Supplementary Materials for

Aryl Amination Using Ligand-Free Ni(II) Salts and Photoredox Catalysis

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General Reagent Information

All solvents were used as received from Sigma-Aldrich. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator using an ice bath for volatile compounds. Chromatographic purification of products was accomplished by flash chromatography on silica gel (Sigma-Aldrich, 230 – 400 mesh or Silicycle, 40-63 µm silica gel, SiliaFlash® F60). All aryl bromides were used as received from Acros, Alfa-Aesar, and Sigma-Aldrich. All amines were purchased from Acros, Alfa-Aesar, and Sigma-Aldrich and were distilled (if liquid) over calcium hydride prior to use. $NiCl_2$•glyme was purchased from Strem Chemical, Inc. and $NiBr_2$•glyme was purchased from Sigma-Aldrich. A 30 W Kessil H150 blue LED (range of emission approximately 380 – 525 nm) was used as the visible light source for each of these reactions.

General Analytical Information

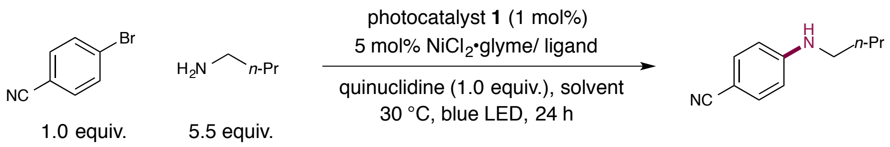
Thin layer chromatography (TLC) was performed on Analtech Uniplate 250 µm or Silicycle 250 µm silica gel plates. Visualization of the developed chromatogram was performed by either fluorescence quenching or potassium permanganate stain. ^1H and ^{13}C NMR spectra were recorded on a Bruker 500 (500 and 125 MHz) instrument, a Bruker AMX-400 spectrometer (400 and 100 MHz) instrument, or a Varian Inova 500 MHz spectrometer (500 and 125 MHz) and are internally referenced to residual protio solvent signals (note: $CDCl_3$ referenced at δ 7.27 and 77.0 ppm, respectively). ^{19}F NMR spectra were recorded on a Bruker 300 (282 MHz) instrument or a Varian Inova 500 MHz spectrometer (471 MHz), and are internally referenced to $CFCl_3$ (note: $CFCl_3$ referenced at δ 0.00 ppm) or *α,α,α*-trifluorotoluene (note: *α,α,α*-trifluorotoluene referenced at δ −63.7 ppm). Data for ^1H NMR are reported as follows: chemical shift (δ ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet , q = quartet, p = pentet, m = multiplet), and coupling constant (Hz). Data for ^{13}C NMR are reported in terms of chemical shift and no special nomenclature is used for equivalent carbons. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer or Thermo Scientific Nicolet iS5 spectrometer (iD5 ATR, diamond) and are reported in terms of frequency of absorption (cm^{-1}). High resolution mass spectra were obtained on an Agilent 6220 Time-of-Flight ESI-LC/MS or Agilent 7200 Accurate-Mass Q-TOF EI-GC/MS at Princeton University mass spectrometry facilities or a Bruker Daltonic APEXIV 4.7 Tesla Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR-MS) at the Department of Chemistry Instrumentation Facility (DCIF) at the Massachusetts Institute of Technology.

Optimization Studies – General Experimental Procedure.

To a solution of base, amine, photocatalyst **1**, and aryl halide in solvent (0.27 M) was added a solution of nickel (II) salt and ligand in solvent that had been sonicated (10 min) prior to addition. The reaction was cooled to –78 °C and degassed by three cycles of freeze, pump (5 min), backfill (with nitrogen gas), and thaw. The reaction was placed 6 cm in front of one 30 W blue LED.

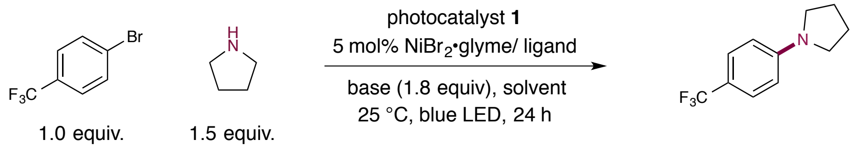
Studies toward the optimization of ligand, base, and solvent.

Part A. Initial optimization of ligand and solvent.[a]



photocatalyst (mol%)	*ligand*	*base*	*solvent*	*product yield (%)**
1	dFbpy	quinuclidine	acetone	0
1	dFbpy	quinuclidine	DMF	22
1	dFbpy	quinuclidine	MeCN	58
1	dFbpy	quinuclidine	DMA	51
1	dMebpy	quinuclidine	DMA	13
1	dtbbpy	quinuclidine	DMA	84
1	phen	quinuclidine	DMA	1
1	terpy	quinuclidine	DMA	6

Part B. Further optimization to arrive at ligand-free conditions.

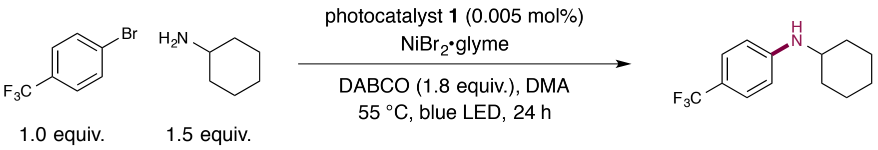


photocatalyst (mol%)	*ligand*	*base*	*solvent*	*product yield (%)**
1	dtbbpy	quinuclidine	MeCN	0
0.02	dtbbpy	quinuclidine	MeCN	21
0.02	dtbbpy	quinuclidine	DMA	30
0.02	dtbbpy	DABCO	DMA	67
0.02	none	DABCO	DMA	95
0.02	none	triethylamine	DMA	27
0.02	none	K_2CO_3	DMA	3
0.02	none	C_2CO_3	DMA	6
0.02	none	KO*t*-Bu	DMA	0

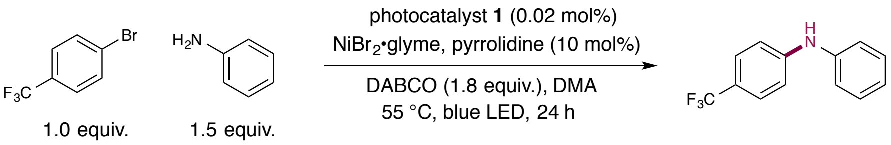
Figure S1. Optimization of ligand, base, and solvent in the metallaphotoredox-catalyzed amination protocol. *All entries are reported as in situ yields determined by ^{1}H NMR using 1,3-benzodioxole as an internal standard. [a] Run using blue LED strips as the source of visible light. DABCO, 1,4-diazabicyclo[2.2.2] octane; dMebpy, 5,5'-dimethyl-2,2'-bipyridine; dtbbpy, 4,4'-di-*tert*-butyl-2,2'-bipyridine; dFbpy, 5,5'-difluoro-2,2'-bipyridine; phen, 1,10-phenanthroline; terpy, terpyridine.

Optimization of nickel loading.

During our optimization studies, we observed that a nickel catalyst loading of 5 mol% was generally efficacious for a wide variety of substrates. However, it is important to note that for several substrates additional tuning of the nickel catalyst loading proved beneficial.



nickel (mol%)	*product yield (%)**
1	44
3	59
5	59
7	44
9	45

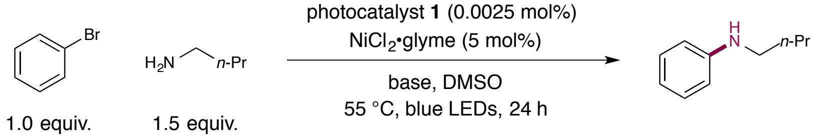


nickel (mol%)	*product yield (%)**	*pyrrolidine-coupled product (%)**
0.5	90	7
1	90	7
3	85	6
5	32	4

Figure S2. Optimization of nickel loading for select substrates. *All entries are reported as in situ yields determined by ^{1}H NMR using 1,3-benzodioxole as an internal standard. DABCO, 1,4-diazabicyclo[2.2.2] octane.

Optimization of base equivalents.

During our optimization studies, we observed that 1.8 equivalents of DABCO was generally efficacious in the cross-coupling of a wide array of aryl halide and amine coupling partners. It is noteworthy, however, that 1.0 equivalent of MTBD was sufficient to achieve highly efficient cross-coupling in most cases involving free base amines as coupling partners. It has also been observed for certain substrates, *e.g.* electron-rich aryl halides, that MTBD often outperforms DABCO. The rationale for this divergence is currently not well-understood.



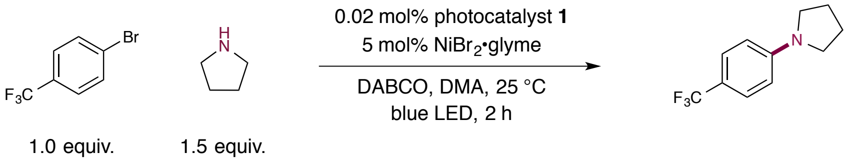
base	*equiv. of base*	*product yield (%)**
DABCO	1.0	35
DABCO	1.2	40
DABCO	1.4	39
DABCO	1.6	43
DABCO	1.8	50
DABCO	2.0	33
MTBD	1.0	84

Figure S3. Optimization of base equivalents for a representative substrate. *All entries are reported as in situ yields determined by ^{1}H NMR using 1,3-benzodioxole as an internal standard. DABCO, 1,4-diazabicyclo[2.2.2] octane; MTBD, 7-methyl-1,5,7-triazabicyclo[4.4.0] dec-5-ene.

Control Experiments

Experiments performed with nickel (II) salt.

To a solution of DABCO (55 mg, 0.490 mmol), pyrrolidine (34 µL, 0.402 mmol) and 4-bromobenzotrifluoride (38 µL, 0.271 mmol) in DMA (0.5 mL) was added photocatalyst **1** (55 µg, 0.0490 µmol) in DMA (6.5 µL). A solution of $NiBr_2$•glyme (4.19 mg, 0.0136 mmol) in DMA (0.5 mL) was then added to the reaction mixture. The solution of $NiBr_2$•glyme and DMA was sonicated for 10 min prior to addition. The reaction was then cooled to –78 °C and degassed by three cycles of freeze, pump (5 min), backfill (with nitrogen gas), and thaw. The reaction was subsequently placed 6 cm in front of one blue LED, with fan cooling, and was irradiated for 2 h.

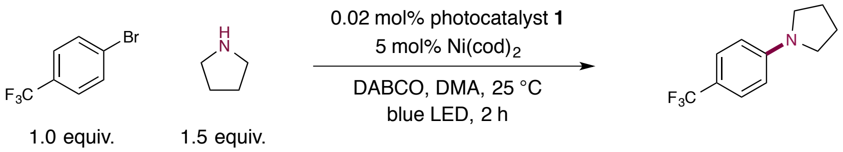


reaction component omitted	*product yield (%)**
light	0
photocatalyst	0
$NiBr_2$•glyme	0
DABCO	62
none	95

Figure S4. Control experiments for the metallaphotoredox-catalzed amination protocol: Ni(II) salt conditions. *All entries are reported as in situ yields determined by ^1H NMR using 1,3-benzodioxole as an internal standard. DABCO, 1,4-diazabicyclo[2.2.2]octane.

Experiments performed with Ni(cod)$_2$.

To a solution of DABCO (55 mg, 0.490 mmol), pyrrolidine (34 µL, 0.402 mmol) and 4-bromobenzotrifluoride (38 µL, 0.271 mmol) in DMA (0.5 mL) was added photocatalyst **1** (55 µg, 0.0490 µmol) in DMA (6.5 µL). The solution was then cooled to –78 °C and degassed by four cycles of freeze, pump (10 min), backfill with nitrogen, and thaw. A solution of Ni(cod)$_2$ (3.73 mg, 0.0136 mmol) in degassed DMA (0.5 mL) was subsequently added by syringe. The reactions were placed 6 cm in front of one blue LED, with fan cooling, and irradiated for 2 h.

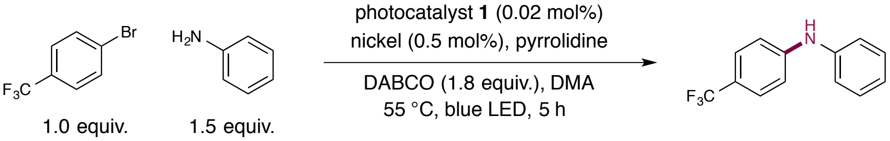


reaction component omitted	*product yield (%)**
light	10
photocatalyst	28
Ni(cod)$_2$	0
DABCO	61
none	95

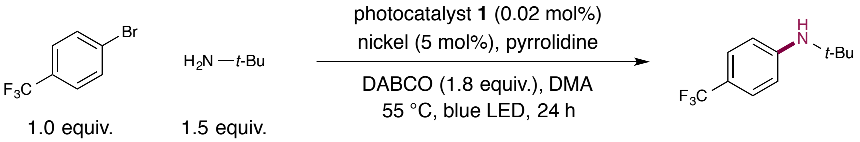
Figure S5. Control experiments for the metallaphotoredox-catalzed amination protocol: Ni(cod)$_2$ conditions.*All entries are reported as in situ yields determined by ^1H NMR using 1,3-benzodioxole as an internal standard. cod, 1,5-cyclooctadiene; DABCO, 1,4-diazabicyclo [2.2.2]octane.

Evaluation of Amines Not Possessing α-Hydrogens

In an attempt to understand the unreactive nature of amines lacking α-hydrogens under the standard metallaphotoredox-catalyzed C–N cross-coupling conditions, a series of experiments were conducted. To test our hypothesis that a β-hydride elimination event was requisite for accessing an active nickel(0) catalyst, we evaluated the reactivity of both aniline and *t*-butyl amine under reaction conditions utilizing a nickel(0) source. Successful cross-coupling of aniline with aryl bromide using Ni(cod)$_2$ in the absence of any additive, such as pyrrolidine, lends support to our hypothesis. Although *t*-butyl amine does not couple under reaction conditions employing Ni(cod)$_2$, we propose that this lack of reactivity stems from the steric bulk around the nitrogen atom.



nickel source	*pyrrolidine (%)*	*product yield (%)**
NiBr$_2$•glyme	0	0
NiBr$_2$•glyme	10	84
Ni(cod)$_2$	0	18

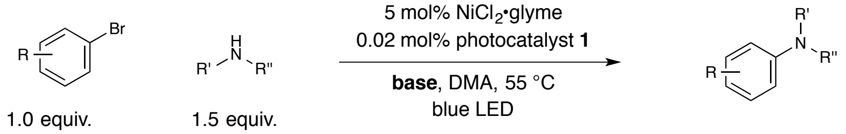


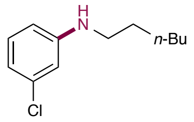
nickel source	*pyrrolidine (%)*	*product yield (%)**
NiCl$_2$•glyme	0	0
NiCl$_2$•glyme	10	0
Ni(cod)$_2$	0	0

Figure S6. Evaluation of select amines lacking α-hydrogens. *All entries are reported as in situ yields determined by ^{1}H NMR using 1,3-benzodioxole as an internal standard. cod, 1,5-cyclooctadiene; DABCO, 1,4-diazabicyclo[2.2.2] octane.

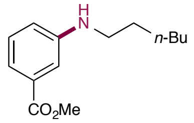
Comparison of results using DABCO and MTBD

To a solution of base (1.8 equiv., 0.490 mmol), amine (1.5 equiv., 0.402 mmol) and aryl bromide (1.0 equiv., 0.271 mmol) in DMA (0.5 mL) was added photocatalyst **1** (0.0490 µmol) in DMA (6.5 µL). A solution of $NiBr_2$•glyme or $NiCl_2$•glyme (0.0136 mmol) in DMA (0.5 mL) was then added to the reaction mixture. The reaction was then cooled to –78 °C and degassed by three cycles of freeze, pump (5 min), backfill (with nitrogen gas), and thaw. The reaction was subsequently placed 6 cm in front of one blue LED, without fan cooling, and was irradiated for 24 h.

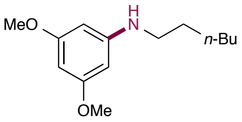




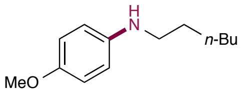
MTBD: 86% yield, 18 h[a]
DABCO: 62% yield, 18 h[b]



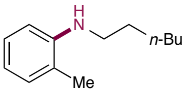
MTBD: 64% yield, 17 h[a]
DABCO: 57% yield, 17h[b]



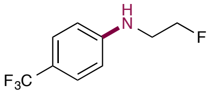
MTBD: 61% yield, 24 h[a,c]
DABCO: 46% yield, 24 h[b,c]



MTBD: 49% yield, 17 h[a,d]
DABCO: 0% yield, 17 h[a,d]



MTBD: 51% yield, 17 h[a,d]
DABCO: 33% yield, 17 h[a,d]



MTBD: 86% yield, 24 h[e]
DABCO: 35% yield, 24 h[e]

Figure S7. Comparison of bases for select substrates. All entries are reported as in situ yields determined by ^1H NMR using 1,3-benzodioxole as an internal standard. DABCO, 1,4-diazabicyclo[2.2.2]octane; Me, methyl; *n*-Bu, *n*-butyl; MTBD, 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene. [a] 1.0 equiv. of MTBD used. [b] 1.8 equiv. of DABCO used.[c] 0.002 mol% photocatalyst **1** used,DMSO used as solvent. [d] 10 mol% $NiCl_2$•glyme used. [e] 3.0 equiv. amine, 4.0 equiv. MTBD, 0.002 mol% photocatalyst **1**, and 7 mol% $NiCl_2$•glyme used.

Amination results employing $Ru(bpy)_3(PF_6)_2$

To a solution of DABCO (55 mg, 0.490 mmol), bromoarene (0.271 mmol), and amine (0.402 mmol) in DMA (0.5 mL) was added $Ru(bpy)_3(PF_6)_2$ as a solution in DMA (3 µL). Then $NiBr_2$•DME (4.19 mg, mmol) was added as a solution in DMA (0.5 mL), which had been sonicated for 10 min. The solution was then cooled to –78 °C and degassed by three cycles of freeze, pump (5 min), backfill with nitrogen, and thaw. The reactions were placed 6 cm in front of one blue LED.

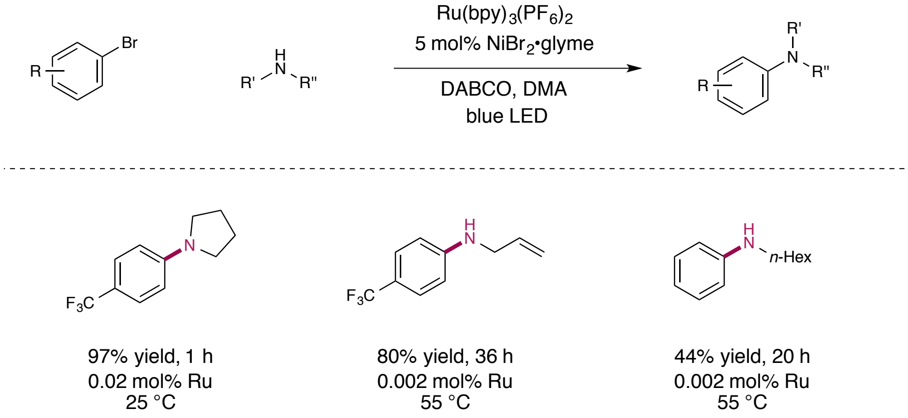


Figure S8. Select substrate yields with Ru(bpy)$_3$(PF$_6$)$_2$ as photocatalyst. All entries are reported as in situ yields determined by ^{1}H NMR using 1,3-benzodioxole as an internal standard. DABCO, 1,4-diazabicyclo[2.2.2]octane; Me, methyl; *n*-Hex, *n*-hexyl; R, H or alkyl group; R', H or alkyl group; R", H or alkyl group; Ru, Ru(bpy)$_3$(PF$_6$)$_2$.

List of substrates currently not able to be coupled

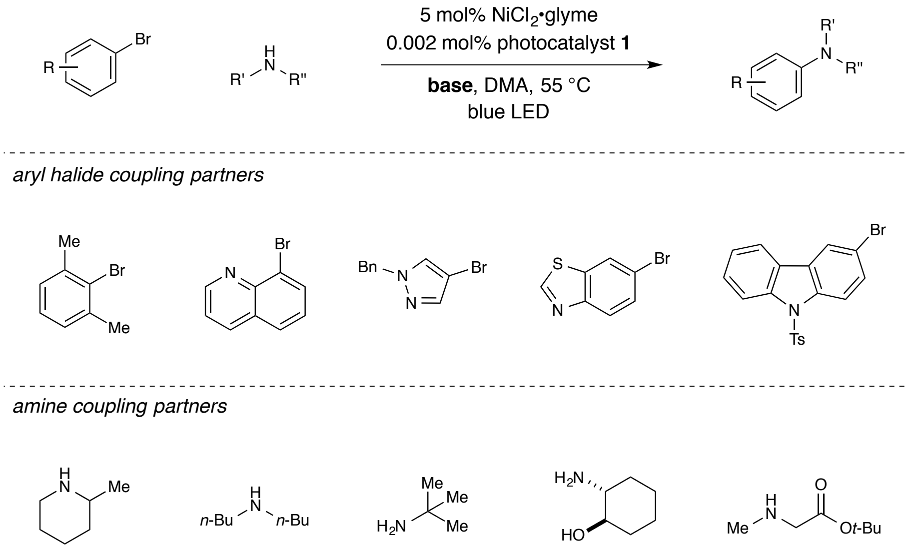
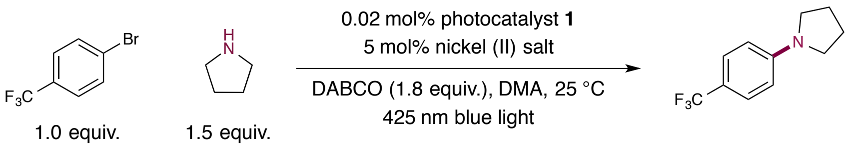


Figure S9. Select substrates that are currently unable to couple in the metallaphotoredox catalyzed amination protocol.

Adaptation of Metallaphotoredox-Catalyzed Amination for Application in Flow Chemistry

All reaction solutions were prepared and degassed according to the general procedure outlined in the General Experimental Procedure. Reactions were evaluated in flow using a Vapourtec E-series Integrated Flow Chemistry System featuring a Vapourtec UV-150 Photochemical Reactor which utilizes a 425 nm blue LED array. For each reaction detailed in Figure S10, the mass balance was accounted for by unreacted aryl bromide starting materials as well as trace amounts of protodehalogenated arene and phenol being observed for each entry.



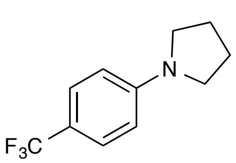
nickel source	*concentration*	*residence time*	*product yield (%)**
$NiBr_2$•glyme	0.27 M	5 min	64
$NiBr_2$•glyme	0.27 M	15 min	81
$NiBr_2•3H_2O$	0.27 M	30 min	93
$NiBr_2•3H_2O$	2.0 M	15 min	95

Figure S10. Adaptation of the metallaphotoredox-catalyzed amination protocol for flow applications. *All entries are reported as in situ yields determined by ^1H NMR using mesitylene as an internal standard. DABCO, 1,4-diazabicyclo[2.2.2]octane.

Experimental Procedures

General Procedure

To an 8 mL vial containing a solution of aryl bromide (1.0 equiv.) and DABCO (1.8 equiv.) or MTBD (1.0 equiv) in DMA (1.5 mL) were added amine (1.5 equiv.), a solution of $NiCl_2$•DME or $NiBr_2$•DME (0.05 equiv.) in DMA or DMSO (1.5 mL), and a solution of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.0002 equiv. or 0.00002 equiv.) in DMA or DMSO (16 µL). The vial was placed under an atmosphere of nitrogen, cooled to – 78 °C, and degassed via vacuum evacuation (5 min), backfilled with nitrogen, and warmed to room temperature. This process was repeated three times, then the vial was sealed with parafilm, placed 6 cm away from one blue LED, and irradiated either under fan cooling (to maintain ambient temperature) or without fan cooling (to heat to approximately 55 °C). After full consumption of arene starting material, the reaction mixture was purified by flash column chromatography on silica gel to afford the desired aniline product.



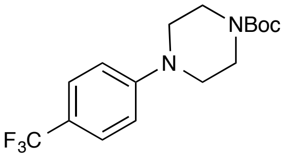
1-(4-(trifluoromethyl)phenyl)pyrrolidine 10

To a solution of 4-bromobenzotrifluoride (114 µL, 0.814 mmol, 1.0 equiv), pyrrolidine (102 µL, 1.221 mmol, 1.5 equiv), and DABCO (164 mg, 1.466 mmol, 1.8 equiv) in DMA (1.5 mL) was added photocatalyst **1** (0.183 mg, 0.0002 equiv) as a solution in DMA (6.5 µL). A solution of $NiBr_2$•glyme (12.56 mg, 0.041 mmol, 0.05 equiv) in DMA (1.5 mL), which had been sonicated for 5 min, was then added. The vial was placed under an atmosphere of nitrogen, cooled to –78 °C, degassed via vacuum evacuation (5 min), backfilled with nitrogen, and warmed to room temperature. This process was repeated three times, and the reaction vial was then sealed with parafilm, placed 6 cm away from one blue LED, and irradiated. The reaction vial was maintained at ambient temperature by cooling with a fan. After 4 h, the reaction mixture was purified directly by flash column chromatography (SiO_2, 0% to 3% diethyl ether in pentane eluent) to give a white solid (167 mg, 0.776 mmol, 75% yield). The spectral data matched that reported in the literature *(35)*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, J = 8.6 Hz, 2H), 6.49 (d, J = 8.6 Hz, 2H), 3.30–3.15 (m, 4H), 2.03–1.90 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 149.6, 126.3 (q, $^3J_{C\text{–}F}$ = 3.75 Hz), 125.2 (q, $^1J_{C\text{–}F}$ = 268.8 Hz), 116.5 (q, $^2J_{C\text{–}F}$ = 32.5 Hz), 110.7, 47.4, 25.4.

^{19}F NMR (282 MHz, $CDCl_3$) δ –61.1 (s, 3F).



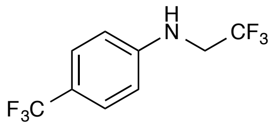
***Tert*-butyl 4-(4-(trifluoromethyl)phenyl)piperazine-1-carboxylate 11**

To a solution of 4-bromobenzotrifluoride (114 µL, 0.814 mmol, 1.0 equiv), *N*-Boc-piperazine (230 mg, 1.236 mmol, 1.5 equiv), and DABCO (164 mg, 1.466 mmol, 1.8 equiv) in DMA (1.5 mL) was added photocatalyst **1** (0.183 mg, 0.0002 equiv) as a solution in DMA (6.5 µL). A solution of $NiBr_2$•glyme (12.56 mg, 0.041 mmol, 0.05 equiv) in DMA (1.5 mL), which had been sonicated for 5 min, was then added. The vial was placed under an atmosphere of nitrogen, cooled to –78 °C, degassed via vacuum evacuation (5 min), backfilled with nitrogen, and warmed to room temperature. This process was repeated three times, and the reaction vial was then sealed with parafilm, placed 6 cm away from one blue LED, and irradiated. The reaction vial was heated to approximately 55 °C by the blue LED without fan cooling. After 24 h, the reaction mixture was purified directly by flash column chromatography (SiO_2, 0% to 10% ethyl acetate in hexanes eluent) to give a white solid (206 mg, 0.623 mmol, 76% yield). The spectral data matched that reported in the literature *(36)*.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.51 (d, *J* = 8.7 Hz, 2H), 6.97 (d, *J* = 8.6 Hz, 2H), 3.60 (t, *J* = 5 Hz, 4H), 3.24 (t, *J* = 5 Hz, 4H), 1.48 (s, 9H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 154.5, 153.1, 126.3 (q, $^3J_{C–F}$ = 3.75 Hz), 124.5 (q, $^1J_{C–F}$ = 268.8 Hz), 120.9 (q, $^1J_{C–F}$ = 32.5 Hz), 115.1, 80.0, 48.0, 28.3.

^{19}F NMR (282 MHz, CDCl$_3$) δ –62.0 (s, 3F).



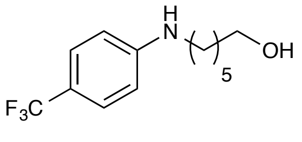
N-(2,2,2-Trifluoroethyl)-4-(trifluoromethyl)aniline 12

To a solution of 4-bromobenzotrifluoride (114 µL, 0.814 mmol, 1.0 equiv), 2,2,2-trifluoroethylamine (97 µL, 1.236 mmol, 1.5 equiv), and DABCO (164 mg, 1.466 mmol, 1.8 equiv) in DMA (1.5 mL) was added photocatalyst **1** (0.165 mg, 0.0002 equiv) as a solution in DMA (6.5 µL). A solution of NiBr$_2$•glyme (12.56 mg, 0.041 mmol, 0.05 equiv) in DMA (1.5 mL), which had been sonicated for 5 min, was then added. The vial was placed under an atmosphere of nitrogen, cooled to –78 °C, degassed via vacuum evacuation (5 min), backfilled with nitrogen, and warmed to room temperature. This process was repeated three times, and the reaction vial was then sealed with parafilm, placed 6 cm away from one blue LED, and irradiated. The reaction vial was heated to approximately 55 °C by the blue LED without fan cooling. After 48 h, the reaction mixture was purified directly by flash column chromatography (SiO$_2$, 0% to 2% diethyl ether in pentane eluent) to give a yellow oil (152 mg, 0.627 mmol, 77% yield). The spectral data matched that reported in the literature *(37)*.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.46 (d, *J* = 8.3 Hz, 2H), 6.72 (d, *J* = 8.5 Hz, 2H), 4.25 (t, *J* = 7.3 Hz, 1H), 3.81 (qd, *J* = 8.8, 7.0 Hz, 2H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 148.9, 126.9 (q, $^3J_{C–F}$ = 3.75 Hz), 124.8 (q, $^1J_{C–F}$ = 268.8 Hz), 124.9 (q, $^1J_{C–F}$ = 227.5 Hz), 120.9 (q, $^2J_{C–F}$ = 32.5 Hz), 112.5, 45.5 (q, $^2J_{C–F}$ = 35.5 Hz).

^{19}F NMR (282 MHz, CDCl$_3$) δ –61.9 (s, 3F), –72.8 (s, 3F).



6-((4-(trifluoromethyl)phenyl)amino)hexan-1-ol 13

To a solution of 4-bromobenzotrifluoride (114 µL, 0.814 mmol, 1.0 equiv), 6-aminohexan-1-ol (143 mg, 1.221 mmol, 1.5 equiv), and DABCO (164 mg, 1.466 mmol, 1.8 equiv) in DMA (1.5 mL) was added photocatalyst **1** (0.165 mg, 0.0002 equiv) as a solution in DMA (19.5 µL). A solution of $NiBr_2$•glyme (12.56 mg, 0.041 mmol, 0.05 equiv) in DMA (1.5 mL), which had been sonicated for 5 min, was then added. The vial was placed under an atmosphere of nitrogen, cooled to –78 °C, degassed via vacuum evacuation (5 min), backfilled with nitrogen, and warmed to room temperature. This process was repeated three times, and the reaction vial was then sealed with parafilm, placed 6 cm away from one blue LED, and irradiated. The reaction vial was maintained at ambient temperature by fan cooling. After 16 h, the reaction was diluted with diethyl ether and extracted with brine (3 x 60 mL), organics dried over $MgSO_4$, and concentrated *in vacuo.* The crude material was purified by flash column chromatography (SiO_2, 0% to 75% diethyl ether in pentane eluent) to give a colorless oil (162 mg, 0.621 mmol, 76% yield).

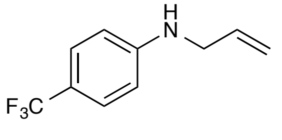
IR (film), ν_{max} 3357, 2934, 2861, 1616, 1535, 1482, 1416, 1319, 1186, 1157, 1100, 1061, 1006, 940, 823 cm^{-1}

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, J = 8.4 Hz, 2H), 6.58 (d, J = 8.4 Hz, 2H), 3.96 (s, 1H), 3.66 (t, J = 6.5 Hz, 2H), 3.25–3.08 (m, 2H), 1.74–1.53 (m, 5H), 1.48–1.36 (m, 4H), 1.25 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 150.9, 126.7 (q, $^3J_{C–F}$ = 4.1 Hz), 125.2 (q, $^1J_{C–F}$ = 270.6 Hz), 118.5 (q, $^2J_{C–F}$ = 32.8 Hz), 111.8, 63.0, 43.5, 32.7, 29.4, 27.0, 25.7.

^{19}F NMR (282 MHz, $CDCl_3$) δ –61.5 (s, 3F).

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{19}F_3NO$([M+H]$^+$) 261.1341, found 261.1343.



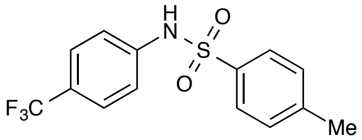
***N*-allyl-4-(trifluoromethyl)aniline 14**

To a solution of 4-bromobenzotrifluoride (114 µL, 0.814 mmol, 1.0 equiv), allyl amine (92 µL, 1.221 mmol, 1.5 equiv), and DABCO (164 mg, 1.466 mmol, 1.8 equiv) in DMA (1.5 mL) was added photocatalyst **1** (0.165 mg, 0.0002 equiv) as a solution in DMA (19.5 µL). A solution of $NiBr_2$•glyme (12.56 mg, 0.041 mmol, 0.05 equiv) in DMA (1.5 mL), which had been sonicated for 5 min, was then added. The vial was placed under an atmosphere of nitrogen, cooled to –78 °C, degassed via vacuum evacuation (5 min), backfilled with nitrogen, and warmed to room temperature. This process was repeated three times, and the reaction vial was then sealed with parafilm, placed 6 cm away from one blue LED, and irradiated. The reaction vial was heated to approximately 55 °C by the blue LED without fan cooling. After 21 h, the reaction mixture was purified directly by flash column chromatography (SiO_2, 0% to 3% diethyl ether in pentane eluent) to give a colorless oil (125 mg, 0.621 mmol, 76% yield). The spectral data matched that reported in the literature *(38)*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, J = 8.3 Hz, 2H), 6.62 (d, J = 8.4 Hz, 2H), 5.93 (ddt, J = 17.2, 10.4, 5.2 Hz, 1H), 5.29 (dd, J = 17.2, 1.6 Hz, 1H), 5.20 (dd, J = 10.3, 1.5 Hz, 1H), 4.13 (s, 1H), 3.85 – 3.78 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 150.6, 134.6, 126.7 (q, $^3J_{C–F}$ = 3.8 Hz), 125.1 (q, $^1J_{C–F}$ = 267.5 Hz), 119.1 (q, $^2J_{C–F}$ = 32.5 Hz), 116.9, 112.1, 46.1.

^{19}F NMR (282 MHz, $CDCl_3$) δ –61.5 (s, 3F).



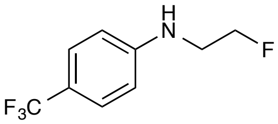
4-methyl-*N*-(4-(trifluoromethyl)phenyl)benzenesulfonamide 15

To an 8 mL vial was added 1-bromo-4-(trifluoromethyl)benzene (116 μL, 0.825 mmol, 1.0 equiv.), MTBD (118 μL, 0.825 mmol, 1.0 equiv.), pyrrolidine (6.9 μL, 0.083 mmol, 0.1 equiv), $NiCl_2$•DME (9.1 mg, 0.041 mmol, 0.05 equiv.), 4-methylbenzenesulfonamide (212 mg, 1.24 mmol, 1.5 equiv.), a solution of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.0002 equiv.) in DMSO (165 μL), and DMSO (2.9 mL, [0.27 M]). The vial was placed under an atmosphere of nitrogen, cooled to –78 °C, degassed via vacuum evacuation (5 min), backfilled with nitrogen, and warmed to room temperature. This process was repeated three times, and the reaction vial was then sealed with parafilm, placed 6 cm away from one blue LED, and irradiated. The reaction vial was heated to roughly 55 °C by the blue LED without the use of a fan. After 19 h, the reaction mixture was purified directly by flash column chromatography (SiO_2, 10% to 50% EtOAc in hexanes eluent) to give a colorless oil (187 mg, 0.594 mmol, 72% yield). No formation of pyrrolidine-coupled product was observed by ^{1}H NMR analysis of the crude reaction mixture. The spectral data matched that reported in the literature *(39)*.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 7.9 Hz, 2H), 7.66 (s, 1H), 7.50 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.3 Hz, 2H), 2.41 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.7, 140.1, 135.6, 130.1, 127.4, 126.7 (q, $^3J_{C–F}$ = 3.8 Hz), 126.5 (q, $^2J_{C–F}$ = 32.8 Hz), 124.0 (q, $^1J_{C–F}$ = 271.7 Hz), 119.6, 21.7.

^{19}F NMR (471 MHz, $CDCl_3$) δ −62.3.



N-(2-fluoroethyl)-4-(trifluoromethyl)aniline 16

To a solution of 4-bromobenzotrifluoride (114 µL, 0.814 mmol, 1.0 equiv), 2-fluoroethylamine hydrogen chloride (243 mg, 2.448 mmol, 3.0 equiv), and MTBD (468 µL, 2.932 mmol, 4.0 equiv) in DMA (1.5 mL) was added photocatalyst **1** (0.021 mg, 0.00002 equiv) as a solution in DMA (2.5 µL). A solution of $NiBr_2$•glyme (17.59 mg, 0.057 mmol, 0.07 equiv) in DMA (1.5 mL), which had been sonicated for 5 min, was then added. The vial was placed under an atmosphere of nitrogen, cooled to –78 °C, degassed via vacuum evacuation (5 min), backfilled with nitrogen, and warmed to room temperature. This process was repeated three times, and the reaction vial was then sealed with parafilm, placed 6 cm away from one blue LED, and irradiated. The reaction vial was heated to approximately 55 °C by the blue LED without fan cooling. After 72 h, the reaction mixture was purified directly by flash column chromatography (SiO_2, 0% to 15% diethyl ether in pentane eluent) to give a colorless oil (137 mg, 0.661 mmol, 81% yield).

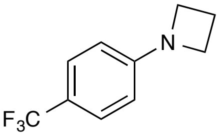
IR (film), ν_{max} 3429, 2965, 1617, 1535, 1321, 1280, 1190, 1161, 1102, 1064, 825 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, J = 8.4 Hz, 2H), 6.64 (d, J = 8.4 Hz, 2H), 4.63 (dt, J = 47.3, 4.9 Hz, 2H), 4.31 (s, 1H), 3.48 (dt, J = 26.6, 4.9 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 150.2, 126.9 (q, $^3J_{C–F}$ = 3.8 Hz), 125.0 (q, $^1J_{C–F}$ = 270.6 Hz), 119.7 (q, $^2J_{C–F}$ = 32.6 Hz), 112.3, 82.3 (d, $^1J_{C–F}$ = 167.9 Hz), 43.8 (d, $^2J_{C–F}$ = 20.3 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ –61.7, –225.0 (tt, $^2J_{H–F}$ = 47.4 Hz, $^3J_{H–F}$ = 26.7 Hz).

HRMS (EI-TOF) m/z calcd. for $C_9H_9F_4N([M+H]^+)$ 207.0671, found 207.0670.



1-(4-(trifluoromethyl)phenyl)azetidine 17

To a solution of 4-bromobenzotrifluoride (114 µL, 0. 814 mmol, 1.0 equiv), azetidine hydrogen chloride (114 mg, 1.218 mmol, 1.5 equiv), and MTBD (220 µL, 1.532 mmol, 1.9 equiv) in DMA (1.5 mL) was added photocatalyst **1** (0.183 mg, 0.0002 equiv) as a solution in DMA (6.6 µL). A solution of $NiCl_2$•glyme (9 mg, 0.041 mmol, 0.05 equiv) in DMA (1.5 mL), which had been sonicated for 5 min, was then added. The vial was placed under an atmosphere of nitrogen, cooled to –78 °C, degassed via vacuum evacuation (5 min), backfilled with nitrogen, and warmed to room temperature. This process was repeated three times, and the reaction vial was then sealed with parafilm, placed 6 cm away from one blue LED, and irradiated with a blue LED. The reaction vial was maintained at 25 °C by fan cooling. After 48 h, the reaction was diluted with diethyl ether and extracted with brine (3 x 60 mL), organics dried over $MgSO_4$, and concentrated *in vacuo.* The crude material was purified by flash column chromatography (SiO_2, 0% to 2% diethyl ether in pentane) as a white solid (114 mg, 70%).

