Supporting Materials to
***Cis*-Chloropalladation of 1,6-Enynes**

*Gangguo Zhu, Zhaoguo Zhang**

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic
Chemistry, Chinese Academy of Sciences, 354 Fenglin Rd., Shanghai 200032, China.

General	S2
Materials	S2
General procedure for the chloropalladation reaction	S2
Analytical data and NMR spectra for 2	S2-S26
GC data for 2	S27-S36

A: General. All reactions and manipulations were conducted in an air atmosphere. Column chromatography was performed using Silica gel (300-400 mesh). ^1H NMR and ^{13}C NMR were recorded on a 300 MHz spectrometers. Chemical shifts were reported in ppm with the solvent resonance as the internal standard.

B: Materials: PdCl_2 was purchased from commercial source was used directly without purification. 1, 6-enyne substrates¹ and the samples in GC analytical were prepared according to the literature.²

C: General method for chloropalladation reaction of 1,6-enynes with PdCl_2

Under Argon or air atmosphere, a 25 mL Schlenk tube was charged with enyne substrate **1** (0.25 mmol), PdCl_2 (0.0125 mmol) and HOAc (5 mL). The mixture was stirred at 50°C and the reaction was monitored by TLC. After the reaction was completed, the reaction mixture was diluted by ether (100 mL) and washed with water, saturated NaHCO_3 , and saturated brine, then dried over MgSO_4 , followed by column chromatography on silica gel to give the product **2**.

¹ (a) Bartlett, A. J.; Laird, T.; Ollis, W. D. *J. C. S. Perkin Trans. I* **1975**, 1315. (b) Oppolzer, W.; Bedoya-Zurita, M.; Switzer, C. Y. *Tetrahedron Lett* **1988**, 29, 6433. (c) Majumdar, K. C.; Jana, G. H. *Can. J. Chem.* **1998**, 76, 297.

² (a) Ma, S.; Lu, X. *J. Chem. Soc. Chem. Commun.* **1990**, 733. (b) Ma, S.; Lu, X. *J. Org. Chem.* **1991**, 56, 5120.

Data for **2a**: ^1H NMR (300 MHz, CDCl_3):³ δ 2.67 (d, $J = 1.8$ Hz, 3 H), 3.82-3.92 (m, 1 H), 4.15 (dd, $J = 9.0, 2.7$ Hz, 1 H), 4.39 (dd, $J = 9.0, 6.9$ Hz, 1 H), 5.14-5.24 (m, 2 H), 5.81 (ddd, $J = 18.0, 10.2, 7.5$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3): δ 167.6, 149.2, 134.3, 124.4, 117.0, 69.5, 44.7, 22.9.

³ (a) Tong, X.; Zhang, Z.; Zhang, X. *J. Am. Chem. Soc.* **2003**, *125*, 6370. (b) Tong, X.; Zhang, Z.; Zhang, X. *J. Am. Chem. Soc.* **2004**, *126*, 7601.

2b ^1H NMR (300 MHz, CDCl_3) : δ 3.40 (s, 3H), 3.91-3.96 (m, 1H), 4.22 (dd, $J = 2.1$, 9.0 Hz, 1H), 4.46 (dd, $J = 7.5$, 9.0 Hz, 1H), 4.70 (d, $J = 13.2$ Hz, 1H), 4.82 (d, $J = 13.2$ Hz, 1H), 5.21-5.28 (m, 2H), 5.77-5.89 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 166.8, 148.4, 133.5, 128.2, 117.6, 69.9, 69.0, 58.1, 44.7.

