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Metal Catalyst-free Substitution of Allylic and Propargylic Phosphates with Diarylmethyl Anions

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Part 1: Experimental

General Information

The ^{1}H (300 or 400 MHz) and ^{13}C NMR (75 or 100 MHz) spectroscopic data were recorded in $CDCl_3$ using Me_4Si ($\delta = 0$ ppm) and the centreline of the triplet ($\delta = 77.1$ ppm), respectively, as internal standards. Signal patterns are indicated as br s (broad singlet), s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). Coupling constants (*J*) are given in Hertz (Hz). Chemical shifts of carbons are accompanied by minus (for C and CH_2) and plus (for CH and CH_3) signs of the attached proton test (APT) experiments. High-resolution mass spectroscopy (HRMS) was performed with a double-focusing mass spectrometer with an ionization mode of positive FAB or EI as indicated for each compound. The solvents that were distilled prior to use are THF (from Na/benzophenone), Et_2O (from Na/benzophenone) and CH_2Cl_2 (from CaH_2). Products were purified by chromatography on silica gel (Kanto, spherical silica gel 60N). Regioselectivity is expressed by % rs or by ratios of the products.

Materials

Alcohol (*R*)-**6**, which had been prepared previously from (*R*)-but-3-yn-2-ol ((*R*)-**117**) of 98% ee,[S1] was converted to (*R*)-**3** (vide infra). (*S*)- and (*R*)-MTPA acids (both 99% ee) were purchased from Aldrich.

GP1: General Procedure for Phosphorylation of Alcohols

To a solution of an alcohol (1 equiv) and *N*-methylimidazole (>1 equiv) in CH_2Cl_2 was added diethyl chlorophosphate (>1 equiv). The solution was stirred at rt and diluted with saturated $NaHCO_3$. The resulting mixture was extracted with EtOAc several times. The combined extracts were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residual oil was purified by chromatography on silica gel to give the phosphate.

Phosphates

(*R*,*E*)-5-((*tert*-Butyldimethylsilyl)oxy)pent-3-en-2-yl diethyl phosphate ((*R*)-3)

(*R*)-**6** (*R*)-**3**

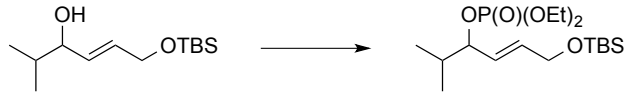
According to GP1 using alcohol (*R*)-**6**[S1] (98% ee, 220 mg, 1.03 mmol), diethyl chlorophosphate (0.22 mL, 1.54 mmol) and *N*-methylimidazole (0.15 mL, 1.85 mmol) in CH_2Cl_2 (5 mL) at rt for 12 h afforded phosphate (*R*)-**3** (343 mg, 95% yield): R_f 0.37 (hexane/EtOAc 1:1); IR (neat) 1472, 1390, 1259, 1035 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.03 (s, 6 H), 0.87 (s, 9 H), 1.28 (dt, $J = 1.0, 7.2$ Hz, 3 H), 1.30 (dt, $J = 1.0, 7.2$ Hz, 3 H), 1.38 (d, $J = 6.3$ Hz, 3 H), 3.99–4.12 (m, 4 H), 4.13–4.18 (m, 2 H), 4.92 (sext., $J = 6.6$ Hz, 1 H), 5.72 (dd, $J = 15.3, 6.0$ Hz, 1 H), 5.79 (dt, $J = 15.3, 3.6$ Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –5.3 (+), 16.1 (+) (d, $J = 7$ Hz), 18.4 (–), 22.3 (+) (d, $J = 5$ Hz), 25.9 (+), 62.7 (–), 63.50 (–) (d, $J = 6$ Hz), 63.54 (–) (d, $J = 6$ Hz), 75.2 (+) (d, $J = 6$ Hz), 129.5 (+) (d, $J = 5$ Hz), 131.5 (+). The ^{1}H and ^{13}C–APT NMR spectra were consistent with those reported.[S1]

(*E*)-6-((*tert*-Butyldimethylsilyl)oxy)hex-4-en-3-yl diethyl phosphate (7)

101 **7**

According to the literature procedure[S1] a mixture of alcohol **101** (193 mg, 0.835 mmol), diethyl chlorophosphate (0.18 mL, 1.25 mmol) and *N*-methylimidazole (0.12 mL, 1.51 mmol) in CH_2Cl_2 (5 mL) was stirred at rt for 12 h to afford phosphate **7** (275 mg, 90% yield): R_f 0.35 (hexane/EtOAc 2:1); IR (neat) 1472, 1390, 1259, 1035, 837 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.07 (s, 6 H), 0.91 (s, 9 H), 0.93 (t, $J = 7.4$ Hz, 3 H), 1.31 (dt, $J = 1.2, 7.2$ Hz, 3 H), 1.33 (dt, $J = 1.2, 7.2$ Hz, 3 H), 1.61–1.83 (m, 2 H), 4.02–4.15 (m, 4 H), 4.16–4.21 (m, 2 H), 4.73 (quint., $J = 7.0$ Hz, 1 H), 5.71 (ddt, $J = 15.4, 7.2, 1.2$ Hz, 1 H), 5.84 (dt, $J = 15.4, 4.3$ Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ –5.3 (+), 9.3 (+), 16.13 (+) (d, $J = 7$ Hz), 16.15 (+) (d, $J = 7$ Hz), 18.4 (–), 25.9 (+), 29.1 (–) (d, $J = 6$ Hz), 62.7 (–), 63.46 (–) (d, $J = 6$ Hz), 63.48 (–) (d, $J = 6$ Hz), 80.4 (+) (d, $J = 6$ Hz), 128.0 (+) (d, $J = 4$ Hz), 132.9 (+). The ^{1}H and ^{13}C–APT NMR spectra were consistent with those reported.[S1]

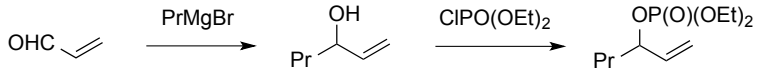
(*E*)-6-((*tert*-Butyldimethylsilyl)oxy)-2-methylhex-4-en-3-yl diethyl phosphate (8)



102 **8**

According to GP1 using alcohol **102** (76 mg, 0.31 mmol), diethyl chlorophosphate (0.067 mL, 0.47 mmol) and *N*-methylimidazole (0.044 mL, 0.56 mmol) in CH_2Cl_2 (2 mL) at rt for 12 h afforded phosphate **8** (113 mg, 95% yield): R_f 0.41 (hexane/EtOAc 2:1); IR (neat) 1471, 1389, 1258, 1037 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.06 (s, 6 H), 0.90 (s, 9 H), 0.92 (d, *J* = 6.8 Hz, 3 H), 0.94 (d, *J* = 6.8 Hz, 3 H), 1.30 (dt, *J* = 1.0, 7.1 Hz, 3 H), 1,32 (dt, *J* = 1.0, 7.1 Hz, 3 H), 1.93 (d of sept., *J* = 6.0, 6.8 Hz, 1 H), 4.02–4.16 (m, 4 H), 4.19 (dm, *J* = 4.2 Hz, 2 H), 4.58 (dt, *J* = 6.0, 7.5 Hz, 1 H), 5.71 (ddt, *J* = 15.4, 7.5, 1.7 Hz, 2 H), 5.84 (ddt, *J* = 15.4, 4.2, 0.6 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ –5.3 (+), 16.1 (+) (d, *J* = 7 Hz), 16.2 (+) (d, *J* = 7 Hz), 17.6 (+), 18.0 (+), 18.4 (–), 25.9 (+), 33.4 (+) (d, *J* = 6 Hz), 62.7 (–), 63.5 (–) (d, *J* = 5 Hz), 84.0 (+) (d, *J* = 6 Hz), 126.1 (+) (d, *J* = 3 Hz), 133.8 (+); HRMS (FAB): m/z calcd for $C_{17}H_{38}O_5PSi$ [$(M+H)^+$] 381.2226, found 381.2218.

Diethyl hex-1-en-3-yl phosphate (9)

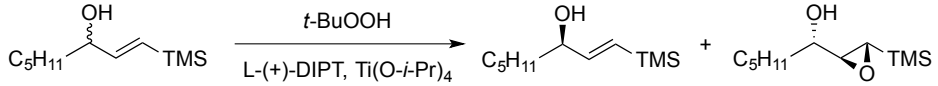


103 **104** **9**

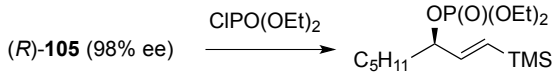
To a suspension of Mg turning (174 mg, 7.16 mmol) in THF (3 mL) was added 1-bromopropane (0.54 mL, 5.97 mmol) dropwise under reflux. The resulting mixture was cooled to rt and diluted with THF (3 mL). Acrolein (**103**) (0.20 mL, 2.99 mmol) was added to the mixture dropwise. The mixture was stirred at rt for 1 h and diluted with saturated NH_4Cl. The resulting mixture was extracted with CH_2Cl_2 three times. The combined extracts were dried over $MgSO_4$ and concentrated to afford crude alcohol **104**, which was used for the next reaction without further purification.

