Supporting Information

An Efficient, Regio- and Stereoselective Palladium Catalyzed Route to Tetrasubstituted Olefins

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General

^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively. 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. All reagents were used directly as obtained commercially. Anhydrous forms of K_2CO_3 , KHCO_3 , DMF, ethyl ether, hexanes, and ethyl acetate were purchased from Fisher Scientific Co.. All palladium salts were donated by Johnson Matthey Inc. and Kawaken Fine Chemicals Co., Ltd.. All boronic acids were donated by Frontier Scientific Co., Ltd..

General procedure for the palladium-catalyzed formation of tetrasubstituted olefins (Table 2)

DMF (8 mL), H_2O (2 mL), KHCO_3 (0.75 mmol), the ArI (0.50 mmol), the boronic acid (0.75 mmol), and the internal alkyne (0.25 mmol) were placed in a 6 dram vial. The contents were stirred and heated in a 100 °C oil bath for 10 min. The $\text{PdCl}_2(\text{PhCN})_2$ catalyst (0.0025 mmol, in 0.1 mL of DMF) was injected. The vial was then heated in an oil bath at 100 °C until palladium black appeared (usually in 3-24 h). The reaction mixture was cooled, quenched with 30 mL of satd NaCl solution, and the aqueous layer was extracted with ethyl ether three times. The combined organic layer was dried over

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anhydrous MgSO₄ and the solvent was evaporated under reduced pressure. The product was isolated by chromatography on a silica gel column.

(Z)-2-(4-Methylphenyl)-1,1-diphenyl-1-propene (1a). White solid after recrystallization from hexane: mp 83-85 °C (lit.¹ mp 84-85 °C); ¹H NMR (300 MHz, CDCl₃) δ 2.13 (s, 3H), 2.28 (s, 3H), 6.90-7.06 (m, 9H), 7.24-7.28 (m, 3H), 7.33-7.38 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 21.36, 23.60, 125.93, 126.72, 127.65, 128.33, 128.81, 129.40, 130.25, 131.09, 135.78, 135.99, 139.17, 141.19, 143.52, 143.98; IR (CDCl₃, cm⁻¹) 3023, 2922, 2856, 1509, and 1490; MS (EI) m/z (rel intensity) 284 (M⁺, 100), 269 (38); HRMS (EI) calcd for C₂₂H₂₀ 284.1565, found: 284.1570.

(Z)-1-(4-Methylphenyl)-1,2-diphenyl-1-propene (1b). White solid after recrystallization from hexane: mp 93-95 °C; ¹H NMR (300 MHz, CDCl₃) δ 2.15 (s, 3H), 2.22 (s, 3H), 6.79-6.87 (m, 4H), 7.18-7.37 (m, 10H); ¹³C NMR (75 MHz, CDCl₃) δ 21.33, 23.65, 126.34, 126.74, 128.12, 128.34, 128.40, 129.53, 130.24, 130.97, 135.38, 135.58, 139.43, 140.33, 144.04, 144.50; IR (CDCl₃, cm⁻¹) 3023, 2922, 1509, and 1490; MS (EI) m/z (rel intensity) 284 (M⁺, 100), 269 (46), 254 (17); HRMS (EI) calcd for C₂₂H₂₀ 284.1565, found: 284.1573.

1-Methyl-4-(triphenylethenyl)-benzene (3). White solid: mp 146-148 °C (lit.² mp 146-148 °C); ¹H NMR (300 MHz, CDCl₃) δ 2.29 (s, 3H), 6.95-7.16 (m, 19H); ¹³C NMR (75 MHz, CDCl₃) δ 21.47, 126.55, 126.60, 127.87, 127.93, 128.65, 131.49, 131.58, 131.62, 136.31, 140.73, 141.01, 141.17, 144.18, 144.21, 144.22 (3 C are missing due to overlap); IR (CDCl₃, cm⁻¹) 3023, 2920, 1508, and 1492; MS (EI) m/z (rel intensity) 346 (M⁺, 100); HRMS (EI) calcd for C₂₇H₂₂ 346.1722, found: 346.1728.

1-Methoxy-4-(triphenylethenyl)benzene (4). Light yellow solid: mp 132-134 °C (lit.³ mp 132-134 °C); ¹H NMR (300 MHz, CDCl₃) δ 3.75 (s, 3H), 6.66 (d, *J* = 8.7 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 7.04-7.15 (m, 15H); ¹³C NMR (75 MHz, CDCl₃) δ 55.32, 113.28, 126.47, 126.48, 126.59, 127.84, 127.96, 129.29, 131.58, 131.60, 131.63, 132.77, 136.35, 140.33, 140.76, 144.22, 144.23, 144.28, 158.32; IR (CDCl₃, cm⁻¹) 3055, 3019, 2954, 2836, 1508, 1491; MS (EI) m/z (rel intensity) 362 (M⁺, 100); HRMS (EI) calcd for C₂₇H₂₂O 362.1671, found: 362.1677.

