Electronic Supplementary Information for "Enantio- and diastereoselective hetero-Diels–Alder reactions between 2-aza-3-silyloxy-1,3-butadienes and aldehydes catalyzed by chiral dirhodium(II) carboxamidates"

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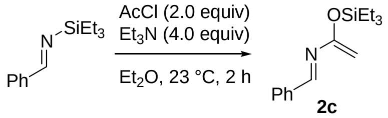
General. Melting points were determined on a Yamato melting point apparatus model MP-21 and are uncorrected. IR spectra were recorded on a JASCO FT/IR-5300 spectrometer and absorbance bands are reported in wavenumber (cm^{-1}). ^{1}H NMR spectra were recorded on JEOL JNM-ECX 400P (400 MHz) spectrometer. Chemical shifts are reported relative to internal standard (tetramethylsilane; δ_H 0.00 or $CDCl_3$; δ_H 7.26). 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-ECX 400P (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. ESI-MS spectra were obtained on a Thermo Scientific Exactive spectrometer. 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-H columns (0.46 cm × 25 cm) from Daicel were used. Retention times (t_R) and peak ratios were determined with JASCO-Chrom NAV 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. Diene **2a, 2b** were prepared according to literature procedure.[1,2]

Experimental Section

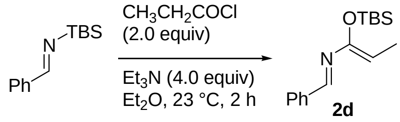
Preparetion of 2-aza-3-triethylsilyloxy-1-phenyl-1,3-butadiene (2c)



To a solution of *N*-triethylsilylbenzylimine (219 mg, 1.0 mmol)[3] and triethylamine (404 mg, 4.0 mmol) in ether (1 mL) was added dropwise a solution of acetyl chloride (157 mg, 2.0 mmol) in ether (1 mL) at 0 °C. After stirring for 2 h at room temperature, the precipitate was filtered through a plug of Celite, and the Celite filter cake was washed with ether (20 mL). The filtrate was concentrated *in vacuo*, and the residue was purified by column chromatography (Wakogel C-200, 2% Et_3N in hexane) to afford **2c** (221 mg, 85%) as a light yellow oil; TLC R_f = 0.78 (2% Et_3N in hexane); IR (film) 2955, 1623, 1603 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.51 (q, J = 8.2 Hz, 6H, $SiCH_2CH_3$), 1.01 (t, J = 8.2 Hz, 9H, $SiCH_2CH_3$), 4.32 (s, 1H, C4–*H*), 4.64 (s, 1H, C4–*H*), 7.43–7.44 (m, 3H, *Ar*), 7.82–7.85 (m, 2H, *Ar*), 8.56 (s, 1H, C1–*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.8 (CH_2), 6.4 (CH_3), 91.7 (CH_2), 128.6 (CH), 129.0 (CH), 131.1 (CH), 135.9 (C), 156.5 (CH), 156.6 (C); EI-HRMS calcd for $C_{15}H_{24}NOSi$

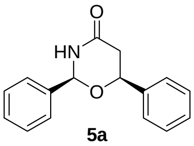
$(M+H)^+$ 262.16217, found 262.16239.

Preparetion of 2-aza-3-*tert*-butyldimethylsilyloxy-1-phenyl-1,3-pentadiene (2d)



According to the procedure for the preparation of **2c**, **2d** was prepared from *N*-*tert*-butyldimethylsilylbenzylimine (439 mg, 2.0 mmol)[4], propionyl chloride (370 mg, 4.0 mmol) and triethylamine (809 mg, 8.0 mmol). The crude product was purified by column chromatography (Wakogel C-200, 2% Et_3N in hexane) to afford **2d** (513 mg, 93%) as a light yellow oil; TLC $R_f = 0.81$ (2% Et_3N in hexane); IR (film) 2930, 1647, 1591 cm^{-1};^1H NMR (400 MHz, $CDCl_3$) δ 0.17 (s, 6H, $Si(CH_3)_2$), 1.04 (s, 9H, $SiC(CH_3)_3$), 1.74 (d, $J = 7.2$ Hz, 3H, C5–H_3), 5.10 (q, $J = 7.2$ Hz, 1H, C4–*H*), 7.41–7.43 (m, 3H, *Ar*), 7.77–7.78 (m, 2H, *Ar*), 8.37 (s, 1H, C1–*H*); δ –3.7 (CH_3), 12.0 (CH_3), 18.4 (C), 25.9 (CH_3), 103.5 (CH), 128.4 (CH), 128.6 (CH), 130.6 (CH), 136.1 (C), 152.7 (C), 153.4 (CH); ESI-HRMS calcd for $C_{15}H_{26}NOSi$ $(M+H)^+$ 276.17782, found 276.17795.

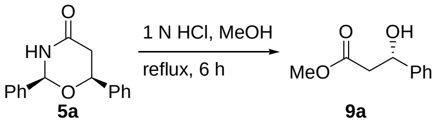
General procedure for asymmetric HDA reaction of 2-az a-3-silyloxydienes with aldehydes: (2*S*,6*S*)-2,6-Diphenyl-1,3-oxazinan-4-one (5a).[5]



5a

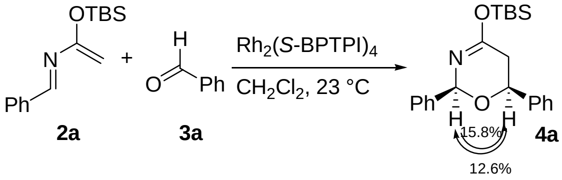
To a solution of benzaldehyde (**3a**) (47.7 mg, 0.45 mmol) in CH_2Cl_2 (0.4 mL) was added $Rh_2(S\text{-BPTPI})_4{\cdot}3H_2O$ (**1**) (4.3 mg, 0.003 mmol, 1 mol %). Then the color of solution was changed from colorless to brown. After stirring for 5 min, a solution of 2-azadiene **2a** (78.4 mg, 0.30 mmol) in CH_2Cl_2 (0.2 mL) added at room temperature. After stirring at this temperature for 24 h, MeOH (ca. 0.1 mL) was added and the mixture was stirred for an additional 0.5 h. The mixture was concentrated *in vacuo* furnished the crude product (118 mg) as a purple solid, which was purified by column chromatography (silica gel, 9:1 $CHCl_3$/EtOAc) to give **5a** (72.2 mg, 95%) as a white solid; mp 173.0–174.0 °C; TLC $R_f = 0.32$ (1:1 $CHCl_3$/EtOAc); $[\alpha]_D^{20}$ –39.8 (*c* 1.03, $CHCl_3$) for 98% ee; IR (KBr) 3242, 1666, 1631 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.77 (m, 2H, C5–*H*), 5.03 (dd, $J = 4.6$, 7.3 Hz, 1H, C6–*H*), 5.93 (s, 1H, C2–*H*), 6.62 (br, 1H, N*H*), 7.31–7.53 (m, 10H, *Ar*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.1 (CH_2), 76.6 (CH), 85.7 (CH), 125.7 (CH), 126.9 (CH), 128.3 (CH), 128.7 (CH), 128.9 (CH), 130.0 (CH), 137.7 (CH), 139.6 (C), 168.8 (C=O); EI-HRMS calcd for $C_{16}H_{15}NO_2$ $(M)^+$ 253.1103, found 253.1099. The enantiomeric excess of **5a** was determined to be 98% by HPLC with a Chiralpak AD-H column (9:1 hexane/*i*-PrOH, 1.0 mL/min): t_R (minor) = 15.3 min for (2*R*,6*R*)-enantiomer; t_R (major) = 17.4 min for (2*S*,6*S*)-enantiomer. A sample for combustion analysis was obtained by recrystallizations from *i*-PrOH as colorless needles (>99% ee); mp 173.5–174.5°C; Anal. Calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.99; H, 5.96; N, 5.56. In order to assign the stereochemistry at C2 and C6, NOE studies were performed on **5a**. Irradiation of C2–H showed NOE with C6–H (12.2%) and the *ortho* proton of the phenyl group (6.0%). Additionally, irradiation of C6–H exhibited NOE with C2–H (12.1%), C5eq–H (5.1%) and the *ortho* proton of the phenyl group (4.6%). These data revealed *cis* relationship between C2–H and C6–H.

Determination of absolute configuration of 5a:
Methyl (*S*)-3-hydroxy-3-phenyl-propionate (9a).[6]



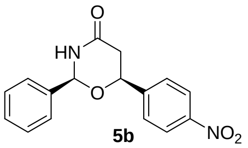
AcCl (0.14 mL, 2 mmol) was added to MeOH (1 mL). This solution was added to a solution of **5a** (40.0 mg, 0.14 mmol, 98% ee) in MeOH (1 mL) at 0 °C. After stirring at reflux temperature for 6 h, the reaction was quenched with saturated $NaHCO_3$ (2 mL), and the whole was extracted with EtOAc (20 mL). The organic layer was washed with water (3 mL) and brine (2 × 3 mL), and dried over anhydrous Na_2SO_4. The solvent was removed *in vacuo* to give the crude product (41 mg) as a yellow oil, which was purified by column chromatography (4:1 hexane/EtOAc) to afford **9a** (26.6 mg, 89%) as a colorless oil; TLC R_f = 0.24 (2:1 hexane/EtOAc); $[\alpha]_D^{22}$ –51.6 (*c* 0.95, $CHCl_3$) for 97% ee [lit.,[6] $[\alpha]_D^{20}$ +46.9 (*c* 1.2, $CHCl_3$) for (*R*)-enantiomer]; ^1H NMR (400 MHz, $CDCl_3$) δ 2.73 (dd, *J* = 4.1, 16.3 Hz, 1H, C2–*H*), 2.77 (dd, *J* = 9.1, 16.3 Hz, 1H, C2–*H*), 3.21 (d, *J* = 3.6, 1H, O*H*), 3.73 (s, 3H, OCH_3), 5.15 (ddd, *J* = 3.6, 4.1, 16.3 Hz, 1H, C3–*H*), 7.28–7.40 (m, 5H, *Ar*). This product **9a** exhibited spectroscopic data identical to (*R*)-**9a**[6], except for the sign of optical rotation. Thus, the preferred absolute stereochemistry of **5a** was determined to be (2*S*,6*S*).

NMR Analysis of 4a.



A solution of diene **2a** (52.3 mg, 0.20 mmol) in CH_2Cl_2 (0.2 mL) was added to a solution of benzaldehyde (**3a**) (23.3 mg, 0.22 mmol) and $Rh_2(S\text{-BPTPI})_4{\cdot}3H_2O$ (**1**) (5.73 mg, 0.004 mmol, 2 mol %) in CH_2Cl_2 (0.05 mL). After stirring for 16 h, the reaction mixture was concentrated *in vacuo* to furnish the crude **4a** (75 mg) as a purple solid; ^1H NMR showed exclusive formation of **4a**; ^1H NMR (400 MHz, C_6D_6) δ 0.35 (s, 3H, SiCH_3), 0.47 (s, 3H, SiCH_3), 1.02 (s, 9H, SiC(CH_3)$_3$), 2.14 (ddd, *J* = 2.3, 4.6, 17.2 Hz, 1H, C5−*H*), 2.20 (ddd, *J* = 2.9, 10.9, 17.2, 1H, C5−*H*), 4.40 (dd, *J* = 4.6, 10.9 Hz, 1H, C2−*H*), 5.95 (s, 1H, C2−*H*), 7.07−7.32 (m, 8H, *Ar*), 7.79−7.81 (m, 2H, *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 (12.6%). Additionally, irradiation of C6−H exhibited NOE with the C2−H (15.8%). These data revealed *cis* relationship between C2−H and C6−H.

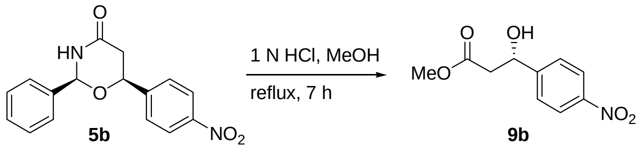
(2*S*,6*S*)-6-(4-nitrophenyl)-2-phenyl-1,3-oxazinan-4-one (5b).



5b

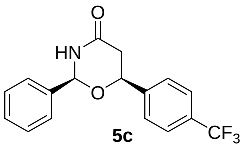
According to the general procedure for asymmetric HDA reaction of 2-aza-3-silyloxydienes with aldehydes, **5b** was prepared from diene **2a** (78.4 mg, 0.30 mmol), *p*-nitrobenzaldehyde (**3b**) (68.0 mg, 0.45 mmol), and Rh$_2$(*S*-BPTPI)$_4$·3H$_2$O (**1**) (4.30 mg, 0.003 mmol, 1 mol %) at 0 °C. The crude product was purified by column chromatography (silica gel, 1:3 hexane/EtOAc) to provide **5b** (87.6 mg, 98%) as a white solid; mp 134.0–135.0 °C; TLC R_f = 0.22 (1:3 hexane/EtOAc); $[\alpha]_D^{19}$ –51.0 (*c* 1.01, CHCl$_3$) for 91% ee; IR (KBr) 3176, 1669, 1602, 1519 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.51 (dd, *J* = 4.1, 17.4 Hz, 1H, C5–*H*), 2.72 (dd, *J* = 11.0, 17.4 Hz, 1H, C5–*H*), 5.06 (dd, 1H, C6–*H*), 5.87 (s, 1H, C2–*H*), 7.12 (br, 1H, N*H*), 7.35–7.48 (m, 7H, *Ar*), 8.12–8.15 (m, 2H, *Ar*); ^{13}C NMR (100 MHz, CDCl$_3$) δ 38.7 (CH$_2$), 75.3 (CH), 85.6 (CH), 123.9 (CH), 126.2 (CH), 126.8 (CH), 128.9 (CH), 130.1 (CH), 137.2 (C), 146.8 (C), 147.5 (C), 168.0 (C=O); EI-HRMS calcd for $C_{17}H_{13}N_2O_4$ $(M–H)^+$ 297.0954, found 297.0871. The enantiomeric excess of **5b** was determined to be 91% by HPLC with a Chiralpak AD-H column (1:1 hexane/*i*-PrOH, 1.0 mL/min): t_R (minor) = 9.7 min for (2*R*, 6*R*)-enantiomer; t_R (major) = 17.6 min for (2*S*, 6*S*)-enantiomer. The preferred absolute configuration of **5b** was not determined. A sample for combustion analysis was obtained by recrystallizations from *i*-PrOH as colorless needles (89% ee); mp 135.5–136.0 °C; Anal. Calcd for $C_{17}H_{14}N_2O_4$: C, 64.42; H, 4.73; N, 9.39. Found: C, 64.46; H, 4.70; N, 9.43.

Determination of absolute configuration of 5b:
Methyl (*S*)-3-hydroxy-3-(4-nitrophenyl) propionate (9b).[7]



According to the procedure for the preparation of **9a**, **9b** was prepared from **5b** (40 mg, 0.13 mmol, 91% ee), AcCl (0.14 mL, 2 mmol) and MeOH (2 mL). The crude product was purified by column chromatography (silica gel, 2:1 hexane/EtOAc) to provide **9b** (28.9 mg, 96%) as a colorless oil; TLC R_f = 0.56 (1:1 hexane/EtOAc); $[\alpha]_D^{19}$ –35.6 (*c* 1.18, CHCl$_3$) for 91% ee [lit.,[7] $[\alpha]_D^{20}$ –37.1 (*c* 1.01, CHCl$_3$) for 94% ee]; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.68–2.79 (m, 2H, C2–*H*), 3.57 (br, 1H, O*H*), 3.75 (s, 3H, OC*H*$_3$), 5.25 (dd, *J* = 4.1, 8.2 Hz, 1H, C3–*H*), 7.56–7.58 (m, 2H, *Ar*), 8.22–8.24 (m, 2H, *Ar*). This product **9b** exhibited spectroscopic data identical to (*S*)-**9b**[7]. Thus, the preferred absolute stereochemistry of **5b** was determined to be (2*S*,6*S*)

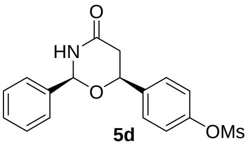
(2*S**,6*S**)-2-Phenyl-6-(4-trifluoromethylphenyl)-1,3-oxazinan-4-one (5c).



5c

According to the general procedure for asymmetric HDA reaction of 2-aza-3-silyloxydienes with aldehydes, **5c** was prepared from diene **2a** (78.4 mg, 0.30 mmol), *p*-trifluoromethylbenzaldehyde (**3c**) (78.3 mg, 0.45 mmol), and Rh$_2$(*S*-BPTPI)$_4$·3H$_2$O (**1**) (4.30 mg, 0.003 mmol, 1 mol %). The crude product was purified by column chromatography (silica gel, 1:2 hexane/EtOAc) to provide **5c** (92.5 mg, 96%) as a white solid; mp 147.0–148.0 °C; TLC R_f = 0.31 (1:3 hexane/EtOAc); $[\alpha]_D^{19}$ –38.6 (*c* 1.02, $CHCl_3$) for 94% ee; IR (KBr) 3161, 1670, 1619 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.63 (dd, *J* = 11.3, 17.2 Hz, 1H, C5–*H*), 2.76 (dd, *J* = 3.6, 17.2 Hz, 1H, C5–*H*), 5.04 (dd, *J* = 3.6, 11.3 Hz, 1H, C6–*H*), 5.88 (s, 1H, C2–*H*), 6.37 (br, 1H, N*H*), 7.32–7.58 (m, 9H, *Ar*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.9 (CH_2), 75.8 (CH), 85.7 (CH), 123.9 (q, *J* = 271 Hz, C), 125.6 (q, *J* = 3.8 Hz, CH), 125.8 (CH), 126.8 (CH), 128.9 (CH), 130.0 (CH), 130.3 (q, *J* = 32.4 Hz, C), 137.4 (C), 143.6 (C), 168.4 (C=O); EI-HRMS calcd for $C_{17}H_{13}NO_2F_3$ $(M–H)^+$ 320.0977, found 320.0892. The enantiomeric excess of **5c** was determined to be 94% by HPLC with a Chiralpak AD-H column (9:1 hexane/*i*-PrOH, 1.0 mL/min): t_R = 15.2 min for minor enantiomer; t_R = 20.6 min for major enantiomer. The preferred absolute configuration of **5c** was not determined. A sample for combustion analysis was obtained by recrystallizations from *i*-PrOH as colorless needles (93% ee); mp 148.0–148.5 °C; Anal. Calcd for $C_{17}H_{14}NO_2F_3$: C, 63.55; H, 4.39; N, 4.36. Found: C, 63.61; H, 4.37; N, 4.29.

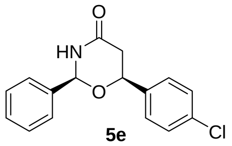
(2*S,6*S**)-6-(4-Mesylphenyl)-2-phenyl-1,3-oxazinan-4-one (5d).**



5d

According to the general procedure for asymmetric HDA reaction of 2-aza-3-silyloxydienes with aldehydes, **5d** was prepared from diene **2a** (78.4 mg, 0.30 mmol), 4-mesyloxybenzaldehyde (**3d**)[8] (90.0 mg, 0.45 mmol), and Rh_2(*S*-BPTPI)$_4$·$3H_2O$ (**1**) (4.30 mg, 0.003 mmol, 1 mol %). The crude product was purified by column chromatography (silica gel, 1:3 hexane/EtOAc) to provide **5d** (101 mg, 97%) as a white solid; mp 141.0–142.5 °C; TLC R_f = 0.45 (EtOAc); $[\alpha]_D^{19}$ –29.9 (*c* 1.04, $CHCl_3$) for 90% ee; IR (KBr) 3174, 1661, 1506, 1347 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.63 (dd, *J* = 10.8, 16.9 Hz, 1H, C5–*H*), 2.76 (dd, *J* = 4.0, 16.9 Hz, 1H, C5–*H*), 3.11 (s, 3H, SO_2CH_3), 5.02 (dd, *J* = 4.0, 10.8 Hz, 1H, C6–*H*), 5.89 (s, 1H, C2–*H*), 7.07 (br, 1H, N*H*), 7.32–7.58 (m, 9H, *Ar*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.3 (CH_3), 38.8 (CH_2), 75.6 (CH), 85.6 (CH), 122.2 (q, *J* = 271 Hz, C), 126.8 (CH), 127.3 (CH), 128.8 (CH), 129.9 (CH), 137.4 (C), 139.0 (C), 148.8 (C), 168.5 (C=O); EI-HRMS calcd for $C_{17}H_{16}NO_5S$ $(M–H)^+$ 346.0827, found 346.0746. The enantiomeric excess of **5d** was determined to be 90% by HPLC with a Chiralpak AD-H column (1:1 hexane/*i*-PrOH, 1.0 mL/min): t_R = 11.7 min for minor enantiomer; t_R = 20.4 min for major enantiomer. The preferred absolute configuration of **5d** was not determined. The preferred absolute configuration of **5d** was not determined. A sample for combustion analysis was obtained by recrystallizations from *i*-PrOH as colorless needles (92% ee); mp 141.5–142.5 °C; Anal. Calcd for $C_{17}H_{17}NO_5S$: C, 58.78; H, 4.93; N, 4.03; S, 9.23. Found: C, 58.77; H, 4.86; N, 4.02; S, 9.20.

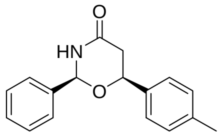
(2*S**,6*S**)-6-(4-Chlorophenyl)-2-phenyl-1,3-oxazinan-4-one (5e).



5e

According to the general procedure for asymmetric HDA reaction of 2-aza-3-silyloxydienes with aldehydes, **5e** was prepared from diene **2a** (78.4 mg, 0.30 mmol), *p*-chlorobenzaldehyde (**3e**) (78.3 mg, 0.45 mmol), and Rh_2(*S*-BPTPI)$_4$·$3H_2O$ (**1**) (4.30 mg, 0.003 mmol, 1 mol %). The crude product was purified by column chromatography (silica gel, 9:1 $CHCl_3$/EtOAc) to provide **5e** (79.6 mg, 93%) as a white solid; mp 149.0–150.0 °C; TLC $R_f = 0.27$ (1:1 $CHCl_3$/EtOAc); $[\alpha]_D^{20}$ –37.5 (*c* 1.14, $CHCl_3$) for 94% ee; IR (KBr) 3170, 1662, 1494 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.71 (dd, *J* = 11.2, 17.4 Hz, 1H, C5–*H*), 2.79 (dd, *J* = 4.5, 17.4 Hz, 1H, C5–*H*), 5.02 (dd, *J* = 4.5, 11.2 Hz, 1H, C6–*H*), 5.93 (s, 1H, C2–*H*), 6.19 (br, 1H, N*H*), 7.32–7.53 (m, 9H, *Ar*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.0 (CH_2), 75.9 (CH), 85.7 (CH), 126.8 (CH), 127.0 (CH), 128.82 (CH), 128.86 (CH), 130.0 (CH), 134.0 (C), 137.5 (C), 138.2 (C), 168.5 (C=O); EI-HRMS calcd for $C_{16}H_{13}NO_2Cl$ $(M–H)^+$ 286.0713, found 286.0631. The enantiomeric excess of **5e** was determined to be 94% by HPLC with a Chiralpak AD-H column (9:1 hexane/*i*-PrOH, 1.0 mL/min): t_R = 17.3 min for minor enantiomer; t_R = 33.3 min for major enantiomer. The preferred absolute configuration of **5e** was not determined. A sample for combustion analysis was obtained by recrystallizations from *i*-PrOH as colorless needles (99% ee); mp 149.5–150.0 °C; Anal. Calcd for $C_{16}H_{14}NO_2Cl$: C, 66.79; H, 4.90; N, 4.87; Cl, 12.32. Found: C, 67.00; H, 4.95; N, 4.89; Cl, 12.15.

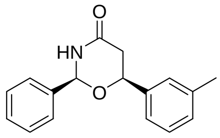
(2*S**,6*S**)-6-(4-Methylphenyl)-2-phenyl-1,3-oxazinan-4-one (5f).



5f

According to the general procedure for asymmetric HDA reaction of 2-aza-3-silyloxydienes with aldehydes, **5f** was prepared from diene **2a** (78.4 mg, 0.30 mmol), *p*-tolualdehyde (**3f**) (54.1 mg, 0.45 mmol), and Rh_2(*S*-BPTPI)$_4$·$3H_2O$ (**1**) (4.30 mg, 0.003 mmol, 1 mol %). The crude product was purified by column chromatography (silica gel, 9:1 $CHCl_3$/EtOAc) to provide **5f** (77.8 mg, 97%) as a white solid; mp 151.0–152.0 °C; TLC $R_f = 0.27$ (1:1 $CHCl_3$/EtOAc); $[\alpha]_D^{21}$ –28.3 (*c* 1.04, $CHCl_3$) for 96% ee; IR (KBr) 3247, 1665, 1632 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H, Ar–C*H*$_3$), 2.73 (s, 1H, C5–*H*), 2.76 (d, *J* = 7.6 Hz, 1H, C5–*H*), 4.98 (t, *J* = 1.4 Hz, 1H, C6–*H*), 5.90 (s, 1H, C2–*H*), 6.52 (br, 1H, N*H*), 7.16–7.51 (m, 9H, *Ar*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1 (CH_3), 38.9 (CH_2), 76.3 (CH), 85.5 (CH), 125.6 (CH), 126.7 (CH), 128.7 (CH), 129.2 (CH), 129.7 (CH), 136.7 (C), 137.8 (C), 138.0 (C), 169.1 (C=O); EI-HRMS calcd for $C_{17}H_{16}NO_2$ $(M–H)^+$ 266.11810, found 266.11799. The enantiomeric excess of **5f** was determined to be 96% by HPLC with a Chiralpak AD-H column (9:1 hexane/*i*-PrOH, 1.0 mL/min): t_R = 15.1 min for minor enantiomer; t_R = 23.1 min for major enantiomer. The preferred absolute configuration of **5f** was not determined. A sample for combustion analysis was obtained by recrystallizations from *i*-PrOH as colorless needles (99% ee); mp 151.0–152.0 °C; Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.16; H, 6.25; N, 5.23.

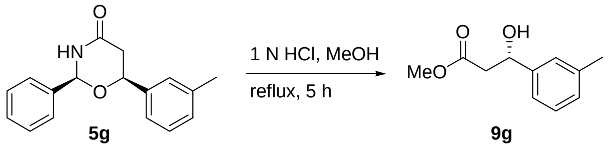
(2*S**,6*S**)-6-(3-Methylphenyl)-2-phenyl-1,3-oxazinan-4-one (5g).



5g

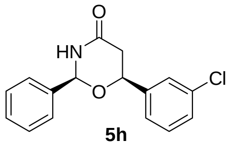
According to the general procedure for asymmetric HDA reaction of 2-aza-3-silyloxydienes with aldehydes, **5g** was prepared from diene **2a** (78.4 mg, 0.30 mmol), *m*-tolualdehyde (**3g**) (54.1 mg, 0.45 mmol), and Rh_2(*S*-BPTPI)$_4$·$3H_2O$ (**1**) (4.30 mg, 0.003 mmol, 1 mol %). The crude product was purified by column chromatography (silica gel, 9:1 $CHCl_3$/EtOAc) to provide **5g** (67.4 mg, 84%) as a white solid; mp 123.0–124.0 °C; TLC R_f = 0.27 (1:1 $CHCl_3$/EtOAc); $[\alpha]_D^{22}$ –26.9 (*c* 1.16, $CHCl_3$) for 92% ee; IR (KBr) 3178, 1679, 1633 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3H, Ar–C*H*$_3$), 2.68 (s, 1H, C5–*H*), 2.69 (s, 1H, C5–*H*), 4.91 (t, *J* = 7.6 Hz, 1H, C6–*H*), 5.84 (s, 1H, C2–*H*), 6.38 (br, 1H, N*H*), 7.05–7.46 (m, 9H, *Ar*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4 (CH_3), 39.0 (CH_2), 76.6 (CH), 85.7 (CH), 122.7 (CH), 126.3 (CH), 126.9 (CH), 128.5 (CH), 128.7 (CH), 129.0 (CH), 129.9 (CH), 137.7 (C), 138.4 (C), 139.6 (C), 169.0 (C=O); EI-HRMS calcd for $C_{17}H_{16}NO_2$ $(M–H)^+$ 266.11810, found 266.11836. A sample for combustion analysis was obtained by recrystallizations from *i*-PrOH as colorless needles (>99% ee); mp 123.5–124.5 °C; Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.20; H, 6.31; N, 5.17.

Determination of enantiomeric excess of 5g:
Methyl (*S*)-3-hydroxy-3-(3-methylphenyl)propionate (9g).[9]



According to the procedure for the preparation of **9a**, **9g** was prepared from **5g** (72.4 mg, 0.27 mmol), AcCl (0.14 mL, 2 mmol) and MeOH (2 mL). The crude product was purified by column chromatography (silica gel, 6:1 hexane/EtOAc) to provide **9g** (28.9 mg, 96%) as a colorless oil; TLC R_f = 0.43 (2:1 hexane/EtOAc); $[\alpha]_D^{20}$ –43.7 (*c* 1.00, $CHCl_3$) for 92% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 2.36 (s, 3H, Ar–C*H*$_3$), 2.71 (dd, *J* = 3.6, 16.3 Hz, 1H, C2–*H*), 2.77 (dd, *J* = 9.1, 16.3 Hz, 1H, C2–*H*), 3.17 (br, 1H, O*H*), 3.74 (s, 3H, OC*H*$_3$), 5.11 (dd, *J* = 3.6, 9.1 Hz, 1H, C3–*H*), 7.09–7.27 (m, 4H, *Ar*). The enantiomeric excess of **9g** was determined to be 92% by HPLC with a Chiralcel OD-H column (19:1 hexane/*i*-PrOH, 1.0 mL/min): t_R = 14.4 min for major enantiomer; t_R = 24.7 min for minor enantiomer. The preferred absolute configuration of **5g** was not determined.

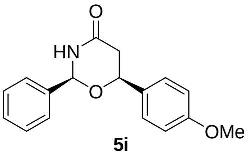
(2*S**,6*S**)-6-(3-Chlorophenyl)-2-phenyl-1,3-oxazinan-4-one (5h).



5h

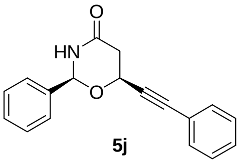
According to the general procedure for asymmetric HDA reaction of 2-aza-3-silyloxydienes with aldehydes, **5h** was prepared from diene **2a** (78.4 mg, 0.30 mmol), *m*-chlorobenzaldehyde (**3h**) (78.3 mg, 0.45 mmol), and Rh_2(*S*-BPTPI)$_4$·$3H_2O$ (**1**) (4.30 mg, 0.003 mmol, 1 mol %). The crude product was purified by column chromatography (silica gel, 9:1 $CHCl_3$/EtOAc) to provide **5h** (79.0 mg, 92%) as a white solid; mp 144.0–145.0 °C; TLC R_f = 0.27 (1:1 $CHCl_3$/EtOAc); $[\alpha]_D^{20}$ –34.0 (*c* 1.02, $CHCl_3$) for 92% ee; IR (KBr) 3167, 1656, 1473 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.71 (dd, *J* = 11.2, 17.4 Hz, 1H, C5–*H*), 2.79 (dd, *J* = 4.5, 17.4 Hz, 1H, C5–*H*), 5.02 (dd, *J* = 4.5, 11.2 Hz, 1H, C6–*H*), 5.92 (s, 1H, C2–*H*), 6.35 (br, 1H, N*H*), 7.30–7.53 (m, 9H, *Ar*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.9 (CH_2), 75.8 (CH), 85.7 (CH), 123.7 (CH), 125.8 (CH), 126.9 (CH), 128.4 (CH), 128.9 (CH), 129.94 (CH), 129.99 (CH), 134.6 (C), 137.5 (C), 141.7 (C), 168.5 (C=O); EI-HRMS calcd for $C_{16}H_{13}NO_2Cl$ $(M–H)^+$ 286.0713, found 286.0634. The enantiomeric excess of **5h** was determined to be 92% by HPLC with a Chiralpak AD-H column (9:1 hexane/*i*-PrOH, 1.0 mL/min): t_R = 16.3 min for major enantiomer; t_R = 17.4 min for minor enantiomer. The preferred absolute configuration of **5h** was not determined. A sample for combustion analysis was obtained by recrystallizations from 1:3 hexane/EtOAc as colorless needles (95% ee); mp 144.5–145.0°C; Anal. Calcd for $C_{16}H_{14}NO_2Cl$: C, 66.79; H, 4.90; N, 4.87; Cl, 12.32. Found: C, 66.90; H, 4.87; N, 4.90; Cl, 12.12.

(2*S**,6*S**)-6-(4-Methylphenyl)-2-phenyl-1,3-oxazinan-4-one (5i).


5i

According to the general procedure for asymmetric HDA reaction of 2-aza-3-silyloxydienes with aldehydes, **5i** was prepared from diene **2a** (78.4 mg, 0.30 mmol), *p*-anisaldehyde (**3i**) (61.2 mg, 0.45 mmol), and Rh_2(*S*-BPTPI)$_4$·$3H_2O$ (**1**) (4.30 mg, 0.003 mmol, 1 mol %) at 30 °C. The crude product was purified by column chromatography (silica gel, 1:2 hexane/EtOAc) to provide **5i** (54.4 mg, 64%) as a white solid; mp 140.5–141.5 °C; TLC R_f = 0.53 (1:3 hexane/EtOAc); $[\alpha]_D^{21}$ –25.0 (*c* 1.01, $CHCl_3$) for 92% ee; IR (KBr) 3174, 1668, 1613, 1251 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.76–2.80 (m, 2H, C5–*H*), 3.80 (s, 3H, ArOCH_3), 4.98 (dd, *J* = 4.5, 10.4 Hz, 1H, C6–*H*), 5.92 (s, 1H, C2–*H*), 6.20 (br, 1H, N*H*), 6.89–6.92 (m, 2H, *Ar*), 7.32–7.52 (m, 7H, *Ar*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.9 (CH_2), 55.2 (CH_3), 76.3 (CH), 85.6 (CH), 114.0 (CH), 126.8 (CH), 127.1 (CH), 128.7 (CH), 129.8 (CH), 131.7 (C), 137.8 (C), 159.5 (C), 169.1 (C=O); EI-HRMS calcd for $C_{17}H_{16}NO_3$ $(M–H)^+$ 283.12084, found 283.1062. The enantiomeric excess of **5i** was determined to be 92% by HPLC with a Chiralpak AD-H column (3:1 hexane/*i*-PrOH, 1.0 mL/min): t_R = 10.4 min for minor enantiomer; t_R = 17.2 min for major enantiomer. The preferred absolute configuration of **5i** was not determined. A sample for combustion analysis was obtained by recrystallizations from *i*-PrOH as colorless needles (91% ee); mp 141.0–142.0 °C; Anal. Calcd for $C_{17}H_{18}NO_3$: C, 72.07; H, 6.05; N, 4.94. Found: C, 71.91; H, 5.93; N, 4.91.

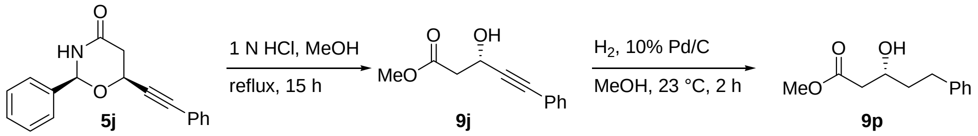
(2*S*,6*S*)-2-Phenyl-6-phenylethynyl-1,3-oxazinan-4-one (5j).



5j

According to the general procedure for asymmetric HDA reaction of 2-aza-3-silyloxydienes with aldehydes, **5j** was prepared from diene **2a** (78.4 mg, 0.30 mmol), phenylpropargylaldehyde (**3j**) (58.6 mg, 0.45 mmol), and $Rh_2(S\text{-BPTPI})_4{\cdot}3H_2O$ (4.30 mg, 0.003 mmol, 1 mol %) at 0 °C. The crude product was purified by column chromatography (silica gel, 9:1 $CHCl_3$/EtOAc) to provide **5j** (82.1 mg, 99%) as a white solid; mp 200–201 °C; TLC $R_f = 0.28$ (2:1 $CHCl_3$/EtOAc); $[\alpha]_D^{21}$ –42.7 (*c* 1.02, $CHCl_3$) for 95% ee; IR (KBr) 2234, 1672 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.82 (dd, *J* = 4.0, 11.3 Hz, 1H, C5–*H*), 2.97 (dd, *J* = 11.3, 17.2 Hz, 1H, C5–*H*), 4.98 (dd, *J* = 4.0, 17.2 Hz, 1H, C6–*H*), 5.82 (s, 1H, C2–*H*), 6.20 (br, 1H, N*H*), 7.28–7.36 (m, 3H, *Ar*), 7.43–7.52 (m, 7H, *Ar*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.0 (CH_2), 65.9 (CH), 85.1 (C), 85.7 (CH), 87.0 (C), 121.6 (C), 127.1 (CH), 128.3 (CH), 128.9 (CH), 129.0 (CH), 130.2 (CH), 131.9 (CH), 137.0 (C), 167.8 (C=O); EI-HRMS calcd for $C_{18}H_{14}NO_2$ $(M–H)^+$ 276.1024, found 276.1015. The enantiomeric excess of **5j** was determined to be 95% by HPLC with a Chiralcel OD-H column (1:1 hexane/*i*-PrOH, 1.0 mL/min): t_R (minor) = 8.2 min for (2*R*,6*R*)-enantiomer; t_R (major) = 14.1 min for (2*S*,6*S*)-enantiomer. A sample for combustion analysis was obtained by recrystallizations from *i*-PrOH as colorless needles (98% ee); mp 208.0–209.0 °C; Anal. Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.96; H, 5.48; N, 5.00. In order to assign the stereochemistry at C2 and C6, NOE studies were performed on **5j**. Irradiation of C2–H showed NOE with C6–H (16.8%) and the *ortho* proton of the phenyl group (9.8%). Additionally, irradiation of C6–H exhibited NOE with C2–H (16.2%) and C5eq–H (4.6%). These data revealed *cis* relationship between C2–H and C6–H.

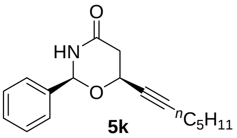
Determination of absolute configuration of 5j:
Methyl (*R*)-3-hydroxy-5-phenylpentanoate (9p).[10]



AcCl (0.14 mL, 2 mmol) was added to MeOH (1 mL). This solution was added to a solution of **5j** (36.0 mg, 0.13 mmol, 95% ee) in MeOH (1 mL) at 0 °C. After stirring at reflux temperature for 15 h, the reaction was quenched with saturated $NaHCO_3$ (2 mL), and the whole was extracted with EtOAc (20 mL). The organic layer was washed with water (3 mL) and brine (2 × 3 mL), and dried over anhydrous Na_2SO_4. The solvent was removed *in vacuo* to give the crude product (40 mg) as a white solid, which was purified by column chromatography (4:1 hexane/EtOAc) to afford **9j** (26.0 mg, 98%) as a colorless oil; TLC R_f = 0.49 (2:1 hexane/EtOAc); $[\alpha]_D^{22}$ +20.9 (*c* 0.90, $CHCl_3$) for 95% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 2.87 (m, 2H, C2–*H*), 3.12 (d, *J* = 6.3 Hz, 1H, O*H*), 3.77 (s, 3H, OC*H*$_3$), 5.00 (m, 1H, C3–*H*), 7.29–7.33 (m, 3H, *Ar*), 7.42–7.44 (m, 2H, *Ar*).