According to GP1 using the above alcohol **104**, diethyl chlorophosphate (0.86 mL, 5.98 mmol) and *N*-methylimidazole (0.59 mL, 7.48 mmol) in CH_2Cl_2 (6 mL) at rt for 1 h afforded phosphate **9** (481 mg, 68% yield from **103**): R_f 0.36 (hexane/EtOAc 2:1); IR (neat) 1264, 985 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, *J* = 7.3 Hz, 3 H), 1.32 (dt, *J* = 1.0, 7.1 Hz, 3 H), 1.33 (dt, *J* = 1.0, 7.1 Hz, 3 H), 1.26–1.48 (m, 2 H), 1.54–1.65 (m, 1 H), 1.66–1.78 (m, 1 H), 4.03–4.16 (m, 4 H), 4.75 (ddt, *J* = 7.1, 6.8, 6.8 Hz, 1 H), 5.20 (dt, *J* = 10.3, 1.0 Hz, 1 H), 5.31 (dt, *J* = 17.3, 1.2 Hz, 1 H), 5.83 (ddd, *J* = 17.3, 10.3, 7.1 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8 (+), 16.1 (+) (d, *J* = 7 Hz), 16.2 (+) (d, *J* = 7 Hz), 18.1 (–), 38.0 (–) (d, *J* = 6 Hz), 63.57 (–) (d, *J* = 6 Hz), 63.59 (–) (d, *J* = 6 Hz), 79.7 (+) (d, *J* = 6 Hz), 117.1 (–), 137.1 (+) (d, *J* = 4 Hz); HRMS (FAB): m/z calcd for $C_{10}H_{22}O_4P$ [$(M+H)^+$] 237.1256, found 237.1255.

(*R*,*E*)-Diethyl (1-(trimethylsilyl)oct-1-en-3-yl) phosphate ((*R*)-10)



105 (racemic) (*R*)-**105** (98% ee) **106**



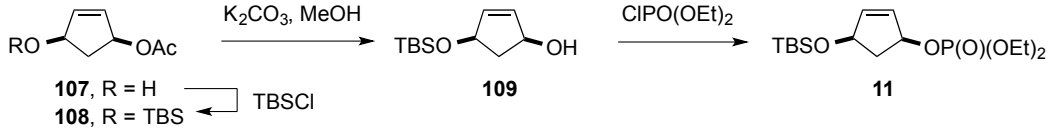
(*R*)-**10**

According to the literature procedure,[S2] a solution of **105** (982 mg, 4.90 mmol), Ti(O-*i*-Pr)$_4$ (1.45 mL, 4.90 mmol) and L-(+)-DIPT (1.24 mL, 5.88 mmol) in CH_2Cl_2 (25 mL) was cooled to –40 °C. A solution of *t*-BuOOH (3.50 M in CH_2Cl_2, 2.10 mL, 7.35 mmol) was added to the solution. The reaction was conducted at –20 °C for 11 h and Me_2S (1.10 mL, 14.9 mmol) was added to quench excess *t*-BuOOH. After 30 min at –20 °C, tartaric acid (10%, 1.0 mL) and NaF (2.91 g, 69 mmol) were added. The mixture was stirred at rt for 30 min and Celite (4.0 g) was added. The mixture was filtered through a pad of Celite. The filtrate was mixed with NaOH (10%, 50 mL) and the mixture was stirred at rt for 10 min. The organic solution was separated, and the aqueous solution was extracted with CH_2Cl_2 twice. The combined extracts were dried over $MgSO_4$ and concentrated to afford a mixture of (*R*)-**105** and **106**. The mixture was subjected to chromatography on silica gel to afford (*R*)-**105** (401 mg, 41% yield) and **106** (426 mg, 40% yield). Alcohol (*R*)-**105** was converted to the MTPA ester to determine 98% ee by ^1H NMR.

According to GP1 using the above alcohol (*R*)-**105** (190 mg, 0.949 mmol), diethyl chlorophosphate (0.21 mL,

1.46 mmol) and *N*-methylimidazole (0.15 mL, 1.90 mmol) in CH_2Cl_2 (3 mL) at rt for 1 h afforded phosphate (*R*)-**10** (266 mg, 83% yield): $[\alpha]_D^{21}$ +8.5 (*c* 0.98, $CHCl_3$); R_f 0.74 (hexane/EtOAc 1:2); IR (neat) 1262, 1250, 1037, 986 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.04 (s, 9 H), 0.85 (d, *J* = 6.8 Hz, 3 H), 1.21–1.40 (m, 12 H), 1.52–1.74 (m, 2 H), 3.99–4.12 (m, 4 H), 4.64–4.73 (m, 1 H), 5.89 (d, *J* = 18.4 Hz, 1 H), 5.95 (dd, *J* = 18.4, 4.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ –1.4 (+), 14.0 (+), 16.2 (+) (*J* = 7 Hz), 22.5 (–), 24.4 (–), 31.5 (–), 35.7 (–) (d, *J* = 6 Hz), 63.5 (–) (d, *J* = 5 Hz), 81.5 (+) (d, *J* = 4 Hz), 132.4 (+), 144.1 (+); HRMS (EI): m/z calcd for $C_{15}H_{33}O_4PSi$ (M^+) 336.1886, found 336.1888.

***cis*-4-((*tert*-Butyldimethylsilyl)oxy)cyclopent-2-en-1-yl diethyl phosphate (11)**

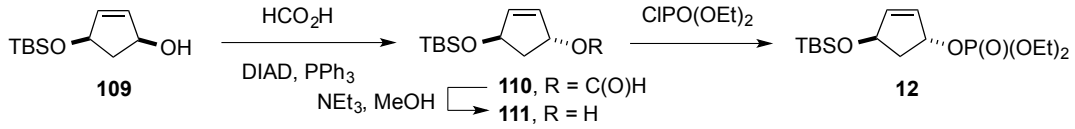


A mixture of alcohol **107**[S3] (1.05 g, 7.38 mmol), TBSCl (1.63 g, 10.8 mmol), imidazole (1.01 g, 14.9 mmol) and a catalytic amount of DMAP in CH_2Cl_2 (10 mL) was stirred at rt for 12 h and diluted with brine. The resulting mixture was extracted with CH_2Cl_2 three times. The combined extracts were washed with brine, dried over $MgSO_4$ and concentrated to afford TBS ether **108**, which was used for the next reaction without further purification.

A mixture of the above ether **108** and K_2CO_3 (2.07 g, 14.9 mmol) in MeOH (15 mL) was stirred at rt for 17 h and diluted with saturated NH_4Cl. The resulting mixture was extracted with EtOAc three times. The combined extracts were dried over $MgSO_4$ and concentrated to give a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to afford alcohol **109** (1.34 g, 85% yield over two steps). The ^1H NMR spectrum was consistent with that reported.[S1,S4,S5]

According to GP1 using alcohol **109** (388 mg, 1.81 mmol), diethyl chlorophosphate (0.39 mL, 2.71 mmol) and *N*-methylimidazole (0.26 mL, 3.30 mmol) in CH_2Cl_2 (10 mL) at rt for 11 h afforded phosphate **11** (566 mg, 89% yield): R_f 0.40 (hexane/EtOAc 1:1); IR (neat) 1261, 1036, 1003 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.04 (s, 3 H), 0.05 (s, 3 H), 0.85 (s, 9 H), 1.30 (t, *J* = 7.2 Hz, 6 H), 1.72 (dt, *J* = 13.4, 5.4 Hz, 1 H), 2.78 (dt, *J* = 13.4, 7.2 Hz, 1 H), 4.07 (quint., *J* = 7.2 Hz, 4 H), 4.59–4.68 (m, 1 H), 5.10–5.20 (m, 1 H), 5.88–5.96 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –4.7 (+), –4.6 (+), 16.1 (+) (d, *J* = 7 Hz), 18.1 (–), 25.8 (+), 42.4 (–) (d, *J* = 4 Hz), 63.7 (–) (d, *J* = 6 Hz), 74.6 (+), 79.9 (+) (d, *J* = 6 Hz), 131.8 (+) (d, *J* = 6 Hz), 139.0 (+). The ^1H and ^{13}C–APT NMR spectra were consistent with those reported.[S1]

***trans*-4-((*tert*-Butyldimethylsilyl)oxy)cyclopent-2-en-1-yl diethyl phosphate (12)**

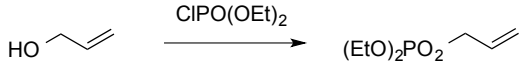


To an ice-cold solution of alcohol **109** (216 mg, 1.01 mmol), PPh_3 (537 mg, 2.05 mmol) and HCO_2H (0.076 mL, 2.01 mmol) in toluene (10 mL) was added DIAD (0.39 mL, 2.02 mmol) dropwise. The mixture was stirred at rt for 12 h and diluted with saturated $NaHCO_3$. The resulting mixture was extracted with EtOAc three times. The combined extracts were dried over $MgSO_4$ and concentrated to give a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to afford formyl ester **110**.

