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# **General information**

Unless otherwise stated, commercial reagents were used without further purification. Organic solvents were distilled and dried over molecular sieves. All reactions were performed under an argon atmosphere using an oven dried Schlenk tube. All compounds were purified by silica gel column chromatography and characterized by using <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy, high resolution MS, and FTIR spectroscopy. NMR spectra were recorded by using a Bruker AV 300 & 400 spectrometer. All chemical shifts ( $\delta$ ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts are related to solvent peaks [CDCl<sub>3</sub>:  $\delta$  =7.26 (<sup>1</sup>H) and 77.00 ppm (<sup>13</sup>C)]. All measurements were performed at room temperature unless otherwise stated. MS were recorded by using a MAT 95-XP (Thermo Electron) (Agilent) instrument. IR spectra were recorded by using an FTIR Nicolet 6700 (Thermo Electron) instrument.

#### General procedure for the hydroamination of isoprene with 4-methoxyaniline

Under an Ar atmosphere, an oven dried Schlenk tube was charged with 4-methoxyaniline (1 mmol, 123 mg), followed by  $Pd(cod)Cl_2$  (5 mol %) and L9 (5 mol %). Toluene (3 mL) and a magnetic stirrer bar were added followed by isoprene (4 equiv) and the reaction mixture was stirred at 100 ° C for the reported time. After completion, the reaction mixture was cooled to rt, diluted with ethyl acetate (10 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography using ethyl acetate/hexane as an eluent to afford the corresponding allylamine derivatives.

**Preparation of (DPEphos)Pd(\pi-allyl)Cl<sup>·</sup> 0.5 CH<sub>2</sub>Cl<sub>2</sub>(4)<sup>1</sup>: In an oven dried 50 mL round bottom flask equipped with a magnetic stir bar were charged with {Pd(\pi-allyl)Cl}<sub>2</sub> (0.137 mmol, 100 mg) and DPEphos (0.274 mmol, 146.8 mg). 10 mL of dry benzene was added to the flask and the resulting solutions were stirred for 15 min. The solution was concentrated under vacuum and the residue was dissolved in 0.5 mL dichloromethane. The solution gave light yellow crystals of <b>4** after diffusion of pentane after 12 h at -35°C. The residue was washed with pentane (5 mL x 2) and dried over vacuum to give 156.5 mg of **4** as a yellowish solid. Yield: 75%; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.20-7.55 (m, 22H), 6.75-6.98 (m, 5H), 5.80-5.85 (m, 1 H), 5.35 (s, 1H), 3.79 (br s, 4H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  =159.1 (t), 134.8, 133.9 (m), 133.3, 132.1 (m), 131.7, 129.6, 129.5, 129.4, 125.3, (m), 122.7 (m), 121.6 (d), 121.2, 78.2 (t, *J* = 15.3 Hz), 54.3. <sup>31</sup>P {<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  =12.8. HRMS (m/z) calcd. for C<sub>39 s</sub>H<sub>34</sub>Cl<sub>2</sub>OP<sub>2</sub>Pd (M)<sup>+</sup>, 763.0649; found 763.01.

# Spectroscopic and analytical data

### 4-Methoxy-*N*-(3-methylbut-2-enyl)aniline (3a)



Yield: 75%; colorless oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 6.71$  (d, J = 8.6 Hz, 2H), 6.52 (d, J = 8.6 Hz, 2H), 5.22-5.28 (m, 1H), 3.5-3.69 (m, s and bs, 6H), 1.67 (s, 3H), 1.62 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 152.3$ , 142.5, 135.6, 121.9, 114.9, 114.4, 56.0, 43.4, 25.9, 18.2; HRMS (EI, m/z) calcd. for C<sub>12</sub>H<sub>17</sub>NO (M)<sup>+</sup>, 191.1300; found 191.1304; IR-ATR (cm<sup>-1</sup>): 3405, 2930, 2831, 1617, 1521, 1467, 1372, 1233, 1037, 908, 818.

## *N*-(3-methylbut-2-enyl)aniline (3b)<sup>2</sup>



Yield: 70%; colorless oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.01-7.20 (m, 2H), 6.46-6.80 (m, 3H), 5.12-5.32 (m, 1H), 3.42-3.71 (m and bs, 3H), 1.77 (s, 3H), 1.72 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  =148.4, 135.6, 129.3, 121.7, 117.3, 113.2, 42.0, 25.7, 18.2; HRMS (EI, m/z) calcd. for C<sub>11</sub>H<sub>15</sub>N (M)<sup>+</sup>, 161.1198; found 161.1199; IR-ATR (cm<sup>-1</sup>): 3421, 3059, 2970, 2877, 1670, 1485, 1429, 1290, 966, 903.

