Supporting Information

The Effects of Molecular Oxygen, Solvent and Light On Iridium-Photoredox/Nickel Dual-Catalyzed Cross-Coupling Reactions

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Materials and Methods

Commercially available reagents were used as obtained except otherwise stated. Cs_2CO_3 and $NiCl_2$•glyme were purchased from Strem Chemicals Inc. $[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$ (**Ir-A**) and $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (**Ir-B**) and $[Ir(dFmppy)_2(dtbbpy)]PF_6$ (**Ir-C**) were synthesized following literature procedures.[1] A new bottle of $Ni(COD)_2$ was used for each experiment and never reused once opened. 100 mL sure-sealed bottles of anhydrous DMF (99.8%), anhydrous DMSO (99.9%), anhydrous MeCN (99.8%), and anhydrous Me_3CCN (98%) were purchased from Sigma Aldrich and used as obtained. Organic solutions were concentrated under reduced pressure on a rotary evaporator using an isopropanol ice-bath for volatile compounds. Chromatographic purification of products was accomplished by silica gel chromatography. Reaction progress was monitored by reversed phase UPLC-MS with DAD and ELSD and a UPLC HSS T3, 2.1 x 30 mm, 1.8 µm column and a gradient of 2 to 98% acetonitrile in water with 0.1% formic acid over 2.0 min at 1 mL/min. Injection volume was 1 µL and the column temperature was 30 °C. Detection was based on electrospray ionization (ESI) in positive and negative polarity, diode-array UV detector from 210 to 400 nm, and evaporative light scattering detector. Thin layer chromatography (TLC) was performed on silica gel 60 F_{254} plates. Visualization of the developed chromatogram was performed with both compact UV-lamp (254/365 nm) and potassium permanganate stain. Compact fluorescent lamp bulbs (helical, 26 W, 1750 lm) were used. Two blue flexible LED strip kits (24 W, 1200 lm, 300 total LEDs, 16.4 ft) were ordered from Solid Apollo (SKU: SA-Blue-KIT1). 34 W blue-LEDs were made from the two flexible blue LED strip kits using an 8 mm Snap & Lite LED Strip Joiner. All reactions were performed

[1] M. S. Lowry, J. I. Goldsmith, J. D. Slinker, R. Rohl, R. A. Pascal, Jr. G. G. Malliaras, S. Bernhard, *Chem. Mater.* **2005**, *17*, 5712.

using borosilicate glass vials of appropriate sizes. ^{1}H- and ^{13}C{1H} NMR spectra were recorded on 400 MHz and 500 MHz for spectrometers and are internally referenced to residual protio solvent signals (note: $CDCl_3$ referenced at 7.26 and 77.0 ppm respectively, and $CO(CD_3)_2$ referenced at 2.05 and 29.9 ppm respectively). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad), integration, and coupling constant (Hz). Data for ^{13}C{1H} NMR are reported in terms of chemical shift and no special nomenclature is used for equivalent carbons. The HRMS were obtained using a hybrid quadrupole time-of-flight mass spectrometer in ESI^{+} mode.

Degassing of non-volatile reaction mixture and solvents: Sparging

A vial containing the reaction mixture or solvent was sealed with a plastic screw cap containing a teflon-lined silicone septum. Inlet nitrogen or argon stream was introduced through a long needle that reached at least half the solution (Figure S1A). An outlet line equipped with a shorter needle that stays above the solution was used to purge out both the inert gas and molecular oxgyen to an oil bubbler as shown in Figure S1A. To ensure complete removal of molecular oxygen from the solution, the degassing was performed with stirring and bubbling for at least 20 – 30 minutes as shown in Figure S1B. After that both the inlet and outlet needles were removed and more parafilm wrap and black tape were quickly applied to the screw cap. The reaction is fully degassed at this point and is ready for irradiation without exposing to air. Note: This degassing technique gave similar result as the freeze-pump-thaw technique when non-volatile reagents and solvents were used.

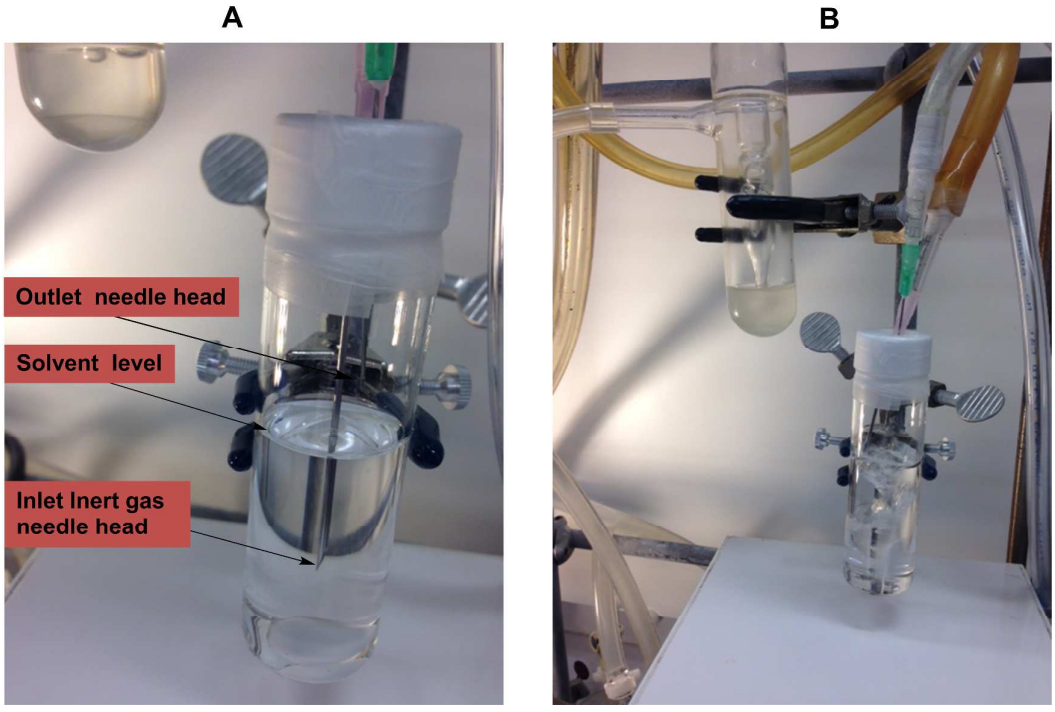


Figure S1. (A) Picture illustration of nitrogen stream degassing of 20 mL of DMF. (B) Picture of DMF undergoing degassing with stirring and nitrogen stream bubbling for 20 minutes.

Freeze-Pump-Thaw procedure of volatile and non-volatile reaction mixture and solvents[2]

1) Place the reaction mixture in an appropriately sized vial equipped with a magnetic stirrer and stopcock glass-joint. Make sure the stopcock is closed. Ensure the vial and all joints are sealed with parafilm and teflon tapes to prevent any air leakage into the vial as shown in Figure S2A.

2) Connect the vial to a Schlenk line (leave the attached hose on vacuum throughout this procedure) and freeze for **15 minutes** at - 78 ^{o}C with an acetone-dry ice bath (-78 ^{o}C cooling is sufficient for DMF solution; liquid nitrogen cooling may be required for other solvents). Before freezing ensure the environment in the flask is free of oxygen to prevent condensation of liquid oxygen upon freezing.

3). When the reaction mixture is frozen, open the stopcock to vacuum and evacuate the atmosphere for **15 minutes** (Figure S2A).

4). Seal the flask by closing the stopcock.

5). Thaw the reaction mixture until it melts by removing the vial from the cooling bath for **15 minutes** (Figure S2B). Gas evolution from the solution may occur but do not to disturb the solution.

6). Reimmerse the vial in the cooling bath and refreeze the reaction mixture (Figure S2A).

7) Repeat steps (3) - (6) until the evolution of gas is no longer observed as the solution thaws. The solution should be put through a ***minimum of three cycles***.

8) Finally, release the vacuum pressure and fill the head space with nitrogen or argon gas and then close the stopcock. The reaction is fully degassed at this point and is ready for irradiation.

[2] M. S. Oderinde, R. D. J. Froese, M. G. Organ, *Angew. Chem. Int. Ed.* **2013**, *52*, 11334.

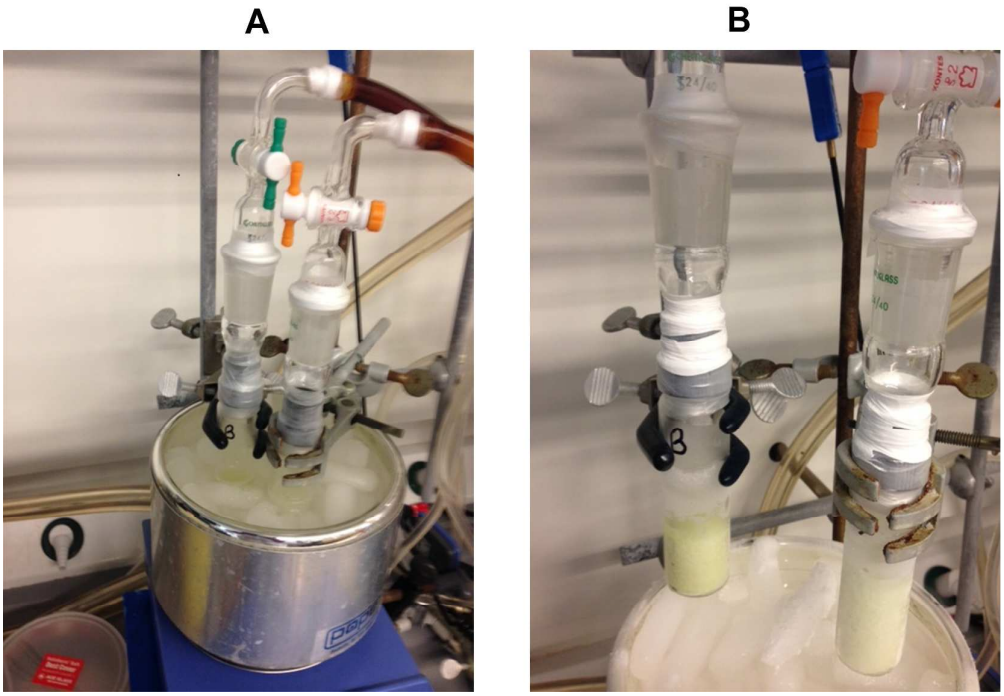


Figure S2. (A) Picture illustration of reaction mixture undergoing freezing and pumping process. (B) Picture illustration of frozen reaction mixture undergoing thawing process.

Headspace purge

As shown in Figure S3, the excess air on top of the reaction mixture can be removed by purging the headspace of the reaction mixture with nitrogen gas for ***only 10 seconds***. The vial is then capped, sealed with parafilm wrap and irradiated.

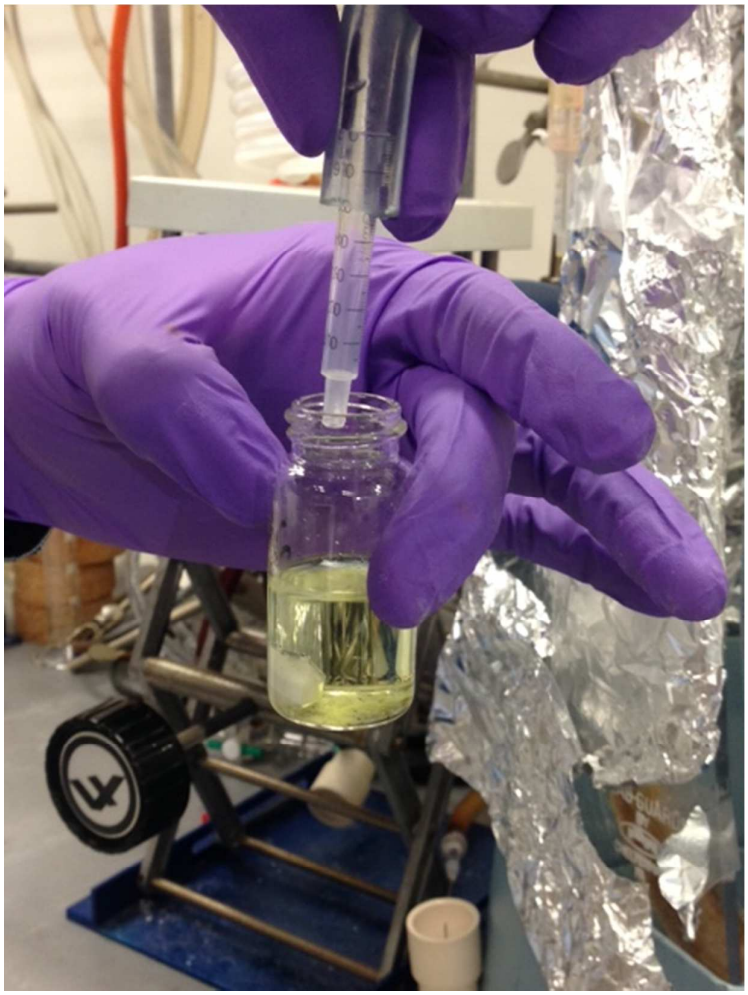


Figure S3. Picture illustration of 10 seconds headspace purge with nitrogen gas.

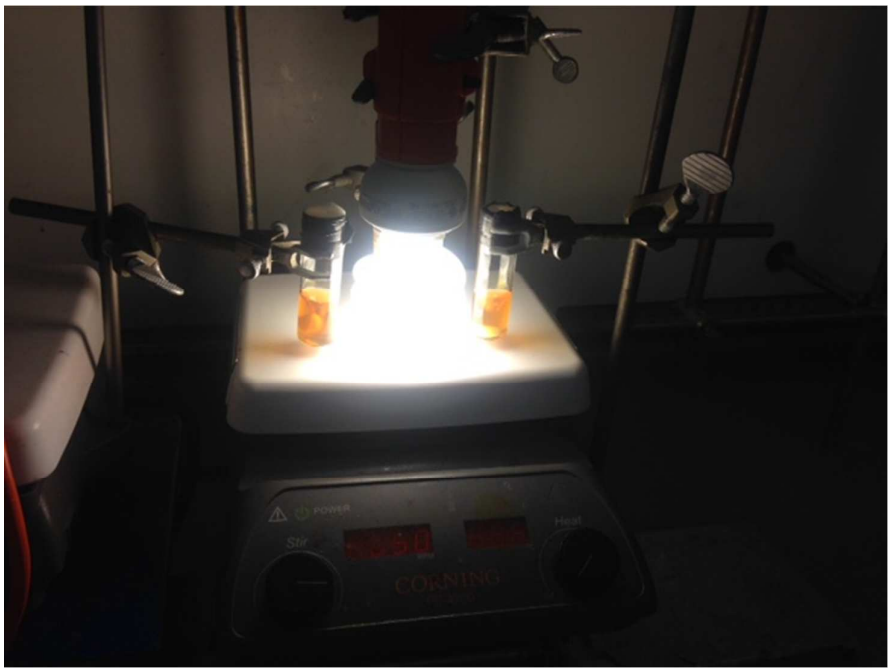


Figure S4. Picture showing two reactions that were prepared inside a nitrogen-filled glove-box and undergoing irradiation with one 26 W CF-lamp inside the fume-hood.

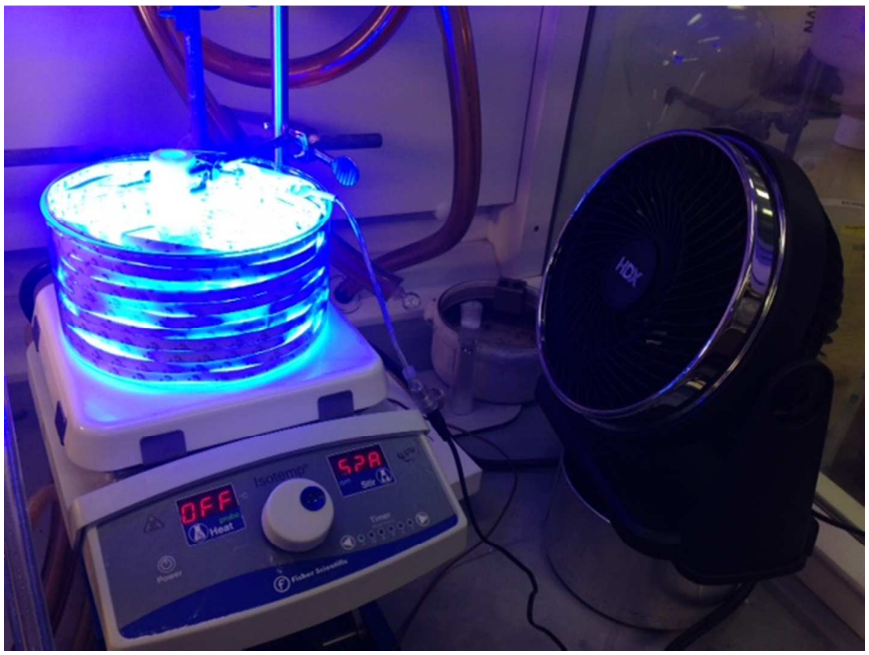
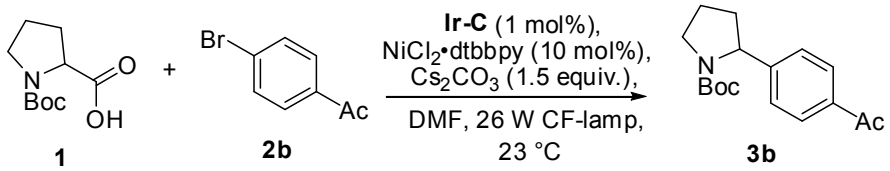


Figure S5. Picture illustration of reaction undergoing irradiation with 34 W blue LED strips and fan cooling.



