## Nickel-Catalyzed Hydrogen-Borrowing Strategy: Chemo-selective Alkylation of Nitriles with Alcohols

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#### [1.1] General Information:

All solvents and reagents were used, as received from the suppliers. TLC was performed on Merck Kiesel gel 60, F<sub>254</sub> plates with the layer thickness of 0.25 mm. Column chromatography was performed on silica gel (100-200 mesh) using a gradient of ethyl acetate and hexane as a mobile phase. <sup>1</sup>H-NMR spectral data were collected using 400 MHz (JEOL) and 500 MHz (Bruker) and <sup>13</sup>C-NMR were recorded at 100 MHz. <sup>1</sup>H-NMR spectral data are given as chemical shifts in ppm followed by multiplicity (*s*- singlet; *d*- doublet; *t*- triplet; *q*-quartet; *m*- multiplet), number of protons and coupling constants. <sup>13</sup>C-NMR chemical shifts are expressed in ppm. HRMS (ESI) spectral data were collected using Bruker High Resolution Mass Spectrometer. GC-MS were recorded using Agilent GC Mass Spectrometer. All the reactions were performed in a close system using Schlenk tube. All nickel salts were purchased from Sigma Aldrich and Alfa Aeser. Nickel(II) 2,4-Pentanedionate (Assay- 95%; CAS Number 3264-82-2; Item Number 018811; HSN Code: 29141990). Potassium *tert*-butoxide was purchased from Avra Synthesis Pvt. Ltd., India. (Purity-98%, CAS No: 865-47-4, Catalog No- ASP2012). Potassium carbonate was purchased from Himedia, India. (Assay-95%; CAS No: 584-08-7, HSN Code: 28364000).

#### General Procedure for Nickel-Catalyzed α-Alkylation of Arylmethyl Nitriles:

**Procedure** [A]: Synthesis of 2,3-diphenylpropanenitrile (**3a**): In a 15 mL oven dried Schlenk tube, benzyl cyanide **1a** (0.50 mmol, 58.5 mg),  $K_2CO_3$  (50 mol%, 34.5 mg), Phen (10 mol%, 9.0 mg), Ni(acac)<sub>2</sub> (5 mol%, 6.4 mg) and benzyl alcohol **2a** (0.75 mmol, 81.0 mg) were added followed by toluene 2.0 mL under an atmosphere of N<sub>2</sub> and the reaction mixture was heated to 140 °C for 36 h in a closed system. The reaction mixture was cooled to room temperature and 3.0 mL of ethyl acetate was added and concentrated under reduced pressure. The residue was purified by column chromatography using a gradient of hexane and ethyl acetate (eluent system) to afford the pure product **3a**. This procedure was used as general procedure [A] for the synthesis of arylmethyl nitriles.

**Procedure [B]:** In a 15 mL oven dried Schlenk tube, nitriles (**1a**, **1b**, **1c**, **1e**, **1f**, **1g** and **1h**) (0.50 mmol),  $K_2CO_3$  (1 equiv.), Phen (10 mol%),  $Ni(acac)_2$  (5 mol%) and the desired alcohols **2** (0.75 mmol) were added followed by toluene 2.0 mL under an atmosphere of  $N_2$  and the reaction mixture was heated to 140 °C for 36 h in a closed system. The reaction mixture was cooled to room temperature and 3.0 mL of ethyl acetate was added and

concentrated under reduced pressure. The residue was purified by column chromatography using a gra-dient of hexane and ethyl acetate (eluent system) to afford the pure product.

**Procedure [C]:** In a 15 mL oven dried Schlenk tube, nitriles (**1a, 1d** and **1i**) (0.50 mmol), NaOH (50 mol%), Phen (10 mol%), NiCl<sub>2</sub>.dme (5 mol%) and the desired alcohols **2** (0.75 mmol) were added followed by toluene 2.0 mL under an atmosphere of N<sub>2</sub> and the reaction mixture was heated to 140 °C for 24 h in a closed system. The reaction mixture was cooled to room temperature and 3.0 mL of ethyl acetate was added and concentrated under reduced pressure. The residue was purified by column chromatography using a gradient of hexane and ethyl acetate (eluent system) to afford the pure product.

**Procedure [D]**: In a 15 mL oven dried Schlenk tube, nitriles (**1a** and **1n**) (0.25 mmol), NaOH (1.0 equiv), Phen (20 mol%), NiCl<sub>2</sub>.dme (10 mol%) and the desired alcohols **2** (2.25 mmol) were added followed by toluene 1.0 mL under an atmosphere of N<sub>2</sub> and the reaction mixture was heated to 140 °C for 36 h in a closed system. The reaction mixture was cooled to room temperature and 3.0 mL of ethyl acetate was added and concentrated under reduced pressure. The residue was purified by column chromatography using a gradient of hexane and ethyl acetate (eluent system) to afford the pure product.

**Procedure [E]**: In a 15 mL oven dried schlenk tube, nitriles (**1e** and **1i**) (0.50 mmol), NaOH (1.0 equiv), Phen (20 mol%), NiCl<sub>2</sub>.dme (10 mol%) and *n*-butanol **2n** (1 ml) was added under an atmosphere of  $N_2$  and the reaction mixture was heated to 140 °C for 36 h in a closed system. The reaction mixture was cooled to room temperature and 3.0 mL of ethyl acetate was added and concentrated under reduced pressure. The residue was purified by column chromatography using a gradient of hexane and ethyl acetate (eluent system) to afford the pure product.

**Procedure [F]**: In a 15 mL oven dried Schlenk tube, 3-phenyl propionitrile **1j** (0.25 mmol), NaOH (1.0 equiv), Phen (20 mol%), NiCl<sub>2</sub>.dme (15 mol%) and the desired alcohols **2** (2.25 mmol) were added followed by toluene 1.0 mL under an atmosphere of N<sub>2</sub> and the reaction mixture was heated to 150 °C for 36 h in a closed system. The reaction mixture was cooled to room temperature and 3.0 mL of ethyl acetate was added and concentrated under reduced pressure. The residue was purified by column chromatography using a gradient of hexane and ethyl acetate (eluent system) to afford the pure product.

