Eur. J. Org. Chem. **2005** · © WILEY-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, 2005 · ISSN 1434–193X

SUPPORTING INFORMATION

Title: Synthesis of Sterically Hindered Biaryls by Zr-Mediated Co-cyclotrimerization of Alkynes
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Experimental Section

All reactions were carried out under inert atmosphere (Ar). THF was distilled from benzophenone and sodium prior to the use. $NiBr_2(PPh_3)_2$[1], the propynoate **3f**[2] and 1-ethynyl-2-methoxynaphthalene[3] were prepared according to previously published procedures. For preparation of new propynoates **3a**, **3b**, **3e** was used the described procedure.[4] The propynoates **3c** and **3d** were prepared by modification of the previously described method.[5] 1-Iodo-2-methylbenzene, 1-iodo-2-methoxybenzene, 1-iodo-2-trifluoromethylbenzene, methyl chloroformate, 3-hexyne, *n*-BuLi (1.6 M solution in hexanes), (-)-menthyl chloroformate were purchased from Aldrich. Trimethylsilylethyne and 2-butyne were purchased from Fluka, Buchs. All other chemicals and solvents were of commercial purity and were used without further purification.

^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Varian Unity Inova 400 spectrometer using tetramethylsilane as an internal standard. Infrared spectra were recorded on a PE-640 Perkin-Elmer spectrometer. Mass spectra were obtained on a ZAB-SEQ VG Analytical spectrometer. Elemental analyses were obtained on a Perkin-Elmer 2400 elemental analyzer. TLC was performed on Merck Silica Gel 60 F_{254} aluminum sheets and column chromatography was performed on Fluka Silica Gel 60.

I. Preparation of the starting material

1. Preparation of 2a and 2b according to Negishi procedure A.[4]

To a solution of methyl propynoate (2 mL, 23 mmol) in THF (5 mL) was added LDA (12.7 mL, 23 mmol) at -78°C and the reaction mixture was stirred for 10 min. Then freshly sublimed $ZnBr_2$ (5.2 g, 23 mmol) in THF (10 mL) was added and the mixture was stirred for additional 10 min at -78°C followed by addition of 1-substituted-2-iodobenzene (20 mmol) and $PdCl_2(PPh_3)_2$ (320 mg, 0.46 mmol). The mixture was allowed to warm up to 20 °C, stirred overnight, quenched with 3M HCl, and extracted with hexane (3×20 mL). Organic fractions were washed with solutions of $NaHCO_3$, NaCl, and dried over Na_2SO_4.

Methyl (2-fluorophenyl)propynoate (3a). Column chromatography on silicagel (10/1 hexane/EtOAc) afforded 1.22 g (34%) of the title compound as a white solid: mp 25-26 °C; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 3.77 (s, 3H), 7.13 (t, J = 7.6 Hz, 1H), 7.17 (td, J = 7.6, 1.4 Hz, 1H), 7.42-7.48 (m, 1H), 7.54-7.58 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si) δ 52.83, 79.77, 84.79 (d, $^3J^{(C-F)}$ = 3.4 Hz), 108.36 (d, $^2J^{(C-F)}$ = 15.2 Hz), 115.82 (d, $^1J^{(C-F)}$ = 20.1 Hz), 124.22 (d, $^4J^{(C-F)}$ = 3.8 Hz), 132.64 (d, $^3J^{(C-F)}$ = 9 Hz), 134.53, 154.04, 162.32, 164.87; IR ($CHCl_3$) nu(tilde) 2231, 1711, 1493, 1435, 1306, 1267, 1229, 1205, 1178, 1154 cm^{-1}; HRMS calcd. for $C_{10}H_7FO_2$ 178.04301, found 178.04257; R_f (9/1 hexan/EtOAc) = 0.23.

