

Supporting Information for

New Efficient Nickel and Palladium Catalyzed Cross-Coupling Reactions Mediated by Tetrabutylammonium Iodide

By Michael Piber[§], Anne Eeg Jensen[§], Mario Rottländer[#] and Paul Knochel^{§*}

[§]Ludwig-Maximilians-Universität München, Institut für Organische Chemie,

Butenandtstr. 5-13, Haus F, 81377 München, Germany.

[#]H. Lundbeck A/S, Othilievej 9, DK-2500 Valby, Denmark.

Paul.Knochel@cup.uni-muenchen.de

General Methods

All reactions were carried out under an argon atmosphere in flame-dried glassware. THF was distilled under argon from sodium benzophenone ketyl. NMP was distilled under argon from calcium hydride. Commercially obtained materials were used without further purification. Column chromatography was performed with 40-63 μm silica gel (Merck). Gas-liquid chromatography was performed on a bonded 5 % phenylmethylpolysiloxan DB 5 capillary column (Megabore, 15 m, 0.53 mm id, 2.65 μm df). NMR spectroscopy was performed with a Bruker AC-300 spectrometer. Infrared spectroscopy was performed with a Nicolet 510 FT-IR-spectrometer and a Perkin-Elmer spectrometer 281. Mass spectra were obtained on a Varian MAT CH 7A. High resolution mass spectra were performed on a Varian MAT 711 (field desorption (FD)). Elemental analysis was performed on a Heraeus CHN-Rapid-Elementaranalysator.

Palladium catalyzed Csp²-Csp³ cross couplings mediated by Bu₄NI.

4-Chlorophenyl(phenyl)methane (4a)¹ Triflate **3a** (261 mg, 1.00 mmol), Pd(dba)₂ (40 mg, 0.07 mmol), dppf (38 mg, 0.07 mmol) and tetrabutylammonium iodide (1.11 g, 3.00 mmol) were dissolved in THF/NMP (1.5 mL, 1:1). To this mixture was added organozinc halide **2a** (1.45 mL, 1.60 mmol, 1.1 M in THF). The reaction mixture was stirred at 60 °C for 2 h. The mixture was

cooled to r.t. and quenched with saturated NH_4Cl solution (1 mL). The aqueous phase was extracted with ether (3 x 3 mL), and the combined organic layers were dried (MgSO_4), filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography (pentane) to give 191 mg (0.94 mmol, 94 %) of the desired product as a clear, colorless oil. $^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ 7.27-6.89 (m, 9 H), 3.85 (s, 2 H). $^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): δ 140.5, 139.6, 131.9, 130.2, 128.8, 128.6, 126.3, 41.2. MS (EI, 70 eV, m/z, rel. int.): 202 (M^+ , 59), 167 (100), 152 (22)

4-Methoxyphenyl(phenyl)methane (4b)² Triflate **3b** (260 mg, 1.01 mmol), $\text{Pd}(\text{dba})_2$ (40 mg, 0.07 mmol), dppf (38 mg, 0.07 mmol) and tetrabutylammonium iodide (1.11 g, 3.00 mmol) were dissolved in THF/NMP (1.5 mL, 1:1). To this mixture was added organozinc halide **2a** (1.45 mL, 1.60 mmol, 1.1 M in THF). The reaction mixture was stirred at 60 °C for 6 h. The mixture was cooled to r.t. and quenched with saturated NH_4Cl solution (1 mL). The aqueous phase was extracted with ether (3 x 3 mL), and the combined organic layers were dried (MgSO_4), filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography (pentane) to give 182 mg (0.92 mmol, 91 %) of the desired product as a clear, colorless oil. $^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ 7.29-7.24 (m, 2 H), 7.21-7.17 (m, 3 H), 7.09 (d, $J=8.5$ Hz, 2 H), 6.82 (d, $J=8.7$ Hz, 2 H), 3.91 (s, 2 H), 3.76 (s, 3 H). $^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): δ 157.9, 141.6, 133.2, 129.8, 128.8, 128.4, 125.9, 113.8, 55.2, 41.0. MS (EI, 70 eV, m/z, rel. int.): 198 (M^+ , 100), 167 (35), 121 (39)