# [1.2] Nickel-Catalysed α-Alkylation of Benzyl Cyanide with Benzyl Alcohols Table S1: Screening of catalyst<sup>a</sup>



Entry	Ni-Catalyst	GC-MS Conversion <b>3a</b> (%)	GC-MS Conversion 3a'
			(%)
1	NiCl <sub>2</sub>	21	22
2	NiBr <sub>2</sub>	17	12
3	Ni(acac) <sub>2</sub>	42	5
4	NiCl <sub>2</sub> .dme	30	10
5	No Catalyst	2	0

Reaction condition: <sup>a</sup>Benzyl cyanide **1a** (0.50 mmol), benzyl alcohol **2a** (0.75 mmol), **Ni-Cat.** (**5 mol%**), phen (10 mol%), *t*-BuOK (15 mol%), toluene (2.0 mL), Schlenk tube under N<sub>2</sub> atmosphere, 130 °C oil bath, 36 h reaction time. Conversions were measured based on **1a**.

**Table S2**: Screening of ligands<sup>a</sup>



Entry	Ligand	GC-MS Conversion <b>3a</b>	GC-MS Conversion 3a'
		(%)	(%)
1		68	2
2		0	3
3		0	0
4		10	28
5		20	30

6		12	8
7	No Ligand	5	_

Reaction condition: <sup>a</sup>Benzyl cyanide **1a** (0.50 mmol), benzyl alcohol **2a** (0.75 mmol), Ni(acac)<sub>2</sub> (5 mol%), **ligand (10 mol%)**, K<sub>2</sub>CO<sub>3</sub> (15 mol%), toluene (2.0 mL), Schlenk tube under N<sub>2</sub> atmosphere, 140 °C oil bath, 36 h reaction time. Conversions were measured based on **1a**.

Table S3: Screening of base<sup>a</sup>

$\begin{array}{c c} \hline \\ \hline \\ 1a \\ \hline \\ 2a \\ \hline \\ toluene, 130 ^{\circ}C, 36 \\ h \\ \hline \\ 3a \\ \hline \\ 3a \\ \hline \\ \\ \\ 3a \\ \hline \\ \\ \\ 3a \\ \hline \\ \\ \\ \\ \\ 3a \\ \hline \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ $	CN + HO	Ni(acac) <sub>2</sub> (5 mol%) Phen (10 mol%) Base (15 mol %) toluene, 130 °C, 36 h	Ph CN +	Ja'
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Entry	Base	GC-MS Conversion 3a	GC-MS Conversion 3a'
		(%)	(%)
1	t-BuONa	27	14
2	t-BuOK	31	5
3	Na <sub>2</sub> CO <sub>3</sub>	14	3
4	K <sub>2</sub> CO <sub>3</sub>	35	1
5	K <sub>3</sub> PO <sub>4</sub>	13	2
6	Cs <sub>2</sub> CO <sub>3</sub>	21	2
7	Et <sub>3</sub> N	2	14
8	Pyridine	2	23
9	N,N di-isopropyl	-	-
	ethylamine		
10 <sup>b</sup>	K <sub>2</sub> CO <sub>3</sub>	68	2

Reaction conditions: <sup>a</sup>Benzyl cyanide **1a** (0.25 mmol), benzyl alcohol **2a** (0.375 mmol), Ni(acac)<sub>2</sub> (5 mol%), phen (10 mol%), **base (15 mol%)**, toluene (2.0 mL), Schlenk tube under N<sub>2</sub> atmosphere, 130 °C oil bath, 36 h reaction time. <sup>b</sup>140 °C. Conversions were measured based on **1a**.

Table S4: Screening of solvents<sup>a</sup>



Entry	Solvent	GC-MS Conversion <b>3a</b> (%)	GC-MS Conversion 3a'
			(%)
1	toluene	68	2
2	<i>p</i> -xylene	26	32
3	1,4 dioxane	-	14
4	DMA	-	_
5	DMF	_	_

Reaction conditions: <sup>a</sup>Benzyl cyanide **1a** (0.50 mmol), benzyl alcohol **2a** (0.75 mmol), Ni(acac)<sub>2</sub> (5 mol%), Phen (10 mol %), K<sub>2</sub>CO<sub>3</sub> (15 mol %), **solvent (2.0 mL**), Schlenk tube under N<sub>2</sub> atmosphere, 140 °C oil bath, 36 h reaction time. Conversions were measured based on **1a**.

**Table S5**: Screening of base equivalence<sup>a</sup>



Entry	K <sub>2</sub> CO <sub>3</sub>	GC-MS Conversion <b>3a</b> (%)	GC-MS Conversion 3a'
	(X mol%)		(%)
1	15	68	2
2	25	76	-
3	50	93 (90%) <sup>b</sup>	-
4	-	41	3

Reaction condition: <sup>a</sup>Benzyl cyanide **1a** (0.50 mmol), benzyl alcohol **2a** (0.75 mmol), Ni(acac)<sub>2</sub> (5 mol%), Phen (10 mol%), K<sub>2</sub>CO<sub>3</sub> (X mol%), toluene (2.0 mL), Schlenk tube under N<sub>2</sub> atmosphere, 140 °C oil bath, 36 h reaction time. <sup>b</sup>Isolated yield. Conversions were measured based on **1a**.

Table S6:	Screening	of benzyl	alcohol	ratio <sup>a</sup>
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[	CN + HO	$ \begin{array}{c}                                     $	Ph CN + CN a 3a'
Entry	Alc.	GC-MS Conversion <b>3a</b> (%)	GC-MS Conversion 3a'
	equivalence		(%)
1	1	33	-
2	1.5	76 (73%)	-
3	1.5	<b>93 (90%)</b> <sup>b,c</sup>	-
4	2.0	67	-

Reaction condition: <sup>a</sup>Benzyl cyanide **1a** (0.50 mmol), benzyl alcohol **2a** (**X equiv.**), Ni(acac)<sub>2</sub> (5 mol%), Phen (10 mol%), K<sub>2</sub>CO<sub>3</sub> (25 mol%), toluene (2.0 mL), Schlenk tube under N<sub>2</sub> atmosphere, 140 °C oil bath, 36 h reaction time. <sup>b</sup>Isolated yield. <sup>c</sup>K<sub>2</sub>CO<sub>3</sub> (50 mol%) was used. Conversions were measured based on **1a**.

