Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

for

Palladium NNC-pincer complex: an efficient catalyst for Allylic Arylation at parts per billion levels

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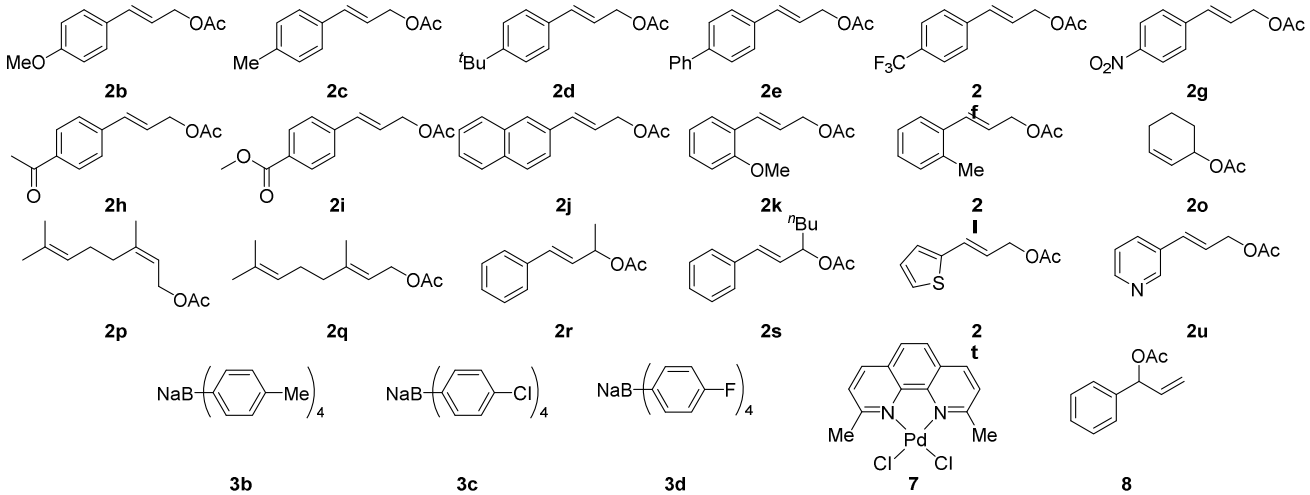
General Information

When manipulations were performed under a nitrogen atmosphere, nitrogen gas was dried by passage through P_2O_5. Commercially available chemicals (purchased from Sigma-Aldrich, TCI, Kanto chemical, Wako Pure Chemical Industries, Nacalai tesque, and Merck) are used without further purification unless otherwise noted. Silica gel was purchased from Kanto chemical (Silica gel 60N, spherical neutral, particle size 40-50μm) or Yamazen corporation (Hi-Flash^{TM} Column Silica gel 40 mm 60 Å). TLC plates were purchased from Merck (TLC Silica gel 60 F_{254}). NMR spectra were recorded on a JEOL JNM A-500 spectrometer (500 MHz for ^{1}H, 125 MHz for ^{13}C) or a JEOL JNM ECS-400 spectrometer (396 MHz for ^{1}H, 100 MHz for ^{13}C). Chemical shifts are reported in δ (ppm) referenced to an internal tetramethylsilane standard for ^{1}H NMR. Chemical shifts of ^{13}C NMR are given related to $CDCl_3$ as an internal standard (δ 77.0). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 25 °C. GC-MS analyses were measured with an Agilent 6890 GC/5973N MS Detector. ESI mass spectra (LRMS and HRMS) were recorded on a JEOL JMS-T100LC spectrometer. Elemental analyses were performed on a J-SCIENCE LAB MICRO CORDER JM10. Melting points were determined using a Yanaco micro melting point apparatus MP-J3 and were uncorrected. IR spectra were obtained using a JASCO FT/IR-460plus spectrometer in ATR mode. Millipore water was obtained from a Millipore Milli-Q Academic A10 purification unit. (*E*)-3-(4-Methoxyphenyl)-2-propen-1-ol acetate (**2b**),[1] (*E*)-3-(4-methylphenyl)-2-propen-1-ol acetate (**2c**),[1] (*E*)-3-(4-*tert*-butylphenyl)-2-propen-1-ol acetate (**2d**),[1] (*E*)-3-(4-phenylphenyl)-2-propen-1-ol acetate (**2e**),[1] (*E*)-3-(4-trifluoromethylphenyl)-2-propen-1-ol acetate (**2f**),[1] (*E*)-3-(4-nitrophenyl)-2-propen-1-ol acetate (**2g**),[1] (*E*)-3-(4-acetylphenyl)-2-propen-1-ol acetate (**2h**),[1] (*E*)-3-((4-methoxycarbonyl)phenyl)-2-propen-1-ol acetate (**2i**),[1] (*E*)-(naphthalene-6-yl)allyl acetate (**2j**),[2] (*E*)-3-((2-methoxycarbonyl)phenyl)-2-propen-1-ol acetate (**2k**),[1] (*E*)-3-(2-methylphenyl)-2-propen-1-ol acetate (**2l**),[1] cyclohex-2-enyl acetate (**2o**),[3] neryl acetate (**2p**),[4] geranyl acetate (**2q**),[4] (*1E*)-1-phenyl-1-buten-3-yl acetate (**2r**),[13] (*1E*)-1-phenyl-1-hepten-3-yl acetate (**2s**),[14] (*E*)-3-(2-thienyl)allyl acetate (**2t**),[1] (*E*)-3-(3-pyridyl)allyl acetate (**2u**),[5] sodium tetraarylborates (**3b-3d**),[6] complex **7**,[17] 1-phenyl-2-propenyl acetate (**8**),[4] 2-phenyl-1,10-phenanthroline,[15] and 2,9-diphenyl-1,10-phenanthlorine[15] were prepared by literature methods.



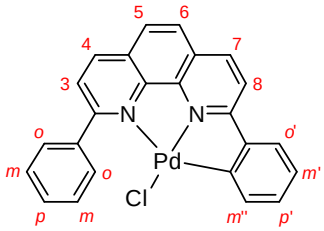
2b **2c** **2d** **2e** **2f** **2g**

2h **2i** **2j** **2k** **2l** **2o**

2p **2q** **2r** **2s** **2t** **2u**

3b **3c** **3d** **7** **8**

Synthesis of Chloro-[2-(9-phenyl-1,10-phenanthrolin-2-yl)phenyl]palladium (1).

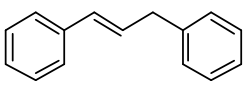


$PdCl_2(MeCN)_2$ (700.0 mg, 2.11 mmol) was added to a solution of 2,9-diphenyl-1,10-phenanthroline (546.1 mg, 2.11 mmol) in a benzene/methanol mixture (20 mL/25 mL). After being stirred for 6 h at 50 °C, a resulting insoluble material was collected by filtration. The obtained material was washed with dichloromethane, methanol, and diethyl ether, and dried in *vacuo* to give **1** (886.2 mg, 1.87 mmol, 89%) as yellow solids. Mp. >300 °C. ^{1}H-NMR (396 MHz, CD_2Cl_2) δ 8.44 (d, *J* = 8.6 Hz, 1H, phen 4-H), 8.43 (d, *J* = 8.6 Hz, 1H, phen 7-H), 7.95 (d, *J* = 8.6 Hz, 1H, phen 8-H), 7.93 (d, *J* = 8.6 Hz, 1H, phen 3-H), 7.87–7.90 (m, 4H, phen 5,6-H, *o*-H), 7.76–7.79 (m, 1H, *m*''-H), 7.53–7.59 (m, 4H, *m*-H, *p*-H, and *o*'-H), 7.15 (td, *J* = 2.0, 7.2 Hz, 1H, *p*'-H), 7.12 (td, *J* = 2.0, 7.2 Hz, 1H, *m*'-H). ^{13}C-NMR (100 MHz, CD_2Cl_2) δ 163.64, 162.92, 151.79, 148.00, 138.20, 137.80, 137.33, 130.91, 130.28, 130.07, 129.15, 128.51, 128.21, 127.82, 126.68, 126.27, 125.26, 124.92, 118.98. IR (ATR): 3046, 2928, 1617, 1585, 1575, 1508, 1499, 1415, 1316, 1147, 1023. 856, 761, 733, 691 cm^{-1}. ESI-TOF-MS *m/z* 437 ([M-Cl]$^+$), 469 ([M-Cl+MeOH]$^+$), 911 ([2M-Cl]$^+$). Anal. Calcd for $C_{24}H_{15}ClN_2Pd \cdot 0.5H_2O$: C, 59.77: H, 3.34; N, 5.81%. Found: C, 59.63: H, 3.26: N, 5.73%.

Typical procedure for the allylic arylation of allylic acetates with sodium tetraarylborates using 1

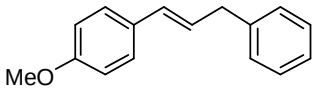
The complex **1** (4.7 mg, 0.01 mmol) was dissolved in methanol (100 mL) to give a stock solution. Under a nitrogen atmosphere, the stock solution (0.1 mL, 1.00 × 10^{-5} mmol), methanol (9.9 mL), and $NaBPh_4$ (6.84 g, 20.0 mmol) were added to a reaction vessel. The resulting solution was degassed via three freeze-pump-thaw cycles. Cinnamyl acetate (1.76 g, 10.0 mmol) was added to the solution. The reaction mixture was stirred at 50 °C for 24 h and allowed to cool to 25 °C. After removal of the solvent, water (50 mL) was added to the residue. The resulting suspension was extracted with *tert*-butyl methyl ether (50 mL × 4). The combined organic layer was dried over Na_2SO_4. The resulting solution was concentrated under reduced pressure. The crude product was chromatographed on silica gel (eluent: hexane) to give 1,1'-[(1*E*)-prop-1-ene-1,3-diyl]dibenzene (**4aa**) (1.69 g, 8.67 mmol, 87%) as colorless oil.

1,1'-[(1*E*)-Prop-1-ene-1,3-diyl]dibenzene (4aa)[7] [CAS: 3412-44-0] (1.69 g, 8.67 mmol, 87%)



^{1}H-NMR (396 MHz, $CDCl_3$) δ 7.37–7.18 (m, 10H, ArH), 6.46 (d, *J* = 15.8 Hz, 1H, -C**H**=CHCH$_2$-), 6.36 (dt, *J* = 15.8, 6.7 Hz, 1H, -CH=C**H**CH$_2$-), 3.55 (d, *J* = 6.7 Hz, 2H, -CH=CHC**H**$_2$-). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 140.19, 137.49, 131.09, 129.26, 128.72, 128.54, 127.15, 126.23, 126.17, 39.40. EI-MS *m/z* 194 (M$^+$).

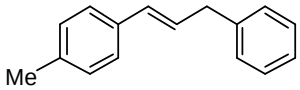
(*E*)-1-(4-Methoxyphenyl)-3-phenylpropene (4ba)[7] [CAS: 35856-81-6] (1.79 g, 7.98 mmol, 80%)



^{1}H-NMR (396 MHz, $CDCl_3$) δ 7.33–7.20 (m, 7H, ArH), 6.83 (d, *J* = 8.7 Hz, 2H, ArH), 6.40 (d, *J* = 15.7 Hz, 1H, -C**H**=CHCH$_2$-), 6.22 (dt, *J* = 15.7, 6.8 Hz, 1H, -CH=C**H**CH$_2$-), 3.80 (s, 3H, -OCH$_3$), 3.53 (d, *J* = 6.8 Hz, 2H, -CH=CHC**H**$_2$-). ^{13}C-NMR (100 MHz, $CDCl_3$) δ

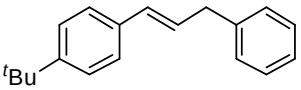
158.80, 140.43, 130.39, 130.27, 128.63, 128.44, 127.19, 127.03, 126.08, 113.88, 55.27, 39.32. EI-MS *m/z* 224 (M^+).

(*E*)-1-(4-Methylphenyl)-3-phenylpropene (4ca)[7] [CAS: 134539-87-0] (1.68 g, 8.07 mmol, 81%)



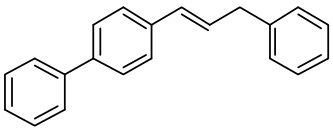
^{1}H-NMR (396 MHz, $CDCl_3$) δ 7.35–7.19 (m, 7H, ArH), 7.10 (d, *J* = 8.3 Hz, 2H, ArH), 6.43 (d, *J* = 15.4 Hz, 1H, -C**H**=CHCH$_2$-), 6.30 (dt, *J* = 15.4, 7.0 Hz, 1H, -CH=C**H**CH$_2$-), 3.54 (d, *J* = 7.0 Hz, 2H, -CH=CHC**H**$_2$-), 2.31 (s, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 140.32, 136.82, 134.65, 130.88, 129.17, 128.65, 128.44, 128.14, 126.11, 125.98, 39.33, 21.15. EI-MS *m/z* 208 (M^+).

(*E*)-1-(4-Methylphenyl)-3-phenylpropene (4da)[8] [CAS: 62056-41-1] (2.32 g, 9.27 mmol, 93%)



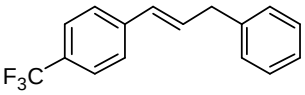
^{1}H-NMR (396 MHz, $CDCl_3$) δ 7.34–7.28 (m, 6H, ArH), 7.25–7.19 (m, 3H, ArH), 6.45 (d, *J* = 15.4 Hz, 1H, -C**H**=CHCH$_2$-), 6.32 (dt, *J* = 15.4, 7.2 Hz, 1H, -CH=C**H**CH$_2$-), 3.54 (d, *J* = 7.2 Hz, 2H, -CH=CHC**H**$_2$-), 1.31 (s, 3Hx3, -C(C**H**$_3$)$_3$). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 150.10, 140.30, 134.65, 130.80, 128.63, 128.42, 128.34, 126.09, 125.80, 125.39, 39.33, 34.48, 31.28. EI-MS *m/z* 250 (M^+).

(*E*)-1-(4-Phenylphenyl)-3-phenylpropene (4ea) [CAS: none] (2.30 g, 8.51 mmol, 85%)



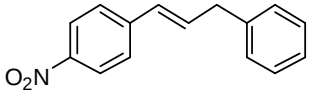
Mp. 90-91 °C. ^{1}H-NMR (396 MHz, $CDCl_3$) δ 7.60–7.52 (m, 4H, ArH), 7.45–7.41 (m, 4H, ArH), 7.35–7.31 (m, 2H, ArH), 7.27–7.21 (m, 4H, ArH), 6.50 (d, *J* = 15.6 Hz, 1H, -C**H**=CHCH$_2$-), 6.41 (dt, *J* = 15.6, 6.5 Hz, 1H, -CH=C**H**CH$_2$-), 3.58 (d, *J* = 6.5 Hz, 2H, -CH=CHC**H**$_2$-). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 140.72, 140.09, 139.79, 136.47, 130.56, 129.36, 128.72, 128.66, 128.48, 127.16, 126.86, 126.50, 126.18, 39.38. IR (ATR): 1600, 1487, 966, 836, 754, 700, 685, 588 cm^{-1}. EI-MS *m/z* 270 (M^+). Anal. Calcd for $C_{21}H_{18}$: C, 93.29: H, 6.71%. Found: C, 93.24: H, 6.71%.

(*E*)-1-(4-trifluoromethylphenyl)-3-phenylpropene (4fa)[9] [CAS: 62056-35-3] (2.50 g, 9.53 mmol, 95%)



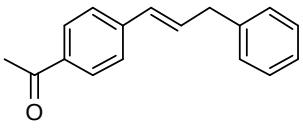
^{1}H-NMR (396 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 2H, ArH), 7.43 (d, *J* = 8.0 Hz, 2H, ArH), 7.35–7.23 (m, 5H, ArH), 6.48–6.46 (m, 2H, -C**H**=C**H**CH$_2$-), 3.57 (d, *J* = 3.7 Hz, 2H, -CH=CHC**H**$_2$-). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 140.93, 139.55, 132.13, 129.79, 128.90 (q, *J* = 32.4 Hz), 128.71, 128.63, 126.41, 126.26, 125.46 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.30 (q, $J_{C\text{-}F}$ = 271.8 Hz), 39.36. EI-MS *m/z* 262 (M^+).

(*E*)-1-(4-Nitrophenyl)-3-phenylpropene (4ga)[7] [CAS: 156904-24-4] (2.27 g, 9.49 mmol, 95%)



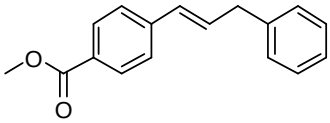
^{1}H-NMR (396 MHz, $CDCl_3$) δ 8.16 (d, *J* = 9.1 Hz, 2H, ArH), 7.47 (d, *J* = 9.1 Hz, 2H, ArH), 7.36–7.32 (m, 2H, ArH), 7.27–7.23 (m, 3H, ArH), 6.57 (dt, *J* = 15.8, 6.3 Hz, 1H, -CH=C**H**CH_2-), 6.50 (d, *J* = 15.8 Hz, 1H, -C**H**=CHCH_2-), 3.61 (brd, *J* = 6.3 Hz, 2H, -CH=CHC**H**$_2$-). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 146.42, 143.82, 138.91, 134.52, 129.00, 128.61, 128.56, 126.43, 126.42, 123.80, 39.32. EI-MS *m/z* 239 (M^+).

(*E*)-1-(4-Acetylphenyl)-3-phenylpropene (4ha) [CAS: none] (1.82 g, 7.72 mmol, 77%)



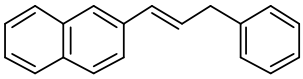
Mp. 37-39 °C. ^{1}H-NMR (396 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.9 Hz, 2H, ArH), 7.43 (d, *J* = 7.9 Hz, 2H, ArH), 7.35–7.31 (m, 2H, ArH), 7.26–7.22 (m, 3H, ArH), 6.56–6.45 (m, 2H, -C**H**=C**H**CH_2-), 3.58 (d, *J* = 5.5 Hz, 2H, -CH=CHC**H**$_2$-), 2.58 (s, 3H, C(O)C**H**$_3$). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 197.53, 142.07, 139.40, 135.53, 132.42, 130.03, 128.67, 128.62, 128.51, 126.30, 126.06, 39.35, 26.47. IR (ATR): 1676, 1598, 1492, 1450, 1409, 1356, 1265, 1181, 976, 957, 938, 808, 738, 696, 595 cm^{-1}. EI-MS *m/z* 236 (M^+). Anal. Calcd for $C_{17}H_{16}O$: C, 86.40: H, 6.82%. Found: C, 86.01: H, 6.81%.

(*E*)-methyl 4-(3-phenylprop-1-enyl)benzoate (4ia)[10] [CAS: 1012036-96-2] (2.32 g, 9.18 mmol, 92%)



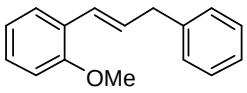
^{1}H-NMR (396 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 2H, ArH), 7.40 (d, *J* = 8.3 Hz, 2H, ArH), 7.34–7.31 (m, 2H, ArH), 7.24 (d, *J* = 7.1 Hz, 3H, ArH), 6.50–6.48 (m, 1H, -C**H**=C**H**CH_2-), 3.91 (s, 3H, -OC**H**$_3$), 3.58 (d, *J* = 5.1 Hz, 2H, -CH=CHC**H**$_2$-). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.82, 141.87, 139.46, 132.13, 130.10, 129.80, 128.61, 128.49, 128.45, 126.27, 125.89, 51.92, 39.33. EI-MS *m/z* 252 (M^+).

(*E*)-1-(2-Naphthyl)-3-phenylpropene (4ja)[11] [CAS: 5751-32-6] (2.41g, 9.87 mmol, 99%)



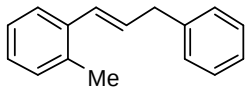
^{1}H-NMR (396 MHz, $CDCl_3$) δ 7.79–7.74 (m, 3H, ArH), 7.70 (s, 1H, ArH), 7.58 (dd, *J* = 8.3, 1.8 Hz, 1H, ArH), 7.46–7.39 (m, 2H, ArH), 7.29–7.22 (m, 5H, ArH), 6.62 (d, *J* = 15.7 Hz, 1H, -C**H**=CHCH_2-), 6.49 (dt, *J* = 15.7, 6.9 Hz, 1H, -CH=C**H**CH_2-), 3.61 (d, *J* = 6.9 Hz, 2H, -CH=CHC**H**$_2$-). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 140.08, 134.87, 133.60, 132.72, 131.09, 129.64, 128.69, 128.49, 128.05, 127.82, 127.59, 126.19, 126.12, 125.73, 125.54, 123.50, 39.42. EI-MS *m/z* 244 (M^+).

(*E*)-1-(2-Methoxyphenyl)-3-phenylpropene (4ka)[10] [CAS: 1246889-00-6] (2.09 g, 9.33 mmol, 93%)



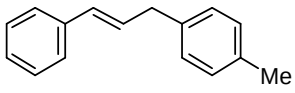
^{1}H-NMR (396 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.5 Hz, 1H, ArH), 7.46–7.41 (m, 2H, ArH), 7.37–7.16 (m, 4H, ArH), 6.92–6.85 (m, 2H, ArH), 6.82 (d, *J* = 15.8 Hz, 1H, -C**H**=CHCH_2-), 6.42 (dt, *J* = 15.8, 7.1 Hz, 1H, -CH=C**H**CH_2-), 3.85 (s, 3H, -OCH_3), 3.57 (d, *J* = 7.1 Hz, 2H, -CH=CHC**H**$_2$-). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 156.35, 140.46, 129.70, 128.57, 128.37, 128.05, 126.52, 126.39, 125.99, 125.68, 120.54, 110.69, 55.32, 39.80. EI-MS *m/z* 224 (M^+).

(*E*)-1-(2-Methylphenyl)-3-phenylpropene (4la)[12] [CAS: 83135-54-0] (1.73 g, 8.30 mmol, 83%)



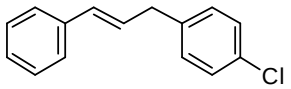
^{1}H-NMR (396 MHz, $CDCl_3$) δ 7.43–7.41 (m, 1H, ArH), 7.33–7.20 (m, 5H, ArH), 7.15–7.13 (m, 3H, ArH), 6.67 (d, *J* = 15.4 Hz, 1H, -C**H**=CHCH$_2$-), 6.23 (dt, *J* = 15.4, 7.3 Hz, 1H, -CH=C**H**CH$_2$-), 3.59 (d, *J* = 7.3 Hz, 2H, -CH=CHC**H**$_2$-), 2.34 (s, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 140.24, 136.54, 135.03, 130.45, 130.14, 128.94, 128.58, 128.44, 127.02, 126.11, 125.99, 125.52, 39.61, 19.83. EI-MS *m/z* 208 (M^+).

