Supporting Information

Nickel-Catalyzed Decyanation of Inert Carbon-Cyano Bonds

Tuhin Patra, Soumitra Agasti, Akanksha and Debabrata Maiti*

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076
E–mail: *dmaiti@chem.iitb.ac.in*

General considerations:

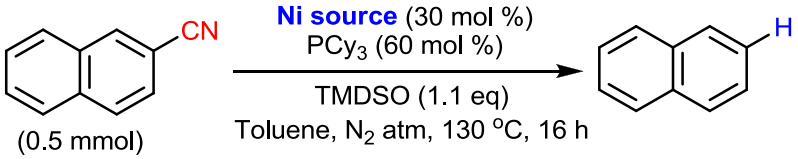
Reagents. Unless otherwise stated, all reactions were carried out under nitrogen atmosphere in screw cap reaction tubes. All the solvents were bought from Merck and dried using standard drying techniques before use. Dry toluene was obtained by passage through alumina and further distilled with sodium wire by using benzophenone as indicator. All cyanides, ligands and silanes were bought from Aldrich and used as received. $Ni(acac)_2$, $Ni(COD)_2$ and PCy_3 were bought from Aldrich and stored under nitrogen in a vacuum atmosphere glovebox. Always $Ni(acac)_2$ and PCy_3 were taken out in small amount for instant use. $Ni(COD)_2$ catalyzed reactions were weighed inside glovebox. All other reagents were purchased from commercial sources and used as received. For column chromatography silica gel (60-120 mesh or 100-200 mesh) from SRL Co. was used. Gradient elution by pet ether/ethyl acetate mixture was performed based on Merck aluminium TLC sheets (silica gel $60F_{254}$).

Analytical information. All isolated compounds are characterized by ^1H NMR, ^{13}C NMR spectroscopy, Gas chromatography mass spectra (GCMS) or HRMS. Copies of the ^1H NMR, ^{13}C NMR can be found in this Supporting Information. Unless otherwise stated, all NMR spectra were recorded on a Bruker 400 MHz instrument (for ^1H NMR) or Bruker 100 MHz instrument (for ^{13}C NMR) and performed in Chloroform-d (99.8 Atom% D, cont. 1.0 V/V% TMS), HRMS data were collected in a Q-TOF micromass (YA-105) in ESI mode. All ^1H NMR spectra are

reported in parts per million (ppm) downfield of TMS and were measured relative to residual $CHCl_3$ (7.27 ppm). All ^{13}C NMR spectra were reported in ppm relative to $CDCl_3$ (77.23 ppm) and were obtained with proton decoupling. Coupling constants, J, are reported in Hertz. All GC analyses were performed on a Agilent 7890A GC system connected with a FID detector using a J & W DB–1 column (10 m, 0.1 mm I.D.). All GCMS analyses were done by Agilent 7890A GC system connected with 5975C inert XL EI/CI MSD (with triple axis detector).

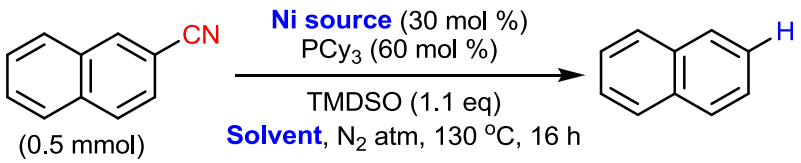
Optimization details for Ni catalyzed reductive decyanation.

(i) Optimization by varying Ni–catalyst:



Entry	Ni–catalyst	GC yield (%)
1	**$Ni(acac)_2$**	**55**
2	$Ni(COD)_2$	51
3	$Ni(OAc)_2.4H_2O$	21
4	$NiCl_2$	5
5	$NiCl_2$.EG-DME	2
6	NiF_2	<1
7	Ni	<1
8	$NiF_2.4H_2O$	2
9	NiO_2	3
10	$NiNO_2$-C	<1
11	$Ni(PPh_3)_4$ + 20% PCy_3	19
12	$Ni(PPh_3)_4$ (No PCy_3 added)	9
13	$Ni(PPh_3)_2(CO)_2$	<1
14	$Ni(Cp)_2$	21
15	$NiBr_2(PBu_3)_2$ (No PCy_3 added)	3
16	$NiBr_2(PBu_3)_2$	35
17	$NiBr_2(PBu_3)_2$ + 20% PCy_3	23

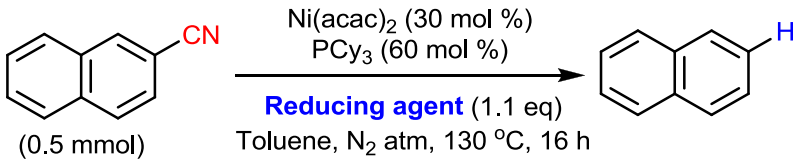
(ii) Optimization with respect to Ni–catalyst and solvent:



Entry	Ni–catalyst	Solvent	GC yield (%)
1	**$Ni(acac)_2$**	**Toluene**	**56**
2	$Ni(acac)_2$	Me-2-pyrrolidinone	53
3	$Ni(acac)_2$	Dioxane	49
4	$Ni(acac)_2$	Pyridine	22
5	$Ni(acac)_2$	Trifluorotoluene	29
6	$Ni(acac)_2$	DMSO	21
7	$Ni(acac)_2$	EG-DME	41
8	$Ni(acac)_2$	Cyclohexane	32
9	$Ni(acac)_2$	Diglyme	26
10	$Ni(OAc)_2$	Toluene	32
11	$Ni(OAc)_2$	Me-2-pyrrolidinone	46
12	$Ni(OAc)_2$	Dioxane	42
13	$Ni(OAc)_2$	Pyridine	34
14	$Ni(OAc)_2$	Trifluorotoluene	36
15	$Ni(OAc)_2$	DMSO	19
16	$Ni(OAc)_2$	EG-DME	48
17	$Ni(OAc)_2$	Cyclohexane	7
18	$Ni(OAc)_2$	Diglyme	40
19	$NiCl_2$	Toluene	7
20	$NiCl_2$	2-MeTHF	8
21	$NiCl_2$	Methylcyclohexane	<1
22	$NiCl_2$	Butyronitrile	3
23	$NiCl_2$	DMF	2
24	$NiCl_2$	Bu_3N	<1
25	$NiCl_2$	Bu_2O	<1

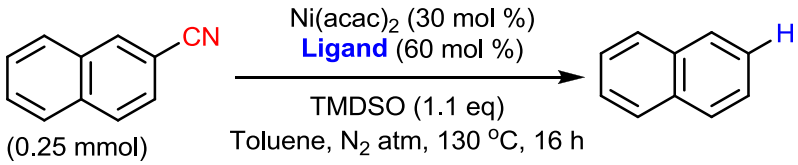
26	$NiCl_2$	m-Xylene	3
27	$NiCl_2$	Dioxane	7
28	$NiCl_2$	2-BuOH	<1
29	$NiCl_2$	DMSO	13
30	$NiCl_2$	Pyridine	46
31	$NiCl_2$	Tetrahydropyran	7
32	$NiCl_2$	Cyclohexane	47
33	$NiCl_2$	Diglyme	17
34	$NiCl_2$	EG-DME	15
35	$NiCl_2$	Trifluorotoluene	12
36	$NiCl_2$	1,2-dimethoxyether	10
37	$NiCl_2$	DCE	5
38	$NiCl_2$	Me_3C-CN	3
39	$NiCl_2$	Toluene	3
40	$NiCl_2$	Me-2-pyrrolidinone	42