A mixture of the above ester **110** and Et_3N (0.014 mL, 0.100 mmol) in MeOH (3 mL) was stirred at rt for 6 h and concentrated to give a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to afford alcohol **111** (206 mg, 95% yield over two steps).

According to GP1 using alcohol **111** (100.3 mg, 0.468 mmol), diethyl chlorophosphate (0.10 mL, 0.695 mmol) and *N*-methylimidazole (0.066 mL, 0.837 mmol) at rt for 10 h afforded phosphate **12** (138 mg, 84% yield): R_f 0.40 (hexane/EtOAc 2:1); IR (neat) 1472, 1370, 1260, 1030 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.06 (s, 6 H), 0.86 (s, 9 H), 1.31 (tm, *J* = 7.2 Hz, 6 H), 2.01 (dddd, *J* = 14.4, 6.6, 3.9, 1.2 Hz, 1 H), 2.30 (ddd, *J* = 14.4, 6.6, 2.1 Hz, 1 H), 4.01–4.18 (m, 4 H), 5.02–5.11 (m, 1 H), 5.44–5.57 (m, 1 H), 5.98 (dt, *J* = 5.5, 2.1 Hz, 1 H), 6.03 (dd, *J* = 5.5, 1.2 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –4.7 (+), 16.2 (+) (d, *J* = 7 Hz), 18.2 (–), 25.9 (+), 42.3 (–) (d, *J* = 5 Hz), 63.7 (–) (d, *J* = 6 Hz), 76.2 (+), 82.3 (+) (d, *J* = 6 Hz), 131.8 (+) (d, *J* = 4 Hz), 141.2 (+); HRMS (FAB): m/z calcd for $C_{15}H_{32}O_5PSi$ [$(M+H)^+$] 351.1757, found 351.1745.

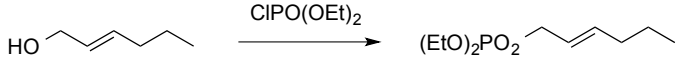
Allyl diethyl phosphate (13)



112 **13**

According to GP1 using alcohol **112** (0.10 mL, 1.47 mmol), diethyl chlorophosphate (0.21 mL, 1.46 mmol) and *N*-methylimidazole (0.13 mL, 1.65 mmol) in CH_2Cl_2 (2 mL) at rt for 12 h afforded phosphate **13** (218 mg, 76% yield): R_f 0.33 (hexane/EtOAc 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.30 (d, J = 7.2 Hz, 6 H), 4.08 (quint., J = 7.2 Hz, 4 H), 4.49 (dd, J = 7.8, 5.6 Hz, 2 H), 5.21 (d, J = 10.2 Hz, 1 H), 5.33 (d, J = 17.1 Hz, 1 H), 5.90 (dd, J = 17.1, 10.2, 5.6 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.1 (+) (d, J = 7 Hz), 63.8 (–) (d, J = 6 Hz), 67.9 (–) (d, J = 5 Hz), 118.1 (–), 132.6 (+) (d, J = 7 Hz). The ^{1}H and ^{13}C NMR spectra were consistent with those reported.[S6]

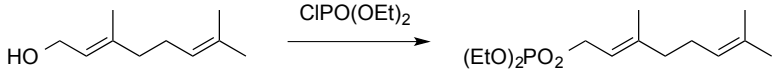
(*E*)-Diethyl hex-2-en-1-yl phosphate (14)



113 **14**

According to GP1 using alcohol **113** (0.50 mL, 4.19 mmol), diethyl chlorophosphate (0.91 mL, 6.29 mmol) and *N*-methylimidazole (0.60 mL, 7.55 mmol) at rt for 13 h afforded phosphate **14** (904 mg, 91% yield): R_f 0.31 (hexane/EtOAc 1:1); IR (neat) 1459, 1393, 1265, 1034 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, J = 7.5 Hz, 3 H), 1.34 (dt, J = 1.0, 7.1 Hz, 6 H), 1.41 (tq, J = 7.0, 7.5 Hz, 2 H), 2.04 (dt, J = 6.4, 7.0 Hz, 2 H), 4.10 (q, J = 7.1 Hz, 2 H), 4.12 (q, J = 7.1 Hz, 2 H), 4.48 (dd, J = 7.2, 6.6 Hz, 2 H), 5.60 (dtt, J = 15.3, 6.4, 1.2 Hz, 1 H), 5.80 (dt, J = 15.3, 6.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5 (+), 16.0 (+) (d, J = 7 Hz), 21.9 (–), 34.1 (–), 63.5 (–) (d, J = 6 Hz), 68.1 (–) (d, J = 6 Hz), 124.5 (+) (d, J = 7 Hz), 136.3 (+); HRMS (FAB): m/z calcd for $C_{10}H_{22}O_4P$ [$(M+H)^+$] 237.1256, found 237.1251. The ^{1}H NMR spectrum was consistent with that reported.[S7]

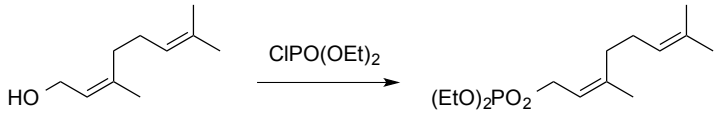
(*E*)-3,7-Dimethylocta-2,6-dien-1-yl diethyl phosphate (15)



114 **15**

According to GP1 using geraniol (**114**) (297 mg, 1.93 mmol), diethyl chlorophosphate (0.42 mL, 2.92 mmol) and *N*-methylimidazole (0.27 mL, 3.42 mmol) in CH_2Cl_2 (2 mL) at rt for 12 h afforded phosphate **15** (517 mg, 92% yield, >97% *E* olefin by ^{13}C NMR): R_f 0.45 (hexane/EtOAc 1:2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.34 (dt, J = 1.2, 7.1 Hz, 6 H), 1.60 (s, 3 H), 1.68 (s, 3 H), 1.71 (s, 3 H), 2.01–2.17 (m, 4 H), 4.11 (dq, J = 7.8, 7.1 Hz, 4 H), 4.57 (t, J = 7.5 Hz, 2 H), 5.09 (tm, J = 6.9 Hz, 1 H), 5.41 (tm, J = 7.2 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.1 (+) (d, J = 7 Hz), 16.4 (+), 17.7 (+), 25.7 (+), 26.2 (–), 39.5 (–), 63.6 (–) (d, J = 6 Hz), 64.1 (–) (d, J = 5 Hz), 118.9 (+) (d, J = 7 Hz), 123.6 (+), 131.9 (–), 142.5 (–). The ^{1}H and ^{13}C NMR spectra were consistent with those reported,[S8] whereas the ^{13}C NMR spectrum in the lit.[S9] is corrected.

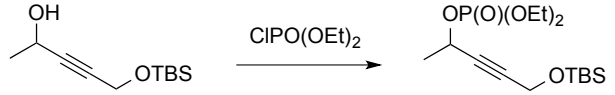
(*Z*)-3,7-Dimethylocta-2,6-dien-1-yl diethyl phosphate (16)



115 **16**

According to GP1 using nerol (**115**) (390 mg, 2.53 mmol), diethyl chlorophosphate (0.55 mL, 3.83 mmol) and *N*-methylimidazole (0.40 mL, 5.07 mmol) in CH_2Cl_2 (25 mL) at rt for 7 h afforded phosphate **16** (521 mg, 71% yield, >97% *Z* olefin by ^{13}C NMR): R_f 0.34 (hexane/EtOAc 2:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.33 (dt, J = 1.0, 7.2 Hz, 6 H), 1.60 (s, 3 H), 1.68 (s, 3 H), 1.77 (s, 3 H), 2.02–2.16 (m, 4 H), 4.10 (dq, J = 8.0, 7.2 Hz, 4 H), 4.54 (t, J = 6.9 Hz, 2 H), 5.04–5.13 (m, 1 H), 5.41 (t, J = 7.2 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.1 (+) (d, J = 7 Hz), 17.7 (+), 23.5 (+), 25.7 (+), 26.6 (–), 32.1 (–), 63.6 (–) (d, J = 6 Hz), 63.8 (–) (d, J = 5 Hz), 119.9 (+) (d, J = 7 Hz), 123.5 (+), 132.3 (–), 142.7 (–). The ^{1}H and ^{13}C NMR spectra were consistent with those reported,[S8] whereas the ^{13}C NMR spectrum in the lit.[S10] is corrected.

