Pd(0)-Catalyzed Highly Selective Synthesis of 1,1-Diarylpropadienes and 1,3-Diarylpropynes From 1-Aryl-1-propynes and Aryl Halides

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Supporting Information

Analytical data	SI-1
¹ H / ¹³ C NMR Spectra	SI-9

The following compounds were prepared according to the procedure described in the Experimental Section.

1. Synthesis of 1-phenyl-1-(1'-naphthyl) propadiene (2b) and

1-(1'-naphthyl)-3-phenyl-1-propyne (3b)

Conditions A: The reaction of 1-phenyl-1-propyne (46 mg, 0.40 mmol), *n*BuLi (0.30 mL, 1.6 M in hexanes, 0.48 mmol), ZnBr₂ (180 mg, 0.80 mmol), Pd(PPh₃)₄ (16 mg, 5 mol%), and α -naphthyl iodide (40 μ l, 0.27 mmol) afforded **2b**¹ (50 mg, 77%) as a liquid. ¹H NMR (300 MHz, CDCl₃) δ = 7.94-7.85 (m, 3 H), 7.60-7.40 (m, 4 H),

7.30-7.20 (m, 5 H), 5.28 (s, 2 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ = 209.0, 136.7, 133.9, 133.7, 131.9, 128.4, 128.3, 128.2, 127.8, 126.8, 126.1, 126.0, 125.8, 125.6, 106.4, 77.7; MS (70 eV): m/z (%): 242 (M^+ , 70.42), 241 (100.00); IR (neat): 1935 cm^{-1} .

Conditions B: The reaction of 1-phenyl-1-propyne (46 mg, 0.40 mmol), LDA (0.40 mL, 2.0 M in pentane/THF/ethylbenzene, 0.80 mmol), ZnBr_2 (180 mg, 0.80 mmol), $\text{Pd}(\text{PPh}_3)_4$ (16 mg, 5 mol%), and α -naphthyl iodide (40 μl , 0.27 mmol) afforded **3b** (44 mg, 67%) as a liquid. ^1H NMR (300 MHz, CDCl_3) δ = 8.41 (d, J = 7.8 Hz, 1 H), 7.89-7.81 (m, 2 H), 7.72 (d, J = 7.2 Hz, 1 H), 7.60-7.53 (m, 4 H), 7.47-7.38 (m, 3 H), 7.34-7.30 (m, 1 H), 4.04 (s, 2 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ = 136.8, 133.5, 133.2, 130.3, 128.6, 128.2, 128.2, 128.0, 126.7, 126.6, 126.3, 126.2, 125.2, 121.3, 92.5, 80.7, 26.1; MS (70 eV): m/z (%): 242 (M^+ , 100.00); IR (neat) 1602, 1495 cm^{-1} ; HRMS calcd for $\text{C}_{19}\text{H}_{14}$ [M^+]: 242.10955, found 242.11168.

2. Synthesis of 1-phenyl-1-(4'-methoxyphenyl) propadiene (**2c**) and

1-(4'-methoxyphenyl)-3-phenyl-1-propyne (**3c**)

Conditions A: The reaction of 1-phenyl-1-propyne (46 mg, 0.40 mmol), $n\text{BuLi}$ (0.30 mL, 1.6 M in hexanes, 0.48 mmol), ZnBr_2 (182 mg, 0.80 mmol), $\text{Pd}(\text{PPh}_3)_4$ (16 mg, 5 mol%), and p -methoxyphenyl iodide (63 mg, 0.27 mmol) afforded **2c**¹ (51 mg, 85%) as a liquid. ^1H NMR (300 MHz, CDCl_3) δ = 7.31-7.14 (m, 7 H), 6.80 (d, J = 8.7 Hz, 2

H), 5.16 (s, 2 H), 3.71 (s, 3 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ = 209.7, 158.9, 136.5, 129.5, 128.4, 128.3, 127.1, 113.9, 108.6, 77.9, 55.3; MS (70 eV): m/z (%): 222 (M^+ , 100.00); IR (neat): 1933 cm^{-1} .