4-Methylphenyl(phenyl)methane (4c)³ Triflate **3c** (249 mg, 1.03 mmol), $\text{Pd}(\text{dba})_2$ (40 mg, 0.07 mmol), dppf (38 mg, 0.07 mmol) and tetrabutylammonium iodide (1.11 g, 3.00 mmol) were dissolved in THF/NMP (1.5 mL, 1:1). To this mixture was added organozinc halide **2a** (1.45 mL, 1.60 mmol, 1.1 M in THF). The reaction mixture was stirred at 60 °C for 2.5 h. The mixture was cooled to r.t. and quenched with saturated NH_4Cl solution (1 mL). The aqueous phase was extracted with ether (3 x 3 mL), and the combined organic layers were dried (MgSO_4), filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography (pentane) to give 174 mg (0.95 mmol, 93 %) of the desired product as a clear, colorless oil. $^1\text{H-NMR}$ (CDCl_3 ,

¹ De Haan, F.P.; Delker, G.L.; Covey, W.D.; Alan, J.; Anisman, M.S. *J. Am. Chem. Soc.* **1984**, *106*, 7038

² Baciocchi, E.; Del Giacco, T.; Elisei, F. *J. Am. Chem. Soc.* **1993**, *115*, 12290

³ Popielarz, R.; Arnold, D. *J. Am. Chem. Soc.* **1990**, *112*, 3068

300 MHz): δ 7.29-7.24 (m, 2 H), 7.21-7.16 (m, 3 H), 7.08 (s, 4 H), 3.93 (s, 2 H), 2.30 (s, 3 H).
 $^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): δ 141.4, 138.1, 135.5, 129.1, 128.9, 128.8, 128.4, 126.0, 41.5, 21.0.
MS (EI, 70 eV, m/z , rel. int.): 182 (M^+ , 83), 167 (100), 91 (29)

Ethyl 4-benzylbenzoate (4d)⁴ Triflate **3d** (297 mg, 1.00 mmol), $\text{Pd}(\text{dba})_2$ (40 mg, 0.07 mmol), dppf (38 mg, 0.07 mmol) and tetrabutylammonium iodide (1.11 g, 3.00 mmol) were dissolved in THF/NMP (1.5 mL, 1:1). To this mixture was added organozinc halide **2a** (1.45 mL, 1.60 mmol, 1.1 M in THF). The reaction mixture was stirred at 60 °C for 4 h. The mixture was cooled to r.t. and quenched with saturated NH_4Cl solution (1 mL). The aqueous phase was extracted with ether (3 x 3 mL), and the combined organic layers were dried (MgSO_4), filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography (pentane/ethyl acetate 95:5) to give 202 mg (0.84 mmol, 84 %) of the desired product as a clear, colorless oil. $^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ 7.96 (d, $J=8.3$ Hz, 2 H); 7.27-7.13 (m, 7 H), 4.33 (q, $J=7.1$ Hz, 2 H), 3.99 (s, 2 H), 1.35 (t, $J=7.1$ Hz, 3 H). $^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): δ 166.4, 146.3, 140.1, 129.7, 128.8, 128.8, 128.5, 128.3, 126.3, 60.7, 41.8, 14.2. MS (EI, 70 eV, m/z , rel. int.): 240 (M^+ , 97), 212 (22), 195 (97), 167 (100), 152 (39), 91 (31)

1-Chloro-4-pentylbenzene (4e)⁵ Triflate **3a** (265 mg, 1.02 mmol), $\text{Pd}(\text{dba})_2$ (40 mg, 0.07 mmol), dppf (38 mg, 0.07 mmol) and tetrabutylammonium iodide (1.11 g, 3.00 mmol) were dissolved in THF/NMP (1.5 mL, 1:1). To this mixture was added organozinc halide **2b** (1.23 mL, 1.60 mmol, 1.3 M in THF). The reaction mixture was stirred at 60 °C for 4 h. The mixture was cooled to r.t. and quenched with saturated NH_4Cl solution (1 mL). The aqueous phase was extracted with ether (3 x 3 mL), and the combined organic layers were dried (MgSO_4), filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography (pentane) to give 171 mg (0.94 mmol, 92 %) of the desired product as a clear, colorless oil. $^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ 7.23 (d, $J=8.4$ Hz, 2 H), 7.10 (d, $J=8.2$ Hz, 2 H), 2.56 (t, $J=7.7$ Hz, 2 H), 1.63-1.53 (m, 2 H), 1.38-1.24 (m, 4 H), 0.88 (t, $J=6.9$ Hz, 3 H). $^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): δ 141.3, 131.2, 129.7, 128.3, 35.2, 31.4, 31.1, 22.5, 14.0. MS (EI, 70 eV, m/z , rel. int.): 182 (M^+ , 43), 125 (100), 105 (45), 91 (23)

