

# A non-symmetric pincer-catalyzed Suzuki-Miyaura arylation of benzyl halides and other non-activated unusual coupling partners

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## 1. General procedures.

All reagents were purchased and used as received except when indicated. Chemical shifts ( $\delta$ ) are given in ppm downfield from Me<sub>4</sub>Si and refer as internal standard to the residual solvent (unless indicated) CDCl<sub>3</sub>: ( $\delta$  = 7.26 for <sup>1</sup>H and 77.00 for <sup>13</sup>C). Coupling constants, *J*, are reported in hertz (Hz). Melting points were determined in a capillary tube and are uncorrected. TLC was carried out on SiO<sub>2</sub>, and the spots were located with UV light. Flash chromatography was carried out on SiO<sub>2</sub>. Drying of organic extracts during work-up of reactions was performed over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Evaporation of solvents was accomplished with a rotatory evaporator.

**2. General Procedure for Suzuki cross-coupling reactions employing  $\alpha$ -bromoenone **2** and arylboronic acids.** Pincer complex **1**<sup>1</sup> (4 mol%) was added to a mixture of bromoenone **2**<sup>2</sup> (1 mmol), arylboronic acid (1.5 mmol), Na<sub>2</sub>CO<sub>3</sub> (2 mmol) and water (1 ml) in a 5 ml round-bottom flask open to the atmosphere. After stirring at 100°C for 12 hours, the reaction mixture was cooled and water (5 ml) was added. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 6 ml). The combined organic extracts were dried over anhydrous sodium sulphate and concentrated *in vacuo*. The residue was dissolved in CDCl<sub>3</sub> and analyzed by <sup>1</sup>H NMR using diethylene glycol dimethyl ether as an internal standard.

**(E)-3,4-Diphenylbut-3-en-2-one (3a).**<sup>2</sup> Yield determined by <sup>1</sup>H-NMR: 74%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 2.32 (s, 3H), 7.03 (m, 2H), 7.18 (m, 5H), 7.39 (m, 3H), 7.65 (s, 1H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 28.4, 128.3, 128.7, 129.5, 129.7, 129.9, 130.0, 131.3, 135.0, 137.4, 139.3, 141.3.

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<sup>1</sup> Inés, B.; SanMartín, R.; Churruga, F.; Domínguez, E.; Urtiaga, M. K.; Arriortua, M. I. *Organometallics* **2008**, *28*, 2833-2839.

<sup>2</sup> Banks, J. C.; Van Mele, D.; Frost, C. G. *Tetrahedron Lett.* **2006**, *47*, 2863-2866.

**(E)-3-(4-Methoxyphenyl)-4-phenylbut-3-en-2-one (3b).**<sup>2</sup> Yield: 86%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ (ppm): 2.33 (s, 3H), 6.92 (m, 1H), 6.95 (m, 1H), 7.07 (m, 4H), 7.19 (m, 3H), 7.61 (s, 1H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ (ppm): 27.9, 55.3, 114.5, 128.3, 128.9, 129.1, 130.7, 130.8, 134.8, 138.8, 140.0, 159.3, 199.9.

**(E)-3-(Naphthalen-1-yl)-4-phenylbut-3-en-2-one (3c).**<sup>2</sup> Yield determined by <sup>1</sup>H-NMR: 38%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ (ppm): 2.13 (s, 3H), 6.93 (m, 2H), 7.00 (m, 2H), 7.14 (m, 1H), 7.32 (m, 1H), 7.47 (m, 3H), 7.74 (m, 1H), 7.92 (m, 3H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ (ppm): 28.4, 125.3, 126.5, 126.8, 127.3, 127.6, 128.8, 129.0, 129.1, 129.8, 131.3, 132.3, 134.3, 134.8, 135.6, 139.0, 140.2, 200.0.

**3. General Procedure for Suzuki cross-coupling reactions employing aryl halides and *n*-butylboronic acid.** Pincer complex **1** (2 mol%) was added to a mixture of aryl halide (1 mmol), *n*-butylboronic acid (1.5 mmol), K<sub>2</sub>CO<sub>3</sub> (2 mmol) and *o*-xylene (2 ml) in a 5 ml round-bottom flask under argon. After stirring at 130°C for 20 hours, the reaction mixture was cooled and water (5 ml) was added. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 6 ml). The combined organic extracts were dried over anhydrous sodium sulphate and concentrated *in vacuo*. The residue was dissolved in CDCl<sub>3</sub> and analyzed by <sup>1</sup>H NMR using diethylene glycol dimethyl ether as an internal standard.

**1-(4-Butylphenyl)ethanone (4a).**<sup>3</sup> Yield: 97%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ (ppm): 0.93 (t, *J*=7.7 Hz, 3H), 1.33 (m, 2H), 1.61 (m, 2H), 2.58 (s, 3H), 2.66 (t, *J* = 7.7 Hz, 2H), 7.26 (d, *J*=8.4, 2H), 7.87 (d, *J*=8.4, 2H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ (ppm): 13.9, 22.3, 26.5, 33.2, 35.7, 128.4, 128.6, 134.9, 148.8, 197.8.

<sup>3</sup>Pérez, I.; Pérez-Sestelo, J.; Sarandeses, L. A. *Org. Lett.* **1999**, *1*, 1267-1269.

