Kumada Coupling of Aryl and Vinyl Tosylates under Mild Conditions

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Supporting Information

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General methods

^1H , ^{13}C , and ^{19}F -NMR spectra were recorded on 400 MHz and 500 MHz Spectrometers. All ^{13}C , and ^{19}F -NMR spectra are proton decoupled. GC and GC-MS analyses were conducted with an HP-1 methyl silicone column. $\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$, $\text{P}(\text{o-tol})_3$, **1** (1-Diphenylphosphino-2-di-tert.-butylphosphinoethylferrocene) and **2** (1-Diphenylphosphino-2-di-tert.-butylphosphinoethylferrocene) and all phenols, ketones and magnesium reagents were purchased and used without further purification. $\text{Pd}(\text{P}(\text{o-tol})_3)_2$,¹ aryl² and alkenyl tosylates³ were synthesized by literature procedures or variations thereof. Particularly for aryl tosylates it is important that no tosyl chloride is left in the substrates since it impedes the coupling reactions. All catalytic reactions were carried out under inert atmosphere in a glove box.

General procedure 1: coupling of aryl tosylates with aryl magnesium bromides.

The reaction conditions and average yields for each reaction are shown in table 1. A typical procedure is given for entry 1.

4-Methoxy-4'-methylbiphenyl.⁴ Into a small vial were placed 7.2 mg $\text{Pd}(\text{P}(\text{o-tol})_3)_2$ (0.010 mmol), 5.4 mg **1** (0.010 mmol), and 278 mg 4-MeOC₆H₄OTs (1.00 mmol). The solids were dissolved in 3 mL of toluene. With a syringe, 1.1 mL of a 1.0 M solution of p-tolylmagnesium bromide (1.10 mmol) in diethyl ether were added to the well stirred solution at room temperature. The vial was closed and the solution was stirred at room temperature in the glovebox for 4 h. The resulting orange suspension was removed from the glovebox, then hydrolyzed with 1.0 M HCl and extracted three times with dichloromethane. The combined organic layers were washed with brine, dried over MgSO_4 , and filtered. After evaporation of the solvent, the crude product was purified by flash column chromatography (silica gel, hexanes, ethyl acetate 95:5) to give 165 mg (83%) of 4-Methoxy-4'-methylbiphenyl. ^1H NMR

(CDCl₃) δ 2.41 (s, 3H), 3.87 (s, 3H), 7.00 (d, J = 8.8 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 8.8 Hz, 2H). ¹³C NMR (CDCl₃) δ 21.5, 55.8, 114.6, 127.0, 128.4, 129.9, 134.2, 136.8, 138.4, 159.4.

4-Methoxy-2'-methylbiphenyl.⁵ 5.8 mg Pd(dba)₂ (0.010 mmol), 5.4 mg **1** (0.010 mmol), 282 mg 4-MeOC₆H₄OTs (1.01 mmol) and 1.0 mL of a 2.0 M solution of o-tolylMgBr (2.00 mmol) were used. The crude material was purified by chromatography (silica gel, hexanes, ethyl acetate 99:1) to give 143 mg (72%) of 4-Methoxy-2'-methylbiphenyl. ¹H NMR (CD₂Cl₂) δ 2.26 (s, 3H), 3.84 (s, 3H), 6.95 (m, 2H), 7.20-7.26 (m, 6H). ¹³C NMR (CD₂Cl₂) δ 20.7, 55.6, 113.9, 126.1, 127.3, 130.2, 130.6, 130.7, 134.7, 135.9, 142.0, 159.1.

2-Methoxy-4'-methylbiphenyl.⁶ 5.8 mg Pd(dba)₂ (0.010 mmol), 5.4 mg **1** (0.010 mmol), 278 mg 2-MeOC₆H₄OTs (1.00 mmol) and 2.0 mL of a 1.0 M solution of p-tolylMgBr (2.00 mmol) were used. The crude material was purified by chromatography (silica gel, hexanes, ethyl acetate 99:1) to give 129 mg (65%) of 4-Methoxy-2'-methylbiphenyl. ¹H NMR (CD₂Cl₂) δ 2.38 (s, 3H), 3.80 (s, 3H), 7.00 (m, 2H), 7.21 (d, J = 4.0 Hz, 2H), 7.27-7.32 (m, 2H), 7.39 (m, 2H). ¹³C NMR (CD₂Cl₂) δ 20.2, 55.9, 111.2, 121.0, 129.2, 130.1, 130.6, 131.4, 131.5, 137.5, 139.5, 157.2.