⁴ Suzuki, H; Masuda, R.; Kubota, H.; Osuka, A. *Chem. Lett.* **1983**, 909

1-Methyl-4-pentylbenzene (4f)⁶ Triflate **3c** (241 mg, 1.00 mmol), Pd(dba)₂ (40 mg, 0.07 mmol), dppf (38 mg, 0.07 mmol) and tetrabutylammonium iodide (1.11 g, 3.00 mmol) were dissolved in THF/NMP (1.5 mL, 1:1). To this mixture was added organozinc halide **2b** (1.23 mL, 1.60 mmol, 1.3 M in THF). The reaction mixture was stirred at 60 °C for 4 h. The mixture was cooled to r.t. and quenched with saturated NH₄Cl solution (1 mL). The aqueous phase was extracted with ether (3 x 3 mL), and the combined organic layers were dried (MgSO₄), filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography (pentane) to give 144 mg (0.89 mmol, 89 %) of the desired product as a clear, colorless oil. ¹H-NMR (CDCl₃, 300 MHz): δ 7.12 (s, 4 H), 2.60 (t, *J*=7.7 Hz, 2 H); 2.35 (s, 3 H), 1.66-1.55 (m, 2 H), 1.38-1.30 (m, 4 H), 0.93 (t, *J*=6.7 Hz, 3 H). ¹³C-NMR (CDCl₃, 75 MHz): δ 139.9, 134.9, 128.9, 128.3, 35.5, 31.5, 22.6, 21.0, 14.0. MS (EI, 70 eV, *m/z*, rel. int.): 162 (M⁺, 48), 105 (100), 91 (15)

4-(4-Ethyloxycarbonylphenyl)butyl pivalate (4g) Triflate **3d** (299 mg, 1.00 mmol), Pd(dba)₂ (40 mg, 0.07 mmol), dppf (38 mg, 0.07 mmol) and tetrabutylammonium iodide (1.11 g, 3.00 mmol) were dissolved in THF/NMP (1.5 mL, 1:1). To this mixture was added organozinc halide **2c** (1.45 mL, 1.60 mmol, 1.1 M in THF). The reaction mixture was stirred at 60 °C for 4 h. The mixture was cooled to r.t. and quenched with saturated NH₄Cl solution (1 mL). The aqueous phase was extracted with ether (3 x 3 mL), and the combined organic layers were dried (MgSO₄), filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography (pentane/ethyl acetate 95:5) to give 282 mg (0.92 mmol, 92 %) of the desired product as a clear, colorless oil. ¹H-NMR (CDCl₃, 300 MHz): δ 7.94 (d, *J*=8.3 Hz, 2 H), 7.22 (d, *J*=8.3 Hz, 2 H), 4.34 (q, *J*=7.2 Hz, 2 H), 4.05 (t, *J*=6.1 Hz, 2 H), 2.67 (t, *J*=7.2 Hz, 2 H), 1.71-1.61 (m, 4 H), 1.36 (t, *J*=7.1 Hz, 3 H), 1.17 (s, 9 H). ¹³C-NMR (CDCl₃, 75 MHz): δ 178.4, 166.5, 147.4, 129.6, 128.2, 128.1, 63.8, 60.7, 38.6, 35.3, 28.1, 27.3, 27.1, 14.2. MS (EI, 70 eV, *m/z*, rel. int.): 306 (M⁺, 4), 260 (76), 176 (100), 163 (27), 131 (58), 57 (48). IR (neat, cm⁻¹): 2976 (s), 2871 (s), 1717 (s), 1611 (s), 1461 (s), 1276 (s). Anal. calcd. for C₁₈H₂₆O₄ (306.40): C 70.56, H 8.55; found: C 70.52, H 8.63

