# Enantioselective Homocrotylboration of Aliphatic Aldehydes

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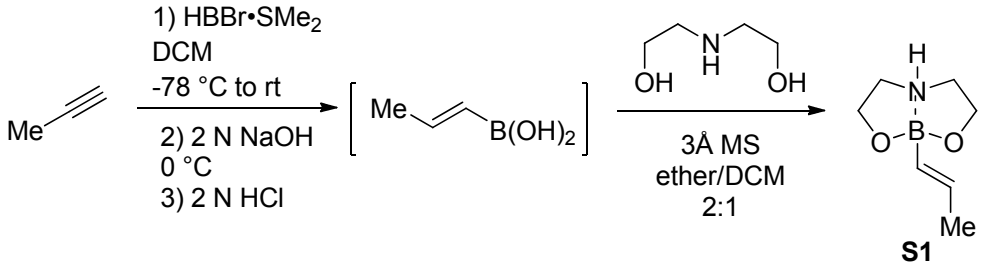
**General Experimental Methods**

Reactions were carried out in oven-dried glassware under a nitrogen atmosphere and were stirred magnetically. The phrase "concentrated" refers to removal of solvents by means of a rotary evaporator attached to a Welch 1400 oil pump (bled to 5-300 mm Hg as needed) followed by removal of residual solvents at < 1 Torr on a vacuum manifold attached to a Welch 1400 vacuum pump. SiliaFlash® F60 (230-400 mesh) from SiliCycle® was used for flash column chromatography unless specifically indicated. Analytical thin layer chromatography (TLC) was performed using silica gel 60 F-254 pre-coated glass plates (0.25 mm). TLC plates were analyzed by short wave UV illumination, or by staining with iodine on silica or dipping in cerium-ammonium-molybdate (CAM) stain (40 g of ammonium pentamolybdate, 1.6 g of cerium (IV) sulfate, 800 mL of diluted sulfuric acid (1:9, with water, v/v)) or vanillin stain (15g vanillin in 250 mL ethanol and 2.5 mL concentrated sulfuric acid) and heating on a hot plate. Tetrahydrofuran (THF), dichloromethane (DCM), toluene and diethyl ether ($Et_2O$) were obtained by degassing with argon and passage through activated alumina columns. $^1H$ and $^{13}C$ NMR spectra were recorded on a Varian Inova 400 MHz in $CDCl_3$ at ambient temperature unless otherwise indicated. Chemical shifts are reported in δ (ppm downfield from tetramethylsilane) and referenced to residual undeuterated solvents (7.26 for $^1H$ NMR and 77.16 for $^{13}C$ NMR). Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet), p (pentet), m (multiplet), app (apparent) and br (broad). IR spectra were recorded on a Varian 640-IR FT-IR spectrometer and are reported in wave numbers ($cm^{-1}$). High performance liquid chromatography (HPLC) analyses were performed on an Agilent 1100 Series instrument equipped with a quaternary pump, using chiral columns (250 × 4.6 mm, 5 μm), monitored by UV absorption. Gas chromotography mass spectroscopy (GC-MS) analyses were performed on an Agilent 7890A GC System and 5975C VL MSD with Triple-Axis Detector. High resolution mass spectra (HRMS) were performed by Mass Spectrometry Laboratory, University of Illinois at Urbana-Champaign using electron impact (EI), chemical ionization (CI) or electrospray ionization (ESI). Optical rotation values were measured on a Jasco Digital Polarimeter using a cell with a path length of 1 dm (c given in g/100 mL).

**Preparation of S1**




Propyne (roughly 4.7 mL, 82.5 mmol) was condensed to a Schlenk flask at -78 °C. A 0 °C solution of $HBBr•SMe_2$ (1 M in DCM, 75 mL) was cannulated to propyne, and then the flasked was firmly sealed, warmed to ambient temperature and stirred for 4 h.

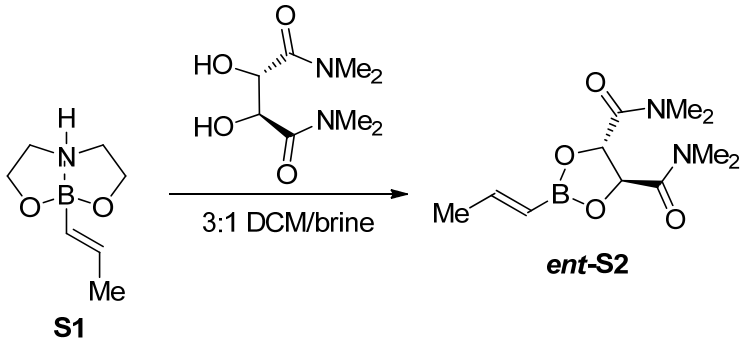
The mixture was then cannulated to 112.5 mL 2 N NaOH at 0 °C, and stirred for 2 h. DCM phase was separated, and the aqueous phase was extrated with $Et_2O$ once. The pH of the aqueous phase was adjusted to 2-3 with 2 N HCl, and extracted with $Et_2O$ four times. All organic phases were combined, dried with $MgSO_4$, filtered and concentrated *in vacuo.*

To the crude boronic acid in 75 mL DCM and 150 mL $Et_2O$ was added diethanolamine (7.2 mL, 75 mmol) and activated 3 Å molecular sieves (15 g). The mixture was stirred vigorously for 2 h, filtered through celite and concentrated. The crude oil was recrystalized from DCM/$Et_2O$ to afford **S1** (10.4 g, 89 %).[1]

$^1$H NMR (400 MHz, $CDCl_3$) δ 6.15–6.02 (m, 1H), 5.96 (dq, 1H, $J$ = 17.4, 6.1), 5.49 (app dd, 1H, $J$ = 17.4, 1.6), 4.03-3.72 (m, 4H), 3.34-3.16 (m, 2 H), 2.81-2.58 (m, 2H), 1.72 (dd, 3H, $J$ = 6.2, 1.4); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 135.2, 63.0, 51.3, 21.4, (**C**-B resonance missing due to boron broadening[2]); IR (neat) 3103, 2954, 2865, 1640, 1453, 1273, 1092, 1058, 990, 859, 729; HRMS (ESI) calcd for $C_7H_{15}NO_2B$ $(M+H)^+$, 156.1196, found 156.1198.

**Representative procedure for preparation of homocrotylation reagent**. ***ent*-1** is illustrated.

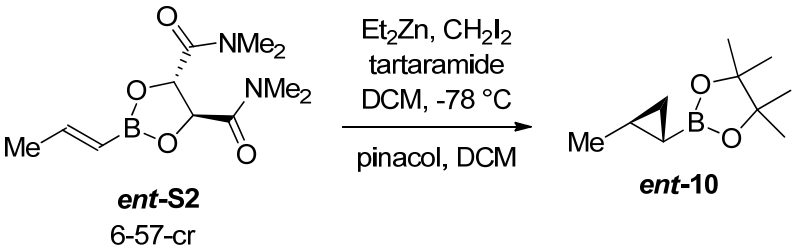
(1) Preparation of ***ent*-S2**




Although ***ent*-S2** can be prepared from condensation of tartaramide diol with commercially available *trans*-1-propen-1-ylboronic acid,[3] it is more economical on a large scale to prepare and use **S1**, which is very stable in storage. **S1** is converted to ***ent*-S2** as follows: (-)-N,N,N',N'-tetramethyl-D-tartaramide ***ent*-9** (2.0 g, 9.79 mmol) and **S1** (1.5 g, 9.79 mmol) were dissolved in 49 mL of DCM. To the mixture was added 16 mL of brine. The reaction was stirred for 30 min. The mixture was thoroughly shaken with brine (16 mL) and 1 N $NaHSO_4$ (12.2 mL, 12.2 mmol) in a separotary funnel. DCM phase was separated, and the aqueous phase was extracted with DCM three times. The combined organic phases were stirred with $MgSO_4$ for 4 h, filtered, concentrated *in vacuo* and pumped overnight, affording ***ent*-S2** (2.1 g, 84 %), which was used without further purification.[4]

$^1$H NMR (400 MHz, $CDCl_3$) δ 6.70 (dq, 1H, $J$ = 17.9, 6.4), 5.58 (s, 2H), 5.45 (app dd, 1H, $J$ = 17.9, 1.6), 3.22 (s, 6H), 2.98 (s, 6H), 1.85 (dd, 3H, $J$ = 6.5, 1.6).

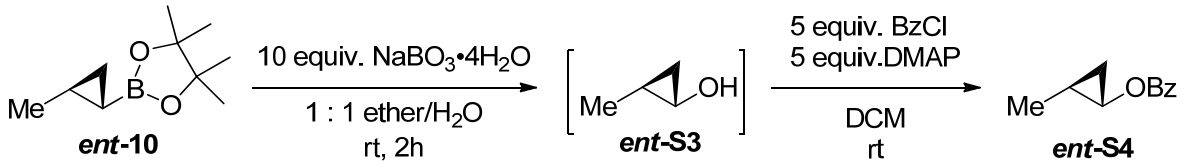
(2) Cyclopropanation



***ent*-S2** (2.1 g, 8.18 mmol) and (-)-N,N,N',N'-tetramethyl-D-tartaramide ***ent*-9** (0.8357 g, 4.09 mmol) were dissolved in DCM (30 mL) at ambient temperature and allowed to stand for 2 h, generating solution A, which was then cooled to -78°C.

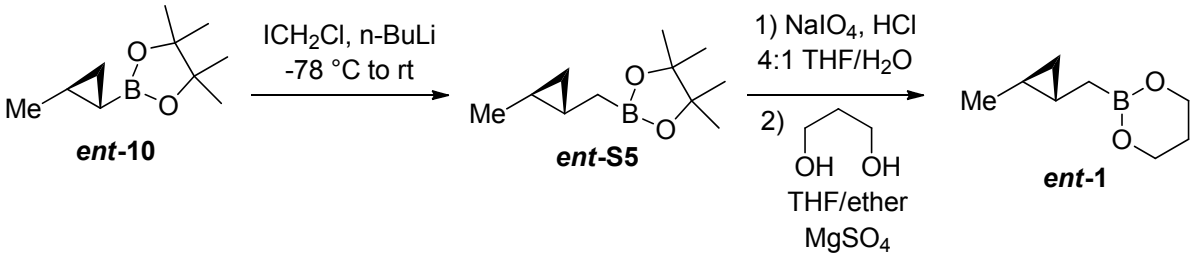
To a DCM (41 mL) solution of $Et_2Zn$ (2.52 mL, 24.6 mmol) was added $CH_2I_2$ (2.97 mL, 36.8 mmol) dropwise at -78 °C, and this mixture was stirred vigorously for 10 min. (Ineffective stirring due to precipitation of zinc salt did not affect the reaction.) The -78 °C solution A was cannulated to carbenoid within 5 min, followed by DCM rinses (5.5 mL × 2). The mixture was stirred at -78 °C for 2 h. 80 mL of saturated aqueous $NH_4Cl$ solution was carefully added to quench the reaction. After addition of $NH_4Cl$, the mixture was stirred at -78 °C for 5 min, taken out of the cooling bath and warmed to ambient temperature. After phase separation, the aqueous phase was extracted with DCM three times. The combined organic phase was dried with $Na_2SO_4$, filtered and concentrated to 20 mL. Pinacol (1.2 g, 9.82 mmol) was added to the crude mixture and the mixture was allowed to stay at ambient temperature and atmosphere overnight. After concentration, the crude mixture was flashed through a short silica column, eluted with 1:1 pentane/ether. The fractions containing product (stained with $I_2$ or CAM) were combined and concentrated to afford ***ent*-10** (1.4 g, 95 %). This material typically contains ~5 % $CH_2$ homologated product, and was used in the next step without purification. It is important to achieve full conversion, as any unreacted alkenylboronate will be homologated to crotylboronate in the next step. The crotylboronate contaminant is undesirable, as it is more reactive than **1**, leading to crotylated impurities in the homocrotylation products.

$^1$H NMR (400 MHz, $CDCl_3$) δ 1.21 (s, 12H), 1.07 (d, 3H, $J$ = 5.8), 0.99-0.88 (m, 1H), 0.70-0.62 (m, 1H), 0.35 (ddd, 1H, $J$ = 9.4, 5.1, 3.3), -0.46 (dt, 1H, $J$ = 9.4, 5.7); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 82.9, 24.86, 24.81, 20.1, 12.8-12.6 (br), 12.4; IR (neat) 2978, 1420, 1314, 1218, 1146, 856; HRMS (EI) calcd for $C_{10}H_{19}O_2B$ ($M^+$) 182.1478, found 182.1480. ***ent*-10** $[\alpha]_D^{20}$ = +42.7° (c 2.06, DCM). Data for **10**: identical to that for ***ent*-10**, except for optical rotation $[\alpha]_D^{20}$ = -38.4° (c 0.88, DCM).




ee % analysis: ***ent*-10** was oxidized to the corresponding alcohol ***ent*-S3** with 10 equiv. of $NaBO_3•4H_2O$ suspended in ether/water biphasic mixture for 2 h. Then the oxidant was filtered and the phases were allowed to separate. The aqueous phase was extracted with $Et_2O$ twice. The combined organic phases were dried over $MgSO_4$, filtered and concentrated. This crude mixture was benzoylated with 5 equiv. of benzoyl chloride and 5 equiv. of 4-(dimethylamino)pyridine (DMAP) in DCM overnight. The ee % of ***ent*-S4** was determined as 98 % by chiral HPLC (Daicel Chiralpak AS-H, hexanes, 0.5 mL/min, 220 nm), $t_R$ (major) = 18.72 min, $t_R$ (minor) = 16.62 min. -97 % ee for **S4**.

(3) Homologation




To a mixture of ***ent*-10** (1.2g, 6.4 mmol) and $ICH_2Cl$ (925 µL, 12.7 mmol) in 51 mL of THF at -78 °C was added n-BuLi (2.5 M in hexanes, 5.1 mL) with a syringe pump over 1 h. The mixture was stirred at -78 °C for an additional 10 min before being allowed to warm to ambient temperature and stirred for an additional 4 h. Saturated aqueous $NH_4Cl$ solution (50 mL) was added to the mixture. The organic phase was separated and the aqueous phase was extracted with $Et_2O$ three times. The combined organic phases were dried with $Na_2SO_4$, filtered and concentrated. The crude mixture was flashed through a short silica column, eluted with 1:1 pentane/ether. The fractions containing product (stained with $I_2$ or CAM) were combined and concentrated to afford ***ent*-S5** (910 mg, 73 %). **S5** obtained by this route contains no *cis*-impurity, in contrast with ***rac*-S5** obtained by direct

cyclopropanation of commercial *trans*-crotylboronate from Aldrich. NMR, IR and HRMS data for ***ent*-S5** was identical to our previous report for ***rac*-S5**.[5]

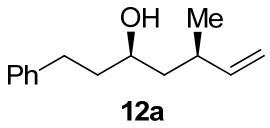
***ent*-S5** $[\alpha]_D^{20}$ = +20.2° (c 0.78, DCM). **S5** $[\alpha]_D^{20}$ = -20.3° (c 1.62, DCM).

Conversion from ***ent*-S5** to ***ent*-1** was performed according to our previous report.[5] NMR, IR and HRMS data for ***ent*-1** was identical to our previous report for ***rac*-1**.[5]

***ent*-1** $[\alpha]_D^{20}$ = +27.6° (c 0.88, DCM). **1** $[\alpha]_D^{20}$ = -24.9° (c 1.02, DCM).

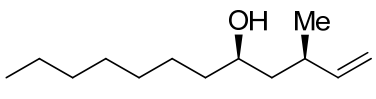
**Homocrotylboration**

All reactions were performed using 0.1 mmol of aldehydes **9** according to the same procedure as in our previous report,[5] for a period indicated in Table 1. ee's % were determined by chiral HPLC directly for compounds **12a**, **12f** and **12g**, or after benzoylation with benzoyl chloride (5 equiv.) and DMAP (10 equiv.) in DCM overnight for compounds **12b**, **12c**, **12d**, and **12e**.



**12a**

17.0 mg, 83 % yield after flash column chromatography, 10 % to 15 % ethyl acetate/hexanes. 97 % ee (Daicel Chiralcel OD-H, 5 % isopropanol/hexanes, 0.5 mL/min, 210 nm), $t_R$ (major) = 21.31 min, $t_R$ (minor) = 14.27 min. NMR and IR data was identical to the literature.[6] HRMS (ESI) calcd for $C_{14}H_{20}ONa$ $(M+Na)^+$ 227.1412, found 227.1422. $[\alpha]_D^{20}$ = +5.8° (c 0.85, DCM).

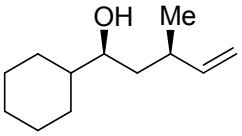


**12b**

17.6 mg, 89 % yield after flash column chromatography, 10 % to 15 % ethyl acetate/hexanes. 97 % ee (Daicel Chiralpak AD-H, hexanes, 0.5 mL/min, 220 nm), $t_R$ (major) = 16.01 min, $t_R$ (minor) = 14.39 min.

$^1$H NMR (400 MHz, $CDCl_3$) δ 5.68 (ddd, 1H, *J* = 17.4, 10.2, 8.2), 5.03 (ddd, 1H, *J* = 17.2, 1.8, 1.0), 4.96 (dd, 1H, *J* = 10.3, 1.6), 3.67-3.58 (m, 1H), 2.50-2.34 (m, 1H), 1.48-1.17 (m, 15H), 1.02 (d, 3H, *J* = 6.8), 0.88 (t, 3H, *J* = 6.8); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 144.4, 113.5, 69.9, 44.4, 38.2, 34.9,

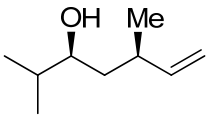
32.0, 29.8, 29.4, 25.8, 22.8, 21.4, 14.2; IR (neat) 3327, 3076, 2923, 2858, 1641, 1458, 1126, 998, 914; HRMS (EI) calcd for $C_{13}H_{25}O$ (M-[H$^-$])$^+$ 197.1906, found 197.1905. $[\alpha]_D^{20}$ = -14.9° (c 0.65, DCM).




**12c**

16.2 mg, 89 % yield after flash column chromatography, 10 % ethyl acetate/hexanes. 97 % ee (Daicel Chiralcel OD-H, hexanes, 0.5 mL/min, 220 nm), $t_R$ (major) = 21.75 min, $t_R$ (minor) = 15.86 min.

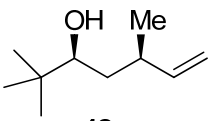
$^1$H NMR (400 MHz, $CDCl_3$) δ 5.65 (ddd, 1H, *J* = 17.2, 10.2, 8.4), 5.02 (ddd, 1H, *J* = 17.2, 1.9, 1.0), 4.96 (dd, 1H, *J* = 10.2, 1.8), 3.44-3.35 (m, 1H), 2.48-2.35 (m, 1H), 1.88-1.56 (m, 4H + water), 1.53-0.90 (m + d, 10H + 3H, *J* = 6.8); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 144.3, 113.6, 73.9, 44.3, 41.2, 35.0, 29.3, 28.0, 26.7, 26.5, 26.4, 21.6; IR (neat) 3361, 3075, 2922, 2854, 1640, 1449, 995, 911; HRMS (EI) calcd for $C_{12}H_{22}O$ ($M^+$) 182.1671, found 182.1670. $[\alpha]_D^{20}$ = -27.9° (c 0.66, DCM).




**12d**

83 % NMR yield, 10.2 mg, 72 % isolated yield after flash column chromatography, eluted with 3:1 pentane/$Et_2O$. 98 % ee (Regis (R,R)-Whelk-O 1, Kromasil, hexanes, 0.5 mL/min, 220 nm), $t_R$ (major) = 25.38 min, $t_R$ (minor) = 23.91 min.

