--Supporting Information--

Ruthenium-Catalyzed [1,n]-Metallotropic Shift (n = 3, 5) of Alkynyl Carbene Complex Intermediates

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(Index)

Synthesis of 1,6-Diacetoxy-2,4-diynes

Procedure 1 (for 1b and 1d-1i) S2

Procedure 2 (for 1j, 1l, and 3) S4

General Procedure of Isomerization Reactions

Properties of Products (2a-2j, 2l, and 4) S5

References S8

To Determine the Configuration of Alkenic Moieties in 2j S9
(NOE Experiments of 2b and 2j)

Selected ¹H and ¹³C NMR Charts

Diyne 1e S10

Diyne 1h S12

Diyne 1j S14

Diyne 1l S16

Triyne 3 S18

Dieneyne 2b S20

Dieneyne 2e S22

Dieneyne 2h S24

Dieneyne 2i S26

Dieneyne 2j S28

Dieneyne 2l S31

Dieneyne 4 S33

Synthesis of 1,6-Diacetoxy-2,4-diynes

Procedure 1 (for symmetric diynes): Diynes **1b**, **1d-i** were prepared from the corresponding propargylic alcohols by using general acetylation methods ($\text{Ac}_2\text{O}/\text{AcCl}/\text{DMAP}$ conditions for primary and secondary alcohols, or $\text{Sc}(\text{OTf})_3$ mediated method¹ for tertiary alcohols) and coupling reactions (Hay coupling conditions² or Swager's conditions³). The typical synthetic procedure was shown below.

1,6-Diacetoxy-1,6-diphenylhexa-2,4-diyne (**1b**).

To a solution of 1-phenyl-2-propyn-1-ol (5.3 g, 40 mmol), triethylamine (8.4 mL, 60 mmol) and 4,4-dimethylaminopyridine (DMAP, 0.39 g, 3.2 mmol) in dichloromethane (80 mL) was slowly added Ac_2O (5.7 mL, 60 mmol) at 0 °C. After stirring at room temperature for 3 h, the reaction mixture was poured into sat. NaHCO_3 aqueous solution. The aqueous layer was extracted with AcOEt (20 mL x 2). The combined organic solution was washed with brine and dried over MgSO_4 . After removal of solvents under reduced pressure, the residue was subjected to short column chromatography on SiO_2 with hexane/ AcOEt (v/v = 10/1) to afford 1-phenyl-2-propynyl acetate in ca. 80% yield.

To a solution of 1-phenyl-2-propynyl acetate (1.7 g, 9.8 mmol), *p*-benzoquinone (0.97 g, 9.0 mmol) and diisopropylamine (2.0 mL, 15 mmol) in toluene (50 mL) was added CuI (19 mg, 0.10 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (14 mg, 0.020 mmol) at room temperature. After stirring at room temperature for 15 h, the solvent was removed under vacuum. The residue was subjected to column chromatography on SiO_2 with hexane/ AcOEt (v/v = 10/1) to afford 1,6-Diacetoxy-1,6-diphenylhexa-2,4-diyne (**1a**) (1.6 g, 4.5 mmol, 46% yield) as a pale yellow oil; IR (neat) 556, 697, 758, 957, 1014, 1218, 1370, 1456, 1746 ($\text{C}=\text{O}$), 2160 ($\text{C}\equiv\text{C}$), 22936, 3035 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 25 °C) δ 2.07 (s, 6H), 6.47 (s, 2H), 7.33-7.39 (m, 6H), 7.44-7.48 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ 20.8, 65.5, 70.6, 76.5, 127.5, 128.6, 129.1, 135.6, 169.2. HRMS (FAB): calcd for $\text{C}_{22}\text{H}_{18}\text{O}_4$ (M^+), 346.1205; found, 346.1198. Anal. Calcd for $\text{C}_{22}\text{H}_{18}\text{O}_4$: C, 76.29; H, 5.24. Found: C, 76.04; H, 5.14.

2,7-Di-*tert*-butylcarbonyloxy-2,7-dimethylocta-3,5-diyne (**1d**).

A white solid (20% yield for 2 steps); mp. 126.4-128.20 °C; IR (KBr) 860, 1118, 1168, 1228, 1283, 1367, 1737 ($\text{C}=\text{O}$), 2157 ($\text{C}\equiv\text{C}$), 2937, 2983 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 1.18 (s, 18H), 1.64 (s, 12H); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C) δ 27.0, 28.5, 39.0, 68.3, 71.3, 80.4, 176.6. HRMS (FAB): calcd for $\text{C}_{20}\text{H}_{30}\text{O}_4$ (M^+), 334.2144; found, 334.2133. Anal. Calcd for $\text{C}_{20}\text{H}_{30}\text{O}_4$: C, 71.82; H, 9.04. Found: C, 71.67; H, 8.78.

1,6-Diacetoxylhexa-2,4-diyne derivative 1e.