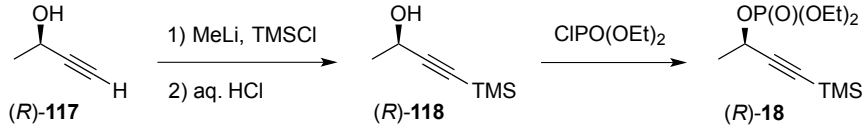
5-((*tert*-Butyldimethylsilyl)oxy)pent-3-yn-2-yl diethyl phosphate (17)



116 **17**

According to GP1 using alcohol **116** (238 mg, 1.11 mmol), diethyl chlorophosphate (0.24 mL, 1.67 mmol) and *N*-methylimidazole (0.158 mL, 2.00 mmol) in CH_2Cl_2 (5 mL) at rt for 11 h afforded phosphate **17** (361 mg, 92% yield): R_f 0.33 (hexane/EtOAc 2:1); IR (neat) 1261, 1037, 1003, 837 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.12 (s, 6 H), 0.91 (s, 9 H), 1.35 (dt, *J* = 2.0, 7.2 Hz, 6 H), 1.57 (d, *J* = 6.4 Hz, 3 H), 4.08–4.20 (m, 4 H), 4.35 (d, *J* = 1.6 Hz, 2 H), 5.09–5.18 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ –5.1 (+), 16.2 (+) (d, *J* = 7 Hz), 18.3 (–), 23.4 (+) (d, *J* = 5 Hz), 25.8 (+), 51.7 (–), 63.9 (–) (d, *J* = 6 Hz), 64.0 (–) (d, *J* = 6 Hz), 64.4 (+) (d, *J* = 5 Hz), 83.0 (–) (d, *J* = 6 Hz), 84.6 (–); HRMS (FAB): m/z calcd for $C_{15}H_{32}O_5PSi$ [$(M+H)^+$] 351.1757, found 351.1767.

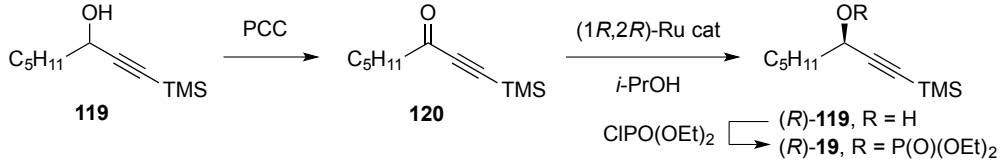
(*R*)-Diethyl (4-(trimethylsilyl)but-3-yn-2-yl) phosphate ((*R*)-18)



(*R*)-**117** (*R*)-**118** (*R*)-**18**

To an ice-cold solution of alcohol (*R*)-**117**[S11] (98% ee by ^1H NMR of the MTPA ester (see part 4 of this supporting info.), 350 mg, 4.99 mmol) in THF (20 mL) was added a solution of MeLi (1.16 M in Et_2O, 9.50 mL, 11.0 mmol) dropwise. The solution was stirred at rt for 1 h and TMSCl (1.60 mL, 12.6 mmol) was added. The solution was stirred at rt for 1 h and 3 N HCl was carefully added until the mixture became acidic. After being stirred for 30 min at rt, the mixture was extracted with Et_2O. The extract was washed sequentially with saturated $NaHCO_3$ and brine, dried over $MgSO_4$ and concentrated to afford (*R*)-**118**, which was diluted with CH_2Cl_2 (10 mL). To the CH_2Cl_2 solution cooled to 0 °C were added *N*-methylimidazole (0.71 mL, 8.99 mmol) and diethyl chlorophosphate (1.08 mL, 7.51 mmol) and the solution was stirred at rt for 5 h. The remaining reagent was quenched by addition of $Me_2N(CH_2)_3NH_2$ (1.90 mL, 15.2 mmol) and the mixture was stirred at rt for 30 min before addition of saturated $NaHCO_3$. The resulting mixture was extracted with CH_2Cl_2 three times. The combined extracts were washed with brine, dried over $MgSO_4$ and concentrated to leave an oil, which was purified by chromatography on silica gel (hexane/EtOAc) to afford (*R*)-**18** (1.05 g, 76% yield): $[\alpha]_D^{21}$ +51 (*c* 1.03, $CHCl_3$); R_f 0.31 (hexane/EtOAc 1:1); IR (neat) 1394, 1034, 989, 847 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.13 (s, 9 H), 1.31 (dt, *J* = 1.2, 7.2 Hz, 3 H), 1.32 (dt, *J* = 1.2, 7.2 Hz, 3 H), 1.52 (d, *J* = 6.6 Hz, 3 H), 4.02–4.18 (m, 2 H), 5.06 (dt, *J* = 7.5, 6.6 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –0.3 (+), 16.1 (+) (d, *J* = 7 Hz), 23.4 (+), 63.8 (–) (d, *J* = 6.5 Hz), 63.9 (–) (d, *J* = 6.5 Hz), 64.6 (+) (d, *J* = 5 Hz), 90.5 (–), 103.4 (–) (d, *J* = 5 Hz); HRMS (EI): m/z calcd for $C_{11}H_{23}O_4PSi$ (M^+) 278.1103, found 278.1098.

(*R*)-Diethyl (1-(trimethylsilyl)oct-1-yn-3-yl) phosphate ((*R*)-19)



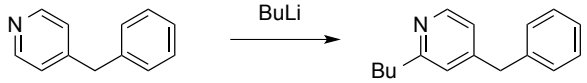
119 **120**

A mixture of alcohol **119** (861 mg, 4.34 mmol), PCC (1.40 g, 6.50 mmol), Celite (2.10 g), and CH_2Cl_2 (20 mL) was stirred vigorously at rt for 1 h and diluted with hexane. The resulting mixture was filtered through a pad of Celite and the filtrate was concentrated to leave an oil, which was purified by chromatography on silica gel to afford ketone **120** (830 mg, 97% yield). RuCl[(1*R*,2*R*)-TsDPEN](*p*-cymene) (269 mg, 0.423 mmol) was neutralized with KOH in CH_2Cl_2, and the mixture was washed with H_2O, dried over CaH_2 and concentrated under vacuum to afford a residue, which was transferred with *i*-PrOH (6 mL) to a solution of ketone **120** (830 mg, 4.23 mmol) in *i*-PrOH (15 mL). The solution was stirred at rt for 11 h and concentrated. The residue was purified by chromatography on silica gel (hexane/EtOAc) to give alcohol (*R*)-**119** (806 mg, 96% yield), which was 93% ee as determined by ^1H NMR spectroscopy of the derived (*S*)- and (*R*)-MTPA esters: ^1H NMR (400 MHz, $CDCl_3$) δ 5.49 (t, *J* = 6.8 Hz, 1 H) (major (*S*)-MTPA ester); δ 5.54 (t, *J* = 6.8 Hz, 1 H) (minor (*R*)-MTPA ester).

According to GP1 using alcohol (*R*)-**119** (93% ee, 188 mg, 0.949 mmol), diethyl chlorophosphate (0.21 mL, 1.46 mmol) and *N*-methylimidazole (0.15 mL, 1.90 mmol) in CH_2Cl_2 (5 mL) at rt for 2 h afforded a mixture of (*R*)-**19** and remaining chlorophosphate, to which $Me_2N(CH_2)_3NH_2$ was added. After 30 min at rt, the mixture was diluted with saturated $NaHCO_3$. The product was extracted with CH_2Cl_2 and purified by chromatography on silica

gel (hexane/EtOAc) to afford phosphate (*R*)-**19** (289 mg, 91% yield): $[\alpha]_D^{21}$ +29 (*c* 0.94, $CHCl_3$): R_f 0.33 (hexane/EtOAc 3:1); IR (neat) 2179, 1252, 1035, 846 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.17 (s, 9 H), 0.90 (t, *J* = 6.9 Hz, 3 H), 1.24–1.54 (m, 12 H), 1.71–1.90 (m, 2 H), 4.06–4.22 (m, 4 H), 4.96 (dt, *J* = 7.5, 6.6 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –0.3 (+), 14.0 (+), 16.1 (+) (d, *J* = 7 Hz), 22.5 (–), 24.4 (–), 31.2 (–), 36.5 (–) (d, *J* = 6 Hz), 63.77 (–) (d, *J* = 6 Hz), 63.85 (–) (d, *J* = 6 Hz), 68.5 (+) (d, *J* = 6 Hz), 91.4 (–), 102.7 (–) (d, *J* = 4 Hz); HRMS (EI): m/z calcd for $C_{15}H_{31}O_4PSi$ (M^+) 334.1729, found 334.1730.

