Base Metal Catalyzed Direct Olefinations of Alcohols with Sulfones
Satyadeep Waiba, Animesh Das, Milan K. Barman and Biplab Maji *

Department of Chemical Sciences, Indian Institute of Science Education and Research Kolkata, Mohanpur 741246, India

E-mail: bm@iiserkol.ac.in

Table of Contents

|   |   |
|---|---|
| 1 | Optimization of reaction conditions | S2 |
| 2 | Mechanistic experiments | S6 |
| 4 | Copies of $^1$H and $^{13}$C NMR spectra | S17 |
1. Optimization of reaction conditions:

Table S1: Screening of different ligands:

| Entry | Ligand | Yield of 3a (%)<sup>b</sup> |
|-------|--------|-----------------------------|
| 1.    | L1     | 85(83)                      |
| 2.    | L2     | 91(89)                      |
| 3.    | L3     | 9                           |
| 4.    | L4     | 45                          |
| 5.    | L5     | 73                          |
| 6.    | L6     | 33                          |
| 7.    | L7     | 60                          |
| 8.    | L8     | 57                          |

<sup>a</sup>Reaction conditions: **1a** (0.15 mmol), **2a** (0.1 mmol), Ni-salt (0.005 mmol), ligand (0.006 mmol), KOH (0.1 mmol) under argon atmosphere at 140 °C in 1,4-dioxane (0.5 mL) for 24 h in a Schlenk tube.

<sup>b</sup>Yields were determined by GC-MS analysis using mesitylene as an internal standard (isolated yields are in parenthesis).
Table S2: Screening of different Ni-salts:

| Entry | Ni-Salt          | Yield of 3a (%)<sup>b</sup> |
|-------|-----------------|-----------------------------|
| 1.    | NiBr<sub>2</sub> | 91(89)                      |
| 2.    | NiCl<sub>2</sub>| 9                           |
| 3.    | Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O | 32                  |
| 4.    | Ni(acac)<sub>2</sub> | 37                  |

<sup>a</sup>Reaction conditions: 1a (0.15 mmol), 2a (0.1 mmol), Ni-salt (0.005 mmol), ligand (0.006 mmol), KOH (0.1 mmol) under argon atmosphere at 140 °C in 1,4-dioxane (0.5 mL) for 24 h in a Schlenk tube. <sup>b</sup>Yields were determined by GC-MS using mesitylene as an internal standard (isolated yields are in parenthesis).

Table S3: Catalyst loading screening:

| Entry | Catalyst loading (x mol%) | Yield of 3a (%)<sup>b</sup> |
|-------|---------------------------|-----------------------------|
| 1.    | 5 mol%                    | 91(89)                      |
| 2.    | 2.5 mol%                  | 68                          |
| 3.    | 1 mol%                    | 61                          |

<sup>a</sup>Reaction conditions: 1a (0.15 mmol), 2a (0.1 mmol), NiBr<sub>2</sub>(x mol%), L<sub>2</sub> (1.2x mol%), KOH (0.1 mmol) under argon atmosphere at 140 °C in 1,4-dioxane (0.5 mL) for 24 h in a Schlenk tube. <sup>b</sup>Yields were determined by GC-MS analysis using mesitylene as an internal standard (isolated yields are in parenthesis). <sup>c</sup>The reaction was performed in the scale of 0.2 mmol.
Table S4: Base screening:

| Entry | Base  | Yield of 3a (%)<sup>b</sup> |
|-------|-------|-----------------------------|
| 1.    | KOH   | 91(89)                      |
| 2.    | t-BuOK | 25                           |
| 3.    | NaOH  | 13                           |
| 4.    | K₂CO₃ | trace                        |
| 5.    | Cs₂CO₃ | trace                       |

<sup>a</sup>Reaction conditions: 1a (0.15 mmol), 2a (0.1 mmol), NiBr₂ (0.005 mmol), L₂ (0.006 mmol), base (0.1 mmol) under argon atmosphere at 140 °C in 1,4-dioxane (0.5 mL) for 24 h in a Schlenk tube.  
<sup>b</sup>Yields were determined by GC-MS analysis using mesitylene as an internal standard (isolated yields are in parenthesis).

