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The reaction of various lithium tributylheteroarylborates with allylic bromides in the presence of copper(I) cyanide furnished the regioselective allylation at the heteroaryl ring.

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Recently, we reported our preliminary results dealing with the regioselective allylation at the 3-position of pyridine by the reaction of copper(I) tributyl 3-pyridyl borate [generated from lithium tributyl 3-pyridyl borate and copper(I) cyanide *in situ*] with allylic bromides [1], which could be adopted for a mild introduction of an allylic substituent having a functional group (*i.e.*, bromo, methoxycarbonyl). We have further examined the reaction of various allylic bromide with several copper(I) tributyl heteroaryl borates. The present paper describes the results including full details of the previous work [1].

Initially, lithium tributyl pyridyl borates **1-4** [derived from corresponding bromopyridines and butyllithium followed by treatment with tributylborane] were subjected to the reaction with allyl bromide **5a**. Thus, treatment of pyridyl borates **1-4** with **5a** without copper(I) cyanide in tetrahydrofuran led to the exclusive formation of betaines **6-8**, with exception of **2** which gave an undetectable mixture. In contrast, allylpyridines **9-12** could be obtained solely from the borates **1-4** and **5a** (1.1 molar equivalents) in the presence of copper(I) cyanide (2.1 molar equivalents).

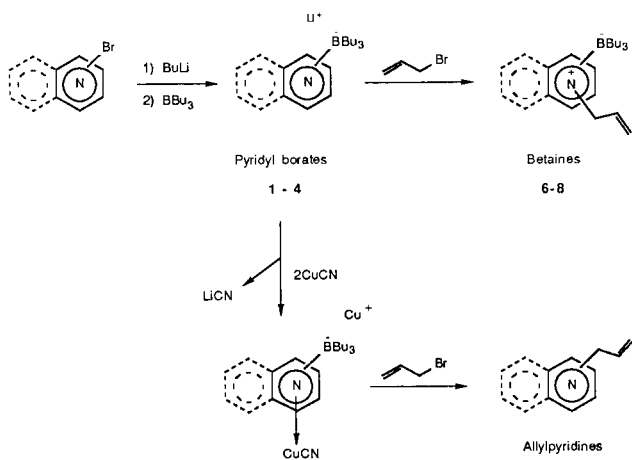


Chart 1

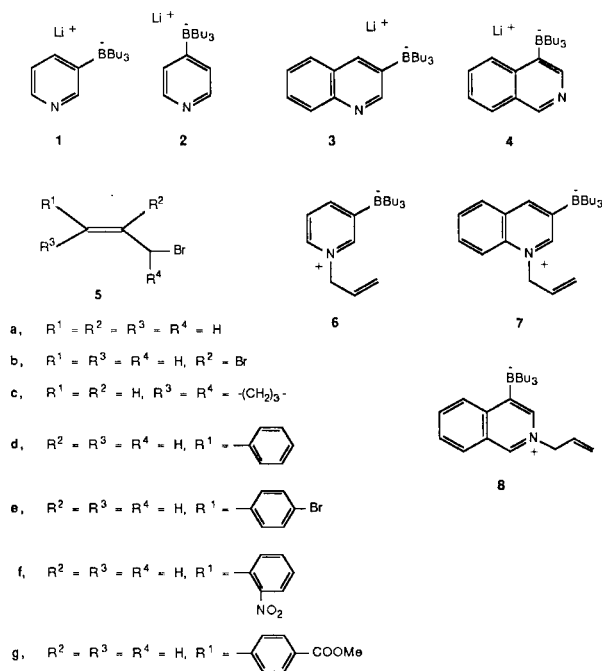


Chart 2

The reaction of borates **1-4** with other allylic bromides **5** in the presence of copper(I) cyanide under the same conditions as above was carried out, and the results are summarized in Table 1. With cinnamyl bromides **5d-5g**, the reaction was accompanied by allylic transposition to some extent, and the product distribution was not so much affected with variation of a substituent on the phenyl ring.

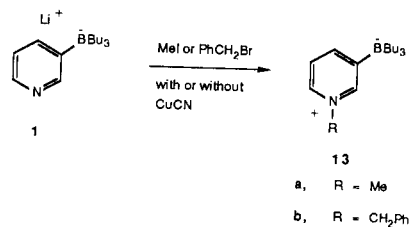


Chart 3

Table 1  
 Allylpyridine Derivatives 9-12

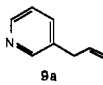
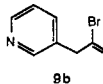
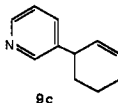
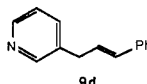
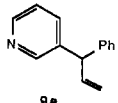
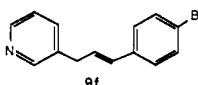
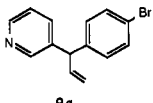
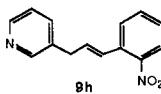
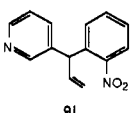
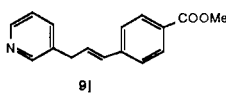
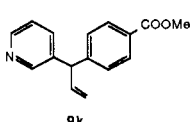
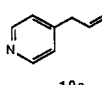
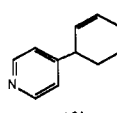
5	Borate	Product	Yield [a] (%)	mp (°C) or bp (°C/mm Hg)	Formula	Analysis (%) or High mass (m/e) Calcd. (Found)
5a	1	 9a	72	bp 78/18 (lit [12] 75/15)		
5b	1	 9b	55	bp 105/18	C <sub>8</sub> H <sub>8</sub> BrN	C, 48.51; H, 4.07; N, 7.07 (C, 48.94; H, 4.25; N, 7.13)
5c	1	 9c	70	bp 125/18 [b] mp 109-111 [c]	C <sub>17</sub> H <sub>16</sub> N <sub>4</sub> O <sub>7</sub> [c]	C, 52.58; H, 4.15; N, 14.43 (C, 52.66; H, 4.25; N, 14.44)
5d	1	 9d	40	bp 120/1 [b]	C <sub>14</sub> H <sub>13</sub> N	C, 86.11; H, 6.71; N, 7.17 (C, 86.29; H, 6.73; N, 7.22)
5d	1	 9e	23	bp 120/1 [b]	C <sub>14</sub> H <sub>13</sub> N	C, 86.11; H, 6.71; N, 7.17 (C, 86.01; H, 6.72; N, 7.28)
5e	1	 9f	41	bp 220/1 [b]	C <sub>14</sub> H <sub>12</sub> BrN	273.0154 and 275.0134 (273.0139 and 275.0124)
5e	1	 9g	30	bp 200/1 [b]	C <sub>14</sub> H <sub>12</sub> BrN	273.0154 and 275.0134 (273.0139 and 275.0100)
5f	1	 9h	39	bp 200/1 [b] mp 158-160 [c]	C <sub>20</sub> H <sub>16</sub> N <sub>5</sub> O <sub>9</sub> [c]	C, 51.18; H, 3.22; N, 14.92 (C, 51.31; H, 3.17; N, 14.81)
5f	1	 9i	18	bp 200/1 [b]	C <sub>14</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub>	240.0099 (240.0091)
5g	1	 9j	38	bp 220/1 [b]	C <sub>16</sub> H <sub>15</sub> NO <sub>2</sub>	253.1101 (253.1089)
5g	1	 9k	27	bp 200/1 [b]	C <sub>16</sub> H <sub>15</sub> NO <sub>2</sub>	253.1101 (253.1082)
5a	2	 10a	48	bp 90/18 mp 165-167 [c] (lit. [13] 167.5-168.5)		
5b	2	 10b	52	bp 140/18 [b] mp 131-134 [c]	C <sub>17</sub> H <sub>16</sub> N <sub>4</sub> O <sub>7</sub> [c]	C, 52.58; H, 4.15; N, 14.43 (C, 52.66; H, 4.12; N, 14.40)

