# Indium(I) Iodide-Catalyzed Regio- and Stereoselective Formal α-Addition of an α-Methylallylboronate to *N*-Acylhydrazones

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# Electronic Supplementary Information

## General Information

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## General Experimental

NMR spectra were recorded on a JEOL JNM-ECX400 spectrometer, operating at 400 MHz for $^1$H NMR, 100 MHz for $^{13}$C NMR and 128 MHz for $^{11}$B NMR. Chemical shifts were reported downfield from TMS or in the scale relative to the corresponding solvent used as an internal reference. IR spectra were measured using a JASCO FT/IR-610 spectrometer. ESI high-resolution mass spectra (ESI-HRMS) were measured with BRUKER DALTONICS BioTOF II. Melting points were measured using a BÜCHI B-545 apparatus and are uncorrected. Preparative thin-layer chromatography was carried out using Wakogel B-5F.

All solvents used in this work were commercially available dry solvents or were distilled under an argon atmosphere. Toluene was freshly distilled from sodium/benzophenone; methanol was distilled from magnesium and stored under argon over molecular sieves 3 Å. Acylhydrazones were synthesized according to a literature-known procedure;[1] prior to their use acylhydrazones were recrystallized and dried (80 °C under high vacuum for several hours). $\alpha$-Substituted pinacolyl allylic boronate **2** was prepared by a literature-known procedure.[2] Indium(I) iodide (powder; 99.999%) was purchased from Aldrich and was used without further purification. All reactions were carried out under an argon atmosphere in well-dried glassware.

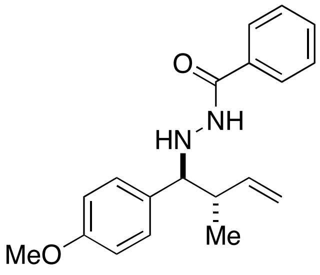
## Typical Procedure for Indium(I)-Catalyzed Addition of **2** to **1a-m**

To a dried septum-capped 5 mL-flask with magnetic stirring bar under an argon atmosphere were added indium(I) iodide (3.0 mg; 5 mol %) and the corresponding *N*-benzoylhydrazone **1a-m** (0.25 mmol). After addition of the indicated dry solvent (500 $\mu$L; 0.5 M) and dry alcohol (1.25 mmol; 5.0 equiv) was added $\alpha$-methylallylboronate **2** (0.375 mmol; 1.5 equiv). The mixture was stirred under an argon atmosphere at the indicated temperature until thin-layer chromatography (TLC) indicated complete conversion of the corresponding *N*-benzoylhydrazone. After addition of an aqueous solution of $K_2CO_3$ (1 M), the phases were separated and the aqueous phase was then extracted with dichloromethane (three times). The combined organic layers were dried ($Na_2SO_4$), filtered and concentrated *in vacuo*. The residues were purified by preparative thin-layer chromatography (PTLC; eluent: *n*-hexane/ethyl acetate = 9:1 to 2:1) to afford the corresponding substituted homoallylic hydrazides **3a-m**.

## Analytical Data for Substituted Homoallylic Hydrazides 3a-m

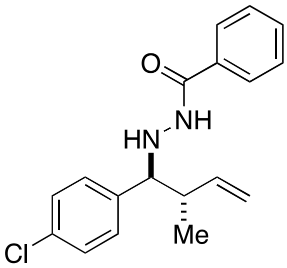
Substituted homoallylic hydrazides **3a-f** and **3l**[1,3,4] as well as substituted homoallylic alcohol **7**[5] are literature-known compounds; obtained analytical data are in agreement with reported data.

Analytical data of new substituted homoallylic hydrazides **3g-k** and **3m** are as follows.