2-Methoxy-2'-methylbiphenyl.⁵ 5.8 mg Pd(dba)₂ (0.010 mmol), 5.4 mg **1** (0.010 mmol), 278 mg 2-MeOC₆H₄OTs (1.01 mmol) and 1.0 mL of a 2.0 M solution of o-tolylMgBr (2.00 mmol) were used. The crude material was purified by chromatography (silica gel; hexanes to elute 2,2'-biphenyl; hexanes, ethyl acetate 95:5 to elute the desired product) to give 129 mg (65%) of 2-Methoxy-2'-methylbiphenyl. ¹H NMR (CD₂Cl₂) δ 2.11 (s, 3H), 3.76 (s, 3H), 6.98-7.03 (m, 2H), 7.11-7.15 (m, 2H), 7.19-7.25 (m, 3H), 7.33-7.39 (m, 1H). ¹³C NMR (CD₂Cl₂) δ 20.0, 55.7, 110.0, 120.8, 125.8, 127.6, 129.0, 129.9, 130.4, 131.2, 137.3, 139.3, 157.0.

2,4,6,4'-Tetramethylbiphenyl.⁷ 5.8 mg Pd(dba)₂ (0.010 mmol), 5.4 mg **1** (0.010 mmol), 290 mg MesOTs (1.00 mmol) and 2.0 mL of a 1.0 M solution of p-tolylMgBr (2.00 mmol) were used. The crude material was purified by chromatography (silica gel, hexanes) and recrystallized from pentane at –35°C to give 84 mg (40%) of 2,4,6,2'-tetramethylbiphenyl. ¹H NMR (CDCl₃) δ 1.99 (s, 6H), 2.30 (s, 3H), 2.38 (s, 3H), 6.91 (s, 2H), 7.00 (d, J = 4.0 Hz, 2H), 7.20 (d, J = 4.0 Hz, 2H). ¹³C NMR (CD₂Cl₂) δ 20.9, 21.1, 21.3, 128.3, 129.4, 129.5 (2 C), 129.6, 129.8, 130.0, 136.2, 136.4, 136.6.

4-Methoxybiphenyl.⁵ 7.2 mg Pd(P(o-tol)₃)₂ (0.010 mmol), 5.4 mg **1** (0.010 mmol), 278 mg 4-MeOC₆H₄OTs (1.10 mmol) and 0.37 mL of a 3.0 M solution of PhMgBr (1.100 mmol) were used. The crude material was purified by chromatography (silica gel, hexanes, ethyl acetate 95:5) to give 157 mg (85%) of 4-Methoxybiphenyl. ¹H NMR (CDCl₃) δ 3.87 (s, 3H), 7.01 (d, J = 8.9 Hz, 2H), 7.33 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.4 Hz, 2H), 7.57 (m, 4H). ¹³C NMR (CDCl₃) δ 55.8, 114.6, 127.1, 127.2, 128.6, 129.1, 134.2, 141.3, 159.6.

4-Fluoro-4'-methoxybiphenyl.⁸ 7.2 mg Pd(P(o-tol)₃)₂ (0.010 mmol), 5.4 mg **1** (0.010 mmol), 278 mg 4-MeOC₆H₄OTs (1.10 mmol) and 0.55 mL of a 2.0 M solution of 4-FC₆H₄MgBr (1.100 mmol) were used. The crude material was purified by chromatography (silica gel, hexanes, ethyl acetate 95:5) to give 162 mg (80%) of 4-Fluoro-4'-methoxybiphenyl. ¹H NMR (CDCl₃) δ 3.86 (s, 3H), 6.98 (d, J = 8.8 Hz, 2H), 7.10 (m, 2H), 7.49 (m, 4H). ¹³C NMR (CDCl₃) δ 55.8, 114.7, 115.9 (d, J = 21 Hz), 128.4, 128.6 (d, J = 8 Hz), 133.2, 137.4, 159.5, 162.5 (d, J = 246 Hz). ¹⁹F NMR (CDCl₃) δ –117.

4-Chloro-4'-methylbiphenyl.⁹ 7.2 mg Pd(P(o-tol)₃)₂ (0.010 mmol), 5.4 mg **1** (0.010 mmol), 283 mg 4-ClC₆H₄OTs (1.00 mmol) and 1.1 mL of a 1.0 M solution of 4-MeC₆H₄MgBr (1.10

mmol) were used. The crude material was purified by chromatography (silica gel, hexanes, ethyl acetate 99:1) and then recrystallized (dissolved in hot diethyl ether, diluted with pentane, left to cool) to give 158 mg (78%) of 4-Chloro-4'-methylbiphenyl. ^1H NMR (CDCl_3) δ 2.41 (s, 3H), 7.26 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H). ^{13}C NMR (CDCl_3) δ 21.5, 127.2, 128.6, 129.3, 130.0, 133.4, 137.5, 137.8, 140.0.