Reaction of 1e with BuLi



1e **29**

To an ice-cold solution of **1e** (74 mg, 0.438 mmol) in THF (1 mL) was added BuLi (1.55 M in hexane, 0.28 mL, 0.434 mmol) dropwise. The solution was stirred at 0 °C for 15 min and H_2O was added to the solution. The resulting mixture was extracted with hexane twice. The combined extracts were washed with brine, dried over $MgSO_4$ and concentrated to afford a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to afford **29** (22 mg, 22% yield): R_f 0.40 (hexane/EtOAc 4:1); IR (neat) 1599, 733, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, *J* = 7.5 Hz, 3 H), 1.37 (sextet, *J* = 7.5 Hz, 2 H), 1.62–1.74 (m, 2 H), 2.73 (t, *J* = 8.1 Hz, 2 H), 3.93 (s, 2 H), 6.91 (d, *J* = 5.3 Hz, 1 H), 6.96 (s, 1 H), 7.14–7.36 (m, 5 H), 8.40 (d, *J* = 5.3 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0 (+), 22.6 (–), 32.1 (–), 38.1 (–), 41.3 (–), 121.5 (+), 123.2 (+), 126.6 (+), 128.7 (+), 129.0 (+), 139.2 (–), 149.2 (+), 150.2 (–), 162.6 (–); HRMS (EI): m/z calcd for $C_{16}H_{19}N$ (M^+) 225.1517, found 225.1517.

GP2: General Procedures for Substitution of Phosphates with Diarylmethanes using BuLi

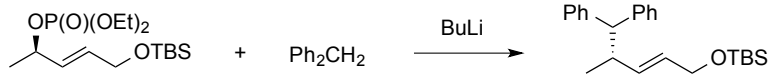
To a solution of diarylmethane **1** (3.3 equiv) in THF was added a solution of BuLi (3 equiv) in hexane dropwise. The solution was stirred at 0 °C–rt for 15 min and cooled to –15 °C. Phosphate (1 equiv) in THF was added to the solution dropwise. The solution was stirred at –15 °C for a specific period of time (usually 15 min) and diluted with saturated NH_4Cl. The resulting mixture was extracted with EtOAc several times. The combined extracts were washed with brine, dried over $MgSO_4$ and concentrated. The residual oil was purified by chromatography on silica gel to afford the corresponding product.

GP3: General Procedures for Substitution of Phosphates with Diarylmethanes using LDA

To an ice-cold solution of *i*-Pr_2NH (3.3 equiv) in THF was added a solution of BuLi (3 equiv) in hexane dropwise. The solution was stirred at 0 °C for 30–60 min and 4-$PyCH_2Ph$ (**1e**) or 2-$PyCH_2Ph$ (**1f**) (3.2 equiv) in THF was added. The solution was stirred at 0 °C for 15 min and cooled to –15 °C. Phosphate (1 equiv) in THF was added to the solution dropwise. The solution was stirred at –15 °C for a specific period of time (usually 15 min) and diluted with saturated NH_4Cl. The product was extracted and purified as mentioned above.

Allylic Products

(*S*,*E*)-*tert*-Butyldimethyl((4-methyl-5,5-diphenylpent-2-en-1-yl)oxy)silane ((*S*)-4)



(*R*)-**3** **1a** (*S*)-**4**

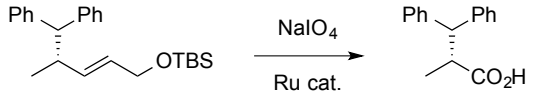
According to GP2 using phosphate (*R*)-**3** (98% ee, 171 mg, 0.485 mmol) in THF (2.5 mL), diphenylmethane (**1a**) (264 mg, 1.57 mmol) and BuLi (1.63 M in hexane, 0.89 mL, 1.45 mmol) in THF (2.5 mL) at –15 °C for 15 min afforded (*S*)-**4** (155 mg, 87% yield, 97% rs by ^1H NMR): $[\alpha]_D^{22}$ –5.0 (*c* 0.83, $CHCl_3$); R_f 0.85 (hexane/EtOAc 1:1); IR (neat) 1598, 1451, 1378, 1254, 1092 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ –0.07 (s, 3 H), –0.06 (s, 3 H), 0.83 (s, 9 H), 0.96 (d, *J* = 6.6 Hz, 3 H), 3.07 (ddq, *J* = 10.6, 5.9, 6.6 Hz, 1 H), 3.60 (d, *J* = 10.6 Hz, 1 H), 3.99 (d, *J* = 4.2 Hz, 2 H), 5.46 (dt, *J* = 15.5, 4.2 Hz, 1 H), 5.52 (dd, *J* = 15.5, 5.9 Hz, 1 H), 7.07–7.30 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ –5.2 (+), 18.4 (–), 19.6 (+), 26.0 (+), 39.9 (+), 58.9 (+), 63.9 (–), 126.0 (+), 126.1 (+), 128.2 (+), 128.3 (+), 128.47 (+), 128.51 (+), 129.0 (+), 134.7 (+), 144.0 (–), 144.3 (–); HRMS (FAB): m/z calcd for $C_{24}H_{33}OSi$ [$(M–H)^+$] 365.2301, found 365.2305.

Determination of enantiomeric purity of (*S*)-**4**.

(*S*)-**4** (*S*)-**121**

To a solution of above (*S*)-**4** (4.9 mg, 0.013 mmol) in THF (1 mL) was added TBAF (1.0 M in THF, 0.13 mL, 0.13 mmol). The solution was stirred at rt for 15 min and diluted with saturated NH_4Cl. The resulting mixture was extracted with EtOAc twice. The combined extracts were dried over $MgSO_4$ and concentrated. The residual oil was purified by chromatography on silica gel (hexane/EtOAc) to afford alcohol (*S*)-**121** (3.3 mg, 98% yield): 96.6% ee by chiral HPLC analysis (Chiralcel AS-H, hexane/*i*-PrOH = 99/1, 0.5 mL/min, 33 °C, t_R (min) = 36.0 (minor (*R*)-isomer), 41.2 (major (*S*)-isomer)); R_f 0.13 (hexane/EtOAc 9:1); IR (neat) 3386, 1598, 1493, 1450, 972, 703 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.98 (d, *J* = 6.6 Hz, 3 H), 1.42–1.72 (br s, 1 H), 3.00–3.16 (m, 1 H), 3.62 (d, *J* = 10.8 Hz, 1 H), 3.84–4.02 (m, 2 H), 5.46–5.63 (m, 1 H), 7.08–7.32 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.7 (+), 40.4 (+), 58.8 (+), 63.8 (–), 126.2 (+), 126.3 (+), 128.2 (+), 128.4 (+), 128.5 (+), 128.6 (+), 128.9 (+), 137.5 (+), 143.9 (–), 144.1 (–); HRMS (FAB): m/z calcd for $C_{18}H_{20}ONa$ [$(M+Na)^+$] 275.1412, found 275.1406.

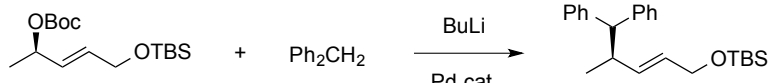
Determination of the absolute configuration of (*S*)-**4**.



(*S*)-**4** (*R*)-**5**

To a suspension of above (*S*)-**4** (132 mg, 0.361 mmol) and $NaIO_4$ (1.23 g, 5.77 mmol) in MeCN (4 mL), CCl_4 (4 mL) and H_2O (6 mL) was added a catalytic amount of $RuCl_3 \cdot nH_2O$. The mixture was stirred at rt for 12 h and diluted with H_2O. The resulting mixture was extracted with CH_2Cl_2 three times. The combined extracts were dried over $MgSO_4$ and concentrated. The residual oil was purified by chromatography on silica gel (hexane/EtOAc) to afford acid (*R*)-**5** (54 mg, 62% yield). The (*R*)-configuration of the acid was determined by comparison of $[\alpha]_D^{21}$ +57 (*c* 1.25, $CHCl_3$) with the lit.[S12] values for the (*S*)-isomer ($[\alpha]_D^{26.5}$ –52.6 ±1.7 (*c* 1.578, $CHCl_3$)). Other characterization data of (*R*)-**5**: R_f 0.13 (hexane/EtOAc 4:1); IR (neat) 3054, 1710, 1265, 740 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.13 (d, *J* = 6.8 Hz, 3 H), 3.31 (dq, *J* = 11.6, 6.8 Hz, 1 H), 4.06 (d, *J* = 11.6 Hz, 1 H), 7.10–7.33 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.2 (+), 44.3 (+), 54.7 (+), 126.6 (+), 126.7 (+), 127.6 (+), 128.2 (+), 128.6 (+), 128.8 (+), 142.1 (–), 142.9 (–), 181.4 (–); HRMS (FAB): m/z calcd for $C_{16}H_{15}O_2$ [$(M–H)^+$] 239.1072, found 239.1072. The ^1H NMR spectrum was consistent with that reported.[S13]

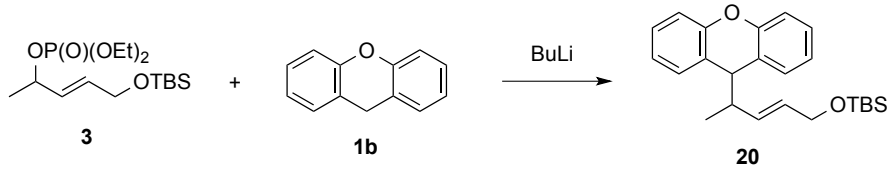
(*R*,*E*)-*tert*-Butyldimethyl((4-methyl-5,5-diphenylpent-2-en-1-yl)oxy)silane ((*R*)-4)