(*E*)-3-(4-Methylphenyl)-1-phenylpropene (4ab)[7] [CAS: 134539-86-9] (1.75 g, 8.40 mmol, 84%)



^{1}H-NMR (396 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.5 Hz, 2H, ArH), 7.29 (d, *J* =7.5 Hz, 2H, ArH), 7.21–7.18 (m, 1H, ArH), 7.15–7.10 (m, 4H, ArH), 6.45 (d, *J* = 15.6 Hz, 1H, -C**H**=CHCH$_2$-), 6.34 (dt, *J* = 15.6, 6.7 Hz, 1H, -CH=C**H**CH$_2$-), 3.51 (d, *J* = 6.7 Hz, 2H, -CH=CHC**H**$_2$-), 2.33 (s, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 137.48, 137.01, 135.62, 130.78, 129.47, 129.14, 128.52, 128.45, 127.00, 126.07, 38.89, 20.99. EI-MS *m/z* 208 (M^+).

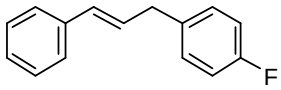
(*E*)-3-(4-Chlorophenyl)-1-phenylpropene (4ac)[7] [CAS: 511234-96-1] (1.34 g, 5.86 mmol, 59%)



^{1}H-NMR (396 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.9 Hz, 2H, ArH), 7.31–7.25 (m, 4H, ArH), 7.24–7.19 (m, 1H, ArH), 7.17 (d, *J* = 7.9 Hz, 2H, ArH), 6.44 (d, *J* = 15.3 Hz, 1H, -C**H**=CHCH$_2$-), 6.31 (dt, *J* = 15.3, 6.7 Hz, 1H, -CH=C**H**CH$_2$-), 3.52 (d, *J* = 6.7 Hz, 2H, -CH=CHC**H**$_2$-).

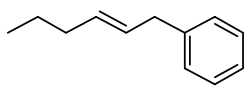
^{13}C-NMR (100 MHz, $CDCl_3$) δ 138.52, 137.17, 131.90, 131.42, 129.98, 128.52, 128.50, 128.49, 127.23, 126.09, 38.56. EI-MS *m/z* 228 (M^+).

(*E*)-3-(4-Fluorophenyl)-1-phenylpropene (4ad)[7] [CAS: 485844-19-7] (1.37 g, 6.45 mmol, 65%)



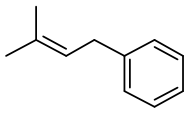
^{1}H-NMR (396 MHz, $CDCl_3$) δ 7.37–7.18 (m, 7H, ArH), 6.99 (t, *J* = 8.1 Hz, 2H, ArH), 6.44 (d, *J* = 15.0 Hz, 1H, -C**H**=CHCH$_2$-), 6.32 (dt, *J* = 15.0, 6.6 Hz, 1H, -CH=C**H**CH$_2$-), 3.52 (d, *J* = 6.6 Hz, 2H, -CH=CHC**H**$_2$-). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 161.45 (d, *J* = 243.3 Hz), 137.26, 135.68 (d, *J* = 3.9 Hz), 131.16, 129.99 (d, *J* = 7.7 Hz), 128.93, 128.49, 127.18, 126.09, 115.18 (d, *J* = 21.0 Hz), 38.43. EI-MS *m/z* 212 (M^+).

(*E*)-1-Phenyl-2-hexene (4ma)[7] [CAS: 78633-31-5] (1.25 g, 7.80 mmol, 78%)



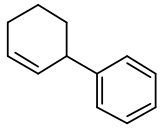
^{1}H-NMR (396 MHz, $CDCl_3$) δ 7.31–7.26 (m, 2H, ArH), 7.20–7.17 (m, 3H, ArH), 5.57 (dt, *J* = 15.0, 5.9 Hz, 1H, -CH=C**H**CH$_2$Ph), 5.50 (dt, *J* = 15.4, 5.9 Hz, 1H, -C**H**=CHCH$_2$Ph), 3.33 (d, *J* = 5.9 Hz, 2H, -CH=CHC**H**$_2$Ph), 2.00 (q, *J* = 6.7 Hz, 2H, -C**H**$_2$CH=CHCH$_2$Ph), 1.40 (sext, *J* = 7.4 Hz, 2H, -C**H**$_2$CH$_2$CH=CHCH$_2$Ph), 0.90 (t, 3H, *J* = 7.4 Hz, -CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 141.12, 131.90, 128.86, 128.46, 128.30, 125.82, 39.06, 34.60, 22.59, 13.69. EI-MS *m/z* 160 (M^+).

2-Methyl-4-phenyl-2-butene (4na)[7] [CAS: 286376-80-5] (1.06 g, 7.25 mmol, 73%)



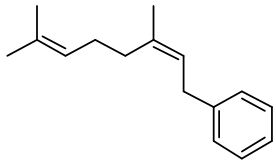
^{1}H-NMR (396 MHz, $CDCl_3$) δ 7.29–7.25 (m, 2H, ArH), 7.19–7.15 (m, 3H, ArH), 5.35–5.30 (m, 2H, $(CH_3)_2C$=C**H**CH_2Ph), 3.34 (d, *J* = 7.1 Hz, 2H, $(CH_3)_2C$=CHC**H**$_2$Ph), 1.74 (s, 3H, -CH_3), 1.72 (s, 3H, -CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 141.79, 132.46, 128.32, 128.28, 125.67, 123.18, 34.35, 25.74, 17.79. EI-MS *m/z* 146 (M^+).

3-Phenylcyclohexene (4oa)[7] [CAS: 15232-96-9] (1.12 g, 7.08 mmol, 71%)



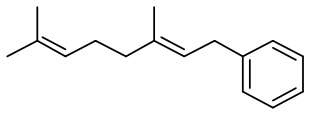
^{1}H-NMR (396 MHz, $CDCl_3$) δ 7.32–7.28 (m, 2H, ArH), 7.23–7.18 (m, 3H, ArH), 5.91–5.88 (m, 1H, -CH=C**H**-CHPh-), 5.73–5.70 (m, 1H, -C**H**=CH-CHPh-), 3.43–3.38 (m, 1H, -CH=CH-C**H**Ph-), 2.11–1.98 (m, 3H, -$(CH_2)_3$-CHPh-), 1.77–1.72 (m, 1H, -$(CH_2)_3$-CHPh-), 1.67–1.51 (m, 2H, -$(CH_2)_3$-CHPh-). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 140.60, 130.13, 128.31, 128.23, 127.69, 125.91, 41.82, 32.61, 24.98, 21.16. EI-MS *m/z* 158 (M^+).

(Z)-3,7-Dimethyl-1-phenyl-2,6-octadiene (4pa)[7] [CAS: 21488-83-5] (1.16 g, 5.39 mmol, 54%)



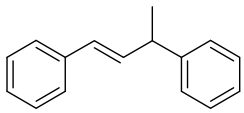
^{1}H-NMR (396 MHz, $CDCl_3$) δ 7.29–7.24 (m, 2H, ArH), 7.19–7.15 (m, 3H, ArH), 5.33 (t, *J* = 7.2 Hz, 1H, -(CH_3)C=C**H**CH_2Ph), 5.16-5.13 (m, 1H, $(CH_3)_2$C=C**H**-**(**$CH_2)_2$-), 3.35 (d, *J* = 7.2 Hz, 2H, -(CH_3)C=CHC**H**$_2$Ph), 2.17–2.10 (m, 4H, $(CH_3)_2$C=CH-**(**C**H**$_2)_2$-), 1.75 (s, 3H, -CH_3), 1.69 (s, 3H, -CH_3), 1.62 (s, 3H, -CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 141.80, 136.14, 131.72, 128.33, 128.31, 125.67, 124.15, 123.81, 34.08, 31.95, 26.56, 25.71, 17.65. EI-MS *m/z* 214 (M^+).

(*E*)-3,7-Dimethyl-1-phenyl-2,6-octadiene (4qa)[7] [CAS: 21488-84-6] (1.38 g, 6.44 mmol, 64%)



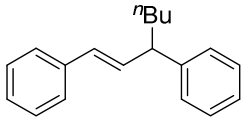
^{1}H-NMR (396 MHz, $CDCl_3$) δ 7.29–7.25 (m, 2H, ArH), 7.20–7.15 (m, 3H, ArH), 5.34 (t, *J* = 7.0 Hz, 1H, -(CH_3)C=C**H**CH_2Ph), 5.10 (t, *J* = 6.9 Hz, 1H, $(CH_3)_2$C=C**H**-**(**$CH_2)_2$-), 3.36 (d, *J* = 7.0 Hz, 2H, -(CH_3)C=CHC**H**$_2$Ph), 2.14–2.09 (m, 2H, $(CH_3)_2$C=CH-**(**C**H**$_2)_2$-), 2.07–2.03 (m, 2H, $(CH_3)_2$C=CH-**(**C**H**$_2)_2$-), 1.71 (s, 3H, -CH_3), 1.68 (s, 3H, -CH_3), 1.60 (s, 3H, -CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 141.75, 136.16, 131.43, 128.33, 128.30, 125.64, 124.25, 123.01, 39.69, 34.16, 26.57, 25.71, 17.68, 16.08. EI-MS *m/z* 214 (M^+).

(*E*)-1,3-Diphenyl-1-butene (4ra)[7] [CAS: 7302-01-4] (1.53 g, 7.35 mmol, 74%)



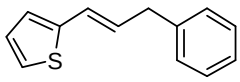
^{1}H-NMR (396 MHz, $CDCl_3$) δ 7.37–7.17 (m, 10H, Ar**H**), 6.40–6.35 (m, 2H), 3.65–3.62 (m, 1H), 1.46 (d, *J* = 7.1 Hz, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 145.60, 137.52, 135.19, 128.47, 127.29, 127.02, 126.20, 126.12, 42.54, 21.20. EI-MS *m/z* 208 (M^+).

(*E*)-1,3-Diphenyl-1-heptene (4sa)[16] [CAS: 485844-22-2] (1.45 g, 5.77 mmol, 58%)



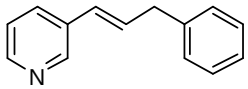
^{1}H-NMR (396 MHz, $CDCl_3$) δ 7.35–7.16 (m, 10H, ArH), 6.41–6.29 (m, 2H), 3.39 (q, *J* = 7.1 Hz, 1H), 1.79 (q, *J* = 7.1 Hz, 2H), 1.36–1.22 (m, 4H) 1.0 (t, *J* = 7.1 Hz, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 144.73, 137.59, 134.48, 129.19, 128.46, 128.44, 127.62, 126.98, 126.14, 126.11, 49.18, 35.62, 29.85, 22.69, 14.05. EI-MS *m/z* 250 (M^+).

(*E*)-1-(2-Thiophene)-3-phenylpropene (4ta)[11] [CAS: 1403462-93-0] (0.029 g, 0.14 mmol, 1%)



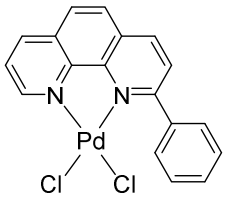
^{1}H-NMR (396 MHz, $CDCl_3$) δ 7.33–7.30 (m, 2H, ArH), 7.26–7.21 (m, 3H, ArH), 7.10 (d, *J* = 4.8 Hz, 1H, thiophene 5-H), 6.93 (dd, *J* = 4.8, 3.2 Hz, 1H, thiophene 4-H), 6.89 (d, *J* = 3.2 Hz, 1H, thiophene 3-H), 6.56 (d, *J* = 15.6 Hz, 1H, -C**H**=CHCH$_2$-), 6.21 (dt, *J* = 15.6, 6.7 Hz, 1H, -CH=C**H**CH$_2$-), 3.51 (d, *J* = 6.7 Hz, 2H, -CH=CHC**H**$_2$-). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 142.58, 139.76, 129.08, 128.67, 128.48, 127.19, 126.21, 124.75, 124.22, 123.46, 39.06. EI-MS *m/z* 200 (M^+).

(*E*)-1-(3-Pyridine)-3-phenylpropene (4ua)[10] [CAS: 1380310-78-0] (0.053 g, 0.27 mmol, 3%)



^{1}H-NMR (396 MHz, $CDCl_3$) δ 8.58 (d, *J* = 1.6 Hz, 1H, ArH), 8.44 (d, *J* = 4.8, 1.6 Hz, 1H, ArH), 7.67 (dt, *J* = 7.9, 1.6 Hz, 1H, ArH), 7.35–7.31 (m, 2H, ArH), 7.25–7.20 (m, 4H, ArH), 6.49–6.39 (m, 2H, -C**H**=C**H**CH$_2$-), 3.57 (d, *J* = 5.1 Hz, 2H, -CH=CHC**H**$_2$-). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 147.97, 147.89, 139.43, 133.05, 132.64, 131.86, 128.64, 128.57, 127.35, 126.36, 123.40, 39.38. FAB-MS *m/z* 196 ([M+1]$^+$).

Synthesis of Dichloro-(2-phenyl-1,10-phenanthroline)palladium (6).



$PdCl_2(MeCN)_2$ (25.9 mg, 0.100 mmol) was added to a solution of 2,9-diphenyl-1,10-phenanthroline (25.6 mg, 0.100 mmol) in CH_2Cl_2. After being stirred for 4 h at 40 °C, a resulting insoluble material was collected by filtration. The obtained material was washed with dichloromethane and hexane, and dried in *vacuo* to give **6** (29.1 mg, 0.067 mmol, 67%) as orange solids. ^{1}H-NMR (396 MHz, DMSO-d_6) δ 9.51(dd, *J* = 1.2, 5.3 Hz, 1H), 8.71 (d, *J* = 8.1 Hz, 1H), 8.67 (dd, *J* = 1.2, 8.3 Hz, 2H), 8.17 (d, *J* = 8.9 Hz, 1H), 8.01 (d, *J* = 8.9 Hz, 1H), 7.90 (dd, *J* = 5.3, 8.3, 2H), 7.88 (d, *J* = 8.1, 2H), 7.42 (d, *J* = 7.9, 2H), 6.87 (t, *J* = 7.9, 1H), 6.66 (t, *J* = 7.9, 2H). ^{13}C-NMR (100 MHz, DMSO-d_6) δ 158.90, 153.94, 145.26, 144.26, 140.22, 139.91, 138.75, 136.77, 130.65, 129.12, 129.02, 128.53, 127.51, 126.99, 125.62, 124.84. ESI-TOF-MS *m/z* 653 ([2M-$PdCl_3$]$^+$).

Experimental Procedure for Scheme 3

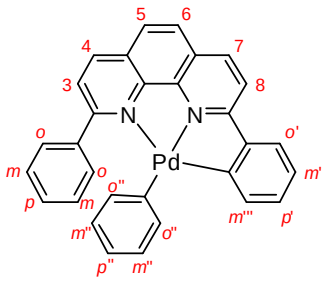
The reaction of 8 with 3a using 1 (Scheme 3a)

Complex **1** (4.7 mg, 0.01 mmol) was dissolved in methanol (100 mL) to give a stock solution. Under a nitrogen atmosphere, the stock solution (0.1 mL, 1.00×10^{-5} mmol), methanol (9.9 mL), and $NaBPh_4$ (**3a**, 6.84 g, 20.0 mmol) were added to a reaction vessel. The resulting solution was degassed via three freeze-pump-thaw cycles. 1-Phenyl-2-propenyl acetate (**8**, 1.76 g, 10.0 mmol) was added to the solution. The reaction mixture was stirred at 50 °C for 24 h and allowed to cool to 25 °C. After removal of the solvent, water (50 mL) was added to the residue. The resulting suspension was extracted with *tert*-butyl methyl ether (50 mL × 4). The combined organic layer was dried over Na_2SO_4. The resulting solution was concentrated under reduced pressure. The crude product was chromatographed on silica gel (eluent: hexane) to give (*E*)-1,3-diphenylpropene (**4a**) (1.46 g, 7.52 mmol, 75%) as colorless oil.

The reaction of the complex 1 with sodium tetraphenylborate (3a) in a NMR tube (Scheme 3b)

In a glove box, the complex **1** (1.0 mg, 2.1×10^{-3} mmol), $NaBPh_4$ (0.7 mg, 2.1×10^{-3} mmol), hexamethylbenzene as an internal standard were placed in a valved NMR tube. THF-d_8 (0.75 mL) was added to the NMR tube. After closed the valve, the NMR tube was taken out from the glove box. The NMR tube was heated in an oil bath at 80 °C for 24 h. After being cooled to 25 °C, the yield of **9** was determined by the ^{1}H NMR analysis to be 96%.

Isolation of Phenyl-[2-(9-phenyl-1,10-phenanthrolin-2-yl)phenyl]palladium (9)



Under a nitrogen atmosphere, $NaBPh_4$ (36.0 mg, 0.106 mmol) was added to a degassed solution of phenyl-[2-(9-phenyl-1,10-phenanthrolin-2-yl)phenyl]palladium (50.0 mg, 0.106 mmol) in THF (35 mL). The reaction mixture was refluxed for 38 h and allowed to cool to 25 °C. After removal of the solvent, the residue was washed with THF (5 mL) and dried in *vacuo*. The crude product was dissolved in CH_2Cl_2 (10 mL) and filtered through Celite. After concentration of the filtrate, the resulting residue was washed with pentane (10 mL) to give phenyl-[2-(9-phenyl-1,10-phenanthrolin-2-yl)phenyl]palladium (32.7 mg, 0.063 mmol, 59%) as orange solids. Mp. 160-164 °C (decomp.). ^{1}H-NMR (396 MHz, CD_2Cl_2) δ 8.50 (d, *J* = 8.7 Hz, 1H, 4-H), 8.43 (d, *J* = 8.7 Hz, 1H, 7-H), 8.11 (d, *J* = 8.3 Hz, 1H, 8-H), 7.91 (d, *J* = 8.7 Hz, 1H, 5-H or 6-H), 7.88 (d, *J* = 8.7 Hz, 1H, 5-H or 6-H), 7.86 (d, *J* = 8.3 Hz, 1H, 3-H), 7.62 (dd, *J* = 1.8, 7.6 Hz, 1H, *o*'-H), 7.52–7.50 (m, 2H, *o*-H), 7.18–7.15 (m, 2H, *o*"-H), 6.98 (dd, *J* = 1.8, 7.6 Hz, 1H, *m*'''-H), 6.92–6.87 (m, 2H, *p*-H and *p*'-H), 6.84–6.80 (m, 3H, *m*-H and *m*'-H), 6.53–6.50 (m, 3H, *m*"-H and *p*"-H). ^{13}C-NMR (100 MHz, CD_2Cl_2) δ 167.68, 161.24, 156.03, 152.58, 148.84, 139.41, 138.00, 137.75, 137.51, 137.22, 130.66, 130.28, 229.73, 129.28, 129.17, 128.51, 127.90, 127.76, 127.19, 126.31, 126.22, 126.18, 124.71, 123.93,

121.31, 118.74. IR (ATR): 3060, 3037, 1620, 1587, 1547, 1509, 1498, 1487, 1463, 1418, 1273, 1149, 1019, 850, 828, 774, 750, 724, 690, 656, 643, 596 cm^{-1}. MALDI-TOF-MS *m/z* 514 ($[M]^+$). Anal. Calcd for $C_{30}H_{20}N_2Pd \cdot 0.5CH_2Cl_2$: C, 68.19: H, 3.87; N, 5.27%. Found: C, 68.29: H, 3.98: N, 5.31%.

The reaction of the complex 9 with cinnamyl acetate (2a) in a NMR tube (Scheme 3c)

In a glove box, complex **9** (1.1 mg, 2.1×10^{-3} mmol) and hexamethylbenzene as an internal standard were placed in a valved NMR tube. THF-d8 (0.75 mL) and a solution of cinnamyl acetate in THF-d_8 (20 μL (concentration is 3.7 mg/200 μL), 2.1×10^{-3} mmol) were added to the NMR tube. After closed the valve, the NMR tube was taken out from the glove box. The NMR tube was heated in an oil bath at 80 °C for 24 h. After being cooled to 25 °C, the yield of **4aa** was determined by the ^1H NMR analysis to be 57%.

The allylic arylation of cinnamyl acetate 2a with sodium tetraphenylborate 3a using 9 (Scheme 3d)

Complex **9** (5.2 mg, 0.01 mmol) was dissolved in methanol (100 mL) to give a stock solution. Under a nitrogen atmosphere, the stock solution (0.1 mL, 1.00×10^{-5} mmol), methanol (9.9 mL), and $NaBPh_4$ (6.84 g, 20.0 mmol) were added to a reaction vessel. The resulting solution was degassed via three freeze-pump-thaw cycles. Cinnamyl acetate (1.76 g, 10.0 mmol) was added to the solution. The reaction mixture was stirred at 50 °C for 24 h and allowed to cool to 25 °C. After removal of the solvent, water (50 mL) was added to the residue. The resulting suspension was extracted with *tert*-butyl methyl ether (50 mL × 4). The combined organic layer was dried over Na_2SO_4. The resulting solution was concentrated under reduced pressure. The crude product was chromatographed on silica gel (eluent: hexane) to give (*E*)-1,3-diphenylpropene (**4aa**) (1.81 g, 9.32 mmol, 93%) as colorless oil.

