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# General Preparation of Highly Functionalized Mixed Cuprates via a Halogen-Copper Exchange

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Typical procedure (**TP**) for the iodine-copper exchange.

A dry and argon flushed 10 mL flask, equipped with a magnetic stirrer and a septum, was charged with 4-iodoacetophenone (1 mmol). Dry THF (2 mL) was added and the solution was added slowly into a dry and argon flushed 25 mL flask, containing the lithium neophylcuprate previously prepared (1.2 mmol) and cooled to  $-30\text{ }^{\circ}\text{C}$ . The mixture was allowed to warm quickly to rt. The I/Cu-exchange was complete within 1 h (checked by GC analysis of reaction aliquots) and the electrophile (0.9 mmol) was added to the mixed organocuprate (**4**). After 0.5 h of stirring at rt, the reaction mixture was quenched with sat.  $\text{NH}_4\text{Cl}$  solution (2 mL) and poured into water (25 mL). The aqueous phase was extracted with diethyl ether (3 x 30 mL). The organic fractions were washed with brine (30 mL), dried ( $\text{MgSO}_4$ ) and concentrated *in vacuo*. Flash chromatography on silica gel furnished the product.

Preparation of ethyl 4-allylbenzoate (**5a**):

Prepared according to **TP** from ethyl 4-iodobenzoate (276 mg, 1.0 mmol), lithium neopentylcuprate (**1**) (1.2 mmol) and allyl bromide (110 mg, 0.9 mmol). Reaction time: 2.5 h. Purification by flash chromatography (pentane/diethyl ether = 99:1) yielded ethyl 4-allylbenzoate (**5a**) as a colourless oil (90 mg, 95 %).

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ,  $25\text{ }^{\circ}\text{C}$ ):  $\delta$  = 7.90 (dd,  $^3J(\text{H,H}) = 8.3\text{ Hz}$  and  $^4J(\text{H,H}) = 1.7\text{ Hz}$ , 2 H), 7.79 (dd,  $^3J(\text{H,H}) = 8\text{ Hz}$  and  $^4J(\text{H,H}) = 1.7\text{ Hz}$ , 2 H), 5.95-5.82 (m, 1 H), 5.05-4.99 (m, 2 H), 4.29 (q,  $^2J(\text{H,H}) = 11\text{ Hz}$  and  $^3J(\text{H,H}) = 7\text{ Hz}$ , 2 H), 3.60 (d,  $^3J(\text{H,H}) = 6.6\text{ Hz}$ , 2 H), 1.31 (t,  $^3J(\text{H,H}) = 7.2\text{ Hz}$ , 3 H).

$^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ,  $25\text{ }^{\circ}\text{C}$ ):  $\delta$  = 165.6, 144.3, 135.4, 128.7, 127.6, 115.5, 59.8, 39.1, 13.3.

**MS** (70 eV, ED):  $m/z$  (%): 190 (26)  $[\text{M}]^+$ , 162 (14), 145 (100), 117 (51), 115 (29), 101 (1).

**IR** (KBr):  $\tilde{\nu}$  = 2980 (s), 1716 (vs), 1640 (m), 1611 (vs), 1575 (m), 1508 (w), 1433 (s), 1367 (s), 1316 (s), 1276 (vs), 1177 (vs), 1105 (vs), 1022 (s), 994 (m), 917 (m), 852 (m), 758 (s), 707 (m).

$\text{C}_{15}\text{H}_{12}\text{O}_2$  :: calc.: C: 75.60, H: 7.42.  
found: C: 76.10, H: 7.55.

Preparation of ethyl 4 benzoyl-benzoate (**5b**):

Prepared according to **TP** from ethyl 4-iodobenzoate (276 mg, 1.0 mmol), lithium neopentylcuprate (**1**) (1.2 mmol) and benzoyl chloride (0.1 mL, 0.9 mmol). Reaction time: 2.5 h. Purification by flash chromatography (pentane/diethyl ether = 95:5) yielded ethyl 4-benzoyl-benzoate (**5b**) as a light yellow oil (400 mg, 87 %).

