Electronic Supporting Information for "Highly enantioselective hetero-Diels–Alder reactions between Rawal's diene and aldehydes catalyzed by chiral dirhodium(II) carboxamidates"

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Experimental Section

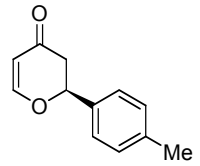
General. Melting points were determined on a Büchi 535 digital melting point apparatus and are uncorrected. IR spectra were recorded on a JASCO FT/IR-5300 spectrometer and absorbance bands are reported in wavenumber (cm^{-1}). ^1H NMR spectra were recorded on JEOL JNM-AL 400 (400 MHz) spectrometer or JEOL JNM-ECA 500 (500 MHz) spectrometer. Chemical shifts are reported relative to internal standard (tetramethylsilane; δ_H 0.00, $CDCl_3$; δ_H 7.26 or CD_2Cl_2; δ_H 5.30). Data are presented as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant and integration. ^{13}C NMR spectra were recorded on JEOL JNM-AL 400 (100 MHz) spectrometer. The following internal references were used ($CDCl_3$; δ 77.0). Optical rotations were measured on a JASCO P-1030 digital polarimeter at the sodium D line (589 nm). EI-MS spectra were obtained on a JEOL JMS-FABmate spectrometer, operating with ionization energy of 70 eV. Column chromatography was carried out on Kanto silica gel 60 N (63–210 mesh). Analytical thin layer chromatography (TLC) was carried out on Merck Kieselgel 60 F_{254} plates with visualization by UV light, anisaldehyde stain solution or phosphomolybdic acid stain solution. Analytical high performance liquid chromatography (HPLC) was performed on a JASCO PU-1580 intelligent HPLC pump with JASCO UV-1575 intelligent UV/VIS detector. Detection was performed at 254 nm. Chiralcel OD-H and Chiralpak AD columns (0.46 cm × 25 cm) from Daicel were used. Retention times (t_R) and peak ratios were determined with JASCO-Borwin analysis system.

All non-aqueous reactions were carried out in flame-dried glassware under argon atmosphere unless otherwise noted. Reagents and solvents were purified by standard means. Dehydrated CH_2Cl_2, acetone, toluene and THF were purchased from Kanto Chemical Co., Inc. Rawal's diene (**2**) was prepared according to literature procedure.[1]

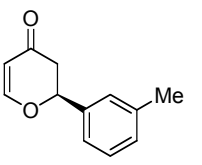
Typical procedure for enantioselective hetero-Diels−Alder (HDA) reaction: (*S*)-2-Phenyl-2,3-dihydro-4*H*-pyran-4-one (5a).[2] A solution of Rawal's diene (**2**) (68.2 mg, 0.3 mmol) in CH_2Cl_2 (0.2 mL) was added to a solution of benzaldehyde (**3a**) (47.7 mg, 0.45 mmol) and Rh_2(*S*-BPTPI)$_4$·3H_2O (**1a**) (4.30 mg, 0.003 mmol, 1 mol %) in CH_2Cl_2 (0.4 mL) at − 40 ºC. The reaction mixture was stirred for 2 h and then diluted with CH_2Cl_2 (1.2 mL). The whole mixture was cooled to −78 ºC, and treated dropwise with 1 M solution of AcCl in CH_2Cl_2 (0.45 mL, 0.45 mmol). After stirring for 30 min, the reaction was quenched with saturated $NaHCO_3$ (3 mL) and extracted with EtOAc (2 x 15 mL). The combined organic layers were washed with water (3 mL) and brine (2 x 3 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished the crude product, which was purified by column chromatography (silica gel 5 g, 6:1 hexane/EtOAc) to provide **5a** (43.5 mg, 83%) as a colorless oil; TLC R_f = 0.34 (2:1 hexane/EtOAc); $[\alpha]_D^{23}$ +109 (*c* 1.09, $CHCl_3$) for 98% ee [lit.,[2] $[\alpha]_D^{23}$ −96.3 (*c* 0.87, $CHCl_3$) for (*R*)-enantiomer]; ^1H NMR (500 MHz, $CDCl_3$) δ 2.65 (ddd, *J* = 1.3, 3.6, 16.9 Hz, 1H, C3-*H*), 2.92 (dd, *J* =14.5, 16.9 Hz, 1H, C3-*H*), 5.43 (dd, *J* = 3.6, 14.5 Hz, 1H, C2-*H*), 5.53 (dd, *J* =1.3, 6.0 Hz, 1H, C5-*H*), 7.37−7.45 (m, 5H, *Ar*), 7.48 (d, *J* = 6.0 Hz, 1H, C6-*H*). Enantiomeric excess of **5a** was determined to be 98% by HPLC with a Chiralcel OD-H column (9:1 hexane/^{i}PrOH, 1.0 mL/min): t_R (major) = 13.4 min for (*S*)-enantiomer; t_R (minor) = 16.0 min for

(*R*)-enantiomer.

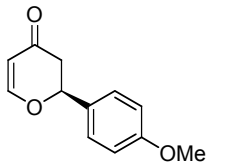
2-(4-Methylphenyl)-2,3-dihydro-4*H*-pyran-4-one (5b).[3] According to the typical procedure for enantioselective HDA reaction, **5b** was prepared from diene **2** (68.2 mg, 0.3 mmol), *p*-tolualdehyde (**3b**) (54.0 mg, 0.45 mmol), and Rh_2(*S*-BPTPI)$_4$·3H_2O (4.30 mg, 0.003 mmol, 1 mol %). The crude product was purified by column chromatography (silica gel, 6:1 hexane/EtOAc) to provide **5b** (43.4 mg, 77%) as a white solid; mp 80.0−81.0 ºC; TLC R_f = 0.35 (2:1 hexane/EtOAc); $[\alpha]_D^{24}$ +128 (*c* 1.16, $CHCl_3$) for 98% ee [lit.,[3] $[\alpha]_D^{19}$ –27.5 (*c* 0.26, $CHCl_3$) for 92% ee of **5b**]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H, ArC*H*$_3$), 2.62 (ddd, *J* = 1.3, 3.6, 16.8 Hz, 1H, C3-*H*), 2.92 (dd, *J* = 14.5, 16.8 Hz, 1H, C3-*H*), 5.39 (dd, *J* = 3.6, 14.5 Hz, 1H, C2-*H*), 5.52 (dd, *J* = 1.3, 5.9 Hz, 1H, C5-*H*), 7.23 (d, *J* = 8.2 Hz, 2H, *Ar*), 7.30 (d, *J* = 8.2 Hz, 2H, *Ar*), 7.47 (d, *J* = 5.9 Hz, 1H, C6-*H*). Enantiomeric excess of **5b** was determined to be 98% by HPLC with a Chiralcel OD-H column (9:1 hexane/^{i}PrOH, 1.0 mL/min): t_R = 10.8 min for major enantiomer; t_R = 12.5 min for minor enantiomer. The preferred absolute configuration of **5b** was not determined.[1]



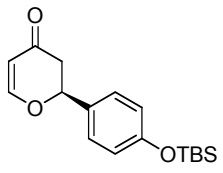
2-(3-Methylphenyl)-2,3-dihydro-4*H*-pyran-4-one (5c).[4] According to the typical procedure for enantioselective HDA reaction, **5c** was prepared from diene **2** (68.2 mg, 0.3 mmol), *m*-tolualdehyde (**3c**) (54.0 mg, 0.45 mol), and Rh_2(*S*-BPTPI)$_4$·3H_2O (4.30 mg, 0.003 mmol, 1 mol %). The crude product was purified by column chromatography (silica gel, 9:1 hexane/EtOAc) to provide **5c** (44.6 mg, 79%) as a colorless oil; TLC R_f = 0.28 (4:1 hexane/EtOAc); $[\alpha]_D^{24}$ +103 (*c* 1.03, $CHCl_3$) for 95% ee [lit.,[4] $[\alpha]_D^{25}$ –103.1 (*c* 0.945, $CHCl_3$) for 99.5% ee of **5c**]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 3H, ArC*H*$_3$), 2.63 (ddd, *J* = 1.4, 3.6, 16.8 Hz, 1H, C3-*H*), 2.92 (dd, *J* = 14.5, 16.8 Hz, 1H, C3-*H*), 5.39 (dd, *J* = 3.6, 14.5 Hz, 1H, C2-*H*), 5.53 (dd, *J* = 1.4, 5.9 Hz, 1H, C5-*H*), 7.19−7.22 (m, 3H, *Ar*), 7.32 (t, *J* = 7.7 Hz, 1H, *Ar*), 7.48 (d, *J* = 5.9 Hz, 1H, C6-*H*). Enantiomeric excess of **5c** was determined to be 95% by HPLC with a Chiralcel OD-H column (9:1 hexane/^{i}PrOH, 1.0 mL/min): t_R = 10.2 min for major enantiomer; t_R = 12.4 min for minor enantiomer. The preferred absolute configuration of **5c** was not determined.



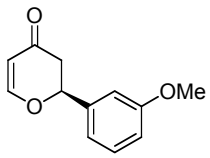
(*S*)-2-(4-Methoxyphenyl)-2,3-dihydro-4*H*-pyran-4-one (5d).[5] According to the typical procedure for enantioselective HDA reaction, **5d** was prepared from diene **2** (68.2 mg, 0.3 mmol), *p*-anisaldehyde (**3d**) (61.2 mg, 0.45 mmol), and Rh_2(*S*-BPTPI)$_4$·3H_2O (4.30 mg, 0.003 mmol, 1 mol %). The crude product was purified by column chromatography (silica gel, 4:1 hexane/EtOAc) to provide **5d** (51.4 mg, 84%) as a white solid; mp 50.5−51.5 ºC; TLC R_f = 0.28 (4:1 hexane/EtOAc); $[\alpha]_D^{23}$ +121 (*c* 1.04, $CHCl_3$) for 99% ee [lit.,[5] $[\alpha]_D^{25}$ –121 (*c* 0.397, $CHCl_3$) for 92% ee of (*R*)-enantiomer]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.63 (ddd, *J* = 1.4, 3.2, 17.2 Hz, 1H, C3-*H*), 2.94 (dd, *J* = 14.5, 17.2 Hz, 1H, C3-*H*), 3.83 (s, 3H, ArOC*H*$_3$), 5.38 (dd, *J* = 3.2, 14.5 Hz, 1H, C2-*H*), 5.51 (dd, *J* = 1.4, 6.3 Hz, 1H, C5-*H*), 6.95 (d, *J* = 8.6 Hz, 2H, *Ar*), 7.34 (d, *J* = 8.6 Hz, 2H, *Ar*), 7.46 (d, *J* = 6.3 Hz, 1H, C6-*H*). Enantiomeric



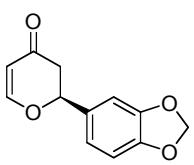
excess of **5d** was determined to be 99% by HPLC with a Chiralcel OD-H column (19:1 hexane/^{i}PrOH, 1.0 mL/min): t_R (major) = 24.4 min for (*S*)-enantiomer; t_R (minor) = 28.0 min for (*R*)-enantiomer.

2-(4-*tert*-Butyldimethylsilyloxyphenyl)-2,3-dihydro-4*H*-pyran-4-one (5e). 

According to the typical procedure for enantioselective HDA reaction, **5e** was prepared from diene **2** (68.2 mg, 0.3 mmol), 4-*tert*-butyldimethylsilyloxy-benzaldehyde (**3e**) (106.4 mg, 0.45 mmol), and Rh_2(*S*-BPTPI)$_4$·3H$_2$O (4.30 mg, 0.003 mmol, 1 mol %). The crude product was purified by column chromatography (silica gel, 9:1 hexane/EtOAc) to provide **5e** (66.3 mg, 73%) as a colorless oil; TLC R_f = 0.31 (4:1 hexane/EtOAc); $[\alpha]_D^{24}$ +95.4 (*c* 1.07, $CHCl_3$) for 98% ee; IR (film) 2955, 1681, 1595, 1513, 1264 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.21 (s, 6H, Si(C*H*$_3$)$_2$), 0.98 (s, 9H, SiC(C*H*$_3$)$_3$), 2.62 (ddd, *J* = 0.7, 4.5, 6.7 Hz, 1H, C3-*H*), 2.92 (dd, *J* = 4.5 17.2 Hz, 1H, C3-*H*), 5.35 (dd, *J* = 6.7, 17.2 Hz, 1H, C3-*H*), 5.15 (dd, *J* = 0.7, 5.9 Hz, 1H, C5-*H*), 6.87 (d, *J* = 5.9 Hz, 1H, C6-*H*), 7.27 (d, *J* = 6.8 Hz, 2H, *Ar*), 7.47 (d, *J* = 6.8 Hz, 2H, *Ar*); ^{13}C NMR (100 MHz, $CDCl_3$) δ −4.5 (CH_3), 18.1 (C), 25.6 (CH_3), 43.1 (CH_2), 80.9 (CH), 107.2 (CH), 120.3 (CH_2), 127.6 (CH_2), 130.3 (C), 156.2 (C), 163.3 (CH), 192.4 (C); EI-HRMS *m/z* calcd for $C_{17}H_{24}O_3Si$ (M^+) 304.14948, found 304.14940. Enantiomeric excess of **5e** was determined to be 98% by HPLC with a Chiralcel OD-H column (19:1 hexane/^{i}PrOH, 1.0 mL/min): t_R = 9.3 min for major enantiomer; t_R = 10.7 min for minor enantiomer. The preferred absolute configuration of **5e** was not determined.

2-(3-Methoxylphenyl)-2,3-dihydro-4*H*-pyran-4-one (5f).[4] 

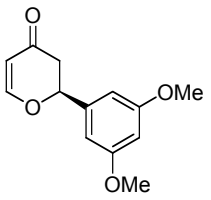
According to the typical procedure for enantioselective HDA reaction, **5f** was prepared from diene **2** (68.2 mg, 0.3 mmol), *m*-anisaldehyde (**3f**) (61.2 mg, 0.45 mmol), and Rh_2(*S*-BPTPI)$_4$·3H$_2$O (4.30 mg, 0.003 mmol, 1 mol %). The crude product was purified by column chromatography (silica gel, 6:1 hexane/EtOAc) to provide **5f** (46.7 mg, 76%) as a colorless oil; TLC R_f = 0.24 (4:1 hexane/EtOAc); $[\alpha]_D^{23}$ +97.8 (*c* 1.19, $CHCl_3$) for 96% ee [lit.,[4] $[\alpha]_D^{25}$ –85.6 (*c* 2.230, $CHCl_3$) for 99.8% ee of **5f**]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.64 (ddd, *J* = 1.3, 3.1, 16.7 Hz, 1H, C3-*H*), 2.93 (dd, *J* = 14.5, 16.7 Hz, 1H, C3-*H*), 3.84 (s, 3H, ArOC*H*$_3$), 5.40 (dd, *J* = 3.1, 14.5 Hz, 1H, C2-*H*), 5.53 (dd, *J* = 1.3, 6.3 Hz, 1H, C5-*H*), 6.91−6.98 (m, 3H, *Ar*), 7.33 (dd, *J* = 7.7, 8.2 Hz, 1H, *Ar*), 7.49 (d, *J* = 6.3 Hz, 1H, C6-*H*). Enantiomeric excess of **5f** was determined to be 96% by HPLC with a Chiralcel OD-H column (9:1 hexane/^{i}PrOH, 1.0 mL/min): t_R = 17.6 min for major enantiomer; t_R = 24.6 min for minor enantiomer. The preferred absolute configuration of **5f** was not determined.

2-(3,4-Methylenedioxyphenyl)-2,3-dihydro-4*H*-pyran-4-one (5g). 

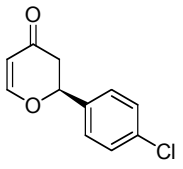
According to the typical procedure for enantioselective HDA reaction, **5g** was prepared from diene **2** (68.2 mg, 0.3 mmol), piperonal (**3g**) (67.5 mg, 0.45 mmol), and Rh_2(*S*-BPTPI)$_4$·3H$_2$O (4.30 mg, 0.003 mmol, 1 mol %). The crude product was purified by column chromatography (silica gel, 6:1 hexane/EtOAc) to provide **5g** (47.9 mg, 73%) as

a white solid; mp 111−112 ºC; TLC R_f = 0.31 (2:1 hexane/EtOAc); $[\alpha]_D^{21}$ +125 (*c* 1.05, $CHCl_3$) for 96% ee; IR (KBr) 3079, 2913, 1671, 1594, 1254 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.61 (ddd, *J* = 1.4, 3.6, 16.8 Hz, 1H, C3-*H*), 2.89 (dd, *J* = 14.5, 16.8 Hz, 1H, C3-*H*), 5.32 (dd, *J* = 3.6, 14.5 Hz, 1H, C2-*H*), 5.51 (dd, *J* = 1.4, 6.3 Hz, 1H, C5-*H*), 6.00 (s, 2H, O*CH*$_2$O), 6.81−6.85 (m, 2H, *Ar*), 6.90 (d, *J* = 1.8 Hz, 1H, *Ar*), 7.45 (d, *J* = 6.3 Hz, 1H, C6-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.2 (CH_2), 80.9 (CH), 101.3 (CH_2), 106.7 (CH), 107.2 (CH), 108.3 (CH), 120.1 (CH), 131.5 (C), 148.0 (C), 163.2 (CH), 192.2 (C); EI-HRMS *m/z* calcd for $C_{12}H_{10}O_4$ (M^+) 218.05791, found 218.05799. Enantiomeric excess of **5g** was determined to be 96% by HPLC with a Chiralcel OD-H column (9:1 hexane/^{i}PrOH, 1.0 mL/min): t_R = 19.3 min for major enantiomer; t_R = 23.4 min for minor enantiomer. The preferred absolute configuration of **5g** was not determined. A sample for combustion analysis was obtained by recrystallizations from hexane as colorless needles (99% ee); mp 112.5-113.5 ºC; Anal Calcd for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62. Found: C, 66.13; H, 4.70.

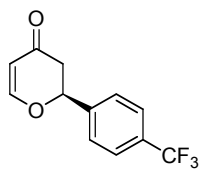
2-(3,5-Dimethoxyphenyl)-2,3-dihydro-4*H*-pyran-4-one (5h). According to the typical procedure for enantioselective HDA reaction, **5h** was prepared from diene **2** (68.2 mg, 0.3 mmol), 3,5-dimethoxybenzaldehyde (**3h**) (74.7 mg, 0.45 mmol), and Rh_2(*S*-BPTPI)$_4$·3H_2O (4.30 mg, 0.003 mmol, 1 mol %). The crude product was purified by column chromatography (silica gel, 4:1 hexane/EtOAc) to provide **5h** (52.8 mg, 75%) as a colorless oil; TLC R_f = 0.31 (2:1 hexane/EtOAc); $[\alpha]_D^{21}$ +75.9 (*c* 1.11, $CHCl_3$) for 90% ee; IR (film) 3071, 2939, 1680, 1590, 1273, 1222 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.65 (ddd, *J* = 1.4, 3.6, 16.8 Hz, 1H, C3-*H*), 2.88 (dd, *J* = 14.5, 16.8 Hz, 1H, C3-*H*), 3.85 (s, 6 H, ArOC*H*$_3$), 5.35 (dd, *J* = 3.6, 14.5 Hz, 1H, C2-*H*), 5.52 (dd, *J* = 1.4, 5.9, Hz, 1H, C5-*H*), 6.46 (t, *J* = 2.2 Hz, 1 H, *Ar*), 6.54 (d, *J* = 2.2Hz, 2H, *Ar*), 7.48 (d, *J* = 6.9 Hz, 1H, C6-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.4 (CH_2), 55.3 (CH_3), 80.9 (CH), 100.4 (CH), 104.0 (CH), 107.3 (CH), 140.0 (C), 161.0 (C), 163.1 (CH), 192.1 (C); EI-HRMS *m/z* calcd for $C_{13}H_{14}O_4$ (M^+) 234.08921, found 234.09016. Enantiomeric excess of **5h** was determined to be 90% by HPLC with a Chiralcel OD-H column (9:1 hexane/^{i}PrOH, 1.0 mL/min): t_R = 17.6 min for major enantiomer; t_R = 24.3 min for minor enantiomer. The preferred absolute configuration of **5h** was not determined.



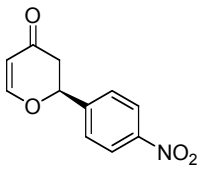
2-(4-Chlorophenyl)-2,3-dihydro-4*H*-pyran-4-one (5i).[6] According to the typical procedure for enantioselective HDA reaction, **5i** was prepared from diene **2** (68.2 mg, 0.30 mmol), 4-chlorobenzaldehyde (**3i**) (63.2 mg, 0.45 mmol), and Rh_2(*S*-BPTPI)$_4$·3H_2O (4.3 mg, 0.003 mmol, 1 mol %). The crude product was purified by column chromatography (silica gel, 4:1 hexane/EtOAc) to provide **5i** (44.3 mg, 71%) as a white solid; mp 70.0–71.0 °C; TLC R_f = 0.34 (2:1 hexane/EtOAc); $[\alpha]_D^{24}$ +100 (*c* 1.33, $CHCl_3$) for 97% ee [lit.,[6] $[\alpha]_D^{25}$ –76.3 (*c* 1.17, $CHCl_3$) for 88% ee of **5i**]; ^1H NMR (400 MHz, $CDCl_3$) δ 2.65 (dd, *J* = 3.6, 16.8 Hz, 1H, C3-*H*), 2.86 (dd, *J* = 14.4, 16.8 Hz, 1H, C3-*H*), 5.41 (dd, *J* = 3.6, 14.4 Hz, 1H, C2-*H*), 5.53 (d, *J* = 6.0 Hz, 1H, C5-*H*), 7.33−7.36 (m, 2H, *Ar*), 7.41-7.47 (m, 2H, *Ar*), 7.47 (d, *J* = 6.0 Hz, 1H, C6-*H*). Enantiomeric excess of **5i** was determined to be 97% by HPLC with a Chiralcel OD-H column (9:1 hexane/^{i}PrOH, 1.0 mL/min): t_R = 14.7 min for major



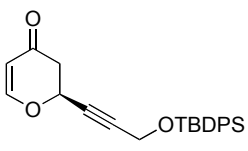
enantiomer; t_R = 18.6 min for minor enantiomer. The preferred absolute configuration of **5i** was not determined.



2-(4-Trifluoromethylphenyl)-2,3-dihydro-4*H*-pyran-4-one (5j).[7] According to the typical procedure for enantioselective HDA reaction, **5j** was prepared from diene **2** (68.2 mg, 0.3 mmol), 4-trifluoromethylbenzaldehyde (**3j**) (78.3 mg, 0.45 mmol), and Rh_2(*S*-BPTPI)$_4$·3H_2O (4.30 mg, 0.003 mmol, 1 mol %). The crude product was purified by column chromatography (silica gel, 9:1 hexane/EtOAc) to provide **5j** (67.5 mg, 93%) as a white solid; mp 48.0−49.0 °C; TLC R_f = 0.25 (2:1 hexane/EtOAc); $[\alpha]_D^{24}$ +50.8 (*c* 1.02, $CHCl_3$) for 95% ee; [lit.,[7] $[\alpha]_D^{24}$ +44.4 (*c* 0.630, $CHCl_3$) for 91% ee of **5j**]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.68 (ddd, *J* = 1.4, 3.2, 16.8 Hz, 1H, C3-*H*), 2.87 (dd, *J* = 14.0, 16.8 Hz, 1H, C3-*H*), 5.50 (dd, *J* = 3.2, 14.0 Hz, 1H, C2-*H*), 5.57 (dd, *J* = 1.4, 6.4 Hz, 1H, C5-*H*), 7.51 (d, *J* = 6.4 Hz, 1H, C6-*H*), 7.52 (d, *J* = 8.2 Hz, 2H, *Ar*), 7.69 (d, *J* = 8.2 Hz, 2H, *Ar*). Enantiomeric excess of **5j** was determined to be 95% by HPLC with a Chiralcel OD-H column (9:1 hexane/^{i}PrOH, 1.0 mL/min): t_R = 12.3 min for major enantiomer; t_R = 17.1 min for minor enantiomer. The preferred absolute configuration of **5j** was not determined.



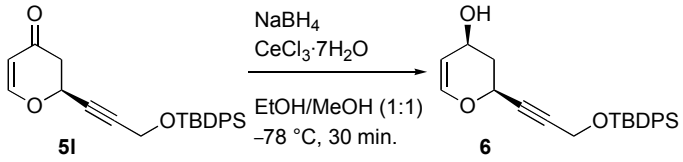
(*S*)-2-(4-Nitrolphenyl)-2,3--dihydro-4*H*-pyran-4-one (5k).[8] According to the typical procedure for enantioselective HDA reaction, **5k** was prepared from diene **2** (68.2 mg, 0.3 mmol), 4-nitrobenzaldehyde (**3k**) (68.0mg, 0.45 mmol), and Rh_2(*S*-BPTPI)$_4$·3H_2O (4.30 mg, 0.003 mmol, 1 mol %). The crude product was purified by column chromatography (silica gel, 3:1 hexane/EtOAc) to provide **5k** (51.3 mg, 78%) as a pale yellow solid; mp 101−102 °C; TLC R_f = 0.25 (2:1 hexane/EtOAc); $[\alpha]_D^{24}$ +58.8 (*c* 1.03, CH_2Cl_2) for 94% ee; [lit.,[8] $[\alpha]_D$ +59 (*c* 0.39, CH_2Cl_2) for (*S*)-enantiomer]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.71 (ddd, *J* = 1.4, 3.6, 16.8 Hz, 1H, C3-*H*), 2.85 (dd, *J* = 14.0, 16.8 Hz, 1H, C3-*H*), 5.56 (dd, *J* = 3.6, 14.0 Hz, 1H, C2-*H*), 5.59 (dd, *J* = 1.4, 6.4 Hz, 1H, C5-*H*), 7.52 (d, *J* = 6.4 Hz, 1H, C6-*H*), 7.60 (d, *J* = 6.8 Hz, 2H, *Ar*), 8.30 (d, *J* = 6.8 Hz, 2H, *Ar*). Enantiomeric excess of **5k** was determined to be 94% by HPLC with a Chiralcel OD-H column (3:1 hexane/^{i}PrOH, 1.0 mL/min): t_R (major) = 20.4 min for (*S*)-enantiomer; t_R (minor) = 30.0 min for (*R*)-enantiomer.