**Table S7**: Temperature Screening<sup>a</sup>

[	CN + HO 1a 2a	Ni(acac) <sub>2</sub> (5 mol%) Phen (10 mol%) K <sub>2</sub> CO <sub>3</sub> (50 mol %) toluene, <b>X</b> °C, 36 h <b>3</b>	a 3a'
Entry	Temp °C	GC-MS Conversion <b>3a</b> (%)	GC-MS Conversion 3a'
			(%)
1	120	20	2
2	130	76	-
3	140	93 (90%) <sup>b</sup>	-

Reaction condition: <sup>a</sup>Benzyl cyanide **1a** (0.50 mmol), benzyl alcohol **2a** (0.75 mmol), Ni(acac)<sub>2</sub> (5 mol%), Phen (10 mol%), K<sub>2</sub>CO<sub>3</sub> (50 mol%), toluene (2.0 mL), Schlenk tube under N<sub>2</sub> atmosphere, **temp** <sup>o</sup>C oil bath, 36 h reaction time. <sup>b</sup>Isolated yield. Conversions were measured based on **1a**.

Table S8: Screening of catalyst loading<sup>a</sup>

	CN 1a	+ HO2a	Ni(acac) <sub>2</sub> (X mol%) Phen (Y mol%) K <sub>2</sub> CO <sub>3</sub> (50 mol%) toluene, 140 °C, 36 h	CN + CN 3a'
Entry	Ni(acac) <sub>2</sub>	Phen	GC-MS Conversion 3a	GC-MS Conversion 3a'
	(X mol%)	(Y mol%)	(%)	(%)
1	2	4	53	3
2	3	6	58	27
3	5	10	<b>93 (90%)</b> <sup>b</sup>	-
4	-	10	<2	-
5	5	-	<5	-
6	-	-	<5	-

Reaction condition: <sup>a</sup>Benzyl cyanide **1a** (0.50 mmol), benzyl alcohol **2a** (0.75 mmol), Ni(acac)<sub>2</sub> (**X mol%**), Phen (**Y mol%**), K<sub>2</sub>CO<sub>3</sub> (50 mol%), toluene (2.0 mL), Schlenk tube

under  $N_2$  atmosphere, 140 °C oil bath, 36 h reaction time. <sup>b</sup>Isolated yield. Conversions were measured based on **1a**.

## [1.3] Deuterium Incorporation Experiments: Scheme S1:



Conversion was calculated by <sup>1</sup>H-NMR integration value

		Deuterium	Deuterium	
		incorporation in	incorporation in	
		Ha position	Hb position	
Signal $\delta$ ppm	7.13 [2H]	3.98 (1H)	3.14 (2H)	
Integral Value	2.0	0.25	0.69	
Calculated		{(1-0.25) / 1} × 100 =	{(2-0.69) / 2} × 100 =	
ratio		75%	66%	

Scheme S2:



Conversion was calculated by <sup>1</sup>H-NMR integration value

		Deuterium	Deuterium	
		incorporation in	incorporation in	
		Ha position	Hb position	
Signal $\delta$ ppm	7.13 [2H]	3.98 (1H)	3.14 (2H)	
Integral Value	2.0	0.57	0.79	
Calculated		$\{(1-0.57) / 1\} \times 100 =$	$\{(2-0.79) / 2\} \times 100 =$	
ratio		43%	61%	

## Scheme S3:



Conversion was calculated by <sup>1</sup>H-NMR integration value

		Deuterium	Deuterium
		incorporation in	incorporation in
		Ha position	Hb position
Signal $\delta$ ppm	7.13 [2H]	3.98 (1H)	3.14 (2H)
Integral Value	2.0	0.70	0.29
Calculated		$\{(1-0.70) / 1\} \times 100 =$	$\{(2-0.29) / 2\} \times 100 =$
ratio		30%	85%

## Scheme S4:



Conversion was calculated by <sup>1</sup>H-NMR integration value

		Deuterium	Deuterium
	incorporation in		incorporation in
		Ha position	Hb position
Signal $\delta$ ppm	7.13 [2H]	3.98 (1H)	3.14 (2H)
Integral Value	2.0	0.82	0.29
Calculated		$\{(1-0.82) / 1\} \times 100 =$	$\{(2-1.21) / 2\} \times 100 =$
ratio		18%	40%

## Calculation of P<sub>H</sub>/P<sub>D</sub>:

Considering individual reaction for the formation of deuterated and non-deuterated product **3a** and **3a-d2**,

In Scheme S4,

For 92% of **2a-d2** deuterium incorporation in the product = 40% For 100% of **2a-d2** deuterium incorporation in the product =  $(40/92) \times 100 \%$ = 43.8% of D Total product (deuterated + non deuterated) yield = 81% Deuterium incorporation in the product = 43.8% of D Total deuterated product =  $(43.8 \times 81) / 100$ = 54.1% Yield of product for non-deuterated reaction = 90% Yield of product for deuterated reaction = 54.1% So,  $P_{\rm H} / P_{\rm D} = 90/54.1$ 



## Scheme S5: 1H-NMR spectra of deuterium compounds 2a-d2, 2a-d1, 1a-d2

## Conversion was calculated by <sup>1</sup>H-NMR integration value

		Deuterium	Deuterium incorporation
		incorporation in	in
		CH <sub>2</sub> position	<b>OH</b> position
Signal $\delta$ ppm	7.24-7.36 (5H)	4.65 (2H)	2.65 (1H)
(Standard)			
Integral Value	5.0	0.16	1.05
(Scheme S5a)			
Calculated ratio		{(2-0.16)/2}×100 = <b>92%</b>	$\{(1-1)\} \times 100 = 0\%$
Integral Value	5.0	2.0	0.02

(Scheme S5b)			
Calculated ratio		$\{(2.0-2.0)/2\} \times 100 = 0\%$	{(1-0.02)}×100 = <b>98%</b>
Signal $\delta$ ppm	7.40-7.31 (5H)	3.74 (2H)	
(Standard)			
Integral Value	5.0	0.06	
(Scheme S5c)			
Calculated ratio		{2.0-0.06/2}×100 = <b>97%</b>	

Scheme S6:

## A: Trapping of Ni-H formation:



**B: Preparation of Cat.B-H:** The catalyst was prepared following literature reported procedure. The Ni-H species, **Cat.B-H** was obtained as pale yellow solid and the solid decomposes very fast in solvent. Characterization data are in agreement with the literature reported data.



Characterization of Cat. B-H: IR: Ni-H 1950 cm<sup>-1</sup>; M.P: (150-151) °C (decompose)<sup>1</sup>.