Methyl (2-chlorophenyl)propynoate (3b). Column chromatography on silicagel (10/1 hexane/EtOAc) afforded 2.8 g (70%) of the title compound as a colorless liquid: ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 3.86 (s, 3H), 7.28 (td, J = 7.5, 1.4 Hz, 1H), 7.37 (td, J = 7.3, 1.7 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 7.6 Hz, 1H), ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si) δ 52.92, 82.63, 84.56, 119.82, 126.65, 129.58, 131.62, 134.68, 137.31, 154.15; R_f (9/1 hexan/EtOAc) = 0.28. Spectral characteristics are in accordance with published data.[6]

2. Preparation of 1-substituted benzene-2-trimethylsilylacetylenes and methyl 2-trimethoxyphenylpropynoate (3c) and (2-methylphenyl)propynoate (3d).[5]

Preparation of 1-substituted benzene-2-trimethylsilylacetylenes. To a mixture of substituted iodobenzene (18.3 mmol) in THF (20 mL) and trimethylsilylacetylene (2.7 g, 27.5 mmol), were added triethylamine (6 mL, 37 mmol), CuI (0.18g, 0.95 mmol) and $Pd(PPh_3)_2Cl_2$ (0.13g, 0.19 mmol) under Ar atmosphere. The reaction mixture was stirred overnight at 20 °C, then quenched with 3M HCl, and extracted with hexane (3×20 mL). Organic fractions were washed with solutions of $NaHCO_3$, NaCl, and dried over Na_2SO_4. Column chromatography on silica gel (9/1 hexane/EtOAc) followed by distillation under reduced pressure provided title compounds. 1-Methyl-2-(1-trimethylsilylethynyl)benzene: 2.6 g (75%). 1-Methoxy-2-(1-trimethylsilylethynyl)benzene: 2.7 g (72%).

Preparation of methyl *ortho*-substituted phenylpropynoates. To a solution of 1-substituted-2-(1-trimethylsilylethynyl)benzene (10.6 mmol) in THF (15 mL) was added *n*-BuLi (6.6 mL of 1.6M solution in hexanes, 10.6 mmol) at -78 °C. The mixture was allowed to warm up to room temperature (20 °C), then cooled back to -78 °C, and methylchloroformate (2 ml, 21.6 mmol) was added. The reaction mixture was allowed to warm up to room temperature, stirred overnight, quenched with 3M HCl, and extracted with hexane (3×20 mL). Organic fractions were washed with solutions of $NaHCO_3$, NaCl, and dried over Na_2SO_4. Column chromatography on silica gel (9/1 hexane/EtOAc) followed by distillation under reduced pressure provided title compounds.

Methyl (2-methoxyphenyl)propynoate (3c). Distillation under reduced pressure afforded 1.2 g (59%) of the title compound as a colorless liquid: ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 3.84 (s, 3H), 3.90 (s, 3H), 6.90-6.96 (m, 2H), 7.40-7.45 (m, 1H), 7.50-7.55 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si) δ 52.66, 55.82, 83.59, 84.20, 108.73, 110.79, 120.50, 132.34, 134.92, 154.59, 161.58; IR (neat) nu(tilde) 2223, 1708, 1493, 1304, 1280, 1249, 1217, 1176 cm^{-1}; R_f (9/1 hexane/EtOAc) = 0.75. Spectral characteristics are in accordance with published data.[4]

Methyl (2-methylphenyl)propynoate (3d). Distillation under reduced pressure afforded 1.1 g (60%) of the title compound as a colorless liquid: ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 2.45 (s, 3H), 3.82 (s, 3H), 7.15-7.20 (m, 1H), 7.22-7.25 (m, 1H), 7.30-7.35 (m, 1H), 7.54 (dd, J = 7.79, 1.52 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si) δ 20.50, 52.71, 84.03, 85.51, 119.34, 125.77, 129.73, 130.63, 133.39, 142.22, 154.57; IR (neat) nu(tilde) 2223, 1709, 1435, 1299, 1285, 1218, 1206, 1178 cm^{-1}; R_f (9/1 hexane/EtOAc) = 0.85. Spectral characteristics are in accordance with published data.[6]