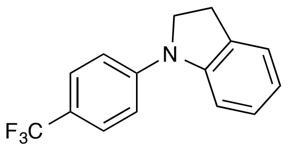
IR (film), ν_{max} 2967, 2928, 2865, 1613, 1528, 1486, 1378, 1317, 1266, 1239, 1156, 1123, 1102, 1063, 1029 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 8.3 Hz, 2H), 6.41 (d, J = 8.4 Hz, 2H), 3.94 (t, J = 7.3 Hz, 4H), 2.41 (p, J = 7.3 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 153.9, 126.4 (q, $^1J_{C\text{–}F}$ = 267.5 Hz), 126.4 (q, $^3J_{C\text{–}F}$ = 3.75 Hz), 118.6 (q, $^2J_{C\text{–}F}$ = 32.5 Hz), 110.4, 52.1, 16.9.

^{19}F NMR (282 MHz, $CDCl_3$) δ –61.4 (s, 3F).

HRMS (ESI-TOF) m/z calcd. for $C_{10}H_{11}F_3N$ ($[M+H]^+$) 201.0765, found 201.0766.



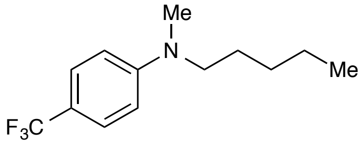
1-(4-(Trifluoromethyl)phenyl)indoline 18

To a solution of 4-bromobenzotrifluoride (114 µL, 0.814 mmol, 1.0 equiv), indoline (137 µL, 1.221 mmol, 1.5 equiv), and DABCO (164 mg, 1.466 mmol, 1.8 equiv) in DMA (1.5 mL) was added photocatalyst **1** (0.165 mg, 0.0002 equiv) as a solution in DMA (6.5 µL). A solution of $NiBr_2$•glyme (12.56 mg, 0.041 mmol, 0.05 equiv) in DMA (1.5 mL), which had been sonicated for 5 min, was then added. The vial was placed under an atmosphere of nitrogen, cooled to –78 °C, degassed via vacuum evacuation (5 min), backfilled with nitrogen, and warmed to room temperature. This process was repeated three times, and the reaction vial was then sealed with parafilm, placed 6 cm away from one blue LED, and irradiated. The reaction vial was heated to approximately 55 °C by the blue LED without fan cooling. After 8 h, the reaction mixture was purified directly by flash column chromatography (SiO_2, 0% to 5% diethyl ether in pentane eluent) to give a white solid (188 mg, 0.623 mmol, 88% yield). The spectral data matched that reported in the literature *(40).*

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, J = 8.5 Hz, 2H), 7.26–7.23 (m, 4H), 7.12 (td, J = 7.7, 1.2 Hz, 1H), 6.83 (td, J = 7.4 Hz, 1.0 Hz, 1H), 4.00 (t, J = 8.4 Hz, 2H), 3.17 (t, J = 8.3 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 146.8, 145.7, 131.9, 127.3, 126.5 (q, $^3J_{C\text{–}F}$ = 3.75 Hz), 125.5, 124.6 (q, $^1J_{C\text{–}F}$ = 268.8 Hz), 122.0 (q, $^2J_{C\text{–}F}$ = 32.5 Hz), 120.3, 116.1, 109.2, 52.0, 28.2.

^{19}F NMR (282 MHz, $CDCl_3$), δ –62.0 (s, 3F).



N-methyl-N-pentyl-4-(trifluoromethyl)aniline 19

To an 8 mL vial was added 1-bromo-4-(trifluoromethyl)benzene (116 μL, 0.825 mmol, 1.0 equiv.), DABCO (166 mg, 1.485 mmol, 1.8 equiv.), $NiBr_2$•DME (25.4 mg, 0.0825 mmol, 0.10 equiv.), N-methylpentan-1-amine (339 μL, 2.475 mmol, 3.0 equiv.), a solution of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.00002 equiv.) in DMA (16.5 μL), and DMA (3.1 mL, [0.27 M]). The vial was placed under an atmosphere of nitrogen, cooled to –78 °C, degassed via vacuum evacuation (5 min), backfilled with nitrogen, and warmed to room temperature. This process was repeated three times, and the reaction vial was then sealed with parafilm, placed 6 cm away from one blue LED, and irradiated. The reaction vial was heated to roughly 55 °C by the blue LED without the use of a fan. After 42 h, the reaction mixture was purified directly by flash column chromatography (SiO_2, 2% to 10% EtOAc in hexanes eluent) to give a colorless oil (148 mg, 0.602 mmol, 73% yield).

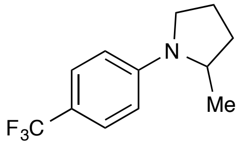
IR (film), ν_{max} 2930, 1616, 1533, 1323, 1102, 1068, 815 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.8 Hz, 2H), 6.7 (d, J = 8.7 Hz, 2H), 3.34 (t, J = 7.4 Hz, 2H), 2.98 (s, 3H), 1.64–1.53 (m, 2H), 1.41–1.26 (m, 4H), 0.92 (t, J = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.3, 126.5 (q, $^3J_{C-F}$ = 3.8 Hz), 123.3 (q, $^1J_{C-F}$ = 270.0 Hz), 117.0 (q, $^2J_{C-F}$ = 32.6 Hz), 110.9, 52.6, 38.4, 29.4, 26.5, 22.7, 14.2.

^{19}F NMR (471 MHz, $CDCl_3$) δ −60.7.

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{19}F_3N$ ($[M+H]^+$) 246.1464, found m/z 246.1450.



2-methyl-1-(4-(trifluoromethyl)phenyl)pyrrolidine 20

To a solution of 4-bromobenzotrifluoride (114 μL, 0.814 mmol, 1.0 equiv), 2-methylpyrrolidine (125 μL, 1.224 mmol, 1.5 equiv), and DABCO (164 mg, 1.466 mmol, 1.8 equiv) in DMA (1.5 mL) was added photocatalyst **1** (0.084 mg, 0.0001 equiv) as a solution in DMA (9.8 μL). A solution of $NiBr_2$•glyme (16.8 mg, 0.055 mmol, 0.07 equiv) in DMA (1.5 mL), which had been sonicated for 5 min, was then added. The vial was placed under an atmosphere of nitrogen, cooled to –78 °C, degassed via vacuum evacuation (5 min), backfilled with nitrogen, and warmed to room temperature. This process was repeated three times, and the reaction vial was then sealed with parafilm, placed 6 cm away from one blue LED, and irradiated. The reaction vial was heated to approximately 55 °C by the blue LED without fan cooling. After 24 h, the reaction was diluted with diethyl ether and extracted with brine (3 x 60 mL), organics dried over $MgSO_4$, and concentrated *in vacuo*. The crude material was purified by flash column chromatography (SiO_2, 0% to 3% diethyl ether in pentane eluent) to give a colorless oil (112 mg, 0.490 mmol, 60% yield).

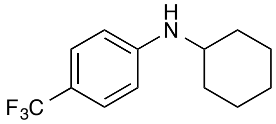
IR (film), ν_{max} 2970, 1614, 1531, 1378, 1323, 1195, 1155, 1104, 1069, 816 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.7 Hz, 2H), 6.56 (d, *J* = 8.7 Hz, 2H), 3.93 (p, *J* = 6.1 Hz, 1H), 3.44 (t, *J* = 8.6 Hz, 1H), 3.20 (q, *J* = 8.4 Hz, 1H), 2.16–1.98 (m, 3H), 1.74 (m, 1H), 1.18 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 149.2, 126.5 (q, $^3J_{C-F}$ = 3.8 Hz), 125.5 (q, $^1J_{C-F}$ = 268.8 Hz), 116.6 (q, $^2J_{C-F}$ = 32.7 Hz), 111.1, 53.8, 48.1, 33.1, 23.3, 19.0.

^{19}F NMR (282 MHz, $CDCl_3$) δ –61.2 (s, 3F).

HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{15}F_3N$ ($[M+H]^+$) 229.1078, found 229.1077.



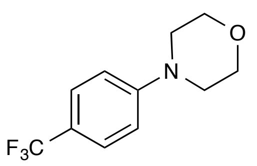
N-cyclohexyl-4-(trifluoromethyl)aniline 21

To a solution of 4-bromobenzotrifluoride (114 µL, 0.814 mmol, 1.0 equiv), cyclohexylamine (279 µL, 2.443 mmol, 3.0 equiv), and DABCO (329 mg, 2.931 mmol, 3.6 equiv) in DMA (1.5 mL) was added photocatalyst **1** (0.041 mg, 0.00005 equiv) as a solution in DMA (4.9 µL). A solution of $NiBr_2$•glyme (12.56 mg, 0.041 mmol, 0.05 equiv) in DMA (1.5 mL), which had been sonicated for 5 min, was then added. The vial was placed under an atmosphere of nitrogen, cooled to –78 °C, degassed via vacuum evacuation (5 min), backfilled with nitrogen, and warmed to room temperature. This process was repeated three times, and the reaction vial was then sealed with parafilm, placed 6 cm away from one blue LED, and irradiated. The reaction vial was heated to approximately 55 °C by the blue LED without fan cooling. After 24 h, the reaction mixture was purified directly by flash column chromatography (SiO_2, 0% to 3% diethyl ether in pentane eluent) to give a white solid (157 mg, 0.645 mmol, 79% yield). The spectral data matched that reported in the literature *(41)*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.5 Hz, 2H), 6.56 (d, *J* = 8.5 Hz, 2H), 3.87 (s, 1H), 3.29 (s, 1H), 2.05 (dd, *J* = 12.8, 4.0 Hz, 2H), 1.77 (dt, *J* = 13.5, 3.9 Hz, 2H), 1.66 (dt, *J* = 12.9, 3.9 Hz, 1H), 1.44 – 1.33 (m, 2H), 1.29 – 1.10 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 149.9, 126.8 (q, $^3J_{C-F}$ = 4.1 Hz), 125.2 (q, $^1J_{C-F}$ = 267.5 Hz), 118.2 (q, $^2J_{C-F}$ = 32.7 Hz), 112.1, 51.5, 33.3, 25.9, 25.0.

^{19}F NMR (282 MHz, $CDCl_3$) δ –61.5 (s, 3F).



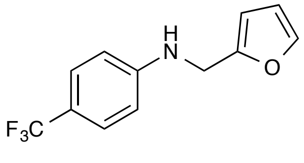
4-(4-(trifluoromethyl)phenyl)morpholine 22

To a solution of 4-bromobenzotrifluoride (115 µL, 0.832 mmol, 1.0 equiv), morpholine (115 µL, 1.232 mmol, 1.5 equiv), and DABCO (166 mg, 1.484 mmol, 1.8 equiv) in DMA (1.5 mL) was added photocatalyst **1** (0.183 mg, 0.0002 equiv) as a solution in DMA (6.6 µL). A solution of $NiCl_2$•glyme (9 mg, 0.041 mmol, 0.05 equiv) in DMA (1.5 mL), which had been sonicated for 5 min, was then added. The vial was placed under an atmosphere of nitrogen, cooled to –78 °C, degassed via vacuum evacuation (5 min), backfilled with nitrogen, and warmed to room temperature. This process was repeated three times, and the reaction vial was then sealed with parafilm, placed 6 cm away from one blue LED, and irradiated. The reaction vial was maintained at ambient temperature by fan cooling. After 8 h, the reaction mixture was purified directly by flash column chromatography (SiO_2, 0% to 10% ethyl acetate in hexanes eluent) to give a white solid (175 mg, 0.631 mmol, 76% yield). The spectral data matched that reported in the literature *(42).*

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, J = 8.6 Hz, 2H), 6.90 (d, J = 8.7 Hz, 2H), 3.81 (t, J = 5.0 Hz, 4H), 3.17 (t, J = 5.0 Hz, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 153.2, 126.3 (q, $^3J_{C\text{–}F}$ = 3.75 Hz), 124.5 (q, $^1J_{C\text{–}F}$ = 270 Hz), 120.9 (q, $^2J_{C\text{–}F}$ = 32.5 Hz), 114.2, 66.5, 48.0.

^{19}F NMR (282 MHz, $CDCl_3$) δ –62.0 (s, 3F).



***N*-(furan-2-ylmethyl)-4-(trifluoromethyl)aniline 23**

To a solution of 4-bromobenzotrifluoride (114 µL, 0.814 mmol, 1.0 equiv), furfuryl amine (132 µL, 1.221 mmol, 1.5 equiv), and DABCO (164 mg, 1.466 mmol, 1.8 equiv) in DMA (1.5 mL) was added photocatalyst **1** (0.165 mg, 0.0002 equiv) as a solution in DMA (19.5 µL). A solution of $NiBr_2$•glyme (12.56 mg, 0.041 mmol, 0.05 equiv) in DMA (1.5 mL), which had been sonicated for 5 min, was then added. The vial was placed under an atmosphere of nitrogen, cooled to –78 °C, degassed via vacuum evacuation (5 min), backfilled with nitrogen, and warmed to room temperature. This process was repeated three times, and the reaction vial was then sealed with parafilm, placed 6 cm away from one blue LED, and irradiated. The reaction vial was heated to approximately 55 °C by the blue LED without fan cooling. After 8 h, the reaction mixture was purified directly by flash column chromatography (SiO_2, 0% to 5% diethyl ether in pentane eluent) to give a white solid (177 mg, 0.733 mmol, 90% yield).

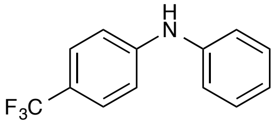
IR (film), ν_{max} 3424, 2922, 1615, 1530, 1483, 1455, 1415, 1320, 1257, 1188, 1163, 1147, 1106, 1062, 1014, 945, 910, 883, 830, 819, 745, 731 cm^{-1}.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.42 (d, *J* = 8.5 Hz, 2H), 7.38 (dd, *J* = 1.8, 0.7 Hz, 1H), 6.68 (d, *J* = 8.5 Hz, 2H), 6.34 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.25 (d, *J* = 3.1 Hz, 1H), 4.36 (s, 3H, CH$_2$ and NH).

^{13}C NMR (125 MHz, CDCl$_3$) δ 151.9, 150.1, 142.3, 126.7 (q, $^1J_{C\text{–}F}$ = 268.8 Hz), 125.0 (q, $^3J_{C\text{–}F}$ = 5.0 Hz), 119.6 (q, $^2J_{C\text{–}F}$ = 32.5 Hz), 112.3, 110.6, 107.5, 41.0.

^{19}F NMR (282 MHz, CDCl$_3$) δ –61.6 (s, 3F).

HRMS (ESI-TOF) m/z calcd. For $C_{12}H_{11}F_3NO$ ([M+H]$^+$) 241.0709, found 241.0722.



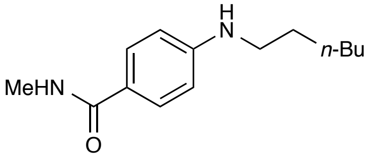
***N*-phenyl-4-(trifluoromethyl)aniline 24**

To a solution of 4-bromobenzotrifluoride (114 μL, 0.814 mmol, 1.0 equiv), aniline (111 μL, 1.221 mmol, 1.5 equiv), pyrrolidine (6.8 μL, 0.081 mmol, 0.1 equiv) and DABCO (164 mg, 1.466 mmol, 1.8 equiv) in DMA (1.5 mL) was added photocatalyst **1** (0.041 mg, 0.00005 equiv) as a solution in DMA (4.9 μL). A solution of NiBr$_2$•glyme (1.26 mg, 0.0041 mmol, 0.005 equiv) in DMA (1.5 mL), which had been sonicated for 5 min, was then added. The vial was placed under an atmosphere of nitrogen, cooled to –78 °C, degassed via vacuum evacuation (5 min), backfilled with nitrogen, and warmed to room temperature. This process was repeated three times, and the reaction vial was then sealed with parafilm, placed 6 cm away from one blue LED, and irradiated. The reaction vial was heated to approximately 55 °C by the blue LED without fan cooling. After 24 h, the reaction mixture was purified directly by flash column chromatography (SiO$_2$, 0% to 3% diethyl ether in pentane eluent) to give a white solid (162 mg, 0.682 mmol, 84% yield). The pyrrolidine-coupled side product was formed in 7% yield, as determined by analysis of the crude reaction mixture by ^{1}H NMR spectroscopy. The spectral data matched that reported in the literature *(43)*.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.35 (t, *J* = 7.9 Hz, 2H), 7.1 (d, *J* = 7.6 Hz, 2H), 7.09 – 7.04 (m, 3H), 5.91 (s, 1H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 146.8, 141.1, 129.6, 126.7 (q, $^3J_{C\text{–}F}$ = 3.75 Hz), 124.6 (q, $^1J_{C\text{–}F}$ = 268.8 Hz), 123.0, 121.7 (q, $^2J_{C\text{–}F}$ = 32.5 Hz), 120.0, 115.3.

^{19}F NMR (282 Hz, CDCl$_3$) δ –62.0 (s, 3F).



4-(hexylamino)-*N*-methylbenzamide 25

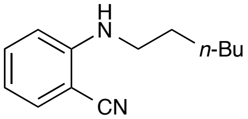
To an 8 mL vial was added 4-bromo-*N*-methylbenzamide (176 mg, 0.825 mmol, 1.0 equiv.), DABCO (166 mg, 1.485 mmol, 1.8 equiv.), $NiCl_2$•DME (9.1 mg, 0.041 mmol, 0.05 equiv.), hexylamine (162 µL, 1.24 mmol, 1.5 equiv.), a solution of Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (0.0002 equiv.) in DMA (165 µL), and DMA (2.9 mL, [0.27 M]). The vial was placed under an atmosphere of nitrogen, cooled to – 78 °C, degassed via vacuum evacuation (5 min), backfilled with nitrogen, and warmed to room temperature. This process was repeated three times, and the reaction vial was then sealed with parafilm, placed 6 cm away from one blue LED, and irradiated. A fan was used to cool the reaction vial to ambient temperature. After 19 h, the reaction mixture was diluted with ethyl acetate (60 mL) and poured into a separatory funnel containing brine (60 mL). The aqueous phase was separated and extracted with ethyl acetate (60 mL). The combined organic extracts were washed again with brine (2 x 30 mL) and concentrated *in vacuo*. The crude reaction mixture was purified by flash column chromatography (SiO_2, 25% to 50% EtOAc in DCM eluent) to give a white solid (135 mg, 0.578 mmol, 70% yield).

IR (film), ν_{max} 3334, 2927, 2360, 1599, 1517, 1193, 832 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.7 Hz, 2H), 6.55 (d, *J* = 8.4 Hz, 2H), 6.04–5.88 (br s, 1H), 4.03–3.86 (br s, 1H), 3.14 (q, *J* = 6.5 Hz, 3H), 2.97 (d, *J* = 4.7 Hz, 3H), 1.68–1.57 (m, 2H), 1.46–1.22 (m, 6H), 0.96–0.83 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.2, 151.1, 128.6, 122.6, 111.7, 43.7, 31.7, 29.5, 26.9, 26.8, 22.8, 14.2.

HRMS (ESI-TOF) m/z calcd. for $C_{14}H_{23}N_2O$ ([M+H]$^+$) 235.1805, found m/z 235.1802.



2-(Hexylamino)benzonitrile 26

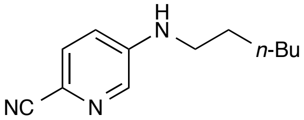
To an 8 mL vial was added 2-bromobenzonitrile (148 mg, 0.813 mmol, 1.0 equiv.), hexylamine (161 µL, 1.219 mmol, 1.5 equiv.), and DABCO (164 mg, 1.466 mmol, 1.8 equiv.) in DMA (1.5 mL) was added photocatalyst **1** (0.021 mg, 0.00002 equiv) as a solution in DMA (2.5 µL). A solution of $NiCl_2$•DME (9.1 mg, 0.041 mmol, 0.05 equiv.) in DMA (1.5 mL), which had been sonicated for five min, was then added. The vial was placed under an atmosphere of nitrogen, cooled to –78 °C, degassed via vacuum evacuation (5 min), backfilled with nitrogen, and warmed to room temperature. This process was repeated three times, and the reaction vial was then sealed with parafilm, placed 6 cm away from one blue LED, and irradiated. The reaction vial was heated to roughly 55 °C by the blue LED without the use of a fan. After 24 h, the reaction mixture was purified directly by flash column chromatography (SiO_2, 0% to 25% EtOAc in hexanes eluent) to give a white solid (137 mg, 0.677 mmol, 83% yield).

IR (film), ν_{max} 3377, 2955, 2928, 2858, 2212, 1606, 1577, 1515, 1460, 1378, 1325, 1291, 1267, 1232, 1165, 1071, 1042 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.39 (m, 2H), 6.69–6.66(m, 2H), 4.52 (s, 1H), 3.24–3.16 (m, 2H), 1.66 (p, *J* = 7.3 Hz, 2H), 1.42 (m, 2H), 1.38–1.29 (m, *J* = 6.8 Hz, 4H), 0.95 (t, *J* = 5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 150.5, 134.4, 132.9, 118.2, 116.3, 110.7, 95.6, 43.5, 31.7, 29.2, 26.8, 22.7, 14.2.

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{19}N_2$ ($[M+H]^+$) 202.1470, found 202.1470 .



5-(Hexylamino)picolinonitrile 27

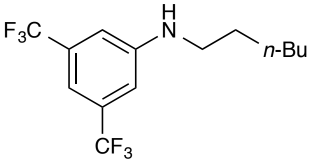
To an 8 mL vial was added 5-bromopicolinonitrile (148 mg, 0.813 mmol, 1.0 equiv.), hexylamine (161 µL, 1.219 mmol, 1.5 equiv.), and DABCO (164 mg, 1.466 mmol, 1.8 equiv.) in DMA (1.5 mL) was added photocatalyst **1** (0.021 mg, 0.00002 equiv) as a solution in DMA (2.5 µL). A solution of $NiCl_2$•DME (9.1 mg, 0.041 mmol, 0.05 equiv.) in DMA (1.5 mL), which had been sonicated for 5 min, was then added. The vial was placed under an atmosphere of nitrogen, cooled to –78 °C, degassed via vacuum evacuation (5 min), backfilled with nitrogen, and warmed to room temperature. This process was repeated three times, and the reaction vial was then sealed with parafilm, placed 6 cm away from one blue LED, and irradiated. The reaction vial was heated to roughly 55 °C by the blue LED without the use of a fan. After 7 h, the reaction was diluted with diethyl ether and extracted with brine (3 x 60 mL). The organics were combined, dried over $MgSO_4$, and concentrated *in vacuo.* The crude product was purified by flash chromatography (SiO_2, 0% to 30% ethyl acetate in hexanes) to give a pale yellow oil (131 mg, 0.644 mmol, 79% yield).

IR (film), ν_{max} 3362, 2954, 2928, 2857, 2220, 1581, 1518, 1468, 1400, 1347, 1316, 1292, 1264, 1209, 1139, 1124, 1086, 1007 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.44 (d, *J* = 8.6 Hz, 1H), 6.78 (dd, *J* = 8.5, 2.9 Hz, 1H), 4.41 (br s, 1H), 3.15 (t, *J* = 7.0 Hz, 2H), 1.64 (p, *J* = 7.3 Hz, 2H), 1.39 (q, *J* = 6.8, 6.3 Hz, 2H), 1.31 (m, 4H), 0.92 (t, *J* = 1.25 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7, 137.3, 129.7, 119.6, 118.9, 116.0, 43.1, 31.6, 28.9, 26.7, 22.6, 14.1.

HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{18}N_3$ ($[M+H]^+$) 203.1423, found 203.1423.



N-hexyl-3,5-bis(trifluoromethyl)aniline 28

To an 8 mL vial was added 1-bromo-3,5-bis(trifluoromethyl)benzene (142 μL, 0.825 mmol, 1.0 equiv.), DABCO (166 mg, 1.485 mmol, 1.8 equiv.), $NiCl_2$•DME (9.1 mg, 0.041 mmol, 0.05 equiv.), hexylamine (162 μL, 1.24 mmol, 1.5 equiv.), a solution of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.00002 equiv.) in DMA (16.5 μL), and DMA (3.1 mL, [0.27 M]). The vial was placed under an atmosphere of nitrogen, cooled to – 78 °C, degassed via vacuum evacuation (5 min), backfilled with nitrogen, and warmed to room temperature. This process was repeated three times, and the reaction vial was then sealed with parafilm, placed 6 cm away from one blue LED, and irradiated. The reaction vial was heated to roughly 55 °C by the blue LED without the use of a fan. After 19 h, the reaction mixture was purified directly by flash column chromatography (SiO_2, 5% to 25% EtOAc in hexanes eluent) to give a colorless oil (240 mg, 0.767 mmol, 93% yield).

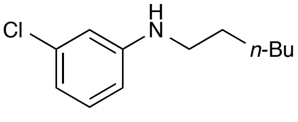
IR (film), ν_{max} 2931, 2326, 1623, 1275, 1170, 1127, 682 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15−7.09 (s, 1H), 6.94−6.88 (s, 2H), 4.09−3.99 (br s, 1H), 3.21−3.09 (m, 2H), 1.65 (p, J = 7.3, 7.2 Hz, 2H), 1.49−1.24 (m, 6H), 0.97−0.85 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.1, 132.5 (q, J_{C-F} = 32.9 Hz), 123.8 (q, J_{C-F} = 272.7 Hz), 111.8, 109.9, 43.8, 31.7, 29.3, 26.9, 22.7, 14.1.

^{19}F NMR (471 MHz, $CDCl_3$) δ −63.3.

HRMS (ESI-TOF) m/z calcd. for $C_{14}H_{18}F_6N$ ($[M+H]^+$) 314.1338, found m/z 314.1341.

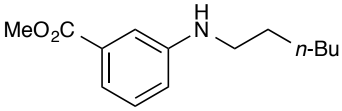


3-chloro-N-hexylaniline 29

To an 8 mL vial was added 1-bromo-3-chlorobenzene (97 μL, 0.825 mmol, 1.0 equiv.), MTBD (118 μL, 0.825 mmol, 1.0 equiv.), $NiCl_2$•DME (9.1 mg, 0.041 mmol, 0.05 equiv.), hexylamine (162 μL, 1.24 mmol, 1.5 equiv.), a solution of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.00002 equiv.) in DMA (16.5 μL), and DMA (3.1 mL, [0.27 M]). The vial was placed under an atmosphere of nitrogen, cooled to −78 °C, degassed via vacuum evacuation (5 min), backfilled with nitrogen, and warmed to room temperature. This process was repeated three times, and the reaction vial was then sealed with parafilm, placed 6 cm away from one blue LED, and irradiated. The reaction vial was heated to roughly 55 °C by the blue LED without the use of a fan. After 17 h, the reaction mixture was purified directly by flash column chromatography (SiO_2, 10% to 25% EtOAc in hexanes eluent) to give a colorless oil (151 mg, 0.718 mmol, 87% yield). The spectral data matched that reported in the literature *(44)*.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.06 (t, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 1H), 6.56 (s, 1H), 6.45 (dd, J = 8.2, 2.2 Hz, 1H), 3.75−3.59 (br s, 1H), 3.08 (t, *J* = 7.1 Hz, 2H), 1.61 (p, *J* = 7.3, 7.2 Hz, 2H), 1.46−1.23 (m, 6H), 0.96−0.83 (m, 3H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 149.7, 135.1, 130.2, 117.0, 112.3, 111.2, 44.0, 31.7, 29.5, 26.9, 22.8, 14.2.



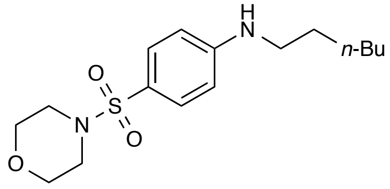
Methyl 3-(hexylamino)benzoate 30

To an 8 mL vial was added methyl 3-bromobenzoate (177 mg, 0.825 mmol, 1.0 equiv.), MTBD (118 µL, 0.825 mmol, 1.0 equiv.), NiCl$_2$•DME (18.2 mg, 0.082 mmol, 0.10 equiv.), hexylamine (162 µL, 1.24 mmol, 1.5 equiv.), a solution of Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (0.00002 equiv.) in DMA (16.5 µL), and DMA (3.1 mL, [0.27 M]). The vial was placed under an atmosphere of nitrogen, cooled to – 78 °C, degassed via vacuum evacuation (5 min), backfilled with nitrogen, and warmed to room temperature. This process was repeated three times, and the reaction vial was then sealed with parafilm, placed 6 cm away from one blue LED, and irradiated. The reaction vial was heated to roughly 55 °C by the blue LED without the use of a fan. After 20 h, the reaction mixture was purified directly by flash column chromatography (SiO$_2$, 10% to 25% EtOAc in hexanes eluent) to give a white solid (165 mg, 0.701 mmol, 85% yield). The spectral data matched that reported in the literature *(45)*.

IR (film), ν_{max} 2930, 2332, 1712, 1525, 1275, 1109, 668 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.37 (d, *J* = 7.6 Hz, 1H), 7.28 (s, 1H), 7.23 (t, *J* = 7.9 Hz, 1H), 6.79 (dd, J = 8.0, 2.5 Hz, 1H), 3.91 (s, 3H), 3.76 (br s, 1H), 3.16 (t, J = 7.1 Hz, 2H), 1.64 (p, J = 7.3, 7.1 Hz, 2H), 1.50−1.27 (m, 6H), 0.93 (t, J = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 167.7, 148.6, 131.1, 129.2, 118.3, 117.3, 113.3, 52.1, 44.0, 31.7, 29.5, 26.9, 22.7, 14.2.



***N*-hexyl-4-(morpholinosulfonyl)aniline 31**

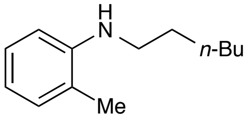
To an 8 mL vial was added 4-((4-bromophenyl)sulfonyl)morpholine (252 mg, 0.825 mmol, 1.0 equiv.), MTBD (118 µL, 0.825 mmol, 1.0 equiv.), NiCl$_2$•DME (9.1 mg, 0.041 mmol, 0.05 equiv.), hexylamine (162 µL, 1.24 mmol, 1.5 equiv.), a solution of Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (0.0002 equiv.) in DMSO (165 µL), and DMSO (2.9 mL, [0.27 M]). The vial was placed under an atmosphere of nitrogen, cooled to –78 °C, degassed via vacuum evacuation (5 min), backfilled with nitrogen, and warmed to room temperature. This process was repeated three times, and the reaction vial was then sealed with parafilm, placed 6 cm away from one blue LED, and irradiated with a blue LED. The reaction vial was heated to roughly 55 °C by the blue LED without the use of a fan. After 19.5 h, the reaction mixture was purified directly by flash column chromatography (SiO_2, 10% to 50% EtOAc in hexanes eluent) to give a white solid (218 mg, 0.668 mmol, 81% yield).

IR (film), ν_{max} 1596, 1343, 1324, 1153, 1112, 1095, 938, 733 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.8 Hz, 2H), 6.59 (t, *J* = 8.8 Hz, 2H), 4.19 (t, *J* = 5.4 Hz, 1H), 3.81–3.65 (m, 4H), 3.16 (t, *J* = 7.1, 5.4 Hz, 2H), 3.96 (dd, *J* = 5.7, 3.8 Hz, 4H), 1.64 (p, *J* = 7.4, 7.1 Hz, 2H), 1.48–1.22 (m, 6H), 0.93–0.88 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 130.1, 121.0, 111.6, 66.2, 46.2, 43.4, 31.6, 29.2, 26.8, 22.7, 14.1.

HRMS (ESI-TOF) m/z calcd. for $C_{16}H_{27}N_2O_3S$ ($[M+H]^+$) 327.1737, found m/z 327.1743.

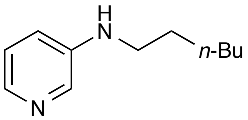


***N*-hexyl-2-methylaniline 32**

To an 8 mL vial was added 1-bromo-2-methylbenzene (99 µL, 0.825 mmol, 1.0 equiv.), MTBD (118 µL, 0.825 mmol, 1.0 equiv.), DABCO (166 mg, 1.485 mmol, 1.8 equiv.), $NiCl_2$•DME (18.2 mg, 0.082 mmol, 0.10 equiv.), hexylamine (162 µL, 1.24 mmol, 1.5 equiv.), a solution of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.00002 equiv.) in DMA (16.5 µL), and DMA (3.1 mL, [0.27 M]). The vial was placed under an atmosphere of nitrogen, cooled to –78 °C, degassed via vacuum evacuation (5 min), backfilled with nitrogen, and warmed to room temperature. This process was repeated three times, and the reaction vial was then sealed with parafilm, placed 6 cm away from one blue LED, and irradiated. The reaction vial was heated to roughly 55 °C by the blue LED without the use of a fan. After 65 h, the reaction mixture was purified directly by flash column chromatography (SiO_2, 10% to 25% EtOAc in hexanes eluent) to give a colorless oil (115 mg, 0.603 mmol, 73% yield). The spectral data matched that reported in the literature *(46)*.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (t, *J* = 7.8 Hz, 1H), 7.06 (d, *J* = 7.3 Hz, 1H), 6.71−6.61 (m, 2H), 3.78−3.28 (br s, 1H), 3.16 (t, *J* = 7.2 Hz, 2H), 2.15 (s, 3H), 1.68 (p, *J* = 7.3, 7.2 Hz, 2H), 1.53−1.20 (m, 6H), 0.98−0.84 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 130.2, 127.3, 121.9, 116.9, 109.9, 44.2, 31.8, 29.7, 27.1, 22.8, 17.6, 14.2.

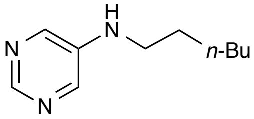


N-hexylpyridin-3-amine 33

To an 8 mL vial was added 3-bromopyridine (79 µL, 0.825 mmol, 1.0 equiv.), DABCO (166 mg, 1.485 mmol, 1.8 equiv.), $NiCl_2$•DME (18.2 mg, 0.082 mmol, 0.10 equiv.), hexylamine (162 µL, 1.24 mmol, 1.5 equiv.), a solution of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.0002 equiv.) in DMA (165 µL), and DMA (2.9 mL, [0.27 M]). The vial was placed under an atmosphere of nitrogen, cooled to –78 °C, degassed via vacuum evacuation (5 min), backfilled with nitrogen, and warmed to room temperature. This process was repeated three times, and the reaction vial was then sealed with parafilm, placed 6 cm away from one blue LED and irradiated. The reaction vial was heated to roughly 55 °C by the blue LED without the use of a fan. After 16 h, the reaction mixture was diluted with ethyl acetate (60 mL) and poured into a separatory funnel containing a solution of 1M NaOH (60 mL). The aqueous phase was separated and extracted with ethyl acetate (60 mL). The combined organic extracts were washed again with brine (2 x 30 mL) and concentrated *in vacuo*. The crude reaction mixture was purified by flash column chromatography (SiO_2, 50% to 100% EtOAc in hexanes eluent) to give a white solid (104 mg, 0.586 mmol, 71% yield). The spectral data matched that reported in the literature *(47).*

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 2.9 Hz, 1H), 7.92 (d, *J* = 4.6 Hz, 1H), 7.05 (dd, *J* = 8.3, 4.6 Hz, 1H), 6.88–6.78 (m, 1H), 3.71 (br s, 1H), 3.09 (t, *J* = 7.3 Hz, 2H), 1.61 (p, *J* = 7.3 Hz, 2H), 1.50–1.17 (m, 6H), 0.99–0.76 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.5, 138.5, 136.1, 123.8, 118.4, 43.7, 31.7, 29.4, 26.9, 22.7, 14.1.



N-hexylpyrimidin-5-amine 34

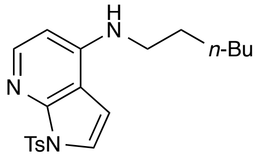
To an 8 mL vial was added 5-bromopyrimidine (130 mg, 0.825 mmol, 1.0 equiv.), DABCO (166 mg, 1.485 mmol, 1.8 equiv.), $NiCl_2$•DME (9.1 mg, 0.041 mmol, 0.05 equiv.), hexylamine (162 µL, 1.24 mmol, 1.5 equiv.), a solution of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.0002 equiv.) in DMSO (165 µL), and DMSO (2.9 mL, [0.27 M]). The vial was placed under an atmosphere of nitrogen, cooled to –78 °C, degassed via vacuum evacuation (5 min), backfilled with nitrogen, and warmed to room temperature. This process was repeated three times, and the reaction vial was then sealed with parafilm, placed 6 cm away from one blue LED and irradiated. A fan was used to cool the reaction vial to ambient temperature. After 15 h, the reaction mixture was purified directly by flash column chromatography (SiO_2, 50% to 100% EtOAc in hexanes eluent) to give a white solid (115 mg, 0.643 mmol, 78% yield).

IR (film), ν_{max} 2360, 2317, 1580, 1433, 1416, 1205 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.08 (s, 2H), 3.81–3.67 (br s, 1H), 3.13 (td, *J* = 7.1, 5.7 Hz, 2H), 1.63 (p, *J* = 7.1 Hz, 2H), 1.48–1.22 (m, 6H), 0.95–0.82 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 148.4, 142.1, 140.7, 43.3, 31.6, 29.3, 26.8, 22.7, 14.1.

HRMS (ESI-TOF) m/z calcd. for $C_{10}H_{18}N_3$ ($[M+H]^+$) 180.1495, found m/z 180.1501.



***N*-hexyl-1-tosyl-1*H*-pyrrolo[2,3-*b*]pyridin-4-amine 35**

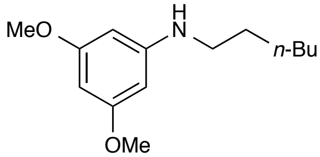
To an 8 mL vial was added 4-bromo-1-tosyl-1*H*-pyrrolo[2,3-*b*]pyridine (289 mg, 0.825 mmol, 1.0 equiv.), DABCO (166 mg, 1.485 mmol, 1.8 equiv.), $NiCl_2$•DME (9.1 mg, 0.041 mmol, 0.05 equiv.), hexylamine (162 µL, 1.24 mmol, 1.5 equiv.), a solution of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.0002 equiv.) in DMA (165 µL), and DMA (2.9 mL, [0.27 M]). The vial was placed under an atmosphere of nitrogen, cooled to –78 °C, degassed via vacuum evacuation (5 min), backfilled with nitrogen, and warmed to room temperature. This process was repeated three times, and the reaction vial was then sealed with parafilm, placed 6 cm away from one blue LED and irradiated. A fan was used to cool the reaction vial to ambient temperature. After 22 h, the reaction mixture was diluted with ethyl acetate (60 mL) and poured into a separatory funnel containing brine (60 mL). The aqueous phase was separated and extracted with ethyl acetate (60 mL). The combined organic extracts were washed again with brine (2 x 30 mL) and concentrated *in vacuo*. The crude reaction mixture was purified by flash column chromatography (SiO_2, 25% to 50% EtOAc in hexanes eluent) to give a white solid (277 mg, 0.750 mmol, 91% yield).

IR (film), ν_{max} 2925, 2359, 1601, 1363, 1180, 1152, 681 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 5.6 Hz, 1H), 8.04 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 4.1 Hz, 1H), 7.24 (d, *J* = 8.3 Hz, 2H), 6.44 (d, *J* = 4.1 Hz, 1H), 6.27 (d, *J* = 5.6 Hz, 1H), 4.32 (t, *J* = 5.4 Hz, 1H), 3.24 (td, *J* = 7.2, 5.6 Hz, 2H), 2.35 (s, 3H), 1.65 (p, *J* = 7.3 Hz, 2H), 1.46–1.20 (m, 6H), 0.94–0.82 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 147.9, 146.8, 144.9, 135.8, 129.6, 128.1, 122.7, 109.6, 101.7, 101.7, 99.6, 43.2, 31.7, 29.4, 26.8, 22.7, 21.8, 14.2.

HRMS (ESI-TOF) m/z calcd. for $C_{20}H_{26}N_3O_2S$ ($[M+H]^+$) 372.1740, found m/z 372.1736.