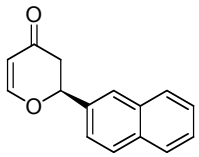
(*S*)-2-(3-*tert*-Butyldiphenylsilyloxyprop-1-ynyl)-2,3-dihydro-4*H*-pyran-4-one (5l).[9] According to the typical procedure for enantioselective HDA reaction, **5l** was prepared from diene **2** (68.2 mg, 0.3 mmol), 4-*tert*-butyldiphenyl- silyloxy-2-butynal (**3l**)[9] (145.1 mg, 0.45 mmol), and Rh_2(*S*-BPTPI)$_4$·3H_2O (4.30 mg, 0.003 mmol, 1 mol %). The crude product was purified by column chromatography (silica gel, 19:1 hexane/EtOAc) to provide **5l** (84.3 mg, 72%) as a pale yellow oil; TLC R_f = 0.38 (4:1 hexane/EtOAc); $[\alpha]_D^{20}$ +122 (*c* 1.08, $CHCl_3$) for 87% ee; [lit.,[9] $[\alpha]_D$ +99.8 (*c* 3.2, $CHCl_3$) for 90% ee of (*S*)-enantiomer]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 (s, 9H, SiC(CH_3)$_3$), 2.64 (s, 1H, C3-*H*), 2.66 (d, *J* = 2.2 Hz, 1H, C3-*H*), 4.36 (d, *J* = 1.4 Hz, 2H, SiOCH_2), 5.14 (dd, *J* = 6.8, 8.2 Hz, 1H, C2-*H*), 5.45 (d, *J* = 6.3 Hz, 1H, C5-*H*), 7.28 (d, *J* = 6.3 Hz, 1H, C6-*H*), 7.38−7.45

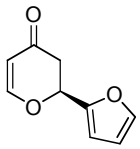
(m, 6H, *Ar*), 7.68−7.70 (m, 4H, *Ar*).

Determination of Enantiomeric Excess of 5l: (2*S*,4*S*)-2-[3-(*tert*-Butyldiphenylsiloxy)prop-1-ynyl]-3,4-dihydro-2*H*-pyran-4-ol (6).[9]

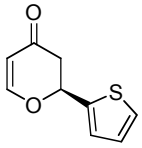


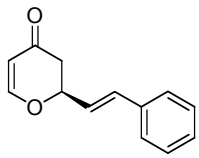
Cerium trichloride heptahydrate (80.4 mg, 0.33 mmol) was added to a stirred solution of **5l** (84.3 mg, 0.22 mmol) in methanol (1.0 mL) and ethanol (1.0 mL). The mixture was cooled to −78 ºC and sodium borohydride (16.7 mg, 0.44 mmol) was added. After stirring for 30 min, the reaction was poured into water (3 mL) and extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine (3 mL) and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* followed by column chromatography (silica gel, 9:1 toluene/EtOAc) provided **6** (67.4 mg, 80%) as a pale yellow oil. TLC R_f = 0.33 (9:1 toluene/EtOAc); $[\alpha]_D^{21}$ +73.5 (*c* 1.00, $CHCl_3$) for 87% ee; [lit.,[9] $[\alpha]_D^{25}$ +69.6 (*c* 1.15, $CHCl_3$) for 90% ee of **6**]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06 (s, 9H, SiC(C*H*$_3$)$_3$), 2.16-2.20 (m, 2H, C3-*H*), 4.12 (dd, *J* = 7.2, 14.5 Hz, 1H, C4-*H*), 4.31 (d, *J* = 1.4 Hz, 2H, SiOC*H*$_2$), 4,89 (t, *J* = 4.1 Hz, 1H, C5-*H*), 5.09 (ddd, *J* = 0.9, 4.1, 6.3 Hz, 1H, C2-*H*), 6.39 (dd, *J* = 0.9, 6.3 Hz, 1H, C6-*H*), 7.37−7.44 (m, 6H, *Ar*), 7.68-7.71 (m, 4H, *Ar*). Enantiomeric excess of **6** was determined to be 87% by HPLC with a Chiralcel OD-H column (50:1 hexane/^{i}PrOH, 1.0 mL/min): t_R (major) = 12.5 min for (*S*)-enantiomer; t_R (minor) = 14.9 min for (*R*)-enantiomer.

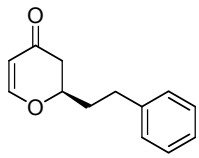
2-(2-Naphthyl)-2,3-dihydro-4*H*-pyran-4-one (5m).[10]  According to the typical procedure for enantioselective HDA reaction, **5m** was prepared from diene **2** (68.2 mg, 0.3 mmol), 2-naphthaldehyde (**3m**) (80.2 mg, 0.45 mmol), and Rh_2(*S*-BPTPI)$_4$·3H_2O (4.30 mg, 0.003 mmol, 1 mol %). The crude product was purified by column chromatography (silica gel, 19:1 hexane/EtOAc) to provide **5m** (59.3 mg, 71%) as a white solid; mp 55.5−56.5 ºC; TLC R_f = 0.28 (4:1 hexane/EtOAc); $[\alpha]_D^{21}$ +95.8 (*c* 1.03, $CHCl_3$) for 96% ee; [lit.,[10] $[\alpha]_D^{22}$ –74.2 (*c* 0.708, $CHCl_3$) for 92.3% ee of **5m**]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.74 (ddd, *J* = 1.0, 3.4, 17.1 Hz, 1H, C3-*H*), 3.02 (dd, *J* = 14.6, 16.1 Hz, 1H, C3-*H*), 5.57 (dd, *J* = 1.0, 5.9 Hz, 1H, C5-*H*), 5.60 (dd, *J* = 3.4, 14.6 Hz, 1H, C2-*H*), 7.50−7.54 (m, 4H, *Ar* and C6-*H*), 7.86−7.92 (m, 4H, *Ar*). Enantiomeric excess of **5m** was determined to be 96% by HPLC with a Chiralcel OD-H column (9:1 hexane/^{i}PrOH, 1.0 mL/min): t_R = 24.6 min for minor enantiomer; t_R = 41.8 min for major enantiomer. The preferred absolute configuration of **5m** was not determined.

(*S*)-2-(2-Furyl)-2,3-dihydro-4*H*-pyran-4-one (5n).[11]  According to the typical procedure for enantioselective HDA reaction, **5n** was prepared from diene **2** (68.2 mg, 0.3 mmol), furfural (**3n**) (43.3 mg, 0.45 mmol), and Rh_2(*S*-BPTPI)$_4$·3H_2O (4.30 mg, 0.003 mmol, 1 mol %). The crude product was purified by column chromatography

(silica gel, 4:1 hexane/EtOAc) to provide **5n** (39.6 mg, 80%) as a white solid; mp 66.0−67.5 ºC; TLC R_f = 0.41 (2:1 hexane/EtOAc); $[\alpha]_D^{21}$ +335 (*c* 1.02, $CHCl_3$) for 90% ee; [lit.,[11] $[\alpha]_D$ –255 (*c* 0.5, $CHCl_3$) for 67% ee of (*R*)-enantiomer]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.72 (ddd, *J* = 0.9, 4.1, 16.7 Hz, 1H, C3-*H*), 3.10 (dd, *J* = 12.7, 16.7 Hz, 1H, C3-*H*), 5.48 (dd, *J* = 3.6, 12.7 Hz, 1H, C2-*H*), 5.51 (dd, *J* = 0.9, 5.9 Hz, 1H, C5-*H*), 6.42 (dd, *J* = 1.8, 3.2 Hz, 1H, *Ar*), 6.46 (d, *J* = 3.2 Hz, 1H, *Ar*), 7.38 (d, *J* = 5.9 Hz, 1H, C6-*H*), 7.48 (d, *J* = 1.8 Hz, 1H, *Ar*). Enantiomeric excess of **5n** was determined to be 90% by HPLC with a Chiralcel OD-H column (50:1 hexane/^{i}PrOH, 1.0 mL/min): t_R (major) = 24.4 min for (*S*)-enantiomer; t_R (minor) = 26.5 min for (*R*)-enantiomer.

2-(2-Thienyl)-2,3-dihydro-4*H*-pyran-4-one (5o).[12]  According to the typical procedure for enantioselective HDA reaction, **5o** was prepared from diene **2** (68.2 mg, 0.3 mmol), 2-thiophencarbaldehyde (**3o**) (50.5 mg, 0.45 mmol), and Rh_2(*S*-BPTPI)$_4$·3H_2O (4.30 mg, 0.003 mmol, 1 mol %). The crude product was purified by column chromatography (silica gel, 4:1 hexane/EtOAc) to provide **5o** (38.3 mg, 71%) as a yellow oil; TLC R_f = 0.38 (2:1 hexane/EtOAc); $[\alpha]_D^{21}$ +248 (*c* 1.08, $CHCl_3$) for 93% ee; [lit.,[12] $[\alpha]_D$ +130 (*c* 1.03, $CHCl_3$) for 52% ee of **5o**]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.83 (ddd, *J* = 0.9, 4.1, 16.8 Hz, 1H, C3-*H*), 3.03 (dd, *J* = 13.1, 16.8 Hz, 1H, C3-*H*), 5.53 (dd, *J* = 0.9, 6.3 Hz, 1H, C5-*H*), 5.68 (dd, *J* = 4.1, 13.1 Hz, 1H, C2-*H*), 7.04 (dd, *J* = 3.6, 5.0 Hz, 1H, *Ar*), 7.12 (d, *J* = 3.6 Hz, 1H, *Ar*), 7.38 (d, *J* = 5.0 Hz, 1H, *Ar*), 7.42 (d, *J* = 6.3 Hz, 1H, C6-*H*). Enantiomeric excess of **5o** was determined to be 93% by HPLC with a Chiralpak AD column (50:1 hexane/^{i}PrOH, 0.7 mL/min): t_R = 34.1 min for major enantiomer; t_R = 38.1 min for minor enantiomer. The preferred absolute configuration of **5o** was not determined.

(*S*)-2-[(*E*)-2-Phenylethenyl]-2,3-dihydro-4*H*-pyran-4-one (5p).[13]  According to the typical procedure for enantioselective HDA reaction, **5p** was prepared from diene **2** (68.2 mg, 0.3 mmol), (*E*)-cinnamaldehyde (**3p**) (59.4 mg, 0.45 mmol), and Rh_2(*S*-BPTPI)$_4$·3H_2O (4.30 mg, 0.003 mmol, 1 mol %). The crude product was purified by column chromatography (silica gel, 6:1 hexane/EtOAc) to provide **5p** (45.1 mg, 75%) as a white solid; mp 49.0−50.0 ºC; TLC R_f = 0.28 (4:1 hexane/EtOAc); $[\alpha]_D^{21}$ +198 (*c* 1.04, CH_2Cl_2) for 97% ee; [lit.,[13] $[\alpha]_D$ –215 (*c* 0.36, CH_2Cl_2) for 99% ee of (*R*)-enantiomer]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.63 (dd, *J* = 3.6, 16.8 Hz, 1H, C3-*H*), 2.74 (dd, *J* = 13.2, 16.8 Hz, 1H, C3-*H*), 5.08 (ddd, *J* = 3.6, 6.4, 13.2 Hz, 1H, C2-*H*), 5.48 (d, *J* = 5.5 Hz, 1H, C5-*H*), 6.30 (dd, *J* = 6.4, 15.8 Hz, 1H, C*H*=CHPh), 6.73 (d, *J* = 15.8 Hz, 1H, CH=C*H*Ph), 7.27−7.42 (m, 6H, *Ar* and C6-*H*). Enantiomeric excess of **5p** was determined to be 97% by HPLC with a Chiralcel OD-H column (3:1 hexane/^{i}PrOH, 1.0 mL/min): t_R (major) = 12.3 min for (*S*)-enantiomer; t_R (minor) = 23.2 min for (*R*)-enantiomer.

(*R*)-2-(2-Phenylethyl)-2,3-dihydro-4*H*-pyran-4-one (5q).[11]  According to the typical procedure for enantioselective HDA reaction, **5q** was prepared from diene **2** (68.2 mg, 0.3 mmol), hydrocinnamaldehyde (**3q**) (60.3 mg, 0.45 mmol), and

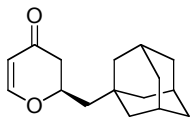
Rh_2(*S*-BPTPI)$_4$·3H_2O (4.30 mg, 0.003 mmol, 1 mol %). The crude product was purified by column chromatography (silica gel, 4:1 hexane/EtOAc) to provide **5q** (56.2 mg, 93%) as a colorless oil; TLC R_f = 0.33 (2:1 hexane/EtOAc); $[\alpha]_D^{21}$ +112.6 (*c* 1.27, $CHCl_3$) for 99% ee; [lit.,[11] $[\alpha]_D^{23}$ –69 (*c* 0.5, $CHCl_3$) for 69% ee of (*S*)-enantiomer]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.97 (m, 1H, C*H*HCH$_2$Ph), 2.16 (m, 1H, C*H*HCH$_2$Ph), 2.42 (ddd, *J* = 0.9, 3.7, 16.8 Hz, 1H, C3-*H*), 2.56 (dd, *J* = 13.1, 16.8 Hz, 1H, C3-*H*), 2.75−2.85 (m, 2H, CH$_2$C*H*$_2$Ph), 4.41 (m, 1H, C2-*H*), 5.41 (dd, *J* = 1.4, 6.4 Hz, 1H, C5-*H*), 7.18−7.24 (m, 3H *Ar*), 7.29−7.33 (m, 2H, *Ar*), 7.39 (d, *J* = 6.4 Hz, 1H, C6-*H*). Enantiomeric excess of **5q** was determined to be 99% by HPLC with a Chiralcel OD-H column (3:1 hexane/^{i}PrOH, 1.0 mL/min): t_R (major) = 12.4 min for (*R*)-enantiomer; t_R (minor) = 23.2 min for (*S*)-enantiomer.

2-Pentyl-2,3-dihydro-4*H*-pyran-4-one (5r).[3] According to the typical procedure for enantioselective HDA reaction, **5r** was prepared from diene **2** (68.2 mg, 0.3 mmol), hexanal (**3r**) (45.0 mg, 0.45 mmol), and Rh_2(*S*-BPTPI)$_4$·3H_2O (4.30 mg, 0.003 mmol, 1 mol %). The crude product was purified by column chromatography (silica gel, 19:1 hexane/EtOAc) to provide **5r** (40.4 mg, 80%) as a colorless oil; TLC R_f = 0.45 (4:1 hexane/EtOAc); $[\alpha]_D^{21}$ +130 (*c* 1.04, $CHCl_3$) for 97% ee; [lit.,[3] $[\alpha]_D^{19}$ –131.4 (*c* 0.54, $CHCl_3$) for 83% ee of **5r**]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, *J* = 6.8 Hz, 3H, C*H*$_3$), 1.30−1.49 (m, 6H, C*H*$_2$C*H*$_2$C*H*$_2$), 1.65 (m, 1H, C2-CH*H*) 1.80 (m, 1H, C2-CH*H*), 2.42 (ddd, *J* = 1.3, 4.5, 16.8 Hz, 1H, C3-*H*), 2.52 (dd, *J* = 13.1, 16.8 Hz, 1H, C3-*H*), 4.41 (ddt, *J* = 4.5, 9.1, 13.1 Hz, 1H, C2-*H*), 5.40 (dd, *J* = 0.9, 5.9 Hz, 1H, C5-*H*), 7.36 (d, *J* = 5.9 Hz, 1H, C6-*H*). Enantiomeric excess of **5r** was determined to be 97% by HPLC with a Chiralcel OD-H column (9:1 hexane/^{i}PrOH, 0.3 mL/min): t_R = 18.6 min for minor enantiomer; t_R = 19.7 min for major enantiomer. The preferred absolute configuration of **5r** was not determined.

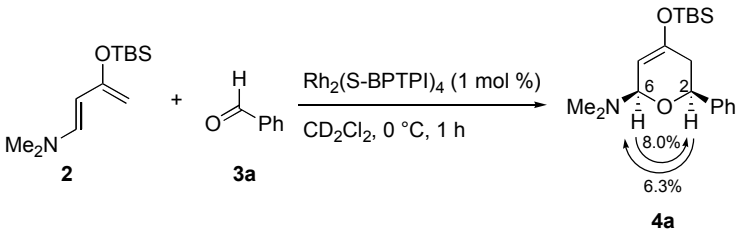
(*R*)-2-(2-*tert*-Butyldimethylsilyloxyethyl)-2,3-dihydro-4*H*-pyran-4-one (5s).[14] According to the typical procedure for enantioselective HDA reaction, **5s** was prepared from diene **2** (68.2 mg, 0.3 mmol), 2-*tert*-butyldimethylsilyloxypropanal (**3s**) (84.7 mg, 0.45 mmol), and Rh_2(*S*-BPTPI)$_4$·3H_2O (4.30 mg, 0.003 mmol, 1 mol %). The crude product was purified by column chromatography (silica gel, 9:1 hexane/EtOAc) to provide **5s** (56.9 mg, 74%) as a colorless oil; TLC R_f = 0.45 (4:1 hexane/EtOAc); $[\alpha]_D^{21}$ +82.2 (*c* 1.08, CH_2Cl_2) for 98% ee; [lit.,[14] $[\alpha]_D^{20}$ –70.0 (*c* 1.00, CH_2Cl_2) for (*S*)-enantiomer]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.04 (s, 6H, Si(C*H*$_3$)$_2$), 0.87 (s, 9H, SiC(C*H*$_3$)$_3$), 1.82 (ddt, *J* = 5.0, 8.6, 17.2, 1H, C2-CH*H*), 2.00 (ddt, *J* = 5.0, 8.6, 14.0 Hz, 1H, C2-CH*H*), 2.46 (dd, *J* = 4.1, 16.8 Hz, 1H, C3-*H*), 2.55 (dd, *J* = 13.1, 16.8 Hz, 1H, C3-*H*), 3.71−3.83 (m, 2H, C*H*$_2$OTBS), 5.40 (d, *J* = 5.9 Hz, 1H, C5-*H*), 7.34 (d, *J* = 5.9 Hz, 1H, C6-*H*). Enantiomeric excess of **5s** was determined to be 98% by HPLC with a Chiralcel OD-H column (50:1 hexane/^{i}PrOH, 1.0 mL/min): t_R (major) = 7.9 min for (*R*)-enantiomer; t_R (minor) = 8.6 min for (*S*)-enantiomer.

(*S*)-2-Cyclohexyl-2,3-dihydro-4*H*-pyran-4-one (5t).[11] According to the typical

procedure for enantioselective HDA reaction, **5t** was prepared from diene **2** (68.2 mg, 0.3 mmol), cyclohexanecarbaldehyde (**3t**) (50.4 mg, 0.45 mmol), and Rh_2(*S*-BPTPI)$_4$·3H_2O (4.30 mg, 0.003 mmol, 1 mol %). The crude product was purified by column chromatography (silica gel, 9:1 hexane/EtOAc) to provide **5t** (38.3 mg, 71%) as a colorless oil; TLC R_f = 0.45 (4:1 hexane/EtOAc); $[\alpha]_D^{21}$ +130 (*c* 1.04, $CHCl_3$) for 95% ee; [lit.,[11] $[\alpha]_D^{23}$ –159 (*c* 0.5, $CHCl_3$) for 76% ee of (*R*)-enantiomer]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.05−1.30 (m, 6H, C_6H_{11}), 1.67−1.90 (m, 5H, C_6H_{11}), 2.38 (ddd, *J* = 1.1, 3.4, 16.6 Hz, 1H, C3-*H*), 2.55 (dd, *J* = 14.4, 16.6 Hz, 1H, C3-*H*), 4.17 (ddd, *J* = 2.3, 3.5, 14.4 Hz, 1H, C2-*H*), 5.39 (dd, *J* = 1.1, 6.3 Hz, 1H, C5-*H*), 7.38 (d, *J* = 6.3 Hz, 1H, C6-*H*). Enantiomeric excess of **5t** was determined to be 95% by HPLC with a Chiralcel OD-H column (19:1 hexane/^{i}PrOH, 0.3 mL/min): t_R (major) = 26.1 min for (*S*)-enantiomer; t_R (minor) = 29.1 min for (*R*)-enantiomer.

2-(1-Adamantylmethyl)-2,3-dihydro-4*H*-pyran-4-one (5u).  According to the typical procedure for enantioselective HDA reaction, **5u** was prepared from diene **2** (68.2 mg, 0.3 mmol), 1-adamantylacetaldehyde (**3u**) (80.2 mg, 0.45 mmol), and Rh_2(*S*-BPTPI)$_4$·3H_2O (4.30 mg, 0.003 mmol, 1 mol %). The crude product was purified by column chromatography (silica gel, 19:1 hexane/EtOAc) to provide **5u** (59.3 mg, 73%) as a white solid; mp 55.5−56.5 ºC; TLC R_f = 0.28 (4:1 hexane/EtOAc); $[\alpha]_D^{21}$ +64.0 (*c* 1.03, $CHCl_3$) for 90% ee; IR (KBr) 2903, 1676, 1593, 1274 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (dd, *J* = 3.2, 5.4 Hz, 1H, C2-CH*H*), 1.52-1.76 (m, 13H, Ad-*H* and C2-C*H*H), 1.97 (s, 3H, Ad-*H*), 2.35 (ddd, *J* = 1.3, 3.6, 16.7 Hz, 1H, C3-*H*), 2.53 (dd, *J* = 13.5, 16.7 Hz, 1H, C3-*H*), 4.60 (ddt, *J* = 3.6, 8.1, 13.5 Hz, 1H, C2-*H*), 5.40 (dd, *J* = 1.3, 5.9 Hz, 1H, C5-*H*), 7.34 (d, *J* = 5.9 Hz, 1H, C6-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.5 (CH), 32.0 (C), 36.8 (CH_2), 42.6 (CH_2), 43.6 (CH_2), 48.8 (CH_2), 76.2 (CH), 106.8 (CH), 163.3 (CH), 193.0 (C); EI-HRMS *m/z* calcd for $C_{16}H_{22}O_2$ (M^+) 246.16198, found 246.16181. Enantiomeric excess of **5u** was determined to be 90% by HPLC with a Chiralcel OD-H column (200:1 hexane/^{i}PrOH, 1.0 mL/min): t_R = 24.1 min for minor enantiomer; t_R = 30.3 min for major enantiomer. The preferred absolute configuration of **5u** was not determined. A sample for combustion analysis was obtained by recrystallizations from hexane as colorless needles (99% ee); mp 59.0−60.0 ºC; Anal Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 78.00; H 9.17.

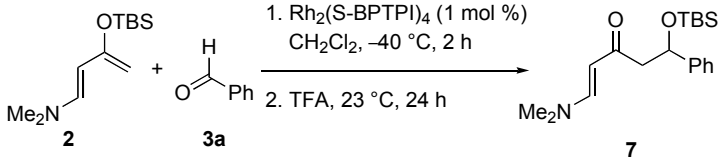
NMR Analysis of 4a.[15]



A solution of diene **2** (11.4 mg, 0.05 mmol) in CD_2Cl_2 (0.05 mL) was added to a solution of benzaldehyde (**3a**) (10.6 mg, 0.10 mmol) and Rh_2(*S*-BPTPI)$_4$·3H_2O (0.72 mg, 0.0005 mmol, 1 mol %) in CD_2Cl_2 (0.05 mL) at 0 ºC. After stirring for 1 h, the reaction mixture was diluted with CD_2Cl_2 (0.4 mL). ^{1}H NMR showed exclusive formation of **4a**; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 0.17

(s, 3H, SiCH_3), 0.19 (s, 3H, SiCH_3), 0.92 (s, 9H, SiC(CH_3)$_3$), 2.15 (ddd, J = 2.3, 3.5, 16.4 Hz, 1H, C3-*H*), 2.41 (ddd, J = 1.6, 10.4, 16.4 Hz, 1H, C3-*H*), 2.61 (s, 6H, N(CH_3)$_2$), 4.61 (dd, J = 3.5, 10.4 Hz, 1H, C2-*H*), 4.81 (dd, J =1.6, 1.8 Hz, 1H, C5-*H*), 4.95 (dd, J = 1.8, 2.3 Hz, 1H, C6-*H*), 7.31−7.39 (m, 5H, *Ar*). In order to assign the stereochemistry at C2 and C6, NOE studies were performed on **4a**. Irradiation of C2-H showed NOE with C6-H (6.3%). Additionally, irradiation of C6-H exhibited NOE with the C2-H (8.0%). These data revealed *cis* relationship between C2-H and C6-H.

Preparation of (*E*)-5-*tert*-Butyldimethylsilyloxy-1-(*N*,*N*-dimethylamino)-5-phenyl-1-penten-3-one (7).



