Supporting Information

Cu-Catalyzed C–N Coupling with Sterically Hindered Partners

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Additional Ligand Evaluation

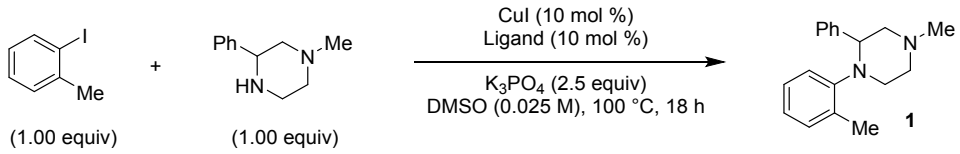

Table S1: Ligands and Complexes Screened by High-Throughput Experimentation

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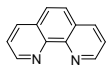
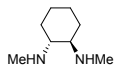
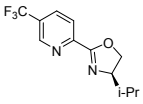
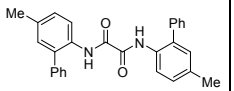
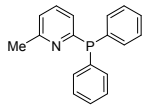
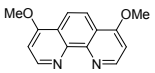
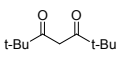
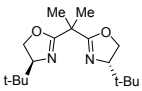
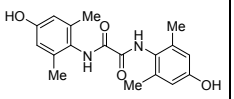
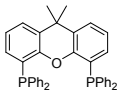
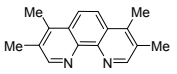
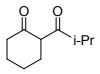
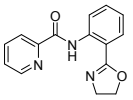
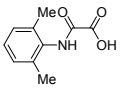
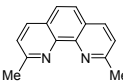
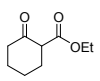
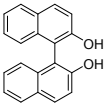
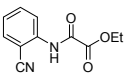
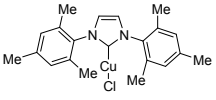
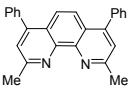
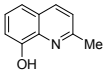
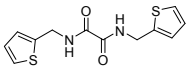
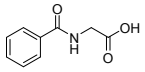
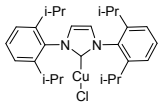
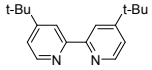
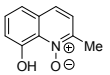
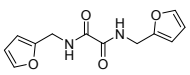
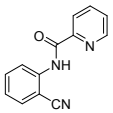
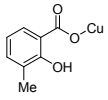
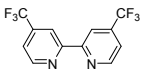
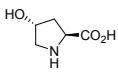
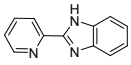
A						
B						
C						 (No CuI added)
D						 (No CuI added)
E						 (No CuI added)
F						 (No CuI added)
G						No Ligand
H					(20 mol %)	

Results of Ligand Evaluation: %Yields of **1** determined by UPLC

Entry	1	2	3	4	5	6
A	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
B	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
C	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
D	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
E	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
F	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
G	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
H	<0.1	<0.1	<0.1	<0.1	<0.1	24.3

High-Throughput Ligand Evaluation: General Procedure

Unless noted, the following steps were conducted in a glovebox under an atmosphere of N_2 with <10 ppm H_2O and O_2.

Ligands and complexes shown in Table S1 were plated into a 96-well reaction block containing 1 mL glass tubes as solutions in DCE or THF, then the solvent was removed in vacuo. When ligands were not fully soluble, they were wet-milled using an IKA probe-type mill and dispensed as stirred suspensions. All ligands and complexes were plated out at a charge of 0.25 µmol per tube, except for PPh_3 (0.50 µmol).

Each tube in the reaction block was charged with a glass bead for agitation purposes, followed by K_3PO_4 (6.25 µmol).

All tubes except those containing Cu complexes (see table) were then charged with a stock solution containing CuI (0.25 µmol) in MeCN (50 µL). The tubes were then evaporated to dryness in a Genevac evaporator under vacuum.

A stock solution containing 2-iodotoluene (2.5 µmol, 1.00 equiv), 1-methyl-3-phenylpiperazine (2.5 µmol, 1.00 equiv) and DMSO (100 µL) was then dispensed to each tube by a Hamilton Star liquid handler.

The tubes were sealed with a Teflon-lined cover, and the plate was placed on a calibrated hotplate/elliptical stirrer pre-set at 100 °C. Stirring was conducted at 300 rpm.

After 18 h, the plate was cooled to room temperature and the following steps were carried out outside the glovebox: The tubes were diluted with MeCN, filtered, and analyzed by UPLC with 4-

chlorobenzonitrile as an internal standard to determine the assay yield of 1-(2-methylphenyl)-2-phenyl-3-methylpiperazine (**1**).

Assay yield Calculation

A sample of product **1** obtained in entry 4, table 1 was isolated by flash column chromatography using 20-35% EtOAc in heptanes as eluent. **1** (0.0017 g) and 4-chlorobenzonitrile (0.0010 g 99+%, Sigma-Aldrich) as internal standard were weighed into a 10-mL volumetric flask, dissolved in 10 mL acetonitrile and injected into a UPLC instrument. The area corresponding to the product (A_{pdt}) and internal standard (A_{std}) was recorded. The relative response factor was determined by using the following formula (AU = absorbance units)

$$Relative\ Response\ Factor\ R = \frac{A(pdt) * wt(std)}{A(std) * wt(pdt)}$$

$$Relative\ Response\ Factor\ R = \frac{(441\ mAU * s) * 1.0\ mg}{(380\ mAU * s) * 1.7\ mg} = 0.68$$

The vials from Table S1 were diluted with an acetonitrile stock solution of 4-chlorobenzonitrile such that each vial contained 0.12 mg 4-chlorobenzonitrile. The vials were analyzed by UPLC and the assay yield was determined by the following formula, with the calculation for **L7** (entry H6, Table S1) given as an example.

$$\%yield = \frac{A(pdt) * wt(std) * 100}{A(std) * R * theor.\ wt(pdt)}$$

$$\%yield = \frac{(92.4\ mAU * s) * 0.12\ mg * 100}{(100\ mAU * s) * 0.68 * 0.67mg} = 24.3\%$$

Additional Notes

Ligands are grouped by general class in Table S1: phenanthroline and bipy derivatives (7 examples), 1,2-diamines (2), 1,3-dicarbonyls (3), amino acids (6), functionalized aryl alcohols (4), bidentate pyridine and oxazoline ligands (5), oxalamides (8), aryl amides (3), phosphines (3), and preformed Cu complexes (4). A blank entry was included to probe the effect of ligandless Cu catalysis.

All ligands and complexes in Table S1 except for H6 (**L7**) are commercially available or were prepared according to literature procedures. See general method B for the preparation of **L7**.

General Methods

Analytical grade solvents and commercially available reagents were purchased from commercial sources and used directly without further purification unless otherwise stated. New bottles of anhydrous DMSO from Aldrich were degassed by freeze-pump-thaw cycles and stored inside a glove box over activated 4 Å molecular sieves. K_3PO_4 was bought from Aldrich as Redi-Dri™ grade and stored inside glove box. Aldrich 99.999% trace metals basis copper(I) iodide was used for the reactions. Thin-layer chromatography (TLC) was carried out on Merck 60 F254 precoated, glass silica plates which were visualized with either ultraviolet light or stained with $KMnO_4$. ^1H NMR and ^{13}C NMR spectra were recorded at room temperature using a Varian I400 or VXR400 (^1H NMR at 400 MHz and $^{13}C\{^1H\}$ NMR at 100 MHz), Varian I500 (^1H NMR at 500 MHz and $^{13}C\{^1H\}$ NMR at 125 MHz). Chemical shifts are reported in ppm with reference to solvent signals [^1H NMR: $CDCl_3$ (7.26 ppm); $^{13}C\{^1H\}$ NMR: $CDCl_3$ (77.2 ppm)]. Signal patterns are indicated as s, singlet; d, doublet; t, triplet, q, quartet; and m, multiplet. Infrared spectra (IR) were obtained on a Bruker Tensor II FTIR Spectrometer analyzed as a thin film and recorded in wavenumbers (cm^{-1}). High resolution Mass spectrometry (HRMS) analysis was obtained using either Agilent 7890B/7250 GC-QTOF system for electron-impact ionization (EI) and reported as m/z (relative intensity) for the molecular ion [M] / suitable fragment ion or Waters/Micromass LCT Classic (ESI-TOF) for electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI) and reported the molecu-lar ion [M+H], [M+Na] or a suitable fragment ion. Flash chromatography was performed using ZEOprep 60 ECO 40-63 µm silica gel. Automated column chromatography was performed on a Biotage Isolera One using Biotage Snap Ultra cartridges (25g, 50g or 100g SiO_2) or a Yamazen Universal Premium column (55g SiO_2) collecting with full spectrum analysis between wavelengths 200-400nm and monitoring wavelengths 254nm and 280nm.

General procedure A for C-N coupling

An oven-dried 16*100 mm size screwcap reaction tube was charged with 4 Å powdered molecular sieves (approx. 400 mg) and sealed with PTFE septa-attached screw cap (See Figure S1). The molecular sieves were then activated by flame-drying the tube under high vacuum for 1 min. Next, the reaction tube was cooled to room temperature and charged with CuI (2-10 mol %), ligand (2-10 mol %) and amine (0.85 mmol, 1.7 equiv). The reaction tube was brought inside a glove box. A magnetic stir bar, K_3PO_4 (2 mmol, 424 mg, 4 equiv), Hantzsch ester (0.5 mmol, 126 mg, 1 equiv), aryl iodide (0.5 mmol, 1 equiv) and degassed anhydrous DMSO (2 mL, 0.25 M) were added. The reaction tube was capped tightly before taking out from the glove box and stirred at 90 °C in a preheated oil bath for 24 h. When the reaction was complete, the mixture was cooled to room temperature and diluted with 20 mL of EtOAc. The organic layer was washed with 20 mL of 10% aqueous LiCl solution. The aqueous layer was back extracted with 10 mL of EtOAc. The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated in a rotary evaporator. The desired product was isolated by flash column chromatography using hexane-ethyl acetate mixture as eluent.

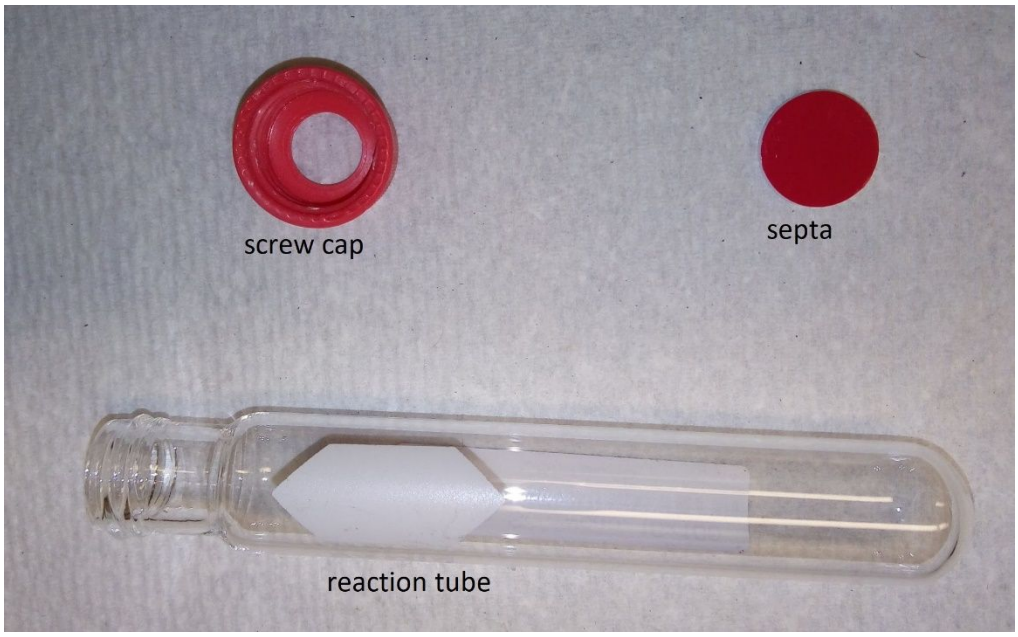
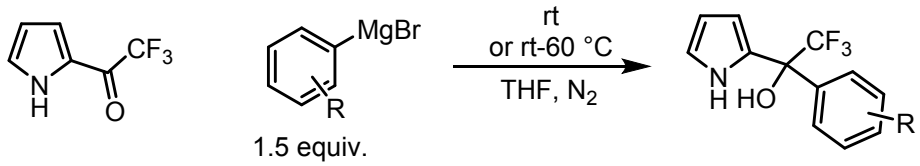


Figure S1: Picture of reaction tube, screwcap and PTFE septa

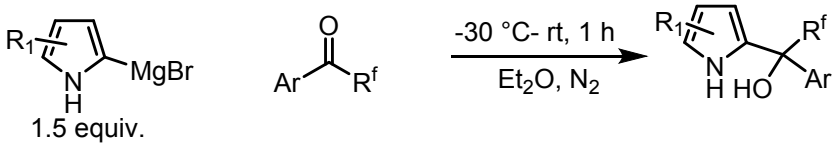
Procedure for ligand synthesis

Ligand Preparation: General method B:



Under a nitrogen atmosphere, a flame dried round-bottom flask was charged with a magnetic stir bar, 2,2,2-trifluoro-1-(1H-pyrrol-2-yl)ethan-1-one (4 mmol) and anhydrous THF (1 M). Aryl Grignard reagent (1.5 equiv) was added dropwise to the solution. The reaction mixture was stirred overnight at room temperature under a positive pressure of nitrogen. After completion the reaction was quenched by adding 10 mL of aqueous 1 N HCl solution. The organic portion was washed with 10 mL of saturated aqueous $NaHCO_3$ and NaCl solution, respectively and dried over anhydrous $MgSO_4$. The desired product was isolated by silica gel flash chromatography using hexane/ ethyl acetate mixture as eluent.

Ligand Preparation: General method C:



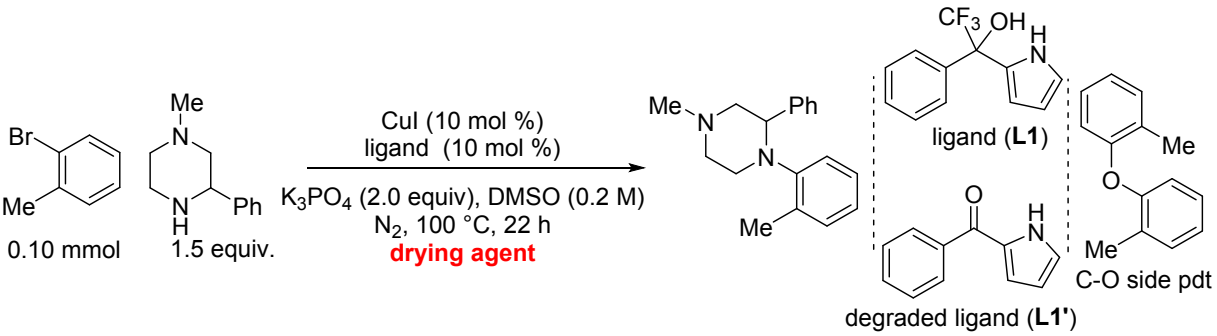
Under a nitrogen atmosphere, a flame dried round-bottom flask was charged with a magnetic stir bar, ketone (4 mmol) and anhydrous Et_2O (1 M). The resulting solution was cooled to -30 °C. Heteroaryl Grignard reagent (1.5 equiv) was added dropwise to the solution while maintaining the internal temperature at -30 °C. The reaction mixture was allowed to warm to the room temperature over 2 h. After completion the reaction was quenched by adding 10 mL of aqueous 1 N HCl solution. The organic portion was separated with 30 mL of ethyl acetate. The organic layer was washed with 10 mL of saturated aqueous $NaHCO_3$ and NaCl solution, respectively and dried over anhydrous $MgSO_4$. The desired product was isolated by silica gel flash chromatography using hexane/ ethyl acetate mixture as eluent.[1]

Optimization details

A. Optimization with aryl bromide:

A-1. Addition of drying agent

Reaction procedure: An over dried 13*100 mm size screwcap reaction tube was charged with a drying agent (approx. 100 mg) and the reaction tube was closed with a rubber septa-attached screw cap. CuI (1.9 mg, 0.01 mmol, 10 mol %), ligand **L** (2.5 mg, 0.01 mmol, 10 mol %) and 1-methyl-3-phenylpiperazine (27.0 mg, 0.15 mmol, 1.5 equiv) were added to the reaction tube. The reaction tube was brought inside an inert atmosphere glove box. Base (0.20 mmol, 2.0 equiv), 1-bromo-2-methylbenzene (17.0 mg, 0.10 mmol, 1.0 equiv) and degassed anhydrous DMSO (0.5 mL, 0.2 M) were added to the tube. The reaction tube was capped tightly, taken out from the glove box and stirred at 100 °C in a preheated oil bath for 22 h. When the reaction was complete, the reaction mixture was cooled to the room temperature and 10 µL of dodecane was added as internal standard. Next, the reaction mixture was diluted with 5 mL of ethyl acetate and analyzed by gas chromatography.



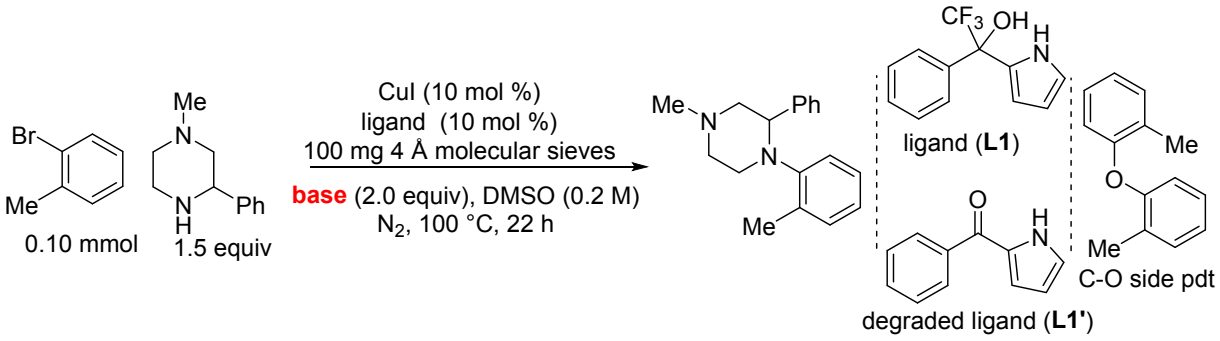
Drying agent	Yield of desired pdt[a]	Yield of C-O side pdt[a]	Unreacted bromide[a]	mol % of L1 after the reaction[a]	mol % of L1' detected[a]
-	17%	23%	40%	6.4 mol %	2.8 mol %

4 Å molecular sieves	18%	1%	78%	3.7 mol %	<1 mol %
Activated silica (60 Å) (100mg)	0%	0%	100%	0 mol %	0 mol %
Activated silica (60 Å) (100 mg) + 100 μL H2O	0 %	0%	96%	3.4 mol %	0.7 mol %
Anhyd. $MgSO_4$ (200 mg)	9%	4%	85%	7 mol %	2.4 mol %

[a]based on gas chromatography analysis

A-2. Optimization of base

Reaction procedure: An over dried 13*100 mm size screwcap reaction tube was charged with a magnetic stir bar and 4 Å powdered molecular sieves (approx. 100 mg) and the reaction tube was closed with a rubber septa-attached screw cap. The molecular sieves were activated by flame drying the tube under high vacuum for 1 min. The reaction tube was cooled to room temperature and charged with CuI (1.9 mg, 0.01 mmol, 10 mol %), ligand **L** (2.5 mg, 0.01 mmol, 10 mol %) and 1-methyl-3-phenylpiperazine (27.0 mg, 0.15 mmol, 1.5 equiv) . The reaction tube was brought inside an inert atmosphere glove box. Base (0.20 mmol, 2 equiv), 1-bromo-2-methylbenzene (17.0 mg, 0.10 mmol, 1.0 equiv) and degassed anhydrous DMSO (0.5 mL, 0.2 M) were added. The reaction tube was capped tightly, taken out of the glove box and stirred at 100 °C in a preheated oil bath for 22 h. When the reaction was complete, the reaction mixture was cooled to room temperature and 10 µL of dodecane was added as internal standard. Next, the reaction mixture was diluted with 5 mL ethyl acetate and analyzed by gas chromatography.



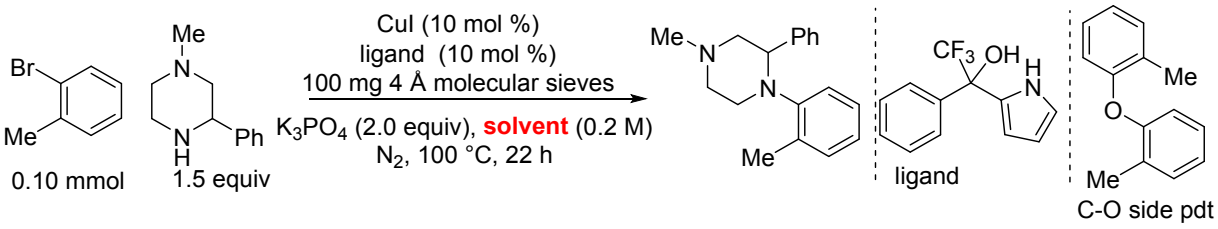
Base	Yield of desired pdt[a]	Yield of C-O side pdt[a]	mol % of L1 after the reaction[a]	mol % of L1' detected[a]
K_3PO_4	**18%**	**2%**	**2.6 mol %**	**<1 mol %**
KO^tBu	1%	0%	0 mol %	10 mol %
NaOAc	14%	4%	7.1 mol %	1 mol %

CsOAc	0 %	0%	9.4 mol %	0 mol %
KOAc	8%	0%	5.1 mol %	<1 mol %
DIPEA	5%	0%	8 mol %	0 mol %
DBU	0%	0%	6 mol %	0 mol %
DABCO	5%	0%	<1 mol %	0 mol %
TMG	0%	0%	<1 mol %	0 mol %
LiHMDS	0%	0%	0 mol %	10 mol %
NaH	1%	1%	2.7 mol %	1.6 mol %

[a]based on gas chromatography analysis

A-3. Optimization of reaction solvent

Reaction procedure: An over dried 13*100 mm size screwcap reaction tube was charged with a magnetic stir bar and 4 Å powdered molecular sieves (approx. 100 mg) and the reaction tube was closed with a rubber septa-attached screw cap. The molecular sieves were activated by flame drying the tube under high vacuum for 1 min. The reaction tube was cooled to room temperature and charged with CuI (1.9 mg, 0.01 mmol, 10 mol %), ligand **L** (2.5 mg, 0.01 mmol, 10 mol %) and 1-methyl-3-phenylpiperazine (27.0 mg, 0.15 mmol, 1.5 equiv). The reaction tube was brought inside an inert atmosphere glove box. K_3PO_4 (42.0 mg, 0.20 mmol, 2.0 equiv), 1-bromo-2-methylbenzene (17.0 mg, 0.10 mmol, 1.0 equiv) and degassed anhydrous solvent (0.5 mL, 0.2 M) were added. The reaction tube was capped tightly, taken out of the glove box and stirred at 100 °C in a preheated oil bath for 22 h. When the reaction was complete, the reaction mixture was cooled to room temperature and 10 µL of dodecane was added as internal standard. Next, the reaction mixture was diluted with 5 mL ethyl acetate and analyzed by gas chromatography.

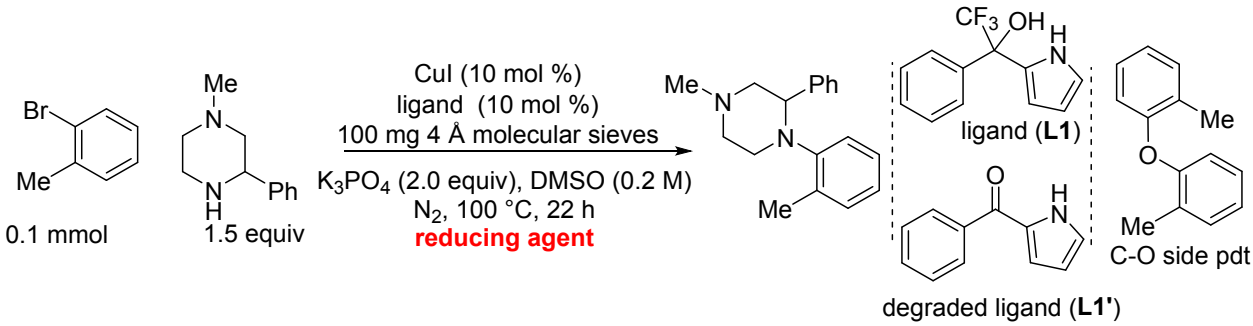


Solvent	Yield of desired pdt[a]	Yield of C-O side pdt[a]	mol % of L1 after the reaction[a]	mol % of L1' detected[a]
1,4 dioxane	0%	0%	nm[b]	nm[b]
MeCN	0%	0%	6.2 mol %	1.8 mol %
DMSO	**18%**	**2%**	**2.6 mol %**	**<1 mol %**
toluene	0%	0%	8.8 mol %	0 mol %
DMA	3%	1%	nm[b]	nm[b]

[a]based on gas chromatography analysis; [b] not measured

A-4. Optimization of reducing agent

Reaction procedure: An over dried 13*100 mm size screwcap reaction tube was charged with a magnetic stir bar and 4 Å powdered molecular sieves (approx. 100 mg) and the reaction tube was closed with a rubber septa-attached screw cap. The molecular sieves were activated by flame drying the tube under high vacuum for 1 min. The reaction tube was cooled to room temperature and charged with CuI (1.9 mg, 0.01 mmol, 10 mol %), ligand **L** (2.5 mg, 0.01 mmol, 10 mol %) and 1-methyl-3-phenylpiperazine (27.0 mg, 0.15 mmol, 1.5 equiv). The reaction tube was brought inside an inert atmosphere glove box. K_3PO_4 (42.0 mg, 0.20 mmol, 2.0 equiv), 1-bromo-2-methylbenzene (17.0 mg, 0.10 mmol, 1.0 equiv), reducing agent (x equiv.) and degassed anhydrous DMSO (0.5 mL, 0.2 M) were added. The reaction tube was capped tightly, taken out of the glove box and stirred at 100 °C in a preheated oil bath for 22 h. When the reaction was complete, the reaction mixture was cooled to room temperature and 10 µL of dodecane was added as internal standard. Next, the reaction mixture was diluted with 5 mL ethyl acetate and analyzed by gas chromatography.



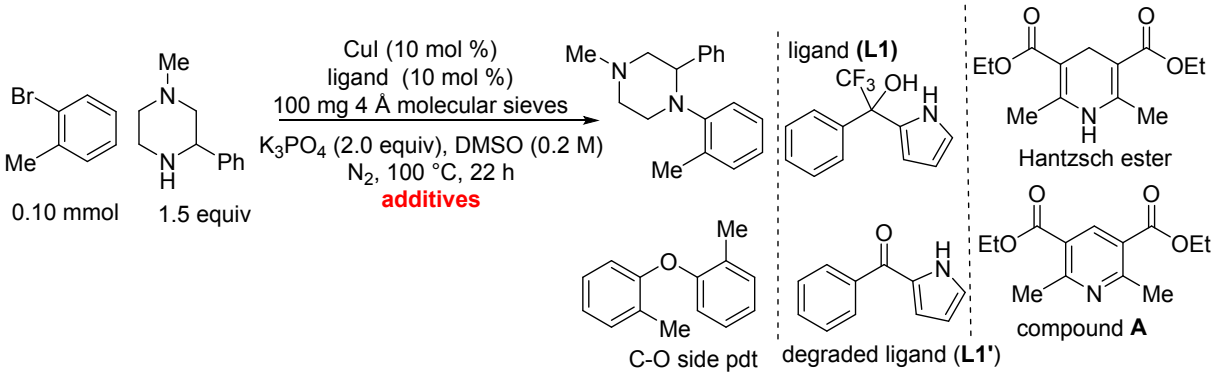
Reducing agent (1 equiv.)	Yield of desired pdt[a]	Yield of C-O side pdt[a]	mol % of L1 after the reaction[a]	mol % of L1' detected[a]
Mn	6%	1%	0 mol %	10 mol %
Zn	7%	0%	1 mol %	3 mol %
Mg	5%	2%	0 mol %	4.9 mol %
In	6%	0%	5.8 mol %	0 mol %
$^{n}Bu_3P$	5%	0%	0 mol %	5.4 mol %
Et_3SiH	8%	0%	2.4 mol %	<1 mol %
tris(trimethylsilyl)silane	0%	0%	nm[b]	nm[b]
Hantzsch ester	**33%**	**3%**	**0 mol %**	**9.4 mol %**
B_2Pin_2	0%	0%	0 mol %	0 mol %
$NaBH_4$	0%	0%	5.3 mol %	0 mol %

$NaB(OAc)_3H$	0%	0%	5.7 mol %	0 mol %
sodium formate	8%	0%	2.8 mol %	2.8 mol %
formic acid	0%	0%	10 mol %	0 mol %
sodium ascorbate (0.5 equiv.)	0%	0%	nm[b]	nm[b]
no reducing agent	**17%**	**2%**	**1 mol %**	**1 mol %**

[a]based on gas chromatography analysis; [b] not measured

A-5. Role of Hantzsch ester

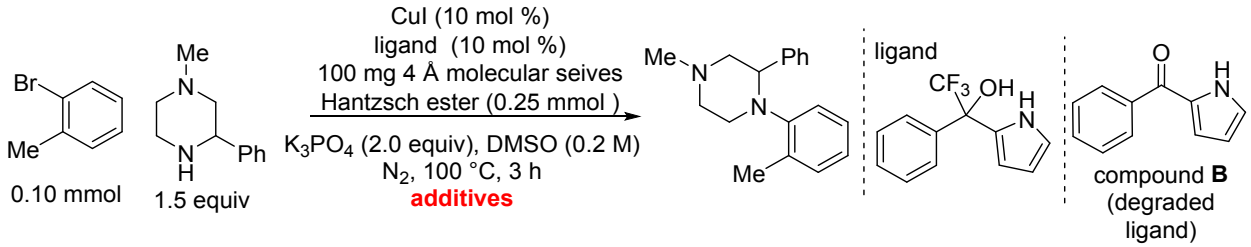
Reaction procedure: An over dried 13*100 mm size screwcap reaction tube was charged with a magnetic stir bar and 4 Å powdered molecular sieves (approx. 100 mg) and the reaction tube was closed with a rubber septa-attached screw cap. The molecular sieves were activated by flame drying the tube under high vacuum for 1 min. The reaction tube was cooled to room temperature and charged with CuI (1.9 mg, 0.01 mmol, 10 mol %), ligand **L** (2.5 mg, 0.01 mmol, 10 mol %) and 1-methyl-3-phenylpiperazine (27.0 mg, 0.15 mmol, 1.5 equiv) . The reaction tube was brought inside an inert atmosphere glove box. K_3PO_4 (42.0 mg, 0.20 mmol, 2.0 equiv), 1-bromo-2-methylbenzene (17.0 mg, 0.10 mmol, 1.0 equiv), additives (x equiv.) and degassed anhydrous DMSO (0.5 mL, 0.2 M) were added. The reaction tube was capped tightly, taken out of the glove box and stirred at 100 °C in a preheated oil bath for 22 h. When the reaction was complete, the reaction mixture was cooled to room temperature and 10 µL of dodecane was added as internal standard. Next, the reaction mixture was diluted with 5 mL ethyl acetate and analyzed by gas chromatography.



Additives	**Yield of desired pdt[a]**	**Yield of C-O side pdt[a]**	**mol % of L1 after the reaction[a]**	**mol % of L1' detected[a]**
Hantzsch ester (1.00 equiv)	34%	3%	2.9 mol %	7.3 mol %
Hantzsch ester (0.50 equiv)	32%	3%	1.8 mol %	8.3 mol %
Hantzsch ester (2.00 equiv)	31%	3 %	0.9 mol %	9 mol %
Hantzsch ester (0.25 equiv)	33%	2%	5.9 mol %	2.7 mol %
Hantzsch ester (1.00 equiv), 3 h	37%	3%	8.9 mol %	0.6 mol %

Hantzsch ester (1.00 equiv) without ligand	0%	0%	-	-
Hantzsch ester (0.25 equiv), 30 mol % ligand, 16 h	52%	3%	18.4 mol %	8.2 mol %
compound **A** (10 mol %)	15%	1%	4.4 mol %	4 mol %

[a]based on gas chromatography analysis

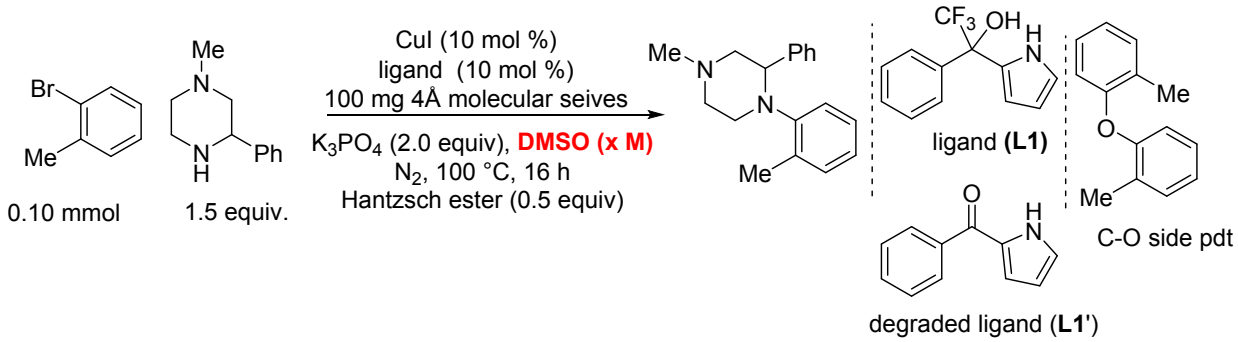


Additives	**Yield of desired pdt[a]**	**Yield of C-O side pdt[a]**	**mol % of L1 after the reaction[a]**	**mol % of L1' detected[a]**
10 mol % of compound **B**	6%	1%	0 mol %	20 mol %
10 mol % of compound **B** without Hantzsch ester	4%	1%	1.2 mol %	9.8 mol %
5 mol % of compound **B**	14%	2%	3.8 mol %	7.8 mol %
5 mol % of compound **B** without Hantzsch ester:	5%	1%	2.4 mol %	4 mol %
2 mol % of compound **B**	17%	3%	3.7 mol %	1.9 mol %
2 mol % of compound **B** without Hantzsch ester	9%	2%	2 mol %	2.9 mol %

[a]based on gas chromatography analysis

A-6. Reaction concentration optimization

Reaction procedure: An over dried 13*100 mm size screwcap reaction tube was charged with a magnetic stir bar and 4 Å powdered molecular sieves (approx. 100 mg) and the reaction tube was closed with a rubber septa-attached screw cap. The molecular sieves were activated by flame drying the tube under high vacuum for 1 min. The reaction tube was cooled to room temperature and charged with CuI (1.9 mg, 0.01 mmol, 10 mol %), ligand **L** (2.5 mg, 0.01 mmol, 10 mol %) and 1-methyl-3-phenylpiperazine (27.0 mg, 0.15 mmol, 1.5 equiv). The reaction tube was brought inside an inert atmosphere glove box. K_3PO_4 (42.0 mg, 0.20 mmol, 2.0 equiv), 1-bromo-2-methylbenzene (17.0 mg, 0.10 mmol, 1.0 equiv), Hantzsch ester (12.5 mg, 0.05 mmol, 0.5 equiv.) and degassed anhydrous DMSO (x M) were added. The reaction tube was capped tightly, taken out of the glove box and stirred at 100 °C in a preheated oil bath for 22 h. When the reaction was complete, the reaction mixture was cooled to room temperature and 10 µL of dodecane was added as internal standard. Next, the reaction mixture was diluted with 5 mL ethyl acetate and analyzed by gas chromatography.

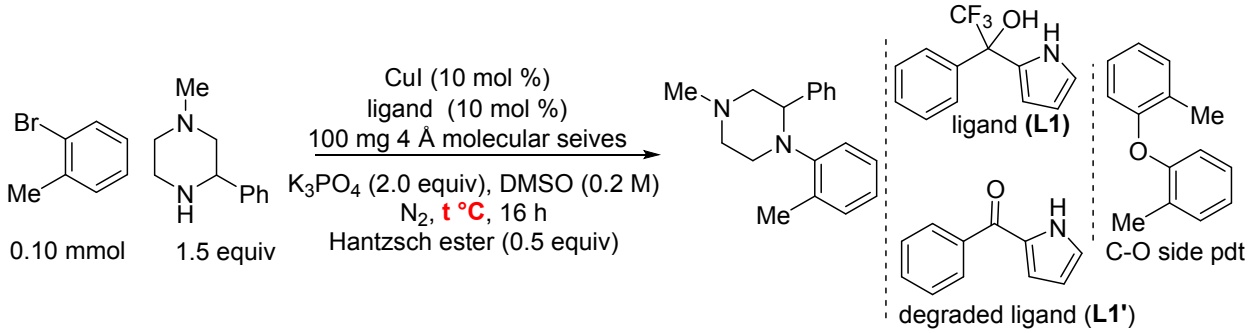


Concentration	Yield of desired pdt[a]	Yield of C-O side pdt[a]	mol % of L1 after the reaction[a]	mol % of L1' detected[a]
0.4 M	31%	3%	0.3 mol %	9.7 mol %
0.2 M	**32%**	**2%**	**2.3 mol %**	**4 mol %**
0.1 M	27%	3%	3.4 mol %	3 mol %
0.067 M	29%	4%	1.9 mol %	1.9 mol %

[a]based on gas chromatography analysis

A-7. Effect of temperature

Reaction procedure: An over dried 13*100 mm size screwcap reaction tube was charged with a magnetic stir bar and 4 Å powdered molecular sieves (approx. 100 mg) and the reaction tube was closed with a rubber septa-attached screw cap. The molecular sieves were activated by flame drying the tube under high vacuum for 1 min. The reaction tube was cooled to room temperature and charged with CuI (1.9 mg, 0.01 mmol, 10 mol %), ligand **L** (2.5 mg, 0.01 mmol, 10 mol %) and 1-methyl-3-phenylpiperazine (27.0 mg, 0.15 mmol, 1.5 equiv). The reaction tube was brought inside an inert atmosphere glove box. K_3PO_4 (42.0 mg, 0.20 mmol, 2.0 equiv), 1-bromo-2-methylbenzene (17.0 mg, 0.10 mmol, 1.0 equiv), Hantzsch ester (12.5 mg, 0.05 mmol, 0.5 equiv.) and degassed anhydrous DMSO (x M) were added. The reaction tube was capped tightly, taken out of the glove box and stirred at t °C in a preheated oil bath for 16 h. When the reaction was complete, the reaction mixture was cooled to room temperature and 10 µL of dodecane was added as internal standard. Next, the reaction mixture was diluted with 5 mL ethyl acetate and analyzed by gas chromatography.

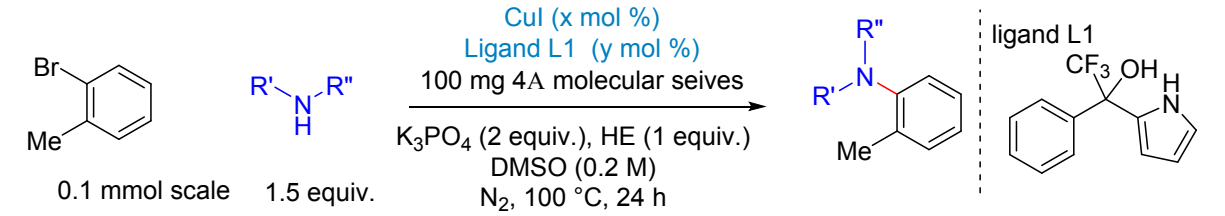


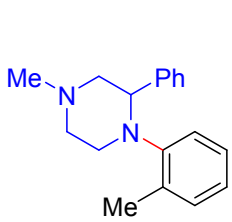
Temp.	Yield of desired pdt[a]	Yield of C-O side pdt[a]	Unreacted bromide[a]	mol % of L1 after the reaction[a]	mol % of L1' detected[a]
80, 24 h	26%	1%	70%	7.4 mol %	0 mol %
90, 24 h	28%	<1%	65%	2.2 mol %	0 mol %
120	28%	3%	80%	0.5 mol %	3.2 mol %
130	18%	3%	70%	0 mol %	2.1 mol %

[a]based on gas chromatography analysis

A-8. Effect of higher catalyst loading

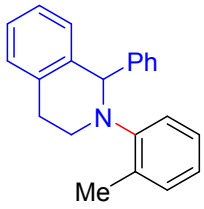
Reaction procedure: An over dried 13*100 mm size screwcap reaction tube was charged with a magnetic stir bar and 4 Å powdered molecular sieves (approx. 100 mg) and the reaction tube was closed with a rubber septa-attached screw cap. The molecular sieves were activated by flame drying the tube under high vacuum for 1 min. The reaction tube was cooled to room temperature and charged with CuI (10-50 mol %), ligand **L** (10-50 mol %) and amine (0.15 mmol, 1.5 equiv). The reaction tube was brought inside an inert atmosphere glove box. K_3PO_4 (42.0 mg, 0.20 mmol, 2.0 equiv), 1-bromo-2-methylbenzene (17.0 mg, 0.10 mmol, 1.0 equiv), Hantzsch ester (25.3 mg, 0.1 mmol, 1 equiv.) and degassed anhydrous DMSO (0.5 mL) were added. The reaction tube was capped tightly, taken out of the glove box and stirred at 100 °C in a preheated oil bath for 24 h. When the reaction was complete, the reaction mixture was cooled to room temperature and 10 µL of dodecane was added as internal standard. Next, the reaction mixture was diluted with 5 mL ethyl acetate and analyzed by gas chromatography.





10 mol % CuI/10 mol % L1:
yield 33 % (unreacted bromide 65 %)

50 mol % CuI/50 mol % L1:
yield 47 % (unreacted bromide 50 %)



10 mol % CuI/10 mol % L1:
yield 45 % (unreacted bromide 55 %)

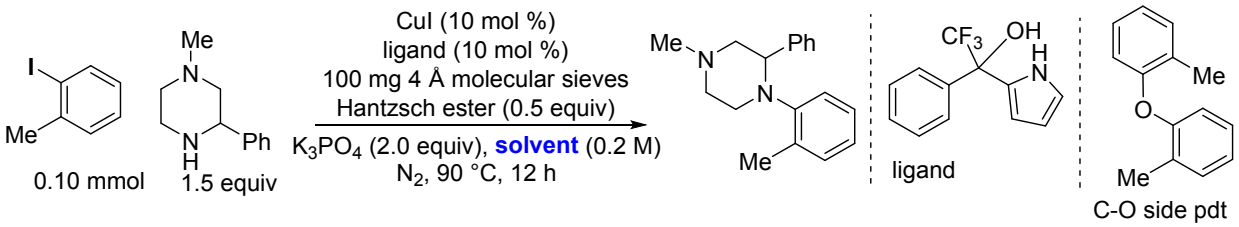
10 mol % CuI/30 mol % L1:
yield 54 % (unreacted bromide 42 %)

50 mol % CuI/50 mol % L1:
yield 55 % (unreacted bromide ~40 %)

B. Optimization with aryl iodide:

B-1. Optimization of solvent

Reaction procedure: An over dried 13*100 mm size screwcap reaction tube was charged with a magnetic stir bar and 4 Å powdered molecular sieves (approx. 100 mg) and the reaction tube was closed with a rubber septa-attached screw cap. The molecular sieves were activated by flame drying the tube under high vacuum for 1 min. The reaction tube was cooled to room temperature and charged with CuI (1.9 mg, 0.01 mmol, 10 mol %), ligand **L** (2.5 mg, 0.01 mmol, 10 mol %) and 1-methyl-3-phenylpiperazine (27.0 mg, 0.15 mmol, 1.5 equiv). The reaction tube was brought inside an inert atmosphere glove box. K_3PO_4 (42.0 mg, 0.20 mmol, 2.0 equiv), 1-iodo-2-methylbenzene (22.0 mg, 0.10 mmol, 1.0 equiv), Hantzsch ester (12.5 mg, 0.05 mmol, 0.5 equiv.) and degassed anhydrous solvent (0.5 mL, 0.2 M) were added. The reaction tube was capped tightly, taken out of the glove box and stirred at 90 °C in a preheated oil bath for 12 h. When the reaction was complete, the reaction mixture was cooled to room temperature and 10 µL of dodecane was added as internal standard. Next, the reaction mixture was diluted with 5 mL ethyl acetate and analyzed by gas chromatography.

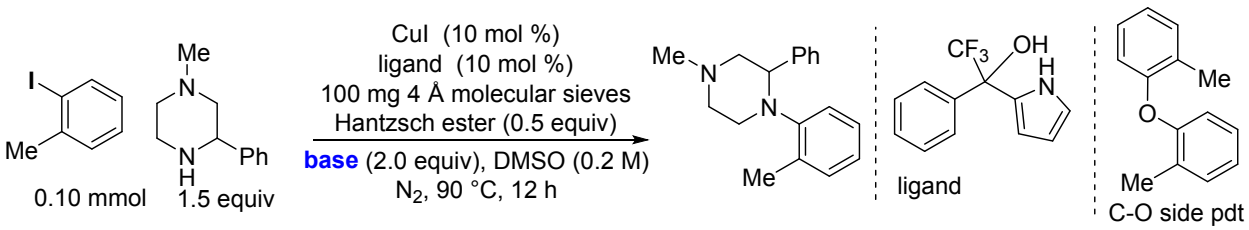


Solvent	Yield of desired pdt[a]	Yield of C-O side pdt[a]	mol % of L1 after the reaction[a]
DMSO	65%	5%	8.4 mol %
DCE	0%	0 %	0 mol %
DCE: DMSO (1:1)	0%	0%	7.3 mol %
$PhCF_3$	0%	0%	7.6 mol %
$PhCF_3$: DMSO (1:1)	17%	<1%	4.2 mol %
THF	5%	<1%	3.7 mol %
THF:DMSO (1:1)	35%	2 %	5.6 mol %
1,4 dioxane	0%	5%	3.8 mol %
1,4 dioxane:DMSO (1:1)	27%	2%	5.8 mol %
DMA	24%	< 1%	3 mol %
DMF	33%	1%	2.4 mol %
MeCN	8%	0%	3.7 mol %

[a]based on gas chromatography analysis

B-2. Optimization of base

Reaction procedure: An over dried 13*100 mm size screwcap reaction tube was charged with a magnetic stir bar and 4 Å powdered molecular sieves (approx. 100 mg) and the reaction tube was closed with a rubber septa-attached screw cap. The molecular sieves were activated by flame drying the tube under high vacuum for 1 min. The reaction tube was cooled to room temperature and charged with CuI (1.9 mg, 0.01 mmol, 10 mol %), ligand **L** (2.5 mg, 0.01 mmol, 10 mol %) and 1-methyl-3-phenylpiperazine (27.0 mg, 0.15 mmol, 1.5 equiv). The reaction tube was brought inside an inert atmosphere glove box. Base (0.20 mmol, 2.0 equiv), 1-iodo-2-methylbenzene (22.0 mg, 0.10 mmol, 1.0 equiv), Hantzsch ester (12.5 mg, 0.05 mmol, 0.5 equiv.) and degassed anhydrous DMSO (0.5 mL, 0.2 M) were added. The reaction tube was capped tightly, taken out of the glove box and stirred at 90 °C in a preheated oil bath for 12 h. When the reaction was complete, the reaction mixture was cooled to room temperature and 10 µL of dodecane was added as internal standard. Next, the reaction mixture was diluted with 5 mL ethyl acetate and analyzed by gas chromatography.

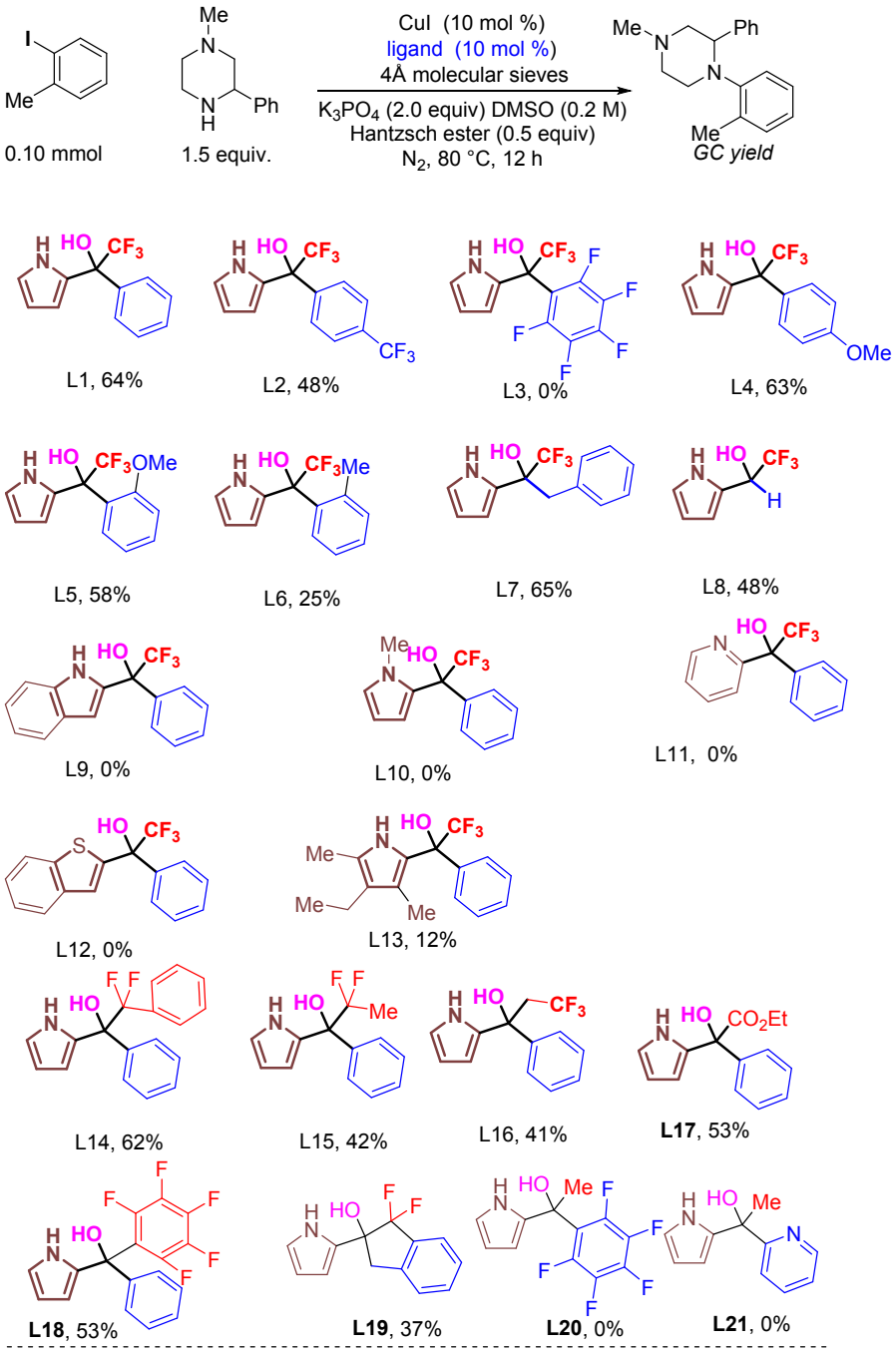


Base	Yield of desired pdt[a]	Yield of C-O side pdt[a]	mol % of L1 after the reaction[a]
K_3PO_4	65%	5%	8.4 mol %
K_2HPO_4	7%	0%	10 mol %
KH_2PO_4	3%	0%	9.6 mol %
Na_2CO_3	18 %	1%	6.8 mol %
K_2CO_3	49 %	7%	3.0 mol %
NaO^tBu	0%	0%	0 mol %
Cs_2CO_3	19%	28%	9 mol %

[a]based on gas chromatography analysis

B-3. Screening of ligand

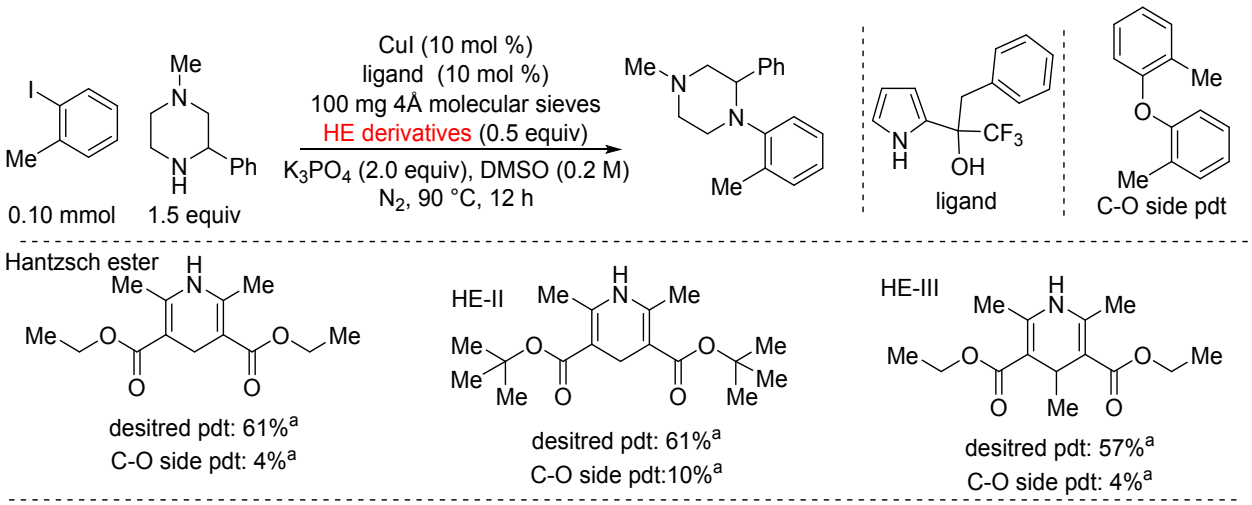
Reaction procedure: An over dried 13*100 mm size screwcap reaction tube was charged with a magnetic stir bar and 4 Å powdered molecular sieves (approx. 100 mg) and the reaction tube was closed with a rubber septa-attached screw cap. The molecular sieves were activated by flame drying the tube under high vacuum for 1 min. The reaction tube was cooled to room temperature and charged with CuI (1.9 mg, 0.01 mmol, 10 mol %), ligand (0.01 mmol, 10 mol %) and 1-methyl-3-phenylpiperazine (27.0 mg, 0.15 mmol, 1.5 equiv). The reaction tube was brought inside an inert atmosphere glove box. K_3PO_4 (42.0 mg, 0.20 mmol, 2.0 equiv), 1-iodo-2-methylbenzene (22.0 mg, 0.10 mmol, 1.0 equiv), Hantzsch ester (12.5 mg, 0.05 mmol, 0.5 equiv.) and degassed anhydrous DMSO (0.5 mL, 0.2 M) were added. The reaction tube was capped tightly, taken out of the glove box and stirred at 80 °C in a preheated oil bath for 12 h. When the reaction was complete, the reaction mixture was cooled to room temperature and 10 µL of dodecane was added as internal standard. Next, the reaction mixture was diluted with 5 mL ethyl acetate and analyzed by gas chromatography.



B-4. Screening of Hantzsch ester derivative

Reaction procedure: An over dried 13*100 mm size screwcap reaction tube was charged with a magnetic stir bar and 4 Å powdered molecular sieves (approx. 100 mg) and the reaction tube was closed with a rubber septa-attached screw cap. The molecular sieves were activated by flame drying the tube under high vacuum for 1 min. The reaction tube was cooled to room temperature and charged with CuI (1.9 mg, 0.01 mmol, 10 mol %), ligand **L** (2.6 mg, 0.01 mmol, 10 mol %) and 1-methyl-3-phenylpiperazine (27.0 mg, 0.15 mmol, 1.5 equiv). The reaction tube was brought inside an inert atmosphere glove box. K_3PO_4 (42.0 mg, 0.20 mmol, 2.0 equiv), 1-iodo-2-methylbenzene (22.0 mg, 0.10 mmol, 1.0 equiv), Hantzsch ester

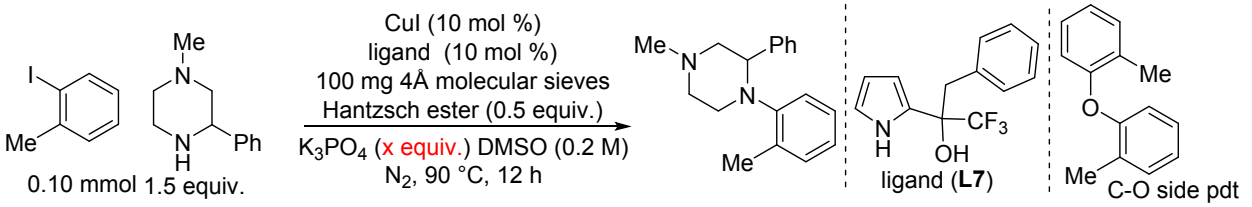
derivative (0.05 mmol, 0.5 equiv.) and degassed anhydrous DMSO (0.5 mL, 0.2 M) were added. The reaction tube was capped tightly, taken out of the glove box and stirred at 90 °C in a preheated oil bath for 12 h. When the reaction was complete, the reaction mixture was cooled to room temperature and 10 µL of dodecane was added as internal standard. Next, the reaction mixture was diluted with 5 mL ethyl acetate and analyzed by gas chromatography.



[a]based on gas chromatography analysis

B-5. Optimization of amount of base

Reaction procedure: An over dried 13*100 mm size screwcap reaction tube was charged with a magnetic stir bar and 4 Å powdered molecular sieves (approx. 100 mg) and the reaction tube was closed with a rubber septa-attached screw cap. The molecular sieves were activated by flame drying the tube under high vacuum for 1 min. The reaction tube was cooled to room temperature and charged with CuI (1.9 mg, 0.01 mmol, 10 mol %), ligand **L** (2.6 mg, 0.01 mmol, 10 mol %) and 1-methyl-3-phenylpiperazine (27.0 mg, 0.15 mmol, 1.5 equiv). The reaction tube was brought inside an inert atmosphere glove box. K_3PO_4 (x equiv), 1-iodo-2-methylbenzene (22.0 mg, 0.10 mmol, 1.0 equiv), Hantzsch ester (12.5 mg, 0.05 mmol, 0.5 equiv.) and degassed anhydrous DMSO (0.5 mL, 0.2 M) were added. The reaction tube was capped tightly, taken out of the glove box and stirred at 90 °C in a preheated oil bath for 12 h. When the reaction was complete, the reaction mixture was cooled to room temperature and 10 µL of dodecane was added as internal standard. Next, the reaction mixture was diluted with 5 mL ethyl acetate and analyzed by gas chromatography.