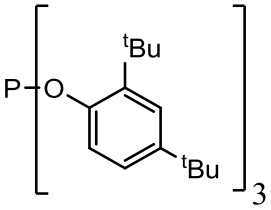
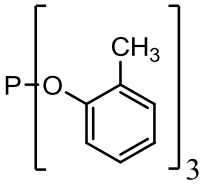
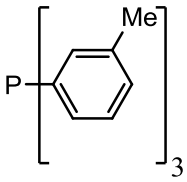
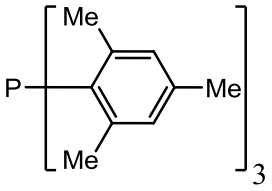
(iii) Optimization by varying reducing agents:

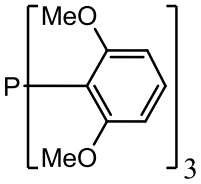
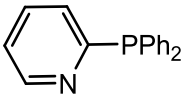
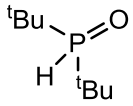
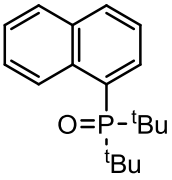
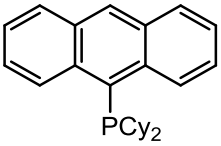
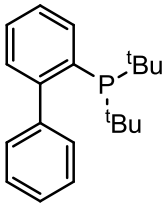
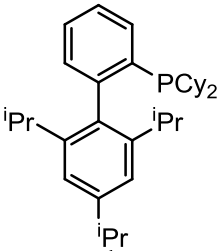


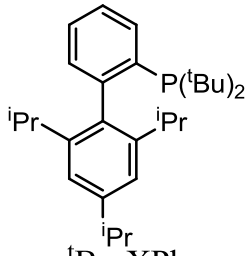
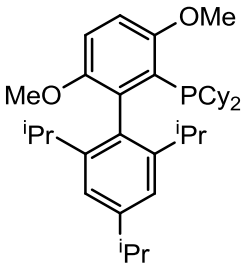
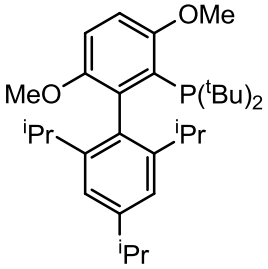
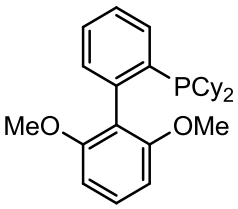
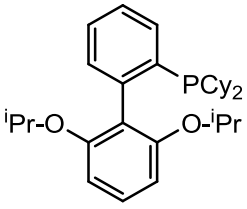
Entry	Reducing agent	GC yield (%)
1	**TMDSO**	**56**
2	Et_3SiH	25
3	$^{i}Pr_3SiH$	<1
4	Ph_2MeSiH	29
5	$(TMS)_3SiH$	44
6	$PhMeSiH_2$	30
7	Ph_2SiH_2	26

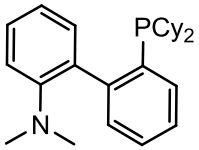
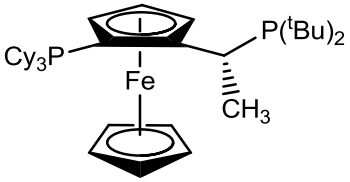
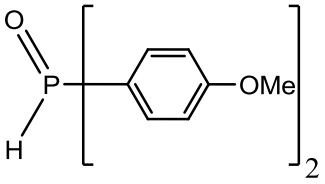
(iv) Optimization with respect to monodentate ligand:



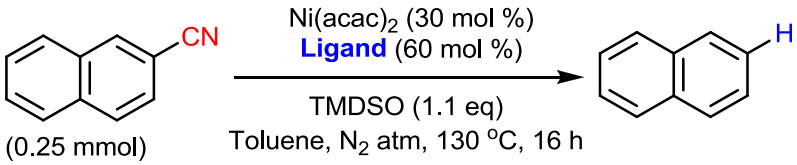
Entry	Ligand	GC yield (%)
1	PBu_3	49
2	PPh_3	16
3	**PCy_3**	**55**
4	$P(OPh)_3$	23
5	Picolinic acid	10
6	L-Proline	<1
7	1,10-Phenanthroline	<1
8		30
9		14
10		17
11		11

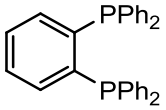
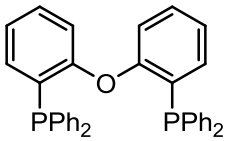
12		32
13		<1
14		11
15		<1
16		21
17	 JohnPhos	12
18	 XPhos	12

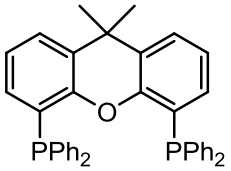
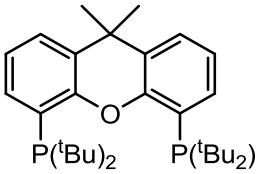
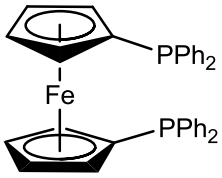
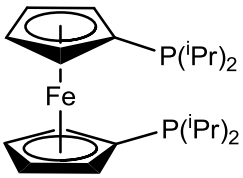
19	 tBu-XPhos	<1
20	 BrettPhos	20
21	 tBu-BrettPhos	15
22	 SPhos	20
23	 RuPhos	24

24	 DavePhos	32
25	 JosiPhos	<1
26		<1

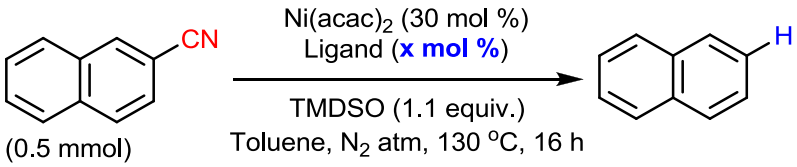
(v) Optimization with respect to bidentate ligand:



Entry	Ligand	GC Yield (%)
1	$Ph_2PCH_2PPh_2$	<1
2	$Ph_2PCH_2CH_2PPh_2$	<1
3	$Ph_2PCH_2CH_2CH_2PPh_2$	<1
4	$Ph_2PCH_2CH_2CH_2CH_2PPh_2$	<1
5		<1
6		<1

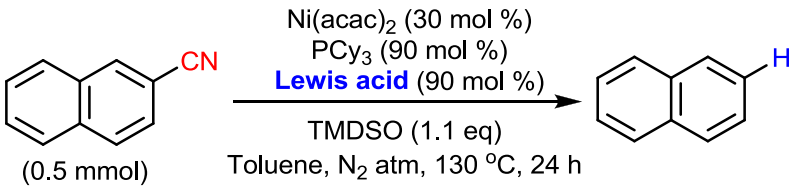
7	 Xantphos	14
8		42
9		<1
10		13

(vi) Optimization with respect to amount of ligand:



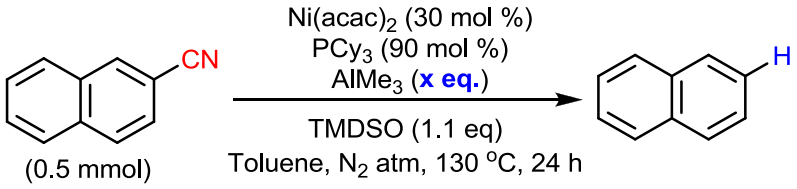
Entry	PCy_3 (mol %)	GC yield (%)
1	30	42
2	60	54
3	**90**	**59**
4	120	59
5	150	57

(vii) Optimization with respect to Lewis acid:



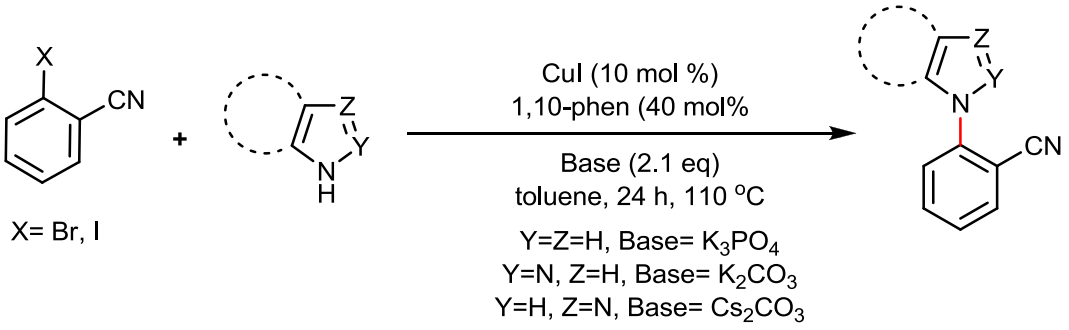
Entry	Lewis acid	GC yield (%)
1	**$AlMe_3$**	**64**
2	$ZnCl_2$	8
3	$FeCl_3$	1
4	$BF_3.Et_2O$	2
5	$AlCl_3$	5
6	BPh_3	29

(viii) Optimization with respect to amount of Lewis acid:



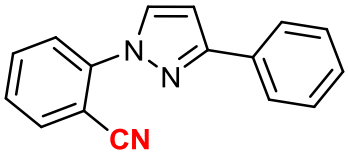
Entry	Lewis acid (equiv.)	GC yield (%)
1	0.5	31
2	1	62
3	2	68
4	**3**	**73**
5	4	70

Experimental procedure for Ni catalyzed reductive decyanation of cyanides.

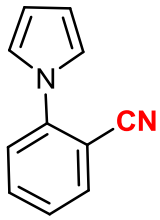


Scheme 1

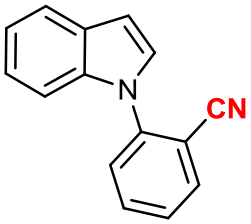
General procedure A for N-arylation of nitrogen heterocycles (Scheme 1).[1] Heterocycle (2 mmol), base (4.2 mmol), CuI (10 mol %), 1,10-phenanthrolene (40 mol %), 2-halobenzonitrile (2.4 mmol) and a stir bar were taken in an oven-dried screw-cap reaction tube. The cap was fitted with a rubber septum and the reaction tube was evacuated and back filled with nitrogen and this sequence was repeated two additional times. Toluene (1 mL) was then added under the positive pressure of nitrogen. The reaction tube was sealed and immersed in pre heated oil bath at 110 °C for 24 h with continuous stirring by a magnetic stirrer. The reaction mixture was removed, allowed to attain room temperature, diluted with 3 mL ethyl acetate, filtered through Celite and eluted with additional 12 mL ethyl acetate. The filtrate was concentrated and the resulting residue was purified by column chromatography using silica gel and pet ether/ethyl acetate as eluent.



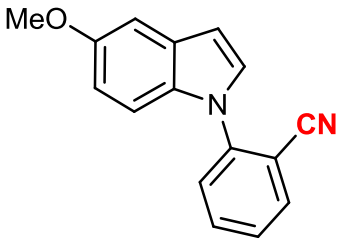
2-(3-Phenyl-1*H*-pyrazol-1-yl)benzonitrile (Table 2, entry 2a-SM). Following general procedure A, 2-Iodobenzonitrile (549 mg, 2.4 mmol), 3-phenyl-1*H*-pyrazole (288 mg, 2.0 mmol), CuI (38 mg, 10 mol%), 1,10-phenanthrolene (144 mg, 40 mol%), K_2CO_3 (580 mg, 4.2 mmol), and toluene (3 mL) were used. Yield 71% (348 mg). m.p. 60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.14 (*q*, J= 4.0, 1H), 7.9 (*d*,J= 8.0, 2H), 7.82 (*d*, J= 8.0, 1H), 7.74 (*td*, J= 8.0, 2.0, 1H), 7.66 (*tt*, J= 8.0, 2.0, 1H), 7.42 (*dt*, J= 6.0, 4.0, 2H), 7.35 (*tq*, J= 5.3, 2.0, 2H), 6.82 (*q*, J= 1.3, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.2, 142.0, 134.8, 134.2, 132.6, 130.7, 128.9, 128.7, 127.1, 126.3, 123.8, 117.4, 106.2, 105.0. GCMS (m/z): 245.1 $[M]^+$.



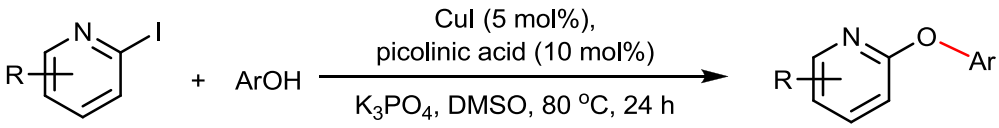
2-(1*H*-Pyrrol-1-yl)benzonitrile (Table 2, entry 2d-SM). Following general procedure A, 2-Bromobenzonitrile (2.18 g, 12 mmol), 1*H*-pyrrole (695 µL, 10 mmol), CuI (190 mg, 10 mol%), 1,10-phenanthroline (720 mg, 40 mol%), K_3PO_4 (4.45 g, 21 mmol) were taken in a round bottom flask and toluene (25 mL) was added under inert atmosphere and refluxed for 24 h at 110 °C. The reaction mixture was removed, allowed to attain room temperature, diluted with 10 mL ethyl acetate, filtered through celite and eluted with additional 30 mL ethyl acetate. The filtrate was concentrated and the resulting residue was purified by column chromatography using pet ether/ ethyl acetate (98:2 v/v) mixture to give the titled compound as brown oil. Isolated yield: 87% (1.46 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76 (*dd*, J= 8.04, 1.32, 1H), 7.65-7.69 (*m*, 1H), 7.43-7.45 (*m*, 1H), 7.39 (*dt*, J= 7.68, 1.12, 1H), 7.11 (*t*, J= 2.14, 2H), 6.41 (*t*, J= 2.16, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.3, 134.7, 134.2, 126.7, 125.3, 121.3, 117.1, 111.4, 107.1. GCMS (m/z): 168.1 $[M]^+$.



