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Supporting Information

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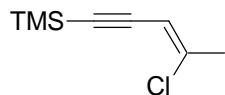
**First Widely Applicable Palladium-Catalyzed *trans*-Selective Monoalkylation of
Unactivated 1,1-Dichloro-1-alkenes and Palladium-Catalyzed Second Substitution
for the Selective Synthesis of (*E*)- or (*Z*)-Trisubstituted Alkenes^{**}**

Ze Tan and Ei-ichi Negishi^{*}

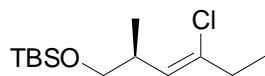
General Procedures. All reactions were run under a dry Ar atmosphere. Reactions were monitored by GC analysis of reaction aliquots. GC analysis was performed on an HP6890 Gas Chromatograph using an HP-5 capillary column (30 m x 0.32 mm, 0.5 μ M film) packed with SE-30 on Chromosorb W. Column chromatography was carried out on 230-400 mesh silica gel. 1 H and 13 C NMR spectra were recorded on a Varian-Inova-300 spectrometer. THF was distilled from sodium/benzophenone. ZnBr₂ was flame-dried under vacuum. Pd(*t*Bu₃P)₂,^a Pd(Cy₃P)₂,^b Pd(DPEphos)Cl₂^c were prepared as reported in the literature. The starting materials were purchased from commercial sources and used as received. Optical rotations were measured on an Autopol III polarimeter.

General procedure for monoalkylation (Representative Procedure A): A flame dried 25-mL round-bottomed flask under argon was charged with 1,1-dichloro-1-alkene (1 mmol), DMF (3 mL) and Pd(DPEphos)Cl₂ (35 mg, 0.05 mmol, 5 mol%). After the addition of the organozinc reagent (1.2 mmol), the reaction mixture was stirred at appropriate temperature until GLC analysis indicated the disappearance of the starting

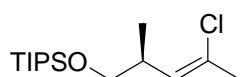
material, and then it was quenched with diluted HCl. After extraction with ether, the combined organic layers were washed with brine, dried over MgSO_4 , filtered and concentrated. The residue was purified by flash column chromatography on silica gel to give the desired product.



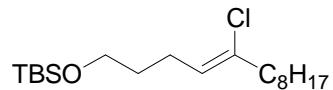
(3Z)-4-Chloro-1-trimethylsilyl-3-penten-1-yne. This compound was prepared according to Representative Procedure A using 1,1-dichloro-4-trimethylsilyl-1-buten-3-yne and Me_2Zn . Yield: 82%; ^1H NMR (CDCl_3 , 300 MHz) d 0.18 (s, 9 H), 2.15 (d, J = 1.3 Hz, 3 H), 5.60 (d, J = 1.3 Hz, 1 H); ^{13}C NMR (CDCl_3 , 75 MHz) d 0.12 (3C), 26.34, 100.23, 100.31, 107.73, 143.26; IR (neat) 2961, 2146, 1594, 1428, 1250 cm^{-1} ; HRMS calcd. for $\text{C}_8\text{H}_{13}\text{ClSi} [\text{M}]^+$ 172.0475, found 172.0473.



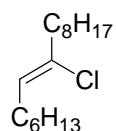
(3Z,2S)-1-tert-Butyldimethylsilyloxy-2-methyl-4-chloro-3-hexene. This compound was prepared according to Representative Procedure A using (3S)-4-*tert*-butyldimethylsilyloxy-1,1-dichloro-3-methyl-1-butene and Et_2Zn . Yield: 85%; $[\alpha]_D^{23}$ +21° (c 0.6, CHCl_3); ^1H NMR (CDCl_3 , 300 MHz) d 0.02 (s, 6 H), 0.88 (s, 9 H), 0.97 (d, J = 6.5 Hz, 3 H), 1.09 (t, J = 7.0 Hz, 3 H), 2.30 (q, J = 7.0 Hz, 2 H), 2.7-2.9 (m, 1 H), 3.35-3.55 (m, 2 H), 5.27 (d, J = 8.2 Hz, 1 H); ^{13}C NMR (CDCl_3 , 75 MHz) d -5.38 (2C), 12.62, 16.38, 18.31, 25.88 (3C), 32.89, 36.29, 66.94, 126.95, 136.34; IR (neat) 1660, 1471, 1462, 1252, 1109, 1089 cm^{-1} ; HRMS calcd. for $\text{C}_{13}\text{H}_{27}\text{ClOSi} [\text{M}]^+$ 262.1520, found 262.1524.



(2Z,4S)-5-Triisopropylsilyloxy-2-chloro-4-methyl-2-pentene. This compound was prepared according to Representative Procedure A using (3S)-1,1-dichloro-3-methyl-4-triisopropylsilyloxy-1-butene, Me₂Zn and NMI. Yield: 73%; [a]_D²³ +24.6° (c 0.48, CHCl₃); ¹H NMR (CDCl₃, 300 MHz) d 1.02 (d, *J* = 6.5 Hz, 3 H), 1.06 (s, 21 H), 2.07 (s, 3 H), 2.7-2.9 (m, 1 H), 3.5-3.7 (m, 2 H), 5.32 (d, *J* = 9.4 Hz, 1 H); ¹³C NMR (CDCl₃, 75 MHz) d 12.01 (3C), 16.39, 17.98 (6C), 26.25, 36.81, 67.20, 128.75, 129.76; IR (neat) 2959, 2943, 2866, 1463, 1383, 1113 cm⁻¹; HRMS calcd. for C₁₅H₃₂ClOSi [M+H]⁺ 291.1911, found 291.1910.

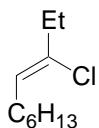


(4Z)-1-*tert*-Butyldimethylsilyloxy-5-chloro-4-tridecene. This compound was prepared according to Representative Procedure A using 5-*tert*-butyldimethylsilyloxy-1,1-dichloro-1-pentene and ⁷OctZnBr. Yield: 83%; ¹H NMR (CDCl₃, 300 MHz) d 0.03 (s, 6 H), 0.88 (bs, 12 H), 1.2-1.4 (m, 10 H), 1.4-1.7 (m, 4 H), 2.1-2.3 (m, 4 H), 3.60 (t, *J* = 6.4 Hz, 2 H), 5.43 (t, *J* = 7.0 Hz, 1 H); ¹³C NMR (CDCl₃, 75 MHz) d -5.31 (2C), 14.10, 18.33, 22.66, 25.01, 25.95 (3C), 27.41, 28.57, 29.23, 29.33, 31.86 (2C), 39.45, 62.65, 124.81, 135.11.

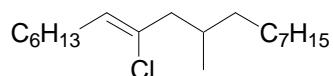


(7Z)-8-Chloro-7-hexadecene. This compound was prepared according to Representative Procedure A using 1,1-dichloro-1-octene and ⁷OctZnBr. Yield: 85%; ¹H NMR (CDCl₃) d 0.88 (t, *J* = 6.7 Hz, 6 H), 1.2-1.45 (m, 18 H), 1.5-1.6 (m, 2 H), 2.15 (q, *J* = 7.0 Hz, 2 H), 2.28 (t, *J* = 7.2 Hz, 2 H), 5.42 (t, *J* = 6.9 Hz, 1 H); ¹³C NMR (CDCl₃, 75 MHz) d 14.07, 22.67, 27.41, 28.50, 28.56, 28.71, 28.91, 29.28, 29.35, 31.70, 31.87, 39.45, 125.37,

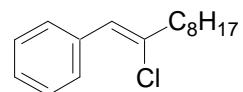
134.68; IR (neat) 1711, 1660, 1466, 1378 cm^{-1} ; LRMS (CI) calcd. for $\text{C}_{16}\text{H}_{31}\text{Cl}$ $[\text{M}]^+$ 258, found 258.



(3Z)-3-Chloro-3-decene. This compound was prepared according to Representative Procedure A using 1,1-dichloro-1-octene and Et_2Zn . Yield: 76%; ^1H NMR (CDCl_3 , 300 MHz) d 0.88 (t, $J = 6.8$ Hz, 3 H), 1.11 (t, $J = 7.3$ Hz, 3 H), 1.2-1.45 (m, 8 H), 2.15 (q, $J = 7.0$ Hz, 2 H), 2.32 (q, $J = 7.3$ Hz, 2 H), 5.44 (t, $J = 7.1$ Hz, 1 H); ^{13}C NMR (CDCl_3 , 75 MHz) d 12.96, 14.32, 22.87, 28.74, 28.95, 28.17, 31.94, 33.08, 124.59, 136.46; LRMS (CI) calcd. for $\text{C}_{10}\text{H}_{19}\text{Cl}$ $[\text{M}]^+$ 174, found 174.

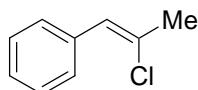


(7Z, 10RS)-8-Chloro-10-methyl-7-octadecene. This compound was prepared according to Representative Procedure A using 1,1-dichloro-1-octene and 2-methyl-1-decanylZnBr. Yield: 70%; ^1H NMR (CDCl_3 , 300 MHz) d 0.8-0.9 (m, 9 H), 1.0-1.2 (m, 1 H), 1.2-1.45 (m, 21 H), 1.7-1.9 (m, 1 H), 1.9-2.35 (m, 4 H), 5.40 (t, $J = 7.0$ Hz, 1 H); ^{13}C NMR (CDCl_3 , 75 MHz) d 14.08, 14.12, 18.93, 22.65, 22.72, 26.92, 28.53, 28.73, 28.92, 29.37, 29.67, 29.91, 30.46, 31.71, 31.95, 36.25, 47.19, 126.70, 133.73; IR (neat) 1711, 1465, 1378, 1089 cm^{-1} .

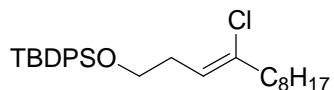


(Z)-2-Chloro-1-phenyl-1-decene. This compound was prepared according to Representative Procedure A using 2,2-dichlorostyrene and $^n\text{OctZnBr}$. Yield: 90%; ^1H NMR (CDCl_3 , 300 MHz) d 0.98 (t, $J = 6.7$ Hz, 3 H), 1.3-1.55 (m, 10 H), 1.65-1.85 (m, 2 H), 7.25-7.35 (m, 5 H); ^{13}C NMR (CDCl_3 , 75 MHz) d 12.96, 14.32, 22.87, 28.74, 28.95, 28.17, 31.94, 33.08, 124.59, 136.46, 137.80, 138.80, 146.50, 146.55, 146.60, 146.65, 146.70, 146.75, 146.80, 146.85, 146.90, 146.95, 147.00, 147.05, 147.10, 147.15, 147.20, 147.25, 147.30, 147.35, 147.40, 147.45, 147.50, 147.55, 147.60, 147.65, 147.70, 147.75, 147.80, 147.85, 147.90, 147.95, 148.00, 148.05, 148.10, 148.15, 148.20, 148.25, 148.30, 148.35, 148.40, 148.45, 148.50, 148.55, 148.60, 148.65, 148.70, 148.75, 148.80, 148.85, 148.90, 148.95, 149.00, 149.05, 149.10, 149.15, 149.20, 149.25, 149.30, 149.35, 149.40, 149.45, 149.50, 149.55, 149.60, 149.65, 149.70, 149.75, 149.80, 149.85, 149.90, 149.95, 149.98, 150.00, 150.02, 150.04, 150.06, 150.08, 150.10, 150.12, 150.14, 150.16, 150.18, 150.20, 150.22, 150.24, 150.26, 150.28, 150.30, 150.32, 150.34, 150.36, 150.38, 150.40, 150.42, 150.44, 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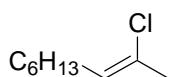
H), 2.52 (t, $J = 6.5$ Hz, 2 H), 6.53 (s, 1 H), 7.3-7.4 (m, 1 H), 7.4-7.45 (m, 2 H), 7.65-7.7 (m, 2 H); ^{13}C NMR (CDCl₃, 75 MHz) d 14.10, 22.66, 27.60, 28.61, 29.23, 29.35, 31.85, 41.18, 124.16, 127.34, 128.09 (2C), 128.96 (2C), 135.14, 135.25; IR (neat) 2954, 2926, 2855, 1642, 1492, 1465, 1447 cm⁻¹; HRMS calcd. for C₁₆H₂₄Cl [M+H]⁺ 251.1566, found 251.1563.



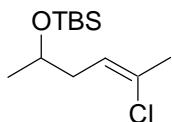
(2Z)-2-Chloro-1-phenyl-1-propene.^d This compound was prepared according to Representative Procedure A using 2,2-dichlorostyrene and Me₂Zn. Yield: 80%; ^1H NMR (CDCl₃, 300 MHz) d 2.28 (s, 3 H), 6.45 (s, 1 H), 7.2-7.4 (m, 3 H), 7.55-7.6 (m, 2 H); ^{13}C NMR (CDCl₃, 75 MHz) d 28.00, 124.72, 127.37, 128.12 (2C), 128.82 (2C), 130.33, 135.25; LRMS (CI) calcd. for C₈H₉Cl [M]⁺ 152, found 152.



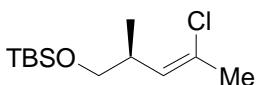
(3Z)-1-tert-Butyldiphenylsilyloxy-4-chloro-3-dodecene. This compound was prepared according to Representative Procedure A using 4-*tert*-butyldiphenylsilyloxy-1,1-dichloro-1-butene and ⁷OctZnBr. Yield: 80%; ^1H NMR (CDCl₃, 300 MHz) d 0.88 (t, $J = 6.9$ Hz, 3 H), 1.05 (s, 9 H), 1.2-1.4 (m, 10 H), 1.45-1.6 (m, 2 H), 2.28 (t, $J = 7.5$ Hz, 2 H), 2.43 (q, $J = 6.7$ Hz, 2 H), 3.70 (t, $J = 6.6$ Hz, 2 H), 5.51 (t, $J = 6.9$ Hz, 1 H), 7.3-7.5 (m, 6 H), 7.6-7.75 (m, 4 H); ^{13}C NMR (CDCl₃, 75 MHz) d 14.09, 12.22, 22.65, 26.83 (3C), 27.41, 28.62, 29.20, 29.34, 31.86, 32.11, 39.55, 62.71, 121.77 (2C), 127.62 (4C), 129.56 (2C), 133.91, 135.58 (4C), 136.31.



