Synthesis of Tetrasubstituted Olefins by Pd-Catalyzed Addition of Arylboronic Acids to Internal Alkynes

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General

The ^1H and ^{13}C NMR spectra were recorded at 300 MHz or 400 MHz and 75 MHz or 100 MHz, respectively. The COESY and NOESY NMR spectra were recorded at 400 MHz. Thin layer chromatography was performed using commercially prepared 60-mesh silica gel plates (Whatman K6F), and visualization was effected with short wavelength UV light (254 nm). Low resolution mass spectra were recorded on a Finnigan TSQ700 triple quadrupole mass spectrometer (Finnigan MAT, San Jose, CA). High resolution mass spectra were recorded on a Kratos MS50TC double focusing magnetic sector mass spectrometer using EI at 70 eV. Anhydrous forms of DMSO, ethyl ether, hexanes, ethyl acetate, and molecular sieves were purchased from Fisher Scientific Co. All palladium salts were donated by Johnson Matthey Inc. and Kawaken Fine Chemicals Co., Ltd. All arylboronic acids were donated by Frontier Scientific Co., Ltd.

General procedure for the synthesis of tetrasubstituted olefins (Table 2)

$\text{Pd}(\text{OAc})_2$ (0.0125 mmol), the internal alkyne (0.25 mmol), the arylboronic acid (1.25 mmol), molecular sieves (4 Å, 0.2 g), and DMSO (2 mL) were placed in a 6-dram vial. The vial was sealed with a septum, degassed, and equipped with O_2 balloon. The contents were stirred at room temperature or at 50 °C for 24 h. The reaction mixture was quenched with 20 mL of satd NaCl solution. The resulting mixture was extracted three times with ethyl ether (30 mL each time). The combined organic layers were dried over anhydrous MgSO_4 and the solvent was evaporated under reduced pressure. The product was isolated by chromatography on a silica gel column.

Characterization data:

1,1,2-Triphenyl-1-butene (1). White solid: mp 80-82 °C (lit.¹ mp 80-81 °C); ^1H NMR (400 MHz, CDCl_3) δ 0.96 (t, J = 7.6 Hz, 3H), 2.50 (q, J = 7.6 Hz, 2H), 6.88-6.93 (m, 2H), 7.00-7.08 (m, 3H), 7.12-7.20 (m, 5H), 7.25-7.39 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.88, 29.27, 125.96, 126.39, 126.84, 127.59, 128.04, 128.38, 129.71, 129.93,

131.01, 139.02, 142.39, 142.44, 143.24, 143.74; IR (CDCl₃, cm⁻¹) 3023, 2959, 2927, 2858, 1598, 1490; MS (EI) m/z (rel intensity) 284 (M⁺, 100), 269 (26); HRMS (EI) calcd for C₂₂H₂₀ 284.1565, found: 284.1572.

(Z)-1,2-Di-(4-methylphenyl)-1-phenyl-1-butene (2). Colorless oil; ¹H NMR (300 MHz, CDCl₃) δ 0.95 (t, *J* = 7.5 Hz, 3H), 2.22 (s, 3H), 2.31 (s, 3H), 2.47 (q, *J* = 7.5 Hz, 2H), 6.80-6.86 (m, 4H), 7.00-7.07 (m, 4H), 7.26-7.36 (m, 5H); ¹³C NMR (75 MHz, CDCl₃) δ 13.90, 21.35, 21.43, 29.31, 126.67, 128.34, 128.36, 128.83, 129.73, 129.78, 130.89, 135.35, 135.79, 138.54, 139.49, 140.47, 141.80, 144.25; IR (CDCl₃, cm⁻¹) 3022, 2958, 2927, 2860, 1598, 1492; MS (EI) m/z (rel intensity) 312 (M⁺, 100), 297 (23); HRMS (EI) calcd for C₂₄H₂₄ 312.1878, found: 312.1886.

(Z)-1,2-Di-(4-methylphenyl)-1,2-diphenylethene (3).² White solid: mp 143-145 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.29 (s, 6H), 6.92-7.00 (m, 8H), 7.03-7.06 (m, 4H), 7.09-7.12 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 21.52, 126.45, 127.81, 128.65, 131.43, 131.63, 136.16, 140.62, 141.17, 144.39; IR (CDCl₃, cm⁻¹) 3050, 3022, 2920, 2860, 1509, 1443; MS (EI) m/z (rel intensity) 360 (M⁺, 100), 345 (22); HRMS (EI) calcd for C₂₈H₂₄ 360.1878, found: 360.1883.

