Supportimg Information

ACTIVATION OF GRUBBS-HOVEYDA SECOND-GENERATION CATALYSTS EMPLOYING AROMATIC LIGANDS BEARING A WIDESPREAD ARYL SUBSTITUENT

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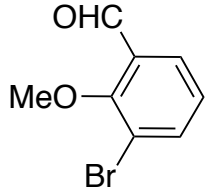
I. Synthesis of catalysts 1i-1m and precursor compounds

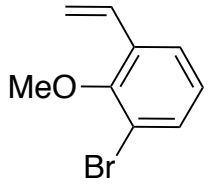
3-Bromo-2-methoxybenzaldehyde 3b[1]



3b

To a solution of 3-bromo-2-hydroxybenzaldehyde **2** (200 mg, 1.0 mmol) and iodomethane (0.19 mL, 3.1 mmol) in DMF was added K_2CO_3 (1.3 g, 9.4 mmol). The mixture was heated to 60 ºC under N_2 in oil bath and stirred for 2 h. 1 M aq. HCl and EtOAc were added to the resulting mixture. The organic phase was separated and the aqueous phase was extracted with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, and evaporated. The residue was purified by column chromatography on silica gel (EtOAc : hexane = 1 : 5) to afford 3-bromo-2-methoxybenzaldehyde **3b** (226.1 mg, quant.). pale yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 4.00 (s, 3H), 7.14 (t, *J* = 15.93 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 2H), 10.37 (s, 1H).

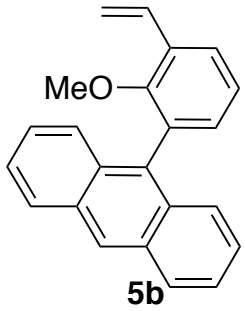
1-Bromo-2-methoxy-3-vinylbenzene 4b[2]



4b

Under N_2 atmosphere, methyltriphenylphosphonium bromide (1.9 g, 5.3 mmol) was dissolved in dry-THF. NHMDS (1.9 M THF solution of 3.6 mL, 6.8 mmol) was slowly added to this solution at -78 ºC. The reaction mixture was stirred at 0 ºC for 2 h and then was cooled to -78 ºC. A solution of 3-bromo-2-methoxybenzaldehyde **3b** (226.1 mg, 1.1 mmol) in dry-THF was syringed into the reaction mixture. The resulting mixture was warmed to 0 ºC and stirred for 3 h. The mixture was quenched with 1 M aq. HCl. After the addition of EtOAc, the organic phase was separated and the aqueous phase was extracted with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, and evaporated. The residue was purified by column chromatography on silica gel (EtOAc : hexane = 1 : 10) to afford 1-bromo-2-methoxy-3-vinylbenzene **4b** (170.3 mg, 76%). pale yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 3.81 (s, 3H), 5.35 (d, *J* = 11.3 Hz, 1H), 5.78 (d, *J* = 17.8 Hz, 1H), 6.94-7.05 (m, 2H), 7.46 (d, *J* = 7.8 Hz, 2H).

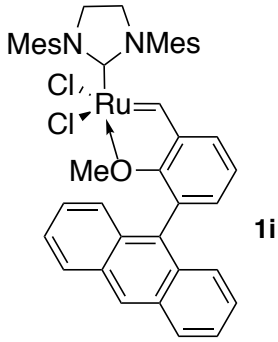
9-(2-Methoxy-3-vinylphenyl)anthracene 5b



5b

To a stirred solution of 1-bromo-2-methoxy-3-vinylbenzene **4b** (170.3 mg, 0.8 mmol) and 9-anthraceneboronic acid (195.2 mg, 0.9 mmol) in mixed solvent (THF : H_2O = 2 : 1) were added K_2CO_3 (552.3 mg, 4.0 mmol) and $Pd(PPh_3)_4$ (46.2 mg, 0.04 mmol). The mixture was heated to reflux in oil bath for 6 h. After cooling the reaction mixture to room temperature, 1M aq. HCl was added, and then the mixture was filtered through a plug of Celite® and washed with EtOAc. The filtrate was extracted with EtOAc. The combined organic phase was washed with brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel ($CHCl_3$: hexane = 1 : 3) to afford 9-(2-methoxy-3-vinylphenyl)anthracene **5b** (43.8 mg, 18%). pale yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 3.10 (s, 3H), 5.39 (d, *J* = 11.1 Hz, 1H), 5.91 (d, *J* = 17.8 Hz, 1H), 7.13-7.23 (m, 1H), 7.30-7.49 (m, 6H), 7.67 (d, *J* = 9.5 Hz, 2H), 7.74 (d, *J* = 9.2 Hz, 1H), 8.05 (d, *J* = 8.1 Hz, 2H), 8.52 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ: 61.1, 76.5, 115.2, 124.0, 125.1, 125.5, 126.2, 126.6, 126.8, 128.4, 130.3, 131.3, 131.7, 132.1, 132.7, 133.2, 156.4; HRMS (FAB+) *m/z* calcd for $C_{23}H_{53}O$ 311.1436, found 311.1399.

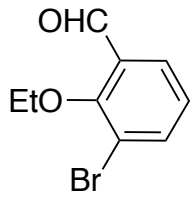
catalyst 1i



1i

To a suspension of 9-(2-methoxy-3-vinylphenyl)anthracene **5b** (37.9 mg, 0.1 mmol) and CuCl (24.2 mg, 0.2 mmol) in dry-CH_2Cl_2 was added Grubbs 2nd (124.4 mg, 0.2 mmol). The reaction mixture was heated at 30 ºC under N_2 and stirred for 3 h. The mixture was concentrated. The residue was purified by column chromatography on the silica gel (dichloromethane : hexane = 5 : 3) to obtain catalyst **1i** (13.7 mg, 15%). green crystal; mp 176.0-177.0 ºC; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 2.37 (s, 6H), 2.48 (s, 12H), 2.93 (s, 3H), 4.14 (s, 4H), 7.07 (t, J = 13.2, 5H), 7.30-7.44 (m, 6H), 7.76-7.82 (d, *J* = 8.64 Hz, 3H), 16.72 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ: 19.3, 21.2, 51.7, 62.7, 122.2, 124.2, 125.4, 126.4, 126.8, 127.6, 128.3, 129.6, 130.6, 131.2, 138.6, 138.8, 146.4, 152.9, 159.8, 293.5; HRMS (FAB+) *m/z* calcd for $C_{43}H_{44}Cl_2N_2ORu$ 776.1874, found 776.1893.

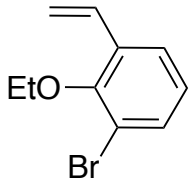
3-Bromo-2-ethoxybenzaldehyde 3c[3]



3c

To a solution of 3-bromo-2-hydroxybenzaldehyde **2** (150 mg, 0.7 mmol) and ethyl iodide (0.20 mL, 2.5 mmol) in DMF was added K_2CO_3 (618.0 mg, 4.5 mmol). The mixture was heated to 60 ºC under N_2 in oil bath and stirred for 2 h. 1 M aq. HCl and EtOAc were added to the resulting mixture. The organic phase was separated and the aqueous phase was extracted with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, and evaporated. The residue was purified by column chromatography on silica gel (EtOAc : hexane = 1 : 5) to afford 3-bromo-2-ethoxybenzaldehyde **3c** (200.2 mg, quant.). pale yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 1.50 (t, *J* = 14.3 Hz, 3H), 4.19 (dd, *J* = 4.1, 13.5 Hz, 2H) 7.12 (d, *J* = 15.9 Hz, 1H), 7.82 (dd, *J* = 7.8, 8.1 Hz, 2H) 10.37 (s, 1H).

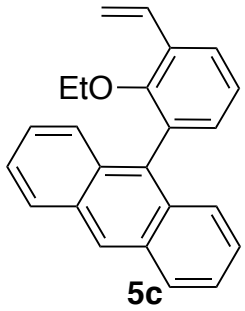
1-Bromo-2-ethoxy-3-vinylbenzene 4c



4c

Under N_2 atmosphere, methyltriphenylphosphonium bromide (1.6 g, 4.5 mmol) was dissolved in dry-THF. NHMDS (1.9 M THF solution of 3.0 mL, 5.7 mmol) was slowly added to this solution at -78 ºC. The reaction mixture was stirred at 0 ºC for 2 h and then was cooled to -78 ºC. A solution of 3-bromo-2-ethoxybenzaldehyde **3c** (200.2 mg, 0.9 mmol) in dry-THF was syringed into the reaction mixture. The resulting mixture was warmed to 0 ºC and stirred for 3 h. The mixture was quenched with 1 M aq. HCl. After the addition of EtOAc, the organic phase was separated and the aqueous phase was extracted with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, and evaporated. The residue was purified by column chromatography on silica gel (EtOAc : hexane = 1 : 10) to afford 1-bromo-2-ethoxy-3-vinylbenzene **4c** (160.2 mg, 81%). pale yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 3.99 (dd, *J* = 3.9, 13.5 Hz, 2H), 5.33 (d, *J* = 10.0 Hz, 1H), 5.76 (d, *J* = 17.8 Hz, 1H), 6.93-7.05 (m, 2H), 7.45 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ: 27.3, 73.5, 110.7, 112.9, 119.3, 125.3, 125.7, 127.7, 130.7, 155.3; HRMS (FAB+) *m/z* calcd for $C_{10}H_{12}BrO$ 227.0072, found 227.0077.

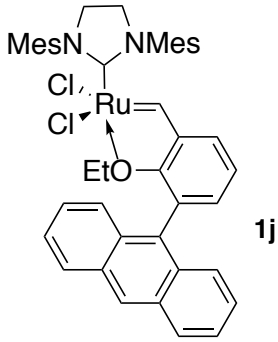
9-(2-Ethoxy-3-vinylphenyl)anthracene 5c



5c

To a stirred solution of 1-bromo-2-ethoxy-3-vinylbenzene **4c** (160.2 mg, 0.7 mmol) and 9-anthraceneboronic acid (172.3 mg, 0.8 mmol) in mixed solvent (THF : H_2O = 2 : 1) were added K_2CO_3 (585.0 mg, 4.2 mmol) and $Pd(PPh_3)_4$ (40.8 mg, 0.04 mmol). The mixture was heated to reflux in oil bath for 6 h. After cooling the reaction mixture to room temperature, 1M aq. HCl was added, and then the mixture was filtered through a plug of Celite® and washed with EtOAc. The filtrate was extracted with EtOAc. The combined organic phase was washed with brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel ($CHCl_3$: hexane = 1 : 3) to afford 9-(2-ethoxy-3-vinylphenyl)anthracene **5c** (51.1 mg, 22%). pale yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 0.56 (t, *J* = 13.8 Hz, 3H), 3.27 (dd, *J* = 3.2, 13.5 Hz, 2H), 5.38 (dd, *J* = 5.4, 10.8 Hz, 1H), 5.91 (dd, *J* = 5.9, 16.2 Hz, 1H), 7.23-7.28 (m, 2H), 7.36-7.46 (m, 5H), 7.67-7.72 (m, 3H), 8.04 (d, *J* = 8.6 Hz, 2H), 8.50 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ: 15.1, 69.5, 114.9, 123.8, 125.1, 125.5, 125.9, 126.8, 128.3, 130.3, 131.3, 131.8, 131.9, 132.0, 132.2, 132.8, 133.6, 155.8; HRMS (FAB+) *m/z* calcd for $C_{24}H_{21}O$ 325.1592, found 325.1552.

catalyst 1j

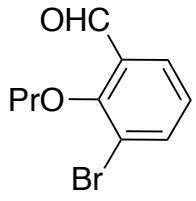


1j

To a suspension of 9-(2-ethoxy-3-vinylphenyl)anthracene **5c** (60.4 mg, 0.2 mmol) and CuCl (36.9 mg, 0.4 mmol) in dry-CH_2Cl_2 was added Grubbs 2nd (158.1 mg, 0.2 mmol). The reaction mixture was heated at 30 ºC under N_2 and stirred for 3 h. The mixture was concentrated. The residue was purified by column chromatography on the silica gel (dichloromethane : hexane = 5 : 3) to obtain catalyst **1j** (42.5 mg, 29%). green crystal; mp 180.0-181.0 ºC; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 0.29 (t, *J* = 13.8 Hz, 3H), 2.34 (bs, 5H), 2.49 (s, 13H), 3.41 (dd, *J* = 3.4, 13.5 Hz, 2H), 4.18 (s, 4H), 7.06 (t, *J* = 7.0 Hz, 5H), 7.29-7.44 (m, 6H), 7.62 (d, *J*= 8.6 Hz, 2H), 7.97 (d, *J* = 8.1 Hz, 2H), 8.44 (s, 1H), 16.77 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ: 13.7, 21.1, 22.8, 51.4, 69.0, 76.5, 122.7, 123.8, 125.4, 126.3, 126.4, 127.0, 127.4, 128.2, 129.4, 130.4, 131.1, 132.8, 135.1, 138.8, 147.2, 152.4, 211.3, 297.9; HRMS (FAB+) *m/z* calcd for $C_{44}H_{46}Cl_2N_2ORu$

790.2031, found 790.2005.

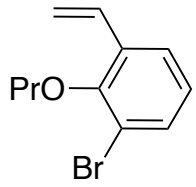
3-Bromo-2-propoxy-benzaldehyde 3d



3d

To a solution of 3-bromo-2-hydroxybenzaldehyde **2** (300 mg, 1.5 mmol) and propyl iodide (0.4 mL, 4.1 mmol) in DMF was added K_2CO_3 (1.2 g, 8.7 mmol). The mixture was heated to 60 ºC under N_2 in oil bath and stirred for 3 h. 1 M aq. HCl and EtOAc were added to the resulting mixture. The organic phase was separated and the aqueous phase was extracted with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, and evaporated. The residue was purified by column chromatography on silica gel (EtOAc : hexane = 1 : 5) to afford 3-bromo-2-propoxy-benzaldehyde **3d** (346.5 mg, 96%). pale yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 1.11 (t, *J* = 15.1 Hz, 3H), 1.86-1.96 (m, 2H), 4.04 (t, *J* = 4.0, 13.2 Hz, 2H) 7.12 (t, *J* = 15.1 Hz, 1H), 7.81 (d, *J* = 7.8 Hz, 2H) 10.37 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 10.5, 23.3, 78.4, 118.5, 125.6, 127.7, 131.2, 139.5, 159.5, 189.3; HRMS (EI+) *m/z* calcd for $C_{10}H_{11}BrO_2$ 241.9942, found 241.9949.

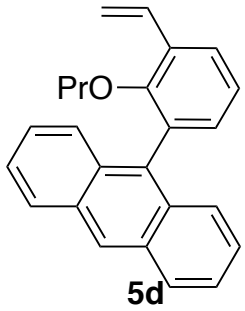
1-Bromo-2-propoxy-3-vinylbenzene 4d



4d

Under N_2 atmosphere, methyltriphenylphosphonium bromide (1.9 g, 5.3 mmol) was dissolved dry-THF. NHMDS (1.9 M THF solution of 3.5 mL, 6.7 mmol) was slowly added to this solution at -78 ºC. The reaction mixture was stirred at 0 ºC for 2 h and then was cooled to -78 ºC. A solution of 3-bromo-2-propoxy-benzaldehyde **3d** (265.7 mg, 1.0 mmol) in dry-THF was syringed into the reaction mixture. The resulting mixture was warmed to 0 ºC and stirred for 3 h. The mixture was quenched with 1 M aq. HCl. After the addition of EtOAc, the organic phase was separated and the aqueous phase was extracted with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, and evaporated. The residue was purified by column chromatography on silica gel (EtOAc : hexane = 1 : 10) to afford 1-bromo-2-propoxy-3-vinylbenzene **4d** (251.7 mg, 96%). pale yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 1.08 (t, *J* = 14.6 Hz, 3H), 1.80-1.93 (m, 2H), 3.85 (t, *J* = 13.0 Hz, 2H), 5.33 (d, *J* = 11.9 Hz, 1H), 5.76 (d, *J* = 17.8 Hz, 1H), 6.92-7.06 (m, 2H), 7.45 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ: 10.5, 23.4, 75.6, 116.0, 118.1, 125.1, 125.5, 131.3, 132.6, 133.3, 153.7; HRMS (FAB+) *m/z* calcd for $C_{11}H_{14}BrO$ 241.0228, found 241.0220.

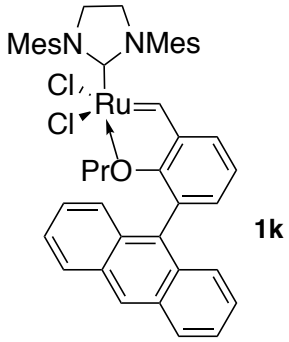
9-(2-Propoxy-3-vinylphenyl)anthracene 5d



5d

To a stirred solution of 1-bromo-2-propoxy-3-vinylbenzene **4d** (73.9 mg, 0.3 mmol) and 9-anthraceneboronic acid (74.9 mg, 0.3 mmol) in mixed solvent (THF : H_2O = 2 : 1) were added K_2CO_3 (211.8 mg, 1.5 mmol) and $Pd(PPh_3)_4$ (17.7 mg, 0.02 mmol). The mixture was heated to reflux in oil bath for 6 h. After cooling the reaction mixture to room temperature, 1M aq. HCl was added, and then the mixture was filtered through a plug of Celite® and washed with EtOAc. The filtrate was extracted with EtOAc. The combined organic phase was washed with brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel ($CHCl_3$: hexane = 1 : 3) to afford 9-(2-propoxy-3-vinylphenyl)anthracene **5d** (49.7 mg, 48%). pale yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ: -0.06 (t, *J* = 14.3 Hz, 3H), 0.98 (dd, *J* = 0.9, 13.5 Hz, 2H), 3.16 (d, *J* = 12.4 Hz, 2H), 5.38 (dd, *J* = 5.3, 10.8 Hz, 1H), 5.91 (dd, *J* = 5.9, 16.2 Hz, 1H), 7.15 (t, *J* = 17.8 Hz, 1H), 7.32-7.48 (m, 6H), 7.68-7.76 (m, 3H), 8.04 (d, *J* = 8.6 Hz, 2H), 8.50 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ: 9.7, 22.9, 75.3, 115.0, 123.9, 125.1, 125.6, 126.0, 126.8, 126.9, 128.4, 131.4, 132.9, 155.8; HRMS (FAB+) *m/z* calcd for $C_{25}H_{23}O$ 339.1749, found 339.1726.

ctalyst 1k

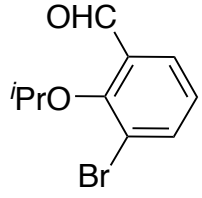


1k

To a suspension of 9-(2-propoxy-3-vinylphenyl)anthracene **5d** (51.1 mg, 0.2 mmol) and CuCl (20.0 mg, 0.2 mmol) in dry-CH_2Cl_2 was added Grubbs 2nd (128.2 mg, 0.2 mmol). The reaction mixture was heated at 30 ºC under N_2 and stirred for 3 h. The mixture was concentrated. The residue was purified by column chromatography on the silica gel (dichloromethane : hexane = 5 : 3) to obtain catalyst **1k** (52.9 mg, 44%). green crystal; mp 164.0-166.5 ºC; ^{1}H NMR (270 MHz, $CDCl_3$) δ: -0.31 (t, *J* = 14.9 Hz, 3H), 0.61 (dd, *J* = 0.6, 13.5 Hz, 2H), 2.35 (bs, 5H), 2.49 (s, 13H), 3.29 (t, *J* = 13.2 Hz, 2H), 4.17 (s, 4H), 7.03-7.10 (m, 5H), 7.30-7.44 (m, 6H), 7.65 (d, *J*= 8.6 Hz, 2H), 7.97 (d, *J* = 8.4 Hz, 2H), 8.45 (s, 1H), 16.79 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ: 8.8, 21.1, 21.5, 51.4, 74.3, 122.6, 124.2, 125.4, 126.3, 127.1, 127.4, 128.1, 129.4, 130.1, 131.2, 132.4, 134.9, 138.8, 147.7, 152.6, 211.0, 298.0; HRMS (FAB+) *m/z* calcd for $C_{45}H_{48}Cl_2N_2ORu$

804.2187, found 804.2202.

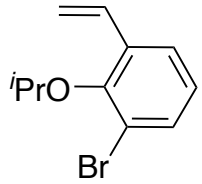
3-Bromo-2-isopropoxybenzaldehyde 3e[4]



3e

To a solution of 3-bromo-2-hydroxybenzaldehyde **2** (100 mg, 0.5 mmol) and 2-iodopropane (249.5μL, 2.5 mmol) in dry-DMF was added K_2CO_3 (552.8 mg, 4.0 mmol). The mixture was heated to 60 ºC under N_2 in oil bath and stirred for 30 min. 1 M aq. HCl and EtOAc were added to the resulting mixture. The organic phase was separated and the aqueous phase was extracted with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, and evaporated. The residue was purified by column chromatography on silica gel (EtOAc : hexane = 1 : 20) to afford 3-bromo-2-isopropoxybenzaldehyde **3e** (119.6 mg, 99%). colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 1.39 (d, J = 6.75 Hz, 6H), 4.52-4.64 (m, 1H), 7.10 (t, J = 7.6 Hz, 1H), 7.81 (d, J = 7.8 Hz, 2H), 10.38 (s, 1H).

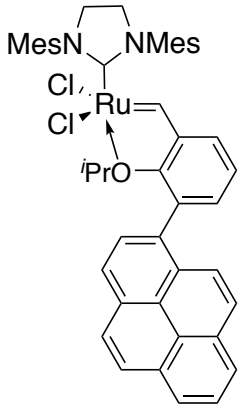
1-Bromo-2-isopropoxy-3-vinylbenzene 4e[4]



4e

Under N_2 atmosphere, methyltriphenylphosphonium bromide (236.6 mg, 0.7 mmol) was dissolved in dry-THF. NHMDS (1.9 M THF solution of 0.7 mL, 1.3 mmol) was slowly added to this solution at -78 ºC. The reaction mixture was stirred at 0 ºC for 2 h and then was cooled to -78 ºC. A solution of 3-bromo-2-isopropoxybenzaldehyde **3e** (80.5 mg, 0.3 mmol) in dry-THF was syringed into the reaction mixture. The resulting mixture was warmed to 0 ºC and stirred for 3 h. The mixture was quenched with 1 M aq. HCl. After the addition of EtOAc, the organic phase was separated and the aqueous phase was extracted with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, and evaporated. The residue was purified by column chromatography on silica gel (EtOAc : hexane = 1 : 10) to afford 1-bromo-2-isopropoxy-3-vinulbenzene **4e** (88.1 mg, quant.). pale yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 1.33 (d, J = 6.8 Hz, 6H), 4.41-4.50 (m, 1H), 5.30 (dd, J = 11.1, 1.4 Hz, 1H), 5.71 (dd, J = 17.6, 1.1 Hz, 1H), 7.07-6.91 (m, 2H), 7.46 (d, J = 7.8 Hz, 2H).

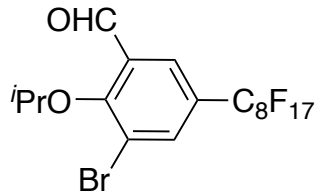
catalyst 1l



1l

To a suspension of 1-(2-isopropoxy-3-vinylphenyl)pyrene **5e** (21.2 mg, 0.0581 mmol) and CuCl (11.1 mg, 0.112 mmol) in dry-CH_2Cl_2 was added Grubbs 2nd (46.9 mg, 0.055 mmol). The reaction mixture was heated at 30 ºC under N_2 and stirred for 3 h. The mixture was concentrated. The residue was purified by column chromatography on the silica gel (dichloromethane : hexane = 5 : 3) to obtain catalyst **1l** (21.8 mg, 45%). green crystal; mp 208 ºC (dec.); ^{1}H NMR (270 MHz, $CDCl_3$) δ: 0.71 (dd, *J* = 45.4, 6.5 Hz, 6H), 2.53 (bs, 18H), 3.99-4.08 (m, 1H), 4.20 (s, 4H), 6.99-7.04 (m, 6H), 7.44-7.48 (m, 1H), 7.95-8.20 (m, 10H), 16.78 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 18.5, 20.7, 20.9, 78.0, 51.0, 122.9, 123.3, 124.4, 124.6, 124.7, 125.3, 125.4, 125.5, 126.2, 127.4, 127.9, 128.0, 128.5, 129.1, 129.4, 131.06, 131.11, 131.4, 134.3, 135.3, 138.9, 140.0, 147.9, 150.0, 211.3, 299.7; HRMS (FAB+) *m/z* calcd for $C_{47}H_{48}Cl_2N_2ORu$ 828.2187, found 828.2161.

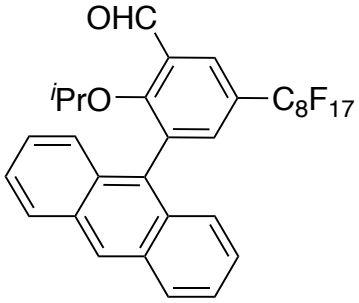
3-Bromo-2-isobutoxy-5-(perfluorooctyl)benzaldehyde 11[5]



11

To a solution of 3-bromo-2-hydroxy-5-(perfluorooctyl)benzaldehyde **10** (1.7 g, 2.67 mmol) and 2-iodopropane (4.5 g, 26.65 mmol) in DMF was added K_2CO_3 (3.0 g, 21.32 mmol). The mixture was heated to 60 ºC under N_2 in oil bath and stirred for 2 h. 1 M aq. HCl and EtOAc were added to the resulting mixture. The organic phase was separated and the aqueous phase was extracted with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, and evaporated. The residue was purified by column chromatography on silica gel (EtOAc : hexane = 1 : 10) to afford 3-bromo-2-isobutoxy-5-(perfluorooctyl)benzaldehyde **11** (1.7 g, 94%). pale yellow crystals; mp 75-76 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 1.43 (d, *J* = 6.2 Hz, 6H), 4.65-4.74 (m, 1H), 8.03 (dd, *J* = 8.9, 2.2 Hz, 2H), 10.38 (s, 1H).