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 8.07 (dd, <sup>3</sup>J(H,H) = 8.4 Hz and <sup>4</sup>J(H,H) = 1.8 Hz, 2 H), 7.74 (dd, <sup>3</sup>J(H,H) = 8 Hz and <sup>4</sup>J(H,H) = 1.8 Hz, 2 H), 7.73 (m, 2 H), 7.53 (dt, <sup>3</sup>J(H,H) = 8 Hz and <sup>4</sup>J(H,H) = 1.4 Hz, 1 H), 7.40 (t, <sup>3</sup>J(H,H) = 8 Hz, 2 H), 4.34 (q, <sup>2</sup>J(H,H) = 11 Hz and <sup>3</sup>J(H,H) = 7 Hz, 2 H), 1.33 (t, <sup>3</sup>J(H,H) = 7 Hz, 3 H).

**<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>, 25 °C): δ = 195.0, 164.8, 140.2, 136.0, 132.6, 131.9, 129.1, 128.7, 128.4, 127.4, 126.2, 60.4, 13.3.

**MS** (70 eV, EI): m/z (%): 254 (48) [M]<sup>+</sup>, 226 (14), 209 (45), 181 (18), 177 (57), 152 (10), 149 (14), 130 (20), 118 (17), 104 (100).

**IR** (KBr):  $\tilde{\nu}$  = 3402 (m, br), 2982 (m), 1720 (vs), 1661 (vs), 1597 (m), 1579 (w), 1448 (m), 1405 (s), 1356 (s), 1369 (s), 1317 (s), 1275 (vs), 1105 (vs), 1020 (m), 939 (m), 927 (m), 851 (w), 769 (w), 715 (s), 698 (m), 657 (m).

**C<sub>15</sub>H<sub>12</sub>O<sub>2</sub>**: calc.: C: 75.57, H: 5.55.  
found: C: 75.41, H: 5.54.

Preparation of ethyl 4-(2,2-dimethyl-1-oxopropyl)-benzoate (**5c**):

Prepared according to **TP** from ethyl 4-iodobenzoate (276 mg, 1.0 mmol), lithium neopentylcuprate (**1**) (1.2 mmol) and pivaloyl chloride (108 mg, 0.9 mmol). Reaction time: 1.5 h. Purification by flash chromatography (pentane/diethyl ether = 95:5) yielded ethyl 4-(2,2-dimethyl-1-oxopropyl)-benzoate (**5c**) as a light yellow oil (350 mg, 83 %).

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 7.99 (dd, <sup>3</sup>J(H,H) = 8.7 Hz and <sup>4</sup>J(H,H) = 1.8 Hz, 2 H), 7.58 (dd, <sup>3</sup>J(H,H) = 8.7 Hz and <sup>4</sup>J(H,H) = 1.8 Hz, 2 H), 4.32 (q, <sup>2</sup>J(H,H) = 11 Hz and <sup>3</sup>J(H,H) = 7 Hz, 2 H), 1.33 (t, <sup>3</sup>J(H,H) = 7 Hz, 3 H), 1.26 (s, 9H).

**<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>, 25 °C): δ = 209.8, 166.2, 143.2, 132.4, 129.6, 127.7, 61.6, 44.7, 28.0, 14.6.

**MS** (70 eV, EI): m/z (%): 235 (3) [M+H]<sup>+</sup>, 189 (8), 177 (100), 149 (20), 121 (5), 103 (6).

**IR** (KBr):  $\tilde{\nu}$  = 3435 (vs, br), 1689 (vs), 1657 (vs), 1597 (m), 1579 (w), 1447 (s), 1402 (s), 1356 (s), 1316 (s), 1277 (vs), 1180 (w), 1072 (s), 939 (m), 928 (m), 850 (m), 794 (m), 736 (m), 699 (vs), 674 (m).