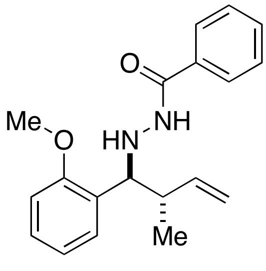
**3g**

***N'*-(1-(4-methoxyphenyl)-2-methylbut-3-enyl)benzohydrazide**[1] (**3g**; Table 3, entry 6): prepared from *N*-benzoylhydrazone **1g** and allylic boronate **2** according to the general procedure for indium(I) iodide-catalyzed additions. White solid (yield: 98%; *syn*:*anti* = 9:91); **mp** = 87.4-88.2 °C; $^1$**H NMR** (CDCl$_3$, 400 MHz): $\delta$ = 0.76 (major, d, *J* = 6.8 Hz, 3H), 1.06 (minor, d, *J* = 6.8 Hz, 3H), 2.35-2.48 (major, m, 1H), 2.57-2.63 (minor, m, 1H), 3.75 (br d, *J* = 9.6 Hz, 1H), 3.80 (s, 3H), 4.97-5.05 (minor, br, 1H), 5.22 (dd, *J* = 1.6 Hz, *J* = 10.0 Hz, 1H), 5.28 (dd, *J* = 1.6 Hz, *J* = 16.8 Hz, 1H), 5.36-5.40 (major, br, 1H), 5.72-5.85 (minor, m, 1H), 5.86-5.99 (major, m, 1H), 6.87 (dd, *J* = 2.4 Hz, *J* = 8.8 Hz, 2H), 7.14-7.55 (m, 8H); $^{13}$**C NMR** (CDCl$_3$, 100 MHz): $\delta$ = 15.6 (minor), 17.8 (major), 41.9 (minor), 44.1 (major), 55.2, 68.0 (major), 68.1 (minor), 113.5 (minor), 113.8 (major), 116.6, 126.7, 128.6, 129.5, 131.6, 132.6, 132.9, 140.1 (minor), 141.5 (major), 159.1, 166.8; **IR** (neat): $\nu$ = 3291, 3065, 3033, 2961, 2932, 2907, 2836, 2247, 1639, 1613, 1579, 1512, 1461, 1304, 1249, 1177, 1037, 910, 827, 810, 733, 693 cm$^{-1}$; **HRMS** (ESI) calcd. for $C_{19}H_{23}N_2O_2^+$ = [M+H]$^+$: *m*/*z* = 311.1754, found: *m*/*z* = 311.1762.



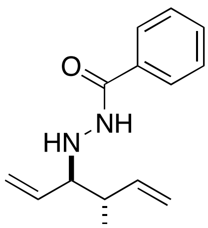
**3h**

***N'*-(1-(4-chlorophenyl)-2-methylbut-3-enyl)benzohydrazide** (**3h**; Table 3, entry 7): prepared from *N*-benzoylhydrazone **1h** and allylic boronate **2** according to the general procedure for indium(I) iodide-catalyzed additions. White solid (yield: 96%; *syn*:*anti* = 4:96); **mp** = 121.9-123.0 °C; $^1$**H NMR** (CDCl$_3$, 400 MHz): $\delta$ = 0.78 (dd, *J* = 2.1 Hz, *J* = 6.9 Hz, 3H), 2.41 (dq, *J* = 6.9 Hz, *J* = 8.9 Hz, 1H), 3.82 (d, *J* = 9.6 Hz, 1H), 5.23 (d, *J* = 10.3 Hz, 1H), 5.28 (d, *J* = 17.4 Hz, 1H), 5.35 (br d, *J* = 6.8 Hz, 1H), 5.92 (ddd, *J* = 3.2 Hz, *J* = 8.9 Hz; *J* = 18.5 Hz, 1H), 7.28-7.32 (m, 5H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 8.3 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 2H); $^{13}$**C NMR** (CDCl$_3$, 100 MHz): $\delta$ = 17.7, 44.0, 67.9, 116.9, 126.7, 128.6, 128.6, 129.8, 131.8, 132.7, 133.3, 139.4, 141.0, 167.2; **IR** (KBr): $\nu$ = 3435, 3290, 3066, 2976, 2928, 2870, 2248, 1639, 1603, 1578, 1530, 1489, 1458, 1312, 1091, 1027, 1014, 997, 908, 821, 794, 733, 693, 648 cm$^{-1}$; **HRMS** (ESI) calcd. for $C_{18}H_{19}ClN_2NaO^+$ = [M+Na]$^+$: *m*/*z* = 337.1078, found: *m*/*z* = 337.1074.



