Indium(I)-catalyzed alkyl–allyl coupling between ethers and an allylborane

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Electronic Supplementary Information (ESI)

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1 General

Nuclear Magnetic Resonance (NMR) spectra were recorded on a JEOL ECX-400, a JEOL ECA-500, or a JEOL ECX-600 spectrometer, operating at 400 MHz, 500 MHz, or 600 MHz for $^1$H NMR, and 100 MHz, 125 MHz, or 150 MHz for $^{13}$C NMR (128 MHz for $^{11}$B NMR). Chemical shifts were reported downfield from tetramethylsilane (TMS). Infra Red (IR) spectra were measured using a JASSO FT/IR-610 spectrometer. High Resolution Mass Spectra (HRMS) were recorded using a JEOL JMS T100TD (DART) spectrometer. Preparative thin-layer chromatography (PTLC) was carried out using Wakogel B-5F from WAKO. All solvents used were commercially available dry solvents that were further dried and degassed appropriately under an argon atmosphere, and stored over activated molecular sieves in an argon box prior to use.

InOTf was prepared according to a reported procedure, and stored in an argon box at $-30$ °C. All other metal salts were purchased from ALDRICH, and stored in an argon box at room temperature. All reactions were carried out under an argon atmosphere in flame-dried glassware. 9-BBN-derived allylborane 2b was synthesized according to a reported method.

2 Starting materials

2.1 Procedure for synthesis of starting materials

To a stirred solution of an alcohol (20 mmol) in dry THF (20 mL) at 0 °C was slowly added NaH (2 equiv). The reaction mixture was further stirred at 0 °C for 1 h before slow addition of MeI (1.5 equiv). The mixture was then allowed to reach to room temperature overnight. Quenching with water followed by extraction (Et$_2$O, 3 × 10mL) and evaporation afforded the corresponding crude ether product, which was then purified by column chromatography to provide substrates 1a–u.

2.2 Analytical data for unknown ethers

1-Bromo-3-(1-methoxyethyl)-benzene (1f):

$^1$H NMR (CDCl$_3$, 600 Hz): $\delta = 1.42$ (s, 3H), 3.23 (s, 3H), 4.23–4.27 (q, $J = 7.2$, 1H), 7.20–7.26 (m, 2H), 7.40–7.46 (m, 2H) ppm.

$^{13}$C NMR (CDCl$_3$, 150 Hz): $\delta = 23.8, 56.6, 79.0, 122.6, 124.8, 129.2, 130.1, 130.5, 146.0$ ppm.

IR (neat): $\nu = 2977, 2930, 2320, 1117, 1068, 998, 871, 668$ cm$^{-1}$.

HRMS (DART): calculated for C$_8$H$_8^{79}$Br$^+$ = [M–OMe$]^{+}$: $m/z = 182.98094$, found: $m/z = 182.98041$.

1-Methoxy-1-(2-thienyl)-ethane (1k):

$^1$H NMR (CDCl$_3$, 600 Hz): $\delta = 1.56$ (s, 3H), 3.27 (s, 3H), 4.56–4.58 (q, $J = 6.9$, 1H), 6.95–6.97 (m, 2H), 7.25–7.26 (m, 1H), ppm.
\[ ^{13}\text{C} \text{NMR (CDCl}_3, 150 \text{ Hz): } \delta = 23.8, 56.2, 74.9, 124.5, 124.7, 126.3, 147.2 \text{ ppm.} \]

\[ \text{IR (neat): } \nu = 2978, 2930, 2820, 1113, 1086, 996, 858, 830, 701 \text{ cm}^{-1}. \]

\[ \text{HRMS (DART): calculated for C}_6\text{H}_7\text{S}^+ = [M-\text{OMe}]^+: m/z = 111.02685, \text{ found: } m/z = 182.02728. \]

3 In(I)-catalyzed coupling reactions

3.1 Procedure for In(I)-catalyzed \text{C–C bond formation}

To a flame-dried 5 ml-screw-vial with magnetic stirring bar in an argon box were added successively InOTf (1–5 mol%), dry toluene or DCM (0.5 M), the corresponding ether 1a–u (0.4 mmol), and allylborane 2b (1.2–2.0 equiv). The reaction mixture was stirred at the indicated temperature for the indicated time until complete consumption of the corresponding electrophile 1 (detected by TLC or \text{H NMR analyses of an aliquot of the reaction mixture}). The crude reaction mixtures were purified -without further treatment- by preparative thin layer chromatography (PTLC; eluant: hexane \(\rightarrow\) hexane/Et\text{2}O = 95:5) or column chromatography (eluant: hexane) to afford the corresponding products 3a–u.

3.2 Analytical data for products

2-(1-Methyl-3-buten-1-yl)-naphthalene (3a):
Prepared from ether 1a and allylborane 2b (1.2 equiv) according to the general procedure with InOTf (1 mol%) in DCM (0.5 M) at 25°C for 90 min. \textit{The obtained analytical data of 3a fit accurately with the reported data.}^5

Colorless liquid.

Yield: 86%.