2-(4-Methylphenyl)naphthalene.⁴ 7.2 mg $\text{Pd}(\text{P}(\text{o-tol})_3)_2$ (0.010 mmol), 5.4 mg **1** (0.010 mmol), 298 mg 2- $\text{C}_{10}\text{H}_7\text{OTs}$ (1.00 mmol) and 1.1 mL of a 1.0 M solution of 4- $\text{MeC}_6\text{H}_4\text{MgBr}$ (1.10 mmol) were used. The crude material was purified by chromatography (silica gel, hexanes, ethyl acetate 99:1) to give 188 mg (86%) of 2-(4-Methylphenyl)naphthalene. ^1H NMR (CDCl_3) δ 2.48 (s, 3H), 7.35 (d, J = 7.8 Hz, 2H), 7.54 (m, 2H), 7.69 (d, J = 7.8 Hz, 2H), 7.79 (dd, J = 8.5, J = 1.9, 2H), 7.93 (m, 3H), 8.09 (d, J = 1.4 Hz, 1H). ^{13}C NMR (CDCl_3) δ 21.6, 125.9, 126.0, 126.2, 126.7, 127.7, 128.1, 128.6, 128.8, 130.1, 133.0, 134.2, 137.6, 138.7, 138.9.

2-(2-Methylphenyl)naphthalene.¹⁰ 7.2 mg $\text{Pd}(\text{P}(\text{o-tol})_3)_2$ (0.010 mmol), 5.4 mg **1** (0.010 mmol), 298 mg 2- $\text{C}_{10}\text{H}_7\text{OTs}$ (1.00 mmol) and 0.55 mL of a 2.0 M solution of 2- $\text{MeC}_6\text{H}_4\text{MgBr}$ (1.100 mmol) were used. The crude was purified by chromatography (silica gel, hexanes, ethyl acetate 99:1) to give 203 mg (93%) of 2-(2-Methylphenyl)naphthalene. ^1H NMR (CDCl_3) δ 2.34 (s, 3H), 7.33 (m, 4H), 7.52 (m, 3H), 7.80 (s, 1H), 7.90 (m, 3H). ^{13}C NMR (CDCl_3) δ 21.0, 126.2, 126.2, 126.6, 127.8, 127.9, 128.1, 128.2, 128.2, 128.4, 130.4, 130.8, 132.7, 133.7, 136.0, 140.0, 142.3.

4,4''-Dimethyl-[1,1':3',1'']terphenyl.¹¹ 7.2 mg $\text{Pd}(\text{P}(\text{o-tol})_3)_2$ (0.010 mmol), 5.4 mg **1** (0.010 mmol), 419 mg $\text{m-C}_6\text{H}_3(\text{OTs})_2$ (1.00 mmol) and 2.2 mL of a 1.0 M solution of 4-

MeC₆H₄MgBr (2.20 mmol) were used. The crude material was purified by chromatography (silica gel, hexanes, ethyl acetate 99:1) and then recrystallized (dissolved in hot diethyl ether, diluted with pentane, left to cool) to give 119 mg (43%) of 2-(4-Methylphenyl)naphthalene. ¹H NMR (CDCl₃) δ 2.43 (6H, s), 7.27 (d, J = 8.8 Hz, 4H), 7.49 (m, 1H), 7.55 (m, 6H), 7.78 (broad, 1H). ¹³C NMR (CDCl₃) δ 21.5, 126.1, 126.2, 127.5, 129.5, 129.9, 137.6, 138.8, 142.0.

1,6-Di-*p*-tolyl-naphthalene. 7.2 mg Pd(P(o-tol)₃)₂ (0.010 mmol), 5.4 mg **1** (0.010 mmol), 468 mg 1,6-C₁₀H₆(OTs)₂ (1.00 mmol) and 2.2 mL of a 1.0 M solution of 4-MeC₆H₄MgBr (2.20 mmol) were used. The crude material was purified by chromatography (silica gel, hexanes, ethyl acetate 99:1) to give 213 mg (69%) of 2-(4-Methylphenyl)naphthalene as a colorless solid. ¹H NMR (CDCl₃) δ 2.48 (s, 3H), 2.52 (s, 3H), 7.37 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.46 (dd, J = 7.1 Hz, J = 1.2 Hz, 1H), 7.48 (d, J = 8.1 Hz, 2H), 7.58 (dd, J = 8.2 Hz, J = 7.2 Hz, 1H), 7.69 (d, J = 8.0 Hz, 2H), 7.74 (dd, J = 8.8 Hz, J = 1.9 Hz, 1H), 7.94 (d, J = 8.1 Hz, 1H), 8.05 (d, J = 8.8 Hz, 1H), 8.14 (d, J = 1.8 Hz, 1H). ¹³C NMR (CDCl₃) δ 21.6, 21.7, 126.0, 126.2, 126.3, 127.1, 127.2, 127.7, 128.1, 129.5, 130.1, 130.4, 131.2, 134.6, 137.4, 137.6, 138.3, 138.5, 138.7, 140.6. Anal. Calcd. for C₂₄H₂₀: C, 93.46; H, 6.54. Found: C, 93.33; H, 6.32.