A solution of diene **2** (68.2 mg, 0.30 mmol) in CH_2Cl_2 (0.2 mL) was added to a solution of benzaldehyde (**3a**) (47.7 mg, 0.45 mmol) and Rh_2(*S*-BPTPI)$_4$·3H_2O (4.30 mg, 0.003 mmol, 1 mol %) in CH_2Cl_2 (0.4 mL) at −40 ºC. The reaction mixture was stirred for 2 h and then diluted with CH_2Cl_2 (1.2 mL). The whole mixture was treated with 10% solution of TFA in THF (0.45 mL). After stirring for 24 h, the reaction was quenched with saturated $NaHCO_3$ (3 mL) and extracted with EtOAc (2 x 10 mL). The combined organic layers were washed with water (3 mL) and brine (2 x 3 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* furnished the crude product, which was purified by column chromatography (silica gel, 1:1 hexane/EtOAc) to provide **7** (54.7 mg, 55%) as a pale yellow oil; TLC R_f = 0.48 (1:3 hexane/EtOAc); $[\alpha]_D^{20}$ −111 (*c* 1.02, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.22 (s, 3H, SiCH_3), −0.07 (s, 3H, SiCH_3), 0.76 (s, 9H, SiC(CH_3)$_3$), 2.42 (dd, J = 4.1, 13.6 Hz, 1H, C4-*H*), 2.61−2.82 (m, 4H, C4-*H*, NCH_3), 2.97 (br, 3H, NCH_3), 4.96 (d, J = 13.2 Hz, C2-*H*), 5.13 (dd, J =4.1, 8.6 Hz, C5-*H*), 7.15 (m, 1H, *Ar*), 7.20−7.24 (m, 2H, *Ar*), 7.29−7.31 (m, 2H, *Ar*), 7.39 (d, J = 13.2, 1H, C1-*H*).

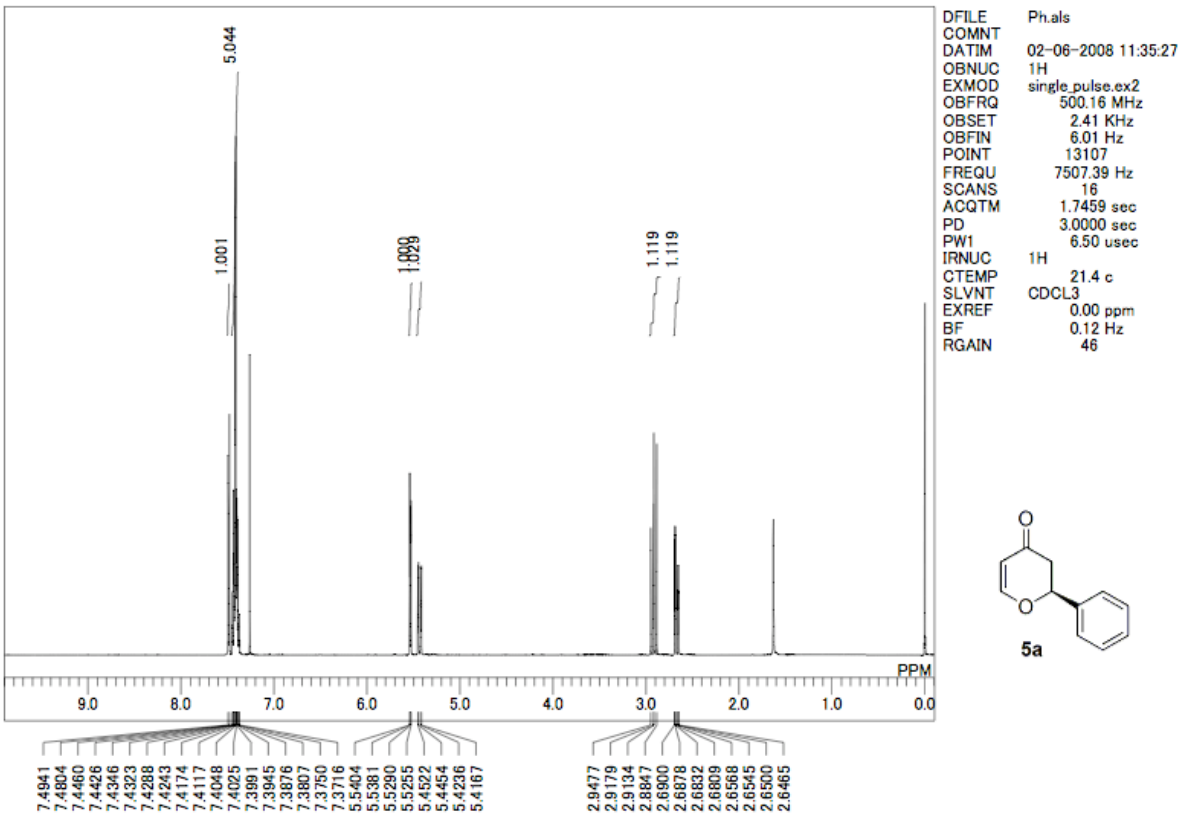
A mixture of **7** (20.0 mg, 0.06 mmol) and Rh_2(*S*-BPTPI)$_4$·3H_2O (0.86 mg, 0.0006 mmol, 1 mol %) in CH_2Cl_2 (0.4 mL) was stirred at 0 ºC for 12 h, but no detectable peaks of the cyclized product (**4a** or **5a**) were observed.

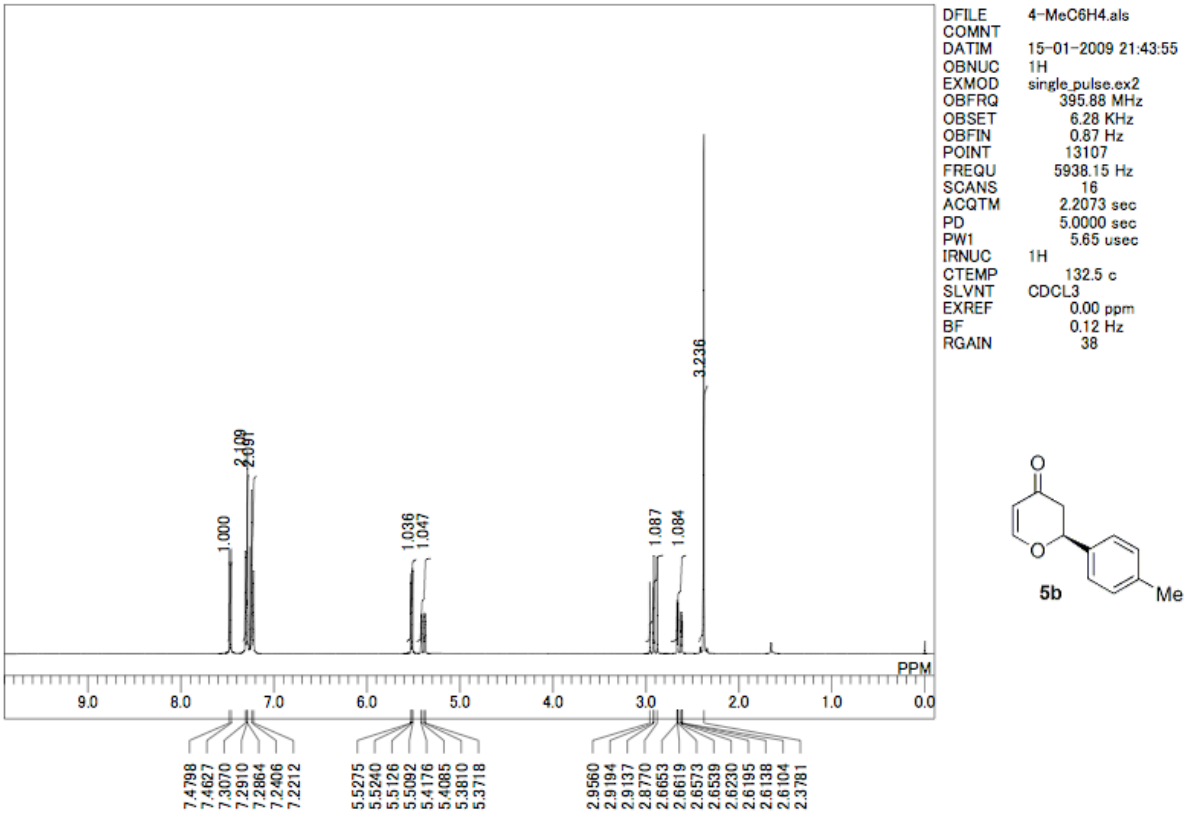
References

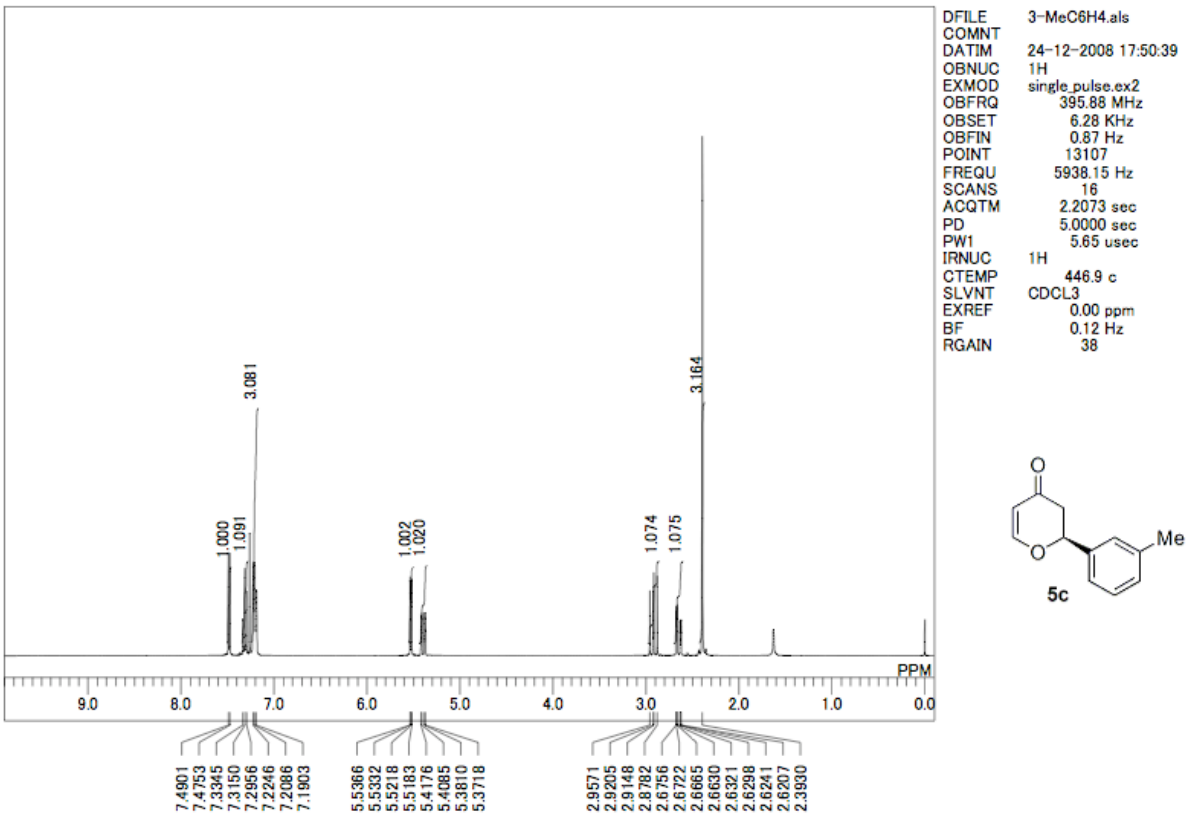
1) S. A. Kozmin, S. He and V. H. Rawal, *Org. Synth*., 2002, **78**, 152.
2) M. Bednarski and S. Danishefsky, *J. Am. Chem. Soc.,* 1986, **108**, 7060.
3) Y. Yamashita, S. Saito, H. Ishitani and S. Kobayashi, *Org. Lett.*, 2002, **4**, 1221.
4) J. Long, J. Hu, X. Shen, B. Ji and K. Ding, *J. Am. Chem. Soc.*, 2002, **124**, 10.
5) J. Mihara, K. Aikawa, T. Uchida, R. Irie and T. Katsuki, *Heterocycles*, 2001, **54**, 395.
6) K. Aikawa, R. Irie and T. Katsuki, *Tetrahedron*, 2001, **57**, 845.
7) S. Kezuka, T. Mita, N. Ohtsuki, T. Ikeno and T. Yamada, *Bull. Chem. Soc. Jpn.*, 2001, **74**, 1333.

8) R. F. Lowe and R. J. Stoodley, *Tetrahedron Lett.*, 1994, **35**, 6351.
9) A. Boyer, G. E. Veitch, E. Beckmann and S. V. Ley, *Angew. Chem., Int. Ed.*, 2009, **48**, 1317.
10) H. Furuno, T. Hayano, T. Kambara, Y. Sugimoto, T. Hanamoto, Y. Tanaka, Y. Z. Jin, T. Kagawa and J. Inanaga, *Tetrahedron*, 2003, **59**, 10509.
11) E. J. Corey, C. L. Cywin and T. D. Roper, *Tetrahedron Lett.*, 1992, **33**, 6907.
12) A. Zulauf, M. Mellah, R. Guillot and E. Schulz, *Eur. J. Org. Chem*., 2008, 2118.
13) S. E. Schaus, J. Brånalt and E. N. Jacobsen, *J. Org. Chem*., 1998, **63**, 403.
14) A. B. Smith, III, R. J. Fox and J. A. Vanecko, *Org. Lett.*, 2005, **7**, 3099.
15) Y. Huang and V. H. Rawal, *Org. Lett*., 2000, **2**, 3321.