2-(1*H*-Indol-1-yl)benzonitrile (Table 2, entry 2e-SM). Following general procedure A, 2-Bromobenzonitrile (437 mg, 2.4 mmol), 1*H*-indole (235 mg, 2.0 mmol), CuI (38 mg, 10 mol%), 1,10-phenanthroline (144 mg, 40 mol%), K_3PO_4 (890 mg, 4.2 mmol) and toluene (3 mL) were used and the titled compound was isolated by 97:3 (v/v) pet ether/ ethyl acetate mixture as white solid. Yield 78% (340 mg). ^{1}H NMR (400 MHz, Chloroform-d) δ. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86 (*dd*, *J* = 7.8, 1.5 Hz, 1H), 7.69 – 7.79 (m, 2H), 7.63 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.50 (td, *J* = 7.7, 7.7, 1.2 Hz, 1H), 7.43 (d, *J* = 3.3 Hz, 1H), 7.33 – 7.40 (m, 1H), 7.20 – 7.30 (m, 2H), 6.76 – 6.81 (dd, *J* = 3.4, 0.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.1, 134.7, 134.1, 129.5, 128.3, 127.6, 127.6, 123.0, 121.6, 121.5, 116.7, 110.4, 110.0, 105.2. GCMS (m/z): 218.0 $[M]^+$.

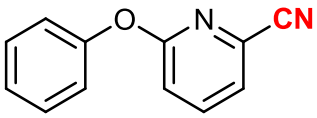


2-(5-Methoxy-1*H*-indol-1-yl)benzonitrile (Table 2, entry 2f-SM). Following general procedure A, 2-Bromobenzonitrile (437 mg, 2.4 mmol), 5-Methoxy-1*H*-indole (235 mg, 2.0 mmol), CuI (38 mg, 10 mol%), 1,10-phenanthroline (144 mg, 40 mol%), K_3PO_4 (890 mg, 4.2 mmol) and toluene (3 mL) were used to prepare the titled compound and isolated by 95:5 pet ether/ ethyl acetate (v/v) mixture as pale yellow solid. Yield 72% (357 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.90- 7.93 (*m*, 1H), 7.81 (*dt*, J= 7.56, 1.56, 1H), 7.54- 7.61 (*m*, 2H), 7.43 (*dd*, J= 3.24, 0.36, 1H), 7.17- 7.20 (*m*, 2H), 6.86 (*dd*, J= 9.04, 2.48, 1H), 6.68 (*dd*, J= 3.28, 0.72, 1H), 3.83 (*s*, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.1, 142.7, 135.5, 132.6, 130.9, 130.3, 129.0, 128.8, 118.4, 117.6, 113.5, 112.2, 110.9, 105.1, 103.8, 56.3. HRMS calculated for ($C_{16}H_{12}N_2O$+H): 249.1028, found 249.1033.

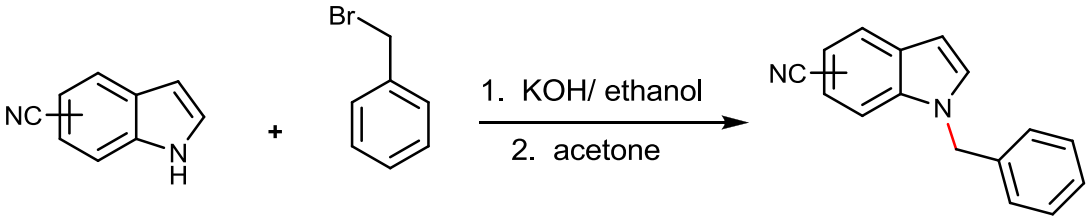


Scheme 3

<u>General procedure B</u> for O-arylation (Scheme 2).[2] An oven-dried screw cap reaction tube with a magnetic stirbar was charged with copper(I) iodide (19 mg, 0.1 mmol, 5 mol%), picolinic acid, **1** (25mg, 0.20 mmol, 10 mol%), aryl iodide (if solid; 2 mmol), ArOH (2.4 mmol) and K_3PO_4 (848 mg, 4 mmol). The tube was evacuated and back-filled with nitrogen. The evacuation/backfill sequence was repeated two additional times. Under a counter flow of nitrogen, remaining liquid reagents were added by syringe, followed by addition of DMSO (2 mL) by syringe. The tube was placed in a preheated oil bath at 80 ºC and the reaction mixture was stirred vigorously for 24 h. The reaction mixture was cooled to room temperature. Ethyl acetate (10 mL) and H_2O (1 mL) were added and the mixture was stirred. The organic layer was separated and the aqueous layer was extracted twice more with ethyl acetate (10 mL). Combined organic layer was dried over Na_2SO_4 and filtered through celite. The filtrate was concentrated and the residue was purified by column chromatography using pet ether/ ethyl acetate as eluent.

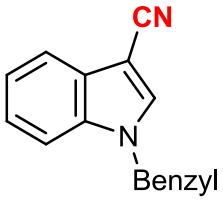


6-Phenoxypicolinonitrile (Table 2, entry 2c-SM). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74 (*t*, J= 8.0, 1H), 7.37 (*q*, J= 8.0, 3H), 7.21 (*t*, J= 8.0, 1H), 7.11 (*tt*, J= 8.0, 2.0, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.0, 153.2, 140.5, 131.1, 130, 125.7, 123.8, 121.5, 117.0, 116.3. GCMS (m/z): 196.0 $[M]^+$.

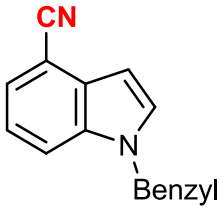


Scheme 2

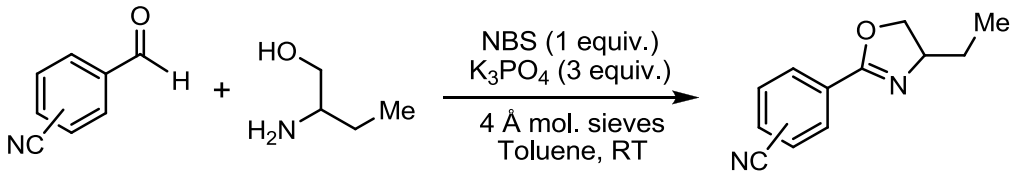
General procedure C for N-benzylation of substituted indoles (Scheme 3).[3] To a solution of substituted indole (2 mmol) in 20 mL ethanol, KOH (168 mg, 3 mmol) was added. The solution was stirred until all the solids dissolved in the solvent. Now the solvent was completely removed from mixture and 20 mL of acetone was added in the mixture, followed by benzyl bromide (238 µL, 2 mmol) was added. Instantly a precipitate was formed. This precipitate was filtered and then the solution was concentrated and pure compound was separated by column chromatography.



1-Benzyl-1*H*-indole-3-carbonitrile (Table 2, entry 2g-SM). Following general procedure C, 3-Cyanoindole (284 mg, 2 mmol) was used to prepare the titled compound and isolated by 98:2 pet ether/ ethyl acetate mixture (v/v) as colorless solid with 91% (423 mg) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81 (*m*, 1H), 7.63 (*s*, 1H), 7.36 (*m*, 6H), 7.17 (*m*, 2H), 5.36 (*s*, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.8, 135.4, 135.2, 129.3, 128.6, 128.1, 127.3, 124.2, 122.5, 120.1, 116.0, 111.0, 86.4, 51.0. GCMS (m/z): 232.1 $[M]^+$.