General procedure 2: coupling of aryl tosylates with alkenyl and alkyl magnesium halides; coupling of alkenyl tosylates with aryl and alkyl magnesium halides.

The reaction conditions and average yields for each reaction are shown in tables 2 and 3. A typical procedure is given for table 2, entry 1.

1-Methoxy-4-(2-methyl-propenyl)-benzene.¹² Into a small vial were placed 3.6 mg Pd(P(o-tol)₃)₂ (0.005 mmol), 2.8 mg **2** (0.005 mmol), and 139 mg 4-MeOC₆H₄OTs (0.50 mmol). The solids were dissolved in 1.5 mL of toluene. With a syringe, 1.1 mL of a 0.5 M solution of 2-methyl-propenylmagnesium bromide in tetrahydrofuran (0.55 mmol) were added to the well

stirred solution at room temperature. The vial was sealed with a PTFE septum, removed from the glovebox and stirred at 80°C for 4 hours. The resulting orange to brown suspension was diluted in 100 mL hexanes and filtered. After evaporation of the solvent, the crude product was purified by flash column chromatography (silica gel, hexanes, ethyl acetate 99:1) to give 71 mg (87%) of 1-Methoxy-4-(2-methyl-propenyl)-benzene. ^1H NMR (CDCl_3) δ 1.86 (d, J = 1.3 Hz, 1H), 1.90 (d, 1.3 Hz, 1H), 3.82 (s, 3H), 6.23 (broad, 1H), 6.88 (d, 8.5 Hz, 2H), 7.18 (d, 8.5 Hz, 2H). ^{13}C NMR (CDCl_3) δ 19.7, 27.2, 55.6, 113.8, 124.9, 130.2, 131.7, 134.4, 158.0.

1-Hexyl-4-methoxy-benzene.¹³ 3.6 mg $\text{Pd}(\text{P}(\text{o-tol})_3)_2$ (0.005 mmol), 2.8 mg **2** (0.005 mmol), 139 mg 4-MeOC₆H₄OTs (0.50 mmol) and 0.28 mL of a 2.0 M solution of nHexMgCl (0.550 mmol) in diethylether were used. The crude material was purified by chromatography (silica gel, hexanes, ethyl acetate 99:1) to give 87 mg (91%) of 1-Hexyl-4-methoxy-benzene. ^1H NMR (CDCl_3) δ 0.90 (m, 3H), 1.33 (m, 6H), 1.60 (m, 2H), 2.56 (m, 2H), 3.80 (s, 3H), 6.85 (d, J = 8.7 Hz, 2H), 7.11 (d, J = 8.7 Hz, 2H). ^{13}C NMR (CDCl_3) δ 14.5, 23.1, 29.4, 32.2, 32.2, 35.5, 55.6, 114.0, 129.6, 135.5, 158.0.

1-Isobutyl-4-methoxy-benzene.¹⁴ 3.6 mg $\text{Pd}(\text{P}(\text{o-tol})_3)_2$ (0.005 mmol), 2.8 mg **2** (0.005 mmol), 139 mg 4-MeOC₆H₄OTs (0.50 mmol) and 0.28 mL of a 2.0 M solution of iBuMgCl (0.550 mmol) in diethylether were used. The solution was stirred at room temperature. The crude was purified by chromatography (silica gel, hexanes, ethyl acetate 99:1) to give 76 mg (92%) of 1-Isobutyl-4-methoxy-benzene. ^1H NMR (CDCl_3) δ 0.91 (d, J = 6.6 Hz, 6H), 1.83 (sept.d, J = 7.2, 6.6 Hz, 1H), 2.43 (d J = 7.2 Hz, 2H), 3.80 (s, 3H), 6.83 (d, J = 8.7 Hz, 2H), 7.07 (d, J = 8.7 Hz, 2H). ^{13}C NMR (CDCl_3) δ 22.7, 30.8, 44.9, 55.6, 113.9, 125.8, 125.9, 129.1, 130.4, 132.2, 132.4, 132.5, 133.4, 134.2, 158.1.