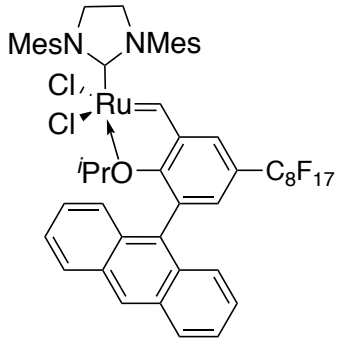
3-(Anthracen-9-yl)-2-isopropoxy-5-(perfluorooctyl)benzaldehyde 12



12

To a stirred solution of 3-bromo-2-isobutoxy-5-(perfluorooctyl)benzaldehyde **11** (196 mg, 0.296 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (15.5 mg, 0.0377 mmol), and 9-anthraceneboronic acid (82.0 mg, 0.369 mmol) in mixed solvent (THF : H_2O = 2 : 1) were added K_3PO_4 (305 mg, 1.44 mmol) and $Pd(OAc)_2$ (5 mg, 0.0223 mmol). The mixture was heated to reflux in oil bath for 24 h. After cooling the reaction mixture to room temperature, 1M aq. HCl was added, and then the mixture was filtered through a plug of Celite® and washed with EtOAc. The filtrate was extracted with EtOAc. The combined organic phase was washed with brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (EtOAc : hexane = 1 : 10) to afford 3-(anthracen-9-yl)-2-isopropoxy-5-(perfluorooctyl)benzaldehyde **12** (119 mg, 53%). white solid; mp 91-92 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.54 (d, *J* = 6.4 Hz, 6H), 3.33-3.42 (m, 1H), 5.44 (d, *J* = 11.1 Hz, 1H), 5.90 (d, *J* = 17.8 Hz, 1H), 7.38-7.50 (m, 6H), 7.64 (d, *J* = 8.6 Hz, 2H), 7.92 (d, *J* = 1.9 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 2H), 8.54 (s, 1H); ^{19}F NMR (466 MHz, $CDCl_3$) δ: -126.0 (2F), -122.5 (2F), -121.7 (4F), -121.4 (2F), -121.0 (2F), -110.3 (2F), -80.6 (4F); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 21.9, 104.6-124.4 (m, C_8F_{17}), 125.4, 125.6, 126.3, 126.7, 127.0, 128.3, 128.5, 128.9, 129.8, 130.3, 130.8, 131.4, 131.8, 138.1, 162.7, 189.9; HRMS (FAB+) *m/z* calcd for $C_{32}H_{20}F_{17}O_2$ 759.1192, found 759.1193.

catalyst 1m

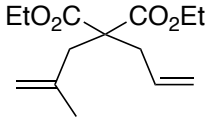


1m

To a suspension of 2-isopropoxy-3-(9-anthracenyl)-5-(perfluorooctyl)-1-vinylbenzene **13** (40.0 mg, 0.053 mmol) and CuCl (16.0 mg, 0.16 mmol) in dry-CH_2Cl_2 was added Grubbs 2nd (45.0 mg, 0.053 mmol). The reaction mixture was heated at 30 ºC under N_2 and stirred for 3 h. The mixture was concentrated. The residue was purified by column chromatography on the silica gel (dichloromethane : hexane = 1 : 5) to obtain

catalyst **1m** (14.1 mg, 22%). green crystal; mp 145 °C (dec.);^{1}H NMR (270 MHz, $CDCl_3$) δ 0.57 (d, *J* = 6.2 Hz, 6H), 2.50 (bs, 18H), 3.90-3.99 (m, 1H), 4.22 (s, 4H), 6.95-7.16 (m, 4H), 7.37-7.47 (m, 5H), 7.59-7.71 (m, 4H), 7.99 (d, *J* = 7.6 Hz, 2H), 8,48 (s, 1H), 16.56 (s, 1H); ^{19}F NMR (466 MHz, $CDCl_3$) δ: 125.9 (2F), -122.6 (2F), -121.8 (6F), -121.0 (2F), -109.8 (2F), -80.6 (3F); HRMS (FAB+) *m/z* calcd for $C_{53}H_{47}Cl_2F_{17}N_2ORu$ 1222.1837, found 1222.1832.

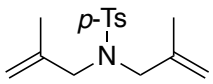
Diethyl 2-allyl-2-(2-methylallyl)malonate 6[4]



6

To a susupension of NaH in 50 % oil (338.0 mg, 14.1 mmol) in dry-THF were slowly added diethyl 2-allylmalonate[4] (1.3 g, 6.3 mmol) and 3-bromo-2-methylprop-1-ene (0.7 mL, 7.0 mmol) under N_2. The reaction mixture was heated to 60 ºC in oil bath and stirred for 24 h. After the addition of 1M aq. HCl, EtOAc was added to the resulting mixture. The organic phase was separated and the aqueous phase was extracted with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, and evaporated. The residue was purified by column chromatography on silica gel (EtOAc : hexane = 1 : 5) to afford diethyl 2-allyl-2-(2-methylallyl)malonate **6** (1.3 g, 81%). colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 1.25 (t, *J* = 13.8, 6.5 Hz, 6H), 1.67 (s, 3H), 2.66-2.70 (m, 4H), 4.09-4.26 (m, 4H), 4.76 (s, 1H), 4.87 (s, 1H), 5.06-5.12 (m, 2H), 5.62-5.77 (m, 1H).

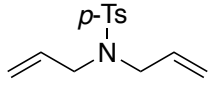
4-Methyl-*N*,*N*-bis(2-methylallyl)benzenesulfonamide 16[4]



16

To a solution of *p*-toluenesulfoneamide (300 mg, 1.8 mmol) in dry-acetone were added K_2CO_3 (2.4 g, 17.5 mmol) and 3-chloro-2-methylprop-1-ene (0.72 mL, 7.3 mmol). The resulting mixture was heated to reflux under N_2 in oil bath and stirred for 12 h. After cooling the reaction mixture to room temperature, the mixture was filtered through a plug of Celite® using pipette with EtOAc and then the filtrate was concentrated. The residue was purified column choromatgraphy on the silica gel (hexane) to give 4-methyl-*N*,*N*-bis(2-methylallyl)benzenesulfonamide **16** (416.2 mg, 85%). colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 1.61 (s, 6H), 2.42 (s, 3H), 3.70 (s, 4H), 4.78 (s, 2H), 4.86 (s, 2H), 7.29 (d, *J* = 8.64 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H).

***N*,*N*-Diallyl-4-methylbenzenesulfonamide 14**[6]



14

To a solution of diallylamine (100.0 mg, 1.03 mmol) in CH_2Cl_2 were added triethylamine (0.23 mL, 1.54 mmol) and

4-methylbenzenesulfonyl chloride (198.5 mg, 1.08 mmol), and the mixture was stirred for 24 h at room temperature. After the addition of saturated NH_4Cl aq., the organic phase was separated and the aqueous phase was extracted with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, and evaporated. The residue was purified by column chromatography on silica gel (EtOAc : hexane = 1 : 5) to afford *N*,*N*-diallyl-4-methylbenzenesulfonamide **14** (84.2 mg, 33%). colorless oil; ^1H NMR (270 MHz, $CDCl_3$) δ: 7.71 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 5.54-5.69 (m, 2H), 5.11-5.18 (m, 4H), 3.80 (d, *J* = 6.2 Hz, 4H), 2.43 (s, 3H).

II. X-Ray structure and structural parameters

Table S1. Crystallographic data of **1e** at 298 K

complex	Anth_metathesis_cat
formula	$C_{45}H_{47}Cl_2N_2ORu$
formula weight	801.80
crystal system	Monoclinic
space group	C2/c
crystal size, mm^3	0.39×0.19×0.11
a, Å	22.4690(8)
b, Å	23.2484(9)
c, Å	15.4089(6)
α, deg	90.00
β, deg	92.46
γ, de	90.00
V, $Å^3$	8041.7(5)
Z	8
d_{alc}, g cm^{-3}	1.325
μ(Mo Kα), mm^{-1}	0.558
reflns used	9418
reflned params	469
R_1 (for $I > 2\sigma(I)$)[a]	0.0269
wR_2 (for all data)[b]	0.0685
GOF on F^2	1.015

[a] $R_1 = \Sigma(|F_0| - |F_c|)/\Sigma|F_0|$. [b] $wR_2 = [\Sigma w(F_0^2 - F_c^2)^2/\Sigma w(F_0^2)^2]^{0.5}$.

III. References

1) M. F. Comber and M. V. Sargent, *J. Chem. Soc. Perkin Trans. 1*, 1991, **11**, 2783.

2) A. Pudleiner and H. Laatssch, *Synthesis*, 1989, **4**, 286.

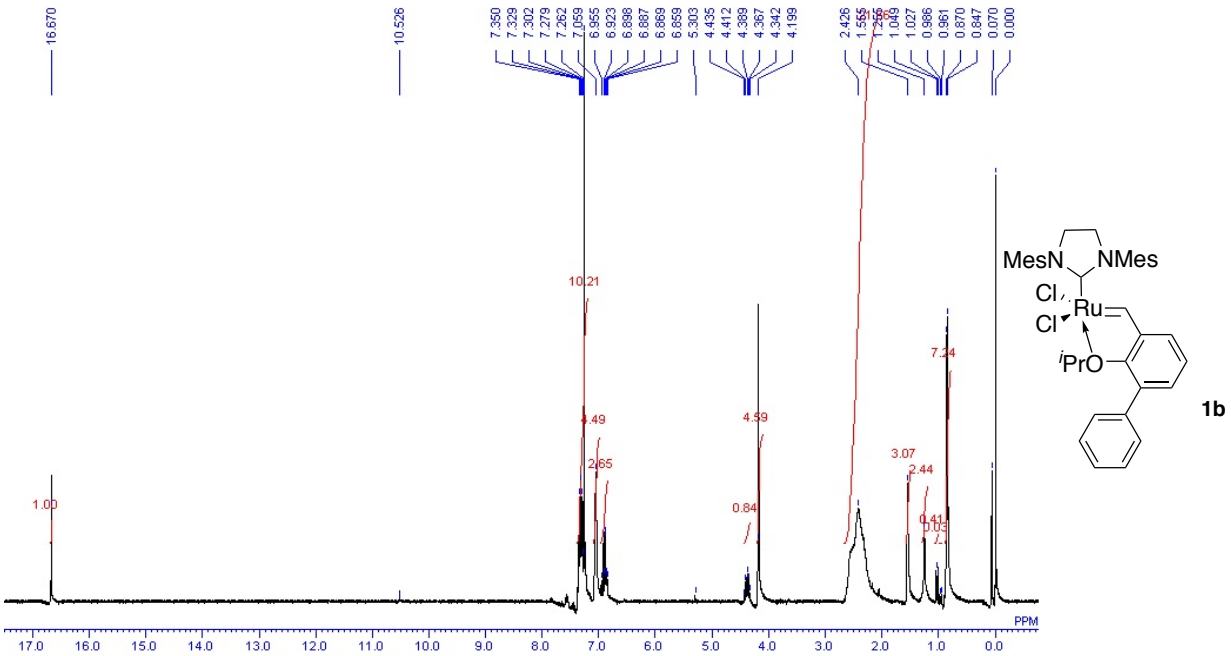
3) A. C. Castro, K. M. Depew, M. J. Grogan, E. B. Holson, B. T. Hopkins, C. W. Johannes, G. F. Keaney, N. O. Koney, T. Liu, D. A. Mann, M. Nevalainen, S. Peluso, L. B. Perez, D. A. Snyder, and T. T. Tibbitts. PCT WO 2008024337 A2, 28 February, 2008.

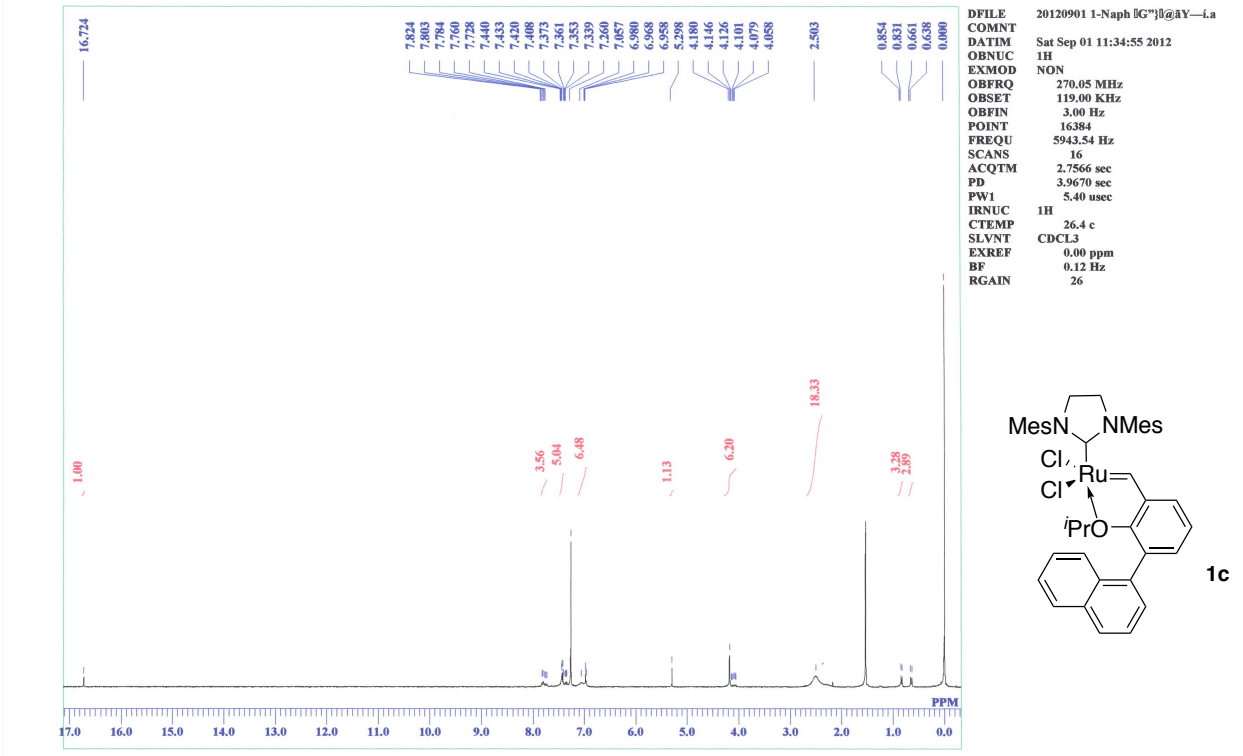
4) Y. Kobayashi, H. Miyazaki, S. Inukai, C. Takagi, R. Makino, K. Shimowaki, R. Igarashi, Y. Sugiyama, S. Nakamura, and M. Matsugi, *Synlett*, 2016, **27**, 2352.

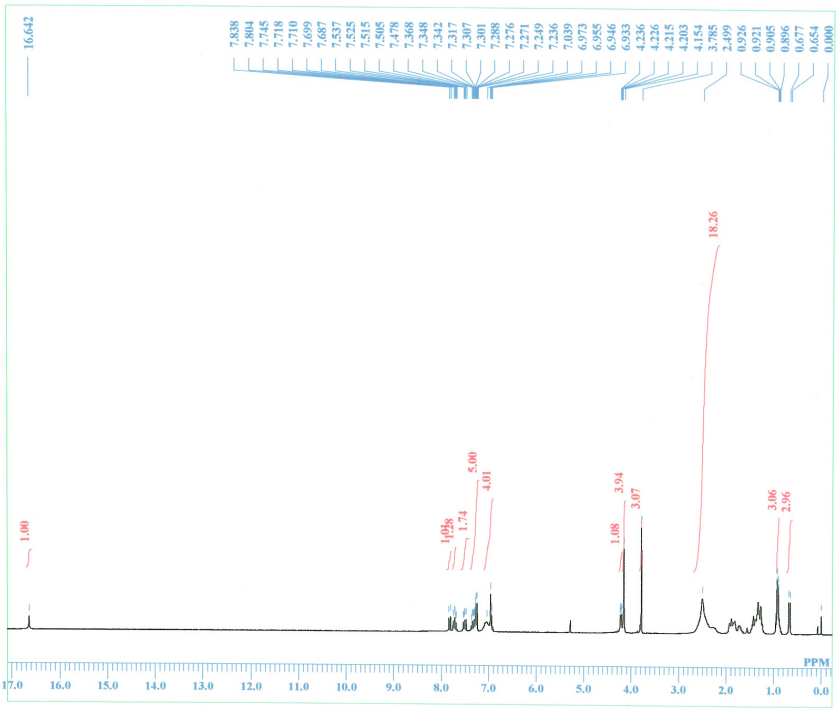
5) Y. Kobayashi, N. Suzumura, Y. Tsuchiya, M. Goto, Y. Sugiyama, T. Shioiri, and M. Matsugi, *Synthesis*, 2017, **49**, 1796.

6) Y. Kobayashi, S. Inukai, N. Kondo, T. Watanabe, Y. Sugiyama, H. Hamamoto, T. Shioiri, and M. Matsugi, *Tetrahedron Lett.*, 2015, **56**, 1363.

IV. Spectra data for products







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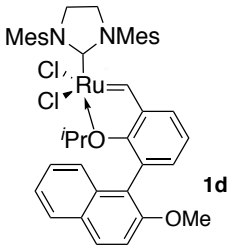

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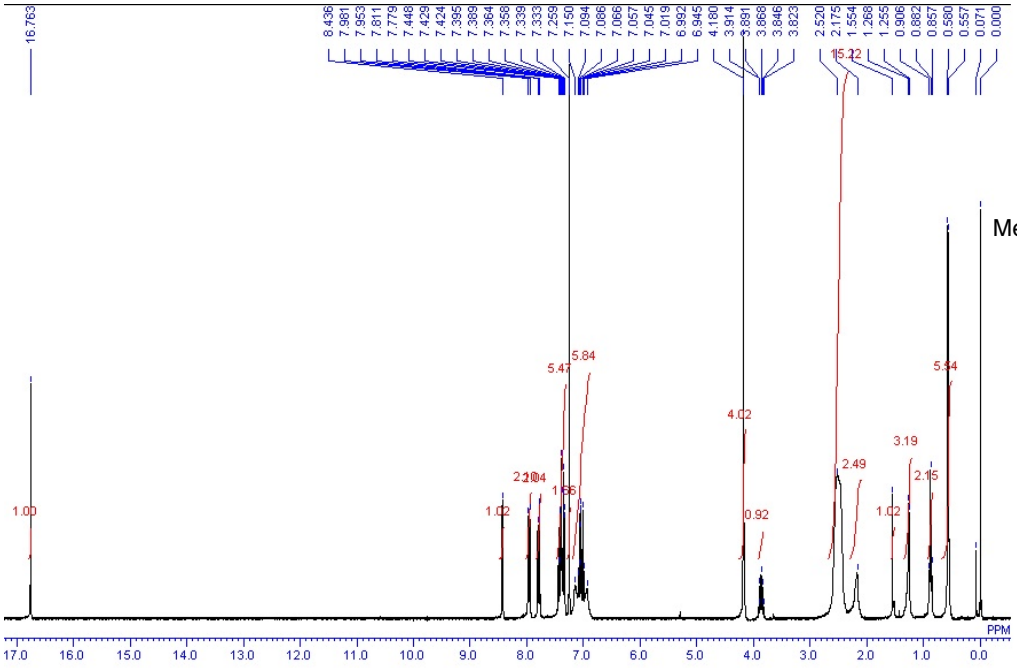

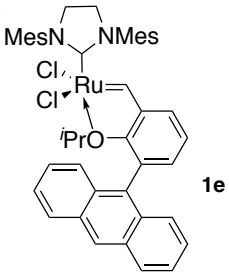

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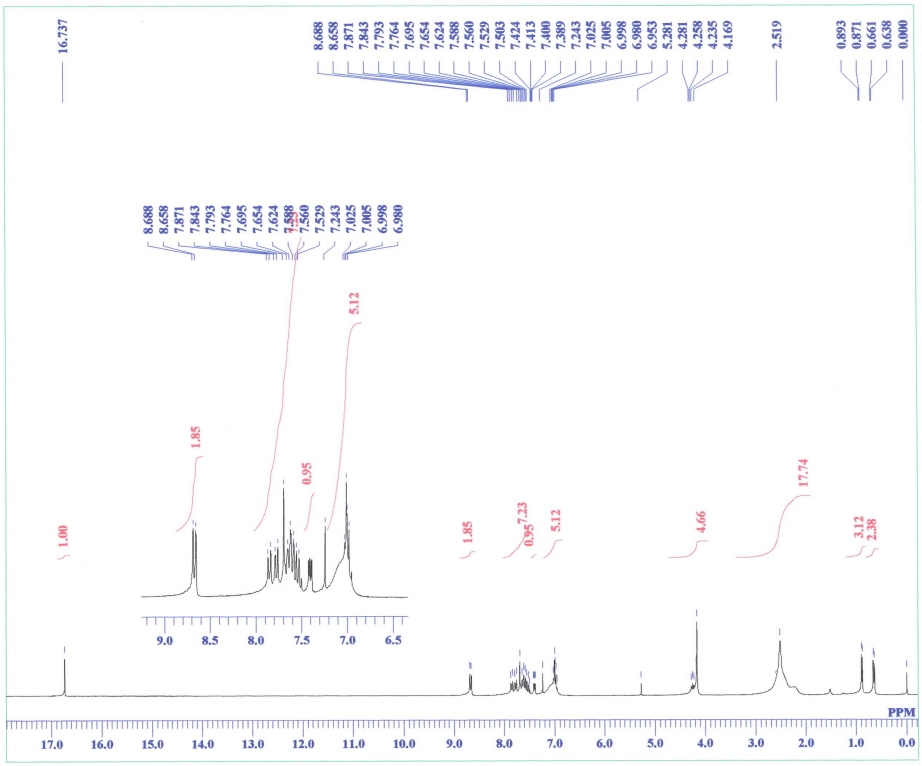
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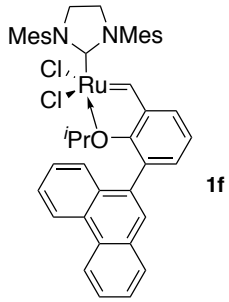
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NMes
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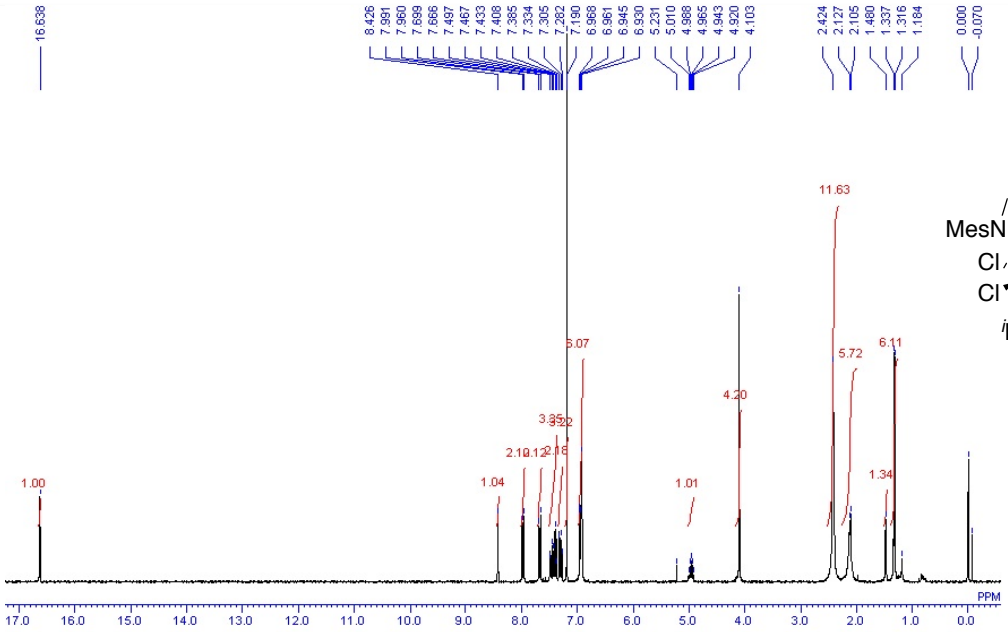
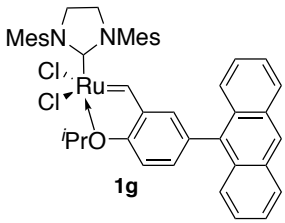
Ru
Cl
iPrO

