Synthesis of symmetrical terphenyl derivatives by PdCl₂-catalyzed

Suzuki-Miyaura reaction of dibromobenzene using

3-(diphenylphosphino)propanoic acid as a ligand

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Supporting Information

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General methods

All the reactions were carried out under air using magnetic stirring unless otherwise noted. ^1H NMR spectral data were recorded on a Bruker DPX-400 spectrometer using TMS as internal standard and CDCl_3 as solvent. Mass spectra were recorded on GC-MS (Agilent 7890A/5975C) instrument under EI model. Column chromatography was performed with silica gel (200-300 mesh) purchased from Qingdao Haiyang Chemical Co., Ltd. All the other reagents were of analytical grade quality, purchased commercially and used as received.

General procedure for Pd-catalyzed Suzuki-Miyaura reactions

The Schlenk tube (5 mL) equipped with a stir bar was charged with PdCl_2 (1.0 mol%), $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{COOH}$ (2.0 mol%), and $\text{K}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ (4.0 equiv.), then 1,4-dibromobenzene (0.5 mmol), phenylboronic acid (1.20 mmol), and DMSO (2.0 ml) were added, and the mixture was stirred at 100 °C until the substrate was completely consumed. After cooling to room temperature, the solution was quenched with water and extracted with EtOAc (3×10 mL). The combined EtOAc extracts were dried over anhydrous Na_2SO_4 and filtrated and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel with PE as the eluent to obtain the desired products.

The NMR spectra data of the products

1,1':4',1''-terphenyl (3a) ^[1]

White solid, Isolated yield = 93 %; mp 211-213 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.68 (s, 4H), 7.67-7.64(m, 4H), 7.49–7.44 (m, 4H), 7.37 (tt, J = 14.8, 7.6 Hz, 2H).

4,4''-dipropyl-1,1':4',1''-terphenyl (3b) ^[2]

White solid, Isolated yield = 94 %; mp 73.2-74 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.65 (s, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 7.7 Hz, 2H), 2.64 (t, *J* = 15.2, 7.6 Hz, 2H), 1.74-1.65(m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H).

4,4''-dipentyl-1,1':4',1''-terphenyl (3c) ^[2]

White solid, Isolated yield = 90 %; mp 174.7-175.4 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.65 (s, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 2.66 (t, *J* = 15.6, 7.6 Hz, 2H), 1.71-1.60 (m, 2H), 1.37-1.34 (m, 4H), 0.91 (t, *J* = 6.8 Hz, 3H).

4,4''-difluoro-1,1':4',1''-terphenyl (3d) ^[3]

White solid, Isolated yield = 90 %; mp 116.4-117.1 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.62-7.57 (m, 8H), 7.17-7.13 (m, 4H),

4,4''-bis(trifluoromethyl)-1,1':4',1''-terphenyl (3e) ^[4]

Creamy white solid, Isolated yield = 85 %; mp 209-210 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.74 (d, *J* = 2.5 Hz, 8H), 7.72 (s, 4H).

3,3'',4,4'',5,5''-hexafluoro-1,1':4',1''-terphenyl (3f) ^[5]

White solid, Isolated yield = 76 %; mp 102.2-102.8 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.59 (s, 4H), 7.23 (dd, *J* = 14.1, 6.4 Hz, 4H).

[1,1':4',1''-terphenyl]-4,4''-dicarbaldehyde (3g) ^[6]

White solid, isolated yield = 75%; mp 272-275 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.65-7.54 (m, 8H), 7.15 (t, *J* = 8.6 Hz, 4H).

3,3''-dimethyl-1,1':4',1''-terphenyl (3h) ^[7]

White solid, Isolated yield = 95 %; mp 141 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.65 (s, 4H), 7.44 (d, *J* = 8.4 Hz, 4H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.17 (d, *J* = 7.5 Hz, 2H), 2.44 (s, 6H).

2,2''-dimethyl-1,1':4',1''-terphenyl (3i) ^[8]

White solid, Isolated yield = 95 %; mp 145.5-146 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.37 (s, 4H), 7.32-7.26 (m, 8H), 2.35 (s, 6H).

1,1':2',1''-terphenyl (3j) ^[9]

White solid, Isolated yield = 43 %; mp 56.2-56.8 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.43 – 7.38 (m, 4H), 7.21-7.16 (m, 6H), 7.15 – 7.11 (m, 4H).

4,4''-bis(trifluoromethyl)-1,1':2',1''-terphenyl (3k) ^[10]

White solid, Isolated yield = 60 %; mp 102.9-103.6 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.49 (ddd, *J* = 5.8, 1.9, 1.2 Hz, 6H), 7.44 (dt, *J* = 5.2, 3.7 Hz, 2H), 7.24 (dd, *J* = 8.7, 0.7 Hz, 4H).

[1,1':2',1''-terphenyl]-4,4''-dicarbaldehyde (3l) ^[11]

Creamy white solid, Isolated yield = 58 %; mp 104.8-106.4 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.98 (s, 1H), 7.75 (dt, *J* = 8.4, 1.6 Hz, 2H), 7.53–7.46 (m, 2H), 7.30 (dd, *J* = 6.4, 1.6 Hz, 2H).

4,4''-difluoro-1,1':2',1''-terphenyl (3m) ^[12]

Faintly yellowy solid, Isolated yield = 57 %; mp 96.8-97.2 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.45–7.35 (m, 4H), 7.10–7.05 (m, 4H), 6.95–6.88 (m, 4H).

2,2''-dimethyl-1,1':3',1''-terphenyl (3n) ^[13]

Colorless clear liquid, Isolated yield = 76%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.39–7.34 (m, 1H), 7.19 (qdd, *J* = 13.1, 5.1, 3.9 Hz, 11H), 2.24 (s, 6H).

4,4''-dipropyl-1,1':3',1''-terphenyl (3o)

White solid, Isolated yield = 39 %; mp 80.1-80.6 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.79 (td, *J* = 1.8, 0.5 Hz, 1H), 7.58 – 7.52 (m, 6H), 7.45–7.20 (m, 5H), 2.67–2.61 (m, 4H), 1.74–1.64 (m, 4H), 0.98 (t, *J* = 7.3 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 141.944, 141.650, 138.602, 129.057, 128.898, 127.053, 125.828, 125.673, 37.718, 24.584, 13.911. HRMS (EI): *m/z* calcd for C₂₄H₂₆ [M]⁺ 314.2035, found 314.2031.

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Copies of NMR

3a: 1,1':4',1''-terphenyl

3b: 4,4''-dipropyl-1,1':4',1''-terphenyl

3c: 4,4''-dipentyl-1,1':4',1''-terphenyl

3d: 4,4''-difluoro-1,1':4',1''-terphenyl

3e: 4,4''-bis(trifluoromethyl)-1,1':4',1''-terphenyl

3f: 3,3'',4,4'',5,5''-hexafluoro-1,1':4',1''-terphenyl

3g: [1,1':4',1''-terphenyl]-4,4''-dicarbaldehyde

3h: 3,3''-dimethyl-1,1':4',1''-terphenyl

3i: 2,2''-dimethyl-1,1':4',1''-terphenyl

3j: 1,1':2',1''-terphenyl

3k: 4,4''-bis(trifluoromethyl)-1,1':2',1''-terphenyl

3l: [1,1':2',1''-terphenyl]-4,4''-dicarbaldehyde

3m: 4,4''-difluoro-1,1':2',1''-terphenyl

3n: 2,2''-dimethyl-1,1':3',1''-terphenyl

3o: 4,4''-dipropyl-1,1':3',1''-terphenyl