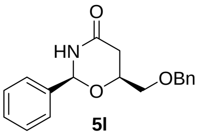
To a solution of **9j** in MeOH (2 mL) was added 10% Pd/C (10 mg), and the resulting mixture was stirred under hydrogen at atmospheric pressure at 23 °C for 2 h. The reaction mixture was then filtered through a plug of Celite, and the Celite filter cake was washed with MeOH (5 mL). The filtrate was concentrated *in vacuo*, and the residue was purified by column chromatography (silica gel, 4:1 hexane/EtOAc) to afford **9p** (25.2 mg, 97%) as a colorless oil; TLC $R_f = 0.45$ (2:1 hexane/EtOAc); $[\alpha]_D^{22}$ +2.0 (*c* 1.01, $CHCl_3$) for 95% ee [lit.,[10] $[\alpha]_D$ –2.68 (*c* 0.67, $CHCl_3$) for (*S*)-enantiomer]; ^1H NMR (400 MHz, $CDCl_3$) δ 1.74 (m, 1H, C4–*H*), 1.80–1.90 (m, 2H, C4–*H*), 2.46 (dd, *J* = 8.6, 16.8 Hz, 1H, C2–*H*), 2.51 (dd, *J* = 3.6, 16.8 Hz, 1H, C2–*H*), 2.66–2.74 (m, 1H, C5–*H*), 2.79–2.86 (m, 1H, C5–*H*), 3.01 (br, 1H, O*H*), 3.71 (s, 3H, OCH_3), 3.99–4.04 (m, 1H, C3–*H*), 7.17–7.22 (m, 2H, *Ar*), 7.26–7.31 (m, 2H, *Ar*), 7.37 (m, 1H, *Ar*). This product **9p** exhibited spectroscopic data identical to (*S*)-**9p**[10], except for the sign of optical rotation. Thus, the preferred absolute stereochemistry of **5j** was determined to be (2*S*,6*S*).

(2*S,6*S**)-6-(2-Heptynyl)-2-phenyl-1,3-oxazinan-4-one (5k)**


5k

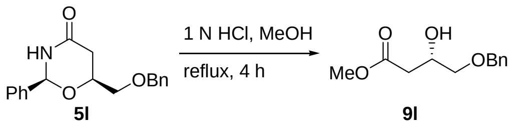
According to the general procedure for asymmetric HDA reaction of 2-aza-3-silyloxydienes with aldehydes, **5k** was prepared from diene **2a** (78.4 mg, 0.30 mmol), 2-octynal (**3k**) (56.0 mg, 0.45 mmol), and $Rh_2(S\text{-BPTPI})_4{\cdot}3H_2O$ (**1**) (4.3 mg, 0.003 mmol, 1 mol %) at 0 °C. The crude product was purified by column chromatography (silica gel, 2:1 hexane/EtOAc) to provide **5k** (76.5 mg, 94%) as a white solid; mp 138.0–139.0 °C; TLC $R_f = 0.52$ (1:3 hexane/EtOAc); $[\alpha]_D^{22}$ –34.8 (*c* 1.06, $CHCl_3$) for 96% ee; IR (KBr) 2251, 1677 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.81 (t, *J* = 7.2 Hz, 3H, CH_2CH_3), 1.19–1.29 (m, 4H, $CH_2CH_2CH_3$), 1.38–1.45 (m, 2H, $C{\equiv}CCH_2CH_2$), 2.11 (m, 2H, $C{\equiv}CCH_2$), 2.49 (dd, *J* = 2.3, 17.1 Hz, 1 H, C5–*H*), 2.59 (dd, *J* = 11.3, 17.1 Hz, 1H, C5–*H*), 4.56 (dd, *J* = 2.2, 11.3 Hz, 1H, C6–*H*), 5.59 (s, 1H, C2–*H*), 7.27–7.36 (m, 6H, N*H* and *Ar*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8 (CH_3), 18.5 (CH_2), 22.0 (CH_2), 27.8 (CH_2), 30.8 (CH_2), 38.1 (CH_2), 65.4 (CH), 76.5 (C), 85.2 (CH), 88.2 (C), 126.9 (CH), 128.6 (CH), 129.8 (CH), 137.1 (C) 168.3 (C=O); EI-HRMS calcd for $C_{17}H_{20}NO_2$ $(M–H)^+$ 270.14940, found 270.14975. The enantiomeric excess of **5k** was determined to be 96% by HPLC with a Chiralpak AD-H column (19:1 hexane/*i*-PrOH, 1.0 mL/min): t_R = 21.1 min for minor enantiomer; t_R = 30.4 min for major enantiomer. The preferred absolute configuration of **5k** was not determined. A sample for combustion analysis was obtained by recrystallizations from *i*-PrOH as colorless needles (98% ee); mp 139.0–139.5 °C; Anal. Calcd for $C_{17}H_{21}NO_2$: C, 75.25; H, 7.80; N, 5.16. Found: C, 74.90; H, 7.59; N, 5.22.

(2*S*,6*S*)-6-Benzyloxymethyl-2-phenyl-1,3-oxazinan-4-one (5l).


5l

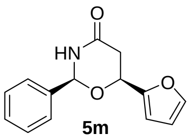
According to the general procedure for asymmetric HDA reaction of 2-aza-3-silyloxydienes with aldehydes, **5l** was prepared from diene **2a** (78.4 mg, 0.30 mmol), benzyloxyacetaldehyde (**3l**) (67.8 mg, 0.45 mmol), and $Rh_2(S\text{-BPTPI})_4{\cdot}3H_2O$ (**1**) (4.3 mg, 0.003 mmol, 1 mol %) at 0 °C. The crude product was purified by column chromatography (silica gel, 9:1 $CHCl_3$/EtOAc) to provide **5l** (65.7 mg, 86%) as a white solid; mp 69.0–70.0 °C; TLC $R_f = 0.23$ (1:1 $CHCl_3$/EtOAc); $[\alpha]_D^{19}$ –19.6 (*c* 1.18, $CHCl_3$) for 97% ee; IR (KBr) 3256, 1668, 1642 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.48 (dd, *J* = 4.1, 17.4 Hz, 1H, C5–*H*), 2.56 (dd, *J* = 11.0, 17.4 Hz, 1H, C5–*H*), 3.57 (dd, *J* = 4.1, 10.5 Hz, 1H, CHC*H*H*O*), 3.65 (dd, *J* = 5.9, 10.5 Hz, 1H, CHCH*H*O), 4.22 (m, 1H, C6–*H*), 4.55 (d, *J* = 12.4 Hz, 1H, OC*H*HPh), 4.59 (d, *J* = 12.4 Hz, 1H, OCH*H*Ph), 5.76 (s, 1H, C2–*H*), 6.19 (br, 1H, N*H*), 7.28–7.47 (m, 10H, *Ar*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.8 (CH_2), 71.6 (CH_2), 73.4 (CH_2), 74.2 (CH), 85.4 (CH), 126.8 (CH), 127.69 (CH), 127.74 (CH), 128.4 (CH), 128.8 (CH), 129.8 (CH), 137.5 (C), 137.6 (C), 168.9 (C=O); EI-HRMS calcd for $C_{18}H_{18}NO_3$ $(M–H)^+$ 296.1287, found 296.1272. The enantiomeric excess of **5l** was determined to be 97% by HPLC with a Chiralcel OD-H column (3:1 hexane/*i*-PrOH, 1.0 mL/min): t_R (minor) = 14.9 min for (2*R*,6*R*)-enantiomer; t_R (major) = 21.4 min for (2*S*,6*S*)-enantiomer. A sample for combustion analysis was obtained by recrystallizations from *i*-PrOH as colorless needles (92% ee); mp 70.5–71.5 °C; Anal. Calcd for $C_{18}H_{19}NO_3$: C, 72.71; H, 6.44; N, 4.71. Found: C, 72.58; H, 6.36; N, 4.70.

Determination of absolute configuration of 5l:
Methyl (*S*)-4-benzyloxy-3-hydroxybutyrate (9l).[7]



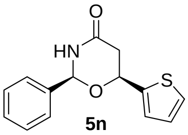
According to the procedure for the preparation of **9a**, **9l** was prepared from **5l** (49.8 mg, 0.17 mmol, 97% ee), AcCl (0.14 mL, 2 mmol) and MeOH (2 mL). The crude product was purified by column chromatography (silica gel, 4:1 hexane/EtOAc) to provide **9l** (30.3 mg, 81%) as a colorless oil; TLC $R_f = 0.40$ (1:1 hexane/EtOAc); $[\alpha]_D^{19}$ –11.0 (*c* 1.51, $CHCl_3$) for 97% ee [lit.,[7] $[\alpha]_D^{20}$ –9.49 (*c* 1.00, $CHCl_3$) for 86% ee]; ^1H NMR (400 MHz, $CDCl_3$) δ 2.56 (d, *J* = 6.3 Hz, 2H, C2–*H*), 2.95 (br, 1H, O*H*), 3.50 (ddd, *J* = 5.9, 9.5, 15.4 Hz, 2H, C4–*H*), 3.70 (s, 3H, OCH_3), 4.25 (m, 1H, C3–*H*), 4.56 (s, 2H, $PhCH_2O$), 7.28–7.38 (m, 5H, *Ar*). This product **9l** exhibited spectroscopic data identical to (*S*)-**9l**[7]. Thus, the preferred absolute stereochemistry of **5l** was determined to be (2*S*,6*S*).

(2*S**,6*S**)-6-Furyl-2-phenyl-1,3-oxazinan-4-one (5m).



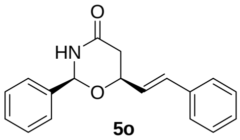
According to the general procedure for asymmetric HDA reaction of 2-aza-3-silyloxydienes with aldehydes, **5m** was prepared from diene **2a** (78.4 mg, 0.30 mmol), furfural (**3m**) (43.2 mg, 0.45 mmol), and $Rh_2(S\text{-BPTPI})_4 \cdot 3H_2O$ (**1**) (4.30 mg, 0.003 mmol, 1 mol %). The crude product was purified by column chromatography (silica gel, 9:1 $CHCl_3$/EtOAc) to provide **5m** (67.8 mg, 93%) as a white solid; mp 177.0–178.5 °C; TLC $R_f = 0.51$ (1:1 $CHCl_3$/EtOAc); $[\alpha]_D^{21}$ +6.57 (*c* 1.09, $CHCl_3$) for 95% ee; IR (KBr) 3176, 2923, 1672, 1396 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.73 (dd, *J* = 3.6, 17.2 Hz, 1H, C5–*H*), 3.09 (dd, *J* = 11.8, 17.2 Hz, 1H, C5–*H*), 5.08 (dd, *J* = 3.6, 11.8 Hz, 1H, C6–*H*), 5.92 (s, 1H, C2–*H*), 6.27 (br, 1H, N*H*), 6.37–6.43 (m, 2H, *Ar*), 7.40–7.50 (m, 6H, *Ar*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 35.0 (CH_2), 70.0 (CH), 85.7 (CH), 108.6 (CH), 110.4 (CH), 127.0 (CH), 128.9 (CH), 130.1 (CH), 137.3 (C), 143.2 (CH), 151.3 (C), 168.5 (C=O); EI-HRMS calcd for $C_{14}H_{12}NO_3$ $(M–H)^+$ 242.0895, found 242.0819. The enantiomeric excess of **5m** was determined to be 95% by HPLC with a Chiralpak AD-H column (9:1 hexane/*i*-PrOH, 1.0 mL/min): t_R = 32.9 min for minor enantiomer; t_R = 37.9 min for major enantiomer. The preferred absolute configuration of **5m** was not determined.

(2*S,6*S**)-2-Phenyl-6-(2-thienyl)-1,3-oxazinan-4-one (5n).**


5n

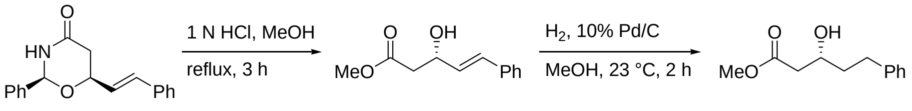
According to the general procedure for asymmetric HDA reaction of 2-aza-3-silyloxydienes with aldehydes, **5n** was prepared from diene **2a** (78.4 mg, 0.30 mmol), 2-thiophencarbaldehyde (**3n**) (50.5 mg, 0.45 mmol), and Rh_2(*S*-BPTPI)$_4$·$3H_2O$ (**1**) (4.30 mg, 0.003 mmol, 1 mol %). The crude product was purified by column chromatography (silica gel, 9:1 $CHCl_3$/EtOAc) to provide **5n** (63.1 mg, 81%) as a white solid; mp 159.0–160.0 °C; TLC R_f = 0.51 (1:1 $CHCl_3$/EtOAc); $[\alpha]_D^{21}$ +10.3 (*c* 1.03, $CHCl_3$) for 96% ee; IR (KBr) 3170, 2921, 1662, 1354 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.88 (dd, *J* = 4.1, 17.2 Hz, 1H, C5–*H*), 2.97 (dd, *J* = 11.3, 17.2 Hz, 1H, C5–*H*), 5.28 (dd, *J* = 4.1, 11.3 Hz, 1H, C6–*H*), 5.94 (s, 1H, C2–*H*), 6.24 (br, 1H, N*H*), 6.99–7.09 (m, 2H, *Ar*), 7.31–7.52 (m, 6H, *Ar*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.9 (CH_2), 72.7 (CH), 85.7 (CH), 125.0 (CH), 126.0 (CH), 126.8 (CH), 126.9 (CH), 128.9 (CH), 130.1 (C), 137.4 (CH), 142.2 (C), 168.2 (C=O); EI-HRMS calcd for $C_{14}H_{12}NO_2S$ $(M–H)^+$ 258.0667, found 258.0587. The enantiomeric excess of **5n** was determined to be 96% by HPLC with a Chiralpak AD-H column (9:1 hexane/*i*-PrOH, 1.0 mL/min): t_R = 22.3 min for minor enantiomer; t_R = 24.4 min for major enantiomer. The preferred absolute configuration of **5n** was not determined.

(2*S*,6*S*)-2-Phenyl-6-[(*E*)-2-phenylethenyl]-1,3-oxazinan-4-one (5o)


5o

According to the general procedure for asymmetric HDA reaction of 2-aza-3-silyloxydienes with aldehydes, **5o** was prepared from diene **2a** (78.4 mg, 0.30 mmol), (*E*)-cinnamaldehyde (**3o**) (59.4 mg, 0.45 mmol), and Rh_2(*S*-BPTPI)$_4$·$3H_2O$ (**1**) (4.3 mg, 0.003 mmol, 1 mol %). The crude product was purified by column chromatography (silica gel, 9:1 $CHCl_3$/EtOAc) to provide **5o** (73.7 mg, 88%) as a white solid; mp 138.0–139.5 °C; TLC R_f = 0.31 (1:1 $CHCl_3$/EtOAc); $[\alpha]_D^{22}$ –21.2 (*c* 1.17, $CHCl_3$) for 96% ee; IR (KBr) 3179, 1670 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.66–2.68 (m, 2H, C5–*H*), 4.67 (m, 1H, C6–*H*), 5.86 (s, 1H, C2–*H*), 6.19 (br, 1H, N*H*), 6.26 (dd, *J* = 6.3, 15.9 Hz, 1H, C*H*=CHPh), 6.68 (d, *J* = 15.9 Hz, 1H, CH=C*H*Ph), 7.24–7.28 (m, 1H, *Ar*), 7.30–7.34 (m, 2H, *Ar*), 7.38–7.40 (m, 2H, *Ar*), 7.43–7.45 (m, 3H, *Ar*), 7.49–7.52 (m, 2H, *Ar*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.2 (CH_2), 75.2 (CH), 85.3 (CH), 126.5 (CH), 126.8 (CH), 126.9 (CH), 128.1 (CH), 128.5 (CH), 128.7 (CH), 129.8 (CH), 132.2 (CH), 135.8 (C), 137.5 (C), 169.1 (C=O); EI-HRMS calcd for $C_{18}H_{17}NO_2$ $(M)^+$ 279.1259, found 279.1255. The enantiomeric excess of **5o** was determined to be 96% by HPLC with a Chiralpak AD-H column (3:1 hexane/*i*-PrOH, 1.0 mL/min): t_R (minor) = 8.2 min for (2*R*,6*R*)-enantiomer; t_R (major) = 9.3 min for (2*S*,6*S*)-enantiomer. A sample for combustion analysis was obtained by recrystallizations from *i*-PrOH as colorless needles (99% ee); mp 138.5–139.5 °C; Anal. Calcd for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.13; N, 5.01. Found: C, 76.42; H, 6.10; N, 5.05.

Determination of absolute configuration of 5o:
Methyl (*R*)-3-hydroxy-5-phenylpentanoate (9p).[10]

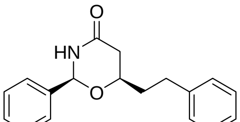


5o **9o** **9p**

AcCl (0.14 mL, 2 mmol) was added to MeOH (1 mL). This solution was added to a solution of **5o** (40 mg, 0.13 mmol, 96% ee) in MeOH (1 mL) at 0 °C. After stirring at reflux temperature for 3 h, the reaction was quenched with saturated $NaHCO_3$ (2 mL), and the whole was extracted with EtOAc (20 mL). The organic layer was washed with water (3 mL) and brine (2 × 3 mL), and dried over anhydrous Na_2SO_4. The solvent was removed *in vacuo* to give the crude product (40 mg) as yellow oil, which was purified by column chromatography (4:1 hexane/EtOAc) to afford **9o** (7.5 mg, 26%) as a colorless oil; TLC R_f = 0.24 (2:1 hexane/EtOAc); $[\alpha]_D^{18}$ –1.2 (*c* 0.38, $CHCl_3$) for 96% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 2.56 (dd, *J* = 5.0, 15.0 Hz, 1H, C2–*H*), 2.71 (dd, *J* = 8.2, 15.0 Hz, 1H, C2–*H*), 3.70 (s, 3H, OCH_3), 4.22 (ddd, *J* = 5.0, 7.7, 8.2, Hz, 1H, C3–*H*), 6.07 (dd, *J* = 7.7, 15.8 Hz, 1H, C4–*H*), 6.62 (d, *J* = 15.8 Hz, 1H, C5–*H*), 7.24–7.42 (m, 5H, *Ar*).

To a solution of **9o** in MeOH (2 mL) was added 10% Pd/C (10 mg), and the resulting mixture was stirred under hydrogen at atmospheric pressure at 23 °C for 2 h. The reaction mixture was then filtered through a plug of Celite, and the Celite filter cake was washed with MeOH (5 mL). The filtrate was concentrated *in vacuo*, and the residue was purified by column chromatography (silica gel, 4:1 hexane/EtOAc) to afford **9p** (7.4 mg, 97%) as a colorless oil; $[\alpha]_D^{22}$ +1.8 (*c* 0.37, $CHCl_3$) for 96% ee [lit.,[10] $[\alpha]_D$ –2.68 (*c* 0.67, $CHCl_3$) for (*S*)-enantiomer]. This product **9p** exhibited spectroscopic data identical to (*S*)-**9p**[10], except for the sign of optical rotation. Thus, the preferred absolute stereochemistry of **5o** was determined to be (2*S*,6*S*).

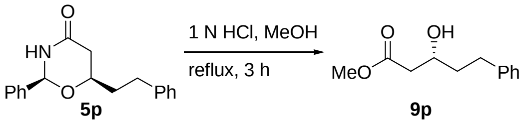
(2*S*,6*R*)-2-Phenyl-6-(2-phenylethyl)-1,3-oxazinan-4-one (5p).



5p

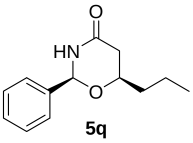
According to the general procedure for asymmetric HDA reaction of 2-aza-3-silyloxydienes with aldehydes, **5p** was prepared from diene **2a** (78.4 mg, 0.30 mmol), hydrocinnamaldehyde (**3p**) (60.3 mg, 0.45 mmol), and $Rh_2(S\text{-BPTPI})_4{\cdot}3H_2O$ (**1**) (4.3 mg, 0.003 mmol, 1 mol %). The crude product was purified by column chromatography (silica gel, 9:1 $CHCl_3$/EtOAc) to provide **5p** (80.0 mg, 95%) as a white solid; mp 128.0–129.5 °C; TLC R_f = 0.36 (1:1 $CHCl_3$/EtOAc); $[\alpha]_D^{22}$ +22.6 (*c* 1.17, $CHCl_3$) for 92% ee; IR (KBr) 3250, 1664, 1633 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.89 (m, 1H, C*H*HCH$_2$Ph), 2.04 (m, 1H, CH*H*CH$_2$Ph), 2.40–2.50 (m, 2H, C5–*H*), 2.70–2.85 (m, 2H, CH$_2$C*H*$_2$Ph), 3.90 (m, 1H, C6–*H*), 5.69 (s, 1H, C2–*H*), 6.20 (br, 1H, N*H*), 7.17–7.23 (m, 3H, *Ar*), 7.28–7.32 (m, 2H, *Ar*), 7.43–7.49 (m, 5H, *Ar*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.0 (CH_2), 36.8 (CH_2), 37.3 (CH_2), 73.8 (CH), 85.4 (CH), 126.0 (CH), 126.7 (CH), 128.36 (CH), 128.42 (CH), 128.8 (CH), 129.7 (CH), 137.9 (C), 141.0 (C), 169.3 (C=O); EI-HRMS calcd for $C_{18}H_{19}NO_2$ $(M)^+$ 281.1416, found 281.1409. Anal. Calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98. Found: C, 76.79; H, 6.86; N, 4.97. A sample for combustion analysis was obtained by recrystallizations from *i*-PrOH as colorless needles (95% ee); mp 128.5–129.5 °C; Anal. Calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98. Found: C, 76.75; H, 6.83; N, 5.01.

Determination of absolute configuration and enantiomeric excess of 5p: Methyl (*R*)-3-hydroxy-5-phenylpentanoate (9p).[10]



According to the procedure for the preparation of **9a**, **9p** was prepared from **5p** (40.0 mg, 0.14 mmol, 92% ee), AcCl (0.14 mL, 2 mmol) and MeOH (2 mL). The crude product was purified by column chromatography (silica gel, 4:1 hexane/EtOAc) to provide **9p** (23.6 mg, 83%) as a colorless oil; $[\alpha]_D^{19}$ +1.9 (*c* 1.09, $CHCl_3$) for 92% ee [lit.,[10] $[\alpha]_D$ –2.68 (*c* 0.67, $CHCl_3$) for (*S*)-enantiomer]. The enantiomeric excess of **9p** was determined to be 92% by HPLC with a Chiralcel OD-H column (19:1 hexane/*i*-PrOH, 1.0 mL/min): t_R (minor) = 19.2 min for (*S*)-enantiomer; t_R (major) = 21.4 min for (*R*)-enantiomer. This product **9p** exhibited spectroscopic data identical to (*S*)-**9p**[10], except for the sign of optical rotation. Thus, the preferred absolute stereochemistry of **5p** was determined to be (2*S*,6*R*).

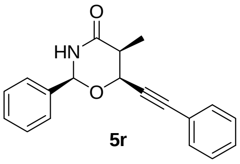
(2*S**,6*R**)-2-Phenyl-6-propyl-1,3-oxazinan-4-one (5q).



5q

According to the general procedure for asymmetric HDA reaction of 2-aza-3-silyloxydienes with aldehydes, **5q** was prepared from diene **2a** (78.4 mg, 0.30 mmol), butyraldehyde (**3q**) (64.9 mg, 0.90 mmol), and Rh_2(*S*-BPTPI)$_4$·3H_2O (**1**) (4.3 mg, 0.003 mmol, 1 mol %). The crude product was purified by column chromatography (silica gel, 9:1 $CHCl_3$/EtOAc) to provide **5q** (60.2 mg, 92%) as a white solid; mp 92.0–93.0 °C; TLC R_f = 0.35 (1:1 $CHCl_3$/EtOAc); $[\alpha]_D^{22}$ –16.7 (*c* 1.22, $CHCl_3$) for 93% ee; IR (KBr) 3212, 1658, 1623 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, *J* = 7.4 Hz, 3H, C*H*$_3$), 1.37–1.58 (m, 3H, C*H*HC*H*$_2$), 1.63–1.73 (m, 1H, CH*H*CH$_2$), 2.32–2.44 (m, 2H, C5–*H*), 3.94 (m, 1H, C6–*H*), 5.72 (s, 1H, C2–*H*), 6.65 (br, 1H, N*H*), 7.36–7.46 (m, 5H, *Ar*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7 (CH_3), 18.0 (CH_2), 37.2 (CH_2), 37.4 (CH_2), 74.5 (CH), 85.1 (CH), 126.6 (CH), 128.5 (CH), 129.4 (CH), 137.9 (C), 169.6 (C=O); EI-HRMS calcd for $C_{13}H_{17}NO_2$ $(M)^+$ 219.1259, found 219.1267. The enantiomeric excess of **5q** was determined to be 93% by HPLC with a Chiralpak AD-H column (9:1 hexane/*i*-PrOH, 1.0 mL/min): t_R = 9.2 min for minor enantiomer; t_R = 11.1 min for major enantiomer. The preferred absolute configuration of **5q** was not determined. A sample for combustion analysis was obtained by recrystallizations from *i*-PrOH as colorless needles (93% ee); mp 93.0–94.0 °C; Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39. Found: C, 71.19; H, 7.86; N, 6.37.

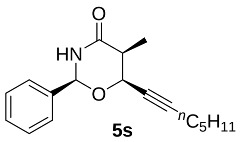
(2*S,5*S**,6*S**)-5-Methyl-2-phenyl-6-phenylethynyl-1,3-oxazinan-4-one (5r).**



5r

According to the general procedure for asymmetric HDA reaction of 2-aza-3-silyloxydienes with aldehydes, **5r** was prepared from diene **2d** (82.6 mg, 0.30 mmol), phenylpropargylaldehyde (**3j**) (58.6 mg, 0.45 mmol), and $Rh_2(S\text{-BPTPI})_4{\cdot}3H_2O$ (**1**) (4.3 mg, 0.003 mmol, 1 mol %) at 0 °C. The crude product was purified by column chromatography (silica gel, 9:1 $CHCl_3$/EtOAc) to provide **5r** (82.9 mg, 95%) as a white solid; mp 173–175 °C; TLC R_f = 0.26 (2:1 $CHCl_3$/EtOAc); $[\alpha]_D^{21}$ –15.5 (*c* 1.01, $CHCl_3$) for 91% ee; IR (KBr) 2236, 1665 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.61 (d, *J* = 7.2 Hz, 3H, C5–C*H*$_3$), 2.74 (dq, *J* = 3.2, 7.2 Hz, 1H, C5–*H*), 5.10 (d, *J* = 3.2 Hz, 1H, C6–*H*), 5.84 (s, 1H, C2–*H*), 6.08 (br, 1H, N*H*), 7.29–7.36 (m, 3H, *Ar*), 7.42–7.51 (m, 7H, *Ar*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7 (CH_3), 40.5 (CH), 69.4 (CH), 83.8 (C), 85.5 (CH), 88.3 (C), 121.8 (C), 127.0 (CH), 128.2 (CH), 128.8 (CH), 128.9 (CH), 130.0 (CH), 131.8 (CH), 137.3 (C), 172.5 (C=O); EI-HRMS calcd for $C_{19}H_{17}NO_2$ $(M)^+$ 291.1259, found 291.1259. The enantiomeric excess of **5r** was determined to be 91% by HPLC with a Chiralcel OD-H column (1:1 hexane/*i*-PrOH, 1.0 mL/min): t_R = 7.2 min for minor enantiomer; t_R = 13.9 min for major enantiomer. A sample for combustion analysis was obtained by recrystallizations from 4:1 hexane/EtOAc as colorless needles (96% ee); mp 184.0–185.0 °C; Anal. Calcd for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.27; H, 5.97; N, 4.78. In order to assign the stereochemistry at C2, C5 and C6, NOE studies were performed on **5r**. Irradiation of C2–H showed NOE with C6–H (15.4%) and the *ortho* proton of the phenyl group (10.3%). Irradiation of C5–H exhibited NOE with C6–H (8.4%) and C5–Me (5.7%). Irradiation of C6–H showed NOE with C2–H (15.4%) and C5–H (8.6%). These data revealed *cis* relationship between C2–H, C5–H and C6–H. The preferred absolute configuration of **5r** was not determined.

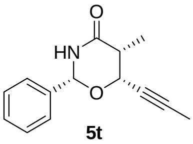
(2*S,5*S**,6*S**)-5-Methyl-2-phenyl-6-(1-heptenyl)-1,3-oxazinan-4-one (5s)**



5s

According to the general procedure for asymmetric HDA reaction of 2-aza-3-silyloxydienes with aldehydes, **5s** was prepared from diene **2d** (82.6 mg, 0.30 mmol), 2-octynal (**3k**) (55.9 mg, 0.45 mmol), and $Rh_2(S\text{-BPTPI})_4{\cdot}3H_2O$ (**1**) (4.3 mg, 0.003 mmol, 1 mol %) at 0 °C. The crude product was purified by column chromatography (silica gel, 2:1 hexane/EtOAc) to provide **5s** (76.2 mg, 89%) as a white solid; mp 109.5–110.5 °C; TLC R_f = 0.53 (1:3 hexane/EtOAc); $[\alpha]_D^{20}$ –14.2 (*c* 1.18, $CHCl_3$) for 92% ee; IR (KBr) 2236, 1665 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, *J* = 6.7 Hz, 3H, CH_2CH_3), 1.28–1.39 (m, 4H, $CH_2CH_2CH_2CH_3$), 1.50–1.54 (m, 5H, C5–CH_3 and C≡CCH_2CH_2), 2.24 (dt, *J* = 1.8, 7.1 Hz, 2H, C≡CCH_2), 2.62 (dq, *J* = 3.5, 10.8 Hz, 1H, C5–*H*), 4.86 (dt, *J* = 1.8, 3.5 Hz, 1H, C6–*H*), 5.77 (s, 1H, C2–*H*), 5.85 (br, 1H, N*H*), 7.40–7.47 (m, 5H, *Ar*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5 (CH_3), 13.9 (CH_3), 18.6 (CH_2), 22.0 (CH_2), 27.9 (CH_2), 30.9 (CH_2), 40.5 (CH), 69.0 (CH), 74.9 (C), 85.3 (CH), 89.6 (C), 126.9 (CH), 128.6 (CH), 129.8 (CH), 137.4 (C), 172.8 (C=O); EI-HRMS calcd for $C_{18}H_{22}NO_2$ $(M-H)^+$ 284.16505, found 284.16485; The enantiomeric excess of **5s** was determined to be 92% by HPLC with a Chiralcel OD-H column (9:1 hexane/*i*-PrOH, 1.0 mL/min): t_R = 10.3 min for minor enantiomer; t_R = 14.3 min for major enantiomer. The preferred absolute configuration of **5s** was not determined. A sample for combustion analysis was obtained by recrystallizations from 4:1 hexane/EtOAc as colorless needles (97% ee); mp 110.0–110.5 °C; Anal. Calcd for $C_{18}H_{23}NO_2$: C, 75.76; H, 8.12; N, 4.91. Found: C, 75.56; H, 7.89; N, 4.93.

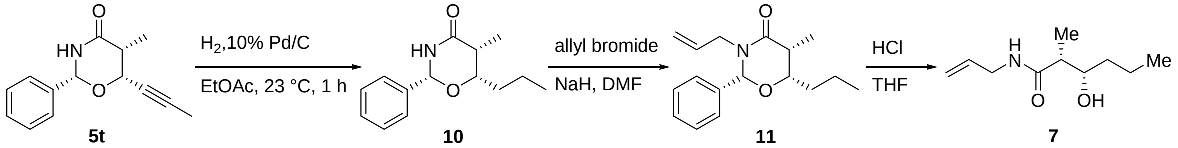
(2*R**,5*R**,6*R**)-5-Methyl-2-phenyl-6-(1-propynyl)-1,3-oxazinan-4-one (5t)



5t

To a solution of diene **2d** (110 mg, 0.40 mmol) and $Rh_2(R\text{-BPTPI})_4\cdot3H_2O$ (**8**) (5.7 mg, 0.004 mmol, 1 mol %) in CH_2Cl_2 (0.4 mL) was added *ca.* 1.5 M solution of 2-butynal (**3r**)[11] in CH_2Cl_2 (0.4 mL) added at –10 °C. After stirring at this temperature for 24 h, MeOH (ca. 0.1 mL) was added and the mixture was stirred for an additional 0.5 h. The mixture was concentrated *in vacuo* furnished the crude product (150 mg) as a purple solid, which was purified by column chromatography (silica gel, 9:1 $CHCl_3$/EtOAc) to give **5t** (83.5 mg, 91%) as a white solid; mp 196.0–197.5 °C; TLC R_f = 0.43 (1:1 $CHCl_3$/EtOAc); $[\alpha]_D^{17}$ +13.2 (*c* 1.08, $CHCl_3$) for 93% ee; IR (KBr) 3169, 1675, 1480 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.45 (d, *J* = 7.2 Hz, 3H, C5–CH_3), 1.87 (d, *J* = 2.3 Hz, 3H, C≡CCH_3), 2.54 (m, 1H, C5–*H*), 4.80 (m, 1H, C6–*H*), 5.74 (s, 1H, C2–*H*), 6.64 (br, 1H, N*H*), 7.38–7.45 (m, 5H, *Ar*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 3.7 (CH_3), 13.6 (CH_3), 40.6 (CH), 69.2 (CH), 74.1 (C), 85.3 (C), 85.4 (CH), 128.0 (CH), 128.8 (CH), 130.0 (CH), 137.3 (C), 172.7 (C=O); EI-HRMS calcd for $C_{14}H_{14}NO_2$ $(M–H)^+$ 228.1103, found 228.1020. The enantiomeric excess of **5t** was determined to be 93% by HPLC with a Chiralpak AD-H column (9:1 hexane/*i*-PrOH, 1.0 mL/min): t_R = 11.0 min for major enantiomer; t_R = 20.3 min for minor enantiomer. The preferred absolute configuration of **5t** was not determined. A sample for combustion analysis was obtained by recrystallizations from *i*-PrOH as colorless needles (91% ee); mp 196.5–197.5 °C; Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.57; H, 6.64; N, 6.15. In order to assign the stereochemistry at C2, C5 and C6, NOE studies were performed on **5t**. Irradiation of C2–H showed NOE with C6–H (9.1%) and the *ortho* proton of the phenyl group (4.2%). Irradiation of C5–H exhibited NOE with C6–H (5.2%) and C5–Me (4.6%). Irradiation of C6–H showed NOE with C2–H (6.6%) and C5–H (6.0%). These data revealed *cis* relationship between C2–H, C5–H and C6–H.

(2*S**,3*S**)-3-Hydroxy-2-methyl-*N*-(2-propenyl)hexanamide (7).



To a solution of **5t** (70.0 mg, 0.31 mmol) in EtOAc (2 mL) was added 10% Pd/C (35 mg), and the resulting mixture was stirred under hydrogen at atmospheric pressure at 23 °C for 1 h. The reaction mixture was then filtered through a plug of Celite, and the Celite filter cake was washed with EtOAc (5 mL). The filtrate was concentrated *in vacuo*, and the residue was purified by column chromatography (silica gel, 1:1 hexane/EtOAc) to afford **10** (65.4 mg, 94%) as a white solid; mp 78.5–80.0 °C; TLC R_f = 0.47 (1:3 hexane/EtOAc); $[\alpha]_D^{19}$ +1.02 (*c* 1.03, $CHCl_3$) for 93% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, *J* = 7.2 Hz, 3H, $CH_2H_2CH_3$), 1.25–1.69 (m, 7H, $CH_2H_2CH_3$ and C5–CH_3), 2.46 (m, 1H, C5–*H*), 3.99 (m, 1H, C6–*H*), 5.73 (s, 1H, C2–*H*), 6.06 (br, 1H, N*H*), 7.40–7.45 (m, 5H, *Ar*).

To a suspension of NaH (10.8 mg, 0.45 mol) in DMF (1 mL) was added a solution of **10** (64.0 mg, 0.27 mmol) and allyl bromide (54.4 mg, 0.45 mmol) at 0 °C. After stirring at 23 °C for 1 h, the reaction was quenched with saturated aqueous NH_4Cl (1 mL), and the whole was extracted with EtOAc (20 mL). The organic layer was washed with water (3 mL) and brine (2 × 3 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* followed by column chromatography (silica gel, 3:1 hexane/EtOAc) provided **11** (70.8 mg, 96%) as a colorless oil; TLC R_f = 0.46 (2:1 hexane/EtOAc); $[\alpha]_D^{21}$ –69.3 (*c* 1.05, $CHCl_3$) for 93% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, *J* = 7.2 Hz, 3H, $CH_2H_2CH_3$), 1.32–1.64 (m, 7H, $CH_2H_2CH_3$ and C5–CH_3), 2.54 (ddd, *J* = 2.3, 7.2, 14.5 Hz, 1H, C5–*H*), 3.03 (ddt, *J* = 1.4, 7.2, 15.4 Hz, 1H, N–C*H*H), 3.94 (m, 1H, C6–*H*), 4.38 (ddt, *J* = 1.8, 4.5, 15.4 Hz, 1H, N–CH*H*), 4.88 (dd, *J* = 1.4, 17.2 Hz, 1H, NCH_2CH=CH*H*), 5.04 (dd, *J* = 1.4, 10.3Hz, 1H, NCH_2CH=C*H*H), 5.61–5.63 (m, 2H, NCH_2CH=CH_2 and C2–*H*), 7.35–7.41 (m, 5H, *Ar*).

To a solution of **11** (65.0 mg, 0.24 mmol) in THF (2 mL) was added a 2*N* aqueous HCl (1 mL). After stirring at 70 °C for 7 h, the reaction was quenched with saturated $NaHCO_3$ (2 mL), and the whole was extracted with EtOAc (20 mL). The organic layer was washed with water (3 mL) and brine (2 × 3 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation *in vacuo* followed by column chromatography (silica gel, 9:1 $CHCl_3$/EtOAc) provided **7** (40.4 mg, 91%) as a white solid; mp 120.0–121.5 °C; TLC R_f = 0.44 (1:1 $CHCl_3$/EtOAc); $[\alpha]_D^{18}$ –11.2 (*c* 1.12, $CHCl_3$) for 93% ee; IR (KBr) 3354, 1639, 1550 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, *J* = 7.4 Hz, 3H, C5–*H*), 1.18 (d, *J* = 7.4 Hz, 3H, C2–CH_3), 1.31–1.36 (m, 2H, C5–*H*), 1.47–1.52 (m, 2H, C5–*H*), 2.32 (ddd, *J* = 2.9, 7.4, 14.3 Hz, 1H, C2–*H*), 3.88–3.91 (m, 3H, C3–*H* and NCH_2), 5.14–5.22 (m, 2H, NCH_2CH=CH_2), 5.85 (m, 1H, NCH_2CH=CH_2), 5.99 (br, 1H,O*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 6.4 (CH_3), 11.2 (CH_3), 19.1 (CH_2), 35.6 (CH_2), 41.5 (CH_2), 44.5 (CH), 71.6 (CH), 116.2 (CH_2), 134.0 (CH), 176.5 (C=O); EI-HRMS calcd for $C_{10}H_{19}NO_2$ $(M)^+$ 185.14158, found 185.14163. A sample for combustion analysis was obtained by recrystallizations from 1:2 hexane/EtOAc as colorless needles; mp 120.5–121.5 °C; Anal. Calcd for $C_{10}H_{19}NO_2$: C, 64.83; H, 10.34; N, 7.56. Found: C, 64.53; H, 10.30; N, 7.58.