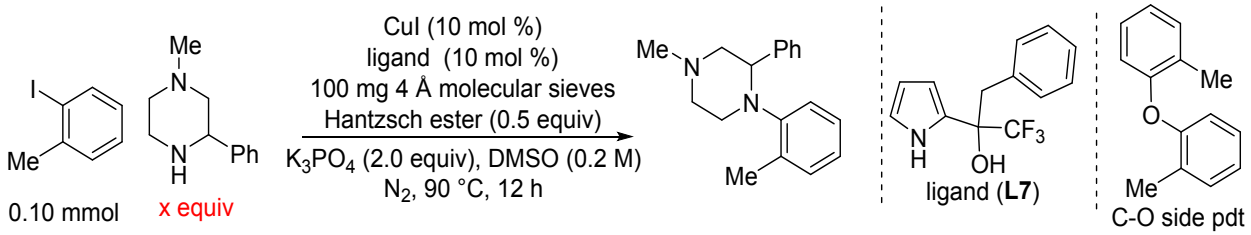
Amount of base	Yield of desired pdt[a]	Yield of C-O side pdt[a]	mol % of L7 after the reaction[a]
1.0 equiv	38%	0%	9 mol %

1.5 equiv	58%	3%	7.8 mol %
2.5 equiv	68%	6%	6 mol %
3.0 equiv	74%	2%	2 mol %
3.0 equiv, 3h	47%	2%	1.7 mol %
4.0 equiv	79%	8%	2.1 mol %

[a]based on gas chromatography analysis

B-6. Optimization of amount of amine

Reaction procedure: An over dried 13*100 mm size screwcap reaction tube was charged with a magnetic stir bar and 4 Å powdered molecular sieves (approx. 100 mg) and the reaction tube was closed with a rubber septa-attached screw cap. The molecular sieves were activated by flame drying the tube under high vacuum for 1 min. The reaction tube was cooled to room temperature and charged with CuI (1.9 mg, 0.01 mmol, 10 mol %), ligand **L** (2.6 mg, 0.01 mmol, 10 mol %) and 1-methyl-3-phenylpiperazine (x equiv). The reaction tube was brought inside an inert atmosphere glove box. K_3PO_4 (42.0 mg, 0.20 mmol, 2 equiv), 1-iodo-2-methylbenzene (22.0 mg, 0.10 mmol, 1.0 equiv), Hantzsch ester (12.5 mg, 0.05 mmol, 0.5 equiv.) and degassed anhydrous DMSO (0.5 mL, 0.2 M) were added. The reaction tube was capped tightly, taken out of the glove box and stirred at 90 °C in a preheated oil bath for 12 h. When the reaction was complete, the reaction mixture was cooled to room temperature and 10 µL of dodecane was added as internal standard. Next, the reaction mixture was diluted with 5 mL ethyl acetate and analyzed by gas chromatography.



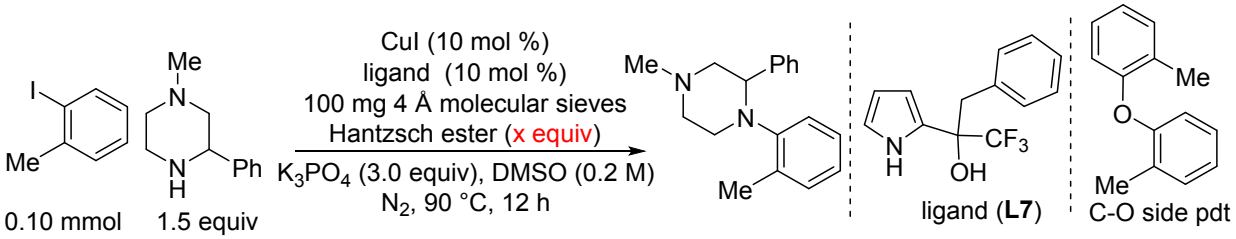
Amount of amine	**Yield of desired pdt[a]**	**Yield of C-O side pdt[a]**	**mol % of L7 after the reaction[a]**
1.0 equiv	60%	3%	2.4 mol %
1.2 equiv	60%	3%	2.9 mol %
1.5 equiv	61%	4%	6 mol %
2.0 equiv	68%	5%	4.5 mol %

[a]based on gas chromatography analysis

B-7. Optimization of amount of Hantzsch ester

Reaction procedure: An over dried 13*100 mm size screwcap reaction tube was charged with a magnetic stir bar and 4 Å powdered molecular sieves (approx. 100 mg) and the reaction tube was closed with a rubber septa-attached screw cap. The molecular sieves were activated by flame drying the tube under high vacuum for 1 min. The reaction tube was cooled to room temperature and charged with CuI (1.9 mg, 0.01 mmol, 10 mol %), ligand **L** (2.6 mg, 0.01 mmol, 10 mol %) and 1-methyl-3-phenylpiperazine (27.0 mg,

0.15 mmol, 1.5 equiv). The reaction tube was brought inside an inert atmosphere glove box. K_3PO_4 (64.0 mg, 0.30 mmol, 3 equiv), 1-iodo-2-methylbenzene (22.0 mg, 0.10 mmol, 1.0 equiv), Hantzsch ester (x equiv.) and degassed anhydrous DMSO (0.5 mL, 0.2 M) were added. The reaction tube was capped tightly, taken out of the glove box and stirred at 90 °C in a preheated oil bath for 12 h. When the reaction was complete, the reaction mixture was cooled to room temperature and 10 µL of dodecane was added as internal standard. Next, the reaction mixture was diluted with 5 mL ethyl acetate and analyzed by gas chromatography.

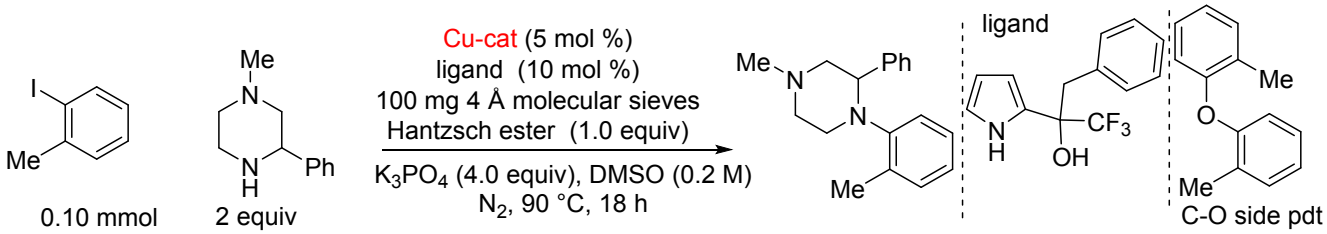


Amount of Hantzsch ester	Yield of desired pdt[a]	Yield of C-O side pdt[a]	mol % of L7 after the reaction[a]
0.1 equiv	59%	3%	2.4 mol %
0.2 equiv	64%	3%	2 mol %
0.5 equiv	66%	2%	2.8 mol %
1.0 equiv	71%	2%	1.6 mol %

[a]based on gas chromatography analysis

B-8. Optimization of copper catalyst

Reaction procedure: An over dried 13*100 mm size screwcap reaction tube was charged with a magnetic stir bar and 4 Å powdered molecular sieves (approx. 100 mg) and the reaction tube was closed with a rubber septa-attached screw cap. The molecular sieves were activated by flame drying the tube under high vacuum for 1 min. The reaction tube was cooled to room temperature and charged with Cu salt (0.005 mmol, 5 mol %), ligand **L** (2.6 mg, 0.010 mmol, 10 mol %) and 1-methyl-3-phenylpiperazine (27.0 mg, 0.150 mmol, 1.5 equiv). The reaction tube was brought inside an inert atmosphere glove box. K_3PO_4 (85.0 mg, 0.40 mmol, 4 equiv), 1-iodo-2-methylbenzene (22.0 mg, 0.100 mmol, 1.0 equiv), Hantzsch ester (25.0 mg, 0.100 mmol, 1.0 equiv.) and degassed anhydrous DMSO (0.5 mL, 0.2 M) were added. The reaction tube was capped tightly, taken out of the glove box and stirred at 90 °C in a preheated oil bath for 18 h. When the reaction was complete, the reaction mixture was cooled to room temperature and 10 µL of dodecane was added as internal standard. Next, the reaction mixture was diluted with 5 mL ethyl acetate and analyzed by gas chromatography.

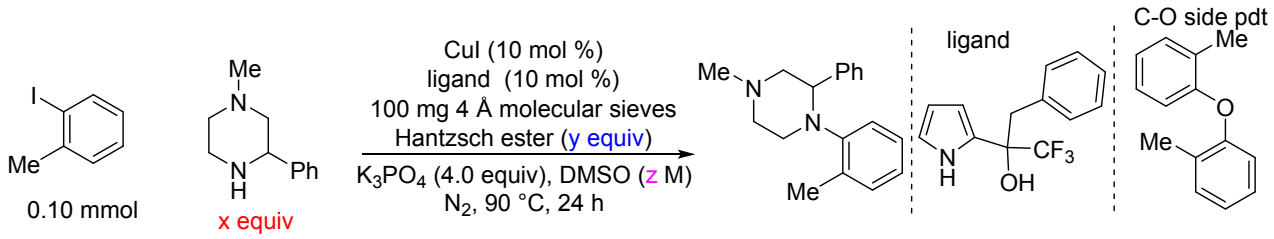


Copper salts	Yield of desired pdt[a]	Yield of C-O side pdt[a]	Unreacted Iodide[a]	mol % of L7 after the reaction[a]
CuI, 10 mol %	93%	6%	7%	5 mol %
CuI	79%	5%	11%	5.9 mol %
$CuBr(PPh_3)_3$	68%	5%	7%	3.8 mol %
$Cu(MeCN)_4BF_4$	72%	13%	12%	8.5 mol %
$Cu(MeCN)_4PF_6$	55%	3%	45%	6.5 mol %
$Cu(OTf)_2$	24%	2%	59%	5.3 mol %
Cu(OTf)toluene	6%	0%	72%	1 mol %
$CuBr(Me_2S)$	78%	4%	13%	4.9 mol %
CuTc	81%	7%	7%	3.7 mol %
CuCl	10%	0%	71%	1 mol %
Cu(triethyl phosphite)I	23%	0%	70%	5.8 mol %
Cu(Mes)	44%	5%	20%	6.6 mol %
$CuCl_2$	70%	4%	19%	5 mol %
$Cu(OAc)_2$	13%	1%	67%	6.6 mol %

[a]based on gas chromatography analysis

B-9. Further optimization of amount of amine, Hantzsch ester and concentration

Reaction procedure: An over dried 13*100 mm size screwcap reaction tube was charged with a magnetic stir bar and 4 Å powdered molecular sieves (approx. 100 mg) and the reaction tube was closed with a rubber septa-attached screw cap. The molecular sieves were activated by flame drying the tube under high vacuum for 1 min. The reaction tube was cooled to room temperature and charged with CuI (1.9 mg, 0.01 mmol, 10 mol %), ligand **L** (2.6 mg, 0.01 mmol, 10 mol %) and 1-methyl-3-phenylpiperazine (x equiv). The reaction tube was brought inside an inert atmosphere glove box. K_3PO_4 (85.0 mg, 0.40 mmol, 4 equiv), 1-iodo-2-methylbenzene (22.0 mg, 0.10 mmol, 1.0 equiv), Hantzsch ester (y equiv.) and degassed anhydrous DMSO (z M) were added. The reaction tube was capped tightly, taken out of the glove box and stirred at 90 °C in a preheated oil bath for 24 h. When the reaction was complete, the reaction mixture was cooled to room temperature and 10 µL of dodecane was added as internal standard. Next, the reaction mixture was diluted with 5 mL ethyl acetate and analyzed by gas chromatography.

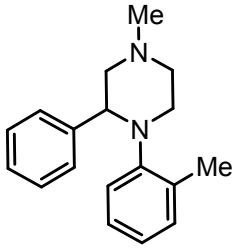


Amt of amine (x equiv)	Amt of HE (y equiv.)	Conc. (z M)	Yield of desired pdt[a]	Yield of C-O side pdt[a]	Unreacted Iodide[a]
2.0 equiv	1.0 equiv	0.20 M	93%	6%	7%
2.0 equiv	0.5 equiv	0.20 M	78%	4%	10%
2.0 equiv	0.5 equiv	0.25 M	80%	10%	7%
2.0 equiv	0.5 equiv	0.30 M	82%	4%	9%
1.5 equiv	1.0 equiv	0.20 M	85%	7%	12%
1.7 equiv	1.0 equiv	0.20 M	83%	14%	6%
1.7 equiv	1.0 equiv	0.25 M	89%	9%	11%

[a]based on gas chromatography analysis

Characterization data for products

4-Methyl-2-phenyl-1-(o-tolyl)piperazine (1):



Following the general procedure A, 4-methyl-2-phenyl-1-(o-tolyl)piperazine was prepared from 2-iodotoluene (0.5 mmol, 61 µL) and 1-methyl-3-phenylpiperazine (0.85 mmol, 150 mg). Desired product was isolated as brown solid. Isolated yield 86% (114 mg).

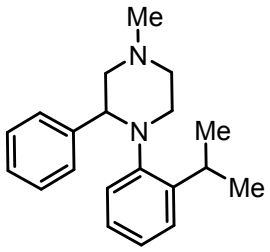
TLC: 0.22 in ethyl acetate.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.28 – 7.20 (m, 2H), 7.13 (t, *J* = 7.5 Hz, 2H), 7.08 (t, *J* = 6.3 Hz, 2H), 7.00 – 6.90 (m, 2H), 6.84 (td, *J* = 7.2, 1.6 Hz, 1H), 4.36 (dd, *J* = 10.1, 2.8 Hz, 1H), 3.17 – 3.05 (m, 1H), 2.96 (dt, *J* = 11.2, 2.4 Hz, 1H), 2.93 – 2.80 (m, 2H), 2.49 – 2.42 (m, 1H), 2.40 (s, 3H), 2.36 (s, 3H), 2.20 (t, *J* = 10.7 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.6, 141.5, 134.3, 130.7, 128.1, 127.7, 126.9, 126.1, 123.9, 122.4, 64.7, 63.6, 55.8, 54.7, 46.0, 17.6.

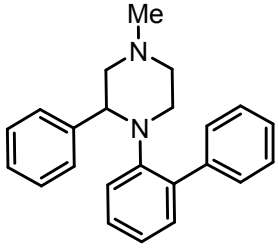
IR (Neat) cm^{-1}: 3024, 2935, 2792, 1599, 1491, 1450, 1370, 1349, 1294, 1253, 1209, 1142, 1112, 1061, 1022, 941, 817, 756, 723, 698.
HRMS (ESI): Calcd. $C_{18}H_{23}N_2$ $[M+H]^+$, 267.1856, Found, 267.1857.

1-(2-Isopropylphenyl)-4-methyl-2-phenylpiperazine (2):



Following the general procedure A, 1-(2-isopropylphenyl)-4-methyl-2-phenylpiperazine was prepared from 1-Iodo-2-isopropylbenzen (0.5 mmol, 80 µL) and 1-methyl-3-phenylpiperazine (0.85 mmol, 150 mg). Desired product was isolated as brown solid. Isolated yield 55% (81 mg).
TLC: 0.22 in ethyl acetate.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 (dt, *J* = 6.0, 1.4 Hz, 2H), 7.15 – 7.07 (m, 3H), 7.06 – 7.00 (m, 2H), 6.96 – 6.88 (m, 2H), 4.30 (dd, *J* = 10.1, 2.9 Hz, 1H), 3.86 (hept, *J* = 6.9 Hz, 1H), 3.01 (dt, *J* = 12.3, 2.9 Hz, 1H), 2.97 – 2.83 (m, 3H), 2.46 (td, *J* = 11.3, 3.2 Hz, 1H), 2.36 (s, 3H), 2.24 (t, *J* = 10.6 Hz, 1H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.2, 145.6, 141.4, 128.1, 128.0, 127.1, 126.5, 125.8, 124.8, 122.6, 64.5, 64.0, 56.7, 55.9, 46.1, 25.8, 24.5, 24.4.
IR (Neat) cm^{-1}: 3025, 2958, 2934, 2866, 2837, 2792, 1599, 1488, 1446, 1293, 1253, 1219, 1209, 1189, 1140, 1127, 1085, 1022, 991, 922, 782, 752, 725.
HRMS (ESI): Calcd. $C_{20}H_{27}N_2$ $[M+H]^+$, 295.2169, Found, 295.2170.

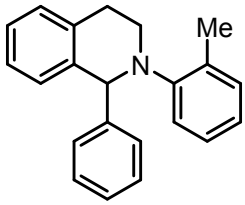
1-([1,1'-Biphenyl]-2-yl)-4-methyl-2-phenylpiperazine (3):



Following the general procedure A, 1-([1,1'-biphenyl]-2-yl)-4-methyl-2-phenylpiperazine was prepared from 2-iodo-1,1'-biphenyl (0.5 mmol, 140 mg) and 1-methyl-3-phenylpiperazine (0.85 mmol, 150 mg). Desired product was isolated as brown solid. Isolated yield 54% (88 mg).
TLC: 0.29 in ethyl acetate.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 – 7.63 (m, 2H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.41 – 7.34 (m, 1H), 7.33 – 7.27 (m, 2H), 7.20 (ddd, *J* = 7.6, 4.8, 3.0 Hz, 3H), 7.16 – 7.10 (m, 1H), 7.05 (td, *J* = 7.6, 1.8 Hz, 1H), 7.02 – 6.94 (m, 2H), 4.26 (dd, *J* = 9.8, 3.0 Hz, 1H), 3.08 (dt, *J* = 12.0, 3.0 Hz, 1H), 2.87 (dt, *J* = 11.3, 2.4 Hz, 1H), 2.78 (td, *J* = 11.5, 2.6 Hz, 1H), 2.60 (dq, *J* = 11.1, 2.5 Hz, 1H), 2.27 (s, 3H), 2.18 (dd, *J* = 11.3, 9.8 Hz, 1H), 2.05 (td, *J* = 11.0, 2.9 Hz, 1H).

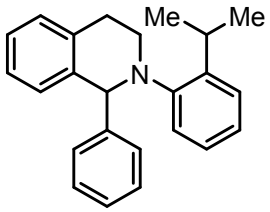
^{13}C NMR (101 MHz, Chloroform-d) δ 148.5, 141.3, 141.1, 137.4, 131.2, 129.4, 128.2, 128.1, 128.1, 127.7, 127.0, 126.8, 123.7, 122.8, 64.0, 63.7, 55.4, 54.3, 45.9.
IR (Neat) cm^{-1}: 2932, 2793, 1530, 1479, 1451, 1371, 1295, 1261, 1207, 1143, 1023, 756, 740, 698.
HRMS (ESI): Calcd. $C_{23}H_{25}N_2$ $[M+H]^+$, 329.2012, Found, 329.2014.

1-Phenyl-2-(o-tolyl)-1,2,3,4-tetrahydroisoquinoline (4):



Following the general procedure A, 1-phenyl-2-(o-tolyl)-1,2,3,4-tetrahydroisoquinoline was prepared from 2-iodotoluene (0.5 mmol, 61 µL) and 1-phenyl-1,2,3,4-tetrahydroisoquinoline (0.85 mmol, 178 mg). Desired product was isolated as white solid. Isolated yield 92% (137 mg). Isolated yield with 2 mol % CuI/ligand: 89% (133 mg).
TLC: 0.54 in 10 % ethyl acetate/ hexanes.
^{1}H NMR (400 MHz, Chloroform-d) δ 7.24 (dd, *J* = 6.7, 1.5 Hz, 2H), 7.21 – 7.10 (m, 5H), 7.04 (ddd, *J* = 6.7, 4.8, 2.2 Hz, 3H), 7.00 – 6.93 (m, 2H), 6.92 – 6.88 (m, 1H), 5.52 (s, 1H), 3.43 – 3.32 (m, 1H), 3.22 – 3.07 (m, 2H), 3.05 – 2.94 (m, 1H), 2.38 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-d) δ 150.3, 143.0, 138.1, 135.5, 134.1, 130.9, 129.6, 128.9, 128.7, 127.7, 126.9, 126.3, 126.1, 125.8, 123.7, 122.9, 65.2, 47.1, 29.3, 18.3.
IR (Neat) cm^{-1}: 3060, 3023, 2920, 1597, 1491, 1451, 1367, 1289, 1277, 1214, 1135, 1108, 1030, 942, 760, 737, 699, 633.
HRMS (ESI): Calcd. $C_{22}H_{22}N$ $[M+H]^+$, 300.1747, Found, 300.1751.

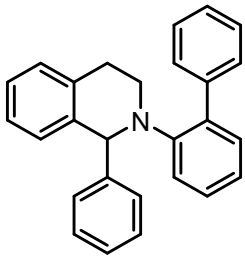
2-(2-Isopropylphenyl)-1-phenyl-1,2,3,4-tetrahydroisoquinoline (5):



Following the general procedure A, 2-(2-isopropylphenyl)-1-phenyl-1,2,3,4-tetrahydroisoquinoline was prepared from 1-Iodo-2-isopropylbenzen (0.5 mmol, 80 µL) and 1-phenyl-1,2,3,4-tetrahydroisoquinoline (0.85 mmol, 178 mg). Desired product was isolated as white solid. Isolated yield 90 % (147 mg). Isolated yield with 5 mol % CuI/ligand: 90 % (147 mg).
TLC: 0.54 in 10 % ethyl acetate/ hexanes.
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.25 – 7.18 (m, 3H), 7.17 – 6.97 (m, 9H), 6.87 (dd, *J* = 8.0, 3.9 Hz, 1H), 5.44 (s, 1H), 3.69 (ddd, *J* = 14.1, 9.1, 5.4 Hz, 1H), 3.37 – 3.10 (m, 3H), 2.97 (d, *J* = 15.3 Hz, 1H), 1.31 – 1.19 (m, 3H), 0.99 (m, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 149.1, 145.9, 138.8, 135.4, 129.9, 128.8, 127.7, 126.9, 126.4, 126.2, 125.8, 124.9, 123.7, 66.8, 29.8, 26.4, 24.4, 24.0.

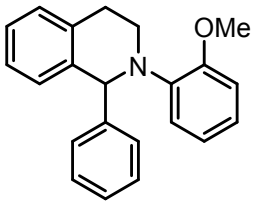
IR (Neat) cm^{-1}: 3060, 3023, 2958, 2922, 2828, 2804, 1596, 1581, 1488, 1447, 1363, 1281, 1207, 1129, 1086, 1034, 941, 743, 728, 699.
HRMS (ESI): Calcd. $C_{24}H_{26}N$ $[M+H]^+$, 328.2060, Found, 328.2060.

2-([1,1'-Biphenyl]-2-yl)-1-phenyl-1,2,3,4-tetrahydroisoquinoline (6):



Following the general procedure A, 2-([1,1'-biphenyl]-2-yl)-1-phenyl-1,2,3,4-tetrahydroisoquinoline was prepared from 2-iodo-1,1'-biphenyl (0.5 mmol, 140 mg) and 1-phenyl-1,2,3,4-tetrahydroisoquinoline (0.85 mmol, 178 mg). Desired product was isolated as white solid. Isolated yield 90 % (162 mg). Isolated yield with 8 mol % CuI/ligand: 89% (160 mg).
TLC: 0.51 in 10 % ethyl acetate/ hexanes.
^{1}H NMR (500 MHz, Chloroform-d) δ 7.62 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.29 (td, *J* = 7.7, 3.0 Hz, 2H), 7.19 (td, *J* = 7.7, 6.3, 3.7 Hz, 6H), 7.08 (dt, *J* = 15.1, 7.9 Hz, 2H), 7.00 – 6.93 (m, 3H), 6.77 (d, *J* = 7.7 Hz, 1H), 5.42 (s, 1H), 3.27 (ddd, *J* = 12.9, 8.5, 4.5 Hz, 1H), 3.12 (dt, *J* = 12.4, 5.1 Hz, 1H), 2.96 – 2.86 (m, 1H), 2.79 (dt, *J* = 16.2, 4.8 Hz, 1H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 149.0, 142.7, 141., 137.51, 136.5, 135.4, 131.4, 129.5, 129.0, 128.7, 128.6, 128.2, 128.0, 127.7, 126.9, 126.7, 126.2, 125.7, 123.1, 122.2, 64.2, 45.7, 28.7.
IR (Neat) cm^{-1}: 3058, 3022, 2916, 2829, 1592, 1493, 1479, 1451, 1433, 1366, 1279, 1218, 941, 763, 740, 698.
HRMS (ESI): Calcd. $C_{27}H_{24}N$ $[M+H]^+$, 362.1903, Found, 362.1904.

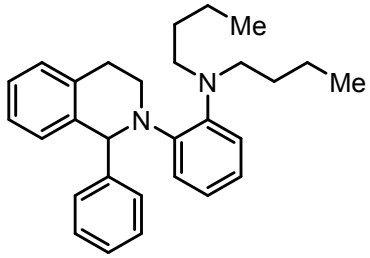
2-(2-Methoxyphenyl)-1-phenyl-1,2,3,4-tetrahydroisoquinoline (7):



Following the general procedure A, 2-(2-methoxyphenyl)-1-phenyl-1,2,3,4-tetrahydroisoquinoline was prepared from 1-iodo-2-methoxybenzene (0.5 mmol, 117 mg) and 1-phenyl-1,2,3,4-tetrahydroisoquinoline (0.85 mmol, 178 mg). Desired product was isolated as white solid and matched with reported spectra[2]. Isolated yield 88% (138 mg).
TLC: 0.24 in 5 % ethyl acetate/ hexanes.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.16 (m, 2H), 7.12 (q, *J* = 5.2, 4.1 Hz, 4H), 7.01 – 6.92 (m, 2H), 6.93 – 6.81 (m, 3H), 6.74 (td, *J* = 7.6, 1.6 Hz, 1H), 6.59 (dd, *J* = 7.9, 1.6 Hz, 1H), 5.91 (s, 1H), 3.92 (s, 3H), 3.49 – 3.37 (m, 1H), 3.36 – 3.26 (m, 1H), 3.20 – 3.07 (m, 1H), 2.96 (dt, *J* = 16.4, 3.8 Hz, 1H).

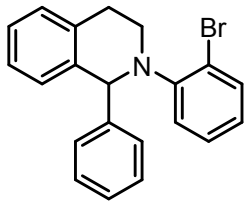
^{13}C NMR (126 MHz, Chloroform-*d*) δ 153.2, 142.2, 140.2, 137.4, 135.2, 129.5, 128.9, 128.8, 127.5, 126.9, 126.4, 125.7, 123.1, 122.2, 121.0, 111.7, 63.0, 55.8, 43.2, 28.9.

N,N-Dibutyl-2-(1-phenyl-3,4-dihydroisoquinolin-2(1H)-yl)aniline (8):



Following the general procedure A, N,N-dibutyl-2-(1-phenyl-3,4-dihydroisoquinolin-2(1H)-yl)aniline was prepared from butyl N,N-dibutyl-2-iodoaniline (0.5 mmol, 166 mg) and 1-phenyl-1,2,3,4-tetrahydroisoquinoline (0.85 mmol, 178 mg). Desired product was isolated as white solid. Isolated yield 50 % (103 mg).
TLC: 0.49 in 10 % ethyl acetate/ hexanes.
^{1}H NMR (400 MHz, Chloroform-d) δ 7.21 (d, *J* = 4.3 Hz, 2H), 7.17 – 7.05 (m, 4H), 7.03 – 6.89 (m, 3H), 6.80 – 6.63 (m, 3H), 6.44 (d, *J* = 7.8 Hz, 1H), 6.24 (s, 1H), 3.45 – 3.23 (m, 4H), 3.13 – 2.98 (m, 3H), 2.96 – 2.86 (m, 1H), 1.50 – 1.37 (m, 4H), 1.32 – 1.18 (m, 4H), 0.89 – 0.77 (m, 6H).
^{13}C NMR (101 MHz, Chloroform-d) δ 144.3, 143.9, 142.0, 137.7, 135.5, 129.7, 129.3, 128.8, 128.7, 127.3, 126.6, 126.3, 125.7, 122.3, 121.6, 120.0, 115.2, 111.8, 60.4, 50.9, 41.6, 29.6, 29.3, 20.9, 14.2.
IR (Neat) cm^{-1}: 3059, 3024, 2955, 2928, 2870, 2860, 2828, 2592, 1504, 1491, 1449, 1373, 1280, 1207, 1132, 1100, 941, 744, 700.
HRMS (ESI): Calcd. $C_{29}H_{37}N_2$ $[M+H]^+$, 413.2951, Found, 413.2953.

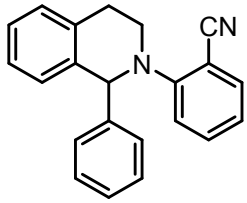
2-(2-Bromophenyl)-1-phenyl-1,2,3,4-tetrahydroisoquinoline (9):



Following the general procedure A, 2-(2-bromophenyl)-1-phenyl-1,2,3,4-tetrahydroisoquinoline was prepared from 1-bromo-2-iodobenzene (0.5 mmol, 141 mg) and 1-phenyl-1,2,3,4-tetrahydroisoquinoline (0.85 mmol, 178 mg). Desired product was isolated as white solid. Isolated yield 50 % (90 mg).
TLC: 0.48 in 10 % ethyl acetate/ hexanes.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 8.0 Hz, 1H), 7.40 – 7.34 (m, 2H), 7.31 (d, *J* = 7.0 Hz, 4H), 7.23 (p, *J* = 3.4 Hz, 3H), 7.09 (d, *J* = 7.7 Hz, 1H), 7.00 (dd, *J* = 8.1, 5.4 Hz, 2H), 5.86 (s, 1H), 3.64 (tt, *J* = 10.3, 6.6 Hz, 1H), 3.40 – 3.28 (m, 2H), 3.14 (dt, *J* = 18.5, 7.5 Hz, 1H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.5, 142.3, 137.5, 135.1, 133.6, 129.5, 129.0, 128.7, 127.8, 127.7, 127.1, 126.5, 125.8, 124.9, 124.7, 121.7, 64.5, 47.1, 29.3.
IR (Neat) cm^{-1}: 3060, 3024, 2921, 2830, 1598, 1582, 1491, 1473, 1452, 1368, 1282, 1044, 941, 754, 741, 700.

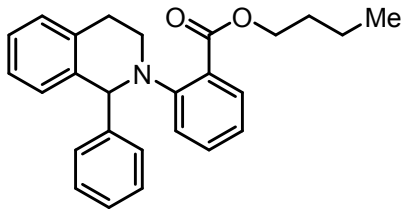
HRMS (ESI): Calcd. $C_{21}H_{19}NBr$ $[M+H]^+$, 364.0695, Found, 364.0697.

2-(1-Phenyl-3,4-dihydroisoquinolin-2(1H)-yl)benzonitrile (10):



Following the general procedure A, 2-(1-phenyl-3,4-dihydroisoquinolin-2(1H)-yl)benzonitrile was prepared from 1-Iodo-2-cyanobenzen (0.5 mmol, 115 mg) and 1-phenyl-1,2,3,4-tetrahydroisoquinoline (0.85 mmol, 178 mg), without Hantzsch ester. Desired product was isolated as yellow oily liquid. Isolated yield 33 % (51 mg).
TLC: 0.21 in 5 % ethyl acetate/ hexanes.
^{1}H NMR (400 MHz, Chloroform-d) δ 7.69 – 7.50 (m, 1H), 7.40 – 7.29 (m, 1H), 7.25 – 7.17 (m, 5H), 7.17 – 7.12 (m, 3H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.99 – 6.93 (m, 2H), 5.84 (s, 1H), 3.75 – 3.60 (m, 1H), 3.61 – 3.45 (m, 1H), 3.23 – 3.08 (m, 1H), 3.06 – 2.94 (m, 1H).
^{13}C NMR (101 MHz, Chloroform-d) δ 154.8, 142.0, 136.5, 134., 134.41, 133.3, 129.0, 128.9, 128., 128.2, 127.4, 126.8, 126.1, 122.2, 122.0, 118.8, 107.4, 64.5, 47.5, 28.9.
IR (Neat) cm^{-1}: 3063, 2953, 2928, 2871, 2211, 1706, 1657, 1599, 1577, 1517, 1491, 1448, 1365, 1267, 1163, 930, 754, 700.
HRMS (EI): Calcd. $C_{22}H_{18}N_2$ $[M]^+$, 310.1465, Found, 310.1463.

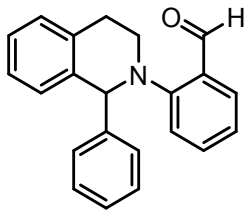
Butyl 2-(1-phenyl-3,4-dihydroisoquinolin-2(1H)-yl)benzoate (11):



Following the general procedure A, butyl 2-(1-phenyl-3,4-dihydroisoquinolin-2(1H)-yl)benzoate was prepared from butyl 2-iodobenzoate (0.5 mmol, 152 mg) and 1-phenyl-1,2,3,4-tetrahydroisoquinoline (0.85 mmol, 178 mg). Desired product was isolated as yellow oily liquid. Isolated yield 39 % (75 mg).
TLC: 0.27in 5 % ethyl acetate/ hexanes.
^{1}H NMR (400 MHz, Chloroform-d) δ 7.62 (d, *J* = 7.7 Hz, 1H), 7.22 (m, 3H), 7.18 – 7.09 (m, 4H), 7.07 – 7.01 (m, 2H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 7.8 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 5.64 (s, 1H), 4.34 – 4.16 (m, 2H), 3.48 (dt, *J* = 13.0, 6.6 Hz, 1H), 3.30 – 3.20 (m, 1H), 3.04 – 2.93 (m, 2H), 1.57 (q, *J* = 7.5 Hz, 2H), 1.34 (p, *J* = 7.6 Hz, 2H), 0.92 – 0.83 (m, 3H).
^{13}C NMR (101 MHz, Chloroform-d) δ 169.0, 150.7, 142.3, 137.3, 135.4, 131.7, 130.7, 129.3, 128.9, 128.5, 127.8, 127.8, 127.1, 126.5, 125.9, 122.7, 122.2, 65.3, 65.1, 47.1, 30.7, 28.9, 19.3, 13.9.
IR (Neat) cm^{-1}: 3062, 3026, 2958, 2931, 2872, 1711, 1679, 1581, 1487, 1448, 1291, 1242, 1148, 1112, 1077, 931, 751. 701.

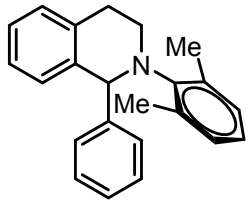
HRMS (ESI): Calcd. $C_{26}H_{28}O_2N$ $[M+H]^+$, 386.2115, Found, 386.2118.

2-(1-Phenyl-3,4-dihydroisoquinolin-2(1H)-yl)benzaldehyde (12):



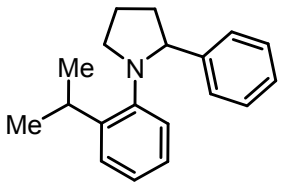
Following the general procedure A, 2-(1-Phenyl-3,4-dihydroisoquinolin-2(1H)-yl)benzaldehyde was prepared from 2-iodobenzaldehyde (0.5 mmol, 116 mg) and 1-phenyl-1,2,3,4-tetrahydroisoquinoline (0.85 mmol, 178 mg). Desired product was isolated as yellow oily liquid. Isolated yield 43 % (67 mg).
TLC: 0.21 in 5 % ethyl acetate/ hexanes.
^{1}H NMR (400 MHz, Chloroform-d) δ 10.44 (s, 1H), 7.81 (d, *J* = 7.7 Hz, 1H), 7.48 – 7.35 (m, 1H), 7.23 (t, *J* = 3.3 Hz, 2H), 7.20 – 7.08 (m, 5H), 7.05 – 6.88 (m, 4H), 5.57 (s, 1H), 3.60 – 3.46 (m, 1H), 3.40 – 3.23 (m, 1H), 3.14 – 2.95 (m, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.1, 155.1, 142.0, 136.7, 135.0, 134.7, 130.5, 129.3, 129.0, 128.7, 128.7, 128.1, 127.4, 126., 126.21, 123.7, 123.1, 67.1, 49.2, 28.6.
IR (Neat) cm^{-1}: 3061, 3026, 2922, 2837, 2747, 1708, 1681, 1658, 1594, 1480, 1449, 1429, 1362, 1283, 1267, 1220, 1158, 930, 745, 700.
HRMS (CI): Calcd. $C_{22}H_{20}ON$ $[M+H]^+$, 314.1539, Found, 314.1544.

2-(2,6-Dimethylphenyl)-1-phenyl-1,2,3,4-tetrahydroisoquinoline (13):



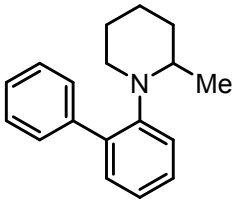
Following the general procedure A, 2-(2,6-dimethylphenyl)-1-phenyl-1,2,3,4-tetrahydroisoquinoline was prepared from 2-iodo-1,3-dimethylbenzene (0.5 mmol, 116 mg) and 1-phenyl-1,2,3,4-tetrahydroisoquinoline (0.85 mmol, 178 mg) and reaction was run for 48 h. Desired product was isolated as white solid. Isolated yield 55% (64 mg).
TLC: 0.51 in 10 % ethyl acetate/ hexanes.
^{1}H NMR (400 MHz, Chloroform-d) δ 7.19 – 7.08 (m, 2H), 7.08 – 6.98 (m, 4H), 6.96 (d, *J* = 7.5 Hz, 1H), 6.88 – 6.79 (m, 2H), 6.79 – 6.72 (m, 3H), 5.29 (s, 1H), 3.48 – 3.36 (m, 1H), 3.18 – 3.07 (m, 1H), 2.96 (t, *J* = 5.7 Hz, 2H), 2.27 (s, 3H), 1.45 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-d) δ 147.2, 143.6, 138.0, 137.5, 136.7, 136.3, 129.1, 129.1, 128.9, 128.9, 128.8, 127.9, 126.9, 126.3, 125.7, 124.8, 64.3, 45.3, 31.5, 19.5, 19.0.
IR (Neat) cm^{-1}: 3060, 3023, 2951, 2916, 2830, 1598, 1491, 1473, 1451, 1374, 1280, 1215, 1146, 1098, 1029, 945, 770, 742, 701.
HRMS (CI): Calcd. $C_{23}H_{24}N$ $[M+H]^+$, 314.1903, Found, 314.1907.

1-(2-Isopropylphenyl)-2-phenylpyrrolidine (14):



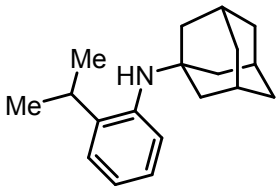
Following the general procedure A, 1-(2-isopropylphenyl)-2-phenylpyrrolidine was prepared from 1-Iodo-2-isopropylbenzen (0.5 mmol, 80 µL) and 2-phenylpyrrolidine (0.85 mmol, 125 mg). Desired product was isolated as white solid. Isolated yield 85% (113 mg). Isolated yield with 5 mol % CuI/ligand: 87% (115 mg).
TLC: 0.37 in 5 % ethyl acetate/ hexanes.
^{1}H NMR (400 MHz, Chloroform-d) δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 7.1 Hz, 3H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 7.9 Hz, 1H), 7.12 – 7.02 (m, 2H), 4.63 (dd, *J* = 8.6, 6.7 Hz, 1H), 3.91 – 3.72 (m, 2H), 3.12 – 2.97 (m, 1H), 2.53 – 2.43 (m, 1H), 2.26 – 2.12 (m, 1H), 2.10 – 1.94 (m, 2H), 1.42 (d, *J* = 6.9 Hz, 3H), 1.25 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.0, 144.6, 143.7, 128.2, 127.2, 126.7, 126.5, 126.0, 123.4, 120.3, 65.5, 56.7, 36.6, 27.0, 24.8, 24.1.
IR (Neat) cm^{-1}: 3061, 3025, 2960, 2926, 2866, 1597, 1488, 1447, 1362, 1261, 1085, 1036, 751, 699.
HRMS (ESI): Calcd. $C_{19}H_{24}N$ $[M+H]^+$, 266.1903, Found, 266.1904.

1-([1,1'-Biphenyl]-2-yl)-2-methylpiperidine (15):



Following the general procedure A, 1-([1,1'-biphenyl]-2-yl)-2-methylpiperidine was prepared from 2-iodo-1,1'-biphenyl (0.5 mmol, 140 mg) and 2-methylpiperidine (0.85 mmol, 84 mg). Desired product was isolated as brown oily liquid. Isolated yield 92% (115 mg). Isolated yield with 8 mol % CuI/ligand: 91% (114 mg).
TLC: 0.63 in 5 % ethyl acetate/ hexanes.
^{1}H NMR (400 MHz, Chloroform-d) δ 7.66 – 7.60 (m, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.35 – 7.27 (m, 3H), 7.19 – 7.10 (m, 2H), 3.05 (pd, *J* = 6.4, 2.7 Hz, 1H), 3.02 – 2.91 (m, 1H), 2.69 – 2.59 (m, 1H), 1.69 – 1.56 (m, 2H), 1.55 – 1.33 (m, 3H), 1.29 – 1.18 (m, 1H), 0.90 (d, *J* = 6.3 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-d) δ 150.5, 141.3, 138.0, 131.1, 129.4, 127.9, 127.8, 126.5, 123.3, 122.4, 53.5, 51.6, 33.3, 26.5, 22.6, 17.2.
IR (Neat) cm^{-1}: 3057, 2961, 2849, 2783, 1593, 1499, 1479, 1432, 1372, 1284, 1244, 1211, 1178, 1113, 1073, 1008, 892, 735, 695.
HRMS (ESI): Calcd. $C_{18}H_{22}N$ $[M+H]^+$, 252.1747, Found, 252.1748.

(3s,5s,7s)-N-(2-Isopropylphenyl)adamantan-1-amine (16):



Following the general procedure A, (3s,5s,7s)-N-(2-isopropylphenyl)adamantan-1-amine was prepared from 2-isopropylbenzen (0.5 mmol, 80 µL) and (3s,5s,7s)-adamantan-1-amine (0.85 mmol, 128 mg). Desired product was isolated as white solid. Isolated yield 93 % (125 mg). Isolated yield with 5 mol % CuI/ligand: 89 % (119 mg).

TLC: 0.40 in 10 % ethyl acetate/ hexanes.

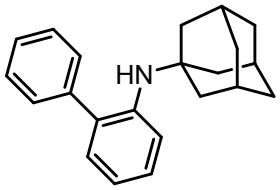
^{1}H NMR (400 MHz, Chloroform-d) δ 7.16 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.09 – 6.98 (m, 2H), 6.80 (ddd, *J* = 8.1, 6.7, 1.9 Hz, 1H), 3.46 (s, 1H), 2.96 (p, *J* = 6.8 Hz, 1H), 2.18 – 2.05 (m, 3H), 1.93 (d, *J* = 3.0 Hz, 6H), 1.75 – 1.61 (m, 6H), 1.24 (d, *J* = 6.8 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.9, 135.8, 125.8, 125.3, 119.0, 118.7, 52.4, 43.8, 36.6, 29.9, 27.6, 22.9.

IR (Neat) cm^{-1}: 2959, 2901, 2848, 1602, 1582, 1511, 1462, 1448, 1355, 1308, 1282, 1265, 1151, 1131, 1099, 1074, 1039, 743.

HRMS (ESI): Calcd. $C_{19}H_{28}N$ $[M+H]^+$, 270.2216, Found, 270.2217.

(3s,5s,7s)-N-([1,1'-biphenyl]-2-yl)adamantan-1-amine (17):



Following the general procedure A, (3s,5s,7s)-N-([1,1'-biphenyl]-2-yl)adamantan-1-amine was prepared from 2-iodo-1,1'-biphenyl (0.5 mmol, 140 mg) and (3s,5s,7s)-adamantan-1-amine (0.85 mmol, 128 mg). Desired product was isolated as white solid. Isolated yield 86% (130 mg). Isolated yield with 5 mol % CuI/ligand: 85% (128 mg).

TLC: 0.33 in 5 % ethyl acetate/ hexanes.

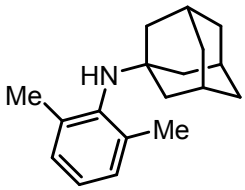
^{1}H NMR (400 MHz, Chloroform-d) δ 7.46 (t, *J* = 7.5 Hz, 2H), 7.42 – 7.33 (m, 3H), 7.20 (ddd, *J* = 8.6, 7.3, 1.7 Hz, 1H), 7.14 – 7.07 (m, 2H), 6.80 (td, *J* = 7.3, 1.2 Hz, 1H), 3.83 (s, 1H), 2.09 (s, 3H), 1.85 (d, *J* = 2.9 Hz, 6H), 1.72 – 1.61 (m, *J* = 3.0 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-d) δ 143.7, 140.2, 130.6, 130.5, 129.7, 128.9, 128.0, 127.2, 117.6, 116.5, 52.2, 43.5, 36.6, 29.8.

IR (Neat) cm^{-1}: 2903, 2848, 1603, 1579, 1509, 1465, 1435, 1356, 1307, 1284, 1267, 1136, 1094, 1008, 739, 703.

HRMS (ESI): Calcd. $C_{22}H_{26}N$ $[M+H]^+$, 304.2060, Found, 304.2059.

(3s,5s,7s)-N-(2,6-dimethylphenyl)adamantan-1-amine (18):



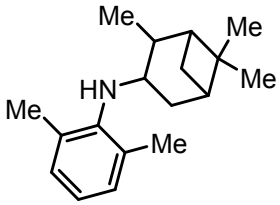
Following the general procedure A, (3s,5s,7s)-N-(2,6-dimethylphenyl)adamantan-1-amine was prepared from 2-iodo-1,3-dimethylbenzene (0.5 mmol, 116 mg) and (3s,5s,7s)-adamantan-1-amine (0.85 mmol, 128 mg) and reaction was ran for 48 h. Desired product was isolated as white solid and matched with reported spetra[3]. Isolated yield 42% (53 mg).

TLC: 0.27 in 5 % ethyl acetate/ hexanes.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.02 (d, *J* = 7.4 Hz, 2H), 6.89 (t, *J* = 7.5 Hz, 1H), 2.73 – 2.42 (m, 1H), 2.37 (s, 6H), 2.05 (s, 3H), 1.81 – 1.76 (m, 6H), 1.68 – 1.57 (m, *J* = 3.0 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-d) δ 143.2, 134.9, 128.5, 123.1, 55.7, 44.5, 36.6, 30.2, 20.8.

N-(2,6-Dimethylphenyl)-2,6,6-trimethylbicyclo[3.1.1]heptan-3-amine (19):



Following the general procedure A, N-(2,6-dimethylphenyl)-2,6,6-trimethylbicyclo[3.1.1]heptan-3-amine was prepared from 2-iodo-1,3-dimethylbenzene (0.5 mmol, 116 mg) and 2,6,6-trimethylbicyclo[3.1.1]heptan-3-amine (0.85 mmol, 130 mg) and reaction was ran for 48 h. Desired product was isolated as colorless oily liquid. Isolated yield 69% (88 mg).

TLC: 0.36 in 5 % ethyl acetate/ hexanes.

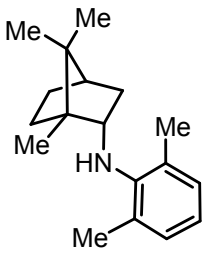
^{1}H NMR (400 MHz, Chloroform-d) δ 6.98 (dd, *J* = 7.6, 3.1 Hz, 2H), 6.85 – 6.74 (m, 1H), 3.71 (dt, *J* = 9.5, 6.1 Hz, 1H), 2.97 (s, 1H), 2.51 – 2.24 (m, 8H), 2.02 – 1.78 (m, 3H), 1.60 (ddt, *J* = 11.7, 5.7, 2.8 Hz, 1H), 1.23 (s, 3H), 1.07 (s, 3H), 0.99 (d, *J* = 3.5 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 145.6, 129.1, 128.3, 121.0, 55.1, 48.6, 48.3, 42.0, 38.6, 37.3, 35.4, 28.1, 23.5, 21.5, 19.5.

IR (Neat) cm^{-1}: 2901, 2872, 1594, 1472, 1450, 1372, 1259, 1221, 1156, 1098, 1027, 934, 790, 759, 742, 704.

HRMS (CI): Calcd. $C_{18}H_{28}N$ $[M+H]^+$, 258.2216, Found, 258.2220.

(1S,2S,4R)-N-(2,6-Dimethylphenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-amine (20):



Following the general procedure A, (1S,2S,4R)-N-(2,6-Dimethylphenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-amine was prepared from 2-iodo-1,3-dimethylbenzene (0.5 mmol, 116 mg) and (1S,2S,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-amine (0.85 mmol, 130 mg) and reaction was ran for 48 h. Desired product was isolated as colorless oily liquid. Isolated yield 41% (52 mg).

TLC: 0.46 in 10 % ethyl acetate/ hexanes.

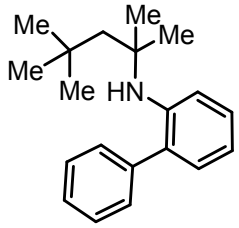
^{1}H NMR (400 MHz, Chloroform-d) δ 7.00 (d, *J* = 7.4 Hz, 2H), 6.78 (t, *J* = 7.5 Hz, 1H), 3.72 – 3.57 (m, 1H), 3.41 (s, 1H), 2.34 (s, 6H), 2.23 (dddd, *J* = 13.5, 10.8, 4.9, 3.1 Hz, 1H), 1.87 (td, *J* = 12.0, 11.2, 3.9 Hz, 2H), 1.70 (t, *J* = 4.5 Hz, 1H), 1.63 – 1.45 (m, 1H), 1.35 (tdt, *J* = 9.4, 6.7, 2.6 Hz, 1H), 1.03 – 0.85 (m, 9H).

^{13}C NMR (101 MHz, Chloroform-d) δ 146.6, 129.2, 127.6, 120.5, 61.6, 49.9, 48.2, 44.9, 38.7, 28.7, 27.6, 20.0, 19.5, 18.8, 14.1.

IR (Neat) cm^{-1}: 2947, 2874, 1594, 1472, 1440, 1387, 1371, 1262, 1220, 1168, 1137, 1107, 1099, 1065, 1033, 988, 937, 758, 738.

HRMS (CI): Calcd. $C_{18}H_{28}N$ $[M+H]^+$, 258.2216, Found, 258.2219.

N-(2,4,4-trimethylpentan-2-yl)-[1,1'-biphenyl]-2-amine (21):



Following the general procedure A, N-(2,4,4-trimethylpentan-2-yl)-[1,1'-biphenyl]-2-amine was prepared from 2-iodo-1,1'-biphenyl (0.5 mmol, 140 mg) and 2,4,4-trimethylpentan-2-amine (0.85 mmol, 110 mg). Desired product was isolated as white solid. Isolated yield 88% (123 mg). Isolated yield with 5 mol % CuI/ligand: 90% (126 mg).

TLC: 0.51 in 10 % ethyl acetate/ hexanes.

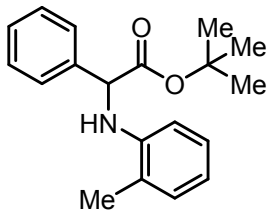
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.41 (m, 2H), 7.41 – 7.32 (m, 3H), 7.25 – 7.16 (m, 1H), 7.07 (dt, *J* = 7.5, 1.8 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.74 (t, *J* = 7.4 Hz, 1H), 3.96 (s, 1H), 1.65 (s, 2H), 1.36 (s, 6H), 0.93 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.2, 140.3, 130.4, 129.8, 129.5, 128.9, 128.1, 127.2, 116.3, 114.1, 55.1, 53.8, 31.8, 31.7, 30.4.

IR (Neat) cm^{-1}: 2949, 2902, 2868, 1603, 1596, 1580, 1510, 1464, 1435, 1384, 1364, 1308, 1281, 1220, 1150, 1052, 1008, 768, 738, 701.

HRMS (CI): Calcd. $C_{20}H_{28}N$ $[M+H]^+$, 282.2216, Found, 282.2217.

tert-Butyl 2-phenyl-2-(o-tolylamino)acetate (22):



Following the general procedure A, tert-butyl 2-phenyl-2-(o-tolylamino)acetate was prepared from 2-iodotoluene (0.5 mmol, 61 µL) and tert-butyl (R)-2-amino-2-phenylacetate hydrogen chloride (0.85 mmol, 206 mg). Desired product was isolated as oily liquid. Isolated yield 87% (129 mg). Isolated yield with 2 mol % CuI/ligand: 84% (124 mg).

TLC: 0.30 in 5 % ethyl acetate/ hexanes.

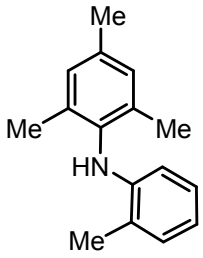
^{1}H NMR (500 MHz, Chloroform-d) δ 7.55 – 7.47 (m, 2H), 7.40 – 7.32 (m, 2H), 7.32 – 7.27 (m, 1H), 7.08 (d, *J* = 7.3 Hz, 1H), 6.98 (td, *J* = 7.8, 1.6 Hz, 1H), 6.69 – 6.61 (m, 1H), 6.34 (d, *J* = 8.0 Hz, 1H), 5.02 (d, *J* = 5.0 Hz, 1H), 4.93 (d, *J* = 5.6 Hz, 1H), 2.30 (s, 3H), 1.40 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.2, 144.3, 138.4, 130.3, 128.7, 128.0, 127.2, 127.1, 122.4, 117.5, 110.8, 82.5, 61.3, 28.0, 17.6.

IR (Neat) cm^{-1}: 2976, 2931, 1727, 1606, 1585, 1510, 1477, 1453, 1368, 1313, 1299, 1255, 1148, 836, 743, 725, 695.

HRMS (CI): Calcd. $C_{19}H_{24}O_2N$ $[M+H]^+$, 298.1802, Found, 298.1804.

2,4,6-Trimethyl-N-(o-tolyl)aniline (23):



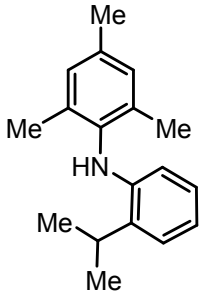
Following the general procedure A, 2,4,6-trimethyl-N-(o-tolyl)aniline was prepared from 2-iodotoluene (0.5 mmol, 61 µL) and 2,4,6-trimethylaniline (0.85 mmol, 115 mg). Desired product was isolated as white solid and matched with reported spetra[4]. Isolated yield 89% (100 mg). Isolated yield with 2 mol % CuI/ligand: 90% (101 mg).

TLC: 0.39 in 5 % ethyl acetate/ hexanes.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 (d, *J* = 7.3 Hz, 1H), 7.08 – 6.94 (m, 3H), 6.75 (t, *J* = 7.4 Hz, 1H), 6.27 – 6.16 (m, 1H), 4.92 (s, 1H), 2.39 (d, *J* = 2.2 Hz, 6H), 2.22 (d, *J* = 2.2 Hz, 6H).

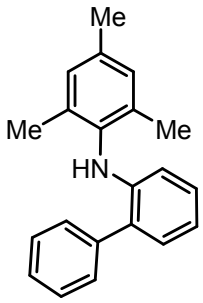
^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.6, 136.1, 135.7, 135.3, 130.3, 129.3, 127.0, 122.2, 117.9, 111.5, 21.0, 18.2, 17.7.

N-(2-Isopropylphenyl)-2,4,6-trimethylaniline (24):



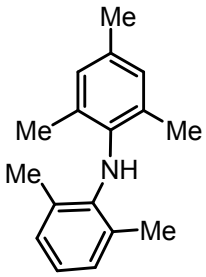
Following the general procedure A, N-(2-isopropylphenyl)-2,4,6-trimethylaniline was prepared from 2-isopropylbenzen (0.5 mmol, 80 µL) and 2,4,6-trimethylaniline (0.85 mmol, 115 mg). Desired product was isolated as white solid and matched with reported spectra.[5] Isolated yield 87% (110 mg). Isolated yield with 5 mol % CuI/ligand: 92% (116 mg).
TLC: 0.39 in 5 % ethyl acetate/ hexanes.
^{1}H NMR (500 MHz, Chloroform-d) δ 7.30 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.07 – 6.96 (m, 3H), 6.89 – 6.81 (m, 1H), 6.24 (dt, *J* = 8.0, 1.5 Hz, 1H), 5.11 (s, 1H), 3.21 (pd, *J* = 6.8, 1.4 Hz, 1H), 2.39 (s, 3H), 2.23 (s, 6H), 1.45 (dd, *J* = 6.8, 1.5 Hz, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 143.2, 136.2, 135.6, 135.1, 132.6, 129.4, 126.6, 125.2, 118.3, 112.3, 27.7, 22.5, 21.0, 18.4.

N-Mesityl-[1,1'-biphenyl]-2-amine (25):



Following the general procedure A, N-mesityl-[1,1'-biphenyl]-2-amine was prepared from 2-iodo-1,1'-biphenyl (0.5 mmol, 140 mg) and 2,4,6-trimethylaniline (0.85 mmol, 115 mg). Desired product was isolated as white solid and matched with reported spectra[5]. Isolated yield 92% (132 mg). Isolated yield with 8 mol % CuI/ligand: 91% (130 mg).
TLC: 0.42 in 5 % ethyl acetate/ hexanes.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.59 (m, 2H), 7.57 – 7.49 (m, 2H), 7.48 – 7.38 (m, 1H), 7.22 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.13 (ddd, *J* = 8.7, 7.5, 1.6 Hz, 1H), 6.97 (s, 2H), 6.84 (td, *J* = 7.4, 1.2 Hz, 1H), 6.27 (dd, *J* = 8.2, 1.1 Hz, 1H), 5.26 (s, 1H), 2.35 (s, 3H), 2.20 (s, 6H).
^{13}C NMR (101 MHz, Chloroform-d) δ 143.6, 139.7, 136.3, 135.6, 135.6, 130.4, 129.5, 129.3, 129.1, 128.7, 127.5, 127.4, 117.6, 111.5, 21.0, 18.4.

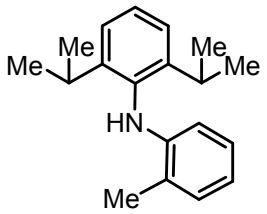
N-(2,6-Dimethylphenyl)-2,4,6-trimethylaniline (26):



Following the general procedure A, N-(2,6-dimethylphenyl)-2,4,6-trimethylanilinewas prepared from 2-iodo-1,3-dimethylbenzene (0.5 mmol, 116 mg) and 2,4,6-trimethylaniline (0.85 mmol, 115 mg) and

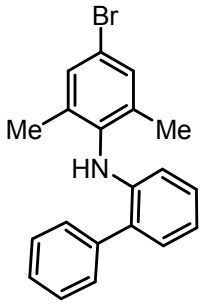
reaction was run for 48 h. Desired product was isolated as white solid and matched with reported spetra.[3] Isolated yield 31% (37 mg).
TLC: 0.38 in 5 % ethyl acetate/ hexanes.
^{1}H NMR (400 MHz, Chloroform-d) δ 6.98 (d, *J* = 7.4 Hz, 2H), 6.87 – 6.79 (m, 3H), 4.72 (s, 1H), 2.27 (s, 3H), 2.06 – 1.93 (m, 12H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.4, 139.1, 131.7, 130.6, 129.3, 128.9, 128.6, 121.1, 20.8, 19.3, 19.2.

2,6-Diisopropyl-N-(o-tolyl)aniline (27):



Following the general procedure A, 2,6-diisopropyl-N-(o-tolyl)aniline was prepared from 2-iodotoluene (0.5 mmol, 61 µL) and 2,6-diisopropylaniline (0.85 mmol, 150 mg) and reaction was run for 60 h. Desired product was isolated as white solid and matched with reported spectra.[4] Isolated yield 68% (90 mg).
TLC: 0.52 in 5 % ethyl acetate/ hexanes.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 (dd, *J* = 8.8, 6.4 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.20 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.02 (td, *J* = 7.7, 1.6 Hz, 1H), 6.74 (td, *J* = 7.4, 1.2 Hz, 1H), 6.20 (dd, *J* = 8.1, 1.1 Hz, 1H), 4.98 (s, 1H), 3.19 (hept, *J* = 6.9 Hz, 2H), 2.42 (s, 3H), 1.22 (dd, *J* = 21.6, 6.9 Hz, 12H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.4, 146.1, 135.8, 130.2, 127.2, 127.1, 123.9, 121., 117.66, 111.5, 28.3, 24.8, 23.1, 17.8.

