Supporting Information

Unified Strategy for Silver-, Base-, and Oxidant-free Direct Arylation of C-H Bonds

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1. General Information

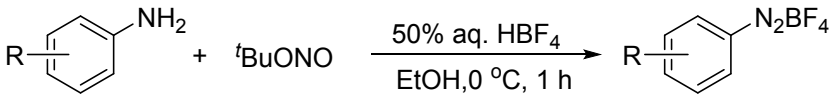
All catalytic experiments were carried out using standard Schlenk techniques. All solvents were reagent grade or better. Deuterated solvents were used as received without any further purification. Most of the chemicals used in catalysis reactions were purified according to standard procedure (or by vacuum distillation/sublimation).[S1] Visible light photoredox catalyst Eosin-Y was purchased from Sigma Aldrich and used as received. Aryl diazonium tetrafluoroborate salts was prepared by previously known procedure.[S2] Pivalamides were prepared by the reaction of the corresponding anilines with trimethylacetyl chloride.[S3] Thin layer chromatography (TLC) analyses were performed on commercial aluminum plates bearing a 0.25 mm layer of Merck Silica gel $60F_{254}$, which were visualized with UV light at 254 nm or under iodine. Column chromatography was performed with SiO_2 (Silicycle Siliaflash F60 (230-400 mesh). ^{1}H NMR (400, 200 or 500 MHz), ^{13}C NMR spectra were recorded on the 100 or 125 MHz NMR spectrometer. Deuterated chloroform was used as the solvent, and chemical shift values (δ) are reported in parts per million relatives to the residual signals of this solvent [δ 7.27 for ^{1}H (chloroform-d), δ 77.0 for ^{13}C (chloroform-d). Abbreviations used in the NMR follow-up experiments: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; sep, septet; m, multiplet. GC analysis was carried out using an HP-5 column (30 m, 0.25 mm, 0.25μ). Mass spectra were obtained on a GCMS-QP 5000 instruments with ionization voltages of 70 eV. High-resolution mass spectra (HRMS) were obtained by fast atom bombardment (FAB) using a double focusing magnetic sector mass spectrometer and electron impact (EI) ionization technique (magnetic sector-electric sector double focusing mass analyzer).

2. Experimental Section

2.1 Synthesis of starting materials

(a) General procedure for the preparation of aryldiazonium tetrafluoroborates

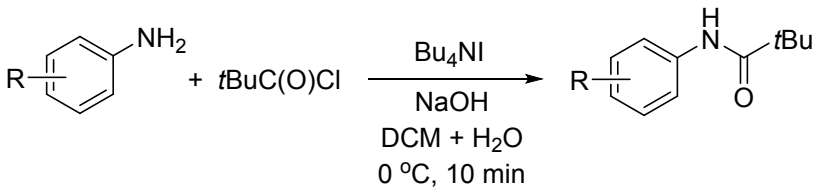
In a 50 mL round-bottom flask, the aniline (10 mmol) was dissolved in a mixture of absolute ethanol (3 mL) and an aqueous solution of HBF_4 (50%, 2.5 mL). The *tert*-butyl nitrite (2.7 mL) was added drop wise to the solution at 0 °C. The mixture was stirred at room temperature for 1 h and diethyl ether (20 mL) was added to precipitate the arenediazonium tetrafluoroborate. The solid was filtered off and washed with diethyl ether (3 × 10 mL). The aryldiazonium tetrafluoroborate was dried *in vacuo* (10^{-3} mbar) for 10 minutes and was then directly used without further purification. Spectral data are agreement with the data available in the literature.[S2]



Scheme S1. Synthesis of aryl diazonium tetrafluoroborates.

(b) General procedure for preparation of pivalamides

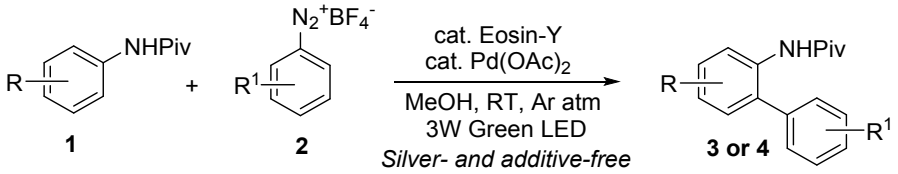
To a 100 mL RB with a magnetic stirring bar, 20 mL water, 15 mL dichloromethane, 15 mmol of aniline and 30 mmol NaOH was taken and cooled to 0 °C. Separately, in a 10 mL conical flask 5 mol% of Bu_4NI (0.75 mmol, 278 mg) was taken in 5 mL dichloromethane and cooled to 0 °C. Similarly in a 25 mL RB with a glass stopper 15 mmol of pivaloyl chloride (1.9 mL) in 10 mL of dichloromethane was taken and cooled to 0 °C. After 10 minutes both the solution of Bu_4NI and pivaloyl chloride were added to the aniline solution simultaneously at once, and was stirred vigorously for another 10 minutes, then to it 20 mL of ice cold water was added, excess base was neutralized with saturated NH_4Cl solution, the organic layer was extracted with dichloromethane (3 x 50 mL), then combined organic layer was washed with brine solution, dried over anhydrous Na_2SO_4, the solvent was removed under reduced pressure. The crude product was recrystallized from 1:1 mixture of dichloromethane and hexane at room temperature (1-2 days). Spectral data are agreement with the data available in the literature.[S3]



Scheme S2. Synthesis of pivalamides.

2.2 General procedure room temperature oxidant- and base-free Eosin-Y/Pd catalyzed C-H arylation of anilides

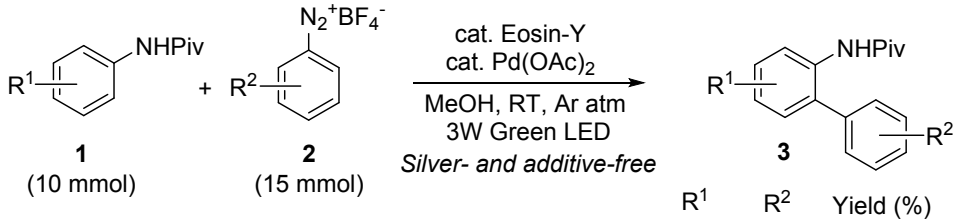
In an oven-dried 15 mL schlenk tube with a magnetic stirring bar was charged with pivalamide 1 (0.2 mmol), aryldiazonium salt **2** (0.3 mmol), Eosin-Y (1 mol %), $Pd(OAc)_2$ (10 mol %), and 1 mL of methanol under argon atm. Then the reaction tube was freezed in liquid N_2, degassed by the freeze-pump-thaw procedure (3×), refilled with argon gas. Then the schlenk tube was placed on a magnetic stirrer with two 3W Green LED light bulbs kept about 5 cm away from it and irradiated at room temperature with constant stirring. After 18 h, the reaction mixture was quenched with saturated 15 mL $NaHCO_3$ solution, and the aqueous layer was extracted with EtOAc (3 x 15 mL). Finally, the combined organic layer was washed with brine solution (15 mL), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel with a mixture of EtOAc and petroleum ether to afford desired *ortho*-arylated product **3** or **4**.



Scheme S3. Room temperature *oxidant-, base-free* Eosin-Y/Pd/catalyzed C-H arylation of anilides.

2.3 General procedure for gram-scale synthesis

In an oven-dried 100 mL schlenk round bottomed flask with a magnetic stirring bar was charged with pivalamide **1** (10 mmol), aryldiazonium salt **2** (15 mmol), $Pd(OAc)_2$ (10 mol %), Eosin-Y (1.0 mol %), and 50 mL of anhydrous methanol under argon atm. Then the reaction tube was freezed in liquid N_2, degassed by the freeze-pump-thaw procedure (3×), refilled with argon gas. Then the round bottomed flask was placed on a magnetic stirrer with two 3 W Green Led light bulbs kept about 5 cm away from it and irradiated at room temperature with constant stirring. After 24 h, the reaction mixture was quenched with saturated 100 mL $NaHCO_3$ solution, and the aqueous layer was extracted with EtOAc (2 x 100 mL). Finally, the combined organic layer was washed with brine solution (100 mL), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel with mixture of EtOAc and petroleum ether to afford desired *ortho*-arylated product in gram-scale.



R^1	R^2	Yield (%)
H	*p*-Cl	**(4a)** 82%
F	*p*-Cl	**(4n)** 87%

Scheme S4. Gram-scale synthesis of C-H arylated anilides.

2.4 Reusability of the homogeneous system

The reusability of present catalytic system was checked by following representative procedure (Sec 2.2). After the first catalytic run between **1a** and **2a** in the presence of catalytic amounts of eosin-Y (1 mol%) and $Pd(OAc)_2$ (10 mol%) in methanol under standard conditions, the yield of the *ortho*-arylated product **3a** observed was 95% (GC yield). In the same reaction vessel were placed fresh **1a** and **2a**, and the reaction was continued further without the addition of catalysts. After 18 h, the yield determined for the second cycle was 91% (GC yield).

2.5. Rate Order Determination

The order for the *ortho* C-H arylation reaction of anilides with various reaction components was determined by the initial rate method. The data of the concentration of the product *vs* time (h) plot was fitted linearly with Origin Pro 8. The slope of the linear fitting is the reaction rate. The order of the reaction was then determined by plotting the log (rate) *vs* log (conc) for a particular component.

2.5.1 Representative Procedure: Rate Order Determination for *N*-(*m*-tolyl)pivalamide

To determine the order for *N*-(*m*-tolyl)pivalamide in the *ortho* C-H arylation of anilides, the initial rates at different initial concentrations of *N*-(*m*-tolyl)pivalamide were recorded. The final data was obtained by averaging the results of two independent runs for each experiment.

In an oven-dried 15 mL schlenk tube with a magnetic stirring bar was charged with 4-chlorobenzenediazonium tetrafluoroborate (136 mg, 0.6 mmol), $Pd(OAc)_2$ (9.0 mg, 0.04 mmol), Eosin-Y (2.6 mg, 0.004 mmol) and specific amount of *N*-(*m*-tolyl)pivalamide (as shown in Table S1). To it 2.0 mL of dry methanol was added, followed by addition of

mesitylene as internal standard (0.056 mL, 0.4 mmol) under argon atm. Then the reaction tube was freezed in liquid N_2, degassed by the freeze-pump-thaw procedure (3×), refilled with argon gas. The temperature of schlenk tube was brought to room temperature, then the schlenk tube was placed on a magnetic stirrer with two 3W Green LED light bulbs kept about 5 cm away from it and irradiated at room temperature with constant stirring. At regular intervals, from the reaction vessel an aliquot of sample was withdrawn to the GC vial. The sample was diluted with methanol and subjected to GC analysis. The concentration of the product **3a** obtained in each sample was determined with respect to the internal standard mesitylene.

Table S1. Rate of *ortho* C-H Arylation Reaction at different Initial Concentration of *N*-(*m*-tolyl)pivalamide.

Experiment no.	Amount of *N*-(*m*-tolyl)pivalamide (mg)	Initial conc. of *N*-(*m*-tolyl)pivalamide [M]	Initial Rate [Mh^{-1}] x 10^{-2}
1	77	0.2	1.6
2	115	0.3	2.1
3	153	0.4	2.4
4	191	0.5	2.8

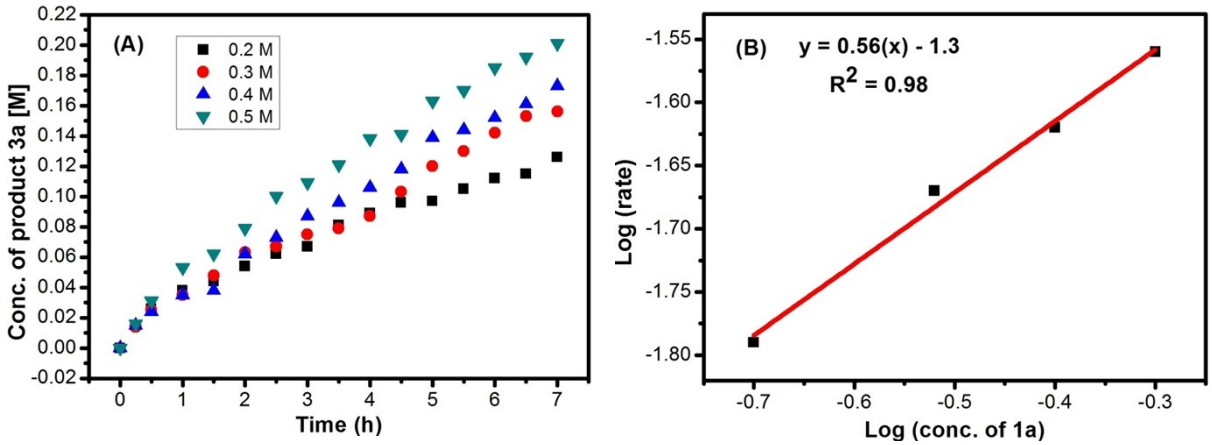


Figure S1. **(A)** Time-dependent formation of **3a** at different initial concentration of *N*-(*m*-tolyl)pivalamide **1a**. **(B)** Plot of log(rate) vs log(conc. of **1a**).

2.5.2 Representative Procedure: Rate Order Determination for 4-chlorobenzenediazonium tetrafluoroborate

To determine the order for 4-chlorobenzenediazonium tetrafluoroborate in the *ortho* C-H arylation of anilides, the initial rates at different initial concentrations of 4-

chlorobenzenediazonium tetrafluoroborate were recorded. The final data was obtained by averaging the results of two independent runs for each experiment.

Representative procedure (Sec 2.5.1) was followed, employing *N*-(*m*-tolyl)pivalamide (76.5 mg, 0.4 mmol), $Pd(OAc)_2$ (9.0 mg, 0.04 mmol), Eosin-Y (2.6 mg, 0.004 mmol), mesitylene as internal standard (0.056 mL, 0.4 mmol) and specific amount of 4-chlorobenzenediazonium tetrafluoroborate (as shown in Table S2) in 2.0 mL of dry methanol.

Table S2. Rate of *ortho* C-H Arylation Reaction at different Initial Concentration of 4-chlorobenzenediazonium tetrafluoroborate.

Experiment no.	4-chlorobenzenediazonium tetrafluoroborate (mg)	Initial conc. of 4-chlorobenzenediazonium tetrafluoroborate [M]	Initial Rate $[Mh^{-1}] \times 10^{-2}$
1	91	0.2	1.8
2	136	0.3	2.0
3	181	0.4	2.1
4	226	0.5	2.2

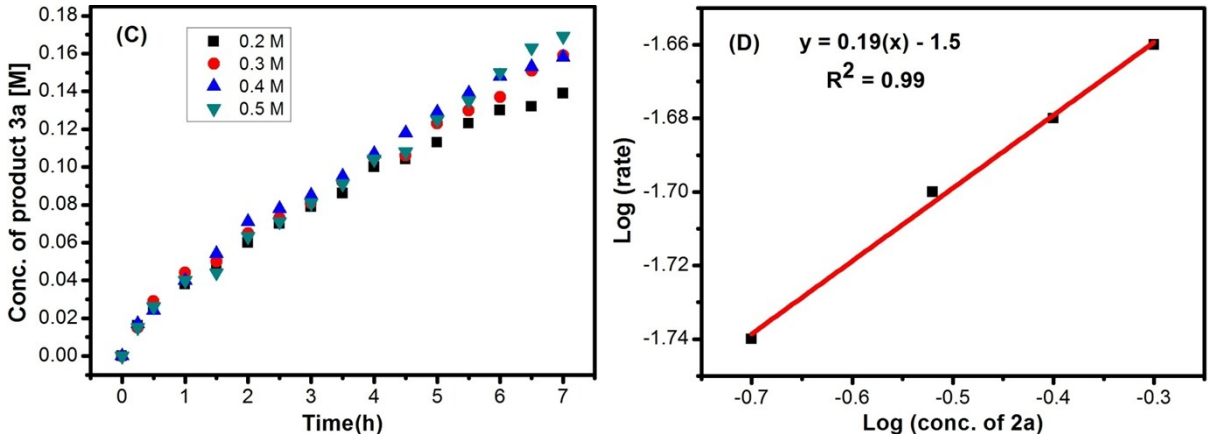


Figure S2. **(A)** Time-dependent formation of **3a** at different initial concentration of 4-chlorobenzenediazonium tetrafluoroborate. **2a. (B)** Plot of log(rate) vs log(conc. of **2a**).

2.5.3 Representative Procedure: Rate Order Determination for Eosin-Y

To determine the order for Eosin-Y in the *ortho* C-H arylation of anilides, the initial rates at different initial concentrations of Eosin-Y were recorded. The final data was obtained by averaging the results of two independent runs for each experiment.

Representative procedure (Sec 2.5.1) was followed, employing *N*-(*m*-tolyl)pivalamide (76.5 mg, 0.4 mmol), 4-chlorobenzenediazonium tetrafluoroborate (136 mg, 0.6 mmol),

$Pd(OAc)_2$ (9.0 mg, 0.04 mmol), mesitylene as internal standard (0.056 mL, 0.4 mmol) and specific amount of Eosin-Y (as shown in Table S3) in 2.0 mL of dry methanol.

Table S3. Rate of *ortho* C-H Arylation Reaction at different Initial Concentration of Eosin-Y.

Experiment no.	Eosin-Y (mg)	Initial conc. of Eosin-Y [M]	Initial Rate $[Mh^{-1}] \times 10^{-2}$
1	2.6	0.002	2.79
2	13	0.01	3.45
3	25.9	0.02	4.40
4	38.9	0.03	4.82

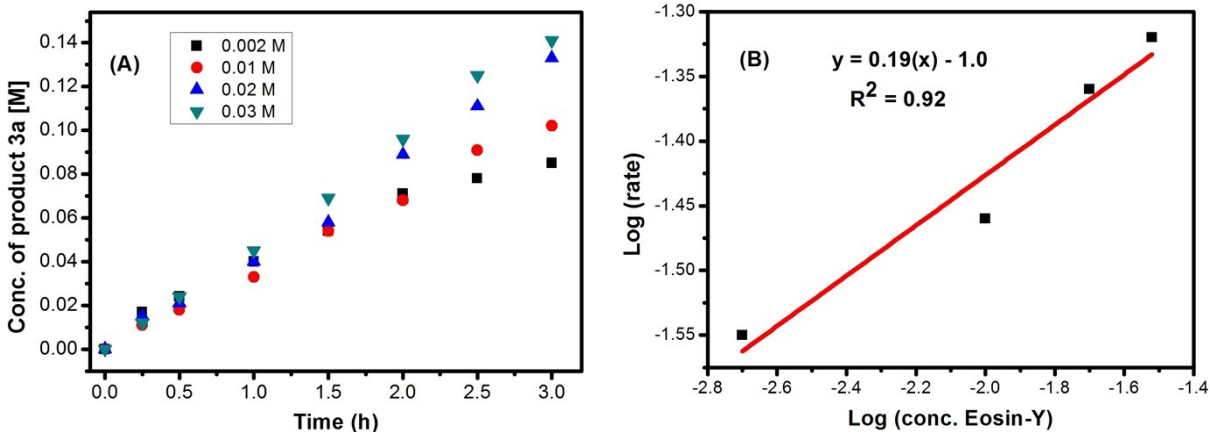


Figure S3. **(A)** Time-dependent formation of **3a** at different initial concentration of Eosin-Y. **(B)** Plot of log(rate) vs log(conc. of Eosin-Y).

2.6.1 Representative Procedure: **Yield determination for $Pd(OAc)_2$ (Figure S4).** To determine the effect of mol% of $Pd(OAc)_2$ in the *ortho* C-H arylation of anilides **3a**, the yields at different initial concentrations of $Pd(OAc)_2$ were recorded.

Representative procedure (Sec 2.2) was followed, employing *N*-(*m*-tolyl)pivalamide (38 mg, 0.2 mmol), 4-chlorobenzenediazonium tetrafluoroborate (38 mg, 0.3 mmol), Eosin-Y (1.3 mg, 0.002 mmol) and specific amount of $Pd(OAc)_2$ (as shown in Table S4) in 1.0 mL of dry methanol.

Table S4. Yield of *ortho* C-H Arylation Reaction at different Initial Concentration of $Pd(OAc)_2$.

Experiment no.	Amount of $Pd(OAc)_2$ (mg)	Initial conc. of $Pd(OAc)_2$ [M]	Yield (%)
1	0.5	0.002	4 (by GC)
2	1.1	0.005	43 (isolated yield)
3	2.2	0.01	61 (isolated yield)
4	4.5	0.02	93 (isolated yield)

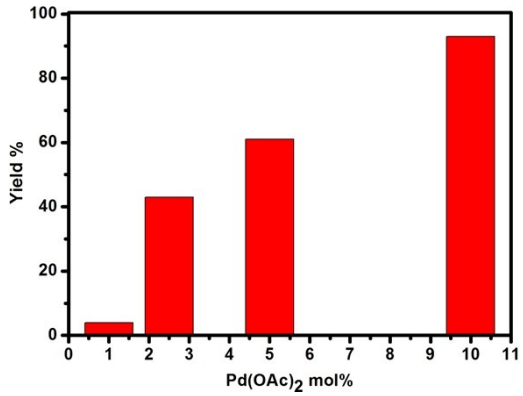


Figure S4.Yield formation of **3a** at different initial concentration of $Pd(OAc)_2$

2.6.2 Representative Procedure: Time-dependent formation of 3a

Representative procedure (Sec 2.5.1) was followed, employing *N*-(*m*-tolyl)pivalamide (76.5 mg, 0.4 mmol), 4-chlorobenzenediazonium tetrafluoroborate (136 mg, 0.6 mmol), $Pd(OAc)_2$ (9.0 mg, 0.04 mmol), mesitylene as internal standard (0.056 mL, 0.4 mmol) and Eosin-Y (2.6 mg, 0.004 mmol), in 2.0 mL of dry methanol. At various time interval, from the reaction vessel an aliquot of sample was withdrawn to the GC vial. The sample was diluted with methanol and subjected to GC analysis. The final data was obtained by averaging the results of two independent runs for each experiment.

Table S5. GC yield of 3a and conversion of 1a at different time intervals.

Experiment no.	Time (h)	Yield of **3a** (%)	Conversion of **1a** (%)
1	0	0	100
2	1	30	70
3	2	45	55
4	3	60	40

5	4	69	31
6	6	84	26
7	8	95	5
8	12	98	2

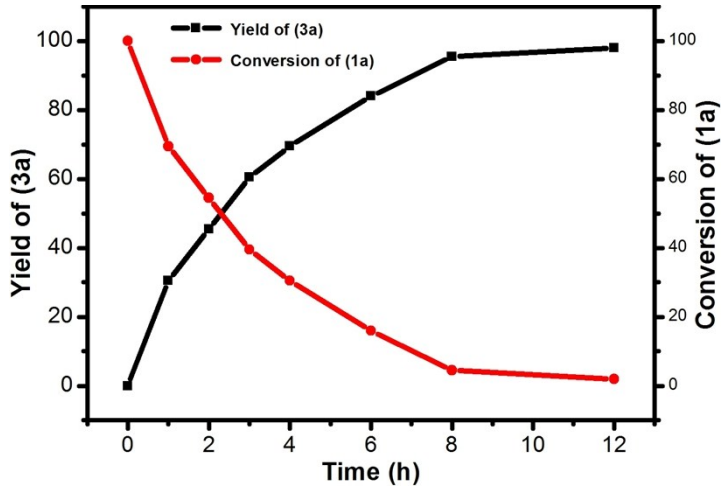
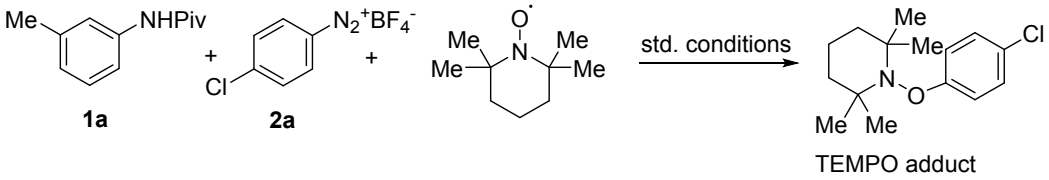


Figure S5. GC yield of **3a** and conversion of **1a** at different time intervals.

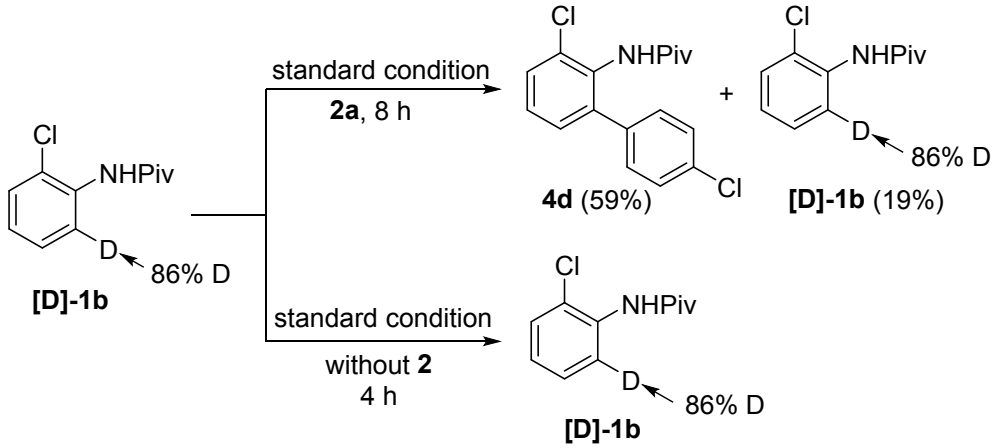
2.7 Mechanistic investigation

2.7.1 Radical trapping experiment



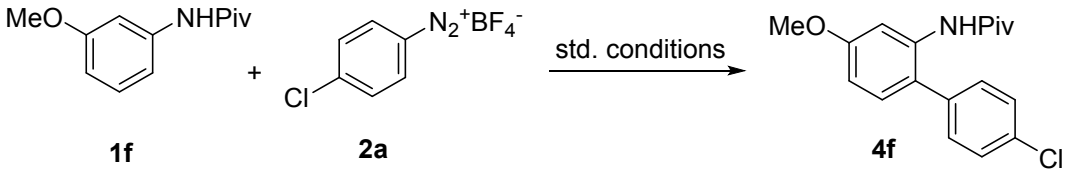
In an oven-dried 15 mL schlenk tube with a magnetic stirring bar was charged with pivalamide **1a** (0.2 mmol), aryldiazonium salt **2a** (0.3 mmol), Eosin-Y (1 mol %), $Pd(OAc)_2$ (10 mol %), and 1 mL of methanol under argon atm. Then the reaction tube was freezed in liquid N_2, degassed by the freeze-pump-thaw procedure (3×), refilled with argon gas. Then the schlenk tube was placed on a magnetic stirrer with two 3W Green LED light bulbs kept about 5 cm away from it and irradiated at room temperature with constant stirring. After 18 h, the reaction mixture was analysed on GC-MS and the formation of *O*-arylated-TEMPO product was observed.

2.7.2 H/D exchange experiments



Deuterium labelled compound **1d** was prepared according to reported literature procedure with 86% deuterium incorporation.[S4] Two independent experiments (i) with **2a** and (ii) without **2a** were performed under standard conditions using freshly distilled dry MeOH. In both the experiments the recovered staring material **1d** showed 86%. Thus, the C-H arylation of the isotopically labeled substrate [D]-**1d** was not accompanied by H/D exchange reactions, which is indicative of a kinetically relevant C-H palladation step.

2.7.3a Light-Dark Experiment



Following representative procedure (Sec 2.5.1), two parallel experiments {A (Light) and B (Dark)} were carried out employing *N*-(3-methoxyphenyl)pivalamide **1f** (83 mg, 0.4 mmol), 4-chlorobenzenediazonium tetrafluoroborate **2a** (136 mg, 0.6 mmol), $Pd(OAc)_2$ (9.0 mg, 0.04 mmol), eosin-Y (2.6 mg, 0.004 mmol) and mesitylene (0.056 mL, 0.4 mmol) as internal standard in 2.0 mL of dry methanol. Initially, the reaction (B) was irradiated with a light source under the standard condition for the first 60 minutes, and then carried out in the dark condition. However, reaction (A) was irradiated with continues irradiation. Continuous sampling was undertaken with the different time intervals, and yield of *ortho*-arylated product (**4f**) was determined by gas chromatography.

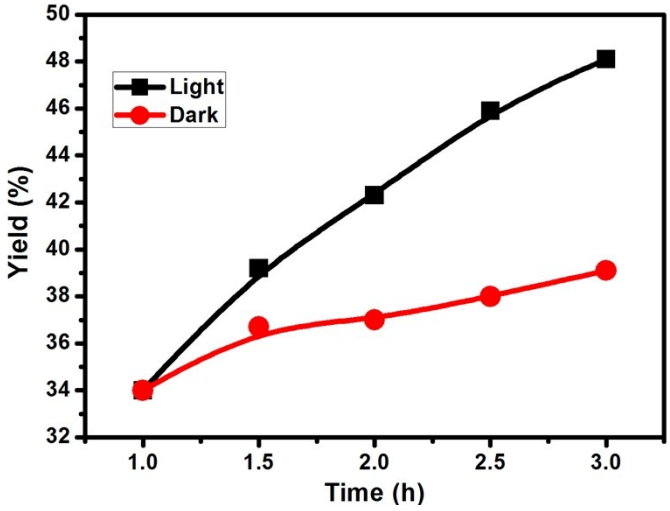


Figure S6. Kinetic profile **4f** at different time intervals for two separate (dark and light) experiments.

2.7.3b Light-Dark Experiment (ON/OFF experiment)

Following representative procedure (Sec 2.5.1), the reaction was carried out employing *N*-(3-methoxyphenyl)pivalamide **1f** (83 mg, 0.4 mmol), 4-chlorobenzenediazonium tetrafluoroborate **2a** (136 mg, 0.6 mmol), $Pd(OAc)_2$ (9.0 mg, 0.04 mmol), eosin-Y (2.6 mg, 0.004 mmol) and mesitylene (0.056 mL, 0.4 mmol) as internal standard in 2.0 mL of dry methanol. The reaction is conducted using alternating intervals of light and dark. In each interval, continuous sampling was undertaken with the different time intervals, and yield of *ortho*-arylated product (**4f**) was determined by gas chromatography.

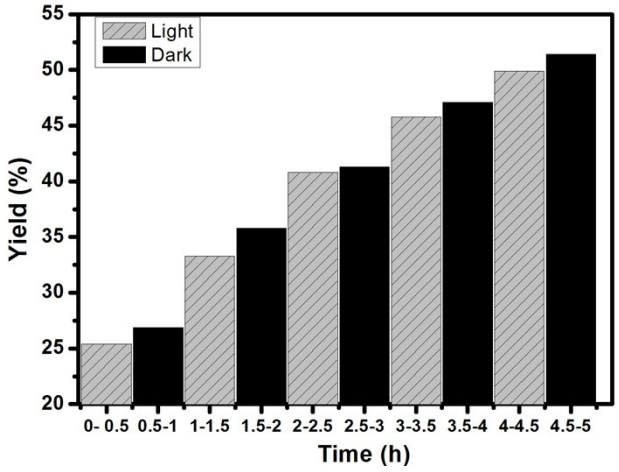


Figure S7. GC yield of **4f** with deferent time intervals (Light-Dark experiment).

2.7.4 Identification of intermediate Pd-complex

To an oven-dried 5 mL screw-capped vial, **1f** (70 mg, 0.33 mmol), $Pd(OAc)_2$ (75mg, 1 equiv.), *N*-Formylglycine (35mg, 1 equiv) and hexafluoroisopropanol (2 mL) were added under argon atm. The mixture was stirred for 3 hr at 100 °C followed by cooling to room temperature. The solution was filtered through a celite pad and submitted to HRMS analysis. HRMS (EI): *m/z* Calcd for [M-H] $C_{15}H_{19}N_2O_5Pd$: 413.0329; Found: 413.0323.

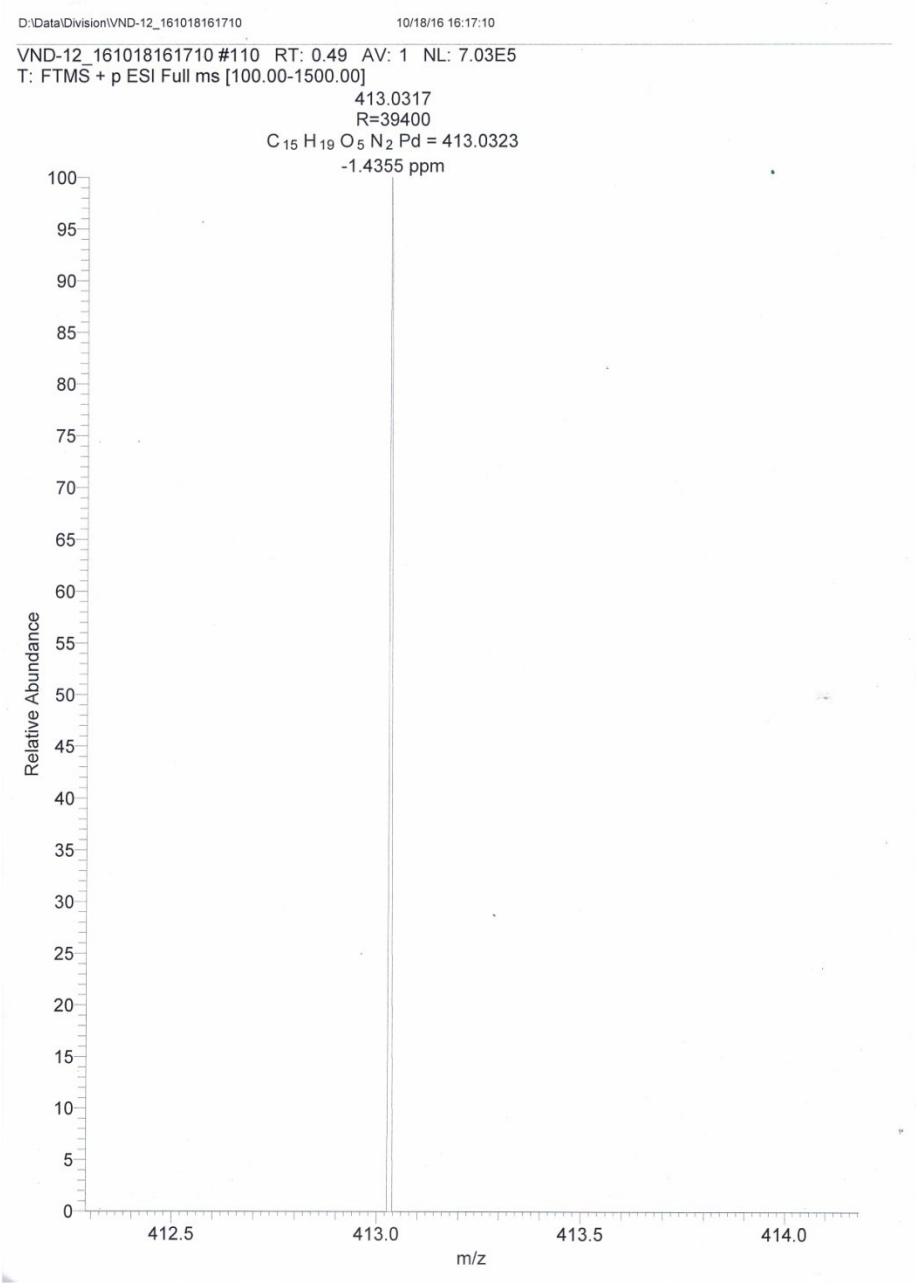


Figure S8. HRMS of intermediate Pd-complex

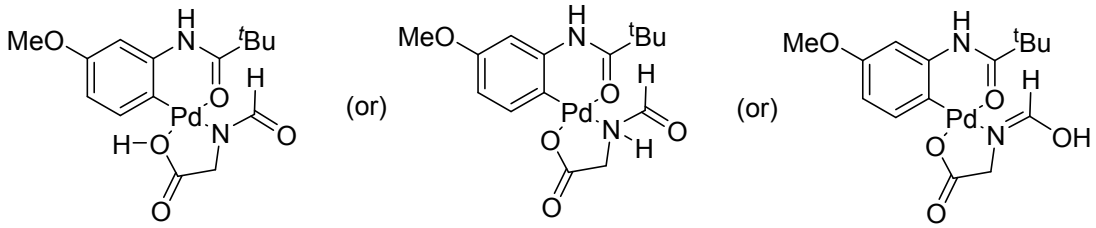


Figure S9. Possible intermediate complexes.

2.8. Effect of other directing group

The effect of substituent on the acyl group of anilides was further studied by changing the *N*-pivaloyl (i.e. *t*-Butyl) group to the *N*-acetyl (i.e. ethyl) group and gave the C-H arylated product in 31% yield only (mono/bis ≈ 2:1). To further extend the scope of the reaction, we investigated different amides such as -$NHCONMe_2$ and -NHTs as the directing groups and found to be not suitable for the present arylation reaction. Due to the favorable conformation of the pivaloyl group good selectivity of the site-selective product was observed.

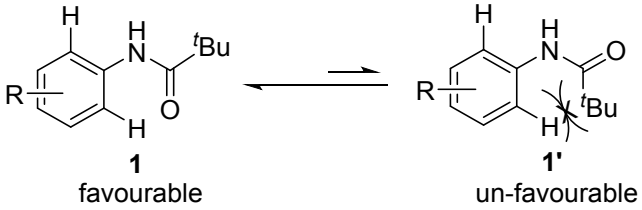
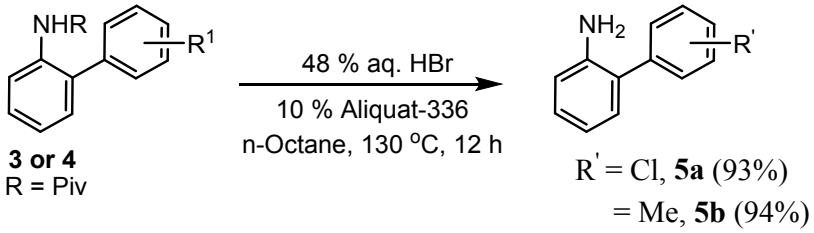


Figure S10. A possible conformation of anilide **1**.

2.9 Diversification of *ortho*-arylaniline derivatives

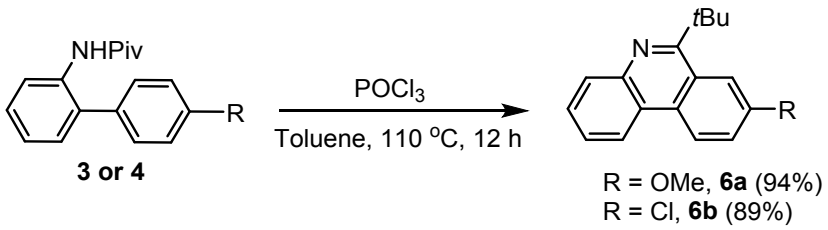
2.9.1 Removal of directing group



To a 10 mL screw-caped tube, *ortho*-aryl pivalamide (0.5 mmol), 10 weight percentage of Aliquat-336, 0.5 mL of 48 % aqueous HBr and 1.0 mL of n-octane were added under argon atm. Then the tube was kept in a preheated oil bath at 130 °C for 12 h. After cooling to room temperature, the reaction mixture was neutralised with saturated Na_2CO_3. The compound was extracted with 25 mL of ethyl acetate three times. Then the organic layer

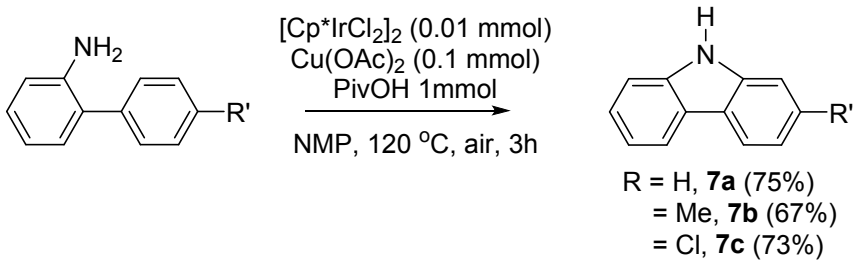
was washed with 25 mL brine solution, dried over anhy. Na_2SO_4 and concentrated in *vacuo*. The residue was purified by column chromatography on silica gel with a mixture of EtOAc in petroleum ether to afford desired *ortho*-arylated anilines (**5**).

2.9.2 Synthesis of phenanthridine



To an oven dried 10 mL sealed tube with magnetic stirring bar was charged *ortho*-arylated pivalamide **3** or **4** (0.2 mmol), $POCl_3$ (0.6 mmol, 0.056 mL). To it 0.5 mL dry Toluene was added under argon atmosphere. The Teflon screw cap was closed and the tube was kept in a preheated oil bath at 110 ^oC, the reaction was continued for 12 h After completion the reaction mixture was quenched by addition of aq. $NaHCO_3$. The mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined extracts were washed with brine solution, dried over anhydrous Na_2SO_4 and concentrated under the reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of hexanes and EtOAc as eluent to afford the corresponding phenanthridine derivatives. Spectral data are agreement with the data available in the literature.[S5]

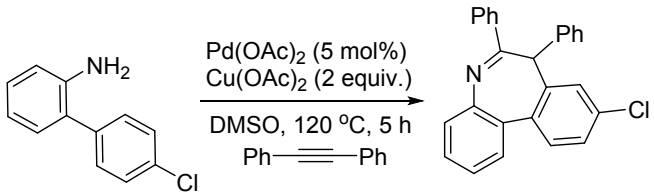
2.9.3 Carbazole synthesis



To a 20 mL two-necked flask with a reflux condenser and a rubber cup were added 2-aryl aniline (0.5 mmol), $[Cp^*IrCl_2]_2$ (0.01 mmol), $Cu(OAc)_2$ (0.1 mmol), PivOH (1.0 mmol) in NMP (3 mL). The resulting mixture was stirred under air at 120 oC for 3h. After cooling, the reaction mixture was extracted with ethyl acetate (100 mL), washed with aqueous $NaHCO_3$ (100 mL, three times), and dried over Na_2SO_4. Purification by column

chromatography on silica gel using hexane-ethyl acetate (10:1, v/v) as eluent gave carbazole. Spectral data are agreement with the data available in the literature.[S6]

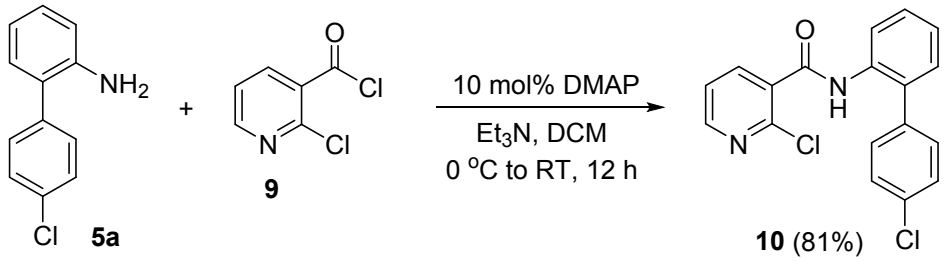
2.9.4 Cyclization with diphenylacetylene



5a **8** (72%)

In a oven-dried, 5.0 mL vial equipped with a stirring bar was charged with $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), $Cu(OAc)_2$ (114.4 mg, 0.63 mmol), **5a** (0.30 mmol) and diphenylacetylene (0.45 mmol), followed by sequential addition of DMSO (3.0 mL). The vial was sealed with a Teflon screw cap and then the reaction mixture was heated at 120 °C for 5 h. After the reaction vessel was cooled to room temperature, the mixture was extracted with EtOAc, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was then purified on silica gel to yield **8** in 72%. Spectral data are agreement with the data available in the literature.[S7]

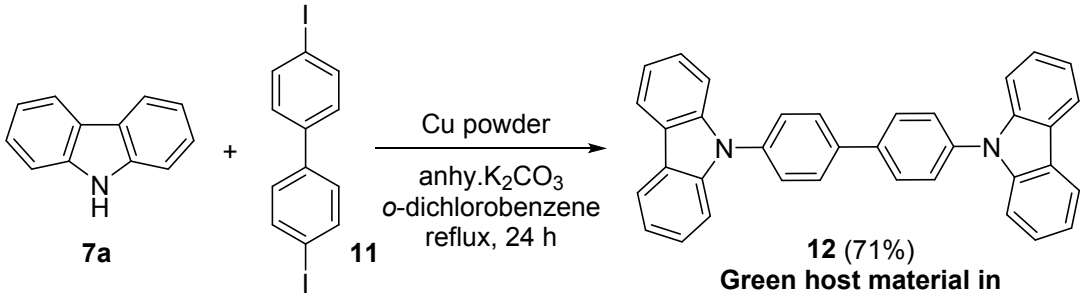
2.9.5 Synthesis of Boscalid[S8]



5a **10** (81%) **Boscalid (BASF)**

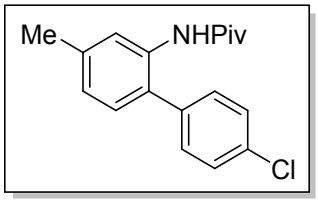
To a stirred solution of 2-chloronicotinoyl chloride **9** (88 mg, 0.5 mmol), 4-dimethylaminopyridine (6 mg, 0.05 mmol) in 4 mL dichloromethane, 4'-chloro-[1,1'-biphenyl]-2-amine **5a** (102 mg, 0.5 mmol), triethylamine (0.14 mL, 1.0 mmol) in dichloromethane (1.0 mL) was added drop wise at 0 °C. The reaction was allowed to stir at 0 °C for 1 h, and another 12 h at room temperature followed by addition of dichloromethane (20 mL) and water (20 mL). The combined organic extracts were dried over Na_2SO_4 and the organic solvent was removed under reduced pressure. The crude residue was purified by column chromatography on silica gel (230-400 mesh) using a mixture of petroleum ether/EtOAc (R_f= 0.5, petroleum ether/EtOAc = 2:1), to afford 2-Chloro-*N*-(4'-chloro-[1,1'-biphenyl]-2-yl)nicotinamide (**10**, 104 mg, 81%) as a white solid.