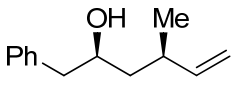
$^1$H NMR (400 MHz, $CDCl_3$) δ 5.66 (ddd, 1H, *J* = 17.2, 10.2, 8.4), 5.03 (ddd, 1H, *J* = 17.2, 1.7, 1.0), 4.97 (dd, 1H, *J* = 10.1, 1.7), 3.44-3.35 (m, 1H), 2.48-2.34 (m, 1H), 1.62 (m, 1H), 1.46-1.30 (m, 3H), 1.03 (d, 3H, *J* = 6.6), 0.905 (d, 3H, *J* = 6.8), 0.902 (d, 3H, *J* = 6.8); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 144.3, 113.6, 74.4, 41.1, 35.1, 34.1, 21.6, 18.8, 17.4; IR (neat) 3389, 3077, 2960, 2878, 1639, 1460, 1134, 994, 914; HRMS (CI) calcd for $C_9H_{17}O$ (M-[H$^-$])$^+$ 141.1280, found 141.1280. $[\alpha]_D^{20}$ = -49.2° (c 0.27, DCM).




**12e**

84 % NMR yield, 9.7 mg, 62 % isolated yield after flash column chromatography, 10:1 pentane/$Et_2O$. 98 % ee (Regis (R,R)-Whelk-O 1, Kromasil , hexanes, 0.5 mL/min, 220 nm), $t_R$ (major) = 17.66 min, $t_R$ (minor) = 20.45 min.

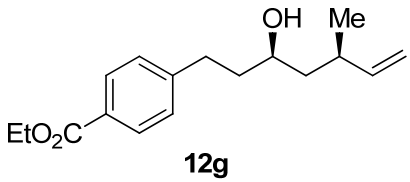
$^1$H NMR (400 MHz, $CDCl_3$) δ 5.62 (ddd, 1H, *J* = 17.2, 10.2, 8.5), 5.03 (ddd, 1H, *J* = 17.2, 1.9, 1.0), 4.97 (dd, 1H, *J* = 10.2, 1.8), 3.23 (br d, 1H, *J* = 10.0), 2.50-2.34 (m, 1H), 1.47-1.22 (m, 3H), 1.04 (d, 3H, *J* = 6.8), 0.88 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 144.2, 113.8, 77.4, 38.6, 35.4, 34.8, 25.8, 21.9; IR (neat) 3395, 3077, 2960, 2873, 1643, 1468, 1394, 1263, 1063, 1007, 918, 821; HRMS (CI) calcd for $C_{10}H_{19}O$ $(M\text{-}[H^-])^+$ 155.1436, found 155.1436. $[\alpha]_D^{20}$ = -50.6° (c 0.45, DCM).




**12f**

15.6 mg, 82 % yield after flash column chromatography, 10 % to 15 % ethyl acetate/hexanes. 97 % ee (Daicel Chiralpak AS-H, 2 % isopropanol/hexanes, 1 mL/min, 210 nm), $t_R$ (major) = 5.53 min, $t_R$ (minor) = 6.03 min.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.36-7.27 (m, 2H), 7.27-7.17 (m, 3H), 5.65 (ddd, 1H, *J* = 17.4, 10.2, 8.2), 5.01 (ddd, 1H, *J* = 17.2, 1.6, 0.8), 4.95 (ddd, 1H, *J* = 10.1, 1.7), 3.91-3.79 (m, 1H), 2.78 (dd, 1H, *J* = 13.5, 4.4), 2.66 (dd, 1H, *J* = 13.5, 8.4), 2.51-2.39 (m, 1H), 1.65-1.38 (m, 3H + water), 1.03 (d, 3H, *J* = 6.8); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 144.1, 138.7, 129.6, 128.7, 126.6, 113.7, 70.6, 44.7, 43.8, 34.9, 21.3; IR (neat) 3412, 3071, 3027, 2959, 2922, 1641, 1604, 1494, 1451, 1078, 1020, 913, 740; HRMS (EI) calcd for $C_{13}H_{18}O$ $(M^+)$ 190.1358, found 190.1357. $[\alpha]_D^{20}$ = +1.7° (c 0.62, DCM).

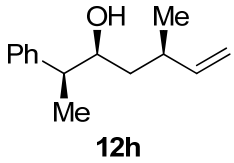



**12g**

24.5 mg, 89 % yield after flash column chromatography, 8:1 ethyl acetate/hexanes. 97 % ee (Daicel Chiralpak AS-H, 2 % isopropanol/hexanes, 1 mL/min, 210 nm), $t_R$ (major) = 17.44 min, $t_R$ (minor) = 12.34 min.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.96 (app d, 2H, *J* = 8.2), 7.25 (app d, 2H, *J* = 8.2), 5.66 (ddd, 1H, *J* = 17.2, 10.2, 8.2), 5.03 (ddd, 1H, *J* = 17.2, 1.6, 1.0), 4.96 (dd, 1H, *J* = 10.2, 1.7), 4.36 (q, 2H, *J* = 7.1), 3.73-3.62 (m, 1H), 2.84 (d of app t, 1H, *J* = 13.7, ~8.0), 2.71 (d of app t, 1H, *J* = 13.7, ~8.2), 2.48-2.33 (m, 1H), 1.87-1.33 (m + t, 5H + 3H + water, *J* = 7.1), 1.02 (d, 3H, *J* = 6.8); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.8, 147.8, 144.1, 129.8, 128.5, 128.2, 113.7, 69.2, 60.9, 44.4, 39.3, 34.9, 32.2, 21.2,

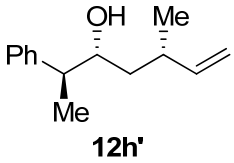
14.5; IR (neat) 3484, 3073, 2965, 2926, 2872, 1711, 1610, 1273, 1105, 914; HRMS (ESI) calcd for $C_{17}H_{25}O_3$ $(M+H)^+$ 277.1804, found 277.1806. $[\alpha]_D^{20}$ = +11.2° (c 1.22, DCM).



**12h**

dr (>20:1) was determined using material partially purified by column chromatography; 10 % ethyl acetate/hexanes, combining all product-containing fractions, together with some fractions before and after. This mixture was then analyzed by LC-MS (ACQUITY UPLC® BEH300 C18 column, 50:50:0.1 acetonitrile/water/formic acid, 0.35 mL/min, 258nm). A second column (10 % ethyl acetate/hexanes) was then performed to afford analytically pure material, 16.9 mg **12h**, 83 % yield.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.37-7.27 (m, 2H), 7.27-7.15 (m, 3H), 5.57 (ddd, 1H, *J* = 17.2, 10.2, 8.4), 4.98 (ddd, 1H, *J* = 17.2, 1.7, 1.0), 4.94 (dd, 1H, *J* = 10.2, 1.8), 3.71 (ddd, 1H, *J* = 9.6, 6.1, 2.9), 2.74 (app p, 1H, *J* = 6.8), 2.45-2.32 (m, 1H), 1.65-1.20 (m + d, 3H + 3H + water, *J* = 7.0), 0.96 (d, 3H, *J* = 6.8); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 144.7, 144.1, 128.6, 128.0, 126.5, 113.7, 74.0, 46.3, 41.7, 35.1, 21.5, 16.0; IR (neat) 3391, 3073, 3027, 2963, 2928, 2876, 1640, 1603, 1493, 1453, 1001, 913, 760; HRMS (ESI) calcd for $C_{14}H_{20}ONa$ $(M+Na)^+$ 227.1412, found 227.1420. $[\alpha]_D^{20}$ = -5.9° (c 0.84, DCM).

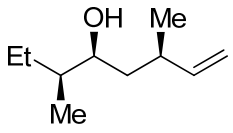


**12h'**

dr (>20:1) was determined using material partially purified by column chromatography; 10 % ethyl acetate/hexanes combining all product-containing fractions, together with some fractions before and after. This mixture was then analyzed by LC-MS (ACQUITY UPLC® BEH300 C18 column, 50:50:0.1 acetonitrile/water/formic acid, 0.35 mL/min, 258nm). A second column (10 % ethyl acetate/hexanes) was then performed to afford 15.9 mg **12h'**, 78 % yield, eluted with 10 % ethyl acetate/hexanes.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.35-7.28 (m, 2H), 7.28-7.20 (m, 3H), 5.65 (ddd, 1H, *J* = 17.2, 10.2, 8.2), 5.01 (ddd, 1H, *J* = 17.2, 1.8, 0.8), 4.96 (dd, 1H, *J* = 10.2, 1.6), 3.72-3.62 (m, 1H), 2.70 (app p, 1H, *J* = 7.0), 2.51-2.38 (m, 1H), 1.66-1.19 (m + d, 3H + 3H + water, *J* = 7.0), 1.01 (d, 3H, *J* = 6.8);

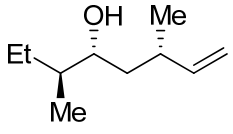
$^{13}$C NMR (100 MHz, $CDCl_3$) δ 144.1, 143.7, 128.6, 128.3, 126.8, 113.7, 74.0, 46.7, 41.8, 34.9, 21.6, 18.0; IR (neat) 3443, 3071, 3027, 2964, 2875, 1640, 1602, 1452, 1005, 911, 762; HRMS (ESI) calcd for $C_{14}H_{20}ONa$ $(M+Na)^+$ 227.1412, found 227.1415. $[\alpha]_D^{20}$ = +21.2° (c 0.80, DCM).



**12i**

87 % NMR yield. dr (>99:1) was analyzed by silylation of the crude mixture (no concentration was performed to avoid any potential loss of diastereomers) with N-methyl-N-(trimethylsilyl)trifluoroacetamide at 70 °C for 1 h, followed by GC-MS analysis (Agilent 19091S-433 HP-5MS 5% phenyl-methyl-siloxane capillary column, 30 m × 250 μm × 0.25 μm, 1 mL/min, 1 min at 60 °C, then 0.1 °C/min to 64 °C). Flash column chromatography was performed to afford 11.8 mg **12i**, 76 % isolated yield, eluted with 10:1 to 20:3 pentane/$Et_2O$.

$^1$H NMR (400 MHz, $CDCl_3$) δ 5.66 (ddd, 1H, *J* = 17.2, 10.3, 8.4), 5.03 (ddd, 1H, *J* = 17.2, 1.8, 1.0), 4.96 (dd, 1H, *J* = 10.3, 1.8), 3.56 (d of app t, 1H, *J* = 9.6, 3.1), 2.46-2.33 (m, 1H), 1.70-1.29 (m, 4H), 1.26 (br s, 1H), 1.23-1.09 (m, 1H), 1.03 (d, 3H, *J* = 6.8), 0.90 (t, 3H, *J* = 7.4), 0.88 (d, 3H, *J* = 6.8); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 144.3, 113.6, 72.7, 41.4, 40.7, 35.1, 26.0, 21.5, 13.6, 12.0; IR (neat) 3360, 3078, 2962, 2929, 2874, 1638, 1458, 1379, 1136, 997, 913; HRMS (CI) calcd for $C_{10}H_{19}O$ $(M-[H^-])^+$ 155.1436, found 155.1437. $[\alpha]_D^{20}$ = -41.0° (c 0.56, DCM).

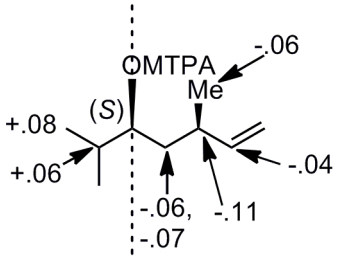


**12i'**

96 % NMR yield. dr (>99 : 1) was analyzed by silylation of crude mixture (no concentration was performed to avoid any potential loss of diastereomers) with N-methyl-N-(trimethylsilyl)trifluoroacetamide at 70 °C for 1 h, followed by GC-MS analysis (Agilent 19091S-433 HP-5MS 5% phenyl-methyl-siloxane capillary column, 30 m × 250 μm × 0.25 μm, 1 mL/min, 1 min at 60 °C, then 0.1 °C/min to 64 °C). Flash column chromatography was performed to afford 12.7 mg **12i'**, 81 % isolated yield, eluted with 10:1 to 20:3 pentane/$Et_2O$.

$^1$H NMR (400 MHz, $CDCl_3$) δ 5.65 (ddd, 1, *J* = 17.2, 10.2, 8.3), 5.03 (ddd, 1, *J* = 17.2, 1.8, 0.8), 4.97 (dd, 1, *J* = 10.2, 1.6), 3.54-3.46 (m, 1), 2.48-2.35 (m, 1), 1.66-1.23 (m, 5), 1.23-1.06 (m, 1), 1.03 (d, 3, *J* = 6.6), 0.90 (t, 3, *J* = 7.4), 0.87 (t, 3, *J* = 6.7); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 144.3, 113.7, 73.4, 41.1, 40.3, 35.1, 25.0, 21.7, 14.7, 11.9; IR (neat) 3358, 3076, 2962, 2928, 2874, 1642, 1459, 1379, 1138, 994, 912; HRMS (CI) calcd for $C_{10}H_{19}O$ (M-[H$^-$])$^+$ 155.1436, found 155.1437. $[\alpha]_D^{20}$ = +29.4° (c 0.64, DCM).

**Mosher Ester Analysis of Absolute Configuration**




*R*- and *S*- MTPA esters were prepared from **12d**.[7] The following ($\delta_S$–$\delta_R$) values were observed between the two derivatives, indicating the *S* configuration of the C–O stereocenter. The absolute configuration of all other homocrotylation products is assigned by analogy to **12d**.

**References and Notes**


[1] Chatette, A. B.; Lebel, H. *Org Synth*, **2004**, *Coll. Vol. 10*, 613; **1999**, *76*, 86.

[2] Due to quadrupole broadening, the NMR signal for carbon directly attached to boron is often too weak to be observed. See: Wrackmeyer, B. *Prog. Nucl. Magn. Reson. Spectrosc.* **1979**, *12*, 227-259.

[3] Tanino, K.; Takahashi, M.; Tomata, Y.; Tokura, H.; Uehara, T.; Narabu, T.; Miyashita, M. *Nat. Chem.* **2011**, *3*, 484-488.

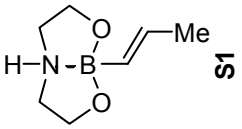
[4] Roush, W. R.; Grover, P. T. *J. Org. Chem.* **1995**, *60*, 3806-3813.

[5] Pei, W.; Krauss, I. J. *J. Am. Chem. Soc.* **2011**, *133*, 18514-18517.

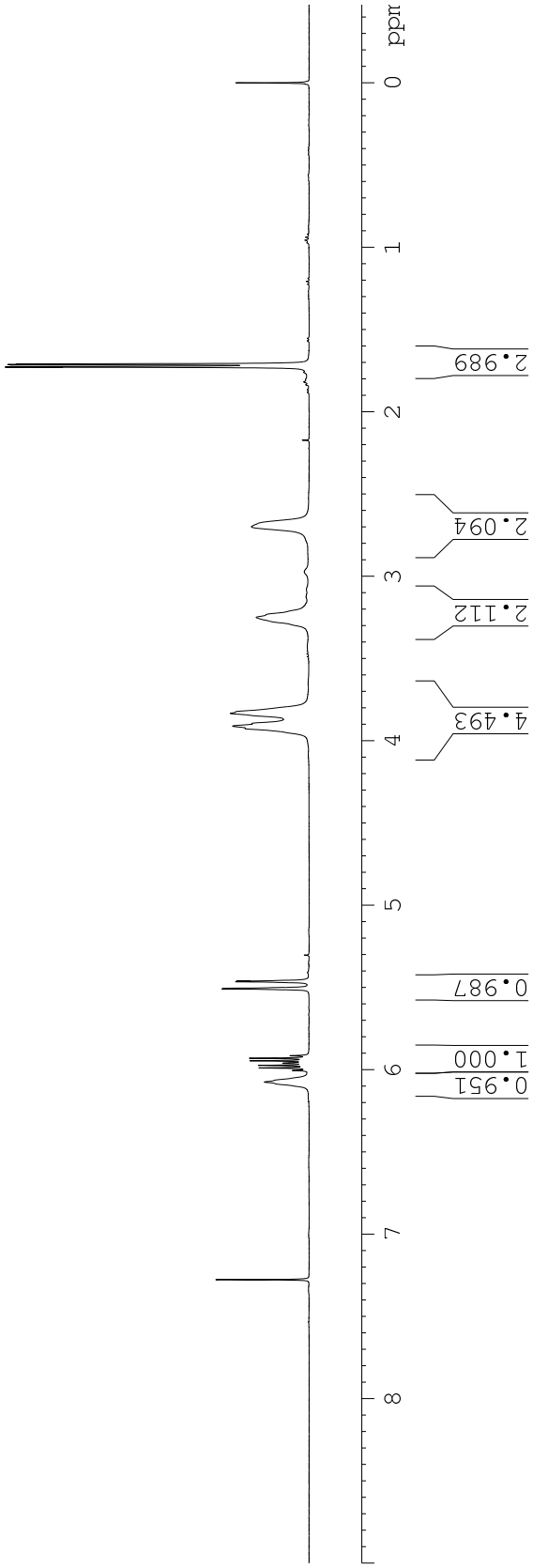
[6] Tamaru, Y.; Kimura, M. *Org Synth*, **2009**, *Coll. Vol. 11*, 327-335; **2006**, *83*, 88-96.

[7] Hoye, T. R.; Jeffrey, C. S.; Shao, F. *Nat. Protocols* **2007**, *2*, 2451-2458.