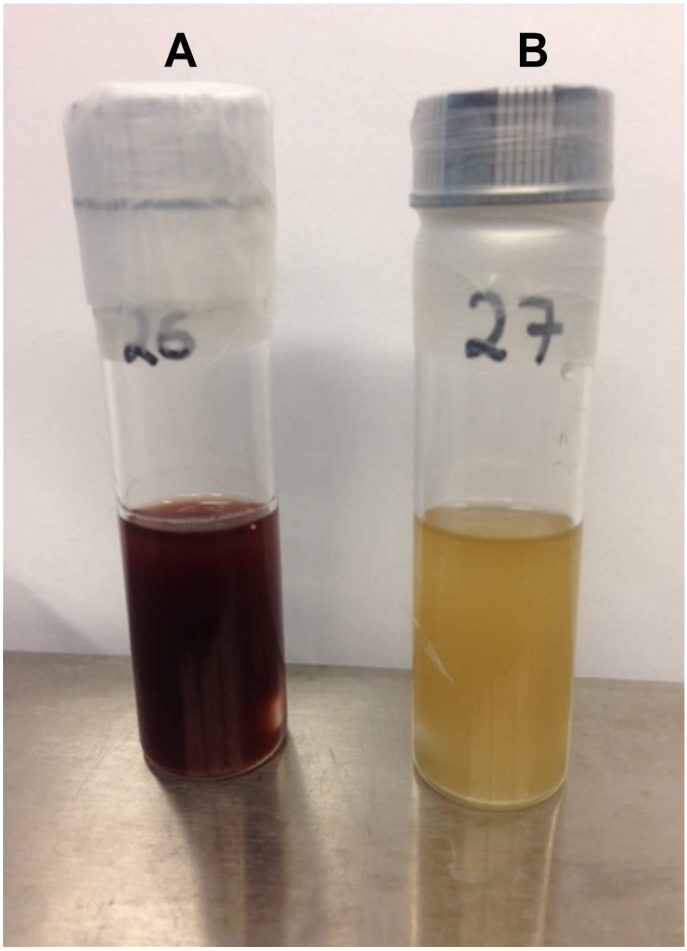
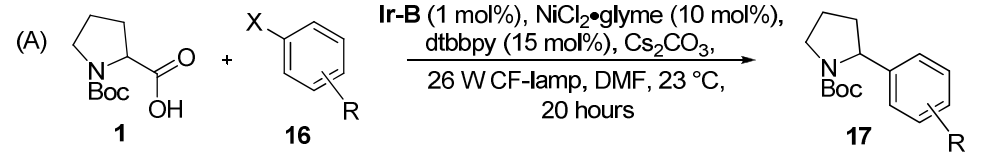
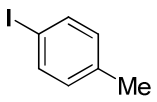
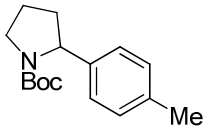
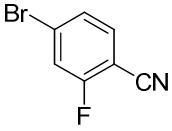
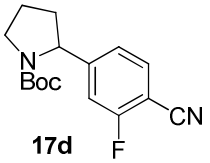
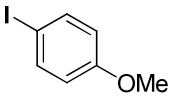
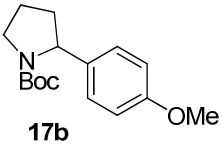
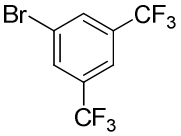
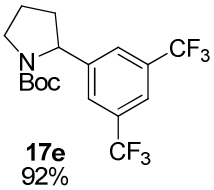
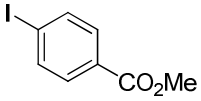
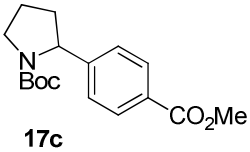
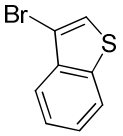
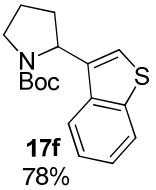
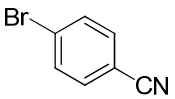
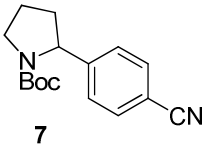
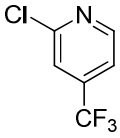
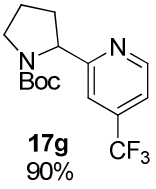
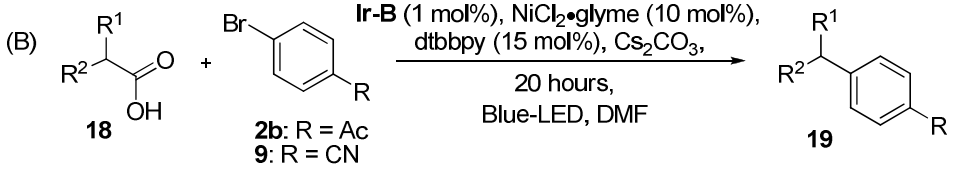


Figure S6. (A) Picture illustration of reaction colour (vial 26) after 20 hours; The reaction mixture was **degassed** by sparging with nitrogen for 20 minutes before irradiation with CF-lamp. (B) Picture illustration of reaction colour (vial 27) after 20 hours; The reaction mixture was only purged with nitrogen for 10 seconds before irradiation with CF-lamp.

Table S1. (A) Aryl halide scope studies with Boc-Pro-OH (**1**). (B) Carboxylic acid scope studies with aryl halides.[a,b]



Aryl halide	Product	Aryl halide	Product
 **2a**	 **3a** 85%	 **16d**	 **17d** 97%
 **16b**	 **17b** 75%	 **16e**	 **17e** 92%
 **16c**	 **17c** 84%	 **16f**	 **17f** 78%
 **9**	 **7** 96%	 **16g**	 **17g** 90%



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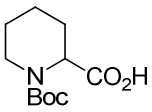
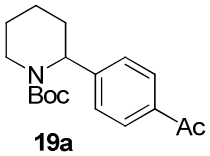
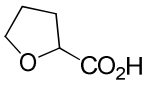
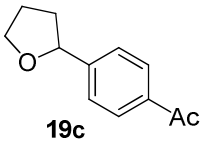
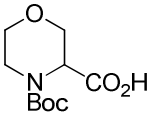
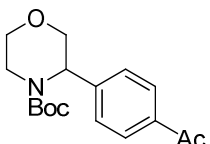
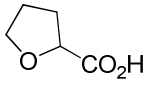
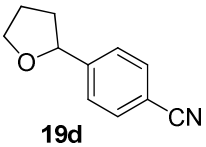
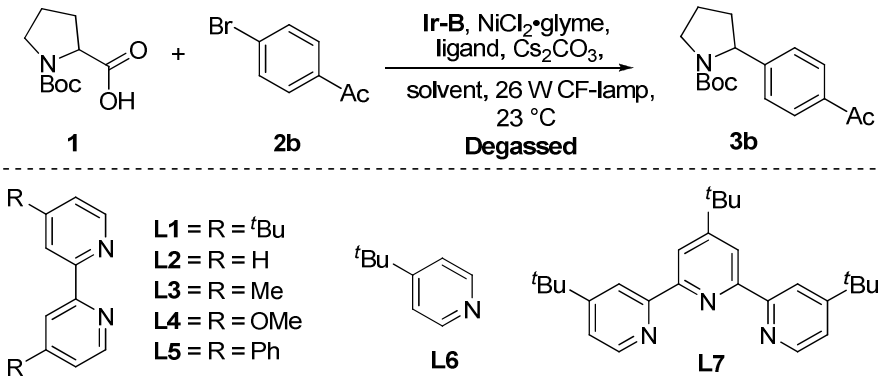
 **18a**	 **19a** 80%	 **18c**	 **19c** 97%
 **18b**	 **19b** 70%	 **18c**	 **19d** 90%

[a]Carboxylic acids: 0.60 mmol., Aryl halides: 0.40 mmol., DMF: 10 mL (0.04 M solution).
[b]The reaction mixtures were only purged with nitrogen for 10 seconds; See condition below.

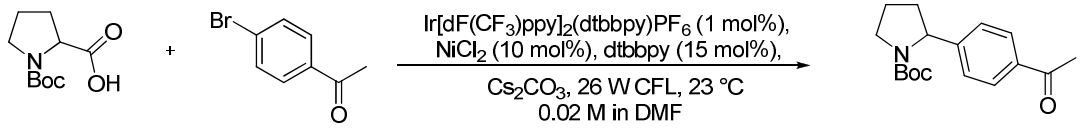
Table S2. Ligand and solvents effect on the Ir-photoredox/nickel dual-catalyzed decarboxylative cross-coupling reaction.[a]



Entry	Solvent	Ligand	Co-solvent	%Yield[b]
1	DMA	**L1**	**-**	**0**
2	NMP	**L1**	**-**	**0**
3	DMF	**L2 - L5**	**-**	**0**
4	DMF	**L6**[c]	**-**	**0**
5	DMF	**L7**	**-**	**0**
6	DMF	**L1**	**MeCN**[d], [e]	**0**
7	DMF	**L1**	**PhCN**[d], [e]	**0**
8	DMF	**L1**	**Me_3CCN**[d], [e]	**90**
9	DMF	**L1**	**Me_3CCN**[d],[e]	**60**
10	DMF	**L1**	**Me_3CCN**[f], [e]	**23**
11	DMF	**L1**	**Me_3CCN**[g] ,[e]	**>95**
12	MeCN	**L1**	**-**	**68**
13	DMF	**L1**	**MeCN**[h],[e]	**90**
14	Me_3CCN	**L1**	**-**	**0**
15	MeCN	**-**	**-**	**0**

[a] Unless otherwise indicated, reactions were carried out with Boc-Pro-OH 1 (0.6 mmol), aryl halide 2 (0.4 mmol), Ir-B (1 mol%), $NiCl_2$•glyme (10 mol%), ligand (L#) (15 mol%), DMF (10 mL, 0.04 M), Cs_2CO_3 (0.6 mmol), irradiated with a 26 W CF-lamp at room temperature for 20 hours; the reaction mixture was degassed by sparging with a nitrogen stream for 20 minutes before irradiation. [b] % Conversion; each reaction was repeated multiple times and monitored by UPLC-MS. [c] 30 mol% was used. [d] Used as a co-solvent in 4:1 (DMF:co-solvent) ratio. [e] 10 mL, 0.04 M reaction [f] Used as a co-solvent in 1:1 (DMF:Me_3CCN) ratio. [g] The reaction was not degassed and only the headspace was purged with N_2 for 10 seconds. [h] Used as a co-solvent in 1:4 (DMF:MeCN) ratio.

Reaction rate studies with and without degassing



A 40 mL vial was charged with $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (**Ir-B**) (4.00 µmol, 0.01 equiv, 4.5 mg), $NiCl_2$•glyme (8.76 mg, 0.04 mmol), 4,4'-di-*tert*-butyl-2,2'-bipyridine (16.1 mg, 0.06 mmol), 4-bromoacetophenone (79.6 mg, 0.40 mmol), Cs_2CO_3 (195.0 mg, 0.60 mmol), Boc-Pro-OH (**1**) (129 mg, 0.60 mmol), magnetic stirring bar and DMF (20 mL). The headspace of the reaction mixture was purged with nitrogen for 10 secs, sealed with a plastic screw cap containing a teflon-lined silicone septum then irradiated with one 26 W CF-lamp clamped at approximately 2 cm away from the reaction vial. An aliquot was removed from the reaction mixture every 30 minutes and analyzed by UPLC-MS and ^{1}H-NMR spectroscopy. The plot of % conversion against time (hours) is shown in Figure S7 as undegassed. When all the O_2 in the reaction mixture is removed by freeze-pump-thaw or inert gas degassing as shown in Figure S1 and S2, no reaction occurred over 72 hours.

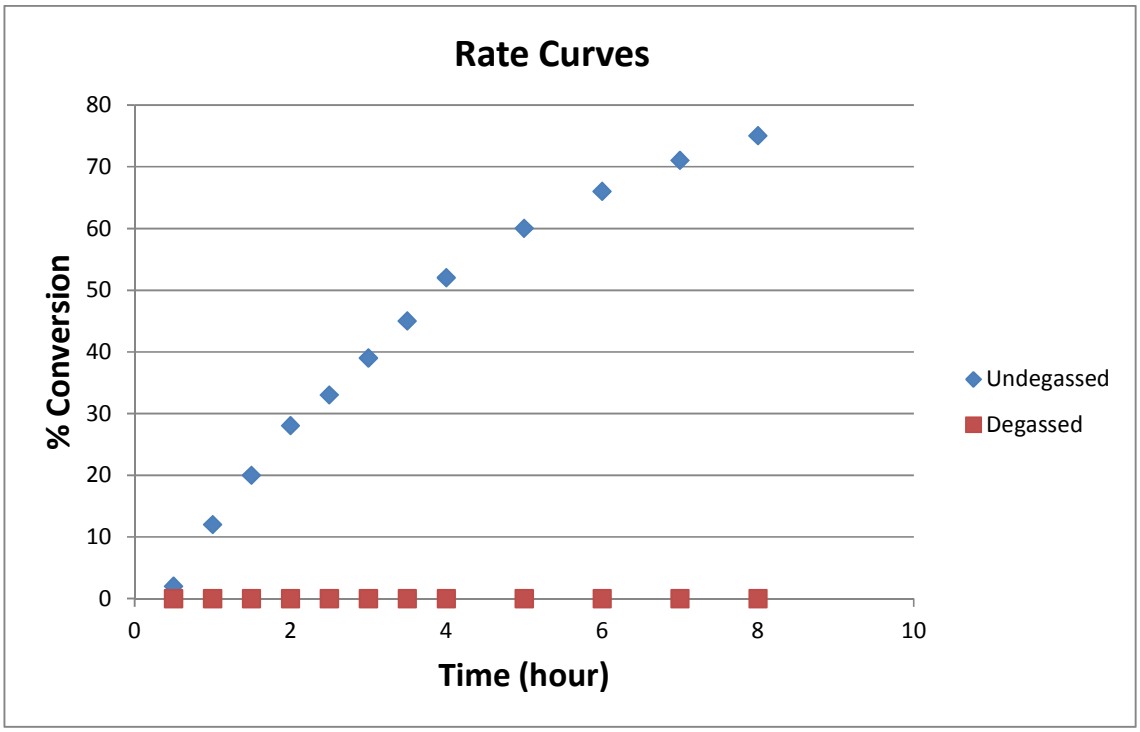
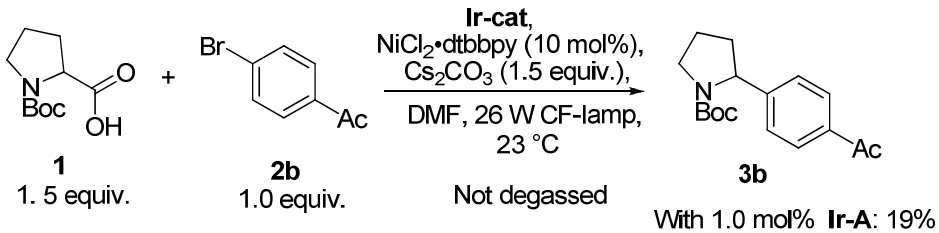


Figure S7. Rate curve of reaction performed with and without degassing.

Reactions with Ir-A, Ir-C and Ir-D photoredox catalysts



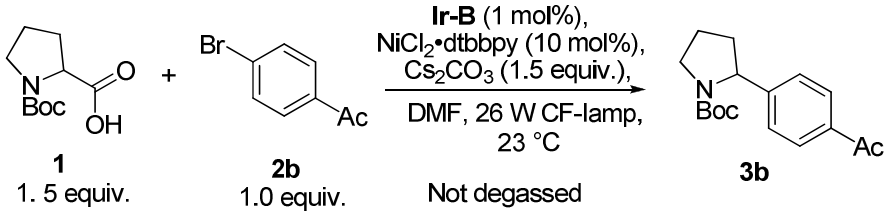
With 1.0 mol% **Ir-A**: 19%

With 1.0 mol% **Ir-C**: 82%

With 1.0 mol% **Ir-D**: 0%

These two separate reactions were carried out according to procedure C above.

Control Experiments: MacMillan-Doyle's reaction

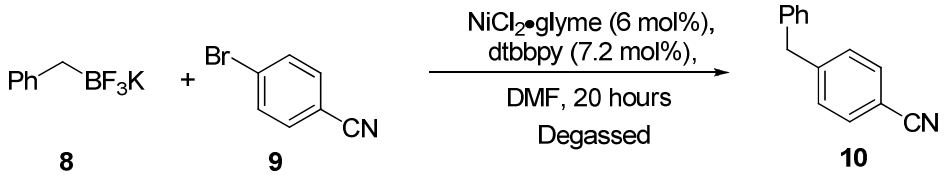


Condition	Product
no light	0%
no **Ir-B**	0%
no $NiCl_2$.glyme	0%
no dtbbpy	0%

These reactions were carried out according to procedure C with each ommision in the table.