#### Scheme S7: Synthetic utility of 3a



**Procedure for synthesis of compound 2,3-diphenylpropan-1-amine [6]**<sup>4</sup>**: 3a** (50 mg, 0.24 mmol) in dry THF (2 mL) was added dropwise to a suspension of LiAlH<sub>4</sub> (14 mg, 0.36 mmol) in dry THF (2 mL) at 0 °C under N<sub>2</sub>. The mixture was stirred overnight, after which the reaction mixture was very slowly quenched with H<sub>2</sub>O (1 mL) and diluted with DCM. The mixture was stirred 20 min. The reaction mixture was cooled to room temperature and 3.0 mL of ethyl acetate was added and concentrated under reduced pressure. The residue was purified by column chromatography using a gradient of hexane and ethyl acetate (15% eluent system) to afford the pure product (Yield: 40%, 20 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.35 (s, 3H), 7.29 (d, *J* = 7.3 Hz, 4H), 7.21-7.19 (m, 3H), 4.90 (dd, *J* = 8.4, 4.9 Hz, 2H), 3.09-2.96 (m, 5H).

## **Procedure for synthesis of compound 2,3-diphenylpropanamide [7]**<sup>3</sup>**:**

**3a** (50 mg, 0.24 mmol) in dry Ethanol (3 mL) was added to a 1(M) NaOH solution. After that, 0.2 mL of 30% H<sub>2</sub>O<sub>2</sub> solution was mixed and stirred for overnight keeping the temperature around 50 °C. The reaction mixture was cooled to room temperature and 3.0 mL of ethyl acetate was added and concentrated under reduced pressure. The residue was purified by column chromatography using a gradient of hexane and ethyl acetate (10% eluent system) to afford the pure product (Yield: 70%, 39 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.34-7.29 (m, 4H), 7.24 (d, *J* = 2.4 Hz, 1H), 7.22-7.18 (m, 2H), 7.17 (t, *J* = 1.6 Hz, 1H), 7.11 (d, *J* = 1.6 Hz, 1H), 7.09 (d, *J* = 1.2 Hz, 1H), 5.25 (s, 2H), 3.64 (t, *J* = 7.4 Hz, 1H), 3.57-3.54 (m, 1H), 3.03-2.97 (m, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  171.6, 136.4, 135.1, 129.2, 129.0, 128.9, 128.7, 128.4, 127.5, 41.8, 40.2.

**Procedure for synthesis of compound 2,3-diphenylpropanoic acid [8]**<sup>2</sup>**:** A suspension of **3a** (50 mg, 0.24 mmol), in a mixture of 0.5 ml 98% H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>O (0.5 ml) and acetic acid (0.3 ml) was reflexed for 24 h. After that the reaction mixture was quenched very slowly with H<sub>2</sub>O (1 mL) and diluted with dichloromethane. The mix-ture was stirred 20 min. The reaction mixture was cooled to room temperature and 3.0 mL of ethyl acetate was added and concentrated under reduced pressure. The residue was purified by column chromatography using a gradient of hexane and ethyl acetate (15% eluent system) to afford the pure product (Yield: 61%, 34 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) *δ* 7.31-7.28 (m, 3H), 7.26 (dd, *J* = 9.1, 4.6 Hz, 2H), 7.23-7.16 (m, 3H), 7.10 (d, *J* = 6.9 Hz, 2H), 3.87-3.83 (m, 1H), 3.40-3.38 (m, 1H), 3.05-3.01 (m, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) *δ* 177.3, 137.3, 136.6, 127.5, 127.3, 127.0, 126.7, 126.2, 125.1, 52.0, 37.9.

## Scheme S8: Practical utility: Higher scale reaction



In a 100 mL oven dried Ace Pressure tube, benzyl cyanide **1a** (4.0 mmol, 468 mg), benzyl alcohol **2a** (6.0 mmol, 648 mg), Ni(acac)<sub>2</sub> (5 mol%, 53 mg), Phen (10 mol%, 72 mg) and  $K_2CO_3$  (50 mol%, 276 mg), were added followed by toluene (7.0 mL) under an atmosphere of N<sub>2</sub> and the reaction mixture was heated at 140 °C for 36 h in a closed system. The reaction mixture was cooled to room temperature and 12.0 mL of ethyl acetate was added and concentrated under reduced pressure. The residue was purified by column chromatography using ethyl acetate/hexane (1:99) (eluent system) to afford the desired product **3a** in 72% yield (596 mg).

### Scheme S9: Determination of reaction order and rate:

Run 1: Reaction was carried out in 2 mL of toluene and yield was calculated by GC

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$							
No.	1a	2a	Ni(acac)	2	Phen	K <sub>2</sub> CO <sub>3</sub>	toluene
	(mmol)	(mmol)	(mmol)		(mmol)	(mmol)	(mL)
Run 1	0.50	0.75	0.025		0.05	0.025	2.0
	Sl. No.	Time (min)		Concentration of <b>1a</b> (mM)		of 1a (mM)	
	1	0			252		1

2	120	235
3	240	218
4	360	201
5	480	188
6	600	175

Run 2: Reaction was carried out in 2 mL of toluene and yield was calculated by GC



No.	1a	2a	$Ni(acac)_2$	Phen	K <sub>2</sub> CO <sub>3</sub>	toluene
	(mmol)	(mmol)	(mmol)	(mmol)	(mmol)	(mL)
Run 2	0.45	0.675	0.0225	0.045	0.0225	2.0

Sl. No.	Time (min)	Concentration of 1a (mM)
1	0	226
2	120	213
3	240	196
4	360	179
5	480	171
6	600	158



Considering steady state approximation for benzyl alcohol

From Run 1: Slope = k [1a] <sup>x</sup>  
- 0.129 = k [0.50] <sup>x</sup>  
From Run 2: Slope = k [1a] <sup>x</sup>  
-0.115 = k [0.45] <sup>x</sup>  
0.129 /- 0.115 = [0.50] <sup>x</sup>/ [0.45] <sup>x</sup>  
1.122 = [1.111] <sup>x</sup>  
Log (1.122) = x. Log (1.111)  
x = 0.049 / 0.046  
= 1.065 
$$\approx$$
 1  
Rate = k [1a] <sup>1</sup>







Scheme S11: Detection of water in reaction mixture by <sup>1</sup>H-NMR

#### Scheme S12: Substrate Scope:



Reaction Conditions: <sup>*a*</sup>**1** (0.50 mmol), aryl alcohols **2** (0.75 mmol), Ni(acac)<sub>2</sub> (0.025 mmol), **L1** (0.05 mmol), K<sub>2</sub>CO<sub>3</sub> (0.25 mmol), toluene (2.0 mL), Schlenk tube under N<sub>2</sub> atmosphere at 140 °C in an oil bath for 36 h. <sup>*b*</sup>*t*-BuOK (0.25 mmol). <sup>*c*</sup>NiCl<sub>2</sub>.dme (0.025 mmol), **L1** (0.05 mmol), NaOH (0.50 mmol), 24 h. <sup>*d*</sup>NiCl<sub>2</sub>.dme (0.025 mmol), **L1** (0.05 mmol), NaOH (0.50 mmol), 36 h. <sup>*e*</sup>K<sub>2</sub>CO<sub>3</sub> (0.5 mmol). <sup>*f*</sup>*t*-BuOK (0.50 mmol). <sup>*g*</sup>K<sub>2</sub>CO<sub>3</sub> (0.75 mmol). <sup>*h*</sup>NaOH (0.5 mmol), 24 h. <sup>*i*</sup>**1j** (0.50 mmol), **2a** (2.5 mmol), NiCl<sub>2</sub>.dme (0.075 mmol), phen (0.2 mmol), NaOH (1.0 mmol), 150 °C oil bath for 36 h. <sup>*j*</sup>GC-MS conversion.