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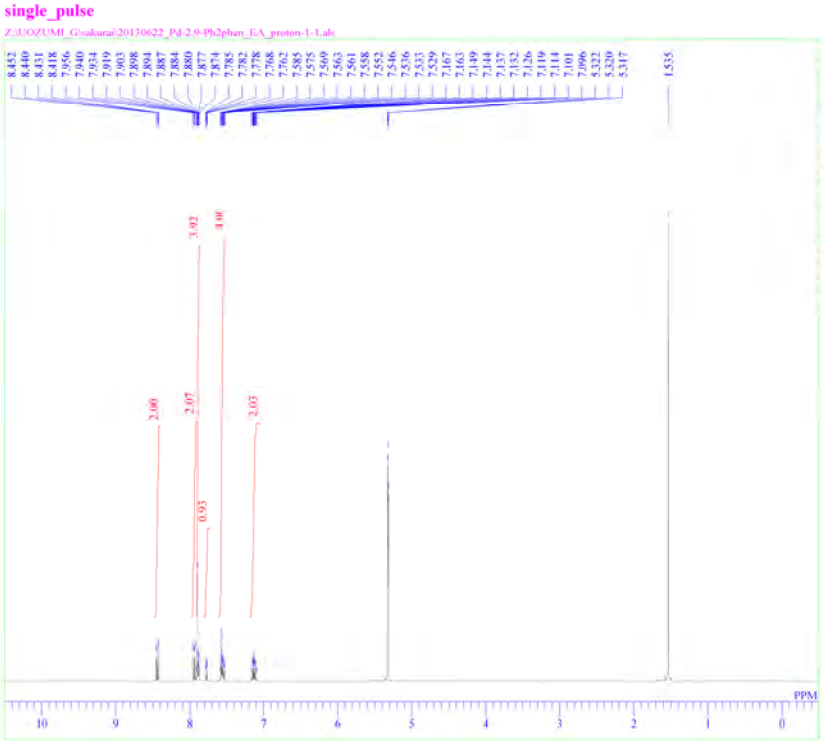
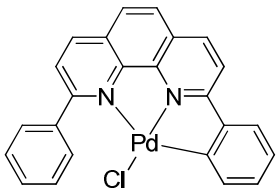
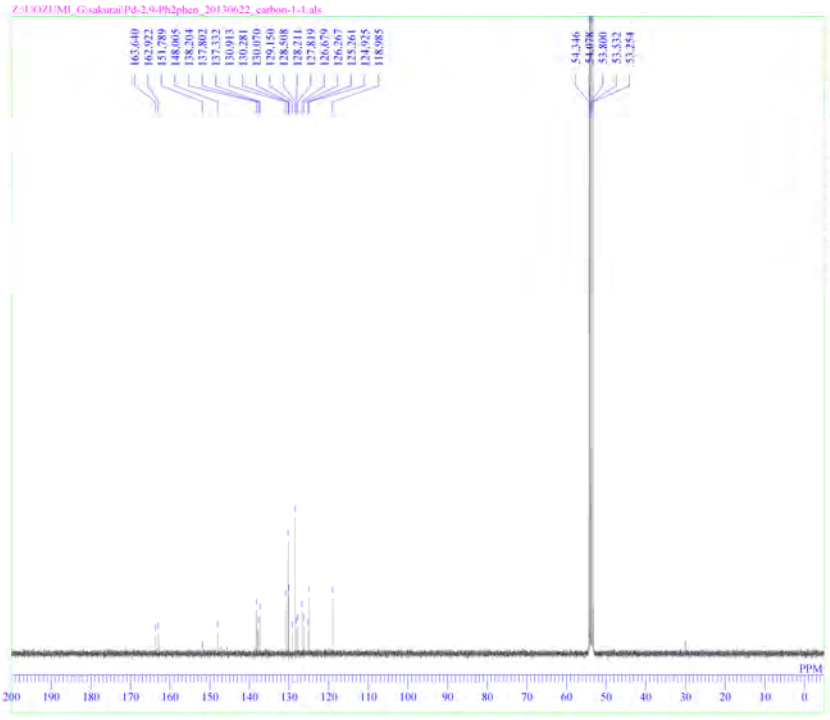
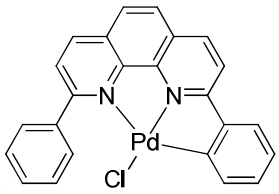
Chloro-[2-(9-phenyl-1,10-phenanthrolin-2-yl)phenyl]palladium (1).

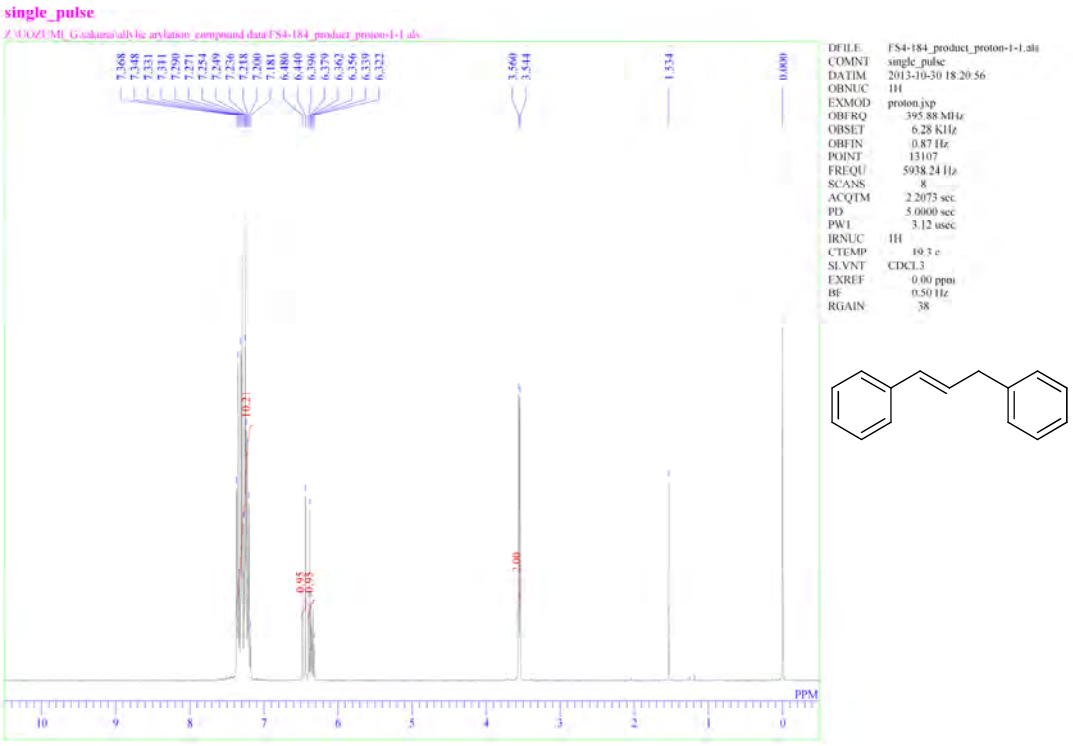


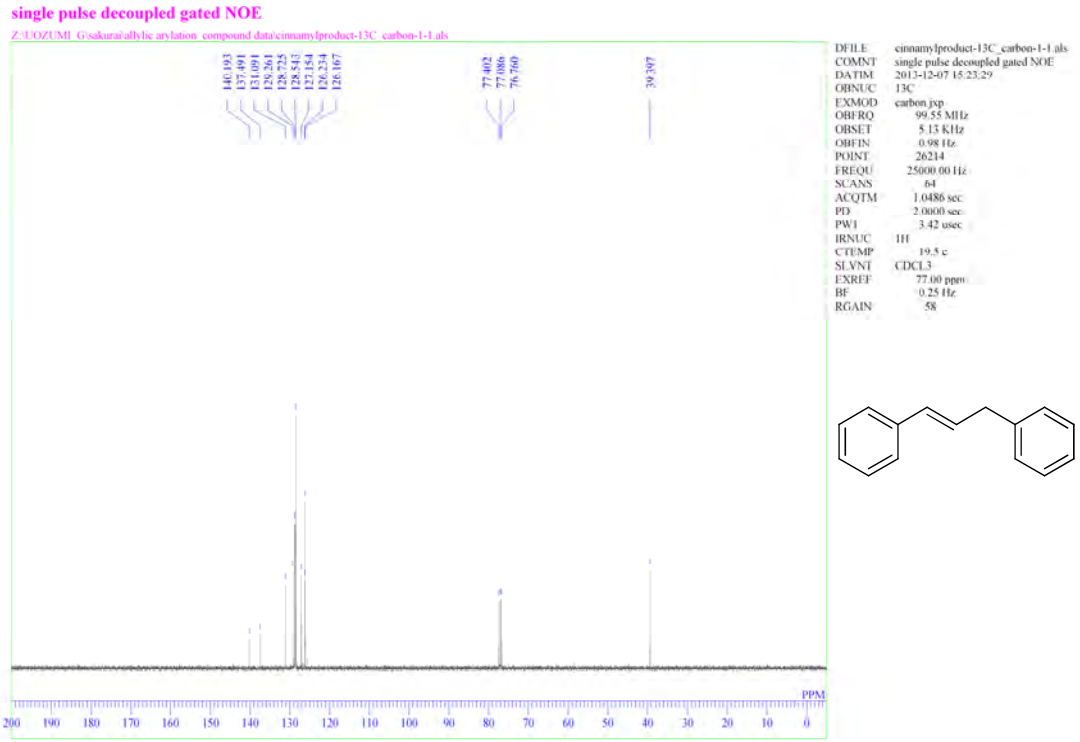




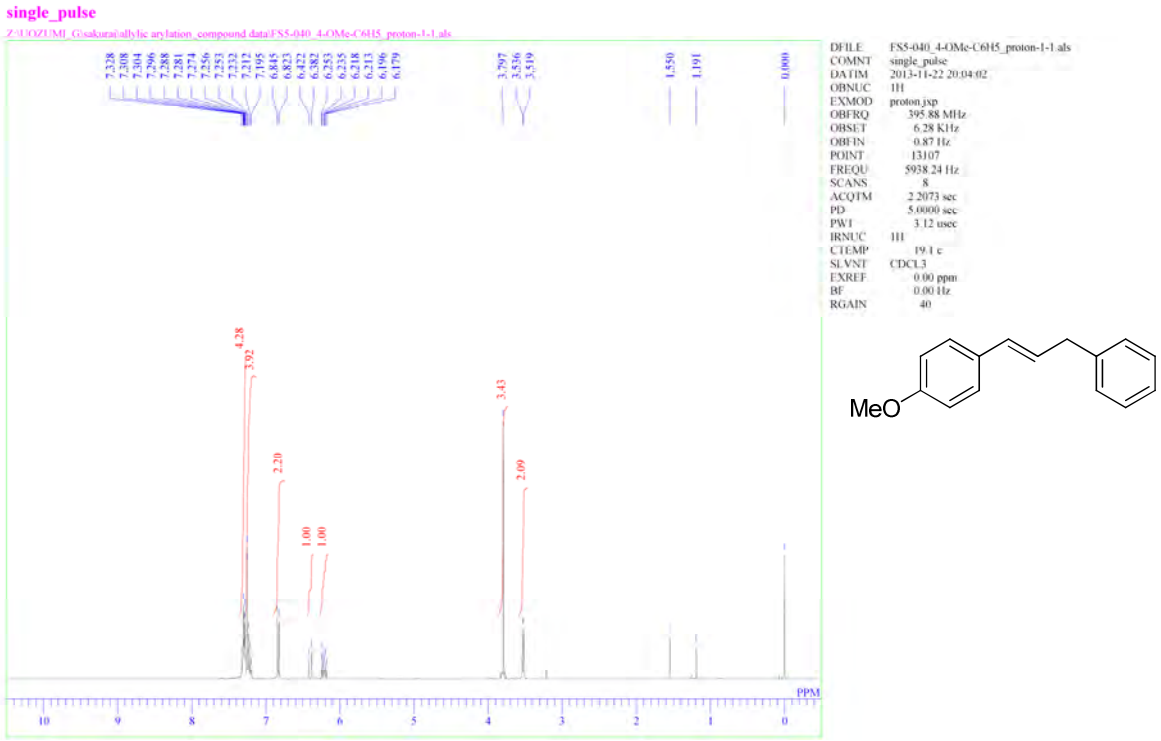


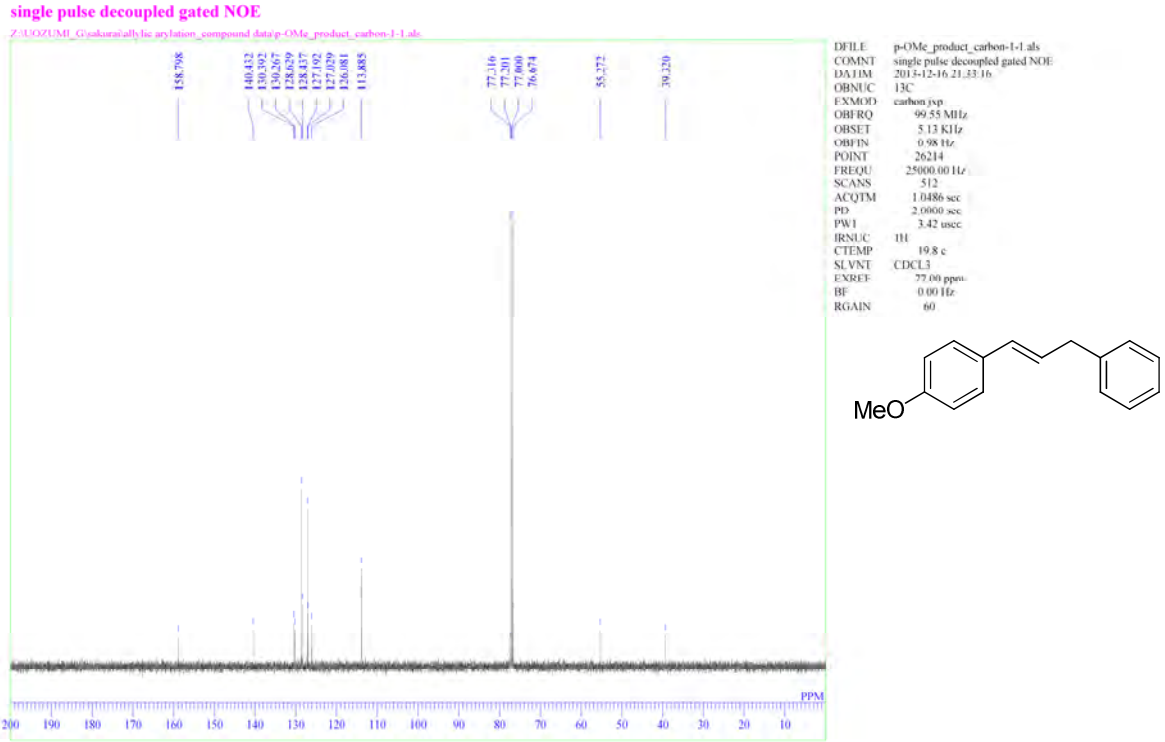
1,1’-[(1*E*)-prop-1-ene-1,3-diyl]dibenzene (4aa)





(*E*)-1-(4-Methoxyphenyl)-3-phenylpropene (4ba)





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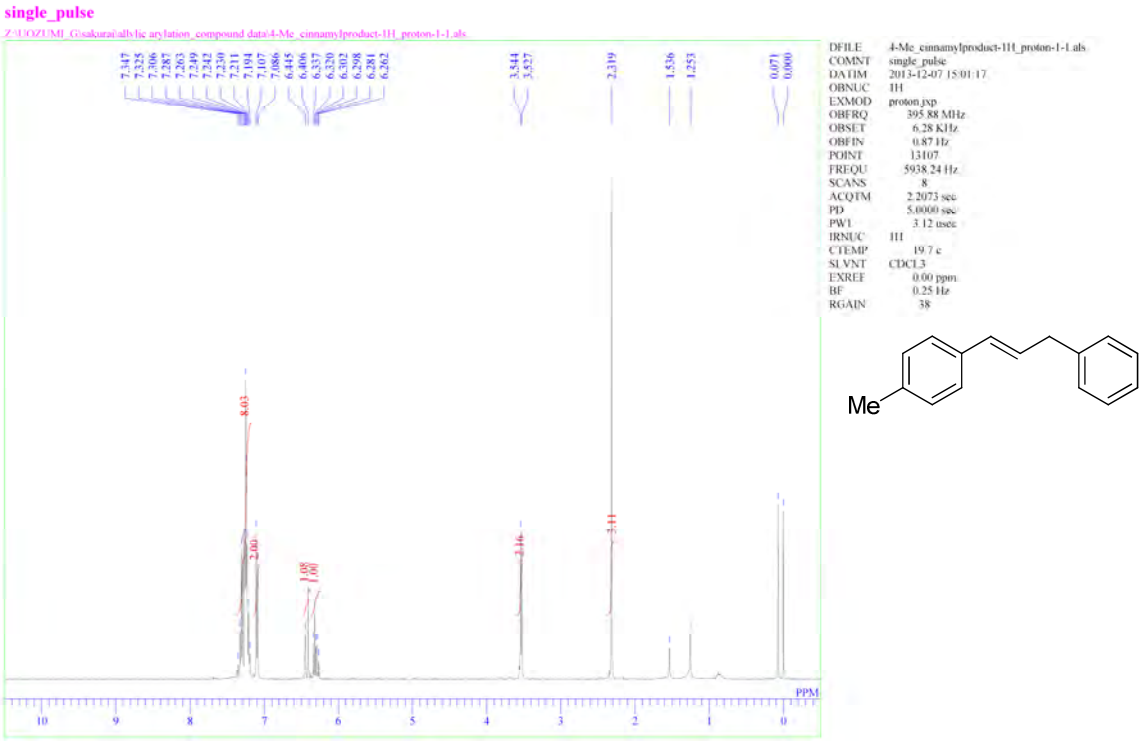

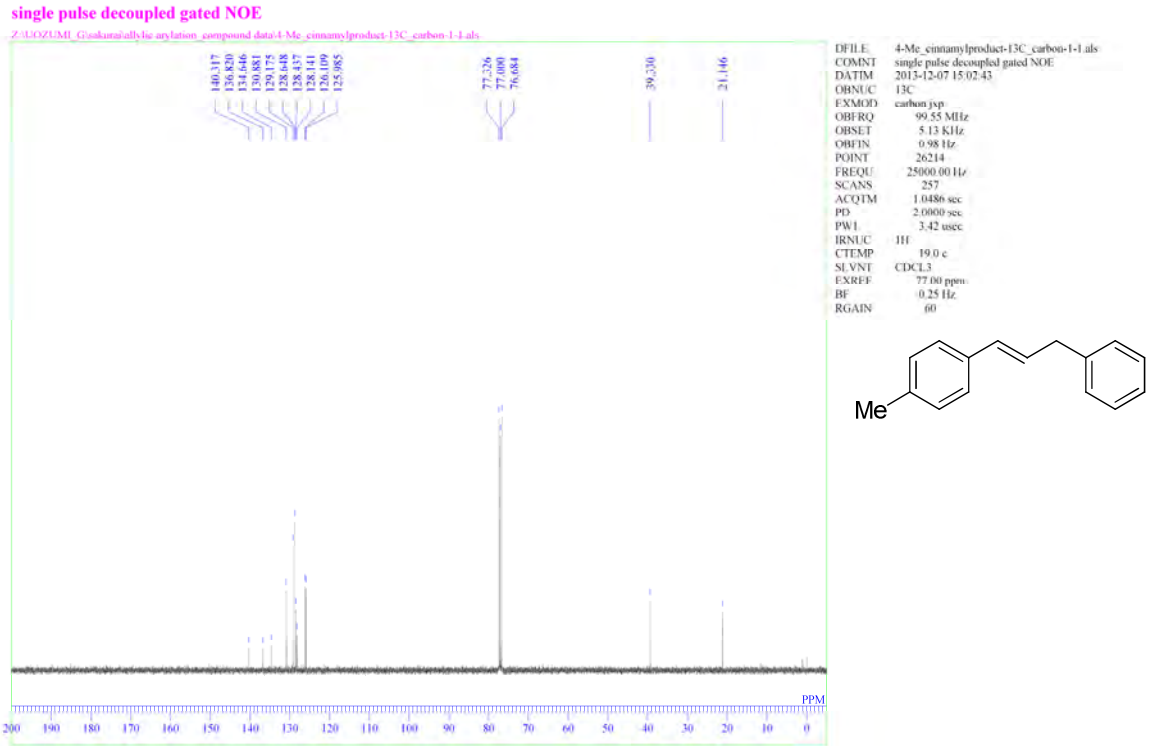

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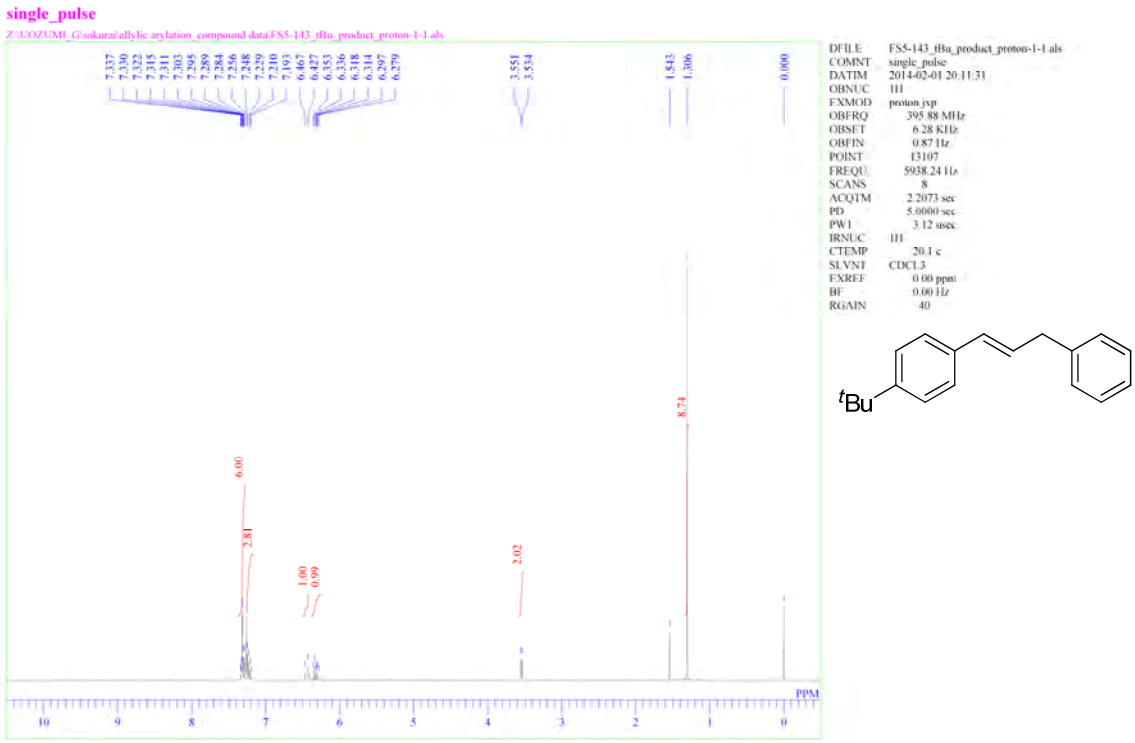