A pale gray solid (64% yield for 2 steps); mp. 79.2-80.9 °C; IR (KBr) 963, 1021, 1134, 1160, 1229, 1267, 1369, 1739 (C=O), 2152 (C≡C), 2858, 2938 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 1.26-1.39 (m, 2H), 1.45-1.69 (m, 10H), 1.80-1.89 (m, 4H), 2.04 (s, 6H), 2.05-2.15 (m, 4H); ¹³C NMR (75 MHz, CDCl₃, 25 °C) δ 21.8, 22.4, 25.0, 36.7, 70.3, 75.3, 79.3, 169.0. HRMS (FAB): calcd for C₂₀H₂₆O₄ (M⁺), 374.1518; found, 374.1512. Anal. Calcd for C₂₀H₂₆O₄: C, 72.70; H, 7.93. Found: C, 72.28; H, 7.92.

1,6-Diacetoxy-1,6-di-*p*-methylphenylhexa-2,4-diyne (1f).

A pale yellow oil (27% yield for 2 steps); IR (neat) 553, 734, 769, 814, 910, 954, 1012, 1219, 1369, 1514, 1744 (C=O), 2159 (C≡C), 2925 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 2.07 (s, 6H), 2.35 (s, 6H), 6.44 (s, 2H), 7.17 (d, *J* = 7.8 Hz, 4H), 7.36 (d, *J* = 7.8 Hz, 4H); ¹³C NMR (75 MHz, CDCl₃, 25 °C) δ 20.9, 21.2, 65.5, 70.6, 76.6, 127.7, 129.4, 132.9, 139.2, 169.5. HRMS (FAB): calcd for C₂₄H₂₂O₄ (M⁺), 374.1518; found, 374.1513. Anal. Calcd for C₂₄H₂₂O₄: C, 76.99; H, 5.92. Found: C, 77.10; H, 6.12.

1,6-Diacetoxy-1,6-di-*p*-bromophenylhexa-2,4-diyne (1g).

A pale brown oil (57% yield for 2 steps); IR (neat) 819, 957, 1012, 1071, 1218, 1370, 1488, 1745 (C=O), 2161 (C≡C), 2935 cm⁻¹; ¹H NMR (270 MHz, CDCl₃, 25 °C) δ 2.10 (s, 6H), 6.42 (s, 2H), 7.33-7.38 (m, 4H), 7.49-7.55 (m, 4H); ¹³C NMR (68 MHz, CDCl₃, 25 °C) δ 20.9, 65.0, 70.9, 76.2, 123.5, 129.3, 131.9, 134.7, 169.3. HRMS (FAB): calcd for C₂₂H₁₆Br₂O₄ (M⁺), 503.9396; found, 503.9391. Anal. Calcd for C₂₂H₁₆Br₂O₄: C, 52.41; H, 3.20. Found: C, 52.37; H, 3.24.

1,6-Diacetoxy-1,6-di-*o*-bromophenylhexa-2,4-diyne (1h).

A pale brown oil (83% yield for 2 steps); IR (neat) 558, 684, 912, 1016, 1216, 1370, 1441, 1471, 1749 (C=O), 2161 (C≡C), 2936, 3063 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 25 °C) δ 2.12 (s, 6H), 6.74 (s, 2H), 7.23 (dd, *J* = 7.2, 7.2 Hz, 2H), 7.36 (dd, *J* = 7.2, 8.0 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 7.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃, 25 °C) δ 20.6, 65.1, 70.9, 75.6, 122.9, 127.7,

129.4, 130.6, 132.9, 134.7, 168.9. HRMS (FAB): calcd for $C_{22}H_{16}Br_2O_4$ (M^+), 503.9396; found, 503.9399.

1,6-Diacetoxy-1,6-di-*p*-methoxyphenylhexa-2,4-diyne (1i).

A colorless oil (73% yield for 2 steps); IR (neat) 830, 953, 1013, 1174, 1218, 1508, 1610, 1748 (C=O), 2146 (C≡C), 2839, 2934 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 2.07 (s, 6H), 3.79 (s, 6H), 6.43 (s, 2H), 6.86-6.89 (m, 4H), 7.39-7.42 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 20.9, 55.2, 65.3, 70.5, 76.7, 114.0, 127.9, 129.2, 160.1, 169.3. HRMS (FAB): calcd for $C_{24}H_{22}O_6$ (M^+), 406.1416; found, 406.1409. Anal. Calcd for $C_{24}H_{22}O_6$: C, 70.92; H, 5.46. Found: C, 71.18; H, 5.37.

Procedure 2 (for asymmetric diynes and triyne 3):

1,6-Diacetoxy-6-methylhepta-2,4-diyne (1l).

To a solution of 3-methyl-1-propyn-3-yl acetate (1.1 g, 8.5 mmol), 2-propyn-1-ol (propargyl alcohol, 1.3 g, 22 mmol), *p*-benzoquinone (2.7 g, 25 mmol) and diisopropylamine (5.6 mL, 40 mmol) in toluene (140 mL) was added CuI (67 mg, 0.35 mmol) and $Pd(PPh_3)_4$ (71 mg, 0.060 mmol) at room temperature. After stirring at room temperature for 12 h, the solvent was removed under vacuum. The residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 10/1) to afford diyne (0.82 g, 4.5 mmol, 53% yield). This diyne was used for the next step.