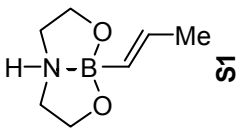
$^{1}$H NMR (400 MHz) of **S1**



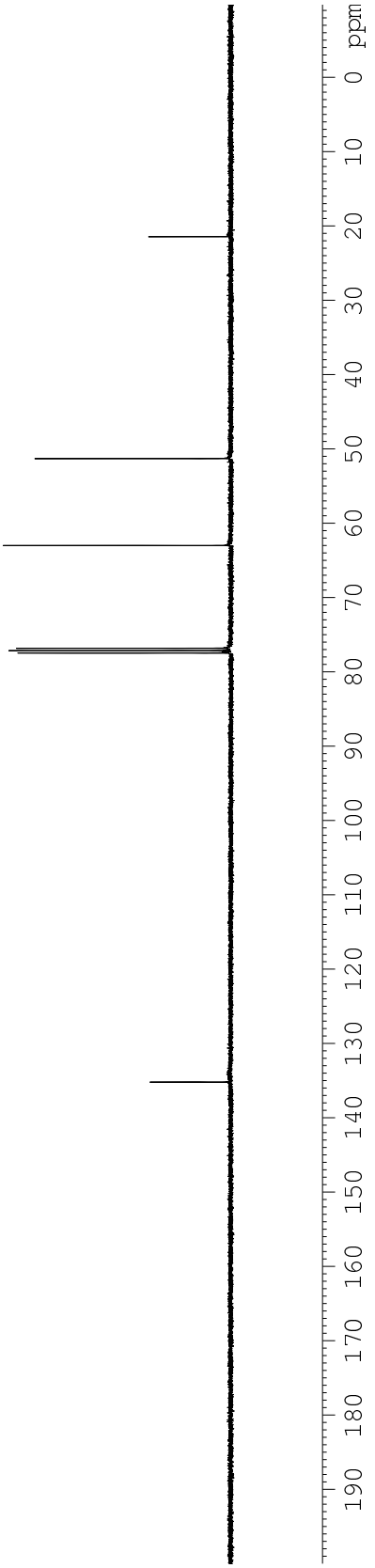

**S1**



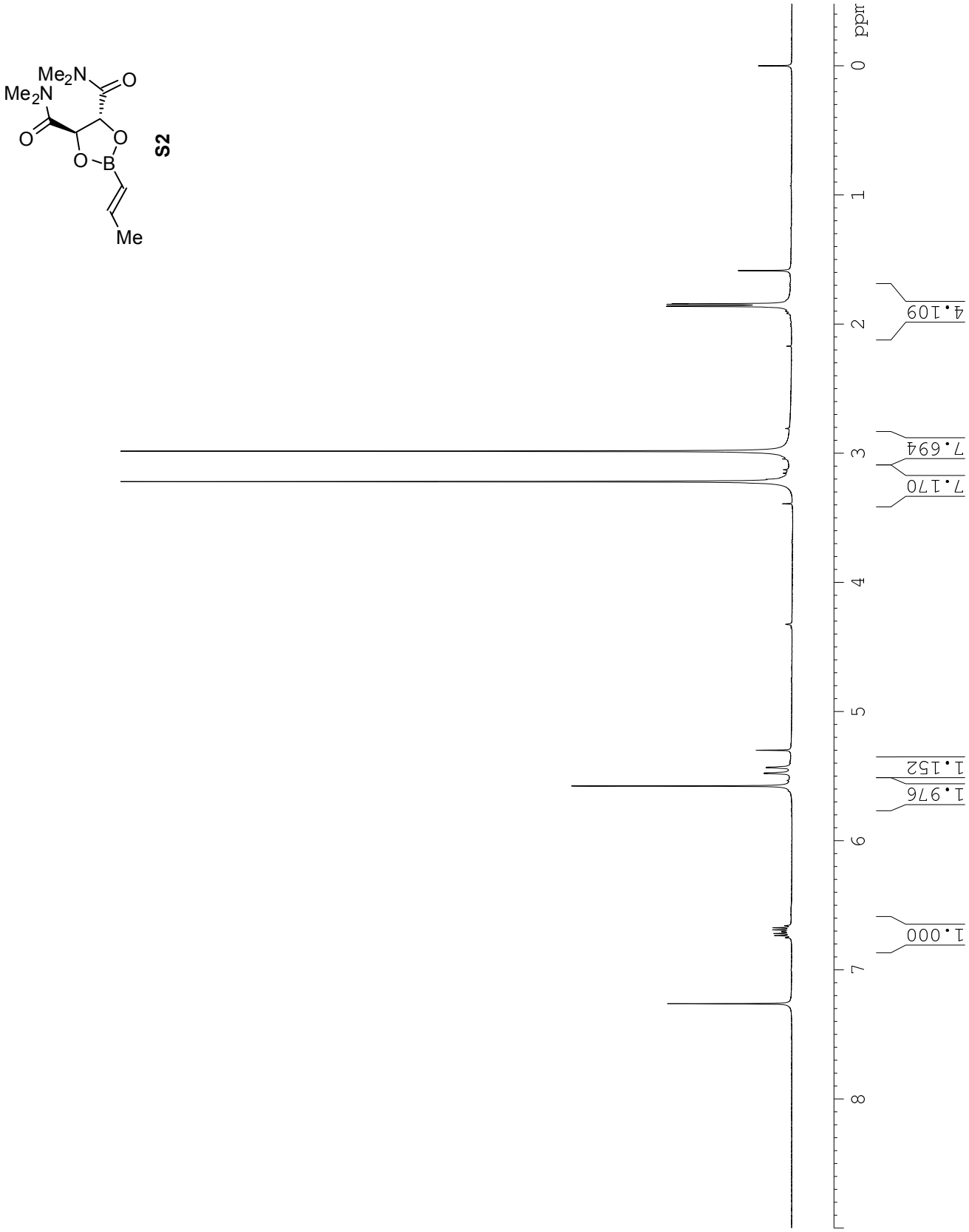
$^{13}$C NMR (100 MHz) of **S1**



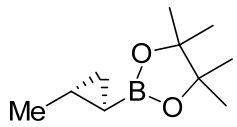

**S1**



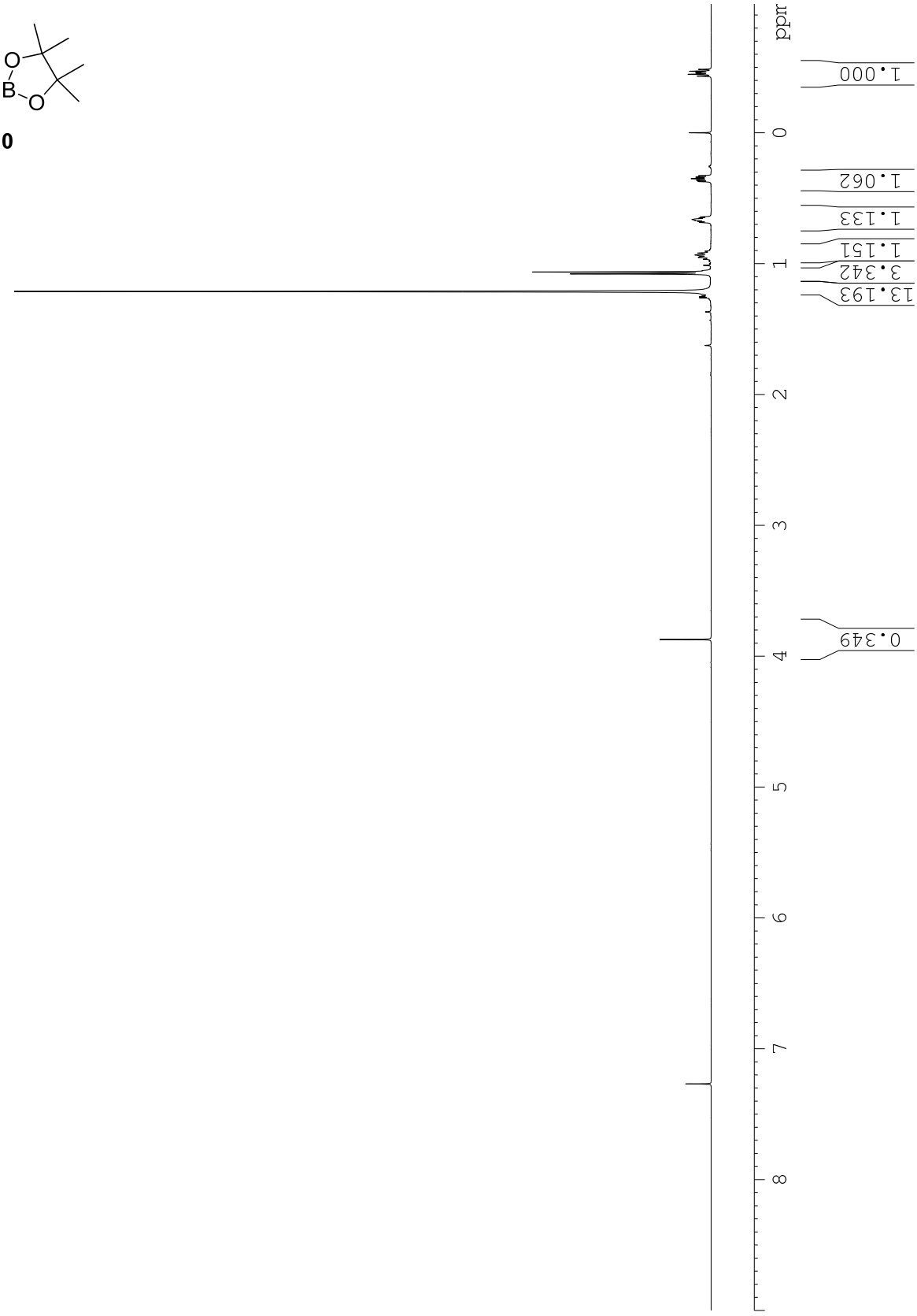
$^{1}$H NMR (400 MHz) of **S2**



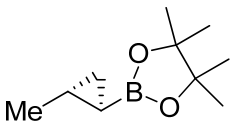
$^{1}$H NMR (400 MHz) of **10**




**10**



$^{13}$C NMR (100 MHz) of **10**

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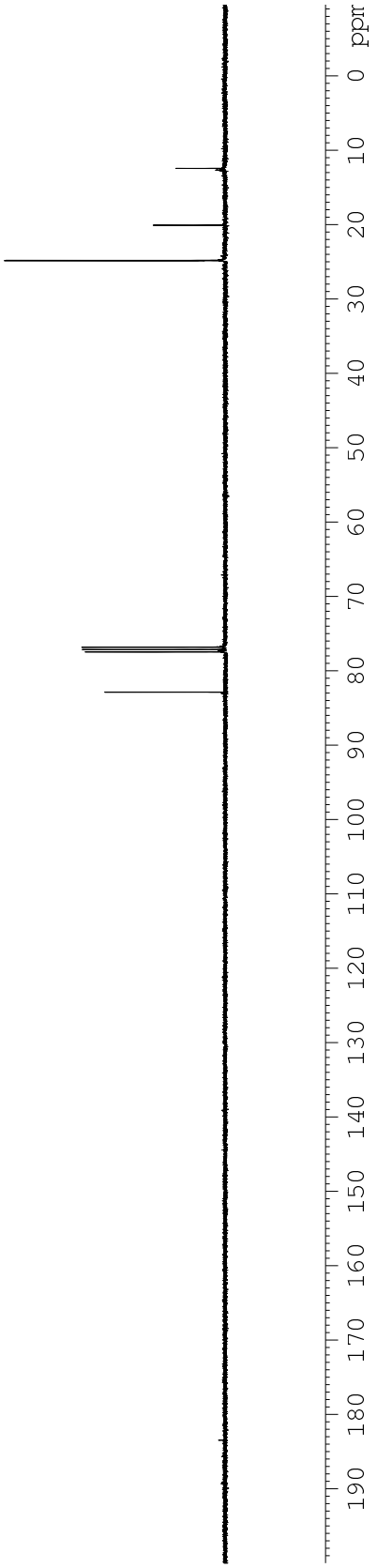
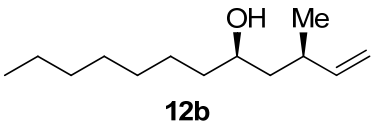
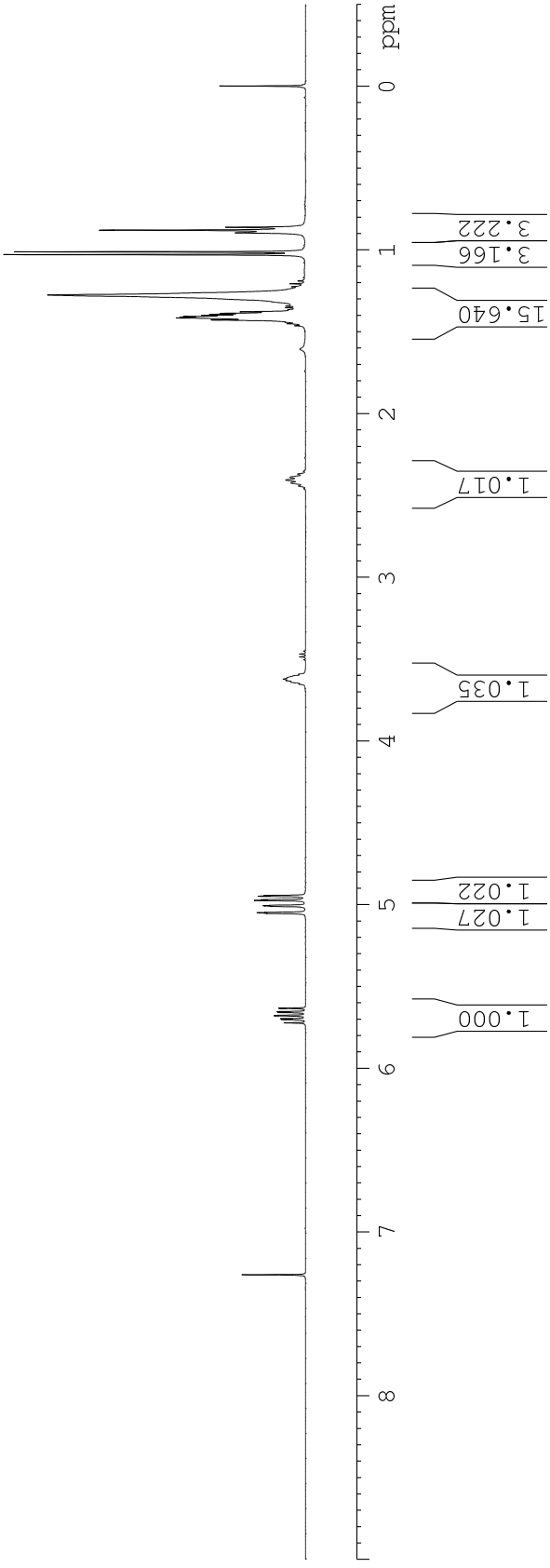