Table 1 (continued)

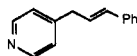
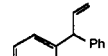
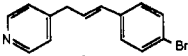
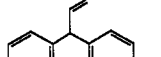
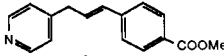
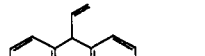
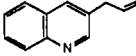
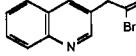
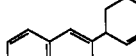
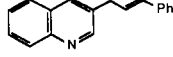
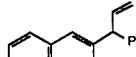
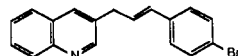
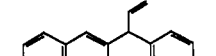
5	Borate	Product	Yield [a] (%)	mp (°C) or bp (°C/mm Hg)	Formula	Analysis (%) or High mass (m/e) Calcd. (Found)
5d	2	 10c	30	bp 130/1 [b]	C <sub>14</sub> H <sub>13</sub> N	C, 86.11; H, 6.71; N, 7.17 (C, 86.02; H, 6.73; N, 7.11)
5d	2	 10d	20	bp 130/1 [b]	C <sub>14</sub> H <sub>13</sub> N + $\frac{1}{10}$ H <sub>2</sub> O	C, 85.33; H, 6.75; N, 7.11 (C, 85.30; H, 6.79; N, 7.18)
5e	2	 10e	28	syrup	C <sub>14</sub> H <sub>12</sub> BrN	273.0154 and 275.0134 (273.0136 and 275.0127)
5e	2	 10f	18	syrup	C <sub>14</sub> H <sub>12</sub> BrN	273.0154 and 275.0134 (273.0139 and 275.0114)
5f	2	 10g	22	syrup	C <sub>16</sub> H <sub>15</sub> NO <sub>2</sub>	253.11089 (253.11059)
5f	2	 10h	20	syrup	C <sub>16</sub> H <sub>15</sub> NO <sub>2</sub>	253.11089 (253.10961)
5a	3	 11a	63	bp 110/1 mp 179-180 [c]	C <sub>18</sub> H <sub>14</sub> N <sub>4</sub> O <sub>7</sub>	C, 54.27; H, 3.54; N, 14.07 (C, 54.19; H, 3.53; N, 13.98)
5b	3	 11b	60	bp 130/1 [b] mp 56-57	C <sub>12</sub> H <sub>10</sub> BrN	C, 58.09; H, 4.06; N, 5.65 (C, 57.91; H, 4.09; N, 5.57)
5c	3	 11c	69	bp 120/1 [b] mp 142-144 [c]	C <sub>24</sub> H <sub>18</sub> N <sub>4</sub> O <sub>7</sub> [c]	C, 57.53; H, 4.14; N, 12.78 (C, 57.44; H, 4.01; N, 12.68)
5d	3	 11d	48	mp 90-91 [d]	C <sub>18</sub> H <sub>15</sub> N	C, 88.13; H, 6.16; N, 5.71 (C, 88.16; H, 6.13; N, 5.60)
5d	3	 11e	20	syrup	C <sub>18</sub> H <sub>15</sub> N	245.12037 (245.11947)
5e	3	 11f	53	mp 92-93 [d]	C <sub>18</sub> H <sub>14</sub> BrN	C, 66.68; H, 4.35; N, 4.32 (C, 66.70; H, 4.35; N, 4.28)
5e	3	 11g	13	syrup mp 125-127 [c]	C <sub>24</sub> H <sub>17</sub> BrN <sub>4</sub> O <sub>7</sub> [c]	C, 52.10; H, 3.10; N, 10.13 (C, 52.19; H, 2.97; N, 10.05)

Table 1 (continued)

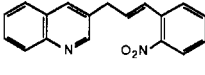
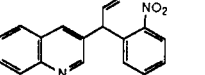
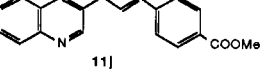
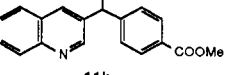
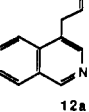

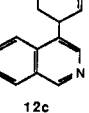
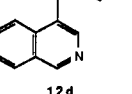
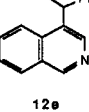
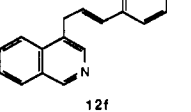
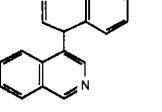
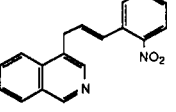
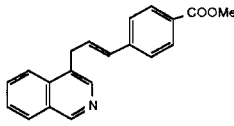
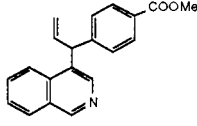


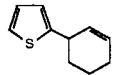
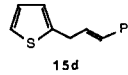


