[Supporting Information]

Ni Single Atoms on Carbon Nitride for Visible-Light-Promoted Full Heterogeneous Dual Catalysis

Minjoon Kwak,[⊥] Jinsol Bok,[⊥] Byoung-Hoon Lee,[⊥] Jongchan Kim, Youngran Seo, Sumin Kim, Hyunwoo Choi, Wonjae Ko, Wytse Hooch Antink, Chan Woo Lee, Guk Hee Yim, Hyojin Seung, Chansul Park, Kug-Seung Lee, Dae-Hyeong Kim, Taeghwan Hyeon,[*] and Dongwon Yoo[*]

This file includes:

[⊥] These authors contributed equally to this work.

[*] To whom correspondence should be addressed.

Email: thyeon@snu.ac.kr (T. H.); dwyoo@snu.ac.kr (D. Y.)

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1. General information

General reagent information

All reagents were obtained from Sigma-Aldrich, Alfa Aesar, Tokyo Chemical Industry, Merck, and Samchun Chemical and used as received without further purification. Thin-layer chromatography (TLC) was run on a SiO_2 plate, then visualized under UV light (254 nm), followed by a phosphomolybdic acid staining solution. Irradiation of the reaction mixture was carried out under commercial blue LED or 40 W blue LED light source (A160WE Tuna Blue Kessil lamp).

Characterization

TEM images were obtained on a JEOL EM-2010 microscope operated at 200 kV. EDS mappings were conducted in STEM mode equipped with a single drift detector (X-MAX^N, Oxford Instruments). Atomic-resolution imaging was performed at 200 kV using a spherical aberration-corrected JEM ARM-200F (Cold FEG Type, JEOL) installed at the National Center for Inter-University Research Facilities at Seoul National University. XPS measurements were conducted using the K-Alpha$^+$ XPS system (Thermo Fisher Scientific) at the Busan Center of the Korea Basic Science Institute (KBSI). The X-ray source of 1,486.6 eV monochromated Al Kα radiation was used. XRD patterns were acquired using a D8 Advance, 2020 (multi-purpose XRD, Cu Kα radiation, Bruker) at the Research Institute Advanced Materials at Seoul National University. X-ray absorption fine structure (XAFS) measurements were made at the 8C nano-probe XAFS beamline (BL8C) of Pohang Light Source (PLS-II) in the 3.0 GeV storage ring with a ring current of 300 mA. The X-ray beam was monochromated by a Si (111) double crystal where the beam intensity was reduced by 30% to eliminate higher-order harmonics. The X-ray beam was then delivered to a secondary source aperture where the beam size was

adjusted to 0.3 mm (v)×1 mm (h). A high voltage (3,000 V) was applied to ionization chambers filled with N_2/Ar mixture gases to detect X-ray intensity. XAFS spectra were collected in both transmission and fluorescence modes. The obtained spectra were processed using Demeter software. ICP-AES analysis was conducted using ICP-730ES (Varian) installed at National Instrumentation Center for Environmental Management at Seoul National University. UV-Vis spectroscopy measurements were conducted using Cary 5G optical spectrometer at KBSI Daegu Center, Korea. Steady-state PL and trPL spectra were recorded using Edinburgh FLS 980 spectrometer. EPR experiments were conducted using EMX micro-9.5/2.7 at 150 K. Samples before, during, and after the reaction were quickly injected to Ar-degassed EPR tubes, and then rapidly frozen using liquid nitrogen for analysis. After the reaction, mixture in EPR tube was regenerated with air and rapidly frozen for further analysis. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 AVANCE, and all chemical shifts are referenced to residual non-deuterated solvent signals (note: $CDCl_3$ referenced at 7.26 and 77.0 ppm respectively). ^{1}H NMR were presented as following: chemical shifts (δ, ppm), integration, coupling constant (Hz), and multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, br = broad, dd = doublet of doublets, td = triplet of doublets, tt = triplet of triplets, m = multiplet). GC-MS spectra were recorded on a GC-MS_5977EI. GC analyses were performed on an Agilent 7890B Gas Chromatograph equipped with an Agilent 5977A Mass Selective Detector. IR spectra were recorded on a Perkin Elmer Spectrum 100 FTIR spectrometer and are reported in wavenumbers (cm^{-1}).

2. Synthesis of CN, NiSAC/CN, and NiNP/CN

Synthesis of CN. CN was synthesized via polymerization of urea. 10 g of urea in sealed alumina boat was treated at 550 °C for 2 h at a muffle furnace.

Introducing single Ni atoms to CN. 200 mg of as-prepared urea-driven CN was suspended in 40 mL of water in 100 mL vial and sonicated for 10 min. Subsequently, 600 μL of $NiCl_2 \cdot 6H_2O$ aqueous solution (10 mg/mL) was added dropwise for 30 seconds to CN suspension and further sonicated for 10 min. The vial was transferred to 70 °C oil bath and heated for 6 h with stirring. The suspension was then rapidly frozen with liquid nitrogen, and freeze-dried for 2 days. Powder was collected and calcined at 250 °C for 2 h (ramping rate: 5 °C/min) in Ar/H_2 (95:5) atmosphere. After calcination was finished, as-obtained powder was washed with 20 mL of ethanol and dried at 60 °C.

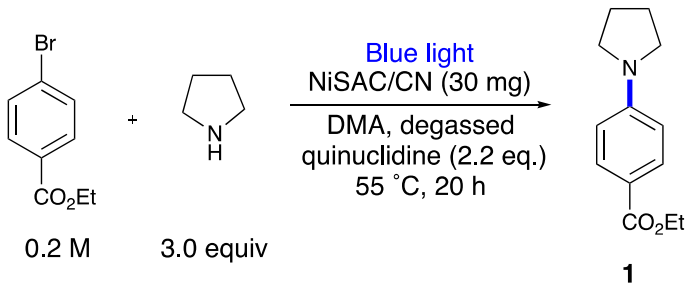
Synthesis of NiNP/CN. For comparison, NiNP/CN was synthesized by photodeposition method.[1] CN (40 mg), TEOA (12 mL), $NiCl_2 \cdot 6H_2O$ aqueous solution (0.1 M, 1.2 mL), and $NaH_2PO_2 \cdot H_2O$ aqueous solution (0.1 M, 8.4 mL) were well mixed in 18.4 mL of water in 50 mL vial. The mixture was degassed with Ar gas for 30 min and then illuminated under UV-Vis light (300 W Xe lamp) for 30 min. After irradiation, the suspension was washed 3 times with 40 mL of water and dried at 60 °C.

3. General procedure for C-N coupling

NiSAC/CN (30 mg, 3 mol% Ni), aryl bromide (0.1 mmol, 1 equiv.), and quinuclidine (0.22 mmol, 2.2 equiv.) were placed into an 8 mL vial equipped with a magnetic stir bar. Subsequently, the amine (0.3 mmol, 3 equiv.) and anhydrous DMA (0.5 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 Ar for 10 min. The mixture was heated and vigorously stirred under blue LED or Kessil LED. After stirring for the respective reaction time, one equivalent of 1,3,5-trimethoxybenzene (0.1 mmol, internal standard) was added. Then, the combined reaction mixture was centrifuged 3 times as diluted with diethyl ether (2 x 2 mL). Then, the supernatant was washed with H_2O (40 mL) and extracted with diethyl ether (3 x 30 mL). The organic layer was dried over anhydrous $MgSO_4$, filtrated, and concentrated under vacuum. The crude product was then diluted with $CDCl_3$ and subjected to ^1H NMR analysis.

4. Reaction optimization

Table S1. Reaction yield of the compound **1** under different amount of NiSAC/CN catalysts.



Entry	Deviation from the standard conditions	Yield (%) *
1	none	79
2	NiSAC/CN (20 mg)	69
3	NiSAC/CN (10 mg)	30

*The yield was determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

5. Catalyst characterization

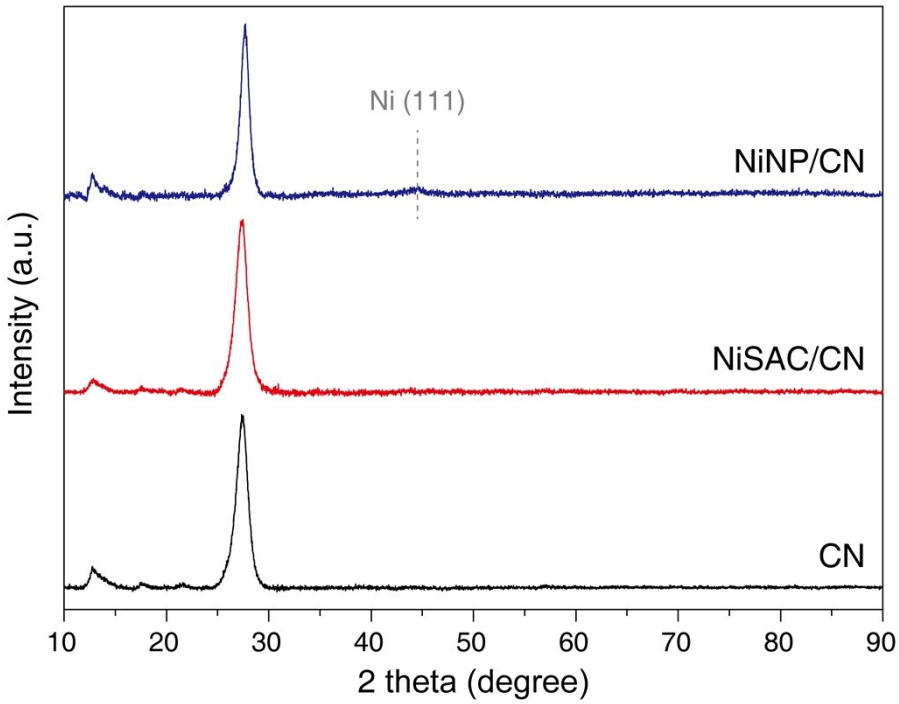


Figure S1. XRD patterns of CN, NiSAC/CN and NiNP/CN.

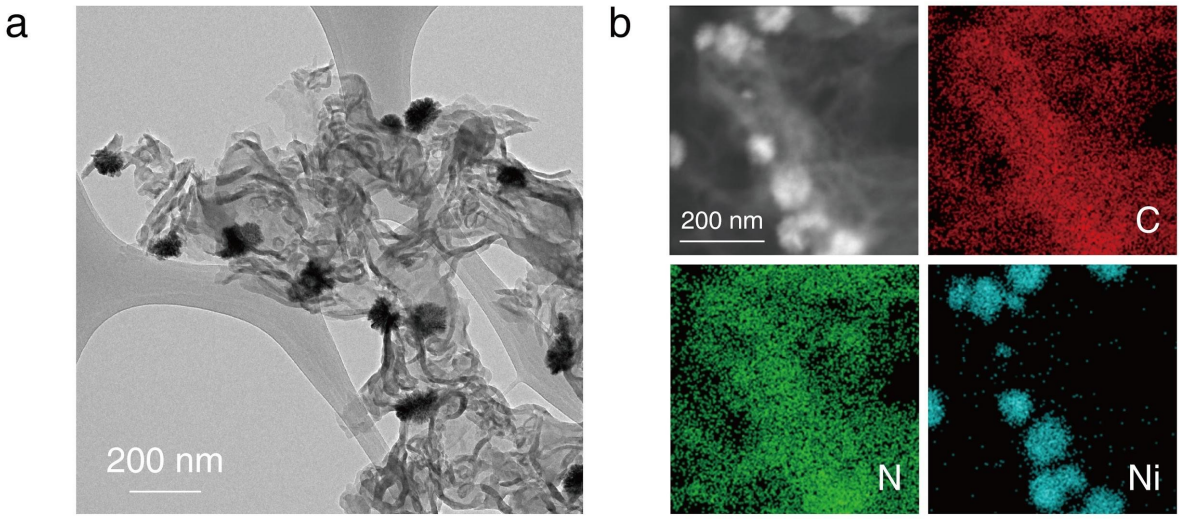
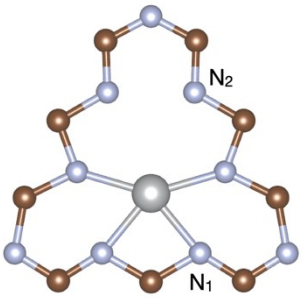


Figure S2. Representative TEM image (a) and EDS elemental mapping image (b) of NiNP/CN.



Shell	R (Å)	N	d (Å)	σ^2 (Å^2)
Ni-N_1	1.99	4.22	0.10	0.0015
Ni-N_2	2.84	2.37	-0.16	0.0005

Figure S3. EXAFS curve-fitting analysis of NiSAC/CN with the schematic model (silver: Ni, grey: N, brown: C) and the resulted fitting parameters.

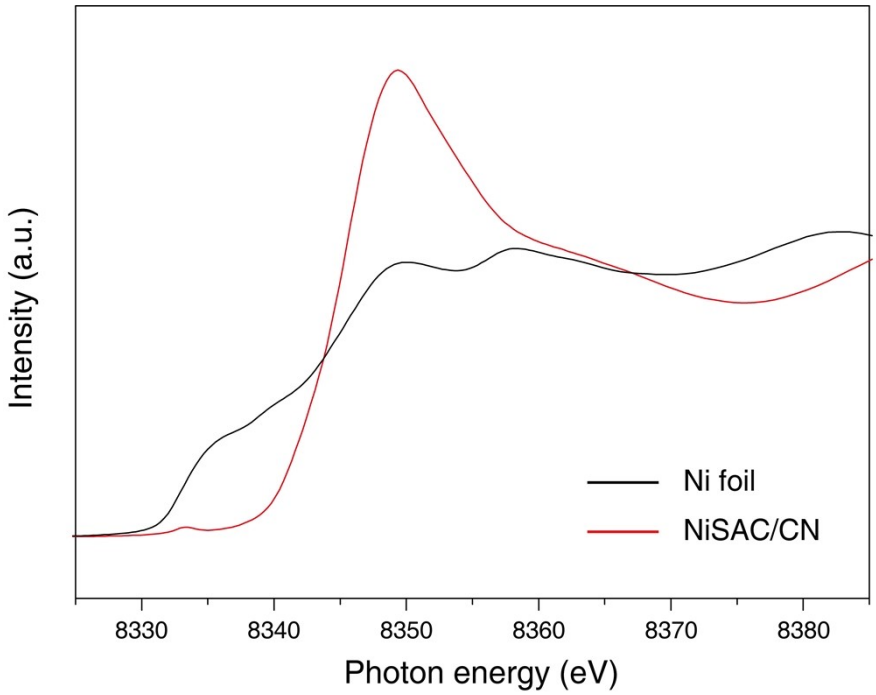


Figure S4. Ni K-edge XANES spectra of Ni foil and NiSAC/CN.