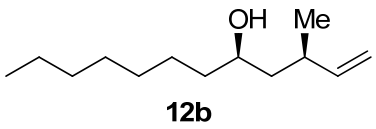
$^{1}$H NMR (400 MHz) of **12b**



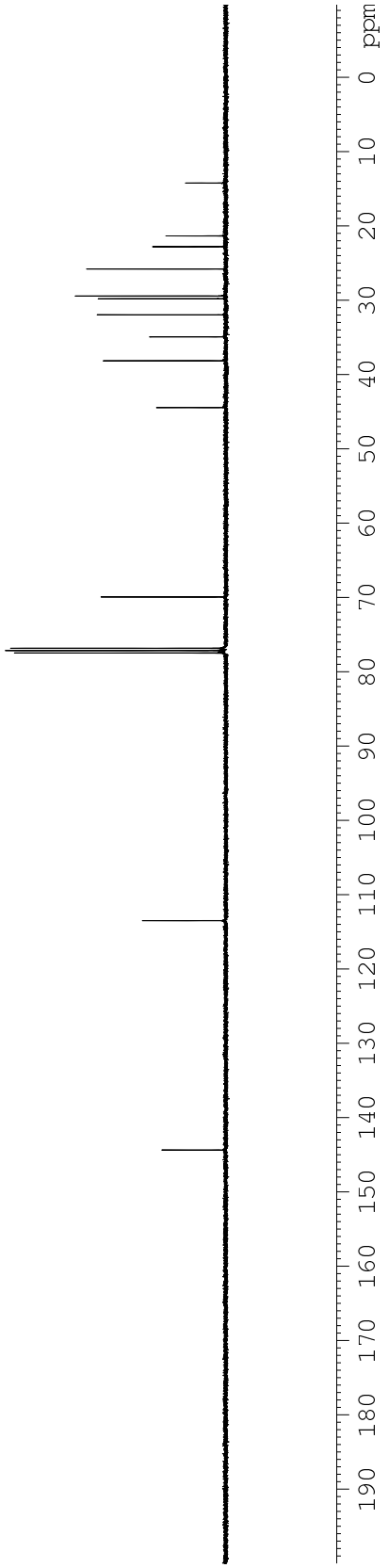

**12b**



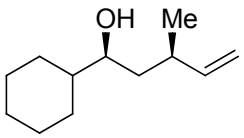
$^{13}$C NMR (100 MHz) of **12b**



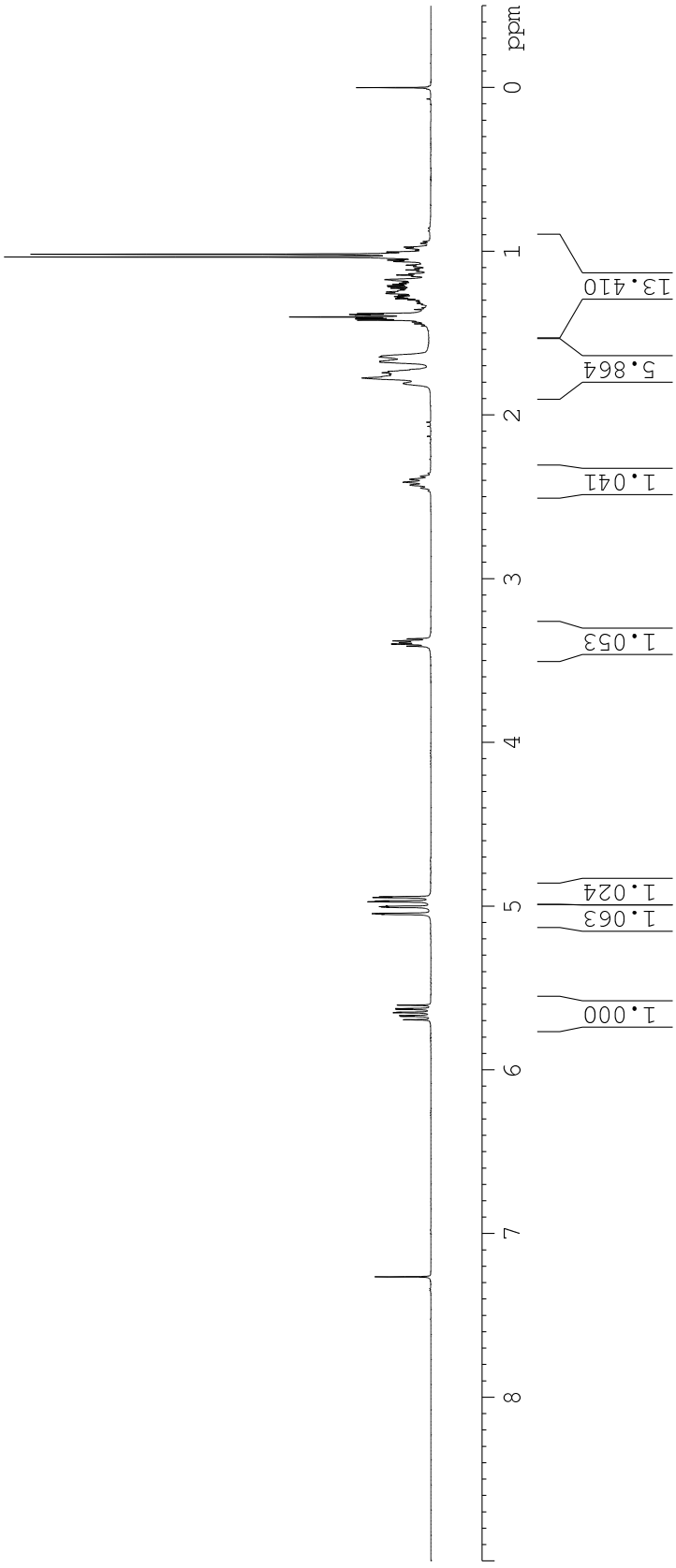

**12b**



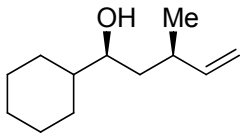
$^{1}$H NMR (400 MHz) of **12c**



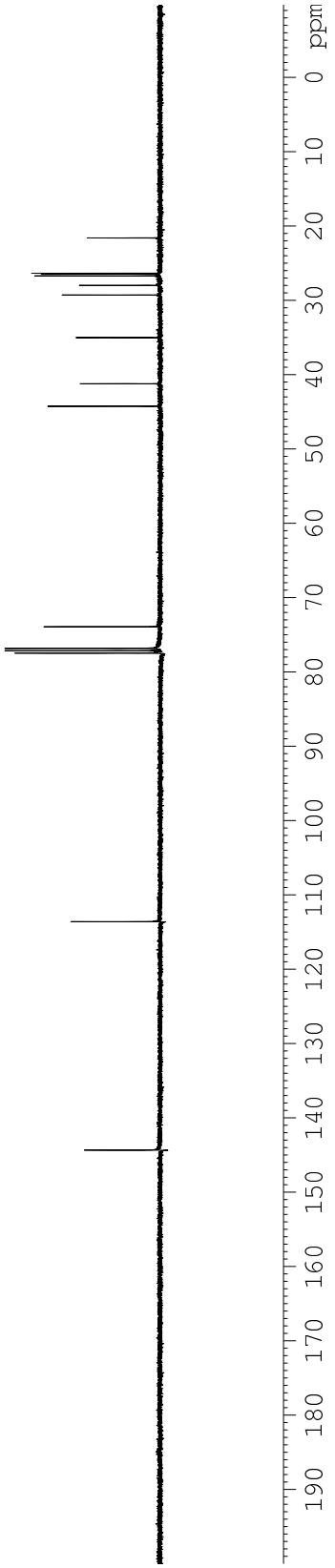

**12c**



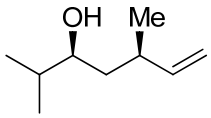
$^{13}$C NMR (100 MHz) of **12c**



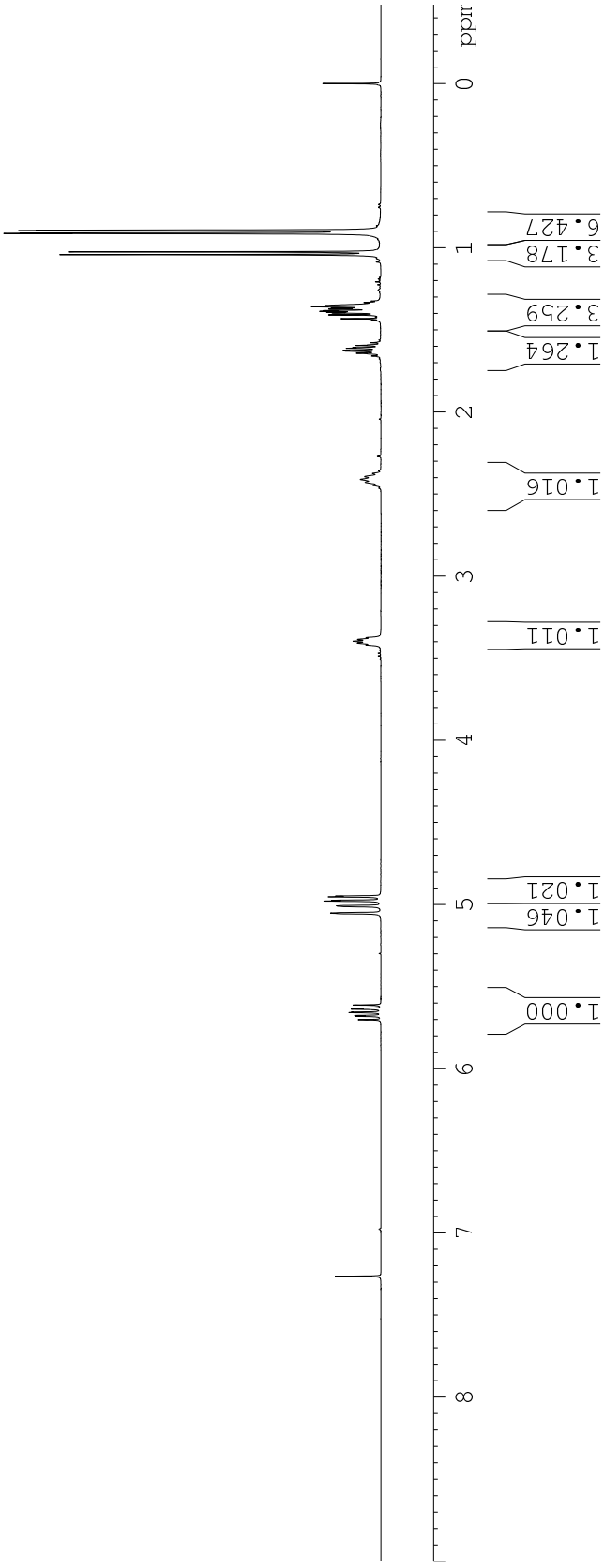

**12c**



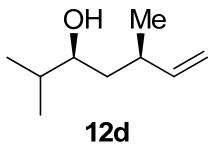
$^{1}$H NMR (400 MHz) of **12d**



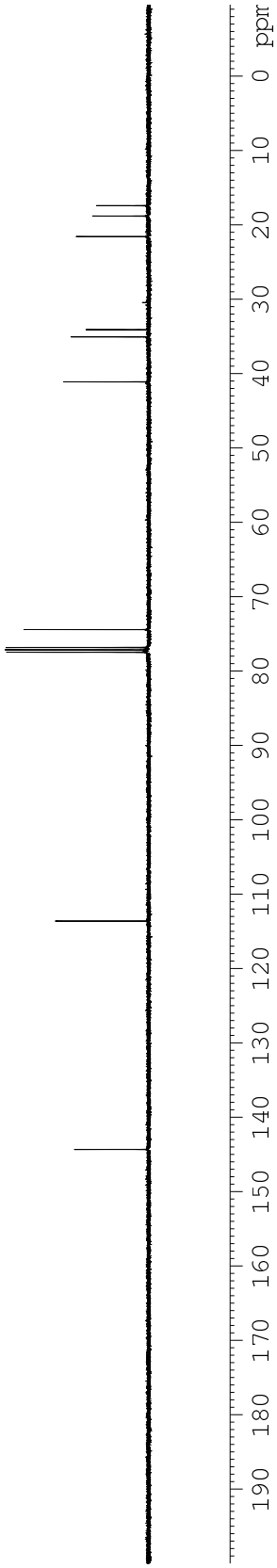

**12d**



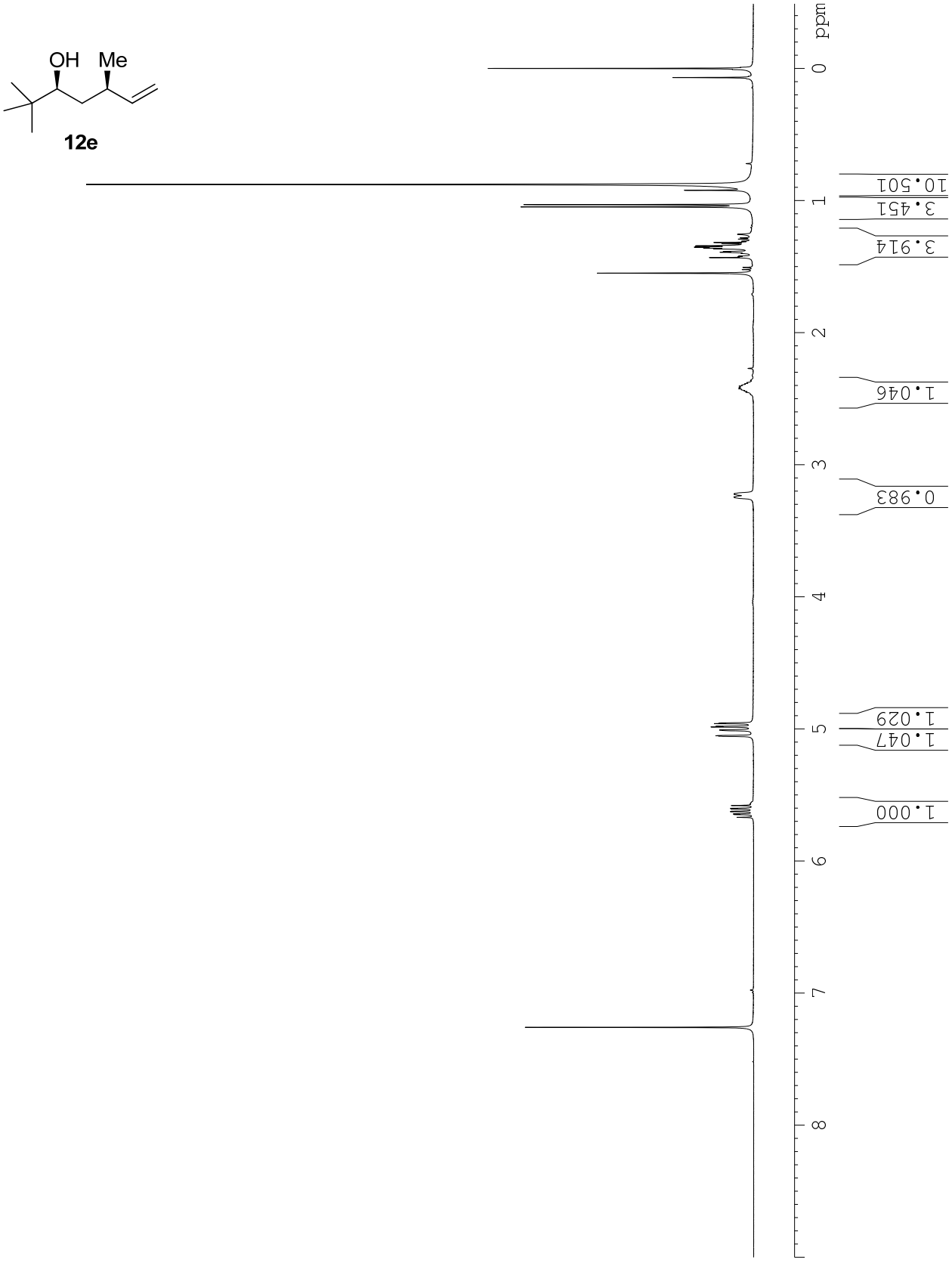
$^{13}$C NMR (100 MHz) of **12d**



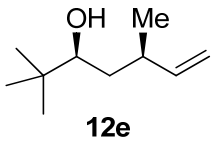

**12d**



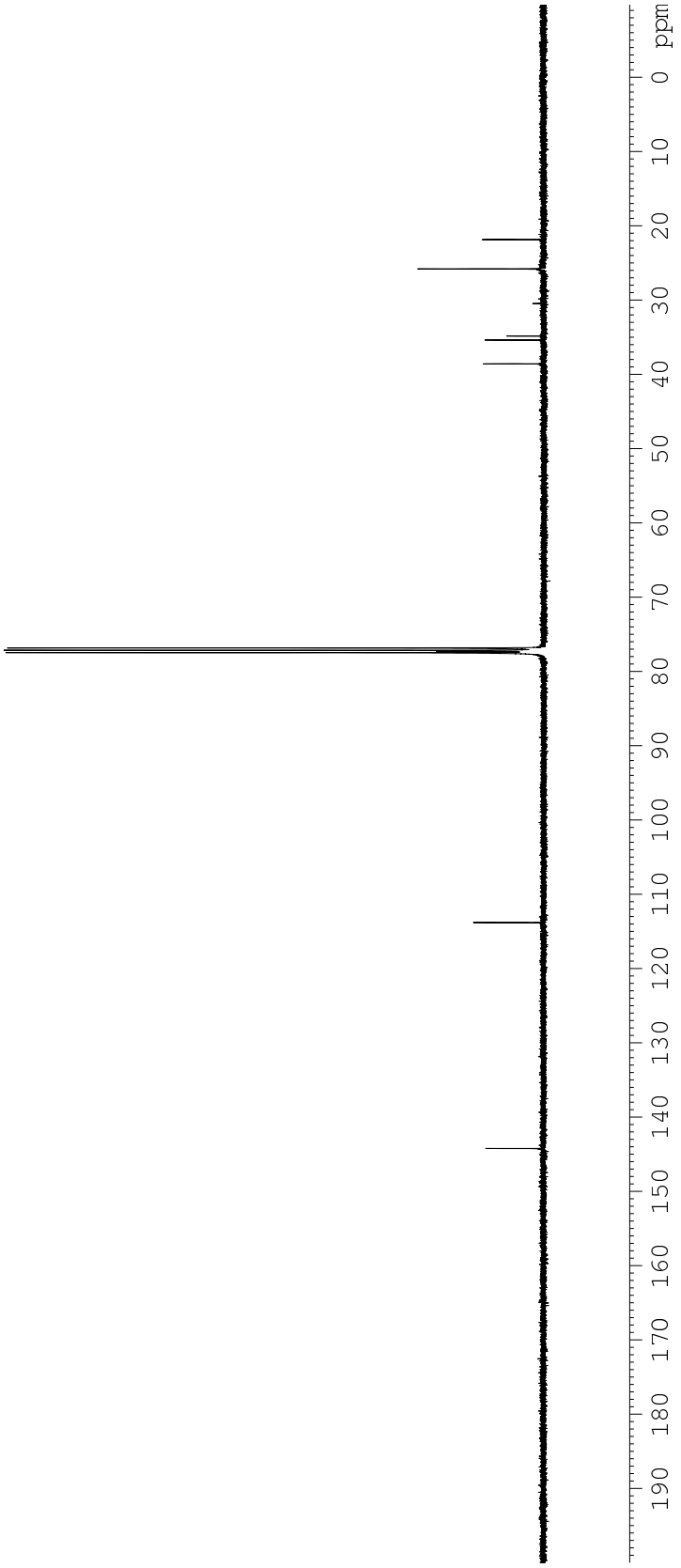
$^{1}$H NMR (400 MHz) of **12e**



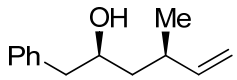
$^{13}$C NMR (100 MHz) of **12e**



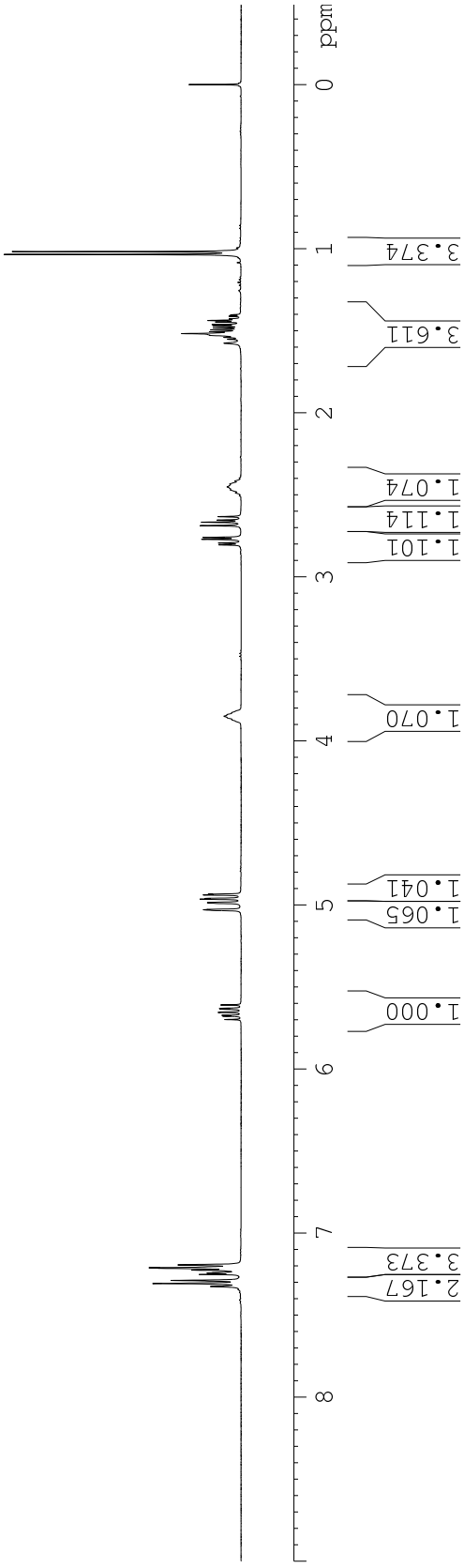

**12e**



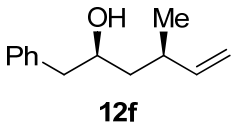
$^{1}$H NMR (400 MHz) of **12f**



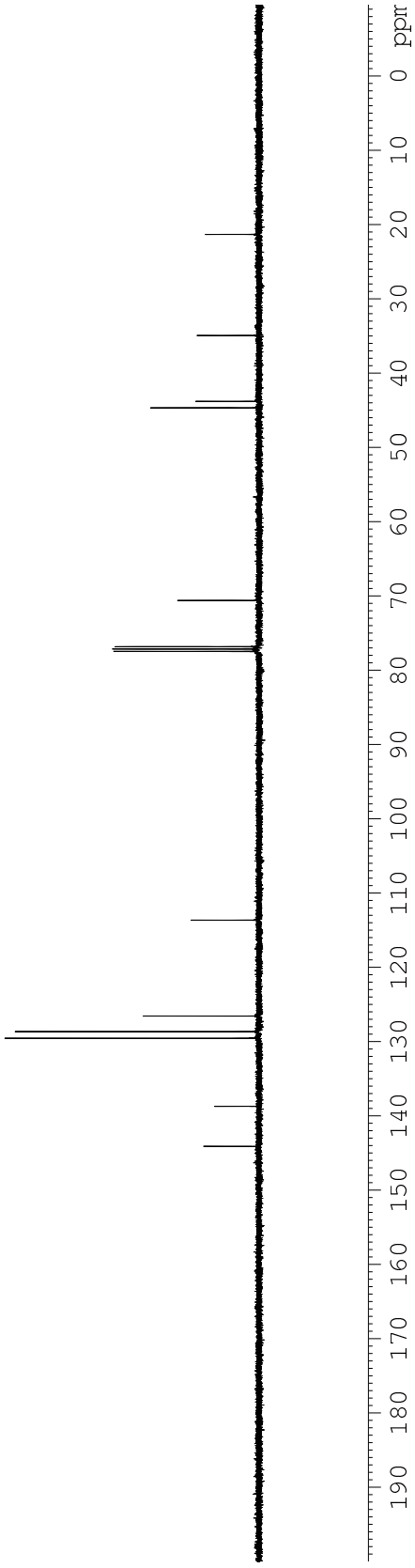

**12f**



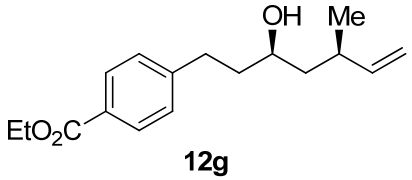
$^{\backslash 13}$C NMR (100 MHz) of **12f**