N-hexyl-3,5-dimethoxyaniline 36

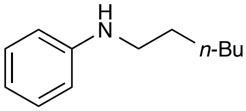
To an 8 mL vial was added 1-bromo-3,5-dimethyoxybenzene (179 mg, 0.825 mmol, 1.0 equiv.), MTBD (118 µL, 0.825 mmol, 1.0 equiv.), $NiCl_2$•DME (9.1 mg, 0.041 mmol, 0.05 equiv.), hexylamine (162 µL, 1.24 mmol, 1.5 equiv.), a solution of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.00002 equiv.) in DMA (16.5 µL), and DMA (3.1 mL, [0.27 M]). The vial was placed under an atmosphere of nitrogen, cooled to –78 °C, degassed via vacuum evacuation (5 min), backfilled with nitrogen, and warmed to room temperature. This process was repeated three times, and the reaction vial was then sealed with parafilm, placed 6 cm away from one blue LED, and irradiated. The reaction vial was heated to roughly 55 °C by the blue LED without the use of a fan. After 42 h, the reaction mixture was purified directly by flash column chromatography (SiO_2, 10% to 25% EtOAc in hexanes eluent) to give a white solid (181 mg, 0.767 mmol, 93% yield).

IR (film), ν_{max} 2927, 2330, 1616, 1595, 1204, 1150, 668 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87 (t, J = 2.1 Hz, 1H), 5.80 (d, J = 2.2 Hz, 2H), 3.76 (s, 6H), 3.73−3.65 (br s, 1H), 3.08 (t, J = 7.2 Hz, 2H), 1.60 (p, J = 7.4, 7.2 Hz), 1.44−1.28 (m, 6H), 0.95−0.87 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 150.5, 91.7, 89.7, 55.3, 44.2, 31.8, 29.6, 27.0, 22.8, 14.2.

HRMS (ESI-TOF) m/z calcd. For $C_{14}H_{24}NO_2$ ($[M+H]^+$) 237.1729, found 237.1728.



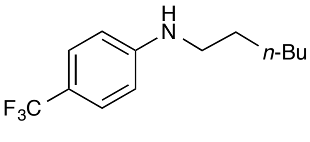
N-hexylaniline

To an 8 mL vial was added bromobenzene (87 µL, 0.825 mmol, 1.0 equiv.), MTBD (118 µL, 0.825 mmol, 1.0 equiv.), $NiCl_2$•DME (9.1 mg, 0.041 mmol, 0.05 equiv.), hexylamine (162 µL, 1.24 mmol, 1.5 equiv.), a solution of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.00002 equiv.) in DMSO (16.5 µL), and DMSO (3.1 mL, [0.27 M]). The vial was placed under an atmosphere of nitrogen, cooled to –78 °C, degassed via vacuum evacuation (5 min), backfilled with nitrogen, and warmed to room temperature. This process was repeated three times, and the reaction vial was then sealed with parafilm, placed 6 cm away from one blue LED, and irradiated. The reaction vial was heated to roughly 55 °C by the blue LED without the use of a fan. After 19 h, the reaction mixture was purified directly by flash column chromatography (SiO_2, 10% to 25% EtOAc in hexanes eluent) to give a colorless oil (134 mg, 0.627 mmol, 76% yield). The spectral data matched that reported in the literature *(48)*.

IR (film), ν_{max} 2925, 2857, 1602, 1505, 1320, 746, 691 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.18 (dd, *J* = 8.5, 7.1 Hz, 2H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 8.3 Hz, 2H), 3.94–3.50 (br s, 1H), 3.11 (t, *J* = 7.2 Hz, 2H), 1.62 (p, *J* = 7.4, 7.1 Hz, 2H), 1.47–1.24 (m, 6H), 0.97–0.85 (m, 3H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 148.6, 129.4, 117.3, 112.9, 44.3, 31.8, 29.7, 27.0, 22.8, 14.2.



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

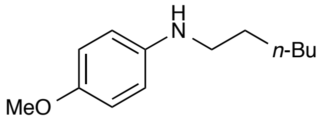
To an 8 mL vial was added 1-bromo-4-(trifluoromethyl)benzene (115 µL, 0.825 mmol, 1.0 equiv.), DABCO (166 mg, 1.485 mmol, 1.8 equiv.), NiCl$_2$•DME (9.1 mg, 0.041 mmol, 0.05 equiv.), hexylamine (162 µL, 1.24 mmol, 1.5 equiv.), a solution of Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (0.0002 equiv.) in DMA (165 µL), and DMA (2.9 mL, [0.27 M]). The vial was placed under an atmosphere of nitrogen, cooled to – 78 °C, degassed via vacuum evacuation (5 min), backfilled with nitrogen, and warmed to room temperature. This process was repeated three times, and the reaction vial was then sealed with parafilm, placed 6 cm away from one blue LED, and irradiated. A fan was used to cool the reaction vial to ambient temperature. After 16 h, the reaction mixture was purified directly by flash column chromatography (SiO$_2$, 10% to 25% EtOAc in hexanes eluent) to give a colorless oil (160 mg, 0.652 mmol, 79% yield). The spectral data matched that reported in the literature *(48).*

IR (film), ν$_{max}$ 2930, 2359, 1616, 1533, 1318, 1105, 822 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.39 (d, *J* = 8.4 Hz, 2H), 6.59 (d, *J* = 8.4 Hz, 2H), 4.25–3.94 (br s, 1H), 3.13 (t, *J* = 7.1 Hz, 2H), 1.63 (p, *J* = 7.4, 7.2 Hz, 2H), 1.47–1.22 (m, 6H), 1.00–0.80 (m, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 150.9, 126.7 (q, $^3J_{C–F}$ = 3.8 Hz), 125.2 (q, $^1J_{C–F}$ = 270.0 Hz), 118.6 (q, $^2J_{C–F}$ = 32.6 Hz), 111.9, 43.7, 31.7, 29.4, 26.9, 22.7, 14.1.

^{19}F NMR (471 MHz, CDCl$_3$) δ −61.0.



***N*-hexyl-4-methoxyaniline**

To an 8 mL vial was added 1-bromo-4-methoxybenzene (104 µL, 0.825 mmol, 1.0 equiv.), MTBD (472 µL, 3.30 mmol, 4.0 equiv.), NiCl$_2$•DME (18.2 mg, 0.082 mmol, 0.10 equiv.), hexylamine (324 µL, 2.48 mmol, 3.0 equiv.), a solution of Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (0.00002 equiv.) in DMSO (16.5 µL), and DMSO (3.1 mL, [0.27 M]). The vial was placed under an atmosphere of nitrogen, cooled to – 78 °C, degassed via vacuum evacuation (5 min), backfilled with nitrogen, and warmed to room temperature. This process was repeated three times, and the reaction vial was then sealed with parafilm, placed 6 cm away from one blue LED, and irradiated. The reaction vial was heated to roughly 55 °C by the blue LED without the use of a fan. After 19 h, the reaction mixture was purified directly by flash column chromatography (SiO_2, 10% to 25% EtOAc in hexanes eluent) to give a colorless oil (152 mg, 0.734 mmol, 89% yield). The spectral data matched that reported in the literature *(48)*.

IR (film), ν_{max} 2927, 2344, 1511, 1234, 1038, 816, 668 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 (d, *J* = 8.9 Hz, 2H), 6.59 (d, *J* = 8.9 Hz, 2H), 3.75 (s, 3H), 3.57 (br s, 1H), 3.06 (t, *J* = 7.1 Hz, 2H), 1.60 (p, *J* = 7.3, 7.1 Hz, 2H), 1.47–1.19 (m, 6H), 0.97–0.83 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 142.9, 115.0, 114.2, 56.0, 45.2, 31.8, 29.8, 27.0, 22.8, 14.2.

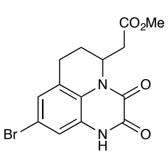
High-throughput Experimentation Using Parallel Photoredox Screening Platform

General Information Section

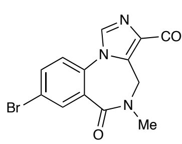
All reagents were used as purchased from commercial suppliers. Solvents were purchased from Sigma-Aldrich, anhydrous, sure-seal quality, and used with no further purification. The reagents and catalysts were purchased from commercial sources and stored in the glovebox. All reactions were performed inside an MBraun glovebox operating with a constant nitrogen purge (oxygen typically < 5 ppm) unless otherwise noted. Reaction experimental design was aided by the use of Accelrys Library Studio. Reactions run at 2.5 μmol scale for the limiting reagent were carried out in 250 μL microvials (Analytical Sales, Cat. No. 10421) in 96-well reaction microplates (Analytical-Sales, Cat. No. 24250). Liquid handling was done using single and multi-channel Eppendorf pipettors (10, 100, 200, and 1000 μL). On completion of solution dosing, the plates were covered by a perfluoroalkoxy alkane (PFA) mat (Analytical-Sales, Cat. No. 96967 and 24261), followed by two silicon rubber mats (Analytical-Sales, Cat. No. 96965 and 24262), and an aluminum cover which was tightly and evenly sealed by 9 screws. The scale-up reactions described below were typically run prior to identification of optimal conditions, and no attempt was made to optimize the isolated yield of material. The goal in these experiments was to isolate pure material for characterization and to provide a standard for quantitative LC analysis. Quantitative analysis was accomplished by reverse phase UPLC (Waters X-BridgeTM BEH 2.5 micron, RP C-18, 2.1 x 50 mm column, eluents: MeCN-H2O containing 0.05% TFA) using an internal standard (1,3,5-trimethoxybenzene). Extinction coefficients for LC analysis were determined by first measuring the molar ratio of a mixture of desired product with internal standard by ^{1}H-NMR analysis, then determining the UV absorption for this mixture by running the same mixture on the UPLC method used for analysis. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 500 (500 MHz) as noted, and are internally referenced to residual protio solvent signals. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration and coupling constant (Hz). Data for ^{13}C NMR are reported in terms of chemical shift. Mass spectra were obtained from an Agilent LC/MSD TOF model G1969A.

Experimental Section – Metallaphotoredox-catalyzed Amination Using the Aryl Halide Informer Library with Piperidine.

Experimental Procedure for Fig. S12. High-throughput experimentation was performed using a parallel photoredox screening platform, following specifications previously detailed in the literature.[14] In a nitrogen filled glovebox, to the collection of eighteen high-complexity aryl halides (2.5 μmol/ reaction) in 250 μL microvials equipped with magnetic stir bars, a solution of piperidine (3.75 μmol, 1.5 eq), base (4.50 μmol, 1.8 eq), $NiCl_2$•glyme (0.125 μmol, 5 mol%), and photocatalyst (0.0002 or 0.00002 μmol, 0.02 or 0.002 mol%) in a solution of DMSO (20 μL) was added. The reaction vials were sealed and stirred at 55 °C for 16 h on a 96-light blue LED-light source (465 nm). The reaction vials were then cooled to ambient temperature and diluted with 100 μL of 5% AcOH in DMSO containing 1,3,5-trimethoxybenzene (0.005 M) and were shaken vigorously. A 25 μL aliquot was removed from each vial, and diluted with 700 μL of MeCN and quantitative UPLC analysis was performed to determine the solution yield compared to a product standard.



X1



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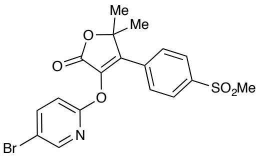

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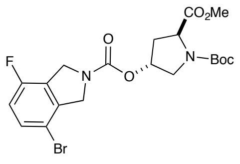

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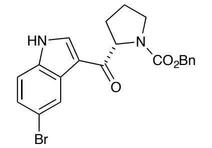

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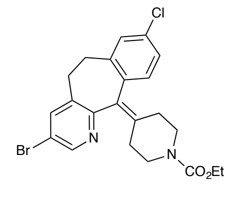

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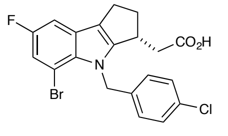

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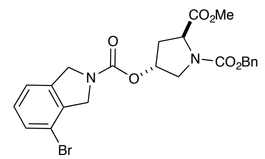

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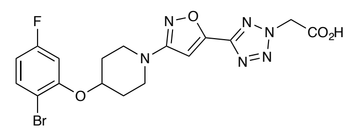
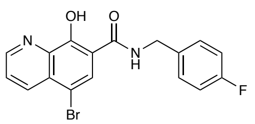


X9



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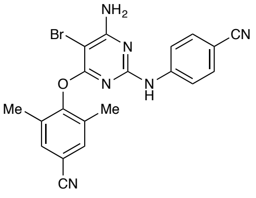

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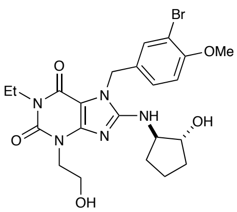

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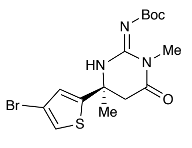

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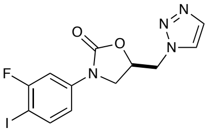

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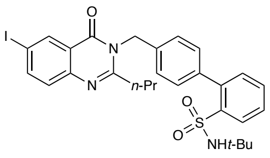

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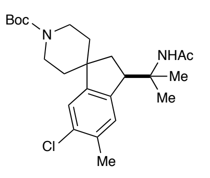

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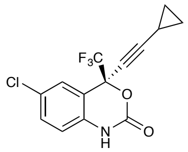

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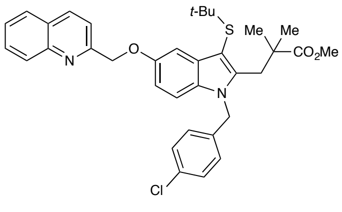


X18

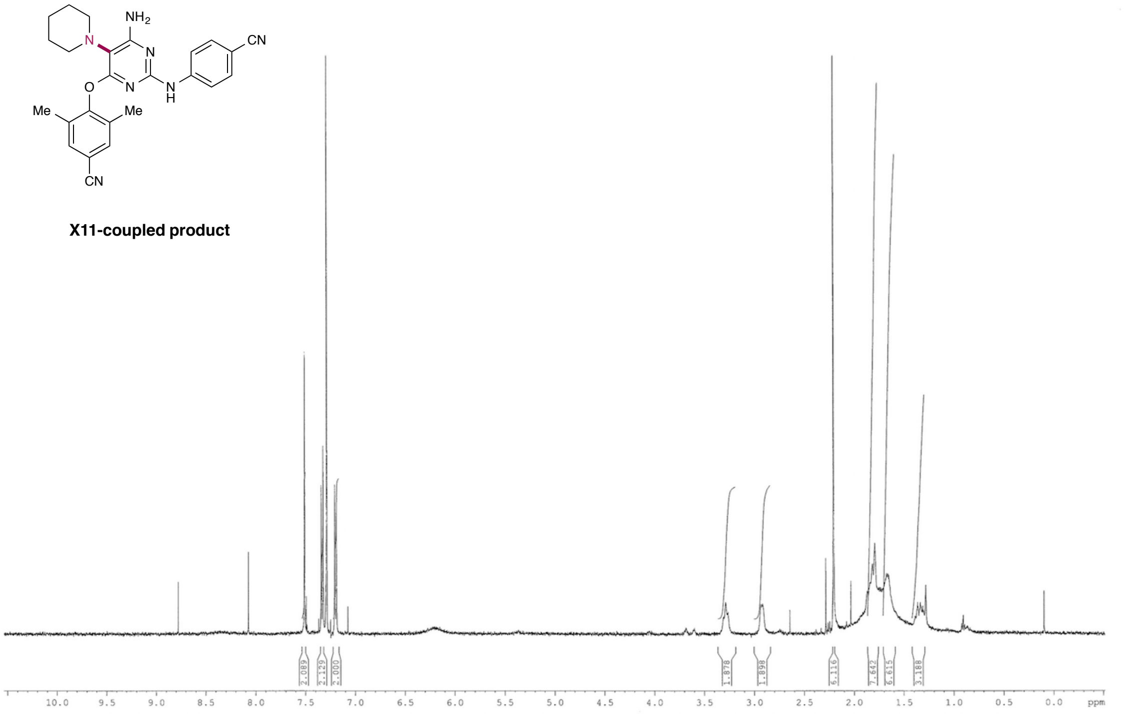
Figure S11. Chemistry informer library used for high throughput experimentation in metallaphotoredox-catalyzed C–N cross coupling

Experimental Procedure for the preparation of X11-coupled product.

In a nitrogen-filled glovebox, a solution of compound X11 (240 μmol, 1.0 eq), piperidine (360 μmol, 1.5 eq), DABCO (432 μmol, 1.8 eq), nickel(II) chloride ethylene glycol dimethyl ether complex (12 μmol, 5 mol%), and $Ru(bpy)_3(PF_6)_2$ (0.048 μmol, 0.02 mol%) in DMSO (1.920 mL) was prepared. This solution was then distributed in 20 μL quantities per vial to a 96-well plate of 250 μL microvials equipped with magnetic stir bars. The reaction vials were sealed and stirred at 55 °C for 16 h on a 96-light blue LED light source (465 nm). The reaction vials were then cooled to ambient temperature and the reactions were recombined and the product was purified by MS-directed HPLC purification.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (s, 2H), 7.35 (d, *J* = 8.65 Hz, 2H), 7.20 (d, *J* = 8.74 Hz, 2H), 3.35 – 3.25 (t, *J* = 11.92 Hz, 2H), 3.00 – 2.90 (d, *J* = 9.68 Hz, 2H), 2.25 (s, 6H), 2.0-1.5 (br m, 4H), 1.4-1,3 (m, 2 H).

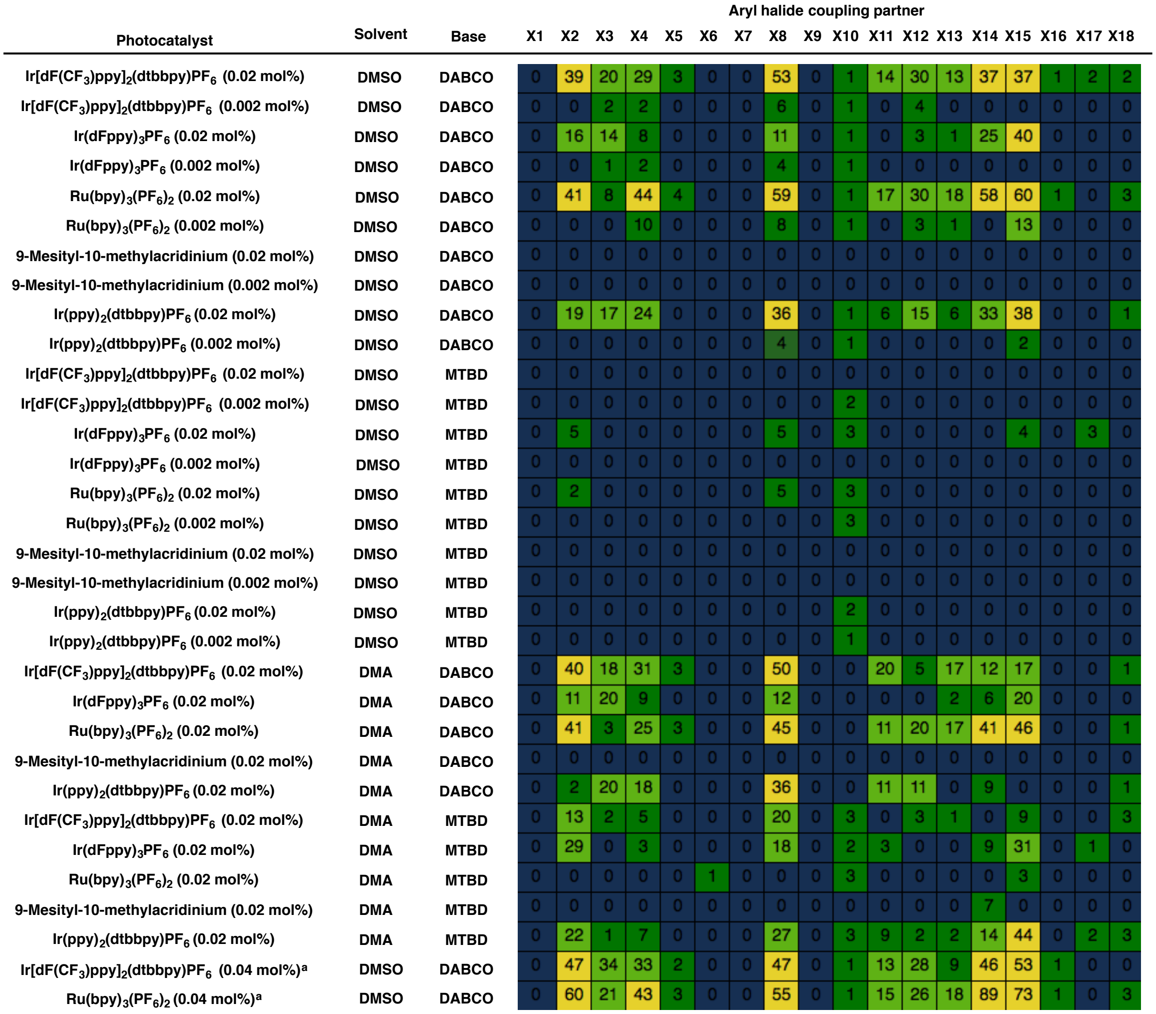
LRMS-ESI m/z calcd. for $C_{25}H_{26}N_7O$: 440.22, found 440.2 $[M+H]^+$



X11-coupled product

Full Results of High Throughput Experimentation.

In the high throughput experimentation conducted employing the metallaphotoredox-catalyzed amination protocol, fourteen of the eighteen aryl halide substrates which comprise the Merck chemistry informer library showed promising to good reactivities. These lead hits can be further optimized to more synthetically useful yields through the evaluation of parameters which have been shown to play important roles in this cross-coupling platform, namely the identity and loading of photocatalyst, solvent choice, reaction temperature, and the loading of nickel catalyst.



			Aryl halide coupling partner																	
Photocatalyst	Solvent	Base	X1	X2	X3	X4	X5	X6	X7	X8	X9	X10	X11	X12	X13	X14	X15	X16	X17	X18
Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (0.02 mol%)	DMSO	DABCO	0	39	20	29	3	0	0	53	0	1	14	30	13	37	37	1	2	2
Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (0.002 mol%)	DMSO	DABCO	0	0	2	2	0	0	0	6	0	1	0	4	0	0	0	0	0	0
Ir(dFppy)$_3$PF$_6$ (0.02 mol%)	DMSO	DABCO	0	16	14	8	0	0	0	11	0	1	0	3	1	25	40	0	0	0
Ir(dFppy)$_3$PF$_6$ (0.002 mol%)	DMSO	DABCO	0	0	1	2	0	0	0	4	0	1	0	0	0	0	0	0	0	0
Ru(bpy)$_3$(PF$_6$)$_2$ (0.02 mol%)	DMSO	DABCO	0	41	8	44	4	0	0	59	0	1	17	30	18	58	60	1	0	3
Ru(bpy)$_3$(PF$_6$)$_2$ (0.002 mol%)	DMSO	DABCO	0	0	0	10	0	0	0	8	0	1	0	3	1	0	13	0	0	0
9-Mesityl-10-methylacridinium (0.02 mol%)	DMSO	DABCO	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
9-Mesityl-10-methylacridinium (0.002 mol%)	DMSO	DABCO	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ir(ppy)$_2$(dtbbpy)PF$_6$ (0.02 mol%)	DMSO	DABCO	0	19	17	24	0	0	0	36	0	1	6	15	6	33	38	0	0	1
Ir(ppy)$_2$(dtbbpy)PF$_6$ (0.002 mol%)	DMSO	DABCO	0	0	0	0	0	0	0	4	0	1	0	0	0	0	2	0	0	0
Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (0.02 mol%)	DMSO	MTBD	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (0.002 mol%)	DMSO	MTBD	0	0	0	0	0	0	0	0	0	2	0	0	0	0	0	0	0	0
Ir(dFppy)$_3$PF$_6$ (0.02 mol%)	DMSO	MTBD	0	5	0	0	0	0	0	5	0	3	0	0	0	0	4	0	3	0
Ir(dFppy)$_3$PF$_6$ (0.002 mol%)	DMSO	MTBD	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ru(bpy)$_3$(PF$_6$)$_2$ (0.02 mol%)	DMSO	MTBD	0	2	0	0	0	0	0	5	0	3	0	0	0	0	0	0	0	0
Ru(bpy)$_3$(PF$_6$)$_2$ (0.002 mol%)	DMSO	MTBD	0	0	0	0	0	0	0	0	0	3	0	0	0	0	0	0	0	0
9-Mesityl-10-methylacridinium (0.02 mol%)	DMSO	MTBD	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
9-Mesityl-10-methylacridinium (0.002 mol%)	DMSO	MTBD	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ir(ppy)$_2$(dtbbpy)PF$_6$ (0.02 mol%)	DMSO	MTBD	0	0	0	0	0	0	0	0	0	2	0	0	0	0	0	0	0	0
Ir(ppy)$_2$(dtbbpy)PF$_6$ (0.002 mol%)	DMSO	MTBD	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0
Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (0.02 mol%)	DMA	DABCO	0	40	18	31	3	0	0	50	0	0	20	5	17	12	17	0	0	1
Ir(dFppy)$_3$PF$_6$ (0.02 mol%)	DMA	DABCO	0	11	20	9	0	0	0	12	0	0	0	0	2	6	20	0	0	0
Ru(bpy)$_3$(PF$_6$)$_2$ (0.02 mol%)	DMA	DABCO	0	41	3	25	3	0	0	45	0	0	11	20	17	41	46	0	0	1
9-Mesityl-10-methylacridinium (0.02 mol%)	DMA	DABCO	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ir(ppy)$_2$(dtbbpy)PF$_6$ (0.02 mol%)	DMA	DABCO	0	2	20	18	0	0	0	36	0	0	11	11	0	9	0	0	0	1
Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (0.02 mol%)	DMA	MTBD	0	13	2	5	0	0	0	20	0	3	0	3	1	0	9	0	0	3
Ir(dFppy)$_3$PF$_6$ (0.02 mol%)	DMA	MTBD	0	29	0	3	0	0	0	18	0	2	3	0	0	9	31	0	1	0
Ru(bpy)$_3$(PF$_6$)$_2$ (0.02 mol%)	DMA	MTBD	0	0	0	0	0	1	0	0	0	3	0	0	0	0	3	0	0	0
9-Mesityl-10-methylacridinium (0.02 mol%)	DMA	MTBD	0	0	0	0	0	0	0	0	0	0	0	0	0	7	0	0	0	0
Ir(ppy)$_2$(dtbbpy)PF$_6$ (0.02 mol%)	DMA	MTBD	0	22	1	7	0	0	0	27	0	3	9	2	2	14	44	0	2	3
Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (0.04 mol%)[a]	DMSO	DABCO	0	47	34	33	2	0	0	47	0	1	13	28	9	46	53	1	0	0
Ru(bpy)$_3$(PF$_6$)$_2$ (0.04 mol%)[a]	DMSO	DABCO	0	60	21	43	3	0	0	55	0	1	15	26	18	89	73	1	0	3

Figure S12. High throughput experimentation results for metallaphotoredox-catalyzed C–N cross coupling. For each entry, yields were determined by UPLC-MS using an internal standard. [a] Run for 48 h using 10 mol% nickel.

Raw data and calculated yields from high throughput experiments

Ir(dF-CF$_3$-ppy)$_2$(dtbbpy) [0.02%], NiCl$_2$ glyme, DABCO, DMSO, 55 °C, 16h

Compound	Product/Standard	Response Factor	Yield
X1	0.00	1.63	0
X2	1.26	1.54	39
X3	0.80	1.22	20
X4	0.60	2.40	29
X5	0.15	1.15	3
X6	0.00	1.58	0
X7	0.00	0.00	0
X8	0.97	2.71	53
X9	0.12	0.00	0
X10	0.03	1.21	1
X11	0.38	1.81	14
X12	0.77	1.98	30
X13	0.35	1.87	13
X14	0.56	3.33	37
X15	1.97	0.93	37
X16	0.03	1.34	1
X17	0.05	1.70	2
X18	0.12	0.68	2

Ir(ppy)$_2$(dtbbpy) [0.02%], NiCl$_2$ glyme, DABCO, DMSO, 55 °C, 16h

Compound	Product/Standard	Response Factor	Yield
X1	0.00	1.63	0
X2	0.63	1.54	19
X3	0.71	1.22	17
X4	0.49	2.40	24
X5	0.00	1.15	0
X6	0.00	1.58	0
X7	0.00	0.00	0
X8	0.67	2.71	36
X9	0.00	0.00	0
X10	0.04	1.21	1
X11	0.18	1.81	6
X12	0.37	1.98	15
X13	0.15	1.87	6
X14	0.50	3.33	33
X15	2.05	0.93	38
X16	0.00	1.34	0
X17	0.00	1.70	0

X18	0.05	0.68	1

Ir(dF-ppy)$_3$ [0.02%], NiCl$_2$ glyme, DABCO, DMSO, 55 °C, 16h

Compound	Product/Standard	Response Factor	Yield
X1	0.00	1.63	0
X2	0.52	1.54	16
X3	0.56	1.22	14
X4	0.17	2.40	8
X5	0.00	1.15	0
X6	0.00	1.58	0
X7	0.06	0.00	0
X8	0.21	2.71	11
X9	0.04	0.00	0
X10	0.04	1.21	1
X11	0.00	1.81	0
X12	0.08	1.98	3
X13	0.04	1.87	1
X14	0.38	3.33	25
X15	2.17	0.93	40
X16	0.00	1.34	0
X17	0.00	1.70	0
X18	0.00	0.68	0

Ru(bpy)$_3$ [0.02%], NiCl$_2$ glyme, DABCO, DMSO, 55 °C, 16h

Compound	Product/Standard	Response Factor	Yield
X1	0.00	1.63	0
X2	1.34	1.54	41
X3	0.31	1.22	8
X4	0.91	2.40	44
X5	0.19	1.15	4
X6	0.00	1.58	0
X7	0.00	0.00	0
X8	1.09	2.71	59
X9	0.18	0.00	0
X10	0.04	1.21	1
X11	0.48	1.81	17
X12	0.77	1.98	30
X13	0.47	1.87	18
X14	0.88	3.33	58
X15	3.25	0.93	60
X16	0.03	1.34	1
X17	0.00	1.70	0
X18	0.19	0.68	3

9-Mesityl-10-methylacridinium [0.02%], NiCl$_2$ glyme [5%], DABCO, DMSO, 55 °C, 16h

Compound	Product/Standard	Response Factor	Yield
X1	0.00	1.63	0
X2	0.00	1.54	0
X3	0.00	1.22	0
X4	0.00	2.40	0
X5	0.00	1.15	0
X6	0.00	1.58	0
X7	0.00	0.00	0
X8	0.00	2.71	0
X9	0.00	0.00	0
X10	0.00	1.21	0
X11	0.00	1.81	0
X12	0.00	1.98	0
X13	0.00	1.87	0
X14	0.00	3.33	0
X15	0.00	0.93	0
X16	0.00	1.34	0
X17	0.00	1.70	0
X18	0.00	0.68	0

Ir(dF-CF$_3$-ppy)$_2$(dtbbpy) [0.02%], NiCl$_2$ glyme, MTBD, DMSO, 55 °C, 16h

Compound	Product/Standard	Response Factor	Yield
X1	0.00	1.63	0
X2	0.00	1.54	0
X3	0.00	1.22	0
X4	0.00	2.40	0
X5	0.00	1.15	0
X6	0.00	1.58	0
X7	0.00	0.00	0
X8	0.00	2.71	0
X9	0.00	0.00	0
X10	0.00	1.21	0
X11	0.00	1.81	0
X12	0.00	1.98	0
X13	0.00	1.87	0
X14	0.00	3.33	0
X15	0.00	0.93	0
X16	0.00	1.34	0
X17	0.00	1.70	0
X18	0.00	0.68	0

$Ir(ppy)_2(dtbbpy)$ [0.02%], $NiCl_2$ glyme, MTBD, DMSO, 55 °C, 16h

Compound	Product/Standard	Response Factor	Yield
X1	0.00	1.63	0
X2	0.00	1.54	0
X3	0.00	1.22	0
X4	0.00	2.40	0
X5	0.00	1.15	0
X6	0.00	1.58	0
X7	0.00	0.00	0
X8	0.00	2.71	0
X9	0.00	0.00	0
X10	0.08	1.21	2
X11	0.00	1.81	0
X12	0.00	1.98	0
X13	0.00	1.87	0
X14	0.00	3.33	0
X15	0.00	0.93	0
X16	0.00	1.34	0
X17	0.00	1.70	0
X18	0.00	0.68	0

$Ir(dF\text{-}ppy)_3$ [0.02%], $NiCl_2$ glyme, MTBD, DMSO, 55 °C, 16h

Compound	Product/Standard	Response Factor	Yield
X1	0.00	1.63	0
X2	0.17	1.54	5
X3	0.00	1.22	0
X4	0.00	2.40	0
X5	0.00	1.15	0
X6	0.00	1.58	0
X7	0.00	0.00	0
X8	0.09	2.71	5
X9	0.00	0.00	0
X10	0.14	1.21	3
X11	0.00	1.81	0
X12	0.00	1.98	0
X13	0.00	1.87	0
X14	0.00	3.33	0
X15	0.21	0.93	4
X16	0.00	1.34	0
X17	0.08	1.70	3
X18	0.00	0.68	0

Ru(bpy)$_3$ [0.02%], NiCl$_2$ glyme, MTBD, DMSO, 55 °C, 16h

Compound	Product/Standard	Response Factor	Yield
X1	0.00	1.63	0
X2	0.07	1.54	2
X3	0.00	1.22	0
X4	0.00	2.40	0
X5	0.00	1.15	0
X6	0.00	1.58	0
X7	0.00	0.00	0
X8	0.09	2.71	5
X9	0.00	0.00	0
X10	0.14	1.21	3
X11	0.00	1.81	0
X12	0.00	1.98	0
X13	0.00	1.87	0
X14	0.00	3.33	0
X15	0.00	0.93	0
X16	0.00	1.34	0
X17	0.00	1.70	0
X18	0.00	0.68	0

9-Mesityl-10-methylacridinium [0.02%], NiCl$_2$ glyme [5%], MTBD, DMSO, 55 °C, 16h

Compound	Product/Standard	Response Factor	Yield
X1	0.00	1.63	0
X2	0.00	1.54	0
X3	0.00	1.22	0
X4	0.00	2.40	0
X5	0.00	1.15	0
X6	0.00	1.58	0
X7	0.00	0.00	0
X8	0.00	2.71	0
X9	0.00	0.00	0
X10	0.00	1.21	0
X11	0.00	1.81	0
X12	0.00	1.98	0
X13	0.00	1.87	0
X14	0.00	3.33	0
X15	0.00	0.93	0
X16	0.00	1.34	0
X17	0.00	1.70	0
X18	0.00	0.68	0

Ir(dF-CF$_3$-ppy)$_2$(dtbbpy) [0.02%], NiCl$_2$ glyme [5%], DABCO, DMA, 55 °C, 16h

Compound	Product/Standard	Response Factor	Yield
X1	0.00	1.63	0
X2	1.30	1.54	40
X3	0.75	1.22	18
X4	0.64	2.40	31
X5	0.12	1.15	3
X6	0.00	1.58	0
X7	0.00	0	0
X8	0.93	2.71	50
X9	0.38	0	0
X10	0.00	1.21	0
X11	0.56	1.81	20
X12	0.11	1.98	5
X13	0.46	1.87	17
X14	0.18	3.33	12
X15	0.92	0.93	17
X16	0.00	1.34	0
X17	0.00	1.7	0
X18	0.08	0.68	1

Ir(ppy)$_2$(dtbbpy) [0.02%], NiCl$_2$ glyme [5%], DABCO, DMA, 55 °C, 16h

Compound	Product/Standard	Response Factor	Yield
X1	0.00	1.63	0
X2	0.08	1.54	2
X3	0.82	1.22	20
X4	0.38	2.40	18
X5	0.00	1.15	0
X6	0.00	1.58	0
X7	0.07	0	0
X8	0.66	2.71	36
X9	0.17	0	0
X10	0.00	1.21	0
X11	0.31	1.81	11
X12	0.27	1.98	11
X13	0.00	1.87	0
X14	0.13	3.33	9
X15	0.00	0.93	0
X16	0.00	1.34	0
X17	0.00	1.7	0
X18	0.11	0.68	1

Ir(dF-ppy)$_3$ [0.02%], NiCl$_2$ glyme [5%], DABCO, DMA, 55 °C, 16h

Compound	Product/Standard	Response Factor	Yield
X1	0.00	1.63	0
X2	0.36	1.54	11
X3	0.82	1.22	20
X4	0.18	2.40	9
X5	0.00	1.15	0
X6	0.00	1.58	0
X7	0.00	0	0
X8	0.23	2.71	12
X9	0.05	0	0
X10	0.00	1.21	0
X11	0.00	1.81	0
X12	0.00	1.98	0
X13	0.07	1.87	2
X14	0.10	3.33	6
X15	1.10	0.93	20
X16	0.00	1.34	0
X17	0.00	1.7	0
X18	0.00	0.68	0

Ru(bpy)$_3$ [0.02%], NiCl$_2$ glyme [5%], DABCO, DMA, 55 °C, 16h

Compound	Product/Standard	Response Factor	Yield
X1	0.00	1.63	0
X2	1.32	1.54	41
X3	0.12	1.22	3
X4	0.51	2.40	25
X5	0.11	1.15	3
X6	0.00	1.58	0
X7	0.00	0	0
X8	0.82	2.71	45
X9	0.11	0	0
X10	0.00	1.21	0
X11	0.31	1.81	11
X12	0.50	1.98	20
X13	0.46	1.87	17
X14	0.62	3.33	41
X15	2.50	0.93	46
X16	0.00	1.34	0
X17	0.00	1.7	0
X18	0.06	0.68	1

9-Mesityl-10-methylacridinium [0.02%], $NiCl_2$ glyme [5%], DABCO, DMA, 55 °C, 16h

Compound	Product/Standard	Response Factor	Yield
X1	0	1.63	0
X2	0	1.54	0
X3	0	1.22	0
X4	0	2.40	0
X5	0	1.15	0
X6	0	1.58	0
X7	0	0	0
X8	0	2.71	0
X9	0	0	0
X10	0	1.21	0
X11	0	1.81	0
X12	0	1.98	0
X13	0	1.87	0
X14	0	3.33	0
X15	0	0.93	0
X16	0	1.34	0
X17	0	1.7	0
X18	0	0.68	0

Ir(dF-CF_3-ppy)$_2$(dtbbpy) [0.02%], $NiCl_2$ glyme [5%], MTBD, DMA, 55 °C, 16h

Compound	Product/Standard	Response Factor	Yield
X1	0.00	1.63	0
X2	0.42	1.54	13
X3	0.10	1.22	2
X4	0.11	2.40	5
X5	0.00	1.15	0
X6	0.00	1.58	0
X7	0.00	0.00	0
X8	0.38	2.71	20
X9	0.12	0.00	0
X10	0.11	1.21	3
X11	0.00	1.81	0
X12	0.07	1.98	3
X13	0.02	1.87	1
X14	0.00	3.33	0
X15	0.49	0.93	9
X16	0.00	1.34	0
X17	0.00	1.70	0
X18	0.23	0.68	3

Ir(ppy)$_2$(dtbbpy) [0.02%], NiCl$_2$ glyme [5%], MTBD, DMA, 55 °C, 16h

Compound	Product/Standard	Response Factor	Yield
X1	0.00	1.63	0
X2	0.73	1.54	22
X3	0.06	1.22	1
X4	0.15	2.40	7
X5	0.00	1.15	0
X6	0.00	1.58	0
X7	0.00	0.00	0
X8	0.50	2.71	27
X9	0.00	0.00	0
X10	0.11	1.21	3
X11	0.26	1.81	9
X12	0.06	1.98	2
X13	0.06	1.87	2
X14	0.20	3.33	14
X15	2.36	0.93	44
X16	0.00	1.34	0
X17	0.07	1.70	2
X18	0.24	0.68	3

Ir(dF-ppy)$_3$ [0.02%], NiCl$_2$ glyme [5%], MTBD, DMA, 55 °C, 16h

Compound	Product/Standard	Response Factor	Yield
X1	0.00	1.63	0
X2	0.93	1.54	29
X3	0.00	1.22	0
X4	0.07	2.40	3
X5	0.00	1.15	0
X6	0.00	1.58	0
X7	0.00	0.00	0
X8	0.33	2.71	18
X9	0.00	0.00	0
X10	0.09	1.21	2
X11	0.08	1.81	3
X12	0.00	1.98	0
X13	0.00	1.87	0
X14	0.14	3.33	9
X15	1.64	0.93	31
X16	0.00	1.34	0
X17	0.04	1.70	1
X18	0.00	0.68	0