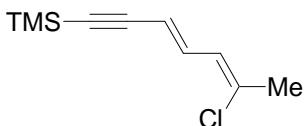
(2Z)-2-Chloro-2-nonene.^e This compound was prepared according to Representative Procedure A using 1,1-dichloro-1-octene, Me₂Zn and NMI. Yield: 75%; ¹H NMR (CDCl₃, 300 MHz) δ 0.88 (t, *J* = 6.7 Hz, 3 H), 1.0-1.6 (m, 8 H), 1.81 (s, 3 H), 2.05-2.3 (m, 2 H), 5.57 (t, *J* = 7.0 Hz, 1 H).



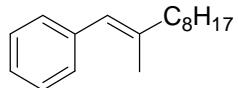
(2Z,5RS)-5-tert-Butyldimethylsilyloxy-2-chloro-2-hexene. This compound was prepared according to Representative Procedure A using (4*RS*)-4-*tert*-butyldimethylsilyloxy-1,1-dichloro-1-pentene, Me₂Zn and NMI. Yield: 85%; ¹H NMR (CDCl₃, 300 MHz) δ 0.03 (s, 6 H), 0.86 (s, 9 H), 1.11 (d, *J* = 5.9 Hz, 3 H), 2.08 (s, 3 H), 2.2-2.35 (m, 2 H), 3.85 (q, *J* = 6.5 Hz, 1 H), 5.48 (t, *J* = 6.5 Hz, 1 H).



(2Z,4S)-5-tert-Butyldimethylsilyloxy-2-chloro-4-methyl-2-pentene. This compound was prepared according to Representative Procedure A using (3*S*)-4-*tert*-butyldimethylsilyloxy-1,1-dichloro-3-methyl-1-butene, Me₂Zn and NMI. Yield: 76%; [a]_D²³ +7.6° (c 0.6, CHCl₃); ¹H NMR (CDCl₃, 300 MHz) δ 0.04 (s, 6 H), 0.89 (s, 9 H), 0.99 (d, *J* = 5.8 Hz, 3 H), 2.07 (s, 3 H), 2.65-2.9 (m, 1 H), 3.35-3.55 (m, 2 H), 5.28 (d, *J* = 8.9 Hz, 1 H); ¹³C NMR (CDCl₃, 75 MHz) δ -5.37 (2C), 16.34, 18.32, 25.91 (3C), 26.27, 36.58, 66.90, 128.65, 129.96; IR (neat) 1666, 1472, 1463, 1252, 1069, 1037, 836 cm⁻¹; HRMS calcd. for C₁₂H₂₅ClOSi [M+H]⁺ 249.1441, found 249.1437.



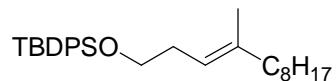
(3E,5Z)-6-Chloro-1-trimethylsilyl-3,5-heptadien-1-yne. This compound was prepared according to Representative Procedure A using 1,1-dichloro-6-trimethylsilyl-1,3-hexadien-5-yne and Me_2Zn . Yield: 82%; ^1H NMR (CDCl_3) δ 0.19 (s, 9 H), 2.18 (s, 3 H), 5.62 (d, $J = 15.6$ Hz, 1 H), 6.10 (d, $J = 10.6$ Hz, 1 H), 6.92 (dd, $J = 10.5, 15.6$ Hz, 1 H).



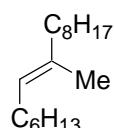
(E)-2-Methyl-1-phenyl-1-decene.^f A flame dried 25-mL three-neck round-bottomed flask under argon was charged with $\text{Ni}(\text{dppp})\text{Cl}_2$ (11 mg, 0.05 mmol, 5 mol%) and ether (5 mL). To the mixture was added (*Z*)-2-Chloro-1-phenyl-1-decene (250 mg, 1 mmol) followed by CH_3MgBr (0.5 mL, 3 M in ether, 1.5 mmol). After refluxing for 2 h, GLC analysis indicated the consumption of the starting material. The mixture was allowed to cool to room temperature, quenched with saturated NH_4Cl and extracted with ether. The combined organic layers were washed with brine, dried over MgSO_4 , filtered and concentrated. The residue was purified by flash column chromatography on silica gel (hexanes) to give the desired product in quantitative yield (229 mg): ^1H NMR (CDCl_3 , 300 MHz) δ 0.89 (t, $J = 6.9$ Hz, 3 H), 1.2-1.4 (bs, 10 H), 1.4-1.6 (m, 2 H), 1.84 (s, 3 H), 2.15 (t, $J = 7.8$ Hz, 2 H), 6.26 (s, 1 H), 7.1-7.4 (m, 5 H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 14.13, 17.75, 22.72, 28.06, 29.36, 29.38, 29.59, 31.95, 40.79, 124.73, 124.74, 127.99, 128.46, 128.59, 128.84, 138.78, 139.40; LRMS (CI) calcd. for $\text{C}_{17}\text{H}_{26}$ $[\text{M}]^+$ 230, found 230.

General procedure for cross-coupling of the (*Z*)-chloroalkenes with Grignard reagents (Representative Procedure B): A flame dried 25-mL three-neck round-bottomed flask under argon was charged with $\text{Pd}(\text{OAc})_2$ (11 mg, 0.05 mmol, 5 mol%),

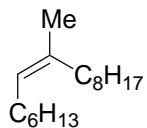
Cyp₃P (24 mg, 0.1 mmol, 10 mol%) and THF (2 mL). The mixture was stirred at 23 °C for 10 min and the (*Z*)-chloroalkene (1 mmol) was added followed by the Grignard reagent (1.5 mmol). The flask was stirred at appropriate temperature until GLC analysis indicated the consumption of the starting material. The mixture was allowed to cool to room temperature, quenched with saturated NH₄Cl and extracted with ether. The combined organic layers were washed with brine, dried over MgSO₄, filtered and concentrated. The residue was purified by flash column chromatography on silica gel to give the desired product.



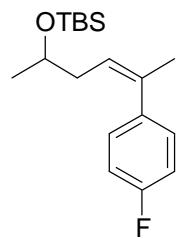
(3Z)-1-*tert*-Butyldimethylsilyloxy-4-methyl-3-dodecene. This compound was prepared according to Representative Procedure B using (3Z)-1-*tert*-butyldiphenylsilyloxy-4-chloro-3-dodecene, Pd(^tBu₃P)₂, and MeMgBr. Yield: 100%; ¹H NMR (CDCl₃, 300 MHz) δ 0.87 (t, *J* = 7.0 Hz, 3 H), 1.05 (s, 9 H), 1.2-1.4 (m, 12 H), 1.54 (s, 3 H), 1.94 (t, *J* = 7.6 Hz, 2 H), 2.26 (q, *J* = 6.9 Hz, 2 H), 3.63 (t, *J* = 7.0 Hz, 2 H), 5.11 (t, *J* = 6.5 Hz, 1 H), 7.3-7.5 (m, 6 H), 7.65-7.75 (m, 4 H); ¹³C NMR (CDCl₃, 75 MHz) δ 14.11, 16.01, 19.19, 22.68, 26.84 (3C), 27.93, 29.29, 29.35, 29.54, 31.56, 31.91, 39.75, 63.85, 120.04 (2C), 127.56 (4C), 129.47 (2C), 134.13, 135.6 (4C), 137.43.



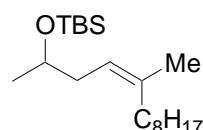
(7E)-8-Methyl-7-hexadecene. This compound was prepared according to Representative Procedure B using (7Z)-8-chloro-7-hexadecene, Pd(^tBu₃P)₂, and MeMgBr. Yield: 95%; ¹H NMR (CDCl₃, 300 MHz) δ 0.88 (t, *J* = 7.0 Hz, 6 H), 1.1-1.5 (m, 20 H), 1.57 (s, 3 H), 1.9-2.1 (m, 4 H), 5.11 (t, *J* = 6.4 Hz, 1 H); IR (neat) 1466, 1378, 974 cm⁻¹.



(7Z)-8-Methyl-7-hexadecene. ¹H NMR (CDCl₃, 300 MHz) δ 0.88 (t, *J* = 6.3 Hz, 6 H), 1.2-1.6 (m, 20 H), 1.67 (s, 3 H), 1.9-2.1 (m, 4 H), 5.11 (t, *J* = 6.9 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 14.09 (2C), 22.72 (2C), 23.42, 27.86, 28.11, 29.14, 29.38, 29.64, 29.68, 30.16, 31.79, 31.89, 31.97, 125.32, 135.36.

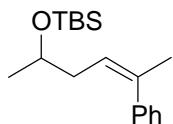


(2Z,5RS)-5-tert-Butyldimethylsilyloxy-2-(4'-fluorophenyl)-2-hexene. This compound was prepared according to Representative Procedure B using (2Z,5RS)-5-*tert*-butyldimethylsilyloxy-2-chloro-2-hexene, Pd(Cy₃P)₂, and 4-PhenylMgBr. Yield: 85%; ¹H NMR (CDCl₃, 300 MHz) δ 0.02 (s, 6 H), 0.87 (s, 9 H), 1.07 (d, *J* = 6.4 Hz, 3 H), 2.01 (s, 3 H), 2.05-2.2 (m, 2 H), 3.7-3.9 (m, 1 H), 5.50 (t, *J* = 7.0 Hz, 1 H), 6.9-7.2 (m, 4 H); ¹³C NMR (CDCl₃, 75 MHz) δ -4.75, -4.62, 18.16, 23.61, 25.79, 25.87 (3C), 39.06, 68.86, 114.71, 114.99, 124.75, 129.50, 129.60, 136.55, 159.89, 163.14; IR (neat) 1603, 1509, 1375, 1253, 1223, 1088, 1004 cm⁻¹.

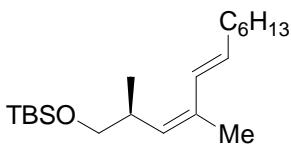


(2RS,4Z)-2-tert-Butyldimethylsilyloxy-5-methyl-4-tridecene. This compound was prepared according to Representative Procedure B using (2Z,5RS)-5-*tert*-butyldimethylsilyloxy-2-chloro-2-hexene, Pd(Cy₃P)₂, and ¹⁰OctMgBr. Yield: 95%; ¹H

NMR (CDCl₃, 300 MHz) d 0.03 (s, 6H), 0.87 (bs, 12 H), 1.09 (d, *J* = 5.8 Hz, 3 H), 1.2-1.4 (m, 12 H), 1.66 (s, 3 H), 1.9-2.25 (m, 4 H), 3.7-3.8 (m, 1 H), 5.10 (t, *J* = 7.1 Hz, 1 H); IR (neat) 1471, 1463, 1376, 1251, 1131, 1084, 1003, 836 cm⁻¹; HRMS calcd. for C₂₀H₄₃OSi [M+H]⁺ 327.3083, found 327.3080.

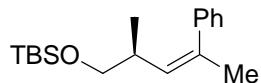


(2Z,5RS)-5-tert-Butyldimethylsilyloxy-2-phenyl-2-hexene. This compound was prepared according to Representative Procedure B using (2Z,5RS)-5-*tert*-butyldimethylsilyloxy-2-chloro-2-hexene, Pd(Cy₃P)₂, and PhMgBr. Yield: 88%; ¹H NMR (CDCl₃, 300 MHz) d 0.01 (s, 6 H), 0.87 (s, 9 H), 1.07 (d, *J* = 6.4 Hz, 3 H), 2.03 (s, 3 H), 2.03-2.3 (m, 2 H), 3.7-3.9 (m, 1 H), 5.53 (t, *J* = 6.7 Hz, 1 H), 7.15-7.4 (m, 5 H); ¹³C NMR (CDCl₃, 75 MHz) d -4.74, -4.64, 18.17, 23.58, 25.76, 25.88 (3C), 39.05, 68.98, 124.31, 126.39, 128.00 (2C), 128.01 (2C), 137.59, 142.14; IR (neat) 1472, 1462, 1375, 1253, 1134, 1090, 1063, 1004 cm⁻¹; HRMS calcd. for C₁₈H₃₁OSi [M+H]⁺ 291.2144, found 291.2141.

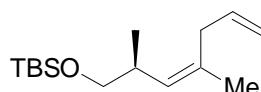


(2S,3Z,5E)-1-tert-Butyldimethylsilyloxy-2,4-dimethyl-3,5-dodecadiene.^g This compound was prepared according to Representative Procedure B using (2Z,4S)-5-*tert*-butyldimethylsilyloxy-2-chloro-4-methyl-2-pentene, Pd(Cy₃P)₂, and (E)-1-OctenylMgBr. Yield: 73%; ¹H NMR (CDCl₃, 300 MHz) d 0.02 (s, 6H), 0.87 (bs, 12 H), 0.95 (d, *J* = 6.6 Hz, 3 H), 1.2-1.4 (m, 8 H), 1.78 (s, 3 H), 2.12 (q, *J* = 7.2 Hz, 2 H), 2.7-2.9 (m, 1 H), 3.3-3.5 (m, 2 H), 4.98 (d, *J* = 9.3 Hz, 1 H), 5.66 (dt, *J* = 6.9, 15.6 Hz, 1 H), 6.41 (d, *J* = 15.6

Hz, 1 H); ^{13}C NMR (CDCl₃, 75 MHz) d -5.34, -5.29, 14.09, 17.59, 18.37, 20.75, 22.63, 25.95 (3C), 28.96, 29.59, 31.77, 33.29, 34.62, 68.07, 127.48, 131.03, 131.27, 132.33; Anal. Calcd. For C₂₀H₄₀OSi: C, 74.00; H, 12.42; found: C, 73.62; H, 12.24.