1f


PPM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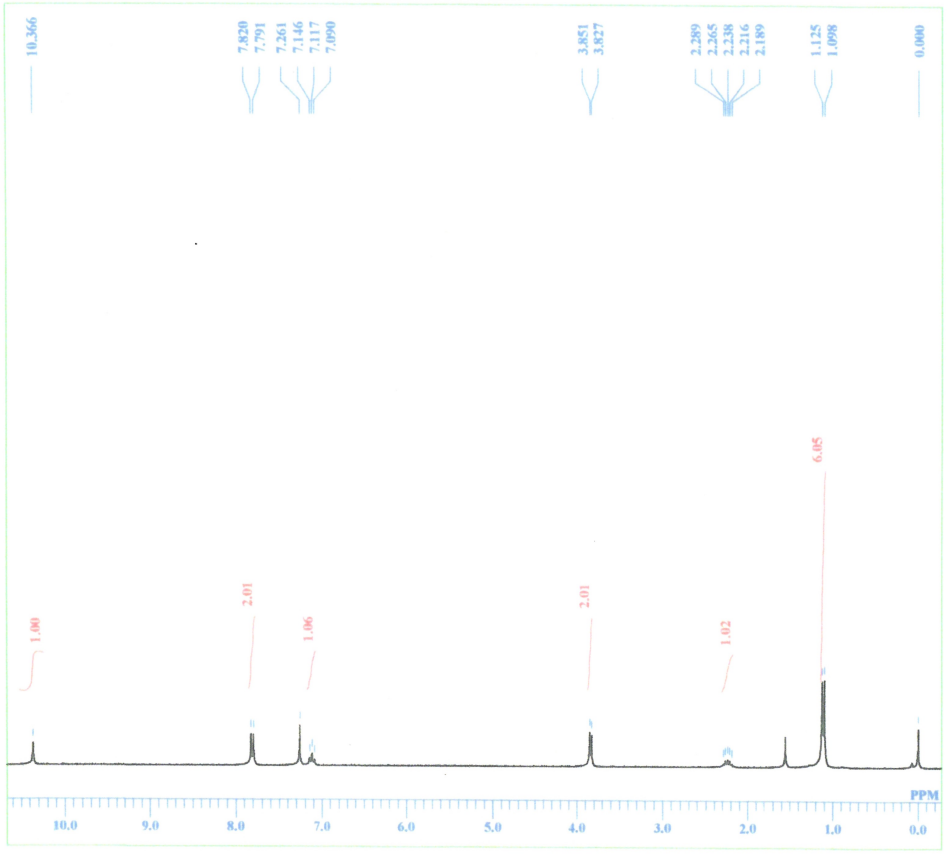
Cl
Ru
Cl
iPrO

1g



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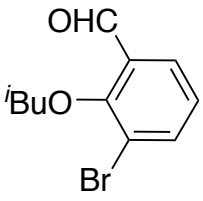
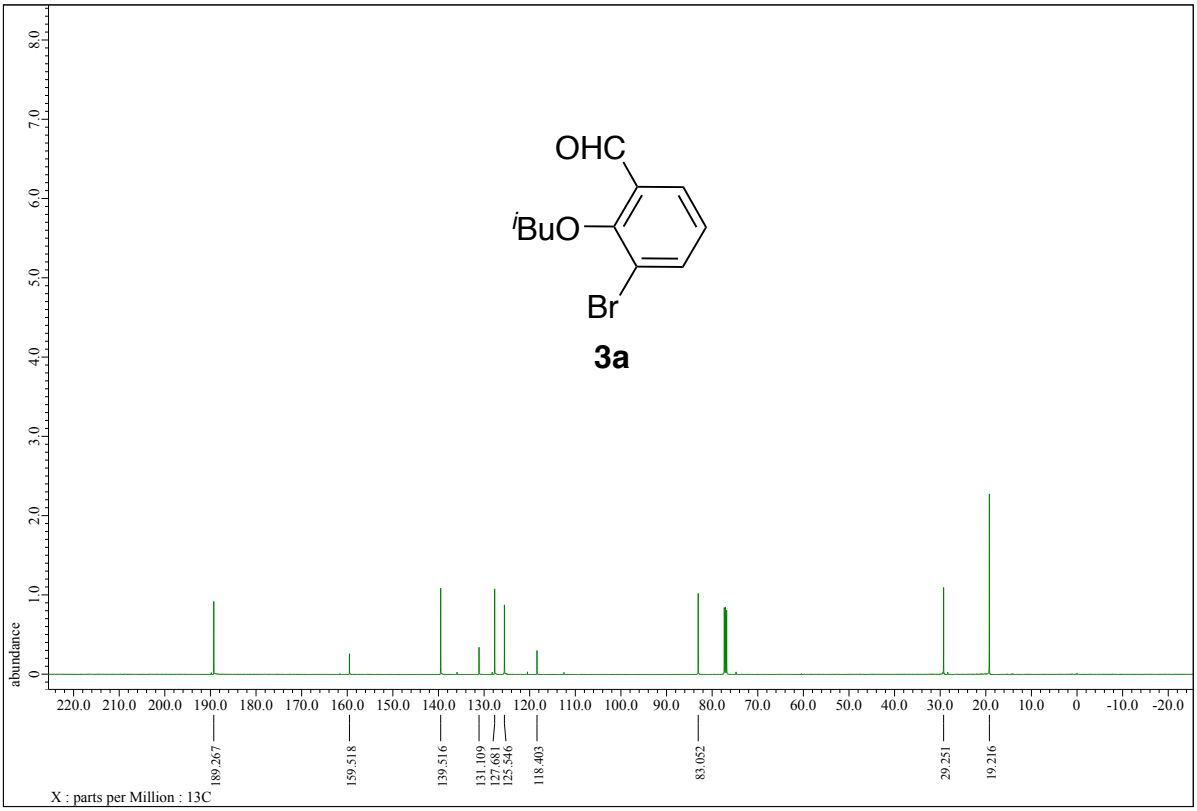
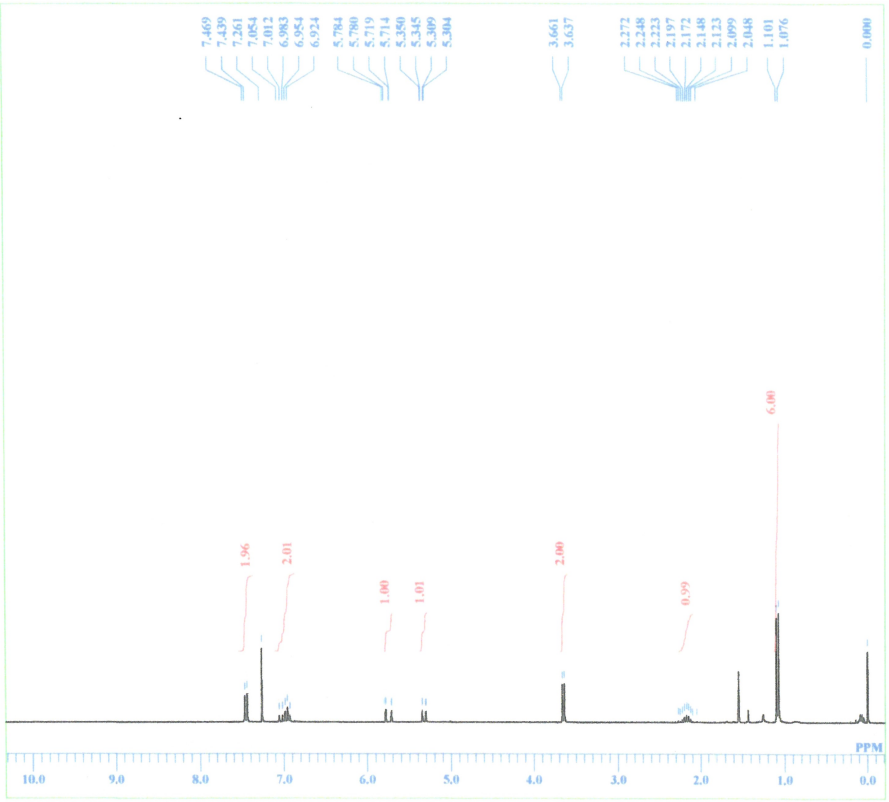


3a



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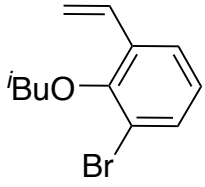

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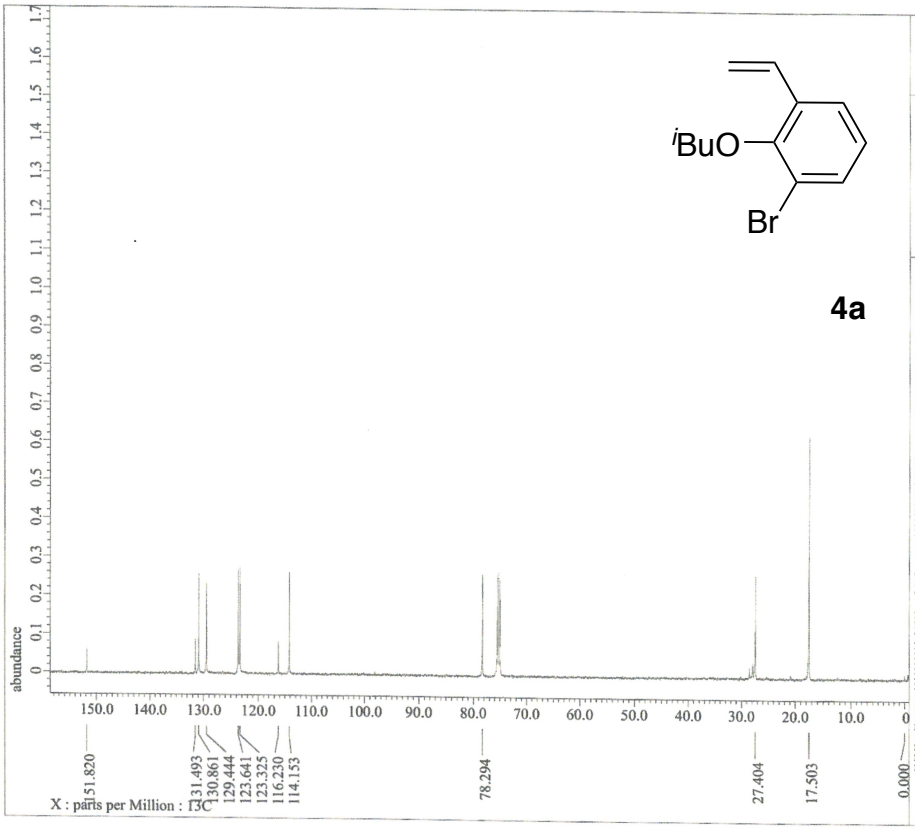

4a

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ppm

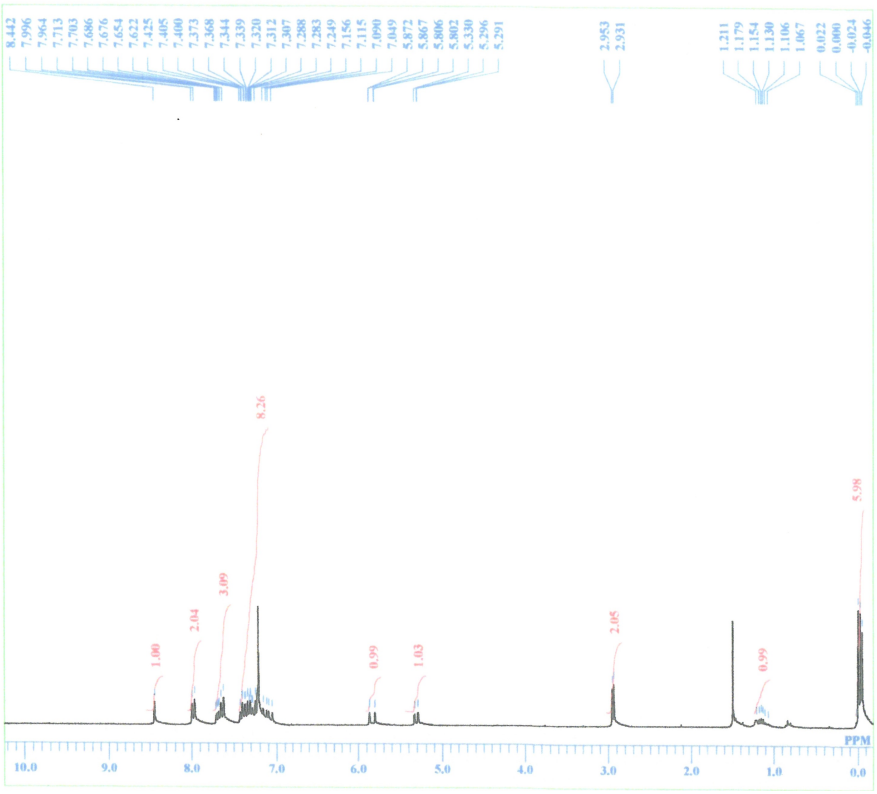
以下に由来：: 20140321inukai03-5.jdf

Filename          = 20140321inukai03-7.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = ft
Solvent           = CHLOROFORM-D
Creation_Time     = 21-MAR-2014 18:10:34
Revision_Time     = 30-JAN-2015 20:05:54
Current_Time      = 30-JAN-2015 20:06:43

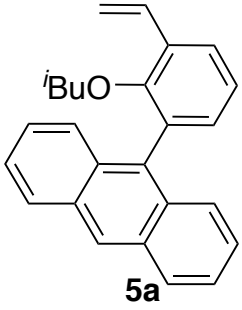
Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

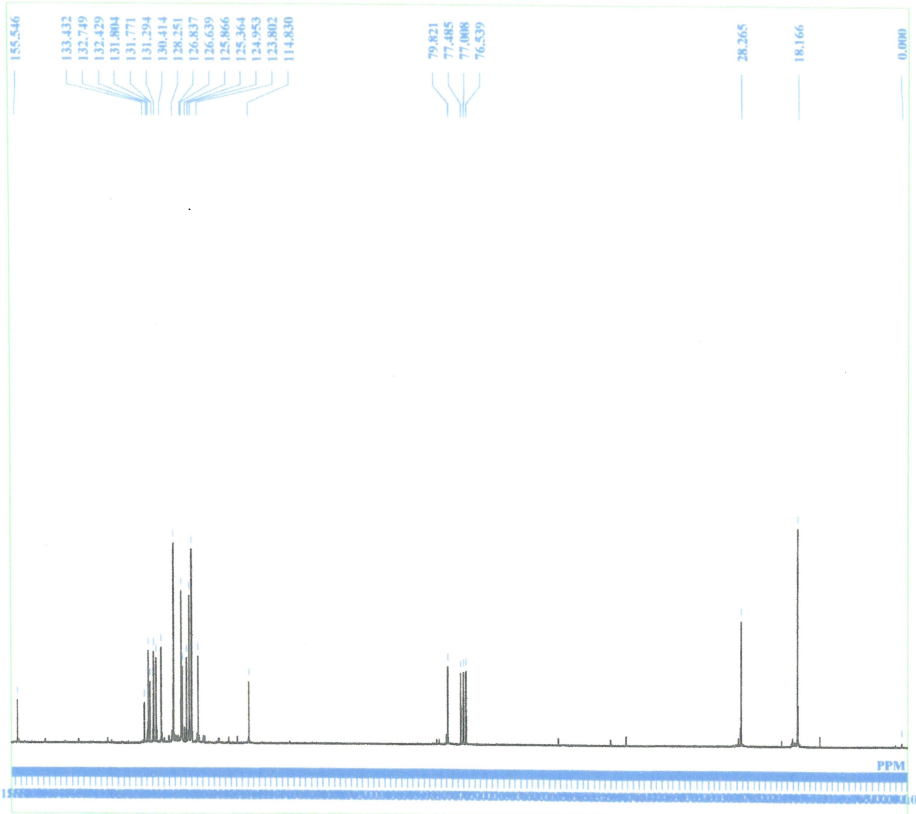
Field_Strength    = 11.62926421[T]  (500[MHz])
X_Acq_Duration    = 0.8388608[s]
X_Domain          = 13C
X_Freq            = 124.5010059[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.1920929[Hz]
X_Sweep           = 39.0625[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.1319398[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 1182
Total_Scans       = 1182

Relaxation_Delay  = 1[s]
Recvr_Gain        = 56
Temp_Cat          = 24.5[dC]
X_90_Width        = 10.8[us]
X_Acq_Time        = 0.8388608[s]
X_Angle           = 30[deg]
X_Atn             = 6.4[dB]
X_Pulse           = 3.6[us]
Irr_Atn_Dec       = 21.74856[dB]
Irr_Atn_Noe       = 21.74856[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 1[s]
Repetition_Time   = 1.8388608[s]
```

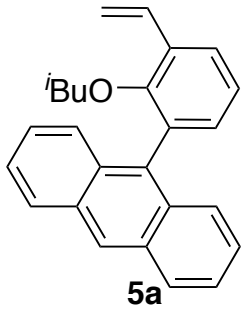


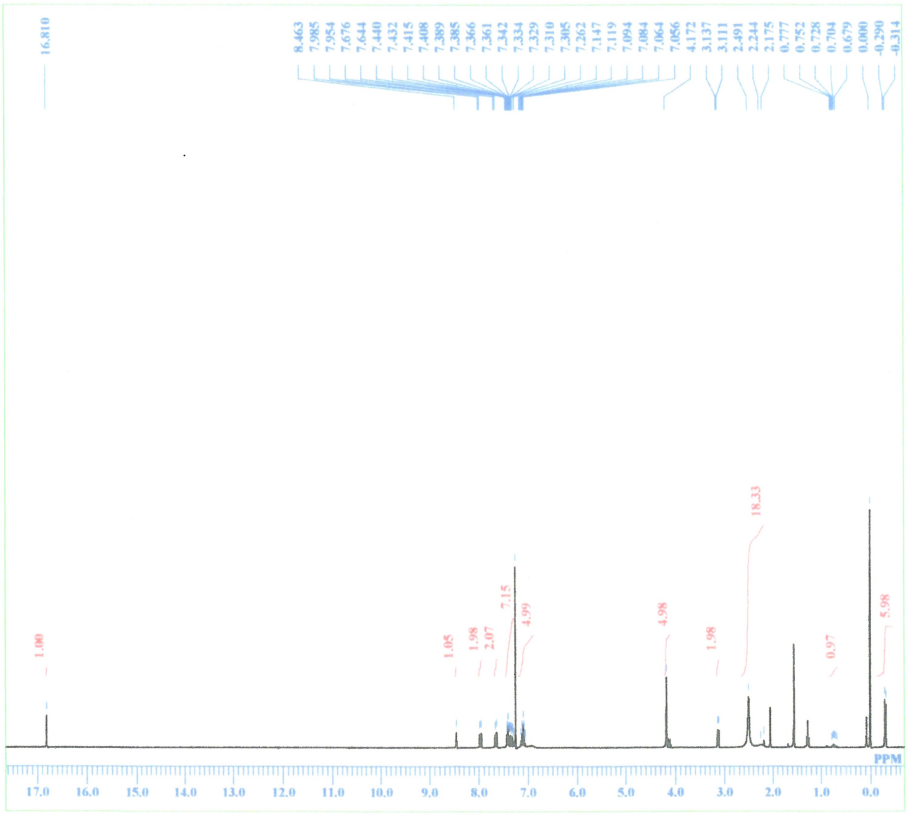
DFILE 20130927 Ligand isobu-9-anth-nontag.als
COMNT
DATIM Thu Dec 05 14:40:39 2013
OBNUC 1H
EXMOD NON
OBFRQ 270.05 MHz
OBSET 112.00 KHz
OBFIN 5800.00 Hz
POINT 8192
FREQU 5401.76 Hz
SCANS 16
ACQTM 1.5165 sec
PD 5.4830 sec
PW1 5.60 usec
IRNUC 1H
CTEMP 23.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 24



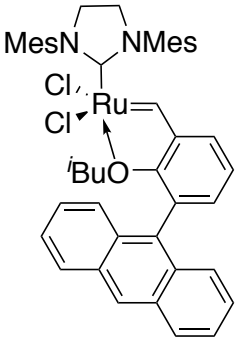


DFILE 20140302 ƒJ0[ƒ{ƒ"[@ibuligand.als
COMNT
DATIM Thu Mar 06 11:07:09 2014
OBNUC 13C
EXMOD BCM
OBFRQ 67.80 MHz
OBSET 135.00 KHz
OBFIN 5200.00 Hz
POINT 32768
FREQU 18306.64 Hz
SCANS 14178
ACQTM 1.7900 sec
PD 1.2100 sec
PW1 4.60 usec
IRNUC 1H
CTEMP 23.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 28

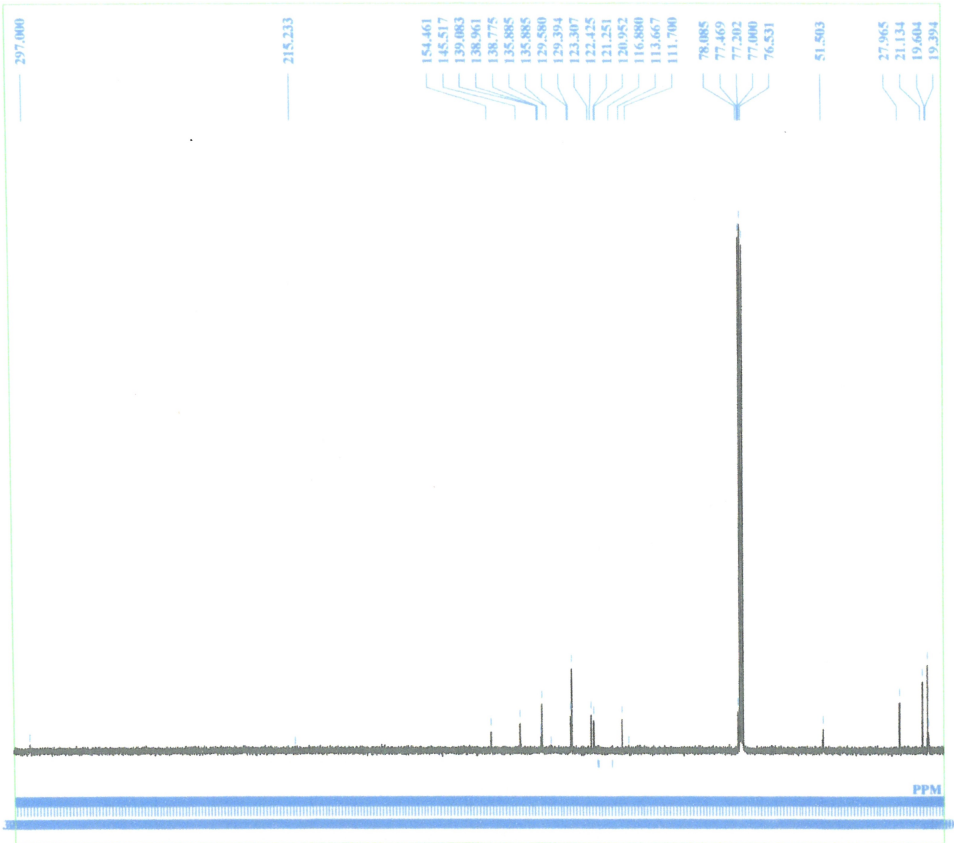




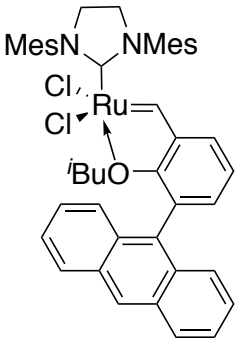
DFILE	isobu-9-anth-nontag.als
COMNT	
DATIM	Thu Dec 19 16:49:21 2013
OBNUC	1H
EXMOD	NON
OBFRQ	270.05 MHz
OBSET	119.00 KHz
OBFIN	3.00 Hz
POINT	16384
FREQU	5943.54 Hz
SCANS	16
ACQTM	2.7566 sec
PD	3.9670 sec
PW1	5.40 usec
IRNUC	1H
CTEMP	21.1 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	25



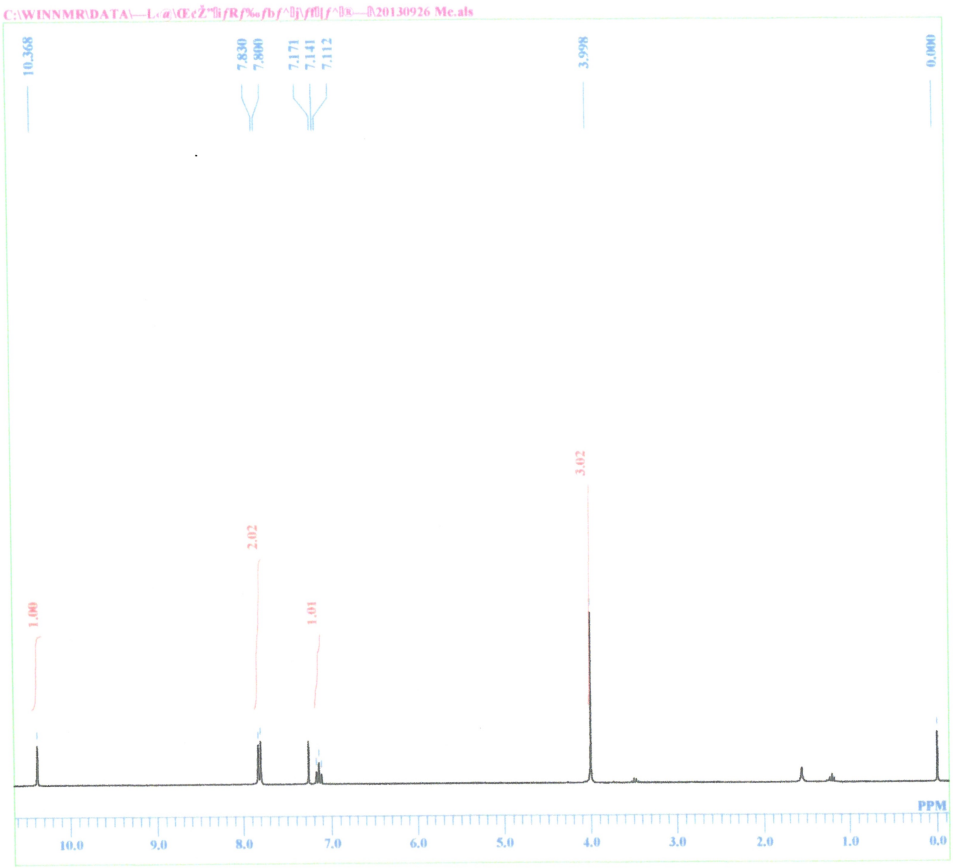
1h



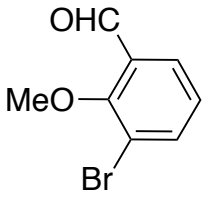
DFILE	*fuf fd@nontag cat.als*
COMNT	
DATIM	Tue Dec 02 09:57:28 2014
OBNUC	13C
EXMOD	BCM
OBFRQ	67.80 MHz
OBSET	135.00 KHz
OBFIN	5200.00 Hz
POINT	65536
FREQU	36036.04 Hz
SCANS	13861
ACQTM	1.8186 sec
PD	1.2100 sec
PW1	4.50 usec
IRNUC	1H
CTEMP	24.6 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	27



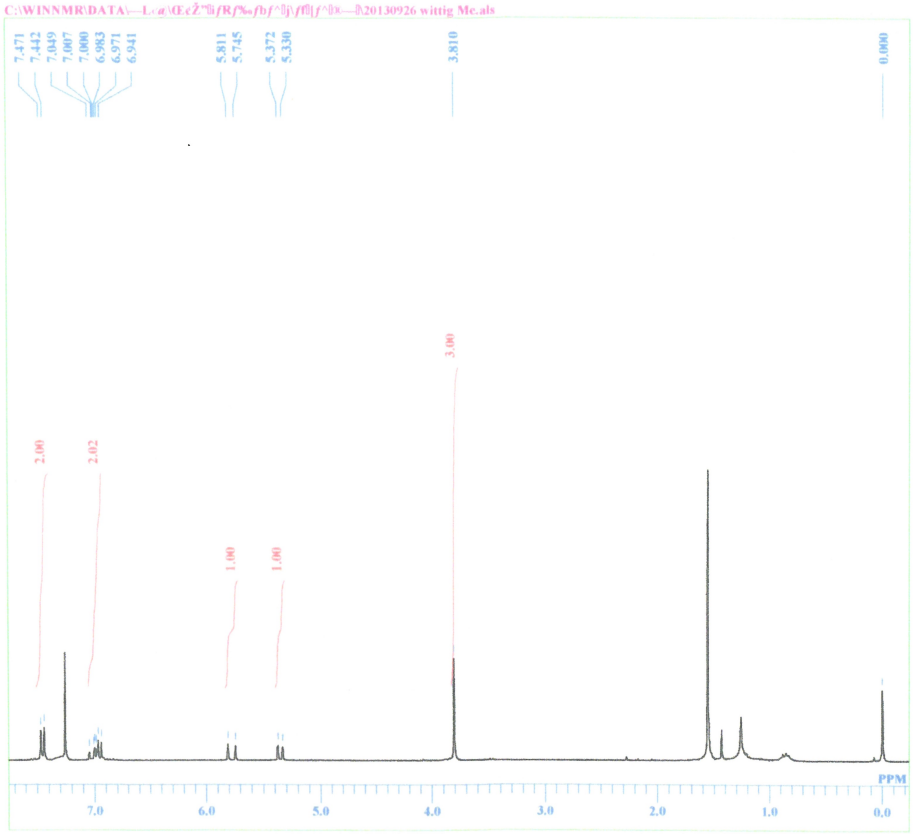
1h



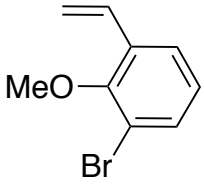
DFILE	20130926 Me.als
COMNT	
DATIM	Mon Jul 29 22:02:08 2013
OBNUC	1H
EXMOD	NON
OBFRQ	270.05 MHz
OBSET	112.00 KHz
OBFIN	5800.00 Hz
POINT	8192
FREQU	5401.76 Hz
SCANS	16
ACQTM	1.5165 sec
PD	5.4830 sec
PW1	5.60 usec
IRNUC	1H
CTEMP	24.5 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	24



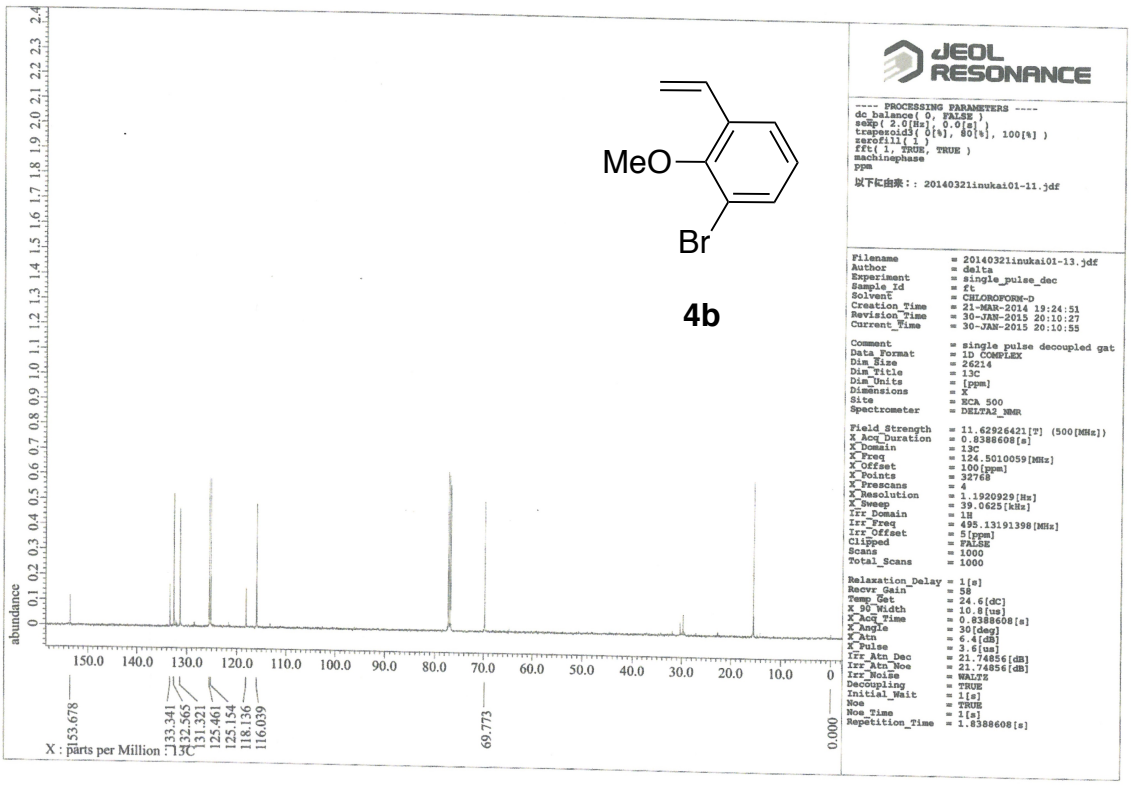
3b