#### 4-Methyl-N-(3-methylbut-2-enyl)aniline (3c)



Yield: 69%; colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 6.91$  (d, J = 8.48 Hz, 2H), 6.47 (d, J = 8.48 Hz, 2H), 5.23-5.27 (m, 1H), 3.75 (bs, 1H), 3.58 (d, J = 8.9 Hz, 2H), 2.16 (s, 3H), 1.66 (s, 3H), 1.62 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 146.2$ , 135.5, 129.9, 126.5, 121.9, 113.4, 42.5, 25.6, 20.6, 18.1; HRMS (EI, m/z) calcd. for C<sub>12</sub>H<sub>17</sub>N (M)<sup>+</sup>, 175.1355; found 175.1355; IR-ATR (cm<sup>-1</sup>): 3415, 3058, 2965, 2827, 1674, 1444, 1400, 1240, 968, 903.

### 4-Ethyl-N-(3-methylbut-2-enyl)aniline (3d)



Yield: 78%; light yellow oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 6.94$  (d, J = 8.80 Hz, 2H), 6.51 (d, J = 8.80 Hz, 2H), 5.24-5.28 (m, 1H), 3.54-3.60 (m, 3H), 2.46 (q, J = 7.6 Hz, 2H), 1.66 (s, 3H), 1.62 (s, 3H), 1.11 (t, J = 7.6 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 146.2$ , 135.5, 133.5, 128.7, 121.7, 113.3, 42.4, 28.0, 25.9, 18.3, 16.1; HRMS (EI, m/z) calcd. for C<sub>13</sub>H<sub>19</sub>N (M)<sup>+</sup>, 189.1510; found 189.1516; IR-ATR (cm<sup>-1</sup>): 3439, 3080, 2918, 2817, 1673, 1480, 1419, 1263, 960, 914.

### 3-Ethyl-N-(3-methylbut-2-enyl)aniline (3e)



Yield: 73%; light yellow oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 6.97$ -7.14 (m, 2H), 6.33-6.49 (m, 3H), 5.23-5.27 (m, 1H), 3.59 (d, J = 8.0 Hz, 2H), 2.49 (q, J = 8.0 Hz, 2H), 1.66 (s, 3H), 1.62 (s, 3H), 1.39 (t, J = 7.8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 148.6$ , 145.6, 135.7, 129.3, 121.9, 117.3, 112.9, 110.5, 42.0, 29.2, 26.1, 18.1, 15.9; HRMS (EI, m/z) calcd. for C<sub>13</sub>H<sub>19</sub>N (M)<sup>+</sup>, 189.1510; found 189.1512; IR-ATR (cm<sup>-1</sup>): 3433, 3090, 2908, 2817, 1670, 1480, 1429, 1243, 966, 954.

### 4-tert-Butyl-N-(3-methylbut-2-enyl)aniline (3f)



Yield: 78%; colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.07-7.17 (m, 3H), 6.46-6.52 (m, 2H), 5.22-5.28 (m, 1H), 3.59 (d, *J* = 6.4 Hz, 2H), 1.66 (s, 3H), 1.62 (s, 3H), 1.20 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 146.2, 140.4, 135.3, 126.1, 121.9, 112.7, 42.4, 34.0, 31.4, 25.9, 18.3;HRMS (EI,m/z) calcd. for C<sub>15</sub>H<sub>23</sub>N (M)<sup>+</sup>, 217.1822; found 217.1825; IR-ATR (cm<sup>-1</sup>): 3433, 3029, 2920, 1760, 1690, 1604, 1437, 1307, 1223, 1103, 957, 844.

# 4-Fluoro-N-(3-methylbut-2-enyl)aniline (3g)



Yield: 83%; colorless oil;<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 6.77-6.83$  (m, 3H), 6.44-6.49 (m, 2H), 5.20-5.25 (m, 1H), 3.56 (d, J = 6.42 Hz, 2H), 1.66 (s, 3H), 1.62 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 156.1$  (d,  $J_{CF} = 238.94$  Hz), 135.8, 128.8 (d,  $J_{CF} = 59.73$  Hz), 125.6, 121.4, 114.9 (d,  $J_{CF} = 134.40$  Hz), 42.8, 25.6, 17.9; HRMS (EI, m/z) calcd. for C<sub>11</sub>H<sub>14</sub>NF (M)<sup>+</sup>, 179.1104; found 179.1104; IR-ATR (cm<sup>-1</sup>): 3411, 3052, 3002, 2950, 1706, 1649, 1600, 1449, 1385, 908.

