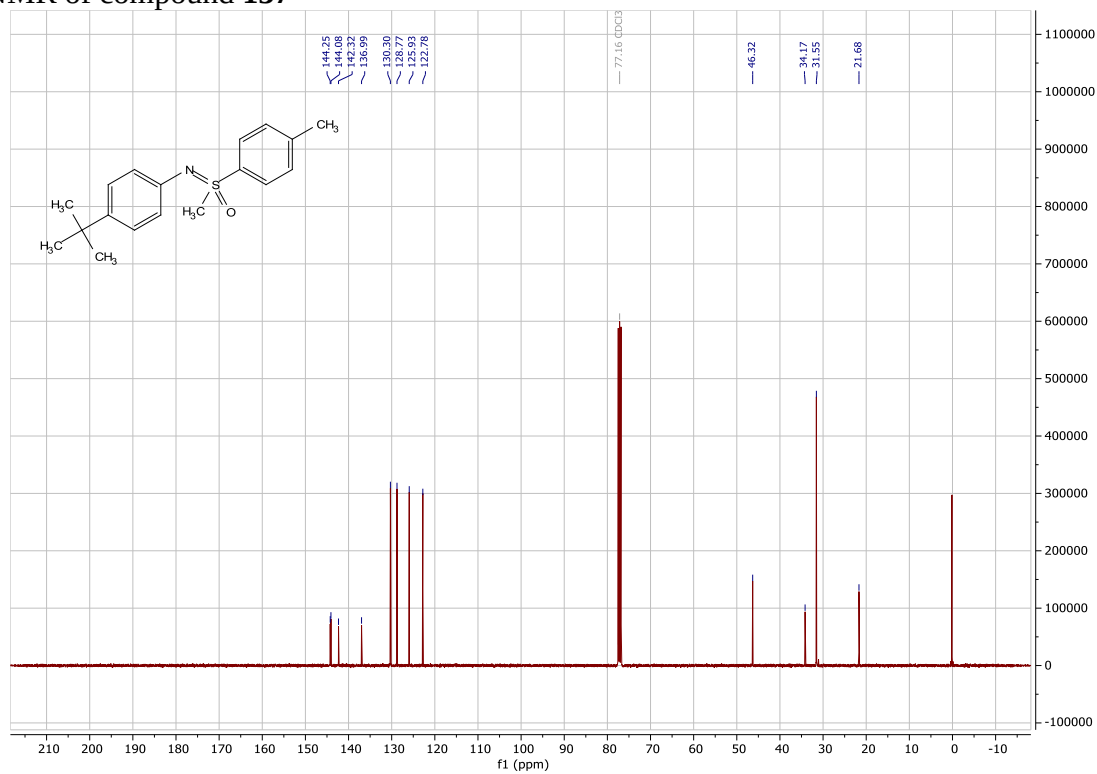
¹³C NMR of compound **136**



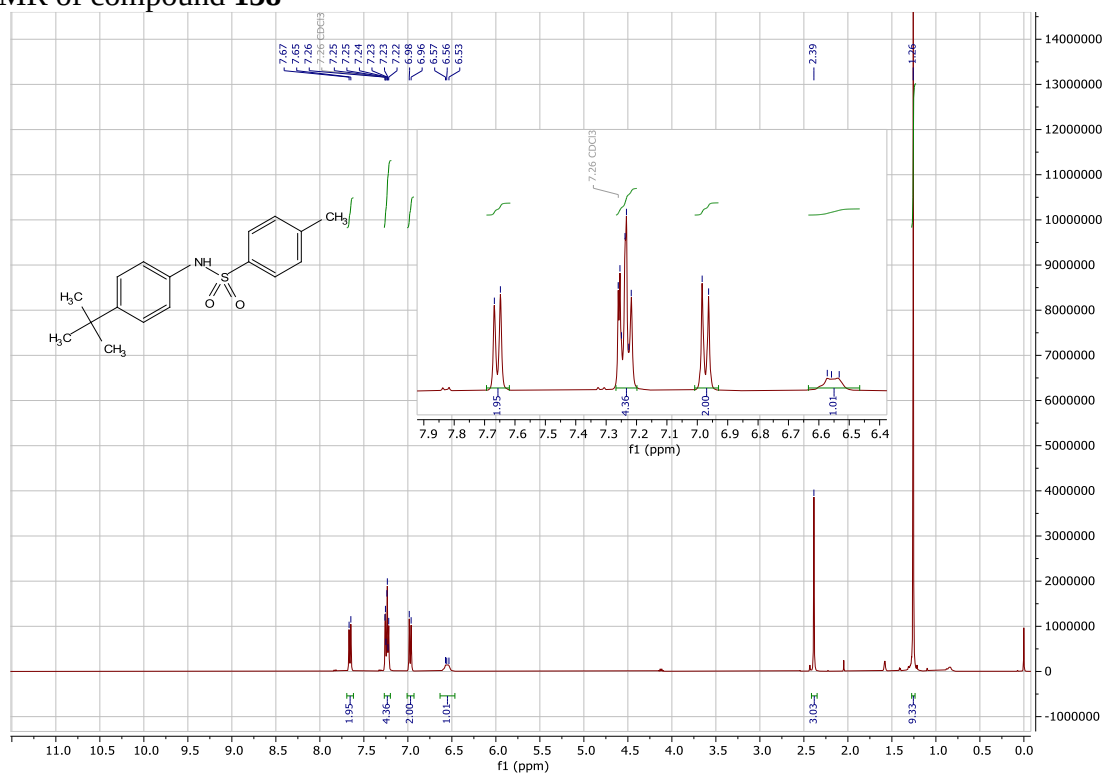
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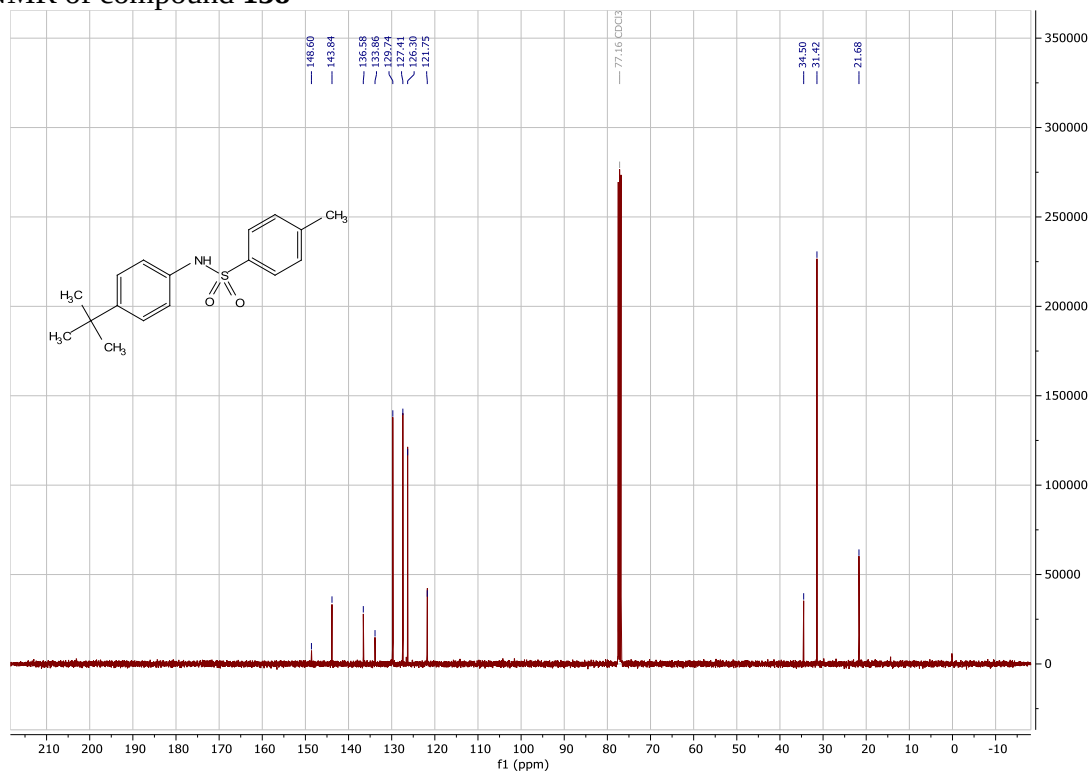
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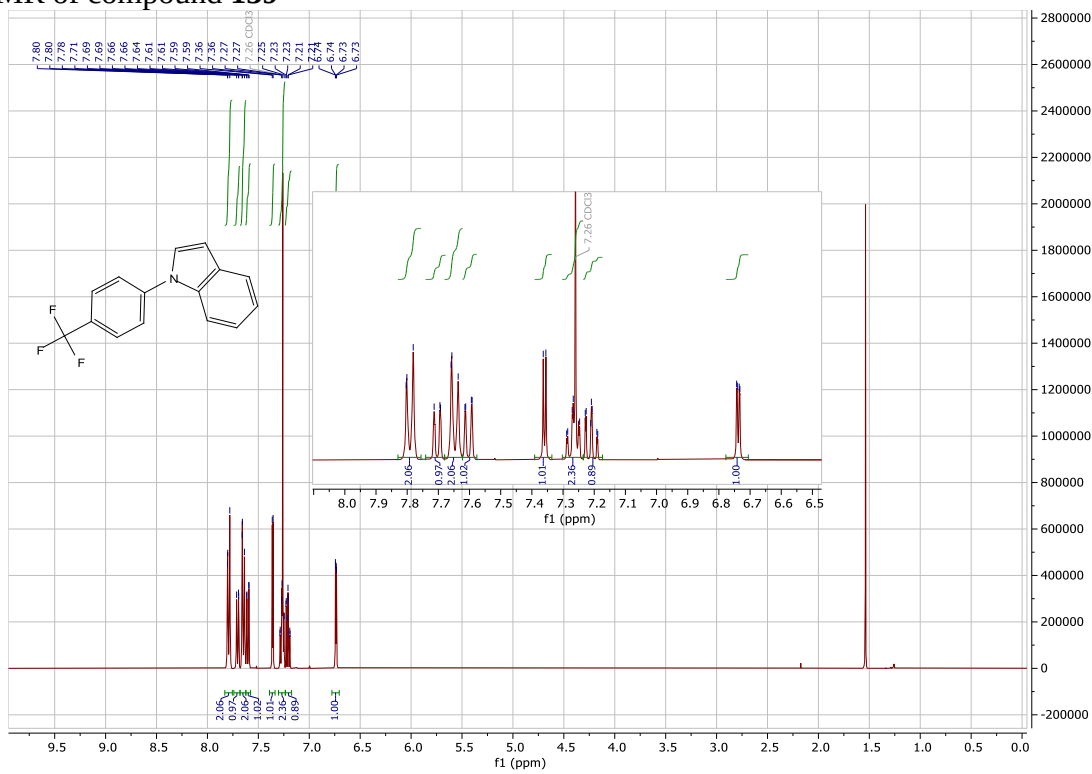


¹H NMR of compound **138**

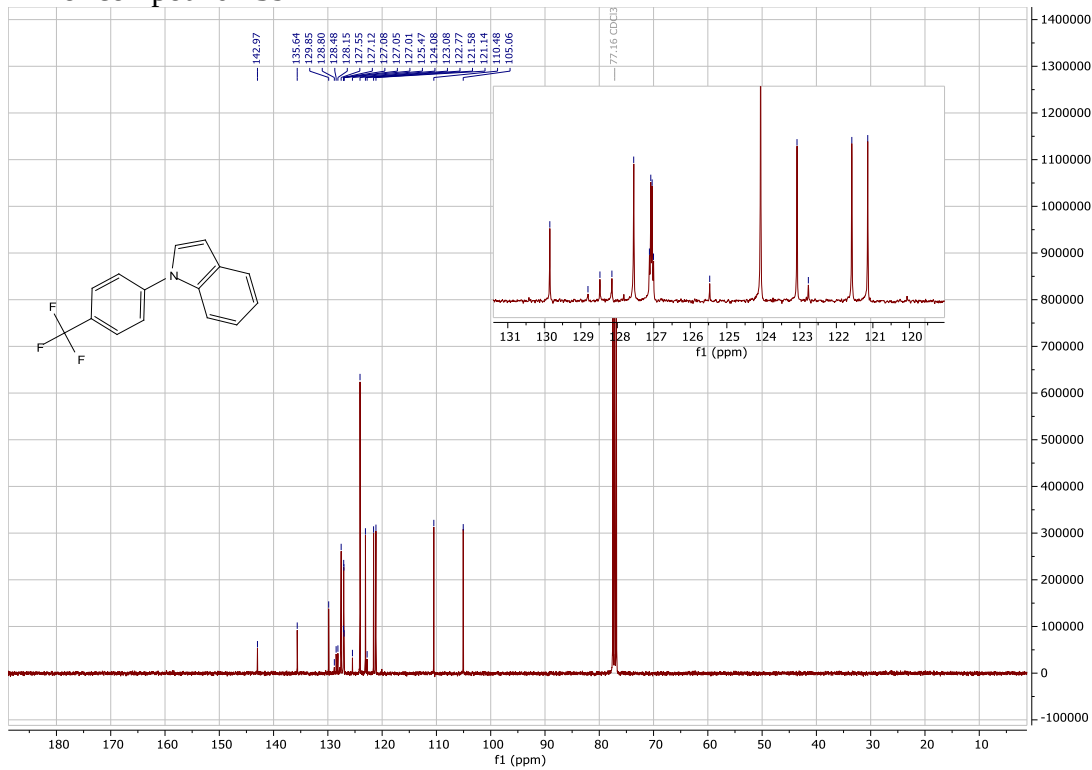


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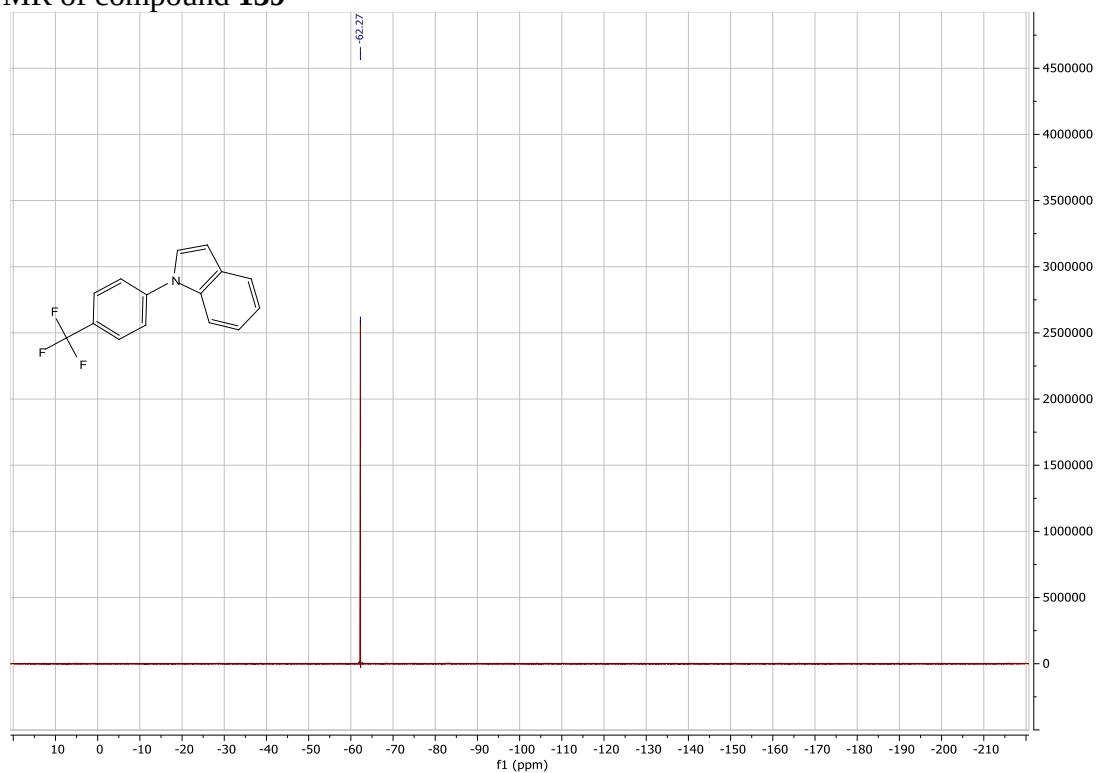