```
DFILE    20130926 wittig Me.als
COMNT
DATIM    Wed Aug 21 21:48:27 2013
OBNUC    1H
EXMOD    NON
OBFRQ      270.05 MHz
OBSET      112.00 KHz
OBFIN      5800.00 Hz
POINT      8192
FREQU      5401.76 Hz
SCANS      16
ACQTM      1.5165 sec
PD         5.4830 sec
PW1        5.60 usec
IRNUC    1H
CTEMP      27.3 c
SLVNT    CDCL3
EXREF      0.00 ppm
BF         0.12 Hz
RGAIN      25
```



4b



4b

JEOL RESONANCE

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

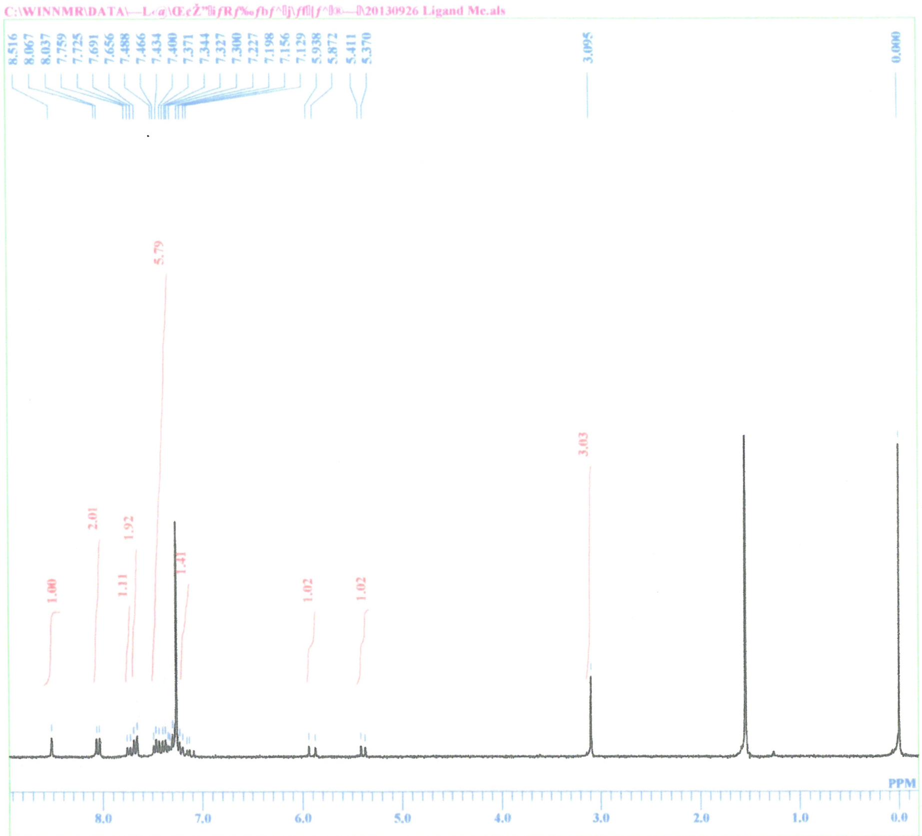
以下に由来：: 20140321inukai01-11.jdf

Filename          = 20140321inukai01-13.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = ft
Solvent           = CHLOROFORM-D
Creation_Time     = 21-MAR-2014 19:24:51
Revision_Time     = 30-JAN-2015 20:10:27
Current_Time      = 30-JAN-2015 20:10:55

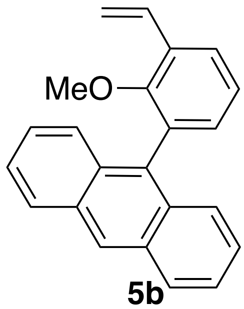
Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = NCA_500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 0.8388608[s]
X_Domain          = 13C
X_Freq            = 124.5010059[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.1920929[Hz]
X_Sweep           = 39.0625[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 1000
Total_Scans       = 1000

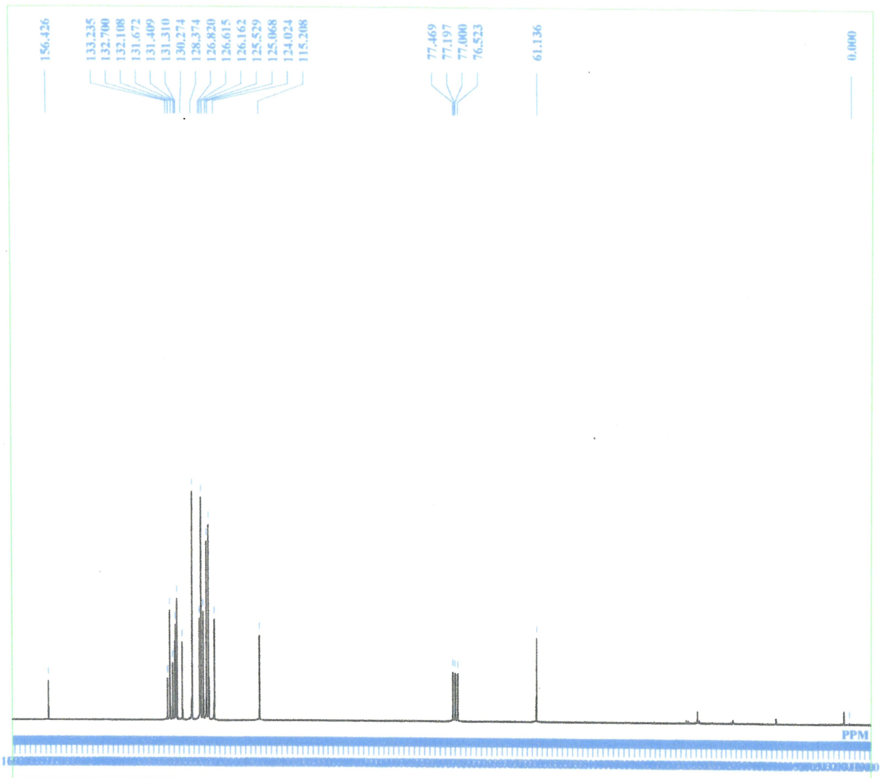
Relaxation_Delay  = 1[s]
Recvr_Gain        = 58
Temp_Get          = 24.6[dC]
X_90_Width        = 10.8[us]
X_Acq_Time        = 0.8388608[s]
X_Angle           = 30[deg]
X_Atn             = 6.4[dB]
X_Pulse           = 3.6[us]
Irr_Atn_Dec       = 21.74856[dB]
Irr_Atn_Noe       = 21.74856[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 1[s]
Repetition_Time   = 1.8388608[s]
```



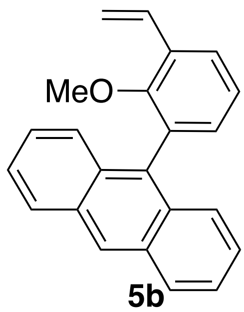
DFILE	20130926 Ligand Me.als
COMNT	
DATIM	Tue Aug 27 18:29:14 2013
OBNUC	1H
EXMOD	NON
OBFRQ	270.05 MHz
OBSET	112.00 KHz
OBFIN	5800.00 Hz
POINT	8192
FREQU	5401.76 Hz
SCANS	8
ACQTM	1.5165 sec
PD	5.4830 sec
PW1	5.60 usec
IRNUC	1H
CTEMP	25.4 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	27



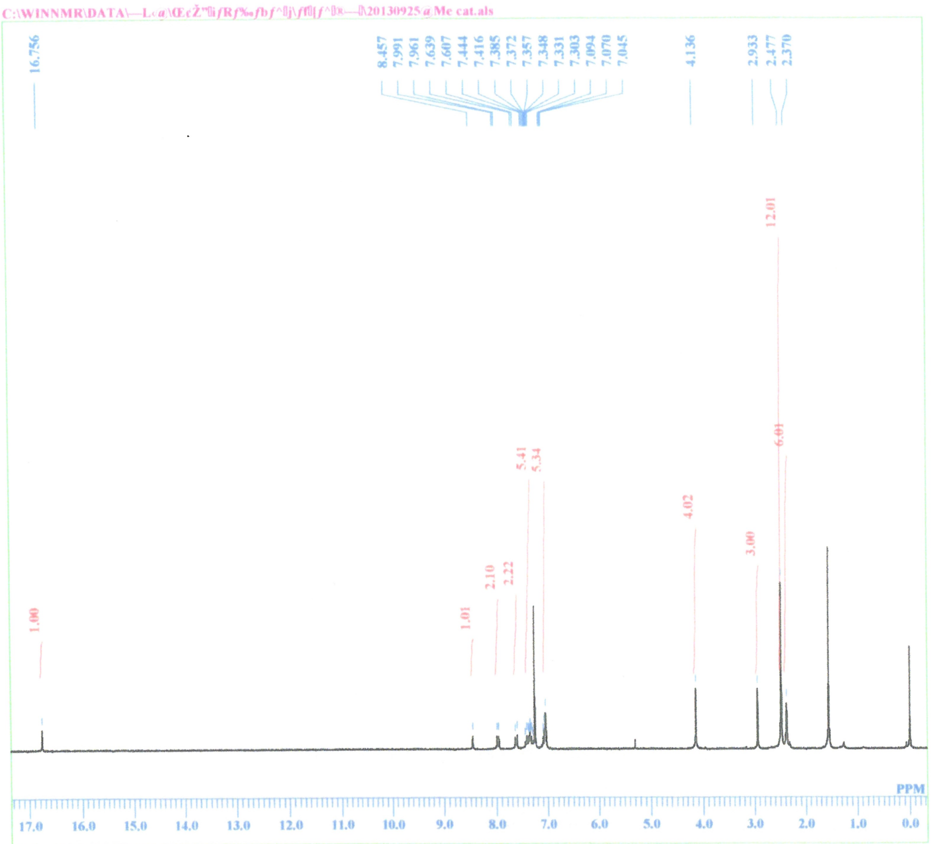
5b



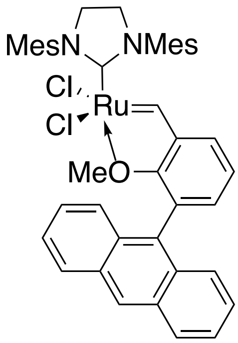
DFILE	20140307 ƒJƒ|ƒ{ƒ"l@Meligand.als
COMNT	
DATIM	Sat Mar 08 11:00:29 2014
OBNUC	13C
EXMOD	BCM
OBFRQ	67.80 MHz
OBSET	135.00 KHz
OBFIN	5200.00 Hz
POINT	32768
FREQU	18306.64 Hz
SCANS	13701
ACQTM	1.7900 sec
PD	1.2100 sec
PW1	4.60 usec
IRNUC	1H
CTEMP	23.4 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	26



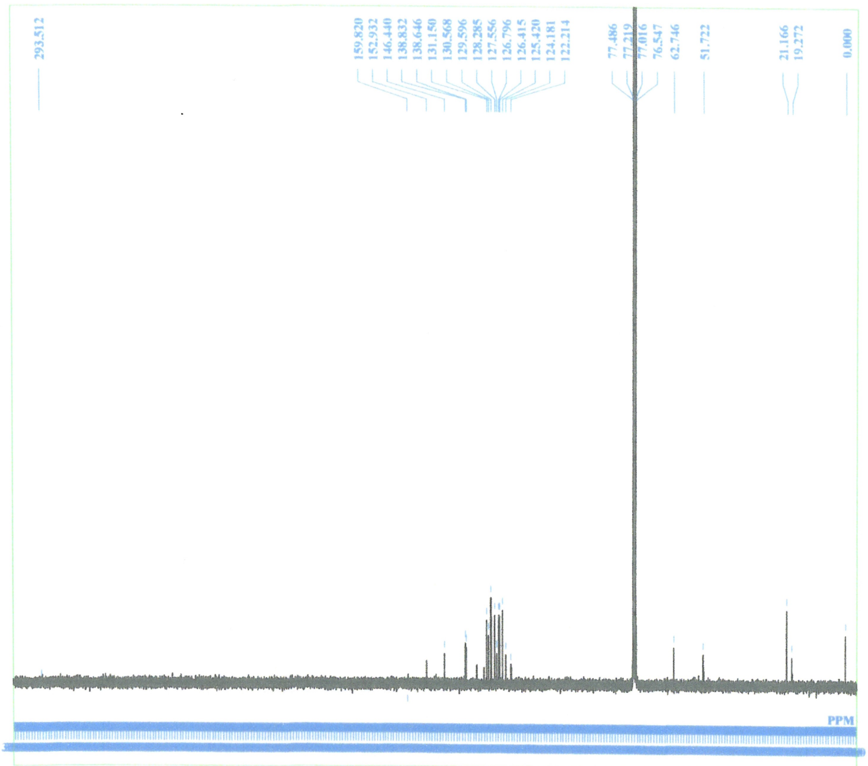
5b



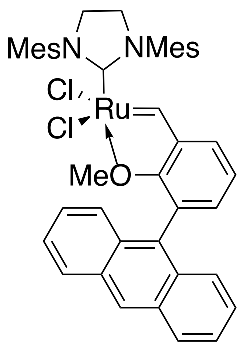
DFILE	20130925@Me cat.als
COMNT	
DATIM	Sun Sep 08 15:22:06 2013
OBNUC	1H
EXMOD	NON
OBFRQ	270.05 MHz
OBSET	119.00 KHz
OBFIN	3.00 Hz
POINT	16384
FREQU	5943.54 Hz
SCANS	16
ACQTM	2.7566 sec
PD	3.9670 sec
PW1	5.40 usec
IRNUC	1H
CTEMP	24.1 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	25



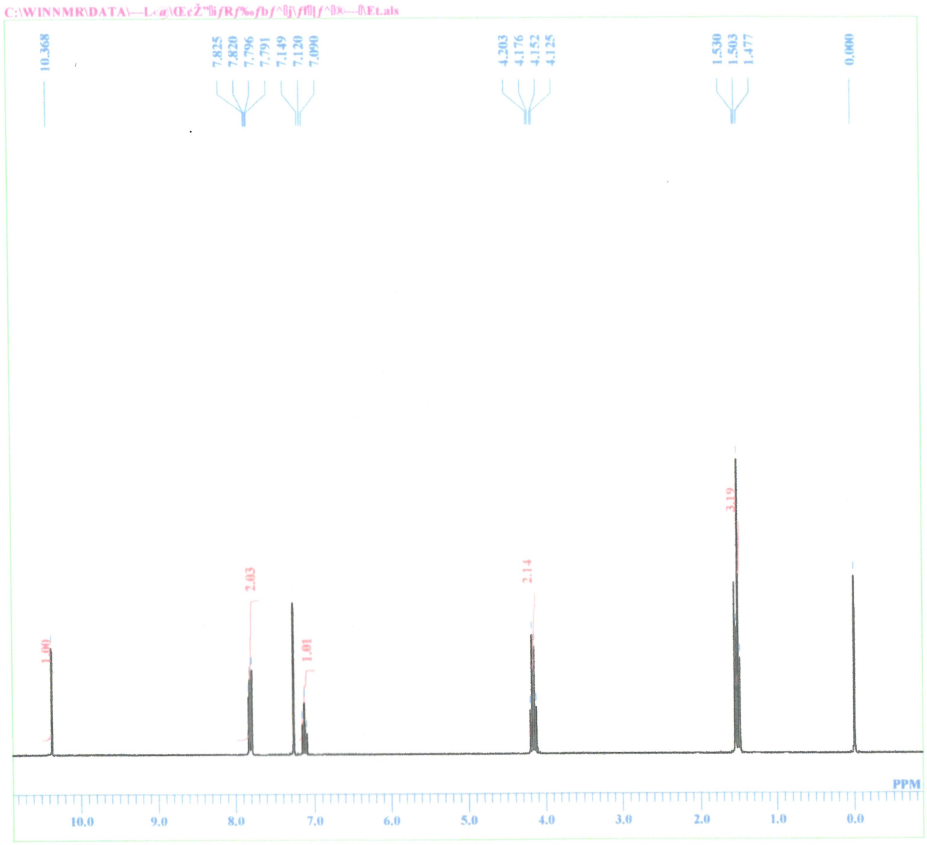
1i



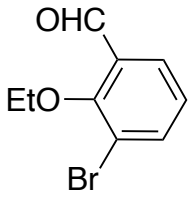
DFILE	20130909 [illegible]@nontag cat.als
COMNT	
DATIM	Mon Sep 09 10:56:09 2013
OBNUC	13C
EXMOD	BCM
OBFRQ	67.80 MHz
OBSET	135.00 KHz
OBFIN	5200.00 Hz
POINT	65536
FREQU	36036.04 Hz
SCANS	14488
ACQTM	1.8186 sec
PD	1.2100 sec
PW1	4.50 usec
IRNUC	1H
CTEMP	24.6 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	26



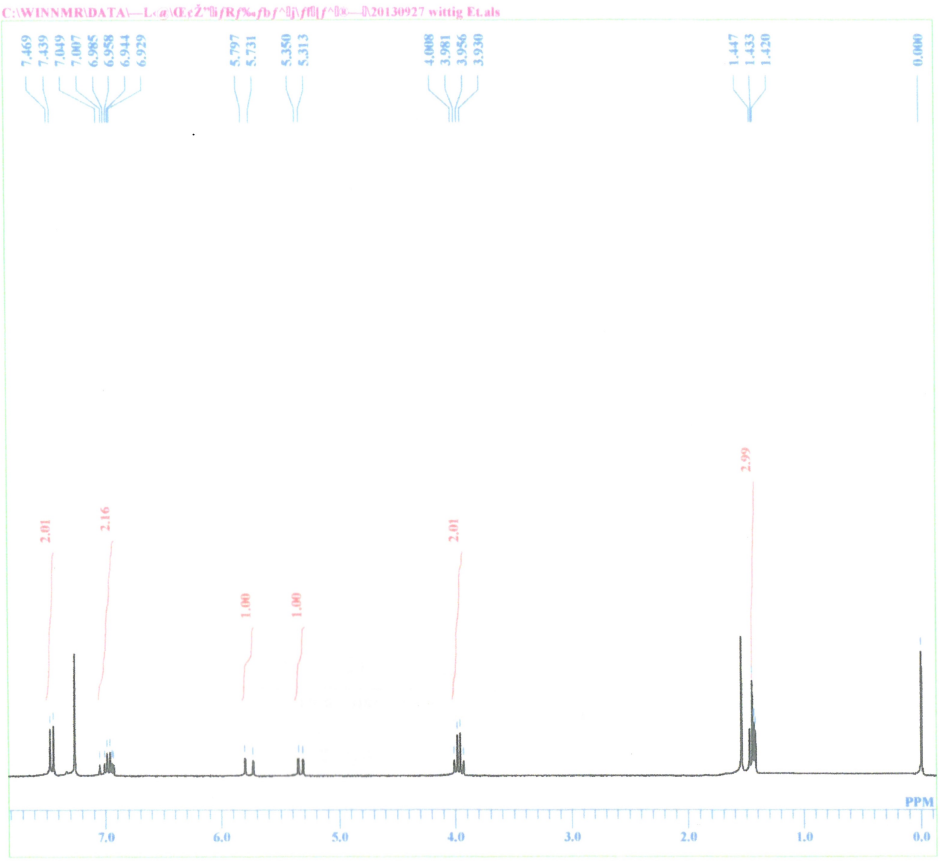
1i



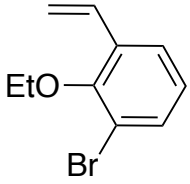
DFILE	Et.als
COMNT	
DATIM	Wed Mar 13 13:25:28 2013
OBNUC	1H
EXMOD	NON
OBFRQ	270.05 MHz
OBSET	112.00 KHz
OBFIN	5800.00 Hz
POINT	8192
FREQU	5401.76 Hz
SCANS	16
ACQTM	1.5165 sec
PD	5.4830 sec
PW1	5.60 usec
IRNUC	1H
CTEMP	25.7 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	25