2.9.6 Synthesis of a Green host material (12)



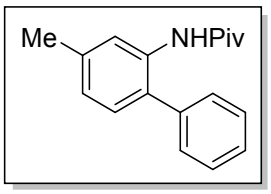
To a 50 mL round bottomed flask carbazole **7a** (2.4 mmol, 334 mg), 4,4'-diiodobiphenyl **11** (1.0 mmol, 406 mg), K_2CO_3 (8.0 mmol, 1.11 g), copper powder (2.8 mmol, 178 mg) and 18-crown-6 (0.2 mmol, 53 mg) were taken under argon atmosphere. To it 20 mL of *o*-dichlorobenzene was added and the mixture was allowed to reflux for 24 h. The reaction mixture was filtered through a small pad of celite and the residue was washed with chloroform. The combined solvents were removed under reduced pressure and the resulted residue was recrystallized from methanol at -20 ^oC to give the product **12** as a white solid (344 mg, 71%).[S9]

3. Characterization Data



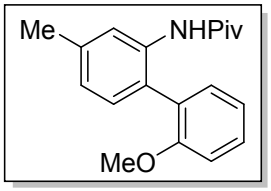
(3a) *N*-(4'-chloro-4-methyl-[1,1'-biphenyl]-2-yl)pivalamide

The title compound was prepared according to the general procedure described above and purified by column chromatography to give the product as a white solid (56 mg, 93%); R*f* = 0.4 (petroleum ether/EtOAc = 10:1), Purified using a mixture of petroleum ether/EtOAc = 20:1; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.08 (s, 1H), 7.38 (d, *J* = 8.6 Hz, 2H), 7.25-7.19 (m, 3H), 7.02 (d, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 2.32 (s, 3H), 1.05 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 176.38, 138.91, 136.62, 134.64, 133.90, 130.76, 129.57, 129.14, 128.40, 125.01, 122.05, 39.77, 27.40, 21.45; HRMS (ESI) m/z calculated for $C_{18}H_{20}ClNO$ $[M+H]^+$ 302.1312; found 302.1306.



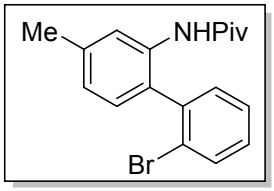
(3b) *N*-(4-methyl-[1,1'-biphenyl]-2-yl)pivalamide

The title compound was prepared according to the general procedure described above and purified by column chromatography to give the product as a white solid (42 mg, 79%); R*f* = 0.4 (petroleum ether/EtOAc = 10:1), Purified using a mixture of petroleum ether/EtOAc = 25:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.25 (s, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.46 (brs, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 7.3 Hz, 2H), 7.15 (d, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 8.3 Hz, 1H), 2.41 (s, 3H), 1.11 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 176.30, 138.46, 138.08, 134.83, 129.48, 129.39, 128.95, 127.82, 124.63, 121.37, 39.74, 27.31, 21.45; HRMS (ESI) m/z calculated for $C_{18}H_{21}NO$ $[M+H]^+$ 268.1701, found .268.1696.



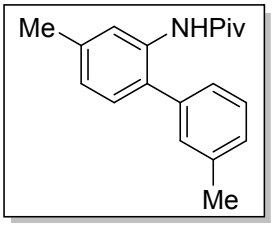
(3c) *N*-(2'-methoxy-4-methyl-[1,1'-biphenyl]-2-yl)pivalamide

The title compound was prepared according to the general procedure described above and purified by column chromatography to give the product as a white solid (46 mg, 78%); R*f* = 0.35 (petroleum ether/EtOAc = 10:1), Purified using a mixture of petroleum ether/EtOAc = 20:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.00 (s, 1H), 7.75 (brs, 1H), 7.41 (t, *J* = 8.4 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.04-7.00 (m, 2H), 3.84 (s, 3), 2.41 (s, 3H), 1.09 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 176.35, 155.84, 138.22, 135.45, 132.21, 130.27, 129.46, 127.32, 127.27, 125.07, 122.67, 121.54, 110.88, 55.74, 39.42, 27.27, 21.38; HRMS (ESI) m/z calculated for $C_{19}H_{23}NO_2$ $[M+H]^+$ 298.1807, found 298.1802.



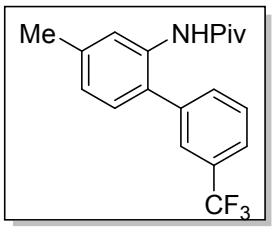
(3d) *N*-(2'-bromo-4-methyl-[1,1'-biphenyl]-2-yl)pivalamide

The title compound was prepared according to the general procedure described above and purified by column chromatography to give the product as a colourless oil (48 mg, 70%); R*f* = 0.3 (petroleum ether/EtOAc = 10:1), Purified using a mixture of petroleum ether/EtOAc = 15:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.14 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.31-7.27 (m, 2H), 7.10 (brs, 1H), 7.06 (d, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 2.42 (s, 3H), 1.05 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 176.22, 139.09, 138.82, 134.92, 132.87, 131.94, 129.74, 129.06, 128.95, 127.94, 124.71, 124.12, 121.76, 39.54, 27.15, 21.53; HRMS (ESI) m/z calculated for $C_{18}H_{20}BrNO$ $[M+H]^+$ 346.0807, found 346.0801.



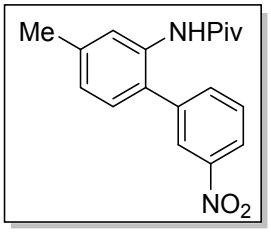
(3e) *N*-(3',4-dimethyl-[1,1'-biphenyl]-2-yl)pivalamide

The title compound was prepared according to the general procedure described above and purified by column chromatography to give the product as a white solid (50 mg, 89%); R*f* = 0.45 (petroleum ether/EtOAc = 10:1), Purified using a mixture of petroleum ether/EtOAc = 25:1; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.25 (s, 1H), 7.52 (brs, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.24-7.12 (m, 4H), 6.98 (d, *J* = 7.7 Hz, 1H), 2.41 (m, 6H), 1.12 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 176.28, 138.65, 138.35, 137.95, 134.82, 130.12, 129.44, 129.35, 128.89, 128.51, 126.39, 124.58, 121.25, 39.77, 27.33, 21.47, 21.38; HRMS (ESI) m/z calculated for $C_{19}H_{23}NO$ $[M+H]^+$ 282.1858, found 282.1852.



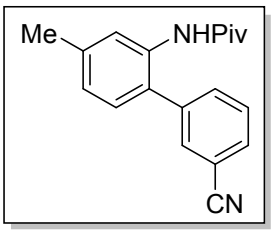
(3f) *N*-(4-methyl-3'-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)pivalamide

The title compound was prepared according to the general procedure described above and purified by column chromatography to give the product as a colourless oil (50 mg, 73%); R*f* = 0.5 (petroleum ether/EtOAc = 10:1), Purified using a mixture of petroleum ether/EtOAc = 30:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.11 (s, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.64 (s, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.26 (brs, 1H), 7.14 (d, *J* = 7.9 Hz, 1H), 7.02 (d, *J* = 7.9 Hz, 1H), 2.40 (s, 3H), 1.11 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 176.48, 139.28, 139.14, 134.52, 132.88, 131.26 (q, $J_{C\text{-}F}$ = 32.2 Hz), 129.63, 129.54, 128.50, 126.12 (q, $J_{C\text{-}F}$ = 3.8 Hz), 125.36, 124.51 (q, $J_{C\text{-}F}$ = 4.0 Hz), 123.86 (q, $J_{C\text{-}F}$ = 272.8 Hz), 122.68, 39.68, 27.27, 21.41; HRMS (ESI) m/z calculated for $C_{19}H_{20}F_3NO$ $[M+H]^+$ 336.1575; found 336.1570.



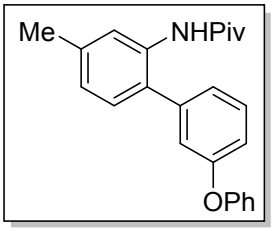
(3g) *N*-(4-methyl-3'-nitro-[1,1'-biphenyl]-2-yl)pivalamide

The title compound was prepared according to the general procedure described above and purified by column chromatography to give the product as a white solid (41 mg, 66%); R*f* = 0.3 (petroleum ether/EtOAc = 10:1), Purified using a mixture of petroleum ether/EtOAc = 10:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25-8.22 (m, 2H), 7.96 (s, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.25 (brs, 1H), 7.17 (d, *J* = 7.8 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 2.41 (s, 3H), 1.13 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 176.47, 148.35, 140.23, 139.67, 135.48, 134.30, 129.82, 129.70, 128.42, 125.95, 124.09, 123.82, 122.47, 39.60, 27.31, 21.34; HRMS (ESI) m/z calculated for $C_{18}H_{20}N_2O_3$ $[M+H]^+$ 313.1552; found 313.1546.



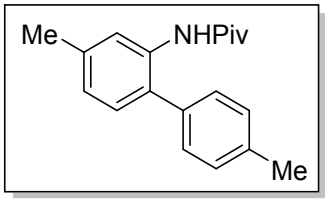
(3h) *N*-(3'-cyano-4-methyl-[1,1'-biphenyl]-2-yl)pivalamide

The title compound was prepared according to the general procedure described above and purified by column chromatography to give the product as a colourless oil (44 mg, 75%); R*f* = 0.5 (petroleum ether/EtOAc = 10:1), Purified using a mixture of petroleum ether/EtOAc = 25:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.98 (s, 1H), 7.69 (d, *J* = 7.1 Hz, 1H), 7.66 (s, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.1 Hz, 1H), 7.17 (brs, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 7.8 Hz, 1H), 2.40 (s, 3H), 1.14 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 176.43, 139.84, 139.59, 134.34, 133.80, 132.81, 131.20, 129.65, 129.55, 128.41, 125.81, 123.55, 118.24, 113.08, 39.63, 27.34, 21.37; HRMS (ESI) m/z calculated for $C_{19}H_{20}N_2O$ $[M+H]^+$ 293.1654; found 293.1648.



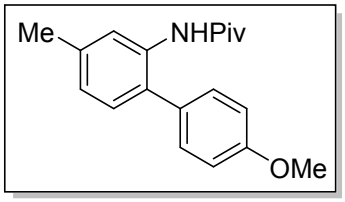
(3i) *N*-(4-methyl-3'-phenoxy-[1,1'-biphenyl]-2-yl)pivalamide

The title compound was prepared according to the general procedure described above and purified by column chromatography to give the product as a colourless oil (64 mg, 89%); R*f* = 0.5 (petroleum ether/EtOAc = 10:1), Purified using a mixture of petroleum ether/EtOAc = 25:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.22 (s, 1H), 7.50 (s, 1H), 7.44 (t, *J* = 8.1 Hz, 1H), 7.37 (t, *J* = 8.1 Hz, 2H), 7.16-7.12 (m, 2H), 7.08 (d, *J* = 7.6 Hz, 1H), 7.06-7.04 (m, 3H), 6.99 (s, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 2.39 (s, 3H), 1.14 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 176.30, 158.12, 156.46, 139.92, 138.74, 134.73, 130.27, 129.89, 129.43, 128.69, 124.68, 123.90, 123.84, 121.45, 119.36, 119.24, 117.78, 39.80, 27.39, 21.46; HRMS (ESI) m/z calculated for $C_{24}H_{25}NO_2$ $[M+H]^+$ 360.1964; found 360.1958.



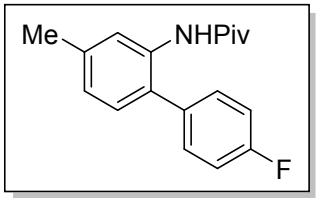
(3j) *N*-(4,4'-dimethyl-[1,1'-biphenyl]-2-yl)pivalamide

The title compound was prepared according to the general procedure described above and purified by column chromatography to give the product as a white solid (51 mg, 90%); R*f* = 0.45 (petroleum ether/EtOAc = 10:1), Purified using a mixture of petroleum ether/EtOAc = 20:1; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.24 (s, 1H), 7.50 (brs, 1H), 7.31-7.20 (m, 4H), 7.11 (d, *J* = 7.7 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 1H), 2.41 (s, 3H), 2.39 (s, 3H), 1.11 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 176.28, 138.20, 137.57, 134.98, 134.88, 129.62, 129.58, 129.22, 124.56, 121.20, 39.74, 27.35, 21.43, 21.17; HRMS (ESI) m/z calculated for $C_{19}H_{23}NO$ $[M+H]^+$ 282.1858, found 282.1852.



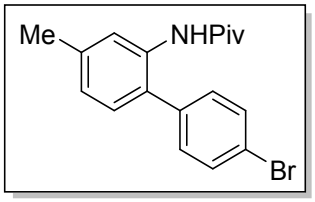
(3k) *N*-(4'-methoxy-4-methyl-[1,1'-biphenyl]-2-yl)pivalamide

The title compound was prepared according to the general procedure described above and purified by column chromatography to give the product as a white solid (56 mg, 94%); R*f* = 0.4 (petroleum ether/EtOAc = 10:1), Purified using a mixture of petroleum ether/EtOAc = 20:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.23 (s, 1H), 7.48 (brs, 1H), 7.27 (d, *J* = 8.7 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 1H), 7.01 (d, *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 7.7 Hz, 1H), 3.86 (s, 3), 2.39 (s, 3H), 1.12 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 176.34, 159.26, 138.22, 135.08, 130.62, 130.23, 129.74, 128.99, 124.62, 121.29, 114.40, 77.05, 55.37, 39.81, 27.44, 21.49; HRMS (ESI) m/z calculated for $C_{19}H_{23}NO_2$ $[M+H]^+$ 298.1807, found 298.1802.



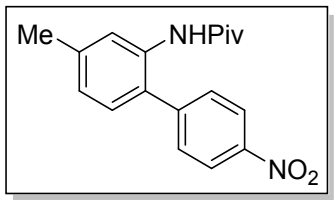
(3l) *N*-(4'-fluoro-4-methyl-[1,1'-biphenyl]-2-yl)pivalamide

The title compound was prepared according to the general procedure described above and purified by column chromatography to give the product as a white solid (51 mg, 89%); R*f* = 0.55 (petroleum ether/EtOAc = 10:1), Purified using a mixture of petroleum ether/EtOAc = 30:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (s, 1H), 7.35-7.30 (m, 3H), 7.17 (t, *J* = 8.7 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 8.8 Hz, 1H), 2.40 (s, 3H), 1.12 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 176.31, 162.32 (d, $J_{C\text{-}F}$ = 248.0 Hz), 138.67, 134.79, 134.03 (d, $J_{C\text{-}F}$ = 3.7 Hz), 131.11 (d, $J_{C\text{-}F}$ = 8.0 Hz), 129.61, 128.50, 124.83, 121.77, 115.91 (d, $J_{C\text{-}F}$ = 21.3 Hz), 39.71, 27.34, 21.42; HRMS (ESI) m/z calculated for $C_{18}H_{20}FNO$ $[M+H]^+$ 286.1654; found 286.1648.



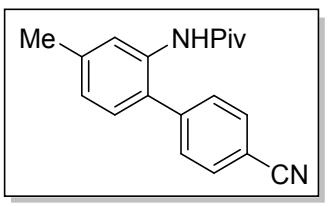
(3m) *N*-(4'-bromo-4-methyl-[1,1'-biphenyl]-2-yl)pivalamide

The title compound was prepared according to the general procedure described above and purified by column chromatography to give the product as a white solid (58 mg, 84%); R*f* = 0.45 (petroleum ether/EtOAc = 10:1), Purified using a mixture of petroleum ether/EtOAc = 20:1; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.15 (s, 1H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.33 (brs, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 7.8 Hz, 1H), 2.39 (s, 3H), 1.13 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 176.31, 138.87, 137.09, 134.55, 132.04, 131.03, 129.48, 128.42, 125.02, 122.13, 121.98, 39.72, 27.37, 21.41; HRMS (ESI) m/z calculated for $C_{18}H_{20}BrNO$ $[M+H]^+$ 346.0807, found 346.0801.



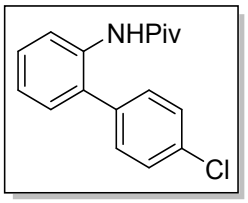
(3n) *N*-(4-methyl-4'-nitro-[1,1'-biphenyl]-2-yl)pivalamide

The title compound was prepared according to the general procedure described above and purified by column chromatography to give the product as a white solid (49 mg, 78%); R*f* = 0.5 (petroleum ether/EtOAc = 15:2), Purified using a mixture of petroleum ether/EtOAc = 15:1; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.32 (d, *J* = 9.0 Hz, 2H), 7.99 (s, 1H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.23 (brs, 1H), 7.16 (d, *J* = 7.8 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 2.41 (s, 3H), 1.14 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 176.45, 147.14, 145.45, 139.91, 134.26, 130.22, 129.54, 128.53, 125.83, 123.96, 123.66, 39.64, 27.35, 21.37; HRMS (ESI) m/z calculated for $C_{18}H_{20}N_2O_3$ $[M+H]^+$ 313.1552; found 313.1546.



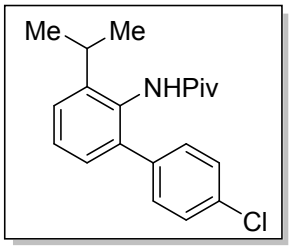
(3o) *N*-(4'-cyano-4-methyl-[1,1'-biphenyl]-2-yl)pivalamide

The title compound was prepared according to the general procedure described above and purified by column chromatography to give the product as a colourless oil (48 mg, 82%); R*f* = 0.45 (petroleum ether/EtOAc = 10:1), Purified using a mixture of petroleum ether/EtOAc = 20:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.02 (s, 1H), 7.76 (d, *J* = 7.9 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.20 (brs, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 7.7 Hz, 1H), 2.40 (s, 3H), 1.13 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 176.40, 143.40, 139.71, 134.27, 132.54, 130.13, 129.45, 128.70, 125.69, 123.33, 118.49, 111.53, 39.66, 27.34, 21.39; HRMS (ESI) m/z calculated for $C_{19}H_{20}N_2O$ $[M+H]^+$ 293.1654; found 293.1648.



(4a) *N*-(4'-chloro-[1,1'-biphenyl]-2-yl)pivalamide

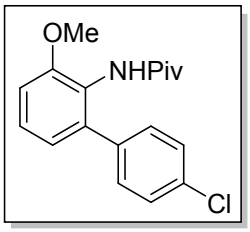
The title compound was prepared according to the general procedure (in gram-scale) described above and purified by column chromatography to give the product as a light yellow solid (2.36 gm, 82%); R*f* = 0.45 (petroleum ether/EtOAc = 10:1), Purified using a mixture of petroleum ether/EtOAc = 25:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (d, *J* = 8.2 Hz, 1H), 7.49-7.46 (m, 2H), 7.40-7.34 (m, 2H), 7.33-7.30 (m, 2H), 7.21 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.19-7.15 (m, 1H),1.13 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 176.30, 136.56, 134.90, 134.10, 131.21, 130.66, 129.75, 129.16, 128.76, 124.22, 121.57, 39.73, 27.38; HRMS (ESI) m/z calculated for $C_{17}H_{18}ClNO$ $[M+H]^+$ 288.1155; found 288.1150.



(4b) *N*-(4'-chloro-3-isopropyl-[1,1'-biphenyl]-2-yl)pivalamide

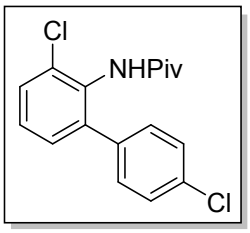
The title compound was prepared according to the general procedure described above and purified by column chromatography to give the product as a white solid (55 mg, 84%); R*f* = 0.45 (petroleum ether/EtOAc = 10:1), Purified using a mixture of petroleum ether/EtOAc = 25:1; ^{1}HNMR (500 MHz, $CDCl_3$): δ = 7.38-7.33 (m, 4H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 7.3 Hz, 1H), 6.75 (s, 1H), 3.05 (sep, *J* = 6.9 Hz, 1H), 1.25 (d, *J* = 6.9 Hz, 6H), 1.11 (s, 9H);

^{13}C NMR (126 MHz, $CDCl_3$): δ = 177.27, 146.93, 139.53, 138.61, 133.17, 131.42, 130.32, 128.13, 127.81, 127.60, 125.62, 38.96, 28.54, 27.42, 23.42; HRMS (ESI) m/z calculated for $C_{20}H_{24}ClNO$ $[M+H]^+$ 330.1625; found 330.1619.



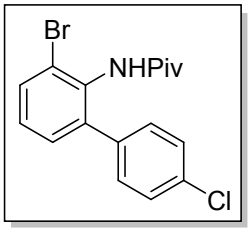
(4c) *N*-(4'-chloro-3-methoxy-[1,1'-biphenyl]-2-yl)pivalamide

The title compound was prepared according to the general procedure described above and purified by column chromatography to give the product as a white solid (55 mg, 87%); R*f* = 0.4 (petroleum ether/EtOAc = 8:1), Purified using a mixture of petroleum ether/EtOAc = 20:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.30 (s, 4H), 7.26 (t, *J* = 8.0 Hz, 1H), 6.94 (brs, 1H), 6.91 (d, *J* = 8.1 Hz, 2H), 3.84 (s, 3H), 1.14 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 176.71, 154.42, 139.50, 138.32, 132.90, 129.79, 128.10, 127.43, 123.21, 122.11, 110.35, 55.94, 39.08, 27.37; HRMS (ESI) m/z calculated for $C_{18}H_{20}ClNO_2$ $[M+H]^+$ 318.1261; found 318.1255.



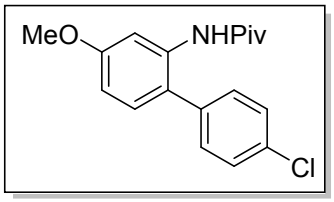
(4d) *N*-(3,4'-dichloro-[1,1'-biphenyl]-2-yl)pivalamide

The title compound was prepared according to the general procedure described above and purified by column chromatography to give the product as a white solid (49 mg, 77%); R*f* = 0.45 (petroleum ether/EtOAc = 8:1), Purified using a mixture of petroleum ether/EtOAc = 20:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.28-7.25 (m, 3H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.05 (s, 1H), 1.14 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 176.53, 141.04, 137.51, 133.56, 132.75, 131.77, 129.89, 129.04, 128.75, 128.27, 128.03, 39.14, 27.31; HRMS (ESI) m/z calculated for $C_{17}H_{17}Cl_2NO$ $[M+H]^+$ 322.0765; found 322.0760.



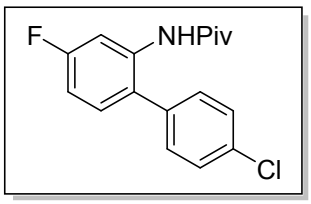
(4e) *N*-(3-bromo-4'-chloro-[1,1'-biphenyl]-2-yl)pivalamide

The title compound was prepared according to the general procedure described above and purified by column chromatography to give the product as a white solid R*f* = 0.45 (petroleum ether/EtOAc = 8:1), Purified using a mixture of petroleum ether/EtOAc = 20:1; (55 mg, 75%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.27-7.24 (m, 3H), 7.20 (t, *J* = 8.2 Hz, 1H), 7.05 (brs, 1H), 1.13 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 176.27, 141.27, 137.77, 133.56, 133.15, 132.24, 129.89, 129.55, 128.45, 128.26, 123.44, 39.17, 27.31; HRMS (ESI) m/z calculated for $C_{17}H_{17}BrClNO$ $[M+H]^+$ 366.0260; found 366.0255.



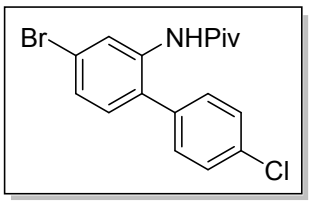
(4f) *N*-(4'-chloro-4-methoxy-[1,1'-biphenyl]-2-yl)pivalamide

The title compound was prepared according to the general procedure described above and purified by column chromatography to give the product as a white solid (62 mg, 97%); R*f* = 0.55 (petroleum ether/EtOAc = 8:1), Purified using a mixture of petroleum ether/EtOAc = 20:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 2.6 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.43 (brs, 1H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 1H), 6.73 (dd, *J* = 8.4, 2.7 Hz, 1H), 3.86 (s, 3H), 1.14 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 176.46, 159.93, 136.42, 136.01, 133.83, 130.91, 130.43, 129.22, 123.09, 110.91, 105.63, 55.46, 39.92, 27.40; HRMS (ESI) m/z calculated for $C_{18}H_{20}ClNO_2$ $[M+H]^+$ 318.1261; found 318.1255.



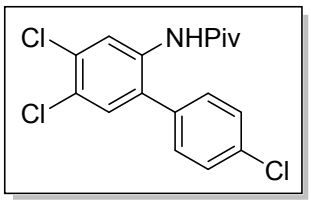
(4g) *N*-(4'-chloro-4-fluoro-[1,1'-biphenyl]-2-yl)pivalamide

The title compound was prepared according to the general procedure described above and purified by column chromatography to give the product as a white solid (57 mg, 94%); R*f* = 0.55 (petroleum ether/EtOAc = 10:1), Purified using a mixture of petroleum ether/EtOAc = 25:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 11.1 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.44 (s, 1H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.15 (t, *J* = 7.8 Hz, 1H), 6.84 (t, *J* = 7.8 Hz, 1H), 1.12 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 176.31, 162.52 (d, J_{C-F} = 245.2 Hz), 136.34 (d, J_{C-F} = 11.6 Hz), 135.61, 134.33, 130.74, 130.66 (d, J_{C-F} = 10.3 Hz), 129.34, 126.36 (d, J_{C-F} = 3.1 Hz), 110.62 (d, J_{C-F} = 21.8 Hz), 108.23 (d, J_{C-F} = 27.6 Hz), 39.83, 27.25; HRMS (ESI) m/z calculated for $C_{17}H_{17}ClFNO$ $[M+H]^+$ 306.1061; found 306.1055.



(4h) *N*-(4-bromo-4'-chloro-[1,1'-biphenyl]-2-yl)pivalamide

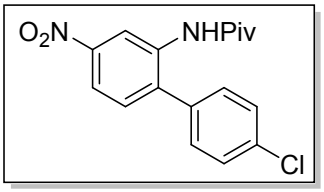
The title compound was prepared according to the general procedure described above and purified by column chromatography to give the product as a white solid (58 mg, 79%); R*f* = 0.4 (petroleum ether/EtOAc = 10:1), Purified using a mixture of petroleum ether/EtOAc = 20:1; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.61 (d, *J* = 2.0 Hz, 1H), 7.48 (d, *J* = 8.6 Hz, 2H), 7.36 (brs, 1H), 7.32-7.26 (m, 3H), 7.06 (d, *J* = 8.2 Hz, 1H), 1.12 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 176.35, 136.05, 135.45, 134.54, 130.84, 130.50, 129.56, 129.41, 127.05, 123.97, 122.53, 39.84, 27.30; HRMS (ESI) m/z calculated for $C_{17}H_{17}BrClNO$ $[M+H]^+$ 366.0260; found 366.0255.



(4i) *N*-(4,4',5-trichloro-[1,1'-biphenyl]-2-yl)pivalamide

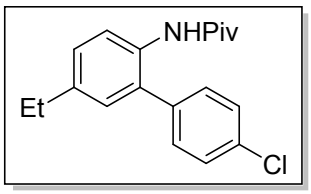
The title compound was prepared according to the general procedure described above and purified by column chromatography to give the product as a white solid (48 mg, 68%); R*f* = 0.55 (petroleum ether/EtOAc = 8:1), Purified using a mixture of petroleum ether/EtOAc = 15:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.57 (s, 1H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.34 (s, 1H),

7.29-7.27 (m, 3H), 1.12 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 176.34, 135.03, 134.35, 134.22, 132.52, 130.76, 130.56, 130.42, 129.56, 127.18, 122.71, 39.85, 27.25; HRMS (ESI) m/z calculated for $C_{17}H_{16}Cl_3NO$ $[M+H]^+$ 356.0376; found 356.0370.



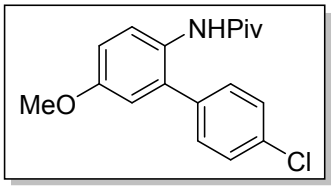
(4j) *N*-(4'-chloro-4-nitro-[1,1'-biphenyl]-2-yl)pivalamide

The title compound was prepared according to the general procedure described above and purified by column chromatography to give the product as a white solid (33 mg, 49%); R*f* = 0.6 (petroleum ether/EtOAc = 5:1), Purified using a mixture of petroleum ether/EtOAc = 15:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.24 (s, 1H), 7.99 (d, *J* = 6.9 Hz, 1H), 7.55-7.53 (m, 3H), 7.37-7.32 (m, 3H), 1.15 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 176.61, 147.98, 136.76, 136.14, 135.53, 134.48, 130.45, 130.25, 129.77, 118.71, 116.26, 77.07, 39.98, 27.29; HRMS (ESI) m/z calculated for $C_{17}H_{17}ClN_2O_3$ $[M+H]^+$ 333.1006; found 333.1000.



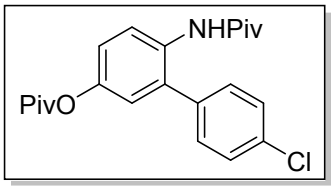
(4k) *N*-(4'-chloro-5-ethyl-[1,1'-biphenyl]-2-yl)pivalamide

The title compound was prepared according to the general procedure described above and purified by column chromatography to give the product as a white solid (54 mg, 85%); R*f* = 0.5 (petroleum ether/EtOAc = 10:1), Purified using a mixture of petroleum ether/EtOAc = 25:1; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 8.4 Hz, 1H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.35-7.26 (m, 3H), 7.22 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.05 (d, *J* = 2.2 Hz, 1H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.24 (t, *J* = 7.6 Hz, 3H), 1.13 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 176.23, 140.38, 136.89, 133.94, 132.48, 131.43, 130.67, 129.14, 129.07, 128.13, 121.91, 39.65, 28.26, 27.42, 15.62; HRMS (ESI) m/z calculated for $C_{19}H_{22}ClNO$ $[M+H]^+$ 316.1468; found 316.1462.



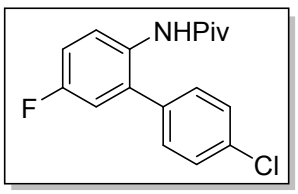
(4l) *N*-(4'-chloro-5-methoxy-[1,1'-biphenyl]-2-yl)pivalamide

The title compound was prepared according to the general procedure described above and purified by column chromatography to give the product as a white solid (59 mg, 93%); R*f* = 0.45 (petroleum ether/EtOAc = 10:1), Purified using a mixture of petroleum ether/EtOAc = 20:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.9 Hz, 1H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.15 (brs, 1H), 6.92 (dd, *J* = 9.1, 3.1 Hz, 1H), 6.77 (d, *J* = 3.2 Hz, 1H), 3.81 (s, 3H), 1.13 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 176.30, 156.34, 136.65, 134.05, 133.63, 130.49, 128.99, 127.90, 124.19, 115.27, 113.56, 55.49, 39.45, 27.40; HRMS (ESI) m/z calculated for $C_{18}H_{20}ClNO_2$ $[M+H]^+$ 318.1261; found 318.1255.



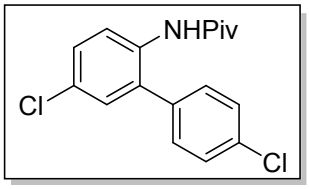
(4m) 4'-chloro-6-pivalamido-[1,1'-biphenyl]-3-yl pivalate

The title compound was prepared according to the general procedure described above and purified by column chromatography to give the product as a white solid (61 mg, 79%); R*f* = 0.55 (petroleum ether/EtOAc = 8:1), Purified using a mixture of petroleum ether/EtOAc = 15:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.31 (d, *J* = 8.9 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 7.30 (brs, 1H), 7.08 (dd, *J* = 8.9, 2.7 Hz, 1H), 6.95 (d, *J* = 2.7 Hz, 1H), 1.35 (s, 9H), 1.13 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 177.12, 176.27, 147.09, 135.75, 134.47, 132.46, 132.23, 130.64, 129.26, 122.71, 122.58, 121.60, 39.74, 39.06, 27.40, 27.12; HRMS (ESI) m/z calculated for $C_{22}H_{26}ClNO_3$ $[M+H]^+$ 388.1679; found 388.1674.



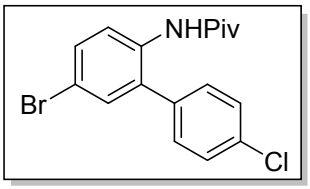
(4n) *N*-(4'-chloro-5-fluoro-[1,1'-biphenyl]-2-yl)pivalamide

The title compound was prepared according to the general procedure described above and purified by column chromatography to give the product as a white solid (2.04 gm, 87%); R*f* = 0.5 (petroleum ether/EtOAc = 10:1), Purified using a mixture of petroleum ether/EtOAc = 20:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.14 (dd, *J* = 9.1, 3.7 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.25 (brs, 1H), 7.05 (dt, *J* = 8.4, 3.5 Hz, 1H), 6.93 (dd, *J* = 8.8, 3.0 Hz, 1H), 1.12 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 176.33, 159.10 (d, $J_{C\text{-}F}$ = 245.2 Hz), 135.55, 134.52, 133.60 (d, $J_{C\text{-}F}$ = 7.6 Hz), 130.90, 130.39, 129.21, 124.04 (d, $J_{C\text{-}F}$ = 8.6 Hz), 116.43 (d, $J_{C\text{-}F}$ = 23.0 Hz), 115.13 (d, $J_{C\text{-}F}$ = 20.9 Hz), 39.55, 27.31; HRMS (ESI) m/z calculated for $C_{17}H_{17}ClFNO$ $[M+H]^+$ 306.1061; found 306.1055.



(4o) *N*-(4',5-dichloro-[1,1'-biphenyl]-2-yl)pivalamide

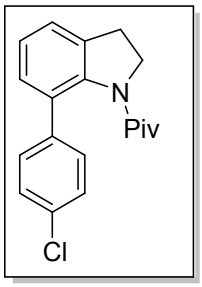
The title compound was prepared according to the general procedure described above and purified by column chromatography to give the product as a white solid (53 mg, 83%); R*f* = 0.5 (petroleum ether/EtOAc = 8:1), Purified by using a mixture of petroleum ether/EtOAc = 15:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.27 (d, *J* = 8.9 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.34 (dd, *J* = 8.7, 2.7 Hz, 1H), 7.32-7.28 (m, 3H), 7.20 (d, *J* = 2.7 Hz, 1H), 1.12 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 176.30, 135.23, 134.69, 133.60, 132.62, 130.48, 129.46, 129.38, 129.14, 128.61, 122.77, 39.77, 27.33; HRMS (ESI) m/z calculated for $C_{17}H_{17}Cl_2NO$ $[M+H]^+$ 322.0765; found 322.0760.



(4p) *N*-(5-bromo-4'-chloro-[1,1'-biphenyl]-2-yl)pivalamide

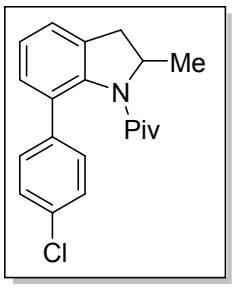
The title compound was prepared according to the general procedure described above and purified by column chromatography to give the product as a white solid (59 mg, 81%); R*f* = 0.45 (petroleum ether/EtOAc = 8:1), Purified using a mixture of petroleum ether/EtOAc = 15:1; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.23 (d, *J* = 8.8 Hz, 1H), 7.52-7.45 (m, 3H), 7.35 (d, *J* = 2.4 Hz, 1H), 7.32-7.26 (m, 3H), 1.11 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 176.31,

135.09, 134.73, 134.13, 132.85, 132.33, 131.59, 130.50, 129.41, 122.93, 116.75, 39.81, 27.34; HRMS (ESI) m/z calculated for $C_{17}H_{17}BrClNO$ $[M+H]^+$ 366.0260; found 366.0255.



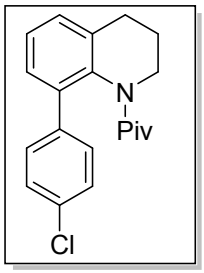
(4q) 1-(7-(4-chlorophenyl)indolin-1-yl)-2,2-dimethylpropan-1-one

The title compound was prepared according to the general procedure described above and purified by column chromatography to give the product as a white solid (50 mg, 81%); R*f* = 0.45 (petroleum ether/EtOAc = 10:1), Purified using a mixture of petroleum ether/EtOAc = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.33 (s, 4H),7.23 (d, *J* = 7.2 Hz, 1H), 7.18-7.14 (m, 2H), 4.20 (t, *J* = 7.6 Hz, 2H), 3.12 (t, *J* = 7.6 Hz, 2H), 1.19 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 177.28, 141.79, 140.03, 134.76, 132.35, 131.87, 128.48, 128.43, 127.88, 125.11, 123.52, 50.63, 39.73, 31.09, 28.01; HRMS (ESI) m/z calculated for $C_{19}H_{21}ClNO$ $[M+H]^+$ 314.1312; found 314.1306.



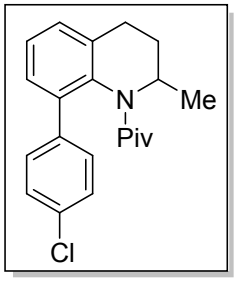
(4r) 1-(7-(4-chlorophenyl)-2-methylindolin-1-yl)-2,2-dimethylpropan-1-one

The title compound was prepared according to the general procedure described above and purified by column chromatography to give the product as a brown solid (58 mg, 89%); R*f* = 0.5 (petroleum ether/EtOAc = 10:1), Purified using a mixture of petroleum ether/EtOAc = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 6.6 Hz, 1H), 7.21-7.17 (m, 2H), 4.78 (quin, *J* = 6.6 Hz, 1H), 3.33 (dd, *J* = 14.9, 6.7 Hz, 1H), 2.62 (d, *J* = 14.9 Hz, 1H), 1.43 (d, *J* = 6.2 Hz, 3H), 1.20 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 177.15, 140.74, 139.76, 134.47, 133.56, 132.36, 128.42, 127.90, 127.85, 125.58, 124.18, 57.03, 40.04, 38.28, 28.52, 20.59; HRMS (ESI) m/z calculated for $C_{20}H_{23}ClNO$ $[M+H]^+$ 328.1468; found328.1463.



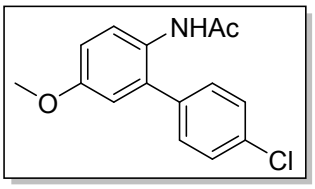
(4s) 1-(8-(4-chlorophenyl)-3,4-dihydroquinolin-1(2H)-yl)-2,2-dimethylpropan-1-one

The title compound was prepared according to the general procedure described above and purified by column chromatography to give the product as a colourless oily liquid (55 mg, 84%); R*f* = 0.45 (petroleum ether/EtOAc = 10:1), Purified using a mixture of petroleum ether/EtOAc = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35-7.31 (m, 7H), 4.40 (s, 1H), 3.40 (s, 1H), 2.85-2.76 (m, 2H), 2.16 (s, 1H), 2.04 (s, 1H), 1.10 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ =176.60, 139.17, 138.80, 137.83, 133.77, 132.31, 129.77, 127.89, 127.82, 127.60, 125.75, 45.15, 39.02, 28.10, 25.73, 24.74; HRMS (ESI) m/z calculated for $C_{20}H_{23}ClNO$ $[M+H]^+$328.1468; found328.1462.



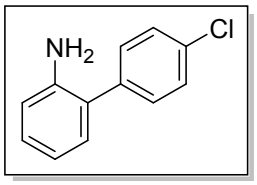
(4t) 1-(8-(4-chlorophenyl)-2-methyl-3,4-dihydroquinolin-1(2H)-yl)-2,2-dimethylpropan-1-one

The title compound was prepared according to the general procedure described above and purified by column chromatography to give the product as a white solid (63 mg, 92%); R*f* = 0.45 (petroleum ether/EtOAc = 10:1), Purified using a mixture of petroleum ether/EtOAc = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 7.19-7.13 (m, 2H), 7.05 (d, *J* = 6.9 Hz, 1H), 4.64-4.61 (m, 1H), 2.90-2.79 (m, 2H), 2.18-2.11 (m, 1H), 1.80-1.77 (m, 1H), 1.30 (d, *J* = 6.5 Hz, 3H), 1.05 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 178.10, 139.66, 139.13, 135.67, 132.34, 131.86, 130.30, 128.09, 127.95, 127.76, 125.46, 77.07, 48.64, 39.73, 29.82, 28.26, 23.56, 18.14; HRMS (ESI) m/z calculated for $C_{21}H_{25}ClNO$ $[M+H]^+$ 342.1625; found342.1619.



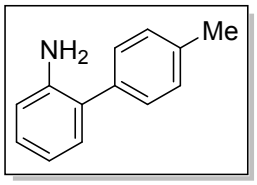
(4u) *N*-(4'-chloro-5-methoxy-[1,1'-biphenyl]-2-yl)acetamide

The title compound was prepared according to the general procedure described above and purified by column chromatography to give the product as a white solid (36 mg, 65%); R*f* = 0.5 (petroleum ether/EtOAc= 1:1), Purified using a mixture of petroleum ether/EtOAc= 1:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 8.7 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 2H),7.31 (d, *J* = 8.5 Hz, 2H), 6.93 (dd, *J* = 9.2, 2.7 Hz, 1H), 6.83 (brs, 1H), 6.78 (d, *J* = 2.5 Hz, 1H), 3.82 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 168.49, 156.76, 136.76, 134.07, 130.40, 129.09, 127.48, 125.12, 115.39, 113.70, 55.52, 24.11; HRMS (ESI) m/z calculated for $C_{15}H_{15}ClNO_2$ $[M+H]^+$, 276.0791; found 276.0785.



(5a) 4'-chloro-[1,1'-biphenyl]-2-amine

The title compound was prepared according to the general procedure described in Sec (2.7.1) and purified by column chromatography to give the product as a light brown oil (75 mg, 93%); R*f* = 0.6 (petroleum ether/EtOAc = 10:1), Purified using a mixture of petroleum ether/EtOAc = 35:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.45-7.41(m, 4H), 7.19 (dt, *J* = 7.7, 1.5 Hz, 1H), 7.12 (dd, *J* = 7.7, 1.5 Hz, 1H), 6.85 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.78 (dd, *J* = 7.9, 1.0 Hz, 1H), 3.74 (brs, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 143.36, 137.85, 133.03, 130.41, 130.29, 128.94, 128.78, 126.24, 118.72, 115.68; HRMS (ESI) m/z calculated for $C_{12}H_{10}ClN$ $[M+H]^+$ 204.0580; found 204.0575.



(5b) 4'-methyl-[1,1'-biphenyl]-2-amine

The title compound was prepared according to the general procedure described in Sec (2.7.1) and purified by column chromatography to give the product as a light brown oil (86 mg, 94%); R*f* = 0.6 (petroleum ether/EtOAc = 10:1), Purified using a mixture of petroleum ether/EtOAc = 35:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.24-7.19 (m, 2H), 6.90 (dt, *J* = 7.2, 0.8 Hz, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 3.74 (s, 2H), 2.48 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 143.50, 136.73, 136.45, 130.37, 129.42, 128.86, 128.22, 127.52, 118.53, 115.46, 21.11; HRMS (ESI) m/z calculated for $C_{13}H_{13}N$ $[M+H]^+$ 184.1126; found 184.1121

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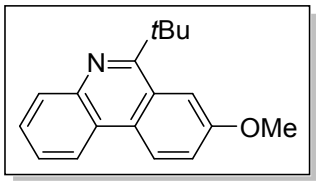
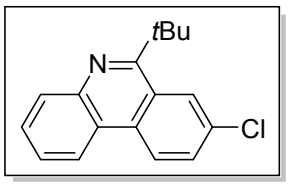


(6a) 6-(*tert*-butyl)-8-methoxyphenanthridine[S5]

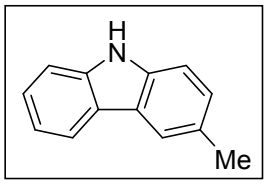
The title compound was prepared according to the general procedure described in Sec (2.7.2) and purified by column chromatography to give the product as a white solid (50 mg, 94%); R*f* = 0.6 (petroleum ether/EtOAc = 10:1), Purified using a mixture of petroleum ether/EtOAc = 35:1; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.61 (d, *J* = 9.2 Hz, 1H), 8.45 (dd, *J* = 7.6, 2.2 Hz, 1H), 8.11 (dd, *J* = 7.4, 2.3 Hz, 1H), 8.01 (d, *J* = 2.6 Hz, 1H), 7.69-7.55 (m, 2H), 7.45 (dd, *J* = 9.1, 2.7 Hz, 1H), 4.01 (s, 3H), 1.75 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 165.68, 157.23, 142.14, 130.20, 128.20, 127.37, 126.49, 125.46, 124.42, 123.46, 121.09, 119.09, 109.66, 55.45, 40.04, 30.95; HRMS (ESI) m/z calculated for $C_{18}H_{19}NO$ $[M+H]^+$ 226.1545; found 226.1539.