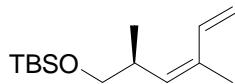


(2Z,4S)-5-tert-Butyldimethylsilyloxy-2-phenyl-4-methyl-2-pentene. This compound was prepared according to Representative Procedure B using (2Z,4S)-5-*tert*-butyldimethylsilyloxy-2-chloro-4-methyl-2-pentene, Pd(OAc)₂/Cyp₃P, and PhZnBr. Yield: 87%; [a]_D²³ +25° (c 0.48, CHCl₃); ^1H NMR (CDCl₃, 300 MHz) d 0.00 (s, 3 H), 0.02 (s, 3 H), 0.89 (s, 9 H), 0.92 (d, *J* = 7.0 Hz, 3 H), 2.03 (s, 3 H), 2.4-2.55 (m, 1 H), 3.3-3.5 (m, 2 H), 5.24 (d, *J* = 10.0 Hz, 1 H), 7.2-7.4 (m, 5 H); ^{13}C NMR (CDCl₃, 75 MHz) d -5.36 (2C), 17.63, 18.36, 25.88, 25.95 (3C), 35.97, 68.16, 126.42, 127.90 (2C), 128.02 (2C), 130.69, 136.68, 142.37; IR (neat) 1471, 1463, 1252, 1104, 1088, 836 cm⁻¹; HRMS calcd. for C₁₈H₃₁OSi [M+H]⁺ 291.2144, found 291.2147.



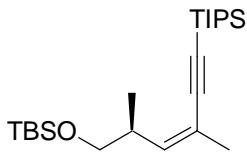
(4Z,6S)-7-tert-Butyldimethylsilyloxy-4,6-dimethyl-1,4-heptadiene. This compound was prepared according to Representative Procedure B using (2Z,4S)-5-*tert*-butyldimethylsilyloxy-2-chloro-4-methyl-2-pentene, Pd(OAc)₂/Cyp₃P, and AllylMgCl. Yield: 83%; [a]_D²³ +18.2° (c 0.66, CHCl₃); ^1H NMR (CDCl₃, 300 MHz) d 0.03 (s, 6 H), 0.89 (s, 9 H), 0.93 (d, *J* = 6.4 Hz, 3 H), 1.67 (s, 3 H), 2.45-2.65 (m, 1 H), 2.65-2.9 (m, 2 H), 3.3-3.5 (m, 2 H), 4.95-5.15 (m, 3 H), 5.7-5.9 (m, 1 H); ^{13}C NMR (CDCl₃, 75 MHz) d -5.36 (2C), 18.04, 18.80, 23.82, 26.38 (3C), 35.85, 37.22, 68.59, 115.55, 129.55, 133.74,

136.85; IR (neat) 1637, 1471, 1463, 1252, 1122, 1085 cm^{-1} ; HRMS calcd. for $\text{C}_{15}\text{H}_{31}\text{OSi}$ $[\text{M}+\text{H}]^+$ 255.2144, found 255.2141.



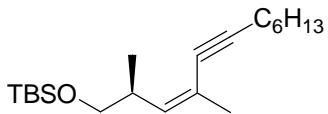
(3Z,5S)-6-tert-Butyldimethylsilyloxy-3,5-dimethyl-1,3-hexadiene.^h This compound was prepared according to Representative Procedure B using (2Z,4S)-5-*tert*-butyldimethylsilyloxy-2-chloro-4-methyl-2-pentene, $\text{Pd}(\text{OAc})_2/\text{Cyp}_3\text{P}$, and vinylMgBr. Yield: 83%; $[\alpha]_D^{23} -4.8^\circ$ (c 0.15, CHCl_3); ^1H NMR (CDCl_3 , 300 MHz) δ 0.02 (s, 6 H), 0.87 (s, 9 H), 0.96 (d, $J = 6.5$ Hz, 3 H), 1.80 (s, 3 H), 2.7-2.9 (m, 1 H), 3.3-3.6 (m, 2 H), 5.05-5.35 (m, 3 H), 6.77 (m, 1 H); ^{13}C NMR (CDCl_3 , 75 MHz) δ -5.38, -5.31, 17.50, 18.34, 19.86, 25.92 (3C), 34.68, 7.95, 113.58, 132.49, 133.98, 134.14; LRMS (CI) calcd. for $\text{C}_{14}\text{H}_{28}\text{OSi}$ $[\text{M}]^+$ 240, found 240.

General procedure for cross-coupling of the (Z)-chloroalkenes with terminal alkynes (Representative Procedure C):ⁱ A flame dried 25-mL three-neck round-bottomed flask with a reflux condenser under argon was charged with $\text{Pd}(\text{MeCN})_2\text{Cl}_2$ (8 mg, 0.03 mmol, 3 mol%), **2** (43 mg, 0.09 mmol, 9 mol%), Cs_2CO_3 (812 mg, 2.5 mmol), followed by anhydrous acetonitrile (3 mL) and the appropriate (Z)-chloroalkene (1 mmol). The slightly yellow suspension was stirred at 23 °C for 25 min. Then alkyne (1.5 mmol) was added via syringe and the mixture was stirred in a heating bath at the desired temperature for the indicated time. The mixture was allowed to cool to room temperature, quenched with saturated NH_4Cl and extracted with ether. The combined organic layers were washed with brine, dried over MgSO_4 , filtered and concentrated. The residue was purified by flash column chromatography on silica gel to give the desired product.

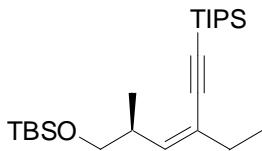


(3Z,5S)-6-tert-Butyldimethylsilyloxy-3,5-dimethyl-1-triisopropylsilyl-3-hexen-1-yne.

This compound was prepared according to Representative Procedure C using (2Z,4S)-5-*tert*-butyldimethylsilyloxy-2-chloro-4-methyl-2-pentene and triisopropylsilylacetylene. Yield: 73%; $[a]_D^{23} +27^\circ$ (c 0.38, CHCl_3); ^1H NMR (CDCl_3 , 300 MHz) d 0.02 (s, 6 H), 0.88 (s, 9 H), 0.99 (d, $J = 7.0$ Hz, 3 H), 1.08 (s, 21 H), 1.83 (s, 3 H), 2.8-3.0 (m, 1 H), 3.35-3.6 (m, 2 H), 5.50 (d, $J = 9.4$ Hz, 1 H); ^{13}C NMR (CDCl_3 , 75 MHz) d -5.36 (2C), 11.34 (3C), 16.73, 18.31, 18.68 (6C), 23.20, 25.89 (3C), 38.28, 67.28, 93.44, 106.52, 118.44, 141.47; HRMS calcd. for $\text{C}_{23}\text{H}_{47}\text{OSi}_2$ $[\text{M}+\text{H}]^+$ 395.3165, found 395.3168.

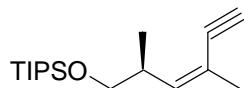


(2S,3Z)-1-tert-Butyldimethylsilyloxy-2,4-dimethyl-3-dodecen-5-yne. This compound was prepared according to Representative Procedure C using (2Z,4S)-5-*tert*-butyldimethylsilyloxy-2-chloro-4-methyl-2-pentene and 1-octyne. Yield: 71%; ^1H NMR (CDCl_3 , 300 MHz) d 0.02 (s, 6 H), 0.88 (bs, 12 H), 0.96 (d, $J = 7.0$ Hz, 3 H), 1.2-1.6 (m, 8 H), 1.79 (s, 3 H), 2.30 (t, $J = 7.0$ Hz, 2 H), 2.75-2.9 (m, 1 H), 3.3-3.6 (m, 2 H), 5.35 (d, $J = 9.3$ Hz, 1 H); IR (neat) 2212, 1463, 1271, 1254 cm^{-1} .



(3Z,5S)-6-tert-Butyldimethylsilyloxy-3-ethyl-5-methyl-1-triisopropylsilyl-3-hexen-1-yne. This compound was prepared according to Representative Procedure C using

(3Z,2S)-1-*tert*-butyldimethylsilyloxy-2-methyl-4-chloro-3-hexene and triisopropylsilylacetylene. Yield: 65%; $[\alpha]_D^{23} +43^\circ$ (c 0.18, CHCl_3); ^1H NMR (CDCl_3 , 300 MHz) d 0.01 (s, 6 H), 0.87 (s, 9 H), 0.98 (d, $J = 7.1$ Hz, 3 H), 1.07 (bs, 24 H), 2.11 (q, $J = 7.0$ Hz, 2 H), 2.8-3.0 (m, 1 H), 3.35-3.6 (m, 2 H), 5.51 (d, $J = 9.4$ Hz, 1 H); ^{13}C NMR (CDCl_3 , 75 MHz) d -5.38, -5.34, 11.35 (3C), 13.27, 16.78, 18.29, 18.68 (6C), 25.89 (3C), 30.39, 38.01, 67.33, 94.20, 105.68, 125.13, 139.97; IR (neat) 2139, 1463, 1384, 1361, 1251, 1116, 1091 cm^{-1} ; HRMS calcd. for $\text{C}_{24}\text{H}_{49}\text{OSi}_2$ $[\text{M}+\text{H}]^+$ 409.3322, found 409.3318.



(3Z,5S)-6-*tert*-Butyldimethylsilyloxy-3,5-dimethyl-3-hexen-1-yne. This compound was prepared according to Representative Procedure C using (2Z,4S)-5-triisopropyl-2-chloro-4-methyl-2-pentene and triethylsilylacetylene followed by deprotection with K_2CO_3 in refluxing MeOH. Yield: 63% over 2 steps; $[\alpha]_D^{23} +41.5^\circ$ (c 0.26, CHCl_3); ^1H NMR (CDCl_3 , 300 MHz) d 1.02 (d, $J = 6.7$ Hz, 3 H), 1.06 (s, 21 H), 1.84 (s, 3 H), 2.8-3.0 (m, 1 H), 3.04 (s, 1 H), 3.45-3.55 (m, 2 H), 5.61 (d, $J = 9.4$ Hz, 1 H); ^{13}C NMR (CDCl_3 , 75 MHz) d 11.99 (3C), 16.70, 18.00 (6C), 22.99, 38.55, 67.58, 80.13, 83.09, 116.88, 142.57; IR (neat) 3313, 2943, 2725, 1463, 1384, 1116, 1090 cm^{-1} ; HRMS calcd. for $\text{C}_{17}\text{H}_{33}\text{OSi}$ $[\text{M}+\text{H}]^+$ 281.2300, found 281.2305.

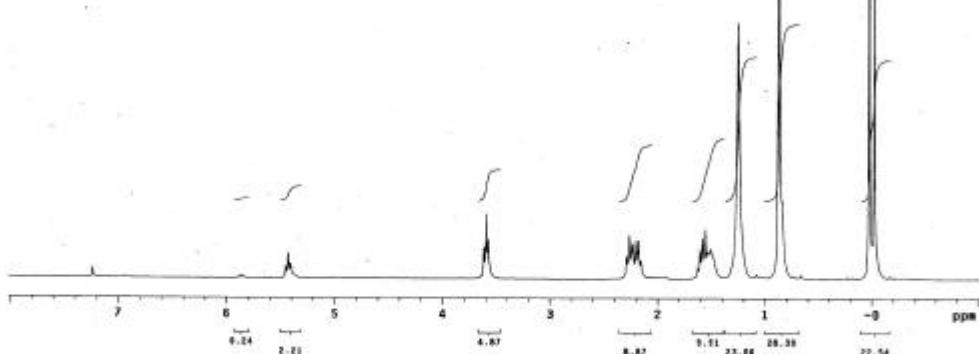
Reference:

- (a) C. Dai, G. C. Fu, *J. Am. Chem. Soc.*, **2001**, *123*, 2719
- (b) T. Yoshida, S. Otsuka, *Inorg. Synth.*, **1990**, *28*, 113.

- (c) M. Kranenburg, Y. E. M. van der Burgt, P. C. J. Kamer, P. W. N. M. van Leeuwen, K. Goubitz, J. Fraanje, *Organometallics*, **1995**, *14*, 3081.
- (d) K. Yates, H. Leung, *J. Org. Chem.*, **1980**, *45*, 1401.
- (e) K. Moughamir, B. Mezgueld, A. Atmani, H. Mestdagh, C. Rolando, *Tetrahedron, Lett.* **1999**, *40*, 59.
- (f) I. Maciagiewicz, P. Dybowski, A. Skowronska, *Tetrahedron*, **2003**, *59*, 6057.
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- (h) E. Brandes, P. A. Grieco, P. Garner, *J. Chem. Soc., Chem. Commun.*, **1988**, *7*, 500.
- (i) D. Gelman, S. L. Buchwald, *Angew. Chem. Int. Ed.*, **2003**, *42*, 5993.

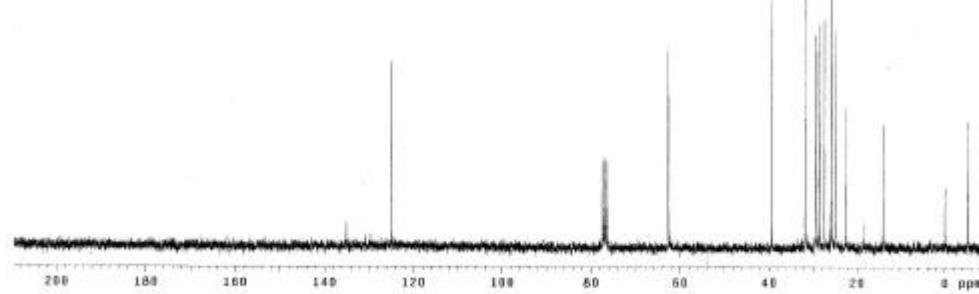
First Widely Applicable Palladium-Catalyzed *trans*-Selective Monoalkylation...