(*R*)-**2** **1a** (*R*)-**4**

To a solution of **1a** (59 mg, 0.35 mmol) in THF (0.5 mL) was added BuLi (1.63 M in hexane, 0.20 mL, 0.33 mmol). The solution was stirred at rt for 15 min and cooled to –15 °C. A solution of (*R*)-**2** (29 mg, 0.092 mmol) and $Pd(PPh_3)_4$ (6 mg, 0.0052 mmol) in THF (0.5 mL) was added to the solution. The solution was stirred at –15 °C for 1 h and diluted with saturated NH_4Cl. The resulting mixture was extracted with EtOAc three times. The combined extracts were washed with brine, dried over $MgSO_4$ and concentrated. The residual oil was purified by chromatography on silica gel (hexane/EtOAc) to afford a mixture of (*R*)-**4** and the regioisomer (28 mg, 83% yield. >99% rs by ^1H NMR). The ^1H NMR spectrum of (*R*)-**4** was consistent with that of (*S*)-**4** obtained above. The product (5.1 mg, 0.014 mmol) in THF (1 mL) was added TBAF (1.0 M in THF, 0.14 mL, 0.14 mmol), and the mixture was stirred at rt for 15 min to obtain the alcohol (3.1 mg, 88% yield), which showed 91.6% ee by chiral HPLC under the conditions mentioned above.

(*E*)-((4-(9*H*-Xanthen-9-yl)pent-2-en-1-yl)oxy)(*tert*-butyl)dimethylsilane (20)

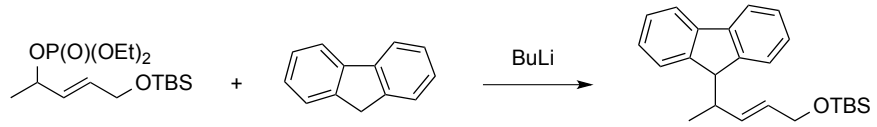


3 **1b** **20**

According to GP2 using phosphate **3** (54 mg, 0.15 mmol) in THF (0.7 mL), 9*H*-xanthene (**1b**) (92 mg, 0.49 mmol) and BuLi (1.55 M in hexane, 0.30 mL, 0.46 mmol) in THF (0.7 mL) at –15 °C for 15 min afforded a

mixture of **20** and the regioisomer (46 mg, 79% yield, 87% rs by ^{1}H NMR). The major product **20**: R_f 0.90 (hexane/EtOAc 1:1); IR (neat) 1577, 1478, 1458, 1255, 753 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ –0.05 (s, 6 H), 0.74 (d, J = 6.9 Hz, 3 H), 0.80 (s, 9 H), 2.34–2.45 (m, 1 H), 3.84 (d, J = 4.2 Hz, 1 H), 3.96 (d, J = 5.0 Hz, 2 H), 5.19 (dt, J = 15.4, 5.0 Hz, 1 H), 5.43 (dd, J = 15.4, 7.7 Hz, 1 H), 6.89–7.18 (m, 8 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ –5.12 (+), –5.10 (+), 15.7 (+), 18.5 (–), 26.1 (+), 45.5 (+), 46.0 (+), 63.8 (–), nine signals (+) for 10 carbons at 116.18, 116.23, 122.7, 122.9, 127.6, 129.3, 129.5, 129.7 and 132.7, 123.3 (–), 124.2 (–), 152.9 (–), 153.1 (–); HRMS (FAB): m/z calcd for $C_{24}H_{32}O_2SiNa$ [(M+Na)$^+$] 403.2069; found 403.2073. Selected signals for the regioisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.77 (dd, J = 15.1, 9.0 Hz, 1 H), 4.85 (dq, J = 15.1, 6.3 Hz, 1 H).

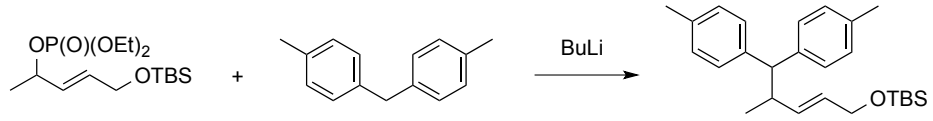
(*E*)-((4-(9*H*-Fluoren-9-yl)pent-2-en-1-yl)oxy)(*tert*-butyl)dimethylsilane (21)



3 **1c** **21**

According to GP2 using phosphate **3** (53 mg, 0.15 mmol) in THF (0.7 mL), 9*H*-fluorene (**1c**) (83 mg, 0.48 mmol) and BuLi (1.55 M in hexane, 0.29 mL, 0.45 mmol) in THF (0.7 mL) at –15 °C for 15 min afforded a mixture of **21** and the regioisomer (45 mg, 81% yield, 85% rs by ^{1}H NMR). The major product **21**: R_f 0.87 and 0.70 (hexane/EtOAc 1:1 and 20:1, respectively); IR (neat) 1717, 1611, 1450, 1254 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ –0.04 (s, 6 H), 0.66 (d, J = 6.8 Hz, 3 H), 0.83 (s, 9 H), 3.02–3.14 (m, 1 H), 3.97 (d, J = 2.2 Hz, 1 H), 4.07 (d, J = 5.1 Hz, 1 H), 5.50 (dt, J = 15.5, 5.1 Hz, 1 H), 5.73 (dd, J = 15.5, 6.1 Hz, 1 H), 7.13–7.33 (m, 4 H), 7.47 (d, J = 7.5 Hz, 2 H), 7.66 (d, J = 7.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ –5.1 (+), 14.7 (+), 18.5 (–), 26.0 (+), 39.4 (+), 52.7 (+), 63.9 (–), eight signals (+) for 10 carbons at 119.7, 124.5, 125.3, 126.6, 126.8, 127.1, 129.1 and 134.2, 141.6 (–), 141.8 (–), 145.3 (–), 146.2 (+); HRMS (FAB): m/z calcd for $C_{24}H_{32}OSiNa$ [(M+Na)$^+$] 387.2120, found 387.2123. Selected signals for the regioisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (d, J = 6.4 Hz, 3 H), 4.78 (dd, J = 15.2, 8.4 Hz, 1 H), 5.24 (dq, J = 15.2, 6.4 Hz, 1 H).

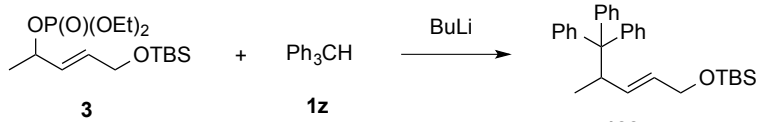
(*E*)-*tert*-Butyldimethyl((4-methyl-5,5-di-*p*-tolylpent-2-en-1-yl)oxy)silane (22)



3 **1d** **22**

According to GP2 using phosphate **3** (53 mg, 0.15 mmol) in THF (0.7 mL), di-*p*-tolylmethane (**1d**) (98 mg, 0.48 mmol) and BuLi (1.60 M in hexane, 0.28 mL, 0.45 mmol) in THF (0.7 mL) at –15 °C for 15 min afforded a mixture of **22** and the regioisomer (57 mg, 95% yield, 92% rs by ^{1}H NMR). The major product **22**: R_f 0.90 (hexane/EtOAc 1:1); IR (neat) 1511, 1461, 1254, 836 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ –0.07 (s, 3 H), –0.06 (s, 3 H), 0.83 (s, 9 H), 0.95 (d, J = 6.6 Hz, 3 H), 2.24 (s, 3 H), 2.26 (s, 3 H), 2.96–3.08 (m, 1 H), 3.53 (d, J = 10.6 Hz, 1 H), 3.99 (d, J = 4.1 Hz, 2 H), 5.41–5.55 (m, 2 H), 6.97–7.21 (m, 8 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ –5.2 (+), 18.4 (–), 19.6 (+), 21.0 (+), 26.0 (+), 39.9 (+), 58.1 (+), 64.1 (–), 127.9 and 128.2 (+), 128.8 (+), 129.0 and 129.2 (+), 135.1 (+), 135.3 and 135.5 (–), 141.3 and 141.6 (–); HRMS (FAB): m/z calcd for $C_{26}H_{38}OSiNa$ [(M+Na)$^+$] 417.2590, found 417.2579. Selected signals for the regioisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.83–2.95 (m, 1 H), 5.26 (dd, J = 15.4, 8.7 Hz, 1 H).