(6b) 6-(*tert*-butyl)-8-chlorophenanthridine[S5]

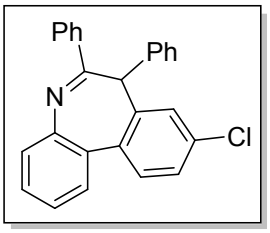
The title compound was prepared according to the general procedure described in Sec (2.7.2) and purified by column chromatography to give the product as a colourless liquid (48.0 mg, 89%); R*f* = 0.6 (petroleum ether/EtOAc = 10:1), Purified using a mixture of petroleum ether/EtOAc = 35:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.61 (d, *J* = 8.8 Hz, 1H), 8.59 (d, *J* = 2.2 Hz, 1H), 8.47 (d, *J* = 7.9 Hz, 1H), 8.13 (d, *J* = 8.2 Hz, 1H), 7.75-7.70 (m, 2H), 7.63 (dt, *J*

= 8.2, 1.2 Hz, 1H), 1.73 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 165.57, 142.81, 132.37, 131.81, 130.36, 129.76, 128.68, 127.54, 126.85, 125.12, 124.62, 122.75, 121.45, 40.16, 31.11; HRMS (ESI) m/z calculated for $C_{17}H_{16}ClN$ $[M+H]^+$ 270.1050; found 270.1044.



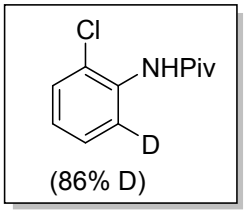
(7b) 3-methyl-9*H*-carbazole[S6]

The title compound was prepared according to the reported literature procedure described in Sec (2.7.3) and purified by column chromatography to give the product as a colourless solid (61.0 mg, 67%); R*f* = 0.6 (petroleum ether/EtOAc = 25:1), Purified using a mixture of petroleum ether/EtOAc = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 7.6 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.93 (s, 1H), 7.41-7.38 (m, 2H), 7.25-7.22 (m, 2H), 7.08 (d, *J* = 8.0 Hz, 1H), 2.54 (s, 3H)); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 139.95, 139.45, 135.99, 125.25, 123.43, 121.03, 120.96, 119.98, 119.31, 110.71, 110.45, 22.03.



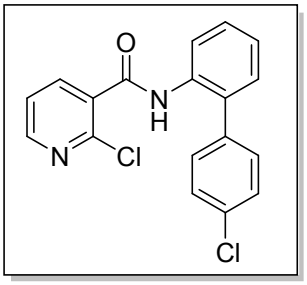
(8) 9-chloro-6,7-diphenyl-7*H*-dibenzo[b,d]azepine[S6]

The title compound was prepared according to the reported literature procedure described in Sec (2.7.4) and purified by column chromatography to give the product as a colourless solid (82 mg, 72%); R*f* = 0.5 (petroleum ether/EtOAc = 10:1), Purified using a mixture of petroleum ether/EtOAc = 20:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.09 (dd, *J* = 7.6, 2.2 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.54-7.51 (m, 3H), 7.48-7.45 (m, 2H), 7.41 (d, *J* = 8.6 Hz, 1H), 7.25 (d, *J* = 8.3 Hz, 1H), 7.17 (t, *J* = 8.6 Hz, 1H), 6.99 (t, *J* = 8.6 Hz, 1H), 6.95-6.92 (m, 3H), 6.78-6.76 (m, 2H), 6.00 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 165.70, 146.08, 140.10, 139.96, 136.54, 135.32, 134.26, 130.97, 130.61, 129.65, 129.32, 128.76, 128.36, 128.00, 127.87, 127.78, 127.63, 126.55, 126.41, 126.28, 124.29, 53.32.



(1d) *N*-(2-chlorophenyl-6-*d*)pivalamide[S7]

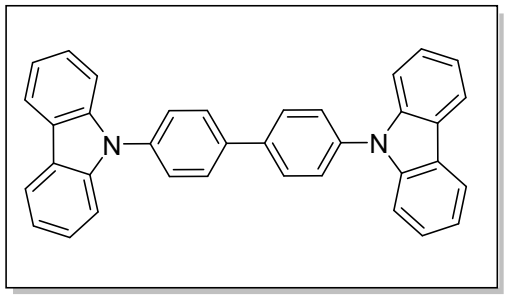
The title compound was prepared according to the reported literature procedure described in Sec (2.7.2) and purified by column chromatography to give the product as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.44 (d, *J* = 7.7 Hz, 0.14H), 8.04 (s, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.31-7.28 (m, 1H), 7.05 (t, *J* = 8.0 Hz, 1H), 1.37 (s, 9H).



2-Chloro-*N*-(4'-chloro-[1,1'-biphenyl]-2-yl)nicotinamide (10)

The title compound was prepared according to the reported literature procedure.[S8]

Yield: 104 mg, (81%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.42 (d, *J* = 4.6 Hz, 1H), 8.39 (d, *J* = 8.4 Hz, 1H),8.17 (s, 1H), 8.11(d, *J* = 7.6 Hz, 1H),7.47-7.44 (m, 1H), 7.43(d, *J* = 8.4 Hz, 2H), 7.35-7.32 (m, 3H), 7.27 (d, *J* = 3.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 162.48, 151.23, 146.65, 140.03, 136.23, 134.37, 134.26, 132.28, 131.05, 130.74, 130.19, 129.23, 128.83, 125.31, 122.84, 122.16; HRMS (ESI) m/z calculated for $C_{21}H_{25}ClNO$ $[M+H]^+$ 343.0405; found 343.0399.



4,4'-di(9H-carbazol-9-yl)-1,1'-biphenyl (12)

The title compound was prepared according to the reported literature procedure.[S9]
Yield: 344 mg (71%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.24 (d, *J* = 7.6 Hz, 4H), 7.95 (d, *J* = 8.4 Hz, 4H), 7.75 (d, *J* = 8.4 Hz, 4H), 7.58 (d, *J* = 8.0 Hz, 4H), 7.51 (t, *J* = 7.6 Hz, 4H),7.38 (t, *J* = 7.3 Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 140.81, 139.24, 137.24, 128.48, 127.46, 126.01, 123.49, 120.37, 120.07, 109.81.

4. References

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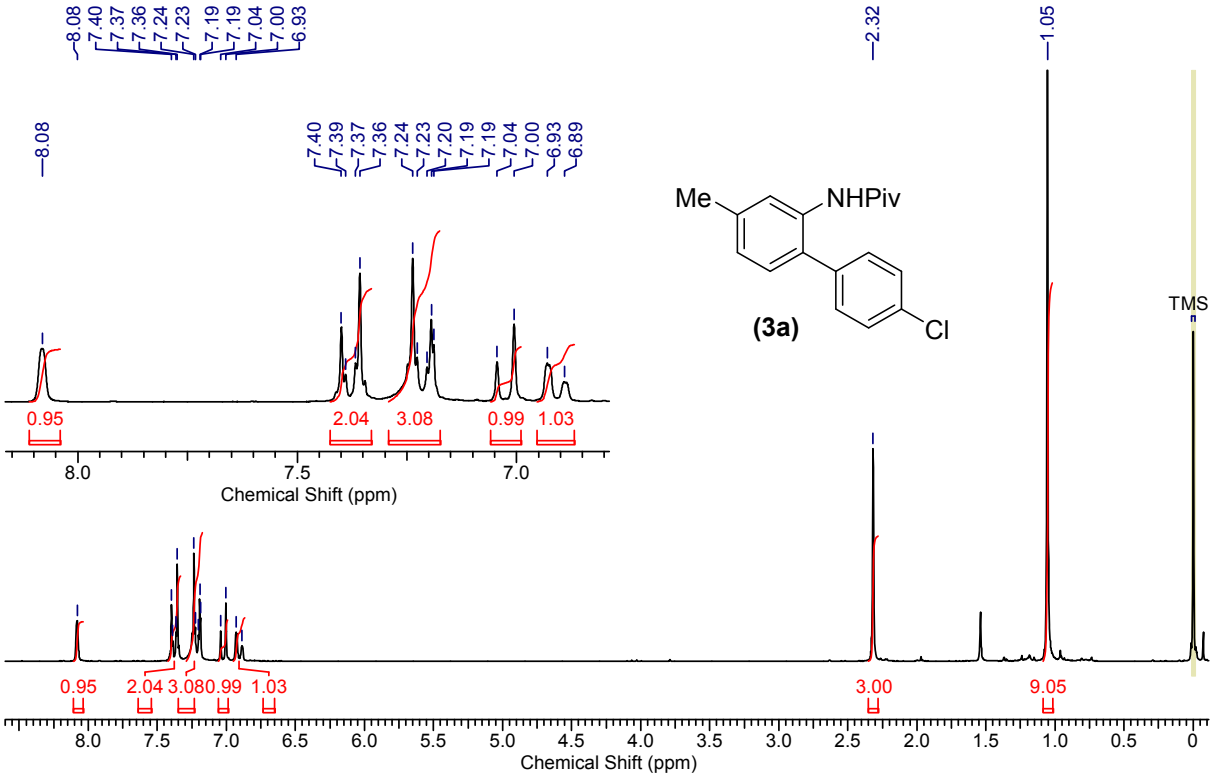
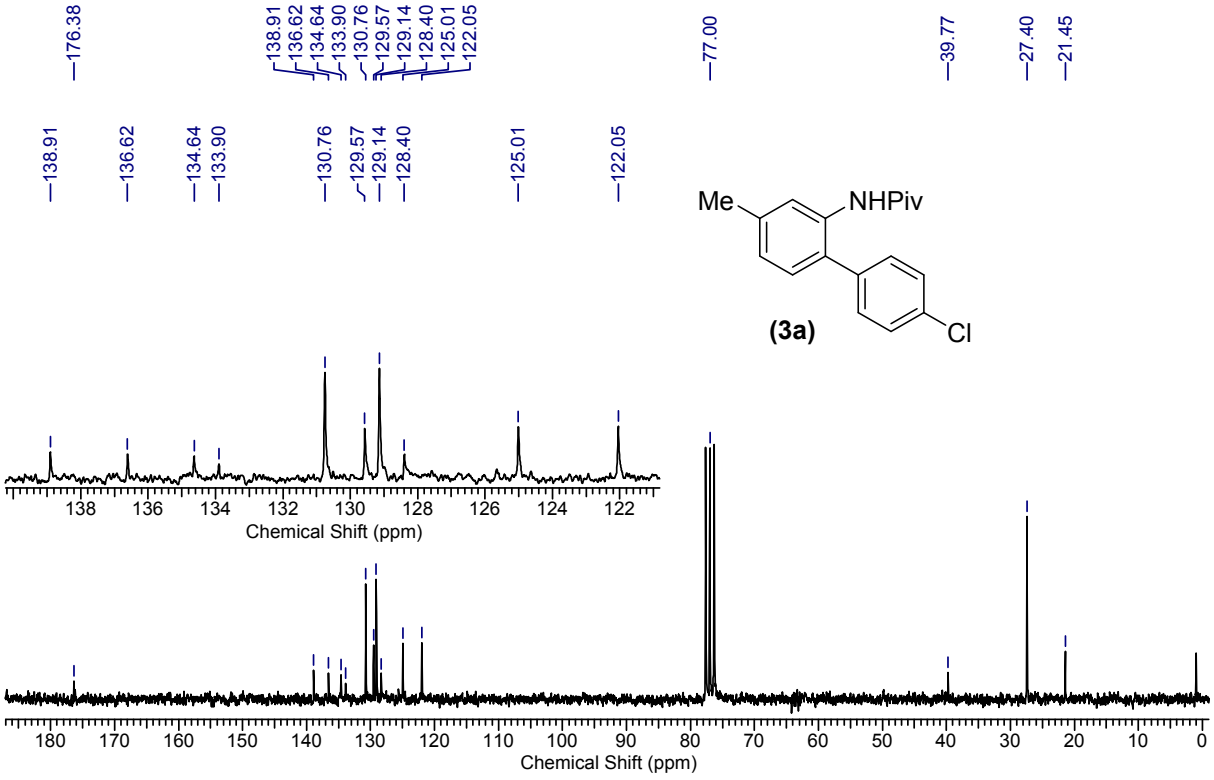
5. Copy of ^{1}H and ^{13}C NMR Spectra



^{1}H NMR of **3a**



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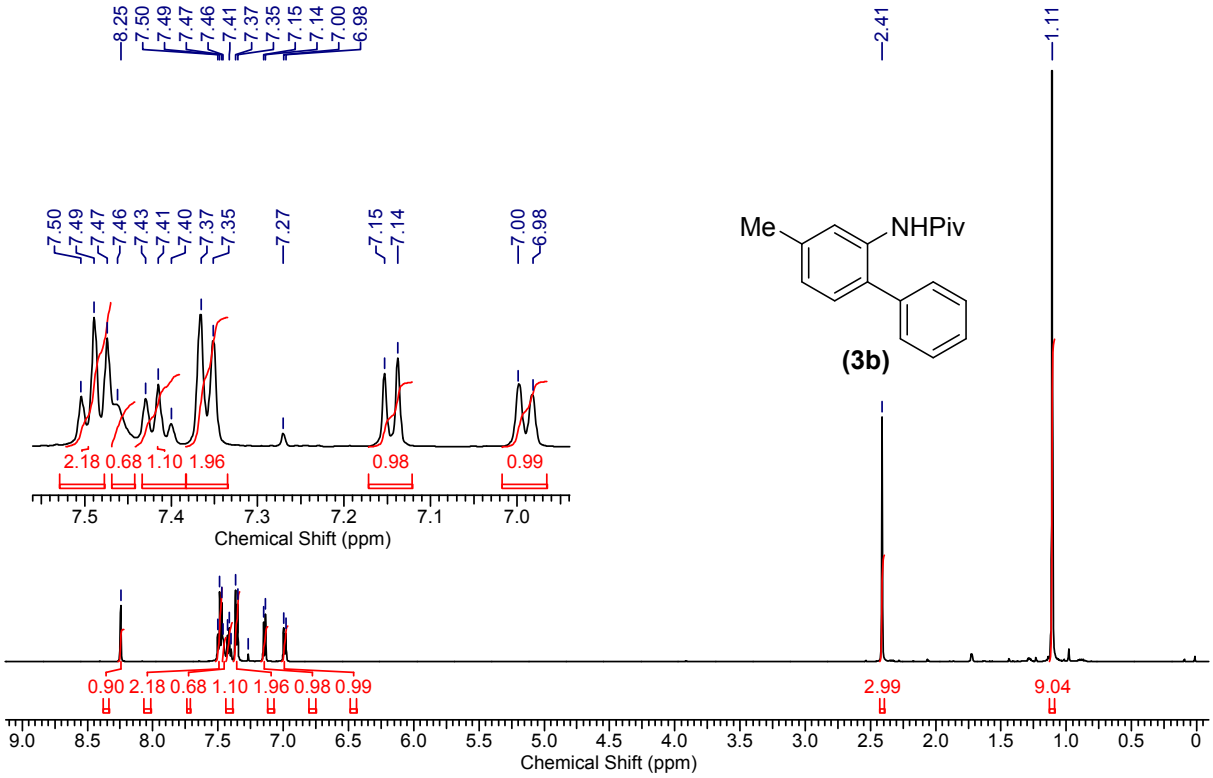
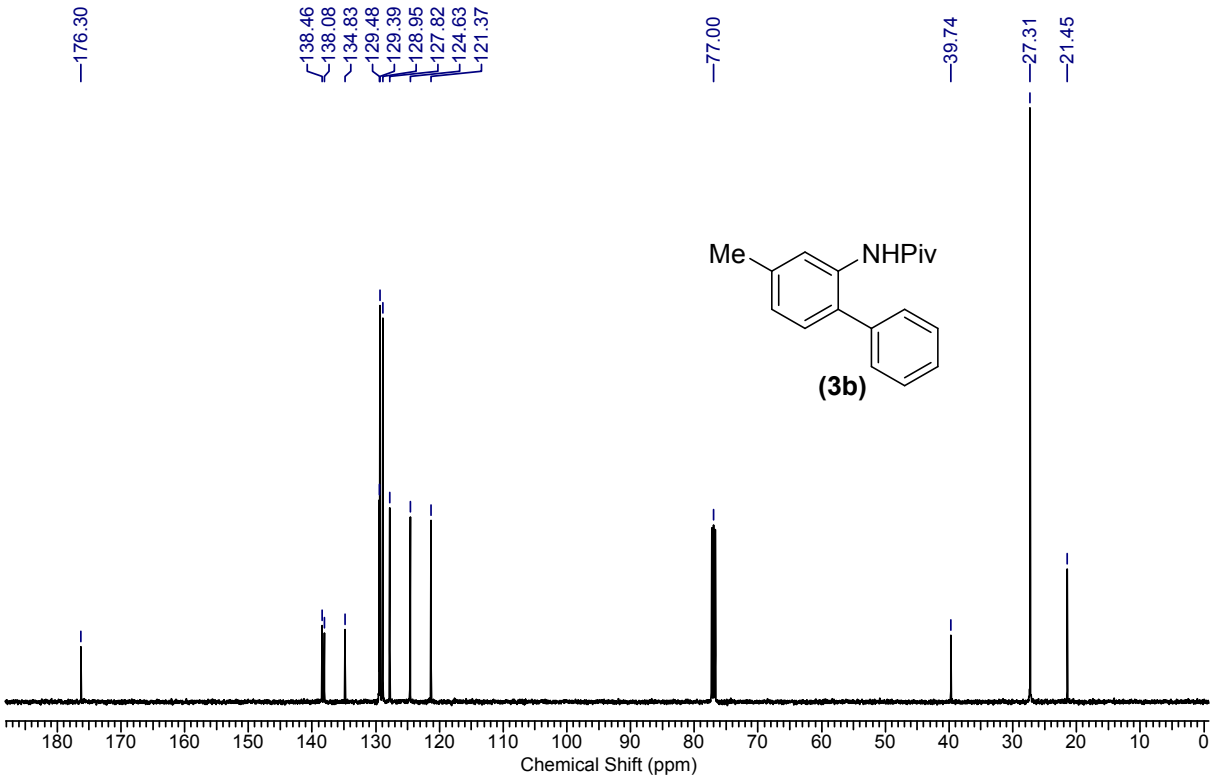


^{1}H NMR of **3b**



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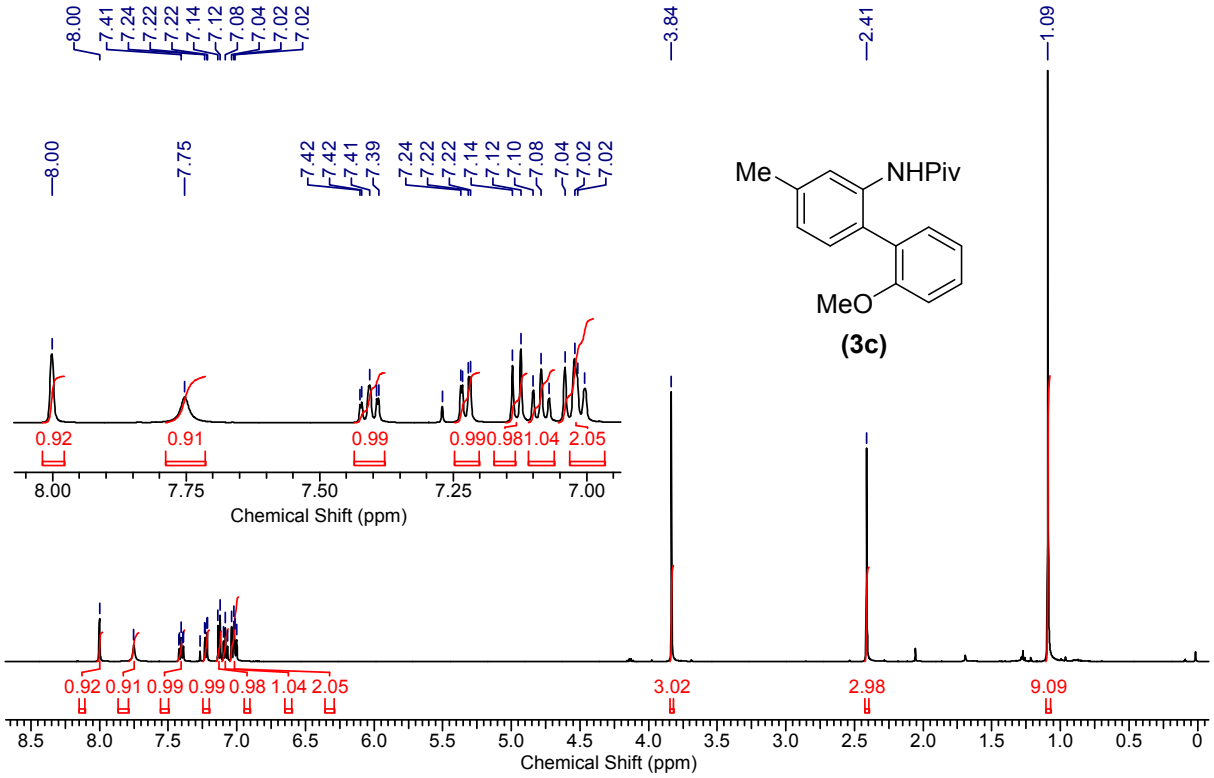
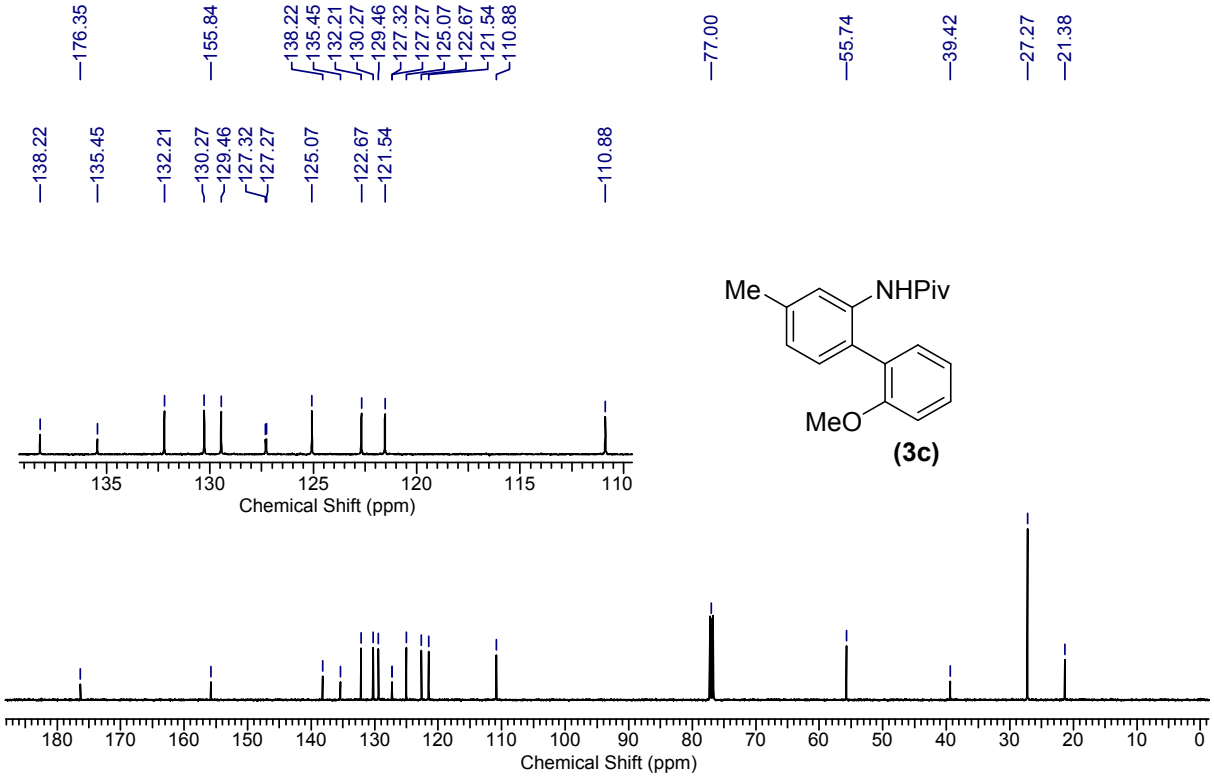


^{1}H NMR of **3c**



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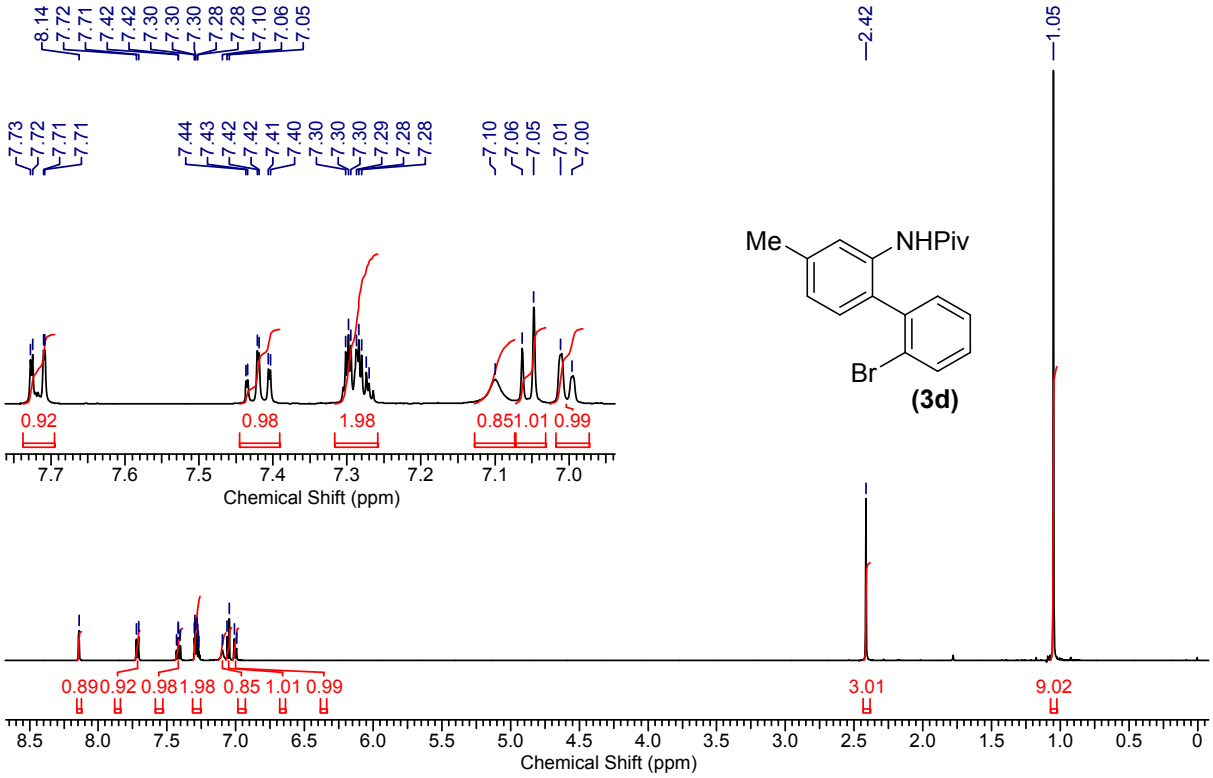

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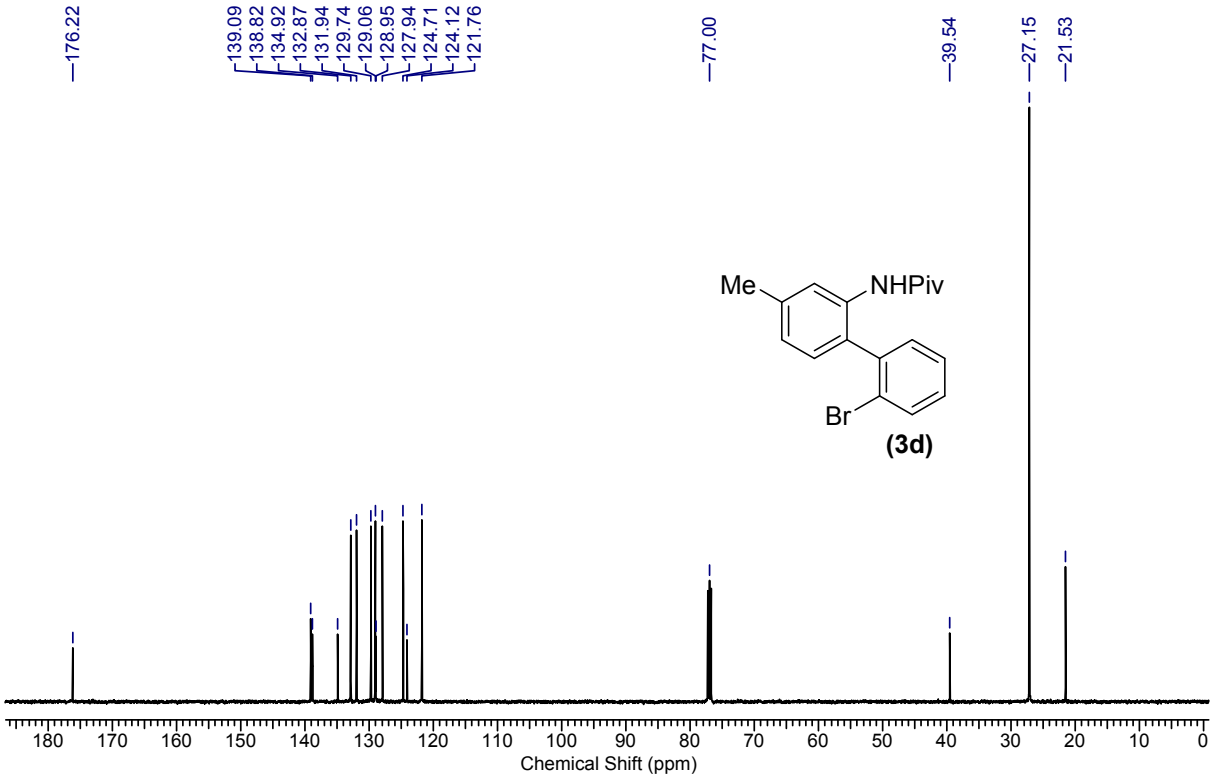

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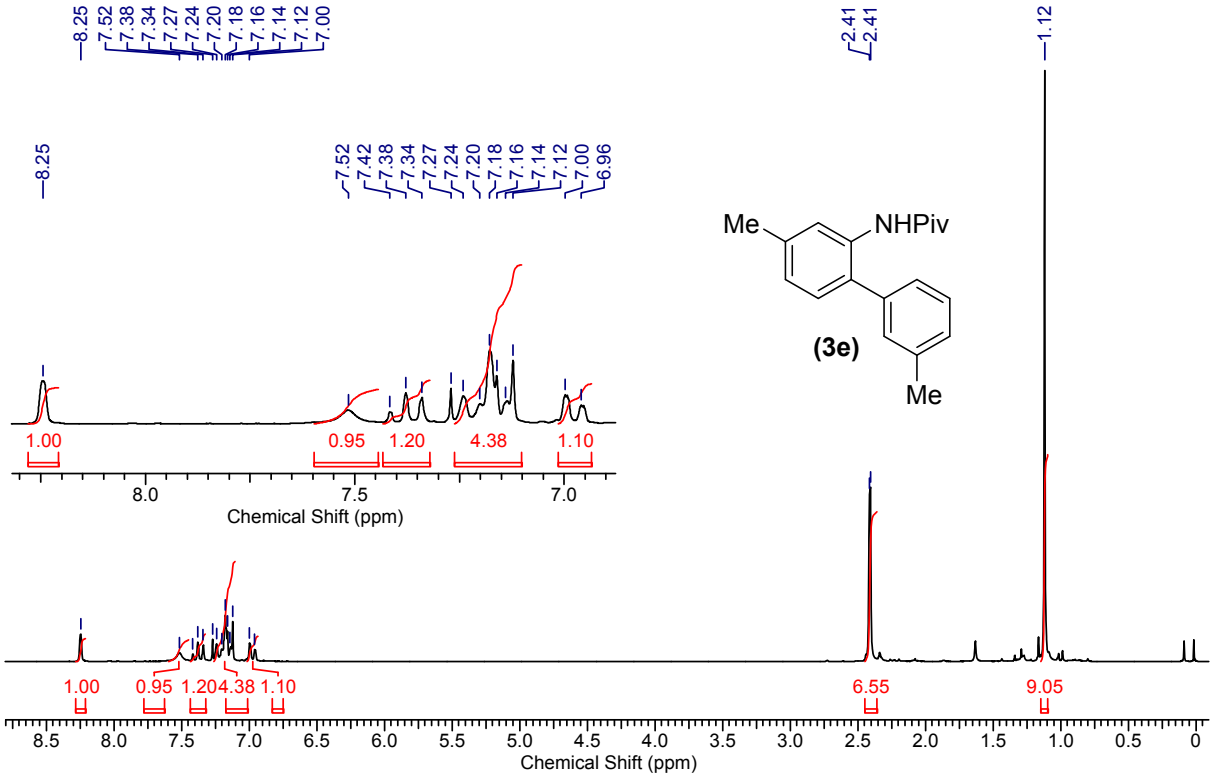

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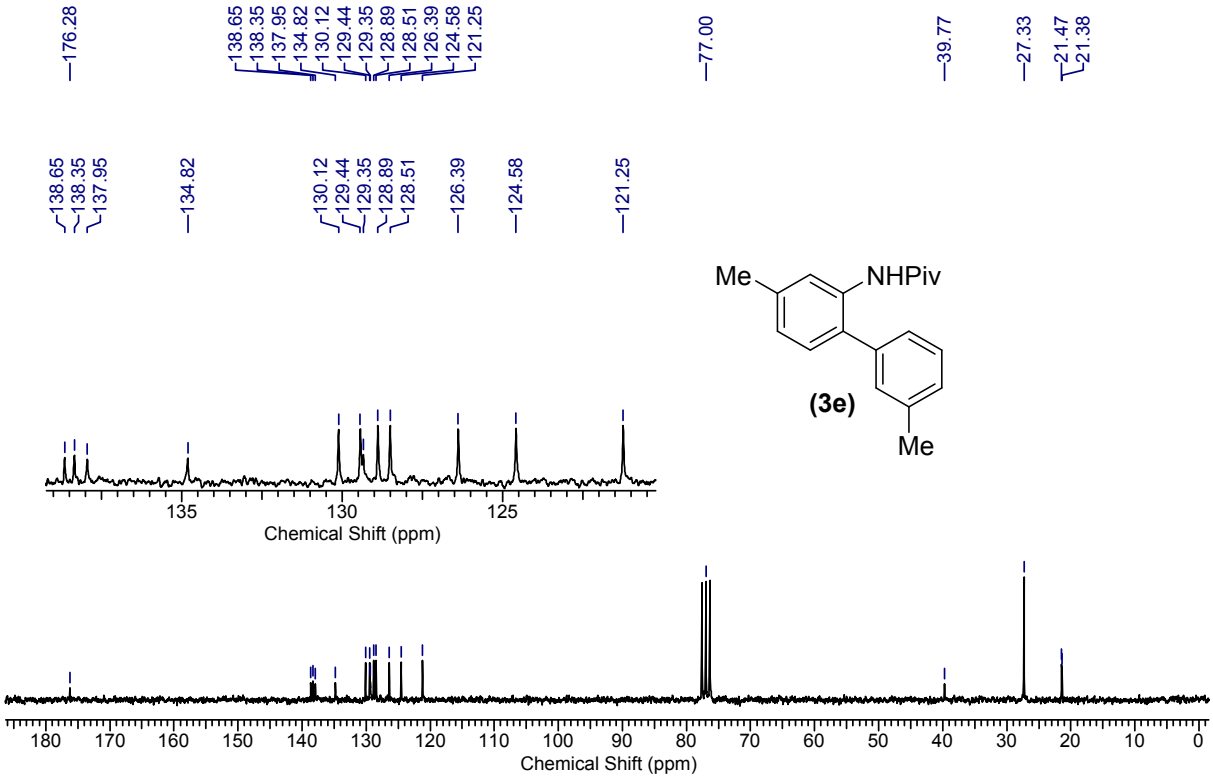

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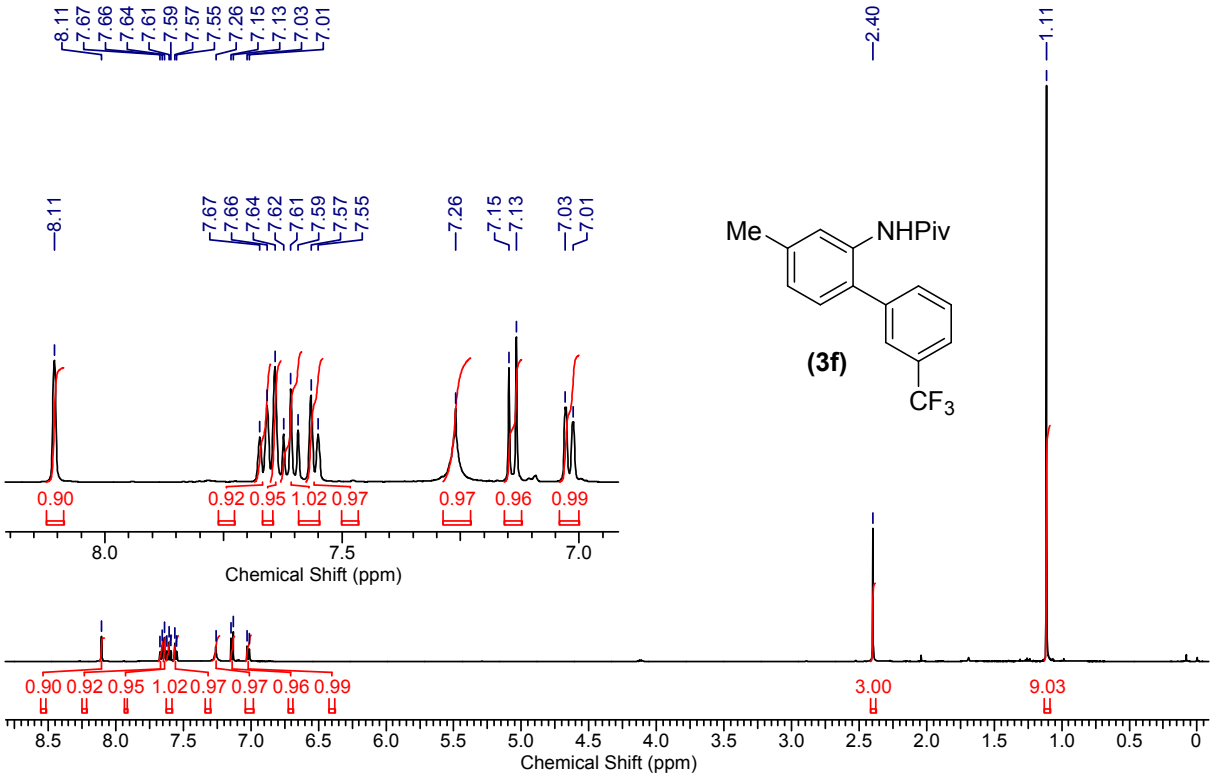

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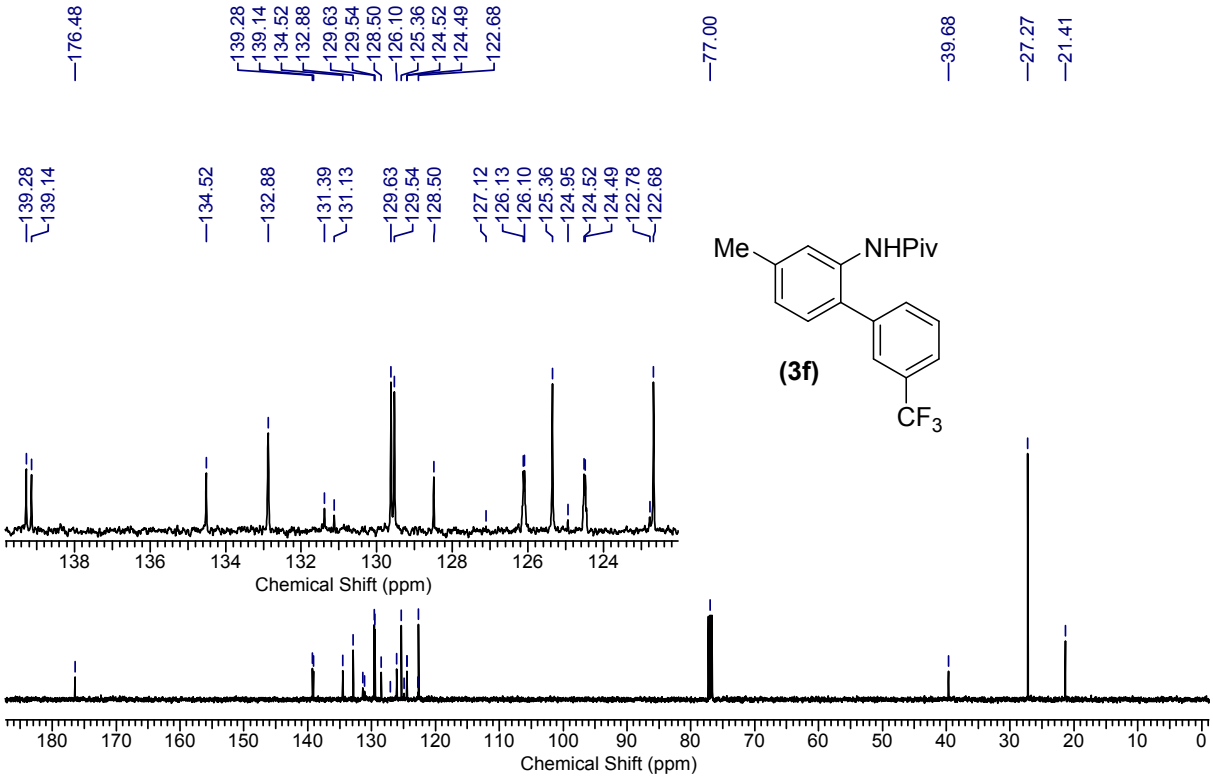

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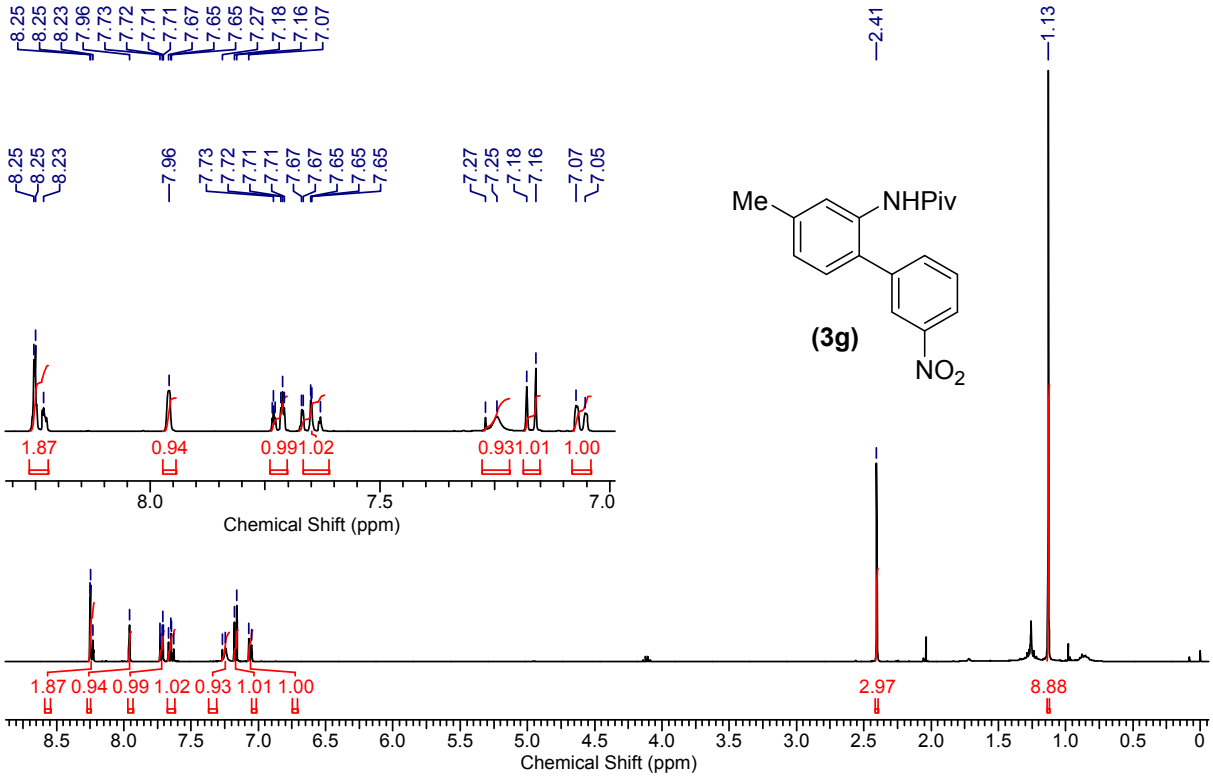