Conditions B: The reaction of 1-phenyl-1-propyne (46 mg, 0.40 mmol), LDA (0.40 mL, 2.0 M in pentane/THF/ethylbenzene, 0.80 mmol), ZnBr_2 (180 mg, 0.80 mmol), $\text{Pd}(\text{PPh}_3)_4$ (16 mg, 5 mol%), and *p*-methoxyphenyl iodide (65 mg, 0.28 mmol) afforded **3c** (58 mg, 94%) as a solid. Mp: 42-43°C (petroleum ether); ^1H NMR (300 MHz, CDCl_3) δ = 7.35-7.15 (m, 7 H), 6.73 (d, J = 8.7 Hz, 2 H), 3.73 (s, 2 H), 3.69 (s, 3 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ = 159.2, 137.0, 132.9, 128.5, 127.9, 126.5, 115.8, 113.8, 85.9, 82.4, 55.2, 25.7; MS (70 eV): m/z (%): 222 (M^+ , 100.00); IR (neat): 1607, 1500, 1246 cm^{-1} ; HRMS calcd for $\text{C}_{16}\text{H}_{14}\text{O}$ [M^+]: 222.10446, found 222.10514.

3. Synthesis of 1-phenyl-1-(4'-methoxycarbonylphenyl) propadiene (**2d**) and

1-(4'-methoxycarbonylphenyl)-3-phenyl-1-propyne (**3d**)

Conditions A: The reaction of 1-phenyl-1-propyne (46 mg, 0.40 mmol), *n*BuLi (0.30 mL, 1.6 M in hexanes, 0.48 mmol), ZnBr_2 (180 mg, 0.80 mmol), $\text{Pd}(\text{PPh}_3)_4$ (8 mg, 5 mol%), and 4-iodobenzoic acid methyl ester (35 mg, 0.13 mmol) afforded **2d** (33 mg, 99%) as a liquid. ^1H NMR (300 MHz, CDCl_3) δ = 7.93 (d, J = 8.6 Hz, 2 H), 7.35 (d, J = 8.6 Hz, 2 H), 7.30-7.20 (m, 5 H), 5.24 (s, 2 H), 3.84 (s, 3 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ = 210.3, 166.9, 141.2, 135.5, 129.7, 128.7, 128.5, 128.5, 128.2, 127.5, 108.8,

78.6, 52.1; MS (70 eV): m/z (%): 250 (M^+ , 100.00); IR (neat): 1931, 1724 cm^{-1} ; HRMS calcd for $\text{C}_{17}\text{H}_{14}\text{O}_2$ [M^+]: 250.09938, found 250.10078.

Conditions B: The reaction of 1-phenyl-1-propyne (46 mg, 0.40 mmol), LDA (0.40 mL, 2.0 M in pentane/THF/ethylbenzene, 0.80 mmol), ZnBr_2 (180 mg, 0.80 mmol), $\text{Pd}(\text{PPh}_3)_4$ (8 mg, 5 mol%), and 4-iodobenzoic acid methyl ester (35 mg, 0.13 mmol) afforded **3d** (33 mg, 99%) as a solid. Mp: 48-50°C (petroleum ether); ^1H NMR (300 MHz, CDCl_3) δ = 7.88 (d, J = 8.7 Hz, 2 H), 7.41 (d, J = 8.7 Hz, 2 H), 7.34-7.15 (m, 5 H), 3.81 (s, 3 H), 3.76 (s, 2 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ = 166.6, 136.2, 131.5, 129.4, 129.1, 128.6, 128.4, 127.9, 126.7, 90.9, 82.0, 52.1, 25.8; MS (70 eV): m/z (%): 250 (M^+ , 100.00); IR (neat): 2219, 1720, 1605, 1275, 1108 cm^{-1} ; (Raman) 2227 cm^{-1} ; Anal. calcd for C, 81.58; H, 5.64. Found: C, 81.40; H, 5.58.

