**Tetrasubstituted Olefin Synthesis via Pd-Catalyzed
Addition of Arylboronic Acids to Internal Alkynes
Using O₂ as an Oxidant**

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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, and visualization was effected with short wavelength UV light (254 nm). Low resolution mass spectra were recorded on a triple quadrupole mass spectrometer. High resolution mass spectra were recorded on a double focusing magnetic sector mass spectrometer using EI at 70 eV. All melting points are uncorrected. All reagents were used as obtained commercially. The product characterization data, ^1H and ^{13}C NMR spectra for compounds **4**, **5**, **7-9**, **14**, **16-18**, **21** can be found in the “Supporting Information” from our previous communication.¹

General procedure for the synthesis of tetrasubstituted olefins (Table 2, eqs. 5 and 6)

$\text{Pd}(\text{OAc})_2$ (0.0125 mmol), the internal alkyne (0.25 mmol), the arylboronic acid (1.25 mmol; 0.5 mmol of *p*-methoxyphenylboronic acid and 0.75 mmol of 3-nitrophenylboronic acid for **eq. 6**), molecular sieves (Fisher Chemicals, type 4 Å, grade 514, 8-12 mesh, beads, 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 an 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.

General procedure for the synthesis of biaryl by homocoupling of aryl boronic acids (Table 3).

$\text{Pd}(\text{OAc})_2$ (0.05 mmol), the arylboronic acid (1.0 mmol), molecular sieves (Fisher Chemicals, type 4 Å, grade 514, 8-12 mesh, beads, 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 an 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:

Ethyl (*E*)-2,3-di-(4-methylphenyl)-butenoate (6) . Colorless liquid: ^1H NMR (400 MHz, CDCl_3) δ 1.31 (t, $J = 7.2$ Hz, 3H), 2.25 (s, 3H), 2.27 (s, 3H), 2.30 (s, 3H), 4.28 (q, $J = 7.2$ Hz, 2H), 6.90-7.00 (m, 8H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.52, 21.43, 21.44, 23.39, 61.11, 128.72, 128.81, 128.86, 129.81, 131.83, 134.41, 136.58, 136.90, 139.08, 142.22, 170.30; IR (CDCl_3 , cm^{-1}) 3022, 2968, 1715, 1598, 1491; MS (EI) m/z (rel intensity) 294 (M^+ , 100), 248 (28); HRMS (EI) calcd for $\text{C}_{20}\text{H}_{22}\text{O}_2$ 294.1620, found: 294.1624.

(*E*)-1,2-Di-(4-methylphenyl)-1-trimethylsilyl-2-phenylethene (11). White solid: mp 88-90 $^{\circ}\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ -0.21 (s, 9H), 2.16 (s, 3H), 2.26 (s, 3H), 6.82-6.96 (m, 8H), 7.25-7.32 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3) δ 0.01, 20.62, 20.66, 126.47, 127.43, 127.52, 127.69, 128.67, 128.91, 129.08, 133.64, 134.89, 139.91, 140.49, 143.17, 144.26, 152.80; IR (CDCl_3 , cm^{-1}) 3026, 2955, 1492; MS (EI) m/z (rel intensity) 356 (M^+ , 100), 341 (86), 284 (8); HRMS (EI) calcd for $\text{C}_{25}\text{H}_{28}\text{Si}$ 356.1960, found: 356.1965.

Diethyl (*Z*)-2,3-di-(4-methylphenyl)-maleate (12). Yellow oil: ^1H NMR (400 MHz, CDCl_3) δ 1.29 (t, $J = 7.2$ Hz, 6H), 2.27 (s, 6H), 4.28 (q, $J = 7.2$ Hz, 4H), 6.97-7.99 (m, 8H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.31, 21.58, 61.86, 129.09, 129.89, 132.02, 138.27, 138.32, 168.57; IR (CDCl_3 , cm^{-1}) 3058, 2983, 1716, 1492; MS (EI) m/z (rel intensity) 352 (M^+ , 100), 337 (11), 307 (48); HRMS (EI) calcd for $\text{C}_{22}\text{H}_{24}\text{O}_4$ 352.1675, found: 352.1680.