**HRMS** for **C<sub>14</sub>H<sub>18</sub>O<sub>3</sub>** (234.2909): calc.: 235.1334 [M+H]<sup>+</sup>  
found: 235.1352 [M+H]<sup>+</sup>

Preparation of ethyl 4-(3-oxocyclohexyl)-benzoate (**5d**):

Prepared according to **TP** from ethyl 4-iodobenzoate (552 mg, 2.0 mmol), lithium neopentylcuprate (**1**) (2.2 mmol), 2-cyclohexen-1-one (0.16 mL, 1.6 mmol) and trimethylsilyl chloride (0.404 mL, 3.2 mmol). Reaction time: 1.5 h. Purification by flash chromatography (pentane/diethyl ether = 95:5) yielded ethyl 4-(3-oxocyclohexyl)-benzoate (**5d**) as a light yellow oil (113 mg, 70 %).

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 7.93 (d, <sup>3</sup>J(H,H) = 8 Hz, 2 H), 7.21 (d, <sup>3</sup>J(H,H) = 8 Hz, 2 H), 4.30 (q, <sup>2</sup>J(H,H) = 11 Hz and <sup>3</sup>J(H,H) = 7 Hz, 2 H), 3.05-2.95 (m, 1H), 2.56-1.50 (m, 8H), 1.32 (t, <sup>3</sup>J(H,H) = 7 Hz, 3 H).

**<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>, 25 °C): δ = 209.3, 165.4, 148.3, 129.0, 128.1, 125.6, 59.9, 47.5, 43.7, 40.1, 31.5, 24.4, 13.3.

**MS** (70 eV, EI): m/z (%): 246 (94) [M]<sup>+</sup>, 218 (2), 201 (100), 189 (9), 177 (17), 148 (14), 145 (49), 131 (89), 117 (50), 102 (22).

**IR** (KBr):  $\tilde{\nu}$  = 2977 (vs), 2934 (s), 2864 (vs), 1719 (m), 1444 (m), 1382 (s), 1350 (m), 1277 (m), 1261 (m), 1123 (vs), 1077 (s), 1043 (m), 1023 (m), 845 (w), 797 (m).

**C<sub>15</sub>H<sub>18</sub>O<sub>3</sub>**: calc.: C: 73.15, H: 7.37.

found: C: 73.44, H: 7.40.

Preparation of diethyl 2-allylterephthalate (**5e**):

Prepared according to **TP** from diethyl 2-bromoterephthalate (630 mg, 2.1 mmol), lithium neopentylcuprate (**1**) (2.2 mmol) and allyl bromide (242 mg, 2 mmol). Reaction time: 1 h. Purification by flash chromatography (pentane/diethyl ether = 99:1) yielded diethyl 2-allylterephthalate (**5e**) as a light yellow oil (400 mg, 76 %).

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 7.87-7.82 (m, 3H), 5.99-5.86 (m, 1H), 5.00-4.97 (m, 2 H), 4.36-4.27 (m, 4 H), 3.60 (d, <sup>3</sup>J(H,H) = 6.6 Hz, 2 H), 1.37-1.30 (m, 3 H).

**<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>, 25 °C): δ = 167.5, 166.3, 141.7, 137.1, 134.5, 133.6, 132.3, 130.8, 128.7, 116.5, 62.0, 61.7, 38.6, 14.7, 14.6.

**MS** (70 eV, EI): m/z (%): 262 (62) [M]<sup>+</sup>, 247 (91), 217 (100), 205 (14), 189 (20), 177 (34), 171 (25), 161 (9), 143 (22), 117 (49), 115 (62).

**IR** (KBr):  $\tilde{\nu}$  = 2980 (s), 2907 (m), 1722 (vs), 1638 (w), 1477 (m), 1407 (m), 1366 (s), 1269 (vs), 1188 (m), 1110 (vs), 1070 (m), 1021 (m), 915 (m), 753 (m), 732 (m).

**HRMS** for C<sub>15</sub>H<sub>18</sub>O<sub>4</sub> (262.3010): calc.: 262.1205 [M]<sup>+</sup>  
found: 262.1210 [M]<sup>+</sup>

Preparation of 2-allylbenzophenone (**5f**):

Prepared according to **TP** from 2-iodobenzophenone (830 mg, 2.7 mmol), lithium neopentylcuprate (**1**) (2.8 mmol) and allyl bromide (302 mg, 2.5 mmol). Reaction time: 1 h. Purification by flash chromatography (pentane) yielded 2-allylbenzophenone (**5f**) as a light yellow oil (480 mg, 80 %).