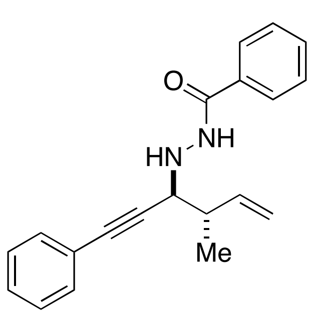
**3i**

***N'*-(1-(2-methoxyphenyl)-2-methylbut-3-enyl)benzohydrazide** (**3i**; Table 3, entry 8): prepared from *N*-benzoylhydrazone **1i** and allylic boronate **2** according to the general procedure for indium(I) iodide-catalyzed additions. White solid (yield: 75%; *syn*:*anti* = 6:94); **mp** = 89.1-90.8 ºC; **$^1$H NMR** (CDCl$_3$, 400 MHz): $\delta$ = 0.85 (major, d, *J* = 6.8 Hz, 3H), 1.07 (minor, d, *J* = 6.8 Hz, 3H), 2.53 (major, dd, *J* = 9.2 Hz, *J* = 16.0 Hz, 1H), 2.70-2.77 (minor, m, 1H), 3.72 (major, s, 3H), 3.76 (minor, s, 3H), 4.43 (major, br d, *J* = 10.0 Hz, 1H), 4.56 (minor, br d, *J* = 10.0 Hz, 1H), 5.21 (dd, *J* = 2.0 Hz, *J* = 10.0 Hz, 1H), 5.27 (dd, *J* = 1.2 Hz, *J* = 17.2 Hz, 1H), 5.42 (br d, *J* = 5.6 Hz, 1H), 5.97-6.06 (m, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 7.00 (dd, *J* = 6.8 Hz, *J* = 8.0 Hz, 1H), 7.20-7.58 (m, 8H); **$^{13}$C NMR** (CDCl$_3$, 100 MHz): $\delta$ = 14.4 (minor), 17.5 (major), 40.4 (minor), 43.5 (major), 55.2 (minor), 55.4 (major), 61.0 (major), 61.6 (minor), 110.6 (minor), 110.7 (major), 114.7 (minor), 116.1 (major), 120.2 (minor), 120.8 (major), 126.7, 128.0, 128.2, 128.5, 129.0, 131.5, 133.1 (minor), 133.2 (major), 141.0 (minor), 141.8 (major), 157.8 (minor), 158.5 (major), 166.6 (minor), 166.7 (major); **IR** (KBr): $\nu$ = 3445, 3292, 3065, 2962, 2932, 2837, 2249, 1652, 1612, 1579, 1512, 1457, 1442, 1420, 1304, 1249, 1176, 1068, 1037, 998, 909, 827, 734, 693, 648 cm$^{-1}$; **HRMS** (ESI) calcd. for $C_{19}H_{22}N_2NaO_2^+$ = [M+Na]$^+$: *m*/*z* = 333.1573, found: *m*/*z* = 337.1576.



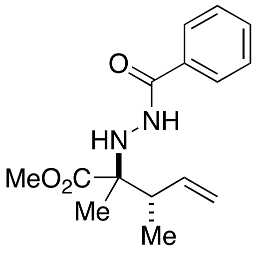
**3j**

***N'*-(4-methyhexa-1,5-dien-3-yl)benzohydrazide** (**3j**; Table 3, entry 9): prepared from *N*-benzoylhydrazone **1j** and allylic boronate **2** according to the general procedure for indium(I) iodide-catalyzed additions. Colorless liquid (yield: 85%; *syn*:*anti* = 9:91); **$^1$H NMR** (CDCl$_3$, 400 MHz): $\delta$ = 1.00 (d, *J* = 6.8 Hz, 3H), 2.24 (dq, *J* = 6.8 Hz, *J* = 8.6 Hz, 1H), 3.25 (t, *J* = 8.8 Hz, 1H), 5.12-5.29 (m, 5H), 5.66 (ddd, *J* = 8.8 Hz, *J* = 10.0 Hz, *J* = 16.8 Hz, 1H), 5.84 (ddd, *J* = 8.8 Hz, *J* = 10.0 Hz, *J* = 16.8 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 6.8 Hz, 2H), 7.77 (br s, 1H); **$^{13}$C NMR** (CDCl$_3$, 100 MHz): $\delta$ = 17.3, 41.5, 67.9, 116.4, 119.5, 126.8, 128.7, 131.7, 133.0, 137.7, 160.9, 166.9; **IR** (neat): $\nu$ = 3446, 3290, 3080, 2978, 2929, 2871, 2249, 1645, 1604, 1578, 1531, 1457, 1419, 1315, 1066, 1027, 996, 909, 734, 694, 648 cm$^{-1}$; **HRMS** (ESI) calcd. for $C_{14}H_{18}N_2NaO^+$ = [M+Na]$^+$: *m*/*z* = 253.1311, found: *m*/*z* = 253.1299.