(E)- 1-(2,4,5-Trimethoxyphenyl)-2,3-di-(4-methylphenyl)-3-phenyl-2-propen-1-one (13). Yellow solid: mp 105-107 °C; ^1H NMR (400 MHz, CDCl_3) δ 2.23 (s, 3H), 2.28 (s, 3H), 3.79 (s, 6H), 3.85 (s, 3H), 6.28 (s, 1H), 6.89-7.01 (m, 8H), 7.09-7.15 (m, 5H), 7.22 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.49, 21.51, 56.17, 56.20, 56.43, 95.90, 113.77, 120.37, 127.62, 128.02, 128.69, 128.72, 130.19, 130.58, 131.27, 135.89, 136.60, 137.05, 139.20, 141.44, 142.89, 142.97, 143.15, 153.88, 154.49, 197.23; IR (CDCl_3 , cm^{-1}) 3025, 1664, 1598, 1492; MS (EI) m/z (rel intensity) 478 (M^+ , 20), 195 (100); HRMS (EI) calcd for $\text{C}_{32}\text{H}_{30}\text{O}_4$ 478.2144, found: 478.2152.

(E)-1,2-Di-(3,4-dimethoxyphenyl)-1-(4-nitrophenyl)-1-butene (15). Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 0.98 (t, $J = 7.2$ Hz, 3H), 2.43 (q, $J = 7.6$ Hz, 2H), 3.49 (s, 3H), 3.63 (s, 3H), 3.76 (s, 3H), 3.83 (s, 3H), 6.35-6.38 (m, 2H), 6.56-6.60 (m, 2H), 6.72-6.73 (m, 2H), 7.40 (d, $J = 8.8$ Hz, 2H), 8.20 (d, $J = 8.8$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.90, 29.03, 55.81, 55.93, 56.00, 56.03, 110.60, 110.98, 113.46, 114.47, 121.65, 123.49, 123.73, 130.61, 134.15, 134.97, 136.41, 143.57, 146.71, 147.70, 148.03, 148.24, 148.71, 150.97; IR (CDCl_3 , cm^{-1}) 3022, 2960, 1598; MS (EI) m/z (rel intensity) 449 (M^+ , 100), 434 (12); HRMS (EI) calcd for $\text{C}_{26}\text{H}_{27}\text{NO}_6$ 449.1838, found: 449.1842.

(E)-1,2-Di-(4-*t*-butylphenyl)-1-(4-nitrophenyl)-1-butene (19). Light yellow solid (mp 135-137 °C); ^1H NMR (400 MHz, CDCl_3) δ 0.96 (t, $J = 7.6$ Hz, 3H), 1.20 (s, 9H), 1.35 (s,

9H), 2.43 (q, $J = 7.6$ Hz, 2H), 6.70-6.73 (m, 2H), 7.00-7.03 (m, 4H), 7.15-7.18 (m, 2H), 7.42 (dd, $J = 1.6, 8.8$ Hz, 2H), 8.22 (dd, $J = 1.6, 8.8$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.92, 29.19, 31.45, 31.54, 34.57, 34.66, 123.72, 124.61, 124.89, 129.29, 130.53, 130.69, 136.77, 138.43, 139.03, 144.14, 146.61, 149.29, 149.71, 151.17; IR (CDCl_3 , cm^{-1}) 3058, 2966, 1492; MS (EI) m/z (rel intensity) 441 (M^+ , 100), 416 (16), 279 (80); HRMS (EI) calcd for $\text{C}_{30}\text{H}_{35}\text{NO}_2$ 441.2668, found: 441.2674.

