

Photo-activation of Pd-catalyzed Sonogashira coupling using a Ru/bipyridine complex as energy transfer agent

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General information: All manipulations were carried out under a nitrogen atmosphere with use of standard Schlenk techniques. DMF and triethylamine were treated with appropriate drying agents, distilled, and stored under argon in the dark. Analytical GC was carried out on a Shimadzu GC-17A gas chromatography equipped with flame ionization detector using a fused capillary column (ULBON HR-1). Mass spectra were obtained on a Shimadzu QP-5000. ^1H NMR spectra were recorded on Bruker AC-200 and JEOL EX-400 spectrometers.

(A) Representative procedure for the coupling reaction in Table 1 and 2. (Table 1, entry 2;

Diphenyl acetylene)

4-Bromobenzene (0.126 g, 0.80 mmol), $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (0.0084 g, 0.032 mmol), and **TB** (0.055 g, 0.064 mmol) were added to a dried Schlenk tube (13mm in diameter) with a teflon stop cock. The vessel was degassed then backfilled with nitrogen followed by addition of DMF (4.0 mL). Then, $\text{P}(t\text{-Bu})_3$ (97.5 μL of a 10 wt% solution in hexane, 0.032mmol), phenylacetylene (105 μL , 0.96 mmol), mesitylene (internal standard: 50 μL , 0.362 mmol) and Et_3N (1.0 mL, 7.18 mmol) were added via a syringe to the stirred reaction mixture under an atmosphere of nitrogen. The irradiation of visible light was carried out by a 150-w Xenon lamp (Ushio SX-UI 150XQ) through a Toshiba Y-42 glass filter and a Sigma-koki CLDF-50S colored filter ($420 < \lambda < 800$ nm). The diameter of the effective irradiation field is 50 mm. For the dark reactions, the Schlenk tube wrapped with an Al-foil was irradiated to make the reaction temperature similar. The yields of products and the consumption of aryl bromides were determined by GC.

(B) Representative procedure for the coupling reaction in Table 2. (Table 2, entry 1;

4-Acetylphenyl phenyl acetylene¹)

The amounts of substrates, $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$, and $\text{P}(t\text{-Bu})_3$ were increased to three times those in procedure (A). The volume of the solvent was not changed, due to prevent the solvent level from exceeding the effective irradiation field. Therefore, the amount of **TB** was not changed

to keep the optimum concentration.

4-Bromoacetophenone (0.475 g, 2.40 mmol), Pd(CH₃CN)₂Cl₂ (0.0252 g, 0.096 mmol), and TB ([Ru(2,2'-bipyridine)₃]₂PF₆) (0.055 g, 0.064 mmol) were added to a dried Schlenk tube (13mm in diameter) with a teflon stop cock. The vessel was degassed then backfilled with nitrogen followed by addition of DMF (4.0 mL). Then, P(*t*-Bu)₃ (292.5 μL of a 10 wt% solution in hexane, 0.096mmol), phenylacetylene (315.9 μL, 2.90 mmol), mesitylene (internal standard: 50 μL, 0.362 mmol) and Et₃N (1.0 mL, 7.18 mmol) were added via a syringe to the stirred reaction mixture in an atmosphere of nitrogen. The irradiation of visible light was carried out by a 150-w Xenon lamp (Ushio SX-UI 150XQ) through a Toshiba Y-42 glass filter and a Sigma-koki CLDF-50S colored filter (800 > λ > 420 nm). The diameter of the effective irradiation field is 50 mm. After 4.0 hours, the reaction mixture was evaporated to dryness and the crude product was extracted from the residue by addition of ether. The purification by chromatography over silica gel 60N (hexane/EtOAc = 95/5) yielded the desired product, 4-Acetylphenyl phenyl acetylene (482 mg, 91%). ¹H NMR (200 MHz, CDCl₃): δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.54-7.52 (m, 2H), 7.33-7.36 (m, 3H), 2.57 (s, 3H).

Table 2, entry 2; 4-Acetylphenyl trimethylsilyl acetylene.² Reaction time: 7 h. Purification by chromatography (hexane/EtOAc = 95/5) yielded the desired product (467 mg, 90%). ¹H NMR (400 MHz, CDCl₃): δ 7.87 (dm, *J* = 8.4Hz, 2H), 7.52 (dm, *J* = 8.4 Hz, 2H), 2.57 (s, 3H), 0.25 (s, 9H).

Table 2, entry 3; 1-Acetylphenyl-1-octyne.³ Reaction time: 14 h. Purification by chromatography (hexane/EtOAc = 95/5) yielded the desired product (405 mg, 74%). ¹H NMR (200 MHz, CDCl₃): δ 7.96 (d, *J* = 8 Hz, 2H), 7.67 (d, *J* = 8 Hz, 2H), 2.51 (s, 3H), 2.43 (t, *J* = 7 Hz, 2H), 1.76-1.31 (m, 8H), 1.00 (t, *J* = 6.5 Hz, 3H).

Table 2, entry 4; 4-Cyanophenyl phenyl acetylene.⁴ Reaction time: 2 h. Purification by chromatography (hexane/EtOAc = 95/5) yielded the desired product (463 mg, 95%). ¹H NMR (400 MHz, CDCl₃): δ 7.65-7.59 (m, 4H), 7.56-7.53 (m, 2H), 7.40-7.37 (m, 3H).

Table 2, entry 5; Diphenyl acetylene.⁵ Reaction time: 8 h. Purification by chromatography (hexane) yielded the desired product (402 mg, 94%). ¹H NMR (200 MHz, CDCl₃): δ 7.54-7.50

(m, 4H), 7.32-7.28 (m, 6H).

Table 2, entry 6; 1-Cyclohexene phenyl acetylene.⁶ Reaction time: 2 h. Purification by chromatography (hexane/EtOAc = 95/5) yielded the desired product (402 mg, 92%). ¹H NMR (200 MHz, CDCl₃): δ 7.43-7.26 (m, 5H), 6.31-6.33 (m, 1H), 2.32-2.20 (m, 4H), 1.78-1.67 (m, 4H).

Table 2, entry 7; 4-Methoxyphenyl phenyl acetylene.⁷ Reaction time: 8 h. Purification by chromatography (hexane/EtOAc = 98/2) yielded the desired product (422 mg, 84%). ¹H NMR (400 MHz, CDCl₃): δ 7.42 (dd, *J* = 8.7, 0.6 Hz, 2H), 7.39 (d, *J* = 2.3 Hz, 2H), 7.20-7.30 (m, 3H), 6.80 (d, *J* = 8.7 Hz, 2H), 3.75 (s, 3H).

Table 2, entry 8; 4-Methylphenyl phenyl acetylene.⁸ Reaction time: 10 h. Purification by chromatography (hexane/EtOAc = 98/2) yielded the desired product (449 mg, 90%). ¹H NMR (200 MHz, CDCl₃): δ 7.52-7.48 (m, 4H), 7.41 (d, *J* = 7.8 Hz, 2H), 7.29-7.26 (m, 3H), 7.10 (d, *J* = 7.81 Hz, 2H), 2.30 (s, 3H).

Table 2, entry 9; 2,6-Dimethylphenyl phenyl acetylene.⁹ Reaction time: 15 h. Purification by chromatography (hexane) yielded the desired product (430 mg, 87%). ¹H NMR (400 MHz, CDCl₃): δ 7.59 (m, 2H), 7.44-7.28 (m, 3H), 7.19 (m, 3H), 2.56 (s, 6H).

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