3. Preparation of methyl (2-trifluoromethylphenyl)propynoate (3e) according to Negishi procedure B.[4] To a solution of $ZnBr_2$ (5.63 g, 25 mmol) in THF (15 mL) was added triethylamine (13.9 mL, 0.1 mol). After 5 minutes 2-iodo-1-trifluoromethylbenzene (3 mL, 21 mmol), methyl propynoate (2.11 g, 25 mmol), and $PdCl_2(PPh_3)_2$ (743 mg, 1.1 mmol) were added. The reaction mixture was stirred overnight, quenched with 3M HCl, and extracted with hexane (3×20 mL). Organic fractions were washed with solutions of $NaHCO_3$, NaCl, and dried over Na_2SO_4. Column chromatography on silica gel (9/1 hexane/EtOAc) afforded 0.76 g (16%) of the title compound as colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 3.83 (s, 3H), 7.55-7.59 (m, 2H), 7.70 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si) δ 52.96, 81.43, 84.74, 116.03 (q, $^1J^{(C\text{-}F)}$ = 349 Hz), 122.97 (q $^2J^{(C\text{-}F)}$ = 272 Hz) 126.15 (q, $^4J^{(C\text{-}F)}$ = 5 Hz), 130.37, 131.62, 132.85 (q, $^3J^{(C\text{-}F)}$ = 31 Hz), 135.29, 153.98; IR ($CHCl_3$) nu(tilde) 3016, 2958, 2233, 1713, 1604, 1577, 1493, 1453, 1436, 1321, 1302, 1287, 1170, 1142, 1061, 1034, 888 cm^{-1}, HRMS calcd for $C_{11}H_7F_3O_2$ 228.03981, found 228.03967; R_f (9/1 hexane/EtOAc) = 0.28.

4. Preparation of (-)-menthyl (2-methylphenyl)-propynoate (8). To a stirred solution of 1-methyl-2-(1-trimethylsilylethynyl)benzene (1.2 g, 7.3 mmol) in THF (15 mL) was added *n*-BuLi (4.6 mL 1.6M solution, 7.4 mmol) at -78 °C and the reaction mixture was allowed to warm up to 20 °C during 1 hour. Then it was again cooled to -78 °C followed by addition of (-)-menthyl chlorformate (1.6 g, 7.3 mmol). The reaction mixture was allowed to warm up to 20 °C, stirred overnight, quenched with 3M HCl, and extracted with hexane (3×20 mL). Organic fractions were washed with solutions of $NaHCO_3$, NaCl, and dried over Na_2SO_4. Column chromatography on silica gel (10/1 hexane/EtOAc) followed by distillation under reduced pressure afforded 1.6 g (73%) of the title compound as yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.81 (d, *J* = 6.9 Hz, 3H), 0.93 (d, *J* = 6.6 Hz, 6H), 1.06-1.16 (m, 2H), 1.25-1.28 (m, 1H), 1.45-1.55 (m, 2H), 1.67-1.74 (m, 2H), 1.90-2.01 (m, 1H), 2.06-2.12 (m, 1H), 2.50 (s, 3H), 4.85 (dt, *J* = 10.8, 4.4 Hz, 1H), 7.17 (td, *J* = 7.6, 1.4 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.32 (td, *J* = 7.5, 1.4 Hz, 1H), 7.55 (dd, *J* = 7.7, 1.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 16.36, 20.58, 20.68, 21.98, 23.50, 26.26, 31.46, 34.13, 40.67, 46.85, 76.29, 84.67, 84.90, 119.59, 125.70, 129.68, 130.45, 133.33, 142.18, 153.94; IR ($CHCl_3$) nu(tilde) 2960, 2208, 1694, 1294, 1276, 1189, 1202, 1151, 980; HRMS calcd for $C_{20}H_{26}O_2$ 298.19328, found 298.19316; $[\alpha]_D^{25}$ -48. 4° (*c* 1, $CHCl_3$); R_f (9/1 hexan/EtOAc) = 0.64.

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