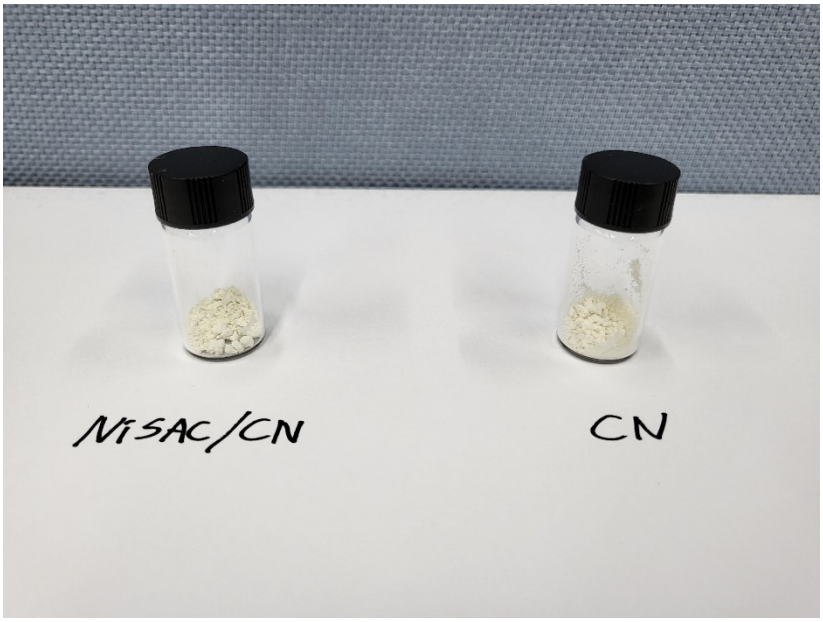


Figure S5. Color of NiSAC/CN (left) and CN (right). Since NiSAC/CN was synthesized via the post-treatment method, not the co-polymerization method, and Ni content was only 0.53 wt%, NiSAC/CN and CN show negligible color change.

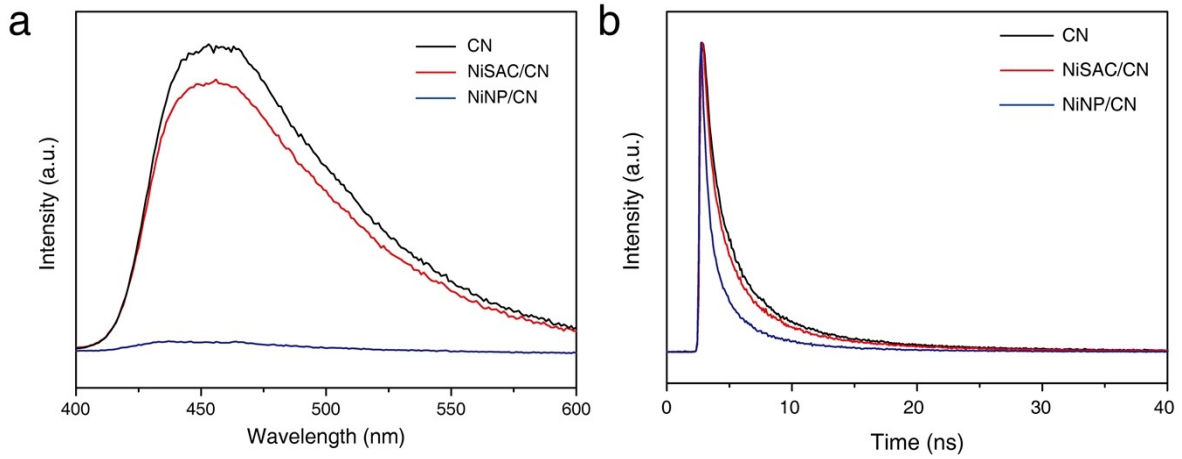


Figure S6. (a) Steady-state PL and (b) time-resolved PL spectra of CN, NiSAC/CN, and NiNP/CN. In time-resolved PL spectra, the PL lifetime of CN, NiSAC/CN, and NiNP/CN are 1.41 ns, 1.07 ns, and 0.63 ns, respectively. Although NiNP/CN shows more efficient electron transfer than NiSAC/CN, NiNP/CN did not mediate the C-N coupling reaction (Table 1, entry 9).

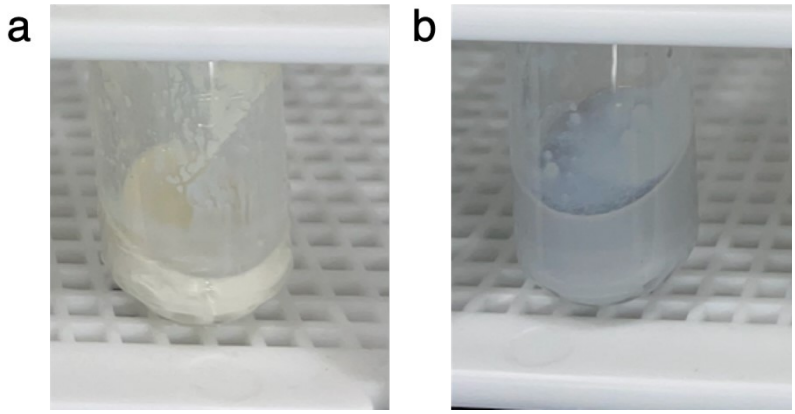


Figure S7. Image of the reaction mixture (a) before light irradiation (b) after 24 h light irradiation when g-CN and nickel precursors were separately introduced.

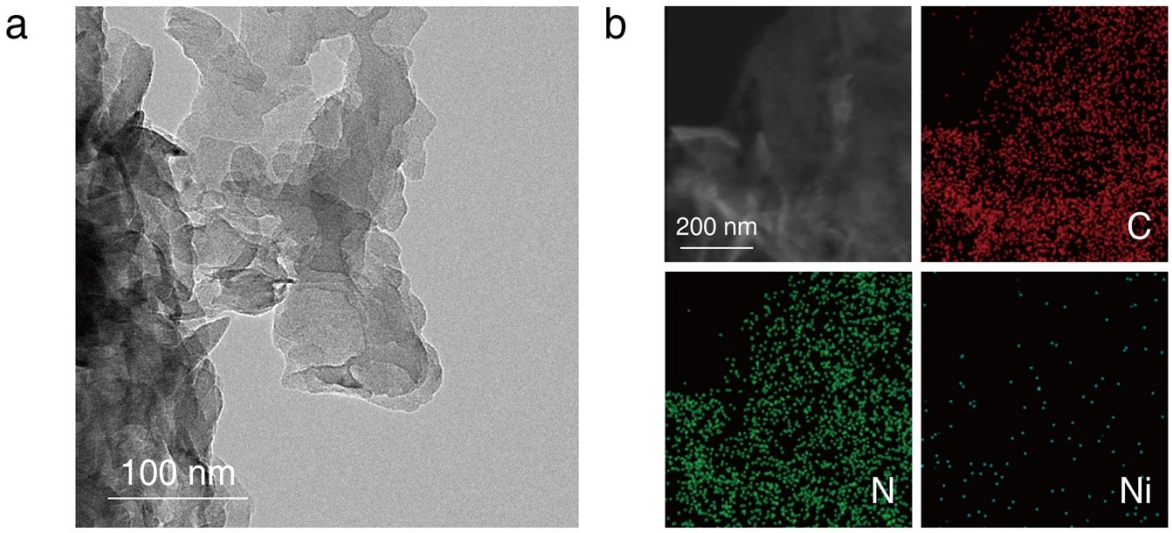


Figure S8. Representative TEM image (a) and EDS elemental mapping image (b) of NiSAC/CN after the model reaction.

6. Recycle test

NiSAC/CN (60 mg, 6 mol% Ni), ethyl 4-iodobenzoate (27.6 mg, 0.1 mmol) and quinuclidine (24.5 mg, 0.22 mmol) were placed into 8 mL vial equipped with a magnetic stir bar. Subsequently, pyrrolidine (21.3 mg, 0.3 mmol), and anhydrous DMA (1 mL) were added, and the vial was sealed with a septum and parafilm. The reaction mixture was sonicated for 5-10 min while degassed with Ar bubbling. After vigorously stirred for 24 h, the reaction mixture was centrifuged and rinsed with hexane (3 x 2 mL). The supernatant was subjected to work up according to general procedure and the yield of product **1** was monitored by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. The recovered catalysts were dried overnight in the vacuum oven at 80 ^{o}C and exploited as the catalyst for further reaction.

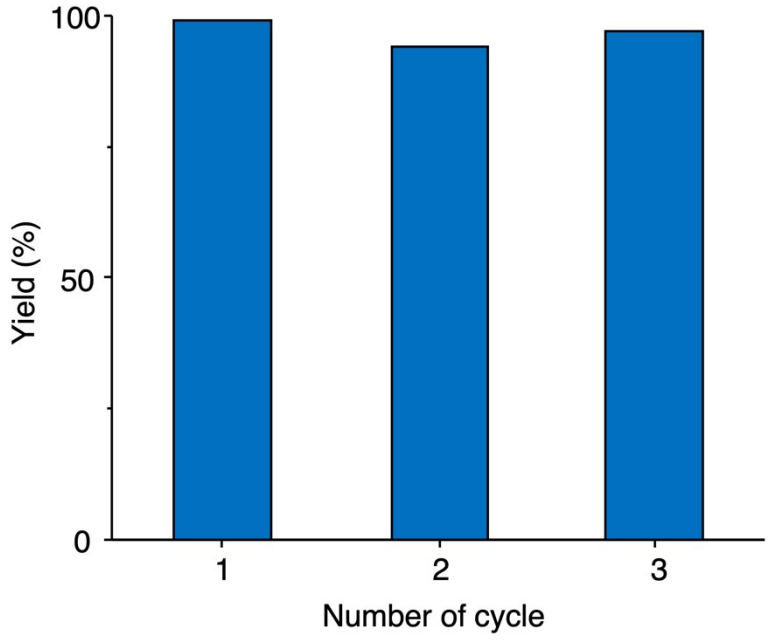


Figure S9. Recycle test for the model reaction producing compound **1**.

7. Hot filtration

Internal standard

To monitor the yield of the product during hot filtration test, the peak area of analyte **2** in GC-MS was obtained from increasing concentration of the analyte from 1 mg/mL to 4 mg/mL (Table S2). As 5 mg/mL of dodecane was used as an internal standard, the response of analyte **2** was calculated and 2.4449 of response factor was obtained.

Hot filtration

NiSAC/CN (90 mg, 3 mol% Ni), 4-bromobenzonitrile (54.6 mg, 0.3 mmol) and quinuclidine (74.1 mg, 0.66 mmol) were placed into 8 mL vial equipped with a magnetic stir bar. Subsequently, pyrrolidine (64.0 mg, 0.9 mmol), dodecane (7.5 mg), and anhydrous DMA (1.5 mL) were added, and the vial was sealed with a septum and parafilm. The reaction mixture was sonicated for 5-10 min while degassed with Ar bubbling. After vigorously stirred for 1 h, 0.5 mL of the hot reaction mixture was centrifuged for 10 min, and the supernatant was transferred to the vial filled with fresh carbon nitride (30 mg). The reaction mixture was degassed by bubbling Ar for 10 min with sonication. The yield of product **2** was monitored by GC-MS using the aforementioned response factor. Over 2 h after hot filtration, the further conversion of starting material was 0.41% and the reaction didn't proceed over the next 3 h (Figure S10). Thus, it is confirmed the reaction is catalyzed on the heterogeneous surface.

Table S2. GC response of 4-(pyrrolidin-1-yl)benzonitrile.

concentration (mg/mL)	A_analyte **2**	A_dodecane	response
1	220275037	434801857	2.533050785
2	576925655	595170022	4.846729789
3	789893996	586711656	6.731534885
4	1119507685	547108906	10.23112284

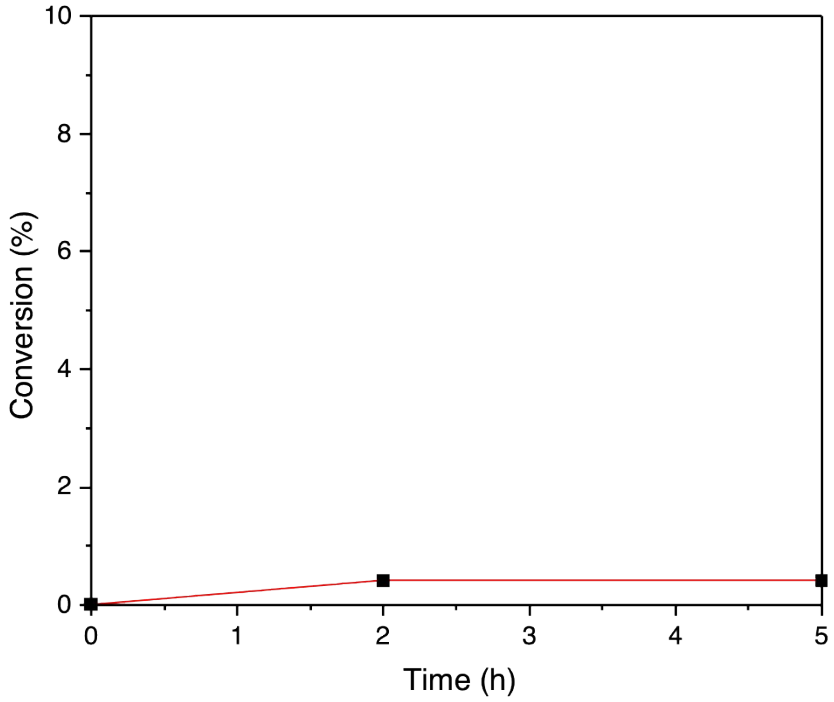


Figure S10. Conversion of the reaction producing compound **2** after hot filtration.

