Supporting Information

Iridium-Catalyzed C-3 Allylation of Indoles with Allylic Alcohols Promoted by Brønsted Acid

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General information

All air-sensitive manipulations were carried out under the nitrogen atmosphere using standard Schlenk techniques. All glassware was oven or flame dried immediately prior to use.

\[ \text{[Ir(COD)Cl]}_2, \quad [\text{Ir}(\text{COD})\text{Cl}]_2, \quad [\text{Ir} \cdot \text{Cp} \cdot \text{Cl}_2], \quad [\text{Ir}(\text{COD})\text{Cl}]_2, \quad [\text{Ir}(\text{COD})(\text{OH})]_2, \quad [\text{Ir}(\text{COD})(\text{OMe})]_2, \quad [\text{Ir(CO)}]_2 \]

allylic alcohols 2b-i, 1-phenyl-1H-indole 1j, 1-Benzyl-1H-indole 1k, 1-(p-Toluenesulfonyl)indole 1l were synthesized according to published procedures. Other reagents were obtained from commercial suppliers and used without further purification. All solvents were obtained from commercial sources and used without further purification, except for THF, which was freshly distilled from sodium benzophenone ketyl under nitrogen.

Products were characterized by \(^1\text{H NMR}, \quad \text{\(^{13}\text{C NMR}, \quad \text{\(^{19}\text{F NMR}, \quad \text{MS}, \quad \text{elemental analyses and IR.}}\)}

Analytical thin-layer chromatography were performed on glass plates precoated with silica gel impregnated with a fluorescent indicator (254 nm), and the plates were visualized by exposure to ultraviolet light. Mass spectra were taken on a Finnigan TSQ Quantum-MS instrument in the electrospray ionization (ESI) mode. IR spectra were recorded on Thermo Scientific Nicolet iS10. \(^1\text{H NMR}, \quad \text{\(^{13}\text{C NMR and \quad \text{\(^{19}\text{F NMR spectra were recorded on an AVANCE 500 Bruker}}\)}

Spectrometer operating at 500 MHz, 125 MHz and 470 MHz in CDCl_3, respectively, and chemical shifts were reported in ppm. Elemental analyses were performed on a Yanagimoto MT3CHN recorder. GC analyses were performed on an Agilent 7890A instrument (Column: Agilent 19091J-413: 30 m \times 320 \mu m \times 0.25 \mu m, carrier gas: H_2, FID detection.\)
The Procedure for Substrate Synthesis

Addition of Vinylimagnesium Bromide to Aryl or Alkyl Aldehydes

Following the procedure of Logan\(^6\): In an oven-dried round-bottom flask, a solution of the aldehyde (10 mmol, 1 equiv) in dry THF (10 mL) was stirred for 10 minutes under nitrogen at 0 °C. To the reaction mixture, the vinylimagnesium bromide (1 M in THF) (12 mmol, 1.2 equiv) was added slowly. After 15 min the reaction was allowed to warm to RT and stirred for an additional 1-3 h. The reaction was quenched with a saturated aqueous NH\(_4\)Cl solution and extracted with diethyl ether. The combined organic layers were washed with brine, dried (MgSO\(_4\)), filtered and evaporated to give the crude allylic alcohols 2b-i that were engaged in the next step without further purification.
General Procedure for Allylation of Indoles

A N₂ purged flame-dried Schlenk tube containing indole 1 (0.200 mmol), [Ir(COD)Cl]₂ (0.004 mmol), were added successively CH₃CN (1 mL), allylic alcohol 2 (0.200 mmol) and H₂SO₄ (1 M in H₂O) (0.010 mmol) via syringe. The reaction mixture was stirred at 50 °C for 5 h. After the reaction was complete, the solvent was removed under reduced pressure. The ratio of regioisomers (branched/linear) was determined by ¹H NMR of the crude reaction mixture. The crude residue was purified by flash column silica gel chromatography (petroleum ether/ethyl acetate: 95:5 to 90:10) to yield the product 3.

References

$^1$H and $^{13}$C NMR Spectra for Compound A, B and 3a-s

$^1$H NMR spectrum (500 MHz, CDCl$_3$) of A

$^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of A
\( ^1H \) NMR spectrum (500 MHz, CDCl\(_3\)) of B

\( ^{13}C \) NMR spectrum (125 MHz, CDCl\(_3\)) of B
$^1$H NMR spectrum (500 MHz, CDCl$_3$) of 3a

$^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of 3a
$^1$H NMR spectrum (500 MHz, CDCl$_3$) of 3b

$^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of 3b
$^1$H NMR spectrum (500 MHz, CDCl$_3$) of 3c

$^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of 3c
$^1$H NMR spectrum (500 MHz, CDCl$_3$) of 3d

$^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of 3d
$^1$H NMR spectrum (500 MHz, CDCl$_3$) of 3e

$^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of 3e
$^1$H NMR spectrum (500 MHz, CDCl$_3$) of 3f

$^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of 3f
$^1$H NMR spectrum (500 MHz, CDCl$_3$) of 3g

$^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of 3g
$^{1}H$ NMR spectrum (500 MHz, CDCl$_3$) of 3h

$^{13}C$ NMR spectrum (125 MHz, CDCl$_3$) of 3h
\[ ^1\text{H} \text{ NMR spectrum (500 MHz, CDCl}_3 \text{) of 3i} \]

\[ ^{13}\text{C} \text{ NMR spectrum (125 MHz, CDCl}_3 \text{) of 3i} \]
$^1$H NMR spectrum (500 MHz, CDCl$_3$) of 3j

$^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of 3j
$^1$H NMR spectrum (500 MHz, CDCl$_3$) of 3k

$^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of 3k
$^1$H NMR spectrum (500 MHz, CDCl$_3$) of 3m

$^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of 3m
$^1$H NMR spectrum (500 MHz, CDCl$_3$) of 3n

$^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of 3n
$^1$H NMR spectrum (500 MHz, CDCl$_3$) of 30

$^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of 30
$^1$H NMR spectrum (500 MHz, CDCl$_3$) of 3p

$^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of 3p
$^1$H NMR spectrum (500 MHz, CDCl$_3$) of 3q

$^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of 3q
$^1$H NMR spectrum (500 MHz, CDCl$_3$) of 3r

$^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of 3r
$^1$H NMR spectrum (500 MHz, CDCl$_3$) of 3s

$^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of 3s