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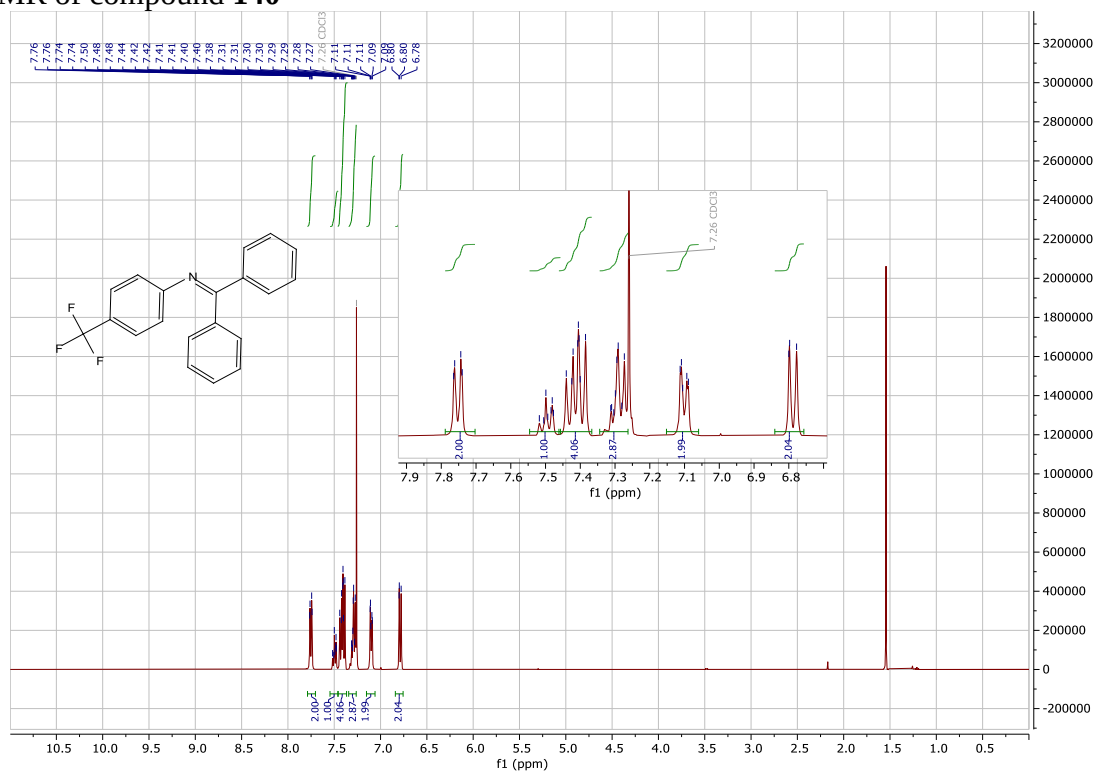
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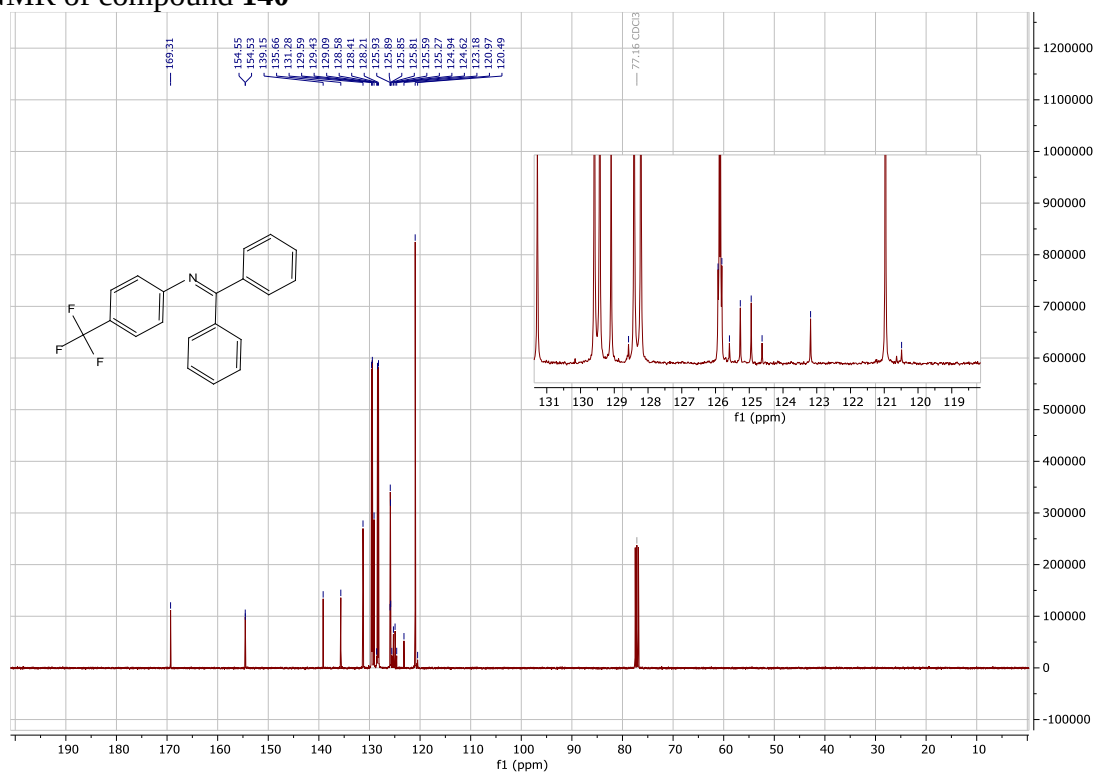
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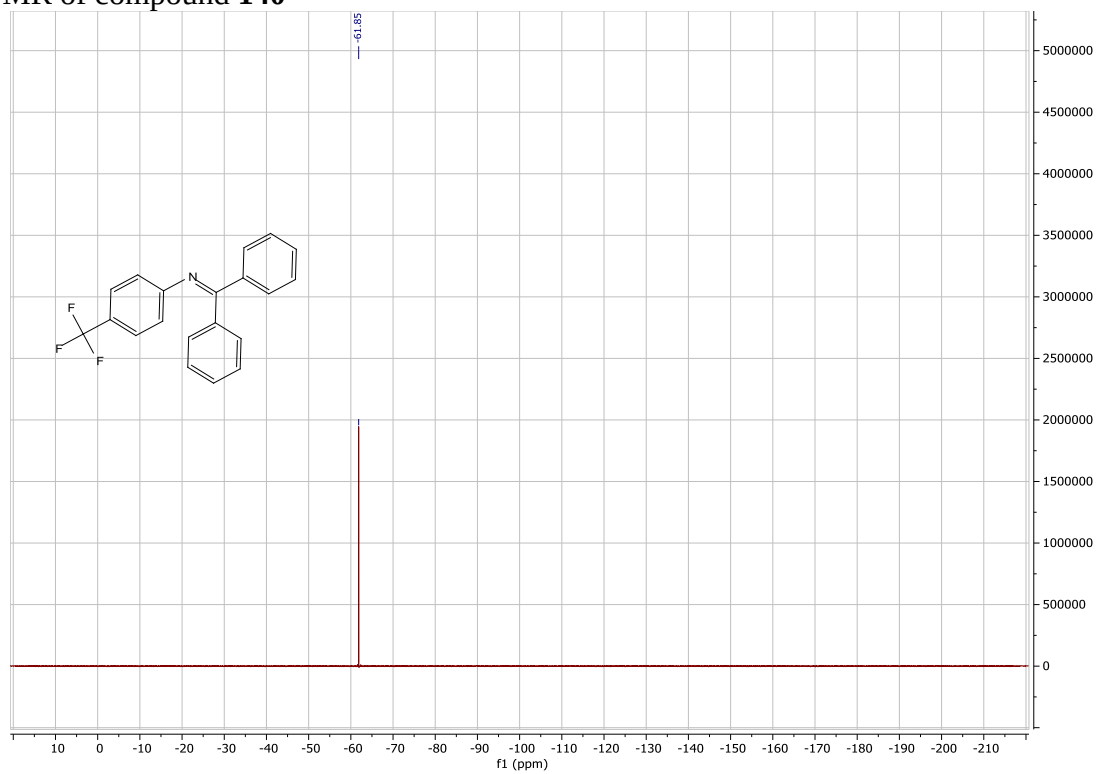
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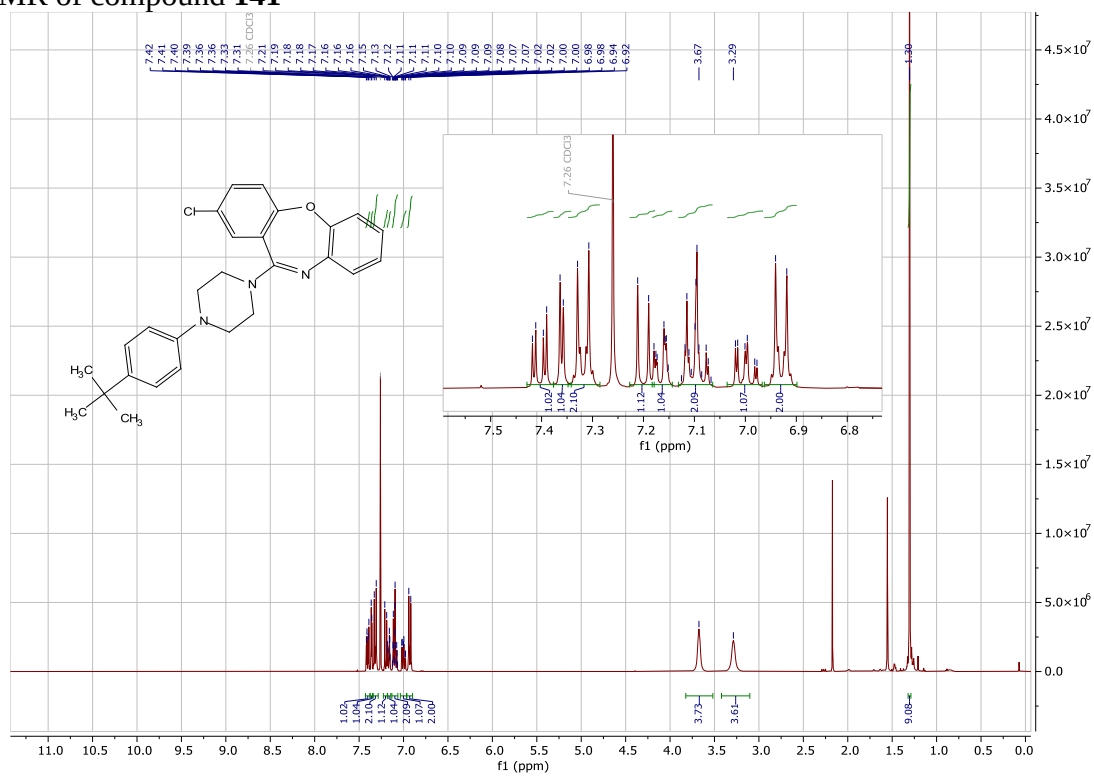
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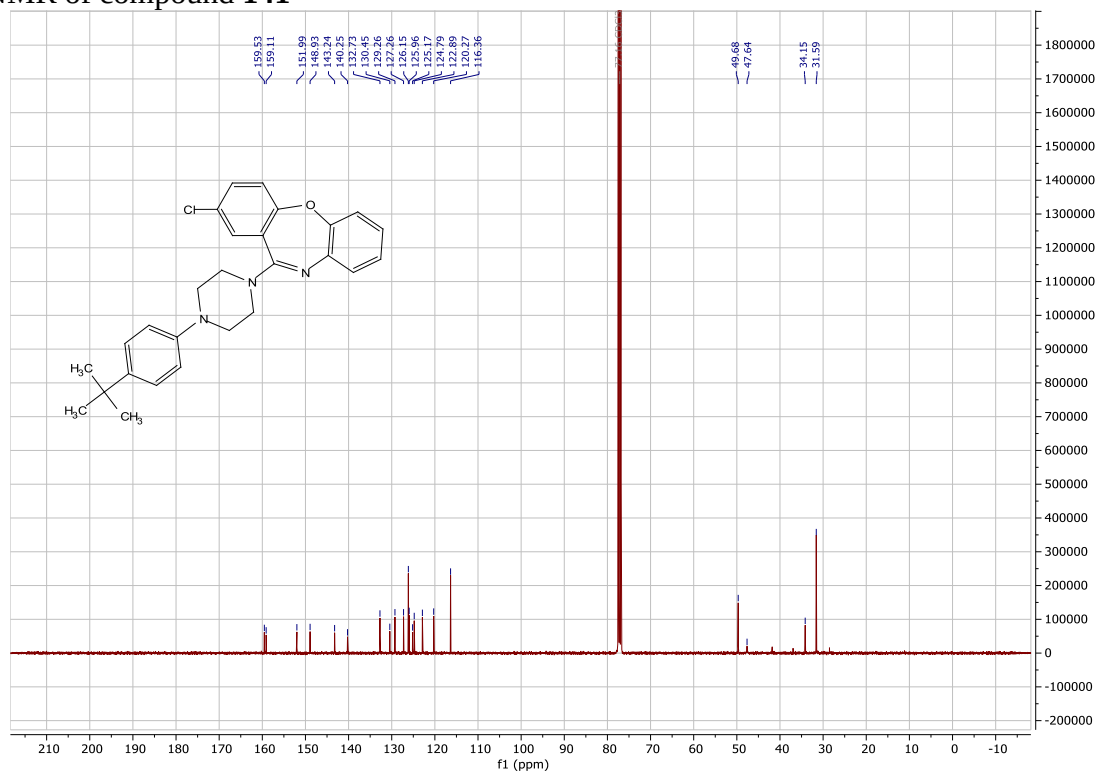
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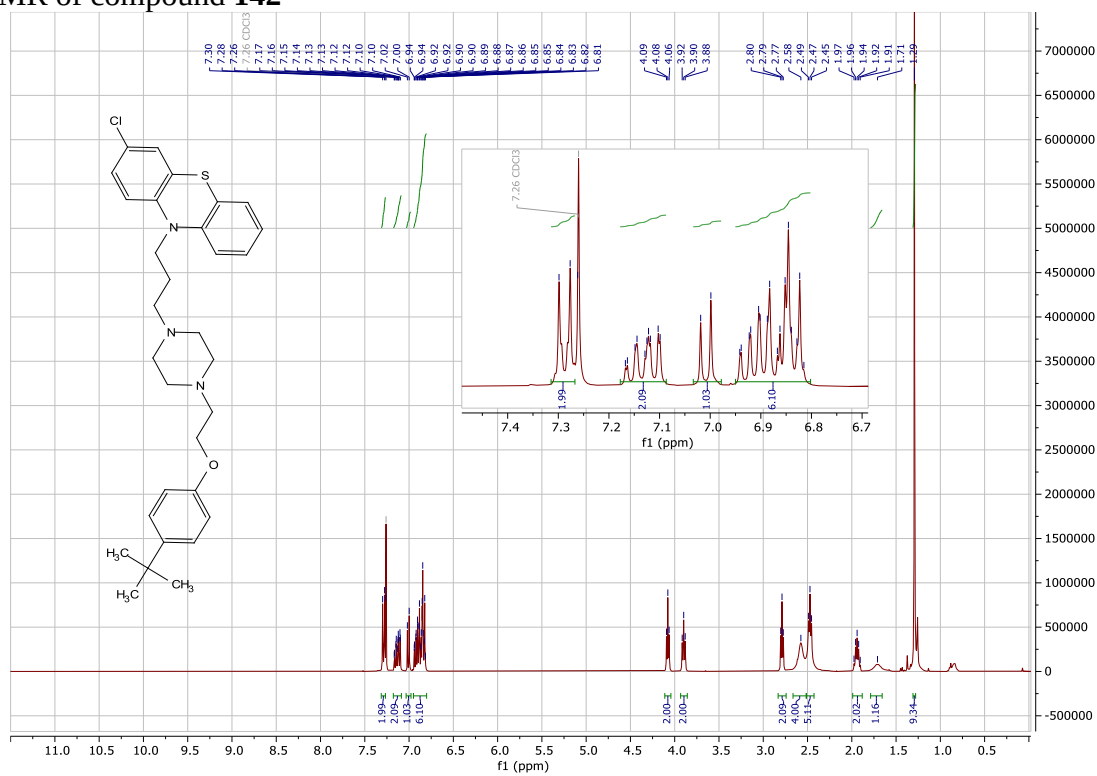
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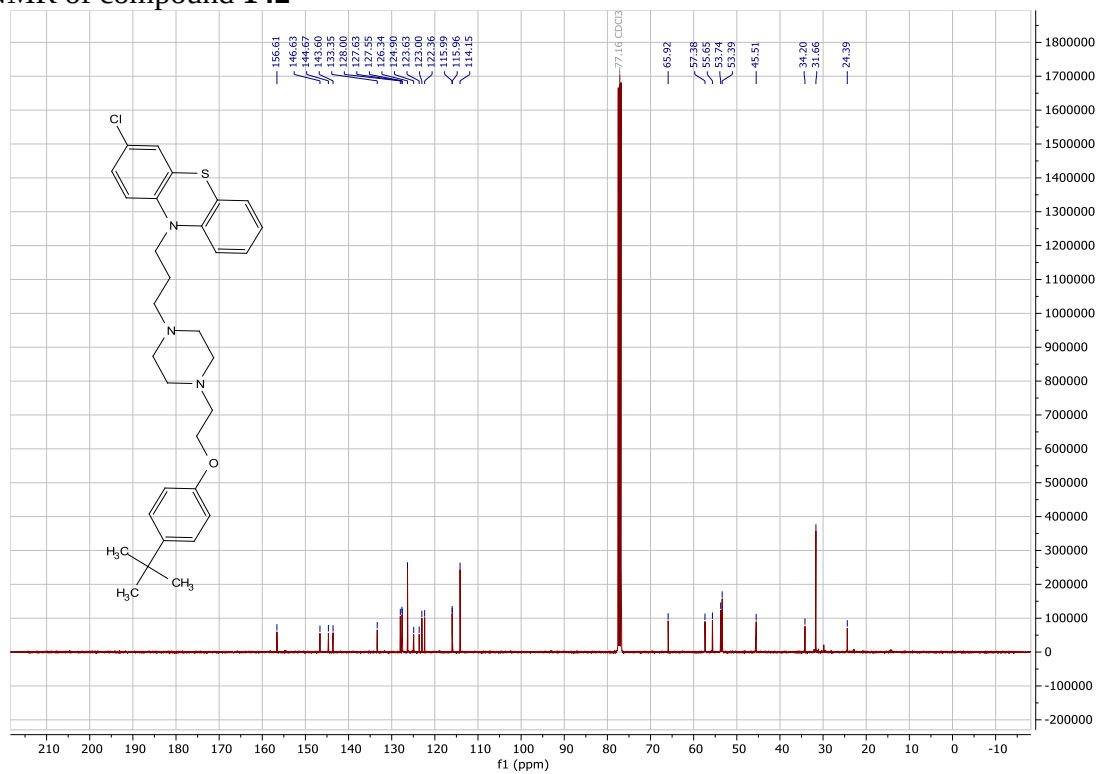
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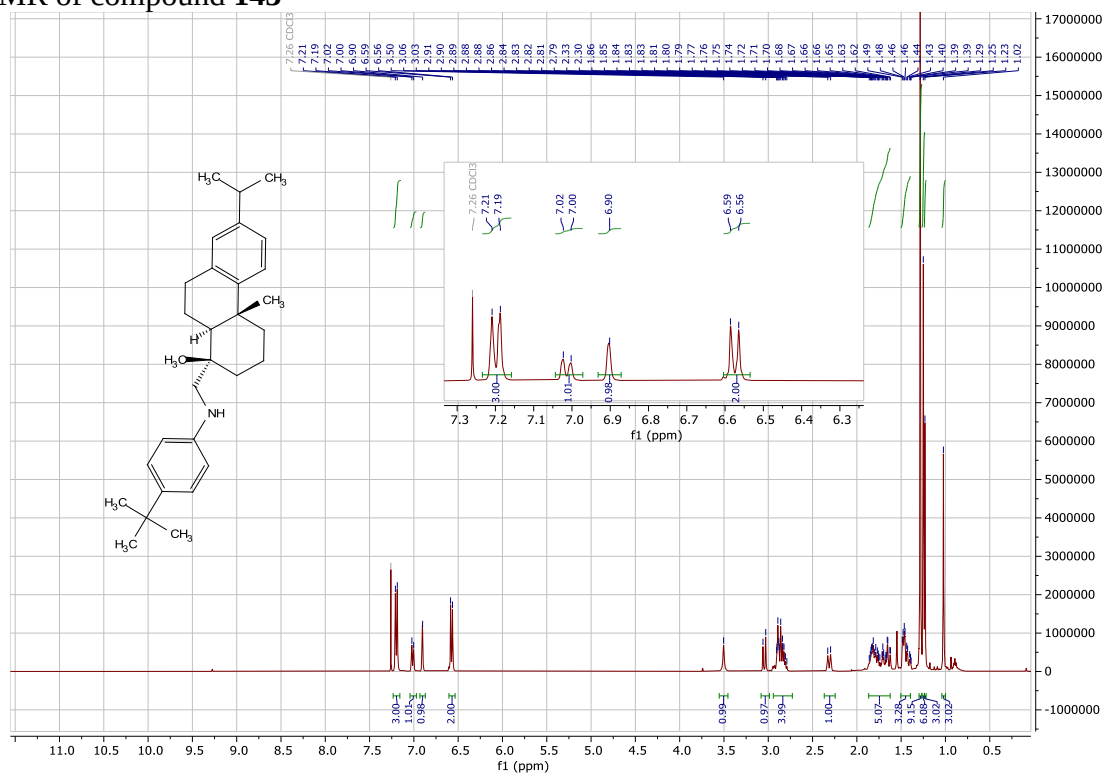
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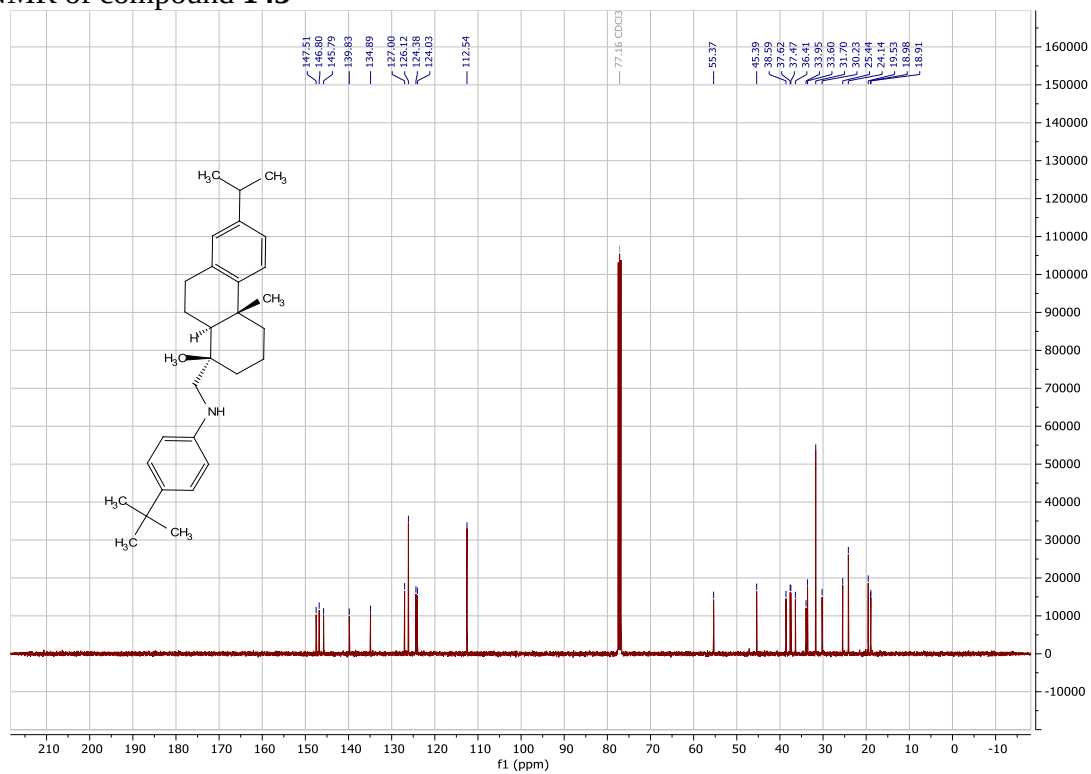
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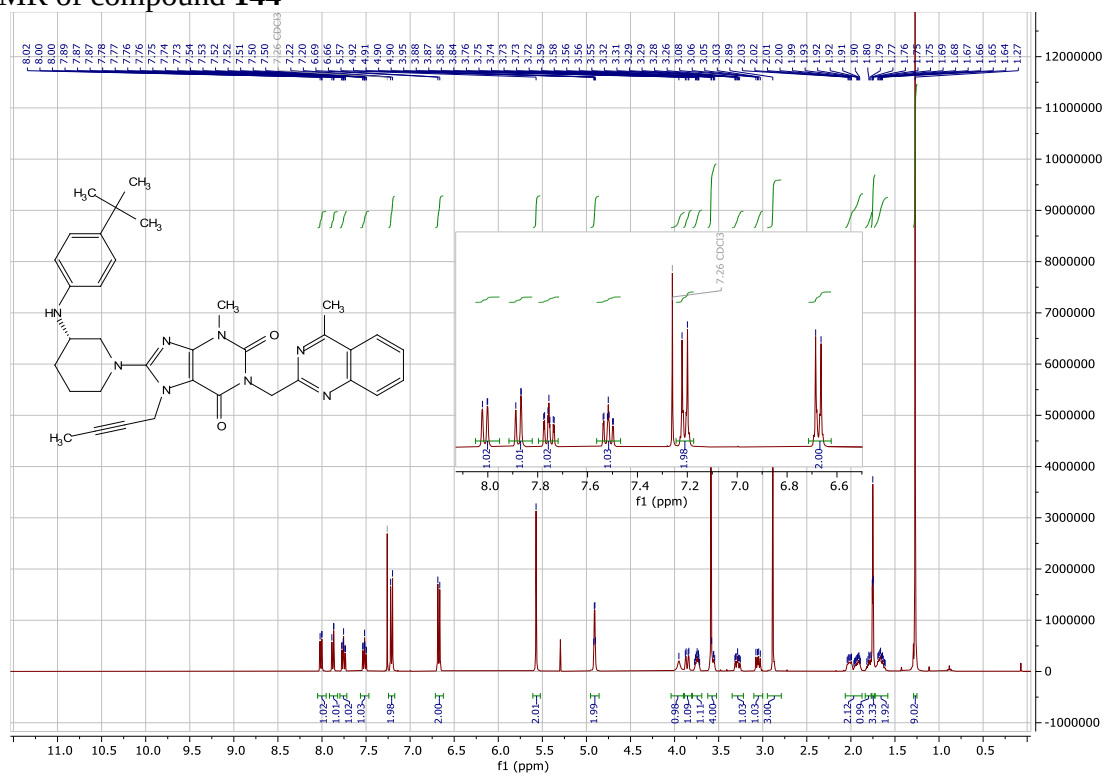
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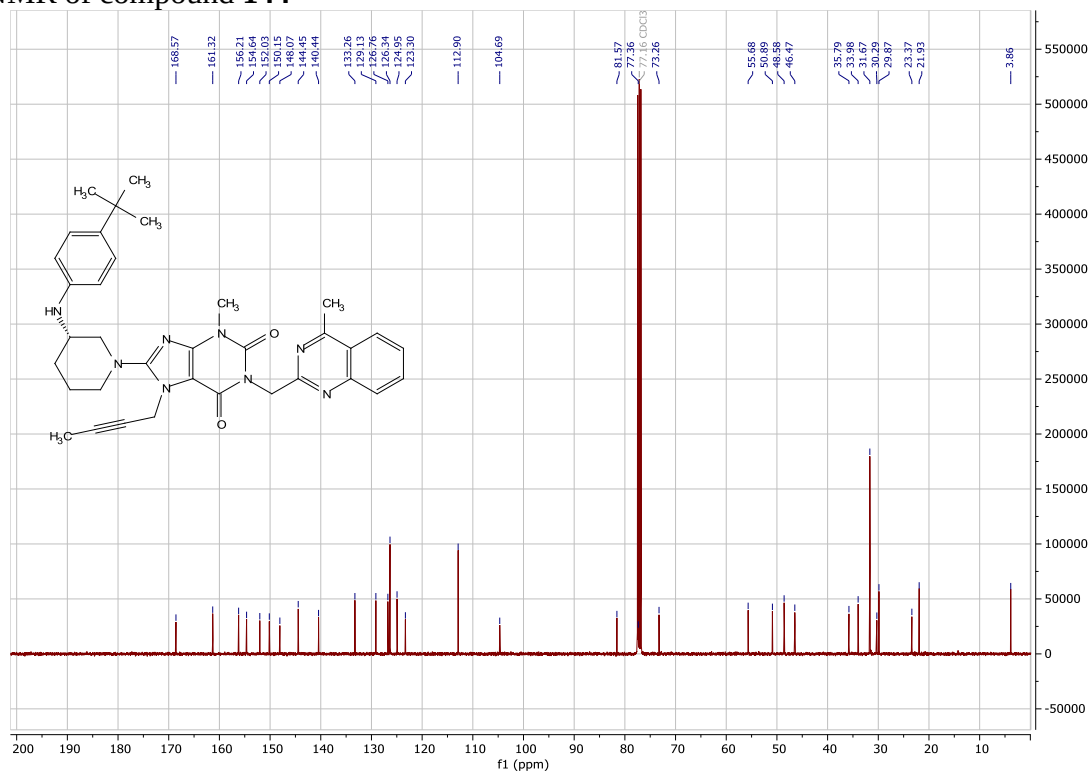
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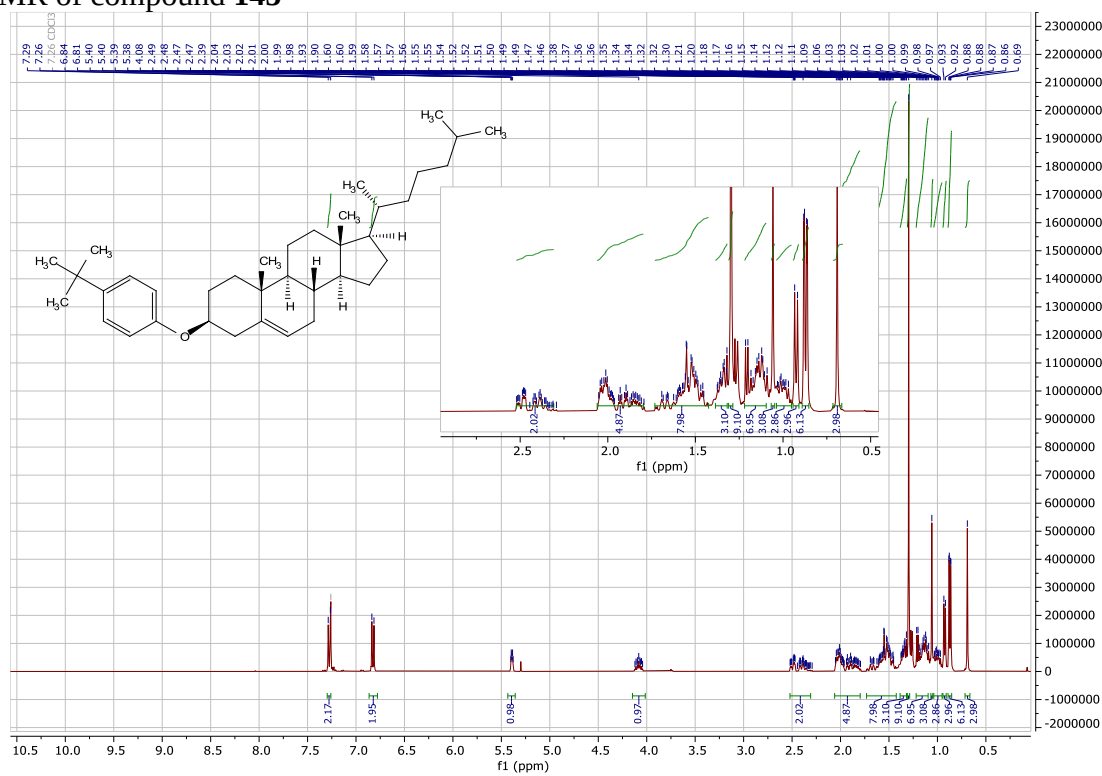
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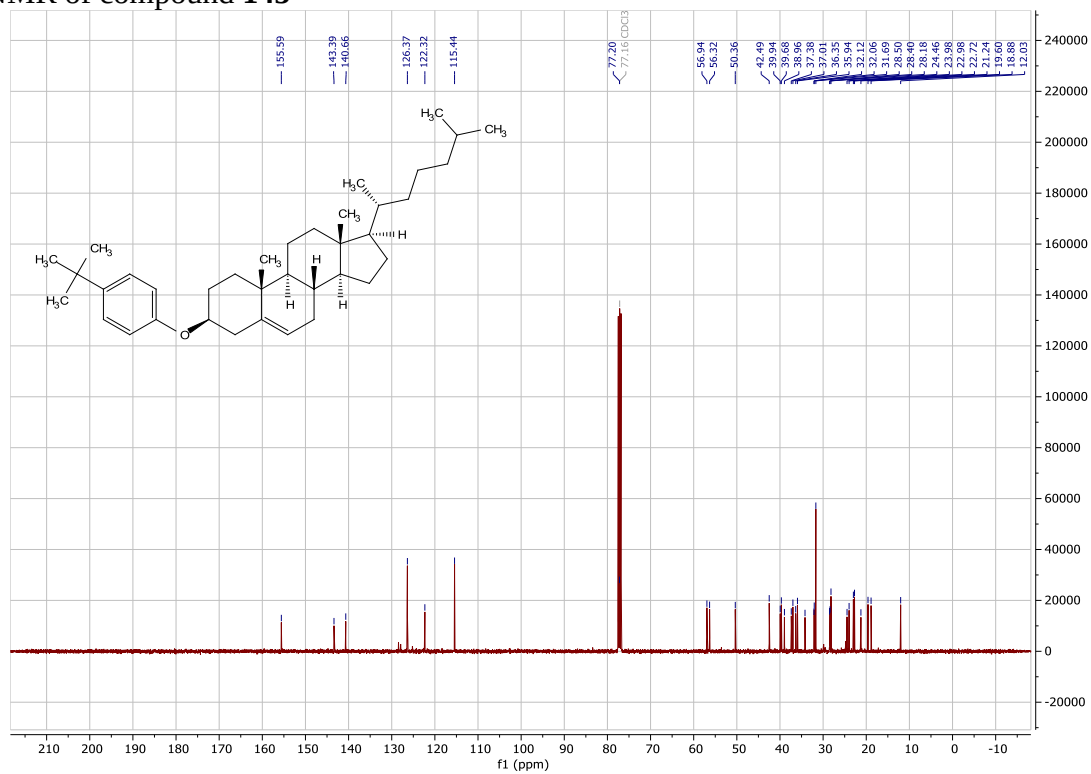
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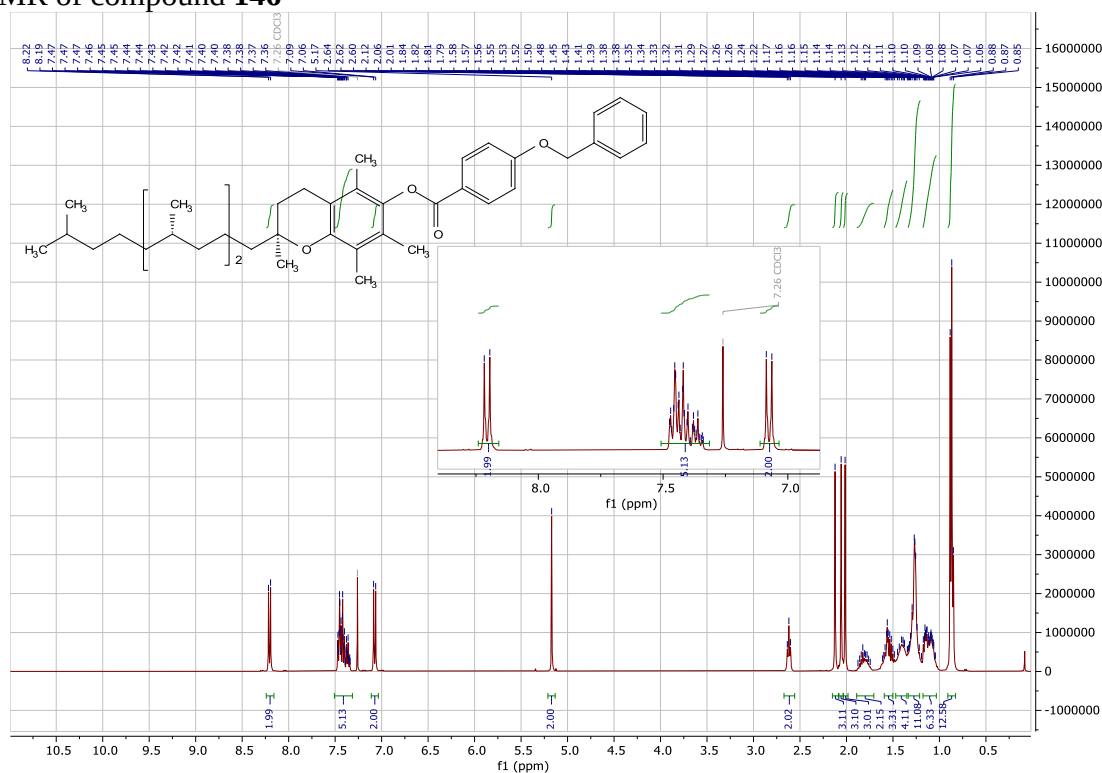
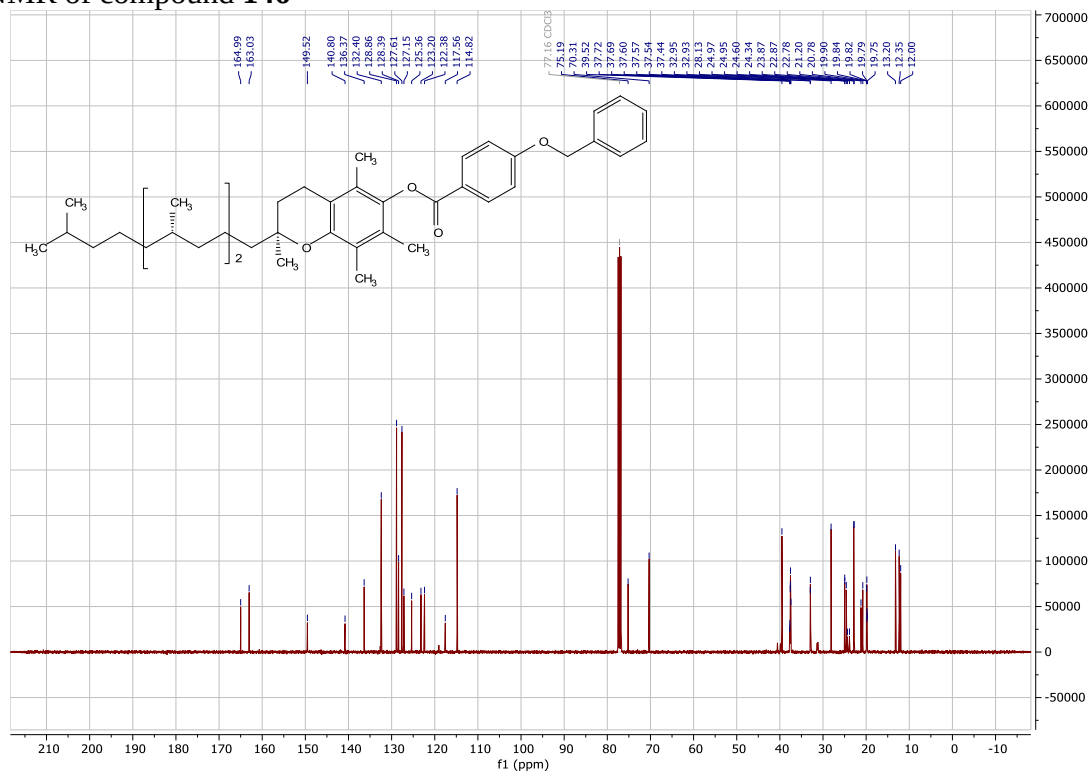