Zu Tan and Ei-ichi Negishi*



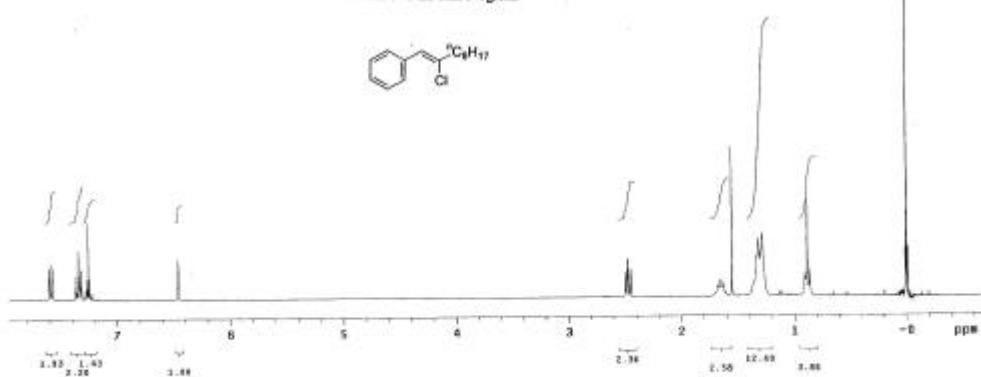
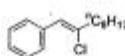
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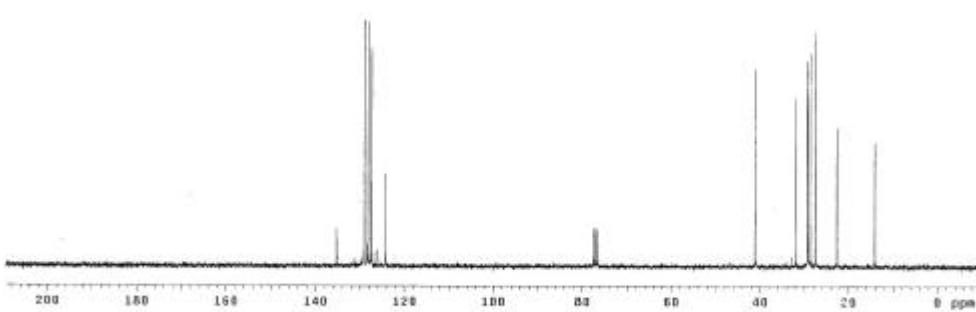
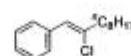
Ze Tan and Ei-ichi Negishi*



INDEX	PRIMACY	PER	HEIGHT
1	10281.168	130.245	1
2	10189.133	129.148	1
3	9726.763	108.386	0.1
4	9661.316	108.482	0.1
5	9644.024	127.337	0.1
6	9348.724	127.337	0.1
7	5025.456	141.431	0.1
8	5067.733	73.888	0.1
9	5773.98	76.575	0.1
10	3185.482	42.278	0.1
11	4843.162	22.352	0.1
12	2323.483	3.347	0.1
13	3784.424	28.227	0.1
14	2187.98	28.686	0.1
15	2081.342	27.598	0.1
16	3798.478	22.837	0.1
17	2081.342	27.598	0.1

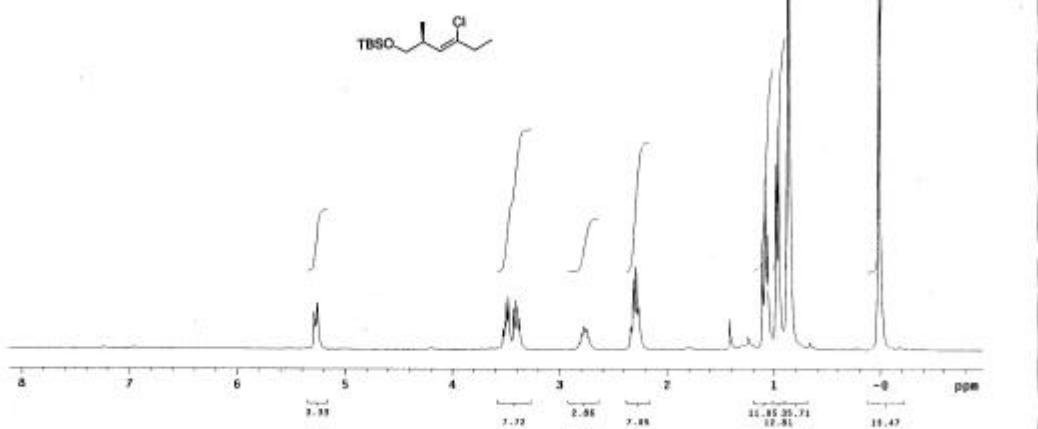
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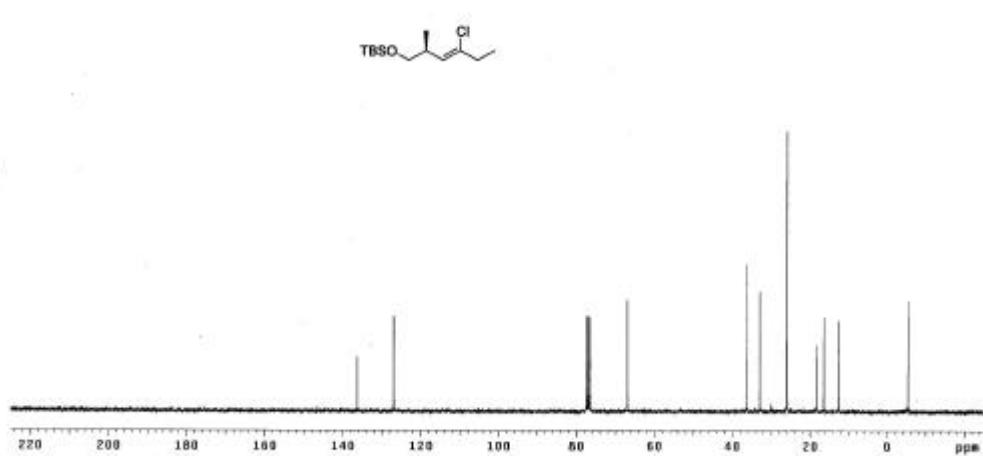
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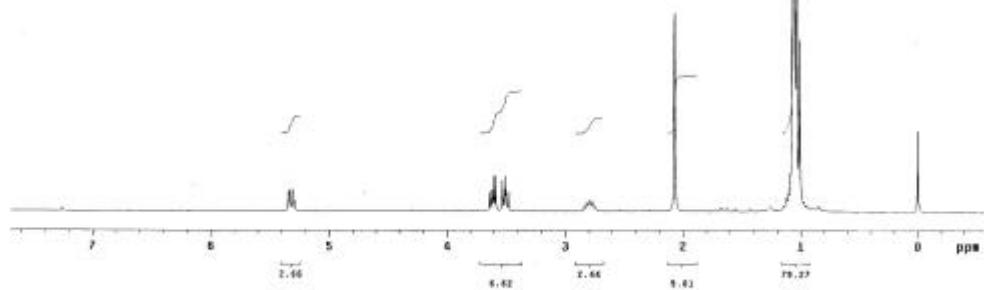
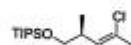
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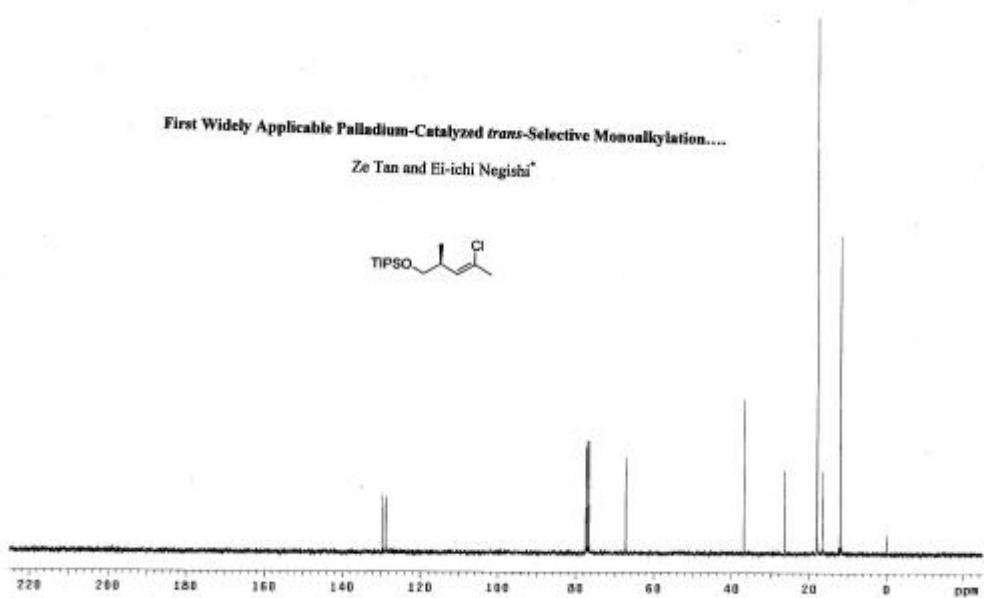
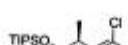
First Widely Applicable Palladium-Catalyzed *trans*-Selective Monoalkylation...

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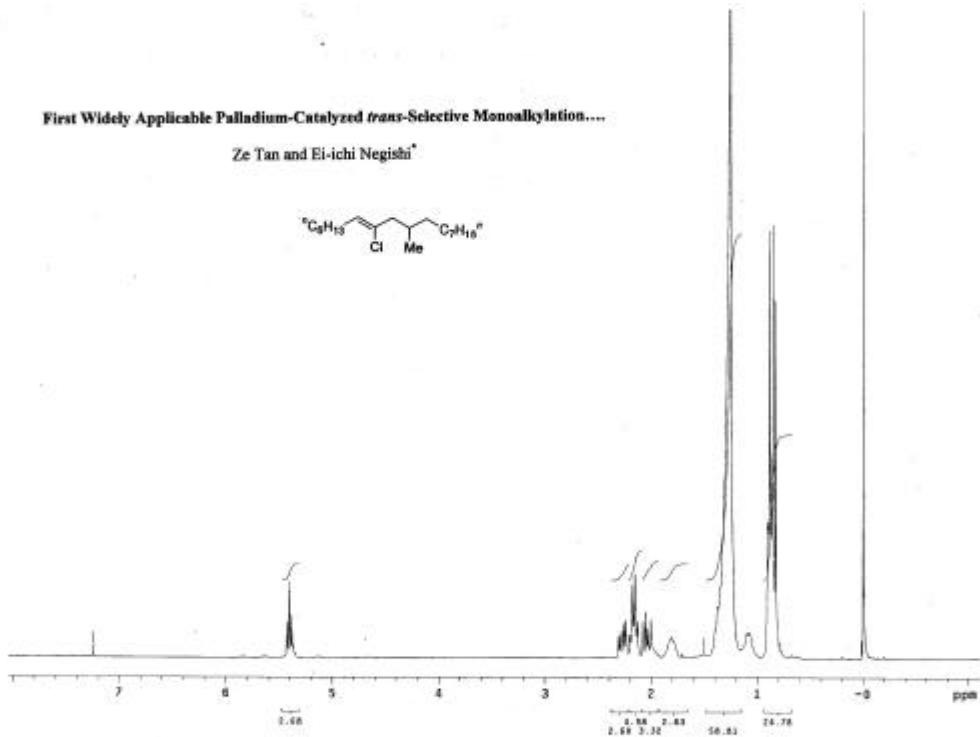
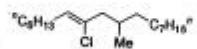
First Widely Applicable Palladium-Catalyzed *trans*-Selective Mannich Reactions

Z. Tan and Ei-ichi Negishi*



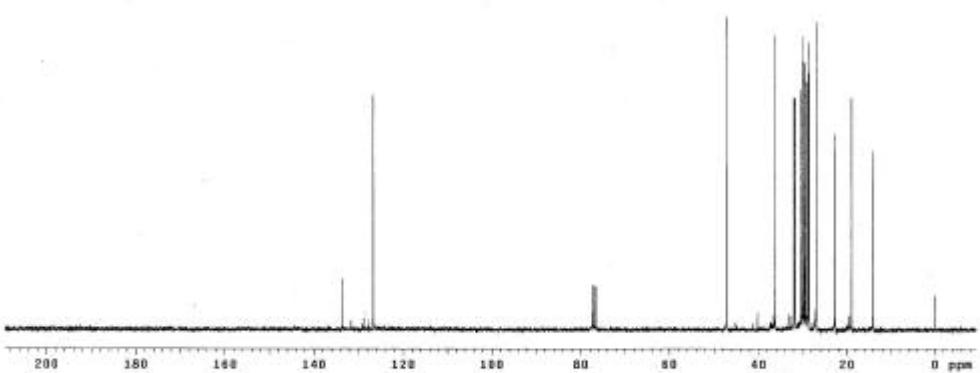
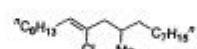
First Widely Applicable Palladium-Catalyzed *trans*-Selective Monoalkylation....

Ze Tan and Ei-ichi Negishi*



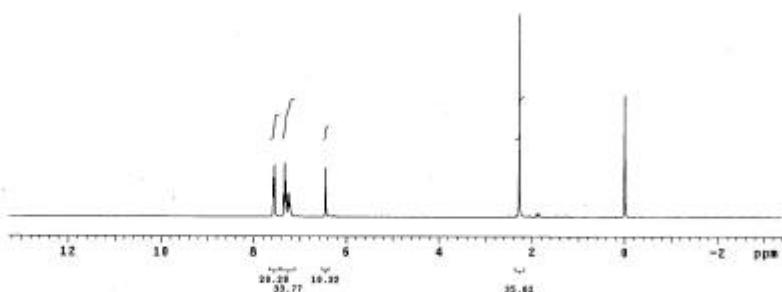
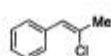
First Widely Applicable Palladium-Catalyzed *trans*-Selective Monoalkylation....

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First Widely Applicable Palladium-Catalyzed *trans*-Selective Monoalkylation....