Table S5: Base loading variation:

| Entry | KOH (mol%) | Yield of 3a (%)<sup>b</sup> |
|-------|-----------|-----------------------------|
| 1.    | 10 mol%   | N.d.                        |
| 2.    | 20 mol%   | trace                       |
| 3.    | 50 mol%   | 13                          |
| 4.    | 100 mol%  | 91(89)                      |

<sup>a</sup>Reaction conditions: 1a (0.15 mmol), 2a (0.1 mmol), NiBr₂ (0.005 mmol), L₂ (0.006 mmol), KOH (x mol%) under argon atmosphere at 140 °C in 1,4-dioxane (0.5 mL) for 24 h in a Schlenk tube.  
<sup>b</sup>Yields were determined by GC-MS using mesitylene as an internal standard (isolated yields are in parenthesis). N.d. = not detected.
Table S6: Solvent variation:

| Entry | Solvent | Yield of 3a (%)<sup>b</sup> |
|-------|---------|-----------------------------|
| 1.    | dioxane | 91(89)                      |
| 2.    | toluene | 35                          |
| 3.    | t-AmOH  | trace                       |
| 4.    | t-BuOH  | trace                       |

<sup>a</sup>Reaction conditions: 1a (0.15 mmol), 2a(0.1 mmol), NiBr<sub>2</sub>(0.005 mmol), L2 (0.006 mmol), KOH (0.1 mmol) under argon atmosphere at 140 °C in solvent (0.5 mL) for 24 h in a Schlenk tube.

<sup>b</sup>Yields were determined by GC-MS analysis using mesitylene as an internal standard (isolated yields are in parenthesis).

Table S7: Control experiments:

| Entry | Deviation | Yield of 3a (%)<sup>b</sup> |
|-------|-----------|-----------------------------|
| 1.    | Without NiBr<sub>2</sub> | 30                          |
| 2.    | Without L2 | 35                          |
| 3.    | Without KOH | 12                          |

<sup>a</sup>Reaction conditions: 1a (0.15 mmol), 2a(0.1 mmol), NiBr<sub>2</sub>(0 or 0.005 mmol), L2 (0 or 0.006 mmol), KOH (0 or 100 mol%) under argon atmosphere at 140 °C in 1,4-dioxane (0.5 mL) for 24 h in a Schlenk tube.

<sup>b</sup>Yields were determined by GC-MS using mesitylene as an internal standard (isolated yields are in parenthesis). N.d. = not detected.
2. Mechanistic experiments:

2.1 Deuterium labelling experiment

In a 15 mL oven dried Schlenk tube NiBr₂ (5 mol%), L₂ (6 mol%), KOH (0.1 mmol), sulfone 1f (36.9 mg, 0.15 mmol) and biphenyl methanol 2c-d₂ (18.6 mg, 0.1 mmol) was charged along with a magnetic stirrer in dioxane (0.5 mL) and the tube was closed before the mixture was placed in a preheated oil bath at 140 °C. After 30h the reaction was stopped and quenched with water and extracted with ethyl acetate (2 x 5 mL). The combined organic phase was dried over sodium sulphate and solvent was removed. Purification of the compound done by column chromatography on silica gel gave the corresponding product in the reported yield.

Figure S1: ¹H NMR of 3p-d obtained from 1f and 2c-d₂.
In a 15 mL oven dried Schlenk tube NiBr$_2$ (5 mol%), L$_2$ (6 mol%), KOH (0.1 mmol), sulfone 1g-d$_2$ (46.4 mg, 0.15 mmol) and alcohol 2d (12.2 mg, 0.1 mmol) was charged along with a magnetic stirrer in dioxane (0.5 mL) and the tube was closed before the mixture was placed in a preheated oil bath at 140 °C. After 24h the reaction was stopped and quenched with water and extracted with ethyl acetate (2 x 5 mL). The combined organic phase was dried over sodium sulphate and solvent was removed. Purification of the compound done by column chromatography on silica gel gave the corresponding product in the reported yield.