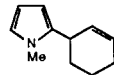
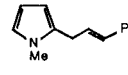
5	Borate	Product	Yield [a] (%)	mp (°C) or bp (°C/mm Hg)	Formula	Analysis (%) or High mass (m/e) Calcd. (Found)
5f	3	 11h	40	syrup	C <sub>18</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub>	290.10555 (290.10636)
5f	3	 11i	10	syrup	C <sub>18</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub>	290.10555 (290.10655)
5g	3	 11j	37	mp 113-115 [e]	C <sub>20</sub> H <sub>17</sub> NO <sub>2</sub>	C, 79.18; H, 5.65; N, 4.62 (C, 78.98; H, 5.71; N, 4.53)
5g	3	 11k	13	syrup	C <sub>20</sub> H <sub>17</sub> NO <sub>2</sub>	303.12530 (303.12560)
5a	4	 12a	61	bp 14 5/15 [b] mp 156-157 [c]	C <sub>18</sub> H <sub>14</sub> N <sub>2</sub> O <sub>7</sub> [c]	C, 54.08; H, 3.54; N, 14.06 (C, 54.15; H, 3.47; N, 14.06)
5b	4	 12b	15	bp 125/1 [b] mp 72-73	C <sub>12</sub> H <sub>10</sub> BrN	C, 58.09; H, 4.06; N, 5.65 (C, 58.22; H, 3.97; N, 5.64)
5c	4	 12c	62	bp 135/1 [b] mp 175-177 [c]	C <sub>21</sub> H <sub>18</sub> N <sub>2</sub> O <sub>7</sub> [c]	C, 57.53; H, 4.14; N, 12.78 (C, 57.47; H, 3.98; N, 12.72)
5d	4	 12d	41	syrup mp 179-180.5 [c]	C <sub>28</sub> H <sub>18</sub> N <sub>2</sub> O <sub>7</sub> [c]	C, 60.76; H, 3.82; N, 11.81 (C, 60.88; H, 3.86; N, 11.98)
5d	4	 12e	14	syrup mp 170-171 [c]	C <sub>24</sub> H <sub>16</sub> N <sub>2</sub> O <sub>7</sub> [c]	C, 60.76; H, 3.82; N, 11.81 (C, 60.92; H, 3.87; N, 11.57)
5e	4	 12f	40	mp 99-100 [f]	C <sub>18</sub> H <sub>14</sub> BrN	C, 66.68; H, 4.35; N, 4.32 (C, 66.74; H, 4.26; N, 4.03)
5e	4	 12g	10	syrup	C <sub>18</sub> H <sub>14</sub> BrN	323.03105 and 325.02897 (323.02914 and 325.02722)
5f	4	 12h	40	mp 111-112 [g]	C <sub>18</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub>	C, 74.47; H, 4.86; N, 9.65 (C, 74.71; H, 4.86; N, 9.73)

Table 1 (continued)

5	Borate	Product	Yield [a] (%)	mp (°C) or bp (°C/mm Hg)	Formula	Analysis (%) or High mass (m/e) Calcd. (Found)
5g	4	 12i	40	mp 114-115 [e]	$C_{20}H_{17}NO_2 + \frac{1}{4} H_2O$	C, 77.65; H, 5.70; N, 4.53 (C, 77.55; H, 5.52; N, 4.37)
5g	4	 12j	10	syrup	$C_{20}H_{17}NO_2$	303.12587 (303.12467)

[a] Isolated yield based on bromopyridine. [b] Bath temperature. [c] Picrate. [d] Recrystallized from ether-hexane. [e] Recrystallized from ethyl acetate-hexane. [f] Recrystallized from ether. [g] Recrystallized from acetone-ether.

Table 2  
2-Allylthiophenes **15** and 2-Allyl-1-methylpyrroles **16**

5	Borate	Product	Yield [a] (%)	bp (°C/mm Hg)	Formula	Analysis (%) or High mass (m/e) Calcd. (Found)
5a	14a	 15a	70	150/760 (lit [14] 155-160/760)		
5b	14a	 15b	52	unstable oil	$C_7H_7BrS$	201.94513 and 203.94323 (201.94513) and (203.94233)
5c		 15c	75	104/18	$C_{10}H_{12}S$	C, 73.12; H, 7.36 (C, 73.19; H, 7.27)
5d		 15d	70	158/18	$C_{13}H_{12}S$	C, 77.95; H, 6.04 (C, 77.99; H, 6.01)
5a		 16a	66	64/18	$C_8H_{11}N + \frac{1}{10} H_2O$	C, 78.13; H, 9.18; N, 11.39 (C, 78.24; H, 9.27; N, 11.13)
5b		 16b	62	unstable oil	$C_8H_{10}BrN$	198.99975 and 200.99781 (199.00095 and 200.99901)
5c		 16c	55	117/18	$C_{11}H_{15}N$	C, 81.94; H, 9.38; N, 8.69 (C, 81.90; H, 9.46; N, 8.54)
5d		 16d	46	110/18	$C_{14}H_{15}N$	C, 85.23; H, 7.66; N, 7.10 (C, 85.34; H, 7.66; N, 7.09)

[a] Isolated yields based on thiophene or 1-methylpyrrole.

When alkyl halides (methyl iodide, benzyl bromide) were subjected to the reaction with **1** under similar conditions as above, formation of betaines **13** [3] was the predominant course of the reaction even in the presence of copper(I) cyanide.

Next, the reaction of borates **14**, **17**, and **19**, substituted with five-membered  $\pi$ -electron excessive heteroaryl groups (*i.e.*, 1-methylpyrrolyl, thiophenyl, 1-methylindolyl) (1 molar equivalent), with **5** (1.1 molar equivalents) in the presence of copper(I) cyanide (1.1 molar equivalents)

Table 3  
 Allylindole Derivatives 18 and 19

5	Borate	Product	Yield [a] (%)	mp (°C) or bp (°C/mm Hg)	Formula	Analysis (%) or High mass (m/e) Calcd. (Found)
5a	17	 18a	71	viscous oil	C <sub>12</sub> H <sub>13</sub> N	171.10480 (171.10620)
5b	17	 18b	53	unstable oil	C <sub>12</sub> H <sub>12</sub> BrN	249.01535 and 251.01328 (249.01575 and 251.01328)
5c	17	 18c	70	viscous oil	C <sub>15</sub> H <sub>17</sub> N	211.13616 (211.13676)
5d	17	 18d	70	viscous oil	C <sub>18</sub> H <sub>17</sub> N	247.13604 (247.13494)
5a	19	 21a	70	bp 142/18	C <sub>12</sub> H <sub>13</sub> N + $\frac{1}{20}$ H <sub>2</sub> O	C, 83.72; H, 7.67; N, 8.14 (C, 83.93; H, 7.54; N, 8.12)
5b	19	 21b	48	unstable oil	C <sub>12</sub> H <sub>12</sub> BrN	249.01543 and 251.01340 (249.01593 and 251.01480)
5c	19	 21c	65	bp 150/1 [b]	C <sub>15</sub> H <sub>17</sub> N	C, 85.26; H, 8.11; N, 6.63 (C, 84.97; H, 8.13; N, 6.51)
5d	19	 21d	40	bp 170/1 [b] mp 72-74	C <sub>18</sub> H <sub>17</sub> N	C, 87.50; H, 6.88; N, 5.62 (C, 87.54; H, 6.90; N, 5.57)
5d	19	 21e	22	symp	C <sub>22</sub> H <sub>25</sub> N	303.19864 (303.19684)
5e	19	 21f	40	mp 111-113 [c]	C <sub>18</sub> H <sub>16</sub> BrN	C, 66.27; H, 4.94; N, 4.29 (C, 66.41; H, 4.94; N, 4.38)
5f	19	 21g	14	symp	C <sub>22</sub> H <sub>24</sub> BrN	381.10921 and 383.10481 (381.10811 and 383.10481)
5g	19	 21h	30	mp 119-120 [c]	C <sub>20</sub> H <sub>19</sub> NO <sub>2</sub>	C, 78.66; H, 6.27; N, 4.59 (C, 78.71; H, 6.34; N, 4.88)

[a] Isolated yield based on 1-methylindole or 3-iodo-1-methylindole. [b] Bath temperature. [c] Recrystallized from acetone-ether.

