Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

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[**]

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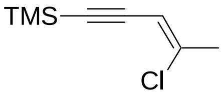
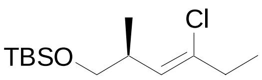
General Procedures. All reactions were run under a dry Ar atmosphere. Reactions were monitored by GC analysis of reaction aliquots. GC analysis was performed on an HP6890 Gas Chromatograph using an HP-5 capillary column (30 m x 0.32 mm, 0.5 μM film) packed with SE-30 on Chromosorb W. Column chromatography 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. $ZnBr_2$ was flame-dried under vacuum. $Pd(^{t}Bu_3P)_2$,[a] $Pd(Cy_3P)_2$,[b] $Pd(DPEphos)Cl_2$[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.

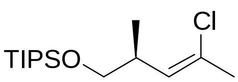
General procedure for monoalkylation (Representative Procedure A): A flame dried 25-mL round-bottomed flask under argon was charged with 1,1-dichloro-1-alkene (1 mmol), DMF (3 mL) and $Pd(DPEphos)Cl_2$ (35 mg, 0.05 mmol, 5 mol%). After the addition of the organozinc reagent (1.2 mmol), the reaction mixture 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.



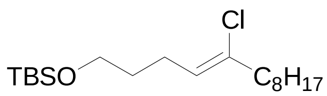
(3*Z*)-4-Chloro-1-trimethylsilyl-3-penten-1-yne. This compound was prepared according to Representative Procedure A using 1,1-dichloro-4-trimethylsilyl-1-buten-3-yne and Me_2Zn. Yield: 82%; ^{1}H NMR ($CDCl_3$, 300 MHz) d 0.18 (s, 9 H), 2.15 (d, *J* = 1.3 Hz, 3 H), 5.60 (d, *J* = 1.3 Hz, 1 H); ^{13}C 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 $C_8H_{13}ClSi$ $[M]^+$ 172.0475, found 172.0473.



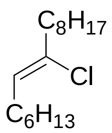
(3*Z*,2*S*)-1-*tert*-Butyldimethylsilyloxy-2-methyl-4-chloro-3-hexene. This compound was prepared according to Representative Procedure A using (3*S*)-4-*tert*-butyldimethylsilyloxy-1,1-dichloro-3-methyl-1-butene and Et_2Zn. Yield: 85%; $[a]_D^{23}$ +21^o (c 0.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) 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 $C_{13}H_{27}ClOSi$ $[M]^+$ 262.1520, found 262.1524.



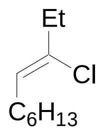
(2*Z*,4*S*)-5-Triisopropylsilyloxy-2-chloro-4-methyl-2-pentene. This compound was prepared according to Representative Procedure A using (3*S*)-1,1-dichloro-3-methyl-4-triisopropylsilyloxy-1-butene, Me_2Zn and NMI. Yield: 73%; $[a]_D^{23}$ +24.6° (c 0.48, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) d 1.02 (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); ^{13}C NMR ($CDCl_3$, 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 $C_{15}H_{32}ClOSi$ $[M+H]^+$ 291.1911, found 291.1910.



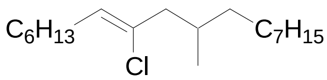
(4*Z*)-1-*tert*-Butyldimethylsilyloxy-5-chloro-4-tridecene. This compound was prepared according to Representative Procedure A using 5-*tert*-butyldimethylsilyloxy-1,1-dichloro-1-pentene and ^{n}OctZnBr. Yield: 83%; ^1H NMR ($CDCl_3$, 300 MHz) d 0.03 (s, 6 H), 0.88 (bs, 12 H), 1.2-1.4 (m, 10 H), 1.4-1.7 (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); ^{13}C NMR ($CDCl_3$, 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.



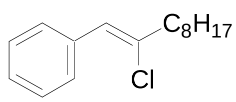
(7*Z*)-8-Chloro-7-hexadecene. This compound was prepared according to Representative Procedure A using 1,1-dichloro-1-octene and ^{n}OctZnBr. Yield: 85%; ^1H NMR ($CDCl_3$) d 0.88 (t, *J* = 6.7 Hz, 6 H), 1.2-1.45 (m, 18 H), 1.5-1.6 (m, 2 H), 2.15 (q, *J* = 7.0 Hz, 2 H), 2.28 (t, *J* = 7.2 Hz, 2 H), 5.42 (t, *J* = 6.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 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 $C_{16}H_{31}Cl$ $[M]^+$ 258, found 258.



(3*Z*)-3-Chloro-3-decene. This compound was prepared according to Representative Procedure A using 1,1-dichloro-1-octene and Et_2Zn. Yield: 76%; ^{1}H 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 $C_{10}H_{19}Cl$ $[M]^+$ 174, found 174.

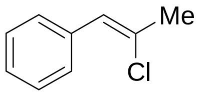


(7*Z*, 10*RS*)-8-Chloro-10-methyl-7-octadecene. This compound was prepared according to Representative Procedure A using 1,1-dichloro-1-octene and 2-methyl-1-decanylZnBr. Yield: 70%; ^{1}H NMR ($CDCl_3$, 300 MHz) d 0.8-0.9 (m, 9 H), 1.0-1.2 (m, 1 H), 1.2-1.45 (m, 21 H), 1.7-1.9 (m, 1 H), 1.9-2.35 (m, 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}.

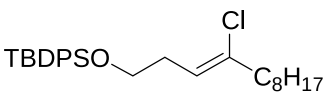


(*Z*)-2-Chloro-1-phenyl-1-decene. This compound was prepared according to Representative Procedure A using 2,2-dichlorostyrene and ^{n}OctZnBr. Yield: 90%; ^{1}H NMR ($CDCl_3$, 300 MHz) d 0.98 (t, *J* = 6.7 Hz, 3 H), 1.3-1.55 (m, 10 H), 1.65-1.85 (m,2

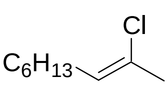
H), 2.52 (t, J = 6.5 Hz, 2 H), 6.53 (s, 1 H), 7.3-7.4 (m, 1 H), 7.4-7.45 (m, 2 H), 7.65-7.7 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) d 14.10, 22.66, 27.60, 28.61, 29.23, 29.35, 31.85, 41.18, 124.16, 127.34, 128.09 (2C), 128.96 (2C), 135.14, 135.25; IR (neat) 2954, 2926, 2855, 1642, 1492, 1465, 1447 cm^{-1}; HRMS calcd. for $C_{16}H_{24}Cl$ [M+H]$^+$ 251.1566, found 251.1563.



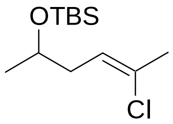
(2*Z*)-2-Chloro-1-phenyl-1-propene.[d] This compound was prepared according to Representative Procedure A using 2,2-dichlorostyrene and Me_2Zn. Yield: 80%; ^{1}H NMR ($CDCl_3$, 300 MHz) d 2.28 (s, 3 H), 6.45 (s, 1 H), 7.2-7.4 (m, 3 H), 7.55-7.6 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) d 28.00, 124.72, 127.37, 128.12 (2C), 128.82 (2C), 130.33, 135.25; LRMS (CI) calcd. for C_8H_9Cl [M]$^+$ 152, found 152.



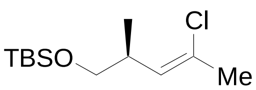
(3*Z*)-1-*tert*-Butyldiphenylsilyloxy-4-chloro-3-dodecene. This compound was prepared according to Representative Procedure A using 4-*tert*-butyldiphenylsilyloxy-1,1-dichloro-1-butene and ^{n}OctZnBr. Yield: 80%; ^{1}H NMR ($CDCl_3$, 300 MHz) d 0.88 (t, J = 6.9 Hz, 3 H), 1.05 (s, 9 H), 1.2-1.4 (m, 10 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 ($CDCl_3$, 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.



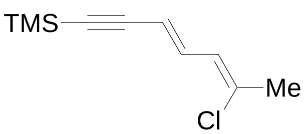
(2*Z*)-2-Chloro-2-nonene.[e] This compound was prepared according to Representative Procedure A using 1,1-dichloro-1-octene, Me_2Zn and NMI. Yield: 75%; ^{1}H NMR ($CDCl_3$, 300 MHz) d 0.88 (t, *J* = 6.7 Hz, 3 H), 1.0-1.6 (m, 8 H), 1.81 (s, 3 H), 2.05-2.3 (m, 2 H), 5.57 (t, *J* = 7.0 Hz, 1 H).



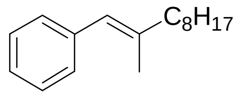
(2*Z*,5*RS*)-5-*tert*-Butyldimethylsilyloxy-2-chloro-2-hexene. This compound was prepared according to Representative Procedure A using (4*RS*)-4-*tert*-butyldimethylsilyloxy-1,1-dichloro-1-pentene, Me_2Zn and NMI. Yield: 85%; ^{1}H NMR ($CDCl_3$, 300 MHz) d 0.03 (s, 6 H), 0.86 (s, 9 H), 1.11 (d, *J* = 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).



(2*Z*,4*S*)-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, Me_2Zn and NMI. Yield: 76%; [a]$_D^{23}$ +7.6^o (c 0.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) d 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); ^{13}C NMR ($CDCl_3$, 75 MHz) d -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 $C_{12}H_{25}ClOSi$ [M+H]$^+$ 249.1441, found 249.1437.



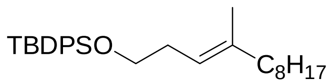
(3*E*,5*Z*)-6-Chloro-1-trimethylsilyl-3,5-heptadien-1-yne. This compound was prepared according to Representative Procedure A using 1,1-dichloro-6-trimethylsilyl-1,3-hexadien-5-yne and Me_2Zn. Yield: 82%; ^{1}H NMR ($CDCl_3$) d 0.19 (s, 9 H), 2.18 (s, 3 H), 5.62 (d, *J* = 15.6 Hz, 1 H), 6.10 (d, *J*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



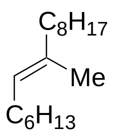
(*E*)-2-Methyl-1-phenyl-1-decene.[f] A flame dried 25-mL three-neck round-bottomed flask under argon was charged with Ni(dppp)Cl_2 (11 mg, 0.05 mmol, 5 mol%) and ether (5 mL). To the mixture was added (*Z*)-2-Chloro-1-phenyl-1-decene (250 mg, 1 mmol) followed by CH_3MgBr (0.5 mL, 3 M in ether, 1.5 mmol). After reluxing 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): ^{1}H NMR ($CDCl_3$, 300 MHz) d 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) d 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 $C_{17}H_{26}$ $[M]^+$ 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 $Pd(OAc)_2$ (11 mg, 0.05 mmol, 5 mol%),

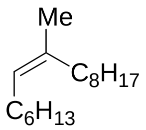
Cyp_3P (24 mg, 0.1 mmol, 10 mol%) and THF (2 mL). The mixture was stirred at 23 °C for 10 min and the (*Z*)-chloroalkene (1 mmol) was added followed by the Grignard reagent (1.5 mmol). The flask was stirred at appropriate temperature until GLC analysis indicated the consumption of the starting material. The mixture was allowed to cool to room temperature, quenched with saturated 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.



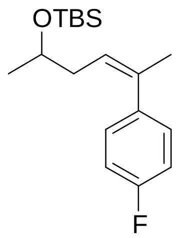
(3*Z*)-1-*tert*-Butyldimethylsilyloxy-4-methyl-3-dodecene. This compound was prepared according to Representative Procedure B using (3*Z*)-1-*tert*-butyldiphenylsilyloxy-4-chloro-3-dodecene, Pd(^{t}Bu$_3$P)$_2$, and MeMgBr. Yield: 100%; ^{1}H NMR ($CDCl_3$, 300 MHz) d 0.87 (t, *J* = 7.0 Hz, 3 H), 1.05 (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); ^{13}C NMR ($CDCl_3$, 75 MHz) d 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.