(*E*)-1-(4-Nitrophenyl)-1,2-diphenyl-1-butene (20). Light yellow solid: mp 140-142 °C; ^1H NMR (300 MHz, CDCl_3) δ 0.99 (t, $J = 7.2$ Hz, 3H), 2.48 (q, $J = 7.5$ Hz, 2H), 6.85-6.88 (m, 2H), 7.04-7.20 (m, 8H), 7.42-7.45 (m, 2H), 8.22-8.25 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.78, 29.30, 123.82, 126.66, 126.98, 127.98, 128.24, 129.72, 130.66, 130.98, 137.17, 141.39, 141.98, 144.62, 146.77, 150.73; IR (CDCl_3 , cm^{-1}) 3022, 1516, 1442; MS (EI) m/z (rel intensity) 329 (M^+ , 100), 300 (21), 253 (28); HRMS (EI) calcd for $\text{C}_{22}\text{H}_{19}\text{NO}_2$ 329.1416, found: 329.1422.

(*E*)-1,2-Di-(2-methoxyphenyl)-1-(4-nitrophenyl)-1-butene (23). Light yellow oil: ^1H NMR (400 MHz, CDCl_3) δ 0.99 (t, $J = 7.2$ Hz, 3H), 2.50 (br, 2H) (the absence of the quartet of the $-\text{CH}_2-$ group is possibly due to the steric bulkiness around this group), 3.56 (s, 3H), 3.77 (s, 3H), 6.61-6.76 (m, 4H), 6.90-7.10 (m, 4H), 7.47-7.50 (m, 2H), 8.13-8.18 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.79, 26.85, 55.36, 55.39, 110.31, 110.81, 120.03, 120.17, 122.54, 123.21, 128.17, 128.52, 130.35, 130.68, 130.78, 131.07, 131.74, 134.97, 146.33, 150.07, 156.84, 156.97; IR (CDCl_3 , cm^{-1}) 3023, 2960, 2870, 1493; MS (EI) m/z (rel intensity) 389 (M^+ , 100), 374 (8); HRMS (EI) calcd for $\text{C}_{24}\text{H}_{23}\text{NO}_4$ 389.1627, found: 389.1632.

(*E*)-1,2-Di-(2-methylphenyl)-1-(4-nitrophenyl)-1-butene (24). Light yellow oil: ^1H NMR (300 MHz, CDCl_3) δ 1.05 (t, $J = 7.2$ Hz, 3H), 2.03 (br, 3H), 2.25 (br, 3H), 2.53 (br, 2H) (the appearance of the broad peaks and the absence of the quartet of $-\text{CH}_2-$ group are possibly due to the steric bulkiness around these groups), 6.88-7.02 (m, 8H), 7.42-7.47 (m, 2H), 8.16-8.21 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.63, 20.13, 20.76, 123.54, 125.17, 125.35, 126.92, 127.37, 129.56, 130.10, 130.43, 135.99, 140.72, 146.43 (the absence of some carbon signals is possibly due to the steric bulkiness around these carbons and possible overlap of some carbon signals); IR (CDCl_3 , cm^{-1}) 3027, 2928, 1508, 1490; MS (EI) m/z (rel intensity) 357 (M^+ , 100), 342 (11), 267 (20); HRMS (EI) calcd for $\text{C}_{24}\text{H}_{23}\text{NO}_2$ 357.1729, found: 357.1736.

