Supporting information
for

Sulfoximinocarbonylation of aryl halides using heterogenous Pd/C catalyst

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1. General information

All reactions were carried out in reaction tubes under CO atmosphere. All the solvents used for the reactions were obtained from Fischer Scientific, India Pvt. Ltd. Reactions were monitored by thin-layer chromatography (TLC) using Merck silica gel 60 F{sub 254} precoated plates (0.25 mm) and visualized by UV fluorescence quenching using appropriate mixture of ethyl acetate and hexanes. Silica gel (particle size: 100-200 mesh) was purchased from Avra and used for column chromatography using hexanes and ethyl acetate mixture as eluent. Pd/C was obtained from Sigma-Aldrich and used directly as received. Various aryl iodides, aryl bromides and substituted sulfides were purchased from Alfa-aesar and Sigma-Aldrich Company. NH-sulfoximines were prepared from commercially available sulphides using literature reported procedure. All the reactions were carried out in temperature controlled IKA magnetic stirrers. {sup 1}H, {sup 13}C and {sup 19}F NMR spectra were recorded on a Bruker 400 MHz. {sup 1}H NMR spectra were reported relative to Me{sub 4}Si (δ 0.0 ppm) or residual CDCl{sub 3} (δ 7.26 ppm) and DMSO-d{sub 6} (δ 2.50 ppm). {sup 13}C NMR were reported relative to CDCl{sub 3} (δ 77.16 ppm) and DMSO-d{sub 6} (δ 39.51 ppm). {sup 19}FNMR were reported relative to C{sub 6}F{sub 6} (δ -164.9 ppm). Chemical shifts were reported in parts per million and multiplicities are as indicated: s (singlet), d (doublet), t (triplet), q (quartet), br s (broad single) and m (multiplet). Coupling constants, J are reported in Hertz. Infrared spectra were recorded on a FTIR 4000 Series Spectrometer using KBr (film). The wave numbers of recorded IR signals are quoted in cm{sup -1}. GC-MS (EI) was recorded on Shimadzu GCMS- QP2010 Ultra using Restek-Rxi-5Sil MS (30 m, 0.25 mmID, 0.25 μm df ) column. High resolution mass spectra (HRMS) were recorded on Q-Tof Micro mass spectrometer.

3. General procedure

3.1. General procedure for aroylation of NH-sulfoximines

Aryl iodide (0.5 mmol), NH-sulfoximine (0.75 mmol), Pd/C (5.3 mg, 1 mol%) and with K{sub 2}CO{sub 3} (0.5 mmol) taken in an oven dried reaction tube equipped magnetic pellet and covered with septum. First the reaction tube was evacuated (10 min) and DMF (1 ml) was added, again it was evacuated (10 min). CO balloon is introduced and stirred at 60°C until the completion of reaction (monitored by TLC). After completion of the reaction, it was allowed to cool to room temperature and extracted with ethyl acetate (3 X 5 mL), followed by brine solution. Then the organic layer was dried over Na{sub 2}SO{sub 4} and concentrated under vacuum. The crude reaction mixture was purified by column chromatography on silica gel (hexanes:ethyl acetate) to get N-arylated sulfoximine 3.
3.2. Experimental procedure for recovery of the Pd/C catalyst

For recycling of Pd/C, the reaction was performed with 4-iodotoluene 1a as substrate in 1.0 mmol scale in optimized reaction conditions such as S-methyl-S-phenyl-NH-sulfoximine 2a (1.5 equiv), K₂CO₃ (1 equiv), and 2 mL DMF under CO balloon at 60 °C. After completion of the reaction, the reaction mixture was allowed to attain room temperature. Then ethyl acetate (5 mL) was added and centrifuged. The liquid decanted to a 50 mL conical flask. This procedure was repeated up to three times and decanted to the same conical flask. After that the catalyst was washed with nano pure water (5 mL) and methanol (5 mL). Finally, the resulting solid particles (Pd/C) dried under vacuum. The dried catalyst was reused for further catalytic cycle. The collected liquid was extracted with ethyl acetate (3 × 10 mL), followed by brine solution. Then the organic phase was dried over Na₂SO₄ and concentrated in vacuum. The resulting reaction mixture was purified by column chromatography on silica gel (hexanes: ethyl acetate) to get N-aroylsulfoximine product 3a.

Mercury Poisoning Test

Mercury poisoning test was also conducted to support that Pd/C is heterogeneous in the reaction medium. Pd/C (10.6 mg, 1 mol%), Hg (8.0 g, 40 mmol, 30 equiv.), 4-Iodotoluene 1a (218 mg, 1.0 mmol, 1.0 equiv.), S-methyl-S-phenyl-sulfoximine 2a (232.83 mg, 1.5 mmol, 1.5 equiv.) were taken in oven dried reaction tube. The reaction tube was evacuated (10 min) and DMF (1 ml) was added, again it was evacuated (10 min) then CO balloon is introduced and stirred at 60°C. After 7 hours, the reaction mixture was allowed to cool to room temperature. Complete inhibition of the reaction was detected and even trace amount of product 3a formation was not observed.

References

4. $^1$H and $^{13}$C spectra for all compounds

**Figure 1**: 400 MHz $^1$H-NMR spectrum of 3a in CDCl$_3$

**Figure 2**: 100 MHz $^{13}$C-NMR spectrum of 3a in CDCl$_3$
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Figure 6: 100 MHz $^{13}$C-NMR spectrum of 3c in CDCl$_3$
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Figure 8: 100 MHz $^{13}$C-NMR spectrum of 3d in CDCl$_3$
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Figure 10: 100 MHz $^{13}$C-NMR spectrum of 3e in CDCl$_3$
Figure 11: 400 MHz $^1$H-NMR spectrum of 3f in CDCl$_3$

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Figure 13: 400 MHz $^1$H-NMR spectrum of 3g in CDCl$_3$

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