Scheme S13: Control experiments and proposed catalytic cycle: Control experiments

On the basis of these control experiments and mechanistic studies, a probable catalytic pathway for the Ni-catalyzed  $\alpha$ -alkylation of nitrile with alcohols is presented in Scheme S13. Primarily, a Ni-catalyzed dehydrogenation of alcohol gave aldehyde **2a'** via Ni-alkoxy species **B** following  $\beta$ -hydride elimination. Thereafter, condensation of aldehyde **2a'** with **1a** resulted the intermediate species **3a'**, which subsequently undergoes chemo-selective hydrogenation to the product **3a** by *in situ* generated Ni-H species. Notably, the overall process released only water as side product, rendering it sustainable

## [1.4] Analytical Data:

**2,3-diphenylpropanenitrile**  $(3a)^5$ : Following the general procedure **A**, the title compound was isolated as a colourless liquid using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 90%, 93 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36-7.29 (m, 3H), 7.29-7.21 (m, 5H), 7.13 (dd, J = 7.6, 1.4Hz, 2H), 4.05-3.91 (m, 1H), 3.19-3.08 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz,

CDCl<sub>3</sub>) *δ* 136.4, 135.3, 129.4, 129.2, 128.8, 128.4, 127.6, 127.5, 120.6, 42.3, 39.9.

**2-phenyl-3-**(p-tolyl)**propanenitrile**  $(3b)^5$ : Following the general procedure A, the title



compound was isolated as a colourless liquid using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 83%, 92 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36-7.34 (m, 3H), 7.28-7.26 (m, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 3.99-3.96 (m, 1H), 3.15-

3.11 (m, 2H), 2.33 (s, 3H).  ${}^{13}C{}^{1}H$  NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  137.2, 135.5, 133.4, 129.5, 129.3, 129.2, 128.3, 127.7, 120.7, 42.0, 40.2, 21.3.

3-(4-ethylphenyl)-2-phenylpropanenitrile (3c): Following the general procedure A, the title



compound was isolated as a colourless liquid using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 61%, 72 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.37-7.31 (m, 3H), 7.28-7.24 (m, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 3.98-3.95

(m, 1H), 3.17-3.08 (m, 2H), 2.62 (q, J = 7.6 Hz, 2H), 1.21 (t, J = 7.6 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  143.4, 135.4, 133.5, 129.1, 129.0, 128.1, 128.1, 127.4, 120.4, 41.8, 39.9, 28.4, 15.5. HRMS (ESI-TOF) m/z: [M]<sup>+</sup> Calculated for C<sub>17</sub>H<sub>17</sub>NNa 258.1253; Found 258.1235.

3-(4-isopropylphenyl)-2-phenylpropanenitrile (3d): Following the general procedure A,



the title compound was isolated as a colourless liquid using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 62%, 77mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36-7.33 (m, 3H), 7.28 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.1

Hz, 2H), 3.96 (dd, J = 8.7, 6.2 Hz, 1H), 3.17-3.08 (m, 2H), 2.91-2.84 (m, 1H), 1.23 (d, J = 6.9 Hz, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  148.0, 135.4, 133.6, 129.1, 129.0, 128.1, 127.4, 126.7, 120.5, 41.9, 40.0, 33.7, 24.0. HRMS (ESI-TOF) m/z: [M]<sup>+</sup> Calculated for C<sub>18</sub>H<sub>19</sub>N 249.1517; Found 249.1596.

**3-(4-methoxyphenyl)-2-phenylpropanenitrile**  $(3e)^5$ : Following the general procedure A, the title compound was isolated as a colourless liquid using silica-gel column chromatography eluting with 2% ethyl acetate in hexane (Yield: 58%, 69 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.35-7.31 (m, 3H), 7.25-7.23 (m, 2H), 7.05-7.03 (m, 2H), 6.83-6.80 (m, 2H), 3.95

(dd, J = 8.0, 6.6 Hz, 1H), 3.78 (s, 3H), 3.15-3.05 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  158.7, 135.1, 130.2, 128.9, 128.2, 128.0, 127.4, 120.4, 113.9, 55.1, 41.3, 40.0.

2-phenyl-3-o-tolylpropanenitrile (3f)<sup>5</sup>: Following the general procedure C, the title



compound was isolated as a colourless liquid using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 67%, 74 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.39-7.24 (m, 6H), 7.18-7.13 (m, 3H), 4.01-3.90 (m, 1H), 3.30-3.09 (m, 2H), 2.23 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100

MHz, CDCl<sub>3</sub>) δ 136.4, 135.6, 134.8, 130.7, 130.1, 129.2, 128.3, 127.6, 127.5, 126.4, 120.6, 39.6, 38.9, 19.3.

3-(4-fluorophenyl)-2-phenylpropanenitrile (3g)<sup>5</sup>: Following the general procedure A, the



title compound was isolated as a colourless liquid using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 70%, 79 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.35 (d, *J* = 5.8 Hz, 2H), 7.25-7.24 (m, 2H), 7.07 (dd, *J* = 9.1, 5.5 Hz, 2H), 6.97 (t, *J* =

8.8 Hz, 3H), 3.98 (dd, J = 8.2, 6.7 Hz, 1H), 3.16-3.12 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  162.2 (d, J = 245 Hz), 134.9, 132.0 (d, J = 3 Hz), 130.9 (d, J = 8 Hz), 129.2, 128.4, 127.6, 120.2, 115.6 (d, J = 21 Hz), 41.4, 39.9.