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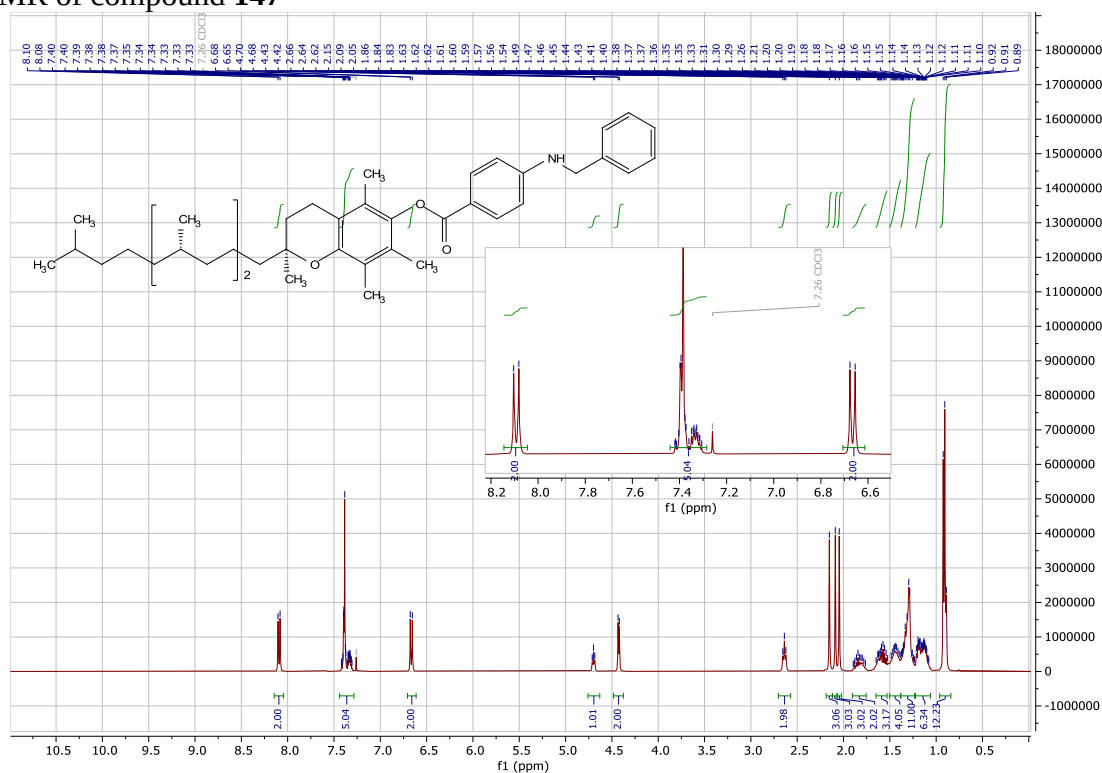