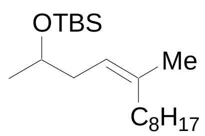
(7*E*)-8-Methyl-7-hexadecene. This compound was prepared according to Representative Procedure B using (7*Z*)-8-chloro-7-hexadecene, Pd(^{t}Bu$_3$P)$_2$, and MeMgBr. Yield: 95%; ^{1}H NMR ($CDCl_3$, 300 MHz) d 0.88 (t, *J* = 7.0 Hz, 6 H), 1.1-1.5 (m, 20 H), 1.57 (s, 3 H), 1.9-2.1 (m, 4 H), 5.11 (t, *J* = 6.4 Hz, 1 H); IR (neat) 1466, 1378, 974 cm^{-1}.



(7*Z*)-8-Methyl-7-hexadecene. ^{1}H NMR ($CDCl_3$, 300 MHz) d 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); ^{13}C NMR ($CDCl_3$, 75 MHz) d 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.

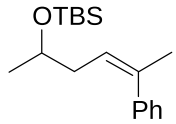


(2*Z*,5*RS*)-5-*tert*-Butyldimethylsilyloxy-2-(4'-fluorophenyl)-2-hexene. This compound was prepared according to Representative Procedure B using (2*Z*,5*RS*)-5-*tert*-butyldimethylsilyloxy-2-chloro-2-hexene**,** Pd(Cy_3P)$_2$**,** and 4-PhenylMgBr. Yield: 85%; ^{1}H NMR ($CDCl_3$, 300 MHz) d 0.02 (s, 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); ^{13}C NMR ($CDCl_3$, 75 MHz) d -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}.

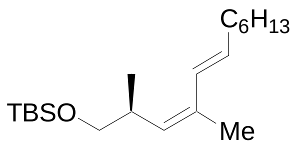


(2*RS*,4*Z*)-2-*tert*-Butyldimethylsilyloxy-5-methyl-4-tridecene. This compound was prepared according to Representative Procedure B using (2*Z*,5*RS*)-5-*tert*-butyldimethylsilyloxy-2-chloro-2-hexene**,** Pd(Cy_3P)$_2$**,** and ^{n}OctMgBr. Yield: 95%; ^{1}H

NMR ($CDCl_3$, 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 $C_{20}H_{43}OSi$ $[M+H]^+$ 327.3083, found 327.3080.

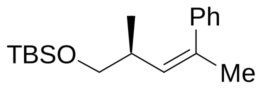


(2*Z*,5*RS*)-5-*tert*-Butyldimethylsilyloxy-2-phenyl-2-hexene. This compound was prepared according to Representative Procedure B using (2*Z*,5*RS*)-5-*tert*-butyldimethylsilyloxy-2-chloro-2-hexene**,** $Pd(Cy_3P)_2$**,** and PhMgBr. Yield: 88%; ^{1}H NMR ($CDCl_3$, 300 MHz) d 0.01 (s, 6 H), 0.87 (s, 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); ^{13}C NMR ($CDCl_3$, 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 $C_{18}H_{31}OSi$ $[M+H]^+$ 291.2144, found 291.2141.

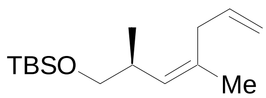


(2*S*,3*Z*,5*E*)-1-*tert*-Butyldimethylsilyloxy-2,4-dimethyl-3,5-dodecadiene.[g] This compound was prepared according to Representative Procedure B using (2*Z*,4*S*)-5-*tert*-butyldimethylsilyloxy-2-chloro-4-methyl-2-pentene**,** $Pd(Cy_3P)_2$**,** and (*E*)-1-OctenylMgBr. Yield: 73%; ^{1}H NMR ($CDCl_3$, 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

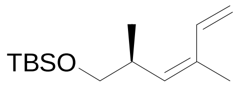
Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) d -5.34, -5.29, 14.09, 17.59, 18.37, 20.75, 22.63, 25.95 (3C), 28.96, 29.59, 31.77, 33.29, 34.62, 68.07, 127.48, 131.03, 131.27, 132.33; Anal. Calcd. For $C_{20}H_{40}OSi$: C, 74.00; H, 12.42; found: C, 73.62; H, 12.24.



(2*Z*,4*S*)-5-*tert*-Butyldimethylsilyloxy-2-phenyl-4-methyl-2-pentene. This compound was prepared according to Representative Procedure B using (2*Z*,4*S*)-5-*tert*-butyldimethylsilyloxy-2-chloro-4-methyl-2-pentene**,** Pd(OAc)$_2$/Cyp$_3$P**,** and PhZnBr. Yield: 87%; [a]$_D^{23}$ +25^o (c 0.48, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 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 ($CDCl_3$, 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 $C_{18}H_{31}OSi$ $[M+H]^+$ 291.2144, found 291.2147.

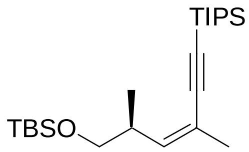


(4*Z*,6*S*)-7-*tert*-Butyldimethylsilyloxy-4,6-dimethyl-1,4-heptadiene. This compound was prepared according to Representative Procedure B using (2*Z*,4*S*)-5-*tert*-butyldimethylsilyloxy-2-chloro-4-methyl-2-pentene**,** Pd(OAc)$_2$/Cyp$_3$P**,** and AllylMgCl. Yield: 83%; [a]$_D^{23}$ +18.2^o (c 0.66, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 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 ($CDCl_3$, 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 $C_{15}H_{31}OSi$ $[M+H]^+$ 255.2144, found 255.2141.

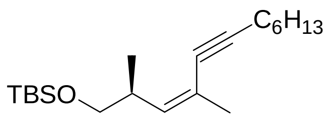


(3*Z*,5*S*)-6-*tert*-Butyldimethylsilyloxy-3,5-dimethyl-1,3-hexadiene.[h] This compound was prepared according to Representative Procedure B using (2*Z*,4*S*)-5-*tert*-butyldimethylsilyloxy-2-chloro-4-methyl-2-pentene**,** $Pd(OAc)_2/Cyp_3P$**,** and vinylMgBr. Yield: 83%; $[a]_D^{23}$ -4.8° (c 0.15, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) d 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) d -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 $C_{14}H_{28}OSi$ $[M]^+$ 240, found 240.

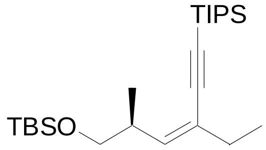
General procedure for cross-coupling of the (*Z*)-chloroalkenes with terminal alkynes (Representative Procedure C):[i] A flame dried 25-mL three-neck round-bottomed flask with a reflux condenser under argon was charged with $Pd(MeCN)_2Cl_2$ (8 mg, 0.03 mmol, 3 mol%), **2** (43 mg, 0.09 mmol, 9 mol%), 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.



(3*Z*,5*S*)-6-*tert*-Butyldimethylsilyloxy-3,5-dimethyl-1-triisopropylsilyl-3-hexen-1-yne. This compound was prepared according to Representative Procedure C using (2*Z*,4*S*)-5-*tert*-butyldimethylsilyloxy-2-chloro-4-methyl-2-pentene and triisopropylsilylacetylene. Yiled: 73%; $[a]_D^{23}$ +27^o (c 0.38, $CHCl_3$); ^{1}H 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 $C_{23}H_{47}OSi_2$ $[M+H]^+$ 395.3165, found 395.3168.

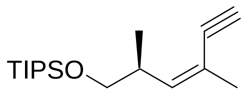


(2*S*,3*Z*)-1-*tert*-Butyldimethylsilyloxy-2,4-dimethyl-3-dodecen-5-yne. This compound was prepared according to Representative Procedure C using (2*Z*,4*S*)-5-*tert*-butyldimethylsilyloxy-2-chloro-4-methyl-2-pentene and 1-octyne. Yiled: 71%; ^{1}H NMR ($CDCl_3$, 300 MHz) d 0.02 (s, 6 H), 0.88 (bs, 12 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}.



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

(3*Z*,2*S*)-1-*tert*-butyldimethylsilyloxy-2-methyl-4-chloro-3-hexene and triisopropylsilylacetylene. Yiled: 65%; $[a]_D^{23}$ +43^o (c 0.18, $CHCl_3$); ^{1}H 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 $C_{24}H_{49}OSi_2$ $[M+H]^+$ 409.3322, found 409.3318.



(3*Z*,5*S*)-6-*tert*-Butyldimethylsilyloxy-3,5-dimethyl-3-hexen-1-yne. This compound was prepared according to Representative Procedure C using (2*Z*,4*S*)-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; $[a]_D^{23}$ +41.5^o (c 0.26, $CHCl_3$); ^{1}H 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 $C_{17}H_{33}OSi$ $[M+H]^+$ 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.

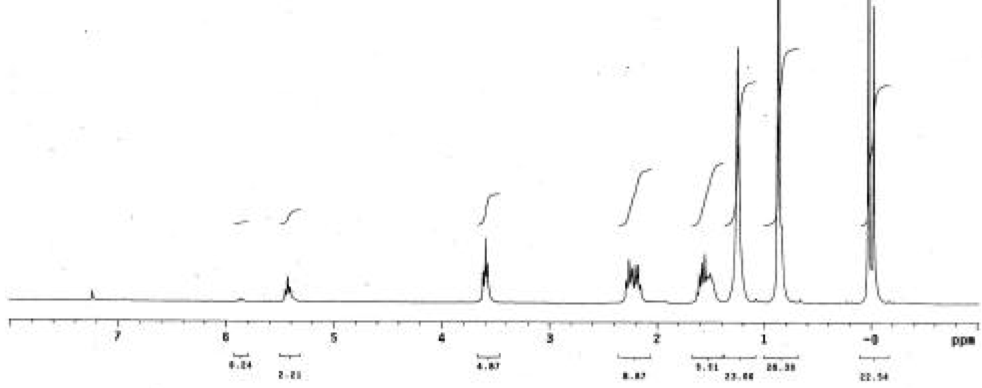
(g) X. Zeng, Q. Hu, M. Qian, E. Negishi, *J. Am. Chem. Soc*., **2003**, *125*, 13626.

(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....