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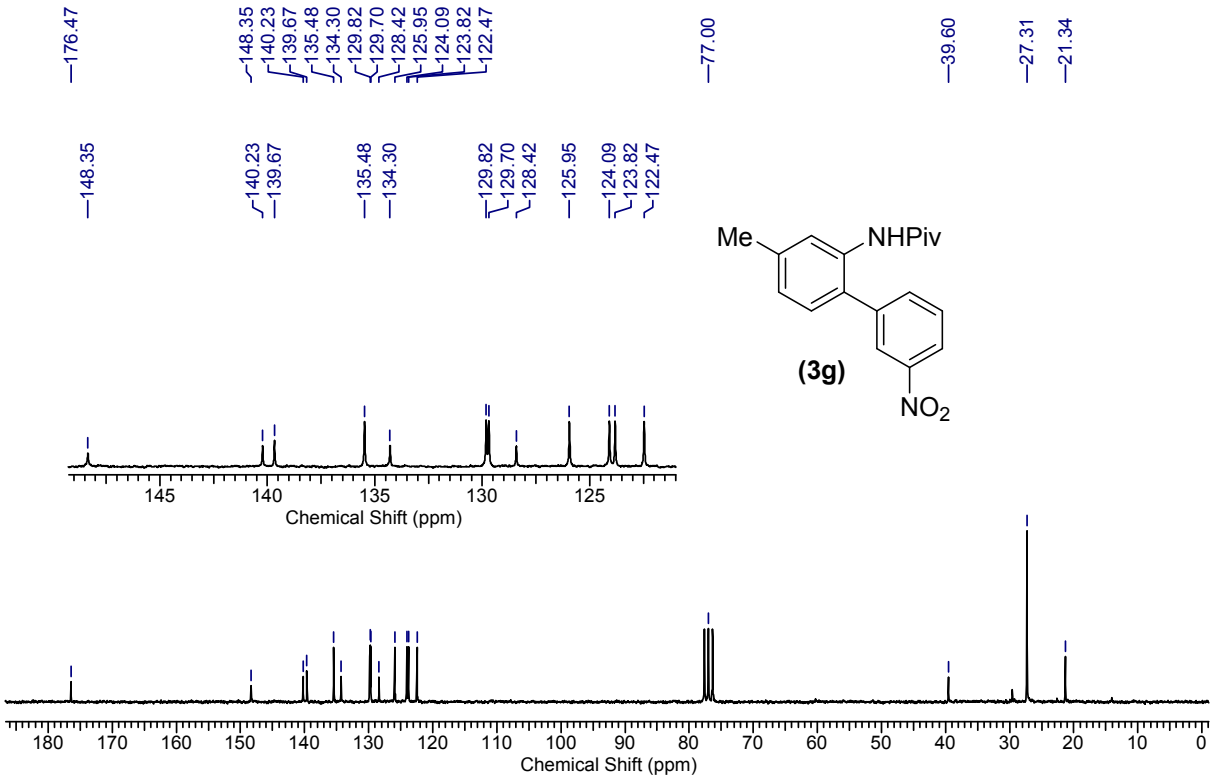

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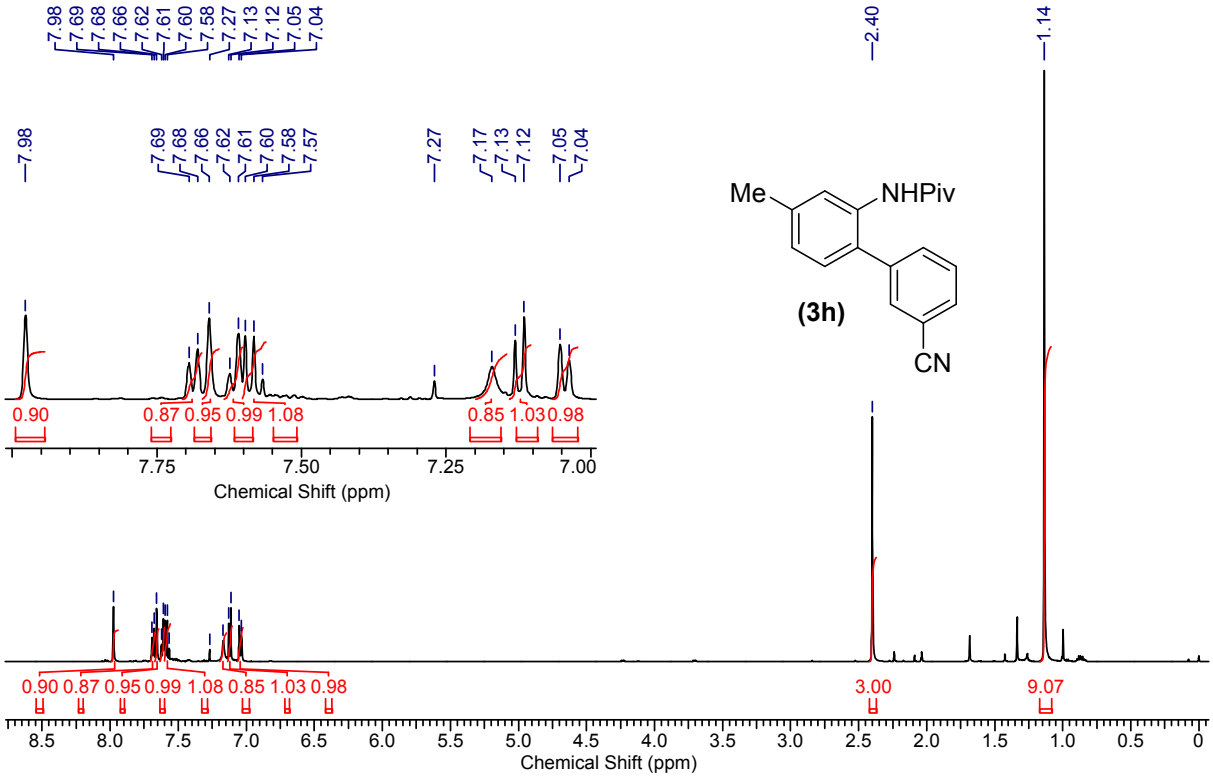

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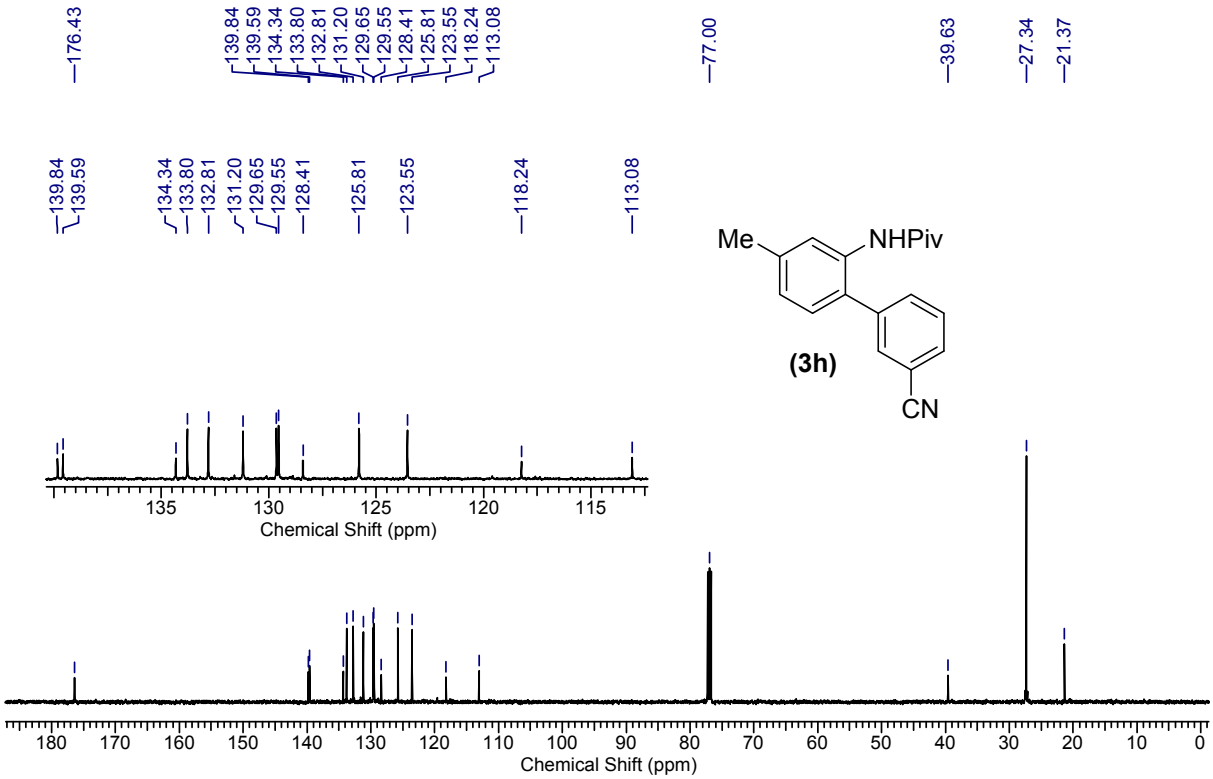

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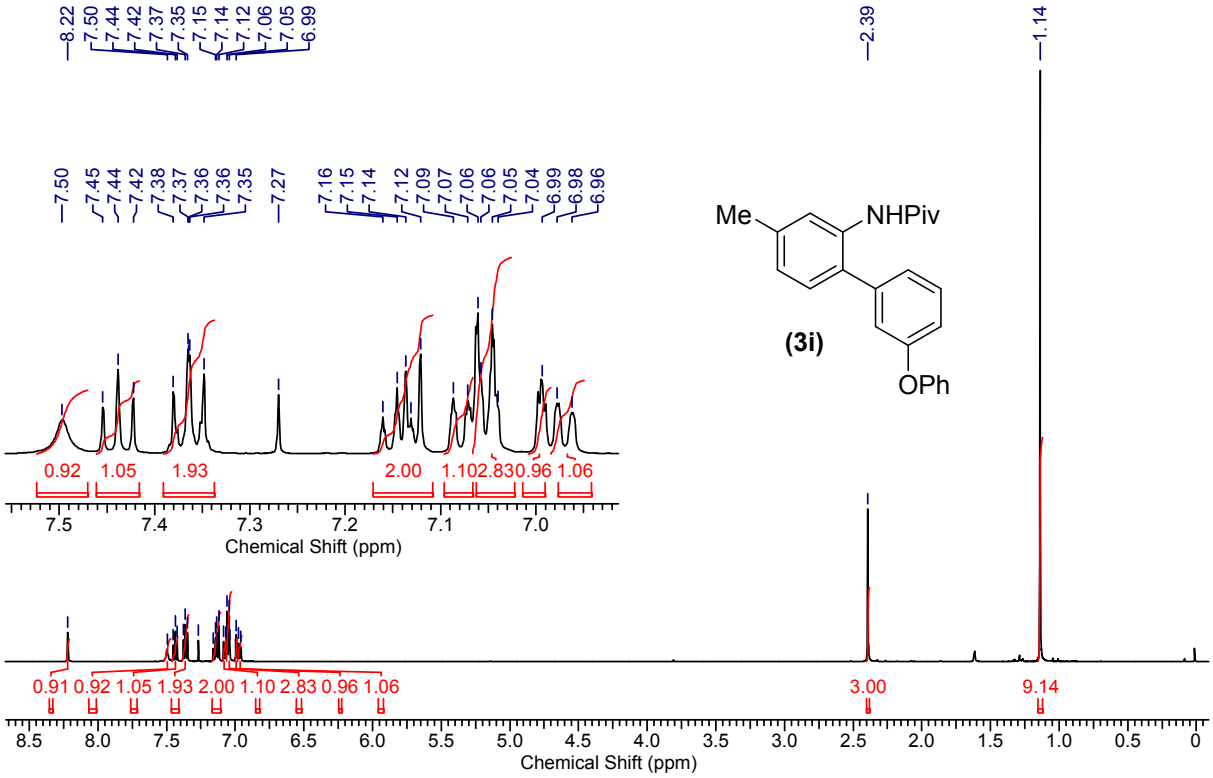

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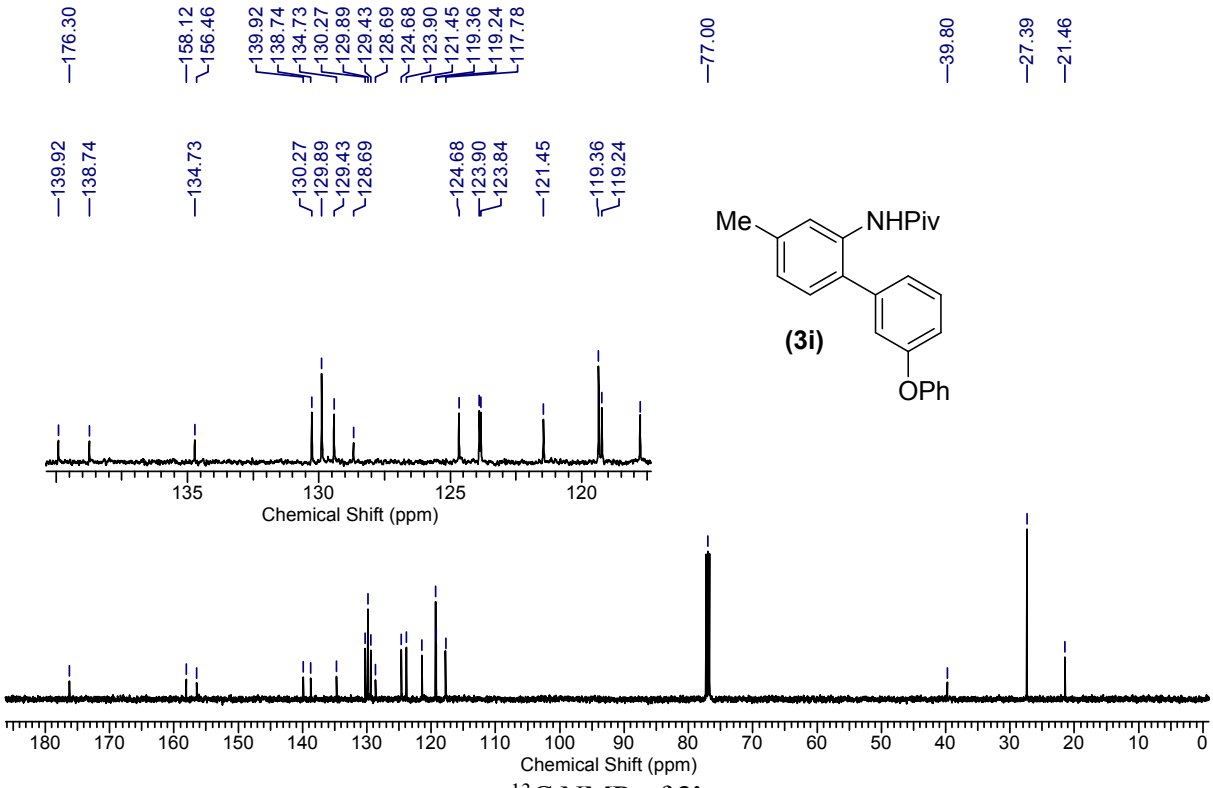

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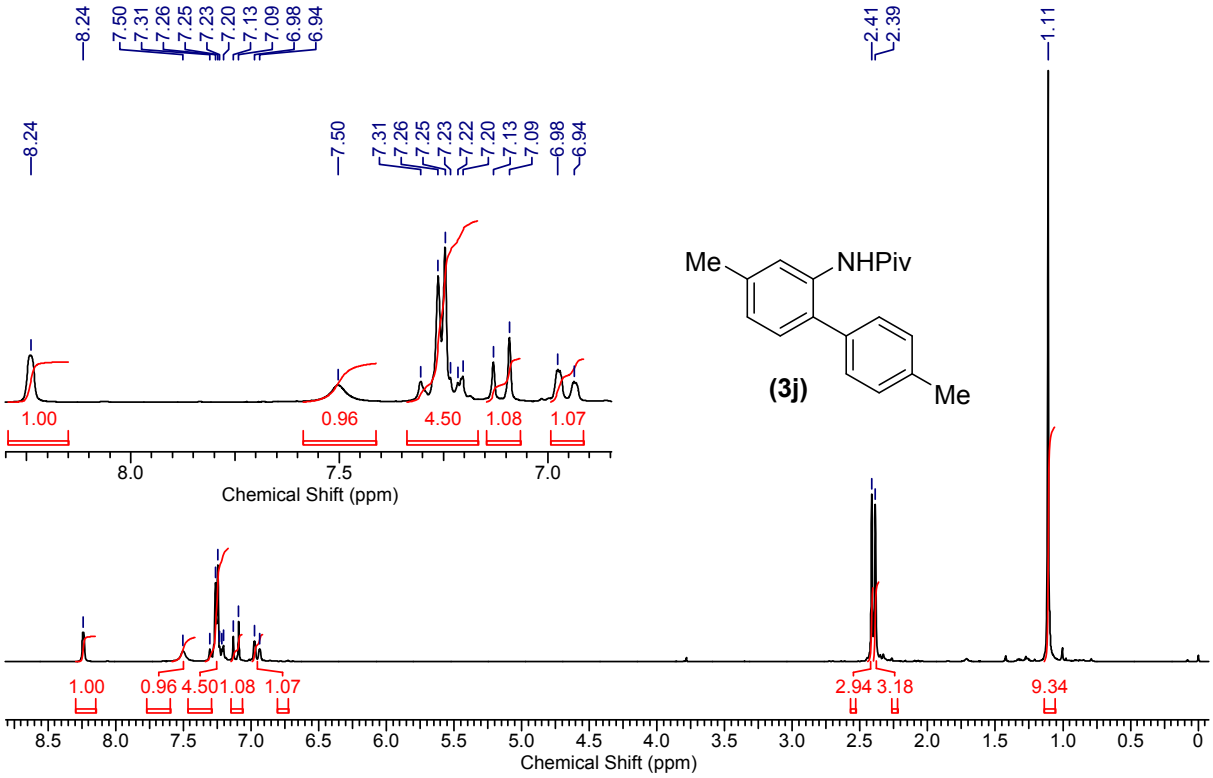

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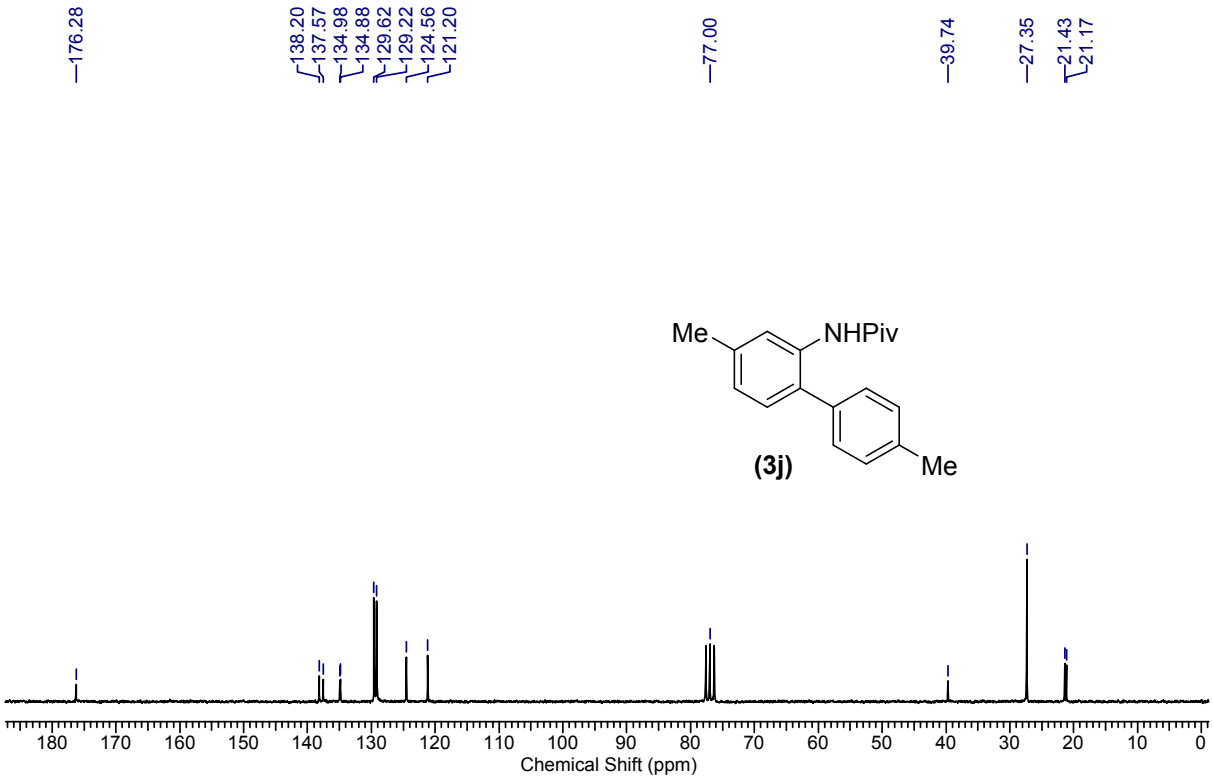

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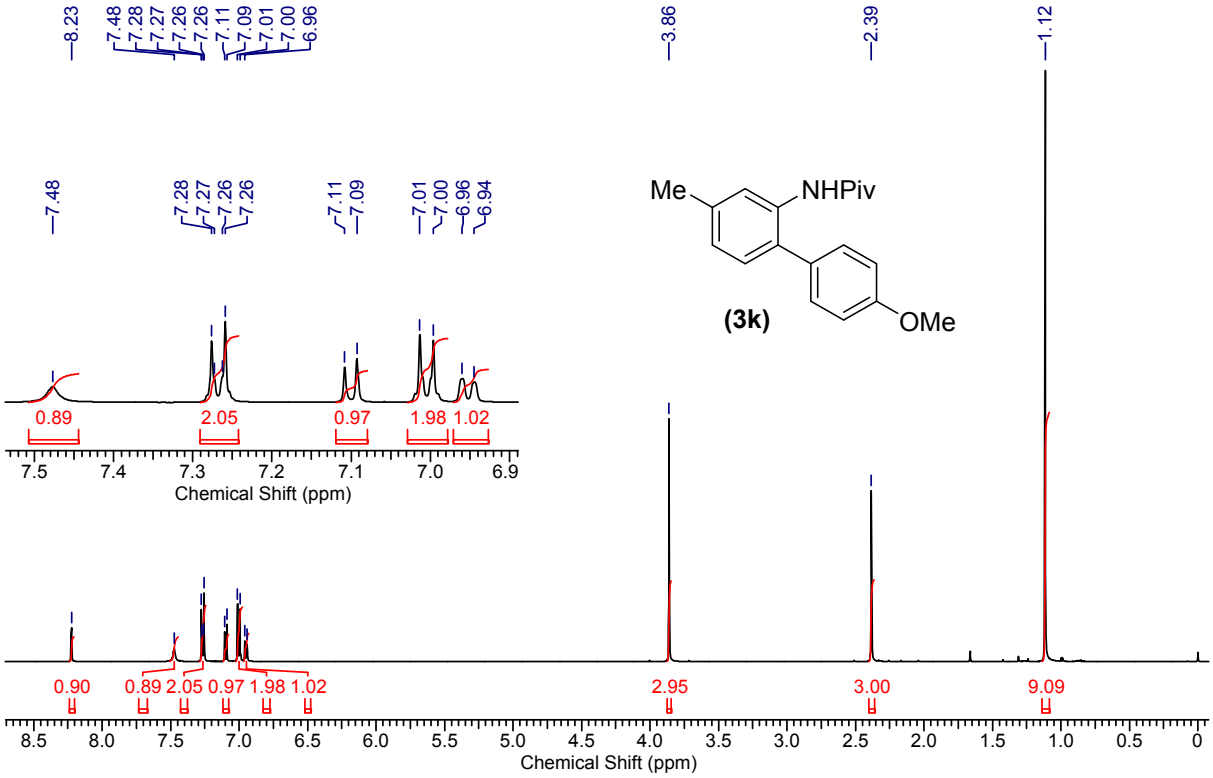

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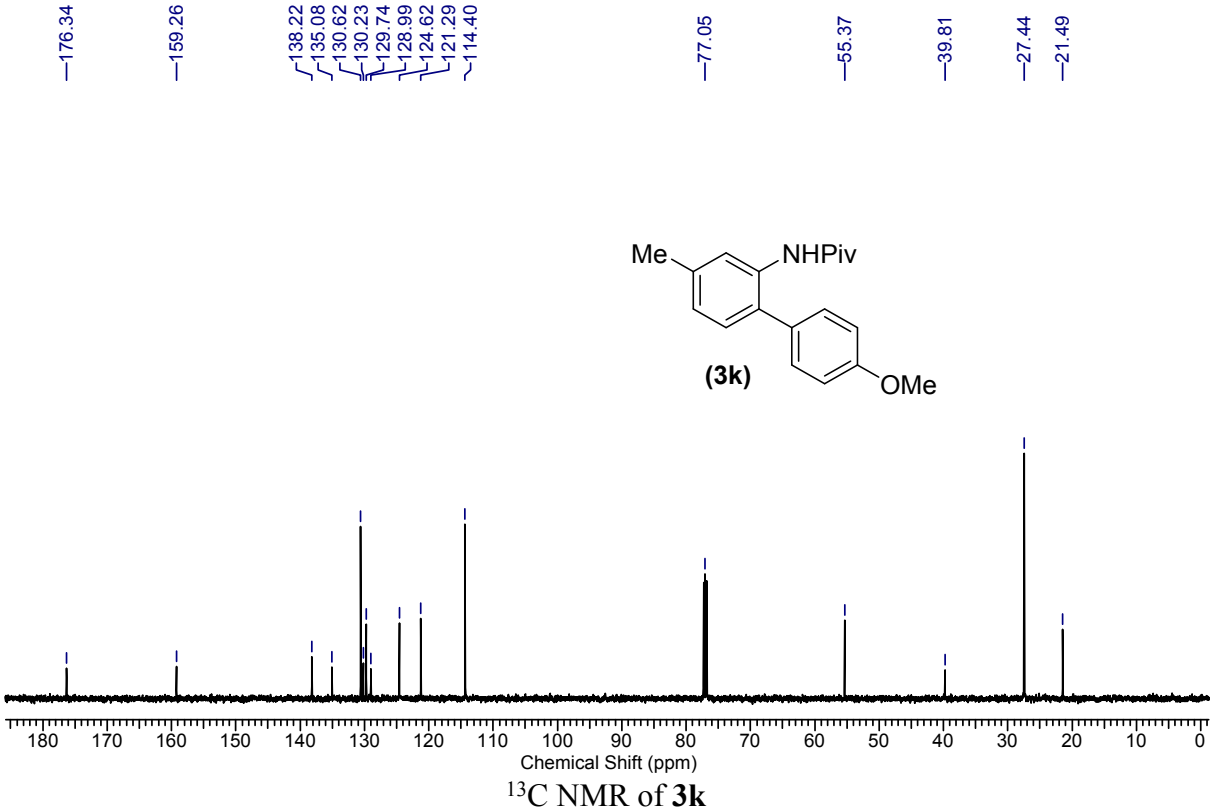

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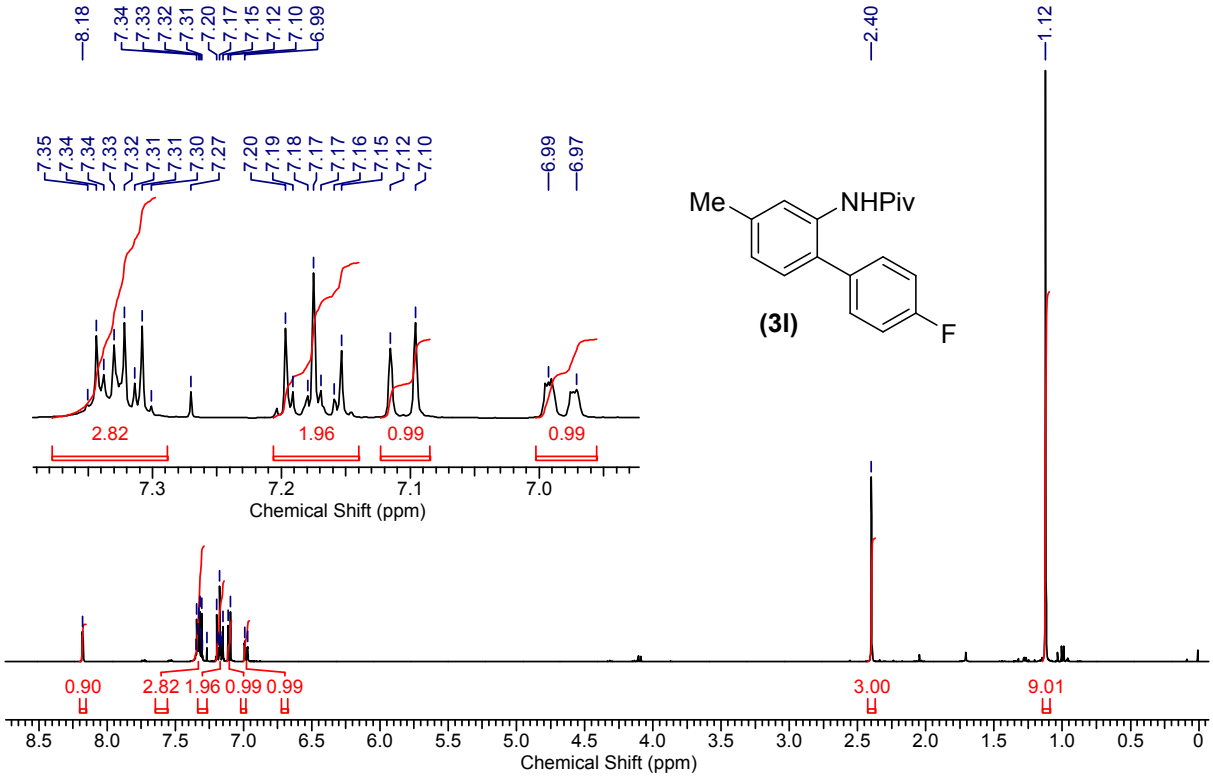

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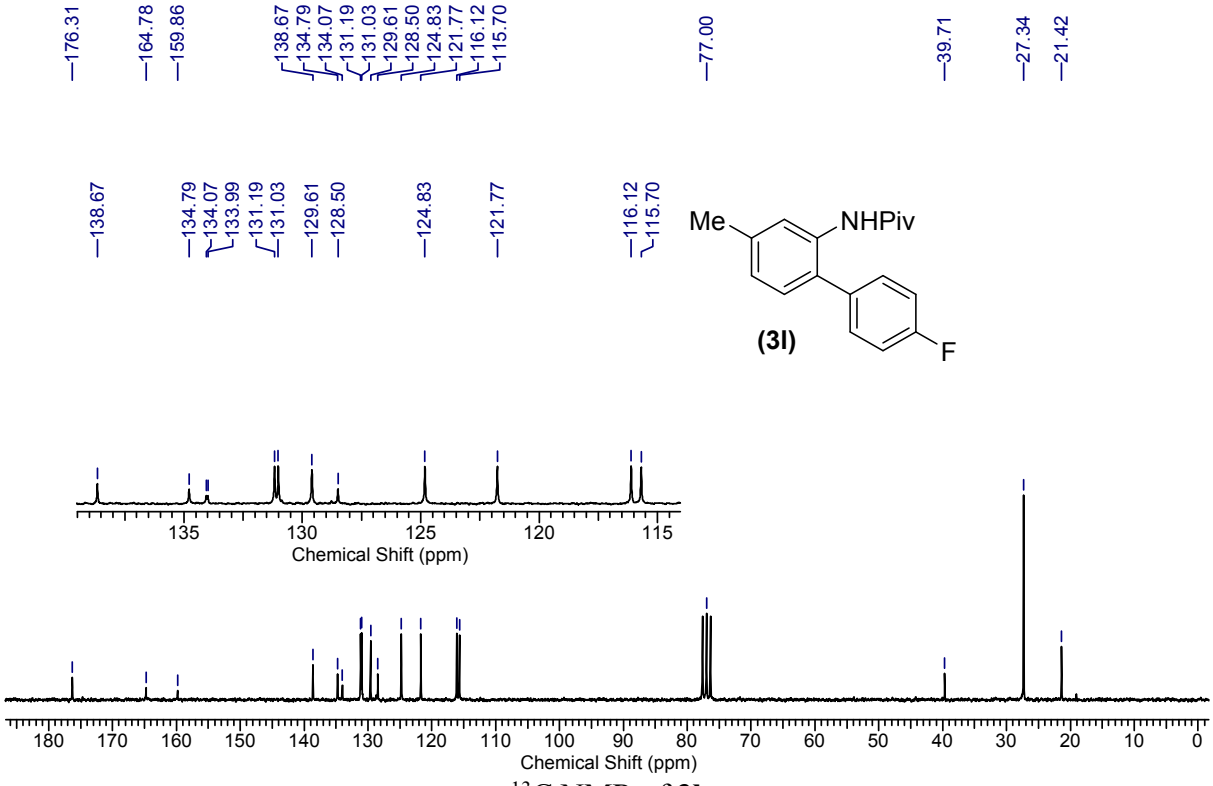

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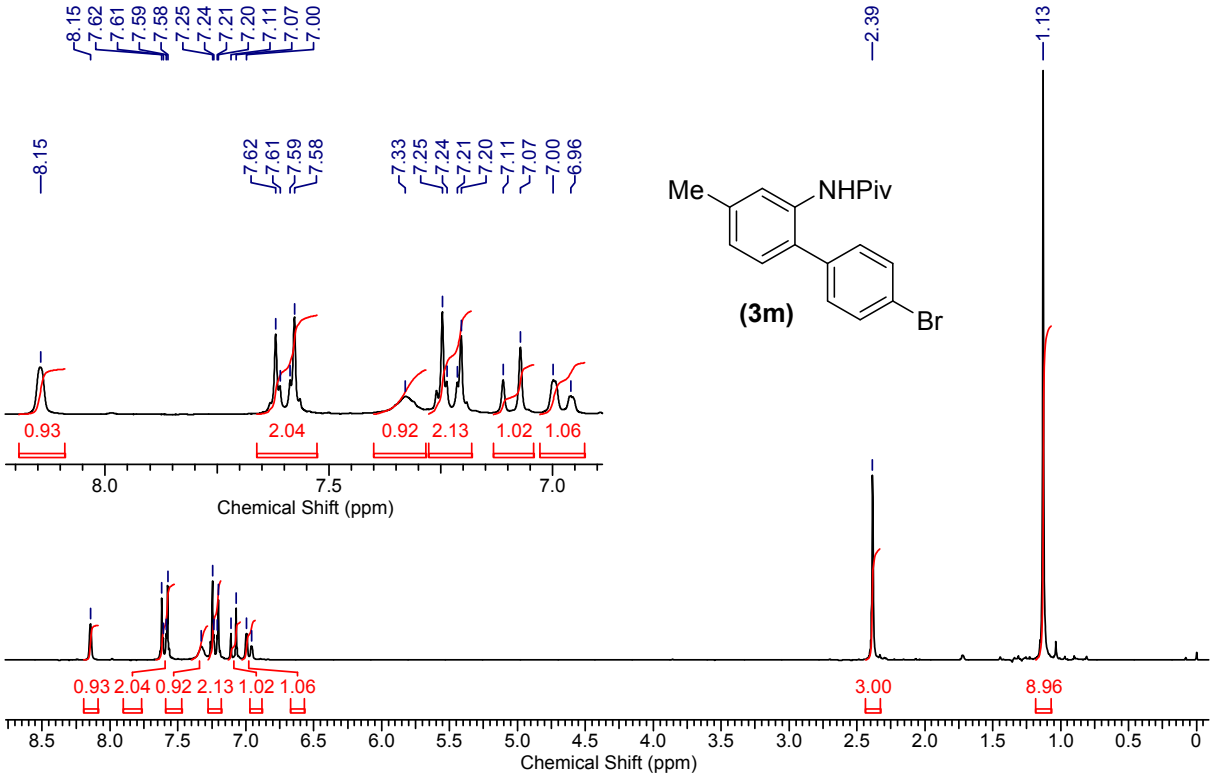

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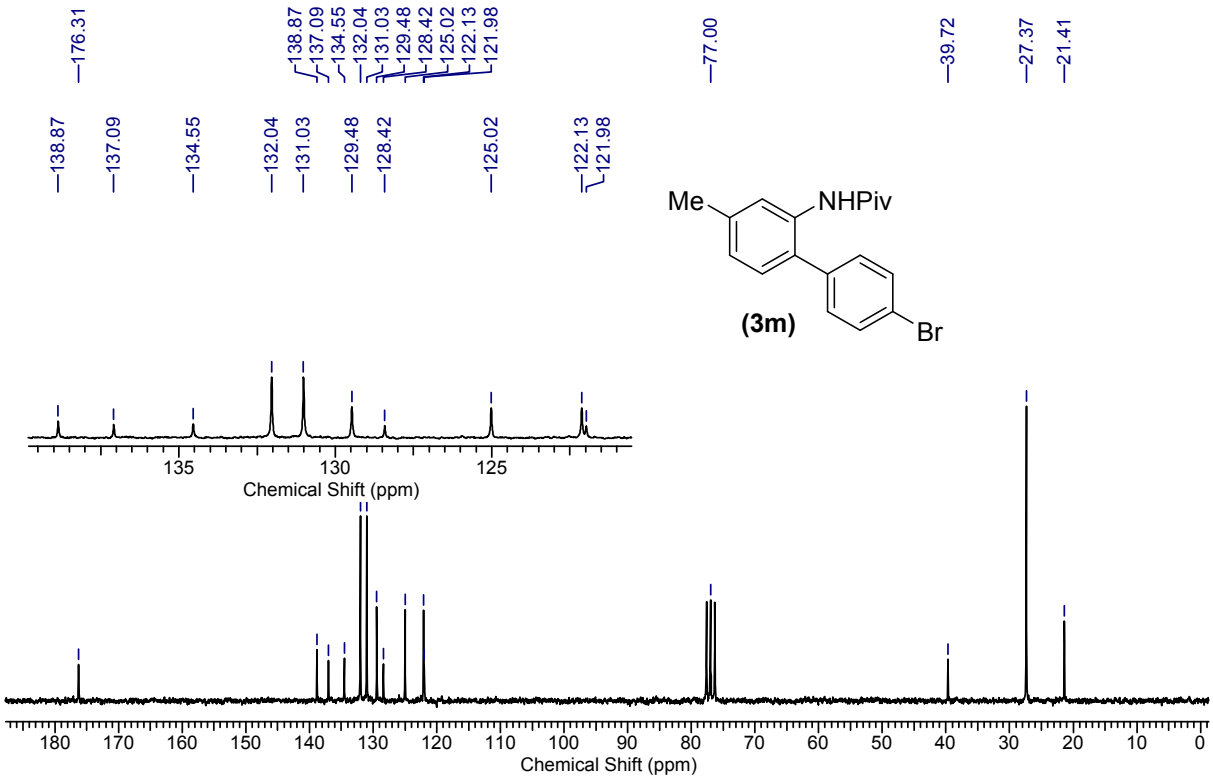

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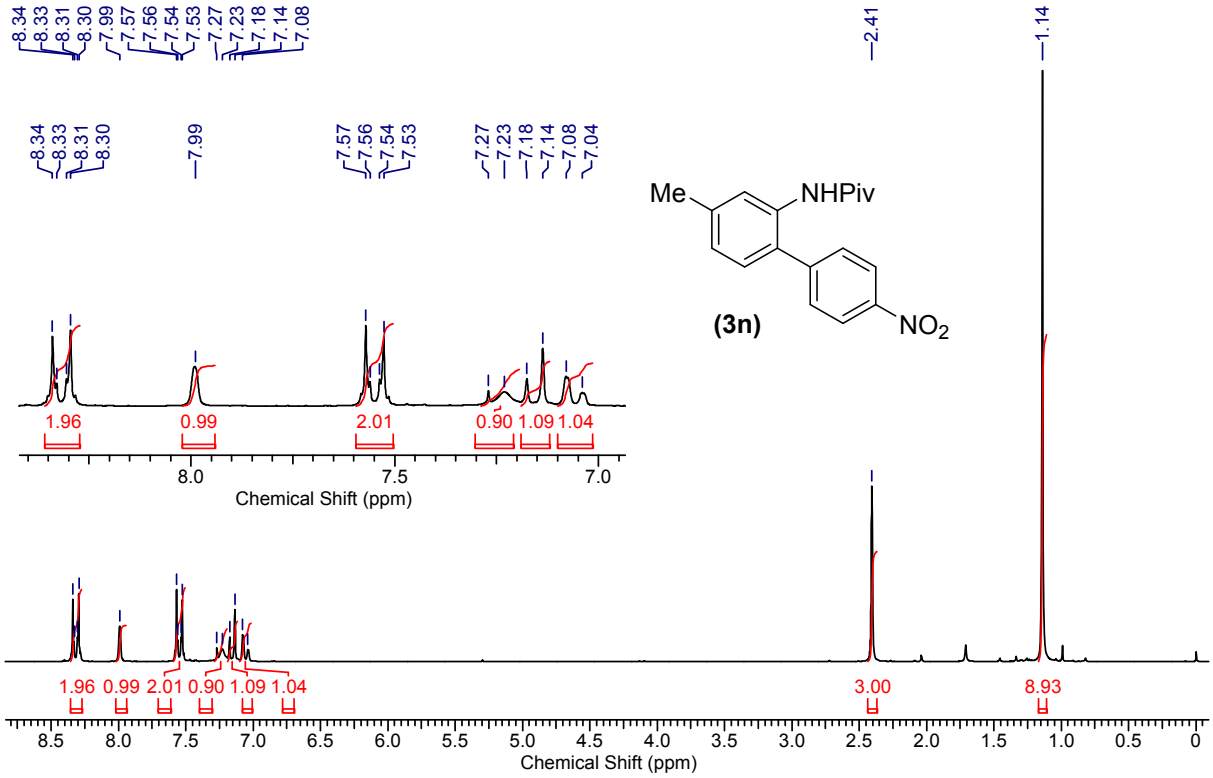

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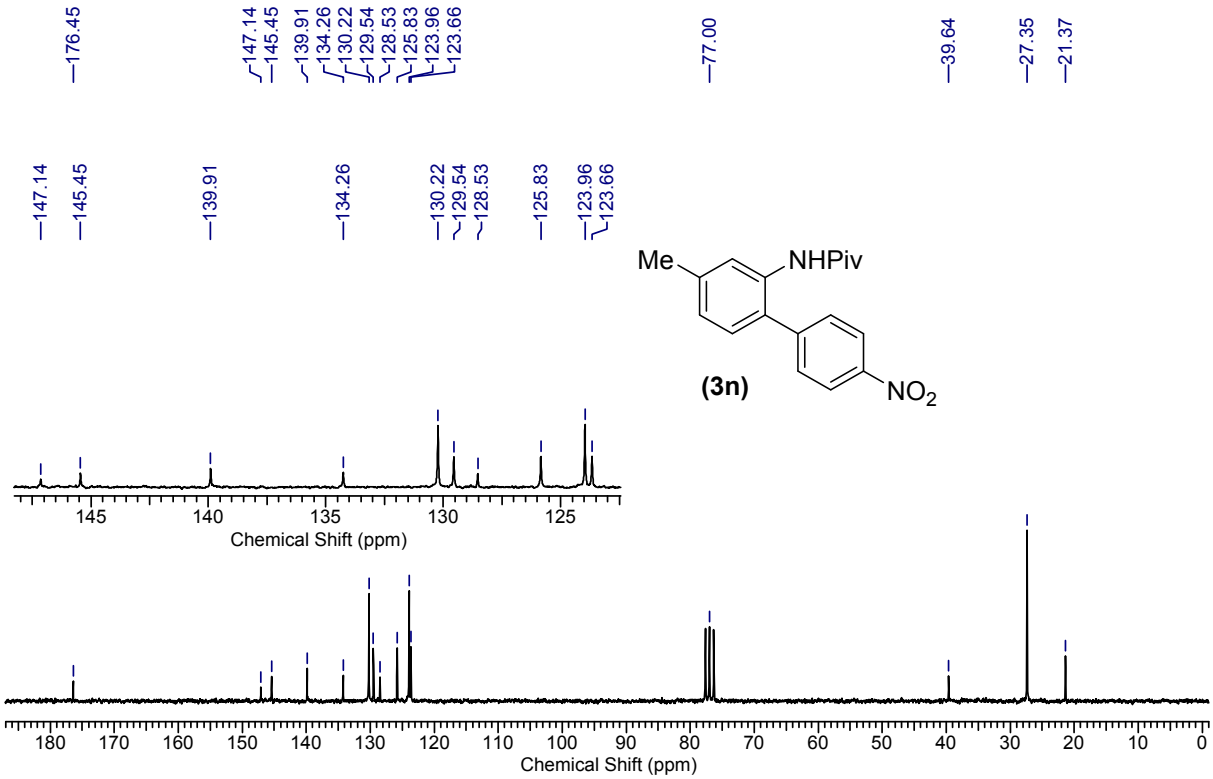