2c ^1H NMR (300 MHz, CDCl_3): δ 0.93 (t, $J = 7.5$ Hz, 3 H), 1.29-1.46 (m, 2 H), 1.53-1.71 (m, 2 H), 2.98-3.23 (m, 2 H), 3.89 (dt, $J = 7.5, 0.9$ Hz, 1 H), 4.15 (dd, $J = 9.0, 1.8$ Hz, 1 H), 4.39 (dd, $J = 9.0, 7.5$ Hz, 1 H), 5.12-5.26 (m, 2 H), 5.82 (ddd, $J = 17.1, 10.2, 7.2$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3): δ 167.5, 154.5, 134.4, 124.2, 116.9, 69.5, 44.8, 34.5, 30.0, 21.8, 13.6.

2d ^1H NMR (300 MHz, CDCl_3): δ 4.00-4.08 (m, 1 H), 4.21 (dd, $J = 9.0, 2.4$ Hz, 1 H), 4.48 (dd, $J = 9.0, 7.2$ Hz, 1 H), 5.30-5.36 (m, 2 H), 5.93 (ddd, $J = 16.8, 9.9, 7.2$ Hz, 1 H), 7.37-7.50 (m, 5 H); ^{13}C NMR (75 MHz, CDCl_3): δ 196.0, 147.9, 135.3, 134.0, 130.3, 128.9, 128.0, 125.3, 117.4, 69.3, 45.8.

2e ^1H NMR (300 MHz, CDCl_3): δ 1.58 (s, 3 H), 1.69 (s, 3 H), 3.24 (s, 3 H), 3.95 (dt, J = 6.6, 1.2 Hz, 1 H), 4.16 (dd, J = 9.0, 0.9 Hz, 1 H), 4.39 (dd, J = 9.0, 6.6 Hz, 1 H), 5.15-5.26 (m, 2 H), 5.87 (ddd, J = 17.1, 10.2, 6.9 Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3): δ 164.9, 156.4, 133.6, 126.6, 116.9, 79.6, 69.1, 51.3, 48.0, 25.7, 24.9; IR (neat, cm^{-1}): 2984 (m), 1764 (m), 1618 (m), 1363 (m), 1178 (m), 1075 (m), 981 (m), 921 (m), 734 (m); MS (EI) m/z (rel): 217 (4.78), 215 (14.86), 200 (6.39), 195 (20.92), 185 (5.54), 165 (20.88), 73 (100.00); Anal. Calcd. for $\text{C}_{11}\text{H}_{15}\text{ClO}_3$: C, 57.27, H, 6.55; Found: C, 57.05, H, 6.46.

2f ^1H NMR (300 MHz, CDCl_3): δ 2.44 (s, 3 H), 2.57 (d, $J = 1.2$ Hz, 3 H), 3.68-3.75 (m, 1 H), 3.80 (d, $J = 1.2$ Hz, 1 H), 3.91 (dd, $J = 10.2, 7.5$ Hz, 1 H), 5.08-5.17 (m, 2 H), 5.73 (ddd, $J = 17.1, 10.2, 7.5$ Hz, 1 H), 7.35 (d, $J = 8.1$ Hz, 2 H), 7.92 (d, $J = 8.1$ Hz, 2 H); ^{13}C NMR (75 MHz, CDCl_3): δ 163.7, 148.2, 145.3, 134.8, 134.5, 129.7, 128.1, 127.8, 116.7, 48.9, 40.8, 22.8, 21.7.

2g ^1H NMR (300 MHz, CDCl_3): δ 2.01-2.04 (m, 3 H), 3.44-3.56 (m, 1 H), 3.82-3.96 (m, 2 H), 4.25-4.43 (m, 2 H), 5.09-5.19 (m, 2 H), 5.81 (ddd, $J = 17.1, 10.2, 7.8$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3): δ 136.8, 135.8, 121.7, 115.6, 73.9, 69.8, 48.3, 23.5.