1-Cyclohexyl-4-methoxy-benzene.¹⁵ 3.6 mg Pd(P(o-tol)₃)₂ (0.005 mmol), 2.7 mg **1** (0.005 mmol), 139 mg 4-MeOC₆H₄OTs (0.50 mmol) and 0.28 mL of a 2.0 M solution of cHexMgCl (0.550 mmol) in diethylether were used. The solution was stirred at room temperature for 16 hours. The crude material was purified by chromatography (silica gel, hexanes, ethyl acetate 99:1) to give 64 mg (67%) of 1-Cyclohexyl-4-methoxy-benzene. ¹H NMR (CDCl₃) δ 1.18-1.33 (m, 1H), 1.33-1.48 (m, 4H), 1.71-1.80 (m, 1H), 1.80-1.92 (m, 4H), 2.40-2.52 (m, 1H), 3.80 (s, 3H), 6.85 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H). ¹³C NMR (CDCl₃) δ 26.6, 27.4, 35.1, 44.1, 55.6, 114.1, 128.0, 140.8, 158.1.

1-Cyclopropyl-4-methoxy-benzene.¹⁶ 3.6 mg Pd(P(o-tol)₃)₂ (0.005 mmol), 2.8 mg **2** (0.005 mmol), 139 mg 4-MeOC₆H₄OTs (0.50 mmol) and 1.1 mL of a 0.5 M solution of cPrMgBr (0.55 mmol) in tetrahydrofuran were used. The crude material was purified by chromatography (silica gel, hexanes, ethyl acetate 99:1) to give 41 mg (55%) of 1-Cyclopropyl-4-methoxy-benzene. ¹H NMR (CDCl₃) δ 0.64 (m, 2H), 0.91 (m, 2H), 1.88 (m, 1H), 3.85 (s, 3H), 6.83 (d, J = 8.7 Hz, 2H), 7.04 (d, J = 8.7 Hz, 2H). ¹³C NMR (CDCl₃) δ 8.9, 15.0, 55.7, 114.2, 127.2, 136.2, 158.0.

1-Benzyl-4-methoxy-benzene.¹⁷ 3.6 mg Pd(P(o-tol)₃)₂ (0.005 mmol), 2.8 mg **2** (0.005 mmol), 139 mg 4-MeOC₆H₄OTs (0.50 mmol) and 0.55 mL of a 1.0 M solution of PhCH₂MgCl (0.550 mmol) in diethylether were used. The solution was stirred at room temperature. The crude material was purified by chromatography (silica gel, hexanes, ethyl acetate 99:1) to give 96 mg (97%) of 1-Benzyl-4-methoxy-benzene. ¹H NMR (CDCl₃) δ 3.80 (s, 3H), 3.96 (s, 2H), 6.86 (d, J = 8.7 Hz, 2H), 7.19, (d, J = 8.7 Hz, 2H), 7.22 (m, 3H), 7.31 (m, 2H). ¹³C NMR (CDCl₃) δ 41.5, 55.7, 114.3, 126.4, 128.9, 129.3, 130.3, 133.7, 142.0, 158.4.

1-Isobutyl-4-trifluoromethyl-benzene.¹⁸ 3.6 mg Pd(P(o-tol)₃)₂ (0.005 mmol), 2.8 mg **2** (0.005 mmol), 139 mg 4-MeOC₆H₄OTs (0.50 mmol) in benzene and 0.28 mL of a 2.0 M solution of iBuMgCl (0.550 mmol) in diethylether were used. The solution was stirred for eight hours at room temperature. The crude material was purified by chromatography (silica gel, hexanes) to give 67 mg (66%) of 1-Isobutyl-4-trifluoromethyl-benzene. ¹H NMR (CDCl₃) δ 0.92 (d, 6.6 Hz, 6H), 1.90 (apparent non., 7.0 Hz, 1H), 2.54 (d, J = 7.2 Hz, 2H), 7.25 (d, J = 7.9 Hz, 2H), 7.53 (d, J = 7.9 Hz, 2H). ¹³C NMR (CDCl₃) δ 22.7, 30.5, 45.6, 124.8 (q, 272 Hz), 125.4 (q, 3.8 Hz), 128.6 (q, 32 Hz), 129.7, 146.2. ¹⁹F NMR (CDCl₃) δ -62.7. Anal. Calcd. for C₁₁H₁₃F₃: C, 65.33; H, 6.48. Found: C, 65.34; H, 6.28.

2-Butyl-naphthalene.¹⁹ 3.6 mg Pd(P(o-tol)₃)₂ (0.005 mmol), 2.7 mg **1** (0.005 mmol), 149 mg 2-C₁₀H₇OTs (0.50 mmol) and 0.28 mL of a 2.0 M solution of iBuMgCl (0.550 mmol) in diethylether were used. The solution was stirred for two hours at room temperature. The crude material was purified by chromatography (silica gel, hexanes, ethyl acetate 99:1) to give 85 mg (92%) of 2-Butyl-naphthalene. ¹H NMR (CDCl₃) δ 0.99 (t, J = 7.3 Hz, 3H), 1.44 (apparent sextet, J = 7.5 Hz, 2H), 1.73 (m, 2H), 2.81 (m, 2H), 7.37 (dd, J = 8.4 Hz, J = 1.7 Hz, 1H), 7.46 (m, 2H), 7.65 (broad, 1H), 7.81 (m, 3H). ¹³C NMR (CDCl₃) δ 14.4, 22.8, 34.0, 36.2, 125.4, 126.2, 126.7, 127.8, 127.9, 128.0, 128.1, 132.4, 134.1, 140.9.