Ze Tan and Ei-ichi Negishi*



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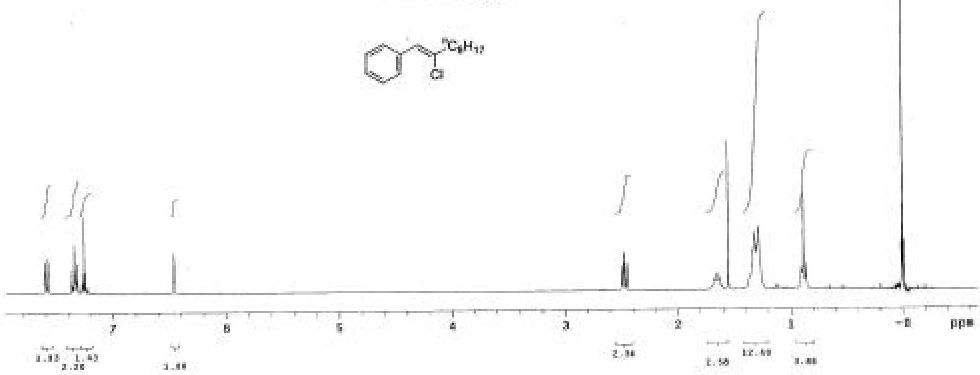

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2	10193.122	135.143	8.8
3	9720.763	128.960	63.7
4	9661.315	128.492	63.3
5	9604.407	127.937	56.4
6	9364.691	124.159	24.1
7	5839.456	77.421	8.6
8	5807.723	77.000	8.9
9	5775.996	76.579	5.7
10	3105.878	41.178	51.8
11	2402.341	31.851	33.7
12	2215.489	29.347	53.8
13	2204.424	29.227	56.6
14	2157.589	28.606	55.1
15	2081.944	27.558	59.7
16	1708.878	22.657	36.9
17	1063.253	14.097	32.9

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

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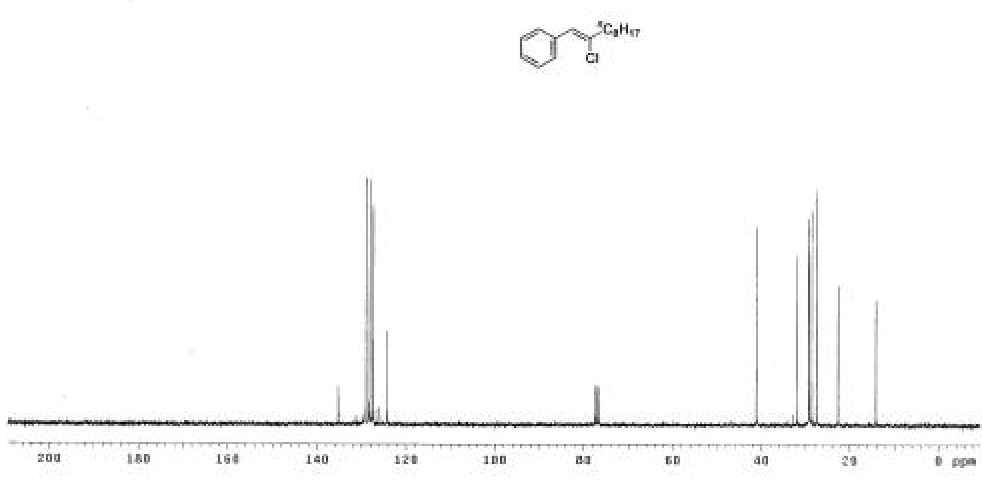

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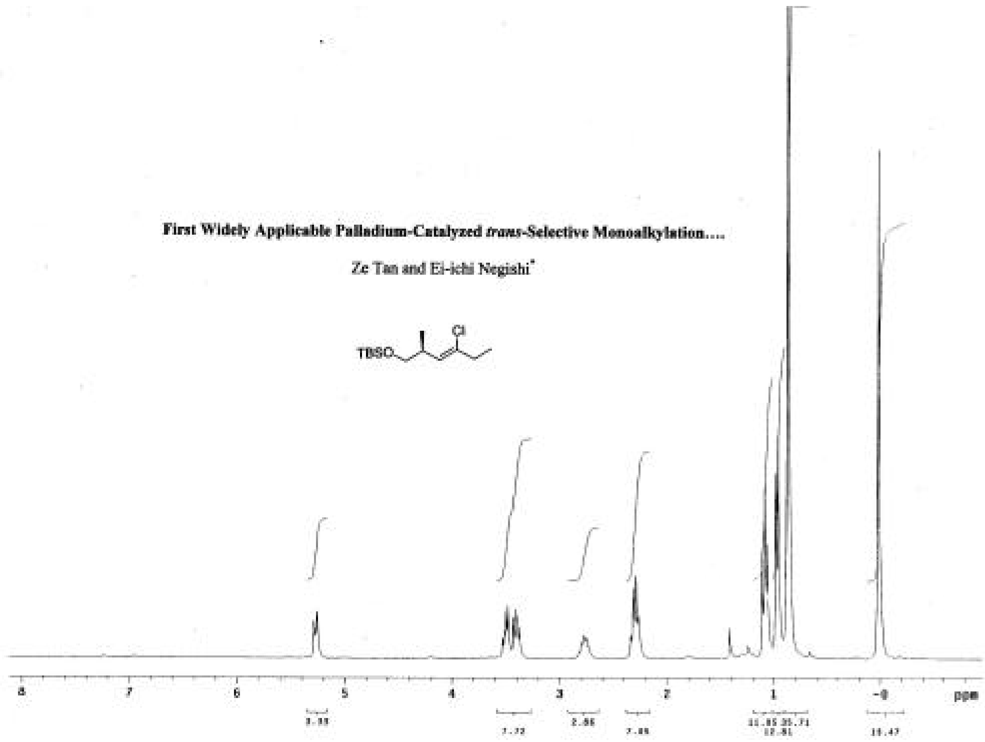

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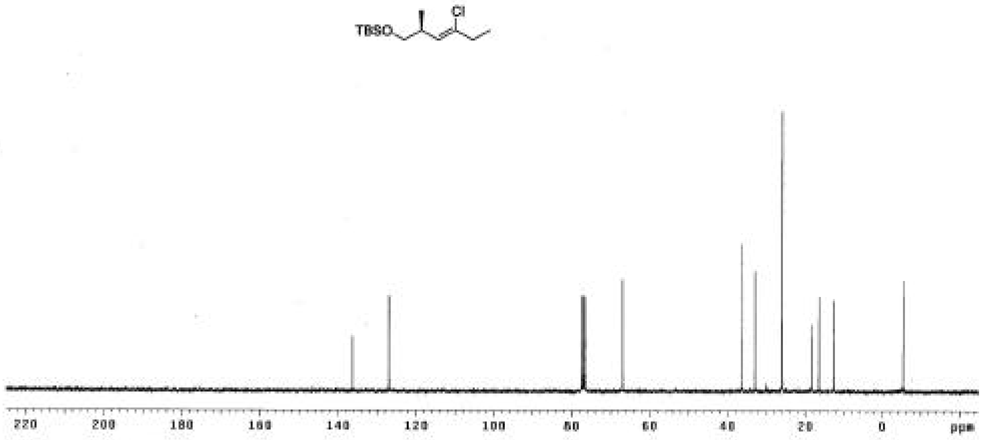

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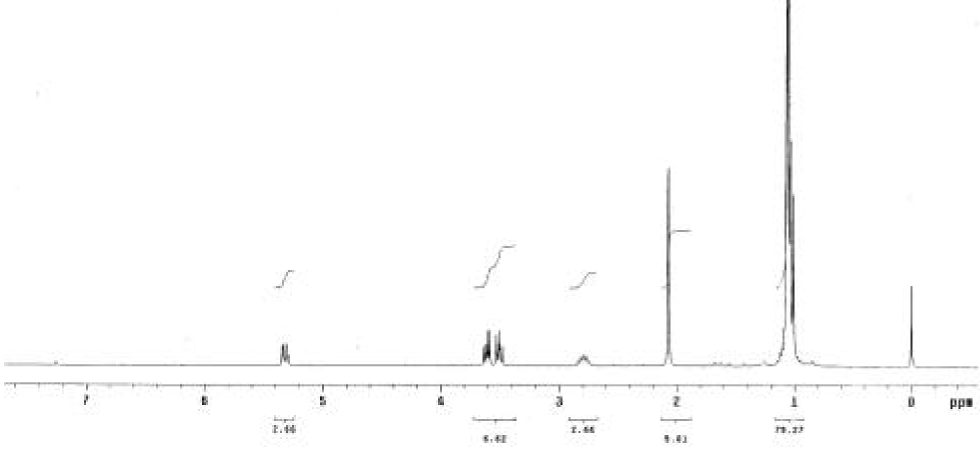

First Widely Applicable Palladium-Catalyzed *trans*-Selective Monoalkylation….

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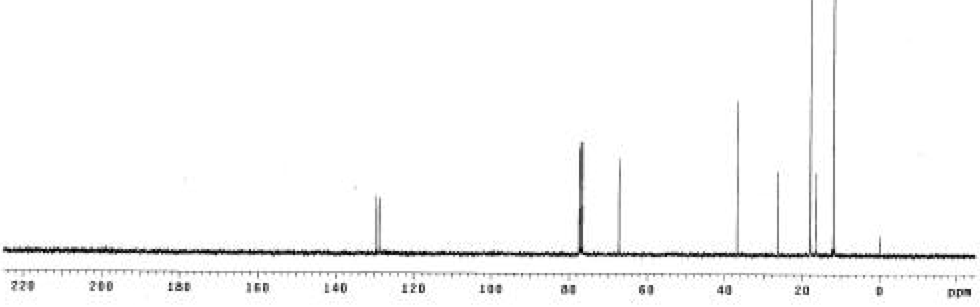

First Widely Applicable Palladium-Catalyzed *trans*-Selective Monoalkylation....

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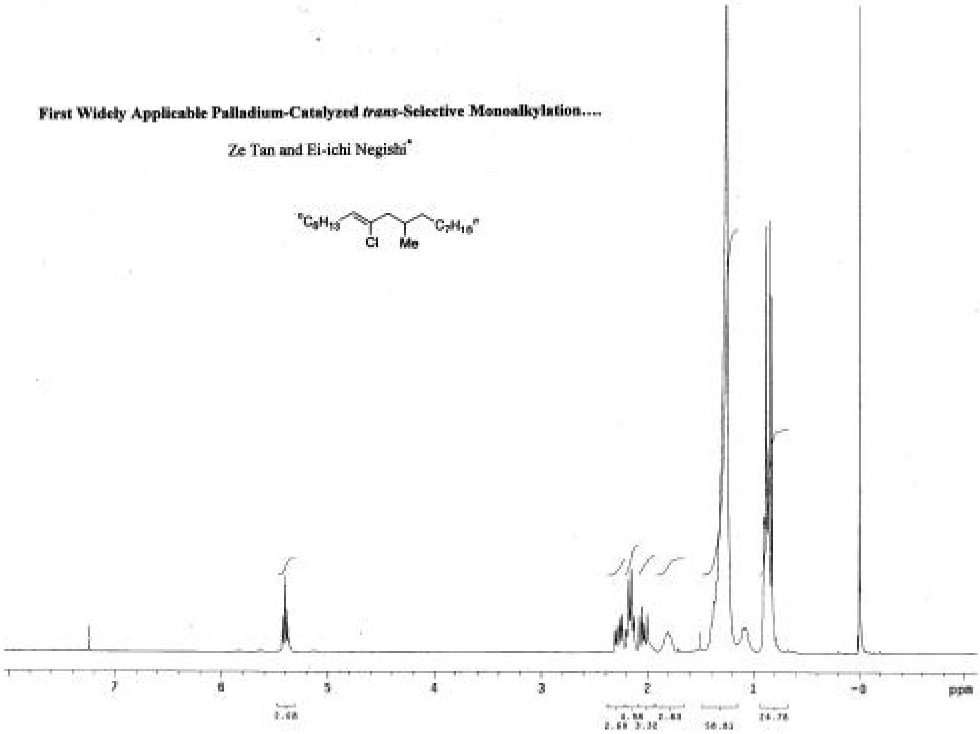

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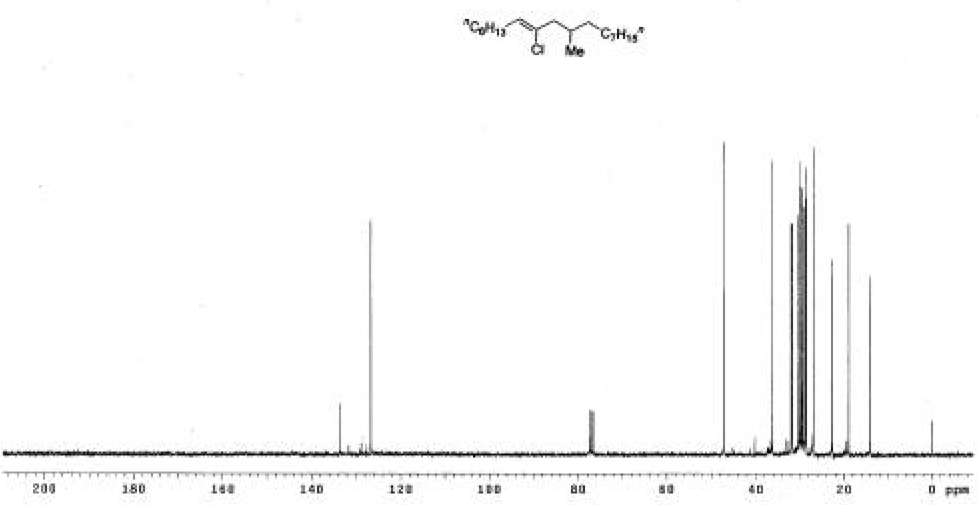