4-Benzyl-1-butene (3b):
Prepared from ether 1b and allylborane 2b (1.5 equiv) according to the general procedure with InOTf (5 mol%) in DCM (0.5 M) at 25°C for 14 h. \textit{The obtained analytical data of 3b fit accurately with the reported data.}^4

Colorless liquid.

Yield 25%.

4-(4-Methoxyphenyl)-1-butene (3c):
Prepared from ether 1c and allylborane 2b (1.2 equiv) according to the general procedure with InOTf (2 mol%) in toluene (0.5 M) at a temperature range from –20°C to room temperature for 14 h. \textit{The obtained analytical data of 3c fit accurately with the reported data.}^5

Colorless liquid.

Yield: 80%.

2-(3-Buten-1-yl)-naphthalene (3d):
Prepared from ether 1d and allylborane 2b (1.5 equiv) according to the general procedure with InOTf (5 mol%).

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mol%) in DCM (0.5 M) at 25 °C for 14 h. The obtained analytical data of 3d fit accurately with the reported data. 

Colorless liquid.
Yield 25%.

(1-Methyl-3-buten-1-yl)-benzene (3e):
Prepared from ether 1e and allylborane 2b (1.2 equiv) according to the general procedure with InOTf (2 mol%) in DCM (0.5 M) at 25 °C for 30 min. The obtained analytical data of 3e fit accurately with the reported data. 

Colorless liquid.
Yield: 73%.

1-H NMR (CDCl3, 600 Hz): δ = 1.22−1.24 (d, J = 6.9, 3H), 2.24−2.29 (m, 1H), 2.33−2.37 (m, 1H), 2.74−2.77 (m, 1H), 4.96−5.00 (m, 2H), 5.64−5.71 (m, 1H), 7.11−7.17 (m, 2H), 7.31−7.34 (m, 2H) ppm.

13C NMR (CDCl3, 150 Hz): δ = 21.3, 39.6, 42.4, 116.3, 122.4, 125.7, 129.0, 129.9, 130.1, 136.5, 149.4 ppm

IR (neat): ν = 2961, 1558, 1540, 1260, 1072, 668 cm−1.


(1-(2-Chloroethyl)-3-buten-1-yl)-benzene (3g):
Prepared from ether 1g and allylborane 2b (1.2 equiv) according to the general procedure with InOTf (5 mol%) in DCM (0.5 M) at 25 °C for 30 min. The obtained analytical data of 3g fit accurately with the reported data. 

Colorless liquid.
Yield: 62%.

1-allyl-1,2,3,4-tetrahydronaphthalene (3h):
Prepared from ether 1h and allylborane 2b (1.2 equiv) according to the general procedure with InOTf (2 mol%) in DCM (0.5 M) at 25 °C for 30 min. The obtained analytical data of 3h fit accurately with the reported data. 

Colorless liquid.
Yield: 83%.

4,4-Diphenyl-1-butene (3i):
Prepared from ether 1i and allylborane 2b (1.2 equiv) according to the general procedure with InOTf (2
mol%) in DCM (0.5 M) at 25°C for 30 min. The obtained analytical data of 3i fit accurately with the reported data.7

Colorless liquid.
Yield: 98%.

4- (p-MeO-phenyl)-4-phenyl-1-butene (3j):
Prepared from ether 1j and allylborane 2b (1.2 equiv) according to the general procedure with InOTf (2 mol%) in DCM (0.5 M) at 25°C for 30 min. The obtained analytical data of 3j fit accurately with the reported data.6

Colorless liquid.
Yield: 94%.

4-(2-Thienyl)-1-pentene (3k):
Prepared from ether 1k and allylborane 2b (1.2 equiv) according to the general procedure with InOTf (5 mol%) in DCM (0.5 M) at 25°C for 30 min.

Colorless liquid.
Yield 45%.

1H NMR (CDCl3, 600 Hz): δ = 1.32–1.33 (d, J = 7.6, 3H), 2.30–2.35 (m, 1H), 2.43–2.47 (m, 1H), 3.10–3.13 (m, 1H), 3.79–3.82 (m, 1H), 5.00–5.06 (m, 2H), 5.73–5.79 (m, 1H), 6.80–6.81 (d, J = 3.48, 1H), 6.91–6.93 (m, 1H), 7.12–7.13 (d, J = 4.8, 1H) ppm.

13C NMR (CDCl3, 150 Hz): δ = 22.3, 35.1, 43.5, 116.5, 122.5, 122.6, 126.4, 136.4, 151.2 ppm.

IR (neat): ν = 3077, 2962, 1515, 1249, 1184, 1038, 911, 808 cm⁻¹.

HRMS (DART): calculated for C₉H₁₃S⁺ = [M+H]⁺: m/z = 153.07380, found: m/z = 153.07387.

(1,1-Dimethyl-3-buten-1-y1)-benzene (3l):
Prepared from ether 1l and allylborane 2b (1.2 equiv) according to the general procedure with InOTf (2 mol%) in DCM (0.5 M) at −20°C for 14 h. The obtained analytical data of 3l fit accurately with the reported data.6

Colorless liquid.
Yield: 40%.