4. Synthesis of 1-phenyl-1-(2'-methylphenyl) propadiene (2e) and

1-(2'-methylphenyl)-3-phenyl-1-propyne (3e)

Conditions A: The reaction of 1-phenyl-1-propyne (46 mg, 0.40 mmol), $n\text{BuLi}$ (0.30 mL, 1.6 M in hexanes, 0.48 mmol), ZnBr_2 (180 mg, 0.80 mmol), $\text{Pd}(\text{PPh}_3)_4$ (16 mg, 5 mol%), and 2-methylphenyliodide (34 μl , 0.27 mmol) afforded **2e** (26 mg, 47%) as a liquid. ^1H NMR (300 MHz, CDCl_3) δ = 7.35-7.20 (m, 9 H), 5.21 (s, 2 H), 2.23 (s, 3H); ^{13}C NMR (75.4 MHz, CDCl_3) δ = 208.3, 137.0, 136.3, 135.4, 130.3, 130.2, 128.4, 127.7, 126.7, 126.7, 126.0, 107.2, 77.6, 20.0; MS (70 eV): m/z (%): 206 (M^+ , 100.00);

IR (neat): 1937 cm^{-1} ; HRMS calcd for $\text{C}_{16}\text{H}_{14}$ [M^+]: 206.10955, found 206.10802.

Conditions B: The reaction of 1-phenyl-1-propyne (46 mg, 0.40 mmol), LDA (0.40 mL, 2.0 M in pentane/THF/ethylbenzene, 0.80 mmol), ZnBr_2 (180 mg, 0.80 mmol), $\text{Pd}(\text{PPh}_3)_4$ (16 mg, 5 mol%), and 2-methylphenyl iodide (34 μL , 0.27 mmol) afforded **3e** (29 mg, 52%) as a liquid. ^1H NMR (300 MHz, CDCl_3) δ = 7.46-7.18 (m, 9 H), 3.89 (s, 2 H), 2.45 (s, 3 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ = 140.1, 136.9, 131.9, 129.3, 128.5, 127.9, 127.8, 126.6, 125.4, 123.4, 91.3, 81.6, 25.9, 20.8, MS (70 eV): m/z (%): 206 (M^+ , 100.00); IR (neat): 1602, 1494 cm^{-1} ; HRMS calcd for $\text{C}_{14}\text{H}_{16}$ [M^+]: 206.10955, found 206.10787.

Synthesis of authentic sample 1-phenyl-3-(2'-methylphenyl)-1-propyne (3e')

Phenyl acetylene (0.11 mL, 1 mmol) was lithiated with *n*BuLi (0.75 mL, 1.6 M in hexanes, 1.20 mmol) at -78°C for 30 min. Then 2-methyl benzyl chloride (0.16 mL, 1.20 mmol) and NaI (15 mg, 0.1 mmol) were added at that temperature. The reaction mixture was allowed to stir at room temperature overnight. After the reaction was complete as monitored by TLC (eluent: petroleum ether (60-90 $^\circ\text{C}$), it was quenched with saturated NH_4Cl and extracted with ether. Drying over MgSO_4 , rotary evaporation, and flash chromatography on silica gel (petroleum ether) afforded **3e'** (51 mg, 25%) as a liquid. ^1H NMR (300 MHz, CDCl_3) δ = 7.51-7.40 (m, 3 H), 7.30-7.16 (m, 6 H), 3.74 (s, 2 H), 2.36 (s, 3 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ = 136.0, 134.9, 131.6, 130.1, 128.3, 128.2, 127.7, 126.8, 126.2, 123.7, 87.2, 82.7, 23.9,

19.3, MS (70 eV): m/z (%): 206 (M^+ , 100.00), IR (neat): 1599, 1490, cm^{-1} ; HRMS calcd for $\text{C}_{14}\text{H}_{16}$ [M^+]: 206.10955, found 206.10981.