Figure S2: $^1$H NMR of 3p-d obtained from 2d and 1g-d$_2$. 
2.2 Kinetic isotope experiment

In an oven dried 15 mL Schlenk tube was charged with NiBr₂ (5 mol%), L₂ (6 mol%), KOH (0.1 mmol), sulfone 1f (36.9 mg, 0.15 mmol) and biphenyl methanol 2c or 2c-d₂ (0.1 mmol) in dioxane (0.5 mL) and the tube was closed before the mixture was placed in a preheated oil bath at 140 °C. After design time (6 h) the reaction was stopped and quenched with water and extracted with ethyl acetate (2 x 5 mL). The combined organic phase was dried over sodium sulphate and solvent was removed and then external standard 1,3,5-trimethoxybenzene (0.1 mmol) and CDCl₃ (1 mL) were added, stirred for 5 minutes and NMR was measured. Yield was determined by comparing the integral with the internal standard.

Figure S3: ¹H NMR for reaction of 1f and 2c.
Figure S4: $^1$H NMR for reaction of 1f and 2c-d$_2$.

2.3 Catalytic experiment with (L2)NiBr$_2$

In a 15 mL oven dried Schlenk tube (L2)NiBr$_2$ (5 mol%), KOH (0.1 mmol), sulfone 1a (0.15 mmol) and benzyl alcohol 2a (0.1 mmol) was charged along with a magnetic stirrer in dioxane (0.5 mL). The tube was closed and stirred in a preheated oil bath at 140 °C for 24 h. The reaction was quenched with water (2 mL) and the organics were extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over Na$_2$SO$_4$, filtered and concentrated. The residue was purified by column chromatography over silica gel (100–200 mesh) with hexane/ethyl acetate mixture as eluent.
2.4 Proof of vinyl sulfone as intermediate and alcohol as the hydride source

![Chemical Reaction Diagram]

In a 15 mL oven dried Schlenk tube NiBr\(_2\) (5 mol%), L\(_2\) (6 mol%), KOH (0.1 mmol), vinyl sulfone 4a (0.1 mmol) and benzyl alcohol 2a (0.1 mmol) was charged along with a magnetic stirrer in dioxane (0.5 mL) and the tube was closed before the mixture was placed in a preheated oil bath at 140 °C. After design time the reaction was stopped and quenched with water. Yield was determined by GC using mesitylene as an internal standard.

In a 15 mL oven dried Schlenk tube NiBr\(_2\) (5 mol%), L\(_2\) (6 mol%), KOH (0.1 mmol), vinyl sulfone 4b (41 mg, 0.1 mmol) and biphenyl methanol 2c-\(d_2\) (18.6 mg, 0.1 mmol) was charged along with a magnetic stirrer in dioxane (0.5 mL) and the tube was closed before the mixture was placed in a preheated oil bath at 140 °C. After 24h time the reaction was stopped and quenched with water and extracted with ethyl acetate (2 x 5 mL). The combined organic phase was dried over sodium sulphate and solvent was removed. Purification of the compound done by column chromatography on silica gel gave the corresponding product in the reported yield.
Figure S5: $^1$H NMR of 3p-d obtained from 4b and 2c-d$_2$.