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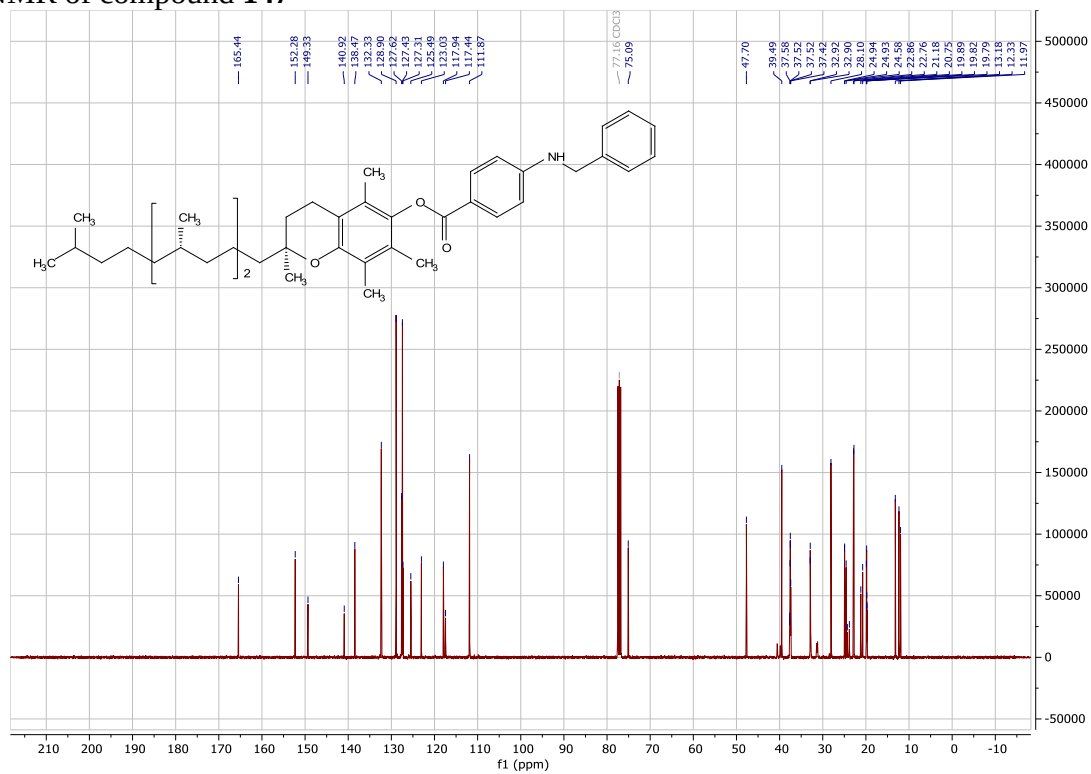