**3k**

***N'*-(4-methyl-1-phenylhex-5-en-1-yn-3-yl)benzohydrazide** (**3k**; Table 3, entry 10): prepared from *N*-benzoylhydrazone **1k** and allylic boronate **2** according to the general procedure for indium(I) iodide-catalyzed additions. Pale yellow solid (yield: 99%; *syn*:*anti* = 5:95); **mp** = 101.8-104.3 ºC; **$^1$H NMR** (CDCl$_3$, 400 MHz): $\delta$ = 1.24 (dd, *J* = 2.1 Hz, *J* = 6.9 Hz, 3H), 2.53 (dq, *J* = 6.2 Hz, *J* = 6.9 Hz, 1H), 4.00 (dd, *J* = 3.4 Hz, *J* = 6.8 Hz, 1H), 5.15 (d, *J* = 10.3 Hz, 1H), 5.21 (d, *J* = 16.5 Hz, 1H), 5.25 (br s, 1H), 5.89 (ddd, *J* = 2.0 Hz, *J* = 8.3 Hz, *J* = 18.3 Hz, 1H), 7.26-7.41 (m, 7H), 7.49 (t, *J* = 6.9 Hz, 1H), 7.77 (d, *J* = 6.9 Hz, 2H), 8.18 (br d, *J* = 6.2 Hz, 1H); **$^{13}$C NMR** (CDCl$_3$, 100 MHz): $\delta$ = 16.7, 41.7, 57.8, 85.1, 87.3, 116.4, 122.7, 126.9, 128.2, 128.6, 131.7, 131.8, 132.7, 140.1, 167.1; **IR** (KBr): $\nu$ = 3299, 3065, 3034, 2975, 2931, 2902, 2860, 2248, 1646, 1602, 1579, 1506, 1490, 1457, 1442, 1372, 1339, 1313, 1169, 1087, 1070, 1027, 1010, 995, 908, 862, 840, 798, 760, 733, 690, 650, 616, 589, 533 cm$^{-1}$; **HRMS** (ESI) calcd. for $C_{20}H_{21}N_2O^+$ = $[M+H]^+$: *m*/*z* = 305.1648, found: *m*/*z* = 305.1645.

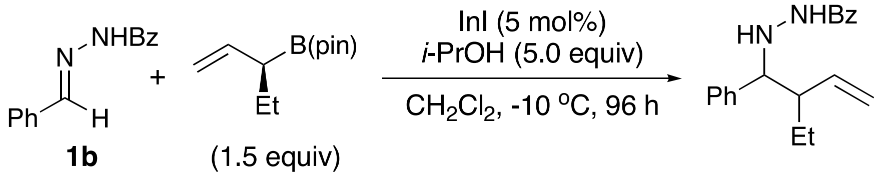


**3m**

**Methyl 2,3-dimethyl-2-(2-(phenylcarbonyl)hydrazinyl)pent-4-enoate (3m**; Table 3, entry 12): prepared from *N*-benzoylhydrazone **1m** and allylic boronate **2** according to the general procedure for indium(I) iodide-catalyzed additions. White solid (yield: 95%; major:minor = 92:8); **mp** = 61.8-63.7 °C; $^1$**H NMR** (CDCl$_3$, 400 MHz): $\delta$ = 1.11 (major, d, *J* = 6.8 Hz, 3H), 1.12 (minor, d, *J* = 6.8 Hz, 3H), 1.35 (major, s, 3H), 1.36 (minor, s, 3H), 2.65-2.77 (m, 1H), 3.75 (s, 3H), 5.10-5.20 (br, 3H), 5.80-5.92 (m, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.71-7.85 (br, 3H); $^{13}$**C NMR** (CDCl$_3$, 100 MHz): $\delta$ = 14.3 (minor), 14.8 (major), 18.1 (minor), 18.7 (major), 43.6 (minor), 44.0 (major), 52.1 (minor), 52.2 (major), 67.7 (major), 68.0 (minor), 116.6 (minor), 117.6 (major), 126.8, 128.6, 131.7, 132.8 (minor), 132.9 (major), 137.7 (major), 138.6 (minor), 166.4 (major), 166.6 (minor), 175.2 (minor), 175.3 (major); **IR** (KBr): $\nu$ = 3282, 3067, 2981, 2950, 2877, 2840, 1733, 1644, 1603, 1579, 1541, 1457, 1381, 1312, 1261, 1191, 1130, 1071, 1027, 997, 922, 793, 694 cm$^{-1}$; **HRMS** (ESI) calcd. for $C_{15}H_{20}N_2NaO_3^+$ = $[M+Na]^+$: *m*/*z* = 299.1366, found: *m*/*z* = 299.1359.

## The Reaction of an Enantiomerically Enriched Boronate with 1b

In the presence of InI (10 mol%) and 2-propanol (5.0 equiv), enantiomerically enriched $\alpha$-ethylallylboronate (88% ee)[6] reacted with **1b** in dichloromethane at -10 °C (see “Typical procedure”) to afford the corresponding homoallylic hydrazide in 99% yield. The product was almost racemic (see below).



99% y, $\alpha$:$\gamma$ = 97:3, *syn*/*anti* = 31:69
9% ee (*syn*), 1% ee (*anti*)

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