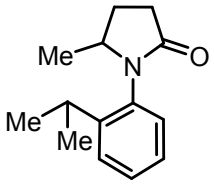
N-(4-Bromo-2,6-dimethylphenyl)-[1,1'-biphenyl]-2-amine (28):



Following the general procedure A, N-(4-bromo-2,6-dimethylphenyl)-[1,1'-biphenyl]-2-amine was prepared from 2-iodo-1,1'-biphenyl (0.5 mmol, 140 mg) and 4-bromo-2,6-dimethylaniline (0.85 mmol, 169 mg). Desired product was isolated as white solid. Isolated yield 63% (110 mg).
TLC: 0.60 in 10 % ethyl acetate/ hexanes.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.34 (m, 2H), 7.31 (dd, *J* = 8.5, 6.8 Hz, 2H), 7.24 – 7.18 (m, 1H), 7.06 (s, 2H), 7.00 (dd, *J* = 7.4, 1.6 Hz, 1H), 6.91 (ddd, *J* = 8.8, 7.5, 1.6 Hz, 1H), 6.64 (td, *J* = 7.4, 1.1 Hz, 1H), 6.01 (dd, *J* = 8.2, 1.1 Hz, 1H), 4.98 (s, 1H), 1.96 (s, 6H).

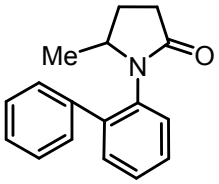
^{13}C NMR (101 MHz, Chloroform-d) δ 142.7, 139.4, 138.6, 137.6, 131.3, 130.5, 129.5, 129.1, 128.7, 127.9, 127.6, 119.1, 118.3, 111.6, 18.4.
IR (Neat) cm^{-1}: 3013, 2920, 2160, 1712, 1578, 1503, 1483, 1433, 1360, 1272, 1220, 863, 744, 701,.
HRMS (CI): Calcd. $C_{20}H_{19}NBr$ $[M+H]^+$, 352.0695, Found, 352.0700.

1-(2-Isopropylphenyl)-5-methylpyrrolidin-2-one (29):



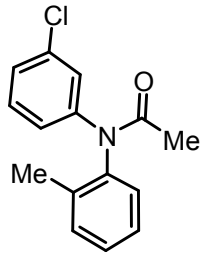
Following the general procedure A, 1-(2-isopropylphenyl)-5-methylpyrrolidin-2-one was prepared from 2-isopropylbenzen (0.5 mmol, 80 µL) and 5-methylpyrrolidin-2-one (0.85 mmol, 85 mg). Desired product was isolated as white solid. Isolated yield 95% (103 mg).
TLC: 0.11 in 30 % ethyl acetate/ hexanes.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.26 (m, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 7.7 Hz, 1H), 4.14 – 3.78 (m, 1H), 3.15 – 2.77 (m, 1H), 2.68 – 2.47 (m, 2H), 2.46 – 2.31 (m, 1H), 1.88 – 1.69 (m, 1H), 1.34 – 0.98 (m, 9H).
^{13}C NMR (101 MHz, Chloroform-d) δ 174.8, 147.8, 130.4, 128.7, 128.1, 126.8, 126.5, 125.8, 57.7, 57.4, 31.3, 30.4, 28.1, 27.9, 24.2, 23.9, 20.6, 20.2.
IR (Neat) cm^{-1}: 2962, 2928, 2868, 1688, 1491, 1450, 1380, 1226, 1131, 757, 660.
HRMS (CI): Calcd. $C_{14}H_{20}ON$ $[M+H]^+$, 218.1539, Found, 218.1541.

1-([1,1'-Biphenyl]-2-yl)-5-methylpyrrolidin-2-one (30):



Following the general procedure A, 1-([1,1'-biphenyl]-2-yl)-5-methylpyrrolidin-2-one was prepared from 2-iodo-1,1'-biphenyl (0.5 mmol, 140 mg) and 5-methylpyrrolidin-2-one (0.85 mmol, 85 mg). Desired product was isolated as white solid and matched with reported spectra[6]. Isolated yield 52 % (65 mg). Isolated yield with 8 mol % CuI/ligand: 52% (65 mg).
TLC: 0.12 in 30 % ethyl acetate/ hexanes.
^{1}H NMR (500 MHz, Chloroform-d) δ 7.53 – 7.31 (m, 8H), 7.27 – 7.13 (m, 1H), 3.21 (s, 1H), 2.49 (ddd, *J* = 17.0, 9.3, 5.3 Hz, 1H), 2.36 (ddd, *J* = 17.1, 9.3, 8.0 Hz, 1H), 2.00 – 1.89 (m, 1H), 1.61 – 1.45 (m, 1H), 0.86 (d, *J* = 6.3 Hz, 3H).
^{13}C NMR (126 MHz, Chloroform-d) δ 175.8, 139.3, 134.9, 130.8, 130.2, 128.6, 128.4, 128.2, 127.6, 55.9, 30.8, 27.7, 20.

N-(3-chlorophenyl)-N-(o-tolyl)acetamide (31):



Following the general procedure A, N-(3-chlorophenyl)-N-(o-tolyl)acetamide was prepared from 2-iodotoluene (0.5 mmol, 61 µL) and N-(3-chlorophenyl)acetamide (0.85 mmol, 144 mg). Desired product was isolated as oily liquid. Isolated yield 68% (88 mg).

TLC: 0.43 in 30 % ethyl acetate/ hexanes.

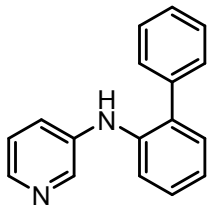
^{1}H NMR (400 MHz, Chloroform-d) δ 7.28 – 7.20 (m, 4H), 7.20 – 7.12 (m, 2H), 7.09 (d, *J* = 7.9 Hz, 1H), 7.05 (s, 1H), 2.13 (s, 3H), 1.89 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-d) δ 170.5, 162.3, 141.2, 136.2, 134.3, 132.0, 129.7, 129.0, 127.7, 125.5, 123.1, 25.1, 24.1, 18.0, 14.4.

IR (Neat) cm^{-1}: 1679, 1589, 1474, 1368, 1314, 1294, 1261, 1097, 1077, 1020, 799, 780, 743.

HRMS (CI): Calcd. $C_{15}H_{15}ONCl$ $[M+H]^+$, 260.0837, Found, 260.0839.

N-([1,1'-biphenyl]-2-yl)pyridin-3-amine (32):



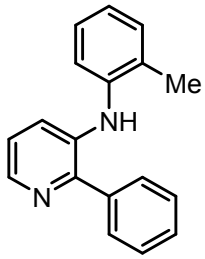
Following the general procedure A, N-([1,1'-biphenyl]-2-yl)pyridin-3-amine was prepared from 2-iodo-1,1'-biphenyl (0.5 mmol, 140 mg) and pyridin-3-amine (0.85 mmol, 80 mg). Desired product was isolated as white solid and matched with reported spectra[7]. Isolated yield 86% (105 mg).

TLC: 0.11 in 20 % ethyl acetate/ hexanes.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.28 (d, *J* = 2.8 Hz, 1H), 8.15 (dd, *J* = 4.7, 1.3 Hz, 1H), 7.47 – 7.40 (m, 4H), 7.39 – 7.32 (m, 3H), 7.32 – 7.25 (m, 2H), 7.15 (dd, *J* = 8.3, 4.7 Hz, 1H), 7.08 (td, *J* = 7.4, 1.3 Hz, 1H), 5.66 (s, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.1, 140.6, 140.2, 139.1, 138.8, 132.6, 131.2, 129.3, 129.0, 128.5, 127.8, 123.8, 123.7, 122.3, 118.2.

2-Phenyl-N-(o-tolyl)pyridin-3-amine (33):



Following the general procedure A, 2-phenyl-N-(o-tolyl)pyridin-3-amine was prepared from 2-iodotoluene (0.5 mmol, 61 µL) and 2-phenylpyridin-3-amine (0.85 mmol, 145 mg). Desired product was isolated as white solid. Isolated yield 68% (88 mg).

TLC: 0.49 in 30 % ethyl acetate/ hexanes.

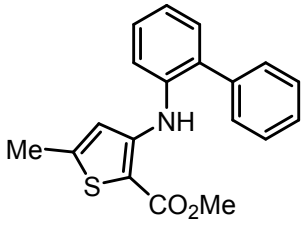
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 (dd, *J* = 4.6, 1.5 Hz, 1H), 7.80 – 7.65 (m, 2H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.46 – 7.39 (m, 1H), 7.31 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.25 – 7.15 (m, 3H), 7.12 (dd, *J* = 8.3, 4.6 Hz, 1H), 7.02 (td, *J* = 7.2, 1.8 Hz, 1H), 5.65 (s, 1H), 2.15 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.73, 1410, 140.0, 138.2, 131.2, 130.3, 129.0, 128.7, 128.6, 127.0, 123.5, 122.8, 122.8, 120.4, 17.9.

IR (Neat) cm^{-1}: 3055, 3023, 2920, 1577, 1501, 1480, 1453, 1434, 1401, 1303, 1250, 1179, 1112, 1018, 792, 738, 699.

HRMS (CI): Calcd. $C_{18}H_{17}N_2$ $[M+H]^+$, 261.1386, Found, 261.1389.

Methyl 3-([1,1'-biphenyl]-2-ylamino)-5-methylthiophene-2-carboxylate (34):



Following the general procedure A, methyl 3-([1,1'-biphenyl]-2-ylamino)-5-methylthiophene-2-carboxylate was prepared from 2-iodo-1,1'-biphenyl (0.5 mmol, 140 mg) and methyl 3-amino-5-methylthiophene-2-carboxylate (0.85 mmol, 146 mg). Desired product was isolated as white solid. Isolated yield 64% (103 mg).

TLC: 0.42 in 10 % ethyl acetate/ hexanes.

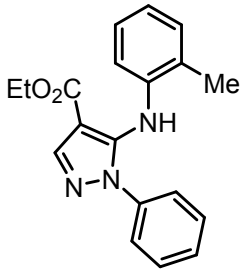
^{1}H NMR (500 MHz, Chloroform-d) δ 8.51 (s, 1H), 7.48 – 7.40 (m, 5H), 7.40 – 7.31 (m, 3H), 7.15 (td, *J* = 7.4, 1.1 Hz, 1H), 6.80 (s, 1H), 3.72 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-d) δ 164.5, 151.2, 146.8, 138.9, 138.8, 134.2, 131.0, 129.3, 128.7, 128.2, 127.6, 123.5, 121.0, 117.1, 101.4, 51.2, 16.4.

IR (Neat) cm^{-1}: 3025, 2948, 1712, 1663, 1567, 1433, 1264, 1236, 1209, 1088, 1056, 760, 744, 700.

HRMS (CI): Calcd. $C_{19}H_{17}O_2NNaS$ $[M+H]^+$, 346.0872, Found, 346.0875.

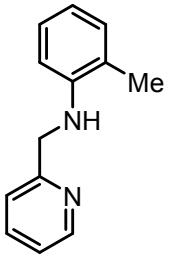
Ethyl 1-phenyl-5-(o-tolylamino)-1H-pyrazole-4-carboxylate (35):



Following the general procedure A, ethyl 1-phenyl-5-(o-tolylamino)-1H-pyrazole-4-carboxylate was prepared from 2-iodotoluene (0.5 mmol, 61 µL) and ethyl 5-amino-1-phenyl-1H-pyrazole-4-carboxylate (0.85 mmol, 196 mg). Desired product was isolated as colorless oily liquid. Isolated yield 55 % (88 mg).

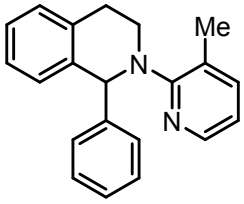
TLC: 0.48 in 20 % ethyl acetate/ hexanes.
^{1}H NMR (400 MHz, Chloroform-d) δ 7.97 (d, *J* = 1.9 Hz, 1H), 7.69 (s, 1H), 7.39 – 7.32 (m, 2H), 7.20 – 7.06 (m, 3H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.72 (dt, *J* = 24.3, 7.6 Hz, 2H), 6.44 (d, *J* = 7.9 Hz, 1H), 4.33 (qd, *J* = 7.1, 2.0 Hz, 2H), 2.32 (d, *J* = 2.0 Hz, 3H), 1.37 (td, *J* = 7.1, 1.9 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-d) δ 164.7, 147.0, 141.1, 139.2, 138.2, 130.4, 128.9, 128.6, 127.4, 126.1, 123.5, 123.0, 119.6, 101.0, 60.1, 18.0, 14.6.
IR (Neat) cm^{-1}: 2979, 1709, 1677, 1596, 1574, 1501, 1459, 1411, 1383, 1233, 1117, 1096, 1078, 970, 780, 756.
HRMS (ESI): Calcd. $C_{19}H_{19}O_2N_3Na$ $[M+Na]^+$, 344.1369, Found, 344.1371.

2-Methyl-N-(pyridin-2-ylmethyl)aniline (36):



Following the general procedure A, 2-methyl-N-(pyridin-2-ylmethyl)aniline was prepared from 2-iodotoluene (0.5 mmol, 61 µL) and pyridin-2-ylmethanamine (0.85 mmol, 92 mg). Desired product was isolated as yellow oily liquid and matched with reported spectra[8]. Isolated yield 91% (90 mg).
TLC: 0.17 in 20 % ethyl acetate/ hexanes.
^{1}H NMR (500 MHz, Chloroform-d) δ 7.65 (td, *J* = 7.7, 1.7 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.19 (dd, *J* = 7.5, 5.0 Hz, 1H), 7.13 (t, *J* = 7.8 Hz, 2H), 6.71 (t, *J* = 7.4 Hz, 1H), 6.61 (d, *J* = 7.9 Hz, 1H), 4.71 (s, 1H), 4.53 (s, 2H), 2.29 (s, 3H).
^{13}C NMR (126 MHz, Chloroform-d) δ 158.6, 149.2, 145.9, 136.6, 130., 127.19, 122.3, 122.1, 121.6, 117.2, 110.2, 49.3, 17.6.

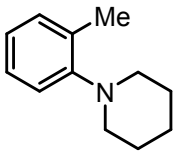
2-(3-Methylpyridin-2-yl)-1-phenyl-1,2,3,4-tetrahydroisoquinoline (37):



Following the general procedure A, 2-(3-methylpyridin-2-yl)-1-phenyl-1,2,3,4-tetrahydroisoquinoline was prepared from 2-iodo-3-methylpyridine (0.5 mmol, 110 mg) and 1-phenyl-1,2,3,4-tetrahydroisoquinoline (0.85 mmol, 178 mg). Desired product was isolated as yellow oily liquid. Isolated yield 52% (78 mg).
TLC: 0.62 in 20 % ethyl acetate/ hexanes.
^{1}H NMR (400 MHz, Chloroform-d) δ 8.10 (dd, *J* = 4.9, 1.8 Hz, 1H), 7.37 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.19 (ddd, *J* = 11.3, 7.3, 1.5 Hz, 2H), 7.15 – 7.06 (m, 6H), 6.93 (d, *J* = 7.7 Hz, 1H), 6.80 (dd, *J* = 7.4, 4.8 Hz, 1H), 6.07 (s, 1H), 3.39 (t, *J* = 5.8 Hz, 2H), 3.19 (dt, *J* = 16.1, 6.1 Hz, 1H), 2.95 (dt, *J* = 16.0, 5.5 Hz, 1H), 2.33 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-d) δ 161.4, 145.4, 144.1, 139.2, 138.4, 135.1, 129.4, 128.9, 128.7, 127.8, 126.9, 126.8, 126.1, 125.8, 118.6, 62.9, 46.2, 29.9, 18.3.

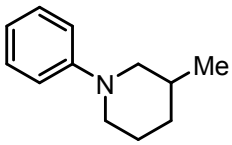
IR (Neat) cm^{-1}: 3059, 3025, 2928, 2028, 2011, 1977, 1599, 1584, 1492, 1421, 1361, 1283, 1258, 1179, 1105, 741, 699.
HRMS (EI): Calcd. $C_{21}H_{20}N_2$ $[M]^+$, 300.1621, Found, 300.1620.

1-(o-tolyl)piperidine (38):



Following the general procedure A, 1-(o-tolyl)piperidine was prepared from 2-iodotoluene (0.5 mmol, 61 µL) and piperidine (0.85 mmol, 71 mg) with 1 mol % CuI/ ligand loading. Desired product was isolated as white solid and matched with reported spetra.[9] Isolated yield 92% (80 mg).
^{1}H NMR (400 MHz, Chloroform-d) δ 7.23 – 7.15 (m, 2H), 7.03 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.98 (td, *J* = 7.3, 1.3 Hz, 1H), 2.94 – 2.80 (m, 4H), 2.34 (s, 3H), 1.74 (p, *J* = 5.7 Hz, 4H), 1.61 (q, *J* = 6.2 Hz, 2H).

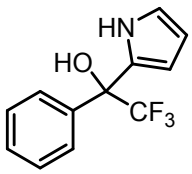
3-methyl-1-phenylpiperidine (39):



Following the general procedure A, 3-methyl-1-phenylpiperidine was prepared from iodobenzene (0.5 mmol, 102 mg) and 3-methylpiperidine (0.85 mmol, 84 mg) with 0.8 mol % CuI/ ligand loading. Desired product was isolated as white solid and matched with reported spetra[10]. Isolated yield 95 % (83 mg).
^{1}H NMR (400 MHz, Chloroform-d) δ 7.39 – 7.17 (m, 2H), 7.06 – 6.91 (m, 2H), 6.83 (td, *J* = 7.3, 1.1 Hz, 1H), 3.72 – 3.53 (m, 2H), 2.65 (td, *J* = 11.7, 3.3 Hz, 1H), 2.34 (dd, *J* = 12.0, 10.3 Hz, 1H), 1.87 – 1.60 (m, 4H), 1.13 – 1.00 (m, 1H), 0.97 (d, *J* = 6.4 Hz, 3H).

Characterization data for ligands

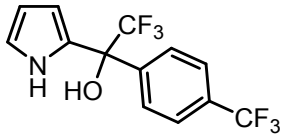
2,2,2-trifluoro-1-phenyl-1-(1H-pyrrol-2-yl)ethan-1-ol (L1):



Following the general procedure **B**, 2,2,2-trifluoro-1-phenyl-1-(1H-pyrrol-2-yl)ethan-1-ol from phenylmagnesium bromide and 2,2,2-trifluoro-1-(1H-pyrrol-2-yl)ethan-1-one (4 mmol, 652mg). Isolated yield 68% (655 mg).
TLC: 0.43 in 20 % ethyl acetate/ hexanes.

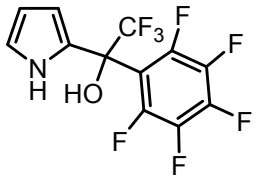
^{1}H NMR (400 MHz, Chloroform-d) δ 8.21 (s, 1H), 7.55 (t, *J* = 4.5 Hz, 2H), 7.46 – 7.34 (m, 3H), 6.76 (d, *J* = 3.1 Hz, 1H), 6.39 (s, 1H), 6.21 (q, *J* = 3.0 Hz, 1H), 3.04 (s, 1H).
^{13}C NMR (101 MHz, Chloroform-d) δ 136.8, 129.2, 128.6, 128.3, 127.5, 125.0 (q, *J* = 286.8 Hz), 119.3, 109.2 (q, *J* = 2.2 Hz) 108.7, 76.4 (q, *J* = 30.3 Hz).
^{19}F NMR (376 MHz, Chloroform-d) δ -76.81.
IR (Neat) cm^{-1}: 3365, 1703, 1363, 1232, 1156, 1105, 1056, 1040, 963, 914, 762, 722, 698.
LRMS (GCMS): m/z 241.1 $[M]^+$

2,2,2-trifluoro-1-(1H-pyrrol-2-yl)-1-(4-(trifluoromethyl)phenyl)ethan-1-ol (L2):



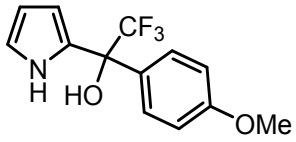
Following the general procedure **B**, 2,2,2-trifluoro-1-(1H-pyrrol-2-yl)-1-(4-(trifluoromethyl)phenyl)ethan-1-ol was prepared from (4-(trifluoromethyl)phenyl)magnesium bromide and 2,2,2-trifluoro-1-(1H-pyrrol-2-yl)ethan-1-one (4 mmol, 652mg). Isolated yield 21% (197 mg) (yield is ~70%, most of the part was isolated as mixture with starting material ketone).
TLC: 0.47 in 20 % ethyl acetate/ hexanes.
^{1}H NMR (500 MHz, Chloroform-d) δ 8.20 (s, 1H), 7.84 – 7.39 (m, 4H), 6.81 (p, *J* = 2.3 Hz, 1H), 6.39 (s, 1H), 6.22 (p, *J* = 2.7 Hz, 1H), 3.01 (s, 1H).
^{13}C NMR (126 MHz, Chloroform-d) δ 140.6, 131.6, 131.3, 128.1, 127.8, 125.8, 125.4, 125.3, 125.3, 125.3, 125.1, 123.5, 122.9, 119.8, 109.6, 109.6, 109.0, 76.2 (q, *J* = 30 Hz).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.86, -76.85.
LRMS (GCMS): m/z 309.1 $[M]^+$

2,2,2-trifluoro-1-(perfluorophenyl)-1-(1H-pyrrol-2-yl)ethan-1-ol (L3):



Following the general procedure **B**, 2,2,2-trifluoro-1-(perfluorophenyl)-1-(1H-pyrrol-2-yl)ethan-1-ol was prepared from (perfluorophenyl)magnesium bromide and 2,2,2-trifluoro-1-(1H-pyrrol-2-yl)ethan-1-one (4 mmol, 652mg). Isolated yield 54% (715 mg)
^{1}H NMR (500 MHz, Chloroform-d) δ 8.44 (s, 1H), 6.85 (q, *J* = 2.2 Hz, 1H), 6.34 (s, 1H), 6.30 – 6.13 (m, 1H), 3.57 (s, 1H).
^{13}C NMR (126 MHz, Chloroform-d) δ 147.2, 145.1, 143.0, 141.0, 139.2, 139.1, 137.3, 137.2, 127.5, 126.1, 125.2, 123.0, 120.7, 119.8, 111.9, 109.0, 108.9, 75.8 (q, *J* = 34 Hz).
^{19}F NMR (376 MHz, Chloroform-d) δ -78.02 (t, *J* = 11.1 Hz), -136.50 (dtt, *J* = 21.9, 10.9, 5.4 Hz), -151.16 (tt, *J* = 21.2, 4.7 Hz), -158.35 – -164.09 (m).
LRMS (GCMS): m/z 331.1 $[M]^+$

2,2,2-trifluoro-1-(4-methoxyphenyl)-1-(1H-pyrrol-2-yl)ethan-1-ol (L4):



Following the general procedure **B**, 2,2,2-trifluoro-1-(4-methoxyphenyl)-1-(1H-pyrrol-2-yl)ethan-1-ol was prepared from (4-methoxyphenyl)magnesium bromide and 2,2,2-trifluoro-1-(1H-pyrrol-2-yl)ethan-1-one (4 mmol, 652mg). Isolated yield 51% (552 mg)

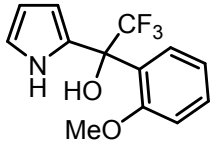
^{1}H NMR (500 MHz, Chloroform-d) δ 8.23 (s, 1H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.09 – 6.83 (m, 2H), 6.75 (td, *J* = 2.7, 1.4 Hz, 1H), 6.38 (dq, *J* = 4.2, 1.5 Hz, 1H), 6.21 (q, *J* = 2.9 Hz, 1H), 3.81 (s, 3H), 3.04 (s, 1H).

^{13}C NMR (126 MHz, Chloroform-d) δ 160.1, 128.9, 128.9, 128.7, 125.0 (q, *J* = 287.3 Hz) 119.2, 113.6, 109.1 (q, *J* = 1.3 Hz), 108.6, 76.1 (q, *J* = 30 Hz), 55.4.

^{19}F NMR (376 MHz, Chloroform-d) δ -77.05.

LRMS (GCMS): m/z 271.1 $[M]^+$

2,2,2-trifluoro-1-(2-methoxyphenyl)-1-(1H-pyrrol-2-yl)ethan-1-ol (L5):



Following the general procedure **B**, 2,2,2-trifluoro-1-(2-methoxyphenyl)-1-(1H-pyrrol-2-yl)ethan-1-ol was prepared from (2-methoxyphenyl)magnesium bromide and 2,2,2-trifluoro-1-(1H-pyrrol-2-yl)ethan-1-one (4 mmol, 652 mg). Isolated yield 58% (628 mg)

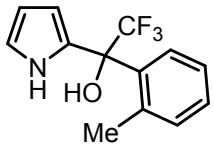
^{1}H NMR (500 MHz, Chloroform-d) 8.56 (s, 1H), 7.43 – 7.28 (m, 1H), 7.18 (d, *J* = 7.9 Hz, 1H), 7.02 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.98 – 6.89 (m, 1H), 6.79 (t, *J* = 2.3 Hz, 1H), 6.62 (d, *J* = 4.3 Hz, 1H), 6.33 (d, *J* = 2.9 Hz, 1H), 6.23 (p, *J* = 2.8 Hz, 1H), 4.00 – 3.84 (m, 3H).

^{13}C NMR (126 MHz, Chloroform-d) δ 157.9, 130.9, 130.6, 127.8, 125.1 (q, *J* = 287.3 Hz), 124.7, 121.7, 118.2, 112.8, 108.5, 78.7 (q, *J* = 31.5 Hz), 56.6.

^{19}F NMR (376 MHz, Chloroform-d) δ -77.10.

LRMS (GCMS): m/z 271.1 $[M]^+$

2,2,2-trifluoro-1-(1H-pyrrol-2-yl)-1-(o-tolyl)ethan-1-ol (L6):



Following the general procedure **B**, 2,2,2-trifluoro-1-(1H-pyrrol-2-yl)-1-(o-tolyl)ethan-1-ol was prepared from *o*-tolylmagnesium bromide and 2,2,2-trifluoro-1-(1H-pyrrol-2-yl)ethan-1-one (4 mmol, 652mg). Desired product was isolated with the 10 % mixture of the starting ketone. The pure product was obtained keepin the mixture in high vacuum. Isolated yield 60% (612 mg)

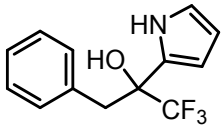
TLC: 0.48 in 20 % ethyl acetate/ hexanes.

^{1}H NMR (400 MHz, Chloroform-d) δ 8.25 (s, 1H), 7.71 (dt, *J* = 8.0, 1.6 Hz, 1H), 7.31 (td, *J* = 7.4, 1.5 Hz, 1H), 7.25 (td, *J* = 7.6, 1.7 Hz, 1H), 7.20 (dd, *J* = 7.4, 1.6 Hz, 1H), 6.76 (td, *J* = 2.7, 1.5 Hz, 1H), 6.37 – 6.06 (m, 2H), 2.90 (s, 1H), 2.05 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 139.0, 134.8, 133.0, 129.3, 128.6, 128.8 (q, *J* = 3 Hz), 125.6, 125.2 (q, *J* = 287.8 Hz), 118.8, 76.9 (q, *J* = 30 Hz), 20.7 (q, *J* = 1 Hz).

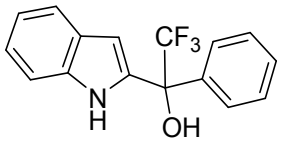
^{19}F NMR (376 MHz, Chloroform-d) δ -75.40.
LRMS (GCMS): m/z 255.1 $[M]^+$

1,1,1-trifluoro-3-phenyl-2-(1H-pyrrol-2-yl)propan-2-ol (L7):



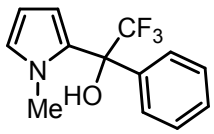
Following the general procedure **C**, 1,1,1-trifluoro-3-phenyl-2-(1H-pyrrol-2-yl)propan-2-ol was prepared from (1H-pyrrol-2-yl)magnesium bromide and 1,1,1-trifluoro-3-phenylpropan-2-one (8 mmol, 1.504 g). Isolated yield 47% (950 mg)
TLC: 0.35 in 20 % ethyl acetate/ hexanes.
^{1}H NMR (400 MHz, Chloroform-d) δ 8.34 (s, 1H), 7.29 (d, *J* = 2.2 Hz, 2H), 7.28 (d, *J* = 2.1 Hz, 1H), 7.07 (dd, *J* = 6.3, 2.8 Hz, 2H), 6.73 (q, *J* = 2.3 Hz, 1H), 6.34 (d, *J* = 3.7 Hz, 1H), 6.27 (q, *J* = 2.9 Hz, 1H), 3.73 – 3.04 (m, 2H), 2.48 (d, *J* = 3.1 Hz, 1H).
^{13}C NMR (101 MHz, Chloroform-d) δ 133.1, 130.8, 128.7, 127.8, 126.8, 125.2 (q, *J* = 285.8 Hz), 118.0, 109.2, 107.2, 75.0 (q, *J* = 29.2 Hz), 41.6.
^{19}F NMR (376 MHz, Chloroform-d) δ -80.26.
IR (Neat) cm^{-1}: 3376, 1700, 1162, 1107, 1088, 1034, 975, 723, 699.
LRMS (GCMS): m/z 255.2 $[M]^+$

2,2,2-trifluoro-1-(1H-indol-2-yl)-1-phenylethan-1-ol (L9):



Following the general procedure **C**, 2,2,2-trifluoro-1-(1H-indol-2-yl)-1-phenylethan-1-ol was prepared from (1H-indol-2-yl)magnesium bromide and trifluoroaetophenone (3 mmol, 421 µL). Isolated yield 65% (567 mg).
^{1}H NMR (400 MHz, Chloroform-d) δ 8.22 (s, 1H), 7.72 – 7.57 (m, 2H), 7.50 – 7.32 (m, 5H), 7.21 (t, *J* = 7.9 Hz, 2H), 6.99 (t, *J* = 7.6 Hz, 1H), 2.97 (s, 1H).
^{13}C NMR (101 MHz, Chloroform-d) δ 137.8, 136.4, 128.6, 128.1, 127.7, 125.2, 125.5 (q, *J* = 287.8 Hz), 123.4 (q, *J* = 3.0 Hz), 122.8, 121.0, 120.4, 114.1, 111.4, 77.2 (q, *J* = 30.3 Hz).
^{19}F NMR (376 MHz, Chloroform-d) δ -76.88.
LRMS (GCMS): m/z 291.2 $[M]^+$

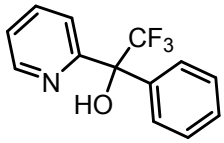
2,2,2-trifluoro-1-(1-methyl-1H-pyrrol-2-yl)-1-phenylethan-1-ol (L10):



Following the general procedure **B**, 2,2,2-trifluoro-1-(1-methyl-1H-pyrrol-2-yl)-1-phenylethan-1-ol was prepared from phenylmagnesium bromide and 2,2,2-trifluoro-1-(1-methyl-1H-pyrrol-2-yl)ethan-1-one (4 mmol, 708 mg). Isolated yield 45% (459 mg).
^{1}H NMR (500 MHz, Chloroform-d) δ 7.42 (dd, *J* = 6.8, 3.1 Hz, 2H), 7.40 – 7.34 (m, 3H), 6.61 (t, *J* = 2.2 Hz, 1H), 6.52 (ddd, *J* = 4.2, 2.7, 1.8 Hz, 1H), 6.14 (dd, *J* = 3.8, 2.7 Hz, 1H), 3.15 (s, 3H), 2.93 (s, 1H).

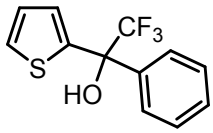
^{13}C NMR (126 MHz, Chloroform-d) δ 136.6, 128.9, 128.3, 128.0, 127.7, 125.5, 124.8 (q, *J* = 287.2 Hz), 110.6 (q, *J* = 2.5 Hz), 106.5, 76.8 (q, *J* = 30.2 Hz), 35.6.
^{19}F NMR (376 MHz, Chloroform-d) δ -71.56 (d, J = 2.0 Hz).
LRMS (GCMS): m/z 255.2 $[M]^+$

2,2,2-trifluoro-1-phenyl-1-(pyridin-2-yl)ethan-1-ol (L11):



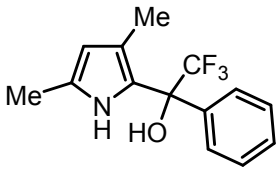
Following the general procedure **C**, 2,2,2-trifluoro-1-phenyl-1-(pyridin-2-yl)ethan-1-ol was prepared from pyridin-2-ylmagnesium bromide and trifluoroaetophenone (4 mmol, 561 µL). Isolated yield 20% (202 mg).
^{1}H NMR (500 MHz, Chloroform-d) δ 8.60 (dt, *J* = 4.9, 1.3 Hz, 1H), 7.74 (td, *J* = 7.8, 1.7 Hz, 1H), 7.67 (d, *J* = 7.5 Hz, 2H), 7.57 – 7.46 (m, 1H), 7.42 – 7.31 (m, 4H), 7.02 (s, 1H).
^{13}C NMR (126 MHz, Chloroform-d) δ 155.0, 147.4, 138.4, 137.6, 128.7, 128.6, 127.1 (q, *J* = 1.2 Hz), 125.1 (q, *J* = 287.2 Hz),124.1, 123.0 (q, *J* = 2.5 Hz), 77.8 (q, *J* = 30.2 Hz).
^{19}F NMR (376 MHz, Chloroform-d) δ -74.77.
LRMS (GCMS): m/z 253.2 $[M]^+$

2,2,2-trifluoro-1-phenyl-1-(thiophen-2-yl)ethan-1-ol (L12):



Following the general procedure **C**, 2,2,2-trifluoro-1-phenyl-1-(thiophen-2-yl)ethan-1-ol was prepared from thiophen-2-ylmagnesium bromide and trifluoroaetophenone (4 mmol, 561 µL). Isolated yield 65% (670 mg).
^{1}H NMR (500 MHz, Chloroform-d) δ 7.62 (q, *J* = 4.7 Hz, 2H), 7.40 (q, *J* = 3.1 Hz, 3H), 7.37 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.23 (d, *J* = 3.8 Hz, 1H), 7.04 – 7.01 (m, 1H), 3.07 (d, *J* = 11.8 Hz, 1H).
^{13}C NMR (126 MHz, Chloroform-d) δ 143.3, 137.9, 129.2, 128.3, 127.3 (q, *J* = 2.5 Hz), 127.1, 127.1, 126.9, 126.1, 123.8, 121.5, 78.0 (q, *J* = 30.2 Hz).
^{19}F NMR (376 MHz, Chloroform-d) δ -76.38.
LRMS (GCMS): m/z 258.2 $[M]^+$

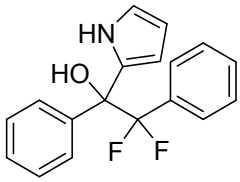
1-(3,5-dimethyl-1H-pyrrol-2-yl)-2,2,2-trifluoro-1-phenylethan-1-ol (L13):



Following the general procedure **B**, 1-(3,5-dimethyl-1H-pyrrol-2-yl)-2,2,2-trifluoro-1-phenylethan-1-ol was prepared from phenylmagnesium bromide and 1-(3,5-dimethyl-1H-pyrrol-2-yl)-2,2,2-trifluoroethan-1-one (4 mmol, 764 mg). Isolated yield 15% (161 mg).
^{1}H NMR (500 MHz, Chloroform-d) δ 8.09 (d, *J* = 9.7 Hz, 1H), 7.55 (dd, *J* = 6.8, 3.3 Hz, 2H), 7.37 (dd, *J* = 4.4, 2.4 Hz, 3H), 5.69 (d, *J* = 2.9 Hz, 1H), 2.91 (s, 1H), 2.24 (s, 3H), 1.58 (s, 3H).

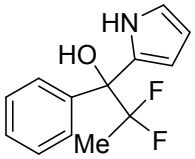
^{13}C NMR (126 MHz, Chloroform-d) δ 138.2, 135.6, 130.3, 129.2, 129.0, 128.4, 127.6, 127.0, 125.4 (q, *J* 287.2 Hz), 122.3, 119.2, 110.2, 76.6 (q, *J* = 29 Hz), 13.0, 11.8.
^{19}F NMR (376 MHz, Chloroform-d) δ -75.09.
LRMS (GCMS): m/z 269.2 $[M]^+$

2,2-difluoro-1,2-diphenyl-1-(1H-pyrrol-2-yl)ethan-1-ol (L14):



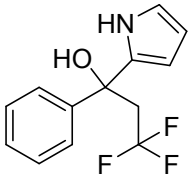
Following the general procedure **C**, 2,2-difluoro-1,2-diphenyl-1-(1H-pyrrol-2-yl)ethan-1-ol was prepared from (1H-pyrrol-2-yl)magnesium bromide and 2,2-difluoro-1,2-diphenylethan-1-one[11] (2 mmol, 764 mg). Isolated yield 64% (382 mg).
^{1}H NMR (400 MHz, Chloroform-d) δ 8.40 (s, 1H), 7.31 (d, *J* = 7.6 Hz, 3H), 7.27 – 7.13 (m, 5H), 7.08 (d, *J* = 7.5 Hz, 2H), 6.75 (td, *J* = 2.8, 1.5 Hz, 1H), 6.37 (qd, *J* = 2.7, 1.5 Hz, 1H), 6.18 (q, *J* = 3.0 Hz, 1H), 2.74 (s, 1H).
^{13}C NMR (126 MHz, Chloroform-d) δ 138.8, 133.7, 131.0, 129.9, 128.3, 127.7, 127.7, 127.4, 127.4, 127.3, 127.3, 122.6 (t, *J* = 255.2 Hz), 118.4, 109.6, 109.6, 109.6, 108.5, 78.4 (t, *J* = 30.0 Hz).
^{19}F NMR (376 MHz, Chloroform-d) δ -102.15, -102.81, -103.06, -103.72.
LRMS (GCMS): m/z 299.2 $[M]^+$

2,2-difluoro-1-phenyl-1-(1H-pyrrol-2-yl)propan-1-ol (L15):



Following the general procedure **C**, 2,2-difluoro-1-phenyl-1-(1H-pyrrol-2-yl)propan-1-ol was prepared from (1H-pyrrol-2-yl)magnesium bromide and 2,2-difluoro-1-phenylpropan-1-one[11] (2.65 mmol, 450 mg). Isolated yield 67% (420 mg).
^{1}H NMR (400 MHz, Chloroform-d) δ 8.36 (s, 1H), 7.59 (dt, *J* = 7.3, 1.6 Hz, 2H), 7.41 – 7.30 (m, 3H), 6.74 (td, *J* = 2.7, 1.5 Hz, 1H), 6.32 (ddd, *J* = 3.9, 2.7, 1.4 Hz, 1H), 6.18 (dt, *J* = 3.6, 2.7 Hz, 1H), 2.80 (s, 1H), 1.55 (t, *J* = 19.2 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-d) δ 139.5, 139.5, 131.2, 128.4, 128.1, 127.3 (t, *J* = 2.0 Hz), 125.1 (*J* = 250.4 Hz), 118.4, 109.1 (t, *J* = 2.0 Hz), 108.3, 77.4 (t, *J*= 26.2 Hz), 19.8 (t, *J* = 27.2).
^{19}F NMR (376 MHz, Chloroform-d) δ -90.59 – -109.59 (m).
LRMS (GCMS): m/z 237.1 $[M]^+$

3,3,3-trifluoro-1-phenyl-1-(1H-pyrrol-2-yl)propan-1-ol (L16):



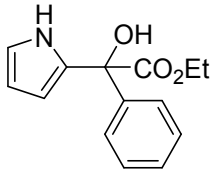
Following the general procedure **C**, 3,3,3-trifluoro-1-phenyl-1-(1H-pyrrol-2-yl)propan-1-ol was prepared from (1H-pyrrol-2-yl)magnesium bromide and 3,3,3-trifluoro-1-phenylpropan-1-one (2.5 mmol, 470 mg). Isolated yield 14% (89 mg).

^{1}H NMR (400 MHz, Chloroform-d) δ 8.11 (s, 1H), 7.50 – 7.40 (m, 2H), 7.40 – 7.32 (m, 2H), 7.32 – 7.28 (m, 1H), 6.71 (tt, *J* = 3.0, 1.5 Hz, 1H), 6.19 (dt, *J* = 16.3, 3.3 Hz, 2H), 3.13 (dd, *J* = 10.2, 2.7 Hz, 2H), 2.58 (s, 1H).

^{19}F NMR (376 MHz, Chloroform-d) δ -58.92 (t, *J* = 10.4 Hz).

LRMS (GCMS): m/z 255.2 $[M]^+$

ethyl 2-hydroxy-2-phenyl-2-(1H-pyrrol-2-yl)acetate (L17):



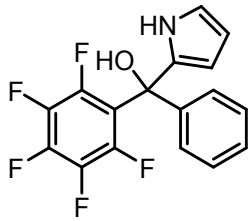
Following the general procedure **C**, ethyl 2-hydroxy-2-phenyl-2-(1H-pyrrol-2-yl)acetate was prepared from (1H-pyrrol-2-yl)magnesium bromide and ethyl 2-oxo-2-phenylacetate (4 mmol, 334 µL). Isolated yield 55% (539 mg).

^{1}H NMR (400 MHz, Chloroform-d) δ 8.61 (s, 1H), 7.43 (dq, *J* = 6.3, 2.9, 2.4 Hz, 2H), 7.37 – 7.30 (m, 3H), 6.76 (td, *J* = 2.7, 1.5 Hz, 1H), 6.32 (ddd, *J* = 3.9, 2.6, 1.5 Hz, 1H), 6.22 (q, *J* = 2.9 Hz, 1H), 4.40 – 4.22 (m, 3H), 1.30 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 173.5, 141.4, 130.5, 128.3, 128.3, 126.7, 118.0, 108.6, 107.7, 77.2, 63.2, 14.1.

LRMS (GCMS): m/z 245.2 $[M]^+$

(perfluorophenyl)(phenyl)(1H-pyrrol-2-yl)methanol (L18):



Following the general procedure **C**, (perfluorophenyl)(phenyl)(1H-pyrrol-2-yl)methanol was prepared from (1H-pyrrol-2-yl)magnesium bromide and (perfluorophenyl)(phenyl)methanone (2 mmol, 544 mg). Isolated yield 52% (352 mg).

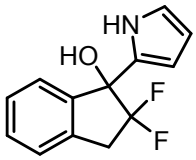
^{1}H NMR (400 MHz, Chloroform-d) δ 8.45 (s, 1H), 7.36 (q, *J* = 3.6 Hz, 3H), 7.29 (dd, *J* = 6.7, 3.1 Hz, 2H), 6.84 (q, *J* = 2.3 Hz, 1H), 6.16 (q, *J* = 3.0 Hz, 1H), 5.81 (p, *J* = 1.7 Hz, 1H), 3.55 (s, 1H).

^{13}C NMR (101 MHz, Chloroform-d) δ 143.9, 133.0, 128.6, 128.5, 126.4, 119.0, 108.8, 108.5.

^{19}F NMR (376 MHz, Chloroform-d) δ -138.81 (dq, *J* = 20.6, 4.6 Hz), -154.55 (t, *J* = 21.2 Hz), -161.66 (td, *J* = 22.6, 7.2 Hz).

LRMS (GCMS): m/z 339.2 $[M]^+$

2,2-difluoro-1-(1H-pyrrol-2-yl)-2,3-dihydro-1H-inden-1-ol (L19):



Following the general procedure **C**, 2,2-difluoro-1-(1H-pyrrol-2-yl)-2,3-dihydro-1H-inden-1-ol was prepared from (1H-pyrrol-2-yl)magnesium bromide and 2,2-difluoro-2,3-dihydro-1H-inden-1-one[11] (1.45 mmol, 245 mg). Isolated yield 31% (105 mg).

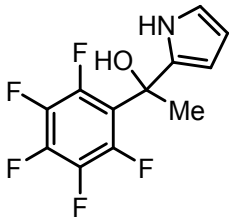
^{1}H NMR (400 MHz, Chloroform-d) δ 8.74 (s, 1H), 7.48 – 7.35 (m, 3H), 7.32 (d, *J* = 7.3 Hz, 1H), 6.84 (q, *J* = 2.4 Hz, 1H), 6.16 (q, *J* = 2.9 Hz, 1H), 5.73 (p, *J* = 1.8 Hz, 1H), 3.42 (ddt, *J* = 16.4, 11.3, 6.4 Hz, 2H), 3.22 (s, 1H).

^{13}C NMR (101 MHz, Chloroform-d) δ 142.3, 142.2, 136.3 (dd, *J* = 6.1, 4.2 Hz), 129.9, 128.7 (t, *J* = 258.5 Hz), 128.3, 128.1, 125.1, 124.9, 119.3, 108.9, 108.2, 80.6 (t, *J* = 23.2 Hz), 38.4 (t, *J* = 25.8 Hz).

^{19}F NMR (376 MHz, Chloroform-d) δ -108.45 – -120.15 (m).

LRMS (GCMS): m/z 235.2 $[M]^+$

1-(perfluorophenyl)-1-(1H-pyrrol-2-yl)ethan-1-ol (L20):



Following the general procedure **C**, 1-(perfluorophenyl)-1-(1H-pyrrol-2-yl)ethan-1-ol was prepared from (1H-pyrrol-2-yl)magnesium bromide and 1-(perfluorophenyl)ethan-1-one (4 mmol, 598 mg). Isolated yield 61% (720 mg).

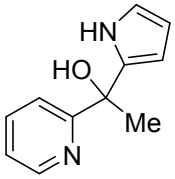
^{1}H NMR (400 MHz, Chloroform-d) δ 8.47 (s, 1H), 6.77 (td, *J* = 2.7, 1.5 Hz, 1H), 6.13 (q, *J* = 2.9 Hz, 1H), 5.96 – 5.80 (m, 1H), 2.95 (s, 1H), 2.08 (t, *J* = 2.7 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-d) δ 135.4, 118.2, 108.6, 105.3, 72.9, 30.2 (t, *J* = 5.1 Hz).

^{19}F NMR (376 MHz, Chloroform-d) δ -139.70 (ddd, *J* = 22.8, 7.1, 3.7 Hz), -153.24 – -158.72 (m), -161.72 (td, *J* = 22.3, 7.0 Hz).

LRMS (GCMS): m/z 277.1 $[M]^+$

1-(pyridin-2-yl)-1-(1H-pyrrol-2-yl)ethan-1-ol (L21):



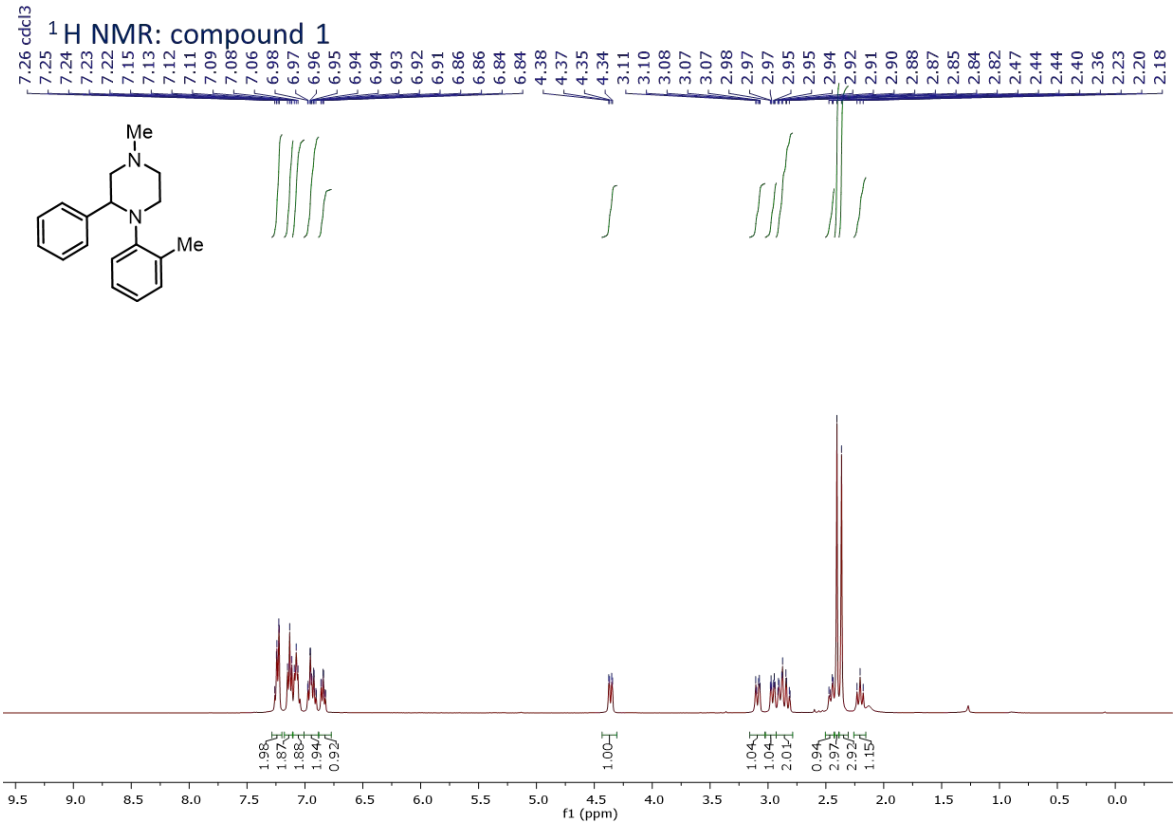
Following the general procedure **C**, 1-(pyridin-2-yl)-1-(1H-pyrrol-2-yl)ethan-1-ol was prepared from (1H-pyrrol-2-yl)magnesium bromide and 1-(pyridin-2-yl)ethan-1-one (4 mmol, 484 mg). Isolated yield 49% (368 mg).

^{1}H NMR (400 MHz, Chloroform-d) δ 8.60 – 8.40 (m, 2H), 7.66 (td, *J* = 7.7, 1.8 Hz, 1H), 7.34 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.19 (ddd, *J* = 7.5, 4.9, 1.1 Hz, 1H), 6.69 (td, *J* = 2.6, 1.5 Hz, 1H), 6.16 (qd, *J* = 3.1, 2.1 Hz, 2H), 5.96 (s, 1H), 1.85 (s, 3H).

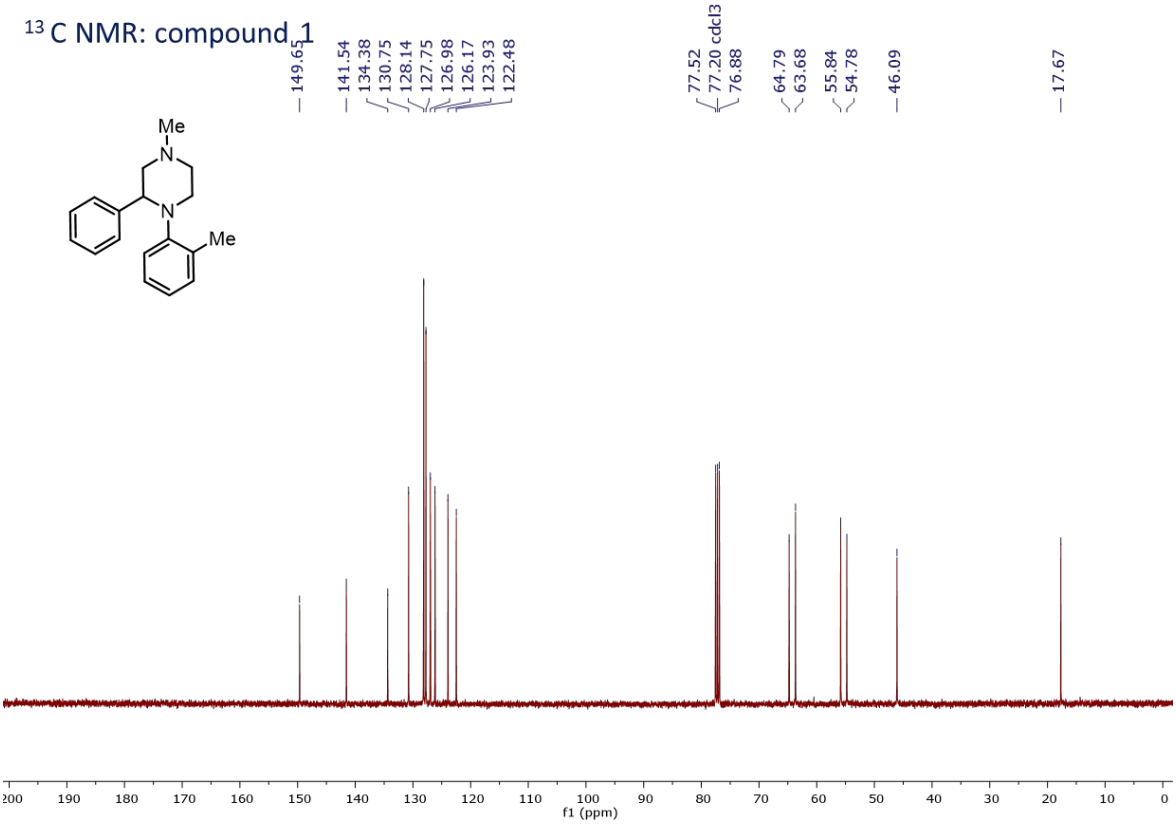
^{13}C NMR (101 MHz, Chloroform-d) δ 163.8, 147.2, 137.4, 136.9, 122.4, 120.2, 117.3, 108.5, 104.9, 72.2, 30.1.
LRMS (GCMS): m/z 188.2 $[M]^+$