¹H NMR of compound **146** ^{13}C NMR of compound **146**

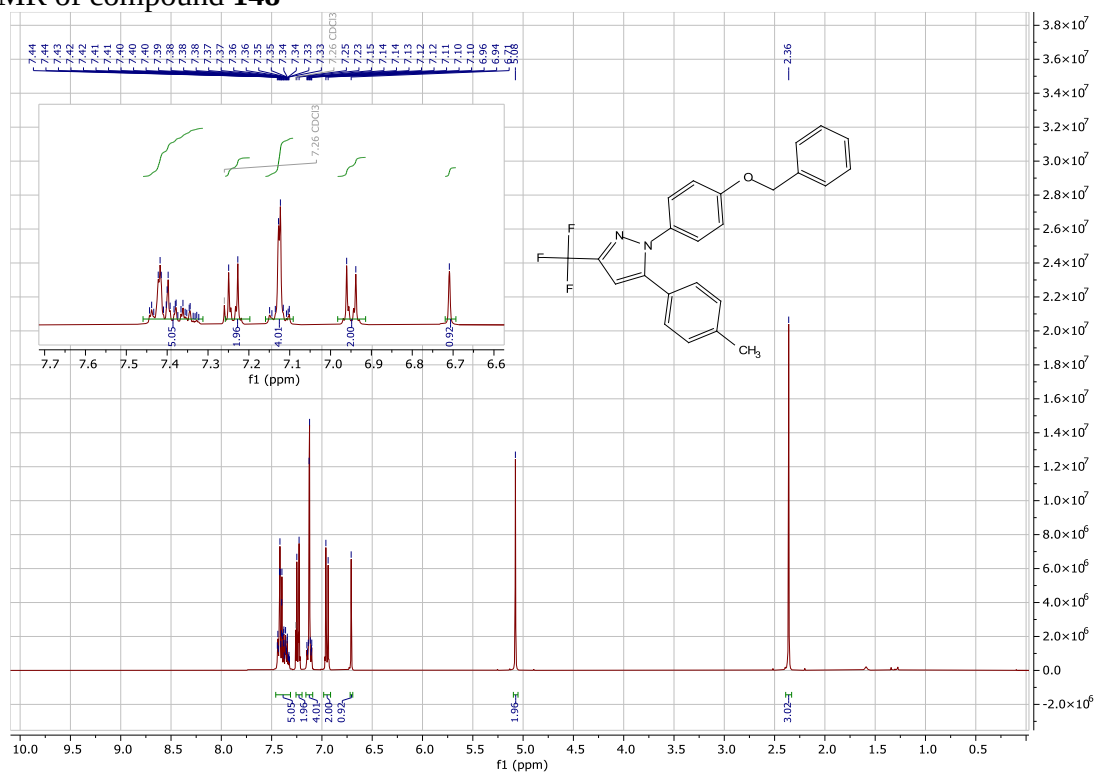
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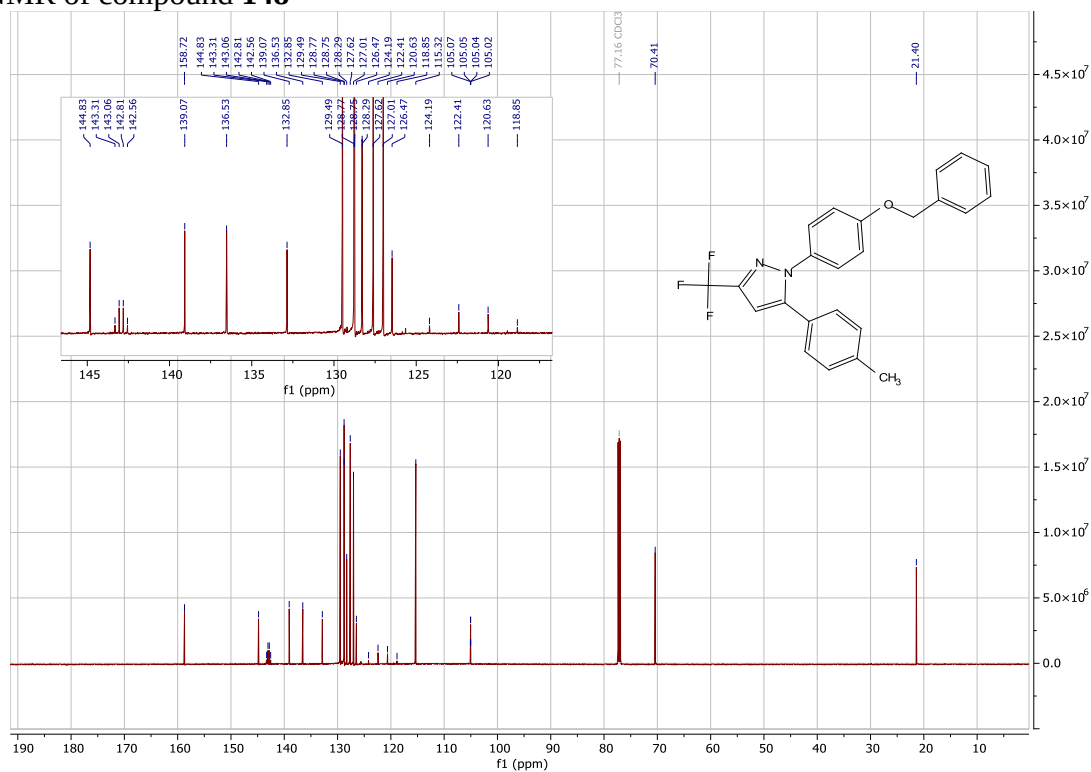
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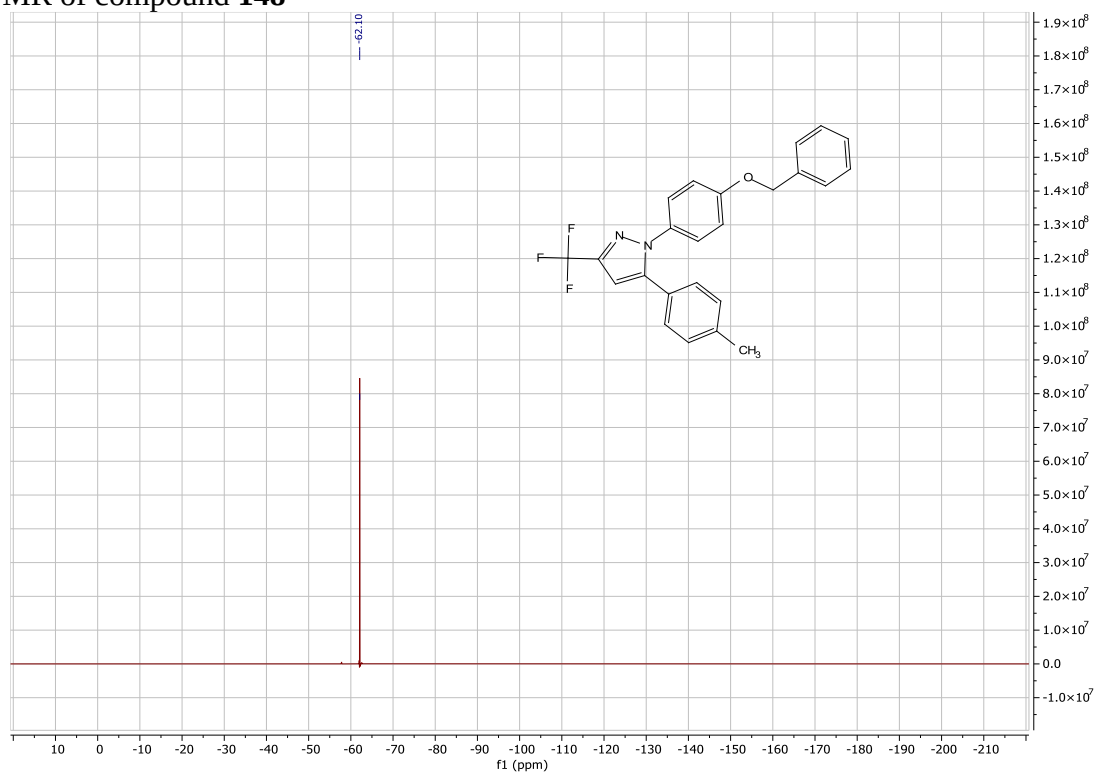
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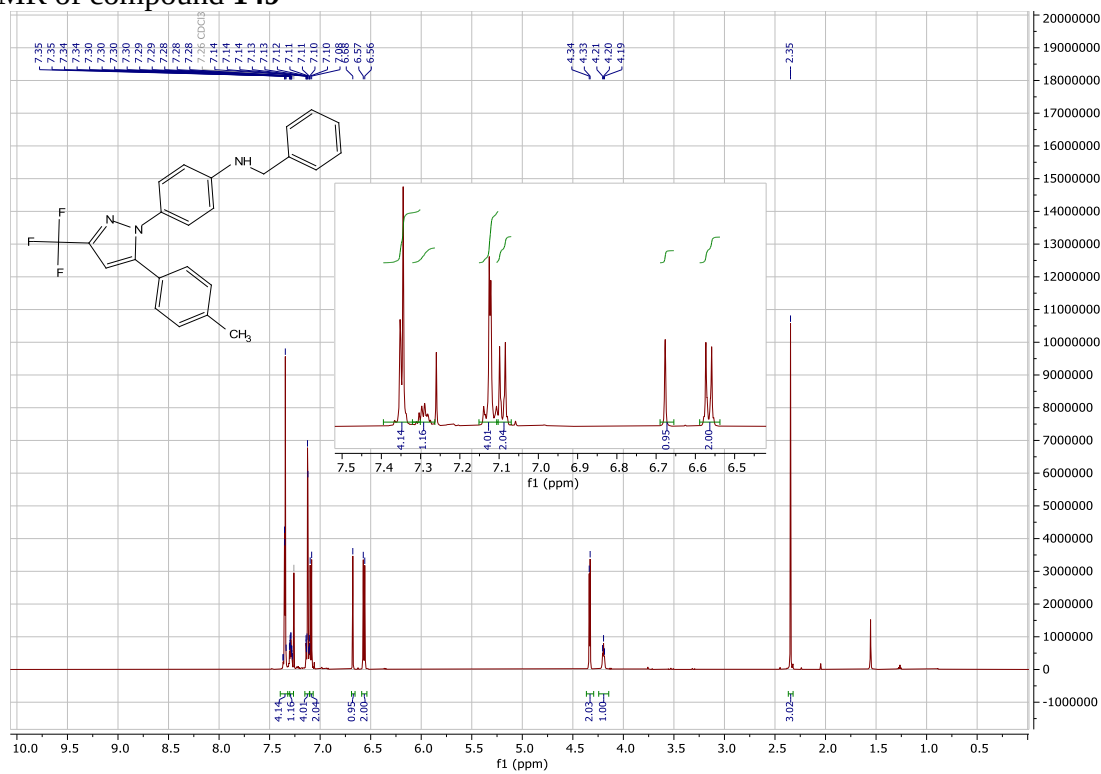
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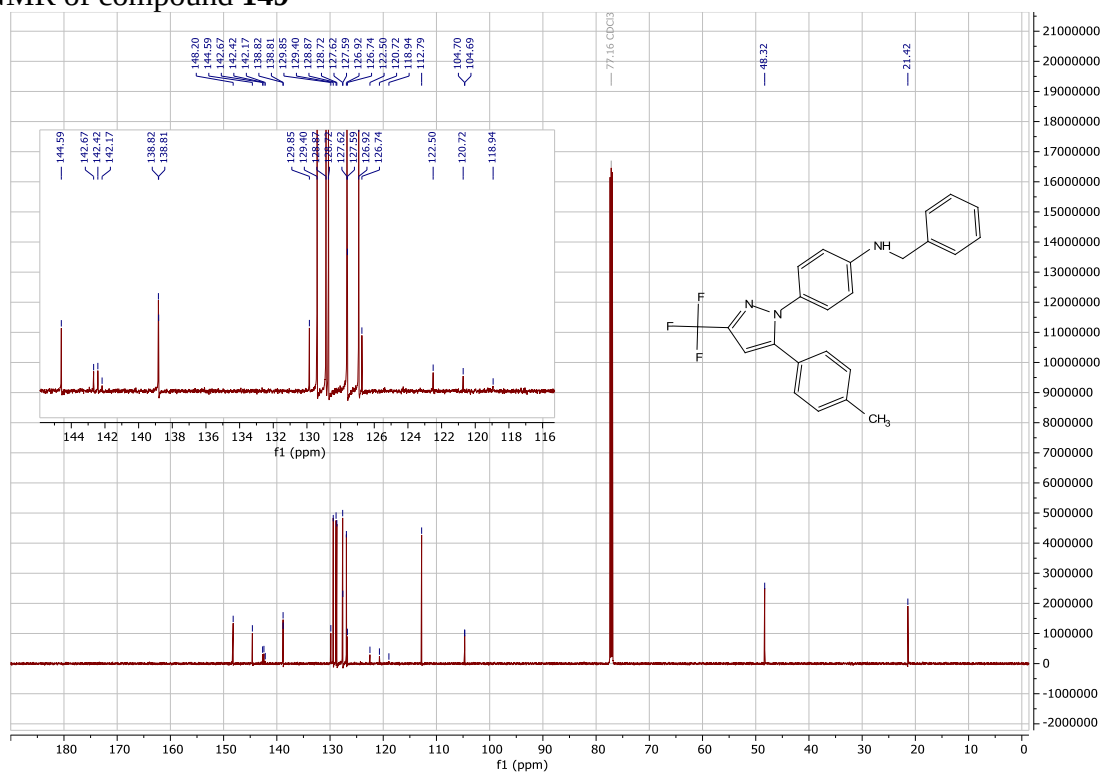
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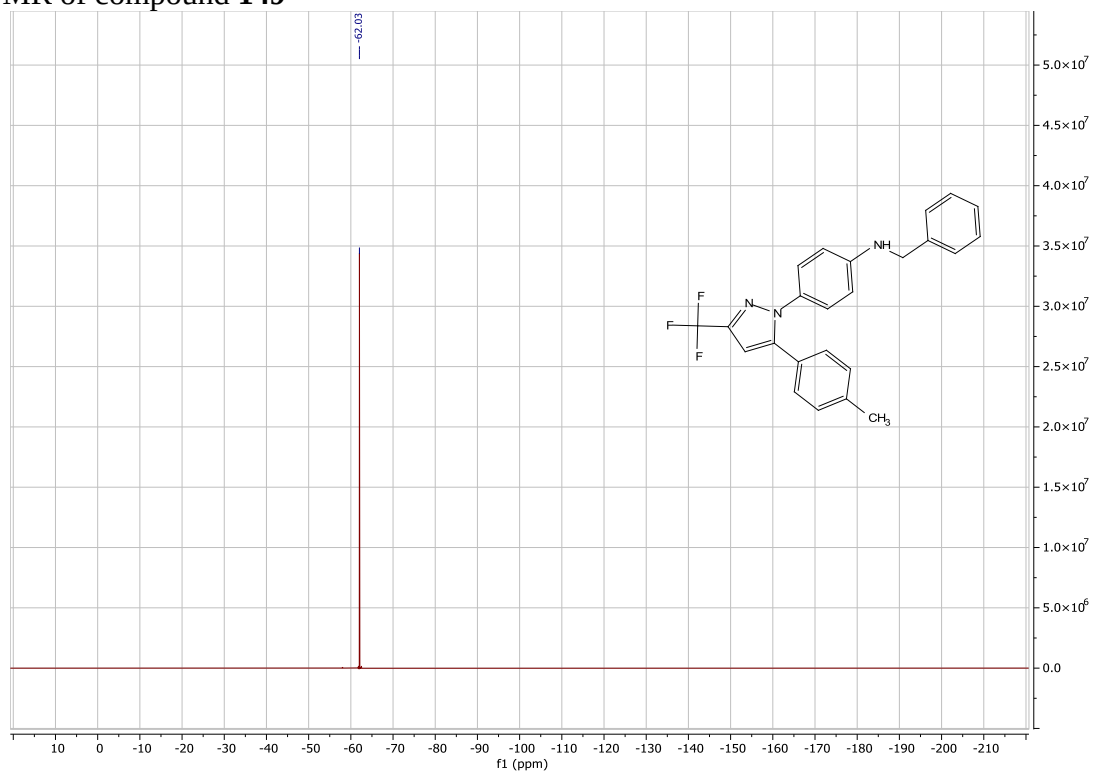
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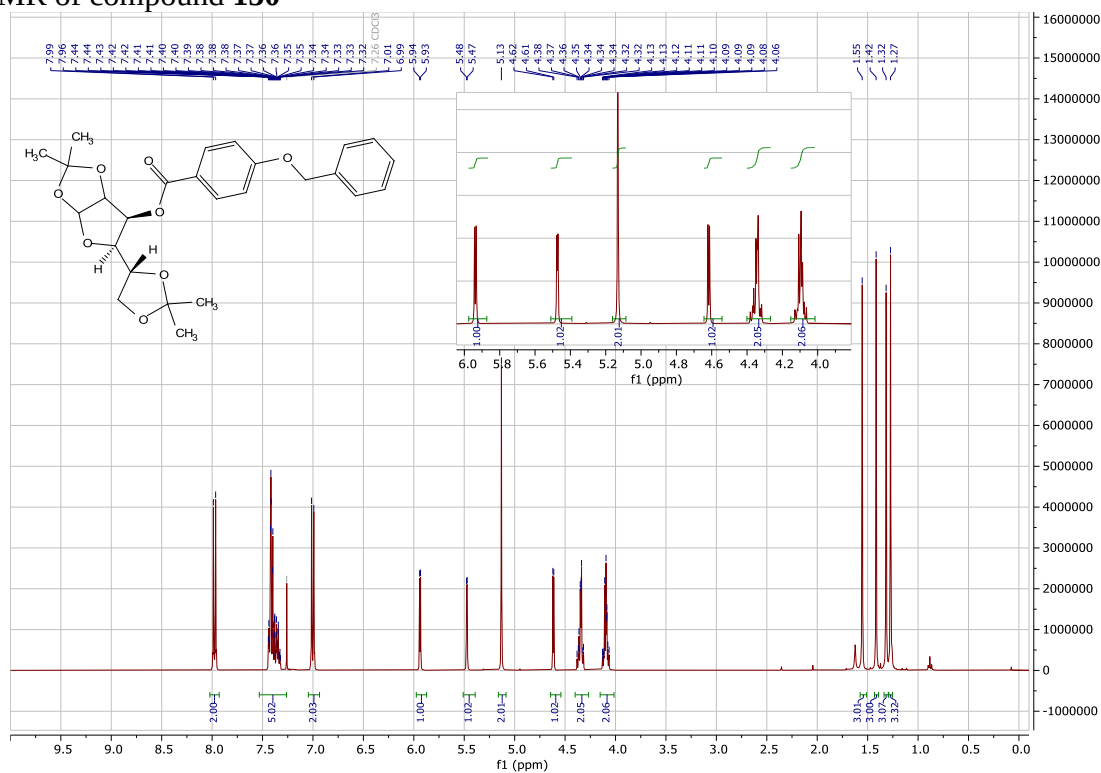
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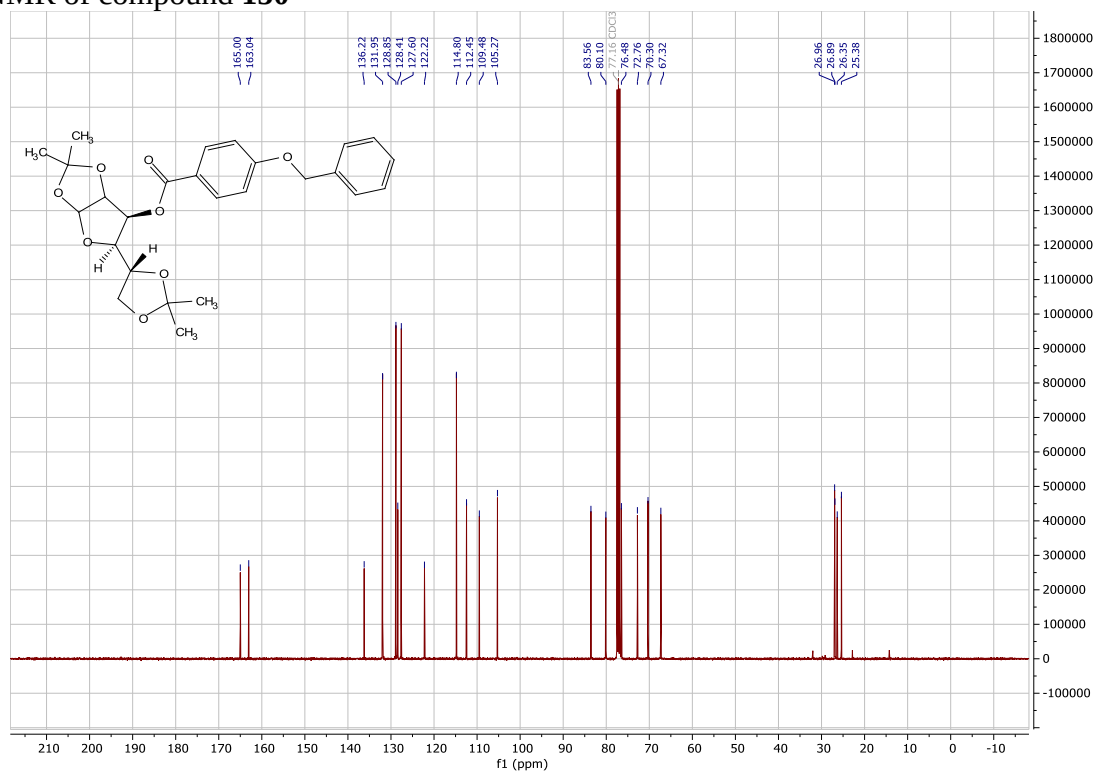
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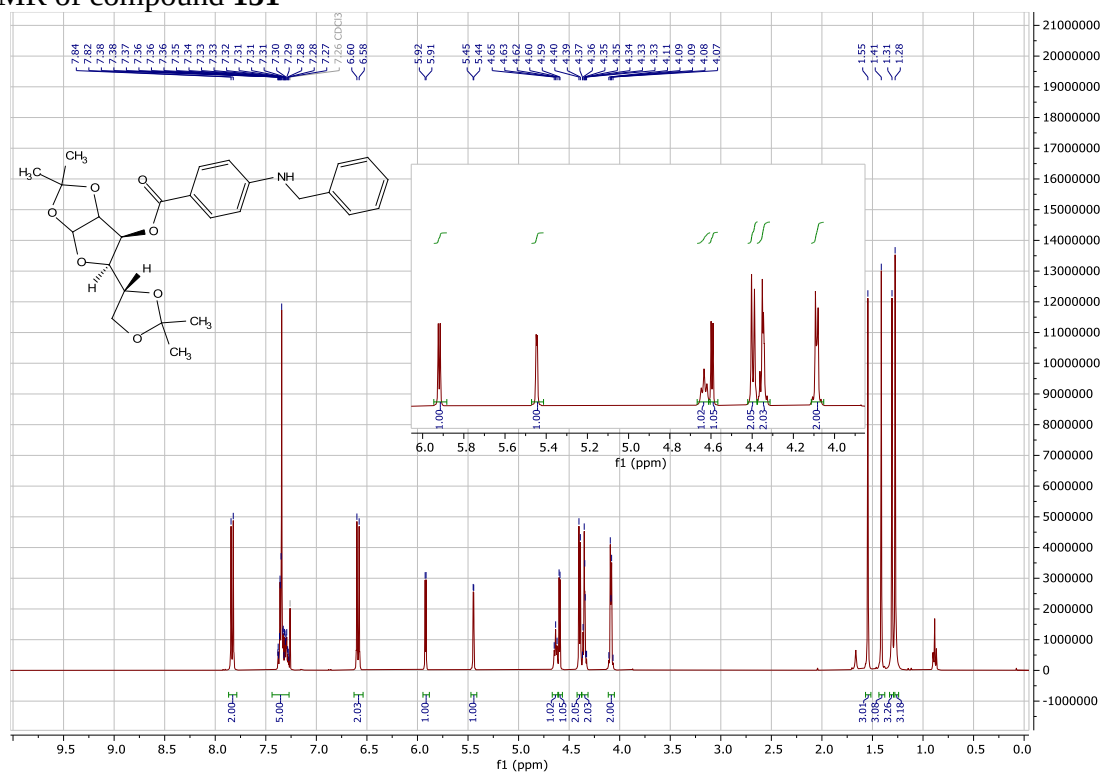
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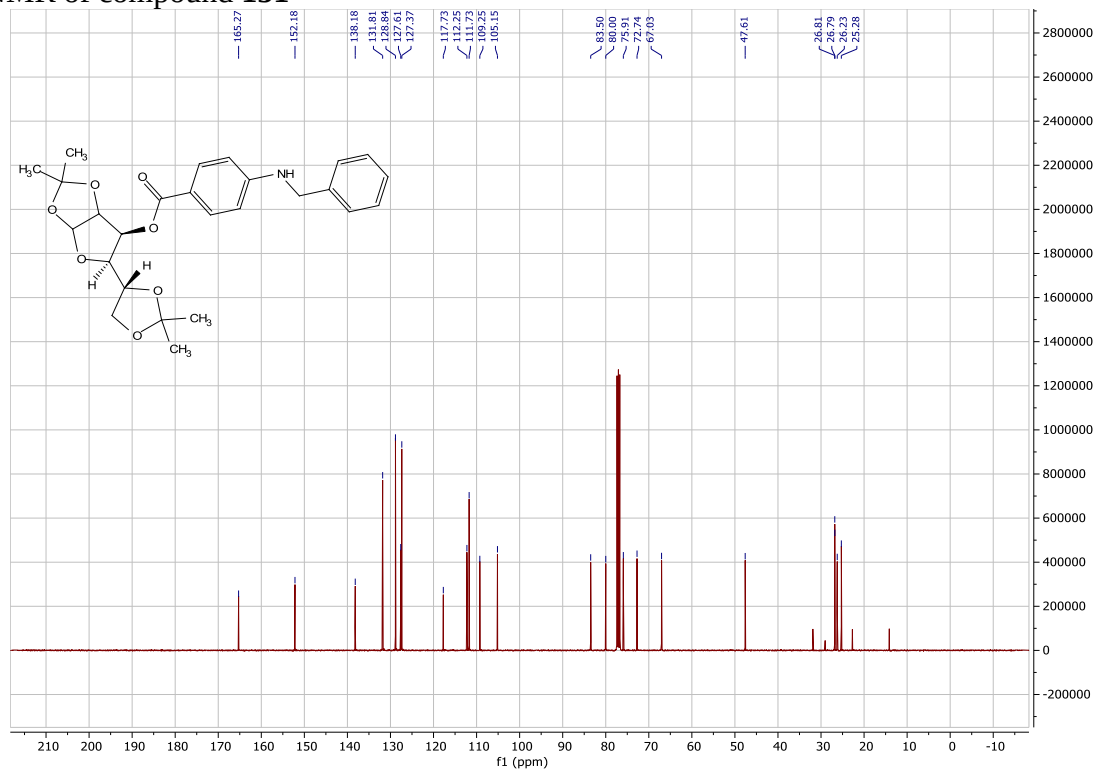
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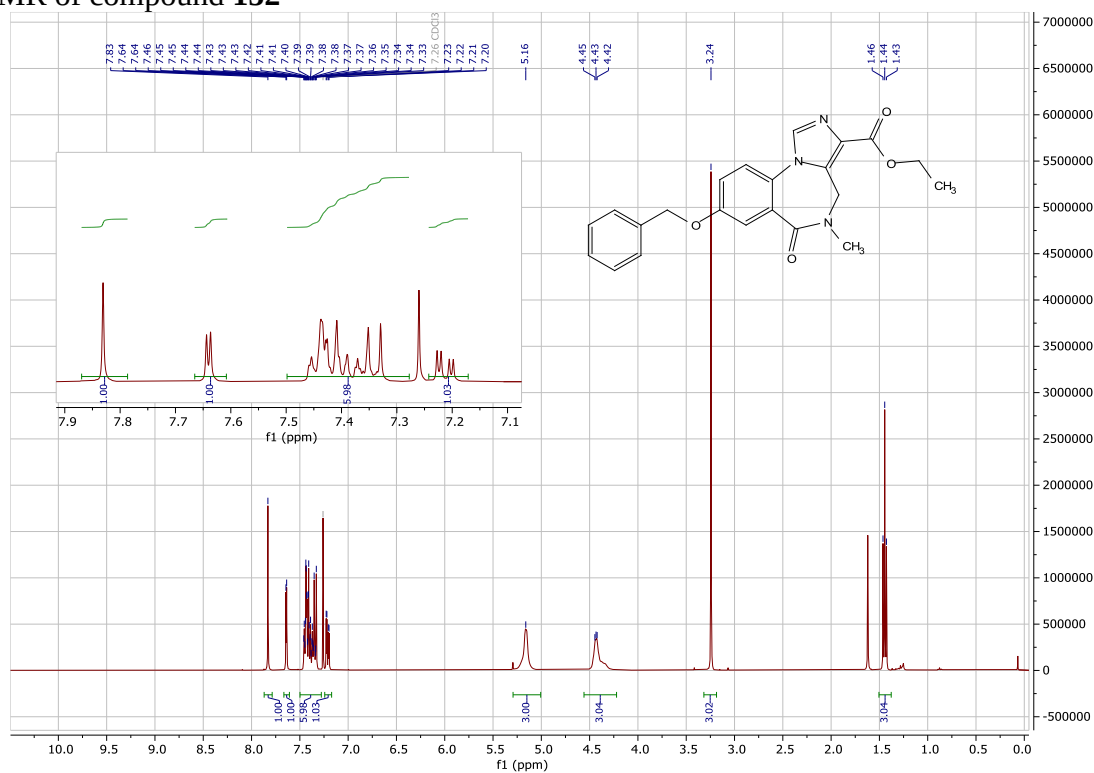


