

Supporting Information

Freedom: A copper-free, oxidant-free and solvent-free palladium catalysed homocoupling reaction.

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General experimental details

¹H NMR spectra were obtained using a Bruker Avance 400 MHz spectrometer. Deuterated chloroform was obtained from Cambridge Isotope Laboratories, Inc., Andover, MA., and used without further purification. GC-MS data was obtained using a Hewlett-Packard 6890 series GC-MS with a Zebron ZB-5, 15 mm × 0.25 mm × 0.25 mm column. All terminal alkynes were purchased from Acros Organics and used without further purification. Palladium(II)trifluoroacetate, palladium(II)acetate, trans-dichlorobis(triphenylphosphine)palladium(II), and tetrakis(triphenylphosphine)palladium(0) were purchased from Strem Chemicals, Inc. and used without further purification. Polymer bound triphenylphosphine-Palladium(0) and polymer bound triphenylphosphine were purchased from Biotage Ltd. Potassium carbonate was purchased from Acros Organics. Simriz 486 Perfluoroelastomer O-rings (6/16" ID × 7/16" OD × 3/32" width) were purchased from Small Parts Inc. The copper rods used to make copper vials were purchased from McMaster-Carr Supply. The Teflon rods used to make Teflon vials were purchased from McMaster-Carr Supply. The stainless steel rods used to make stainless steel vials were purchased from McMaster-Carr Supply. Ball-milling was carried out in an 8000M SpexCertiprep Mixer/Mill purchased from Spex certiprep.

Typical procedure for the homocoupling of terminal alkynes with free Palladium catalyst

In all cases, the phenylacetylene was used as the limiting reagent. Phenylacetylene (0.200 g, 1.96 mmol), free palladium catalyst (0.049 mmol), potassium carbonate (0.270 g, 1.96 mmol), were added to a custom-made 2.0 × 0.5 inch screw capped stainless steel vial inserted with a perfluoroelastomer O-ring, along with a 1/8" inch stainless steel ball bearing. After placement of the vial in a Spex Certiprep 8000M mixer/mill, the reagents were ball milled for 16.7 hours. The resulting mixture was removed from the vial, dissolved with ethyl acetate, filtered, and the organic layer was extracted with ethyl acetate using a separatory funnel and dried over anhydrous magnesium sulfate. The organic layer was removed under reduced pressure to affording the crude product. Then crude product purified by flash column chromatography on silica gel using pentane as eluent to afford pure product. ¹H-NMR and GC-MS were performed to assess the extent and purity of the reaction products. All of the products are known and were characterized by comparison of their spectral data with those of authentic samples.

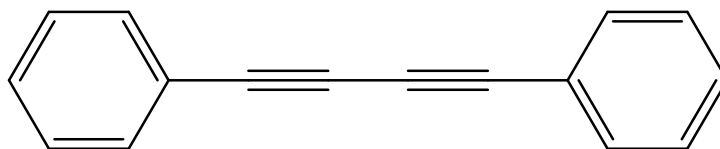
Typical procedure for the homocoupling of terminal alkynes with polymer-supported Palladium

catalyst

In all cases, the phenylacetylene was used as the limiting reagent. Phenylacetylene (0.200 g, 1.96 mmol), polymer-supported tetrakis(triphenylphosphine)palladium(0) (2 % cross-linked with divinylbenzene) (0.022 g, 0.049 mmol), potassium carbonate (0.270 g, 1.96 mmol), were added to a custom-made 2.0 × 0.5 inch screw capped stainless steel vial inserted with a perfluoroelastomer O-ring, along with a 1/8" inch stainless steel ball bearing. After placement of the vial in a Spex Certiprep 8000M mixer/mill, the reagents were ball milled for 16.7 hours. The resulting mixture was removed from the vial, dissolved with ethyl acetate, filtered, and the organic layer was extracted with ethyl acetate using a separatory funnel and dried over anhydrous magnesium sulfate. The organic layer was removed under reduced pressure to affording the crude product. Then crude product purified by flash column chromatography on silica gel using pentane as eluent to afford pure product. Following filtration, the polymer support reagent can be recycled and reuse. ¹H-NMR and GC-MS were performed to assess the extent and purity of the reaction products. All of the products are known and were characterized by comparison of their spectral data with those of authentic samples.