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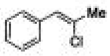

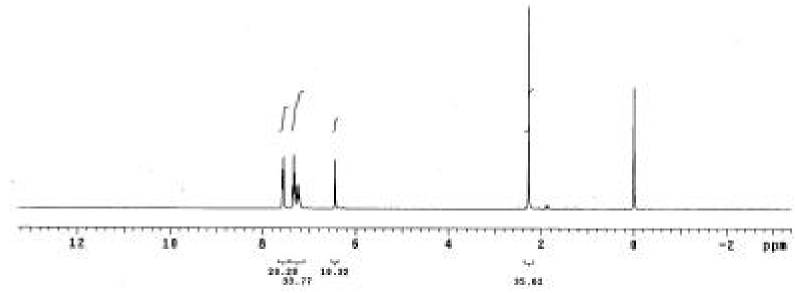

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4	9665.707	128.115	114.9
5	9607.389	127.367	63.8
6	9407.372	124.717	33.7
7	5838.828	77.421	33.3
8	5806.163	77.000	33.6
9	5778.374	76.578	32.7
10	2112.135	28.001	[illegible]
11	-1.958	-0.026	

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

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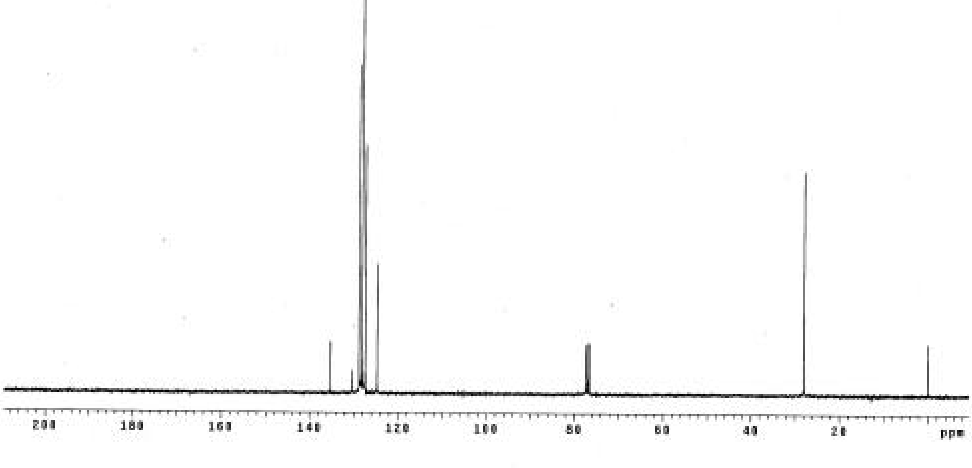

INDEX	FREQUENCY	PPM	HEIGHT
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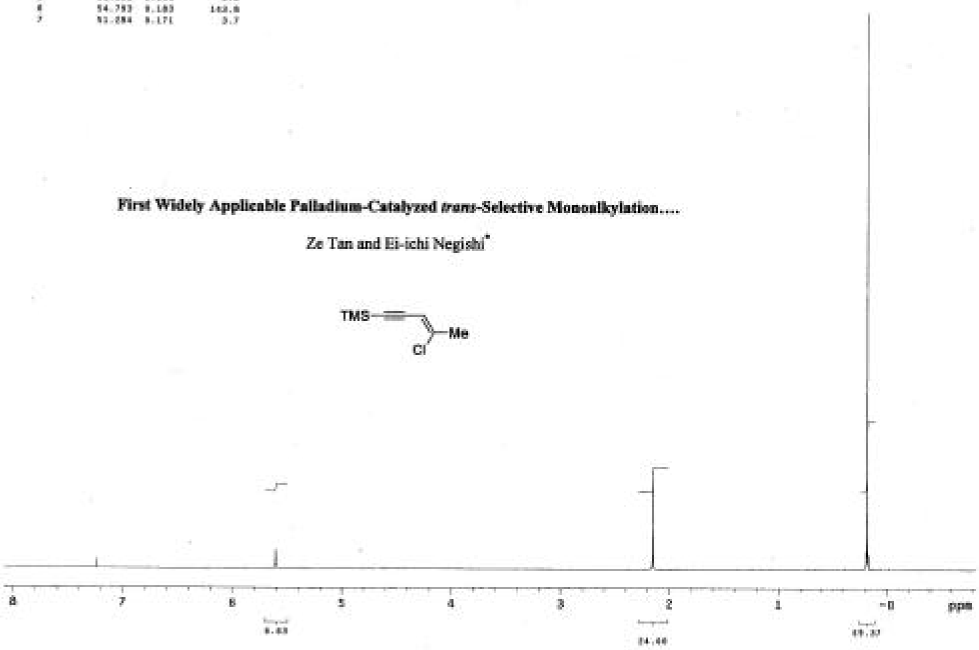
4	645.021	2.150	22.2
5	58.392	0.195	4.8
6	54.793	0.183	142.8
7	51.284	0.171	3.7

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

Ze Tan and Ei-ichi Negishi*



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2	8104.165	107.447	34.4
3	7546.156	100.022	19.4
4	5839.459	77.421	10.6
5	5807.219	76.993	11.0
6	5775.492	76.573	10.9
7	1965.211	26.055	52.3
8	-11.945	-0.158	76.8

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

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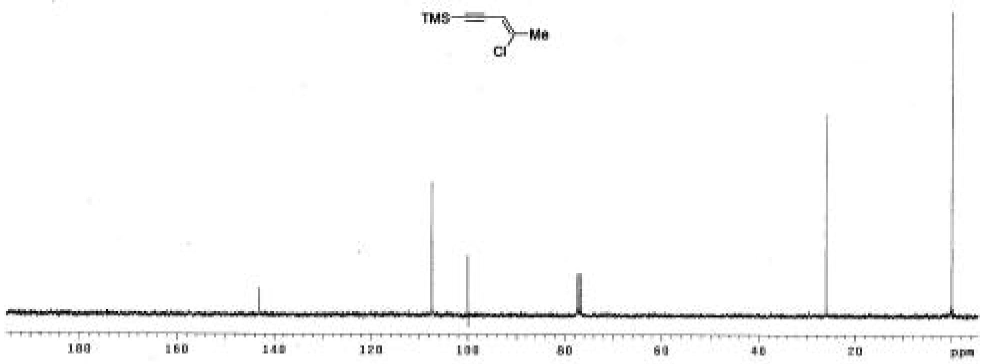
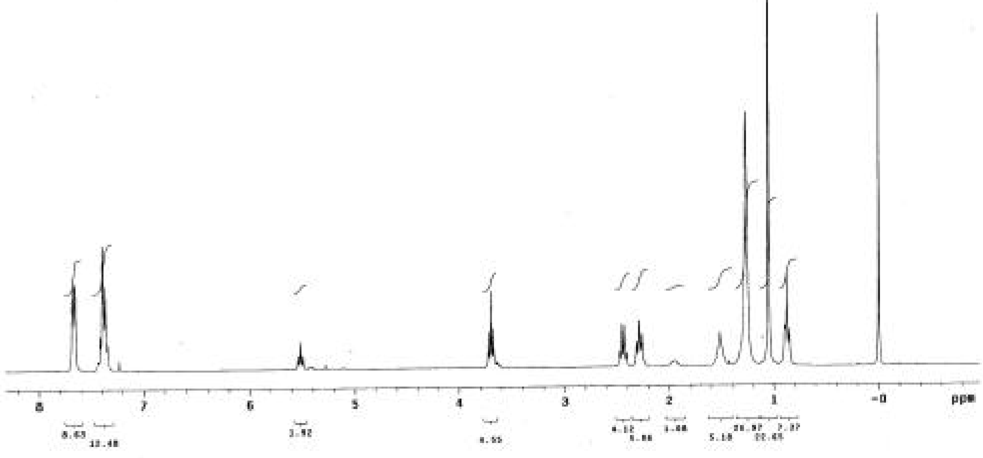




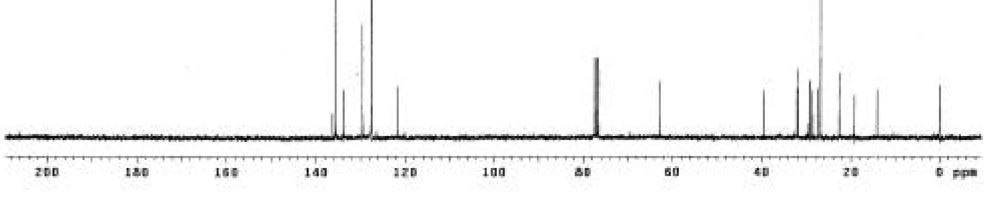
First Widely Applicable Palladium-Catalyzed *trans*-Selective Monoalkylation….

Ze Tan and Ei-ichi Negishi*

INDEX	FREQUENCY	PPM	HEIGHT
1	10251.631	136.367	6.3
2	10226.738	135.579	78.8
3	10100.837	133.918	12.5
4	9772.590	129.564	23.6
5	9766.946	129.484	5.1
6	9626.440	127.621	68.8
7	9621.908	127.581	8.7
8	9184.778	121.766	13.3
9	5840.332	77.427	26.8
10	5808.181	77.008	21.6
11	5776.374	76.578	26.7
12	4729.881	62.706	14.7
13	2982.673	39.545	12.8
14	2422.368	32.114	13.9
15	2403.223	31.869	18.9
16	2213.363	29.343	15.2
17	2202.788	29.203	14.6
18	2158.478	28.616	12.6
19	2067.318	27.407	13.9
20	2024.888	26.833	39.5
21	1708.758	22.653	16.9
22	1449.383	19.215	11.1
23	1062.824	14.088	12.5
24	-0.488	-0.006	13.7

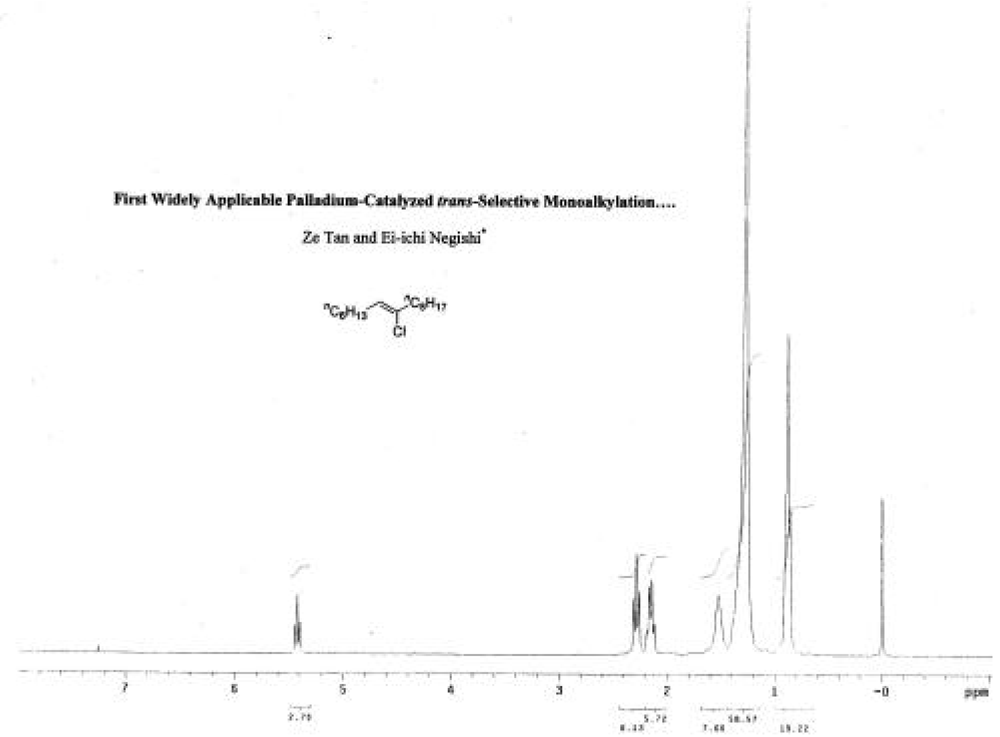
First Widely Applicable Palladium-Catalyzed *trans*-Selective Monoalkylation….