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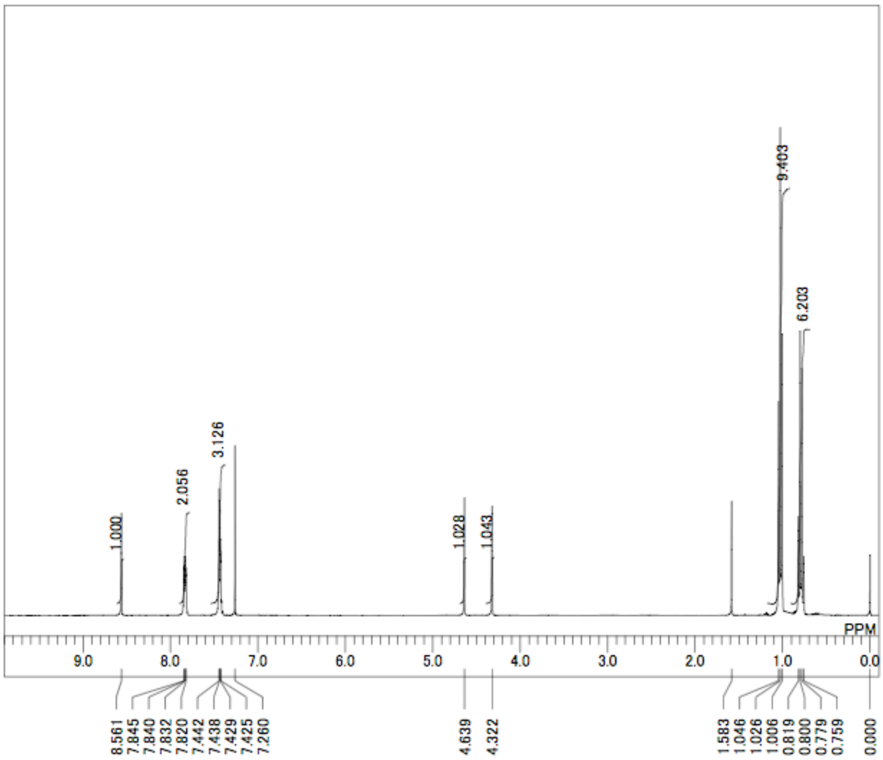

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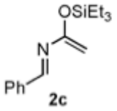

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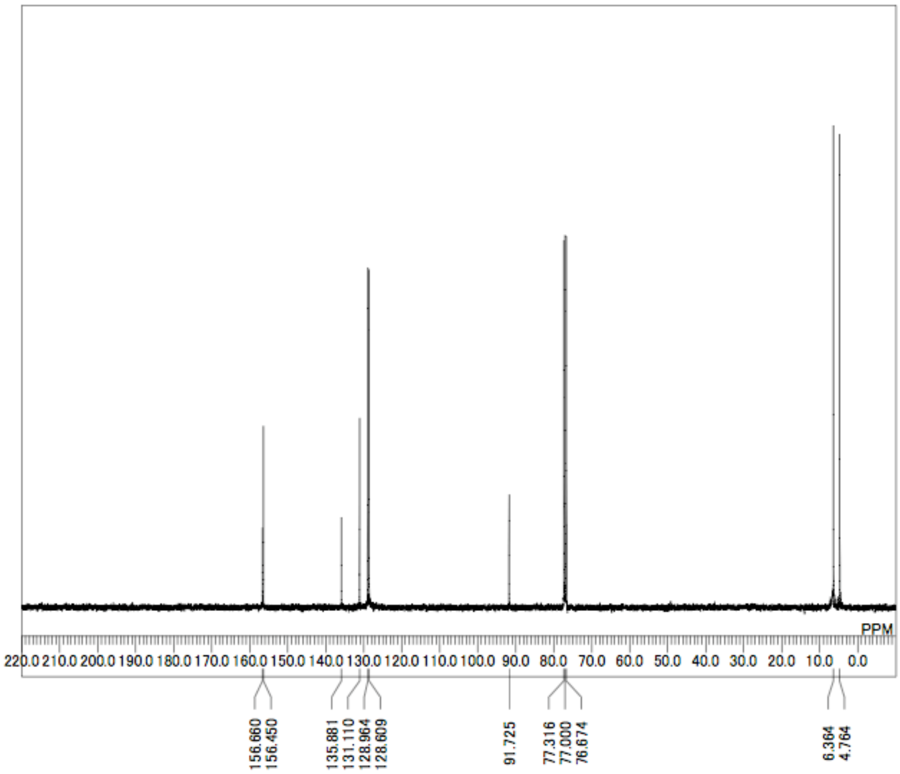

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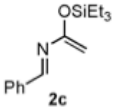

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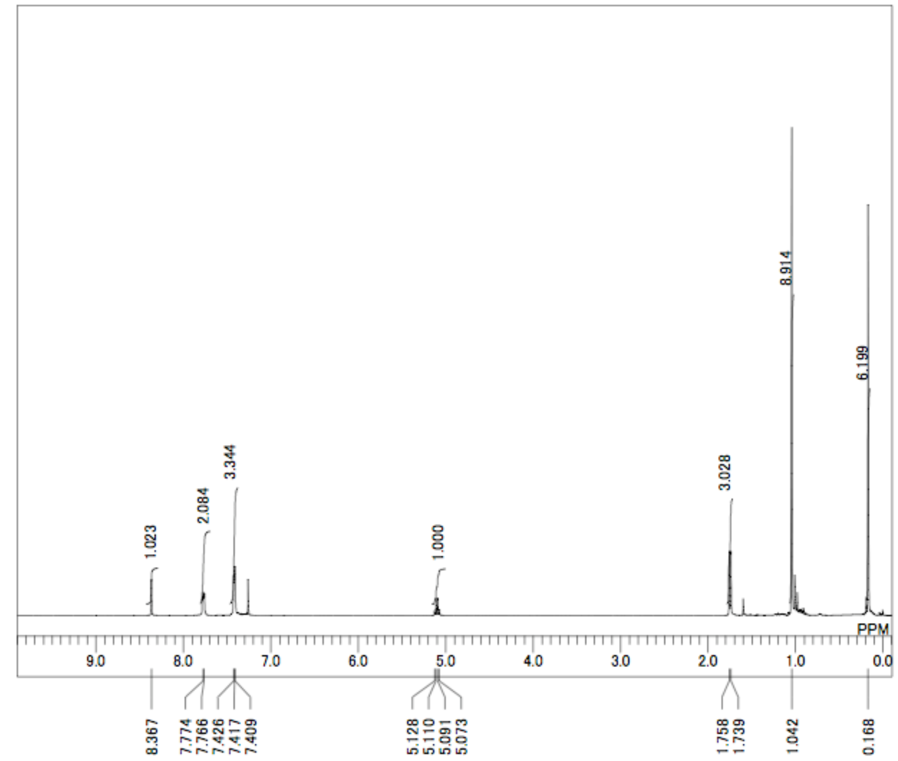

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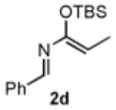

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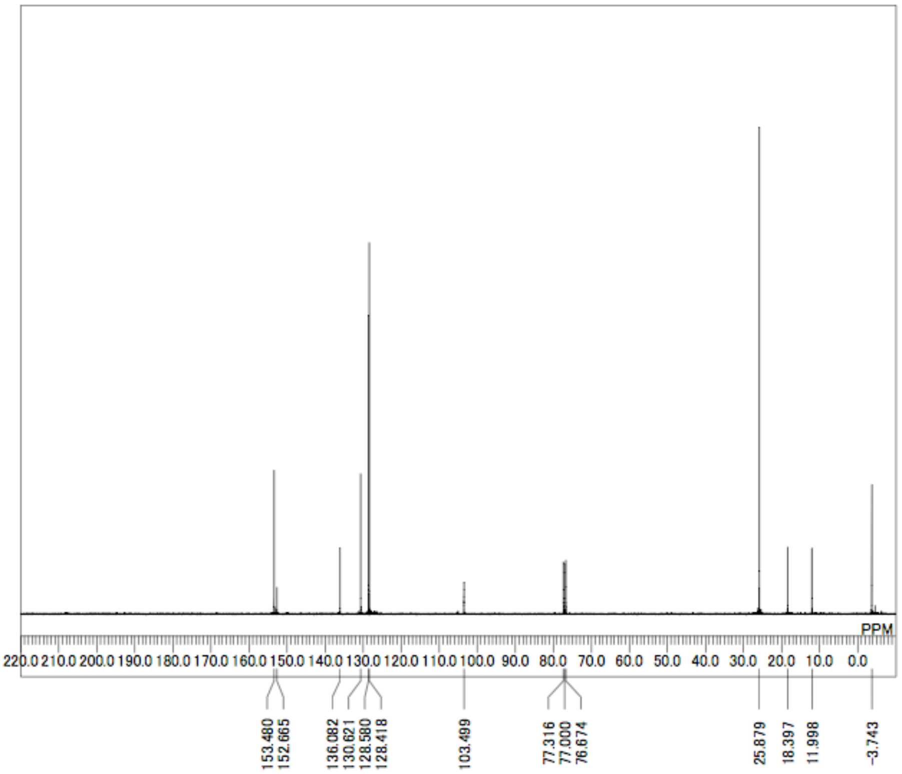

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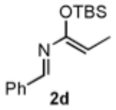

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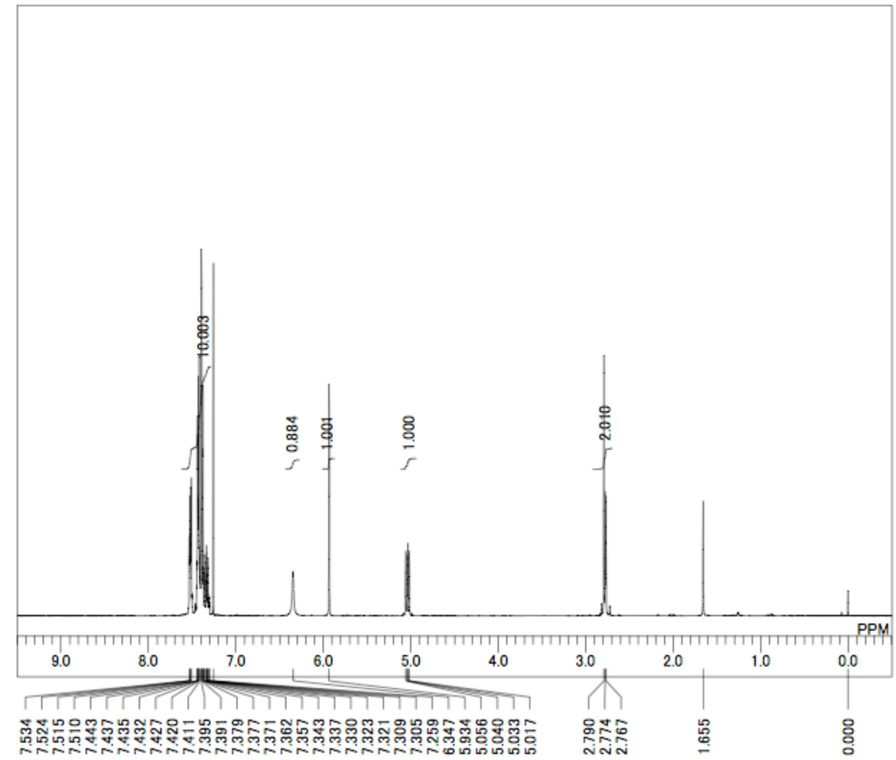

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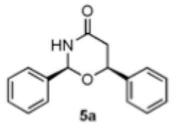

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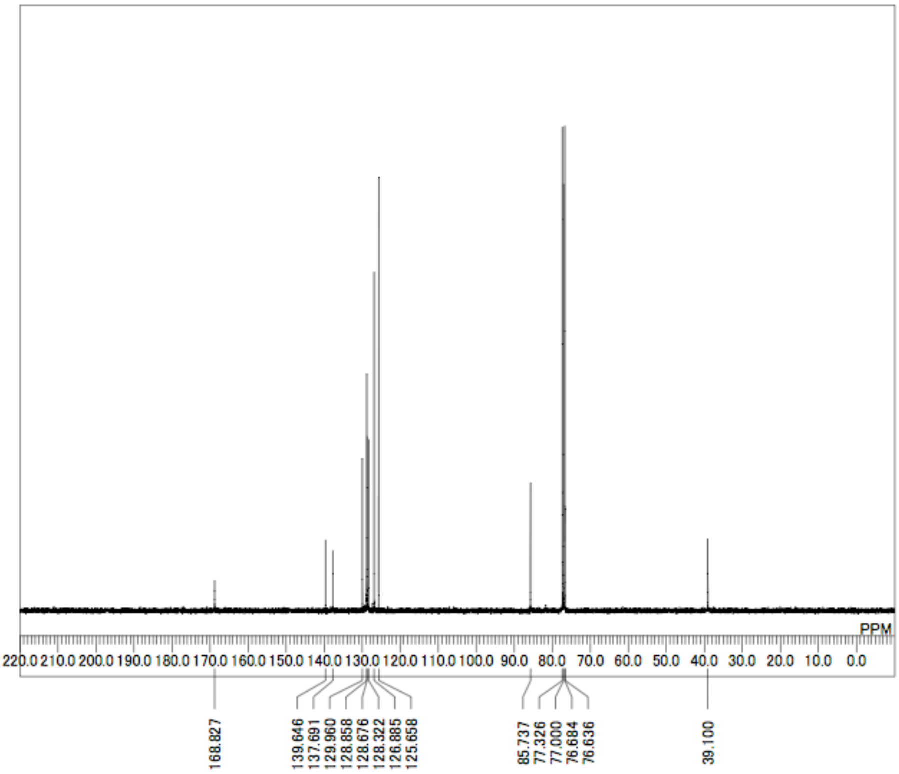

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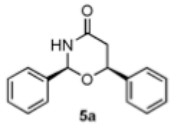

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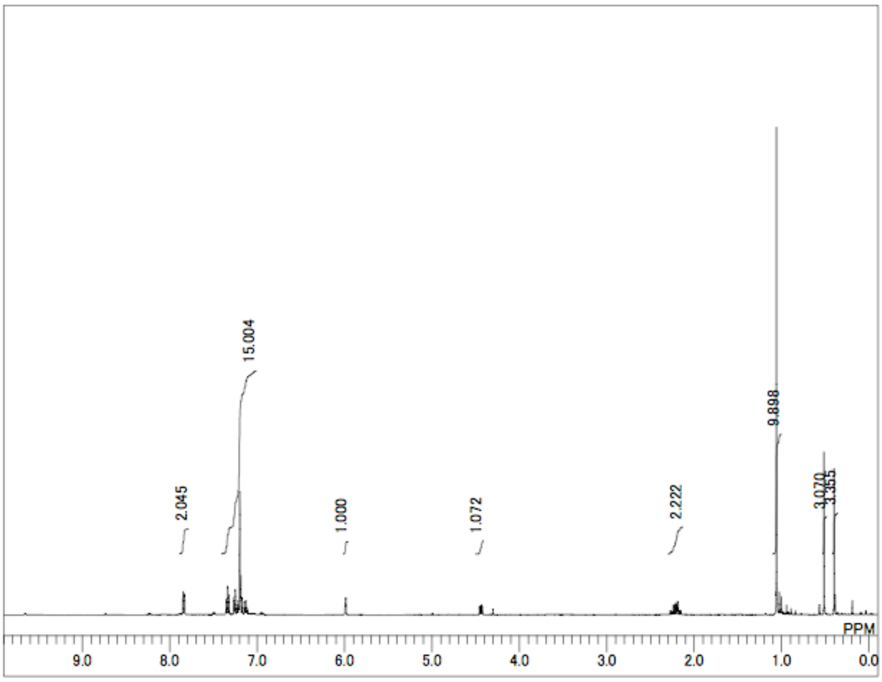

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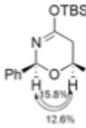

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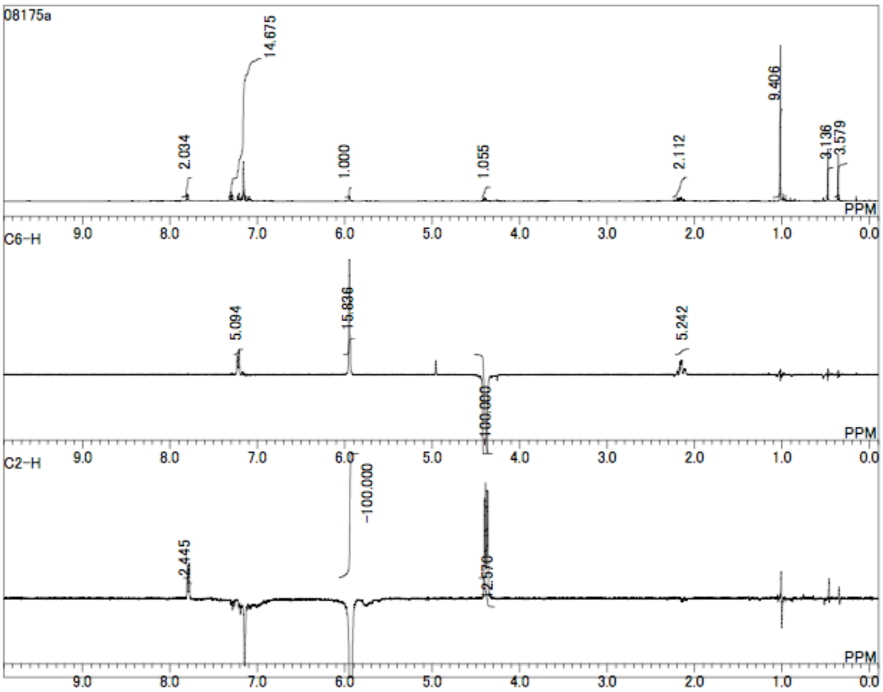

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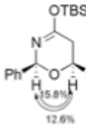

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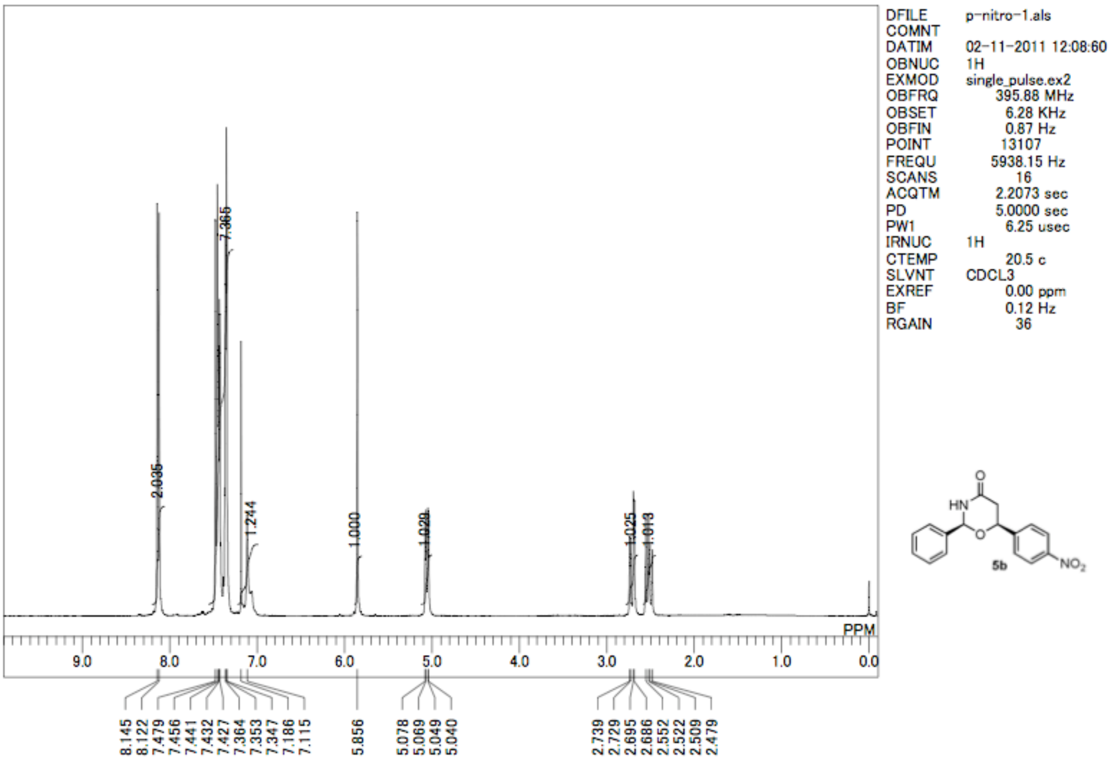

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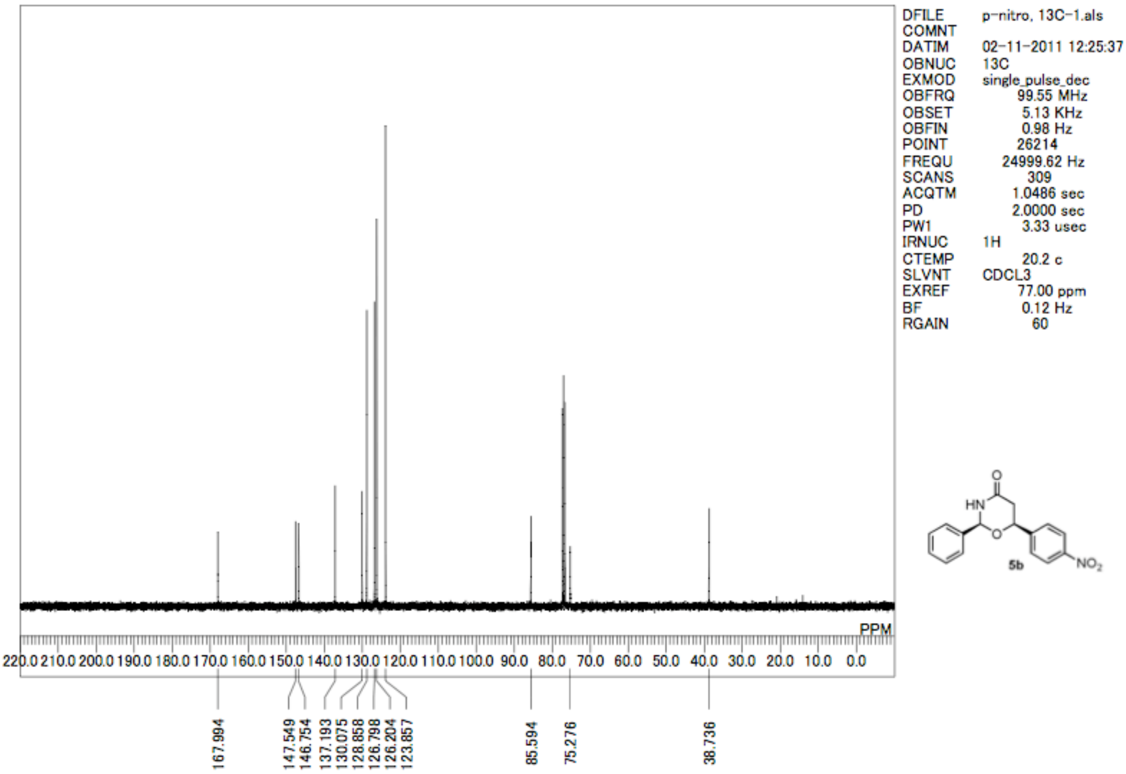

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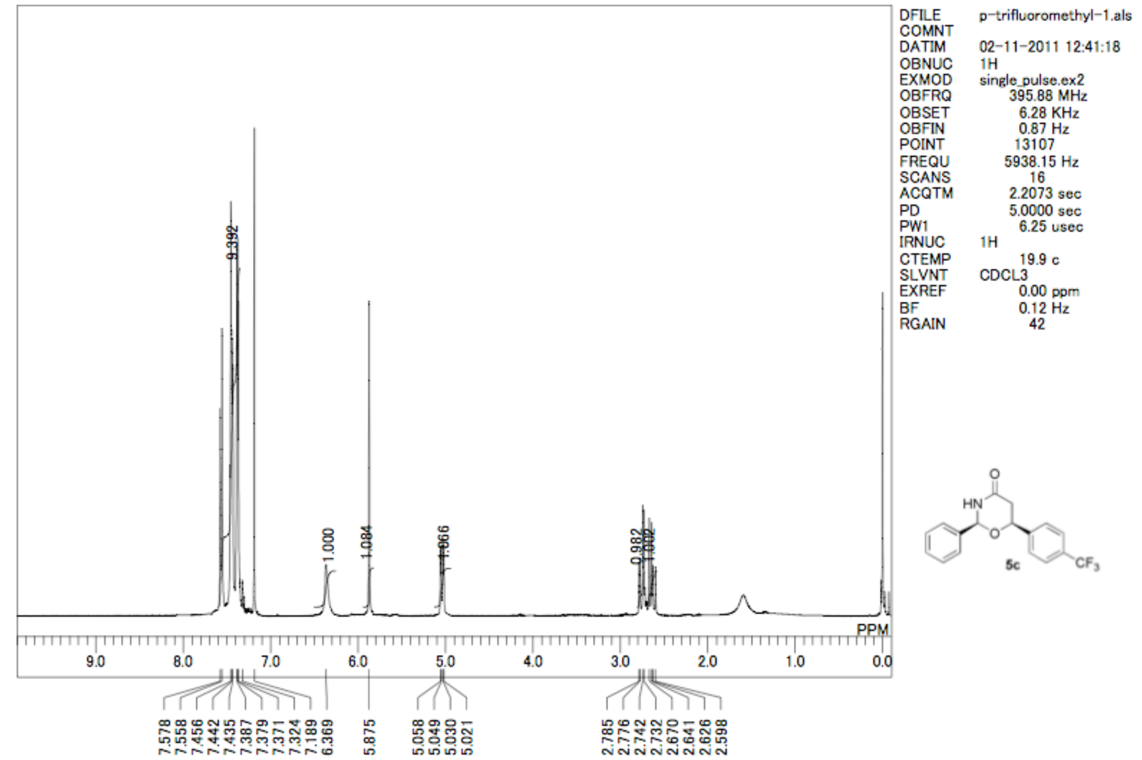

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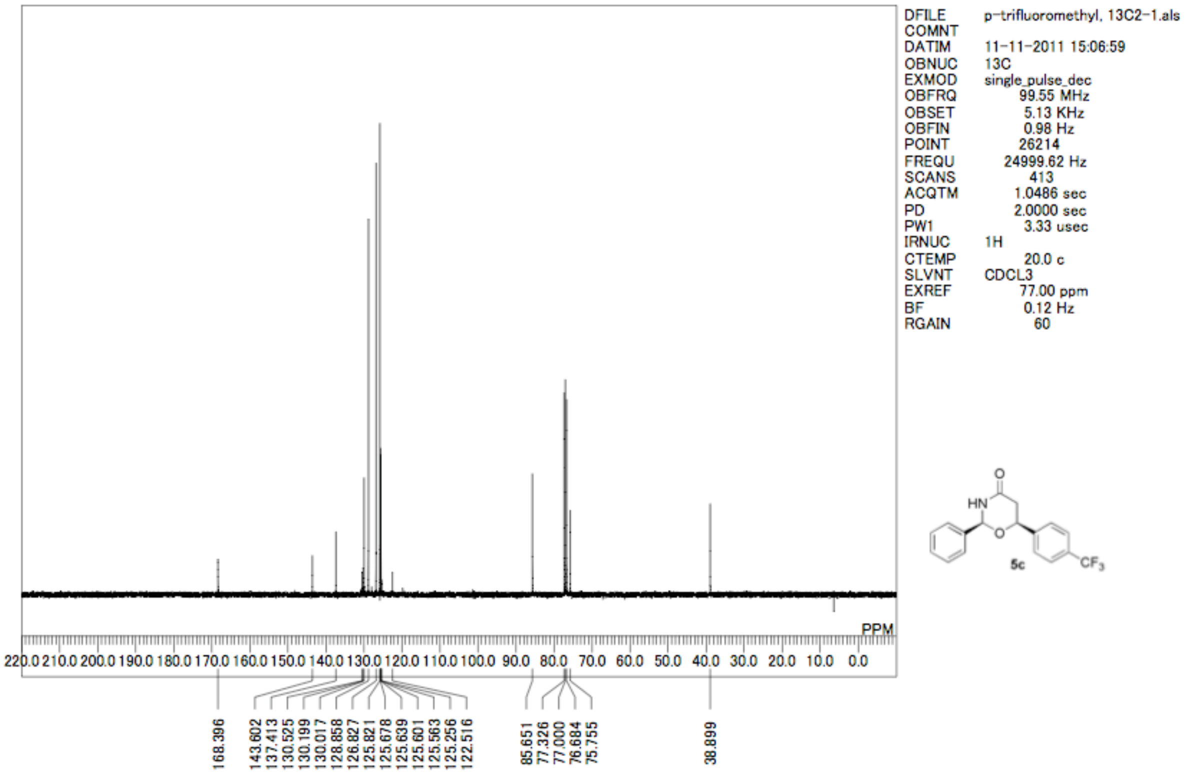
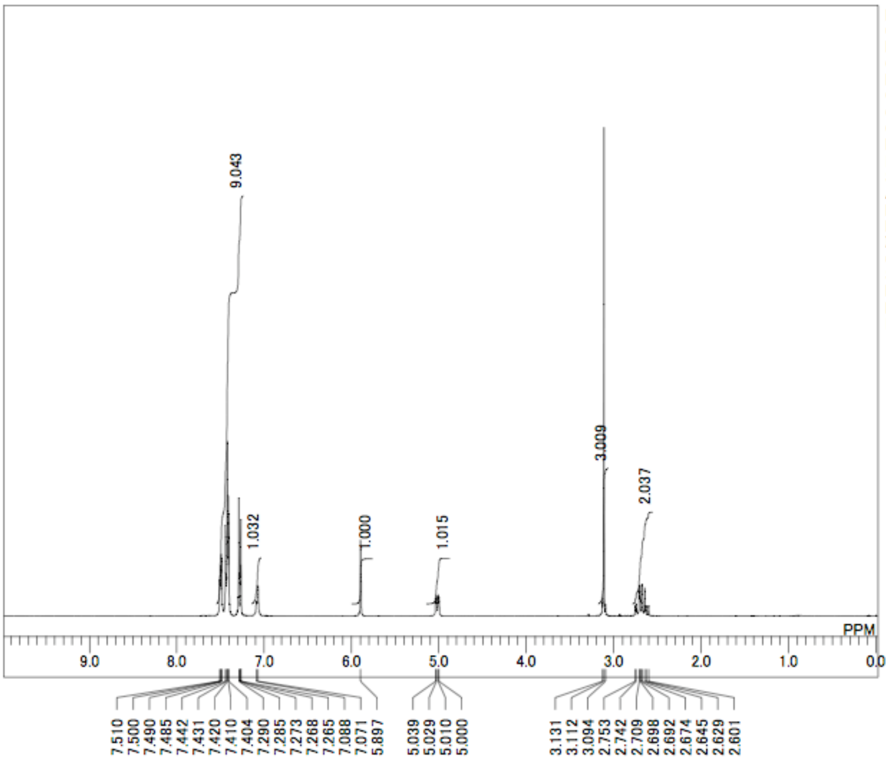
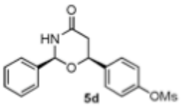
OBSET 6.28 KHz
OBFIN 0.87 Hz
POINT 13107
FREQU 5938.15 Hz
SCANS 16
ACQTM 2.2073 sec
PD 5.0000 sec
PW1 6.25 usec
IRNUC 1H
CTEMP 19.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 42



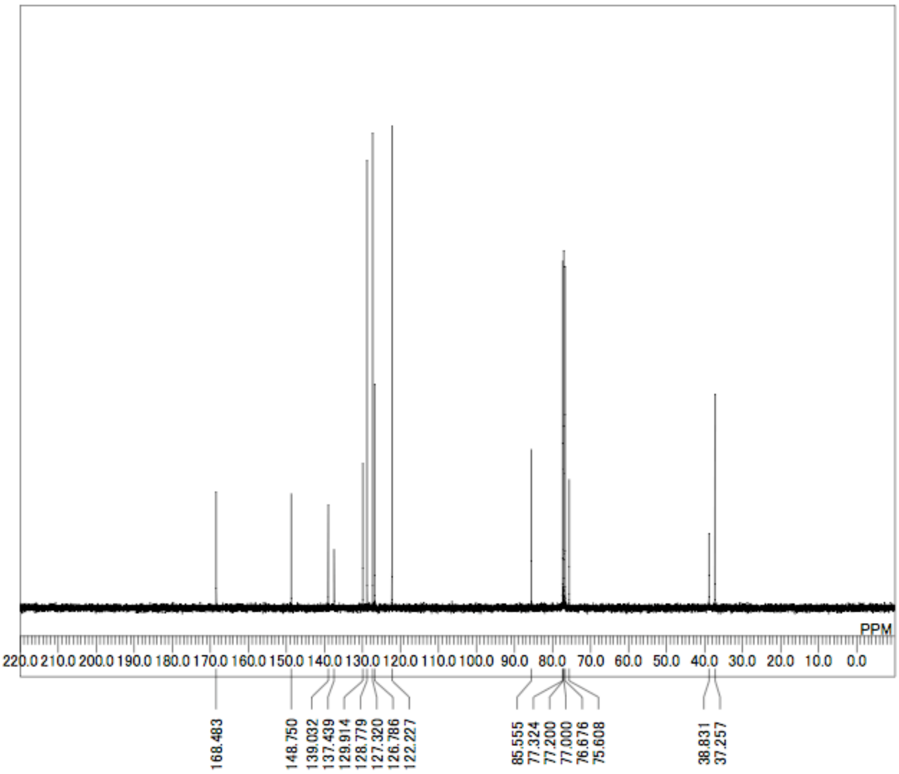
DFILE p−trifluoromethyl, 13C2−1.als
COMNT
DATIM 11−11−2011 15:06:59
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 99.55 MHz
OBSET 5.13 KHz
OBFIN 0.98 Hz
POINT 26214
FREQU 24999.62 Hz
SCANS 413
ACQTM 1.0486 sec
PD 2.0000 sec
PW1 3.33 usec
IRNUC 1H
CTEMP 20.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60



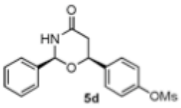
DFILE	p-mesyl.als
COMNT	
DATIM	12-11-2011 15:41:18
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	391.78 MHz
OBSET	8.51 KHz
OBFIN	3.34 Hz
POINT	13107
FREQU	5882.26 Hz
SCANS	16
ACQTM	2.2282 sec
PD	5.0000 sec
PW1	5.62 usec
IRNUC	1H
CTEMP	19.7 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	28



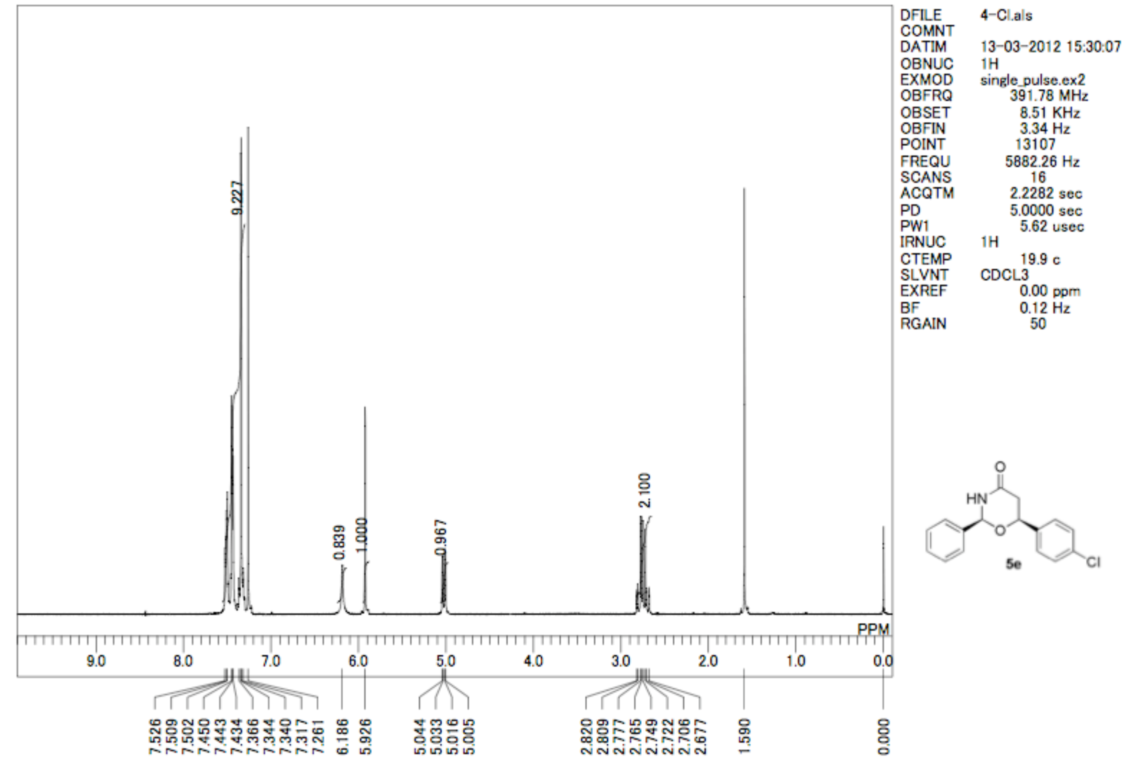
5d



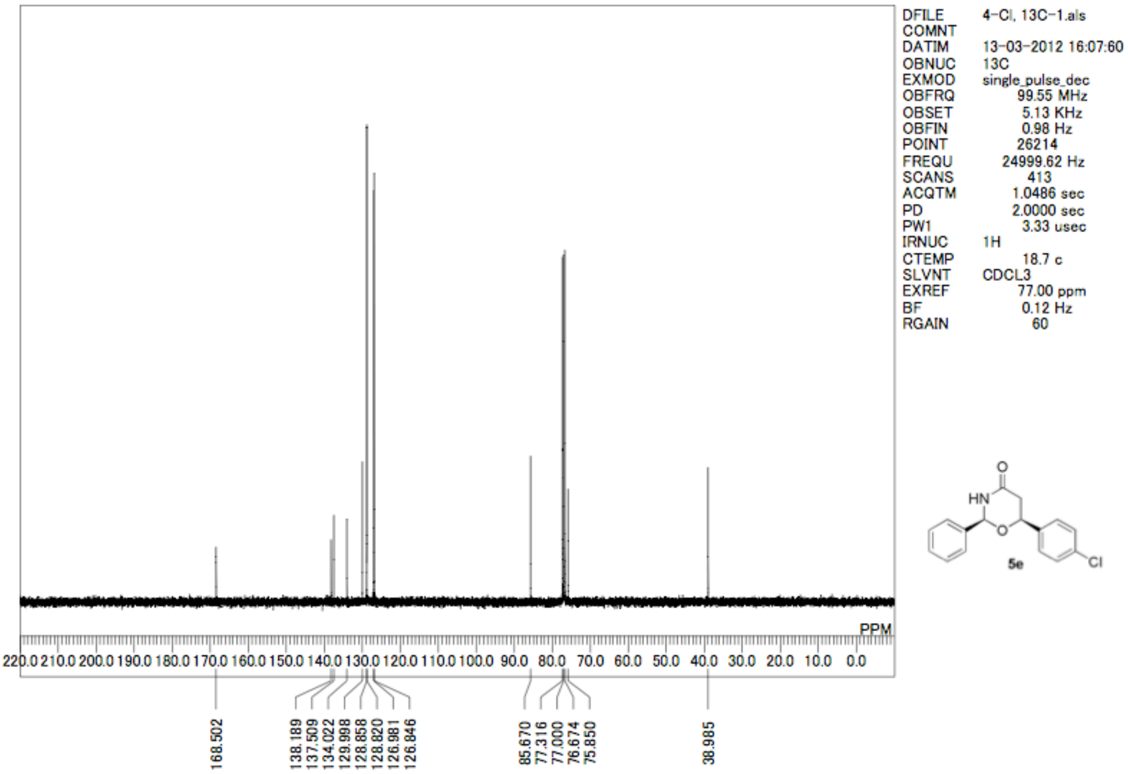
DFILE	p-mesyl, 13C.als
COMNT	
DATIM	12-11-2011 16:12:54
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	98.52 MHz
OBSET	4.64 KHz
OBFIN	8.74 Hz
POINT	26214
FREQU	24630.17 Hz
SCANS	324
ACQTM	1.0643 sec
PD	2.0000 sec
PW1	2.83 usec
IRNUC	1H
CTEMP	19.7 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