NMR Spectra

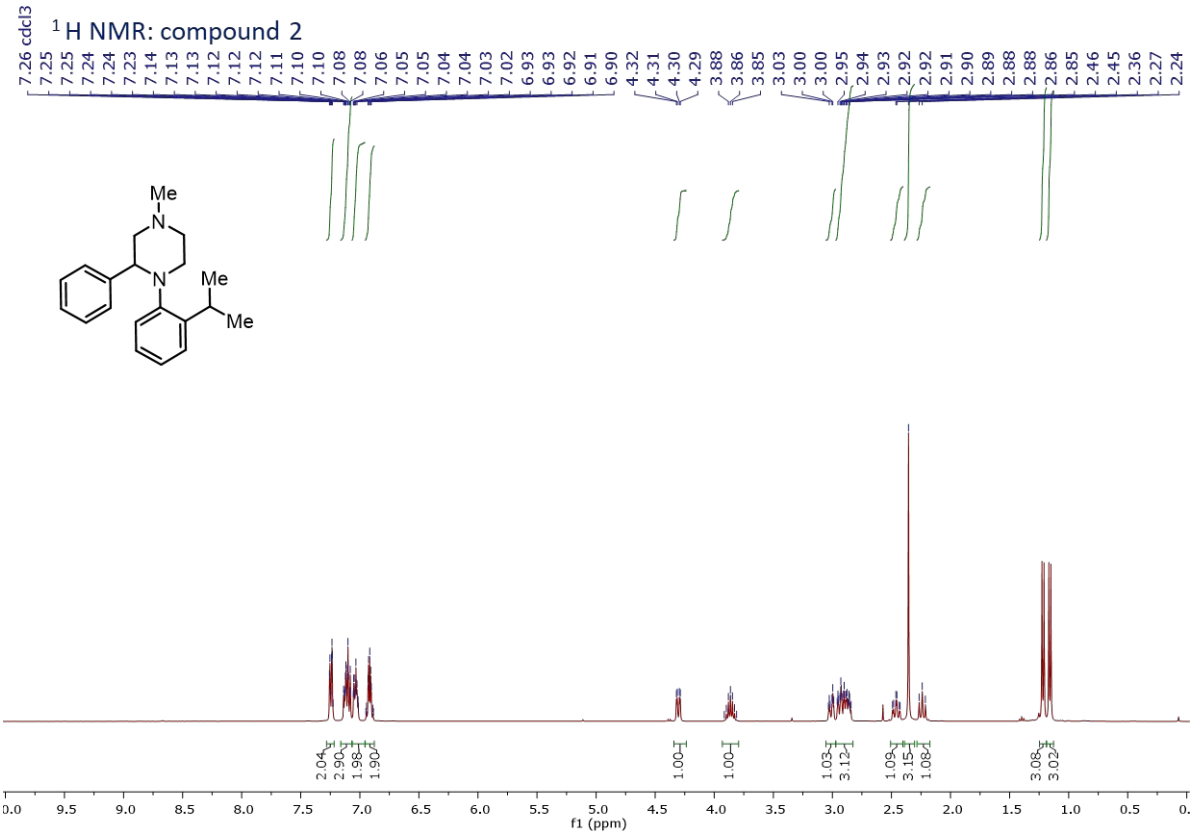
^{1}H NMR: compound 1



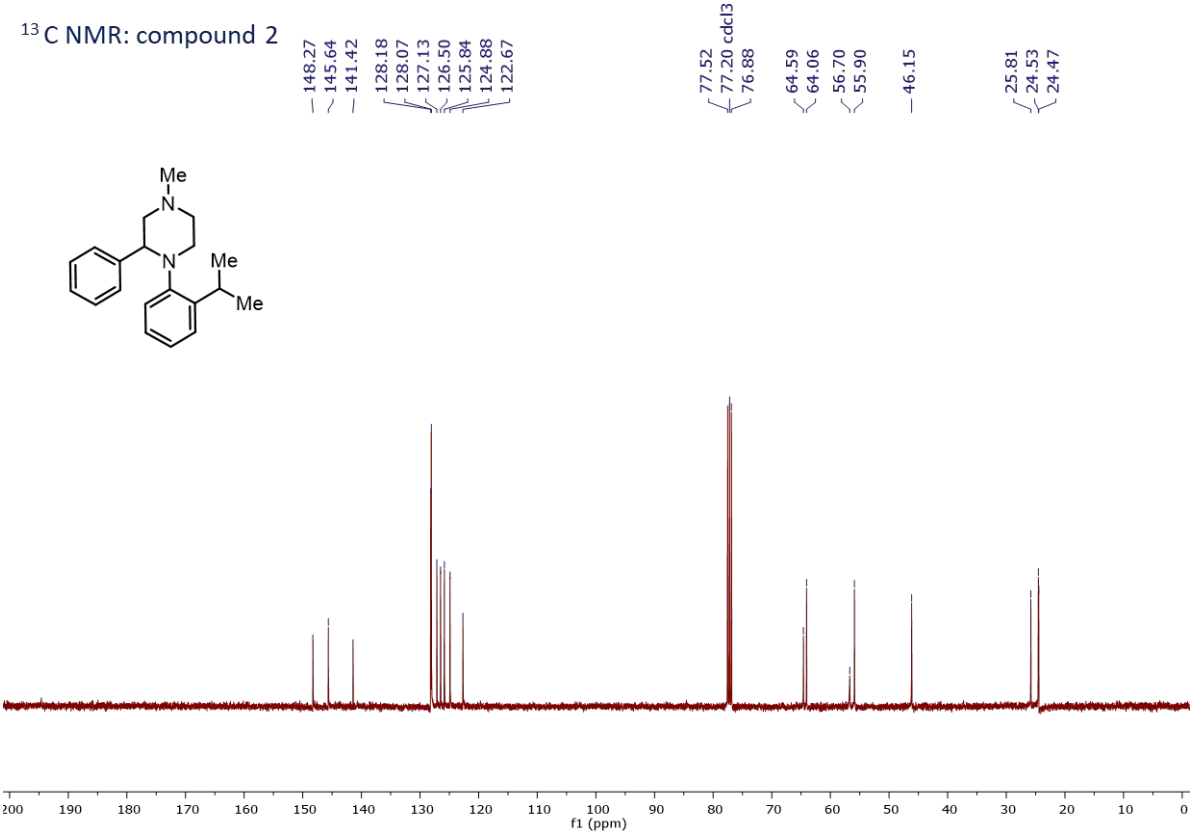
^{13}C NMR: compound 1



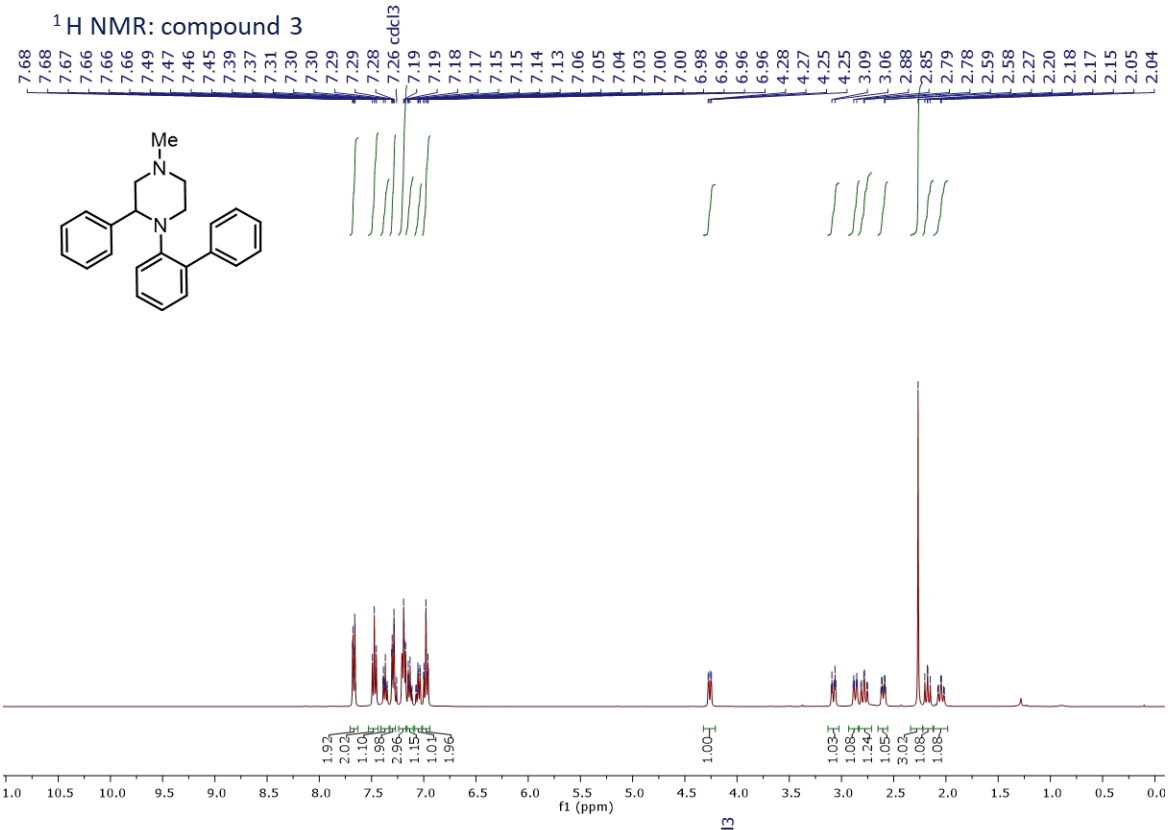
^{1}H NMR: compound 2



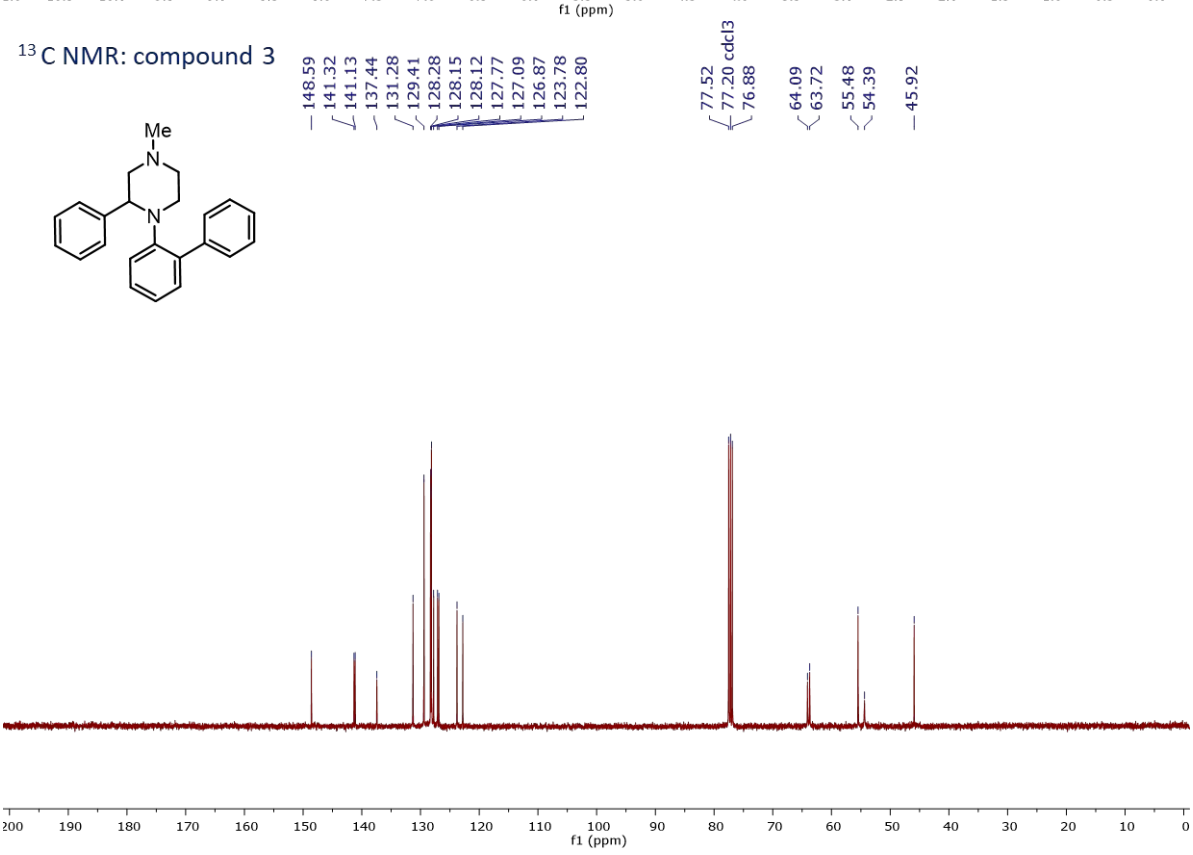
^{13}C NMR: compound 2



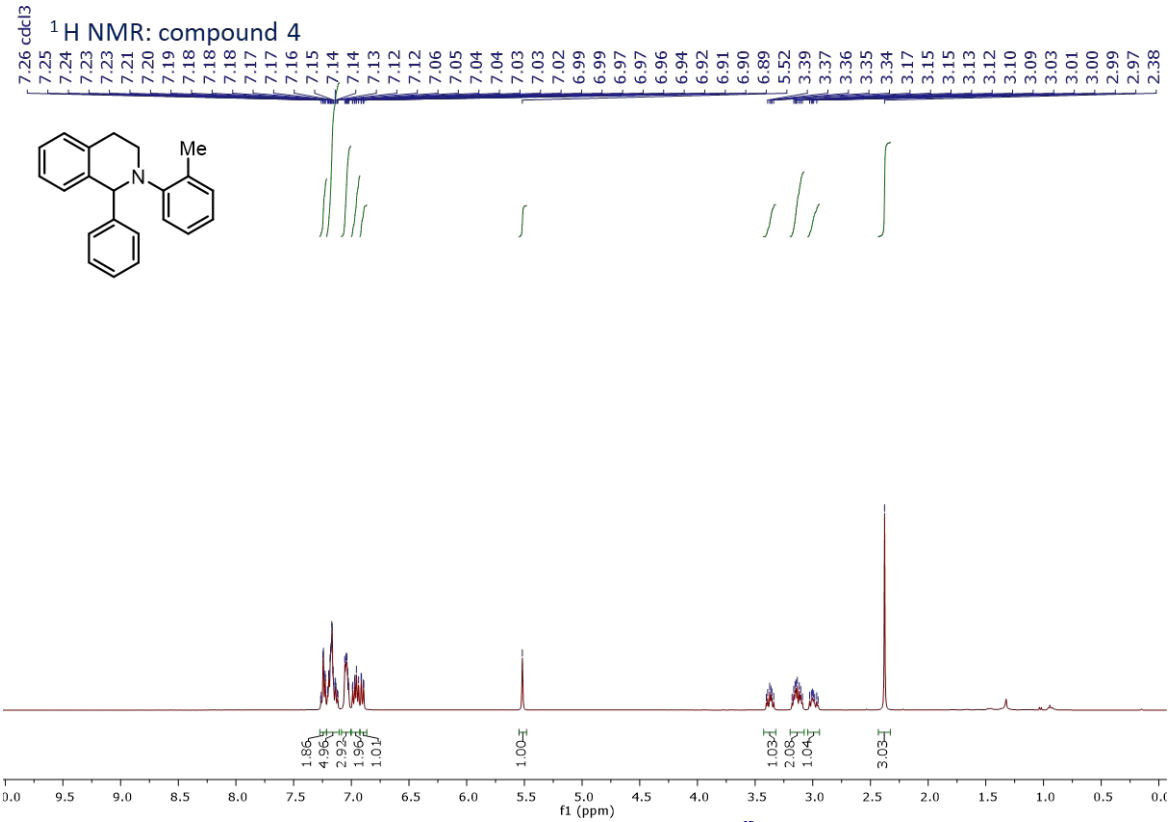
^{1}H NMR: compound 3



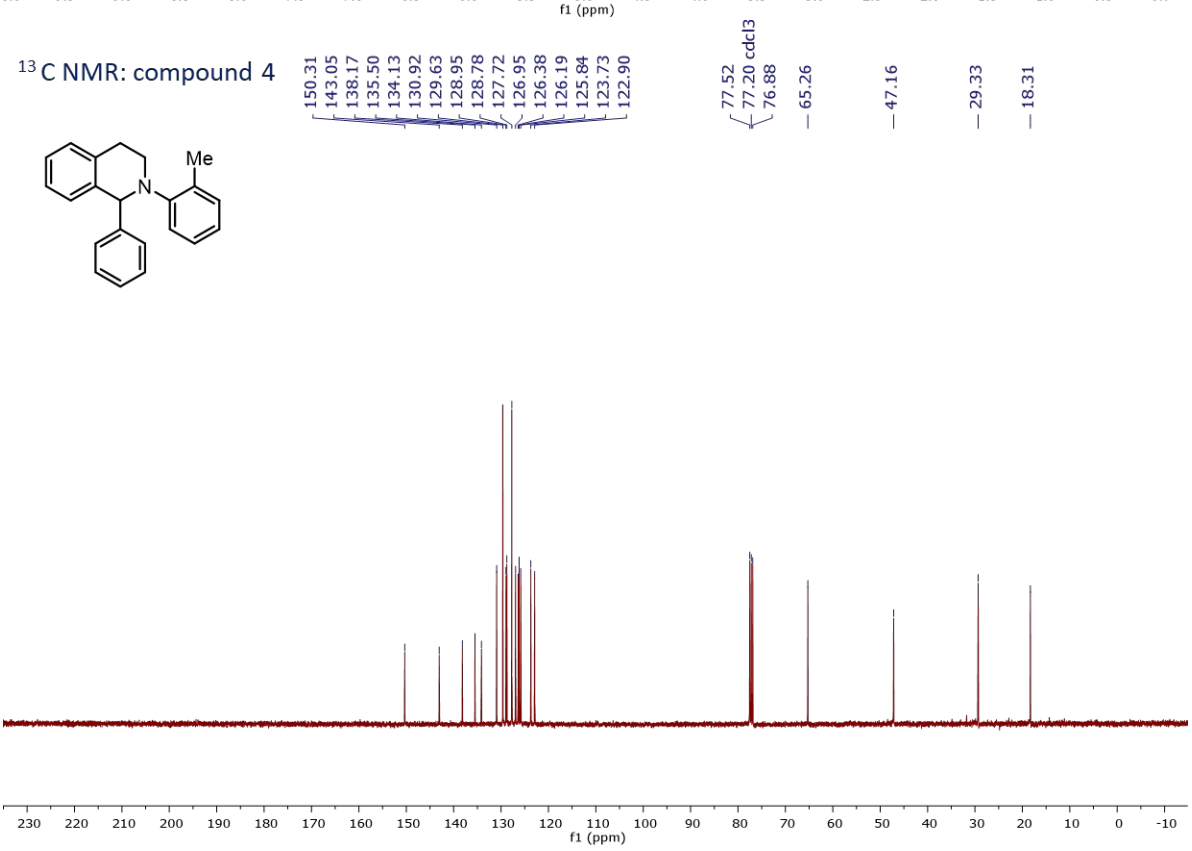
^{13}C NMR: compound 3

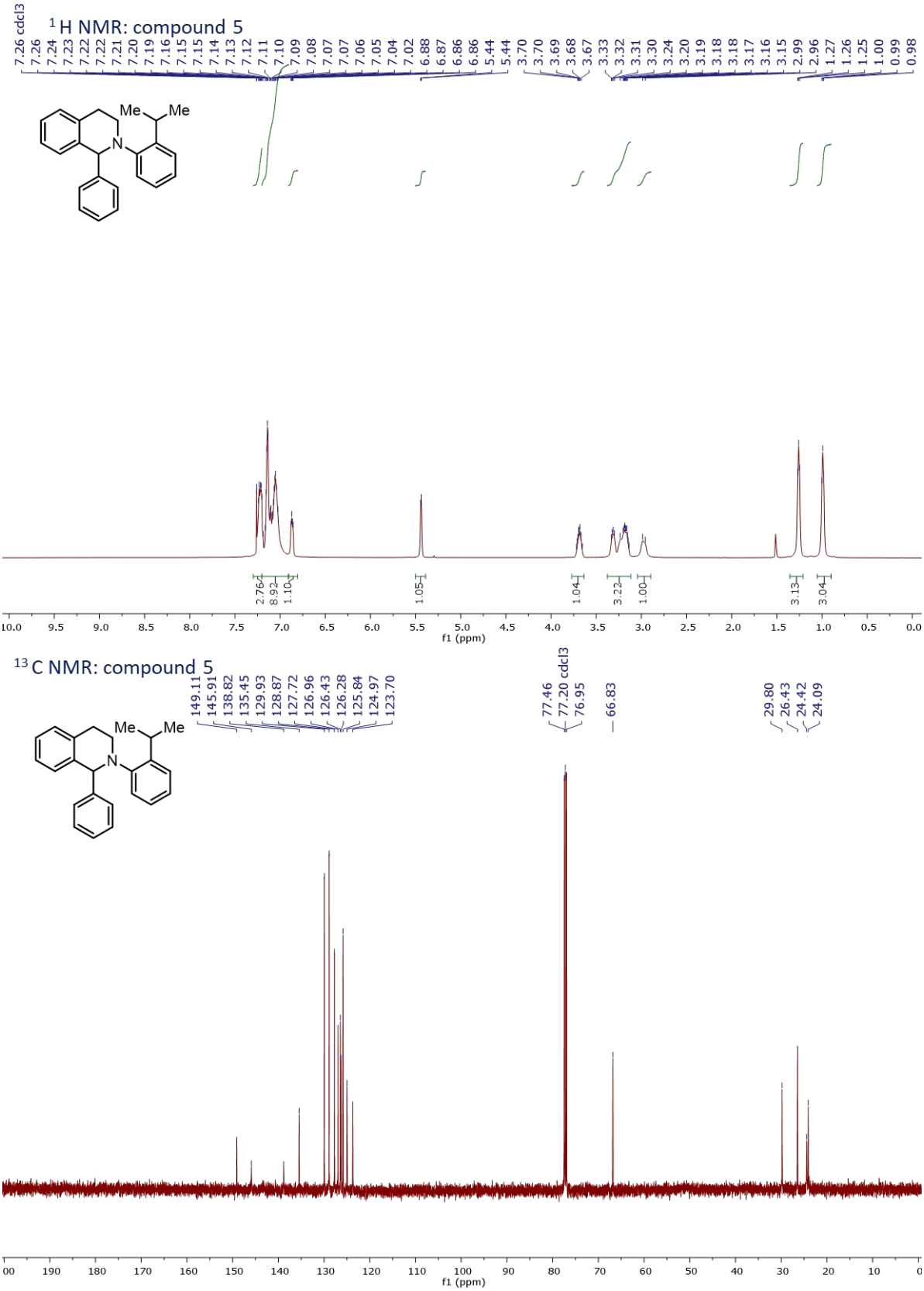


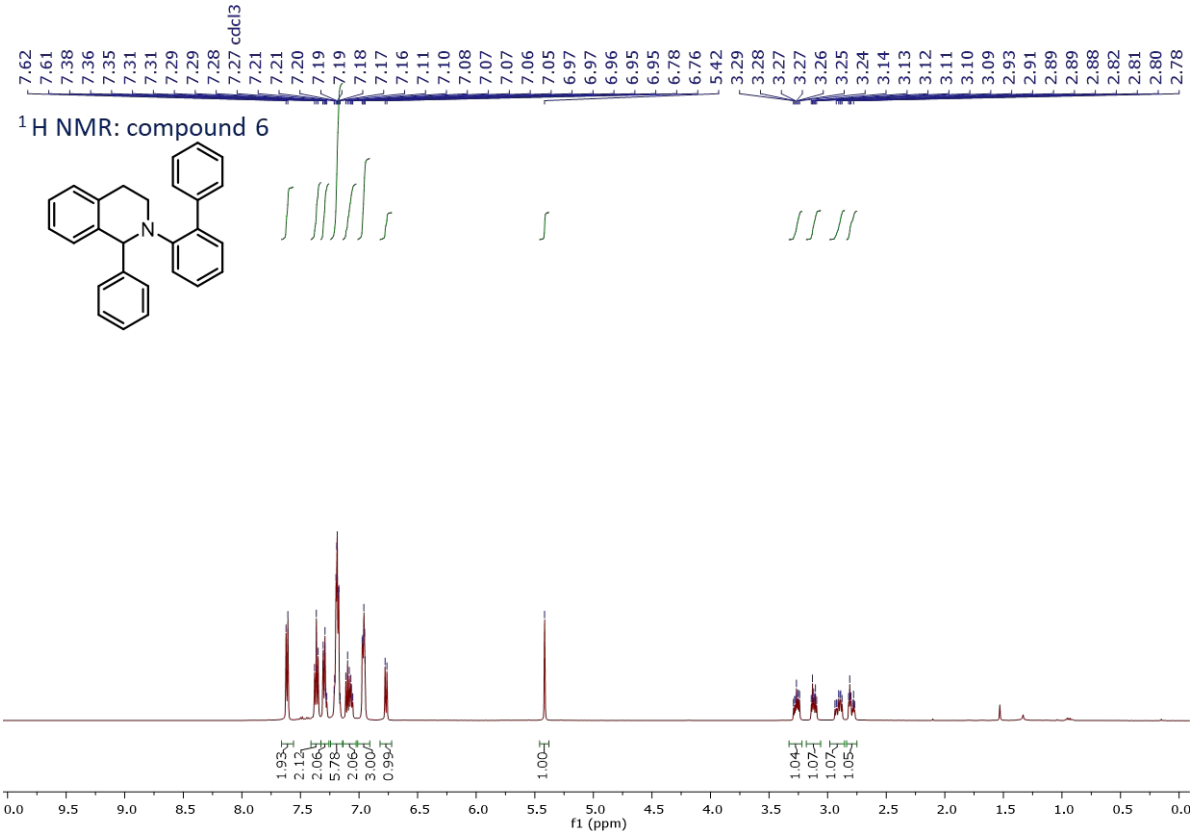
^{1}H NMR: compound 4

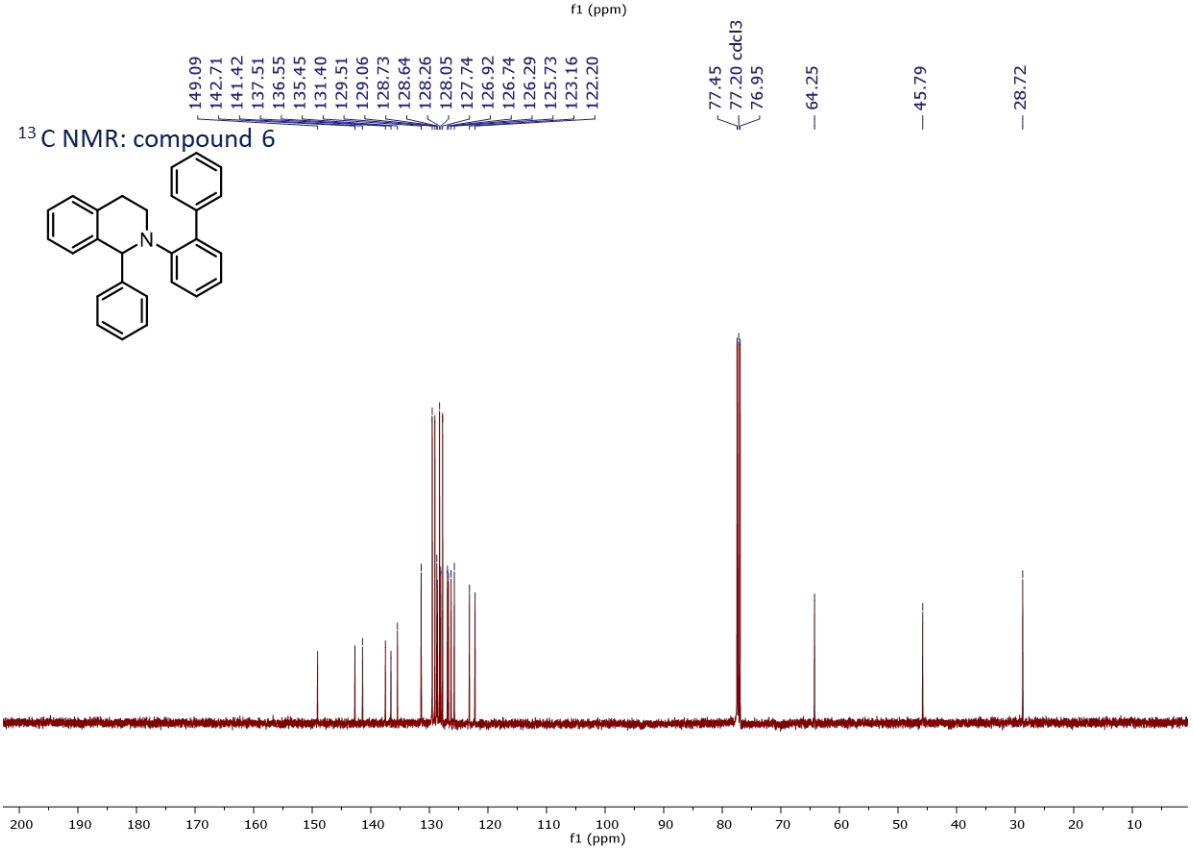


^{13}C NMR: compound 4

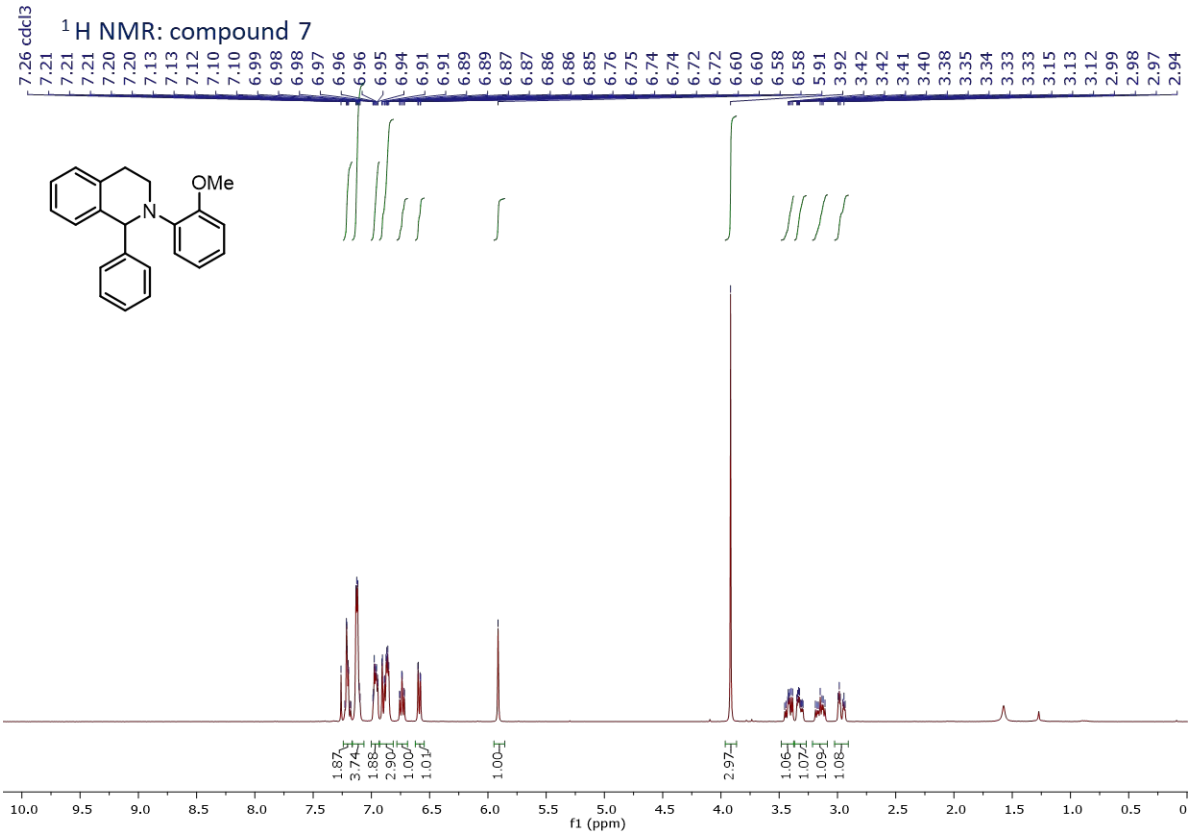



1H NMR: compound 5
7.26 cdcl3
7.26 7.26 7.24 7.23 7.22 7.22 7.21 7.20 7.19 7.16 7.15 7.15 7.14 7.13 7.12 7.11 7.10 7.09 7.08 7.07 7.07 7.06 7.05 7.04 7.02 6.88 6.87 6.86 6.86 6.86 5.44 5.44 3.70 3.70 3.69 3.68 3.67 3.33 3.32 3.31 3.30 3.24 3.20 3.19 3.18 3.18 3.17 3.16 3.15 2.99 2.96 1.27 1.26 1.25 1.00 0.99 0.98
Me
Me
N
2.76
8.92
1.10
1.05
1.04
3.22
1.00
3.13
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
13C NMR: compound 5
149.11 145.91 138.82 135.45 129.93 128.87 127.72 126.96 126.43 126.28 125.84 124.97 123.70
77.46 77.20 cdcl3 76.95
66.83
29.80 26.43 24.42 24.09
Me
Me
N
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

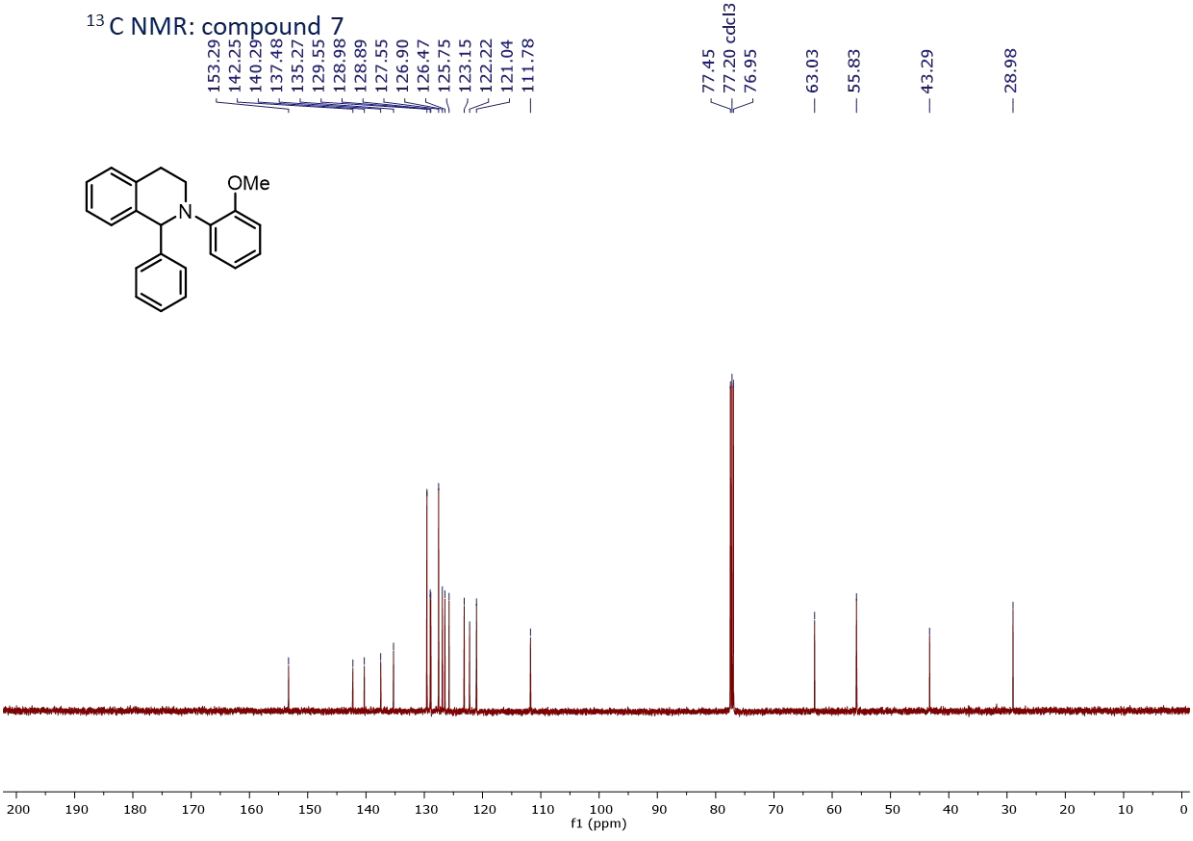

7.62 7.61 7.38 7.36 7.35 7.31 7.31 7.29 7.29 7.28 7.27 cdcl3 7.21 7.21 7.20 7.19 7.19 7.18 7.17 7.16 7.11 7.10 7.08 7.07 7.07 7.06 7.05 6.97 6.97 6.96 6.95 6.95 6.78 6.76 5.42 3.29 3.28 3.27 3.27 3.26 3.25 3.24 3.14 3.13 3.12 3.11 3.10 3.09 2.93 2.91 2.89 2.89 2.88 2.82 2.81 2.80 2.78
1H NMR: compound 6
1.93 2.12 2.06 5.78 2.06 3.00 0.99 1.00 1.04 1.07 1.07 1.05
f1 (ppm)


149.09 142.71 141.42 137.51 136.55 135.45 131.40 129.51 129.06 128.73 128.64 128.26 128.05 127.74 126.92 126.74 126.29 125.73 123.16 122.20 77.45 77.20 cdcl3 76.95 64.25 45.79 28.72
13C NMR: compound 6
f1 (ppm)

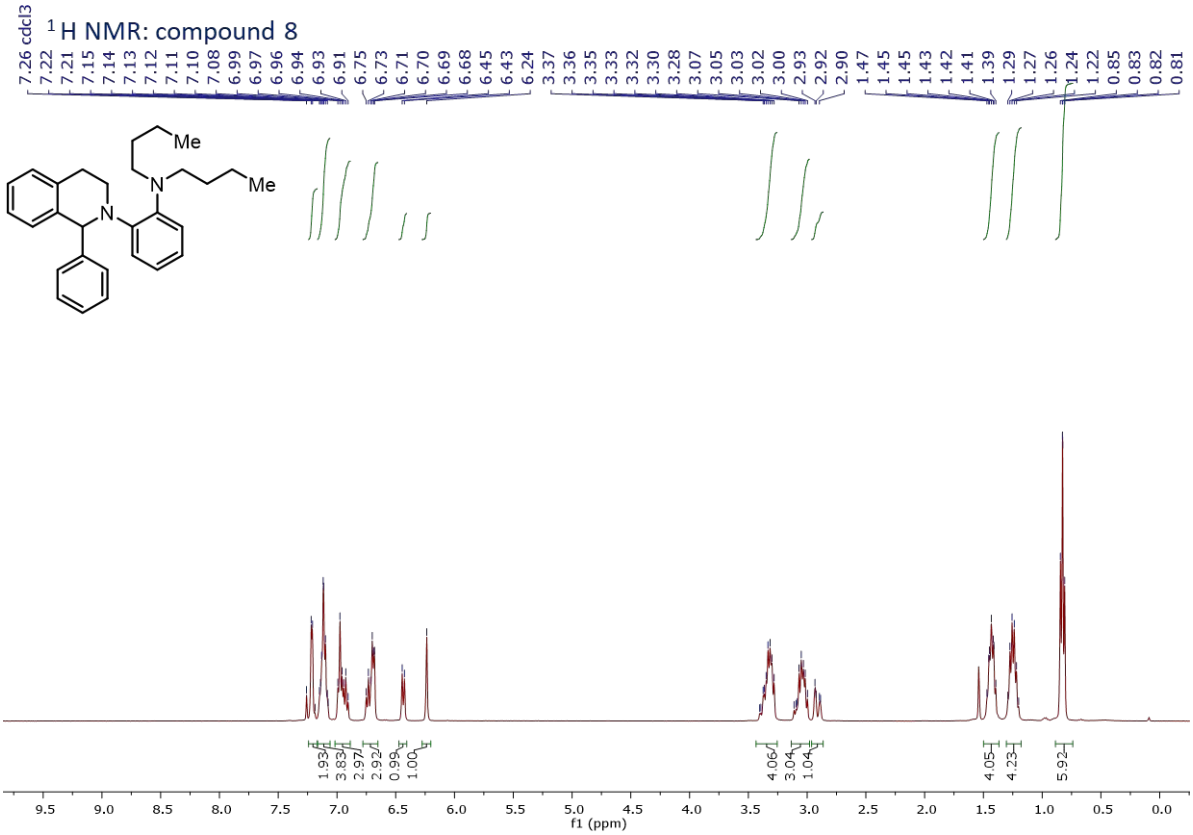
^{1}H NMR: compound 7



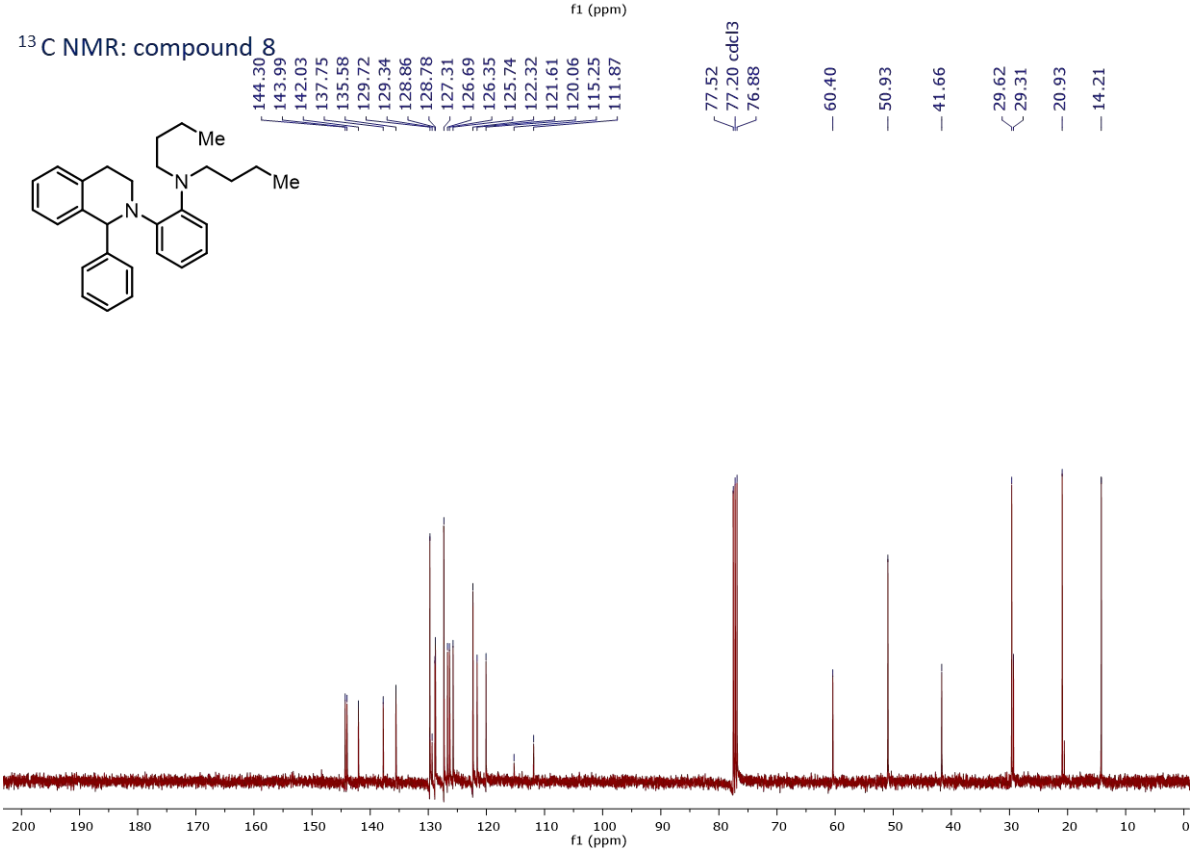
^{13}C NMR: compound 7



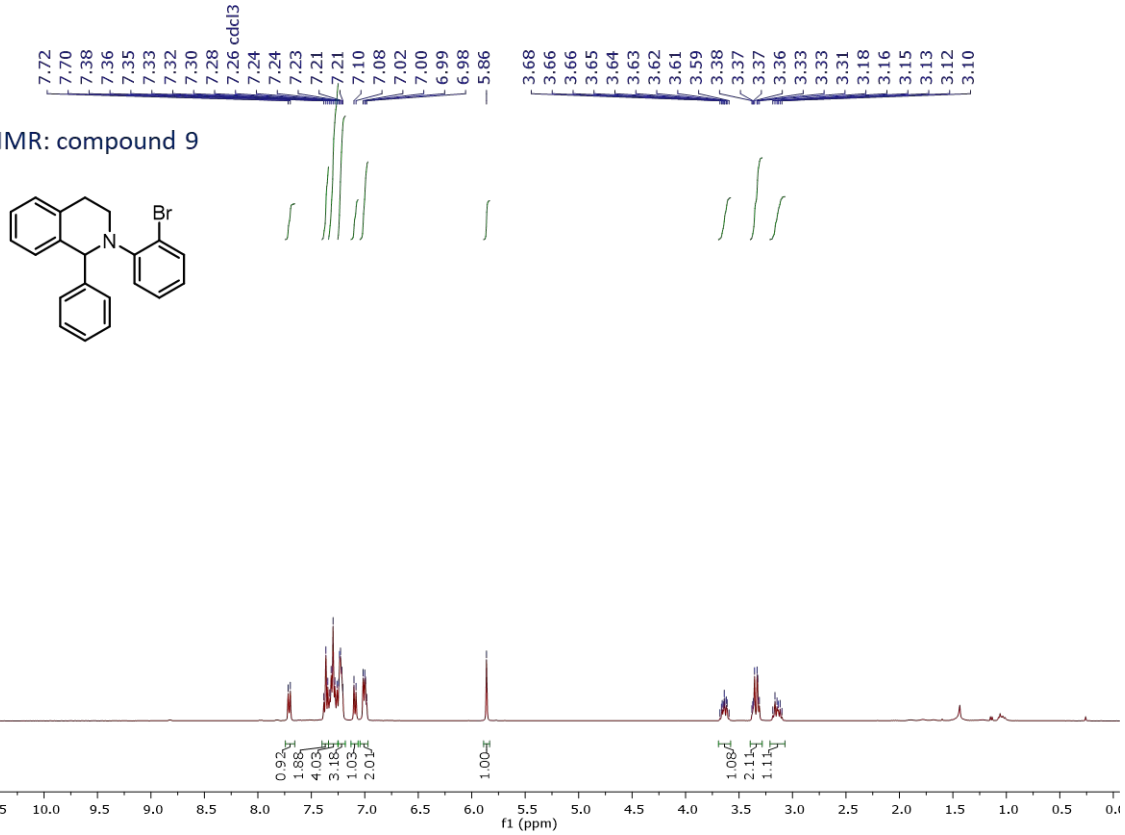
^{1}H NMR: compound 8



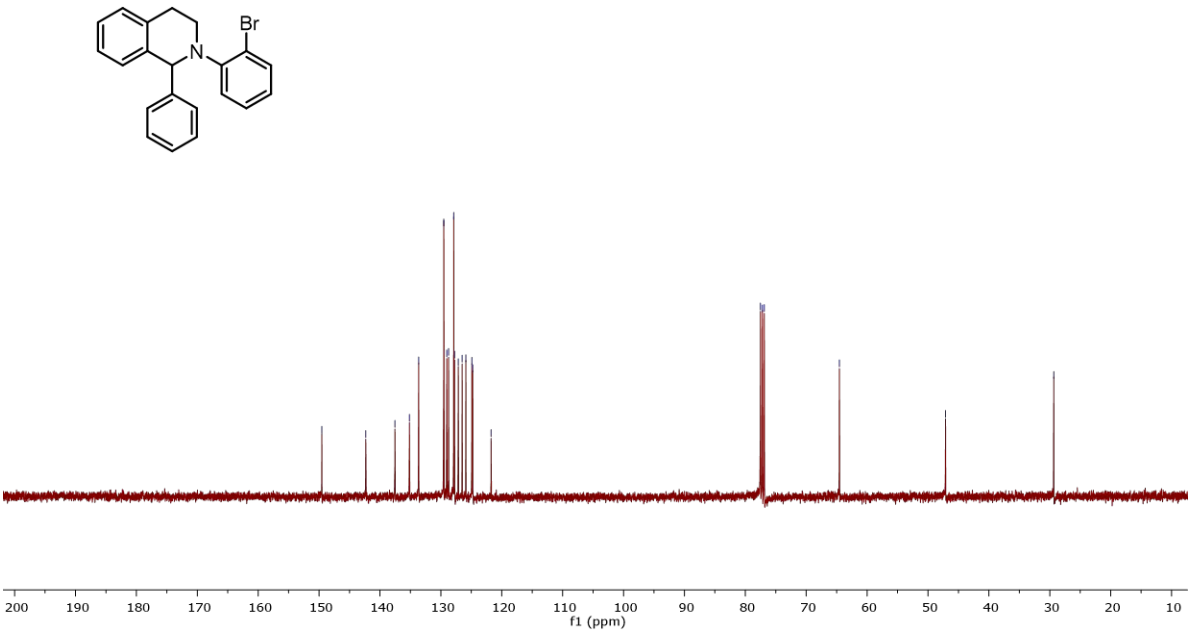
^{13}C NMR: compound 8



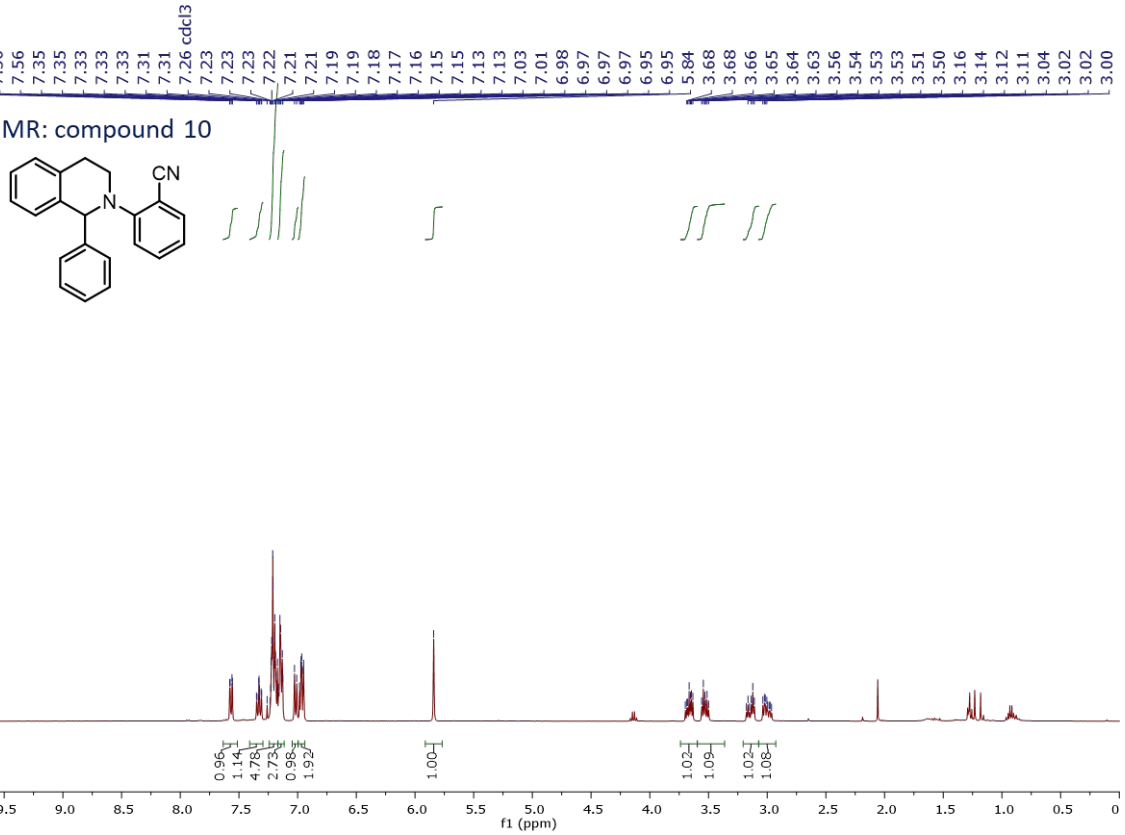
^{1}H NMR: compound 9



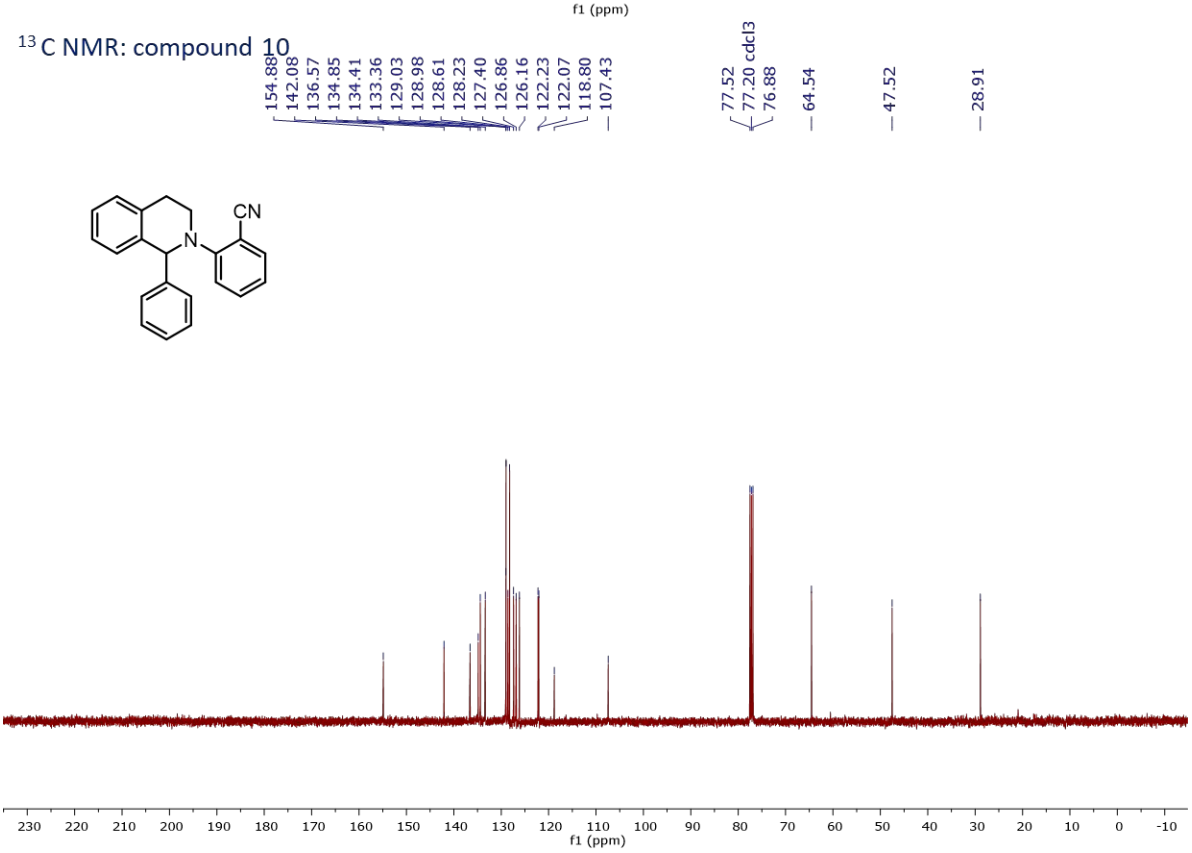
^{13}C NMR: compound 9

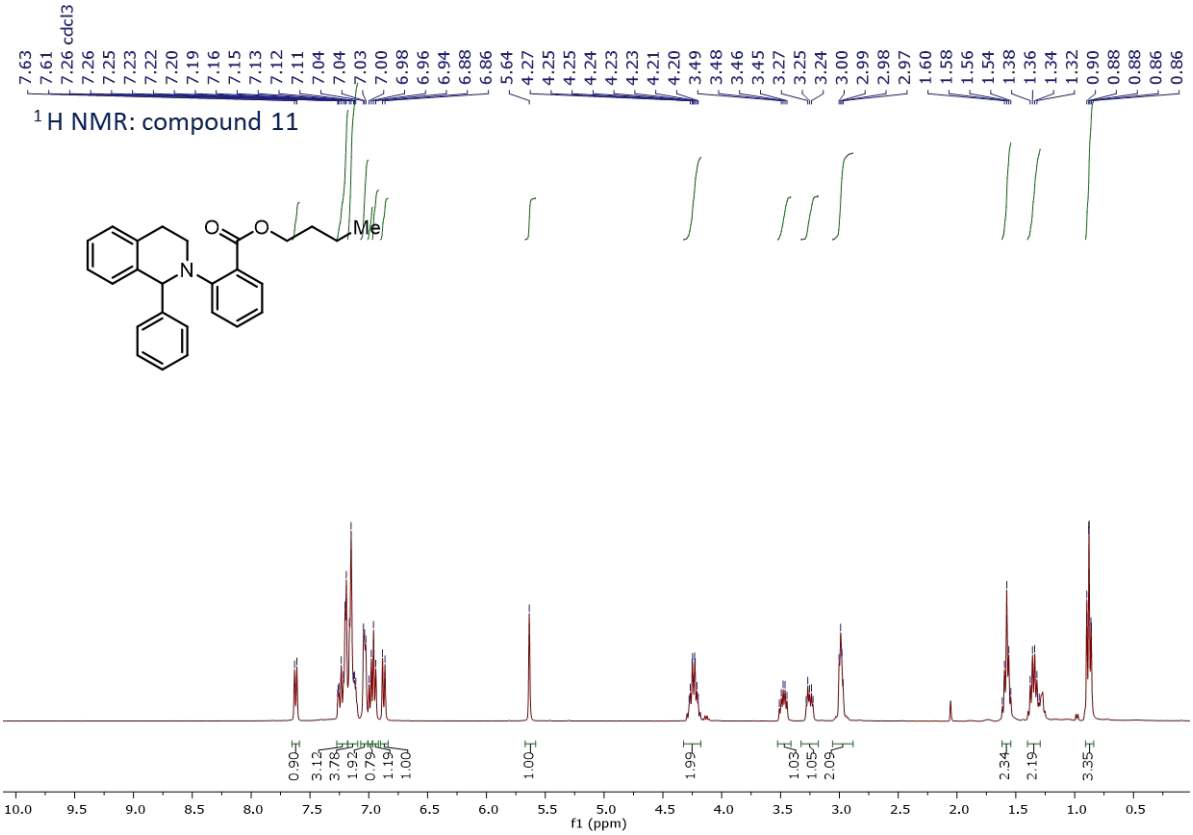


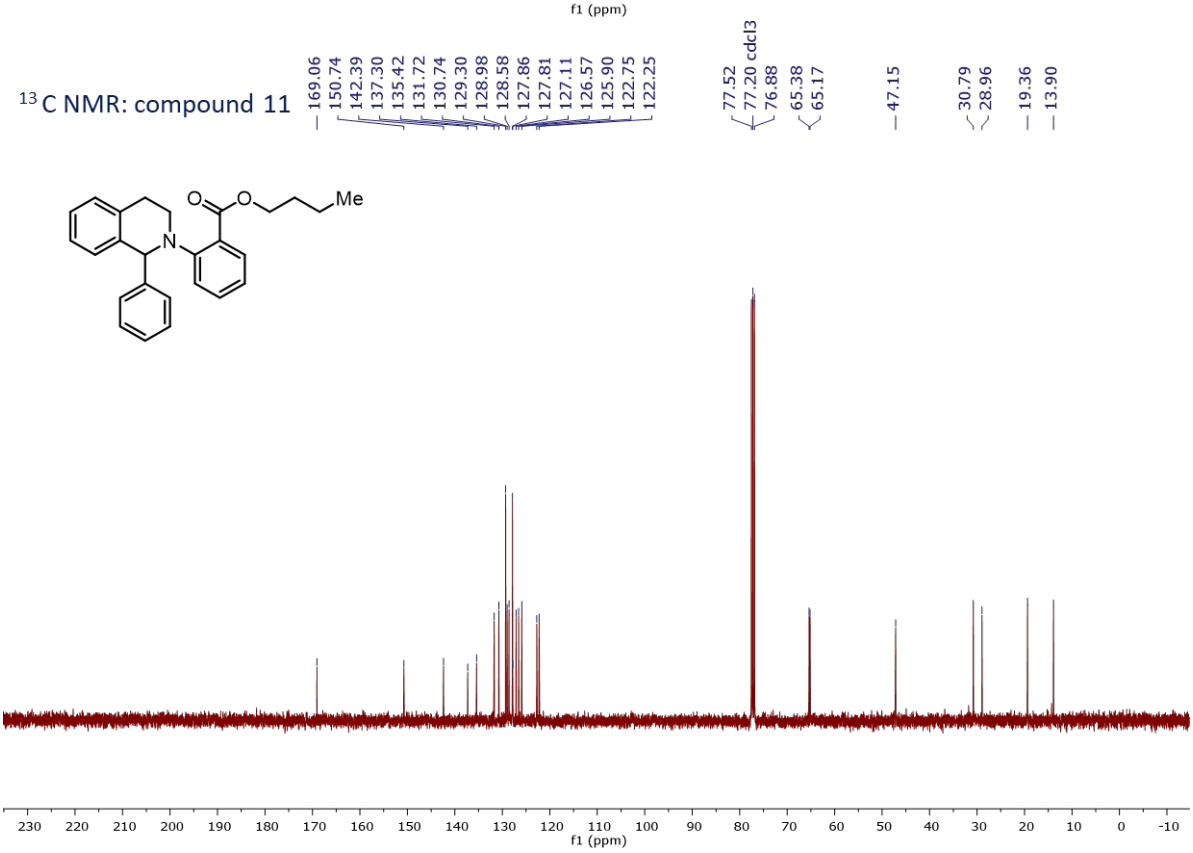
^{1}H NMR: compound 10

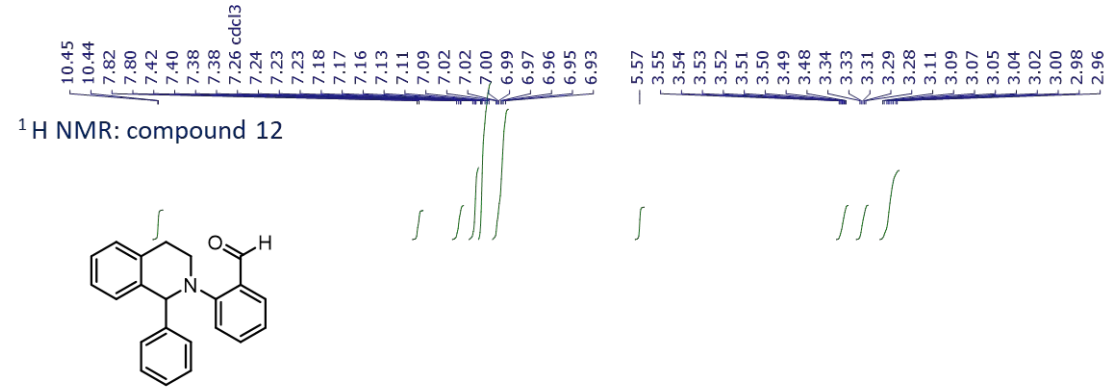


^{13}C NMR: compound 10

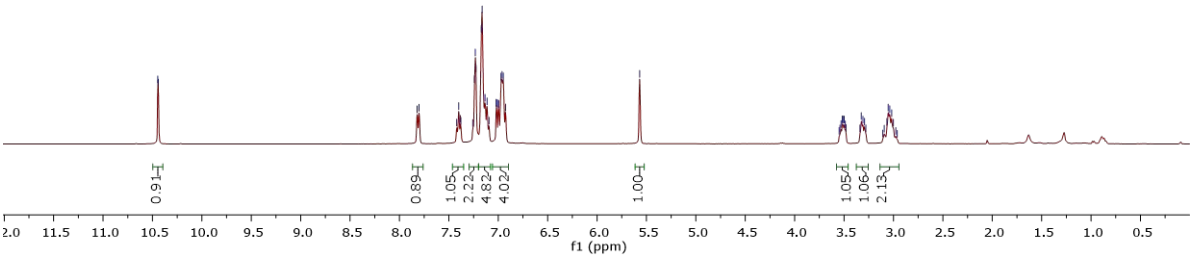


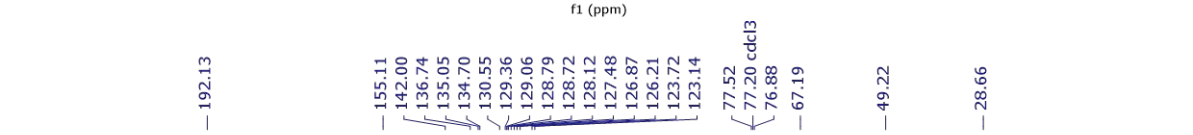

7.63 7.61 7.26 cdcl3 7.26 7.25 7.23 7.22 7.20 7.19 7.16 7.15 7.13 7.12 7.11 7.04 7.04 7.03 7.00 6.98 6.96 6.94 6.88 6.86 5.64 4.27 4.25 4.25 4.24 4.23 4.23 4.21 4.20 3.49 3.48 3.46 3.45 3.27 3.25 3.24 3.00 2.99 2.98 2.97 1.60 1.58 1.56 1.54 1.38 1.36 1.34 1.32 0.90 0.88 0.88 0.86 0.86
1H NMR: compound 11
O
O
Me
N
0.90 3.12 3.78 1.92 0.79 1.19 1.00 1.00 1.99 1.03 1.05 2.09 2.34 2.19 3.35
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