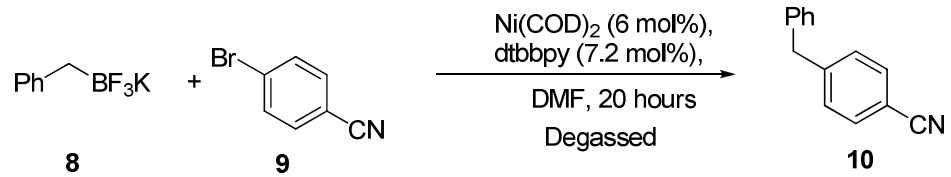
Control Experiments: Molander's reaction

(A)



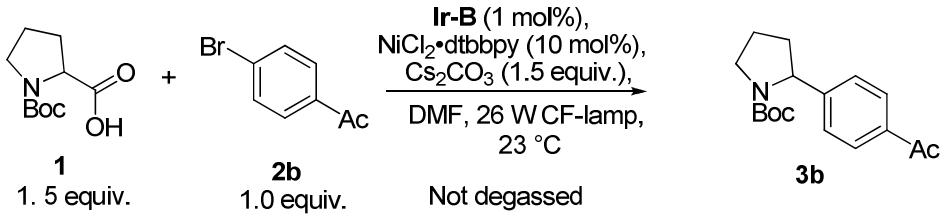
8 (1. 5 equiv.) **9** (1.0 equiv.) **10** 0%

(B)



8 (1. 5 equiv.) **9** (1.0 equiv.) **10** 0%

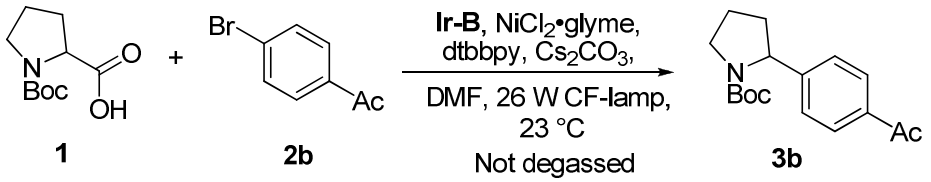
Effect of excess O_2



1 1. 5 equiv. **2b** 1.0 equiv. Not degassed **3b**

Without headspace purge: 80%

Effect of KO_2



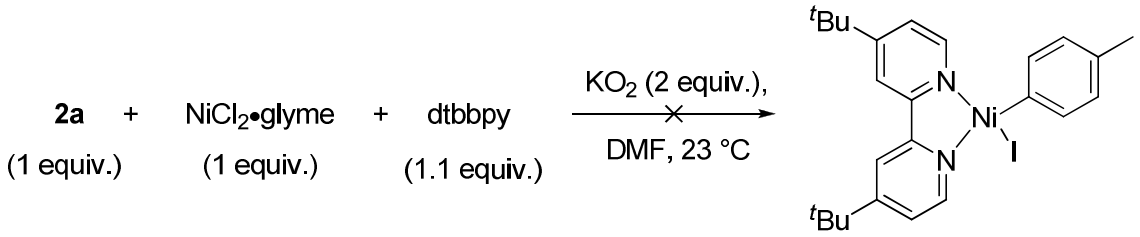
1 **2b** **3b**

With 1.0 equiv. of KO_2: 55%

With 0.5 equiv. of KO_2: 75%

With 0.1 equiv. of KO_2: 95%

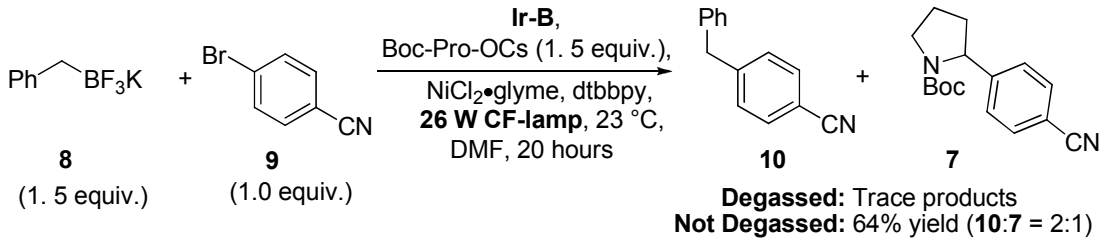
Oxidative additive studies with KO_2



Scheme S1. Reaction of $NiCl_2$•dtbbpy, **2a** and KO_2 to detect oxidative addition.

In this reaction, only both the $NiCl_2$•dtbbpy and **2a** were observed after 24 hours. The addition of 1 equiv. of either $AgBF_4$ or AgOTf as halides scavenger did not influence the reaction. Likewise, the irradiation of the reaction mixture with either 26 W CF-lamps or 34 W blue LEDs did not promote oxidative addition. Our inability to detect any oxidative addition product together with the known reduction potentials for $O_2^{\bullet-}$ ($E_{½}^{red}$ [$O_2/O_2^{\bullet-}$] = –0.865 V *vs.* SCE in DMF) and $Ni^{(II)}$ ($E_{½}^{red}$ [$Ni^{(II)}/Ni^{(0)}$] = –1.20 V *vs.* SCE in DMF) suggests that $O_2^{\bullet-}$ itself is not reducing $NiCl_2$•dtbbpy by a SET process.

Procedures for scheme 4 in the manuscript

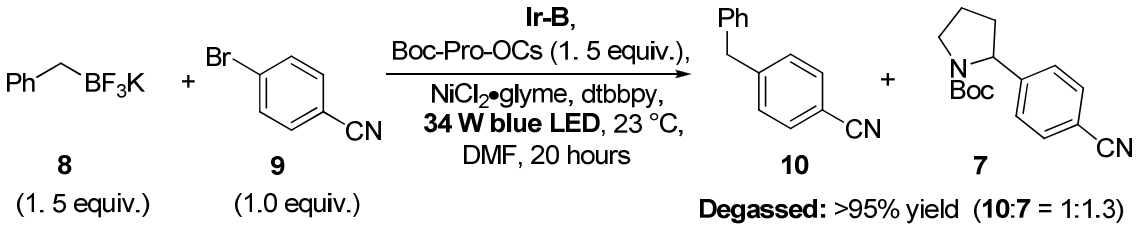


Degassed: A 10 mL vial was charged with $NiCl_2$•glyme (6.60 mg, 0.03 mmol, 0.06 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (9.7 mg, 0.04 mmol, 0.072 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (**Ir-B**) (11.0 mg, 10.00 μmol, 0.02 equiv), 4-bromobenzonitrile (**9**) (91.0 mg, 0.50 mmol, 1.0 equiv.), $BnBF_3K$ (**8**) (149.0 mg, 0.75 mmol, 1.5 equiv), Boc-Pro-OH (161.0 mg, 0.75 mmol, 1.5 equiv.), Cs_2CO_3 (244 mg, 0.75 mmol, 1.5 equiv.), a magnetic stirrer, and DMF (5 mL) . The vial was sealed, wrapped with parafilm and sparged with nitrogen for 20 minutes according to Figure S1. The vial was again wrapped twice with parafilm and white tapes to prevent any air-leak into the reaction during irradiation. The reaction mixture was then irradiated for 24 hours with a 26 W CF-lamp clamped at approximately 2 cm away from the reaction vial. UPLC-MS before work up and ^1H NMR analysis of the crude reaction after work up both showed trace products.

Not degassed: A 10 mL vial was charged with $NiCl_2$•glyme (6.60 mg, 0.03 mmol, 0.06 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (9.7 mg, 0.04 mmol, 0.072 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (**Ir-B**) (11.10 mg, 10.00 μmol, 0.02 equiv.), 4-bromobenzonitrile (**9**) (91.0 mg, 0.50 mmol, 1.0 equiv.), $BnBF_3K$ (**8**) (149.0 mg, 0.75 mmol, 1.5 equiv.), Boc-Pro-OH (161.0 mg, 0.75 mmol, 1.5 equiv.), Cs_2CO_3 (244 mg, 0.75 mmol, 1.5 equiv.), a magnetic stirrer, and DMF (10 mL) . The headspace of the reaction mixture was purged with nitrogen for 10 seconds according to Figure S3.

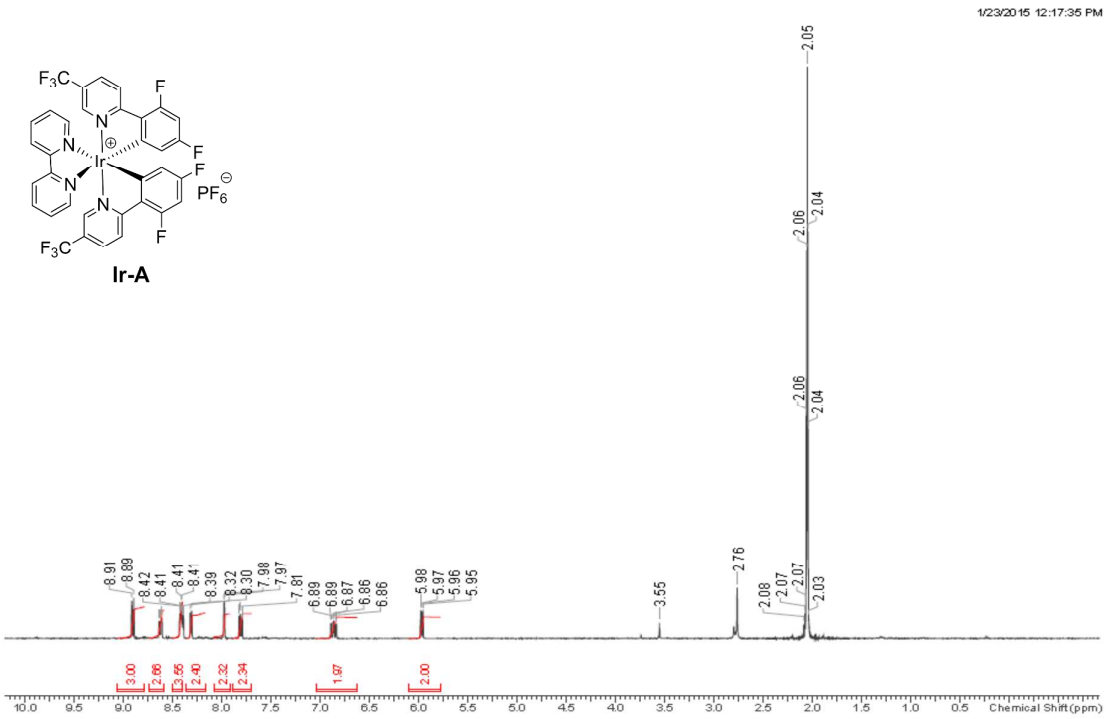
The vial was sealed, and wrapped with parafilm. The reaction mixture was then irradiated for 24 hours with a 26 W CF-lamp clamped at approximately 2 cm away from the reaction vial. UPLC-MS analysis before work up and ^{1}H-NMR analysis of the crude reaction after work up both showed 64% conversion to **10:7** (2:1 ratio).

Procedures for Scheme 5 in the manuscript

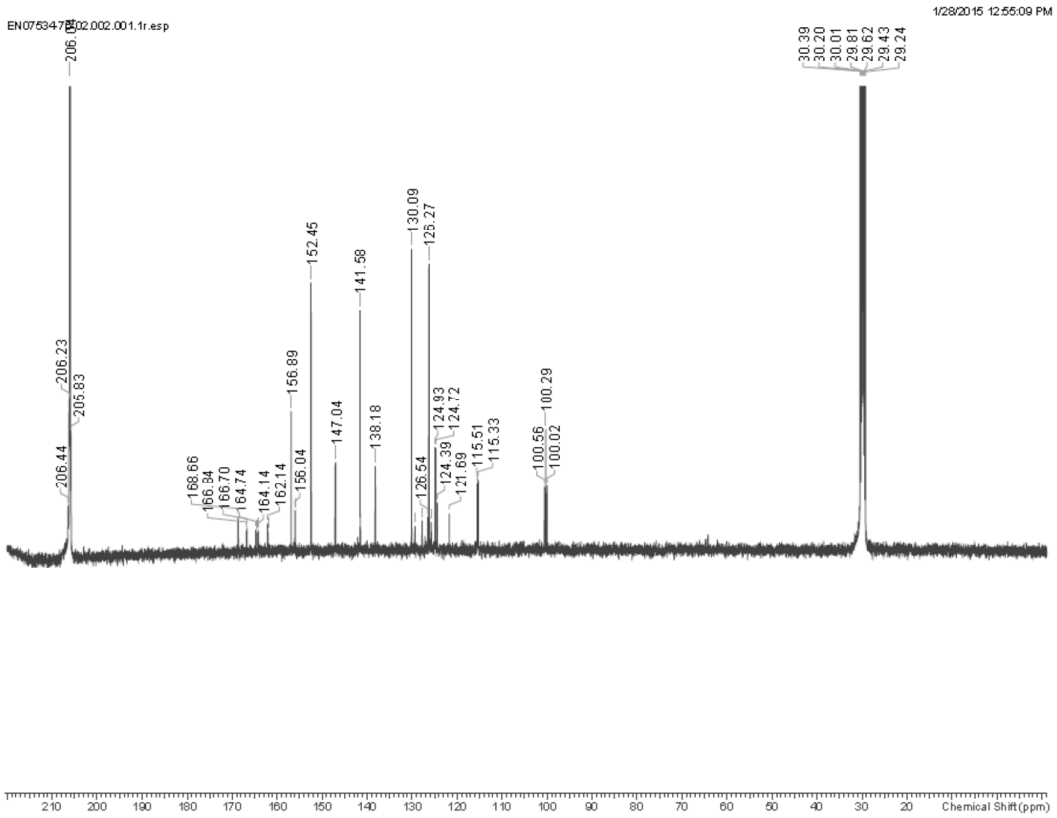


A 10 mL vial was charged with $NiCl_2$•glyme (6.60 mg, 0.03 mmol, 0.06 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (9.7 mg, 0.04 mmol, 0.072 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (**Ir-B**) (11.0 mg, 10.00 μmol, 0.02 equiv), 4-bromobenzonitrile (**9**) (91.0 mg, 0.50 mmol, 1.0 equiv.), $BnBF_3K$ (**8**) (149.0 mg, 0.75 mmol, 1.5 equiv), Boc-Pro-OH (161.0 mg, 0.75 mmol, 1.5 equiv.), Cs_2CO_3 (244 mg, 0.75 mmol, 1.5 equiv.), a magnetic stirrer, and DMF (10 mL) . The vial was sealed, wrapped with parafilm and sparged with nitrogen for 20 minutes according to Figure S1. The vial was again wrapped twice with parafilm and white tapes to prevent any air-leak into the reaction during irradiation. The reaction mixture was then irradiated for 24 hours with 34 W blue LEDs as illustrated in Figure S5. UPLC-MS analysis before work up and ^{1}H NMR analysis of the crude reaction after work up both showed showed > 95% conversion to **10:7** (1:1.3 ratio).

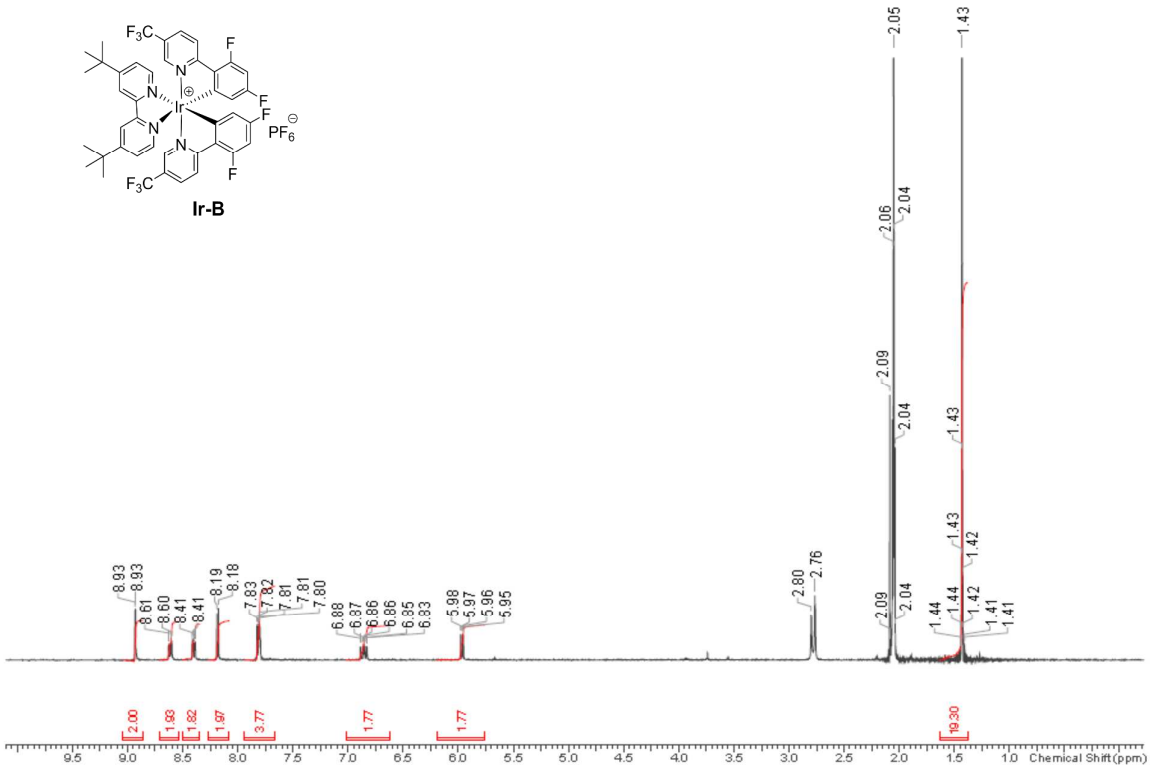
^{1}H-NMR Spectrum of [Ir(dF(CF$_3$)ppy)$_2$(bpy)]PF$_6$ (Ir-A)