Ru(bpy)$_3$ [0.02%], NiCl$_2$ glyme [5%], MTBD, DMA, 55 °C, 16h

Compound	Product/Standard	Response Factor	Yield
X1	0.00	1.63	0
X2	0.00	1.54	0
X3	0.00	1.22	0
X4	0.00	2.40	0
X5	0.00	1.15	0
X6	0.03	1.58	1
X7	0.00	0.00	0
X8	0.00	2.71	0
X9	0.00	0.00	0
X10	0.11	1.21	3
X11	0.00	1.81	0
X12	0.00	1.98	0
X13	0.00	1.87	0
X14	0.00	3.33	0
X15	0.19	0.93	3
X16	0.00	1.34	0
X17	0.00	1.70	0
X18	0.00	0.68	0

9-Mesityl-10-methylacridinium [0.02%], NiCl$_2$ glyme [5%], MTBD, DMA, 55 °C, 16h

Compound	Product/Standard	Response Factor	Yield
X1	0.00	1.63	0
X2	0.00	1.54	0
X3	0.00	1.22	0
X4	0.00	2.40	0
X5	0.00	1.15	0
X6	0.00	1.58	0
X7	0.00	0.00	0
X8	0.00	2.71	0
X9	0.00	0.00	0
X10	0.11	1.21	3
X11	0.00	1.81	0
X12	0.00	1.98	0
X13	0.00	1.87	0
X14	0.00	3.33	0
X15	0.36	0.93	7
X16	0.00	1.34	0
X17	0.00	1.70	0
X18	0.00	0.68	0

Ir(dF-CF$_3$-ppy)$_2$(dtbbpy) [0.002%], NiCl$_2$ glyme, DABCO, DMSO, 55 °C, 16h

Compound	Product/Standard	Response Factor	Yield
X1	0.00	1.63	0
X2	0.00	1.54	0
X3	0.08	1.22	2
X4	0.05	2.40	2
X5	0.00	1.15	0
X6	0.00	1.58	0
X7	0.00	0.00	0
X8	0.11	2.71	6
X9	0.00	0.00	0
X10	0.03	1.21	1
X11	0.00	1.81	0
X12	0.09	1.98	4
X13	0.00	1.87	0
X14	0.00	3.33	0
X15	0.00	0.93	0
X16	0.00	1.34	0
X17	0.00	1.70	0
X18	0.00	0.68	0

Ru(bpy)$_3$ [0.002%], NiCl$_2$ glyme, DABCO, DMSO, 55 °C, 16h

Compound	Product/Standard	Response Factor	Yield
X1	0.00	1.63	0
X2	0.00	1.54	0
X3	0.00	1.22	0
X4	0.20	2.40	10
X5	0.00	1.15	0
X6	0.00	1.58	0
X7	0.00	0.00	0
X8	0.15	2.71	8
X9	0.00	0.00	0
X10	0.04	1.21	1
X11	0.00	1.81	0
X12	0.08	1.98	3
X13	0.03	1.87	1
X14	0.00	3.33	0
X15	0.71	0.93	13
X16	0.00	1.34	0
X17	0.00	1.70	0
X18	0.00	0.68	0

$Ir(ppy)_2(dtbbpy)$ [0.002%], $NiCl_2$ glyme, DABCO, DMSO, 55 °C

Compound	Product/Standard	Response Factor	Yield
X1	0.00	1.63	0.0
X2	0.00	1.54	0.0
X3	0.00	3.90	0.0
X4	0.00	2.40	0.0
X5	0.00	1.15	0.0
X6	0.00	1.58	0.0
X7	0.00	0.00	0.0
X8	0.08	2.71	4.3
X9	0.00	1.83	0.0
X10	0.04	1.21	1.0
X11	0.00	1.81	0.0
X12	0.00	1.98	0.0
X13	0.00	1.87	0.0
X14	0.00	3.33	0.0
X15	0.10	0.93	1.8
X16	0.00	1.34	0.0
X17	0.00	1.70	0.0
X18	0.00	0.68	0.0

$Ir(dF\text{-}ppy)_3$ [0.002%], $NiCl_2$ glyme, DABCO, DMSO, 55 °C

Compound	Product/Standard	Response Factor	Yield
X1	0.00	1.63	0.0
X2	0.00	1.54	0.0
X3	0.05	3.90	3.9
X4	0.05	2.40	2.4
X5	0.00	1.15	0.0
X6	0.00	1.58	0.0
X7	0.00	0.00	0.0
X8	0.08	2.71	4.5
X9	0.00	1.83	0.0
X10	0.04	1.21	0.9
X11	0.00	1.81	0.0
X12	0.00	1.98	0.0
X13	0.00	1.87	0.0
X14	0.00	3.33	0.0
X15	0.00	0.93	0.0
X16	0.00	1.34	0.0
X17	0.00	1.70	0.0
X18	0.00	0.68	0.0

Ir(dF-CF$_3$-ppy)$_2$(dtbbpy) [0.002%], NiCl$_2$ glyme, MTBD, DMSO, 55 °C

Compound	Product/Standard	Response Factor	Yield
X1	0	1.63	0.0
X2	0	1.54	0.0
X3	0	3.90	0.0
X4	0	2.40	0.0
X5	0	1.15	0.0
X6	0	1.58	0.0
X7	0	0.00	0.0
X8	0	2.71	0.0
X9	0	1.83	0.0
X10	0.067279334	1.21	1.6
X11	0	1.81	0.0
X12	0	1.98	0.0
X13	0	1.87	0.0
X14	0	3.33	0.0
X15	0	0.93	0.0
X16	0	1.34	0.0
X17	0	1.70	0.0
X18	0	0.68	0.0

Ir(ppy)$_2$(dtbbpy) [0.002%], NiCl$_2$ glyme, MTBD, DMSO, 55 °C

Compound	Product/Standard	Response Factor	Yield
X1	0	1.63	0.0
X2	0	1.54	0.0
X3	0	3.90	0.0
X4	0	2.40	0.0
X5	0	1.15	0.0
X6	0	1.58	0.0
X7	0	0.00	0.0
X8	0	2.71	0.0
X9	0	1.83	0.0
X10	0.059672133	1.21	1.4
X11	0	1.81	0.0
X12	0	1.98	0.0
X13	0	1.87	0.0
X14	0	3.33	0.0
X15	0	0.93	0.0
X16	0	1.34	0.0
X17	0	1.70	0.0
X18	0	0.68	0.0

Ir(dF-ppy)$_3$ [0.002%], NiCl$_2$ glyme, MTBD, DMSO, 55 °C

Compound	Product/Standard	Response Factor	Yield
X1	0	1.63	0.0
X2	0	1.54	0.0
X3	0	3.90	0.0
X4	0	2.40	0.0
X5	0	1.15	0.0
X6	0	1.58	0.0
X7	0.071115803	0.00	0.0
X8	0	2.71	0.0
X9	0	1.83	0.0
X10	0	1.21	0.0
X11	0	1.81	0.0
X12	0	1.98	0.0
X13	0	1.87	0.0
X14	0	3.33	0.0
X15	0	0.93	0.0
X16	0	1.34	0.0
X17	0	1.70	0.0
X18	0	0.68	0.0

Ru(bpy)$_3$ [0.002%], NiCl$_2$ glyme, MTBD, DMSO, 55 °C

Compound	Product/Standard	Response Factor	Yield
X1	0	1.63	0.0
X2	0	1.54	0.0
X3	0	3.90	0.0
X4	0	2.40	0.0
X5	0	1.15	0.0
X6	0	1.58	0.0
X7	0	0.00	0.0
X8	0	2.71	0.0
X9	0	1.83	0.0
X10	0.127043439	1.21	3.1
X11	0	1.81	0.0
X12	0	1.98	0.0
X13	0	1.87	0.0
X14	0	3.33	0.0
X15	0	0.93	0.0
X16	0	1.34	0.0
X17	0	1.70	0.0
X18	0	0.68	0.0

Ir(dF-CF$_3$-ppy)$_2$(dtbbpy) [0.04%], NiCl$_2$ glyme [10%], DABCO, DMSO, 55 °C, 48h

Compound	Product/Standard	Response Factor	Yield
X1	0.00	1.63	0
X2	1.54	1.54	47
X3	1.40	1.22	34
X4	0.77	2.40	37
X5	0.09	1.15	2
X6	0.00	1.58	0
X7	0.00	0.00	0
X8	0.86	2.71	47
X9	0.33	0.00	0
X10	0.05	1.21	1
X11	0.36	1.81	13
X12	0.70	1.98	28
X13	0.23	1.87	9
X14	0.69	3.33	46
X15	2.87	0.93	53
X16	0.04	1.34	1
X17	0.00	1.70	0
X18	0.00	0.68	0

Ru(bpy)$_3$ [0.04%], NiCl$_2$ glyme [10%], DABCO, DMSO, 55 °C, 48h

Compound	Product/Standard	Response Factor	Yield
X1	0.00	1.63	0
X2	1.94	1.54	60
X3	0.86	1.22	21
X4	0.90	2.40	43
X5	0.13	1.15	3
X6	0.00	1.58	0
X7	0.00	0.00	0
X8	1.02	2.71	55
X9	0.37	0.00	0
X10	0.06	1.21	1
X11	0.43	1.81	15
X12	0.65	1.98	26
X13	0.48	1.87	18
X14	1.34	3.33	89
X15	3.92	0.93	73
X16	0.04	1.34	1
X17	0.00	1.70	0
X18	0.21	0.68	3

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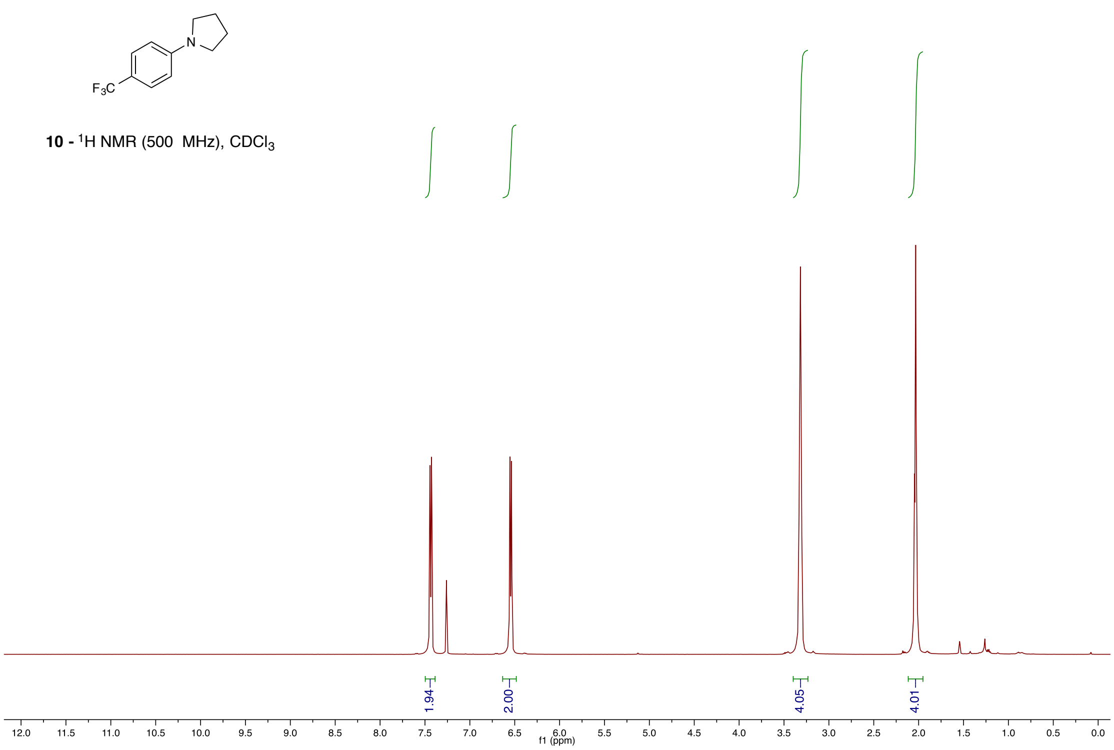
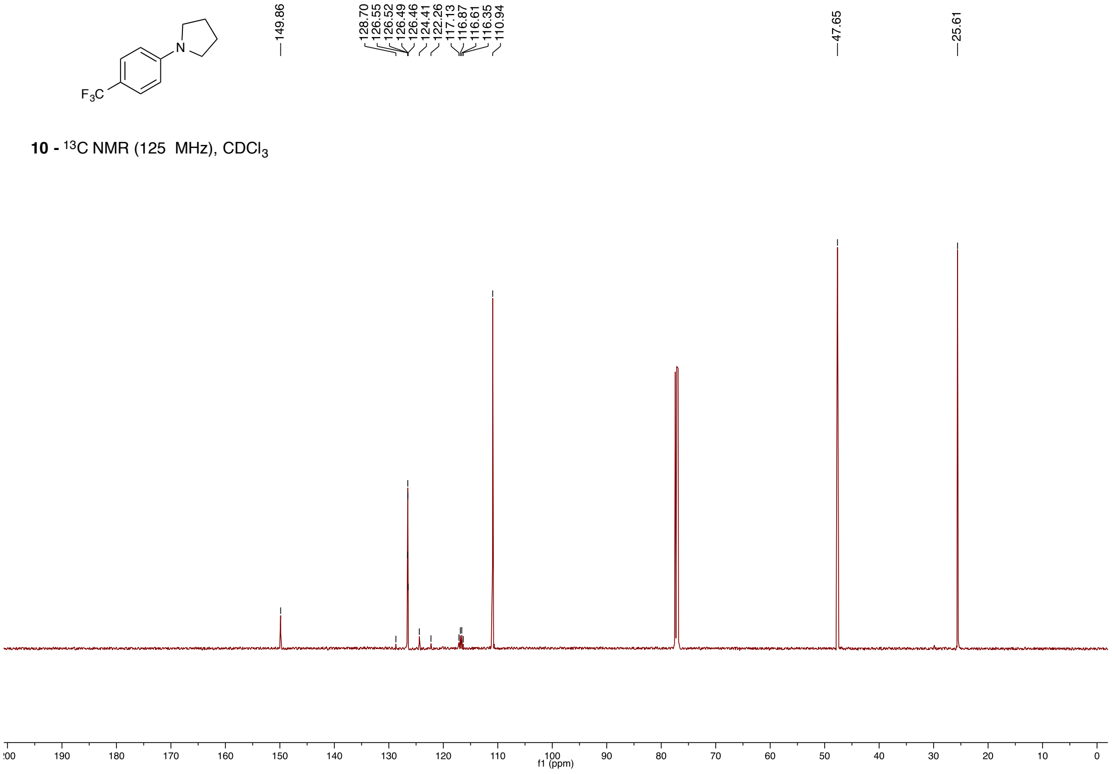
NMR Spectra


10 - ^{1}H NMR (500 MHz), $CDCl_3$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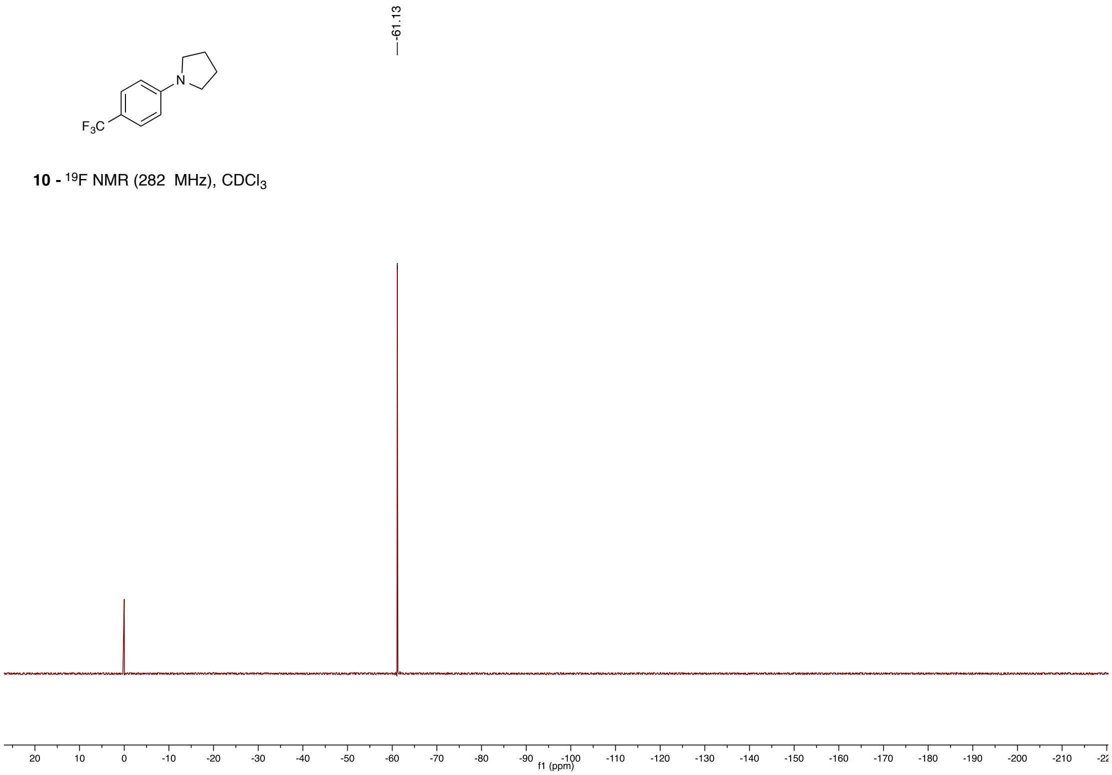
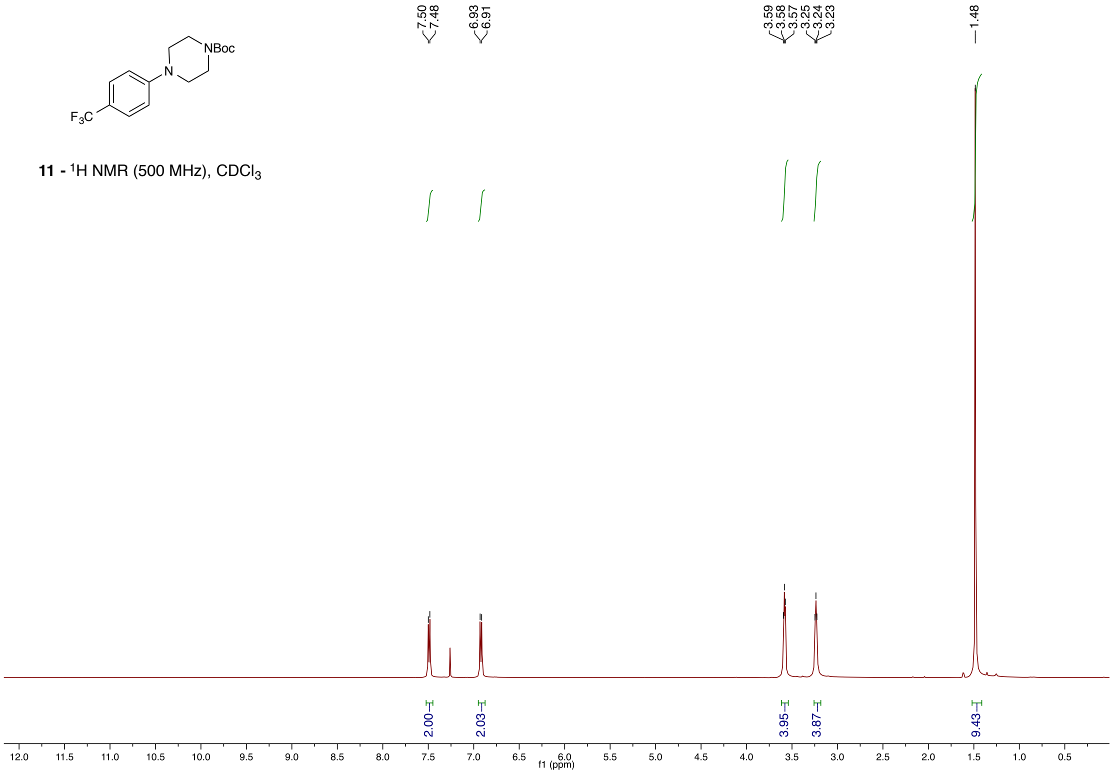


10 - ^{19}F NMR (282 MHz), CDCl$_3$



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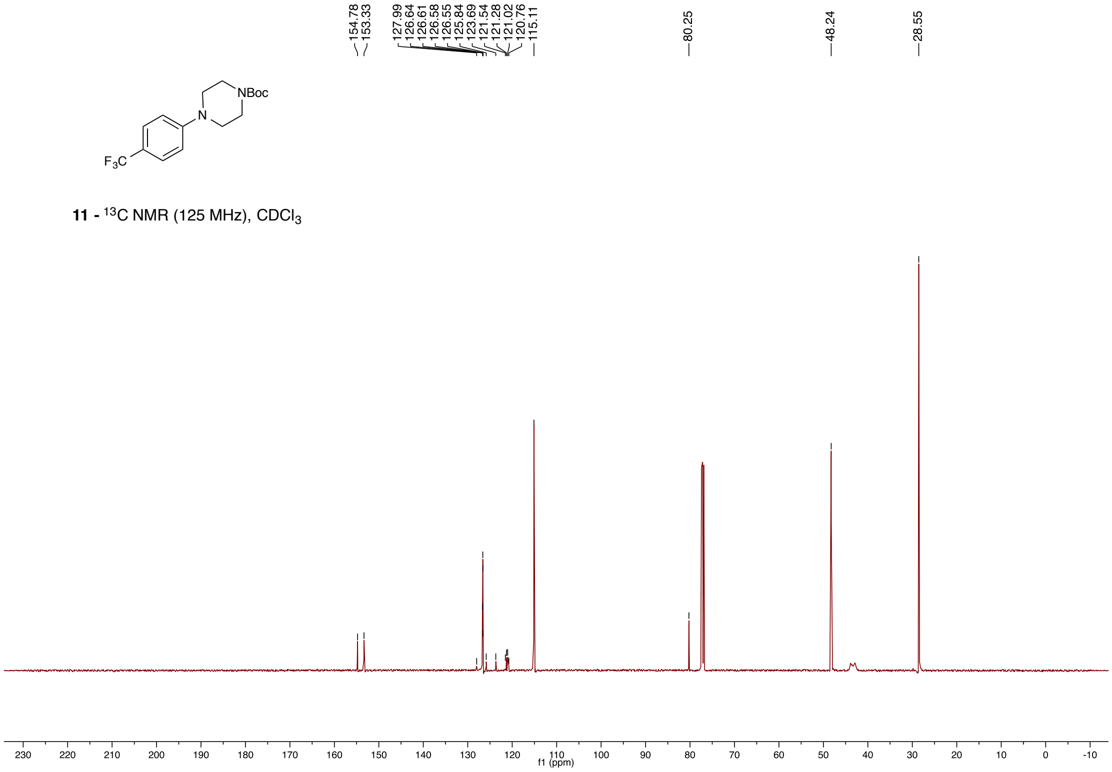

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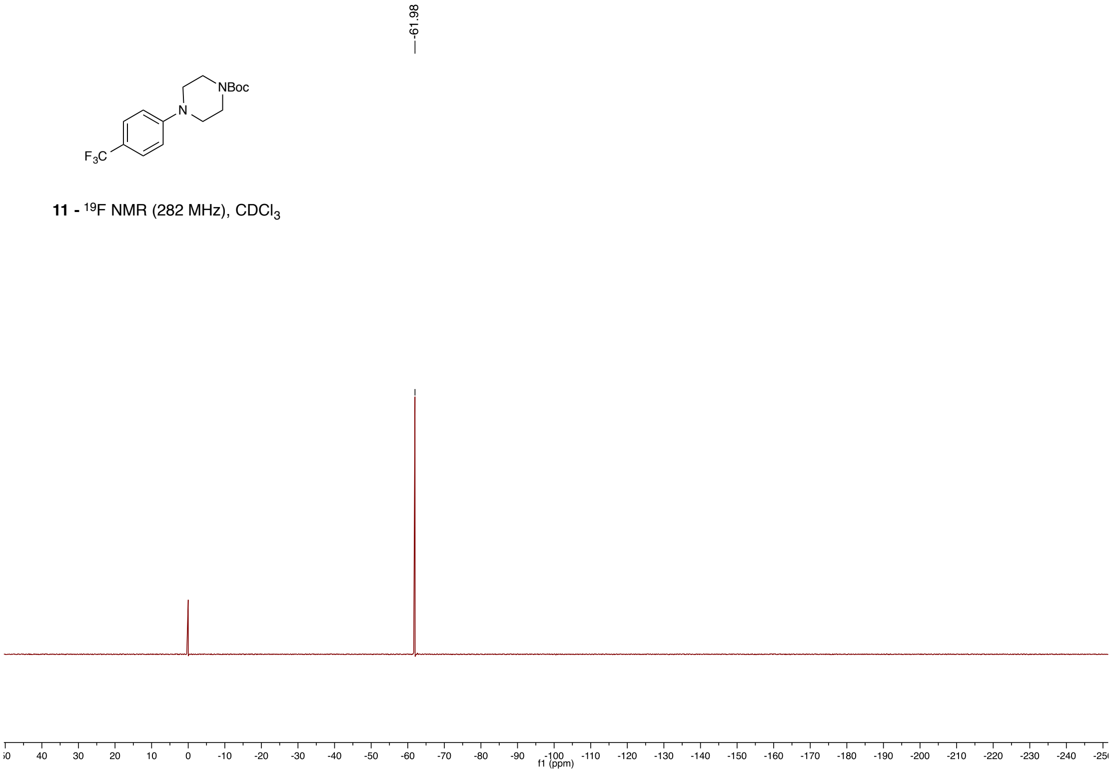

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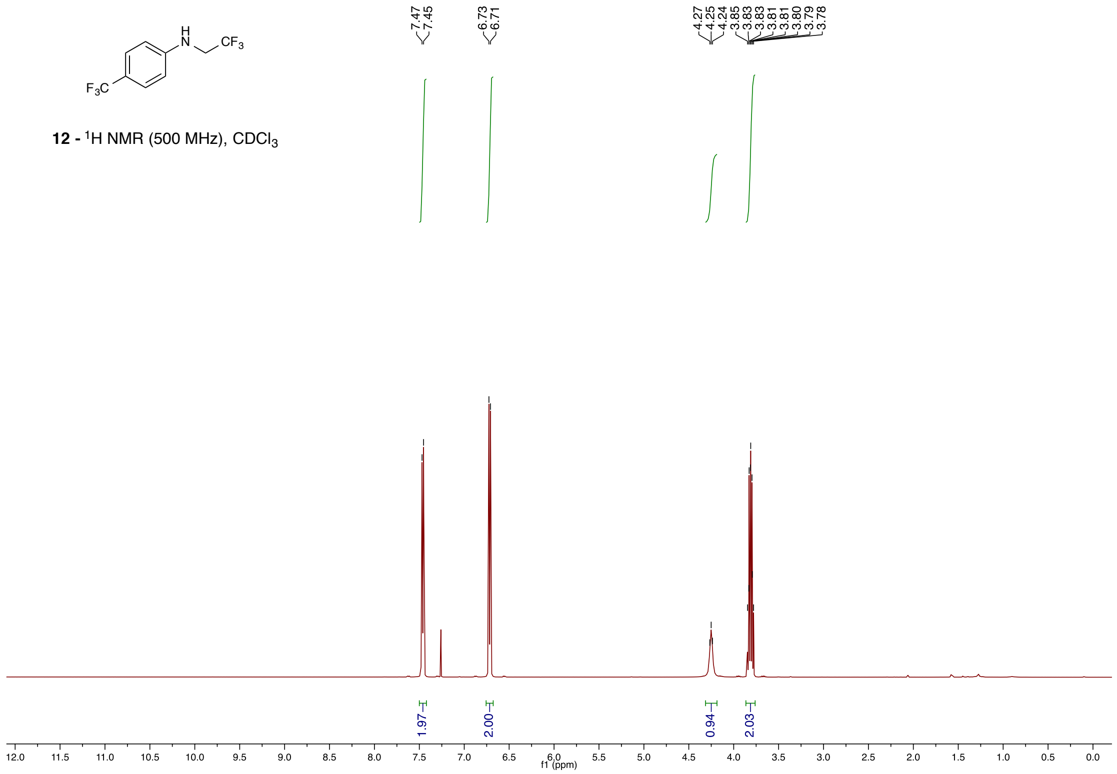

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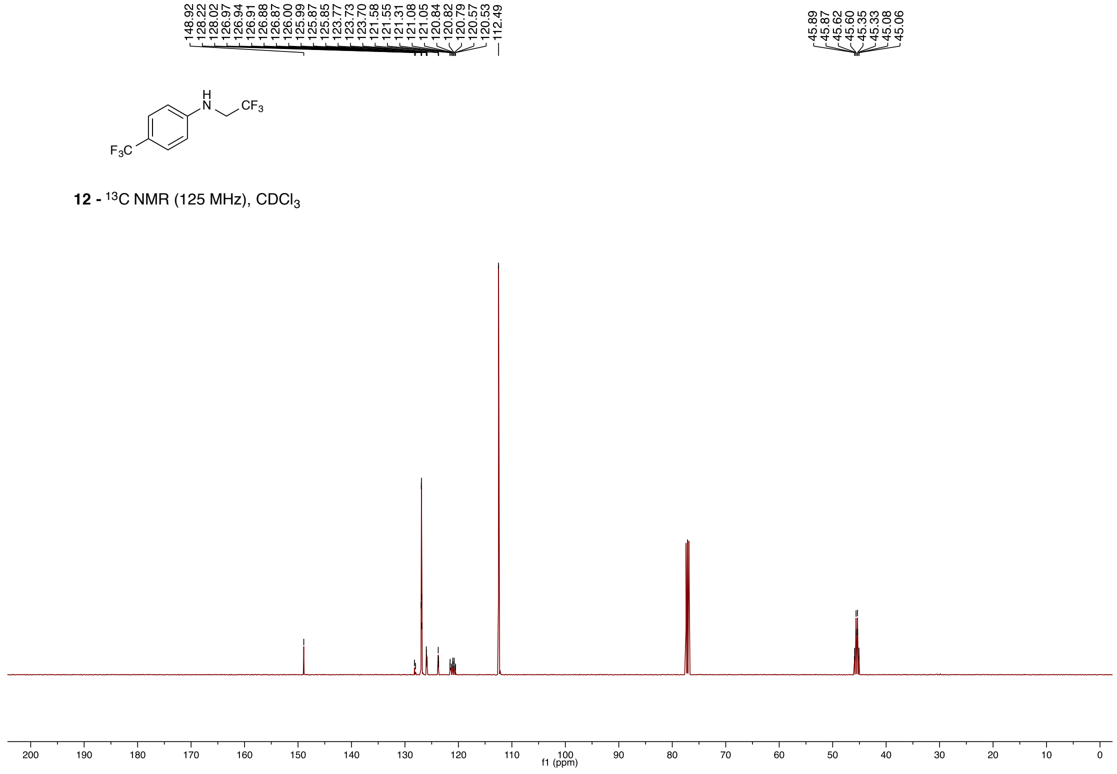

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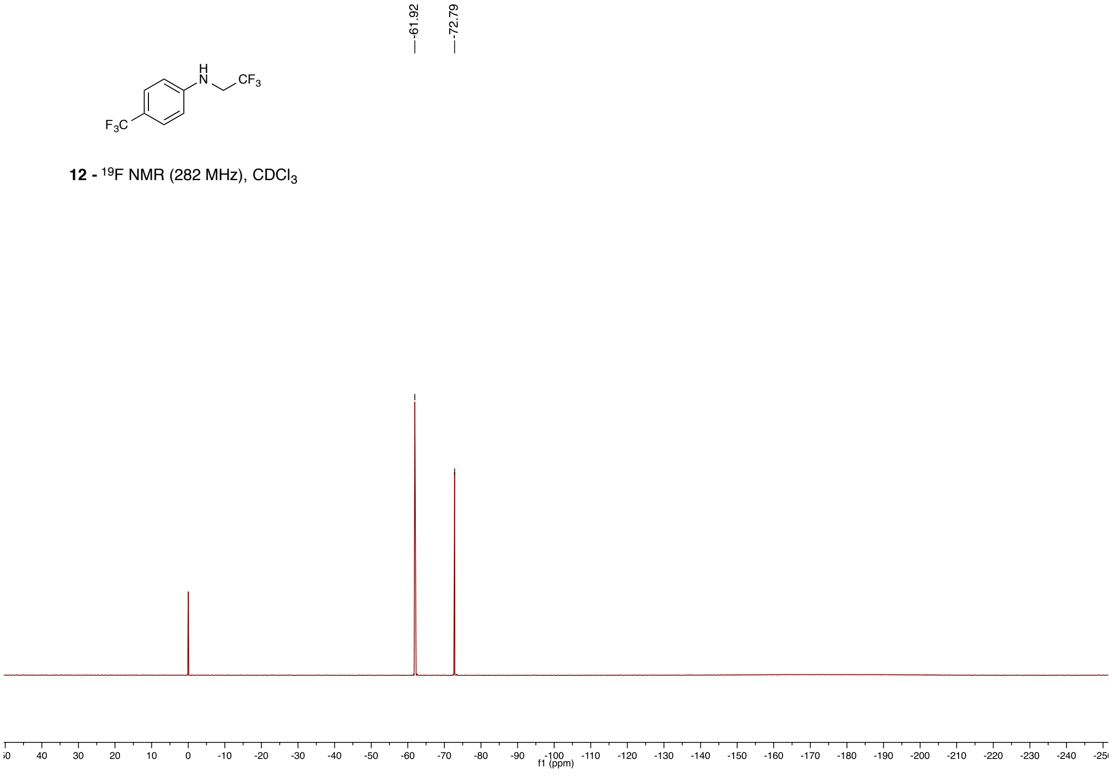

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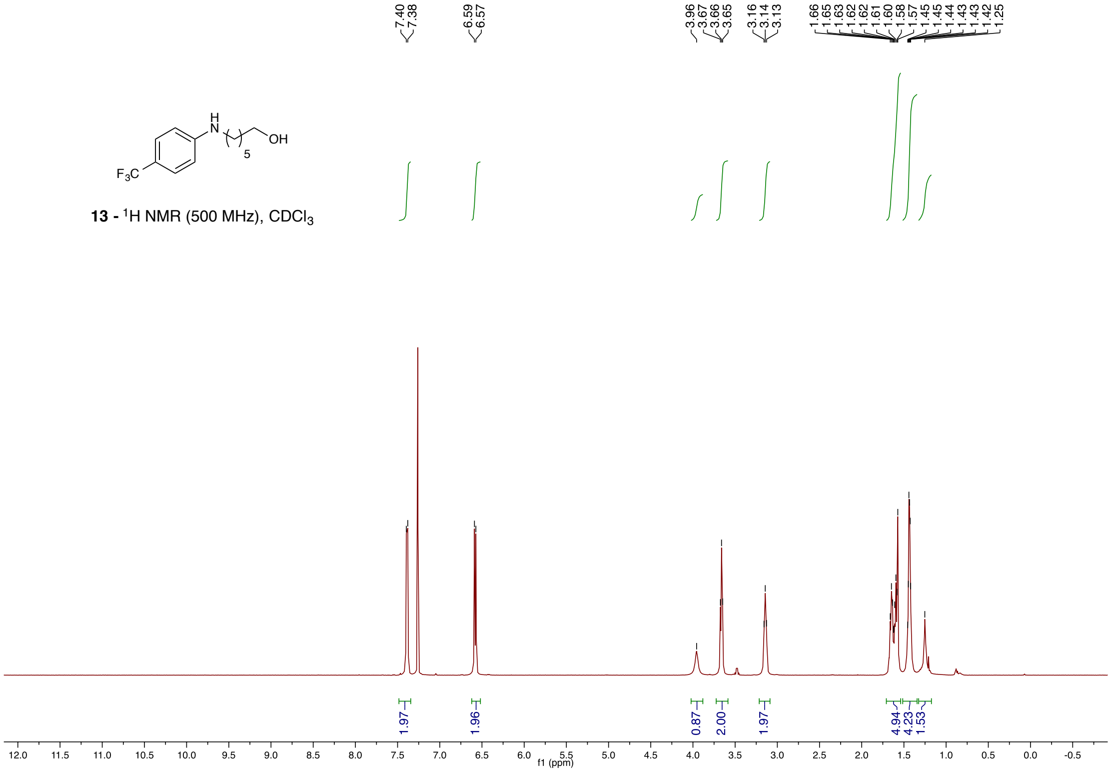

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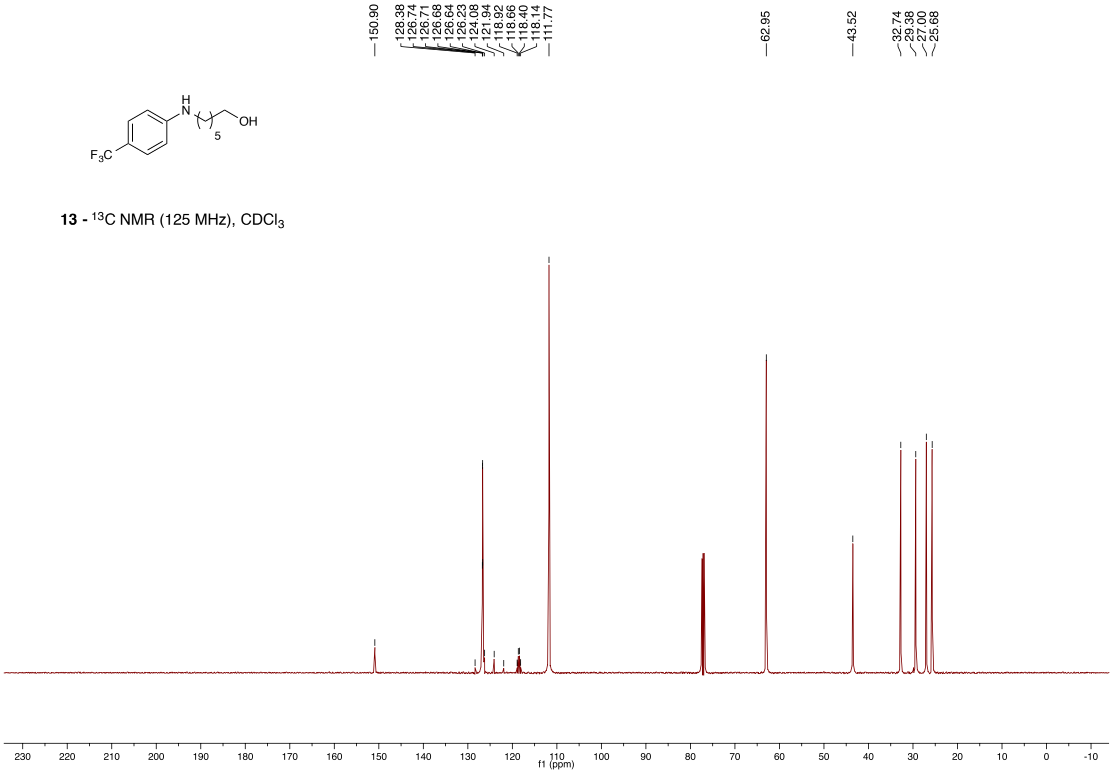

