Supplementary Materials for

Overcoming Limitations in Dual Photoredox/Nickel catalyzed C–N Cross-Couplings due to Catalyst Deactivation

Sebastian Gisbertz,[1,2] Susanne Reischauer[1,2] & Bartholomäus Pieber[1*]

[1]*Department of Biomolecular Systems, Max-Planck-Institute of Colloids and Interfaces, Am Mühlenberg 1, 14476 Potsdam, Germany*

[2]*Department of Chemistry and Biochemistry, Freie Universität Berlin, Am Mühlenberg 1, 14476 Potsdam, Germany*

**Corresponding author*
Email: bartholomaeus.pieber@mpikg.mpg.de

TABLE OF CONTENTS

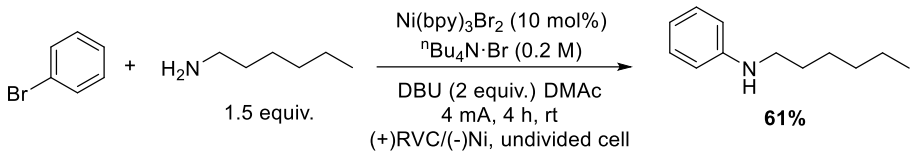
1. General remarks

Substrates, reagents, and solvents were purchased from commercial suppliers and used without further purification. Methyl 4-(trifluoromethylsulfonyloxy)benzoate,[1] methyl 4-(tosyloxy)benzoate[2], methyl 4-((methylsulfonyl)oxy)benzoate[3] and *N-tert*-butylisopropylamine (BIPA)[4] were prepared according to literature procedures. ^{1}H-, ^{13}C- and ^{19}F-NMR spectra were obtained using a Varian 400 spectrometer (400 MHz, Agilent), an Ascend^{TM} 400 spectrometer (400 MHz, cryoprobe, Bruker) and a Varian 600 spectrometer (600 MHz, Agilent) at 298 K, and are reported in ppm relative to the residual solvent peaks. Peaks are reported as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, with coupling constants in Hz. Analytical thin layer chromatography (TLC) was performed on pre-coated TLC-sheets, ALUGRAM Xtra SIL G/UV$_{254}$ sheets (Macherey-Nagel) and visualized with 254 nm light or staining solutions followed by heating. Purification of final compounds was carried out by flash chromatography on the Reveleris X2 Flash Chromatography System from GRACE using prepacked columns with 40 μm silica gel. Silica 60 M (0.04-0.063 mm) silica gel (Sigmal Aldrich) was used for dry loading of the crude compounds on the flash chromatography system. Centrifugation was carried out using an Eppendorf 5430 centrifuge. High-resolution mass spectral data were obtained using a Waters XEVO G2-XS 4K spectrometer with the XEVO G2-XS QTOF capability kit. Emission spectra of LED lamps were recorded using 10 in. (24.5 cm) integrating sphere (Labsphere, Inc. Model LMS 1050) equipped with a diode array detector (International Light, Model RPS900). The UV/Vis spectrum of Ir(ppy)$_2$(dtbbpy)PF$_6$ was recorded using a UVmini-1240 spectrometer (Shimadzu).Inductively coupled plasma - optical emission spectrometry (ICP-OES) was carried out using a Horiba Ultra 2 instrument equipped with photomultiplier tube detection. FTIR spectra were recorded on a Thermo Scientific Nicolet iD5 spectrometer. Diffuse reflectance UV/Vis spectra of powders were recorded on a Shimadzu UV-2600 spectrometer equipped with an integrating sphere. For XRD measurements, a Bruker D8 Advanced X-ray diffractometer with Cu Kα radiation was used. Scanning electron microscopy (SEM) images were obtained on a LEO 1550-Gemini microscope. Energy-dispersive X-ray (EDX) investigations were conducted on a Link ISIS-300 system (Oxford Microanalysis Group) equipped with a Si(Li) detector and an energy resolution of 133 eV. X-ray photoelectron spectroscopic (XPS) measurements were carried out with a CISSY set-up, equipped with a SPECS XR 50 X-ray gun with Mg Kα excitation radiation (1254.6 eV) and combined with a lens analyzer module (CLAM) under ultra-high vacuum (UHV, 1.5x10-8 Pa). The calibration was performed using

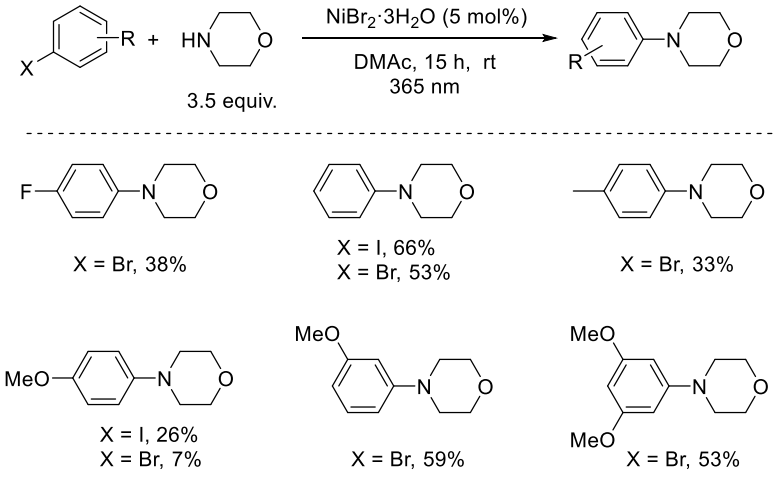
the Au 4f7/2 (84.0 eV) binding energy scale as reference. Quantitative analysis and decovolution were achieved using “peakfit” and “Igor” software with Lorenzian-Gaussian functions and Shirley background deletion in photoemission spectra. The STEM images were acquired using a double-corrected Jeol ARM200F, equipped with a cold field emission gun. For the investigation, the acceleration voltage was set to 200kV, the emission was put to 5µA and a condenser aperture with a diameter of 20µm was used. With these settings, the microscope reaches a lattice resolution below 1Å. The STEM specimens were prepared by dissolving a powder sample of the material in ethanol, sonicating the solution for 15 minutes and finally dropping a few drops onto a copper TEM grid coated with holey carbon film. Once the solution had dried off, the specimens were investigated.

2. Literature analysis: aryl halides without electron withdrawing groups

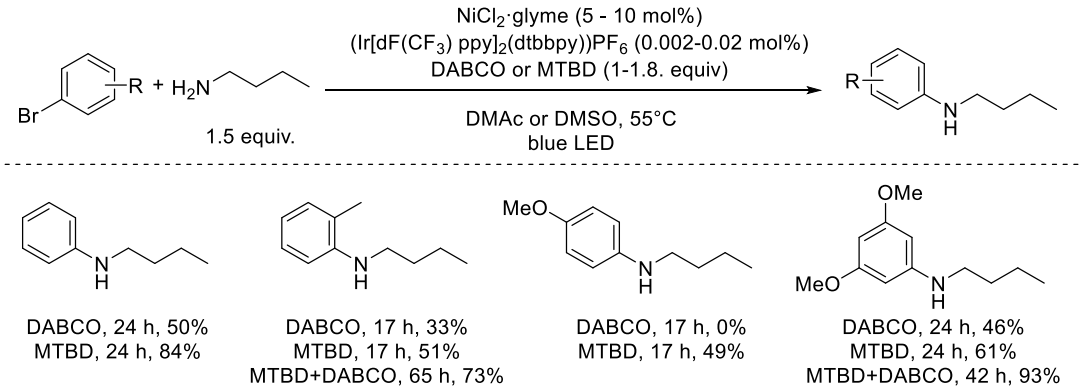
a) Electrochemically driven, Ni-catalyzed amination[5]



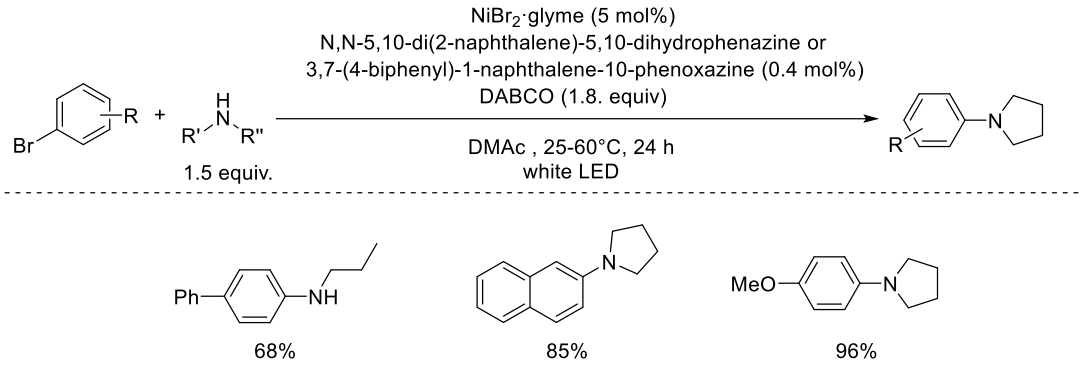
b) UV-light mediated, Ni-catalyzed amination[6]



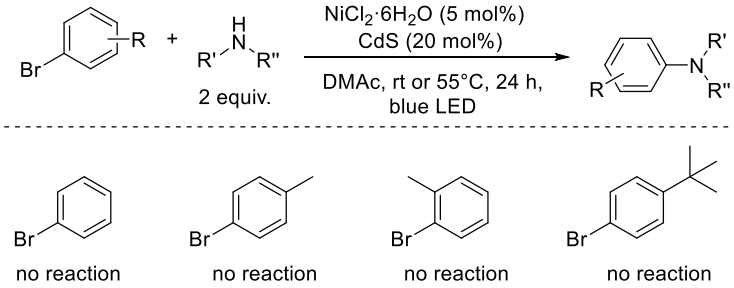
c) Dual nickel/photoredox catalyzed amination using (Ir[dF(CF3)ppy]2(dtbbpy))PF6[7]



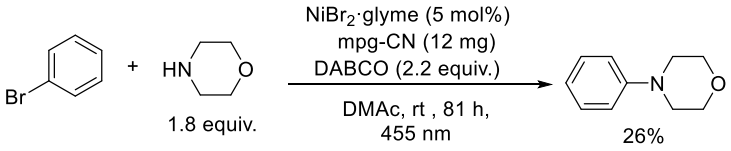
d) Dual nickel/photoredox catalyzed amination using organic dyes[8]



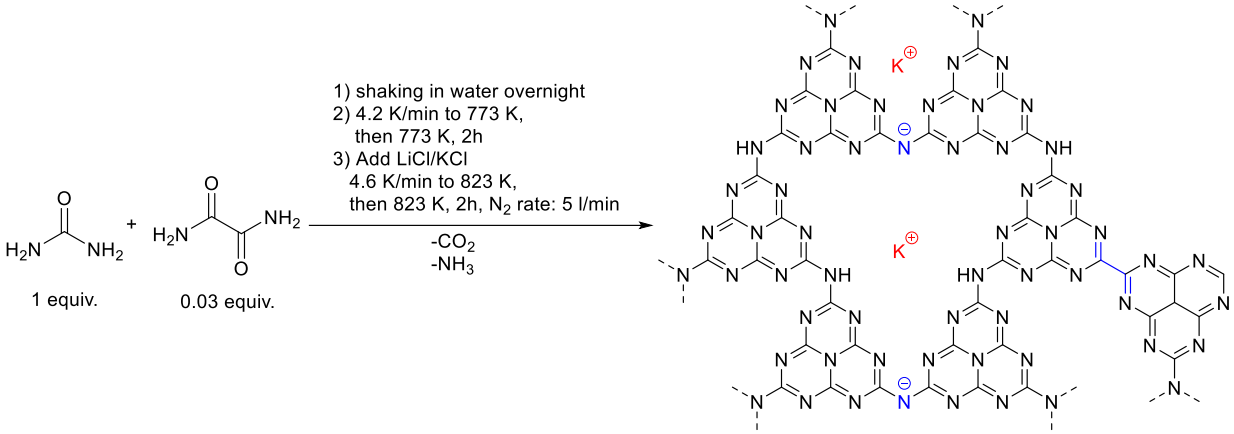
e) Dual nickel/photoredox catalyzed amination using CdS[9]



e) Dual nickel/photoredox catalyzed amination using mpg-CN[10]



3. Preparation of CN-OA-m



Scheme S1. Synthesis of CN-OA-m

The synthesis for CN-OA-m was carried out using a slightly adapted version of the literature procedure (Scheme S1)[11]: For each batch of the photocatalyst, urea (10 g, 166.5 mmol) and oxamide (0.5 g, 5.7 mmol) were mixed in 10 ml of DI water to generate a homogeneous mixture. After drying at 373 K, the resulting solids were grinded, transferred into a crucible with a cover and heated up in an air-oven with a heating rate of 4.3 K/min to 773 K. After keeping the mixture for 2h at 773 K, the sample was allowed to cool to room temperature. Subsequently, KCl (3.3 g, 44.3 mmol) and LiCl (2.7 g, 63.7 mmol) were added and the solids were grinded to obtain a homogeneous mixture which was heated in an inert atmosphere (N_2 flow: 5 mL/min) to 823 K with a heating rate of 4.6 K/min. After keeping the mixture for 2 h at 823 K, the sample was allowed to cool to room temperature and the resulting solids were collected on a filter paper and washed with H_2O (3 x 100 mL). The resulting yellow material was dried at 373 K (average yield per batch: ~425 mg). All analytical data (FTIR, UV/Vis, XRD, SEM, etc.; see Section 7) are in full agreement with those published in the literature.[11]

The cost of CN-OA-m was calculated to be 4.0 € g^{-1} based on the prices of urea, oxamide, LiCl and KCl from Sigma-Aldrich (Merck).[12] As a comparison, the price of $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ is 883 € g^{-1}.[12]

The UV/Vis spectrum of CN-OA-m shows a strong absorption up to ~460 nm and a comparably weaker absorption band up to ~700 nm (Figure S1, A) which are attributed to the π-π* electron transition of the sp^2 hybridization of C and N in the heptazine framework and n-π* electron transition involving the lone pairs of the edge nitrogen atoms in the heptazine units,

respectively.[11] The capability of harvesting low energy light is therefore superior compared to Ir and Ru photocatalysts (see Figure S1, B for the UV/Vis spectrum of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ as a representative example) which have only a low absorption band between 400 and 500 nm in the visible region, which corresponds to the metal-to-ligand charge transfer transition.

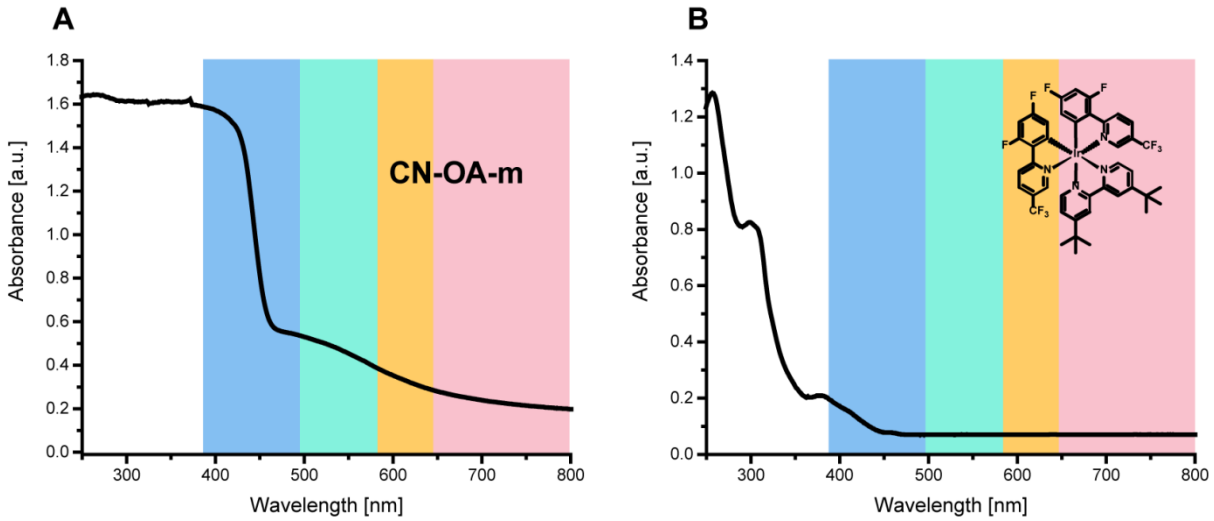


Figure S1. UV/VIS-absorption spectra of CN-OA-m (**A**) and $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (**B**).

4. Setup for photochemical reactions

A flexible, red/green/blue LED strip[13] (RGB, 5m, 24 W/strip; Tween Light, BAHAG AG, Germany) was wrapped around a 115 mm borosilicate crystallization dish (Figure S2, A). Blue, green, red or white (illumination of all three LED colors - red/green/blue) light was used at full power for all experiments (For emission spectra of a single diode, see Figure S3). The evaporating dish was filled with ethylene glycol and the temperature was set to 40°C to maintain a constant temperature. The sealed, cylindrical reaction vessels (16 x 100 mm) were placed at the same distance from the LED strip during all experiments (Figure S2, A). All reactions were performed with a stirring speed of 600 (1 mL) or 1400 rpm (3 or 6 mL). For large scale aminations a flexible, red/green/blue LED strip (RGB, 5m, 24 W/strip; Tween Light, BAHAG AG, Germany) was wrapped around a mm borosilicate beaker (Figure S2, B). The scale-up reaction was performed in a sealed, cylindrical reaction vessel (25 x 140 mm) with a stirring speed of 700 rpm and without additional heating (Figure S2, B).

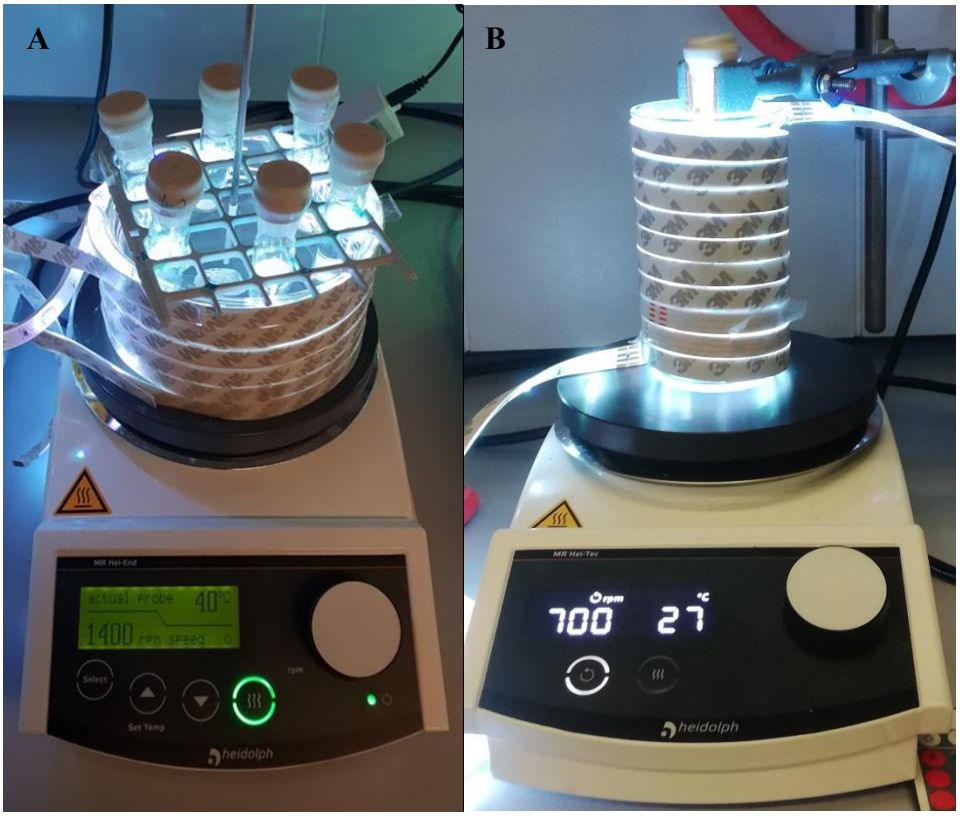


Figure S2. Experimental setup for general photochemical reactions (**A**) and for the scale-up reaction (**B**).

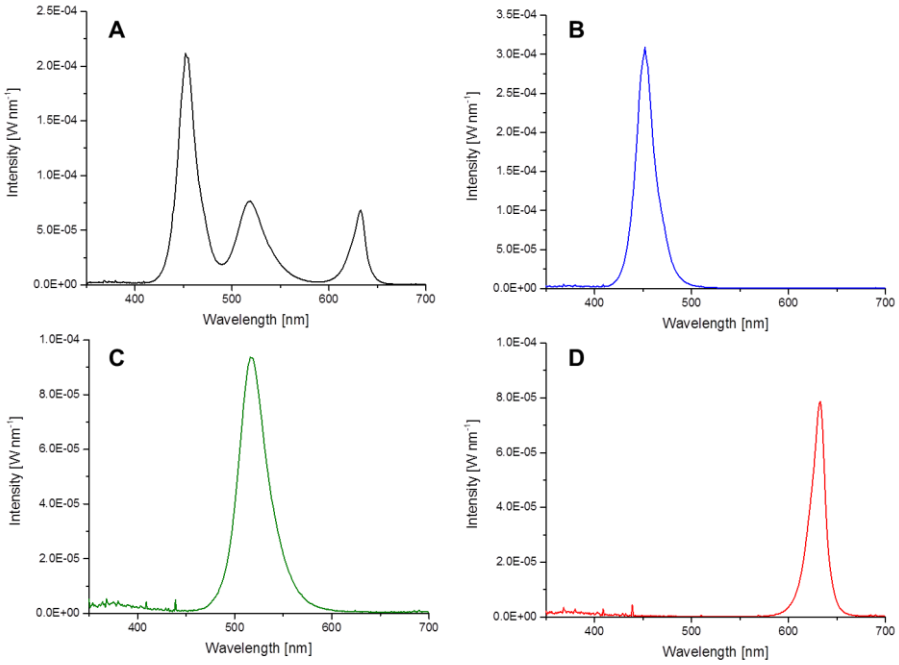


Figure S3. Emission spectra of the LED strips used for photochemical reactions. All experiments were carried out at maximum power. **A**: white light. **B**: blue light only. **C**: green light only. **D**: red light only.

A Kessil® PR 160-370nm lamp, a stir plate and a fan for cooling was used for UV-light experiments (Figure S4, A). All experiments were carried out with maximum lamp power. The sealed reaction vessels (16 x 100 mm) were placed at the same distance (4 cm) from the light source during all experiments. All reactions were performed with vigorous stirring.

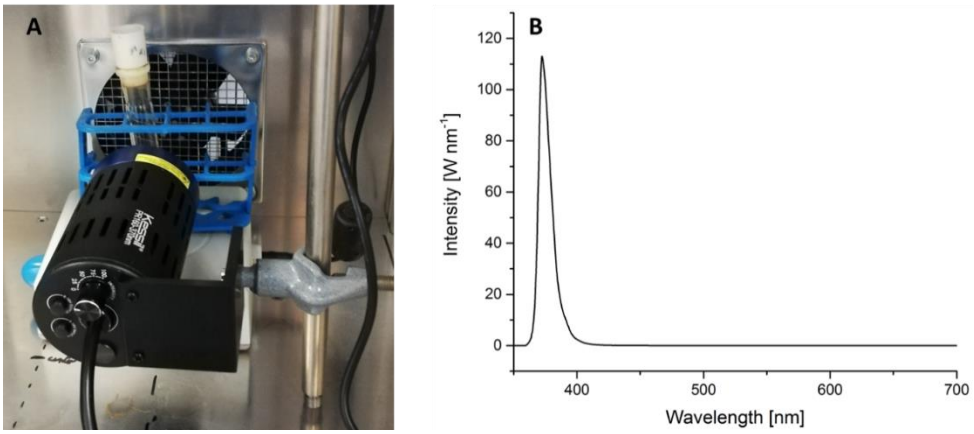


Figure S4. **A**: Picture of the Set-up for UV-light experiments **B**: Emission spectra of the Kessil® PR 160-370nm lamp used for photochemical reactions. All experiments were carried out at maximum power.

5. Reaction optimization

5.1 General experimental procedure for screening experiments

An oven dried vial (16 x 100 mm) equipped with a stir bar was charged with methyl 4-bromobenzoate (0.3 mmol, 64.5 mg, 1 equiv.), the base (0.9 mmol, 3.0 equiv.), the Ni^{II} catalyst (30 µmol, 10 mol%) and the carbon nitride material (10 mg). Subsequently, pyrrolidine (0.45 mmol, 37.0 µL, 1.5 equiv.) and the solvent (anhydrous, 3 mL) were added and the vial was sealed with a septum and Parafilm. The reaction mixture was sonicated for 5-10 min followed by stirring for 5 min until a fine dispersion of the solids was achieved and the mixture was then degassed by bubbling N_2 for 10 min. The mixture was irradiated in the photoreactor at 40 °C with rapid stirring (1400 rpm). After the respective reaction time, one equivalent of 1,3,5-trimethoxybenzene (0.3 mmol, 50.5 mg) was added. An aliquot of the reaction mixture (~300 µL) was filtered, diluted with DMSO-d_6 and subjected to ^{1}H-NMR analysis. (Alternatively, 1.5 mL $CDCl_3$ and 3 mL H_2O were added and the vial was sealed and vigorously shaken. After phase separation, the $CDCl_3$ layer was carefully removed using a syringe, filtered, and analyzed by ^{1}H-NMR.) For representative NMR spectra, see Figure S5.

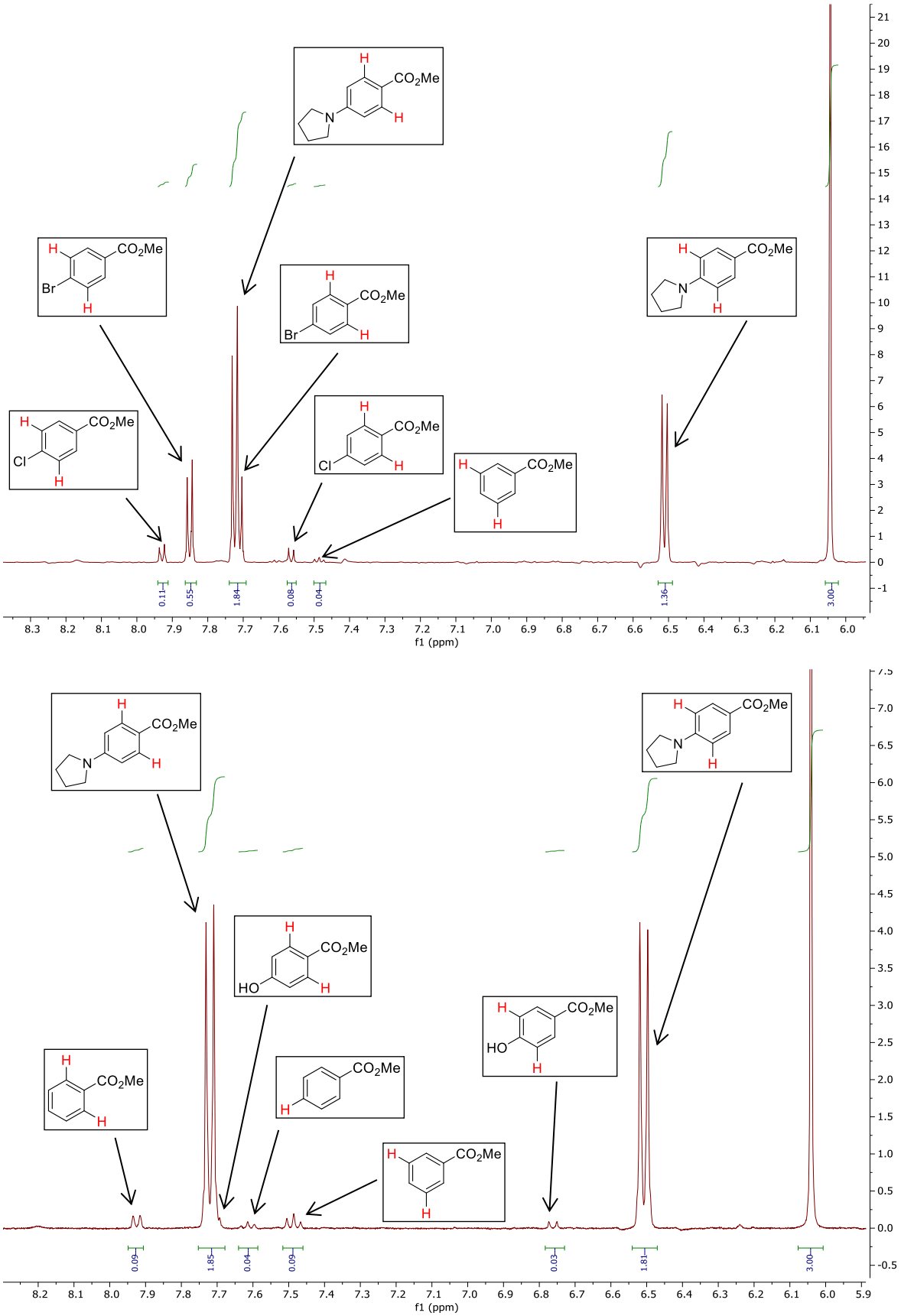
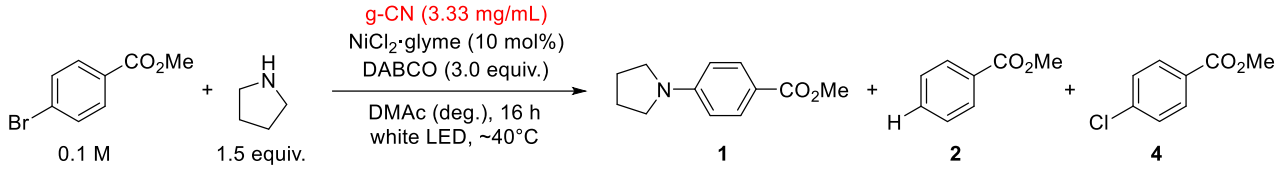


Figure S5. Examples of ^{1}H-NMR spectra for determining NMR yields.

5.2 Screening of carbon nitride material

Table S1. Screening of carbon nitride materials.[a]



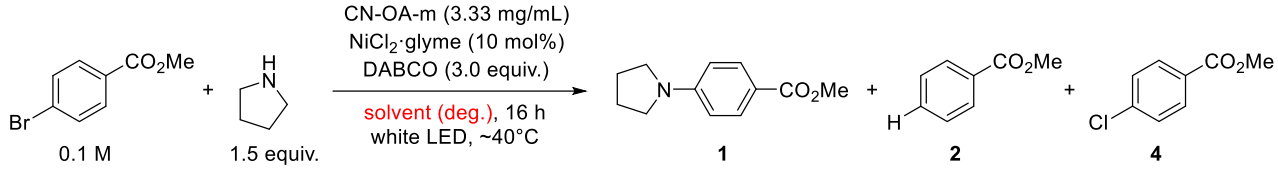
Entry	CN catalyst	Conversion [%][b]	1 [%][c]	2 [%][c]	4 [%][c]
1	CN-OA-m	73	65	2	5
2	$CMB_{0.05}$-CN	25	21	2	trace
3	mpg-CN	23	19	trace	trace
4	PHIK	18	14	trace	trace
5	CNS_{600}	9	6	trace	trace

[a]Reaction conditions: methyl 4-bromobenzoate (0.3 mmol), pyrrolidine (0.45 mmol), $NiCl_2$·glyme (10 mol%), DABCO (0.9 mmol), carbon nitride (10 mg), DMAc (anhydrous, 3 mL), white LEDs at 40 °C for 16h. [b]Conversion of methyl 4-bromobenzoate determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [c]NMR yields determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard.

Several carbon nitride materials were tested: Mesoporous graphitic carbon nitride (mpg-CN),[14] a modified carbon nitride derived from a cyanuric acid/melamide/barbituric acid complex ($CMB_{0.05}$-CN),[15] a sulfur-doped material (CNS_{600}),[16] a strongly oxidizing potassium poly(heptazine imide) (K-PHI),[17] and a carbon nitride derivative prepared *via* co-condensation of urea and oxamide followed by post-calcination in a molten salt (CN-OA-m),[11] all using white LED (RGB) irradiation at a constant temperature of 40 °C.

5.3 Solvent screening

Table S2. Solvent screening.[a]

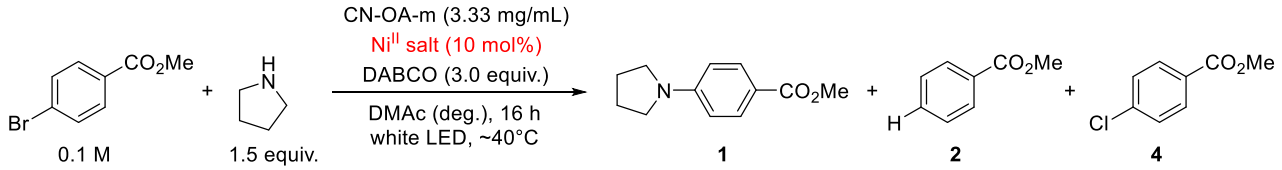


Entry	Solvent	Conversion [%][b]	1 [%][c]	2 [%][c]	4 [%][c]
1	DMAc	74	66	2	4
2	DMSO	28	24	trace	trace
3	DMF	n.d.o[d]	18	trace	trace
4	MeCN	19	14	trace	trace
5	diglyme	15	11	trace	trace
6	toluene	6	6	trace	trace
7	DCM	11	trace	trace	trace

[a]Reaction conditions: methyl 4-bromobenzoate (0.3 mmol), pyrrolidine (0.45 mmol), $NiCl_2$·glyme (10 mol%), DABCO (0.9 mmol), CN-OA-m (10 mg), solvent (anhydrous, 3 mL), white LEDs at 40 °C for 16h. [b]Conversion of methyl 4-bromobenzoate determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [c]NMR yields determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [d] not detected due to overlapping peaks.

5.4 Screening of Ni^{II} sources

Table S3. Screening Ni^{II} sources.[a]



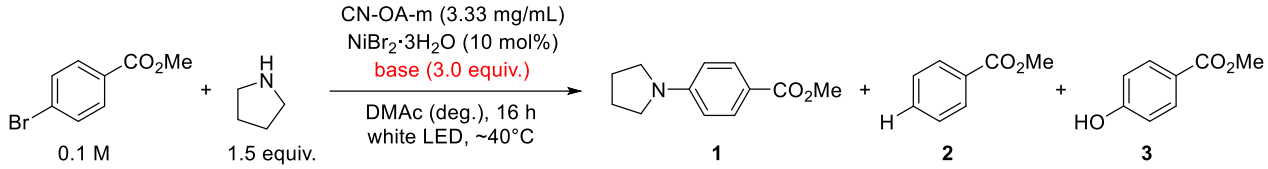
Entry	Ni^{II} catalyst	Conversion [%][b]	1 [%][c]	2 [%][c]	4 [%][c]	Price [€ mol^{-1}][d]
1	NiI_2	90	86	2	n.d.	2063
2	$NiBr_2$·glyme	87	80	3	n.d.	10431
3	$NiCl_2$	85	76	4	5	110
4	$NiBr_2$	74	72	trace	n.d.	411
5	$NiBr_2·3H_2O$	71	68	3	n.d.	116
6	$NiCl_2$·glyme	74	66	trace	9	4161
7	$Ni(ClO_4)_2·6H_2O$	62	59	trace	n.d.	171
8	$Ni(NO_3)_2·6H_2O$	52	52	trace	n.d.	49
9	$Ni(OTf)_2$	55	51	3	n.d.	12917
10	$NiCl_2·6H_2O$	45	35	4	2	71
11	$Ni(BF_4)_2·6H_2O$	24	23	2	n.d.	223
12	$Ni(TMHD)_2$	10	5	2	n.d.	35294
13	$Ni(OAc)_2·4H_2O$	9	5	4	n.d.	28
14	$Ni(SO_4)2·6H_2O$	9	4	2	n.d.	41
15	$Ni(acac)_2$	3	n.d.	trace	n.d.	620

[a]Reaction conditions: methyl 4-bromobenzoate (0.3 mmol), pyrrolidine (0.45 mmol), Ni^{II} catalyst(10 mol%), DABCO (0.9 mmol), CN-OA-m (10 mg), DMAc (anhydrous, 3 mL), white LEDs at 40 °C for 16h. [b]Conversion of methyl 4-bromobenzoate determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [c]NMR yields determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [d]Prices according to Sigma Aldrich (Merck)[x].

$NiBr_2·3H_2O$ gave the best combination of price, selectivity (chloride formation in case of $NiCl_2$), activity and handling (NiI_2 and $NiBr_2$ are highly hygroscopic).

5.5 Base screening

Table S4. Base screening.[a]



Entry	Base	Conversion [%][b]	1 [%][c]	2 [%][c]	3 [%][c]
1	TMP[d]	quant.	91	3	2
2	BIPA[e]	90	89	trace	n.d.[f]
3	DABCO[g]	71	68	3	trace
4	K_2HPO_4	68	63	4	trace
5	dimethylaniline	59	62	n.d.	n.d.
6	$CaCO_3$	65	61	trace	trace
7	2,6-lutidine	62	60	3	n.d.
8	without base	65	58	4	trace
9	tetramethylguanidine	53	43	n.d.	n.d.
10	DIPEA[h]	49	42	6	n.d.
11	Et_3N	42	35	5	trace
12	DMAP[i]	43	31	6	trace
13	K_3PO_4	33	21	trace	trace
14	DBU[j]	27	19	trace	trace
15	Na_2CO_3	17	14	trace	trace
16	$NaHCO_3$	14	8	4	trace
17	NaO*t*Bu	29	5	trace	trace
18	KOH	quant.	4	n.d.	n.d.
19	NaOH	quant.	n.d.	n.d.	n.d.
20	K_2CO_3	8	n.d.	trace	n.d.
21	NaH_2PO_4	10	n.d.	n.d.	n.d.

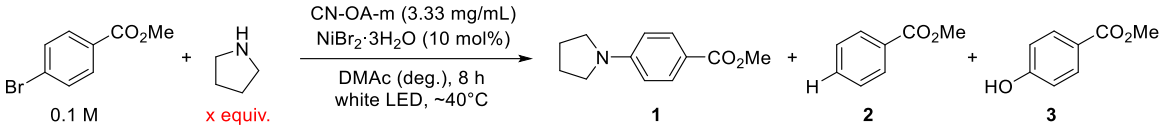
Entry	Base	Conversion [%][b]	1 [%][c]	2 [%][c]	3 [%][c]
22	LiOH	43	n.d.	n.d.	n.d.
23	Cs_2CO_3	11	n.d.	5	trace
24	CsF	7	n.d.	trace	n.d.
25	CsOAc	2	n.d.	n.d.	n.d.
26	HMDS[k]	quant.	n.d.	n.d.	n.d.

[a]Reaction conditions: methyl 4-bromobenzoate (0.3 mmol), pyrrolidine (0.45 mmol), $NiBr_2 \cdot 3H_2O$ (10 mol%), base (0.9 mmol), CN-OA-m (10 mg), DMAc (anhydrous, 3 mL), white LEDs at 40 °C for 16h. [b]Conversion of methyl 4-bromobenzoate determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [c]NMR yields determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [d]2,2,6,6-tetramethylpiperidin [e]*N-tert*-butylisopropylamine. [f]not detected. [g]1,4-diazabicyclo[2.2.2]octane. [h]*N,N*-diisopropylethylamine. [i]4-(dimethylamino)pyridine. [j]1,8-diazabicyclo[5.4.0]undec-7-ene. [k]Gexamethyldisilazane

N-tert-butylisopropylamine (BIPA) and 2,2,6,6-tetramethylpiperidine (TMP) gave best results. No C-N coupling between the aryl halide and these secondary, sterically hindered amines was observed. The absence of a base resulted in 58% yield indicating that the amine substrate can play several roles simultaneously (substrate, ligand, base). All other tested bases did not significantly increase the yield compared to the base-free method.

5.6 Screening of conditions

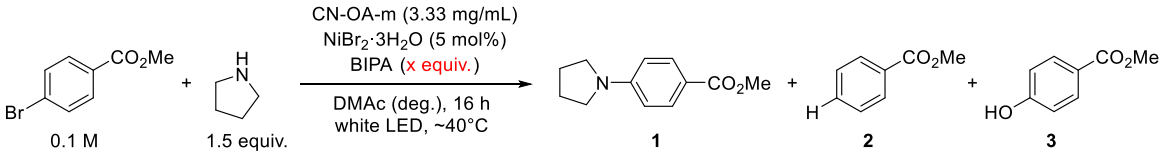
Table S5. Screening of amine equivalents for the base-free method.



Entry	Pyrrolidine [equiv.]	Conversion [%][b]	1 [%][c]	2 [%][c]	3 [%][c]
1	1	33	24	4	1
2	1.5	53	43	6	1
3	2.0	67	59	7	1
4	2.5	91	83	6	2
5	3.0	quant.	94	5	2
6	3.5	quant.	92	6	3

[a]Reaction conditions: methyl 4-bromobenzoate (0.3 mmol), pyrrolidine (x equiv.), $NiBr_2 \cdot 3H_2O$ (10 mol%), CN-OA-m (10 mg), DMAc (anhydrous, 3 mL), white LEDs at 40 °C for 8 h. [b]Conversion of methyl 4-bromobenzoate determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [c]NMR yields determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard.

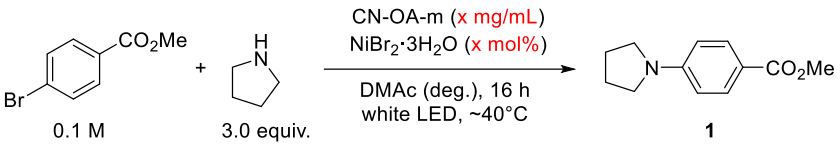
Table S6. Screening of base (BIPA) equivalents for reactions with 1.5 equiv. pyrrolidine.[a]



Entry	BIPA [equiv.]	Conversion [%][b]	1 [%][c]	2 [%][c]	3 [%][c]
1	-	65	58	5	n.d.[d]
2	0.5	68	58	5	3
3	1	87	81	4	2
4	1.5	91	82	5	n.d.
5	2.0	92	84	5	n.d.

[a]Reaction conditions: methyl 4-bromobenzoate (0.3 mmol), pyrrolidine (0.45 mmol), $NiBr_2 \cdot 3H_2O$ (5 mol%), CN-OA-m (10 mg), BIPA (0-2 equiv.), DMAc (anhydrous, 3 mL), white LEDs at 40 °C for 16 h. [b]Conversion of methyl 4-bromobenzoate determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [c]NMR yields determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [d]not detected.

Table S7. Effect of the amount of $NiBr_2 \cdot 3H_2O$ and CM-OA-m on the yield of **1**.[a]

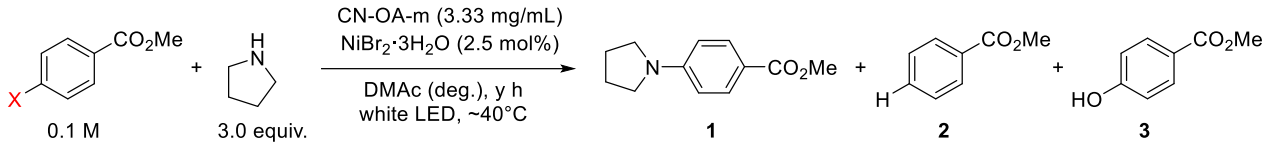


Entry	$NiBr_2 \cdot 3H_2O$ [mol%]	CN-OA-m [g/mL]	Conversion [%][b]	1 [%][c]
1	10	3.33	quant.	95
2	5	3.33	quant.	98
3	5	1.66	quant.	97
4	2.5	1.66	quant.	98
5	1	1.66	47	47
6	2.5	0.88	56	56

[a]Reaction conditions: methyl 4-bromobenzoate (0.3 mmol), pyrrolidine (0.9 mmol), $NiBr_2 \cdot 3H_2O$ (y mol%), base (0.9 mmol), CN-OA-m (x mg), DMAc (anhydrous, 3 mL), white LEDs at 40 °C for 16h. [b]Conversion of methyl 4-bromobenzoate determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [c]NMR yields determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard.

5.7 Screening of aryl (pseudo)halides

Table S8. Screening of aryl (pseudo)halides.[a]

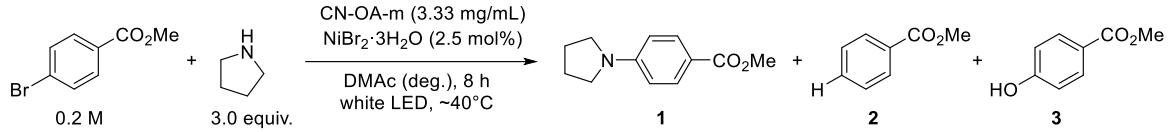


Entry	X	Time [h]	Conversion [%][b]	1 [%][c]	2 [%][c]	3 [%][c]
1	I	8	quant.	99	1	n.d.
2	Br	8	quant.	98	2	1
3	Cl	168	76	72	4	n.d.
4	OTf	72	75	67	5	2
5	OTs	16	2	n.d.	n.d.	n.d.
6	OMs	16	5	n.d.	n.d.	4

[a]Reaction conditions: aryl (pseudo)halide (0.3 mmol), pyrrolidine (0.9 mmol), $NiBr_2 \cdot 3H_2O$ (2.5 mol%), CN-OA-m (10 mg), DMAc (anhydrous, 3 mL), white LEDs at 40 °C for x h. [b]Conversion of methyl 4-bromobenzoate determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [c]NMR yields determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [d]not detected.

5.8 Control studies

Table S9. Control studies.[a]

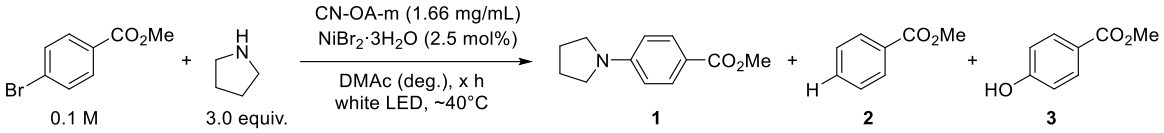


Entry	Deviation from standard conditions	Conversion [%][b]	1 [%][c]	2 [%][c]	3 [%][c]
1	None	quant.	98	2	n.d.[d]
2	dtbbpy[e] (2.5 mol%) as ligand	48	45	2	n.d.
3	No CN-OA-m	5	n.d.	2	1
4	No $NiBr_2 \cdot 3H_2O$	5	n.d.	n.d.	n.d.
5	No light	<1	n.d.	n.d.	n.d.
6	No degassing	10	10	n.d.	n.d.

[a]Reaction conditions: methyl 4-bromobenzoate (1.2 mmol), pyrrolidine (3.6 mmol), $NiBr_2 \cdot 3H_2O$ (2.5 mol%), CN-OA-m (20 mg), DMAc (anhydrous, 6 mL), white LEDs at 40 °C for 8 h. [b]Conversion of methyl 4-bromobenzoate determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [c]NMR yields determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [d]not detected. [e]4,4′-Di-tert-butyl-2,2′-bipyridyl.