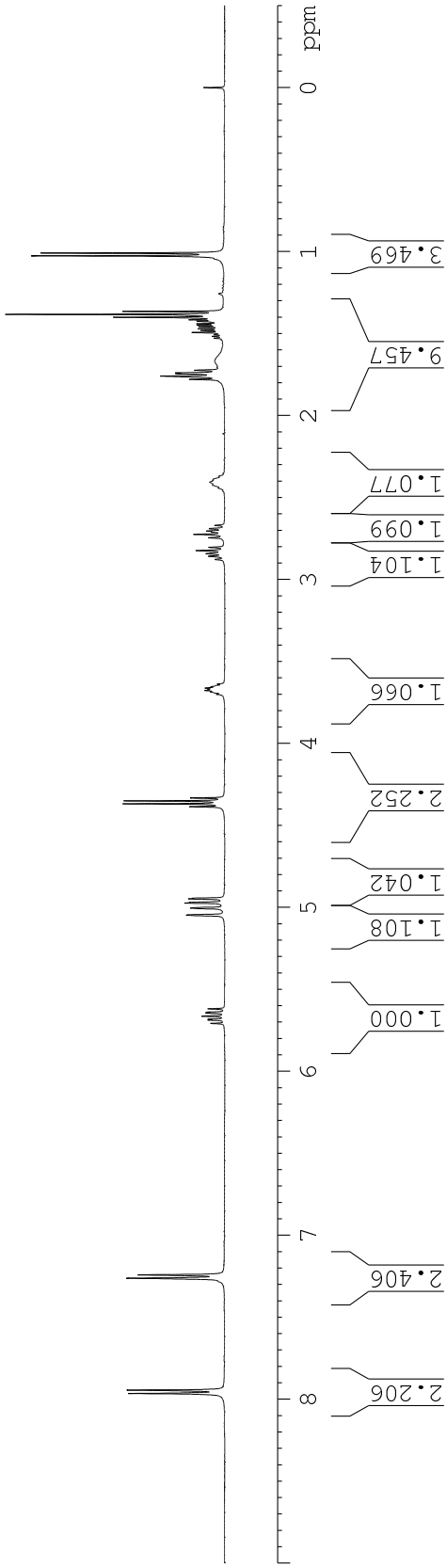

**12f**



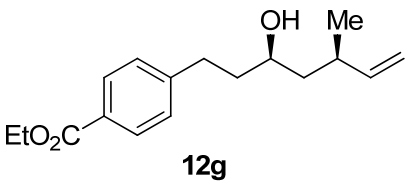
$^{1}$H NMR (400 MHz) of **12g**



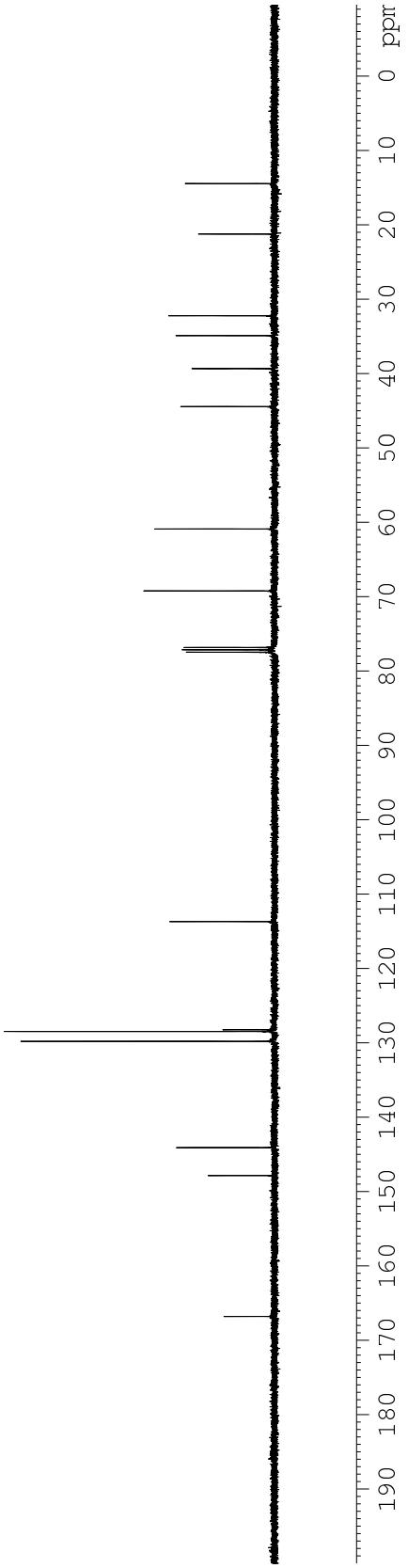

**12g**



$^{13}$C NMR (100 MHz) of **12g**




**12g**



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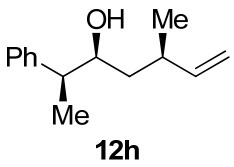
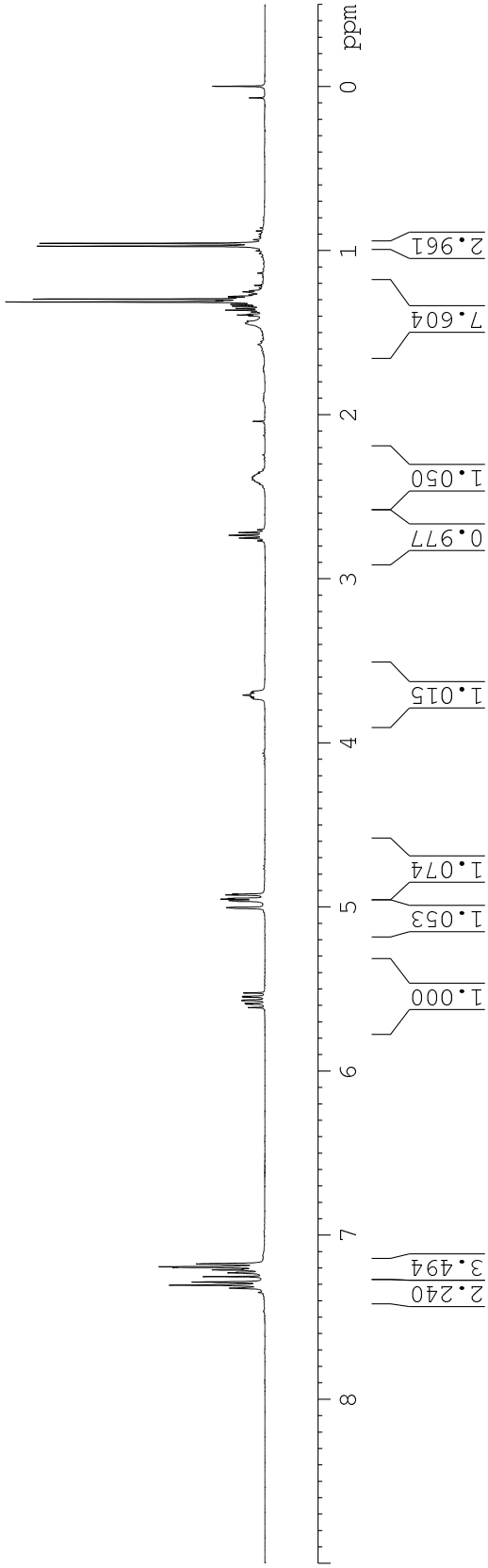
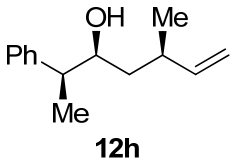