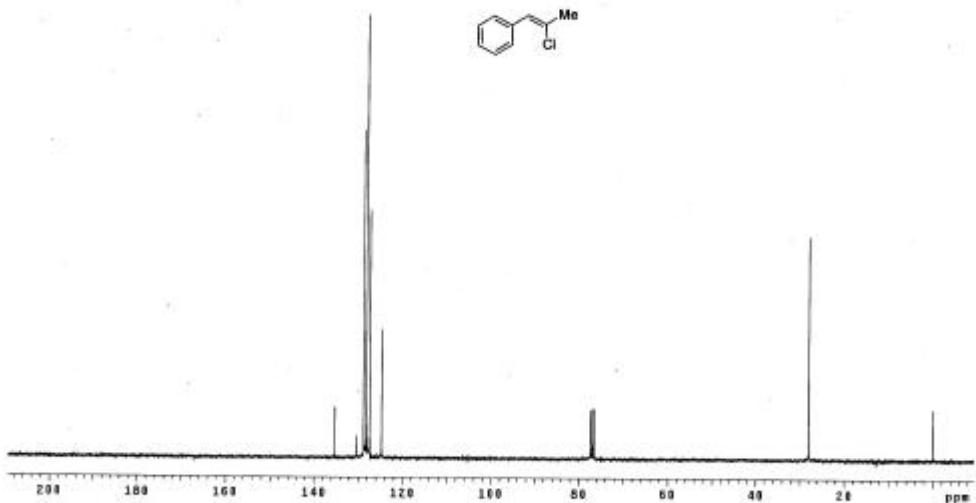
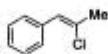
Ze Tan and Ei-ichi Negishi*



INDEX	FREQUENCY	PPM	HEIGHT
1	19281.558	135.246	19.0
2	3838.451	130.325	5.1
3	8718.586	128.416	64.5
4	9893.707	128.115	314.7
5	8859.143	127.913	34.8
6	3887.377	324.717	32.7
7	5828.829	77.421	12.3
8	5898.161	77.300	33.6
9	5776.374	78.379	32.7
10	2112.339	29.091	..
11	-1.888	-9.026	..

First Widely Applicable Palladium-Catalyzed *trans*-Selective Monoalkylation....

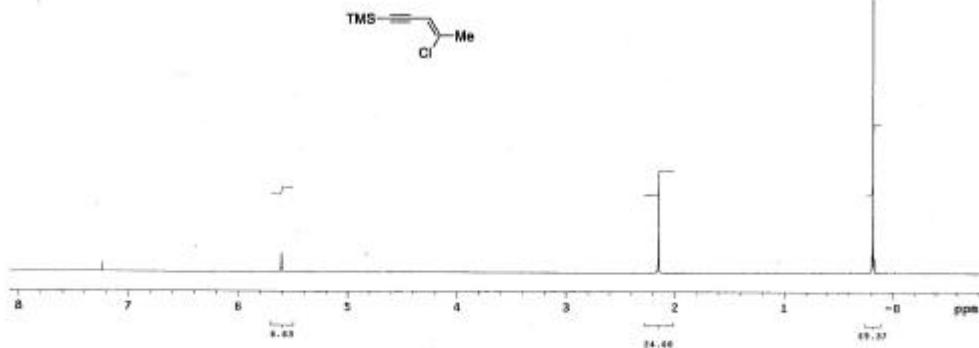
Ze Tan and Ei-ichi Negishi*



INDEX	FREQUENCY	PPM	HEIGHT
1	1662.193	5.838	4.8
2	1664.619	5.833	4.7
3	845.425	2.135	2.5
4	845.425	2.135	2.5
5	56.393	8.195	6.8
6	54.793	8.183	16.5
7	53.284	8.171	3.7

First Widely Applicable Palladium-Catalyzed *trans*-Selective Monoalkylation....

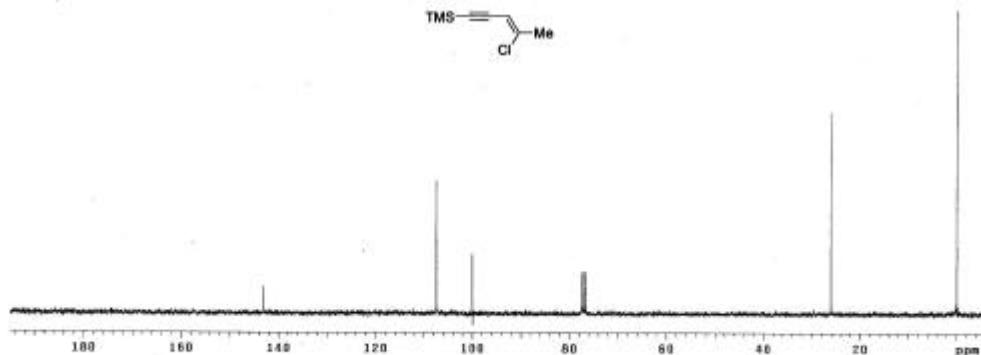
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INDEX	FREQUENCY	PPM	HEIGHT
1	13763.852	142.875	8.0
2	8389.459	137.447	34.4
3	7344.219	132.772	19.4
4	5839.458	77.931	18.8
5	5887.219	76.953	11.0
6	5776.482	76.573	18.9
7	1285.211	28.995	92.3
8	-01.985	-9.158	78.9

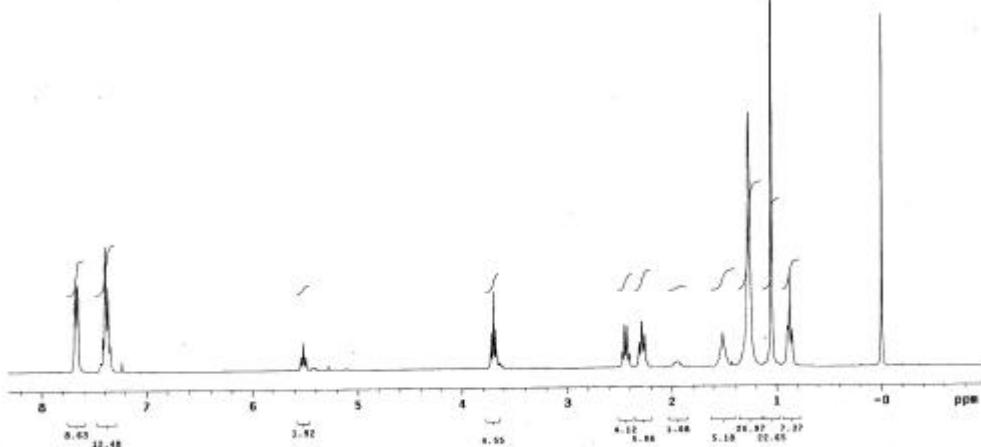
First Widely Applicable Palladium-Catalyzed *trans*-Selective Monoalkylation....

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First Widely Applicable Palladium-Catalyzed *trans*-Selective Monosalkylation...

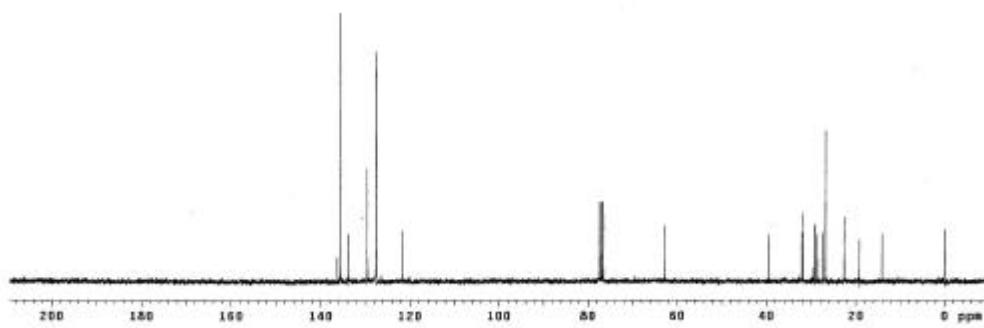
Ze Tan and Ei-ichi Negishi



INDEX	FREQUENCY	PPW	PERCENT
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2	10,076,716	135,578	7.0
3	10,140,837	132,918	7.0
4	9,716,957	125,444	5.5
5	9,765,946	125,484	5.5
6	9,836,440	127,621	5.7
7	9,921,798	127,581	5.7
8	10,164,778	132,788	6.2
9	10,244,778	132,788	6.2
10	5,806,103	77,888	3.5
11	5,376,274	76,578	3.5
12	4,729,665	62,798	2.8
13	4,232,366	56,214	2.5
14	2,423,366	32,214	1.5
15	2,485,215	31,869	1.5
16	2,323,383	28,343	1.5
17	2,022,768	29,232	1.2
18	2,022,768	29,232	1.2
19	2,457,436	37,497	1.8
20	2,824,668	45,933	20.5
21	7,798,718	22,659	10.5
22	10,449,393	29,259	13.1
23	10,822,822	32,169	14.0
24	10,822,822	32,169	14.0
25	9,335	11,335	5.2

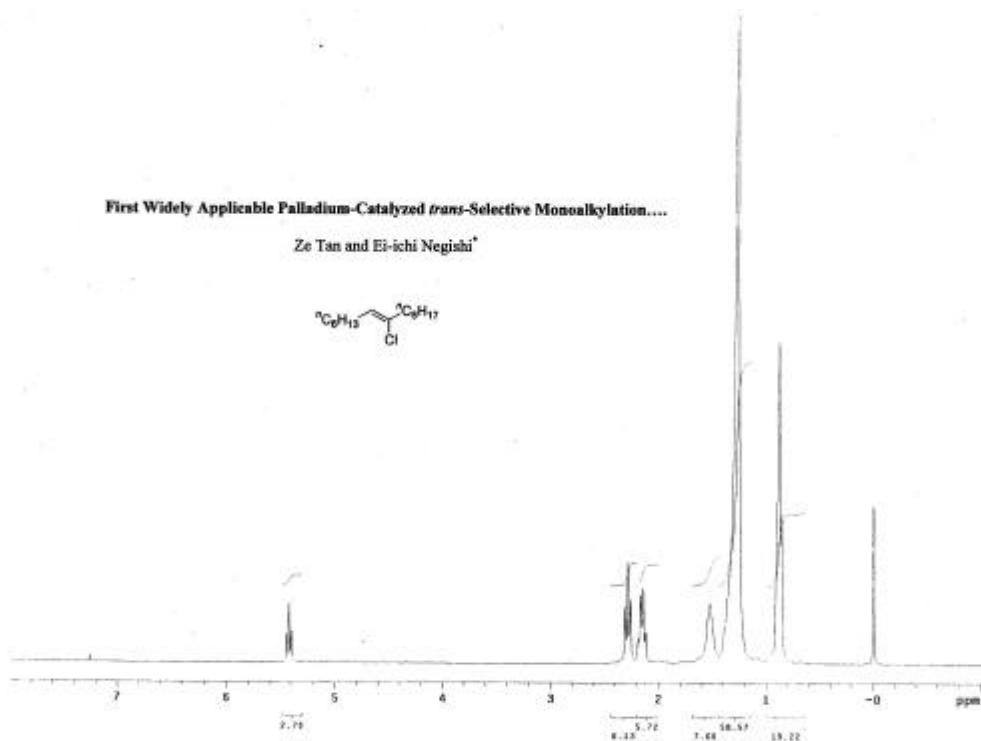
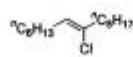
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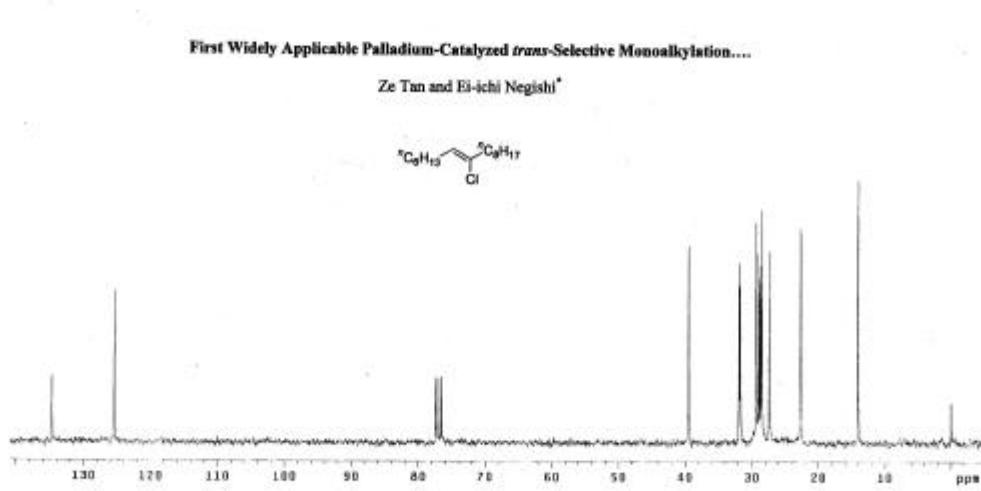
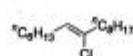
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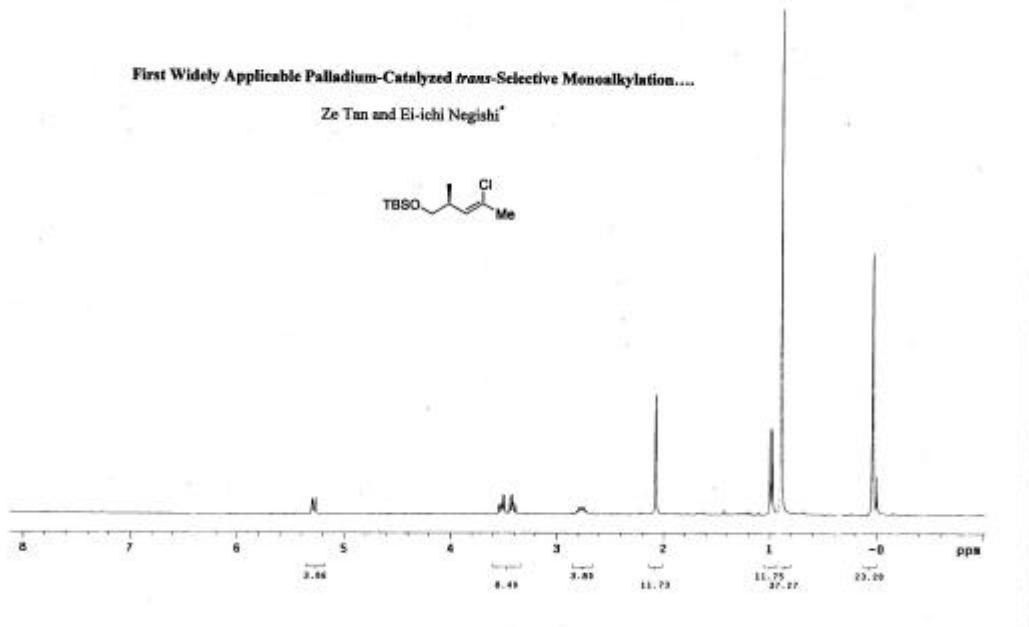
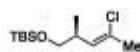
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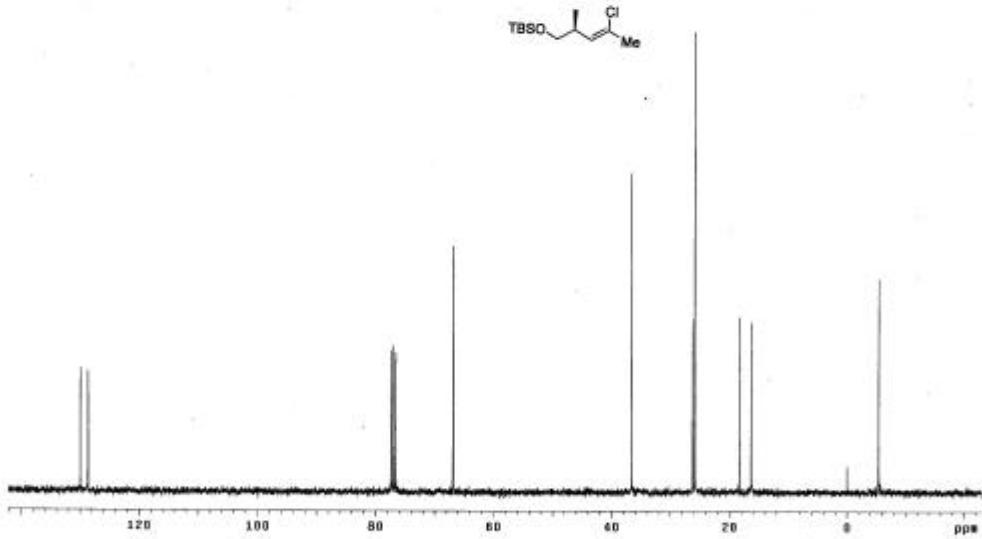
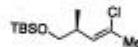
Ze Tan and Ei-ichi Negishi*