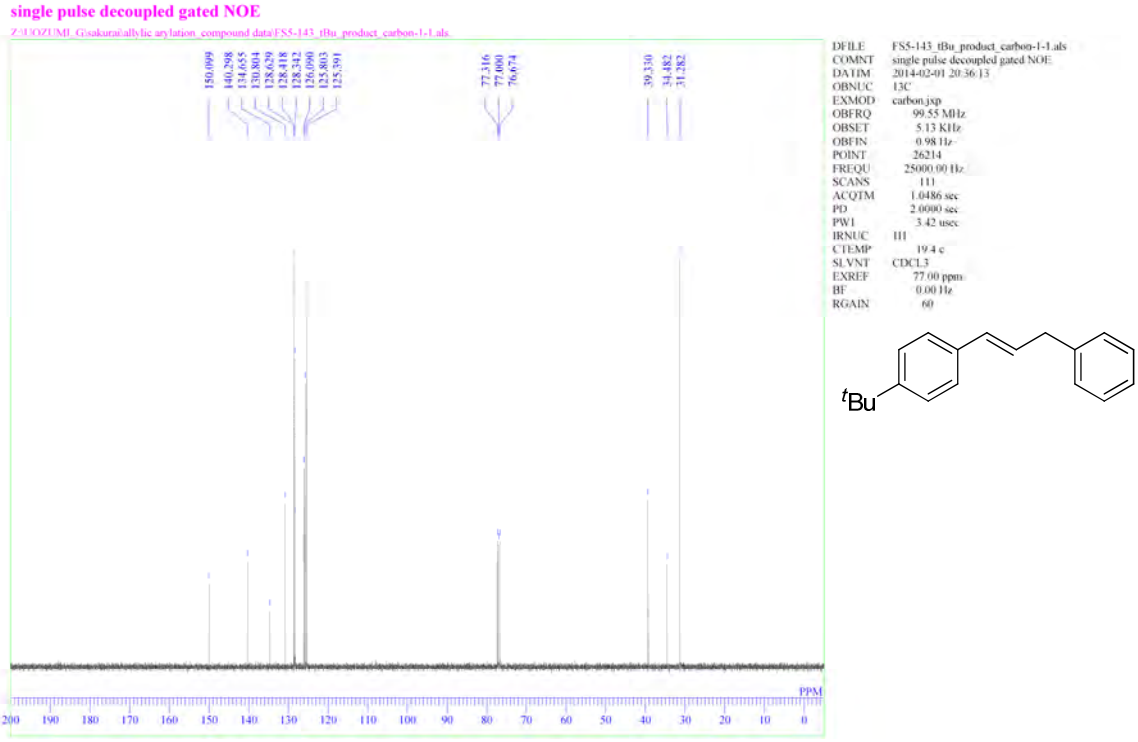

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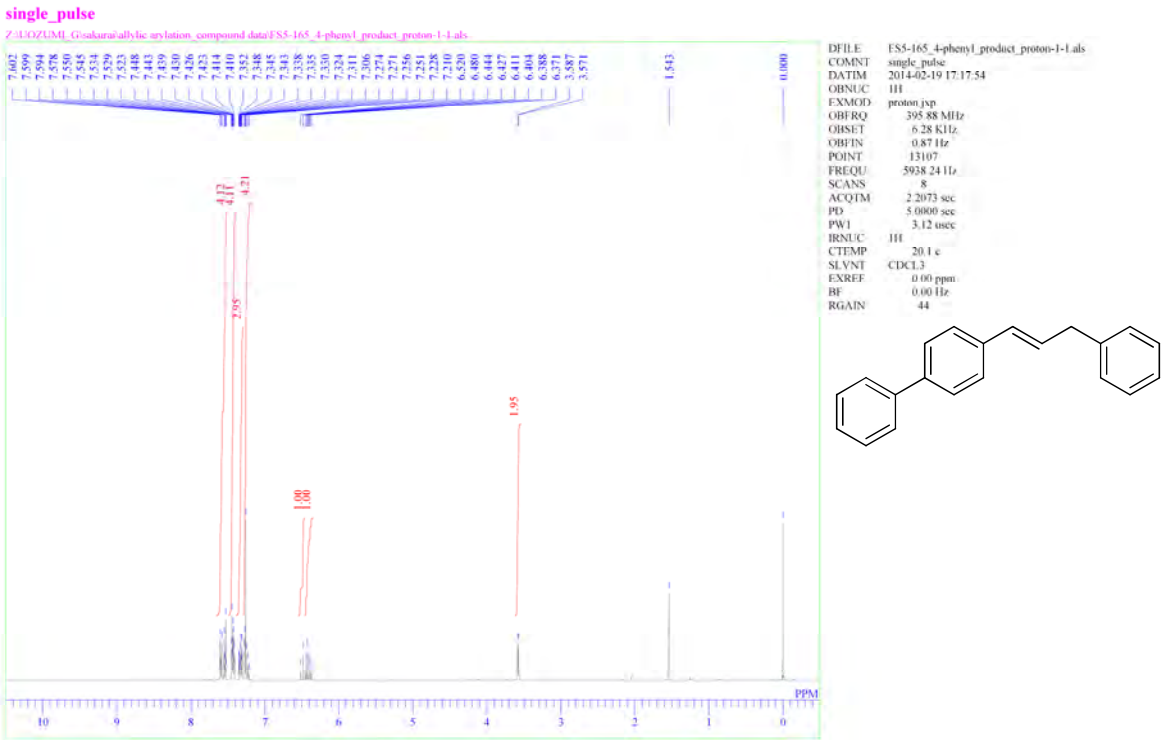

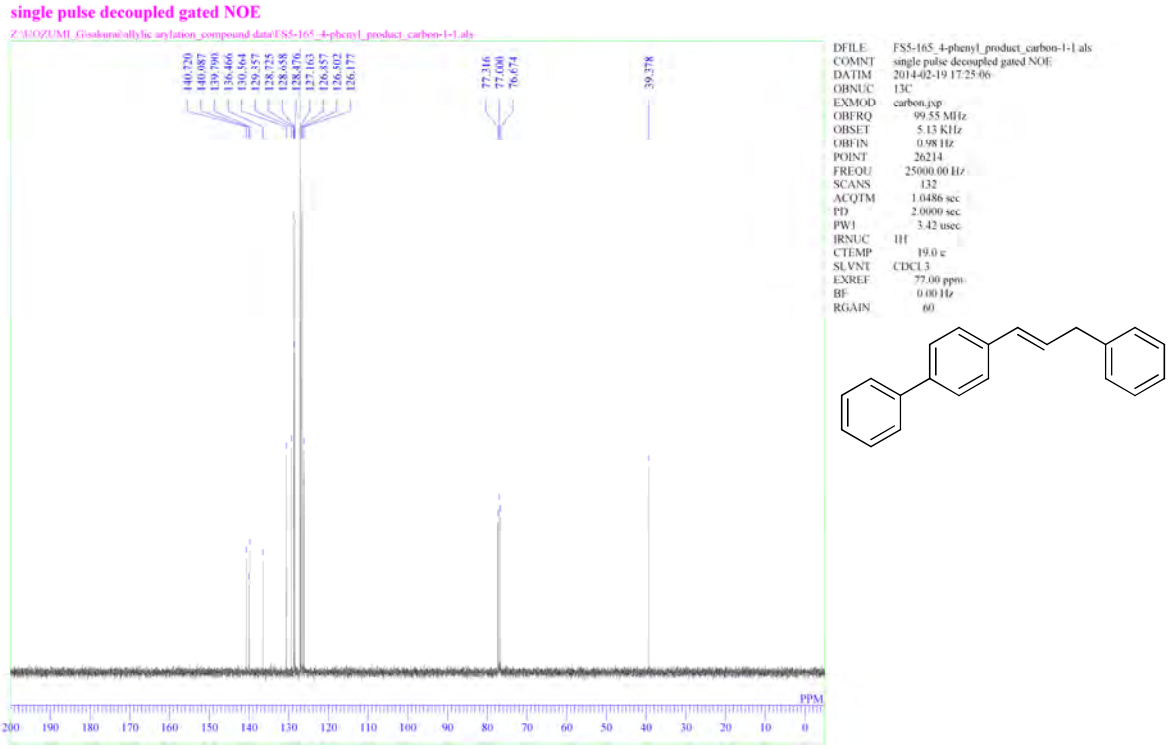

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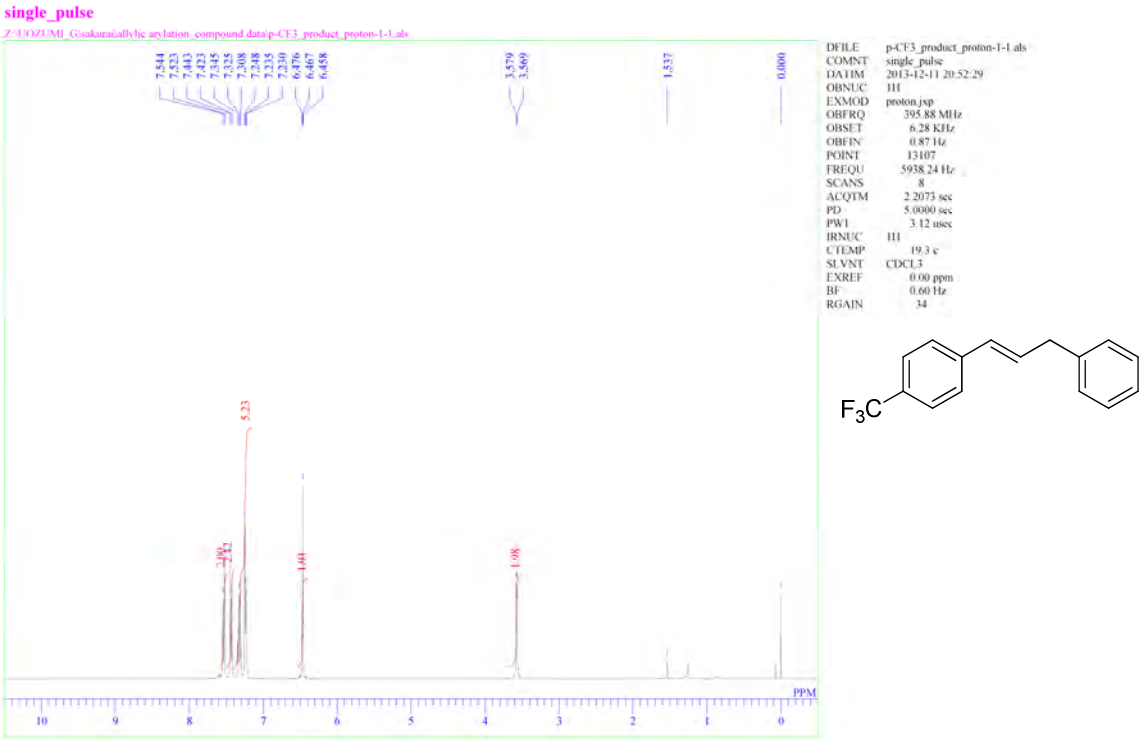

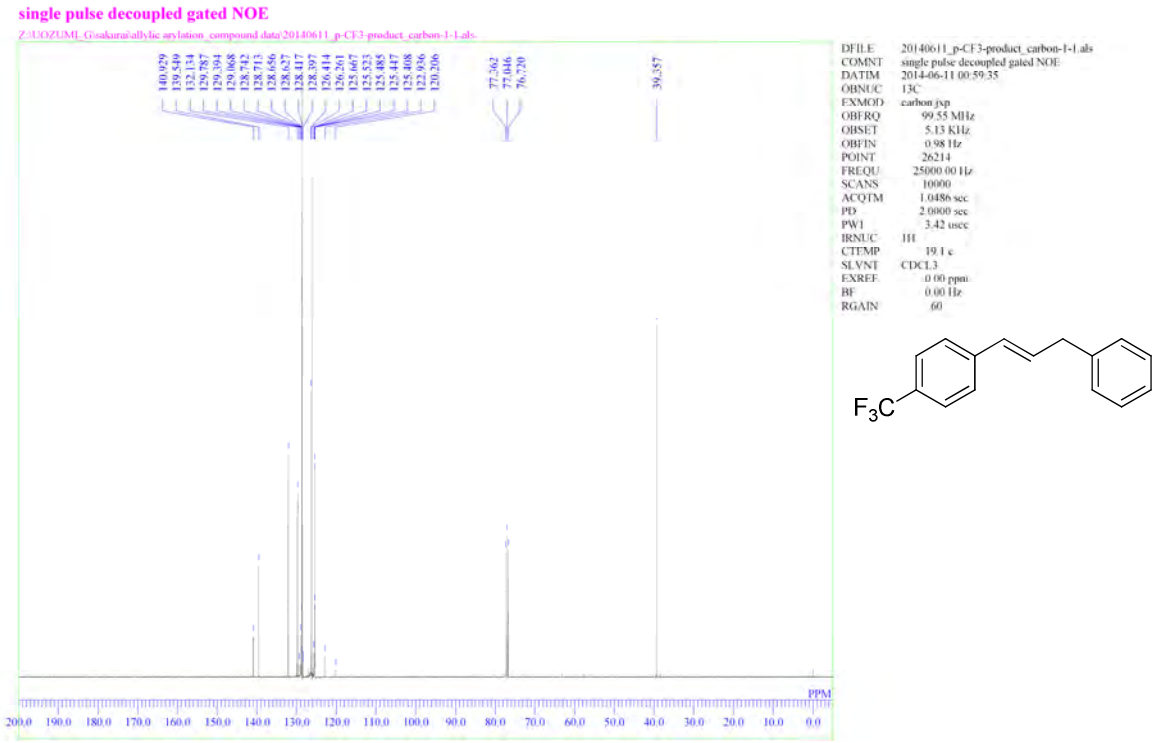

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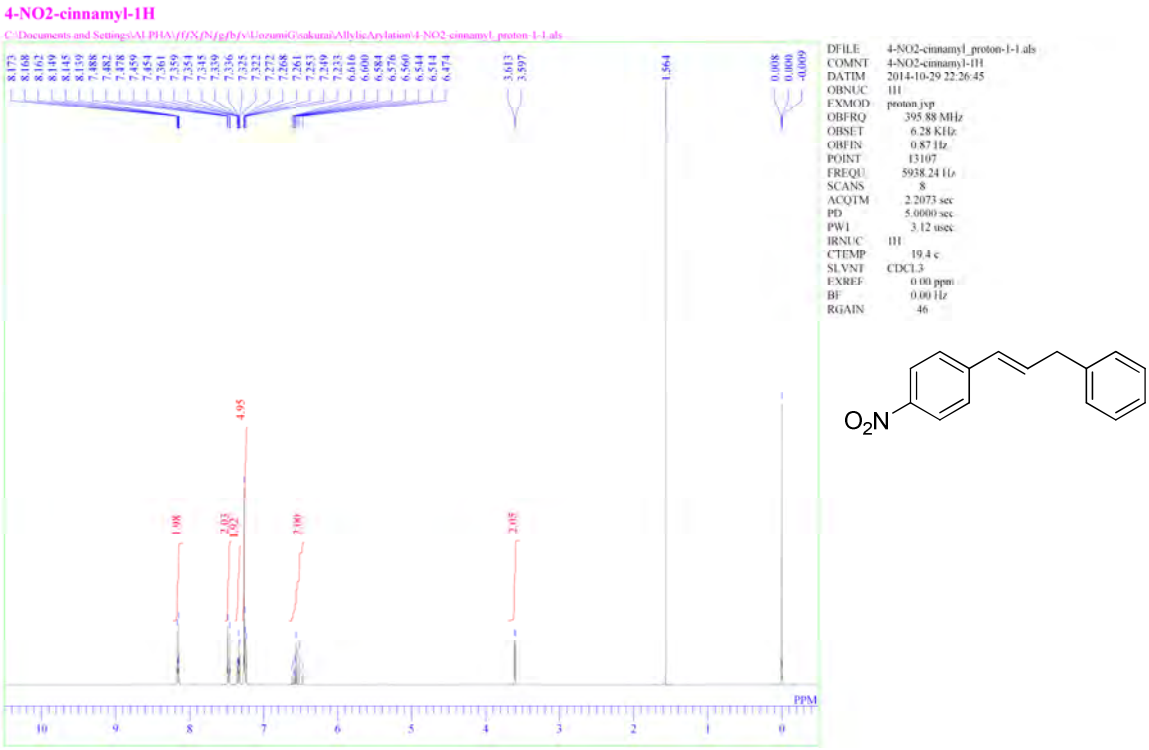

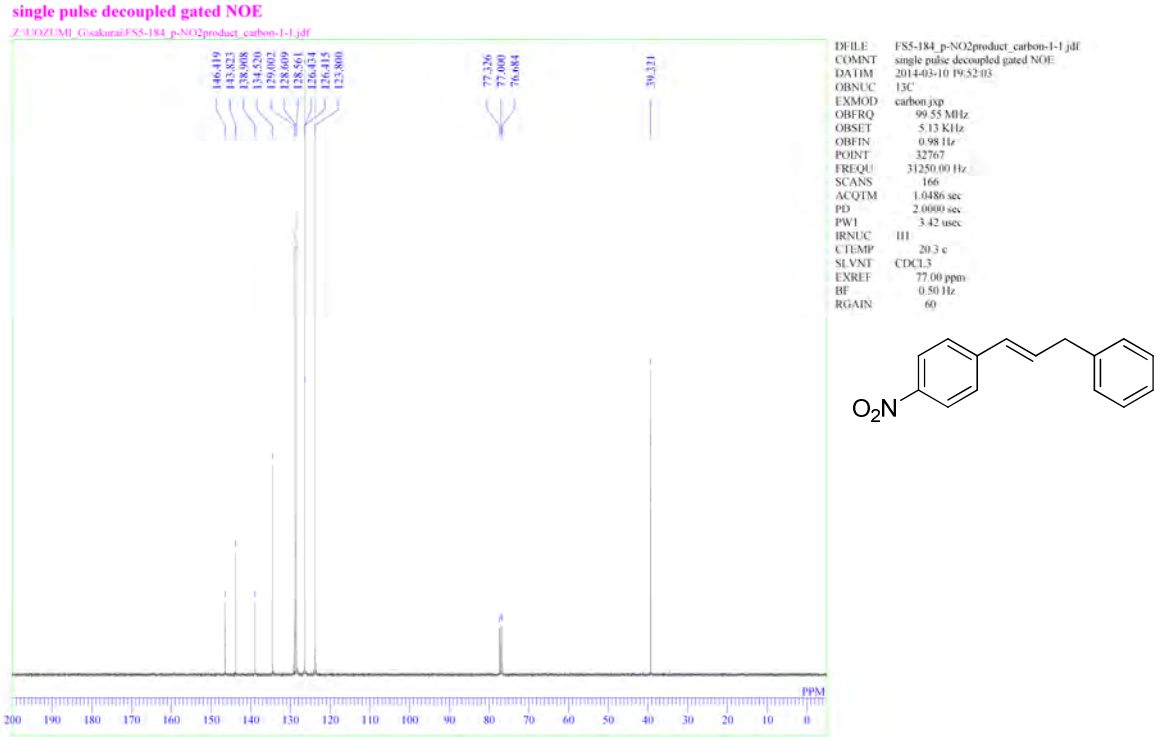

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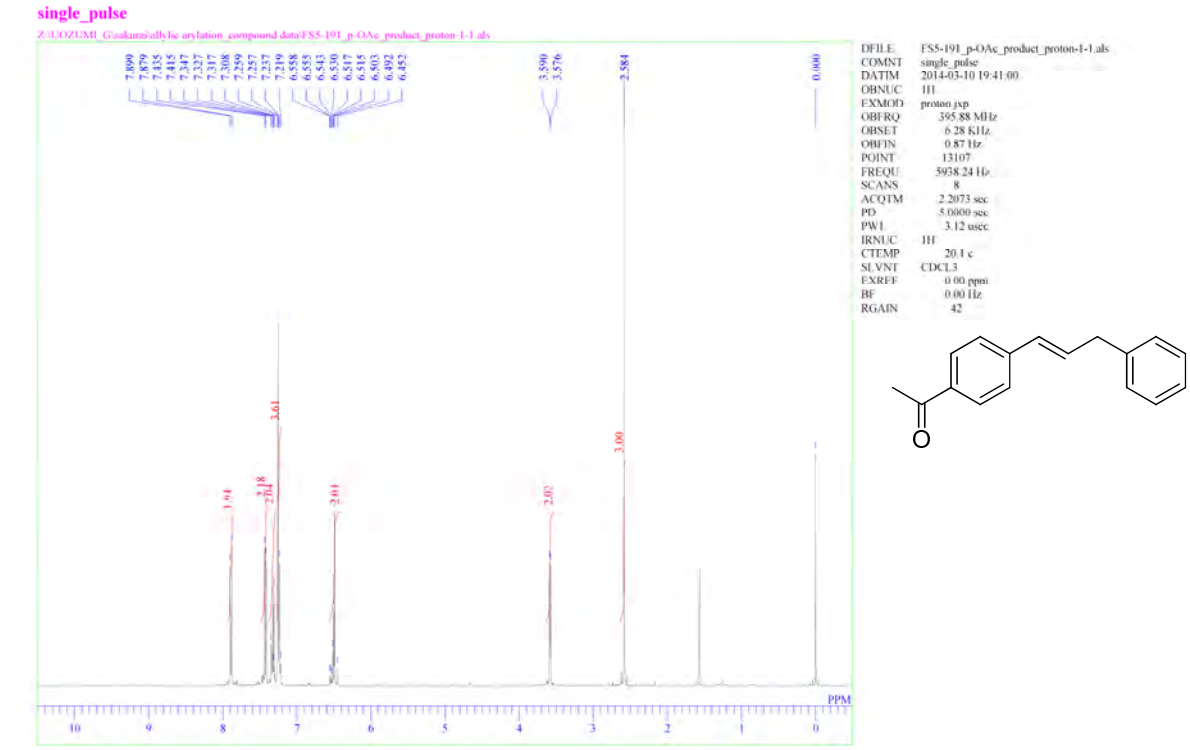