8. Magnified EPR spectra

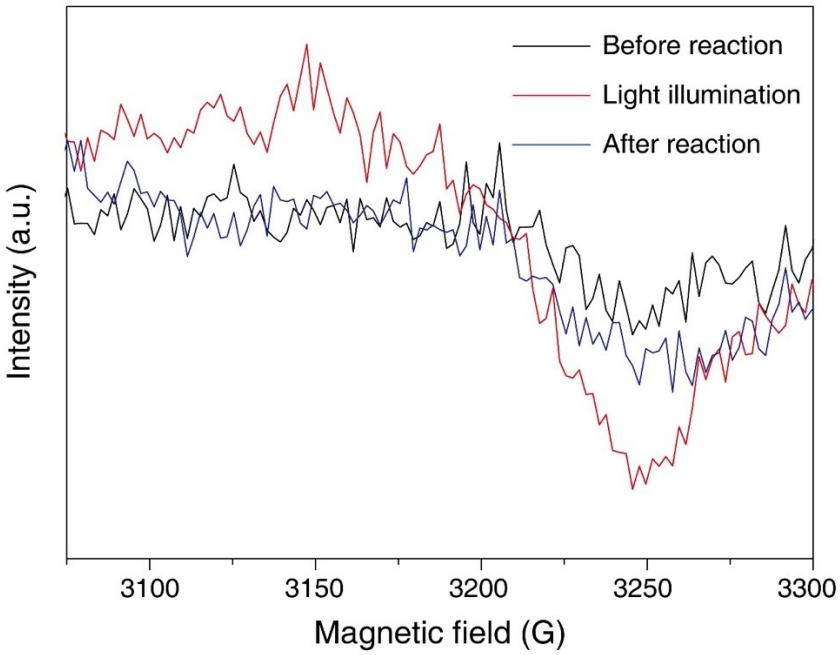


Figure S11. Magnified quasi *in situ* EPR spectra of the reaction mixture at 150 K in various conditions.

9. Mechanism study

Hammett plot

NiSAC/CN (30 mg, 3 mol% Ni) and *para*-substituted aryl iodide (0.1 mmol) were placed into 8 mL vial equipped with a magnetic stir bar. Subsequently, pyrrolidine (1 mmol), dodecane (0.1 mmol), and anhydrous DMA (0.5 mL) were added, and the vial was sealed with a septum and parafilm. The reaction mixture was sonicated for 5-10 min while degassed with Ar bubbling. The conversion of starting material was monitored by GC-MS.

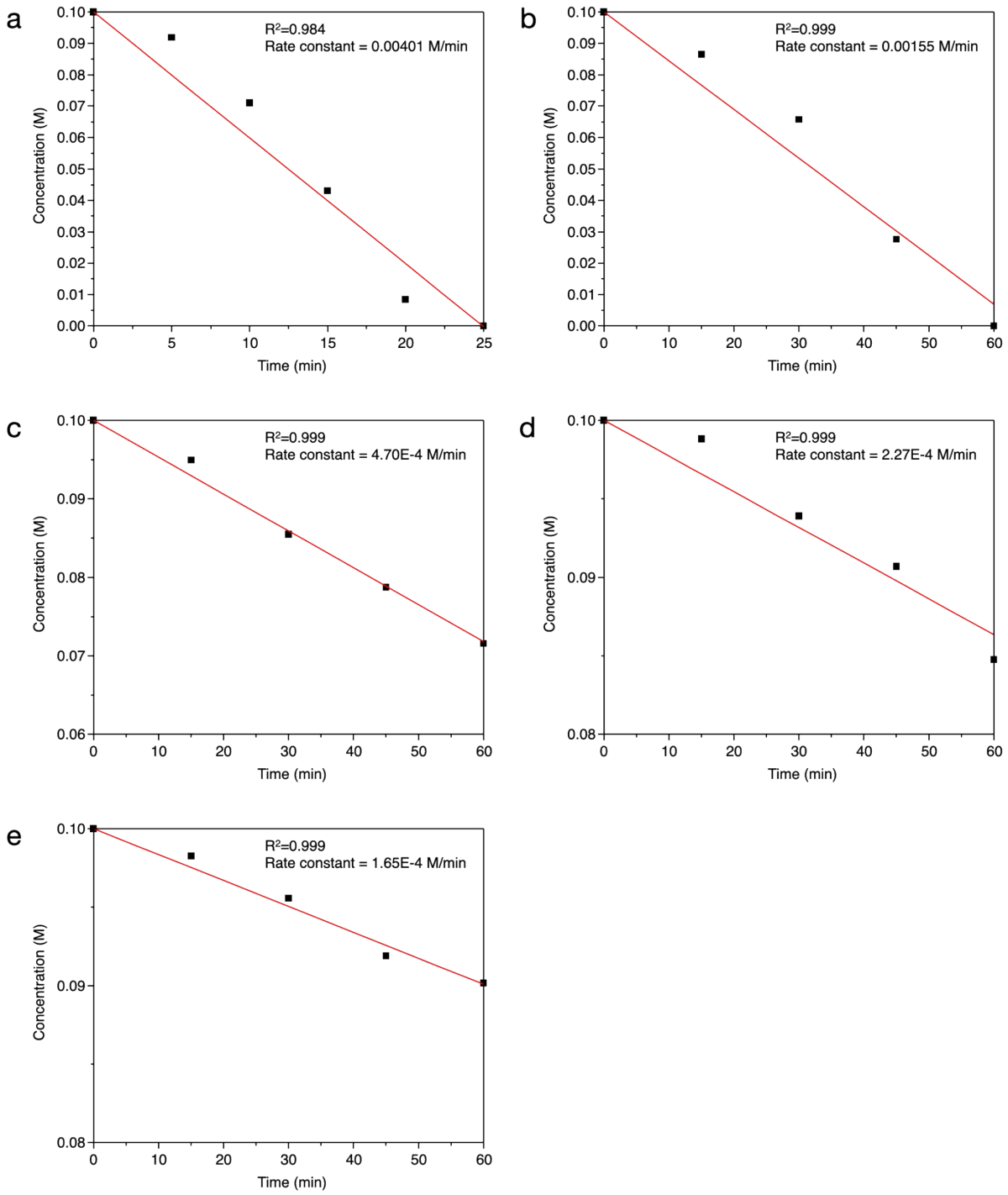


Figure S12. Reaction progress of C-N coupling between pyrrolidine and *para*-substituted aryl iodides (a) 4-iodobenzotrifluoride (b) 1-chloro-4-iodobenzene (c) iodobenzene (d) 4-iodotoluene (e) 4-iodoanisole.

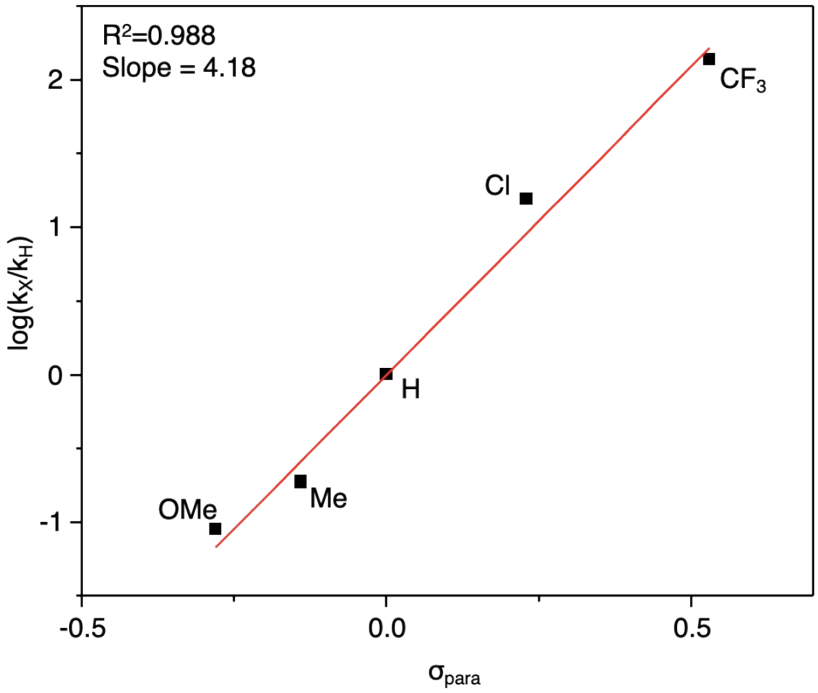


Figure S13. The Hammett plot of C-N coupling of *para*-substituted aryl iodides.

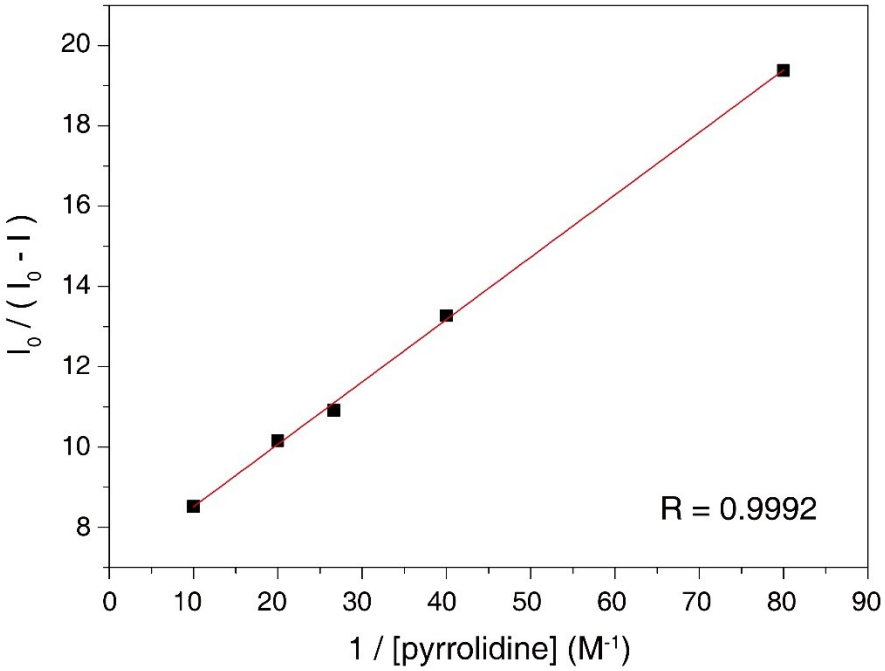
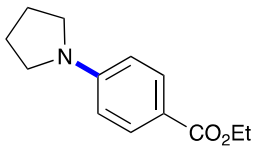


Figure S14. Linear fitting of data from emission quenching experiment.[2,3]

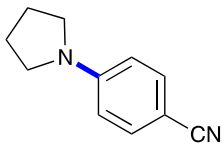
10. Detailed procedure and characterization for C-N coupling



Ethyl 4-(pyrrolidin-1-yl)benzoate (1): The compound was prepared following the aforementioned general procedure using ethyl 4-bromobenzoate (22.9 mg, 0.1 mmol), pyrrolidine (21.3 mg, 0.3 mmol), quinuclidine (24.5 mg, 0.22 mmol), NiSAC/CN (30 mg, 3 mol% Ni), and DMA (0.5 mL). The reaction mixture was vigorously stirred for 20 h at 55 ^{o}C in the presence of blue LED. The reaction mixture was subjected to work up according to general procedure.

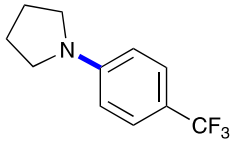
White solid (79%), ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88 (2H, *J*=8.9 Hz, d), 6.44 (2H, *J*=8.9 Hz, d), 4.30 (2H, *J*=7.1 Hz, q), 3.28-3.25 (4H, m), 1.98-1.95 (4H, m), 1.35 (3H, *J*=7.1 Hz, t)

The above ^{1}H NMR is in agreement with previously published data.[4]



4-(Pyrrolidin-1-yl)benzonitrile (2): The compound was prepared following the aforementioned general procedure using 4-bromobenzonitrile (18.2 mg, 0.1 mmol), pyrrolidine (21.3 mg, 0.3 mmol), quinuclidine (24.5 mg, 0.22 mmol), NiSAC/CN (30 mg, 3 mol% Ni), and DMA (0.5 mL). The reaction mixture was vigorously stirred for 14 h at 55 ^{o}C in the presence of blue LED. The reaction mixture was subjected to work up according to general procedure. White solid (99%), ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 (2H, *J*=8.8 Hz, d), 6.49 (2H, *J*=8.8 Hz, d), 3.33-3.30 (4H, m), 2.05-2.02 (4H, m)

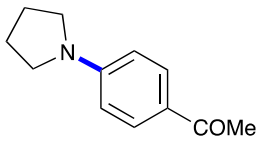
The above ^{1}H NMR is in agreement with previously published data.[5]



1-(4-(Trifluoromethyl)phenyl)pyrrolidine (3): The compound was prepared following the aforementioned general procedure using 4-bromobenzotrifluoride (22.5 mg, 0.1 mmol), pyrrolidine (21.3 mg, 0.3 mmol), quinuclidine (24.5 mg, 0.22 mmol), NiSAC/CN (30 mg, 3 mol% Ni), and DMA (0.5 mL). The reaction mixture was vigorously stirred for 24 h at 55 °C in the presence of blue LED. The reaction mixture was subjected to work up according to general procedure.

White solid (97%), ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 (2H, *J*=8.6 Hz, d), 6.54 (2H, *J*=8.6 Hz d), 3.33-3.30 (4H, m), 2.05-2.02 (4H, m)

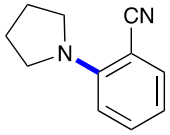
The above ^{1}H NMR is in agreement with previously published data.[5]



1-(4-(Pyrrolidin-1-yl)phenyl)ethan-1-one (4): The compound was prepared following the aforementioned general procedure using 4-bromobenzotrifluoride (19.9 mg, 0.1 mmol), pyrrolidine (21.3 mg, 0.3 mmol), quinuclidine (24.5 mg, 0.22 mmol), NiSAC/CN (30 mg, 3 mol% Ni), and DMA (0.5 mL). The reaction mixture was vigorously stirred for 72 h at 55 °C in the presence of blue LED. The reaction mixture was subjected to work up according to general procedure.

White solid (45%), ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86 (2H, *J*=8.8 Hz, d), 6.51 (2H, *J*=8.8 Hz, d), 3.38-3.35 (4H, m), 2.50 (3H, s), 2.05-2.02 (4H, m)

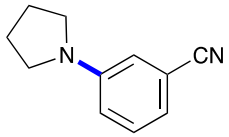
The above ^{1}H NMR is in agreement with previously published data.[6]



2-(Pyrrolidin-1-yl)benzonitrile (5): The compound was prepared following the aforementioned general procedure using 2-bromobenzonitrile (18.2 mg, 0.1 mmol), pyrrolidine (21.3 mg, 0.3 mmol), quinuclidine (24.5 mg, 0.22 mmol), NiSAC/CN (30 mg, 3 mol% Ni), and DMA (0.5 mL). The reaction mixture was vigorously stirred for 22 h at 55 ^{o}C in the presence of blue LED. The reaction mixture was subjected to work up according to general procedure.

Transparent oil (82%), ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45-7.42 (1H, m), 7.34-7.29 (1H, m), 6.66-6.62 (2H, m), 3.62-3.58 (4H, m), 2.02-1.98 (4H, m)

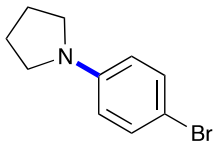
The above ^{1}H NMR is in agreement with previously published data.[5]



3-(Pyrrolidin-1-yl)benzonitrile (6): The compound was prepared following the aforementioned general procedure using 3-bromobenzonitrile (18.2 mg, 0.1 mmol), pyrrolidine (21.3 mg, 0.3 mmol), quinuclidine (24.5 mg, 0.22 mmol), NiSAC/CN (30 mg, 3 mol% Ni), and DMA (0.5 mL). The reaction mixture was vigorously stirred for 72 h at 55 ^{o}C in the presence of blue LED. The reaction mixture was subjected to work up according to general procedure.