2-Isobutyl-naphthalene.²⁰ 3.6 mg Pd(P(o-tol)₃)₂ (0.005 mmol), 2.7 mg **1** (0.005 mmol), 149 mg 2-C₁₀H₇OTs (0.50 mmol) and 0.28 mL of a 2.0 M solution of iBuMgCl (0.550 mmol) in diethylether were used. The solution was stirred for two hours at room temperature. The crude material was purified by chromatography (silica gel, hexanes, ethyl acetate 99:1) to give 86 mg (93%) of 2-Butyl-naphthalene. ¹H NMR (CDCl₃) δ 0.99 (d, J = 6.6 Hz, 6H), 2.02 (apparent non., J = 6.7 Hz, 1H), 2.68 (d, J = 7.2 Hz, 2H), 7.35 (dd, J = 8.3 Hz, J = 1.6 Hz,

1H), 7.47 (m, 2H), 7.62 (broad, 1H), 7.82 (m, 3H). ¹³C NMR (CDCl₃) δ 22.9, 30.6, 46.1, 125.4, 126.2, 127.6, 127.9, 128.0, 128.0, 128.4, 132.4, 134.0, 139.7.

2-Benzyl-naphthalene.²¹ 3.6 mg Pd(P(o-tol)₃)₂ (0.005 mmol), 2.7 mg **1** (0.005 mmol), 149 mg 2-C₁₀H₇OTs (0.50 mmol) and 0.55 mL of a 1.0 M solution of PhCH₂MgCl (0.550 mmol) in diethylether were used. The solution was stirred for two hours at room temperature. The crude material was purified by chromatography (silica gel, hexanes, ethyl acetate 99:1) to give 106 mg (97%) of 2-Benzyl-naphthalene. ¹H NMR (CDCl₃) δ 4.20 (s, 2H), 7.27 (m, 3H), 7.36 (m, 3H), 7.49 (m, 2H), 7.69 (broad, 1H), 7.83 (m, 3H). ¹³C NMR (CDCl₃) δ 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.

1-(4-*tert*-Butyl-cyclohex-1-enyl)-4-methyl-benzene.²² 2.6 mg Pd₂(dba)₃·CHCl₃ (0.0025 mmol), 2.7 mg **1** (0.005 mmol), 154 mg toluene-4-sufonic acid 4-*tert*-butyl-cyclohex-1-enylester (0.50 mmol) and 0.55 mL of a 1.0 M solution of 4-MeC₆H₄MgBr (0.550 mmol) in diethylether were used. The crude material was purified by chromatography (silica gel, hexanes) to give 92 mg (81%) of 1-(4-*tert*-Butyl-cyclohex-1-enyl)-4-methyl-benzene as a colorless oil. ¹H NMR (CDCl₃) δ 0.93 (s, 9H), 1.35 (m, 2H), 1.99 (m, 2H), 2.26 (m, 1H), 2.35 (s, 3H), 2.43 (m, 1H), 2.53 (m, 1H), 6.11 (m, 1H), 7.13 (d, J = 7.9 Hz, 2H), 7.29 (d, J 0 7.9 Hz, 2H). ¹³C NMR (CDCl₃) δ 21.4, 24.8, 27.7, 27.9, 29.3, 32.6, 44.2, 124.5, 125.2, 129.3, 136.5, 136.6, 139.8.

1-(6-methyl-cyclohex-1-enyl)-4-methyl-benzene.²³ 2.6 mg Pd₂(dba)₃·CHCl₃ (0.0025 mmol), 2.7 mg **1** (0.005 mmol), 133 mg toluene-4-sufonic acid 6-methyl-cyclohexy-1-enylester (0.50 mmol) and 0.55 mL of a 1.0 M solution of 4-MeC₆H₄MgBr (0.550 mmol) in diethylether were used. The crude material was purified by chromatography (silica gel, hexanes) to give

66 mg (71%) of 1-Methyl-4-(6-methyl-cyclohex-1-enyl)-benzene as a colorless oil (mixture of isomers). ^1H NMR (CDCl_3) δ 0.93 (d, J = 7.1 Hz, 3H), 1.56-1.73 (m, 3H), 1.81-1.93 (m, 1H), 2.14 (m, 2H), 2.33 (s, 3H), 2.81 (m, 1H), 5.85 (td, J = 3.9 Hz, J = 1.1 Hz), 7.11 (d, J = 8.1 Hz, 2H), 7.20 (d, J = 8.1 Hz, 2H). ^{13}C NMR (CDCl_3) δ 19.5, 20.9, 21.7, 26.9, 31.0, 31.7, 125.4, 126.7, 129.5, 136.6, 140.5, 143.3. Anal. Calcd. for $\text{C}_{14}\text{H}_{18}$: C, 90.26; H, 9.74. Found: C, 90.19; H, 9.71.