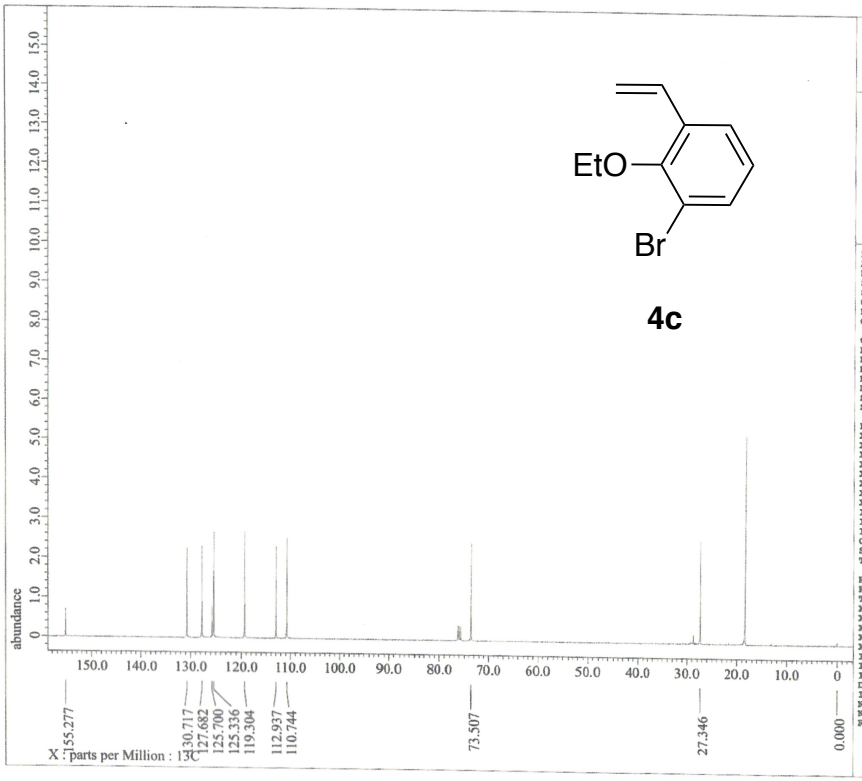
3c



DFILE 20130927 wittig Et.als
COMNT
DATIM Mon Mar 18 13:15:33 2013
OBNUC 1H
EXMOD NON
OBFRQ 270.05 MHz
OBSET 112.00 KHz
OBFIN 5800.00 Hz
POINT 8192
FREQU 5401.76 Hz
SCANS 16
ACQTM 1.5165 sec
PD 5.4830 sec
PW1 5.60 usec
IRNUC 1H
CTEMP 24.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 25



4c

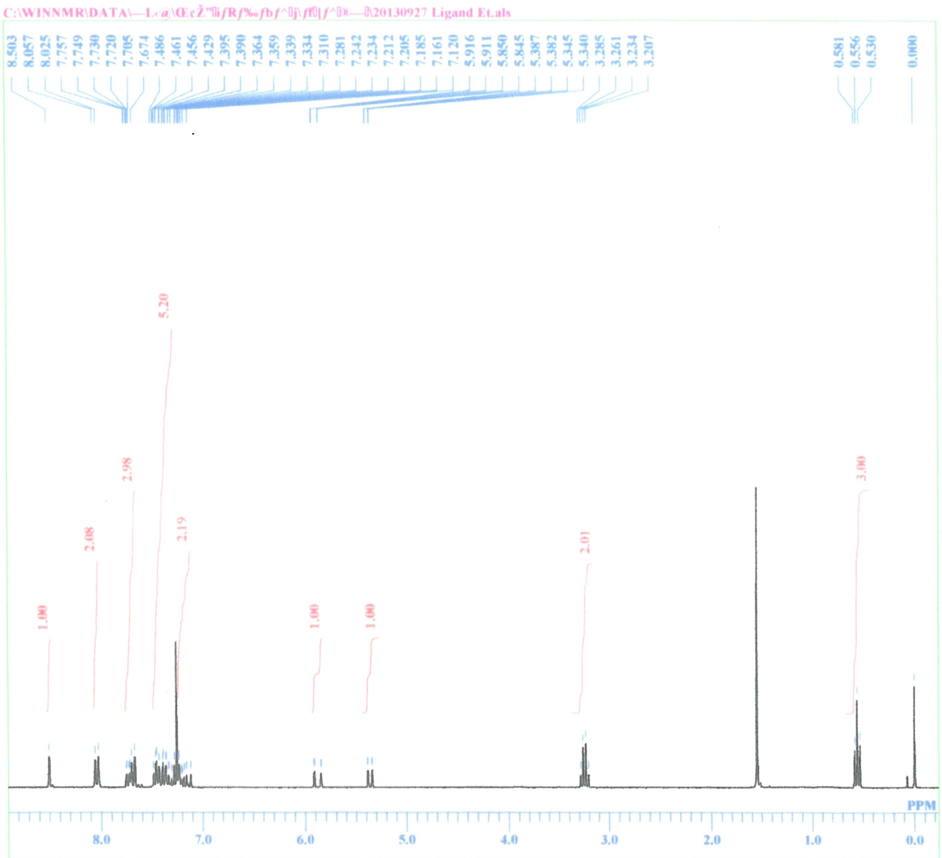


4c

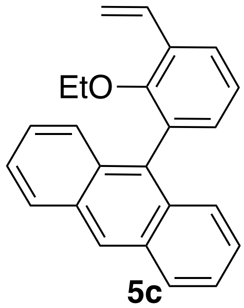
JEOL RESONANCE

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid3( 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
以下に由来：: 1d_13c_sumple01-8.jdf
```

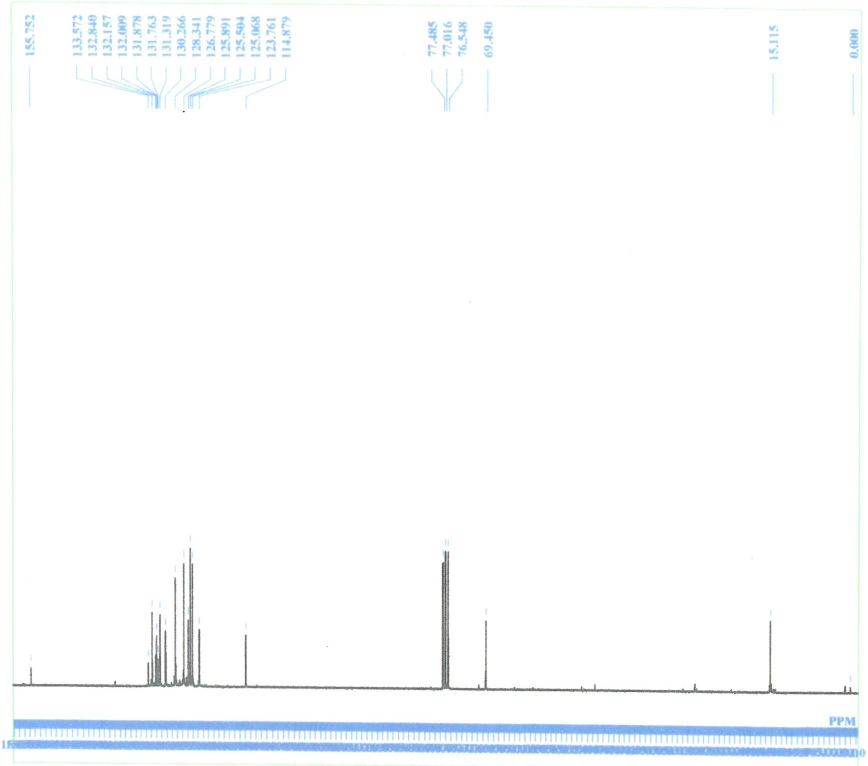
Filename	= 1d_13c_sumple01-10.jdf
Author	= dalta
Experiment	= single_pulse_dec
Sample_Id	= inu
Solvent	= CHLOROFORM-D
Creation_Time	= 24-MAR-2014 13:14:29
Revision_Time	= 30-JAN-2015 20:13:16
Current_Time	= 30-JAN-2015 20:13:53
Comment	= single pulse decoupled gat
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
Dim_Title	= 13C
Dim_Units	= [ppm]
Dimensions	= X
Site	= RCA 500
Spectrometer	= DELTA2_NMR
Field_Strength	= 11.62926421[T] (500[MHz])
X_Acq_Duration	= 0.8388608[s]
X_Domain	= 13C
X_Freq	= 124.5010059[MHz]
X_Offset	= 100[ppm]
X_Points	= 32768
X_Prescans	= 4
X_Resolution	= 1.1920929[Hz]
X_Sweep	= 39.0625[kHz]
Irr_Domain	= 1H
Irr_Freq	= 495.13191398[MHz]
Irr_Offset	= 5[ppm]
Clipped	= FALSE
Scans	= 1000
Total_Scans	= 1000
Relaxation_Delay	= 1[s]
Recvr_Gain	= 58
Temp_Set	= 24.5[dC]
X_90_Width	= 10.8[us]
X_Acq_Time	= 0.8388608[s]
X_Angle	= 30[deg]
X_Atn	= 6.4[dB]
X_Pulse	= 3.6[us]
Irr_Atn_Dec	= 21.74856[dB]
Irr_Atn_Noe	= 21.74856[dB]
Irr_Noise	= WALTZ
Decoupling	= TRUE
Initial_Wait	= 1[s]
Noe	= TRUE
Noe_Time	= 1[s]
Repetition_Time	= 1.8388608[s]



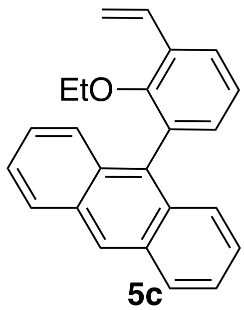
DFILE 20130927 Ligand Et.als
COMNT
DATIM Thu Jun 20 17:20:34 2013
OBNUC 1H
EXMOD NON
OBFRQ 270.05 MHz
OBSET 112.00 KHz
OBFIN 5800.00 Hz
POINT 8192
FREQU 5401.76 Hz
SCANS 16
ACQTM 1.5165 sec
PD 5.4830 sec
PW1 5.60 usec
IRNUC 1H
CTEMP 25.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 24



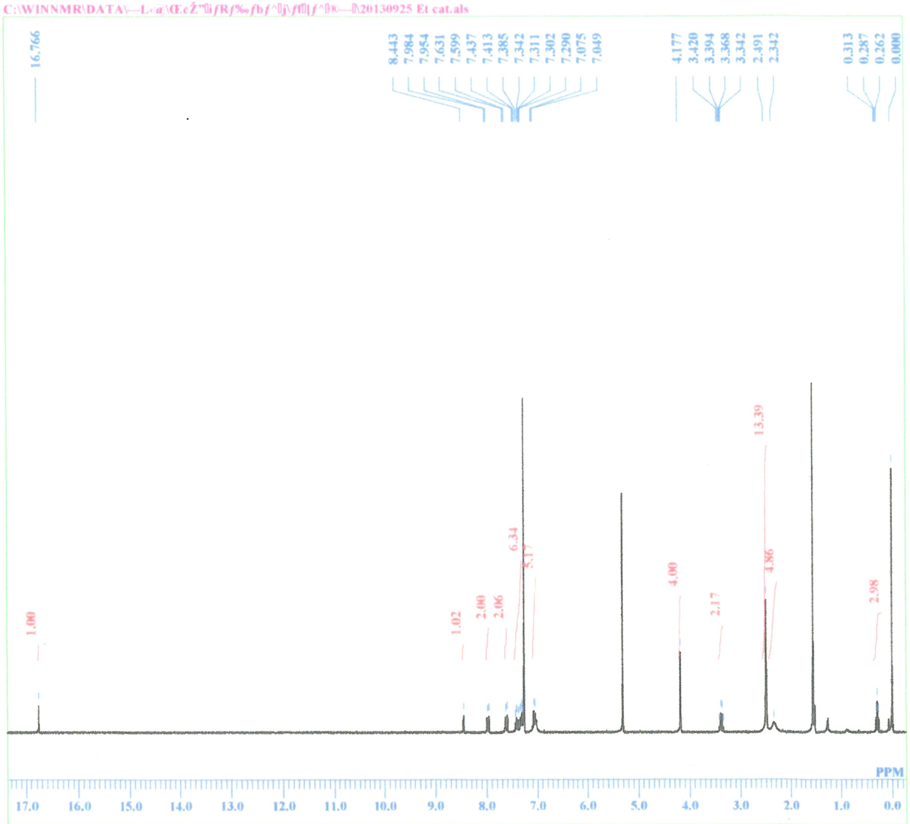
5c



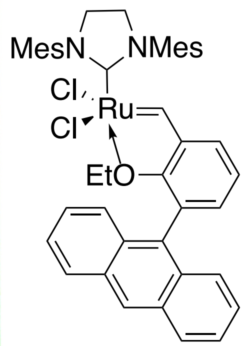
DFILE 20140302 Etligand.als
COMNT
DATIM Sun Mar 02 11:06:20 2014
OBNUC 13C
EXMOD BCM
OBFRQ 67.80 MHz
OBSET 135.00 KHz
OBFIN 5200.00 Hz
POINT 32768
FREQU 18306.64 Hz
SCANS 14788
ACQTM 1.7900 sec
PD 1.2100 sec
PW1 4.60 usec
IRNUC 1H
CTEMP 24.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 28



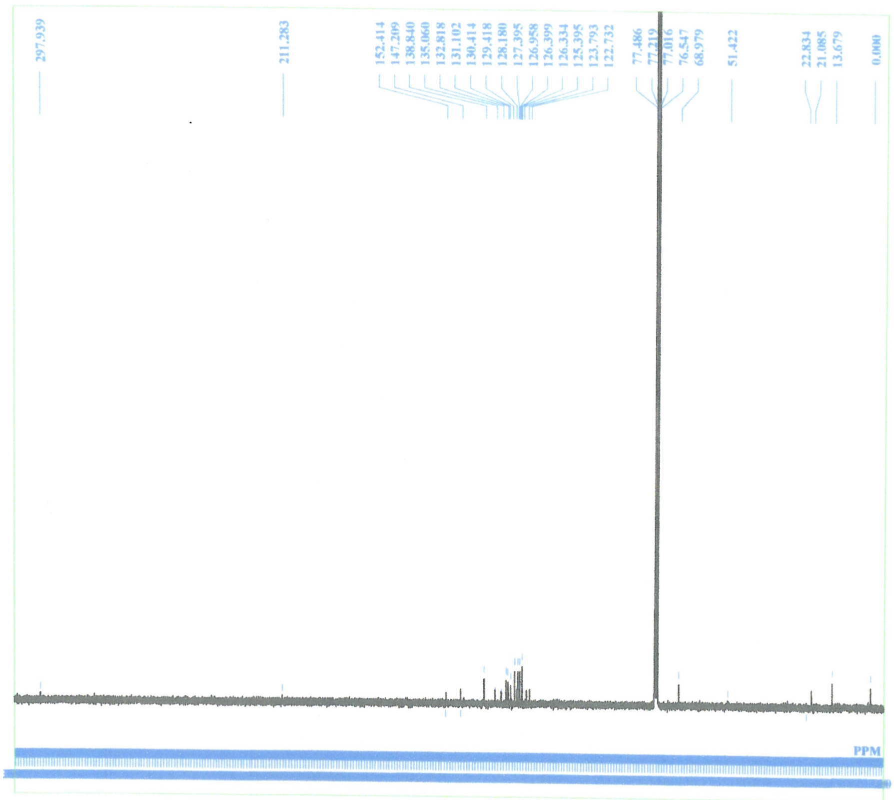
5c



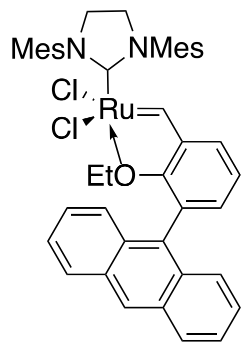
DFILE 20130925 Et cat.als
COMNT
DATIM Sun Jul 28 14:57:08 2013
OBNUC 1H
EXMOD NON
OBFRQ 270.05 MHz
OBSET 119.00 KHz
OBFIN 3.00 Hz
POINT 16384
FREQU 5943.54 Hz
SCANS 16
ACQTM 2.7566 sec
PD 3.9670 sec
PW1 5.40 usec
IRNUC 1H
CTEMP 24.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 27



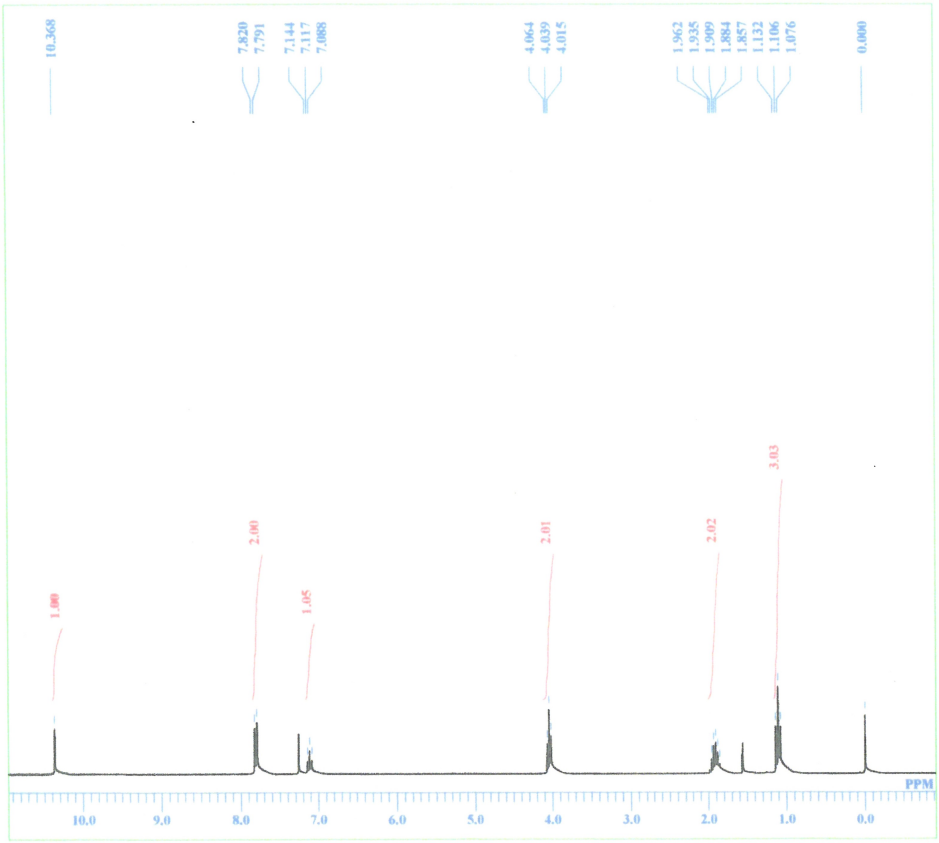
1j



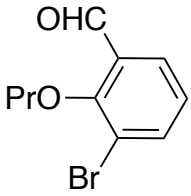
DFILE 20130731 ...
COMNT H18,11,16 tomioka
DATIM Wed Jul 31 11:16:18 2013
OBNUC 13C
EXMOD BCM
OBFRQ 67.80 MHz
OBSET 135.00 KHz
OBFIN 5200.00 Hz
POINT 65536
FREQU 36036.04 Hz
SCANS 14475
ACQTM 1.8186 sec
PD 1.2100 sec
PW1 4.50 usec
IRNUC 1H
CTEMP 24.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 24



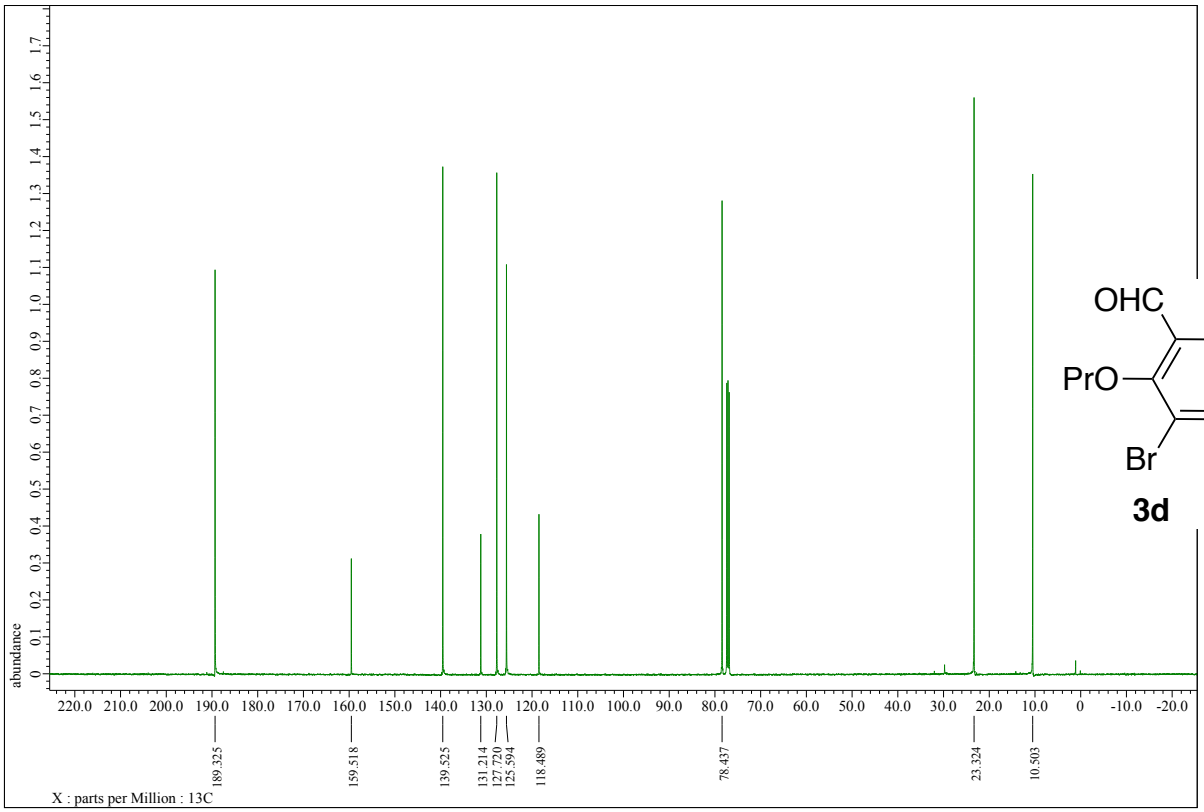
1j

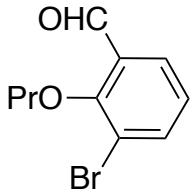


DFILE 20130129 Pr.als
COMNT
DATIM Wed Apr 17 13:51:10 2013
OBNUC 1H
EXMOD NON
OBFRQ 270.05 MHz
OBSET 112.00 KHz
OBFIN 5800.00 Hz
POINT 8192
FREQU 5401.76 Hz
SCANS 16
ACQTM 1.5165 sec
PD 5.4830 sec
PW1 5.60 usec
IRNUC 1H
CTEMP 24.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 23

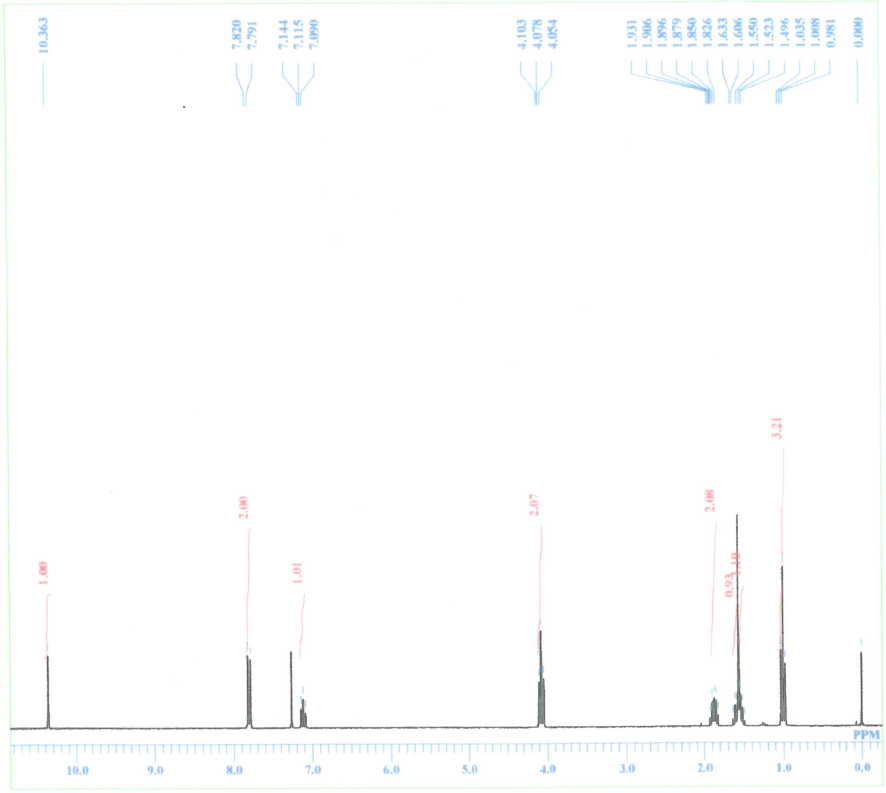


3d

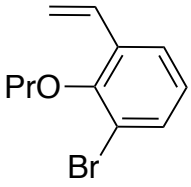




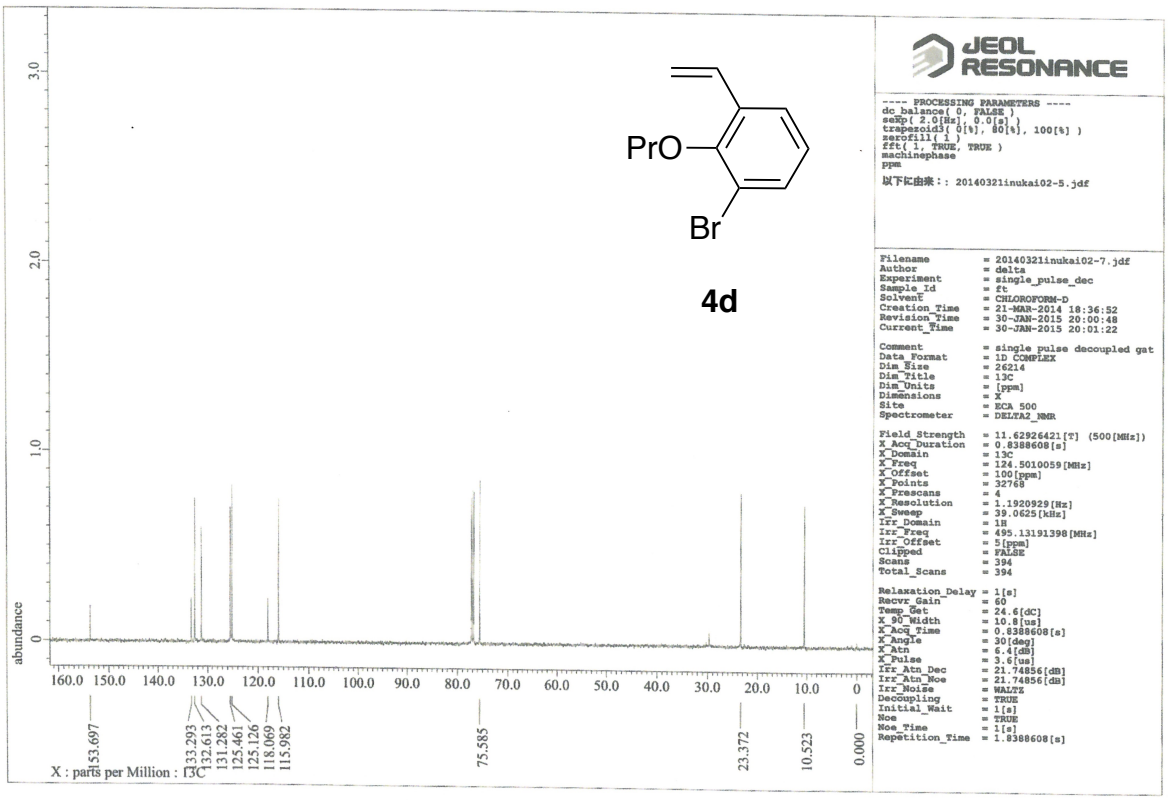
3d