169.06 150.74 142.39 137.30 135.42 131.72 130.74 129.30 128.98 128.58 127.86 127.81 127.11 126.57 125.90 122.75 122.25 77.52 77.20 cdcl3 76.88 65.38 65.17 47.15 30.79 28.96 19.36 13.90
13C NMR: compound 11
O
O
Me
N
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

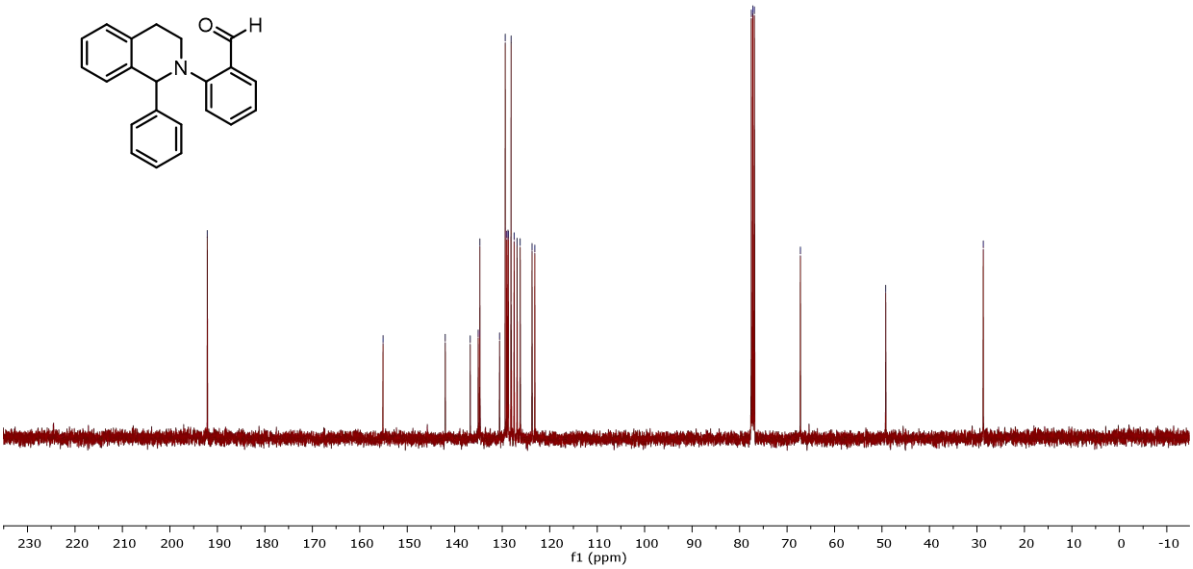


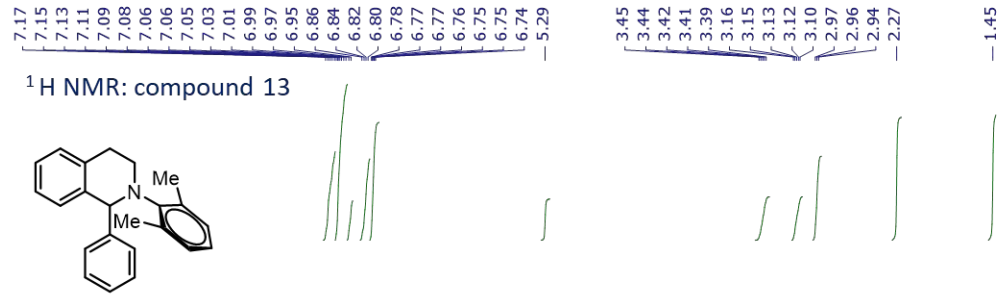
^{1}H NMR: compound 12



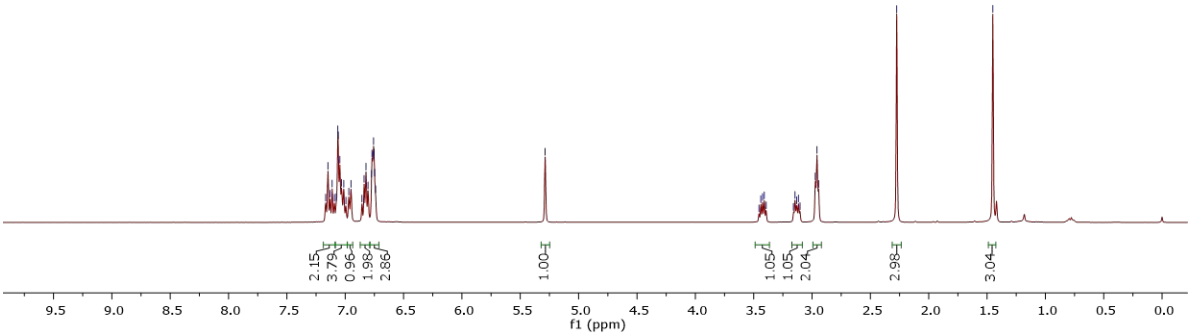


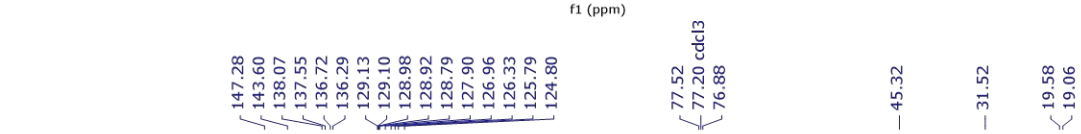
^{13}C NMR: compound 12



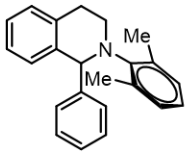


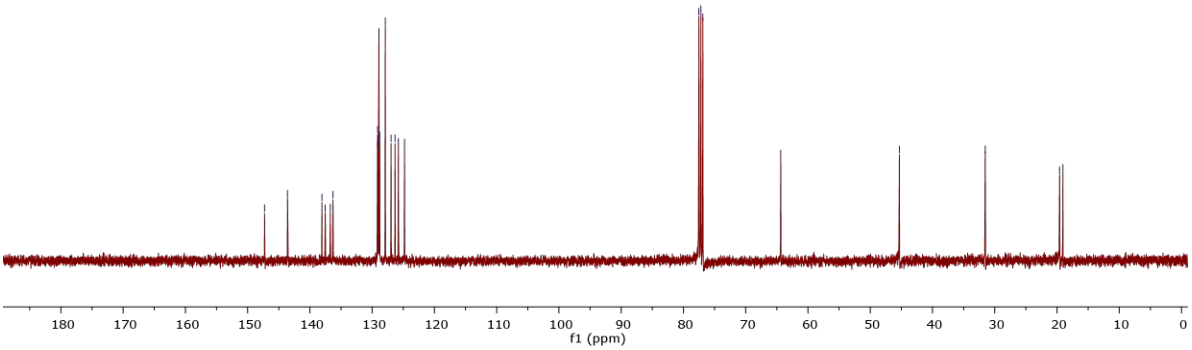
^{1}H NMR: compound 13



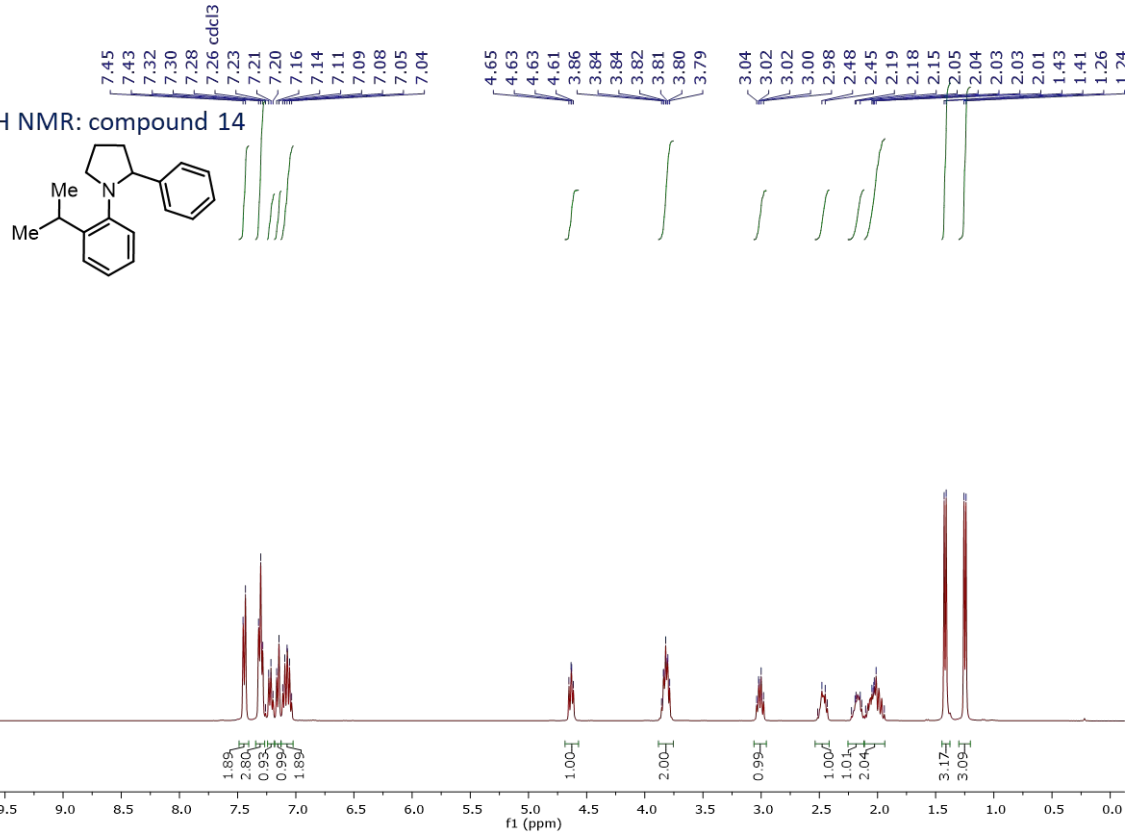


^{13}C NMR: compound 13

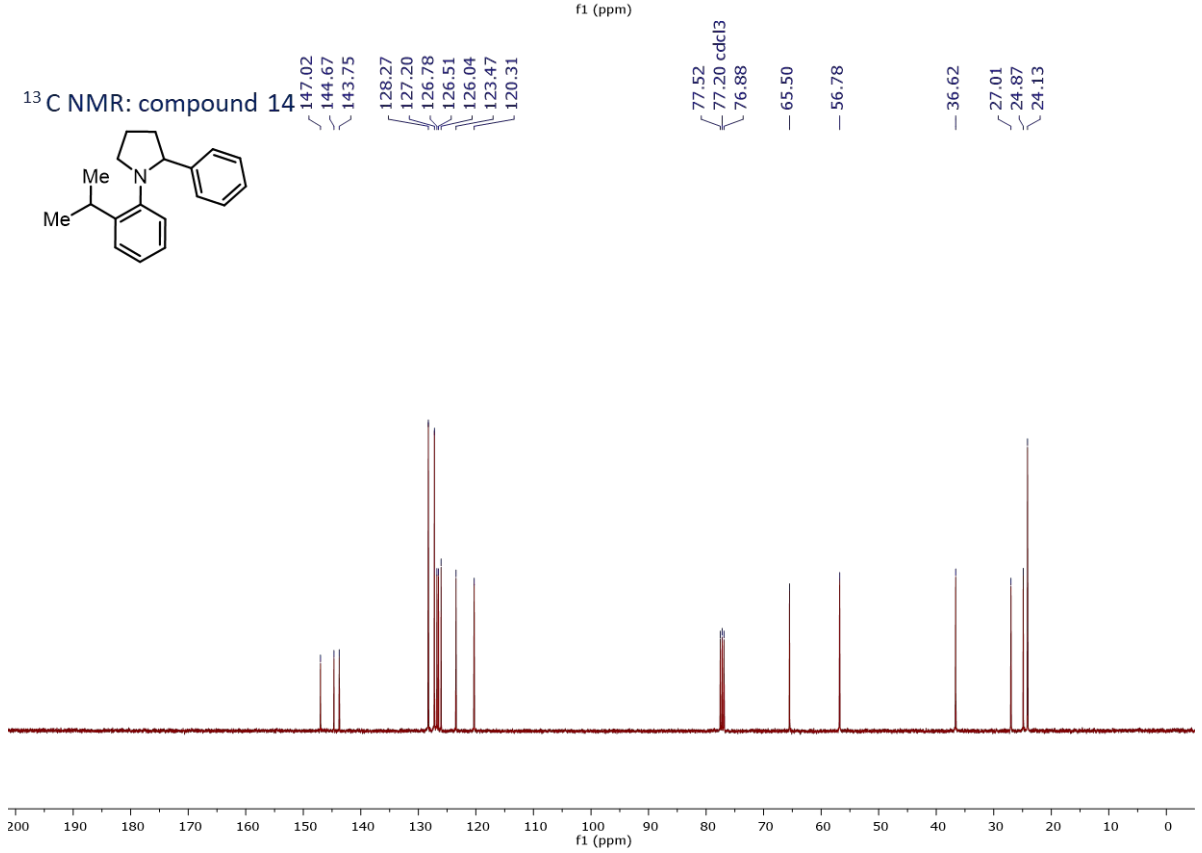




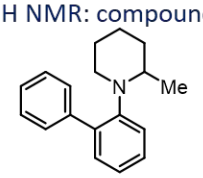
^{1}H NMR: compound 14



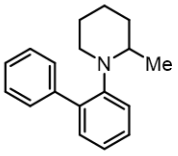
^{13}C NMR: compound 14



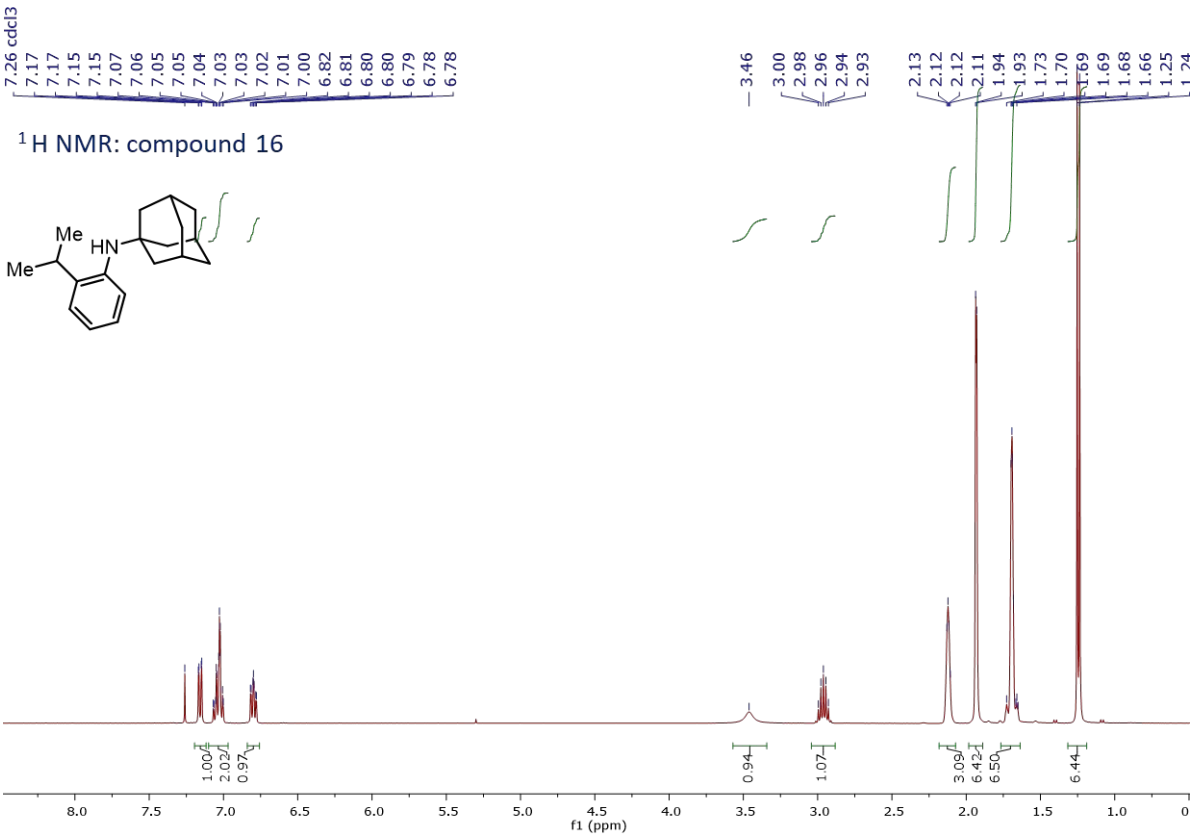
^{1}H NMR: compound 15



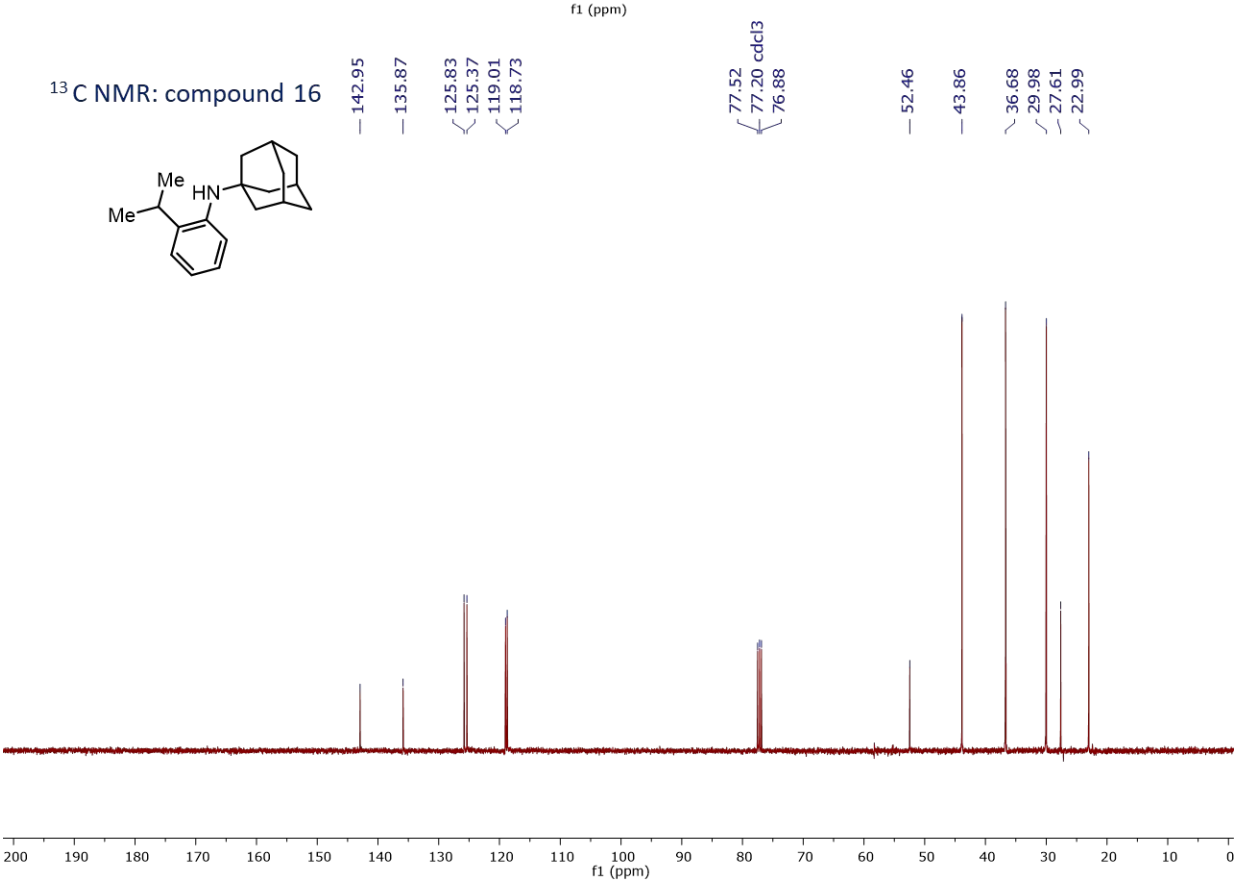
^{13}C NMR: compound 15



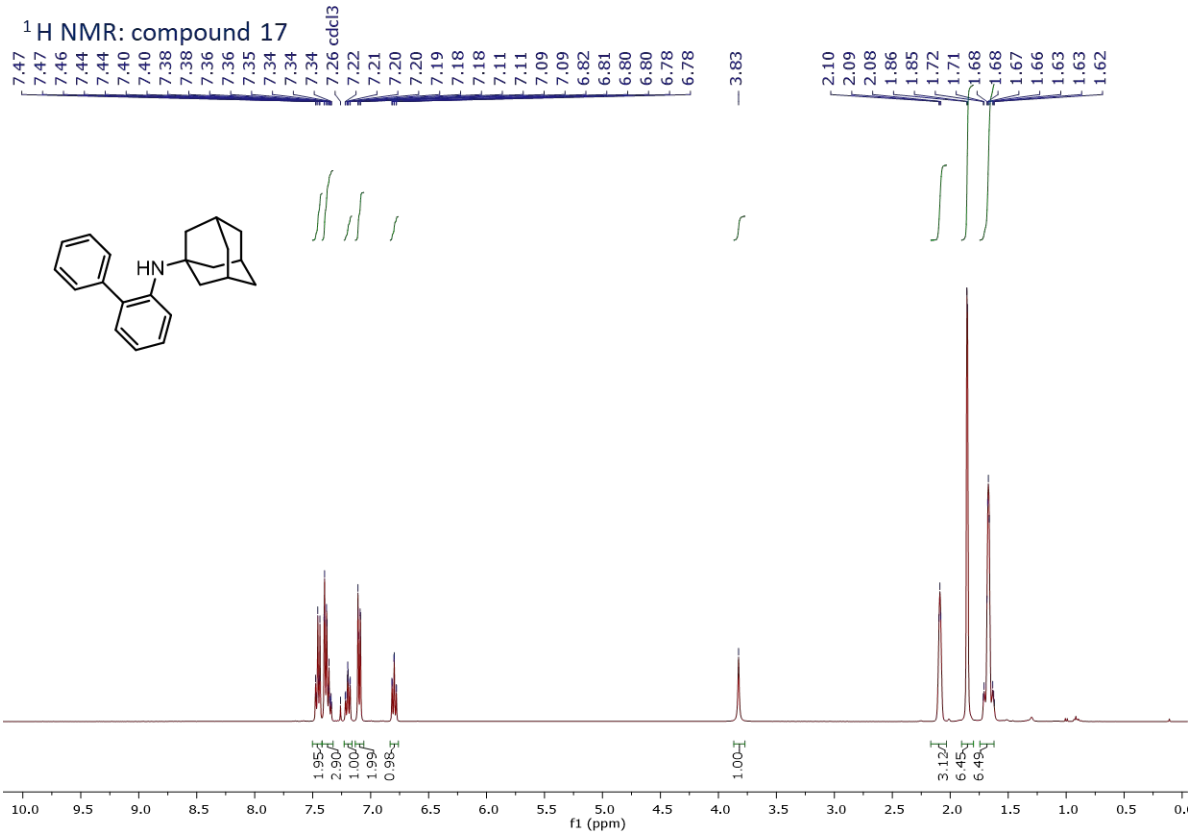
^{1}H NMR: compound 16



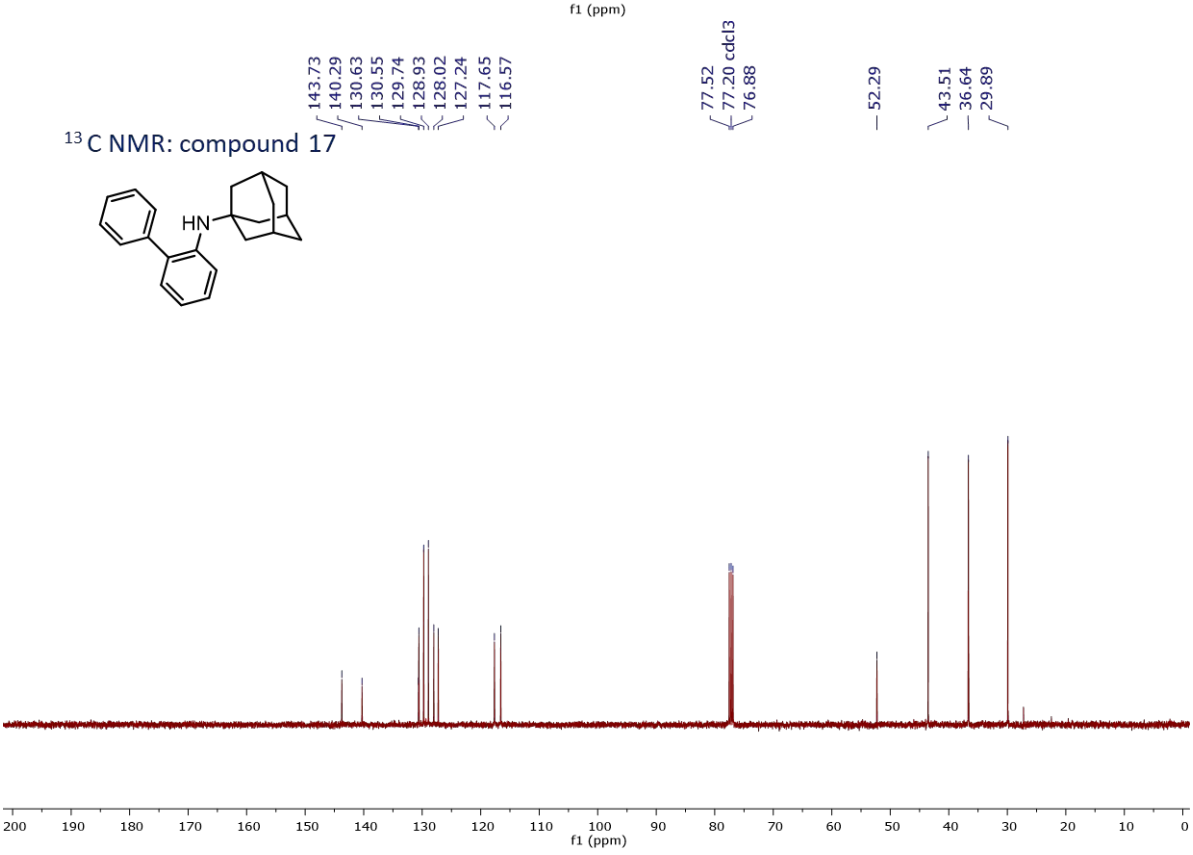
^{13}C NMR: compound 16



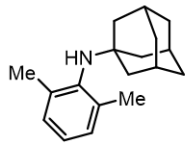
^{1}H NMR: compound 17



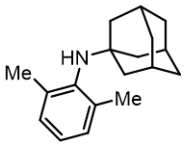
^{13}C NMR: compound 17



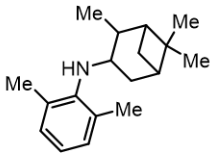
^{1}H NMR: compound 18



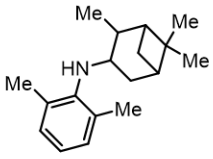
^{13}C NMR: compound 18



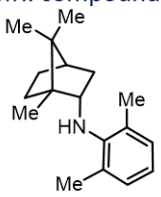
^{1}H NMR: compound 19



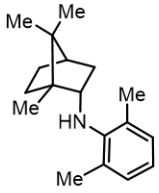
^{13}C NMR: compound 19

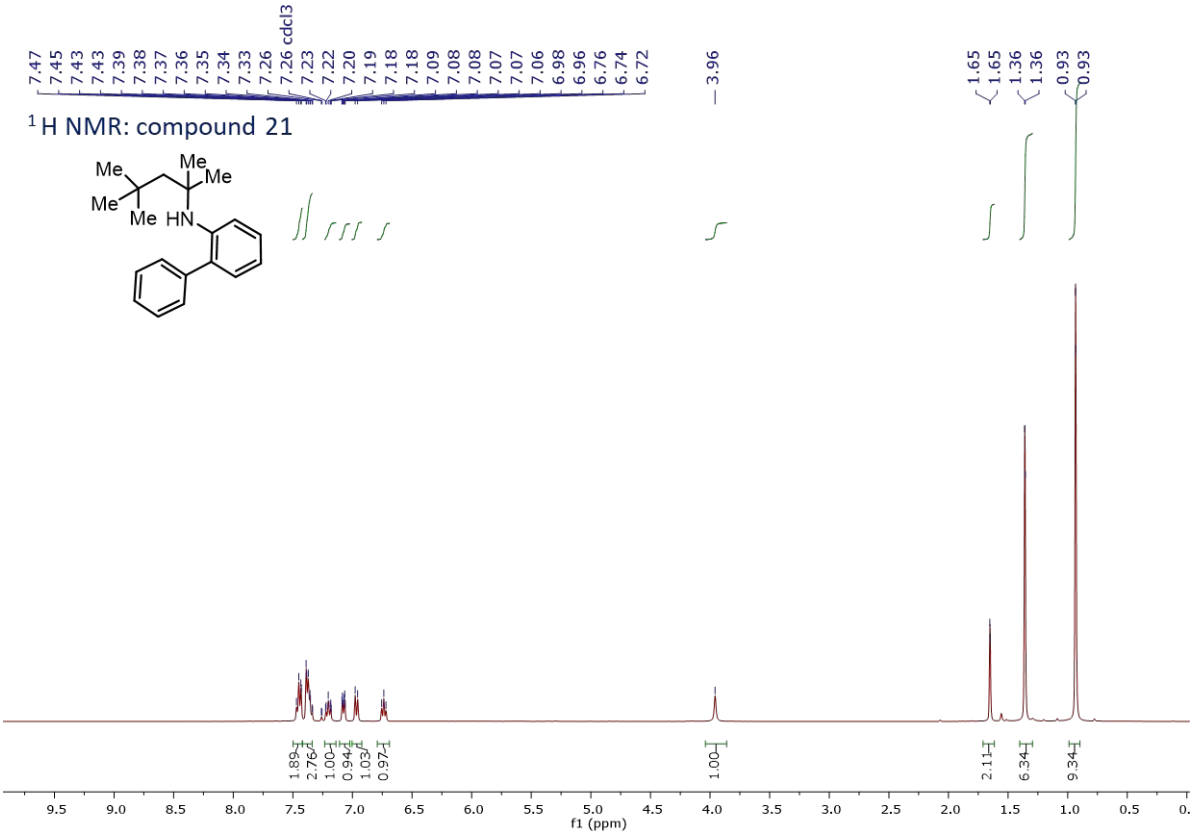


^{1}H NMR: compound 20

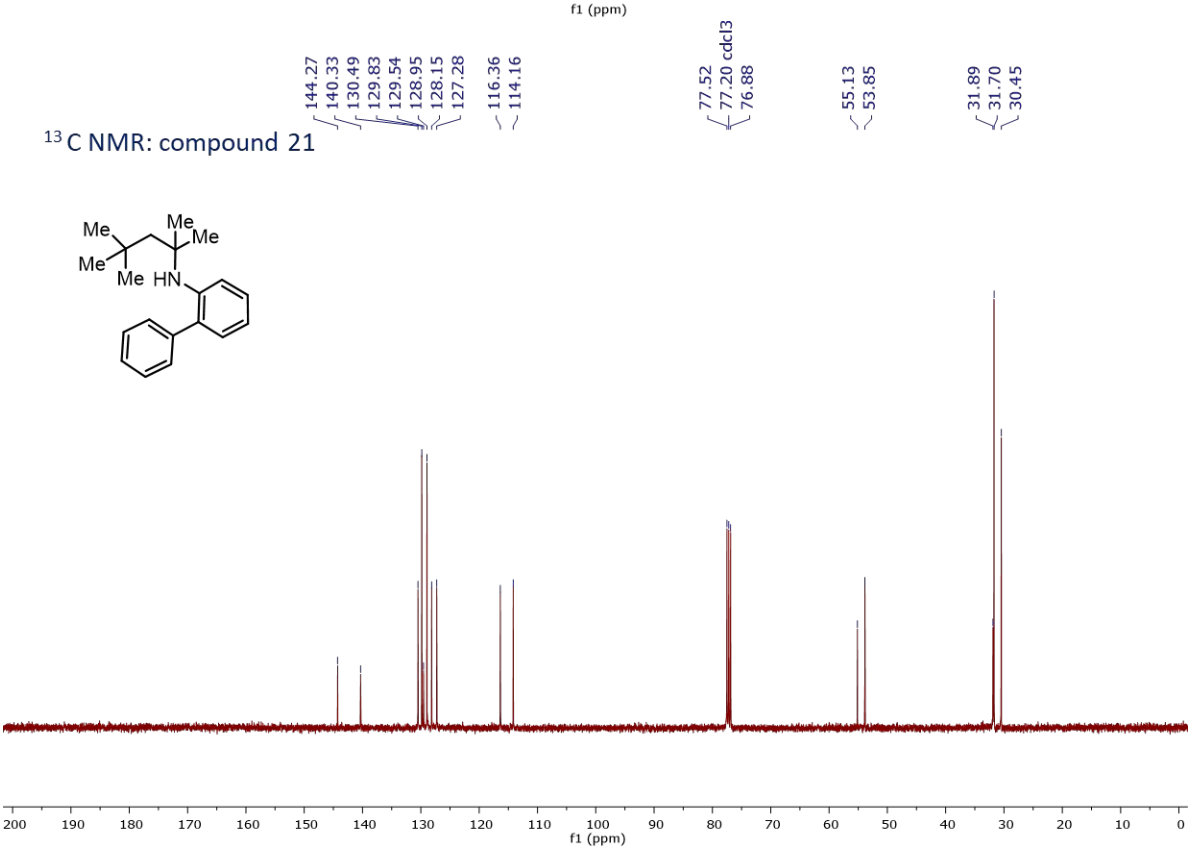


^{13}C NMR: compound 20

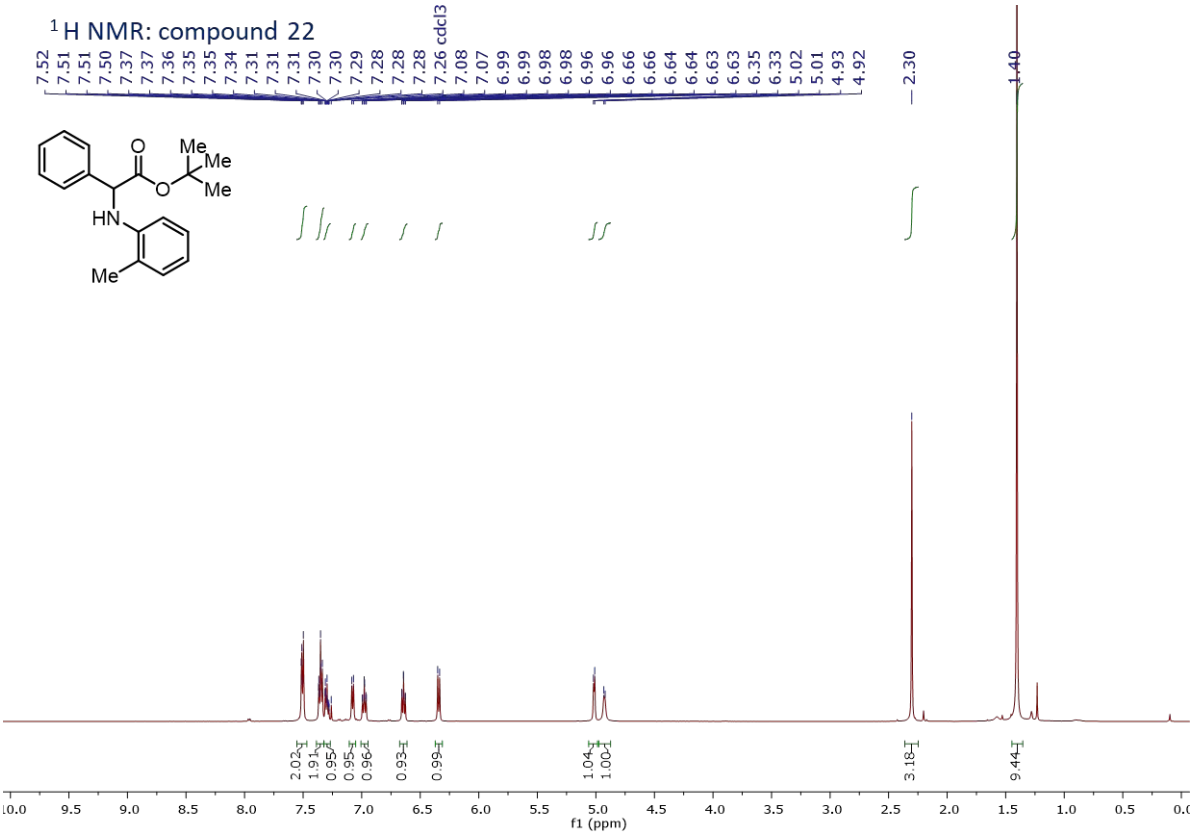


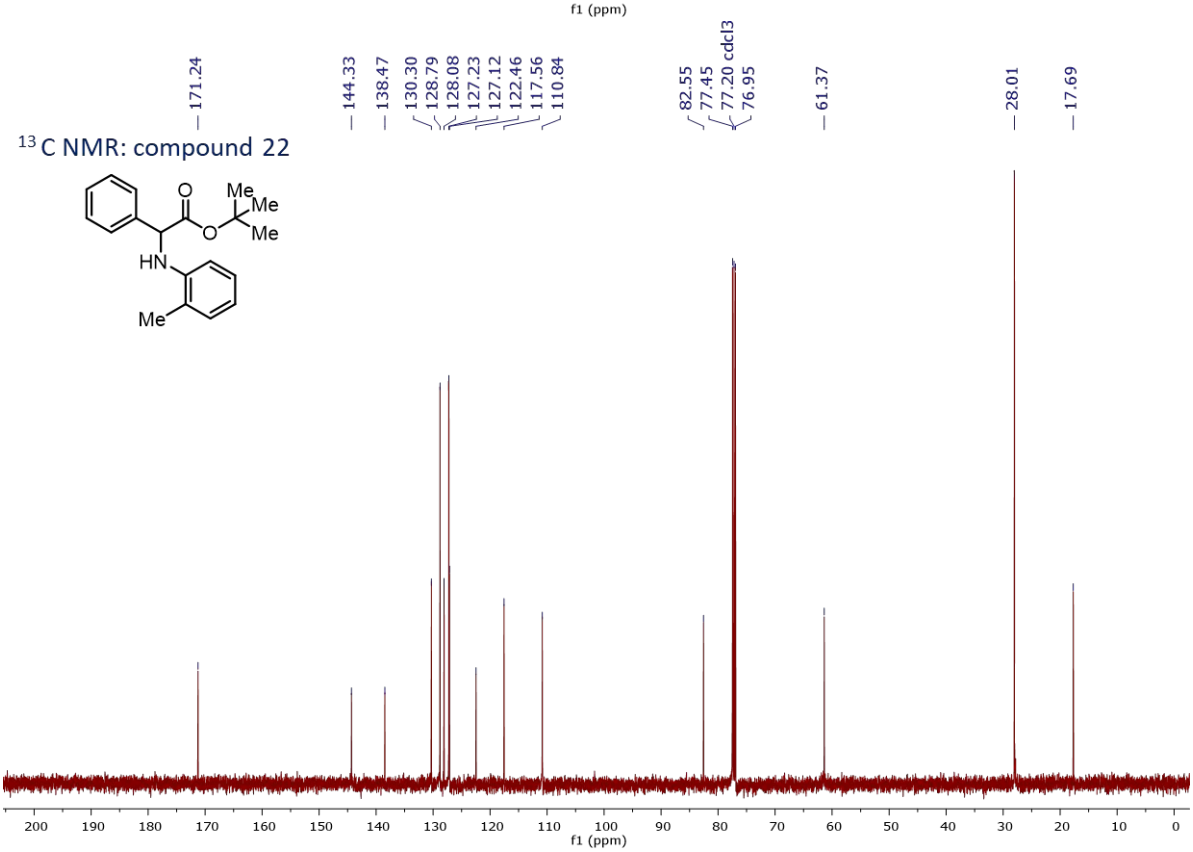


^{1}H NMR: compound 21

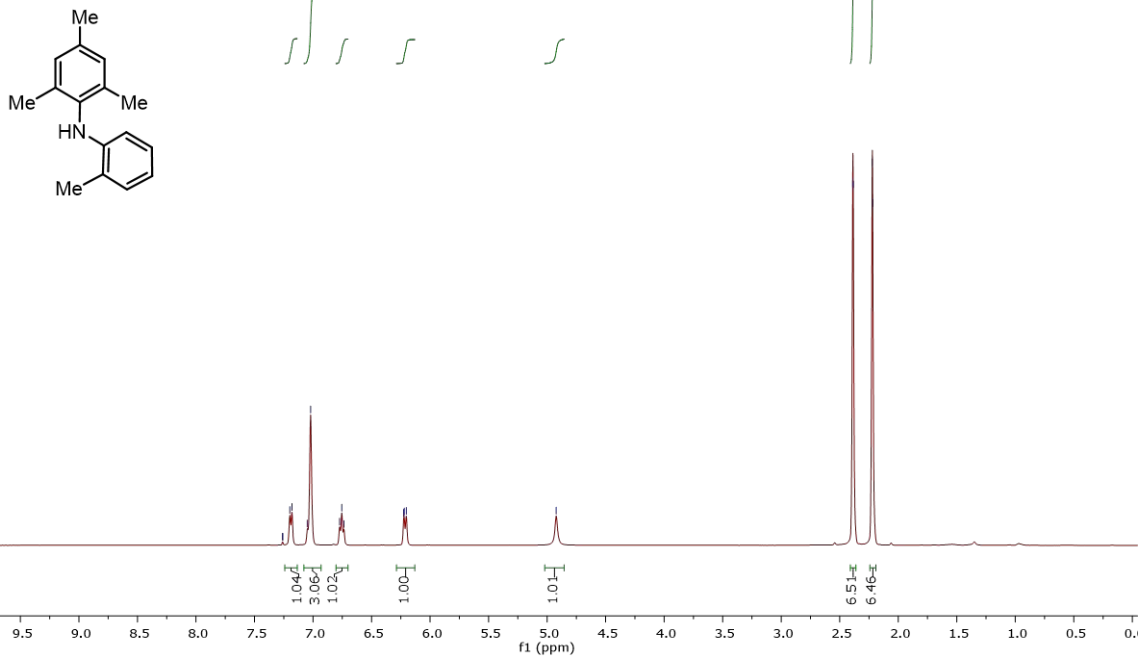


^{13}C NMR: compound 21

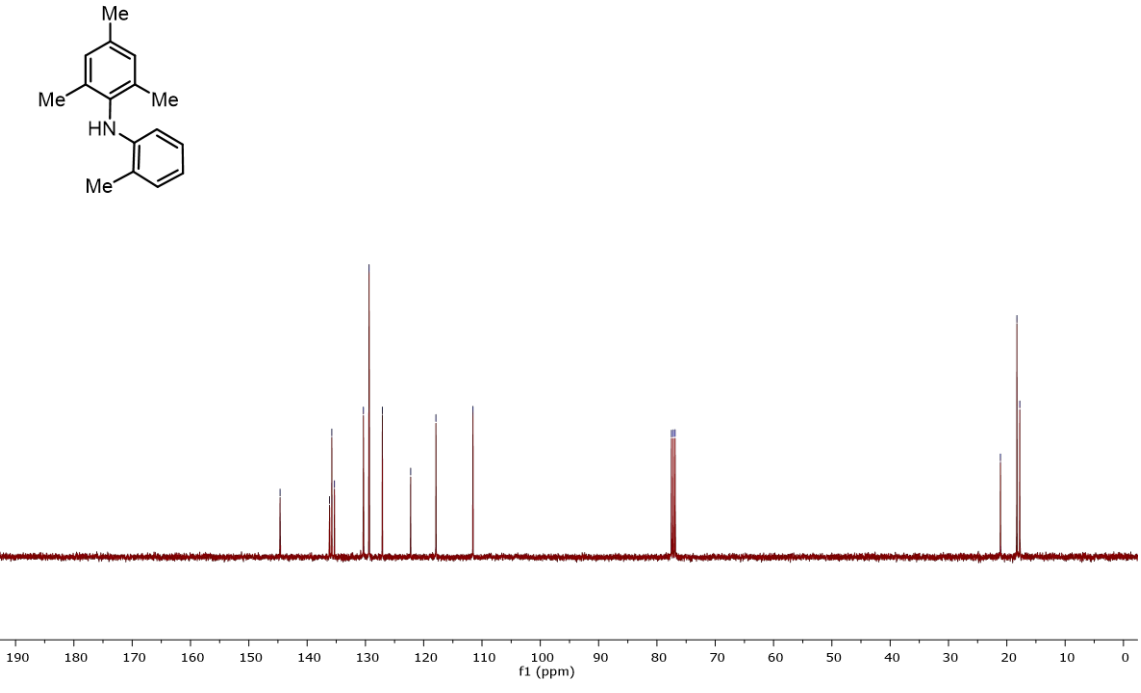

1H NMR: compound 22
7.52 7.51 7.51 7.50 7.37 7.37 7.36 7.35 7.35 7.34 7.31 7.31 7.31 7.30 7.30 7.29 7.28 7.28 7.28 7.26 cdcl3 7.08 7.07 6.99 6.99 6.98 6.98 6.96 6.96 6.66 6.66 6.64 6.64 6.63 6.63 6.35 6.33 5.02 5.01 4.93 4.92
2.30
1.40
O
Me
Me
Me
O
HN
Me
2.02 1.91 0.95 0.95 0.96 0.93 0.99 1.04 1.00 3.18 9.44
f1 (ppm)


13C NMR: compound 22
171.24
144.33
138.47
130.30
128.79
128.08
127.23
127.12
122.46
117.56
110.84
82.55
77.45
77.20 cdcl3
76.95
61.37
28.01
17.69
O
Me
Me
Me
O
HN
Me
f1 (ppm)