2j ¹H NMR (300 MHz, CDCl₃): δ 3.71-3.80 (m, 1 H), 3.86 (dd, *J* = 8.4, 3.3 Hz, 1 H), 4.05 (dd, *J* = 8.4, 6.3 Hz, 1 H), 4.28 (d, *J* = 13.5 Hz, 1 H), 4.49 (dd, *J* = 13.5, 1.8 Hz, 1 H), 5.17-5.32 (m, 2 H), 5.90 (ddd, *J* = 17.4, 9.9, 7.2 Hz, 1 H), 7.26-7.40 (m, 5 H); ¹³C NMR (75 MHz, CDCl₃): δ 139.7, 138.1, 135.4, 128.6, 128.3, 127.7, 124.7, 116.3,

73.3, 70.5, 49.3.

2h ¹H NMR (300 MHz, CDCl₃): δ 0.92 (t, *J* = 7.2 Hz, 3 H), 1.21-1.40 (m, 2 H), 1.50-1.62 (m, 2 H), 2.22 (t, *J* = 7.2 Hz, 2 H), 3.49-3.58 (m, 1 H), 3.84 (dd, *J* = 8.7, 2.4 Hz, 1 H), 3.92 (dd, *J* = 8.7, 6.3 Hz, 1 H), 4.30 (d, *J* = 12.9 Hz, 1 H), 4.40 (d, *J* = 12.9 Hz, 1 H), 5.08-5.19 (m, 2 H), 5.81 (ddd, *J* = 17.1, 10.2, 7.2 Hz, 1 H); ¹³C NMR (75

S12

5.83 (ddd, $J = 17.4, 10.5, 6.9$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3): δ 136.8, 136.4, 135.6, 115.2, 72.0, 69.1, 51.1, 39.9, 29.6; IR (neat, cm^{-1}): 2966 (m), 2855 (m), 1638 (m), 1459 (m), 1364 (m), 1203 (m), 1081 (m), 993 (m), 933 (m), 734 (m); MS (EI) m/z (rel): 201 (M^+ , ^{37}Cl , 11.70), 199 (M^+ , ^{35}Cl , 28.06), 185 (16.27), 165 (89.40), 155 (6.48), 145 (27.37), 135 (17.97); Anal. Calcd. for $\text{C}_{11}\text{H}_{17}\text{ClO}$: HRMS: Calcd: 239.0605 (M+K), Found: 239.0600.

2k: ^1H NMR (300 MHz, CDCl_3): δ 1.54-1.74 (m, 4 H), 1.98-2.35 (m, 4 H), 3.55-3.63 (m, 1 H), 3.79 (dd, $J = 8.4, 3.6$ Hz, 1 H), 3.99 (dd, $J = 8.4, 6.3$ Hz, 1 H), 4.27-4.42 (m, 2 H), 5.10-5.22 (m, 2 H), 5.70-5.75 (m, 1 H), 5.84 (ddd, $J = 17.4, 9.9, 7.5$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3): δ 136.9, 135.9, 135.8, 129.2, 128.2, 115.7, 73.2, 70.4, 48.3, 26.4, 25.2, 22.3, 21.7; IR (neat, cm^{-1}): 2934 (m), 2859 (m), 1639 (m), 1437 (m), 1269 (m), 1070 (m), 921 (m), 734 (m); MS (EI) m/z (rel): 226 (M^+ , ^{37}Cl , 3.55), 224 (M^+ , ^{35}Cl , 11.44), 194 (15.16), 189 (22.42), 169 (15.64), 159 (34.03), 141 (62.63), 135 (100.00), 115 (72.63); Anal. Calcd. for $\text{C}_{13}\text{H}_{17}\text{ClO}$: HRMS: Calcd: 224.0968, Found: 224.0976.

2I: ¹H NMR (300 MHz, CDCl₃): δ 3.76 (s, 3 H), 3.91 (dd, *J* = 6.9, 6.0 Hz, 1 H), 4.20 (dd, *J* = 9.6, 2.4 Hz, 1 H), 4.44 (dd, *J* = 9.6, 7.8 Hz, 1 H), 5.11-5.30 (m, 3 H), 5.41 (dd, *J* = 13.2, 0.9 Hz, 1 H), 5.79 (ddd, *J* = 16.8, 9.9, 6.9 Hz, 1 H), 6.80-6.96 (m, 4 H); ¹³C NMR (75 MHz, CDCl₃): δ 166.9, 154.5, 151.5, 147.6, 133.3, 128.4, 117.7, 116.5,

70.1, 65.7, 55.6, 44.7.