Copies of $^{1}H/^{13}C$ NMR spectra



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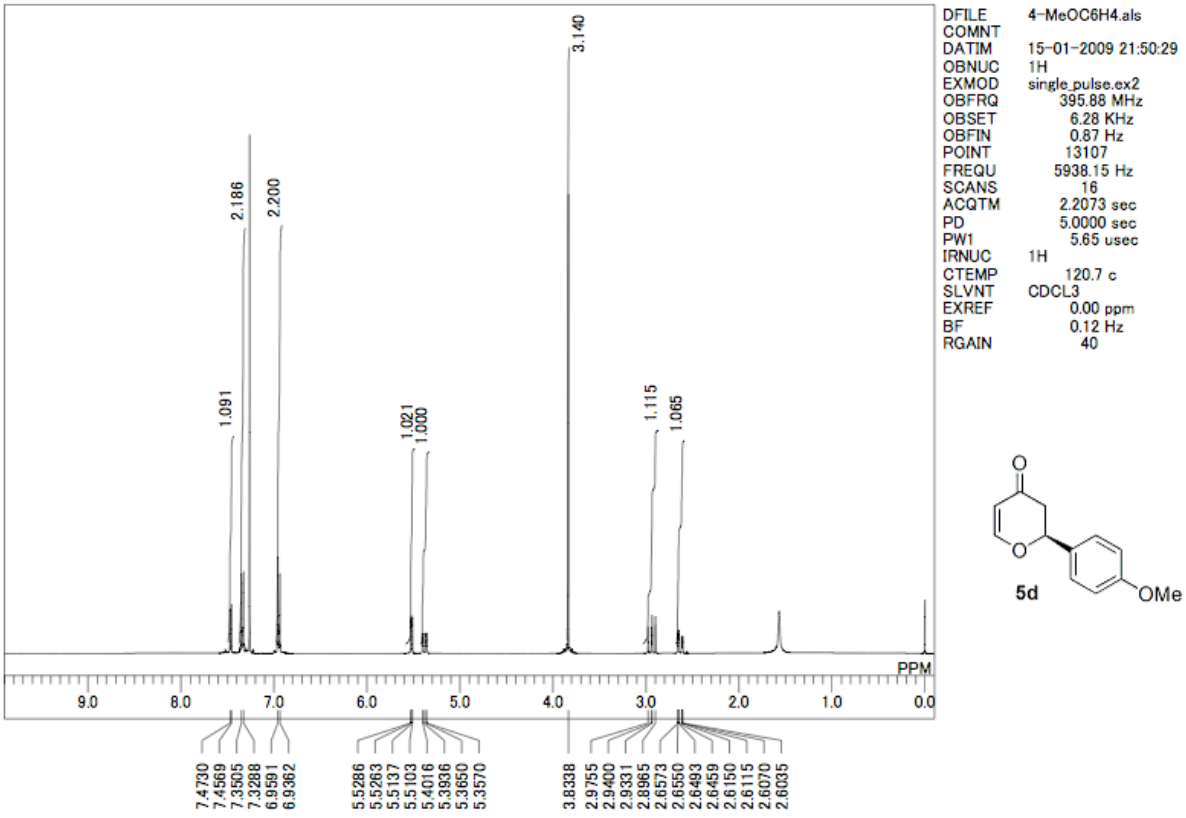
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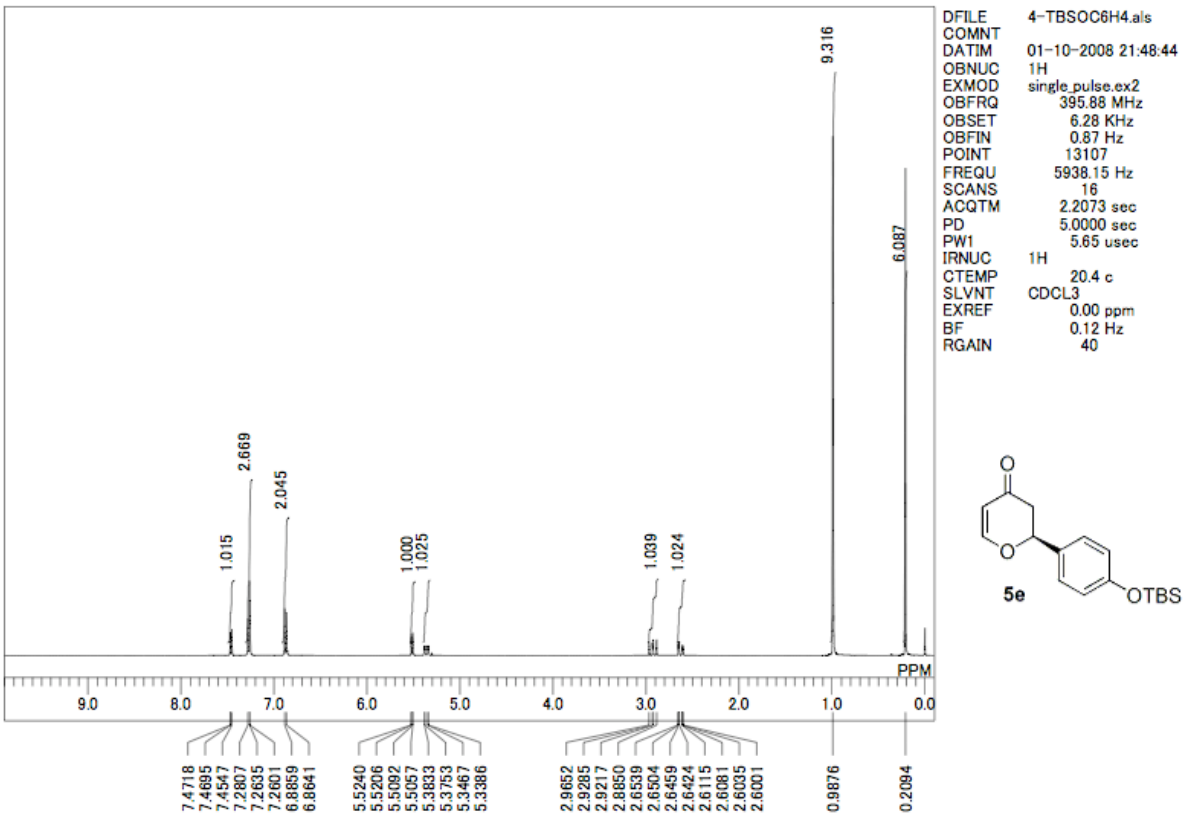
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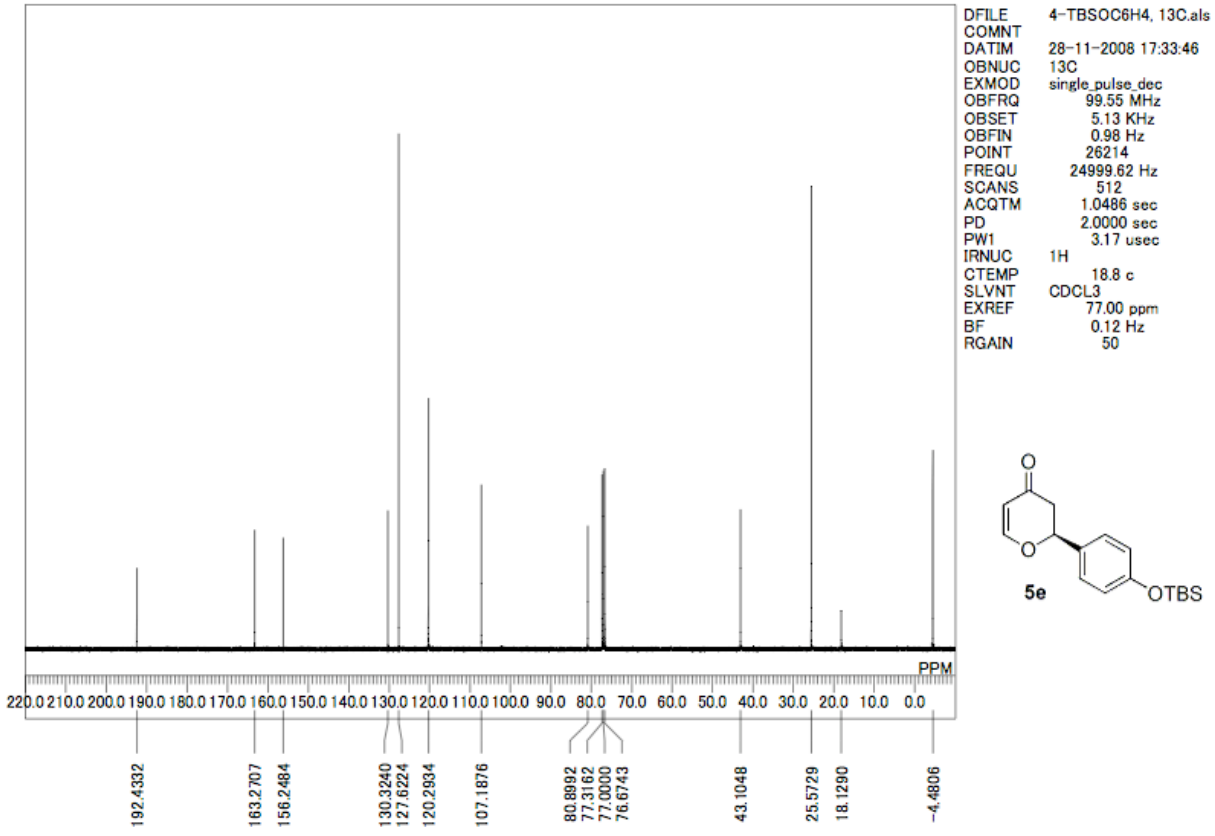
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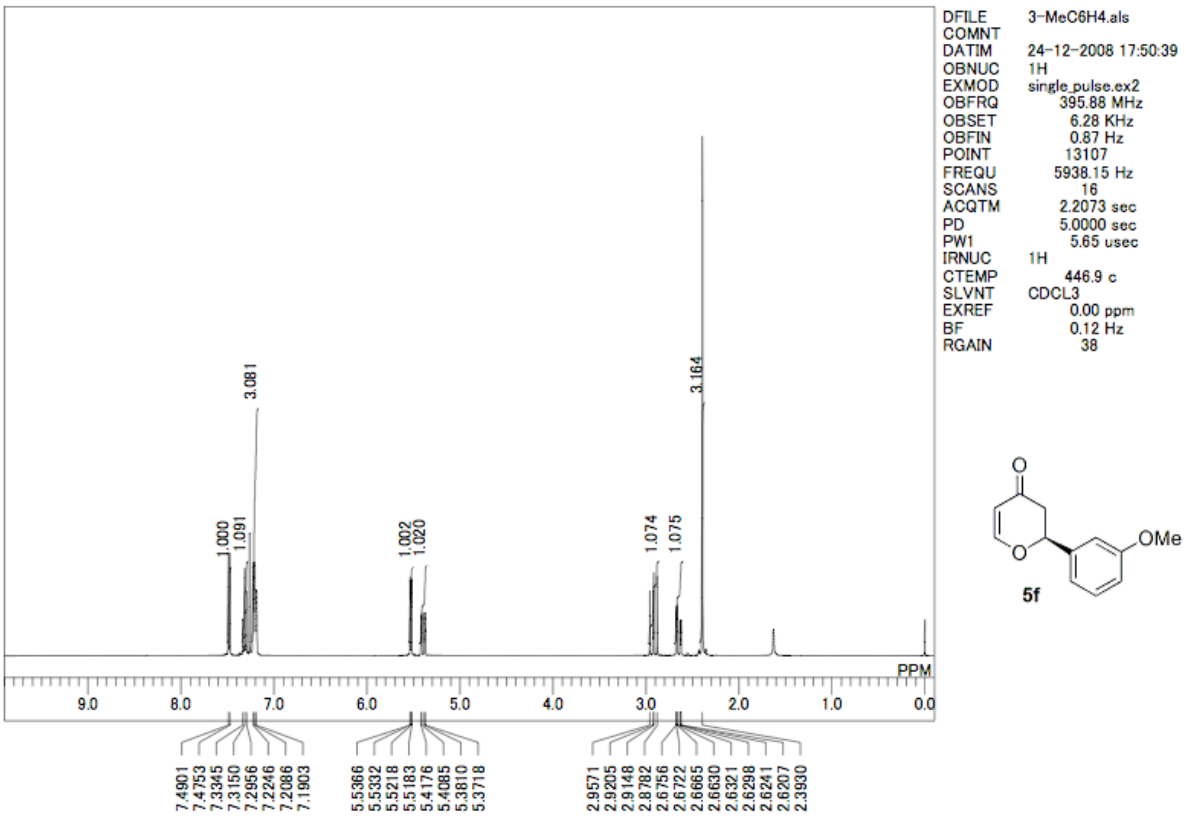
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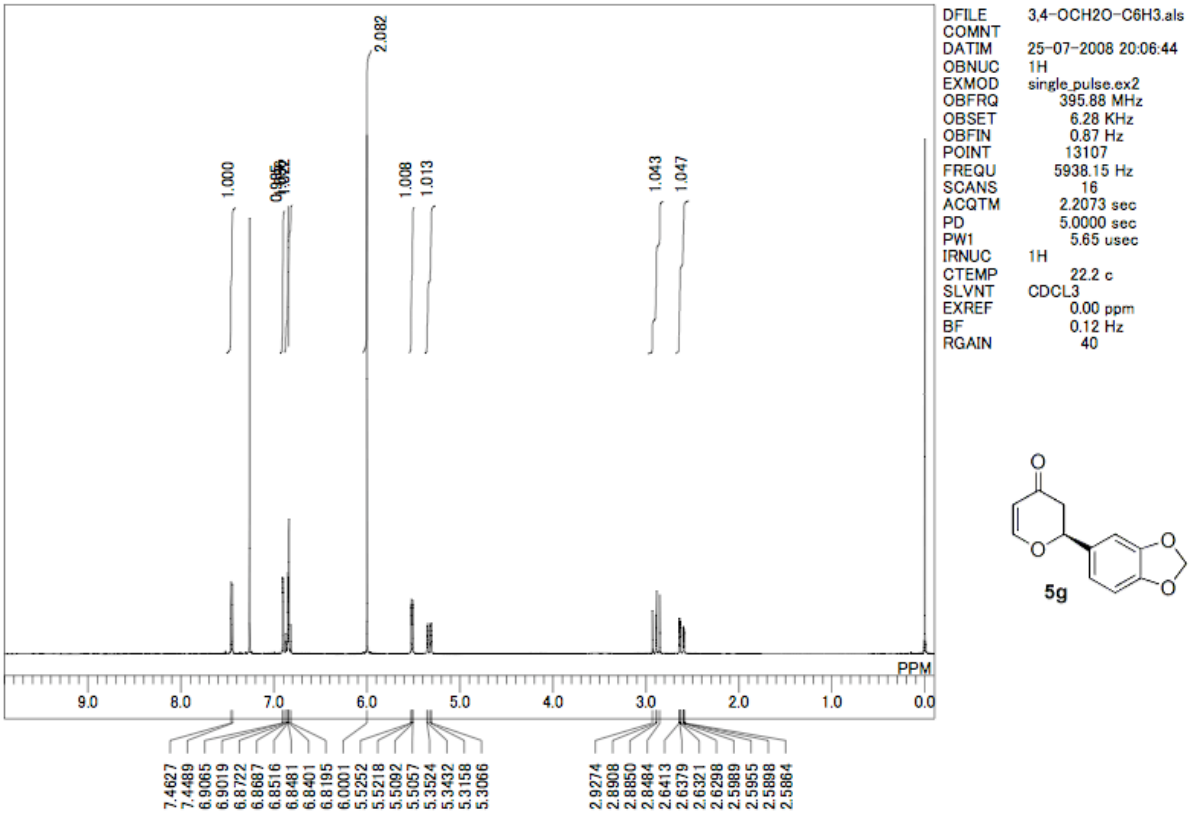
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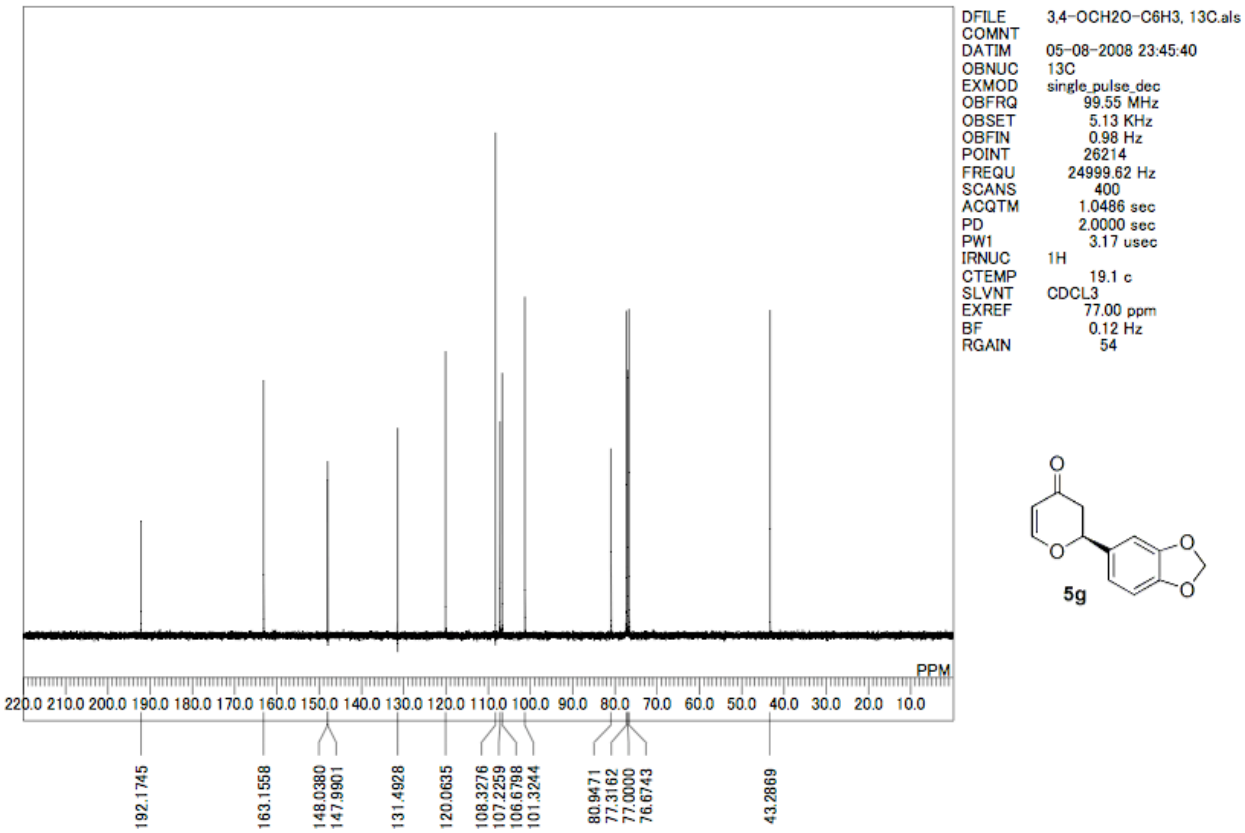
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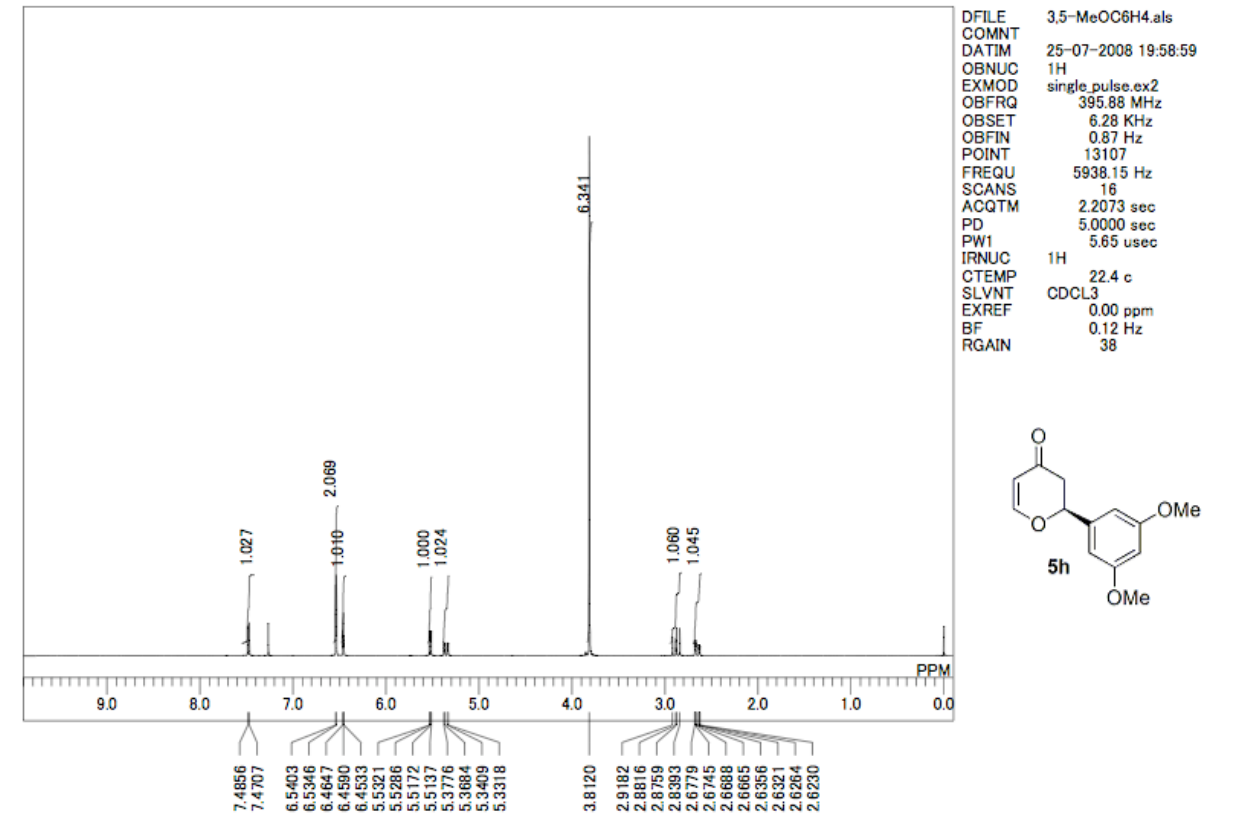
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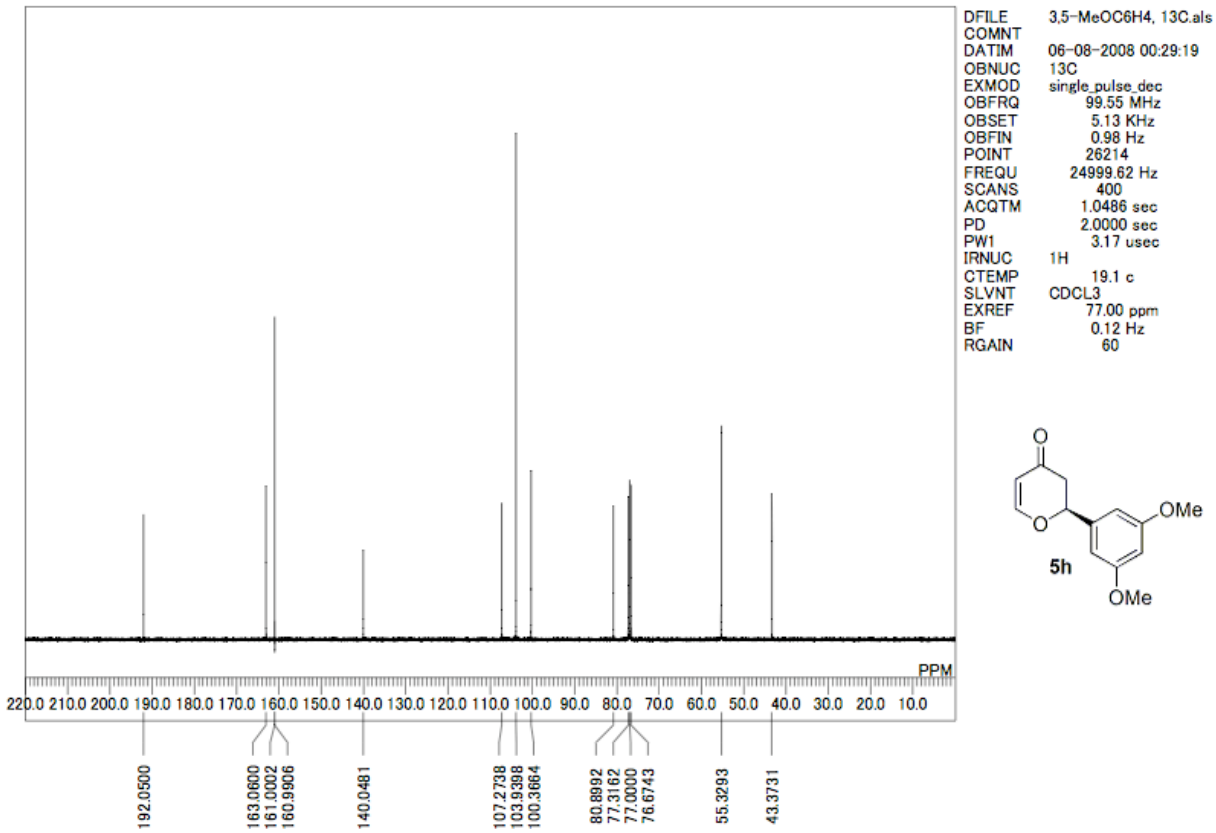
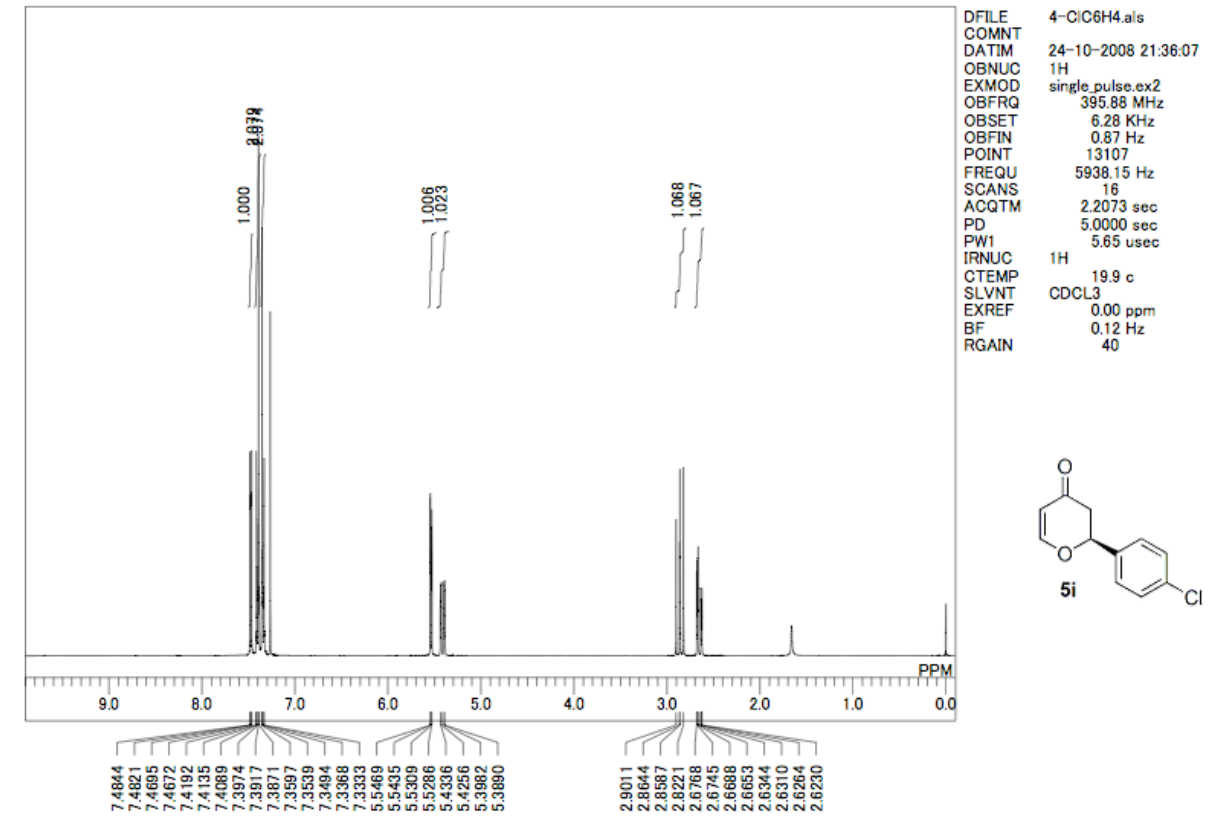
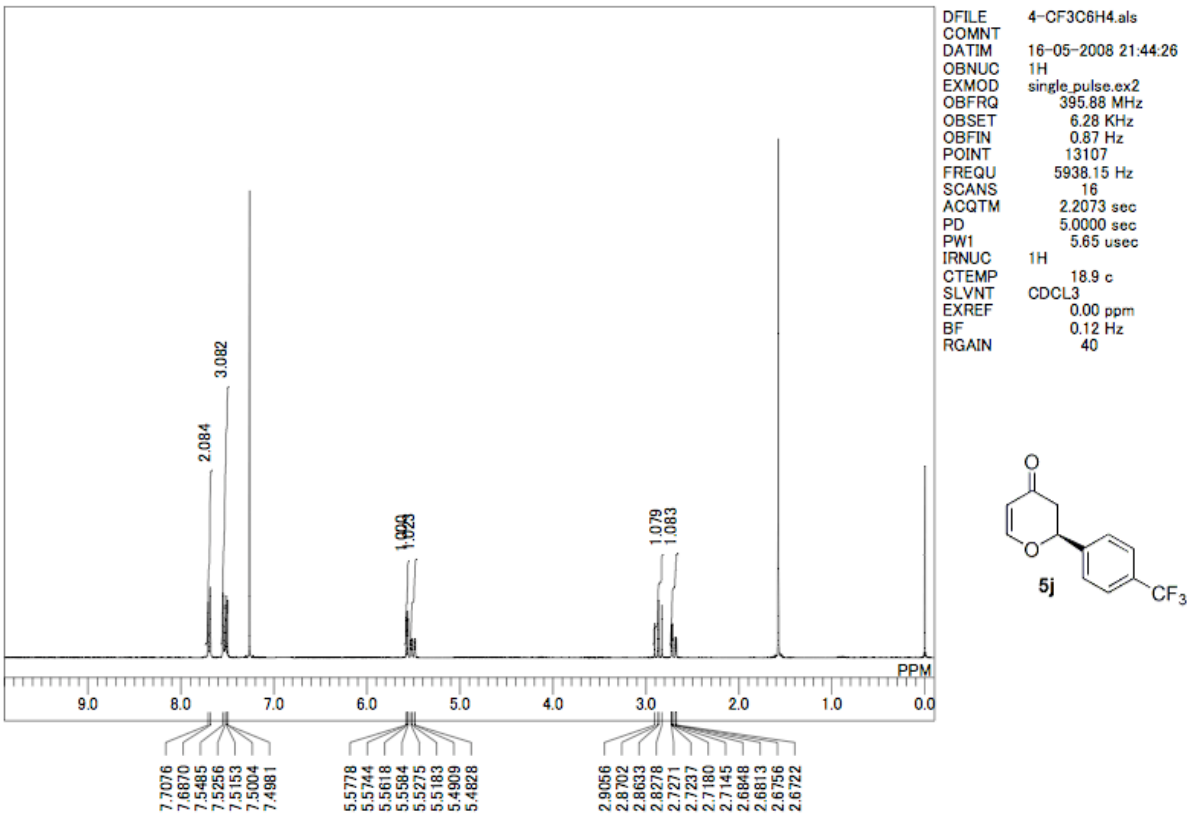
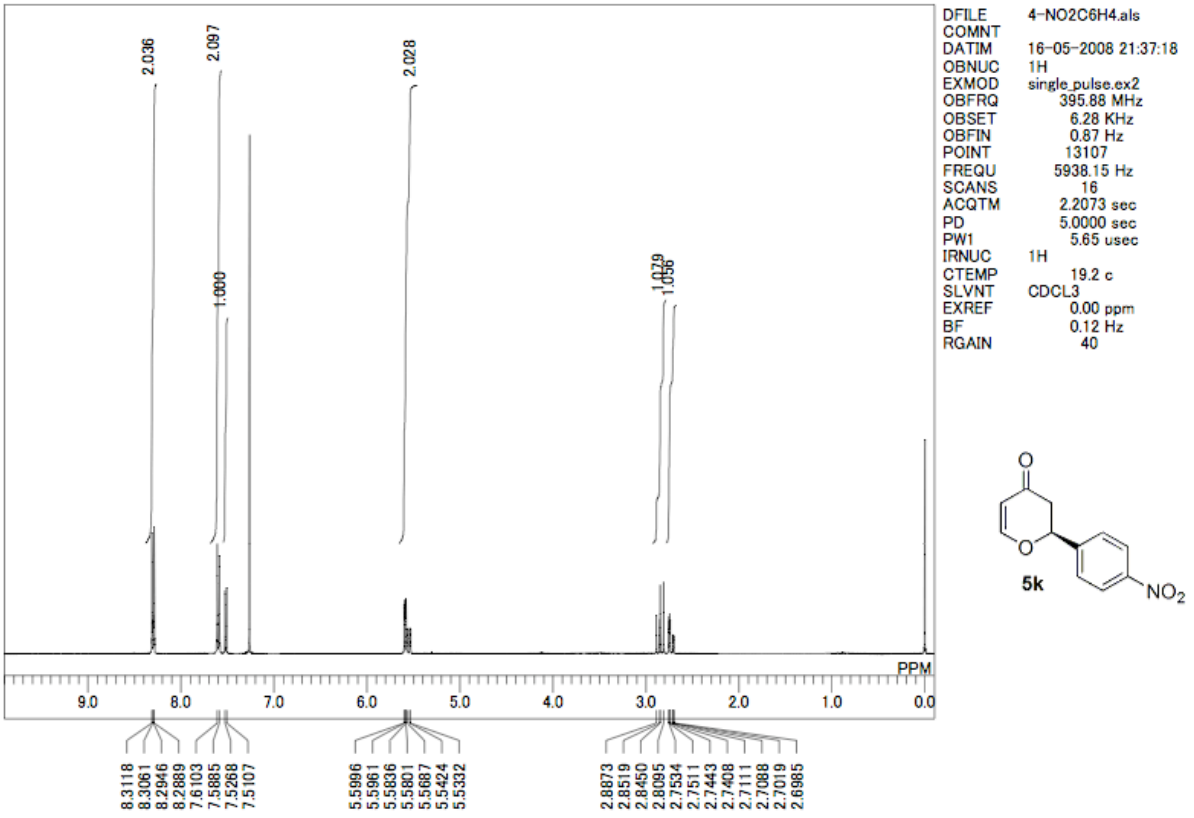
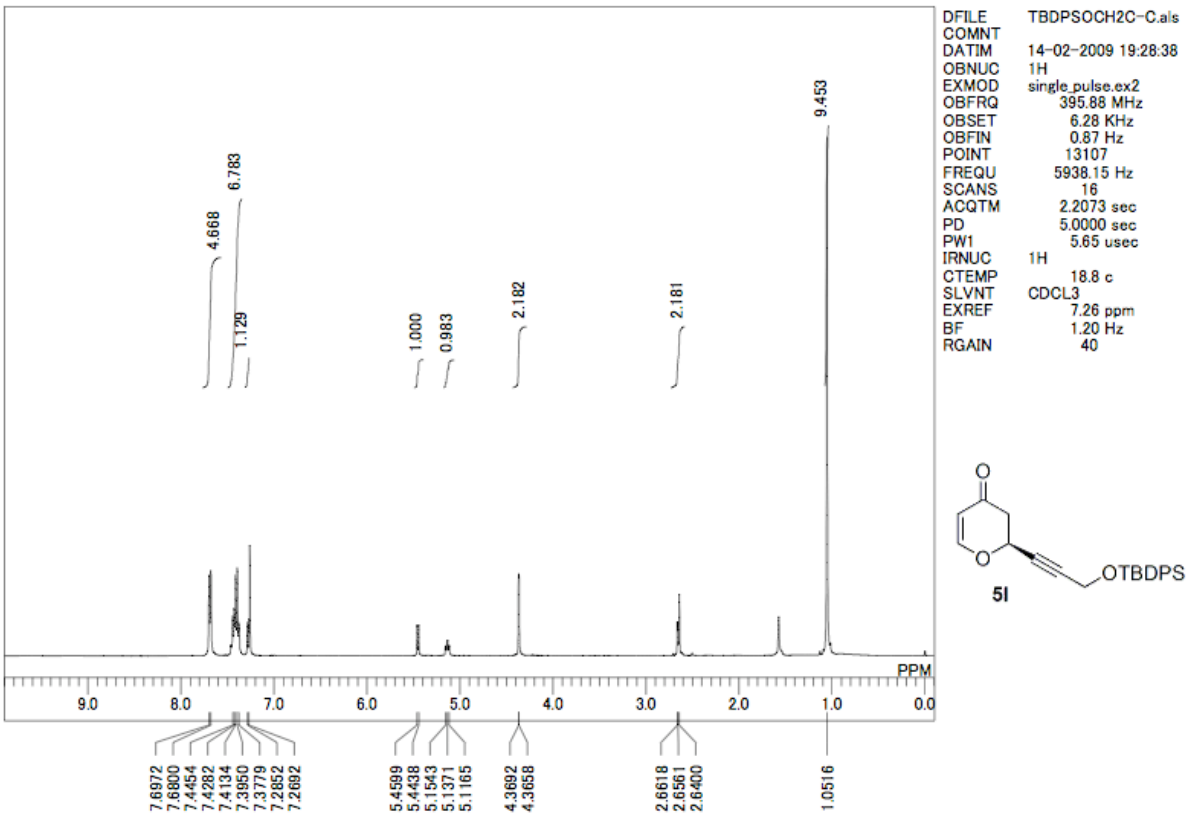
OMe
5h