Table 4

## IR and NMR Spectral Data of Allylpyridines 9-12

Compound	IR, cm <sup>-1</sup>	NMR (deuteriochloroform) $\delta$			
			<b>10h</b>	1720, 1672, 1594, 1544 [a]	3.83 (s, 3H), 4.50-5.40 (m, 3H), 5.96-6.50 (m, 1H), 6.90-7.30 (m, 4H), 7.93 (d, 2H, J = 8 Hz), 8.30-8.65 (m, 2H)
<b>9a</b>	1682, 1640, 1594, 1576 [a]	3.32 (d, 2H, J = 6 Hz), 4.90-5.20 (m, 2H), 5.60-6.15 (m, 1H), 7.00-7.20 (m, 1H), 7.30-7.50 (m, 1H), 8.25-8.50 (m, 2H)	<b>11a</b>	1608, 1574, 1496 [a]	3.36 (d, 2H, J = 6 Hz), 4.86-5.20 (m, 2H), 5.60-6.15 (m, 1H), 7.20-7.70 (m, 4H), 8.02 (d, 1H, J = 7 Hz), 8.73 (d, 1H, J = 2 Hz)
<b>9b</b>	1630, 1576, 1478 [a]	3.70 (s, 2H), 5.45 (d, 1H, J = 1 Hz), 5.56 (d, 1H, J = 1 Hz), 7.00-7.30 (m, 1H), 7.40-7.60 (m, 1H), 8.30-8.50 (m, 2H)	<b>11b</b>	1628, 1606, 1568, 1494 [a]	3.73 (s, 2H), 5.40-5.60 (m, 2H), 7.20-8.30 (m, 5H), 8.65 (d, 1H, J = 2 Hz)
<b>9c</b>	1672, 1650, 1574, 1478 [a]	1.35-2.20 (m, 6H), 3.20-3.50 (m, 1H), 5.40-6.00 (m, 2H), 7.00-7.20 (m, 1H), 7.40-7.55 (m, 1H), 8.30-8.50 (m, 2H)	<b>11c</b>	1615, 1572 [a]	1.40-2.20 (m, 6H), 3.30-3.70 (m, 1H), 5.50-6.05 (m, 2H), 7.20-8.20 (m, 5H), 8.72 (s, 1H)
<b>9d</b>	1648, 1598, 1576 [a]	3.53 (d, 2H, J = 6 Hz), 6.00-6.55 (m, 2H), 7.00-7.40 (m, 6H), 7.40-7.65 (m, 1H), 8.30-8.60 (m, 2H)	<b>11d</b>	1608, 1595, 1570, 1494 [a]	3.53 (d, 2H, J = 5 Hz), 6.20-6.50 (m, 2H), 7.00-7.90 (m, 9H), 8.03 (d, 1H, J = 8 Hz), 8.70 (s, 1H)
<b>9e</b>	1668, 1638, 1602, 1576 [a]	4.66 (d, 1H, J = 6 Hz), 4.80-5.30 (m, 2H), 6.00-6.45 (m, 1H), 7.00-7.50 (m, 7H), 8.30-8.55 (m, 2H)	<b>11e</b>	1638, 1622, 1602, 1572 [a]	4.80-5.40 (m, 3H), 6.00-6.60 (m, 1H), 7.00-8.20 (m, 10H), 8.66 (d, 1H, J = 1 Hz)
<b>9f</b>	1650, 1590, 1580, 1486 [a]	3.47 (d, 2H, J = 5 Hz), 6.15-6.30 (m, 2H), 7.00-7.50 (m, 6H), 8.30-8.50 (m, 2H)	<b>11f</b>	1648, 1622, 1606, 1588, 1568 [b]	3.56 (d, 2H, J = 5 Hz), 6.25 (s, 2H), 6.90-7.20 (m, 9H), 8.70 (s, 1H)
<b>9g</b>	1668, 1640, 1588, 1578 [a]	4.55-5.35 (m, 3H), 5.90-6.40 (m, 1H), 6.90-7.50 (m, 6H), 8.30-8.50 (m, 2H)	<b>11g</b>	1638, 1604, 1572, 1486 [a]	4.82 (d, 1H, J = 6 Hz), 5.00-5.42 (m, 2H), 6.00-6.50 (m, 1H), 7.00 (d, 2H, J = 8 Hz), 7.30-8.20 (m, 9H), 8.65 (d, 1H, J = 2 Hz)
<b>9h</b>	1644, 1608, 1574, 1524 [a]	3.55 (d, 2H, J = 6 Hz), 6.00-6.40 (m, 2H), 6.70-8.00 (m, 6H), 8.30-8.60 (m, 2H)	<b>11h</b>	1644, 1608, 1572, 1518 [a]	3.70 (d, 2H, J = 7 Hz), 6.00-6.45 (m, 1H), 6.70-8.20 (m, 10H), 8.73 (s, 1H)
<b>9i</b>	1638, 1608, 1574, 1524 [a]	4.80-5.60 (m, 3H), 5.95-6.45 (m, 1H), 7.00-7.95 (m, 6H), 8.30-8.50 (m, 2H)	<b>11i</b>	1647, 1608, 1574, 1528 [a]	4.93 (dd, 1H, J = 1, 8 Hz), 5.46 (d, 1H, J = 9 Hz), 5.69 (d, 1H, J = 6 Hz), 5.90-6.40 (m, 1H), 7.10-8.10 (m, 9H), 8.67 (s, 1H)
<b>9j</b>	1722, 1658, 1608, 1582 [a]	3.48 (d, 2H, J = 5 Hz), 3.82 (s, 3H), 6.30-6.45 (m, 2H), 7.05-7.55 (m, 4H), 7.90 (d, 2H, J = 8 Hz), 8.45 (br s, 2H)	<b>11j</b>	1712, 1606, 1506, 1494 [b]	3.60-3.75 (m, 2H), 3.82 (s, 3H), 6.40-6.55 (m, 2H), 7.20-8.10 (m, 9H), 8.83 (s, 1H)
<b>9k</b>	1722, 1680, 1638, 1612 [a]	3.83 (s, 3H), 4.66-5.40 (m, 3H), 6.00-6.45 (m, 1H), 7.00-7.50 (m, 4H), 7.92 (d, 2H, J = 8 Hz), 8.40 (br s, 2H)	<b>11k</b>	1722, 1620, 1610, 1575 [a]	3.73 (s, 3H), 4.92 (d, 1H, J = 6 Hz), 5.03-5.40 (m, 2H), 6.05-6.50 (m, 1H), 7.10-8.20 (m, 9H), 8.67 (d, 1H, J = 2 Hz)
<b>10a</b>	1704, 1650, 1600, 1550 [a]	3.30 (d, 2H, J = 6 Hz), 4.90-5.20 (m, 2H), 5.60-6.10 (m, 1H), 7.00 (d, 2H, J = 5 Hz), 8.40 (d, 2H, J = 5 Hz)	<b>12a</b>	1640, 1624, 1586 [a]	3.70 (d, 2H, J = 6 Hz), 4.85-5.20 (m, 2H), 5.70-6.30 (m, 1H), 7.35-8.10 (m, 4H), 8.30 (s, 1H), 9.03 (s, 1H)
<b>10b</b>	1674, 1600, 1544 [a]	1.30-2.20 (m, 6H), 3.10-3.45 (m, 1H), 5.40-6.00 (m, 1H), 7.03 (d, 2H, J = 6 Hz), 8.40 (d, 2H, J = 6 Hz)	<b>12b</b>	1620, 1582, 1568, 1504 [b]	4.02 (s, 2H), 5.36 (d, 1H, J = 1 Hz), 5.50 (d, 1H, J = 1 Hz), 7.40-8.10 (m, 4H), 8.38 (br s, 1H), 9.15 (br s, 1H)
<b>10c</b>	1688, 1638, 1602, 1582 [a]	3.43 (d, 2H, J = 5 Hz), 5.98-6.55 (m, 2H), 6.95-7.40 (m, 7H), 8.40 (br s, 2H)	<b>12c</b>	1645, 1622, 1582 [a]	1.30-2.30 (m, 6H), 3.80-4.20 (m, 1H), 5.60-6.10 (m, 2H), 7.30-8.10 (m, 4H), 8.30 (s, 1H), 8.98 (s, 1H)
<b>10d</b>	1670, 1637, 1596, 1540 [a]	4.50-5.30 (m, 3H), 5.90-6.40 (m, 1H), 6.85-7.30 (m, 7H), 8.40 (br s, 2H)	<b>12d</b>	1666, 1624, 1602, 1584, 1572 [a]	3.70-3.90 (m, 2H), 6.25-6.50 (m, 2H), 7.00-8.00 (m, 9H), 8.32 (s, 1H), 9.01 (s, 1H)
<b>10e</b>	1688, 1640, 1600, 1599 [a]	3.46 (d, 2H, J = 5 Hz), 6.20-6.40 (m, 2H), 7.00-7.50 (m, 6H), 8.45 (d, 2H, J = 5 Hz)	<b>12e</b>	1674, 1638, 1622, 1602, 1548 [a]	4.75-5.40 (m, 3H), 6.15-6.60 (m, 1H), 7.00-8.00 (m, 9H), 8.30 (s, 1H), 9.03 (s, 1H)
<b>10f</b>	1670, 1596 [a]	4.56 (d, 1H, J = 6 Hz), 4.80-5.35 (m, 2H), 5.90-6.50 (m, 1H), 6.80-7.65 (m, 6H), 8.40 (d, 2H, J = 5 Hz)	<b>12f</b>	1642, 1622, 1582, 1568, 1504 [b]	3.75 (d, 2H, J = 5 Hz), 6.26 (s, 2H), 6.80-8.00 (m, 8H), 8.30 (s, 1H), 9.09 (s, 1H)
<b>10g</b>	1724, 1642, 1606 [a]	3.40-3.60 (m, 2H), 3.83 (s, 3H), 6.25-6.45 (m, 2H), 7.00-7.40 (m, 4H), 7.80-8.00 (m, 2H), 8.30-8.60 (m, 2H)	<b>12g</b>	1674, 1630, 1622, 1584 [a]	4.75-5.40 (m, 3H), 6.10-6.60 (m, 1H), 6.90-8.00 (m, 8H), 8.30 (s, 1H), 9.10 (s, 1H)