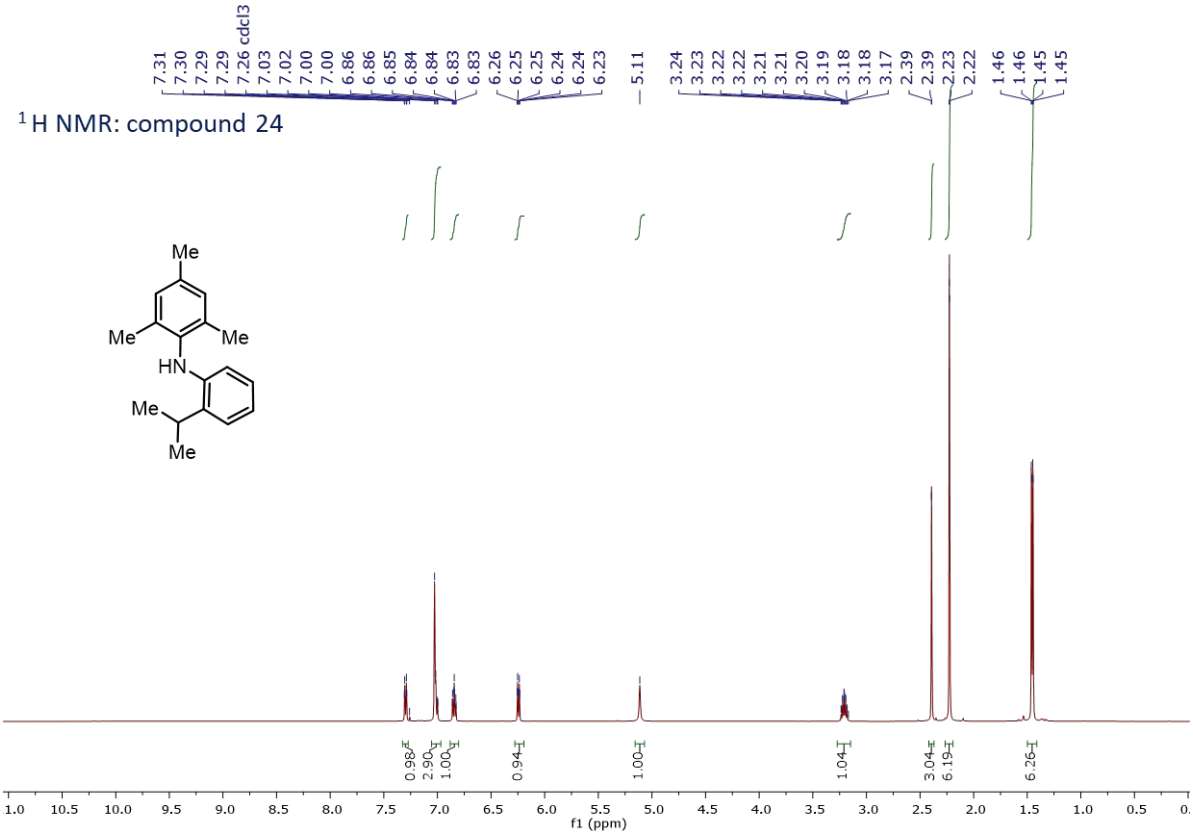
^{1}H NMR: compound 23



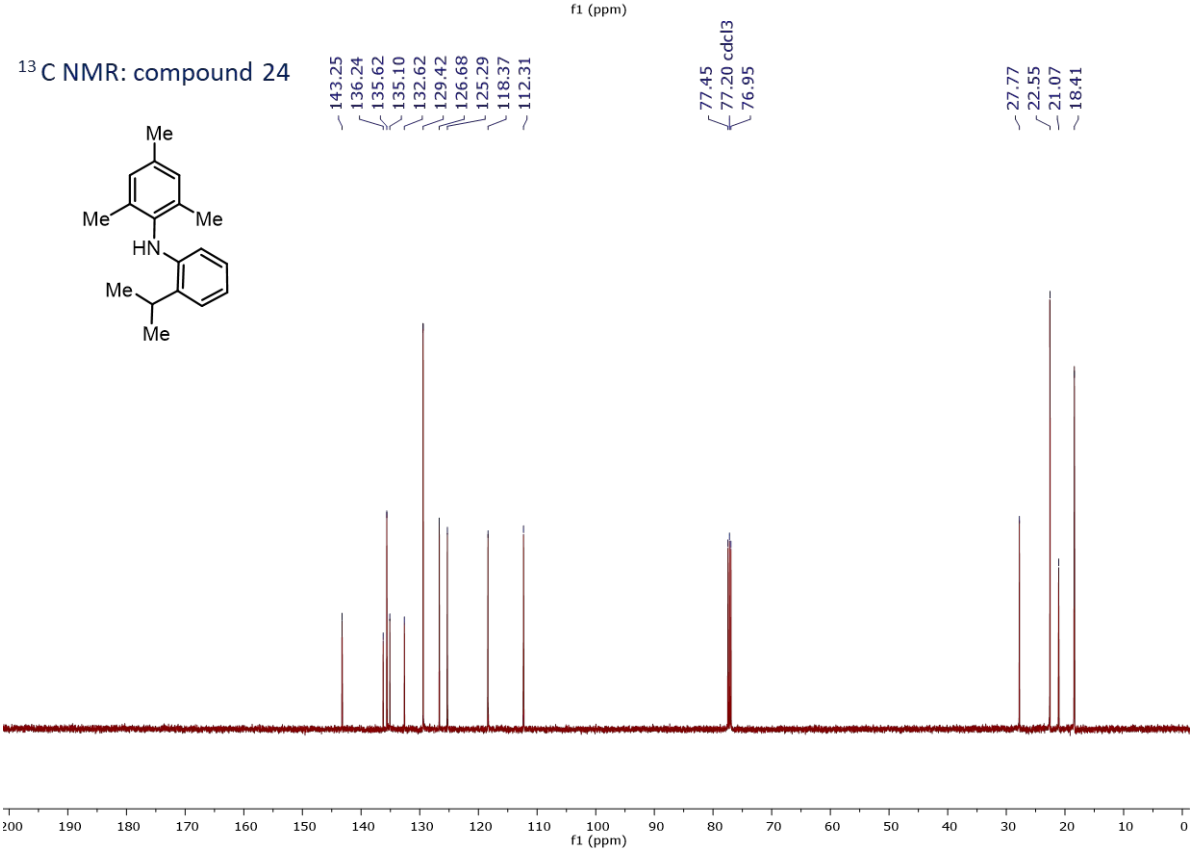
^{13}C NMR: compound 23



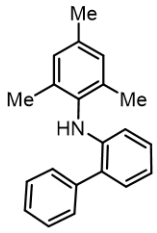
^{1}H NMR: compound 24



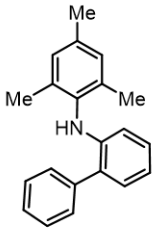
^{13}C NMR: compound 24



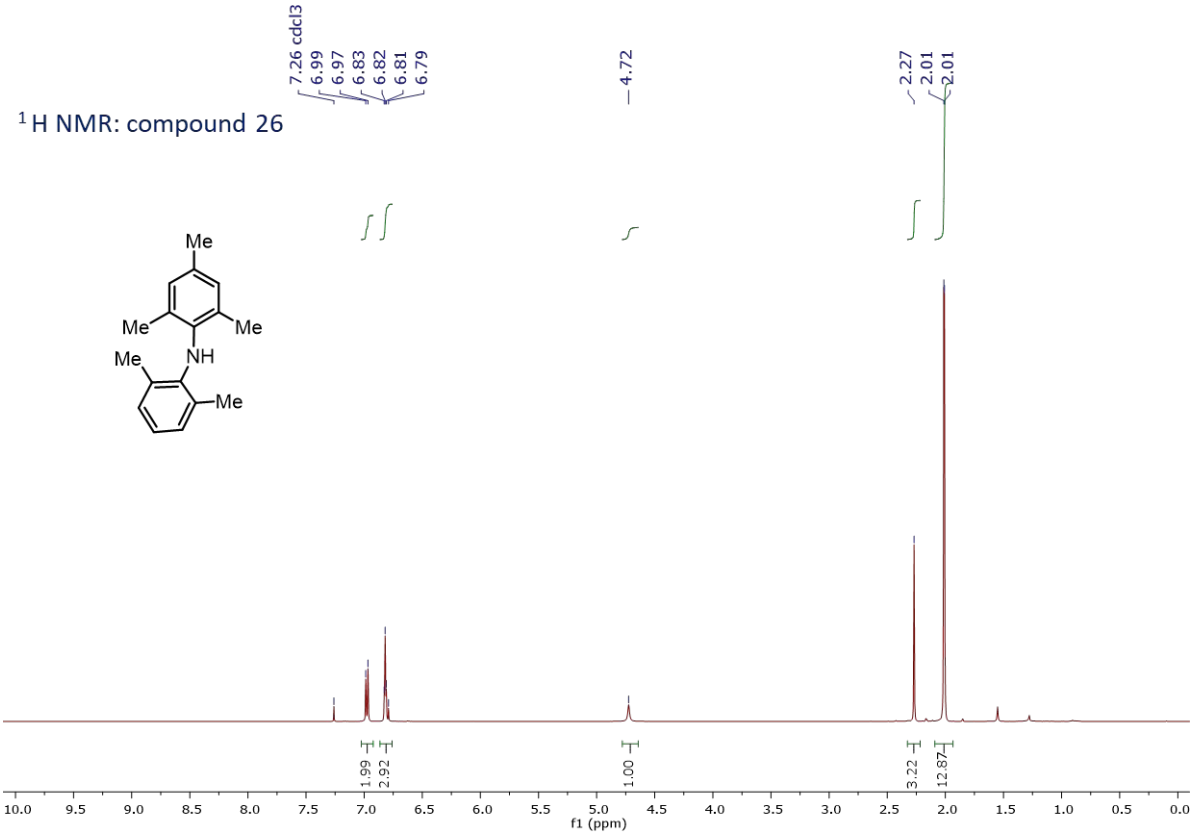
^{1}H NMR: compound 25



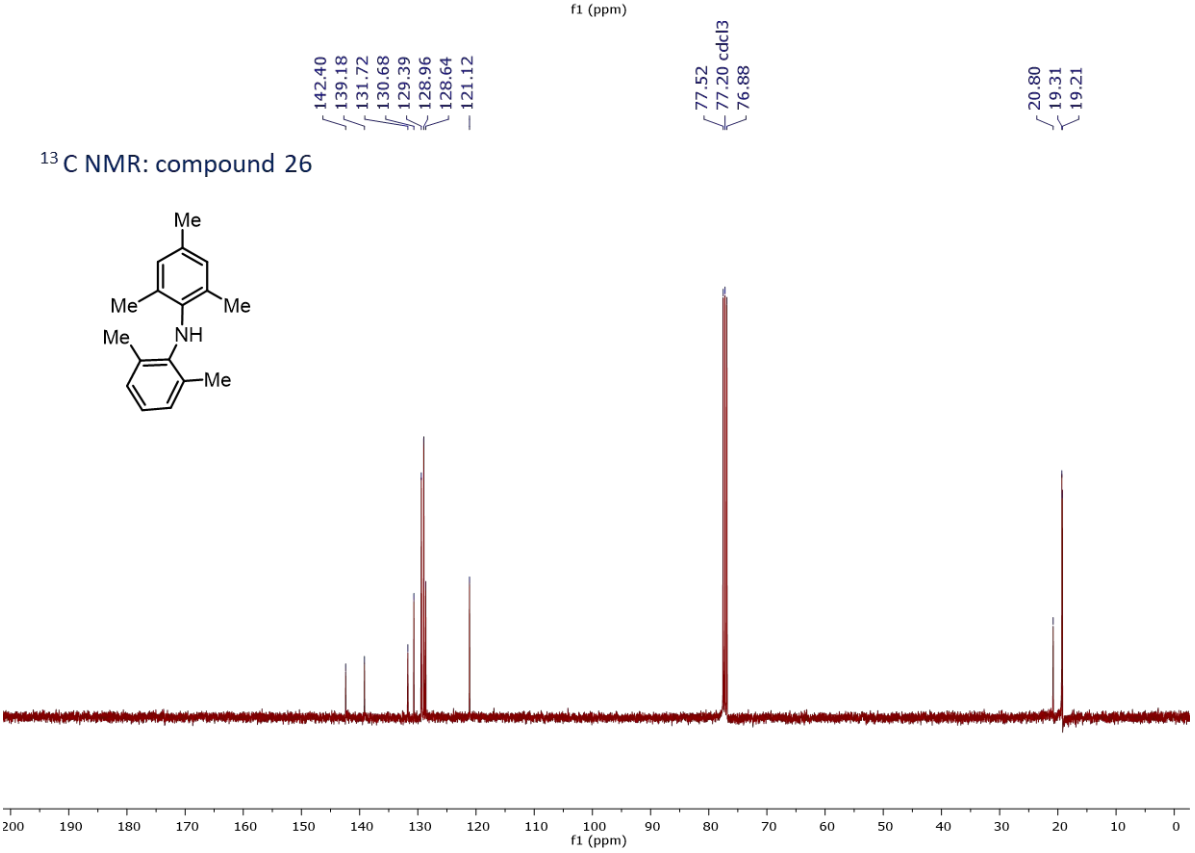
^{13}C NMR: compound 25

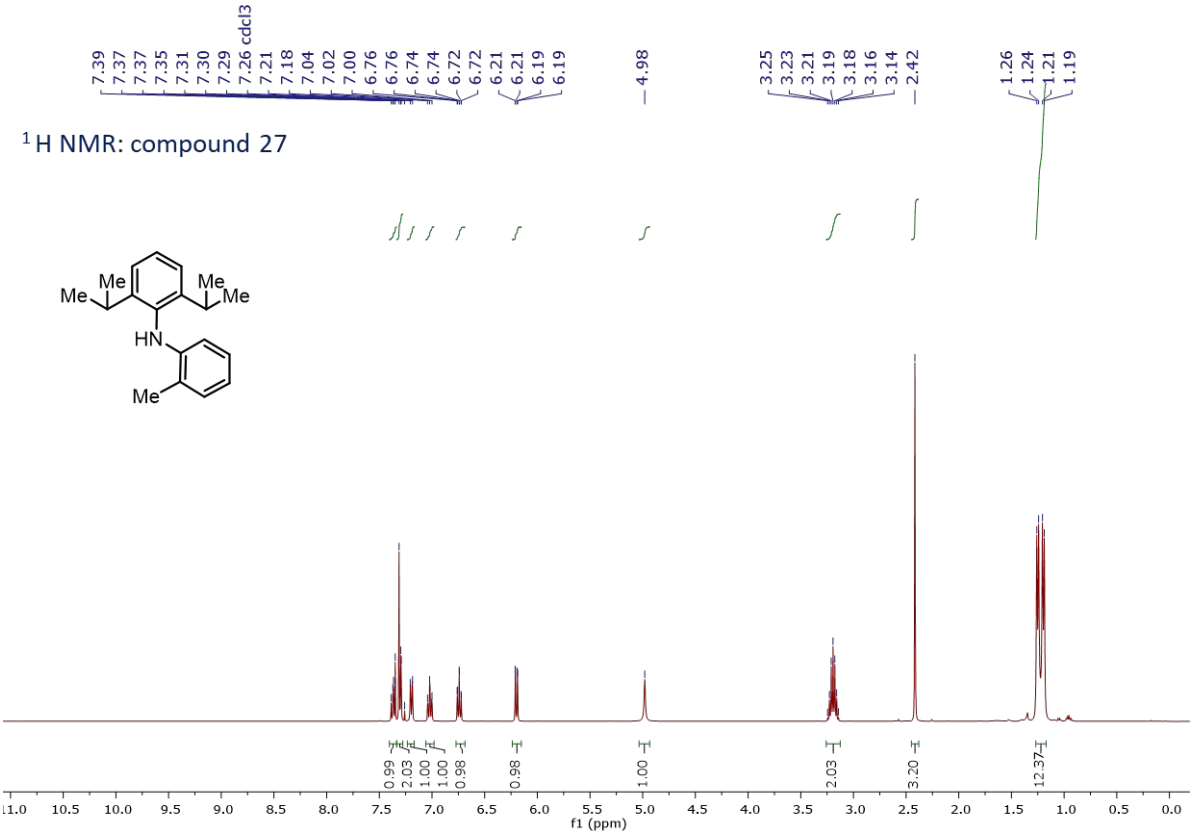


[1] H NMR: compound 26

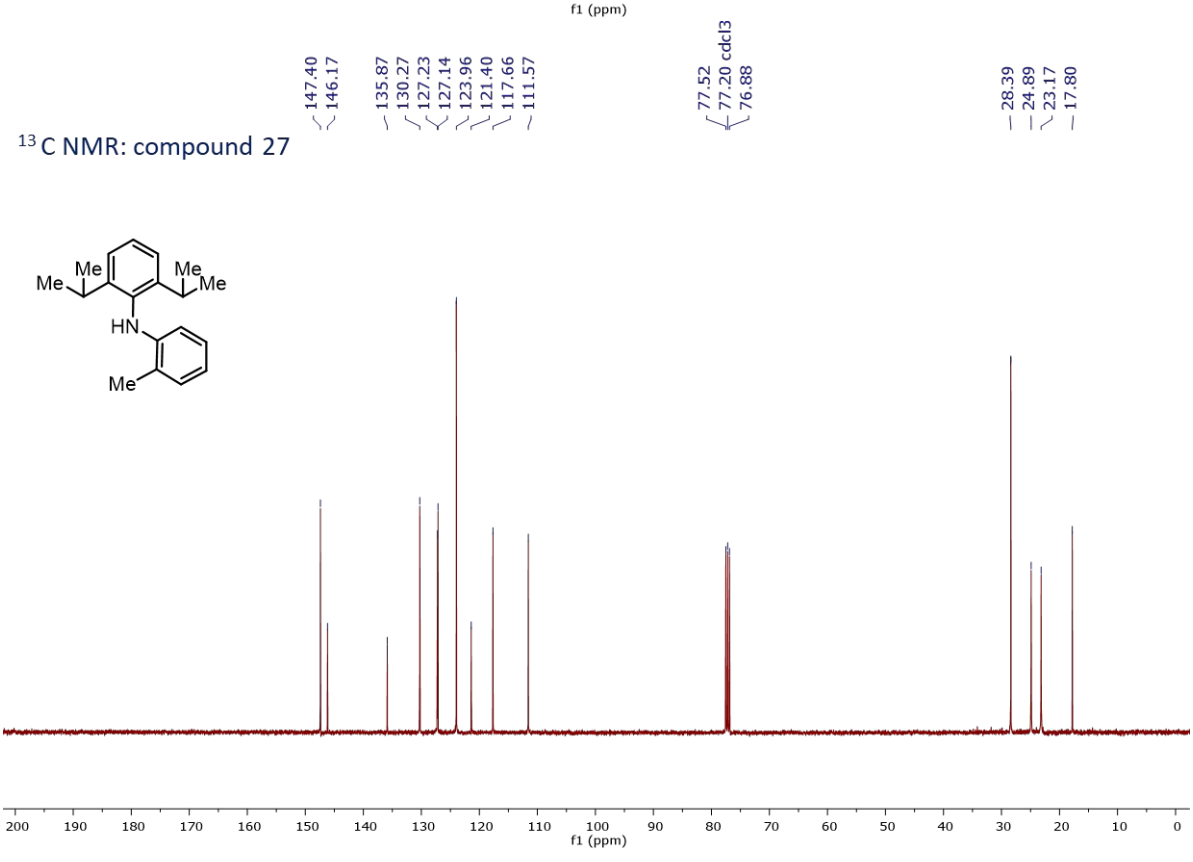


[13] C NMR: compound 26

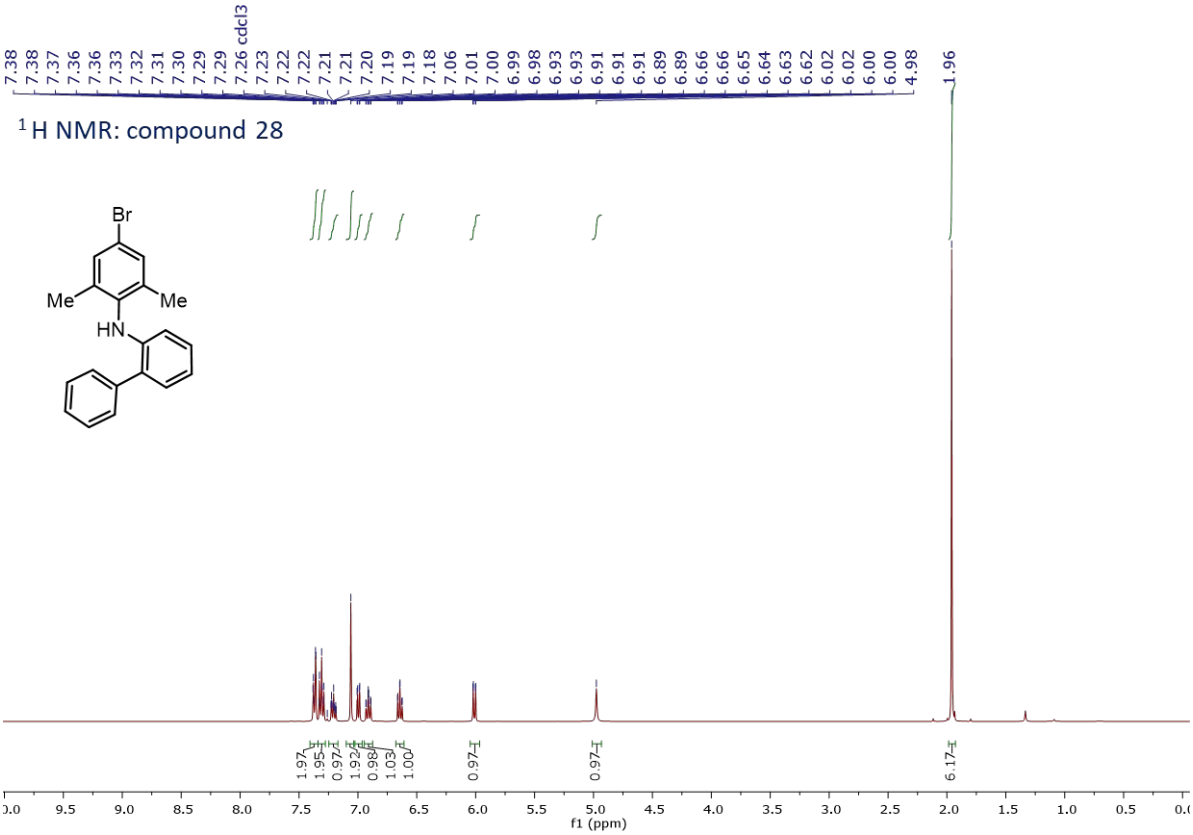




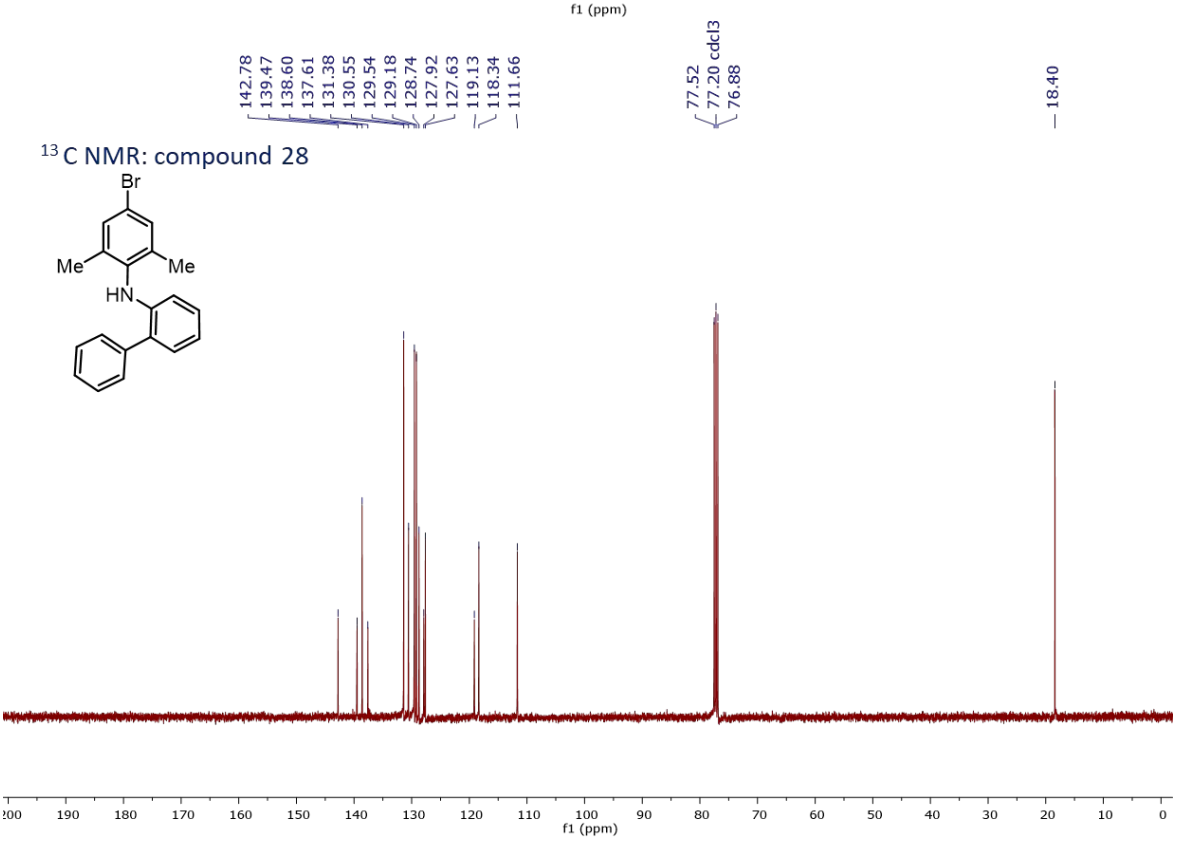
^{1}H NMR: compound 27



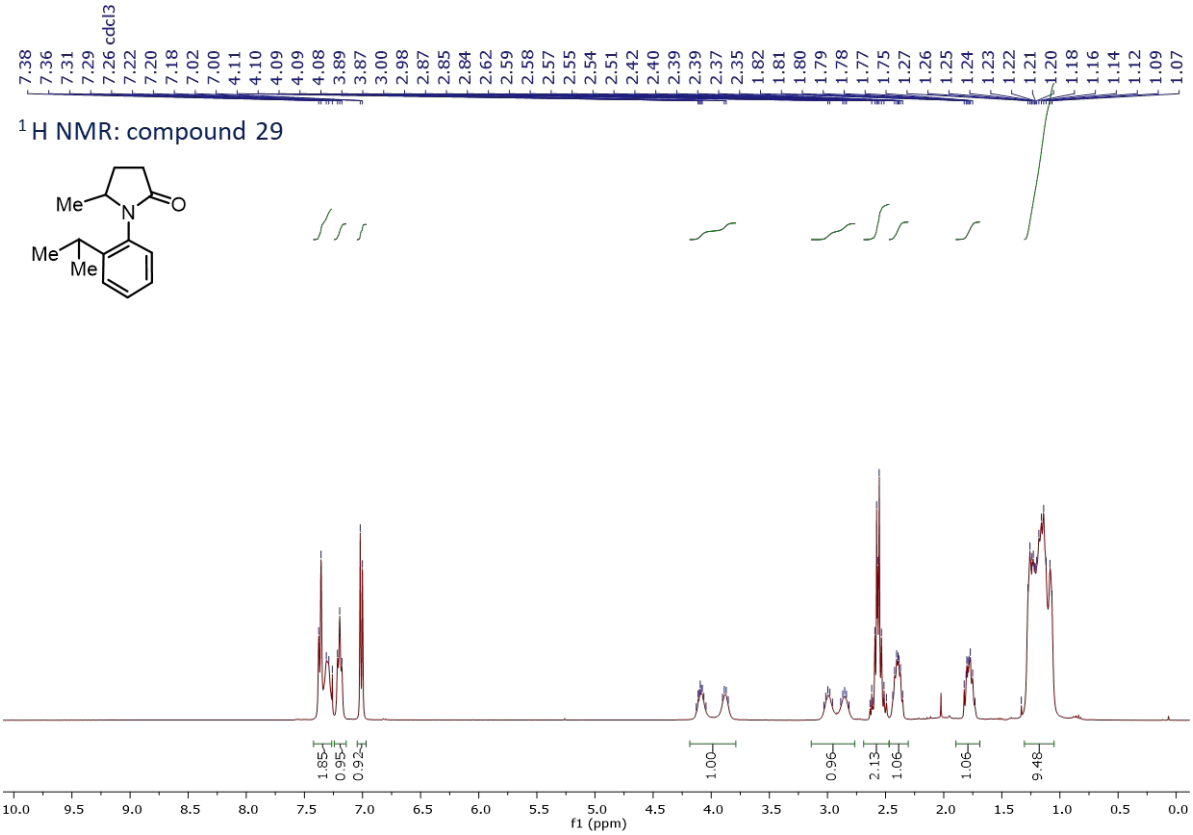
^{13}C NMR: compound 27

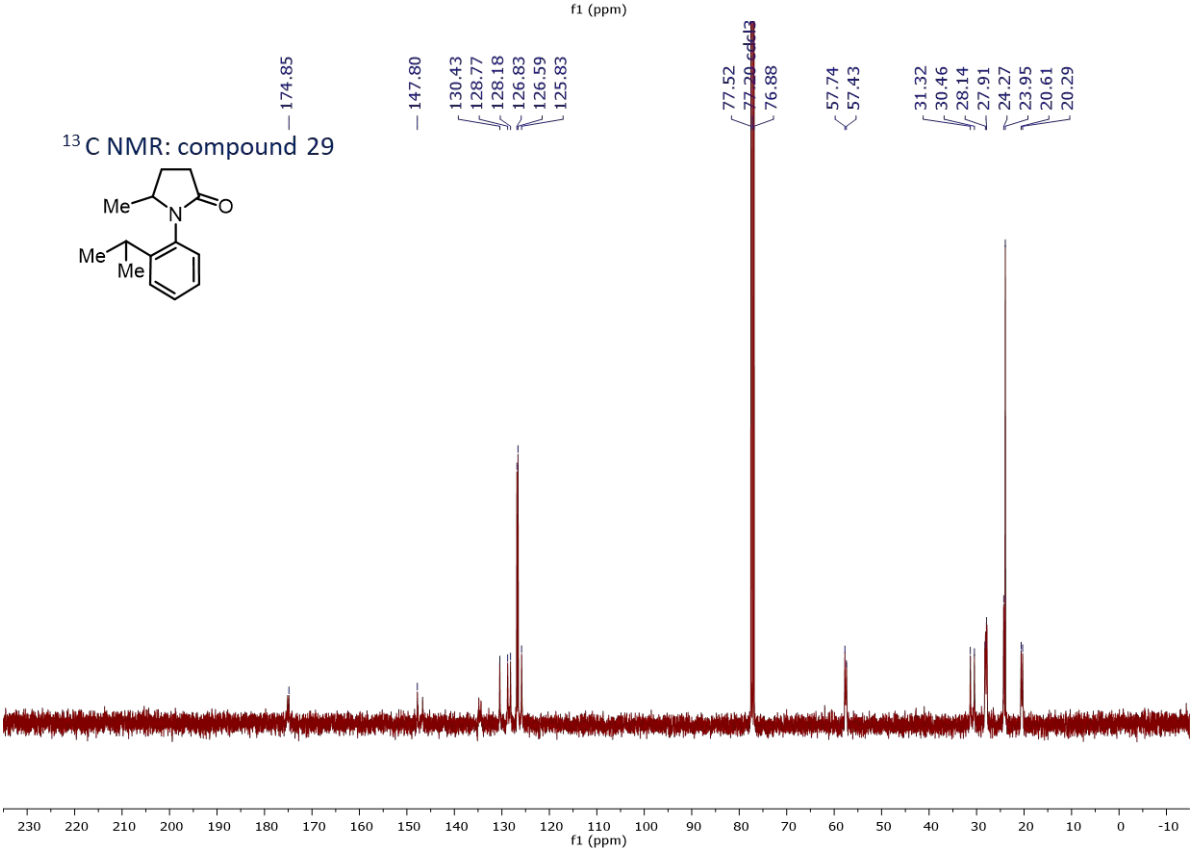


^{1}H NMR: compound 28

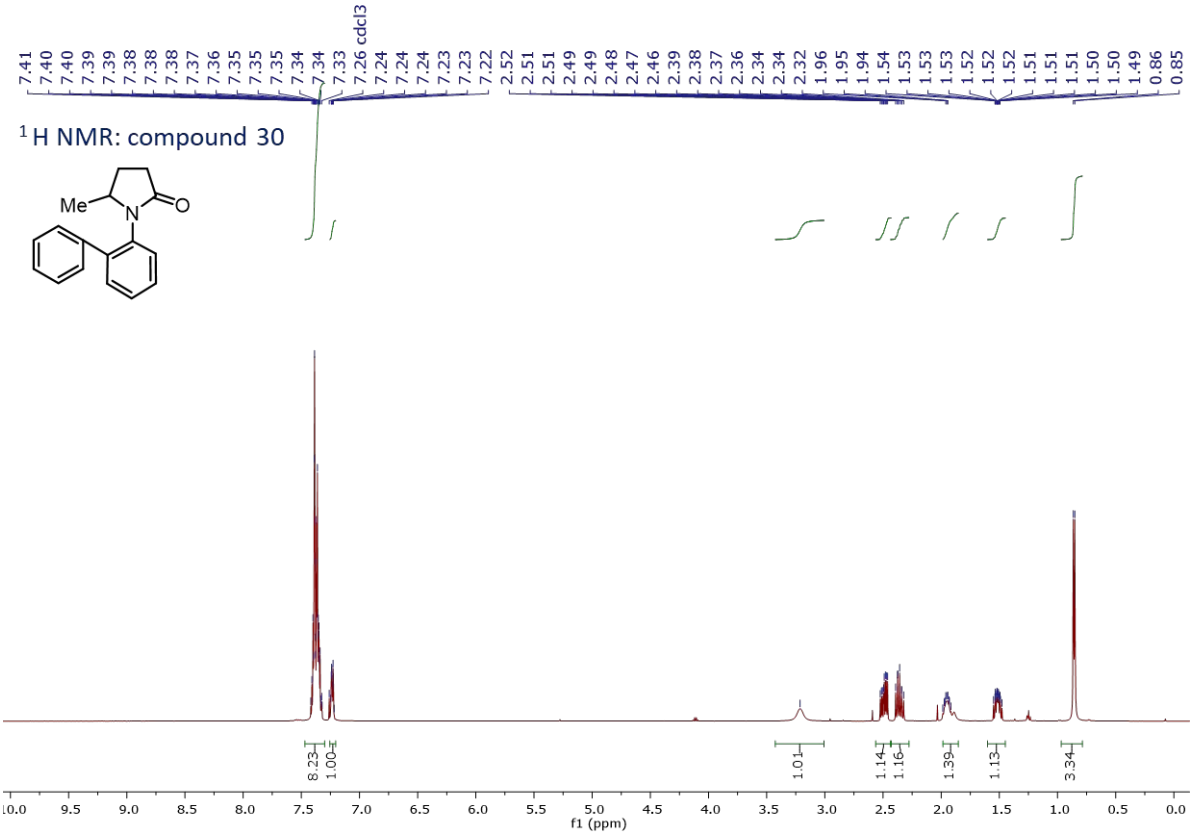


^{13}C NMR: compound 28

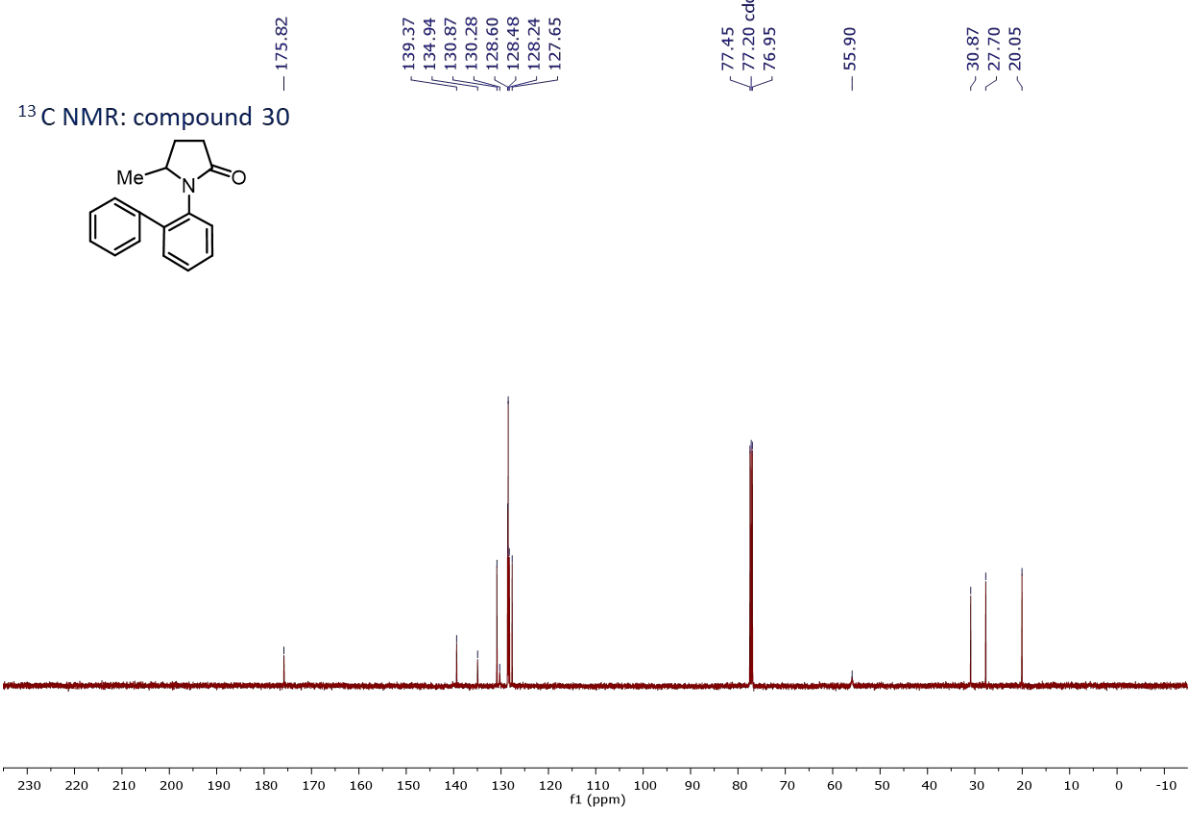

7.38 7.36 7.31 7.29 7.26 cdcl3 7.22 7.20 7.18 7.02 7.00 4.11 4.10 4.09 4.09 4.08 3.89 3.87 3.00 2.98 2.87 2.85 2.84 2.62 2.59 2.58 2.57 2.55 2.54 2.51 2.42 2.40 2.39 2.39 2.37 2.35 1.82 1.81 1.80 1.79 1.78 1.77 1.75 1.27 1.26 1.25 1.24 1.23 1.22 1.21 1.20 1.18 1.16 1.14 1.12 1.09 1.07
1H NMR: compound 29
Me
N
O
Me
Me
1.85
0.95
0.92
1.00
0.96
2.13
1.06
1.06
9.48
f1 (ppm)


174.85
147.80
130.43
128.77
128.18
126.83
126.59
125.83
77.52
77.20 cdcl3
76.88
57.74
57.43
31.32
30.46
28.14
27.91
24.27
23.95
20.61
20.29
13C NMR: compound 29
Me
N
O
Me
Me
f1 (ppm)