2m ^1H NMR (300 MHz, CDCl_3): δ 0.90 (t, $J = 6.9$ Hz, 3 H), 1.19-1.33 (m, 2 H), 1.42-1.55 (m, 2 H), 2.19 (t, $J = 6.9$ Hz, 2 H), 2.45 (s, 3 H), 3.14 (dd, $J = 9.6, 6.6$ Hz, 1 H), 3.40 (dd, $J = 9.6, 1.8$ Hz, 1 H), 3.45-3.53 (m, 1 H), 3.66 (d, $J = 13.8$ Hz, 1 H), 3.85-4.08 (m, 1 H), 5.03-5.13 (m, 1 H), 5.69 (ddd, $J = 17.4, 9.9, 6.9$ Hz, 1 H),

7.32-7.38 (m, 2 H), 7.68-7.74 (m, 2 H); ^{13}C NMR (75 MHz, CDCl_3): δ 143.9, 137.4, 135.2, 134.7, 132.4, 129.7, 128.9, 128.4, 127.8, 127.7, 126.9, 116.4, 52.5, 51.0, 47.0, 21.5.

2n ^1H NMR (300 MHz, CDCl_3): δ 2.43 (s, 3 H), 3.32-3.42 (m, 2 H), 3.64-3.75 (m, 2 H), 4.06 (dd, J = 14.7, 1.8 Hz, 1 H), 5.10-5.23 (m, 2 H), 5.75 (ddd, J = 17.4, 10.2, 6.9 Hz, 1 H), 7.25-7.40 (m, 7 H), 7.63 (d, J = 8.4 Hz, 2 H); ^{13}C NMR (75 MHz, CDCl_3): δ 143.9, 137.4, 135.3, 134.7, 132.5, 129.7, 129.0, 128.5, 127.8, 127.7, 126.9, 116.4, 52.5, 51.0, 47.1, 21.5; IR (neat, cm^{-1}): 3083 (m), 1598 (m), 1446 (m), 1350 (m), 1163 (m), 1093 (m), 912 (m), 815 (m), 733 (m); MS (EI) m/z (rel): 375 (M^+ , ^{37}Cl , 1.62), 373 (M^+ , ^{35}Cl , 3.97), 338 (55.91), 218 (64.76), 189 (25.77), 182 (41.47), 155 (100.00); Anal. Calcd. for $\text{C}_{20}\text{H}_{20}\text{ClNO}_2\text{S}$: HRMS: Calcd: 374.0982 ($\text{M}+\text{H}$), Found: 374.0976.

2q ^1H NMR (300 MHz, CDCl_3): δ 3.55-3.63 (m, 1 H), 3.81-3.94 (m, 2 H), 4.07 (s, 2 H), 4.27-4.45 (m, 2 H), 4.53 (s, 2 H), 5.12-5.23 (m, 2 H), 5.80 (ddd, $J = 17.4, 9.9, 7.5$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3): δ 141.9, 137.4, 135.1, 128.5, 127.90, 127.87, 127.81, 122.4, 116.2, 73.3, 72.0, 70.9, 69.4, 48.6; IR (neat, cm^{-1}): 3032 (m), 2860 (m), 1756 (m), 1727 (m), 1678 (m), 1638 (m), 1497 (m), 1455 (m), 1359 (m), 1206 (m), 1077 (m), 992 (m), 925 (m), 737 (m); MS (EI) m/z (rel): 173 ($\text{M}^+ - \text{Bn}$, 3.05), 156 (13.54), 149 (2.51), 128 (3.92), 121 (5.42), 105 (12.10), 91 (100.00); Anal. Calcd. for $\text{C}_{15}\text{H}_{17}\text{ClO}_2$: HRMS: Calcd: 287.0815 ($\text{M} + \text{Na}$), Found: 287.0809.