2.5 Probing the involvement of Ni-H species:

**Preparation of Ni-H complex**

\[
\text{PCy}_3 + \text{NiBr}_2 \xrightarrow{0.4 \text{ mmol} \quad 0.2 \text{ mmol}} \xrightarrow{\text{EtOH, reflux, 6h}} \xrightarrow{\text{PCy}_3} \xrightarrow{\text{Br-Ni-Br, PCy}_3} \xrightarrow{\text{NaBH}_4 (1\text{eq})} \xrightarrow{\text{C}_6\text{H}_6; \text{EtOH (5:1, 3 mL)}} \xrightarrow{\text{PCy}_3} \xrightarrow{\text{Br-Ni-H, PCy}_3} \xrightarrow{\text{L6-Ni-H}}
\]

The catalyst was prepared according to literature procedure.\textsuperscript{12, 13} The L6-Ni-H species was obtained as pale yellow solid and used for further reactions.

**Catalytic experiment with Ni-H complex**

In a 15 mL oven dried Schlenk tube L6-Ni-H (5 mol%), KOH (0.1 mmol), sulfone 1a (0.15 mmol) and benzyl alcohol 2a (0.1 mmol) was charged along with a magnetic stirrer in dioxane (0.5 mL). The tube was closed and stirred in a preheated oil bath at 140 °C for 24 h. The reaction was
quenched with water (2 mL) and the organics were extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over Na$_2$SO$_4$, filtered and concentrated. The residue was purified by column chromatography over silica gel (100–200 mesh) with hexane/ethyl acetate mixture as eluent.

**Catalytic experiment with Ni-H complex and vinyl sulfone 4a:**

In a 15 mL oven dried Schlenk tube L6-Ni-H (5 mol%), KOH (0.1 mmol), vinyl sulfone 4a (0.1 mmol) and benzyl alcohol 2a (0.1 mmol) was charged along with a magnetic stirrer in dioxane (0.5 mL). The tube was closed and stirred in a preheated oil bath at 140 °C for 24 h. The reaction was quenched with water (2 mL) and the organics were extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over Na$_2$SO$_4$, filtered and concentrated. The residue was purified by column chromatography over silica gel (100–200 mesh) with hexane/ethyl acetate mixture as eluent.
2.6 Probing the Ni-alkoxy intermediate:

Preparation of Ni-H complex

In a 15 mL oven dried Schlenk tube (L2)NiBr₂ (0.1 mmol), t-BuOK (0.2 mmol) and benzyl alcohol 2a (0.2 mmol) was charged along with a magnetic stirrer in dioxane (1 mL) and the tube was closed before the mixture was placed in a preheated oil bath at 140 °C. After design time the reaction was stopped and the solvent was dried under vacuum. The black powder obtained was used directly for further reaction. HRMS calcd for C₂₁H₁₉N₂NiO₂ [M +] 389.0800, found 389.1976.

Catalytic experiment with Ni-H complex:

In a 15 mL oven dried Schlenk tube Ni-Alkoxy (10 mol%), KOH (0.1 mmol), sulfone 1a (0.15 mmol) and benzyl alcohol 2a (0.1 mmol) was charged along with a magnetic stirrer in dioxane (0.5 mL). The tube was closed and stirred in a preheated oil bath at 140 °C for 24 h. The reaction was quenched with water (2 mL) and the organics were extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography over silica gel (100–200 mesh) with hexane/ethyl acetate mixture as eluent.
2.7 Isolation of byproduct:

\[
\text{PhSO}_2\text{Ph} + \text{PhOH} \xrightarrow{\text{NiBr}_2 \ (5 \text{ mol})} \text{PhPh} + \text{PhSO}_2\text{K}
\]

In a 15 mL oven dried Schlenk tube NiBr\(_2\) (5 mol%), L\(_2\) (6 mol%), KOH (0.1 mmol), sulfone 1a (0.15 mmol) and benzyl alcohol 2a (0.1 mmol) was charged along with a magnetic stirrer in dioxane (0.5 mL) and the tube was closed before the mixture was placed in a preheated oil bath at 140°C. After design time the reaction was stopped and the precipitate was filtered, washed with DCM. White solid. 19.5 mg, 72%.