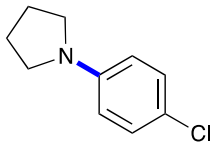
White solid (37%), ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.26-7.22 (1H, m), 6.90-6.88 (1H, m), 6.73-6.71 (2H, m), 3.28-3.25 (4H, m), 2.05-2.01 (4H, m)

The above ^{1}H NMR is in agreement with previously published data.[5]



1-(4-Bromophenyl)pyrrolidine (7): The compound was prepared following the aforementioned general procedure using 1,4-dibromobenzene (23.6 mg, 0.1 mmol), pyrrolidine (21.3 mg, 0.3 mmol), quinuclidine (24.5 mg, 0.22 mmol), NiSAC/CN (30 mg, 3 mol% Ni), and DMA (0.5 mL). The reaction mixture was vigorously stirred for 24 h at 55 °C in the presence of blue LED. The reaction mixture was subjected to work up according to general procedure. White solid (67%), ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27 (2H, *J*=9.0 Hz, d), 6.42 (2H, *J*=9.0 Hz, d), 3.25-3.22 (4H, m), 2.02-1.99 (4H, m)

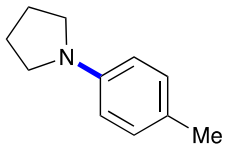
The above ^{1}H NMR is in agreement with previously published data.[5]



1-(4-Chlorophenyl)pyrrolidine (8): The compound was prepared following the aforementioned general procedure using 1-bromo-4-chlorobenzene (19.1 mg, 0.1 mmol), pyrrolidine (21.3 mg, 0.3 mmol), quinuclidine (24.5 mg, 0.22 mmol), NiSAC/CN (30 mg, 3 mol% Ni), and DMA (0.5 mL). The reaction mixture was vigorously stirred for 24 h at 55 °C in the presence of blue LED. The reaction mixture was subjected to work up according to general procedure.

White solid (33%), ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.15 (2H, *J*=8.8 Hz, d), 6.46 (2H, *J*=8.8 Hz, d), 3.26-3.23 (4H, m), 2.02-1.99 (4H, m)

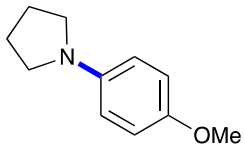
The above ^{1}H NMR is in agreement with previously published data.[5]



1-(*p*-Tolyl)pyrrolidine (9): The compound was prepared following the aforementioned general procedure using 4-bromotoluene (17.1 mg, 0.1 mmol), pyrrolidine (21.3 mg, 0.3 mmol), quinuclidine (24.5 mg, 0.22 mmol), NiSAC/CN (30 mg, 3 mol% Ni), LiCl (4.2 mg, 0.1 mmol) and DMA (0.5 mL). The reaction mixture was vigorously stirred for 48 h at 55 ^{o}C in the presence of blue LED. The reaction mixture was subjected to work up according to general procedure.

White solid (29%), ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.04 (2H, *J*=8.3 Hz, d), 6.51 (2H, *J*=8.3 Hz, d), 3.28-3.24 (4H, m), 2.26 (3H, s), 2.01-1.98 (4H, m)

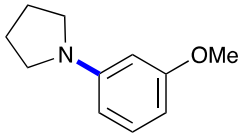
The above ^{1}H NMR is in agreement with previously published data.[7]



1-(4-Methoxyphenyl)pyrrolidine (10): The compound was prepared following the aforementioned general procedure using 4-bromoanisole (18.7 mg, 0.1 mmol), pyrrolidine (21.3 mg, 0.3 mmol), quinuclidine (24.5 mg, 0.22 mmol), NiSAC/CN (30 mg, 3 mol% Ni), LiCl (4.2 mg, 0.1 mmol) and DMA (0.5 mL). The reaction mixture was vigorously stirred for 48 h at 55 ^{o}C in the presence of blue LED. The reaction mixture was subjected to work up according to general procedure.

White solid (22%), ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.88 (2H, *J*=9.0 Hz, d), 6.57 (2H, *J*=9.0 Hz, d), 3.79 (3H, s), 3.28-3.25 (4H, m), 2.03-2.00 (4H, m)

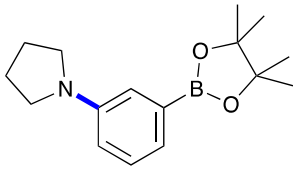
The above ^{1}H NMR is in agreement with previously published data.[8]



1-(3-Methoxyphenyl)pyrrolidine (11): The compound was prepared following the aforementioned general procedure using 3-bromoanisole (18.7 mg, 0.1 mmol), pyrrolidine (21.3 mg, 0.3 mmol), quinuclidine (24.5 mg, 0.22 mmol), NiSAC/CN (30 mg, 3 mol% Ni), and DMA (0.5 mL). The reaction mixture was vigorously stirred for 48 h at 55 ^{o}C in the presence of blue LED. The reaction mixture was subjected to work up according to general procedure.

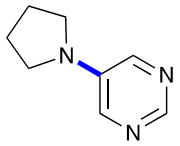
Yellow oil (24%), ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.15-7.11 (1H, m), 6.25-6.19 (2H, m), 6.12-6.11 (1H, m), 3.80 (3H, s), 3.29-3.25 (4H, m), 2.00-1.97 (4H, m)

The above ^{1}H NMR is in agreement with previously published data.[7]



1-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrrolidine (12): The compound was prepared following the aforementioned general procedure using 3-bromophenyl boronic acid pinacol ester (28.3 mg, 0.1 mmol), pyrrolidine (21.3 mg, 0.3 mmol), quinuclidine (24.5 mg, 0.22 mmol), NiSAC/CN (30 mg, 3 mol% Ni), and DMA (0.5 mL). The reaction mixture was vigorously stirred for 72 h at 55 ^{o}C in the presence of blue LED. The reaction mixture was subjected to work up according to general procedure.

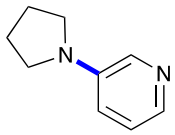
Transparent oil (50%), ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.24-7.20 (1H, m), 7.12-7.10 (1H, m), 7.01-7.01 (1H, m), 6.66-6.64 (1H, m), 3.30-3.27 (4H, m), 1.98-1.94 (4H, m), 1.32 (12H, s), ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.4, 128.4, 121.8, 117.5, 114.5, 83.4, 47.6, 25.3, 24.8, HRMS : m/z calculated for $C_{16}H_{24}BNO_2$:273.1900; found 273.1901, FT-IR (film) 2976 (arom. CH), 1599 and 1573 (arom. CC), 1438 (CH), 1333 (arom. CN), 1271 (CN), 1143 (CO) cm^{-1}



5-(Pyrrolidin-1-yl)pyrimidine (13): The compound was prepared following the aforementioned general procedure using 5-bromopyrimidine (15.9 mg, 0.1 mmol), pyrrolidine (21.3 mg, 0.3 mmol), quinuclidine (24.5 mg, 0.22 mmol), NiSAC/CN (30 mg, 3 mol% Ni), and DMA (0.5 mL). The reaction mixture was vigorously stirred for 24 h at 55 ^{o}C in the presence of blue LED. The reaction mixture was subjected to work up according to general procedure.

Transparent oil (63%), ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.55 (1H, s), 8.05 (2H, s), 3.33-3.29 (4H, m), 2.07-2.03 (4H, m)

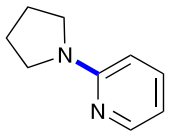
The above ^{1}H NMR is in agreement with previously published data.[5]



3-(Pyrrolidin-1-yl)pyridine (14): The compound was prepared following the aforementioned general procedure using 3-bromopyridine (15.8 mg, 0.1 mmol), pyrrolidine (21.3 mg, 0.3 mmol), quinuclidine (24.5 mg, 0.22 mmol), NiSAC/CN (30 mg, 3 mol% Ni), and DMA (0.5 mL). The reaction mixture was vigorously stirred for 26 h at 55 ^{o}C in the presence of blue LED. The reaction mixture was subjected to work up according to general procedure.

Transparent oil (64%), ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.97-7.89 (2H, m), 7.10-7.07 (1H, m), 6.80-6.77 (1H, m), 3.29-3.25 (4H, m), 2.02-1.99 (4H, m)

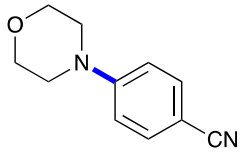
The above ^{1}H NMR is in agreement with previously published data.[5]



2-(Pyrrolidin-1-yl)pyridine (15): The compound was prepared following the aforementioned general procedure using 2-bromopyridine (15.8 mg, 0.1 mmol), pyrrolidine (35.5 mg, 0.5 mmol), quinuclidine (24.5 mg, 0.22 mmol), NiSAC/CN (30 mg, 3 mol %Ni), and DMA (0.5 mL). The reaction mixture was vigorously stirred for 72 h at 55 °C in the presence of blue LED. The reaction mixture was subjected to work up according to general procedure.

Transparent oil (32%), ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.16-8.14 (1H, m), 7.44-7.40 (1H, m), 6.52-6.50 (1H, m), 6.36-6.34 (1H, m), 3.46-3.43 (4H, m), 2.02-1.99 (4H, m)

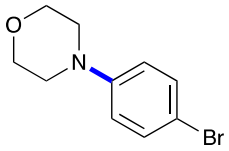
The above ^{1}H NMR is in agreement with previously published data.[7]



4-Morpholinobenzonitrile (16): The compound was prepared following the aforementioned general procedure using 4-bromobenzonitrile (18.2 mg, 0.1 mmol), morpholine (26.1 mg, 0.3 mmol), quinuclidine (24.5 mg, 0.22 mmol), NiSAC/CN (30 mg, 3 mol% Ni), and DMA (0.5 mL). The reaction mixture was vigorously stirred for 18 h at 55 °C in the presence of blue LED. The reaction mixture was subjected to work up according to general procedure.

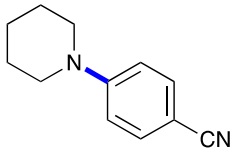
White solid (92%), ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52 (2H, *J*=8.6 Hz, d), 6.86 (2H, *J*=8.6 Hz, d), 3.85 (4H, *J*=4.8 Hz, t), 3.28 (4H, *J*=4.8 Hz, t)

The above ^{1}H NMR is in agreement with previously published data.[9]



4-(4-Bromophenyl)morpholine (17): The compound was prepared following the aforementioned general procedure using 1,4-bromobenzene (23.6 mg, 0.1 mmol), morpholine (26.1 mg, 0.3 mmol), quinuclidine (24.5 mg, 0.22 mmol), NiSAC/CN (30 mg, 3 mol% Ni), and DMA (0.5 mL). The reaction mixture was vigorously stirred for 48 h at 55 °C in the presence of blue LED. The reaction mixture was subjected to work up according to general procedure. White solid (76%), ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34 (2H, *J*=9.0 Hz, d), 6.76 (2H, *J*=9.0 Hz, d), 3.84 (4H, *J*=4.8 Hz, t), 3.10 (4H, *J*=4.8 Hz, t)

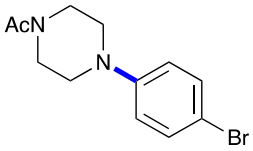
The above ^{1}H NMR is in agreement with previously published data.[10]



4-(Piperidin-1-yl)benzonitrile (18): The compound was prepared following the aforementioned general procedure using 4-bromobenzonitrile (18.2 mg, 0.1 mmol), piperidine (25.5 mg, 0.3 mmol), quinuclidine (24.5 mg, 0.22 mmol), NiSAC/CN (30 mg, 3 mol% Ni), and DMA (0.5 mL). The reaction mixture was vigorously stirred for 24 h at 55 °C in the presence of blue LED. The reaction mixture was subjected to work up according to general procedure.

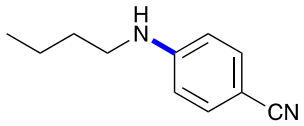
White solid (69%), ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46 (2H, *J*=9.0 Hz, d), 6.84 (2H, *J*=9.0 Hz, d), 3.33-3.31 (4H, m), 1.68-1.65 (6H, m)

The above ^{1}H NMR is in agreement with previously published data.[6]



1-(4-(4-Bromophenyl)piperazin-1-yl)ethan-1-one (19): The compound was prepared following the aforementioned general procedure using 1,4-dibromobenzene (23.6 mg, 0.1 mmol), pyrrolidine (38.5 mg, 0.3 mmol), quinuclidine (24.5 mg, 0.22 mmol), NiSAC/CN (30 mg, 3 mol% Ni), and DMA (0.5 mL). The reaction mixture was vigorously stirred for 24 h at 70 °C in the presence of blue LED. The reaction mixture was subjected to work up according to general procedure.