To a solution of diyne (4.5 mmol), triethylamine (0.95 mL, 6.8 mmol) and 4,4-dimethylaminopyridine (DMAP, 45 mg, 0.37 mmol) in dichloromethane (10 mL) was slowly added Ac_2O (0.65 mL, 6.8 mmol) at 0 °C. After stirring at room temperature for 3 h, the reaction mixture was poured into sat. $NaHCO_3$ aqueous solution. The aqueous layer was extracted with AcOEt (10 mL x 2). The combined organic solution was washed with brine and dried over $MgSO_4$. After removal of solvents under reduced pressure, the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 10/1) to afford 1,6-Diacetoxy-6-methylhepta-2,4-diyne (**1j**) (0.85 g, 3.8 mmol, 84% yield) as a colorless oil; IR (neat) 1029, 1131, 1221, 1371, 1748 (C=O), 2161 (C≡C), 2990 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.66 (s, 6H), 2.03 (s, 3H), 2.10 (s, 3H), 4.73 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 20.6, 21.7, 28.6, 52.3, 68.1, 70.5, 71.5, 73.9, 80.1, 169.0, 169.8. HRMS (FAB): calcd for $C_{12}H_{14}O_4$ (M^+), 222.0892; found, 222.0892.

1,6-Diacetoxy-6-methyl-1-phenylhepta-2,4-diyne (1j).

A colorless oil (23% yield for 2 steps); IR (neat) 699, 959, 1016, 1131, 1224, 1370, 1746 (C=O), 2166 (C≡C), 2990 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 1.66 (s, 6H), 2.02 (s, 3H), 2.10 (s, 3H), 6.47 (s, 1H), 7.26-7.42 (m, 3H), 7.45-7.50 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C) δ 20.9, 21.7, 28.6, 65.7, 68.2, 71.0, 71.5, 76.1, 80.8, 127.7, 128.7, 129.2, 136.0, 169.2, 169.5. HRMS (FAB): calcd for $\text{C}_{12}\text{H}_{14}\text{O}_4$ (M^+), 298.1205; found, 298.1201.

2,9-Diacetoxy-2,9-dimethyldeca-3,5,7-triyn-3-ene (3).

A colorless oil (12% yield for 2 steps); IR (neat) 837, 961, 1016, 1131, 1179, 1241, 1337, 1368, 1746 (C=O), 2222 (C≡C), 2940, 2990 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 25 °C) δ 1.66 (s, 12H), 2.02 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ 21.7, 28.6, 63.7, 69.2, 71.5, 79.0, 168.9. HRMS (FAB): calcd for $\text{C}_{16}\text{H}_{18}\text{O}_4$ (M^+), 274.1205; found, 274.1202.

General Procedure of Isomerization Reactions.

To a solution of diyne **1** (0.5 mmol) and ethyl vinyl ether (0.14 mL, 1.5 mmol) in 1,2-dichloroethane (DCE, 2.5 mL) was added $[\text{RuCl}_2(\text{CO})_3]_2$ (13 mg, 0.025 mmol) at room temperature. After stirring at 50 °C for 48 h, the solvent was removed under reduced pressure and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt as eluents to afford the corresponding products **2**.

3,6-diacetoxy-2,7-dimethylocta-2,6-diene-4-yne (2a).

A white solid (98% [79% yield without ethyl vinyl ether]); mp. 47.0-48.9 °C; IR (KBr) 545, 875, 1117, 1305, 1372, 1751 (C=O), 2189 (C≡C), 2914 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 25 °C) δ 1.70 (s, 6H), 1.94 (s, 6H), 2.17 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ 17.6, 20.5, 20.6, 85.8, 125.1, 133.7, 168.2. Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_4$: C, 67.18; H, 7.25. Found: C, 66.94; H, 7.29.

(1Z,5E)-2,5-diacetoxy-1,6-diphenylhexa-1,5-diene-3-yne (2b).

A pale yellow solid (84% yield); mp. 90.3-91.5 °C; IR (KBr) 689, 763, 963, 1016, 1178, 1200, 1372, 1753 (C=O), 2189 (C≡C), 2931, 3039 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 25 °C) δ 2.23 (s, 3H), 2.27 (s, 3H), 6.54 (s, 1H), 6.64 (s, 1H), 7.28-7.39 (m, 6H), 7.47 (d, J = 6.8 Hz, 2H), 7.74 (d, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ 20.9, 21.0, 84.6, 91.0, 127.3, 128.2, 128.3, 128.6, 128.6, 128.7, 128.7, 128.8, 128.9, 129.2, 132.5, 133.1, 167.3, 168.6. HRMS (FAB): calcd for $\text{C}_{22}\text{H}_{18}\text{O}_4$ (M^+), 346.1205; found, 346.1200. Anal. Calcd for $\text{C}_{22}\text{H}_{18}\text{O}_4$: C, 76.29; H, 5.14. Found: C, 75.82; H, 5.14.

3,6-dibenzoyloxy-2,7-dimethylocta-2,6-diene-3-yne (2c).