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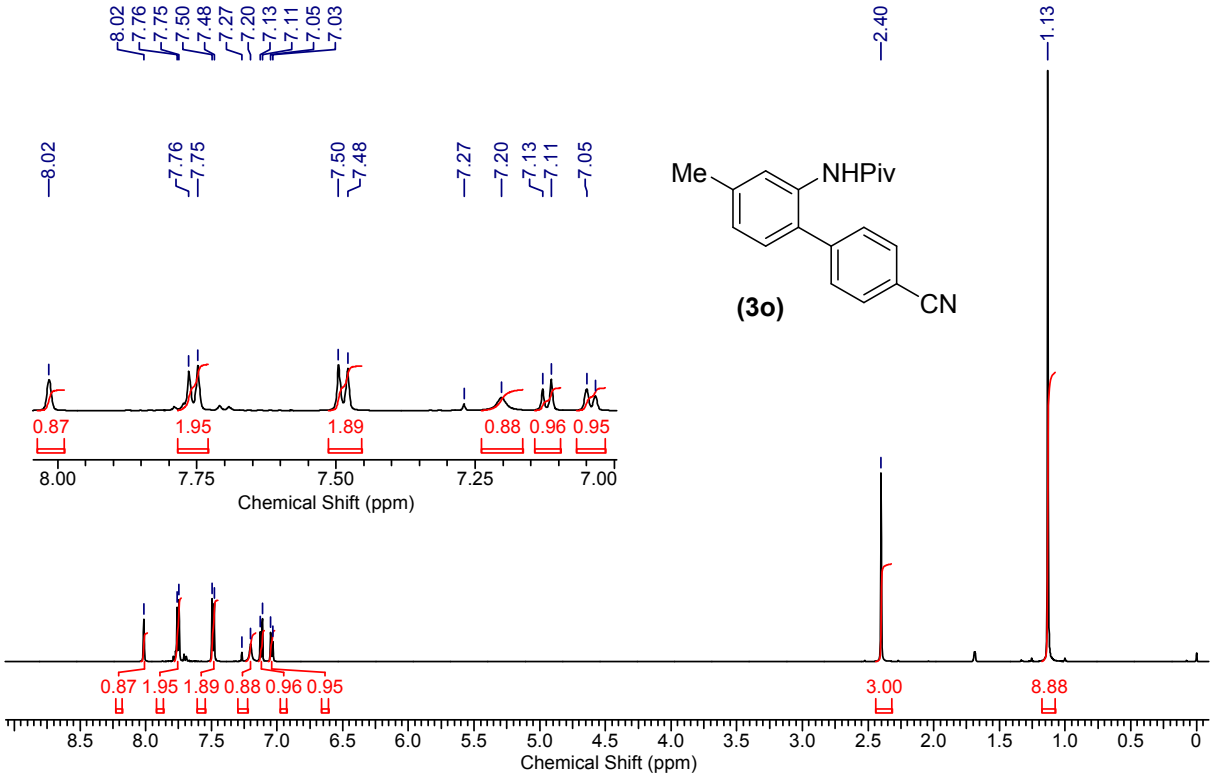

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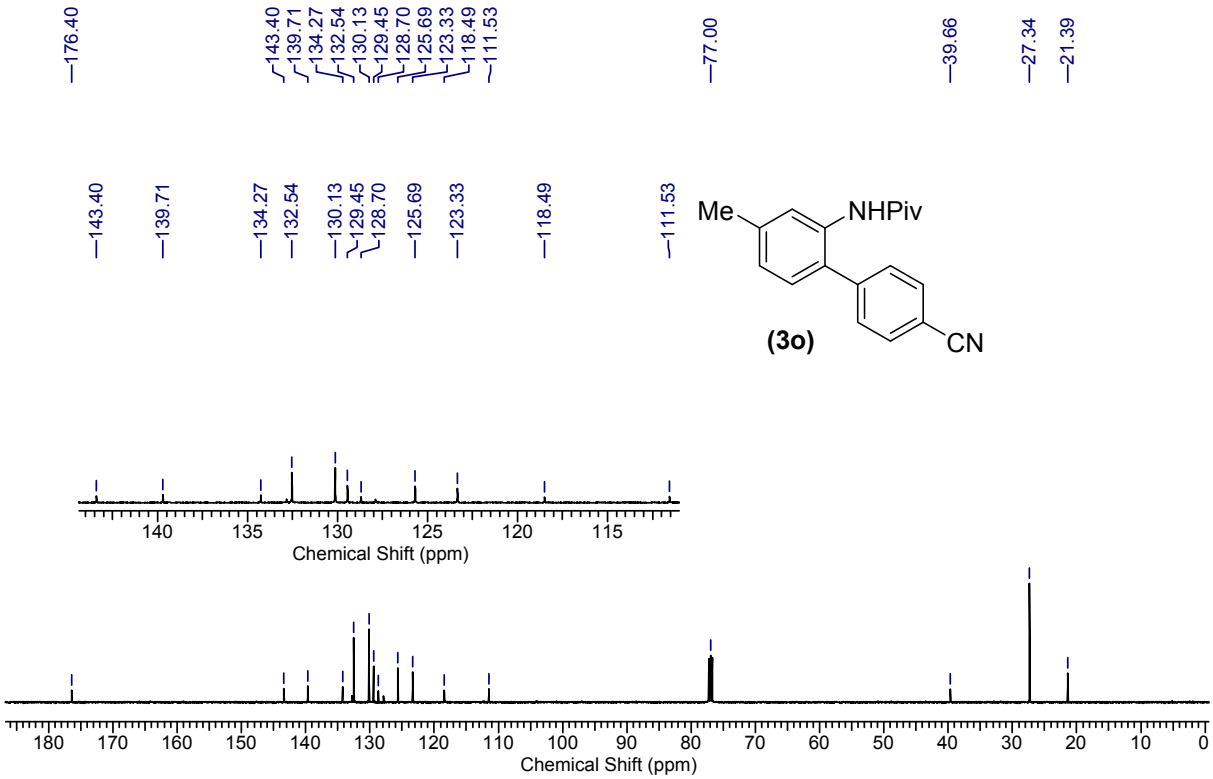

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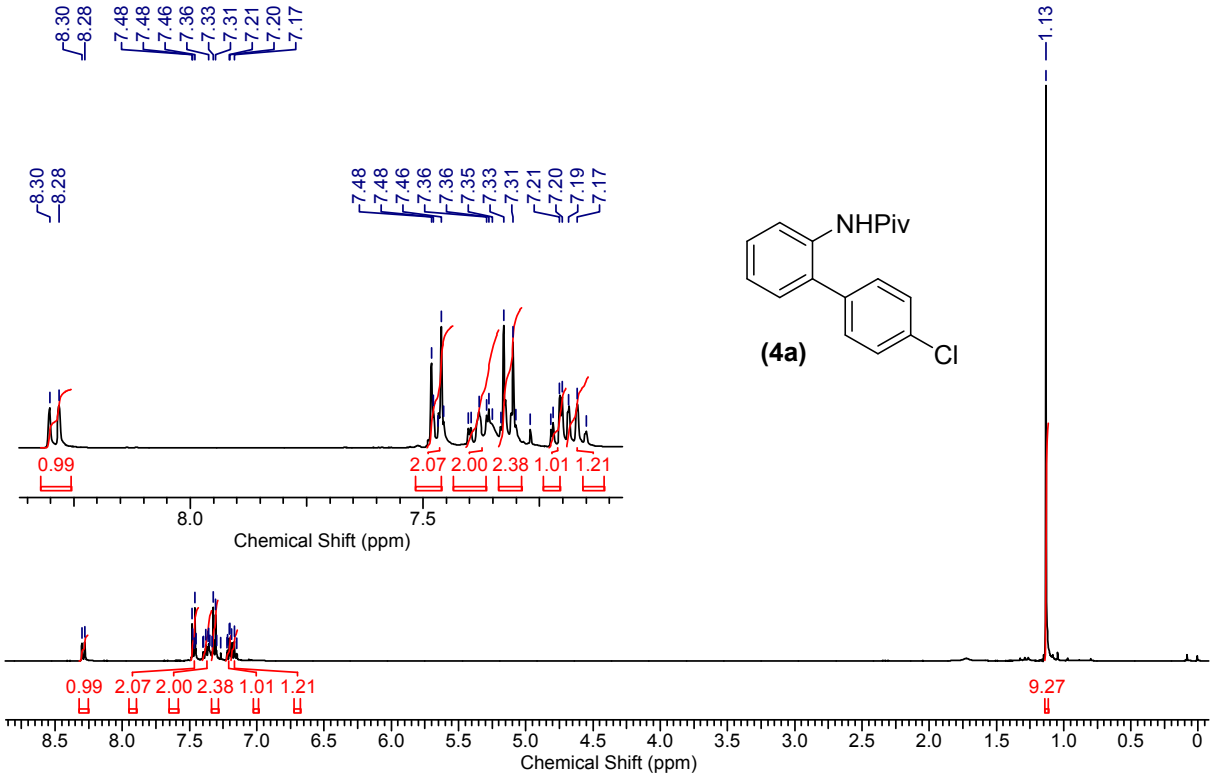

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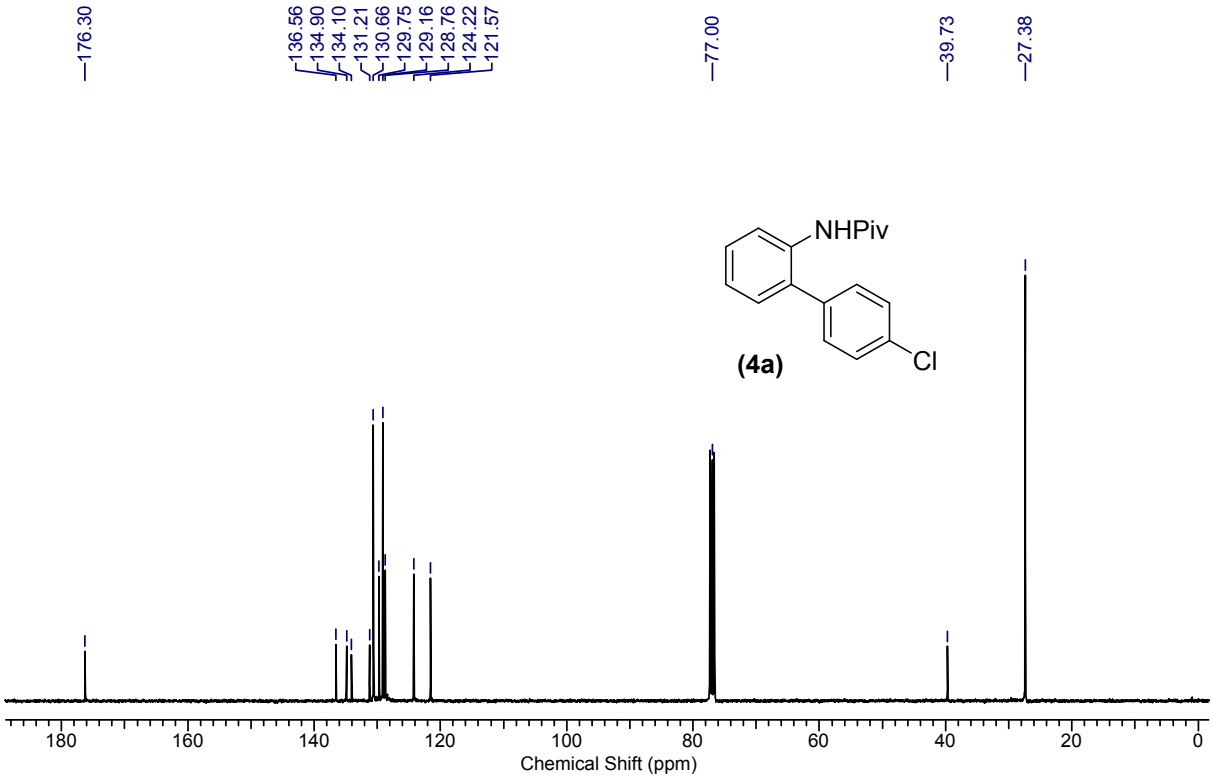

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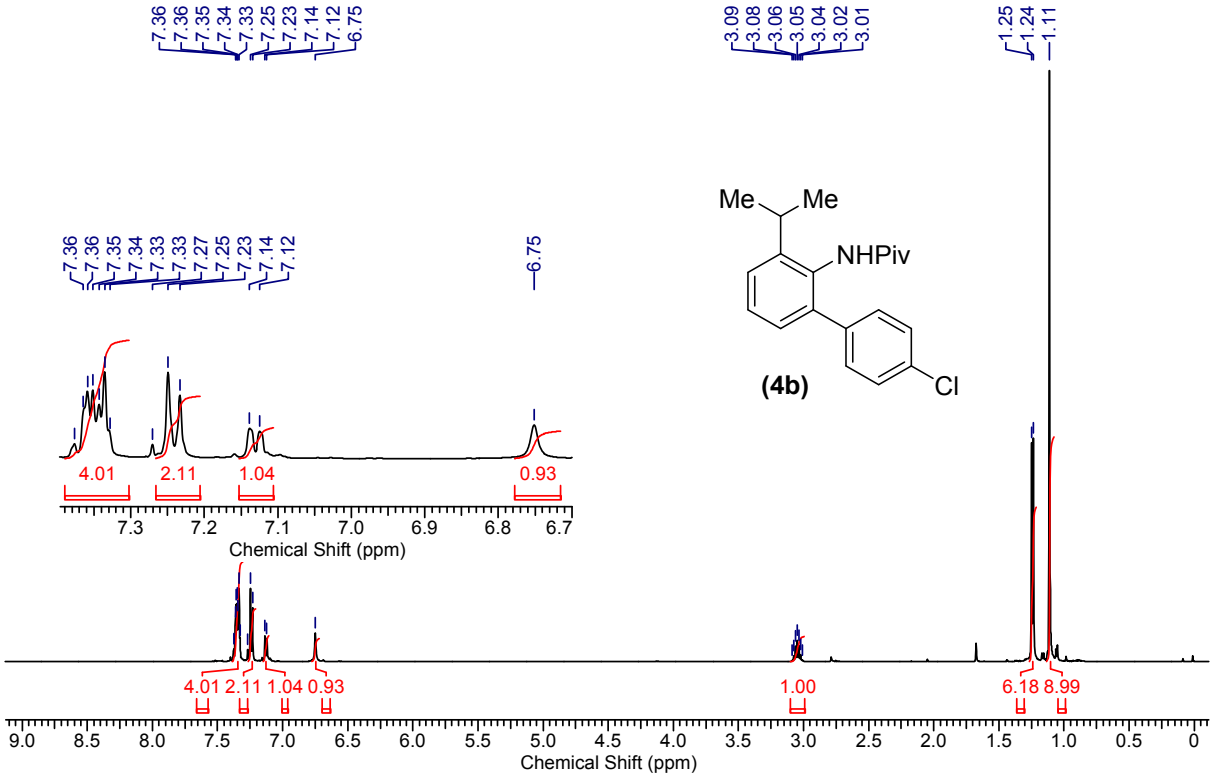

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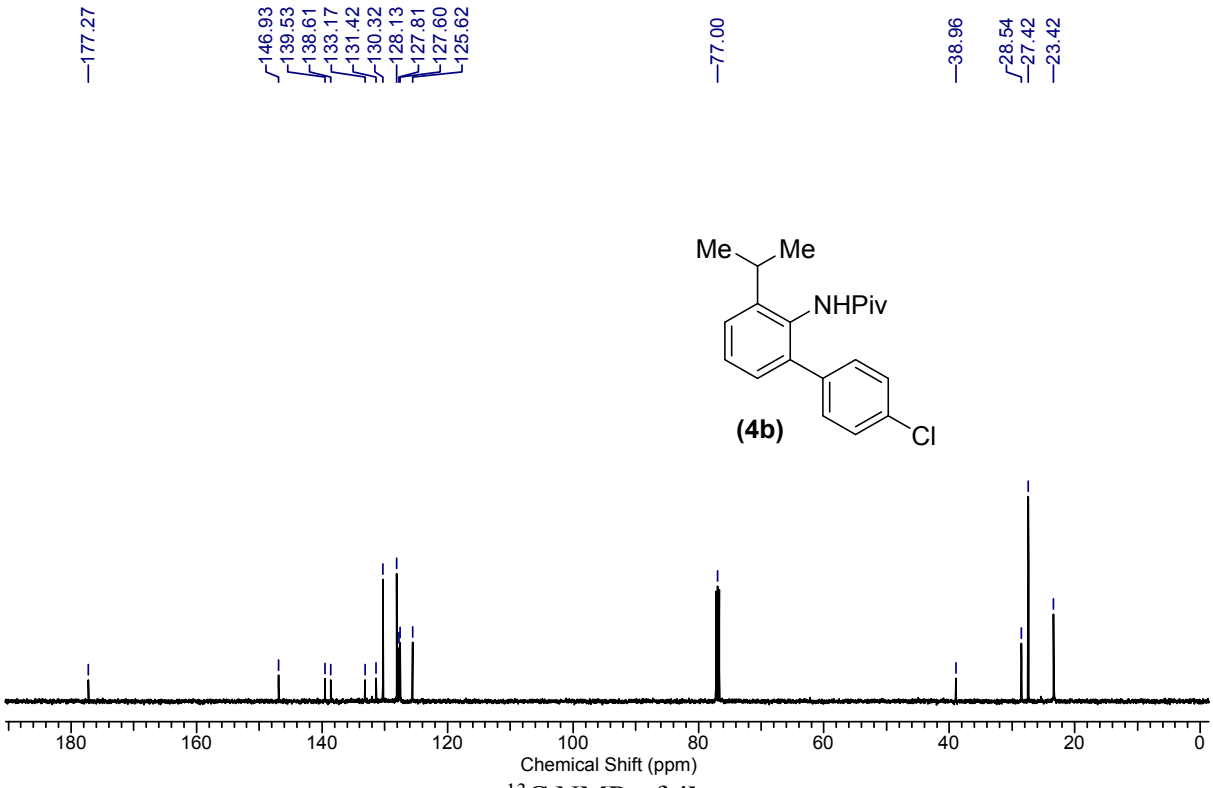

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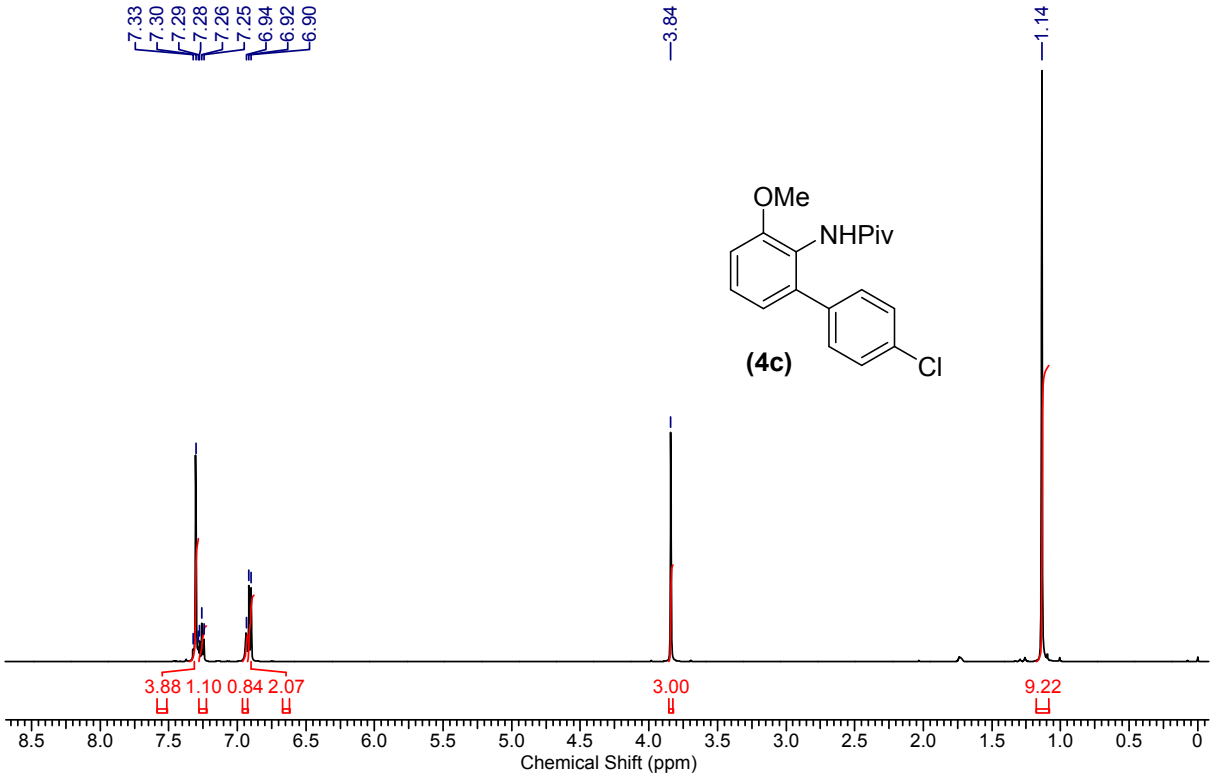

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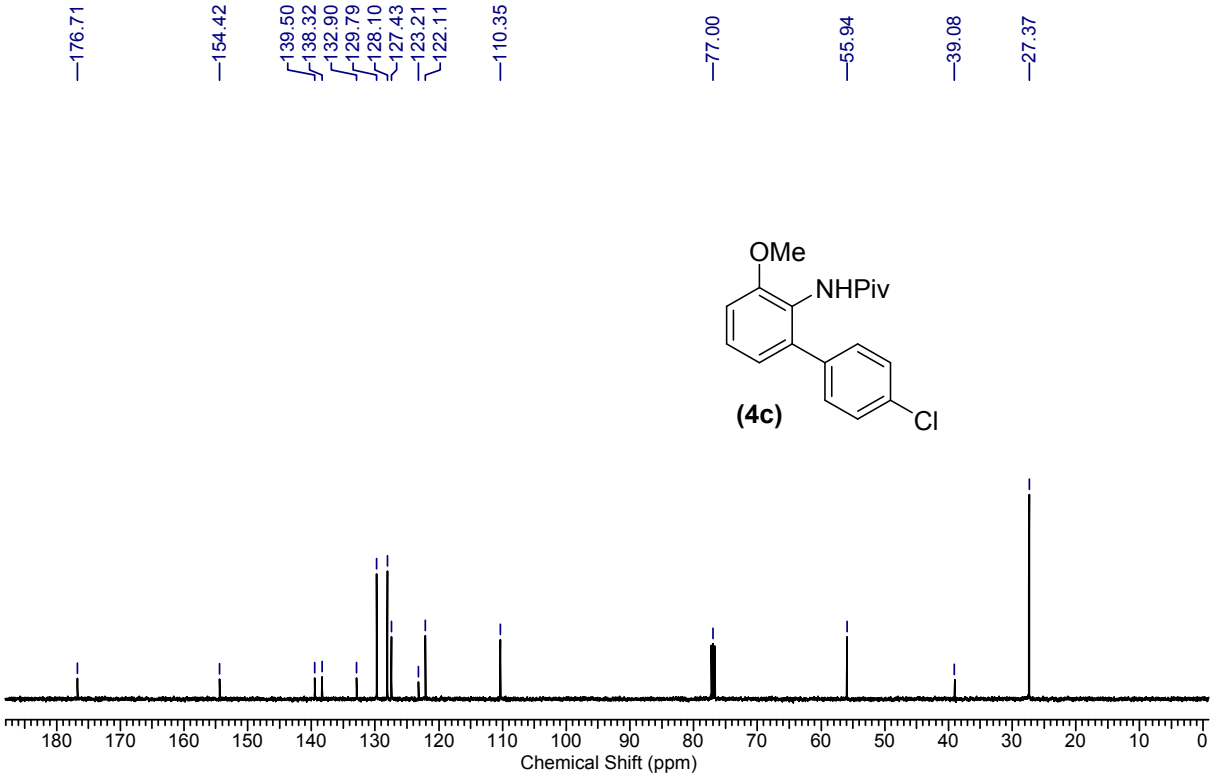

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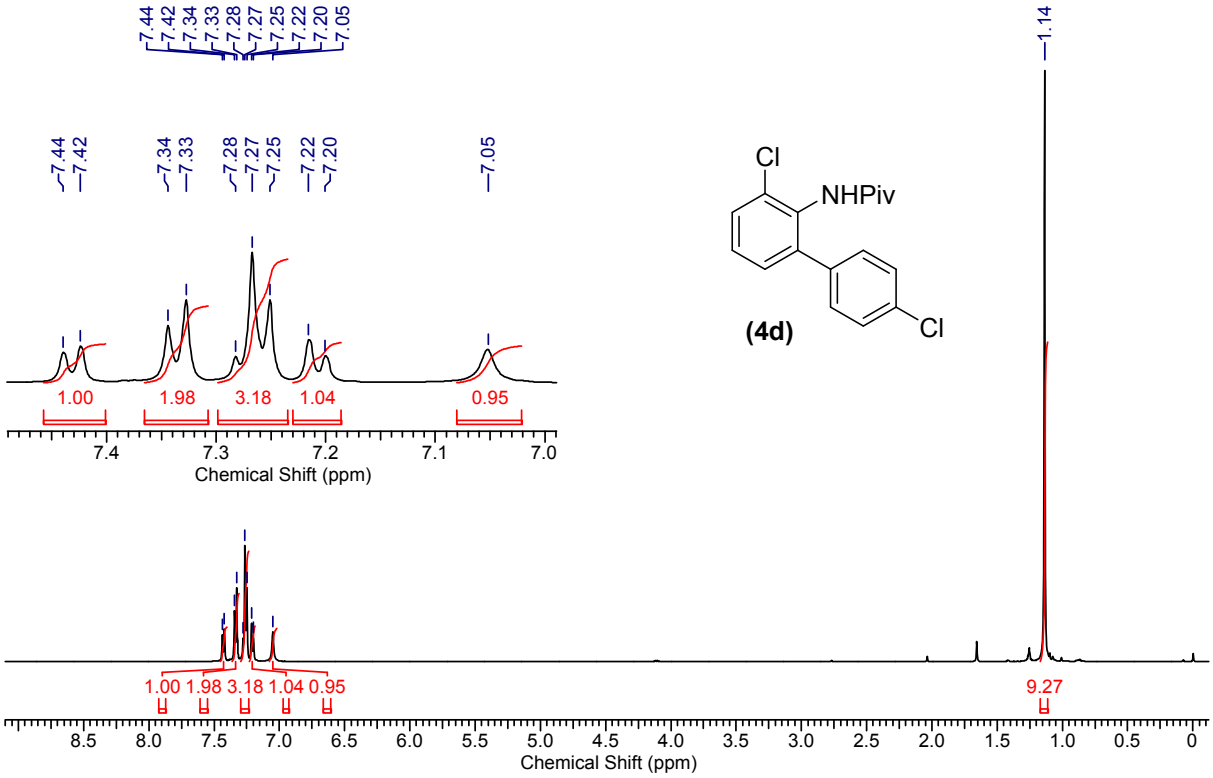

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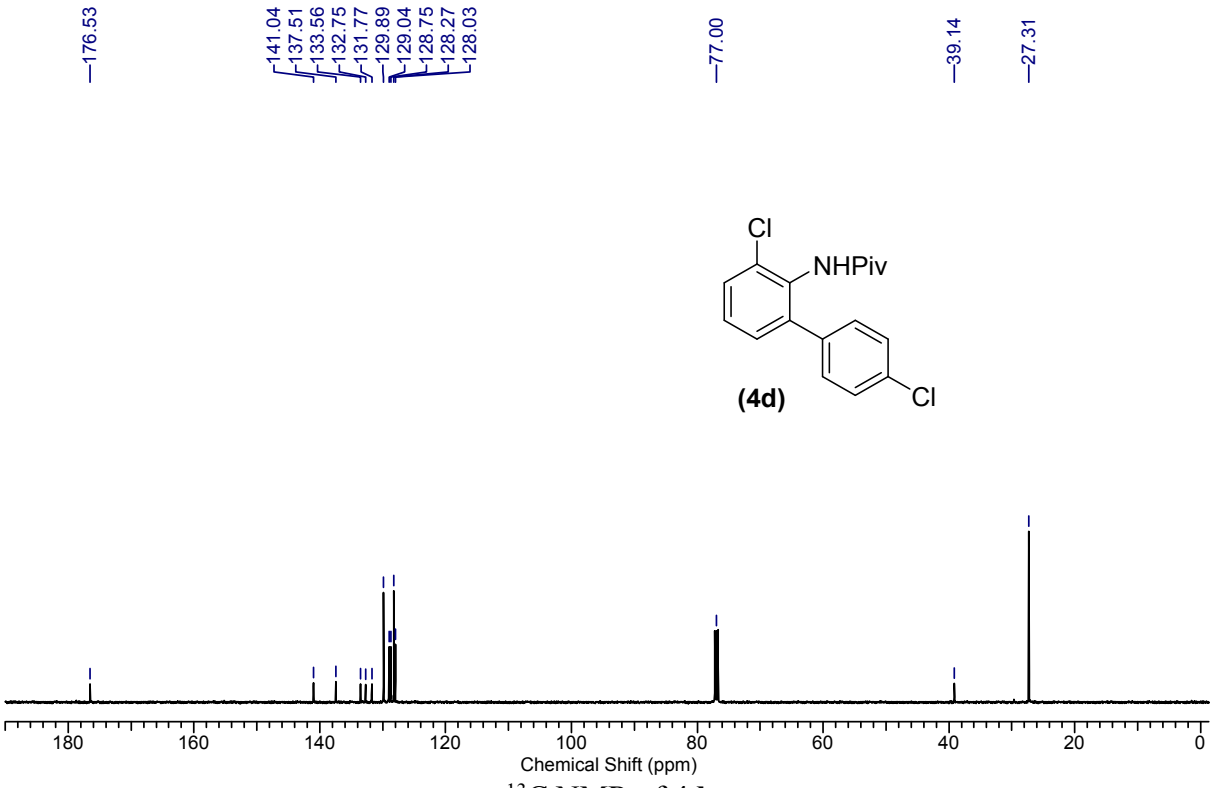

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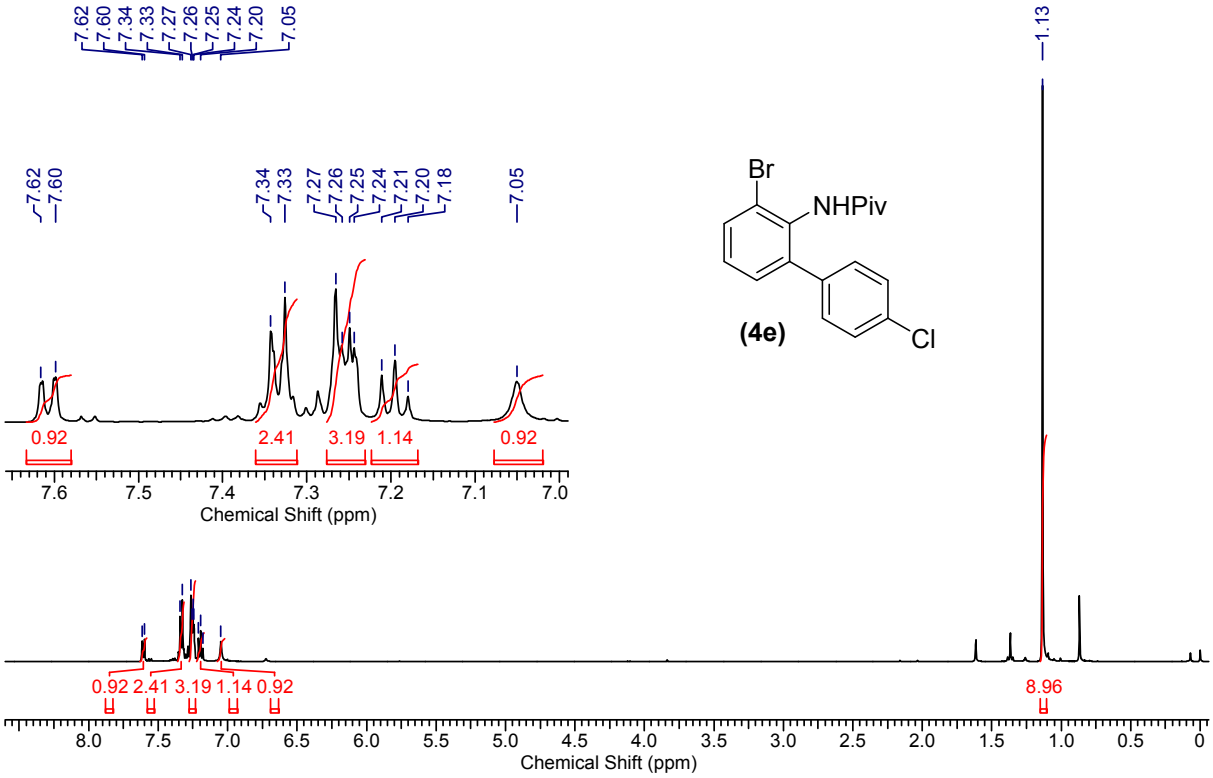

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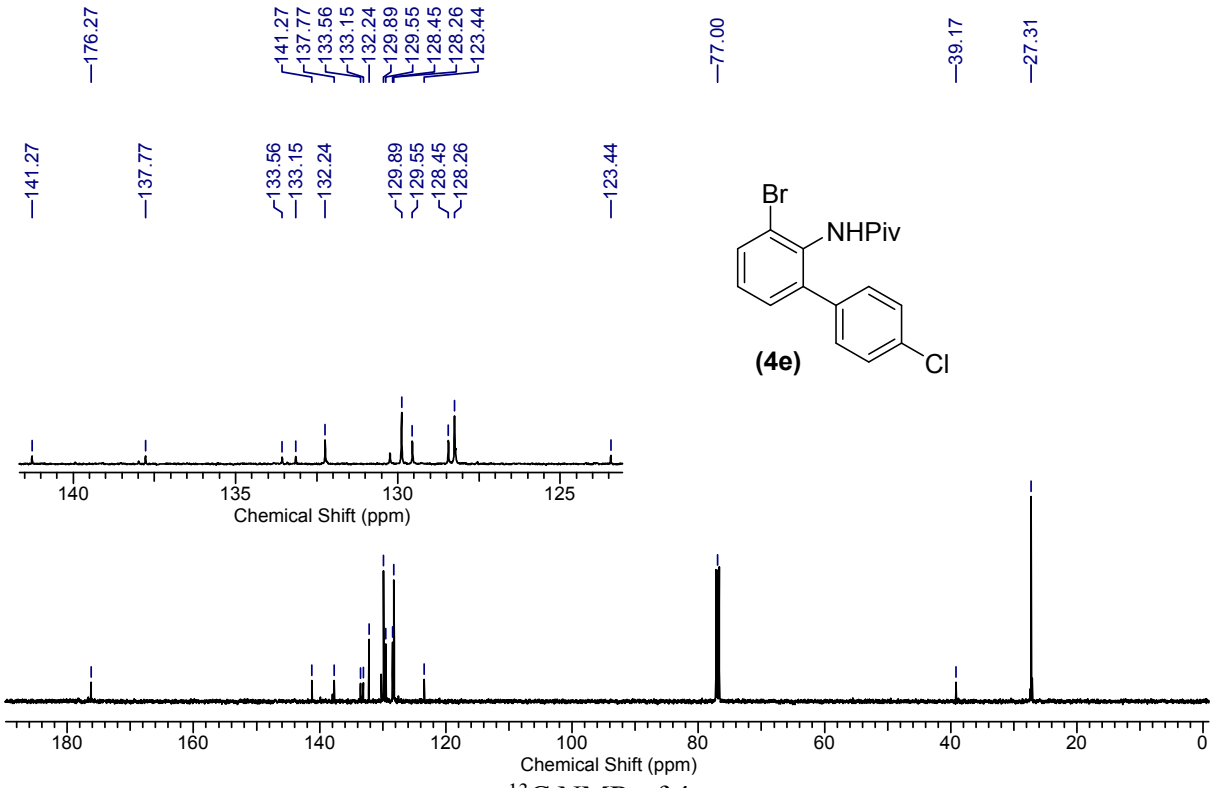

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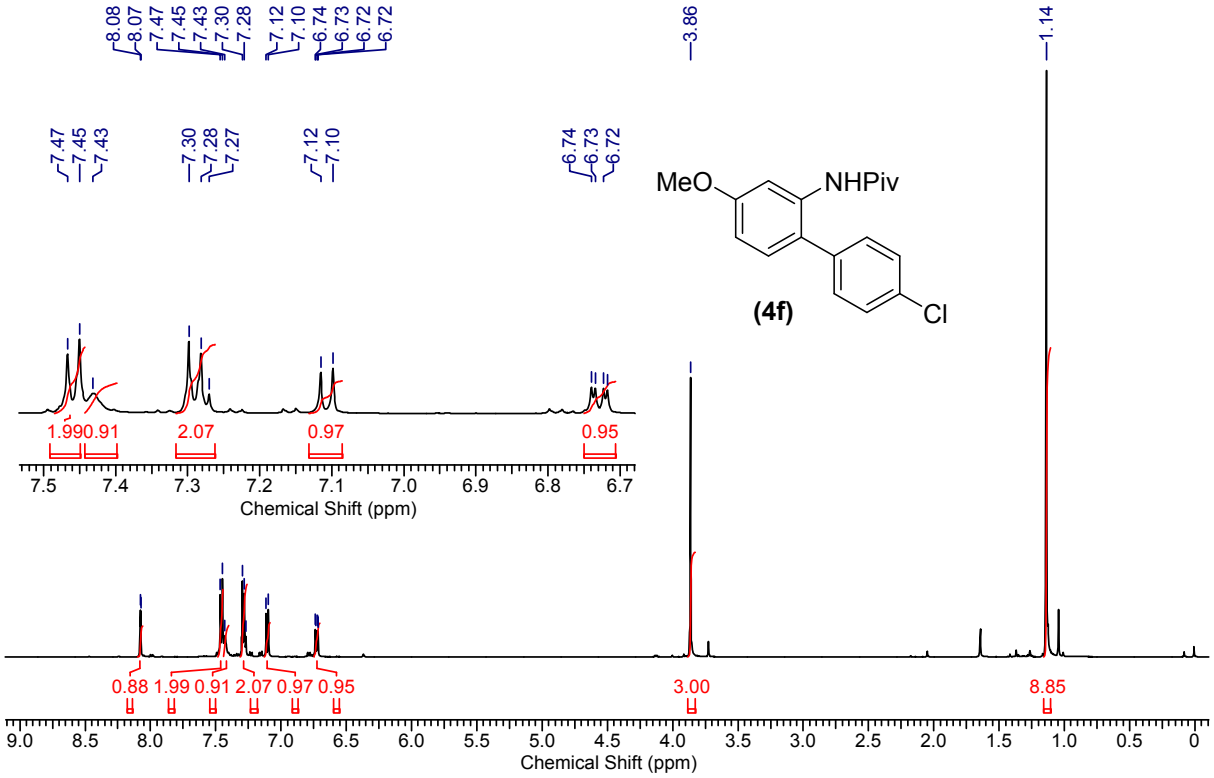

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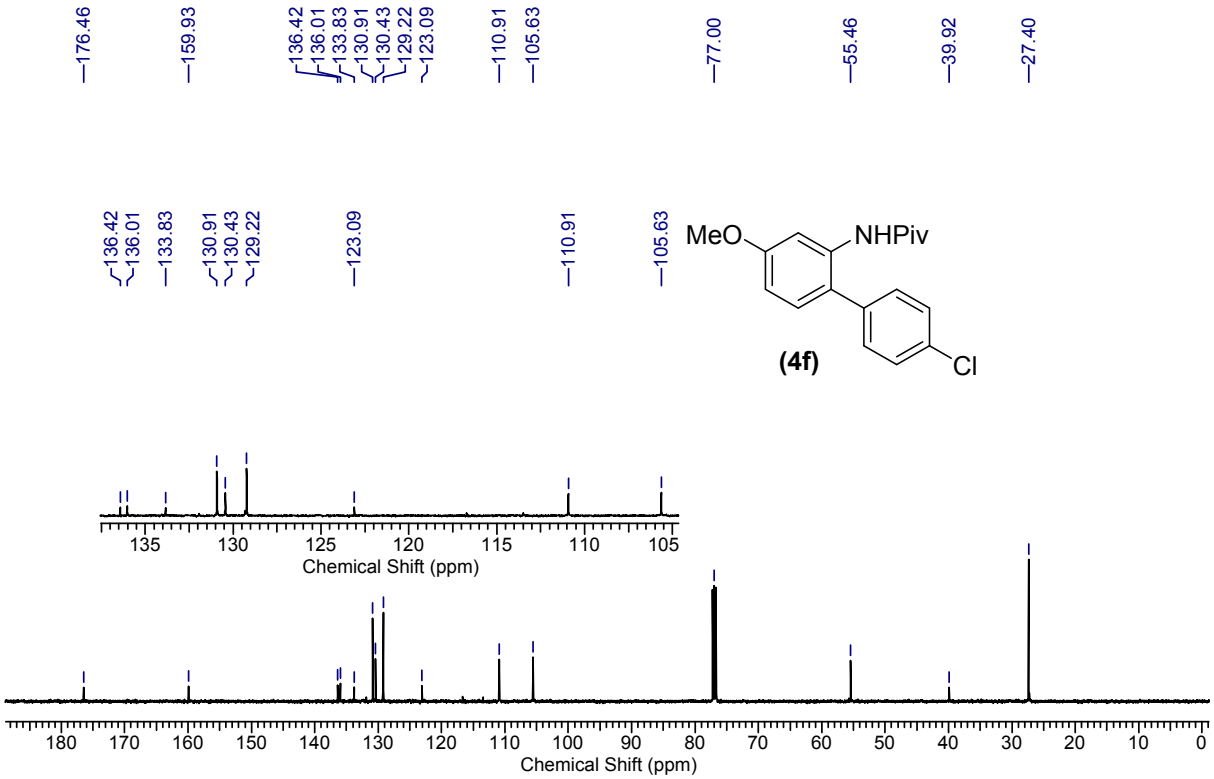

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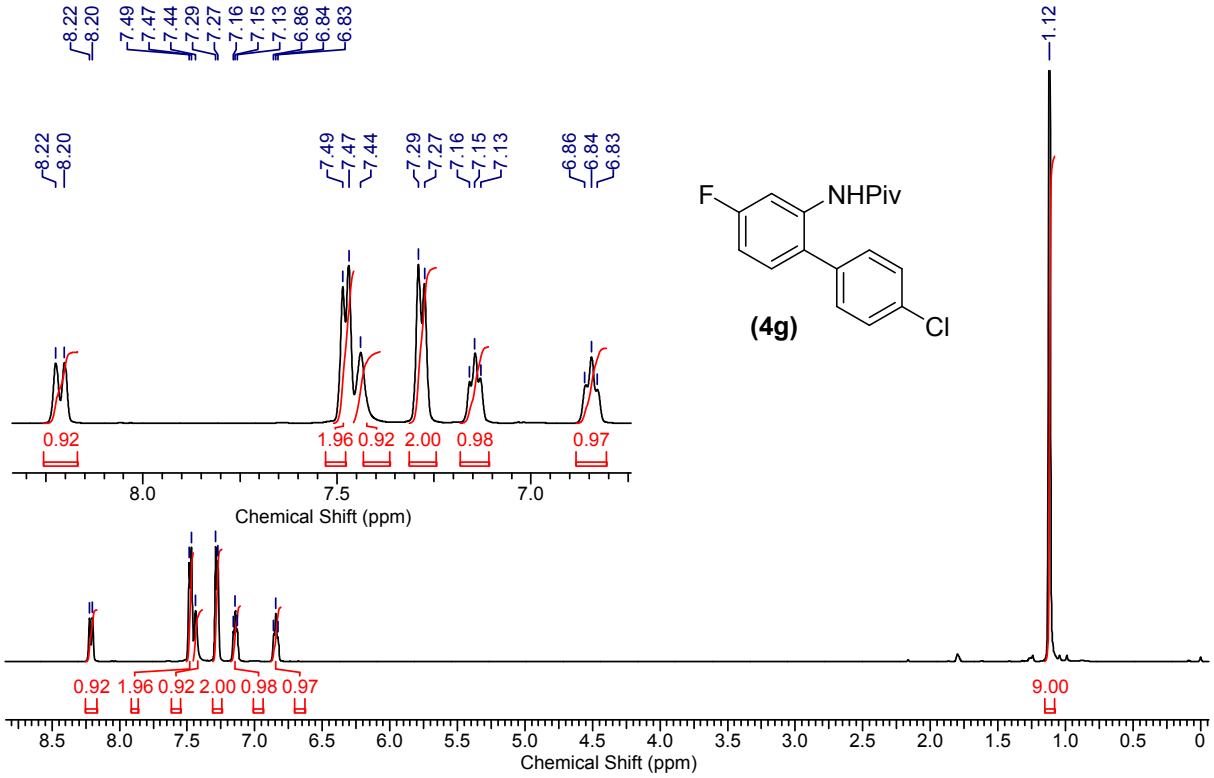

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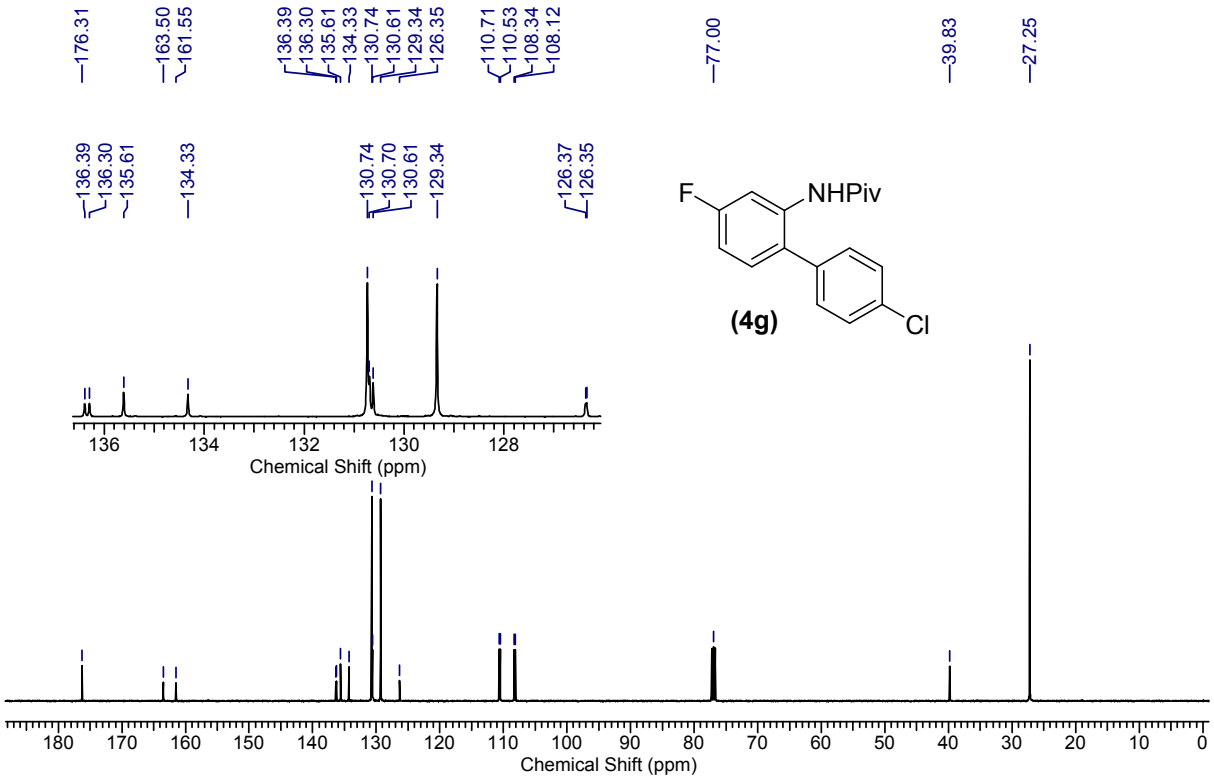