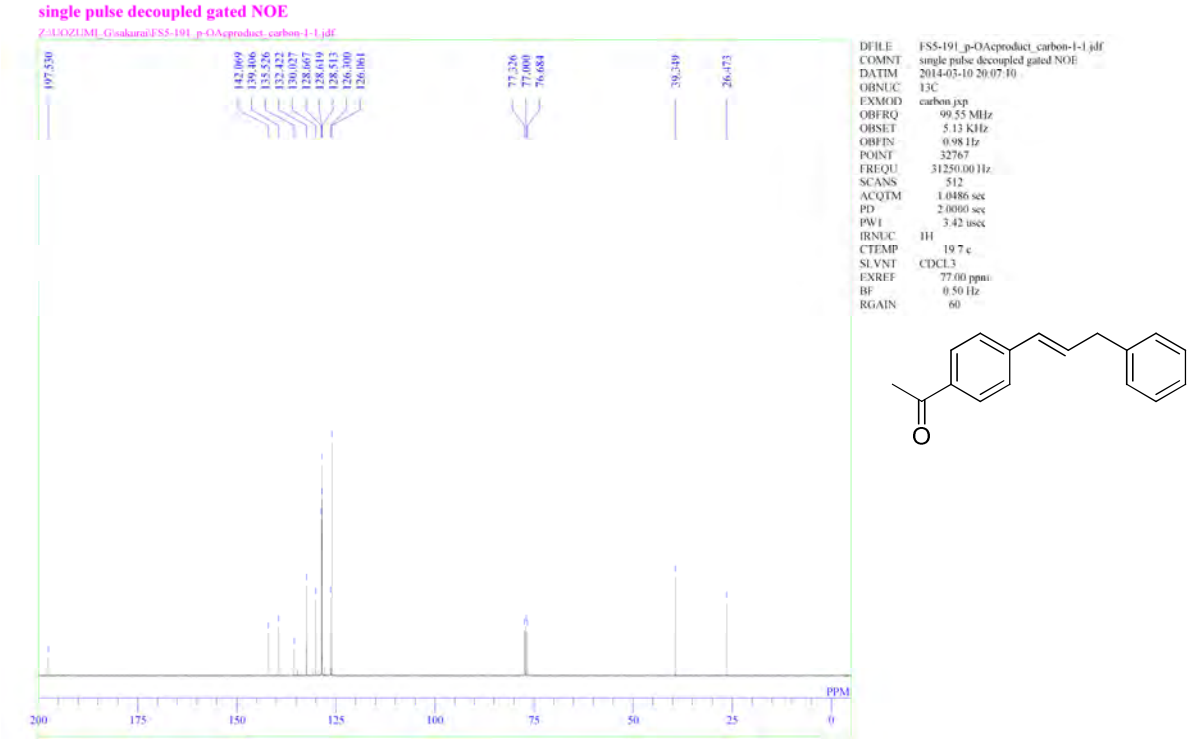

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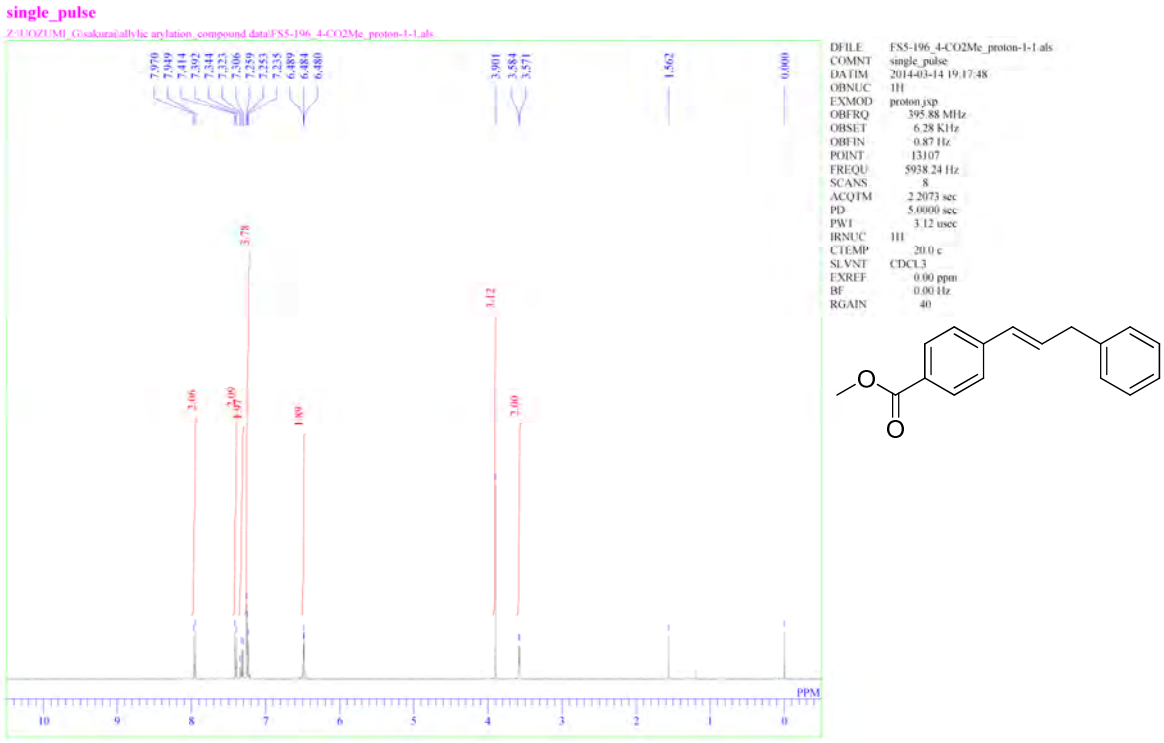

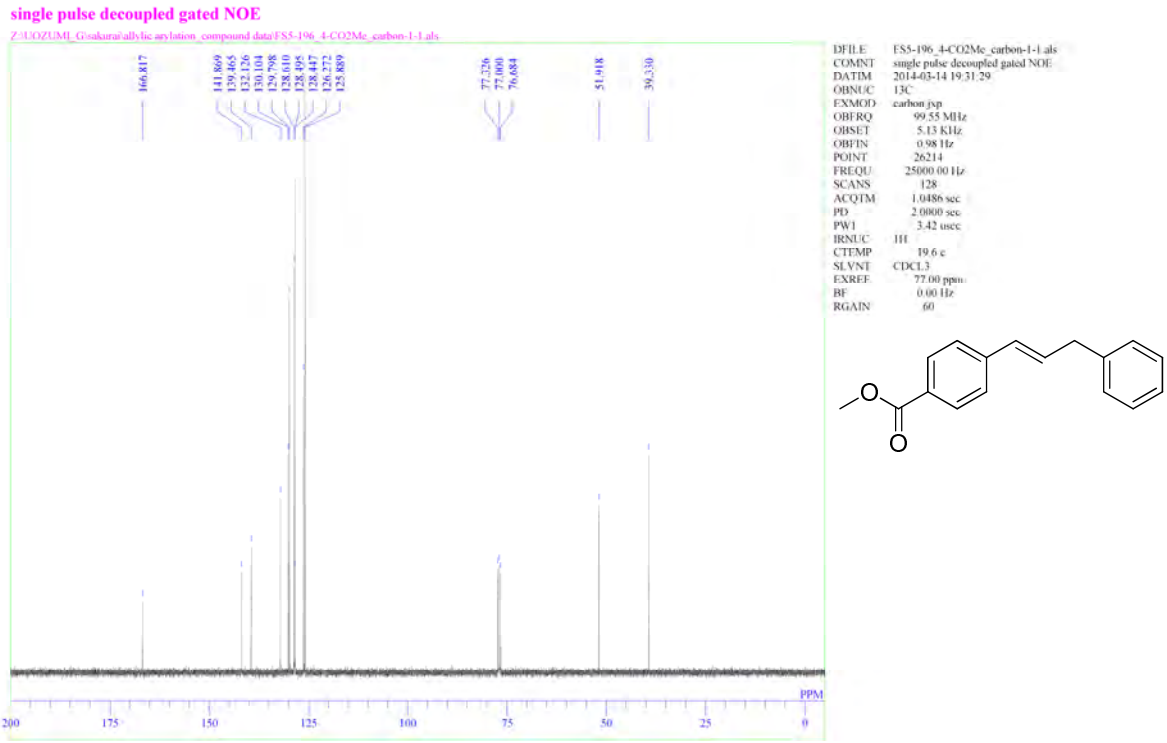

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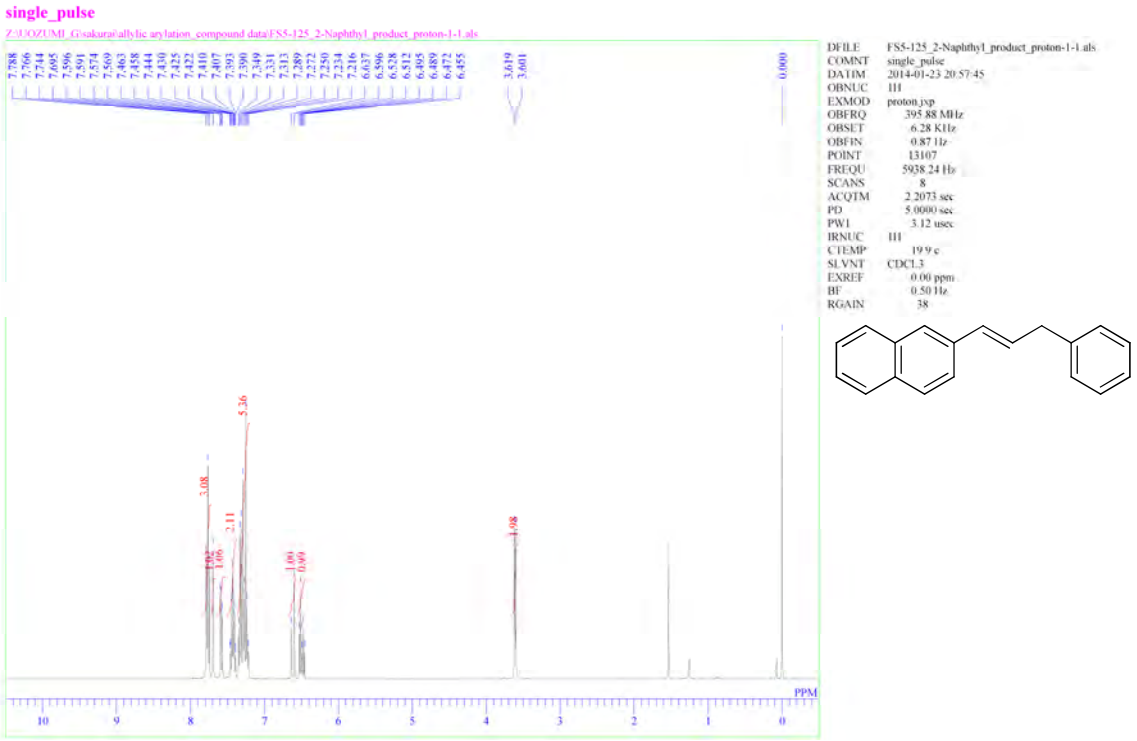

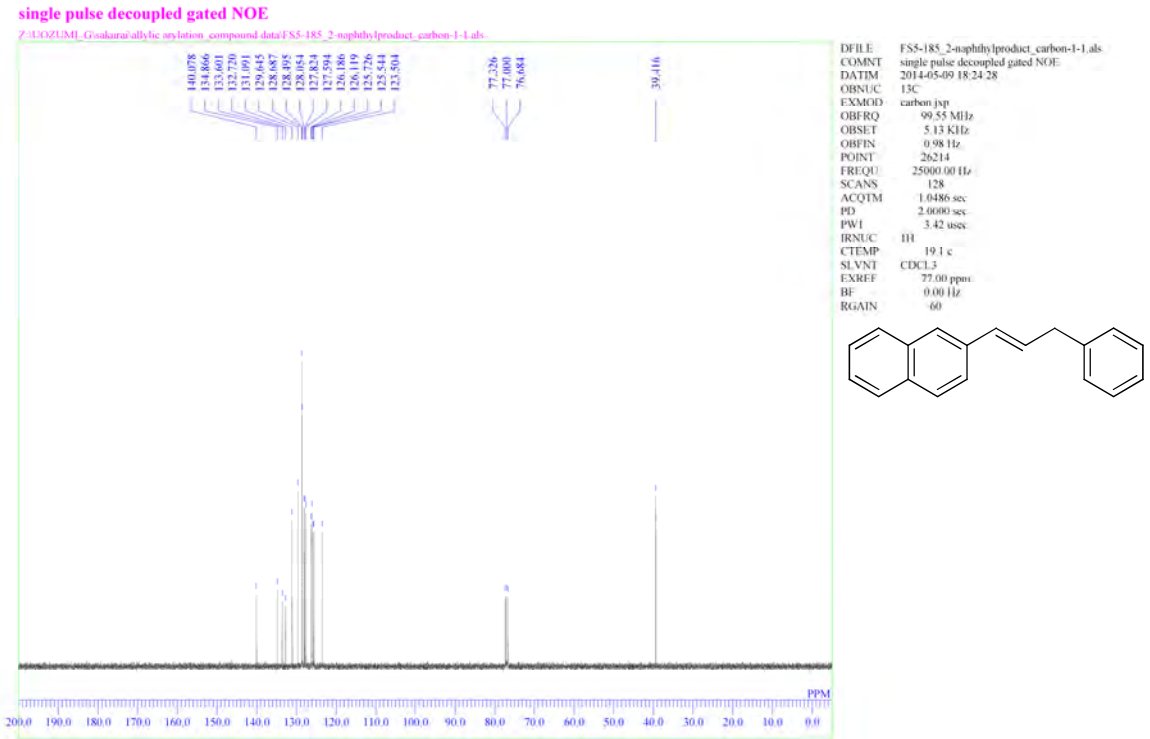

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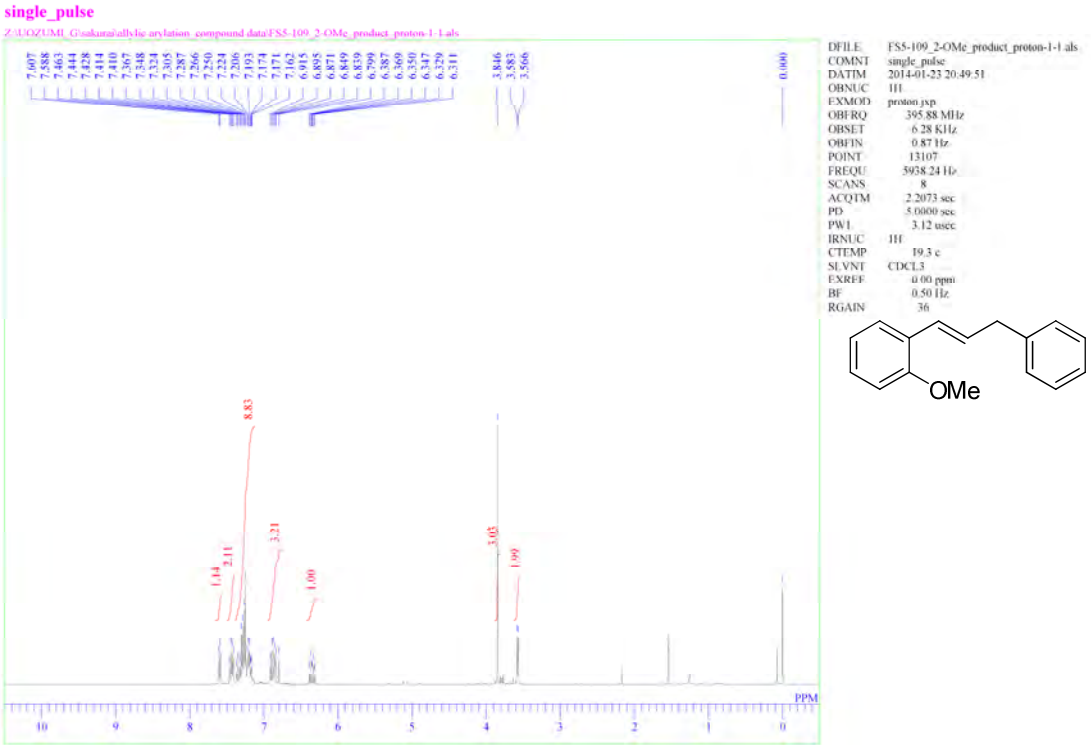
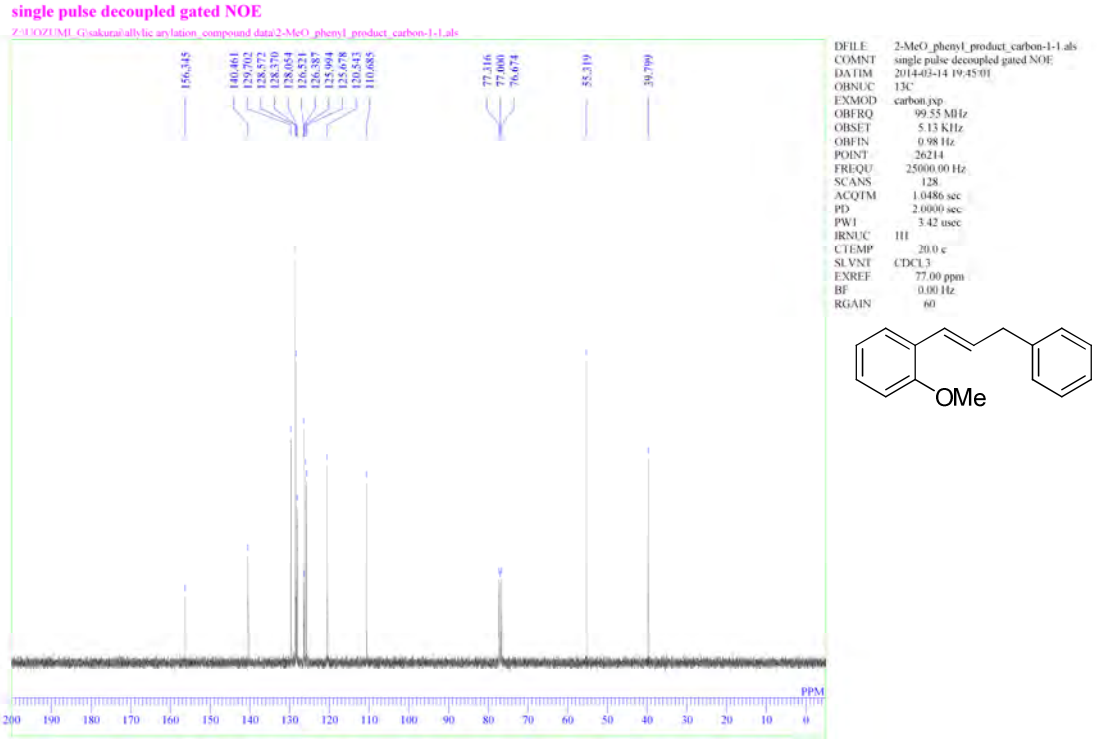
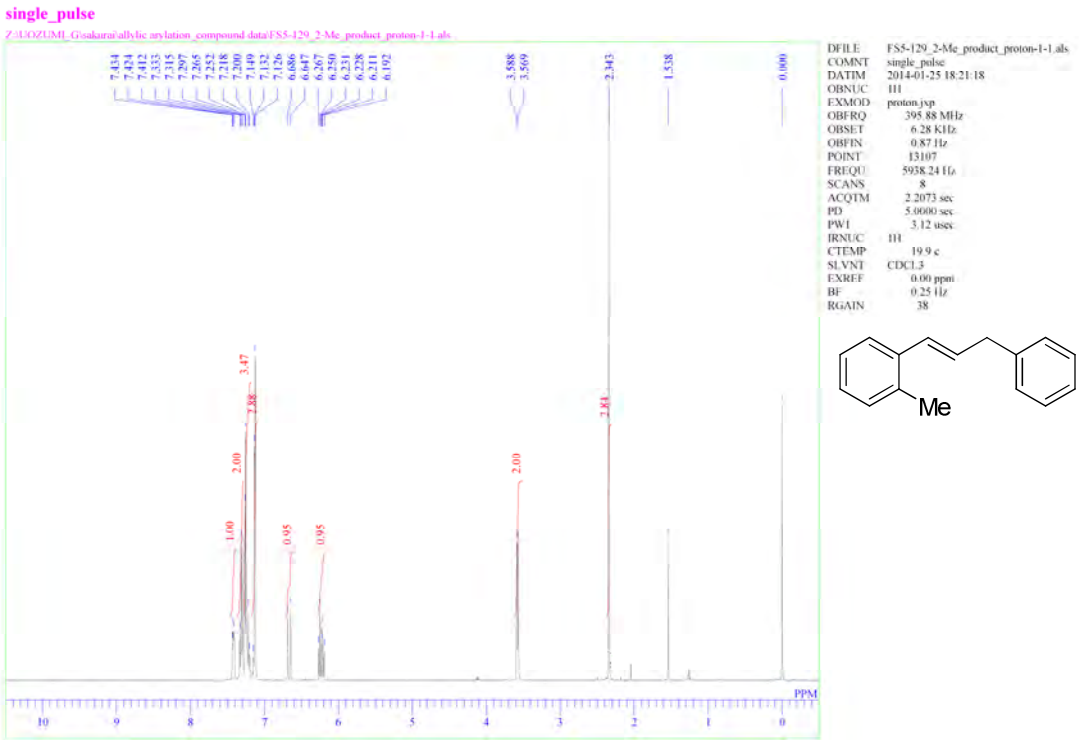
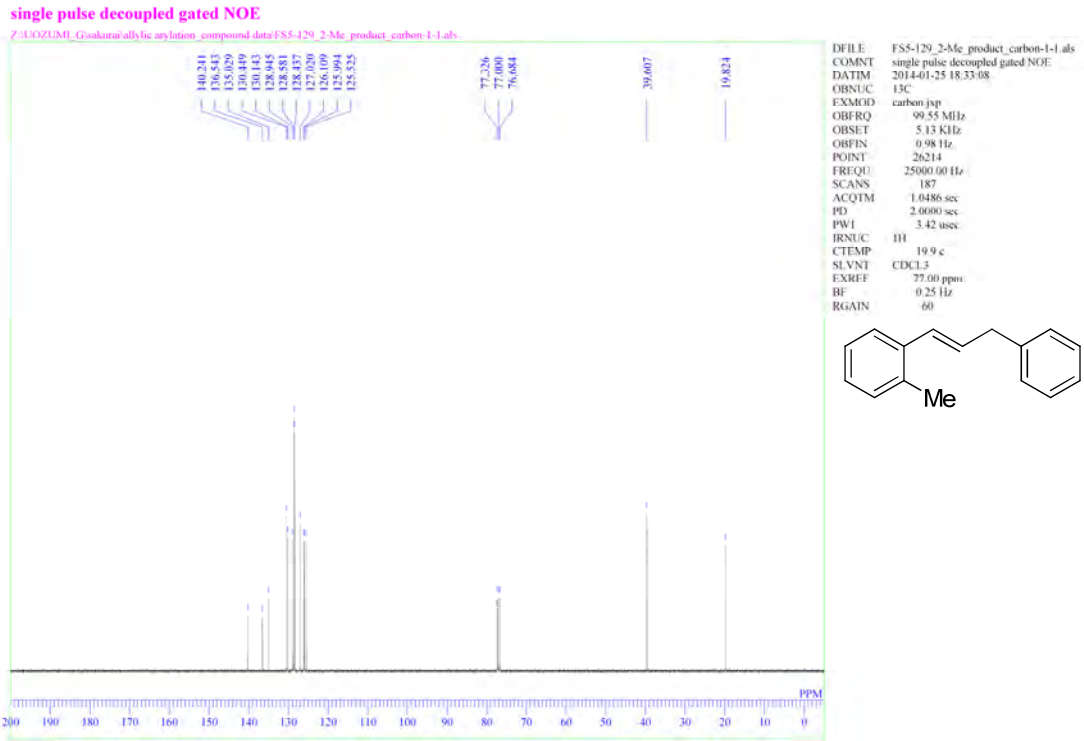