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 7.88-7.80 (m, 3 H), 7.60-7.28 (m, 6 H), 6.01-5.81 (m, 1H), 5.06-4.96 (m, 2 H), 4.36-4.27 (m, 4 H), 3.46 (d, <sup>3</sup>J(H,H) = 6.6 Hz, 2 H).

**<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>, 25 °C): δ = 196.9, 136.6, 136.2, 134.5, 132.5, 131.6, 130.4, 129.6, 128.3, 127.9, 116.0, 39.6.

**MS** (70 eV, EI): m/z (%): 222 (40), 207 (100), 178 (10), 165 (15), 145 (22), 115 (30), 105 (9), 91 (5), 77 (27).

**IR** (KBr):  $\tilde{\nu}$  = 3511 (w, br), 3062 (m), 2956(vs), 2926 (vs), 2855 (s), 1666 (vs), 1598 (vs), 1580 (s), 1477 (s), 1465 (s), 1448 (vs), 1364 (s), 1315 (vs), 1269 (vs), 1154 (m), 999 (m), 928 (vs), 762 (vs), 702 (vs), 639 (s).

**HRMS** for C<sub>16</sub>H<sub>14</sub>O (224.2545): calc.: 224.0837 [M]<sup>+</sup>  
found: 224.0829 [M]<sup>+</sup>

Preparation of 2-methylbenzophenone (**5g**):

Prepared according to **TP** from 2-iodobenzophenone (620 mg, 2.0 mmol), lithium neopentylcuprate (**1**) (2.2 mmol) and methyl iodide (0.12 mL, 1.9 mmol). Reaction time: 1 h. Purification by flash chromatography (pentane/diethyl ether gradient) yielded 2-methylbenzophenone (**5g**) as a light yellow oil (300 mg, 80 %).

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 7.74-7.71 (m, 3 H), 7.50 (tt, <sup>3</sup>J(H,H) = 7.3 Hz and <sup>4</sup>J(H,H) = 1.3 Hz, 1 H), 7.40-7.14 (m, 5 H), 2.25 (s, 3 H).

**<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>, 25 °C): δ = 199.0, 139.0, 138.1, 137.1, 133.5, 130.6, 130.5, 128.9, 128.8, 125.8, 113.9, 20.4.

**MS** (70 eV, EI): m/z (%): 195 (100) [M]<sup>+</sup>, 178 (15), 165 (10), 152 (8), 119 (34), 105 (30), 91 (55), 77 (45), 65 (20), 51 (15), 39 (10).

**IR** (KBr):  $\tilde{\nu}$  = 3511 (w, br), 3062 (m), 2936(vs), 2855 (w), 1676 (vs), 1562 (s), 1470 (s), 1458 (s), 1384 (m), 1315 (s), 1134 (w), 902 (m), 757 (vs), 701 (s).

**HRMS** for C<sub>14</sub>H<sub>12</sub>O (196.2445): calc.: 196.0888 [M]<sup>+</sup>  
found: 196.0881 [M]<sup>+</sup>

Preparation of 2,2-dimethyl-1-[4-(2-propenyl)phenyl]-1-propanone (**5h**):

Prepared according to **TP** from 4-iodophenyl *t*-butyl ketone (290 mg, 1.0 mmol), lithium neopentylcuprate (**1**) (1.2 mmol) and allyl bromide (109 mg, 0.9 mmol). Reaction time: 1.5 h. Purification by flash chromatography (pentane/diethyl ether 100:1) yielded 2,2-dimethyl-1-[4-(2-propenyl)phenyl]-1-propanone (**5f**) as a light yellow oil (170 mg, 93 %).

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 7.60 (d, <sup>3</sup>J(H,H) = 8.3 Hz, 2 H), 7.14 (d, <sup>3</sup>J(H,H) = 8.3 Hz, 2 H), 5.94-5.80 (m, 1 H), 5.04-4.98 (m, 2 H), 3.33 (d, <sup>3</sup>J(H,H) = 6.6 Hz, 2 H), 1.26 (s, 9 H).