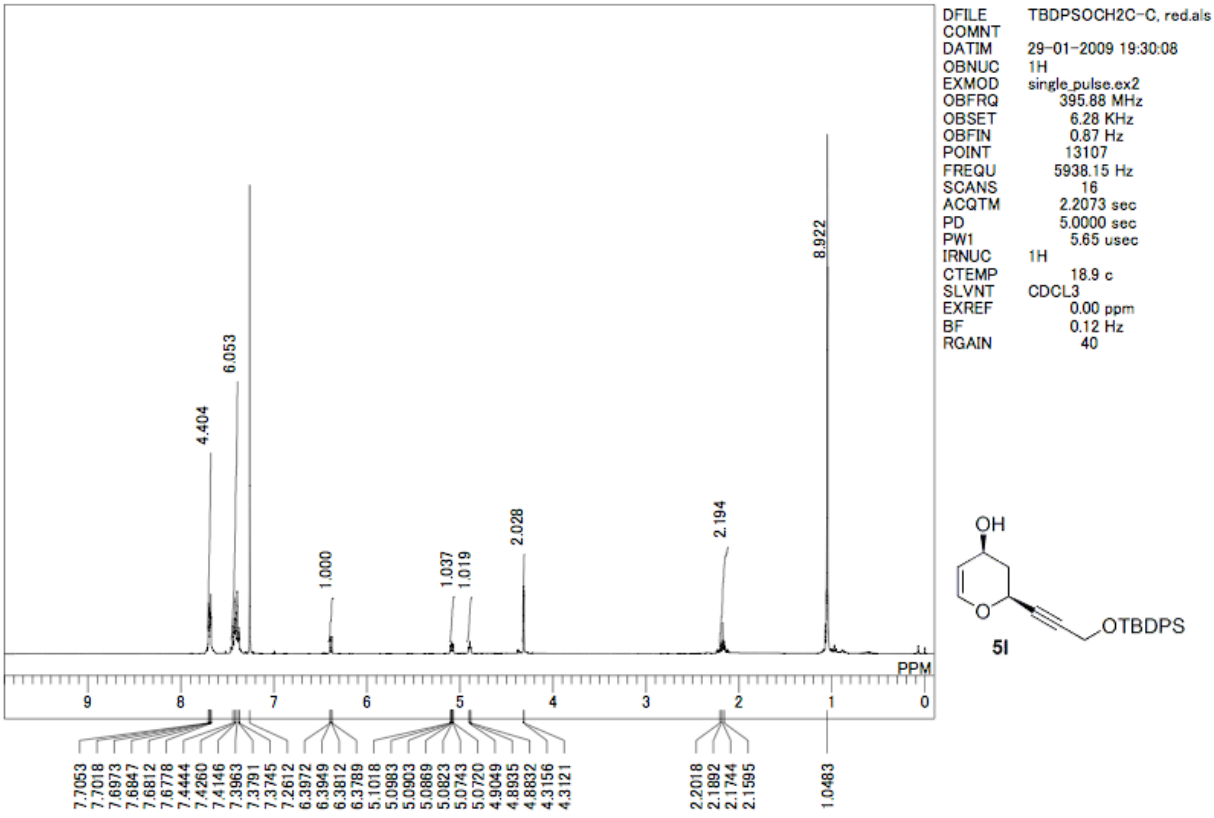

DFILE 3,5-MeOC6H4, 13C.als
COMNT
DATIM 06-08-2008 00:29:19
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 99.55 MHz
OBSET 5.13 KHz
OBFIN 0.98 Hz
POINT 26214
FREQU 24999.62 Hz
SCANS 400
ACQTM 1.0486 sec
PD 2.0000 sec
PW1 3.17 usec
IRNUC 1H
CTEMP 19.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60
OMe
OMe
5h
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
192.0500
163.0600
161.0002
160.9906
140.0481
107.2738
103.9398
100.3664
80.8992
77.3162
77.0000
76.6743
55.3293
43.3731

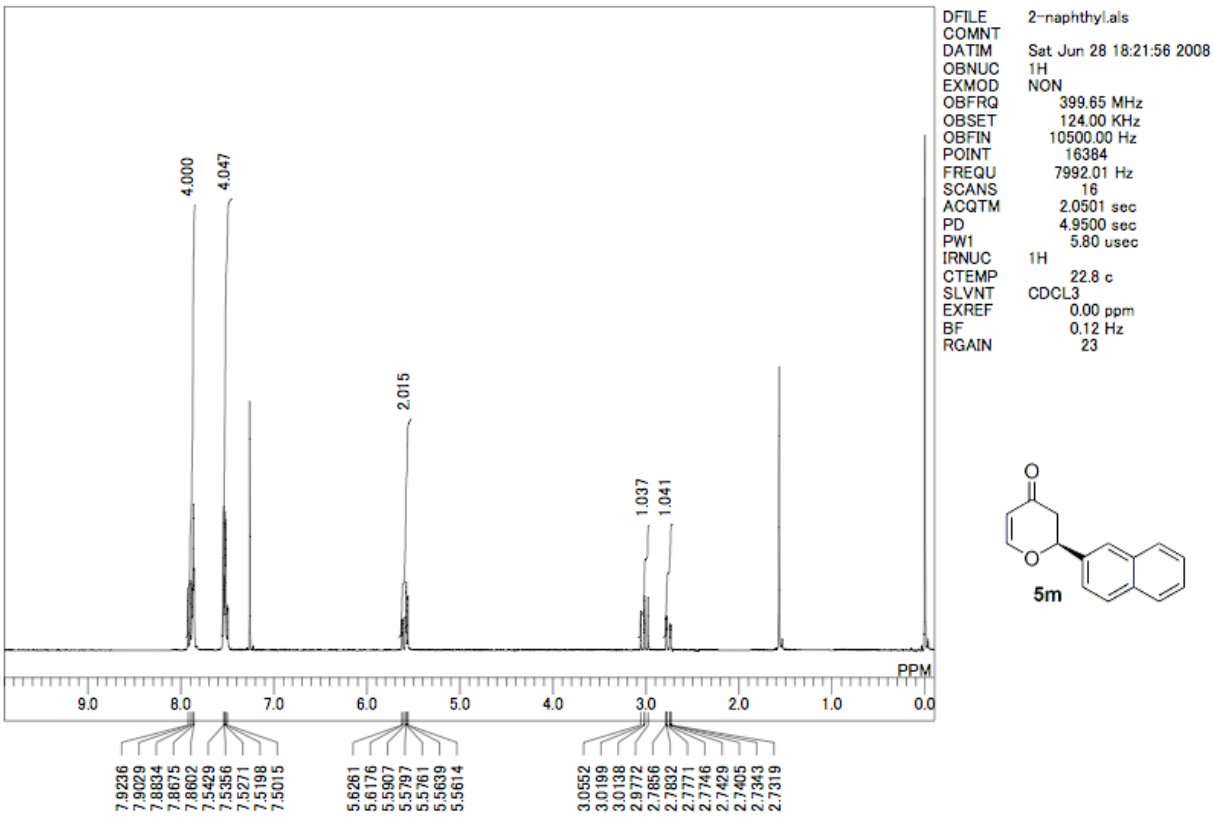

DFILE 4-ClC6H4.als
COMNT
DATIM 24-10-2008 21:36:07
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 395.88 MHz
OBSET 6.28 KHz
OBFIN 0.87 Hz
POINT 13107
FREQU 5938.15 Hz
SCANS 16
ACQTM 2.2073 sec
PD 5.0000 sec
PW1 5.65 usec
IRNUC 1H
CTEMP 19.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 40
Cl
5i
PPM
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
1.000
2.879
2.878
1.006
1.023
1.068
1.067
7.4844
7.4821
7.4695
7.4672
7.4192
7.4135
7.4089
7.3974
7.3917
7.3871
7.3597
7.3539
7.3494
7.3368
7.3333
5.5469
5.5435
5.5309
5.5286
5.4336
5.4256
5.3982
5.3890
2.9011
2.8644
2.8587
2.8221
2.6768
2.6745
2.6688
2.6653
2.6344
2.6310
2.6264
2.6230


DFILE 4-CF3C6H4.als
COMNT
DATIM 16-05-2008 21:44:26
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 395.88 MHz
OBSET 6.28 KHz
OBFIN 0.87 Hz
POINT 13107
FREQU 5938.15 Hz
SCANS 16
ACQTM 2.2073 sec
PD 5.0000 sec
PW1 5.65 usec
IRNUC 1H
CTEMP 18.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 40
2.084
3.082
1.079
1.083
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.7076
7.6870
7.5485
7.5256
7.5153
7.5004
7.4981
5.5778
5.5744
5.5618
5.5584
5.5275
5.5183
5.4909
5.4828
2.9056
2.8702
2.8633
2.8278
2.7271
2.7237
2.7180
2.7145
2.6848
2.6813
2.6756
2.6722
O
O
5j
CF3


DFILE 4-NO2C6H4.als
COMNT
DATIM 16-05-2008 21:37:18
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 395.88 MHz
OBSET 6.28 KHz
OBFIN 0.87 Hz
POINT 13107
FREQU 5938.15 Hz
SCANS 16
ACQTM 2.2073 sec
PD 5.0000 sec
PW1 5.65 usec
IRNUC 1H
CTEMP 19.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 40
2.036
2.097
1.000
2.028
1.079
1.056
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.3118
8.3061
8.2946
8.2889
7.6103
7.5885
7.5268
7.5107
5.5996
5.5961
5.5836
5.5801
5.5687
5.5424
5.5332
2.8873
2.8519
2.8450
2.8095
2.7534
2.7511
2.7443
2.7408
2.7111
2.7088
2.7019
2.6985
O
O
5k
NO2

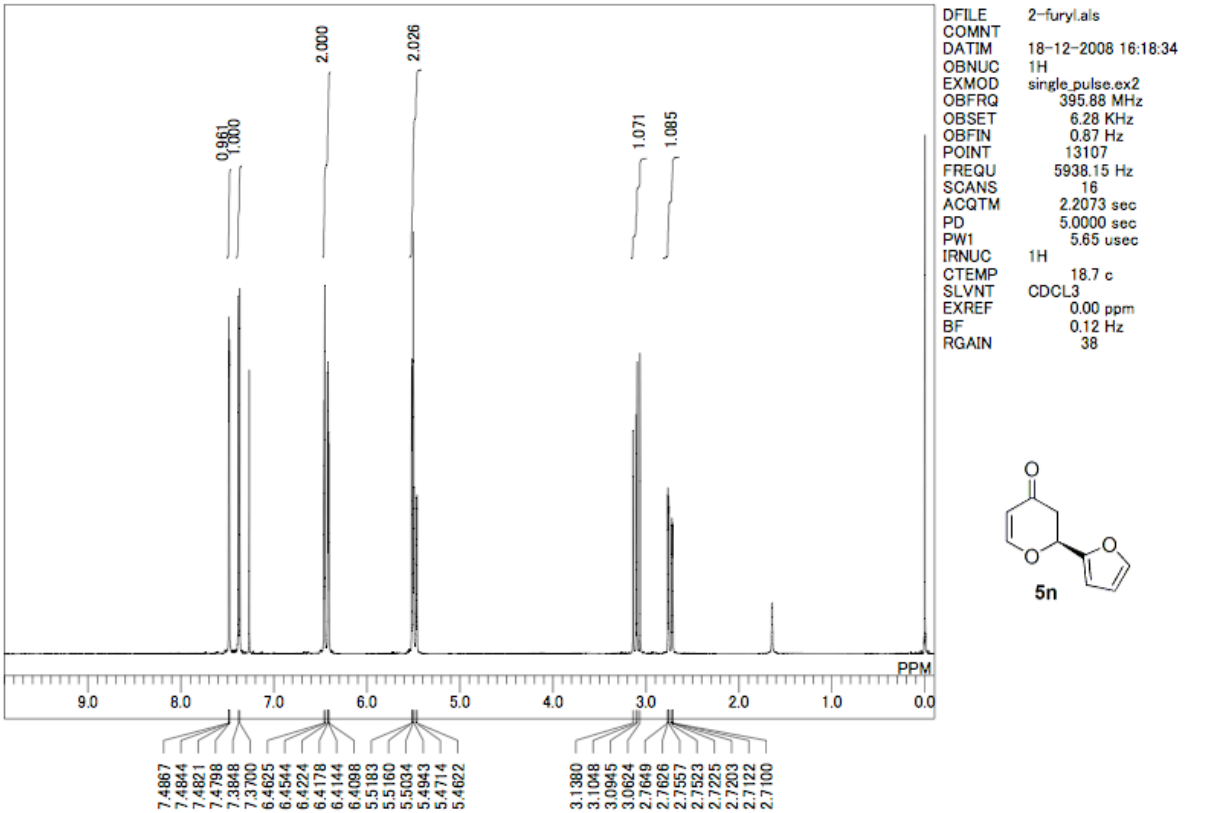

DFILE TBDPSOCH2C-C.als
COMNT
DATIM 14-02-2009 19:28:38
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 395.88 MHz
OBSET 6.28 KHz
OBFIN 0.87 Hz
POINT 13107
FREQU 5938.15 Hz
SCANS 16
ACQTM 2.2073 sec
PD 5.0000 sec
PW1 5.65 usec
IRNUC 1H
CTEMP 18.8 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 1.20 Hz
RGAIN 40
9.453
6.783
4.668
1.129
1.000
0.983
2.182
2.181
PPM
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
7.6972 7.6800 7.4454 7.4282 7.4134 7.3950 7.3779 7.2852 7.2692
5.4599 5.4438 5.1543 5.1371 5.1165
4.3692 4.3658
2.6618 2.6561 2.6400
1.0516
O
O
OTBDPS
5l


DFILE TBDPSOCH2C-C, red.als
COMNT
DATIM 29-01-2009 19:30:08
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 395.88 MHz
OBSET 6.28 KHz
OBFIN 0.87 Hz
POINT 13107
FREQU 5938.15 Hz
SCANS 16
ACQTM 2.2073 sec
PD 5.0000 sec
PW1 5.65 usec
IRNUC 1H
CTEMP 18.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 40
8.922
6.053
4.404
1.000
1.037
1.019
2.028
2.194
PPM
9 8 7 6 5 4 3 2 1 0
7.7053 7.7018 7.6973 7.6847 7.6812 7.6778 7.4444 7.4260 7.4146 7.3963 7.3791 7.3745 7.2612
6.3972 6.3949 6.3812 6.3789
5.1018 5.0983 5.0903 5.0869 5.0823 5.0743 5.0720 4.9049 4.8935 4.8832 4.3156 4.3121
2.2018 2.1892 2.1744 2.1595
1.0483
OH
O
OTBDPS
5l


4.000
4.047
2.015
1.037
1.041
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.9236
7.9029
7.8834
7.8675
7.8602
7.5429
7.5356
7.5271
7.5198
7.5015
5.6261
5.6176
5.5907
5.5797
5.5761
5.5639
5.5614
3.0552
3.0199
3.0138
2.9772
2.7856
2.7832
2.7771
2.7746
2.7429
2.7405
2.7343
2.7319
DFILE 2-naphthyl.als
COMNT
DATIM Sat Jun 28 18:21:56 2008
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 16
ACQTM 2.0501 sec
PD 4.9500 sec
PW1 5.80 usec
IRNUC 1H
CTEMP 22.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 23

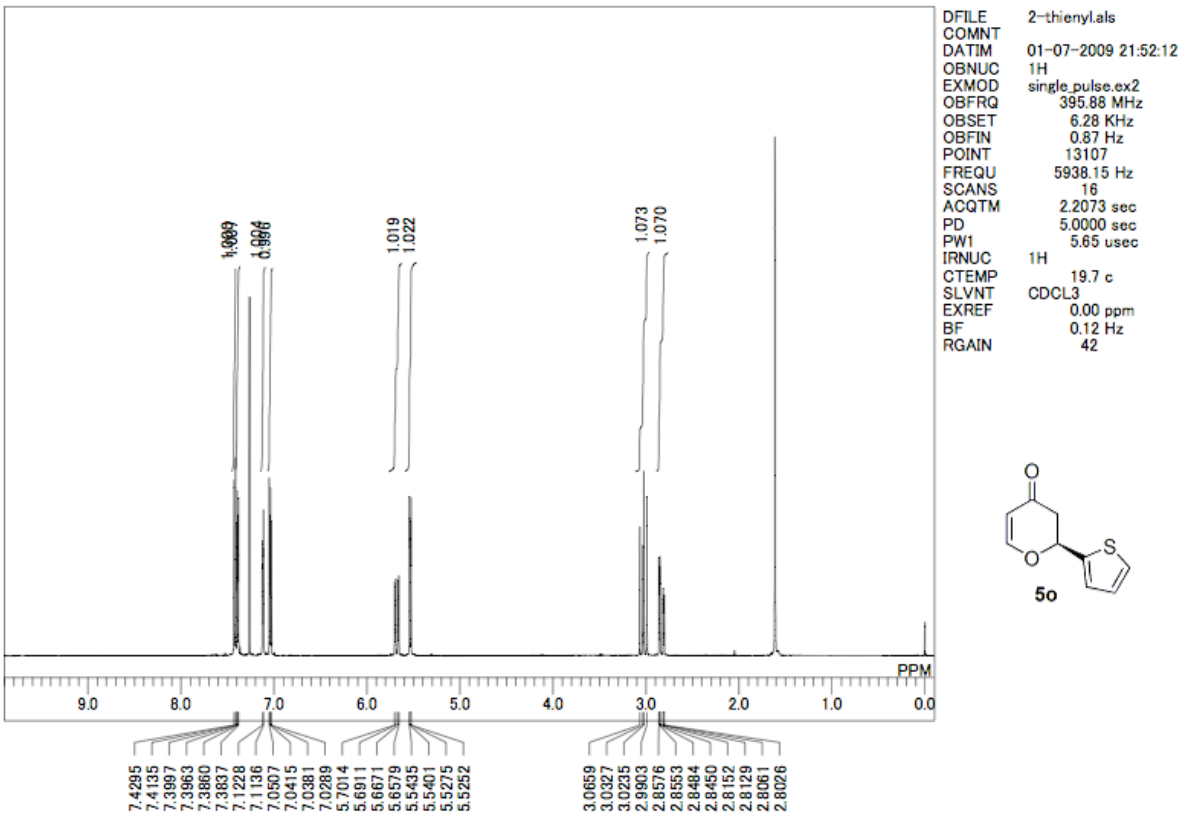
O
O

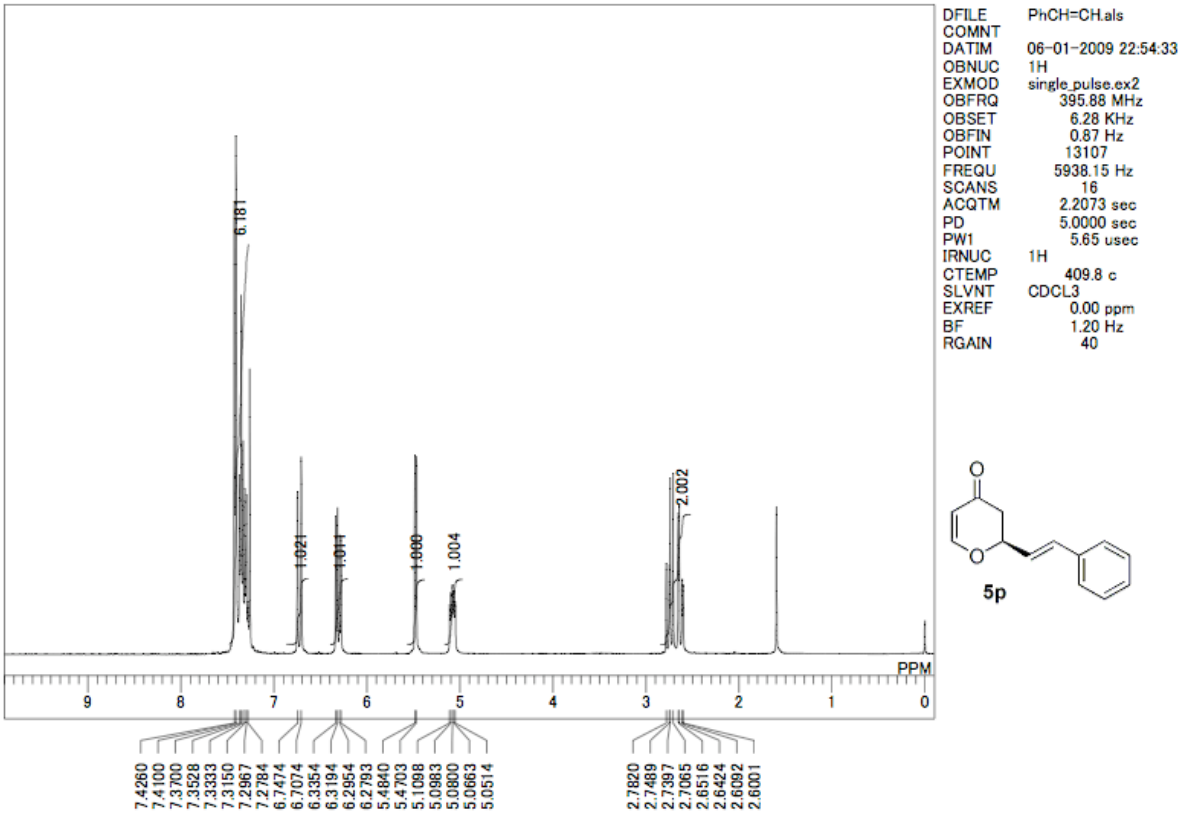
5m

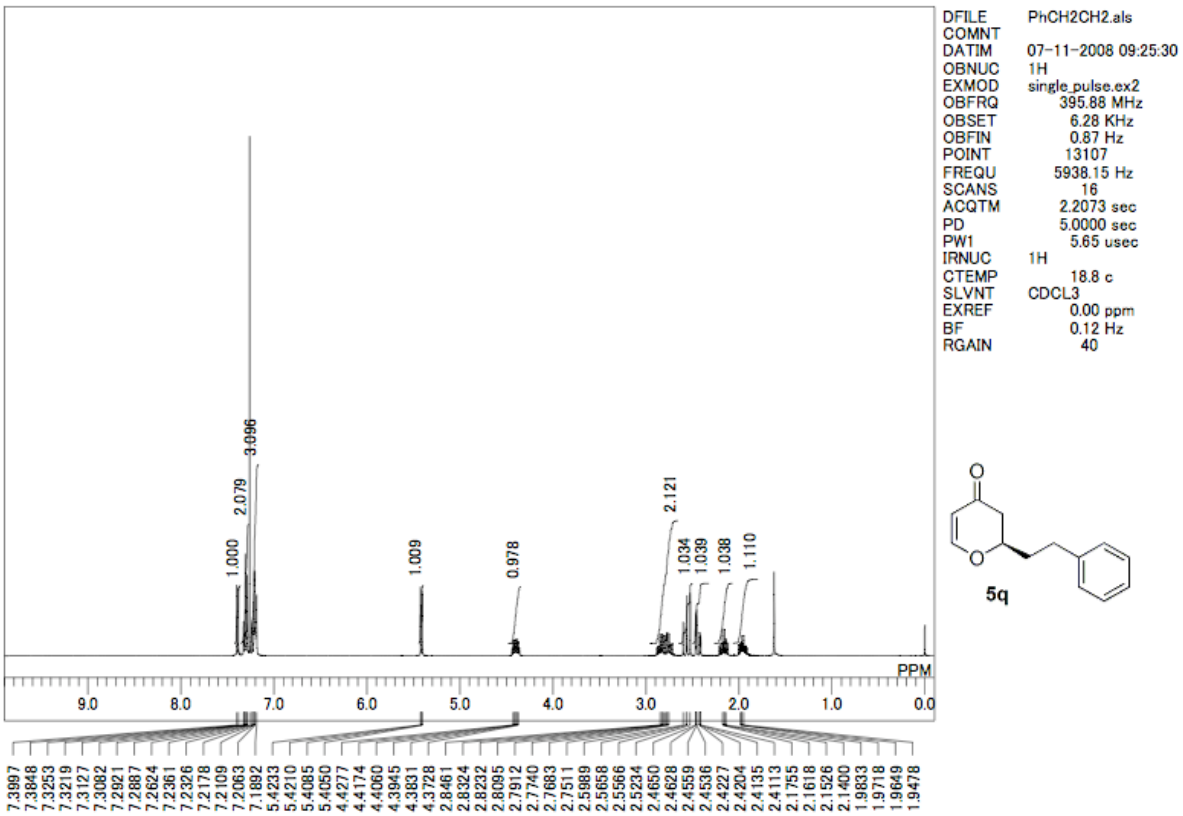

0.961
1.000
2.000
2.026
1.071
1.085
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.4867
7.4844
7.4821
7.4798
7.3848
7.3700
6.4625
6.4544
6.4224
6.4178
6.4144
6.4098
5.5183
5.5160
5.5034
5.4943
5.4714
5.4622
3.1380
3.1048
3.0945
3.0624
2.7649
2.7626
2.7557
2.7523
2.7225
2.7203
2.7122
2.7100
DFILE 2-furyl.als
COMNT
DATIM 18-12-2008 16:18:34
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 395.88 MHz
OBSET 6.28 KHz
OBFIN 0.87 Hz
POINT 13107
FREQU 5938.15 Hz
SCANS 16
ACQTM 2.2073 sec
PD 5.0000 sec
PW1 5.65 usec
IRNUC 1H
CTEMP 18.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 38