5.9 Time/Wavelength study

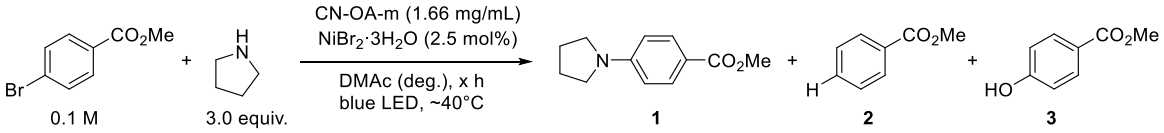
Table S10. Time study using white light.



Entry	Time [h]	Conversion [%][b]	1 [%][c]	2 [%][c]	3 [%][c]
1	1	25	24	n.d.[d]	n.d.
2	2	39	38	n.d.	n.d.
3	3	48	48	trace	n.d.
4	4	77	76	1	n.d.
5	5	87	83	2	n.d.
6	6	91	91	2	n.d.
7	7	97	94	3	n.d.
8	8	quant.	96	2	1

[a]Reaction conditions: methyl 4-bromobenzoate (0.6 mmol), pyrrolidine (1.8 mmol), $NiBr_2 \cdot 3H_2O$ (2.5 mol%), CN-OA-m (10 mg), DMAc (anhydrous, 6 mL), white LEDs at 40 °C for x h. [b]Conversion of methyl 4-bromobenzoate determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [c]NMR yields determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [d]not detected.

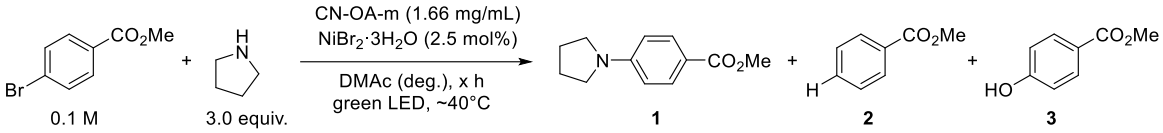
Table S11. Time study using blue light.



Entry	Time [h]	Conversion [%][b]	1 [%][c]	2 [%][c]	3 [%][c]
1	2	51	51	n.d.[d]	n.d.
2	4	77	80	trace	n.d.
3	5.5	quant.	>99	trace	n.d.

[a]Reaction conditions: methyl 4-bromobenzoate (0.6 mmol), pyrrolidine (1.8 mmol), $NiBr_2 \cdot 3H_2O$ (2.5 mol%), CN-OA-m (10 mg), DMAc (anhydrous, 6 mL), blue LEDs at 40 °C for x h. [b]Conversion of methyl 4-bromobenzoate determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [c]NMR yields determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [d]not detected.

Table S12. Time study using green light.



Entry	Time [h]	Conversion [%][b]	1 [%][c]	2 [%][c]	3 [%][c]
1	4	10	10	n.d.[d]	n.d.
2	8	21	20	n.d.	n.d.
3	24	69	68	n.d.	n.d.
4	48	quant.	>99	n.d.	n.d.

[a]Reaction conditions: methyl 4-bromobenzoate (0.6 mmol), pyrrolidine (1.8 mmol), $NiBr_2 \cdot 3H_2O$ (2.5 mol%), CN-OA-m (10 mg), DMAc (anhydrous, 6 mL), green LEDs at 40 °C for x h. [b]Conversion of methyl 4-bromobenzoate determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [c]NMR yields determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [d]not detected.

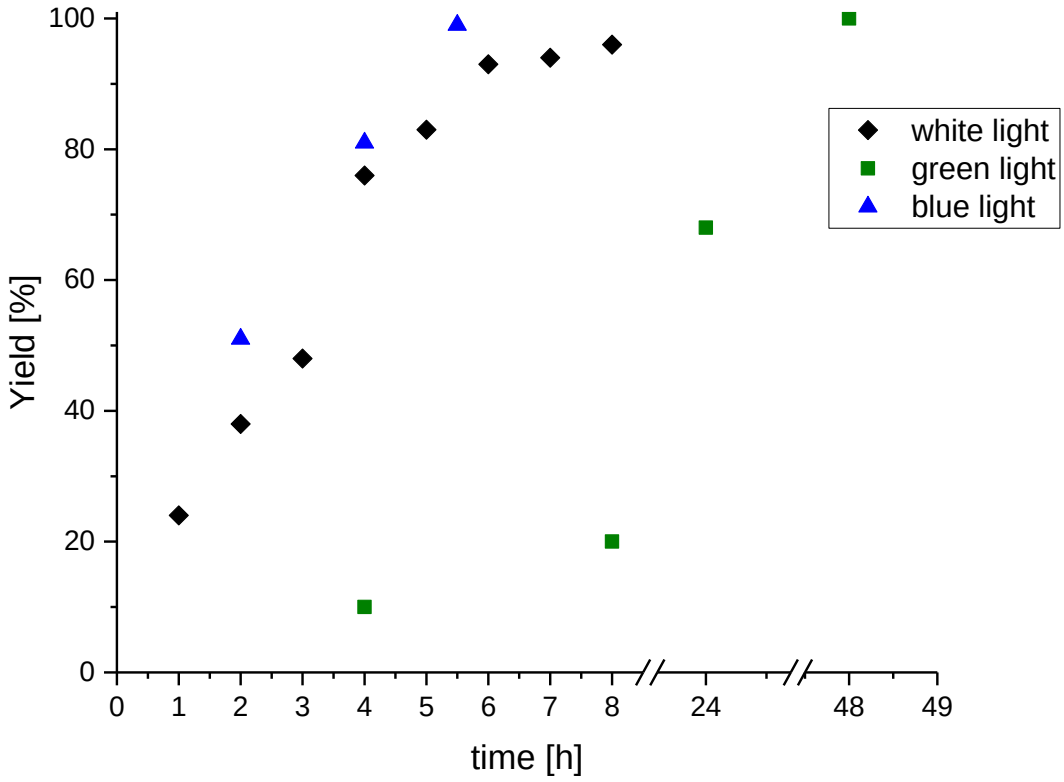


Figure S6. Time study using blue, green and white light for model reaction.

For ICP-OES experiments, the reaction mixture was centrifuged at 3000 rpm for 20 min and the liquid phase was carefully separated and analyzed by ^{1}H-NMR. The carbon nitride was washed with DMAc (anhydrous, 6 mL, followed by centrifugation at 3000 rpm for 20 min and separation of the liquid phase), water (6 mL, followed by centrifugation at 3000 rpm for 20 min and separation of the liquid phase) and lyophilized (overnight) before analysis.

Table S13: ICP-OES measurements of the nickel content on the new and recovered CN-OA-m after 8 h white light and 48 h green light standard reaction.

Sample	Ni [mg/g CN]	% adsorbed Ni
CN-OA-m new	0.117	/
CN-OA-m white light standard reaction 1	14.2	16.1
CN-OA-m green light standard reaction	13.8	15.7

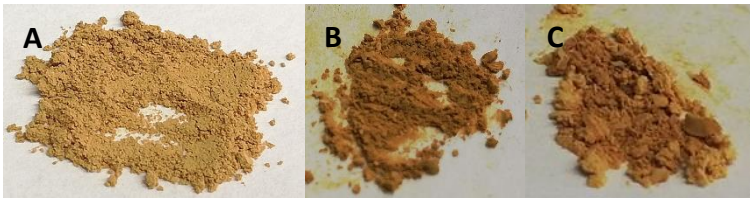


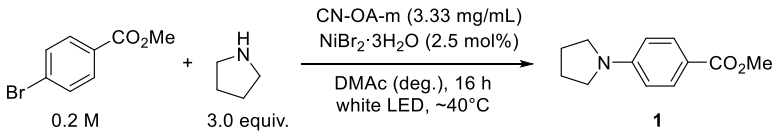
Figure S7. Fresh CN-OA-m (**A**), CN-OA-m after 8 h white light irradiation for standard reaction (**B**) and CN-OA-m after 48 h green light irradiation for standard reaction (**C**).

Note: Although 1.66 mg mL^{-1} of CN-OA-m is suitable for the C-N cross-coupling, a higher loading (3.33 mg mL^{-1}) was used for further experiments in order to obtain enough material for material characterization (ICP-OES, EDX, SEM, TEM, etc).

6. Recycling studies

An oven dried vial (13 x 80 mm) equipped with a stir bar was charged with CN-OA-m (20 mg), 4-bromomethylbenzoate (258.0 mg, 1.2 mmol, 1.0 equiv.) and $NiBr_2 \cdot 3H_2O$ (8.2 mg, 30 µmol, 2.5 mol%). Subsequently, pyrrolidine (256.0 mg, 295.6 µl, 3.6 mmol, 3.0 equiv.) and DMAc (anhydrous, 6 mL) were added and the vial was sealed with a septum and Parafilm. The reaction mixture was sonicated for 5-10 min followed by stirring for 5 min until fine dispersion of the solids was achieved and the mixture was then degassed by bubbling N_2 for 10 min. The mixture was irradiated in the photoreactor (white light or green light) at 40 °C with rapid stirring (1400 rpm). After the respective reaction time, one equivalent of 1,3,5-trimethoxybenzene (202.0 mg, 1.2 mmol) was added and the mixture was stirred for 5 min. The reaction mixture was centrifuged at 3000 rpm for 20 min and the liquid phase was carefully separated and analyzed by ^{1}H-NMR. The carbon nitride was washed with DMAc (anhydrous, 6 mL, followed by centrifugation at 3000 rpm for 20 min and separation of the liquid phase), lyophilized (overnight) and reused in the next reaction.

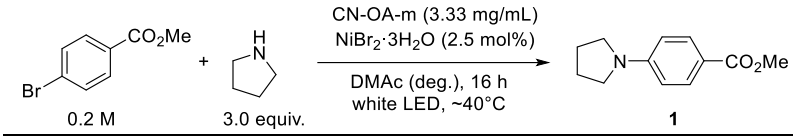
Table S14. Reusability of CN-OA-m using white light.[a]



Cycle	1 [%][b]
1	99
2	98
3	43
4	27
5	33

[a]Reaction conditions: methyl 4-bromobenzoate (1.2 mmol), pyrrolidine (3.6 mmol), $NiBr_2 \cdot 3H_2O$ (2.5 mol%), CN-OA-m (20 mg - reused), DMAc (anhydrous, 6 mL), white LEDs at 40 °C for 16h. [b]NMR yields determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard.

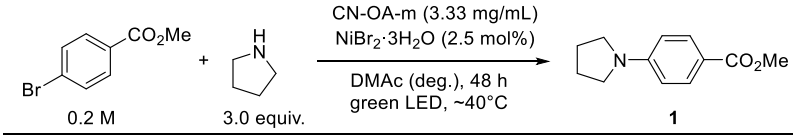
Table S15. Reusability of CN-OA-m without additional $NiBr_2 \cdot 3H_2O$ using white light.[a]



Cycle	1 [%][b]
1	99
2[c]	1

[a]Reaction conditions: methyl 4-bromobenzoate (1.2 mmol), pyrrolidine (3.6 mmol), $NiBr_2 \cdot 3H_2O$ (2.5 mol%), CN-OA-m (20 mg - reused), DMAc (anhydrous, 6 mL), white LEDs at 40 °C for 16h. [b]NMR yields determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [c]No $NiBr_2 \cdot 3H_2O$ added.

Table S16. Reusability of CN-OA-m using green light.[a]



Cycle	1 [%][b]
1	99
2	99
3	98
4	98
5	94

[a]Reaction conditions: methyl 4-bromobenzoate (1.2 mmol), pyrrolidine (3.6 mmol), $NiBr_2 \cdot 3H_2O$ (2.5 mol%), CN-OA-m (20 mg - reused), DMAc (anhydrous, 6 mL), green LEDs at 40 °C for 48h. [b]NMR yields determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard.

Table S17: ICP-OES measurements of the nickel content on recovered CN-OA-m after white light and green light recyclability tests.

Sample	Ni [mg/g CN]	% adsorbed Ni
CN-OA-m white light recyclability tests	60.5	13.7
CN-OA-m green light recyclability tests	38.8	8.8

Figure S8. Fresh CN-OA-m (**A**), CN-OA-m after recyclability tests with white light irradiation (**B**) and CN-OA-m after recyclability tests with green light irradiation (**C**).

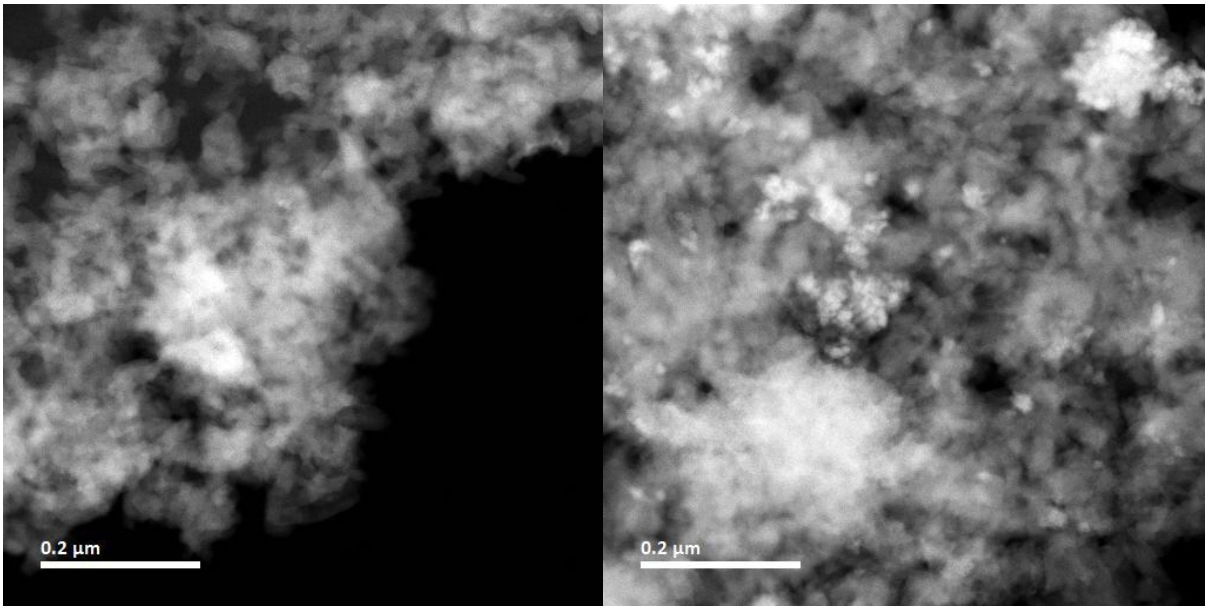


Figure S9. HAADF-STEM brightfield images show almost no nickel particle agglomerates (bright spots) on CN-OA-m after recyclability tests with green light irradiation (left) and a significant amount of agglomerates after recyclability tests with white light irradiation (right).

7. Scale-up of amination

An oven dried vial (25 x 140 mm) (Figure S10, A) equipped with a stir bar was charged with $NiBr_2 \cdot 3H_2O$ (54.5 mg, 0.2 mmol, 2.5 mol%), methyl 4-bromobenzoate (1.720 g, 8.0 mmol, 1 equiv.) and CN-OA-m (133.3 mg). Subsequently, pyrrolidine (1.706 g, 1.97 ml, 24.0 mmol, 3 equiv.) and DMAc (anhydrous, 6 mL) were added and the vial was sealed with a septum and parafilm. The reaction mixture was sonicated for 10 min and the mixture was then degassed by bubbling N_2 for 30 min and stirring the reaction mixture. The mixture was irradiated in a beaker wrapped with a LED-band (Figure S2, B) at ~40°C with rapid stirring (700 rpm). The completion of the reaction (14 h) was confirmed by taking an aliquot and measuring ^{1}H-NMR of the crude mixture in DMSO-d^6. The catalyst was removed by centrifugation (3000 rpm, 20 min) and the liquid phase was diluted with H_2O (200 mL) and extracted with ethyl acetate (3 x 200 mL). The combined organic phases were washed with H_2O (200 mL), a sat. $NaHCO_3$ solution (200 ml), and brine (200 mL), dried over Na_2SO_4 and concentrated. The crude product was purified by flash column chromatography (SiO_2, Hexane/EtOAc; gradient 0-5% ethyl acetate in hexane; 2. Isocratic 5% ethyl acetate in hexane)) on a Grace™ Reveleris™ system using a 24 g cartridge to afford (1-(4-methylbenzoate)pyrrolidine) (**1**) in 93 % (1.5338 g, 7.47 mmol) as a white solid (Figure S11).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.7 Hz, 2H), 6.46 (d, *J* = 8.7 Hz, 2H), 3.83 (s, 3H), 3.40 – 3.09 (m, 4H), 2.05 – 1.86 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 167.57, 150.79, 131.31, 116.16, 110.62, 51.37, 47.47, 25.41. HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{16}NO_2$ [$(M+H)^+$]: 206.1176; found: 206.116.

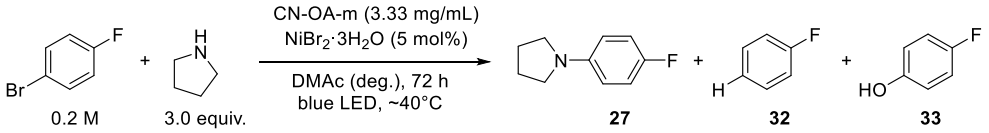
These data are in full agreement with those previously published in the literature.[18]

Figure S10. Vessel dimensions of vial for scale-up reaction (**A**) and vial for "standard scale" reactions (**B**).

Figure S11. Isolated product (1-(4-methylbenzoate)pyrrolidine) (**1**) from 8 mmol scale**.**

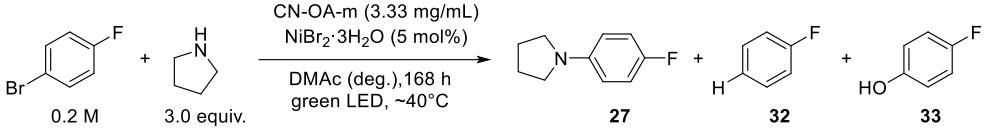
8. Studies on the reaction of 4-bromofluorobenzene with pyrrolidine.

Procedure A: Dual CN-OA-m/Ni catalysis with irradiation at 450 nm



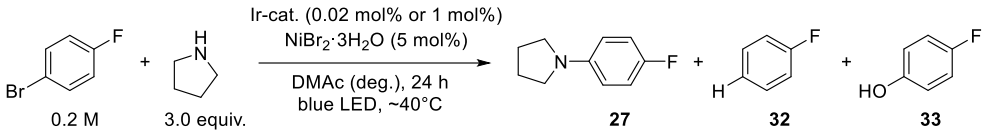
An oven dried vial (19 x 80 mm) equipped with a stir bar was charged with the CN-OA-m (20 mg), 4-bromofluorobenzene (210.0 mg, 131.8 µl, 1.2 mmol, 1.0 equiv.) and $NiBr_2 \cdot 3H_2O$ (16.4 mg, 60 µmol, 5.0 mol%). Subsequently, pyrrolidine (256.0 mg, 295.6 µl, 3.6 mmol, 3.0 equiv.) and DMAc (anhydrous, 6 mL) were added and the vial was sealed with a septum and Parafilm. The reaction mixture was sonicated for 5-10 min followed by stirring for 5 min until fine dispersion of the solids was achieved and the mixture was then degassed by bubbling N_2 for 10 min. The mixture was irradiated in the photoreactor (blue light function of RGB LED strip) at 40 °C with rapid stirring (1400 rpm). After 72 h, one equivalent of 1,3,5-trimethoxybenzene (1.2 mmol) was added and the mixture was stirred for 5 min. An aliquot of the reaction mixture (~300 µL) was filtered, diluted with DMSO-d_6 and subjected to ^{1}H-NMR analysis.

Procedure B: Dual CN-OA-m/Ni catalysis with irradiation at 520 nm



An oven dried vial (19 x 80 mm) equipped with a stir bar was charged with the CN-OA-m (20 mg), 4-bromofluorobenzene (210.0 mg, 131.8 µl, 1.2 mmol, 1.0 equiv.) and (16.4 mg, 60 µmol, 5.0 mol%). Subsequently, pyrrolidine (256.0 mg, 295.6 µl, 3.6 mmol, 3.0 equiv.) and DMAc (anhydrous, 6 mL) were added and the vial was sealed with a septum and Parafilm. The reaction mixture was sonicated for 5-10 min followed by stirring for 5 min until fine dispersion of the solids was achieved and the mixture was then degassed by bubbling N_2 for 10 min. The mixture was irradiated in the photoreactor (green light function of RGB LED strip) at 40 °C with rapid stirring (1400 rpm). After 168 h, one equivalent of 1,3,5-trimethoxybenzene (1.2 mmol) was added and the mixture was stirred for 5 min. An aliquot of the reaction mixture (~300 µL) was filtered, diluted with DMSO-d_6 and subjected to ^{1}H-NMR analysis.

Procedure Ir: Dual Ir/Ni catalysis with irradiation at 420 nm



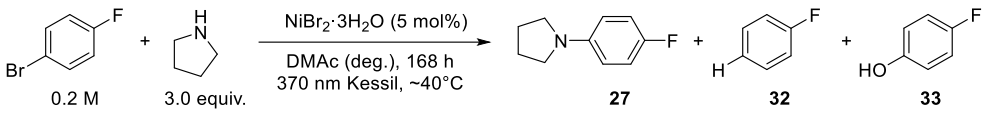
Ir1: An oven dried vial (19 x 80 mm) equipped with a stir bar was charged with 4-bromofluorobenzene (210.0 mg, 131.8 µl, 1.2 mmol, 1.0 equiv.) and $NiBr_2 \cdot 3H_2O$ (16.4 mg, 60 µmol, 5.0 mol%) and a solution of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.27 mg, 0.02 mol%). in DMAc (48 µl). Subsequently, pyrrolidine (256.0 mg, 295.6 µl, 3.6 mmol, 3.0 equiv.) and DMAc (anhydrous, 6 mL) were added and the vial was sealed with a septum and Parafilm.

Ir2: An oven dried vial (19 x 80 mm) equipped with a stir bar was charged with 4-bromofluorobenzene (52.5 mg, 33.0 µl, 0.3 mmol, 1.0 equiv.), $NiBr_2 \cdot 3H_2O$ (4.1 mg, 15 µmol, 5.0 mol%) and a solution of Ir $[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (3.37 mg, 1 mol%). in DMAc (600 µl). Subsequently, pyrrolidine (64.0 mg, 73.9 µl, 0.9 mmol, 3.0 equiv.) and DMAc (anhydrous, 2.4 mL) were added and the vial was sealed with a septum and Parafilm.

The reaction mixture was sonicated for 5-10 min followed by stirring for 5 min and the mixture was then degassed by bubbling N_2 for 10 min. The mixture was irradiated in the photoreactor (blue light function of LED-band) at 40 °C with rapid stirring (1400 rpm). After 24 h, one equivalent of 1,3,5-trimethoxybenzene (Ir1: 202.0 mg, 1.2 mmol/ Ir2: 50.5 mg, 0.3 mmol) was added and the mixture was stirred for 5 min. An aliquot of the reaction mixture (~300 µL) was filtered, diluted with DMSO-d_6 and subjected to ^{1}H-NMR analysis.

Note: In case if procedure C2, the formation of small amounts of black particles was observed after the reaction.

Procedure UV: Ni catalysis with irradiation at 370 nm

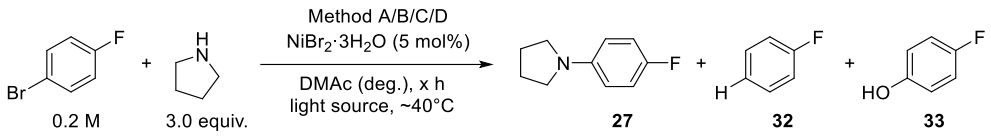


An oven dried vial (19 x 80 mm) equipped with a stir bar was charged 4-bromofluorobenzene (210.0 mg, 131.8 µl, 1.2 mmol, 1.0 equiv.) and $NiBr_2 \cdot 3H_2O$ (16.4 mg, 60 µmol, 5.0 mol%). Subsequently, pyrrolidine (256.0 mg, 295.6 µl, 3.6 mmol, 3.0 equiv.) and DMAc (anhydrous, 6 mL) were added and the vial was sealed with a septum and Parafilm. The reaction mixture was sonicated for 5-10 min followed by stirring for 5 min and the mixture was then degassed by bubbling N_2 for 10 min. The mixture was irradiated with UV light using the Kessil® PR 160-370 nm lamp with rapid stirring (~800 rpm) and cooling by a fan. After 3 h (**UV1**), 15 h (**UV2**), 72 h (**UV3**) and 168 h (**UV4**) one equivalent of 1,3,5-trimethoxybenzene (202.0 mg, 1.2 mmol) was added and the mixture was stirred for 5 min. An aliquot of the reaction mixture (~300 µL) was filtered, diluted with DMSO-d_6 and subjected to ^{1}H-NMR analysis.

Note: The color of the reaction solution changed from yellowish to black and a significant amount of black particles was formed.

The reaction mixtures of procedure A, B, and D were centrifuged at 3000 rpm for 20 min. The carbon nitride from the blue (procedure A) and green light experiment (procedure B) and the black particles formed during the UV-light experiment (procedure D) were washed with DMAc (anhydrous 6 mL, followed by centrifugation at 3000 rpm for 20 min and separation of the liquid phase) and acetone (6 mL, followed by centrifugation at 3000 rpm for 20 min and separation of the liquid phase), lyophilized (overnight) and subjected to FTIR, UV-Vis, XRD, UV-Vis, ICP-OES, EDX, XPS as well as SEM and TEM analysis. For comparison, an unused sample of CN-OA-m from the same batch was also analyzed.

Table S18. Coupling of 4-bromofluorobenzene and pyrrolidine using different light sources and catalysts.



Entry	Procedure	Conversion [%][a]	27 [%][b]	32 [%][b]	33 [%][b]
1	A	93	70	6	9
2	A	92	69	7	8
3	A	91	68	6	9
4	A	92	63	7	6
5	A	87	60	7	9
6	A	18	6	2	n.d.[c]
7	A	22	5	n.d.	3
8	B	quant.	91	5	2
9	B	quant.	89	1	10
10	B	quant.	89	9	1
11	B	99	86	9	2
12	B	quant.	88	1	10
13	B	97	86	2	9
14	B	quant.	84	9	n.d.
15	Ir1	quant.	77	7	4
16	Ir2	79	33	20	13
17	UV1	18	7	3	n.d.
18	UV2	39	17	9	4
19	UV3	94	26	32	16
20	UV4	quant.	10	23	9

[a]Conversion of 4-bromofluorobenzene determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [b]NMR yields determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [c]not detected.

8.1 Powder X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS)

The powder X-ray diffraction spectra (PXRD) of the black material generated during the UV-light experiment (Table S18, Entry 17) showed diffraction peaks at 44°, 51° and 76° that could be assigned to the (1 1 1), (2 0 0), (2 2 0) planes of nickel(0) (Figure S12). Spectra of the recovered CN-OA-m (Table 17, Entry 7 & 8) materials show a characteristic peak at 27.4°, which corresponds to the in-planar structural packing and inter-planar stacking peaks of the aromatic systems of CN-OA-m. Nickel(0) (diffraction peaks at 44°, 51° and 76°) was detected in the material recovered from experiment using blue LEDs (Method A), and, although in significantly lower quantity, in the material recovered from the experiment using green LEDs (Method B).

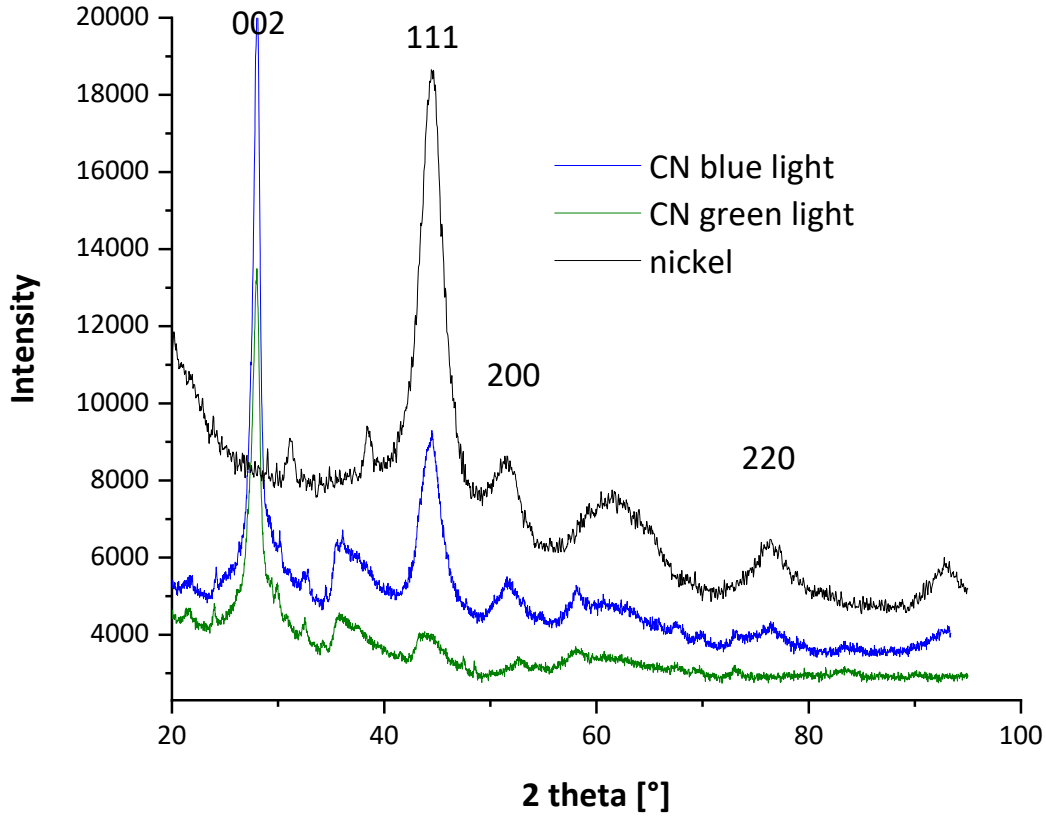


Figure S12. XRD measurements of the material generated by UV-light (black line), CN-OA-m after method A with blue light irradiation (blue line) and CN-OA-m after method B with green light irradiation (green line).

XPS scans of the solid material generated during UV light experiments and CN-OA-m recovered from the experiments using blue (Method A) and green LED (Method B) irradiation confirmed the presence of nickel in both samples (Figure S13). High-resolution XPS analysis spectra for core levels of Ni2p confirm the presence of Ni^{2+} and Ni^{0} at 854.6 (± 0.02) eV and 852.3 (± 0.02) eV, for CN-OA-m recovered from method A (blue light) and the material generated during UV light irradiation (Figure S13, A). Only Ni^{2+} (854.6 (± 0.02) eV) species were detected in the CN-OA-m sample recovered from the experiment using method B (green light).The high-resolution XPS spectra of the C 1s core level spectra shows typical C-C and N-C=N bonding signals for all CN-OA-m samples (Figure S13, B). The N 1s spectra contain two main peaks that are typical for carbon nitrides and can be assigned to i) sp2 bonded nitrogen in tri-s-triazine groups (C-N=C), and ii) sp3 amino groups(C-NH) for all CN-OA-m samples. The calculated elemental composition indicates a two times higher concentration of nickel on CN-OA-m recovered from method A (blue light) compared to CN-OA-m recovered from method B (green light) (Table S19).

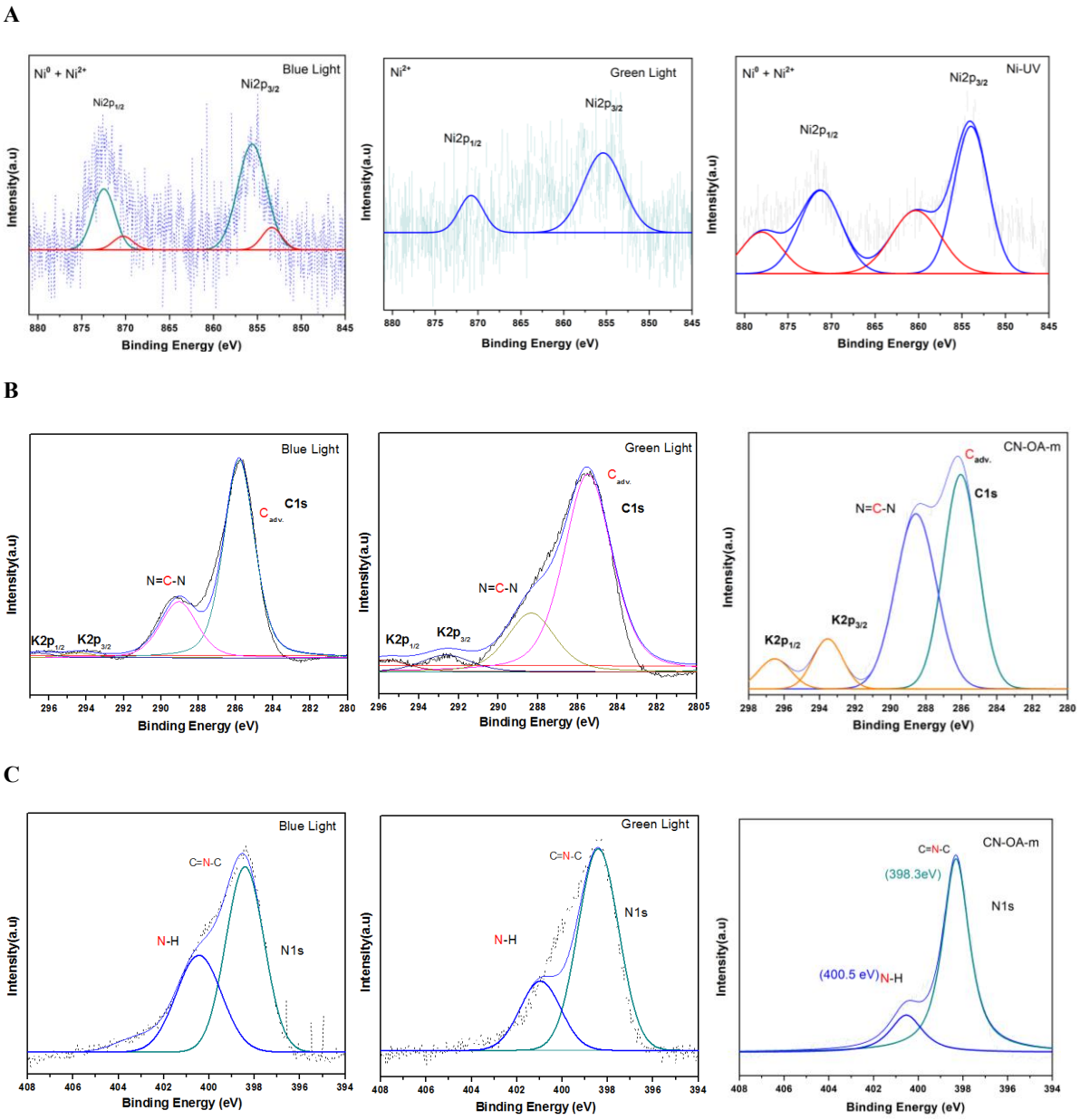


Figure S13. **A)** High-resolution XPS analysis spectra for core levels of Ni $2p_{3/2}$: CN-OA-m recovered from experiments using method A (blue light) and method B (green light), and the heterogeneous material generated during UV-light experiments(Ni-UV). **B)** High-resolution XPS analysis spectra for core levels of C 1s: CN-OA-m recovered from experiments using method A (blue light) and method B (green light), and unused CN-OA-m. **C)** High-resolution XPS analysis spectra for core levels of N 1s: CN-OA-m recovered from experiments using method A (blue light) and method B (green light), and unused CN-OA-m. has been deconvoluted using *Lorenzian-Gaussian* peak fitting functions with Shirley background deletion.

Table S19. XPS Elemental composition of CN-OA-m and CN-OA-m recovered from experiments using method A and B.

Sample	% w/w N	% w/w C	% w/w K	% w/w Ni
CN-OA-m	57.257	41.191	1.552	---
CN-OA-m blue light[a]	61.094	37.718	0.365	0.822
CN-OA-m green light[b]	59.021	39.983	0.709	0.377

[a]Sample recovered from experiment described in Table S18, Entry 7. [b]Sample recovered from experiment described in Table S18, Entry 8.

8.2 Scanning transmission electron microscopy (STEM)

8.2.1 CN-OA-m recovered from method A (blue LEDs) and method B (green LEDs)

Scanning transmission electron microscopy (STEM) was used to visualize nickel particles on the surface of the recovered CN-OA-m. High-angle annular dark-field (HAADF) images show round- to oval-shaped particles with sizes ranging 10-20 nm. The polycrystalline particle consist of smaller ones (1-5 nm), which agglomerated on the surface (Figure S14 and S15). The images show the porous structure of CN-OA-m containing particles that show a diffraction pattern indicating Ni-species deposition. The exact lattice of a selected nickel particle is shown in higher resolution. The STEM images of CN-OA-m recovered from experiments using method B (green LED) (Figure S15) show a significantly lower amount of (agglomerated) nickel particles compared to using method A (blue LED, Figure S14). This confirms the results obtained using XRD (Figure S12), XPS (Figure S13), EDX (Table S20) and ICP-OES (Table S21) analysis.

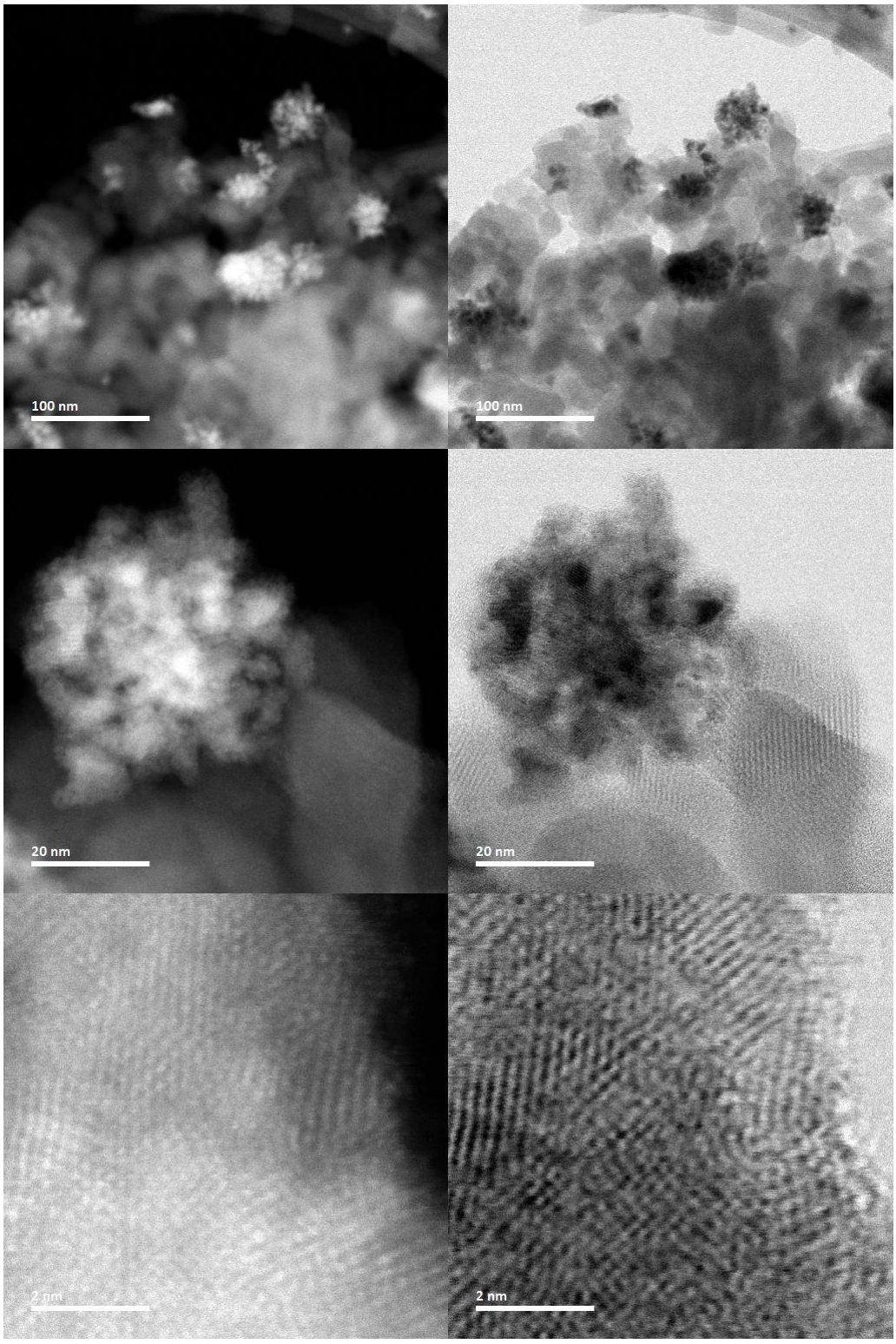


Figure S14. HAADF-STEM brightfield (left)/darkfield (right) images showing nickel particles (bright spots in brightfield and dark spots in darkfield) on CN-OA-m recovered from the experiment using method A (blue LED).

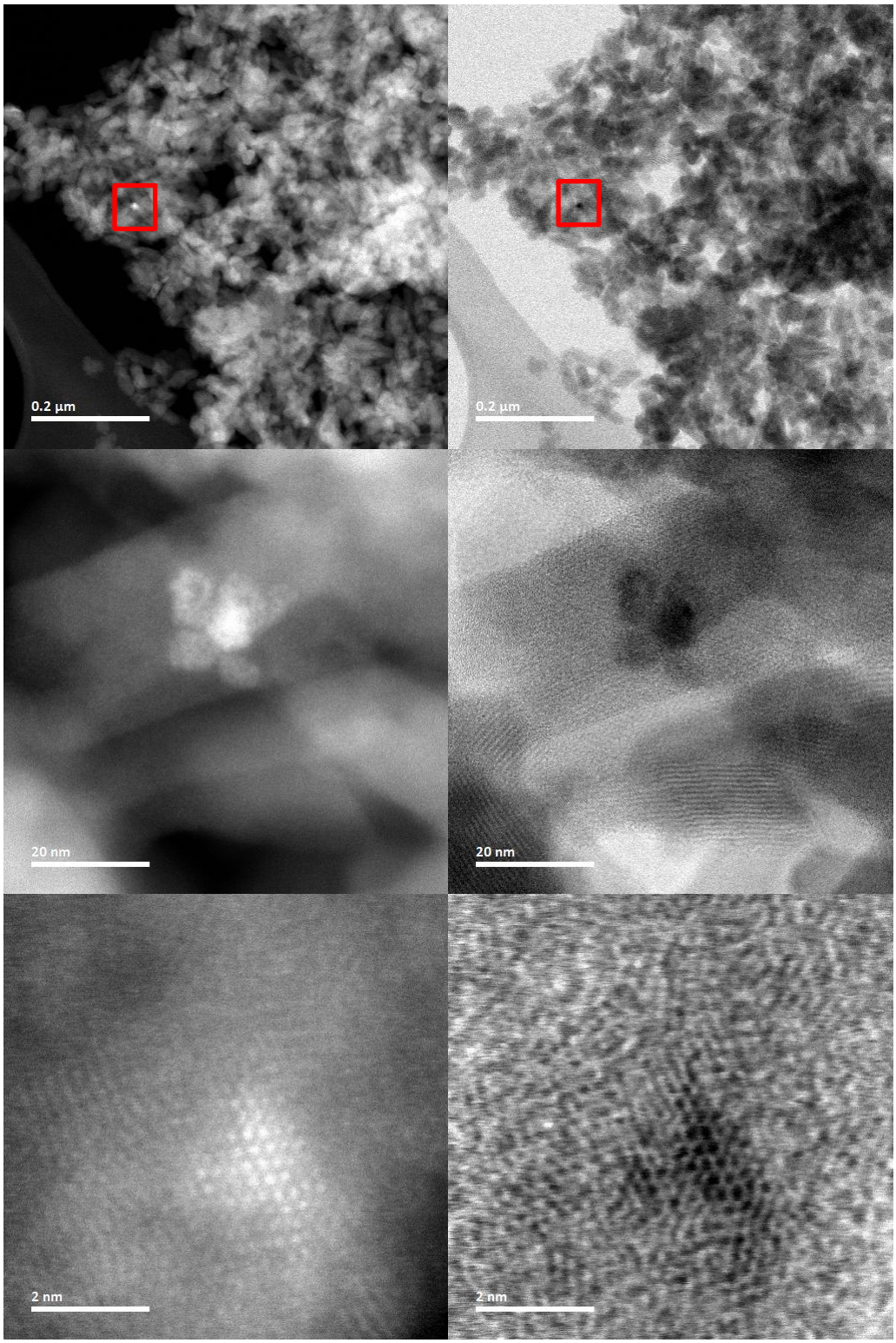


Figure S15. HAADF-STEM brightfield (left)/darkfield (right) showing a nickel particle (bright spot in brightfield and dark spot in darkfield) on CN-OA-m recovered from the experiment using method B (green LED).

8.2.2 Heterogeneous material generated during experiments using the UV method (photocatalyst-free and UV-light)

The STEM image shows the solid material formed using method C (UV-light). Although the particle mainly consists of nickel, lighter elements can be additionally identified. EDX analysis (Table S20) shows the presence of carbon, indicating that agglomerated nickel species incorporate organic materials. This is in agreement with the low mass-balance observed during these reactions (e.g. Table S18, Entry 20), suggesting substrate/product degradation presumably by the high energy light source.

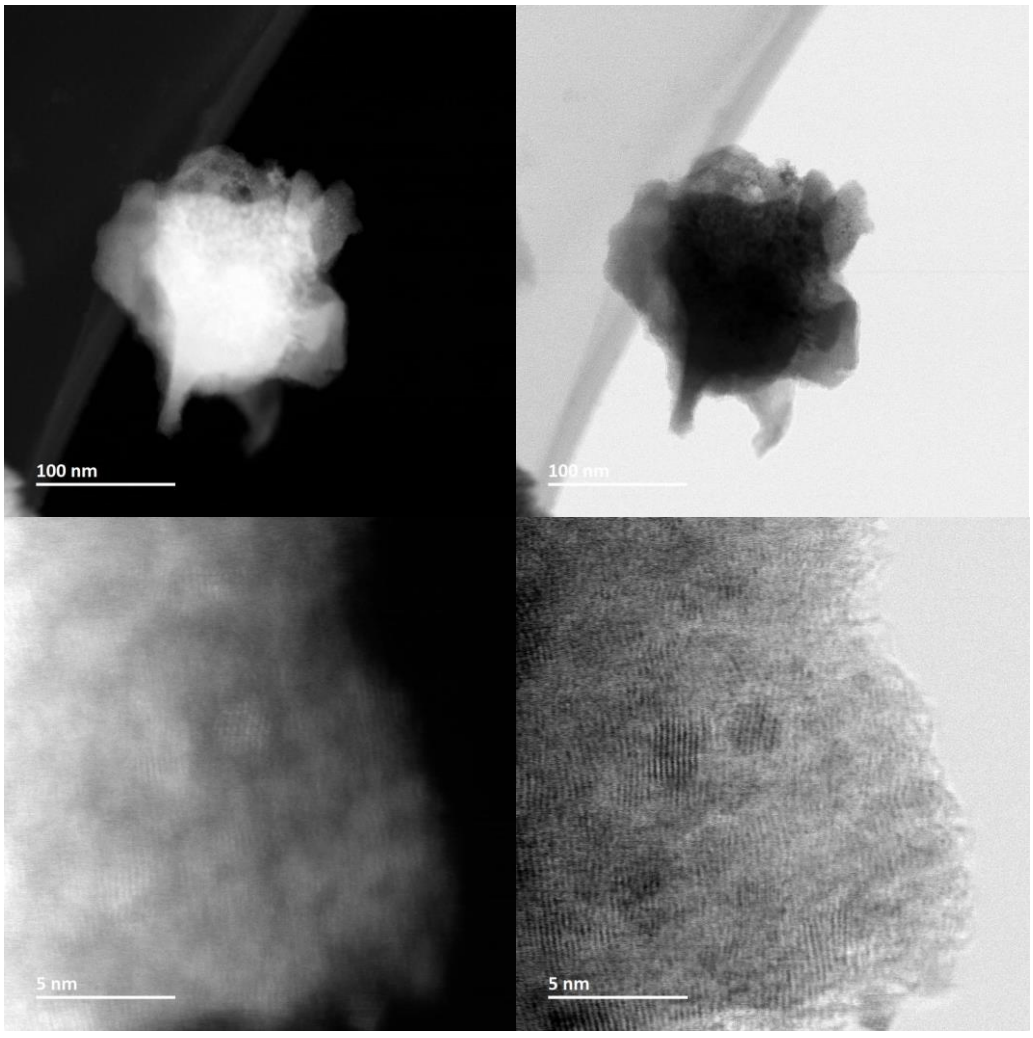


Figure S16. HAADF-STEM brightfield (left)/darkfield (right) images of nickel particles (bright spots in brightfield and dark spots in darkfield) after UV-light method (photocatalyst-free).