A white solid (97% yield); mp. 88.2-90.0 °C; IR (KBr) 704, 1023, 1119, 1174, 1256, 1453, 1601, 1735 (C=O), 2200 (C≡C), 2916, 2981 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 1.75 (s, 6H), 2.00 (s, 6H), 7.45 (dd, J = 7.5, 7.5 Hz, 4H), 7.55-7.62 (m, 2H), 8.08-8.13 (m, 4H); ¹³C NMR (75 MHz, CDCl₃, 25 °C) δ 17.8, 20.8, 86.1, 125.4, 128.4, 129.4, 130.1, 133.3, 134.3, 164.1. Anal. Calcd for C₂₄H₂₂O₄: C, 76.99; H, 5.92. Found: C, 76.85; H, 5.96.

3,6-di-*tert*-butylcarbonyloxy-2,7-dimethylocta-2,6-diene-3-yne (2d).

A white solid (91% yield); mp. 72.6-74.0 °C; IR (KBr) 884, 1031, 1109, 1227, 1275, 1307, 1366, 1396, 1457, 1478, 1751 (C=O), 2223 (C≡C), 2913, 2936, 2974 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 1.19 (s, 18H), 1.60 (s, 6H), 1.84 (s, 6H); ¹³C NMR (75 MHz, CDCl₃, 25 °C) δ 17.3, 20.4, 26.9, 38.8, 85.7, 125.5, 132.5, 175.6. HRMS (FAB): calcd for C₂₀H₃₀O₄ (M⁺), 334.2144; found, 334.2135. Anal. Calcd for C₂₀H₃₀O₄: C, 71.82; H, 9.04. Found: C, 71.76; H, 8.88.

2,5-diacetoxyhexa-1,5-diene-3-yne derivative 2e.

A yellow oil (89% yield); IR (neat) 758, 1218, 1371, 1449, 1749 (C=O), 2184 (C≡C), 2858, 2935 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 1.48-1.58 (m, 8H), 1.58-1.67 (m, 4H), 2.06-2.19 (m, 10H containing dimethyl 6H at δ 2.16), 2.34-2.43 (m, 4H); ¹³C NMR (75 MHz, CDCl₃, 25 °C) δ 20.6, 26.1, 26.8, 27.1, 27.8, 30.8, 85.7, 122.2, 140.6, 168.4. HRMS (FAB): calcd for C₂₀H₂₆O₄ (M⁺), 330.1831; found, 330.1830.

(1*Z*,5*E*)-2,5-diacetoxy-1,6-di-*p*-methylphenylhexa-1,5-diene-3-yne (2f).

A white solid (70% yield); mp. 108.7-109.9 °C; IR (KBr) 209, 812, 880, 961, 1018, 1176, 1200, 1371, 1510, 1755 (C=O), 2189 (C≡C), 3025 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 2.22 (s, 3H), 2.28 (s, 3H), 2.35 (s, 3H), 2.36 (s, 3H), 7.13-7.19 (m, 4H), 7.37 (d, J = 8.1 Hz, 2H), 7.63 (d, J = 8.1 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃, 25 °C) δ 20.9, 20.9, 21.4, 21.4, 84.7, 91.3, 127.3, 127.6, 128.1, 128.6, 128.8, 129.1, 129.2, 129.4, 129.7, 130.4, 139.0, 139.0, 167.6, 168.9. Anal. Calcd for C₂₄H₂₂O₄: C, 76.99; H, 5.92. Found: C, 77.18; H, 5.98.

(1Z,5E)-2,5-diacetoxy-1,6-di-*p*-bromophenylhexa-1,5-diene-3-yne (2g).

A pale yellow solid (90% yield); mp. 138.5-139.7 °C; IR (KBr) 815, 884, 962, 1010, 1074, 1178, 1198, 1488, 1747 (C=O), 1763 (C=O), 2202 (C≡C), 3045 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 2.24 (s, 3H), 2.28 (s, 3H), 6.47 (s, 1H), 6.58 (s, 1H), 7.33 (d, *J* = 8.7 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.49 (d, *J* = 8.7 Hz, 2H), 7.60 (d, *J* = 8.7 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃, 25 °C) δ 20.8, 20.9, 84.7, 91.3, 123.0, 123.0, 126.3, 128.0, 128.7, 129.1, 130.1, 130.7, 131.4, 131.6, 131.9, 167.3, 168.6 (one aromatic carbon peak seems to be measured together with others). HRMS (FAB): calcd for C₂₂H₁₆Br₂O₄ (M⁺), 503.9396; found, 503.9394. Anal. Calcd for C₂₂H₁₆Br₂O₄: C, 52.41; H, 3.20. Found: C, 52.24; H, 3.30.

(1Z,5E)-2,5-diacetoxy-1,6-di-*o*-bromophenylhexa-1,5-diene-3-yne (2h).

A pale yellow oil (85% yield); mp. = 49.1-50.8 °C; IR (KBr) 665, 743, 1022, 1089, 1123, 1201, 1370, 1435, 1465, 1767 (C=O), 2192 (C≡C), 2925, 3052 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 25 °C) δ 2.16 (s, 3H), 2.27 (s, 3H), 6.79 (s, 1H), 6.99 (s, 1H), 7.14 (dd, *J* = 7.6, 8.0 Hz, 1H), 7.18 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.28 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.36 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.57-7.61 (m, 3H), 8.13 (d, *J* = 8.0 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃, 25 °C) δ 20.8, 21.0, 84.6, 89.9, 124.1, 124.6, 125.9, 127.1, 127.2, 128.0, 129.7, 129.7, 129.8, 130.0, 130.1, 132.5, 132.7, 133.0, 167.2, 168.4 (two aromatic carbon peaks seem to be measured together with others). HRMS (FAB): calcd for C₂₂H₁₆Br₂O₄ (M⁺), 503.9396; found, 503.9395.