White solid (75%), m.p.: 135.4 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36 (2H, *J*=9.0 Hz, d), 6.79 (2H, *J*=9.0 Hz, d), 3.77-3.60 (4H, m), 3.16-3.10 (4H, m), 2.13 (3H, s), ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.0, 149.9, 132.0, 118.2, 112.7, 49.5, 49.1, 46.0, 41.2, 21.3, HRMS : m/z calculated for $C_{12}H_{15}BrN_2O$:282.0368; found 282.0364, FT-IR (solid) 2973 and 2830 (arom. CH), 1642 (CO), 1495 (arom. CC), 1430 (CH), 1332 (arom. CN), 1222 (arom. CN), 654 (CBr) cm^{-1}



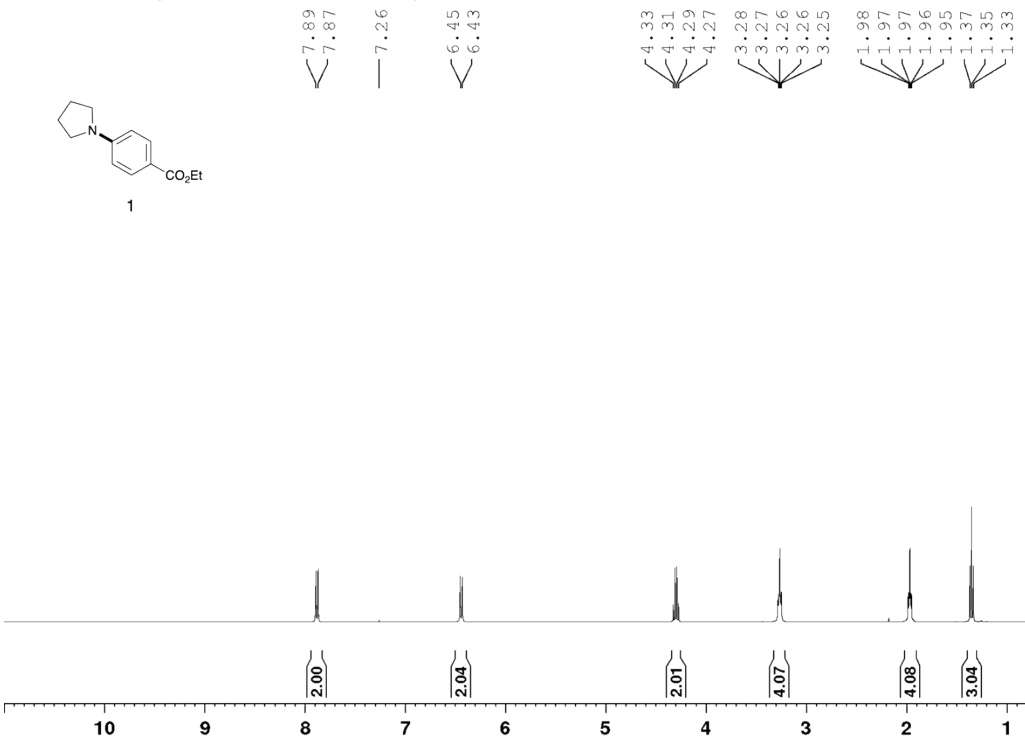
4-(Butylamino)benzonitrile (20): The compound was prepared following the aforementioned general procedure using 4-bromobenzonitrile (18.2 mg, 0.1 mmol), n-butylamine (21.9 mg, 0.3 mmol), quinuclidine (24.5 mg, 0.22 mmol), NiSAC/CN (30 mg, 3 mol% Ni), and DMA (0.5 mL). The reaction mixture was vigorously stirred for 24 h at 55 °C in the presence of Kessil blue lamp. The reaction mixture was subjected to work up according to general procedure.

Transparent oil (99%), ^{1}H NMR ($CDCl_3$) δ: 7.41 (2H, *J*=8.8 Hz, d), 6.54 (2H, *J*=8.8 Hz, d), 4.17 (1H, br), 3.15 (2H, *J*=7.2 Hz, q), 1.61 (2H, *J*=7.2 Hz, quin), 1.43 (2H, *J*=7.2 Hz, hex), 0.96 (3H, *J*=7.2 Hz, t)

The above ^{1}H NMR is in agreement with previously published data.[11]

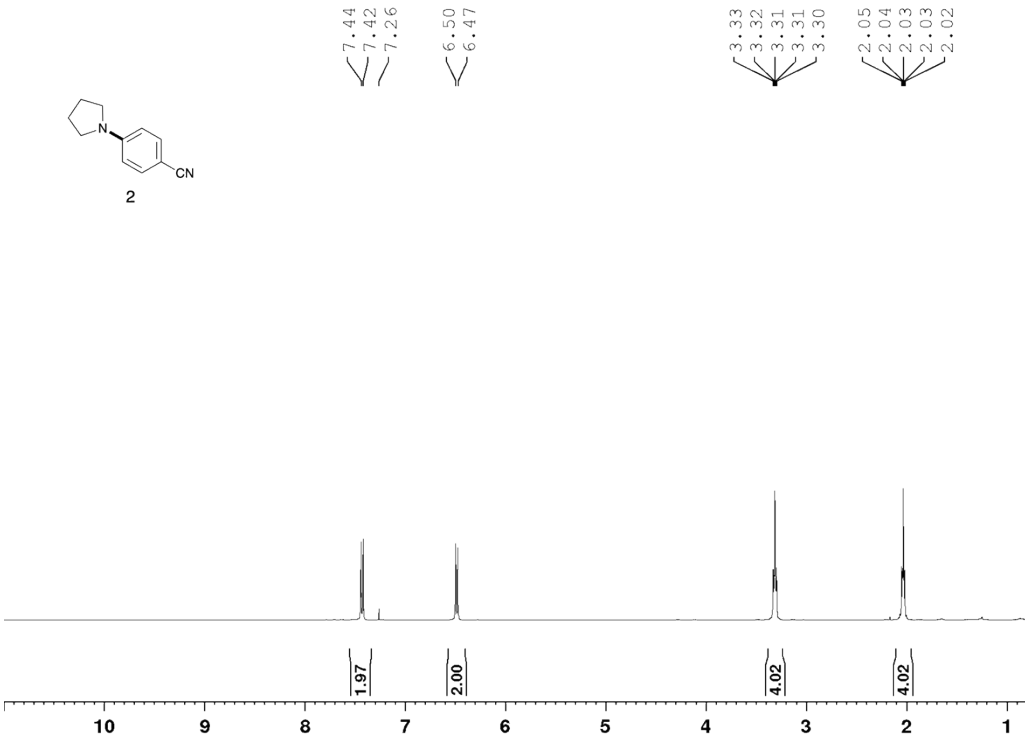
11. ^{1}H and ^{13}C NMR spectra of compounds