8.3 Scanning electron microscopy (SEM)

SEM images of the new and recovered CN-OA-m samples showed a porous texture that was not altered during the catalytic transformation (Figure S17).

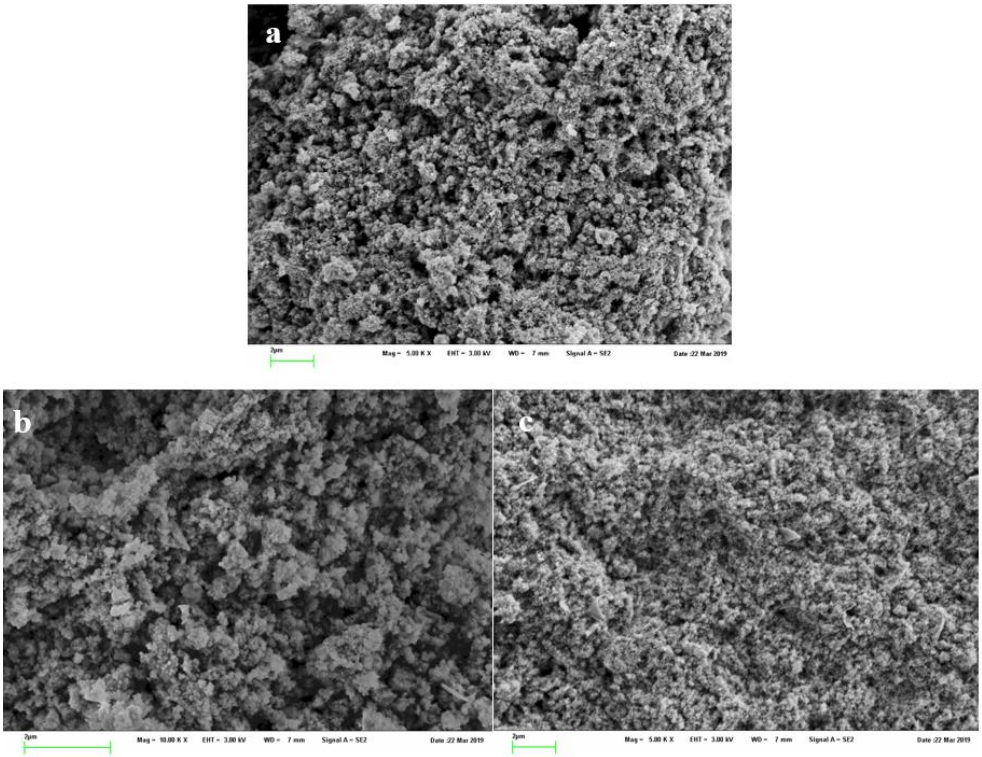


Figure S17- SEM images of CN-OA-m new (**A**), CN-OA-m recovered from the cross-coupling using blue light (Table S18, Entry 7) (**B**), and CN-OA-m recovered from the cross-coupling using green light (Table S18, Entry 8) (**C**).

8.4 Energy-dispersive X-ray spectroscopy (EDX) and inductively coupled plasma atomic emission spectroscopy (ICP-OES)

Elemental analysis via EDX (Table S20) and ICP-OES (Table S21) analysis of the recovered CN-OA-m samples shows a 3 times higher Ni concentration for the blue light experiment. The material from the blue light experiment contains ~12-14 w/w % Ni suggesting that ~70% of the homogeneous nickel catalyst were deposited on the CN-OA-m during the model reaction. The material from the green light experiment contains ~3-4 w/w % Ni suggesting that ~70% of the homogeneous nickel catalyst were deposited on the CN-OA-m during the model reaction.

Table S20: EDX elemental composition acquired from new and recovered CN-OA-m.

Sample	% w/w N	% w/w C	% w/w O	% w/w K	% w/w Ni
CN-OA-m	42.56	37.59	3.65	1.06	0.05
CN-OA-m from Method A (blue light)[a]	36.25	30.27	7.16	8.60	13.90
CN-OA-m from Method B (green light)[b]	47.19	29.46	7.79	8.86	3.38
Solid from UV-experiment[c]	22.8	21.00	18.92	-	26.71

[a]Sample recovered from experiment described in Table S18, Entry 7. [b]Sample recovered from experiment described in Table S18, Entry 8. [c]Sample recovered from experiment described in Table S18, Entry 17.

Table S21: ICP-OES measurements of the nickel content on the new and recovered CN-OA-m.

Sample	Ni [mg/g CN]	% absorbed Ni
CN-OA-m new	0.69	0.39
CN-OA-m from Method A (blue light)[a]	126	71.2
CN-OA-m from Method B (green light)[b]	35.5	20.1

[a]Sample recovered from experiment described in Table S18, Entry 7.
[b]Sample recovered from experiment described in Table S18, Entry 8.

8.5 Fourier-transform infrared spectroscopy (FTIR) and Ultraviolet–visible spectroscopy (UV-VIS)

FTIR spectra of the new and recovered CN-OA-m samples were identical (Figure S18).

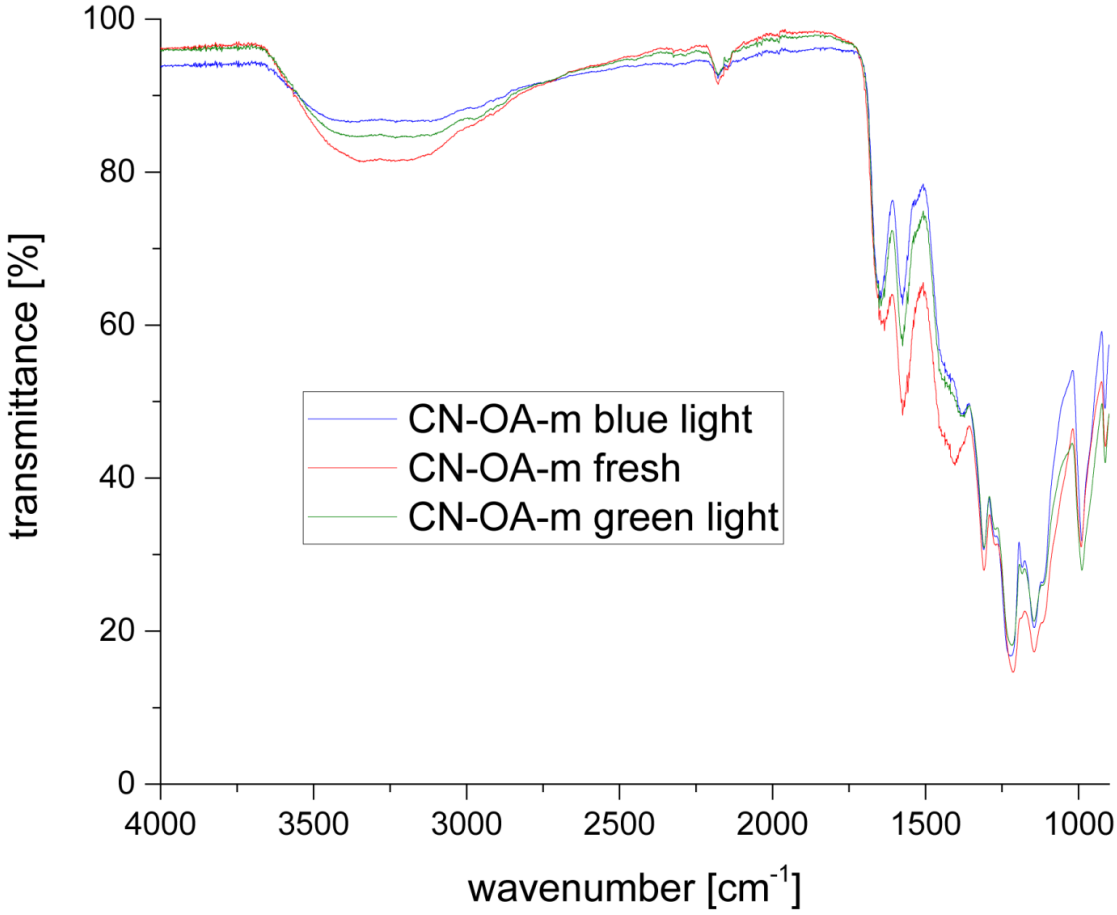


Figure S18. FTIR spectra of CN-OA-m new (red), CN-OA-m recovered from the cross-coupling using blue light (blue), and CN-OA-m recovered from the cross-coupling using green light (green).

The UV-Vis spectra of the CN-OA-m recovered from the cross-coupling using green light and CN-OA-m recovered from the cross-coupling using blue showed an increased absorption in the visible region (>460 nm) compared to a unused CN-OA-m sample.

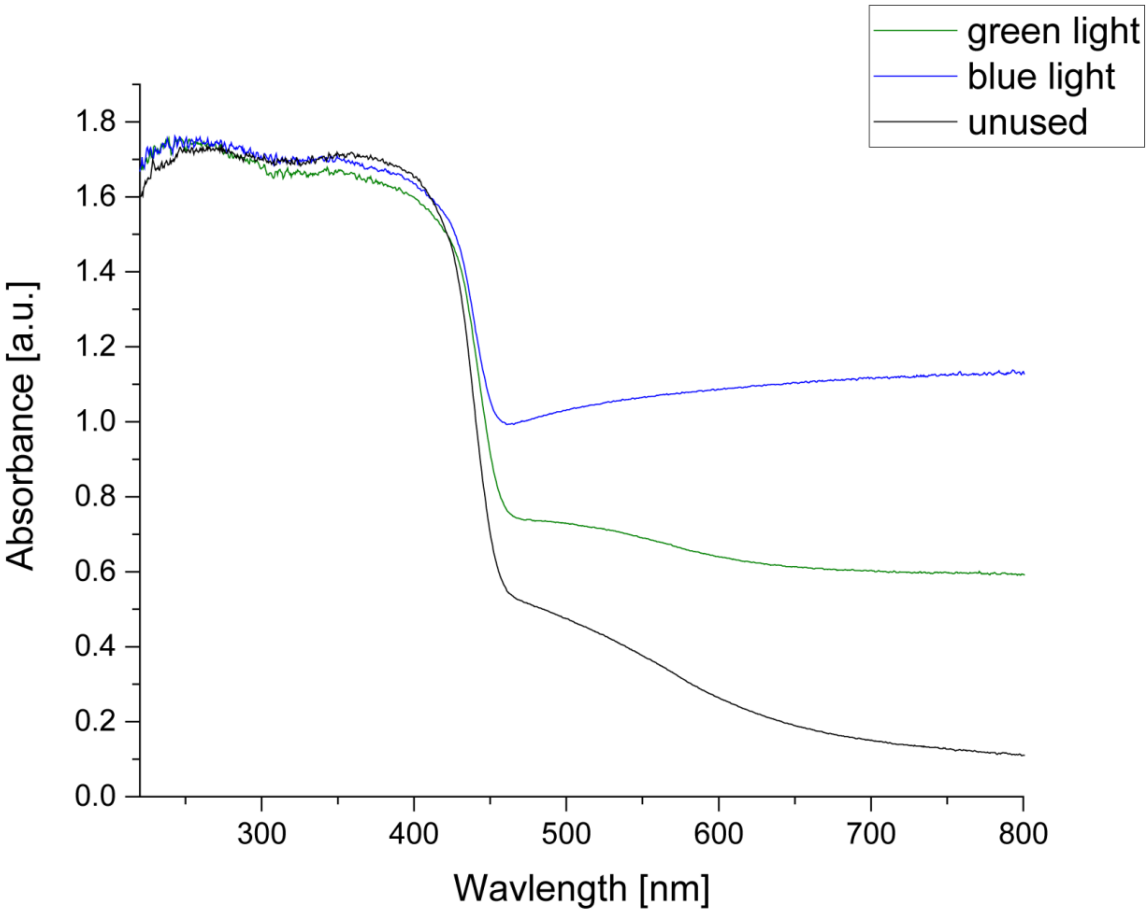
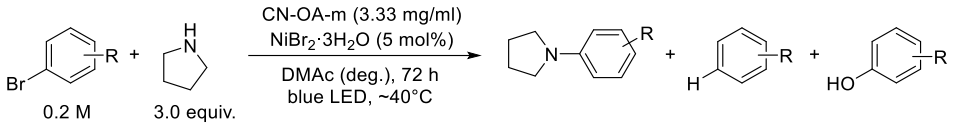


Figure S19. UV/Vis absorption spectra of CN-OA-m new (grey), CN-OA-m recovered from the cross-coupling using blue light (blue), and CN-OA-m recovered from the cross-coupling using green light (green).

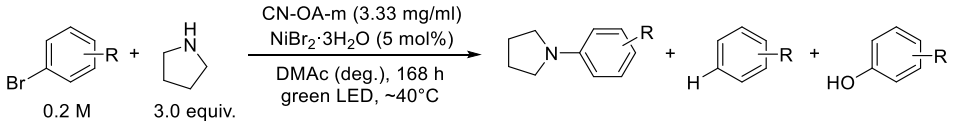
9. Studies on the reaction of bromobenzene, 3-bromotoluene, 1-bromo-4-*tert*-butylbenzene, and 4-bromoanisole with pyrrolidine.

Procedure A: Dual CN-OA-m/Ni catalysis with irradiation at 450 nm



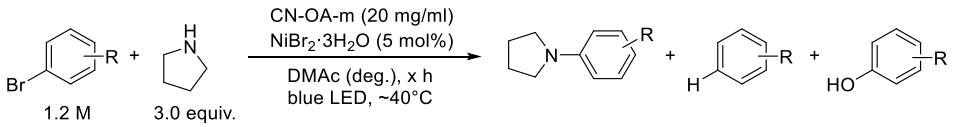
An oven dried vial (19 x 80 mm) equipped with a stir bar was charged with the CN-OA-m (20 mg), aryl bromide (1.2 mmol, 1.0 equiv.) and $NiBr_2 \cdot 3H_2O$ (16.4 mg, 60 µmol, 5.0 mol%). Subsequently, pyrrolidine (256.0 mg, 295.6 µl, 3.6 mmol, 3.0 equiv.) and DMAc (anhydrous, 6 mL) were added and the vial was sealed with a septum and Parafilm. The reaction mixture was sonicated for 5-10 min followed by stirring for 5 min until fine dispersion of the solids was achieved and the mixture was then degassed by bubbling N_2 for 10 min. The mixture was irradiated in the photoreactor (blue light function of RGB LED strip) at 40 °C with rapid stirring (1400 rpm). After 72 h, one equivalent of 1,3,5-trimethoxybenzene (1.2 mmol) was added and the mixture was stirred for 5 min. An aliquot of the reaction mixture (~300 µL) was filtered, diluted with DMSO-d_6 and subjected to ^{1}H-NMR analysis.

Procedure B: Dual CN-OA-m/Ni catalysis with irradiation at 520 nm



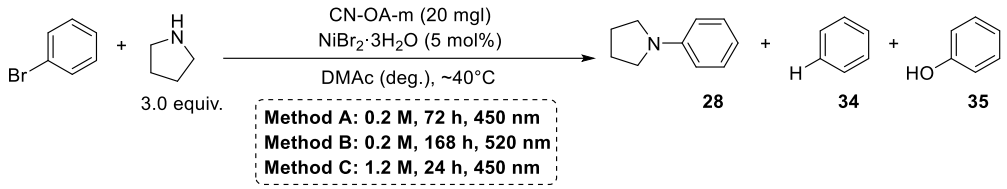
An oven dried vial (19 x 80 mm) equipped with a stir bar was charged with the CN-OA-m (20 mg), aryl bromide (1.2 mmol, 1.0 equiv.) and $NiBr_2 \cdot 3H_2O$ (16.4 mg, 60 µmol, 5.0 mol%). Subsequently, pyrrolidine (256.0 mg, 295.6 µl, 3.6 mmol, 3.0 equiv.) and DMAc (anhydrous, 6 mL) were added and the vial was sealed with a septum and Parafilm. The reaction mixture was sonicated for 5-10 min followed by stirring for 5 min until fine dispersion of the solids was achieved and the mixture was then degassed by bubbling N_2 for 10 min. The mixture was irradiated in the photoreactor (green light function of RGB LED strip) at 40 °C with rapid stirring (1400 rpm). After 168 h, one equivalent of 1,3,5-trimethoxybenzene (1.2 mmol) was added and the mixture was stirred for 5 min. An aliquot of the reaction mixture (~300 µL) was filtered, diluted with DMSO-d_6 and subjected to ^{1}H-NMR analysis.

Procedure C: Dual CN-OA-m/Ni catalysis with irradiation at 450 nm and higher concentration (1.2 M)



An oven dried vial (19 x 80 mm) equipped with a stir bar was charged with the CN-OA-m (20 mg), aryl bromide (1.2 mmol, 1.0 equiv.) and $NiBr_2 \cdot 3H_2O$ (16.4 mg, 60 µmol, 5.0 mol%). Subsequently, pyrrolidine (256.0 mg, 295.6 µl, 3.6 mmol, 3.0 equiv.) and DMAc (anhydrous, 1 mL) were added and the vial was sealed with a septum and Parafilm. The reaction mixture was sonicated for 5-10 min followed by stirring for 5 min until fine dispersion of the solids was achieved and the mixture was then degassed by bubbling N_2 for 10 min. The mixture was irradiated in the photoreactor (blue light function of RGB LED strip) at 40 °C with moderate stirring (600 rpm). After respective reaction time, one equivalent of 1,3,5-trimethoxybenzene (202.0 mg, 1.2 mmol) was added and the mixture was stirred for 5 min. An aliquot of the reaction mixture (~300 µL) was filtered, diluted with DMSO-d_6 and subjected to ^{1}H-NMR analysis.

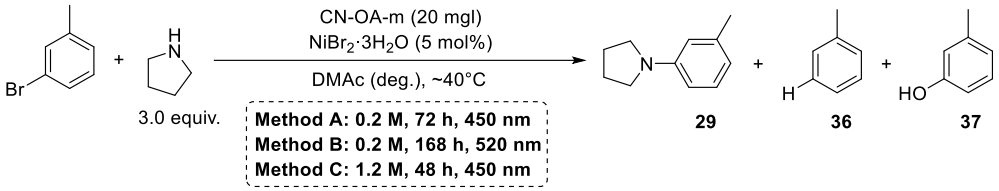
Table S22. Coupling of bromobenzene and pyrrolidine using methods A-C.



Entry	Procedure	Conversion [%][a]	28 [%][b]	34 [%][b]	35 [%][b]
1	A	quant.	74	8	11
2	A	quant.	68	11	10
3	A	quant.	67	11	12
4	A	quant.	66	10	11
5	A	67	44	7	6
6	A	56	32	5	4
7	B	quant.	94	4	3
8	B	quant.	93	4	3
9	B	quant.	91	5	5
10	B	quant.	90	4	4
11	B	quant.	88	4	5
12	B	quant.	87	4	5
13	C	quant.	86	8	4
14	C	quant.	85	7	3
15	C	99	85	8	3
16	C	quant.	85	9	3
17	C	quant.	84	8	3
18	C	quant.	84	9	3
19	C[d]	quant.	85	5	2
20	C[d]	quant.	82	5	1

[a]Conversion of bromobenzene determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [b]NMR yields determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [c]not detected. [d]Carried out using 520 nm LEDs and 168 h reaction time.

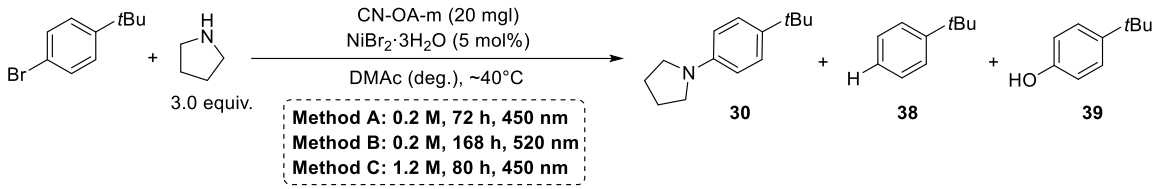
Table S23. Coupling of 3-bromotoluene and pyrrolidine using methods A-C.



Entry	Procedure	Conversion [%][a]	29 [%][b]	36 [%][b]	37 [%][b]
1	A	quant.	74	17	6
2	A	quant.	72	17	6
3	A	quant.	72	18	4
4	A	quant.	61	18	12
5	A	64	31	12	9
6	A	52	20	13	8
7	B	quant.	93	5	4
8	B	quant.	86	10	4
9	B	quant.	85	10	5
10	B	quant.	84	10	5
11	B	quant.	84	10	7
12	B	quant.	83	10	6
13	C	quant.	85	14	2
14	C	quant.	84	14	3
15	C	quant.	83	14	3
16	C	quant.	83	14	3
17	C	quant.	82	15	3
18	C	quant.	81	16	3
19	C[d]	quant.	80	6	0

[a]Conversion of 3-bromotoluene determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [b]NMR yields determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [c]not detected. [d]Carried out using 520 nm LEDs and 168 h reaction time.

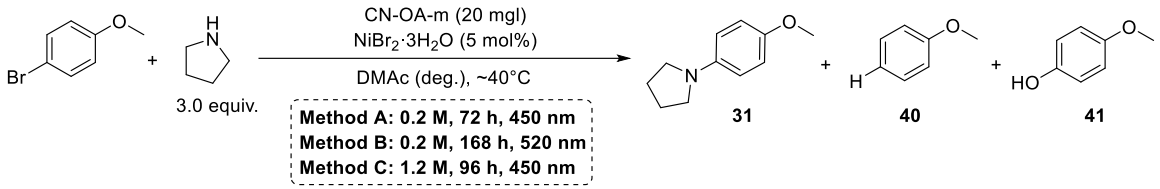
Table S24. Coupling of 4-bromotertbutylbenzene and pyrrolidine using methods A-C.



Entry	Procedure	Conversion [%][a]	30 [%][b]	38 [%][b]	39 [%][b]
1	A	98	70	13	9
2	A	99	69	17	7
3	A	quant.	67	14	8
4	A	88	57	16	9
5	A	82	53	15	9
6	A	90	52	13	7
7	B	quant.	92	5	3
8	B	96	90	4	2
9	B	94	87	3	3
10	B	91	85	3	2
11	B	57	50	4	2
12	B	30	28	1	2
13	C	quant.	82	9	2
14	C	quant.	80	9	1
15	C	quant.	80	9	2
16	C	quant.	80	9	2
17	C	quant.	80	9	3
18	C	quant.	80	10	3
19	C[d]	91	82	4	0

[a]Conversion of 4-bromotertbutylbenzene determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [b]NMR yields determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [c]not detected. [d]Carried out using 520 nm LEDs and 72 h reaction time.

Table S25. Coupling of 4-bromoansiole and pyrrolidine using methods A-C.

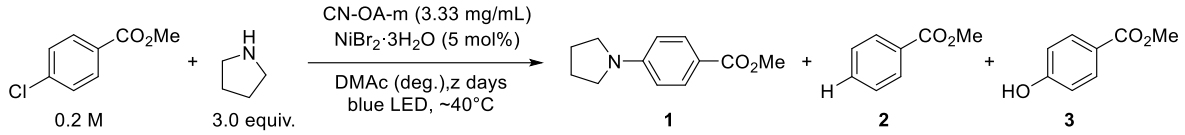


Entry	Procedure	Conversion [%][a]	31 [%][b]	40 [%][b]	41 [%][b]
1	A	86	80	6	n.d.[c]
2	A	91	78	12	2
3	A	90	72	10	5
4	A	66	53	8	2
5	A	43	32	4	2
6	A	13	4	n.d.	2
7	B	82	77	7	0
8	B	83	77	6	0
9	B	76	68	6	0
10	B	68	60	4	4
11	B	68	60	4	3
12	B	58	52	4	2
13	C	quant.	81	8	5
14	C	quant.	80	11	5
15	C	quant.	80	11	5
16	C	quant.	80	8	4
17	C	quant.	79	11	4
18	C	quant.	77	9	6
19	C[d]	quant.	84	8	1
20	C[d]	quant.	83	8	0

[a]Conversion of 4-bromoanisole determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [b]NMR yields determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [c]not detected. [d]Carried out using 520 nm LEDs and 168 h reaction time.

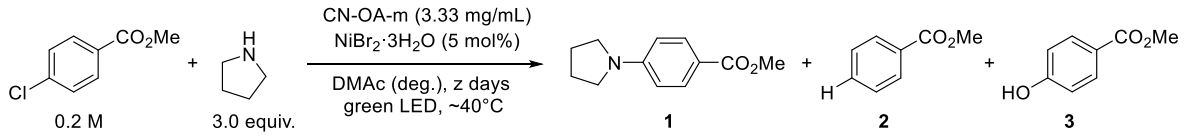
10. Studies on the reaction of methyl 4-chlorobenzoate

Procedure A: Dual CN-OA-m/Ni catalysis with irradiation at 450 nm



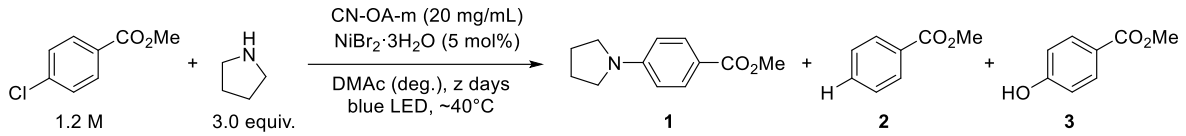
An oven dried vial (19 x 80 mm) equipped with a stir bar was charged with the CN-OA-m (20 mg), methyl 4-chloromethylbenzoate (204.7 mg, 1.2 mmol, 1.0 equiv.) and $NiBr_2 \cdot 3H_2O$ (16.4 mg, 60 µmol, 5.0 mol%). Subsequently, pyrrolidine (64.0 mg, 295.6 µl, 3.6 mmol, 3.0 equiv.) and DMAc (anhydrous, 6 mL) were added and the vial was sealed with a septum and Parafilm. The reaction mixture was sonicated for 5-10 min followed by stirring for 5 min until fine dispersion of the solids was achieved and the mixture was then degassed by bubbling N_2 for 10 min. The mixture was irradiated in the photoreactor (blue light of LED-band) at 40 °C with rapid stirring (1400 rpm). After respective reaction time, one equivalent of 1,3,5-trimethoxybenzene (202.0 mg, 1.2 mmol) was added and the mixture was stirred for 5 min. An aliquot of the reaction mixture (~300 µL) was filtered, diluted with DMSO-d_6 and subjected to ^{1}H-NMR analysis.

Procedure B: Dual CN-OA-m/Ni catalysis with irradiation at 520 nm



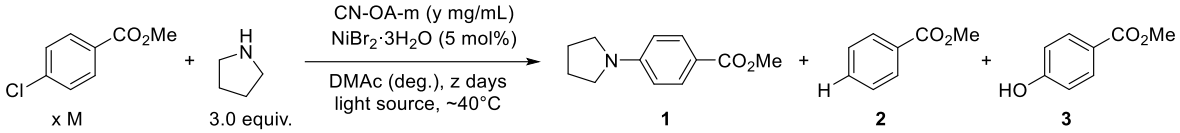
An oven dried vial (19 x 80 mm) equipped with a stir bar was charged with the CN-OA-m (20 mg), methyl 4-chloromethylbenzoate (204.7 mg, 1.2 mmol, 1.0 equiv.) and $NiBr_2 \cdot 3H_2O$ (16.4 mg, 60 µmol, 5.0 mol%). Subsequently, pyrrolidine (64.0 mg, 295.6 µl, 3.6 mmol, 3.0 equiv.) and DMAc (anhydrous, 6 mL) were added and the vial was sealed with a septum and Parafilm. The reaction mixture was sonicated for 5-10 min followed by stirring for 5 min until fine dispersion of the solids was achieved and the mixture was then degassed by bubbling N_2 for 10 min. The mixture was irradiated in the photoreactor (blue light of LED-band) at 40 °C with rapid stirring (1400 rpm). After respective reaction time, one equivalent of 1,3,5-trimethoxybenzene (202.0 mg, 1.2 mmol) was added and the mixture was stirred for 5 min. An aliquot of the reaction mixture (~300 µL) was filtered, diluted with DMSO-d_6 and subjected to ^{1}H-NMR analysis.

Procedure C: Dual CN-OA-m/Ni catalysis with irradiation at 450 nm and higher concentration (1.2 M)



An oven dried vial (19 x 80 mm) equipped with a stir bar was charged with the CN-OA-m (20 mg), methyl 4-chloromethylbenzoate (204.7 mg, 1.2 mmol, 1.0 equiv.) and $NiBr_2 \cdot 3H_2O$ (16.4 mg, 60 µmol, 5.0 mol%). Subsequently, pyrrolidine (64.0 mg, 295.6 µl, 3.6 mmol, 3.0 equiv.) and DMAc (anhydrous, 1 mL) were added and the vial was sealed with a septum and Parafilm. The reaction mixture was sonicated for 5-10 min followed by stirring for 5 min until fine dispersion of the solids was achieved and the mixture was then degassed by bubbling N_2 for 10 min. The mixture was irradiated in the photoreactor (blue light or green function of LED-band) at 40 °C with moderate stirring (600 rpm). After respective reaction time, one equivalent of 1,3,5-trimethoxybenzene (202.0 mg, 1.2 mmol) was added and the mixture was stirred for 5 min. An aliquot of the reaction mixture (~300 µL) was filtered, diluted with DMSO-d_6 and subjected to ^{1}H-NMR analysis.

Table S26. Coupling of methyl 4-chlorobenzoate and pyrrolidine using methods A-C.



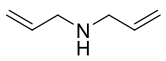
Entry	Method	Time [days]	Conversion [%][a]	1 [%][b]	2 [%][b]	3 [%][b]
1	A	3	47	37	2	n.d.[c]
2	A	7	78	65	7	3
3	A	14	91	65	16	7
4	B	3	59	41	1	12
5	B	7	76	72	4	n.d.
6	B	14	89	83	n.d.	9
7	C	1	79	75	3	1
8	C	2	97	92	3	2
9	C	3	97	89	4	2
10	C	4	99	89	3	2

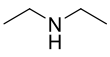
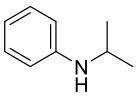
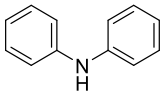
[a]Conversion of methyl 4-chlorobenzoate determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [b]NMR yields determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [c]not detected

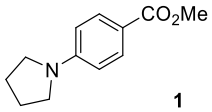
11. Scope and limitations

General experimental procedure. An oven dried vial (13 x 95 mm) equipped with a stir bar was charged with $NiBr_2 \cdot 3H_2O$ (8.2 mg, 30 µmol, 2.5 mol%), aryl bromide (1.2 mmol, 1 equiv.) and CN-OA-m (20 mg). Subsequently, the amine (3.6 mmol, 3 equiv.) and DMAc (anhydrous, 6 mL) were added and the vial was sealed with a septum and parafilm. The reaction mixture was sonicated for 5-10 min and the mixture was then degassed by bubbling N_2 for 10 min. The mixture was irradiated in the batch reactor (described above) at 40°C with rapid stirring (1400 rpm). After the respective reaction time, one equivalent of 1,3,5-trimethoxybenzene (202.0 mg, 1.2 mmol, internal standard) was added. An aliquot (~300 µL) of the reaction mixture was diluted with DMSO-d_6 and subjected to ^{1}H-NMR analysis. After full consumption of the arene starting material, the liquid phase was diluted with H_2O (40 mL) and extracted with ethyl acetate (3 x 30 mL). The combined organic phases were washed with H_2O (40 mL), $NaHCO_3$ solution (40 ml) and brine (40 mL), dried over Na_2SO_4 and concentrated. The crude product was purified by flash column chromatography (SiO_2, Hexane/EtOAc, dichloromethane/EtOAc or dichloromethane/MeOH) on a Grace™ Reveleris™ system using a 12 g cartridge to afford the desired product. The final product was characterized by ^{1}H-NMR, ^{13}C-NMR, ^{19}F-NMR and HRMS (ESI-TOF).

Unsuccessful amines



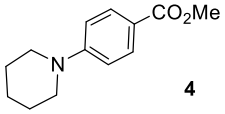


1

1-(4-methylbenzoate)pyrrolidine. From pyrrolidine (256.0 mg, 295.6 µl, 3.6 mmol, 3.0 equiv.) and 4-bromomethylbenzoate (258.0 mg, 1.2 mmol, 1.0 equiv.). Reaction time: 8 h. Purification with flash chromatography (1. gradient 0-5% ethyl acetate in hexane; 2. Isocratic 5% ethyl acetate in hexane) afforded the title compound (231.1 mg, 1.13 mmol, 94%) as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.7 Hz, 2H), 6.46 (d, *J* = 8.7 Hz, 2H), 3.83 (s, 3H), 3.40 – 3.09 (m, 4H), 2.05 – 1.86 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 167.58, 150.79, 131.32, 116.17, 110.62, 51.37, 47.47, 25.41. HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{16}NO_2$ [$(M+H)^+$]: 206.1176; found: 206.1158.

These data are in full agreement with those previously published in the literature.[18]

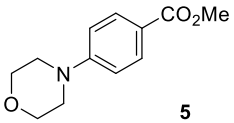


4

Methyl 4-(piperidin-1-yl)benzoate. From piperidine (306.5 mg, 356.4 µl, 3.6 mmol, 3.0 equiv.) and 4-bromomethylbenzoate (258.0 mg, 1.2 mmol, 1.0 equiv.). Reaction time: 72 h. Double amount of $NiBr_2 \cdot 3H_2O$ (16.4 mg, 60 µmol, 5.0 mol%) was used. Purification with flash chromatography (1. gradient 0-5% ethyl acetate in hexane; 2. Isocratic 5% ethyl acetate in hexane) afforded the title compound (225.8 mg, 1.03 mmol, 86%) as a white solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.87 (d, J = 9.1 Hz, 2H), 6.82 (d, J = 9.0 Hz, 2H), 3.83 (s, 3H), 3.28 (m, 4H), 1.67 – 1.56 (m, 6H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.18, 154.46, 131.19, 118.61, 113.52, 51.49, 48.73, 25.35, 24.32. HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{18}NO_2$ [$(M+H)^+$]: 220.1332 ; found: 220.1340.

These data are in full agreement with those previously published in the literature.[19]

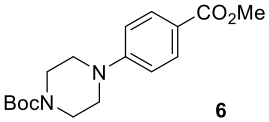


5

Methyl 4-morpholinobenzoate. From morpholine (313.6 mg, 313.6 µl, 3.6 mmol, 3.0 equiv.) and 4-bromomethylbenzoate (258.0 mg, 1.2 mmol, 1.0 equiv.). Reaction time: 16 h. Purification with flash chromatography (gradient 0-2% ethyl acetate in DCM; 2. Isocratic 2% ethyl acetate in DCM) afforded the title compound (255.5 mg, 1.15 mmol, 96%) as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, J = 9.0 Hz, 2H), 6.86 (d, J = 9.0 Hz, 2H), 3.92 – 3.72 (m, 7H), 3.26 (d, J = 5.1 Hz, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.04, 154.15, 131.21, 120.34 113.50, 66.59, 51.71, 47.72. HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{16}NO_3$ [$(M+H)^+$]: 222.1125; found: 222.1139.

These data are in full agreement with those previously published in the literature.[20]

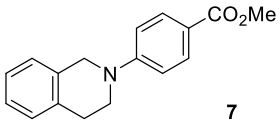


6

***tert*-Butyl 4-(4-(methoxycarbonyl)phenyl)piperazine-1-carboxylate.** From *tert*-butyl piperazine-1-carboxylate (335.3 mg, 1.8 mmol, 3.0 equiv.) and 4-bromomethylbenzoate (129.0 mg, 0.6 mmol, 1.0 equiv.) using 5 mol% $NiBr_2 \cdot 3H_2O$ (8.2 mg, 60 µmol) and pyrrolidine (4.3 mg, 4.9 µl, 0.06 mmol, 10 mol%) as additive. Reaction time: 24 h. Purification with flash chromatography (1. gradient 0-3% ethyl acetate in DCM; 2. Isocratic 3% ethyl acetate in DCM) afforded the title compound (146.2 mg, 0.45 mmol, 76%) as a white solid. The pyrrolidine-coupled side-product was formed in 10% yield, as determined by analysis of the crude mixture by ^{1}H NMR spectroscopy.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (d, J = 8.9 Hz, 2H), 6.85 (d, J = 8.9 Hz, 2H), 3.86 (s, 3H), 3.57 (m, 4H), 3.29 (m, 4H), 1.48 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.48, 155.09, 154.41, 131.69, 120.63, 114.42, 80.56, 52.15, 47.98, 43.46, 28.92, 28.78. HRMS (ESI-TOF) m/z calcd. for $C_{17}H_{25}N_2O_4$ [$(M+H)^+$]: 321.1809; found: 321.1818

These data are in full agreement with those previously published in the literature.[19]

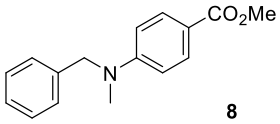


7

Methyl 4-(3,4-dihydroisoquionolin-2(1*H*)-yl)benzoate. From 1,2,3,4-tetrahydroisoquinoline (479.5 mg, 456.7 µl, 3.6 mmol, 3.0 equiv.) and 4-bromomethylbenzoate (258.0 mg, 1.2 mmol, 1.0 equiv.). Reaction time: 16 h. Purification with flash chromatography (1. gradient 0-5% ethyl acetate in hexane; 2. Isocratic 5% ethyl acetate in hexane) afforded the title compound (281.6 mg, 1.06 mmol, 88%) as a white solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 9.0 Hz, 2H), 7.23 – 7.13 (m, 4H), 6.86 (d, *J* = 9.0 Hz, 2H), 4.49 (s, 2H), 3.88 (s, 3H), 3.62 (t, *J* = 5.9 Hz, 2H), 2.97 (t, *J* = 5.8 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.29, 153.00, 135.02, 133.80, 131.36, 128.22, 126.73, 126.51, 126.37, 118.29, 112.10, 51.56, 49.01, 44.78, 29.04. HRMS (ESI-TOF) m/z calcd. for $C_{17}H_{18}NO_2$ [$(M+H)^+$]: 268.1332; found: 268.1344

These data are in full agreement with those previously published in the literature.[21]

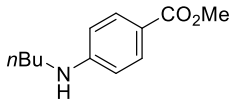


8

Methyl 4-(benzyl(methyl)amino)benzoate. From *N*-methylbenzylamine (438.6 mg, 467.1 µl, 3.6 mmol, 3.0 equiv.) and 4-bromomethylbenzoate (258.0 mg, 1.2 mmol, 1.0 equiv.). Reaction time: 72 h. Purification with flash chromatography (1.gradient 0-4% ethyl acetate in hexane; 2. Isocratic 4% ethyl acetate in hexane) afforded the title compound (245.4 mg, 0.96 mmol, 80%) as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 9.1 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.20 (d, *J* = 7.1 Hz, 2H), 6.71 (d, *J* = 9.1 Hz, 2H), 4.62 (s, 2H), 3.86 (s, 3H), 3.12 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.39, 152.75, 137.79, 131.43, 128.78, 127.20, 126.46, 117.37, 110.88, 55.92, 51.52, 38.69. HRMS (ESI-TOF) m/z calcd. for $C_{16}H_{18}NO_2$ [$(M+H)^+$]: 256.1332; found: 256.1344

These data are in full agreement with those previously published in the literature.[22]

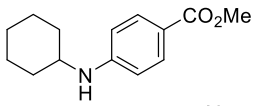


9

Methyl 4-(butylamino)benzoate. From *n*-butylamine (263.3 mg, 355.8 µl, 3.6 mmol, 3.0 equiv.) and 4-bromomethylbenzoate (258.0 mg, 1.2 mmol, 1.0 equiv.) using 5 mol% $NiBr_2 \cdot 3H_2O$ (16.4 mg, 60 µmol,). Reaction time: 72 h. Purification with flash chromatography (1. gradient 0-8% ethyl acetate in hexane; 2. Isocratic 8% ethyl acetate in hexane) afforded the title compound (223.2 mg, 1.08 mmol, 90%) as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, J = 8.6 Hz, 2H), 6.52 (d, J = 8.6 Hz, 2H), 4.21 (brs, 1H), 3.83 (s, 3H), 3.16 – 3.07 (m, 2H), 1.63 – 1.52 (m, 2H), 1.41 (h, J = 7.3, 6.9 Hz, 2H), 0.94 (td, J = 7.3, 1.0 Hz, 3H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.40, 152.24, 131.52, 117.77, 111.26, 51.46, 43.01, 31.35, 20.21, 13.84. HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{18}NO_2$ $[(M+H)^+]$: 208.1332; found: 208.1342.

These data are in full agreement with those previously published in the literature.[23]

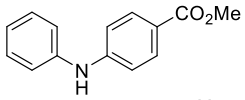


10

Methyl 4-(cyclohexylamino)benzoate. From cyclohexylamine (357.0 mg, 415.4 µl, 3.6 mmol, 3.0 equiv.) and 4-bromomethylbenzoate (258.0 mg, 1.2 mmol, 1.0 equiv.) using 5 mol% $NiBr_2 \cdot 3H_2O$ (16.4 mg, 60 µmol,). Reaction time: 72 h. Purification with flash chromatography (1. gradient 0-5% ethyl acetate in hexane; 2. Isocratic 5% ethyl acetate in hexane) afforded the title compound (203.2 mg, 0.87 mmol, 73%) as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, J = 8.8 Hz, 2H), 6.51 (d, J = 8.9 Hz, 2H), 4.01 (brs, 1H), 3.83 (s, 3H), 3.30 (m, 1H), 2.06 – 2.00 (m, 2H), 1.81 – 1.73 (m, 2H), 1.69 – 1.61 (m, 1H), 1.42 – 1.32 (m, 2H), 1.28 – 1.13 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.36, 151.10, 131.60, 117.56, 111.59, 51.47, 51.24, 33.10, 25.73, 24.87. HRMS (ESI-TOF) m/z calcd. for $C_{14}H_{20}NO_2$ $[(M+H)^+]$: 234.1489; found: 234.1500.

These data are in full agreement with those previously published in the literature.[24]

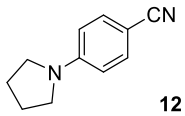


11

Methyl 4-(butylamino)benzoate. From aniline (335.5 mg, 329.2 µl, 3.6 mmol, 3.0 equiv.) and 4-bromomethylbenzoate (258.0 mg, 1.2 mmol, 1.0 equiv.) using 5 mol% $NiBr_2 \cdot 3H_2O$ (8.2 mg, 60 µmol) and pyrrolidine (4.3 mg, 4.9 µl, 0.06 mmol, 10 mol) as well as *N-tert*-butylisopropylamine (BIPA) (414.8 mg, 570.6 µl, 3.6 mmol, 3.0 equiv.) as additives Reaction time: 72 h. Purification with flash chromatography (1. gradient 0-10% ethyl acetate in hexane; 2. Isocratic 10% ethyl acetate in hexane) afforded the title compound (246.7 mg, 1.09 mmol, 90%) as a white solid. The pyrrolidine-coupled side-product was formed in 2% yield, as determined by analysis of the crude mixture by ^{1}H NMR spectroscopy.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, J = 8.1 Hz, 2H), 7.34 (m, 2H), 7.18 (d, J = 7.7 Hz, 2H), 7.07 (t, J = 7.4 Hz, 1H), 6.99 (d, J = 8.6 Hz, 2H), 6.19 (brs, 1H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.08, 148.16, 140.88, 131.50, 129.51, 123.07, 120.94, 120.42, 114.56, 51.77. HRMS (ESI-TOF) m/z calcd. for $C_{14}H_{14}NO_2$ $[(M+H)^+]$: 228.1019; found: 228.1033.

These data are in full agreement with those previously published in the literature.[25]

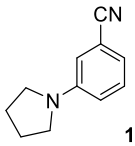


12

1-(4-benzonitrile)pyrrolidine. From pyrrolidine (256.0 mg, 295.6 µl, 3.6 mmol, 3.0 equiv.) and 4-bromobenzonitrile (218.4 mg, 1.2 mmol, 1.0 equiv.). Reaction time: 24 h. Purification with flash chromatography (1. gradient 0-5% ethyl acetate in hexane; 2. Isocratic 5% ethyl acetate in hexane) afforded the title compound (189.6mg, 1.11 mmol, 92%) as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 8.8 Hz, 2H), 6.48 (d, *J* = 8.9 Hz, 2H), 3.32 – 3.28 (m, 4H), 2.09 – 1.94 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ= 150.00, 133.43, 121.11, 111.47, 96.38, 47.51, 25.44. HRMS (ESI-TOF) m/z calcd. for $C_{11}H_{13}N_2$ $[(M+H)^+]$: 173.1074; found: 173.1081.