1-(1,3-Dimethyl-but-1-enyl)-4-methyl-benzene. 2.6 mg $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (0.0025 mmol), 2.8 mg **2** (0.005 mmol), 127.2 mg toluene-4-sulfonic acid 1-isopropyl-propenylester (0.500 mmol) and 0.55 mL of a 1.0 M solution of 4-MeC₆H₄MgBr in diethylether were used. The crude material was purified by chromatography (silica gel, hexanes) to give 37 mg (43%) of 1-(1,3-Dimethyl-but-1-enyl)-4-methyl-benzene as a colorless oil. ^1H NMR (CDCl_3) δ 1.04 (d, J = 6.6 Hz, 6H), 2.03 (d, J = 1.3 Hz, 3H), 2.34 (s, 3H), 2.68 (dsept., J = 9.1 Hz, J = 6.6 Hz, 1H), 5.58 (dq, J = 9.1 Hz, J = 1.3 Hz, 1H), 7.12 (d, J = 7.8 Hz, 2H), 7.29 (d, J = 7.8 Hz, 2H). ^{13}C NMR (CDCl_3) δ 16.1, 21.4, 23.4, 28.3, 125.9, 129.2, 132.5, 135.8, 136.4, 141.6. Anal. Calcd. for $\text{C}_{13}\text{H}_{18}$: C, 89.59; H, 10.41. Found: C, 89.27; H, 10.43.

4-tert-Butyl-1-isobutyl-cyclohexene. 5.2 mg $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (0.005 mmol), 5.4 mg **1** (0.010 mmol), 308.4 mg toluene-4-sulfonic acid 4-tert-butyl-cyclohex-1-enylester (1.000 mmol) in 3 mL toluene and 0.55 mL of a 2.0 M solution of *i*BuMgCl in diethylether were used. Stirring for one hour in the glove-box. The crude material was purified by chromatography (silica gel, hexanes) to give 159 mg (82%) of 4-tert-Butyl-1-isobutyl-cyclohexene as a colorless oil. ^1H NMR (CDCl_3) δ 0.83 (d, J = 6.2 Hz, 3H), 0.85 (d, J = 6.2 Hz, 3H), 0.86 (s, 9H), 1.07-1.30 (m, 2H), 1.64-1.87 (m, 5H), 1.89-2.06 (m, 3H), 5.36 (m, 1H). ^{13}C NMR (CDCl_3) δ 22.6, 23.2, 24.8, 26.4, 27.2, 27.6, 30.1, 32.6, 44.7, 47.8, 122.6, 137.2. Anal. Calcd. for $\text{C}_{14}\text{H}_{26}$: C, 86.52; H, 13.48. Found: C, 86.58; H, 13.28.

(1-Isobutyl-vinyl)-benzene.²⁴ 2.6 mg Pd₂(dba)₃·CHCl₃ (0.0025 mmol), 2.7 mg **1** (0.005 mmol), 137 mg toluene-4-sulfonic acid 1-phenyl-vinylester (0.50 mmol) and 0.28 mL of a 2.0 M solution of iBuMgCl (0.550 mmol) in diethylether were used. The reaction was carried out at room temperature. The crude material was purified by chromatography (silica gel, hexanes) to give 24 mg (30%) of (1-Isobutyl-vinyl)-benzene as a colorless oil. ¹H NMR (CDCl₃) δ 0.86 (d, J = 6.6 Hz, 6H), 1.65 (non., J = 6.7 Hz, 1H), 2.38 (dd, J = 7.2 Hz, J = 1.1 Hz, 2H), 5.02 (m, 1H), 5.25 (d, J = 1.8 Hz, 1H), 7.25 (m, 1H), 7.31 (m, 2H), 7.38, (m, 2H). ¹³C NMR (CDCl₃) δ 22.7, 26.8, 30.1, 45.5, 52.9, 53.2, 53.4, 53.7, 54.0, 113.8, 126.7, 127.6, 128.6, 141.9, 148.2.