**<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 208.7, 143.8, 136.9, 136.5, 128.8, 128.6, 116.8, 44.5, 40.4, 28.5.

**MS** (70 eV, EI): m/z (%): 202 (1) [M]<sup>+</sup>, 145 (100), 115 (18), 101 (2).

**IR** (KBr):  $\tilde{\nu}$  = 2968 (s), 2906 (s), 1672 (vs), 1606 (vs), 1477 (m), 1402 (s), 1366 (m), 1277 (s), 1171 (s), 962 (s), 916 (m), 824 (m), 759 (m), 560 (w).

**HRMS** for C<sub>14</sub>H<sub>18</sub>O (202.2921): calc.: 202.1358 [M]<sup>+</sup>  
found: 202.1330 [M]<sup>+</sup>

Preparation of 3-[4-(2,2-dimethylpropanoyl)phenyl]cyclohexanone (**5i**):

Prepared according to **TP** from 4-iodophenyl *t*-butyl ketone (290 mg, 1.0 mmol), lithium neopentylcuprate (**1**) (1.2 mmol), 2-cyclohexen-1-one (0.12 mL, 1.2 mmol) and trimethylsilyl chloride (0.303 mL, 2.4 mmol). Reaction time: 2 h. Purification by flash chromatography (pentane/diethyl ether 9:1) yielded 3-[4-(2,2-dimethylpropanoyl)phenyl]cyclohexanone (**5f**) as a light yellow oil (150 mg, 60 %).

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 7.63 (d, <sup>3</sup>J(H,H) = 8.3 Hz, 2 H), 7.18 (d, <sup>3</sup>J(H,H) = 8.3 Hz, 2 H), 3.03-2.93 (m, 1 H), 2.56-1.49 (m, 8 H), 1.27 (s, 9 H).

**<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 210.8, 208.7, 147.7, 137.1, 129.0, 127.4, 126.7, 48.9, 44.9, 44.5, 41.5, 32.9, 28.5, 25.8.

**MS** (70 eV, EI): m/z (%): 258 (1) [M]<sup>+</sup>, 201 (100), 144 (1), 131 (3), 115 (4), 103 (2).

**IR** (KBr):  $\tilde{\nu}$  = 3413 (m, br), 2935 (vs), 2870 (s), 1712 (vs), 1671 (vs), 1606 (s), 1477 (s), 1448 (m), 1414 (m), 1395 (m), 1366 (s), 1276 (s), 1198 (m), 1172 (vs), 962 (vs), 842 (m), 768 (m), 710 (w).

**HRMS** for C<sub>17</sub>H<sub>22</sub>O<sub>2</sub> (258.3554): calc.: 258.1620 [M]<sup>+</sup>  
found: 258.1629 [M]<sup>+</sup>

Preparation of 4-acetylbenzophenone (**5j**):

Prepared according to **TP** from 4-iodoacetophenone (240 mg, 1.0 mmol), lithium neophylcuprate (**2**) (1.2 mmol) and benzoyl chloride (0.1 mL, 0.9 mmol). Reaction time: 1.5 h. Purification by flash chromatography (pentane/diethyl ether = 9:1) yielded 4-acetylbenzophenone (**5j**) as a light yellow oil (155 mg, 77 %).

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 7.98 (dd, <sup>3</sup>J(H,H) = 8 Hz and <sup>4</sup>J(H,H) = 1.8 Hz, 2 H), 7.79 (dd, <sup>3</sup>J(H,H) = 8 Hz and <sup>4</sup>J(H,H) = 1.8 Hz, 2 H), 7.73 (m, 2 H), 7.55 (dt, <sup>3</sup>J(H,H) = 8 Hz and <sup>4</sup>J(H,H) = 1.4 Hz, 1 H), 7.43 (t, <sup>3</sup>J(H,H) = 8 Hz, 2 H), 2.59 (s, 3 H).