(1Z,5E)-2,5-diacetoxy-1,6-di-*p*-methoxyphenylhexa-1,5-diene-3-yne (2i).

A pale yellow oil (16% yield); IR (neat) 526, 732, 827, 957, 1031, 1085, 1177, 1257, 1303, 1369, 1463, 1511, 1605, 1764 (C=O), 2181 (C≡C), 2935 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 2.22 (s, 3H), 2.28 (s, 3H), 3.82 (s, 6H), 6.49 (s, 1H), 6.56 (s, 1H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃, 25 °C) δ 20.9, 21.0, 52.3, 52.3, 84.7, 91.4, 113.8, 114.1, 125.2, 126.0, 126.7, 126.8, 127.2, 128.4, 130.2, 130.8, 159.9, 160.1, 167.7, 169.0. HRMS (FAB): calcd for C₂₄H₂₂O₆ (M⁺), 406.1416; found, 406.1416.

(1E)-2,5-diacetoxy-6-methyl-1-phenylhepta-1,5-diene-3-yne (2j).

A colorless oil (93% yield); IR (neat) 509, 609, 693, 756, 878, 919, 958, 1013, 1115, 1207, 1299, 1372, 1447, 1490, 1628, 1769 (C=O), 2197 (C≡C), 2915 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 1.72 (s, 3H), 1.97 (s, 3H), 2.19 (s, 3H), 2.45 (s, 3H), 6.48 (s, 1H), 7.23-7.36 (m, 3H), 7.44 (d, J = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C) δ 17.8, 20.5, 20.7, 21.0, 84.2, 87.7, 125.0, 126.0, 128.4, 128.5, 129.1, 129.1, 133.3, 135.5, 167.5, 168.5. HRMS (FAB): calcd for $\text{C}_{18}\text{H}_{18}\text{O}_4$ (M^+), 298.1205; found, 298.1207.

2,5-diacetoxy-6-dimethylhepta-1,5-diene-3-yne (2l).

A pale yellow oil (79% yield); IR (neat) 1017, 1118, 1198, 1371, 1624, 1769 (C=O), 2203 (C≡C) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 25 °C) δ 1.71 (s, 3H), 1.94 (s, 3H), 2.17 (s, 3H), 2.18 (s, 3H), 5.24 (s, 2H), 5.32 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ 17.8, 17.8, 20.6, 20.8, 83.1, 86.0, 112.2, 124.6, 135.7, 168.0, 168.3 (one vinylic carbon peak seems to be measured together with others at δ 112.2 or 135.7). HRMS (FAB): calcd for $\text{C}_{12}\text{H}_{15}\text{O}_4$ ($\text{M}+\text{H}^+$), 223.0970; found, 223.0970.

3,8-diacetoxy-2,9-dimethyldeca-2,8-diene-4,6-diyne (4).

A yellow solid (70% yield); mp. = 53.7-55.2 °C; IR (KBr) 545, 874, 1114, 1146, 1207, 1374, 1643, 1765 (C=O), 2139 (C≡C), 2914 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 25 °C) δ 1.72 (s, 6H), 1.97 (s, 6H), 2.18 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ 18.1, 20.5, 20.8, 76.3, 77.0, 125.1, 137.6, 168.3. HRMS (FAB): calcd for $\text{C}_{16}\text{H}_{18}\text{O}_4$ (M^+), 274.1205; found, 274.1214.

References

- 1) Ishihara, K.; Kubota, M.; Kurihara, H.; Yamamoto, H. *J. Org. Chem.* **1996**, *61*, 4560.
- 2) Hay, A. S. *J. Org. Chem.* **1962**, *27*, 3320
- 3) Williams, V. E.; Swager, T. M. *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 4669.

To Determine the Stereochemistry of Alkenic Moieties in **2j** (NOE Experiments of **2b** and **2j**)

The stereochemistry of **2j** is indirectly determined as follows:

Step 1: To determine the stereochemistry of alkenic parts of **2b** on the basis of chemical shift values of analogous vinyl protons.

- (1) Rotem *et al.* have reported that the chemical shift of vinyl proton of *Z*-acetoxystilbene is larger than that of *E*-isomer.
- (2) The results of nOe measurement of **2b** are shown below. [δ 6.64 (vinylic)-7.74 (*o*-position)], [δ 6.54 (vinylic)-7.47 (*o*-position)]: both of these pairs shows >10% of nOe effects.

Based on these two facts, the pair of chemical shifts, [δ 6.54 (vinylic)-7.47 (*o*-position)] in **2b** should be derived from *E*-configuration.

Step 2: To determine the stereochemistry in **2j**.

By comparing between both pairs of chemical shifts of **2b** and **2j-major**, we finally proposed that the alkenic stereochemistry in **2j-major** is *E*. This assignment is also supported by the pair of chemical shift in **2j-minor** [δ 6.58 (vinylic)-7.71 (*o*-position)], because this pair is so similar to that of *Z*-part in **2b**.