⁵ Konishi, H.; Yokota, K.; Ichihashi, Y.; Okano, T.; Kiji, J. *Chem. Lett.* **1980**, 1423

⁶ Alonso, F.; Barba, I.; Yus, M. *Tetrahedron* **1990**, *46*, 2069

1-Pentyl-1-cyclohexene (4h)⁷ Triflate **3e** (233 mg, 1.01 mmol), Pd(dba)₂ (40 mg, 0.07 mmol), dppf (38 mg, 0.07 mmol) and tetrabutylammonium iodide (1.11 g, 3.00 mmol) were dissolved in THF/NMP (1.5 mL, 1:1). To this mixture was added organozinc halide **2b** (1.14 mL, 1.60 mmol, 1.4 M in THF). The reaction mixture was stirred at 60 °C for 1 h. The mixture was cooled to r.t. and quenched with saturated NH₄Cl solution (1 mL). The aqueous phase was extracted with ether (3 x 3 mL), and the combined organic layers were dried (MgSO₄), filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography (pentane) to give 117 mg (0.77 mmol, 76 %) of the desired product as a clear, colorless oil. ¹H-NMR (CDCl₃, 300 MHz): δ 5.39 (m, 1 H), 1.99-1.89 (m, 6 H), 1.63-1.54 (m, 4 H), 1.39-1.24 (m, 6 H), 0.89 (t, *J*=8.2 Hz, 3 H). ¹³C-NMR (CDCl₃, 75 MHz): δ 138.1, 120.5, 38.1, 31.7, 28.3, 27.4, 25.3, 23.1, 22.6, 22.5, 14.1. MS (EI, 70 eV, *m/z*, rel. int.): 152 (M⁺, 13), 95 (29), 81 (100), 67 (27)

1-Cyclohexenyl(phenyl)methane (4i)⁸ Triflate **3e** (235 mg, 1.02 mmol), Pd(dba)₂ (40 mg, 0.07 mmol), dppf (38 mg, 0.07 mmol) and tetrabutylammonium iodide (1.11 g, 3.00 mmol) were dissolved in THF/NMP (1.5 mL, 1:1). To this mixture was added organozinc halide **2a** (1.45 mL, 1.60 mmol, 1.1 M in THF). The reaction mixture was stirred at 60 °C for 1 h. The mixture was cooled to r.t. and quenched with saturated NH₄Cl solution (1 mL). The aqueous phase was extracted with ether (3 x 3 mL), and the combined organic layers were dried (MgSO₄), filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography (pentane) to give 147 mg (0.85 mmol, 84 %) of the desired product as a clear, colorless oil. ¹H-NMR (CDCl₃, 300 MHz): δ 7.34-7.29 (m, 2 H), 7.24-7.20 (m, 3 H), 5.50 (m, 1 H), 3.28 (s, 2 H), 2.12-2.01 (m, 2 H), 1.95-1.83 (m, 2 H), 1.66-1.54 (m, 4 H). ¹³C-NMR (CDCl₃, 75 MHz): δ 140.4, 137.2, 128.9, 128.1, 125.8, 122.9, 44.7, 28.1, 25.3, 22.9, 22.4. MS (EI, 70 eV, *m/z*, rel. int.): 172 (M⁺, 47), 129 (19), 115 (28), 91 (67), 81 (100), 53 (27)

Nickel catalyzed Csp³-Csp³ cross couplings mediated by Bu₄NI.

Preparation of benzylic zinc bromides: A 25 mL flask charged with cut zinc foil (1.5 g, 22.5 mmol) and a stirring bar was flame dried and flushed with argon. THF (1 mL) and 1,2-dibromoethane (402 mg, 2.3 mmol) was added and the zinc activated by heating to reflux, then

⁷ D'Onofrio, F; Scettri, A. *Synthesis* 1985, 1159

allowing to cool down. This procedure was repeated until foam no longer occurred as result of heating, occasionally releasing the pressure of the flask. The mixture was cooled to 0 °C before adding benzyl bromide (1.8 g, 7.5 mmol) in THF (5 mL) dropwise (0.1 drop/sec). The mixture was kept at 0 °C until the reaction had completed (checked by GC, app. 2 hours). The solution was concentrated to 2-3 M under vacuum before use.