Table 4 (continued)

Compound	IR, cm <sup>-1</sup>	NMR (deuteriochloroform) $\delta$
<b>12h</b>	1622, 1608, 1586, 1574, 1518 [b]	3.93 (d, 2H, J = 6 Hz), 6.10-6.45 (m, 1H), 6.80-8.10 (m, 8H), 8.35 (s, 1H), 9.06 (s, 1H)
<b>12i</b>	1708, 1646, 1620, 1606, 1586 [b]	3.89 (s, 3H), 3.80-4.10 (m, 2H), 6.45-6.60 (m, 2H), 7.15-8.10 (m, 9H), 8.35 (s, 1H), 9.09 (s, 1H)
<b>12j</b>	1722, 1624, 1610, 1584 [a]	3.83 (s, 3H), 4.70-5.50 (m, 3H), 6.10-6.60 (m, 1H), 7.10-8.00 (m, 9H), 8.30 (s, 1H), 9.09 (s, 1H)

[a] Film. [b] Potassium bromide.

Table 5

IR and NMR Spectral Data of **15** and **16**

Compound	IR (film), cm <sup>-1</sup>	NMR (deuteriochloroform) $\delta$
<b>15a</b>	1642, 1430	3.42 (d, 2H, J = 6 Hz), 4.90-5.20 (m, 2H), 5.60-6.15 (m, 1H), 6.50-7.15 (m, 3H)
<b>15b</b>	1630	3.86 (s, 2H), 5.43 (d, 1H, J = 1 Hz), 5.56 (d, 1H, J = 1 Hz), 6.75-7.00 (m, 2H), 7.12 (dd, 1H, J = 2, 5 Hz)
<b>15c</b>	1650, 1530	1.50-2.30 (m, 6H), 5.73 (s, 2H), 6.67-6.95 (m, 2H), 7.02 (dd, 1H, J = 1, 6 Hz)
<b>15d</b>	1645, 1638, 1600	3.75 (d, 2H, J = 5 Hz), 6.30-6.50 (m, 2H), 6.70-7.50 (m, 8H)
<b>16a</b>	1704, 1642	3.27 (d, 2H, J = 6 Hz), 3.44 (s, 3H), 4.80-5.20 (m, 2H), 5.70-6.10 (m, 3H), 6.40-6.60 (m, 1H)
<b>16b</b>	1632, 1494	3.46 (s, 3H), 3.55 (s, 2H), 5.28 (d, 1H, J = 1 Hz), 5.41 (d, 1H, J = 1 Hz), 5.85-6.10 (m, 2H), 6.46-6.65 (m, 1H)
<b>16c</b>	1690, 1645, 1492	1.40-2.20 (m, 6H), 3.48 (s, 3H), 3.30-3.60 (m, 1H), 5.60-6.10 (m, 2H), 6.40-6.60 (m, 1H)
<b>16d</b>	1640, 1600, 1494	3.46 (s, 3H), 3.35-3.60 (m, 2H), 5.80-6.10 (m, 2H), 6.15-6.40 (m, 2H), 6.40-6.55 (m, 1H), 6.95-7.30 (m, 5H)

under similar conditions as above were examined.