2j-minor: ^1H NMR (300 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ 1.74 (s, 3H), 1.98 (s, 3H), 2.18 (s, 3H), 2.20 (s, 3H), 6.58 (s, 1H), 7.23-7.36 (m, 3H), 7.71 (d, $J = 7.8$ Hz, 2H)

(ref.): The chemical shift of vinyl proton in *Z*-acetoxystilbene is larger than that of *E*-isomer.

Figure 1. Determination of the Alkenic Stereochemistry in **2b** and **2j**.

C:\WINMR98\COMMON\DEFAULT.ALS
hexyl(S)-1(H)

¹H NMR of 1h

D:\exp401-500\o-Br(S)-1(H).als
o-Br(S)-1(H)

DFILE D:\exp401-500\o-Br(S)-1(H).als
COMNT o-Br(S)-1(H)
DATIM Sat Jan 07 00:20:34 2006
OBNUC 1H
EXMOD NON
OBFREQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 16384
FREQ 8000.0 Hz
SCANS 16
ACQTM 2.048 sec
PD 4.952 sec
PWL 7.5 us
IRNUC 1H
CTEMP 23.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.00 Hz
YG
IG
RGAIN 13

¹³C NMR of 1h

C:\WINNR98\COMMON_DEFAULT.ALS
o-Br (S)-1 (C)

DFILE C:\WINNR98\COMMON_DEFAULT.ALS
COMNT o-Br (S)-1 (C)
DATIM Sat Jan 07 00:27:11 2006
OBNUC 13C
EXHOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 27173.9 Hz
SCANS 64
ACQTM 1.206 sec
PD 3.794 sec
PWL 4.4 us
IRNUC 1H
CTEMP 24.6 C
SINT CDCL3
EXREF 77.00 ppm
BF 1.00 Hz
YG
YG2
IG
RGAIN 33

¹H NMR of 1j

C:\WINMR98\COMMON_DEFAULT.ALS
exp398-2 (H)

MENUF NON
OENUC 1H
OFR 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
PW1 5.7 us
DEADT 97.2 us
PREDL 0.2000 ms
IWT 1.0 sec
POINT 32768
SPO 32768
TIMES 16
SCANS 16
DUMMY 1
FREQU 6013.2 Hz
FLT 3000 Hz
DELAY 66.7 us
ACQTM 5.449 sec
PD 1.551 sec
ADBIT 16.00
RGAIN 18
BF 0.10 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD NON
EXPCM NON:Single.coupled:PW1_ACQTM_PD
IRNUC 1H
IFR 300.40 MHz
IRSET 130.00 KHz
IRFIN 1150.0 Hz
IRRFW 40 us
IRATN 511
DFILE C:\WINMR98\COMMON_DEFAULT.ALS
SF TH5
LKSET 25.60 KHz
LKFIN 52.0 Hz
LKLEV 200
LGAIN 25
LKPHS 139
LKSIG 1411
CSPED 15 Hz
FILDC
FILDF

C:\WINNR98\COMMON_DEFAULT.ALS
exp398-2(C)

```

MENUF BCM
ORNUC 13C
OFR 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
PW1 4.5 us
DEADT 27.2 us
PREDL 0.2000 ms
IWT 1.0 sec
POINT 32768
SPO 32768
TIMES 5000
SCANS 217
DUMY 1
FREQU 20408.1 Hz
FLT 10200 Hz
DELAY 19.6 us
ACQTM 1.606 sec
PD 3.394 sec
ADEIT 16.00
RGAIN 25
BF 0.10 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD BCM
EXPCM Bilevel.complete.decoupling:Set
IRNUC 1H
IFR 300.40 MHz
IRSET 130.00 KHz
IRFIN 1150.0 Hz
IRPW 40 us
IRATN 511
DFILE
SF C:\WINNR98\COMMON\_DEFAULT.ALS
TH5
LKSET 25.60 KHz
LKFIN 52.0 Hz
LKLEV 200
LGAIN 25
LKPHS 139
LKSIG 1290
CSFED 15 Hz
FLDC
FLDF

```

C:\WINNMR98\COMMON_DEFAULT.ALS
exp403-1 (H)

```

C:\WINNR98\COMMON\_DEFAULT.ALS
exp403-1(H)
Fri Jan 06 22:23:38 2006
1H
OBNUC 1H
EXMOD NON
399.65 MHz
124.00 KHz
10500.0 Hz
16384
8000.0 Hz
16
2.048 sec
4.952 sec
7.5 us
1H
IRNUC 1H
CTEMP 23.4 C
CDCL3
SLVNT
EXREF 0.00 ppm
BF 1.00 Hz
YG
IG
IG 17
RGAIN

```

¹³C NMR of 1l

C:\WINNMR98\COMMON_DEFAULT.ALS
exp403-1(C)

DFILE C:\WINNMR98\COMMON_DEFAULT.ALS
COMNT exp403-1(C)
DATIM Fri Jan 06 22:36:36 2006
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREOU 27173.9 Hz
SCANS 145
ACQTM 1.206 sec
PD 3.794 sec
FVL 4.4 us
IRNUC 1H
CTEMP 24.4 C
SIVNT CDCL3
EXREF 77.00 ppm
BF 1.00 Hz
YG
YG2
IG
RGAIN 34