**1-"Butyl-4-methoxybenzene (4b).**<sup>4</sup> Yield determined by <sup>1</sup>H-NMR: 61%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ (ppm): 0.96 (t, *J*=7.3 Hz, 3H), 1.40 (m, 2H), 1.60 (m, 2H), 2.59 (t, *J*=7.6 Hz, 2H), 3.82 (s, 3H), 6.86 (d, *J*=8.5 Hz, 2H), 7.13 (d, *J*=8.4 Hz 2H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ (ppm): 13.6, 22.3, 33.9, 34.7, 55.2, 113.6, 129.2, 134.9, 157.6.

**1-"Butyl-4-nitrobenzene (4c).**<sup>4</sup> Yield determined by <sup>1</sup>H-NMR: 68%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ (ppm): 0.92 (t, *J*=7.2 Hz, 3H), 1.36 (m, 2H), 1.60 (m, 2H), 2.70 (t, *J*=7.8 Hz, 2H), 7.35 (d, *J*=8.7 Hz 2H), 8.14 (d, *J*=8.7 Hz, 2H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ (ppm): 13.8, 22.2, 33.0, 35.5, 123.5, 129.1, 146.2, 150.8.

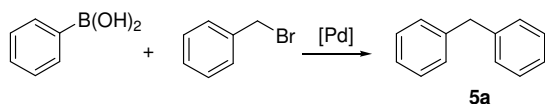
**4-"Butylbenzotrile (4d).**<sup>5</sup> Yield determined by <sup>1</sup>H-NMR: 74%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ (ppm): 0.93 (t, *J*=7.2 Hz, 3H), 1.35 (m, 2H), 1.60 (m, 2H), 2.66 (t, *J*=7.6 Hz, 2H), 7.27 (d, *J*=7.6 Hz, 2H), 7.55 (d, *J*=7.6 Hz, 2H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ (ppm): 13.7, 22.1, 32.9, 35.7, 109.3, 119.1, 129.1, 131.9, 148.5.

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<sup>4</sup> Kondolff, I.; Doucet, H.; Santelli, M. *Tetrahedron* **2004**, *60*, 3813-3818.

<sup>5</sup> Kataoka, N.; Shelby, Q.; Stambuli, J.; Hartwing, F. *J. Org. Chem.* **2002**, *67*, 5553-5566.

#### 4. Selected Suzuki coupling assays between phenylboronic acid and benzyl bromide



Entry	reaction conditions <sup>a</sup>	5a (%) <sup>b</sup>
1	<b>1</b> (2 mol%), K <sub>2</sub> CO <sub>3</sub> , MeOH, 100°C	52
2	<b>1</b> (2 mol%), K <sub>2</sub> CO <sub>3</sub> , EtOH, 100°C	33
3	<b>1</b> (2 mol%), K <sub>2</sub> CO <sub>3</sub> , MeOH:H <sub>2</sub> O (3:1), 100°C	-
4	<b>1</b> (2 mol%), K <sub>2</sub> CO <sub>3</sub> , H <sub>2</sub> O, 100°C	61
5	<b>1</b> (2 mol%), Na <sub>2</sub> CO <sub>3</sub> , H <sub>2</sub> O, 100°C	67
6	<b>1</b> (2 mol%), Na <sub>2</sub> CO <sub>3</sub> , H <sub>2</sub> O, 120°C	44
7	<b>1</b> (2 mol%), Na <sub>2</sub> CO <sub>3</sub> , H <sub>2</sub> O, 80°C	10
8 <sup>c</sup>	<b>1</b> (2 mol%), Na <sub>2</sub> CO <sub>3</sub> , H <sub>2</sub> O, 80°C	12
9	<b>1</b> (1 mol%), Na <sub>2</sub> CO <sub>3</sub> , H <sub>2</sub> O, 100°C	67
10	<b>1</b> (10 <sup>-1</sup> mol%), Na <sub>2</sub> CO <sub>3</sub> , H <sub>2</sub> O, 100°C	67
11	<b>1</b> (10 <sup>-2</sup> mol%), Na <sub>2</sub> CO <sub>3</sub> , H <sub>2</sub> O, 100°C	13
12	<b>1</b> (10 <sup>-3</sup> mol%), Na <sub>2</sub> CO <sub>3</sub> , H <sub>2</sub> O, 100°C	-
13 <sup>d</sup>	<b>1</b> (10 <sup>-1</sup> mol%), Na <sub>2</sub> CO <sub>3</sub> , H <sub>2</sub> O, 100°C	38
14 <sup>e</sup>	<b>1</b> (10 <sup>-1</sup> mol%), Na <sub>2</sub> CO <sub>3</sub> , H <sub>2</sub> O, 100°C	65
15 <sup>c,e</sup>	<b>1</b> (10 <sup>-1</sup> mol%), Na <sub>2</sub> CO <sub>3</sub> , H <sub>2</sub> O, 100°C	62

<sup>a</sup> 1.5 equiv. of phenylboronic acid, 1.0 equiv. of benzyl bromide, and 2.0 eq. of base were employed for a reaction time of 3h. <sup>b</sup> Determined by <sup>1</sup>H-NMR on the basis of the amount of starting benzyl bromide. Diethylene glycol dimethyl ether was used as internal standard. <sup>c</sup> The mixture was allowed to react for 24h. <sup>d</sup> 1.0 equiv. of phenylboronic acid were used. <sup>e</sup> 2.0 equiv. of phenylboronic acid were used.