Ze 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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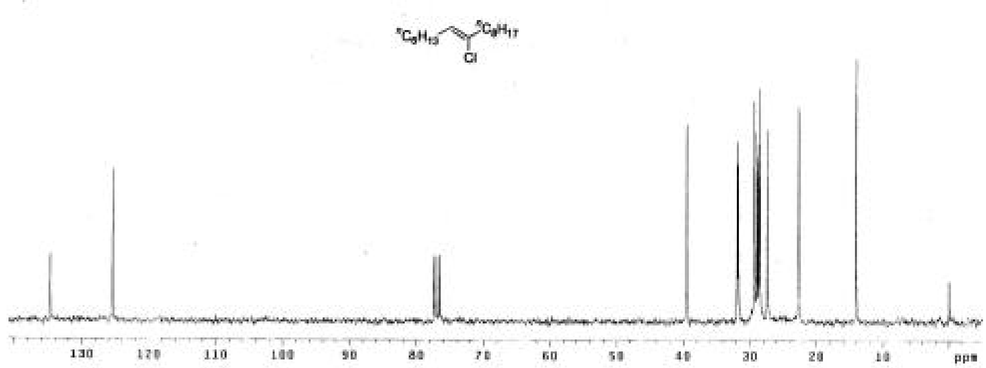

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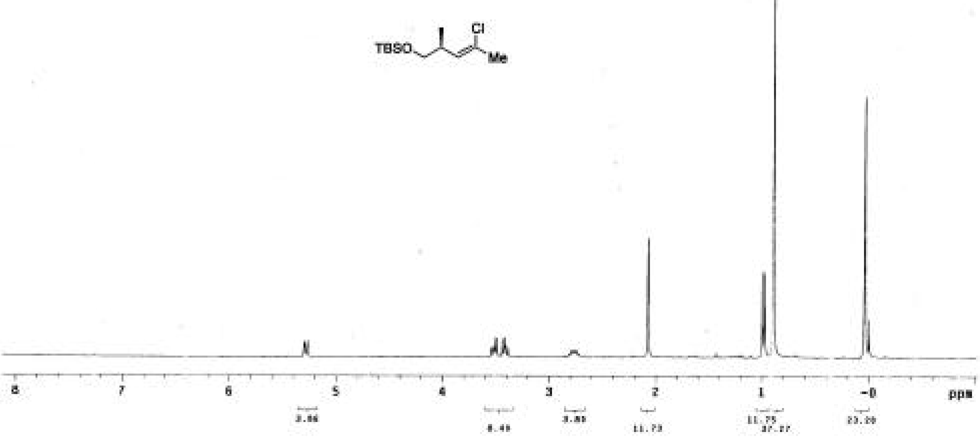
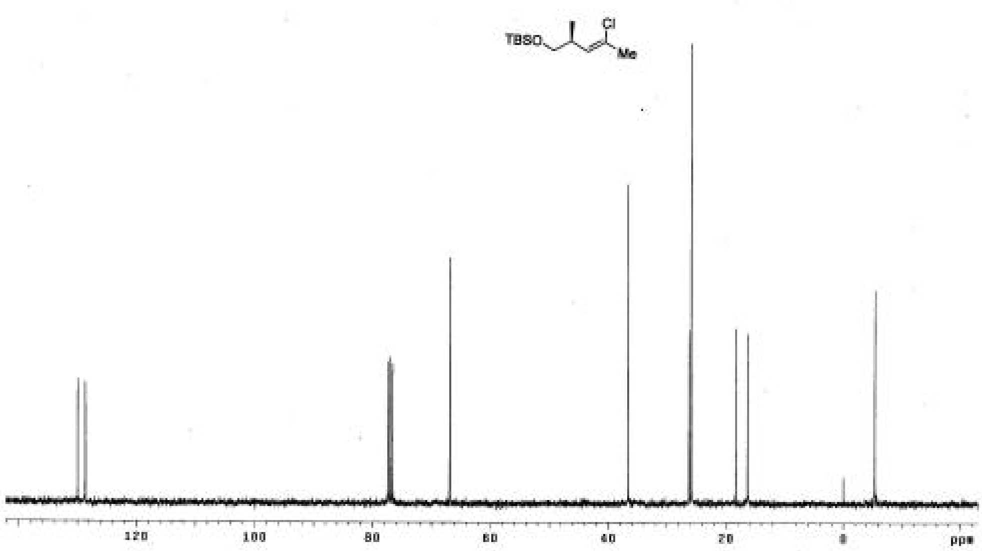


INDEX	FREQUENCY	PPM	HEIGHT
1	9802.124	129.959	31.0
2	9762.155	128.660	30.8
3	5838.945	77.427	36.5
4	5808.811	77.004	37.0
5	5776.876	76.580	35.8
6	5045.611	66.896	63.2
7	2758.566	36.579	82.3
8	1981.959	26.285	44.6
9	1954.987	25.907	118.7
10	1381.775	18.320	45.1
11	1232.177	16.336	43.7
12	-1.198	-0.016	6.7
13	-404.830	-5.367	55.0

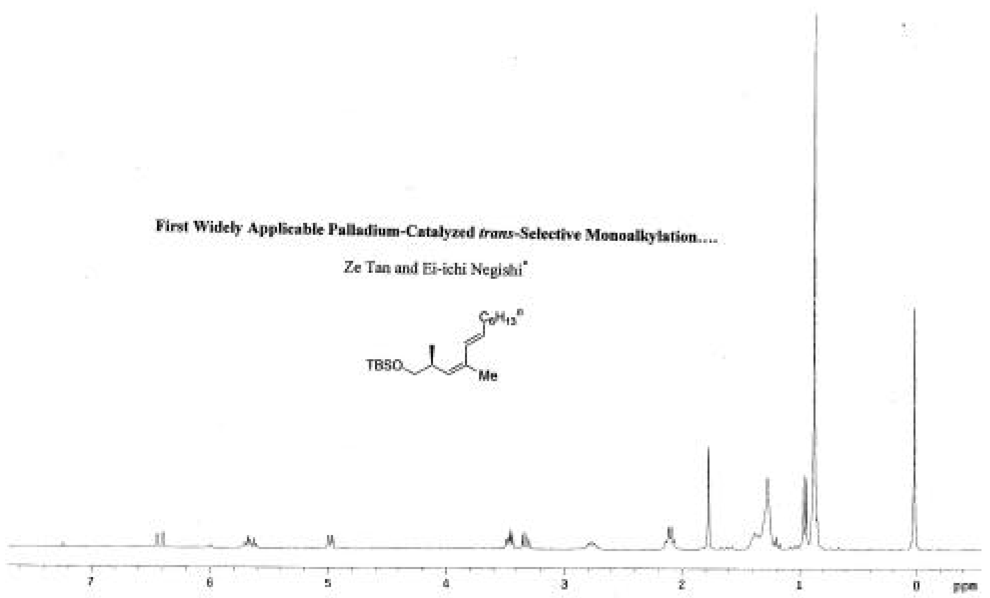
First Widely Applicable Palladium-Catalyzed *trans*-Selective Monoalkylation….

Ze 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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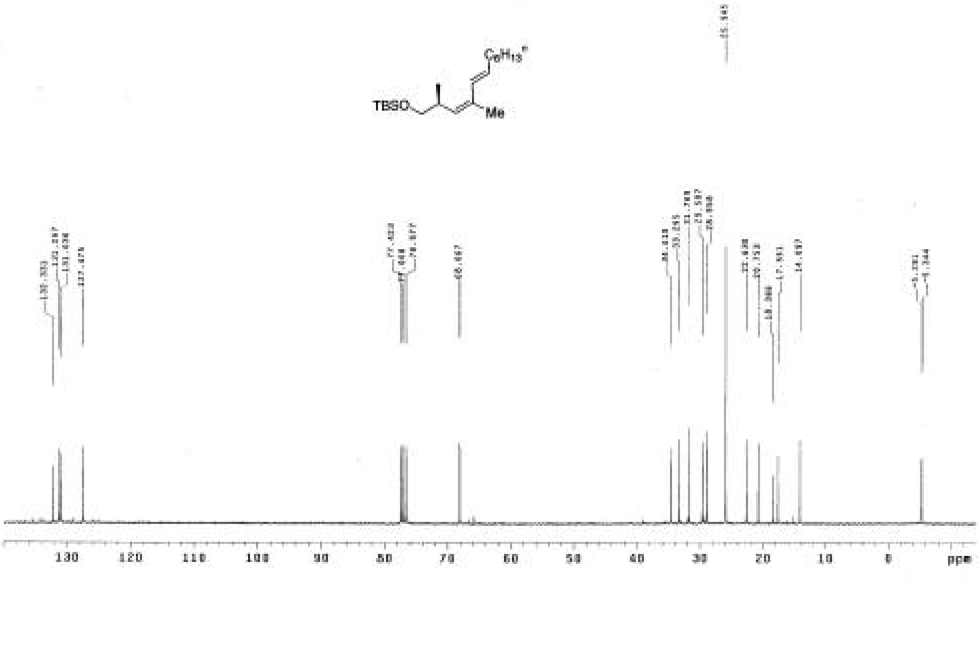

First Widely Applicable Palladium-Catalyzed *trans*-Selective Monoalkylation....

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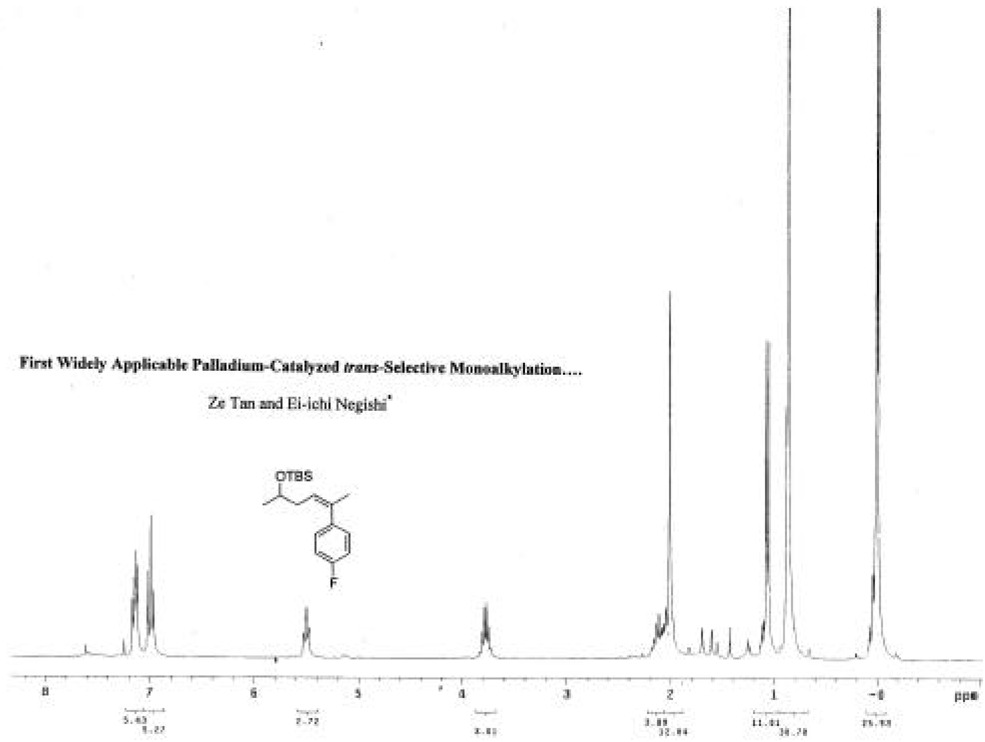
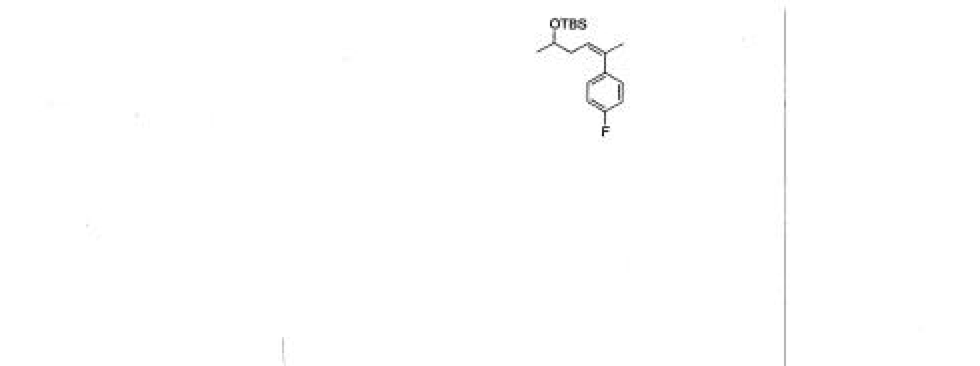