(*E*)-1-(2-Methylphenyl)-3-phenylpropene (4la)





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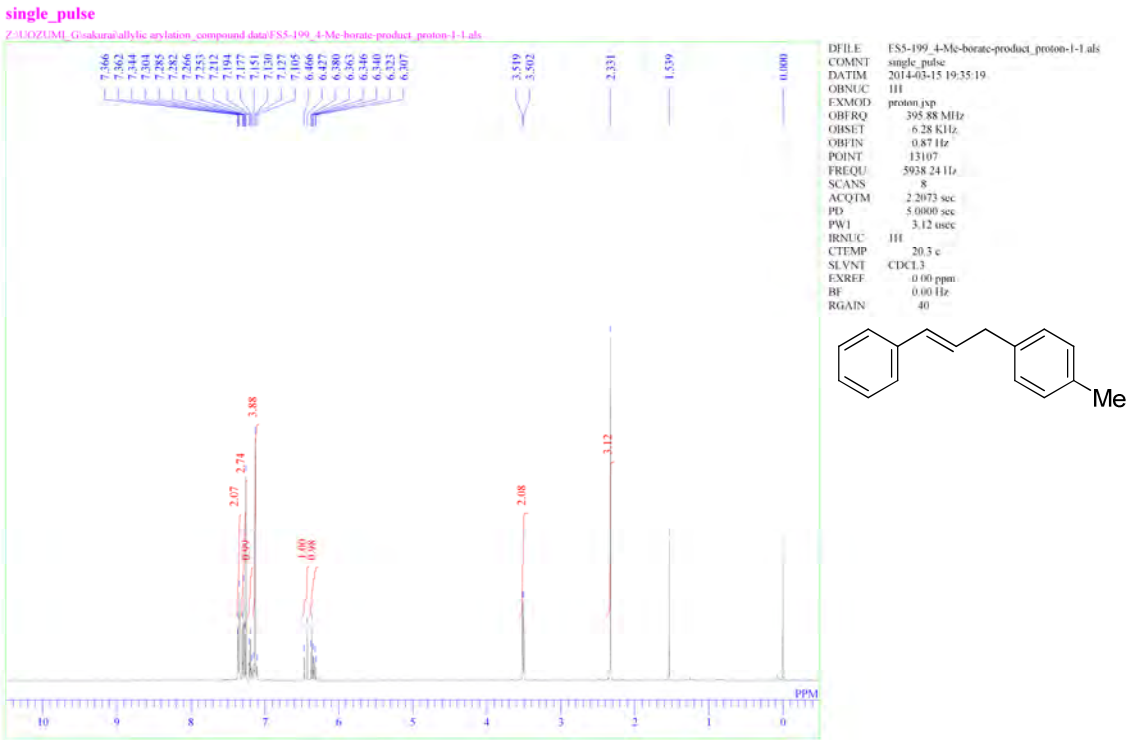
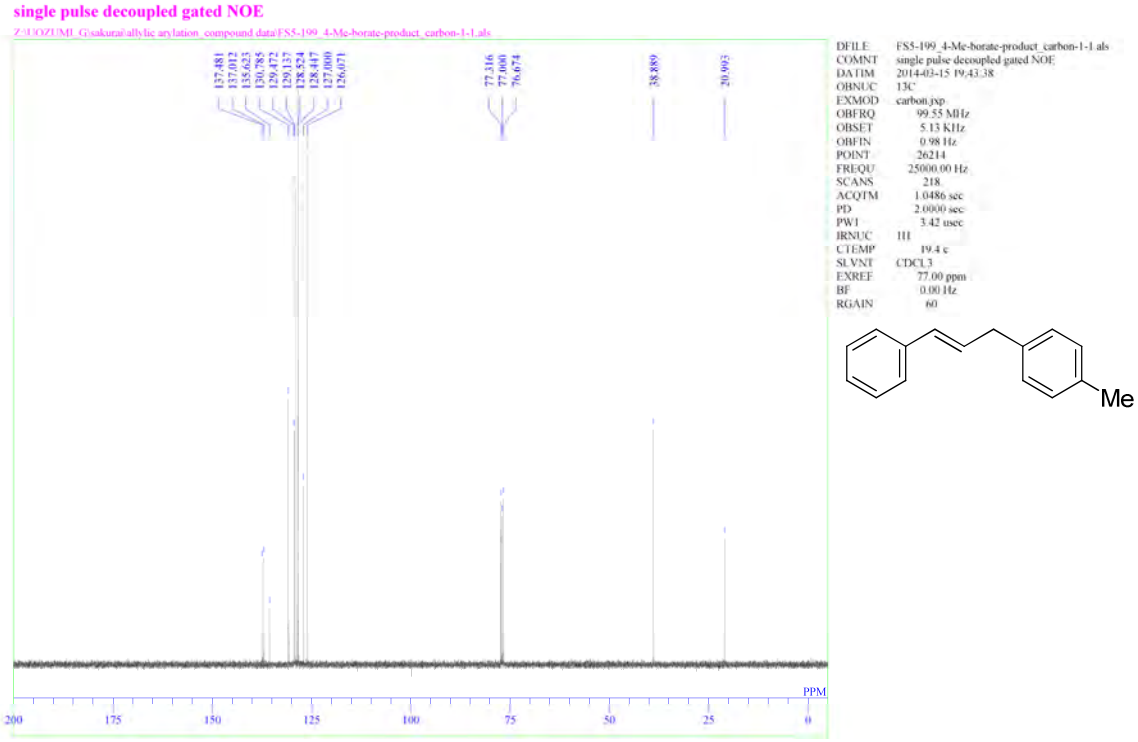
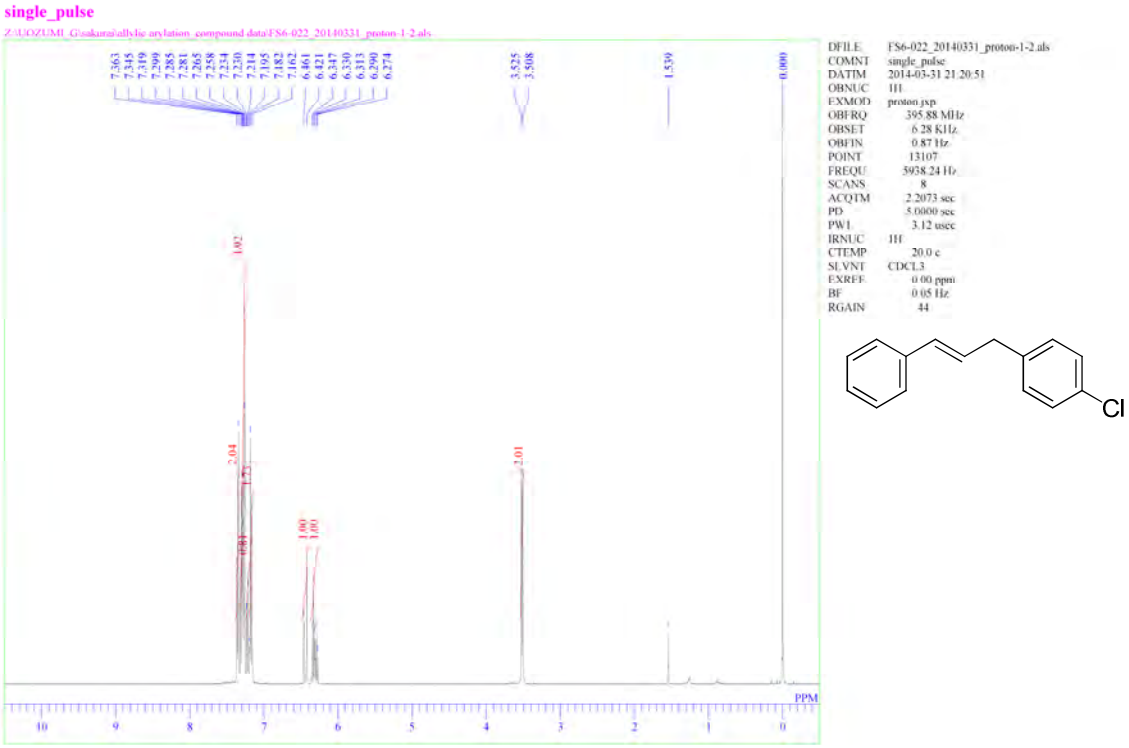
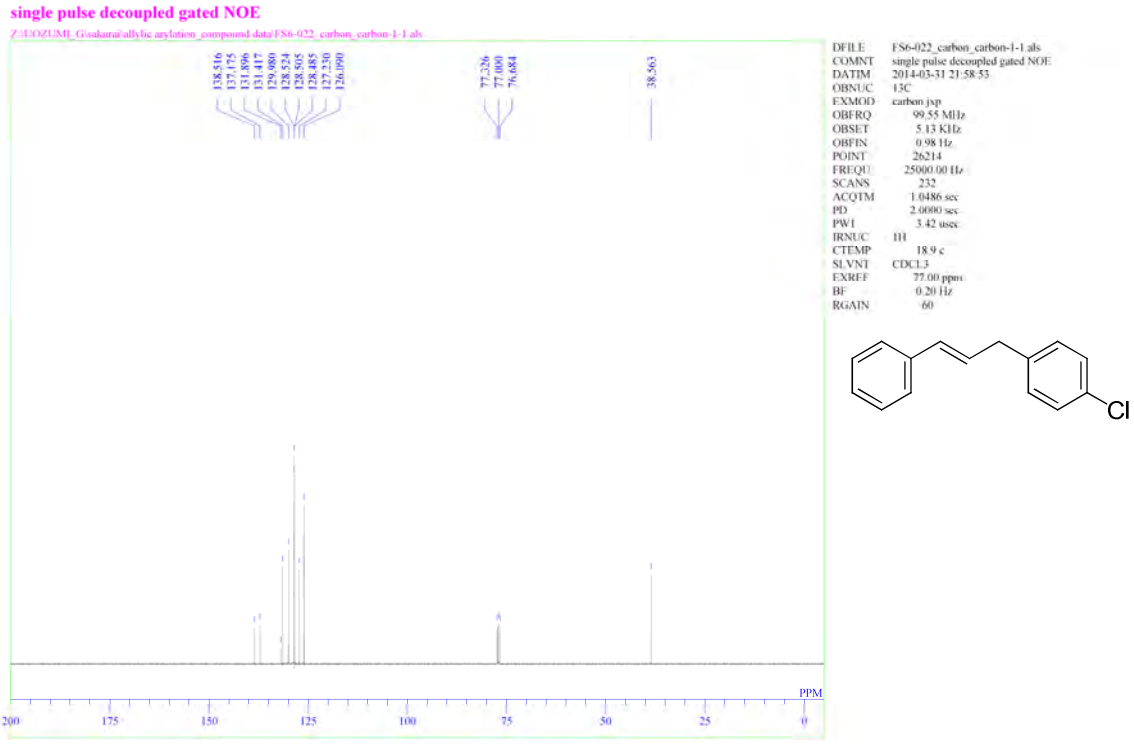


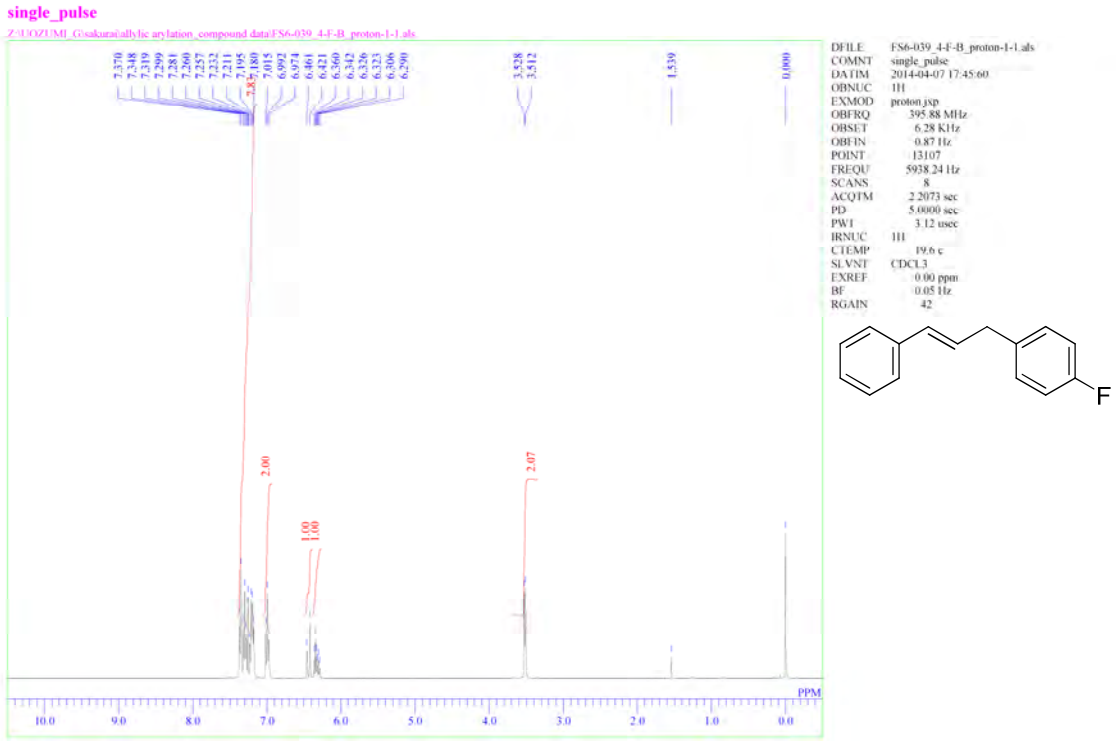


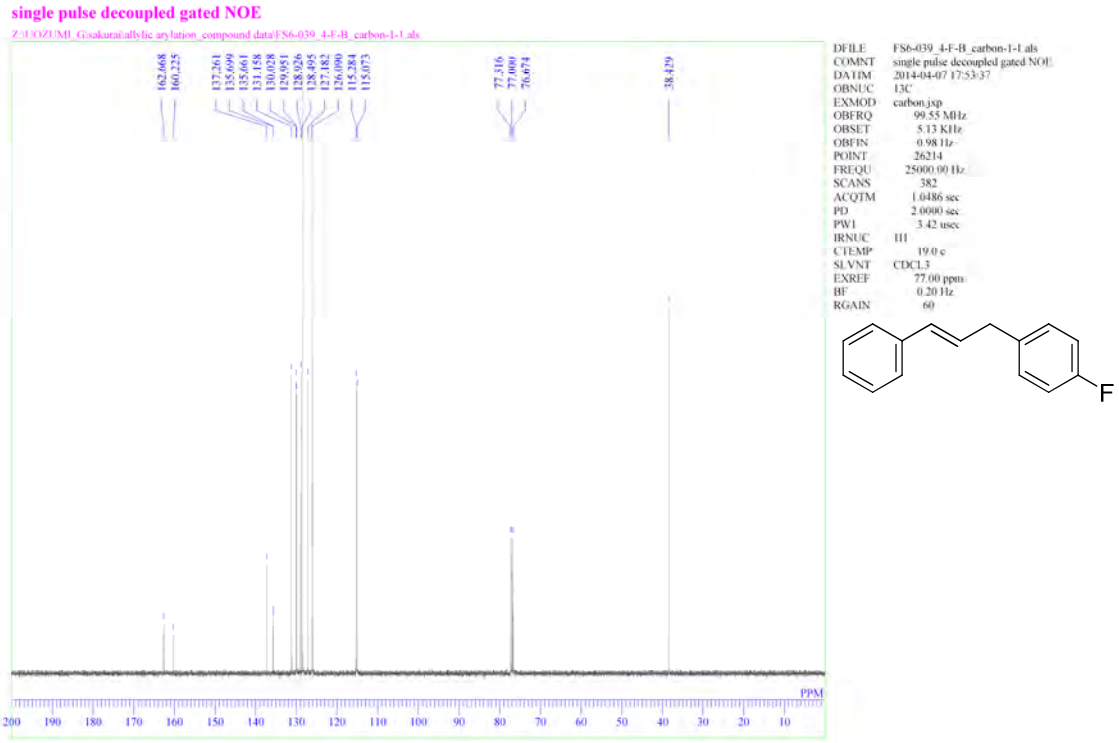
(*E*)-3-(4-Chlorophenyl)-1-phenylpropene (4ac)



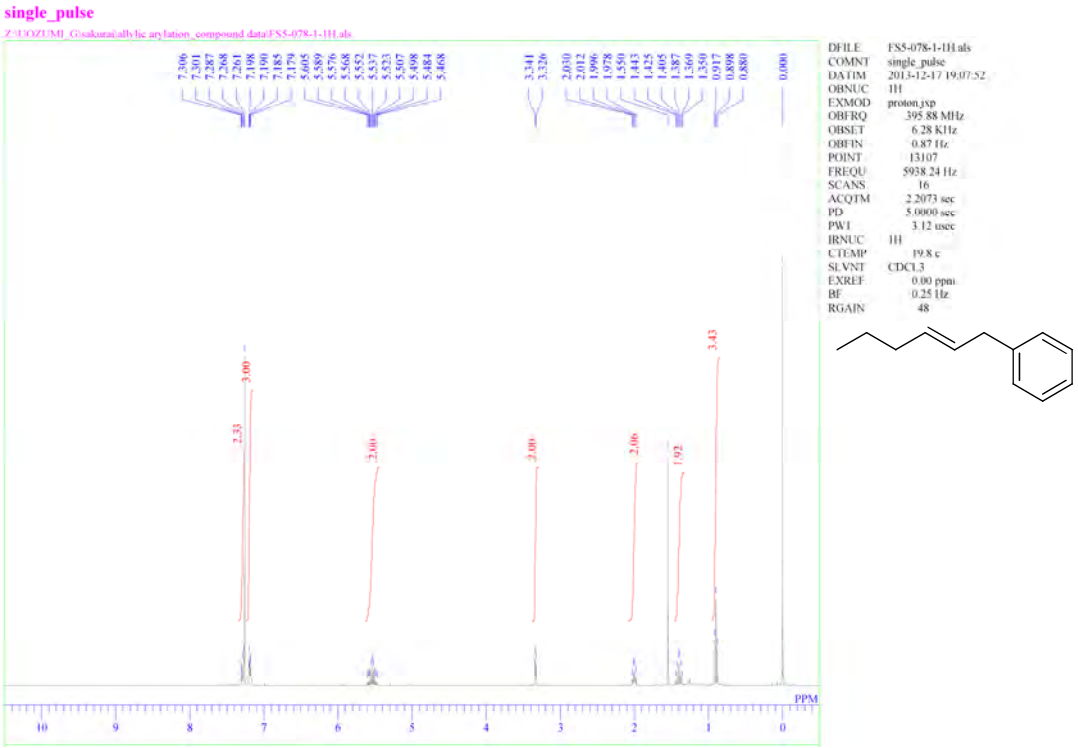


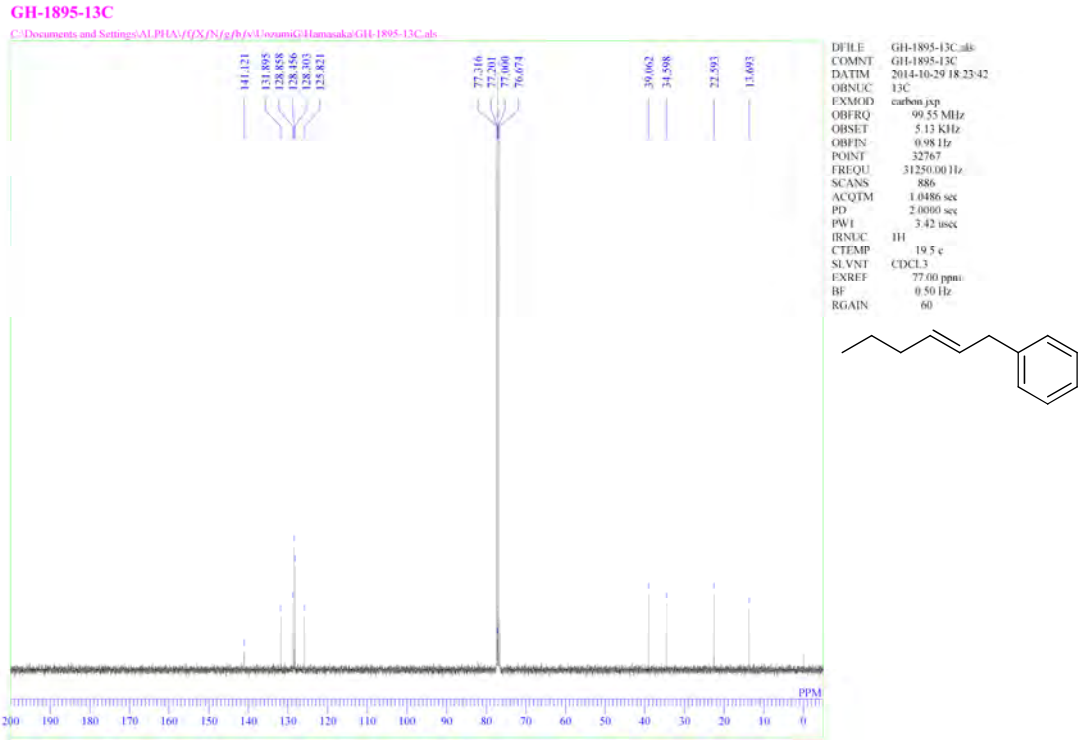
(*E*)-3-(4-Fluorophenyl)-1-phenylpropene (4ad)