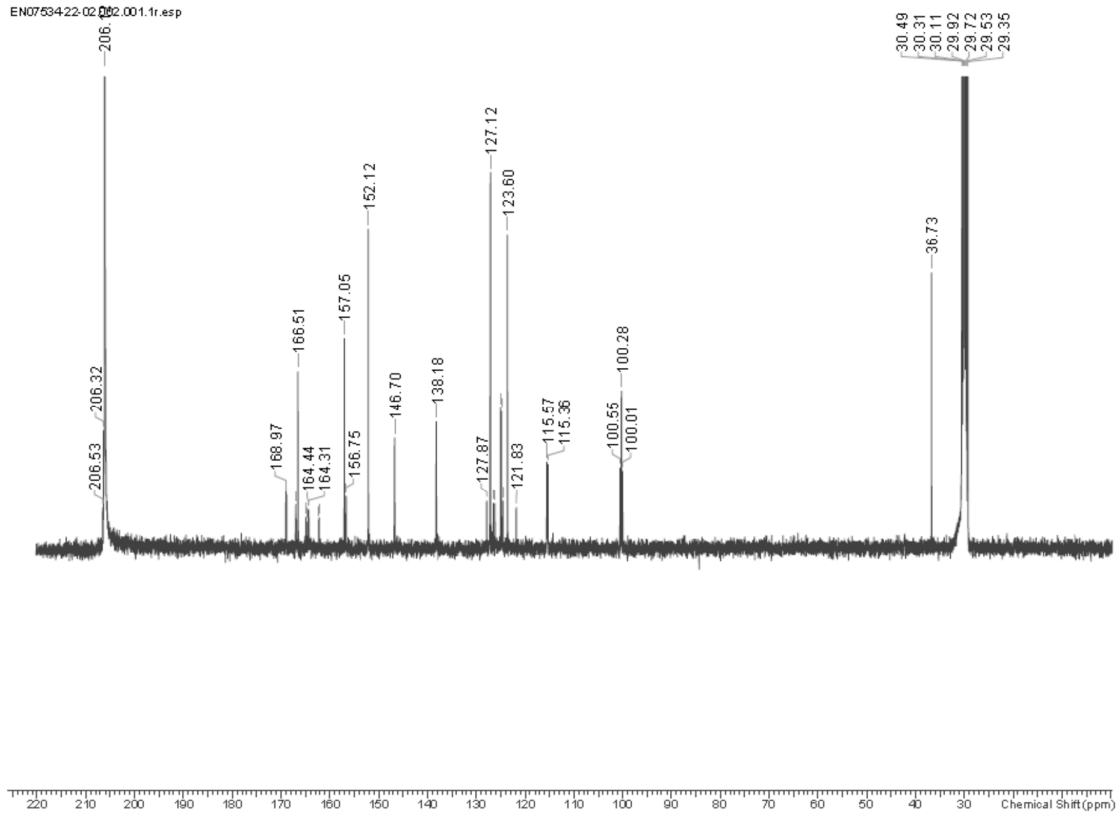
^{13}C-NMR Spectrum of [Ir(dF(CF$_3$)ppy)$_2$(bpy)]PF$_6$ (Ir-A)



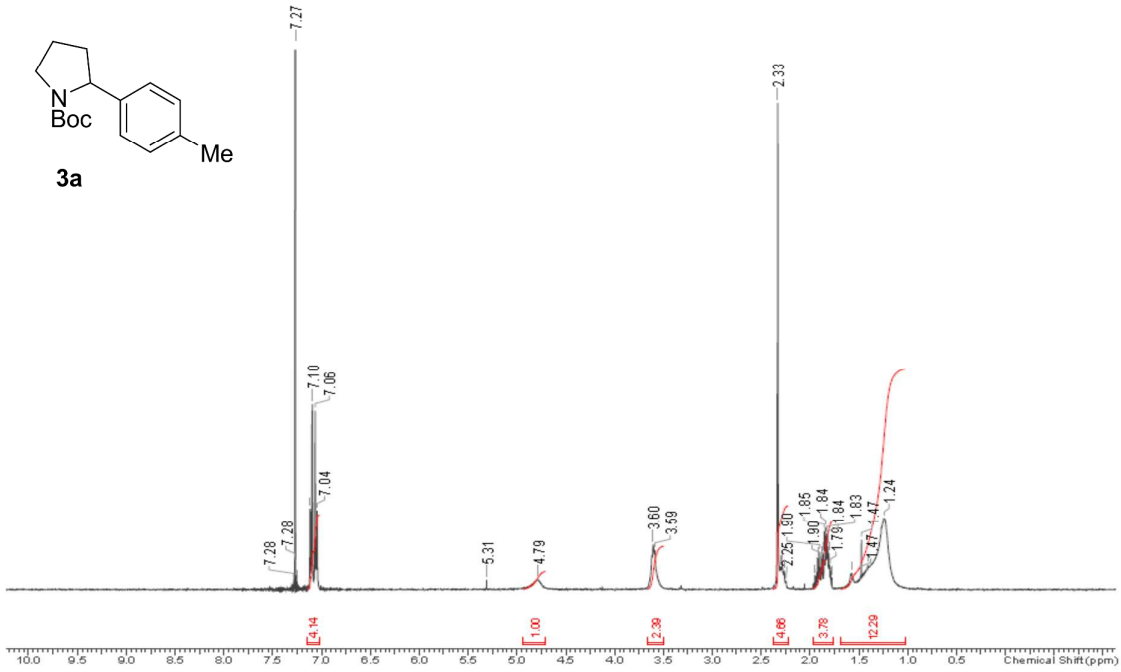
^{1}H-NMR Spectrum of [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (Ir-B)



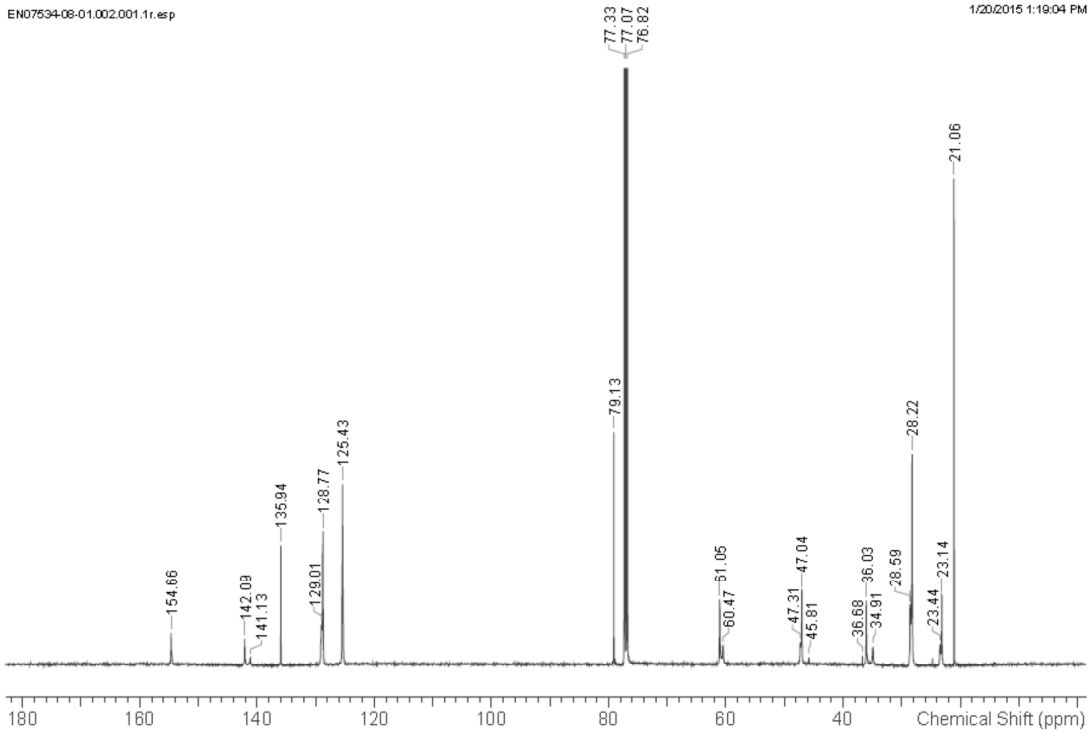
^{13}C-NMR Spectrum of [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (Ir-B)



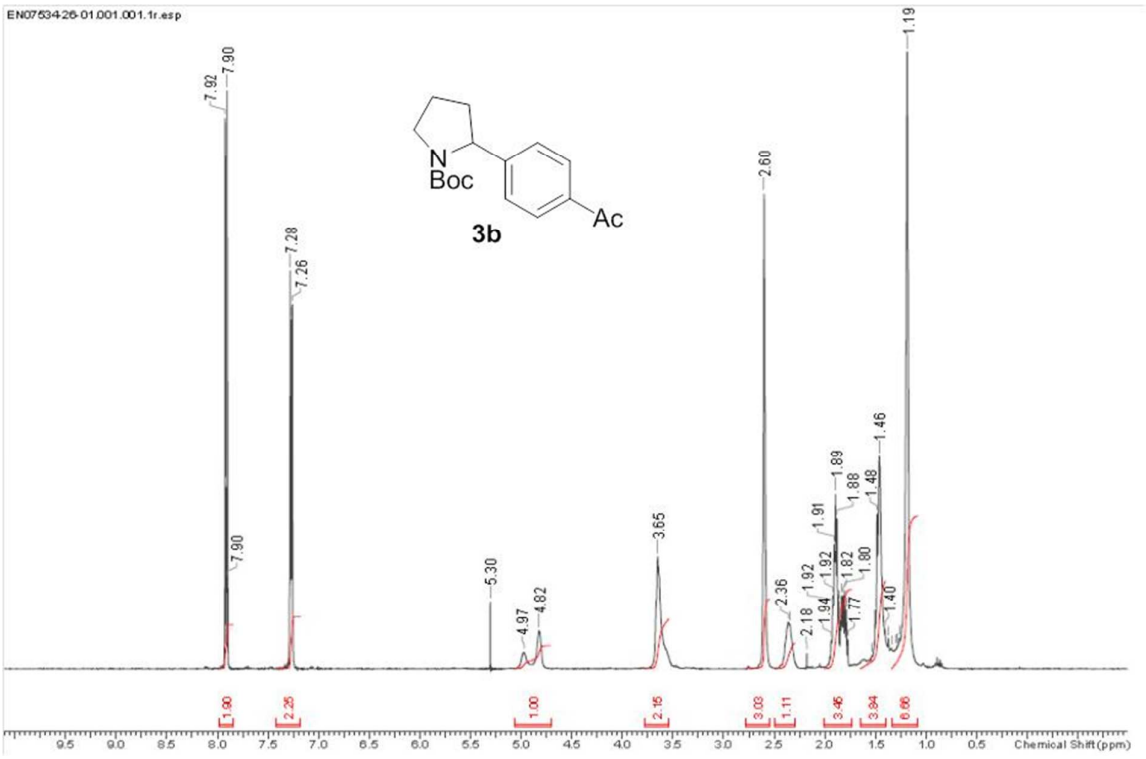
^{1}H-NMR Spectrum of *tert*-Butyl 2-(*p*-tolyl)pyrrolidine-1-carboxylate (3a)



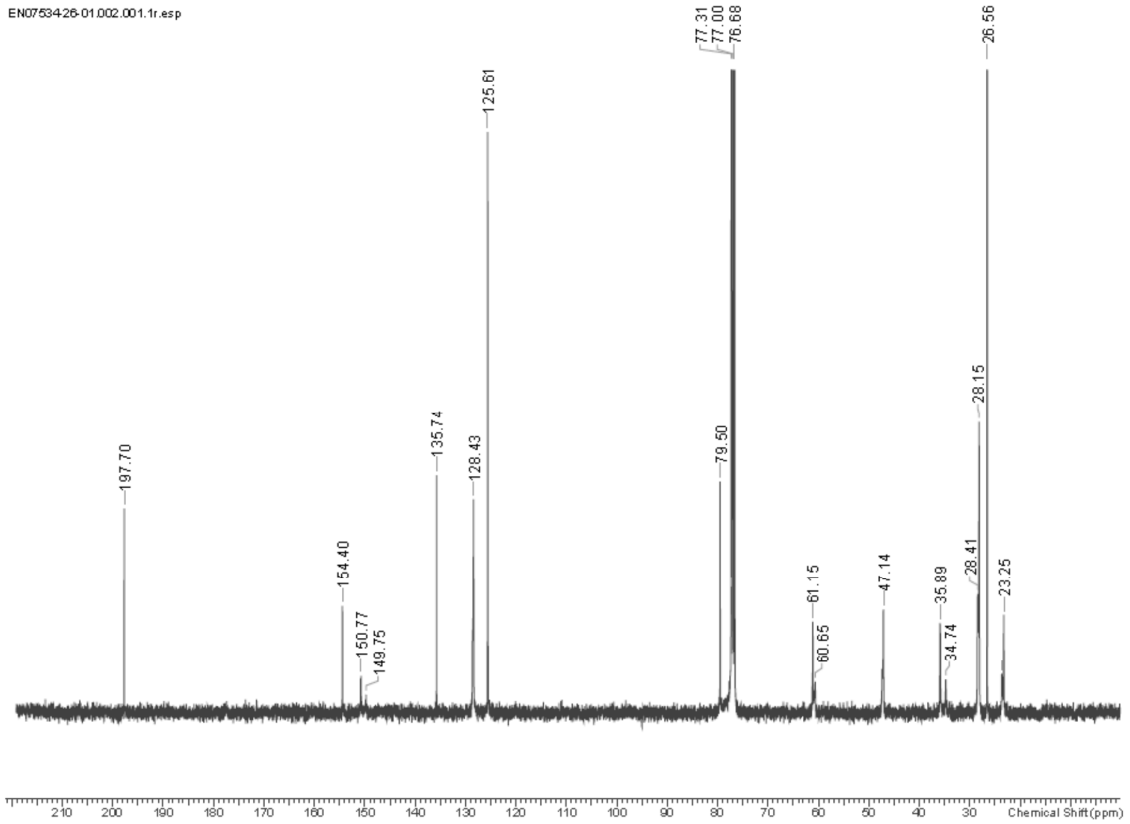
^{13}C-NMR Spectrum of *tert*-Butyl 2-(*p*-tolyl)pyrrolidine-1-carboxylate (3a)



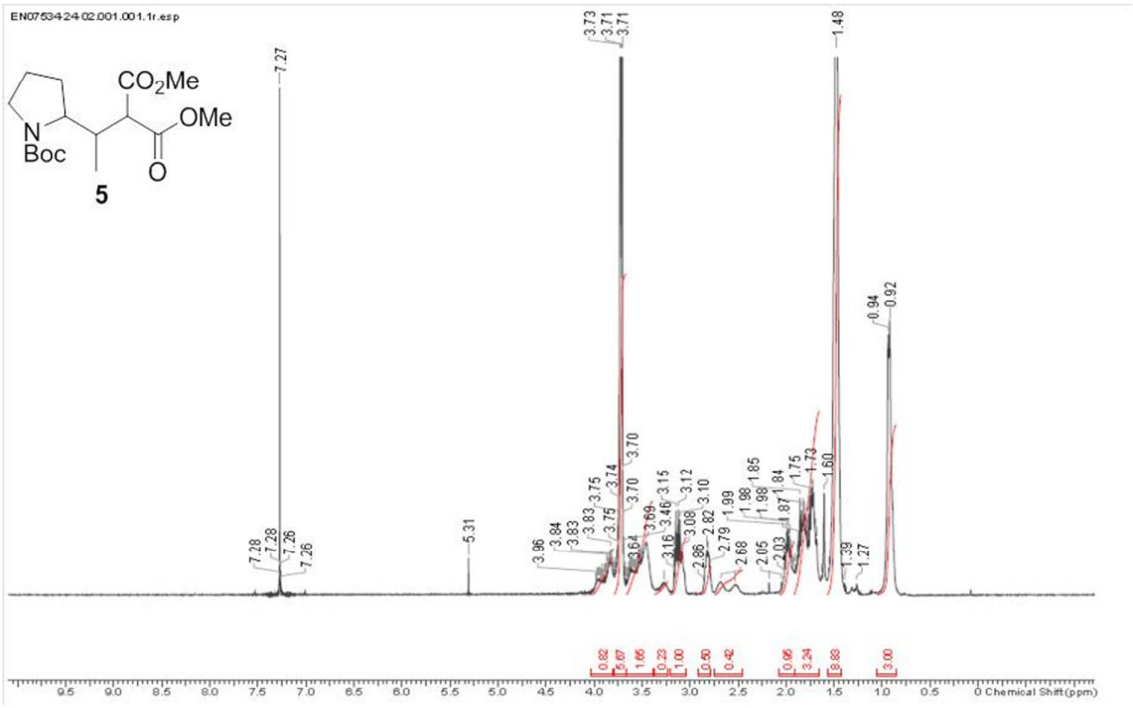
^{1}H-NMR Spectrum of *tert*-Butyl 2-(4-acetylphenyl)pyrrolidine-1-carboxylate (3b)