D:\exp401-500\exp404-1(H).als
exp404-1(H)

```

D:\exp401-500\exp404-1(H).als
exp404-1(H)
Fri Jan 06 20:00:35 2006
1H
ONUC 1H
EXMOD NON
329.65 MHz
OBFRQ 124.00 KHz
OBSET 10500.0 Hz
OBFIN 16384
POINT 8000.0 Hz
FREQU 16
SCANS 2.048 sec
ACQTM 4.952 sec
PD 7.5 us
PWL 1H
IRNUC 23.9 c
CTEMP
SLVNT CDC13
EXREF 0.00 ppm
BF 1.00 Hz
YG
YG2
IG
RGAIN 19

```

2

C:\WINNMR98\COMMON_DEFAULT.ALS
exp404-1(C)

DFILE C:\WINNMR98\COMMON_DEFAULT.ALS
COMNT exp404-1(C)
DATIM Fri Jan 06 20:07:31 2006
CNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 27173.9 Hz
SCANS 72
ACQTM 1.206 sec
PD 3.794 sec
PW1 4.4 us
IRNUC 1H
CTEMP 24.7 C
SIVNT CDCL3
EXREF 77.00 ppm
BF 1.00 Hz
YG
YG2
IG
RGAIN 34

¹H NMR of 2b

C:\WINNMR98\COMMON_DEFAULT.ALS
Rh

DFILE C:\WINNMR98\COMMON_DEFAULT.ALS
COMNT Rh
DATIM Mon Dec 12 18:02:11 2005
ORNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 16384
FREQU 8000.0 Hz
SCANS 8
ACQTM 2.048 sec
PD 4.952 sec
PWL 7.5 us
IRNUC 1H
CTEMP 27.7 c
SIVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
YG
YG2
IG
RGAIN 19

C:\WINNMR98\COMMON_DEFAULT.ALS
Ph

DFILE C:\WINNMR98\COMMON_DEFAULT.ALS
 COMNT Ph
 DATIM Mon Dec 12 18:10:48 2005
 OBNUC 13C
 EXMOD BCM
 OBFRQ 100.40 MHz
 OBSET 125.00 KHz
 OBFIN 10500.0 Hz
 POINT 32768
 FREQ 27173.9 Hz
 SCANS 161
 ACQTM 1.206 sec
 PD 1.794 sec
 PW 4.4 us
 IRNUC 1H
 CTEMP 26.9 c
 SLYNT CDCL3
 EXREF 77.00 ppm
 BF 0.12 Hz
 YG
 YG2
 IG
 RGAIN 34

¹H NMR of 2e

D:\exp301-400\exp364-2(H).als
exp364-2(H)

DFILE D:\exp301-400\exp364-2(H).als
CONNT exp364-2(H)
DATIM Sat Dec 10 05:23:40 2005
OBNUC 1H
EXMOD NON
OBPRQ 399.65 MHz
OBSEI 124.00 KHz
OBFIN 10500.0 Hz
POINT 16384
FREQU 8000.0 Hz
SCANS 16
ACQTM 2.048 sec
PD 4.952 sec
FwI 7.5 us
IRNUC 1H
CTEMP 24.3 c
SIVNT CDCL3
EXREF 0.00 ppm
BF 1.00 Hz
YG
YG2
IG
RGAIN 12

D:\exp301-400\exp364-2(C).als
exp364-2(C)

DFILE D:\exp301-400\exp364-2(C).als

COMNT exp364-2(C)

DATIM Sat Dec 10 05:30:31 2005

OBNUC 13C

EXMOD BCM

OBPRQ 100.40 MHz

OBSET 125.00 KHz

OBFIN 10500.0 Hz

POINT 32768

FREQU 27173.9 Hz

SCANS 48

ACQTM 1.206 sec

PD 3.794 sec

PWL 4.4 us

IRNUC 1H

CTEMP 24.6 c

SLVNT CDCL3

EXREF 77.00 ppm

BF 1.00 Hz

YG

YG2

IG

RGAIN

33

¹H NMR of 2h

C:\WINNR98\COMMON_DEFAULT.ALS
O-Br (P)-1 (H)

DFILE C:\WINNR98\COMMON_DEFAULT.ALS
COMNT O-Br (P)-1 (H)
DATIM Fri Jan 06 23:02:00 2006
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 16384
FREQU 8000.0 Hz
SCANS 16
ACQTM 2.048 sec
PD 4.952 sec
FSL 7.5 us
IRNUC 1H
CTEMP 23.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.00 Hz
YG
YG2
IG
RGAIN 19

¹³C NMR of 2h

C:\WINNR98\COMMON_DEFAULT.ALS
O-Br (P)-1 (C)

DFILE C:\WINNR98\COMMON_DEFAULT.ALS
COMNT O-Br (P)-1 (C)
DATIM Fri Jan 06 23:17:31 2006
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 27173.9 Hz
SCANS 176
ACQTM 1.206 sec
PD 3.794 sec
PWI 4.4 us
IRNUC 1H
CTEMP 24.6 C
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.00 Hz
YG
YG2
IG
RGAIN 34