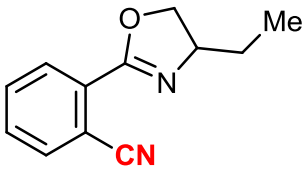


1-Benzyl-1*H*-indole-4-carbonitrile (Table 2, entry 2h-SM). Following general procedure C, 4-Cyanoindole (285 mg, 2 mmol) was used. The titled compound was isolated by 98:2 pet ether/ ethyl acetate mixture (v/v) as colorless solid with 93% (432 mg) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49 (*m*, 2H), 7.32 (*m*, 4H), 7.20 (*dd*, *J* = 8.2, 7.4 Hz, 1H), 7.10 (*m*, 2H), 6.78 (*dd*, J= 3.2, 0.6, 1H), 5.38 (*s*, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.7, 136.1, 131.2, 130.2, 129.2, 128.2, 126.9, 125.3, 121.5, 118.9, 114.7, 103.5, 101.0, 50.7. GCMS (m/z): 232.1 $[M]^+$.



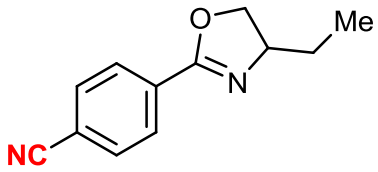
Scheme 4

<u>General procedure D</u> for the preparation of Cyanooxazoline (Scheme 4).[4] A round bottom flask with magnetic stirbar was charged with molecular sieves (4 Å) and cyanobenzaldehyde. The flask was put into vaccum/nitrogen sequences for three times using inlet stopper and immediately a septum was put. Then dry toluene and 2-aminobutanol were put through syringes. A N_2 balloon was fitted and the solution mixture was stirred at room temperature for overnight. K_3PO_4 and NBS were added and stirred again at room temperature for 4 h, filtered through sintered bed using ethyl acetate as washing solvent. The filtrate was concentrate and purified with column chromatography (neutral alumina column).

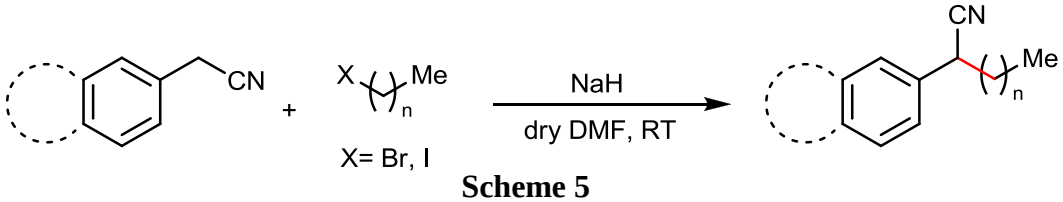


2-(4-Ethyl-4,5-dihydrooxazol-2-yl)benzonitrile (Table 2, entry 2i-SM). Following general procedure D the titled compound was synthesized using 2-Cyanobenzaldehyde (2 mmol) and isolated by using neutral alumina column (CAUTION: compound decomposes in silica column)

with 95:5 pet ether/ ethyl acetate (v/v) as colorless liquid in 68% yield (272 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03 (*dd*, J= 7.8, 1.6, 1H), 7.77 (*dd*, J= 7.6, 1.2, 1H), 7.64 (*dt*, J= 7.6, 1.6, 1H), 7.57 (*dt*, J= 7.6, 1.6, 1H), 4.56 (*dd*, J= 9.4, 8.2, 1H), 4.35 (*m*, 1H), 4.14 (*t*, J= 8.0, 1H), 1.78 (*s*, J= 7.4, 1H), 1.67 (*s*, J= 7.0, 1H), 1.04 (*t*, J= 7.4, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.1, 134.7, 132.6, 131.2, 130.3, 118.0, 112.0, 106.1, 73.0, 68.6, 28.8, 10.2. GCMS (m/z): 200.2 $[M]^+$.

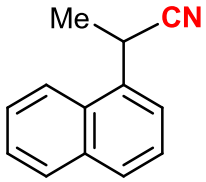


4-(4-Ethyl-4,5-dihydrooxazol-2-yl)benzonitrile (Table 2, entry 2j-SM). Following general procedure D, 4-Cyanobenzaldehyde (2 mmol) was used. The titled compound was isolated by using neutral alumina column (CAUTION: compound decomposes in silica column) with 95:5 pet ether/ ethyl acetate (v/v) as colorless liquid in 76% yield (304 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03 (*dd*, J= 8.4, 1.6, 2H), 7.69 (*dd*, J= 8.8, 2.0, 2H), 4.53 (*dt*, J= 8.4, 1.2, 1H), 4.29 (*dq*, J= 7.6, 1.6, 1H), 4.09 (*dt*, J= 8.0, 1.6, 1H), 1.75 (*ds*, J= 7.6, 1.6, 1H), 1.63 (*ds*, J= 7.2, 1.2, 1H), 1.01 (*dt*, J= 7.2, 1.2, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.7, 131.9, 131.9, 128.6, 118.1, 114.4, 72.4, 68.1, 28.4, 10.0. HRMS calculated for ($C_{12}H_{12}N_2O$+H): 201.0950, found 201.0947.

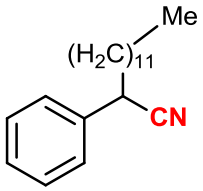


Scheme 5

<u>General procedure E</u> for the preparation of *α*-substituted benzyl cyanide (Scheme 5). To a stirred suspension of NaH (226 mg, 5.46 mmol) in dry DMF (7 mL), *α*–aryl acetonitrile (5.2 mmol) was added dropwise over a period of 5 min at 0 °C. After the mixture was stirred for 30 min, alkyl bromide (5 mmol) was added at room temperature. The mixture was stirred at room temperature for 15 h. Reaction mixture was quenched with ice cold water (10 mL) and extracted with Et_2O (3*10 mL). The combined organic layers was washed with saturated $NaHCO_3$ and brine solution and dried over Na_2SO_4. Desired compound was obtained from the column chromatography of the concentrated organic layer using pet ether/ ethyl acetate as eluent.



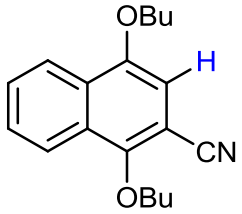
2-(Naphthalen-1-yl)propanenitrile (Table 3, entry 3e-SM). Following general procedure E the titled compound was synthesized using 2-(naphthalene-1-yl)acetonitrile (780 µL, 5.2 mmol) and methyl iodide (310 µL, 5 mmol) and isolated by pet ether as colorless liquid with 86% yield (778 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91 (*m*, 2H), 7.83 (*m*, 1H), 7.71 (*dd*, J= 7.1,1.2, 1H), 7.54 (*m*, 3H), 4.57 (*q*, J= 7.2, 1H), 1.73 (*d*, J= 7.2, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 133.9, 132.6, 129.7, 129.2, 128.8, 126.8, 126.0, 125.5, 124.5, 122.0, 121.8, 28.1, 20.4. GCMS (m/z): 181.0 $[M]^+$.



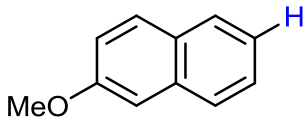
2-Phenyltetradecanenitrile (Scheme 3, entry 4a). The titled compound was synthesized following general procedure E using benzyl cyanide (600 µL, 5.2 mmol) and 1-bromododecane (1.2mL, 5 mmol) and was purified using 230-400 mesh silica with 96:4 pet ether/ ethyl acetate (v/v) as colorless liquid with 69% yield (985 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35- 7.42 (*m*, 2H), 7.29- 7.32 (*m*, 3H), 3.74- 3.78 (*m*, 1H), 1.80-1.98 (*m*, 2H), 1.25 (*s*, 20H), 0.87 (*t*, J= 6.0, 3H). GCMS (m/z): 285.2 $[M]^+$.