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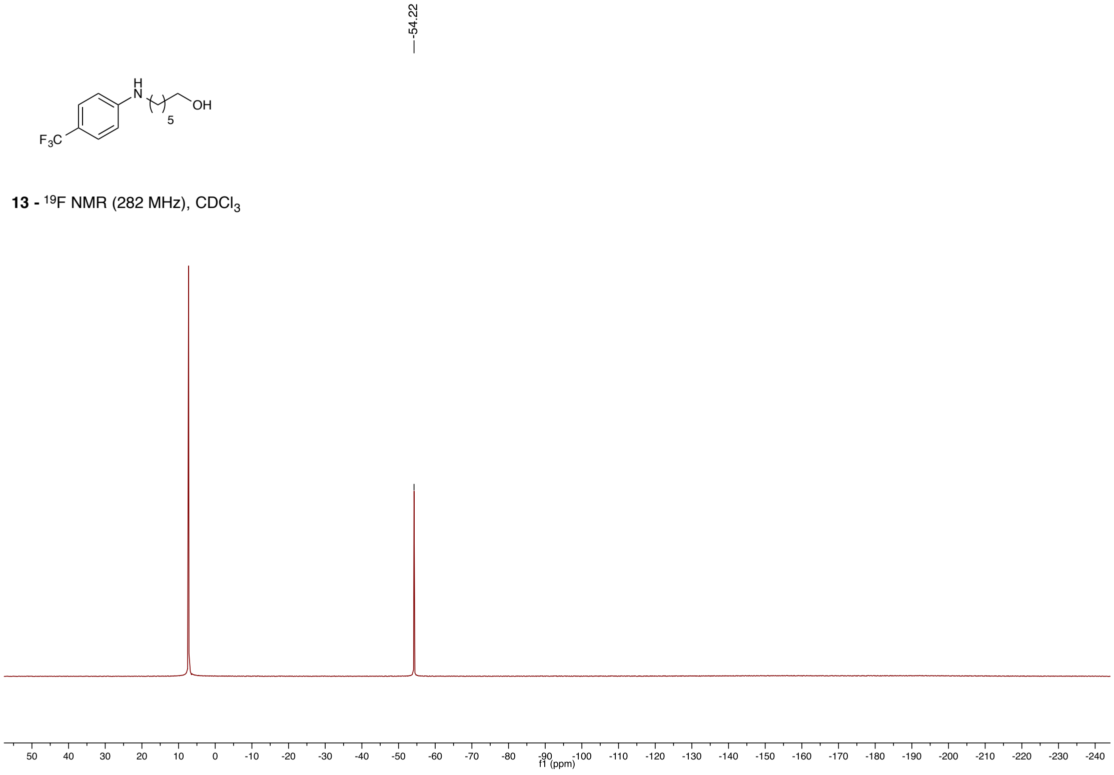

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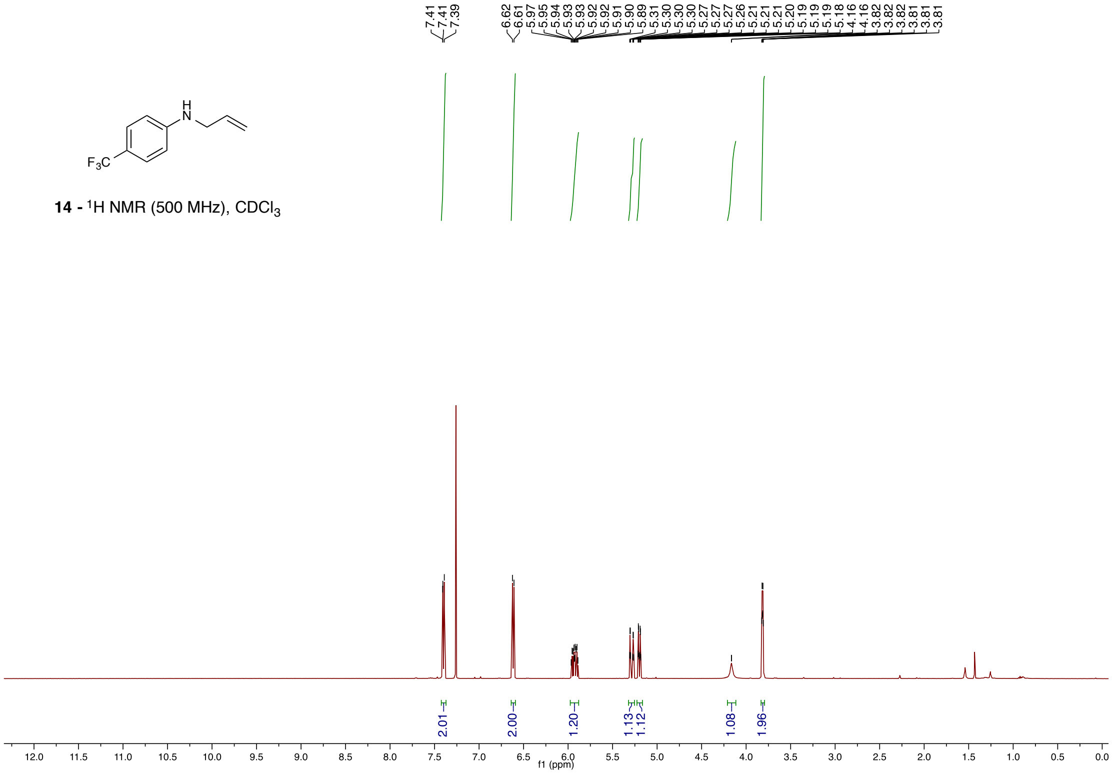

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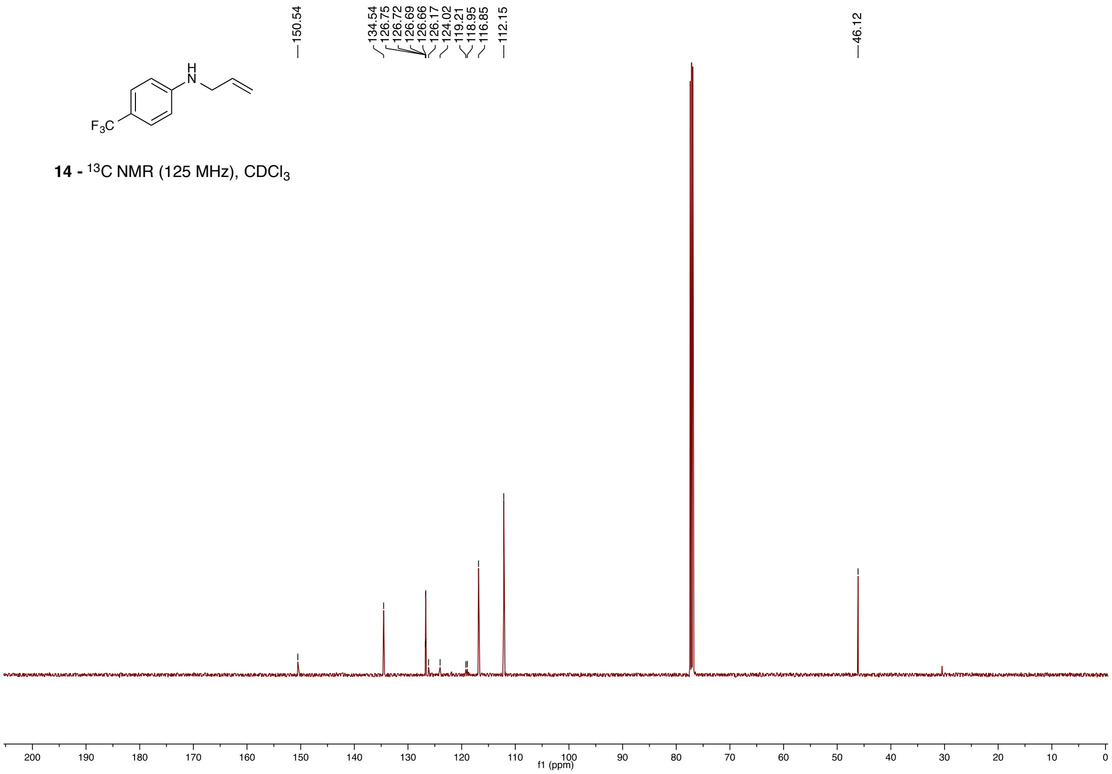

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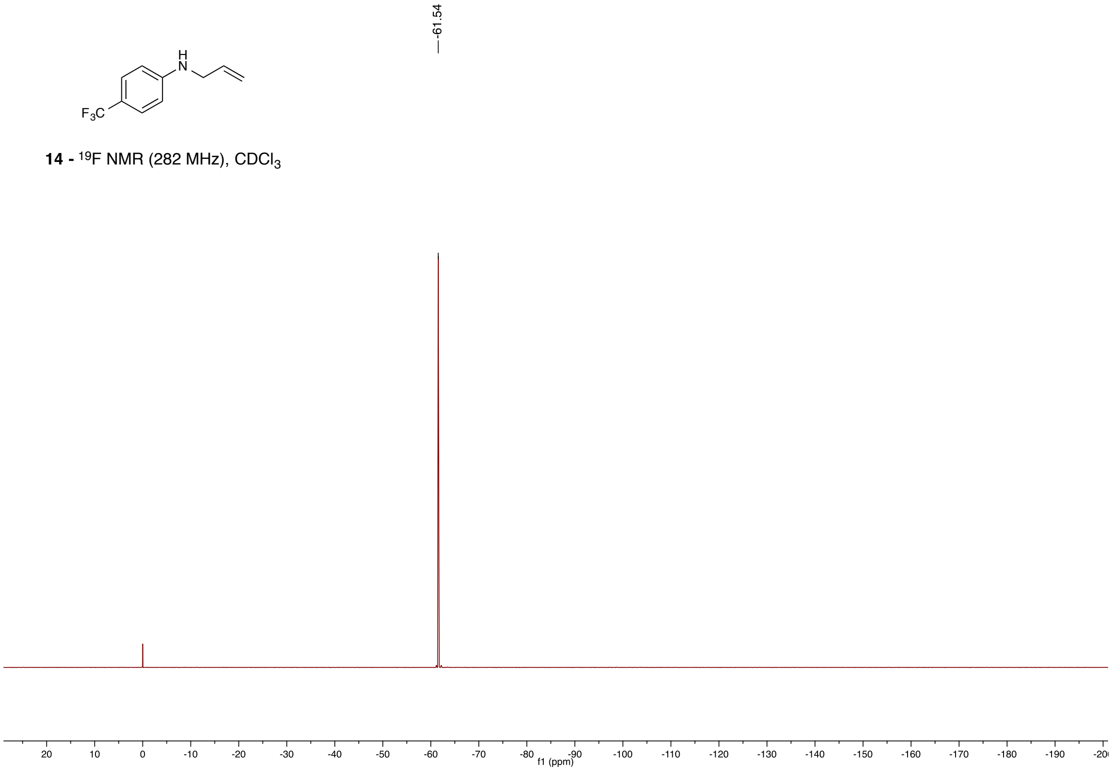
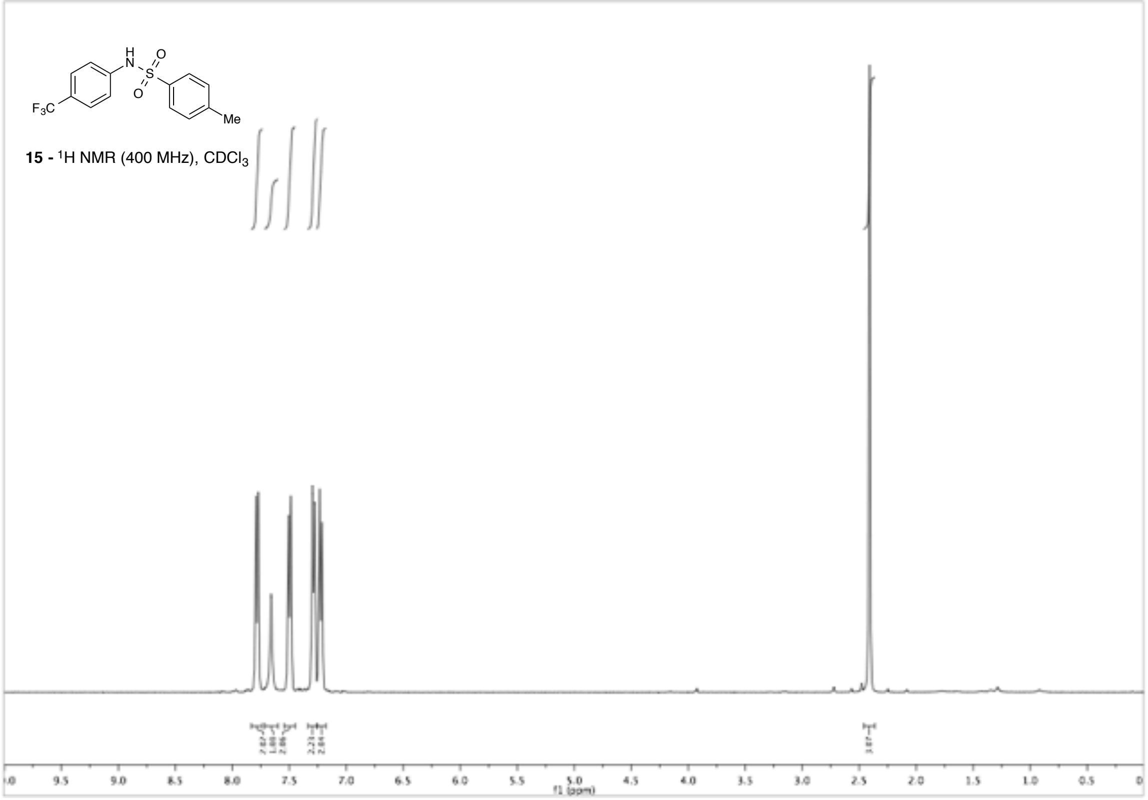
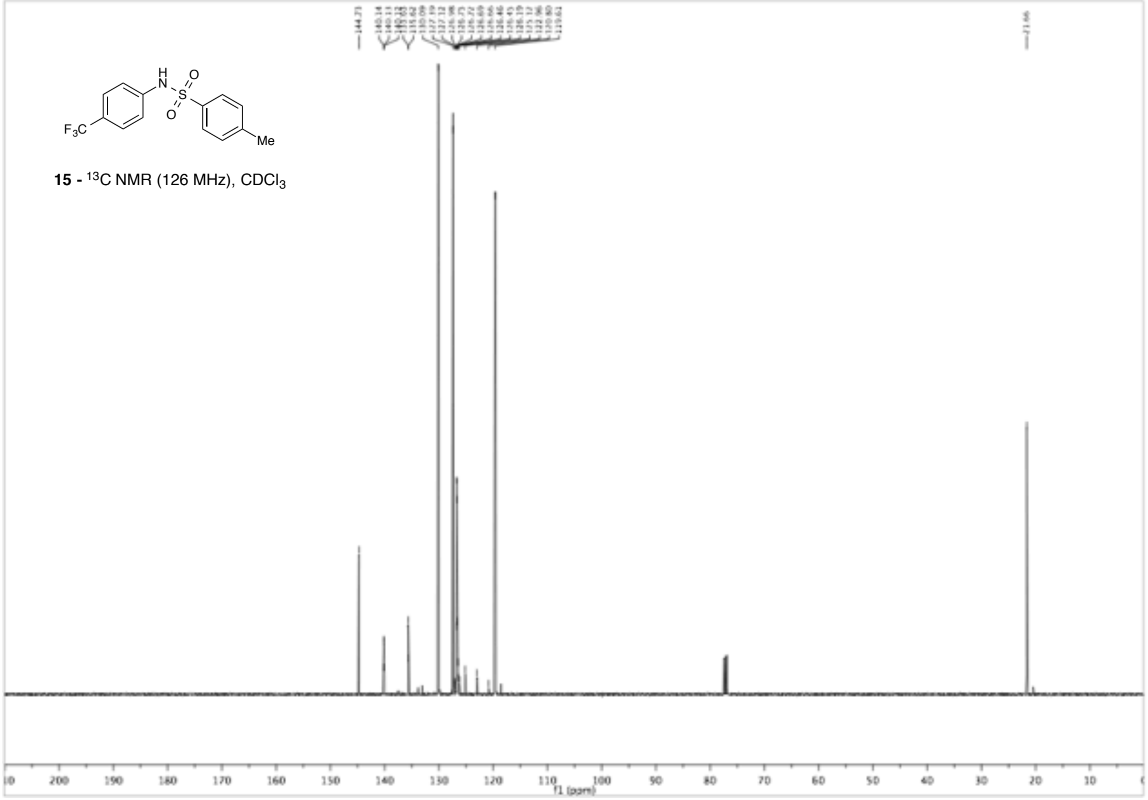


