Supporting Information

Palladium-catalyzed oxidative alkynylation of alkenes via C–C bond cleavage under oxygen atmosphere

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General Methods. NMR spectra were recorded on JEOL EX-400 (^1H NMR, 400 MHz; ^{13}C NMR, 100 MHz) and JEOL GSX-270 (^1H NMR, 270 MHz; ^{13}C NMR, 67.8 MHz) instruments for solutions in CDCl_3 with Me_4Si as an internal standard: the following abbreviations are used; s: singlet, d: doublet, t: triplet, q: quartet, qui: quintet, m: multiplet. FT–IR spectra (thin film for liquids) were recorded on a Nicolet Impact 400 spectrometer. Column chromatography on SiO_2 was performed with Merck silica gel 60. Elemental analysis was done at the Microanalytical Center of Kyoto University.

Commercially available organic and inorganic compounds were used without further purification except for the solvent, which was distilled by the known method before use.

Typical Procedure for palladium-catalyzed oxidative alkynylation of alkenes under oxygen: A mixture of $\text{Pd}(\text{acac})_2$ (0.02 mmol), pyridine (0.4 mmol), MS3A (40 mg) and toluene (1.0 mL) in a 10-mL schlenk tube fitted with an oxygen balloon was stirred at room temperature. After few minutes, alkene (0.2 mmol) and alcohol (0.20 mmol) in toluene (1.0 mL) were added and the mixture was stirred at 80 °C under oxygen until the reaction had reached completion by monitoring with TLC analysis. The reaction mixture was cooled to room temperature and then filtered through a pad of Florisil. The filtrate was concentrated under vacuum to give an oil, which was subjected to column chromatography on SiO_2 with EtOAc-hexane (2/98) as eluent. GLC yield was determined using bibenzyl as an internal standard.

5-Phenylpent-2-en-4-ynoic acid butyl ester (4): Colorless oil; IR(neat): 1715 and 2200 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 0.95 (t, $J = 7.3$ Hz, 3H), 1.41 (sextet, $J = 7.4$ Hz, 2H), 1.66 (quint, $J = 7.3$ Hz, 2H), 4.18 (t, $J = 6.8$ Hz, 2H), 6.31 (d, $J = 15.6$ Hz, 1H), 6.98 (d, $J = 15.6$ Hz, 1H), 7.34–7.38 (m, 3H), 7.47–7.48 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 13.8, 19.2, 30.7, 64.7, 86.3, 98.2, 122.1, 124.9, 128.4, 129.2, 130.0, 131.8, 165.8. Anal. Calcd for $\text{C}_{15}\text{H}_{16}\text{O}_2$: C, 78.92; H, 7.06. Found: C, 79.21; H, 7.17.

(3-Hexylbut-3-en-1-ynyl)benzene (6): Colorless oil; IR(neat): 2200 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3): δ 0.89 (t, $J = 6.8$ Hz 3H), 1.26–1.43 (m, 6H), 1.59 (quint, $J = 7.3$ Hz, 2.0 H), 2.24 (t, $J = 7.6$ Hz, 2H), 5.28 (d, $J = 1.6$ Hz, 1H), 5.40 (d, $J = 2.0$ Hz, 1H), 7.09–7.35 (m, 3H), 7.41–7.45 (m, 2H); ^{13}C NMR (67.8 MHz, CDCl_3): δ 14.2, 22.7, 28.2, 28.7, 31.7, 37.3, 89.0, 89.9, 120.9, 123.3, 128.0, 131.5, 131.8.. Anal. Calcd for $\text{C}_{16}\text{H}_{20}$: C, 90.51; H, 9.49. Found: C, 90.41; H, 9.66.

Cyclopent-2-enylethynylbenzene (7): Colorless oil; ^1H NMR (270 MHz, CDCl_3): δ 1.26–2.07 (m, 1H), 2.27–2.40 (m, 2H), 2.45–2.58 (m, 1H), 3.69–3.71 (m, 1H), 5.72–5.76 (m, 1H), 5.85 (dd, $J = 2.3, 5.4$ Hz, 1H), 7.25–7.27 (m, 3H), 7.37–7.41 (m, 2H); ^{13}C NMR (67.8 MHz, CDCl_3): δ 31.6, 32.0, 36.4, 80.6, 92.6, 123.9, 127.5, 128.1, 131.2, 131.6, 131.9. Anal. Calcd for $\text{C}_{13}\text{H}_{12}$: C, 92.81; H, 7.19. Found: C, 93.02; H, 7.26.

Cyclopent-3-enylethynylbenzene (8): ^1H NMR (270 MHz, CDCl_3): δ 2.45–2.58 (m, 2H), 2.72–2.81 (m, 2H), 3.23 (quint, $J = 8.1$, 1H), 5.72–5.76 (m, 1H), 7.25–7.27 (m, 3H), 7.37–7.41 (m, 2H); ^{13}C NMR (67.8 MHz, CDCl_3): δ 28.5, 40.3, 79.9, 94.4, 124.0, 127.5, 128.1, 129.4, 131.6.