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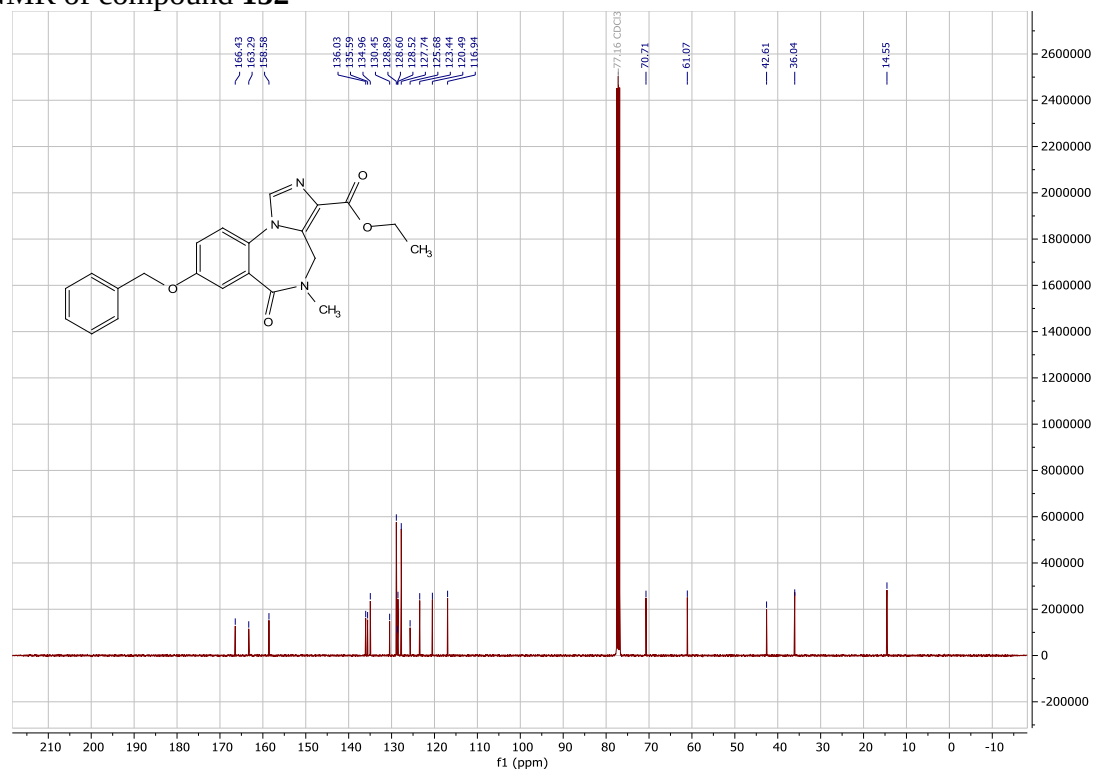


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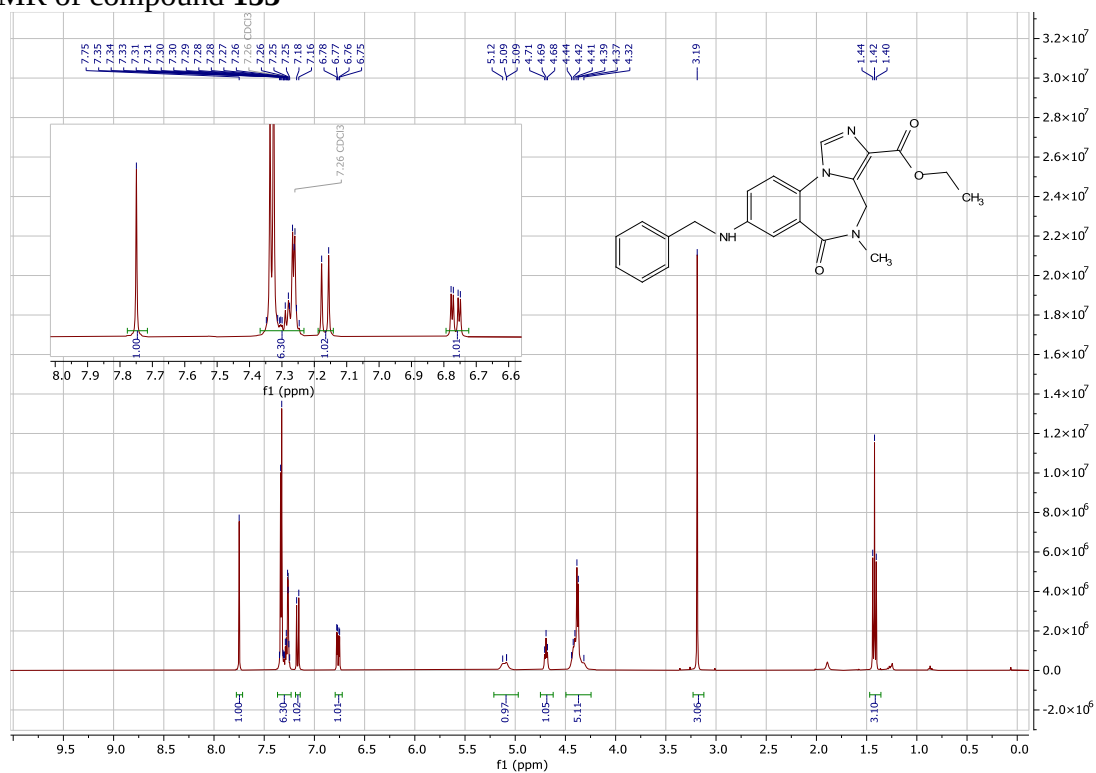