**<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>, 25 °C): δ = 197.9, 196.3, 141.7, 140.0, 137.3, 133.4, 130.5, 130.4, 129.2, 128.9, 128.5, 27.3.

**MS** (70 eV, EI): m/z (%): 224 (29) [M]<sup>+</sup>, 209 (90), 181 (8), 167 (100), 153 (11), 147 (20), 119 (3), 105 (34).

**IR** (KBr):  $\tilde{\nu}$  = 3435 (vs, br), 1689 (vs), 1657 (vs), 1597 (m), 1579 (w), 1447 (s), 1402 (s), 1356 (s), 1316 (s), 1277 (vs), 1180 (w), 1072 (s), 939 (m), 928 (m), 850 (m), 794 (m), 736 (m), 699 (vs), 674 (m).

**HRMS** for C<sub>15</sub>H<sub>12</sub>O<sub>2</sub> (224.2545): calc.: 224.0837 [M]<sup>+</sup>  
found: 224.0829 [M]<sup>+</sup>

Preparation of 3-(4-acetylphenyl)cyclohexanone (**5k**):

Prepared according to **TP** from 4-iodoacetophenone (240 mg, 1.0 mmol), lithium neophylcuprate (**2**) (1.2 mmol), 2-cyclohexen-1-one (0.12 mL, 1.2 mmol) and trimethylsilyl chloride (0.303 mL, 2.4 mmol). Reaction time: 2h. Purification by flash chromatography (pentane/diethyl ether = 6:4) yielded 3-(4-acetylphenyl)cyclohexanone (**5k**) as a colourless oil (140 mg, 68 %).

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 7.85 (d, <sup>3</sup>J(H,H) = 8.3 Hz, 2 H), 7.24 (d, <sup>3</sup>J(H,H) = 8.3 Hz, 2 H), 3.06-2.96 (m, 1 H), 2.50 (s, 3 H), 2.46-1.66 (m, 8 H).

**<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>, 25 °C): δ = 228.5, 210.6, 150.0, 136.2, 129.3, 127.2, 48.8, 45.0, 41.5, 32.8, 27.0, 25.8.

**MS** (70 eV, EI): m/z (%): 216 (27) [M]<sup>+</sup>, 201 (100), 181 (11), 173 (8), 147 (3), 131 (16), 115 (4), 103 (4).

**IR** (KBr):  $\tilde{\nu}$  = 3430 (m, br), 2935 (vs), 2870 (s), 1712 (vs), 1657 (vs), 1606 (s), 1477 (s), 1448 (m), 1414 (m), 1395 (m), 1366 (s), 1276 (s), 1198 (m), 1172 (vs), 962 (vs), 842 (m), 768 (m), 710 (w).

**C<sub>14</sub>H<sub>16</sub>O<sub>2</sub>**: calc.: C: 77.75, H: 7.46.  
found: C: 77.76, H: 7.40.

Preparation of 2-acetylbenzaldehyde (**5l**):

Prepared according to **TP** from 2-iodobenzaldehyde (230 mg, 1 mmol), lithium neopentylcuprate (**1**) (1.2 mmol) and acetyl chloride (0.07 mL, 1.1 mmol). Reaction time: 4.5 h. Purification by flash chromatography (pentane/diethyl ether = 9:1) yielded 2-acetylbenzaldehyde (**5l**) as a colourless oil (103 mg, 70 %).

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 10.19 (s, 1 H), 7.92-7.72 (m, 2 H), 7.64-7.55 (m, 2 H), 2.69 (s, 3 H).

**<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>, 25 °C): δ = 193.9, 190.3, 140.0, 137.3, 133.4, 130.5, 130.4, 128.9, 28.3.

**MS** (70 eV, EI): m/z (%): 148 (3) [M]<sup>+</sup>, 133 (24), 120 (2), 111 (1), 105 (100), 91 (8), 85 (3).

**IR** (KBr):  $\tilde{\nu}$  = 3379 (m, br), 2924 (m), 2856 (m), 1732 (vs), 1696 (vs), 1637 (w), 1599 (m), 1574 (w), 1434 (w), 1407 (w), 1286 (m), 1209 (m), 1175 (w), 1079 (w), 996 (m), 917 (m), 754 (s), 636 (w).