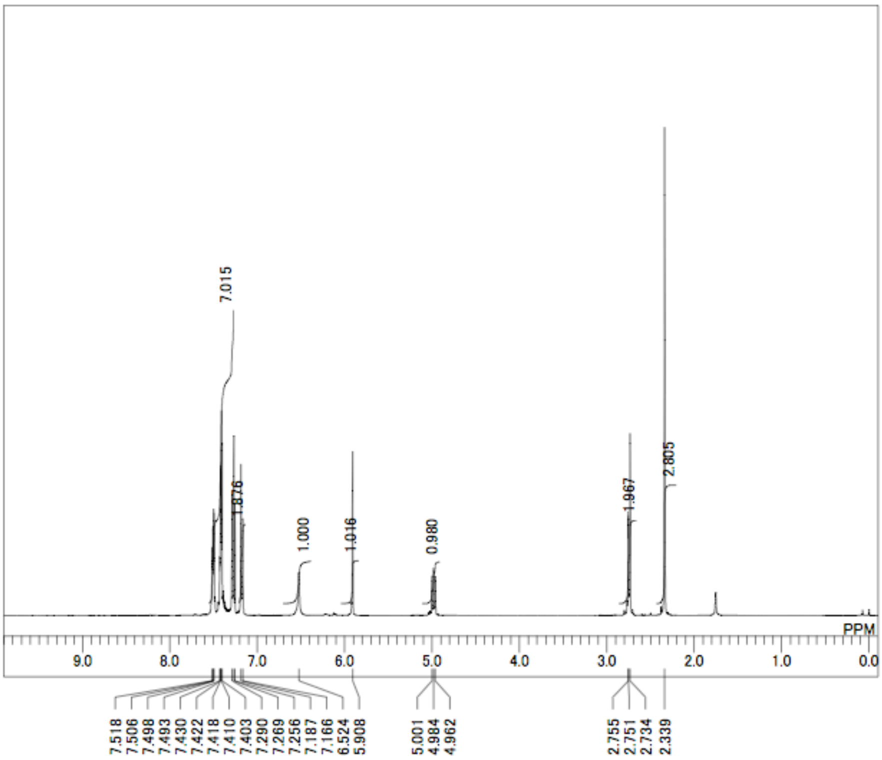
5d



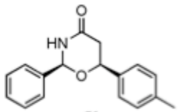
DFILE 4-Cl.als
COMNT
DATIM 13-03-2012 15:30:07
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 391.78 MHz
OBSET 8.51 KHz
OBFIN 3.34 Hz
POINT 13107
FREQU 5882.26 Hz
SCANS 16
ACQTM 2.2282 sec
PD 5.0000 sec
PW1 5.62 usec
IRNUC 1H
CTEMP 19.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 50



DFILE 4-Cl, 13C-1.als
COMNT
DATIM 13-03-2012 16:07:60
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 413
ACQTM 1.0486 sec
PD 2.0000 sec
PW1 3.33 usec
IRNUC 1H
CTEMP 18.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60



```
DFILE     p-methyl.als
COMNT
DATIM     18-11-2011 09:53:44
OBNUC     1H
EXMOD     single_pulse.ex2
OBFRQ          391.78 MHz
OBSET            8.51 KHz
OBFIN            3.34 Hz
POINT           13107
FREQU         5882.26 Hz
SCANS              16
ACQTM          2.2282 sec
PD             5.0000 sec
PW1              5.62 usec
IRNUC     1H
CTEMP            19.3 c
SLVNT     CDCL3
EXREF            0.00 ppm
BF               0.12 Hz
RGAIN              36
```



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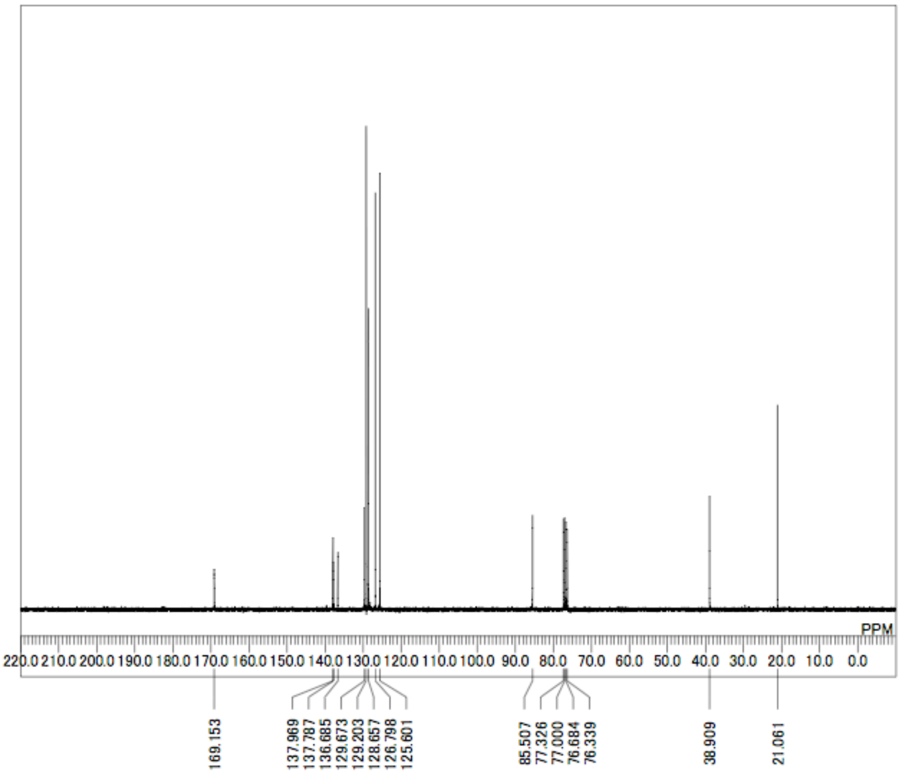
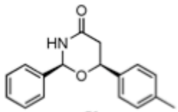
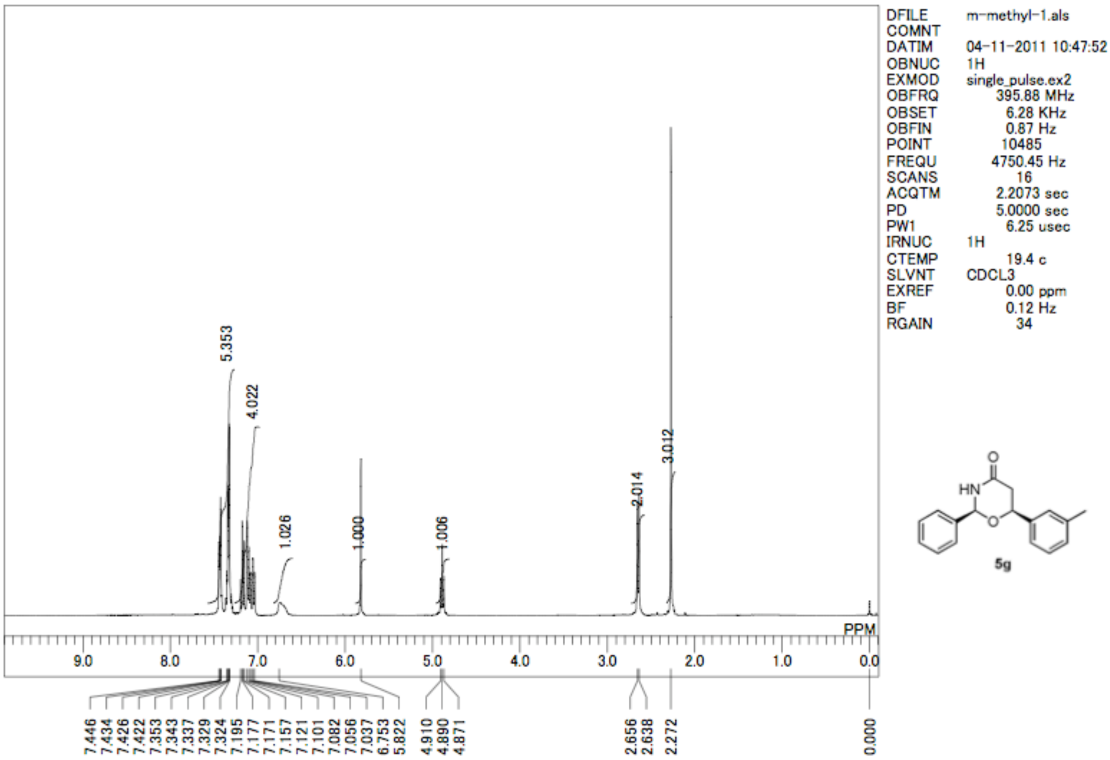
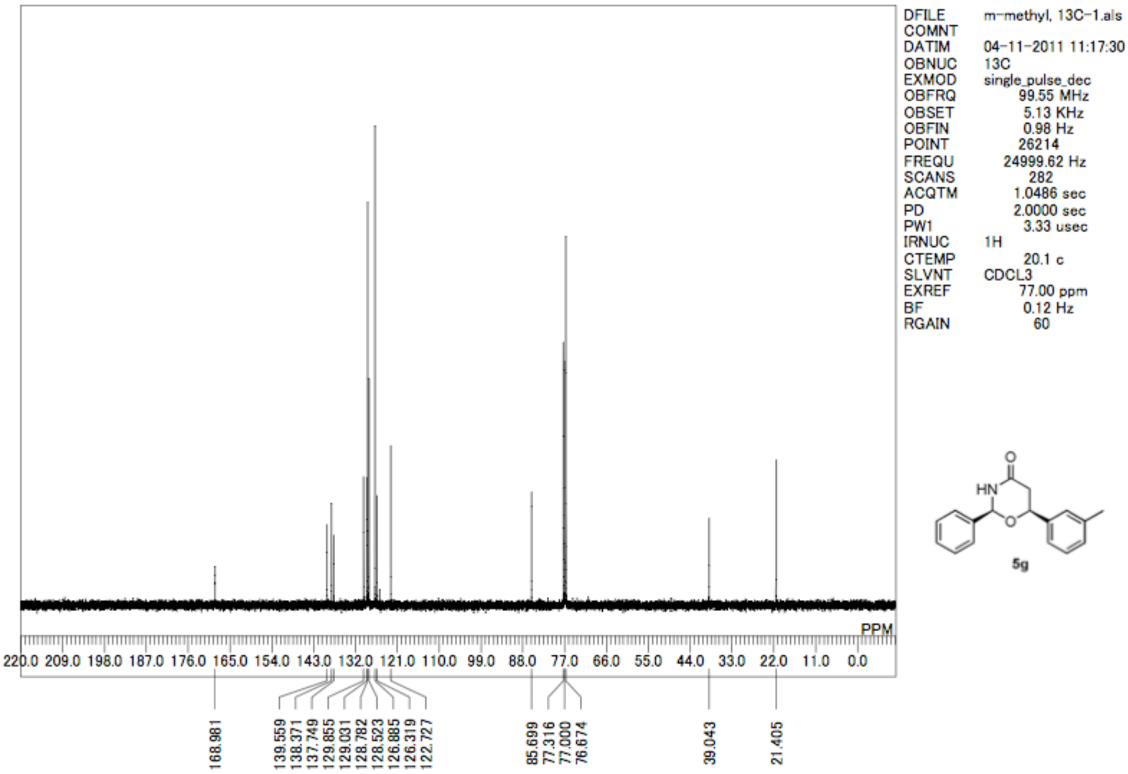


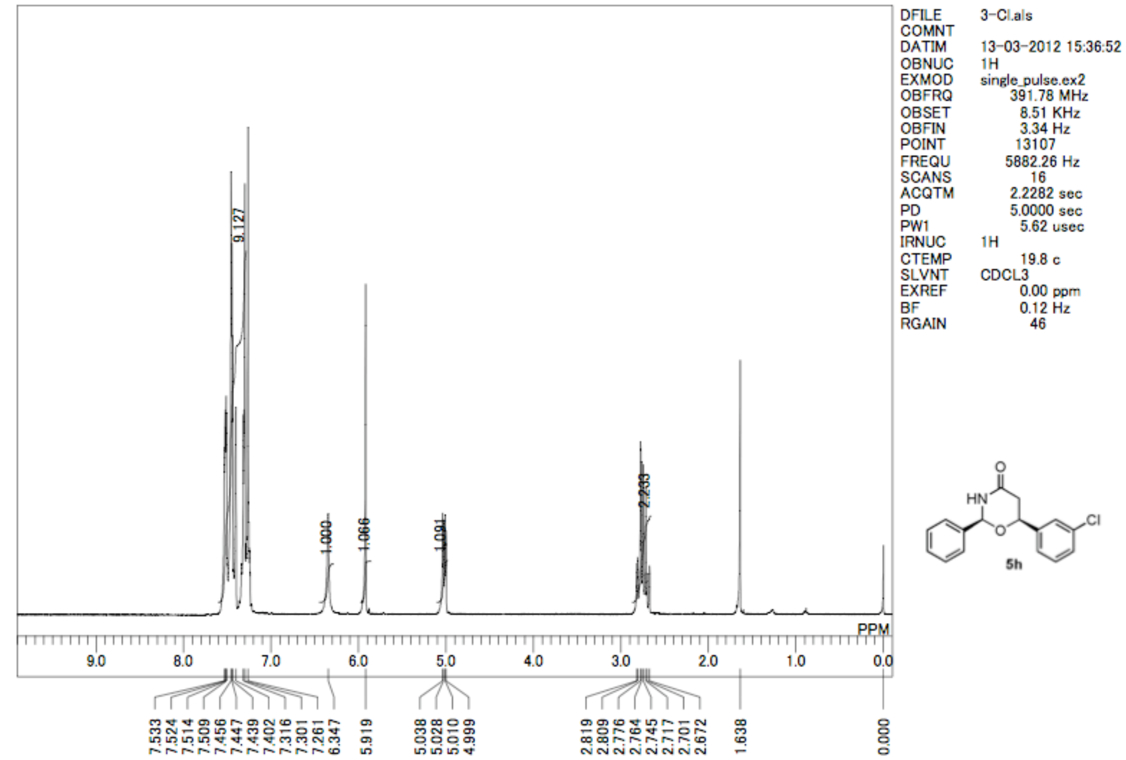
```
DFILE     p-methyl, 13C-1.als
COMNT
DATIM     24-11-2011 16:45:26
OBNUC     13C
EXMOD     single_pulse_dec
OBFRQ           99.55 MHz
OBSET            5.13 KHz
OBFIN            0.98 Hz
POINT           26214
FREQU        24999.62 Hz
SCANS             254
ACQTM          1.0486 sec
PD             2.0000 sec
PW1              3.33 usec
IRNUC     1H
CTEMP            19.2 c
SLVNT     CDCL3
EXREF           77.00 ppm
BF               0.12 Hz
RGAIN              60
```

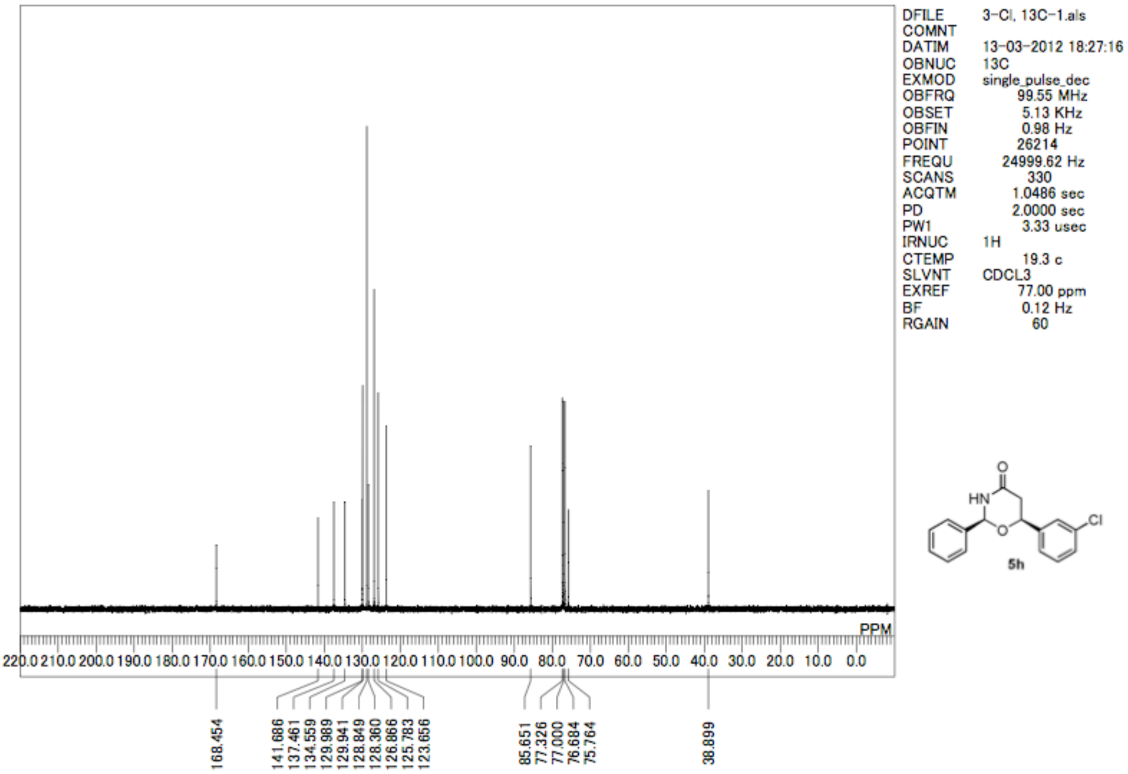


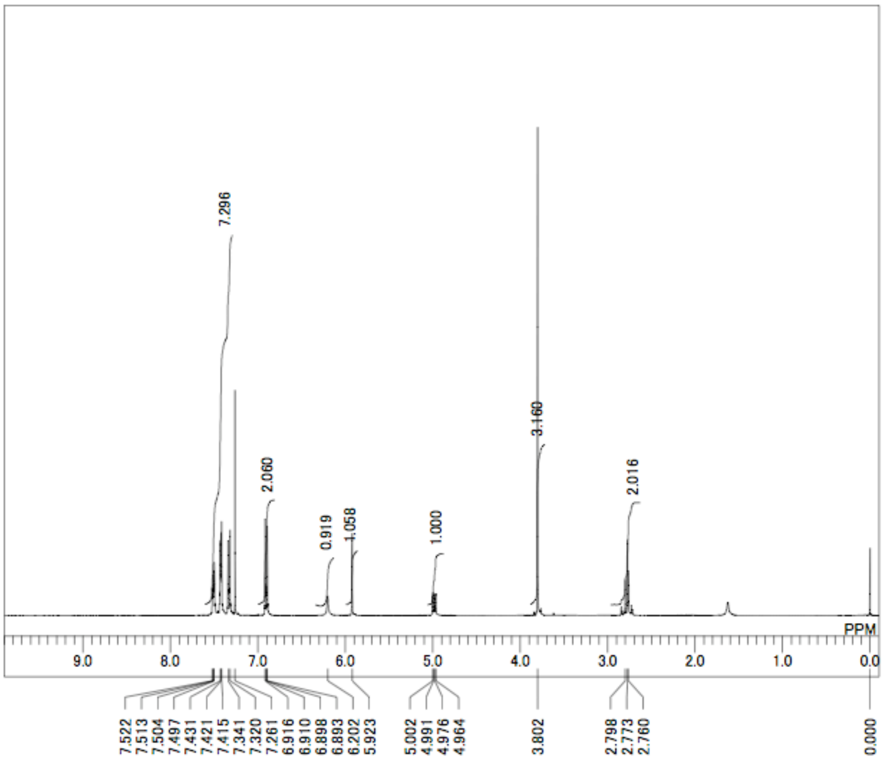
5f


DFILE m-methyl-1.als
COMNT
DATIM 04-11-2011 10:47:52
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 395.88 MHz
OBSET 6.28 KHz
OBFIN 0.87 Hz
POINT 10485
FREQU 4750.45 Hz
SCANS 16
ACQTM 2.2073 sec
PD 5.0000 sec
PW1 6.25 usec
IRNUC 1H
CTEMP 19.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 34
5.353
4.022
1.026
1.000
1.006
2.014
3.012
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.446
7.434
7.426
7.422
7.353
7.343
7.337
7.329
7.324
7.195
7.177
7.171
7.157
7.121
7.101
7.082
7.056
7.037
6.753
5.822
4.910
4.890
4.871
2.656
2.638
2.272
0.000
HN
O
O
5g

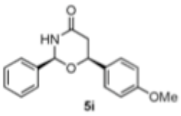

DFILE m-methyl, 13C-1.als
COMNT
DATIM 04-11-2011 11:17:30
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 99.55 MHz
OBSET 5.13 KHz
OBFIN 0.98 Hz
POINT 26214
FREQU 24999.62 Hz
SCANS 282
ACQTM 1.0486 sec
PD 2.0000 sec
PW1 3.33 usec
IRNUC 1H
CTEMP 20.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60
PPM
220.0
209.0
198.0
187.0
176.0
165.0
154.0
143.0
132.0
121.0
110.0
99.0
88.0
77.0
66.0
55.0
44.0
33.0
22.0
11.0
0.0
168.981
139.559
138.371
137.749
129.855
129.031
128.782
128.523
126.885
126.319
122.727
85.699
77.316
77.000
76.674
39.043
21.405
HN
O
O
5g


DFILE 3-Cl.als
COMNT
DATIM 13-03-2012 15:36:52
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 391.78 MHz
OBSET 8.51 KHz
OBFIN 3.34 Hz
POINT 13107
FREQU 5882.26 Hz
SCANS 16
ACQTM 2.2282 sec
PD 5.0000 sec
PW1 5.62 usec
IRNUC 1H
CTEMP 19.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 46
9.127
1.000
1.066
1.091
2.233
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.533
7.524
7.514
7.509
7.456
7.447
7.439
7.402
7.316
7.301
7.261
6.347
5.919
5.038
5.028
5.010
4.999
2.819
2.809
2.776
2.764
2.745
2.717
2.701
2.672
1.638
0.000
O
HN
O
Cl
5h

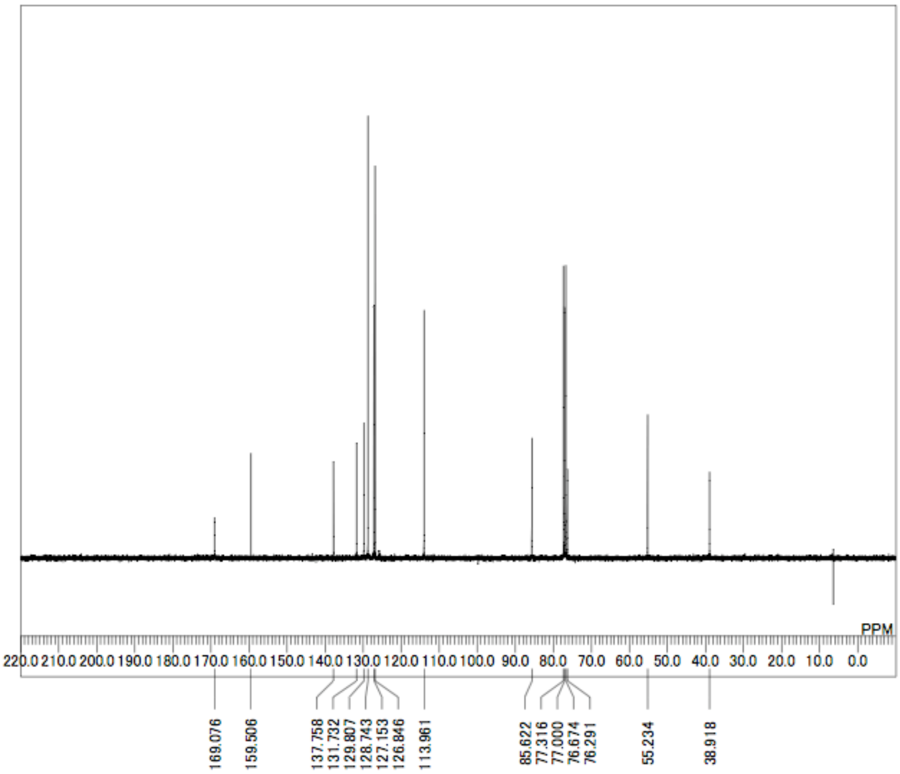

DFILE 3-Cl, 13C-1.als
COMNT
DATIM 13-03-2012 18:27:16
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 99.55 MHz
OBSET 5.13 KHz
OBFIN 0.98 Hz
POINT 26214
FREQU 24999.62 Hz
SCANS 330
ACQTM 1.0486 sec
PD 2.0000 sec
PW1 3.33 usec
IRNUC 1H
CTEMP 19.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
168.454
141.686
137.461
134.559
129.989
129.941
128.849
128.360
126.866
125.783
123.656
85.651
77.326
77.000
76.684
75.764
38.899
O
HN
O
Cl
5h



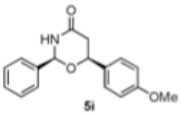
DFILE	p−anis.als
COMNT	
DATIM	03−12−2011 18:28:01
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
POINT	13107
FREQU	5938.15 Hz
SCANS	16
ACQTM	2.2073 sec
PD	5.0000 sec
PW1	6.25 usec
IRNUC	1H
CTEMP	19.9 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	40



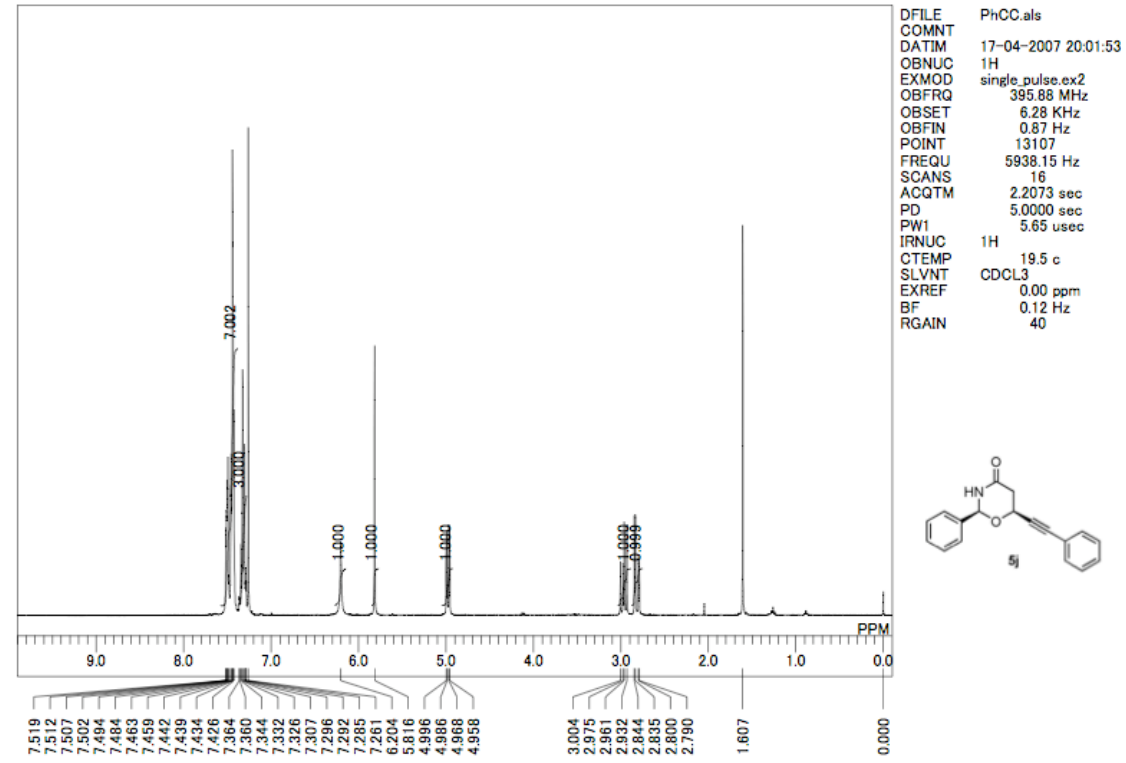
5i



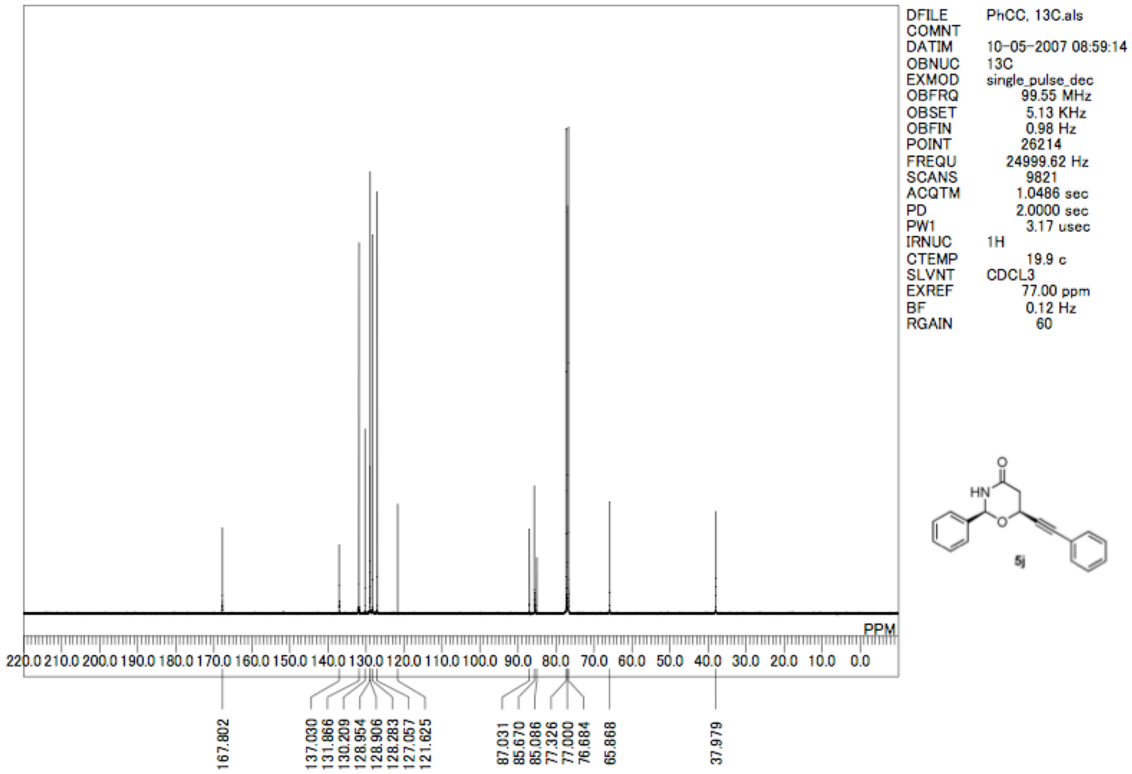
DFILE	p−anis, 13C−1.als
COMNT	
DATIM	08−12−2011 11:19:40
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	26214
FREQU	24999.62 Hz
SCANS	723
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.33 usec
IRNUC	1H
CTEMP	18.9 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



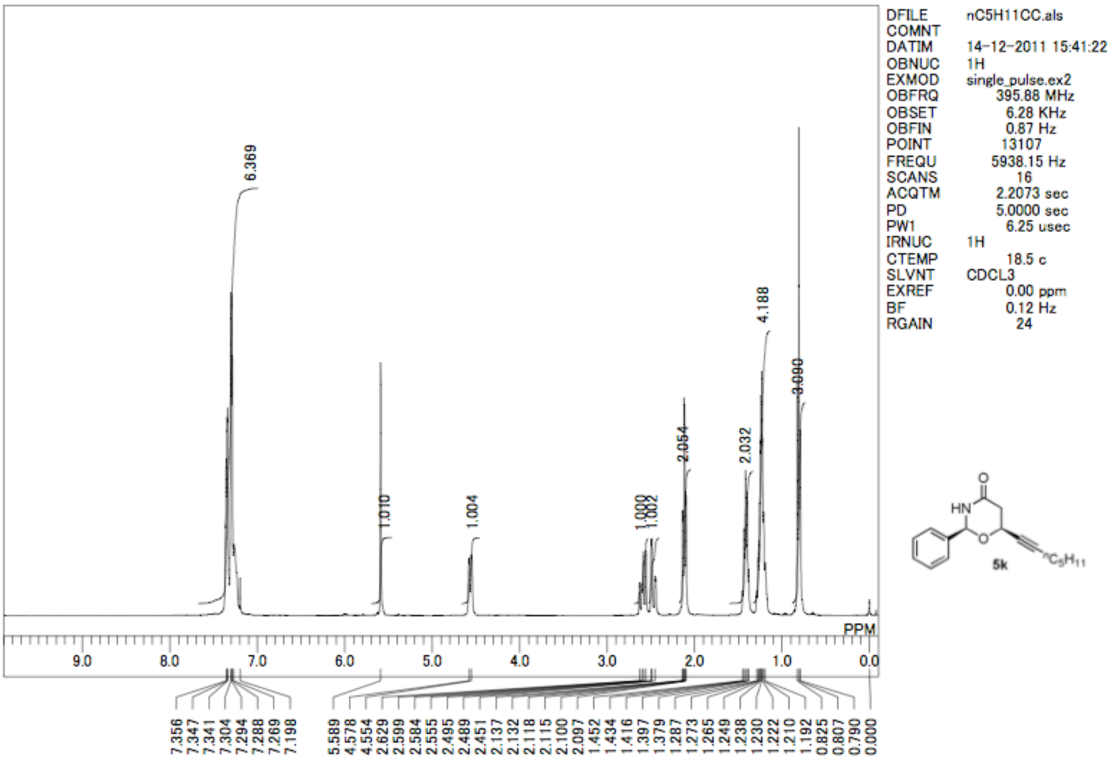
5i

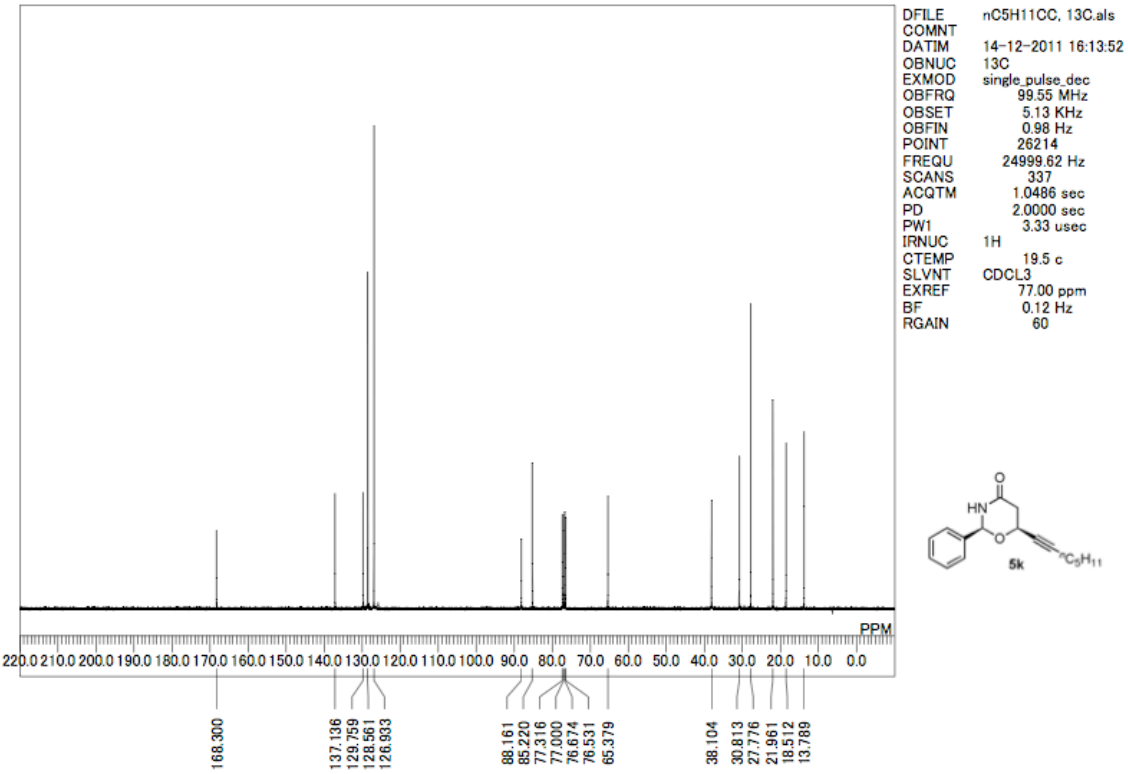


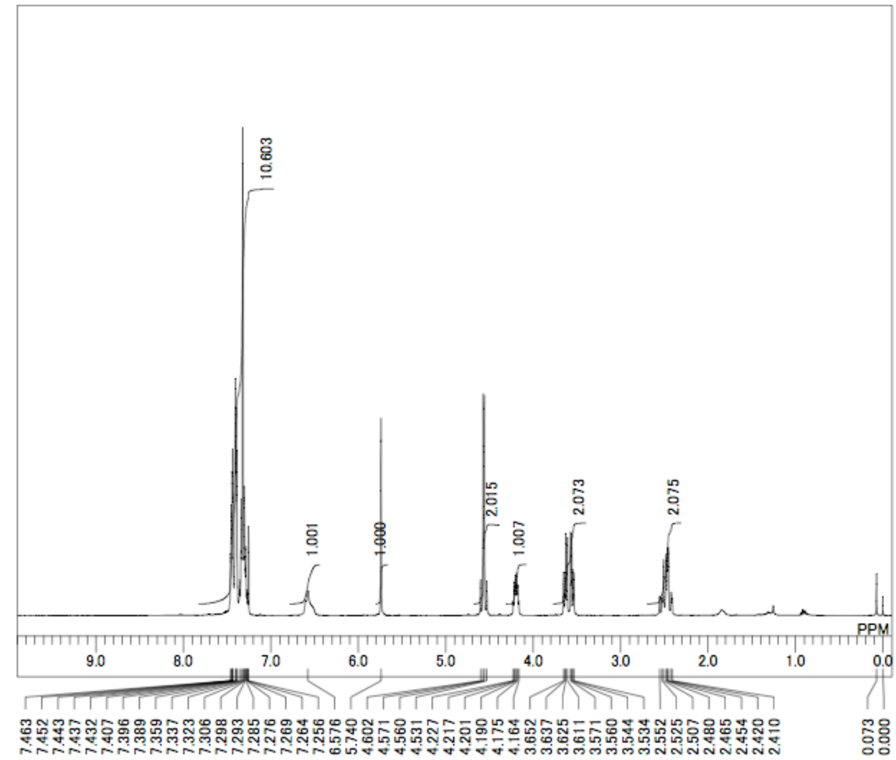
DFILE PhCC.als
COMNT
DATIM 17-04-2007 20:01:53
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 395.88 MHz
OBSET 6.28 KHz
OBFIN 0.87 Hz
POINT 13107
FREQU 5938.15 Hz
SCANS 16
ACQTM 2.2073 sec
PD 5.0000 sec
PW1 5.65 usec
IRNUC 1H
CTEMP 19.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 40