**5. General Procedure for Suzuki cross-coupling reactions employing benzyl bromides and aryl boronic acids.** Pincer complex **1** (0.1 mol%) was added to a mixture of benzyl bromide (1 mmol), arylboronic acid (1.5 mmol), Na<sub>2</sub>CO<sub>3</sub> (2 mmol) and water (1 ml) in a 5 ml round-bottom flask open to the atmosphere. After stirring at 100°C for 3 hours, the reaction mixture was cooled and water (5 ml) was added. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 6 ml). The combined organic extracts

were dried over anhydrous sodium sulphate and concentrated *in vacuo*. The residue was dissolved in CDCl<sub>3</sub> and analyzed by <sup>1</sup>H NMR using diethylene glycol dimethyl ether as an internal standard.

**Diphenylmethane (5a).**<sup>6</sup> Yield determined by <sup>1</sup>H-NMR: 67%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ (ppm): 4.14 (s, 2H), 7.24-7.30 (m, 6H), 7.43 (t, *J*=7.5 Hz 4H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ (ppm): 42.2, 126.3, 128.7, 129.2, 141.3.

**1-Benzyl-4-methoxy-benzene (5b).**<sup>6</sup> Yield determined by <sup>1</sup>H-NMR: 92%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ (ppm): 3.81 (s, 3H), 3.96 (s, 2H), 6.86 (d, *J*=8.5 Hz, 2H), 7.18 (d, *J*=8.5 Hz, 2H), 7.24-7.29 (m, 3H), 7.32 (t, *J*=7.3 Hz, 2H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ (ppm): 41.2, 55.4, 114.0, 126.1, 128.6, 129.0, 130.0, 133.4, 141.7, 158.1.

**4-Benzyl-1,2-dimethoxy-benzene (5c).**<sup>7</sup> Yield determined by <sup>1</sup>H-NMR: 82%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ (ppm): 3.84-3.87 (2 s, 6H), 3.96 (s, 3H), 6.74-6.83 (m, 3H), 7.20-7.34 (m, 5H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ (ppm): 41.4, 55.7, 55.8, 111.1, 111.2, 112.2, 120.7, 120.8, 125.9, 128.3, 128.6, 133.5, 141.2, 147.3, 148.8.

**1-Benzyl-naphthalene (5d).**<sup>8</sup> Yield determined by <sup>1</sup>H-NMR: 71%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ (ppm): 4.53 (s, 2H), 7.24-7.31 (m, 3H), 7.32-7.40 (m, 3H), 7.47-7.56 (m, 3H), 7.85 (d, *J*=8.4 Hz, 1H), 7.91-9.97 (m, 1H), 8.05-8.12 (m, 1H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ (ppm): 39.2, 124.4, 125.7, 126.1, 126.2, 127.5, 127.5, 128.6, 128.8, 128.9, 132.3, 134.1, 136.8, 140.8.

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<sup>6</sup> Molander, G. A.; Elia, M. D. *J. Org. Chem.* **2006**, *71*, 9198-9202.

<sup>7</sup> Tsuchimoto, T.; Tobita, K.; Hiyama, T.; Fukazawa, S. *J. Org. Chem.* **1997**, *62*, 6997-7005.

<sup>8</sup> McLaughlin, M. *Org. Lett.* **2005**, *7*, 4875-4878.

**2-Benzyl-naphthalene (5e).**<sup>9</sup> Yield determined by <sup>1</sup>H-NMR: 82%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ (ppm): 4.20 (s, 2H), 7.25-7.29 (m, 3H), 7.32-7.40 (m, 3H), 7.47-7.51 (m, 2H), 7.69 (s, 1H), 7.81-7.85 (m, 3H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ (ppm): 42.6, 125.8, 126.4, 126.6, 127.6, 128.0, 128.1, 128.1, 128.5, 128.8, 129.0, 129.5, 132.5, 134.1, 139.1, 141.4.

**2-(4-Methoxy-benzyl)-naphthalene (5f).**<sup>10</sup> Yield determined by <sup>1</sup>H-NMR: 82%. M.p. (EtAcO:hexane 4:6): 54-56°C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ (ppm): 3.81 (s, 3H), 4.11 (s, 2H), 6.85-6.88 (m, 2H), 7.16-7.19 (m, 2H), 7.33 (dd, *J*=8.4, 1.7 Hz, 1H), 7.43-7.48 (m, 2H), 7.64 (s, 1H), 7.76-7.83 (m, 3H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ (ppm): 41.2, 55.2, 113.9, 125.3, 125.9, 126.9, 127.5, 127.5, 127.6, 128.0, 129.9, 132.0, 133.1, 133.6, 139.0, 158.0.

**2-(3,4-Dimethoxy-benzyl)-naphthalene (5g).** Yield: 76%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ (ppm): 3.83 (s, 3H), 3.87 (s, 3H), 4.11 (s, 2H), 6.77-6.81 (m, 3H), 7.33 (dd, *J*=8.4, 1.7 Hz, 1H), 7.43-7.47 (m, 2H), 7.64 (s, 1H), 7.77-7.83 (m, 3H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ (ppm): 41.6, 55.7, 55.8, 111.2, 112.3, 120.9, 125.3, 125.9, 126.8, 127.5, 127.5, 127.6, 128.0, 132.0, 133.5, 133.5, 138.8, 147.4, 148.9. MS *m/z* (%): 278.13 (100), 247.11 (60), 231.08 (14), 203.08 (24). HRSM *m/z*: calcd. for C<sub>19</sub>H<sub>18</sub>O<sub>2</sub>: 278.1307; found: 278.1303.

