Supporting Information

New Synthesis of Biaryls *via* Rh-catalyzed Decarbonylative Suzuki-Coupling of Carboxylic Anhydrides with Arylboroxines

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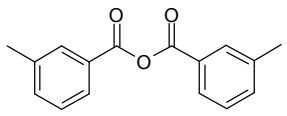
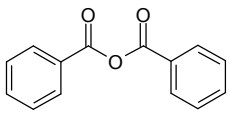
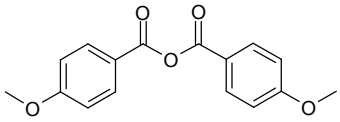
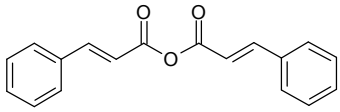
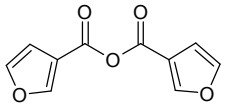
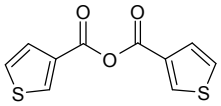
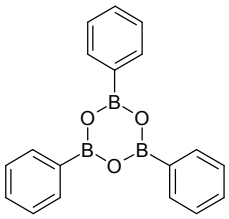
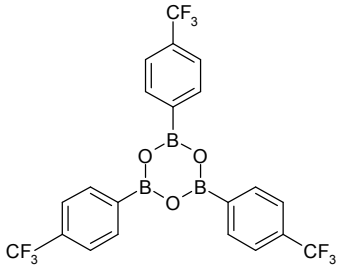
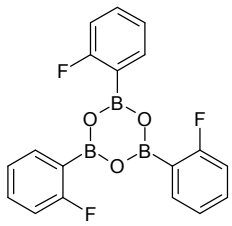
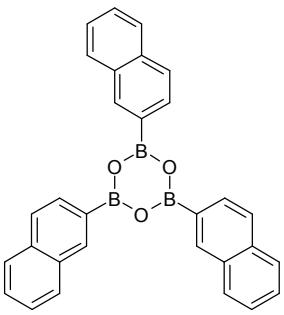
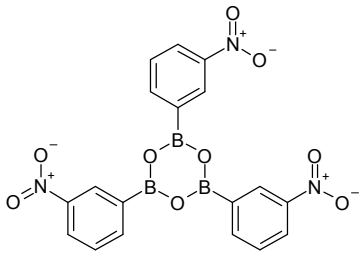
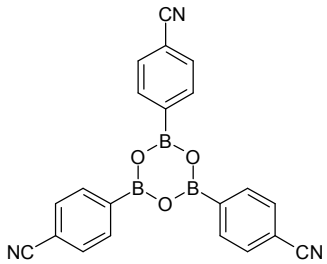
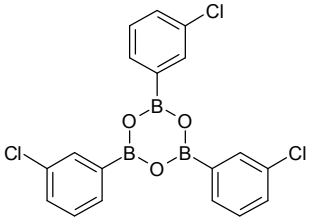
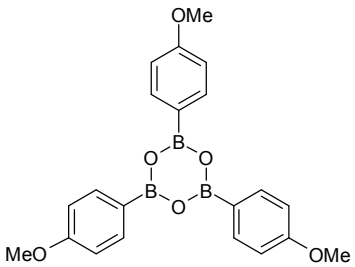
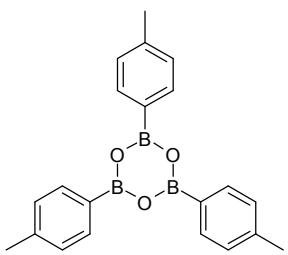
Structures of the Anhydrides **1a** – **1f**

 **1a**	 **1b**
 **1c**	 **1d**
 **1e**	 **1f**

Boroxines **3a- 3i**

 **3a**	 **3b**	 **3c**
 **3d**	 **3e**	 **3f**
 **3g**	 **3h**	 **3i**

General Procedure:

Synthesis of 3-methylbiphenyl **6a**: A flame-dried 20 mL reaction vessel equipped with a pressure equalizer and magnetic stirrer was charged with 2,4,6-triphenylboroxine (**3a**) (0.50 mmol, 155 mg), and dry potassium fluoride (0.10 mmol, 5.80 mg). The reaction vessel is closed and dried for 15 minutes *in vacuo* at 100 °C. After cooling to room temperature, di-μ-chlorotetrakis(η^2-ethylene)dirhodium(I) (5.80 mg, 0.015 mmol) and 3-methylbenzoic anhydride (**1a**) (254 mg, 1.00 mmol) were added *via* syringe as a stock solution in 4 mL anhydrous mesitylene. The mixture was then stirred at 160 °C and the progress of the reaction was monitored by GC. After completion of the reaction (usually after 8 h), the volatiles were removed *in vacuo* and the residue was purified by column chromatography (SiO_2, hexane), yielding **6a** as a white solid (108 mg, 64 %). The product was identified by means of ^{1}H and ^{13}C NMR as well as by GC-MS and HRMS to be 3-methylbiphenyl, CAS registry number [643-93-6]. The side product **7a** (40 mg, 20 %), CAS registry number [643-65-2], was isolated after further elution with hexanes / ethyl acetate.