INDEX	FREQUENCY	PPM	HEIGHT
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2	8782.155	128.668	39.8
3	8888.945	77.427	36.5
4	8888.945	77.427	37.6
5	5776.878	76.589	35.8
6	9145.611	58.096	93.2
7	2738.888	35.579	60.3
8	1981.939	24.285	44.9
9	1232.172	18.328	10.7
10	1232.172	18.328	45.1
11	1232.172	18.328	43.7
12	-41.192	-9.416	6.7
13	-484.039	-5.367	55.0

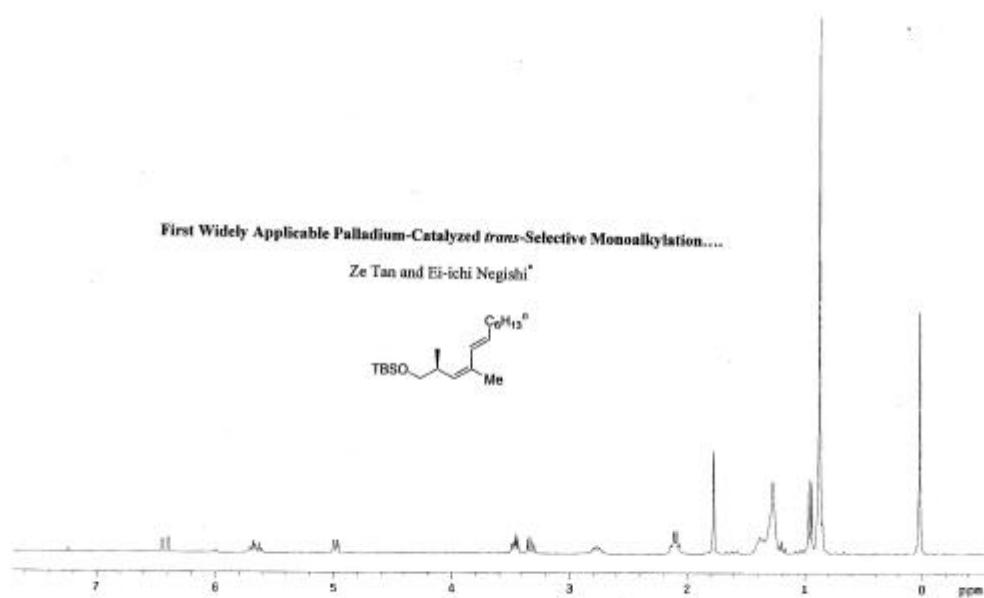
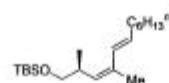
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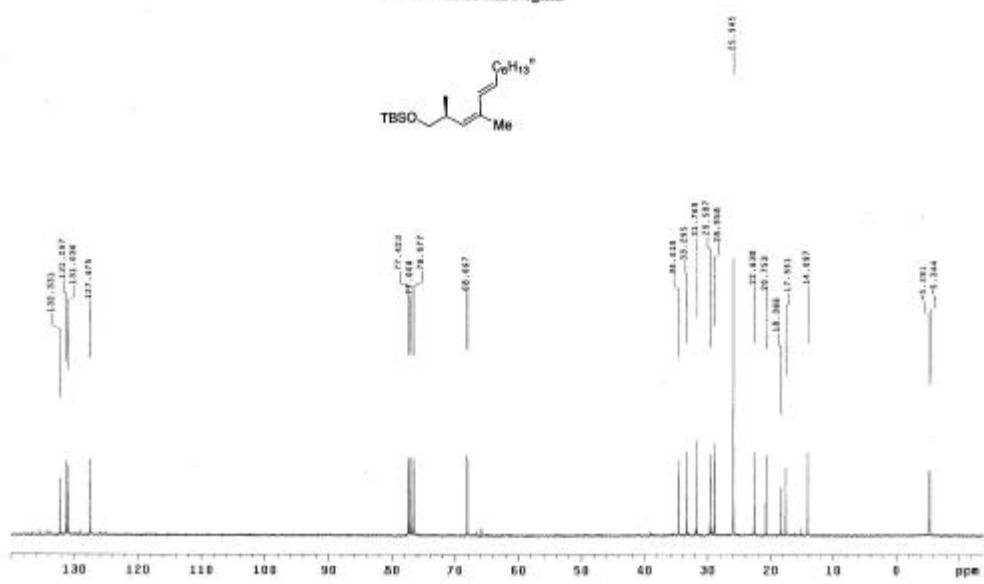
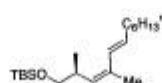
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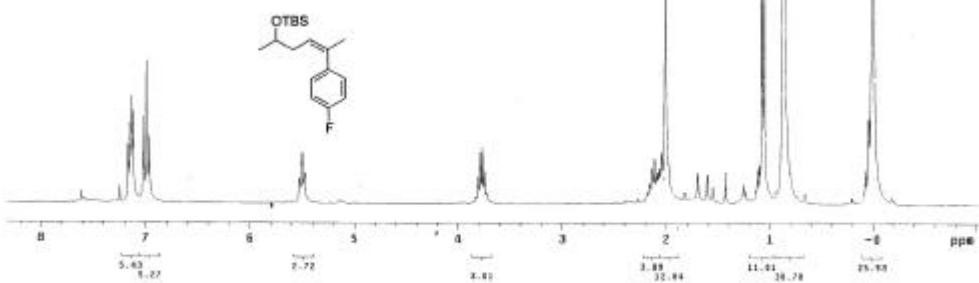
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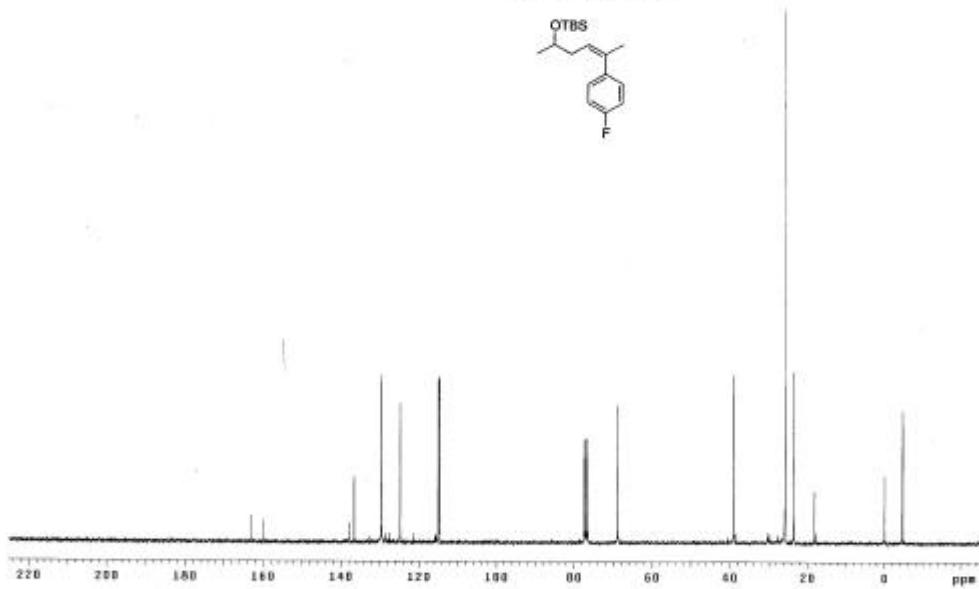
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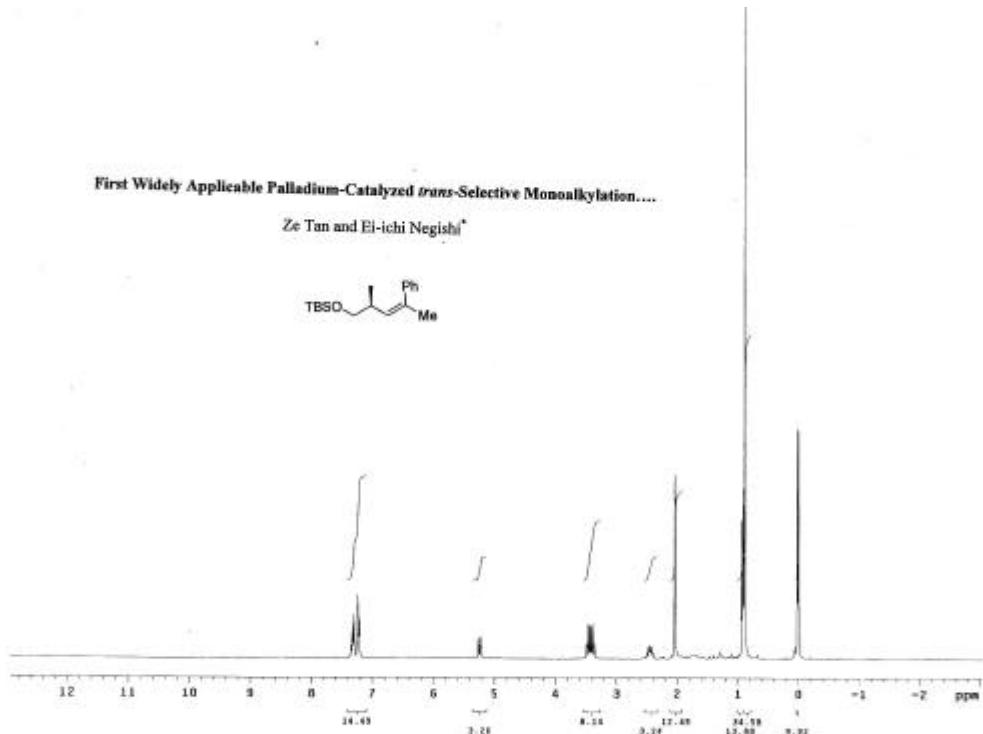
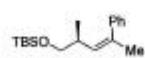
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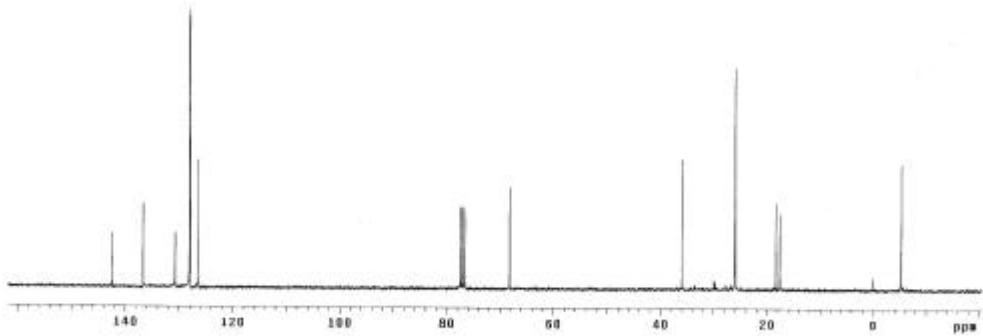
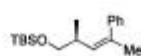
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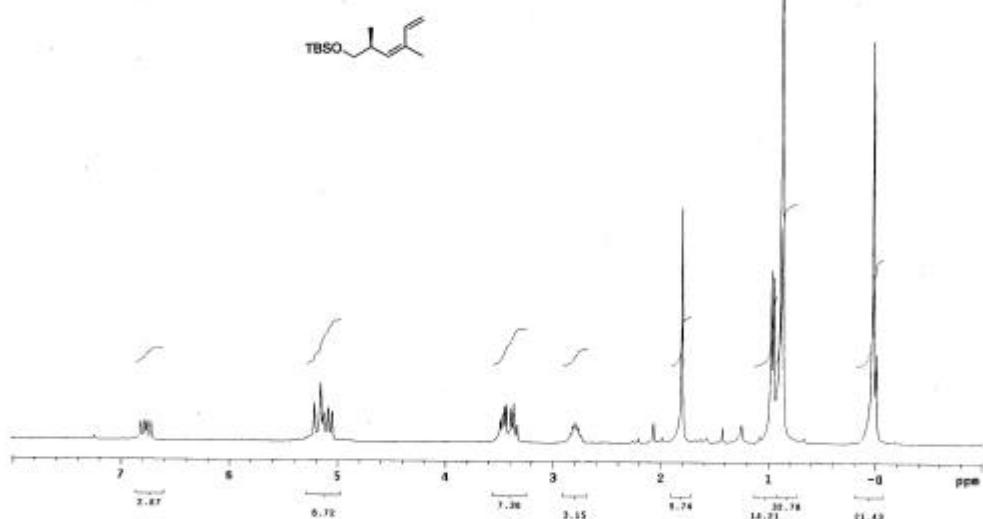
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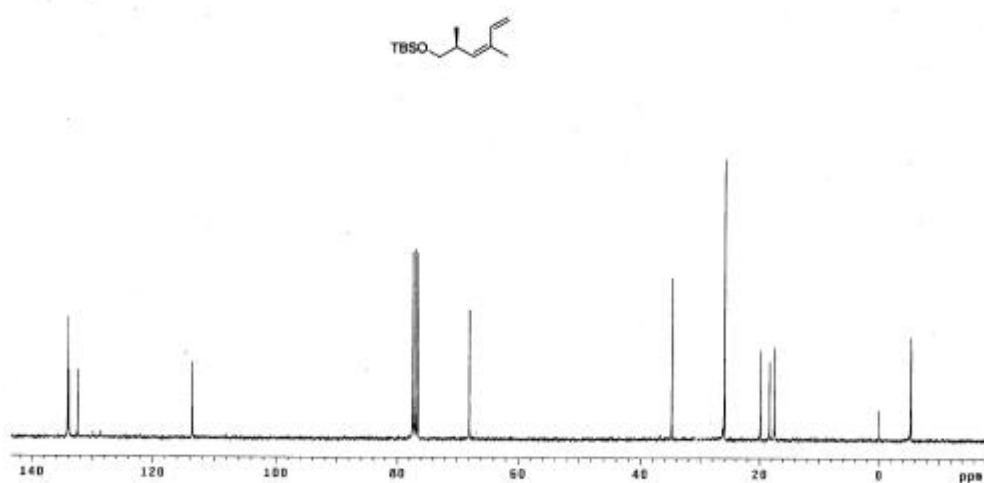
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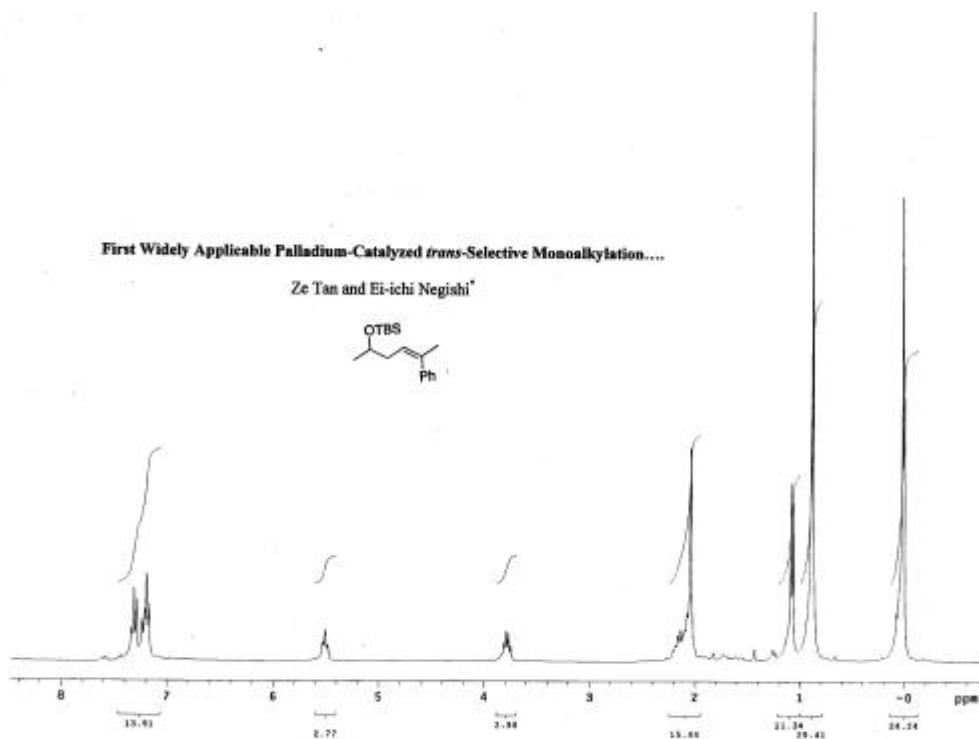
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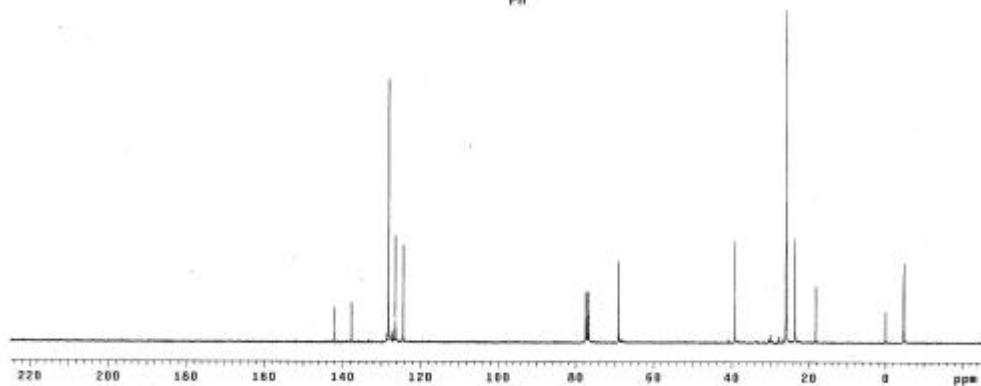
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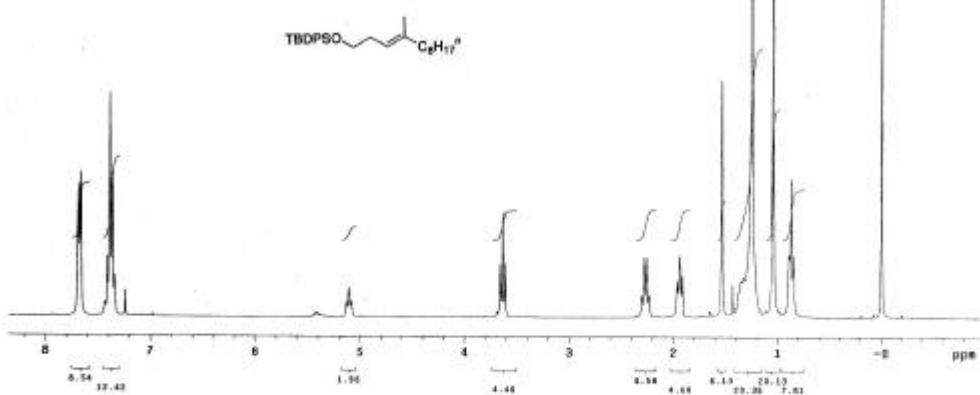
First Widely Applicable Palladium-Catalyzed *trans*-Selective Monoalkylation....