These data are in full agreement with those previously published in the literature.[26]

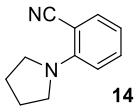


13

1-(3-benzonitrile)pyrrolidine. From pyrrolidine (256.0 mg, 295.6 µl, 3.6 mmol, 3.0 equiv.) and 3-bromobenzonitrile (218.4 mg, 1.2 mmol, 1.0 equiv.). Reaction time: 24 h. No internal standard (1,3,5-trimethoxybenzene was used) due to poor separation from the product during flash chromatography. Purification with flash chromatography (1. gradient 0-5% ethyl acetate in hexane; 2. Isocratic 5% ethyl acetate in hexane) afforded the title compound (180.4 mg, 1.05 mmol, 87%) as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.23 (m, 1H), 6.90 (m, 1H), 6.77 – 6.69 (m, 2H), 3.34 – 3.23 (m, 4H), 2.13 – 1.99 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.62, 129.73, 119.95, 118.50, 115.78, 114.24, 112.63, 47.55, 25.46.HRMS (ESI-TOF) m/z calcd. for $C_{11}H_{13}N_2$ [$(M+H)^+$]: 173.1074; found: 173.1080

These data are in full agreement with those previously published in the literature.[27]

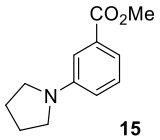


14

1-(2-benzonitrile)pyrrolidine. From pyrrolidine (256.0 mg, 295.6 µl, 3.6 mmol, 3.0 equiv.) and 2-bromobenzonitrile (218.4 mg, 1.2 mmol, 1.0 equiv.) using 5 mol% $NiBr_2 \cdot 3H_2O$ (8.2 mg, 60 µmol). Reaction time: 72 h. No internal standard (1,3,5-trimethoxybenzene was used) due to poor separation from the product during flash chromatography. Purification with flash chromatography (eluents: 1. gradient 0-5% ethyl acetate in hexane; 2. Isocratic 5% ethyl acetate in hexane) afforded the title compound (190.5 mg, 1.11 mmol, 92%) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (m, 1H), 7.31 (m, 1H), 6.67 – 6.59 (m, 2H), 3.63 – 3.53 (m, 4H), 2.03 – 1.94 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.04, 135.72, 133.40, 121.51, 115.86, 114.24, 94.27, 49.81, 25.76. HRMS (ESI-TOF) m/z calcd. for $C_{11}H_{13}N_2$ [$(M+H)^+$]: 173.1074; found: 173.1081

These data are in full agreement with those previously published in the literature.[1]

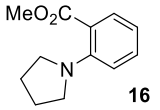


15

1-(3-methylbenzoate)pyrrolidine. From pyrrolidine (256.0 mg, 295.6 µl, 3.6 mmol, 3.0 equiv.) and 3-bromomethylbenzoate (258.0 mg, 1.2 mmol, 1.0 equiv.). Reaction time: 24 h. No internal standard (1,3,5-trimethoxybenzene was used) due to poor separation from the product during flash chromatography. Purification with flash chromatography (1. gradient 0-5% ethyl acetate in hexane; 2. Isocratic 5% ethyl acetate in hexane) afforded the title compound (218.4 mg, 1.06 mmol, 89%) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 7.6 Hz, 1H), 7.25 (t, *J* = 7.8 Hz, 1H), 7.22 – 7.91 (s, 1H), 6.71 (m, 1H), 3.89 (s, 3H), 3.29 (t, J = 6.6 Hz, 4H), 2.00 (t, J = 6.6 Hz, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.89, 147.78, 130.73, 129.02, 116.39, 115.93, 112.38, 52.00, 47.70, 25.48. HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{16}NO_2$ [$(M+H)^+$]: 206.17556; found: 206.1185.

These data are in full agreement with those previously published in the literature.[20]

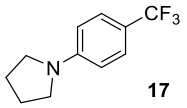


16

1-(2-methylbenzoate)pyrrolidine. From pyrrolidine (256.0 mg, 295.6 µl, 3.6 mmol, 3.0 equiv.) and 2-bromomethylbenzoate (258.0 mg, 1.2 mmol, 1.0 equiv.) using 5 mol% $NiBr_2 \cdot 3H_2O$ (8.2 mg, 60 µmol). Reaction time: 72 h. No internal standard (1,3,5-trimethoxybenzene was used) due to poor separation from the product during flash chromatography. Purification with flash chromatography (1. gradient 0-5% ethyl acetate in hexane; 2. Isocratic 5% ethyl acetate in hexane) afforded the title compound (87.2 mg, 0.42 mmol, 35%) as a colourless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (m, 1H), 7.31 (t, *J* = 8.7 Hz, 1H), 6.79 (m, 1H), 6.71 (t, *J* = 7.4 Hz, 1H), 3.88 (s, 3H), 3.28 – 3.19 (m, 4H), 1.99 – 1.88 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.57, 147.93, 131.79, 131.08, 117.09, 115.63, 113.95, 52.00, 50.87, 25.88. HRMS (ESI-TOF) m/z calcd. for $C_{12}H_{16}NO_2$ [$(M+H)^+$]: 206.17556; found: 206.1185.

These data are in full agreement with those previously published in the literature.[28]

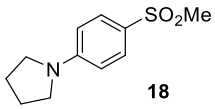


17

1-(4-(trifluoromethyl)phenyl)pyrrolidine. From pyrrolidine (256.0 mg, 295.6 µl, 3.6 mmol, 3.0 equiv.) and 4-bromobenzotrifluoride (270.0 mg, 168.0 µl, 1.2 mmol, 1.0 equiv.). Reaction time: 8 h. Purification with flash chromatography (1. gradient 0-3% ethyl acetate in hexane; 2. Isocratic 3% ethyl acetate in hexane) afforded the title compound (238.2 mg, 1.11 mmol, 92%) as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 8.7 Hz, 2H), 6.58 (d, *J* = 8.7 Hz, 2H), 3.37 – 3.27 (m, 4H), 2.10 – 2.00 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.76, 126.38 (q, *J* = 3.7 Hz), 125.42 (q, *J* = 269.9 Hz), 116.56 (q, *J* = 32.5 Hz), 110.84, 47.53, 25.48. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -60.58(s, 3F). HRMS (ESI-TOF) m/z calcd. for $C_{11}H_{13}F_3N$ [$(M+H)^+$]: 216.0922 ; found: 216.1008.

These data are in full agreement with those previously published in the literature.[29]

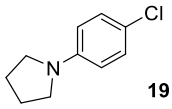


18

1-(4-(methylsulfonyl)phenyl)pyrrolidine. From pyrrolidine (256.0 mg, 295.6 µl, 3.6 mmol, 3.0 equiv.) and 4-bromopheyl methylsulfone (282.1 mg, 1.2 mmol, 1.0 equiv.). Reaction time: 24 h. Purification with flash chromatography (1. gradient 0-2% ethyl acetate in DCM; 2. Isocratic 2% ethyl acetate in DCM) afforded the title compound (251.0 mg, 1.11 mmol, 93%) as a white solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.9 Hz, 2H), 6.51 (d, *J* = 9.0 Hz, 2H), 3.30 – 3.24 (m, 4H), 2.94 (s, 3H), 2.05 – 1.93 (m, 4H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 150.89, 129.02, 125.04, 110.98, 47.61, 45.13, 25.39. HRMS (ESI-TOF) m/z calcd. for $C_{11}H_{16}NO_2S$ [$(M+H)^+$]: 226.0897; found: 226.0907.

These data are in full agreement with those previously published in the literature.[30]

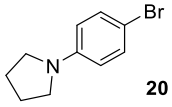


19

1-(4-chlorophenyl)pyrrolidine. From pyrrolidine (256.0 mg, 295.6 µl, 3.6 mmol, 3.0 equiv.) and 4-bromochlorobenzene (229.7 mg, 1.2 mmol, 1.0 equiv.). Reaction time: 24 h. Purification with flash chromatography (1. gradient 0-2% ethyl acetate in hexane; 2. Isocratic 2% ethyl acetate in hexane) afforded the title compound (196.8 mg, 1.08 mmol, 90%) as a white solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.17 (d, *J* = 8.9 Hz, 2H), 6.48 (d, *J* = 8.9 Hz, 2H), 3.28 – 3.18 (m, 4H), 2.06 – 1.97 (m, 4H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 146.49, 128.81, 120.04, 112.61, 47.73, 25.48. HRMS (ESI-TOF) m/z calcd. for $C_{10}H_{13}ClN$ [$(M+H)^+$]: 182.0731; found: 182.0738.

These data are in full agreement with those previously published in the literature.[18]

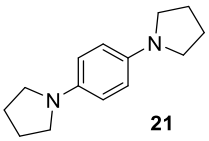


20

1-(4-bromophenyl)pyrrolidine. From pyrrolidine (256.0 mg, 295.6 µl, 3.6 mmol, 3.0 equiv.) and 1,4-dibromobenzene (283.1 mg, 1.2 mmol, 1.0 equiv.). Reaction time: 24 h. Purification with flash chromatography (1. gradient 0-2% ethyl acetate in hexane; 2. Isocratic 2% ethyl acetate in hexane) afforded the title compound (218.4 mg, 0.97 mmol, 80%) as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 8.9 Hz, 2H), 6.42 (d, *J* = 8.9 Hz, 2H), 3.29 – 3.16 (m, 4H), 2.05 – 1.96 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.82, 131.68, 113.19, 107.08, 47.68, 25.50. HRMS (ESI-TOF) m/z calcd. for $C_{10}H_{13}BrN$ [$(M+H)^+$]: 226.0226; found: 226.0231.

These data are in full agreement with those previously published in the literature.[31]

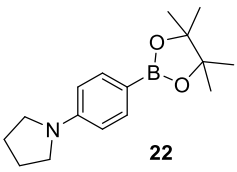


21

1-di(4-pyrrolidin-1yl)benzene. From pyrrolidine (853.3 mg, 985.3 µl, 12.0 mmol, 10 equiv.) and 1,4-dibromobenzene (283.1 mg, 1.2 mmol, 1.0 equiv.). Reaction time: 144 h. Purification with flash chromatography (1. gradient 0-5% ethyl acetate in hexane; 2. Isocratic 5% ethyl acetate in hexane) afforded the title compound (157.3 mg, 0.73 mmol, 61%) as a white solid. For analysis via NMR spectroscopy, the final product was treated with deuterated trifluoro acetic acid in D_2O.

^{1}H NMR (400 MHz, deuterium oxide) δ 7.17 (s, 4H), 3.20 (m, 8H), 1.68 (m, 8H). ^{13}C NMR (101 MHz, deuterium oxide) δ 143.24, 126.02, 61.01, 25.62. HRMS (ESI-TOF) m/z calcd. for $C_{14}H_{21}N_2$ [$(M+H)^+$]: 217.1700; found: 217.1709

These data are in full agreement with those previously published in the literature.[32]

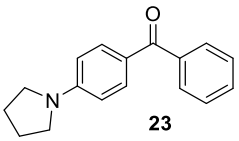


22

1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)phenyl)pyrrolidine. From pyrrolidine (256.0 mg, 295.6 µl, 3.6 mmol, 3.0 equiv.) and 4-bromomethyl-phenylboronic acid pinacol ester (339.6 mg, 1.2 mmol, 1.0 equiv.). Reaction time: 48 h. No internal standard (1,3,5-trimethoxybenzene was used) due to poor separation from the product during flash chromatography. Purification with flash chromatography (1. gradient 0-10% ethyl acetate in hexane; 2. Isocratic 2% ethyl acetate in hexane) afforded the title compound (284.3 mg, 1.04 mmol, 87%) as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8.6 Hz, 2H), 6.55 (d, *J* = 8.6 Hz, 2H), 3.39 – 3.17 (m, 4H), 2.13 – 1.92 (m, 4H), 1.35 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.00, 136.24, 113.94, 110.93, 83.06, 47.40, 25.46, 24.88. HRMS (ESI-TOF) m/z calcd. for $C_{16}H_{25}BNO_2$ [$(M+H)^+$]: 274.1973; found: 274.1987.

These data are in full agreement with those previously published in the literature.[33]

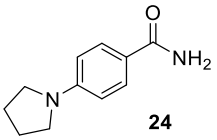


23

phenyl(4-(pyrrolidin-1-yl)phenyl)methanone. From pyrrolidine (256.0 mg, 295.6 µl, 3.6 mmol, 3.0 equiv.) and 4-bromobenzophenone (313.3 mg, 1.2 mmol, 1.0 equiv.). Reaction time: 48 h. Purification with flash chromatography (1. gradient 0-5% ethyl acetate in hexane; 2. Isocratic 5% ethyl acetate in hexane) afforded the title compound (281.9 mg, 1.12 mmol, 93%) as a white solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.9 Hz, 2H), 7.72 – 7.66 (m, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.45 – 7.37 (m, 2H), 6.51 (d, *J* = 8.9 Hz, 2H), 3.38 – 3.27 (m, 4H), 2.02 – 1.95 (m, 4H).^{13}C NMR (151 MHz, Chloroform-*d*) δ 195.01, 150.88, 139.51, 132.90, 130.95, 129.37, 127.97, 124.20, 110.63, 47.58, 25.42. HRMS (ESI-TOF) m/z calcd. for $C_{17}H_{17}NO$ [$(M+H)^+$]: 252.1383; found: 252.1394.

These data are in full agreement with those previously published in the literature.[34]

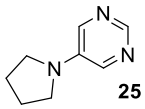


24

1-(4-benzamide)pyrrolidine. From pyrrolidine (256.0 mg, 295.6 µl, 3.6 mmol, 3.0 equiv.) and 4-bromobenzamide (240.0 mg, 1.2 mmol, 1.0 equiv.). Reaction time: 72 h. Purification with flash chromatography (1. gradient 0-5% methanol in DCM; 2. Isocratic 5% methanol in DCM) afforded the title compound (175.0 mg, 0.92 mmol, 77%) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.69 (d, J = 8.8 Hz, 2H), 7.58 – 7.52 (brs, 1H), 6.86 – 6.80 (brs, 1H), 6.47 (d, J = 8.8 Hz, 2H), 3.23 (s, 4H), 1.92 (s, 4H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.05, 149.49, 129.08, 120.24, 110.47, 47.22, 25.01. HRMS (ESI-TOF) m/z calcd. for $C_{11}H_{15}N_2O$ [$(M+H)^+$]: 191.1179; found: 191.1188.

These data are in full agreement with those previously published in the literature.[35]

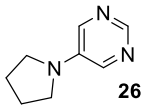


25

5-(4-pyrrolidin-1yl)pyrimidine. From pyrrolidine (256.0 mg, 295.6 µl, 3.6 mmol, 3.0 equiv.) and 5-bromopyrimidine (190.8 mg, 1.2 mmol, 1.0 equiv.) using 5 mol% $NiBr_2 \cdot 3H_2O$ (16.4 mg, 60 µmol). Reaction time: 72 h. Purification with flash chromatography (1. gradient 0-50% ethyl acetate in hexane with 1% Et_3N; 2. Isocratic 50% ethyl acetate in hexane with 1% Et_3N) afforded the title compound (141.3 mg, 0.95 mmol, 79%) as a colorless solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.47 (s, 1H), 7.97 (s, 2H), 3.32 – 3.16 (m, 4H), 2.06 – 1.90 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.60, 141.09, 139.35, 46.84, 25.27. HRMS (ESI-TOF) m/z calcd. for $C_8H_{12}N_3$ [$(M+H)^+$]: 150.1026 ; found: 150.1033.

These data are in full agreement with those previously published in the literature.[36]

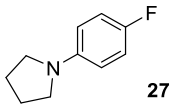


26

3-(pyrrolidin-1yl)pyridine. From pyrrolidine (256.0 mg, 295.6 µl, 3.6 mmol, 3.0 equiv.) and 3-bromopyridine (189.6 mg, 115.6 µl, 1.2 mmol, 1.0 equiv.) using 5 mol% $NiBr_2 \cdot 3H_2O$ (16.4 mg, 60 µmol). Reaction time: 72 h. Purification with flash chromatography (1. gradient 0-40% ethyl acetate in hexane with 1% Et_3N; 2. Isocratic 40% ethyl acetate in hexane with 1% Et_3N) afforded the title compound (135.2 mg, 0.91 mmol, 76%) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 – 7.81 (m, 2H), 7.03 (m, 1H), 6.72 (m, 1H), 3.21 (m, 4H), 2.00 – 1.87 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.68, 136.74, 134.23, 123.49, 117.60, 47.19, 25.32. HRMS (ESI-TOF) m/z calcd. for $C_9H_{13}N_2$ [$(M+H)^+$]: 149.1074 ; found: 149.1081

These data are in full agreement with those previously published in the literature.[37]

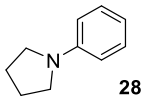


27

1-(4-fluorophenyl)pyrrolidine. From pyrrolidine (256.0 mg, 295.6 µl, 3.6 mmol, 3.0 equiv.) and 4-bromofluorobenzene (210.0 mg, 131.8 µl, 1.2 mmol, 1.0 equiv.) using 5 mol% $NiBr_2 \cdot 3H_2O$ (16.4 mg, 60 µmol). Reaction time: 72 h. Purification with flash chromatography (1. gradient 0-3% ethyl acetate in hexane; 2. Isocratic 3% ethyl acetate in hexane) afforded the title compound (128.8 mg, 0.78 mmol, 65 %) as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.99 – 6.89 (m, 2H), 6.52 – 6.44 (m, 2H), 3.30 – 3.19 (m, 4H), 2.05 – 1.96 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.81 (d, *J* = 233.3 Hz), 144.78, 115.48 (d, *J* = 22.0 Hz), 112.05 (d, *J* = 7.1 Hz), 48.10, 25.50. ^{19}F NMR (564 MHz, Chloroform-*d*) δ -131.00 (s, 1F). HRMS (ESI-TOF) m/z calcd. for $C_{10}H_{13}FN$ $[(M+H)^+]$: 166.1027 ; found: 166.1033.

These data are in full agreement with those previously published in the literature.[31]

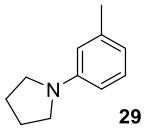


28

1-phenylpyrrolidine. From pyrrolidine (256.0 mg, 295.6 µl, 3.6 mmol, 3.0 equiv.) and bromobenzene (188.4 mg, 125.6 µl, 1.2 mmol, 1.0 equiv.). using 5 mol% $NiBr_2 \cdot 3H_2O$ (16.4 mg, 60 µmol). Reaction time: 72 h. Purification with flash chromatography (1. gradient 0-2% ethyl acetate in hexane; 2. Isocratic 2% ethyl acetate in hexane) afforded the title compound (136.9 mg, 0.93 mmol, 77%) as a colourless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 (m, 2H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 2H), 3.43 – 3.30 (m, 4H), 2.13 – 2.05 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.04, 129.25, 115.49, 111.77, 47.71, 25.61. HRMS (ESI-TOF) m/z calcd. for $C_{10}H_{14}N$ $[(M+H)^+]$: 148.1121; found: 148.1122.

These data are in full agreement with those previously published in the literature.[18]

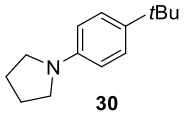


29

1-(m-tolyl)pyrrolidine. From pyrrolidine (256.0 mg, 295.6 µl, 3.6 mmol, 3.0 equiv.) and 3-bromotoluene (188.4 mg, 145.6 µl, 1.2 mmol, 1.0 equiv.) using 5 mol% $NiBr_2 \cdot 3H_2O$ (16.4 mg, 60 µmol). Reaction time: 72 h. Purification with flash chromatography (1. gradient 0-2% ethyl acetate in hexane; 2. Isocratic 2% ethyl acetate in hexane) afforded the title compound (134.0 mg, 0.93 mmol, 69%) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24-7.16 (t, *J* = 8.8 Hz, 1H), 6.58 (d, *J* = 7.4 Hz, 1H), 6.51 – 6.44 (m, 2H), 3.35 (m, 4H), 2.41 (s, 3H), 2.11 – 2.00 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.13, 138.86, 129.09, 116.44, 112.45, 108.99, 47.68, 25.56, 21.98. HRMS (ESI-TOF) m/z calcd. for $C_{11}H_{16}N$ [$(M+H)^+$]: 162.1278; found: 162.1282.

These data are in full agreement with those previously published in the literature.[29]

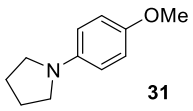


30

1-(4-(tert-butyl)phenyl)pyrrolidine. From pyrrolidine (256.0 mg, 295.6 µl, 3.6 mmol, 3.0 equiv.) and 4-bromotertbutylbenzene (255.7 mg, 208.8 µl, 1.2 mmol, 1.0 equiv.) using 5 mol% $NiBr_2 \cdot 3H_2O$ (16.4 mg, 60 µmol). Reaction time: 72 h. Purification with flash chromatography (1. gradient 0-3% ethyl acetate in hexane; 2. Isocratic 3% ethyl acetate in hexane) afforded the title compound (203.2 mg, 1.00 mmol, 83%) as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 (d, J = 7.0 Hz, 2H), 6.64 (d, J = 7.0 Hz, 2H), 3.42 – 3.30 (m, 4H), 2.11 – 2.02 (m, 4H), 1.40 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.94, 138.03, 125.99, 111.43, 47.79, 33.82, 31.70, 25.56. HRMS (ESI-TOF) m/z calcd. for $C_{14}H_{22}N$ [$(M+H)^+$]: 204.1747; found: 204.1759.

These data are in full agreement with those previously published in the literature.[18]



31

1-(4-methoxyphenyl)pyrrolidine. From pyrrolidine (256.0 mg, 295.6 µl, 3.6 mmol, 3.0 equiv.) and 4-bromoanisole (224.4 mg, 150.2 µl, 1.2 mmol, 1.0 equiv.) using 5 mol% $NiBr_2 \cdot 3H_2O$ (16.4 mg, 60 µmol). Reaction time: 72 h. No internal standard (1,3,5-trimethoxybenzene was used) due to poor separation from the product during flash chromatography. Purification with flash chromatography (1. gradient 0-5% ethyl acetate in hexane; 2. Isocratic 5% ethyl acetate in hexane) afforded the title compound (154.7 mg, 0.87 mmol, 73%) as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.88 (d, J = 8.1 Hz, 2H), 6.57 (d, J = 8.1 Hz, 2H), 3.78 (s, 3H), 3.32 – 3.18 (m, 4H), 2.07 – 1.94 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.75, 143.25, 115.01, 112.59, 56.01, 48.24, 25.41.HRMS (ESI-TOF) m/z calcd. for $C_{11}H_{16}NO$ $[(M+H)^+]$: 178.1227; found: 178.1236

These data are in full agreement with those previously published in the literature.[18]

12. References

1 Yu, P. & Morandi, B. Nickel-Catalyzed Cyanation of Aryl Chlorides and Triflates Using Butyronitrile: Merging Retro-hydrocyanation with Cross-Coupling. *Angew. Chem. Int. Ed.* **56**, 15693-15697 (2017).

2 Wang, J., Zhao, J. & Gong, H. Nickel-catalyzed methylation of aryl halides/tosylates with methyl tosylate. *Chem. Commun.* **53**, 10180-10183 (2017).

3 Mori, A., Mizusaki, T., Ikawa, T., Maegawa, T., Monguchi, Y. & Sajiki, H. Mechanistic Study of a Pd/C-Catalyzed Reduction of Aryl Sulfonates Using the Mg–MeOH–NH4OAc System. *Chem. Eur. J.* **13**, 1432-1441 (2007).

4 Brown, H. C., Kanth, J. V. B., Dalvi, P. V. & Zaidlewicz, M. Molecular Addition Compounds. 15. Synthesis, Hydroboration, and Reduction Studies of New, Highly Reactive tert-Butyldialkylamine−Borane Adducts. *J. Org. Chem.* **64**, 6263-6274 (1999).

5 Kawamata, Y., Vantourout, J. C., Hickey, D. P., Bai, P., Chen, L., Hou, Q., Qiao, W., Barman, K., Edwards, M. A., Garrido-Castro, A. F., deGruyter, J. N., Nakamura, H., Knouse, K., Qin, C., Clay, K. J., Bao, D., Li, C., Starr, J. T., Garcia-Irizarry, C., Sach, N., White, H. S., Neurock, M., Minteer, S. D. & Baran, P. S. Electrochemically Driven, Ni-Catalyzed Aryl Amination: Scope, Mechanism, and Applications. *J. Am. Chem. Soc.* **141**, 6392-6402 (2019).

6 Lim, C.-H., Kudisch, M., Liu, B. & Miyake, G. M. C–N Cross-Coupling via Photoexcitation of Nickel–Amine Complexes. *J. Am. Chem. Soc.* **140**, 7667-7673 (2018).

7 Corcoran, E. B., Pirnot, M. T., Lin, S., Dreher, S. D., DiRocco, D. A., Davies, I. W., Buchwald, S. L. & MacMillan, D. W. C. Aryl amination using ligand-free Ni(II) salts and photoredox catalysis. *Science* **353**, 279-283 (2016).

8 Du, Y., Pearson, R. M., Lim, C.-H., Sartor, S. M., Ryan, M. D., Yang, H., Damrauer, N. H. & Miyake, G. M. Strongly Reducing, Visible-Light Organic Photoredox Catalysts as Sustainable Alternatives to Precious Metals. *Chem. Eur. J.* **23**, 10962-10968 (2017).

9 Liu, Y.-Y., Liang, D., Lu, L.-Q. & Xiao, W.-J. Practical heterogeneous photoredox/nickel dual catalysis for C–N and C–O coupling reactions. *Chem. Commun.* **55**, 4853-4856 (2019).

10 Ghosh, I., Khamrai, J., Savateev, A., Shlapakov, N., Antonietti, M. & König, B. Organic semiconductor photocatalyst can bifunctionalize arenes and heteroarenes. *Science* **365**, 360-366 (2019).

11 Zhang, G., Li, G., Lan, Z.-A., Lin, L., Savateev, A., Heil, T., Zafeiratos, S., Wang, X. & Antonietti, M. Optimizing Optical Absorption, Exciton Dissociation, and Charge Transfer of a Polymeric Carbon Nitride with Ultrahigh Solar Hydrogen Production Activity. *Angew. Chem. Int. Ed.* **56**, 13445-13449 (2017).

12 (https://www.sigmaaldrich.com (Germany; 2019 October 16).).

13 https://www.bauhaus.info/led-baender/tween-light-led-band/p/22517610?gclid=EAIaIQobChMIoLWto9zl3wIVTZSyCh3YDweqEAQYASABEgJmRfD_BwE&s_kwcid=AL!5677!3!190027496787!!!g!462716337331!&pla_prpaid=462716337331&ef_id=EAIaIQobChMIoLWto9zl3wIVTZSyCh3YDweqEAQYASABEgJmRfD_BwE:G:s&pla_adgrid=41635814775&pla_campid=225980581&pla_prch=online&pla_prid=22517610&cid=PSEGoo225980581_41635814775&pla_adt=pla (Germany; 2019 October 16).

14 Goettmann, F., Fischer, A., Antonietti, M. & Thomas, A. Chemical Synthesis of Mesoporous Carbon Nitrides Using Hard Templates and Their Use as a Metal-Free Catalyst for Friedel–Crafts Reaction of Benzene. *Angew. Chem. Int. Ed.* **45**, 4467-4471 (2006).

15 Shalom, M., Guttentag, M., Fettkenhauer, C., Inal, S., Neher, D., Llobet, A. & Antonietti, M. In Situ Formation of Heterojunctions in Modified Graphitic Carbon Nitride: Synthesis and Noble Metal Free Photocatalysis. *Chem. Mater.* **26**, 5812-5818 (2014).

16 Zhang, J., Sun, J., Maeda, K., Domen, K., Liu, P., Antonietti, M., Fu, X. & Wang, X. Sulfur-mediated synthesis of carbon nitride: Band-gap engineering and improved functions for photocatalysis. *Energy Environ. Sci.* **4**, 675-678 (2011).

17 Savateev, A., Pronkin, S., Epping, J. D., Willinger, M. G., Wolff, C., Neher, D., Antonietti, M. & Dontsova, D. Potassium Poly(heptazine imides) from Aminotetrazoles: Shifting Band Gaps of Carbon Nitride-like Materials for More Efficient Solar Hydrogen and Oxygen Evolution. *ChemCatChem* **9**, 167-174 (2017).

18 Hamid, M. H. S. A., Allen, C. L., Lamb, G. W., Maxwell, A. C., Maytum, H. C., Watson, A. J. A. & Williams, J. M. J. Ruthenium-Catalyzed N-Alkylation of Amines

and Sulfonamides Using Borrowing Hydrogen Methodology. *J. Am. Chem. Soc.* **131**, 1766-1774 (2009).

19 Sandtorv, A. H. & Stuart, D. R. Metal-free Synthesis of Aryl Amines: Beyond Nucleophilic Aromatic Substitution. *Angew. Chem. Int. Ed.* **55**, 15812-15815 (2016).

20 Urgaonkar, S., Xu, J.-H. & Verkade, J. G. Application of a New Bicyclic Triaminophosphine Ligand in Pd-Catalyzed Buchwald−Hartwig Amination Reactions of Aryl Chlorides, Bromides, and Iodides. *J. Org. Chem.* **68**, 8416-8423 (2003).

21 Lin, S.-X., Sun, G.-J. & Kang, Q. A visible-light-activated rhodium complex in enantioselective conjugate addition of α-amino radicals with Michael acceptors. *Chem. Commun.* **53**, 7665-7668 (2017).

22 Wolfe, J. P. & Buchwald, S. L. Scope and Limitations of the Pd/BINAP-Catalyzed Amination of Aryl Bromides. *J. Org. Chem.* **65**, 1144-1157 (2000).

23 Xie, X., Zhang, T. Y. & Zhang, Z. Synthesis of Bulky and Electron-Rich MOP-type Ligands and Their Applications in Palladium-Catalyzed C−N Bond Formation. *J. Org. Chem.* **71**, 6522-6529 (2006).

24 Liu, K.-J., Zeng, X.-L., Zhang, Y., Wang, Y., Xiao, X.-S., Yue, H., Wang, M., Tang, Z. & He, W.-M. Palladium-Catalyzed Reductive Coupling of Nitroarenes with Phenols-leading to N-Cyclohexylanilines. *Synthesis* **50**, 4637-4644 (2018).

25 Suárez-Pantiga, S., Hernández-Ruiz, R., Virumbrales, C., Pedrosa, M. R. & Sanz, R. Reductive Molybdenum-Catalyzed Direct Amination of Boronic Acids with Nitro Compounds. *Angew. Chem. Int. Ed.* **58**, 2129-2133 (2019).

26 Desmarets, C., Schneider, R. & Fort, Y. Nickel(0)/Dihydroimidazol-2-ylidene Complex Catalyzed Coupling of Aryl Chlorides and Amines. *J. Org. Chem.* **67**, 3029-3036 (2002).

27 Wolfe, J. P., Tomori, H., Sadighi, J. P., Yin, J. & Buchwald, S. L. Simple, Efficient Catalyst System for the Palladium-Catalyzed Amination of Aryl Chlorides, Bromides, and Triflates. *J. Org. Chem.* **65**, 1158-1174 (2000).

28 Yoshida, H., Morishita, T. & Ohshita, J. Direct Access to Anthranilic Acid Derivatives via CO2 Incorporation Reaction Using Arynes. *Org. Lett.* **10**, 3845-3847 (2008).

29 Brenner, E., Schneider, R. & Fort, Y. Nickel-catalysed couplings of aryl chlorides with secondary amines and piperazines. *Tetrahedron* **55**, 12829-12842 (1999).

30 Johnson, T. C., Elbert, Bryony L., Farley, A. J. M., Gorman, T. W., Genicot, C., Lallemand, B., Pasau, P., Flasz, J., Castro, J. L., MacCoss, M., Dixon, D. J., Paton, R. S., Schofield, C. J., Smith, M. D. & Willis, M. C. Direct sulfonylation of anilines mediated by visible light. *Chem. Sci.* **9**, 629-633 (2018).

31 Hollmann, D., Bähn, S., Tillack, A., Parton, R., Altink, R. & Beller, M. A novel salt-free ruthenium-catalyzed alkylation of aryl amines. *Tetrahedron Lett.* **49**, 5742-5745 (2008).

32 Ju, Y. & Varma, R. S. An Efficient and Simple Aqueous N-Heterocyclization of Aniline Derivatives: Microwave-Assisted Synthesis of N-Aryl Azacycloalkanes. *Org. Lett.* **7**, 2409-2411 (2005).

33 Lim, S., Song, D., Jeon, S., Kim, Y., Kim, H., Lee, S., Cho, H., Lee, B. C., Kim, S. E., Kim, K. & Lee, E. Cobalt-Catalyzed C–F Bond Borylation of Aryl Fluorides. *Org. Lett.* **20**, 7249-7252 (2018).

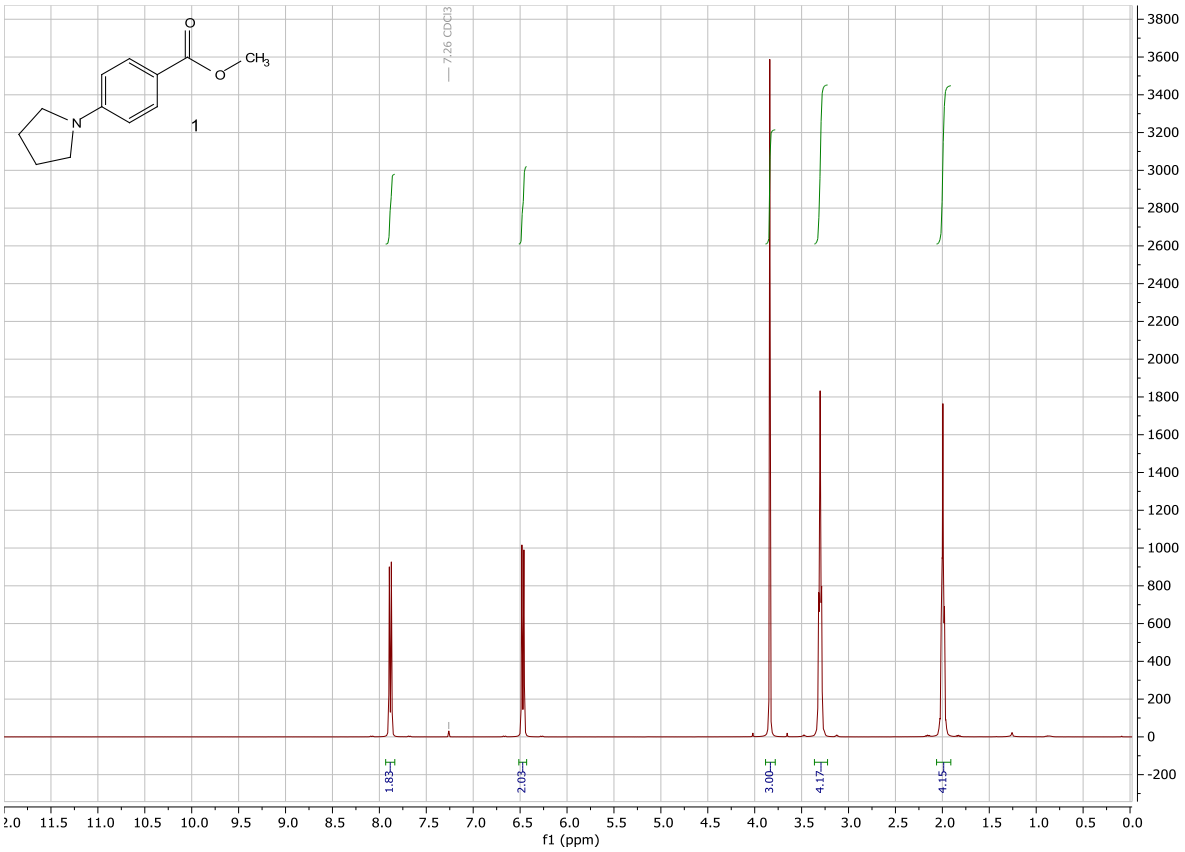
34 Wolfe, J. P. & Buchwald, S. L. Palladium-Catalyzed Amination of Aryl Triflates. *J. Org. Chem.* **62**, 1264-1267 (1997).

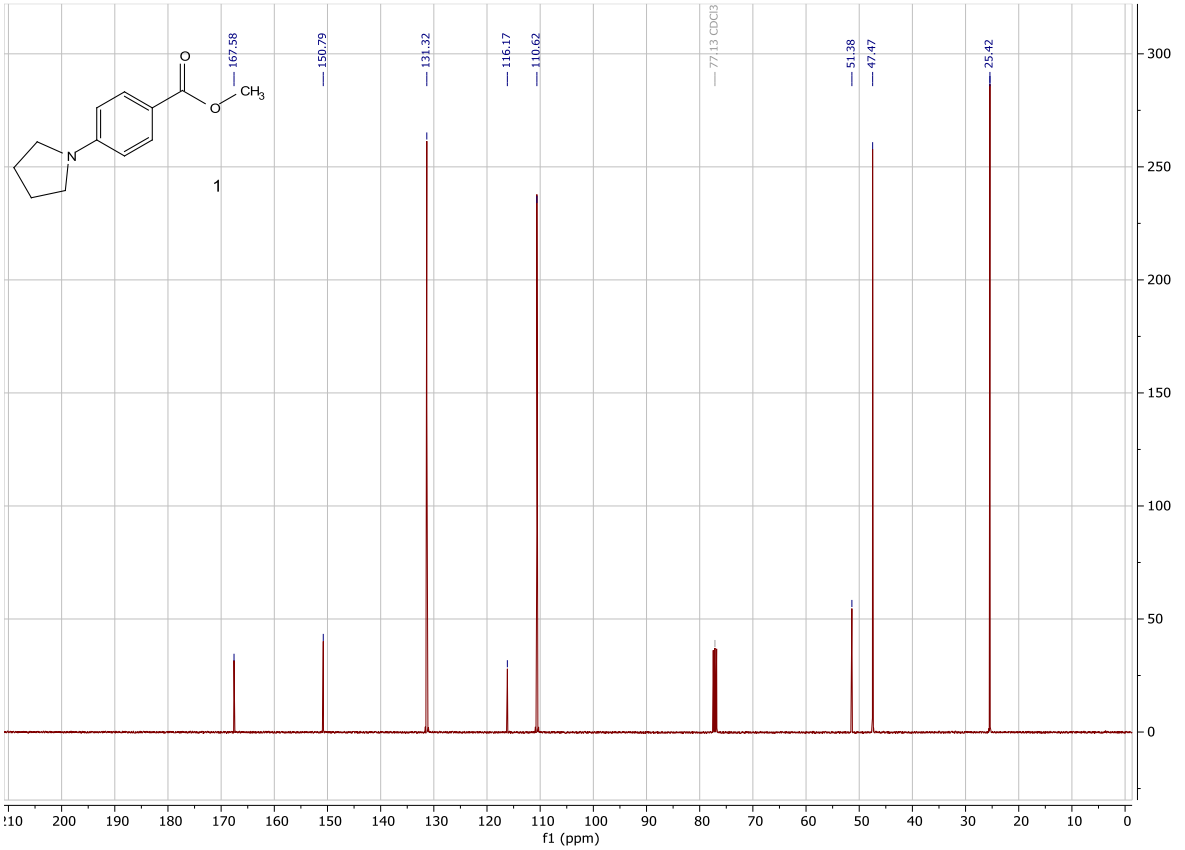
35 Lakshminarayana, N., Prasad, Y. R., Gharat, L., Thomas, A., Narayanan, S., Raghuram, A., Srinivasan, C. V. & Gopalan, B. Synthesis and evaluation of some novel dibenzo[b,d]furan carboxylic acids as potential anti-diabetic agents. *Eur. J. Med. Chem.* **45**, 3709-3718 (2010).

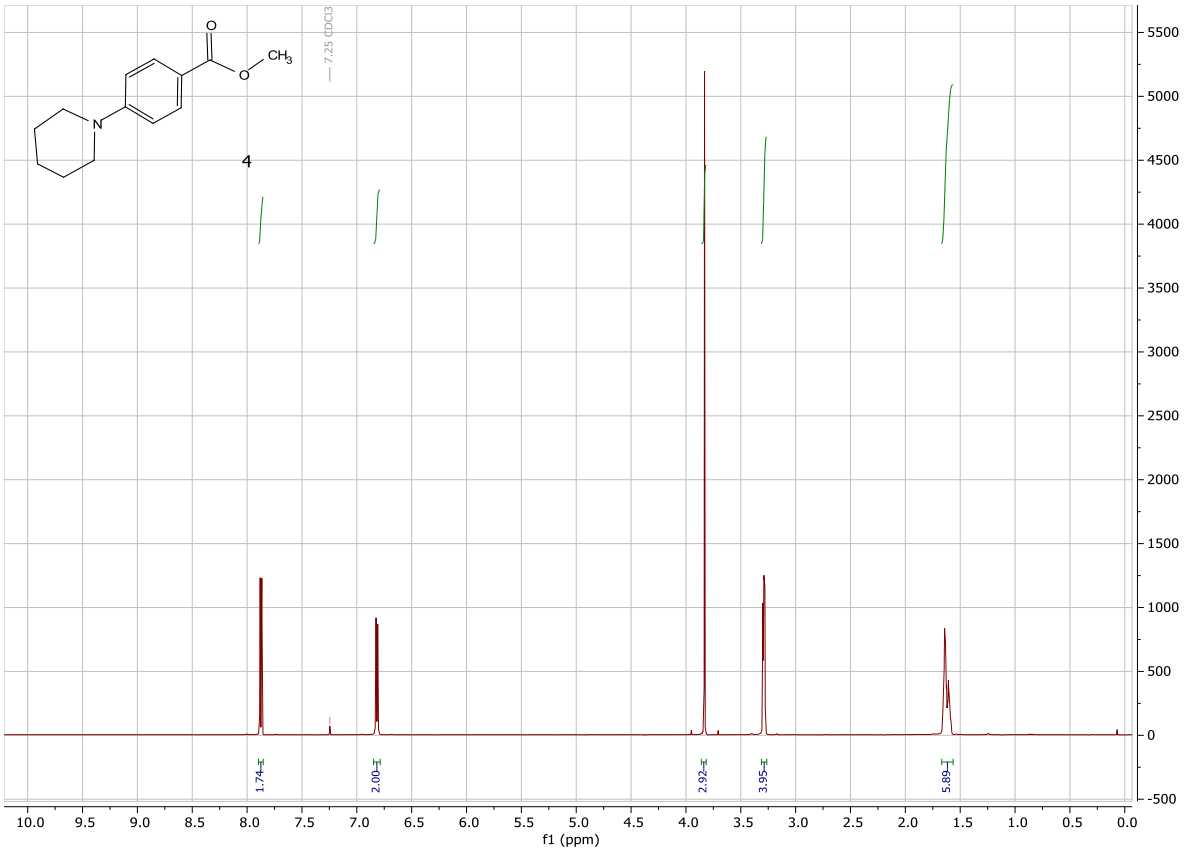
36 Charles, M. D., Schultz, P. & Buchwald, S. L. Efficient Pd-Catalyzed Amination of Heteroaryl Halides. *Org. Lett.* **7**, 3965-3968 (2005).

37 Maiti, D., Fors, B. P., Henderson, J. L., Nakamura, Y. & Buchwald, S. L. Palladium-catalyzed coupling of functionalized primary and secondary amines with aryl and heteroaryl halides: two ligands suffice in most cases. *Chem. Sci.* **2**, 57-68 (2011).