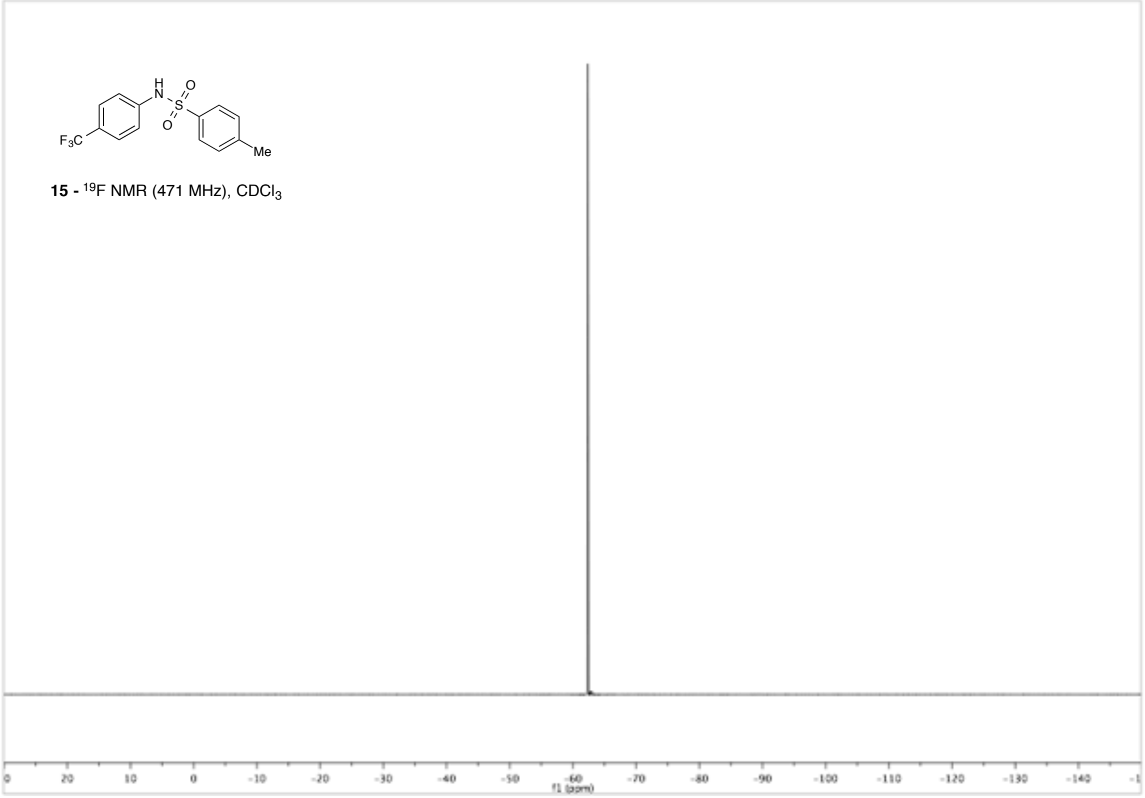
14 - ^{19}F NMR (282 MHz), CDCl$_3$



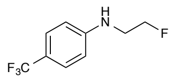
15 - ^{1}H NMR (400 MHz), CDCl$_3$



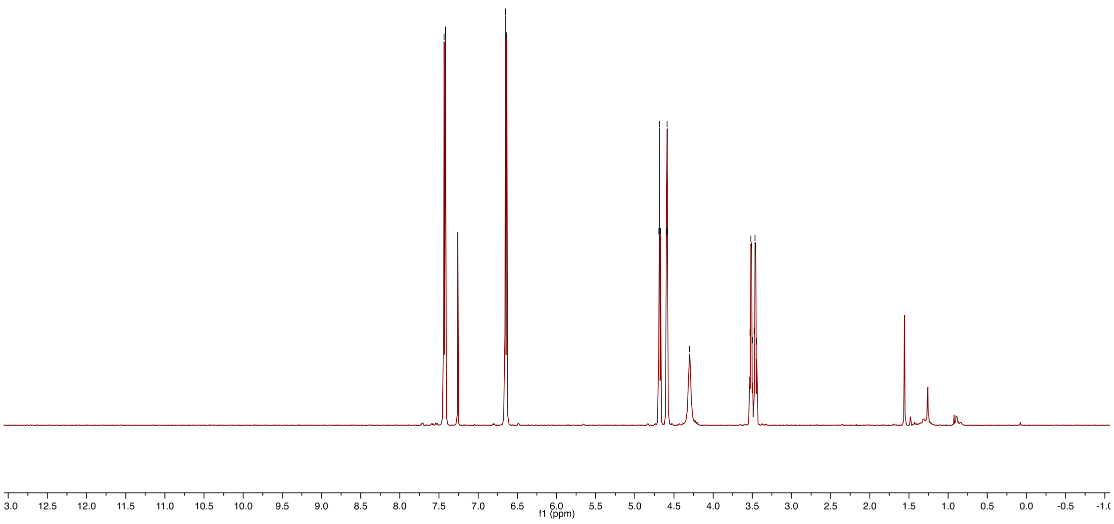
15 - ^{13}C NMR (126 MHz), CDCl$_3$

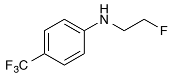


15 - ^{19}F NMR (471 MHz), CDCl$_3$

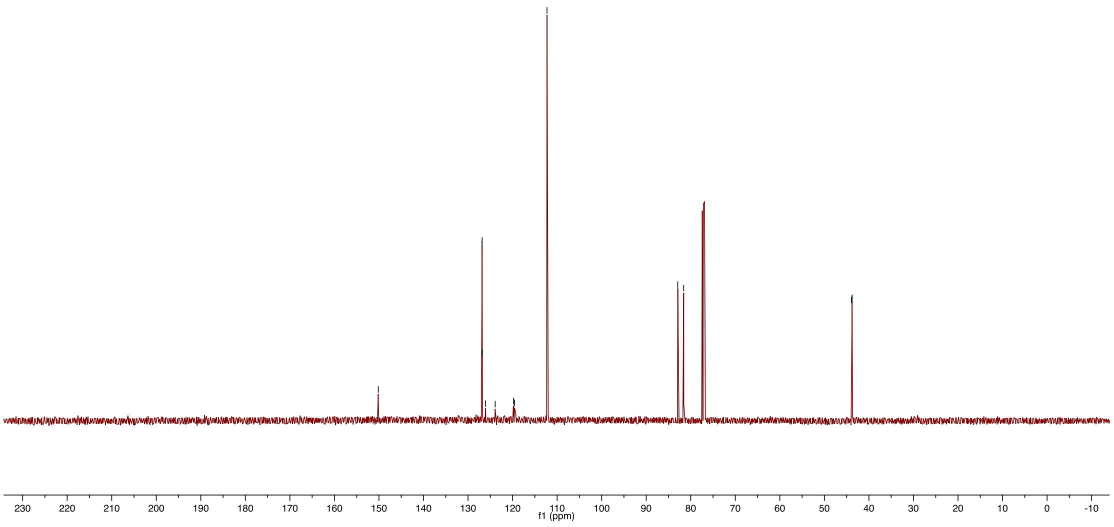


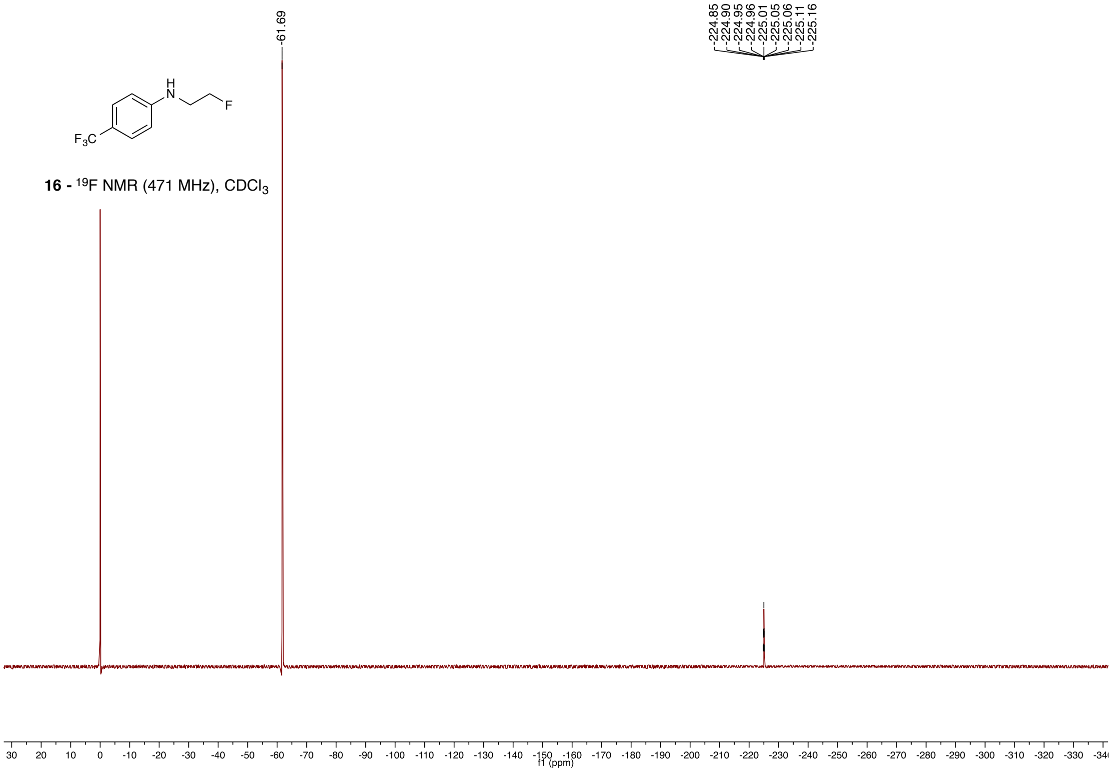
16 - ^{1}H NMR (500 MHz), $CDCl_3$



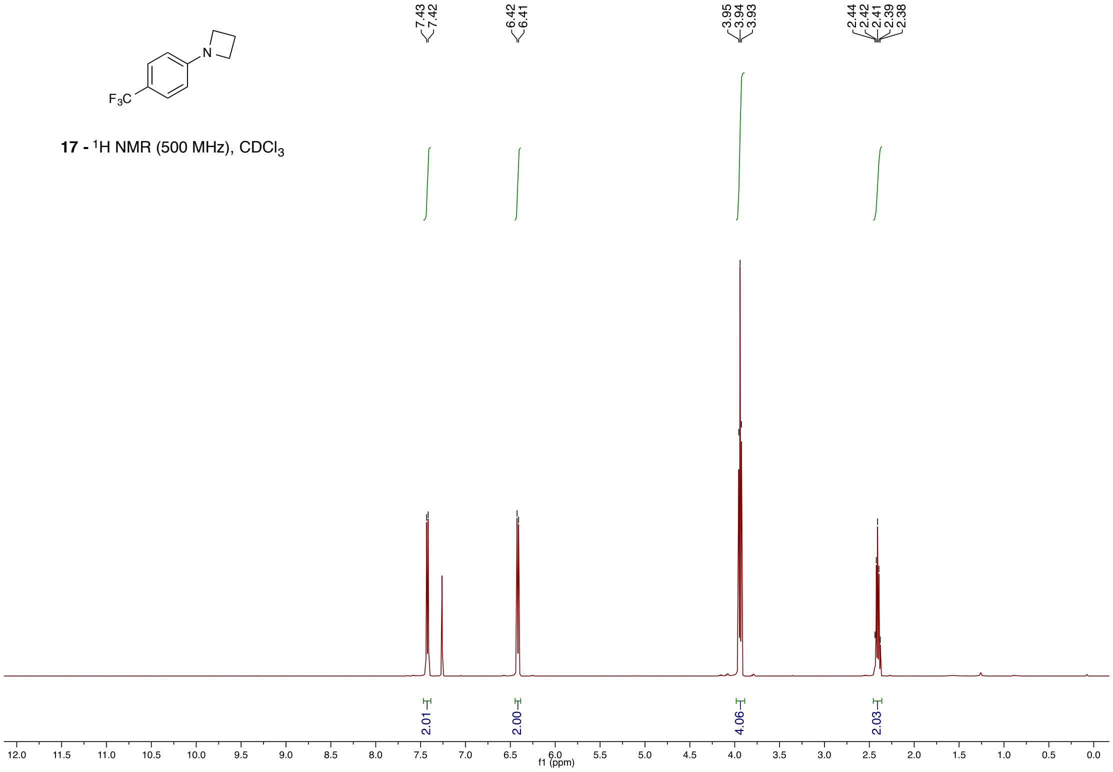


16 - ^{13}C NMR (125 MHz), $CDCl_3$

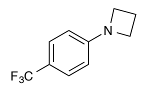




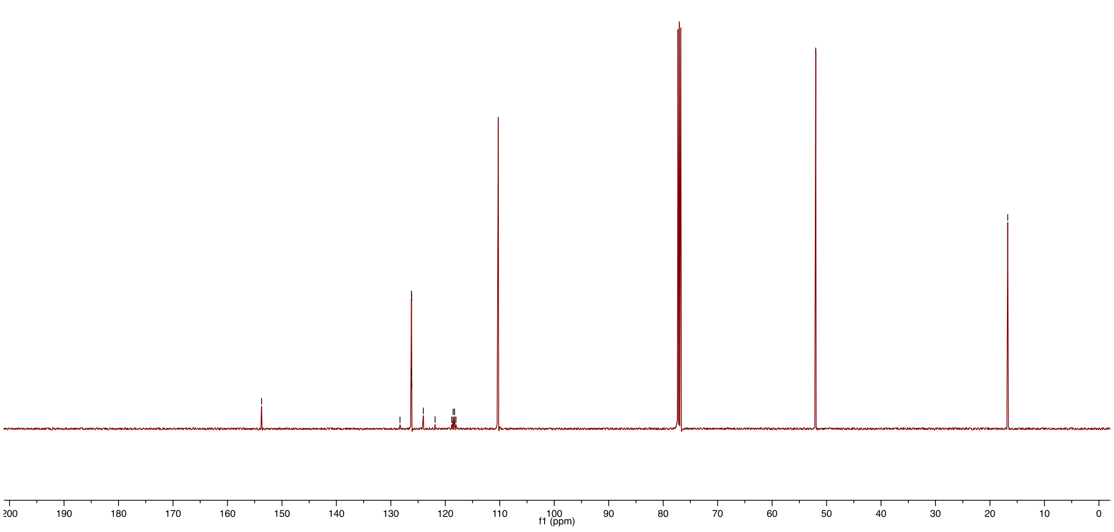
16 - ^{19}F NMR (471 MHz), CDCl$_3$

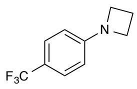


17 - ^{1}H NMR (500 MHz), CDCl$_3$

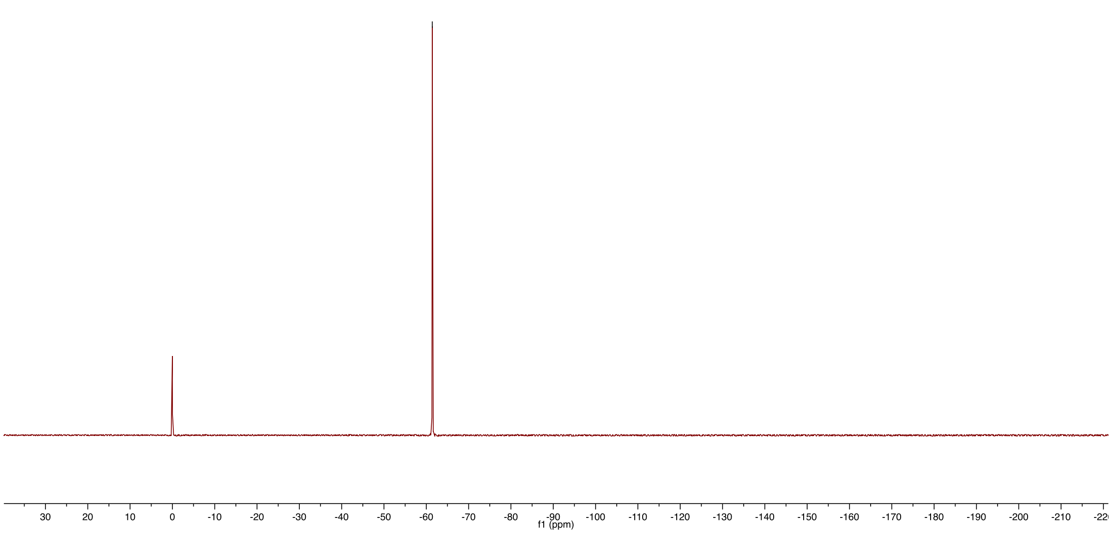


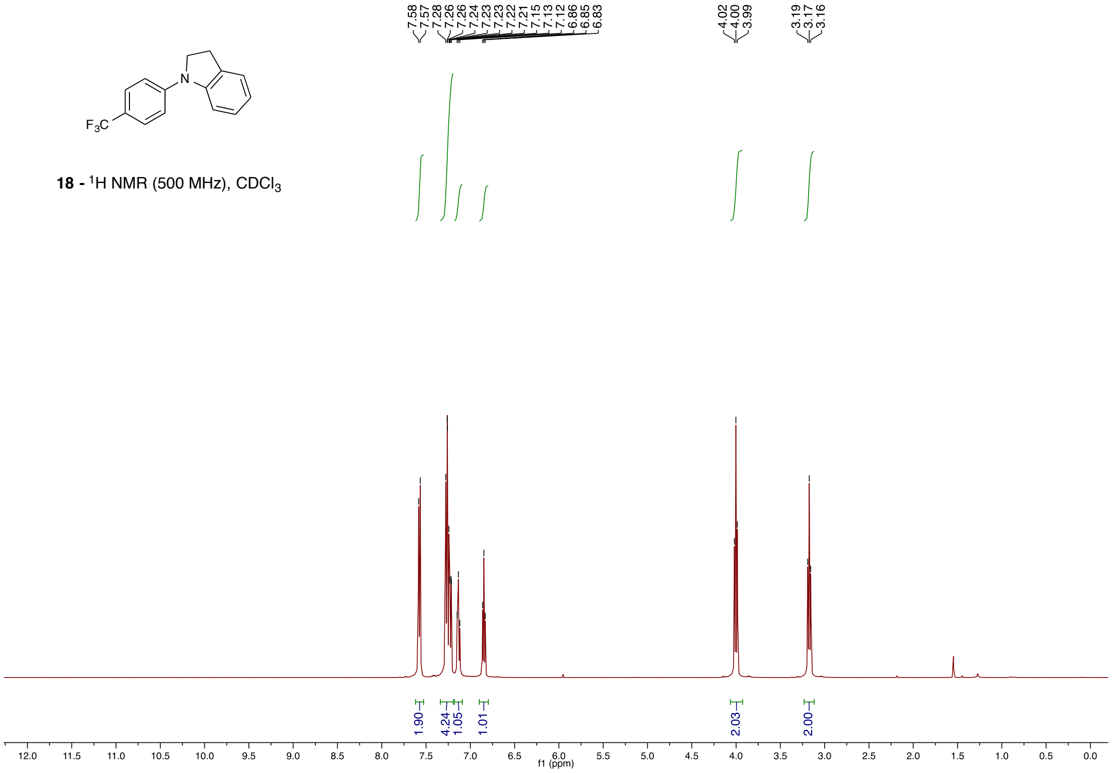
17 - ^{13}C NMR (125 MHz), CDCl$_3$



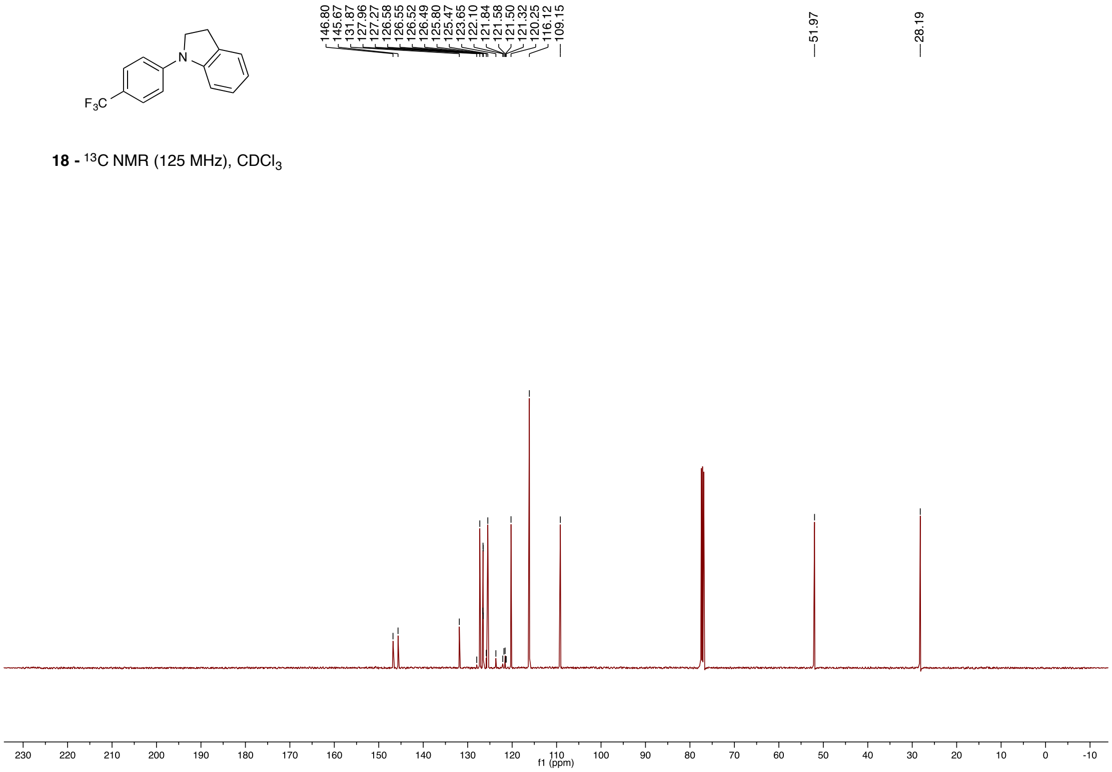


17 - ^{19}F NMR (282 MHz), CDCl$_3$

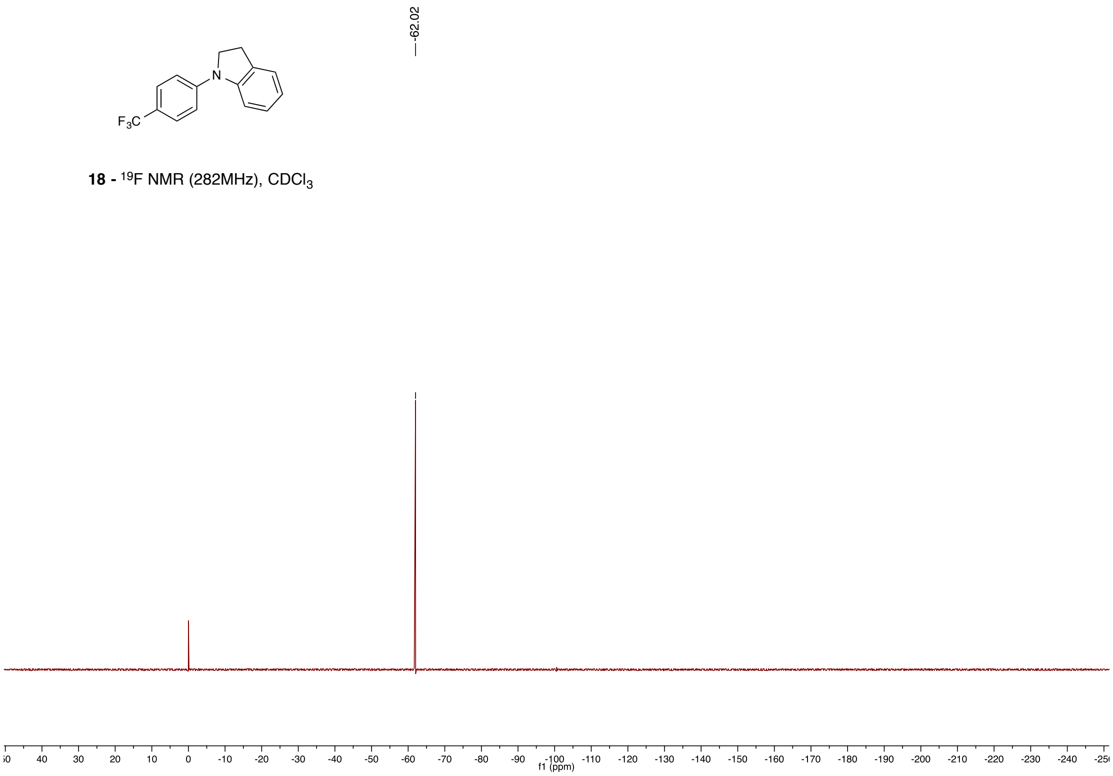




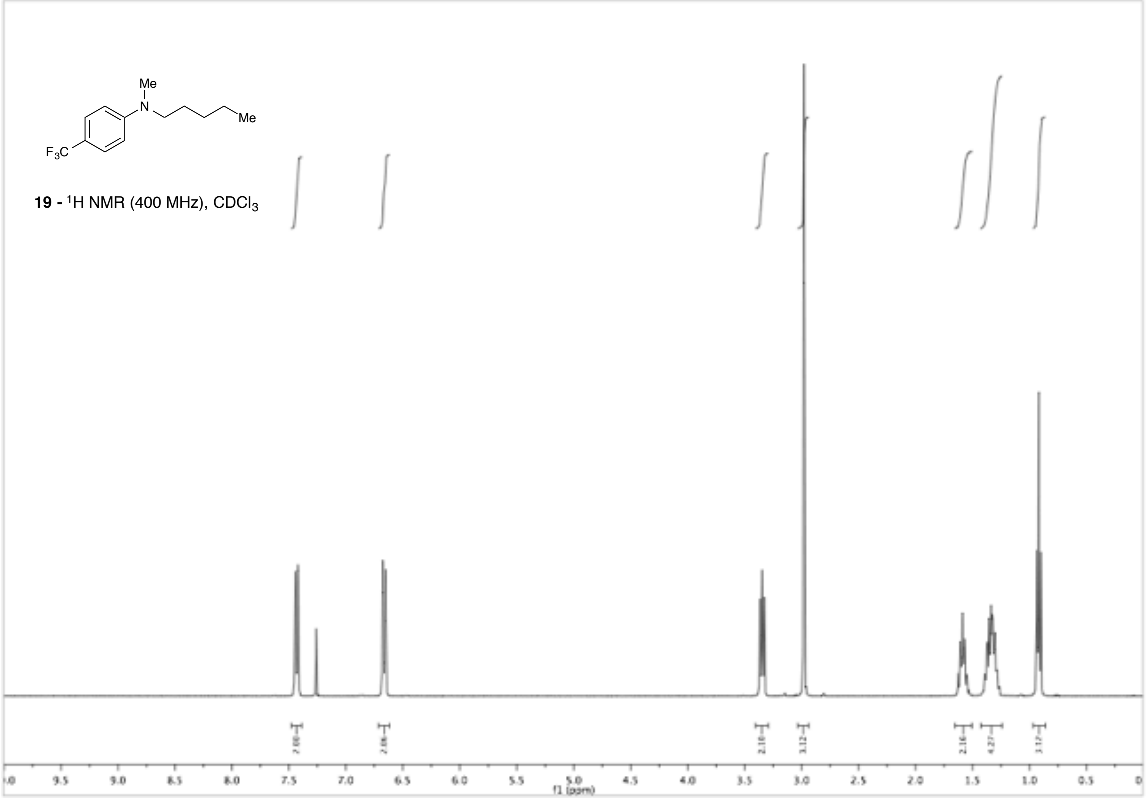
18 - ^{1}H NMR (500 MHz), $CDCl_3$



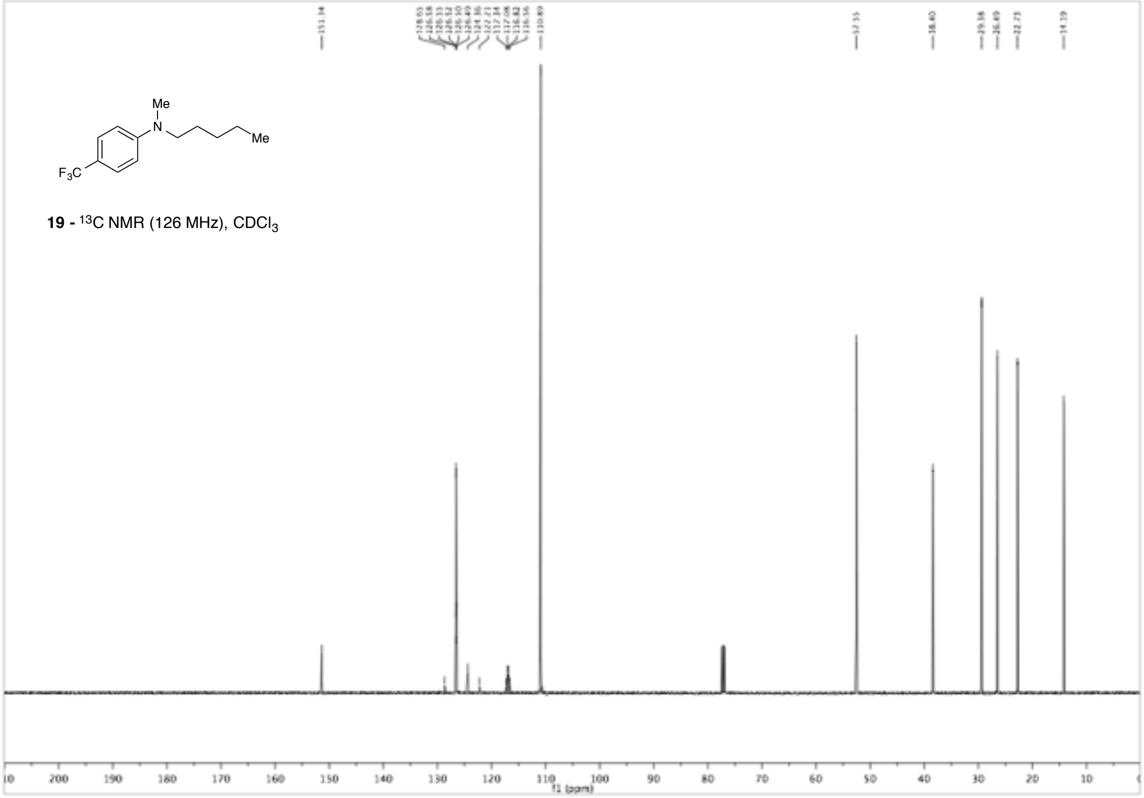
18 - ^{13}C NMR (125 MHz), $CDCl_3$



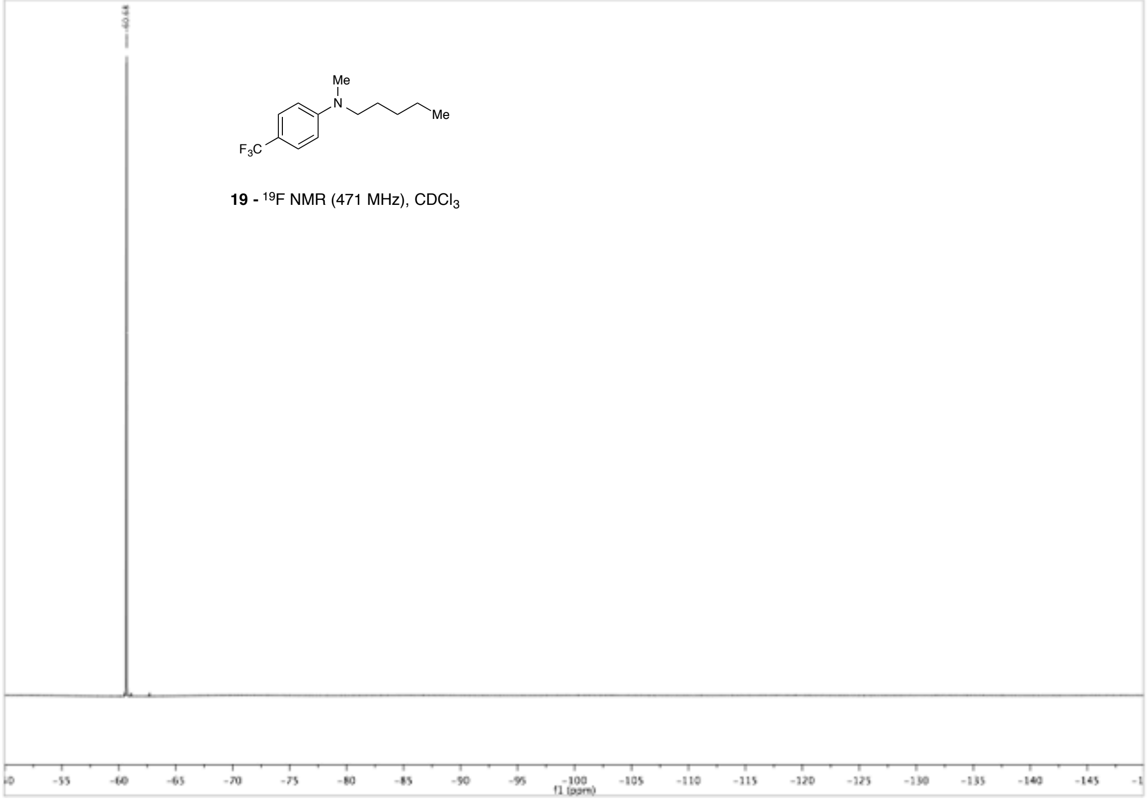
18 - ^{19}F NMR (282MHz), CDCl$_3$



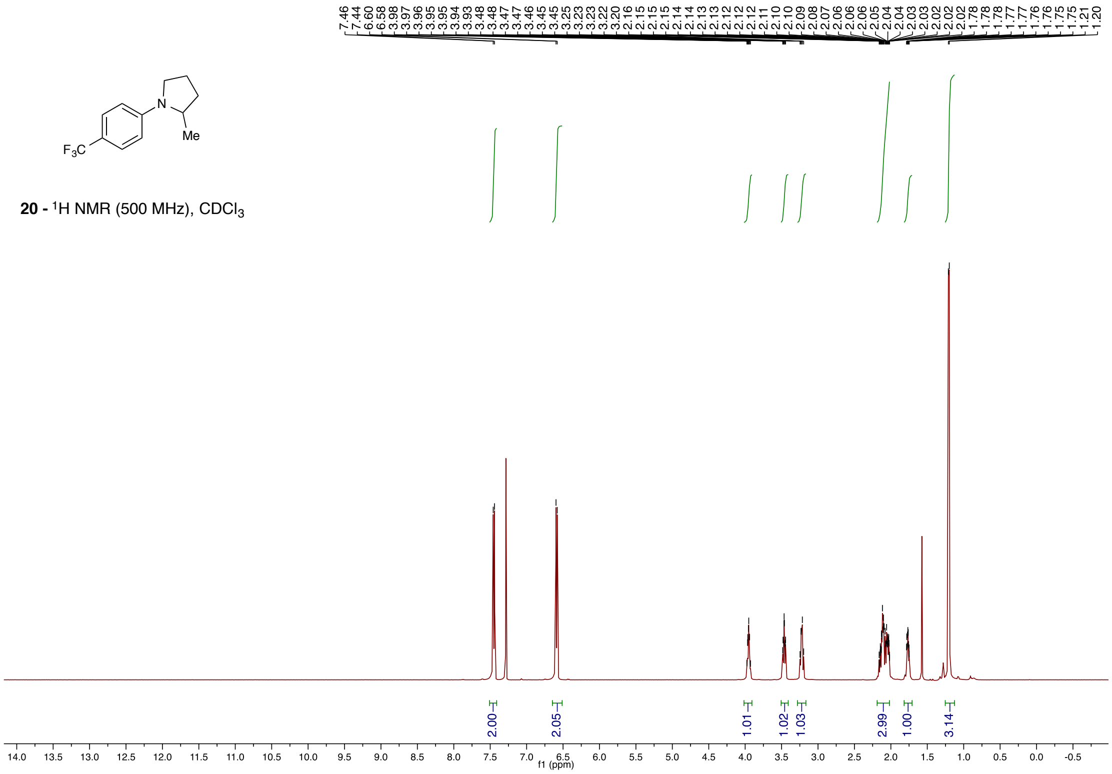
19 - ^{1}H NMR (400 MHz), CDCl$_3$



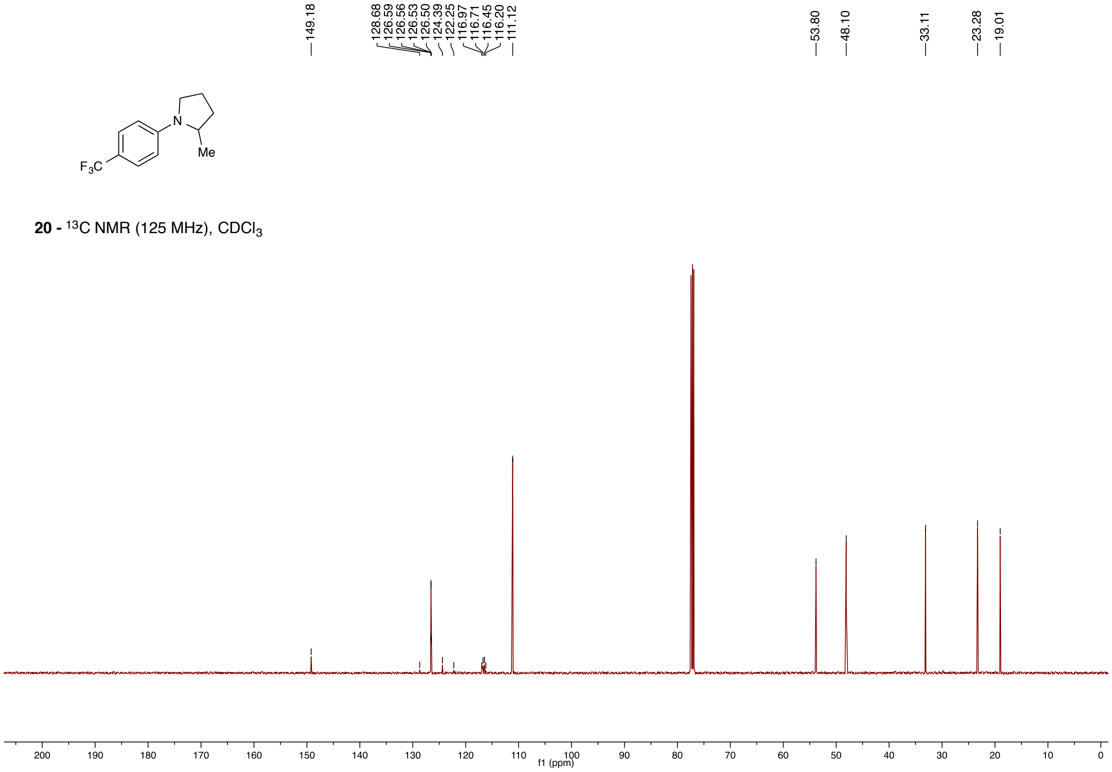
19 - ^{13}C NMR (126 MHz), $CDCl_3$



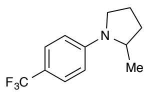
19 - ^{19}F NMR (471 MHz), $CDCl_3$



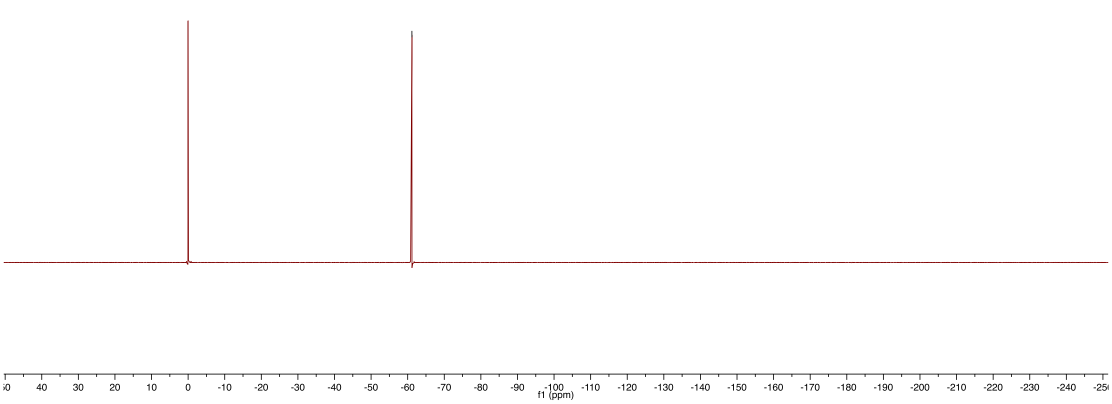
20 - ^{1}H NMR (500 MHz), $CDCl_3$