<u>General procedure F</u> for the reductive decyanation of aryl cyanide with 15-20 mol% catalyst loading. An oven dried resealable screw cap standard reaction tube containing a magnetic stirbar was charged with aryl cyanide (0.5 mmol), $Ni(acac)_2$ (15-20 mol%), PCy_3 (30-40 mol%). The tube was then evacuated and back-filled with nitrogen. The evacuation/backfill sequence was repeated two additional times. Under a counter flow of nitrogen, TMDSO (0.5 mmol), $AlMe_3$ in toluene solution (1.5 mmol) and toluene (1 mL) were added by syringe. The tube was placed in a preheated oil bath at 130 °C and the reaction mixture was stirred vigorously for 24 h. The reaction mixture was cooled to room temperature, diluted with 3 mL ethyl acetate and filtered through celite, eluting with additional 10 mL of ethyl acetate. The filtrate was concentrated and the resulting residue was purified by column chromatography.

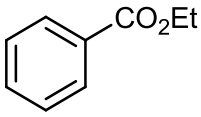
General procedure G for the reductive decyanation of aryl cyanide with 30 mol% catalyst loading. An oven dried resealable screw cap standard reaction tube containing a magnetic stirbar was charged with aryl cyanide (0.5 mmol), $Ni(acac)_2$ (30 mol%, 0.15 mmol), PCy_3 (90 mol%, 0.45 mmol). The tube was then evacuated and back-filled with nitrogen. The evacuation/backfill sequence was repeated two additional times. Under a counter flow of nitrogen, TMDSO (0.5 mmol), $AlMe_3$ in toluene solution (1.5 mmol) and toluene (1 mL) were added by syringe. The tube was placed in a preheated oil bath at 130 °C and the reaction mixture was stirred vigorously for 24 h. The reaction mixture was cooled to room temperature, diluted with 3 mL ethyl acetate and filtered through celite, eluting with additional 10 mL of ethyl acetate. The filtrate was concentrated and the resulting residue was purified by column chromatography.



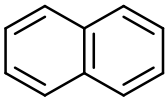
1,4-Dibutoxy-2-naphthonitrile (Table 1, entry 1a). Following general procedure F with 15 mol% $Ni(acac)_2$ the titled compound was obtained as white solid (114 mg, 77%) after the elution with 98:2 pet ether/ethyl acetate (v/v) from silica column. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.22-8.27 (*m*, 1H), 8.09- 8.14 (*m*, 1H), 7.54- 7.62 (*m*, 2H), 6.67 (*s*, 1H), 4.27 (*t*, J= 8.0, 2H), 4.07 (*t*, J= 8.0, 2H), 1.58-2.0 (*m*, 4H), 1.50- 1.52 (*m*, 4H), 1.0 (*t*, J= 8.0, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.7, 151.1, 151.1, 129.1, 128.7, 128.5, 128.5, 127.7, 123.0, 122.8, 118.0, 104.3, 99.6, 76.2, 68.5, 32.6, 31.3, 19.6, 19.4, 14.1, 14.0. GCMS (m/z): 297.2 $[M]^+$.



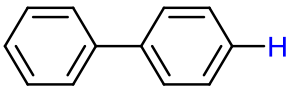
2-Methoxynaphthalene (Table 1, entry 1b). Following general procedure F with 15 mol% $Ni(acac)_2$ and elution with pet ether from silica column gave the titled compound as white solid (55 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (*m*, 3H), 7.45 (*ddd*, J= 8.2, 6.8, 1.3, 1H), 7.35 (*ddd*, J= 8.0, 6.8,1.3, 1H), 7.16 (*m*, 2H), 3.93 (*s*, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.8, 134.8, 129.6, 129.1, 127.8, 127.2, 126.9, 126.6, 123.8, 118.9, 105.9, 55.5. GCMS (m/z): 158.0 $[M]^+$.



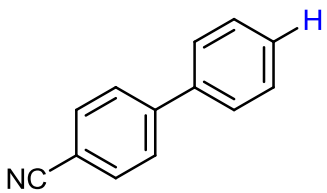
Ethyl benzoate (Table 1, entry 1c and 1h). The general procedure F was followed with 15 mol% $Ni(acac)_2$ and elution by 98:2 pet ether/ethyl acetate (v/v) from silica column gave **1c** as colorless liquid (59 mg, 79%). General procedure F with 20 mol% $Ni(acac)_2$ gave 44% yield (33 mg) and general procedure G led to 49% yield (37 mg) for **1h**. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.07-8.04 (*m*, 2H), 7.55 (*tt*, J= 8.0, 2.0, 1H), 7.43 (*qt*, J= 10.0, 1.3, 2H), 4.38 (*q*, J= 8.0, 2H), 1.4 (*t*, J= 8.0, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.8, 133.0, 130.7, 129.7, 128.5, 61.1, 14.5. GCMS (m/z): 150.0 $[M]^+$.



Naphthalene (Table 1, entry 1d and 1e). General procedure F was followed for both cyanonaphthalene with 20 mol% $Ni(acac)_2$ and purification with silica column using pet ether gave the titled compound as white solid with 52% yield (33 mg) for both cases. Again general procedure G led to 70% (45 mg) and 68% (44 mg) yield, respectively for 1-cyanonaphthalene and 2-cyanonaphthalene. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (*dd*, J= 6.1, 3.3, 4H), 7.52 (*dp*, J= 6.3, 3.7, 3.7, 3.0, 3.0, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 133.6, 128.1, 126.0. GCMS (m/z): 128.0 $[M]^+$.

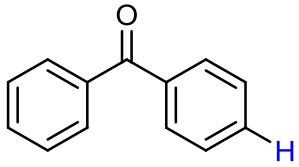


Biphenyl (Table 1, entry 1f). Following general procedure F with 20 mol% $Ni(acac)_2$ and after isolation from silica column by pet ether, biphenyl was obtained as white solid (42 mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65 (*ddd*, J= 8.1, 2.2, 1.0, 4H), 7.50 (*m*, 4H), 7.40 (*m*, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.4, 128.9, 127.4, 127.4. GCMS (m/z): 154.1 $[M]^+$.

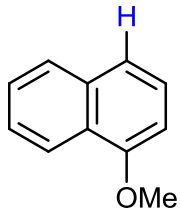


4-Cyanobiphenyl (Table 1, entry 1g). Following general procedure F with 15 mol% $Ni(acac)_2$ titled compound was obtained as white solid (51 mg, 57%) after isolation by 95:5 pet ether/ ethyl

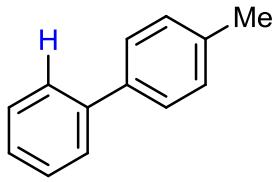
acetate (v/v) mixture. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 – 7.76 (m, 4H), 7.57 – 7.63 (m, 2H), 7.46 – 7.53 (m, 2H), 7.40 – 7.46 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.9, 139.4, 132.8, 129.3, 128.9, 128.0, 127.4, 119.2, 111.1. GCMS (m/z): 179.0 $[M]^+$.



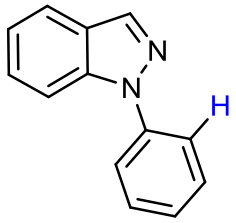
Benzophenone (Table 1, entry 1i). Following general procedure G titled compound was isolated by 98:2 pet ether/ ethyl acetate (v/v) mixture as white solid (48 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81 (*d*, J= 8.4, 4H), 7.58 (*t*, J= 7.2, 2H), 7.48 (*t*, J= 8.0, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 197.0, 137.8, 132.6, 130.2, 128.5. GCMS (m/z): 182.0 $[M]^+$.