Synthesis of 3-methyl-4'trifluormethylbiphenyl **6b**: Compound **6b** was synthesized following the above procedure from 3-methylbenzoic anhydride (**1a**) (254 mg, 1.00 mmol) and 2,4,6-tris-(4-trifluoromethylphenyl)boroxine (**3b**) (257 mg, 0.50 mmol). After purification by column chromatography (SiO_2, Hexane) **6b** was obtained as a white solid (155 mg, 0.66 mmol, 66 %); ^{1}H-NMR (300.1 MHz, $CDCl_3$): 7.60-7.56 (m, 4H), 7.33-7.22 (m, 3H), 7.13 (m, 1H), 2.34 (s, 3H) ppm; ^{13}C-NMR (75.5 MHz, $CDCl_3$): 145.3, 140.2, 139.0, 129.3 (q, ^2J = 32 Hz), 129.3, 129,3, 128.4, 127.8, 126.5 (q, ^1J = 270 Hz), 126.1 (q, ^3J = 4 Hz), 124.8, 21.8 ppm; MS (EI, 70 eV): m/z (%) = 236 (100, $[M]^+$), 217 (5), 167 (29), 152 (6), 91 (3); HRMS (EI) calc. for $C_{14}H_{11}F_3$ $[M]^+$: 236.081285, found: 236.080898.

Synthesis of 2-fluoro-3'-methylbiphenyl **6c**: Compound **6c** was synthesized following the above procedure from 3-methylbenzoic anhydride (**1a**) (254 mg, 1.00 mmol) and 2,4,6-tris-(2-fluorophenyl)boroxine (**3c**) (182 mg, 0.50 mmol). After purification by column chromatography (SiO_2, Hexane) **6c** was obtained as a white solid (90 mg, 0.48 mmol, 48 %); ^{1}H-NMR (300.1 MHz, $CDCl_3$): 7.33-7.23 (m, 4H), 7.21-7.16 (m, 1H), 7.12-7.00 (m, 3H), 2.31 (s, 3H) ppm; ^{13}C-NMR (75.5 MHz, $CDCl_3$): 158.7 (^1J(C-F) = 248 Hz), 137.5, 135.3, 129.0, 128.6, 128.4, 128.3, 128.0, 127.9, 125.7, 123.8, 115.6 (^3J(C-F) = 23 Hz), 21.0 ppm; MS (EI, 70 eV): m/z (%) = 186 (100, $[M]^+$), 183 (14), 170 (9), 165 (21), 133 (4); HRMS (EI) calc. for $C_{13}H_{11}F$ $[M]^+$: 186.084478, found: 186.084697.

Synthesis of 2-m-*tolylnaphtalin* **6d**: Compound **6d** was synthesized following the above procedure from 3-methylbenzoic anhydride (**1a**) (254 mg, 1.00 mmol) and 2,4,6-tris-(2-naphtyl)boroxine (**3d**) (231 mg, 0.50 mmol). After purification by column chromatography (SiO_2, hexane) **6d** was obtained as a white solid (100 mg, 0.45 mmol, 45 %). The spectroscopic data of the product was identical with that reported in literature for 2-m-tolylnaphtalin CAS registry number: [36821-15-5].

Synthesis of 3-methyl-3'-nitrobiphenyl **6e**: Compound **6e** was synthesized following the above procedure from 3-methylbenzoic anhydride (**1a**) (254 mg, 1.00 mmol) and 2,4,6-tris-(3-nitrophenyl)boroxine (**3e**) (223 mg, 0.50 mmol). After purification by column chromatography (SiO_2, hexane / ethyl acetate 10:1) **6e** was obtained as a yellow solid (130 mg, 0.61 mmol, 61 %). The spectroscopic data of the product was identical with that reported in literature for 3-methyl-3'-nitrobiphenyl, CAS registry number: [952-03-04].

Synthesis of 3'-methylbiphenyl-4-carbonitrile **6f**: Compound **6f** was synthesized following the above procedure from 3-methylbenzoic anhydride (**1a**) (254 mg, 1.00 mmol) and 2,4,6-tris-(4-benzonitrile)boroxine (**3f**) (207 mg, 0.50 mmol). After purification by column chromatography (SiO_2, hexane / ethyl acetate 10:1) **6f** was obtained as a white solid (110 mg, 0.57 mmol, 57 %); ^{1}H-NMR (300.1 MHz, $CDCl_3$): 7.69 (cm, 4H), 7.41-7.33 (m, 3H), 7.26-7.21 (m, 1H), 2.43 (s, 3H) ppm; ^{13}C-NMR (75.5 MHz, $CDCl_3$): 146.2, 139.6, 139.2, 132.9, 129.8, 129.4, 128.4, 128.1, 124.8, 119.4, 111.2, 21.9 ppm; MS (EI, 70 eV): m/z (%) = 193 (100, $[M]^+$), 190 (11), 177 (6), 165 (15), 152 (3); HRMS (EI) calc. for $C_{14}H_{11}N$ $[M]^+$: 193.089149, found: 193.088972.