O
O
O

5n

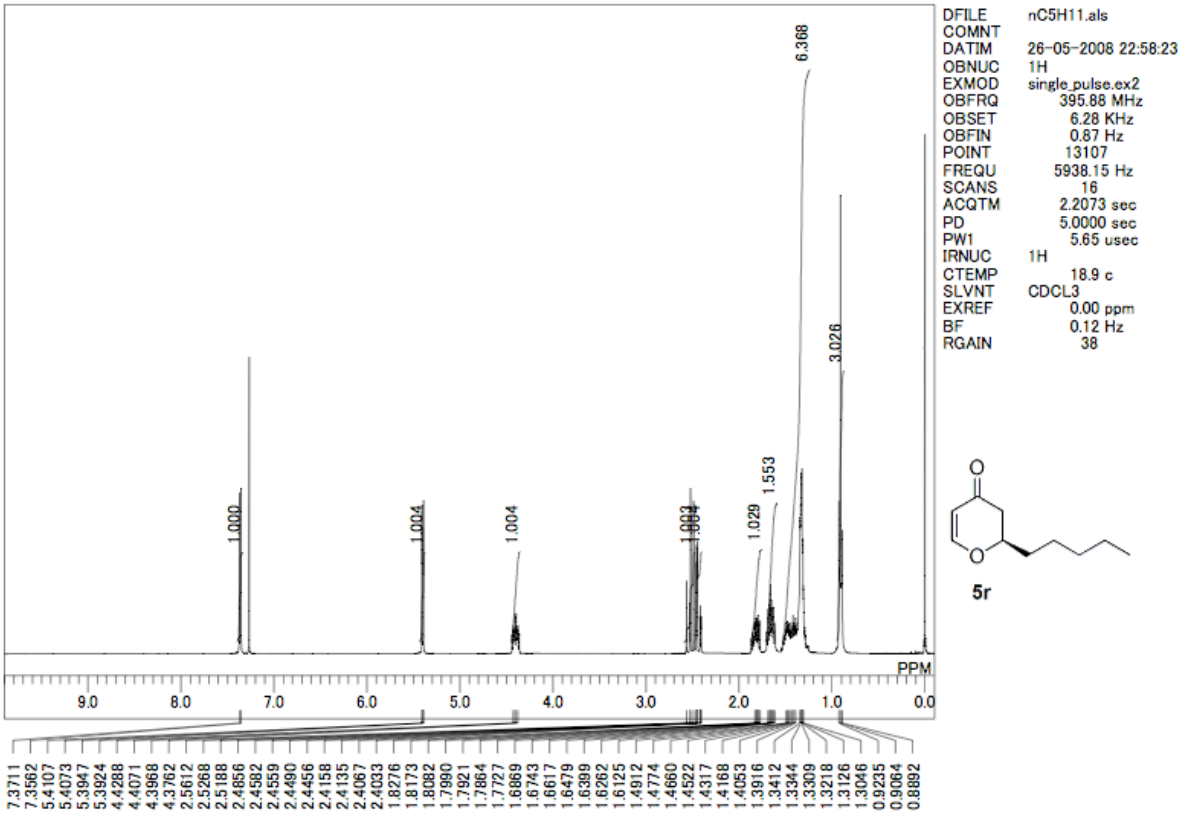

DFILE 2-thienyl.als
COMNT
DATIM 01-07-2009 21:52:12
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 395.88 MHz
OBSET 6.28 KHz
OBFIN 0.87 Hz
POINT 13107
FREQU 5938.15 Hz
SCANS 16
ACQTM 2.2073 sec
PD 5.0000 sec
PW1 5.65 usec
IRNUC 1H
CTEMP 19.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 42
1.019
1.022
1.073
1.070
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.4295
7.4135
7.3997
7.3963
7.3860
7.3837
7.1228
7.1136
7.0507
7.0415
7.0381
7.0289
5.7014
5.6911
5.6671
5.6579
5.5435
5.5401
5.5275
5.5252
3.0659
3.0327
3.0235
2.9903
2.8576
2.8553
2.8484
2.8450
2.8152
2.8129
2.8061
2.8026
O
O
S
5o


DFILE PhCH=CH.als
COMNT
DATIM 06-01-2009 22:54:33
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 395.88 MHz
OBSET 6.28 KHz
OBFIN 0.87 Hz
POINT 13107
FREQU 5938.15 Hz
SCANS 16
ACQTM 2.2073 sec
PD 5.0000 sec
PW1 5.65 usec
IRNUC 1H
CTEMP 409.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 40
6.181
1.021
1.011
1.000
1.004
2.002
PPM
9
8
7
6
5
4
3
2
1
0
7.4260
7.4100
7.3700
7.3528
7.3333
7.3150
7.2967
7.2784
6.7474
6.7074
6.3354
6.3194
6.2954
6.2793
5.4840
5.4703
5.1098
5.0983
5.0800
5.0663
5.0514
2.7820
2.7489
2.7397
2.7065
2.6516
2.6424
2.6092
2.6001
O
O
5p


DFILE PhCH2CH2.als
COMNT
DATIM 07-11-2008 09:25:30
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 395.88 MHz
OBSET 6.28 KHz
OBFIN 0.87 Hz
POINT 13107
FREQU 5938.15 Hz
SCANS 16
ACQTM 2.2073 sec
PD 5.0000 sec
PW1 5.65 usec
IRNUC 1H
CTEMP 18.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 40
1.000
2.079
3.096
1.009
0.978
2.121
1.034
1.039
1.038
1.110
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.3997
7.3848
7.3253
7.3219
7.3127
7.3082
7.2921
7.2887
7.2624
7.2361
7.2326
7.2178
7.2109
7.2063
7.1892
5.4233
5.4210
5.4085
5.4050
4.4277
4.4174
4.4060
4.3945
4.3831
4.3728
2.8461
2.8324
2.8232
2.8095
2.7912
2.7740
2.7683
2.7511
2.5989
2.5658
2.5566
2.5234
2.4650
2.4628
2.4559
2.4536
2.4227
2.4204
2.4135
2.4113
2.1755
2.1618
2.1526
2.1400
1.9833
1.9718
1.9649
1.9478

O
O

5q


DFILE nC5H11.als
COMNT
DATIM 26-05-2008 22:58:23
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 395.88 MHz
OBSET 6.28 KHz
OBFIN 0.87 Hz
POINT 13107
FREQU 5938.15 Hz
SCANS 16
ACQTM 2.2073 sec
PD 5.0000 sec
PW1 5.65 usec
IRNUC 1H
CTEMP 18.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 38
6.368
3.026
1.553
1.029
1.000
1.004
1.004
1.003
1.004
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.3711
7.3562
5.4107
5.4073
5.3947
5.3924
4.4288
4.4071
4.3968
4.3762
2.5612
2.5268
2.5188
2.4856
2.4582
2.4559
2.4490
2.4456
2.4158
2.4135
2.4067
2.4033
1.8276
1.8173
1.8082
1.7990
1.7921
1.7864
1.7727
1.6869
1.6743
1.6617
1.6479
1.6399
1.6262
1.6125
1.4912
1.4774
1.4660
1.4522
1.4317
1.4168
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1.3916
1.3412
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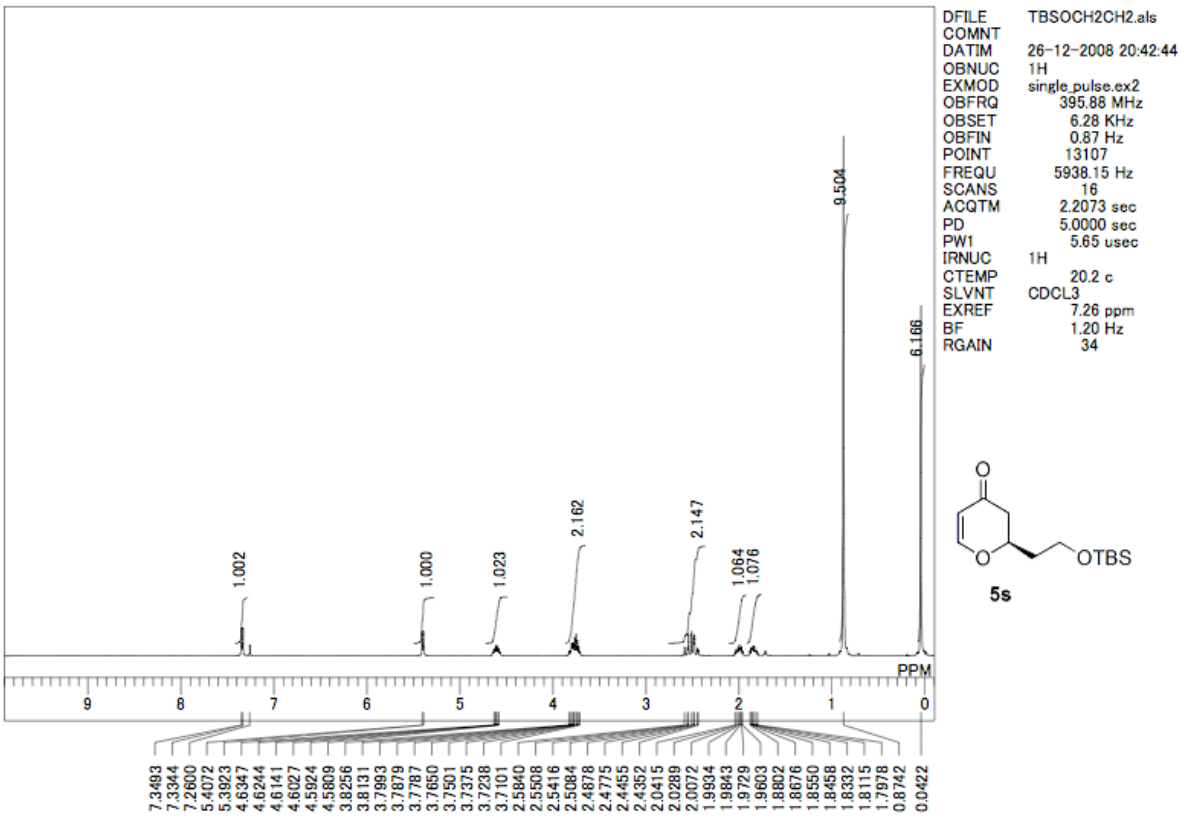
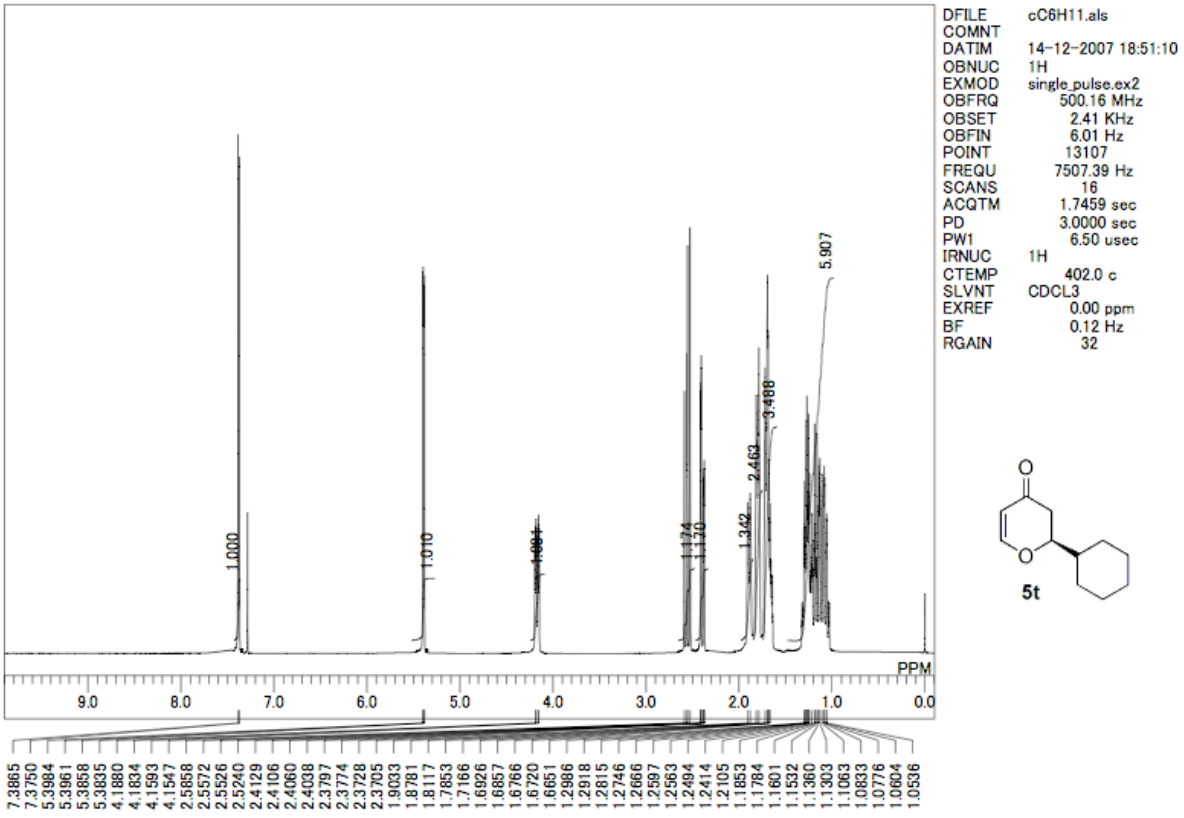
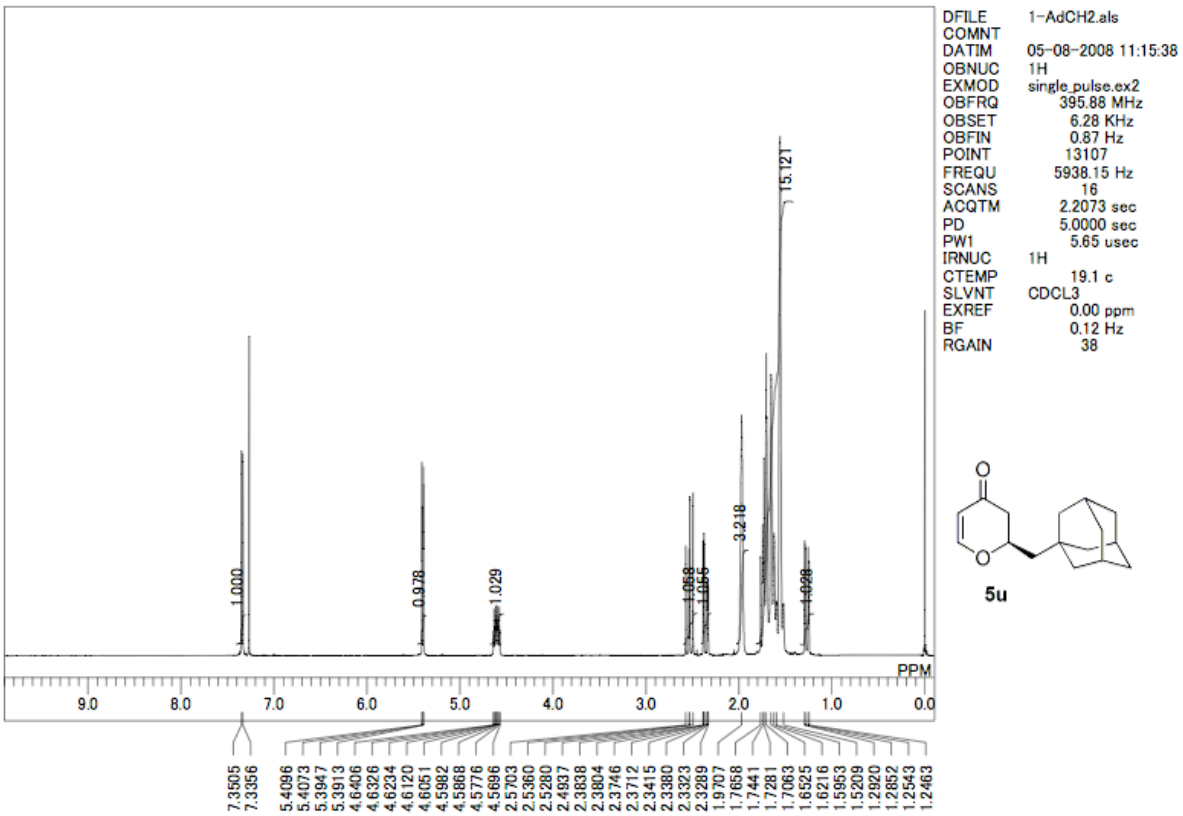
1.3218
1.3126
1.3046
0.9235
0.9064
0.8892

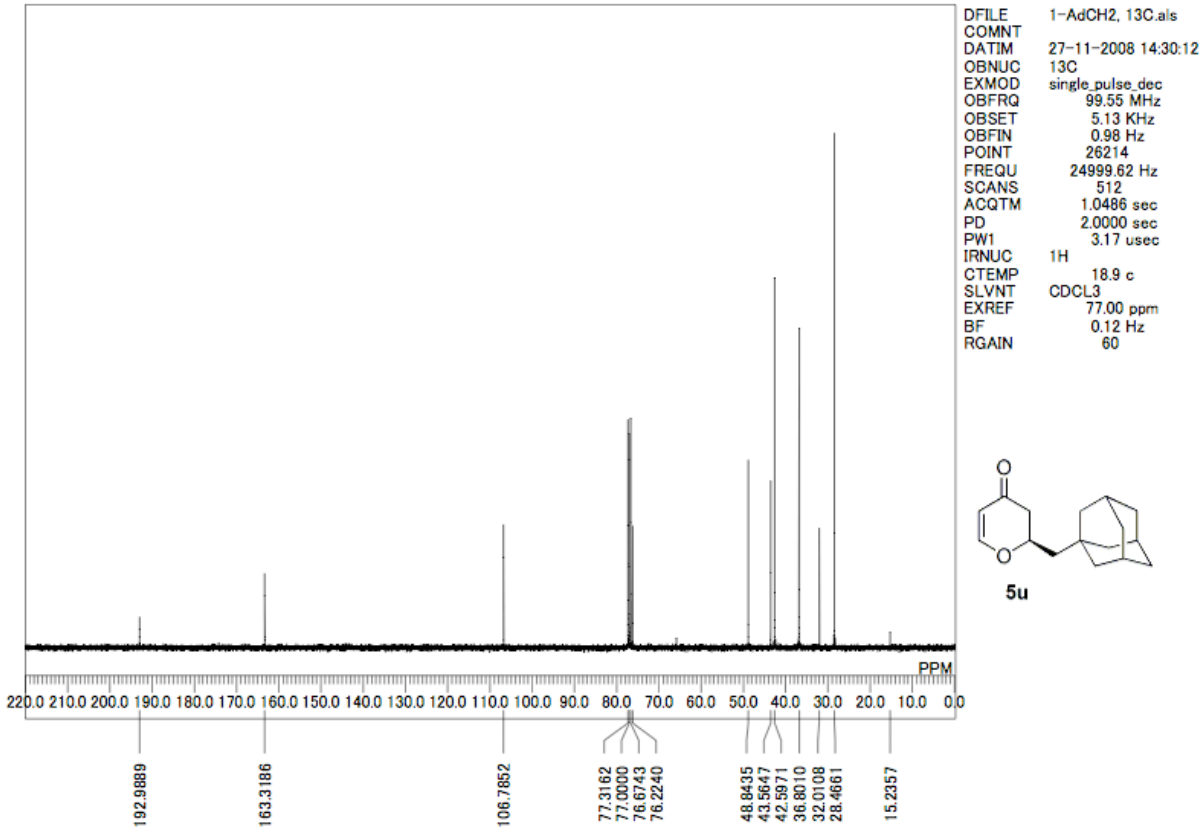
O
O

5r

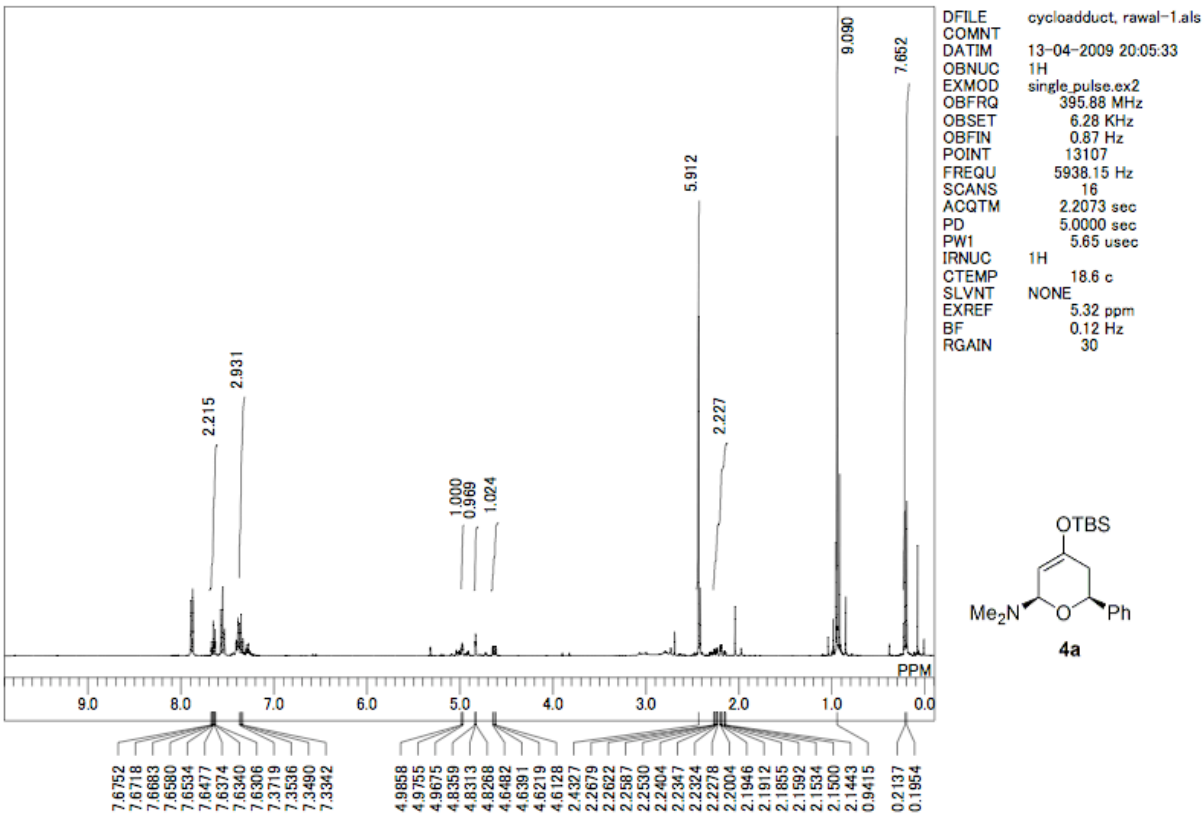

DFILE TBSOCH2CH2.als
COMNT
DATIM 26-12-2008 20:42:44
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 395.88 MHz
OBSET 6.28 KHz
OBFIN 0.87 Hz
POINT 13107
FREQU 5938.15 Hz
SCANS 16
ACQTM 2.2073 sec
PD 5.0000 sec
PW1 5.65 usec
IRNUC 1H
CTEMP 20.2 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 1.20 Hz
RGAIN 34
9.504
6.166
2.162
2.147
1.002
1.000
1.023
1.064
1.076
PPM
9 8 7 6 5 4 3 2 1 0
7.3493 7.3344 7.2600 5.4072 5.3923 4.6347 4.6244 4.6141 4.6027 4.5924 4.5809 3.8256 3.8131 3.7993 3.7879 3.7787 3.7650 3.7501 3.7375 3.7238 3.7101 2.5840 2.5508 2.5416 2.5084 2.4878 2.4775 2.4455 2.4352 2.0415 2.0289 2.0072 1.9934 1.9843 1.9729 1.9603 1.8802 1.8676 1.8550 1.8458 1.8332 1.8115 1.7978 0.8742 0.0422
O
O
OTBS
5s