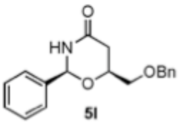
DFILE PhCC, 13C.als
COMNT
DATIM 10-05-2007 08:59:14
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 99.55 MHz
OBSET 5.13 KHz
OBFIN 0.98 Hz
POINT 26214
FREQU 24999.62 Hz
SCANS 9821
ACQTM 1.0486 sec
PD 2.0000 sec
PW1 3.17 usec
IRNUC 1H
CTEMP 19.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60


6.369
1.010
1.004
1.000
1.002
2.054
2.032
4.188
3.090
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.356
7.347
7.341
7.304
7.294
7.288
7.269
7.198
5.589
4.578
4.554
2.629
2.599
2.584
2.555
2.495
2.489
2.451
2.137
2.132
2.118
2.115
2.100
2.097
1.452
1.434
1.416
1.397
1.379
1.287
1.273
1.265
1.249
1.238
1.230
1.222
1.210
1.192
0.825
0.807
0.790
0.000
DFILE nC5H11CC.als
COMNT
DATIM 14-12-2011 15:41:22
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 6.25 usec
IRNUC 1H
CTEMP 18.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 24
HN
O
O
$^nC_5H_{11}$
5k

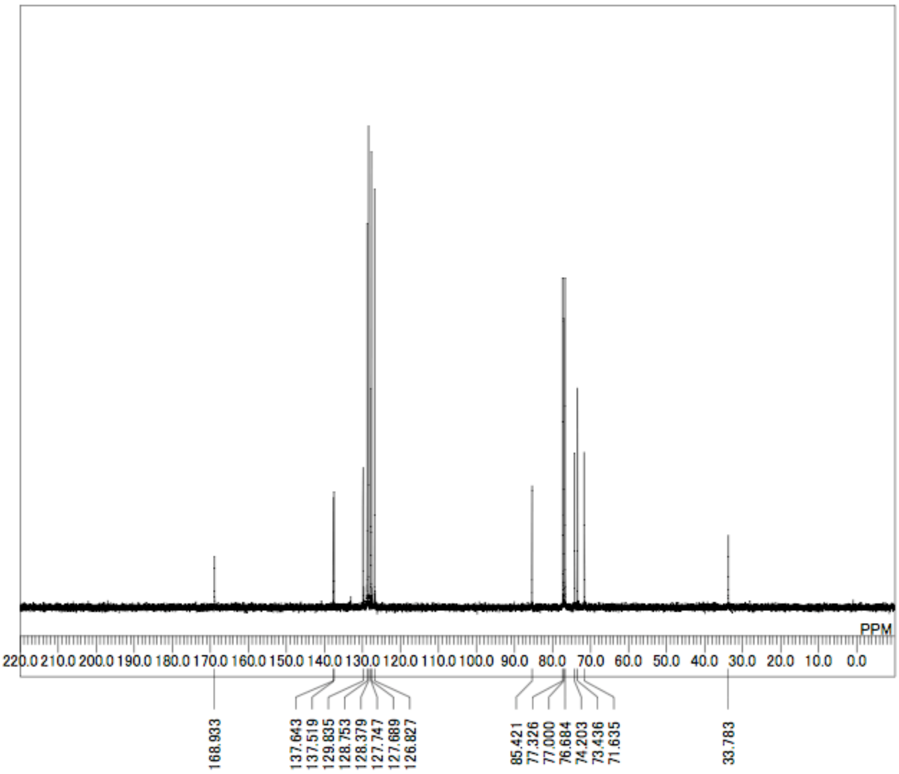

PPM
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
168.300
137.136
129.759
128.561
126.933
88.161
85.220
77.316
77.000
76.674
76.531
65.379
38.104
30.813
27.776
21.961
18.512
13.789
DFILE nC5H11CC, 13C.als
COMNT
DATIM 14-12-2011 16:13:52
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 337
ACQTM 1.0486 sec
PD 2.0000 sec
PW1 3.33 usec
IRNUC 1H
CTEMP 19.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60
HN
O
O
$^nC_5H_{11}$
5k



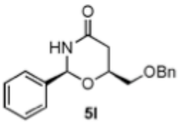
DFILE	BnOCH2.als
COMNT	
DATIM	25-01-2008 15:09:58
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
POINT	13107
FREQU	5938.15 Hz
SCANS	16
ACQTM	2.2073 sec
PD	5.0000 sec
PW1	5.65 usec
IRNUC	1H
CTEMP	18.1 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	34



5l



DFILE	BnOCH2, 13C.als
COMNT	
DATIM	30-01-2008 19:52:40
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	619
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.17 usec
IRNUC	1H
CTEMP	17.9 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	56



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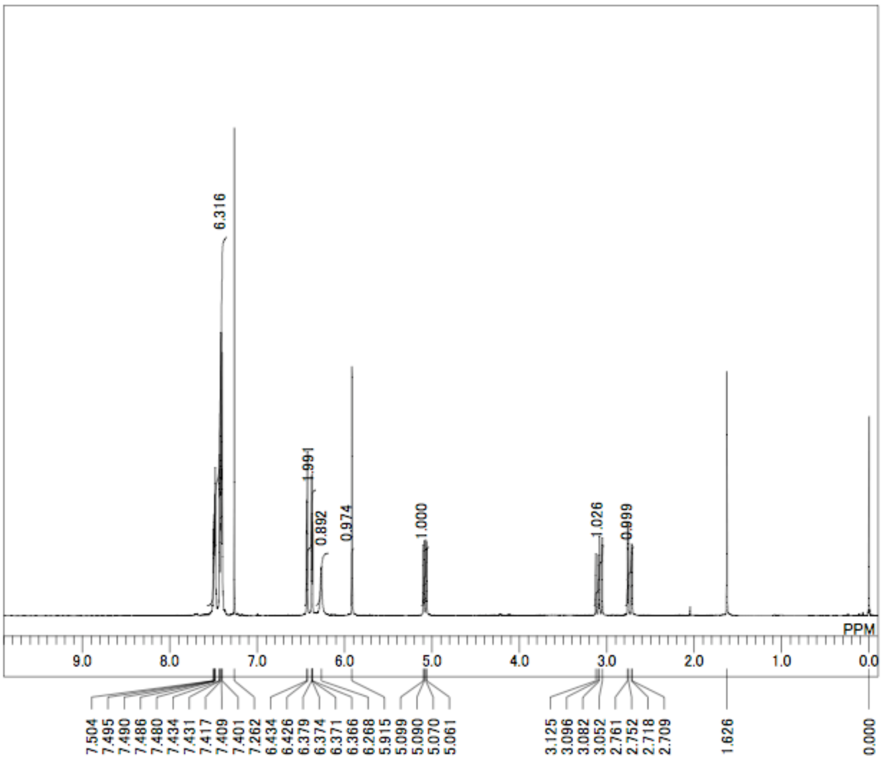
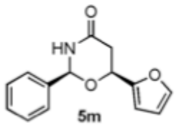
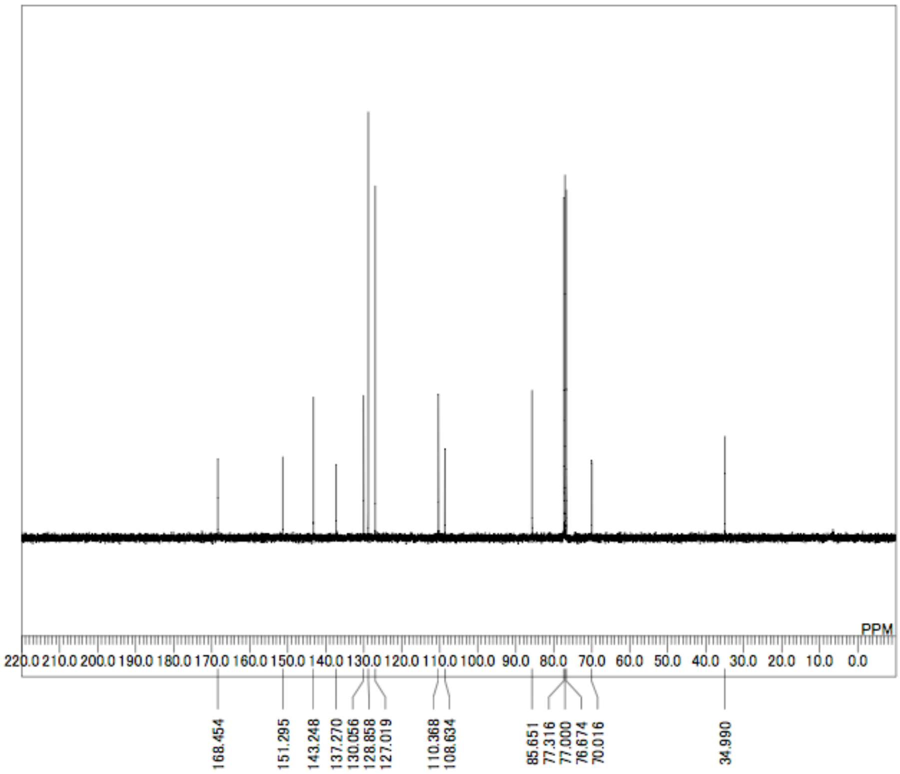


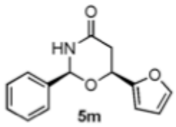
DFILE	furyl.als
COMNT	
DATIM	14-04-2012 20:29:10
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
POINT	13107
FREQU	5938.15 Hz
SCANS	16
ACQTM	2.2073 sec
PD	5.0000 sec
PW1	6.25 usec
IRNUC	1H
CTEMP	406.7 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	40



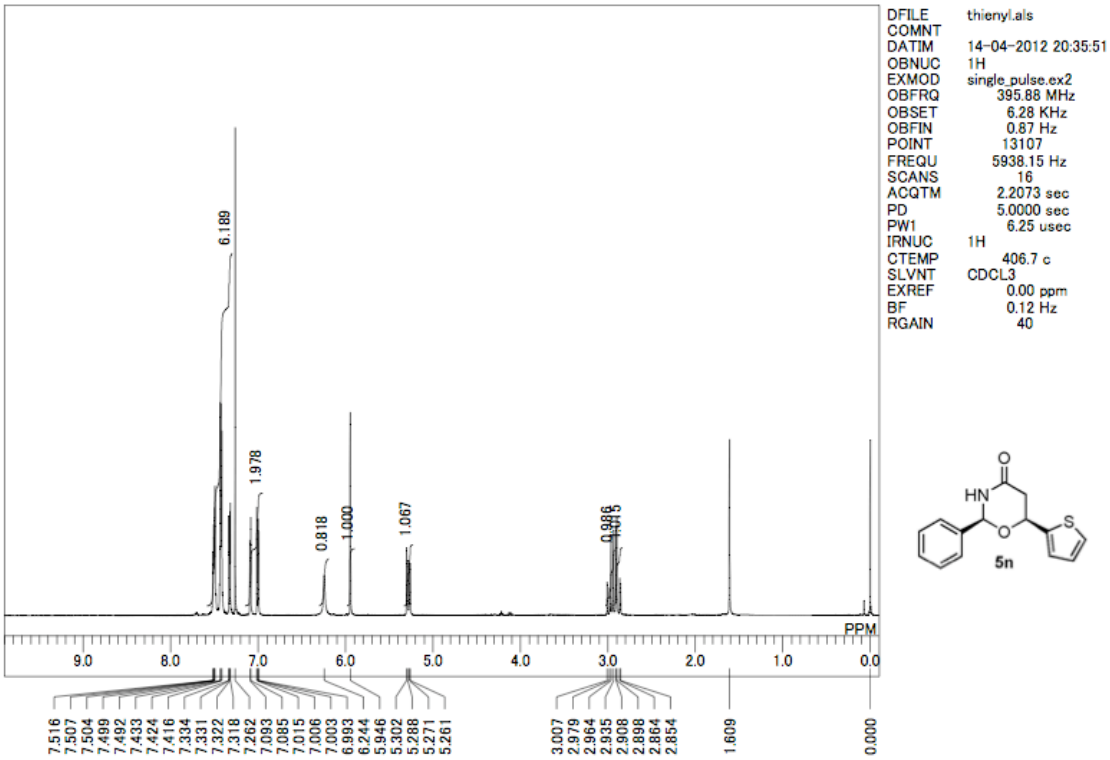
5m



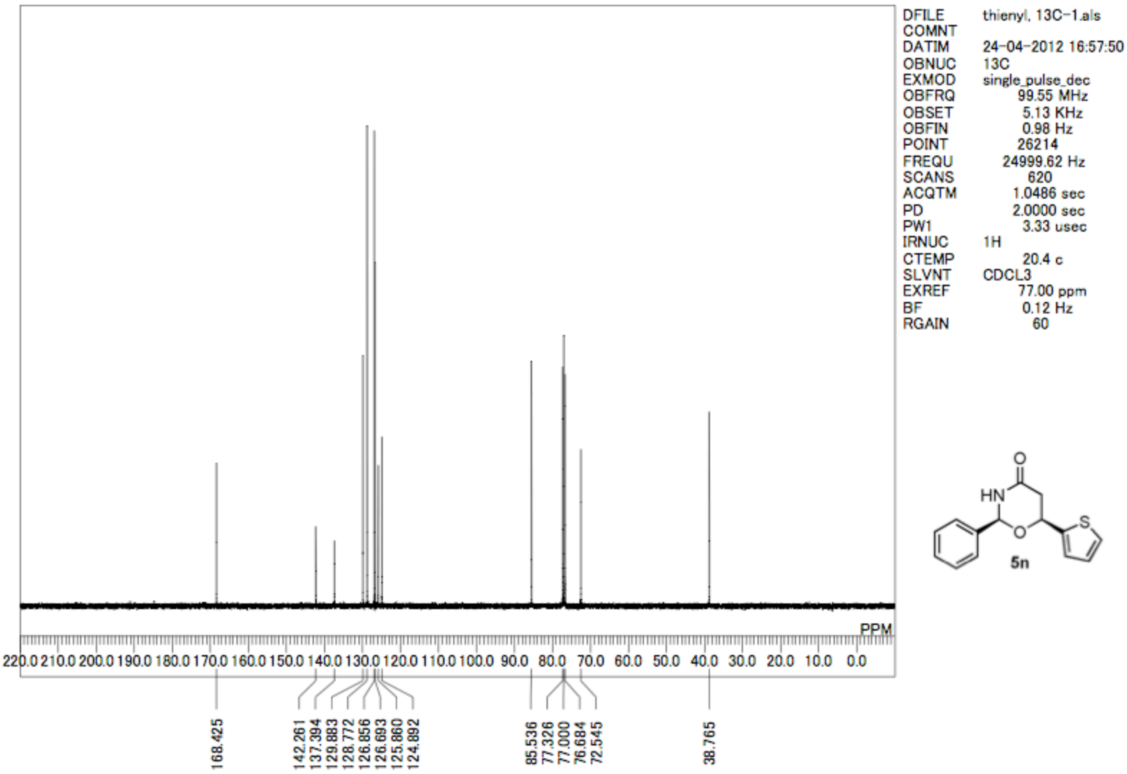
DFILE	furyl, 13C-1.als
COMNT	
DATIM	17-04-2012 18:26:38
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	26214
FREQU	24999.62 Hz
SCANS	419
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.33 usec
IRNUC	1H
CTEMP	406.6 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



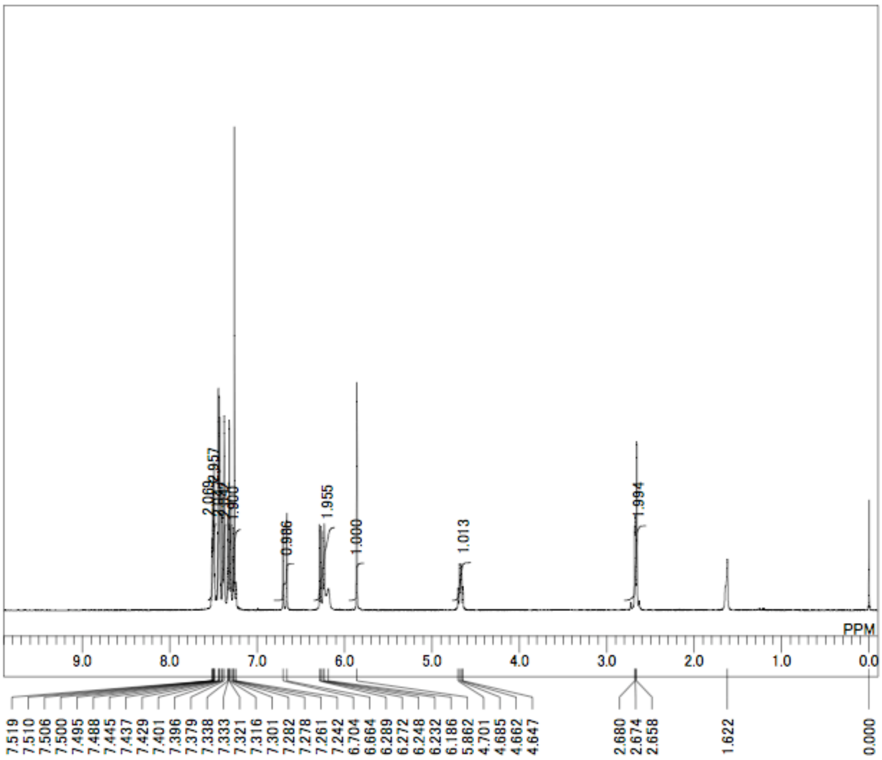
5m



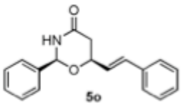
```
DFILE   thienyl.als
COMNT
DATIM   14-04-2012 20:35:51
OBNUC   1H
EXMOD   single_pulse.ex2
OBFRQ        395.88 MHz
OBSET          6.28 KHz
OBFIN          0.87 Hz
POINT        13107
FREQU      5938.15 Hz
SCANS           16
ACQTM        2.2073 sec
PD           5.0000 sec
PW1            6.25 usec
IRNUC   1H
CTEMP         406.7 c
SLVNT   CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN           40
```



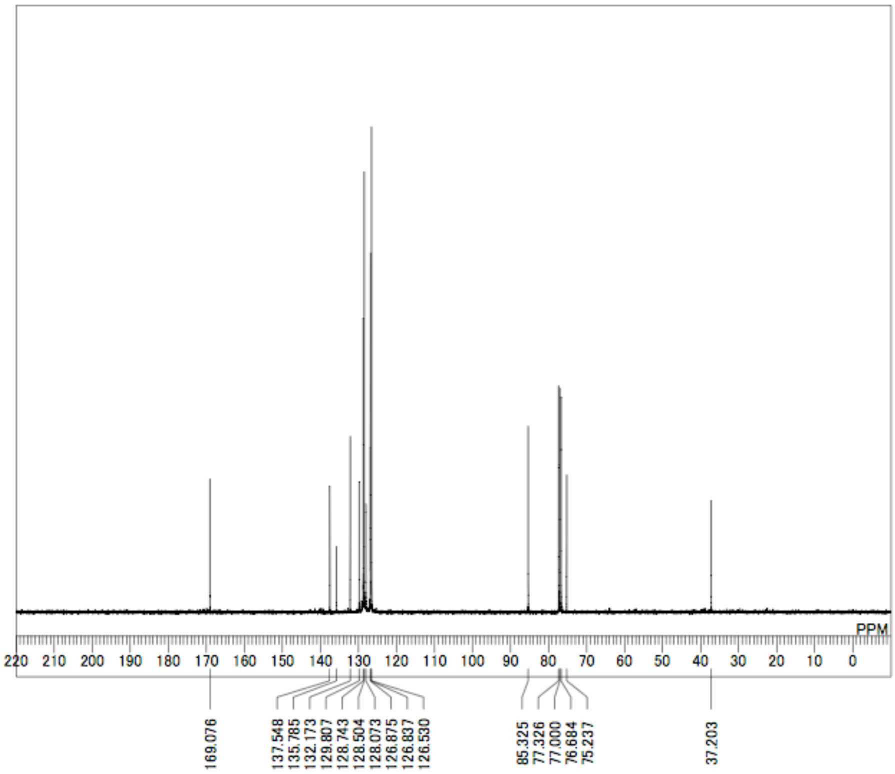
```
DFILE   thienyl, 13C-1.als
COMNT
DATIM   24-04-2012 16:57:50
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ         99.55 MHz
OBSET          5.13 KHz
OBFIN          0.98 Hz
POINT        26214
FREQU     24999.62 Hz
SCANS          620
ACQTM        1.0486 sec
PD           2.0000 sec
PW1            3.33 usec
IRNUC   1H
CTEMP          20.4 c
SLVNT   CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN           60
```



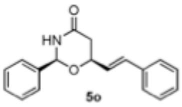
DFILE	PhC=C.als
COMNT	
DATIM	29-01-2008 16:41:59
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
POINT	16384
FREQU	7422.80 Hz
SCANS	16
ACQTM	2.2073 sec
PD	5.0000 sec
PW1	5.65 usec
IRNUC	1H
CTEMP	17.8 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	40



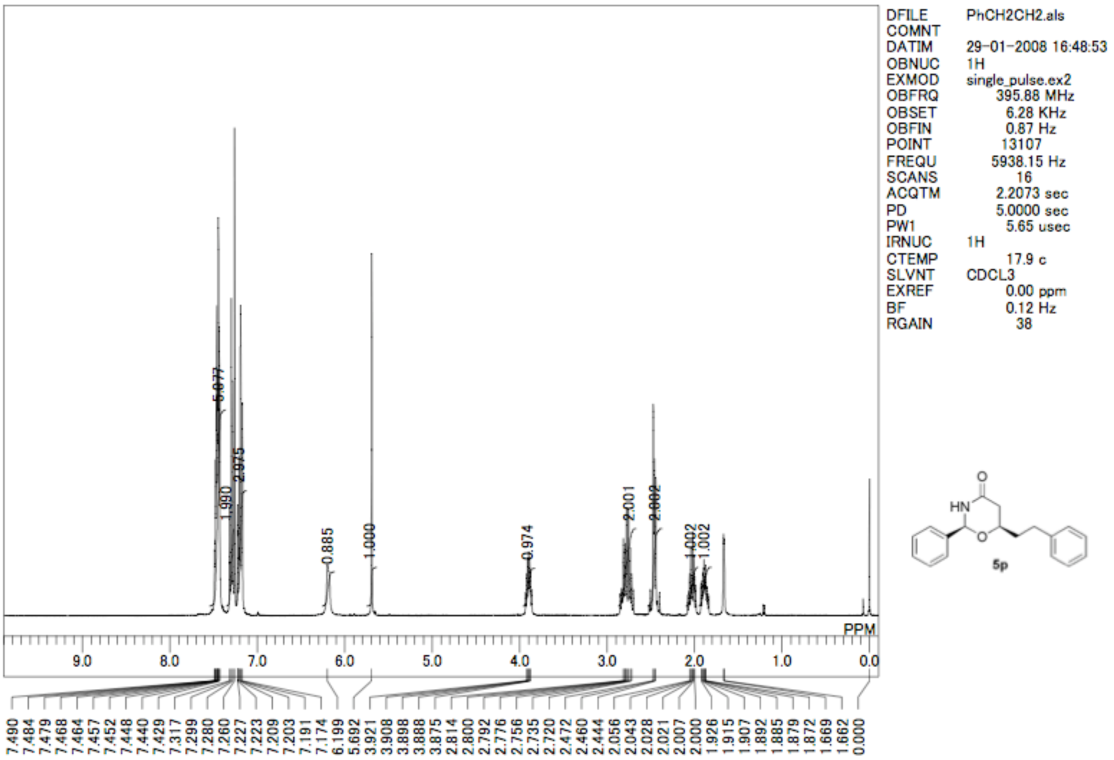
5o



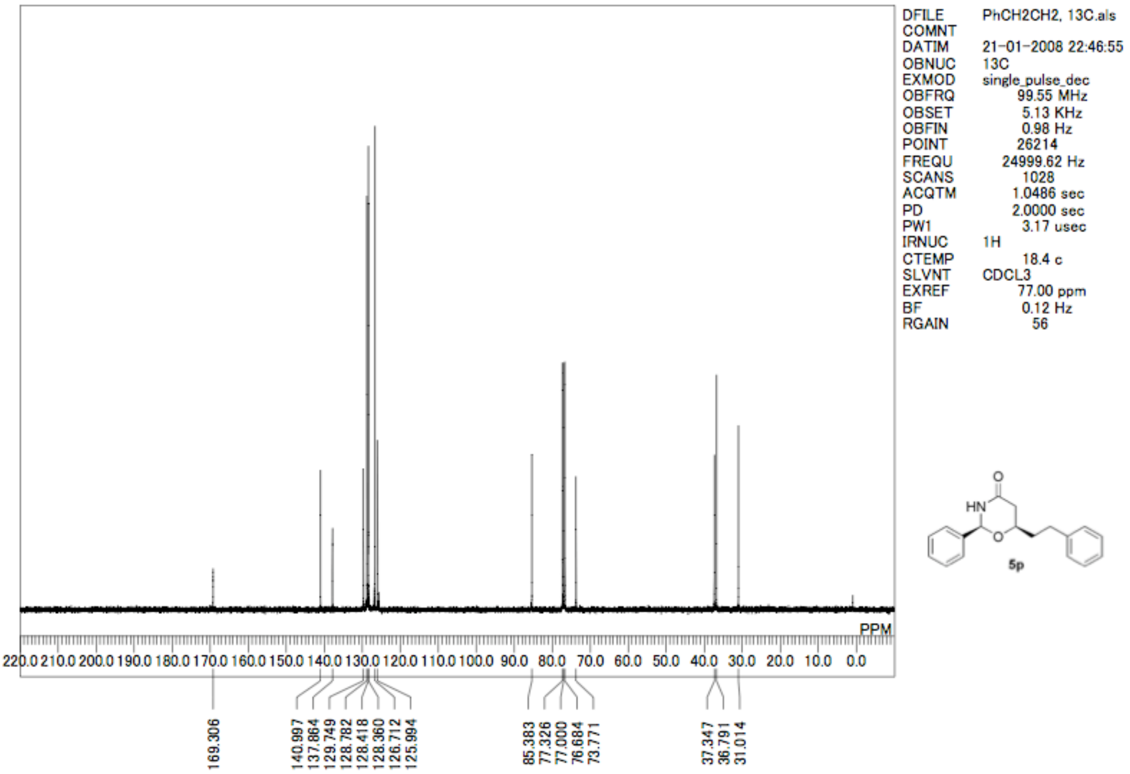
DFILE	PhC=C, 13C.als
COMNT	
DATIM	22-01-2008 23:10:09
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	26214
FREQU	24999.62 Hz
SCANS	1028
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.17 usec
IRNUC	1H
CTEMP	18.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	56



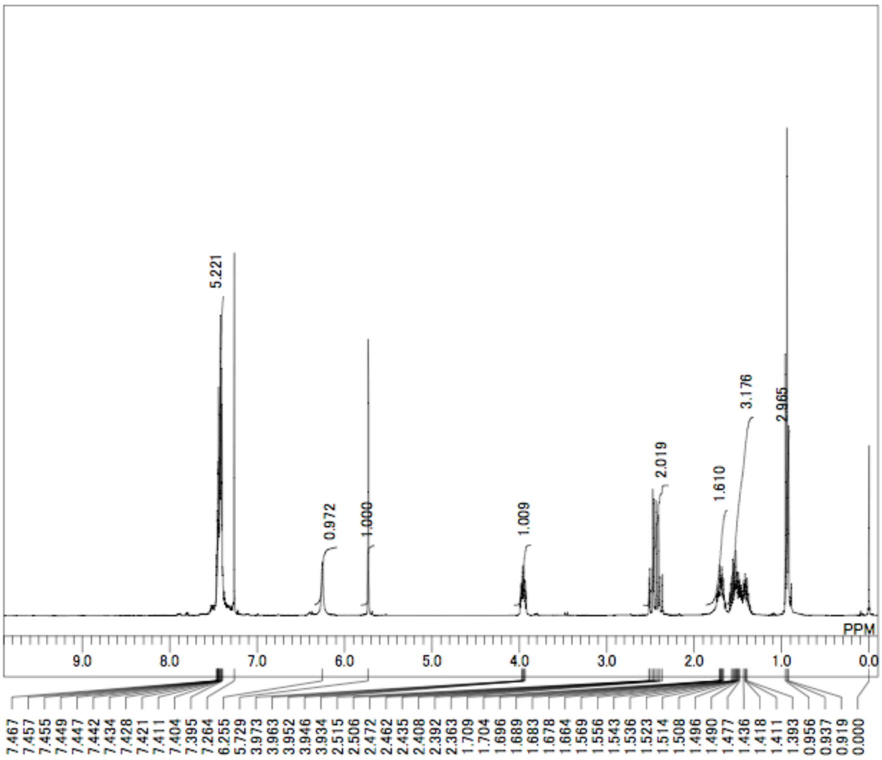
5o



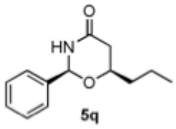
DFILE	PhCH2CH2.als
COMNT	
DATIM	29-01-2008 16:48:53
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
POINT	13107
FREQU	5938.15 Hz
SCANS	16
ACQTM	2.2073 sec
PD	5.0000 sec
PW1	5.65 usec
IRNUC	1H
CTEMP	17.9 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	38



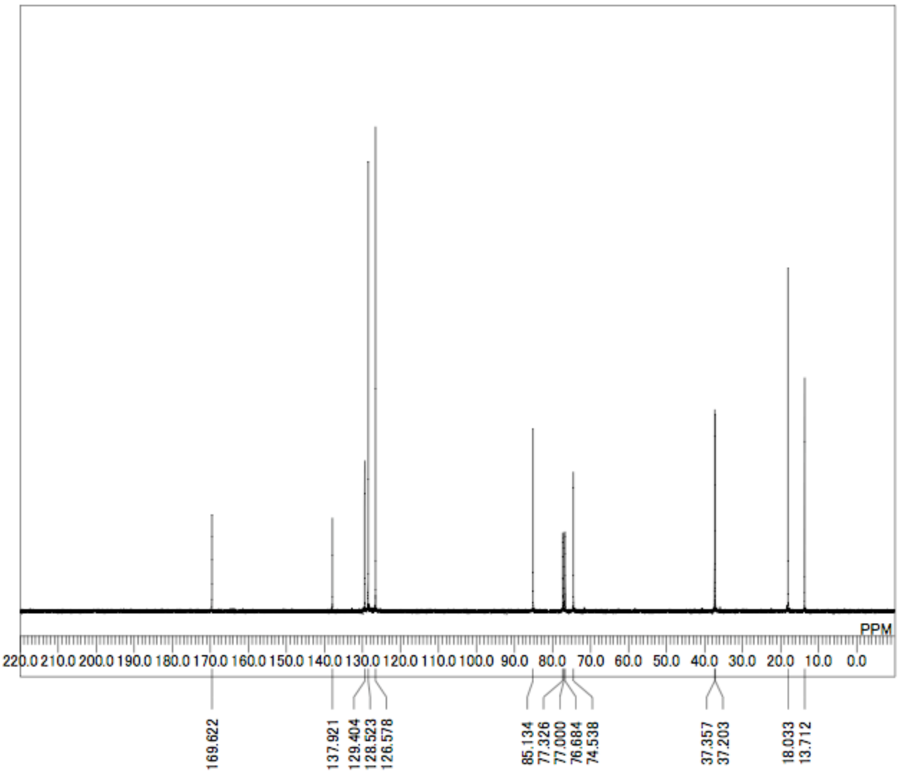
DFILE	PhCH2CH2, 13C.als
COMNT	
DATIM	21-01-2008 22:46:55
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	26214
FREQU	24999.62 Hz
SCANS	1028
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.17 usec
IRNUC	1H
CTEMP	18.4 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	56



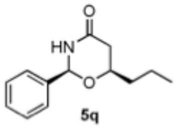
DFILE	Pr.als
COMNT	
DATIM	07-11-2007 15:43:29
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
POINT	13107
FREQU	5938.15 Hz
SCANS	16
ACQTM	2.2073 sec
PD	5.0000 sec
PW1	5.65 usec
IRNUC	1H
CTEMP	19.7 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	38



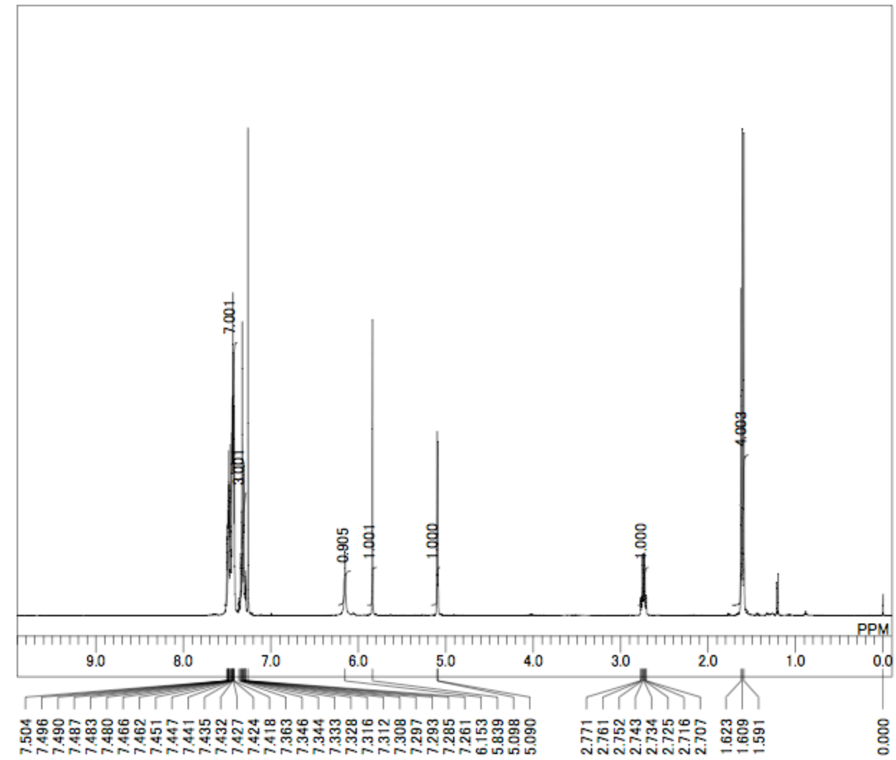
5q



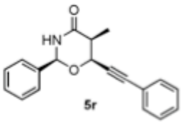
DFILE	Pr, 13C.als
COMNT	
DATIM	23-01-2008 22:47:02
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	26214
FREQU	24999.62 Hz
SCANS	260
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.17 usec
IRNUC	1H
CTEMP	18.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	58



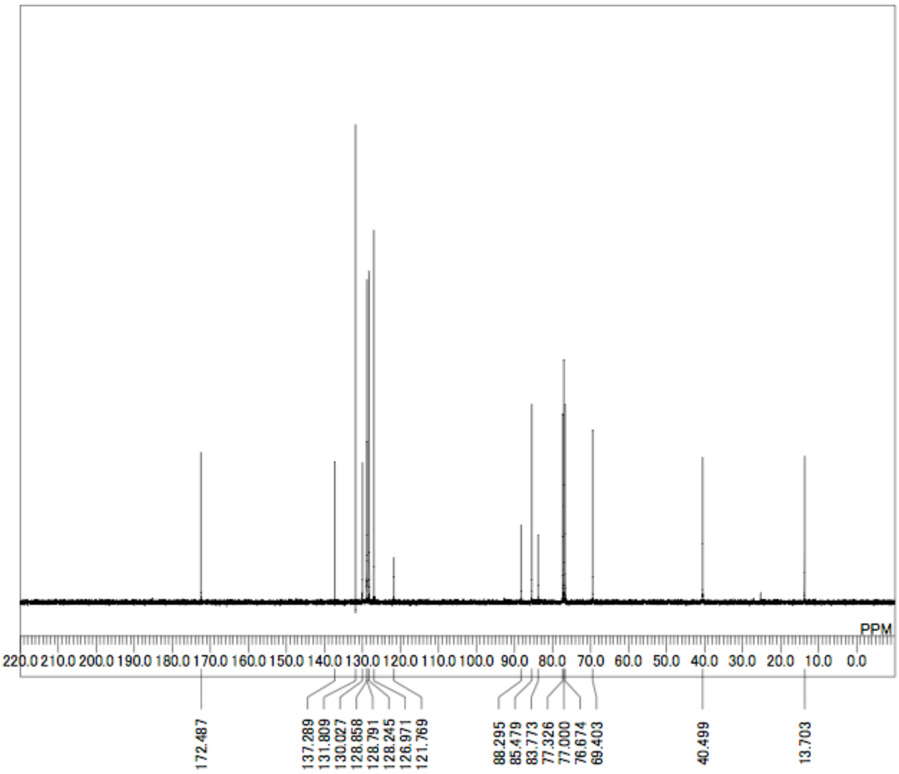
5q



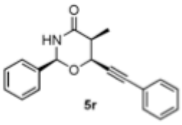
```
DFILE   Me, PhCC.als
COMNT
DATIM   09-05-2007 22:10:13
OBNUC   1H
EXMOD   single_pulse.ex2
OBFRQ      395.88 MHz
OBSET        6.28 KHz
OBFIN        0.87 Hz
POINT       13107
FREQU     5938.15 Hz
SCANS          16
ACQTM      2.2073 sec
PD         5.0000 sec
PW1          5.65 usec
IRNUC   1H
CTEMP        19.9 c
SLVNT   CDCL3
EXREF        0.00 ppm
BF           0.12 Hz
RGAIN          40
```