(*E*)-*tert*-Butyldimethyl((4-methyl-5,5,5-triphenylpent-2-en-1-yl)oxy)silane (122)

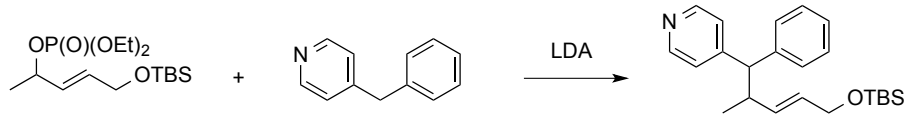


3 **1z** **122**

According to GP2 using phosphate **3** (41 mg, 0.116 mmol) in THF (0.5 mL), Ph_3CH (**1z**) (92 mg, 0.377 mmol) and BuLi (1.61 M in hexane, 0.22 mL, 0.354 mmol) in THF (1 mL) at –15 °C for 15 min afforded a mixture of **122** and the regioisomer (32 mg, 61% yield, 84% rs by ^{1}H NMR). The major product **122**: R_f 0.85 (hexane/EtOAc 2:1); IR (neat) 1597, 1494, 1254, 836, 704 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ –0.07 (s, 3 H), –0.05 (s, 3 H), 0.82 (s, 9 H), 0.90 (d, J = 6.4 Hz, 3 H), 4.01 (d, J = 4.5 Hz, 2 H), 4.14 (quint., J = 6.4 Hz, 1 H), 5.45 (dt, J = 15.6, 4.5 Hz, 1 H), 5.64 (dd, J = 15.6, 6.3 Hz, 1 H), 7.08–7.42 (m, 15 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –5.2 (+), 17.2 (+), 18.4 (–),

26.0 (+), 39.0 (+), 61.2 (–), 64.0 (–), 125.6 (+), 127.4 (+), 130.1 (+) (br s), 130.3 (+), 132.5 (+), 145.7 (br s); HRMS (FAB): m/z calcd for $C_{30}H_{39}OSi$ [$(M+H)^+$] 443.2770; found 443.2770. Selected signals for the regioisomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ –0.11 (s, 3 H), –0.09 (s, 3 H), 0.83 (s, 9 H), 1.58 (dd, *J* = 6.3, 1.5 Hz, 3 H), 5.14 (ddq, *J* = 15.0, 8.1, 1.5 Hz, 1 H), 5.64 (dq, *J* = 15.0, 6.3 Hz, 1 H).

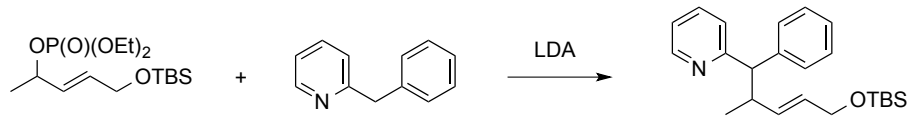
(*E*)-4-(5-((*tert*-Butyldimethylsilyl)oxy)-2-methyl-1-phenylpent-3-en-1-yl)pyridine (23)



3 **1e** **23**

According to GP3 using phosphate **3** (47 mg, 0.13 mmol) in THF (0.5 mL), 4-benzylpyridine (**1e**) (73 mg, 0.43 mmol), *i*-Pr_2NH (0.062 mL, 0.445 mmol) and BuLi (1.55 M in hexane, 0.26 mL, 0.403 mmol) in THF (1.5 mL) at –15 °C for 8 h afforded **23** (37 mg, 78% yield, 92% rs by ^{1}H NMR), which was a mixture of the diastereomers (51:49 by ^{1}H NMR): R_f 0.52 (hexane/EtOAc 3:1); IR (neat) 1597, 1416, 1254, 1070, 836 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ –0.071 and –0.055 (2s, 3 H), –0.062 and –0.051 (2s, 3 H), 0.82 (s, 9 x 0.51 H), 0.83 (s, 9 x 0.49 H), 0.97 and 0.98 (2d, *J* = 6.6 and 6.6 Hz, 3 H), 3.00–3.14 (m, 1 H), 3.59 and 3.60 (2d, *J* = 10.8 and 10.5 Hz, 1 H), 3.94–4.04 (m, 2 H), 5.42–5.54 (m, 2 H), 7.12–7.32 (m, 7 H), 8.42–8.50 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ –5.2 (+), 18.4 (–), 19.4 and 19.5 (+), 25.9 and 26.0 (+), 39.4 and 39.7 (+), 58.3 (+), 63.6 and 63.7 (–), 123.6 and 123.9 (+), 126.7 and 126.8 (+), 128.2 and 128.5 (+), 128.6 and 128.8 (+), 129.7 and 129.9 (+), 133.5 and 133.6 (+), 142.1 and 142.4 (–), 149.8 and 150.0 (+), 152.9 and 153.1 (–); HRMS (FAB) m/z calcd for $C_{23}H_{34}NOSi$ [$(M+H)^+$] 368.2410, found 368.2405.

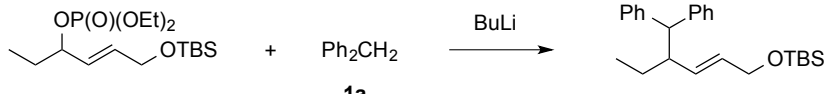
(*E*)-2-(5-((*tert*-Butyldimethylsilyl)oxy)-2-methyl-1-phenylpent-3-en-1-yl)pyridine (24)



3 **1f** **24**

According to GP3 using phosphate **3** (49 mg, 0.139 mmol) in THF (0.5 mL), 2-benzylpyridine (**1f**) (76 mg, 0.45 mmol), *i*-Pr_2NH (0.061 mL, 0.435 mmol) and BuLi (1.55 M in hexane, 0.27 mL, 0.42 mmol) in THF (1.5 mL) at –15 °C for 15 min afforded **24** (43 mg, 84% yield, 94% rs by ^{1}H NMR), which was a mixture of the diastereomers (51:49 by ^{1}H NMR): R_f 0.72 (hexane/EtOAc 3:1); IR (neat) 1588, 1471, 1433, 1254 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ –0.07 (s, 6 x 0.51 H), –0.06 (s, 6 x 0.49 H), 0.83 (s, 9 H), 0.90–0.98 (m, 3 H), 3.23–3.38 (m, 1 H), 3.75 (d, *J* = 10.8 Hz, 1 H), 3.92–4.00 (m, 2 H), 5.38–5.56 (m, 2 H), 6.98–7.57 (m, 8 H), 8.52 and 8.57 (2d, *J* = 4.5 and 4.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ –5.2 and –5.1 (+), 18.40 and 18.42 (–), 19.1 and 19.3 (+), 26.0 (+), 40.06 and 40.11 (+), 60.8 and 60.9 (+), 63.89 and 63.93 (–), 121.2 and 121.3 (+), 123.49 and 123.50 (+), 126.3 and 126.5 (+), six signals (+) for 3 carbons at 128.3, 128.46 (+), 128.52, 128.7, 129.06, and 129.14, 134.4 and 134.6 (+), 136.2 and 136.4 (+), 142,69 and 142.73 (–), 149.3 and 149.5 (+), 163.1 and 163.2 (–); HRMS (FAB): m/z calcd for $C_{23}H_{34}NOSi$ [$(M+H)^+$] 368.2410, found 368.2411.

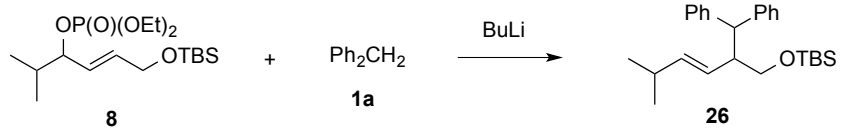
(*E*)-((4-Benzhydrylhex-2-en-1-yl)oxy)(*tert*-butyl)dimethylsilane (25)



7 **1a** **25**

According to GP2 using phosphate **7** (47 mg, 0.13 mmol) in THF (0.7 mL), **1a** (72 mg, 0.41 mmol) and BuLi (1.63 M in hexane, 0.24 mL, 0.39 mmol) in THF (0.7 mL) at –15 °C for 15 min afforded **25** (39 mg, 80% yield, 91% rs by ^{1}H NMR): R_f 0.90 (hexane/EtOAc 1:1); IR (neat) 1599, 1494, 1451, 1255, 1075 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ –0.082 (s, 3 H), –0.077 (s, 3 H), 0.82 (t, *J* = 7.5 Hz, 3 H), 0.83 (s, 9 H), 1.04–1.20 (m, 1 H), 1.39–1.51 (m, 1 H), 2.73–2.84 (m, 1 H), 3.73 (d, *J* = 10.6 Hz, 1 H), 3.97 (dd, *J* = 5.0, 1.4 Hz, 2 H), 5.28 (ddt, *J* = 15.4, 8.8, 1.4 Hz, 1 H), 5.42 (dt, *J* = 15.4, 5.0 Hz, 1 H), 7.04–7.31 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ –5.21 (+), –5.19 (+), 11.7 (+), 18.4 (–), 26.0 (+), 26.1 (–), 47.9 (+), 57.2 (+), 63.8 (–), 125.9 (+), 126.1 (+), 128.25 (+), 128.26 (+), 128.5 (+), 128.6 (+), 131.3 (+), 132.6 (+), 144.1 (–), 144.4 (–); HRMS (FAB): m/z calcd for $C_{25}H_{36}OSiNa$ [$(M+Na)^+$] 403.2433, found 403.2434.