1-Chloro-4-(triphenylethenyl)benzene (5). White solid: mp 165-167 °C; ¹H NMR (300 MHz, CDCl₃) δ 6.95-7.15 (m, 19H); ¹³C NMR (75 MHz, CDCl₃) δ 126.82, 126.88, 126.92, 127.93, 128.02, 128.11, 128.15, 131.48, 131.50, 131.53, 132.42, 132.88, 139.88, 141.82, 142.46, 143.53, 143.60, 143.66; IR (CDCl₃, cm⁻¹) 3055, 3025 and 1491; MS (EI) m/z (rel intensity) 366 (M⁺, 100); HRMS (EI) calcd for C₂₆H₁₉Cl 366.1175, found: 366.1181.

(Z)-1-(3,5-Difluorophenyl)-2-(4-methoxyphenyl)-1,2-diphenylethylene (6). White solid: mp 131-133 °C; ¹H NMR (300 MHz, CDCl₃) δ 3.78 (s, 3H), 6.57-6.60 (m, 3H), 6.71 (d, *J* = 8.7 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 7.00-7.13 (m, 10H); ¹³C NMR (75 MHz, CDCl₃) δ 55.37, 101.77, 102.11, 102.45, 113.61, 114.15, 114.25, 114.38, 114.48, 126.96, 127.04, 127.93, 128.12, 128.17, 128.24, 131.41, 131.48, 132.52, 132.70, 135.38, 138.07, 142.59, 142.99, 143.44, 147.73, 158.86, 161.06, 161.24, 164.35, 164.52 (the more ¹³C peaks are due to ¹⁹F splitting); IR (CDCl₃, cm⁻¹) 3021, 2930, 2837, 1618, 1592, and 1508; MS (EI) m/z (rel intensity) 398 (M⁺, 100); HRMS (EI) calcd for C₂₇H₂₀F₂O 398.1482, found: 398.1490.

(Z)-2-(4-Methylphenyl)-1,1-diphenyl-1-butene (7a).⁴ White solid after recrystallization from hexane: mp 114-116 °C; ¹H NMR (300 MHz, CDCl₃) δ 0.94 (t, *J* = 7.5 Hz, 3H), 2.28 (s, 3H), 2.48 (q, *J* = 7.5 Hz, 2H), 6.88-7.03 (m, 9H), 7.23-7.37 (m, 5H); ¹³C NMR (75 MHz, CDCl₃) δ 13.88, 21.39, 29.20, 125.82, 126.71, 127.56, 128.33, 128.75, 129.70, 129.76, 130.98, 135.86, 138.66, 139.24, 142.31, 143.43, 143.94; IR (CDCl₃, cm⁻¹) 3033, 2977, 1490, and 1442; MS (EI) m/z (rel intensity) 298 (M⁺, 100), 283 (23); HRMS (EI) calcd for C₂₃H₂₂ 298.1722, found: 298.1726.

3-(4-Methylphenyl)-4,4-diphenyl-3-buten-2-one (8a) and (E)-4-(4-methylphenyl)-3,4-diphenyl-3-buten-2-one (8b). Yellow solid (mixture); ¹H NMR (300 MHz, CDCl₃) δ 2.09 (2 sets of singlets, 3H), 2.28 (2 sets of singlets, 3H), 6.88-7.35 (m, 14H); IR (CDCl₃, cm⁻¹) 3023, 2922, 1683, 1509, 1490, and 1443; MS (EI) m/z (rel intensity) 312 (100), 311(88), 297 (45) and 269 (65); HRMS (EI) calcd for C₂₃H₂₀O 312.1514, found: 312.1522.

Ethyl 2-(4-methylphenyl)-3,3-diphenylpropenoate (9a) and ethyl (E)-3-(4-methylphenyl)-2,3-diphenylpropenoate (9b). Yellow solid (mixture); ¹H NMR (300

MHz, CDCl₃) δ 0.97 (2 sets of triplets, J = 7.2 Hz, 3H), 2.28 (2 sets of singlets, 3H), 4.02 (2 sets of quartets, J = 7.2 Hz, 2H), 6.89-7.32 (m, 14H); IR (CDCl₃, cm⁻¹) 3023, 2985, 1717, 1508, 1490, and 1443; MS (EI) m/z (rel intensity) 342 (M^+ , 14), 252 (100), 207 (27), 179 (45), 178 (53); HRMS (EI) calcd for C₂₄H₂₂O₂ 342.1620, found: 342.1629.

(*E*)-1-(4-Trifluoromethylphenyl)-1-(4-methylphenyl)-2-phenylpropene (10a).