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



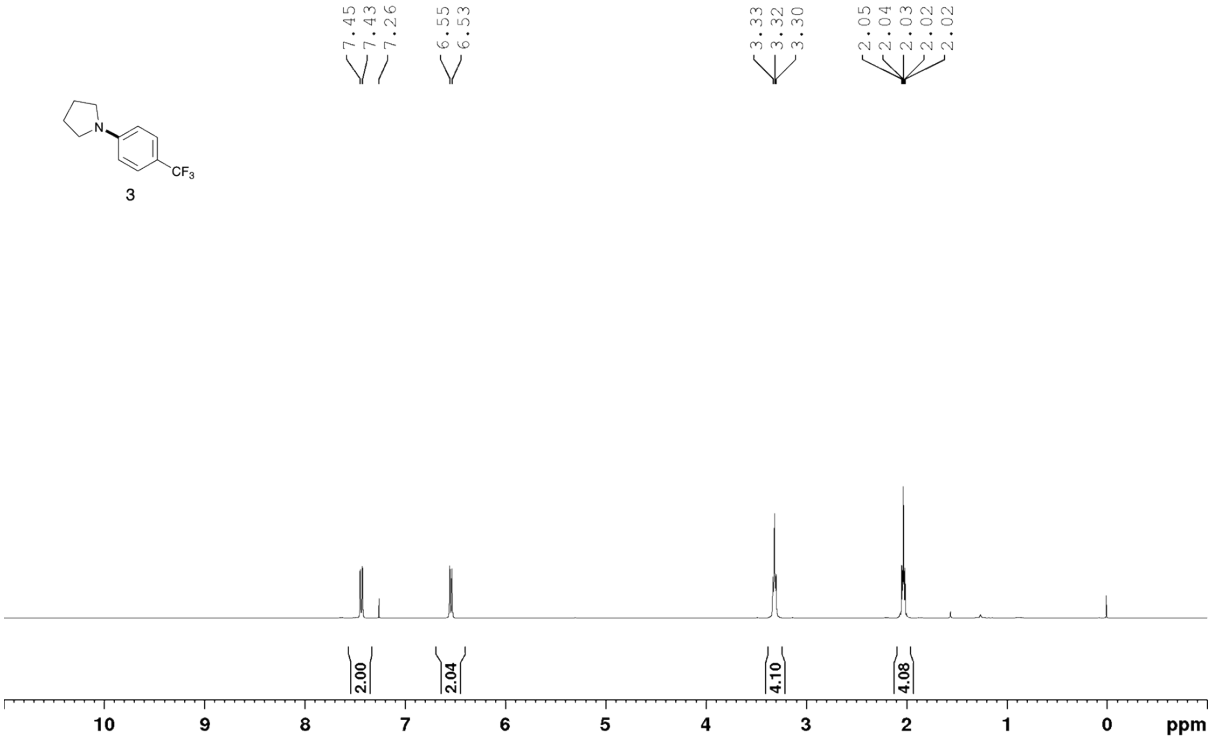
1

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



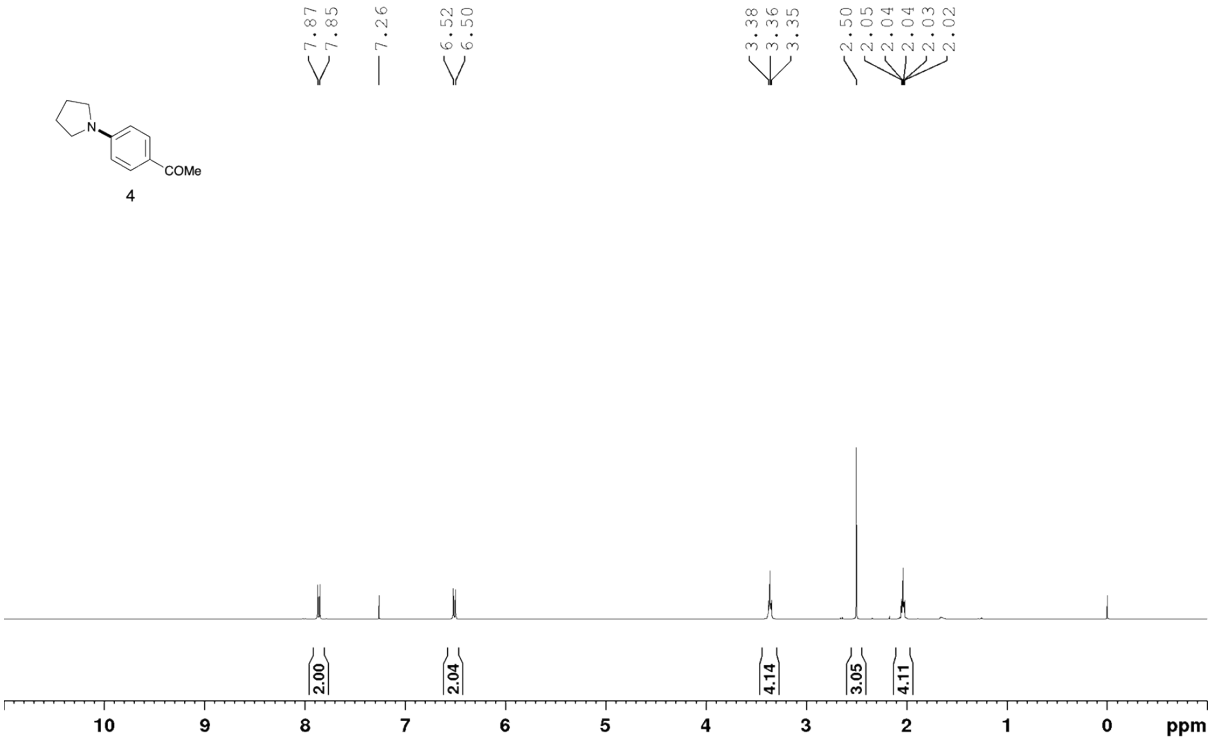
2

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



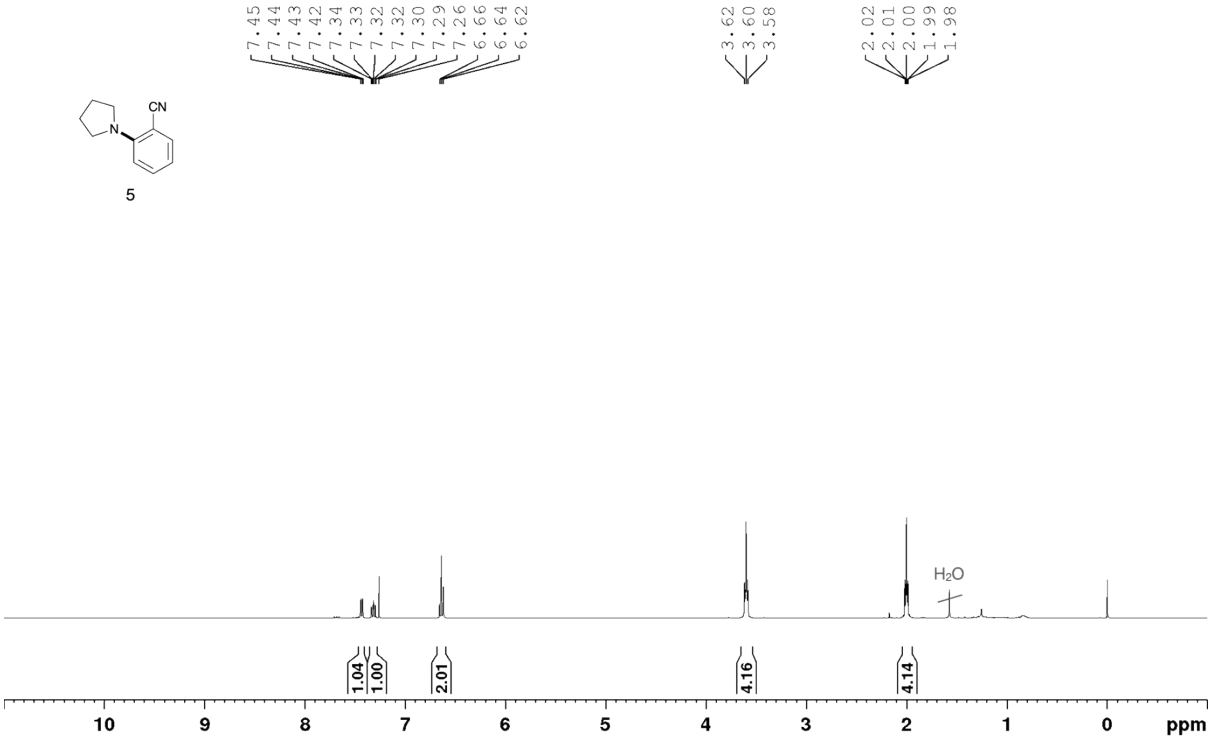
3

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

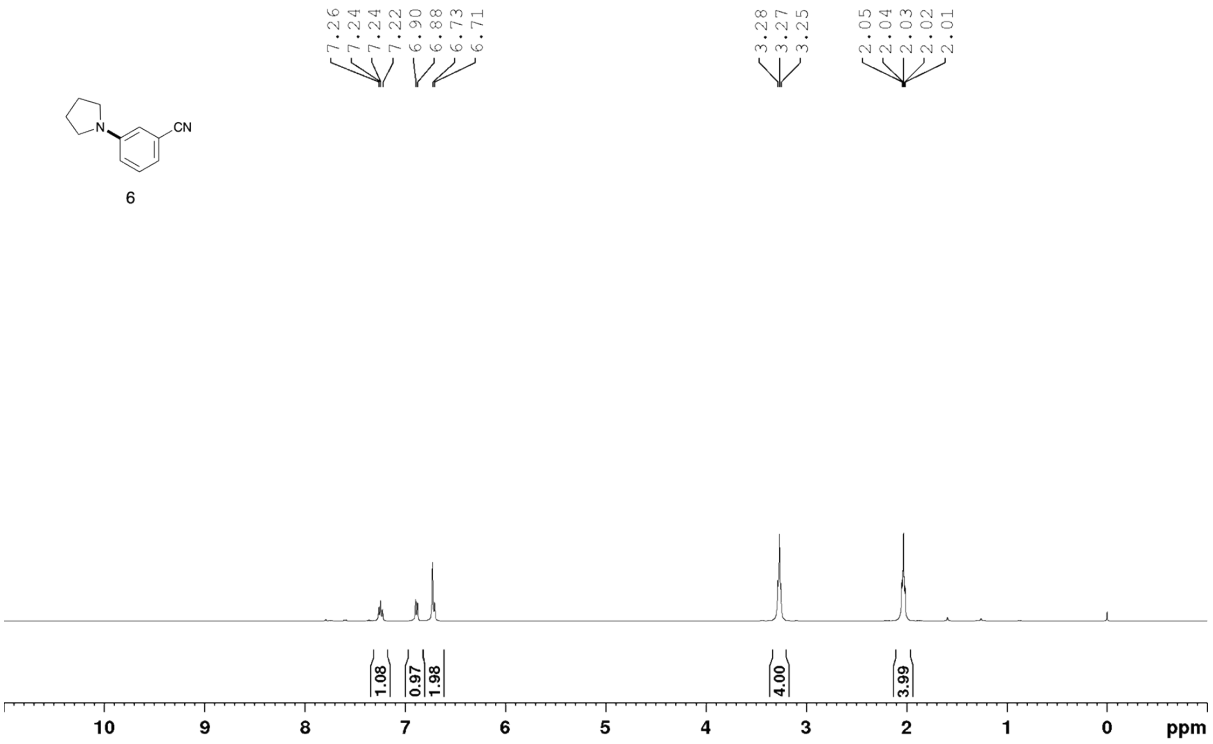


4

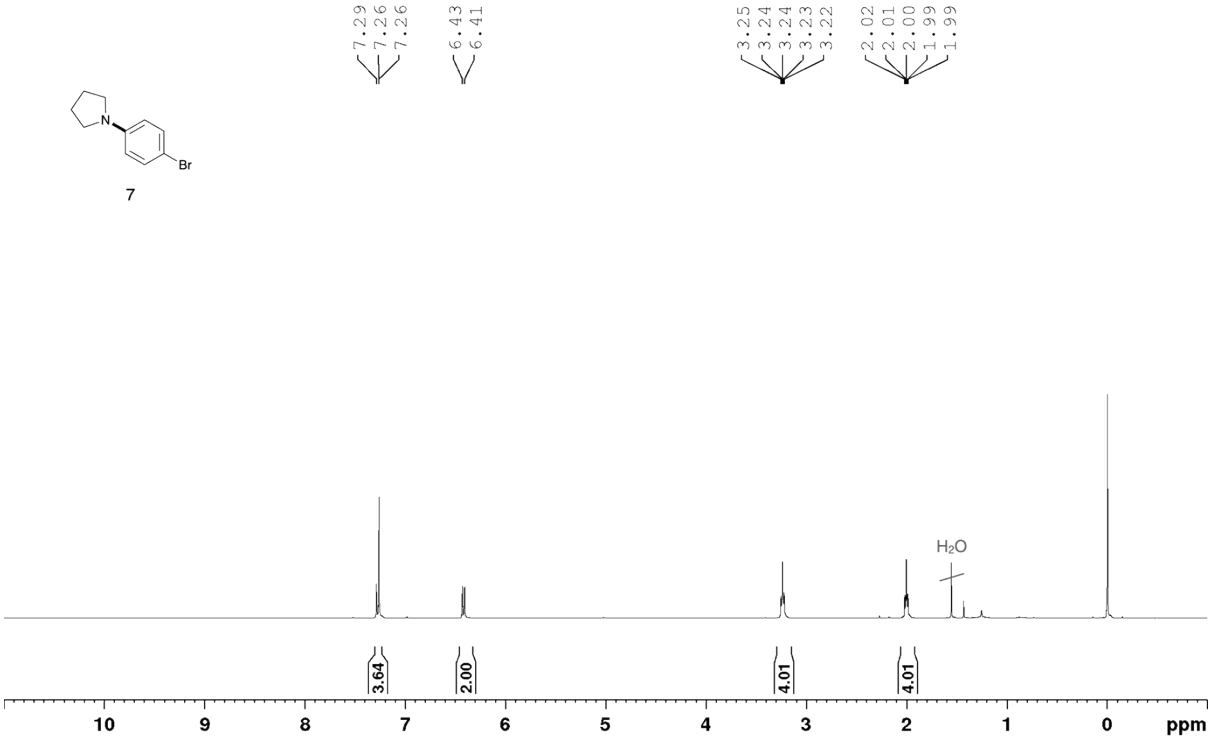
^{1}H NMR ($CDCl_3$, 400 MHz)



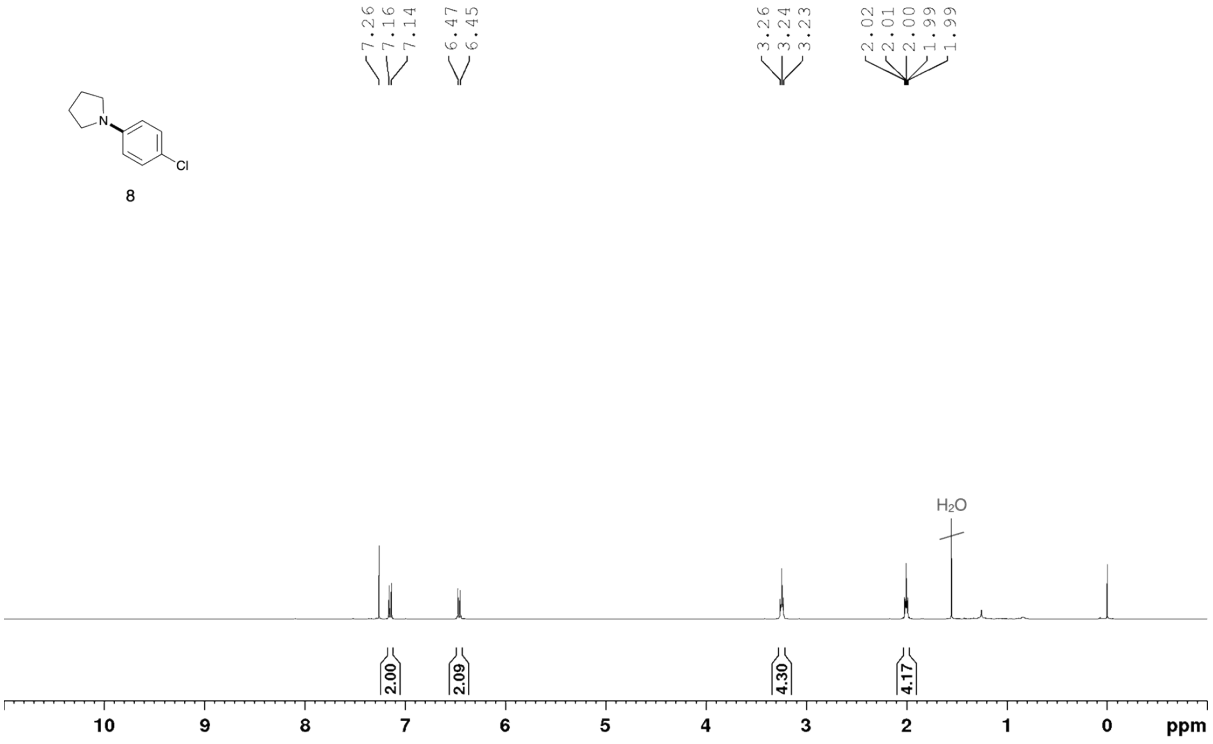
^{1}H NMR ($CDCl_3$, 400 MHz)



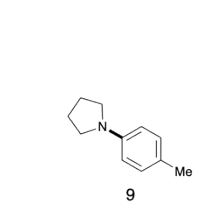
^{1}H NMR ($CDCl_3$, 400 MHz)



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

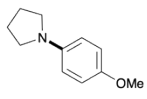


^{1}H NMR ($CDCl_3$, 400 MHz)



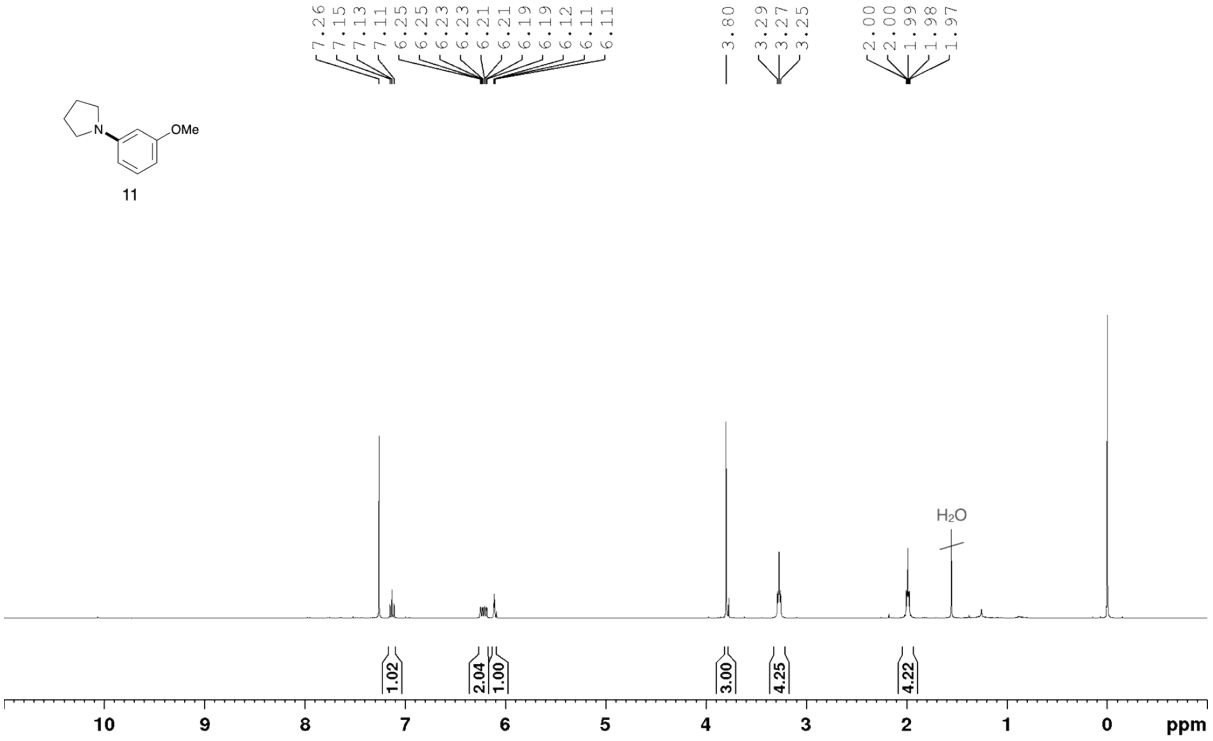
9

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

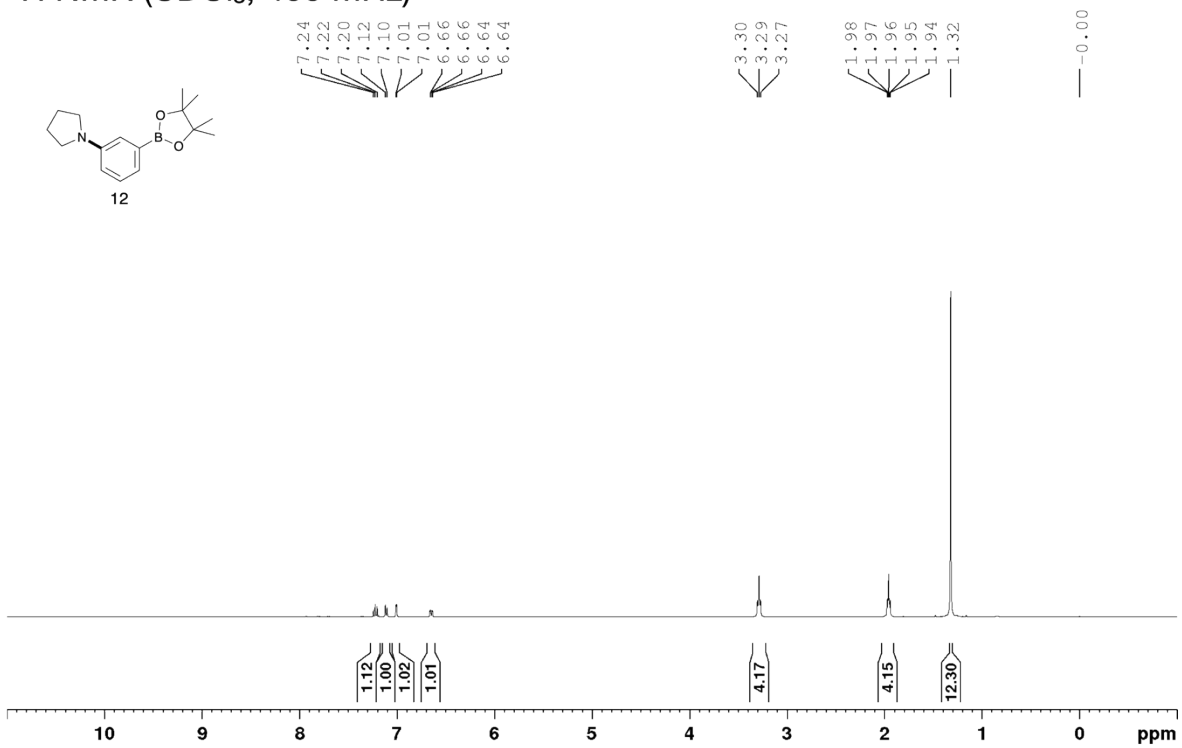


10

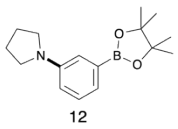
^{1}H NMR ($CDCl_3$, 400 MHz)



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

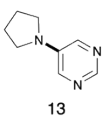


^{13}C NMR ($CDCl_3$, 100 MHz)