12. Copies of NMR spectra



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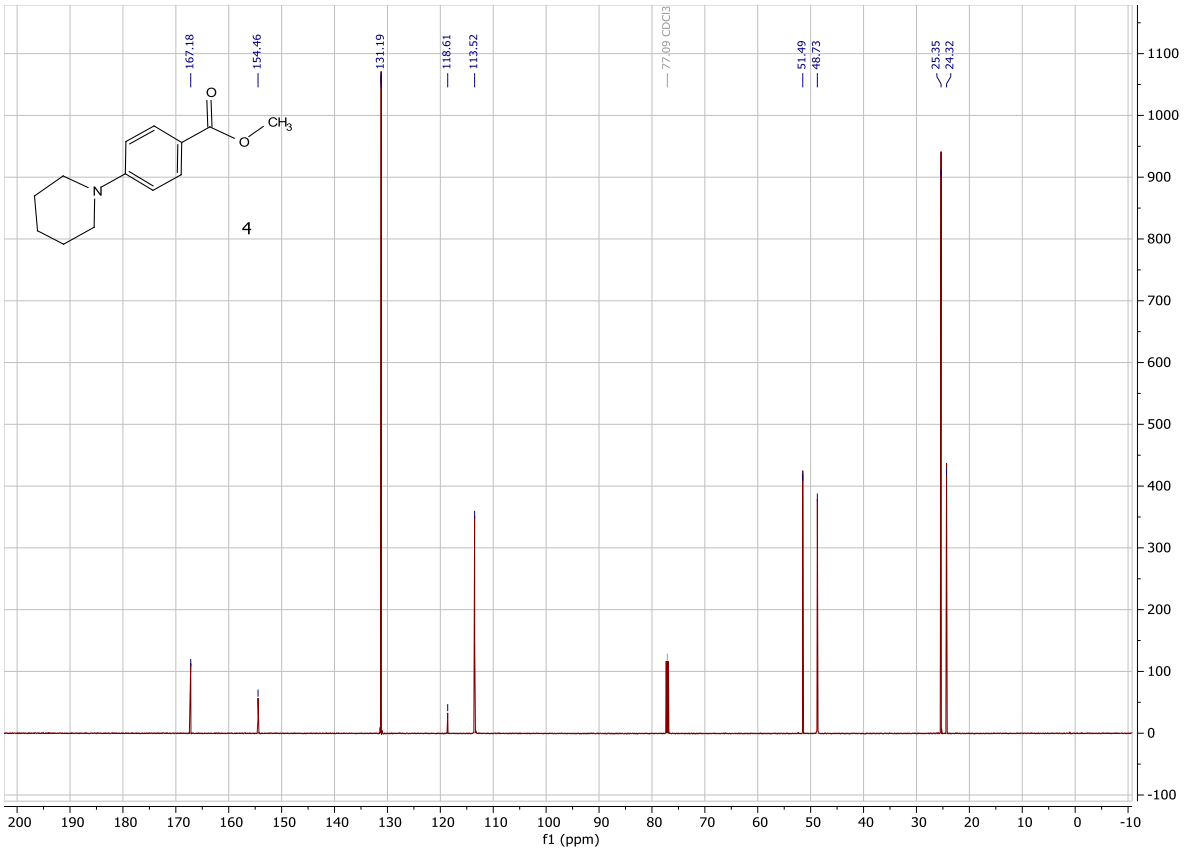
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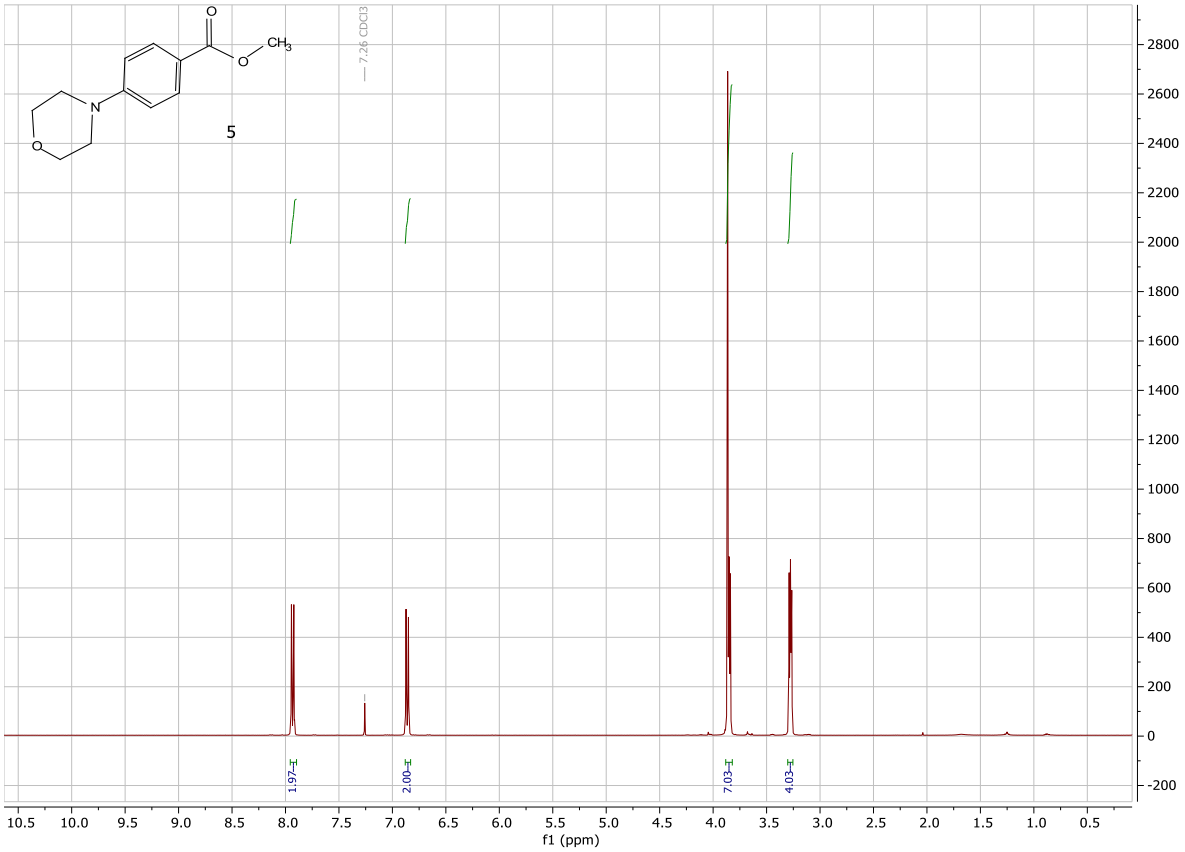
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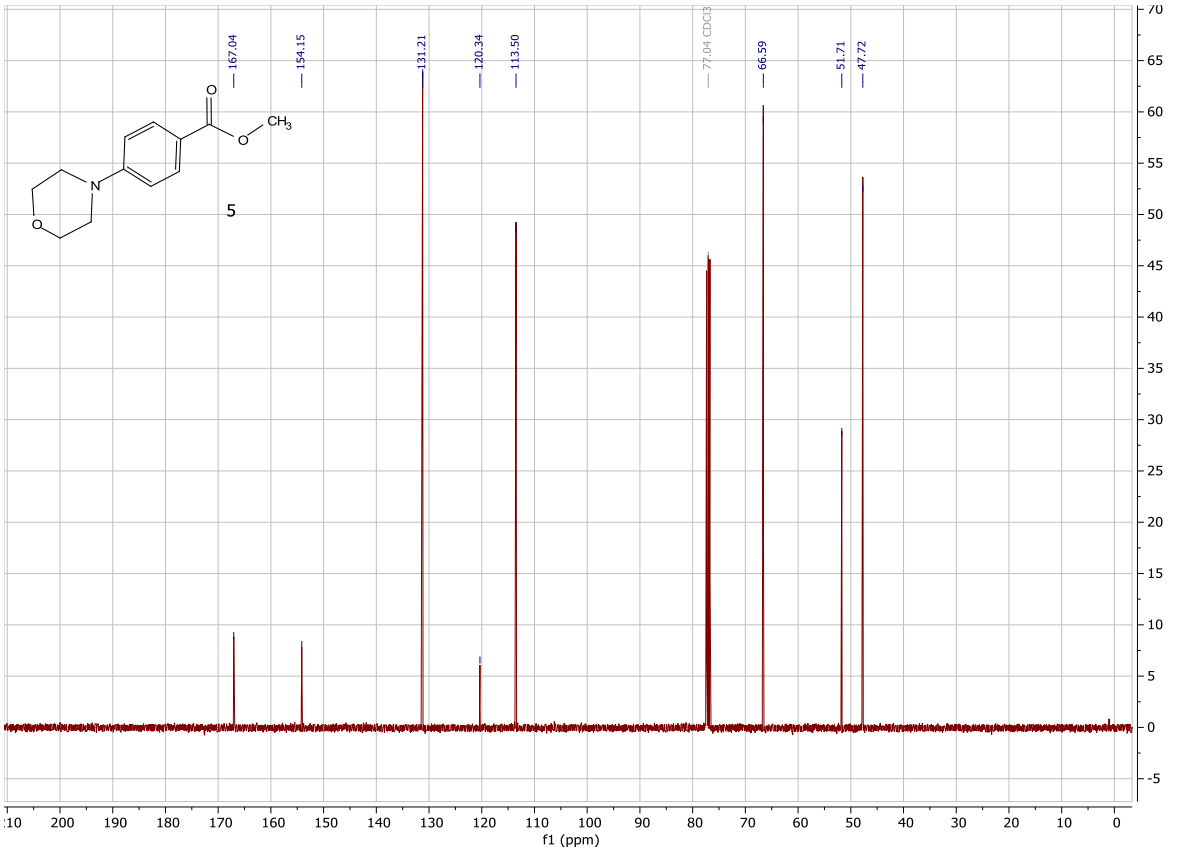
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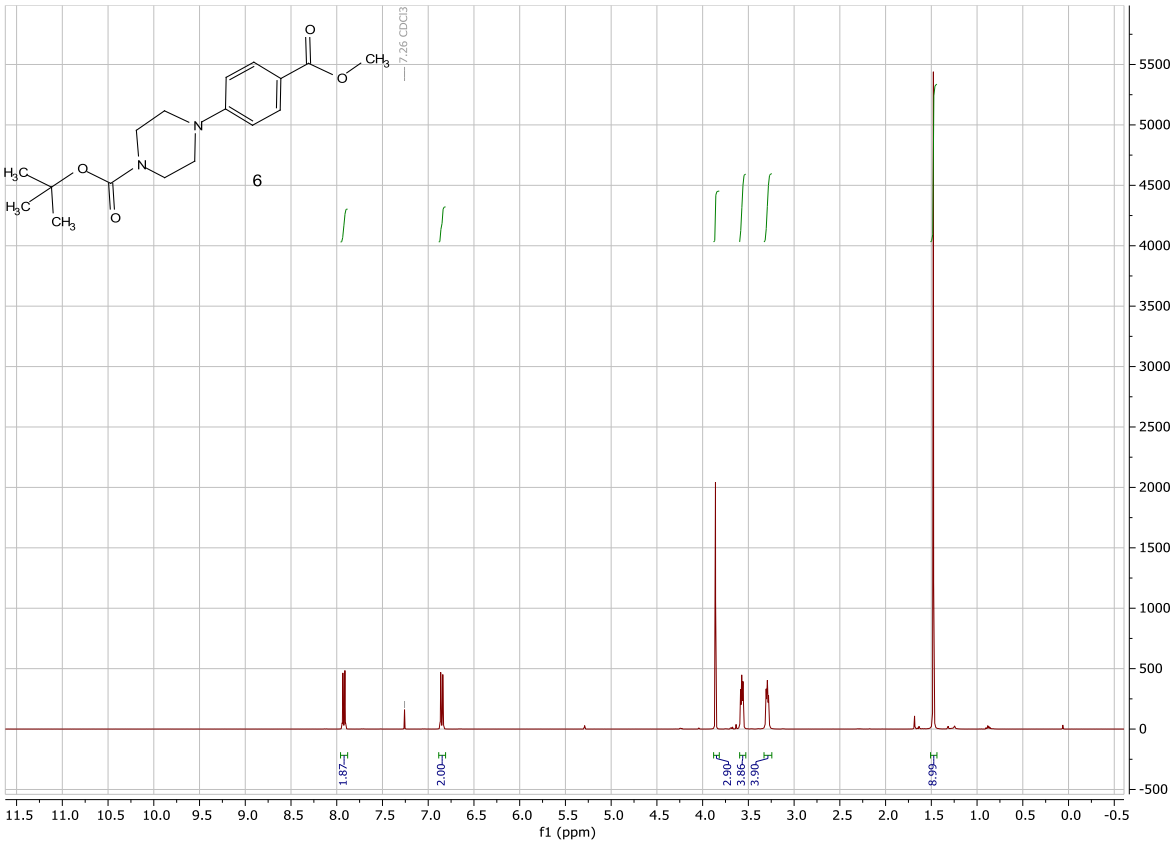
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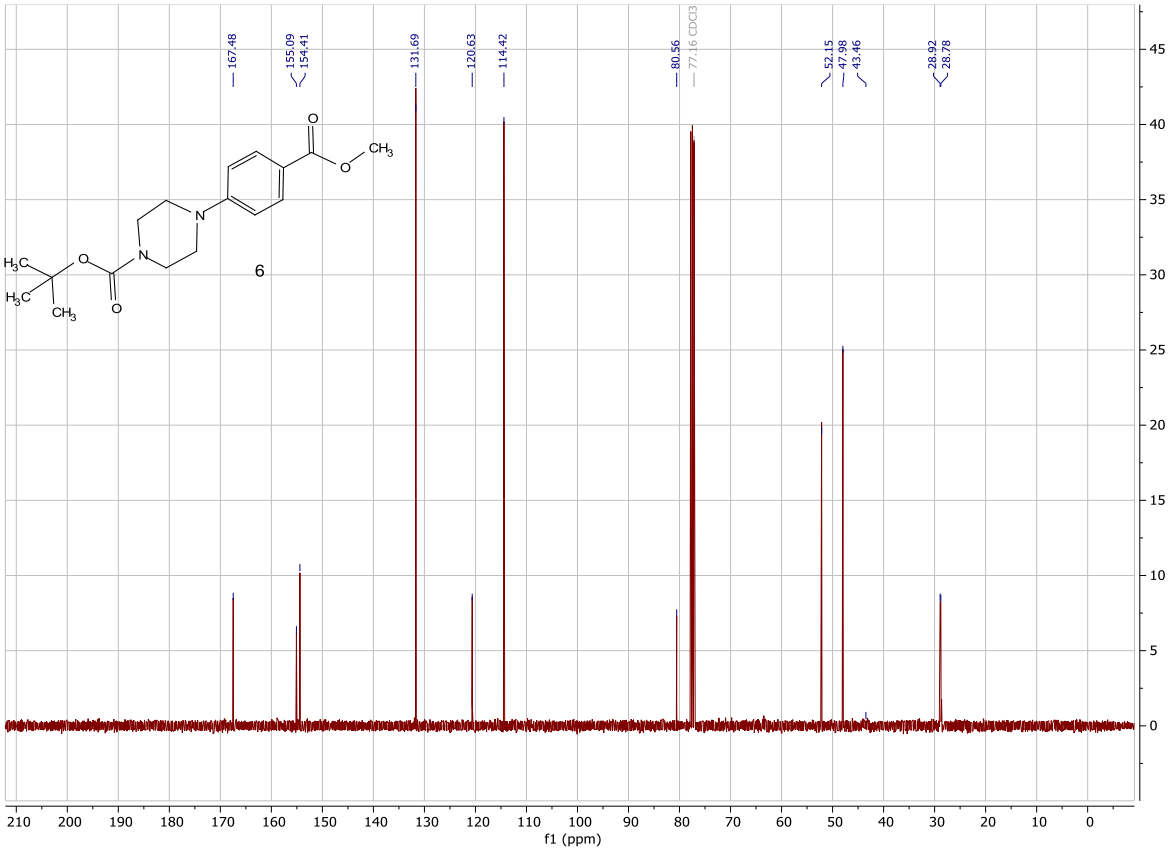
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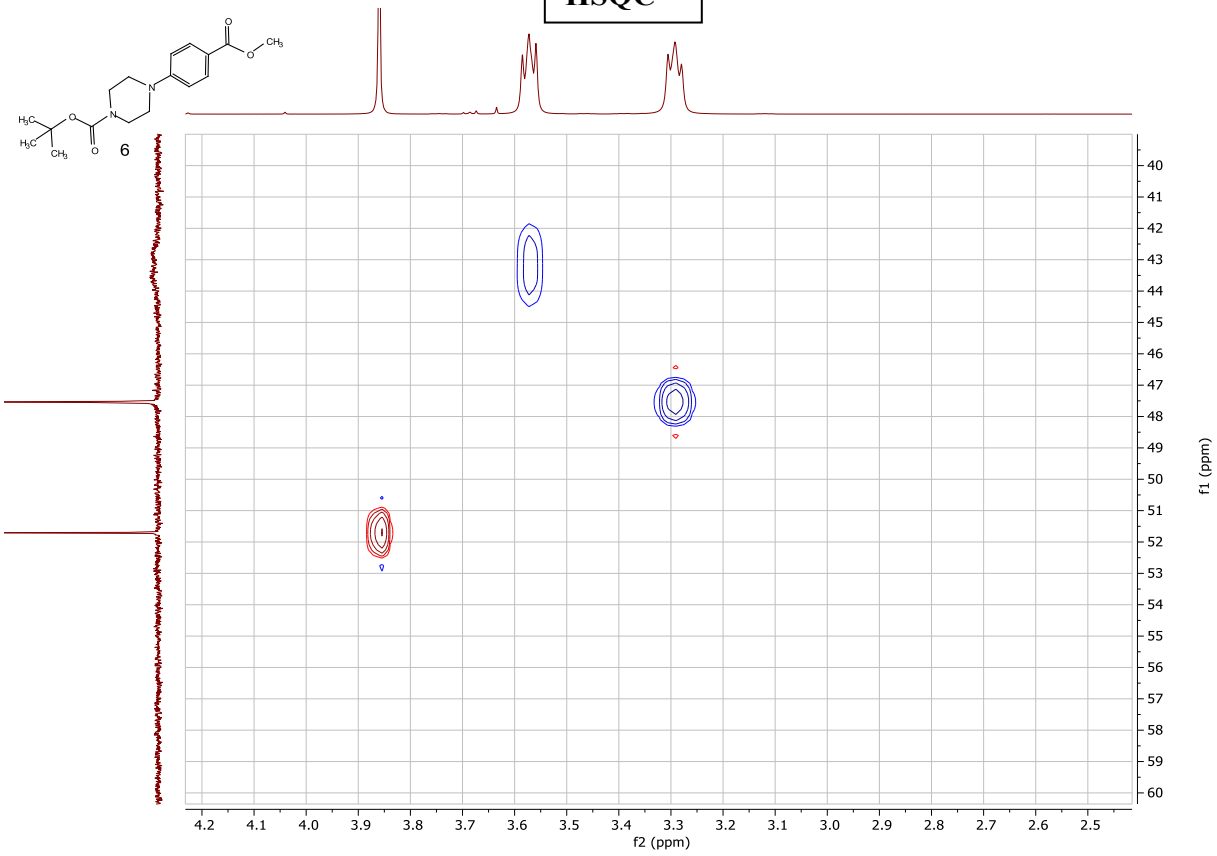

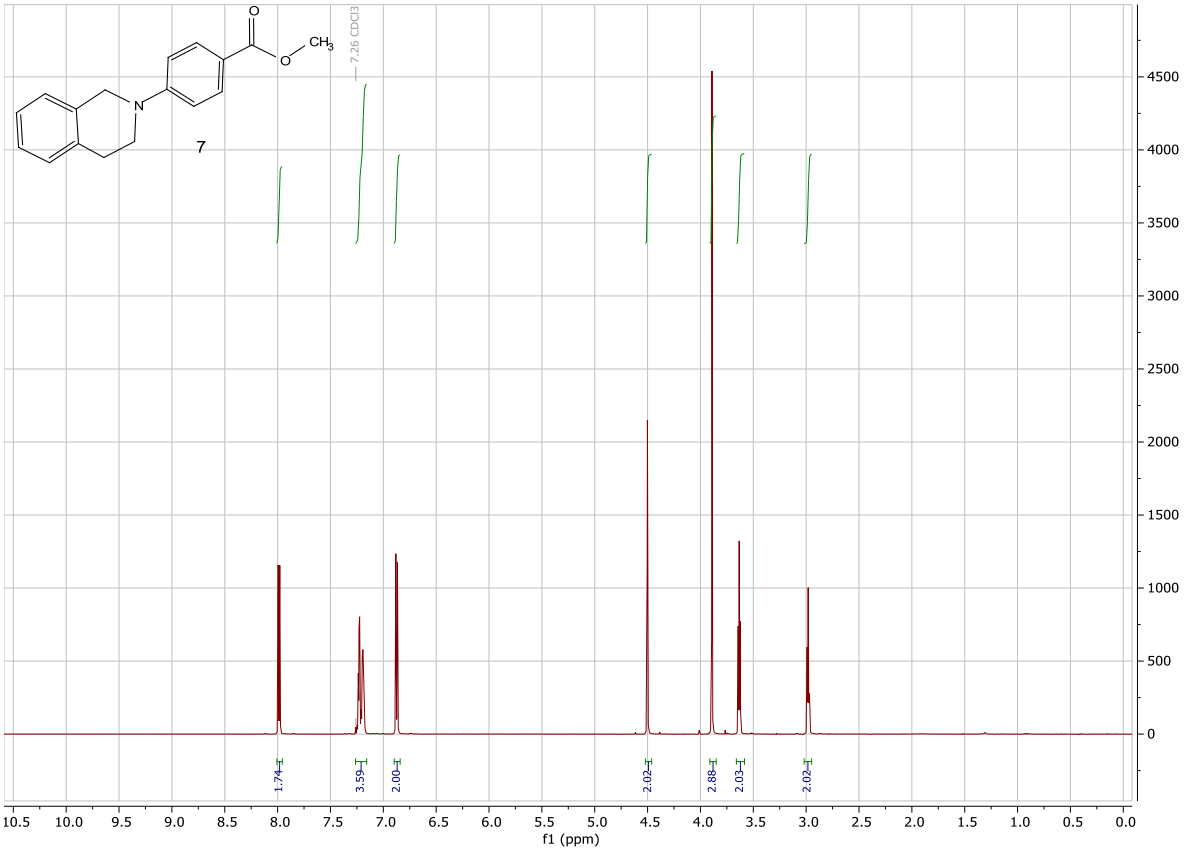

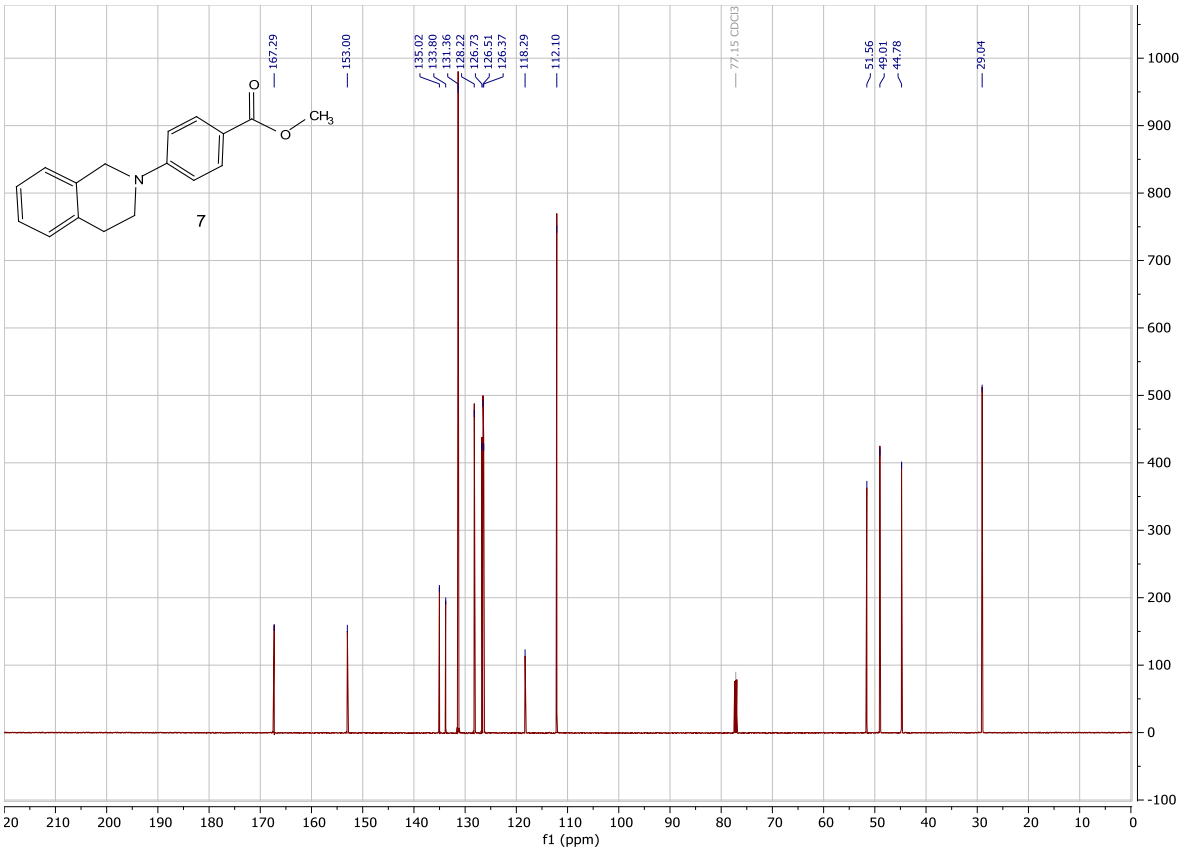
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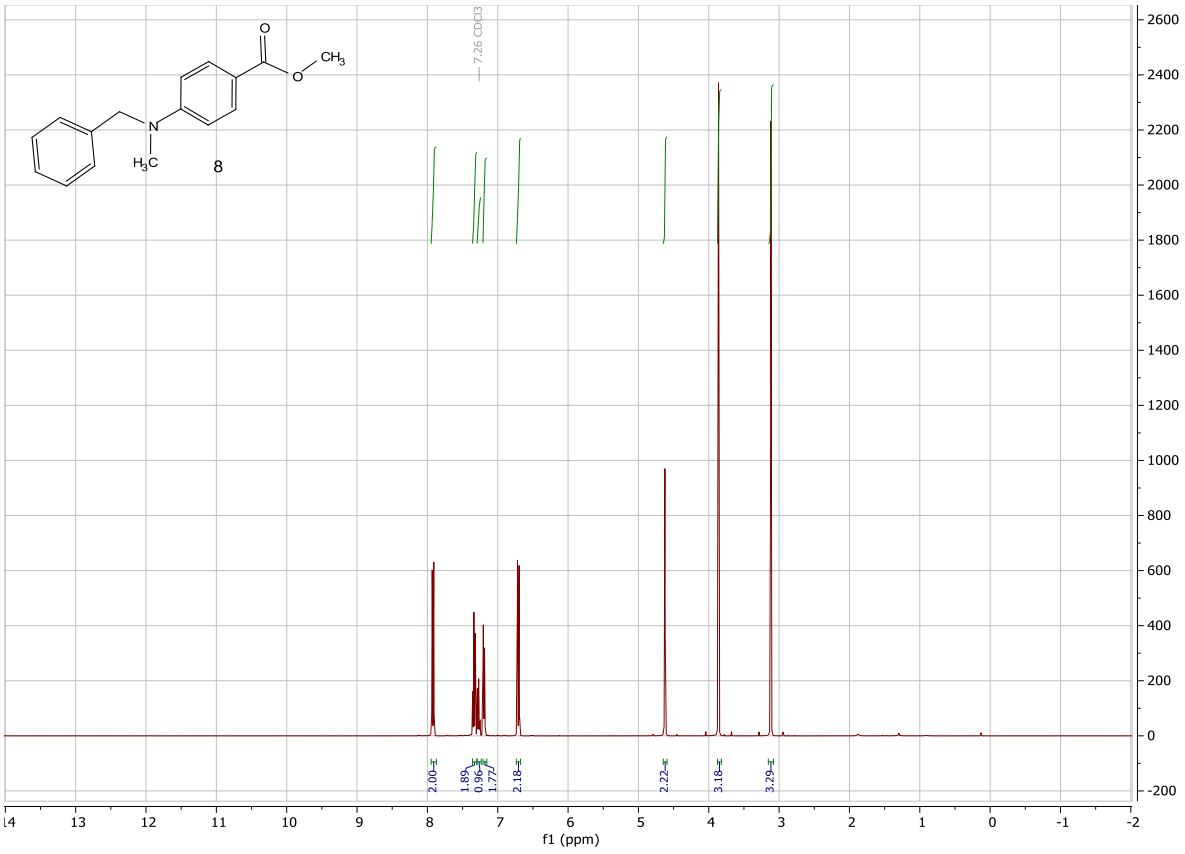
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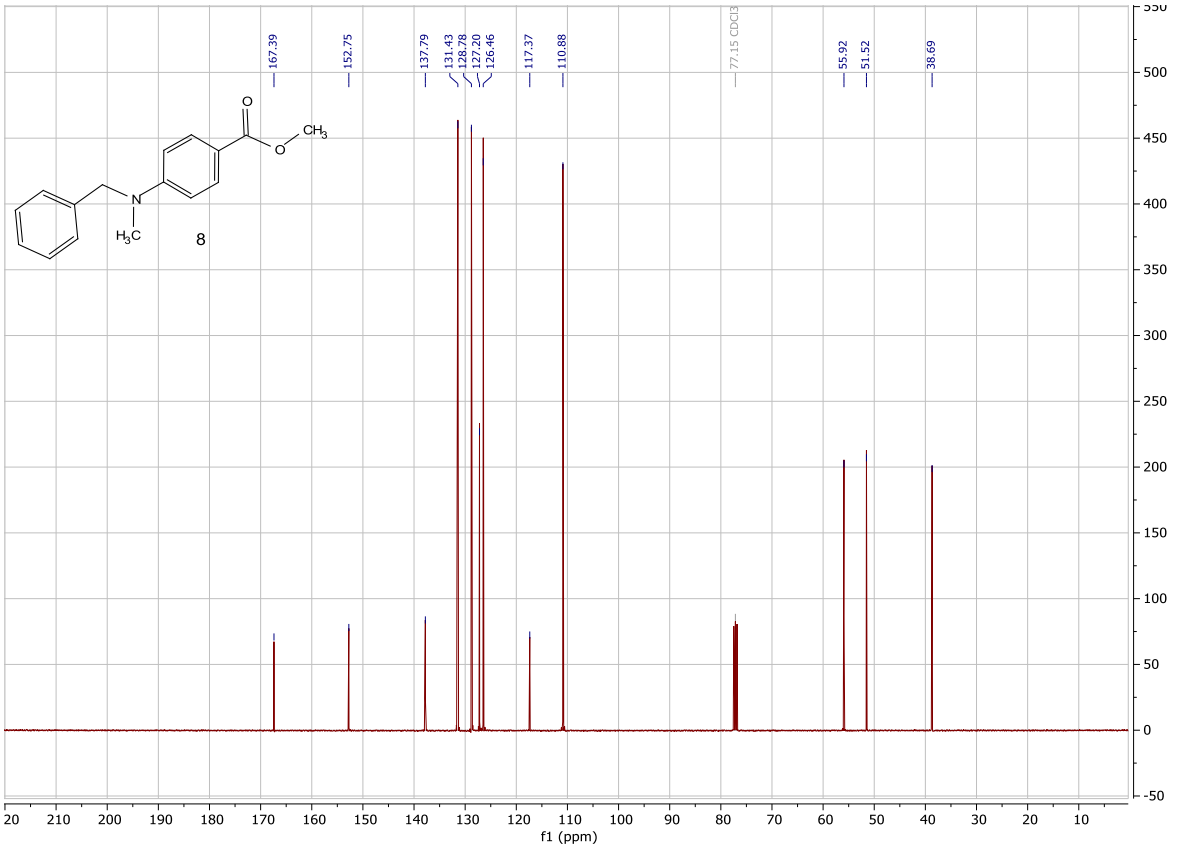
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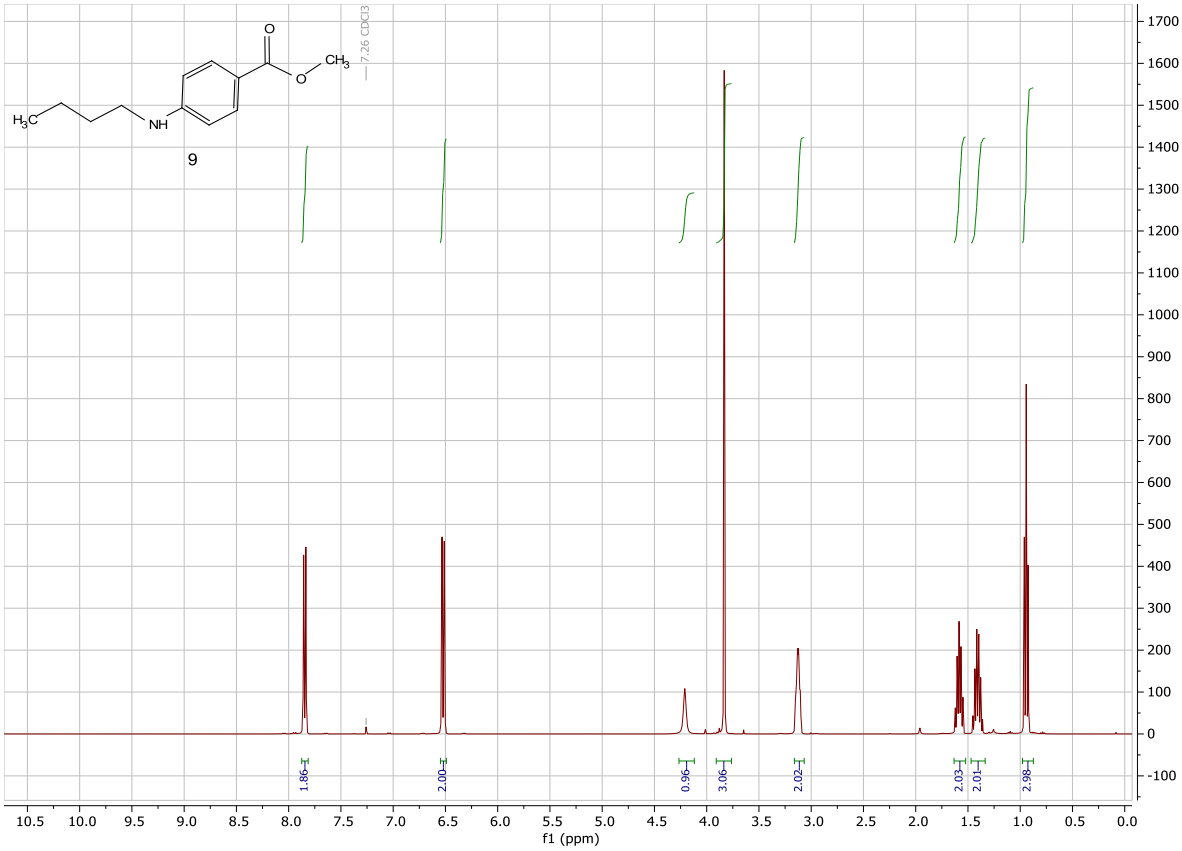
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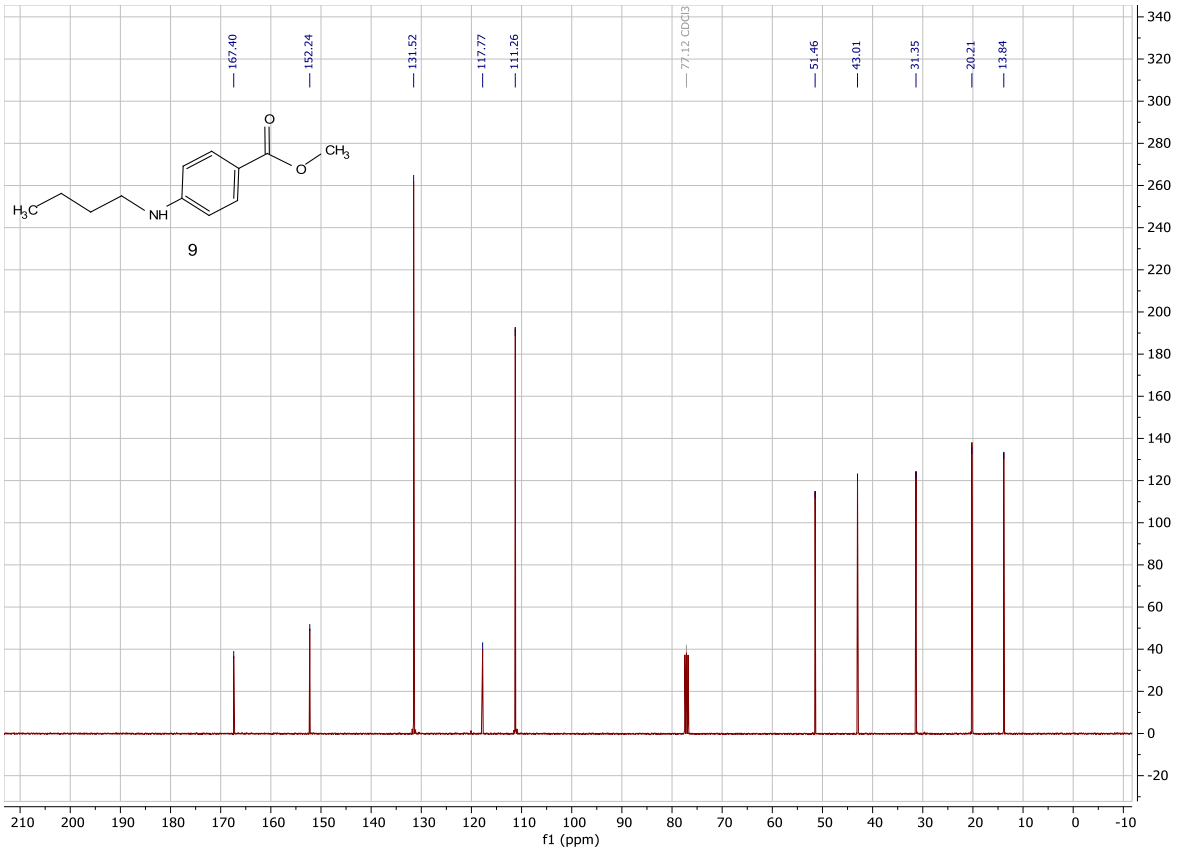
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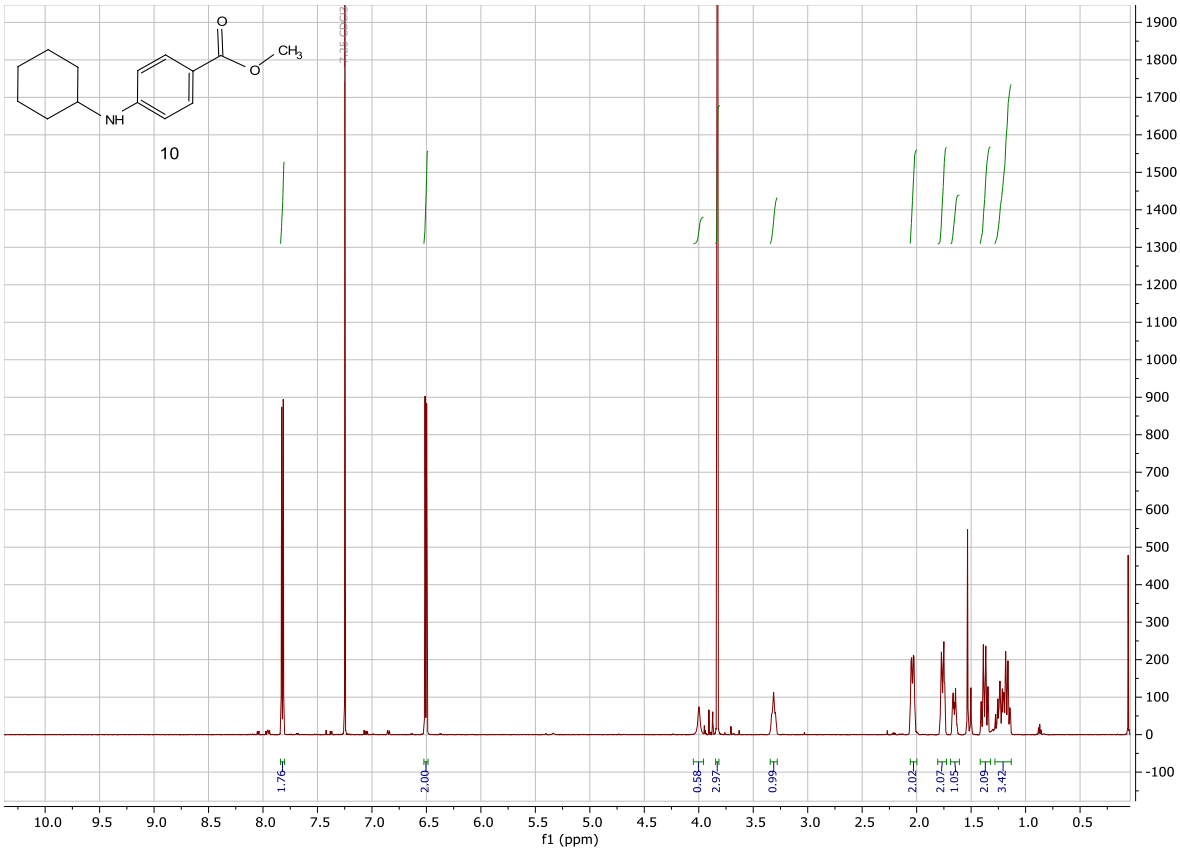
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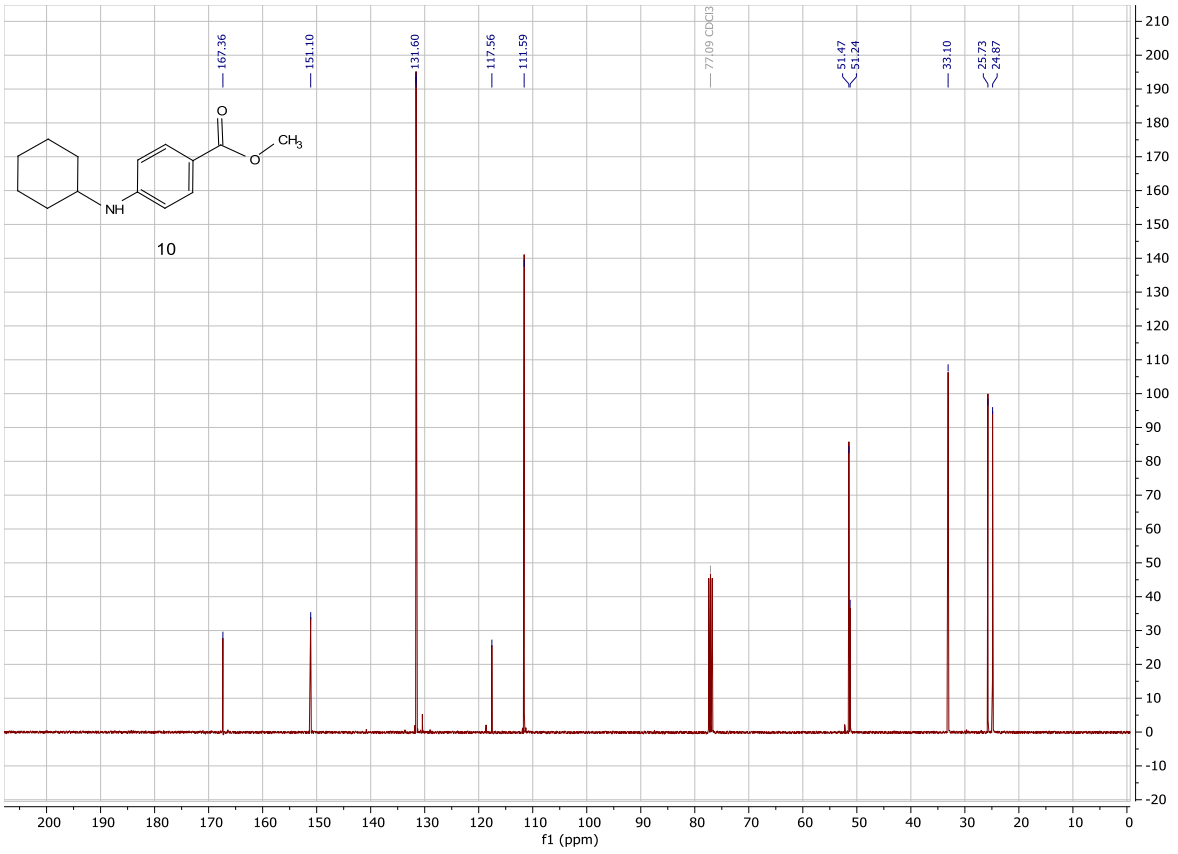
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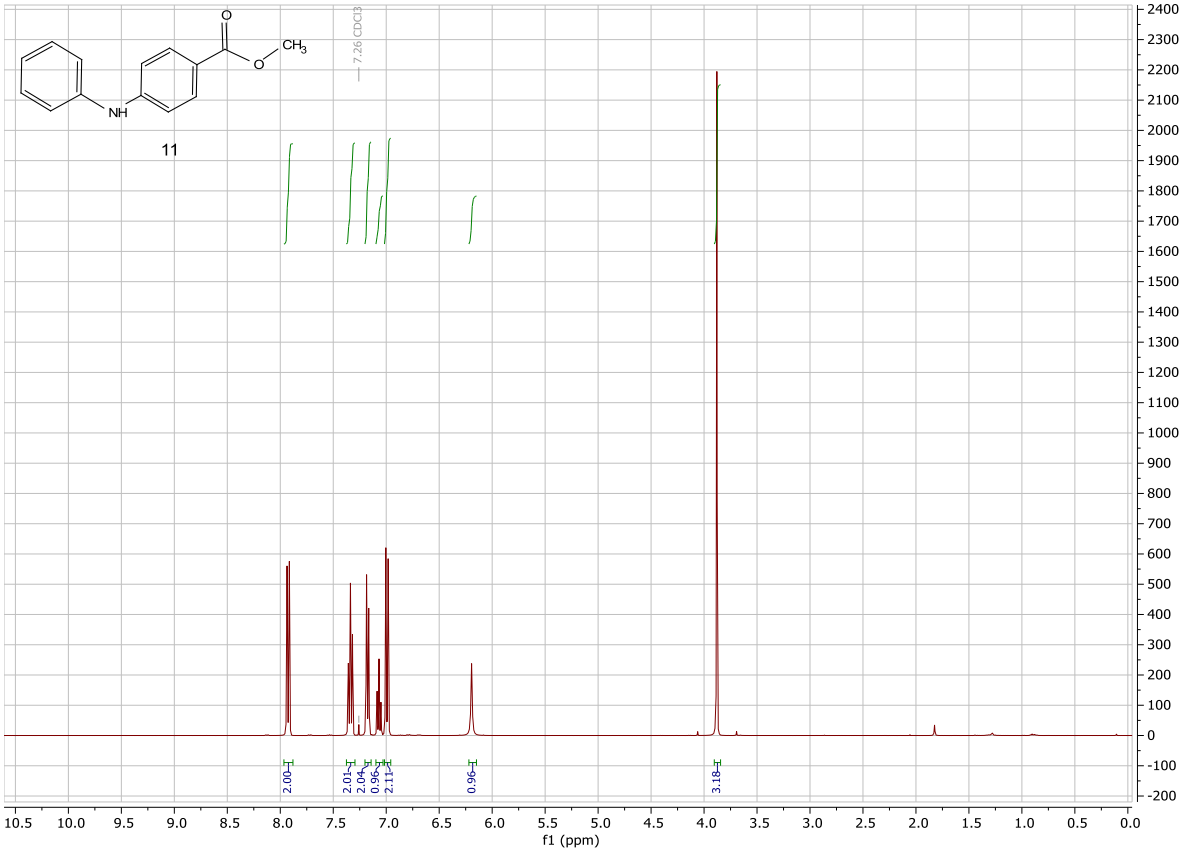
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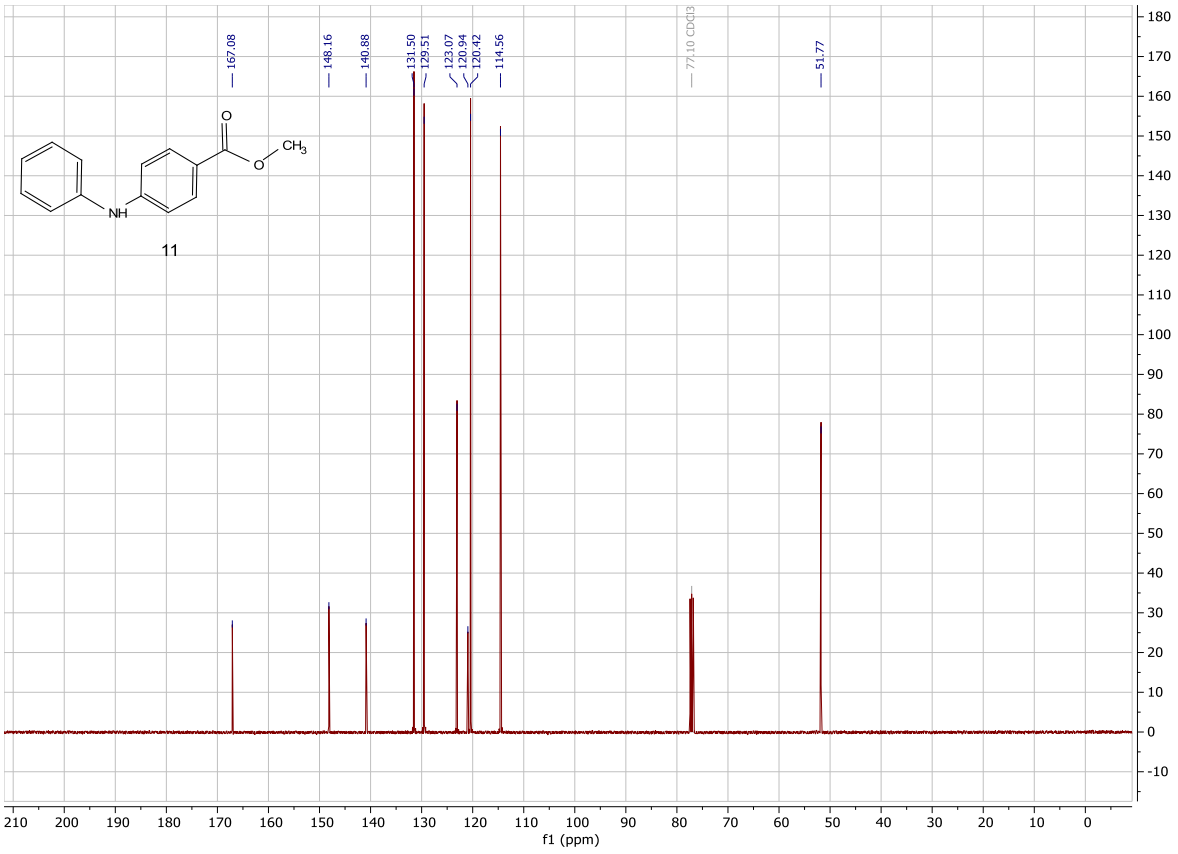
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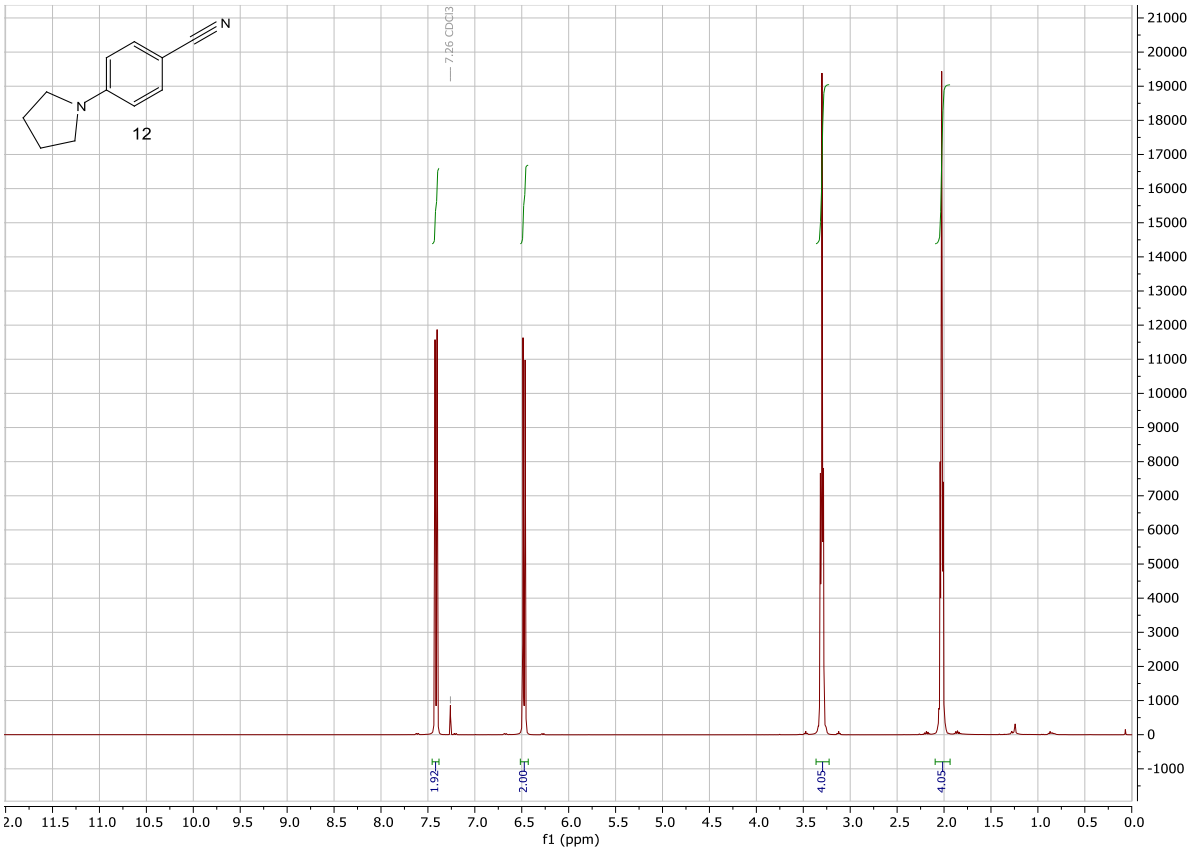
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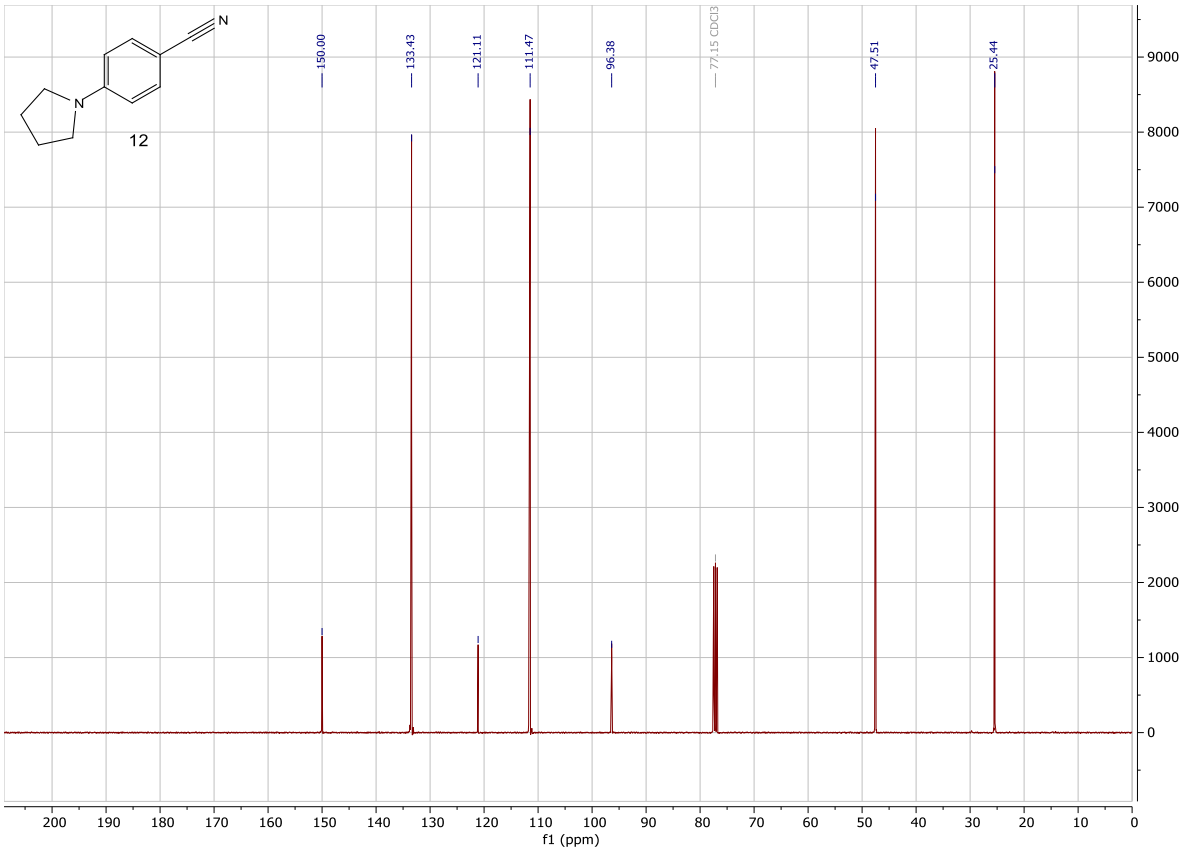
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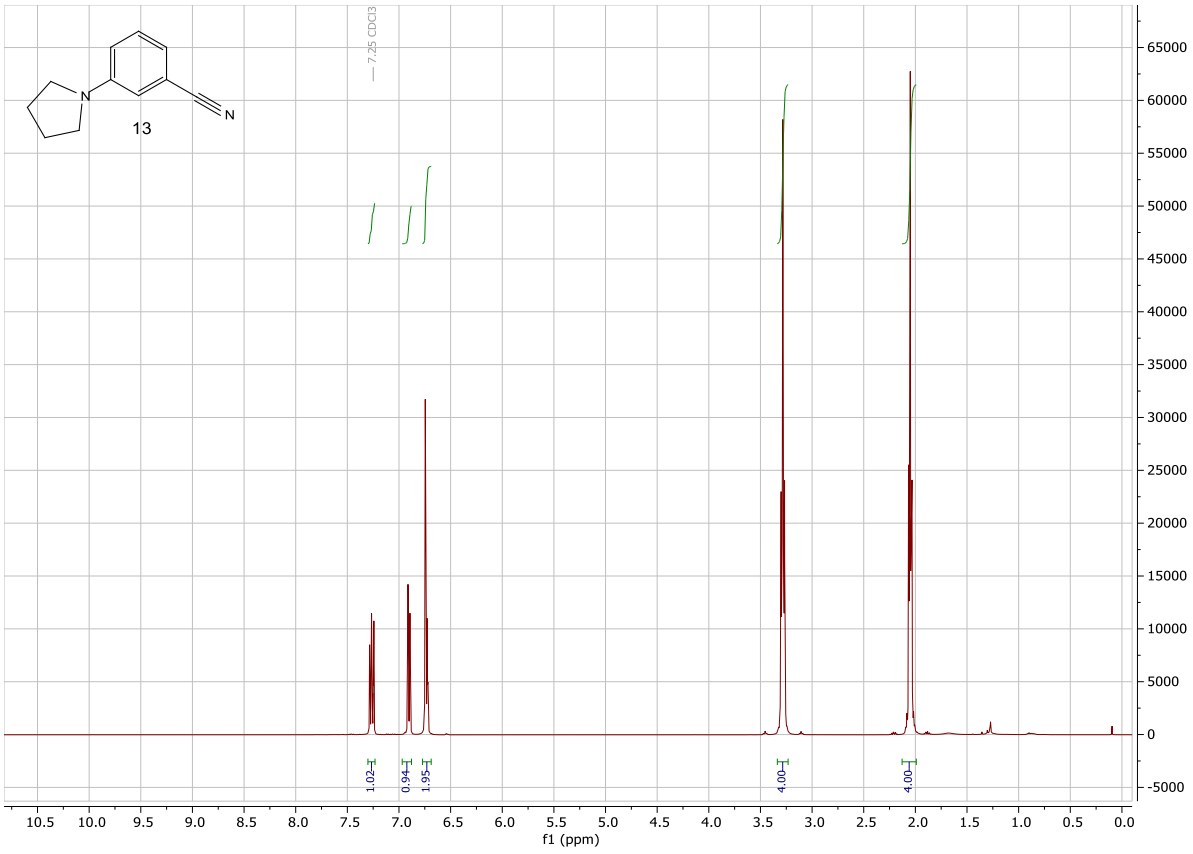
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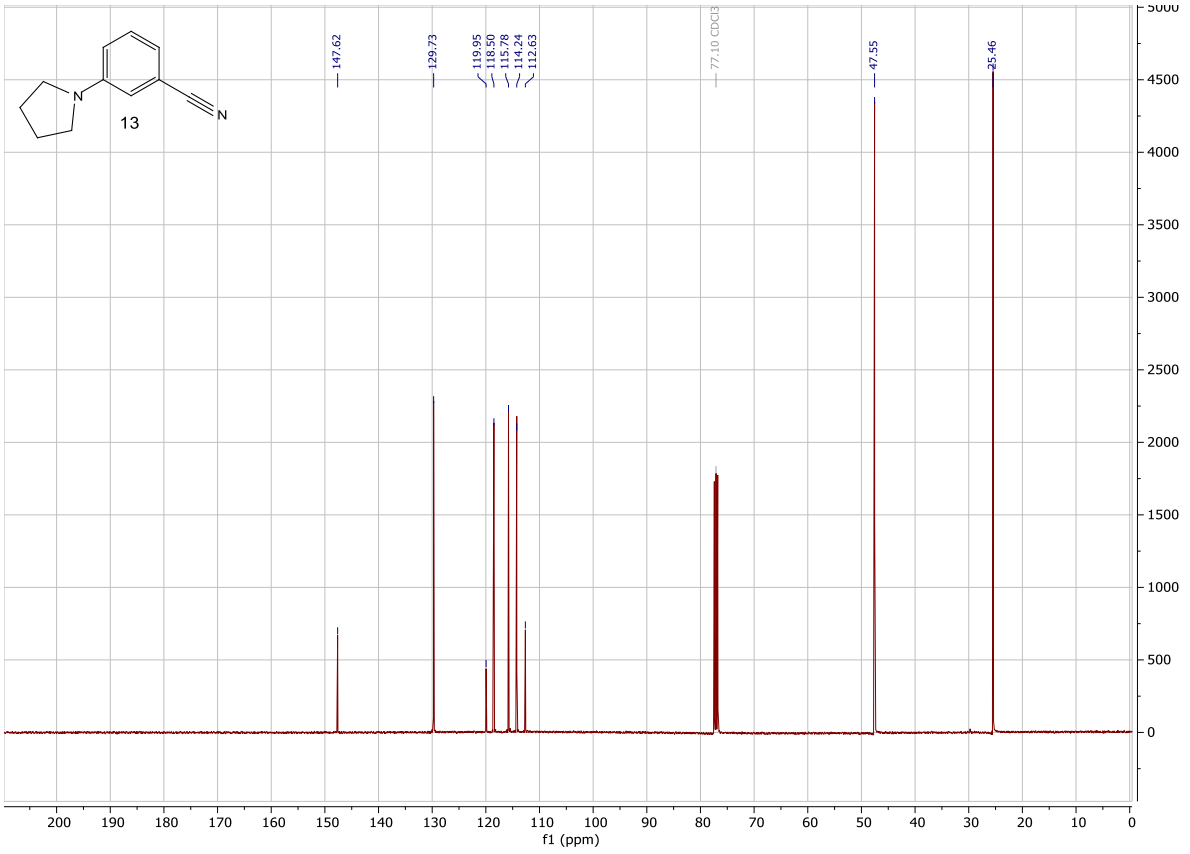
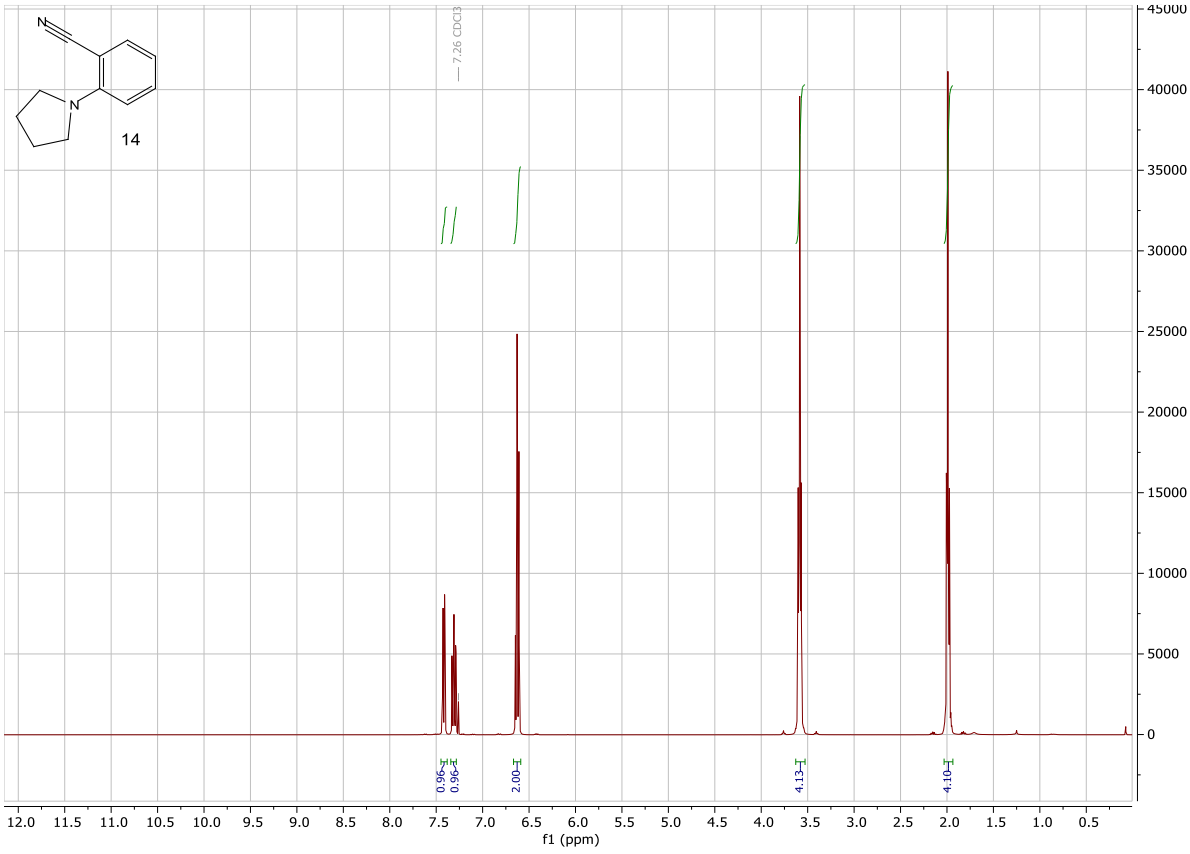
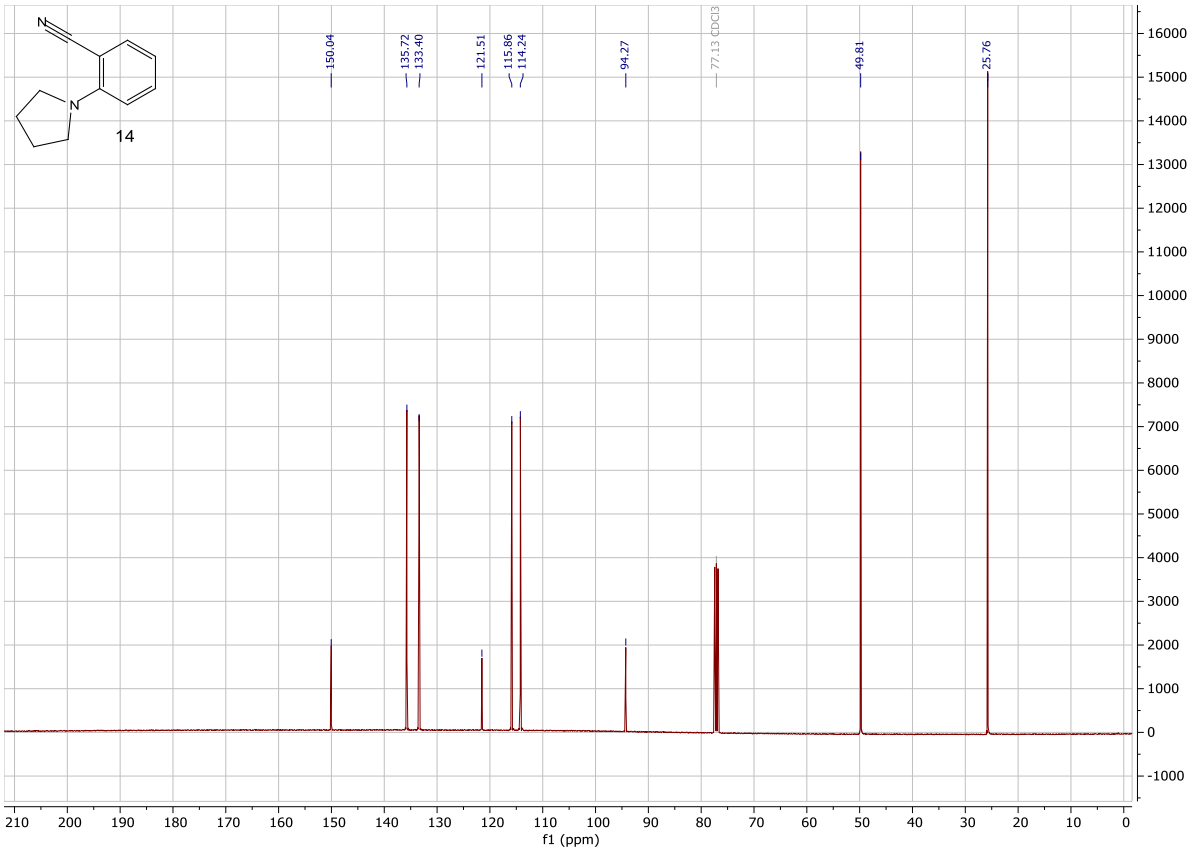
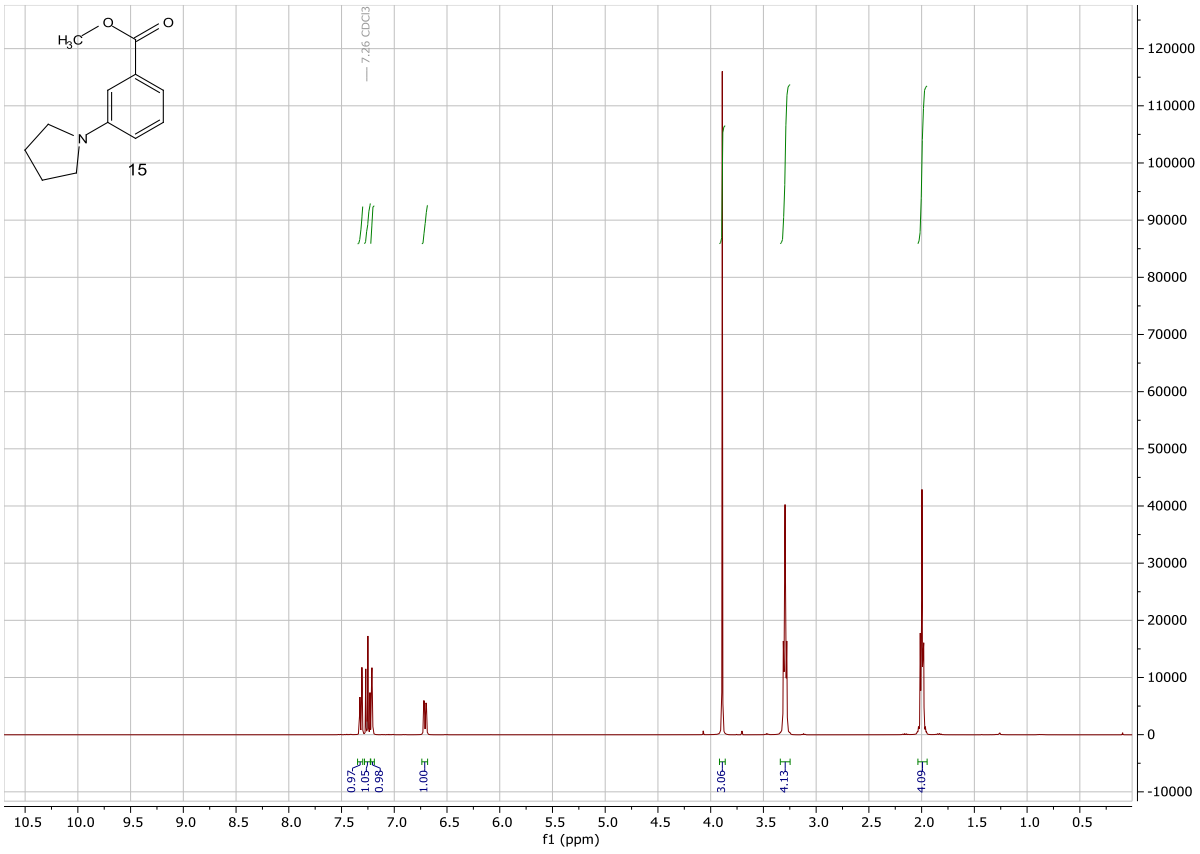
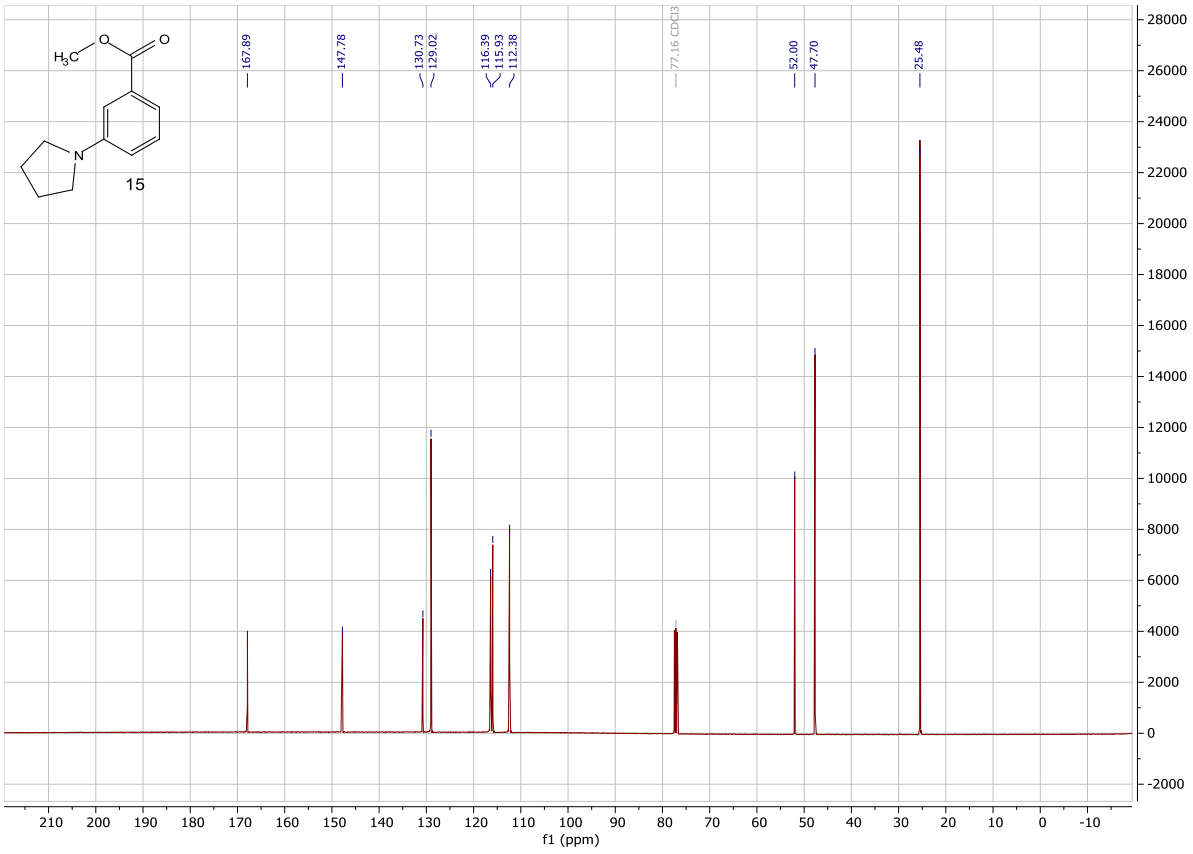
0.94
1.95
4.00
4.00
f1 (ppm)