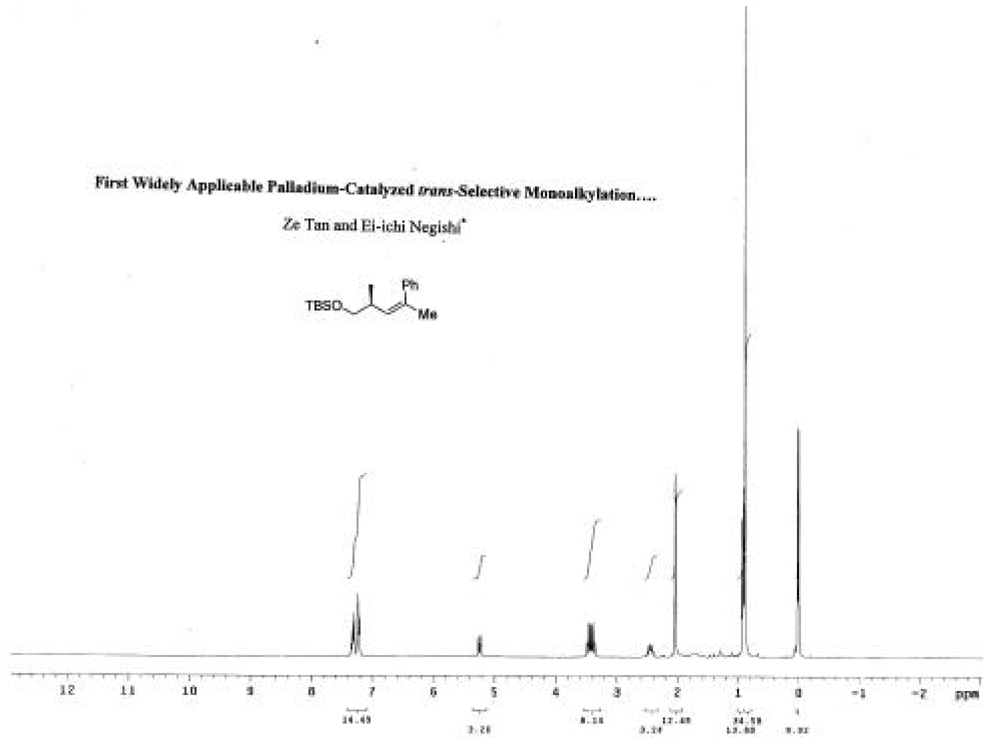
First Widely Applicable Palladium-Catalyzed *trans*-Selective Monoalkylation....

Ze Tan and Ei-ichi Negishi*



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

Ze Tan and Ei-ichi Negishi*



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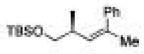

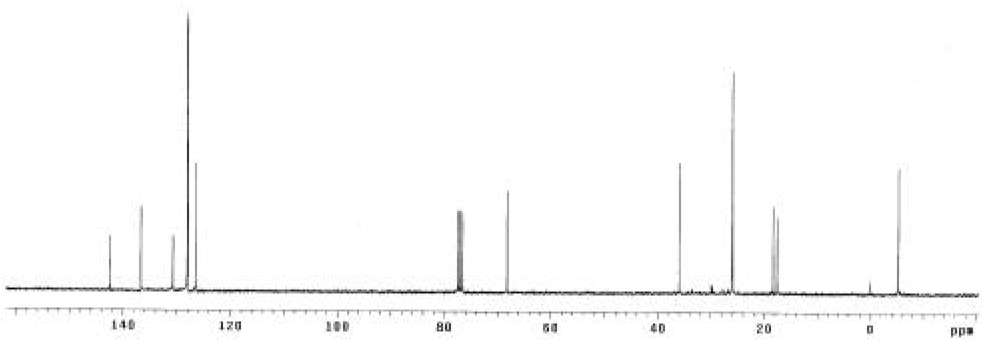

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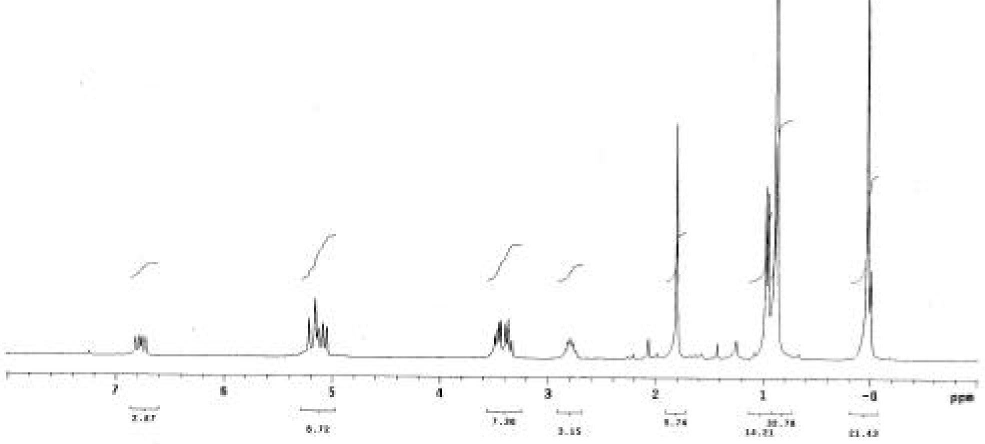

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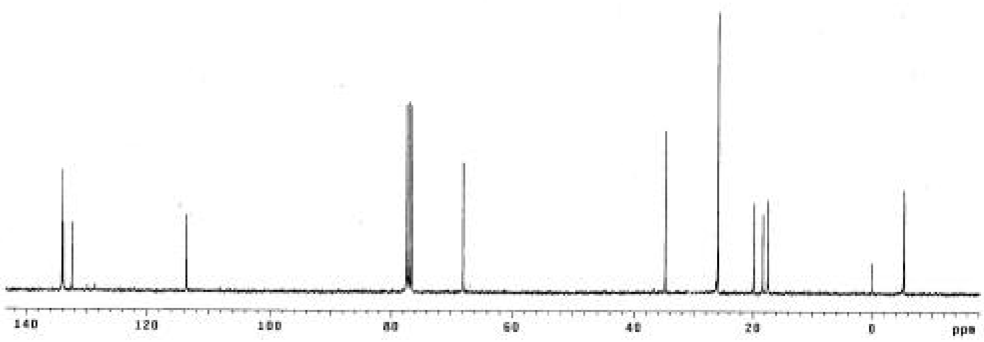

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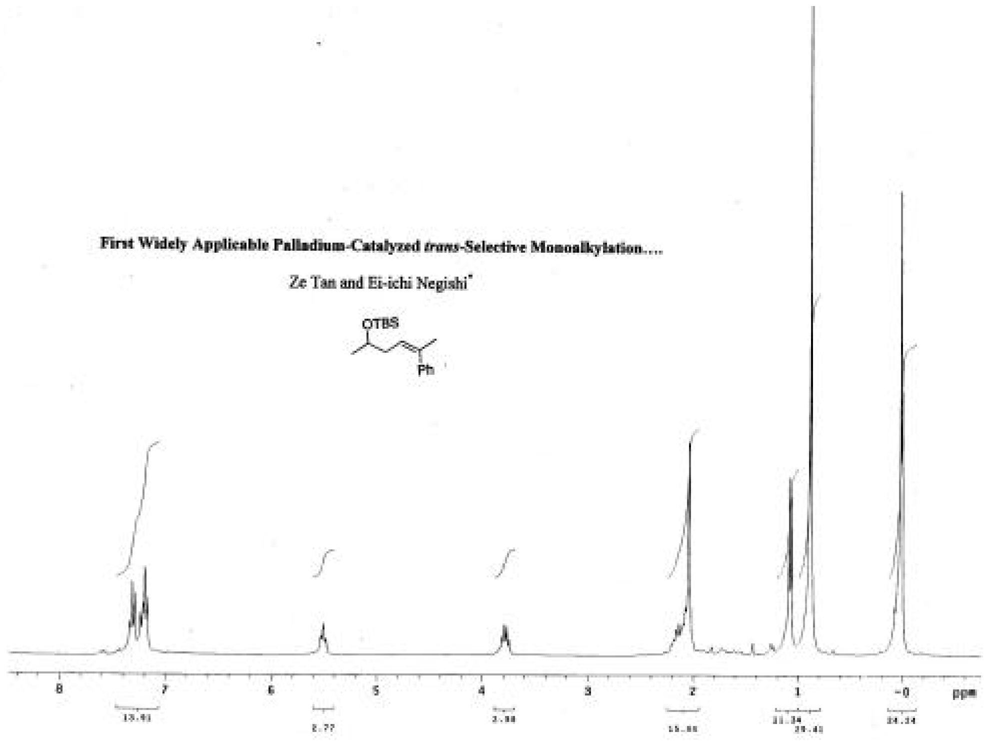

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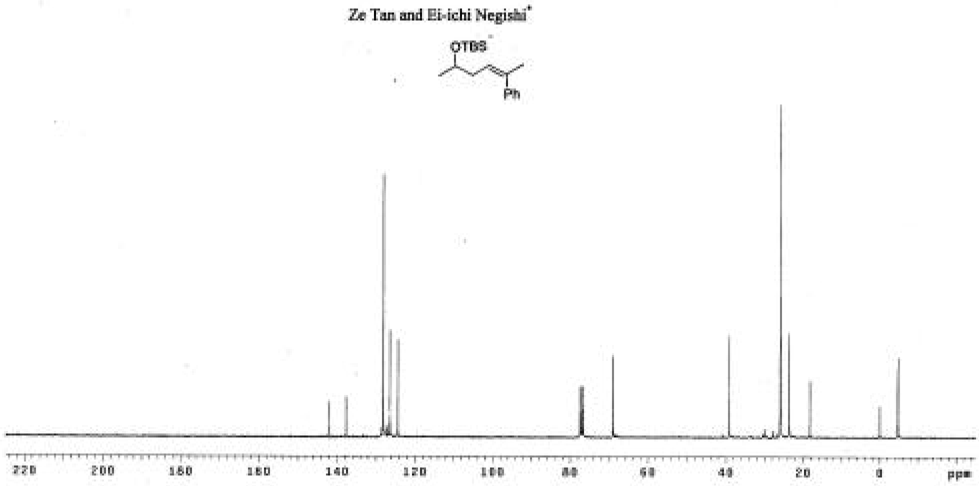