(*Z,Z*)-4,7-Di-(4-methoxyphenyl)-5,6-dipropyl-4,6-decadiene (27a). Light yellow oil: ^1H NMR (400 MHz, CDCl_3) δ 0.77-0.83 (m, 12H), 1.16-1.40 (m, 8H), 1.55-1.58 (m, 2H), 1.99-2.03 (m, 2H), 2.18-2.30 (m, 4H), 3.81 (s, 6H), 6.75 (d, $J = 8.8$ Hz, 4H), 7.10 (d, $J = 8.8$ Hz, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.44, 15.11, 21.73, 22.98, 36.21, 36.57, 55.40, 112.95, 129.78, 136.05, 136.52, 139.19, 157.72; IR (CDCl_3 , cm^{-1}) 3023, 2958, 2930, 2871, 1601, 1492; MS (EI) m/z (rel intensity) 434 (M^+ , 65), 121 (100); HRMS (EI) calcd for $\text{C}_{30}\text{H}_{42}\text{O}_2$ 434.3185, found: 434.3190.

Dimethyl (*Z,Z*)-4,4'-(1,3-butadiene-1,4-diyl)-1,2,3,4-tetrapropyl-bis-benzoate(27d). Colorless liquid: ^1H NMR (400 MHz, CDCl_3) δ 0.72-0.77 (m, 6H), 0.88-0.95 (m, 6H),

1.05-1.11 (m, 4H), 1.40-1.50 (m, 4H), 1.75-1.85 (m, 2H), 2.10-2.25 (m, 6H), 3.91 (s, 6H), 6.91-6.96 (m, 4H), 7.80-7.86 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.29, 15.11, 21.68, 23.12, 35.83, 36.82, 52.20, 127.55, 128.85, 128.92, 137.12, 140.15, 148.92, 167.51; IR (CDCl_3 , cm^{-1}) 3026, 1710, 1599, 1491; MS (EI) m/z (rel intensity) 490 (M^+ , 56), 448 (98), 415 (82), 163 (100); HRMS (EI) calcd for $\text{C}_{31}\text{H}_{42}\text{O}_4$ 490.3083, found: 490.3090.

(Z,Z)-4,7-Di-(3-nitrophenyl)-5,6-dipropyl-4,6-decadiene (27e). Light yellow liquid: ^1H NMR (400 MHz, CDCl_3) δ 0.72-0.79 (m, 6H), 0.90-1.10 (m, 10H), 1.56-1.66 (m, 4H), 1.92-2.33 (m, 8H), 6.89-6.93 (m, 2H), 7.20-7.28 (m, 2H), 7.46-7.48 (m, 2H), 7.95-8.00 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.24, 15.30, 21.90, 23.27, 35.62, 36.35, 121.09, 123.71, 128.29, 134.82, 136.52, 140.29, 144.95, 147.69; IR (CDCl_3 , cm^{-1}) 3026, 2960, 2928, 2871, 1600, 1491; MS (EI) m/z (rel intensity) 464 (M^+ , 100), 421 (42), 286 (50); HRMS (EI) calcd for $\text{C}_{28}\text{H}_{36}\text{N}_2\text{O}_4$ 464.2675, found: 464.2683.

(E)-2-(4-Methoxyphenyl)-1-(3-nitrophenyl)-1-phenyl-1-butene (28). Light yellow liquid: ^1H NMR (400 MHz, CDCl_3) δ 0.95 (t, $J = 7.2$ Hz, 3H), 2.48 (q, $J = 7.2$ Hz, 2H), 3.75 (s, 3H), 6.71-6.75 (m, 2H), 7.00-7.05 (m, 2H), 7.15-7.38 (m, 7H), 7.76 (s, 1H), 7.83-7.88 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.74, 29.33, 55.39, 113.86, 120.93, 125.74, 127.40, 128.50, 128.75, 129.71, 130.93, 133.33, 136.39, 137.10, 142.44, 144.75, 145.34, 147.93, 158.56; IR (CDCl_3 , cm^{-1}) 3026, 2930, 1599, 1492; MS (EI) m/z (rel intensity) 359 (M^+ , 100), 344 (11); HRMS (EI) calcd for $\text{C}_{23}\text{H}_{21}\text{NO}_3$ 359.1521, found: 359.1526.

References

- (1) Zhou, C.; Larock, R. C. *Org. Lett.* **2005**, 7, 259.