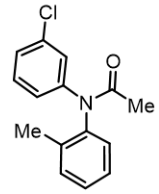
^{1}H NMR: compound 30



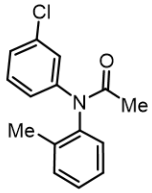
^{13}C NMR: compound 30

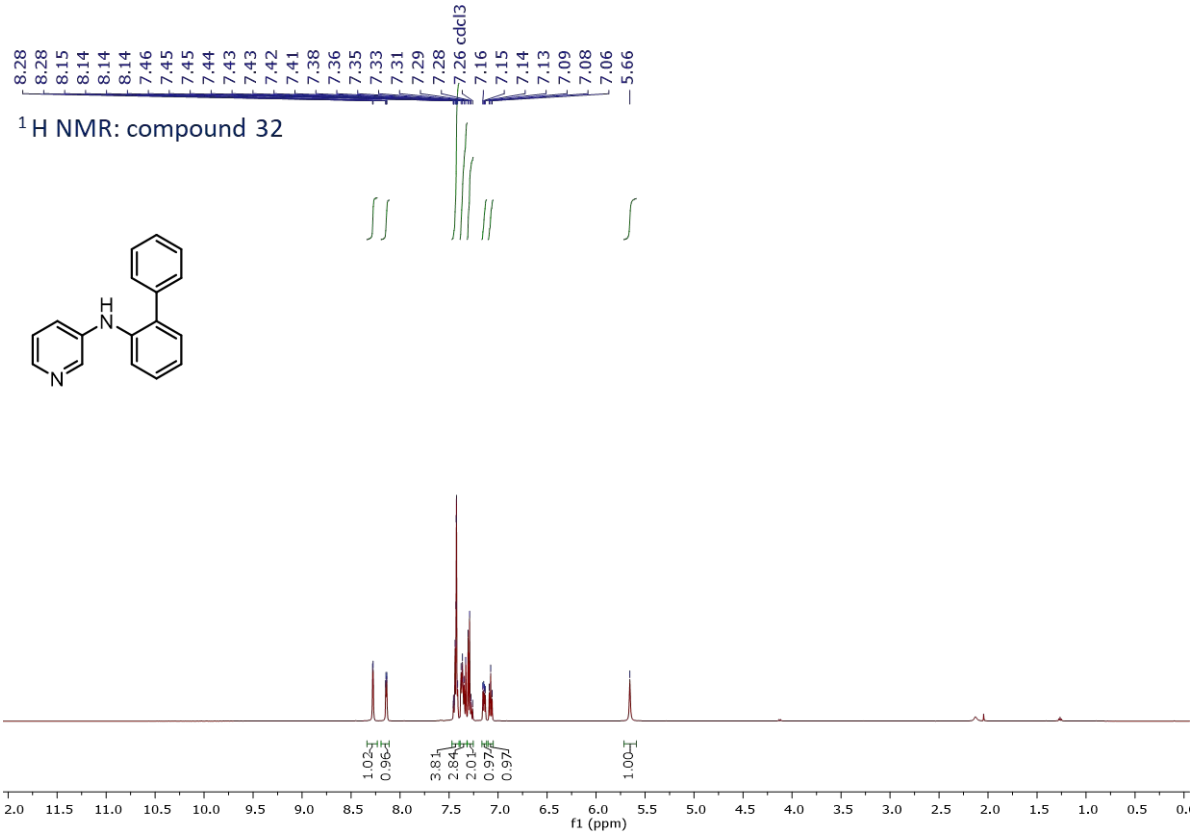


^{1}H NMR: compound 31

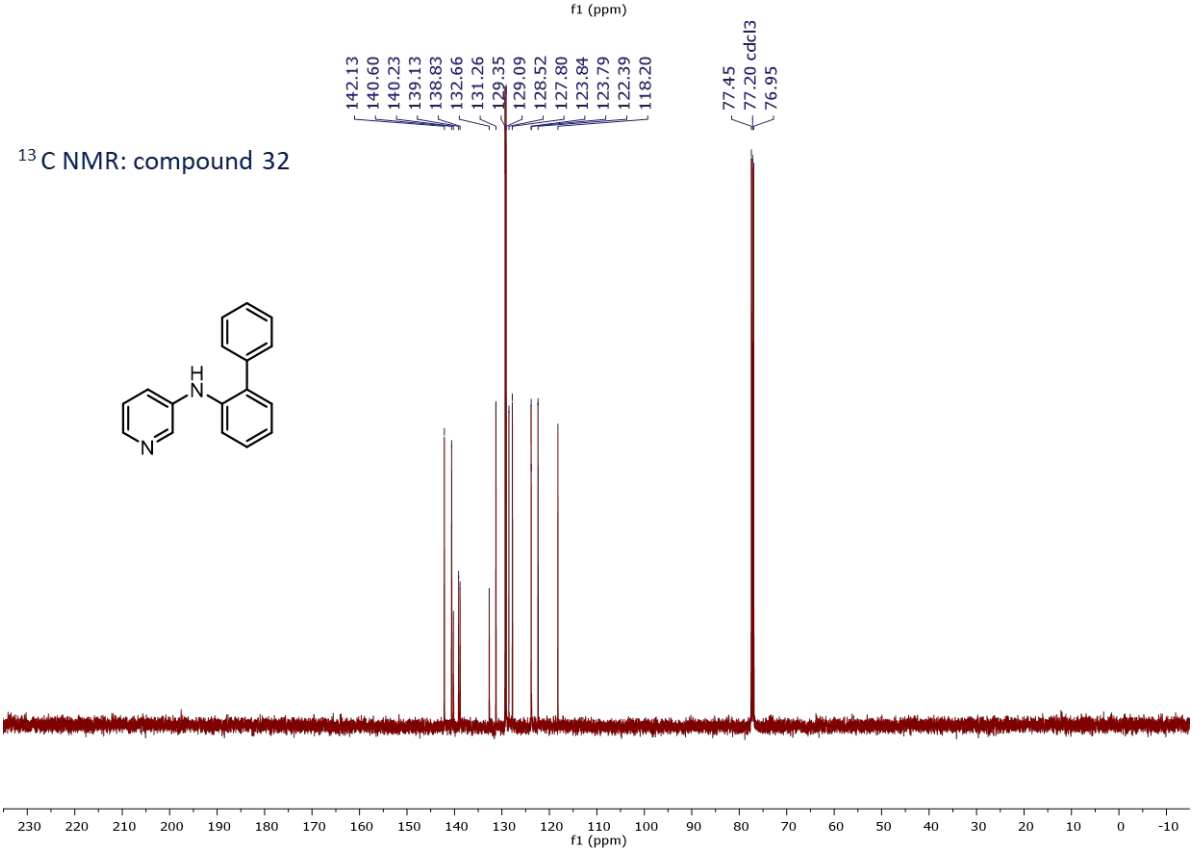


^{13}C NMR: compound 31



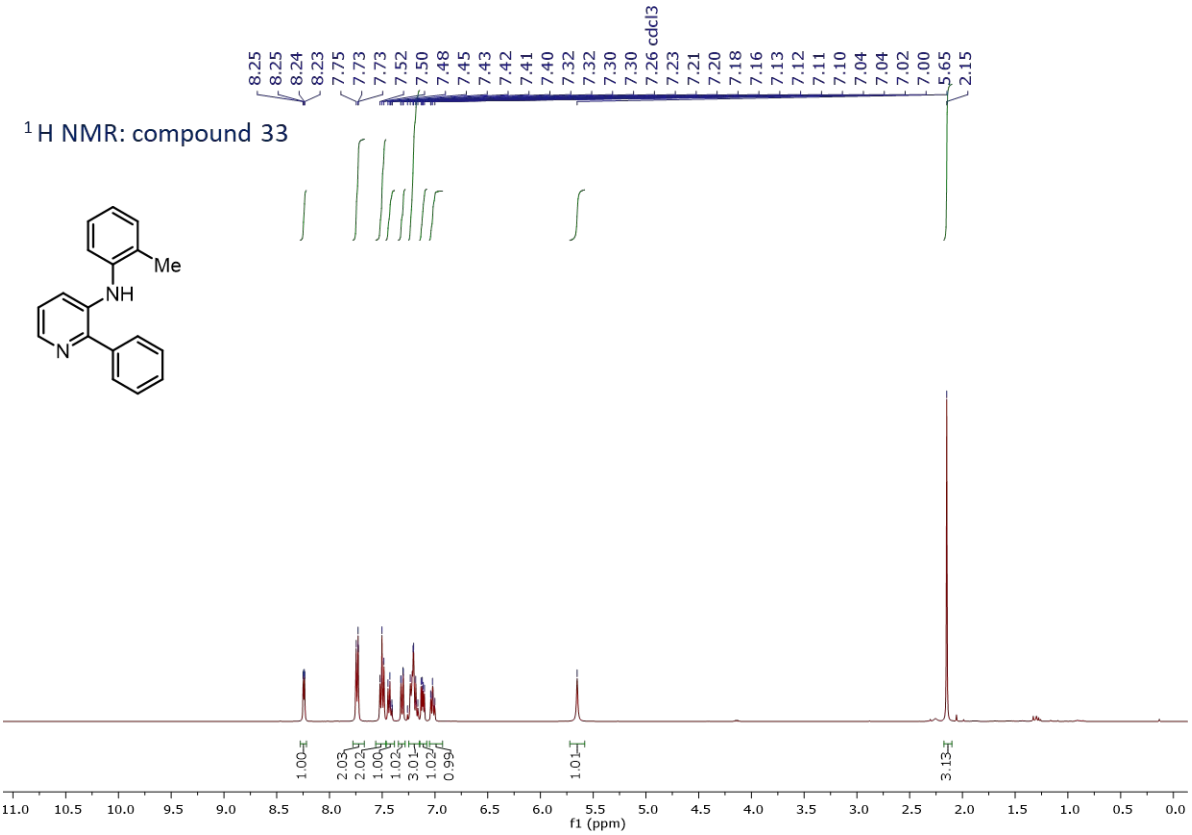


^{1}H NMR: compound 32

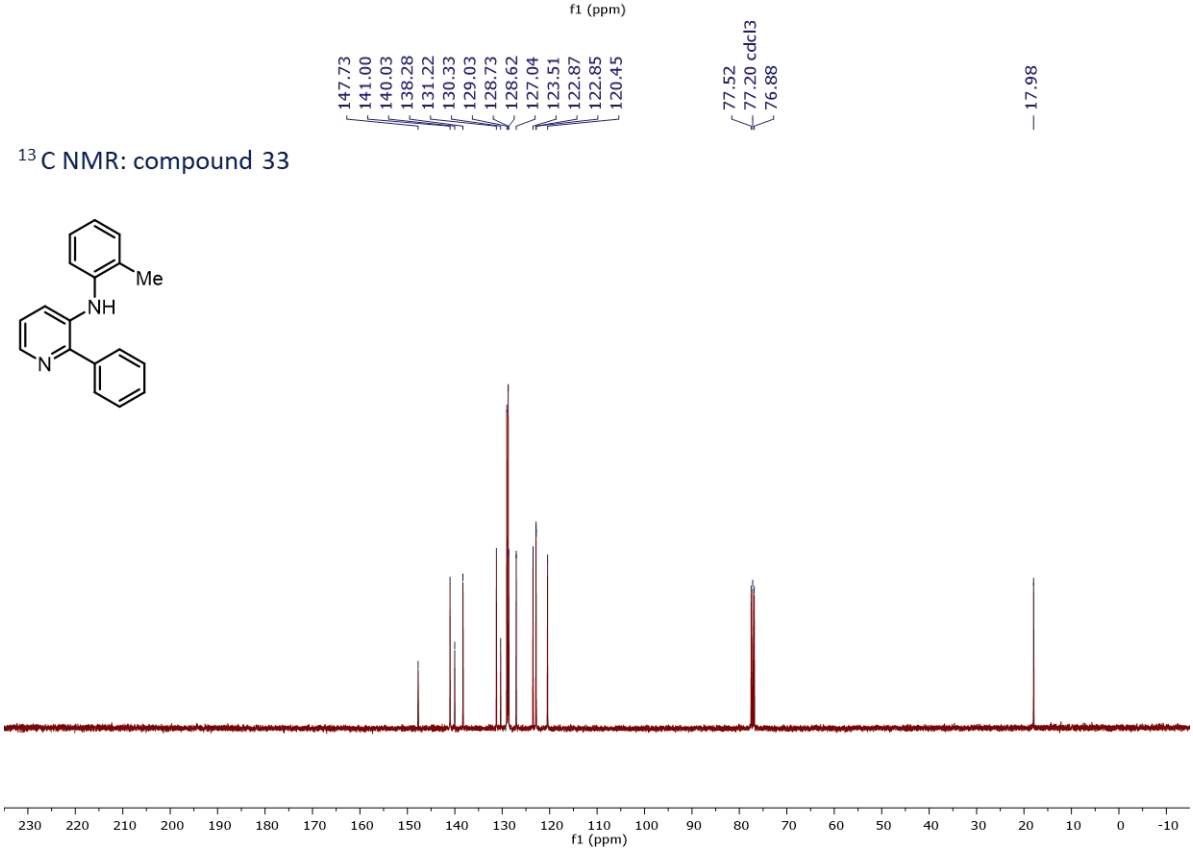


^{13}C NMR: compound 32

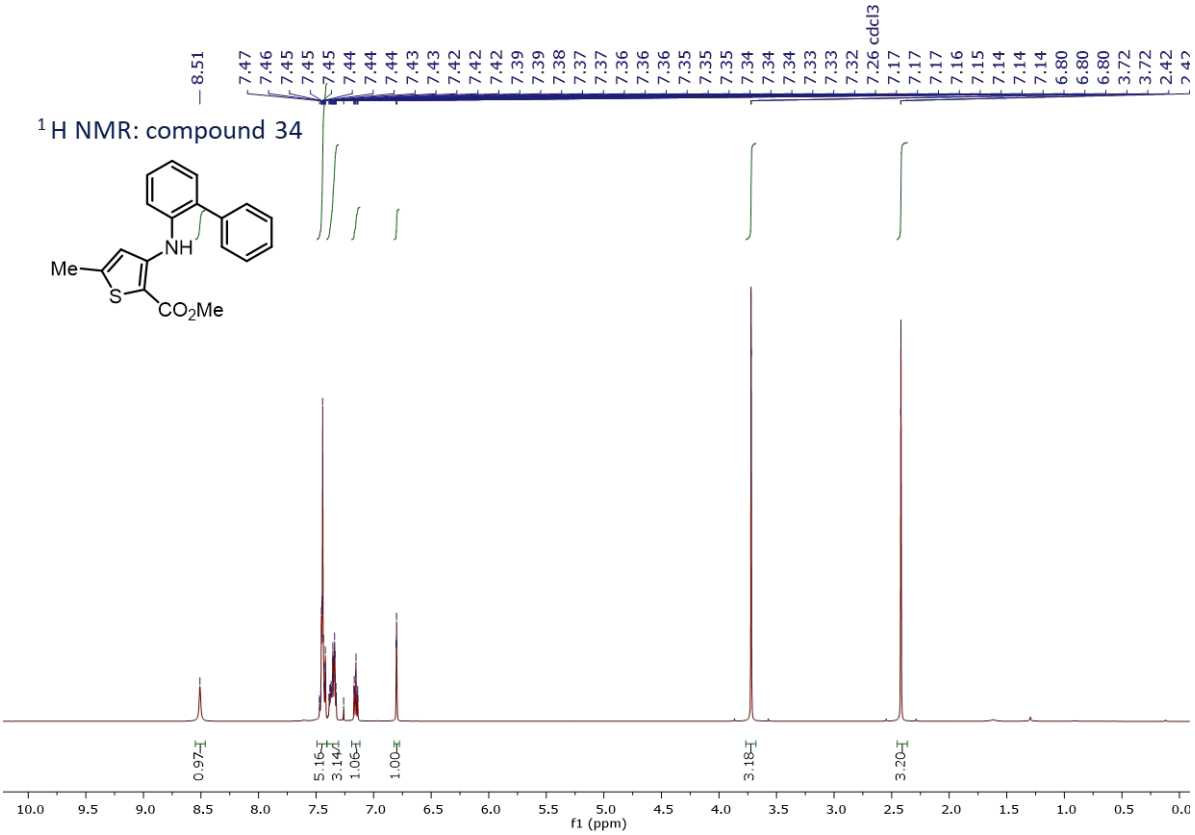
[1] H NMR: compound 33



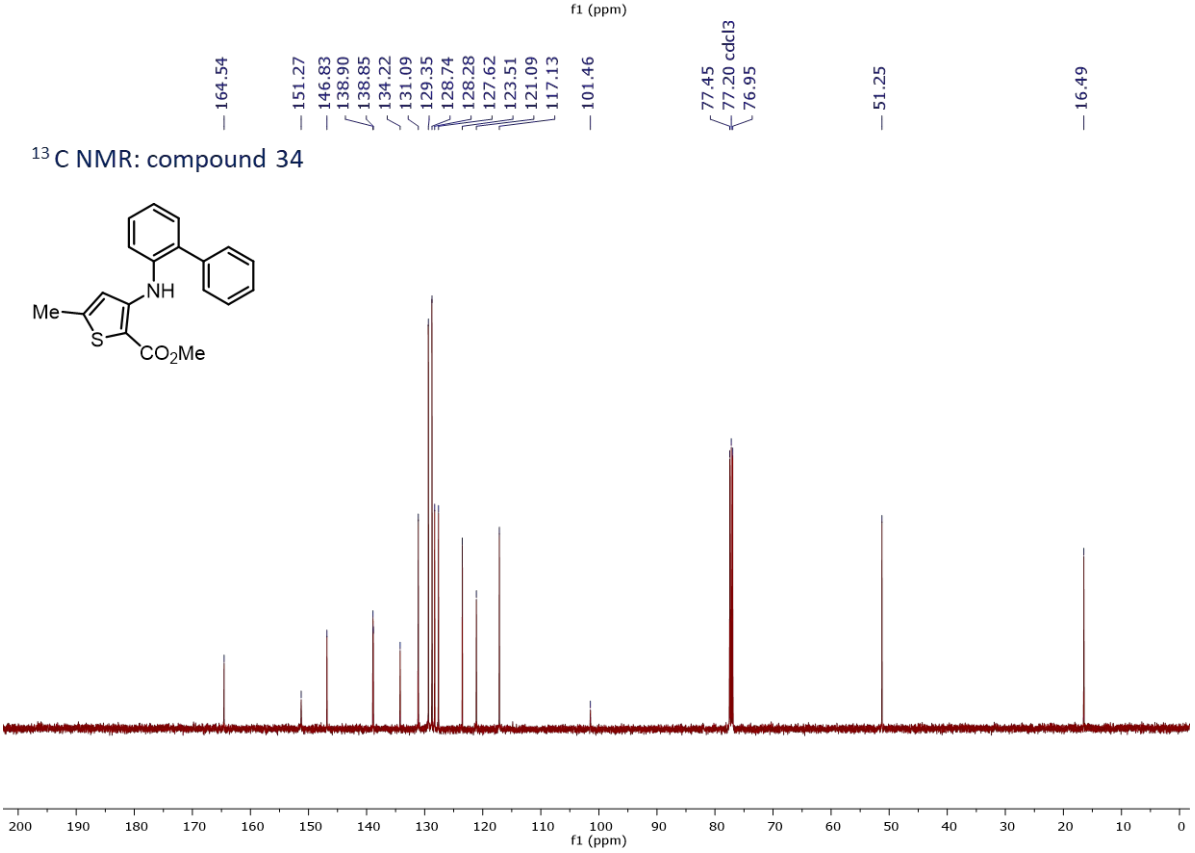
[13] C NMR: compound 33



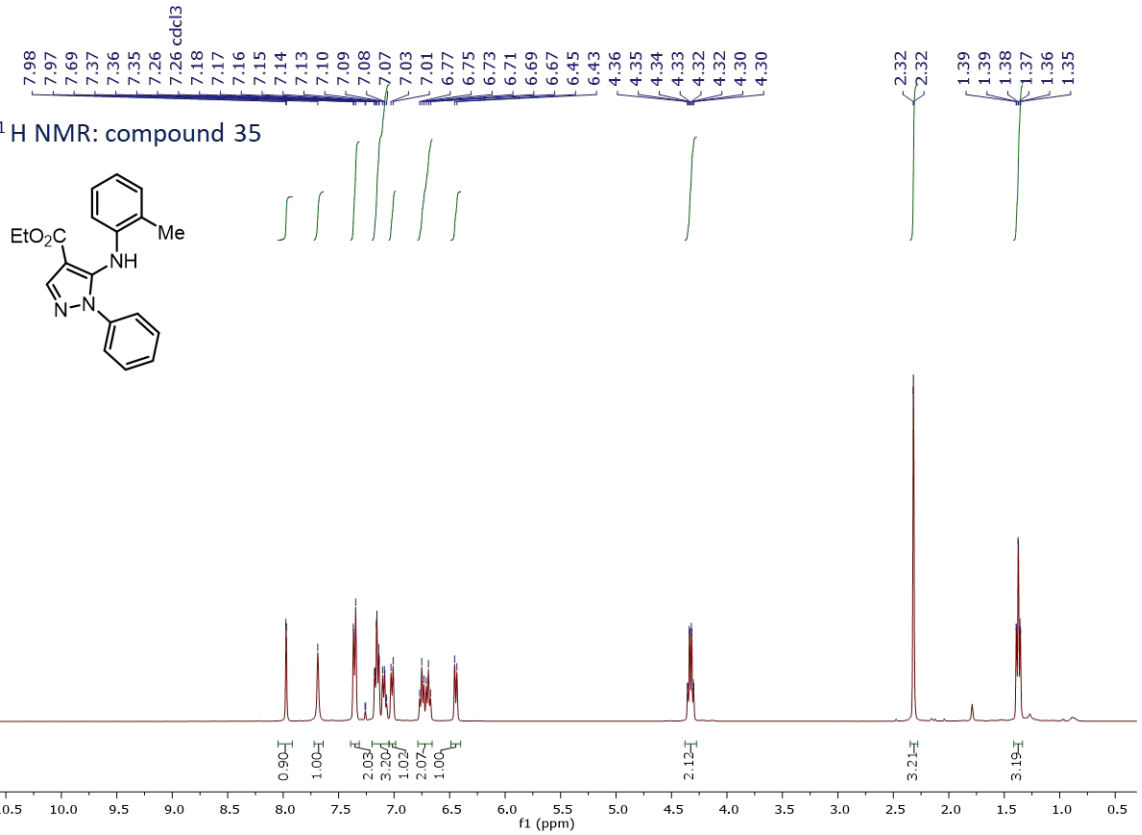
^{1}H NMR: compound 34



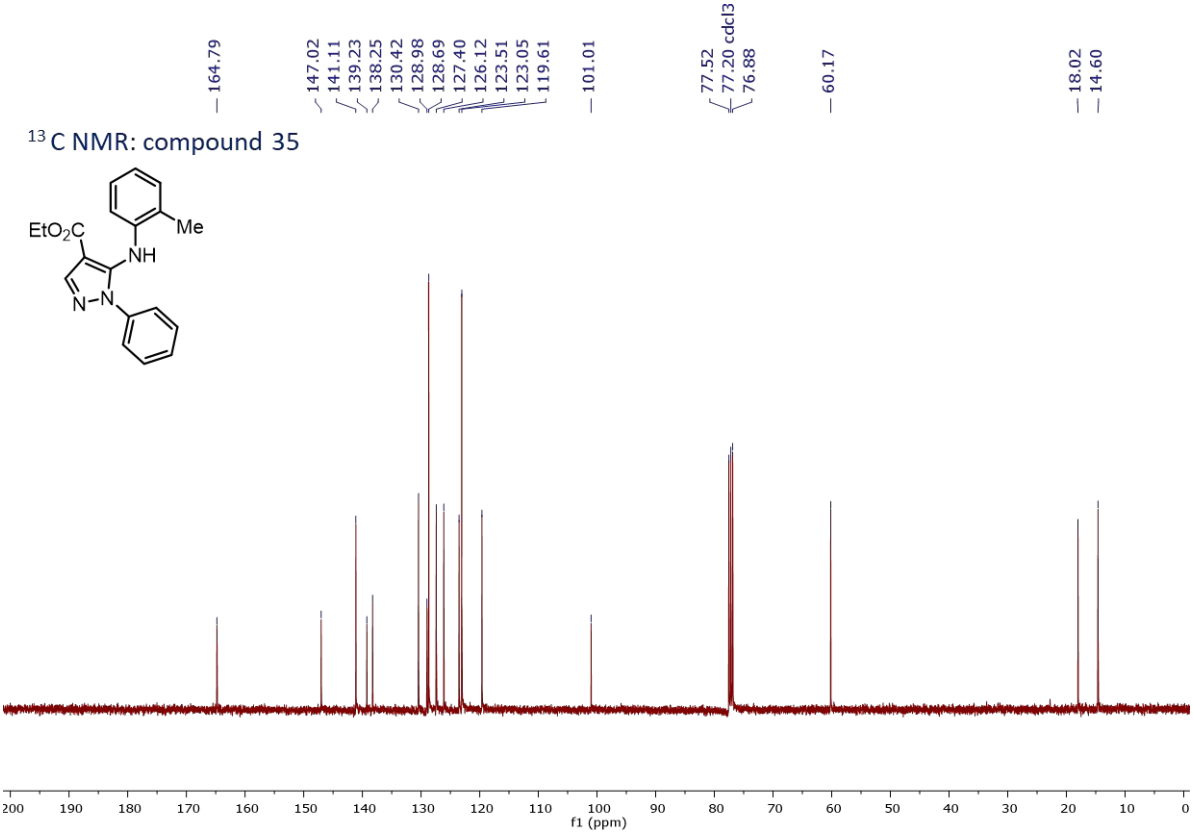
^{13}C NMR: compound 34

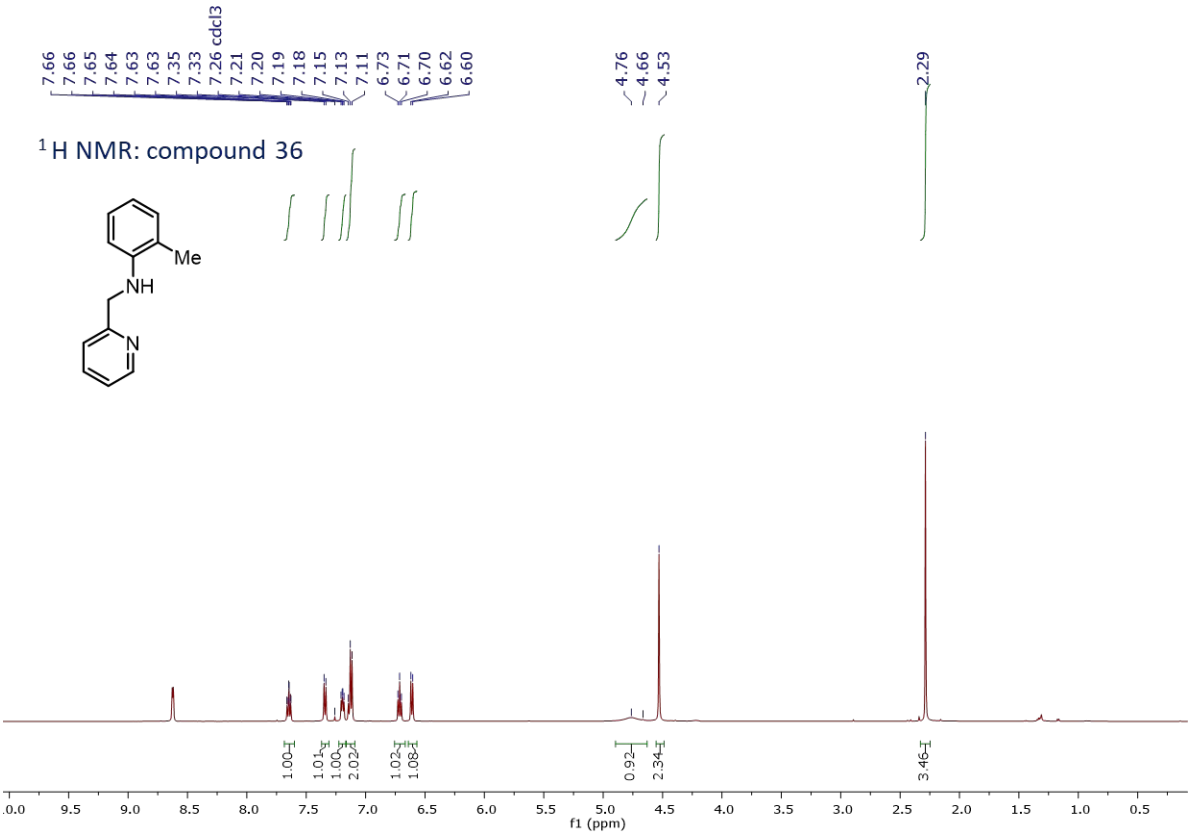


^{1}H NMR: compound 35

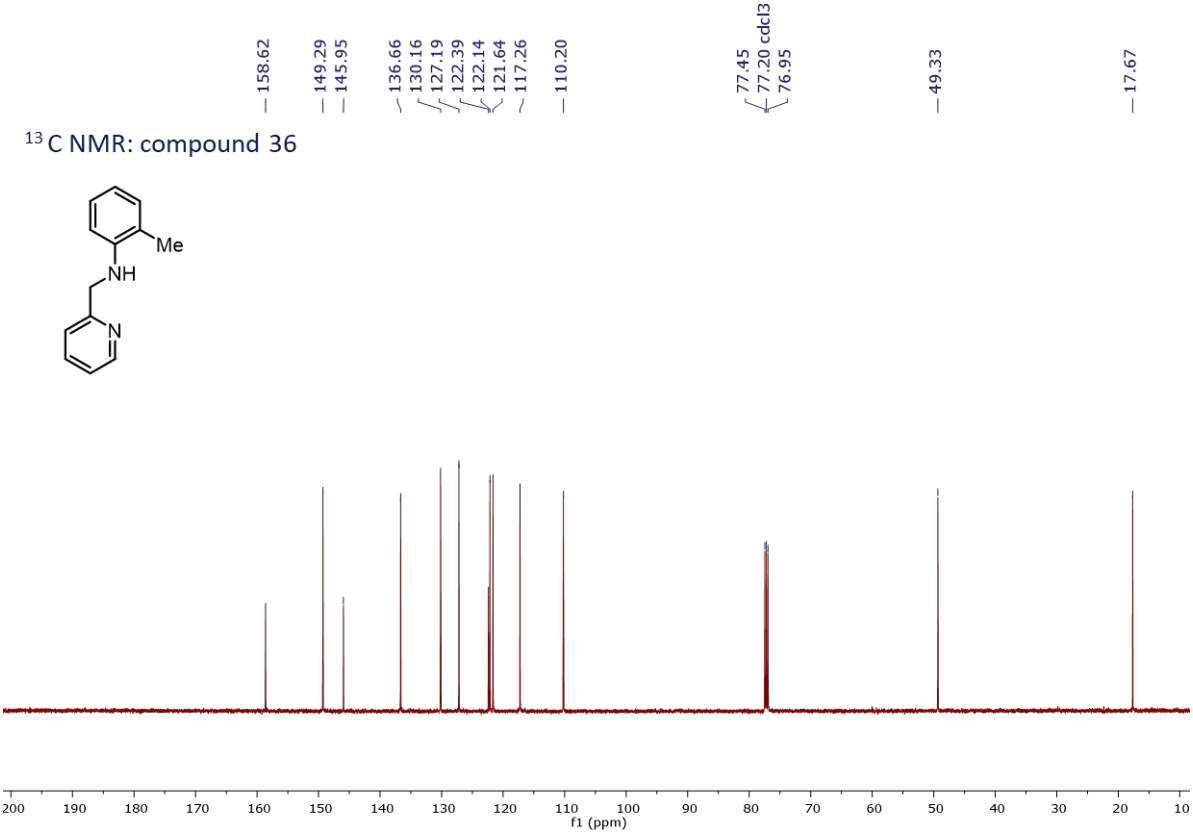


^{13}C NMR: compound 35



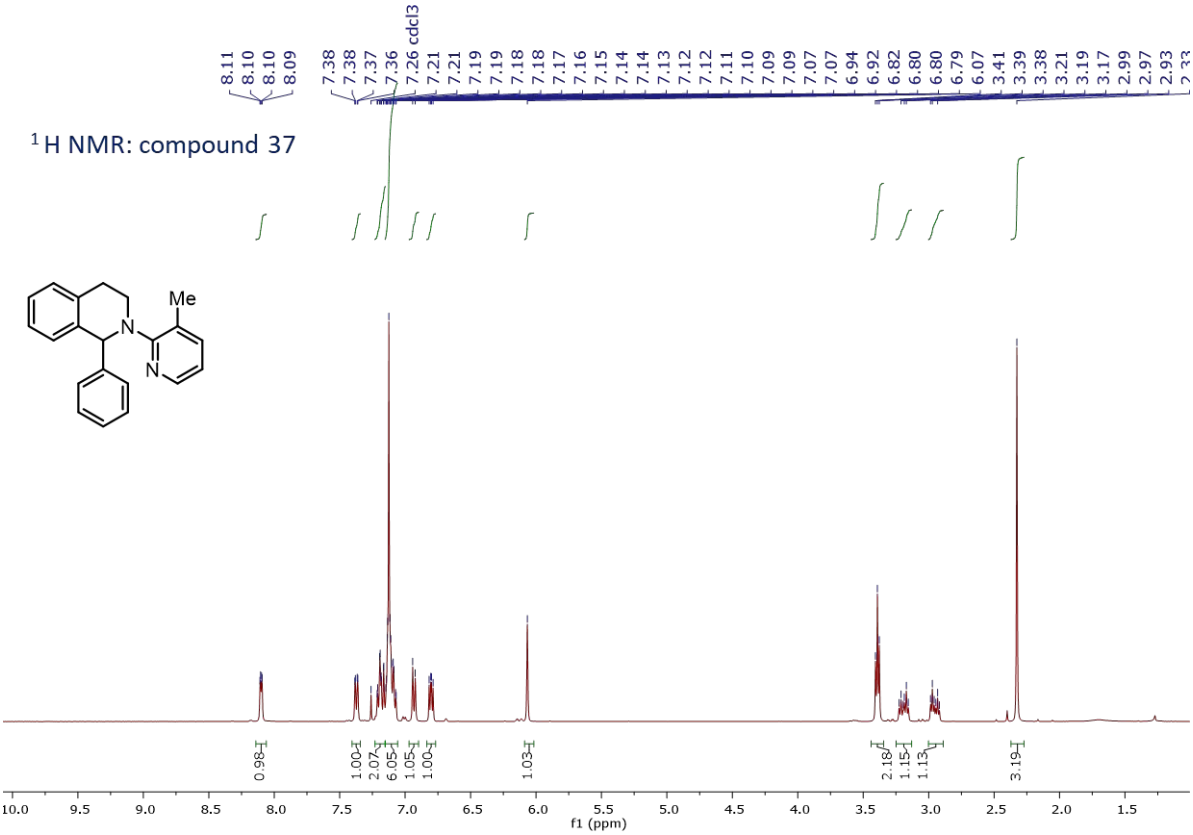


^{1}H NMR: compound 36

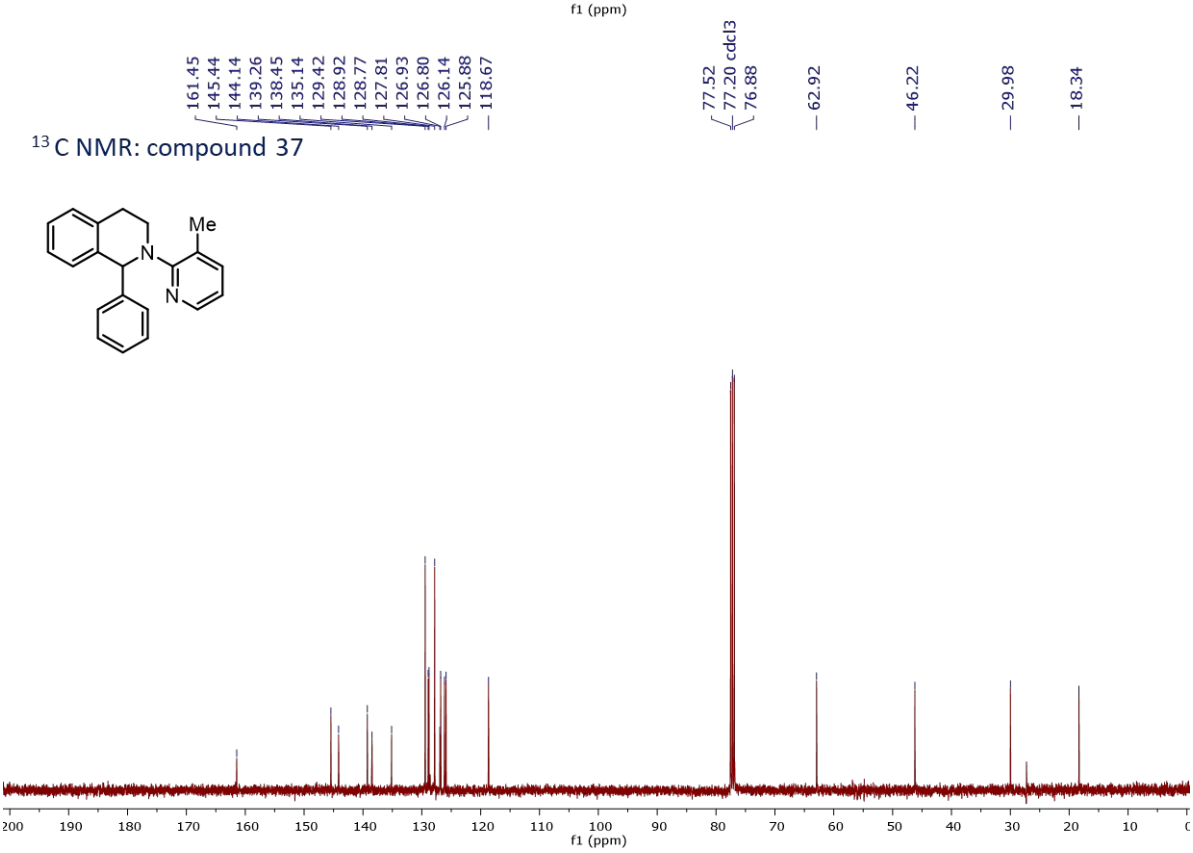


^{13}C NMR: compound 36

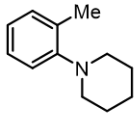
^{1}H NMR: compound 37



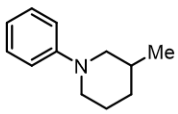
^{13}C NMR: compound 37



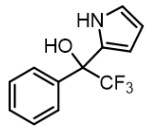
^{1}H NMR: compound 38



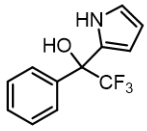
^{13}C NMR: compound 39



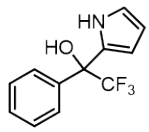
^{1}H NMR: L1



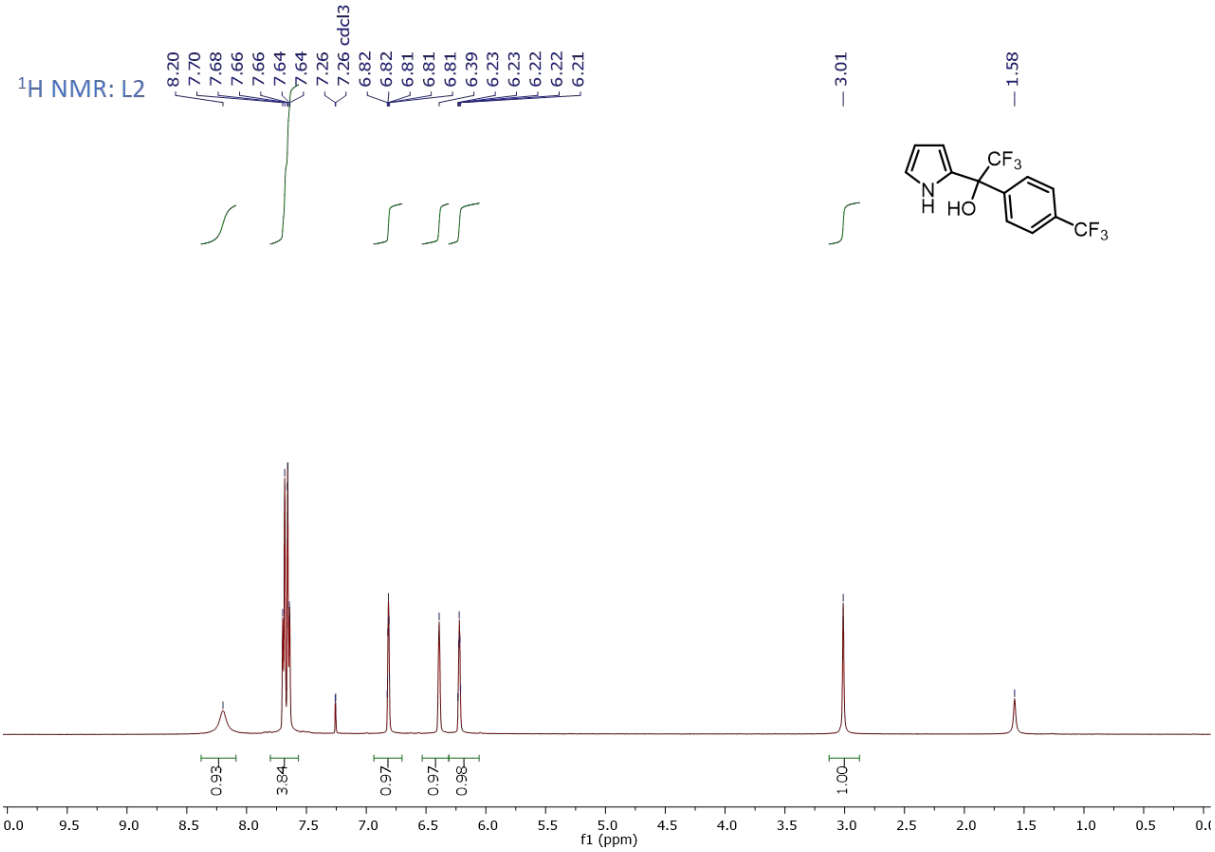
^{13}C NMR: L1



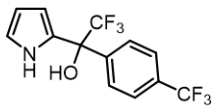
^{19}F NMR: L1



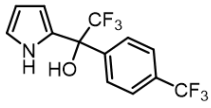
^{1}H NMR: L2



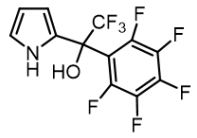
^{13}C NMR: L2

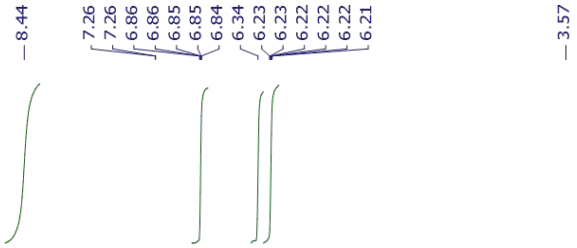


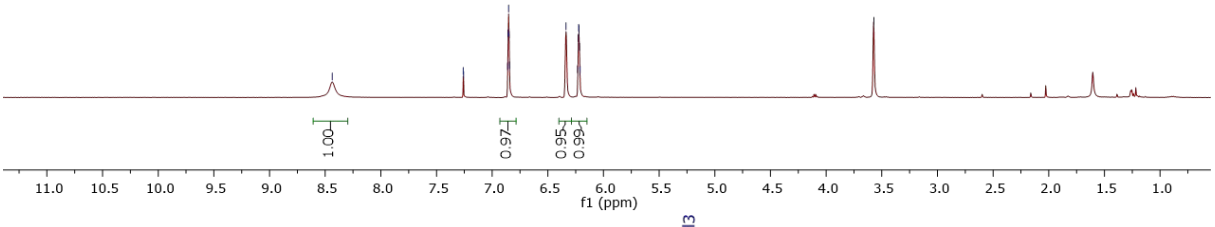
^{19}F NMR: L2

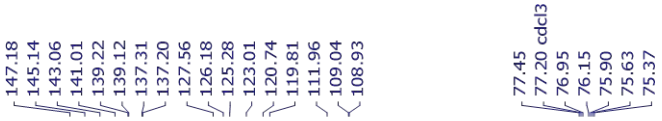


^{1}H NMR: L3

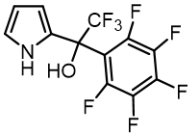




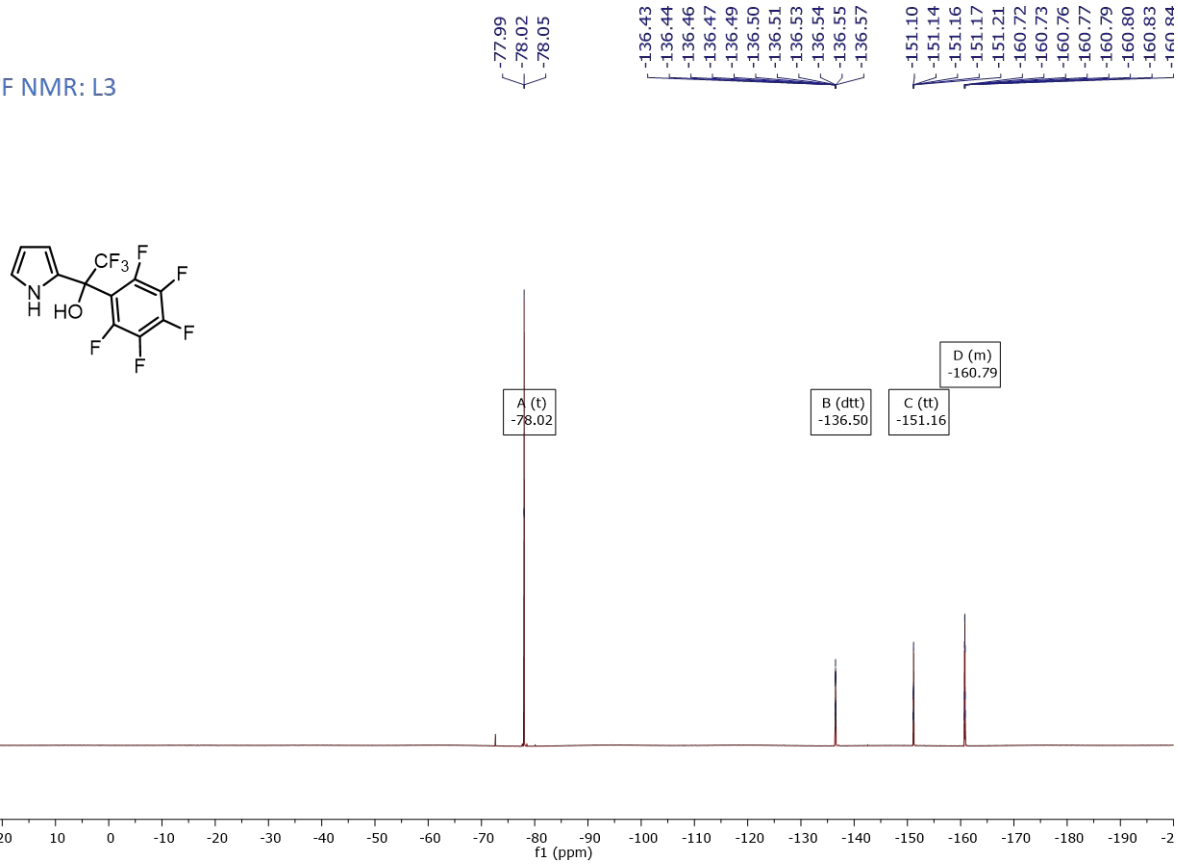




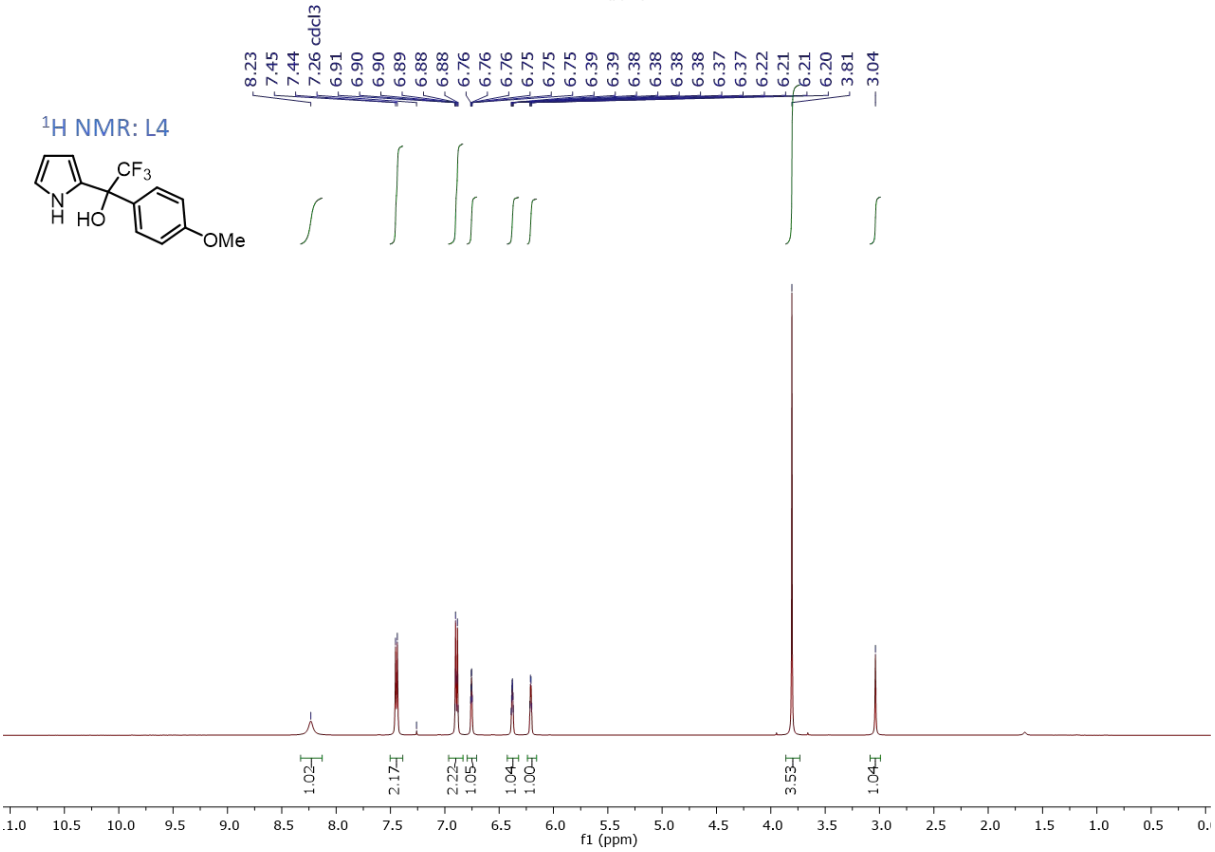
^{13}C NMR: L3

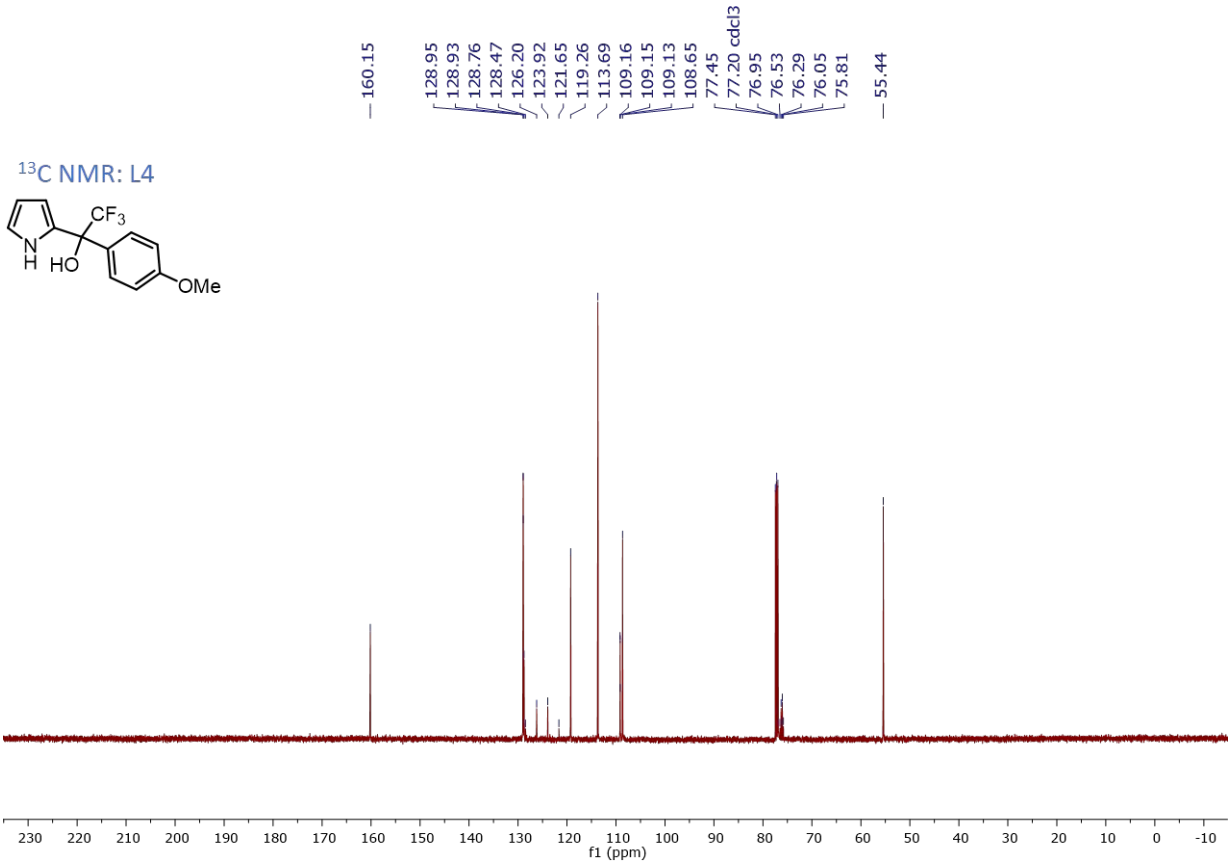


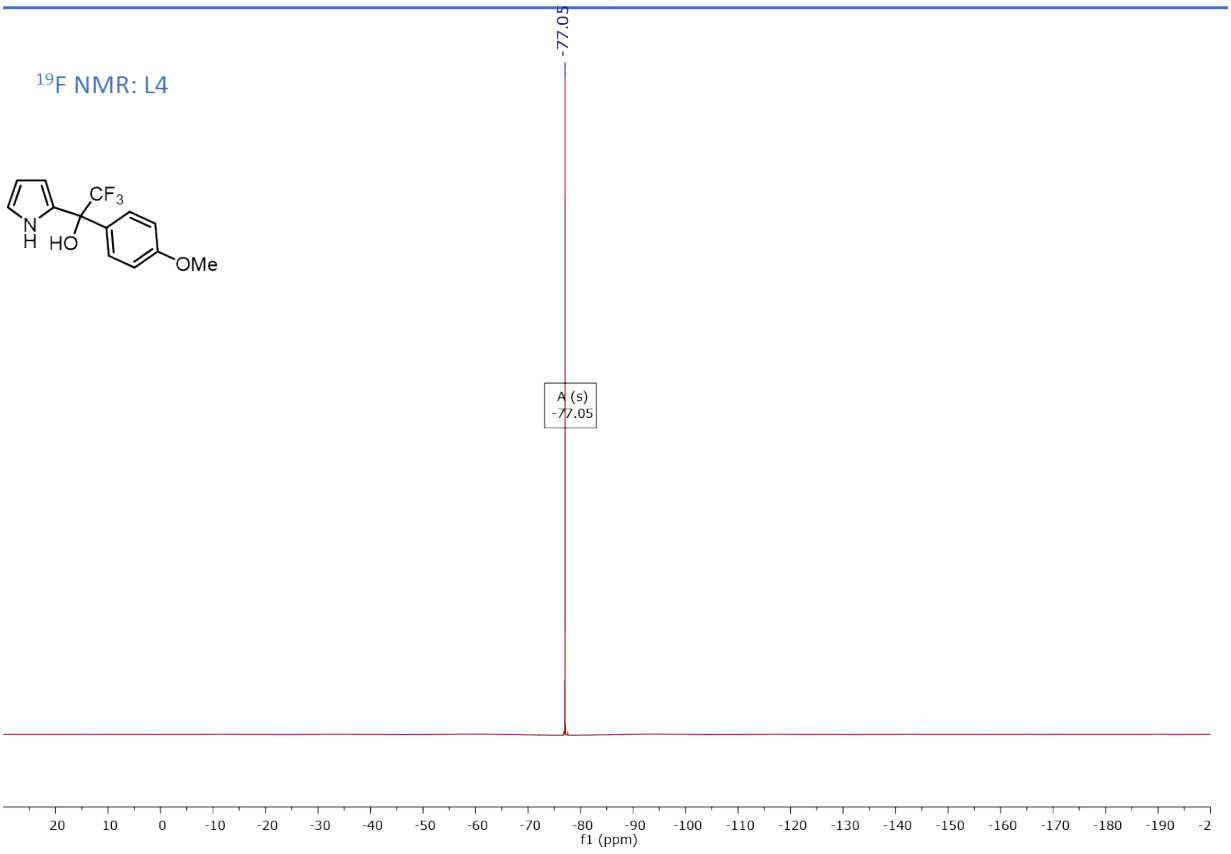
^{19}F NMR: L3



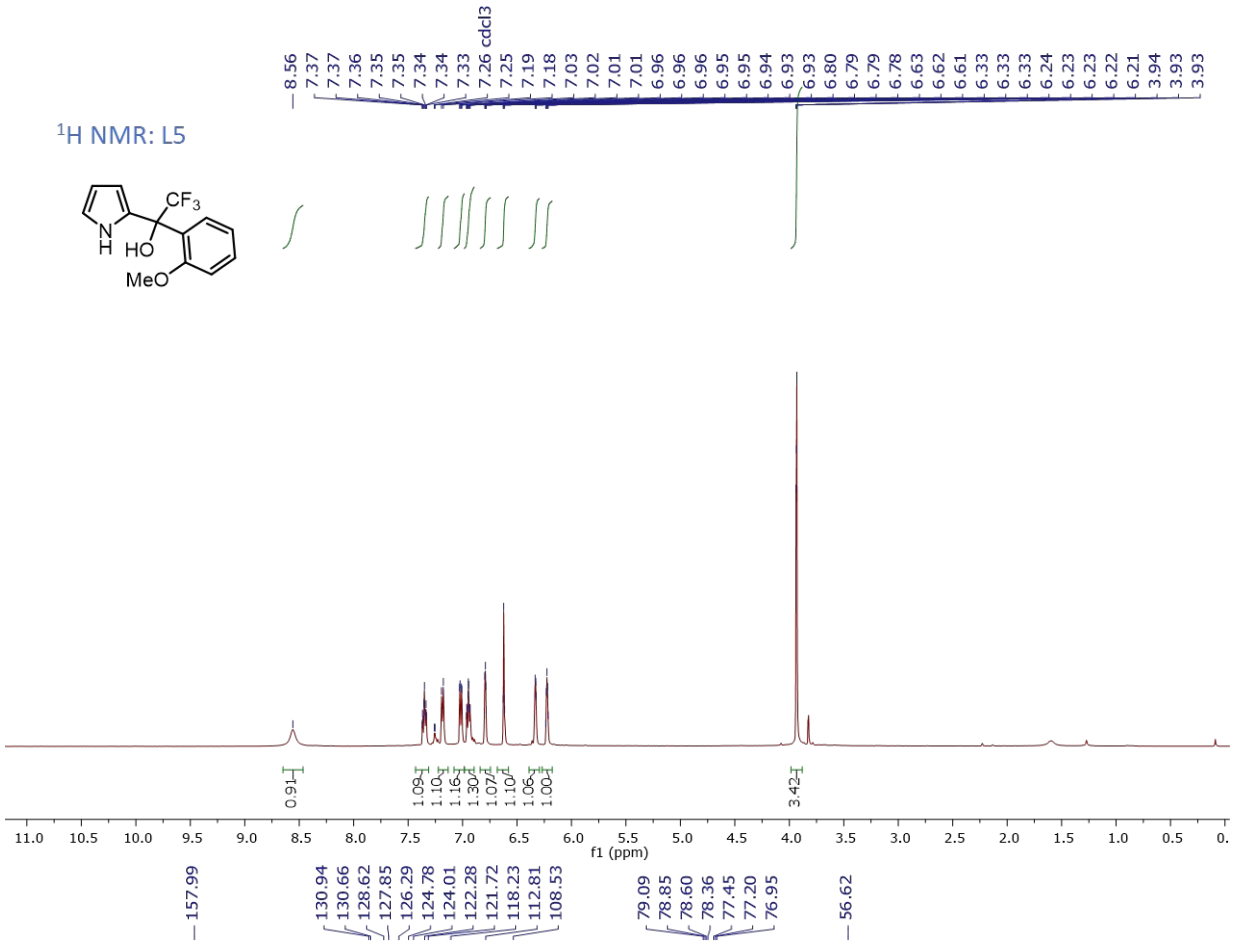
^{1}H NMR: L4



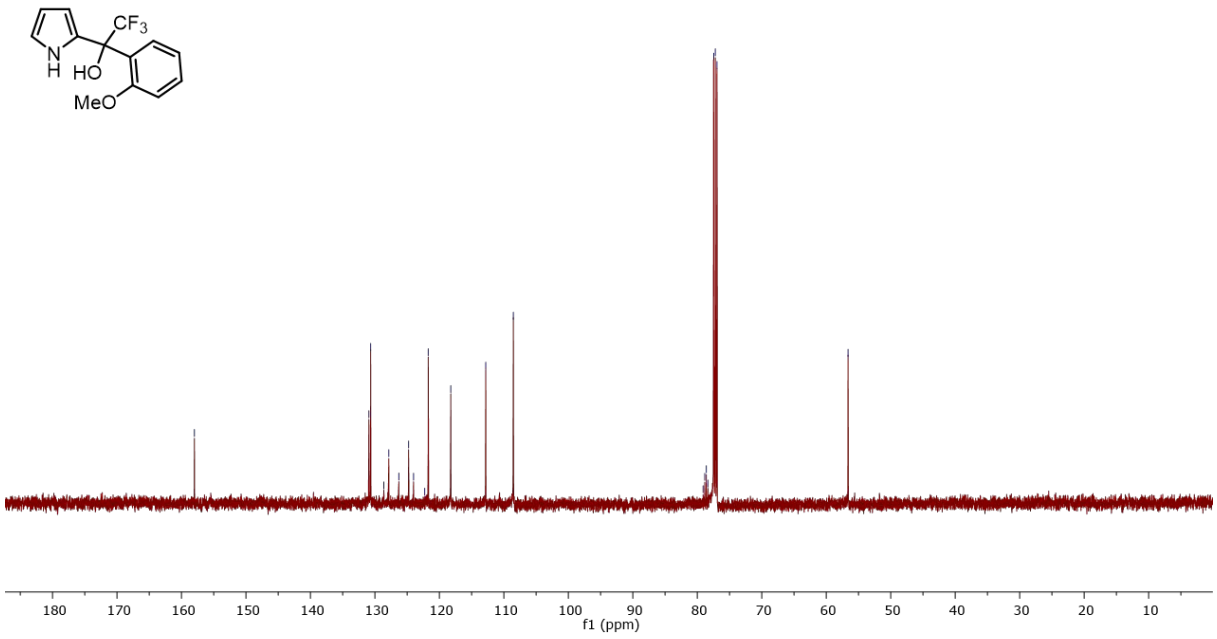

160.15
128.95
128.93
128.76
128.47
126.20
123.92
121.65
119.26
113.69
109.16
109.15
109.13
108.65
77.45
77.20 cdcl3
76.95
76.53
76.29
76.05
75.81
55.44
13C NMR: L4
CF3
N
H
HO
OMe
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-77.05
19F NMR: L4
CF3
N
H
HO
OMe
A (s)
-77.05
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
f1 (ppm)

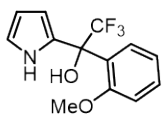
^{1}H NMR: L5



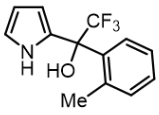
^{13}C NMR: L5

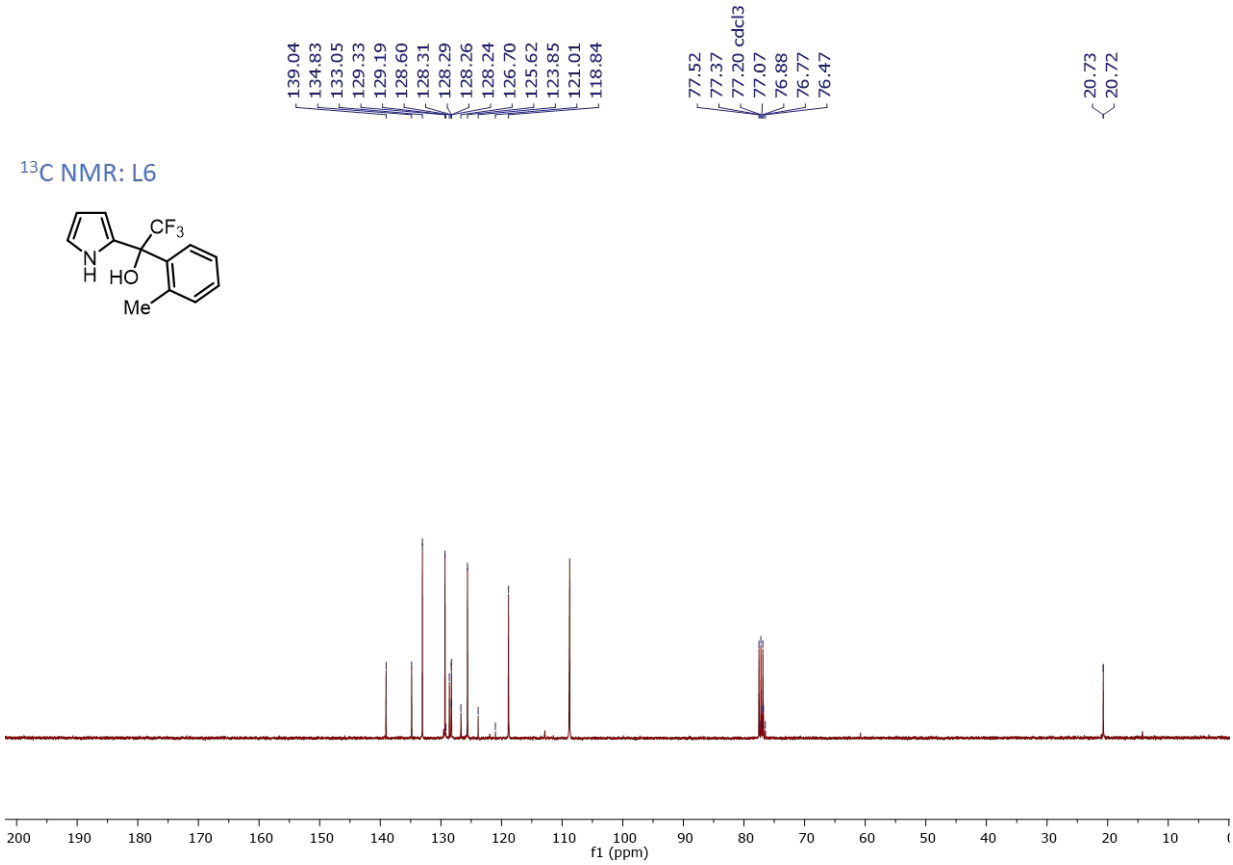


^{19}F NMR: L5

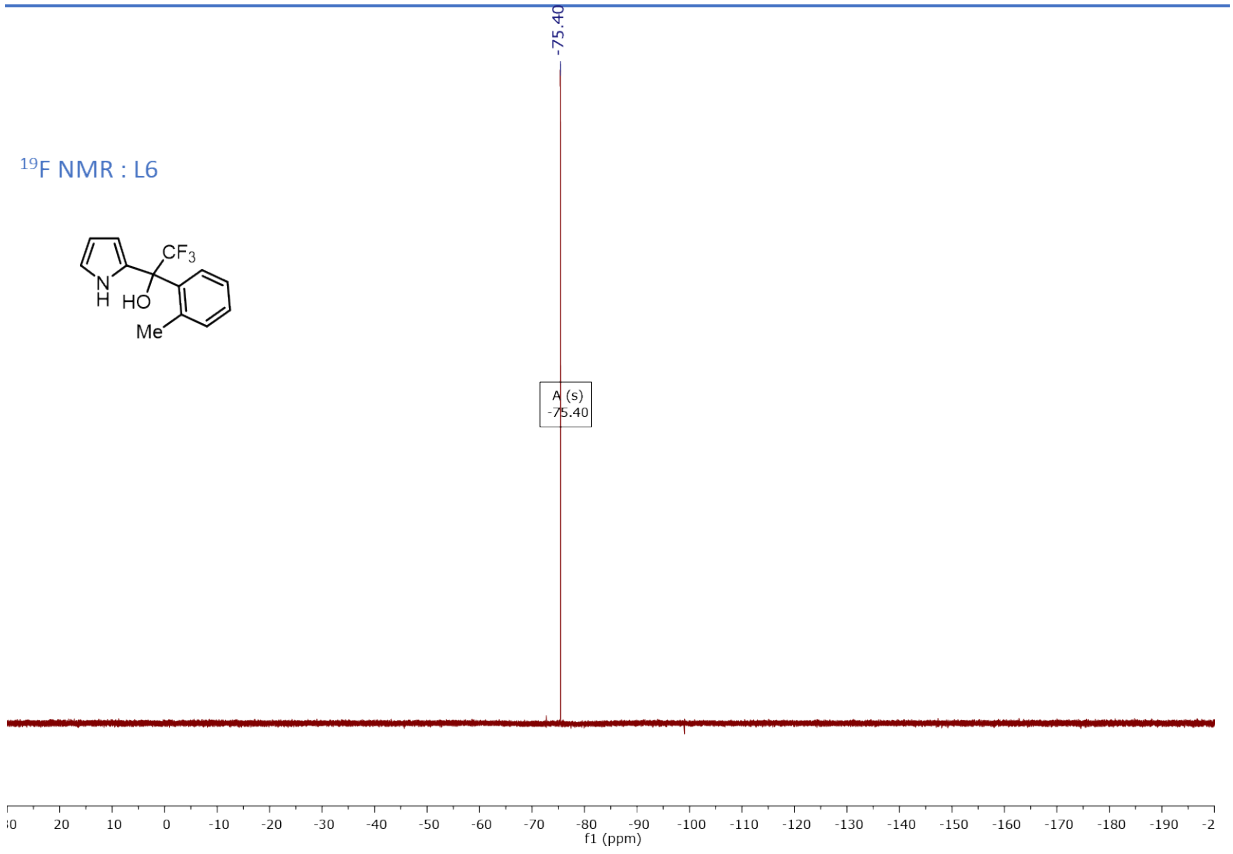


^{1}H NMR: L6



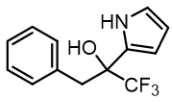


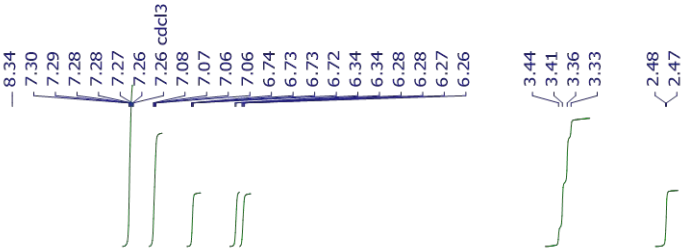
^{13}C NMR: L6

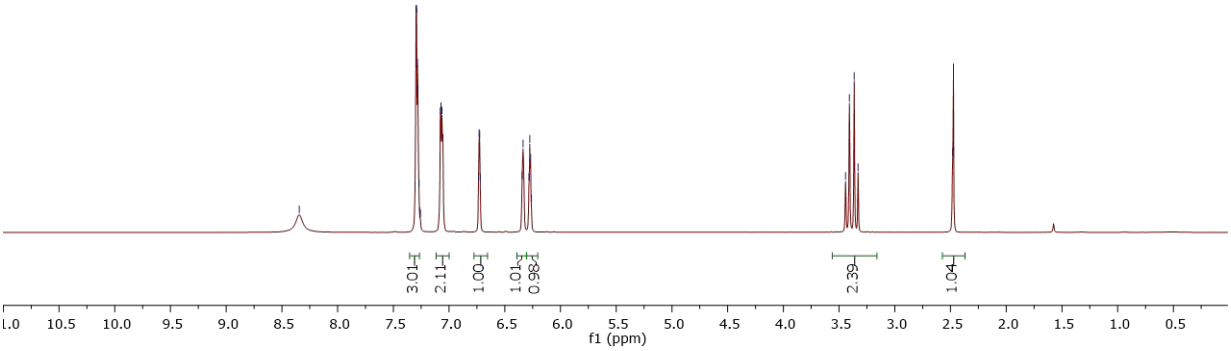


^{19}F NMR : L6

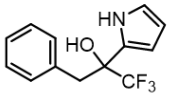
^{1}H NMR: L7



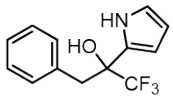




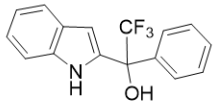
^{13}C NMR: L7



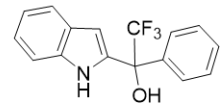
^{19}F NMR : L7

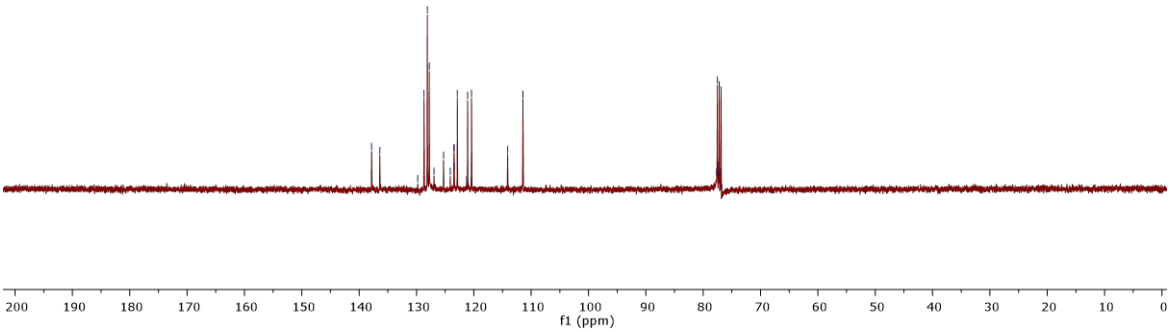


^{1}H NMR: L9

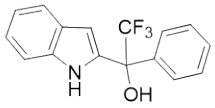


^{13}C NMR: L9

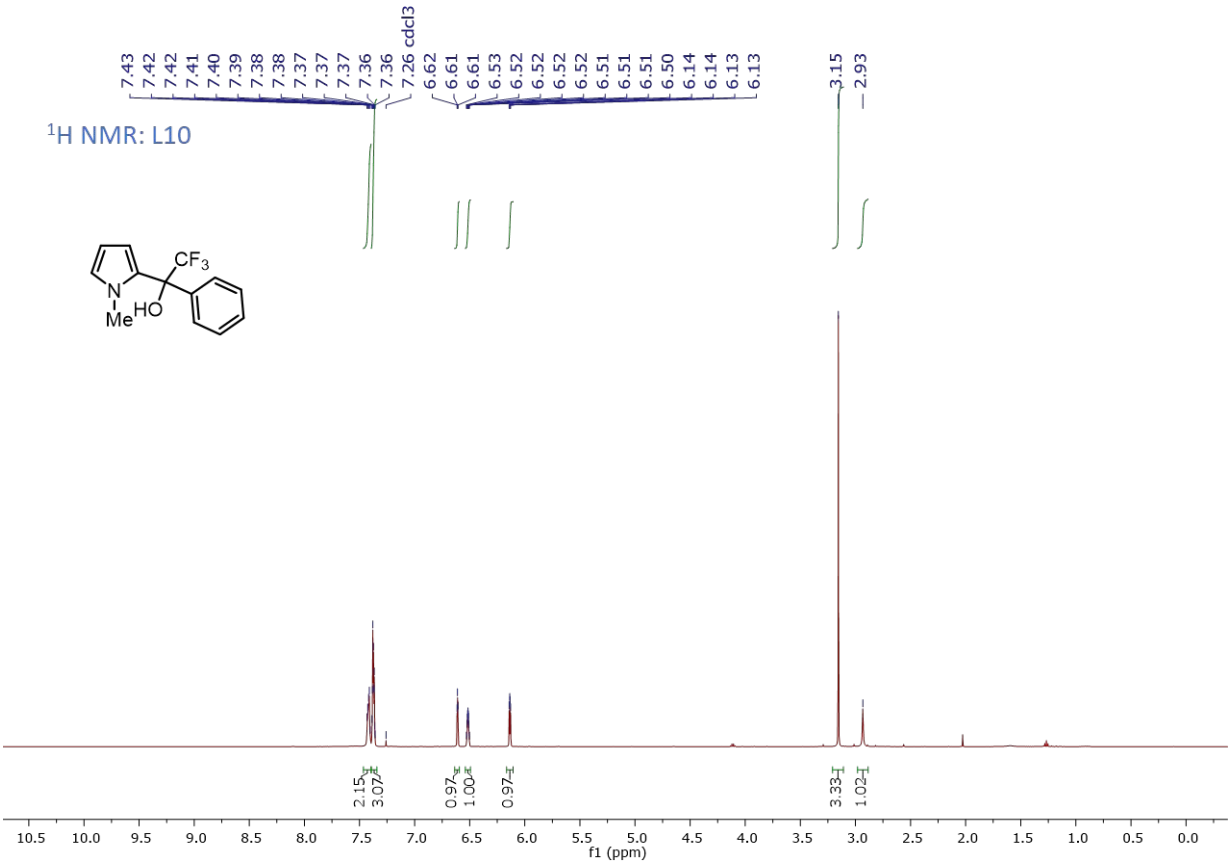




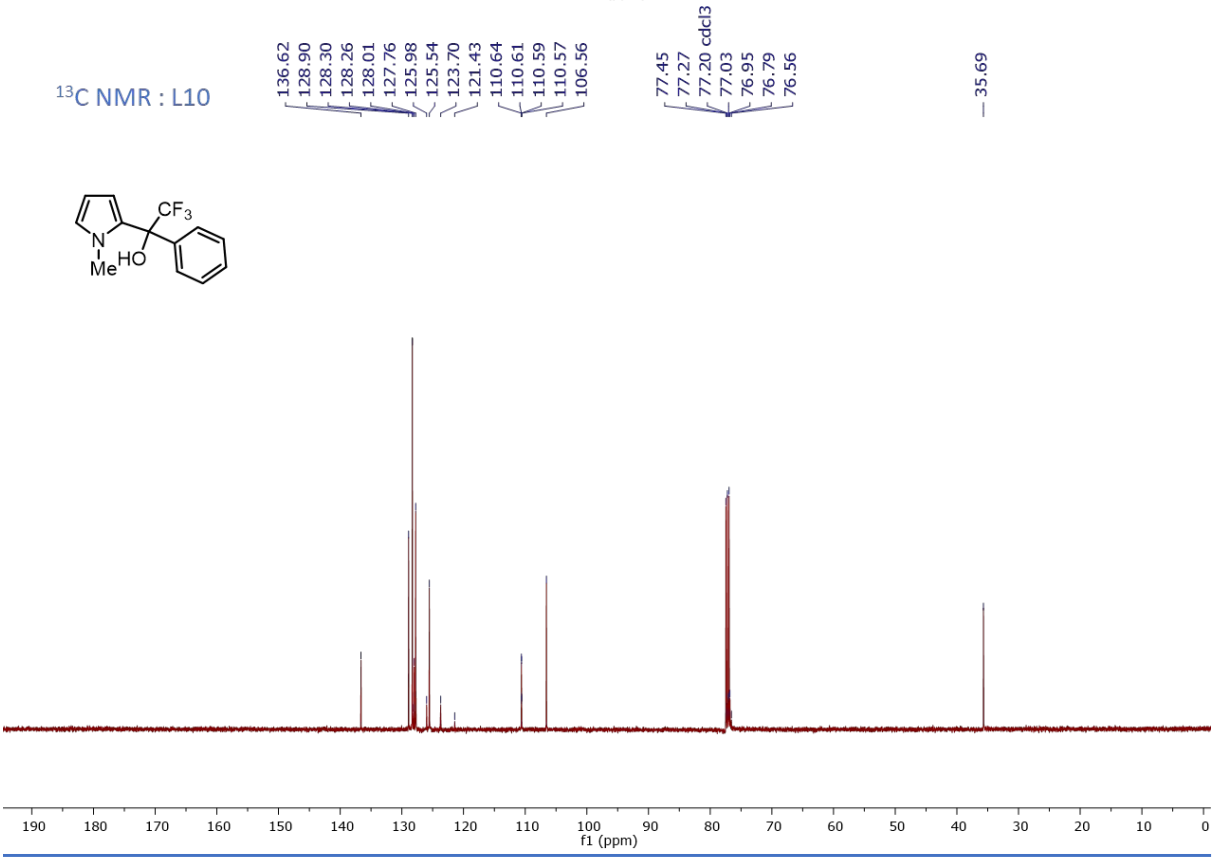
^{19}F NMR : L9



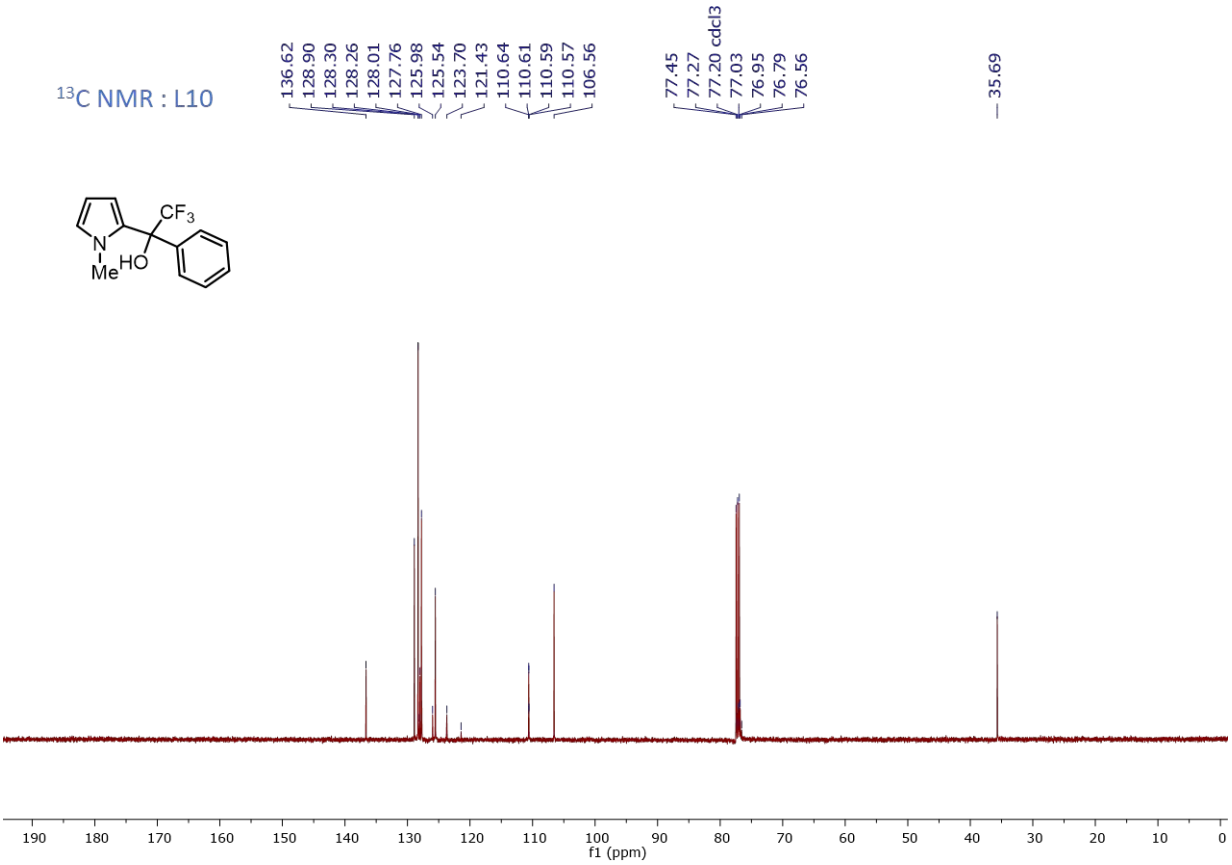
^{1}H NMR: L10



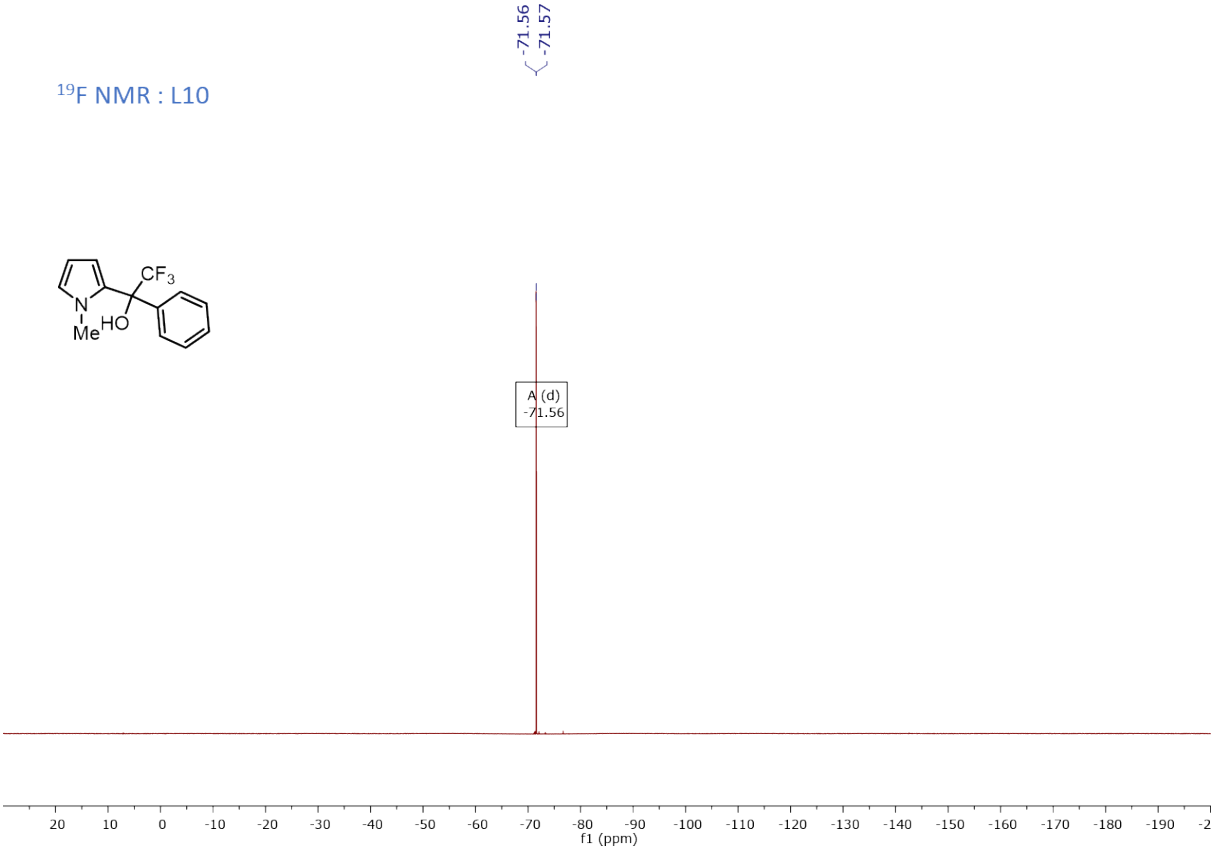
^{13}C NMR : L10



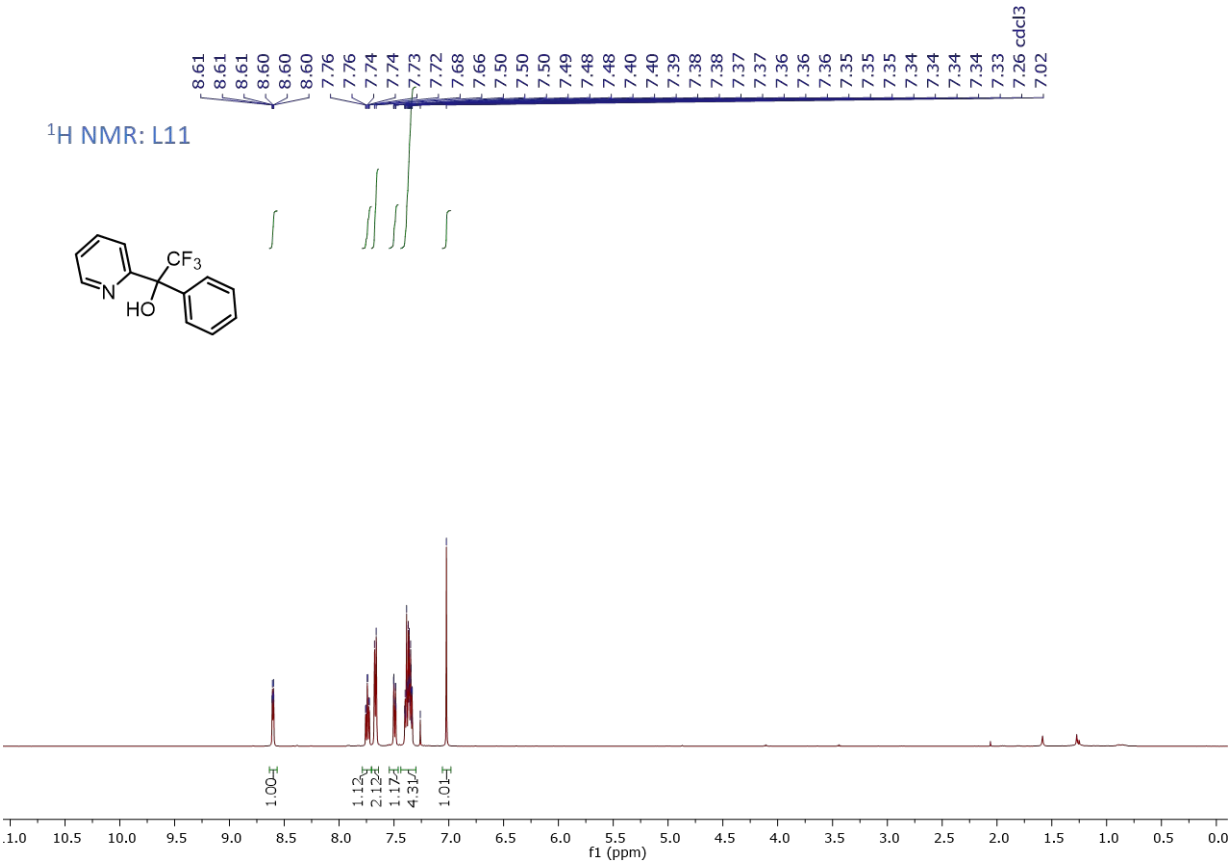
^{13}C NMR : L10



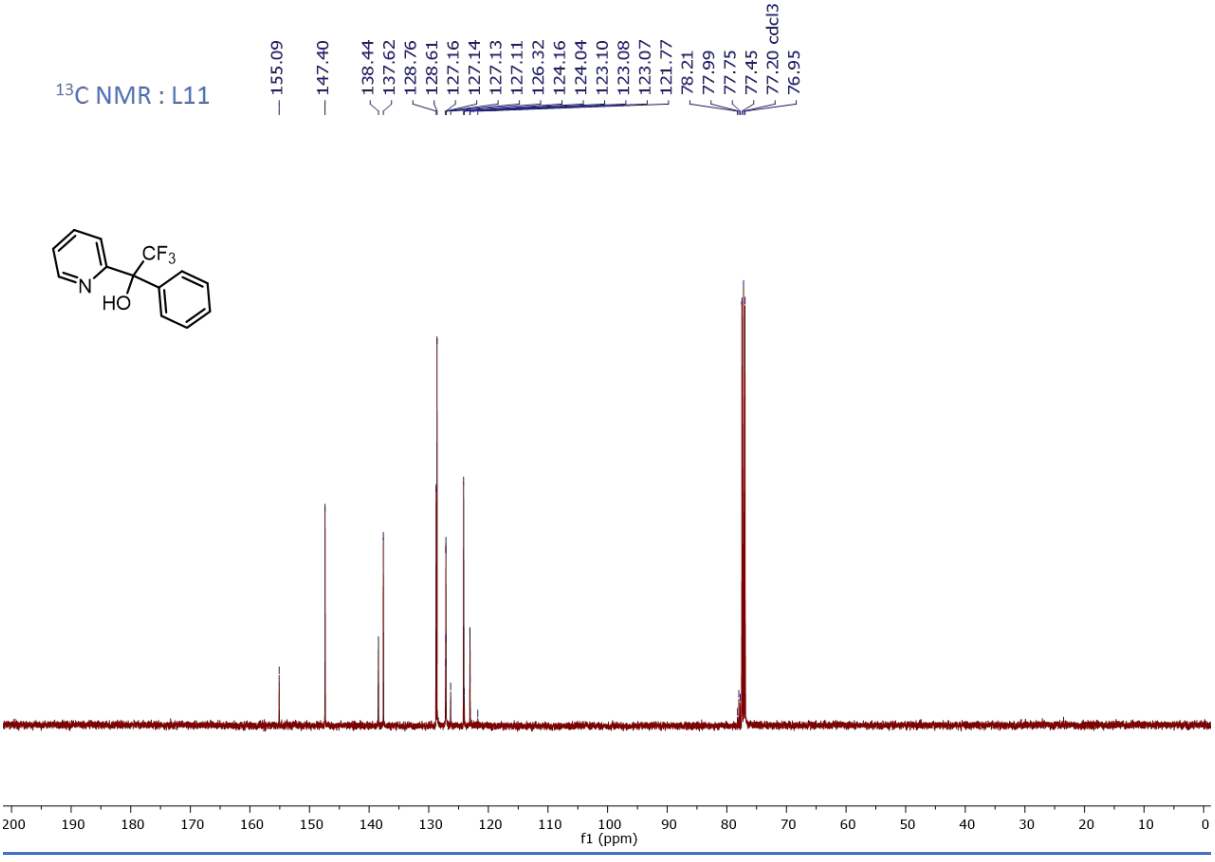
^{19}F NMR : L10



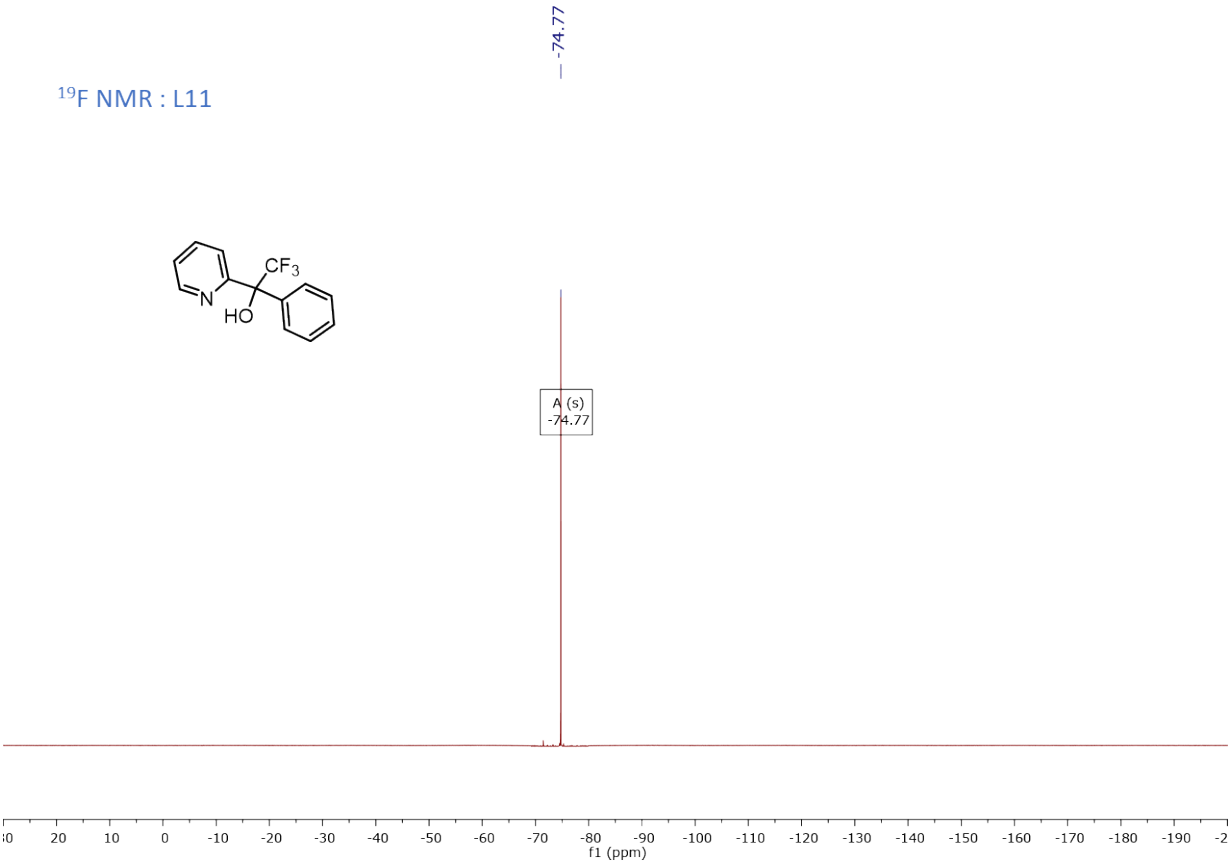
^{1}H NMR: L11



^{13}C NMR : L11



^{19}F NMR : L11



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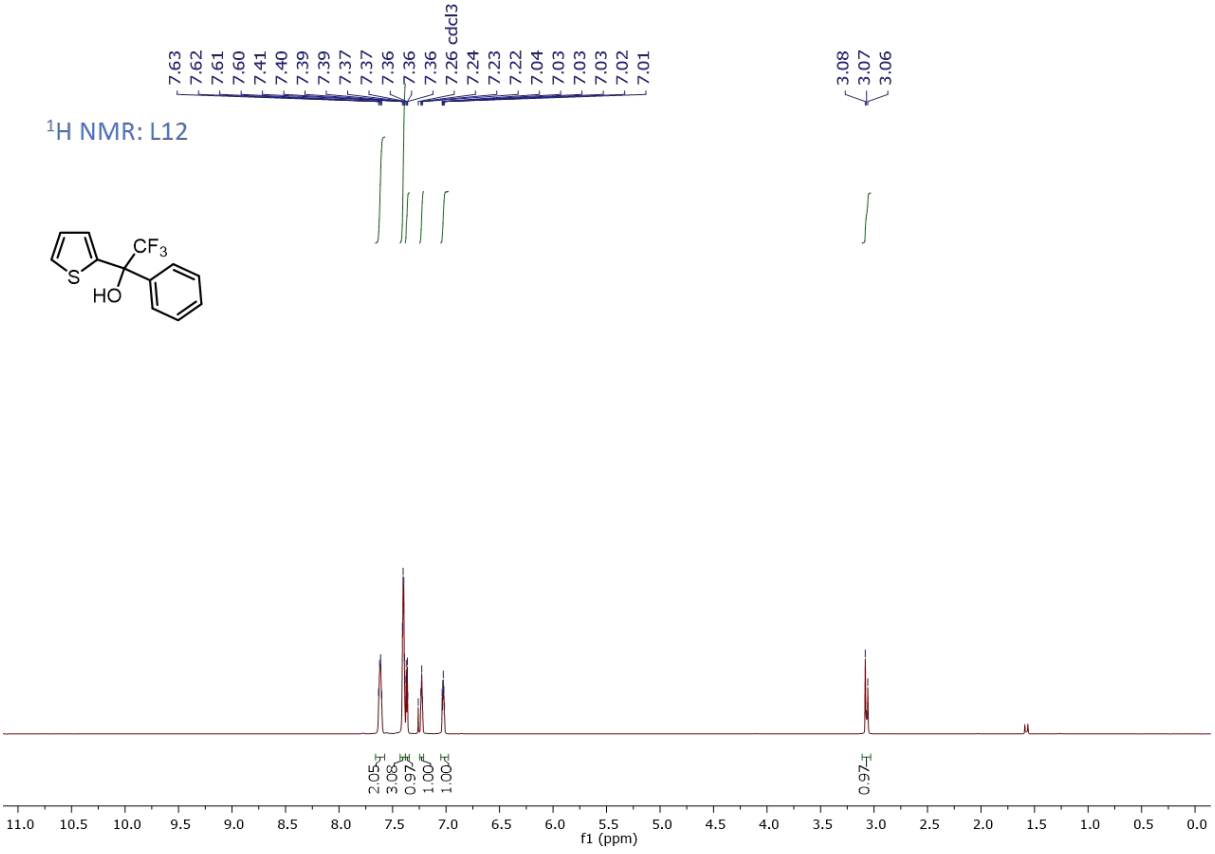