Experimental characterization data for compounds

1,4-Diphenyl buta-1,3-diyne (2a)



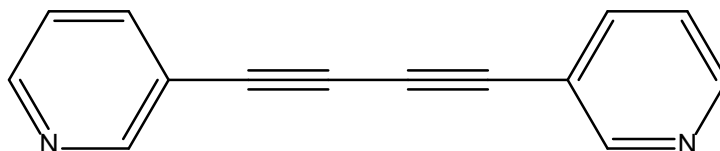
2a

¹H NMR (CDCl₃, 400 MHz): δ (ppm) = 7.56-7.54 (m, 4H), 7.40-7.35 (m, 6H)

¹³C NMR (CDCl₃, 100 MHz): δ (ppm) = 132.5, 129.2, 128.4, 121.8, 81.5, 73.9.

GC-MS: m/z: 202 [M⁺].

3-(4-(Pyridin-3-yl)buta-1,3-diyne)pyridine (2b)



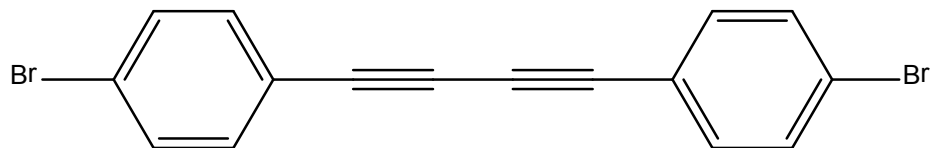
2b

¹H NMR (CDCl₃, 400 MHz): δ (ppm) = 7.29-7.32 (m, 2H), 7.83 (d, 2H), 8.60 (2H), 8.78 (s, 2H)

^{13}C NMR (CDCl_3 , 100 MHz): δ (ppm) = 76.6, 79.1, 118.8, 123.1, 139.4, 149.5, 153.1

GC-MS: m/z : 204 [M^+].

1,4-bis(4-bromophenyl)buta-1,3-diyne (2c)



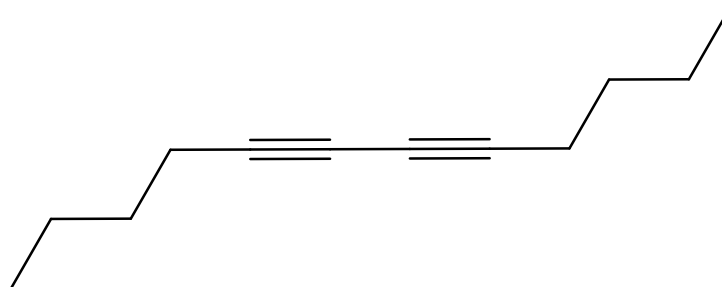
2c

^1H NMR (CDCl_3 , 400 MHz): δ (ppm) = 7.38 (d, $J=8.0$ Hz, 4H), 7.48 (d, $J=8.0$ Hz, 4H)

^{13}C NMR (CDCl_3 , 100 MHz): δ (ppm) = 74.7, 81.0, 120.3, 123.8, 131.8, 133.8

GC-MS: m/z : 358 [M^+].

Dodeca-5,7-diyne (2d)



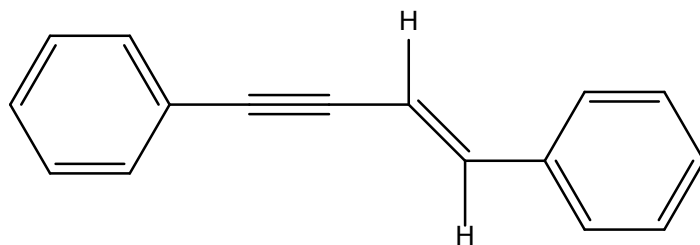
2d

^1H NMR (CDCl_3 , 400 MHz): δ (ppm) = 0.90 (t, 6H), 1.38-1.44 (m, 4H), 1.47-1.52 (m, 4H), 2.25 (t, 4H)

^{13}C NMR (CDCl_3 , 100 MHz): δ (ppm) = 13.5, 18.8, 21.9, 30.3, 65.2, 77.4

GC-MS: m/z : 162 [M^+].

(E)-1,4-Diphenylbut-1-en-3-yne (3a)



3a

^1H NMR (CDCl_3 , 400 MHz): δ (ppm) = 7.47 (d, 2H), 7.43 (d, 2H), 7.35 - 7.25 (m, 6H), 7.05 (d, $J=16.0$ Hz, 1H), 6.39 (d, $J=16.0$ Hz, 1H);

^{13}C NMR (CDCl_3 , 100 MHz): δ (ppm) = 141.2, 136.3, 131.5, 128.7, 128.6, 128.3, 128.2, 126.3, 123.4, 108.1, 91.8, 88.9

GC-MS: m/z : 204 [M^+].