```
DFILE     20130926 wittig Pro-9-anth-nontag.als
COMNT
DATIM     Fri Jul 26 18:21:02 2013
OBNUC     1H
EXMOD     NON
OBFRQ       270.05 MHz
OBSET       112.00 KHz
OBFIN      5800.00 Hz
POINT        8192
FREQU      5401.76 Hz
SCANS          16
ACQTM       1.5165 sec
PD          5.4830 sec
PW1         5.60 usec
IRNUC     1H
CTEMP       25.1 c
SLVNT     CDCL3
EXREF       0.00 ppm
BF          0.12 Hz
RGAIN          23
```



4d



4d

JEOL RESONANCE

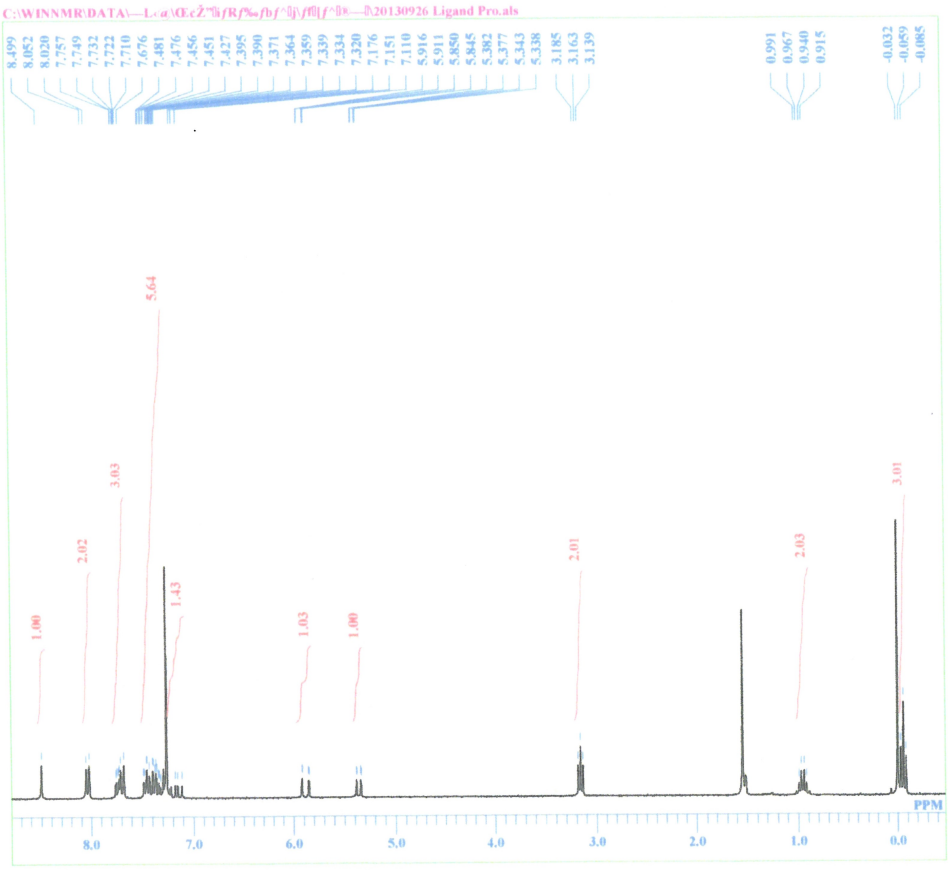
```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
setXp( 2.0[Hz], 0.0[s] )
trapezoid3( 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
以下に由来：: 20140321inukai02-5.jdf
```

```
Filename          = 20140321inukai02-7.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = ft
Solvent           = CHLOROFORM-D
Creation_Time     = 21-MAR-2014 18:36:52
Revision_Time     = 30-JAN-2015 20:00:48
Current_Time      = 30-JAN-2015 20:01:22

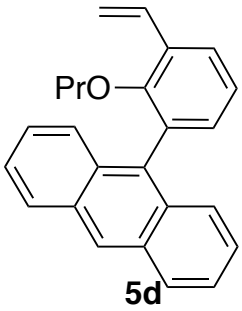
Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

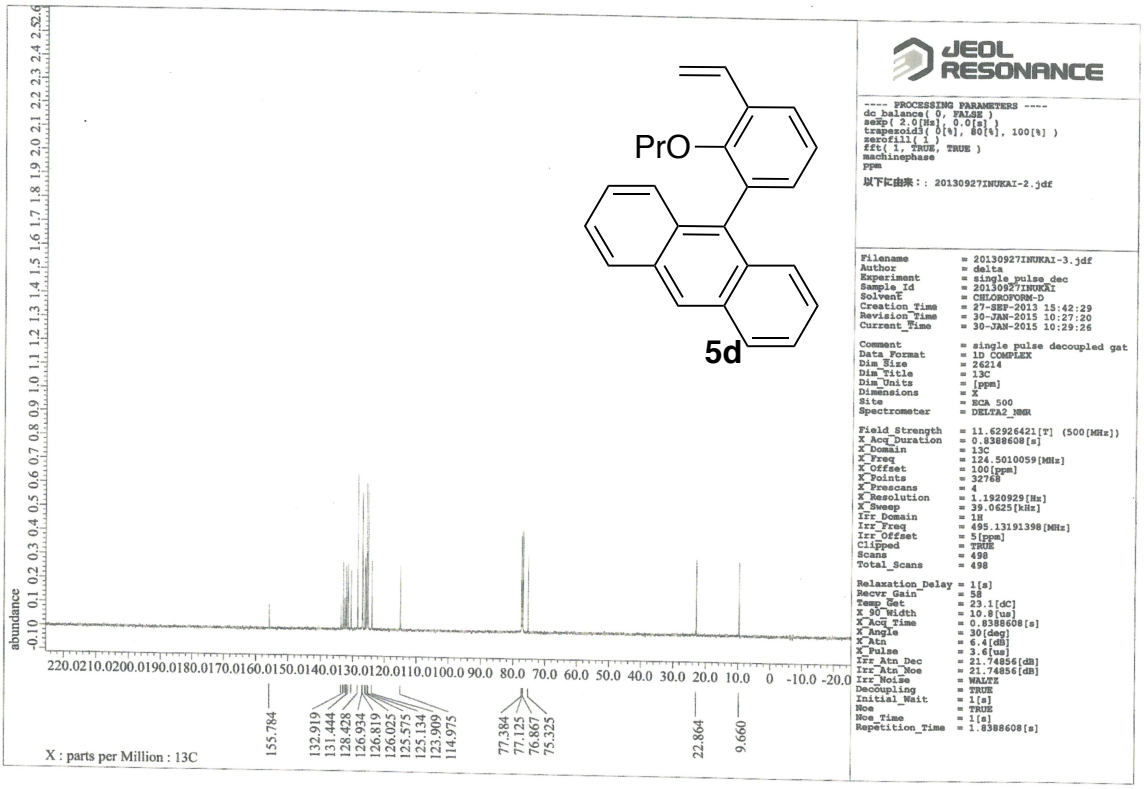
Field_Strength    = 11.62926421[T]  (500[MHz])
X_Acq_Duration    = 0.8388608[s]
X_Domain          = 13C
X_Freq            = 124.5010059[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.1920929[Hz]
X_Sweep           = 39.0625[kHz]
Irr_Domain        = 1H
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 394
Total_Scans       = 394

Relaxation_Delay  = 1[s]
Recvr_Gain        = 60
Temp_Get          = 24.6[dC]
X_90_Width        = 10.8[us]
X_Acq_Time        = 0.8388608[s]
X_Angle           = 30[deg]
X_Atn             = 6.6[dB]
X_Pulse           = 3.6[us]
Irr_Atn_Dec       = 21.74856[dB]
Irr_Atn_Noe       = 21.74856[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 1[s]
Repetition_Time   = 1.8388608[s]
```



DFILE	20130926 Ligand Pro.als
COMNT	
DATIM	Sat Jun 29 10:27:45 2013
OBNUC	1H
EXMOD	NON
OBFRQ	270.05 MHz
OBSET	112.00 KHz
OBFIN	5800.00 Hz
POINT	8192
FREQU	5401.76 Hz
SCANS	16
ACQTM	1.5165 sec
PD	5.4830 sec
PW1	5.60 usec
IRNUC	1H
CTEMP	25.1 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	26

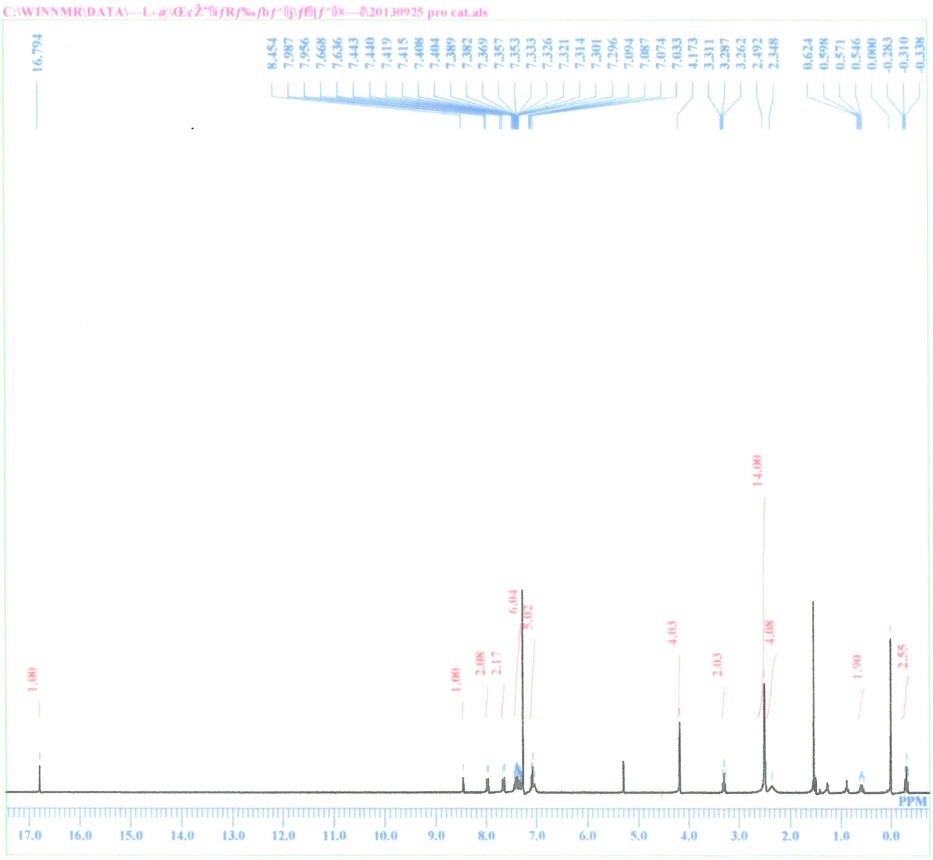




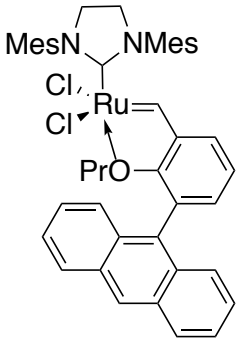
JEOL RESONANCE

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
em&p( 2.0[Hz], 0.0[s] )
trapezoid3( 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
以下に由来：: 20130927INUKAI-2.jdf
```

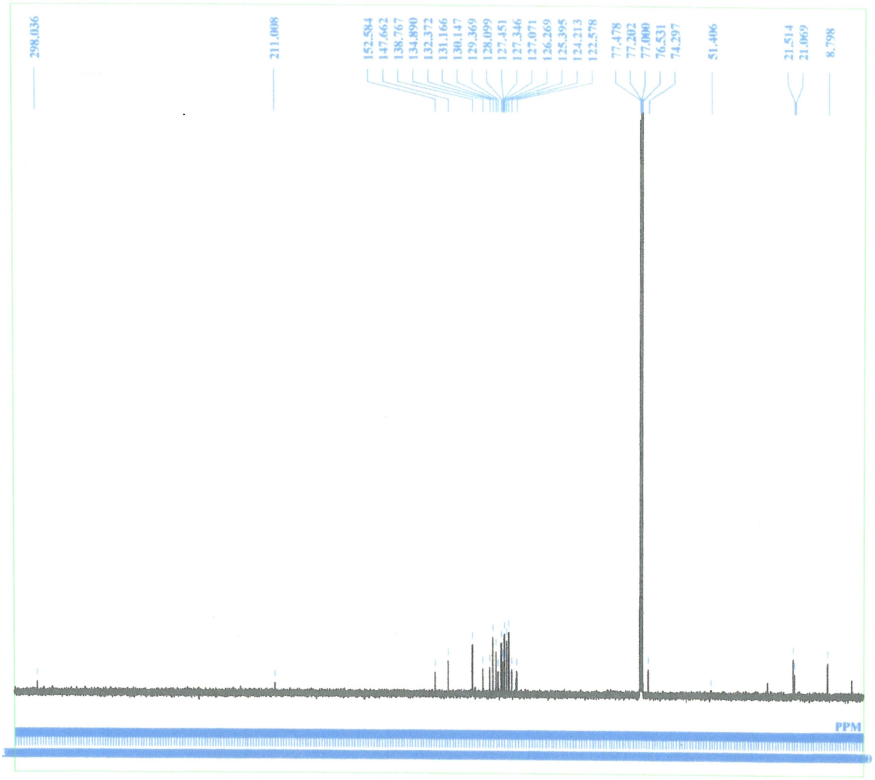
Filename	= 20130927INUKAI-3.jdf
Author	= delta
Experiment	= single_pulse_dec
Sample_Id	= 20130927INUKAI
Solvent	= CHLOROFORM-D
Creation_Time	= 27-SEP-2013 15:42:29
Revision_Time	= 30-JAN-2015 10:27:20
Current_Time	= 30-JAN-2015 10:29:26
Comment	= single pulse decoupled gat
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
Dim_Title	= 13C
Dim_Units	= [ppm]
Dimensions	= X
Site	= RCA 500
Spectrometer	= DELTA2_NMR
Field_Strength	= 11.62926421[T] (500[MHz])
X_Acq_Duration	= 0.8388608[s]
X_Domain	= 13C
X_Freq	= 124.5010059[MHz]
X_Offset	= 100[ppm]
X_Points	= 32768
X_Prescans	= 4
X_Resolution	= 1.1920929[Hz]
X_Sweep	= 39.0625[kHz]
Irr_Domain	= 1H
Irr_Freq	= 495.13191398[MHz]
Irr_Offset	= 5[ppm]
Clipped	= TRUE
Scans	= 498
Total_Scans	= 498
Relaxation_Delay	= 1[s]
Recvr_Gain	= 58
Temp_Get	= 23.1[dC]
X_90_Width	= 10.8[us]
X_Acq_Time	= 0.8388608[s]
X_Angle	= 30[deg]
X_Atn	= 6.4[dB]
X_Pulse	= 3.6[us]
Irr_Atn_Dec	= 21.74856[dB]
Irr_Atn_Noe	= 21.74856[dB]
Irr_NoiSe	= WALTZ
Decoupling	= TRUE
Initial_Wait	= 1[s]
Noe	= TRUE
Noe_Time	= 1[s]
Repetition_Time	= 1.8388608[s]



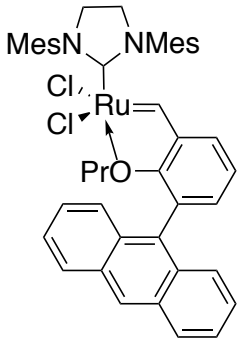
DFILE	20130925 pro cat.als
COMNT	
DATIM	Sun Jun 30 14:52:11 2013
OBNUC	1H
EXMOD	NON
OBFRQ	270.05 MHz
OBSET	119.00 KHz
OBFIN	3.00 Hz
POINT	16384
FREQU	5943.54 Hz
SCANS	16
ACQTM	2.7566 sec
PD	3.9670 sec
PW1	5.40 usec
IRNUC	1H
CTEMP	25.5 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	26



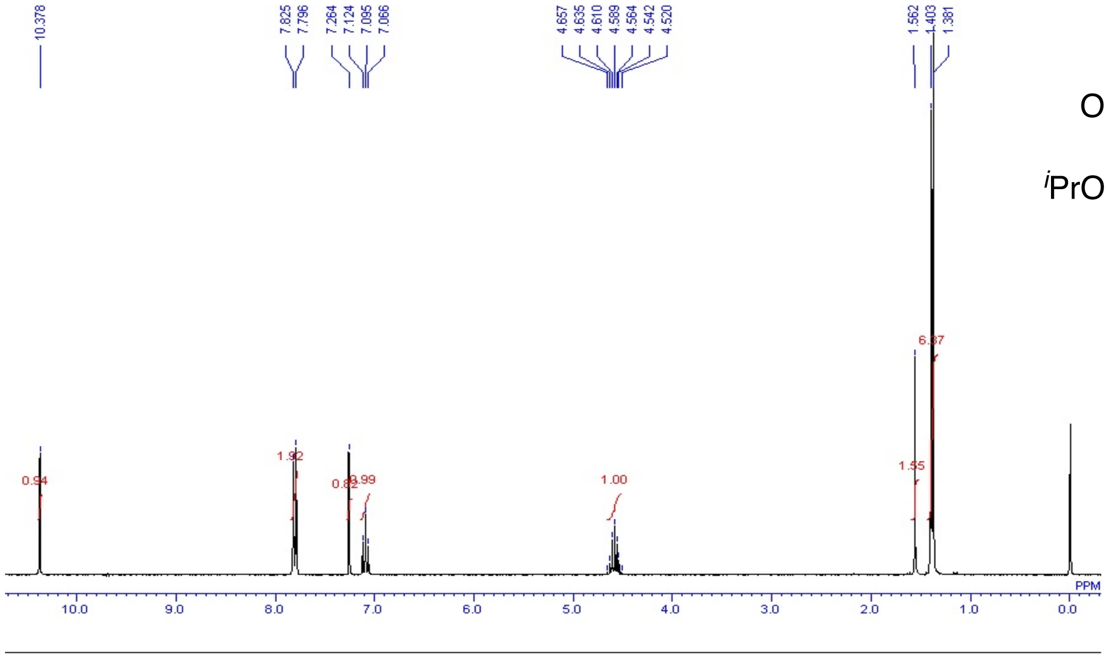
1k

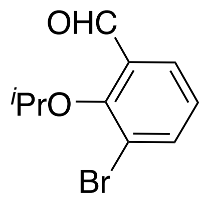


DFILE	20130527 fJl[f{f^l@fvflfsfd@nontag cat.
COMNT	H18,11,16 tomioka
DATIM	Mon Jul 01 11:05:43 2013
OBNUC	13C
EXMOD	BCM
OBFRQ	67.80 MHz
OBSET	135.00 KHz
OBFIN	5200.00 Hz
POINT	65536
FREQU	36036.04 Hz
SCANS	14333
ACQTM	1.8186 sec
PD	1.2100 sec
PW1	4.50 usec
IRNUC	1H
CTEMP	24.7 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	26

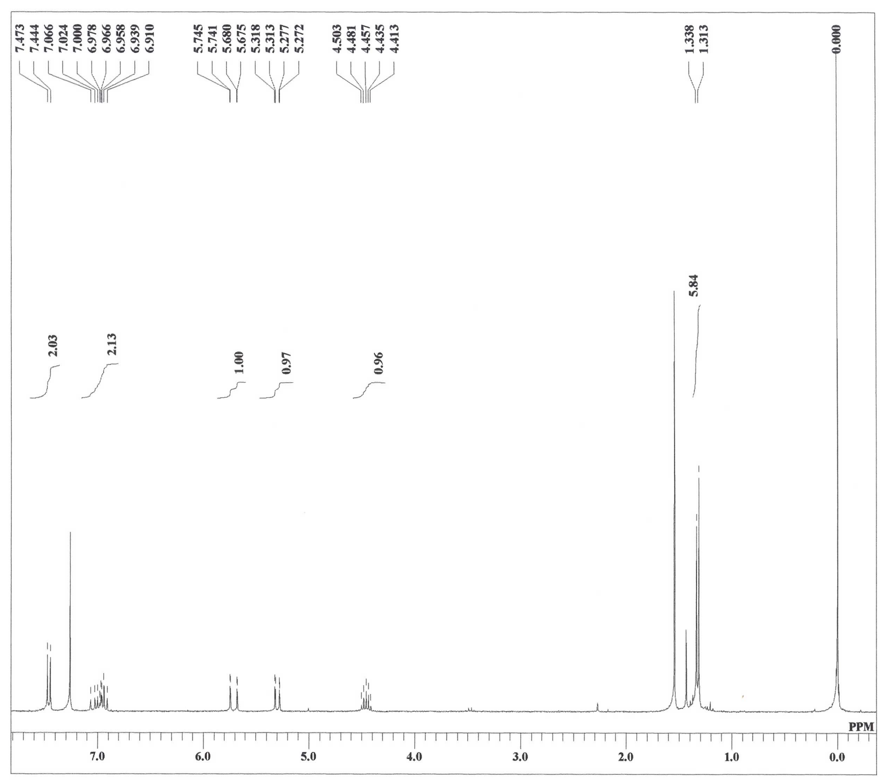


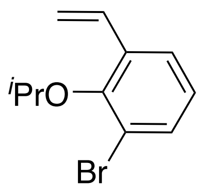
1k


10.378
7.825 7.796 7.264 7.124 7.095 7.066
4.657 4.635 4.610 4.589 4.564 4.542 4.520
1.562 1.403 1.381
0.94 1.92 0.82 0.99 1.00 1.55 6.67
PPM
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0