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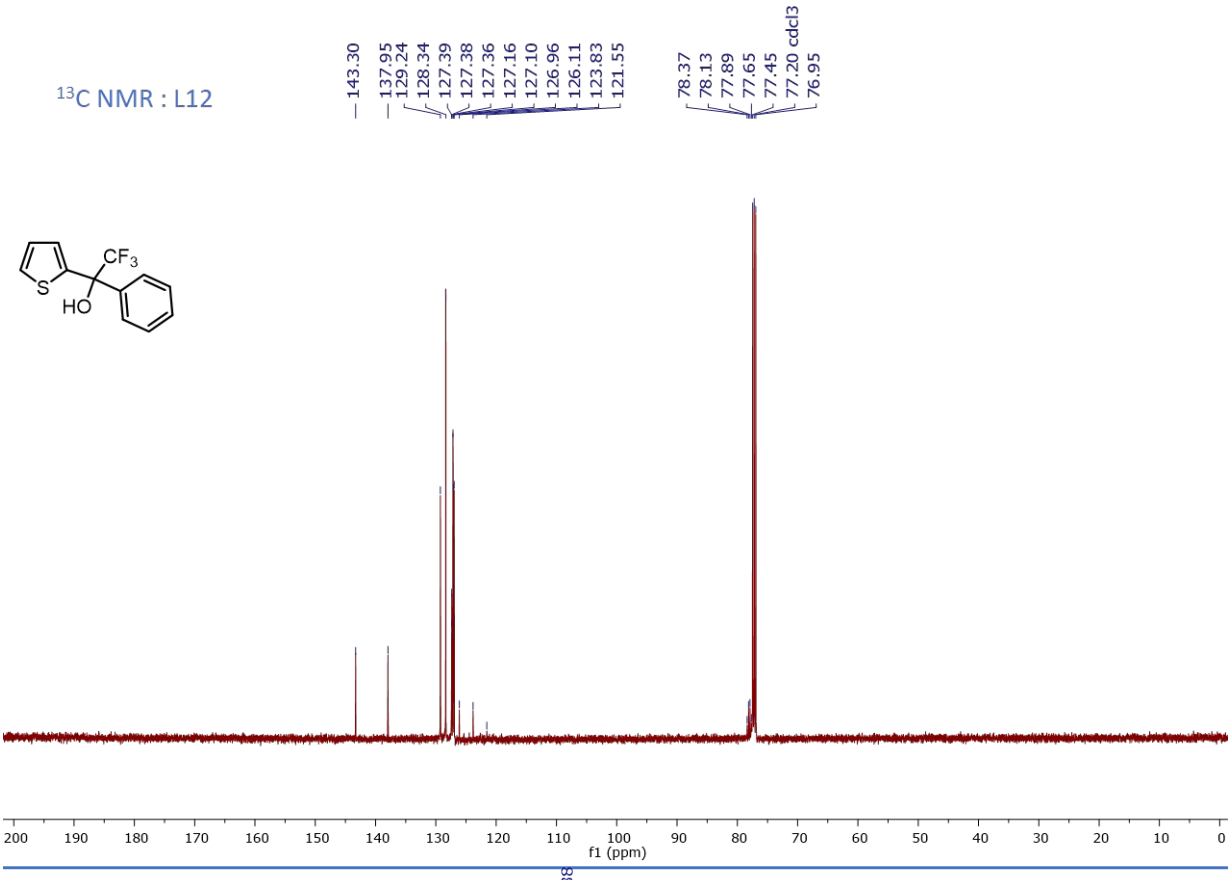

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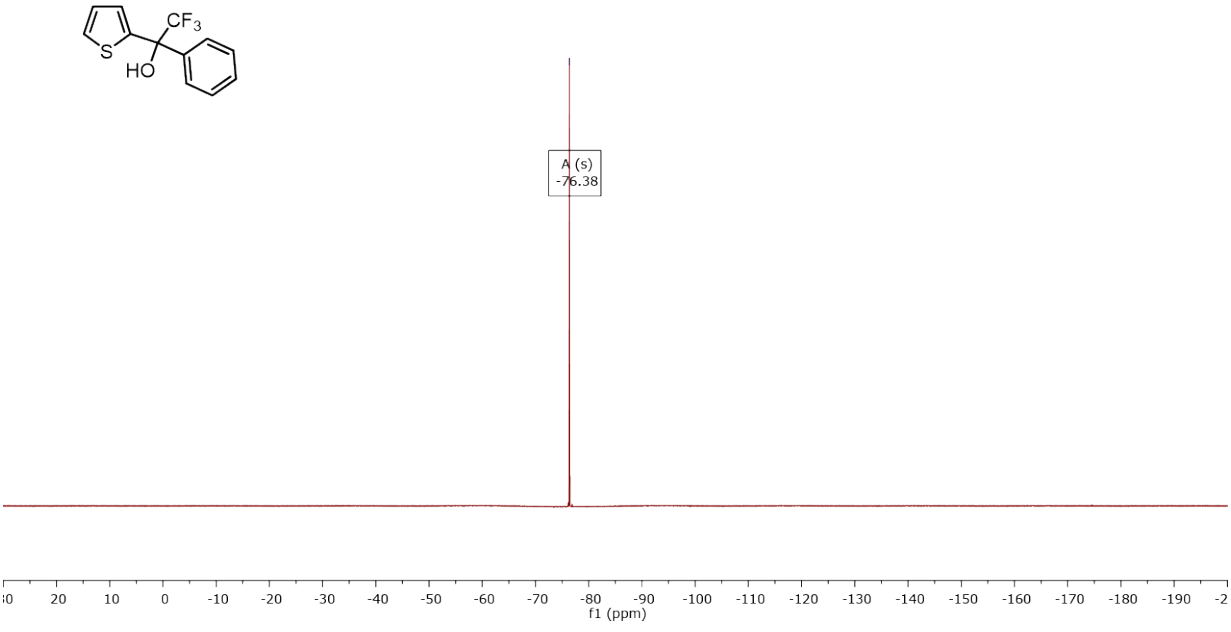

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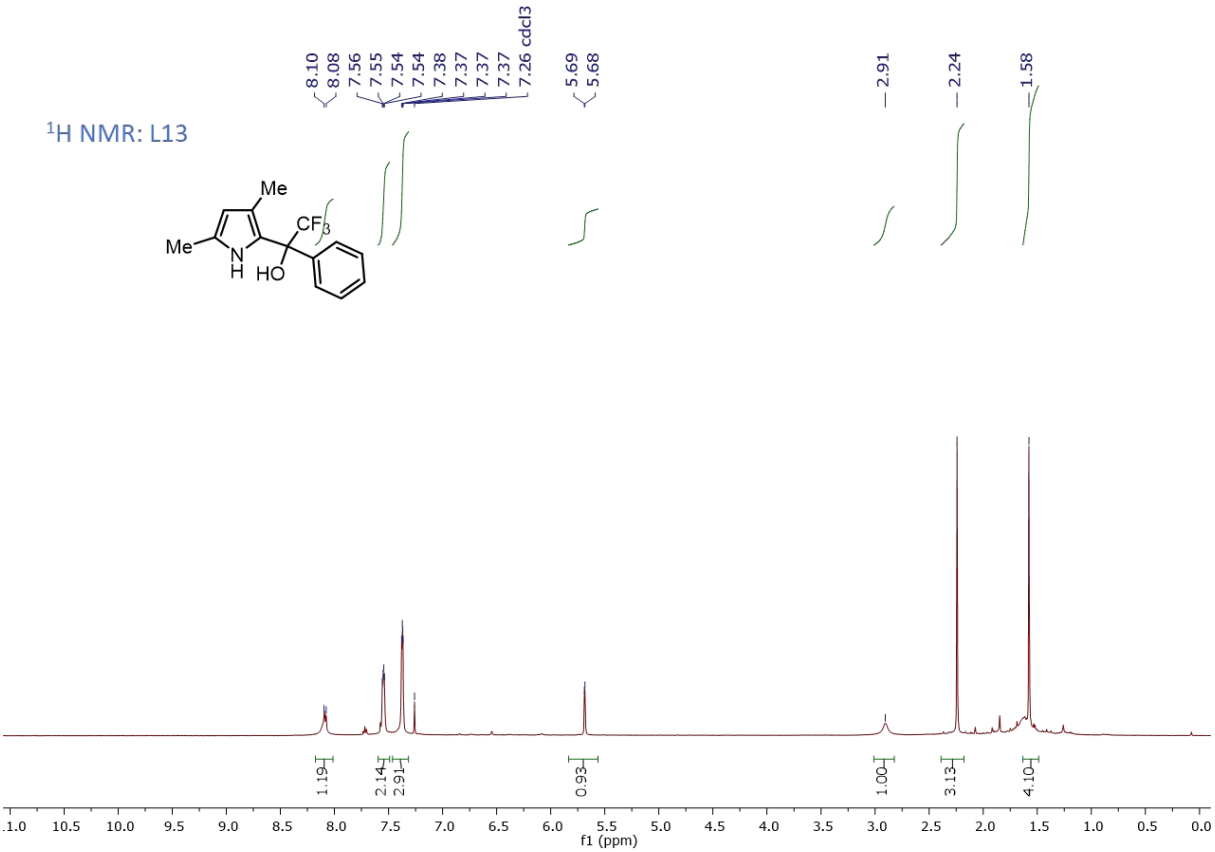

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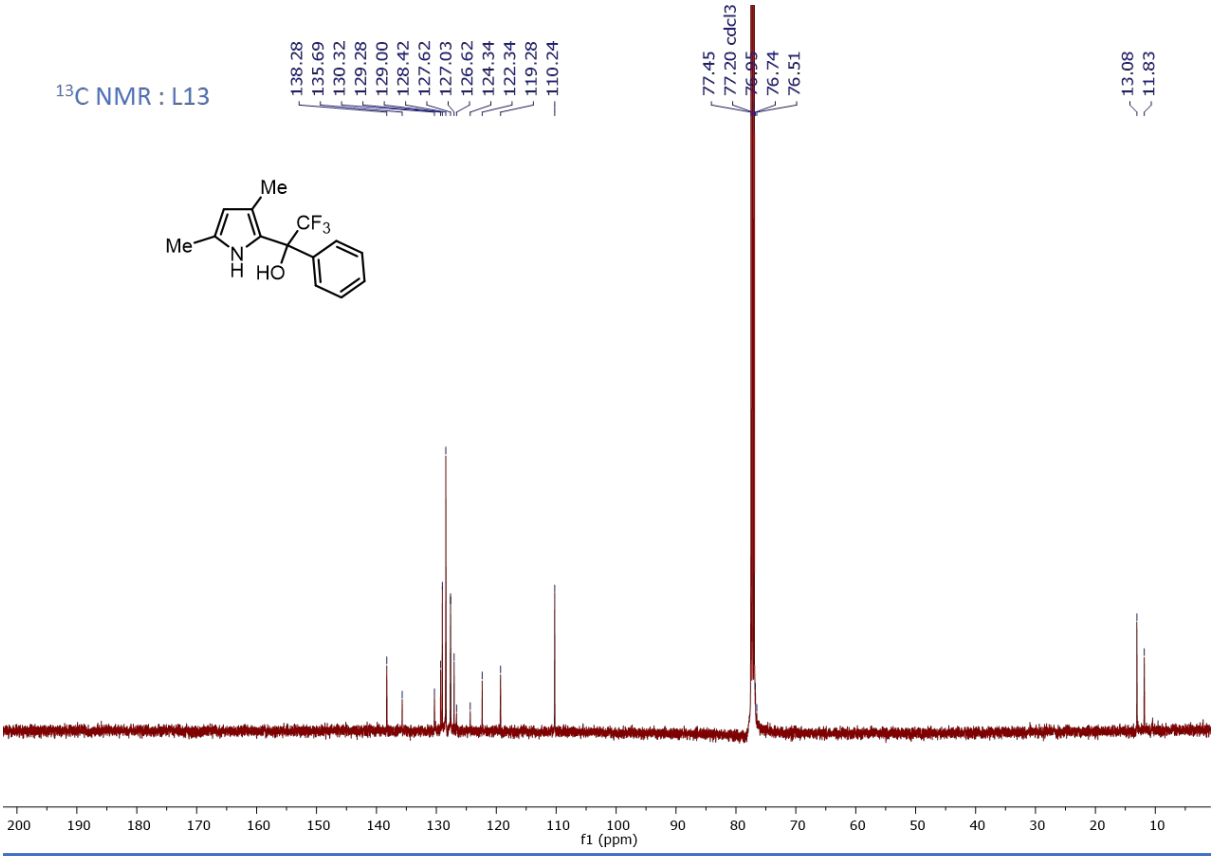
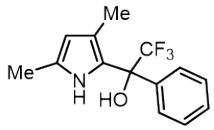


^{19}F NMR : L13



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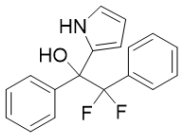
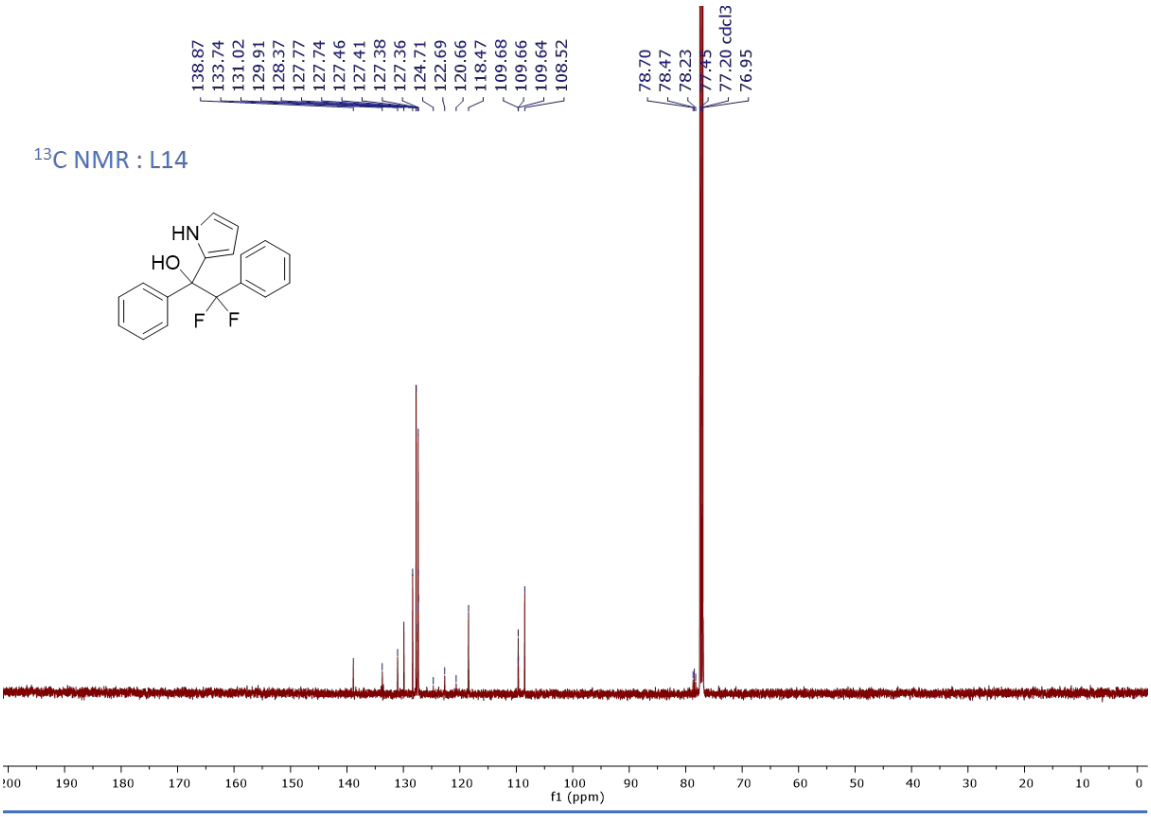
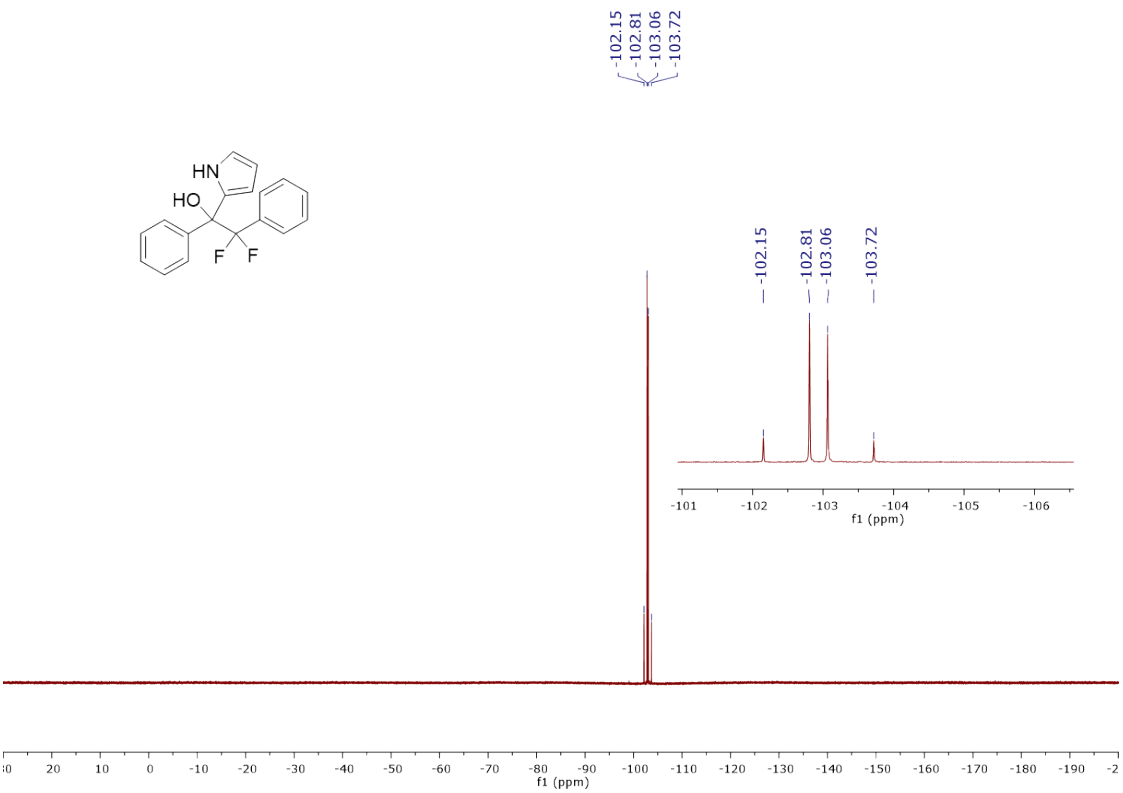
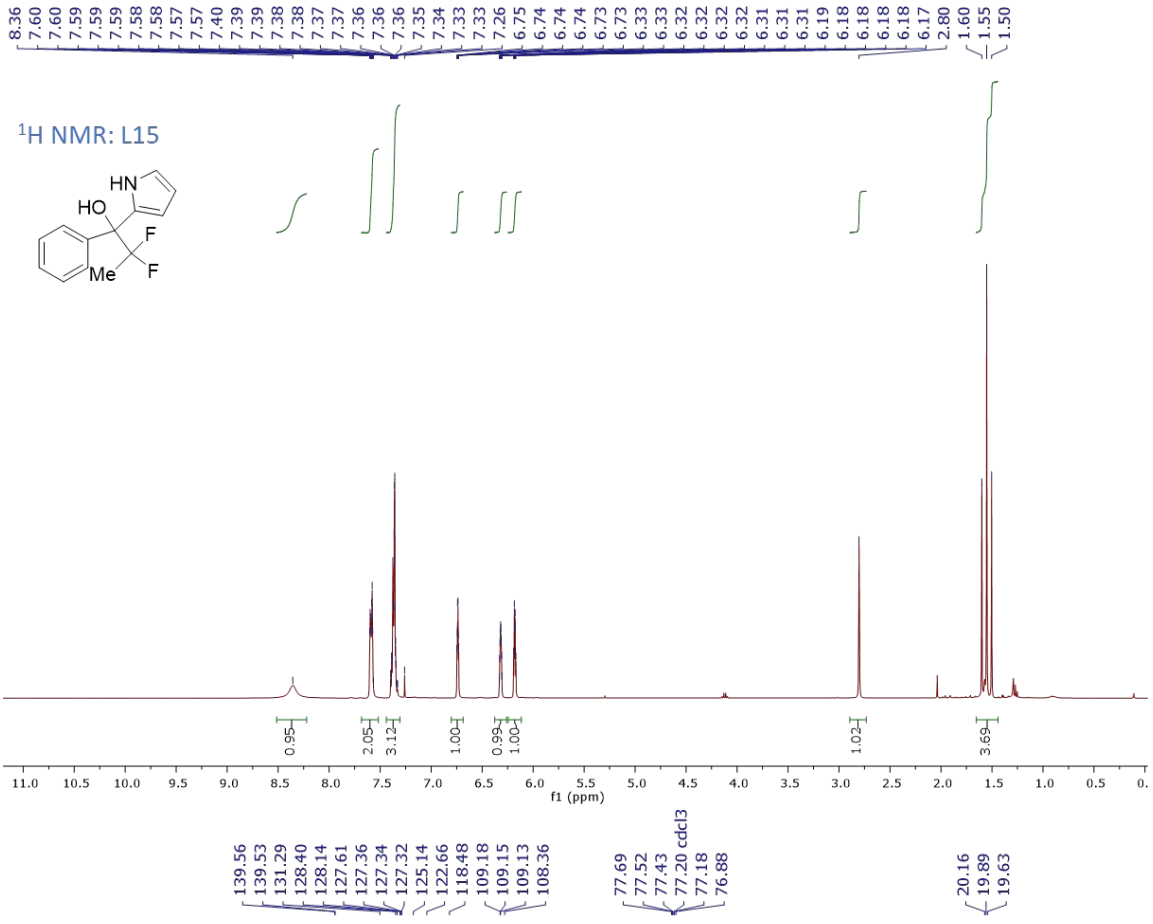
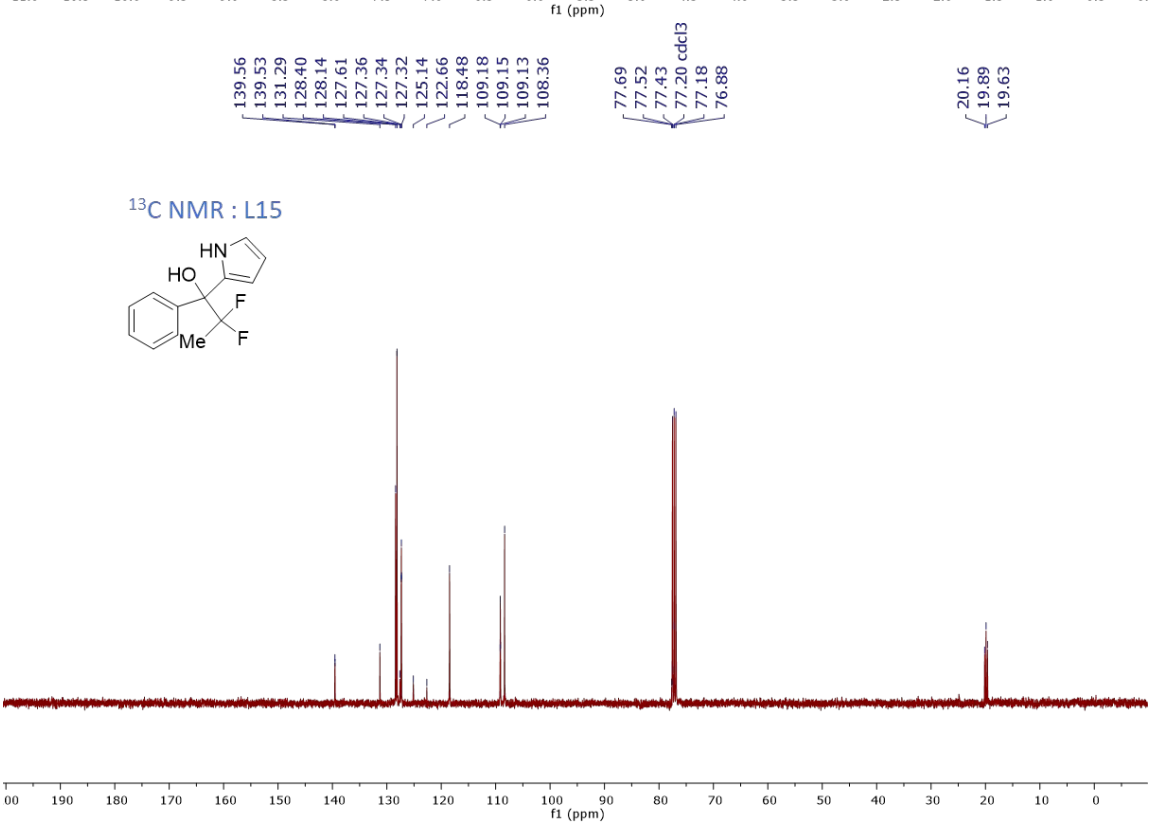


^{13}C NMR : L14

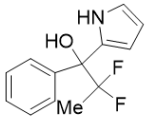

138.87
133.74
131.02
129.91
128.37
127.77
127.74
127.46
127.41
127.38
127.36
124.71
122.69
120.66
118.47
109.68
109.66
109.64
108.52
78.70
78.47
78.23
77.45
77.20 cdcl3
76.95
HN
HO
F
F
f1 (ppm)


-102.15
-102.81
-103.06
-103.72
HN
HO
F
F
f1 (ppm)

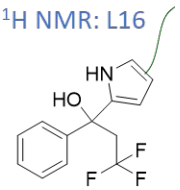

8.36 7.60 7.60 7.59 7.59 7.59 7.58 7.58 7.57 7.57 7.40 7.39 7.39 7.38 7.38 7.37 7.37 7.36 7.36 7.36 7.35 7.34 7.33 7.33 7.26 6.75 6.74 6.74 6.74 6.73 6.73 6.33 6.33 6.32 6.32 6.32 6.32 6.31 6.31 6.31 6.19 6.18 6.18 6.18 6.18 6.17 2.80 1.60 1.55 1.50
1H NMR: L15
HN
HO
F
F
Me
0.95 2.05 3.12 1.00 0.99 1.00 1.02 3.69
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)


139.56 139.53 131.29 128.40 128.14 127.61 127.36 127.34 127.32 125.14 122.66 118.48 109.18 109.15 109.13 108.36
77.69 77.52 77.43 77.20 cdcl3 77.18 76.88
20.16 19.89 19.63
13C NMR : L15
HN
HO
F
F
Me
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

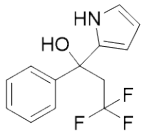
^{19}F NMR : L15



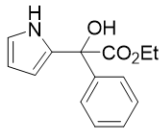
^{1}H NMR: L16



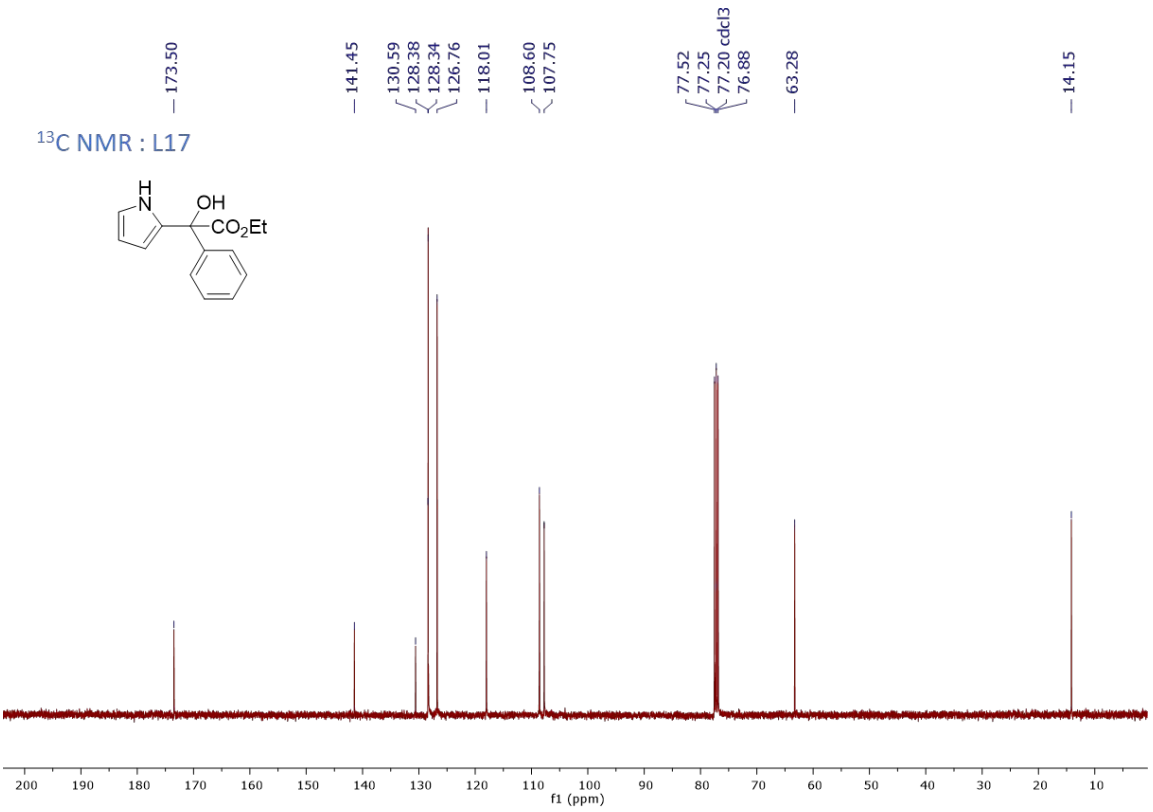
^{19}F NMR : L16



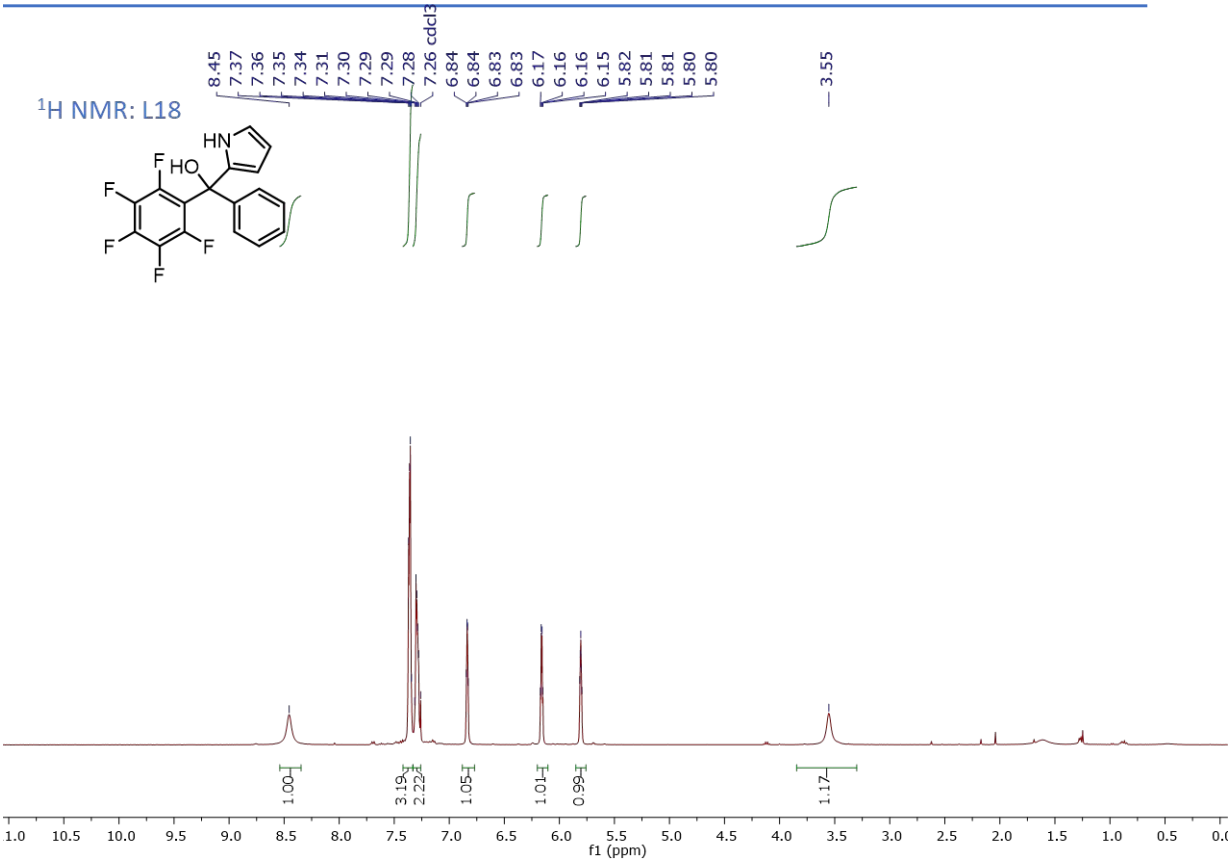
^{1}H NMR: L17



^{13}C NMR : L17

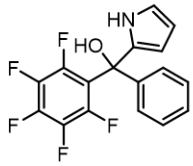


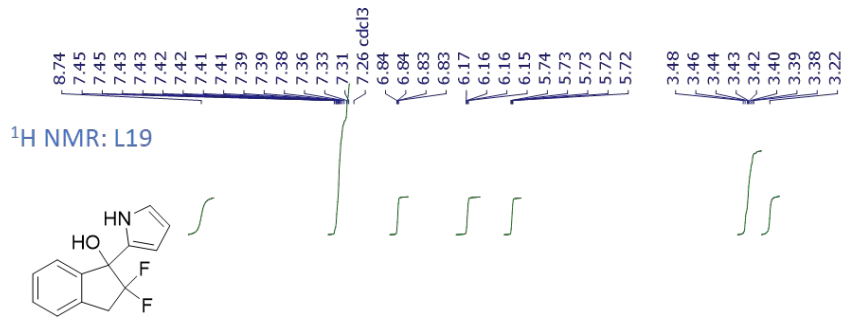
^{1}H NMR: L18



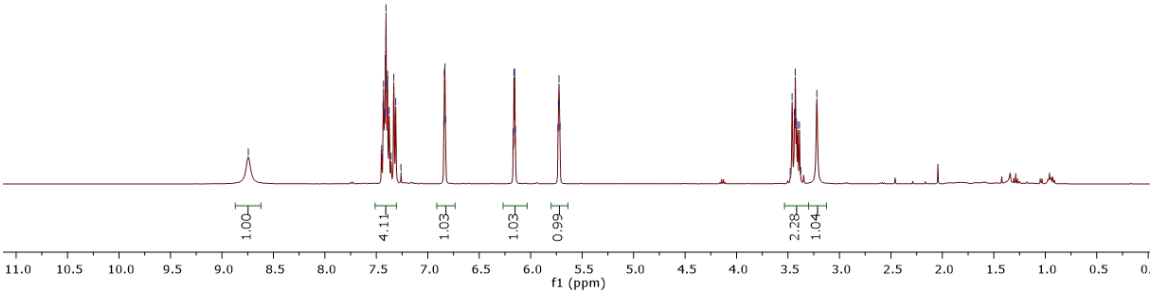
^{13}C NMR : L18

^{19}F NMR : L18

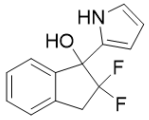


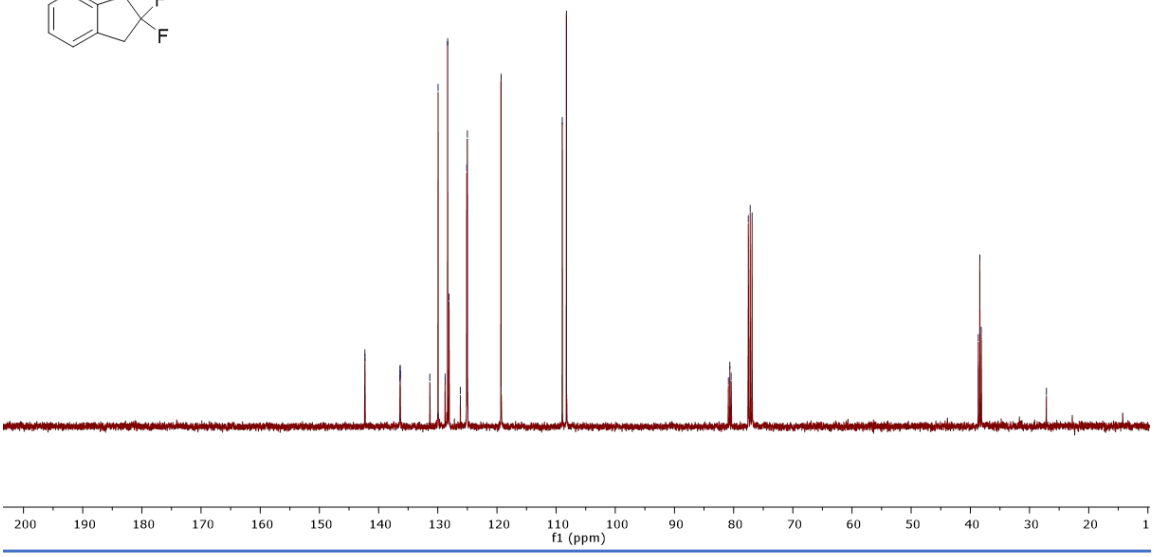


^{1}H NMR: L19

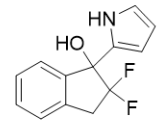


^{13}C NMR : L19

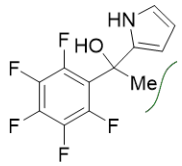




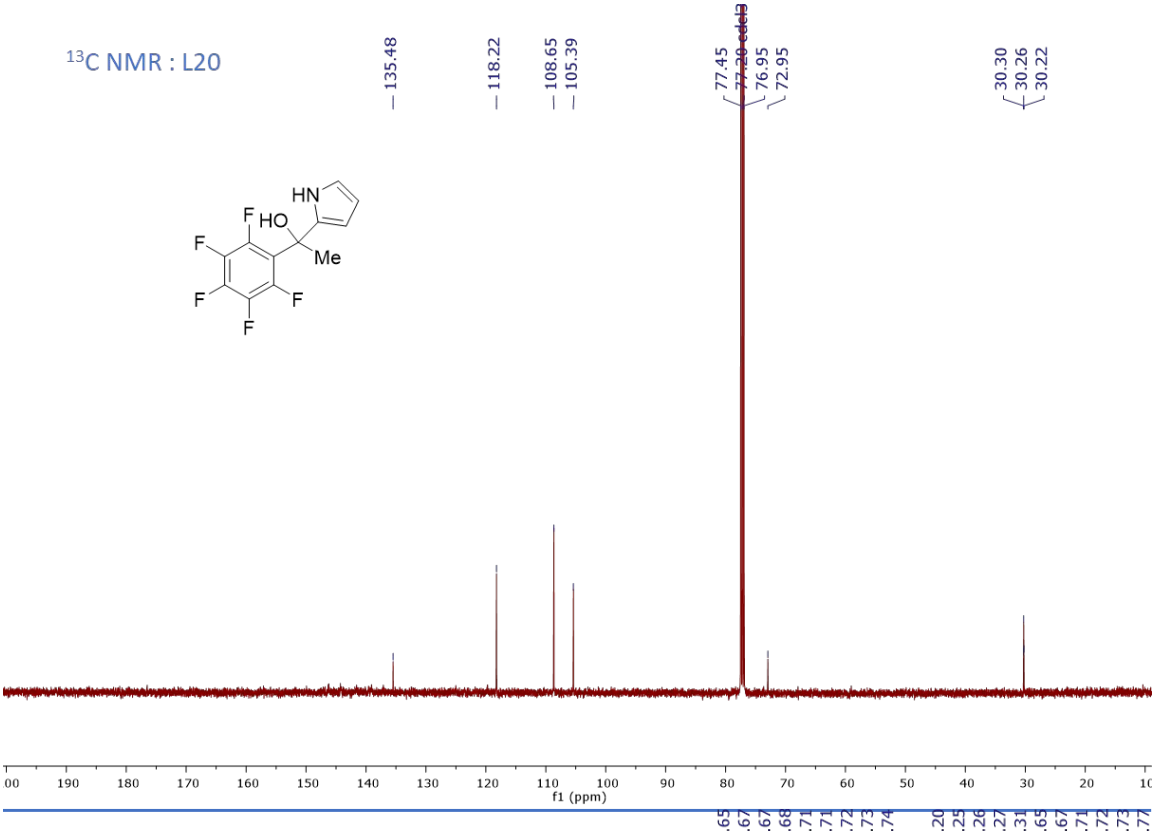
^{19}F NMR : L19



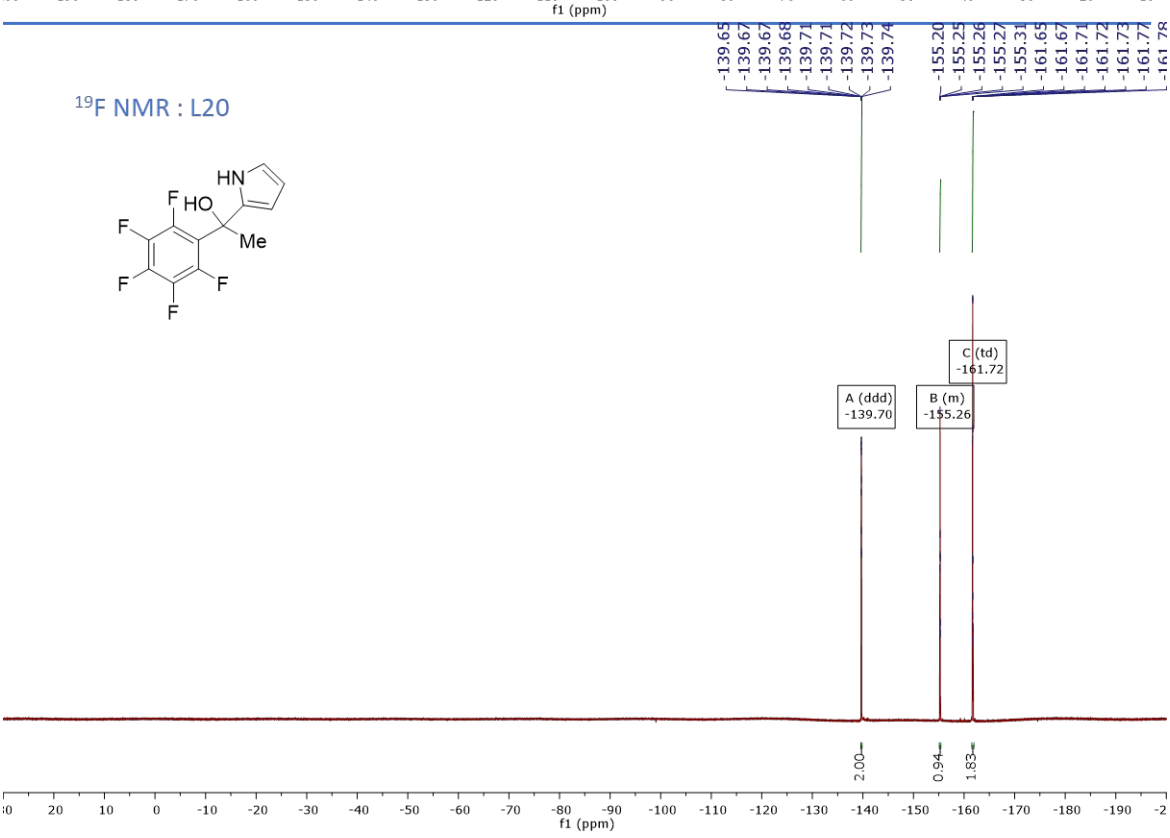
^{1}H NMR: L20

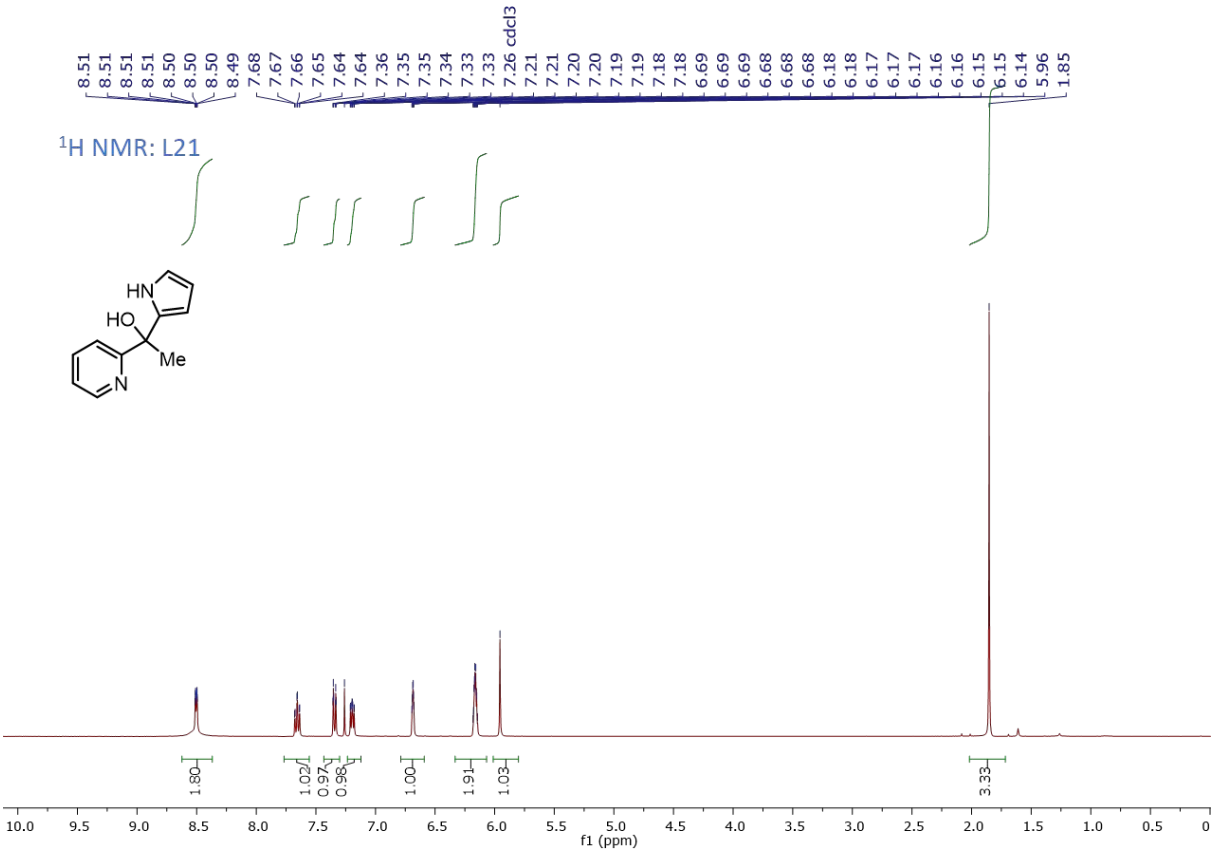


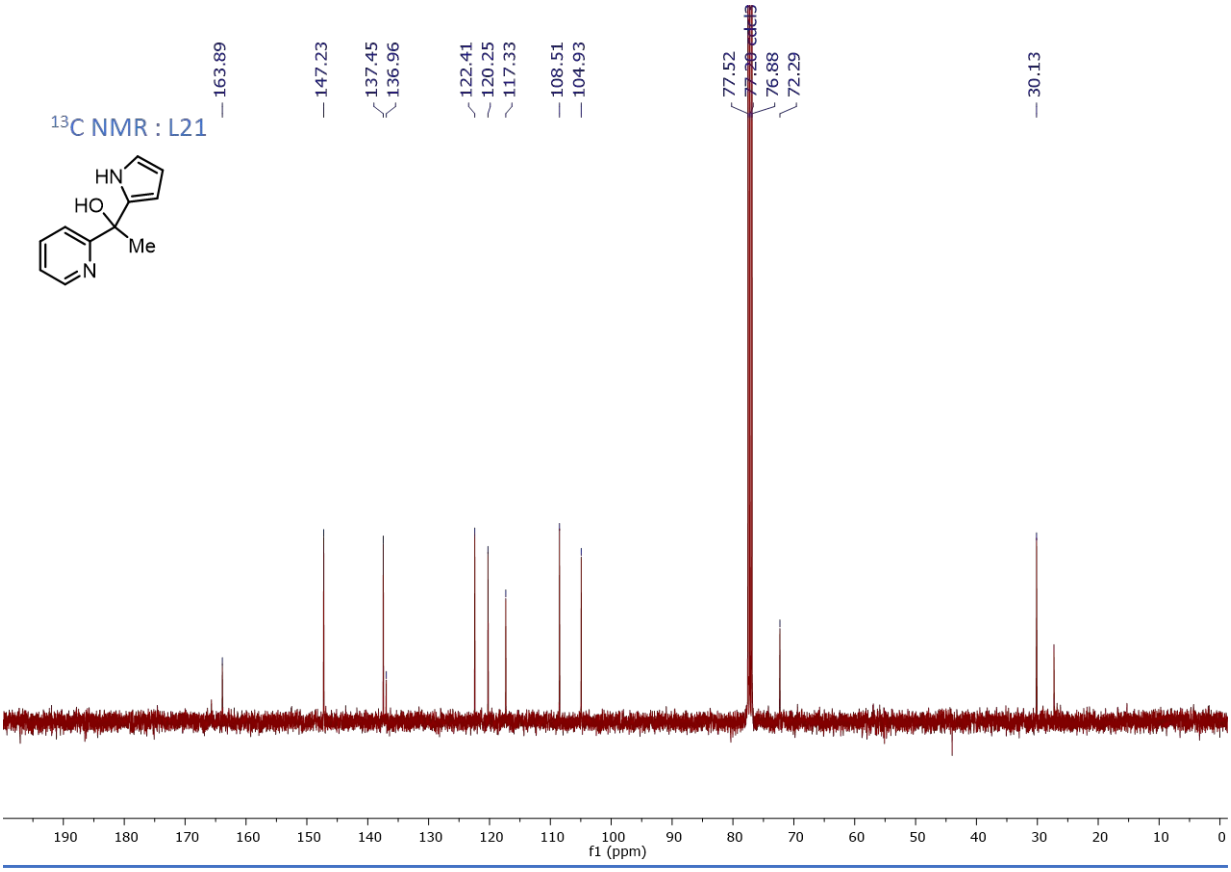
^{13}C NMR : L20



^{19}F NMR : L20




8.51 8.51 8.51 8.51 8.50 8.50 8.50 8.49 7.68 7.67 7.66 7.65 7.64 7.64 7.36 7.35 7.35 7.34 7.33 7.33 7.26 cdcl3 7.21 7.21 7.20 7.20 7.19 7.19 7.18 7.18 6.69 6.69 6.69 6.68 6.68 6.68 6.18 6.17 6.17 6.17 6.16 6.16 6.15 6.15 6.14 5.96 1.85
1H NMR: L21
HN
HO
Me
N
1.80 1.02 0.97 0.98 1.00 1.91 1.03 3.33
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)


163.89 147.23 137.45 136.96 122.41 120.25 117.33 108.51 104.93 77.52 77.20 cdcl3 76.88 72.29 30.13
13C NMR : L21
HN
HO
Me
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

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