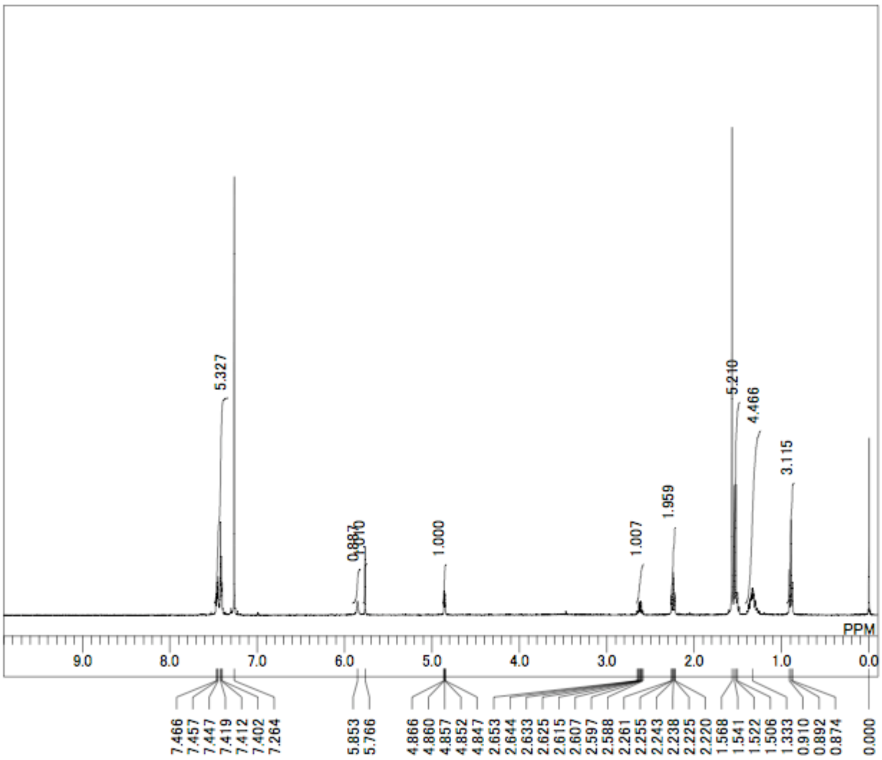
5r



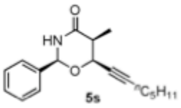
```
DFILE   Me, PhCC, 13C.als
COMNT
DATIM   09-05-2007 23:26:58
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ       99.55 MHz
OBSET        5.13 KHz
OBFIN        0.98 Hz
POINT       26214
FREQU    24999.62 Hz
SCANS         512
ACQTM      1.0486 sec
PD         2.0000 sec
PW1          3.17 usec
IRNUC   1H
CTEMP        19.5 c
SLVNT   CDCL3
EXREF       77.00 ppm
BF           0.12 Hz
RGAIN          60
```



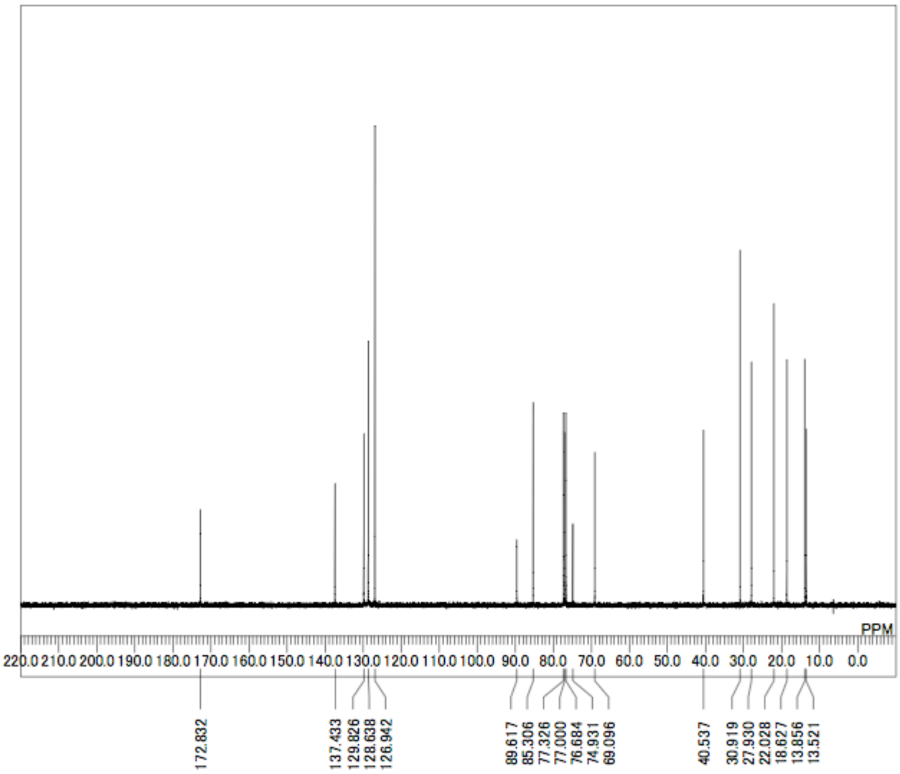
5r



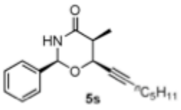
DFILE	Me, octyl.als
COMNT	
DATIM	10-12-2011 15:13:45
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	391.78 MHz
OBSET	8.51 KHz
OBFIN	3.34 Hz
POINT	13107
FREQU	5882.26 Hz
SCANS	16
ACQTM	2.2282 sec
PD	5.0000 sec
PW1	5.62 usec
IRNUC	1H
CTEMP	19.3 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	50



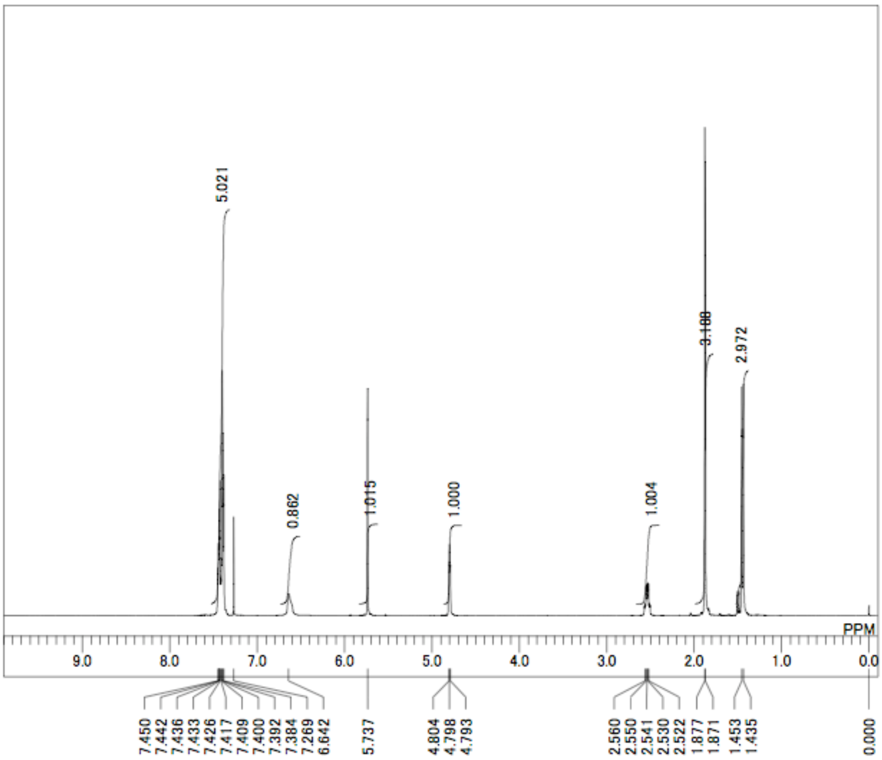
5s



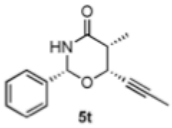
DFILE	Me, octyl, 13C-1.als
COMNT	
DATIM	10-12-2011 15:44:05
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	26214
FREQU	24999.62 Hz
SCANS	377
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.33 usec
IRNUC	1H
CTEMP	19.2 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



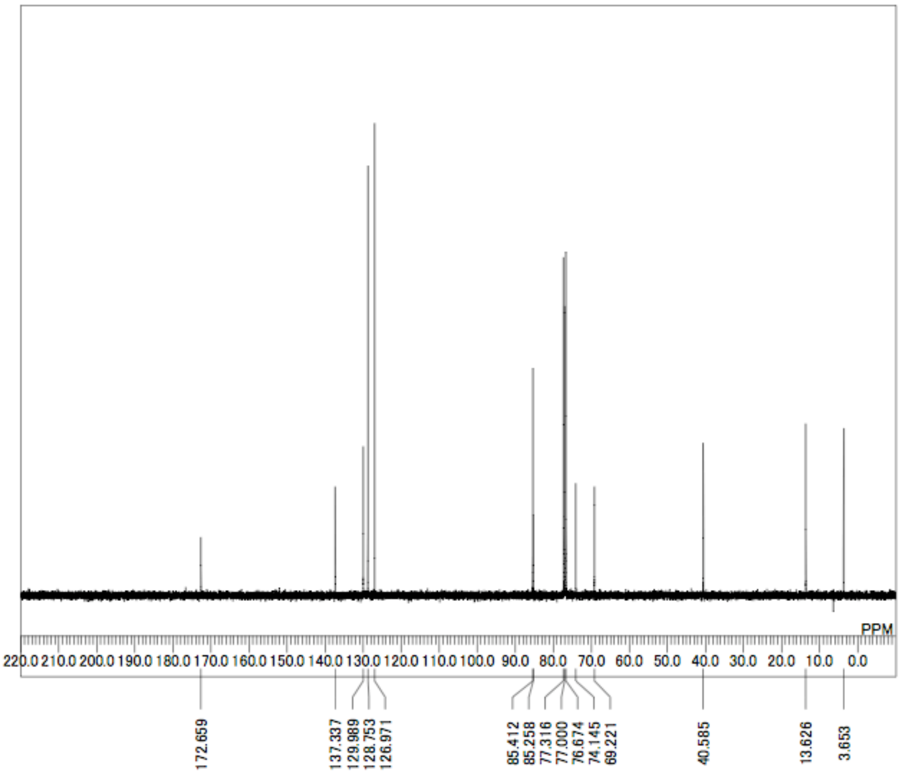
5s



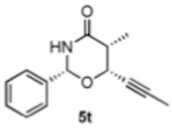
```
DFILE    Me, CH3CC.als
COMNT
DATIM    04-01-2012 15:07:00
OBNUC    1H
EXMOD    single_pulse.ex2
OBFRQ       395.88 MHz
OBSET         6.28 KHz
OBFIN         0.87 Hz
POINT        13107
FREQU      5938.15 Hz
SCANS           16
ACQTM       2.2073 sec
PD          5.0000 sec
PW1           6.25 usec
IRNUC    1H
CTEMP         18.3 c
SLVNT    CDCL3
EXREF         0.00 ppm
BF            0.12 Hz
RGAIN           34
```



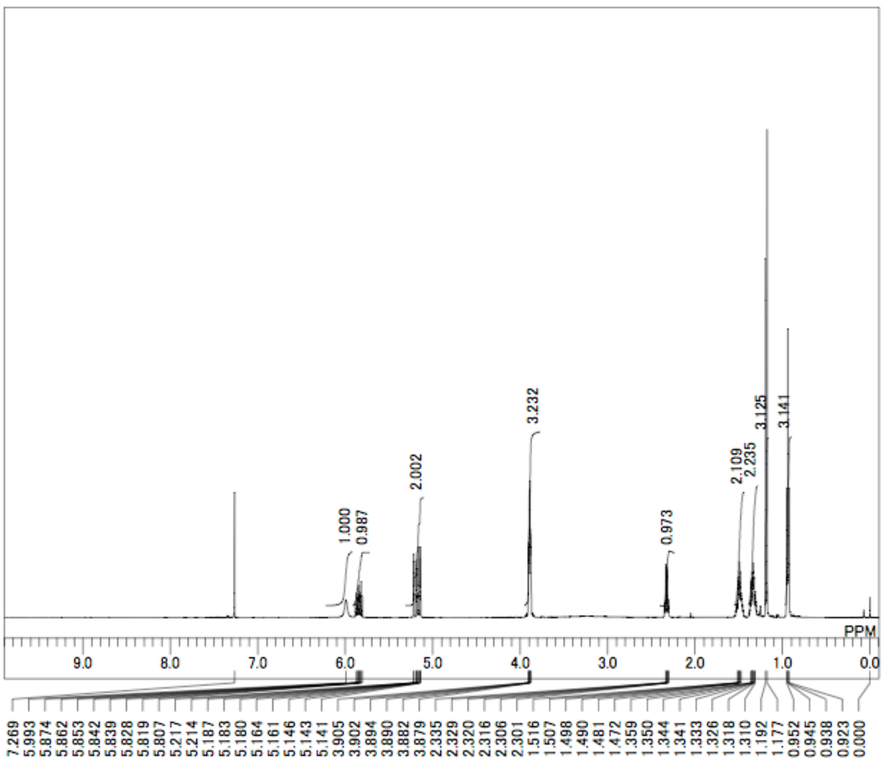
5t



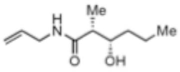
```
DFILE    Me, CH3CC, 13C-1.als
COMNT
DATIM    04-01-2012 15:42:07
OBNUC    13C
EXMOD    single_pulse_dec
OBFRQ        99.55 MHz
OBSET         5.13 KHz
OBFIN         0.98 Hz
POINT        26214
FREQU     24999.62 Hz
SCANS          390
ACQTM       1.0486 sec
PD          2.0000 sec
PW1           3.33 usec
IRNUC    1H
CTEMP         18.9 c
SLVNT    CDCL3
EXREF        77.00 ppm
BF            0.12 Hz
RGAIN           60
```



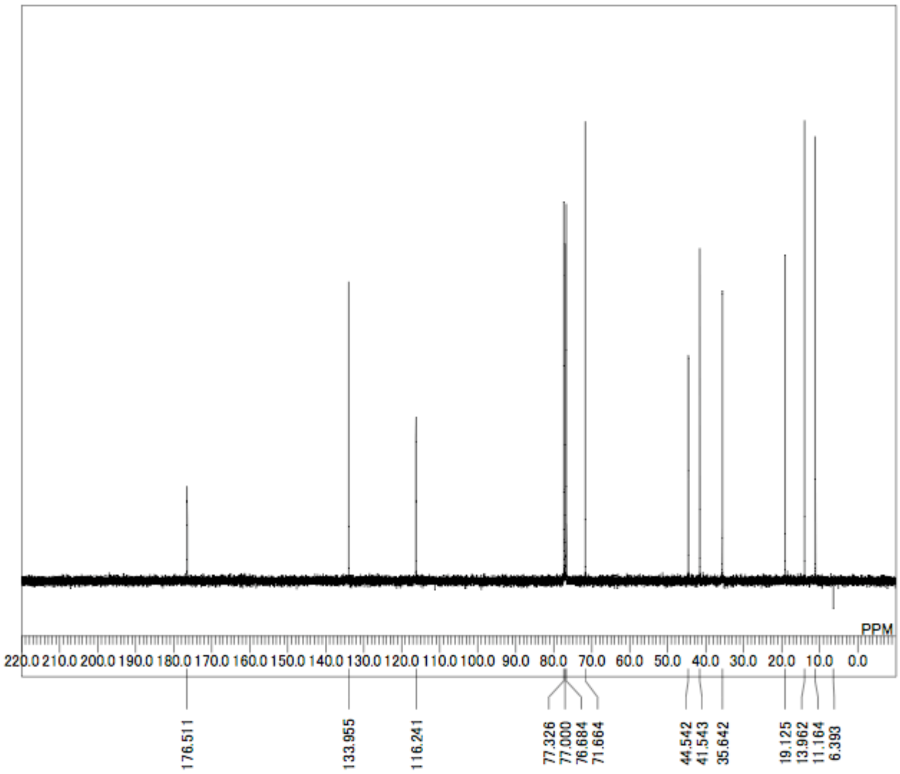
5t



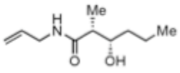
DFILE	amide.als
COMNT	
DATIM	06-01-2012 14:22:01
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.39 Hz
SCANS	16
ACQTM	1.7459 sec
PD	3.0000 sec
PW1	6.50 usec
IRNUC	1H
CTEMP	18.7 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	46



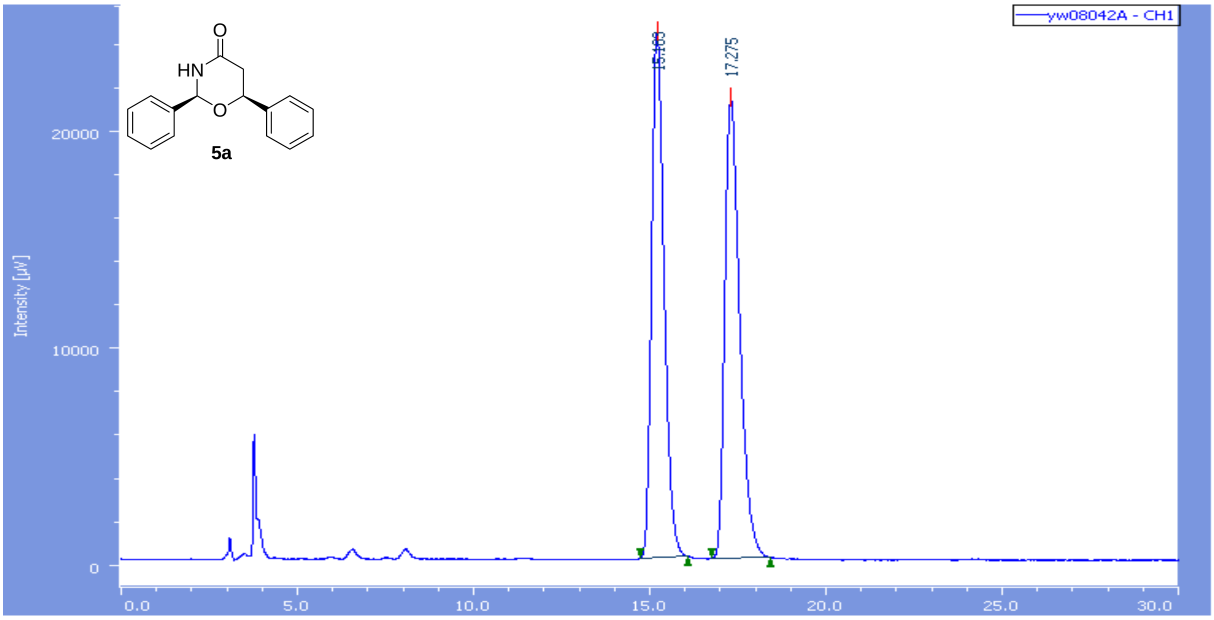
7

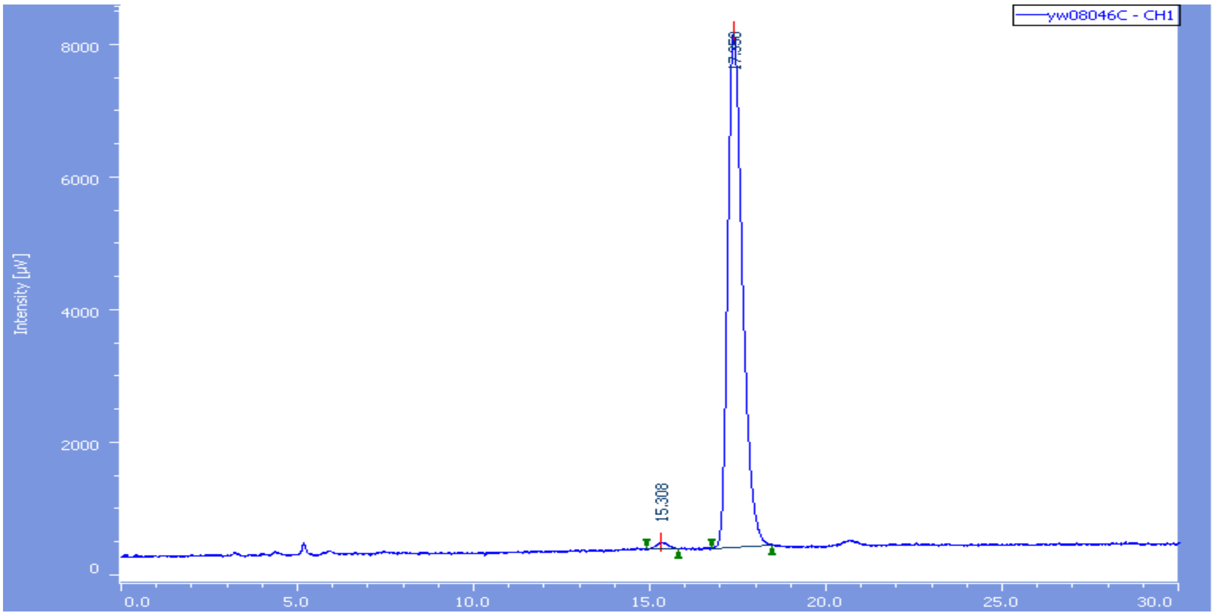


DFILE	amide, 13C.als
COMNT	
DATIM	07-01-2012 19:04:26
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	26214
FREQU	24999.62 Hz
SCANS	361
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.33 usec
IRNUC	1H
CTEMP	19.6 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



7



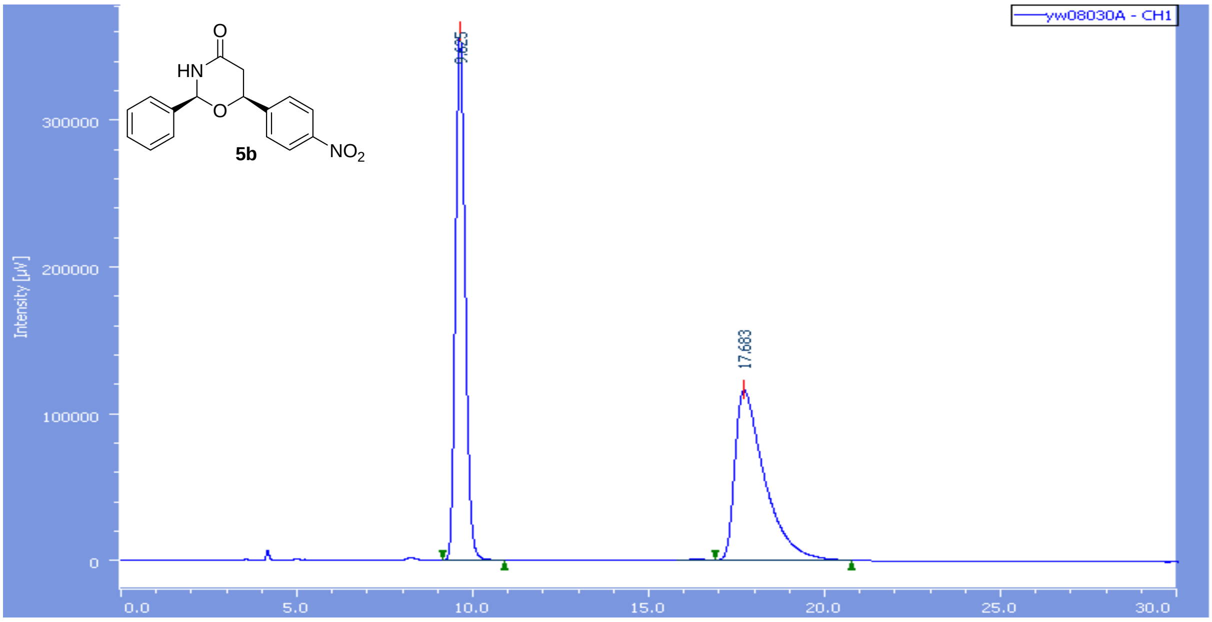


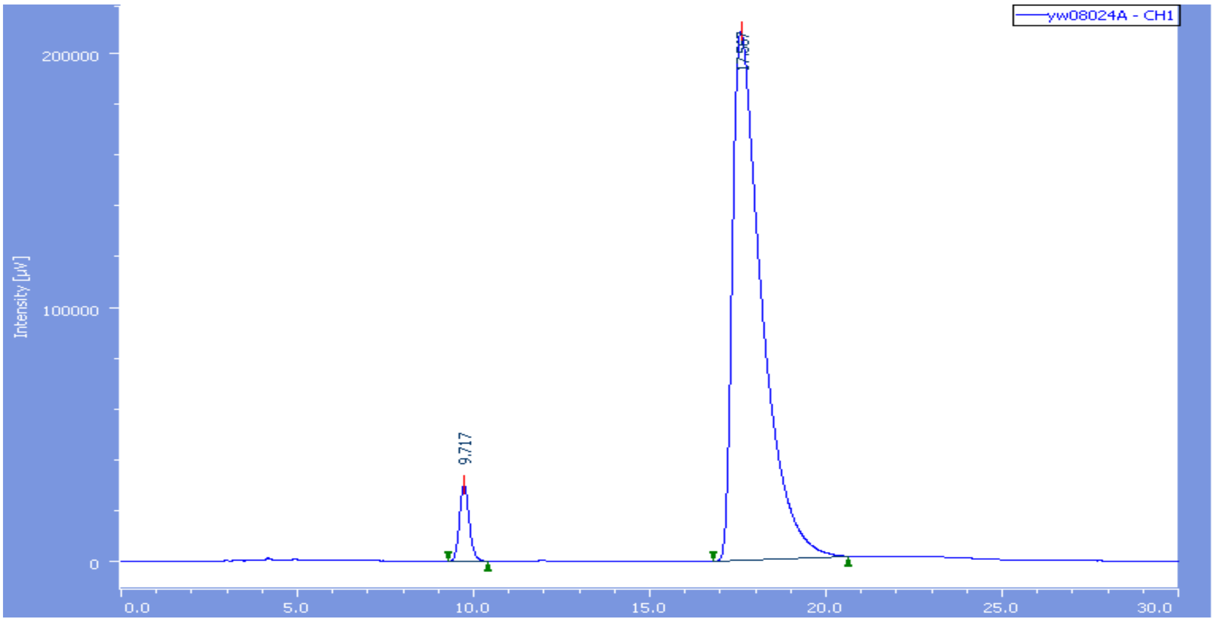
5a (racemate)

Peak No.	**Time (min)**	**Area [m V. Sec]**	**Area %**
1	15.18	618563	49.83
2	17.28	622652	50.17

5a

Peak No.	**Time (min)**	**Area [m V. Sec]**	**Area %**
1	15.31	2416	1.06
2	17.36	226185	98.94



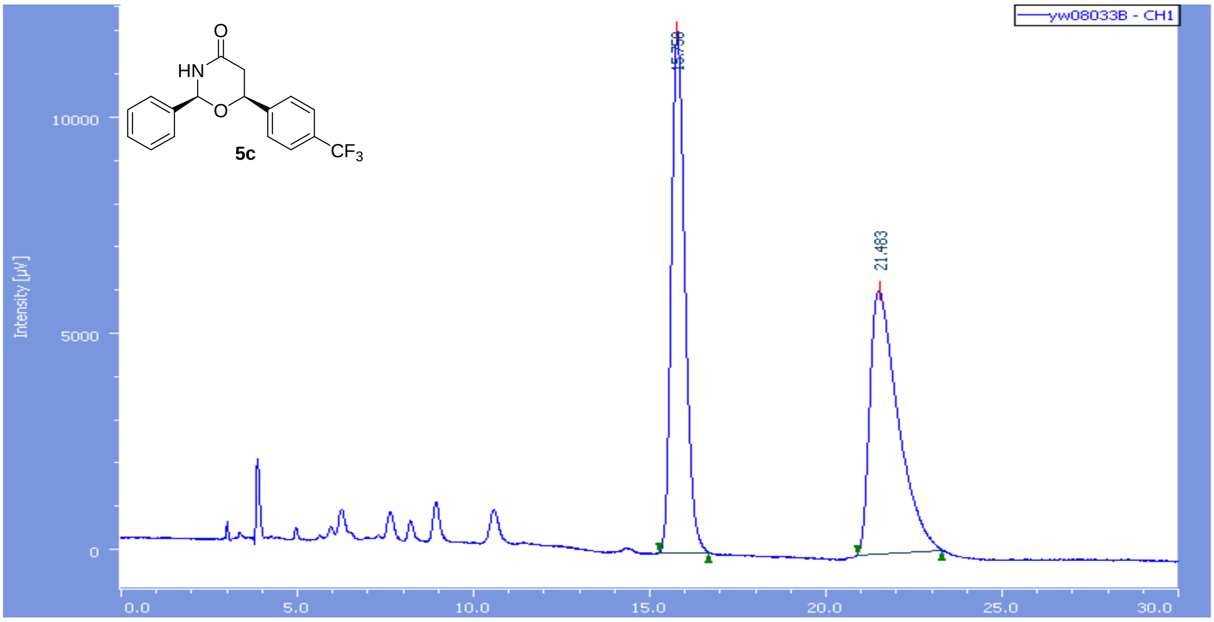


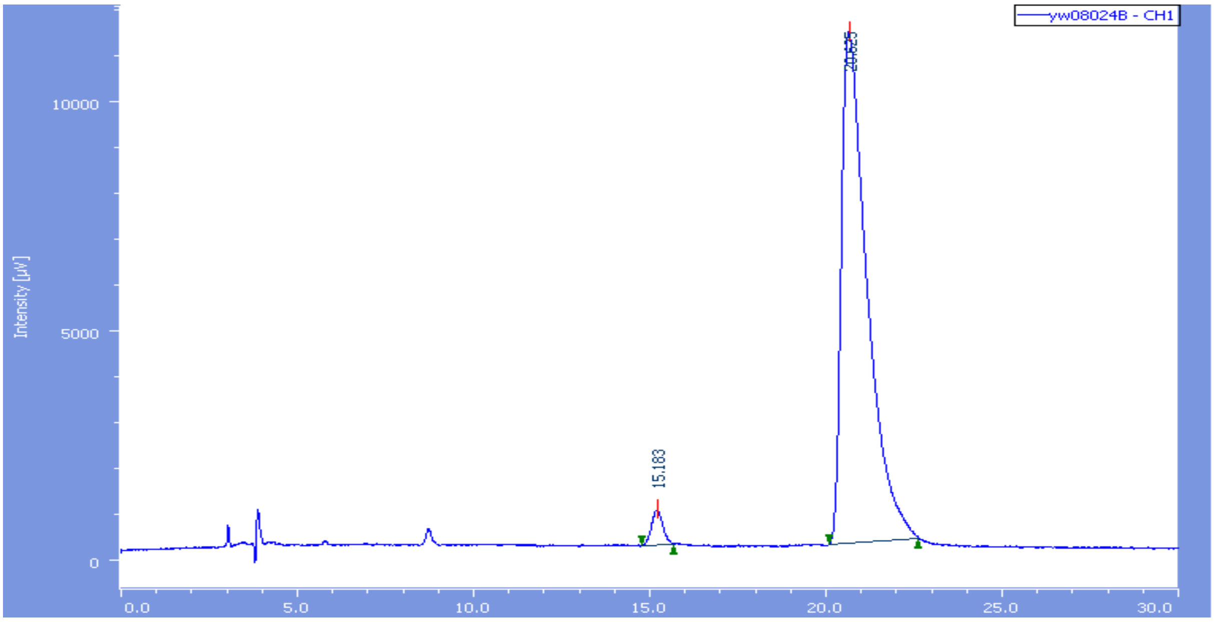
5b (racemate)

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	9.63	6837382	50.28
2	17.68	6761453	49.72

5b

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	9.72	574974	4.58
2	17.56	11987345	95.42



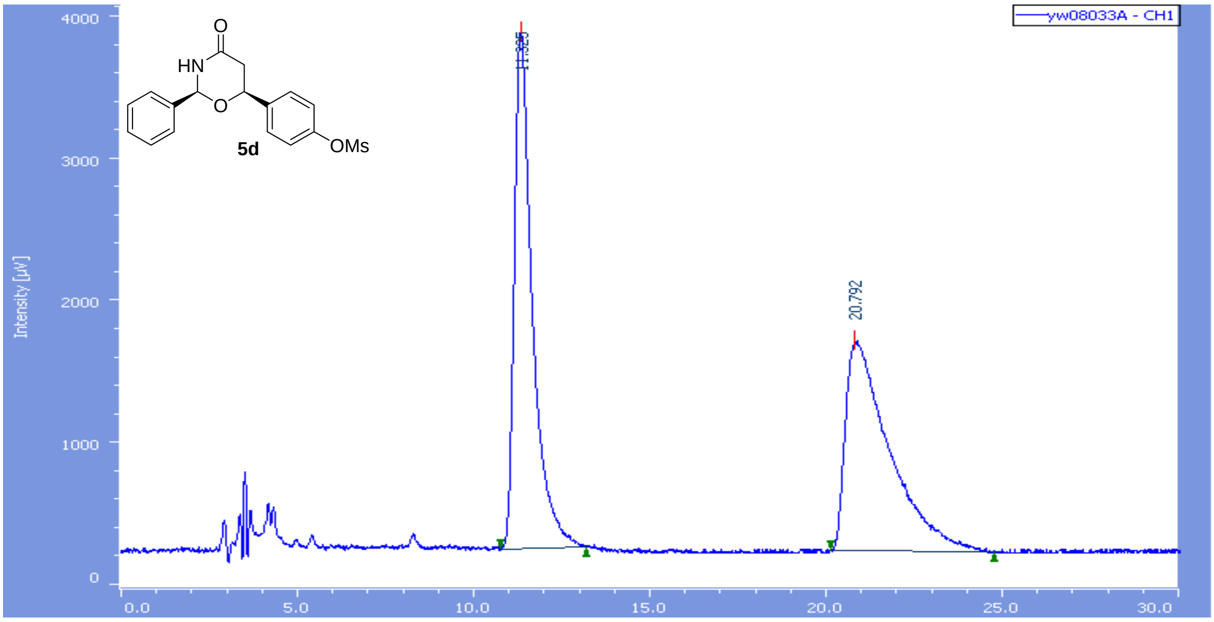


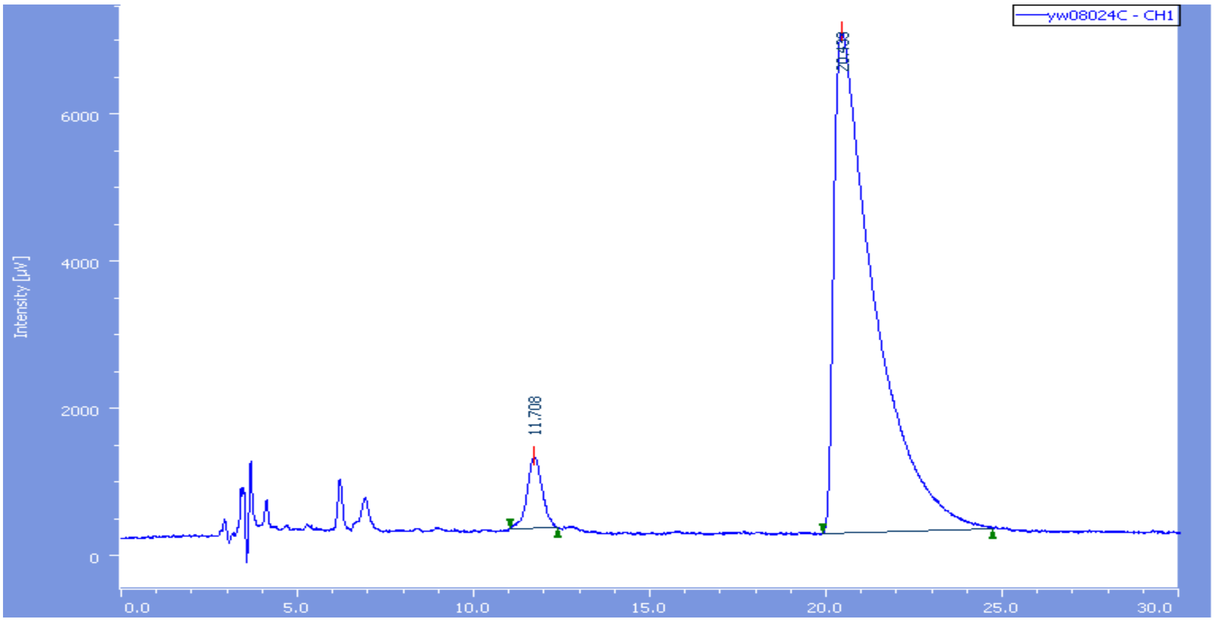
5c (racemate)

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	15.76	334578	49.75
2	21.48	337952	50.25

5c

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	15.18	16738	2.88
2	20.63	564681	97.12



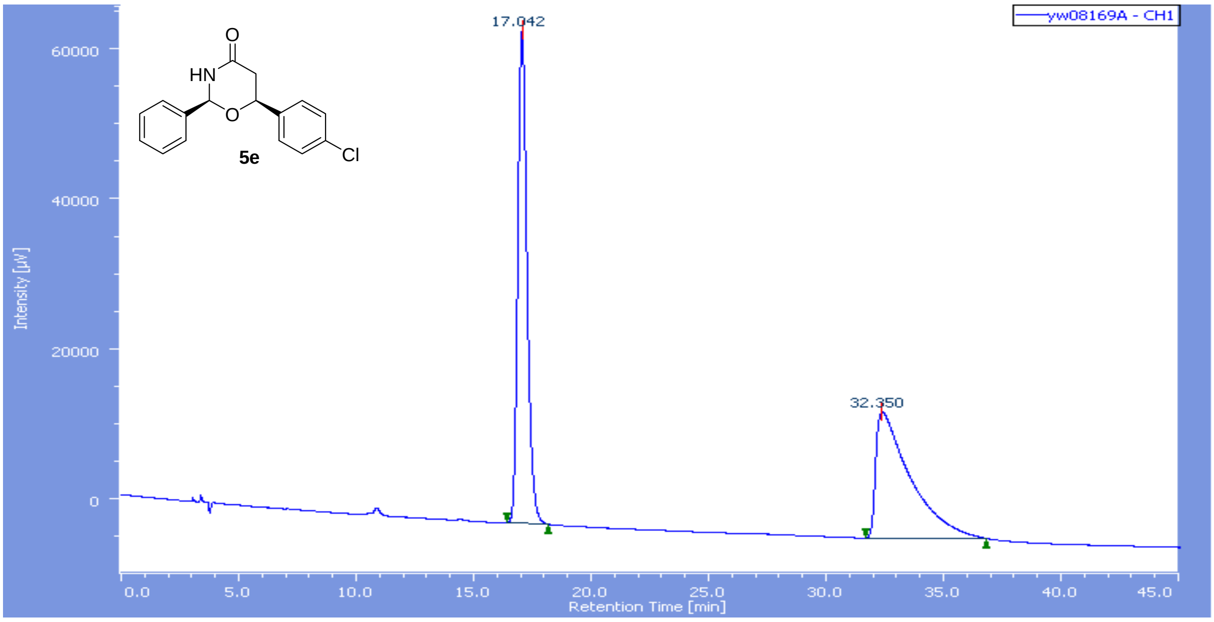


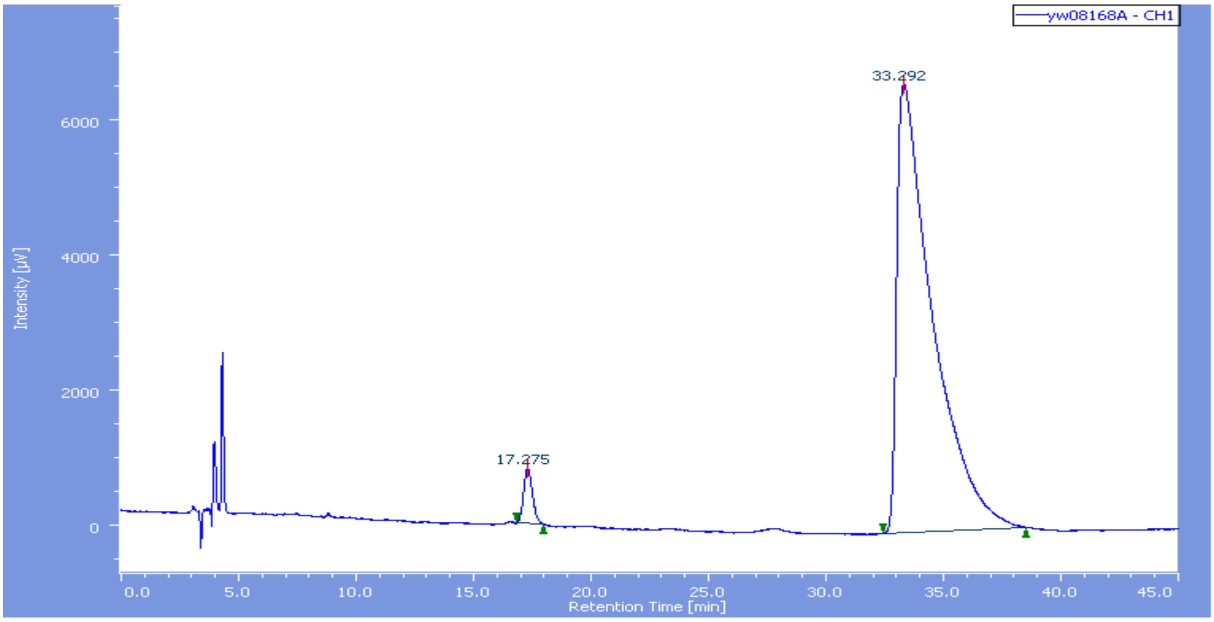
5d (racemate)