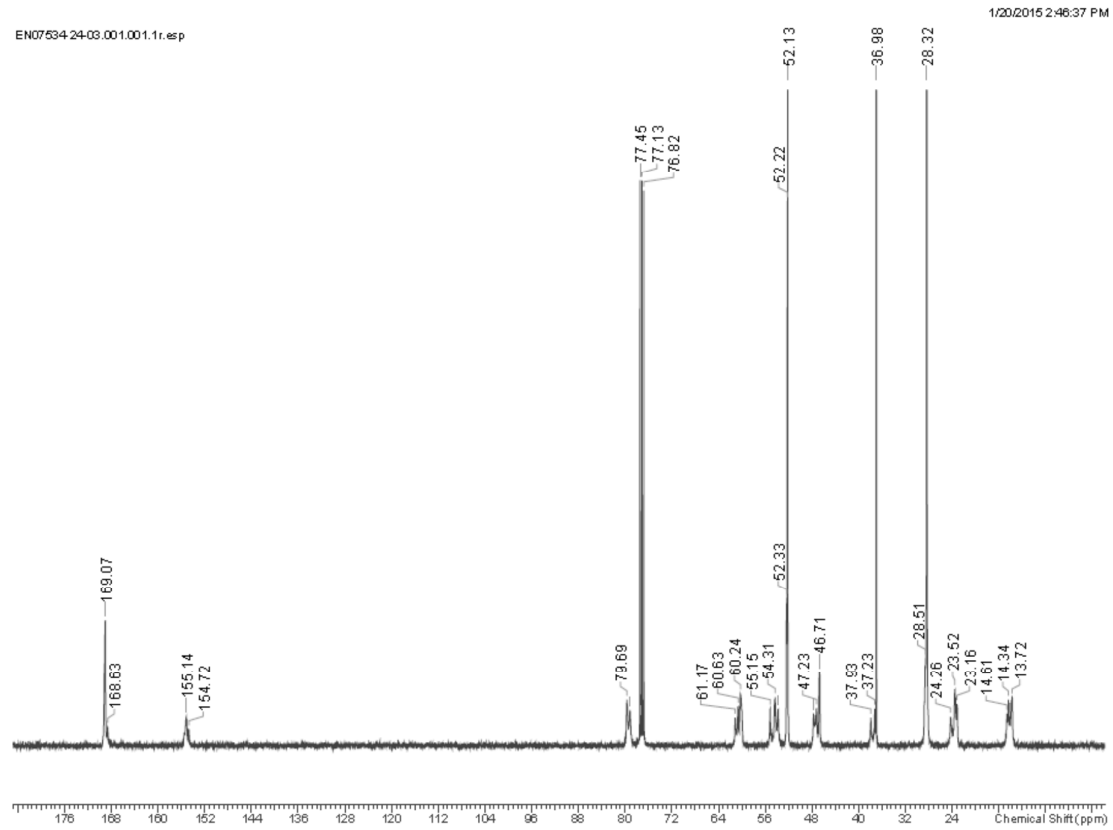
^{13}C-NMR Spectrum of *tert*-Butyl 2-(4-acetylphenyl)pyrrolidine-1-carboxylate (3b)



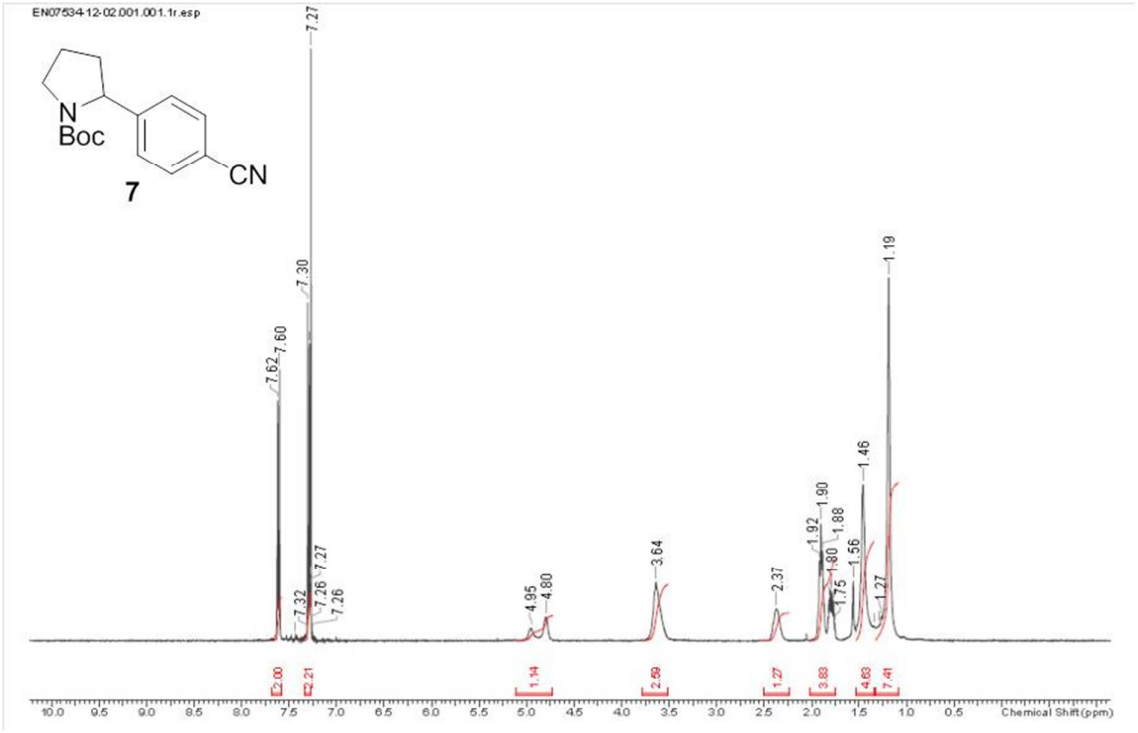
^{1}H-NMR Spectrum of Dimethyl 2-(1-(1-(*tert*-butoxycarbonyl)pyrrolidin-2-yl)ethyl)malonate (5)



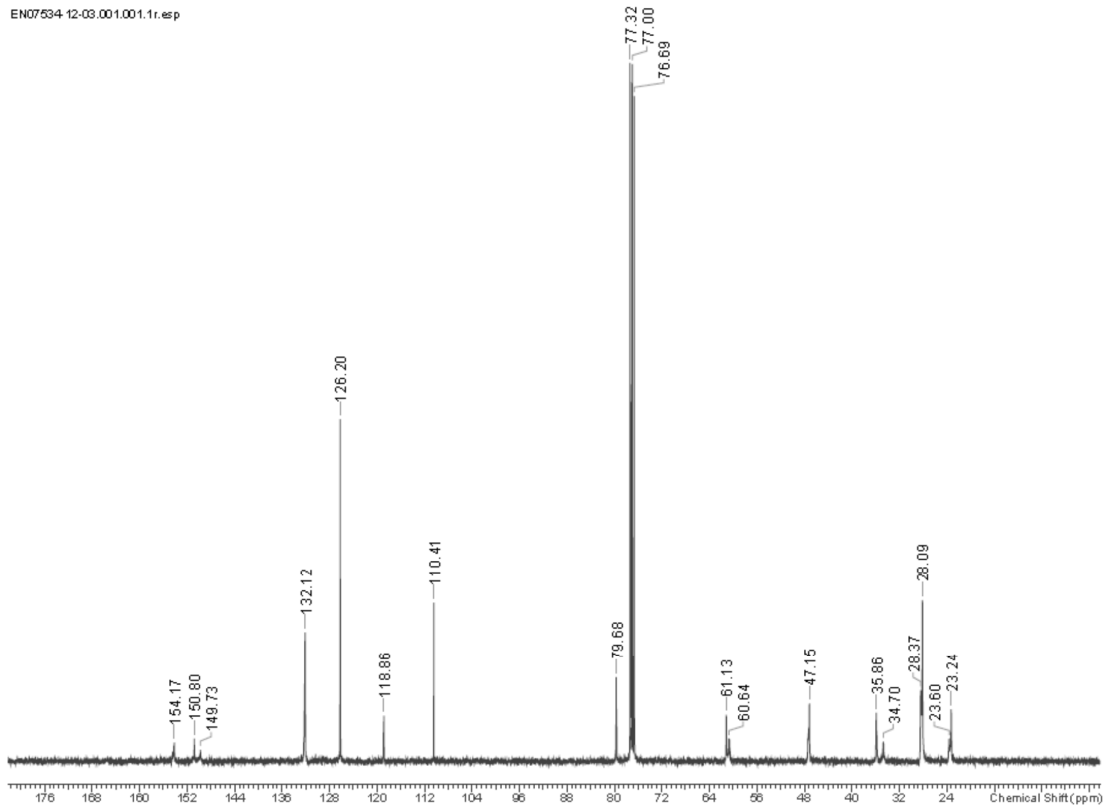
^{13}C-NMR Spectrum of Dimethyl 2-(1-(1-(*tert*-butoxycarbonyl)pyrrolidin-2-yl)ethyl)malonate (5)



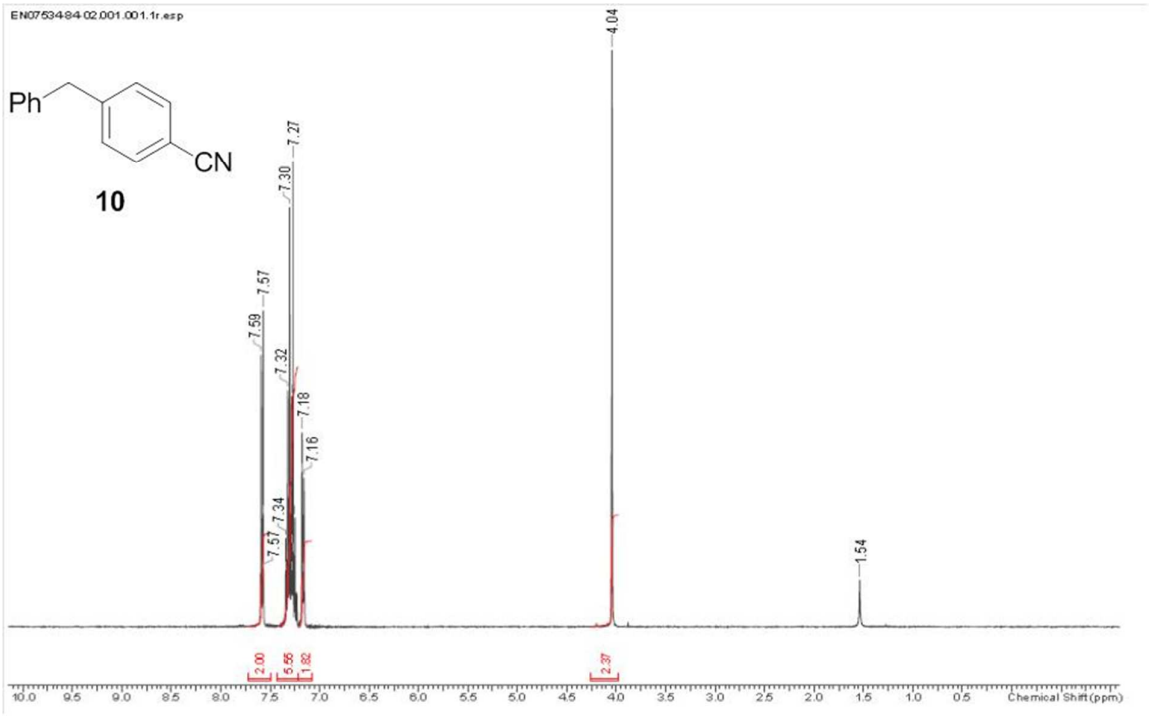
^{1}H-NMR Spectrum of *tert*-Butyl 2-(4-cyanophenyl)pyrrolidine-1-carboxylate (7)



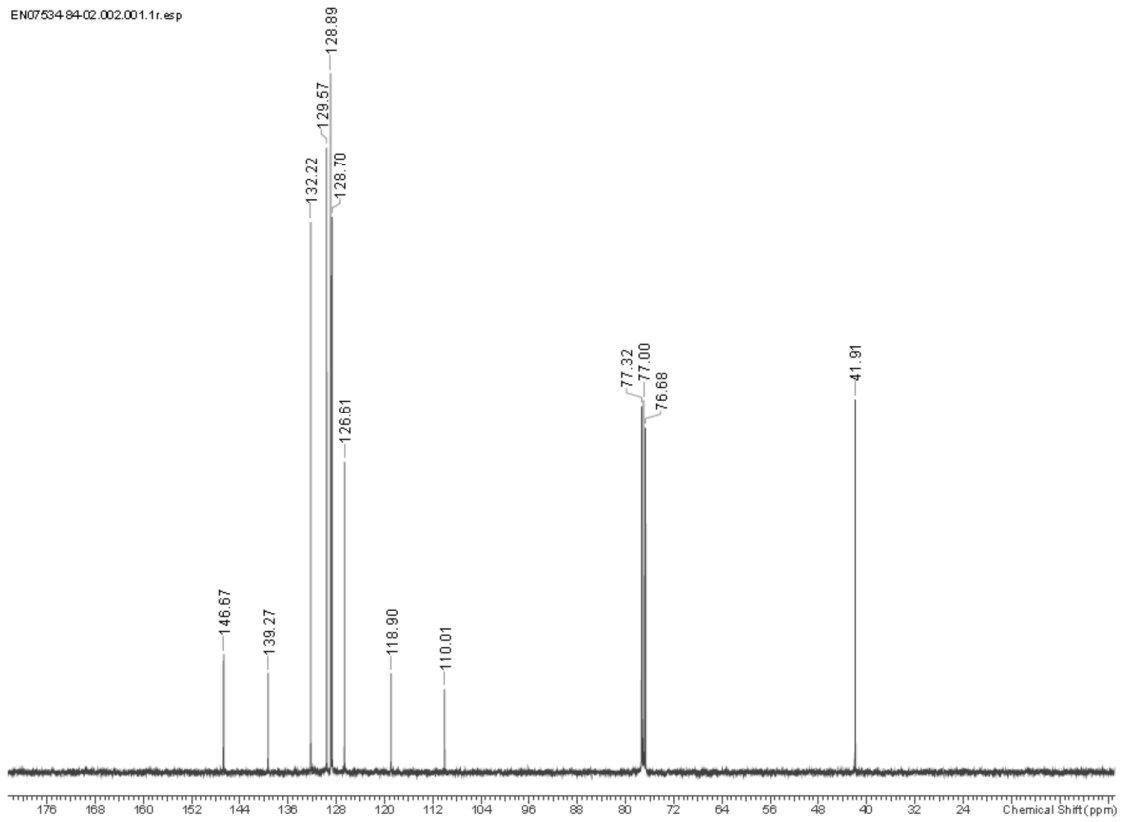
^{13}C-NMR Spectrum of *tert*-Butyl 2-(4-cyanophenyl)pyrrolidine-1-carboxylate (7)



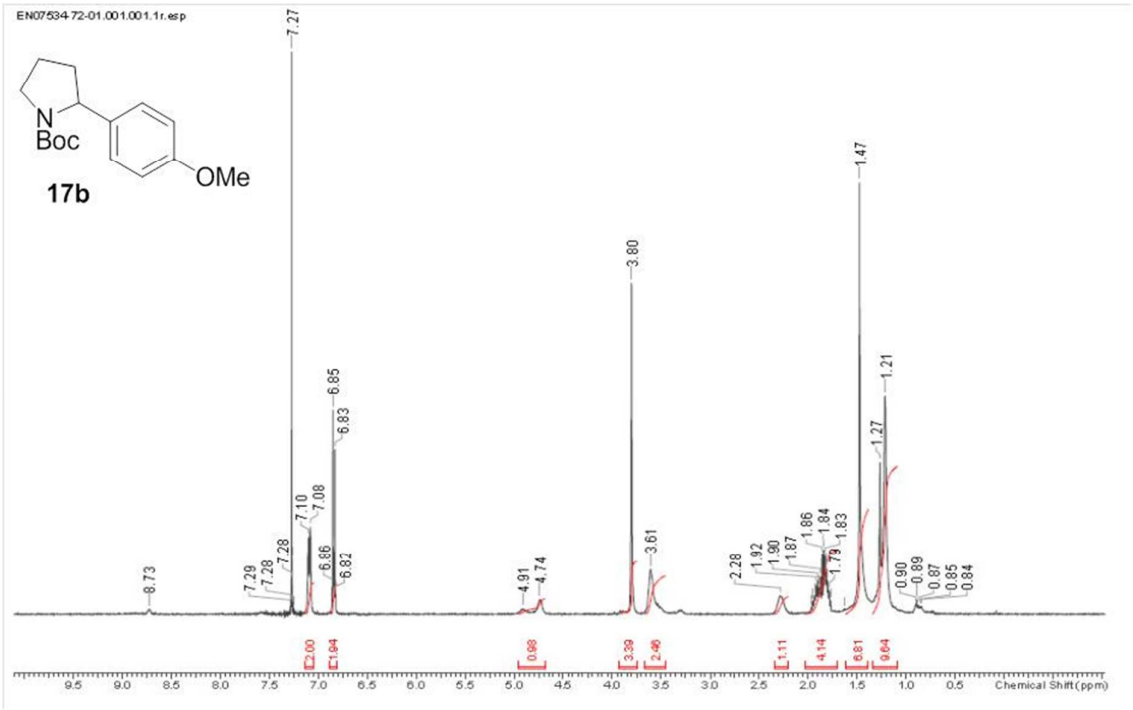
^{1}H-NMR Spectrum of 4-Benzylbenzonitrile (10)