¹H NMR of 2i

D:\exp401-500\exp402-1 (H).als
exp402-1 (H)

DFILE D:\exp401-500\exp402-1 (H).als
COMNT exp402-1 (H)
DATIM Mon Jan 16 18:39:24 2006
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 6013.2 Hz
SCANS 16
ACQTM 5.449 sec
PD 1.551 sec
PWL 5.7 us
IRNUC 1H
CTEMP 23.2 C
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.00 Hz
YG
YG2
IG
RGAIN 19

D:\exp401-500\exp402-1(C).als
exp402-1(C)

D:\exp401-500\exp402-1(C).als
COMNT exp402-1(C)
DATIM Mon Jan 16 18:55:37 2006
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 185
ACQTM 1.606 sec
PD 3.394 sec
PW1 4.5 us
IRNUC 1H
CTEMP 23.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.00 Hz
YG
YG2
IG
RGAIN 25

¹H NMR of 2j-mixture

C:\WINMR98\COMMON_DEFAULT.ALS
exp405-2(H)

DFILE C:\WINMR98\COMMON_DEFAULT.ALS
CONNT exp405-2(H)
DATIM Fri Jan 13 17:04:26 2006
OBNUC 1H
EXMOD NON
OBFREQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 16384
FREQU 8000.0 Hz
SCANS 16
ACQTM 2.048 sec
PD 4.952 sec
PWL 7.5 us
IRNUC 1H
CTEMP 23.9 c
SIVNT CDCL3
EXREF 0.00 ppm
BF 1.00 Hz
YG2
IG
RGAIN 12

¹H NMR of 2j-major

C:\WINNMR98\COMMON\DEFAULT.ALS
exp405' (H)

C:\WINNMR98\COMMON_DEFAULT.ALS
exp405' (C)

MENUF BCM
OBNUC 13C

75.45 MHz
124.00 KHz
1840.0 Hz
4.5 us
27.2 us
0.2000 ms
1.0 sec
32768
32768
5000
152
20408.1 Hz
10200 Hz
19.6 us
1.606 sec
3.394 sec
16.00
26
0.10 Hz
0.00
0.00
90.00
100.00

EXMOD BCM
EXPCM Bilevel.complete.decoupling: Set
IRNUC 1H
IRF 300.40 MHz
IRSET 130.00 KHz
IRFIN 1150.0 Hz
IRPW 40 us
IRATN 511
DFILE C:\WINNMR98\COMMON_DEFAULT.ALS
TH5

SF 25.60 KHz
LKSET 52.0 Hz
LKFIN 200
LKLEV 22
LGAIN 169
LKPHS 486
LKSIG 17 Hz
CSFED
FILDC
FILDF

¹H NMR of 2l

C:\WINMR98\COMMON_DEFAULT.ALS
exp406' (H)

DFILE C:\WINMR98\COMMON_DEFAULT.ALS
COMNT exp406' (H)
DATIM Wed Jan 18 12:02:58 2006
QBNUC 1H
EXMOD NON
CEFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 16384
FREQ 8000.0 Hz
SCANS 16
ACQTM 2.048 sec
PD 4.952 sec
PWL 7.5 us
IRNUC 1H
CTEMP 23.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 10.00 Hz
YG
YG2
IG
RGAIN 14

C:\WINNMR98\COMMON_DEFAULT.ALS
exp406' (C)

DFILE C:\WINNMR98\COMMON_DEFAULT.ALS
COMNT exp406' (C)
DATIM Wed Jan 18 12:41:45 2006
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBRIN 10500.0 Hz
POINT 32768
FREQU 27173.9 Hz
SCANS 456
ACQTM 1.206 sec
PD 3.794 sec
PWL 4.4 us
IRNUC 1H
CTEMP 25.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 10.00 Hz
YG
YG2
IG
RGAIN 34

¹H NMR of 4

C:\WINNR98\COMMON_DEFAULT.ALS
MF-158-4(400)H

DFILE C:\WINNR98\COMMON_DEFAULT.ALS
COMNT MF-158-4(400)H
DATIM Fri Jul 16 20:03:53 2004
OBNUC 1H
EXMOD NON
OBFREQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 16384
FREQ 8000.0 Hz
SCANS 16
ACQTM 2.048 sec
PD 4.952 sec
PWL 7.0 us
IRNUC 1H
CTEMP 25.1 C
SLVNT CDCL3
EXREF 0.00 Ppm
BF 0.12 Hz
YG
YG2
IG
RGAIN 17

¹³C NMR of 4

C:\WINNMR98\COMMON_DEFAULT.ALS
MF-158-4 (400) C

DEFILE C:\WINNMR98\COMMON_DEFAULT.ALS
COMNT MF-158-4 (400) C
DATIM Fri Jul 16 20:35:05 2004
OENUC I3C
EXMOD BCM

OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQ 27173.9 Hz
SCANS 582
ACQTM 1.206 sec
PD 1.794 sec
PW1 4.5 us
IRNUC 1H
CTEMP 24.9 C
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
YG
IG
RGAIN 33