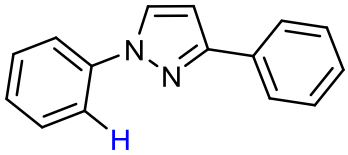
1-Methoxynaphthalene (Table 1, entry 1j). The general procedure G was followed and elution with pet ether from silica column gave the titled compound as colorless liquid (56 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.27- 8.44 (*m*, 1H), 7.79- 7.98 (*m*, 1H), 7.39- 7.63 (*m*, 4H), 6.86 (*dq*, J= 7.4,1.4,1.4,1.2, 1H), 4.04 (*s*, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.6, 134.6, 127.6, 126.6, 126.0, 125.7, 125.3, 122.1, 120.4, 103.9, 55.6. GCMS (m/z): 158.0 $[M]^+$.



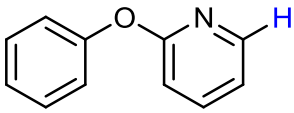
4-Methylbiphenyl (Table 1, entry 1k). Following general procedure G titled compound was isolated from silica column by pet ether as white solid (68 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48-7.53 (*m*, 2H), 7.40-7.44 (*m*, 2H), 7.32-7.38 (*m*, 2H), 7.22- 7.28 (*m*, 1H), 7.16-7.20 (m. 2H), 2.32 (*s*, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.4, 138.6, 137.2, 129.7, 128.9, 127.2, 127.2, 21.3. GCMS (m/z): 168.1 $[M]^+$.



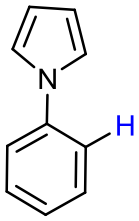
1-Phenyl-1*H*-indzole (Table 2, entry 2a). Procedure F with 20 mol% $Ni(acac)_2$ was followed and the titled compound was obtained in 95% (92 mg) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.14 (*s*, 1H), 7.67 (d, *J* = 7.8 Hz, 4H), 7.47 (t, *J* = 7.5, 7.5 Hz, 2H) 7.33 (dt, *J* = 26.5, 7.3, 7.3 Hz, 2H), 7.17 (d, *J* = 7.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.9, 140.4, 135.6, 129.7, 127.3, 126.9, 123.0, 121.7, 121.5. GCMS (m/z): 194.0 $[M]^+$.



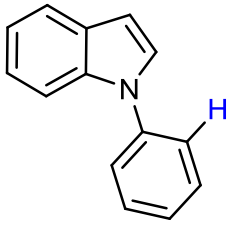
1,3-Diphenyl-1*H*-pyrazole (table 2, entry 2b). General procedure F with 20 mol% $Ni(acac)_2$ was followed and the titled compound was obtained in 94% yield (104 mg) as white solid. m.p. 81ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.68 (dd, *J* = 5.0, 2.5 Hz, 1H), 7.57 (dd, *J* = 8.4, 2.7 Hz, 2H), 7.25 (dt, *J* = 11.8, 7.7, 7.7 Hz, 4H), 7.17 (t, *J* = 7.4, 7.4 Hz, 1H), 7.07 (t, *J* = 7.4, 7.4 Hz, 1H), 6.54 (dd, *J* = 4.3, 2.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.9, 140.2, 133.2, 129.4, 128.7, 128.1, 128.0, 126.3, 125.9, 119.0, 105.1. GCMS (m/z): 220.1 $[M]^+$.



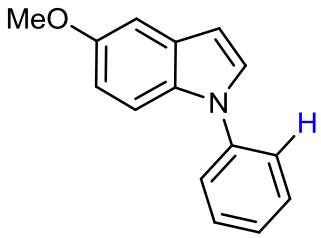
2-Phenoxypyridine (Table 2, entry 2c). General procedure F with 20 mol% $Ni(acac)_2$ was followed to obtain the titled compound in 56% yield (48 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11 (dd, *J* = 5.0, 2.0 Hz, 1H), 7.51 – 7.66 (m, 1H), 7.26 – 7.37 (m, 2H), 7.01 – 7.15 (m, 3H), 6.85 – 6.92 (m, 1H), 6.77 – 6.85 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (101 MHz, $cdcl_3$) δ 111.6, 118.6, 121.3, 124.8, 129.8, 139.6, 147.8, 154.2, 163.8. GCMS (m/z): 171.0 $[M]^+$.[1]



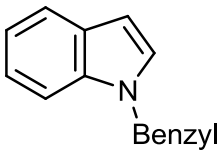
1-Phenyl-1*H*-pyrrole (Table 2, entry 2d). Following general procedure G and isolating by 98:2 pet ether/ethyl acetate (v/v) the titled compound was obtained as white solid in 98% (76 mg) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59 (d, J = 4.8 Hz, 4H), 7.45 (q, J = 4.8, 4.5, 4.5 Hz, 1H), 7.37 (t, J = 2.4, 2.4 Hz, 2H), 6.67 – 6.81 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.3, 129.1, 125.0, 119.8, 118.7, 110.3. GCMS (m/z): 143.0 $[M]^+$.



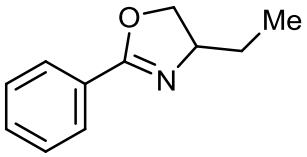
1-Phenyl-1*H*-indole (Table 2, entry 2e). General procedure G was followed and the titled compound was obtained as colorless oil in 83% (80 mg) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75 (*d*, J= 8.4, 1H), 7.63 (*d*, J= 8.0, 1H), 7.56 (*d*, J= 4.4, 4H), 7.35- 7,42 (*m*, 2H), 7.21- 7.31 (*m*, 2H), 6.75 (*d*, J= 3.2, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.9, 136.0, 129.8, 129.4, 128.1, 126.6, 124.5, 122.5, 121.3, 120.5, 110.6, 103.7. GCMS (m/z): 193.1 $[M]^+$.



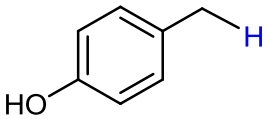
5-Methoxy-1-phenyl-1*H*-indole (Table 2, entry 2f). Procedure G was followed and the titled compound was obtained in 97% (108 mg) yield as colorless liquid after elution with 95:5 pet ether/ethyl acetate mixture (v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (ddd, J = 4.3, 2.9, 1.7 Hz, 5H), 7.37 (dddd, J = 8.2, 5.2, 3.4, 1.8 Hz, 2H), 7.21 (t, J = 2.4, 2.4 Hz, 1H), 6.95 (dt, J = 9.0, 2.5, 2.5 Hz, 1H), 6.66 (q, J = 2.2, 2.2, 1.3 Hz, 1H), 3.92 (d, J = 1.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.7, 140.1, 131.2, 130.0, 129.8, 128.5, 126.4, 124.1, 112.6, 111.5, 103.4, 102.8, 56.0. GCMS (m/z): 223.1 $[M]^+$.



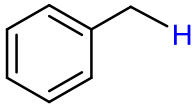
1-Benzyl-1*H*-indole (Table 2, entry 2g and 2h). Following procedure G the titled compound was obtained in 81% (84 mg) for **2g** and 72% (74.5 mg) for **2h** as colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64-7.73 (*m*, 1H), 7.20 (*ddd*, 4H), 7.18-7.23 (*m*, 1H), 7.11-7.18 (*m*, 4H), 6.59 (*dd*, J=3.1, 0.9, 1H), 5.35 (*s*, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.7, 136.4, 128.9, 128.8, 128.4, 127.7, 126.9, 121.8, 121.1, 119.7, 109.8, 101.8, 50.2. GCMS (m/z): 207.1 $[M]^+$.