5. Synthesis of 1-phenyl-1-(4'-cyanophenyl) proadiene (2f) and

1-(4'-cyanophenyl)-3-phenyl-1-propyne (3f)

Conditions A: The reaction of 1-phenyl-1-propyne (46 mg, 0.40 mmol), *n*BuLi (0.30 mL, 1.6 M in hexanes, 0.48 mmol), ZnBr_2 (180 mg, 0.80 mmol), $\text{Pd}(\text{PPh}_3)_4$ (16 mg, 5 mol%), and *p*-cyanophenyliodide (33 mg, 0.14 mmol) afforded **2f** (30 mg, 96%) as a solid. Mp: 87-89°C (petroleum ether); ^1H NMR (300 MHz, CDCl_3) δ = 7.53 (d, J = 8.7 Hz, 2 H), 7.38 (d, J = 8.7 Hz, 2 H), 7.34-7.20 (m, 5 H), 5.27 (s, 2 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ = 210.3, 141.4, 134.8, 132.1, 128.6, 128.6, 128.4, 127.7, 118.9, 110.5, 108.4, 79.0; MS (70 eV): m/z (%): 217 (M^+ , 100.00); IR (neat): 2226, 1925, 1602 cm^{-1} ; Anal. calcd for $\text{C}_{16}\text{H}_{11}\text{N}$: C, 88.45; H, 5.10; N, 6.45. Found: C, 88.13; H, 5.05; N, 6.30. In this reaction, < 4% **1-phenyl-3-(4'-cyanophenyl)-1-propyne (3f')**

was also formed as a liquid. ^1H NMR (300 MHz, CDCl_3) δ = 7.59 (d, J = 8.1 Hz, 2 H), 7.49 (d, J = 8.1 Hz, 2 H), 7.42-7.37 (m, 2 H), 7.31-7.20 (m, 3 H), 3.85 (s, 2 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ = 142.3, 132.4, 131.6, 128.7, 128.3, 128.2, 123.0, 118.9,

110.6, 85.5, 83.7, 26.0; MS (70 eV): m/z (%): 217 (M^+ , 100.00); IR (neat): 2229 cm^{-1} ; HRMS calcd for $\text{C}_{16}\text{H}_{11}\text{N}$ [M^+]: 217.08915, found: 217.08881.

Conditions B: The reaction of 1-phenyl-1-propyne (46 mg, 0.40 mmol), LDA (0.40 mL, 2.0 M in pentane/THF/ethylbenzene, 0.80 mmol), ZnBr_2 (180 mg, 0.80 mmol), $\text{Pd}(\text{PPh}_3)_4$ (8 mg, 5 mol%), and *p*-cyanophenyl iodide (30 mg, 0.13 mmol) afforded **3f** (26 mg, 92%) as a solid. Mp: 41-43°C (petroleum ether); ^1H NMR (300 MHz, CDCl_3) δ = 7.50 (d, J = 8.7 Hz, 2 H), 7.43 (d, J = 8.7 Hz, 2 H), 7.36-7.18 (m, 5H), 3.78 (s, 2 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ = 135.9, 132.1, 131.9, 128.7, 128.6, 127.9, 126.9, 118.5, 111.1, 92.6, 81.2, 25.8; MS (m/z) 217 (M^+ , 100.00); IR (neat): 2227, 1604, 1495 cm^{-1} ; Anal. calcd for $\text{C}_{16}\text{H}_{11}\text{N}$: C, 88.45; H, 5.10; N, 6.45. Found: C, 88.01; H, 4.98; N, 6.30.

6. Synthesis of 1-phenyl-1-(4'-biphenyl) propadiene (**2g**) and

1-phenyl-3-(4'-biphenyl)-1-propyne (**3g**)

Conditions A: The reaction of 1-(4'-biphenyl)-1-propyne (77 mg, 0.40 mmol), *n*BuLi (0.38 mL, 1.6 M in hexanes, 0.60 mmol), ZnBr_2 (180 mg, 0.80 mmol), $\text{Pd}(\text{PPh}_3)_4$ (23 mg, 5 mol%), and iodobenzene (67 μL , 0.60 mmol) afforded **2g** (85 mg, 79%) as a solid. Mp: 72-73°C (petroleum ether); ^1H NMR (300 MHz, CDCl_3) δ = 7.68-7.62 (m,

4 H), 7.51-7.39 (m, 10 H), 5.35 (s, 2 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ = 210.0, 140.7, 140.0, 136.1, 135.2, 131.9, 128.8, 128.7, 128.5, 128.4, 127.3, 127.1, 127.0, 108.9, 78.2; MS (70 eV): m/z (%): 268 (M^+ , 100.00); IR (neat): 1930 cm^{-1} ; Anal. calcd for $\text{C}_{21}\text{H}_{16}$: C, 93.99; H, 6.01. Found: C, 94.02; H, 6.09.