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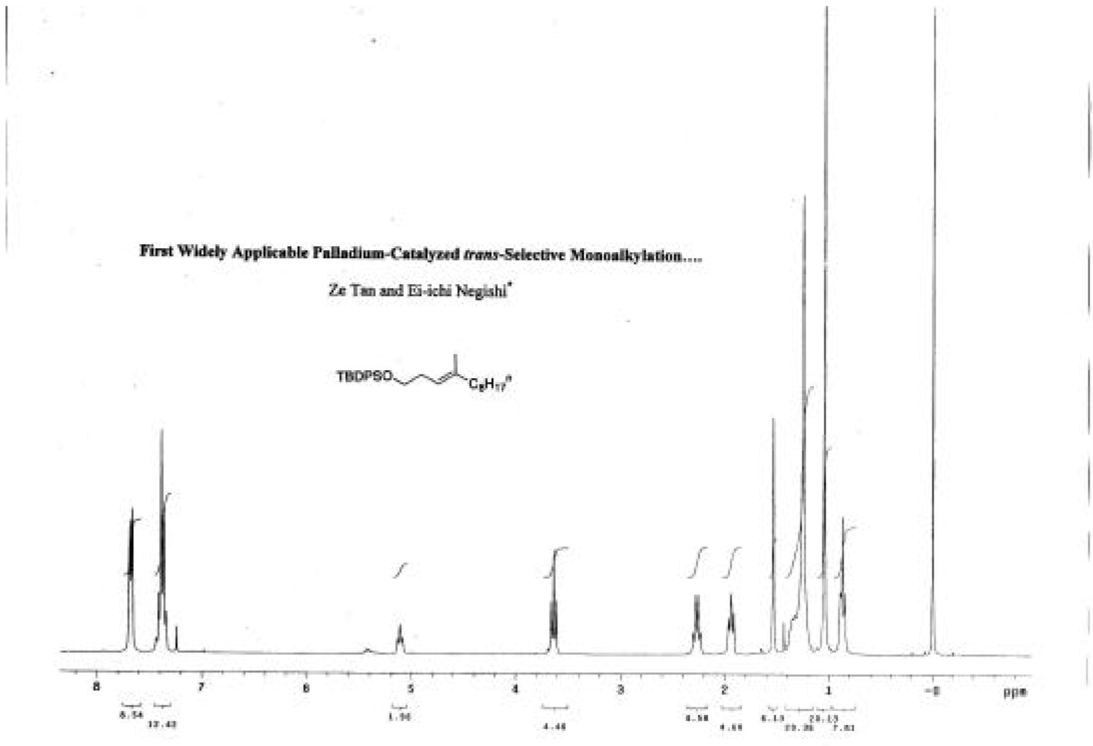

First Widely Applicable Palladium-Catalyzed *trans*-Selective Monoalkylation....

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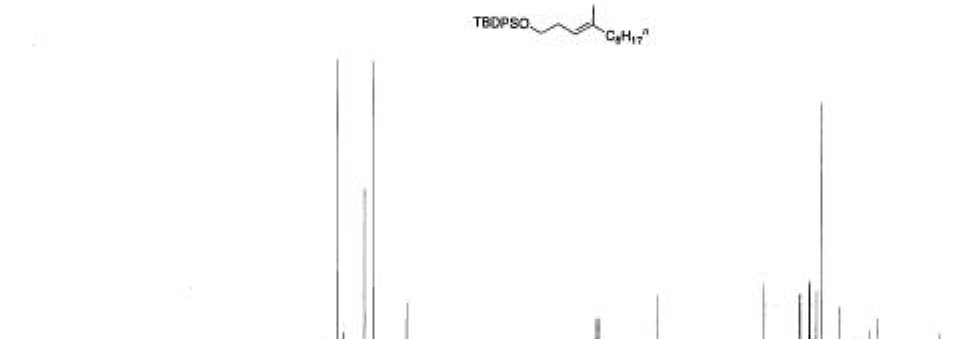
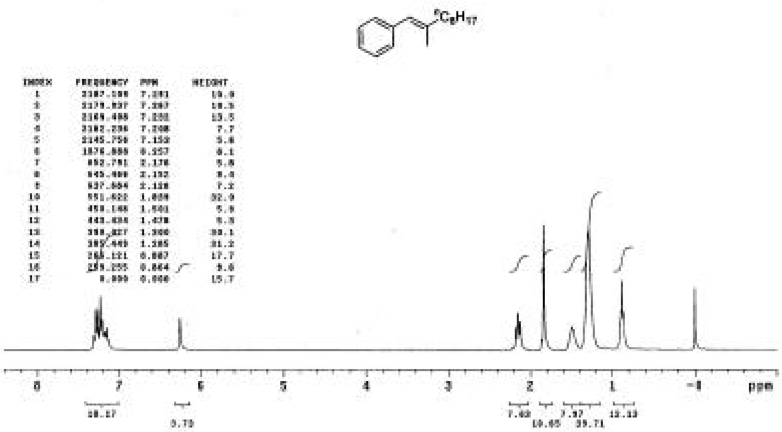


Videly Applicable Palladium-Catalyzed *trans*-Selective Monoalkylation....

Ze Tan and Ei-ichi Negishi*



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

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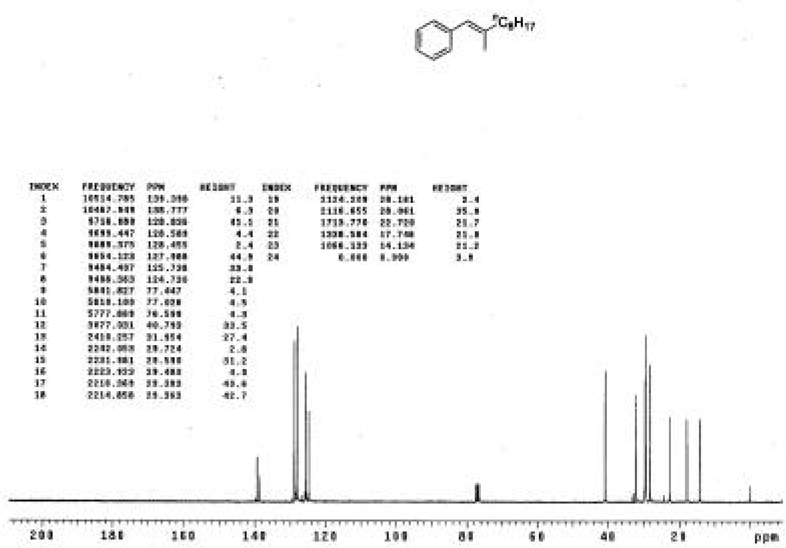

First Widely Applicable Palladium-Catalyzed *trans*-Selective Monoalkylation....

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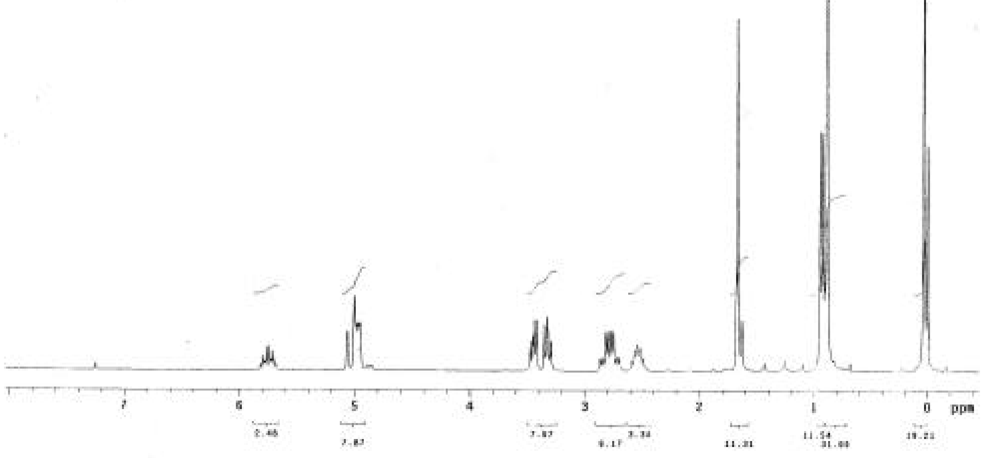

INDEX	FREQUENCY	PPM	HEIGHT
1	10321.491	136.865	9.7
2	10087.397	133.741	10.1
3	9771.870	129.551	17.4
4	8715.821	115.546	18.9
5	5173.372	68.590	17.6
6	2807.071	37.217	19.5
7	2703.686	35.846	17.1
8	1989.693	26.380	58.1
9	1796.505	23.819	18.6
10	1418.118	18.802	18.3
11	1360.589	18.039	15.8

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

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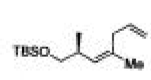