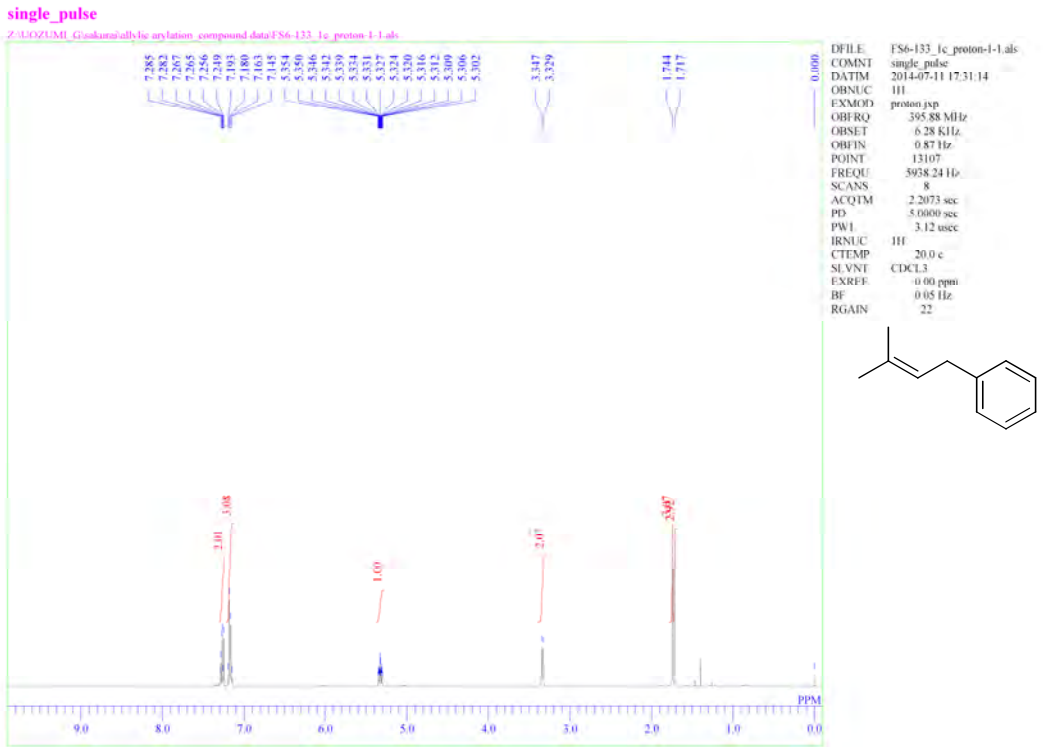


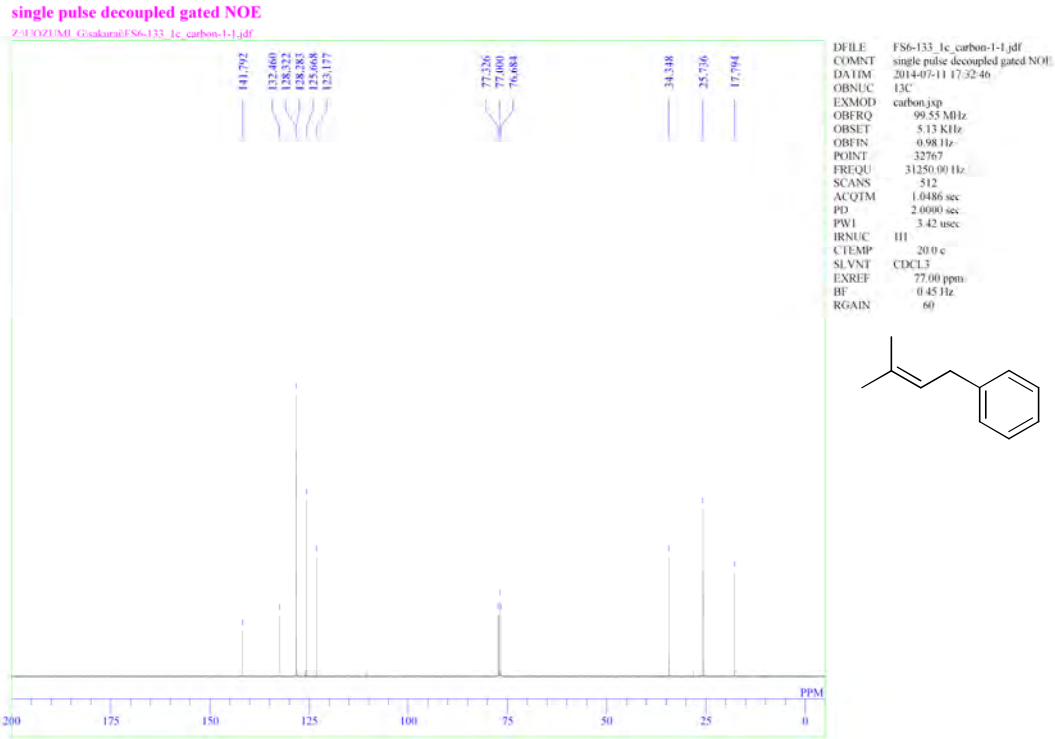
(*E*)-1-Phenyl-2-hexene (4ma)





2-Methyl-4-phenyl-2-butene (4na)





3-Phenylcyclohexene (4oa)

single_pulse

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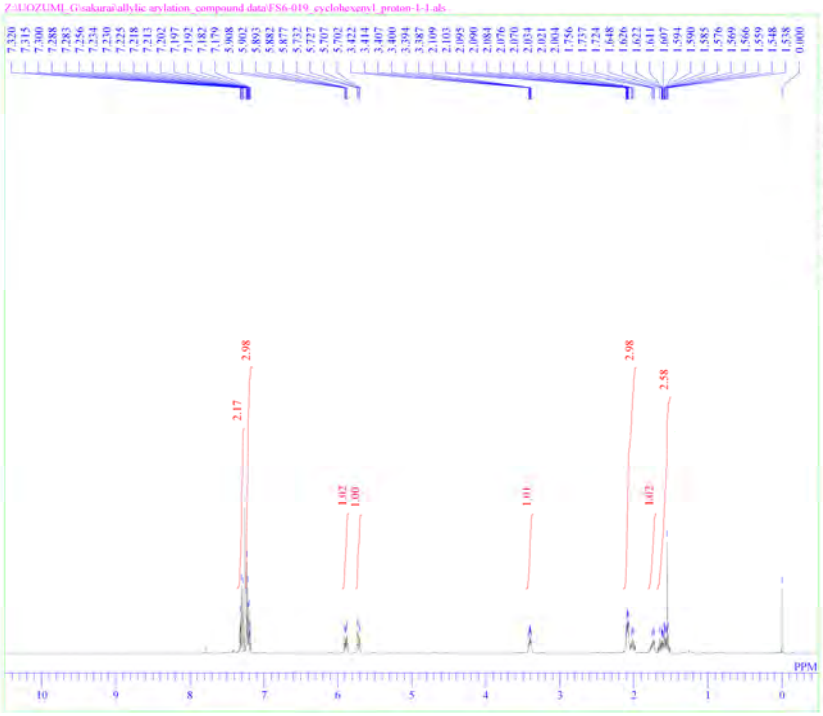

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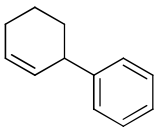
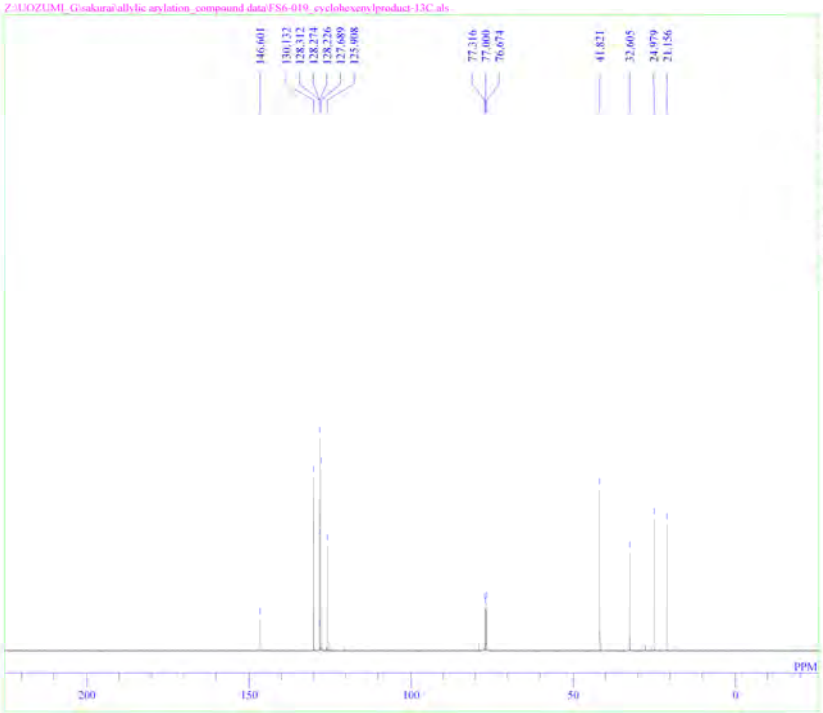
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
POINT	13107
FREQU	5938.24 Hz
SCANS	8
ACQTM	2.2073 sec
PD	5.0000 sec
PW1	3.12 usec
IRNUC	1H
CTEMP	19.8 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.00 Hz
RGAIN	38



single pulse decoupled gated NOE

Z:\UOZUMI_G\sakurai\allylic arylation_compound data\ES6-019_cyclohexenylproduct-13C.als



DFILE	ES6-019_cyclohexenylproduct-13C.als
COMNT	single pulse decoupled gated NOE
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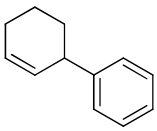
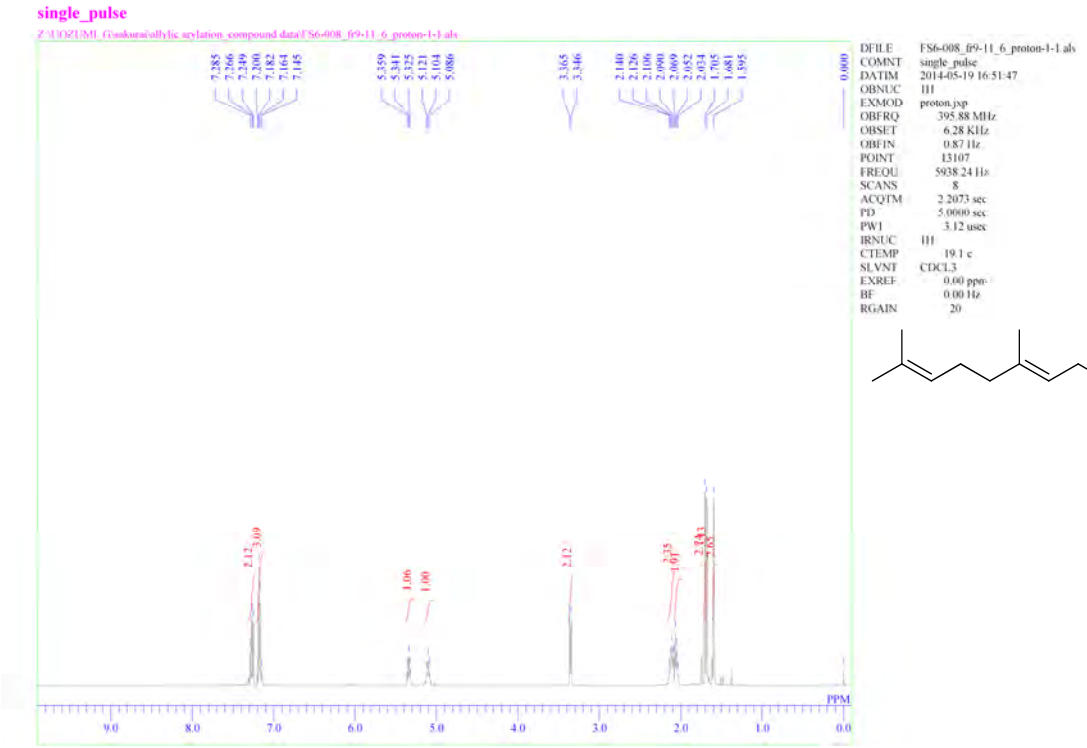
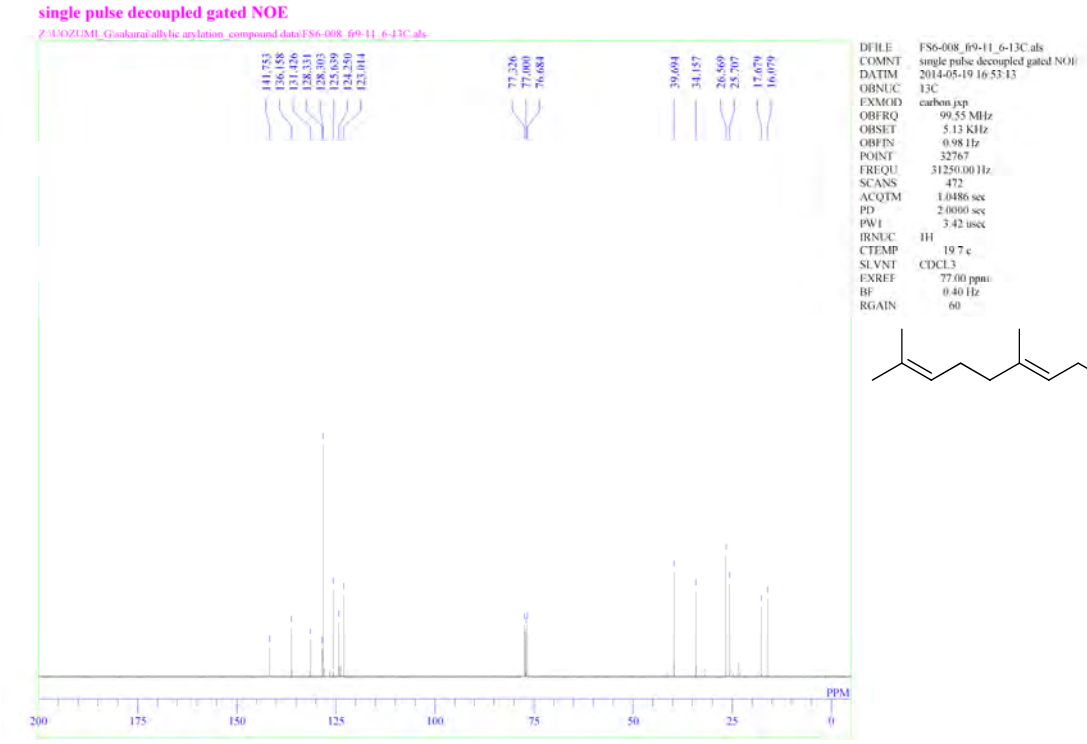
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	32767
FREQU	31250.00 Hz
SCANS	512
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.42 usec
IRNUC	1H
CTEMP	19.4 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.50 Hz
RGAIN	60



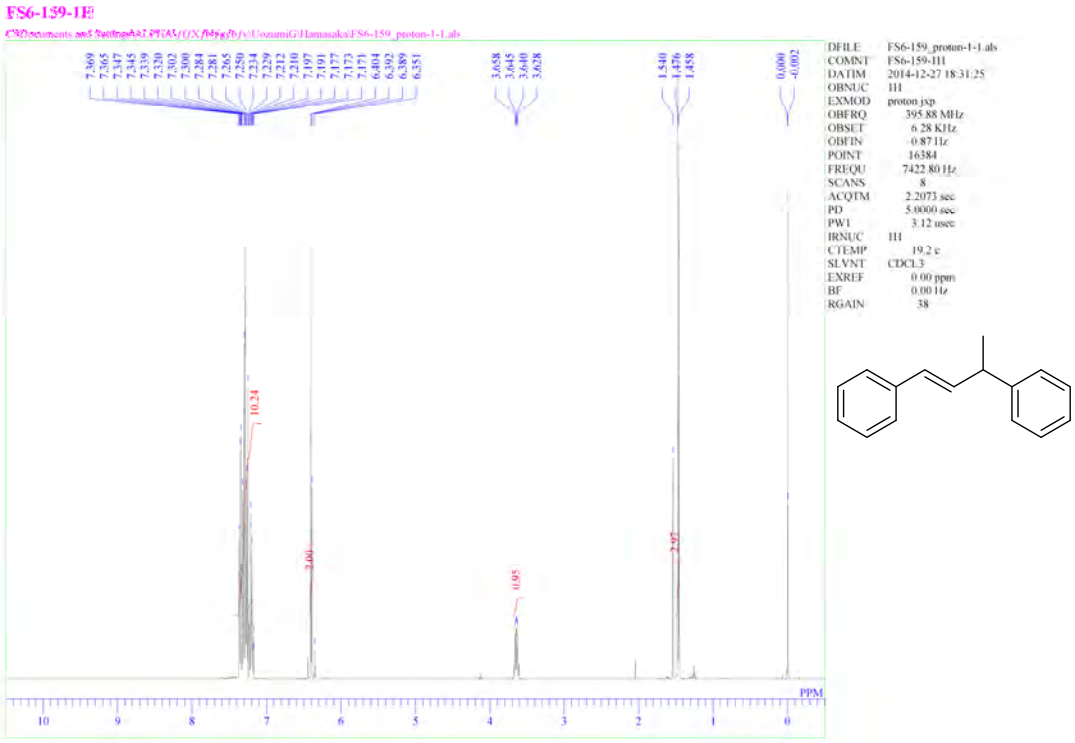
(Z)-3,7-Dimethyl-1-phenyl-2,6-octadiene (4pa)

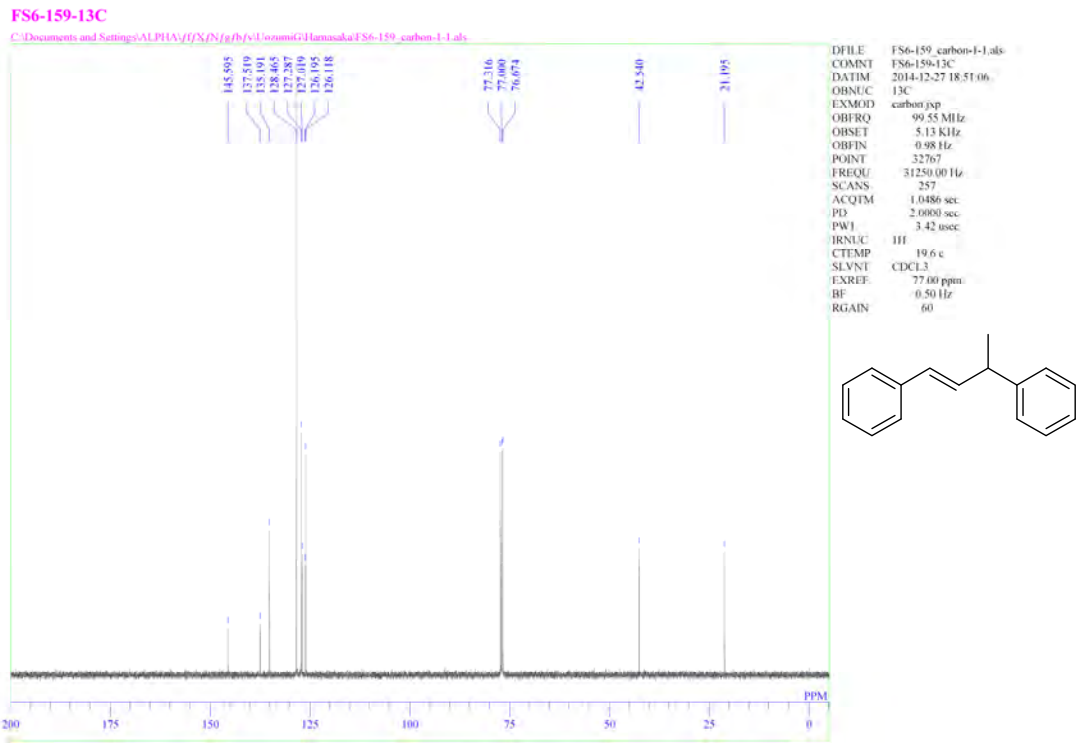
(*E*)-3,7-Dimethyl-1-phenyl-2,6-octadiene (4qa)



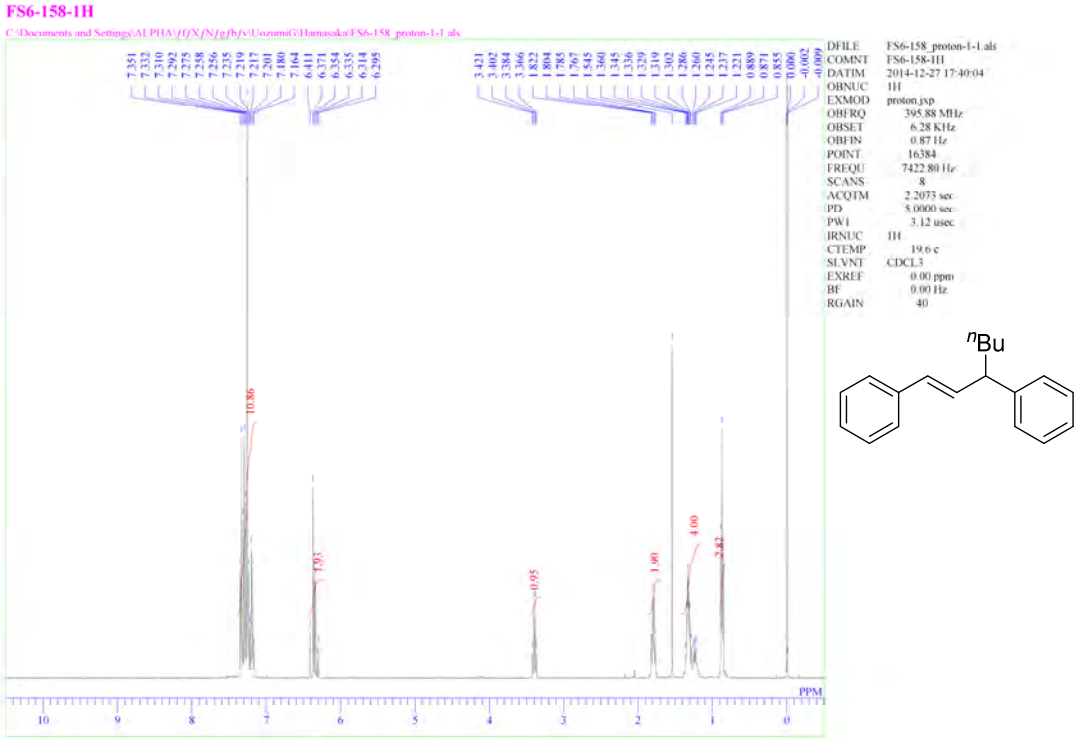


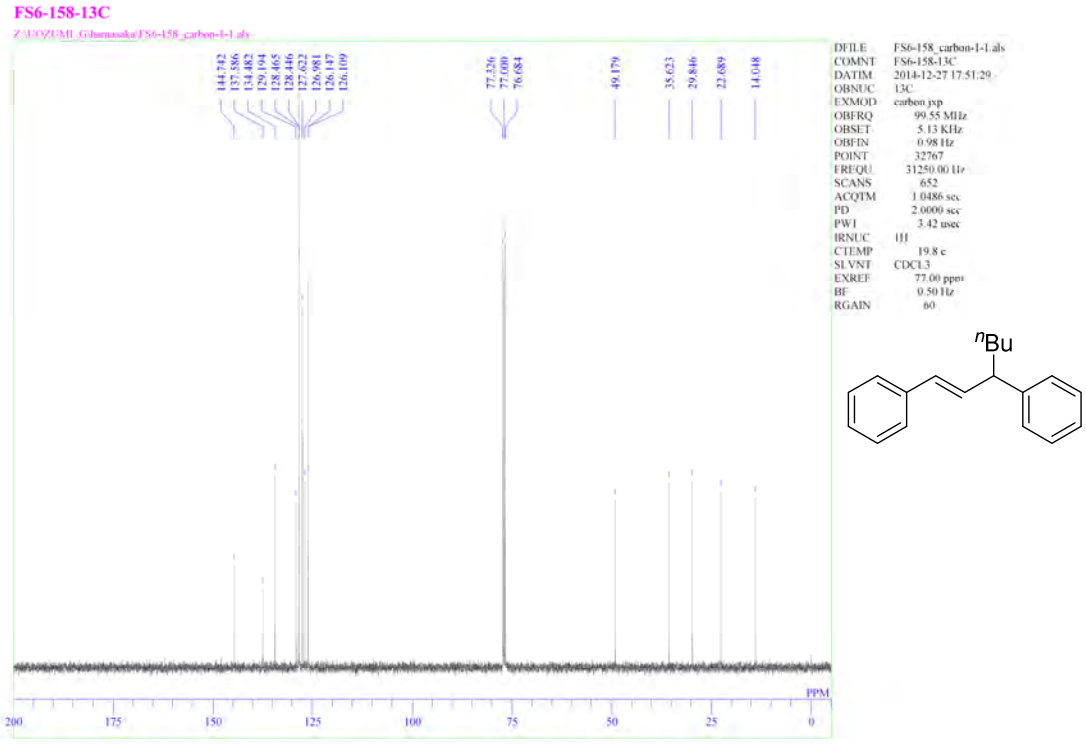
(*E*)-1,3-Diphenyl-1-butene (4ra)