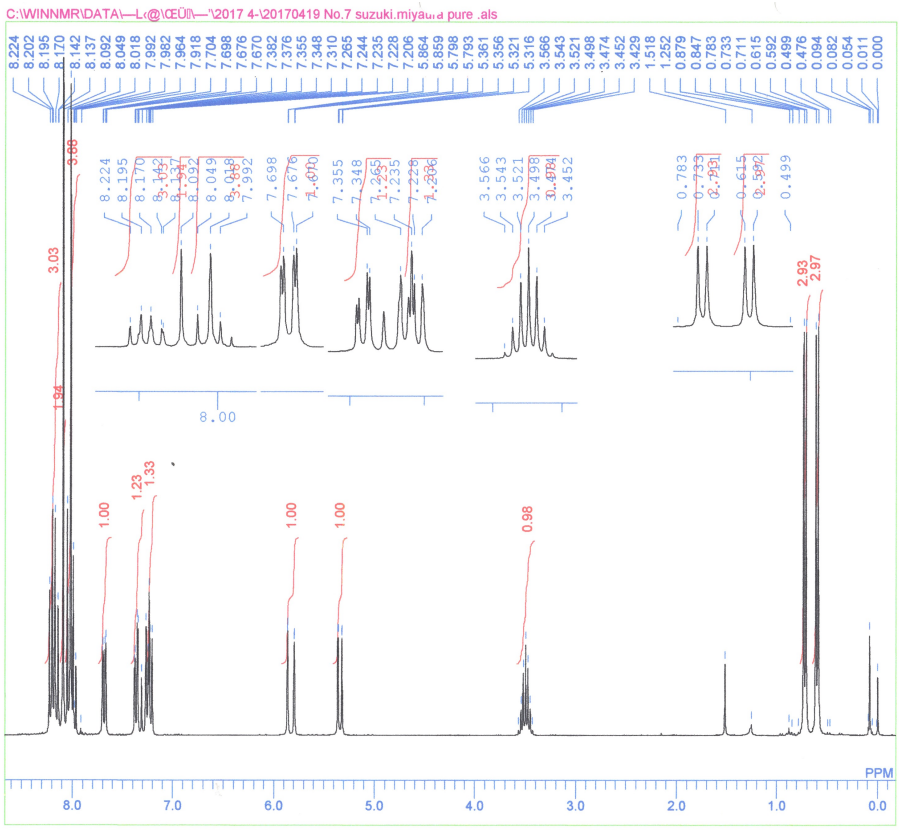

OHC
iPrO
Br

3e

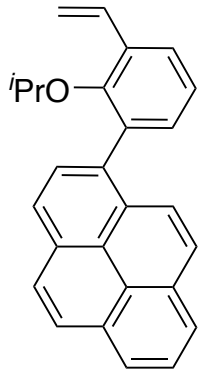

7.473 7.444 7.066 7.024 7.000 6.978 6.966 6.958 6.939 6.910
5.745 5.741 5.680 5.675 5.318 5.313 5.277 5.272
4.503 4.481 4.457 4.435 4.413
1.338 1.313
0.000
2.03 2.13 1.00 0.97 0.96 5.84
PPM
7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
DFILE 20120731
COMNT
DATIM Tue Jul 31 14:13:48 2012
OBNUC 1H
EXMOD NON
OBFRQ 270.05 MHz
OBSET 112.00 KHz
OBFIN 5800.00 Hz
POINT 8192
FREQU 5401.76 Hz
SCANS 16
ACQTM 1.5165 sec
PD 5.4830 sec
PW1 5.60 usec
IRNUC 1H
CTEMP 25.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 25


iPrO
Br

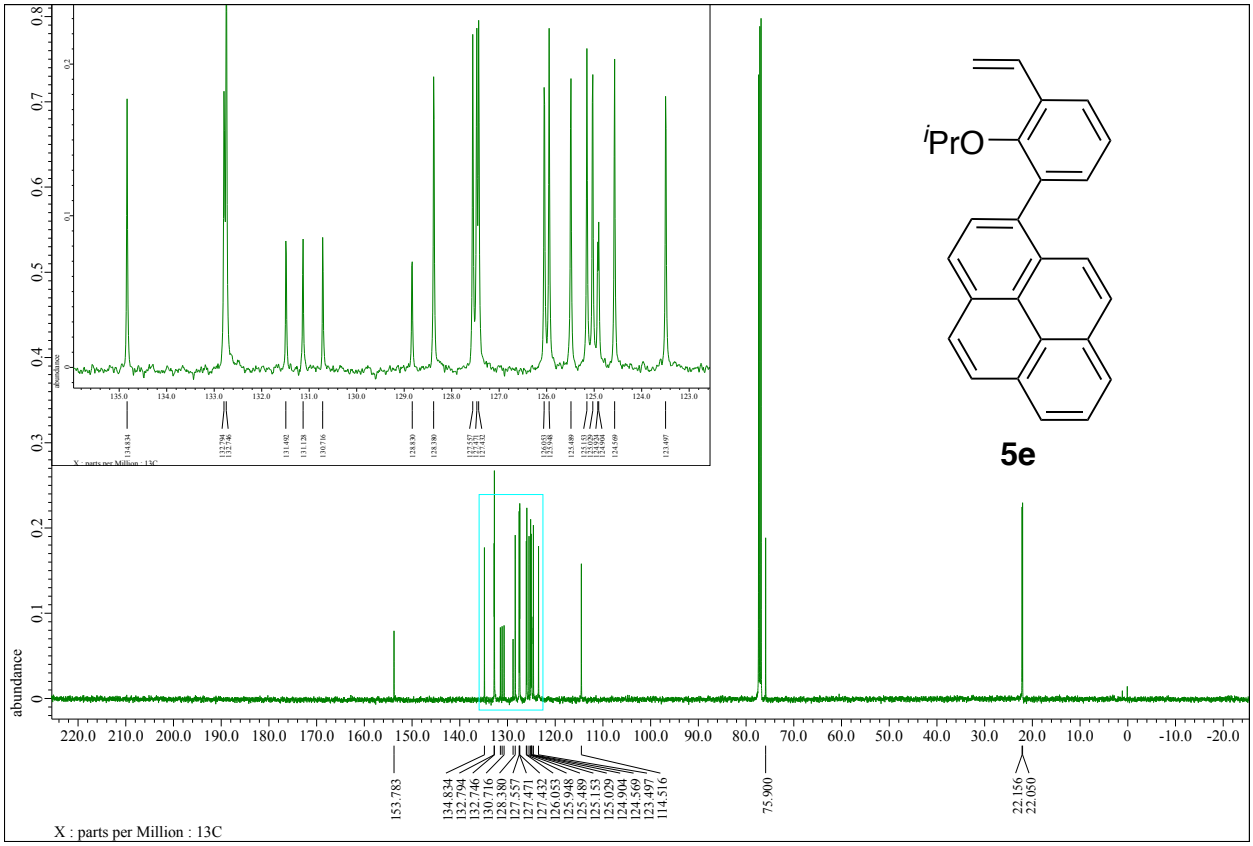
4e



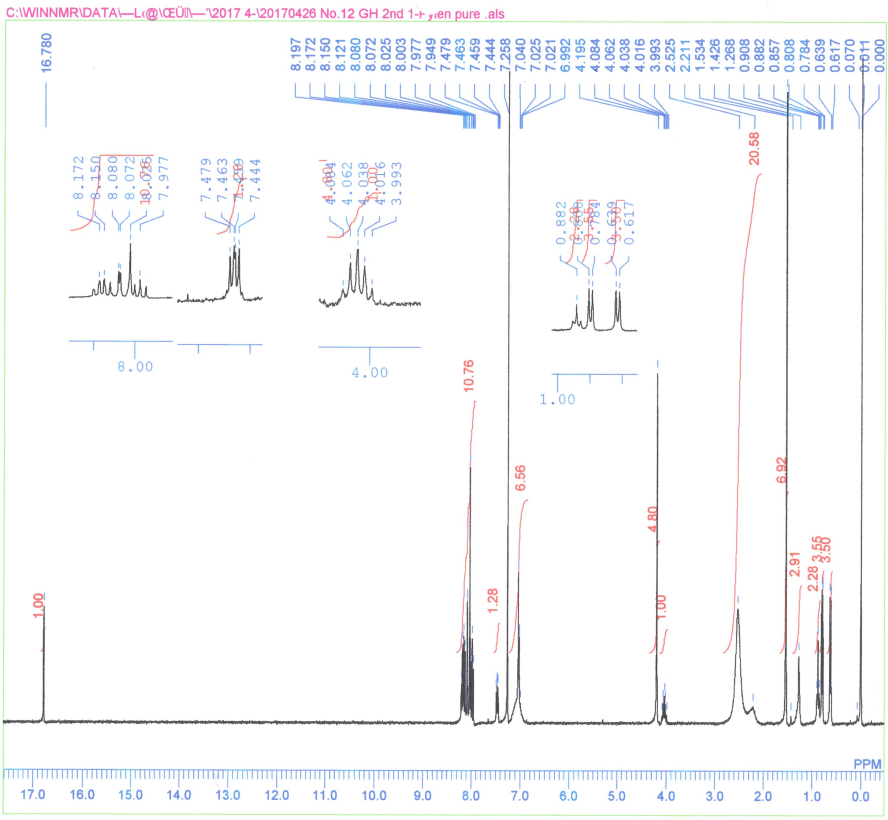
DFILE 20170419 No.7 suzuki.miyaura pure .als
COMNT
DATIM Wed Apr 19 13:17:04 2017
OBNUC 1H
EXMOD NON
OBFRQ 270.05 MHz
OBSET 112.00 KHz
OBFIN 5800.00 Hz
POINT 16384
FREQU 5401.76 Hz
SCANS 16
ACQTM 3.0331 sec
PD 3.9670 sec
PW1 7.50 usec
IRNUC 1H
CTEMP 25.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 17



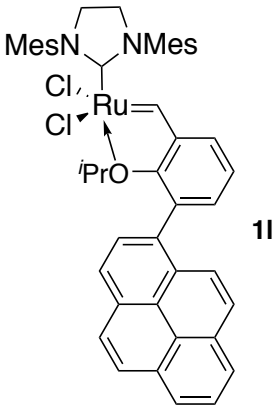
5e



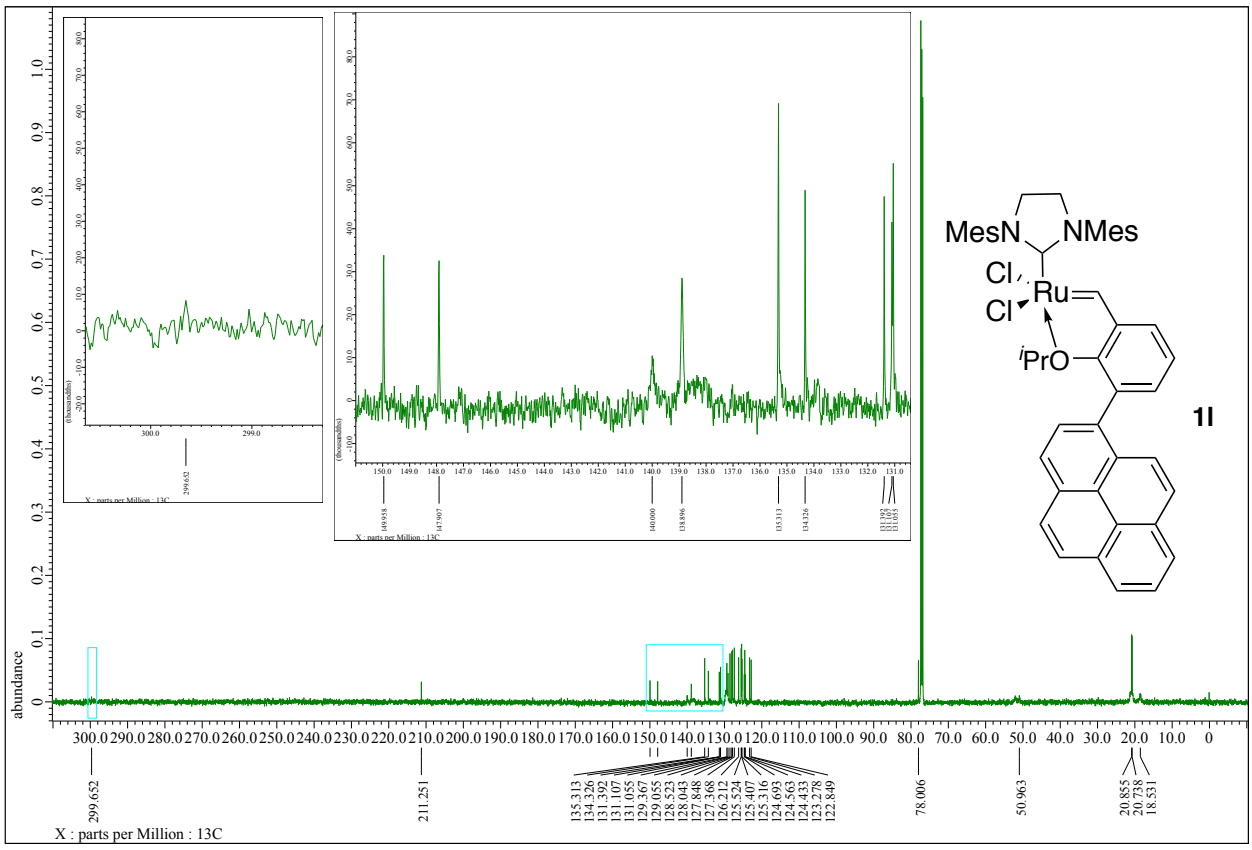
5e



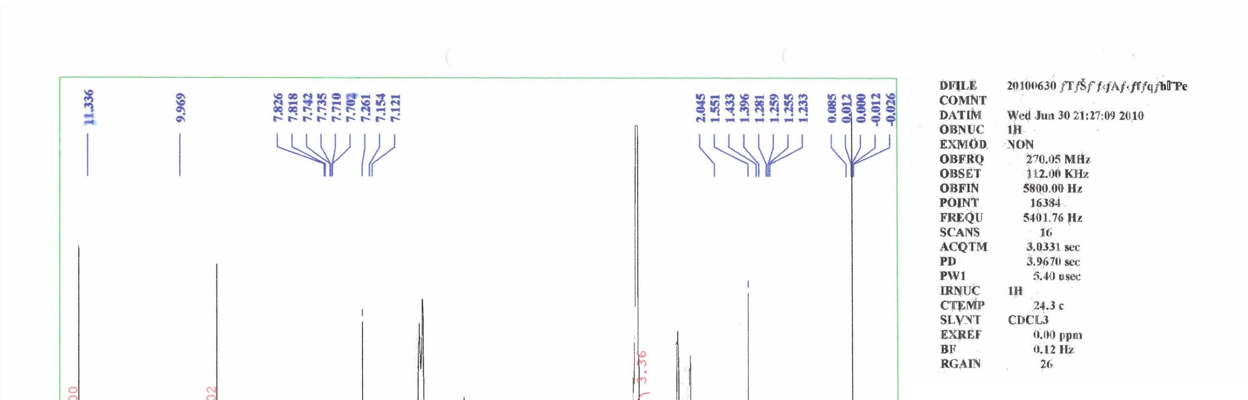

```
DFILE    20170426 No.12 GH 2nd 1-Pylen pure .als
COMNT
DATIM    Wed Apr 26 16:44:49 2017
OBNUC    1H
EXMOD    NON
OBFRQ      270.05 MHz
OBSET      112.00 KHz
OBFIN     5800.00 Hz
POINT       16384
FREQU     6999.12 Hz
SCANS          16
ACQTM      2.3409 sec
PD         3.9670 sec
PW1         7.50 usec
IRNUC    1H
CTEMP      25.5 c
SLVNT    CDCL3
EXREF      0.00 ppm
BF         0.12 Hz
RGAIN        25
```

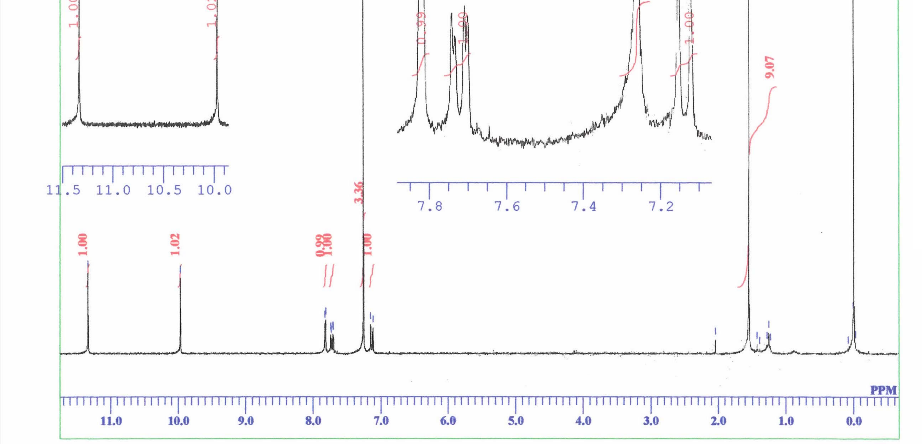


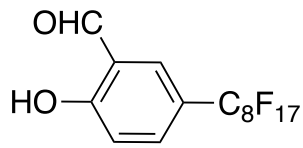
1l



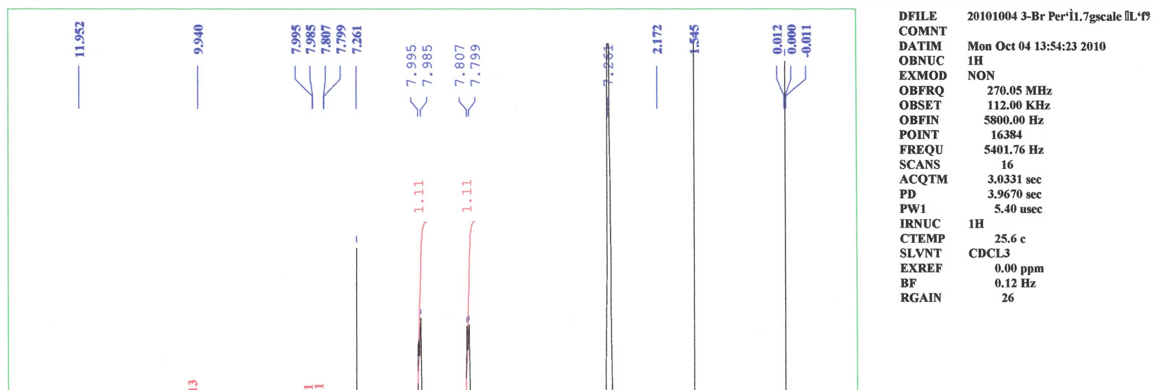
1l

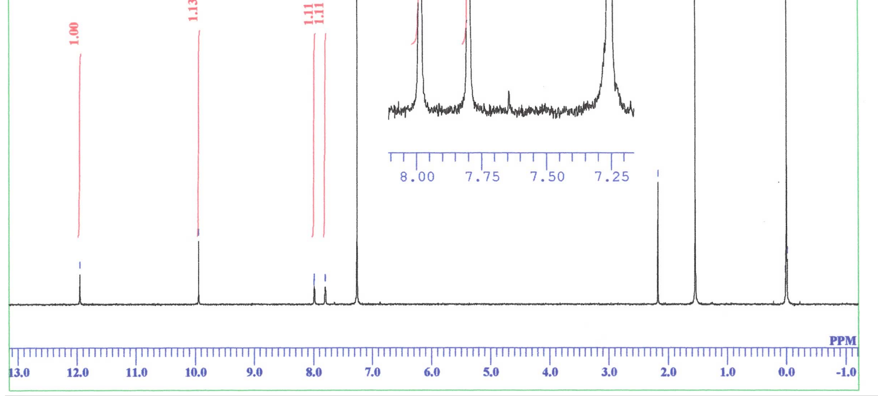

DFILE 20100630
COMNT
DATIM Wed Jun 30 21:27:09 2010
OBNUC 1H
EXMOD NON
OBFRQ 270.05 MHz
OBSET 112.00 KHz
OBFIN 5800.00 Hz
POINT 16384
FREQU 5401.76 Hz
SCANS 16
ACQTM 3.0331 sec
PD 3.9670 sec
PW1 5.40 usec
IRNUC 1H
CTEMP 24.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 26
11.336
9.969
7.826
7.818
7.742
7.735
7.710
7.702
7.261
7.154
7.121
2.045
1.551
1.433
1.396
1.281
1.259
1.255
1.233
0.085
0.012
0.000
-0.012
-0.026
PPM

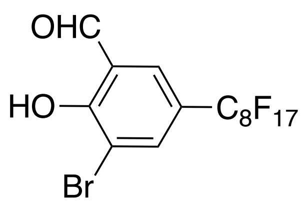



OHC
HO
C_8F_{17}

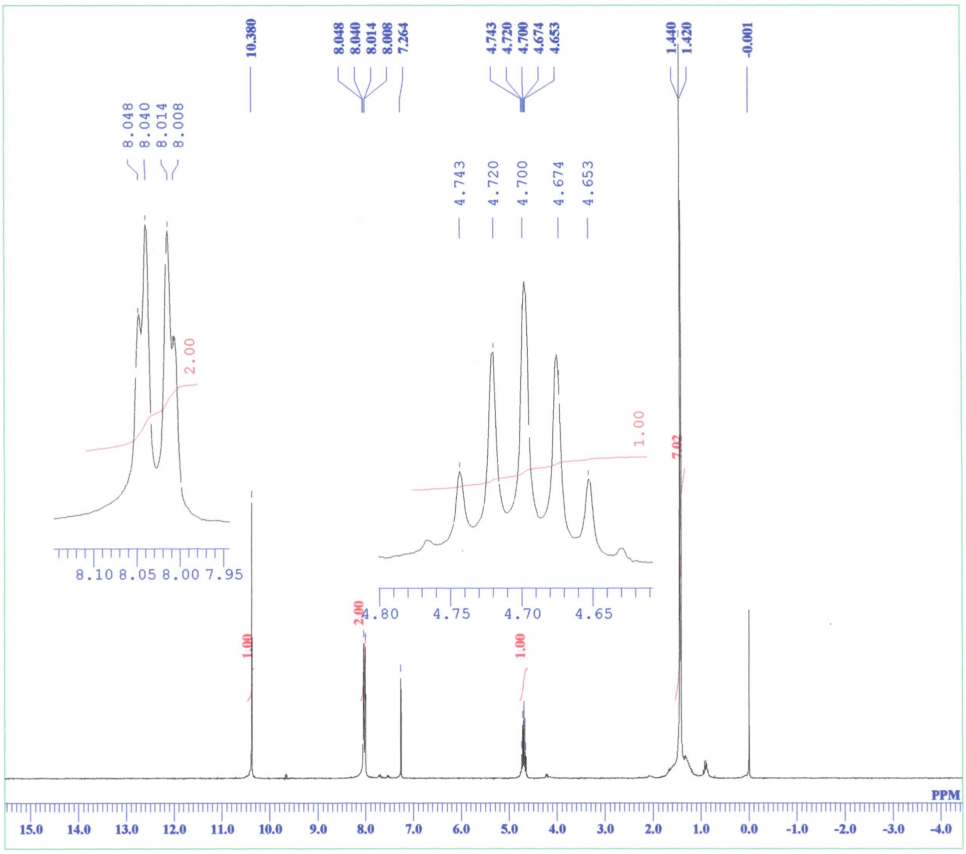
9

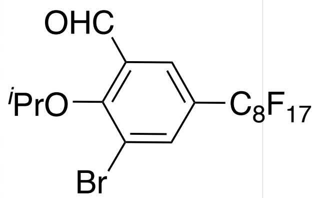

DFILE 20101004 3-Br
COMNT
DATIM Mon Oct 04 13:54:23 2010
OBNUC 1H
EXMOD NON
OBFRQ 270.05 MHz
OBSET 112.00 KHz
OBFIN 5800.00 Hz
POINT 16384
FREQU 5401.76 Hz
SCANS 16
ACQTM 3.0331 sec
PD 3.9670 sec
PW1 5.40 usec
IRNUC 1H
CTEMP 25.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 26
11.952
9.940
7.995
7.985
7.807
7.799
7.261
2.172
1.545
0.012
0.000
-0.011
PPM



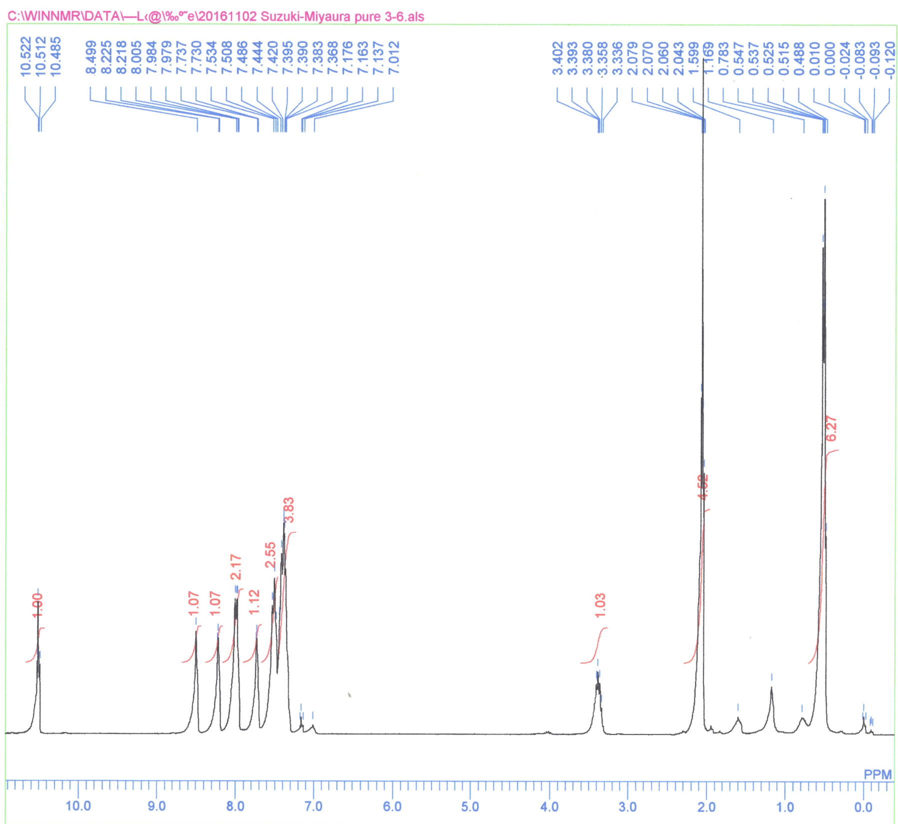

OHC
HO
C_8F_{17}
Br

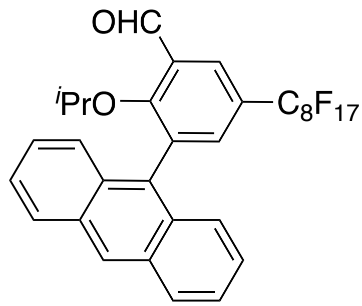
10


10.380
8.048
8.040
8.014
8.008
7.264
4.743
4.720
4.700
4.674
4.653
1.440
1.420
-0.001
PPM
DFILE 20100708 Br Perf iso-i.als
COMNT
DATIM Thu Jul 08 22:38:07 2010
OBNUC 1H
EXMOD NON
OBFRQ 270.05 MHz
OBSET 112.00 KHz
OBFIN 5800.00 Hz
POINT 16384
FREQU 5401.76 Hz
SCANS 16
ACQTM 3.0331 sec
PD 3.9670 sec
PW1 5.40 usec
IRNUC 1H
CTEMP 24.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 20