3-(4-chlorophenyl)-2-phenylpropanenitrile (3h)<sup>5</sup>: Following the general procedure A, the



title compound was isolated as a colourless liquid using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 61%, 73 mg).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36-7.32 (m, 3H), 7.26-7.22 (m, 4H), 7.03 (d, *J* = 8.4 Hz, 2H), 4.00-3.96 (m, 1H), 3.18-3.08 (m,

2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  134.7, 134.5, 133.3, 130.6, 129.1, 128.7, 128.3, 127.4, 120.0, 41.4, 39.5.

3-(3-bromophenyl)-2-phenylpropanenitrile (3i): Following the general procedure A, the



title compound was isolated as a colourless liquid using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 45%, 64 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.41-7.33 (m, 4H), 7.26-7.24 (m, 3H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.07 (d, *J* = 7.7 Hz, 1H), 3.98

(dd, J = 8.2, 6.5 Hz, 1H), 3.17-3.06 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  138.5, 134.8, 132.2, 130.6, 130.2, 129.2, 128.4, 128.0, 127.5, 122.6, 120.0, 41.7, 39.5. HRMS (ESI-TOF) m/z: [M]<sup>+</sup> Calculated for C<sub>15</sub>H<sub>12</sub>BrNNa 308.0045; Found 308.0042.

**2-phenyl-3-(4-(trifluoromethyl)phenyl)propanenitrile** (**3j**)<sup>5</sup>: Following the general



procedure **B**, the title compound was isolated as a colourless liquid using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 80%, 110 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.53 (d, J = 8.4 Hz, 2H), 7.36-7.32 (m, 3H), 7.24-7.21 (m, 4H), 4.03 (d, J =

6.7 Hz, 1H), 3.24-3.18 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.0 (q, J = 2 Hz), 134.5, 129.9, 129.6, 129.2, 128.5, 127.4, 125.6 (q, J = 8 Hz), 124.0 (d, J = 271 Hz), 119.86, 41.8, 39.3.

**3-(furan-2-yl)-2-phenylpropanenitrile (3k)**<sup>6</sup>: Following the general procedure C, the title



compound was isolated as a colourless liquid using silica-gel column chromatography eluting with 2% ethyl acetate in hexane (Yield: 56%, 55 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.30-7.26 (m, 4H), 7.23-7.18 (m, 2H), 6.23-6.22 (m, 1H), 6.04 (d, J = 3.2 Hz, 1H), 4.09-4.06 (m, 1H), 3.23-3.17 (m, 1H), 3.13-3.04 (m, 1H).<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.0, 142.1,

135.0, 129.2, 128.41, 127.6, 120.2, 110.6, 108.3, 37.2, 34.7.

2-phenyl-3-(pyridin-2-yl)propanenitrile (31)<sup>5</sup>: Following the general procedure C, the title compound was isolated as a colourless liquid using silica-gel column chromatography eluting with 3% ethyl acetate in hexane (Yield: 80%, 83 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.61 (d, J = 4.8 Hz, 1H), 7.63-7.60 (m, CN 31 1H), 7.36 (d, J = 4.1 Hz, 4H), 7.34-7.30 (m, 1H), 7.20 (dd, J = 7.4, 5.0 Hz, 1H), 7.13 (d, J = 7.7 Hz, 1H), 4.49 (dd, J = 9.2, 6.6 Hz, 1H), 3.38-3.26 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 156.1, 149.6, 136.4, 135.4, 129.0, 128.1, 127.3, 123.8, 122.3, 120.5, 44.1, 37.2.

**3-(naphthalen-1-yl)-2-phenylpropanenitrile** (**3m**)<sup>6</sup>: Following the general procedure **A**, the



title compound was isolated as a white solid using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 87%, 112 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.93 (dd, J = 13.7, 8.1 Hz, 2H), 7.81 (d, J = 8.2 Hz, 1H), 7.59-7.50 (m, 2H), 7.42-7.31 (m, 7H), 4.18 (dd, J =8.7, 6.7 Hz, 1H), 3.69-3.58 (m, 2H).  ${}^{13}C{}^{1}H{}$  NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ 

135.6, 133.9, 132.2, 131.2, 129.2, 129.1, 128.3, 128.2, 127.3, 126.5, 125.8, 125.5, 125.4, 122.6, 120.4, 39.6, 38.8.

**3-phenyl-2-**(p-tolyl)**propanenitrile**  $(4a)^7$ : Following the general procedure **B**, the title



compound was isolated as a colourless liquid using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 63%, 70 mg).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.31-7.26 (m, 3H), 7.16-7.15 (m, 6H), 3.99-3.95 (m, 1H), 3.21-3.09 (m, 2H), 2.36 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100

MHz, CDCl<sub>3</sub>) δ 137.9, 136.3, 132.1, 129.6, 129.1, 128.5, 127.2, 127.2, 120.5, 42.1, 39.4, 21.0.

3-(4-methoxyphenyl)-2-(p-tolyl)propanenitrile (4b)<sup>8</sup>: Following the general procedure B,



the title compound was isolated as a colourless liquid using silica-gel column chromatography eluting with 2% ethyl acetate in hexane (Yield: 52%, 65 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.16-7.11 (m, 4H), 7.05-7.02 (m, 2H), 6.82-6.80 (m, 2H), 3.91 (dd, *J* = 8.1, 6.5 Hz,

1H), 3.78 (s, 3H), 3.13-3.02 (m, 2H), 2.34 (s, 3H).  ${}^{13}C{}^{1}H$  NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  158.8, 137.9, 132.3, 130.3, 129.6, 128.5, 127.3, 120.6, 114.0, 55.2, 41.4, 39.7, 21.0.

3-(3-methoxyphenyl)-2-phenylpropanenitrile (4c)<sup>7</sup>: Following the general procedure **B**, the title compound was isolated as a colourless liquid using silica-gel column chromatography eluting with 2% ethyl acetate in hexane (Yield: 53%, 63 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.29-7.26 (m, 4H), 7.15 (dd, J = 5.5, 1.7 Hz, 2H), 6.85 (d, J = 7.8 Hz, 2H), 6.76 (d, J = 1.9 Hz, 1H), 3.98-3.94 (m, 1H), 3.77 (s, 3H), 3.18-3.13 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ 

 $159.9,\,136.6,\,136.3,\,130.0,\,129.2,\,128.6,\,127.4,\,120.3,\,119.7,\,113.7,\,113.1,\,55.3,\,42.1,\,39.8.$ 

**2-(2-methoxyphenyl)-3-phenylpropanenitrile**  $(4d)^{11}$ : Following the general procedure C, the title compound was isolated as a colourless liquid using silica-gel column chromatography eluting with 2% ethyl acetate in hexane (Yield: 56%, 66 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.33-7.24 (m, 5H), 7.19 (d, J = 6.5 Hz, 2H), 6.97-6.88 (m, 2H), 4.40 (dd, J = 8.9, 5.4 Hz, 1H), 3.84 (s,

3H), 3.16-3.02 (m, 2H).  ${}^{13}C{}^{1}H$  NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  156.0, 137.1, 129.5, 129.4, 129.4, 128.5, 128.4, 127.1, 123.5, 120.4, 110.9, 55.9, 40.0, 34.2.