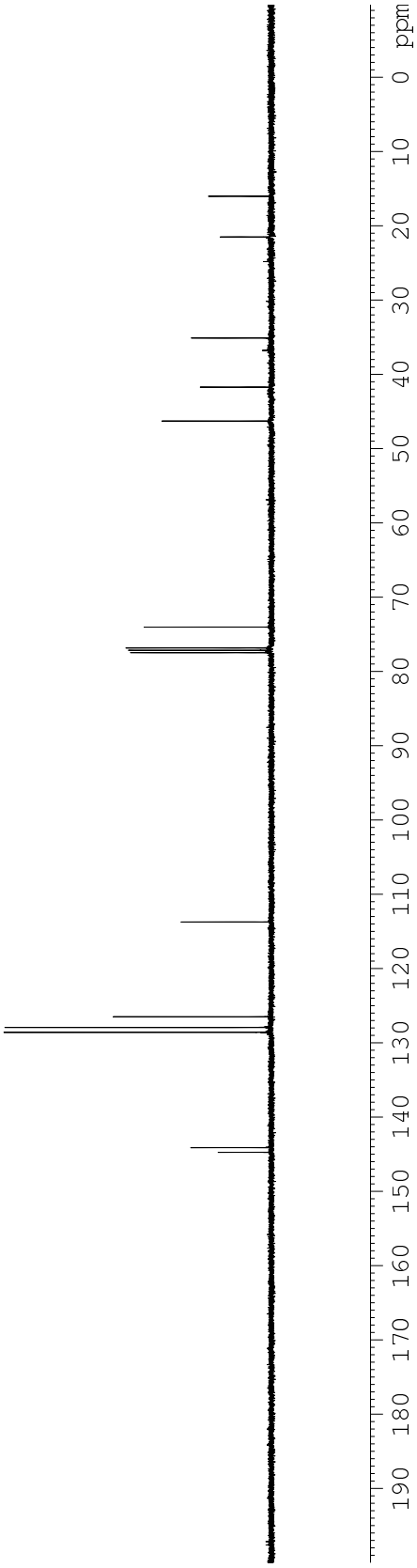

**12h**



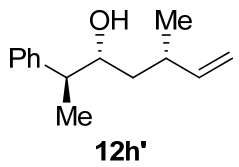
$^{13}$C NMR (100 MHz) of **12h**



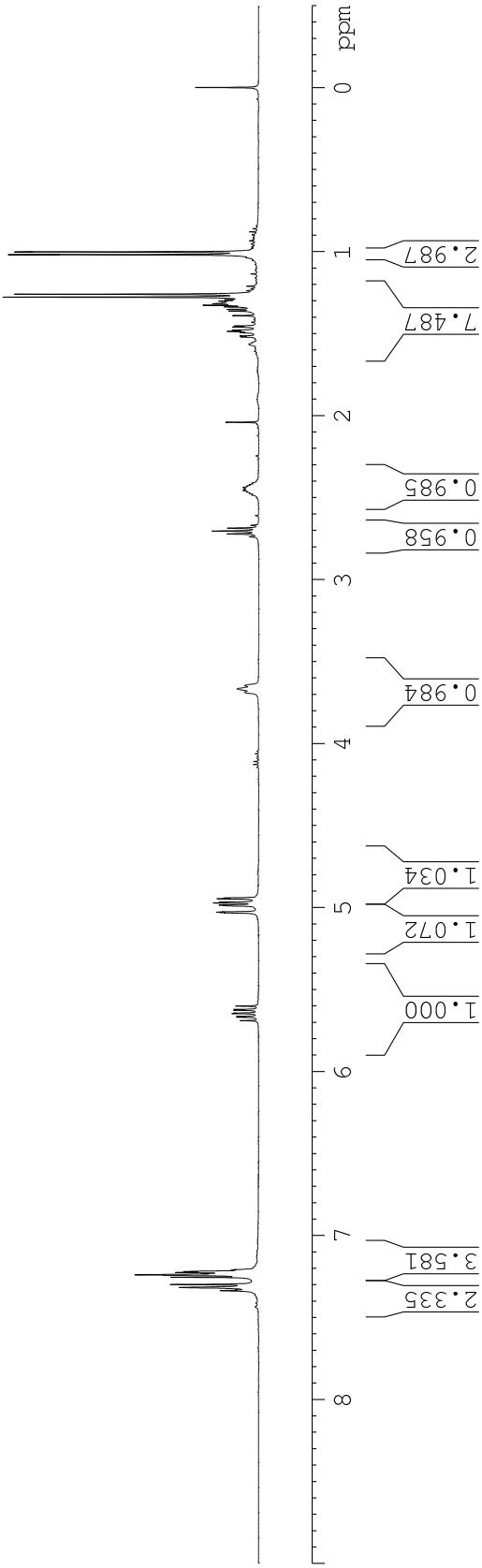

**12h**



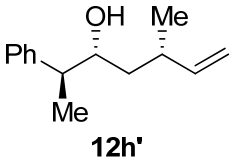
$^{1}$H NMR (400 MHz) of **12h'**



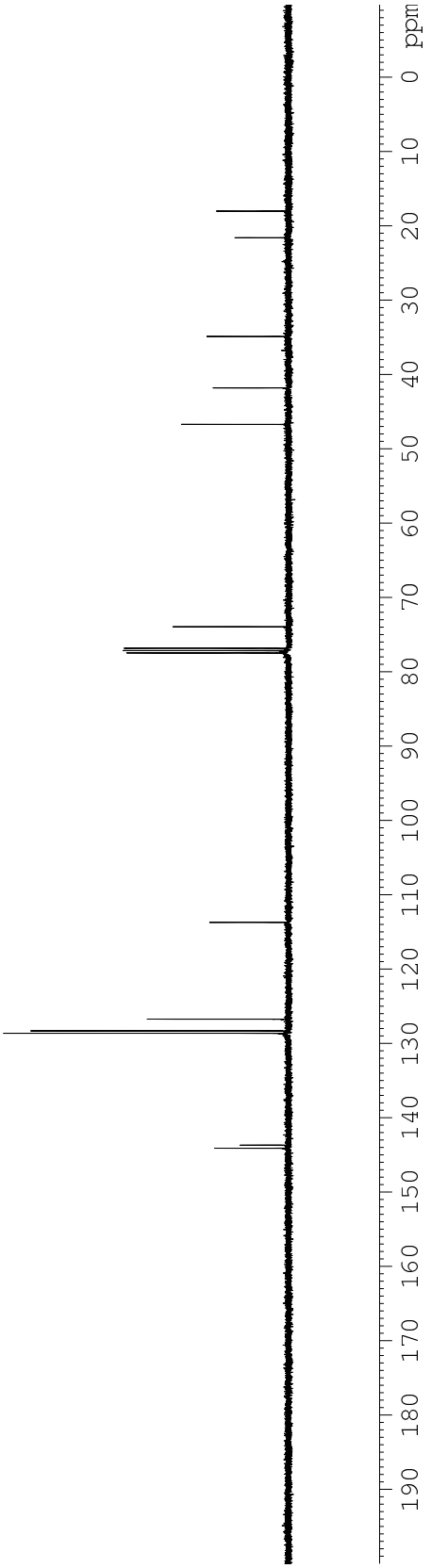

**12h'**



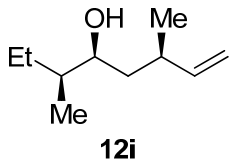
$^{13}$C NMR (100 MHz) of **12h'**



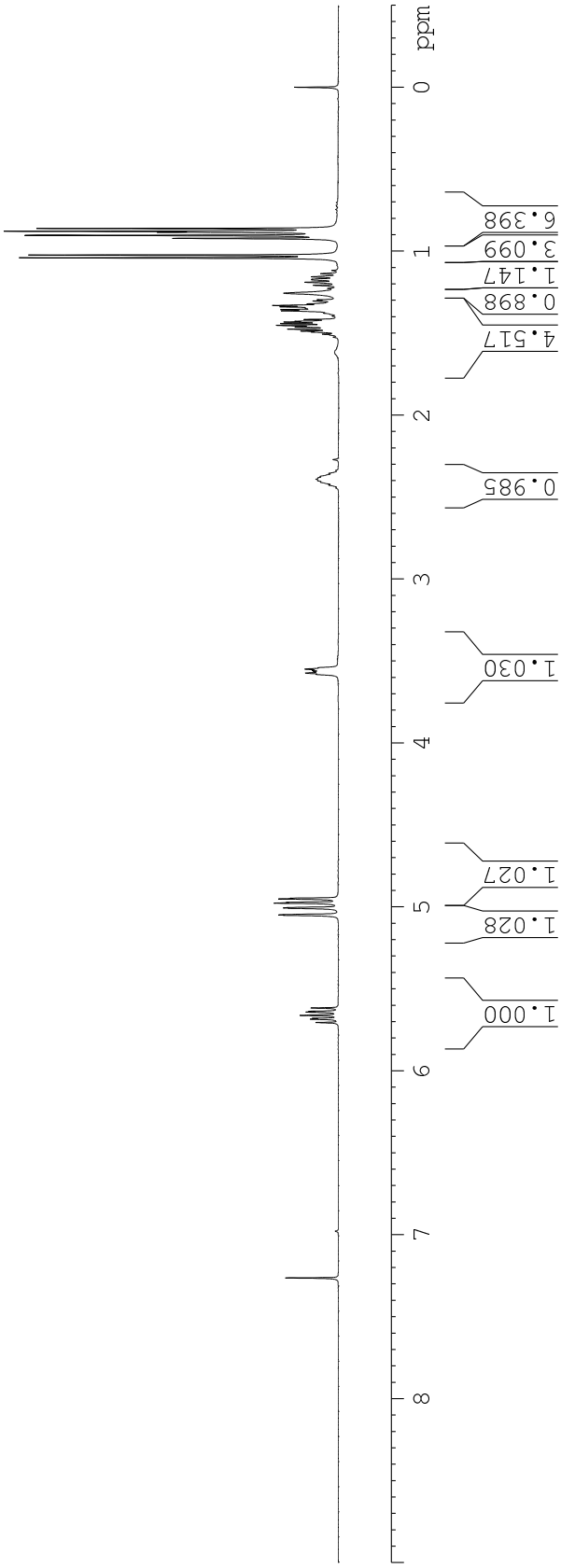

**12h'**



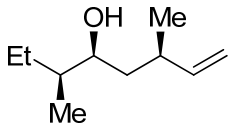
$^{1}$H NMR (400 MHz) of **12i**



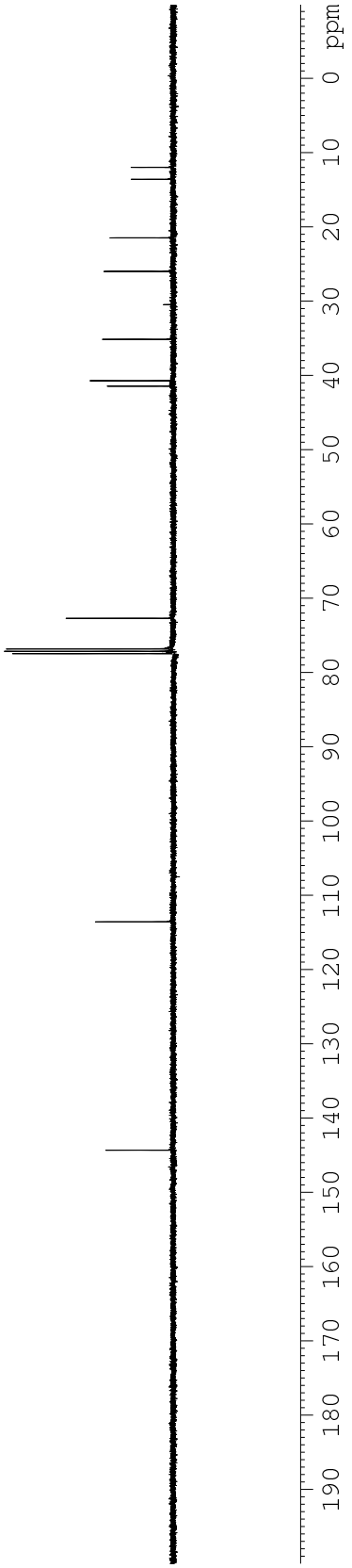

**12i**



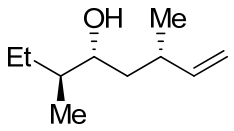
$^{13}$C NMR (100 MHz) of **12i**



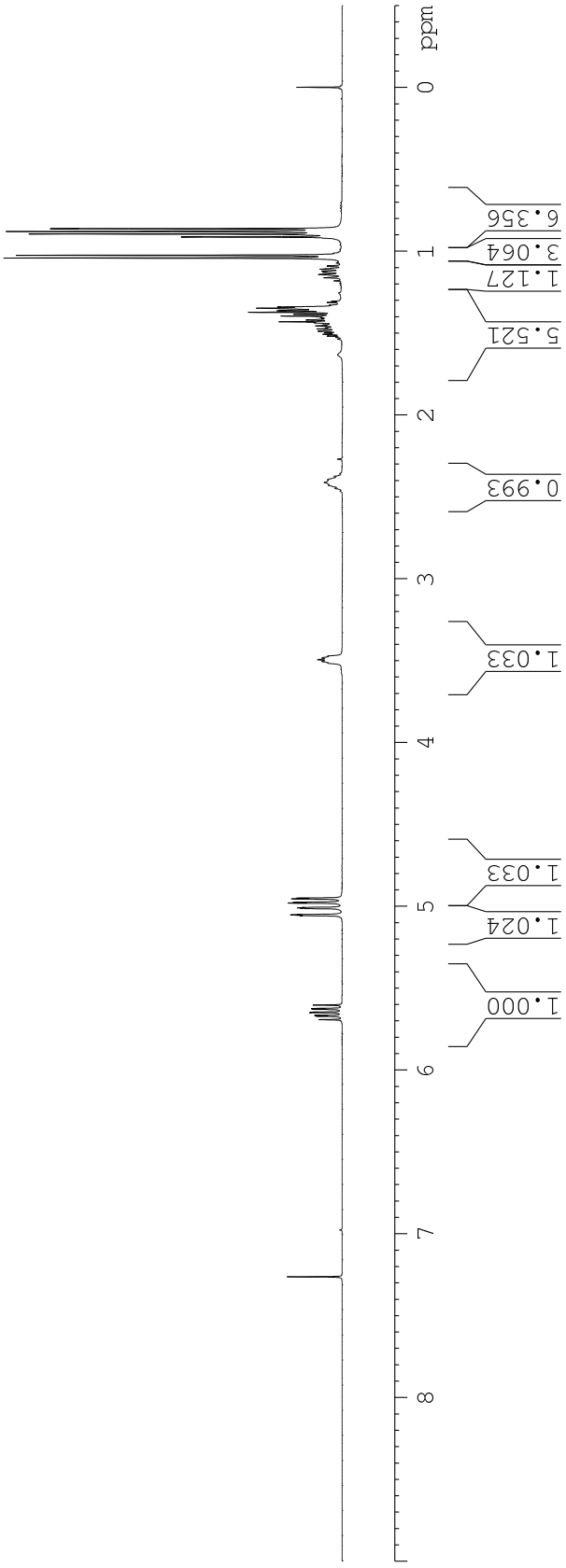

**12i**



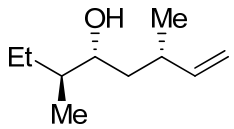
$^{1}$H NMR (400 MHz) of **12i'**



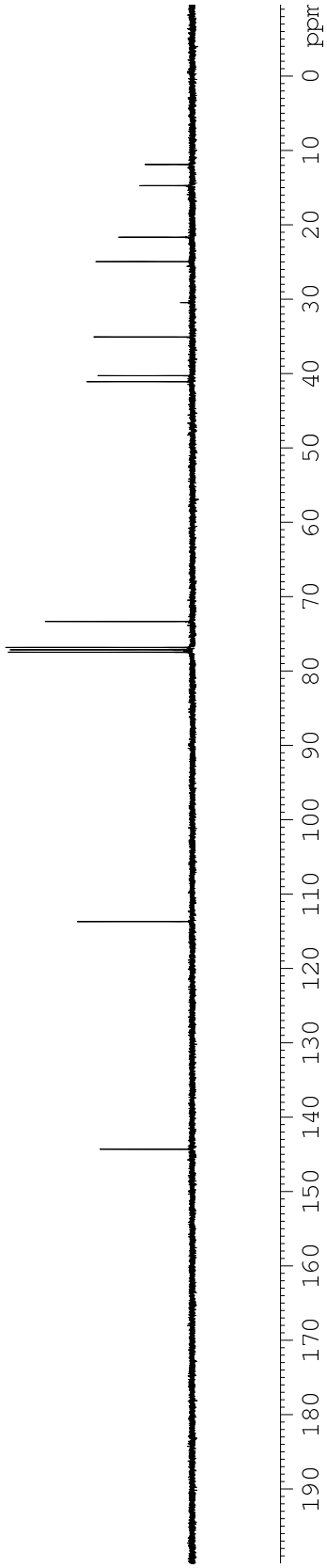

**12i'**



$^{13}$C NMR (100 MHz) of **12i'**

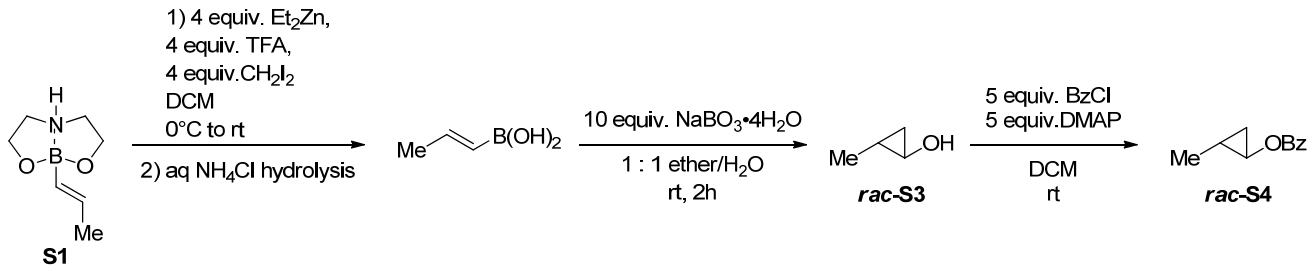



**12i'**

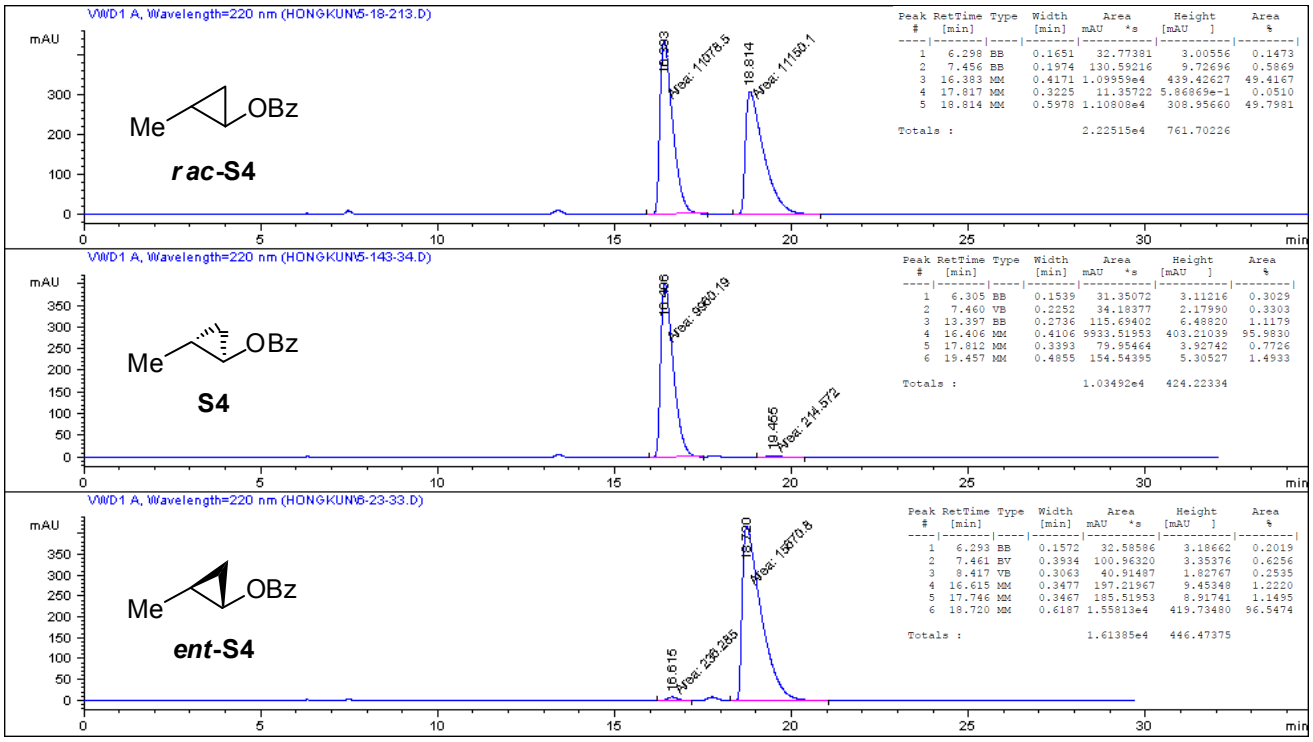


HPLC chromatograms

**S4** and ***ent*-S4**

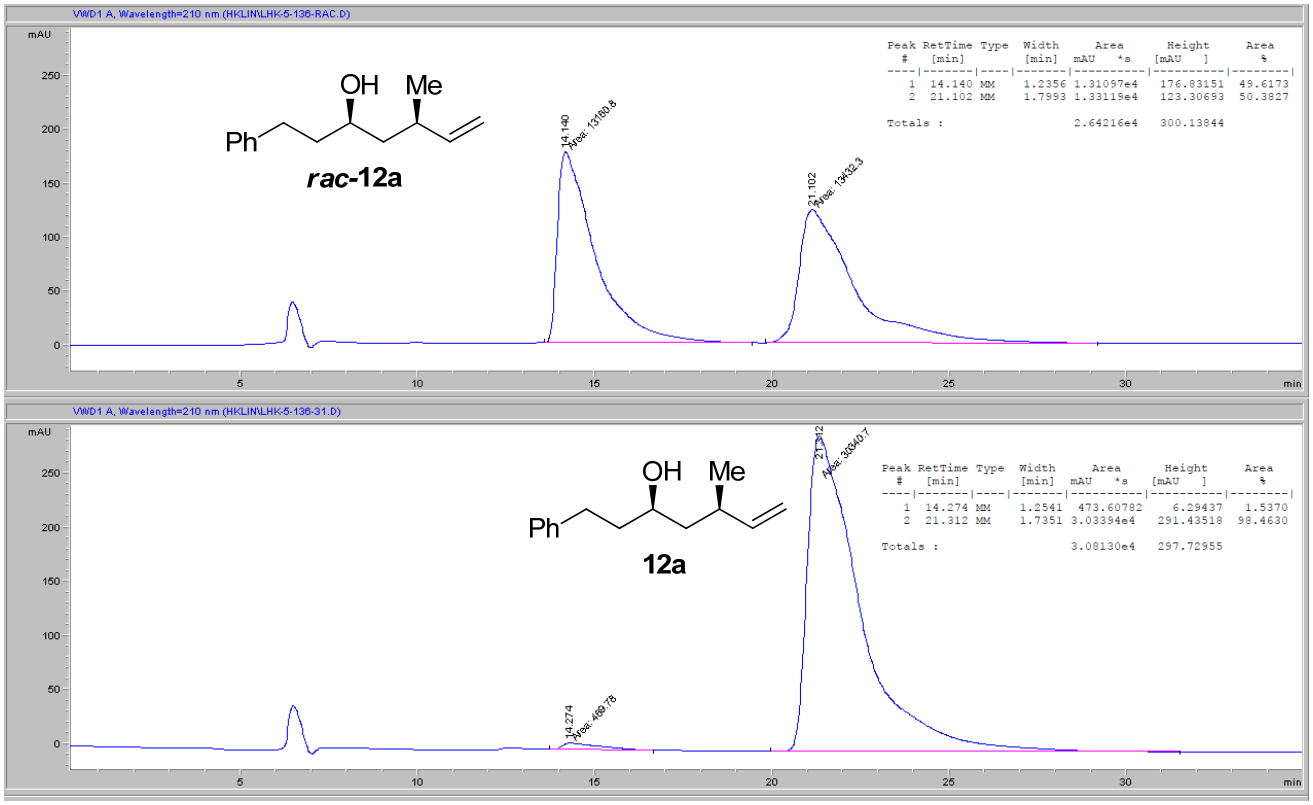



Racemic **S4** was prepared from **S1** by cyclopropanation, oxidation and benzoylation.

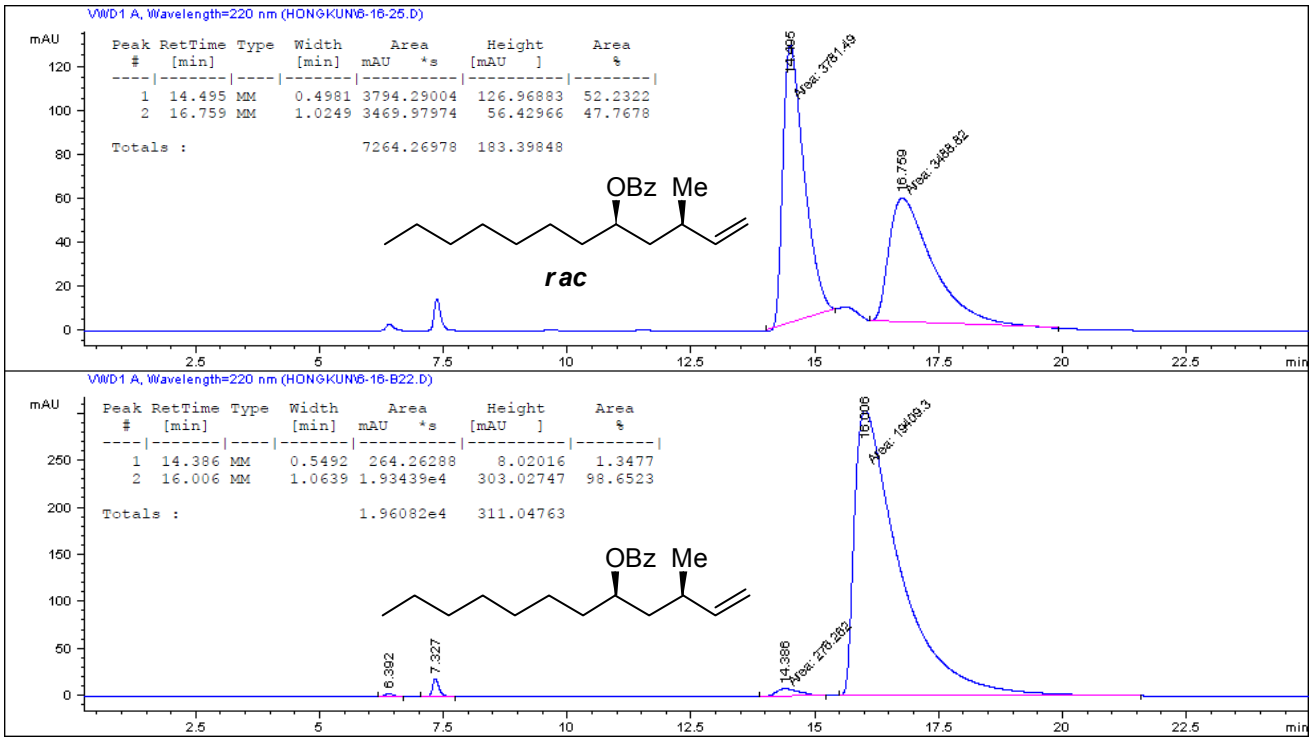


All racemic homocrotylation compounds were prepared from our racemic **1**, containing 5 % *cis*-cyclopropane, resulting in a shoulder peak in all racemic HPLC chromatograms.

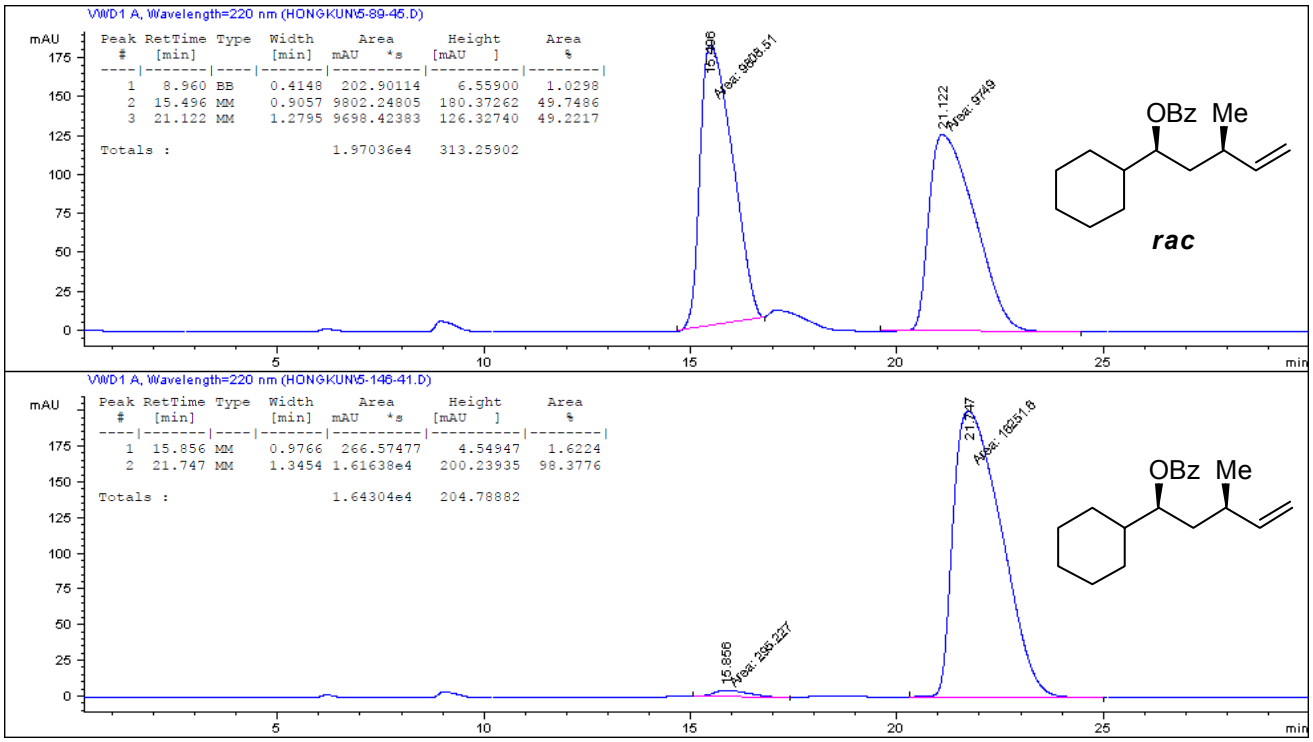
**12a**



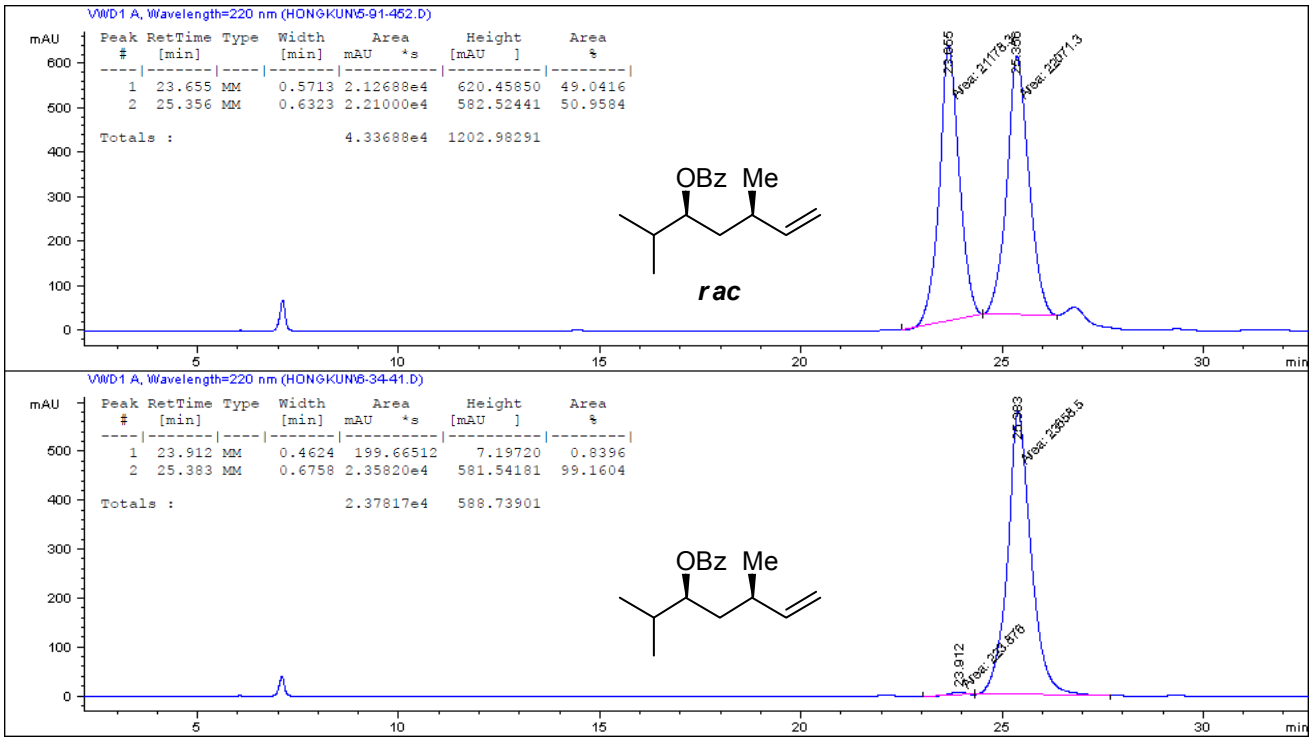
## 12b


VWD1 A, Wavelength=220 nm (HONGKUN\6-16-25.D)
mAU
Peak RetTime Type Width Area Height Area
# [min] [min] mAU *s [mAU ] %
1 14.495 MM 0.4981 3794.29004 126.96883 52.2322
2 16.759 MM 1.0249 3469.97974 56.42966 47.7678
Totals : 7264.26978 183.39848
14.495
Area: 3781.49
16.759
Area: 3488.82
OBz Me
rac
VWD1 A, Wavelength=220 nm (HONGKUN\6-16-B22.D)
mAU
Peak RetTime Type Width Area Height Area
# [min] [min] mAU *s [mAU ] %
1 14.386 MM 0.5492 264.26288 8.02016 1.3477
2 16.006 MM 1.0639 1.93439e4 303.02747 98.6523
Totals : 1.96082e4 311.04763
16.006
Area: 19409.3
OBz Me
6.392
7.327
14.386
Area: 276.382
min