## 4-Chloro-N-(3-methylbut-2-enyl)aniline (3h)



Yield: 70%; light yellow oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.03-7.06 (m, 3H), 6.47-6.50 (m, 2H), 5.20-5.25 (m, 1H), 3.58 (d, *J* = 6.06 Hz, 2H), 1.67 (s, 3H), 1.63 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 146.5, 136.3, 129.1, 122.3, 120.9, 114.3, 42.6, 25.8, 18.0; HRMS (EI, m/z) calcd. for C<sub>11</sub>H<sub>14</sub>NCl (M)<sup>+</sup>, 195.0804; found 195.0809; IR-ATR (cm<sup>-1</sup>): 3412, 3042, 2911, 1568, 1469, 1425, 1392, 1105, 968, 951, 857.

## 3-Methyl-N-(naphthalen-2-ylmethyl)but-2-en-1-amine (3i)



Yield: 62%; colorless oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.29-8.04 (m, 7H), 5.07-5.12 (m, 1H), 4.00 (s, 2H), 2.35-2.39 (m, 2H), 1.53 (bs, 1H), 1.25 (m, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$ = 145.9, 136.7, 133.8, 131.9, 128.7, 127.7, 126.1, 125.6, 123.9, 112.6, 54.85, 45.3, 27.0, 21.7; HRMS (EI, m/z): calcd. for C<sub>16</sub>H<sub>19</sub>N(M)<sup>+</sup>, 225.1511; found: 225.1512; IR-ATR (cm<sup>-1</sup>): 3407, 3025, 2933, 1640, 1511, 1494, 1448, 1380, 1247, 1124, 967.

## 4-(3-Methylbut-2-enyl)morpholine (major isomer) (3j)



Colorless oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 5.64-5.82$ (m, 1H), 3.61-3.65 (m, 4H), 2.75-2.84 (m, 2H), 2.39-2.49 (m, 4H), 1.57 (s, 3H), 1.53 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 139.3$ , 125.1, 67.8, 53.6, 46.5, 22.2, 14.6; HRMS (ESI-TOF, m/z) calcd. for C<sub>9</sub>H<sub>18</sub>NO (M+H)<sup>+</sup>, 156.1382; found 156.1380; IR-ATR (cm<sup>-1</sup>): 2974, 2855, 1681, 1421, 1248, 903, 726, 649.

### 4-(3-Methylbut-3-en-2-yl)morpholine (minor isomer) (3j')

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.96-5.09(m, 2H), 3.61-3.69 (m, 4H), 2.31-2.49 (m, 1H), 2.22-2.39 (m, 4H), 1.18 (s, 3H), 1.07 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  =132.5, 122.8, 67.3, 67.2, 51.1, 16.3, 13.2.

### N-(cyclohex-2-enyl)-4-methoxyaniline (3k)<sup>2</sup>

Yield: 95%; colorless oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 6.81-6.90$  (m, 2H), 6.63-6.71 (m, 2H), 5.63-5.79 (m, 2H), 3.89 (bs, 2H), 3.72 (s, 3H), 2.00-2.02 (m, 2H), 1.85-1.89 (m, 1H), 1.49-1.69 (m, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 152.1$ , 141.1, 129.9, 129.8, 115.0, 55.8, 49.1, 29.0, 25.2, 19.8; HRMS (EI, m/z) calcd. for C<sub>13</sub>H<sub>17</sub>NO (M)<sup>+</sup>, 203.1310; found 203.1318; IR-ATR (cm<sup>-1</sup>): 3419, 2976, 2887, 1678, 1483, 1419, 1270, 903.

### *N*-(cyclohex-2-enyl)aniline (3l)<sup>2</sup>



Yield: 95%; colorless oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.01-7.22 (m, 2H), 6.50-6.80 (m, 3H), 5.70-5.90 (m, 2H), 3.98 (bs, 1H), 3.75 (br s, 1H), 2.03-2.08 (m, 2H), 1.89-1.93 (m, 1H), 1.59-1.69 (m, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 147.2, 130.2, 129.4, 128.6, 117.2, 113.3, 47.9, 28.9, 25.2, 19.7; HRMS (EI, m/z) calcd. for C<sub>12</sub>H<sub>15</sub>N (M)<sup>+</sup>, 173.1204; found 173.1209; IR-ATR (cm<sup>-1</sup>): 3432, 3022, 2887, 1680, 1570, 1447, 1240, 902.