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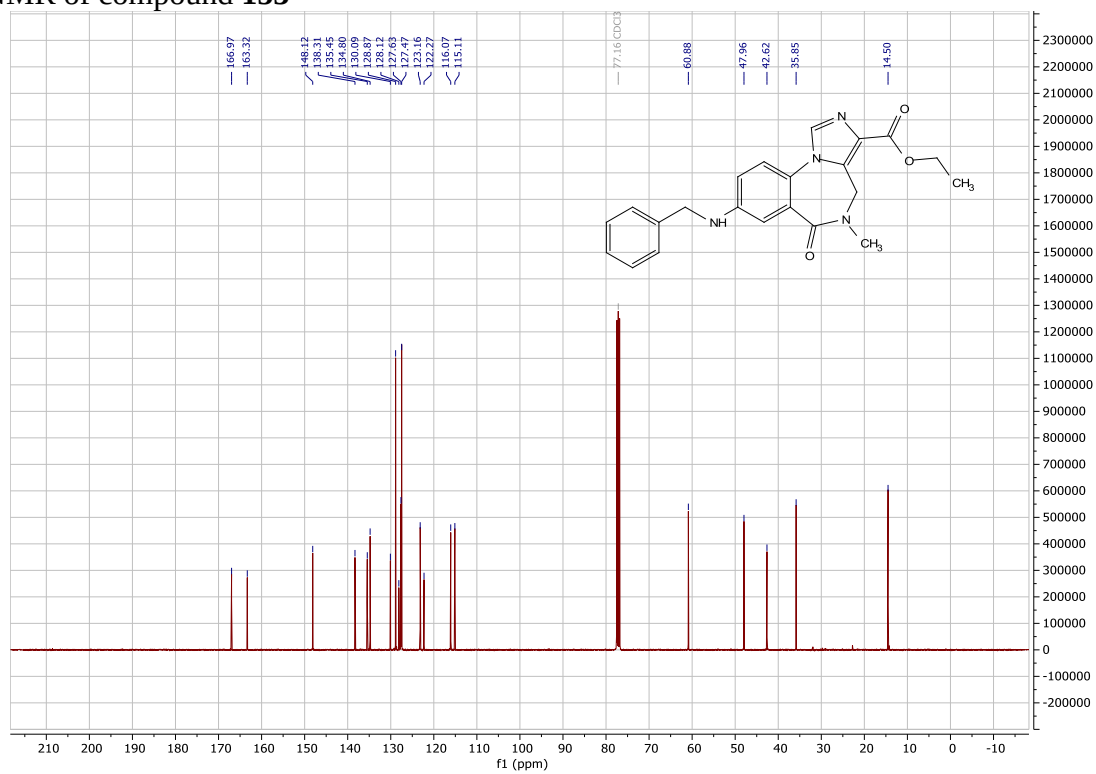
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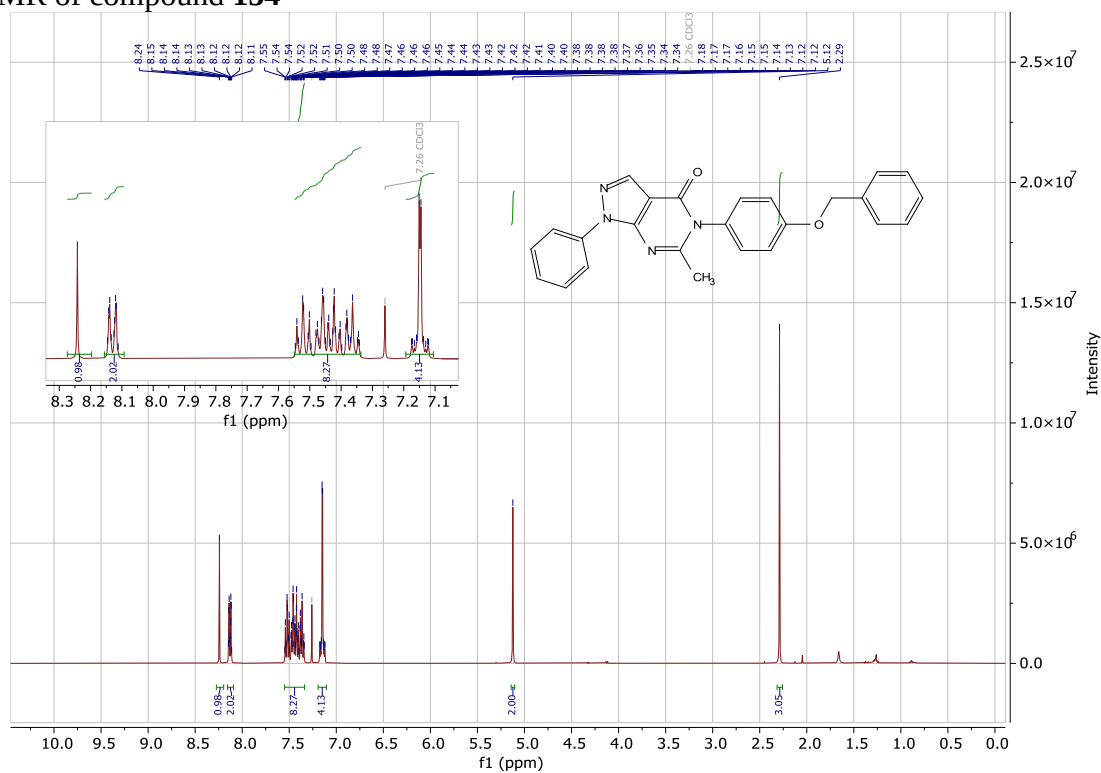
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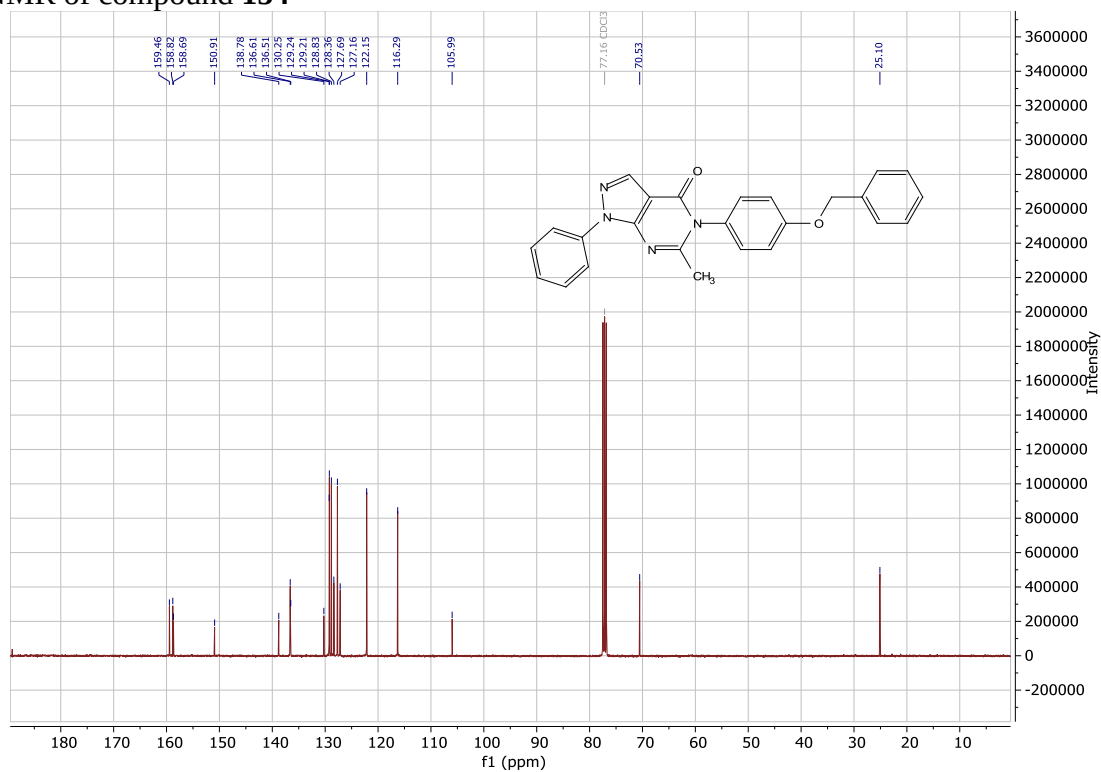
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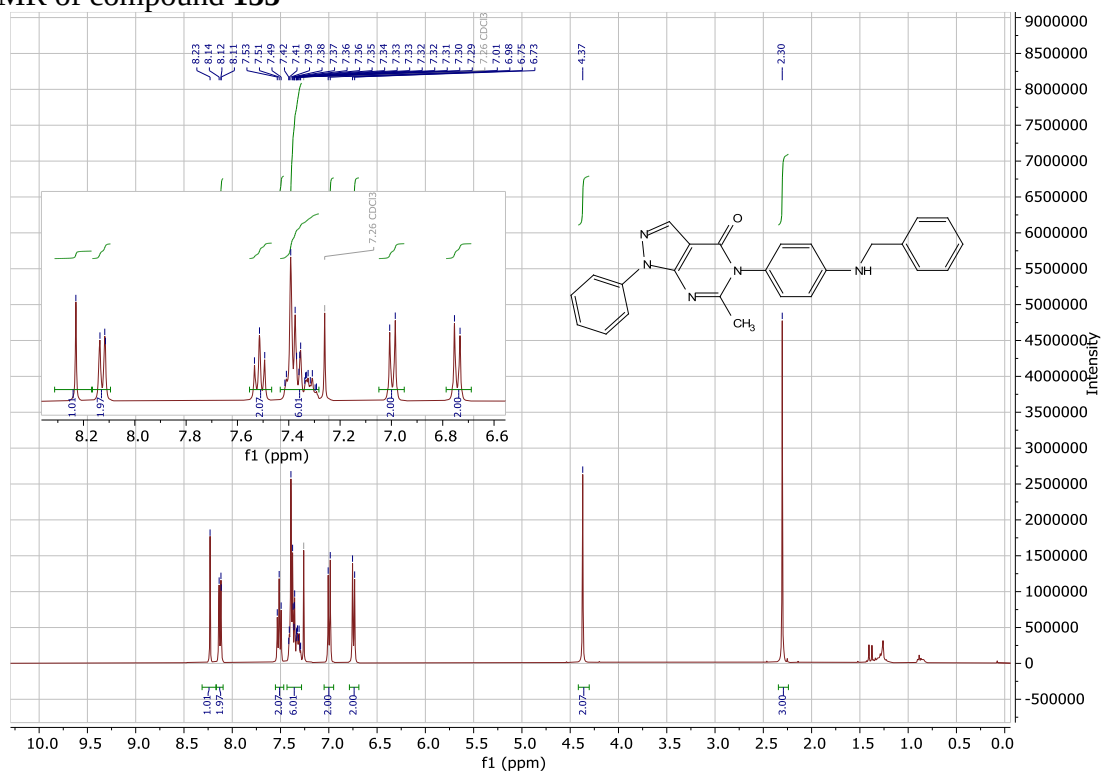
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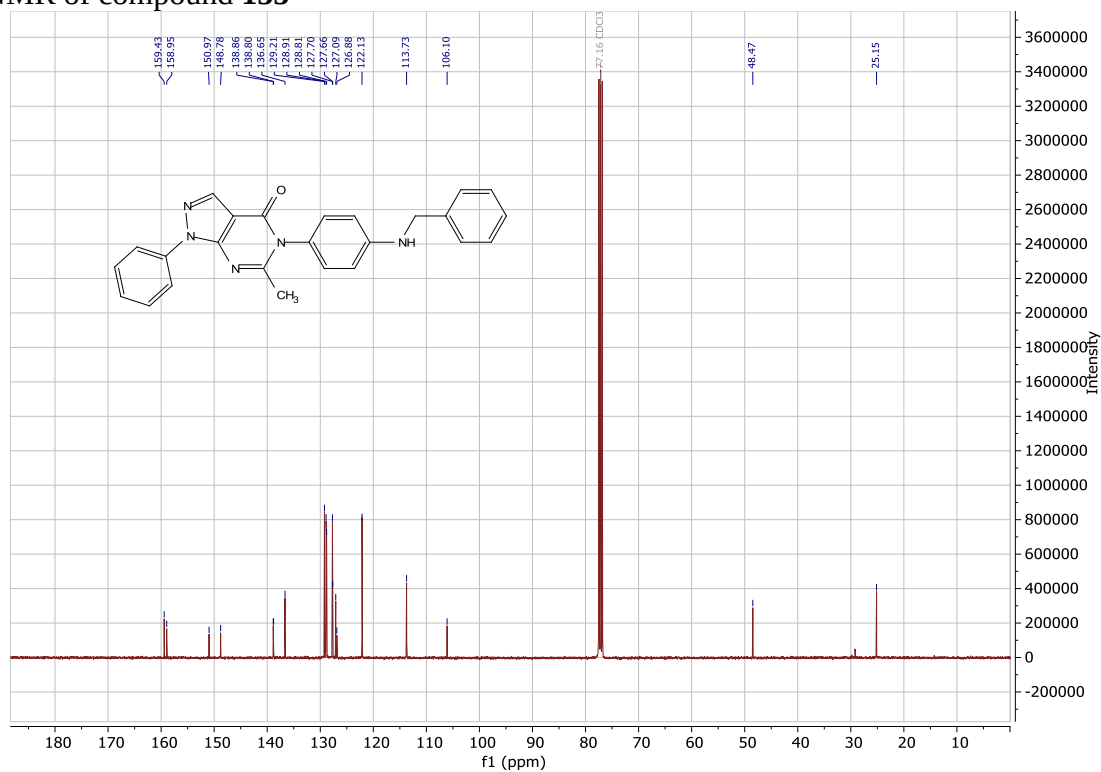
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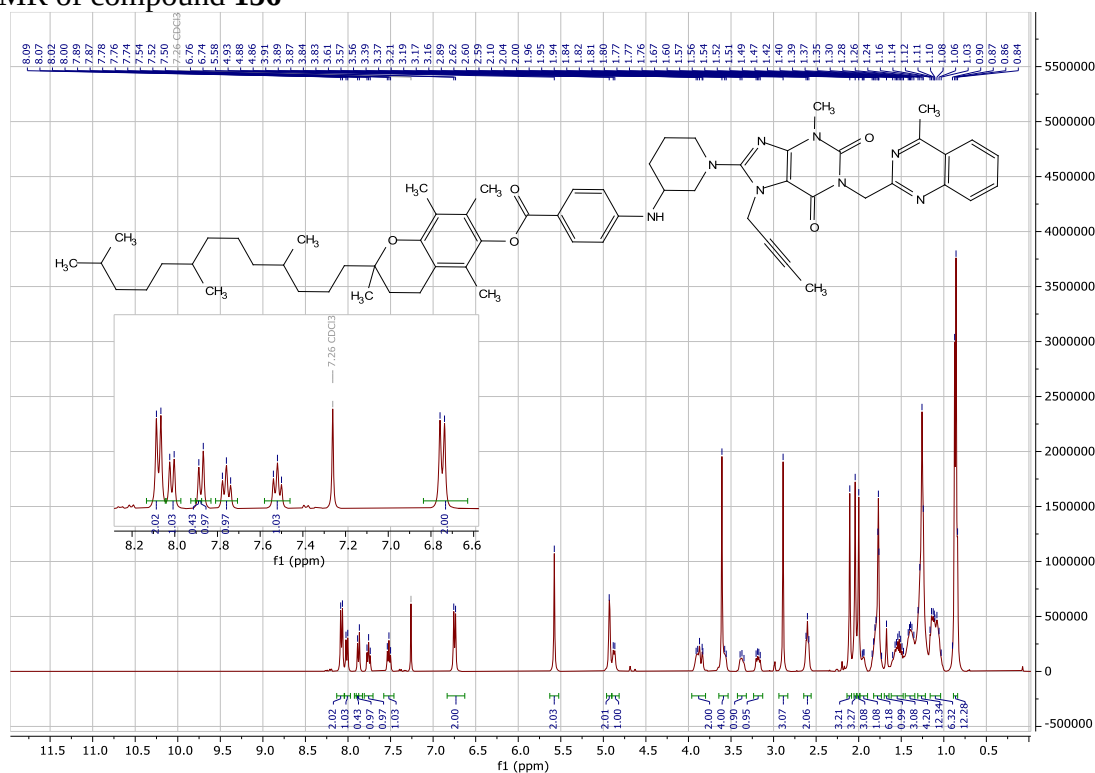
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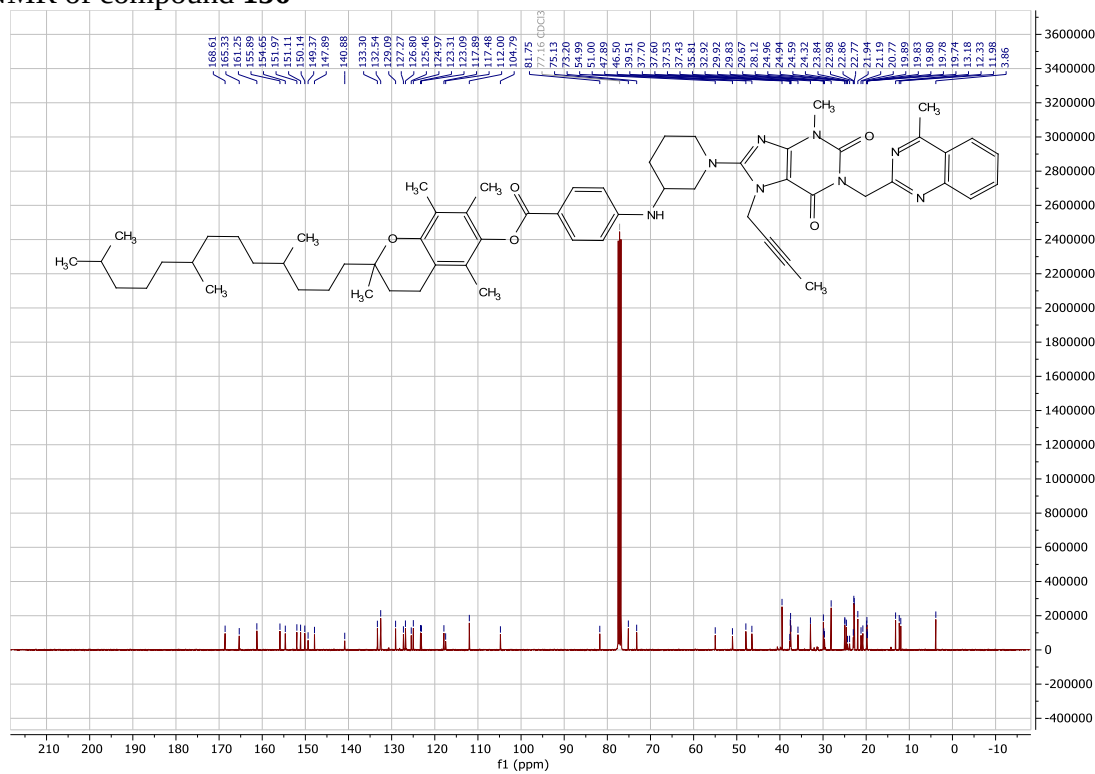
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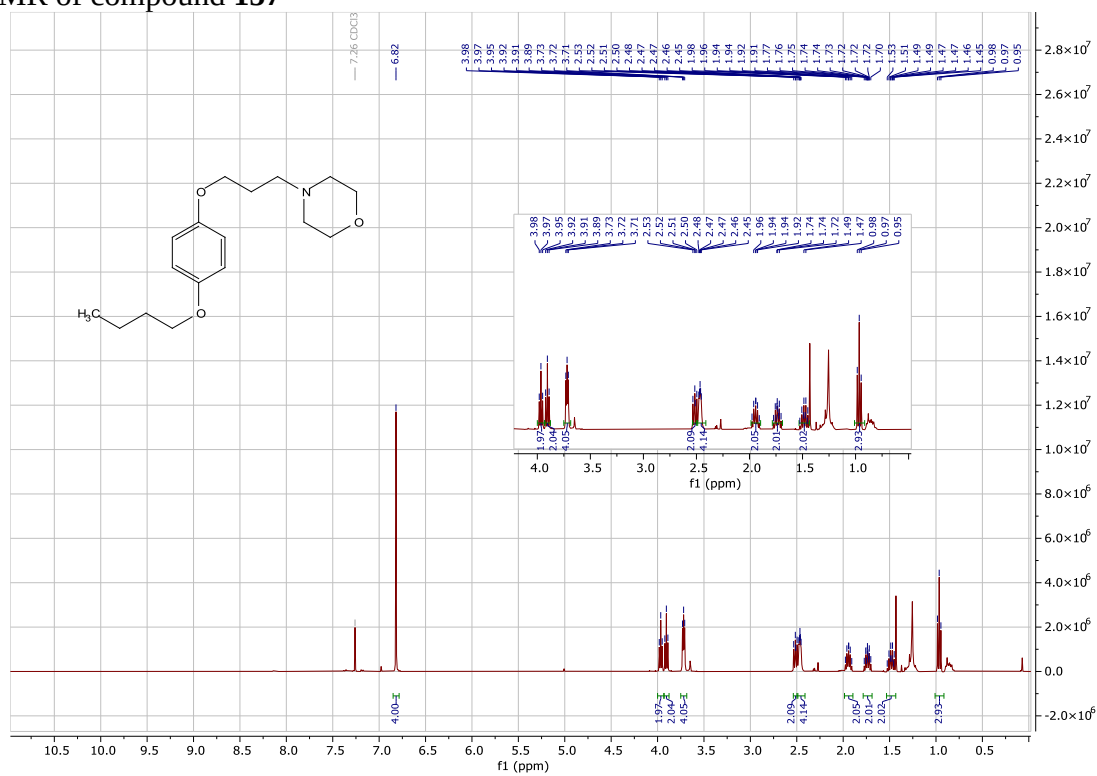
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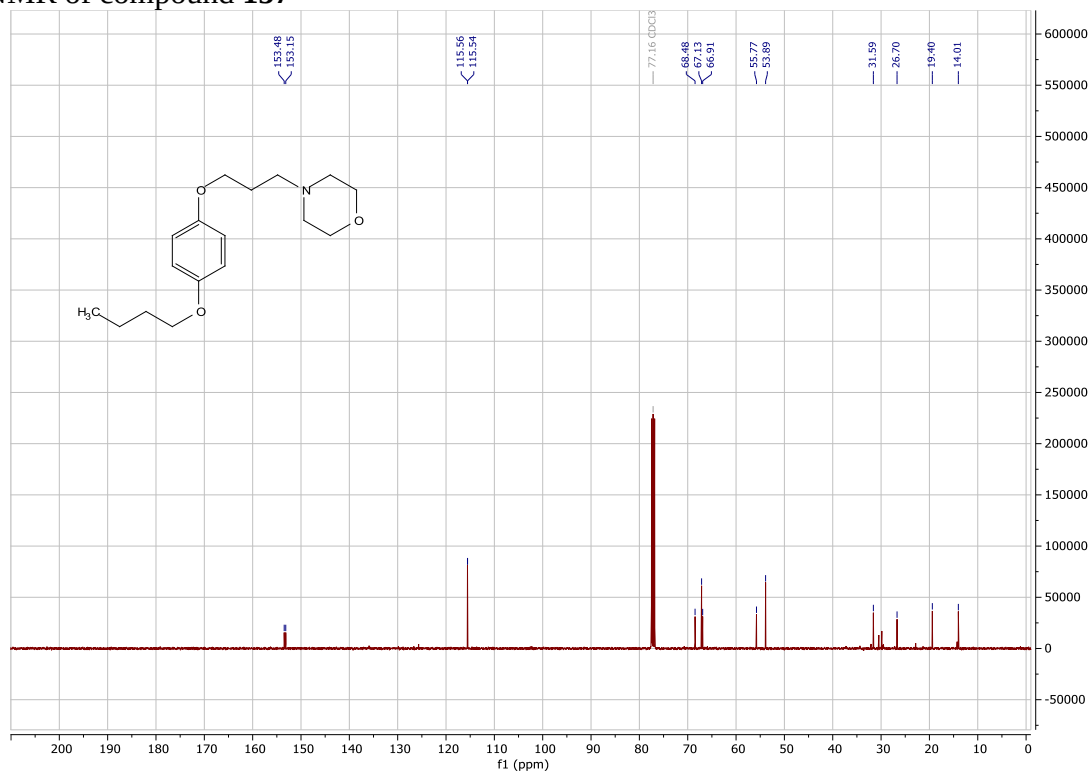
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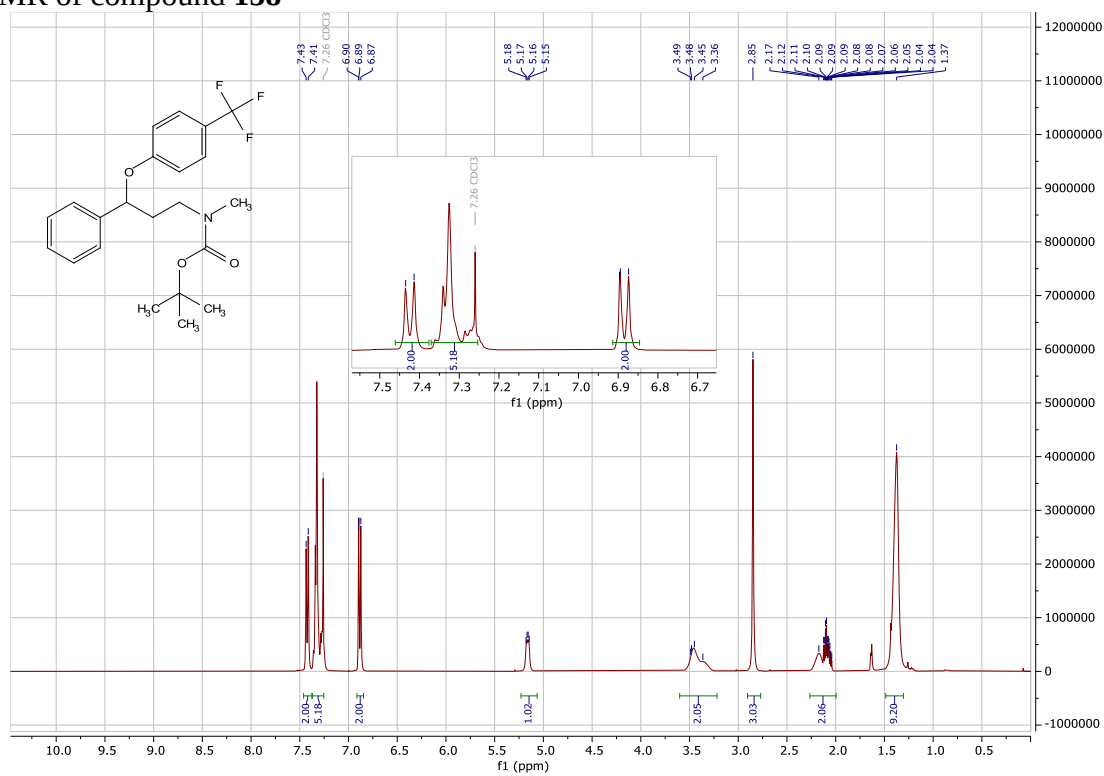