**2,4'-Methylenedinaphthalene (5h).** Yield: >99%. M.p. : (EtOAc/Hexanes, 4:6) 89-91 °C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ (ppm): 4.7 (s, 2H), 7.43-7.58 (m, 7H), 7.72 (s, 1H), 7.80-7.99 (m, 5H), 7.98 (d, *J*=8.0 Hz, 1H), 8.11 (d, *J*=7.4 Hz, 1H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ (ppm): 39.1, 124.2, 125.7, 125.5, 125.5, 125.9, 126.0, 126.9, 127.2, 127.4, 127.4, 127.5, 127.6, 127.9, 128.6, 132.1, 132.1, 133.6, 133.9, 136.4, 138.1. MS *m/z* (%): 268.12 (100),

<sup>9</sup> Limmert, M. E.; Roy, A. H.; Hartwing, J. F. *J. Org. Chem.* **2005**, *70*, 9364-9370.

<sup>10</sup> Utley, J. H. P.; Rozenberg, G. G. *Tetrahedron* **2002**, *58*, 5251-5265.

267.12 (67), 265.10 (22), 253.10 (31), 252.09 (31). HRSM m/z: calcd. for C<sub>21</sub>H<sub>16</sub>: 268.1252; found: 268.1250.

**2-(2,4,6-Trimethyl-benzyl)-naphthalene (5i).** Yield: 19%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ (ppm): 2.26 (s, 6H), 2.36 (s, 3H), 4.20 (s, 2H), 6.96 (s, 2H), 7.28 (dd, *J*=8.4, 1.5 Hz, 1H), 7.35 (s, 1H), 7.39-7.45 (m, 2H), 7.69-7.82 (m, 3H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ (ppm): 20.1, 20.9, 34.9, 125.1, 125.5, 125.8, 127.0, 127.5, 127.5, 127.9, 128.9, 131.9, 133.5, 133.6, 135.7, 137.1, 137.6. MS m/z (%): 260.15 (98), 245.13 (100), 230.10 (30), 215.08 (22), 141.07 (21), 132.09 (68), 115.05 (17). HRSM m/z: calcd. for C<sub>20</sub>H<sub>20</sub>: 260.1565; found: 260.1559.

**1-(4-Nitro-benzyl)-naphthalene (5j).**<sup>11</sup> Yield determined by <sup>1</sup>H-NMR: 69%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ (ppm): 4.54 (s, 2H), 7.31-7.34 (s, 3H), 7.45-7.52 (m, 3H), 7.82-7.92 (s, 3H), 8.10-8.13 (m, 2H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ (ppm): 38.9, 123.7, 123.8, 125.5, 125.8, 126.3, 127.6, 127.9, 128.9, 129.3, 131.7, 134.0, 134.7, 146.4, 148.5.

**4-Benzyl-benzonitrile (5k).**<sup>8</sup> Yield determined by <sup>1</sup>H-NMR: 61%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ (ppm): 4.06 (s, 2H), 7.17-7.20 (m, 3H), 7.26-7.30 (m, 2H), 7.36-7.38 (m, 2H), 7.60-7.62 (m, 2H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ (ppm): 42.6, 110.9, 119.9, 127.6, 129.8, 130.1, 131.0, 133.4, 141.2, 148.8.

**4-(4-Methoxybenzyl)benzonitrile (5l).**<sup>6</sup> Yield determined by <sup>1</sup>H-NMR: 94%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ (ppm): 3.69 (s, 3H), 3.87 (s, 2H), 6.76 (d, *J*=8.7 Hz, 2H), 6.98 (d, *J*=8.7 Hz, 2H), 7.17 (d, *J*=8.5 Hz, 2H), 7.45 (d, *J*=8.5 Hz, 2H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ (ppm): 41.0, 55.2, 109.8, 114.1, 118.9, 129.4, 129.9, 131.3, 132.2, 147.2, 158.3.

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<sup>11</sup> Inoh, J.-I.; Satoh, T.; Pivsa-Art, S.; Miura, M.; Nomura, M. *Tetrahedron Lett.* **1998**, *39*, 4673-4676.

**4-Naphthalen-1-ylmethyl-benzonitrile (5m).** Yield: 82%. M.p. : (EtAcO:Hexanes 2:8): 86-88 °C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ (ppm): 4.49 (s, 2H), 7.26-7.33 (m, 3H), 7.45-7.55 (m, 5H), 7.81-7.92 (m, 3H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ (ppm): 39.0, 109.9, 118.9, 123.8, 125.5, 125.7, 126.2, 127.6, 127.7, 128.8, 129.2, 131.7, 132.1, 133.9, 134.7, 146.3. MS m/z (%): 243.10 (100), 242.10 (38), 228.07 (10). HRSM m/z: calcd. for C<sub>18</sub>H<sub>13</sub>N: 243.1048; found: 243.1047.

**1-Benzyl-4-trifluoromethyl-benzene (5n).**<sup>8</sup> Yield determined by <sup>1</sup>H-NMR: 82%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ (ppm): 4.09 (s, 2H), 7.16-7.42 (m, 7H), 7.59 (d, *J*=8.1 Hz, 2H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ (ppm): 41.7, 124.4 (q, *J* = 272 Hz), 125.4 (q, *J*=4 Hz), 126.5, 128.5 (q, *J*=33 Hz), 128.6, 128.9, 129.2, 140.0, 145.3.