Synthesis of 3-chloro-3'-methylbiphenyl **6g**: Compound **6g** was synthesized following the above procedure from 3-methylbenzoic anhydride (**1a**) (254 mg, 1.00 mmol) and 2,4,6-tris-(3-chlorophenyl)boroxine (**3g**) (207 mg, 0.50 mmol). After purification by column chromatography (SiO_2, hexane) **6f** was obtained as a white solid (110 mg, 0.55 mmol, 55 %). The spectroscopic data of the product was identical with that reported in literature for 3-chloro-3'-methylbiphenyl, CAS registry number: [952-03-04].

Synthesis of 4-methoxy-3'-methylbiphenyl **6h**: Compound **6h** was synthesized following the above procedure from 3-methylbenzoic anhydride (**1a**) (254 mg, 1.00 mmol) and 2,4,6-tris-(4-methoxyphenyl)boroxine (**3h**) (201 mg, 0.50 mmol). After purification by column chromatography (SiO_2, hexane / ethyl acetate 10:1) **6h** was obtained as a white solid (75 mg,

0.38 mmol, 38 %). The spectroscopic data of the product was identical with that reported in literature for 4-methoxy-3'-methylbiphenyl, CAS registry number: [17171-17-4].

Synthesis of biphenyl **6i**: Compound **6i** was synthesized following the above procedure from benzoic anhydride (**1b**) (226 mg, 1.00 mmol) and 2,4,6-triphenylboroxine (**3a**) (0.50 mmol, 155 mg). After purification by column chromatography (SiO_2, hexane) **6i** was obtained as a white solid (85 mg, 0.55 mmol, 55 %). The spectroscopic data of the product was identical with that reported in literature for biphenyl, CAS registry number: [92-52-4].

Synthesis of 4-methoxybiphenyl **6j**: Compound **6j** was synthesized following the above procedure from anisic anhydride (**1c**) (286 mg, 1.00 mmol) and 2,4,6-triphenylboroxine (**3a**) (0.50 mmol, 155 mg). After purification by column chromatography (SiO_2, hexane / ethyl acetate 10:1) **6j** was obtained as a white solid (65 mg, 0.35 mmol, 35 %). The spectroscopic data of the product was identical with that reported in literature for 4-methoxybiphenyl, CAS registry number: [613-37-6].

Synthesis of stilbene **6k**: Compound **6k** was synthesized following the above procedure from cinnamatic anhydride (**1d**) (278 mg, 1.00 mmol) and 2,4,6-triphenylboroxine (**3a**) (0.50 mmol, 155 mg). After purification by column chromatography (SiO_2, hexane) **6k** was obtained as a white solid (30 mg, 0.16 mmol, 16 %). The spectroscopic data of the product was identical with that reported in literature for stilbene, CAS registry number: [103-30-0].

Synthesis of 3,4'-dimethylbiphenyl **6l**: Compound **6l** was synthesized following the above procedure from 3-methylbenzoic anhydride (**1a**) (254 mg, 1.00 mmol) and 2,4,6-tris-(4-methylphenyl)boroxine (**3i**) (0.50 mmol, 177mg). After purification by column chromatography (SiO_2, hexane) **6l** was obtained as a white solid (105 mg, 0.57 mmol, 57 %). The spectroscopic data of the product was identical with that reported in literature for 3,4'-dimethylbiphenyl, CAS registry number: [7383-90-6].

Synthesis of 3-phenylfurane **6m**: Compound **6m** was synthesized following the above procedure from furane-3-carboxylic anhydride (**1e**) (206 mg, 1.00 mmol) and 2,4,6-triphenylboroxine (**3a**) (0.50 mmol, 155 mg). After purification by column chromatography (SiO_2, hexane) **6m** was obtained as a white solid (30 mg, 0.21 mmol, 21 %). The spectroscopic data of the product was identical with that reported in literature for 3-phenylfurane, CAS registry number: [13679-41-9].

Synthesis of 3-phenylthiophene (**6n**): Compound **6n** was synthesized following the above procedure from thiophene-3-carboxylic anhydride (**1f**) (238 mg, 1.00 mmol) and 2,4,6-triphenylboroxine (**3a**) (0.50 mmol, 155 mg). After purification by column chromatography (SiO_2, hexane) **6n** was obtained as a white solid (35 mg, 0.35 mmol, 21 %). The spectroscopic data of the product was identical with that reported in literature for 3-phenylthiophene, CAS registry number: [2404-87-7].