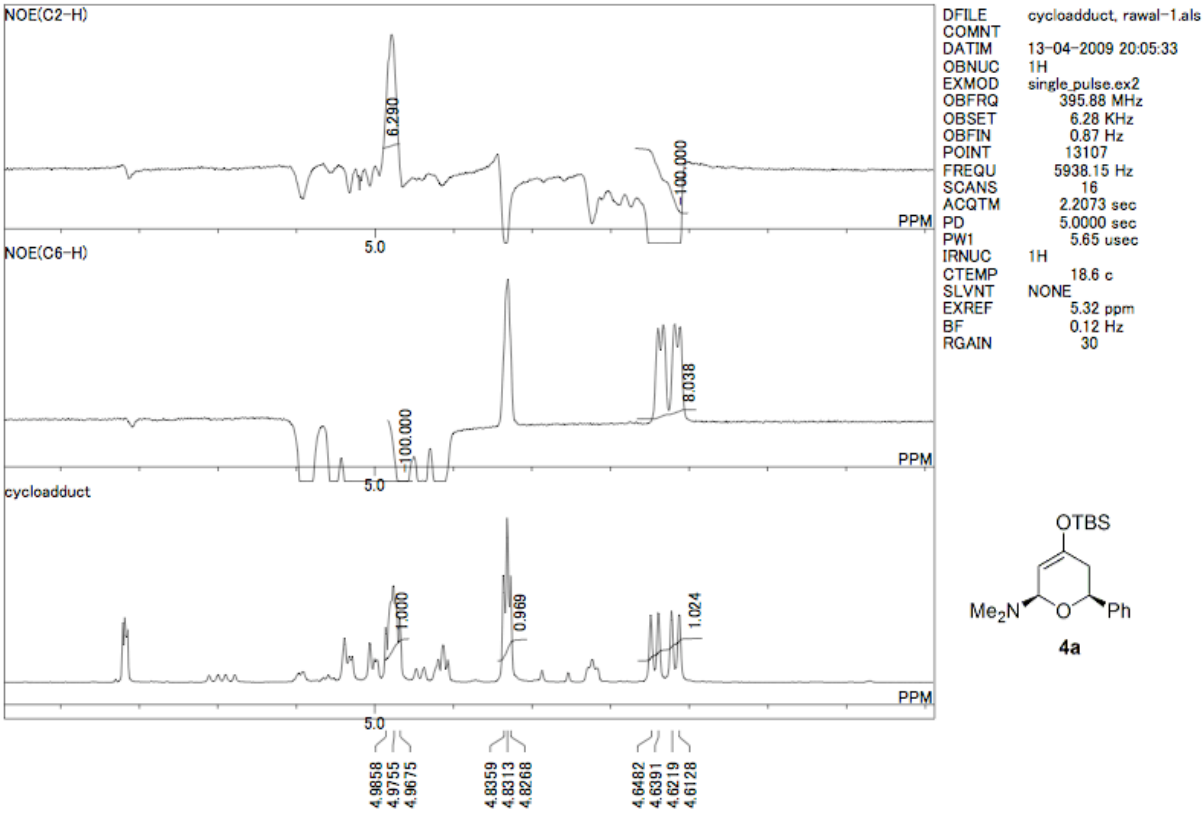

DFILE cC6H11.als
COMNT
DATIM 14-12-2007 18:51:10
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 16
ACQTM 1.7459 sec
PD 3.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 402.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 32
5.907
3.488
2.463
1.342
1.174
1.130
1.010
1.000
1.091
PPM
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
7.3865 7.3750 5.3984 5.3961 5.3858 5.3835 4.1880 4.1634 4.1593 4.1547 2.5858 2.5572 2.5526 2.5240 2.4129 2.4106 2.4060 2.4038 2.3797 2.3774 2.3728 2.3705 1.9033 1.8781 1.8117 1.7853 1.7166 1.6926 1.6657 1.6766 1.6720 1.6651 1.2986 1.2918 1.2815 1.2746 1.2666 1.2597 1.2563 1.2494 1.2414 1.2105 1.1853 1.1784 1.1601 1.1532 1.1360 1.1303 1.1063 1.0833 1.0776 1.0604 1.0536
O
O
5t


DFILE 1-AdCH2.als
COMNT
DATIM 05-08-2008 11:15:38
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 395.88 MHz
OBSET 6.28 KHz
OBFIN 0.87 Hz
POINT 13107
FREQU 5938.15 Hz
SCANS 16
ACQTM 2.2073 sec
PD 5.0000 sec
PW1 5.65 usec
IRNUC 1H
CTEMP 19.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 38
1.000
0.978
1.029
1.068
1.055
3.218
15.121
1.028
PPM
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
7.3505 7.3356 5.4096 5.4073 5.3947 5.3913 4.6406 4.6326 4.6234 4.6120 4.6051 4.5982 4.5868 4.5776 4.5696 2.5703 2.5360 2.5280 2.4937 2.3838 2.3804 2.3746 2.3712 2.3415 2.3380 2.3323 2.3289 1.9707 1.7658 1.7441 1.7281 1.7063 1.6525 1.6216 1.5953 1.5209 1.2920 1.2852 1.2543 1.2463
5u

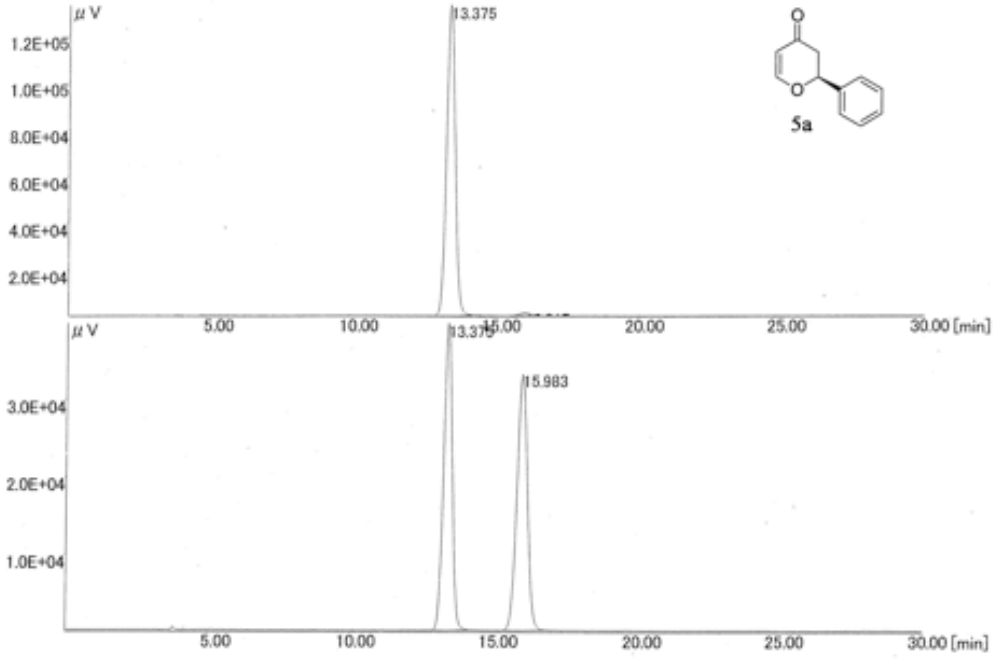

DFILE 1-AdCH2, 13C.als
COMNT
DATIM 27-11-2008 14:30:12
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 99.55 MHz
OBSET 5.13 KHz
OBFIN 0.98 Hz
POINT 26214
FREQU 24999.62 Hz
SCANS 512
ACQTM 1.0486 sec
PD 2.0000 sec
PW1 3.17 usec
IRNUC 1H
CTEMP 18.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
192.9889 163.3186 106.7852 77.3162 77.0000 76.6743 76.2240 48.8435 43.5647 42.5971 36.8010 32.0108 28.4661 15.2357
5u

NMR Analysis of 4a





Copies of Chromatogram

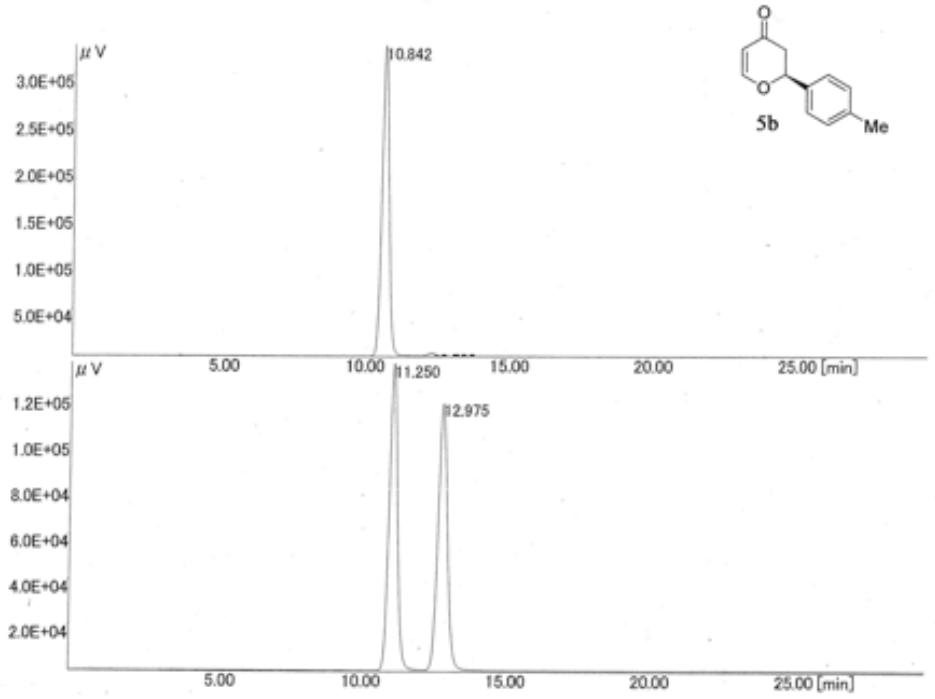


5a

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	13.38	2836312	98.92
2	16.02	30925	1.08

5a (racemate)

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	13.38	841208	50.03
2	15.98	840110	49.97

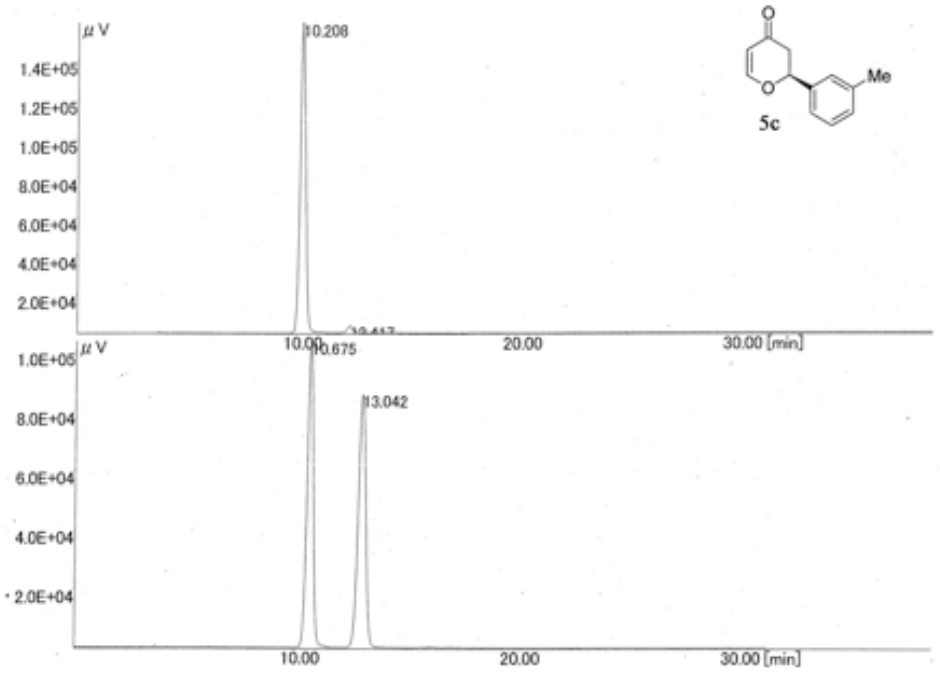


5b

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	10.84	5718572	98.98
2	12.50	58926	1.02

5b (racemate)

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	11.25	2657864	50.01
2	12.98	2657006	49.99



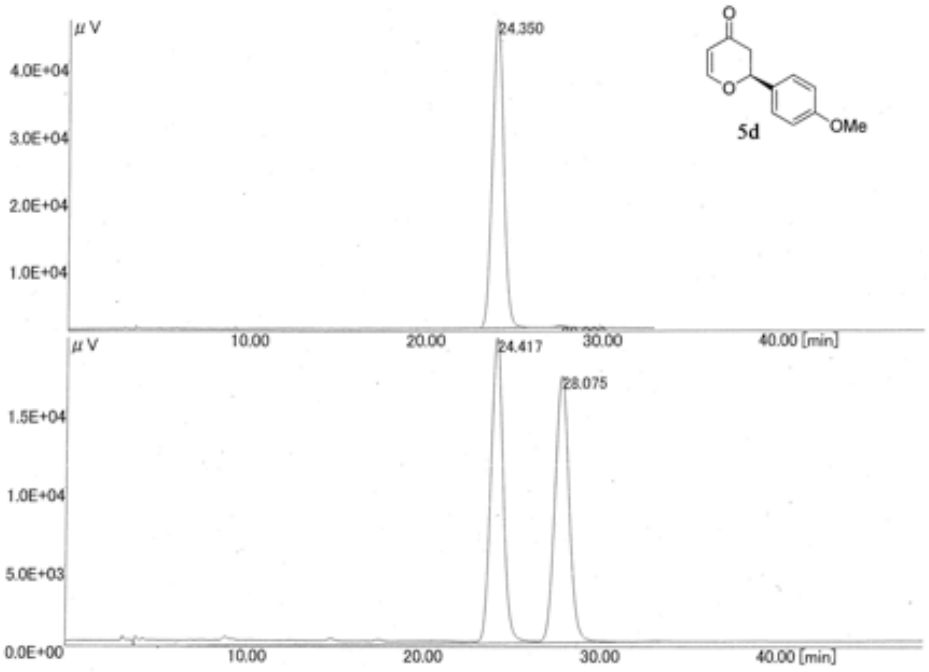
5c

5c

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	10.20	2698561	97.50
2	12.42	69203	2.50

5c (racemate)

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	10.68	1968148	50.05
2	13.04	1964131	49.95

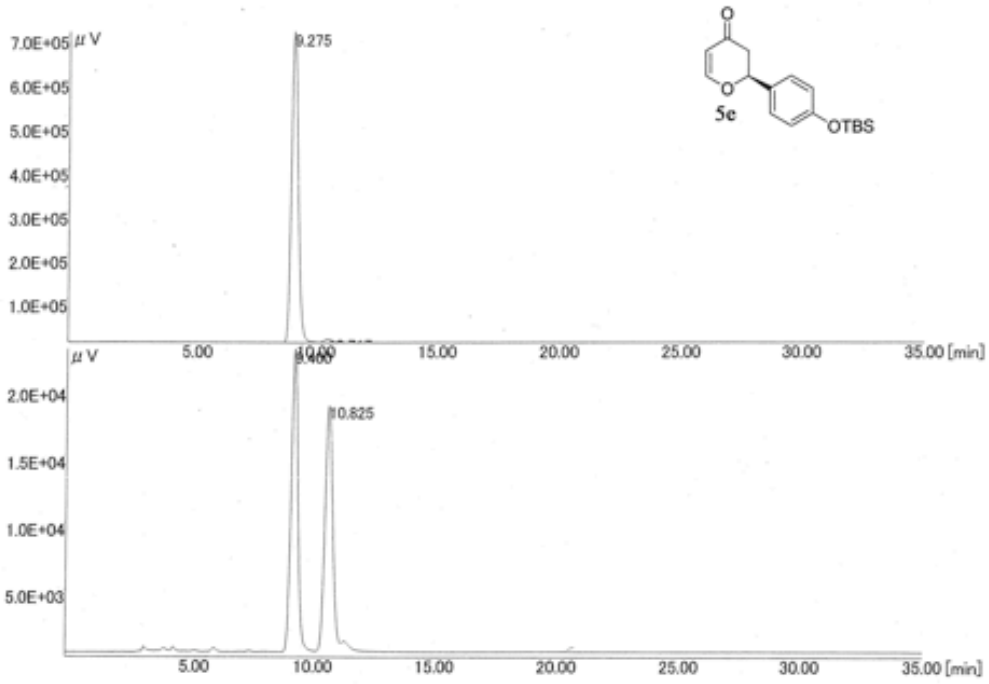


5d

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	24.35	2002734	99.46
2	28.00	10892	0.54

5d (racemate)

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	24.42	936347	50.23
2	28.08	927834	49.77

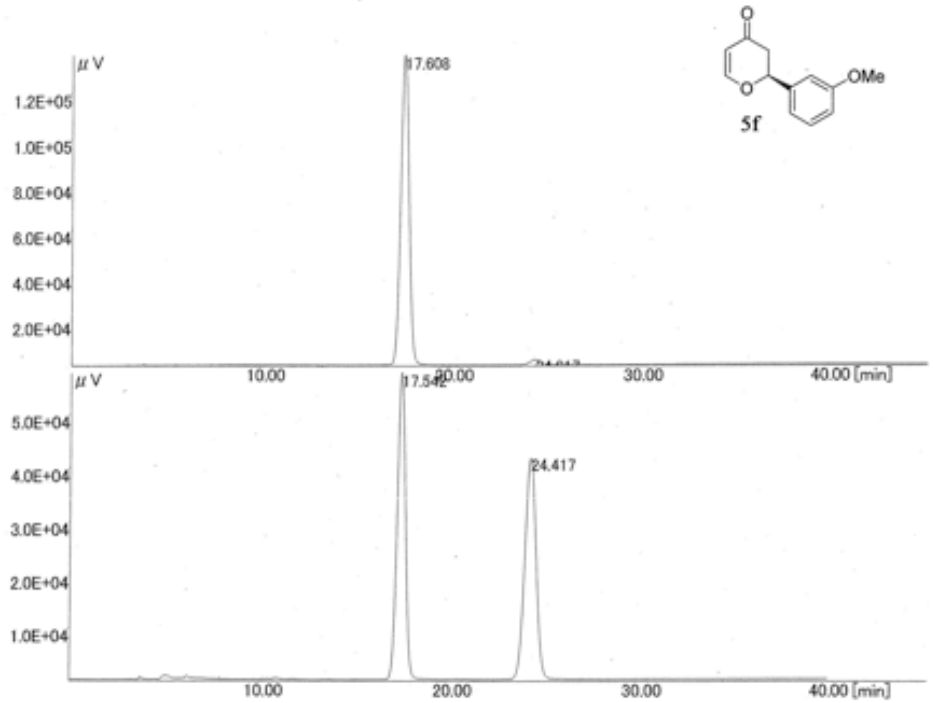


5e

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	9.28	13434523	98.87
2	10.72	153518	1.13

5e (racemate)

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	9.40	419920	50.35
2	10.83	413938	49.65

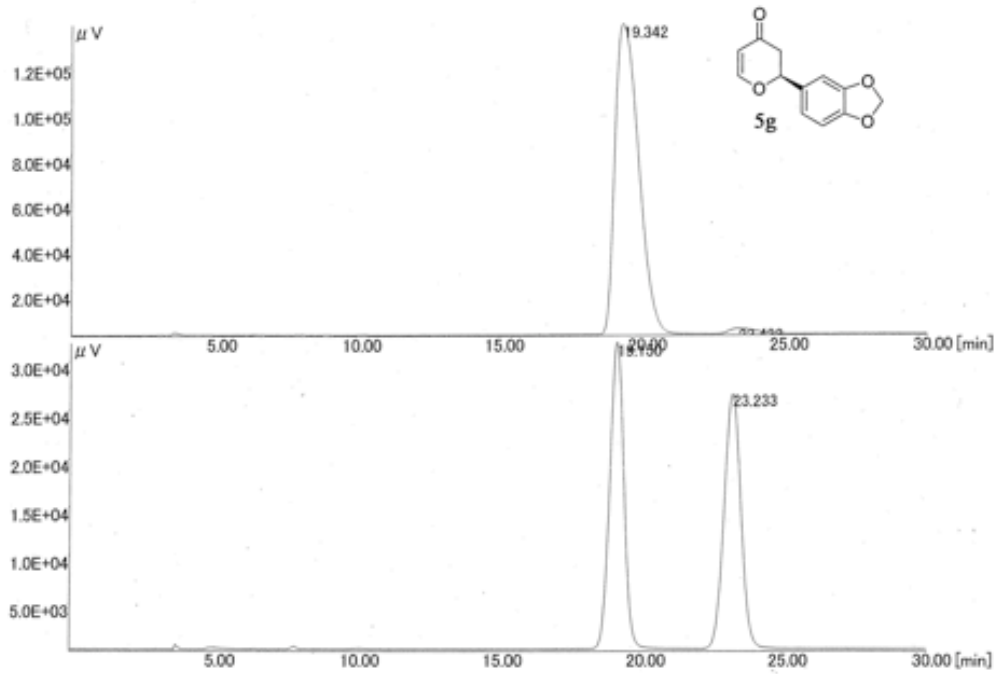


5f

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	17.61	4068653	97.75
2	24.62	93543	2.25

5f (racemate)

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	17.54	1708413	50.07
2	24.42	1703726	49.93

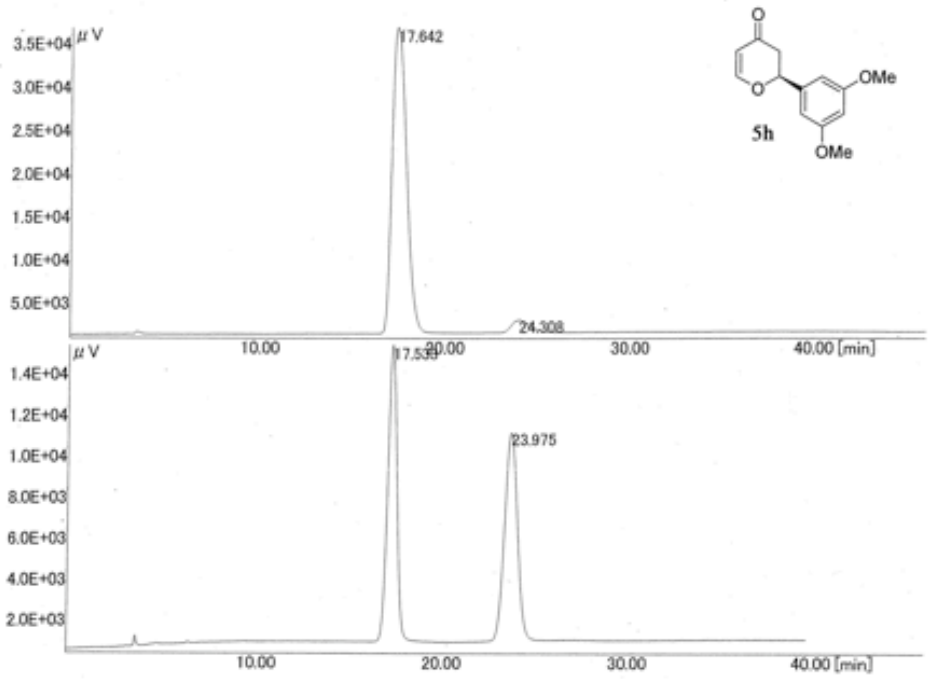


5g

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	19.34	7914760	98.02
2	23.43	159489	1.98

5g (racemate)

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	19.15	1087198	50.02
2	23.23	1086320	49.98

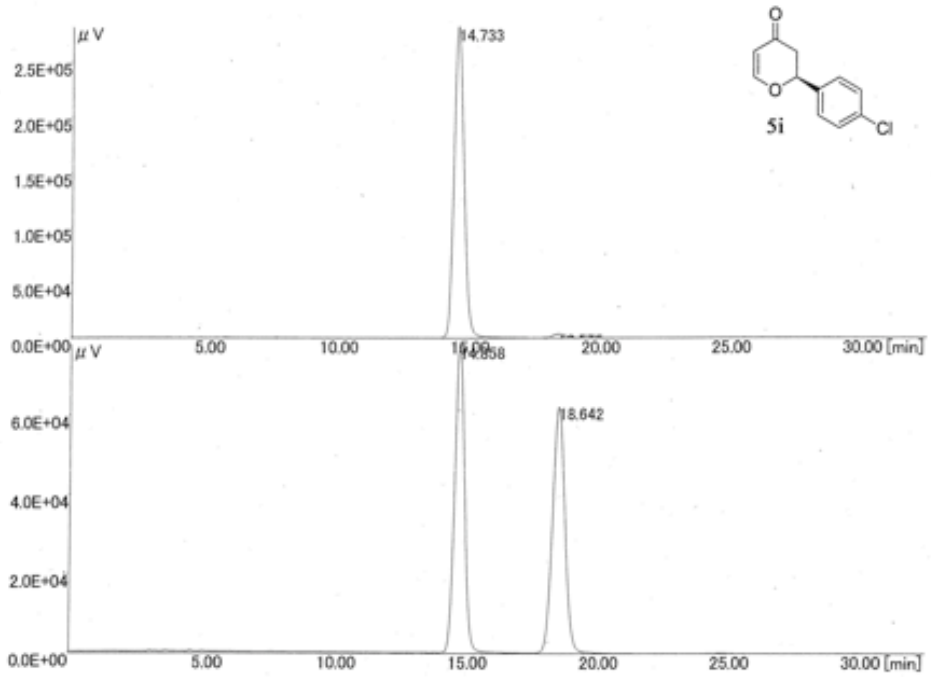


5h

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	17.64	1881568	94.95
2	24.31	100071	5.05

5h (racemate)

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	17.53	513447	50.12
2	23.98	510887	49.88

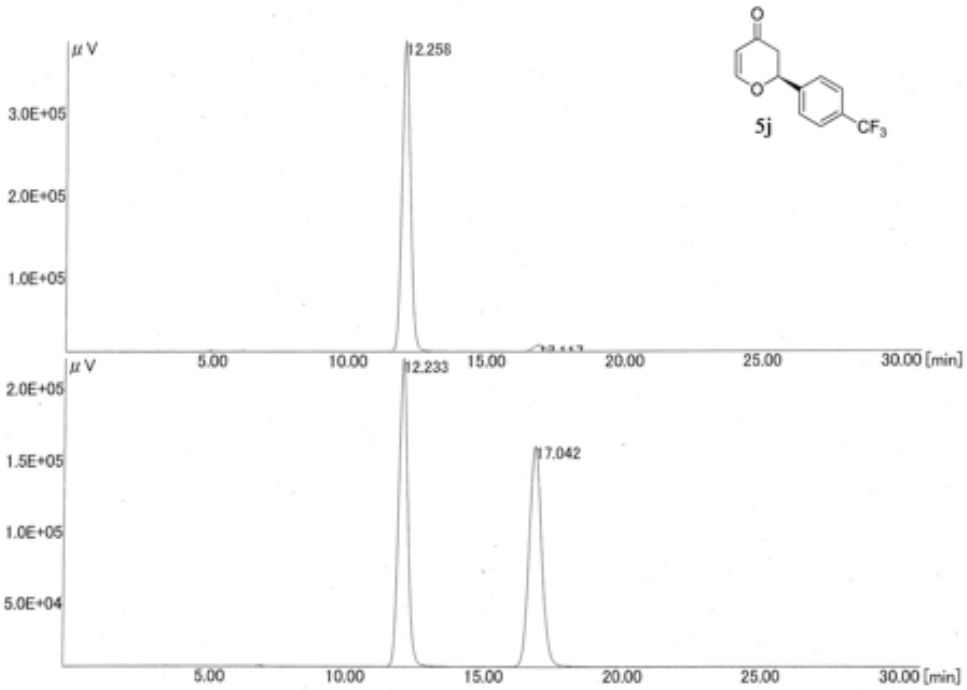


5i

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	14.73	7304830	98.65
2	18.58	100264	1.35