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	11.33	128712	50.23
2	20.79	127514	49.77

5d

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	11.71	28601	5.05
2	20.43	538002	94.95



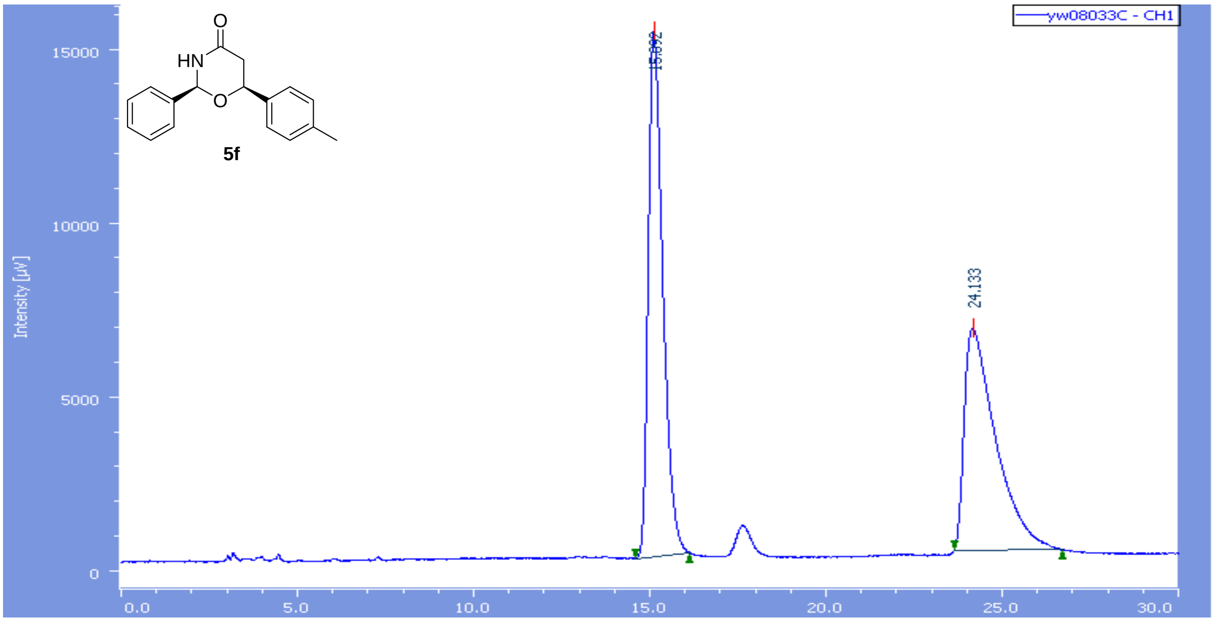


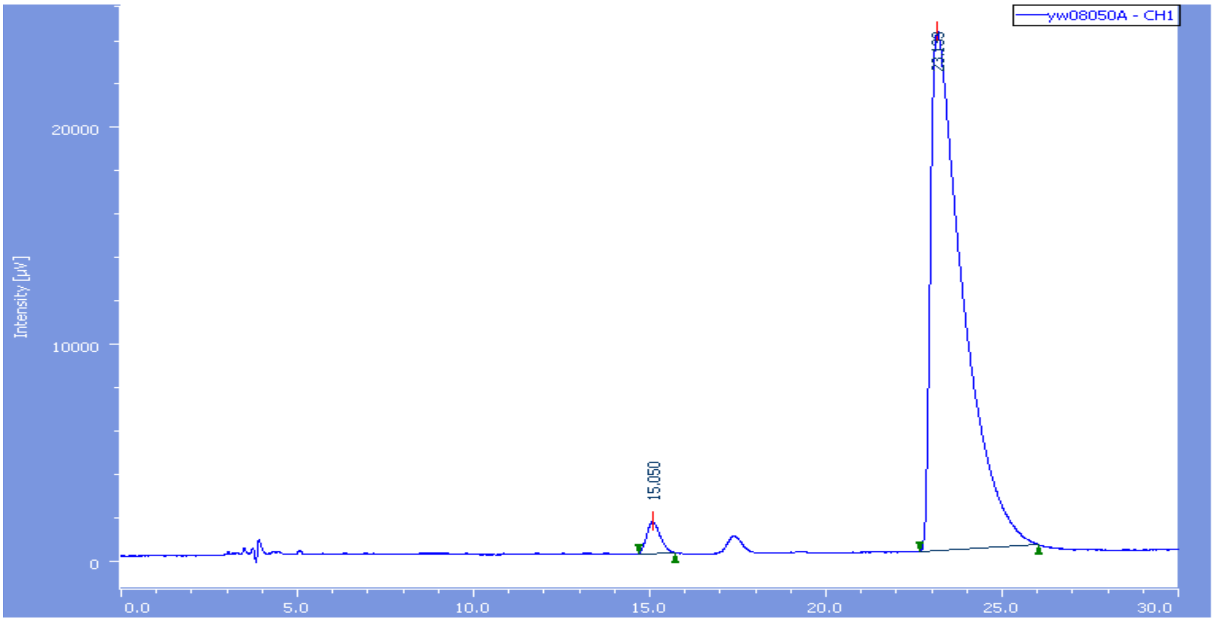
5e (racemate)

PeakNo.	Time (min)	Area [m V. Sec]	Area %
1	17.04	1748875	50.00
2	32.35	1748212	50.00

5e

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	17.28	21161	2.94
2	33.29	699008	97.06



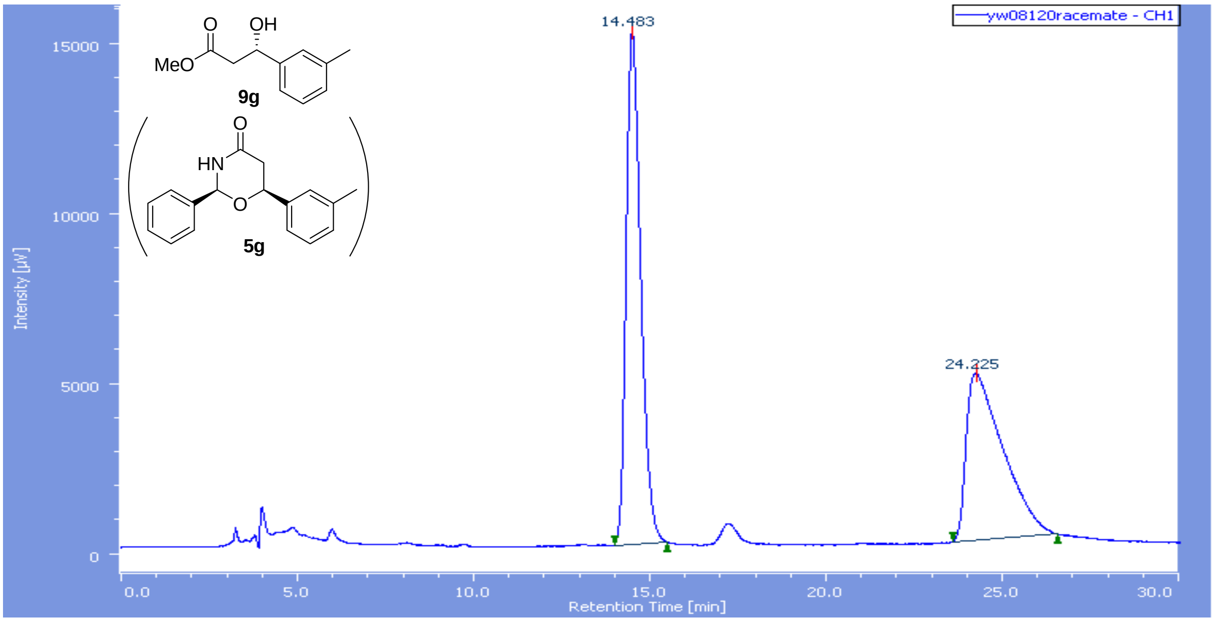


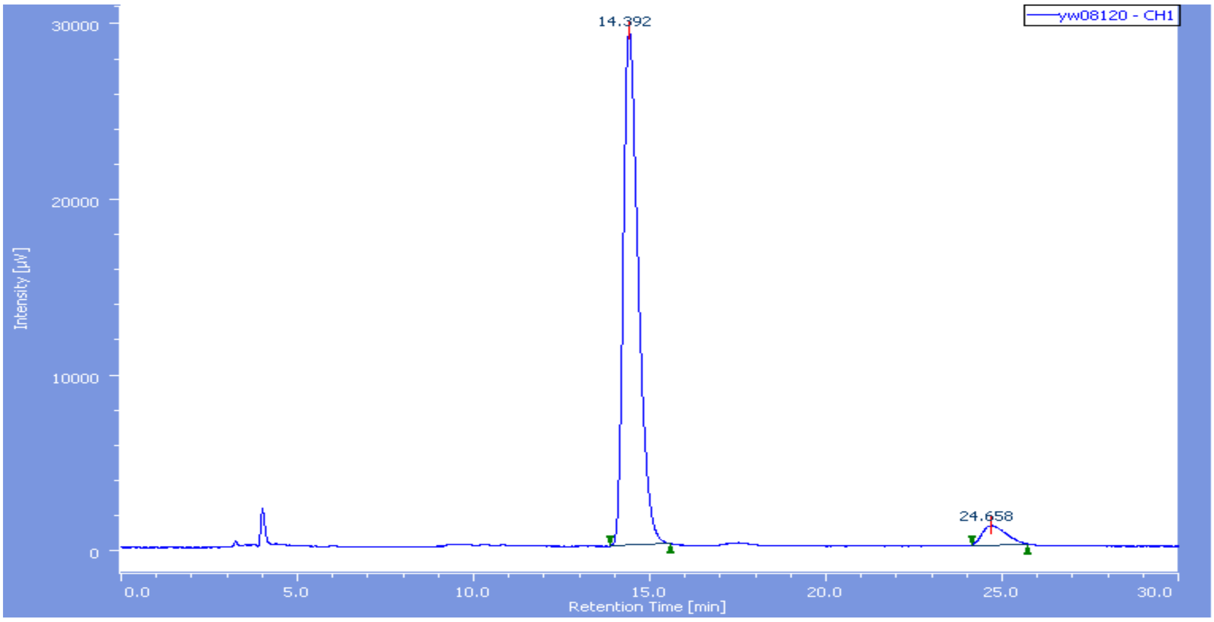
5f (racemate)

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	15.09	432413	49.85
2	24.13	434893	50.15

5f

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	15.05	34666	2.22
2	23.13	1526881	97.78



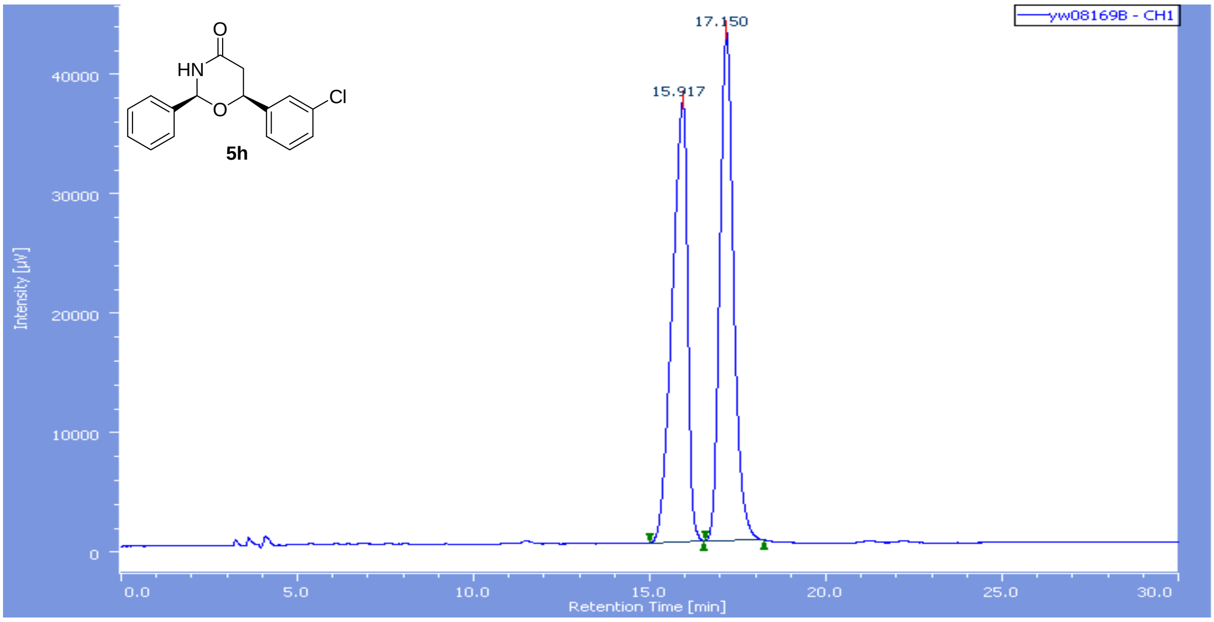


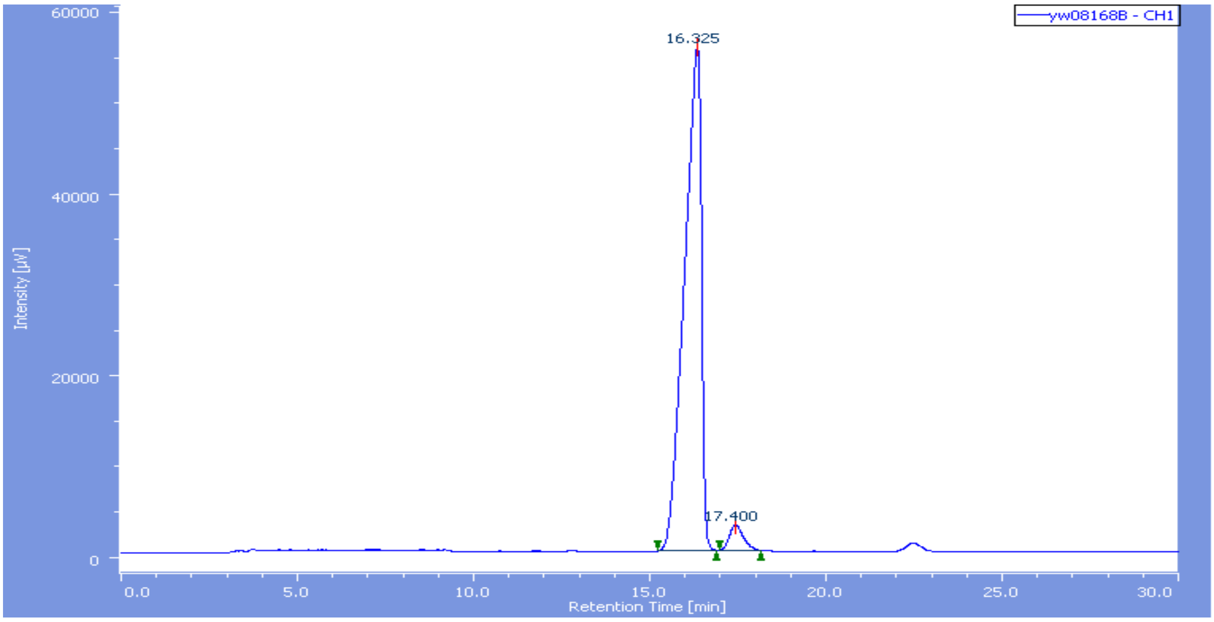
9g (racemate)

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	14.48	446570	50.76
2	24.21	433125	49.24

9g

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	14.39	878008	4.06
2	24.66	37155	95.94



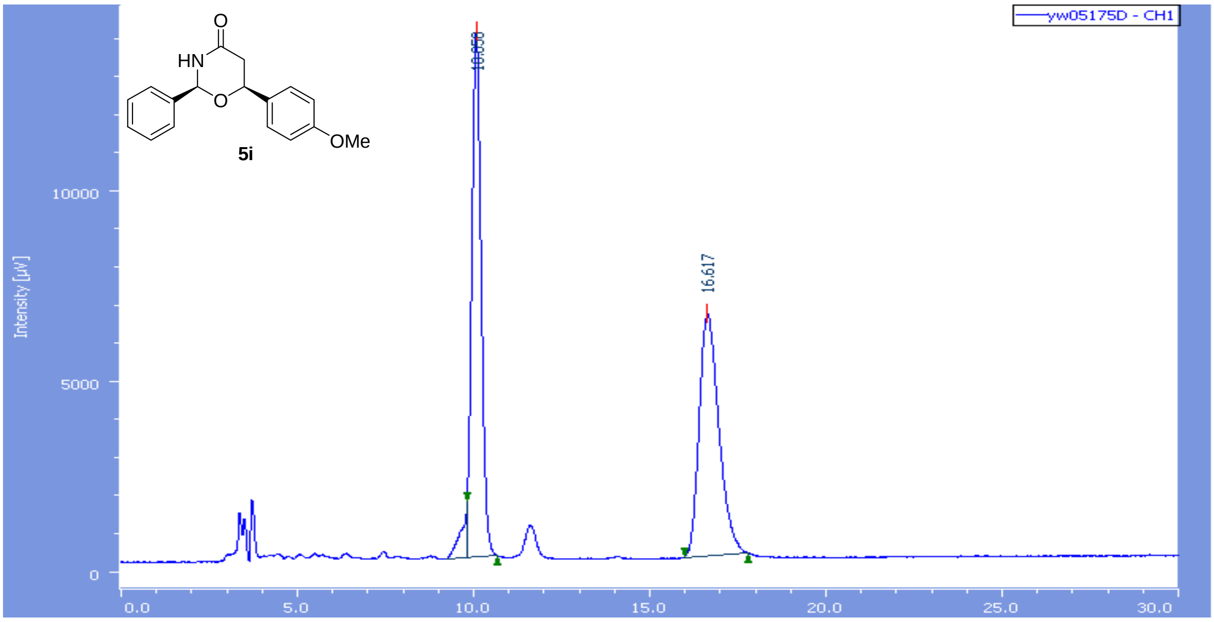


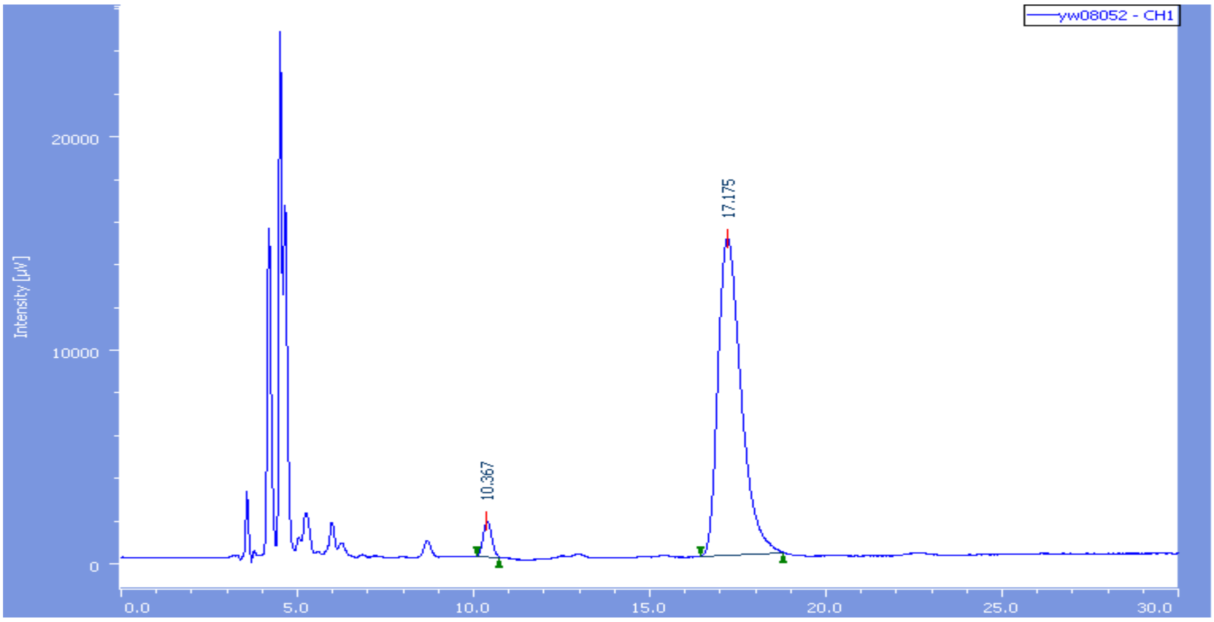
5h (racemate)

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	15.92	1142620	50.00
2	17.15	1142401	50.00

5h

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	16.33	1854828	95.97
2	17.40	77886	4.03



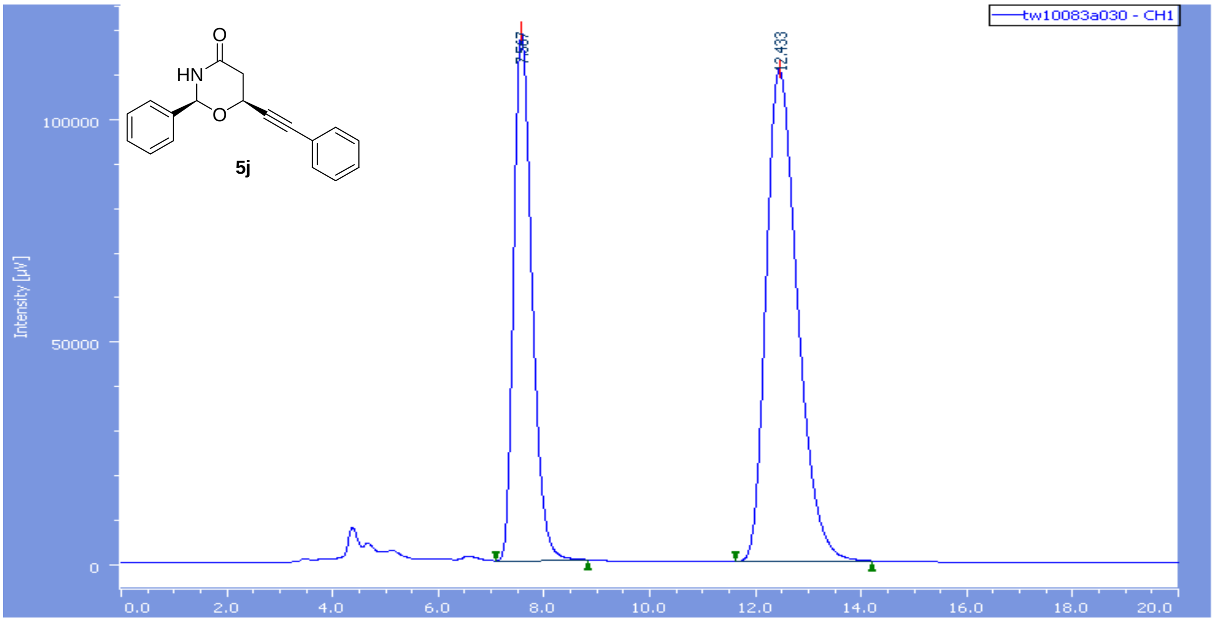


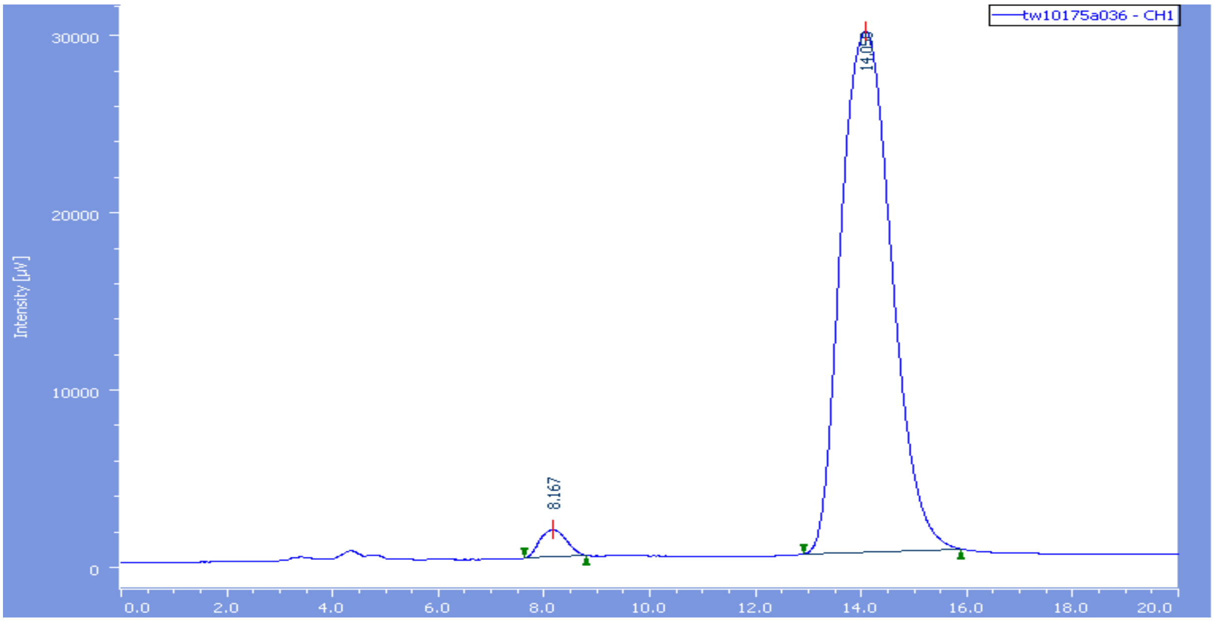
5i (racemate)

Peak No.	**Time (min)**	**Area [m V. Sec]**	**Area %**
1	10.06	254511	49.80
2	16.62	256513	50.20

5i

Peak No.	**Time (min)**	**Area [m V. Sec]**	**Area %**
1	10.37	28062	3.99
2	17.18	674969	96.01



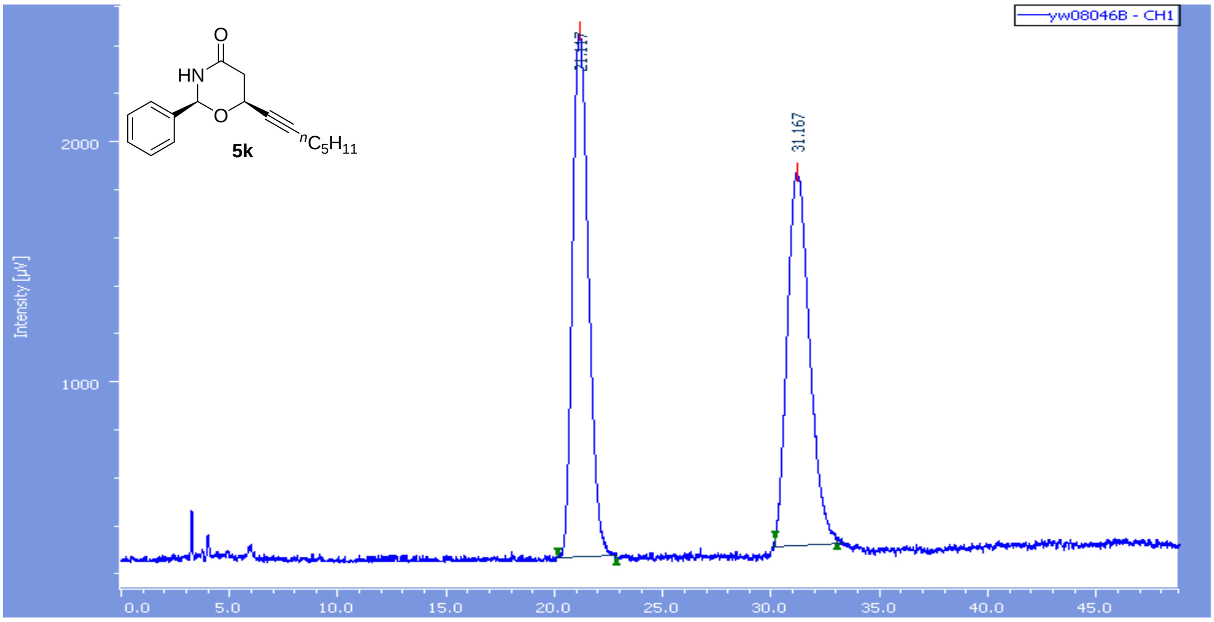


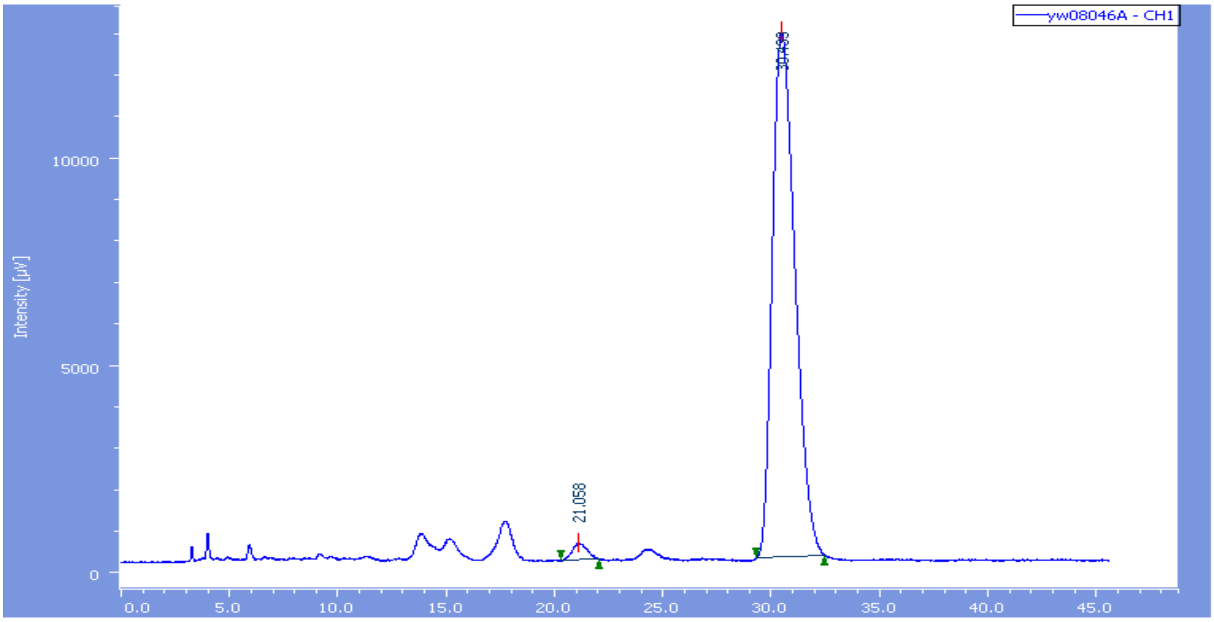
5j (racemate)

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	7.57	4556110	49.97
2	12.43	4561453	50.03

5j

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	8.17	53782	2.68
2	14.06	1952977	97.32



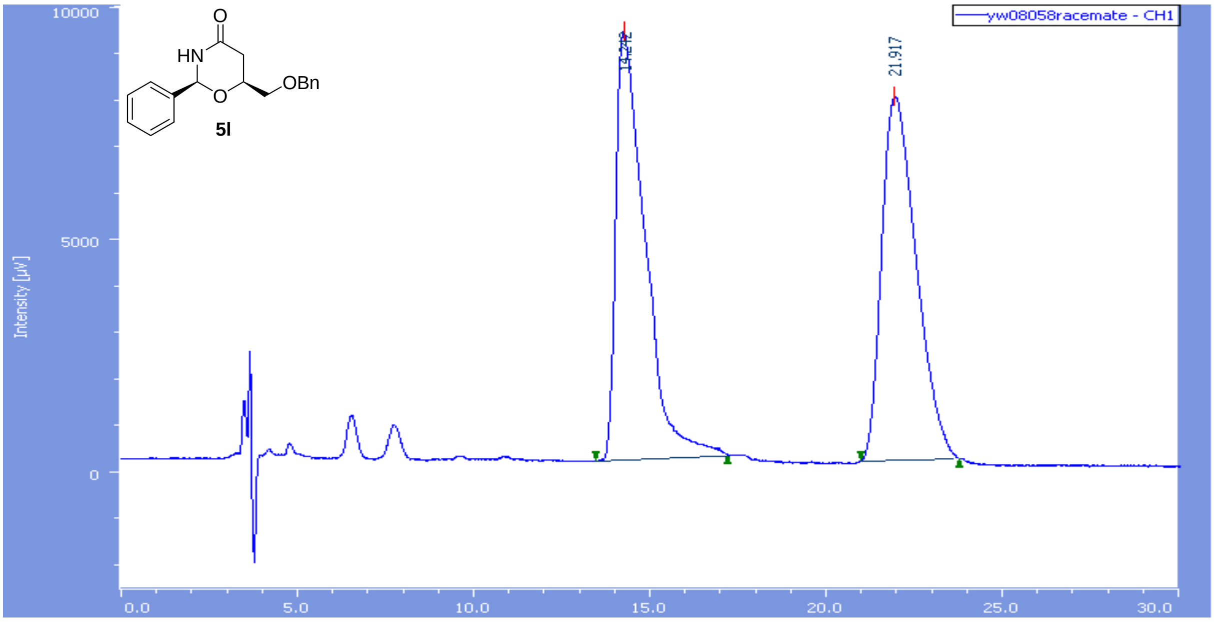


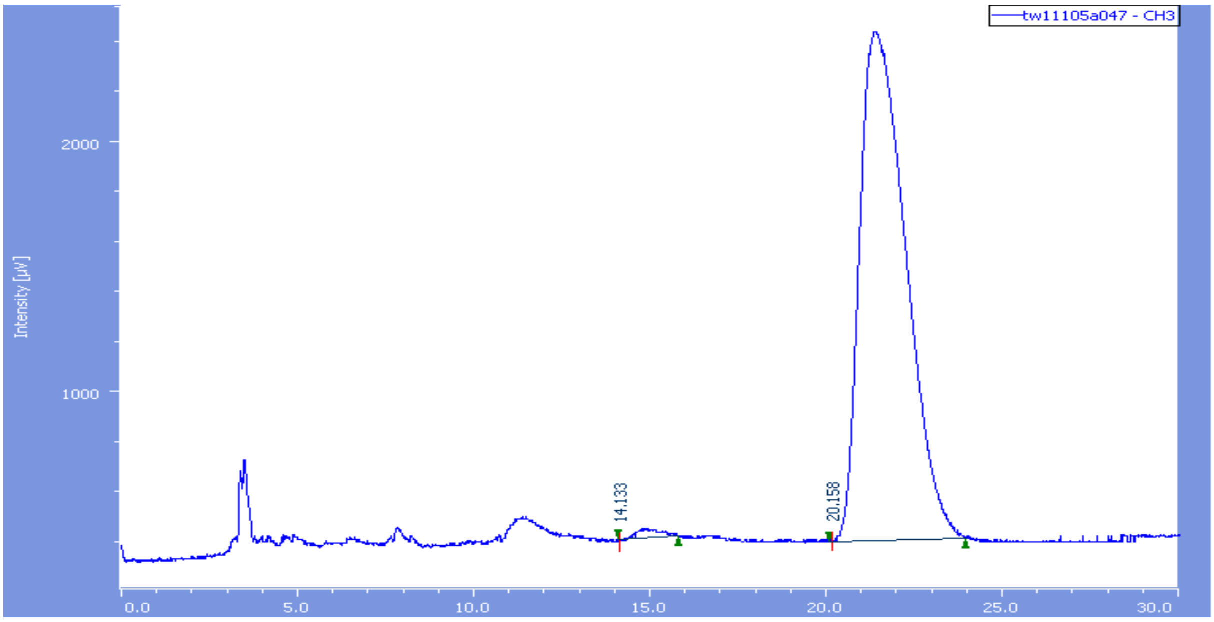
5k (racemate)

Peak No.	**Time (min)**	**Area [m V. Sec]**	**Area %**
1	21.12	111894	50.15
2	31.17	111237	49.85

5k

Peak No.	**Time (min)**	**Area [m V. Sec]**	**Area %**
1	21.06	18751	2.00
2	30.43	916885	98.00