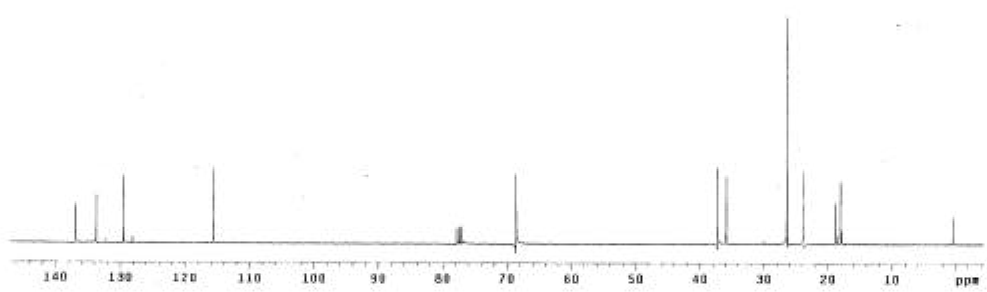

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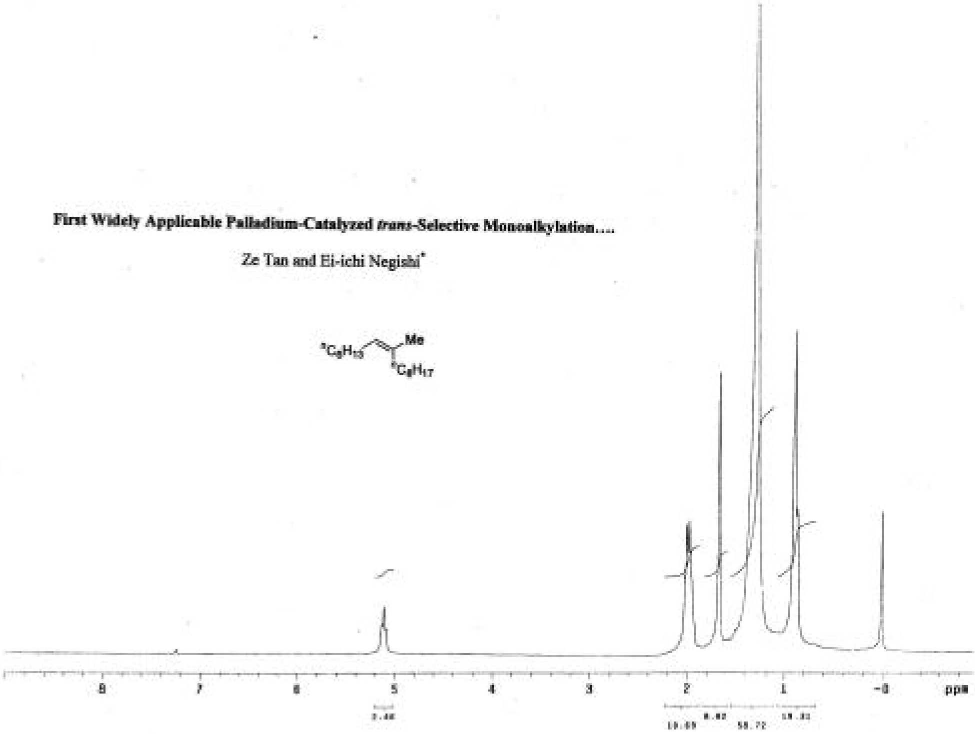
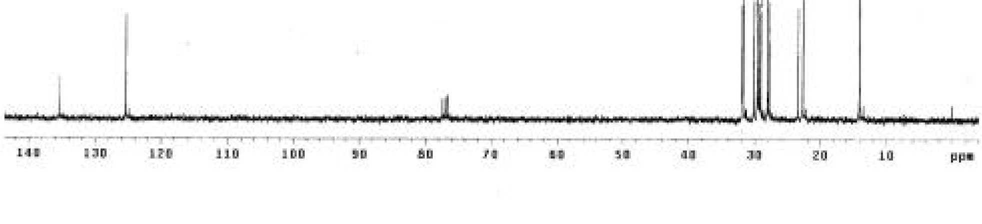
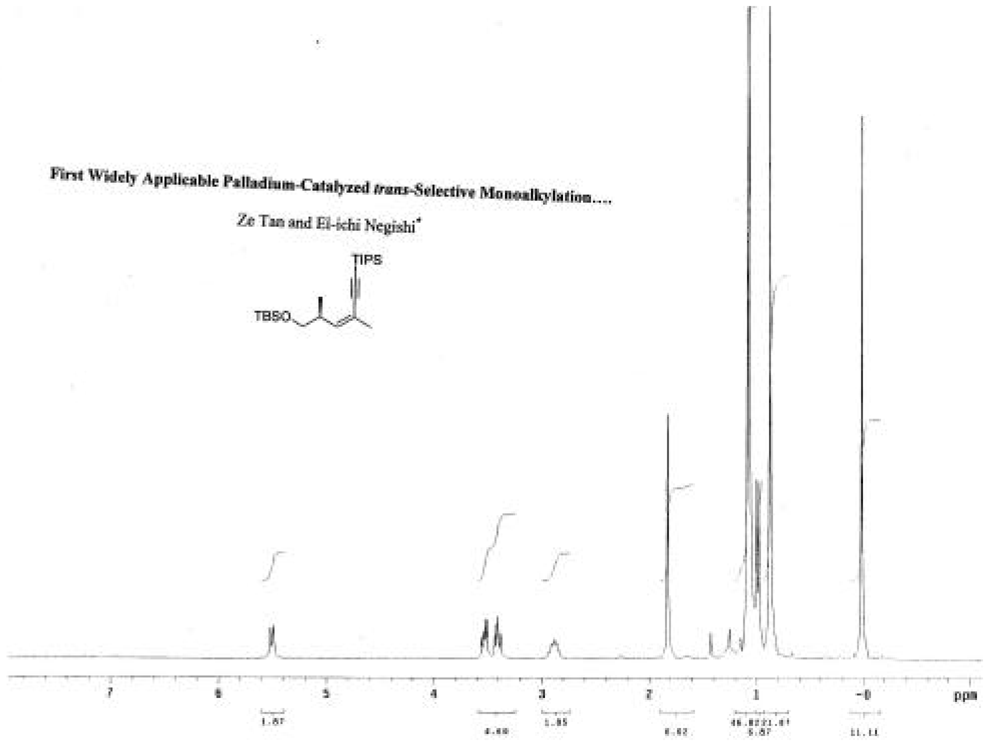


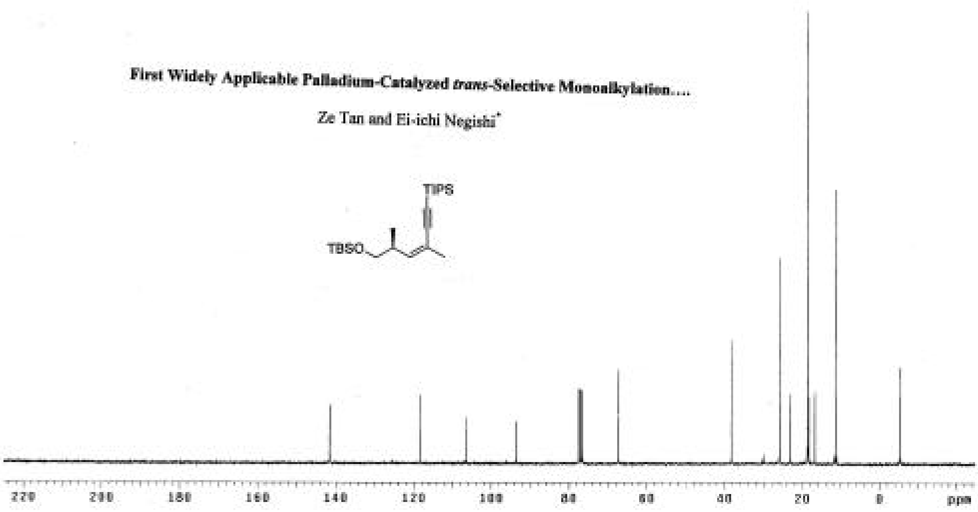
INDEX	FREQUENCY	PPM	HEIGHT
1	10210.357	135.358	16.8
2	9452.345	125.321	27.3
3	2411.606	31.971	29.6
4	2405.269	31.887	25.5
5	2398.476	31.792	34.1
6	2274.511	30.158	38.8
7	2236.452	29.678	33.5
8	2235.487	29.637	32.8
9	2215.418	29.377	30.9
10	2187.798	29.137	31.7
11	2124.381	28.111	31.6
12	2101.188	27.855	35.9
13	1768.141	23.414	28.5
14	1713.767	22.720	41.1
15	1063.416	14.098	45.7

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

Ze Tan and Ei-ichi Negishi*

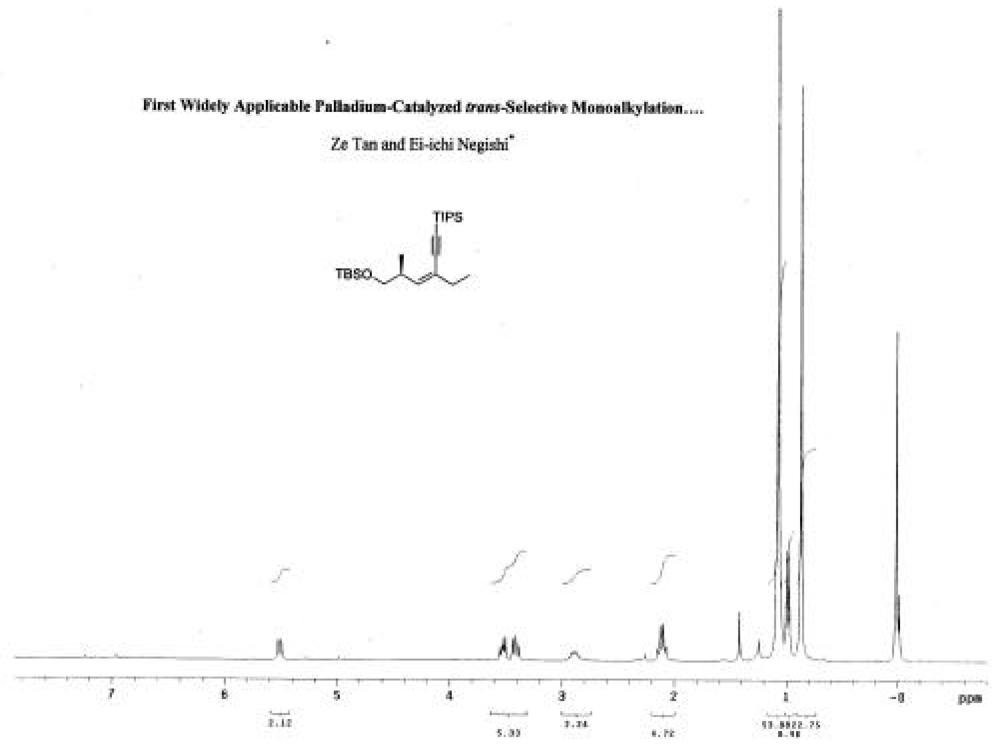



First Widely Applicable Palladium-Catalyzed trans-Selective Monoalkylation....
Ze Tan and Ei-ichi Negishi*
TIPS
TBSO
7
6
5
4
3
2
1
-0
ppm
1.87
4.00
1.85
6.02
46.82
21.67
5.87
11.11


First Widely Applicable Palladium-Catalyzed trans-Selective Monoalkylation....
Ze Tan and Ei-ichi Negishi*
TIPS
TBSO
220
200
180
160
140
120
100
80
60
40
20
0
ppm

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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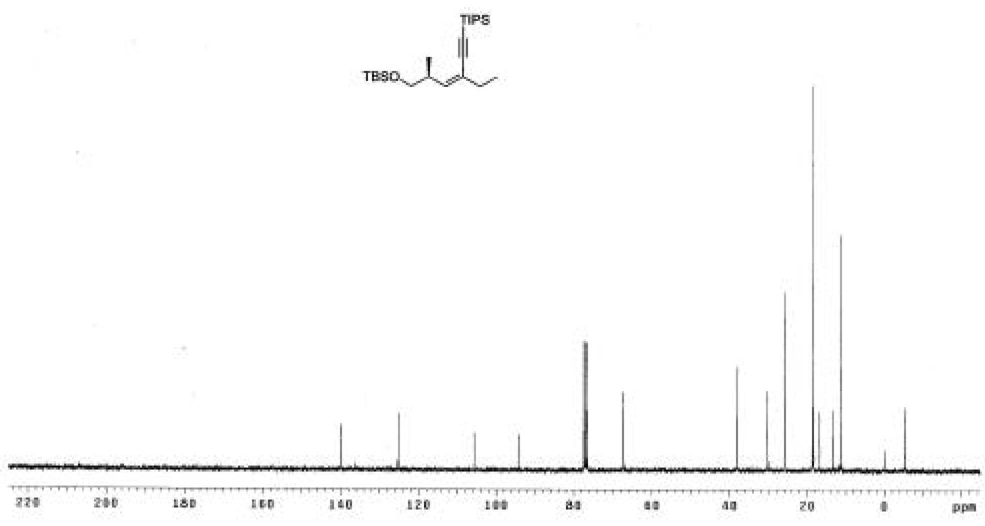

First Widely Applicable Palladium-Catalyzed *trans*-Selective Monoalkylation....

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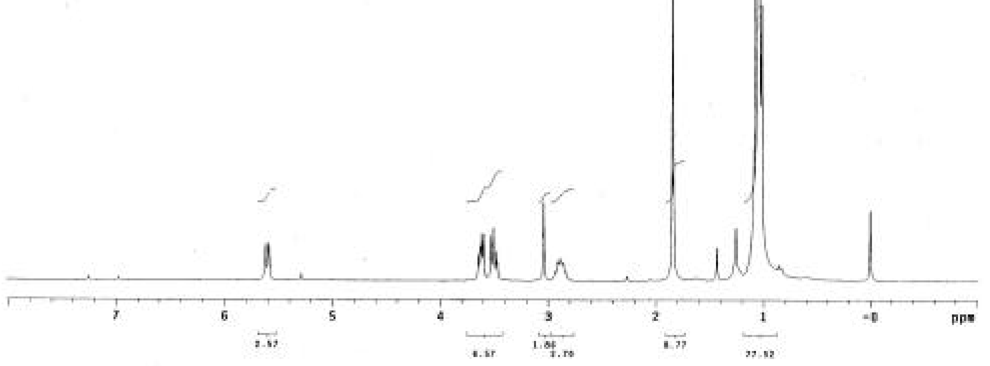

INDEX	FREQUENCY	PPM	HEIGHT
1	10753.294	142.569	19.8
2	8815.697	116.879	13.9
3	6267.177	83.092	7.7
4	6043.923	80.132	19.8
5	5839.858	77.423	25.2
6	5807.723	77.000	25.5
7	5775.789	76.577	18.8
8	5098.021	67.575	20.3
9	2893.298	38.345	19.3
10	1734.285	22.992	21.1
11	1357.886	18.003	124.6
12	1259.583	16.699	18.3
13	904.156	11.988	84.1
14	-1.765	-0.023	3.5

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

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