**1-Methoxy-4-(4-(trifluoromethyl)benzyl)benzene (5o).**<sup>12</sup> Yield determined by <sup>1</sup>H-NMR: 86%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ (ppm): 3.79 (s, 3H), 3.97 (s, 2H), 6.85 (d, *J*=8.7 Hz, 2H), 7.09 (d, *J*=8.1 Hz, 2H), 7.28 (d, *J*=8.7 Hz, 2H), 7.53 (d, *J*=8.1 Hz, 2H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ (ppm): 40.8, 55.2, 114.0, 124.3 (q, *J*=269.9 Hz), 125.3 (q, *J*=3.5 Hz), 128.3 (q, *J*=31.9 Hz), 129.0, 129.9, 132.0, 145.7, 158.2.

**1-(4-Trifluoromethyl-benzyl)-naphthalene (5p).** Yield >99%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ (ppm): 4.54 (s, 2H), 7.33-7.37 (m, 3H), 7.49-7.60 (m, 5H), 7.87 (d, *J*=8.2 Hz, 1H), 7.94-8.00 (m, 2H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ (ppm): 38.8, 123.9, 124.3 (q, *J*=271.8 Hz), 125.3 (q, *J*=3.7 Hz), 125.5, 125.7, 126.2, 127.5, 127.6, 128.4 (q, *J*=32.3 Hz), 128.8, 128.9, 131.9, 134.0, 135.5, 144.8. MS m/z (%): 286.09 (100), 217.10 (55), 215.08 (31), 202.07 (15). HRSM m/z: calcd. for C<sub>18</sub>F<sub>3</sub>: 286.0969; found: 286.0959.

<sup>12</sup> Itami, K.; Minero, M.; Kamei, T.; Yoshida, J.-I. *Org. Lett.* **2002**, *4*, 3635-3638.

**1-Benzyl-4-methyl-benzene (5q).**<sup>8</sup> Yield determined by <sup>1</sup>H-NMR: 73%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ (ppm): 2.43 (s, 3H), 4.06 (s, 2H), 7.18-7.24 (m, 4H), 7.28-7.33 (m, 3H), 7.37-7.43 (m, 2H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ (ppm): 21.2, 41.7, 126.2, 128.6, 129.0, 129.1, 129.3, 135.7, 138.3, 141.6.

**1-Methoxy-4-(4-methylbenzyl)benzene (5r).**<sup>13</sup> Yield determined by <sup>1</sup>H-NMR: 59%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ (ppm): 2.23 (s, 3H), 3.69 (s, 3H), 3.80 (s, 2H), 6.74 (d, *J*=8.6 Hz, 2H), 6.96-7.02 (m, 6H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ (ppm): 21.0, 40.6, 55.2, 123.8, 128.7, 129.1, 129.8, 133.5, 135.4, 138.5, 157.9.