(E)-2,3-Di-(4-methylphenyl)-3-phenylpropenal (4). Light yellow solid: mp 145-146 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.28 (s, 3H), 2.31 (s, 3H), 6.87-6.90 (m, 2H), 6.93-7.00 (m, 4H), 7.04-7.07 (m, 2H), 7.27-7.31 (m, 2H), 7.41-7.45 (m, 3H), 9.68 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 21.59, 21.61, 128.41, 128.80, 129.13, 129.74, 131.29, 131.40, 131.94, 133.52, 137.35, 138.25, 139.08, 139.67, 139.69, 160.55, 194.15; IR (CDCl₃, cm⁻¹) 3052, 3025, 2919, 2852, 2720, 1669, 1508, 1443; MS (EI) m/z (rel intensity) 312 (M⁺, 100), 297 (29), 252 (13); HRMS (EI) calcd for C₂₃H₂₀O 312.1514, found: 312.1520.

(*E*)-2,3-Di-(4-methylphenyl)-3-phenyl-2-propen-1-ol (5). White solid: mp 93-96 °C; ^1H NMR (400 MHz, CDCl_3) δ 1.27 (s, 1H), 2.22 (s, 3H), 2.29 (s, 3H), 4.45 (s, 2H), 6.81 (d, $J = 8.0$ Hz, 2H), 6.86 (m, $J = 8.0$ Hz, 2H), 7.02 (d, $J = 8.0$ Hz, 2H), 7.11 (d, $J = 8.0$ Hz, 2H), 7.29-7.38 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.41, 21.46, 65.43, 127.39, 128.46, 128.54, 129.29, 129.91, 129.96, 130.80, 136.29, 136.69, 137.43, 138.03, 139.59, 142.46, 142.83; IR (CDCl_3 , cm^{-1}) 3597, 3053, 2986, 2925, 2854, 1509, 1443; MS (EI) m/z (rel intensity) 314 (M^+ , 100), 266 (14), 252 (15); HRMS (EI) calcd for $\text{C}_{23}\text{H}_{22}\text{O}$ 314.1671, found: 314.1676.

Ethyl (*E*)-2,3-di-(4-methylphenyl)-3-phenylpropenoate (6). White solid: mp 127-129 °C; ^1H NMR (300 MHz, CDCl_3) δ 0.96 (t, $J = 7.2$ Hz, 3H), 2.28 (s, 3H), 2.30 (s, 3H), 4.01 (q, $J = 7.2$ Hz, 2H), 6.89-7.03 (m, 8H), 7.28-7.33 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.94, 21.49, 21.52, 61.06, 128.28, 128.49, 128.80, 129.20, 129.44, 129.95, 131.11, 133.48, 135.00, 137.29, 137.63, 138.04, 143.15, 145.59, 171.09; IR (CDCl_3 , cm^{-1}) 3053, 3024, 2918, 2871, 1715, 1509, 1445; MS (EI) m/z (rel intensity) 356 (M^+ , 100), 282 (22), 266 (33); HRMS (EI) calcd for $\text{C}_{25}\text{H}_{24}\text{O}_2$ 356.1776, found: 356.1781.

Ethyl (*E*)-2,3-di-(4-methylphenyl)-3-(trimethylsilyl)propenoate (7). Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 0.13 (s, 9H), 1.30 (t, $J = 7.2$ Hz, 3H), 2.20 (s, 3H), 2.23 (s, 3H), 4.23 (q, $J = 7.2$ Hz, 2H), 6.71 (d, $J = 8.0$ Hz, 2H), 6.88-6.96 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 0.01, 14.28, 21.26, 21.33, 61.24, 127.80, 128.33, 128.47, 129.30, 134.63, 134.80, 136.45, 139.37, 144.05, 151.39, 169.98; IR (CDCl_3 , cm^{-1}) 3020, 2980, 2922, 1716, 1506, 1442; MS (EI) m/z (rel intensity) 352 (M^+ , 18), 337 (100), 309 (30); HRMS (EI) calcd for $\text{C}_{22}\text{H}_{28}\text{SiO}_2$ 352.1859, found: 352.1865.

(E)-1,2-Di-(4-methylphenyl)-1-(4-nitrophenyl)-1-butene (8). Yellow solid: mp 136-138 °C; ^1H NMR (400 MHz, CDCl_3) δ 0.95 (t, $J = 7.2$ Hz, 3H), 2.20 (s, 3H), 2.28 (s, 3H), 2.43 (q, $J = 7.2$ Hz, 2H), 6.73 (d, $J = 8.0$ Hz, 2H), 6.85 (d, $J = 8.0$ Hz, 2H), 7.00-7.03 (m, 4H), 7.40 (d, $J = 8.0$ Hz, 2H), 8.20 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.84, 21.38, 21.47, 29.31, 123.77, 128.72, 128.99, 129.57, 130.65, 130.86, 136.18, 136.48, 136.66, 138.44, 139.22, 143.96, 146.66, 151.29; IR (CDCl_3 , cm^{-1}) 3057, 3022, 2970, 2932, 1516, 1442; MS (EI) m/z (rel intensity) 357 (M^+ , 100), 342 (19); HRMS (EI) calcd for $\text{C}_{24}\text{H}_{23}\text{NO}_2$ 357.1729, found: 357.1736.