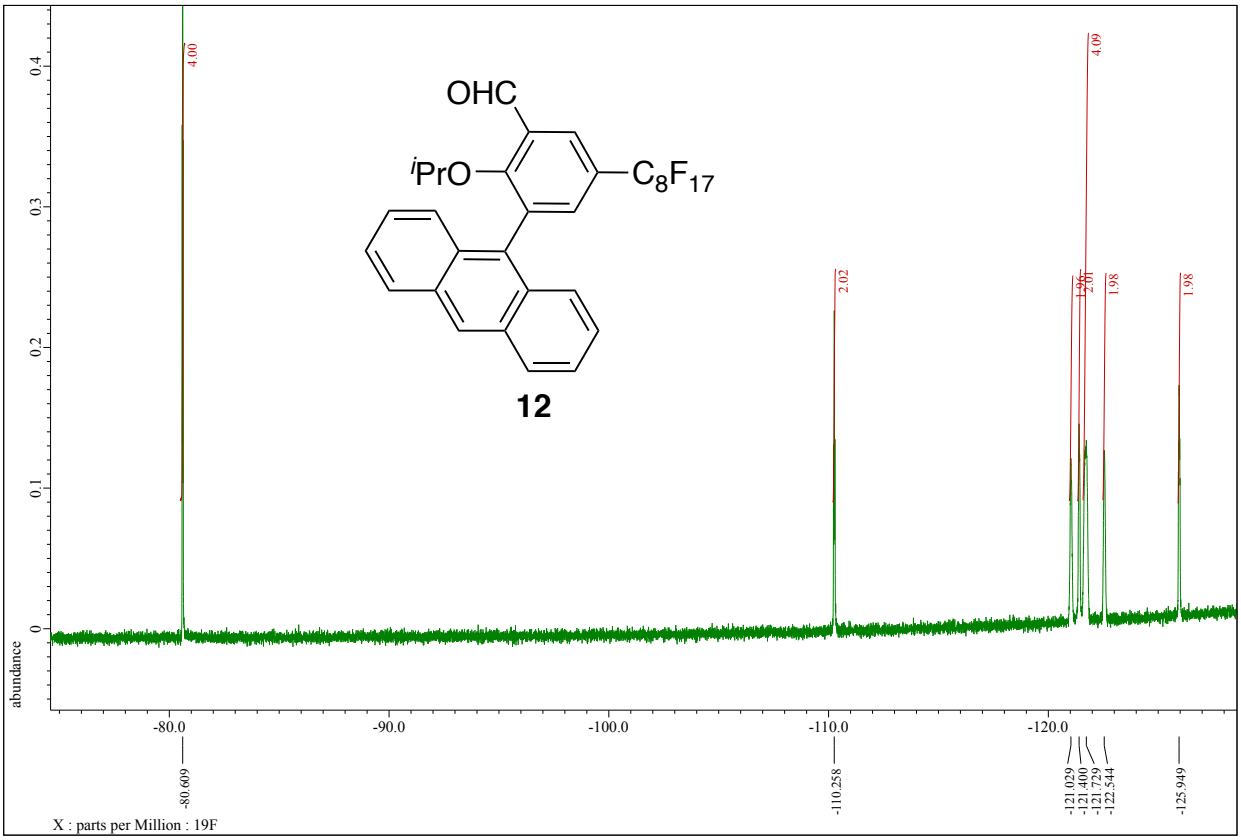

OHC
^{i}PrO
C_8F_{17}
Br

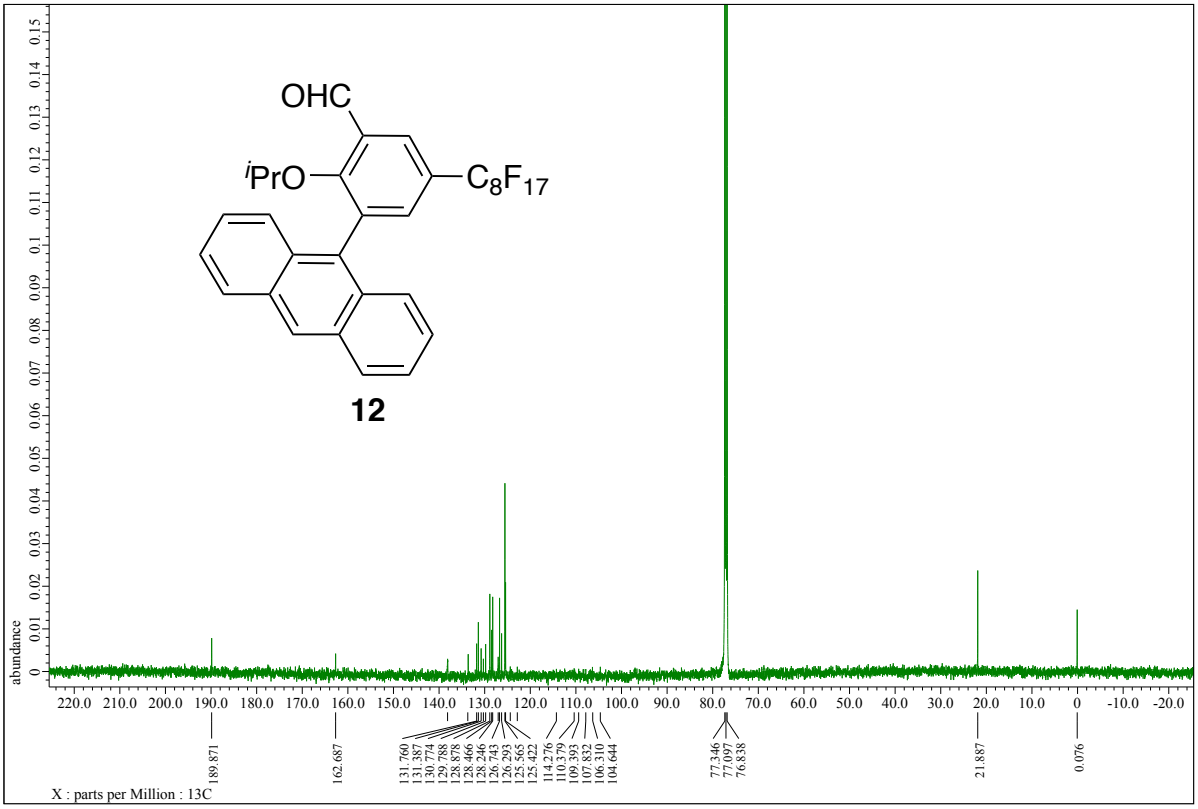
11

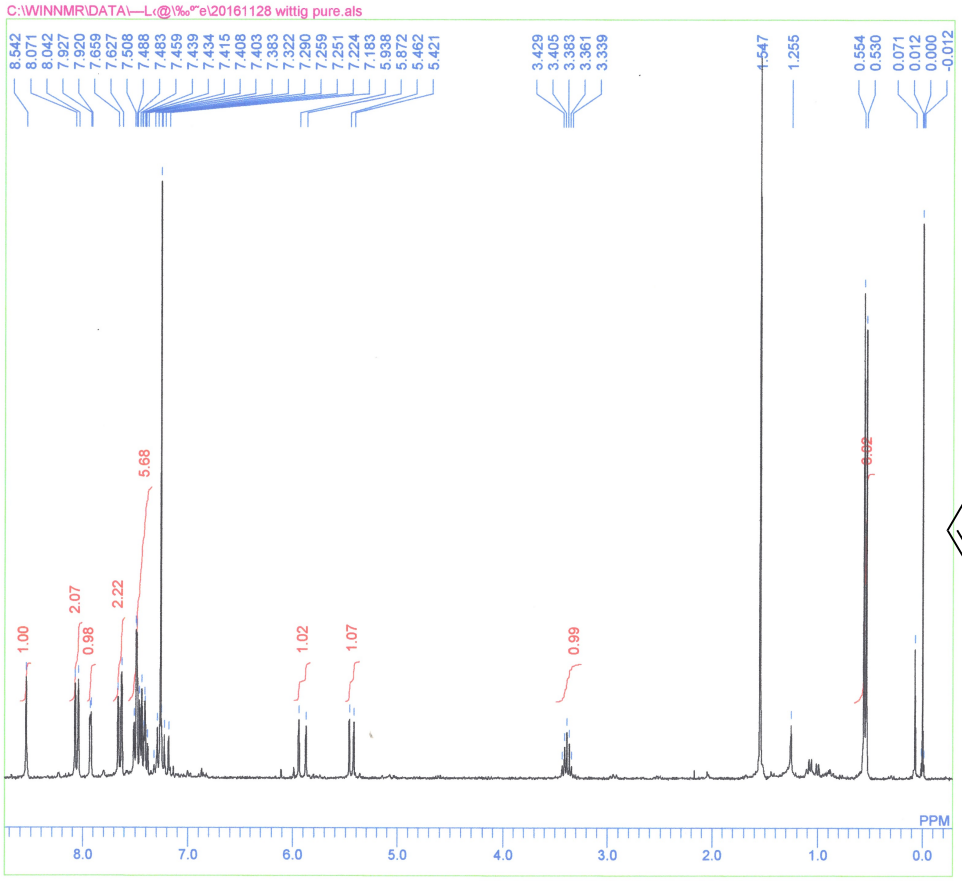

C:\WINNMR\DATA\20161102 Suzuki-Miyaura pure 3-6.als
PPM
DFILE 20161102 Suzuki-Miyaura pure 3-6.als
COMNT
DATIM Wed Nov 02 18:46:48 2016
OBNUC 1H
EXMOD NON
OBFRQ 270.05 MHz
OBSET 112.00 KHz
OBFIN 5800.00 Hz
POINT 8192
FREQU 5401.76 Hz
SCANS 16
ACQTM 1.5165 sec
PD 5.4830 sec
PW1 5.60 usec
IRNUC 1H
CTEMP 27.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 17


OHC
^{i}PrO
C_8F_{17}

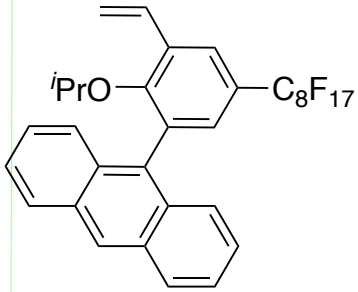
12


OHC
iPrO
C8F17
12
4.00
2.02
4.09
2.01
1.98
1.98
abundance
-80.0
-90.0
-100.0
-110.0
-120.0
-80.609
-110.258
-121.029
-121.400
-121.729
-122.544
-125.949
X : parts per Million : 19F

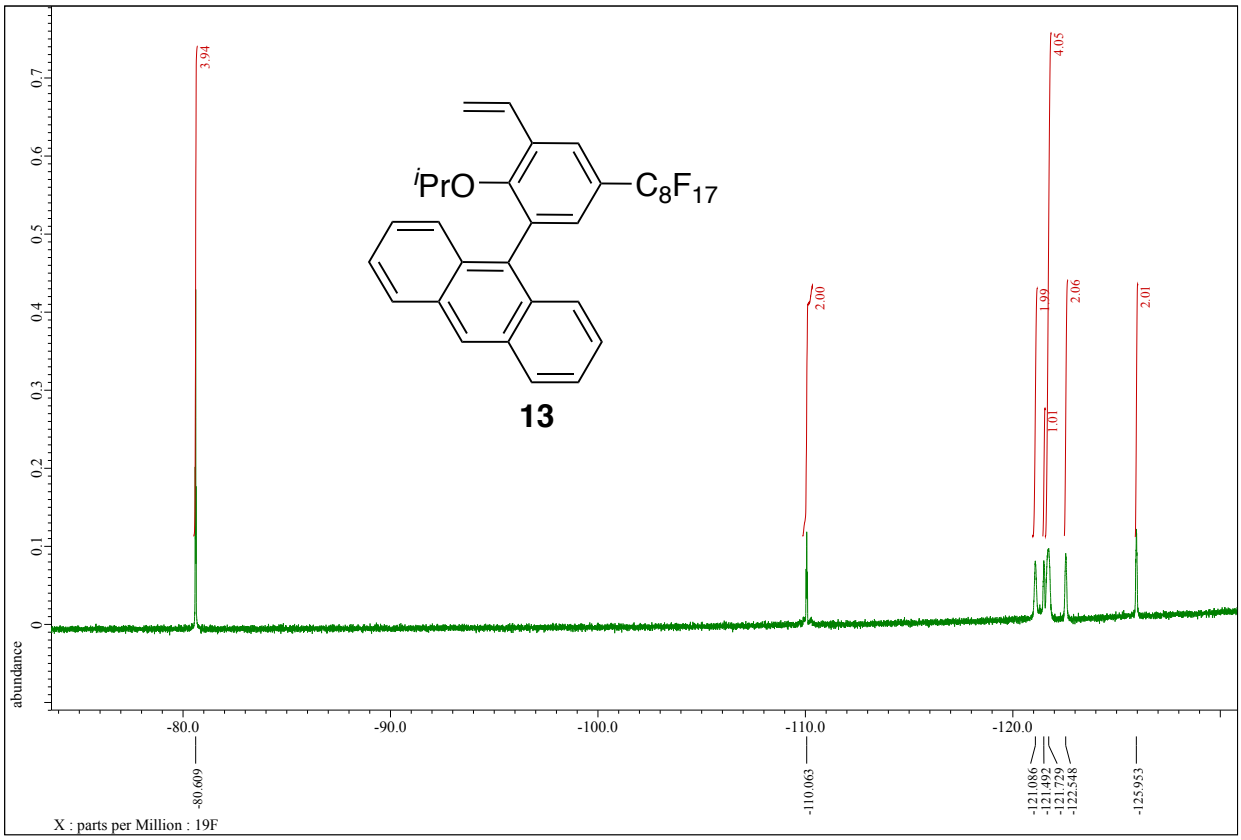

OHC
iPrO
C8F17
12
abundance
189.871
162.687
131.760
131.387
130.774
129.788
128.878
128.466
128.246
126.743
126.293
125.565
125.422
114.276
110.379
109.393
107.832
106.310
104.644
77.346
77.097
76.838
21.887
0.076
X : parts per Million : 13C



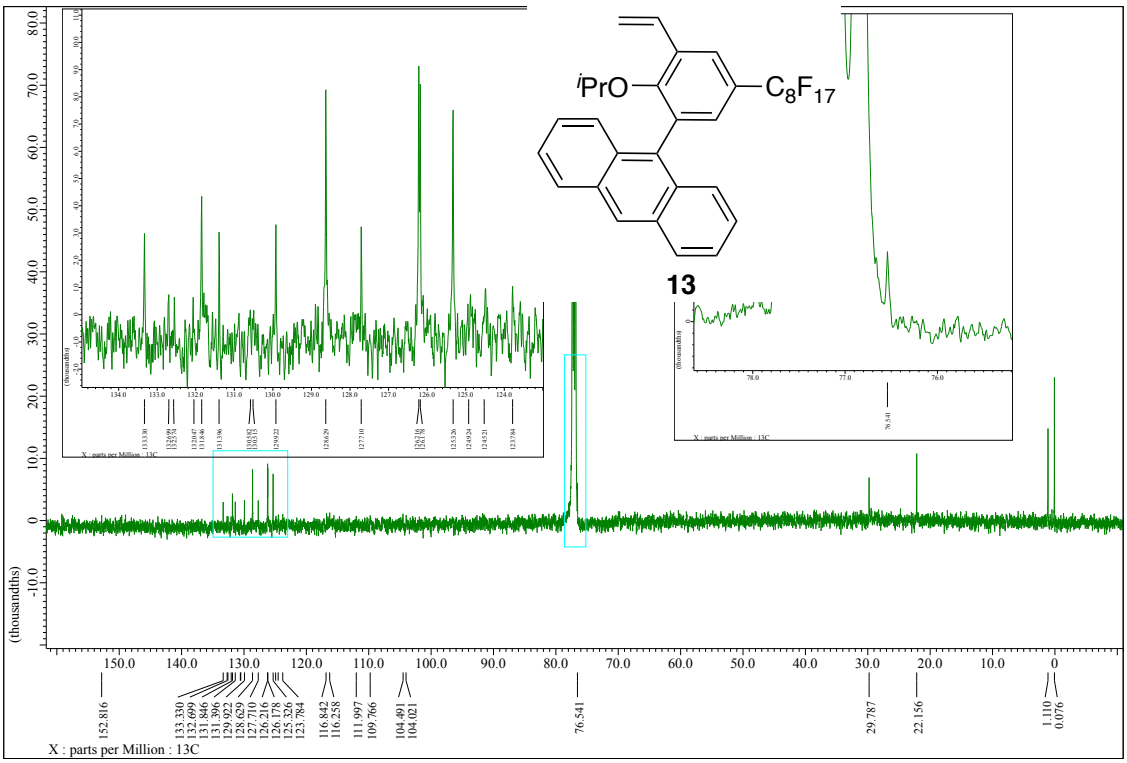
DFILE 20161128 wittig pure.als
COMNT
DATIM Mon Nov 28 12:28:38 2016
OBNUC 1H
EXMOD NON
OBFRQ 270.05 MHz
OBSET 112.00 KHz
OBFIN 5800.00 Hz
POINT 8192
FREQU 5401.76 Hz
SCANS 16
ACQTM 1.5165 sec
PD 5.4830 sec
PW1 5.60 usec
IRNUC 1H
CTEMP 23.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 25

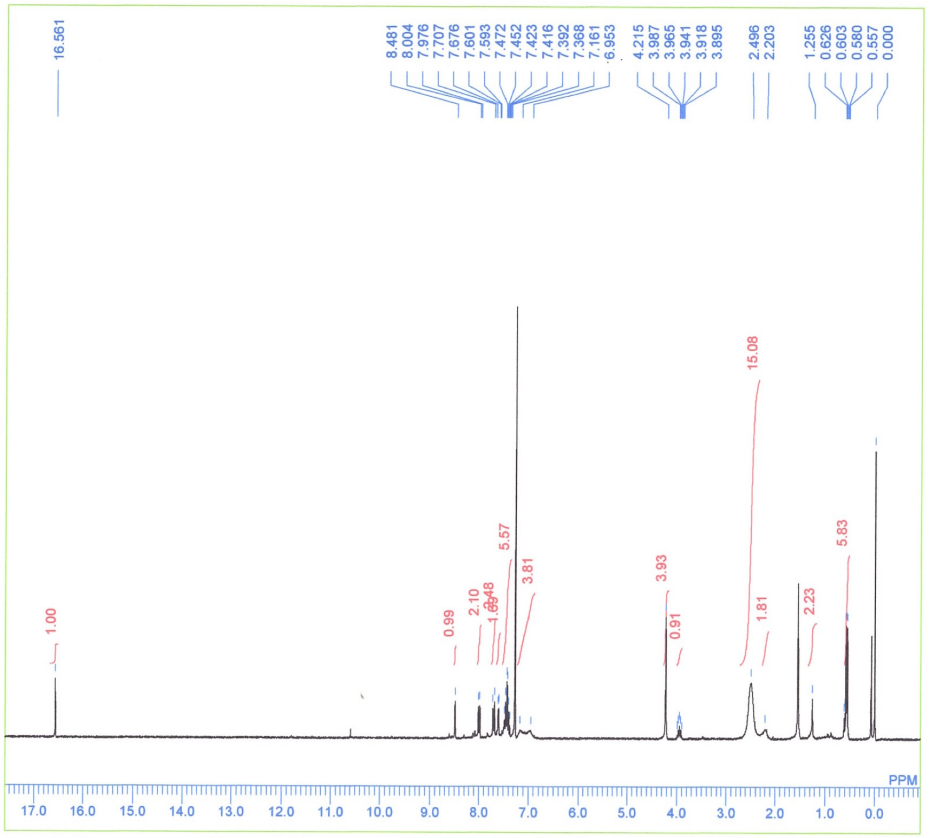


13

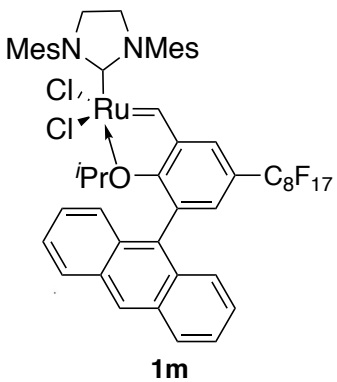


13

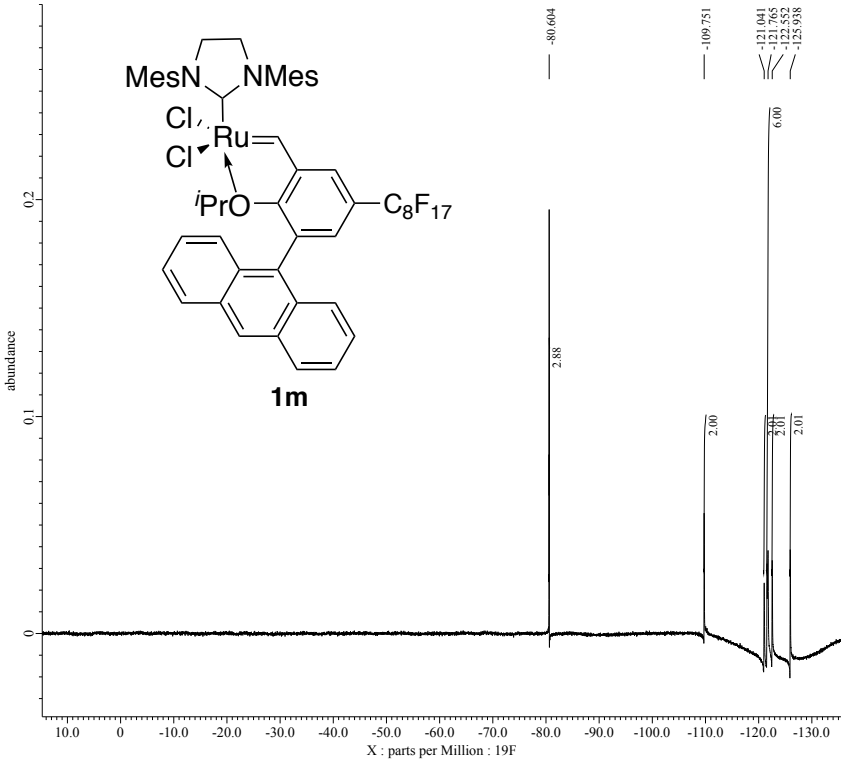




DFILE 20161130 f-GH 2nd genaration.als
COMNT
DATIM Wed Nov 30 17:32:17 2016
OBNUC 1H
EXMOD NON
OBFRQ 270.05 MHz
OBSET 119.00 KHz
OBFIN 3.00 Hz
POINT 16384
FREQU 5943.54 Hz
SCANS 16
ACQTM 2.7566 sec
PD 3.9670 sec
PW1 5.40 usec
IRNUC 1H
CTEMP 24.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 26



1m

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Filename          = 19Fcat11-6.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = 19Fcat11
Solvent           = CHLOROFORM-D
Creation_Time     = 26-FEB-2018 21:15:42
Revision_Time     = 26-FEB-2018 23:38:04
Current_Time      = 26-FEB-2018 23:38:50

Comment           = single_pulse
Data_Format       = 1D REAL
Dim_Size          = 26214
Dim_Title         = 19F
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 0.13631488[s]
X_Domain          = 19F
X_Freq            = 465.88941346[MHz]
X_Offset          = 0[ppm]
X_Points          = 32768
X_Prescans        = 1
X_Resolution      = 7.33595628[Hz]
X_Sweep           = 240.38461538[kHz]
Irr_Domain        = 19F
Irr_Freq          = 465.88941346[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 19F
Tri_Freq          = 465.88941346[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 1000
Total_Scans       = 1000

Relaxation_Delay = 5[s]
Recvr_Gain        = 48
Temp_Set          = 22.7[dC]
X_90_Width        = 15[us]
X_Acq_Time        = 0.13631488[s]
X_Angle           = 45[deg]
X_Atn             = 6.6[dB]
X_Pulse           = 7.5[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
RepetitIon_Time   = 5.13631488[s]
```