Ze Tan and Ei-ichi Negishi*



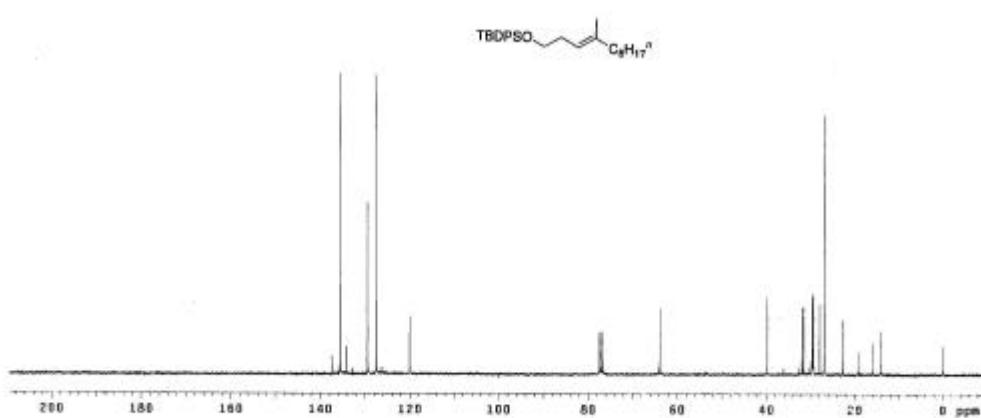
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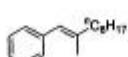
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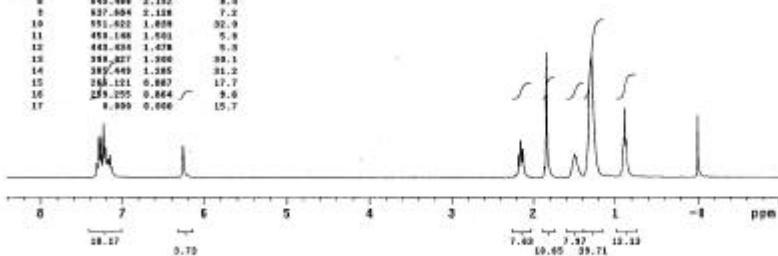


Videly Applicable Palladium-Catalyzed *trans*-Selective Monoalkylation...

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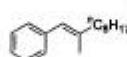


INDEX	FREQUENCY	PPM	HEIGHT
1	2359.008	7.081	13.9
2	2359.009	7.079	13.9
3	2349.498	7.255	13.5
4	2342.258	7.255	7.7
5	2145.758	7.152	5.8
6	1829.989	6.257	8.1
7	415.176	5.78	9.8
8	845.498	2.132	8.4
9	827.304	2.132	7.2
10	551.622	1.858	92.9
11	459.148	1.601	5.8
12	459.148	1.674	5.9
13	389.268	0.908	3.0
14	389.494	1.285	31.2
15	263.121	0.887	17.7
16	253.255	0.884	9.6
17	8.099	0.006	15.7

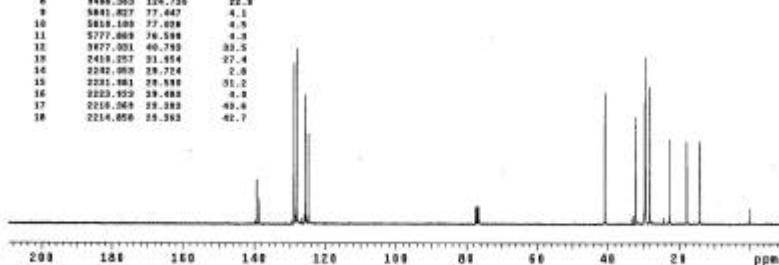


First Widely Applicable Palladium-Catalyzed *trans*-Selective Monoalkylation...

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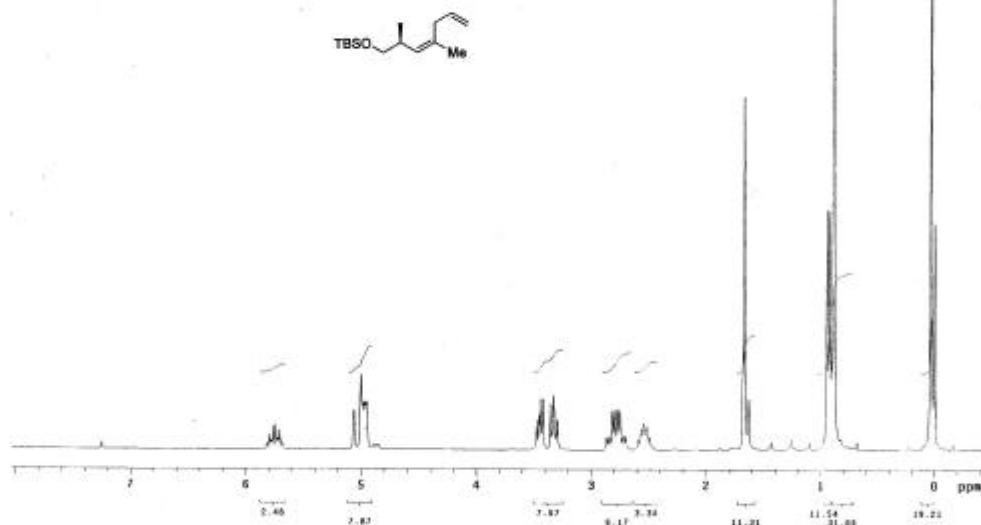


INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	16487.781	139.595	11.3	19	3124.288	28.181	2.4
2	16487.781	139.577	11.3	20	1124.285	28.181	2.4
3	5718.499	128.838	45.1	21	1735.778	23.759	21.7
4	5693.497	128.568	4.4	22	1328.584	17.768	21.8
5	8888.375	128.455	2.4	23	1066.133	14.136	21.2
6	8884.128	127.768	44.9	24	6.088	8.009	3.8
7	2458.164	124.736	22.4				
8	3468.263	124.736	2.4				
9	5881.827	77.447	4.1				
10	5818.107	77.038	4.5				
11	5777.881	76.598	4.3				
12	3977.091	40.749	33.5				
13	2458.164	38.724	27.4				
14	2382.008	38.724	2.8				
15	2221.981	28.558	31.2				
16	2223.952	28.488	4.8				
17	2218.369	28.383	49.6				
18	2214.056	28.383	42.7				



First Widely Applicable Palladium-Catalyzed *trans*-Selective Monoalkylation....