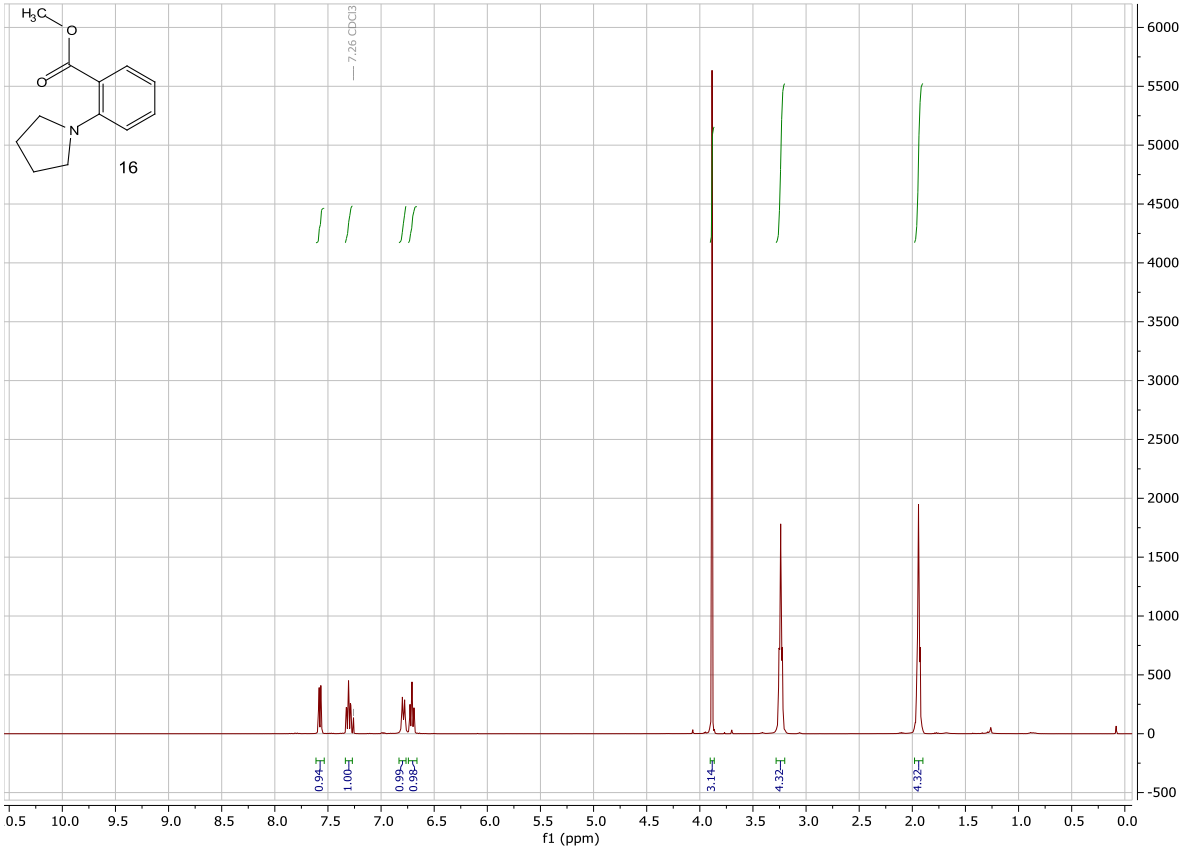

13
147.62
129.73
119.95
118.50
115.78
114.24
112.63
77.10 CDCl3
47.55
35.46
f1 (ppm)

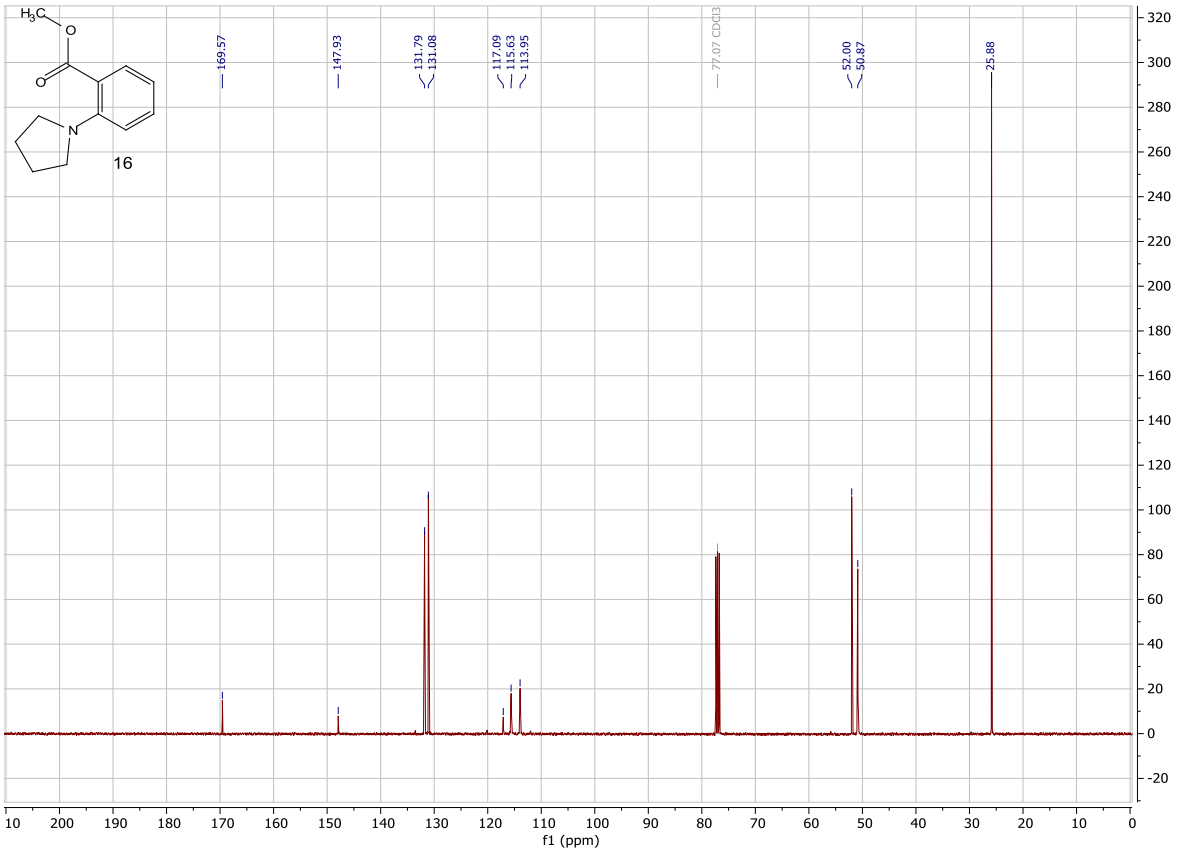

14
7.26 CDCl3
0.96
0.96
2.00
4.13
4.10
f1 (ppm)

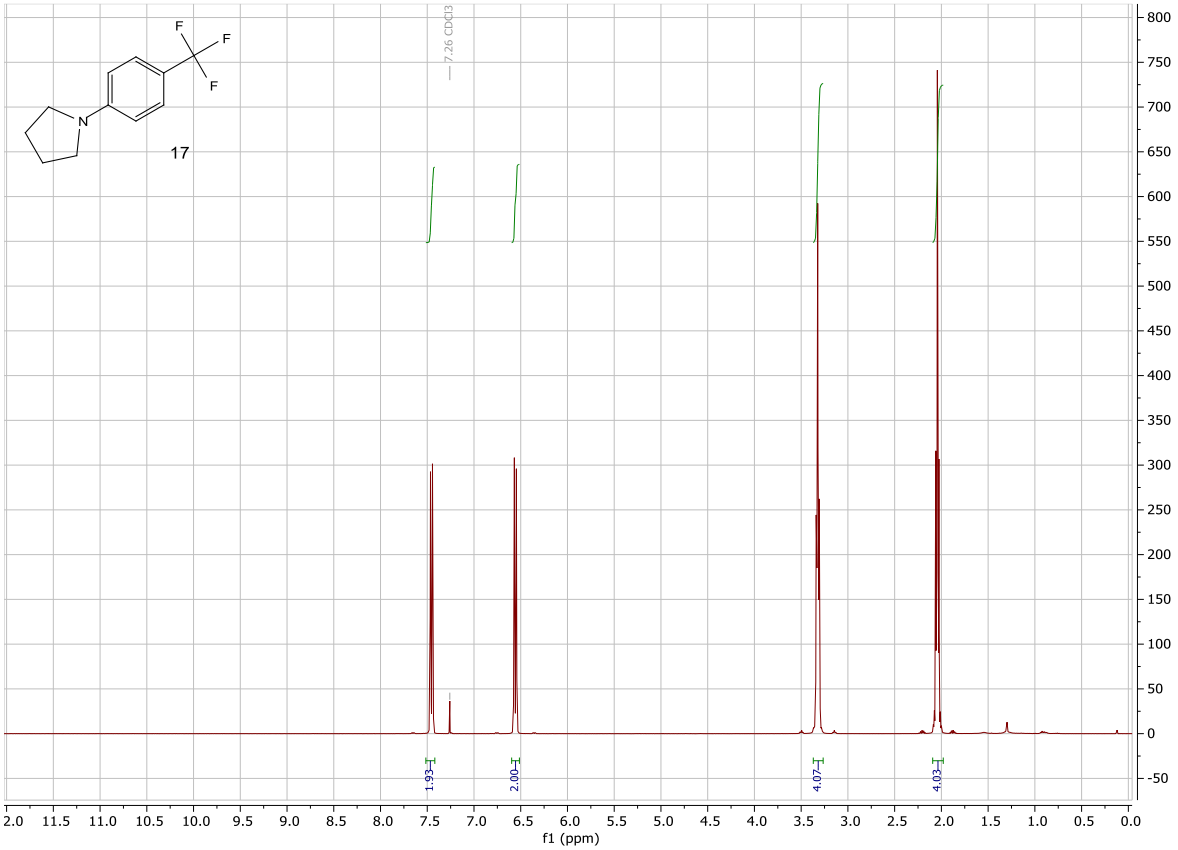

N
N
14
150.04
135.72
133.40
121.51
115.86
114.24
94.27
77.13 CDCl3
49.81
25.76
f1 (ppm)

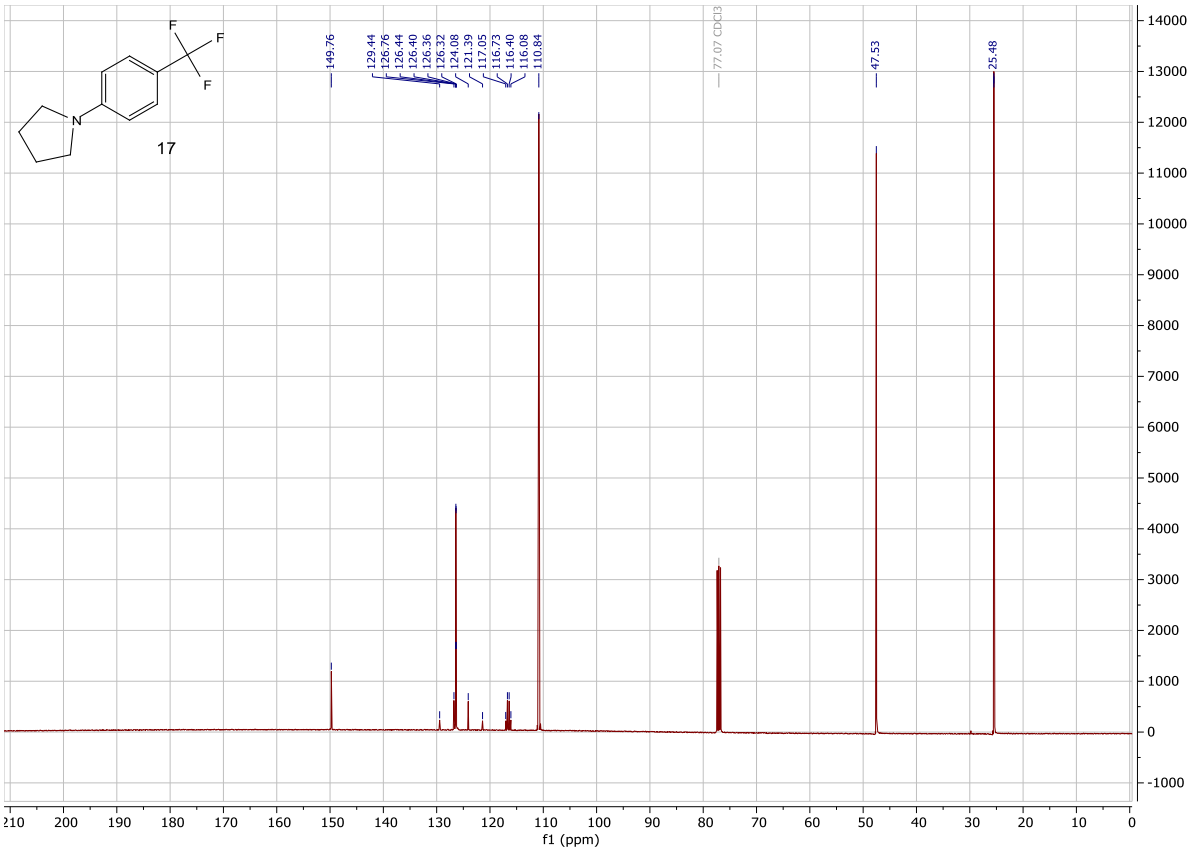

H3C
O
O
N
15
7.26 CDCl3
0.97
1.05
0.98
1.00
3.06
4.13
4.09
f1 (ppm)

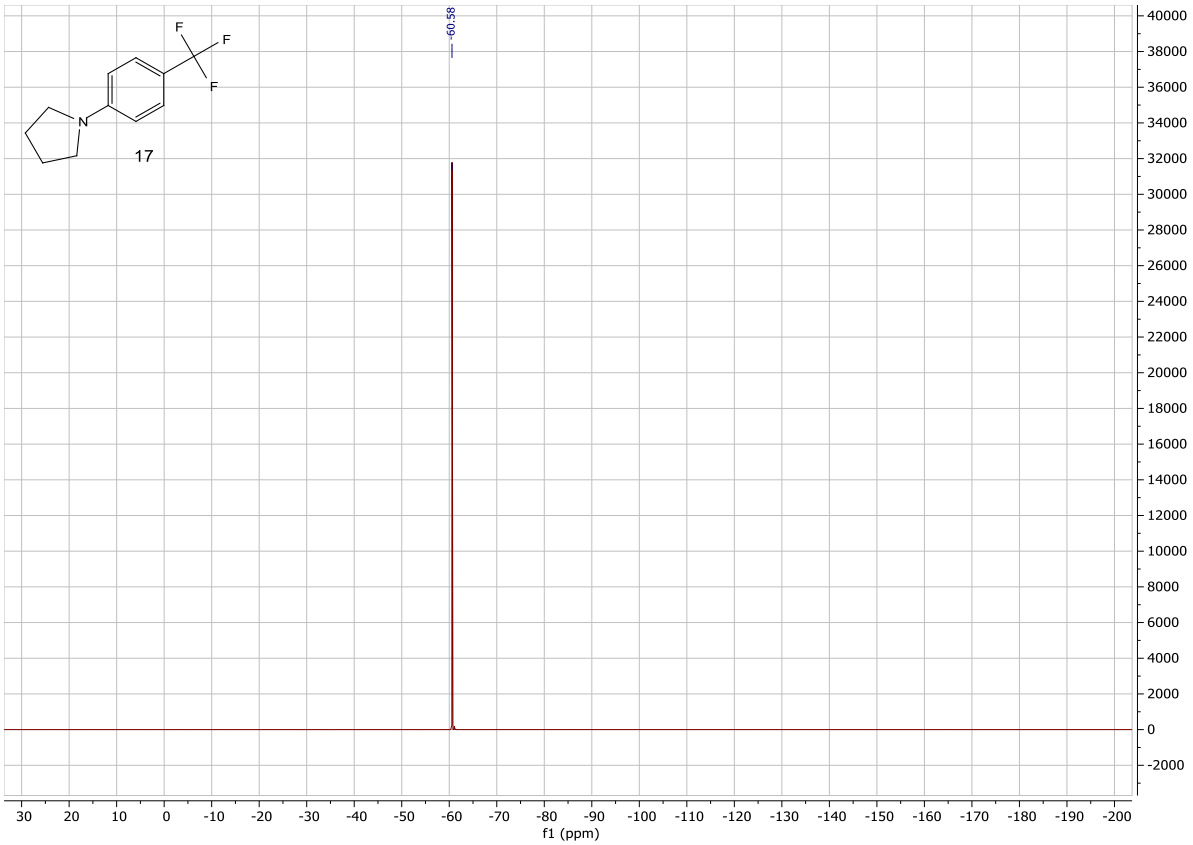

15
167.89
147.78
130.73
129.02
116.39
115.93
112.38
77.16 CDCl3
52.00
47.70
25.48
f1 (ppm)

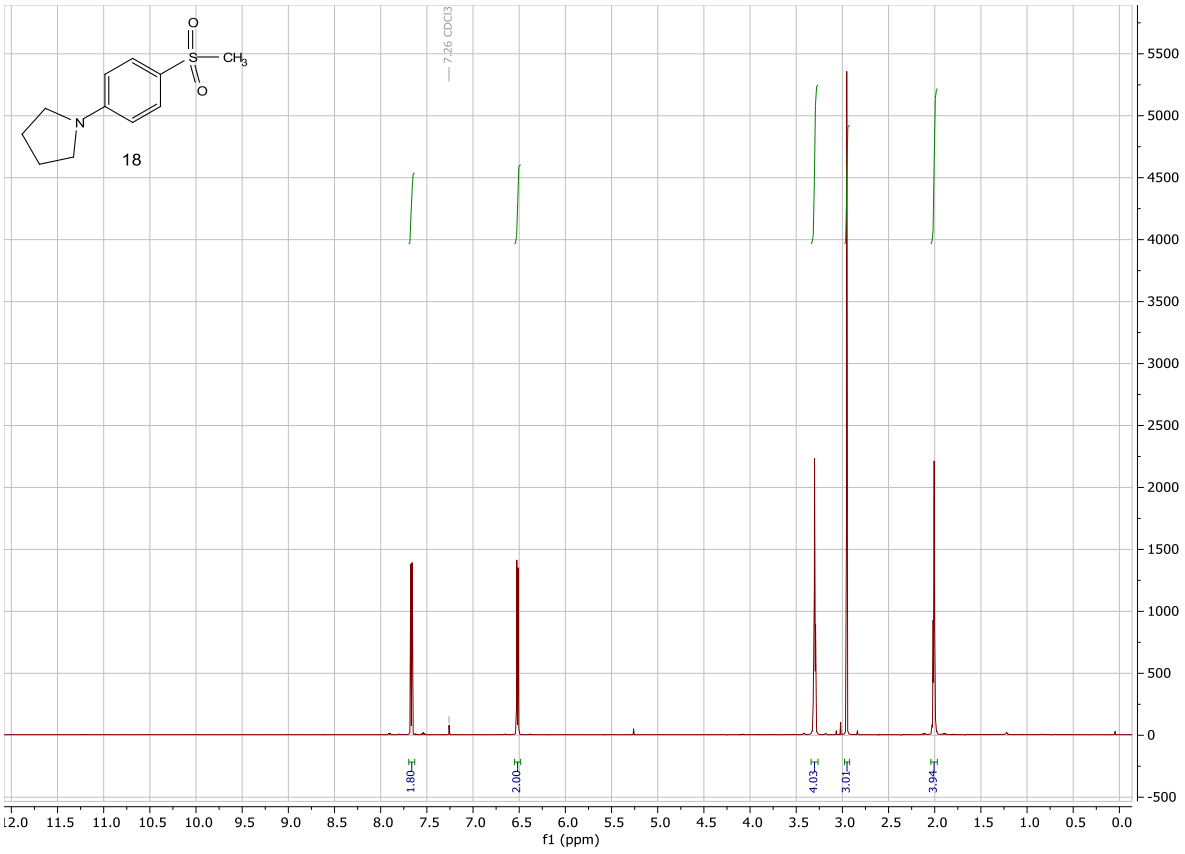

16
7.26 CDCl3
0.94
1.00
0.99
0.98
3.14
4.32
4.32
f1 (ppm)

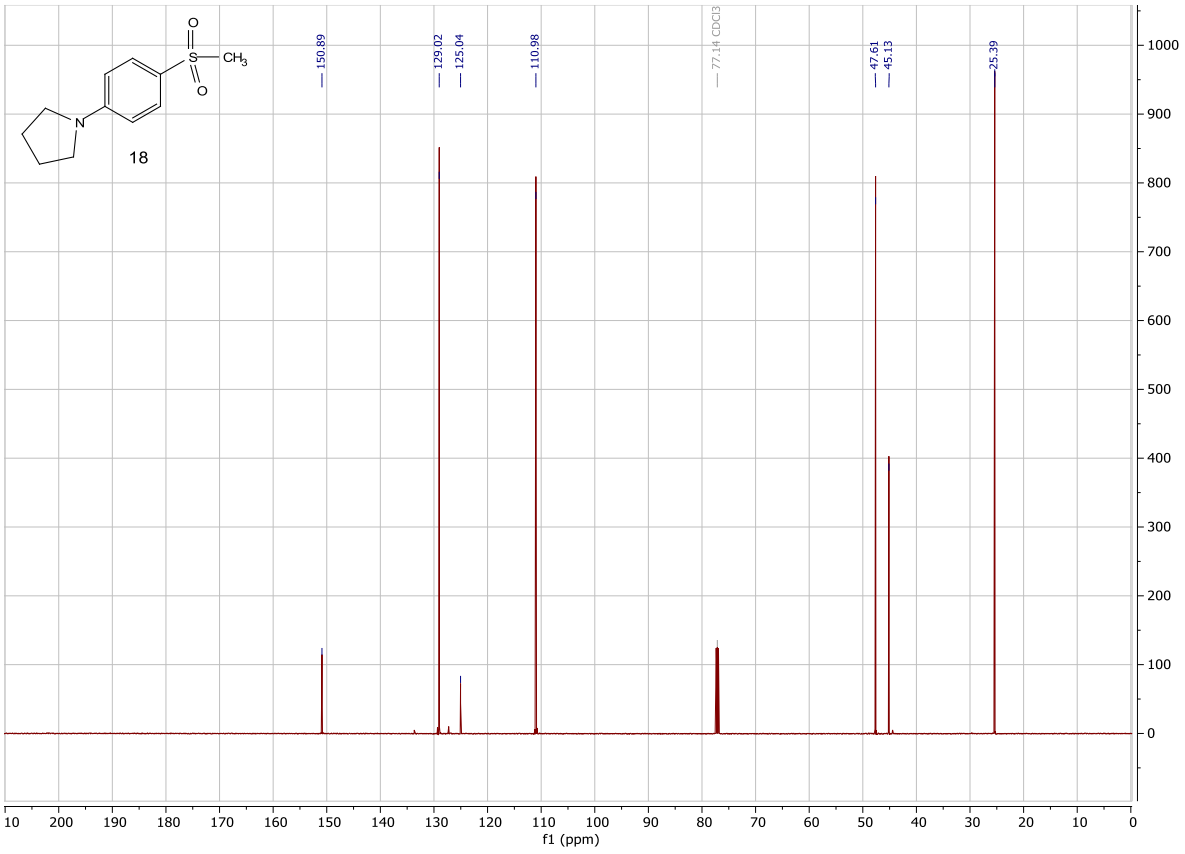

16
169.57
147.93
131.79
131.08
117.09
115.63
113.95
77.07 CDCl3
52.00
50.87
25.88
f1 (ppm)