S20

4.14-4.23 (m, 4H), 5.00-5.07 (m, 2H), 5.64-5.76 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3):
 δ 171.2, 171.1, 137.9, 136.0, 124.0, 114.8, 61.7, 59.6, 46.2, 39.5, 38.7, 23.6, 13.99,
 13.96.

E-**2s** ^1H NMR (300 MHz, CDCl_3): δ 3.82 (t, $J = 7.2$ Hz, 1 H), 4.18 (dd, $J = 9.0, 2.4$ Hz, 1 H), 4.40 (dd, $J = 9.0, 7.2$ Hz, 1 H), 5.25-5.29 (m, 2 H), 5.82 (ddd, $J = 16.8, 9.9, 7.2$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3): δ 166.7, 141.9, 134.1, 127.4, 117.3, 69.3, 47.1, 25.7.

Z-2s: ^1H NMR (300 MHz, CDCl_3): δ 2.50 (d, $J = 1.2$ Hz, 3 H), 3.75-3.86 (m, 1 H), 4.06 (dd, $J = 9.0, 2.7$ Hz, 1 H), 4.37 (dd, $J = 9.0, 7.5$ Hz, 1 H), 5.12-5.25 (m, 2 H), 5.82 (ddd, $J = 18.3, 10.8, 8.1$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3): δ 167.2, 135.0, 133.5, 125.1, 117.4, 68.6, 45.2, 28.9.

E-**2t**: ^1H NMR (300 MHz, CDCl_3): δ 3.95-4.04 (m, 1 H), 4.24 (dd, $J = 9.3, 2.1$ Hz, 1 H), 4.49 (dd, $J = 9.3, 7.5$ Hz, 1 H), 5.32-5.40 (m, 2 H), 5.94 (ddd, $J = 17.4, 10.2, 7.5$, Hz, 1 H), 7.35-7.46 (m, 5 H); ^{13}C NMR (75 MHz, CDCl_3): δ 165.0, 140.2, 137.5, 133.7, 129.9, 128.7, 128.4, 128.9, 117.6, 69.0, 47.9.

Z-2t: ¹H NMR (300 MHz, CDCl₃): δ 3.70-3.78 (m, 1 H), 4.02 (dd, *J* = 8.7, 2.7 Hz, 1 H), 4.33 (dd, *J* = 8.7, 7.2 Hz, 1 H), 4.77-5.01 (m, 2 H), 5.65 (ddd, *J* = 17.7, 10.2, 7.8 Hz, 1 H), 7.37-7.40 (m, 5 H); ¹³C NMR (75 MHz, CDCl₃): δ 167.6, 139.6, 135.2,

132.9, 129.8, 128.3, 127.9, 127.5, 117.5, 69.0, 46.3.

GC trace for *Z*-2t

GC trace for *E*-2t

Area Percent Report

rted By : Signal
 ltiplier : 1.0000
 lution : 1.0000

gnal 1: FID1 A,

ak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	1.415	PB S	0.0132	1.85842e5	2.12730e5	98.85892
2	3.730	BB	0.0455	1979.78723	688.71021	1.05315
3	6.137	PB	0.0980	165.30037	25.05363	0.08793

GC for **2t**:(E/Z=91/9)

GC data for **2a**:

GC data for **2d**:

GC data for **2c**:

GC data for **2b**:

GC trace of pure **Z-2s**

GC trace of pure *E*-2s

=====
Area Percent Report
=====

ted By : Signal
tiplier : 1.0000
ution : 1.0000

nal 1: FID1 A,

k	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	3.732	BV	0.0380	1709.09167	665.28485	93.89624
2	6.456	BB	0.0663	111.10017	25.76314	6.10376

GC for **2s**: (E/Z=94/6)