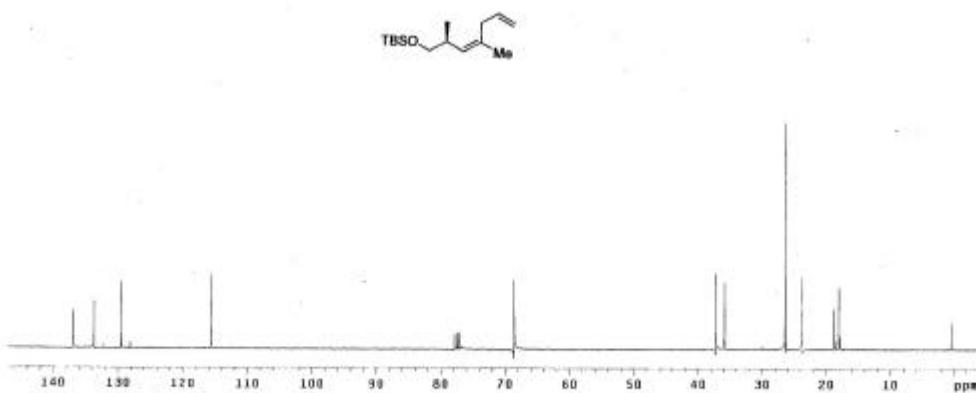
Ze Tan and Ei-ichi Negishi*



INDEX	FRQUENCY	PPM	HEIGHT
1	13321.491	131.065	9.7
2	10882.397	135.741	12.1
3	8771.378	128.551	17.6
4	8735.821	119.548	38.9
5	5173.599	109.559	27.8
6	2887.971	97.217	5.5
7	2723.685	95.846	37.5
8	1381.693	39.388	38.3
9	1296.505	29.819	28.4
10	1218.118	38.842	28.3
11	1340.349	28.328	15.8

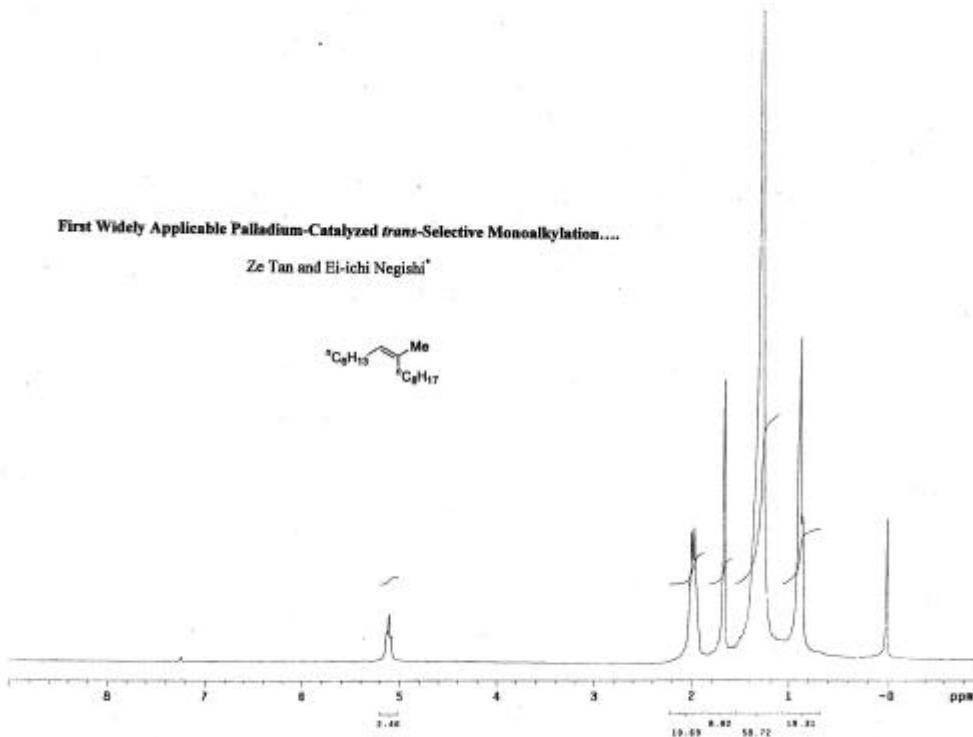
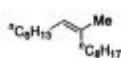
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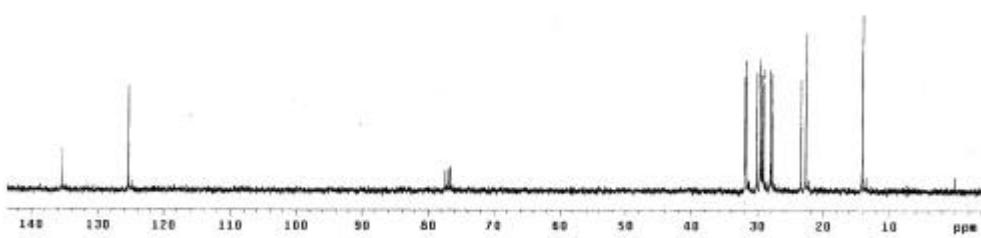
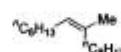
Ze Tan and Ei-ichi Negishi*



SPECIES	ENDOWMENT	ENV	WEIGHT
1	18218.337	195.358	36
2	8492.345	125.322	37
3	2411.466	31.875	38
4	2495.350	31.887	35
5	3398.470	31.792	34
6	2274.931	28.258	33
7	2274.931	28.258	33
8	2339.418	28.879	34
9	2339.418	28.879	34
10	2187.798	29.127	31
11	2124.386	28.111	31
12	2381.288	27.055	39
13	2764.345	25.414	28
14	2323.262	22.720	41

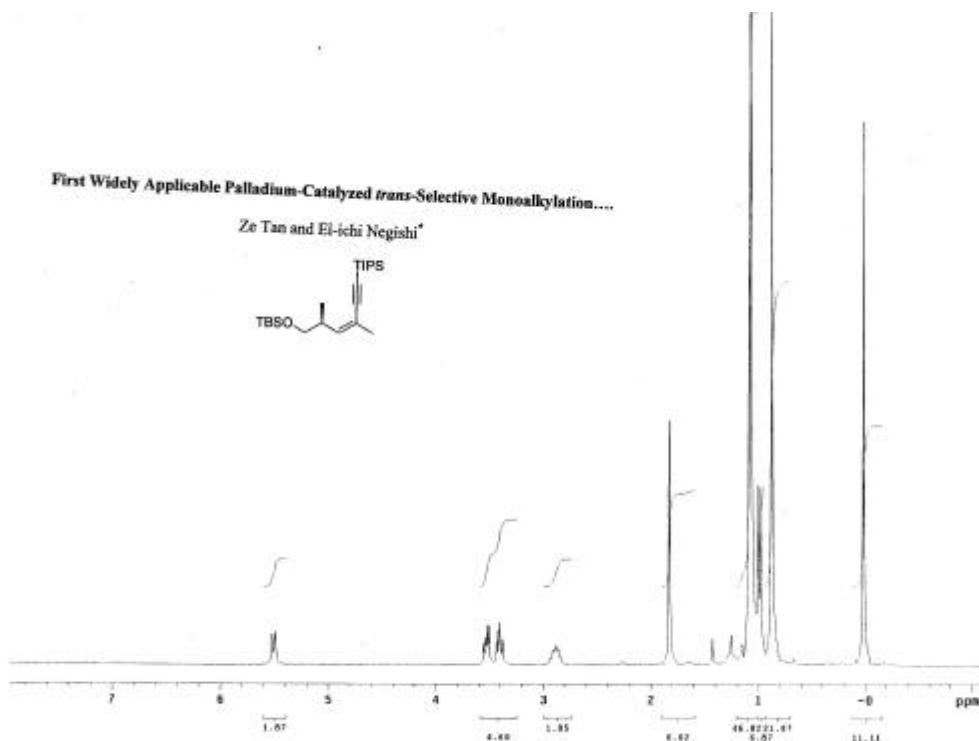
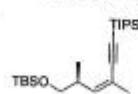
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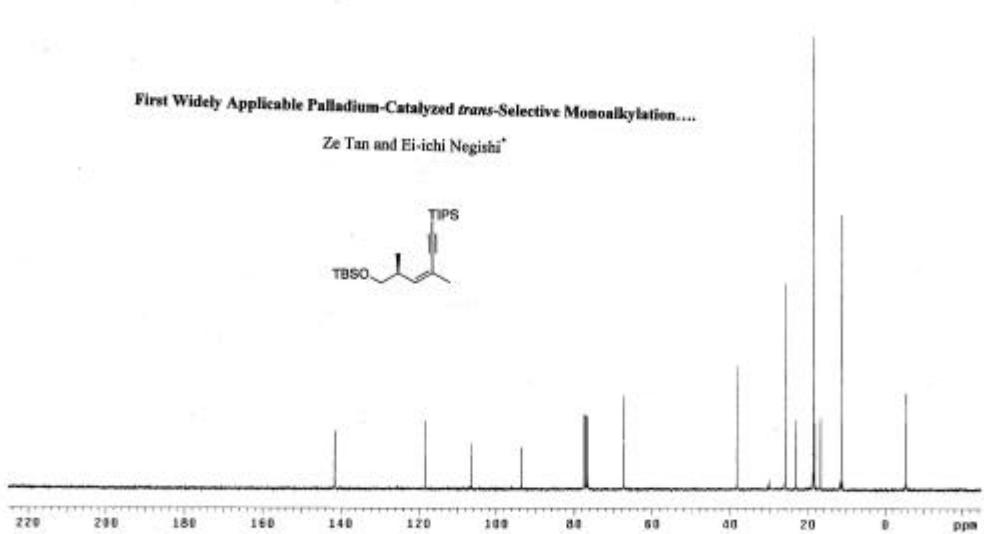
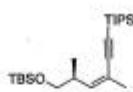
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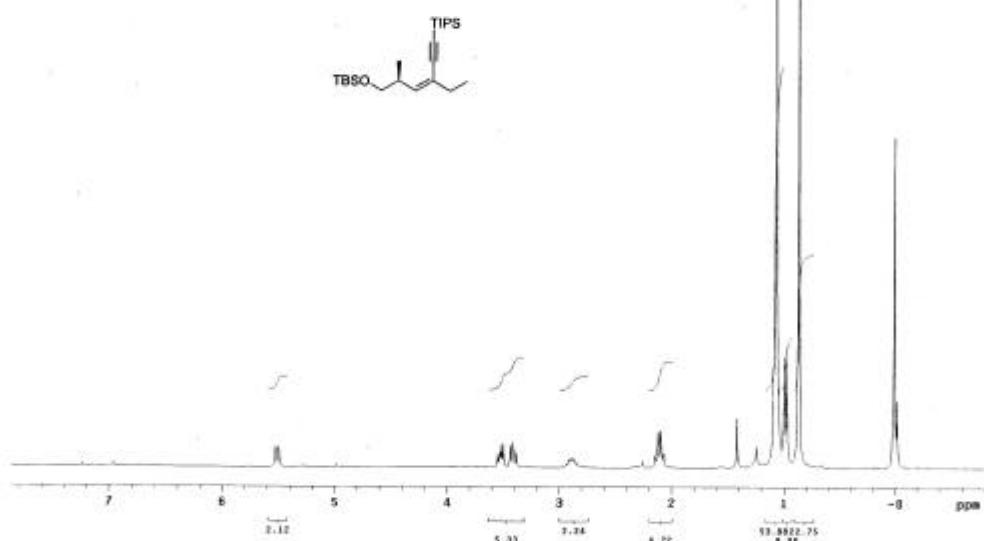
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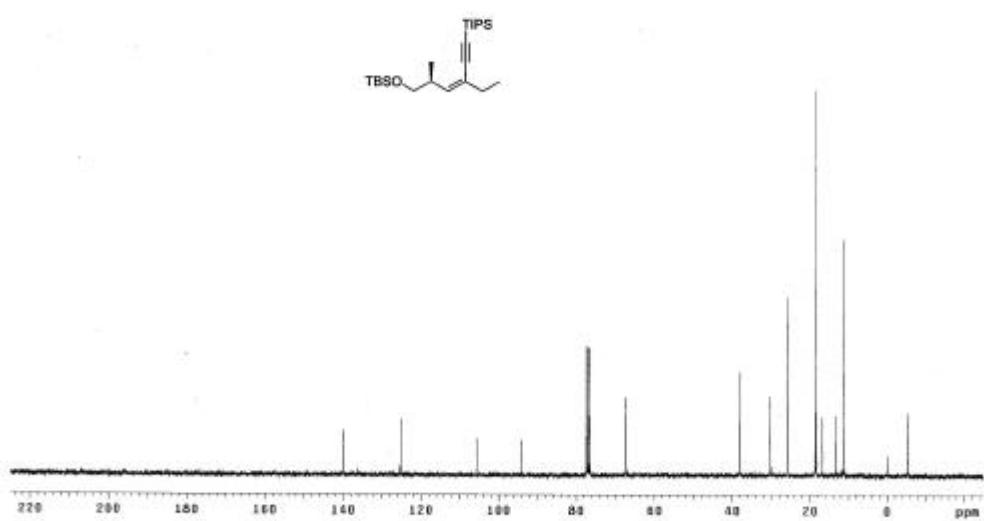
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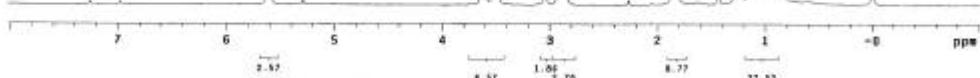
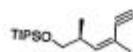
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First Widely Applicable Palladium-Catalyzed *trans*-Selective Monoalkylation....

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DRDX	PROTONICITY	PPM	ABSORBT
1		10753.774	342.588
2		9815.497	326.879
3		6267.177	89.881
4		6249.973	88.170
5		5884.961	77.131
6		5863.923	76.388
7		5715.788	76.577
8		5498.812	67.575
9		2892.212	38.345
10		1734.285	22.887
11		1227.545	18.343
12		1259.593	18.399
13		884.156	11.369
14		-2.785	-9.923

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