5i (racemate)

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	14.86	2006011	49.92
2	18.64	2012464	50.08

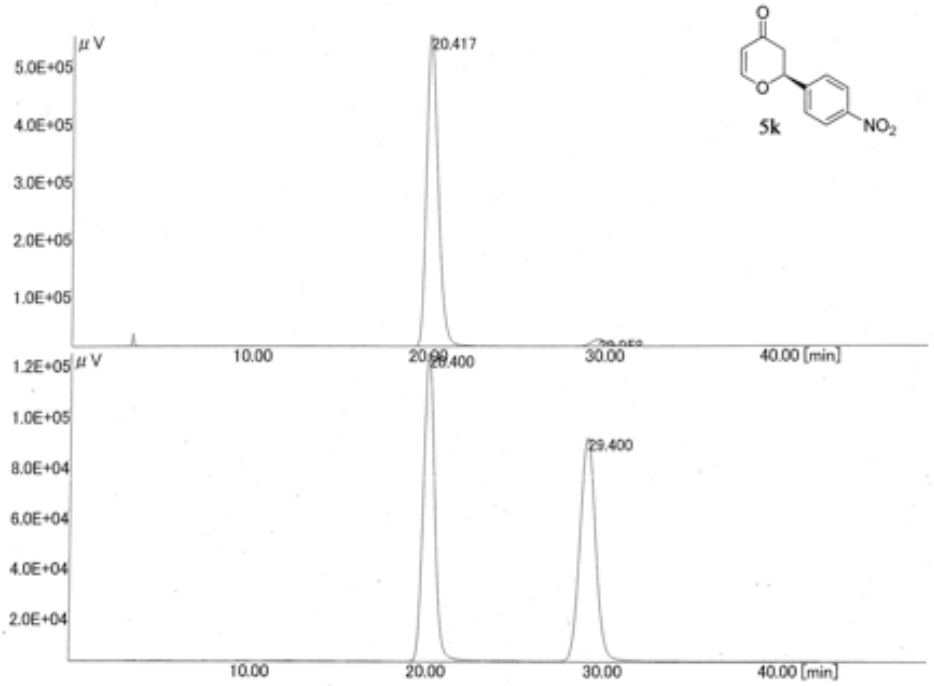


5j

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	12.26	8000145	97.27
2	17.12	224876	2.73

5j (racemate)

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	12.23	4845107	50.01
2	17.04	4842498	49.99

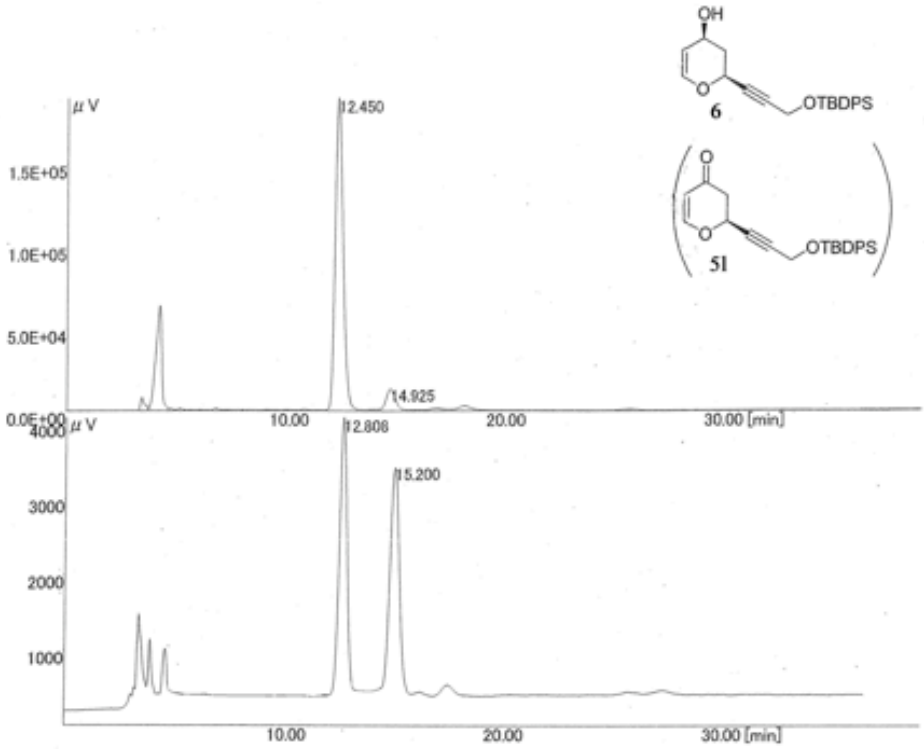


5k

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	20.42	2433829	97.21
2	29.96	698763	2.79

5k (racemate)

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	20.40	5342988	49.95
2	29.40	5353856	50.05

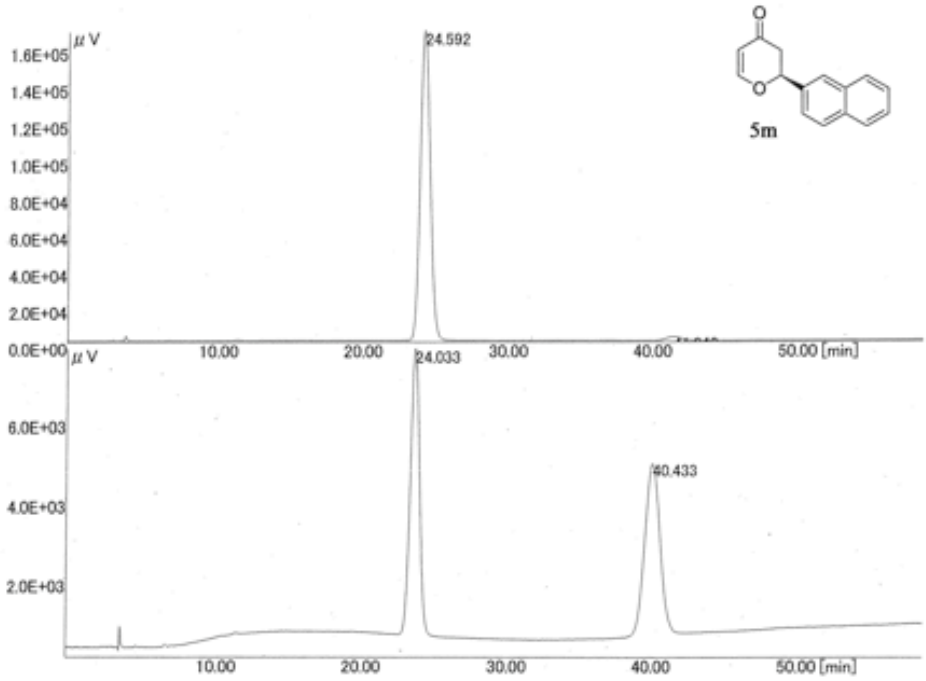


6

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	12.45	4910883	93.47
2	14.93	343034	6.53

6 (racemate)

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	12.81	101227	50.20
2	15.20	100414	49.80



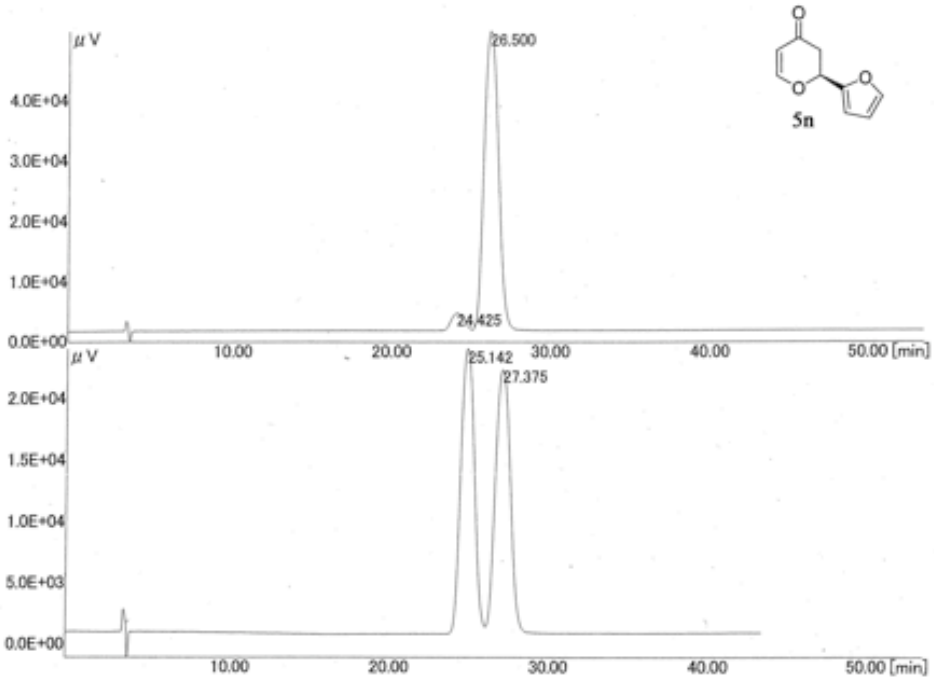
5m

5m

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	24.59	7790089	98.19
2	41.84	143395	1.81

5m(racemate)

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	24.03	311989	49.91
2	40.43	313069	50.09

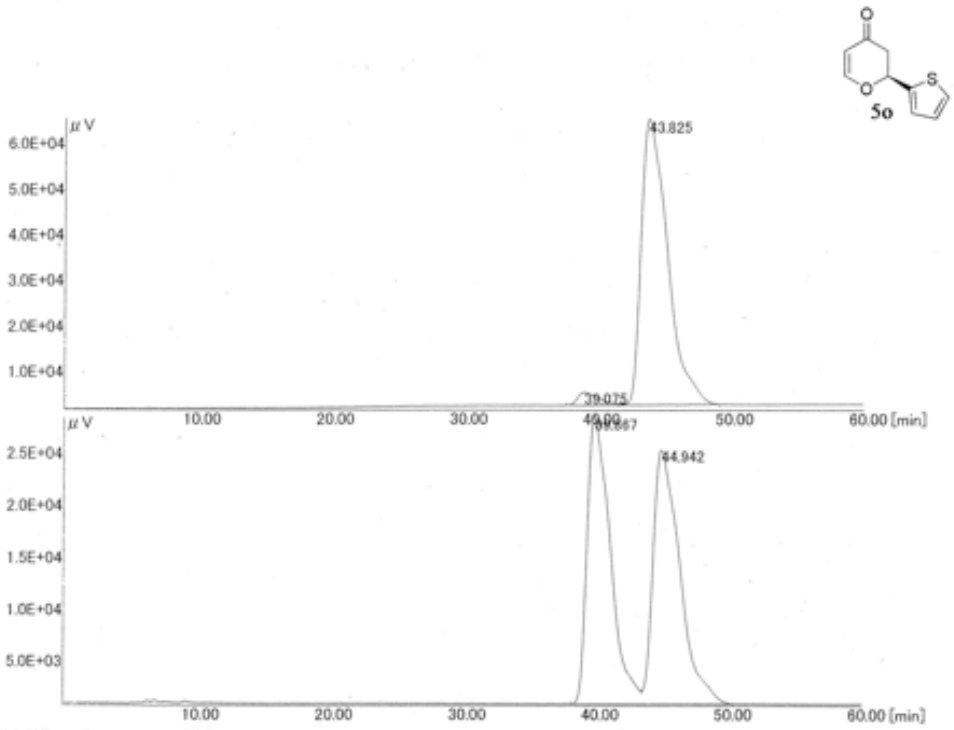


5n

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	24.43	153324	4.73
2	26.50	3088074	95.27

5n (racemate)

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	25.14	1370819	49.88
2	27.38	1377353	50.12

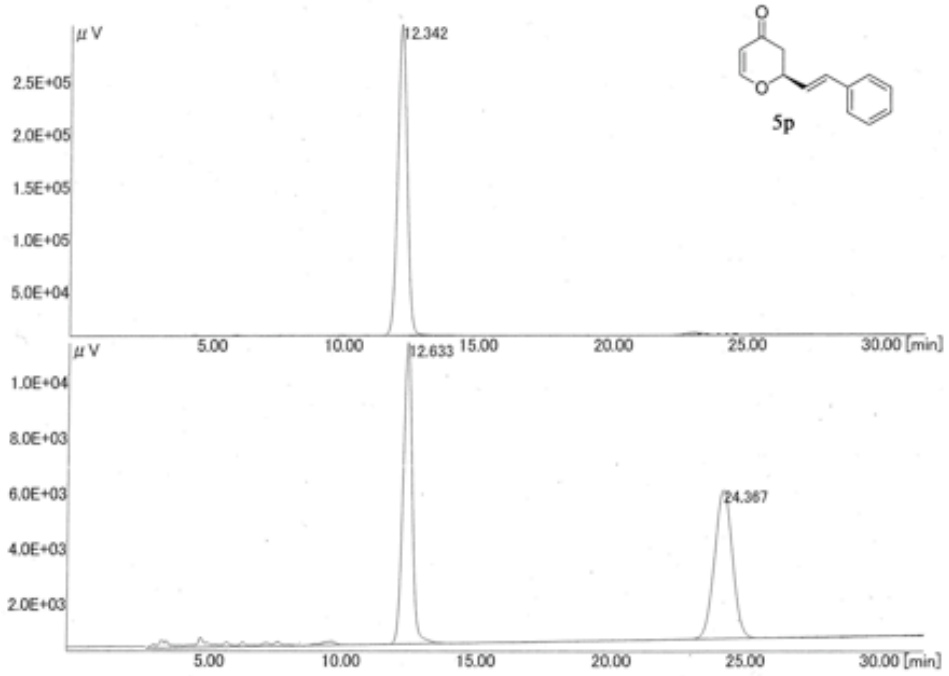


5o

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	39.08	312658	3.51
2	43.83	8600748	96.49

5o (racemate)

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	39.87	3358083	49.62
2	44.94	3409195	50.38



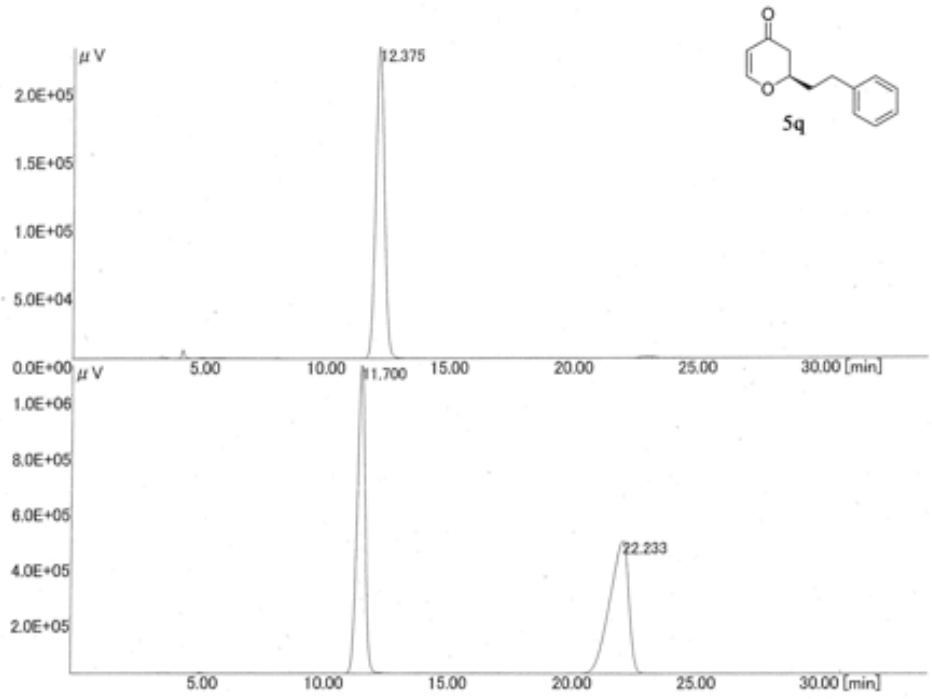
5p

5p

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	12.34	7244612	98.72
2	23.23	93917	1.28

5p (racemate)

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	12.63	256094	50.17
2	24.37	254267	49.83

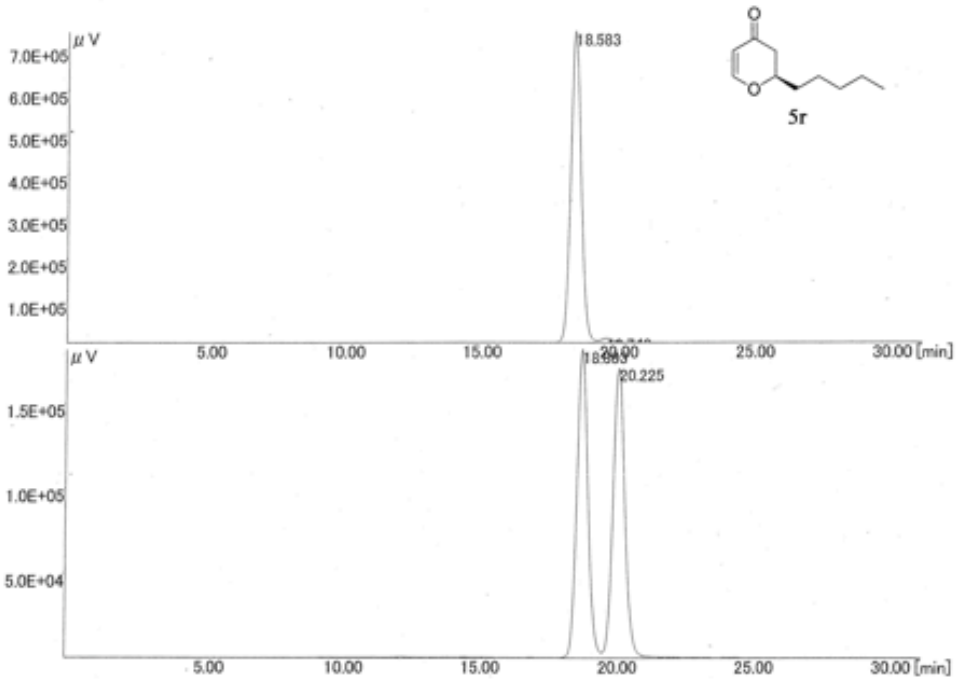


5q

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	12.38	5376813	99.28
2	23.19	38906	0.72

5q (racemate)

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	11.70	24537247	49.86
2	22.23	24673748	50.14

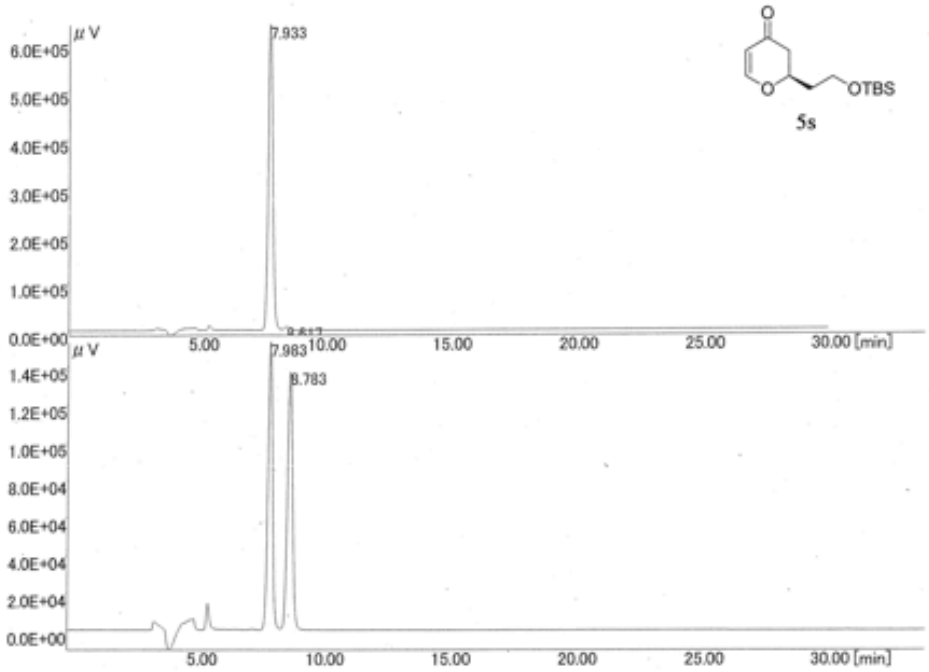


5r

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	18.58	19350232	98.54
2	19.74	286326	1.46

5r (racemate)

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	18.88	4995612	49.77
2	20.23	5041790	50.23

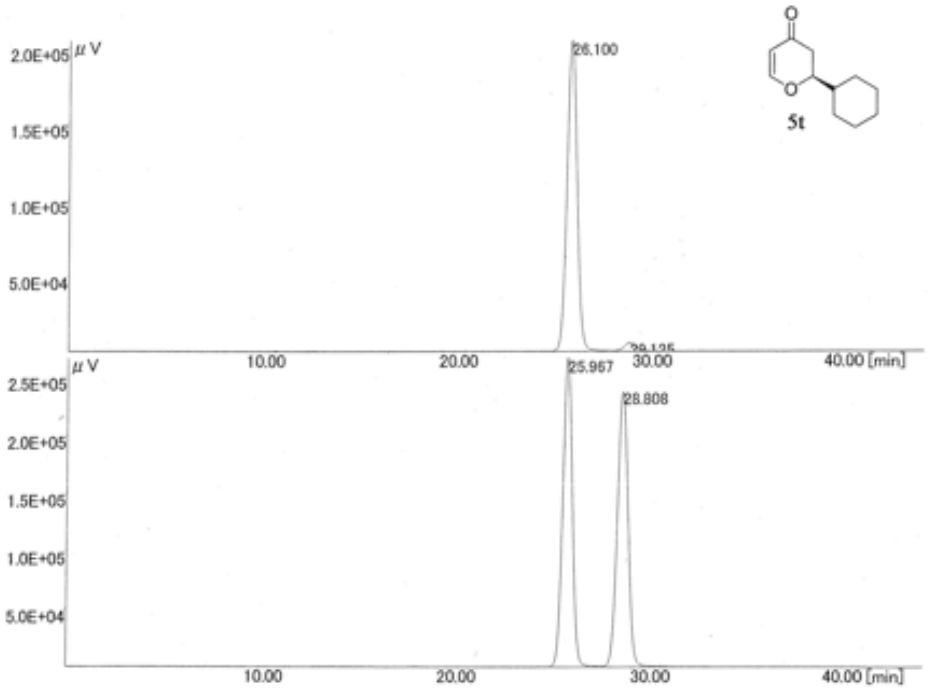


5s

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	7.93	7882415	99.05
2	8.62	75289	0.95

5s (racemate)

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	7.98	1904967	49.92
2	8.78	1910097	50.08



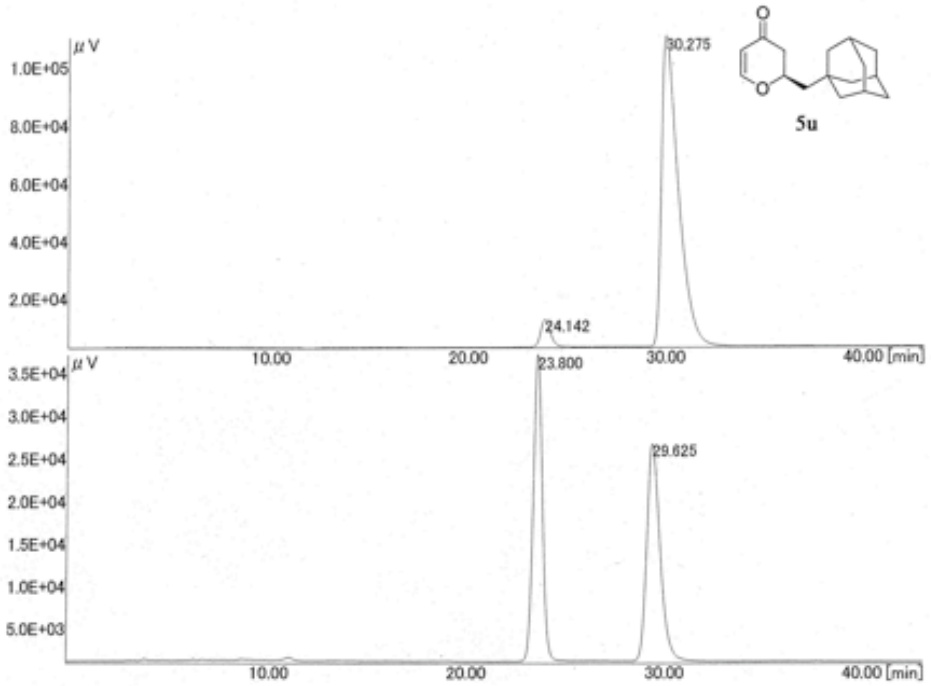
5t

5t

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	26.10	7109642	97.33
2	29.13	195250	2.67

5t (racemate)

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	25.97	8839714	50.00
2	28.81	8838594	50.00



5u

5u

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	24.14	321841	4.80
2	30.28	6386333	95.20

5u (racemate)

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	23.80	115704	49.68
2	29.63	117183	50.32