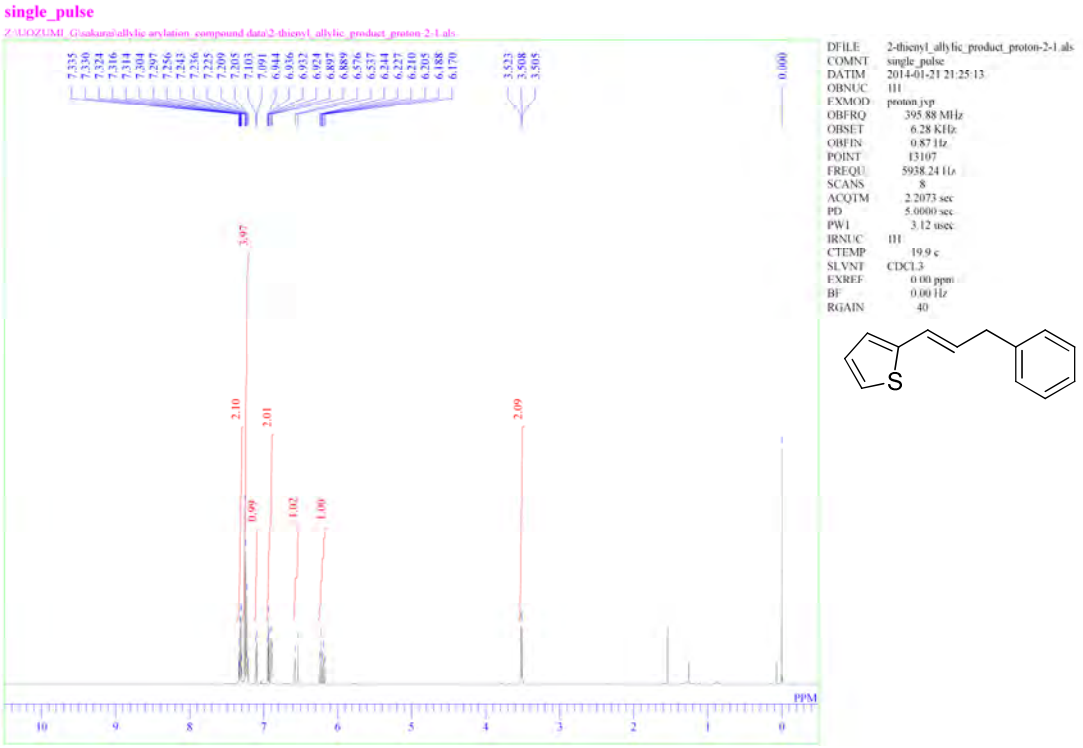


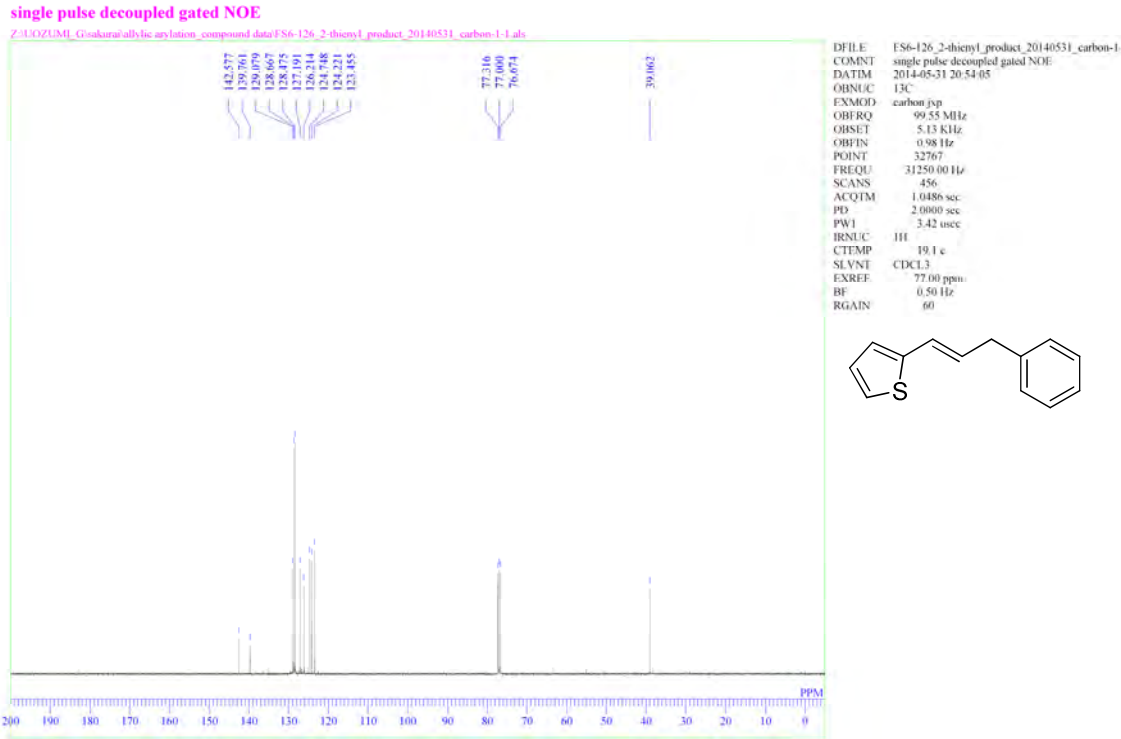
(*E*)-1,3-Diphenyl-1-heptene (4sa)





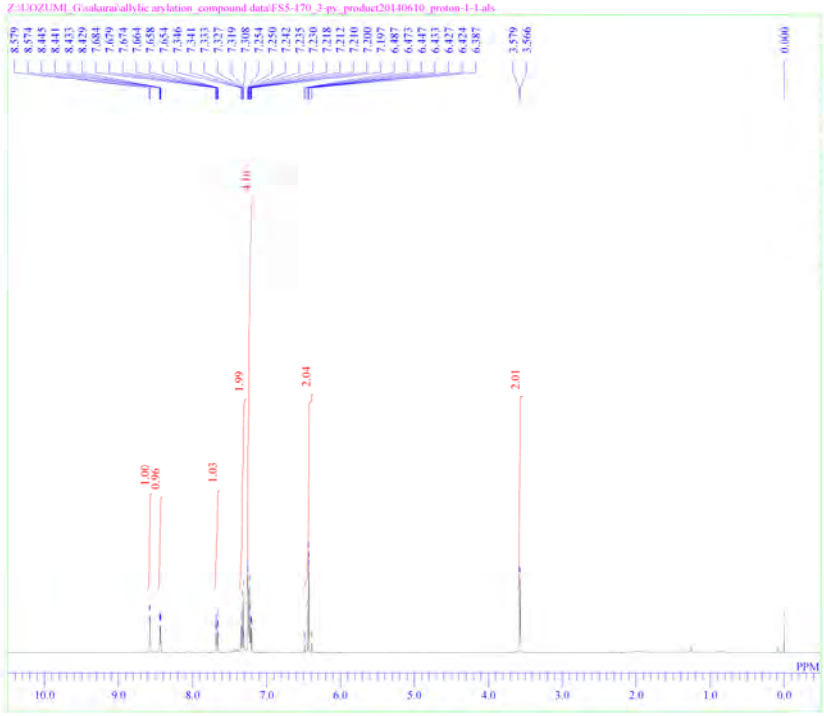
(*E*)-1-(2-Thiophene)-3-phenylpropene (4ta)



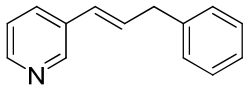


(*E*)-1-(3-Pyridine)-3-phenylpropene (4ua)

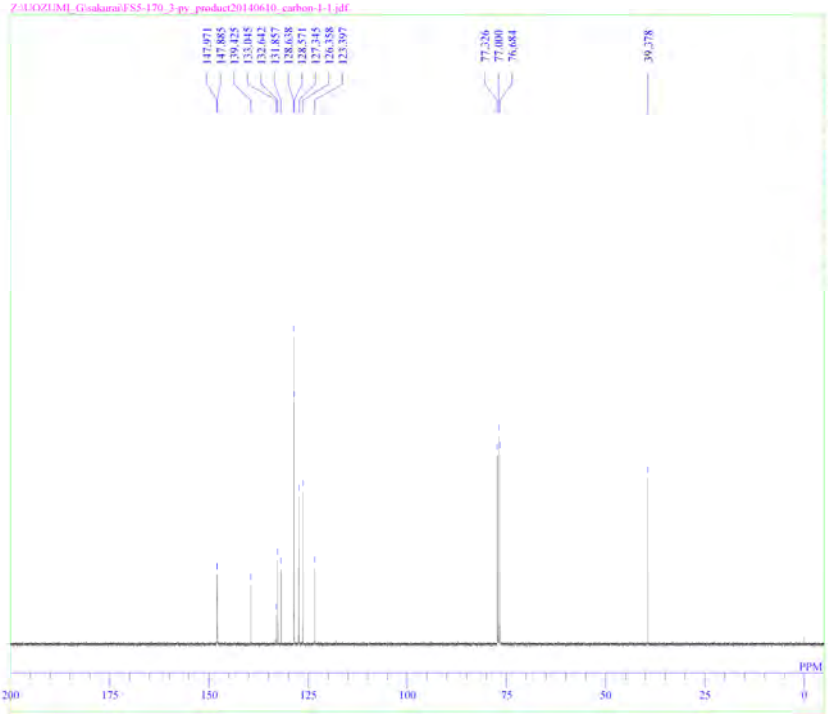
single_pulse



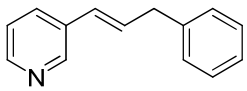
DFILE	FS5-170_3-py_product20140610_proton-1-1.als
COMNT	single_pulse
DATIM	2014-06-10 21:24:26
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
POINT	13107
FREQU	5938.24 Hz
SCANS	8
ACQTM	2.2073 sec
PD	5.0000 sec
PW1	3.12 usec
IRNUC	1H
CTEMP	19.2 c
SLVNT	CDCl3
EXREF	0.00 ppm
BF	0.00 Hz
RGAIN	30



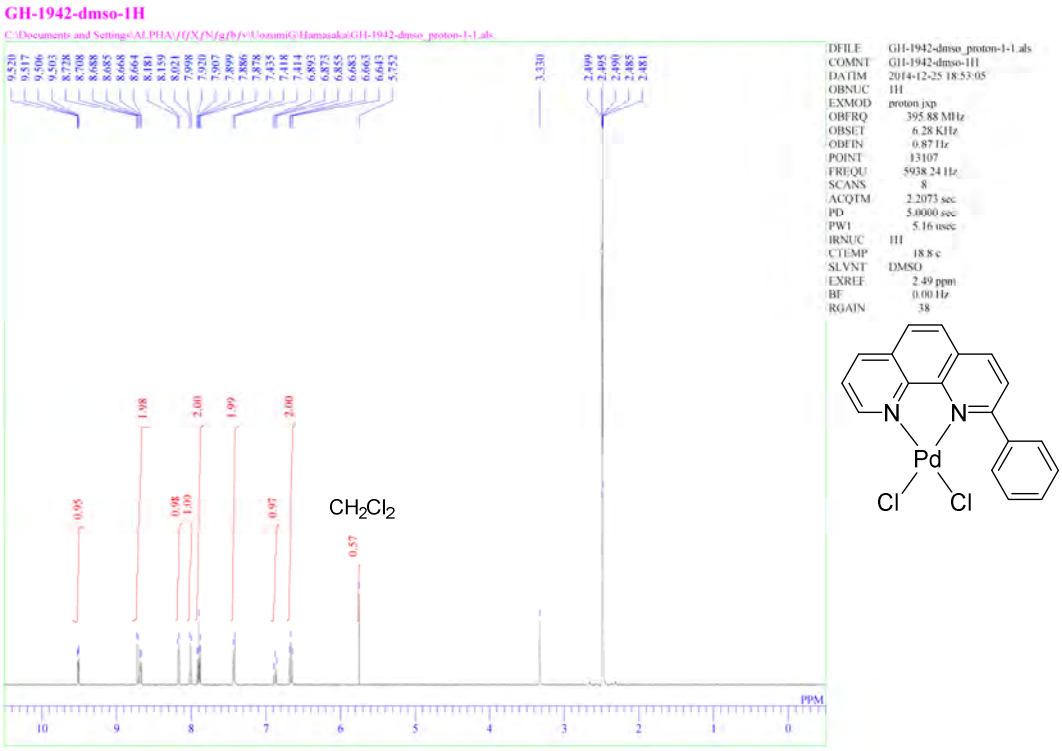
single pulse decoupled gated NOE

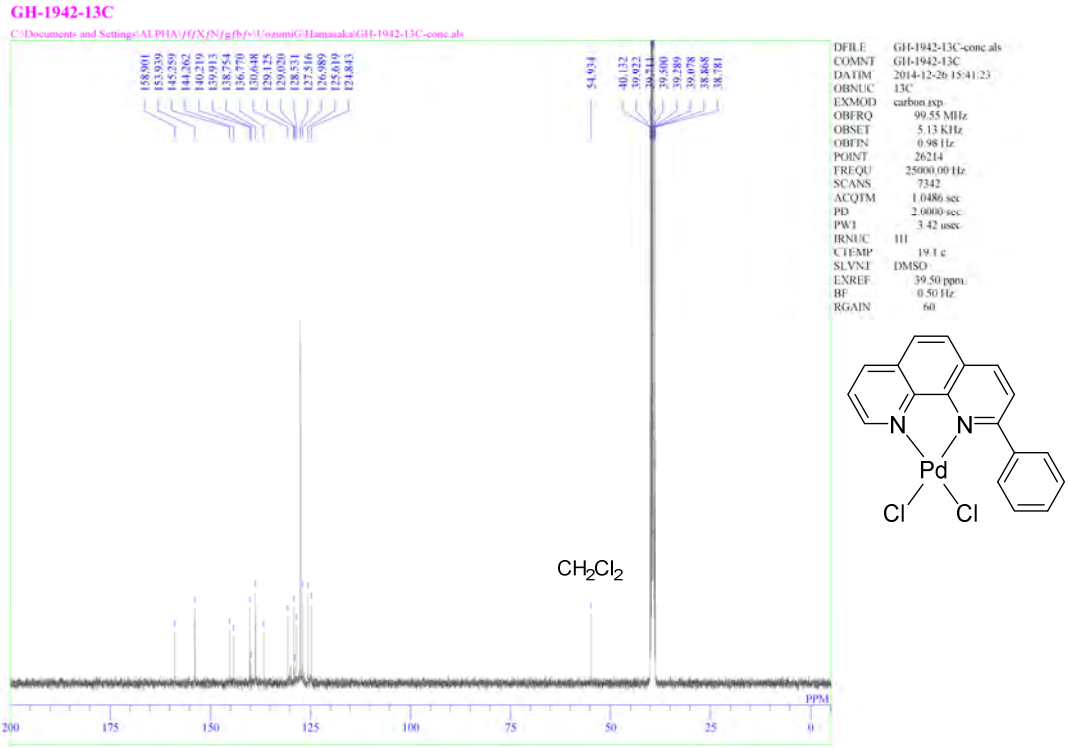


DFILE	FS5-170_3-py_product20140610_carbon-1-1.jdf
COMNT	single pulse decoupled gated NOE
DATIM	2014-06-10 21:41:45
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	32767
FREQU	31250.00 Hz
SCANS	536
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.42 usec
IRNUC	1H
CTEMP	19.2 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	0.50 Hz
RGAIN	60



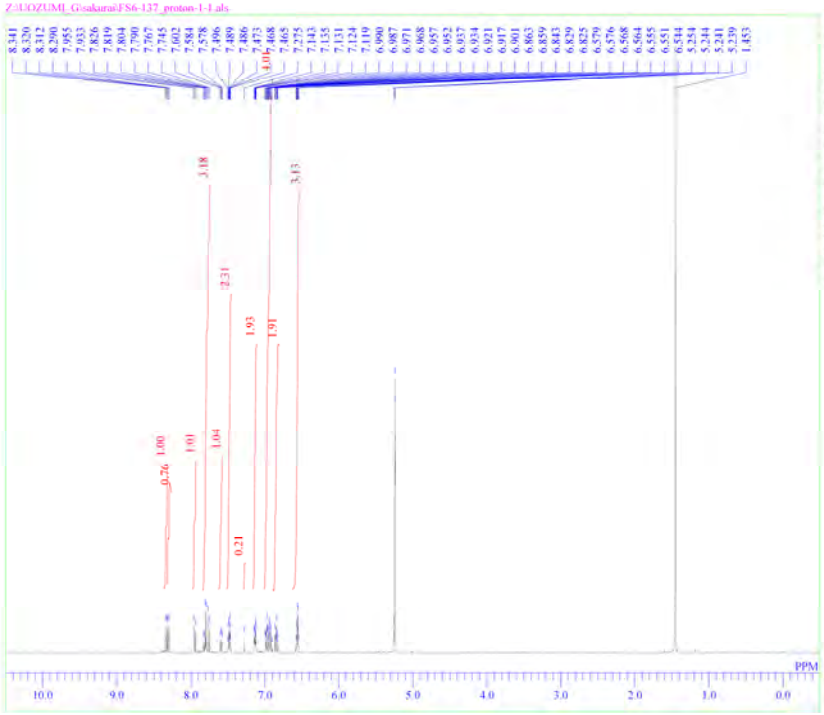
Dichloro-(2-phenyl-1,10-phenanthroline)palladium (6)



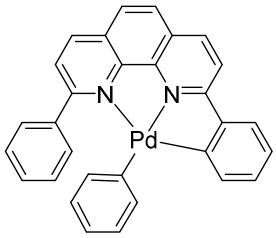


Phenyl-[2-(9-phenyl-1,10-phenanthrolin-2-yl)phenyl]palladium (9)

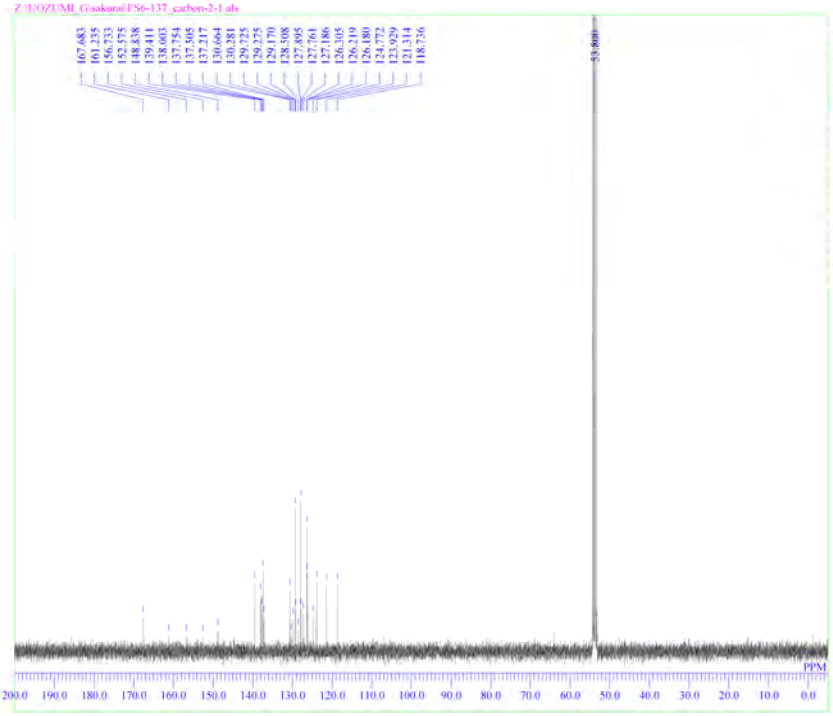
single_pulse




```
DFILE   FS6-137_proton-1-1.als
COMNT   single_pulse
DATIM   2014-08-13 15:06:48
OBNUC   1H
EXMOD   proton.jxp
OBFRQ   395.88 MHz
OBSET   6.28 KHz
OBFIN   0.87 Hz
POINT   13107
FREQU   5938.24 Hz
SCANS   16
ACQTM   2.2073 sec
PD      5.0000 sec
PW1     3.12 usec
IRNUC   1H
CTEMP   20.2 c
SLVNT   CD2CL2
EXREF   0.00 ppm
BF      0.50 Hz
RGAIN   50
```



single pulse decoupled gated NOE




```
DFILE   FS6-137_carbon-2-1.als
COMNT   single pulse decoupled gated NOE
DATIM   2014-08-13 22:03:08
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ   99.55 MHz
OBSET   5.13 KHz
OBFIN   0.98 Hz
POINT   26214
FREQU   25000.00 Hz
SCANS   12658
ACQTM   1.0486 sec
PD      2.0000 sec
PW1     3.42 usec
IRNUC   1H
CTEMP   19.4 c
SLVNT   CD2CL2
EXREF   53.80 ppm
BF      0.00 Hz
RGAIN   60
```