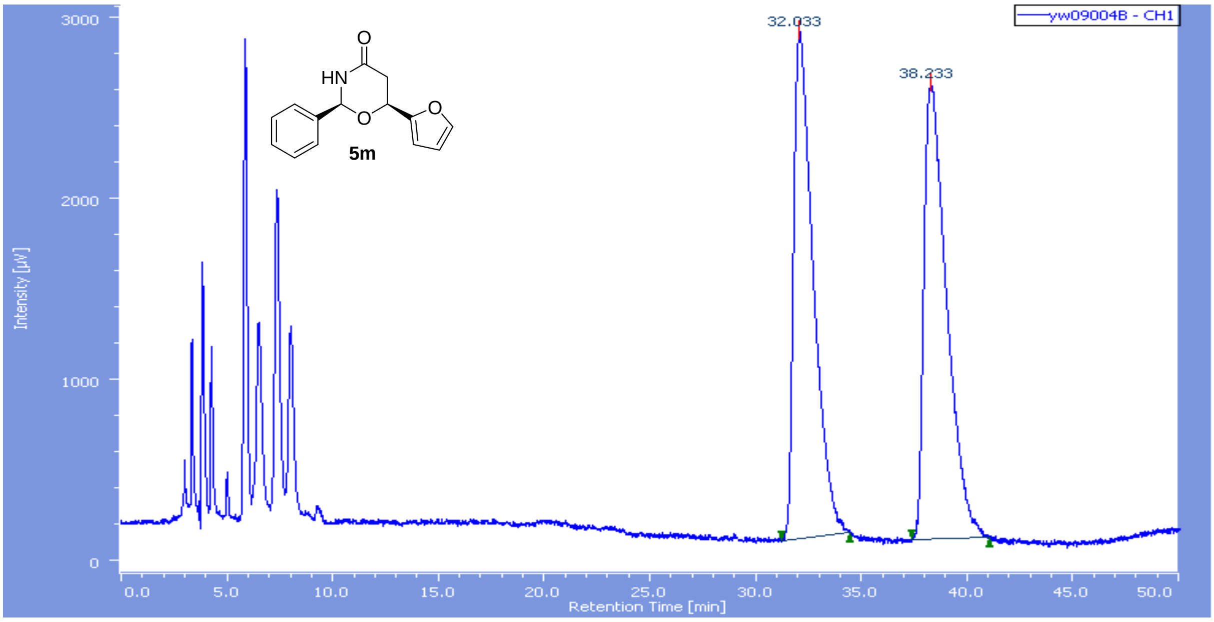


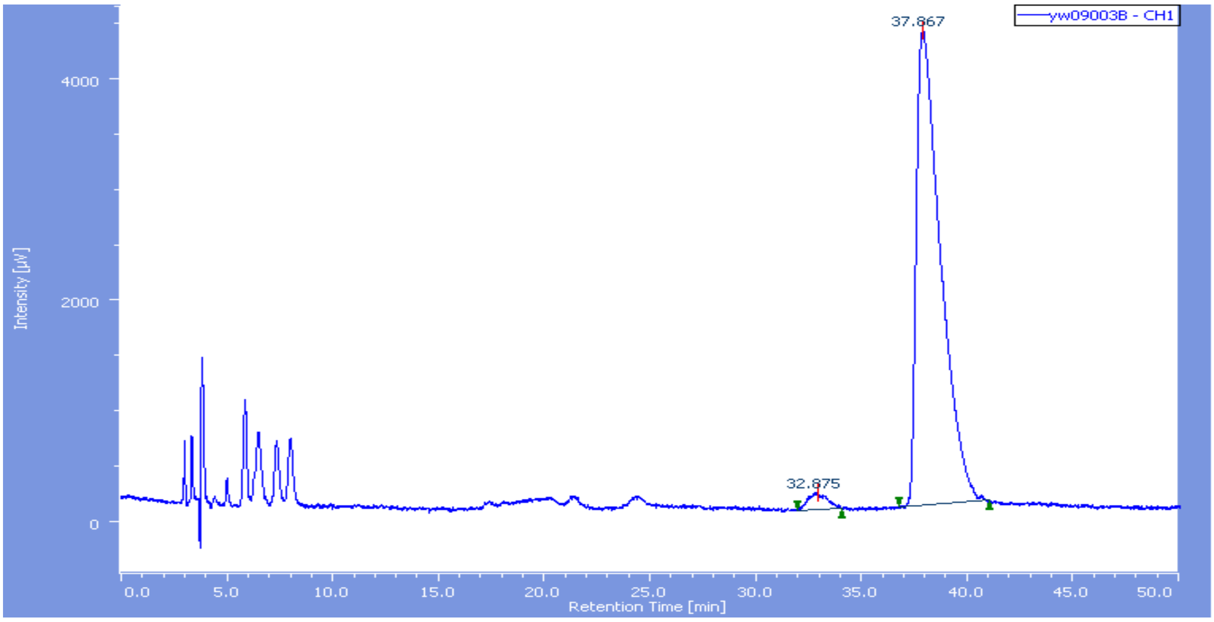
5l (racemate)

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	14.24	542287	49.93
2	21.92	543770	50.07

5l

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	14.89	2633	1.39
2	21.37	186845	98.61



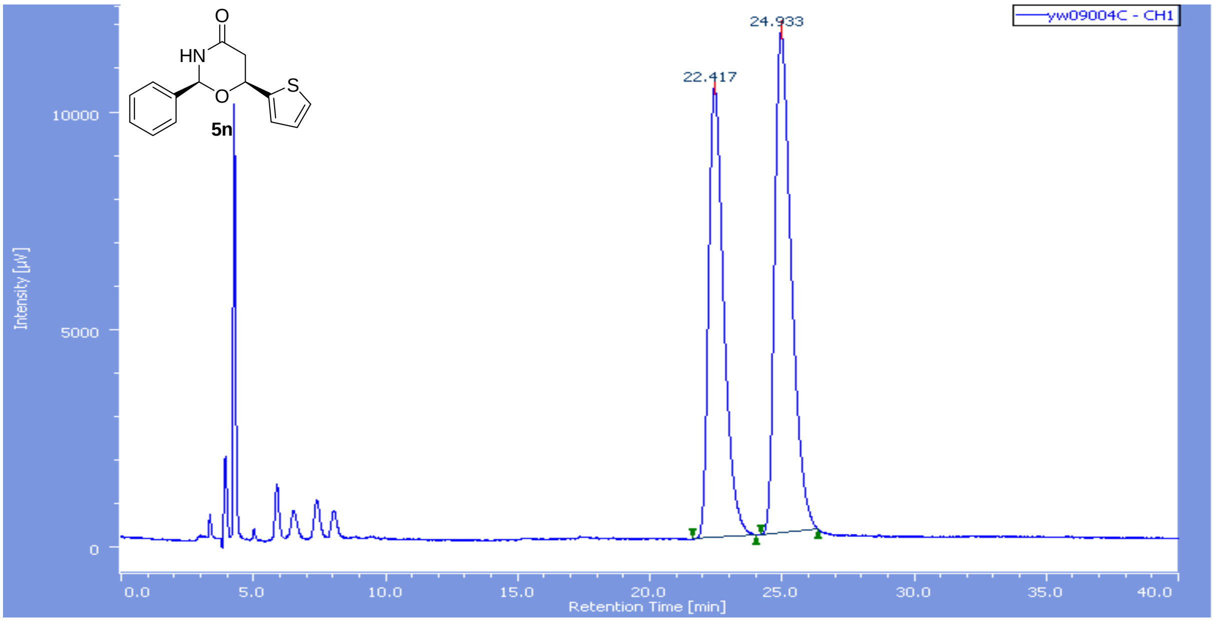


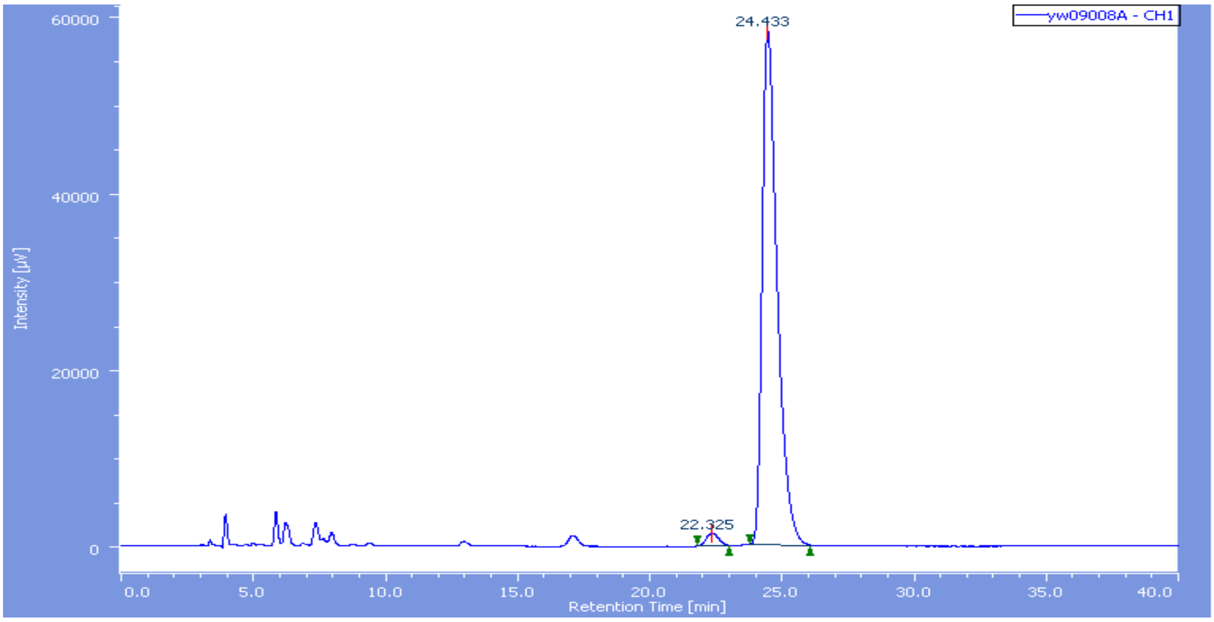
5m (racemate)

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	32.03	182366	49.58
2	21.92	185412	50.42

5m

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	32.88	9442	2.70
2	37.87	340778	97.30



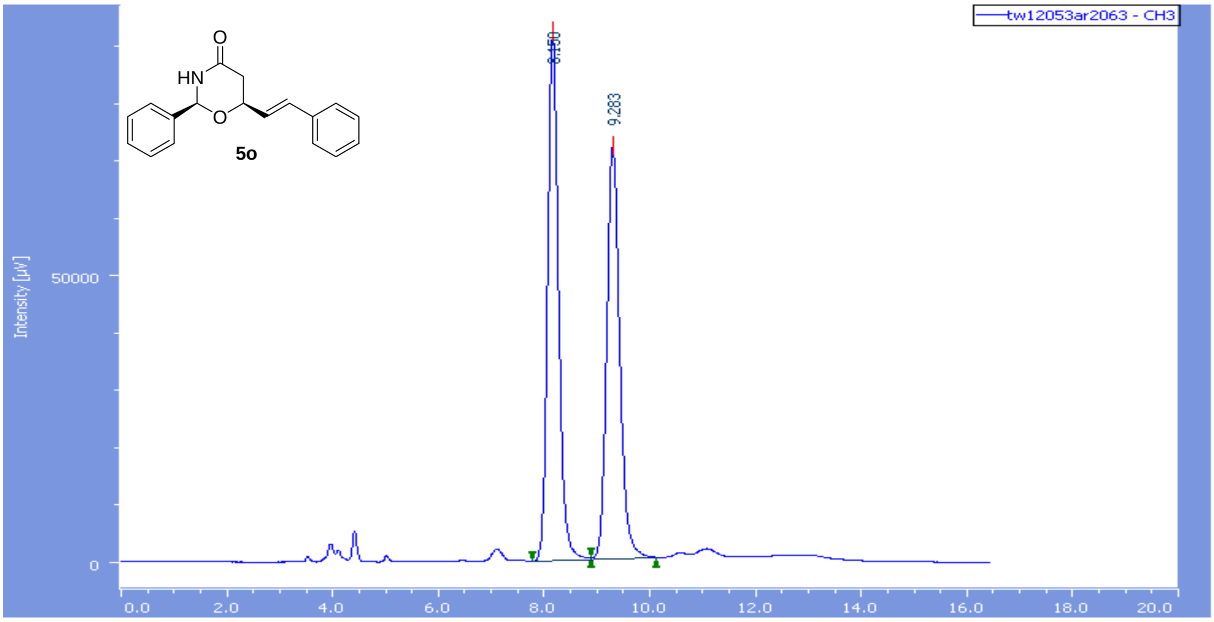


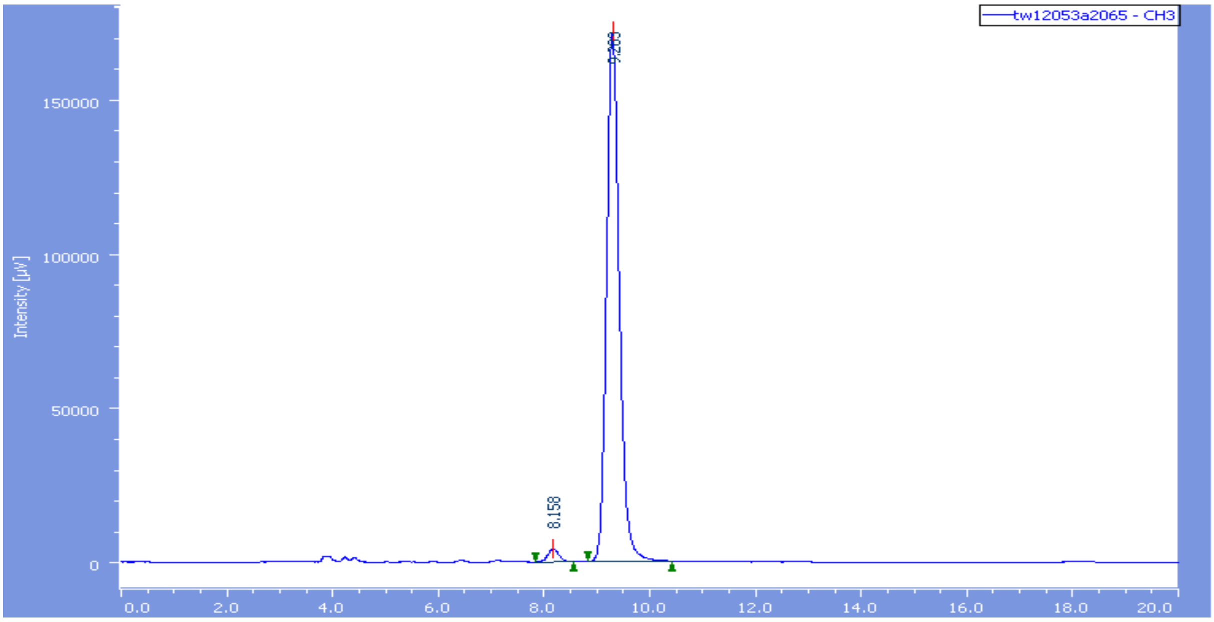
5n (racemate)

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	22.42	441738	49.33
2	24.93	453638	50.67

5n

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	22.33	46226	1.98
2	24.43	2291619	98.02



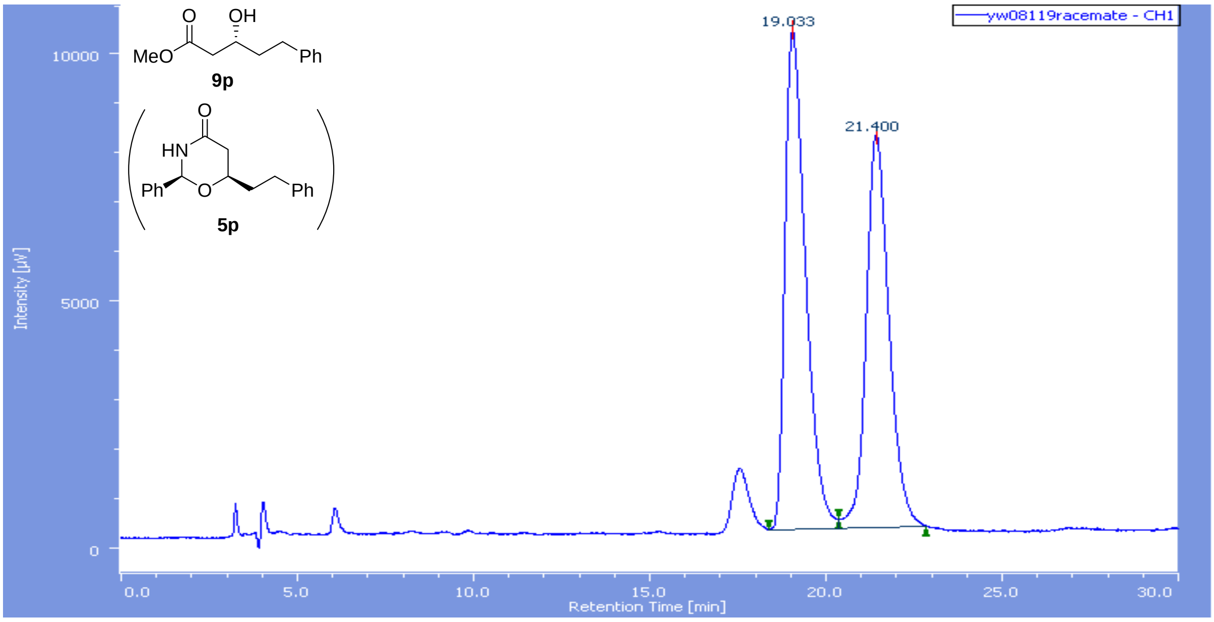


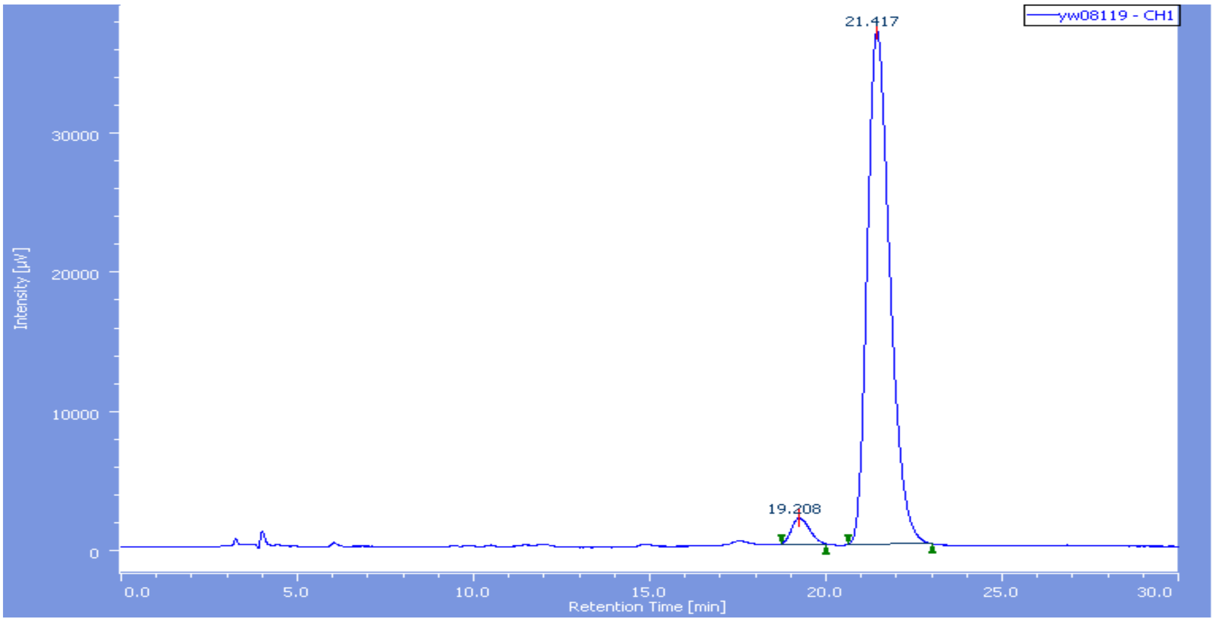
5o (racemate)

Peak No.	**Time (min)**	**Area [m V. Sec]**	**Area %**
1	8.15	1313541	50.21
2	9.28	1302371	49.79

5o

Peak No.	**Time (min)**	**Area [m V. Sec]**	**Area %**
1	8.16	60080	2.04
2	9.28	2881232	97.96



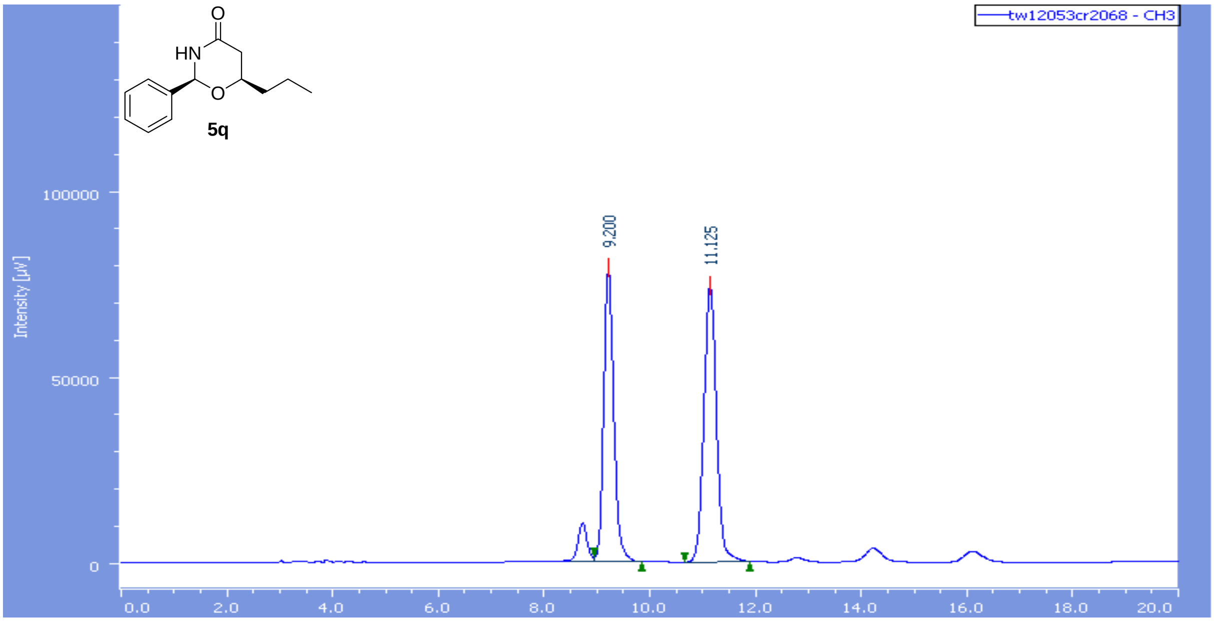


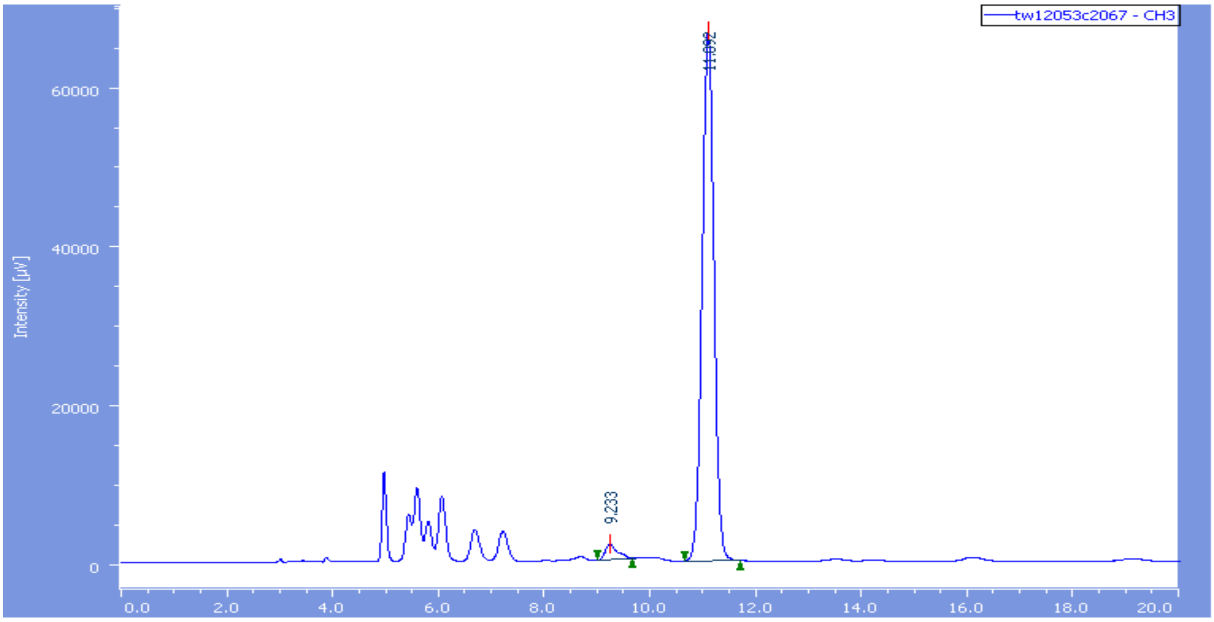
9p (racemate)

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	19.03	399044	50.32
2	21.40	393938	49.68

9p

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	19.21	66123	3.87
2	21.42	1642780	96.13



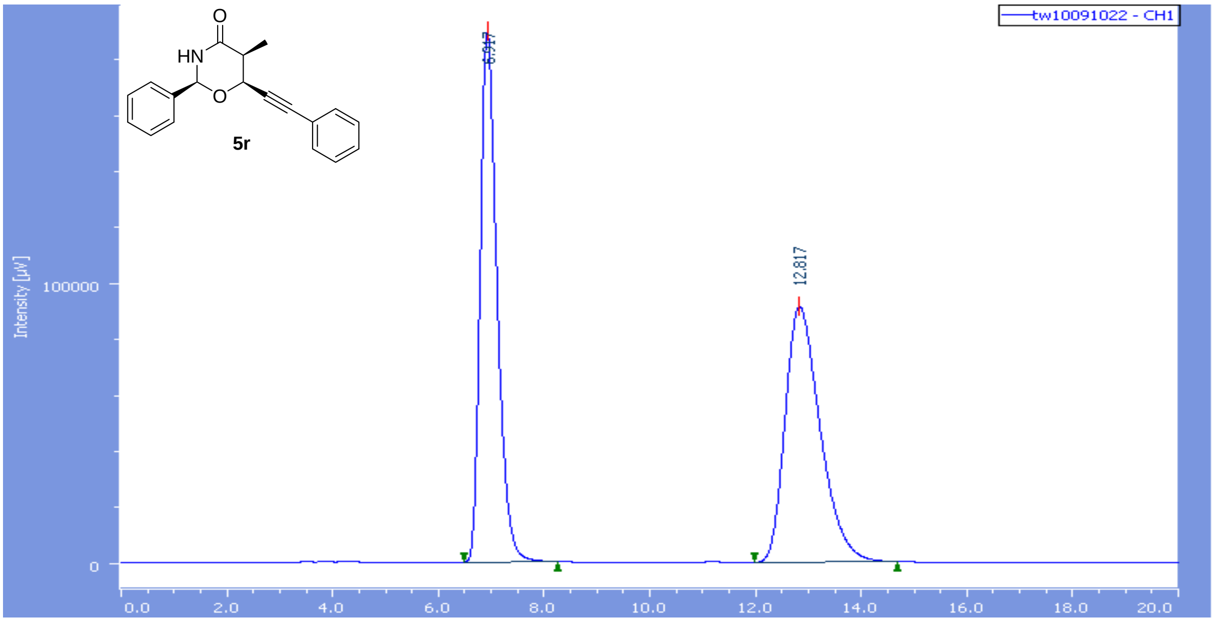


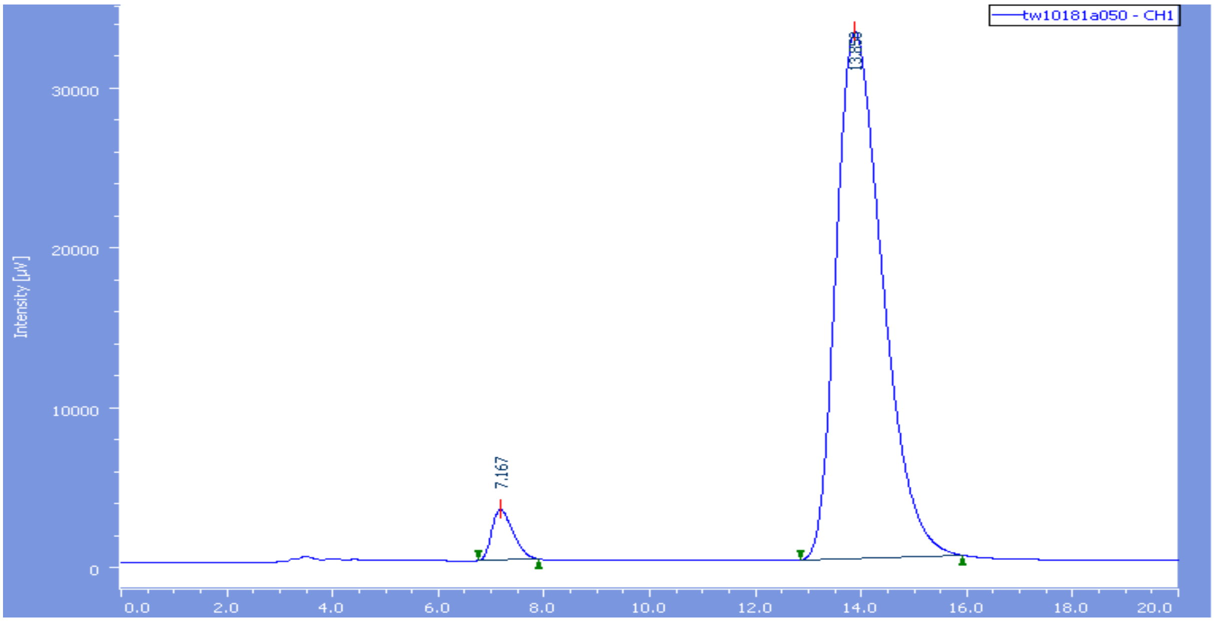
5q (racemate)

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	9.20	1244922	50.47
2	11.13	1221583	49.53

5q

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	9.23	36717	3.44
2	11.09	1030646	96.56



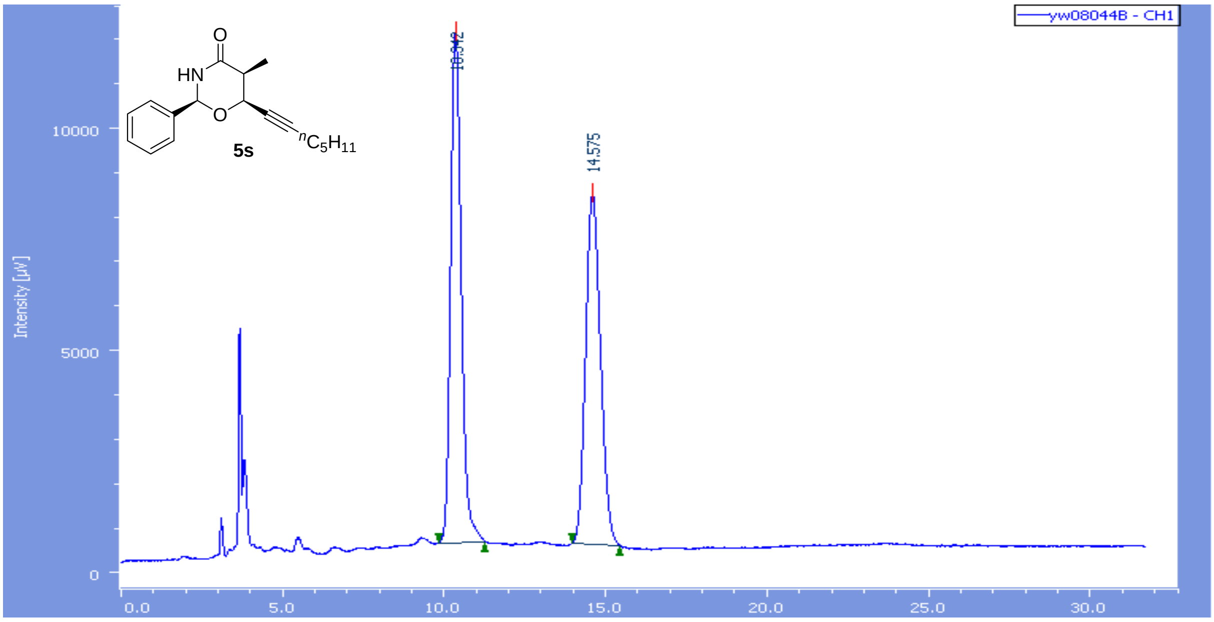


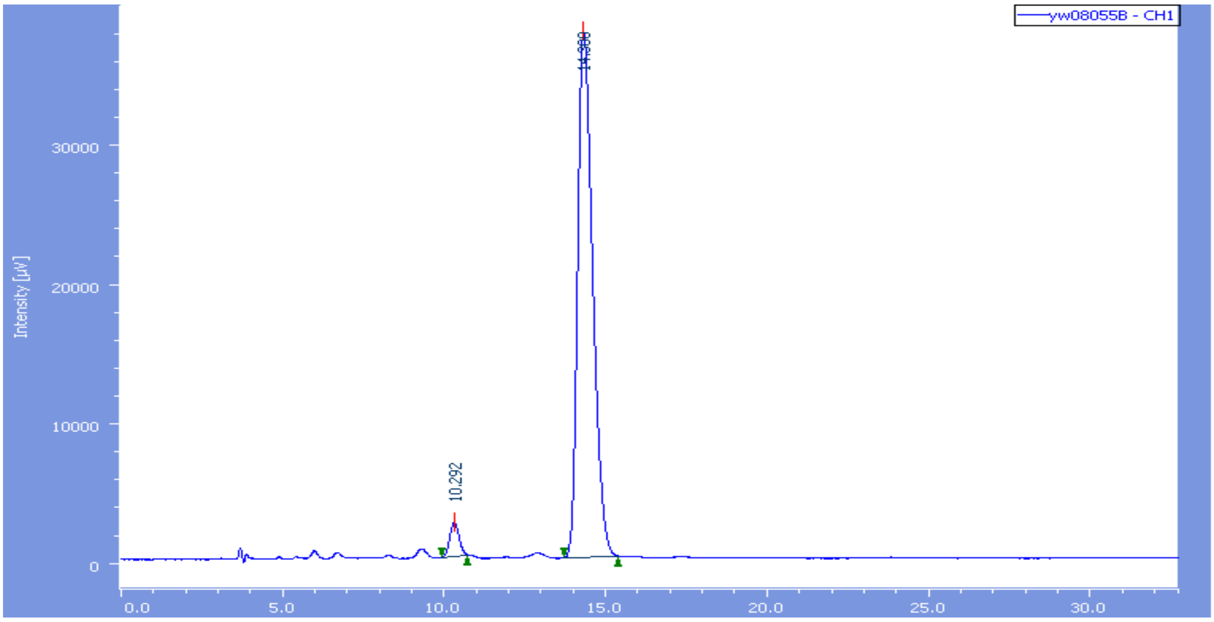
5r (racemate)

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	6.92	4177546	49.89
2	12.82	4196476	50.11

5r

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	7.17	92105	4.41
2	13.86	1996462	95.59



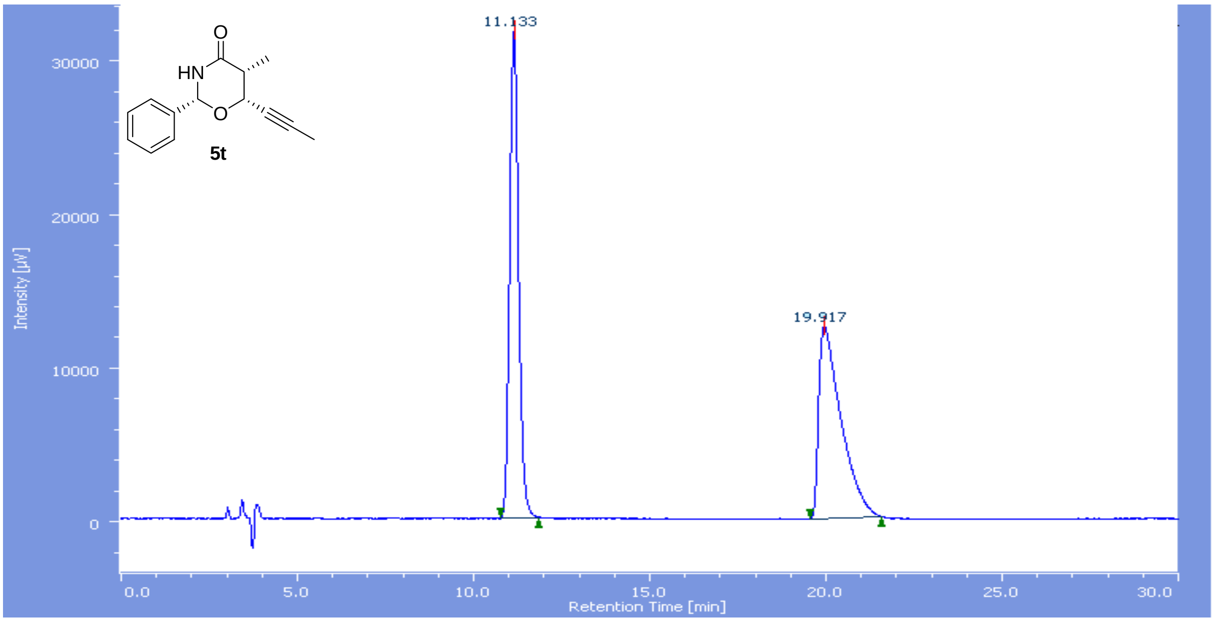


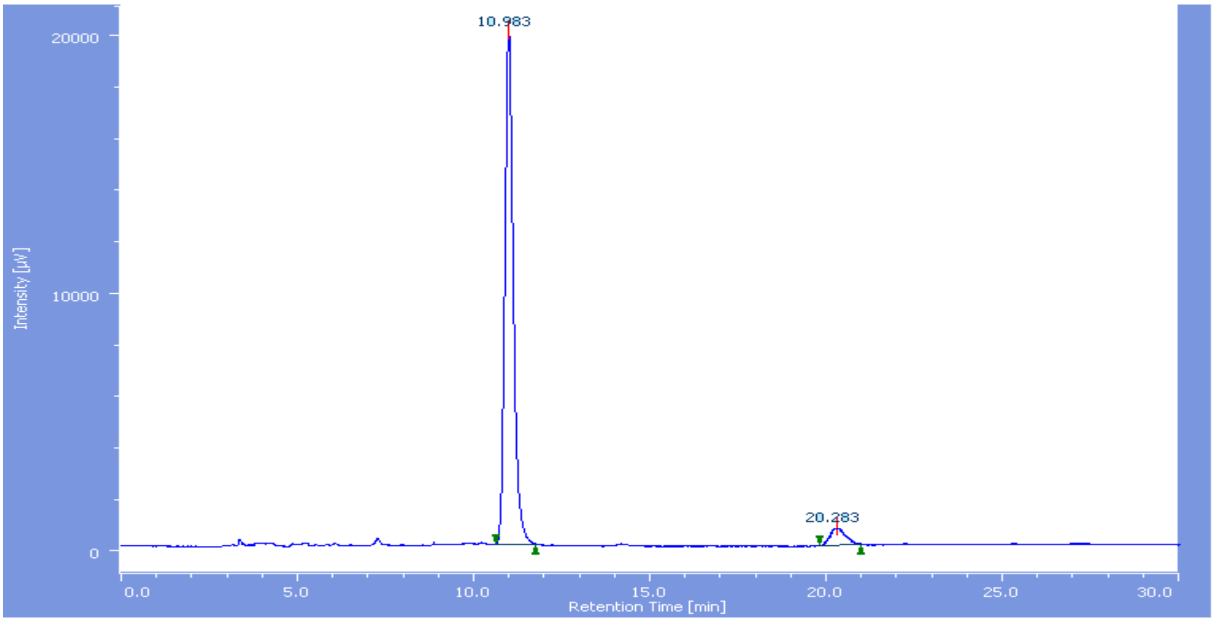
5s (racemate)

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	10.34	253278	50.06
2	14.58	252574	49.94

5s

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	10.29	47637	3.77
2	14.30	1217429	96.23





5t (racemate)

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	11.13	557353	50.28
2	19.92	551208	49.72

5t

Peak No.	Time (min)	Area [m V. Sec]	Area %
1	10.98	333129	96.46
2	20.28	12213	3.54