## *N*-(cyclohex-2-enyl)-2-bromoaniline (3m)<sup>2</sup>



Yield: 40%; colorless oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.21-7.42 (m, 2H), 6.59-6.73 (m, 2H), 5.79-5.90 (m, 2H), 4.29-4.32 (m, 1H), 3.98 (br s, 1H), 2.03-2.08 (m, 2H), 1.88-1.94 (m, 1H), 1.59-1.67 (m, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 144.1, 132.5, 130.9, 129.1, 128.8, 117.3, 111.4, 110.5, 48.1, 28.7, 25.2, 19.7; HRMS (EI, m/z) calcd. for C<sub>12</sub>H<sub>14</sub>BrN (M)<sup>+</sup>, 251.0310; found 251.0317; IR-ATR (cm<sup>-1</sup>): 3429, 2986, 2247, 1618, 1475, 1420, 1279, 913.

# N-(cyclohex-2-enyl)-4-cyanoaniline (3n)



Yield: 49%; colorless oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.32-7.49 (m, 2H), 6.69-6.83 (m, 2H), 5.74-5.89 (m, 2H), 4.29-4.35 (m, 1H), 4.12 (br s, 1H), 2.03-2.10 (m, 2H), 1.88-1.97 (m, 1H), 1.61-1.77 (m, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 150.7, 134.5, 133.6, 130.1, 118.3, 112.8, 110.5, 49.7, 28.7, 25.3, 19.9; HRMS (EI, m/z) calcd. for C<sub>13</sub>H<sub>14</sub>N<sub>2</sub> (M)<sup>+</sup>, 198.1157; found 198.1154; IR-ATR (cm<sup>-1</sup>): 3429, 2986, 2347, 2275, 1608, 1555, 1435, 1420, 1279.

## *N*-(cyclohex-2-enyl)-4-trifluoromethylaniline (30)<sup>2</sup>



Yield: 77%; colorless oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.40-7.42 (m, 2H), 6.59-6.63 (m, 2H), 5.70-5.92 (m, 2H), 4.20-4.28 (m, 2H), 2.09-2.10 (m, 2H), 1.88-1.91 (m, 1H), 1.69-1.73 (m, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 149.9, 130.9, 127.1, 126.8 (q), 125.4 (d), 118.1 (q), 112.7, 48.3, 28.2, 25.3, 19.9; HRMS (EI, m/z) calcd. for C<sub>13</sub>H<sub>14</sub>F<sub>3</sub>N (M)<sup>+</sup>, 241.1078; found 241.1073; IR-ATR (cm<sup>-1</sup>): 3434, 2916, 2877, 1648, 1534, 1467, 1443, 1259.

## N-(cyclohex-2-enyl)-4-chloroaniline (3p)



Yield: 82%; colorless oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.18-7.32 (m, 2H), 6.78-6.88 (m, 2H), 5.80-5.89 (m, 2H), 4.10-4.18 (m, 2H), 2.19-2.23 (m, 2H), 1.86-1.91 (m, 1H), 1.77-1.79 (m, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 147.3, 133.8, 132.5, 129.4, 128.2, 116.1, 48.5, 28.2, 25.3, 19.9; HRMS (EI, m/z) calcd. for C<sub>12</sub>H<sub>14</sub>ClN (M)<sup>+</sup>, 207.0815; found 207.0819; IR-ATR (cm<sup>-1</sup>): 3431, 2946, 2877, 1678, 1544, 1437, 1412, 1293.

### *N*-(cyclohex-2-enyl)-3-ethylaniline (3q)<sup>2</sup>



Yield: 78%; colorless oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.10-7.22 (m, 2H), 6.61-6.68 (m, 2H), 5.70-5.79 (m, 2H), 4.32 (q, *J* = 7.2 Hz, 2H), 4.10-4.18 (m, 1H), 3.45 (br s, 1H), 2.09-2.13 (m, 2H), 1.81-1.87 (m, 1H), 1.70-1.75 (m, 3H), 1.39 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 147.3, 130.8, 130.4, 128.4, 127.2, 122.8, 116.1, 110.3, 48.5, 29.6, 28.2, 25.3, 19.9, 14.8; HRMS (EI, m/z) calcd. for C<sub>14</sub>H<sub>19</sub>N (M)<sup>+</sup>, 201.1517; found 201.1513; IR-ATR (cm<sup>-1</sup>): 3435, 2916, 2870, 1658, 1584, 1473, 1417, 1265.