Conditions B: The reaction of 1-(4'-biphenyl)-1-propyne (77 mg, 0.40 mmol), LDA (0.40 mL, 2.0 M in pentane/THF/ethylbenzene, 0.80 mmol), ZnBr_2 (180 mg, 0.80 mmol), $\text{Pd}(\text{PPh}_3)_4$ (16 mg, 5 mol%), and iodobenzene (30 μl , 0.27 mmol) afforded **3g** (48 mg, 66%) as a solid. Mp: 40-42°C (petroleum ether); ^1H NMR (300 MHz, CDCl_3) δ = 7.66-7.30 (m, 14 H), 3.92 (s, 2 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ = 140.9, 139.6, 135.8, 131.6, 128.7, 128.4, 128.2, 127.8, 127.3, 127.2, 127.0, 123.6, 87.4, 82.7, 25.4; MS (70 eV): m/z (%): 268 (M^+ , 100.00); IR (neat) $1597, 1488\text{ cm}^{-1}$; (Raman) 2233 cm^{-1} ; HRMS calcd for $\text{C}_{21}\text{H}_{16}$ [M^+]: 268.12520, found: 268.12623.

References:

1. Ma S.; Zhang A. *J. Org. Chem.* 1998, **63**, 9601.

hqw-6-116-re-c

Archive directory: /export/home/masm/vnmrSYS/data

Sample directory:

File: CARBON

Pulse Sequence: s2pu1

Zxh-1-6-2-c

Archive directory: /export/home/masm/vnarsys/data
Sample directory:
File: CARBON

Pulse Sequence: s2pu1

3a

25.686

hqw-6-135-c

Archive directory: /export/home/masm/vnmrsys/data

Sample directory:

File: CARBON

Pulse Sequence: s2pu1

3b

hqw-6-128-1-c

Archive directory: /export/home/masm/vnmrsys/data

Sample directory:

File: CARBON

Pulse Sequence: s2pu1

3b

hqw-6-136-1-c

Archive directory: /export/home/masm/vnmrSYS/data

Sample directory:

File: CAG80N

Pulse Sequence: s2pu1

hqw-6-129-c

Archive directory: /export/home/masm/vnmrSYS/data

Sample directory:

File: CARBON

Pulse Sequence: s2pu1

hqw-6-133-c

Archive directory: /export/home/masm/vnmr/sys/data

Sample directory:

File: CARBON

Pulse Sequence: s2pu1

hqw-6-130-c

Archive directory: /export/home/masm/vnmrSYS/data

Sample directory:
File: CARBON

Pulse Sequence: s2pu1

hqw-6-137

Pulse Sequence: s2pu1

Solvent: CDCl₃

Ambient temperature
Mercury-800BB "QMC300"

Relax. delay 0.800 sec
Pulse 45.0 degrees
Acq. time 1.500 sec
Width 17482.5 Hz
176 repetitions

OBSERVE C13, 75.4420979 MHz

DECOUPLE H1, 300.0295498 MHz

Power 38 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 4 hr, 23 min, 36 sec

2e

zxh-1-67

Archive directory: /export/home/masm/vnmrSYS/data

Sample directory:

Pulse Sequence: s2pul

3e

91.334

81.564
77.420
77.000
76.573

25.861
20.793

3.737

2.364

0.000

7.517
7.487
7.442
7.414
7.384
7.338
7.306
7.302
7.283
7.279
7.276
7.251
7.242

3.777

0.000

3f

hqw-6-132-c

Archive directory: /export/home/masm/vnmrsys/data

Sample directory:

File: CARBON

Pulse Sequence: s2pu1

3f

hqw-6-143-c

Archive directory: /export/home/masm/vnmr/sys/data

Sample directory:

File: CARBON

Pulse Sequence: s2pu1

— 25.394