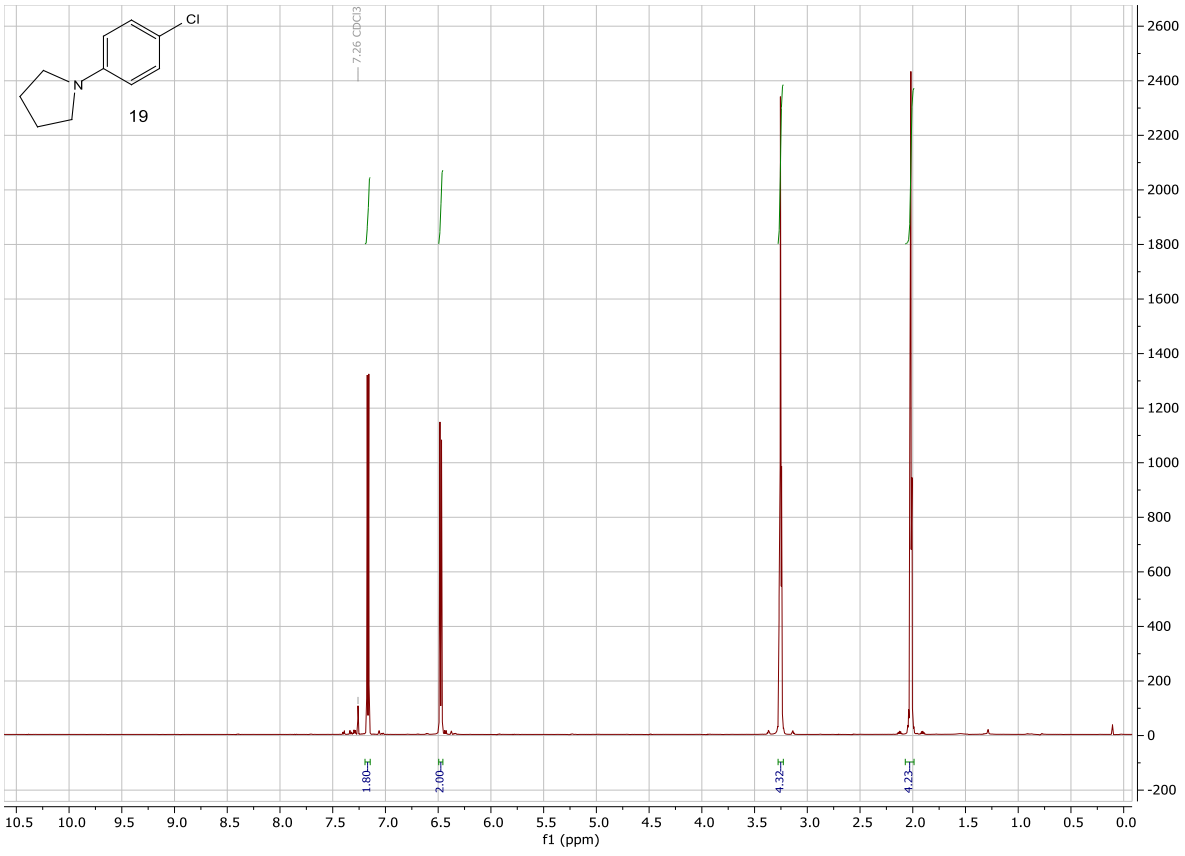

17
7.26 CDCl3
1.93
2.00
4.07
4.03
f1 (ppm)

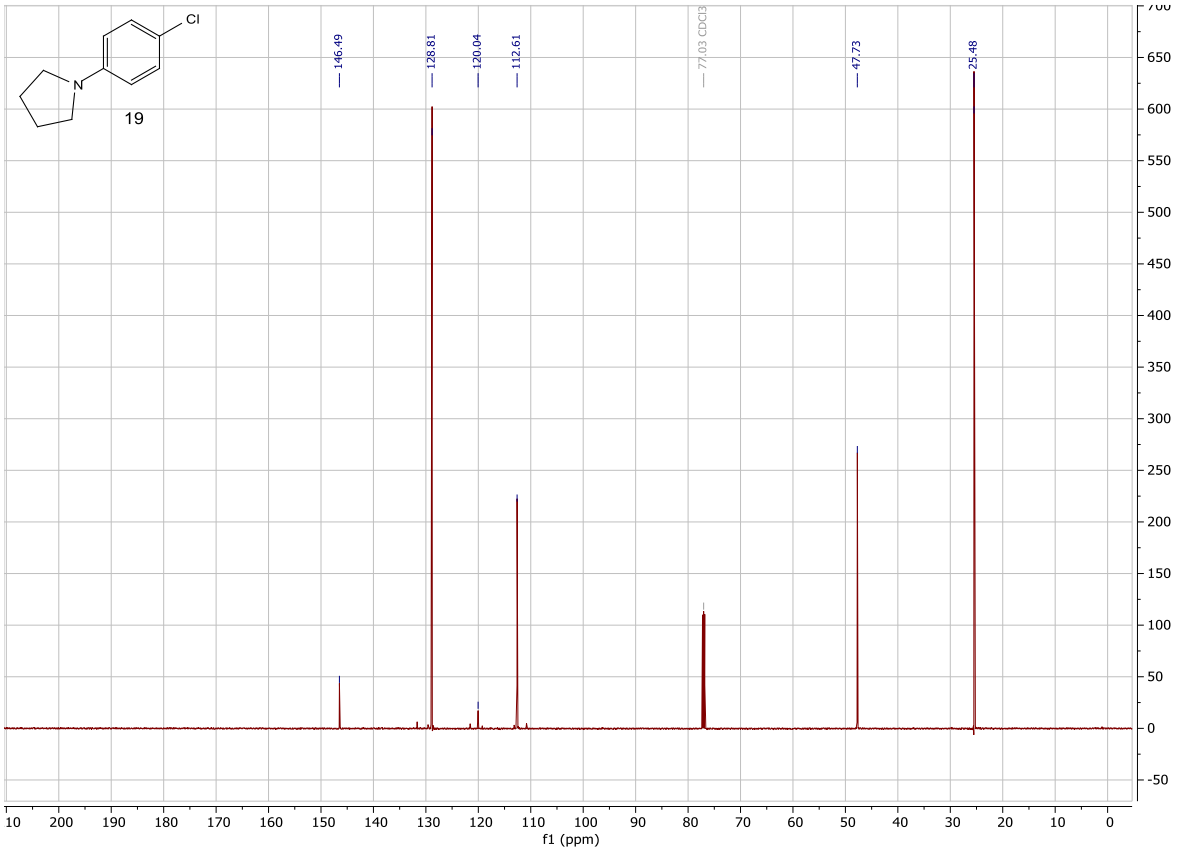

F
F
F
N
17
149.76
129.44
126.76
126.44
126.40
126.36
126.32
124.08
121.39
117.05
116.73
116.40
116.08
110.84
77.07 CDCl3
47.53
25.48
f1 (ppm)

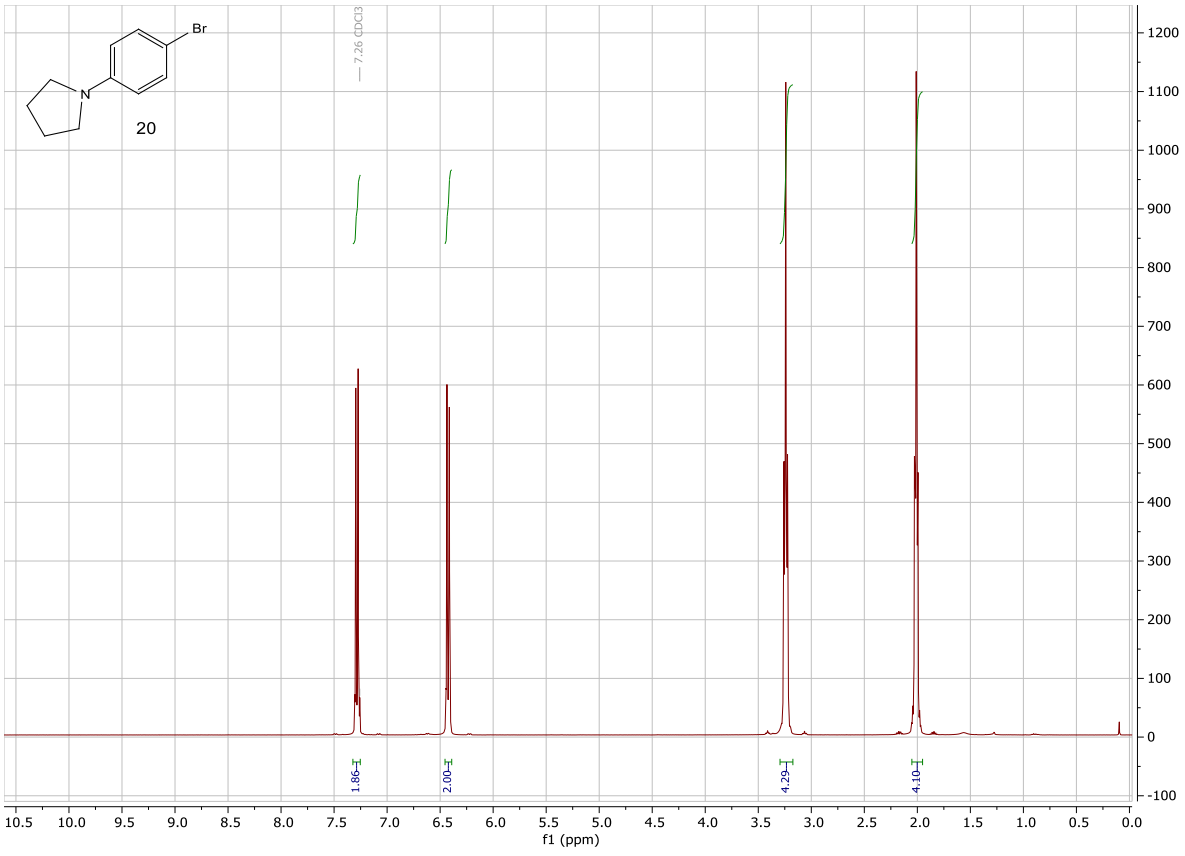

F
F
F
N
17
-60.58
f1 (ppm)

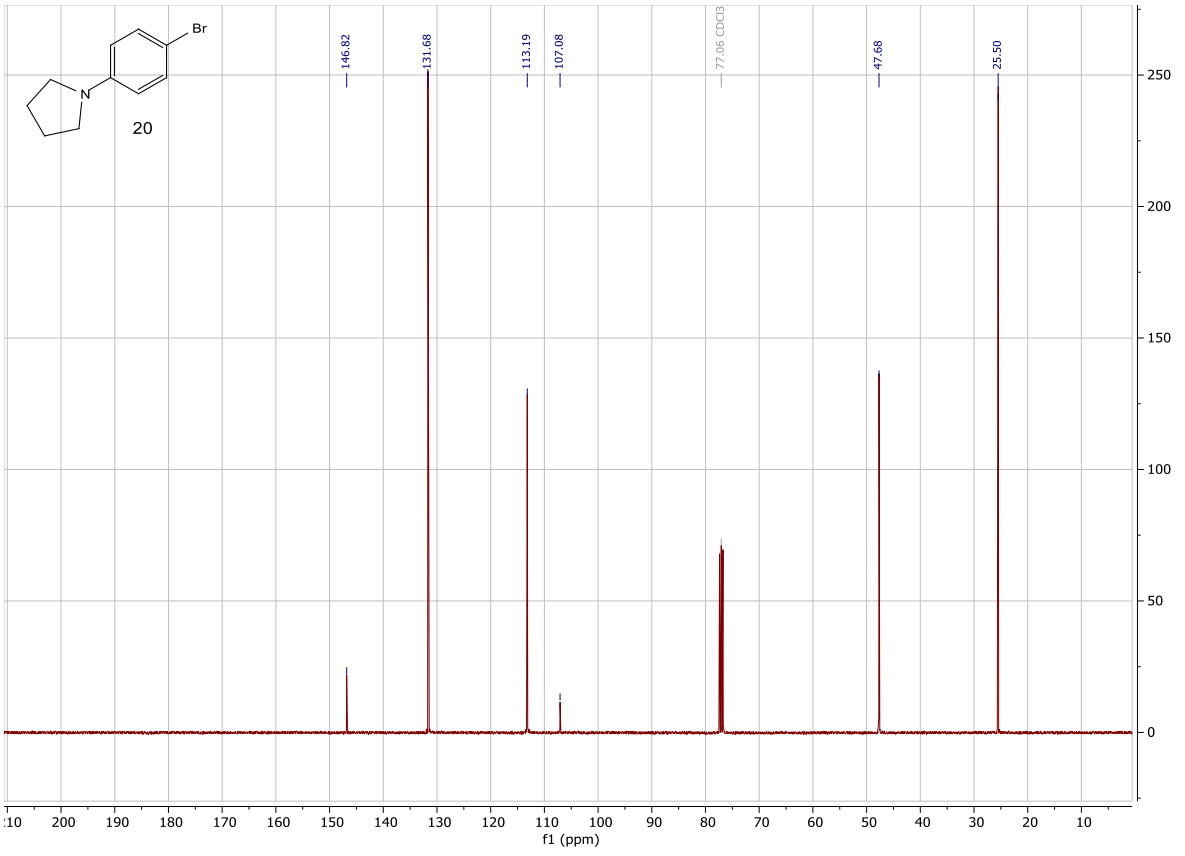

18
7.26 CDCl3
1.80
2.00
4.03
3.01
3.94
f1 (ppm)

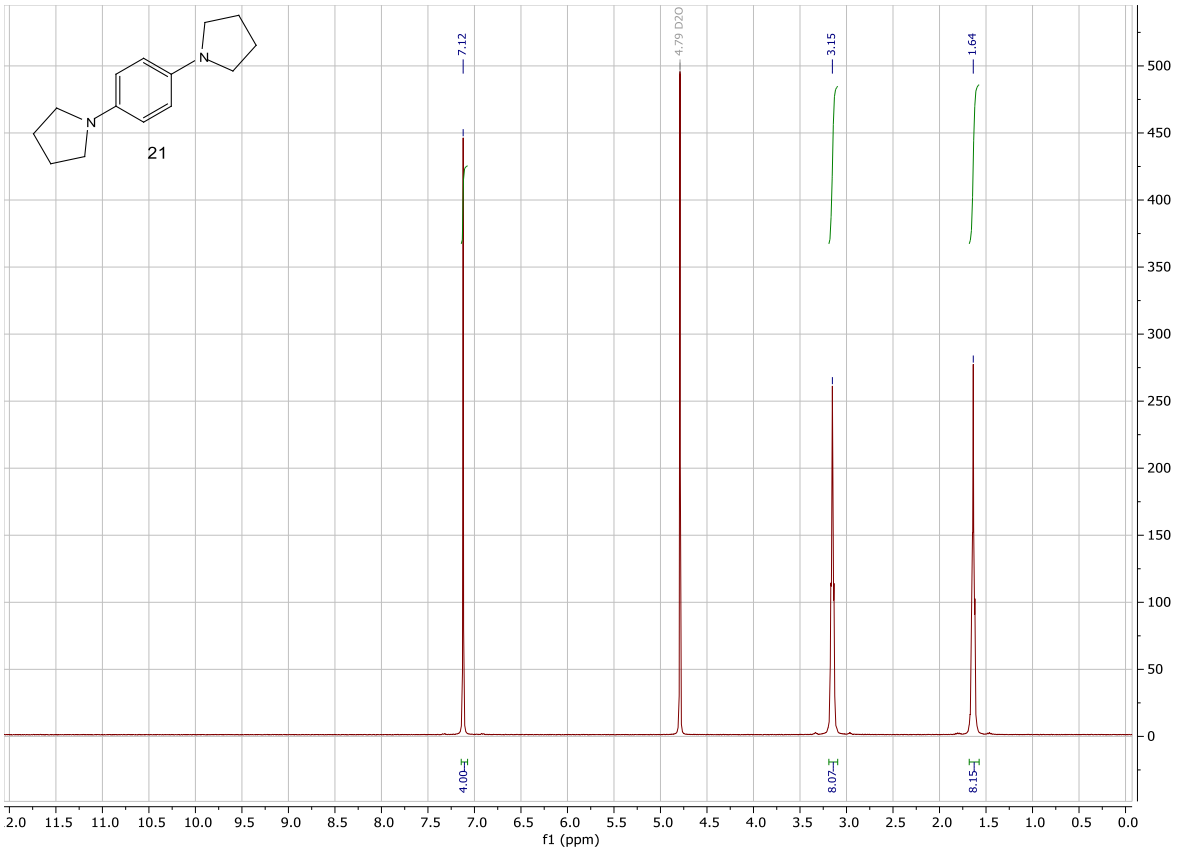

18
150.89
129.02
125.04
110.98
77.14 CDCl3
47.61
45.13
25.39
f1 (ppm)

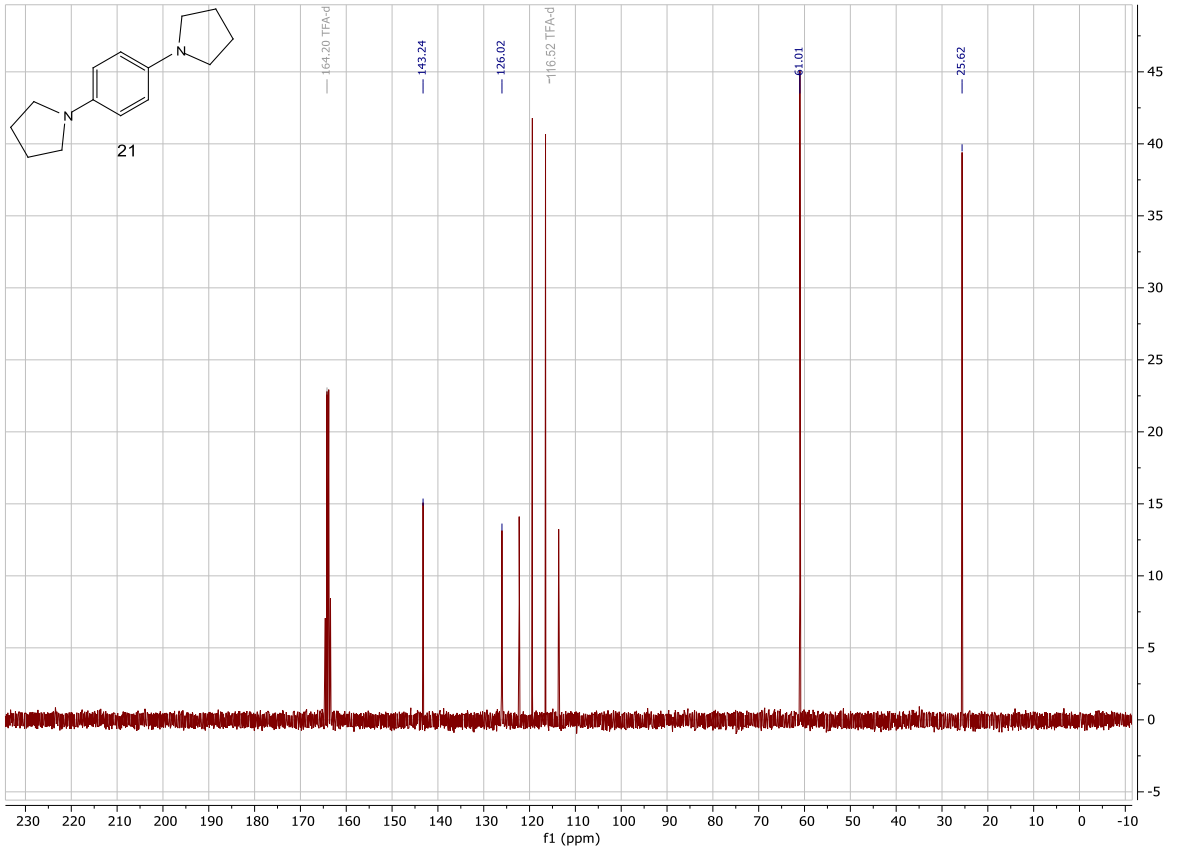

Cl
N
19
7.26 CDCl3
1.80
2.00
4.32
4.23
f1 (ppm)

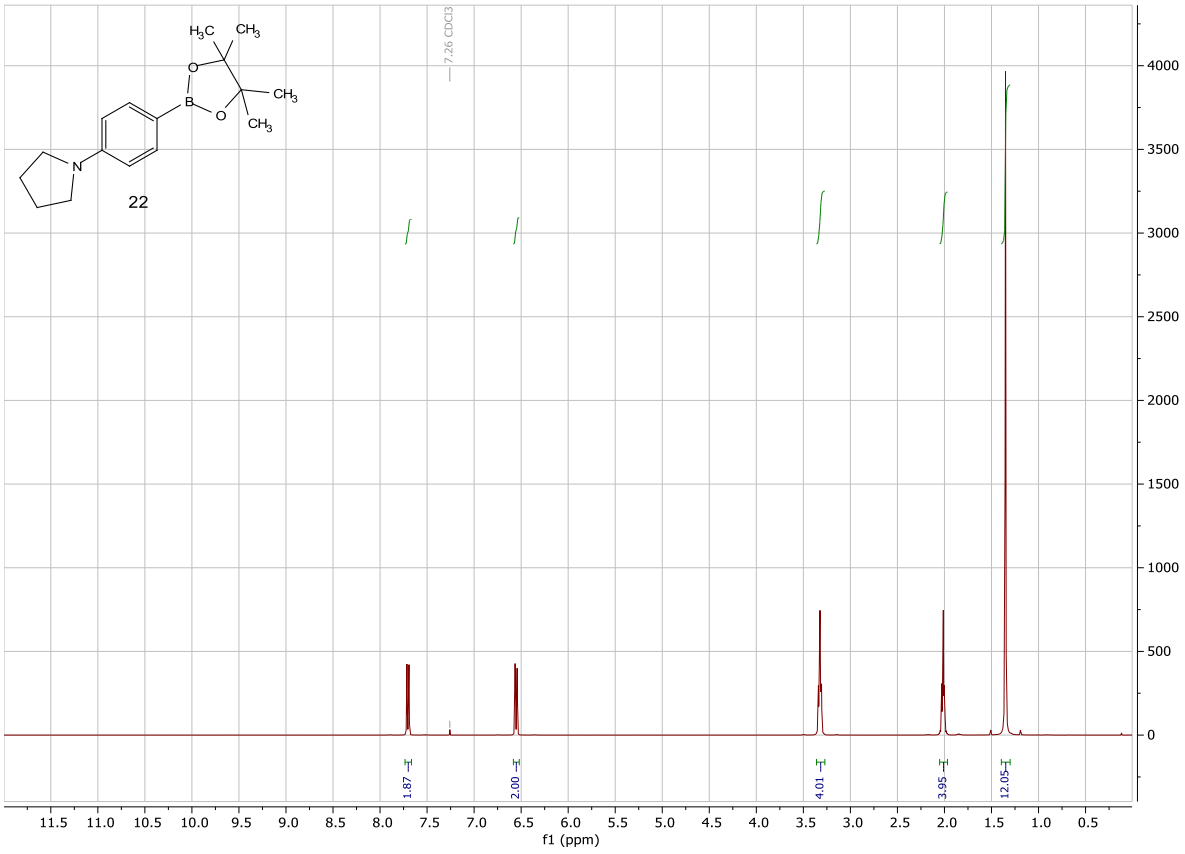

Cl
N
19
146.49
128.81
120.04
112.61
77.03 CDCl3
47.73
25.48
f1 (ppm)

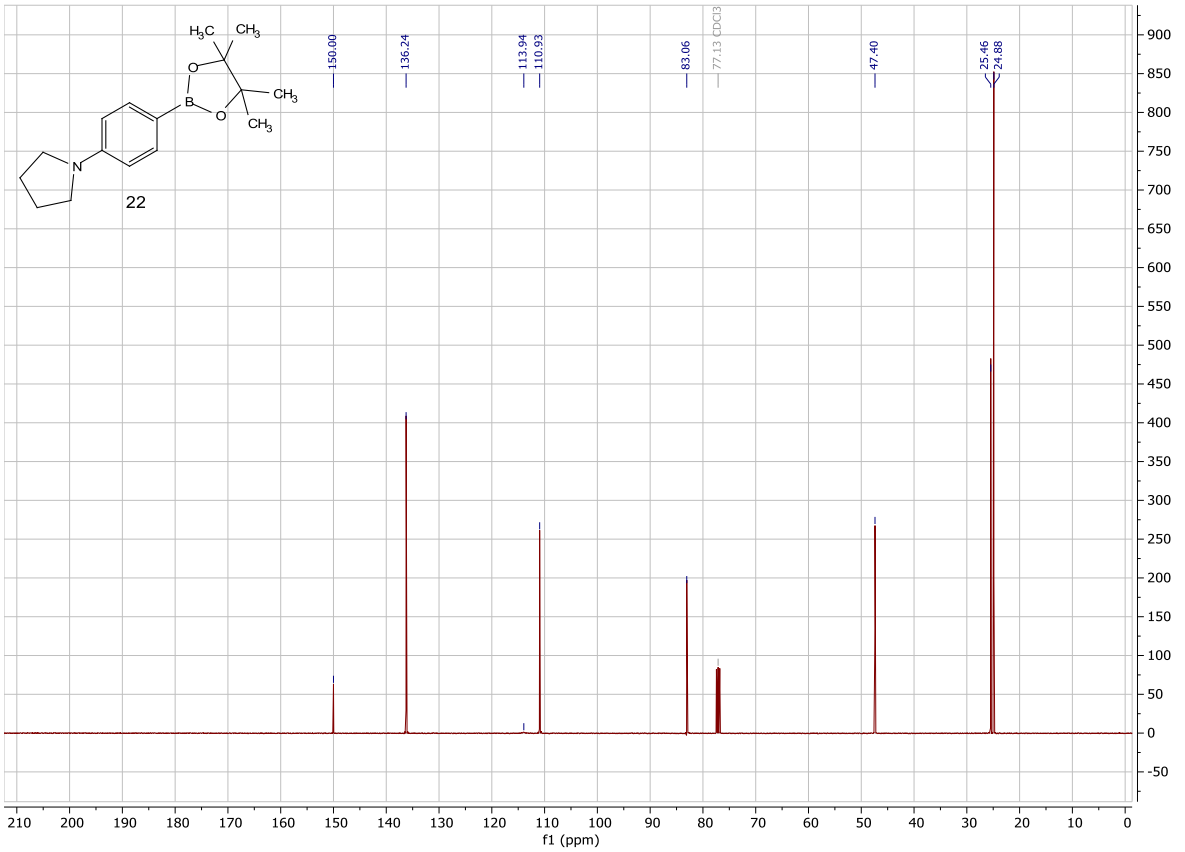

Br
N
20
7.26 CDCl3
1.86
2.00
4.29
4.10
f1 (ppm)

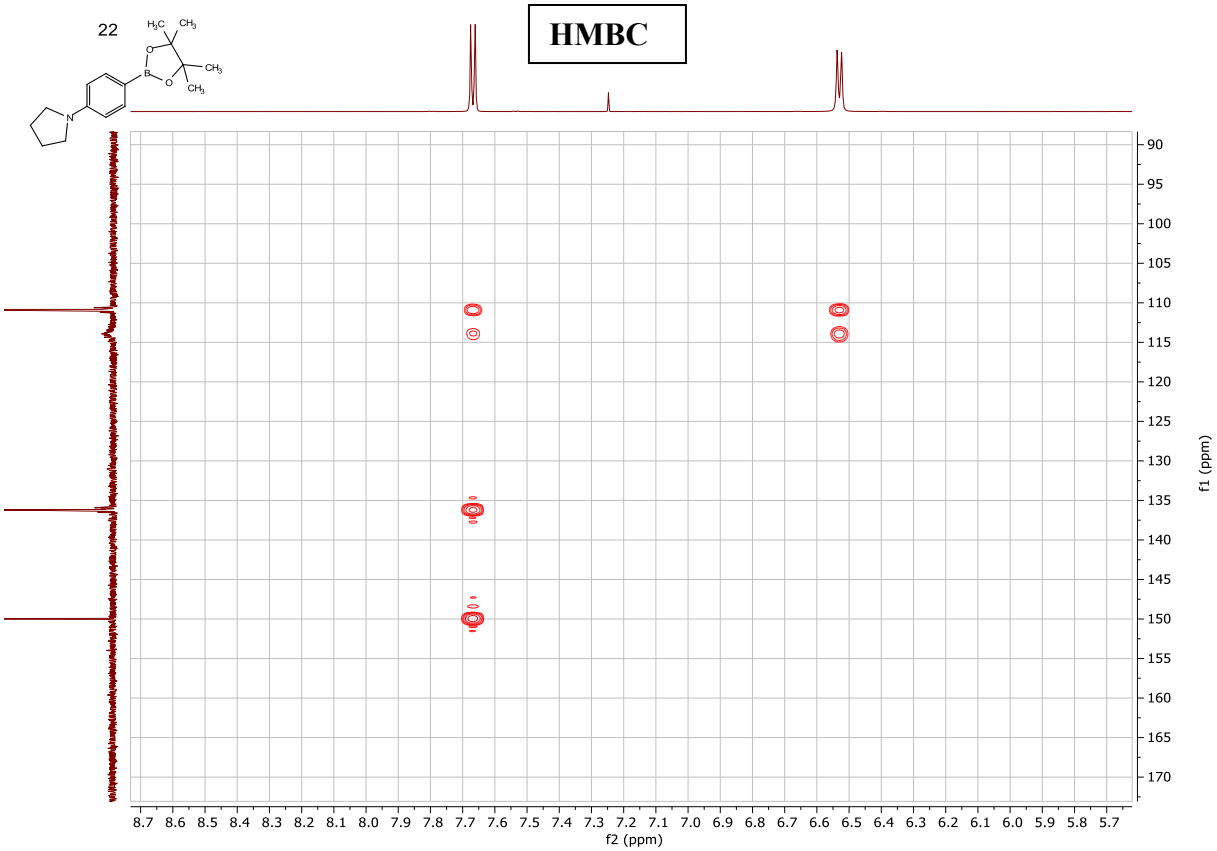

Br
N
20
146.82
131.68
113.19
107.08
77.06 CDCl3
47.68
25.50
f1 (ppm)

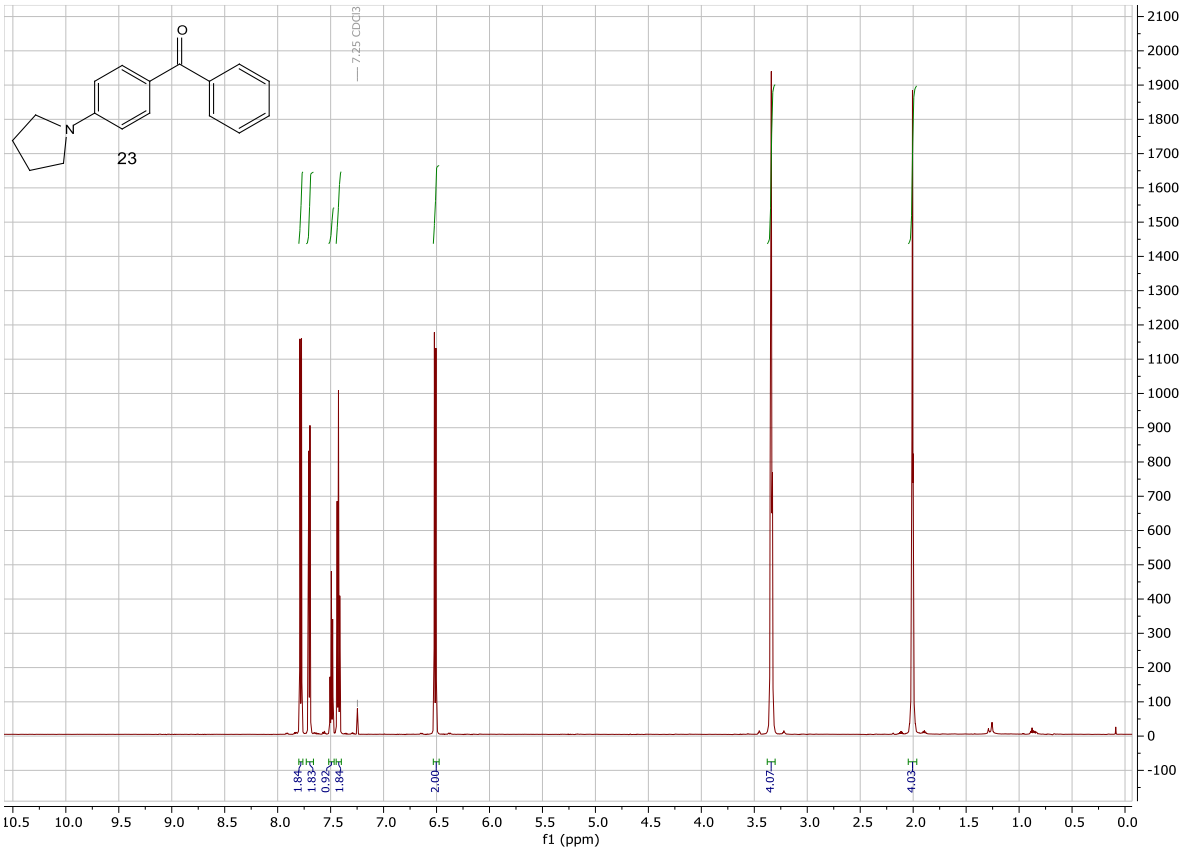

21
7.12
4.79 D2O
3.15
1.64
4.00
8.07
8.15
f1 (ppm)

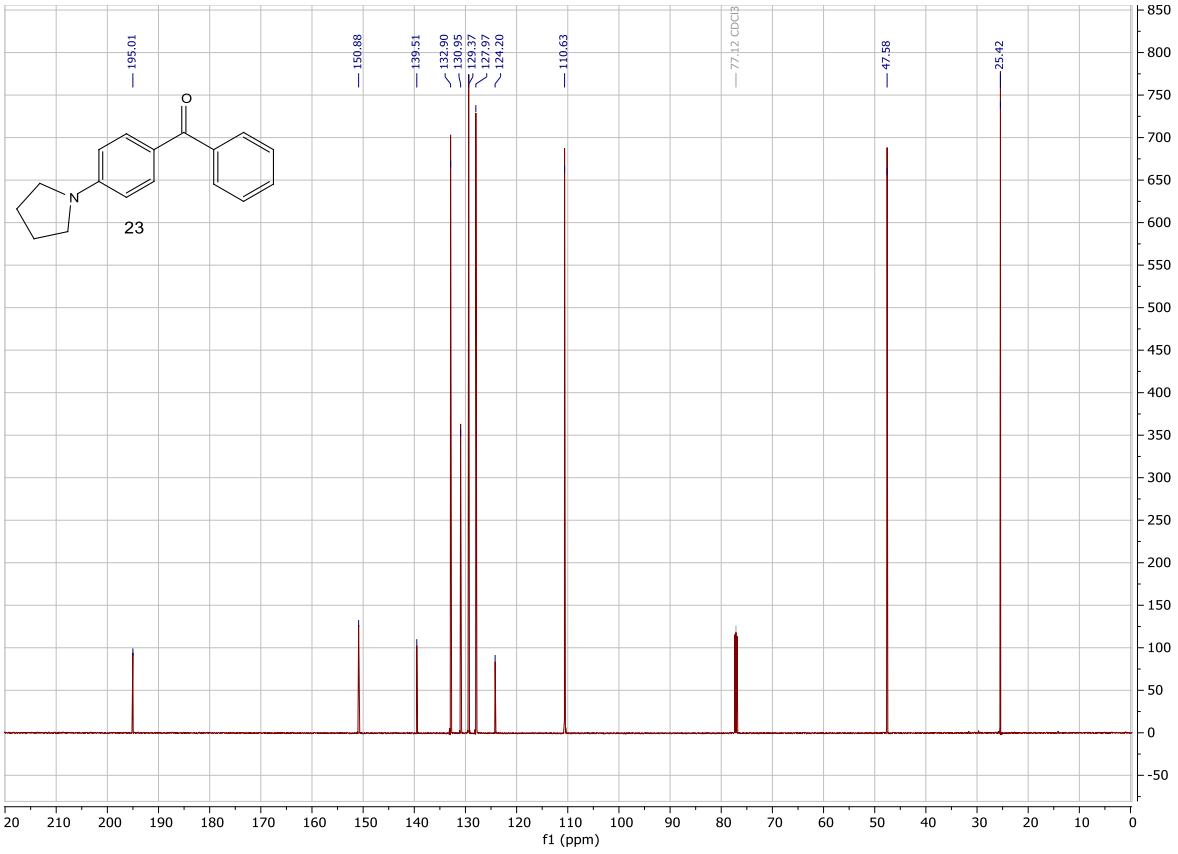

21
164.20 TFA-d
143.24
126.02
116.52 TFA-d
61.01
25.62
f1 (ppm)

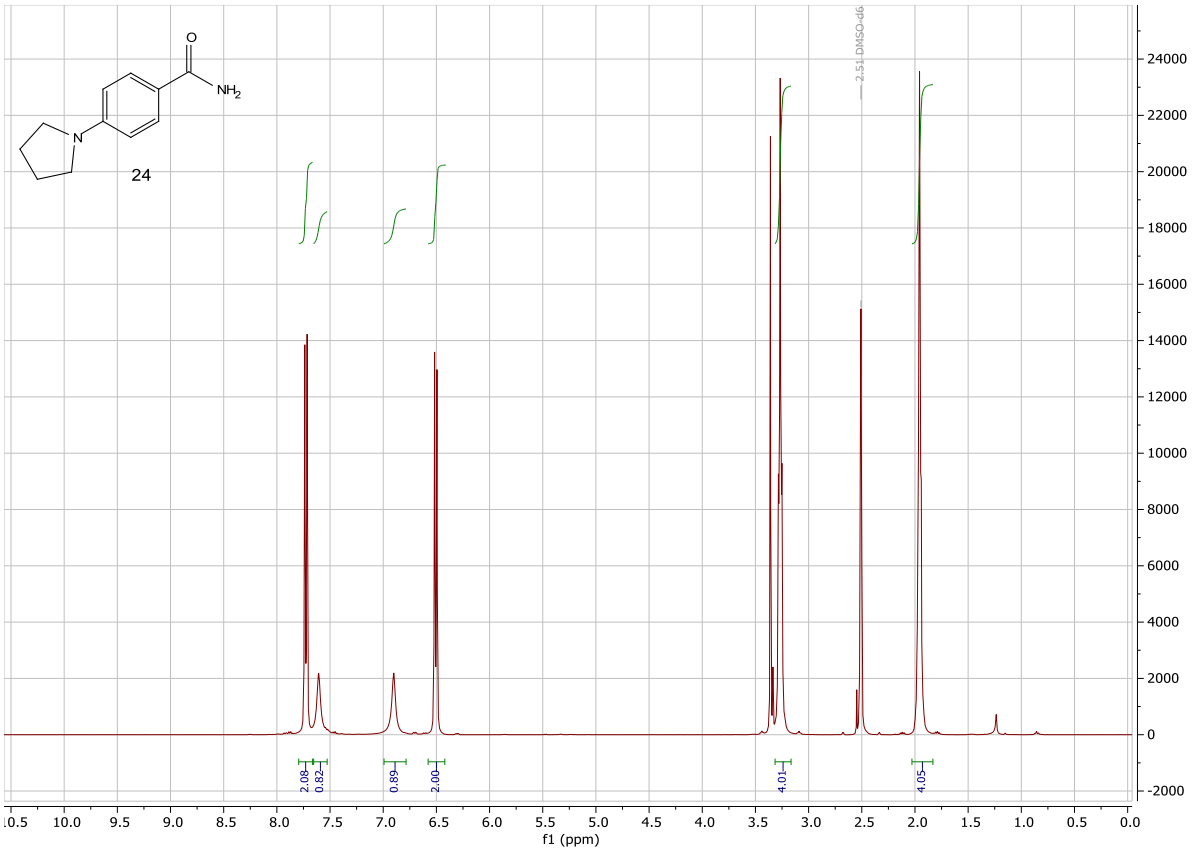

22
7.26 CDCl3
1.87
2.00
4.01
3.95
12.05
f1 (ppm)

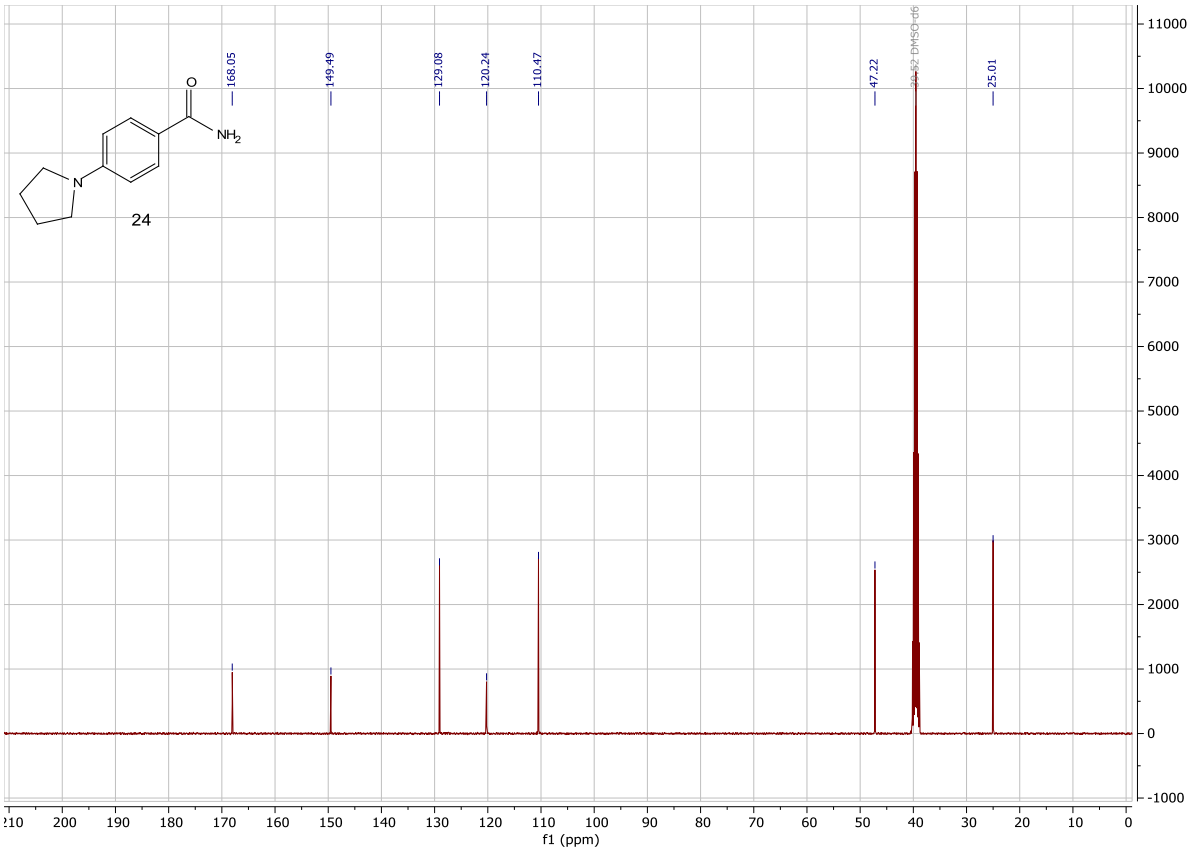

22
150.00
136.24
113.94
110.93
83.06
77.13 CDCl3
47.40
25.46
24.88
f1 (ppm)

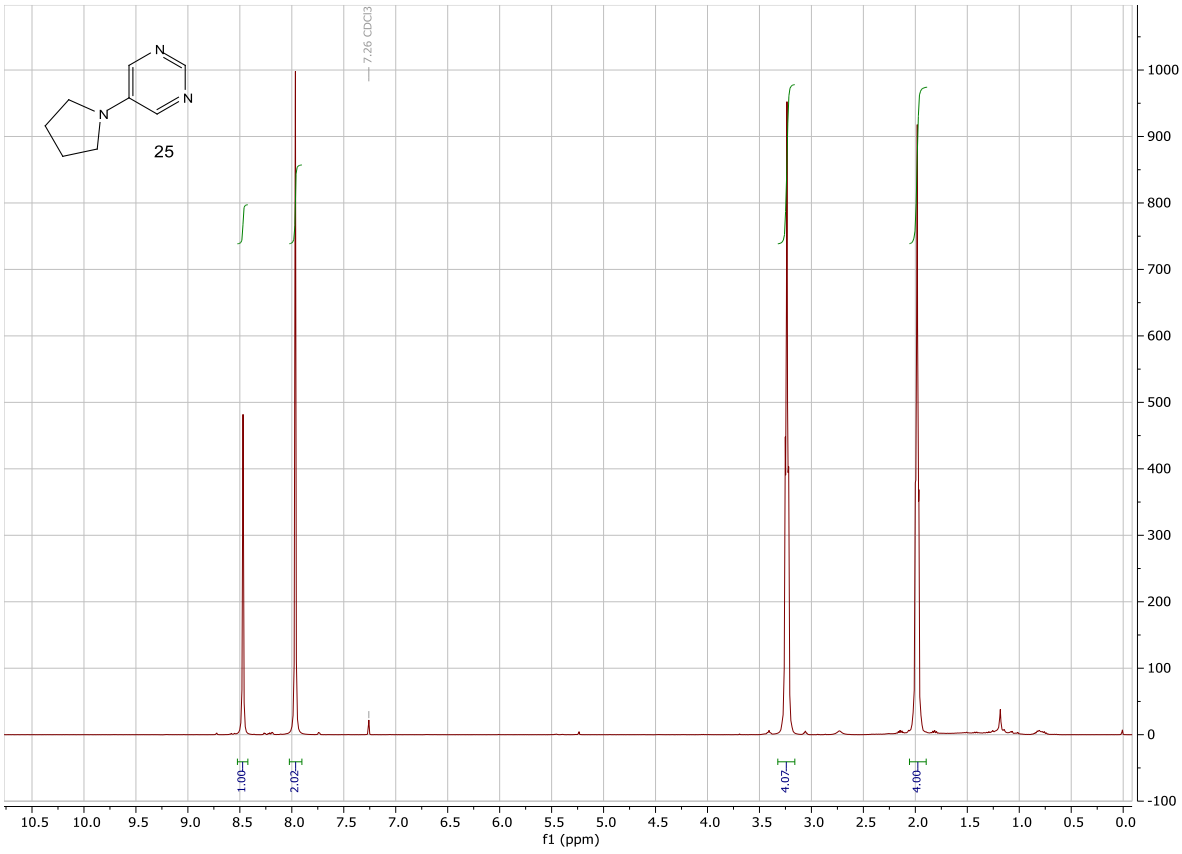

HMBC
22
f2 (ppm)
f1 (ppm)