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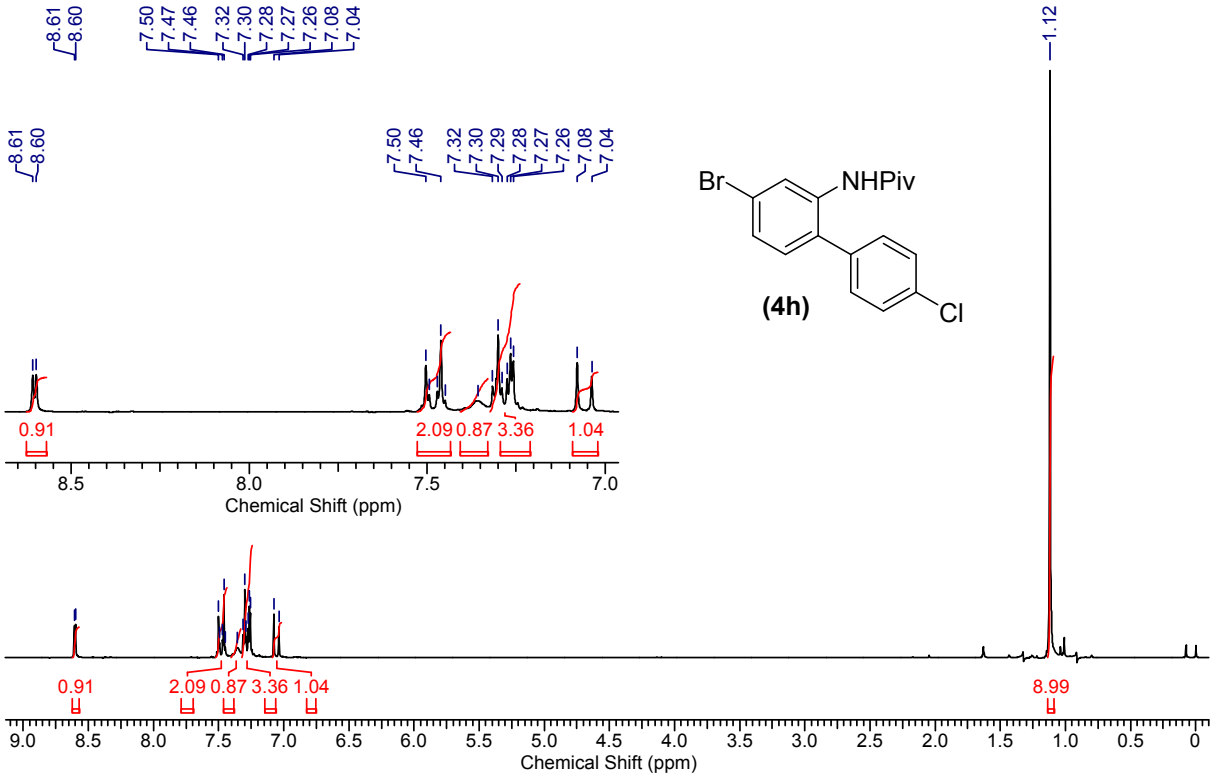

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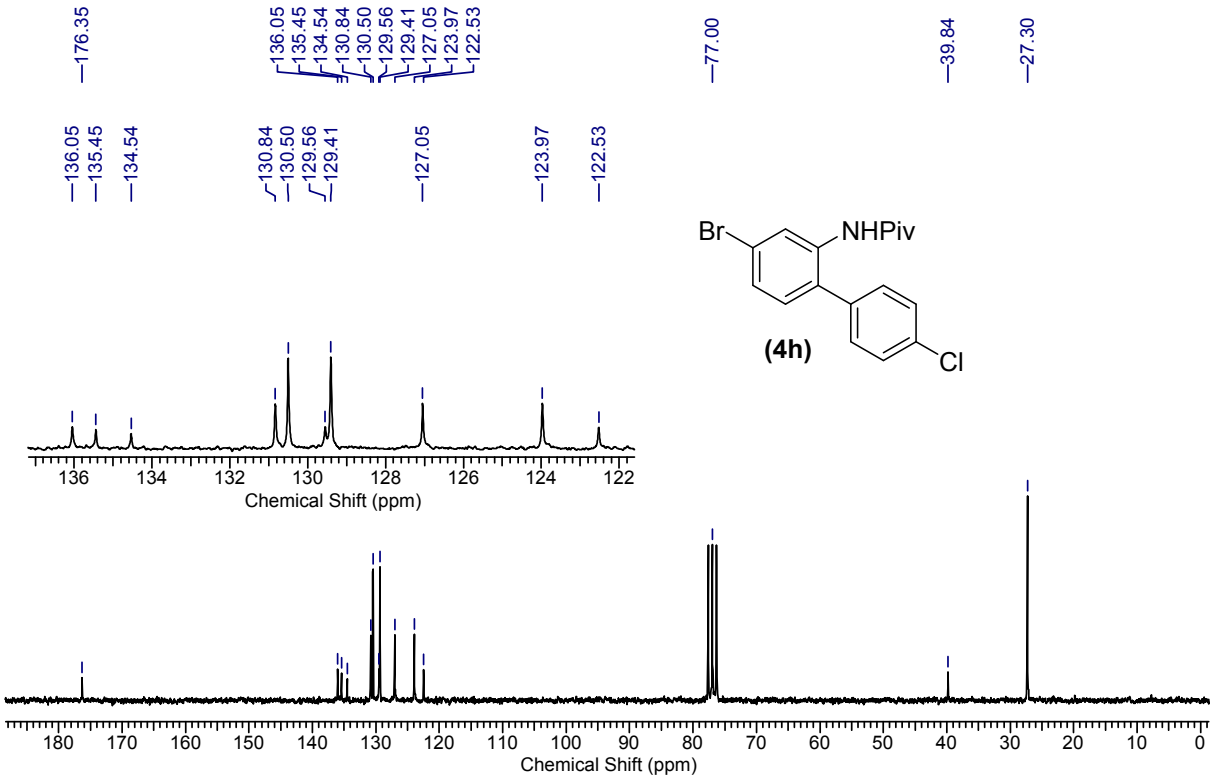

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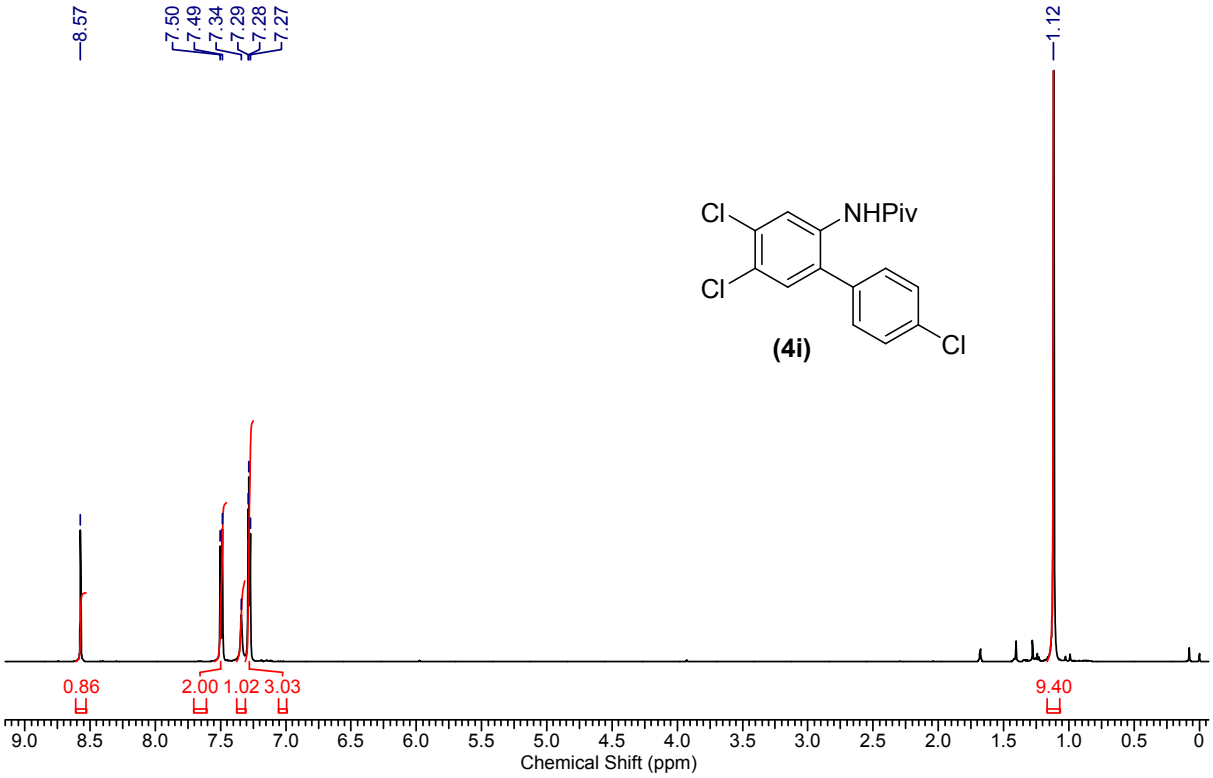

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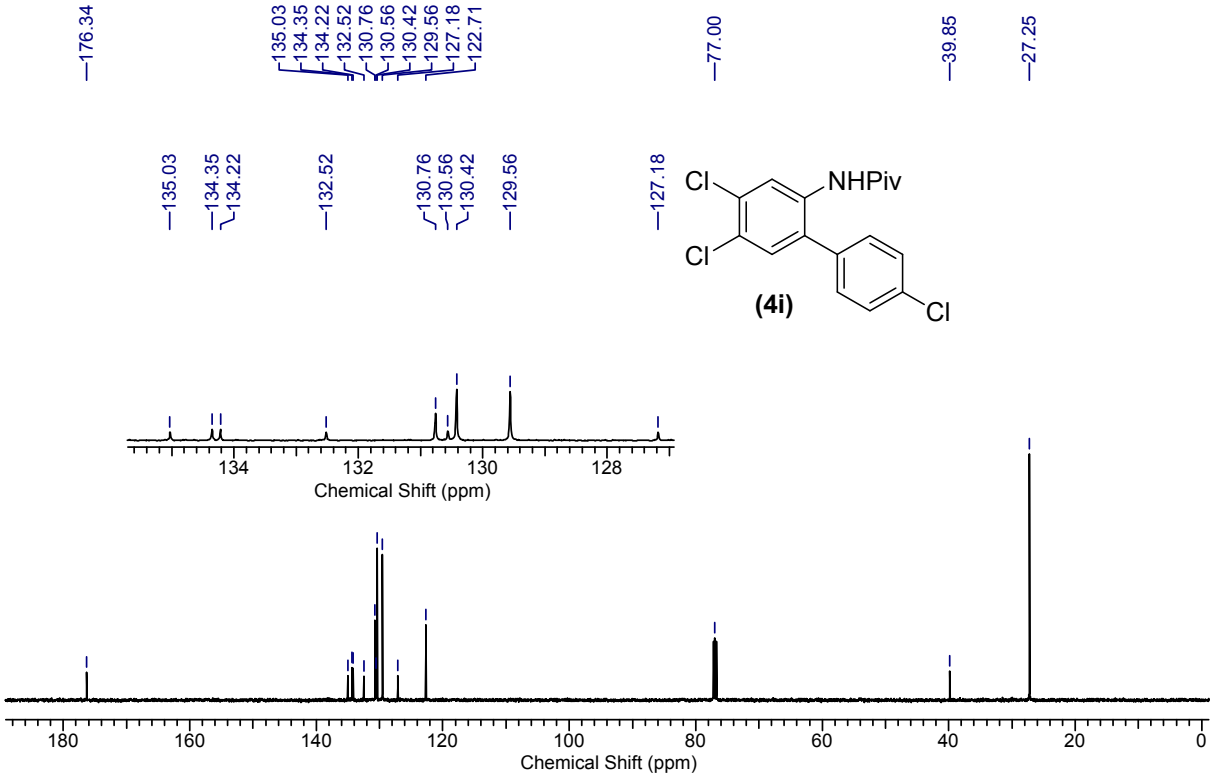

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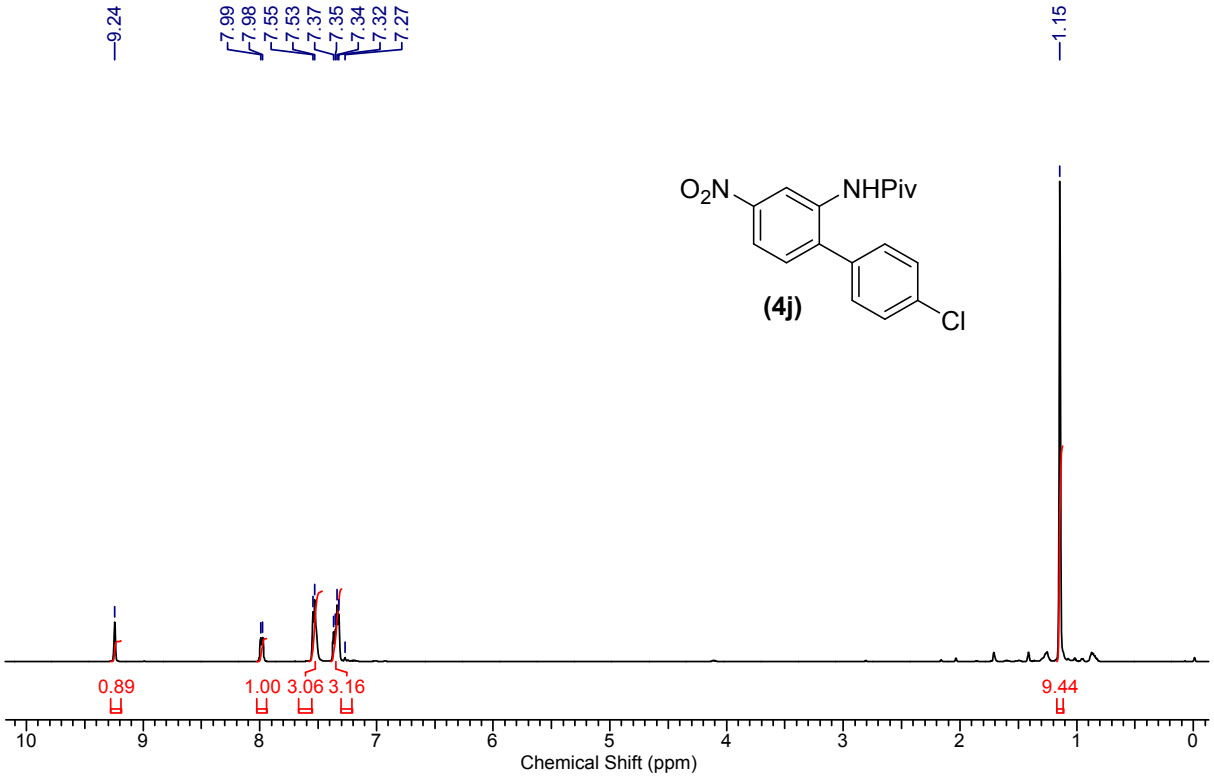

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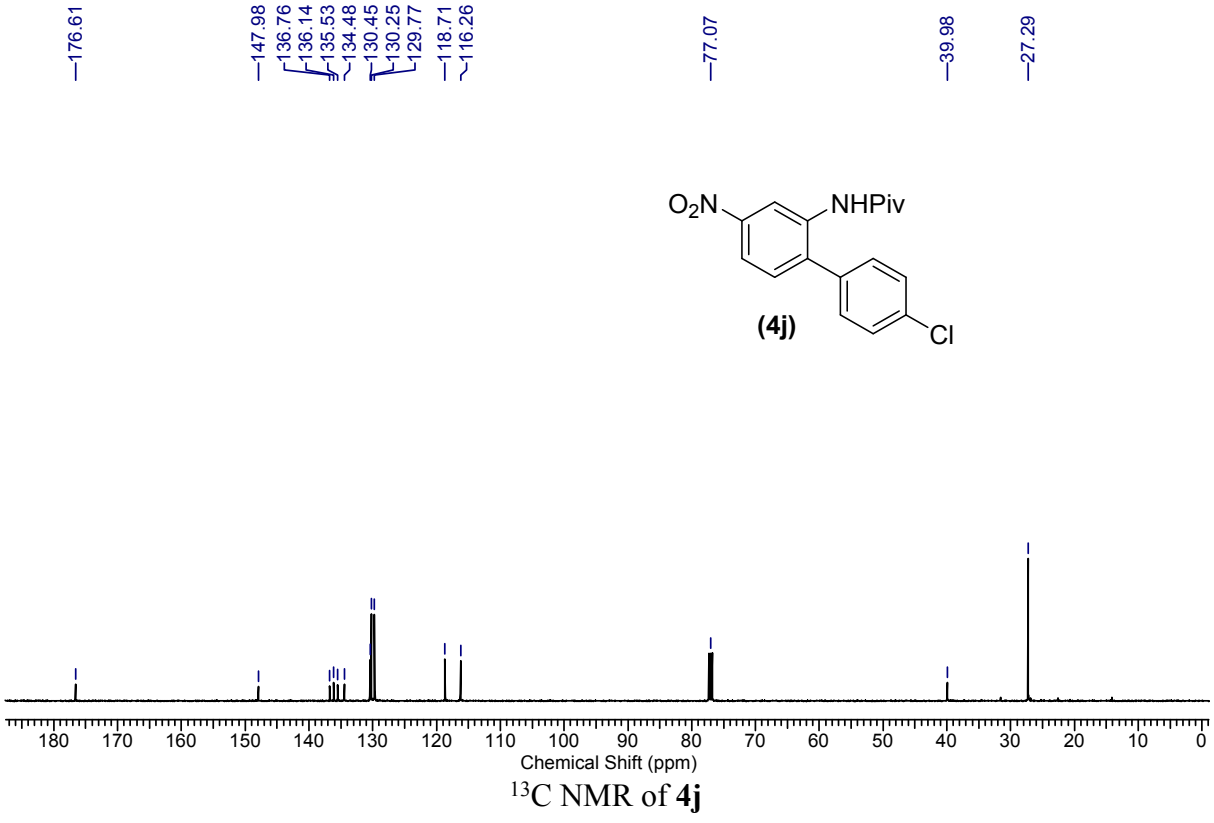

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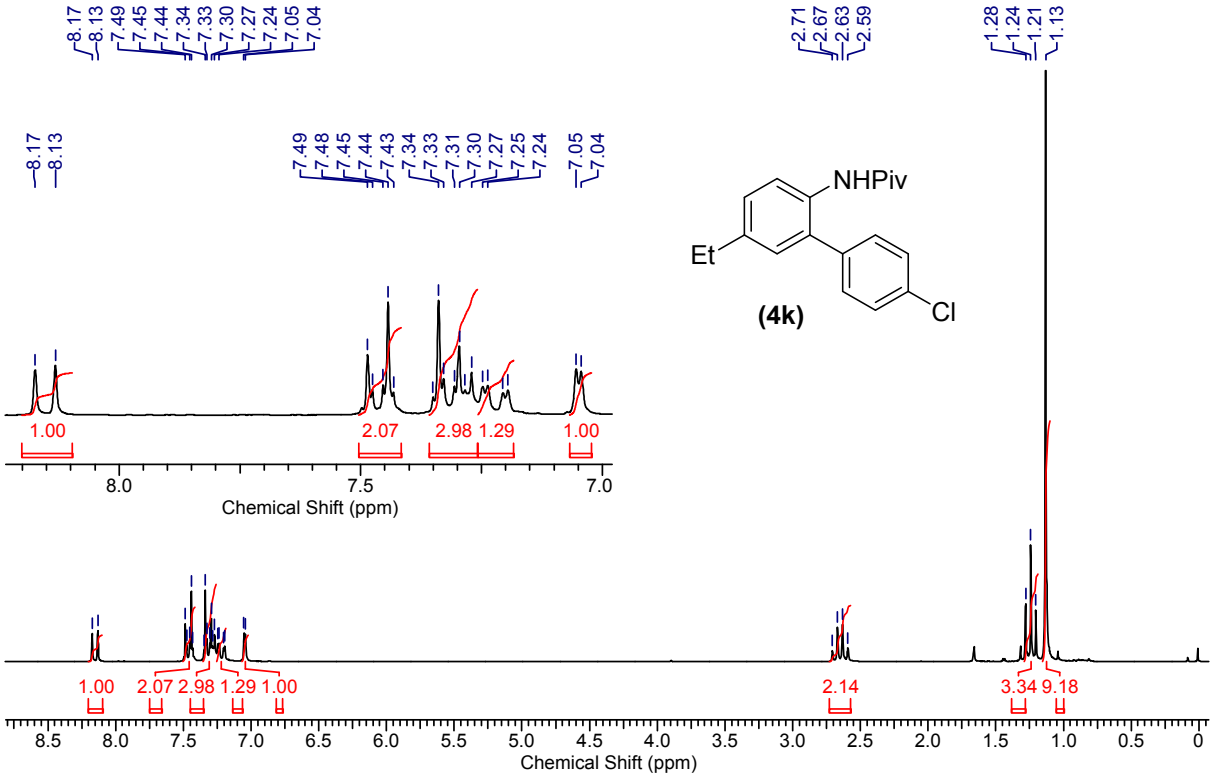

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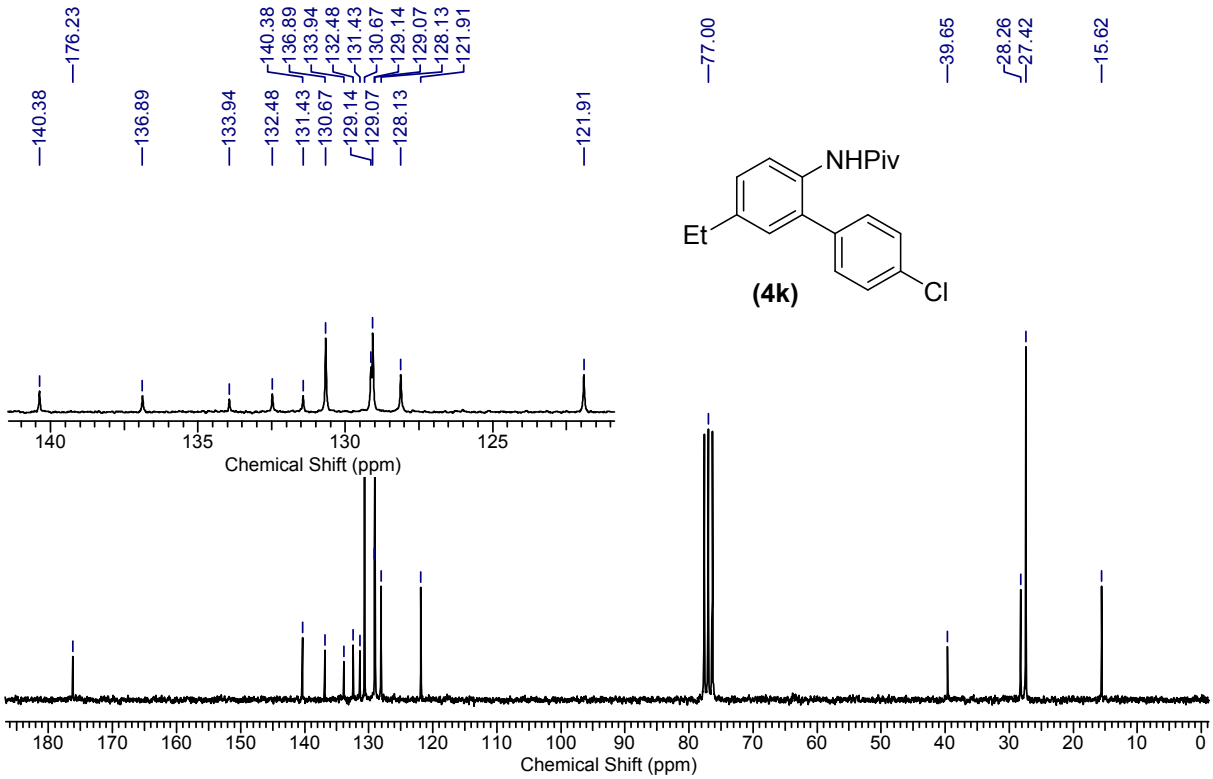

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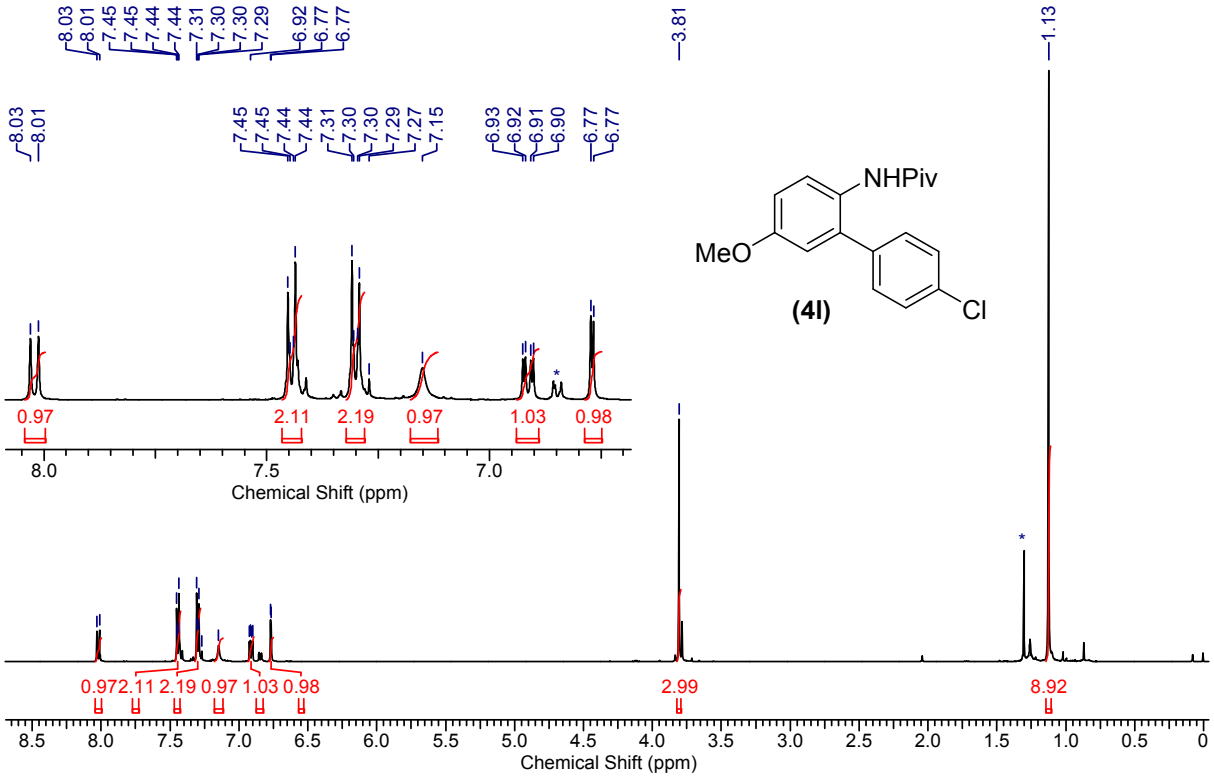
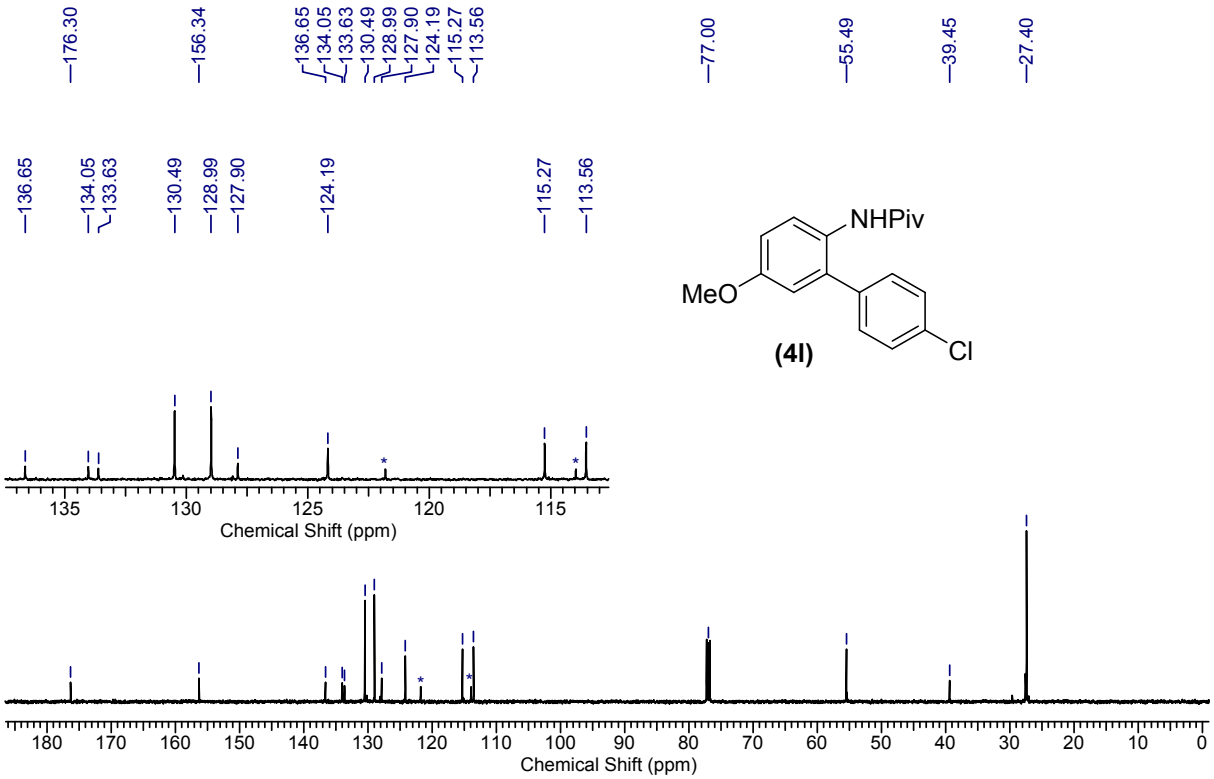
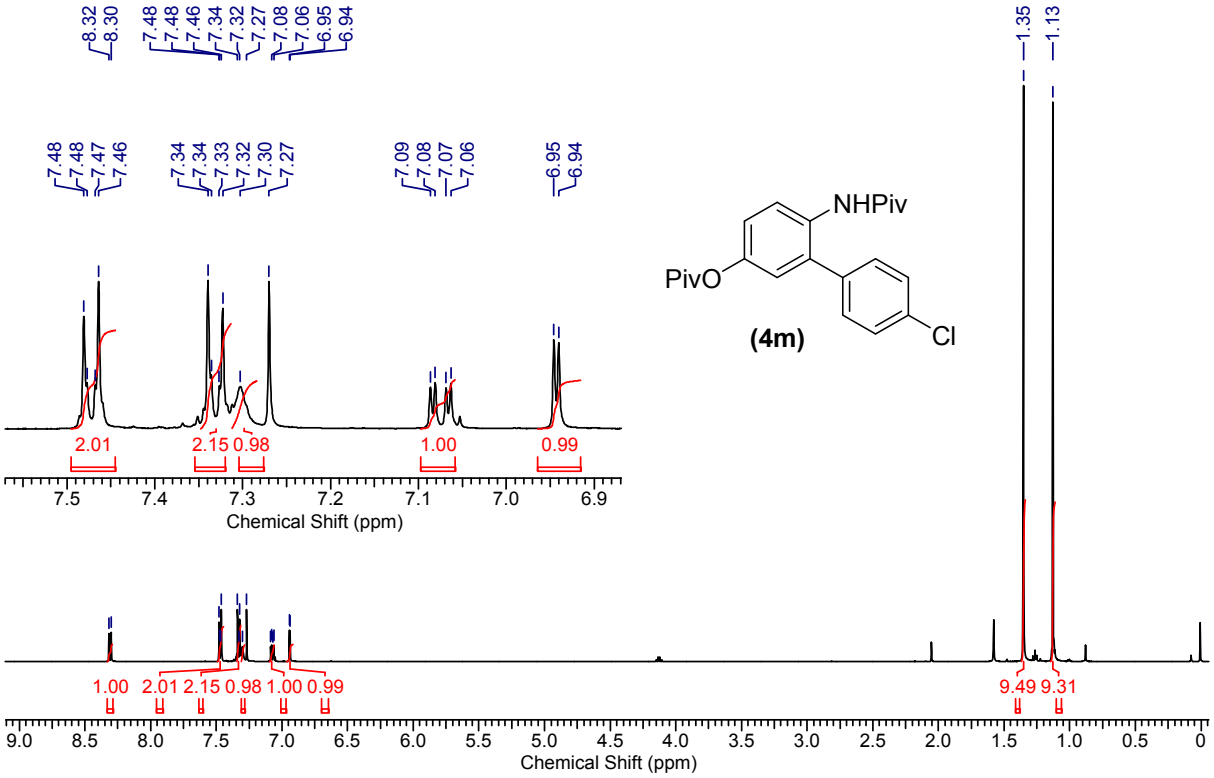