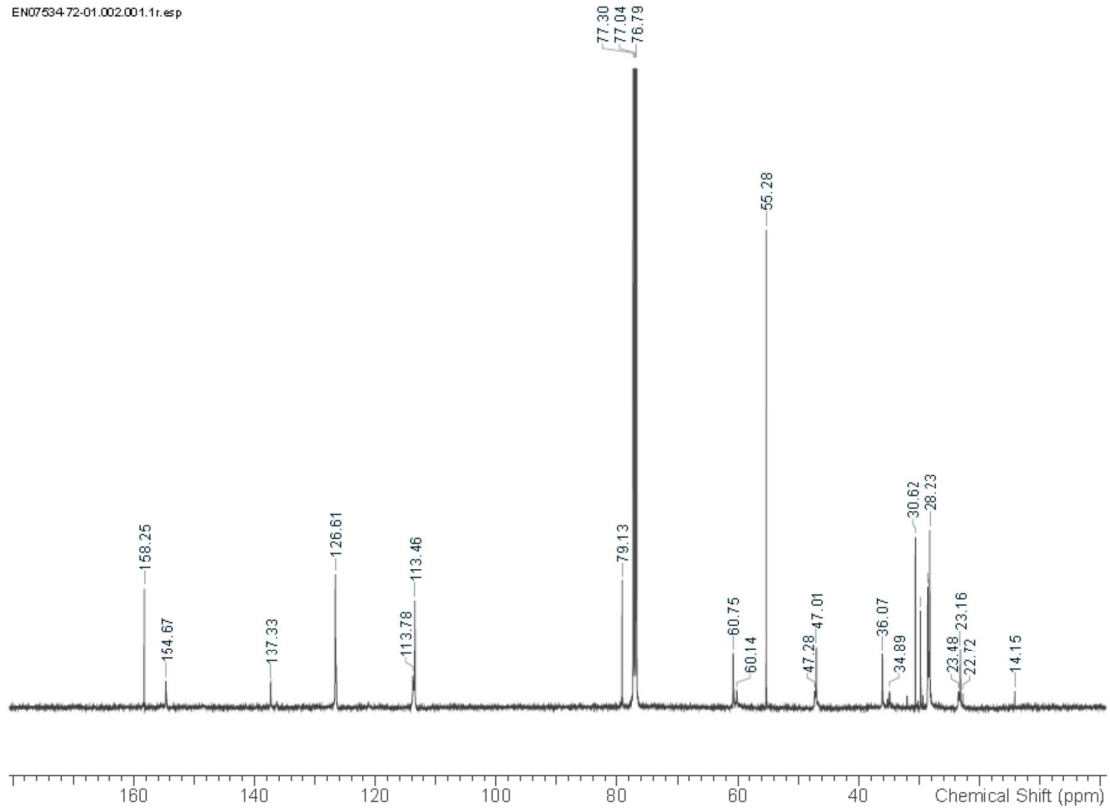
^{13}C-NMR Spectrum of 4-Benzylbenzonitrile (10)



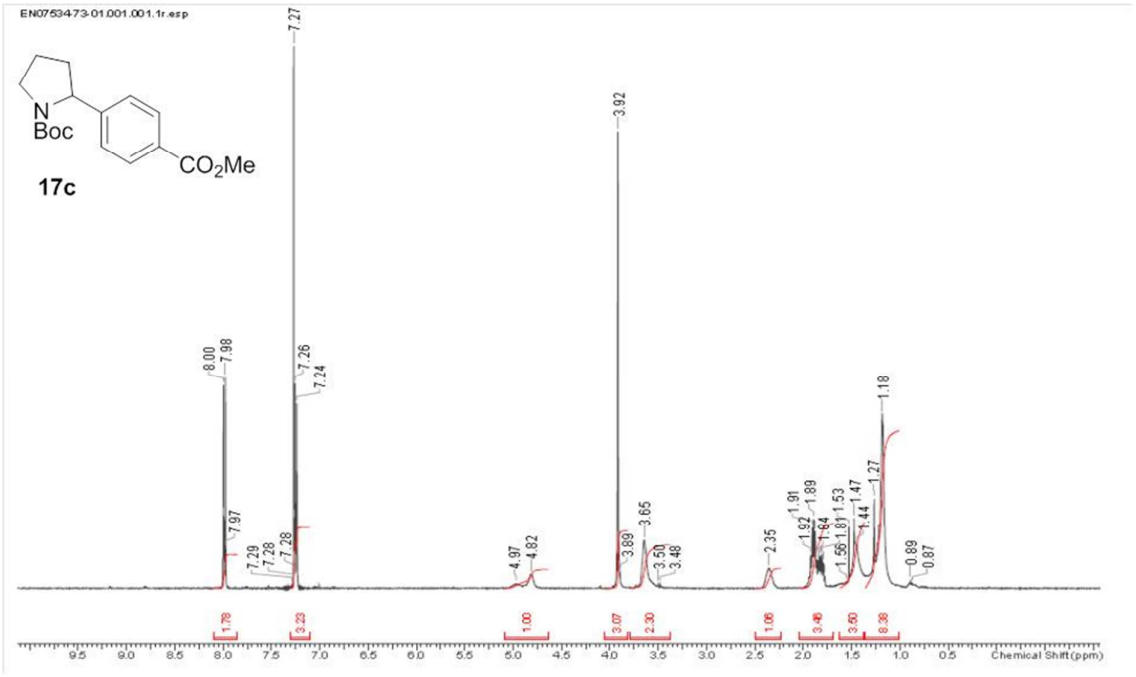
^{1}H-NMR Spectrum of *tert*-Butyl 2-(4-methoxyphenyl)pyrrolidine-1-carboxylate (17b)



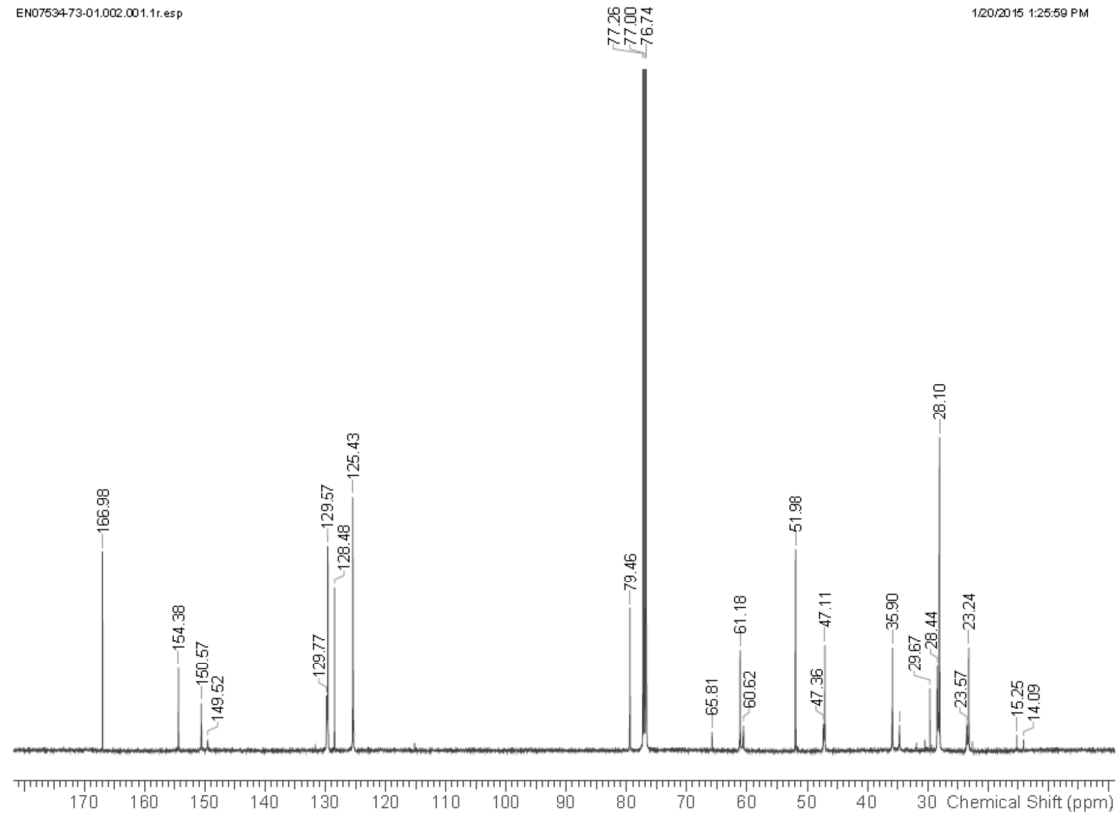
^{13}C-NMR Spectrum of *tert*-Butyl 2-(4-methoxyphenyl)pyrrolidine-1-carboxylate (17b)



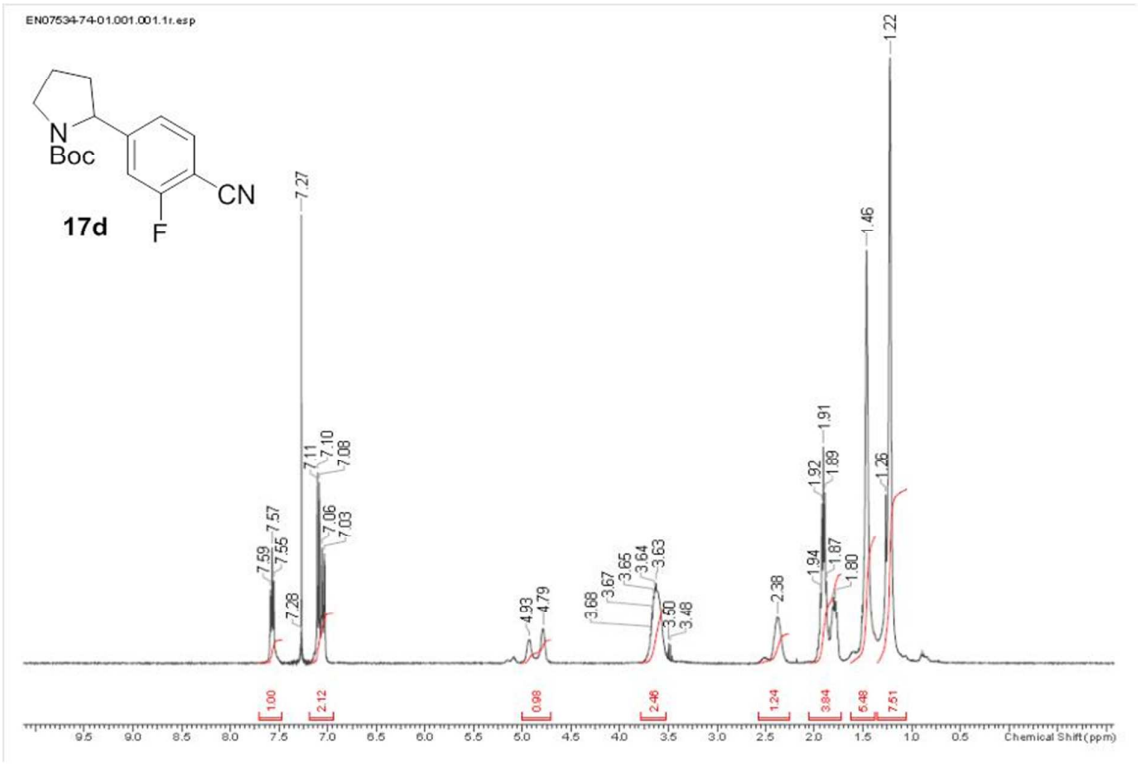
^{1}H-NMR Spectrum of *tert*-Butyl 2-(4-(methoxycarbonyl)phenyl)pyrrolidine-1-carboxylate (17c)



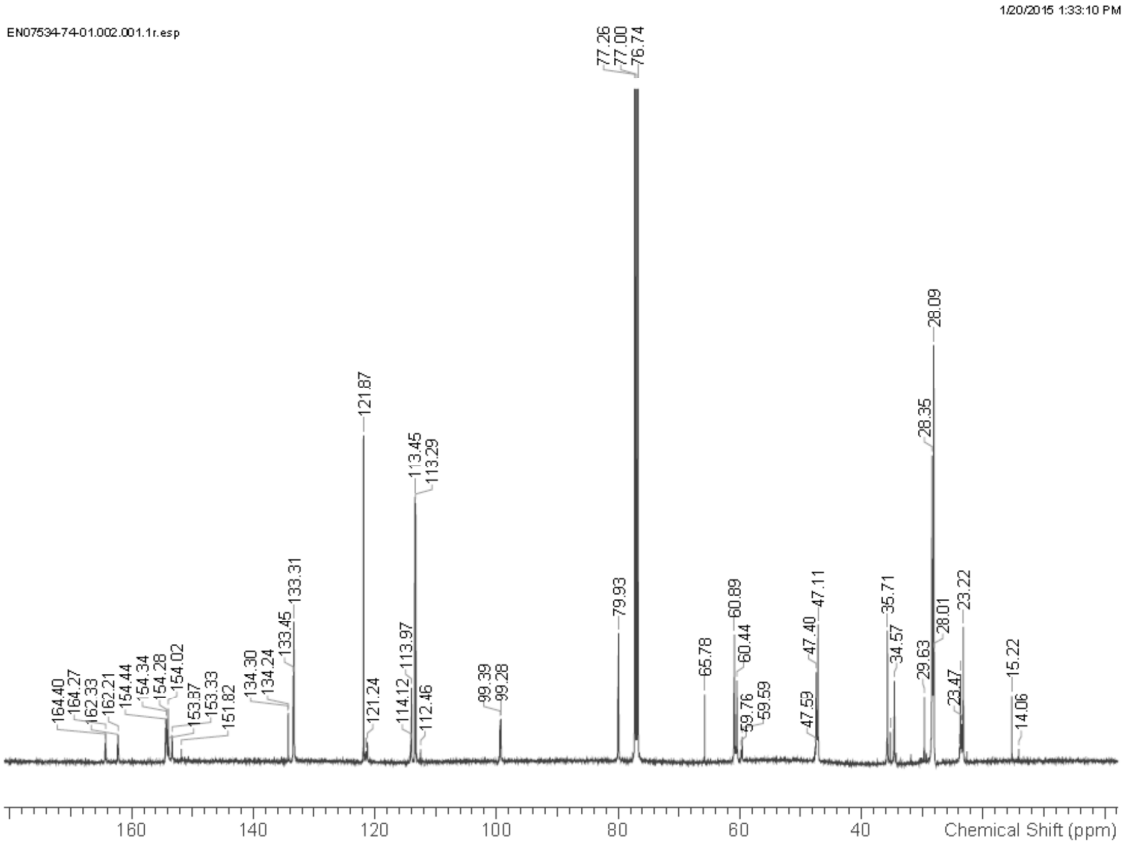
^{13}C-NMR Spectrum of *tert*-Butyl 2-(4-(methoxycarbonyl)phenyl)pyrrolidine-1-carboxylate (17c)



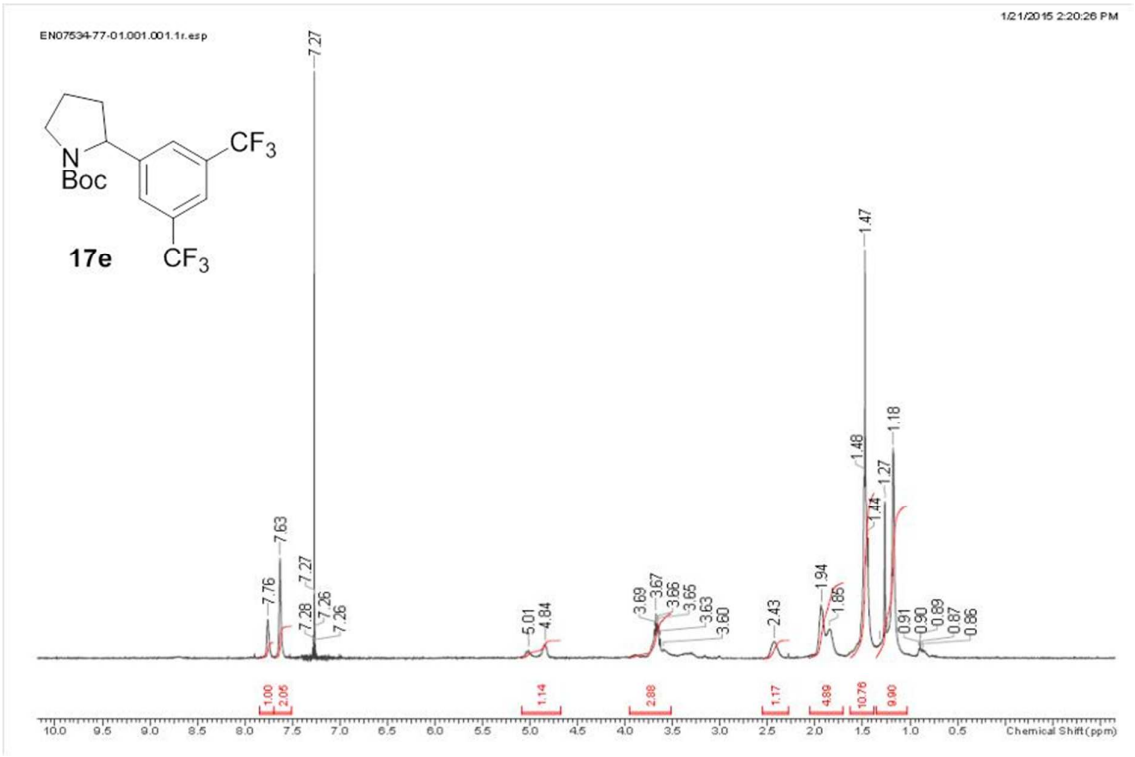
^{1}H-NMR Spectrum of *tert*-Butyl 2-(4-cyano-3-fluorophenyl)pyrrolidine-1-carboxylate (17d)