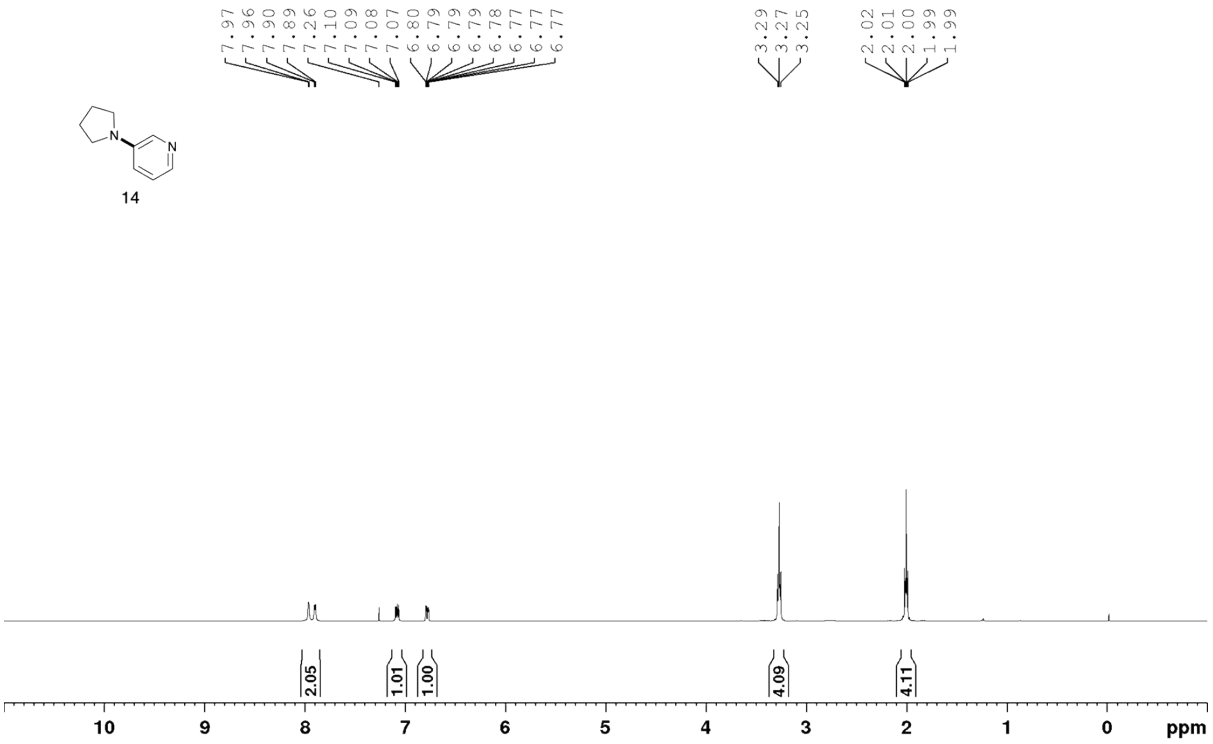
12

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



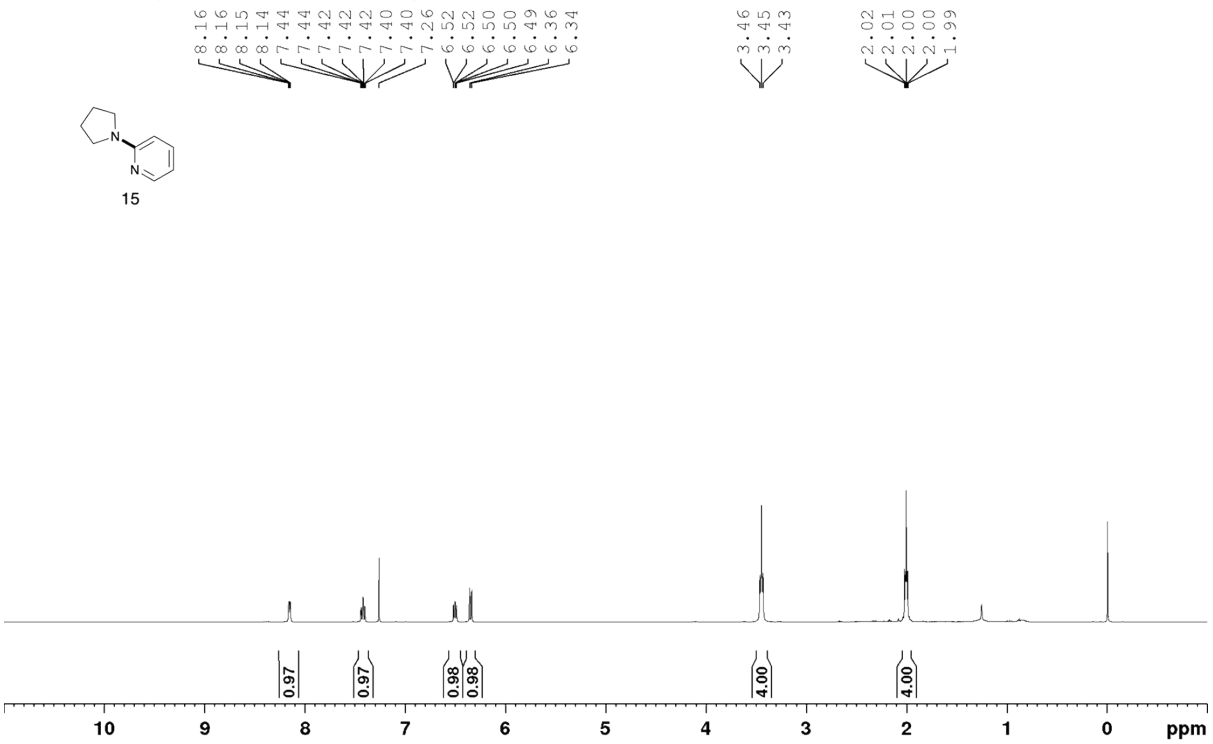
13

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



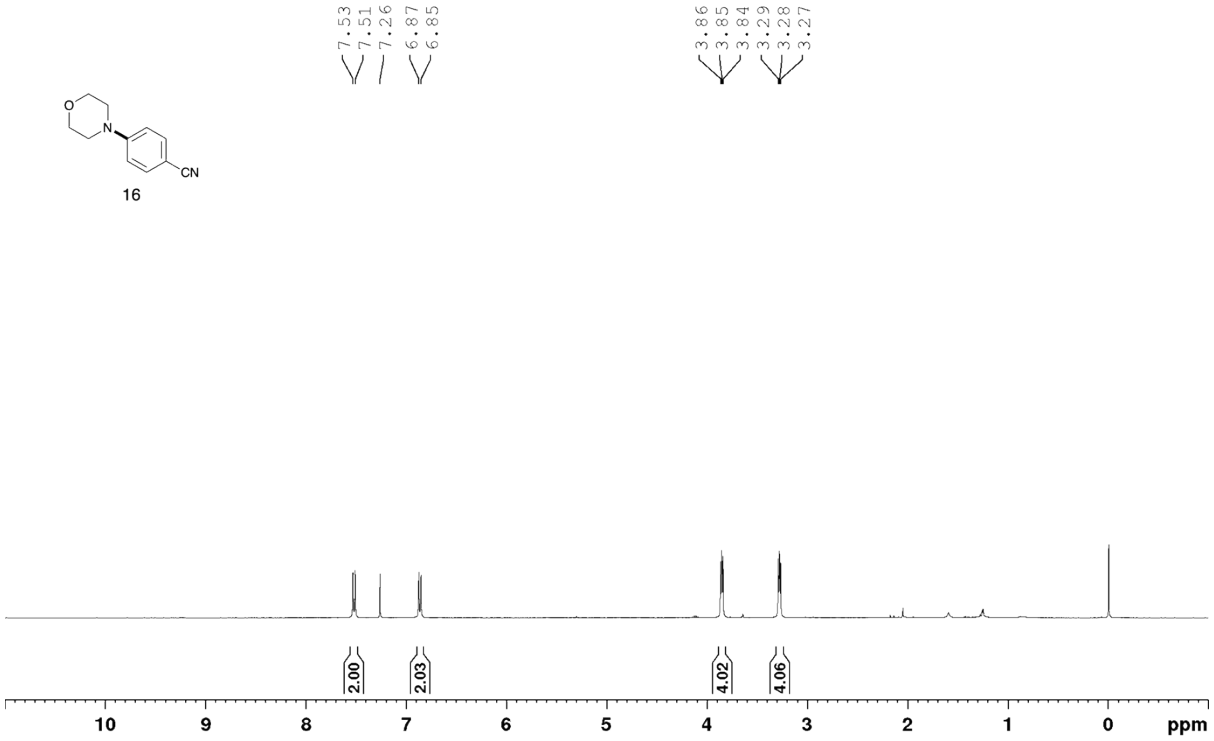
14

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



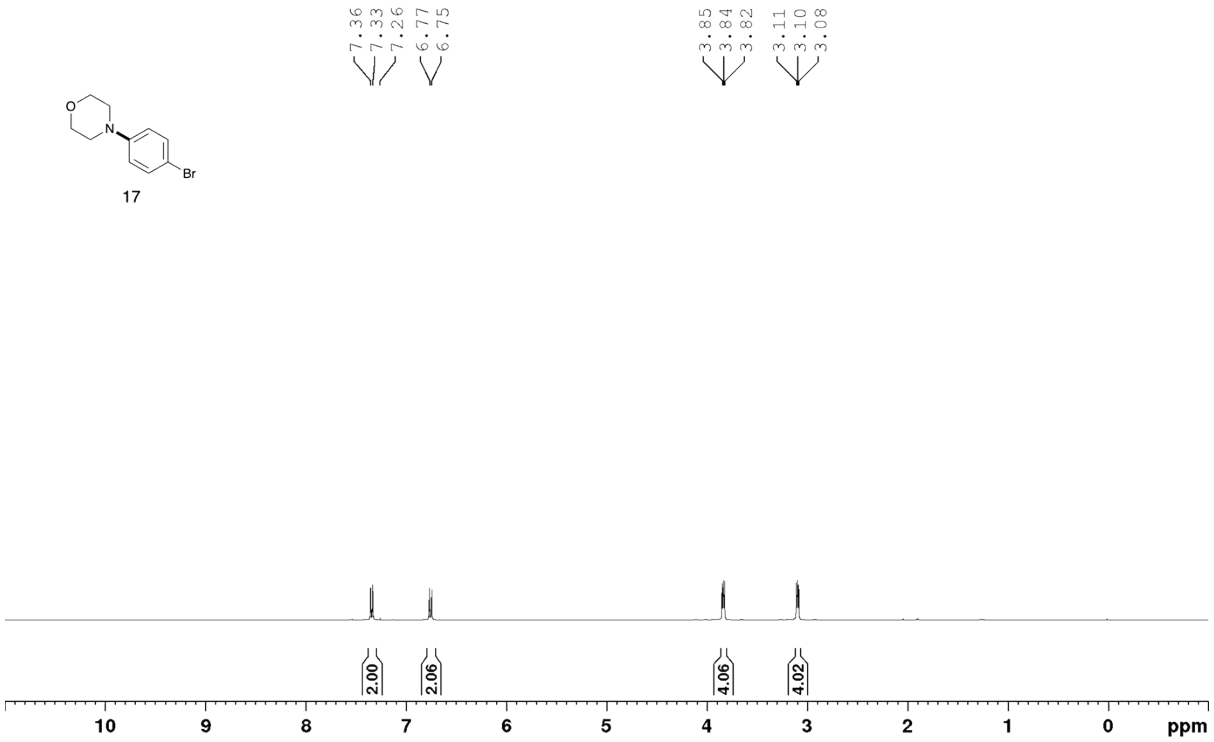
15

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



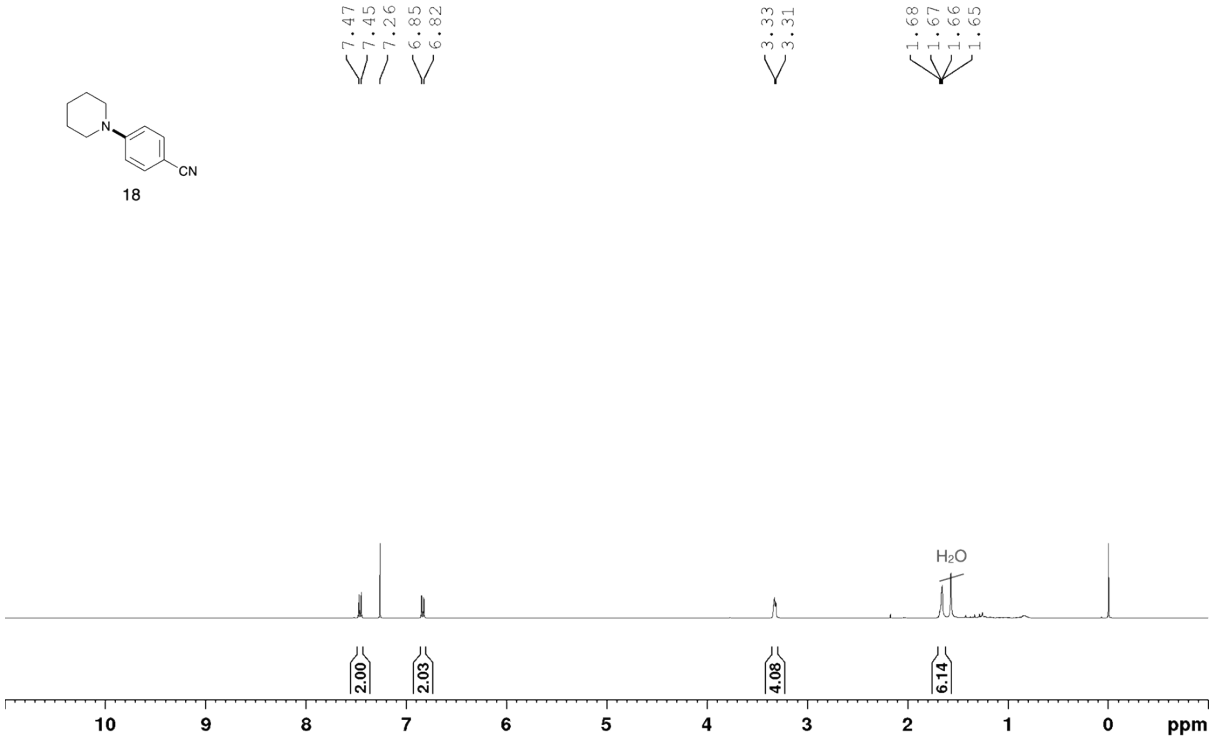
16

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

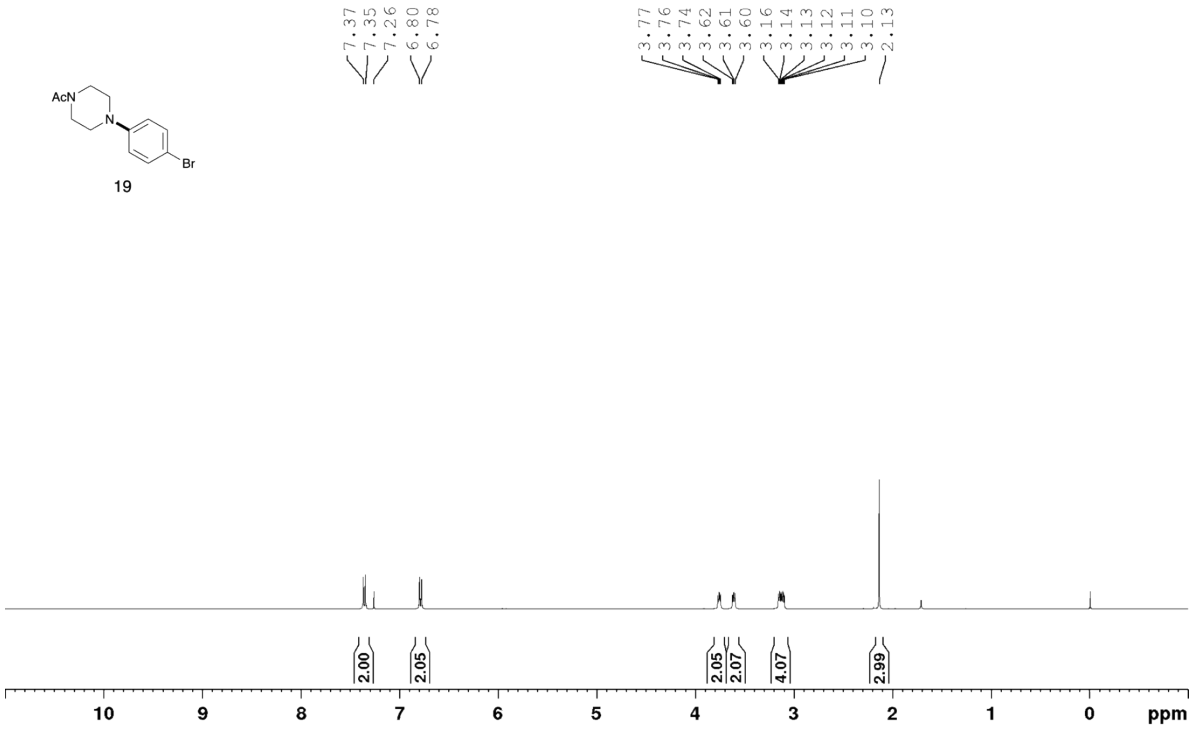


17

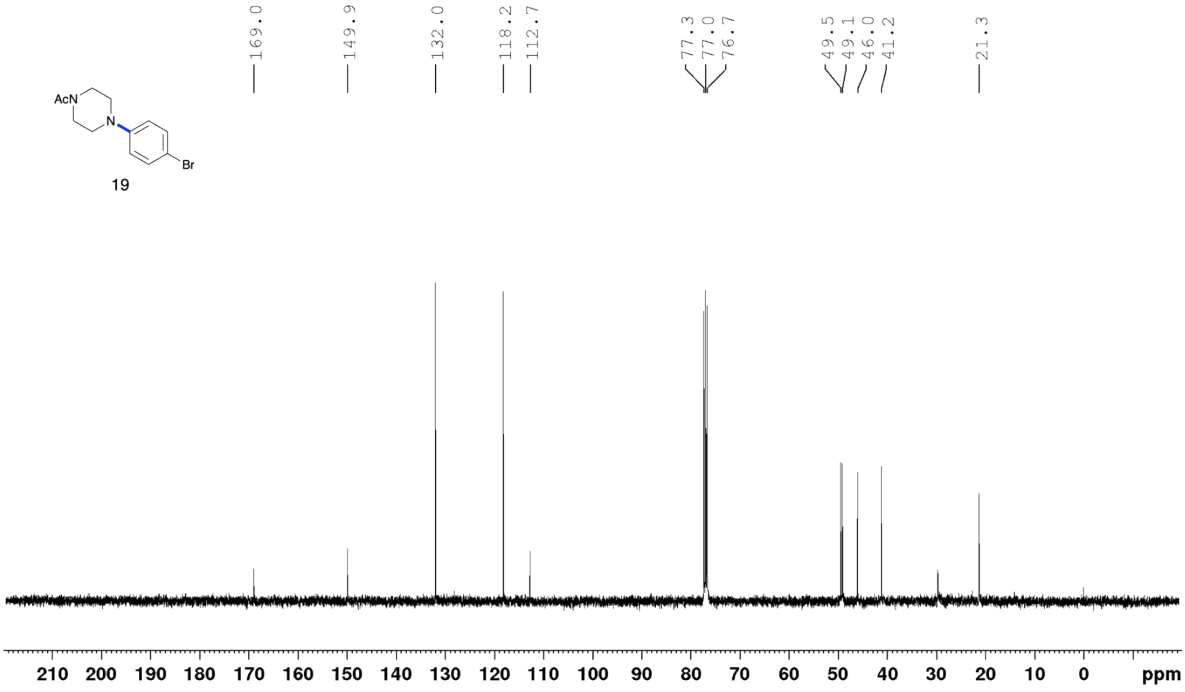
^{1}H NMR ($CDCl_3$, 400 MHz)



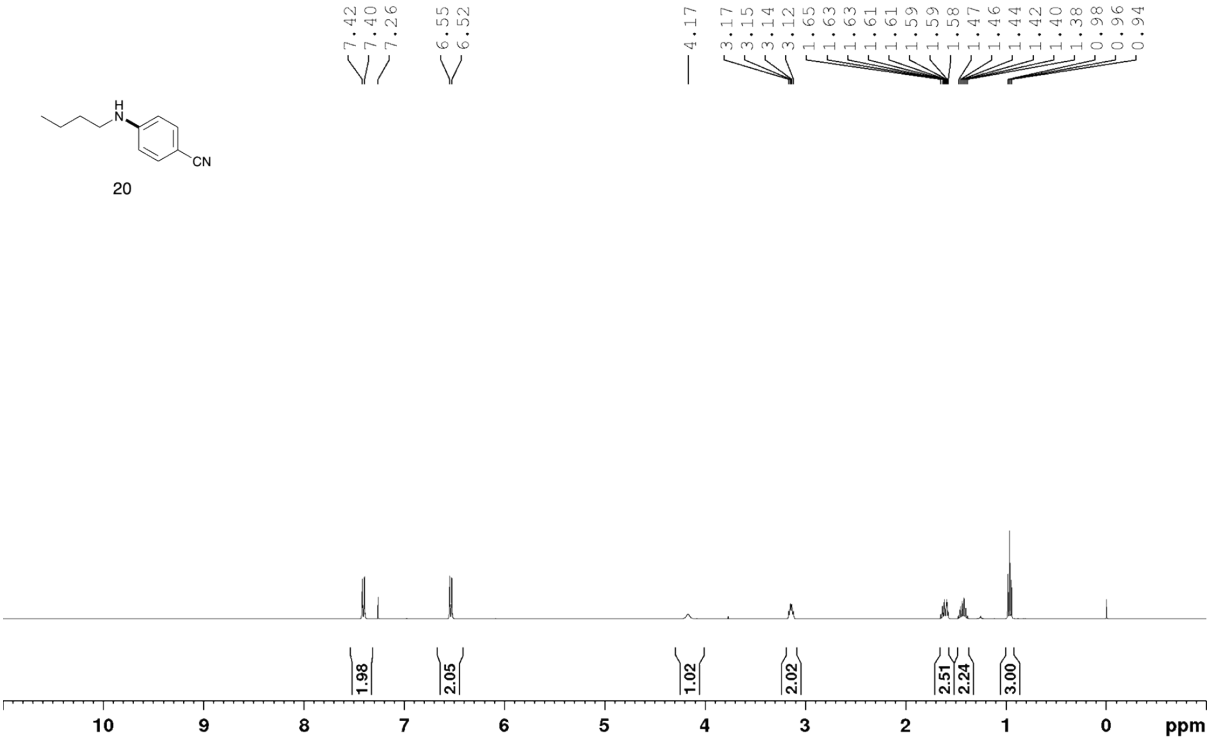
^{1}H NMR ($CDCl_3$, 400 MHz)



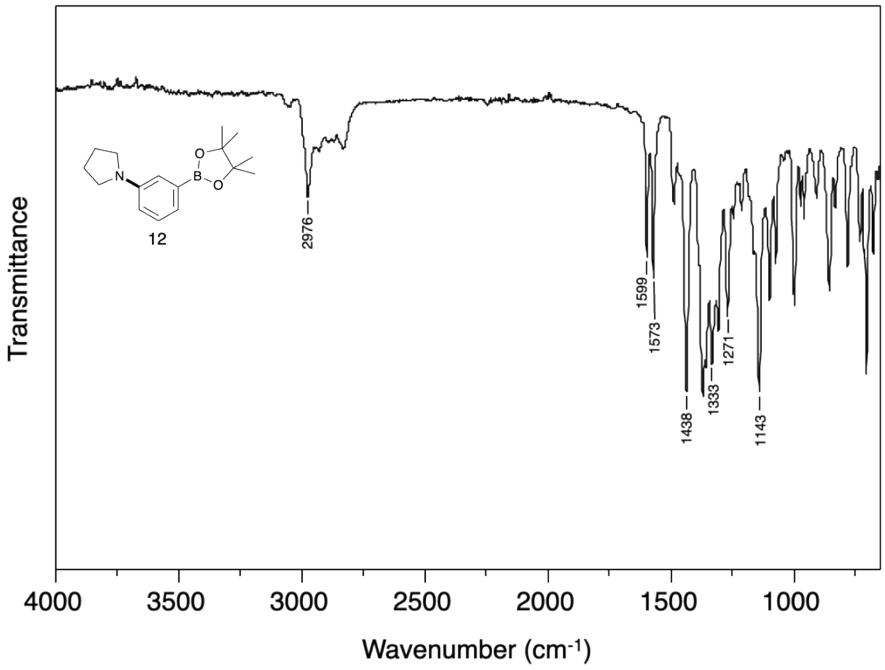
^{13}C NMR ($CDCl_3$, 100 MHz)

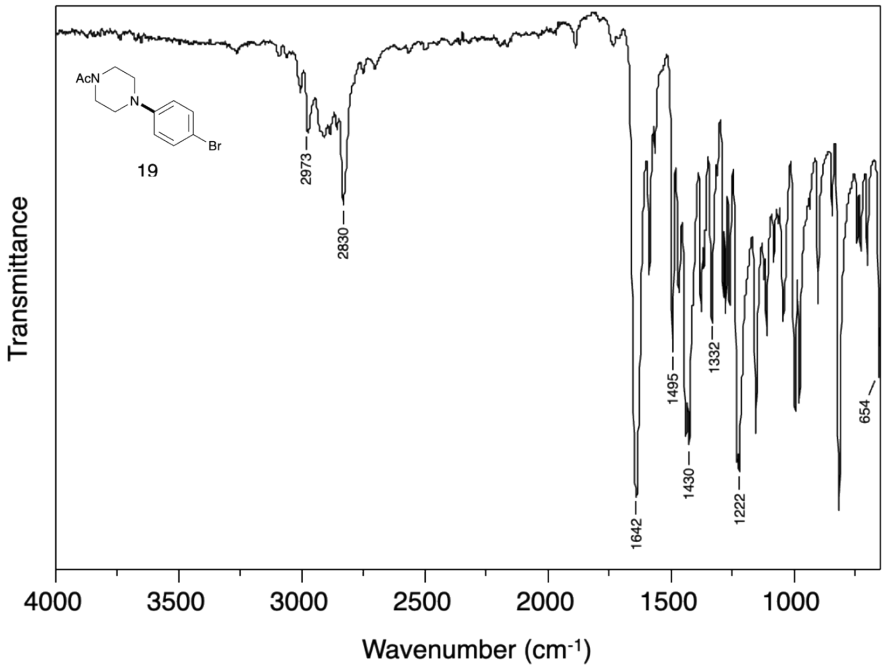


^{1}H NMR ($CDCl_3$, 400 MHz)



12. FT-IR spectra of compounds 12 and 19





13. Abbreviations list

SAC: single-atom catalyst

CN: carbon nitride

NiSAC/CN: single Ni atoms supported on carbon nitride

XRD: X-ray diffraction

NiNP/CN: Ni nanoparticles supported on CN

TEM: transmission electron microscopy

EDS: energy dispersive X-ray spectroscopy

STEM: scanning transmission electron microscopy

HAADF-STEM: high-angle annular dark-field scanning transmission electron microscopy

EXAFS: extended X-ray absorption fine structure spectroscopy