White solid after recrystallization from ethanol: mp 105-107 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.14 (s, 3H), 2.23 (s, 3H), 6.77 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 8.4 Hz, 2H), 7.16-7.22 (m, 5H), 7.38 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 21.34, 23.58, 125.30, 125.34, 125.37, 125.41, 125.91, 126.67, 128.21, 128.60, 128.68, 129.40, 130.56, 130.90, 136.04, 136.66, 138.20, 139.55, 143.86, 147.71, 147.73 (the extra peaks are due to ¹⁹F splitting); IR (CDCl₃, cm⁻¹) 3023, 2920, 1615, 1509, 1490, 1441, and 1325; MS (EI) m/z (rel intensity) 352 (M^+ , 100), 351 (62), 337 (31), 336 (31), 322 (18); HRMS (EI) calcd for C₂₃H₁₉F₃ 352.1439, found: 352.1444.

(*E*)-1-(4-Methylphenyl)-2-phenyl-1-(5-pyrimidyl)propene (11a).

White solid, recrystallized from 40:1 hexane/ethyl acetate: mp 109-111 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.18 (s, 3H), 2.22 (s, 3H), 6.73 (d, J = 8.0 Hz, 2H), 6.87 (d, J = 8.0 Hz, 2H), 7.14-7.20 (m, 5H), 8.64 (s, 2H), 9.13 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 21.33, 23.57, 127.11, 128.33, 128.93, 129.20, 130.86, 132.39, 136.66, 137.55, 138.41, 139.46, 143.00, 156.59, 157.84; IR (CDCl₃, cm⁻¹) 3022, 2920, 1547, 1510, 1442, and 1409; MS (EI) m/z (rel intensity) 286 (M^+ , 100), 271 (32), 215 (59), 213 (31); HRMS (EI) calcd for C₂₀H₁₈N₂ 286.1470, found: 286.1476.

(*E*)-1-(4-Methylphenyl)-1-(4-nitrophenyl)-2-phenylpropene (12a).

Yellow solid, recrystallized from 40:1 hexane/ethyl acetate: mp 136-138 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.15 (s, 3H), 2.22 (s, 3H), 6.73 (d, J = 8.0 Hz, 2H), 6.86 (d, J = 8.0 Hz, 2H), 7.15-7.20 (m, 5H), 7.42 (d, J = 8.8 Hz, 2H), 8.21 (d, J = 8.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 21.32, 23.59, 123.75, 126.92, 128.27, 128.76, 129.33, 130.91, 131.18, 136.40, 137.63, 137.71, 139.10, 143.46, 146.66, 151.03; IR (CDCl₃, cm⁻¹) 3022, 2920, 1592, 1515, and 1491; MS (EI) m/z (rel intensity) 329 (M^+ , 100), 314 (17); HRMS (EI) calcd for C₂₂H₁₉NO₂ 329.1416, found: 329.1423.

(E)-2-(4-Methylphenyl)-1-(4-nitrophenyl)-1-phenylpropene (12b). Yellow solid, recrystallized from 10:1 hexane/acetone: mp 141-143 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.15 (s, 3H), 2.29 (s, 3H), 6.86-6.89 (m, 2H), 7.00-7.09 (m, 7H), 7.41 (d, *J* = 8.8 Hz, 2H), 8.22 (d, *J* = 8.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 21.37, 23.56, 123.75, 126.62, 128.04, 128.96, 129.24, 131.05, 131.20, 136.72, 137.35, 138.18, 140.19, 142.30, 146.63, 150.97; IR (CDCl₃, cm⁻¹) 3023, 2921, 1595, 1515, and 1493; MS (EI) *m/z* (rel intensity) 329 (M⁺, 100), 314 (15); HRMS (EI) calcd for C₂₂H₁₉NO₂ 329.1416, found: 329.1423.

(Z)-1-(4-Methoxyphenyl)-1,2-diphenyl-1-butene (13a).⁵ White solid, recrystallized from hexane: mp 116-118 °C (lit. mp 116-119 °C); ¹H NMR (300 MHz, CDCl₃) δ 0.96 (t, *J* = 7.5 Hz, 3H), 2.48 (q, *J* = 7.5 Hz, 2H), 3.69 (s, 3H), 6.56 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 7.14-7.20 (m, 10H); ¹³C NMR (75 MHz, CDCl₃) δ 13.87, 29.30, 55.24, 113.01, 126.28, 126.78, 128.14, 128.36, 129.72, 129.96, 132.14, 135.72, 138.50, 141.56, 142.69, 144.10, 157.74; IR (CDCl₃, cm⁻¹) 3019, 2969, 2932, 2871, 2834, 1606, 1508, 1492, and 1441; MS (EI) *m/z* (rel intensity) 314 (M⁺, 100), 299 (35), 284 (19); HRMS (EI) calcd for C₂₃H₂₂O 314.1671, found: 314.1680.

References

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Figure 1. NOESY H-H interaction

2.223
2.152

7.369
7.366
7.346
7.298
7.289
7.286
7.278
7.276
7.263
7.260
7.204
7.199
7.192
7.186
7.178
6.873
6.846
6.815
6.787

23.650
21.329

77.703
77.279
76.856

144.495
144.041
140.330
139.433
135.577
135.381
130.967
130.239
129.528
128.400
128.339
128.123
126.737
126.339

13a

13a

NOESY

COESY

COESY

NOESY

COESY

NOESY

NOESY

13a