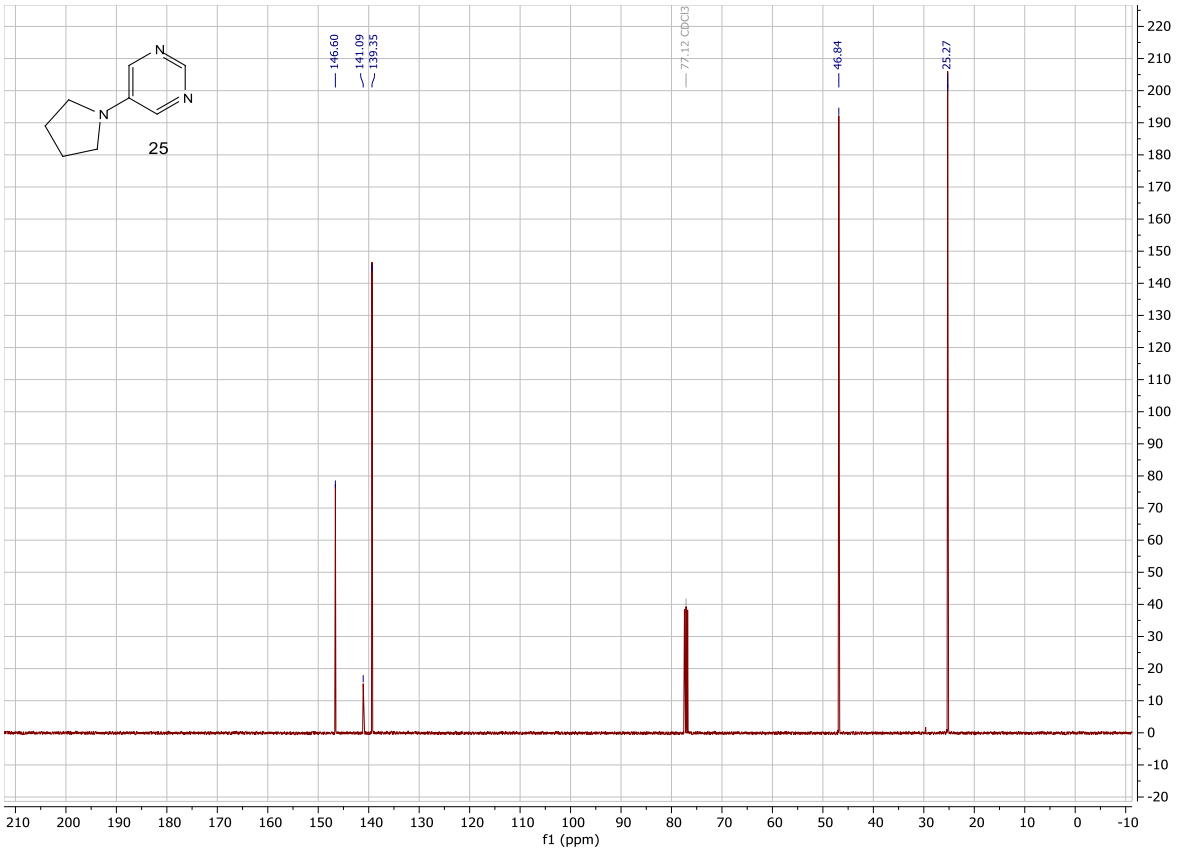

23
7.25 CDCl3
1.84
1.83
0.92
1.84
2.00
4.07
4.03
f1 (ppm)

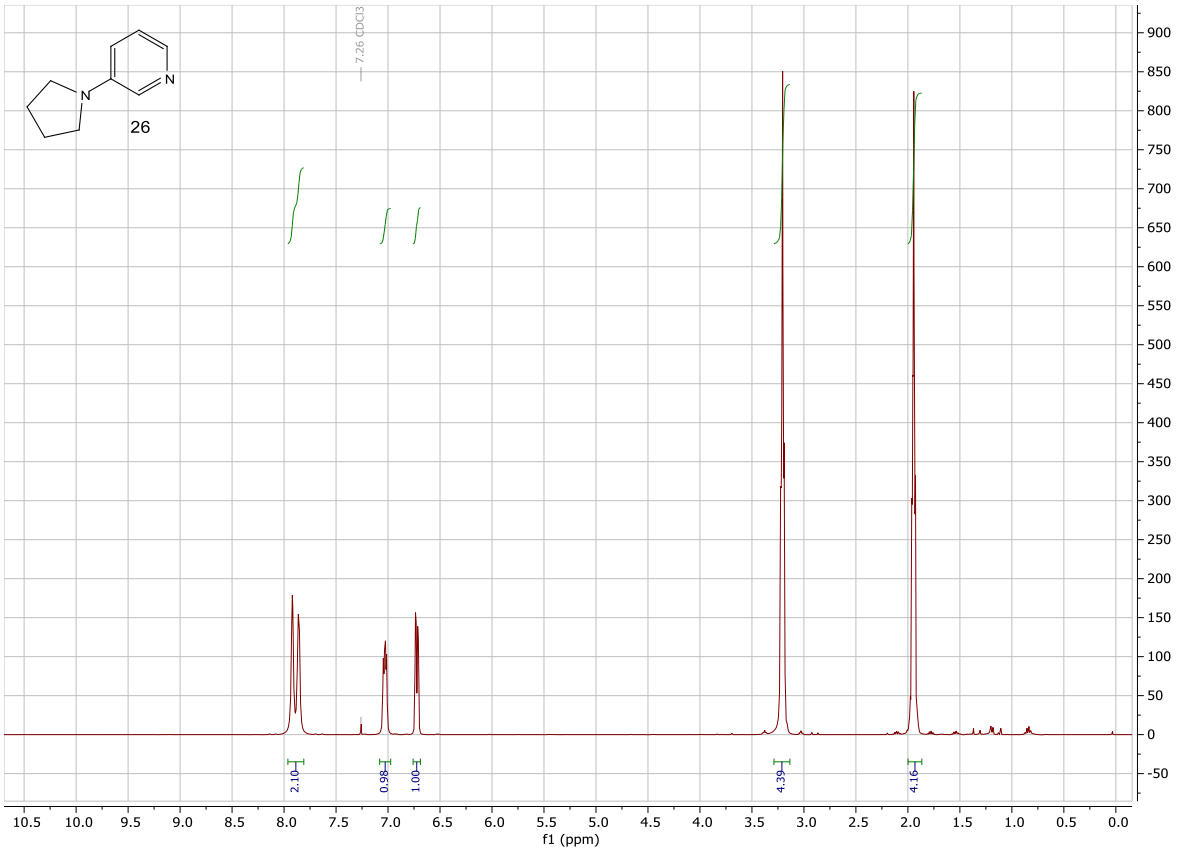

195.01
150.88
139.51
132.90
130.95
129.37
127.97
124.20
110.63
77.12 CDCl3
47.58
25.42
O
N
23
f1 (ppm)

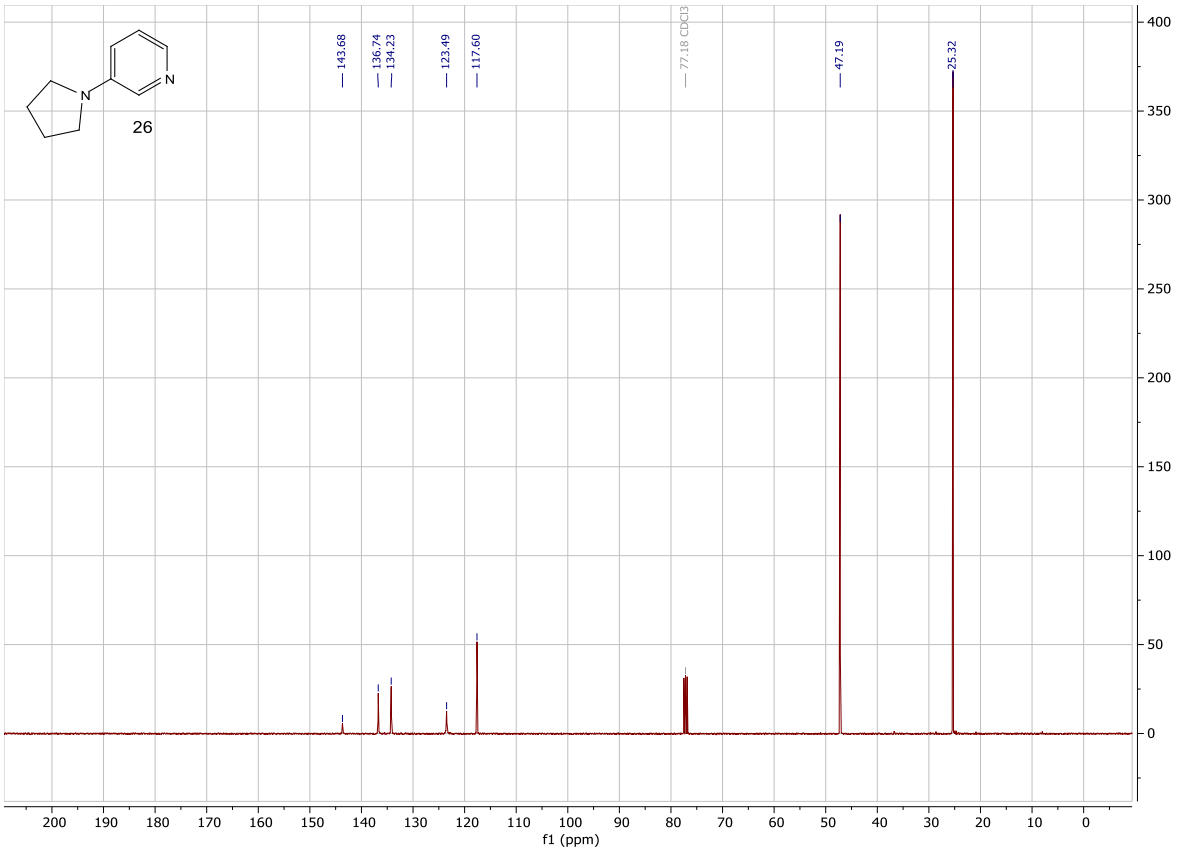

O
NH2
N
24
2.51 DMSO-d6
2.08
0.82
0.89
2.00
4.01
4.05
f1 (ppm)

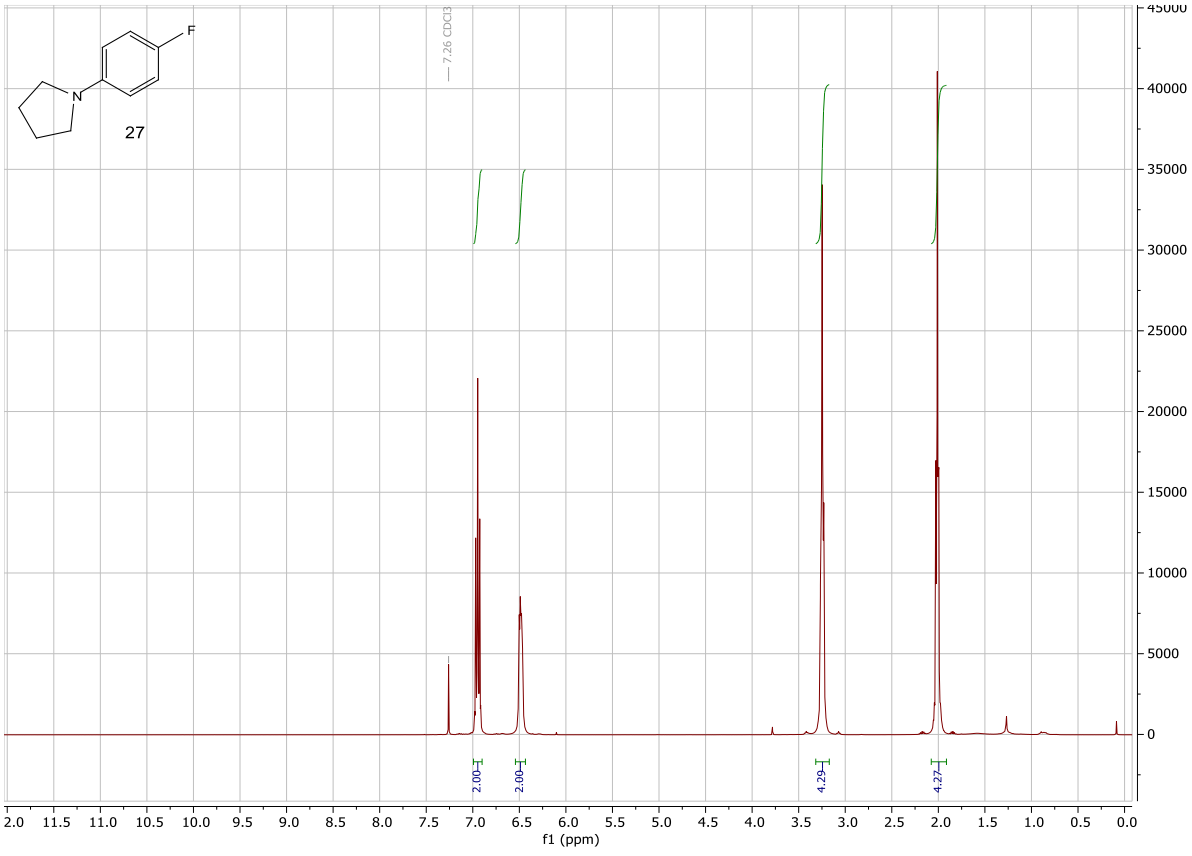

168.05
149.49
129.08
120.24
110.47
47.22
39.52 DMSO-d6
25.01
O
NH2
N
24
f1 (ppm)

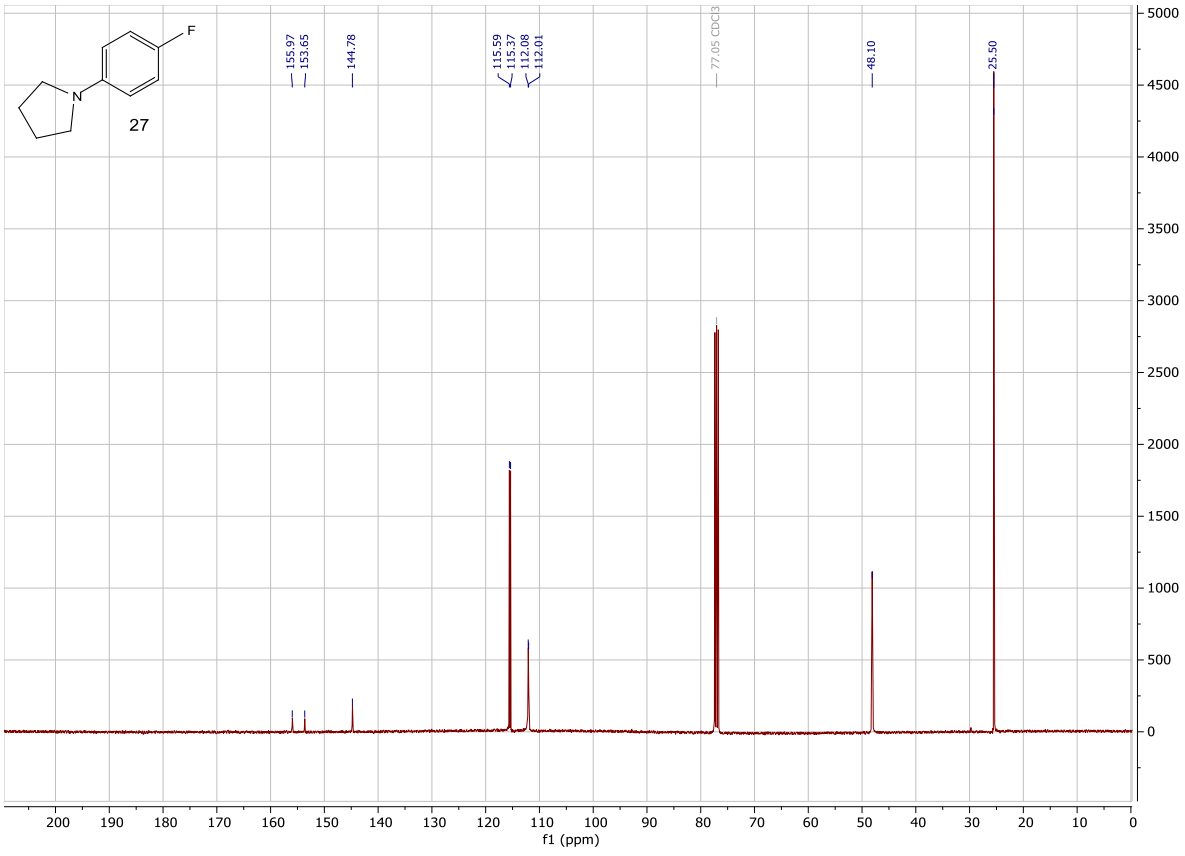

7.26 CDCl3
N
N
N
25
1.00
2.02
4.07
4.00
f1 (ppm)

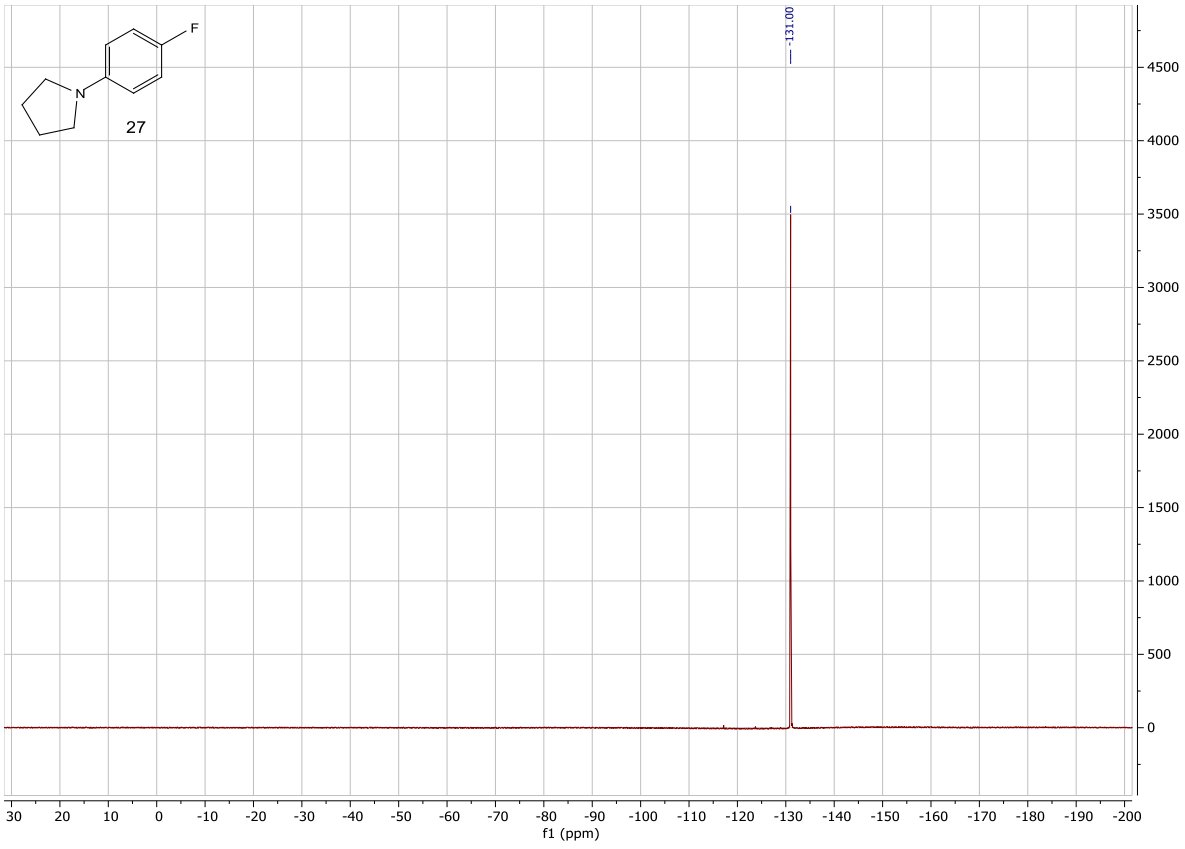

25
146.60
141.09
139.35
77.12 CDCl3
46.84
25.27
f1 (ppm)

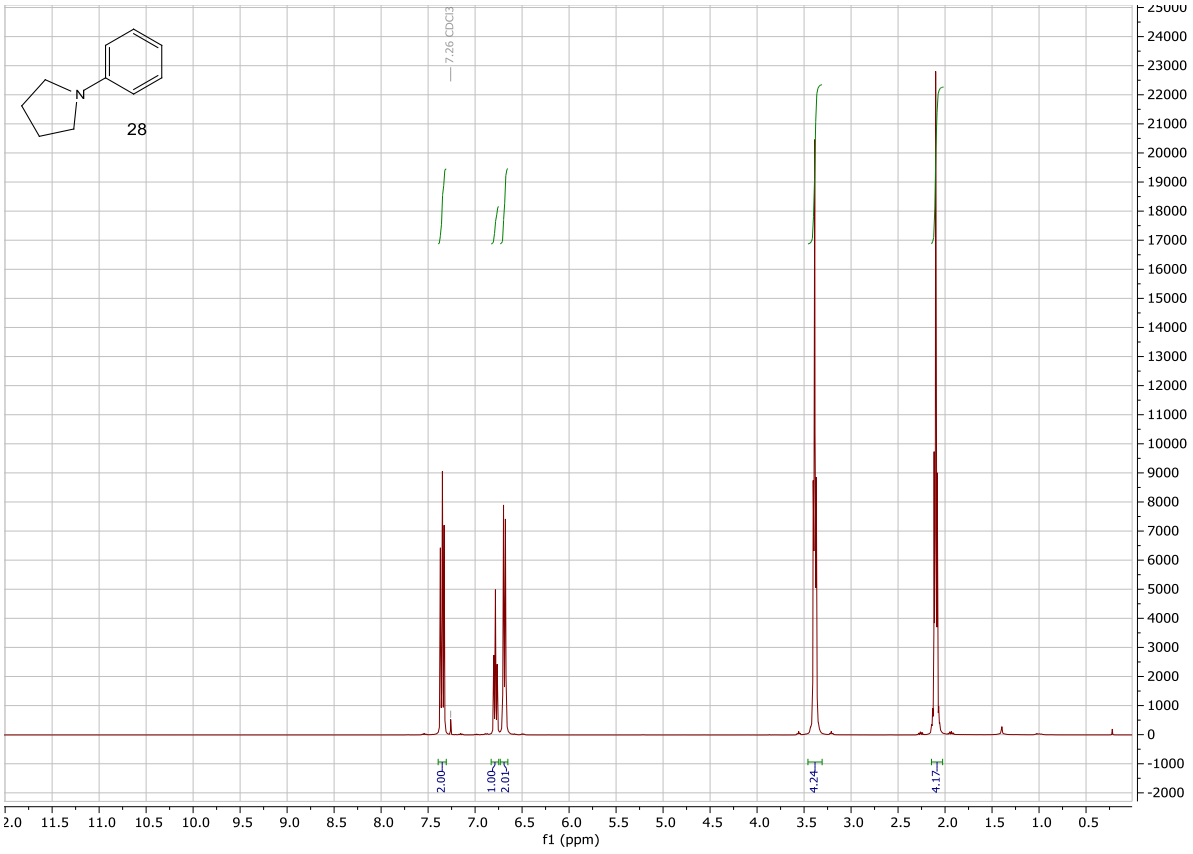

26
7.26 CDCl3
2.10
0.98
1.00
4.39
4.16
f1 (ppm)

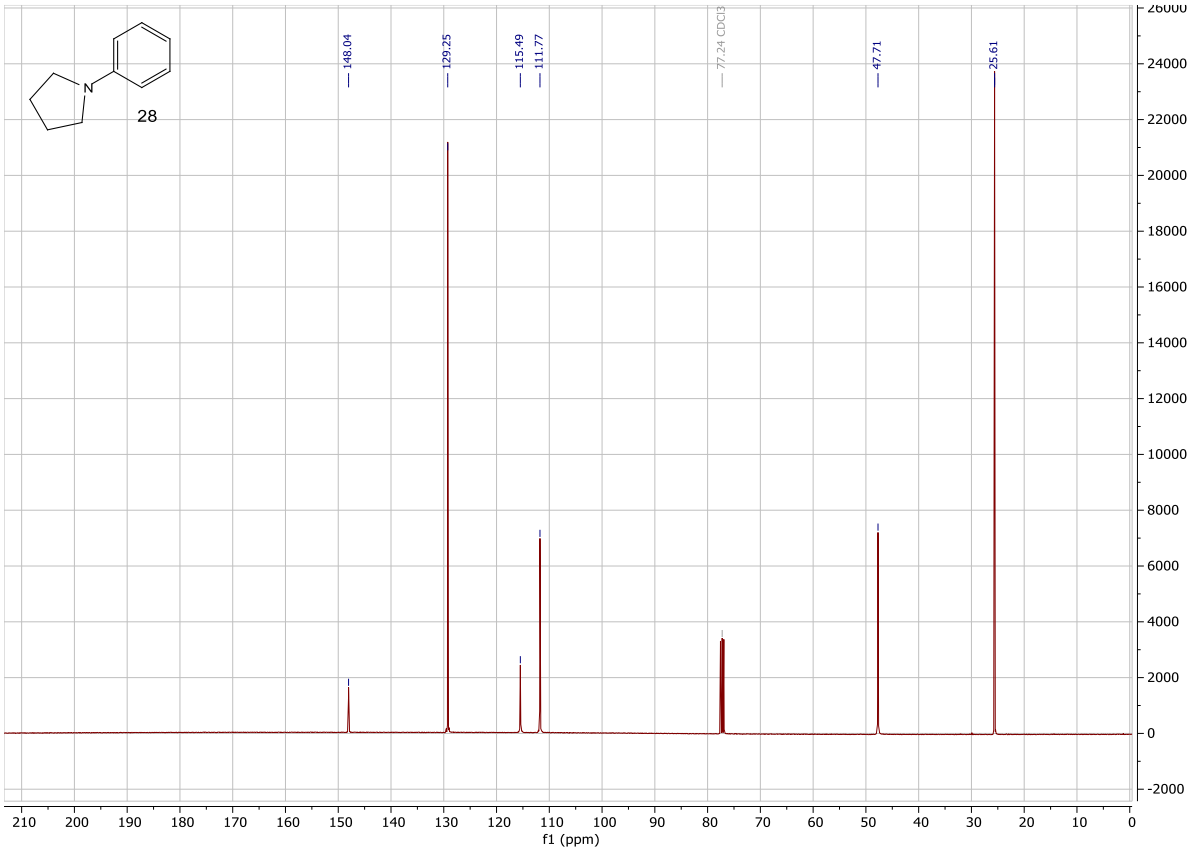

26
143.68
136.74
134.23
123.49
117.60
77.18 CDCl3
47.19
25.32
f1 (ppm)

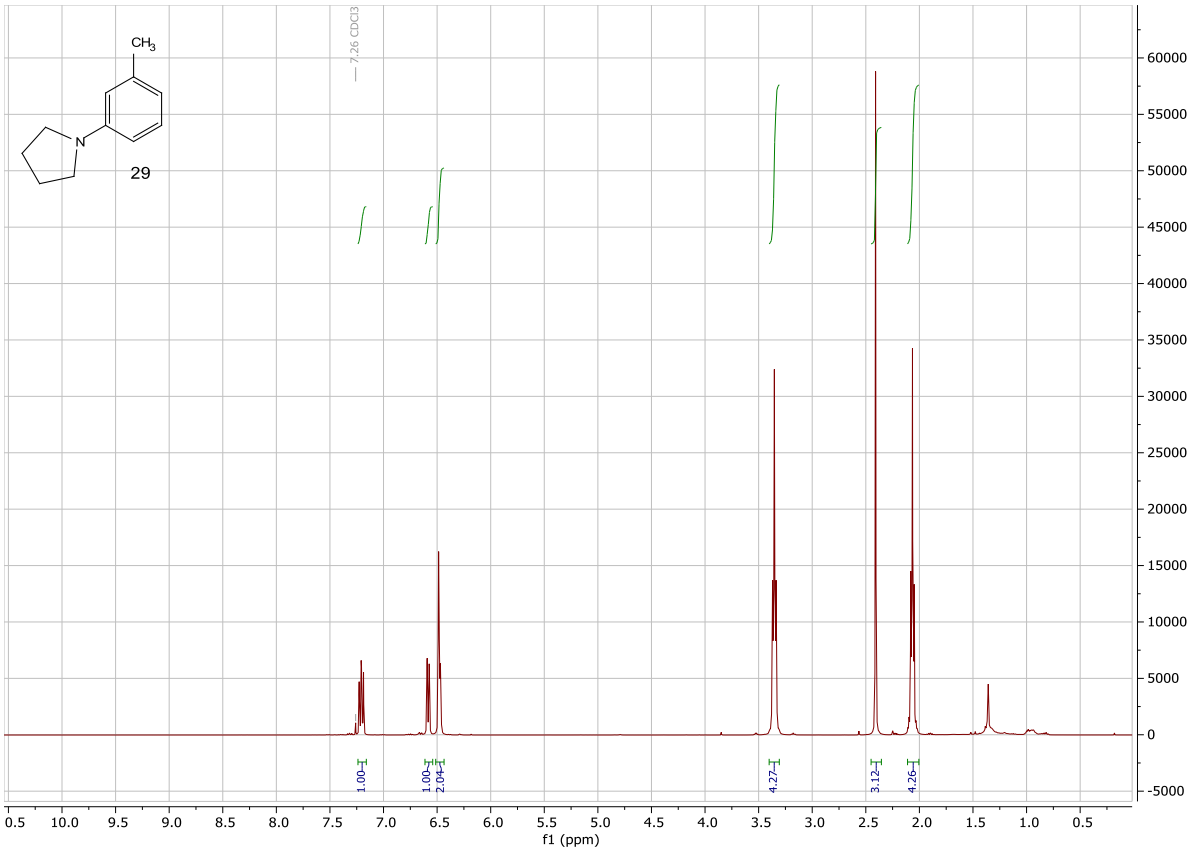

27
7.26 CDCl3
2.00
2.00
4.29
4.27
f1 (ppm)

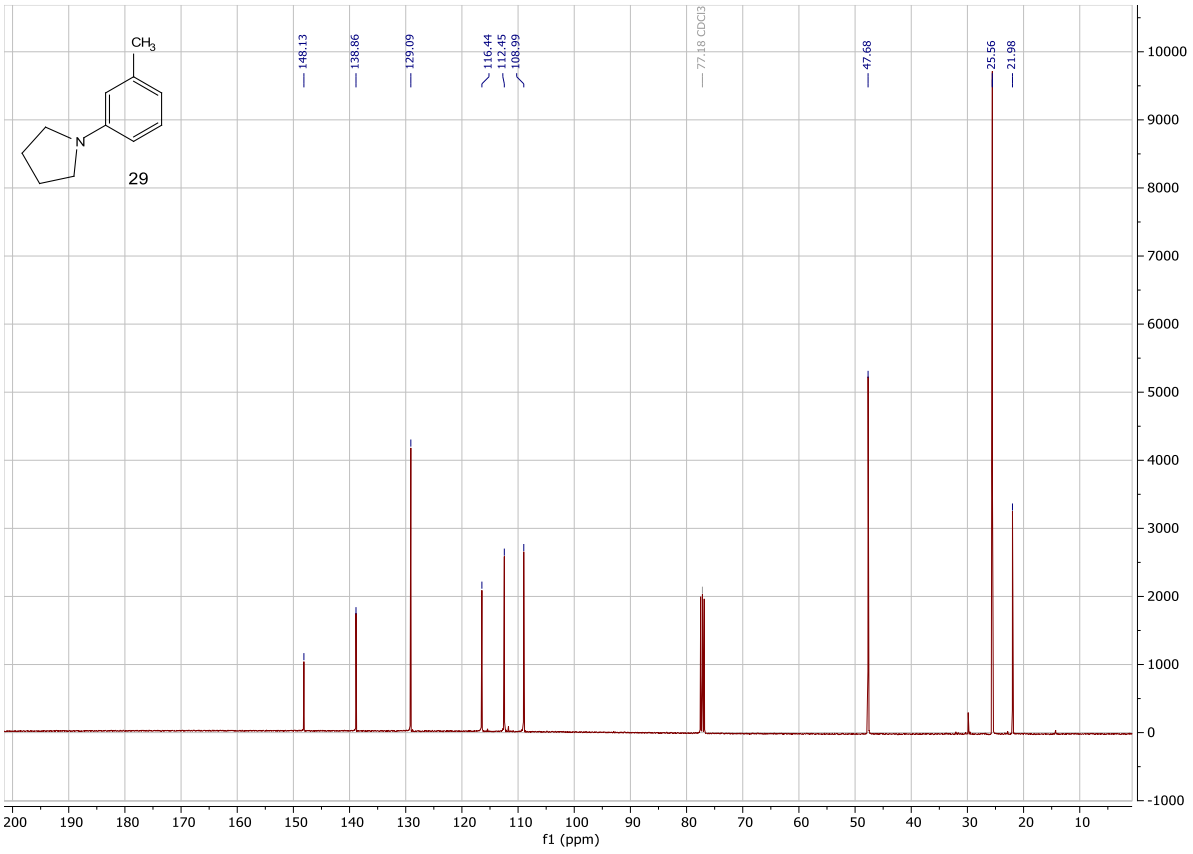

F
N
27
155.97
153.65
144.78
115.59
115.37
112.08
112.01
77.05 CDCl3
48.10
25.50
f1 (ppm)

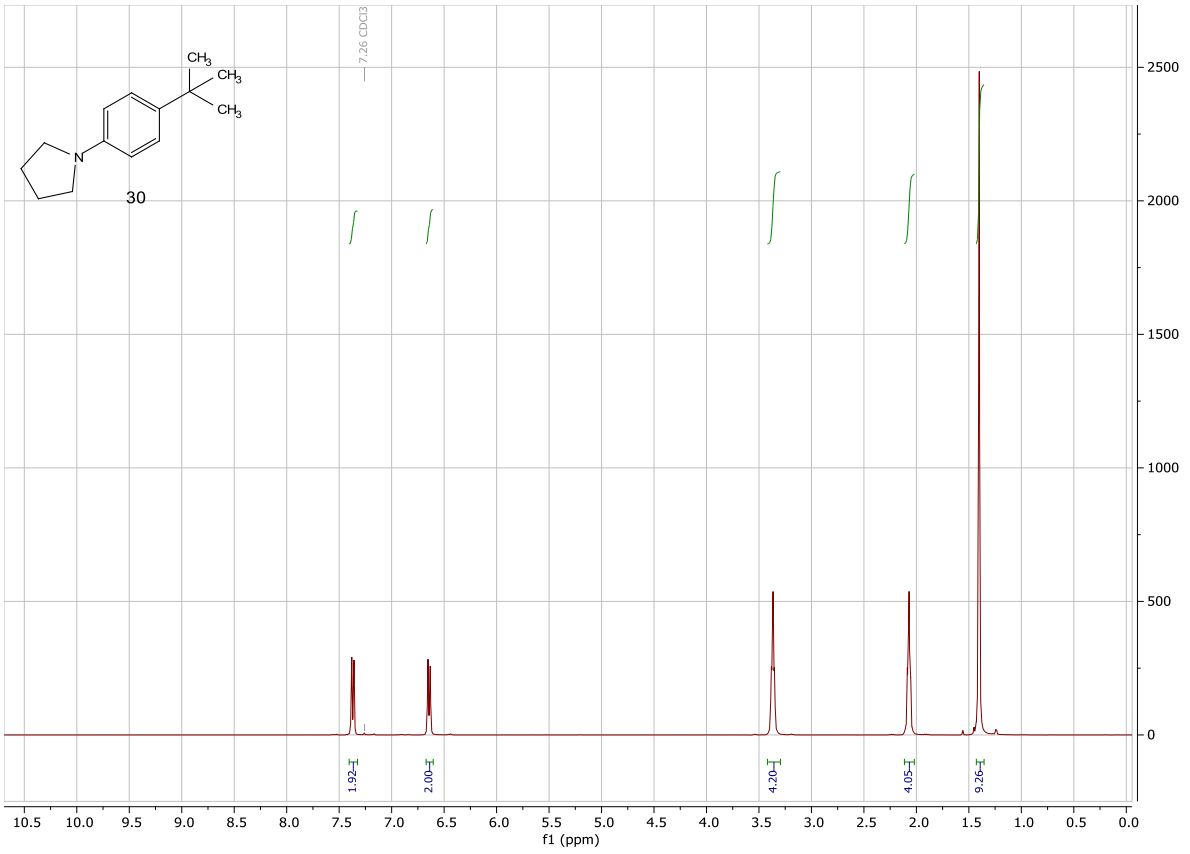

F
N
27
-131.00
f1 (ppm)

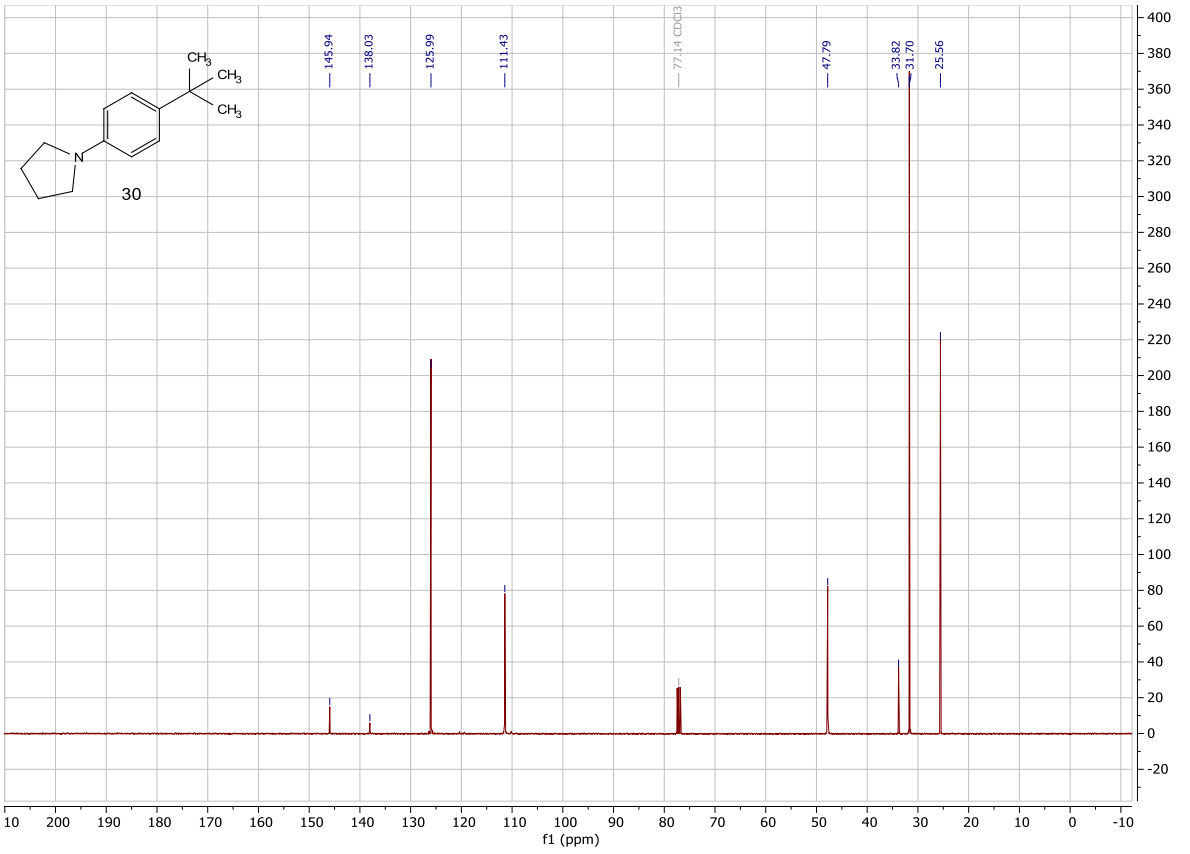

28
7.26 CDCl3
2.00
1.00
2.01
4.24
4.17
f1 (ppm)

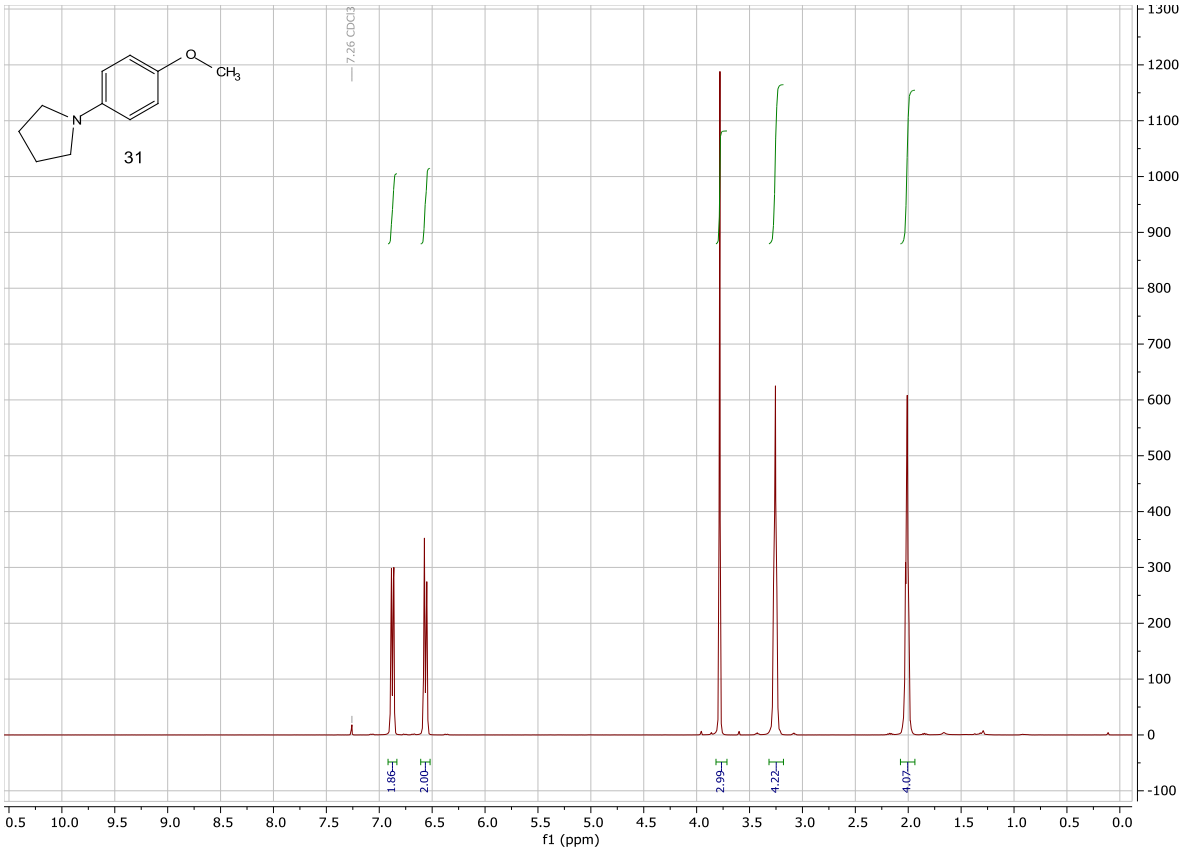

28
148.04
129.25
115.49
111.77
77.24 CDCl3
47.71
25.61
f1 (ppm)

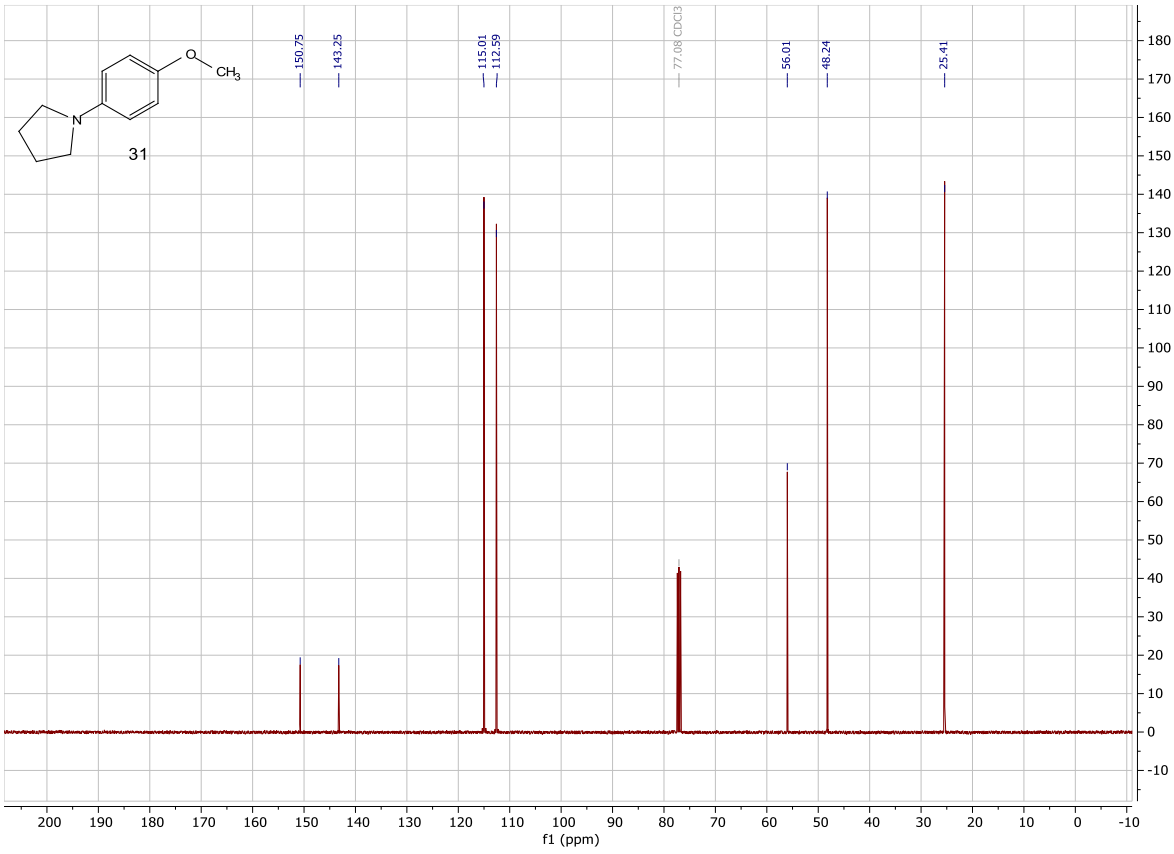

CH3
N
29
7.26 CDCl3
1.00
1.00
2.04
4.27
3.12
4.26
f1 (ppm)


CH3
N
29
148.13
138.86
129.09
116.44
112.45
108.99
77.18 CDCl3
47.68
25.56
21.98
f1 (ppm)


CH3
CH3
CH3
N
30
7.26 CDCl3
1.92
2.00
4.20
4.05
9.26
f1 (ppm)


CH3
CH3
CH3
N
30
145.94
138.03
125.99
111.43
77.14 CDCl3
47.79
33.82
31.70
25.56
f1 (ppm)


31
7.26 CDCl3
1.86
2.00
2.99
4.22
4.07
f1 (ppm)


31
150.75
143.25
115.01
112.59
77.08 CDCl3
56.01
48.24
25.41
f1 (ppm)