When borates **14** [derived from thiophene or 1-methylpyrrole with *t*-butyllithium [4] followed by treatment with tributylborane] were allowed to react with **5a** in the absence of copper(I) cyanide, 2-allylthiophene **15a** (13% yield) and 2-butylthiophene (10% yield) were obtained from **14a**, and **14b** afforded a fairly unstable oil. As is evident from Table 2, highly regioselective allylation at the 2-position of thiophene and 1-methylpyrrole could be attained with copper(I) cyanide. Unlike the instances of the pyridyl borates **1-4**, in the present case an allylic transposition was not observed on the reaction with **5d**.

Table 6

IR and NMR Spectral Data of **18** and **21**

Compound	IR, cm <sup>-1</sup>	NMR (deuteriochloroform) $\delta$
<b>18a</b>	1640, 1616, 1552 1514 [a]	3.50 (dd, 2H, J = 2, 7 Hz), 3.73 (s, 3H), 4.90-5.30 (m, 2H), 5.80-6.30 (m, 1H), 6.82 (s, 1H), 6.90-7.40 (m, 3H), 7.50-7.80 (m, 1H)
<b>18b</b>	1628, 1614, 1568 [a]	3.60 (s, 3H), 3.82 (s, 2H), 5.46 (d, 2H, J = 10 Hz), 6.90 (s, 1H), 7.00-7.30 (m, 3H), 7.40-7.60 (m, 2H)
<b>18c</b>	1612, 1570, 1550, 1512 [a]	1.50-2.30 (m, 6H), 3.50 (s, 3H), 3.90-4.20 (m, 1H), 5.77 (s, 2H), 6.76 (s, 1H), 7.00-7.30 (m, 3H), 7.50-7.70 (m, 1H)
<b>18d</b>	1615, 1598, 1578, 1550 [a]	3.66 (d, 2H, J = 5 Hz), 3.75 (s, 3H), 6.40-6.60 (m, 2H), 6.87 (s, 1H), 7.00-7.50 (m, 8H), 7.55-7.75 (m, 1H)
<b>21a</b>	1670, 1642, 1614 [a]	3.47 (s, 3H), 3.30-3.60 (m, 2H), 4.80-5.20 (m, 2H), 5.70-6.10 (m, 1H), 6.20 (s, 1H), 6.90-7.30 (m, 3H), 7.40-7.60 (m, 1H)
<b>21b</b>	1630, 1548, 1514 [a]	3.46 (s, 3H), 3.75 (s, 2H), 5.30 (d, 1H, J = 1 Hz), 5.44 (d, 1H, J = 1 Hz), 6.27 (s, 1H), 6.95-7.30 (m, 3H), 7.40-7.60 (m, 1H)
<b>21c</b>	1610, 1536, 1470 [a]	1.40-2.20 (m, 6H), 3.60 (s, 3H), 3.40-3.70 (m, 1H), 5.60-6.00 (m, 2H), 6.16 (s, 1H), 6.85-7.30 (m, 3H), 7.40-7.60 (m, 9H)
<b>21d</b>	1625, 1615, 1595, 1542 [b]	3.53 (s, 3H), 3.50-3.70 (m, 2H), 6.20-6.40 (m, 3H), 6.95-7.60 (m, 9H)
<b>21e</b>	1615, 1600 [a]	0.80-1.05 (m, 3H), 1.20-1.70 (m, 4H), 2.70 (t, 2H, J = 6 Hz), 3.46 (s, 3H), 3.50-3.70 (m, 2H), 6.30-6.50 (m, 2H), 7.00-7.75 (m, 9H)
<b>21f</b>	1646, 1608, 1582, 1548 [b]	3.56 (s, 3H), 3.50-3.70 (m, 2H), 6.15-6.40 (m, 3H), 6.90-7.60 (m, 8H)
<b>21g</b>	1700, 1650, 1616, 1588 [a]	0.80-1.06 (m, 3H), 1.10-1.70 (m, 4H), 2.70 (t, 2H, J = 7 Hz), 3.60 (s, 3H), 3.50-3.70 (m, 2H), 6.20-6.40 (m, 2H), 6.90-7.60 (m, 8H)
<b>21h</b>	1718, 1644, 1606, 1582 [b]	3.52 (s, 3H), 3.45-3.65 (m, 2H), 3.80 (s, 3H), 6.20-6.45 (m, 3H), 6.80-7.30 (m, 5H), 7.35-7.60 (m, 1H), 7.85 (d, 2H, J = 8 Hz)

[a] Film. [b] Potassium bromide.

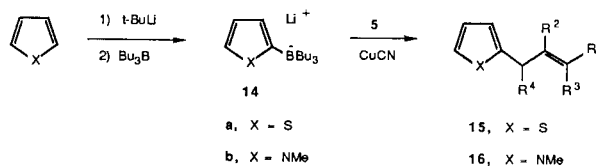


Chart 4



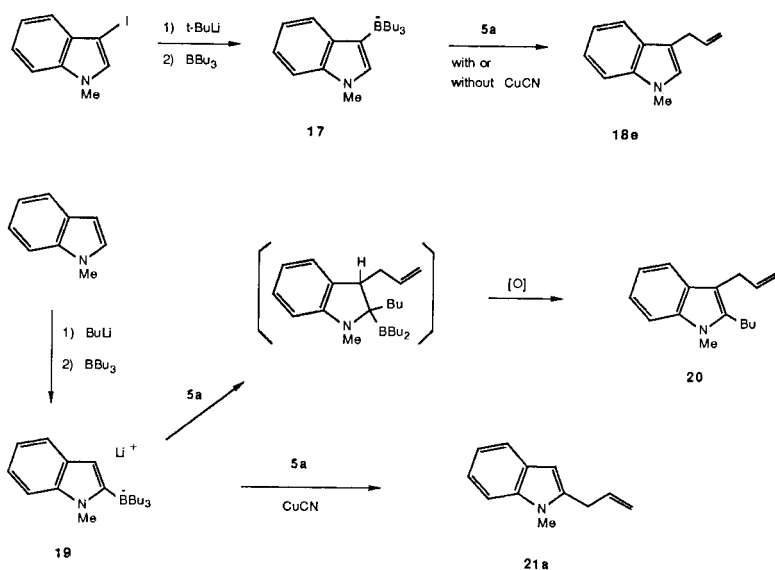


Chart 5

Noticeable results were obtained from the reaction of tributyl 1-methyl-3-indolyl borate **17** [derived from 3-iodo-1-methylindole and *t*-butyllithium followed by treatment with tributylborane], and tributyl 1-methyl-2-indolyl borate **19** [5] with **5**.