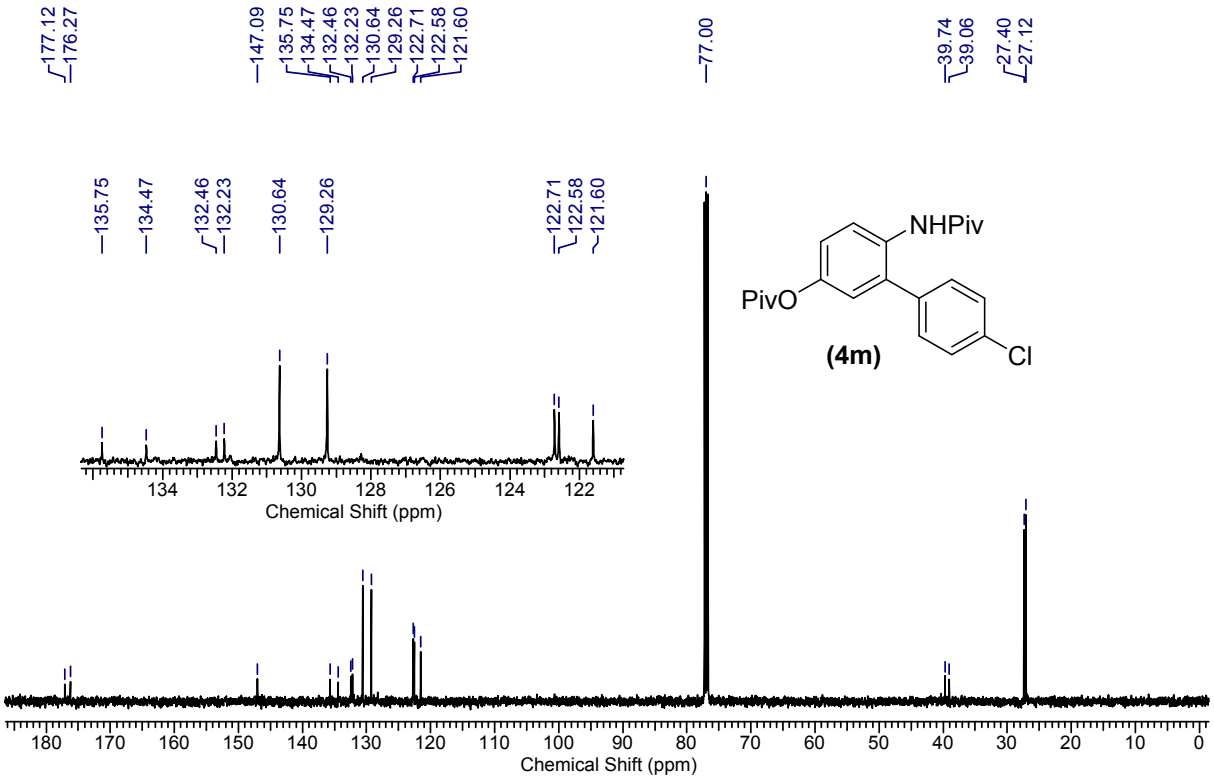
^{1}H NMR of **4l**



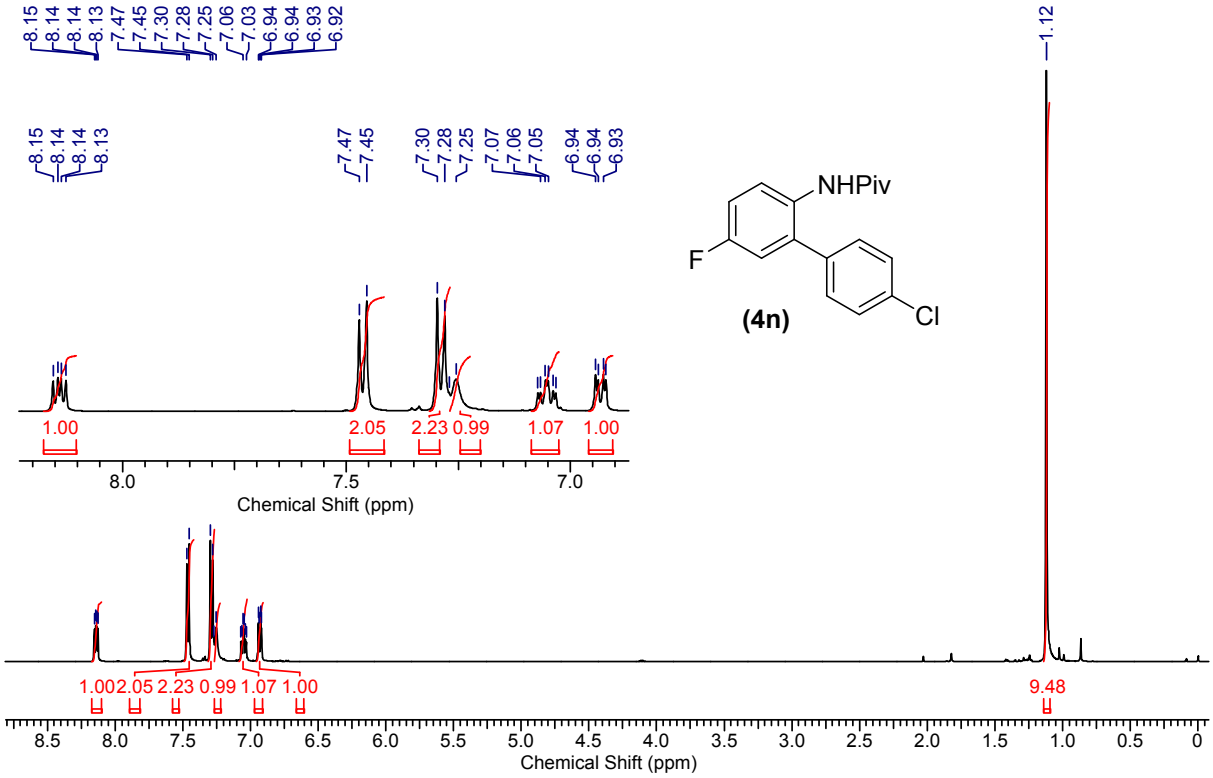
^{13}C NMR of **4l**



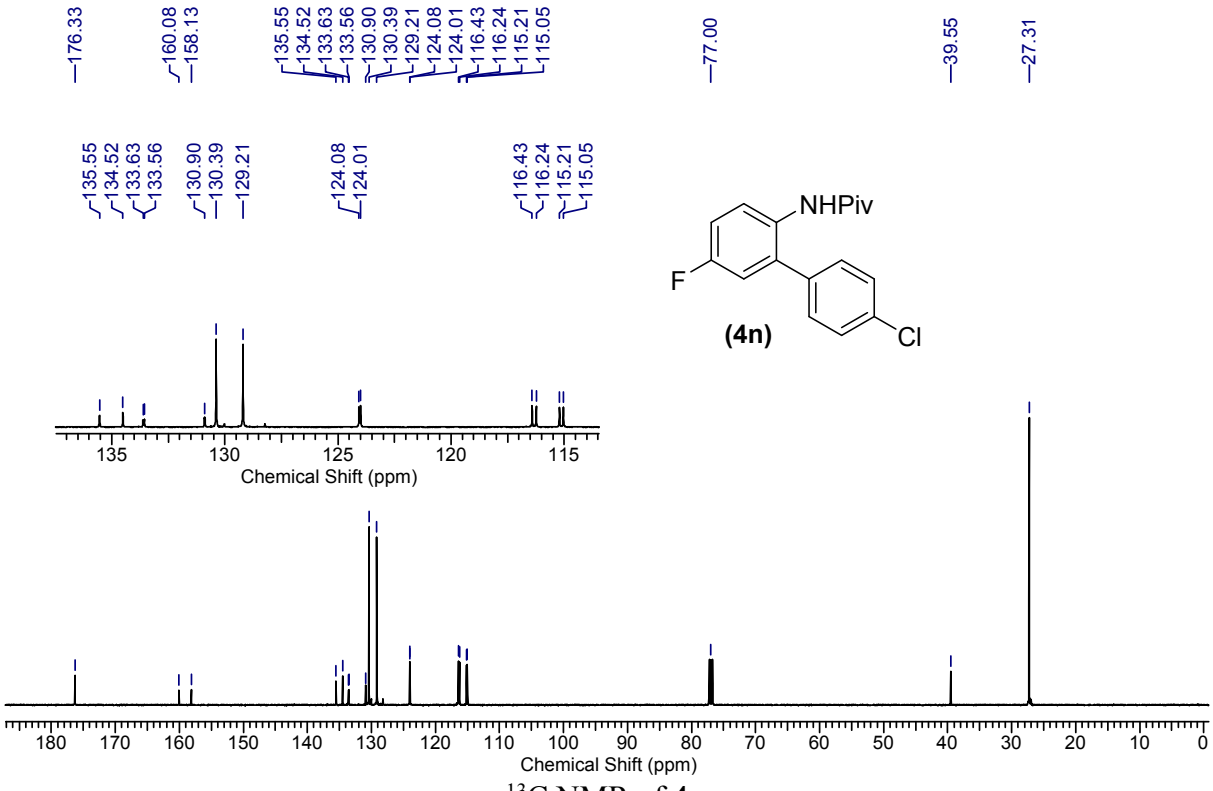
^{1}H NMR of **4m**



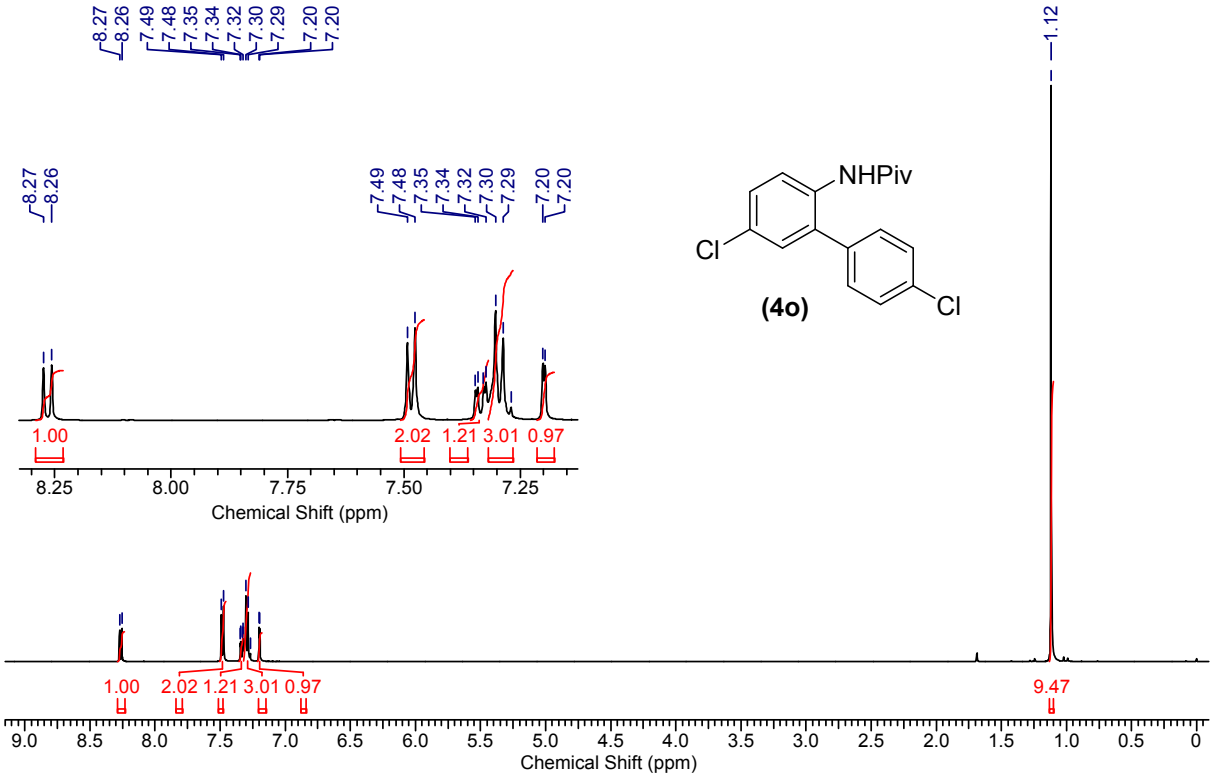
^{13}C NMR of **4m**



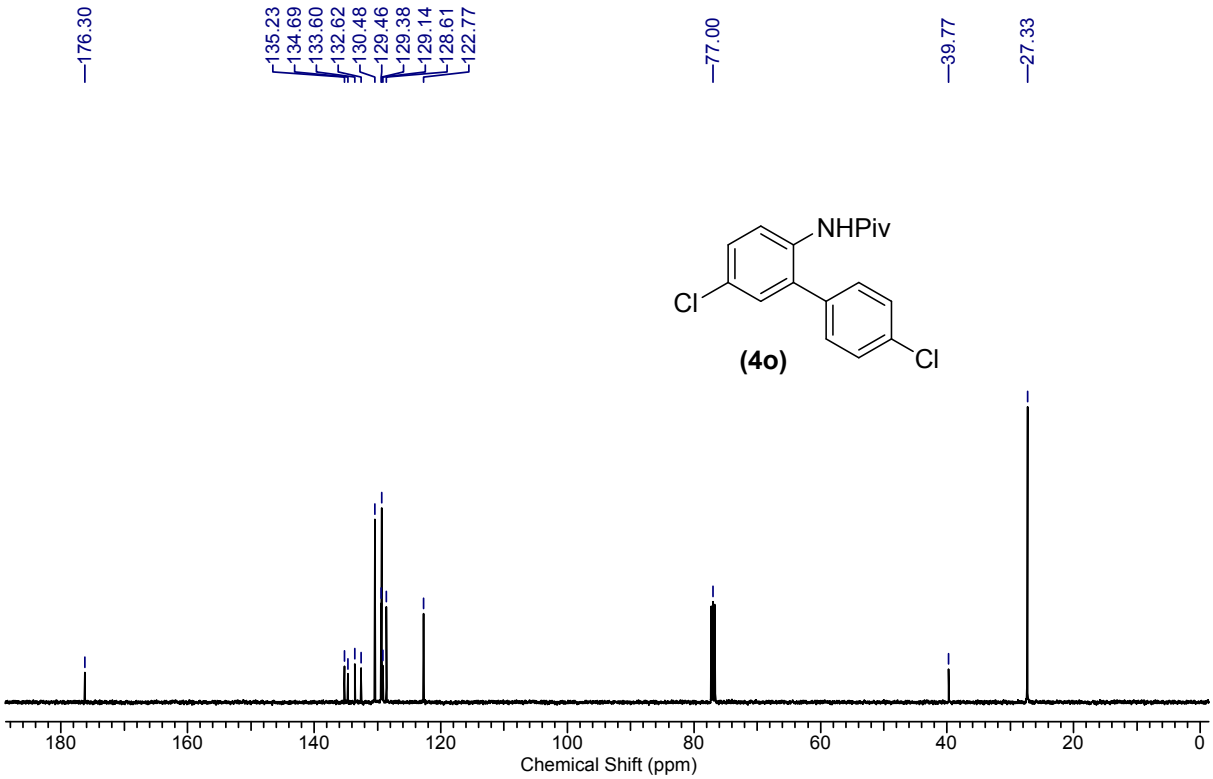
^{1}H NMR of **4n**



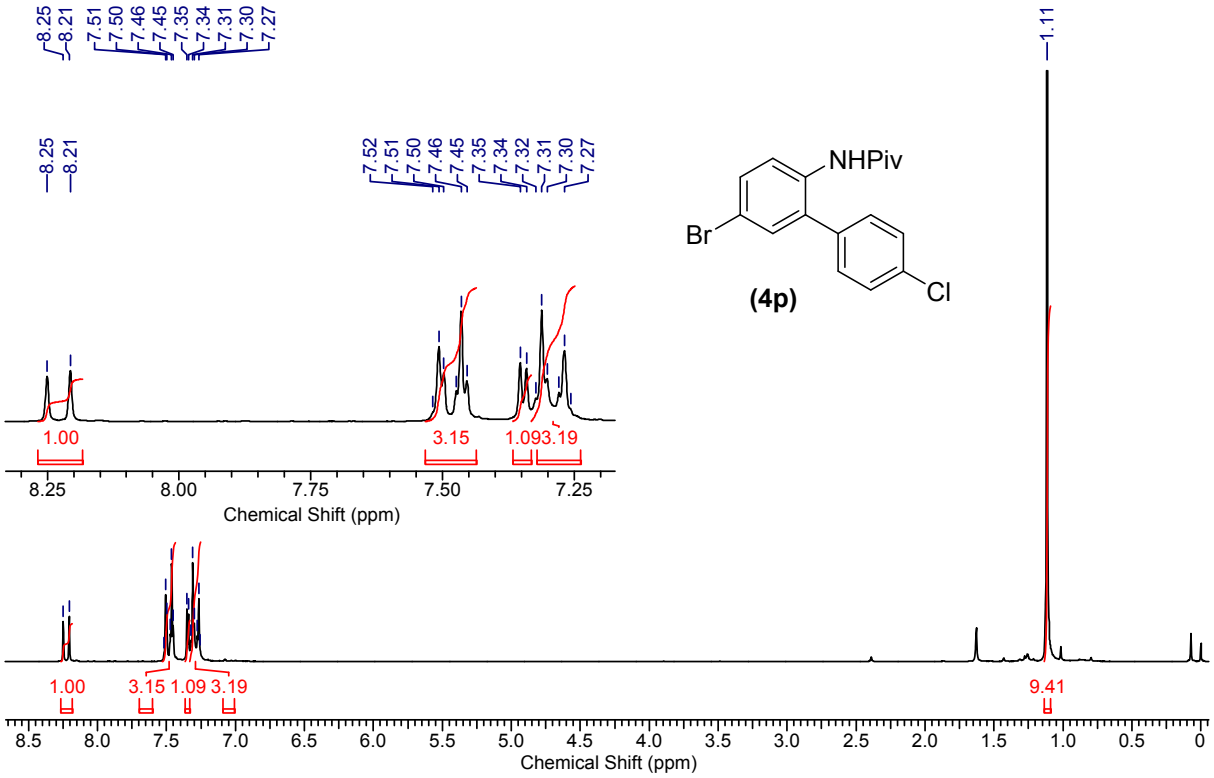
^{13}C NMR of **4n**



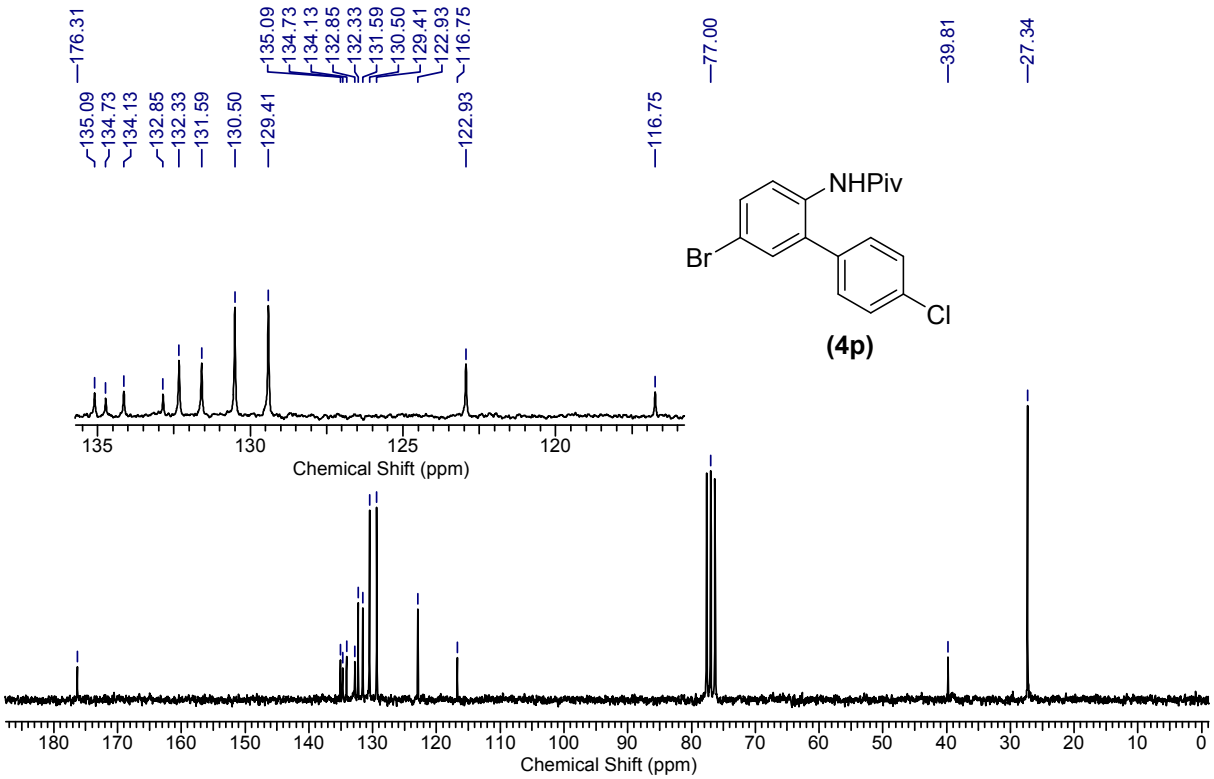
^{1}H NMR of **4o**



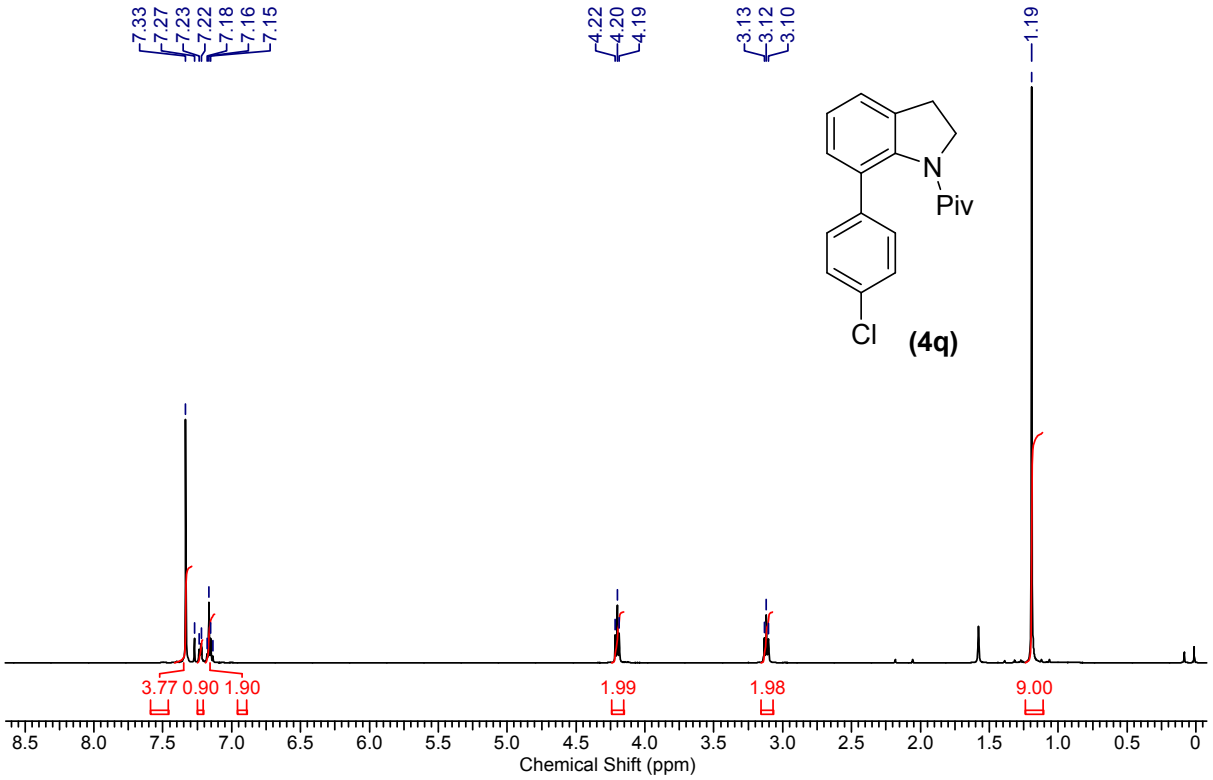
^{13}C NMR of **4o**



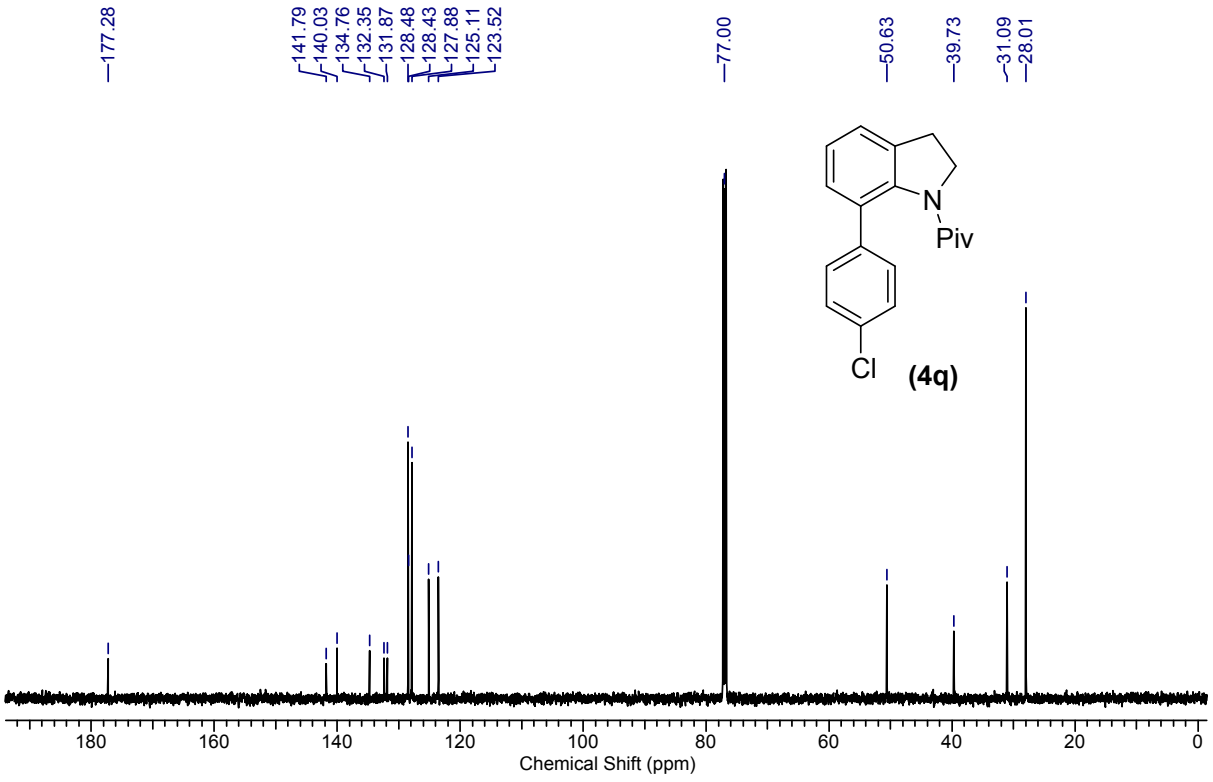
^{1}H NMR of **4p**



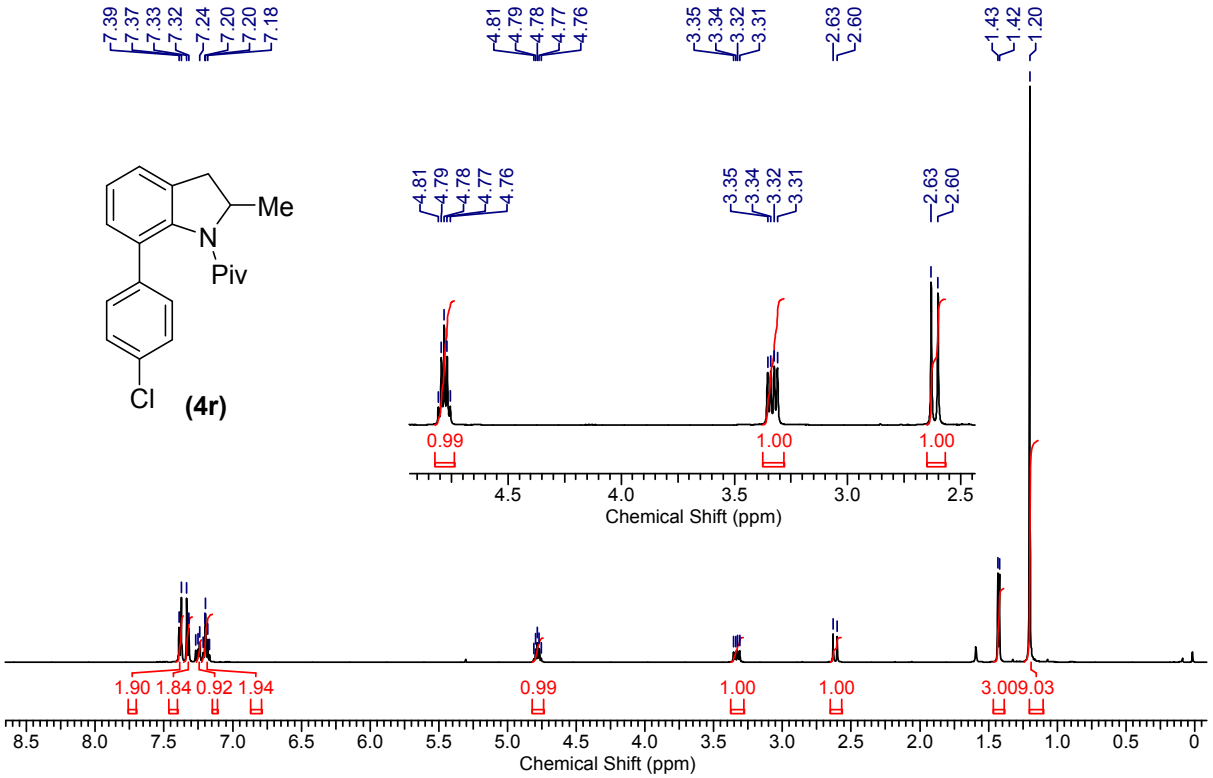
^{13}C NMR of **4p**



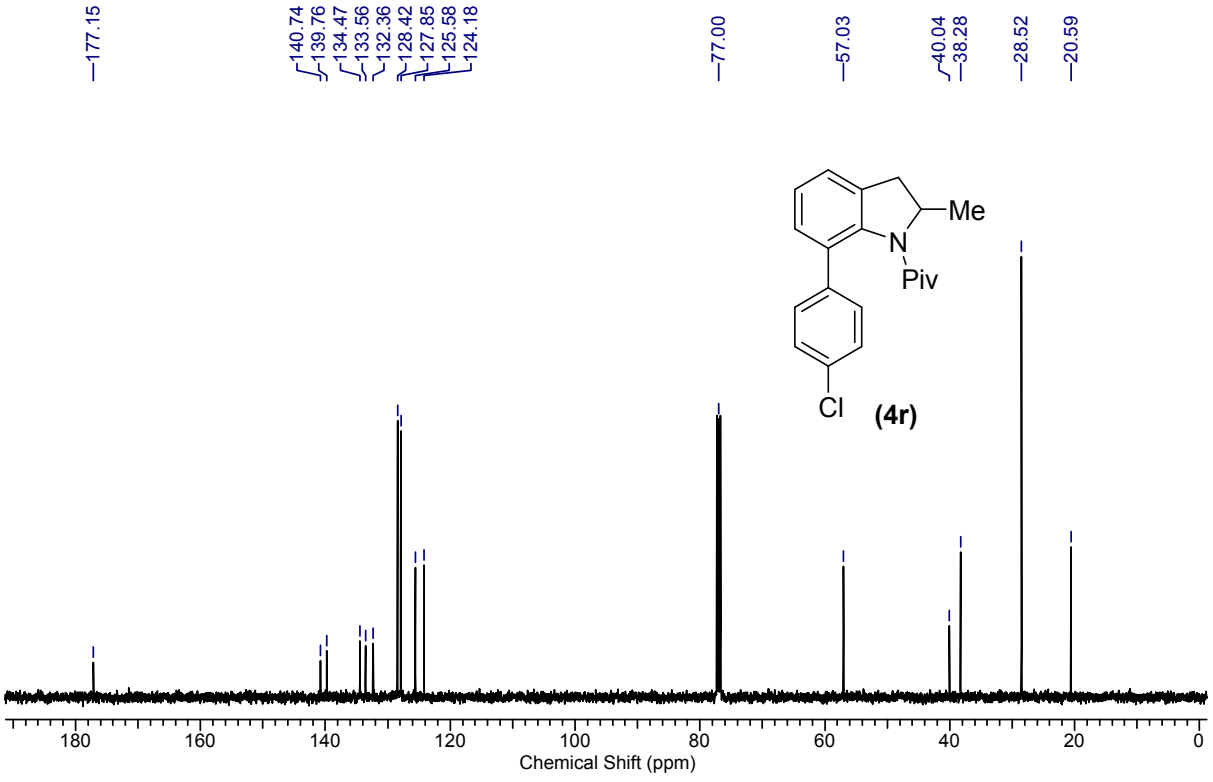
^{1}H NMR of **4q**



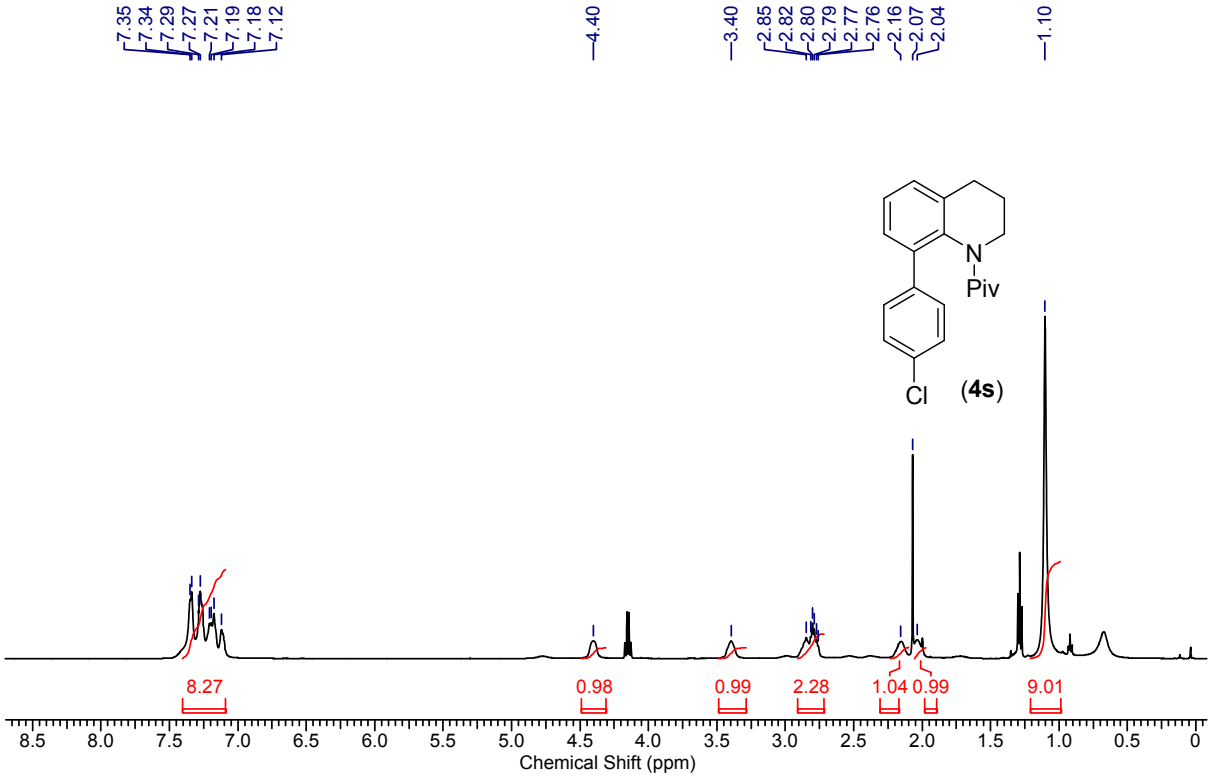
^{13}C NMR of **4q**



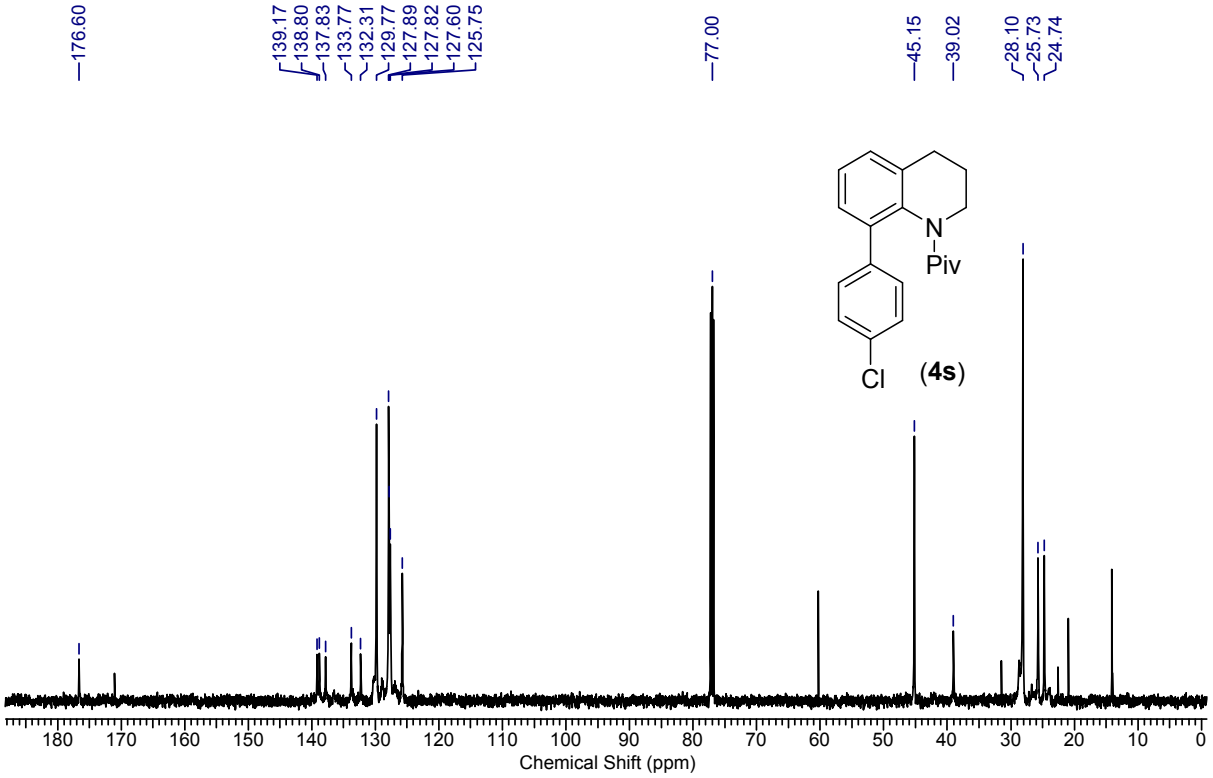
^{1}H NMR of **4r**



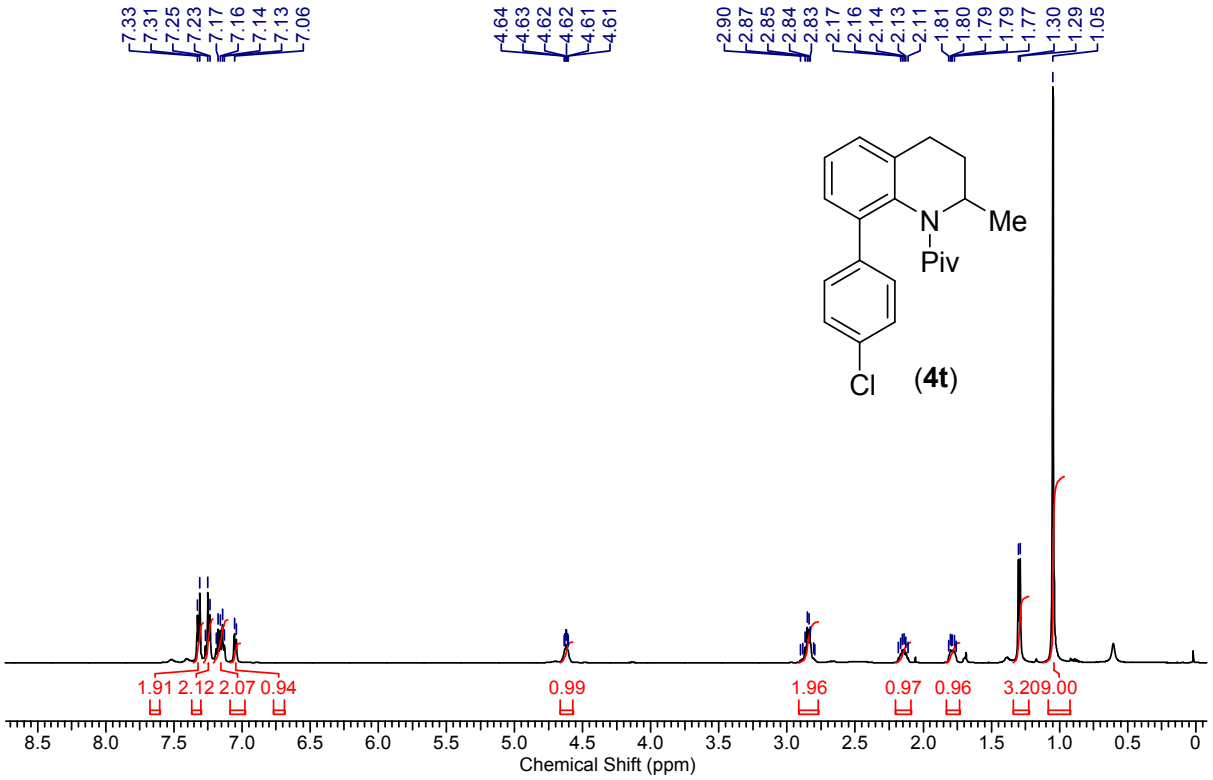
^{13}C NMR of **4r**



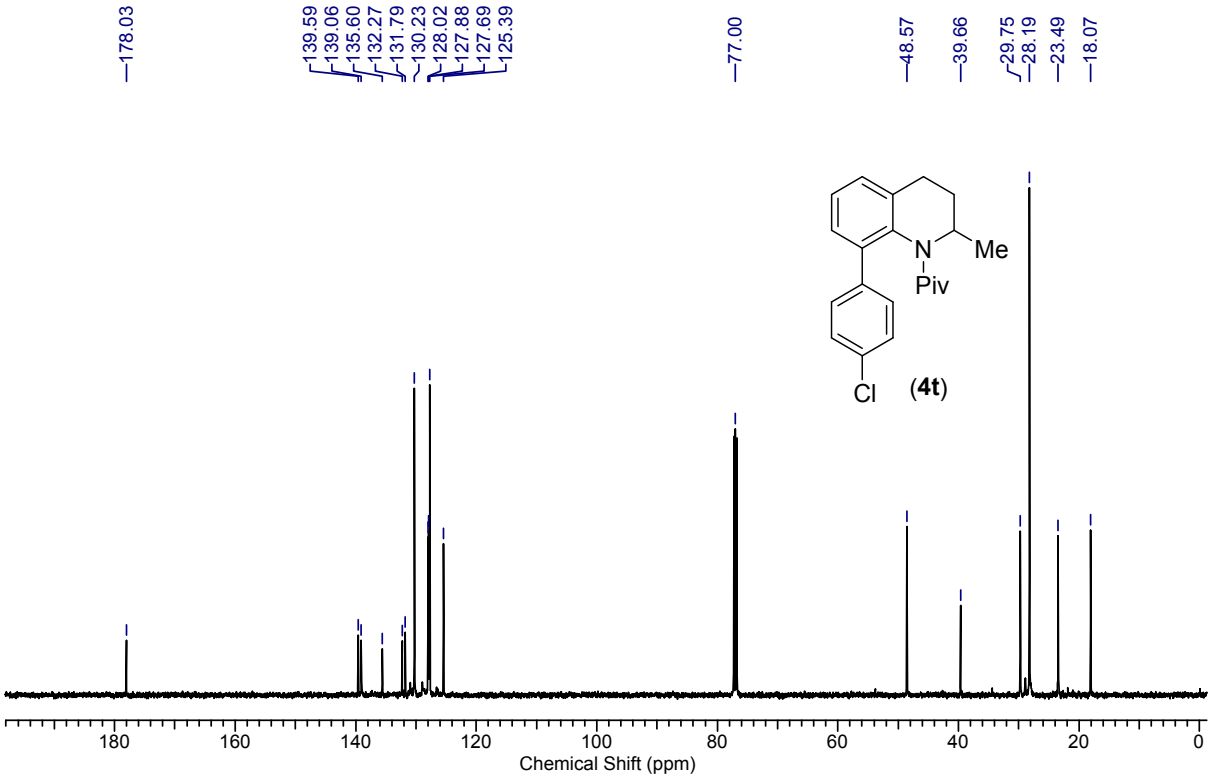
^{1}H NMR of **4s**



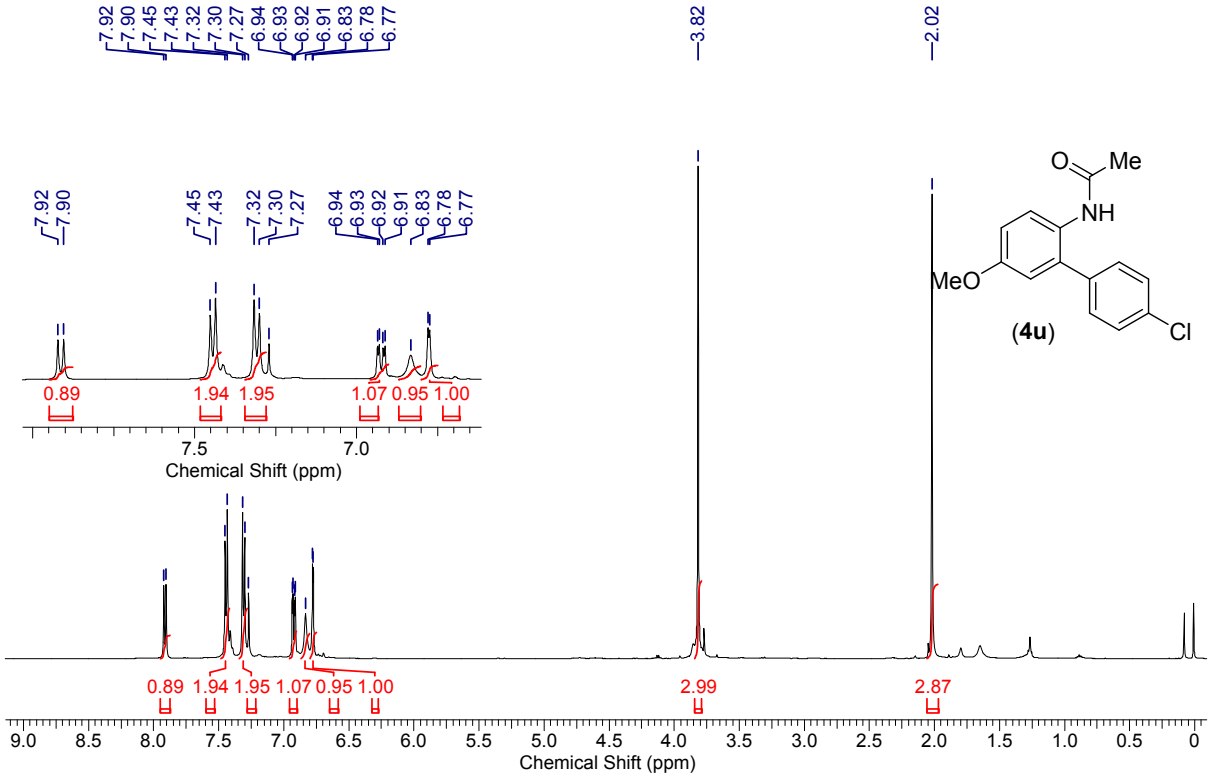
^{13}C NMR of **4s**



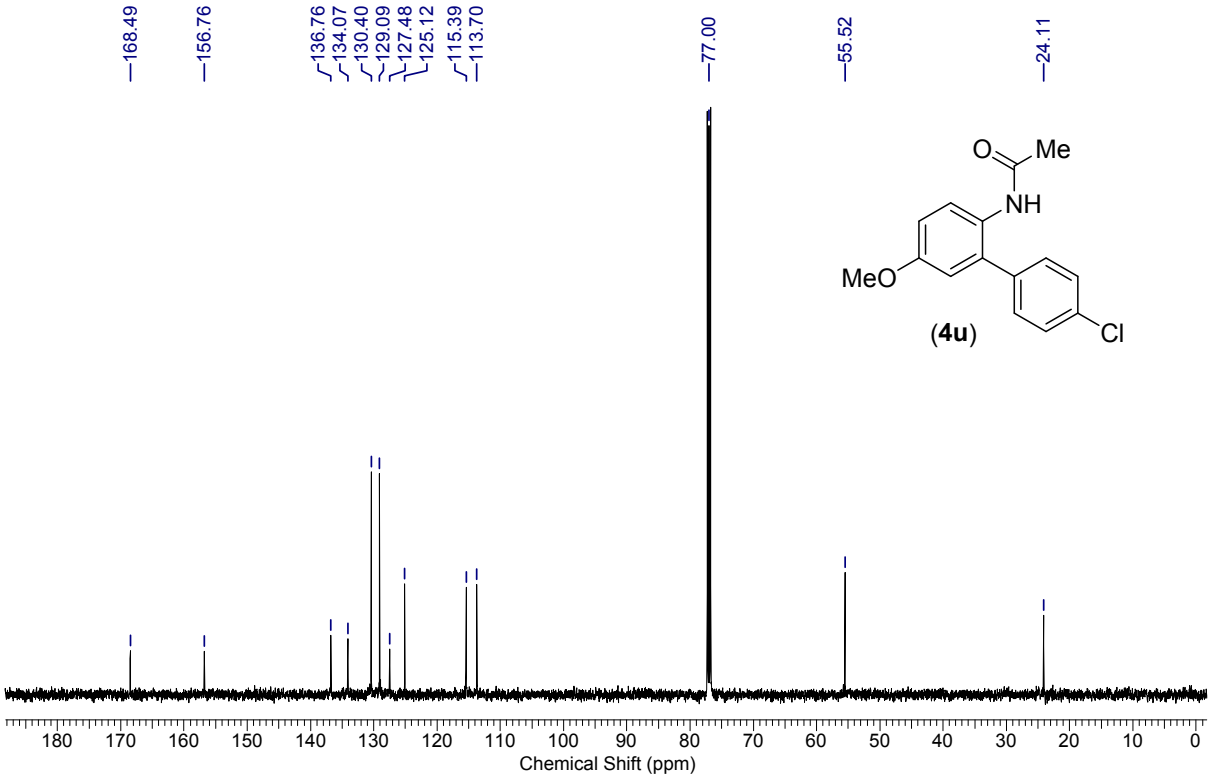
^{1}H NMR of **4t**



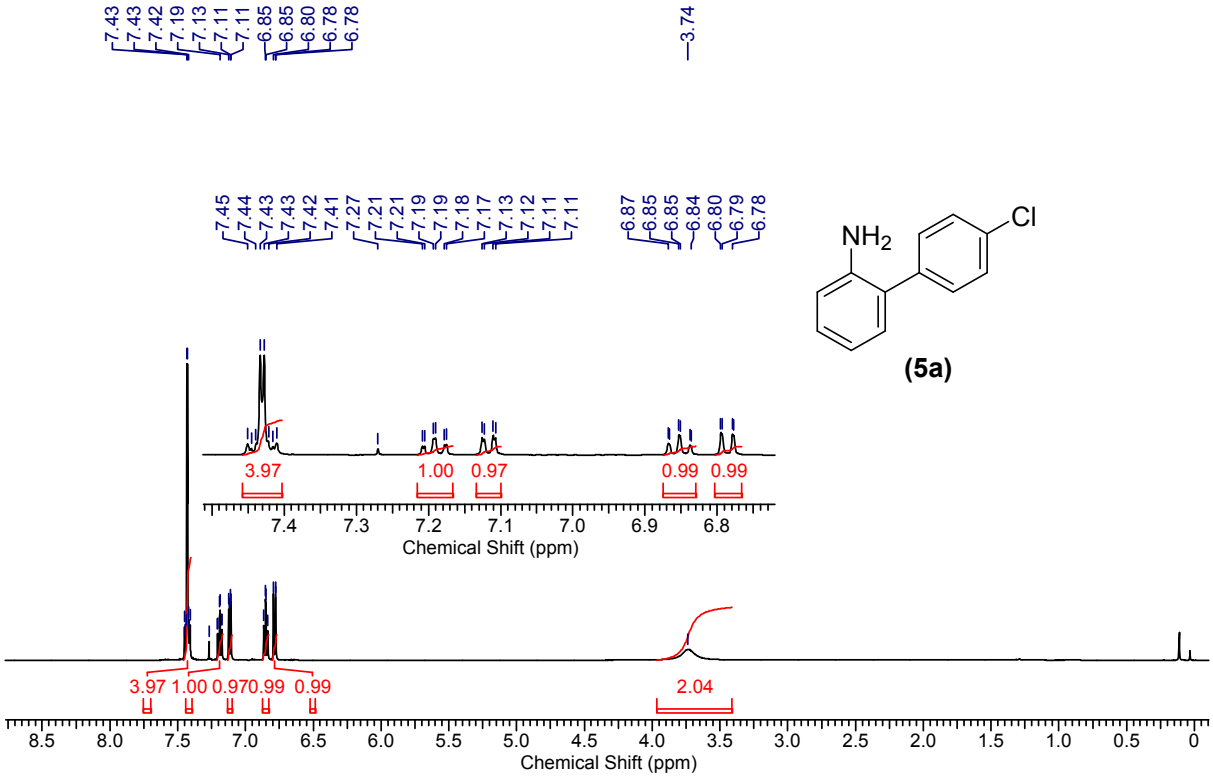