1-(1,1-Dimethyl-3-buten-1-yl)-4-methoxy-benzene (3m):
Prepared from ether 1m and allylborane 2b (1.2 equiv) according to the general procedure with InOTf (2 mol%) in DCM (0.5 M) at −20°C for 5 h.

Colorless liquid.
Yield: 78%.

1H NMR (CDCl3, 600 Hz): δ = 1.28 (s, 6H), 2.33–2.34 (d, J = 6.9, 2H), 3.79 (s, 3H), 4.93–4.97 (m, 2H), 5.52–5.59 (m, 1H), 6.84–6.65 (d, J = 8.9, 2H), 7.25–7.47 (d, J = 8.9, 2H) ppm.

13C NMR (CDCl3, 150 Hz): δ = 28.7, 36.9, 48.9, 55.2, 113.3, 116.8, 126.8, 135.7, 141.3, 157.3 ppm.

IR (neat): ν = 3077, 2962, 1515, 1249, 1184, 1038, 911, 808 cm⁻¹.
HRMS (DART): calculated for C_{13}H_{19}O^{+} = [M+H]^{+}: m/z = 191.14359, found: m/z = 191.14370.

4-(4,4,4-Triphenyl)-1-butane (3n):
Prepared from ether 1n and allylborane 2b (1.2 equiv) according to the general procedure with InOTf (2 mol%) in DCM (0.5 M) at 25 °C for 30 min. *The obtained analytical data of 3n fit accurately with the reported data.*
White solid.
Yield 95%.

(3-Methyl-1,5-hexadien-1-yl)-benzene (3o-L):

![Diagram of 3o-L](image)

Prepared from ether 1o and allylborane 2b (1.2 equiv) according to the general procedure with InOTf (2 mol%) in DCM (0.5 M) at 25 °C for 30 min. *The obtained analytical data of 3o fit accurately with the reported data.*
Colorless liquid.
Yield 93%, L:B = 1:1.

1,5-Hexadien-1-yl-benzene (3p-L):

![Diagram of 3p-L](image)

Prepared from ether 1p and allylborane 2b (1.2 equiv) according to the general procedure with InOTf (5 mol%) in DCM (0.5 M) at 25 °C for 14 h. *The obtained analytical data of 3p fit accurately with the reported data.*
Colorless liquid.
Yield: 30%, L:B = 6:1.

(3-Methyl-5-hexen-1-ynyl)benzene (3q-L):

![Diagram of 3q-L](image)

Prepared from ether 1q and allylborane 2b (1.2 equiv) according to the general procedure with InOTf (5 mol%) in DCM (0.5 M) at 25 °C for 5h. *The obtained analytical data of 3q fit accurately with the reported data.*
reported data.\textsuperscript{10}
Colorless liquid.
Yield: 60\%, L:B=12:1.

1-Methyl-4-(1-methylethenyl)-6-(2-propenyl)-cyclohexene (3r):

\[
\begin{array}{c}
\text{Me} \\
\text{Me} \\
\text{3r (syn:anti = 4:1)}
\end{array}
\]

Prepared from ether 1r and allylborane 2b (1.2 equiv) according to the general procedure with InOTf (2 mol\%) in DCM (0.5 M) at 25 °C for 14 h. The obtained analytical data of 3r fit accurately with the reported data.\textsuperscript{11}
Colorless liquid.

p-4-Pentenylanisole (3t):
Prepared from ether 1t and allylborane 2b (2.0 equiv) according to the general procedure with InOTf (5 mol\%) under neat conditions at 60 °C for 48 h.
Colorless liquid.
Yield 58\%.

\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 Hz): \(\delta = 1.57–1.65\) (m, 2H), 1.98–2.03 (m, 2H), 2.47–2.51 (t, \(J = 7.7\), 2H), 3.70 (s, 3H), 4.88–4.97 (m, 2H), 5.70–5.80 (m, 1H), 6.73–6.76 (d, \(J = 8.7\), 2H), 7.00–7.03 (d, \(J = 8.7\), 2H) ppm.

\textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 Hz): \(\delta = 30.8, 33.2, 34.4, 55.2, 113.7, 114.6, 129.3, 134.5, 138.7, 157.7\) ppm.

IR (neat): \(v = 3073, 2962, 2834, 1244, 1038, 911, 828\) cm\textsuperscript{-1}.

HRMS (DART): calculated for C\textsubscript{12}H\textsubscript{17}O\textsuperscript{+} = [M+H]\textsuperscript{+}: \(m/z = 177.12794\), found: \(m/z = 177.12837\).

1- Allyladamantane (3u):
Prepared from ether 1u and allylborane 2b (1.2 equiv) according to the general procedure with InOTf (5 mol\%) in DCM (0.5 M) at 25 °C for 14 h. The obtained analytical data of 3u fit accurately with the reported data.\textsuperscript{4}
Colorless liquid.
Yield 73\%.

4 References


Me: 93% (L:B = 1.1:1)
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