Subjecting **17** to the reaction with **5a** produced 3-allyl-1-methylindole **18a** irrespective of whether copper(I) cyanide was present or not, *i.e.*, in 71% yield with copper(I) cyanide, and in 33% yield without copper(I) cyanide.

Although the principle product from **19** with **5a** was 3-allyl-2-butyl-1-methylindole **20** as was expected from the known path [6], the remarkable activation of C<sub>2</sub>-B bond of **19** was realized by using copper(I) cyanide in the reaction to afford exclusive formation of 2-allyl-1-methylindole **21a** in 70% yield. The reactions of indolyl borates **17** and **19** with **5** were also examined, and the results are summarized in Table 3.

The reaction of **17** with **5d** in the presence of copper(I) cyanide produced 3-cinnamyl-1-methylindole **18d** as the sole product, whereas a similar treatment of **19** with **5d** led to the formation of 2-cinnamyl-1-methylindole **21d** in 40% yield and 2-butyl-3-cinnamylindole **21e** in 22% yield.

## EXPERIMENTAL

All melting points were determined with a Yanagimoto micro melting point apparatus, and are uncorrected.

Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl before use.

The ir spectra were recorded with a Hitachi 270-30 spectrometer. The nmr spectra were determined with a Hitachi R-40 and a JEOL FX-90Q spectrometers. Chemical shifts are reported relative to internal tetramethylsilane and given in  $\delta$ -value. Coupling constants are reported in

Hertz and splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. The mass spectra were recorded on a JEOL JMS-QH100 and a JEOL JMS-D300 spectrometers.

Column chromatography and flash chromatography were performed on silica gel 70-230 and 230-400 mesh ASTM obtained from Merck, respectively.

### Typical Procedure for Betaines 6-8: Tributyl 1-Allyl-3-pyridinio Borate 6.

Tributylborane (1M solution in hexane, 5 ml) was added to a solution of 3-lithiopyridine [2] [derived from 3-bromopyridine (785 mg, 5 mmoles) and butyllithium (1.5M solution in hexane, 3.4 ml) in ether (30 ml)] at  $-70^\circ$  under a nitrogen atmosphere. The mixture was stirred for 1 hour at the same temperature, and then room temperature overnight. The mixture was concentrated *in vacuo*, and dissolved in tetrahydrofuran (20 ml) under a nitrogen atmosphere. After the mixture was cooled to  $-30^\circ$ , allyl bromide **5a** (665 mg, 5.5 mmoles) was added, the whole was gradually warmed to room temperature, and stirred overnight. After treatment with 10% aqueous sodium hydroxide (10 ml) and 30% aqueous hydrogen peroxide (2 ml) under ice-cooling, the mixture was diluted with ethyl acetate (60 ml), washed with brine (40 ml), and dried over magnesium sulfate. The solvent was removed and the residue was purified by flash chromatography with hexane:ethyl acetate (3:1) to give 948 mg (63% yield) of **6** as a viscous oil; ir (film):  $\nu$  1624, 1604, 1490, 1454  $\text{cm}^{-1}$ ; nmr (deuteriochloroform):  $\delta$  0.10-1.45 (m, 27H), 4.88 (d, 2H,  $J = 6$  Hz), 5.10-5.55 (m, 2H), 5.70-6.30 (m, 1H), 7.30-7.60 (m, 1H), 7.70-7.90 (m, 1H), 8.17 (d, 1H,  $J = 1$  Hz), 8.40 (d, 1H,  $J = 6$  Hz); ms: (ei) Calcd. for C<sub>16</sub>H<sub>27</sub>BN [(M-C<sub>4</sub>H<sub>9</sub>)<sup>+</sup>]: 244.22182. Found: 244.22362; ms: (ci with methane) Calcd. for C<sub>20</sub>H<sub>37</sub>BN [(MH)<sup>+</sup>]: 302.30192. Found: 302.30192.

Borates **3** and **4** were formed from treatment of 3-lithioquinoline [7] and 4-lithioisoquinoline [8] with tributylborane, respectively, in the same manner as described for **1**, and betaines **7** and **8** were obtained by the same treatment as described for **6**. Tributyl 1-allyl-3-quinolinyl borate **7** was obtained in 70% yield and recrystallized from ethyl acetate-hexane, mp  $72-73^\circ$ ; ir (potassium bromide):  $\nu$  1582, 1564, 1514  $\text{cm}^{-1}$ ; nmr (deuteriochloroform):  $\delta$  0.20-1.50 (m, 27H), 4.90-5.50 (m, 4H), 5.80-6.25 (m, 1H), 7.50-8.00 (m, 4H), 8.63 (s, 1H), 8.75 (s, 1H).

Anal. Calcd. for C<sub>24</sub>H<sub>38</sub>BN: C, 82.04; H, 10.90; N, 3.99. Found: C, 82.09; H, 10.97; N, 3.96.

Tributyl 2-allyl-4-isoquinolinyl borate **8** was obtained as an unstable

syrup in 60% yield; ir (film):  $\nu$  1656, 1628, 1604, 1514  $\text{cm}^{-1}$ ; nmr (deuteriochloroform):  $\delta$  0.45-1.60 (m, 27H), 4.93 (d, 2H,  $J = 5$  Hz), 5.10-5.53 (m, 2H), 5.80-6.20 (m, 1H), 7.40-8.00 (m, 4H), 8.43 (s, 1H), 9.03 and 9.13 (two singlets, 1H); ms: (ei) Calcd. for  $\text{C}_{20}\text{H}_{29}\text{BN}(\text{M}-\text{C}_6\text{H}_5)^+$ : 294.24097. Found: 294.23927; ms: (Ci with methane) Calcd. for  $\text{C}_{24}\text{H}_{39}\text{BN}(\text{MH})^+$ : 352.31754. Found: 352.31984.