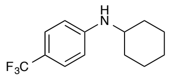


20 - ^{13}C NMR (125 MHz), $CDCl_3$

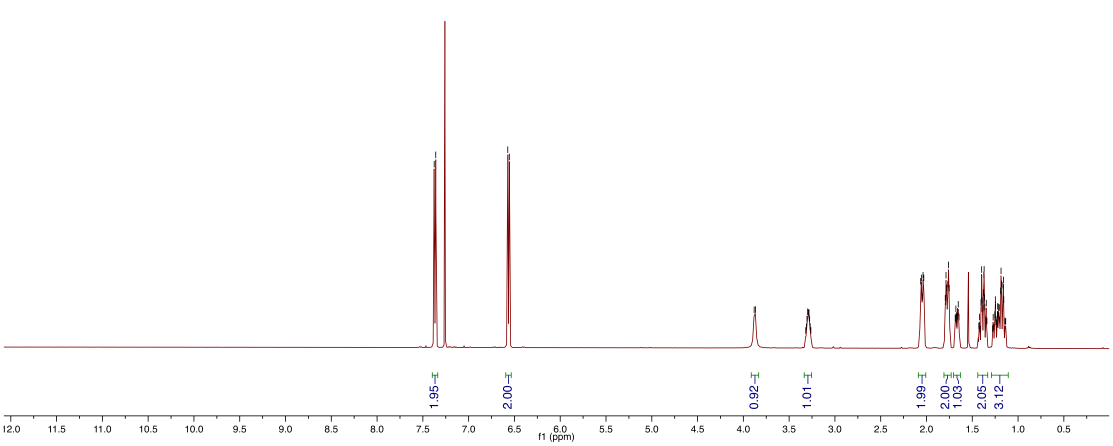


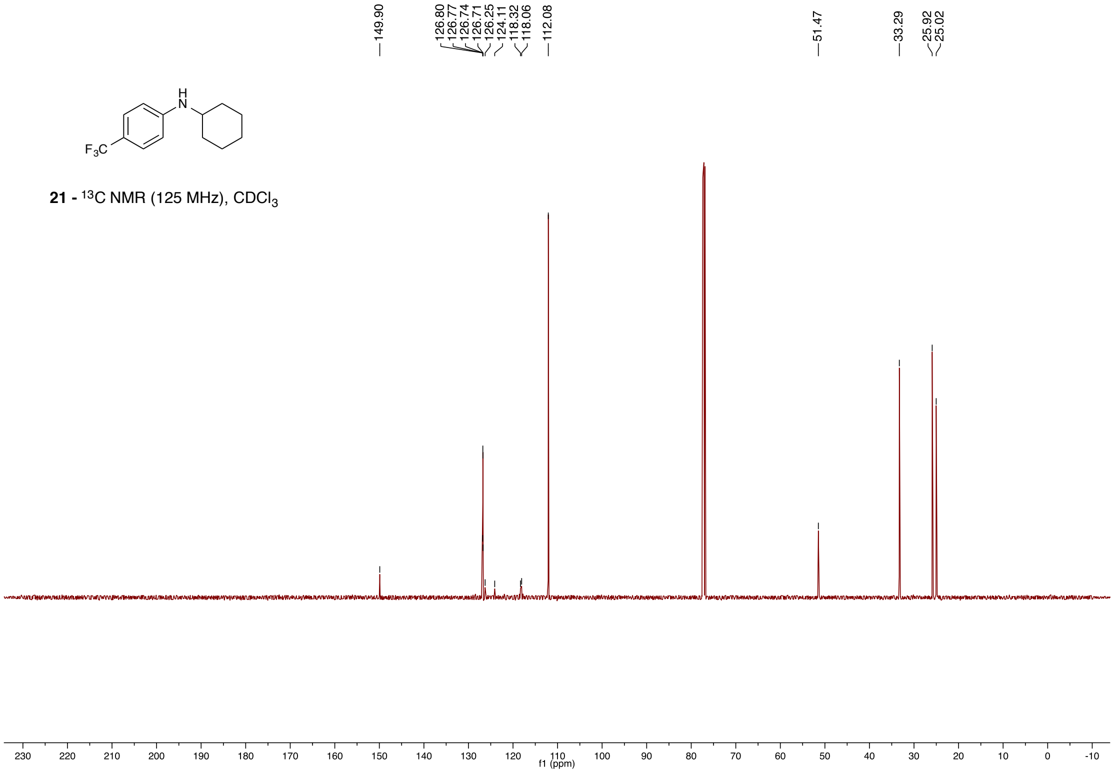
20 - ^{19}F NMR (282 MHz), CDCl$_3$



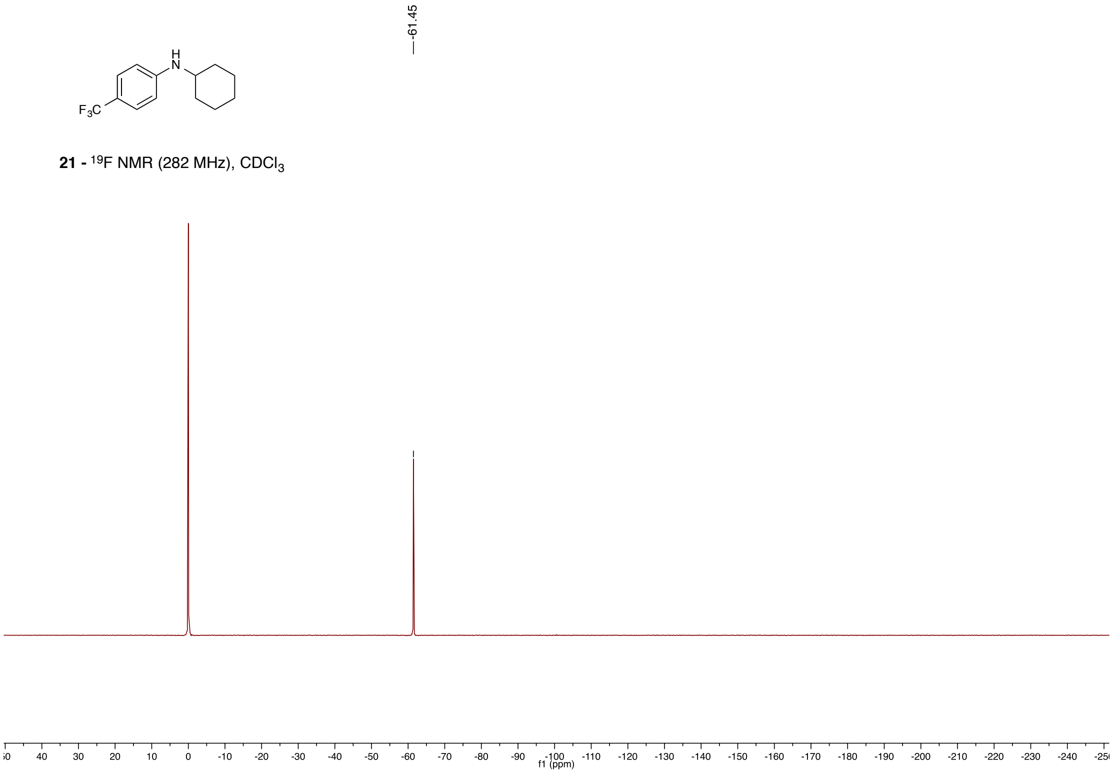


21 - ^{1}H NMR (500 MHz), CDCl$_3$

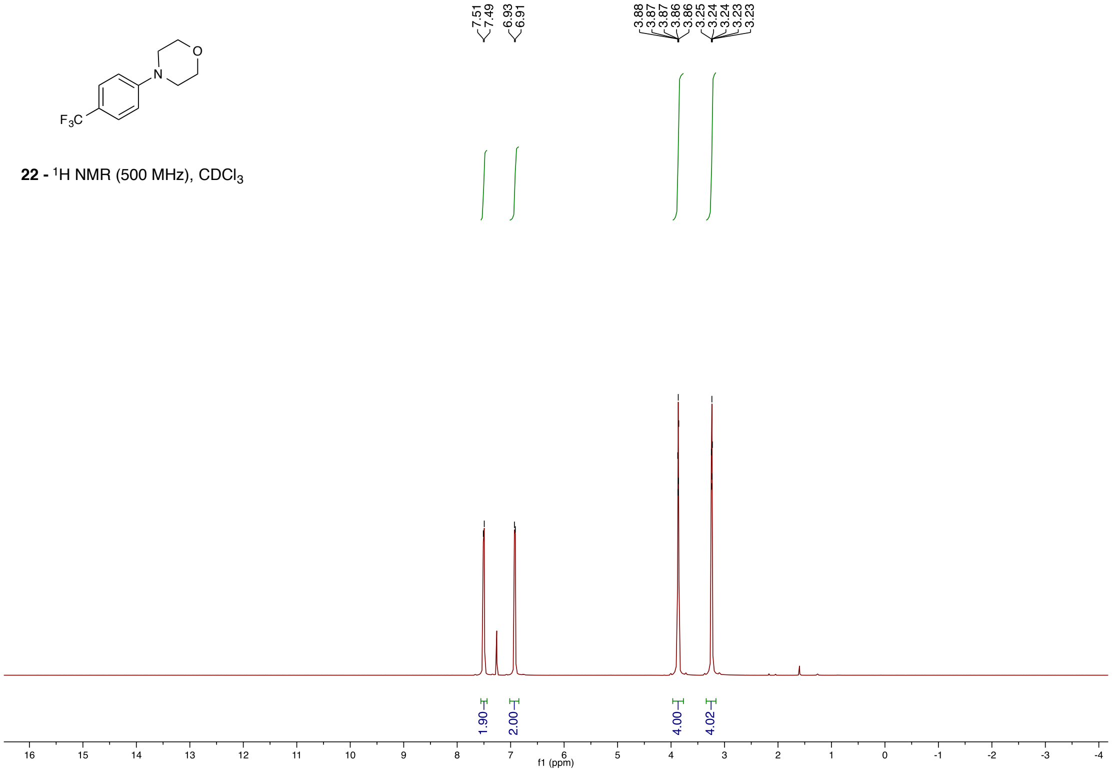




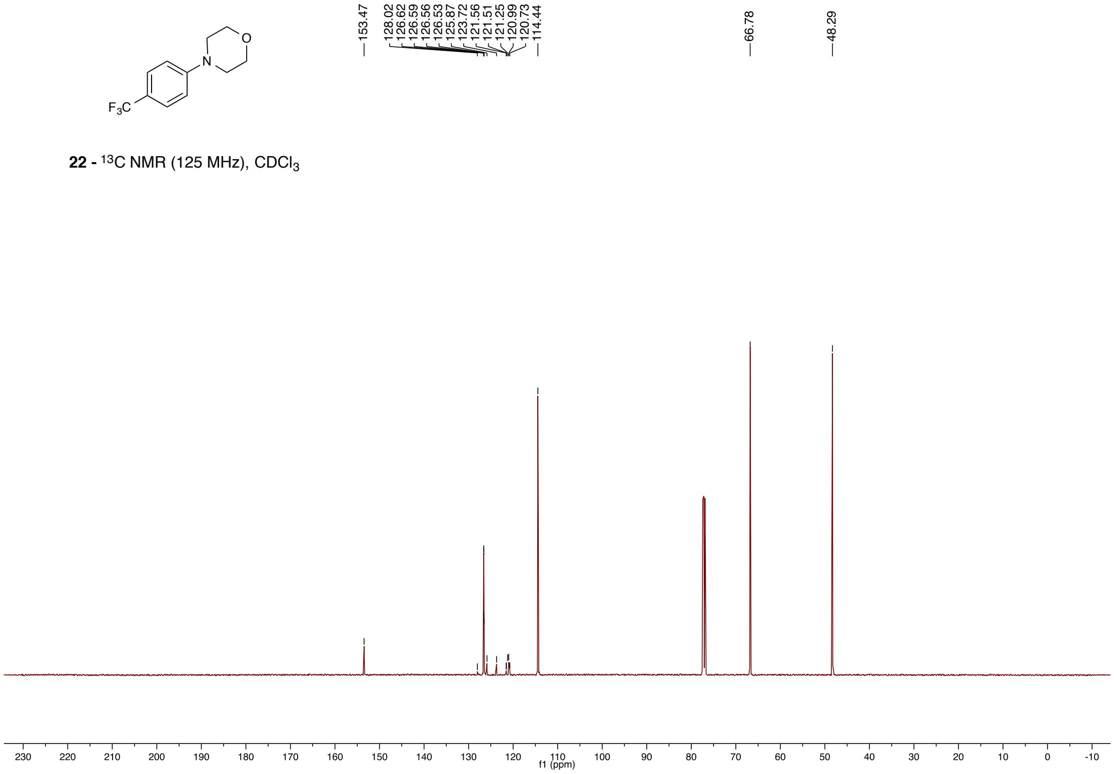
21 - ^{13}C NMR (125 MHz), $CDCl_3$



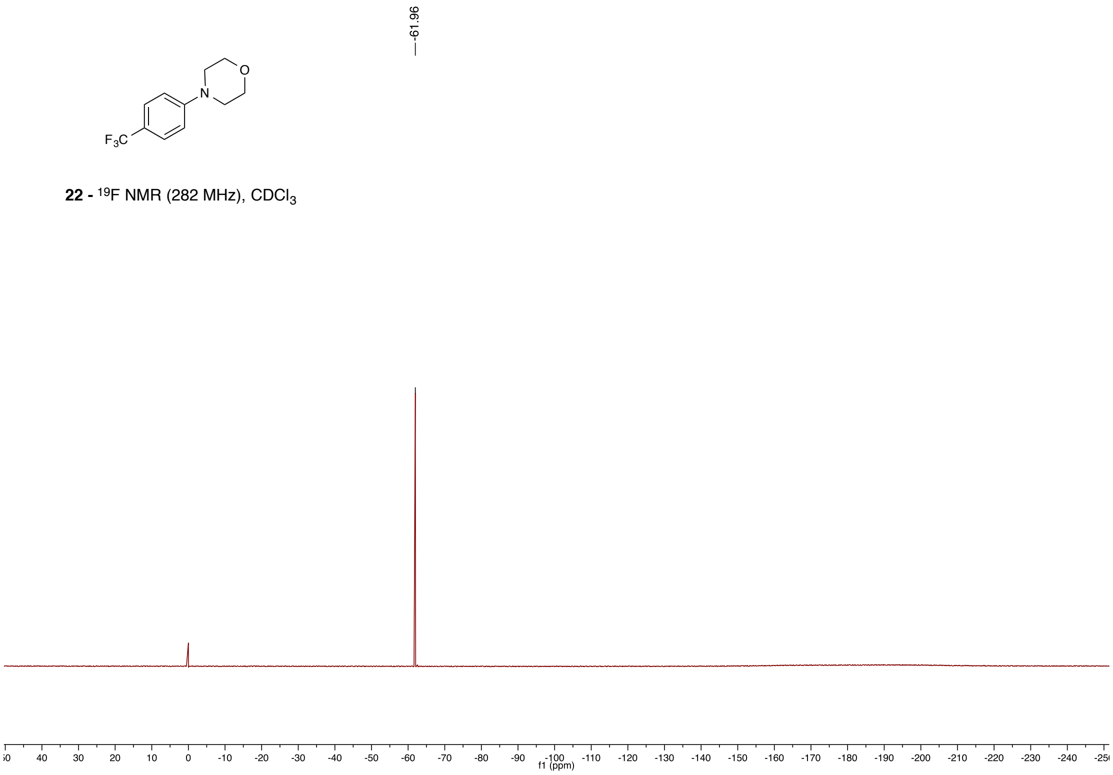
21 - ^{19}F NMR (282 MHz), $CDCl_3$



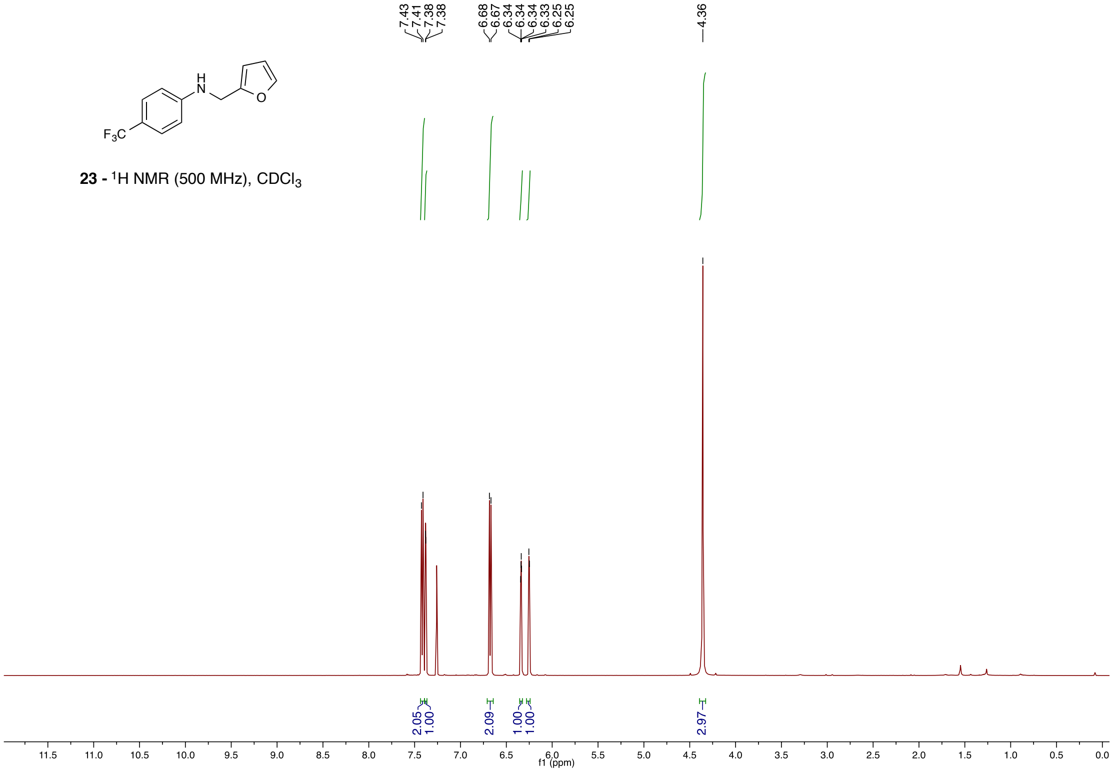
22 - ^{1}H NMR (500 MHz), $CDCl_3$



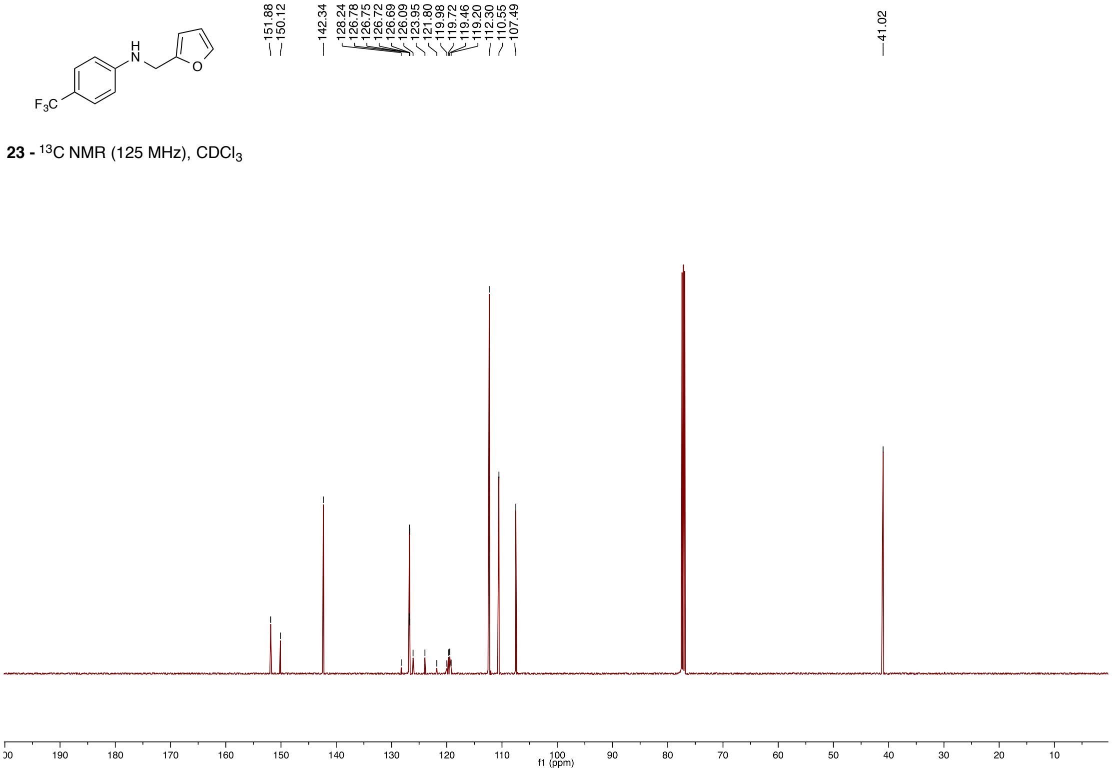
22 - ^{13}C NMR (125 MHz), $CDCl_3$



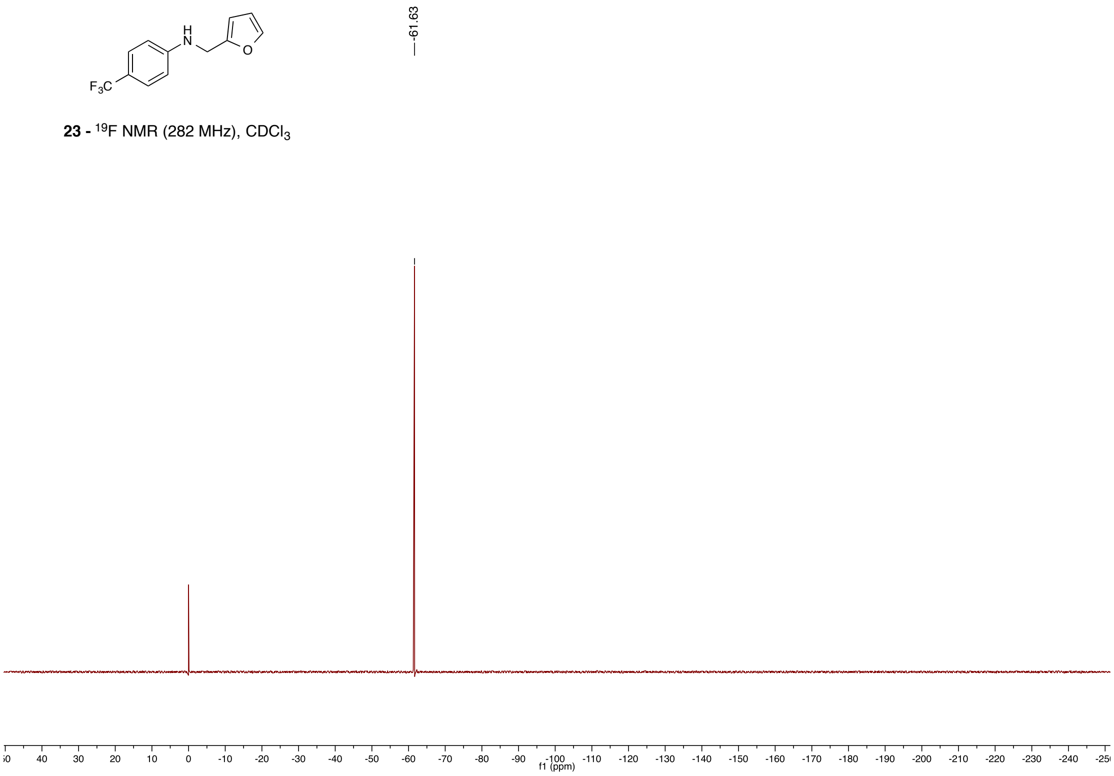
22 - ^{19}F NMR (282 MHz), CDCl$_3$



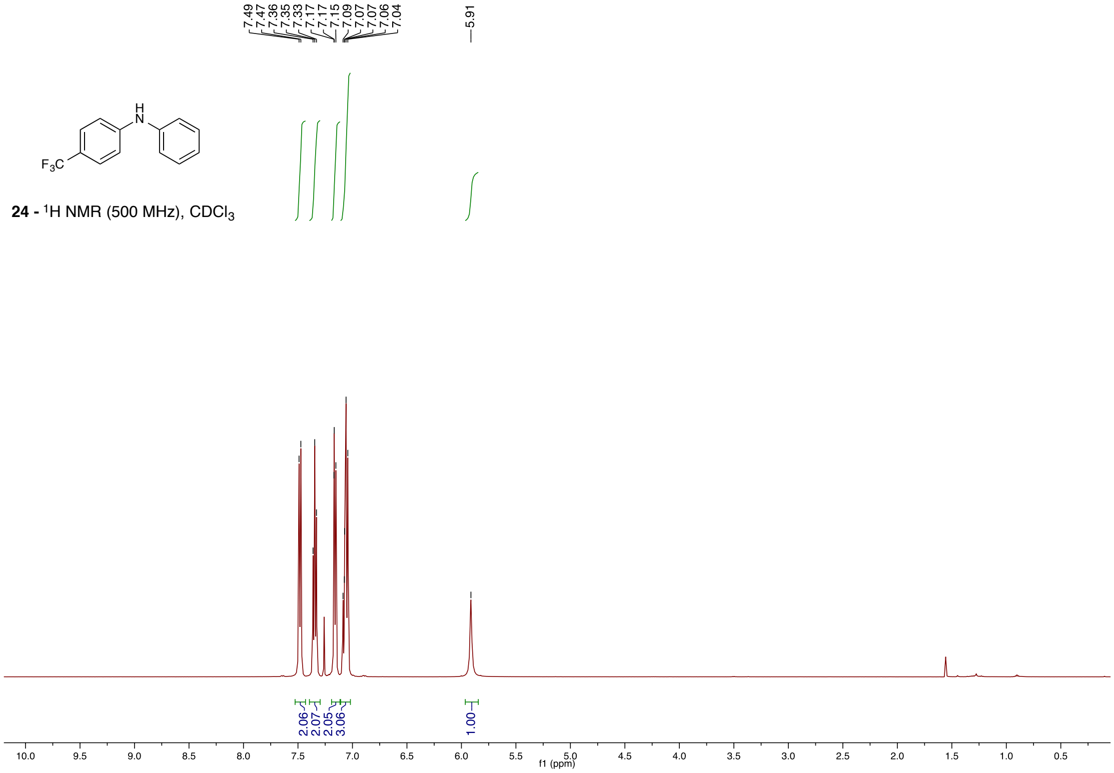
23 - ^{1}H NMR (500 MHz), CDCl$_3$



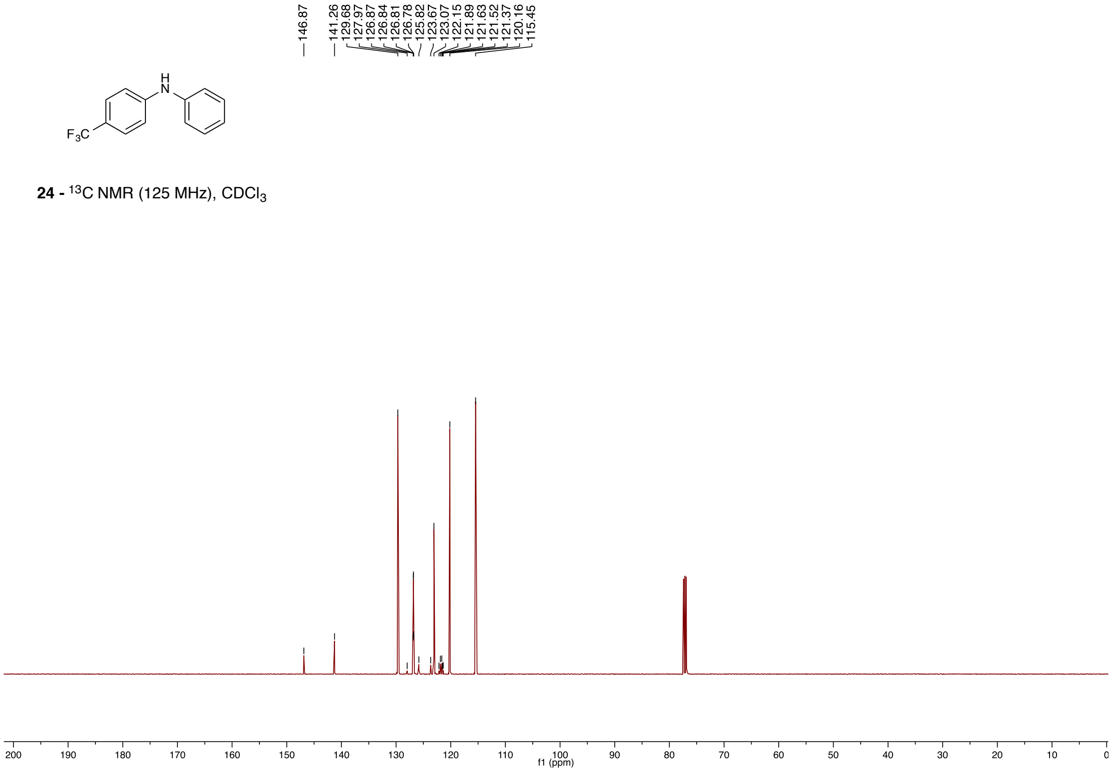
23 - ^{13}C NMR (125 MHz), CDCl$_3$



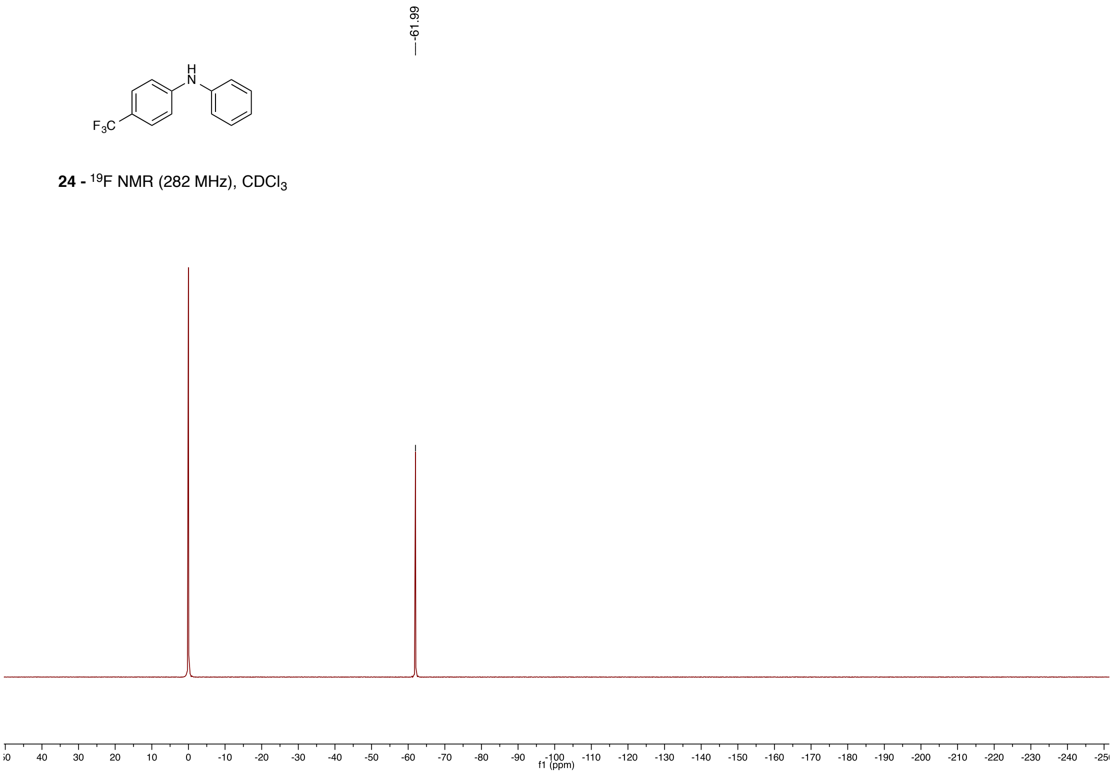
23 - ^{19}F NMR (282 MHz), CDCl$_3$



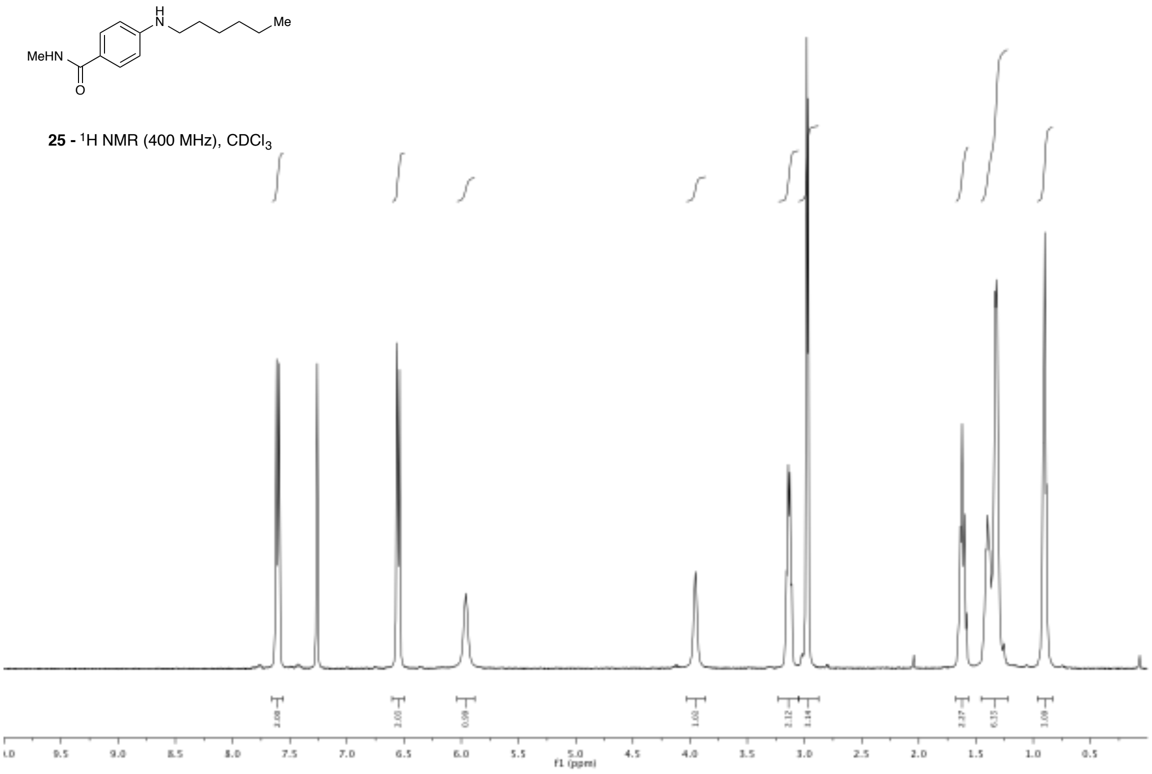
24 - ^{1}H NMR (500 MHz), CDCl$_3$



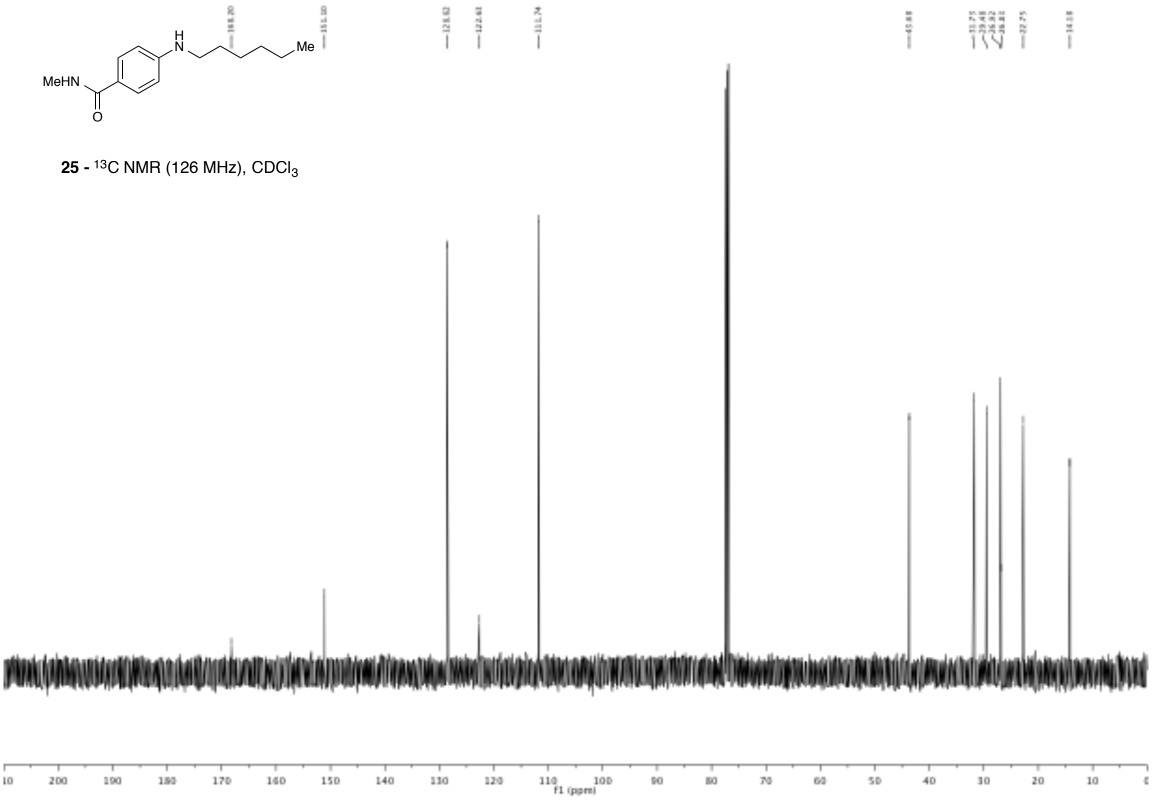
24 - ^{13}C NMR (125 MHz), CDCl$_3$



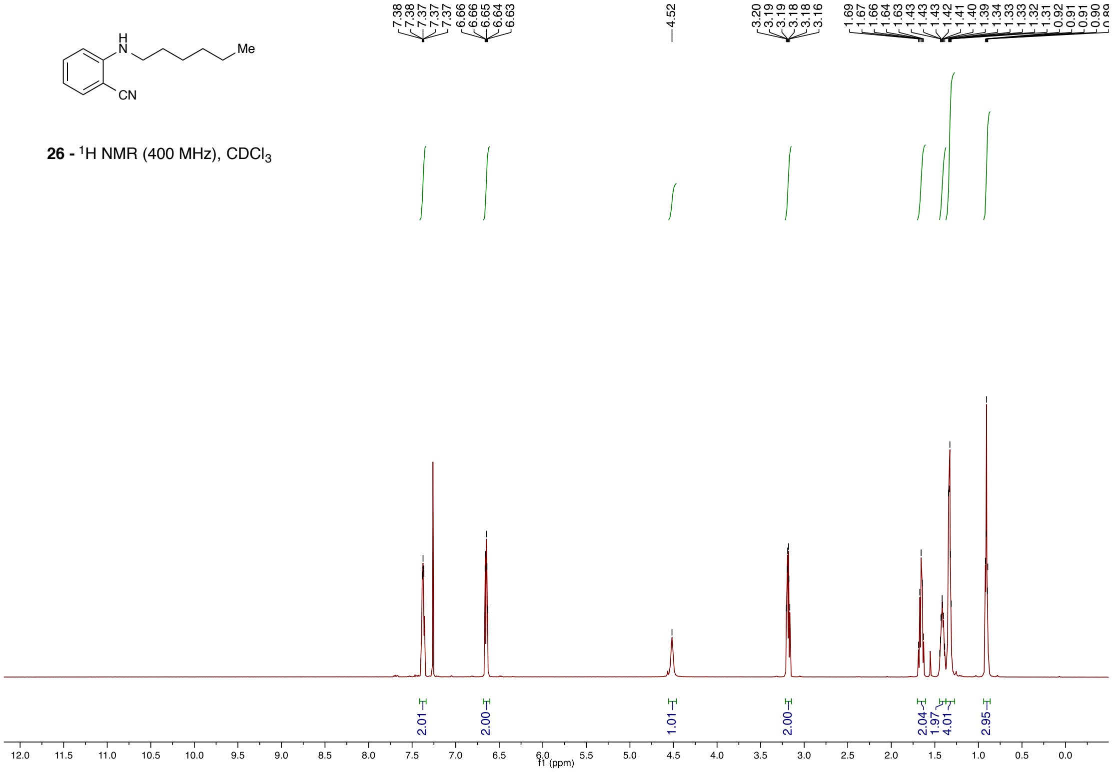
24 - ^{19}F NMR (282 MHz), $CDCl_3$



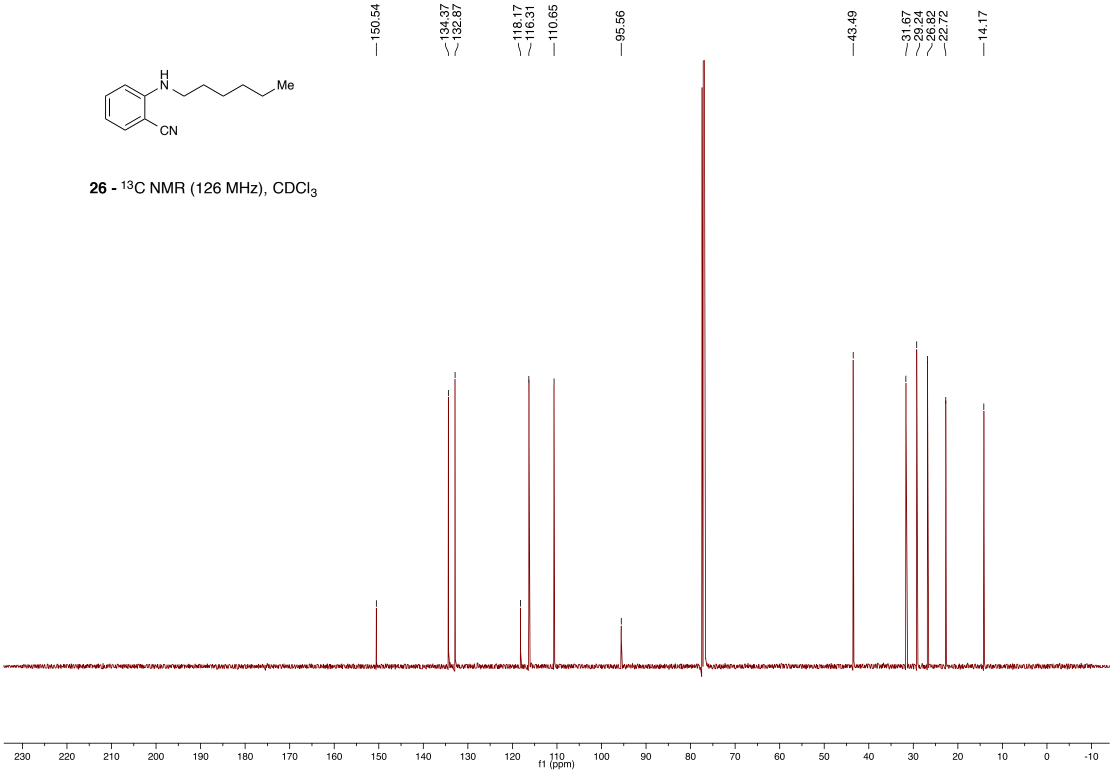
25 - ^{1}H NMR (400 MHz), $CDCl_3$



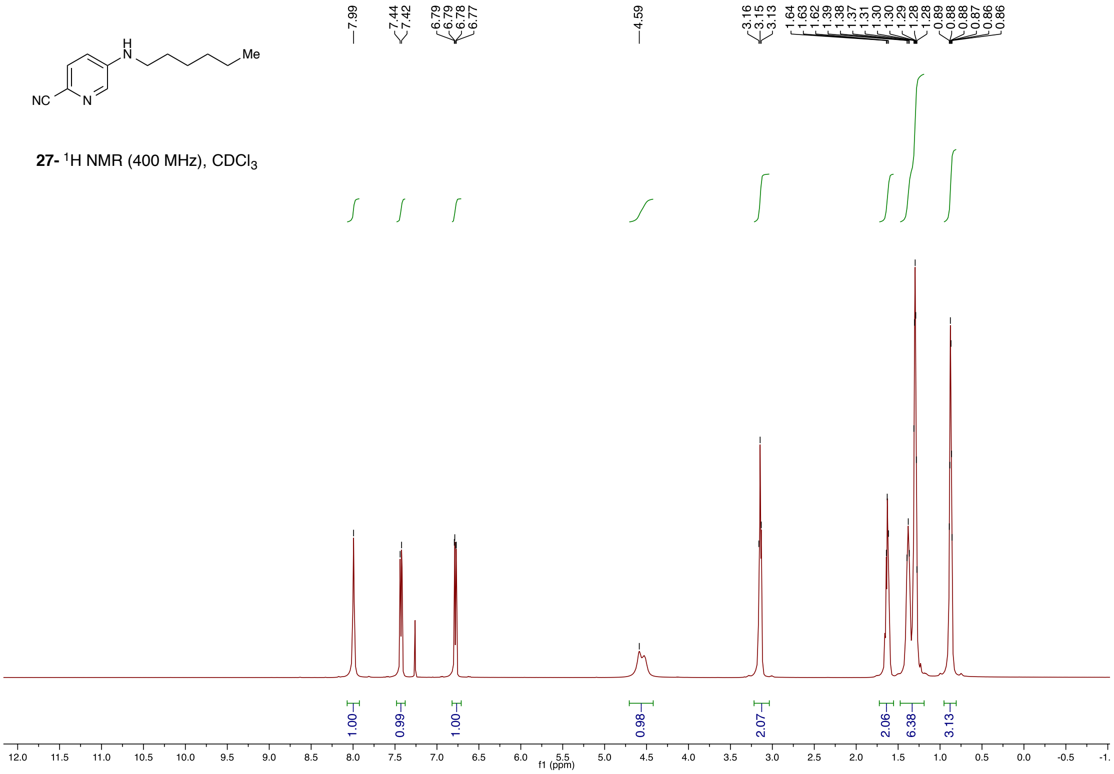
25 - ^{13}C NMR (126 MHz), CDCl$_3$



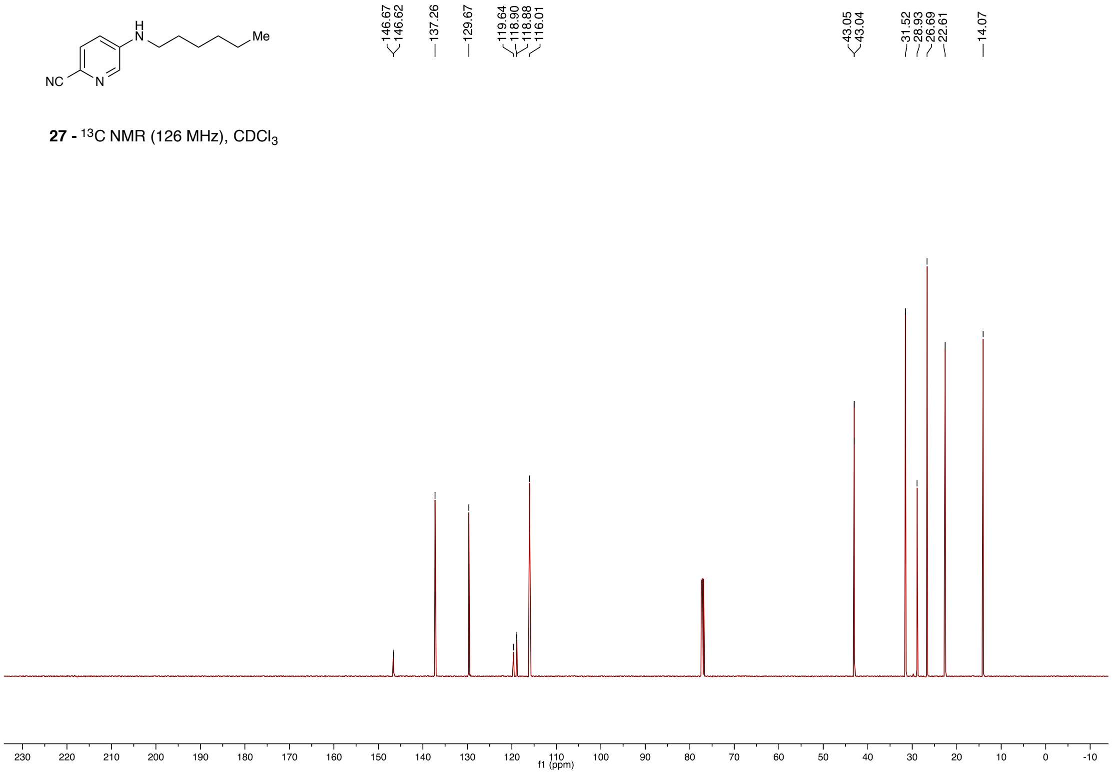
26 - ^{1}H NMR (400 MHz), CDCl$_3$



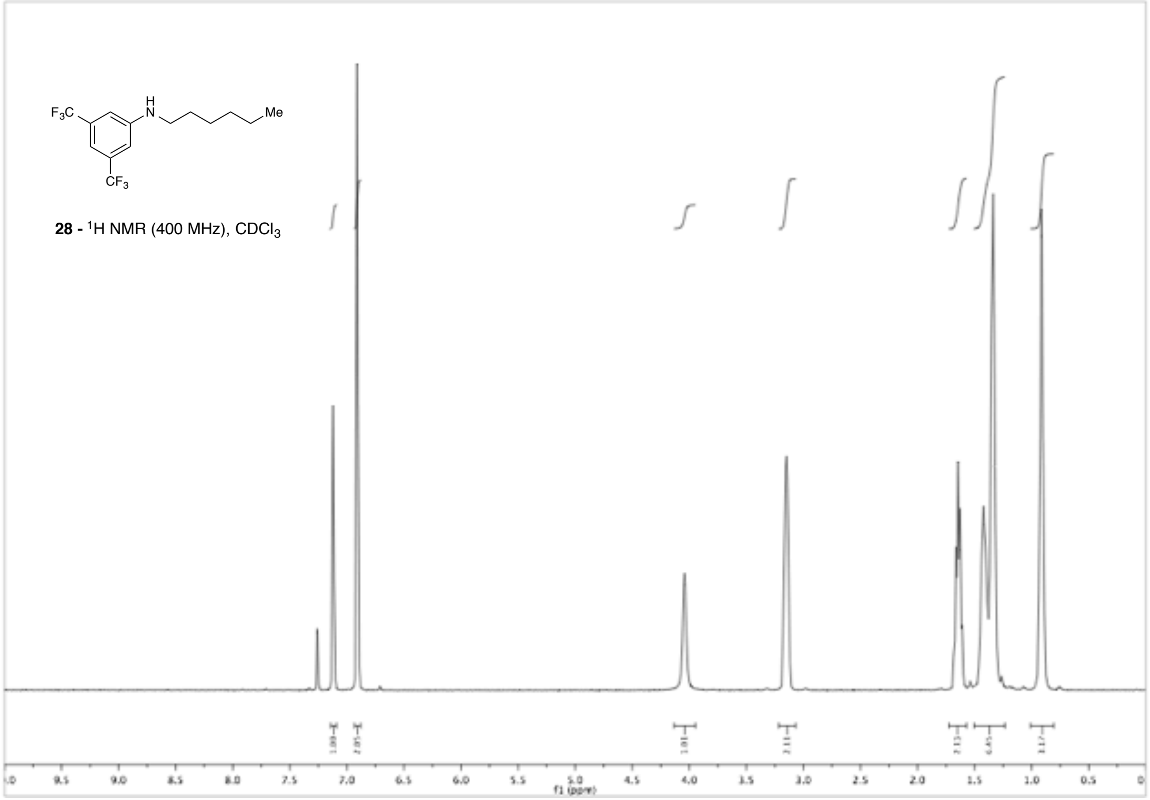
26 - ^{13}C NMR (126 MHz), CDCl$_3$