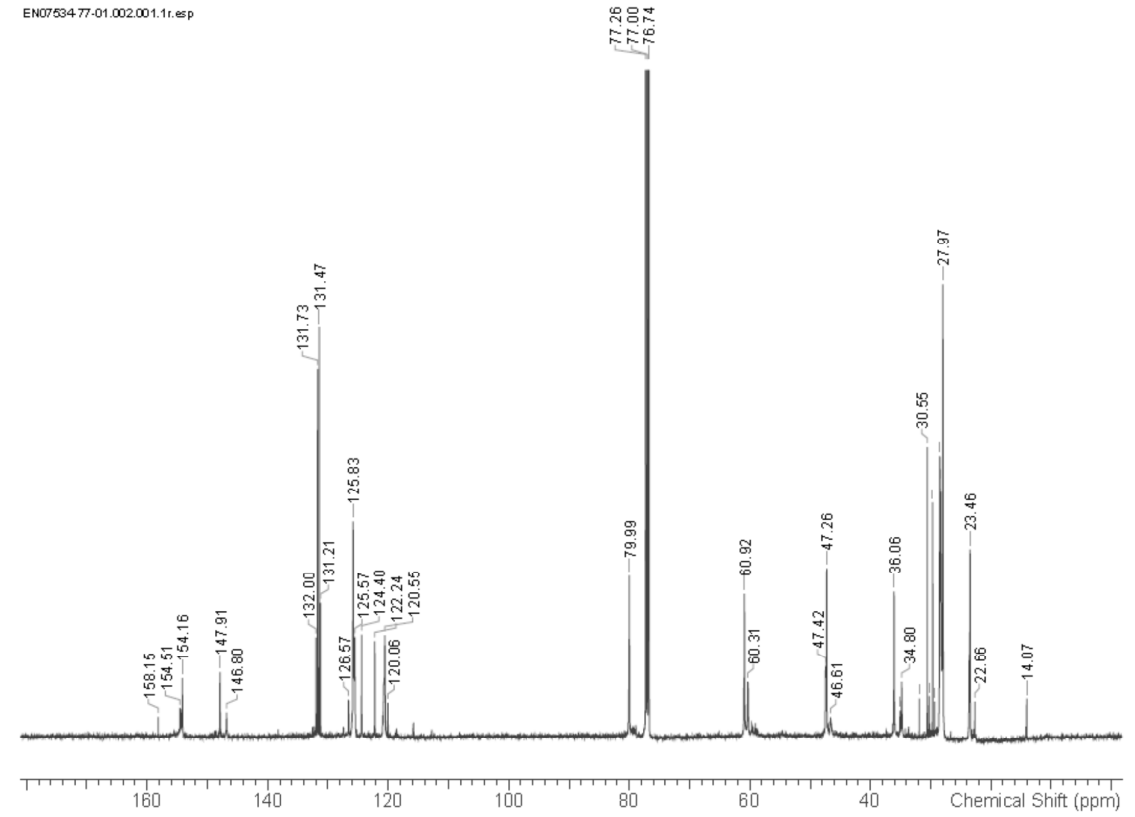
^{13}C-NMR Spectrum of *tert*-Butyl 2-(4-cyano-3-fluorophenyl)pyrrolidine-1-carboxylate (17d)



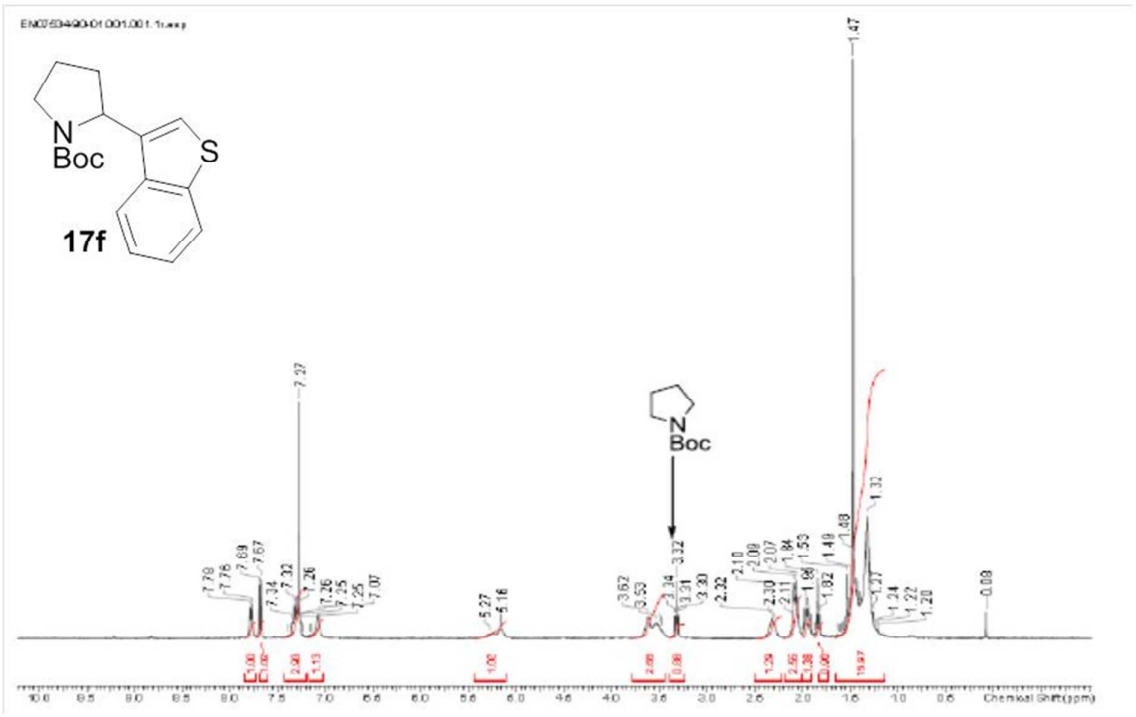
[1]H-NMR Spectrum of *tert*-Butyl 2-(3,5-bis(trifluoromethyl)phenyl)pyrrolidine-1-carboxylate (17e)



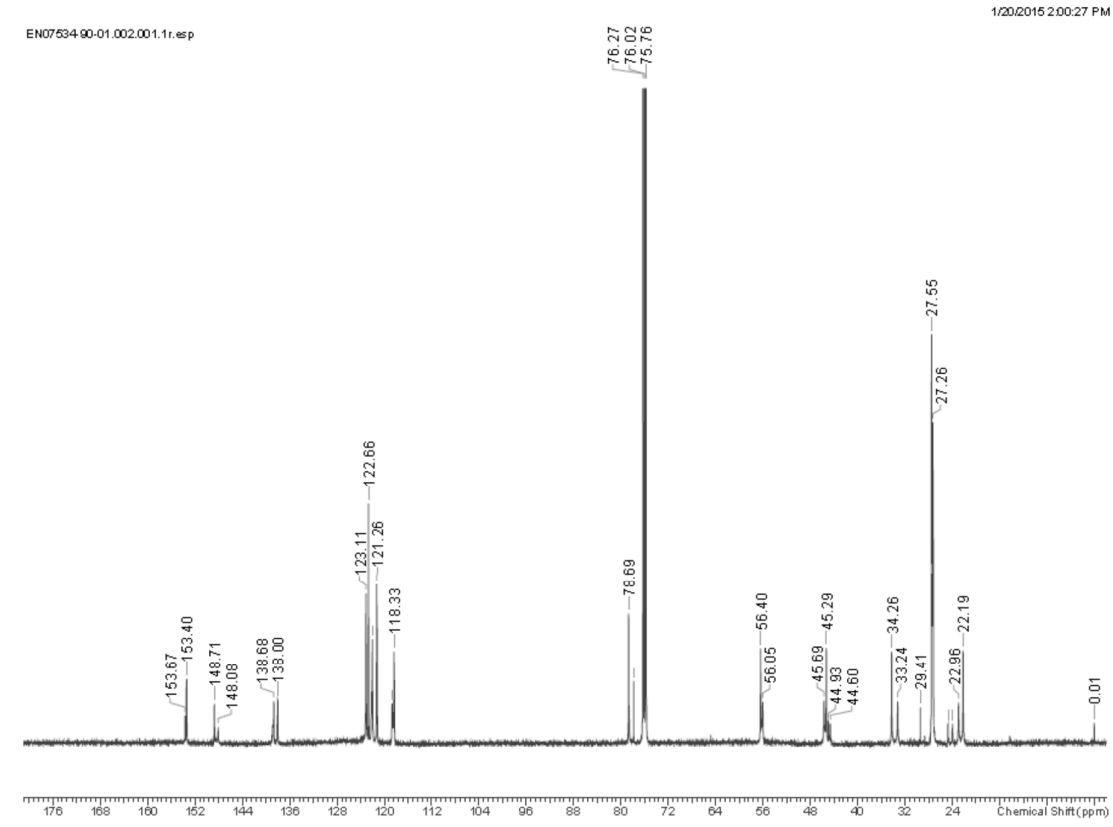
[13]C-NMR Spectrum of *tert*-Butyl 2-(3,5-bis(trifluoromethyl)phenyl)pyrrolidine-1-carboxylate (17e)



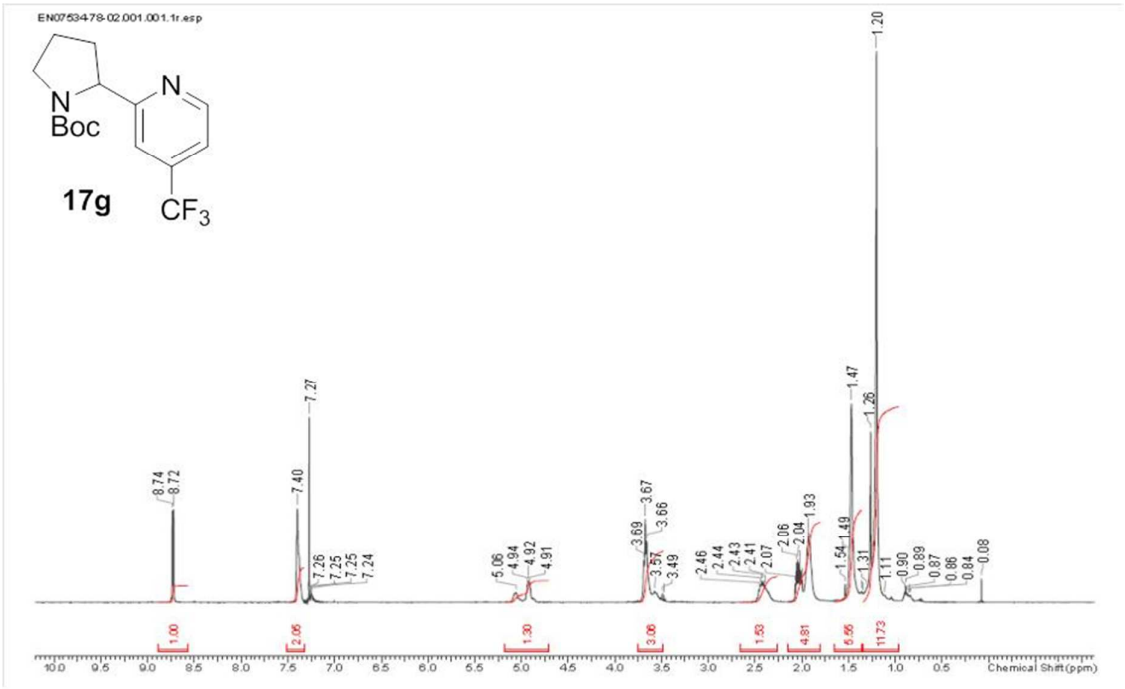
^{1}H-NMR Spectrum of *tert*-Butyl 2-(benzo[β]thiophen-3-yl)pyrrolidine-1-carboxylate (17f)



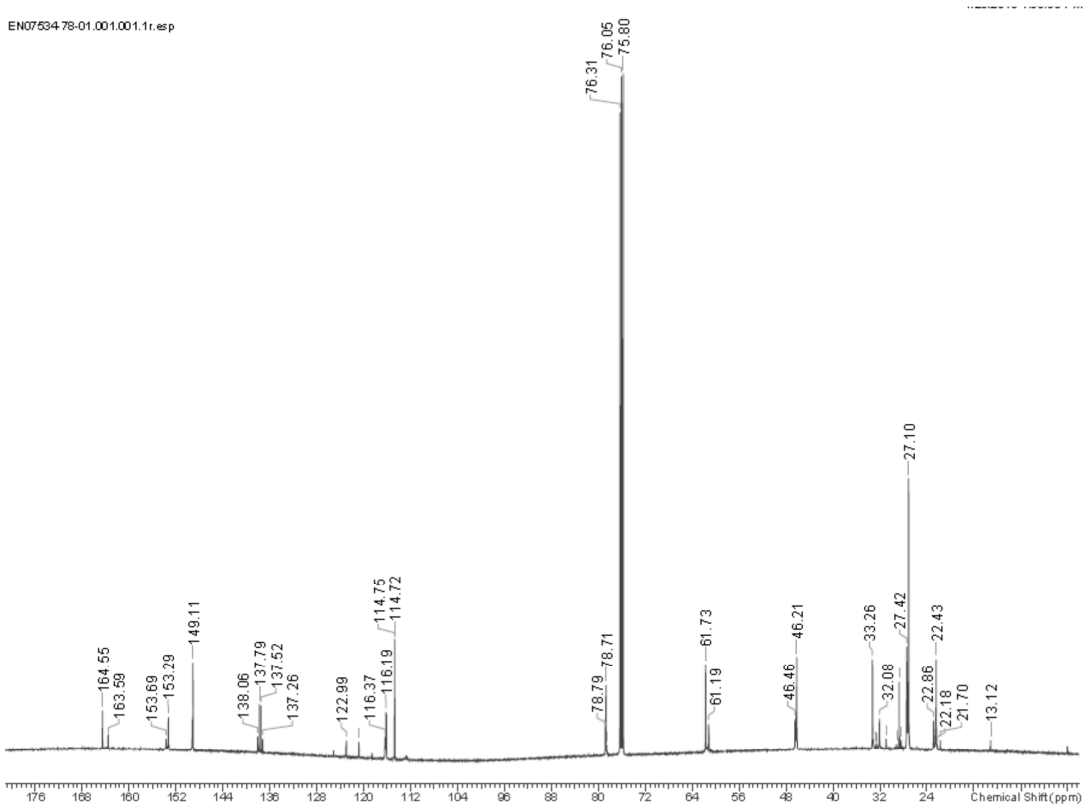
^{13}C-NMR Spectrum of *tert*-Butyl 2-(benzo[β]thiophen-3-yl)pyrrolidine-1-carboxylate (17f)



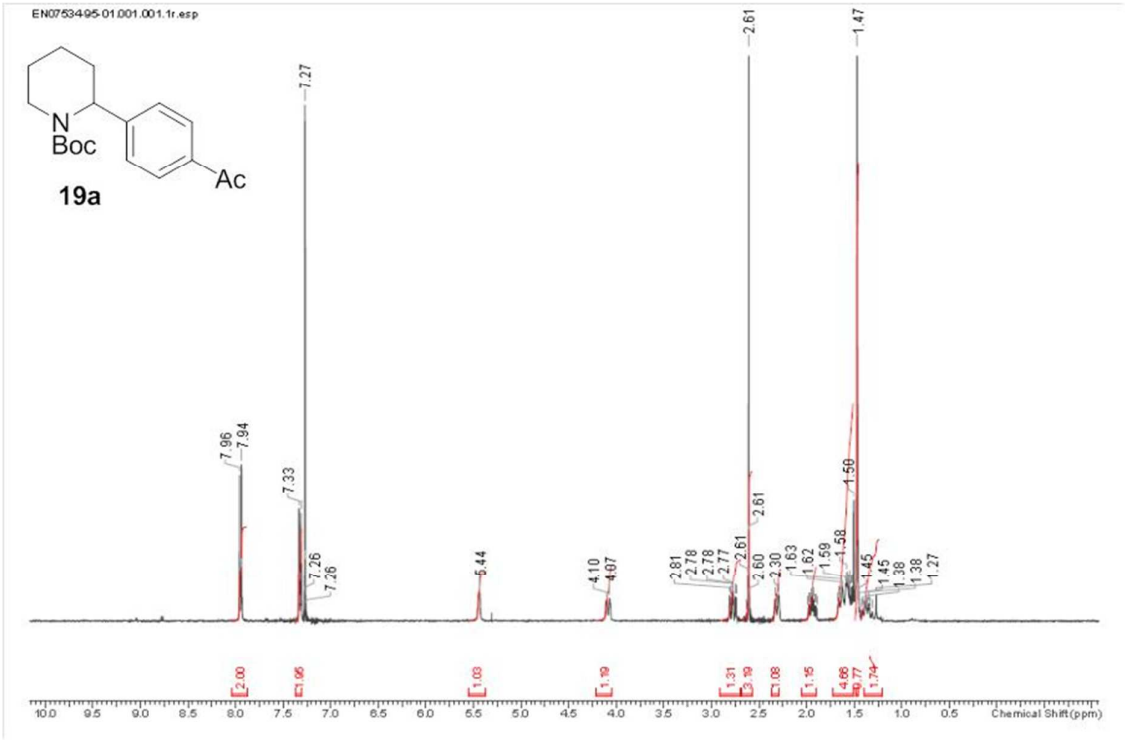
^{1}H-NMR Spectrum of *tert*-Butyl 2-(4-(trifluoromethyl)pyridin-2-yl)pyrrolidine-1-carboxylate (17g)