2-(3,4-dimethoxyphenyl)-3-phenylpropanenitrile (4e)<sup>12</sup>: Following the general procedure



**B**, the title compound was isolated as a colourless liquid using silica-gel column chromatography eluting with 5% ethyl acetate in hexane (Yield: 65%, 87 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.40 (d, J = 4.0 Hz, 1H), 7.32-7.29 (m, 3H), 7.15 (d, J = 7.0 Hz, 2H), 6.84 (d, J = 8.5 Hz, 1H),

6.66 (s, 1H), 3.97 (t, J = 7.3 Hz, 1H), 3.90 (s, 3H), 3.83 (s, 3H), 3.24-3.12 (m, 2H). <sup>13</sup>C{<sup>1</sup>H}

NMR (100 MHz, CDCl<sub>3</sub>) δ 149.1, 148.8, 136.3, 129.4, 129.2, 128.7, 127.4, 120.6, 119.8, 111.3, 110.5, 55.9, 42.2, 39.2.

**2-(4-fluorophenyl)-3-phenylpropanenitrile**  $(4f)^{13}$ : Following the general procedure **B**, the title compound was isolated as a colourless liquid using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 47%, 53 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.30-7.25 (m, 3H), 7.21-7.17 (m, 2H), CN 4f 7.09 (dd, J = 7.5, 1.8 Hz, 2H), 7.04-7.00 (m, 2H), 3.96-3.96 (m, 1H), 3.20-3.07 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  162.5 (d, J = 247 Hz), 136.0, 131.0 (d, J =3 Hz), 129.5 (d, *J* = 5 Hz), 129.1, 128.9, 120.3, 116.3 (d, *J* = 21 Hz), 115.8, 42.2, 39.1.

**2-(4-chlorophenyl)-3-phenylpropanenitrile**  $(4g)^8$ : Following the general procedure **B**, the



title compound was isolated as a colourless liquid using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 53%, 64 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.35 (d, J = 8.3 Hz, 2H), 7.32 (t, J = 7.0 Hz, 3H), 7.20 (d, J = 8.2 Hz, 2H), 7.14 (d, J = 6.9 Hz, 2H), 4.02 (t, J

= 7.2 Hz, 1H), 3.24-3.12 (m, 2H).  ${}^{13}C{}^{1}H$  NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  135.9, 134.3, 133.7, 129.4, 129.3, 129.0, 128.8, 127.6, 120.1, 42.1, 39.2.

**2-(4-bromophenyl)-3-phenylpropanenitrile**  $(4h)^7$ : Following the general procedure **B**, the title compound was isolated as a colourless liquid using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 30%, 43 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.47 (d, J = 8.7 Hz, 2H), 7.29-7.28 CN (m, 3H), 7.10 (d, J = 8.7 Hz, 4H), 3.97 (t, J = 7.6 Hz, 1H), 3.21-3.07 (m,

2H).  ${}^{13}C{}^{1}H{}$  NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  135.8, 134.2, 132.2, 129.9, 129.5, 129.1, 128.8, 122.4, 120.0, 42.0, 39.3.

2-(benzo[d][1,3]dioxol-5-yl)-3-phenylpropanenitrile (4i): Following the general procedure



4h

C, the title compound was isolated as a colourless liquid using silica-gel column chromatography eluting with 3% ethyl acetate in hexane (Yield: 80%, 100 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.30-7.24 (m, 3H), 7.13 (dd, J = 9.1, 2.8 Hz, 2H), 6.76-6.74 (m, 2H), 6.69-6.67 (m, 1H), 5.97 (s, 2H)

2H), 3.90 (dd, J = 8.1, 6.6 Hz, 1H), 3.18-3.05 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ 148.3, 147.6, 136.3, 129.3, 128.9, 128.7, 127.5, 121.1, 120.5, 108.6, 107.9, 101.5, 42.3, 39.5. HRMS (ESI-TOF) m/z: [M]<sup>+</sup> Calculated for C<sub>16</sub>H<sub>13</sub>NO<sub>2</sub> 251.0946; Found 251.0952.





compound was isolated as a colorless liquid using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 50%, 29 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.36-7.33 (m, 5H), 7.31-7.28 (m,

2H), 7.26-7.24 (m, 5H), 3.06-3.03 (m, 1H), 2.93 (d, J = 7.1 Hz, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  136.8, 129.0, 128.8, 127.3, 115.0, 38.0, 35.9.

2-(3,4-dimethoxyphenyl)hexanenitrile (5a)<sup>7</sup>: Following the general procedure E, the title



compound was isolated as a colourless liquid using silica-gel column chromatography eluting with 5% ethyl acetate in hexane (Yield: 38%, 22 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.84 (d, *J* = 1.6 Hz, 2H), 6.80 (s, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 3.69 (dd, *J* = 8.5, 6.4 Hz, 1H), 1.92-

1.80 (m, 2H), 1.37-1.34 (m, 4H), 0.90 (t, J = 7.2 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  149.4, 148.8, 128.5, 121.3, 119.6, 111.4, 110.3, 56.0, 37.1, 35.7, 29.2, 22.2, 13.9.

2-(benzo[d][1,3]dioxol-5-yl)hexanenitrile (5b)<sup>4</sup>: Following the general procedure E, the title



compound was isolated as a colourless liquid using silica-gel column chromatography eluting with 2% ethyl acetate in hexane (Yield: 47%, 25 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.25-7.22 (m, 1H), 6.77-6.74 (m, 2H), 5.97- 5.94 (m, 2H), 3.68-3.48 (m, 1H), 1.87-1.84 (m, 2H),

1.43-1.35 (m, 4H), 0.89-0.87 (m, 3H).<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  148.3, 147.4, 129.8, 121.1, 120.8, 108.6, 107.7, 101.5, 37.1, 35.7, 29.1, 22.2, 13.9.