Typical Procedure A: Nickel catalysed cross-coupling of benzylzinc bromide and alkyl iodides. Preparation of 1,5-Diphenyl-1-pentanone (6a). A dried and argon-flushed 10 mL two-necked flask was charged with Ni(acac)₂ (74 mg, 0.3 mmol) and evacuated for 5 min. Dry THF (2 mL), NMP (1 mL), 4-iodobutyrophenone (820 mg, 3 mmol), 4-fluorostyrene (**1**; 74 mg, 0.6 mmol) and tetrabutylammonium iodide (3.3 g, 9 mmol) were successively added at r.t. The mixture was cooled to -35 °C before slowly adding a solution of benzylzinc bromide (2.5 M, 7.5 mmol) in dry THF. The flask was then allowed to warm to 0 °C, and after 1 hour to 10 °C. The reaction was complete in 16 hours, after which it was quenched with saturated aqueous NH₄Cl solution (2 mL) and extracted with ether (4 x 50-75 mL). The combined organic phases were dried (MgSO₄) before removing the solvents *in vacuo*. Flash chromatography on silica gel (pentane/ether 20:1) furnished the cross-coupling product **6a** as a colourless oil (476 mg, 67 %). IR (KBr): 3025 (w), 2935 (m), 1686 (s), 1597 (m), 1496 (m), 1448 (s), 750 (m), 691 (s). ¹H NMR (300 MHz, CDCl₃): δ 7.84 - 7.06 (m, 10H), 2.84 (t, *J* = 7.1 Hz, 2H), 2.53 (t, *J* = 7.3 Hz, 2H), 1.92 - 1.54 (m, 4H). ¹³C NMR (75 MHz, CDCl₃): δ 200.4, 142.4, 137.2, 133.1, 128.7, 128.6, 128.5, 128.2, 125.9, 38.6, 36.0, 31.3, 24.2. MS (EI, 70 eV): 238 (2), 120 (12), 105 (12), 71 (41), 42 (100). HRMS: calc. for C₁₇H₁₈O, 238.1352; found: 238.1355.

The products **6b–6f** were prepared according to this method.

1-Phenylnonane (6b): Prepared from octyl iodide (720 mg, 3 mmol). Reaction time: 4 hour at 0 °C. Purification by flash chromatography (100 % pentane) yielded **6b** as a colourless oil (470 mg, 77 %). IR (KBr): 3026.7 (m), 2925.0 (s), 2854.2 (s), 1604.6 (w), 1496.0 (m), 1453.5 (m), 697.3 (s). ¹H NMR (300 MHz, CDCl₃): δ 7.23 - 6.83 (m, 5H), 2.53 (t, *J* = 7.6 Hz, 2H), 1.54 (p, *J* = 7.6 Hz, 2H), 1.24 - 1.19 (m, 12H), 0.81 (t, *J* = 6.7 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 142.8, 128.3, 128.1, 125.4, 76.5, 35.9, 31.8, 31.4, 29.5, 29.4, 29.2, 22.6, 14.0. MS (EI, 70 eV):

⁸ Cristol, S.J.; Ilenda, C.S. *J. Am. Chem. Soc.* **1975**, *97*, 5862

204 (42), 105 (13), 91 (100), 71 (12), 57 (14), 43 (26), 41 (20), 29 (12). HRMS: calc. for $C_{16}H_{24}$, 204.1870; found: 204.1874.

5-Phenylpentyl pivalate (6c): Prepared from 4-iodobutyl pivalate (850 mg, 3 mmol). Reaction time: 4 hour at 0 °C. Purification by flash chromatography (pentane/ether 20:1) yielded **6c** as a colourless oil (603 mg, 81 %). IR (KBr): 3026.6 (s), 2935.1 (s), 2859.6 (s), 1728.8 (s), 1453.8 (s), 1157.9 (m), 1036.6 (m). 1H NMR (200 MHz, $CDCl_3$): δ 7.20 - 7.08 (m, 5H), 3.97 (t, $J = 6.5$ Hz, 2H), 2.55 (t, $J = 7.5$ Hz, 2H), 1.64 - 1.30 (m, 6H), 1.27 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 179.0, 142.4, 128.4, 128.3, 125.7, 64.3, 38.7, 35.8, 31.0, 28.5, 27.2, 25.5. MS (EI, 70 eV): 146 (100), 117 (64), 104 (81), 91 (87), 57 (76), 41 (21), 28 (21). Anal. Calc. for $C_{16}H_{24}O_2$: C, 77.38; H, 9.74. Found: C, 77.70; H, 9.72.