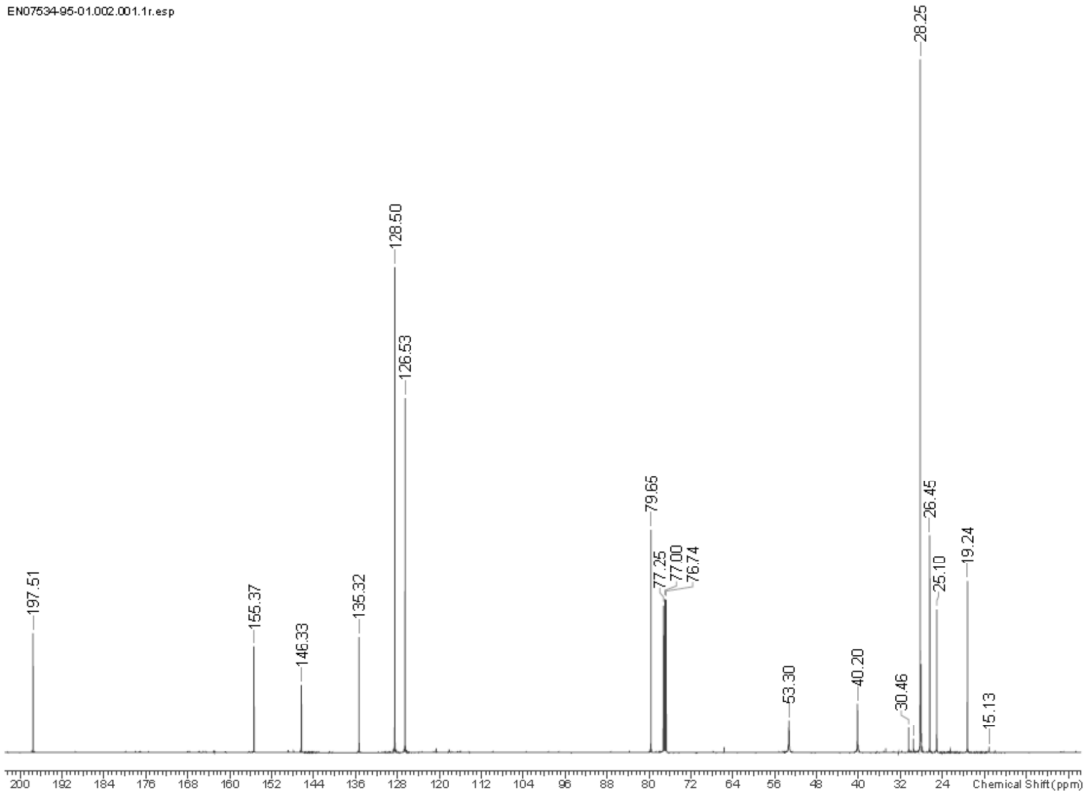
^{13}C-NMR Spectrum of *tert*-Butyl 2-(4-(trifluoromethyl)pyridin-2-yl)pyrrolidine-1-carboxylate (17g)



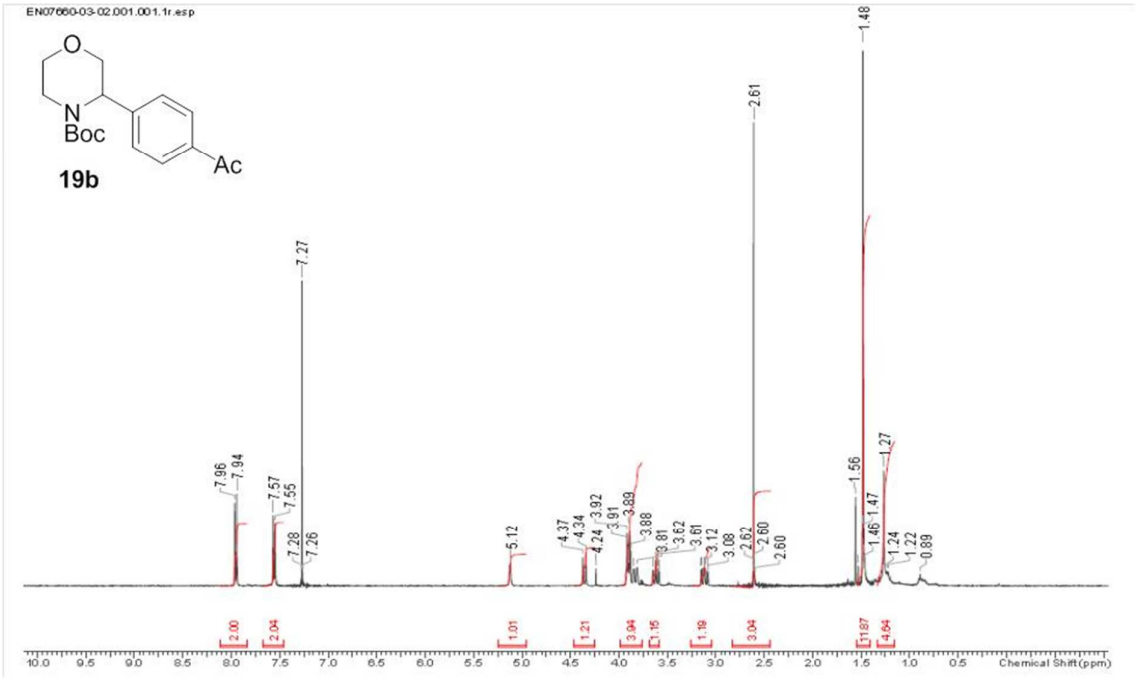
^{1}H-NMR Spectrum of *tert*-Butyl 2-(4-acetylphenyl)piperidine-1-carboxylate (19a)



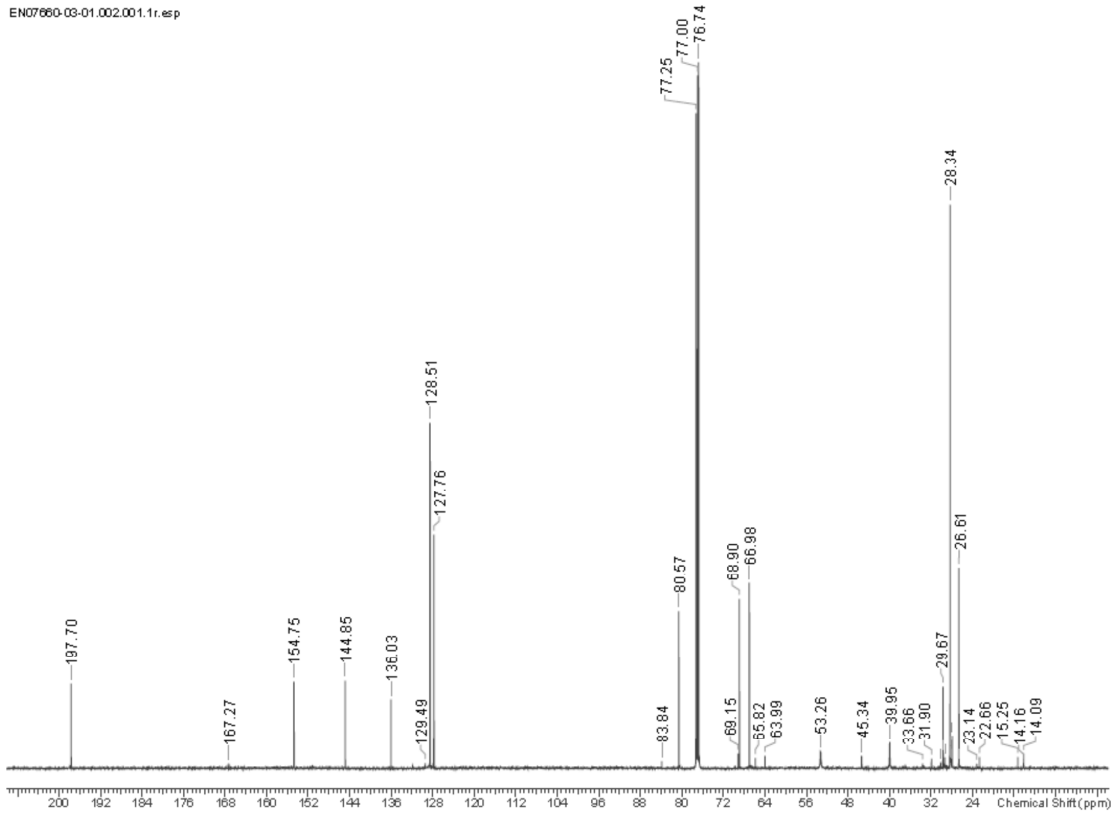
^{13}C-NMR Spectrum of *tert*-Butyl 2-(4-acetylphenyl)piperidine-1-carboxylate (19a)



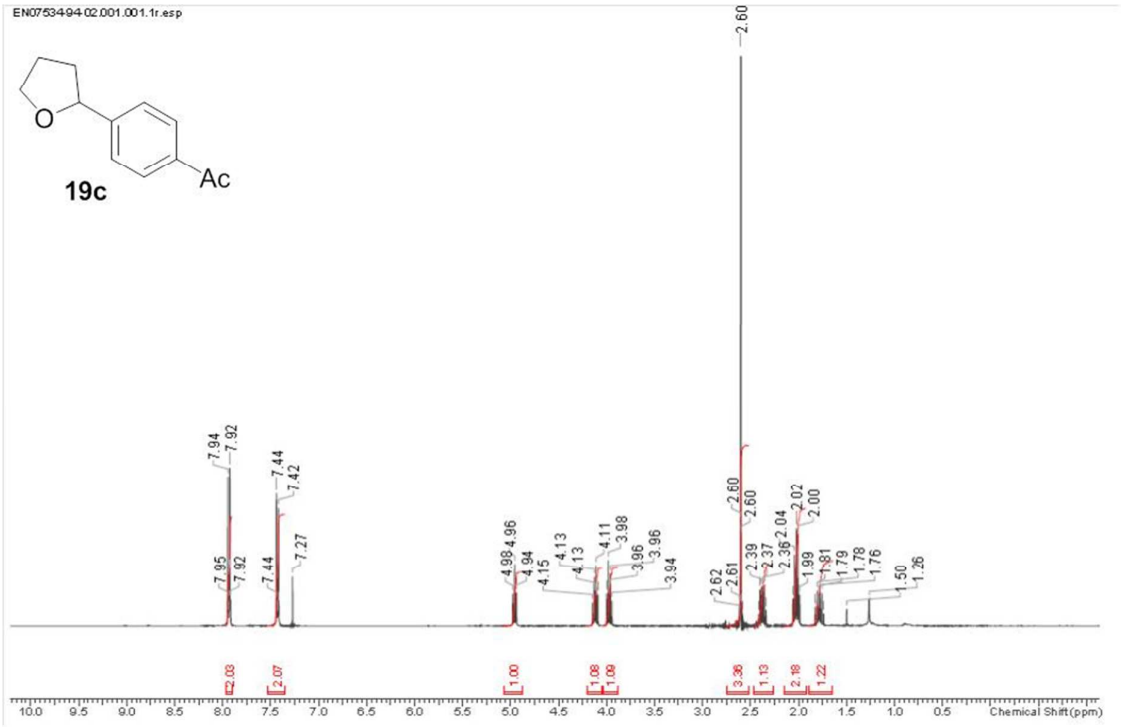
^{1}H-NMR Spectrum of *tert*-butyl 3-(4-acetylphenyl)morpholine-4-carboxylate (19b)



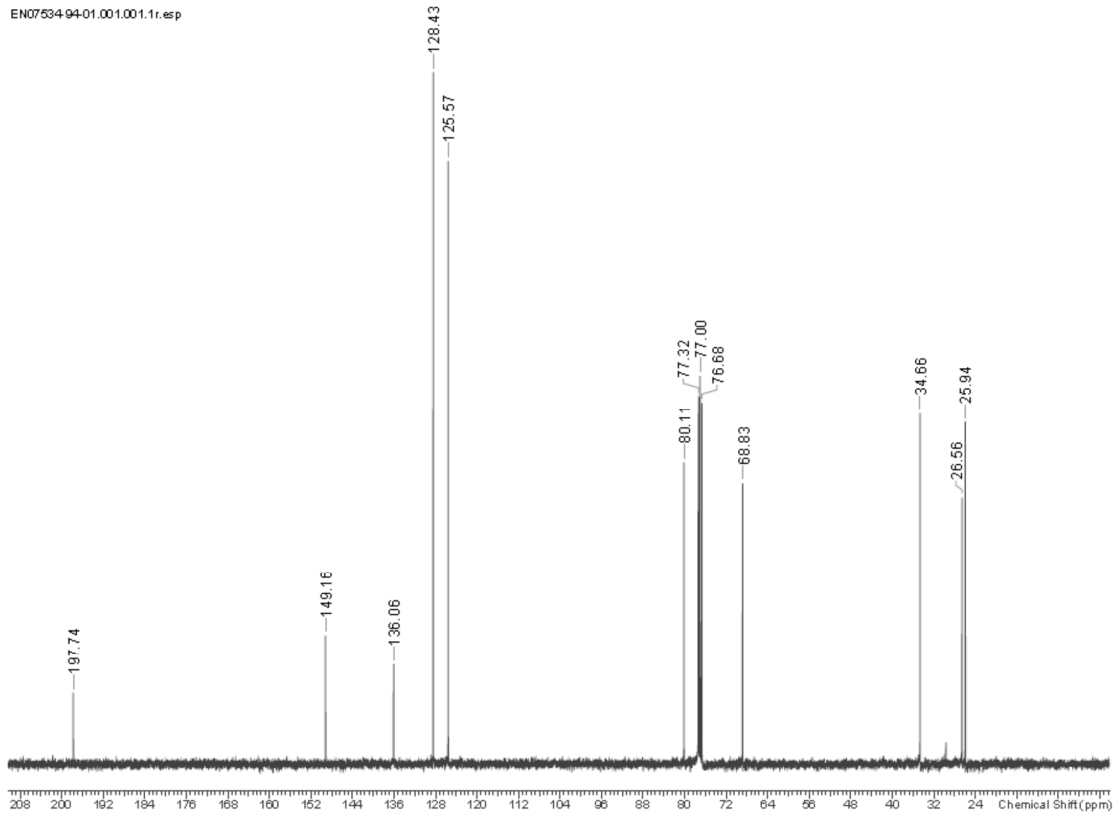
^{13}C-NMR Spectrum of *tert*-butyl 3-(4-acetylphenyl)morpholine-4-carboxylate (19b)



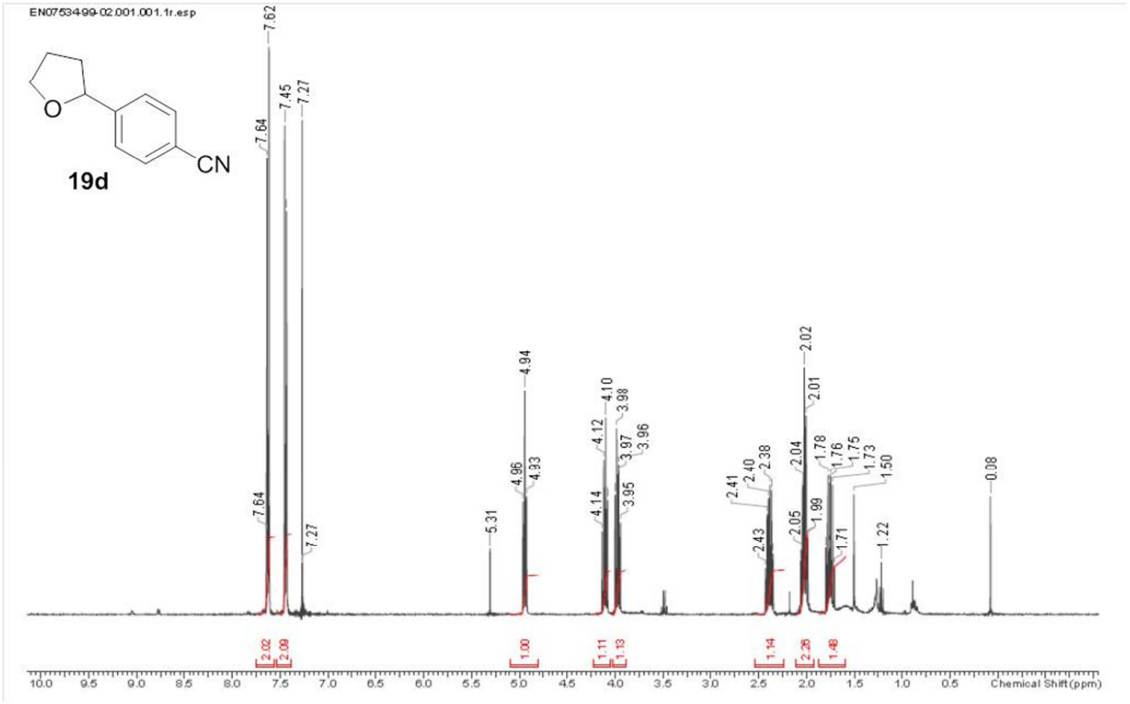
^{1}H-NMR Spectrum of 1-(4-(tetrahydrofuran-2-yl)phenyl)ethan-1-one (19c)



^{13}C-NMR Spectrum of 1-(4-(tetrahydrofuran-2-yl)phenyl)ethan-1-one (19c)



^{1}H-NMR Spectrum of 4-(tetrahydrofuran-2-yl)benzonitrile (19d)



^{13}C-NMR Spectrum of 4-(tetrahydrofuran-2-yl)benzonitrile (19d)