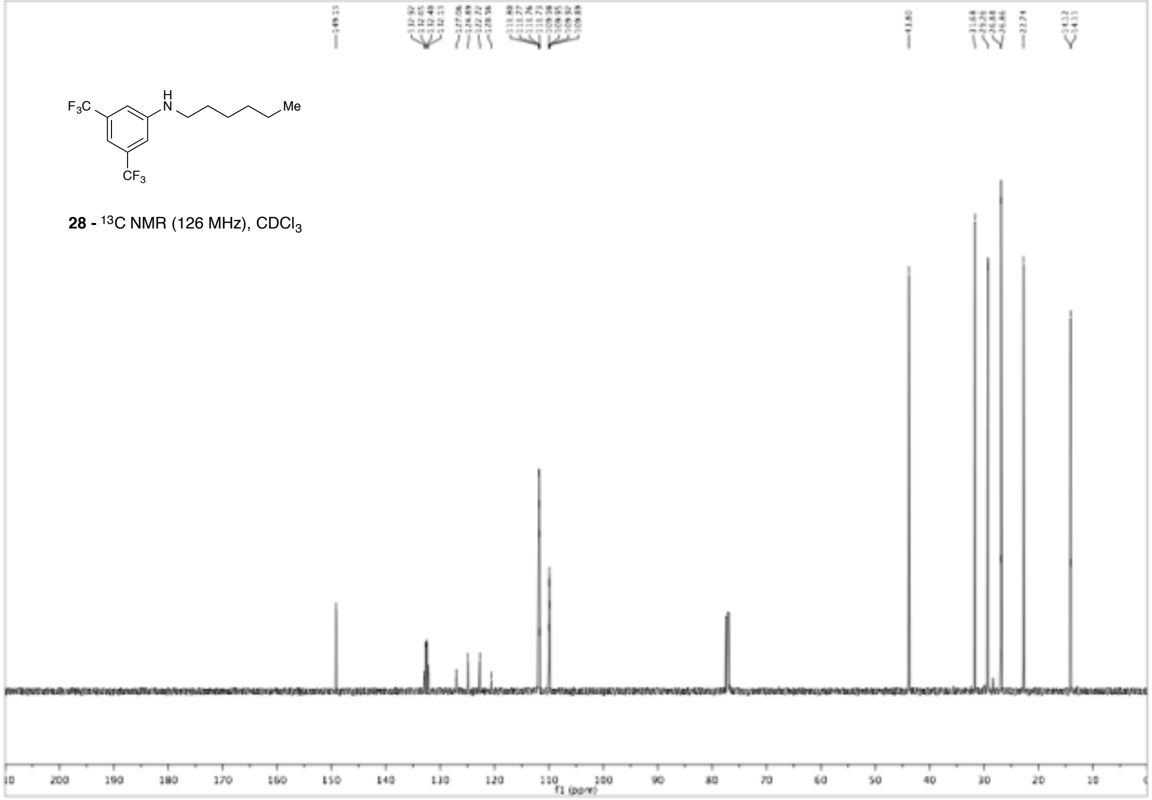
27- ^{1}H NMR (400 MHz), CDCl$_3$



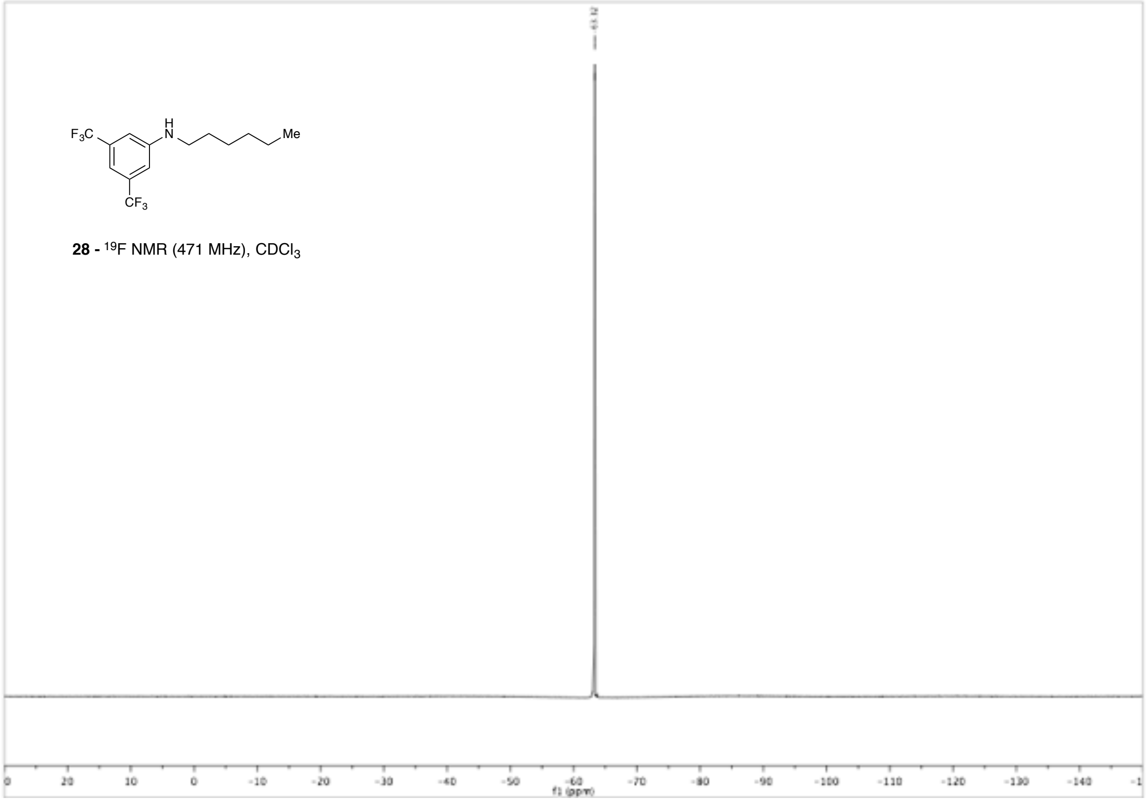
27 - ^{13}C NMR (126 MHz), CDCl$_3$



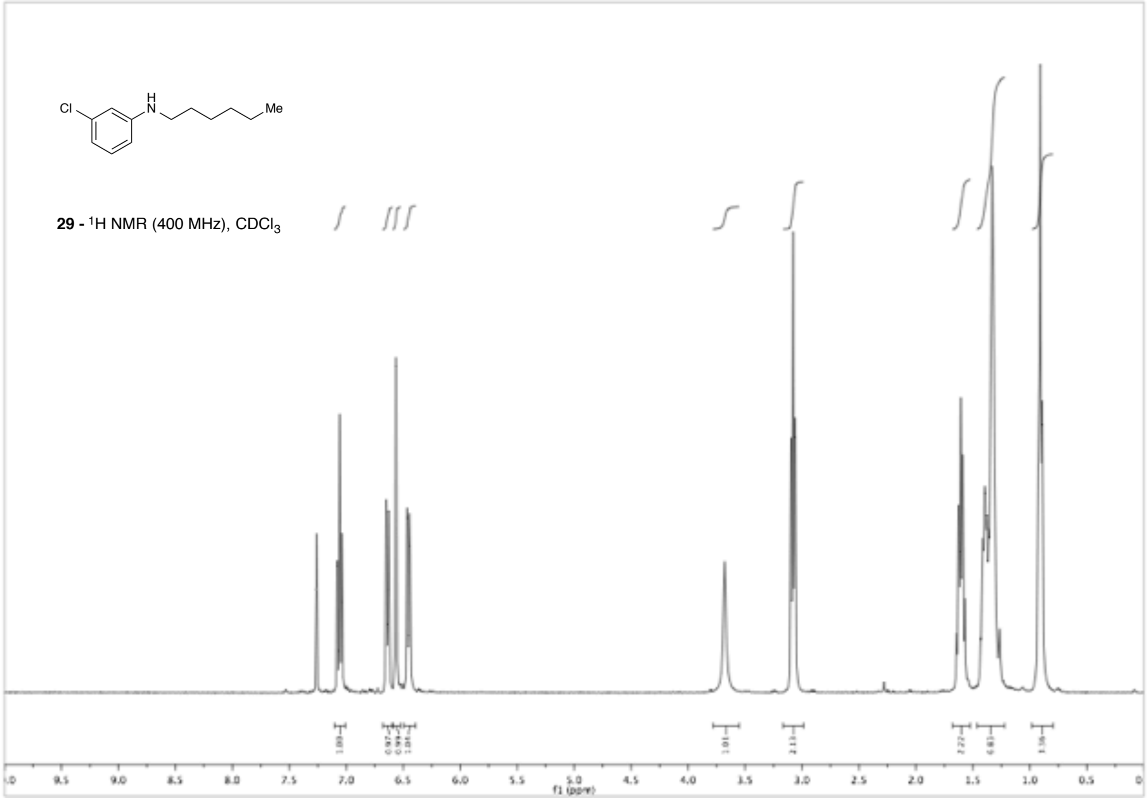
28 - ^{1}H NMR (400 MHz), CDCl$_3$

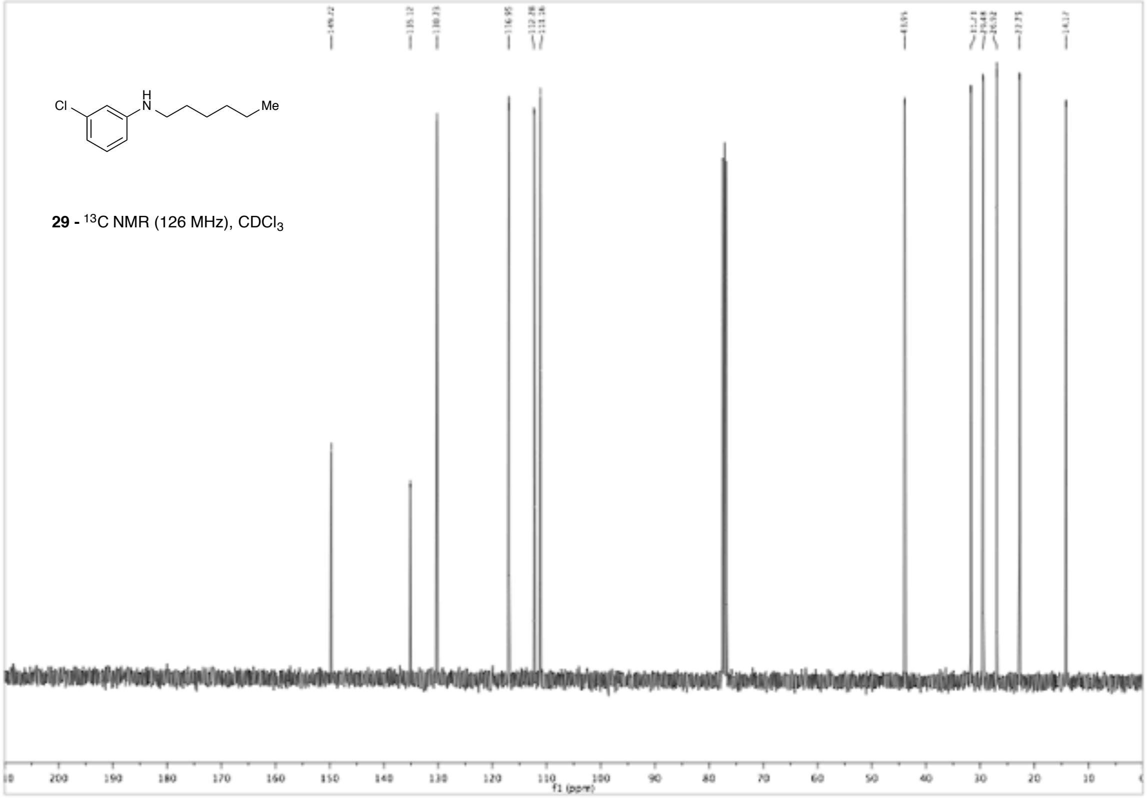


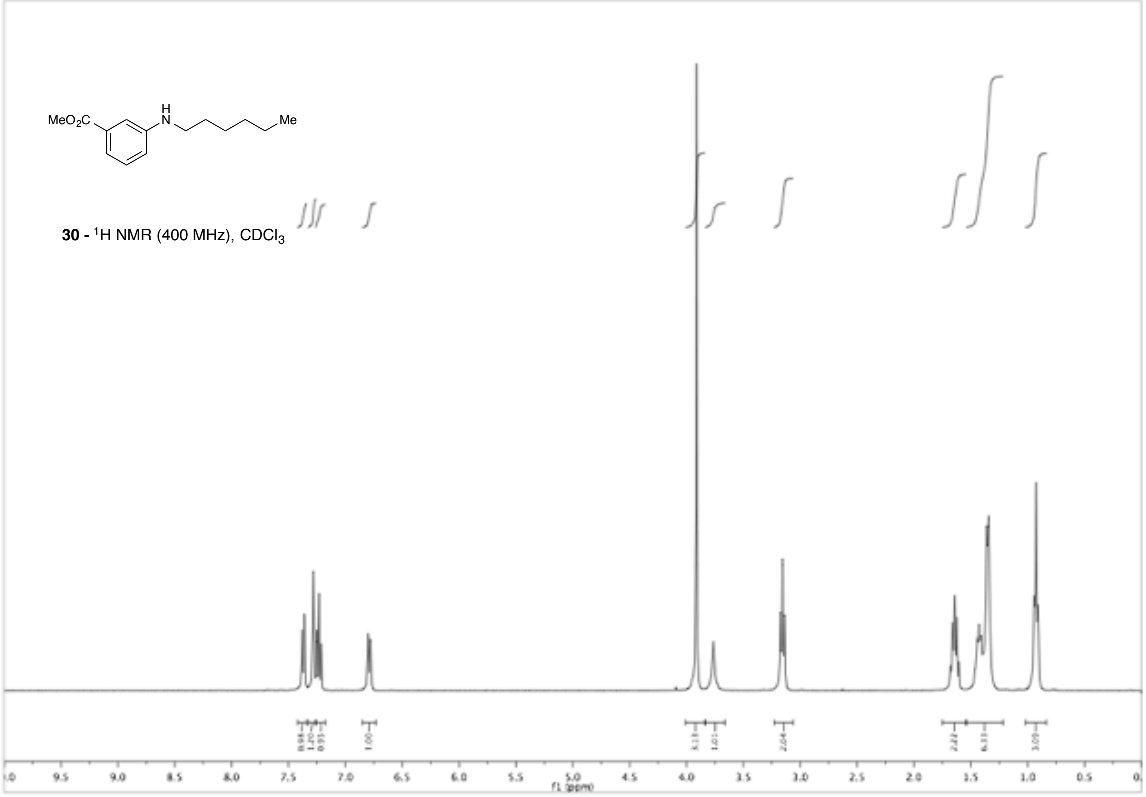
28 - ^{13}C NMR (126 MHz), CDCl$_3$



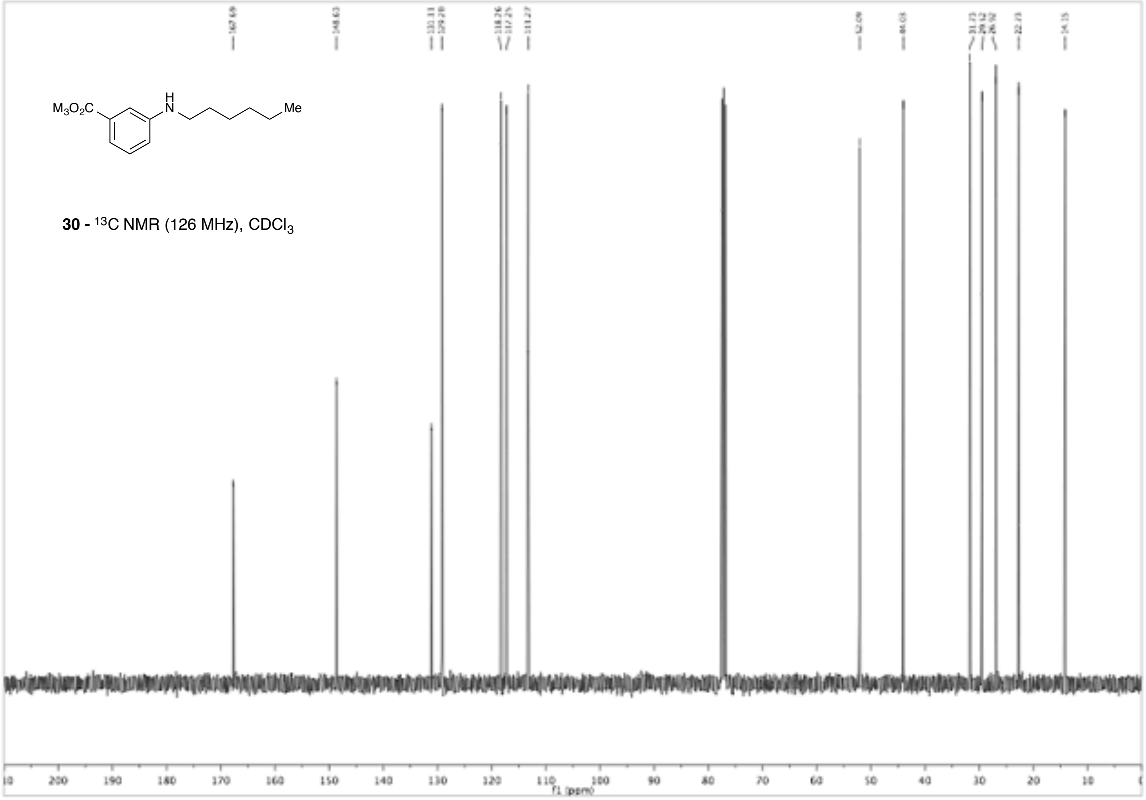
28 - ^{19}F NMR (471 MHz), CDCl$_3$


29 - ^{1}H NMR (400 MHz), $CDCl_3$

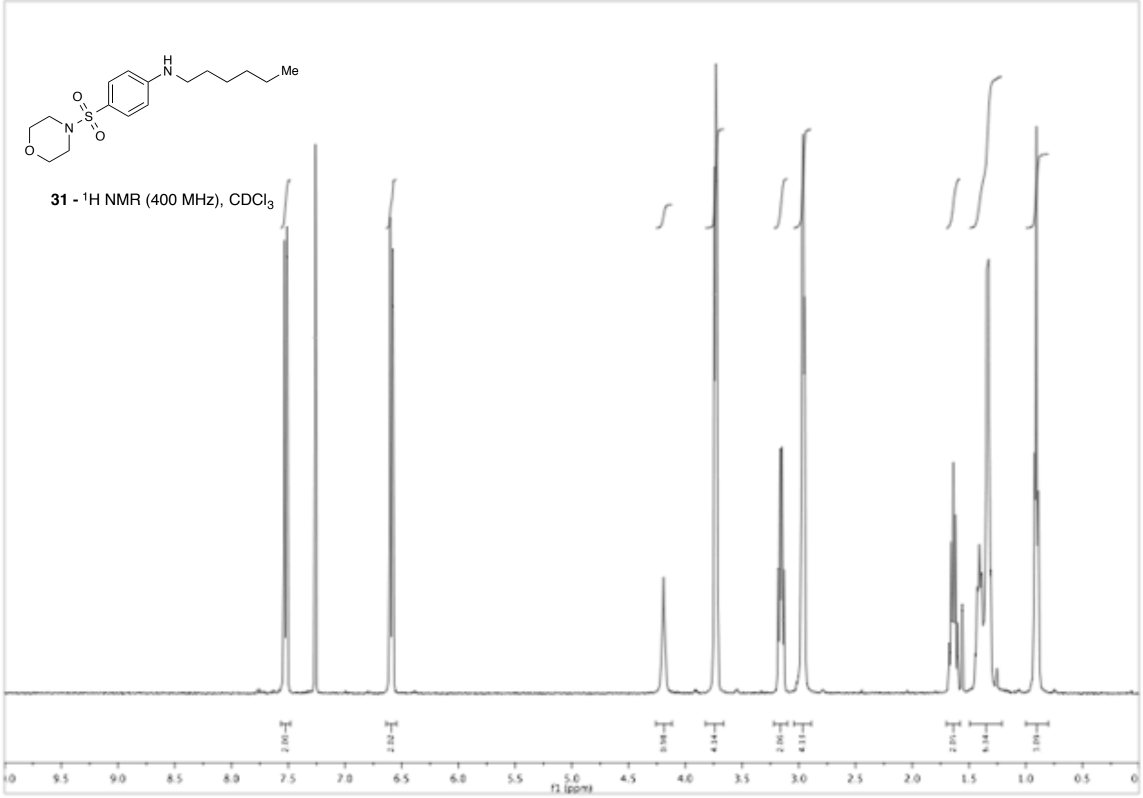

29 - ^{13}C NMR (126 MHz), $CDCl_3$



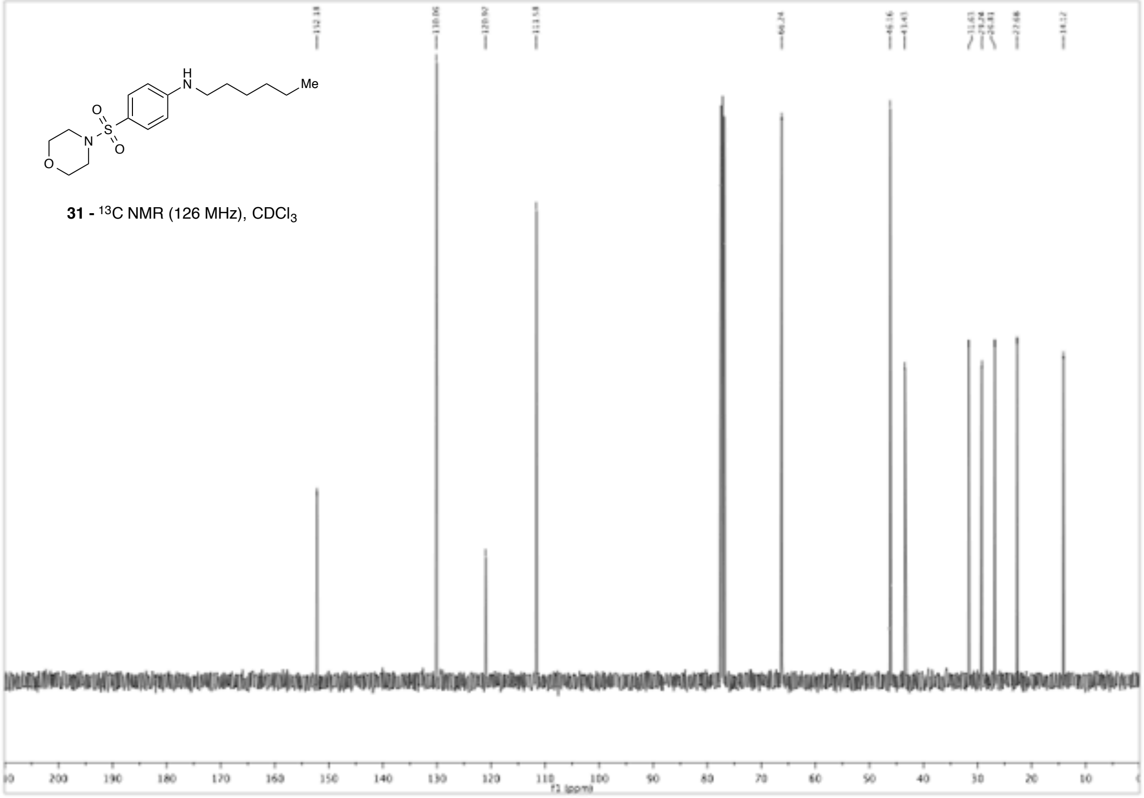
30 - ^{1}H NMR (400 MHz), $CDCl_3$



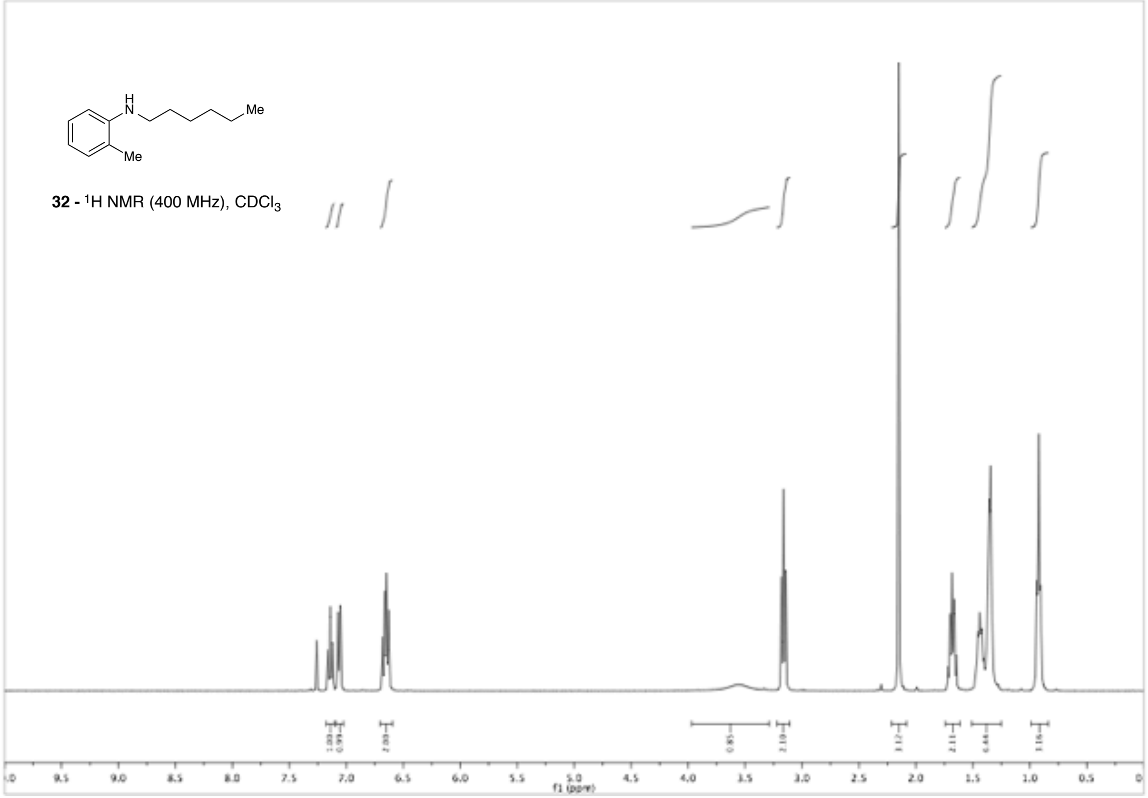
30 - ^{13}C NMR (126 MHz), $CDCl_3$



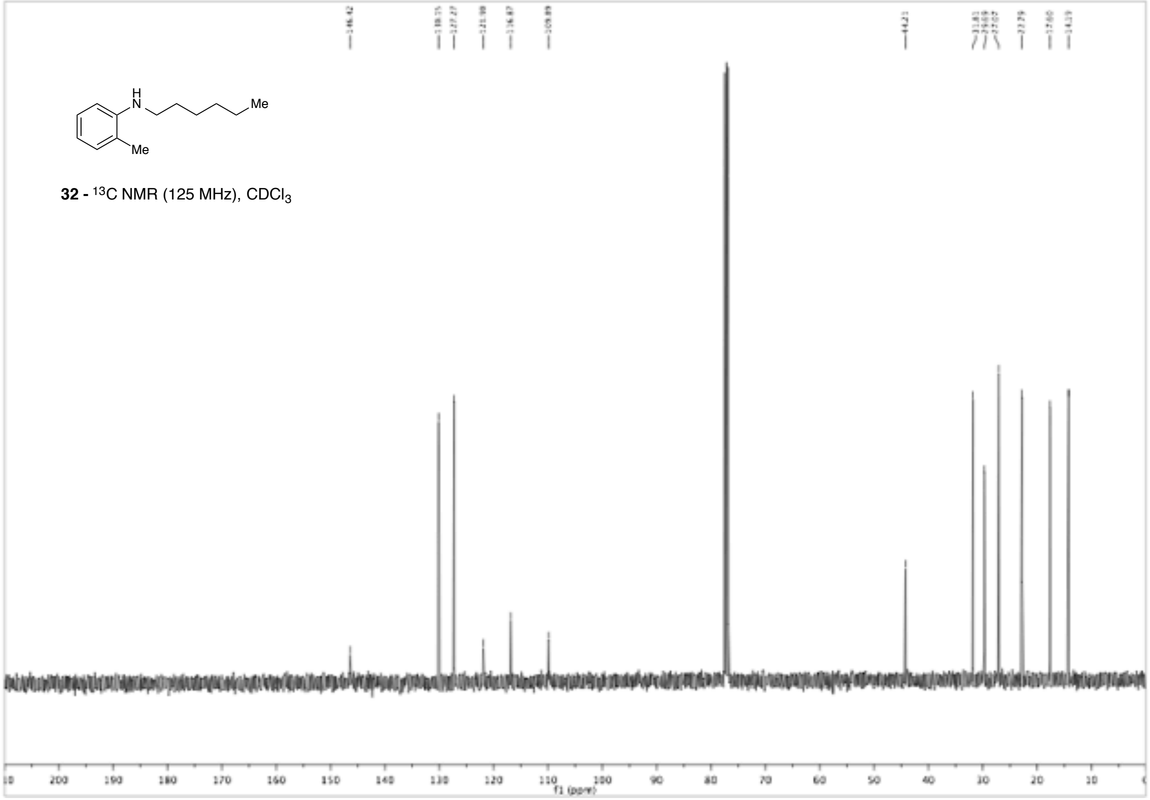
31 - ^{1}H NMR (400 MHz), CDCl$_3$



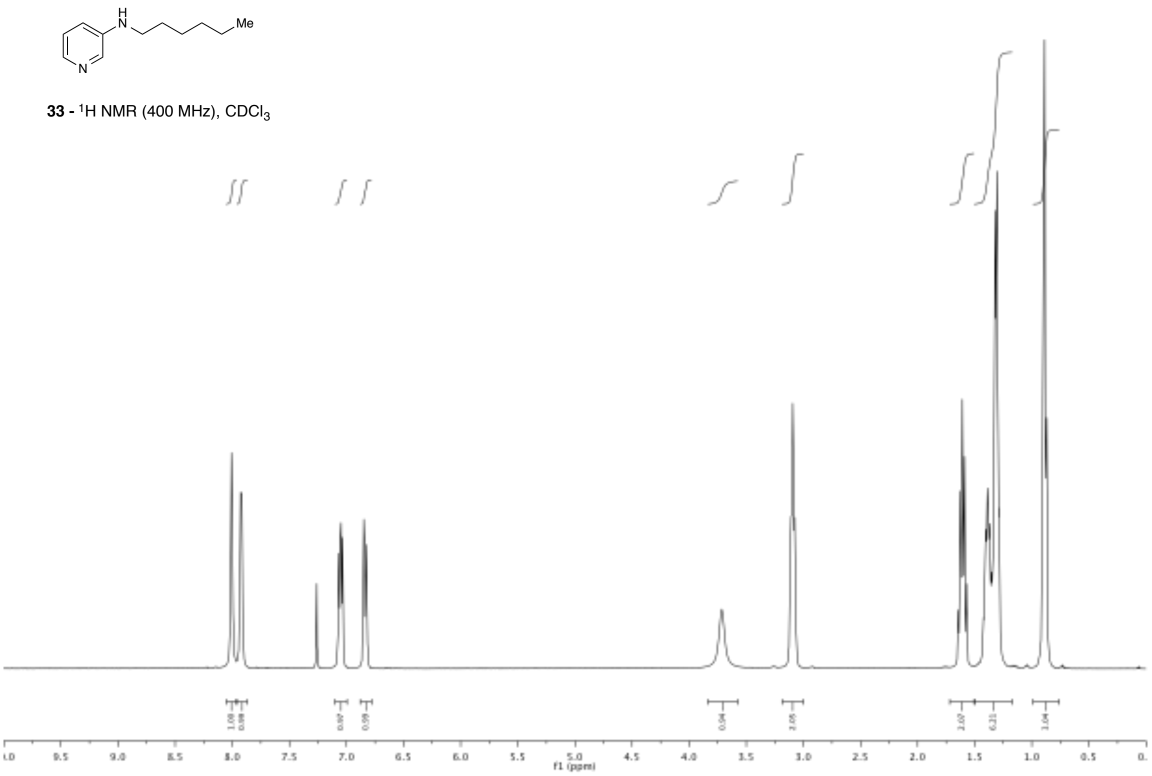
31 - ^{13}C NMR (126 MHz), CDCl$_3$



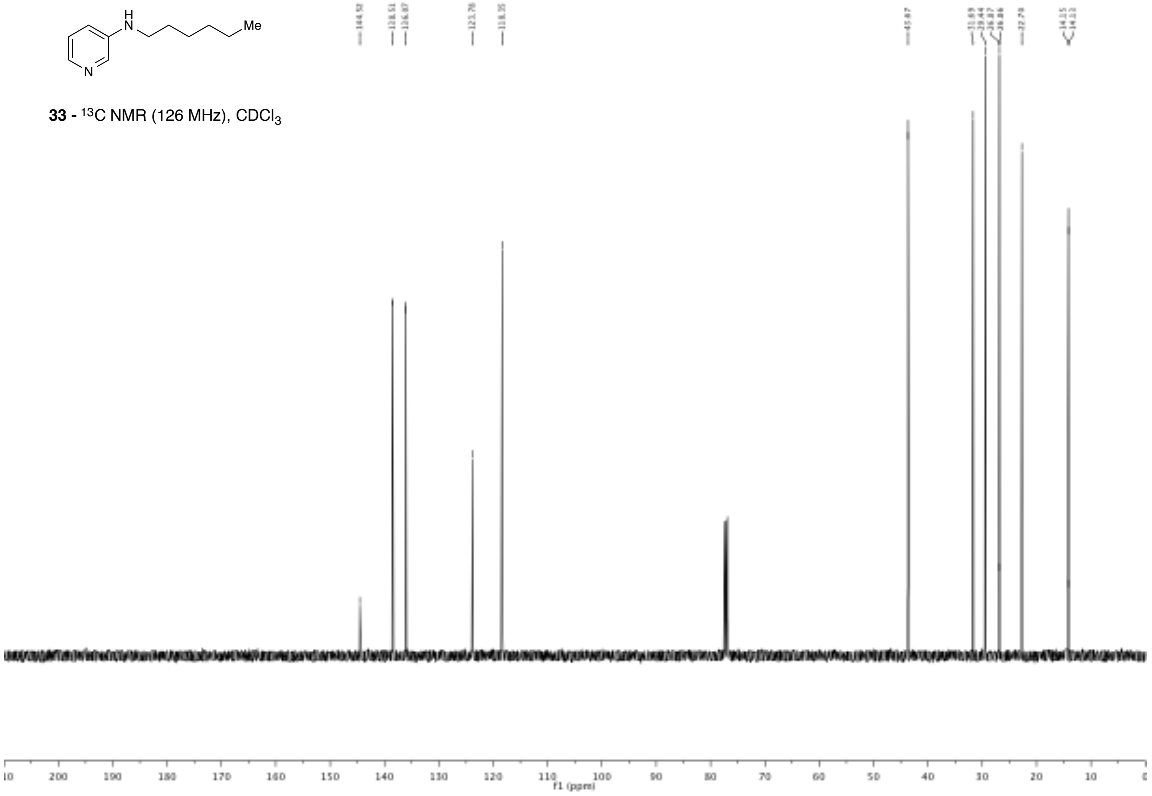
32 - ¹H NMR (400 MHz), CDCl$_3$



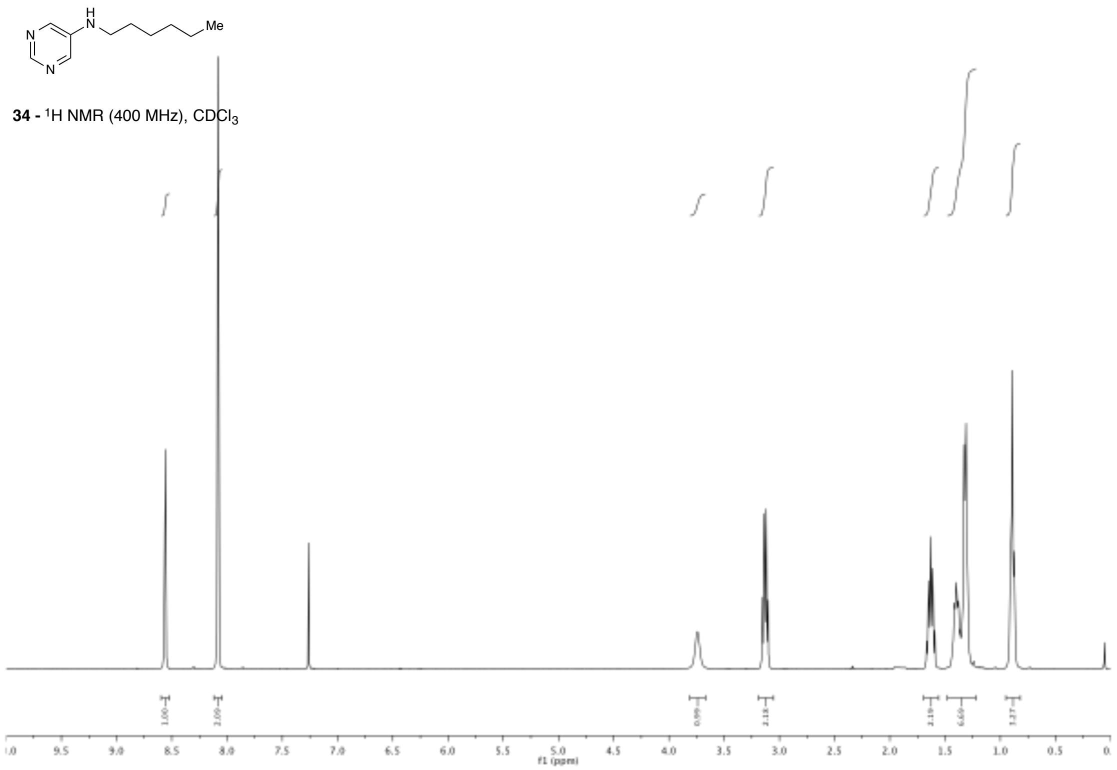
32 - ¹³C NMR (125 MHz), CDCl$_3$



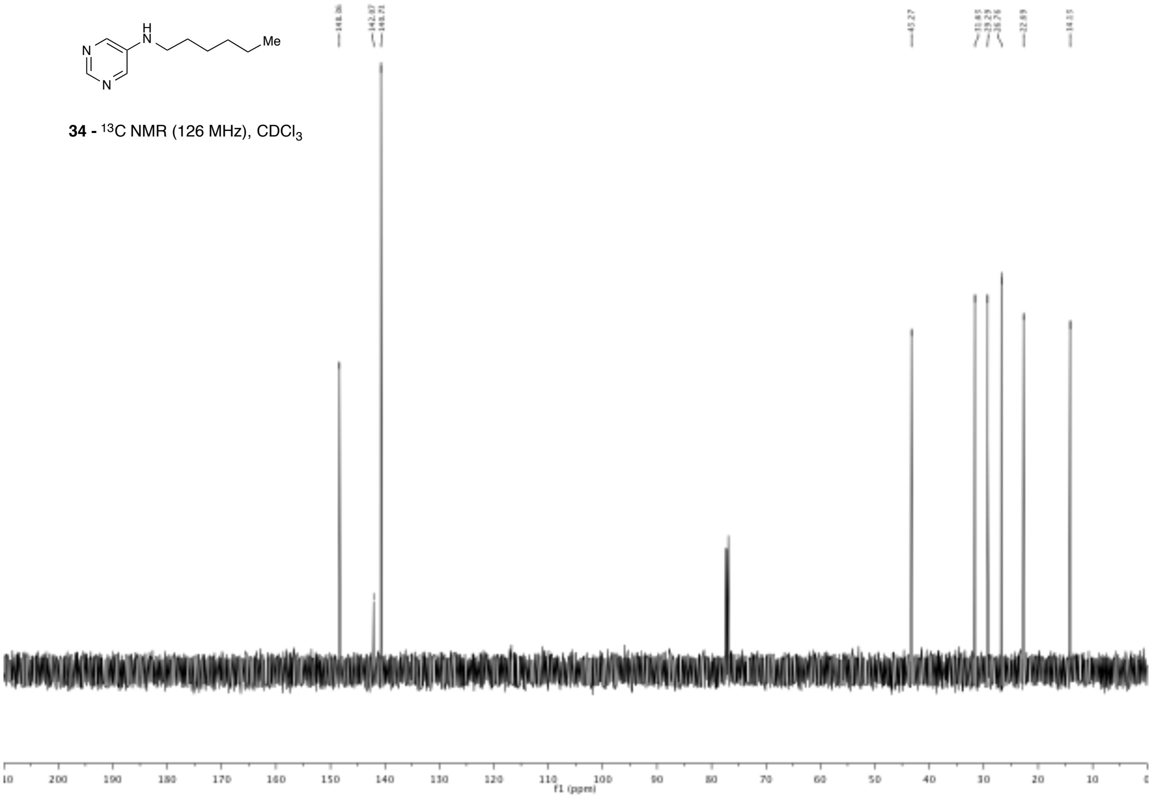
33 - ^{1}H NMR (400 MHz), CDCl$_3$



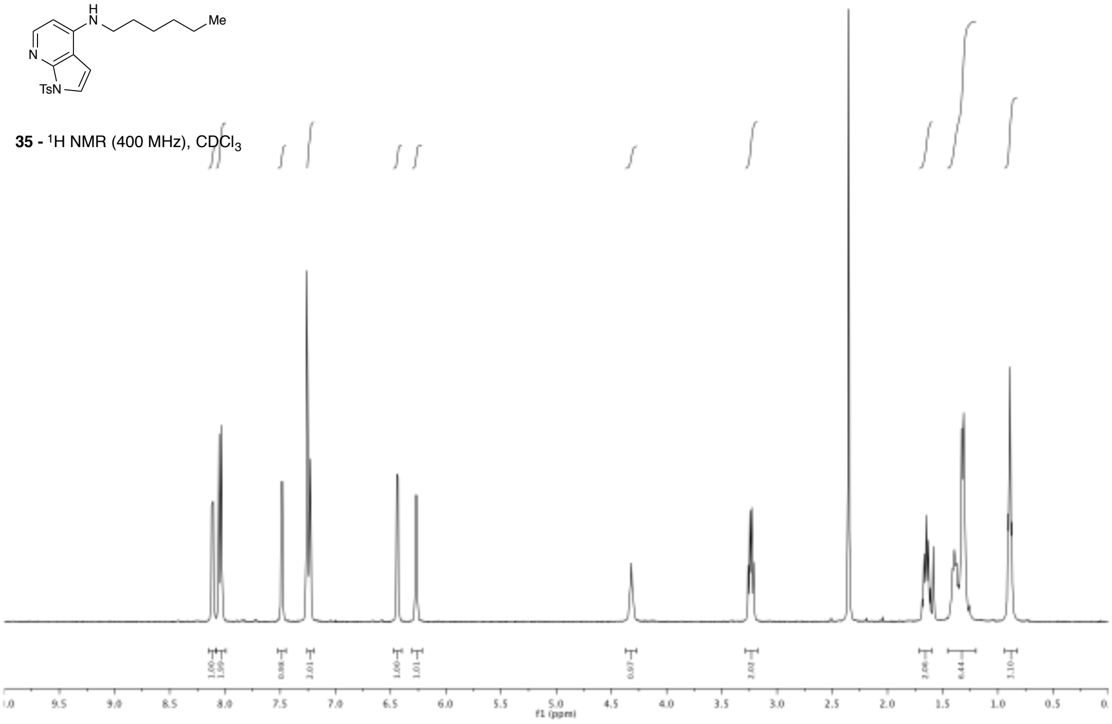
33 - ^{13}C NMR (126 MHz), CDCl$_3$



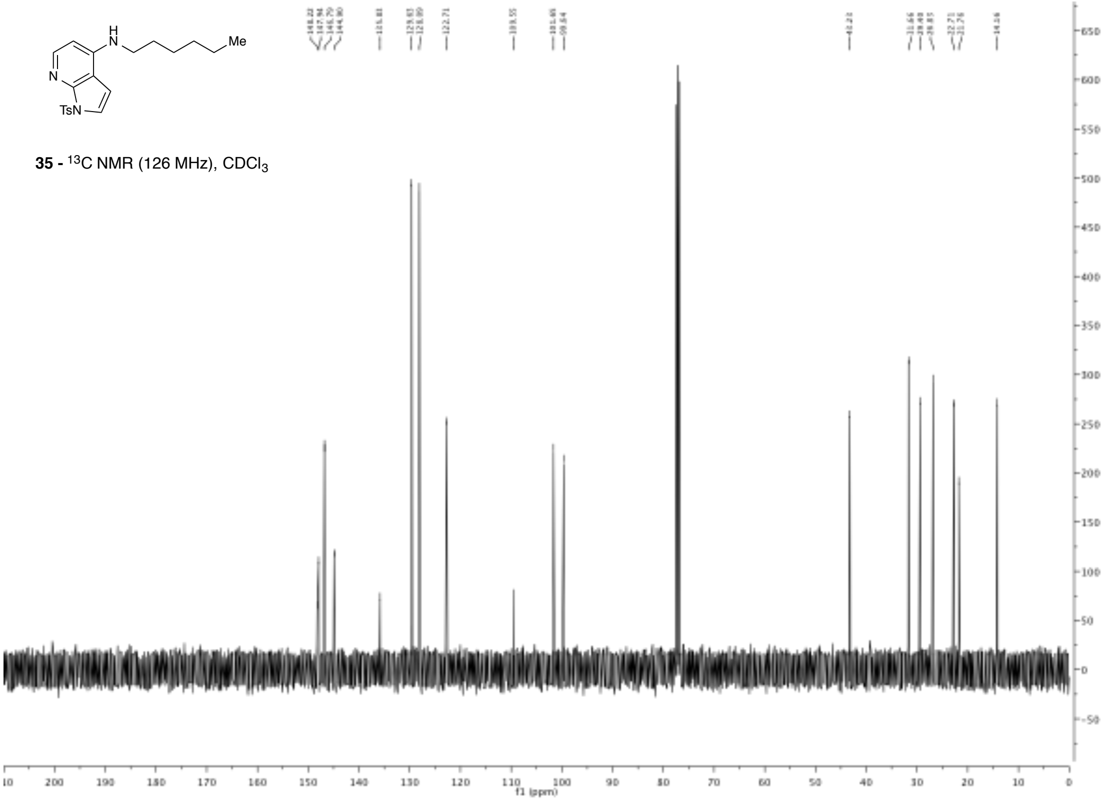
34 - ^{1}H NMR (400 MHz), $CDCl_3$



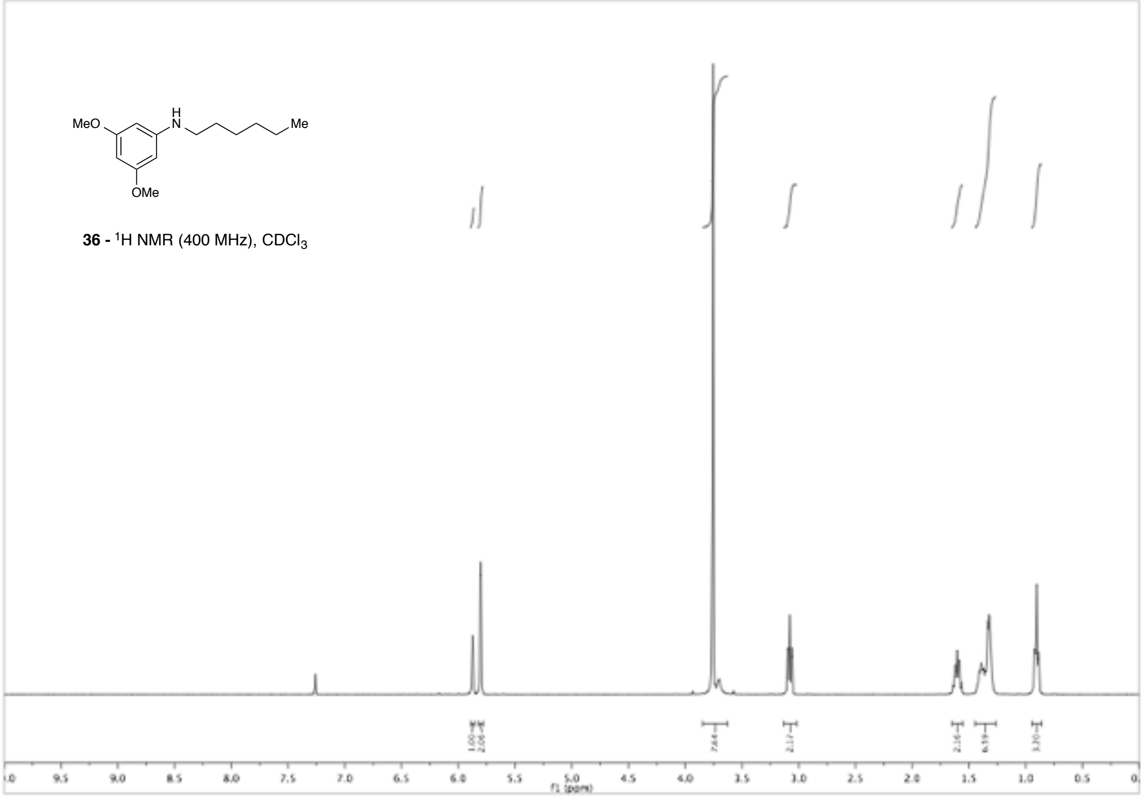
34 - ^{13}C NMR (126 MHz), $CDCl_3$



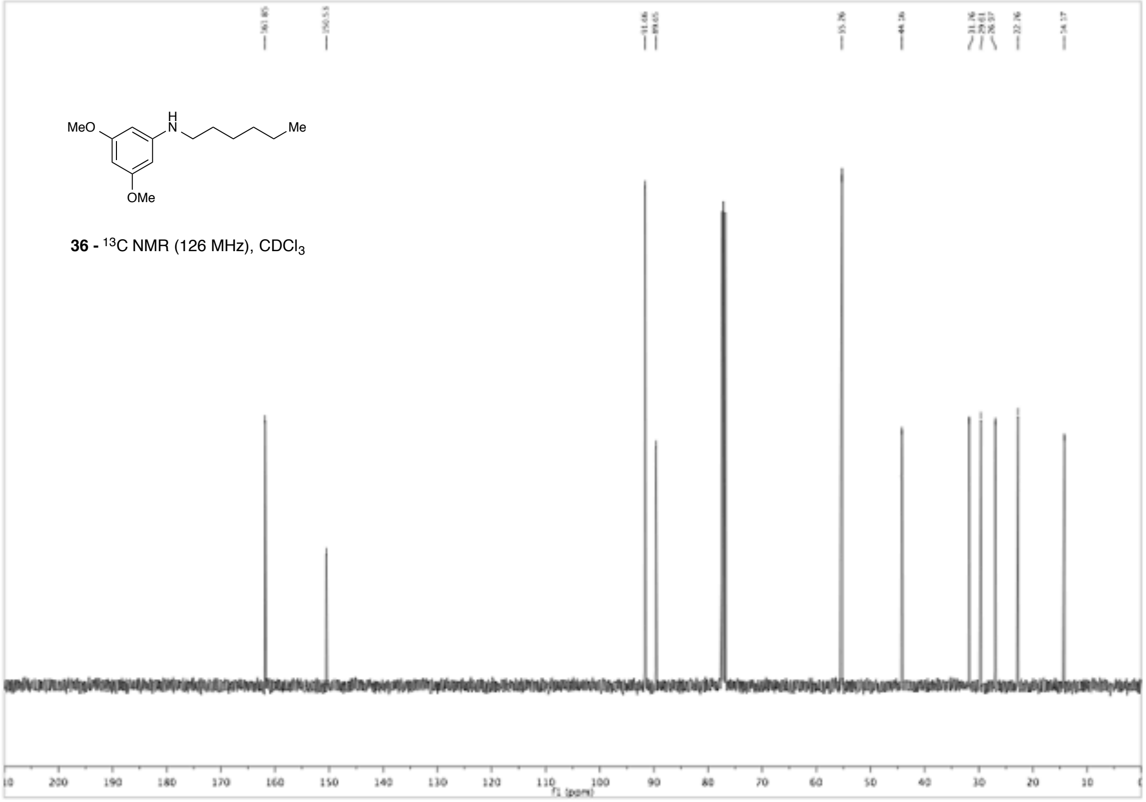
35 - ^{1}H NMR (400 MHz), CDCl$_3$



35 - ^{13}C NMR (126 MHz), CDCl$_3$



36 - ^{1}H NMR (400 MHz), CDCl$_3$



36 - ^{13}C NMR (126 MHz), CDCl$_3$