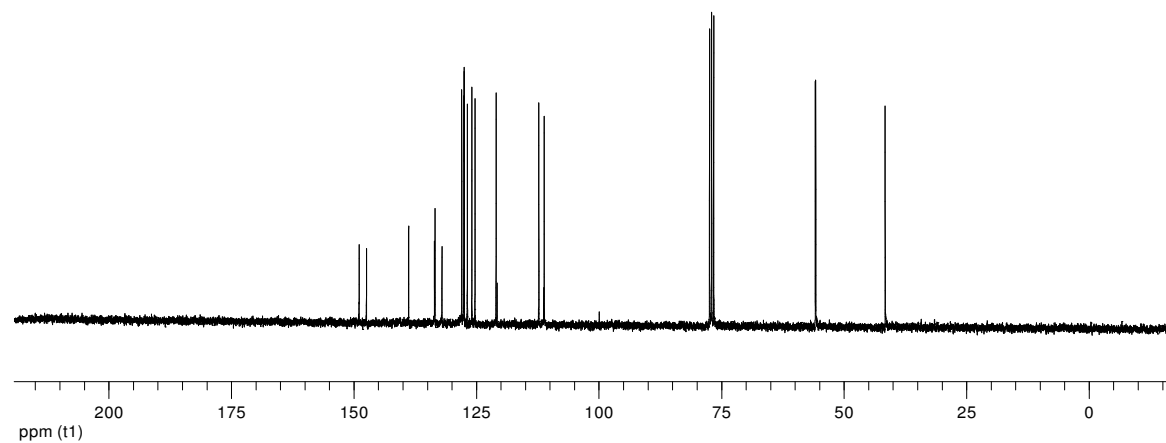
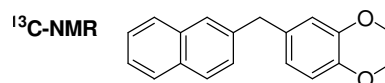
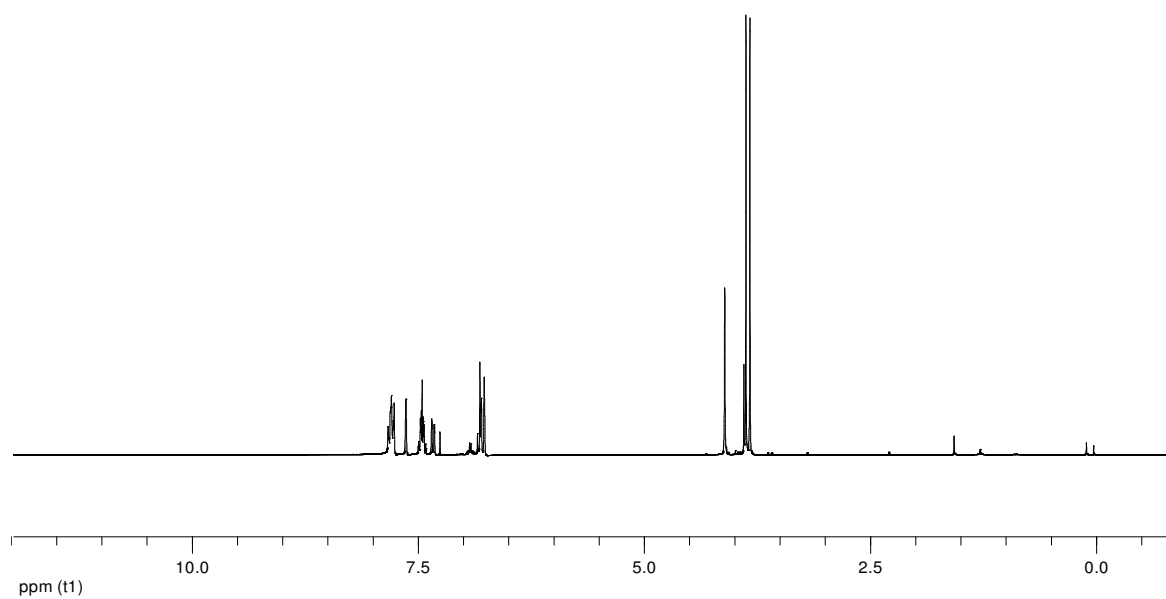
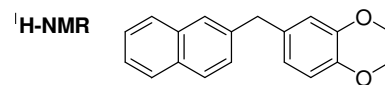
**6. General Procedure for Suzuki cross-coupling reactions employing benzyl chlorides and aryl boronic acids.** Pincer complex **1** (2 mol%) was added to a mixture of benzyl chloride (1 mmol), arylboronic acid (1.5 mmol), Na<sub>2</sub>CO<sub>3</sub> (2 mmol) and water (1 ml) in a sealed tube. After stirring at 150°C for 3 hours, the reaction mixture was cooled and water (5 ml) was added. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 6 ml). The combined organic extracts were dried over anhydrous sodium sulphate and concentrated *in vacuo*. The residue was dissolved in CDCl<sub>3</sub> and analyzed by <sup>1</sup>H NMR using diethylene glycol dimethyl ether as an internal standard.

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<sup>13</sup> Kofinf, C. C.; Knochel, P. *Org. Lett.* **2006**, *8*, 4121-4124.

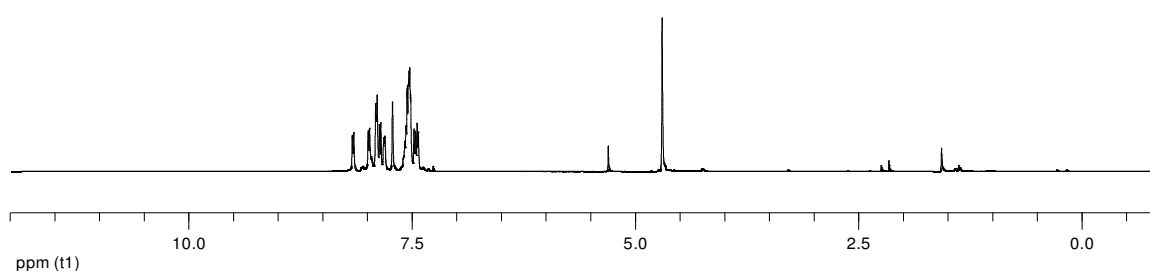
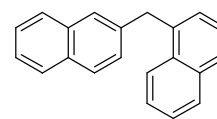
7.  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra of new compounds.

2-(3,4-Dimethoxy-benzyl)-naphthalene (5g).

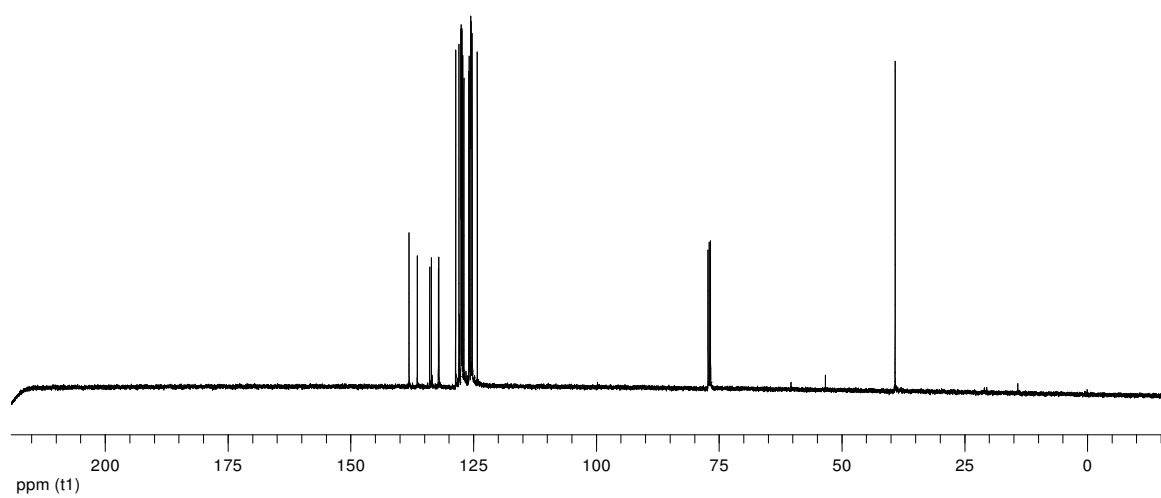
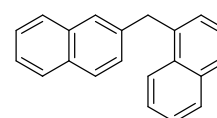