(1-Isobutyl-propenyl)-benzene. 2.6 mg Pd₂(dba)₃·CHCl₃ (0.0025 mmol), 2.7 mg **1** (0.005 mmol), 144 mg toluene-4-sulfonic acid 1-phenyl-propenylester (0.50 mmol) and 0.28 mL of a 2.0 M solution of iBuMgCl (0.550 mmol) in diethylether were used. The reaction was carried out at room temperature. The crude material was purified by chromatography (silica gel, hexanes) to give 71 mg (82%) of (1-Isobutyl-propenyl)-benzene as a colorless oil. ¹H NMR (CDCl₃) δ 0.77 (d, J = 6.6 Hz, 6H), 1.52 (apparent non., J = 7.1 Hz, 1H), 1.71 (d, J = 6.9 Hz, 3H), 2.32 (d, J = 7.3 Hz, 2H), 5.69 (q, J = 6.9 Hz, 1H), 7.08-7.28 (m, 5H). ¹³C NMR (CDCl₃) δ 14.8, 22.8, 27.6, 38.6, 124.2, 126.7, 126.8, 128.5, 140.9, 144.3. Anal. Calcd. for C₁₄H₁₈: C, 90.26; H, 9.74. Found: C, 90.19; H, 9.71.

(1-Cycloheptylidene-3-methyl-butyl)-benzene. 2.6 mg Pd₂(dba)₃·CHCl₃ (0.0025 mmol), 2.7 mg **1** (0.005 mmol), 171 mg toluene-4-sulfonic acid cyclohexylidene-phenyl-methylester (0.50 mmol) and 0.28 mL of a 2.0 M solution of iBuMgCl (0.550 mmol) in diethylether were used. The reaction was carried out at 80°C. The crude material was purified by chromatography (silica gel, hexanes) to give 99 mg (87%) of (1-Cycloheptylidene-3-methyl-butyl)-benzene as a colorless oil. ¹H-NMR, CD₂Cl₂, δ = 0.93 (d, J = 6.6 Hz, 6H), 1.51 (m, 3H), 1.65 (m, 4H), 2.02

(m, 2H), 2.32 (d, $J = 7.3$ Hz, 2H), 2.38 (m, 2H), 7.14 (m, 2H), 7.25 (m, 1H), 7.34 (m, 2H). ^{13}C
NMR (CDCl_3) δ 22.8, 27.1, 27.4, 28.7, 29.1, 31.2, 32.8, 43.1, 126.0, 128.2, 129.4, 132.1,
136.9, 144.6. Anal. Calcd. for $\text{C}_{17}\text{H}_{24}$: C, 89.41; H, 10.59. Found: C, 89.28; H, 10.68.

t1e1 (Table 1 entry 1)

t1e2

S16

10-83

t1e3

S18

VIP number VIP1294884

t1e3

PROTON CD2C12 usr2 Limment 1

Current Data Parameters
 NAME JU108-2004-Lim
 EXPNO 20
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20040708
 Time 15.34
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 PULPROG zg30
 TO 65536
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 NS 16
 DS 2
 SWH 10330.578 Hz
 FIDRES 0.157632 Hz
 AQ 3.1719923 sec
 RG 90.5
 DM 48.400 usec
 DE 6.50 usec
 TE 300.0 K
 D1 1.00000000 sec

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 P1 10.50 usec
 PL1 0.00 dB
 SF01 500.1330885 MHz

F2 - Processing parameters
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 SF 500.1300939 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
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 F1P 11.000 ppm
 F1 5501.43 Hz
 F2P -1.000 ppm
 F2 -500.13 Hz
 PPMCM 0.60000 ppm/cm
 HZCM 300.07805 Hz/cm

VIP number VIP1294884
t1e3
C13CPD CD2C12 usr2 Limmert 1

Current Data Parameters
NAME Ju108-2004-Lim
EXPNO 21
PROCNO 1

F2 - Acquisition Parameters
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Time 15.44
INSTRUM spect
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PULPROG zgpg30
TD 65536
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DS 4
SWH 31446.541 Hz
FIDRES 0.479836 Hz
AQ 1.0420724 sec
RG 8192
DM 15.900 usec
DE 6.50 usec
TE 300.0 K
D1 2.0000000 sec
d11 0.0300000 sec
d12 0.0000000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 7.30 usec
PL1 5.00 dB
SF01 125.771519 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 18.00 dB
PL13 18.00 dB
SF02 500.1320005 MHz

F2 - Processing parameters
SI 32768
SF 125.7578912 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
FAP 245.000 ppm
F1 27037.95 Hz
F2 53.000 ppm
F2 -626.79 Hz
PPMCM 11.00000 ppm/cm
HZCM 1383.33679 Hz/cm

t1e4

tle5

t1e13

t1e14

tle15

tle16

t2e1

t2e2

t2e4

t2e5

t2e6

t2e7

t3e6

t3e7

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