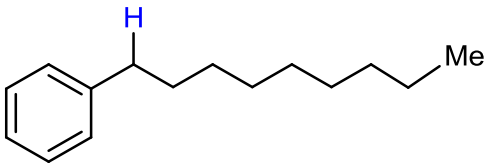
4-Ethyl-2-phenyl-4,5-dihydrooxazole (Table 2, entry 2i and 2j). General procedure G was followed and the titled compound was obtained as colorless liquid in 86% (75 mg) and 74% (65 mg) yield respectively for **2i** and **2j**. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86 (dd, J = 7.8, 2.9 Hz, 2H), 7.23 – 7.44 (m, 3H), 4.29 – 4.41 (m, 1H), 4.06 – 4.19 (m, 1H), 3.86 – 4.02 (m, 1H), 1.58 – 1.76 (m, 1H), 1.43 – 1.57 (m, 1H), 0.82 – 0.96 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.5, 131.3, 128.3, 127.8, 72.3, 67.9, 28.6, 10.0. GCMS (m/z): 175.1 $[M]^+$.



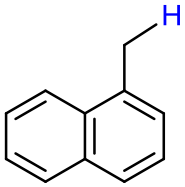
4-Methylphenol (Table 3, entry 3a). General procedure G was followed and the titled compound was obtained by 90:10 pet ether/ethyl acetate mixtures (v/v) as colorless liquid in 78% (42 mg) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.98-7.18 (*m*, 2H), 6.76 (t*d*, J= 6.0,2.6, 2H), 4.64 (*s*, 1H), 2.29 (*s*, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.3, 130.3, 130.2, 115.3, 20.6. GCMS (m/z): 108.0 $[M]^+$.



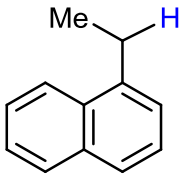
Toluene (Table 3, entry 3b). General procedure G was followed using *m*-xylene as solvent and yield was determined by GC due to high volatility of product using *n*-decane as internal standard. GC yield 82%. (N. B. Same amount of $AlMe_3$ in toluene was added in the standard product mixture also).



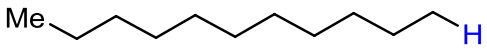
Nonylbenzene (Table 3, entry 3c). General procedure G was followed and the titled compound was obtained as colorless liquid in 79% (80.6 mg) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29-7.34 (*m*, 2H), 7.19- 7.22 (*m*, 3H), 2.64 (*t*, J= 6.0, 2H), 1.30- 1.44 (*m*, 14H), 0.92 (*t*, J= 8, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.1, 128.6, 128.4, 125.7, 36.2, 32.1, 31.8, 29.8, 29.6, 22.9, 14.3. GCMS (m/z): 204.2 $[M]^+$.



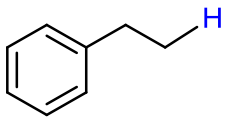
1-Methylnaphthalene (Table 3, entry 3d). General procedure G was followed and yield was determined by GC using *n*-decane as internal standard. GC yield: 71%.



1-Ethylnaphthalene (Table 3, entry 3e). General procedure G was followed and the titled compound was obtained in 68% (53 mg) yield as colorless liquid after elution with pet ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.09 (*dq*, J= 8.5, 1.1, 0.9, 1H), 7.88 (*dd*, J= 8.1,1.5, 1H), 7.74 (*d*, J= 8.1, 1H), 7.47-7.57 (*m*, 2H), 7.44 (*dd*, J= 8.1, 7.0, 1H), 7.38 (*d*, J= 8.0, 1H), 3.16 (*q*, J= 8.0, 2H), 1.42 (*t*, J= 8.0, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.5, 134.0, 131.9, 128.9, 126.6, 125.8, 125.6, 125.0, 123.9, 26.1, 15.3. GCMS (m/z): 156.1 $[M]^+$.

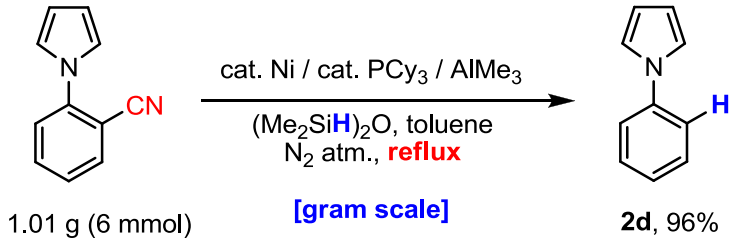


Undecane (Table 3, entry 3f). General procedure G was followed and the titled compound was obtained as colorless liquid in 61% (47.6 mg) yield after elution with pet ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.59- 1.63 (*m*, 2H), 1.2- 1.4 (*m*, 16H), 0.80- 0.96 (*t*, J= 6.4, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 31.9, 29.7, 29.3, 22.6, 14.1. GCMS (m/z): 156.2 $[M]^+$.



Ethylbenzene (Table 3, entry 3g). General procedure G was followed and yield was determined by GC due to high volatility of product using *n*-decane as internal standard. GC yield 67%.

Large scale reaction (Scheme 3, entry 2d):



A two neck round bottom flask fitted with septum and with magnetic stirbar was charged with 2-(1*H*-pyrrol-1-yl)benzonitrile (1.01 gm, 6 mmol), $Ni(acac)_2$ (1.8 mmol, 463 mg), PCy_3 (5.4 mmol, 1.52 gm) and fitted with reflux condenser under nitrogen atmosphere. Then toluene (8 mL), TMDSO (6.0 mmol, 1.5 mL), and $AlMe_3$ in toluene (18.0 mmol, 1.6 mL) were added sequentially. Finally the round bottom flask was immersed into oil bath at 130 °C and stirred under reflux condition in nitrogen atmosphere for 24 h. Finally the RB was cooled, the reaction mixture was filtered through celite using 25 mL ethyl acetate as washing solvent. The filtrate was concentrated and purified by 100-200 mesh silica and 97:3 pet ether/ethyl acetate (v/v) to give the desired decyanated product as white solid in 96% yield (824 mg).

Isolation of *trans*-[$Ni(PCy_3)_2(CN)_2$] and reactivity study:

Trans-[$Ni(PCy_3)_2(CN)_2$] was isolated from entries **1f** (biphenyl), **1g** (4-cyanobiphenyl), **1i** (benzophenone), **3f** (undecane) in ~10-15% yield (colorless crystal). CIF file is not included since the crystal structure is already reported.[5] HRMS calculated for ($C_{38}H_{66}N_2NiP_2$+H): 671.4133, found 671.4131. Attempted decyanation of 1-cyanonphthalene with this isolated crystal of *trans*-[$Ni(PCy_3)_2(CN)_2$] as catalyst (30 mol%) resulted in 95% yield of 1-cyanonaphthalene (recovered starting material). This reaction shows the catalytic inefficiency of *trans*-[$Ni(PCy_3)_2(CN)_2$]. Formation of catalytically inactive stable *trans*-[$Ni(PCy_3)_2(CN)_2$] can possibly account for low yields of desired product in some cases.

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