**HRMS** for C<sub>10</sub>H<sub>10</sub>O (148.1586): calc.: 148.0524 [M]<sup>+</sup>  
found: 148.0538 [M]<sup>+</sup>

Preparation of 2-allylbenzaldehyde (**5m**):

Prepared according to **TP** from 2-iodobenzaldehyde (210 mg, 0.9 mmol), lithium neopentylcuprate (**1**) (1.2 mmol) and allyl bromide (110 mg, 0.9 mmol). Reaction time: 4.5 h. Purification by flash chromatography (pentane/diethyl ether = 98:2) yielded 2-allylbenzaldehyde (**5m**) as a colourless oil (100 mg, 80 %).

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 10.20 (s, 1 H), 7.77 (dd, <sup>3</sup>J(H,H) = 7.6 Hz and <sup>4</sup>J(H,H) = 1.3 Hz, 1 H), 7.46 (td, <sup>3</sup>J(H,H) = 7.5 Hz and <sup>4</sup>J(H,H) = 1.4 Hz, 1 H), 7.32 (t, <sup>3</sup>J(H,H) = 7.5 Hz, 1 H), 7.21 (t, <sup>3</sup>J(H,H) = 7.6 Hz, 1 H), 6.03-5.90 (m, 1 H), 5.04-4.88 (m, 2 H), 3.75 (d, <sup>3</sup>J(H,H) = 6.2 Hz, 2 H).

**<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>, 25 °C): δ = 191.3, 141.2, 135.9, 132.9, 130.6, 130.1, 125.9, 115.4, 35.5.

**MS** (70 eV, EI): m/z (%): 146 (19) [M]<sup>+</sup>, 131 (100), 128 (39), 118 (47), 117 (63), 155 (80), 103 (48).

**IR** (KBr):  $\tilde{\nu}$  = 2934 (vs, br), 2859 (vs, br), 1732 (vs), 1694 (vs), 1584 (w), 1579 (w), 1434 (m), 1368 (s), 1240 (vs), 1175 (w), 1112 (s), 1015 (s), 957 (m), 758 (s), 714 (m), 648 (w).

**HRMS** for C<sub>10</sub>H<sub>10</sub>O (146.1858): calc.: 146.0732 [M]<sup>+</sup>  
found: 146.0729 [M]<sup>+</sup>

Preparation of 2-allyl-3-methyl-2-cyclohexen-1-one (**8**):

Prepared according to **TP** from 2-iodo-3-methyl-cyclohexen-1-one (240 mg, 1 mmol), lithium neopentylcuprate (**1**) (1.2 mmol) and allyl bromide (110 mg, 0.9 mmol). Reaction time: 3.5 h. Purification by flash chromatography (pentane/diethyl ether = 96:4) yielded 2-allyl-3-methyl-cyclohexen-1-one (**8**) as a colourless oil (100 mg, 74 %).

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 5.73-5.64 (m, 1 H), 4.90-4.84 (m, 2 H), 2.99 (d, <sup>3</sup>J(H,H) = 6 Hz, 2 H), 2.63-1.90 (m, 6 H), 1.86 (s, 3 H).

**<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>, 25 °C): δ = 198.6, 157.2, 136.2, 126.7, 114.7, 38.1, 33.3, 29.6, 22.6, 21.6.

**MS** (70 eV, EI): m/z (%): 150 (43) [M]<sup>+</sup>, 135 (100), 131 (4), 122 (9), 119 (14), 117 (22), 107 (20).

**IR** (KBr):  $\tilde{\nu}$  = 2924 (m), 2868 (m), 1666 (vs), 1636 (s), 1430 (m), 1379 (m), 1360 (w), 1261 (w), 1191 (w), 1016 (w), 996 (w), 910 (m), 799 (w).

**HRMS** for C<sub>10</sub>H<sub>14</sub>O (150.2176): calc.: 150.1045 [M]<sup>+</sup>  
found: 150.1062 [M]<sup>+</sup>