\(^1\)H NMR (400 MHz, D\(_2\)O) \(\delta\) 7.67 (dd, \(J = 7.5, 1.5\) Hz, 2H), 7.56 (m, \(J = 4.9, 3.2\) Hz, 3H). \(^{13}\)C NMR (126 MHz, D\(_2\)O) \(\delta\) 153.4, 130.5, 129.0, 123.3. HRMS calcd for [C\(_6\)H\(_5\)O\(_2\)S]~ [M]\(^-\) 141.0016, found 141.0019.

**Figure S6**: \(^1\)H NMR of the by-product.
2.8 Detection of aldehyde

In a 15 mL oven dried Schlenk tube (L2)NiBr2 (5 mol%), KOH (0.1 mmol), and benzyl alcohol 2a (0.1 mmol) was charged along with a magnetic stirrer in dioxane (0.5 mL) and the tube was closed before the mixture was placed in a preheated oil bath at 140 °C. After designated time the reaction was stopped and quenched with water. The reaction mixture was analyzed by GC MS using mesitylene as an internal standard.
Figure S8: GC spectra for detection of aldehyde.
3. Copies of $^1$H and $^{13}$C NMR spectra:

**Figure S9**: $^1$H NMR spectra of 3a.

**Figure S10**: $^{13}$C NMR spectra of 3a.
Figure S11: $^1$H NMR spectra of 3b.

Figure S12: $^{13}$C NMR spectra of 3b.
Figure S13: $^1$H NMR spectra of 3c.

Figure S14: $^{13}$C NMR spectra of 3c.
Figure S15: $^1$H NMR spectra of 3d.

Figure S16: $^{13}$C NMR spectra of 3d.
Figure S17: $^1$H NMR spectra of 3e.

Figure S18: $^{13}$C NMR spectra of 3e.
Figure S19: $^1$H NMR spectra of 3f.

Figure S20: $^{13}$C NMR spectra of 3f.
Figure S21: $^1$H NMR spectra of 3g.

Figure S22: $^{13}$C NMR spectra of 3g.
Figure S23: $^1$H NMR spectra of 3h.

Figure S24: $^{13}$C NMR spectra of 3h.
Figure S25: $^1$H NMR spectra of 3i.

Figure S26: $^{13}$C NMR spectra of 3i.
Figure S27: $^{19}$F NMR spectra of 3i.

Figure S28: $^1$H NMR spectra of 3j.
**Figure S29:** $^{13}$C NMR spectra of 3j.

**Figure S30:** $^1$H NMR spectra of 3k.
Figure S31: $^{13}$C NMR spectra of 3k.

Figure S32: $^1$H NMR spectra of 3l.
Figure S33: $^{13}$C NMR spectra of 3l.

$^{13}$C NMR (126 Mhz) in CDCl$_3$

Figure S34: $^1$H NMR spectra of 3m.

$^1$H NMR (400 Mhz) in CDCl$_3$
Figure S35: $^{13}$C NMR spectra of 3m.

Figure S36: $^1$H NMR spectra of 3n.
Figure S37: $^{13}$C NMR spectra of $3n$.

Figure S38: $^1$H NMR spectra of $3o$. 
Figure S39: $^{13}$C NMR spectra of 3o.

Figure S40: $^1$H NMR spectra of 3p.
Figure S41: $^{13}$C NMR spectra of 3p.
1-methoxy-4-vinylbenzene, 3q

Reaction mixture NMR in CDCl₃

Figure S42: $^1$H NMR spectra of 3q.
Figure S43: $^1$H NMR spectra of 3r.
Figure S44: $^1$H NMR spectra of 3s.
Figure S45: $^1$H NMR spectra of 3t.
Figure S46: $^1$H NMR spectra of 3u.

Figure S47: $^{13}$C NMR spectra of 3u.
**Figure S48:** $^1$H NMR spectra of 3v.

2-vinylthiophene, 3v

Reaction mixture NMR in CDCl$_3$
Figure S49: $^1$H NMR spectra of 3w.
Figure S50: $^1$H NMR spectra of 3x.

Figure S51: $^{13}$C NMR spectra of 3x.