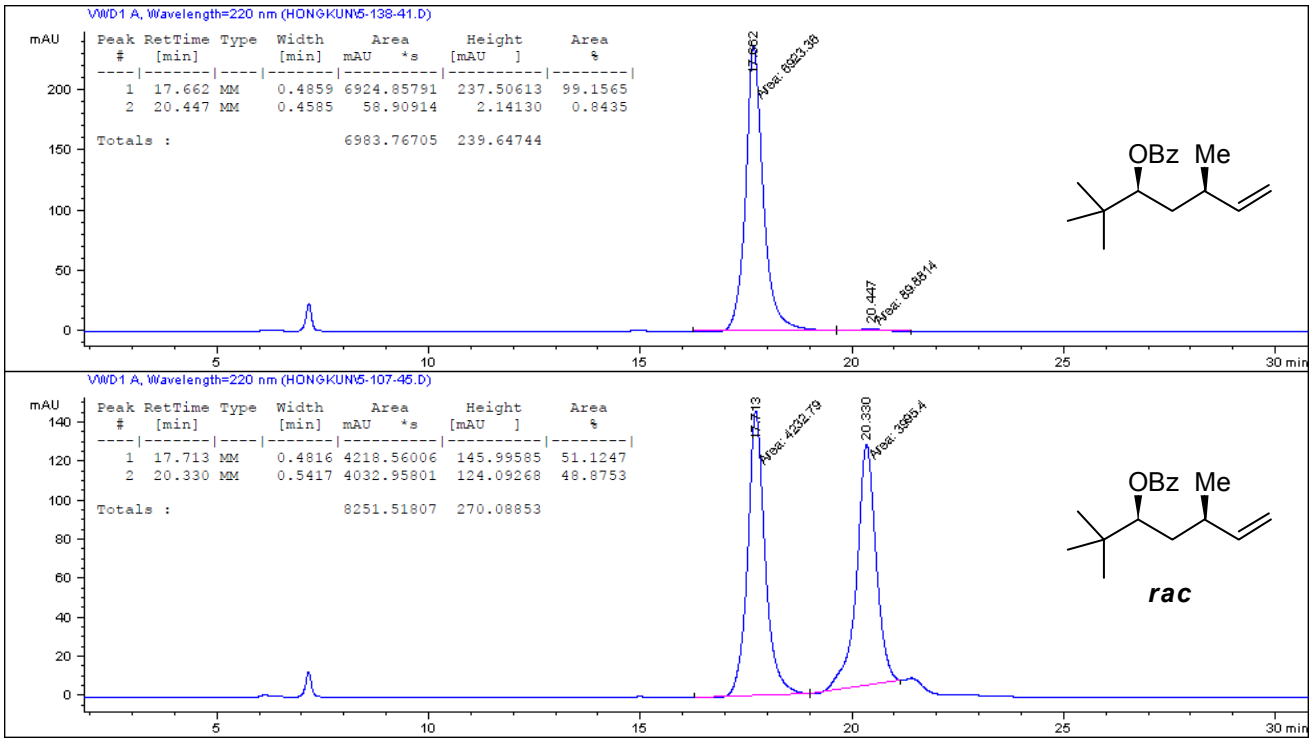
## 12c


VWD1 A, Wavelength=220 nm (HONGKUN\5-89-45.D)
mAU
Peak RetTime Type Width Area Height Area
# [min] [min] mAU *s [mAU ] %
1 8.960 BB 0.4148 202.90114 6.55900 1.0298
2 15.496 MM 0.9057 9802.24805 180.37262 49.7486
3 21.122 MM 1.2795 9698.42383 126.32740 49.2217
Totals : 1.97036e4 313.25902
15.496
Area: 9808.51
21.122
Area: 9749
OBz Me
rac
VWD1 A, Wavelength=220 nm (HONGKUN\5-146-41.D)
mAU
Peak RetTime Type Width Area Height Area
# [min] [min] mAU *s [mAU ] %
1 15.856 MM 0.9766 266.57477 4.54947 1.6224
2 21.747 MM 1.3454 1.61638e4 200.23935 98.3776
Totals : 1.64304e4 204.78882
21.747
Area: 16251.8
OBz Me
15.856
Area: 266.227
min

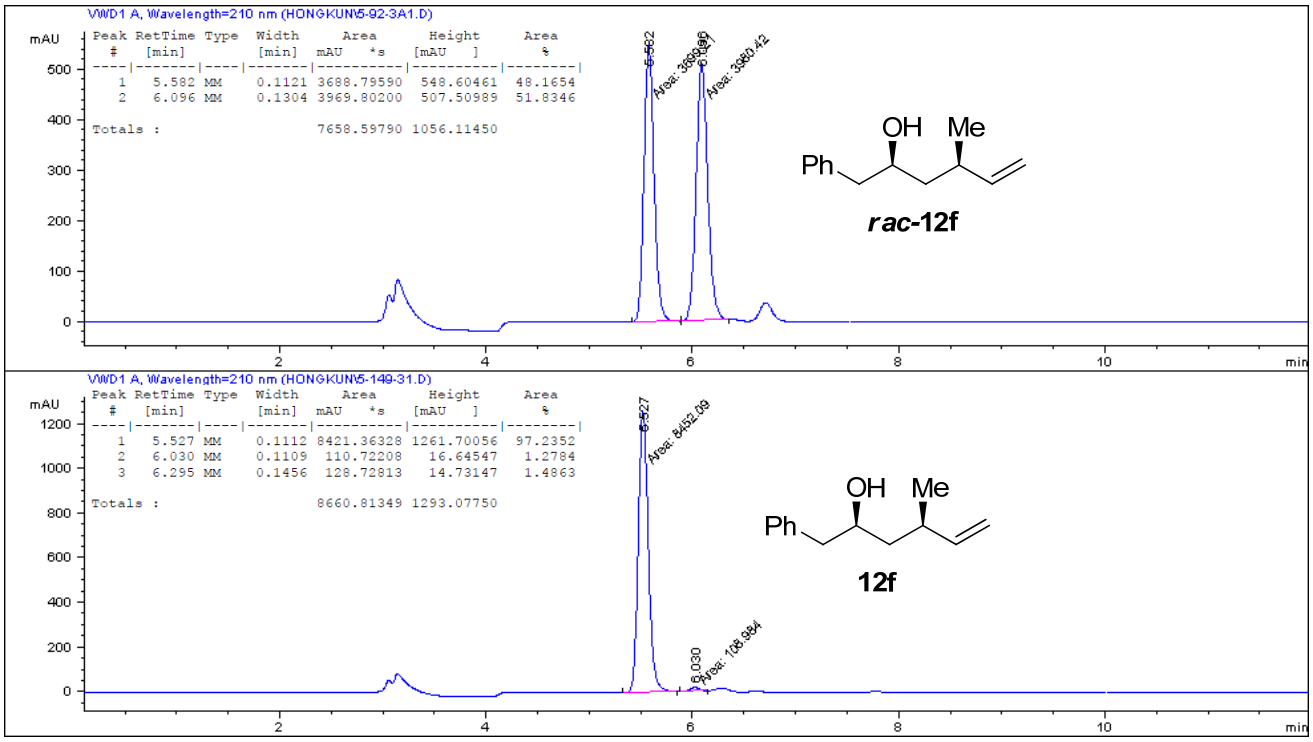
## 12d


VWD1 A, Wavelength=220 nm (HONGKUN\5-91-452.D)
Peak RetTime Type Width Area Height Area
# [min] [min] mAU *s [mAU ] %
1 23.655 MM 0.5713 2.12688e4 620.45850 49.0416
2 25.356 MM 0.6323 2.21000e4 582.52441 50.9584
Totals : 4.33688e4 1202.98291
OBz Me
rac
VWD1 A, Wavelength=220 nm (HONGKUN\6-34-41.D)
Peak RetTime Type Width Area Height Area
# [min] [min] mAU *s [mAU ] %
1 23.912 MM 0.4624 199.66512 7.19720 0.8396
2 25.383 MM 0.6758 2.35820e4 581.54181 99.1604
Totals : 2.37817e4 588.73901
OBz Me
mAU
min

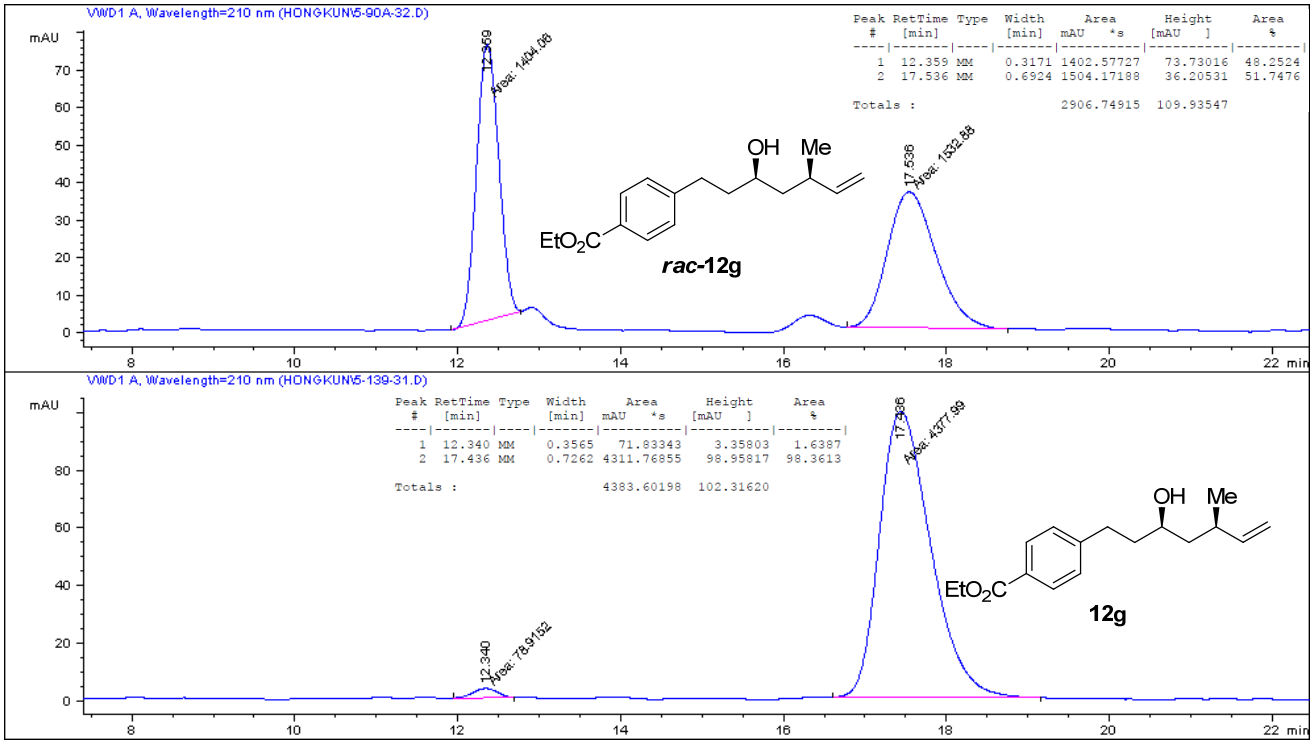
## 12e


VWD1 A, Wavelength=220 nm (HONGKUN\5-138-41.D)
Peak RetTime Type Width Area Height Area
# [min] [min] mAU *s [mAU ] %
1 17.662 MM 0.4859 6924.85791 237.50613 99.1565
2 20.447 MM 0.4585 58.90914 2.14130 0.8435
Totals : 6983.76705 239.64744
OBz Me
VWD1 A, Wavelength=220 nm (HONGKUN\5-107-45.D)
Peak RetTime Type Width Area Height Area
# [min] [min] mAU *s [mAU ] %
1 17.713 MM 0.4816 4218.56006 145.99585 51.1247
2 20.330 MM 0.5417 4032.95801 124.09268 48.8753
Totals : 8251.51807 270.08853
OBz Me
rac
mAU
min

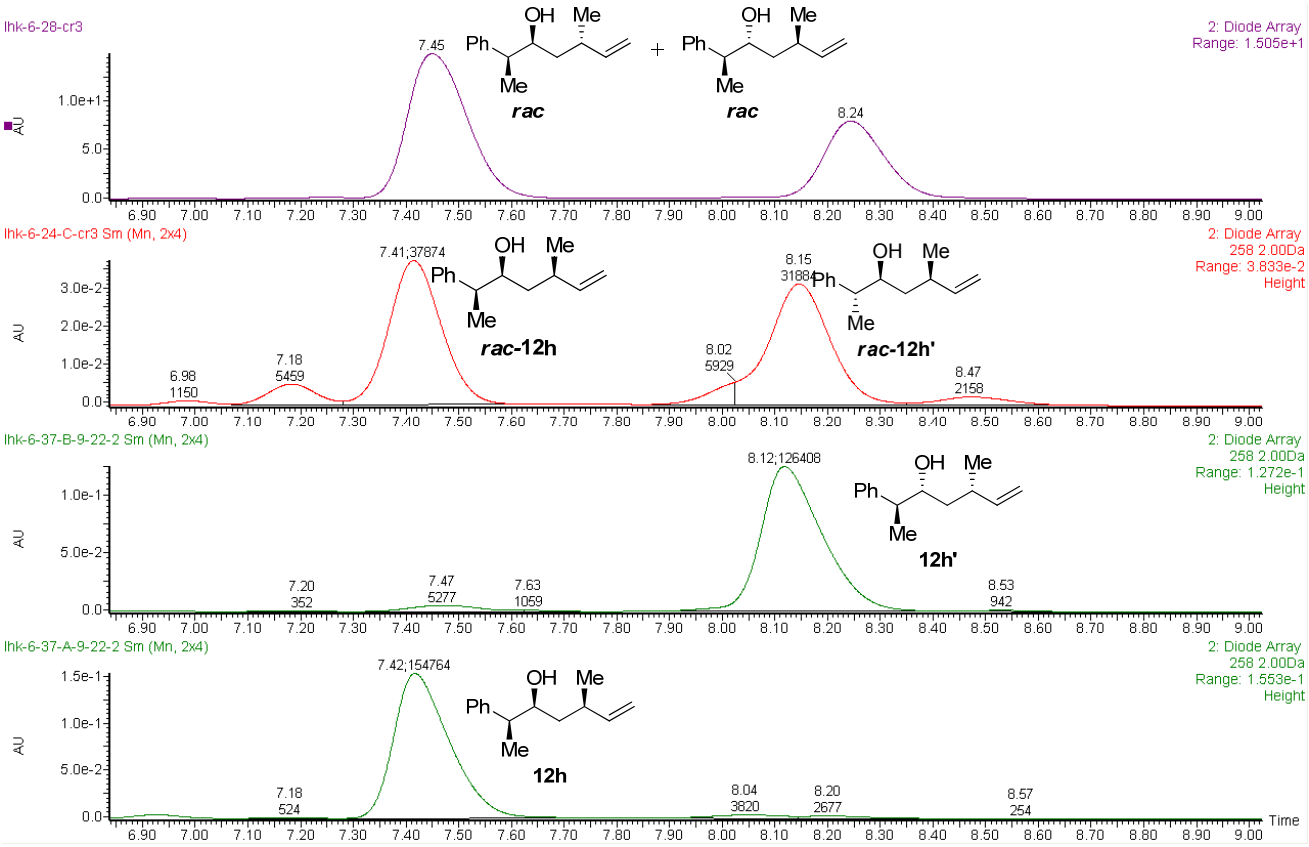
## 12f


VWD1 A, Wavelength=210 nm (HONGKUN\5-92-3A1.D)
Peak RetTime Type Width Area Height Area
# [min] [min] mAU *s [mAU ] %
1 5.582 MM 0.1121 3688.79590 548.60461 48.1654
2 6.096 MM 0.1304 3969.80200 507.50989 51.8346
Totals : 7658.59790 1056.11450
OH Me
Ph
rac-12f
VWD1 A, Wavelength=210 nm (HONGKUN\5-149-31.D)
Peak RetTime Type Width Area Height Area
# [min] [min] mAU *s [mAU ] %
1 5.527 MM 0.1112 8421.36328 1261.70056 97.2352
2 6.030 MM 0.1109 110.72208 16.64547 1.2784
3 6.295 MM 0.1456 128.72813 14.73147 1.4863
Totals : 8660.81349 1293.07750
OH Me
Ph
12f
mAU
min

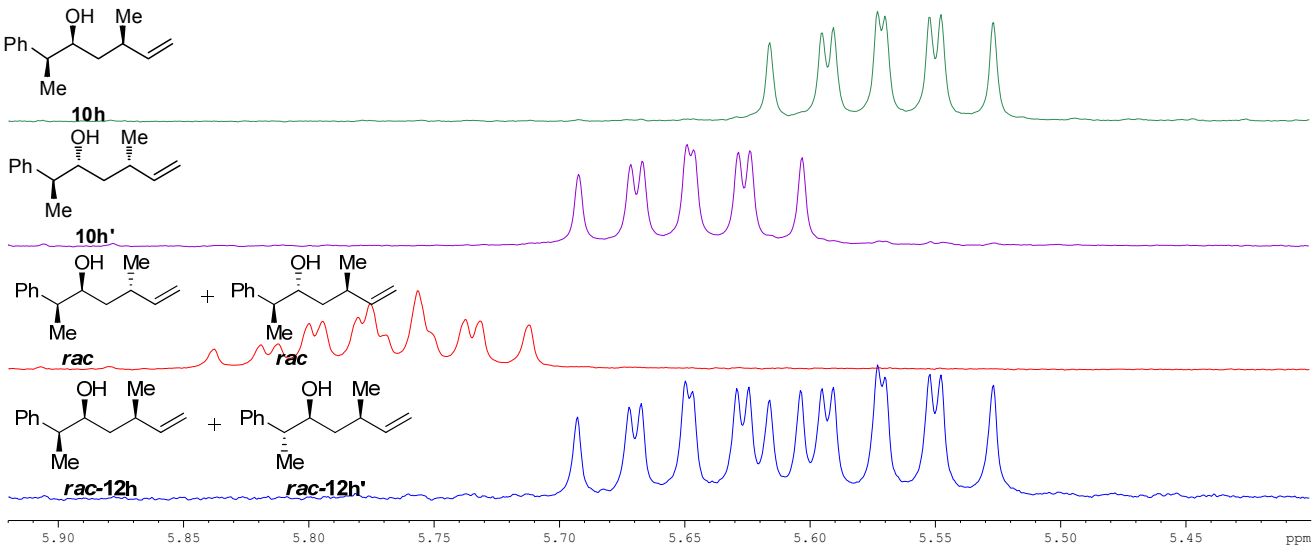
## 12g


VWD1 A, Wavelength=210 nm (HONGKUN\5-90A-32.D)
Peak RetTime Type Width Area Height Area
# [min] [min] mAU *s [mAU ] %
1 12.359 MM 0.3171 1402.57727 73.73016 48.2524
2 17.536 MM 0.6924 1504.17188 36.20531 51.7476
Totals : 2906.74915 109.93547
OH Me
EtO2C
rac-12g
VWD1 A, Wavelength=210 nm (HONGKUN\5-139-31.D)
Peak RetTime Type Width Area Height Area
# [min] [min] mAU *s [mAU ] %
1 12.340 MM 0.3565 71.83343 3.35803 1.6387
2 17.436 MM 0.7262 4311.76855 98.95817 98.3613
Totals : 4383.60198 102.31620
OH Me
EtO2C
12g
mAU
min