2-phenyloctanenitrile (5c)<sup>3</sup>: Following the general procedure **D**, the title compound was



isolated as a colourless liquid using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 53%, 27 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.31 (dd, J = 8.9, 5.8 Hz, 2H), 7.25 (dd, J = 9.6, 4.1 Hz,

3H), 3.70 (dd, J = 8.6, 6.3 Hz, 1H), 1.92-1.73 (m, 2H), 1.47-1.33 (m, 2H), 1.27-1.18 (m, 6H), 0.80 (t, J = 6.9 Hz, 3H).<sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  136.1, 129.0, 128.0, 127.2, 120.9, 37.5, 35.9, 31.5, 28.6, 27.0, 22.6, 14.0.

2-(4-methoxyphenyl)nonanenitrile (5d): Following the general procedure D, the title



compound was isolated as a colourless liquid using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 80%, 49 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.21-7.14 (m, 2H), 6.89-6.79 (m, 2H), 3.73 (s, 3H), 3.63 (dd, *J* 

= 8.5, 6.4 Hz, 1H), 1.89-1.68 (m, 2H), 1.20-1.18 (m, 10H), 0.78 (d, J = 7.1 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H}

NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  158.1, 127.3, 126.9, 120.1, 113.2, 54.2, 35.4, 34.8, 30.6, 27.8, 27.8, 25.9, 21.4, 12.9. HRMS (ESI-TOF) m/z: [M]<sup>+</sup> Calculated for C<sub>16</sub>H<sub>23</sub>NONa 268.1672; Found 268.1689.

2-phenyldodecanenitrile (5e): Following the general procedure D, the title compound was



isolated as a colourless liquid using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 65%, 42 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.33-7.28 (m, 2H), 7.26-7.23 (m, 3H), 3.97 (t, *J* = 6.8 Hz, 1H), 3.69 (dd,

J = 8.6, 6.3 Hz, 1H), 1.90-1.74 (m, 2H), 1.57-1.51 (m, 1H), 1.45-1.33 (m, 2H), 1.19-1.17 (m, 10H), 0.82-0.78 (m, 5H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  136.1, 129.0, 128.0, 127.2, 121.0, 37.4, 35.9, 31.9, 29.5, 29.3, 29.0, 28.6, 27.0, 25.9, 22.7, 14.1. HRMS (ESI-TOF) m/z: [M]<sup>+</sup> Calculated for C<sub>18</sub>H<sub>28</sub>N 258.2216; Found 258.2249.

3-cyclopropyl-2-phenylpropanenitrile (5f)<sup>5</sup>: Following the general procedure **D**, the title



compound was isolated as a colourless liquid using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 80%, 34 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.32-7.24 (m, 5H), 3.79 (dd, J = 8.4, 6.3 Hz, 1H), 1.89-1.77 (m, 1H), 1.65 (dd, J = 13.8, 6.6 Hz, 1H), 0.82-0.75 (m,

2H), 0.50-0.46 (m, 1H), 0.15-0.09 (m, 1H), 0.07-0.03 (m, 1H).  $^{13}C{^{1}H}$  NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  135.0, 128.0, 127.0, 126.4, 120.1, 40.1, 36.9, 7.8, 3.8, 3.5.

3-cyclopropyl-2-(4-methoxyphenyl)propanenitrile (5g)<sup>7</sup>: Following the general procedure



**D**, the title compound was isolated as a colourless liquid using silicagel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 83%, 42 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.30-7.26 (m, 2H), 6.94-6.90 (m, 2H), 3.86-3.82 (m, 4H), 1.91-1.85 (m, 1H), 1.74-1.69

(m, 1H), 0.90-0.78 (m, 1H), 0.64-0.49 (m, 2H), 0.18-0.13 (m, 2H).<sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  159.2, 128.4, 127.9, 121.3, 114.3, 55.3, 41.1, 37.0, 8.8, 4.7, 4.4.

**3-cyclopropyl-2-(4-methoxyphenyl)propanenitrile** (**5h**)<sup>6</sup>: Following the general procedure **D**, the title compound was isolated as a colourless liquid using silica-gel



**D**, the title compound was isolated as a colourless liquid using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 52%, 28 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.41-7.35 (m, 2H), 7.35-7.27 (m, 3H), 3.88-3.82 (m, 1H), 1.92-1.80 (m, 2H), 1.72-1.61 (m, 4H), 1.55-

1.48 (m, 1H), 1.33-1.13 (m, 4H), 1.02-0.89 (m, 2H).<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  136.6, 129.0, 128.8, 127.2, 121.2, 34.6, 32.6, 30.2, 30.0, 28.8, 25.7, 25.2, 24.3.

**2,5-diphenylpent-4-enenitrile** (5i)<sup>14</sup>: Following the general procedure **D**, the title compound



was isolated as a colourless liquid using silica-gel column chromatography eluting with 2% ethyl acetate in hexane (Yield: 34%, 20 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.77-7.75 (m, 2H), 7.60 (d, *J* = 7.3 Hz, 2H), 7.44 (s, 1H), 7.40-7.35 (m, 2H), 7.31-7.27 (m, 2H), 7.21

(s, 1H), 7.17-7.15 (m, 2H), 4.03-3.94 (m, 1H), 3.21-3.11 (m, 2H).  ${}^{13}C{}^{1}H$  NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  141.6, 138.8, 134.4, 132.9, 129.9, 129.6, 129.1, 128.4, 127.5, 126.0, 120.2, 42.0, 39.4.

5,9-dimethyl-2-phenyldec-8-enenitrile (5j)<sup>5</sup>: Following the general procedure D, the title



compound was isolated as a colourless liquid using silica-gel column chromatography eluting with 1% ethyl acetate in hexane (Yield: 47%, 30 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.40-7.35 (m, 2H), 7.32-7.29 (m, 3H), 5.07-5.03 (m, 1H), 3.75-3.71(m, 1H),

1.94-1.86 (m, 4H), 1.67 (d, J = 0.9 Hz, 3H), 1.57 (s, 3H), 1.47-1.42 (m, 2H), 1.33-1.25 (m, 2H), 1.17-1.09 (m, 1H), 0.87 (d, J = 6.5 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  129.1, 128.1, 127.3, 127.3, 124.6, 121.0, 37.8, 36.7, 34.2, 33.7, 32.0, 25.8, 25.5, 19.5, 17.7.

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# [1.6] Copies of <sup>1</sup>H and <sup>13</sup>C NMR spectra for selected compounds.





















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