## 2,4'-Methylenedinaphthalene (5h).

<sup>1</sup>H-NMR

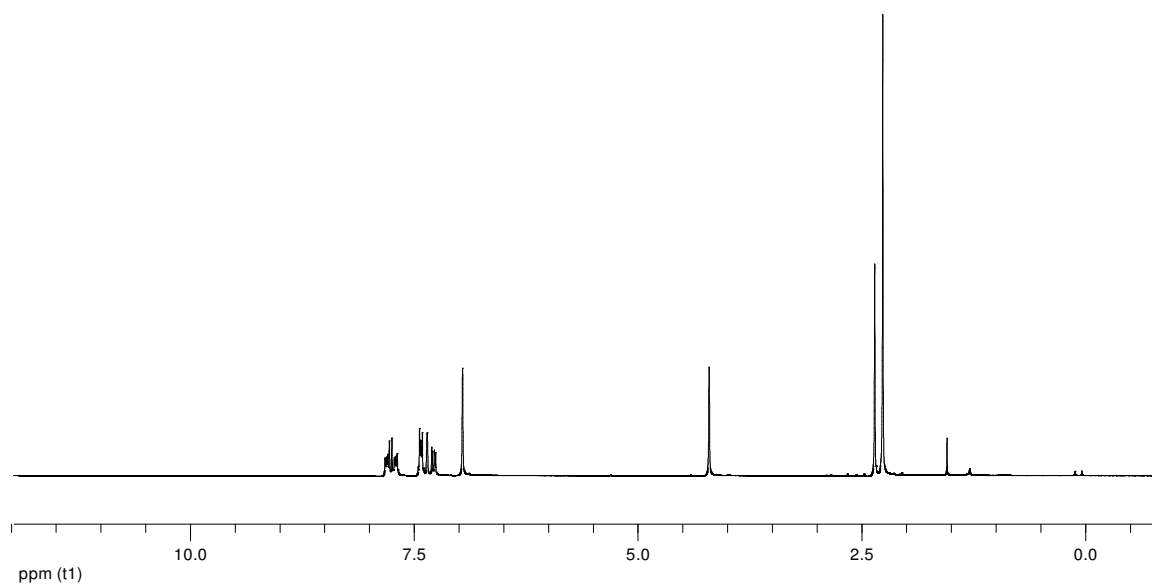
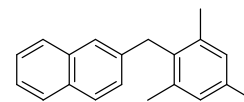


<sup>13</sup>C-NMR

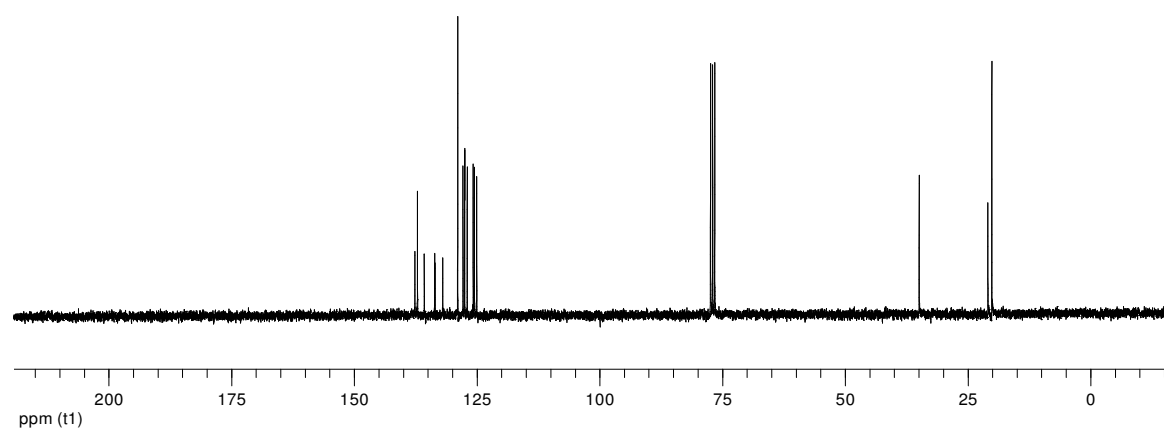
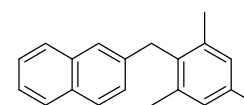