(E)-1,2-Di-(4-methoxyphenyl)-1-(4-nitrophenyl)-1-butene (9). Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 0.95 (t, $J = 7.2$ Hz, 3H), 2.42 (q, $J = 7.2$ Hz, 2H), 3.70 (s, 3H), 3.77 (s, 3H), 6.59 (d, $J = 7.6$ Hz, 2H), 6.72-6.76 (m, 4H), 7.04 (d, $J = 8.4$ Hz, 2H), 7.38 (d, $J = 8.4$ Hz, 2H), 8.20 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.88, 29.17, 55.31, 55.37, 113.39, 113.68, 123.76, 130.65, 130.85, 132.20, 133.70, 134.69, 136.10, 143.23, 146.61, 151.41, 158.03, 158.40; IR (CDCl_3 , cm^{-1}) 3033, 2963, 2932, 2836, 1605, 1509, 1441; MS (EI) m/z (rel intensity) 389 (M^+ , 100), 374 (20); HRMS (EI) calcd for $\text{C}_{24}\text{H}_{23}\text{NO}_4$ 389.1627, found: 389.1634.

(Z)-1,2-Di-[4-tetrahydropyranyl-2-oxy]phenyl-1-(4-nitrophenyl)-1-butene (10). Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 0.92 (t, $J = 7.6$ Hz, 3H), 1.57-1.69 (m, 6H), 1.78-1.97 (m, 6H), 2.43 (q, $J = 7.6$ Hz, 2H), 3.52-3.62 (m, 2H), 3.82-3.98 (m, 2H), 5.26-5.28 (m, 1H), 5.35-5.37 (m, 1H), 6.70-6.75 (m, 4H), 6.86 (d, $J = 8.8$ Hz, 2H), 7.02 (d, $J = 8.8$ Hz, 2H), 7.38 (d, $J = 8.8$ Hz, 2H), 8.19 (d, $J = 8.8$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.89, 19.19, 19.27, 25.40, 25.45, 29.24, 30.62, 30.70, 62.52, 62.59, 96.60, 96.74, 115.80, 116.13, 123.72, 130.67, 130.76, 132.11, 134.57, 135.46, 136.174, 143.31, 146.59, 151.39, 155.61, 155.98; IR (CDCl_3 , cm^{-1}) 3332, 2948, 2871, 1702, 1608, 1512,

1440; MS (EI) m/z (rel intensity) 529 (M^+ , 25), 445 (100); HRMS (EI) calcd for $C_{32}H_{35}NO_6$ 529.2464, found: 529.2474.

(Z)-1,2-Di-(3,4-methylenedioxyphenyl)-1-(4-nitrophenyl)-1-butene (11). Yellow solid: mp 127-129 °C; 1H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, J = 7.2 Hz, 3H), 2.36 (q, J = 7.2 Hz, 2H), 5.85 (s, 2H), 5.92 (s, 2H), 6.30-6.33 (m, 2H), 6.52-6.67 (m, 4H), 7.36 (d, J = 8.8 Hz, 2H), 8.20 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.79, 29.36, 101.12, 101.16, 108.06, 108.35, 109.86, 111.14, 123.24, 123.80, 124.76, 130.49, 135.23, 136.02, 136.47, 143.71, 146.22, 146.48, 146.72, 147.33, 147.62, 150.83; IR ($CDCl_3$, cm^{-1}) 3072, 2971, 2895, 1593, 1516, 1435; MS (EI) m/z (rel intensity) 417 (M^+ , 100), 356 (23); HRMS (EI) calcd for $C_{24}H_{19}NO_6$ 417.1212, found: 417.1217.

(Z)-1,2-Di-(3,5-difluorophenyl)-1-(4-nitrophenyl)-1-butene (12). Yellow oil; 1H NMR (400 MHz, $CDCl_3$) δ 0.96 (t, J = 7.2 Hz, 3H), 2.40 (q, J = 7.2 Hz, 2H), 6.37-6.40 (m, 2H), 6.56-6.68 (m, 4H), 7.38 (d, J = 8.4 Hz, 2H), 8.26 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.45, 29.25, 102.84, 103.01, 103.09, 103.26, 103.36, 103.51, 112.21, 112.28, 112.39, 112.46, 113.37, 113.44, 113.55, 113.62, 115.57, 123.98, 124.16, 129.49, 130.36, 136.52, 144.05, 144.18, 144.21, 144.27, 147.33, 148.24, 161.47, 161.60, 161.82, 161.95, 163.95, 164.08, 164.29, 164.42; IR ($CDCl_3$, cm^{-1}) 3050, 3025, 2968, 2871, 1590, 1516, 1442; MS (EI) m/z (rel intensity) 312 (M^+ , 61), 269 (60), 191 (100); HRMS (EI) calcd for $C_{22}H_{15}NO_2F_4$ 401.1039, found: 401.1046.

Reference

- Okamoto, Y.; Yoshikawa, Y.; Hayashi, T. *J. Organomet. Chem.* **1989**, 359, 143.
- Oda, H.; Morishita, M.; Fugami, K.; Sano, H.; Kosugi, M. *Chem. Lett.* **1996**, 9, 811.