ICP-OES: inductively coupled plasma optical emission spectroscopy

XANES: X-ray absorption near edge structure

XPS: X-ray photoelectron spectroscopy

DMA: dimethylacetamide

DABCO: diazabicyclo[2,2,2]octane

TEOA: triethanolamine

TEMPO: (2,2,6,6-tetramethylpiperidin-1-yl)oxyl

PL: photoluminescence

EPR: electron paramagnetic resonance

References

1. L. Kong, Y. Dong, P. Jiang, G. Wang, H. Zhang and N. Zhao, *J. Mater. Chem. A*, 2016, **4**, 9998-10007.
2. S. Singh, K. Sharma and S. K. Awasthi, *RSC Adv.*, 2015, **5**, 85854-85861.
3. R. Nasri, L. P. Bidel, N. Rugani, V. Perrier, F. Carrière, E. Dubreucq and C. Jay-Allemand, *Molecules*, 2019, **24**, 2888.
4. I. Ghosh, J. Khamrai, A. Savateev, N. Shlapakov, M. Antonietti and B. König, *Science*, 2019, **365**, 360-366.
5. S. Gisbertz, S. Reischauer and B. Pieber, *Nat. Catal.*, 2020, **3**, 611-620.
6. Y.-Y. Liu, D. Liang, L.-Q. Lu and W.-J. Xiao, *Chem. Commun.*, 2019, **55**, 4853-4856.
7. M. T. La, S. Kang and H.-K. Kim, *J. Org. Chem.*, 2019, **84**, 6689-6696.
8. R. N. Baig and R. S. Varma, *RSC Adv.*, 2014, **4**, 6568-6572.
9. C.-H. Lim, M. Kudisch, B. Liu and G. M. Miyake, *J. Am. Chem. Soc.*, 2018, **140**, 7667-7673.
10. Y.-B. Huang, C.-T. Yang, J. Yi, X.-J. Deng, Y. Fu and L. Liu, *J. Org. Chem.*, 2011, **76**, 800-810.
11. J. Louie, M. S. Driver, B. C. Hamann and J. F. Hartwig, *J. Org. Chem.*, 1997, **62**, 1268-1273.