**2-(2,4,6-Trimethyl-benzyl)-naphthalene (5i).**

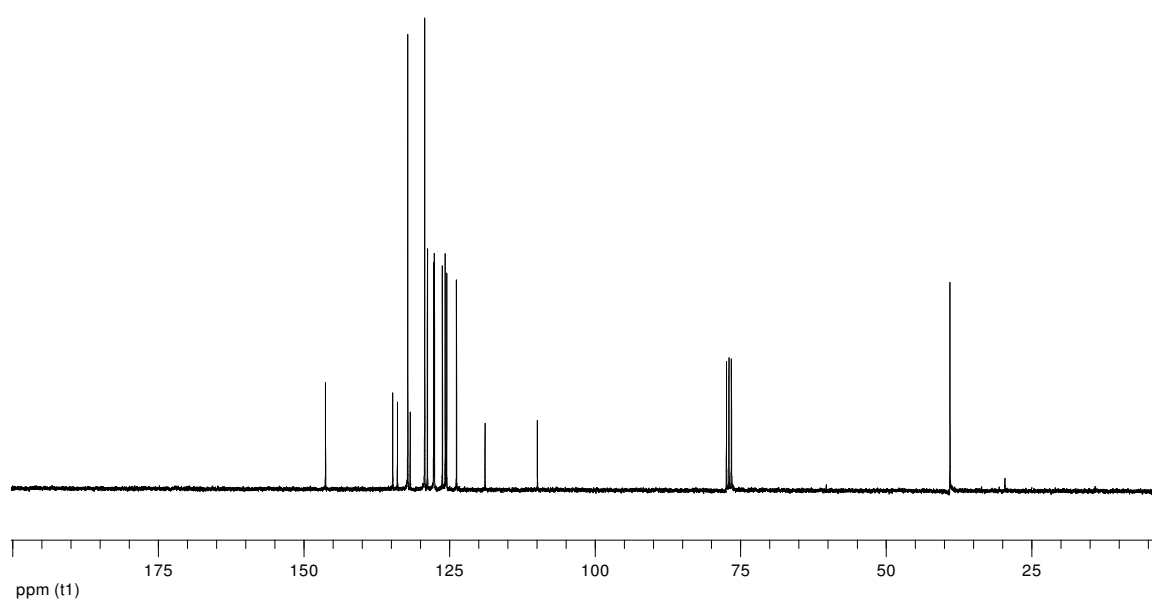
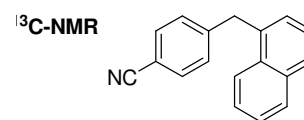
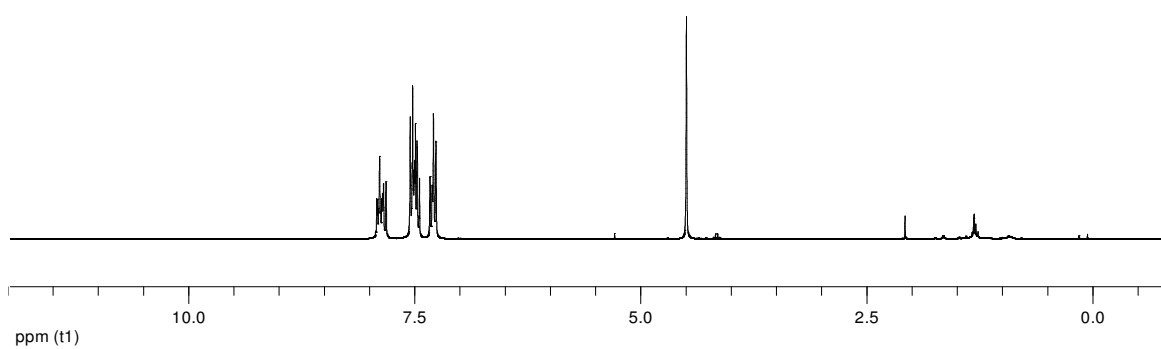
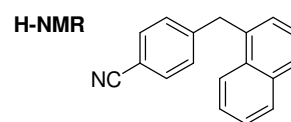
<sup>1</sup>H-NMR



<sup>13</sup>C-NMR

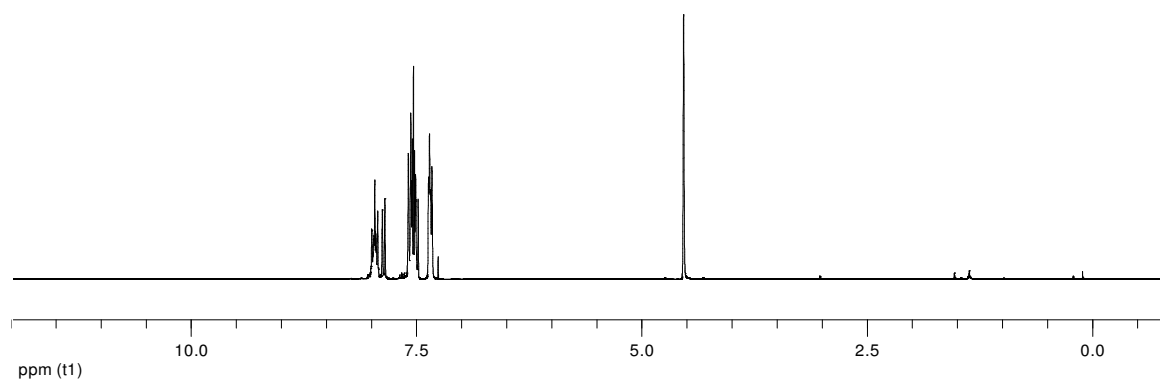
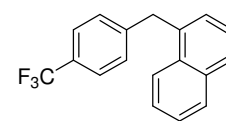


### 4-Naphthalen-1-ylmethyl-benzonitrile (5m).



# 1-(4-Trifluoromethyl-benzyl)-naphthalene (5p).

H-NMR



<sup>13</sup>C-NMR