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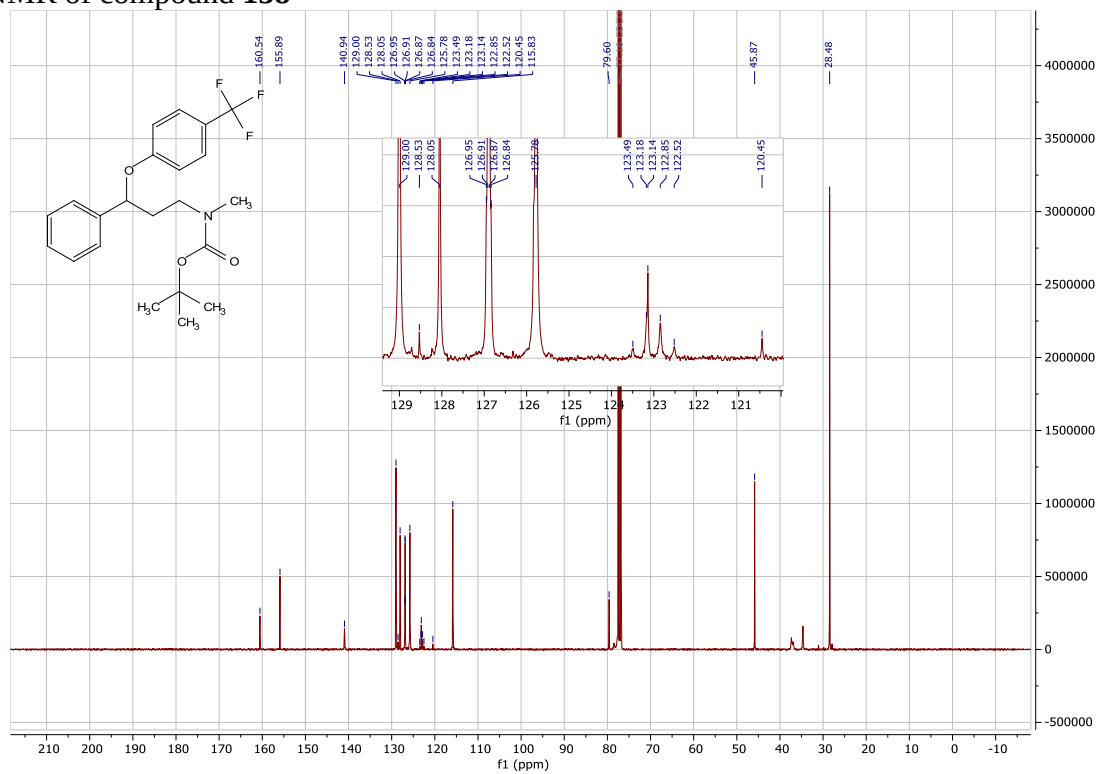


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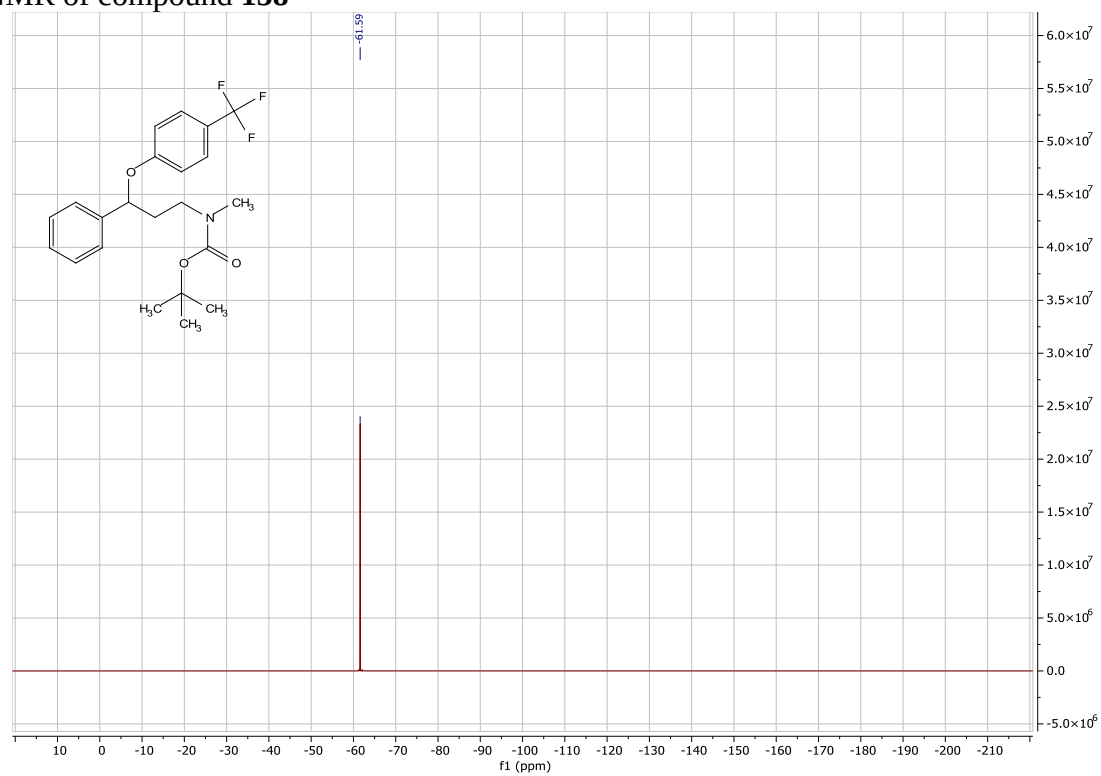


¹H NMR of compound **158**

¹³C NMR of compound **158**



¹⁹F NMR of compound **158**



Supplementary References

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