#### Typical Procedure for Allylpyridines 9-12: 3-Allylpyridine 9a.

Borate **1** was derived from 3-bromopyridine (1.41 g, 9 mmoles) and butyllithium (1.5M solution in hexane, 6 ml) in ether (50 ml) followed by treatment with tributylborane (1M solution in hexane, 9 ml) by the previously reported method [2], and ether was removed *in vacuo*. The residue was dissolved in tetrahydrofuran (20 ml) and added dropwise to a suspension of copper(I) cyanide (1.7 g, 18.9 mmoles) in tetrahydrofuran (20 ml) at  $-30^\circ$  under a nitrogen atmosphere. After stirring for 20 minutes, allyl bromide **5a** (1.19 g, 9.9 mmoles) was added, the whole was gradually warmed to room temperature, and stirred overnight. The mixture was treated with 10% aqueous sodium hydroxide (10 ml) and 30% aqueous hydrogen peroxide (3 ml) solutions under ice-cooling, diluted with ethyl acetate (60 ml), washed with brine (40 ml), and dried over magnesium sulfate. The solvent was removed and the residue was purified by flash chromatography with hexane: ethyl acetate (2:1) to give 800 mg (75% yield) of **9a**.

Allylpyridines **9-12** were obtained by the same procedure as described above, and the results are summarized in Table 1. Tributyl 4-pyridyl borate **2** was formed from tributylborane (1M solution in hexane, 6 ml) and 4-lithiopyridine [9] [derived from 4-bromopyridine (942 mg, 6 mmoles) and butyllithium (1.5M solution in hexane, 4 ml) in ether].

#### Typical Procedure for 2-Allylthiophenes 15 and 2-Allyl-1-methylpyrroles 16: 2-Allyl-1-methylpyrrole 16a.

Tributylborane (1M solution in hexane, 10 ml) was added to a solution of 2-lithio-1-methylpyrrole [4] [derived from 1-methylpyrrole (810 mg, 10 mmoles) and *t*-butyllithium (1.8M solution in pentane, 6.5 ml) in tetrahydrofuran (30 ml)] at  $-70^\circ$  under a nitrogen atmosphere, the mixture was stirred for 1 hour, and then gradually warmed to room temperature. This solution of borate **14b** was added to a suspension of copper(I) cyanide (979 mg, 11 mmoles) in tetrahydrofuran (20 ml) at  $-30^\circ$  under a nitrogen atmosphere, and the whole was stirred for 20 minutes. Allyl bromide **5a** (1.32 g, 11 mmoles) was added, the mixture was slowly warmed to room temperature, and stirred overnight. After treatment with 10% aqueous sodium hydroxide (15 ml) and 30% aqueous hydrogen peroxide (5 ml) solutions under ice-cooling, the mixture was diluted with ethyl acetate (60 ml), washed with brine (40 ml), and dried over magnesium sulfate. The solvent was removed and the residue was purified by flash chromatography with hexane to give 799 mg (66% yield) of **16a**.

Borate **14a** was formed from thiophene (840 mg, 10 mmoles) and *t*-butyllithium (1.8M solution in pentane, 6.5 ml) followed by treatment with tributylborane (1M solution in hexane, 10 ml) in the same manner as described for **14b**. The reactions of **14** with **5** were performed in the same manner as described above (Table 2).

#### 3-Allyl-2-butyl-1-methylindole 20.

Allyl bromide **5a** (660 mg, 5.5 mmoles) was added to a solution of borate **19** [derived from 1-methylindole (655 mg, 5 mmoles) and butyllithium (1.5M solution in hexane, 3.5 ml) followed by treatment with tributylborane (1M solution in hexane, 5 ml) in tetrahydrofuran (30 ml) according to the Levy's method [5]] at  $-30^\circ$  under a nitrogen atmosphere, the whole was gradually warmed to room temperature, and stirred overnight. After treatment with 10% aqueous sodium hydroxide (10 ml) and

30% aqueous hydrogen peroxide (5 ml) solutions under ice-cooling, the mixture was diluted with ethyl acetate (60 ml), washed with brine (40 ml), and dried over magnesium sulfate. The solvent was removed and the residue was purified by flash chromatography with hexane to give 795 mg (70% yield) of **20** as a viscous oil, bp  $130^\circ$  (1 mm Hg) (bath temperature); ir (film):  $\nu$  1638, 1615, 1565, 1472  $\text{cm}^{-1}$ ; nmr (deuteriochloroform):  $\delta$  0.90 (t, 3H,  $J = 7$  Hz), 1.13-1.73 (m, 4H), 2.66 (t, 2H,  $J = 7$  Hz), 3.53 (s, 3H), 3.30-3.75 (m, 2H), 4.83-5.26 (m, 2H), 5.70-6.25 (m, 1H), 6.90-7.25 (m, 4H), 7.40-7.60 (m, 1H); ms: (ei) 227 ( $\text{M}^+$ ).

Anal. Calcd. for  $\text{C}_{16}\text{H}_{21}\text{N}$ : C, 84.53; H, 9.31; N, 6.16. Found: C, 84.40; H, 9.29; N, 6.14.

#### 2-Allyl-1-methylindole 21a.

A solution of borate **19** in tetrahydrofuran (30 ml) was formed in the same manner as described above, and added to a suspension of copper(I) cyanide (490 mg, 5.5 mmoles) in tetrahydrofuran (20 ml) at  $-30^\circ$  under a nitrogen atmosphere, and the whole was stirred for 20 minutes. Allyl bromide **5a** (665 mg, 5.5 mmoles) was added, the mixture was gradually warmed to room temperature, and stirred overnight. After treatment with 10% aqueous sodium hydroxide (10 ml) and 30% aqueous hydrogen peroxide (5 ml) under ice-cooling, the mixture was diluted with ethyl acetate (60 ml), washed with brine (40 ml), and dried over magnesium sulfate. The solvent was removed and the residue was purified by flash chromatography with hexane to give 634 mg (70% yield) of **21a** (Table 3).

Borate **17** was formed from 3-iodo-1-methylindole [10] (711 mg, 3 mmoles) and *t*-butyllithium (1.8M solution in pentane, 2 ml) [11] followed by treatment with tributylborane (1M solution in hexane, 3 ml) in the same manner as described for **19**, and reactions of **17** and **19** with **5** in the presence of copper(I) cyanide were carried out in the same manner as described above (Table 3).

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Anal. Calcd. for  $\text{C}_{18}\text{H}_{34}\text{BN}$ : C, 78.54; H, 12.54; N, 5.09. Found: C, 78.63; H, 12.48; N, 5.01.
- [4] Tributyl 1-benzyl-3-pyridinyl borate **13b**, viscous oil; 45% yield; ir (film):  $\nu$  1604, 1488, 1454, 1428  $\text{cm}^{-1}$ ; nmr (deuteriochloroform):  $\delta$  0.10-0.60 (m, 27H), 5.30 (s, 2H), 7.00-7.75 (m, 7H), 8.20-8.50 (m, 2H); ms: (ei) Calcd. for  $\text{C}_{24}\text{H}_{38}\text{BN}$ : 351.30973. Found: 351.31023.
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