Phenyl (4-phenylbutyl) sulfide (6d): Prepared from 3-iodopropyl phenyl sulfide (830 mg, 3 mmol). Reaction time: 1 hour at 0 °C followed by 10 hours at r.t. Purification by flash chromatography (pentane/ether 20:1) yielded **6d** as white crystals (457 mg, 63 %). IR (KBr): 3060.0 (m), 2932.8 (s), 2856.3 (m), 1583.8 (m), 1480.4 (s), 1452.4 (s), 1438.6 (s), 1091.9 (m), 1025.3 (m). 1H NMR (300 MHz, $CDCl_3$): δ 7.20 - 7.02 (m, 10H), 2.81 (t, $J = 7.0$ Hz, 2H), 2.50 (t, $J = 7.3$ Hz, 2H), 1.69 - 1.42 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.1, 138.5, 129.1, 128.8, 128.4, 128.3, 125.8, 35.4, 33.6, 30.4, 28.7. MS (EI, 70 eV): 242 (100), 110 (53), 91 (77), 28 (20). HRMS: calc. for $C_{16}H_{18}S$, 242.1120; found: 242.1125.

Ethyl 4-(5-phenyl-5-oxopentyl) benzoate (6e): Prepared from 4-iodobutyrophenone (820 mg, 3 mmol) and 4-carbethoxybenzylzinc bromide (2.31 g, 7.5 mmol). Reaction time: 1 hour at 0 °C followed by 16 hours at r.t. Purification by flash chromatography (pentane/ether 20:1) yielded **6e** as white crystals (660 mg, 71 %). IR (KBr): 3066.3 (m), 2929.9 (m), 1705.2 (s), 1682.0 (s), 1608.5 (s), 1281.4 (s), 1180.2 (m), 1109.4 (m), 1022.3 (m). 1H NMR (200 MHz, $CDCl_3$): δ 8.25 - 7.01 (m, 9H), 4.29 (q, $J = 7.1$, 2H), 2.95 - 1.64 (m, 8H), 1.31 (t, $J = 7.1$, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.1, 167.0, 147.7, 146.4, 138.1, 133.0, 129.7, 128.6, 128.5, 128.2, 60.8, 37.5, 35.9, 30.8, 23.9, 14.4. MS (EI, 70 eV): 310 (45), 281 (20), 265 (23), 191 (49), 163 (100), 144 (45), 131 (51), 120 (74), 105 (97), 90 (33), 77 (55). HRMS: calc. for $C_{20}H_{22}O_3$, 310.1571; found: 310.1570.

3-(5-Phenyl-5-oxopentyl)benzotrile (6f): Prepared from 4-iodobutyrophenone (820 mg, 3 mmol) and 3-cyanobenzyl zinc bromide (1.96 g, 7.5 mmol). Reaction time: 1 hour at 0 °C followed by 16 hours at 10 °C. Purification by flash chromatography (pentane/ether 20:1) yielded **6f** as pale yellow crystals (582 mg, 74 %). IR (KBr): 3056.2 (m), 2942.8 (s), 2867.6 (m), 2226.1 (s), 1727.0 (s), 887.1 (m), 754.1 (s). ¹H NMR (200 MHz, CDCl₃): δ 7.90 - 7.19 (m, 9H), 2.94 (t, *J* = 6.8, 2H), 2.64 (t, *J* = 7.2, 2H), 1.74 - 1.62 (m, 4H). ¹³C NMR (75 MHz, CDCl₃): δ 200.0, 143.3, 137.5, 132.9, 132.8, 131.7, 129.5, 128.9, 128.4, 127.8, 112.7, 38.0, 35.2, 30.5, 23.5. MS (EI, 70 eV): 263 (22), 133 (23), 120 (70), 105 (100), 77 (30). HRMS: calc. for C₁₈H₁₇NO, 263.1312; found: 263.1311.