## *N*-cyclohept-2-en-1-ylaniline (3r)<sup>2</sup>



Yield: 53%; colorless oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 7.13-7.24$  (m, 2H), 6.48-6.68 (m, 3H), 5.55-5.83 (m, 2H), 4.13 (br d, J = 8.3 Hz, 1H), 3.44-3.54 (m, 1H), 2.12-2.29 (m, 2H), 1.88-2.10 (m, 4H), 1.44-1.65 (m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 146.4$ , 136.7, 131.6, 129.4, 117.9, 114.1, 54.5, 33.7, 28.6, 28.5, 26.6; HRMS (EI, m/z): calcd. for C<sub>13</sub>H<sub>17</sub>N(M)<sup>+</sup>, 187.1350; found: 187.1355; IR-ATR (cm<sup>-1</sup>): 3409, 3027, 2892, 1672, 1599, 1449, 1420, 1364, 1269, 1068, 966, 905.

### (E)-N-(pent-2-enyl)aniline (3s)



Yield: 49%; colorless oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.15-7.28 (m, 2H), 6.63-6.80 (m, 3H), 5.59-5.75 (m, 2H), 3.90-3.98 (bs, 1H), 3.70-3.75 (m, 2H), 1.66-1.69 (m, 2H), 1.28-1.34 (m, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 146.4, 133.9, 129.1, 125.5, 115.2, 113.9, 50.9, 21.7, 17.7; HRMS (EI): calcd. for C<sub>11</sub>H<sub>15</sub>N (M)<sup>+</sup>, 161.1204; found: 161.1209; IR-ATR (cm<sup>-1</sup>): 3433, 3027, 2892, 1672, 1555, 1449, 1420, 1364, 1269, 1068, 966, 905, 728.

### (E)-N-(4-phenylbut-2-enyl)aniline (3t)



Yield: 55%; colorless oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.04-7.14 (m, 5H), 6.47-6.66 (m, 5H), 5.24-5.31 (m, 1H), 4.99-5.06 (m, 1H), 3.57-3.65 (m, 3H), 1.98-2.06 (m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 147.8, 139.4, 131.7, 129.2, 123.9, 122.0, 121.1, 117.9, 113.5, 112.8, 42.2, 39.7; HRMS (ESI-TOF, m/z) calcd. for  $C_{16}H_{17}N$  (M)<sup>+</sup>, 223.1361; found 223.1369;IR-ATR (cm<sup>-1</sup>): 3408, 3037, 2928, 1608, 1553, 1400, 1351, 1274, 1106, 1021, 903.

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- 2. O. Löber, M. Kawatsura and J. F. Hartwig, J. Am. Chem. Soc. 2001, 123, 4366-4367



<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) spectrum of 4-Methoxy-*N*-(3-methylbut-2-enyl)aniline(**3a**)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of 4-Methyl-*N*-(3-methylbut-2-enyl)aniline(**3c**)



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of 4-Methyl-*N*-(3-methylbut-2-enyl)aniline(**3c**)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of 4-Ethyl-*N*-(3-methylbut-2-enyl)aniline(**3d**)







<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of 3-Ethyl-*N*-(3-methylbut-2-enyl)aniline (3e)



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of 3-Ethyl-*N*-(3-methylbut-2-enyl)aniline (3e)







<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) spectrum of 4-Fluoro-*N*-(3-methylbut-2-enyl)aniline (**3g**)



<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) spectrum of 4-Fluoro-*N*-(3-methylbut-2-enyl)aniline (**3g**)





<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) spectrum of 3-Methyl-*N*-(naphthalen-2-ylmethyl)but-2-en-1-amine (**3i**)



<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) spectrum of 3-Methyl-*N*-(naphthalen-2-ylmethyl)but-2-en-1-amine (3i)





<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) spectrum of (*E*)-*N*-(pent-2-enyl)aniline (**3s**)



<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) spectrum of (*E*)-*N*-(4-phenylbut-2-enyl)aniline (**3t**)