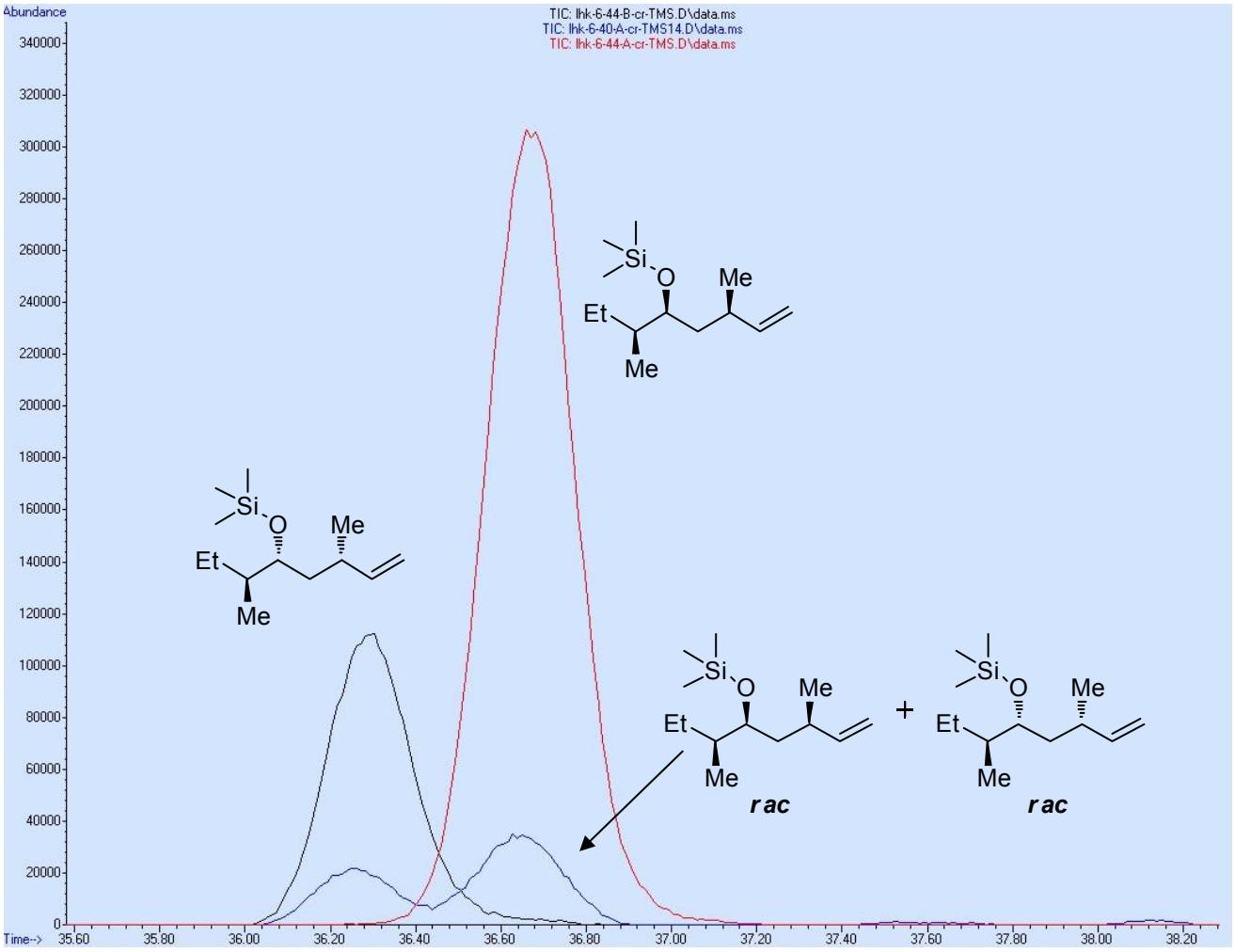
LC-MS chromatogram of **12h**/**h'**




$^{1}$H-NMR overlay of **12h**/**12h'** samples used in dr analysis



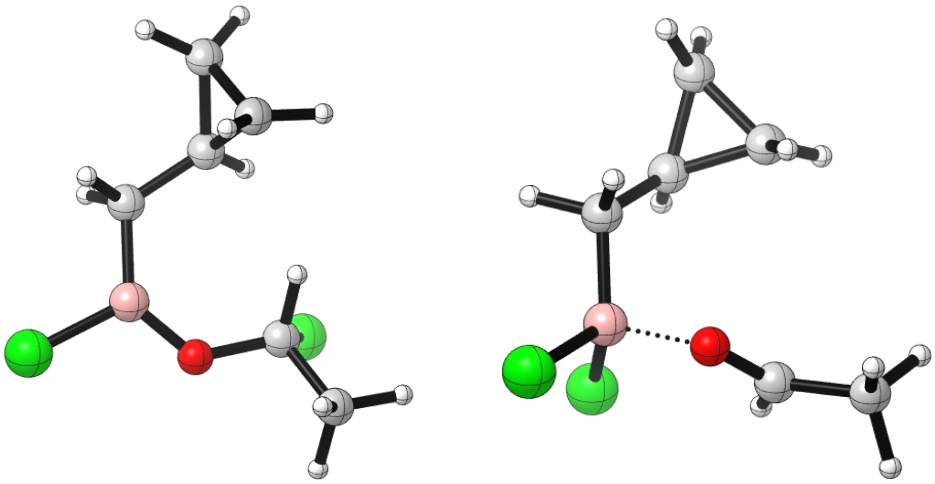
GC-MS chromatogram of **12i/i'**



## General Computational Methods

All calculations were performed with the Gaussian 09 package.[1] Geometries were fully optimized in the gas phase and characterized by frequency calculations using B3LYP functional and 6-31G* basis set. Free energies were calculated for each stationary point.

Reference 1:
Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.



**16-Me**
**ΔΔG = 0.0 kcal/mol**

**19-Me**
**ΔΔG = 5.9 kcal/mol**

**Figure S1. Optimized structures of 16 and 19.**

## Cartesian coordinates of stationary points

### TS-O

| | | | |
|---|---|---|---|
| B | 0.33011272 | -0.09661836 | 0.00000000 |
| C | 1.47924472 | -1.32190536 | -0.04057100 |
| C | 2.64816172 | -1.00573336 | 0.76075300 |
| C | 3.64915172 | 0.46982664 | 0.16505600 |
| H | 0.92697772 | -2.11826136 | 0.47369900 |
| H | 1.72856172 | -1.63790936 | -1.05777200 |
| C | 4.02667272 | -1.04068836 | 0.33101000 |
| H | 4.78671272 | -1.21717036 | 1.08984200 |
| H | 4.23259672 | -1.55119736 | -0.60820500 |
| H | 2.47143572 | -0.82622636 | 1.81977000 |
| H | 4.27480172 | 1.06468564 | 0.82424100 |
| H | 3.71730172 | 0.72916264 | -0.88707300 |
| C | 2.05417272 | 1.55975864 | 0.40676900 |
| H | 1.85497272 | 1.42317964 | 1.47416900 |
| C | 2.62947372 | 2.91676164 | 0.04999800 |
| H | 1.84384672 | 3.66348864 | 0.21424700 |
| H | 3.48939872 | 3.18256264 | 0.67183900 |
| H | 2.91271972 | 2.95749664 | -1.00600500 |
| O | 1.10134372 | 1.16700964 | -0.40042300 |
| O | -0.68145928 | -0.34773136 | -0.97422300 |
| O | -0.10804728 | 0.02022964 | 1.38263700 |
| C | -1.29984928 | 0.75977864 | 1.58157300 |
| C | -1.87810528 | 0.39054064 | -0.82237600 |
| C | -2.39995628 | 0.30985264 | 0.61610500 |
| H | -2.61485128 | -0.01572636 | -1.52729000 |
| H | -1.71647728 | 1.44926164 | -1.09358200 |
| H | -3.29596628 | 0.93410564 | 0.73819000 |
| H | -2.67544928 | -0.72806436 | 0.84198400 |
| H | -1.11560828 | 1.84079164 | 1.43923000 |
| H | -1.61226128 | 0.62056364 | 2.62499700 |

Sum of electronic and zero-point Energies= -603.460589
Sum of electronic and thermal Energies= -603.447974
Sum of electronic and thermal Enthalpies= -603.447030
Sum of electronic and thermal Free Energies= -603.498727
Imaginary frequency: -496.76 $cm^{-1}$

### TS-Cl

| | | | |
|---|---|---|---|
| B | 0.49114331 | 0.12882448 | 0.00000000 |
| C | 1.32543031 | -1.27966152 | -0.21757700 |
| C | 2.62761131 | -1.25138852 | 0.46276200 |
| C | 3.76477931 | 0.00618448 | -0.19187900 |
| H | 0.71830931 | -2.05446252 | 0.26704800 |
| H | 1.43075631 | -1.53228852 | -1.27848500 |
| C | 3.89072631 | -1.58547752 | -0.12429400 |
| H | 4.69691231 | -1.91136352 | 0.52733100 |
| H | 3.88780831 | -2.05589052 | -1.10450300 |
| H | 2.60434131 | -1.10855152 | 1.54175900 |
| H | 4.59881931 | 0.40551248 | 0.37666800 |
| H | 3.75281831 | 0.27182548 | -1.24441400 |
| Cl | 0.00948031 | 0.25432548 | 1.84723000 |
| Cl | -0.99117969 | 0.21028748 | -1.10180800 |
| C | 2.54123731 | 1.35360248 | 0.31072000 |
| H | 2.46862831 | 1.21269548 | 1.39259600 |
| C | 3.30216131 | 2.60050448 | -0.09322200 |

| | | | |
|---|---|---|---|
| H | 2.70176331 | 3.46293548 | 0.21667600 |
| H | 4.27786931 | 2.66554348 | 0.39613800 |
| H | 3.42766731 | 2.65097748 | -1.17868900 |
| O | 1.40230431 | 1.22580148 | -0.35022300 |

Sum of electronic and zero-point Energies= -1255.592233
Sum of electronic and thermal Energies= -1255.581620
Sum of electronic and thermal Enthalpies= -1255.580676
Sum of electronic and thermal Free Energies= -1255.628261
Imaginary frequency: -421.09 $cm^{-1}$

**TS-LA**

| | | | |
|---|---|---|---|
| B | 0.04025765 | 0.16103060 | 0.00000000 |
| C | -0.62250635 | -1.18034740 | -0.66250600 |
| C | -2.08650035 | -1.16890940 | -0.48612400 |
| C | -2.60657335 | -1.29797740 | 1.22323400 |
| H | -0.43687435 | -1.08875140 | -1.74059700 |
| H | -0.19383635 | -2.12106840 | -0.31830300 |
| C | -2.86453535 | -2.27669840 | -0.02344700 |
| H | -3.91544635 | -2.33228240 | -0.29337100 |
| H | -2.36829235 | -3.23735640 | 0.08529400 |
| H | -2.62886335 | -0.32804940 | -0.91496800 |
| H | -3.58913135 | -1.00199340 | 1.57709400 |
| H | -1.99841535 | -1.85171840 | 1.93148300 |
| C | -1.77571135 | 0.36179460 | 1.57218300 |
| H | -2.29221835 | 1.02517960 | 0.87021400 |
| C | -2.16878335 | 0.58257460 | 3.02042200 |
| H | -1.76776035 | 1.55526360 | 3.32746200 |
| H | -3.25363935 | 0.59992760 | 3.15672300 |
| H | -1.72599935 | -0.18124640 | 3.66568500 |
| O | -0.47048535 | 0.26981860 | 1.40899000 |
| O | 1.58266565 | 0.12103160 | 0.18935300 |
| O | -0.34993535 | 1.28031260 | -0.80458500 |
| B | 2.50387065 | -1.16750340 | 0.28852300 |
| Cl | 1.72742865 | -2.29404740 | 1.59734300 |
| Cl | 2.39499265 | -1.98615640 | -1.40455500 |
| C | 4.02131265 | -0.78023140 | 0.65524600 |
| C | 4.49698065 | -0.79260540 | 1.97966800 |
| C | 4.93156765 | -0.38111440 | -0.34308100 |
| C | 5.80635865 | -0.42377340 | 2.29440700 |
| H | 3.83137065 | -1.10851940 | 2.77739600 |
| C | 6.24124465 | -0.00785840 | -0.03743900 |
| H | 4.60987365 | -0.37642740 | -1.38067000 |
| C | 6.68526365 | -0.02702540 | 1.28592200 |
| H | 6.14131665 | -0.45280940 | 3.32884300 |
| H | 6.91821865 | 0.28939860 | -0.83515600 |
| H | 7.70686965 | 0.25711660 | 1.52701400 |
| C | 0.15253165 | 2.55854460 | -0.45842400 |
| C | 2.07908265 | 1.41802960 | 0.66599500 |
| C | 1.67086765 | 2.50882160 | -0.31406700 |
| H | -0.14714235 | 3.25901360 | -1.24644800 |
| H | -0.29498535 | 2.91261160 | 0.48662900 |
| H | 2.05779265 | 3.47012160 | 0.04934700 |
| H | 2.13099265 | 2.30627660 | -1.28802900 |
| H | 1.65386065 | 1.58391460 | 1.66110800 |
| H | 3.15833965 | 1.33842960 | 0.74950200 |

Sum of electronic and zero-point Energies= -1780.368915
Sum of electronic and thermal Energies= -1780.347307

Sum of electronic and thermal Enthalpies= -1780.346363
Sum of electronic and thermal Free Energies= -1780.439773
Imaginary frequency: -396.63 $cm^{-1}$

**TS-2**

| | | | |
|---|---|---|---|
| B | 0.49114331 | 0.01610306 | 0.00000000 |
| C | 1.66225731 | -1.04980894 | -0.42463200 |
| C | 2.96250731 | -0.71512694 | 0.20615700 |
| C | 3.58018131 | 0.83950006 | -0.29514700 |
| H | 1.35814631 | -2.03252794 | -0.04408600 |
| H | 1.76353931 | -1.12472994 | -1.51419600 |
| C | 4.22866631 | -0.69092394 | -0.44398100 |
| H | 2.97289431 | -0.71201494 | 1.29637500 |
| H | 4.34677831 | 1.36248206 | 0.26852200 |
| H | 3.46936531 | 1.16114706 | -1.32619200 |
| Cl | 0.13704731 | -0.19825994 | 1.87466700 |
| Cl | -1.04319269 | -0.21500994 | -1.01056300 |
| C | 2.12922931 | 1.74517706 | 0.36835000 |
| H | 2.16848931 | 1.49729606 | 1.43369000 |
| C | 2.48188531 | 3.19085306 | 0.07136000 |
| H | 1.68880831 | 3.81510506 | 0.49718100 |
| H | 3.43375831 | 3.48457106 | 0.52326000 |
| H | 2.51144231 | 3.37409606 | -1.00678100 |
| O | 1.01597331 | 1.36842606 | -0.24837500 |
| C | 5.53339131 | -0.90150894 | 0.28715700 |
| H | 5.79026631 | -1.96768394 | 0.27358500 |
| H | 6.35280431 | -0.35345594 | -0.18982300 |
| H | 5.46390631 | -0.58623094 | 1.33352000 |
| H | 4.23310431 | -0.97248194 | -1.49560100 |

Sum of electronic and zero-point Energies= -1294.883532
Sum of electronic and thermal Energies= -1294.871195
Sum of electronic and thermal Enthalpies= -1294.870251
Sum of electronic and thermal Free Energies= -1294.921639
Imaginary frequency: -341.02 $cm^{-1}$

**TS-4**

| | | | |
|---|---|---|---|
| B | -0.33011272 | -0.01610306 | 0.00000000 |
| C | -1.10188572 | -1.40478406 | -0.45052900 |
| C | -2.45750072 | -1.48242406 | 0.08420700 |
| C | -3.74578972 | -0.14823106 | -0.32862000 |
| H | -0.51871572 | -2.20611206 | 0.02148600 |
| H | -1.07699472 | -1.53471306 | -1.53683100 |
| C | -3.66165772 | -1.68087606 | -0.67933000 |
| H | -4.47262872 | -2.25317406 | -0.22973100 |
| H | -3.52790472 | -1.89025806 | -1.73913900 |
| H | -2.54592872 | -1.52733306 | 1.16817200 |
| Cl | -0.11381572 | -0.01800506 | 1.89375800 |
| Cl | 1.28988228 | 0.16172694 | -0.87430800 |
| C | -2.39233472 | 1.24470194 | 0.13881400 |
| H | -2.42779872 | 1.11016294 | 1.22245800 |
| C | -3.06726872 | 2.49034494 | -0.39840700 |
| H | -2.52456772 | 3.35409094 | 0.00317100 |
| H | -4.11456072 | 2.58219694 | -0.10655300 |
| H | -2.98244672 | 2.52175394 | -1.48852000 |
| O | -1.21171672 | 1.07482394 | -0.41755600 |
| H | -3.87390272 | 0.35395494 | -1.28405100 |
| C | -4.83282572 | 0.07374394 | 0.71603300 |

| | | | |
|---|---|---|---|
| H | -4.83505172 | 1.08349894 | 1.13466800 |
| H | -5.82363872 | -0.11352406 | 0.28380900 |
| H | -4.70759972 | -0.61972106 | 1.55565500 |

Sum of electronic and zero-point Energies= -1294.872834
Sum of electronic and thermal Energies= -1294.860782
Sum of electronic and thermal Enthalpies= -1294.859838
Sum of electronic and thermal Free Energies= -1294.910468
Imaginary frequency: -436.40 $cm^{-1}$

**TS-6**

| | | | |
|---|---|---|---|
| B | 0.13687600 | -0.22542352 | -0.00295096 |
| C | 1.33142100 | -1.25307052 | 0.44490404 |
| C | 2.64589700 | -0.56707752 | 0.56078104 |
| C | 3.18674900 | 0.00846248 | -0.96709696 |
| H | 1.06976800 | -1.63598752 | 1.43867604 |
| H | 1.40584600 | -2.11032852 | -0.23553196 |
| C | 3.89247600 | -1.07952752 | 0.10441904 |
| H | 2.69350000 | 0.25931048 | 1.26901904 |
| H | 3.98713700 | 0.72988748 | -1.10156396 |
| H | 2.97697400 | -0.61042252 | -1.83342796 |
| Cl | -0.30162300 | 0.88806748 | 1.49478904 |
| Cl | -1.36711200 | -1.15895952 | -0.57353396 |
| C | 1.79684300 | 1.19011748 | -1.18834596 |
| O | 0.62719500 | 0.56809848 | -1.14240196 |
| C | 2.03365200 | 2.41942748 | -0.32293396 |
| H | 3.02717500 | 2.83791048 | -0.51697496 |
| H | 1.28333900 | 3.16367248 | -0.61238796 |
| H | 1.90002200 | 2.23475748 | 0.74219704 |
| H | 2.05790100 | 1.40188948 | -2.23187996 |
| C | 5.22094800 | -0.64637552 | 0.67417304 |
| H | 5.50572800 | -1.32794552 | 1.48505904 |
| H | 6.01304800 | -0.67805552 | -0.08137796 |
| H | 5.17223700 | 0.36592548 | 1.08852504 |
| H | 3.87525400 | -2.06962052 | -0.34732296 |

Sum of electronic and zero-point Energies= -1294.874905
Sum of electronic and thermal Energies= -1294.862621
Sum of electronic and thermal Enthalpies= -1294.861677
Sum of electronic and thermal Free Energies= -1294.912941
Imaginary frequency: -326.72 $cm^{-1}$

**16**

| | | | |
|---|---|---|---|
| B | -0.28180354 | 0.41867956 | 0.00000000 |
| C | 1.11045446 | -0.22892244 | -0.37517000 |
| C | 1.34870746 | -1.72791444 | -0.27505800 |
| C | 1.75862446 | -2.36036144 | 1.03932600 |
| H | 1.32615846 | 0.10698856 | -1.40290700 |
| H | 1.86260046 | 0.29928656 | 0.23069000 |
| C | 2.75234946 | -2.25022144 | -0.09270600 |
| H | 3.03890446 | -3.15889944 | -0.61501700 |
| H | 3.55543646 | -1.52373244 | 0.00669000 |
| H | 0.71074146 | -2.33446844 | -0.91468100 |
| H | 1.37405546 | -3.34575544 | 1.29133100 |
| H | 1.89608146 | -1.70680044 | 1.89815500 |
| Cl | -0.35377754 | 2.21294356 | -0.04292600 |
| C | -1.76085354 | -1.50595344 | 0.49062800 |
| C | -2.91715054 | -1.66462244 | 1.45452200 |
| H | -3.18792654 | -2.71799044 | 1.55928200 |

```
 H                -2.61820054   -1.27268344    2.43305900
 H                -3.78401854   -1.10112344    1.10005000
 O                -1.46587154   -0.14126644    0.35747400
 Cl               -2.22488854   -2.18998744   -1.15315300
 H                -0.88023954   -2.07392044    0.78483100
Sum of electronic and zero-point Energies=          -1255.633572
Sum of electronic and thermal Energies=             -1255.621895
Sum of electronic and thermal Enthalpies=           -1255.620950
Sum of electronic and thermal Free Energies=        -1255.673056
```

**19**

```
 B                -0.57165861    0.61191628    0.00000000
 C                 0.79195439   -0.13977972   -0.37328300
 C                 2.03439639    0.30662528    0.38103500
 C                 2.89716939    1.44292228   -0.13597900
 H                 0.62135439   -1.21089172   -0.19315000
 H                 0.96389739   -0.04489972   -1.45516900
 C                 3.41222939    0.02282628   -0.16270700
 H                 4.20072839   -0.25094072    0.53342100
 H                 3.48348639   -0.47006772   -1.12924700
 H                 1.94411139    0.24844228    1.46436000
 H                 3.34371939    2.13554628    0.57448200
 H                 2.63047139    1.89447128   -1.08951900
 Cl               -0.98098961    0.60677028    1.82515400
 Cl               -2.02150661    0.14019828   -1.03766800
 C                -0.15924361    3.12556328    0.32165200
 H                -0.23461861    2.96549528    1.40331100
 C                 0.13549739    4.47519228   -0.21563300
 H                -0.61463761    5.18432728    0.15844500
 H                 1.10380139    4.81157628    0.17905900
 H                 0.15040239    4.47630528   -1.30669100
 O                -0.33203761    2.16037328   -0.43199100
Sum of electronic and zero-point Energies=          -1255.623634
Sum of electronic and thermal Energies=             -1255.611280
Sum of electronic and thermal Enthalpies=           -1255.610336
Sum of electronic and thermal Free Energies=        -1255.663576
```