^{13}C NMR of **4t**



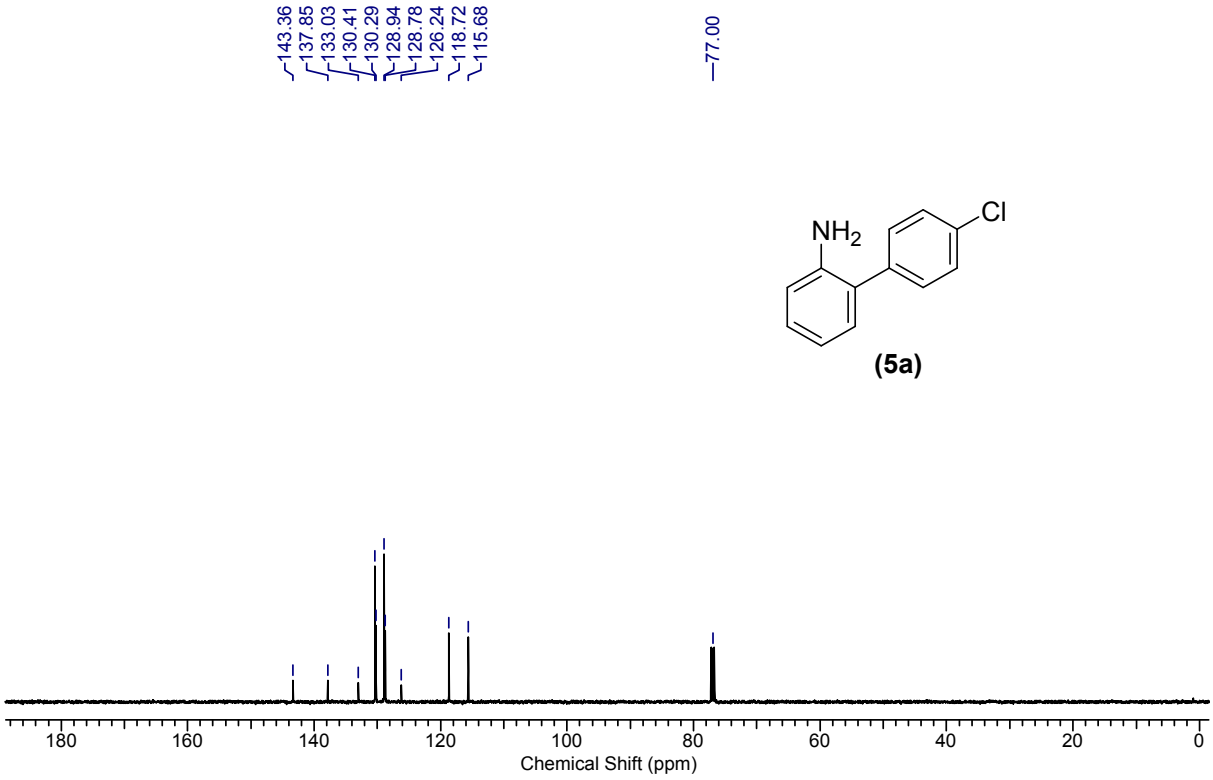
^{1}H NMR of **4u**



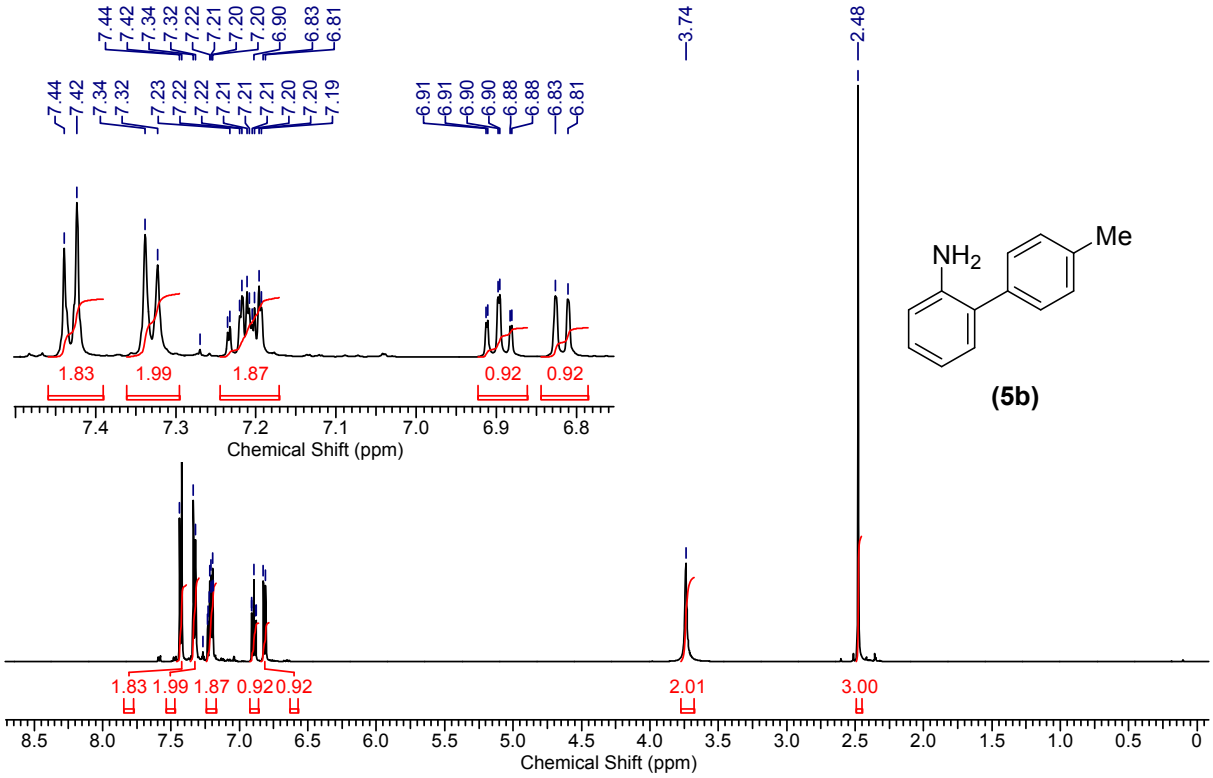
^{13}C NMR of **4u**



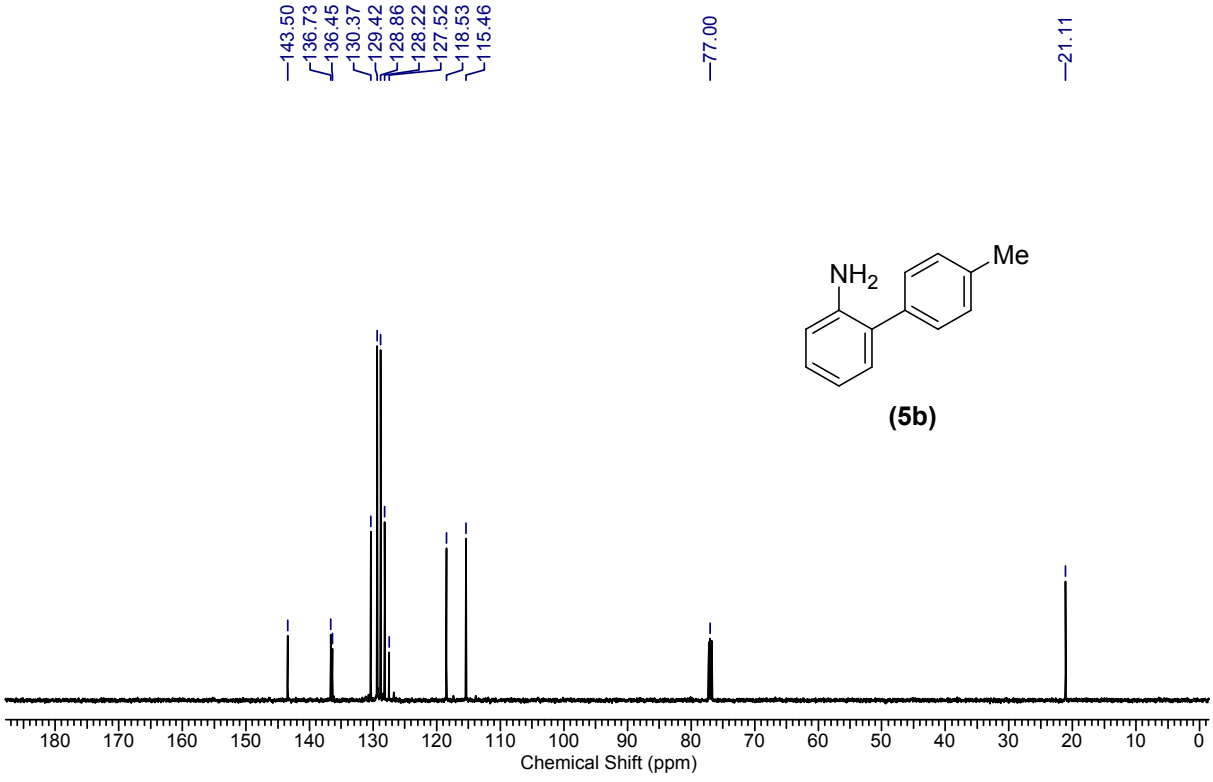
^{1}H NMR of **5a**



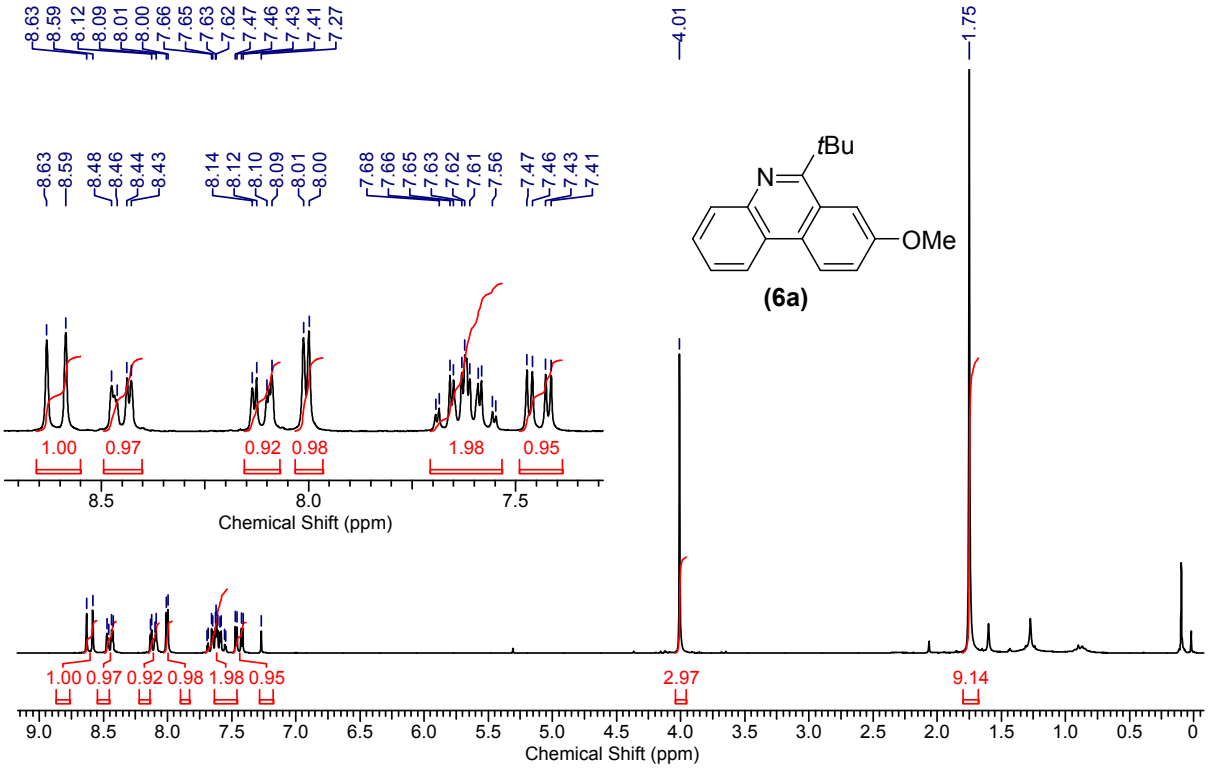
^{13}C NMR of **5a**



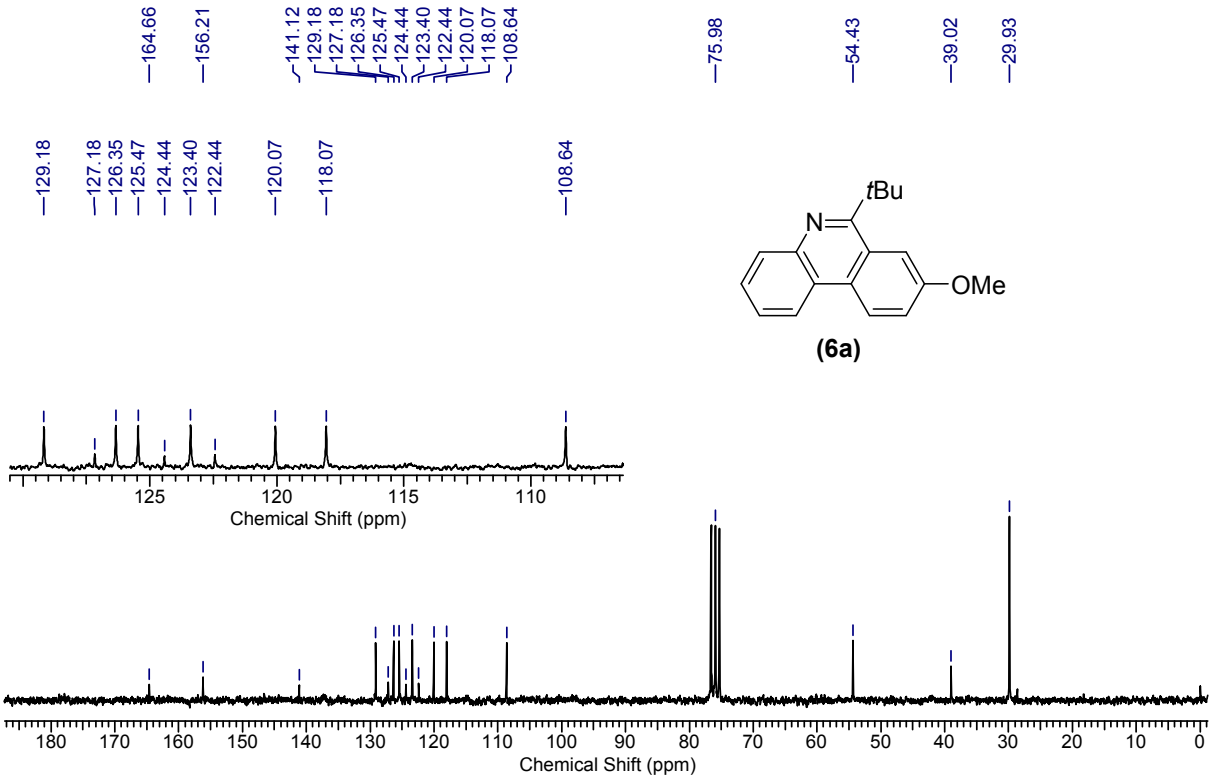
^{1}H NMR of **5b**



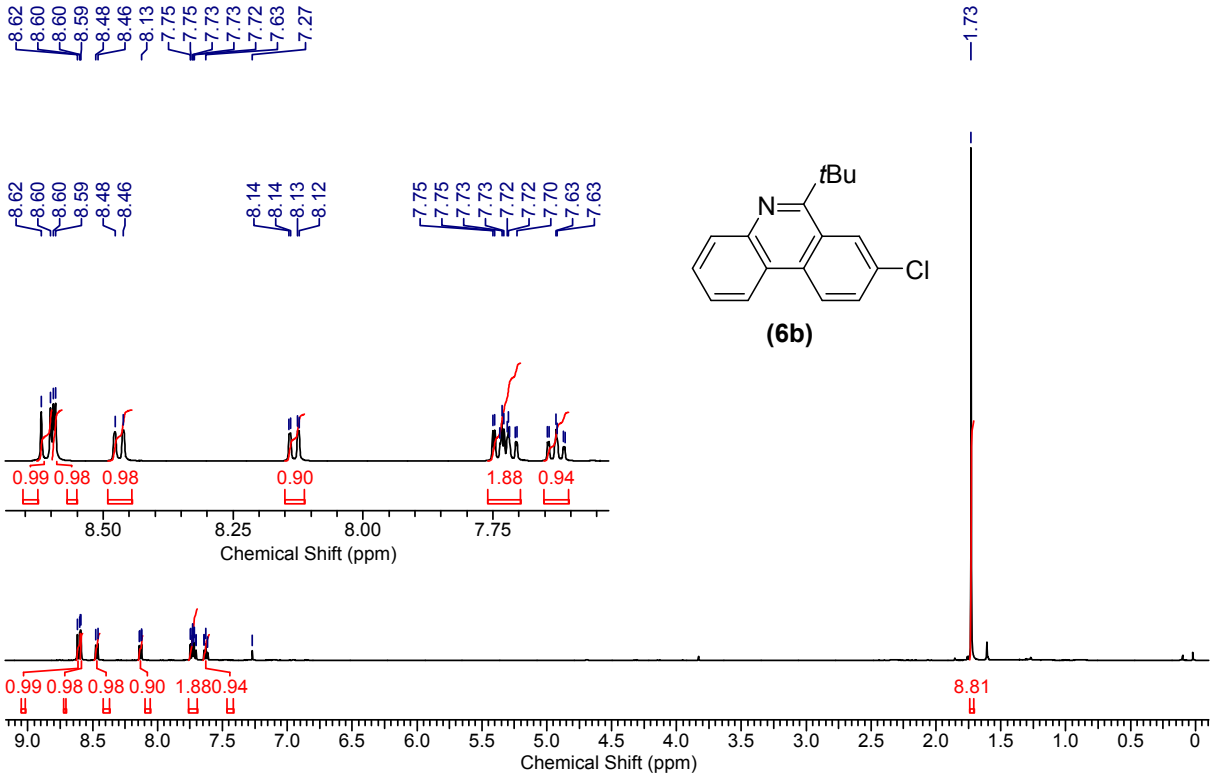
^{13}C NMR of **5b**



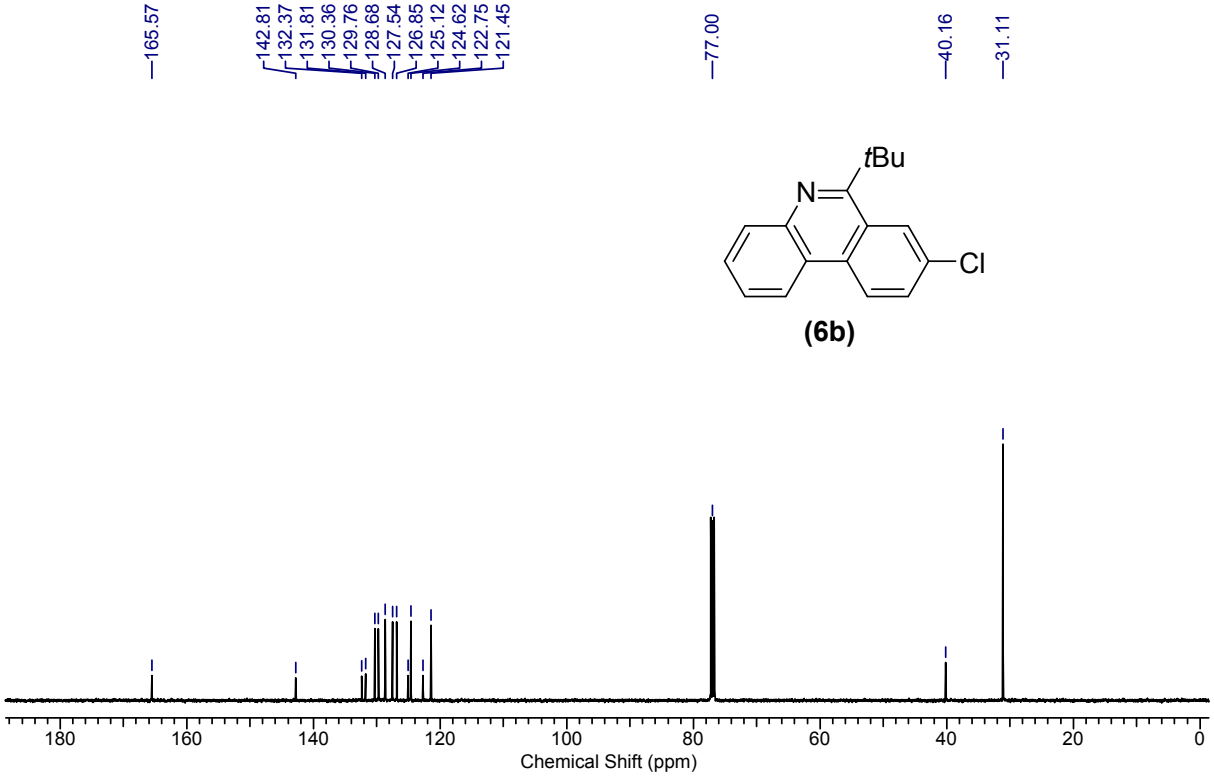
^{1}H NMR of **6a**



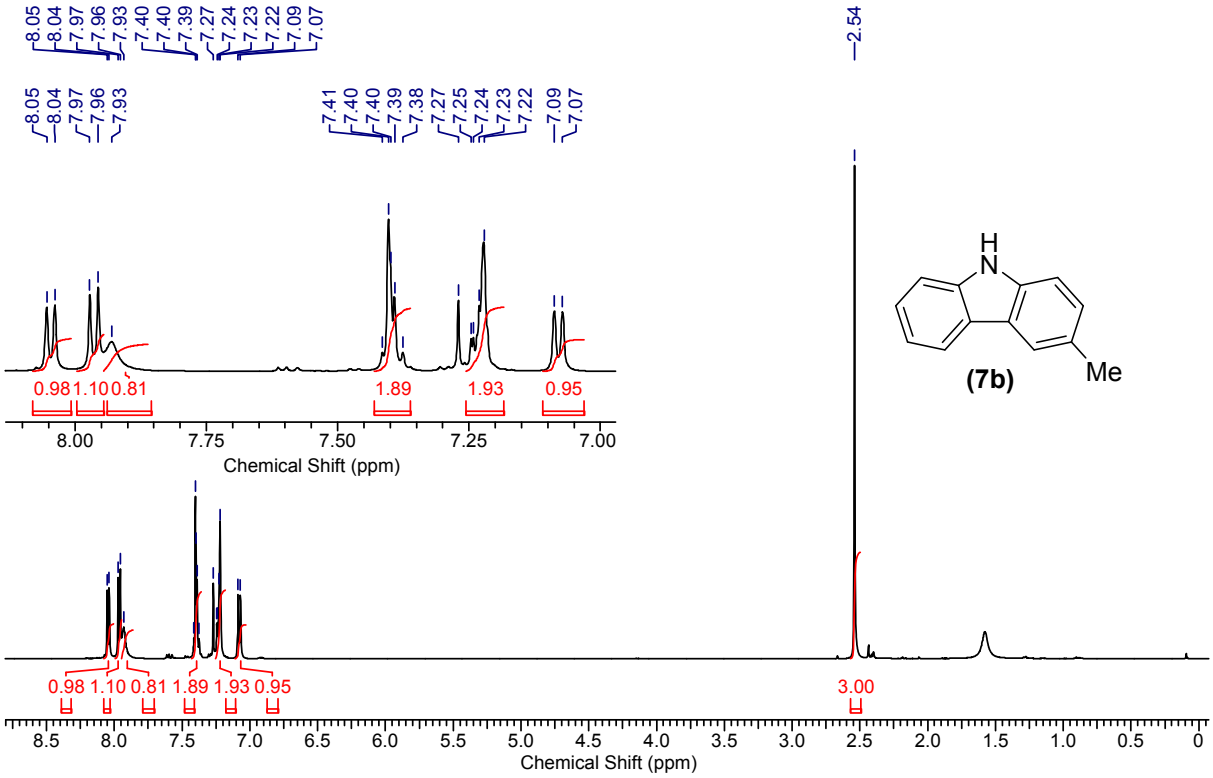
^{13}C NMR of **6a**



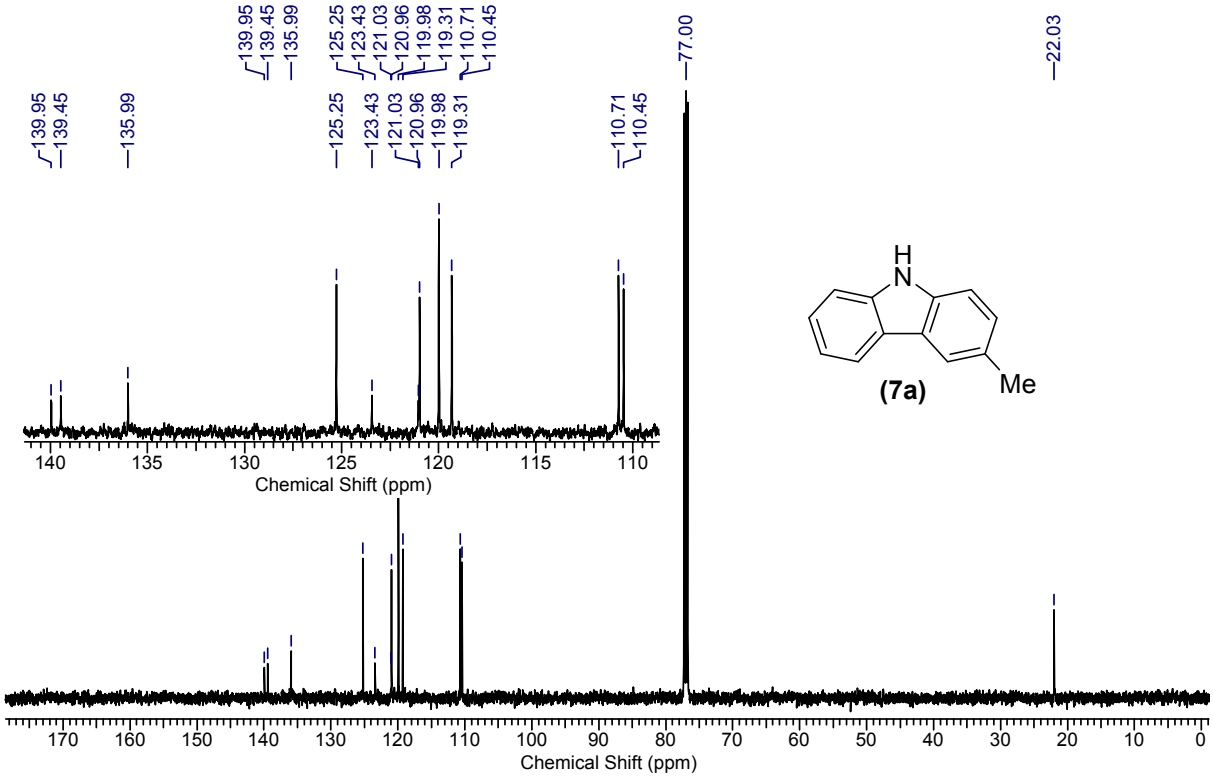
^{1}H NMR of **6b**



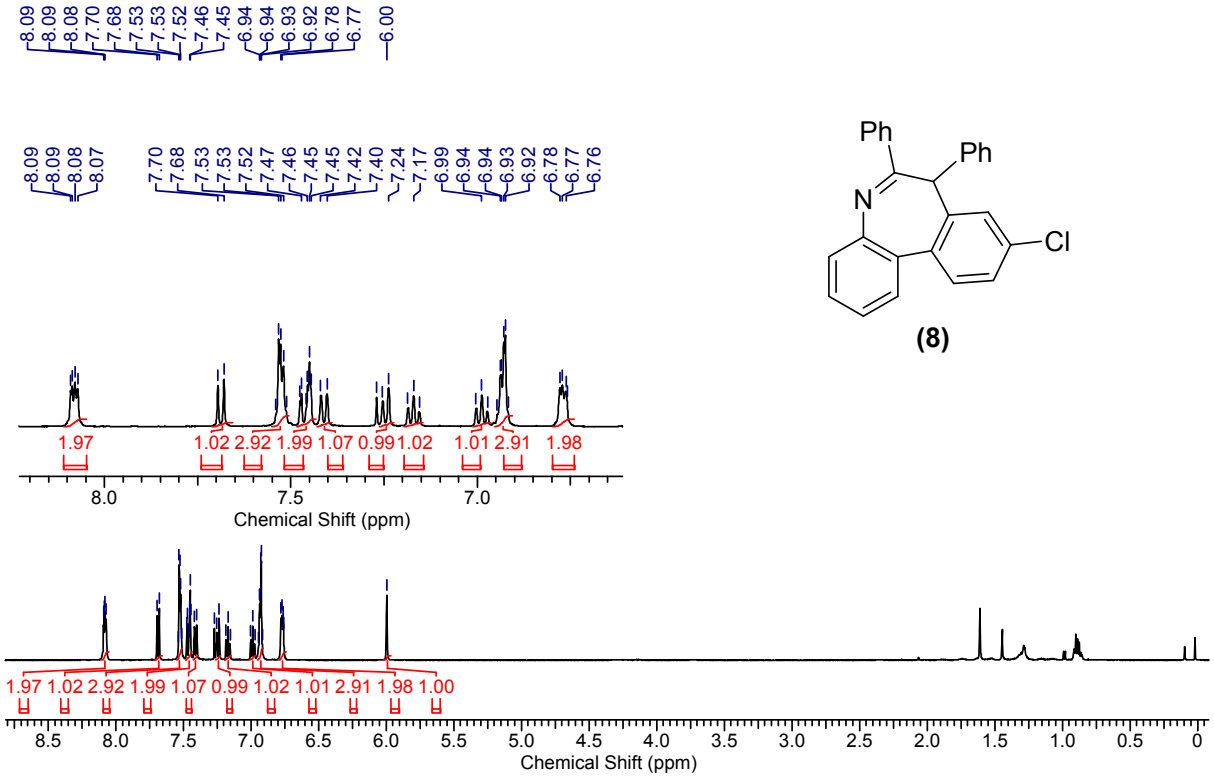
^{13}C NMR of **6b**



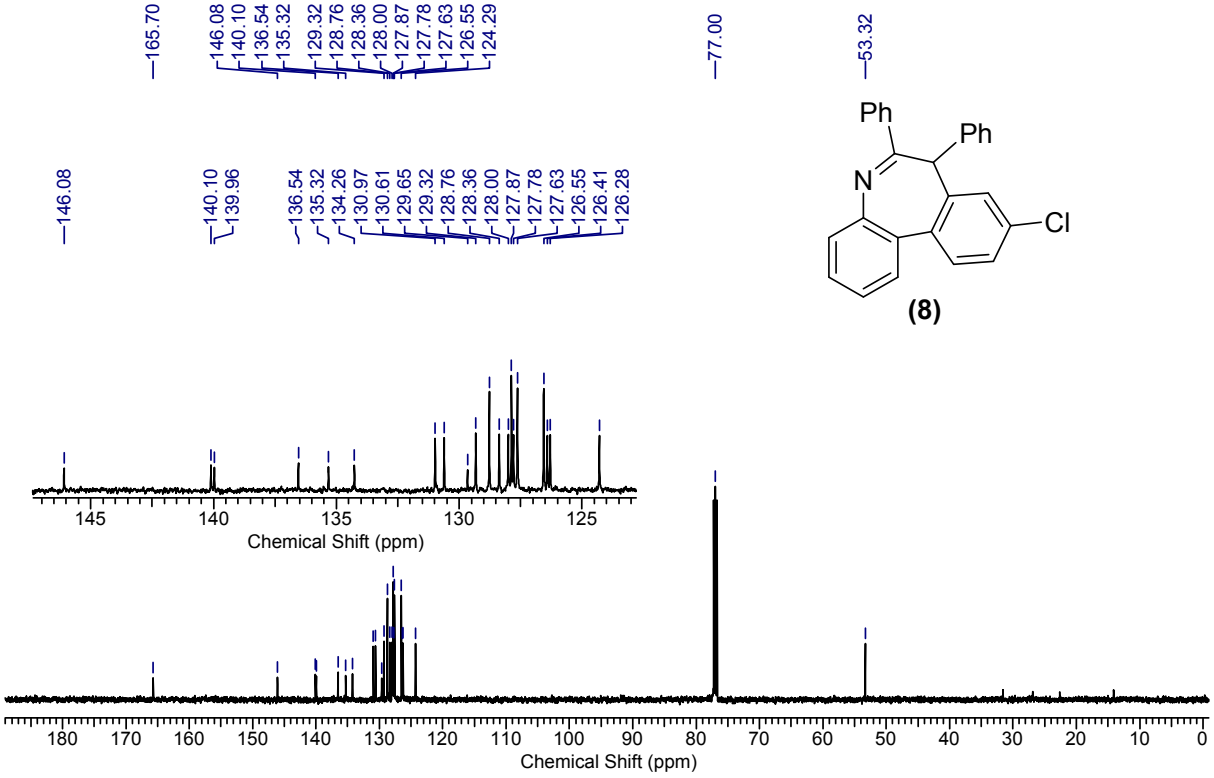
^{1}H NMR of **7a**



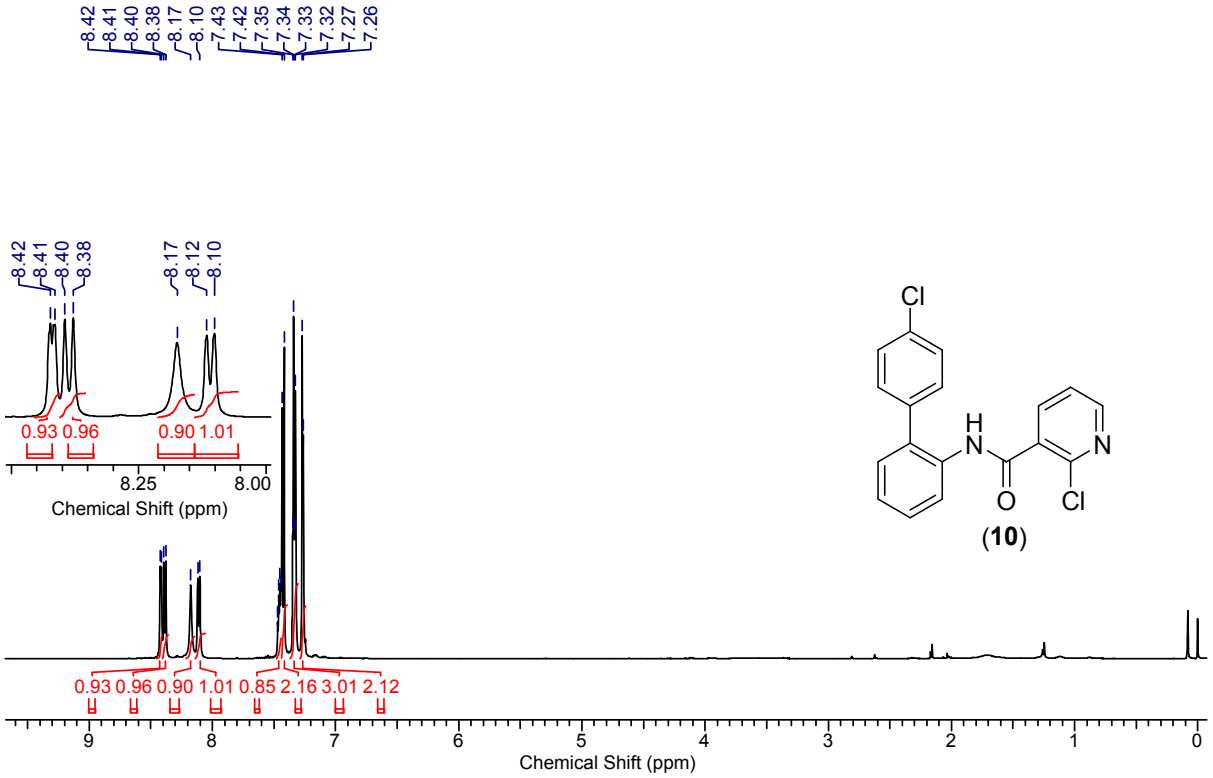
^{13}C NMR of **7a**



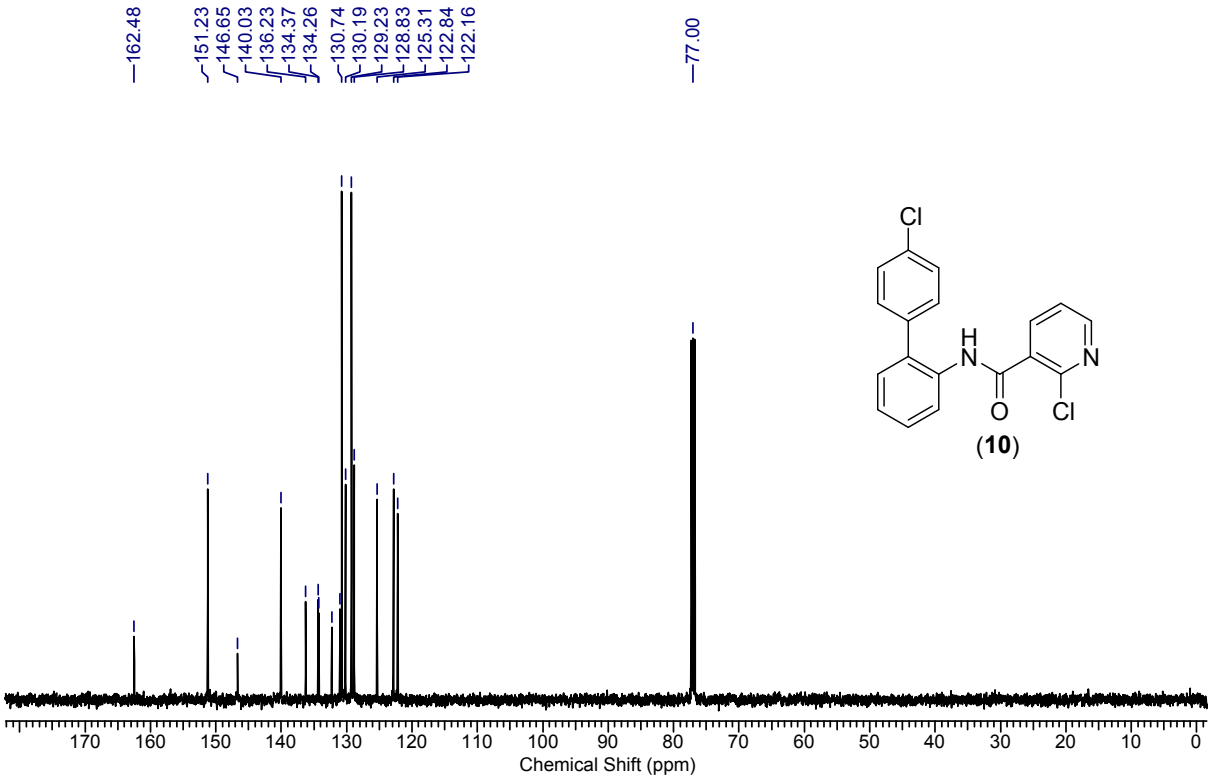
^{1}H NMR of **8**



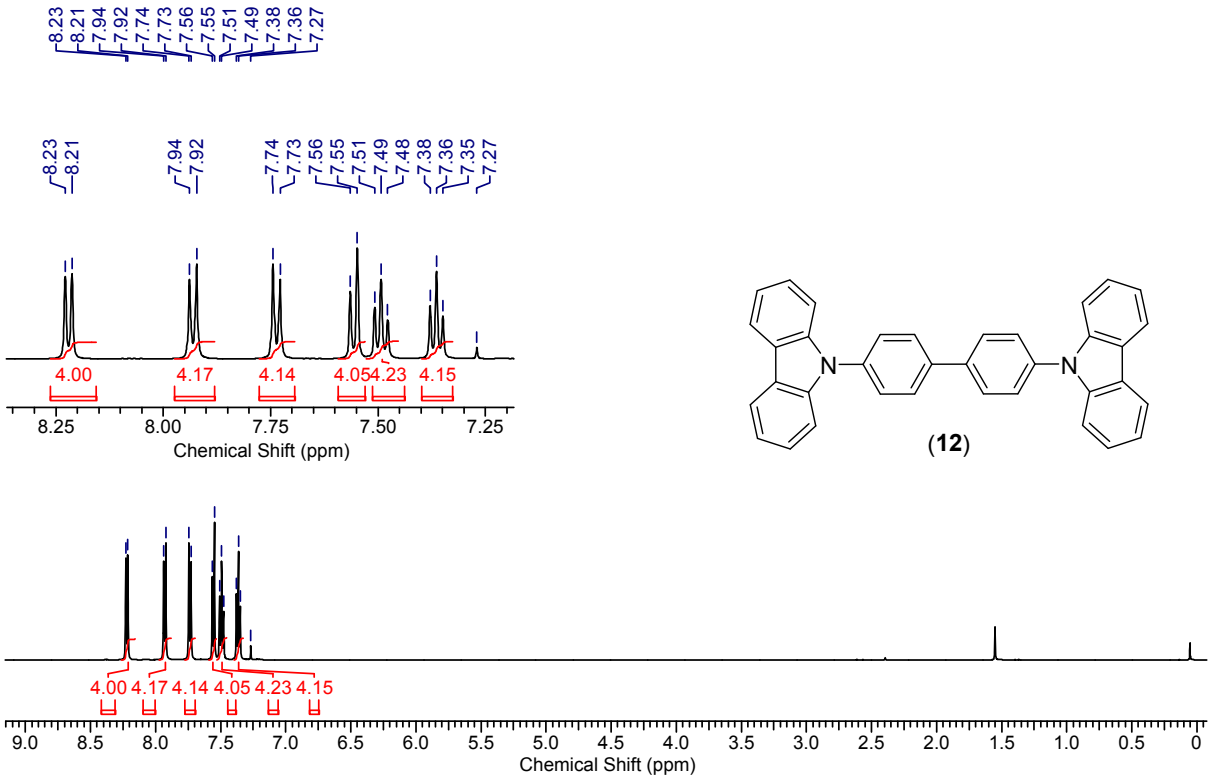
^{13}C NMR of **8**



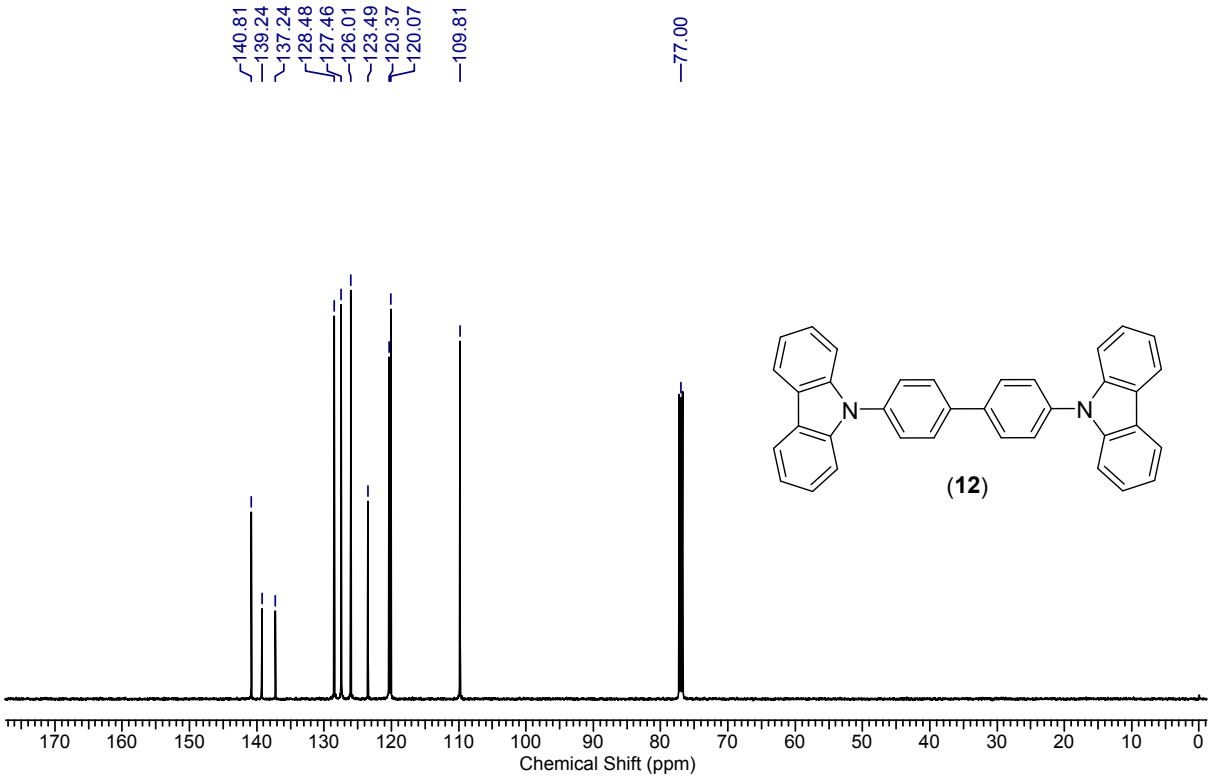
^{1}H NMR of **10**



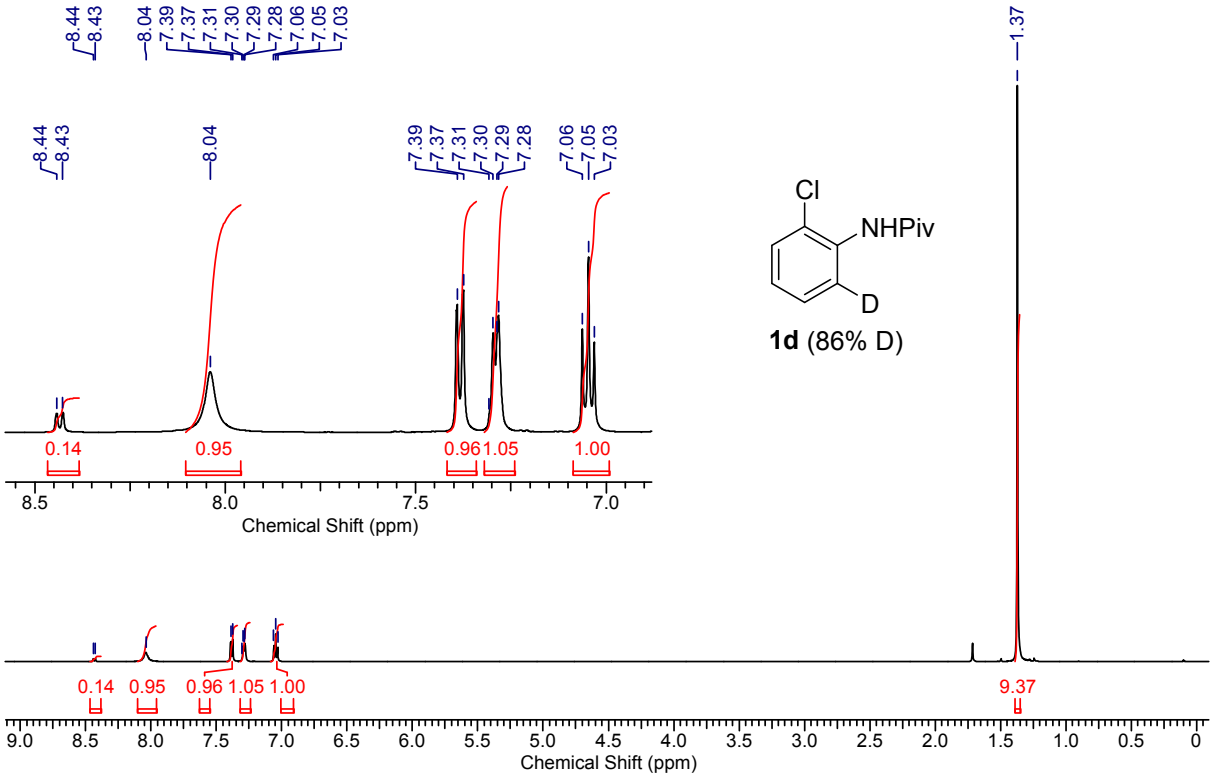
^{13}C NMR of **10**



^{1}H NMR of **12**



^{13}C NMR of **12**



1d (86% D)

^{1}H NMR of **1d**