$Pd(PhCN)_2Cl_2/P(t\text{-}Bu)_3$: A Versatile Catalyst for Sonogashira Reactions of Aryl Bromides at Room Temperature

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Supporting Information

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Representative Procedure (Table 1, Entry 4; 4-Methoxyphenyl phenyl acetylene). $Pd(PhCN)_2Cl_2$ (11.5 mg, 0.030 mmol) and CuI (3.9 mg, 0.020 mmol; stored under argon or nitrogen) are added to a dry, 4-mL septum-capped vial, which is then sparged with argon and charged with dioxane (1.0 mL; Aldrich Sure/Seal™ anhydrous/99.8%). $P(t\text{-}Bu)_3$ (260 μL of a 0.25 M solution in dioxane; 0.065 mmol), $HN(i\text{-}Pr)_2$ (166 μL, 1.20 mol; Aldrich Sure/Seal™ 99.5%), 4-bromoanisole (127 μL, 1.00 mmol), and phenylacetylene (131 μL, 1.20 mmol) are added via syringe to the stirred reaction mixture. During the reaction, precipitation of $[H_2N(i\text{-}Pr)_2]Br$ is observed. After 1.0 hours, the reaction mixture is diluted with EtOAc (5 mL), filtered through a small pad of silica gel (with EtOAc rinsings), concentrated, and purified by flash chromatography (50:1 pentane:EtOAc), which yielded the desired product, 4-methoxyphenyl phenyl acetylene[1] (201 mg, 94%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.51 (m, 4H), 7.33 (m, 3H), 6.90 (m, 2H), 3.84 (s, 3H).

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Table 1, Entry 1: Diphenylacetylene.[1] Reaction time: 0.5 h. Purification by flash chromatography (100:1 pentane:Et_2O) furnished the product in 94% yield (167 mg) as a colorless solid. ^1H NMR (300 MHz, $CDCl_3$): δ 7.60-7.40 (m, 10H).

Table 1, Entry 2: 1-Phenyl-1-octyne.[2] Reaction time: 5 h. Purification by flash chromatography (150:1 pentane:Et_2O) furnished the product in 70% yield (130 mg) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ 7.44-7.19 (m, 5H), 2.46-2.39 (m, 2H), 1.75-1.19 (m, 8H), 0.92 (s, 3H).

Table 1, Entry 3: 2-Methyl-4-phenyl-3-butyn-2-ol.[3] Reaction time: 4 h. Purification by flash chromatography (10:1 pentane:EtOAc) furnished the product in 91% yield (146 mg) as a colorless solid. ^1H NMR (300 MHz, $CDCl_3$): δ 7.44 (m, 2H), 7.33 (m, 3H), 2.21 (s, 1H), 1.62 (s, 6H).

Table 1, Entry 5: Hexyl 4-methoxyphenyl acetylene.[4] Reaction time: 6 h. Purification by flash chromatography (100:1 pentane:Et_2O) furnished the product in 93% yield (201 mg) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ 7.33 (m, 2H), 6.81 (m, 2H), 3.79 (s, 3H), 2.38 (m, 2H), 1.61-1.10 (m, 8H), 0.90 (m, 3H).

Table 1, Entry 6: 4-(4-Methoxyphenyl)-2-methyl-3-butyn-2-ol.[5] Reaction time: 8 h. Purification by flash chromatography (6:1 pentane:EtOAc) furnished the product in 95% yield (181 mg) as a colorless solid. ^1H NMR (300 MHz, $CDCl_3$): δ 7.34 (m, 2H), 6.82 (m, 2H), 3.81 (s, 3H), 2.10 (s, 1H), 1.62 (s, 6H).

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Table 1, Entry 7: 4-Methoxyphenyl trimethylsilyl acetylene.[6] Reaction time: 3 h. Purification of the crude reaction mixture by flash chromatography (50:1 pentane: EtOAc, plus 3% NEt_3 to deactivate the silica gel) furnished the product in 90% yield (183 mg) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40 (m, 2H), 6.82 (m, 2H), 3.82 (s, 3H), 0.25 (s, 9H).

Table 1, Entry 8: 4-Dimethylaminophenyl phenyl acetylene.[7] Reaction time: 2.0 h. Purification of the crude reaction mixture by flash chromatography (30:1 pentane:EtOAc) furnished the product in 94% yield (207 mg) as a slightly-yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 (m, 2H), 7.42 (m, 2H), 7.33 (m, 2H), 6.42 (m, 3H), 3.01 (s, 6H).

Table 1, Entry 9: 4-Acetylphenyl phenyl acetylene.[8] Reaction time: 3 h. Purification by flash chromatography (3:1 pentane:EtOAc) furnished the product in 95% yield (192 mg) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.89 (m, 2H), 7.48 (m, 2H), 2.60 (s, 3H), 2.51 (s, 1H), 1.63 (s, 6H).

Table 1, Entry 10: Phenyl *o*-tolyl acetylene.[1] Reaction time: 2.0 h. Purification by flash chromatography (60:1 pentane:EtOAc) furnished the product in 94% yield (180 mg) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53-7.18 (m, 9H), 2.53, (s, 3H).

Table 1, Entry 11: 1-(*o*-Tolyl)-3-methyl-1-butyn-3-ol.[9] Reaction time: 5 h. Purification by flash chromatography (6:1 pentane:EtOAc) furnished the product in

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84% yield (146 mg) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44-7.10 (m, 4H), 2.43 (s, 3H), 2.15 (s, 1H), 1.66 (s, 6H).

Table 1, Entry 12: 2,6-Dimethylphenyl phenyl acetylene.[10] Reaction time: 15 h (90% conversion). Purification by flash chromatography (100:1 pentane:EtOAc) furnished the product in 63% yield (130 mg) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 (m, 2H), 7.44-7.28 (m, 3H), 7.19 (m, 3H), 2.56, (s, 6H).

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