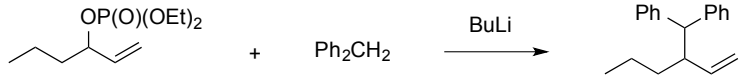
(*E*)-((2-Benzhydryl-5-methylhex-3-en-1-yl)oxy)(*tert*-butyl)dimethylsilane (26)



8 **1a** **26**

According to GP2 using phosphate **8** (28 mg, 0.0746 mmol) in THF (0.5 mL), **1a** (41 mg, 0.241 mmol) and BuLi (1.60 M in hexane, 0.14 mL, 0.224 mmol) in THF (0.5 mL) at –15 °C for 1 h afforded a mixture of **26** and the regioisomer (23 mg, 77% yield, 81% rs by ^{1}H NMR). The major product **26**: R_f 0.85 and 0.51 (hexane/EtOAc 1:1 and 20:1, respectively); IR (neat) 1470, 1253, 1106, 835 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ –0.08 (s, 3 H), –0.05 (s, 3 H), 0.73 (d, *J* = 6.7 Hz, 3 H), 0.81 (d, *J* = 6.7 Hz, 3 H), 0.88 (s, 9 H), 2.08 (d of sext, *J* = 6.6, 6.7 Hz, 1 H), 2.85–2.96 (m, 1 H), 3.42 (dd, *J* = 9.7, 5.2 Hz, 1 H), 3.51 (dd, *J* = 9.7, 3.8 Hz, 1 H), 4.04 (d, *J* = 10.3 Hz, 2 H), 5.18 (dd, *J* = 15.5, 8.3 Hz, 1 H), 5.27 (dd, *J* = 15.5, 6.6 Hz, 1 H), 7.04–7.35 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ –5.43 (+), –5.35 (+), 18.4 (–), 22.4 (+), 22.5 (+), 26.0 (+), 31.2 (+), 49.0 (+), 52.5 (+), 65.2 (–), 125.8 (+), 126.1 (+), 127.5 (+), 128.0 (+), 128.38 (+), 128.43 (+), 129.2 (+), 140.0 (+), 143.7 (–), 144.1 (–); HRMS (FAB): m/z calcd for $C_{26}H_{37}OSi$ [$(M–H)^+$] 393.2614, found 393.2621. Selected signals for the minor product: ^{1}H NMR (400 MHz, $CDCl_3$) δ –0.10 (s, 3 H), –0.09 (s, 3 H), 5.64 (dd, *J* = 15.3, 7.2 Hz, 1 H), 5.77 (dt, *J* = 15.3, 4.3 Hz, 1 H).

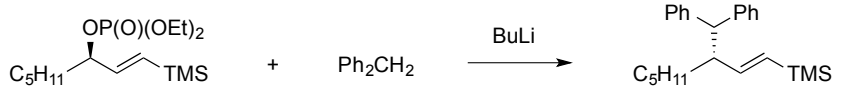
(2-Ethylbut-3-ene-1,1-diyl)dibenzene (27)



9 **1a** **27**

The general procedure GP2 was applied to this reaction except for reaction temperature of –78 °C. Briefly, phosphate **9** (24 mg, 0.10 mmol) in THF (1.0 mL) was added to a mixture of **1a** (56 mg, 0.33 mmol) and BuLi (1.60 M in hexane, 0.20 mL, 0.32 mmol) in THF (4.0 mL) at –78 °C and the solution was stirred for 15 min to afford a mixture of **27** and the regioisomer **34** (20 mg, 81% yield, 78% rs by ^{1}H NMR). The major product **27**: R_f 0.87 (hexane/EtOAc 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80 (t, *J* = 7.0 Hz, 3 H), 1.06–1.46 (m, 4 H), 2.83–2.93 (m, 1 H), 3.72 (d, *J* = 10.6 Hz, 2 H), 4.88 (dd, *J* = 16.9, 1.9 Hz, 1 H), 4.90 (dd, *J* = 10.5, 1.9 Hz, 1 H), 5.44 (ddd, *J* = 16.9, 10.5, 9.1 Hz, 1 H). Selected signals for the regioisomer **34**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.74 (dd, *J* = 7.8, 6.6 Hz, 2 H), 3.95 (t, *J* = 7.8 Hz, 1 H). The ^{1}H NMR spectrum of **34** was consistent with that of the same compound obtained from phosphate **14** and **1a** (vide infra).

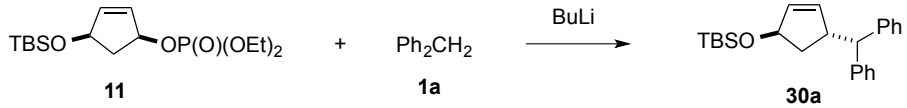
(*R*,*E*)-(3-Benzhydryloct-1-en-1-yl)trimethylsilane ((*R*)-28)



(*R*)-**10** **1a** (*R*)-**28**

According to GP2 using phosphate (*R*)-**10** (98% ee, 46 mg, 0.137 mmol) in THF (1 mL), **1a** (73 mg, 0.435 mmol) and BuLi (1.60 M in hexane, 0.26 mL, 0.416 mmol) in THF (1 mL) at –15 °C for 15 min afforded (*R*)-**28** (38 mg, 80% yield, >99% rs by ^{1}H NMR): 96% ee as determined by HPLC analysis (Chiralcel OJ-H, hexane/*i*-PrOH = 99.5/0.5, 0.1 mL/min, 35 °C, t_R (min) = 54.2 (major (*R*)-isomer)), 61.9 (minor (*S*)-isomer); $[\alpha]_D^{21}$ –50 (*c* 0.86, $CHCl_3$); R_f 0.81 (hexane/EtOAc 3:1); IR (neat) 1616, 1495, 1451, 1247, 868, 838, 701 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.15 (s, 9 H), 1.11 (t, *J* = 6.8 Hz, 3 H), 1.34–1.74 (m, 8 H), 3.06–3.17 (m, 1 H), 4.00 (d, *J* = 10.4 Hz, 1 H), 5.70 (d, *J* = 18.4 Hz, 1 H), 5.87 (dd, *J* = 18.4, 8.4 Hz, 1 H), 7.31–7.61 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ –1.3 (+), 14.1 (+), 22.6 (–), 26.9 (–), 31.8 (–), 32.7 (–), 51.1 (+), 57.5 (+), 125.8 (+), 126.1 (+), 128.0 (+), 128.4 (+), 128.5 (+), 128.7 (+), 131.8 (+), 144.1 (–), 144.2 (–), 149.2 (+); HRMS (EI): m/z calcd for $C_{24}H_{34}Si$ (M^+) 350.2430, found 350.2429.

***trans*-((4-Benzhydrylcyclopent-2-en-1-yl)oxy)(*tert*-butyl)dimethylsilane (30a)**

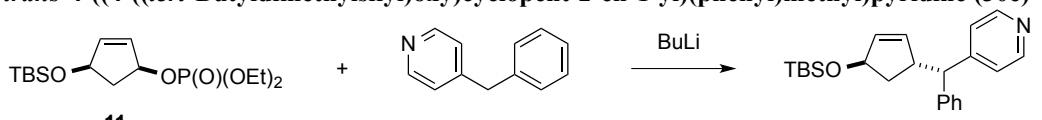


11 **1a** **30a**

According to GP2 using phosphate **11** (35 mg, 0.100 mmol) in THF (0.5 mL), **1a** (60 mg, 0.36 mmol) and

BuLi (1.63 M in hexane, 0.19 mL, 0.31 mmol) in THF (0.5 mL) at –15 °C for 15 min afforded a mixture of **30a**, cis isomer **31a** and the regioisomer **32a** in a ratio of 87:1:12 by ^{1}H NMR (26 mg, 71% yield). The major product **30a**: R_f 0.92 (hexane/EtOAc 1:1); IR (neat) 1716, 1495, 1450, 1254, 1046 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.03 (s, 6 H), 0.86 (s, 9 H), 1.77–1.91 (m, 2 H), 3.52 (d, J = 11.2 Hz, 1 H), 3.75–3.85 (m, 1 H), 4.82–4.90 (m, 1 H), 5.67 (dm, J = 5.7 Hz, 1 H), 5.72 (dt, J = 5.7, 2.0 Hz, 1 H), 7.12–7.31 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ –4.5 (+), 18.4 (–), 26.1 (+), 40.0 (–), 48.8 (+), 58.2 (+), 77.4 (+), 126.27 (+), 126.28 (+), 128.07 (+), 128.15 (+), 128.51 (+), 128.53 (+), 134.1 (+), 137.4 (+), 144.3 (–), 144.6 (–); HRMS (FAB): m/z calcd for $C_{24}H_{32}OSiNa$ [(M+Na)$^+$] 387.2120, found 387.2120.

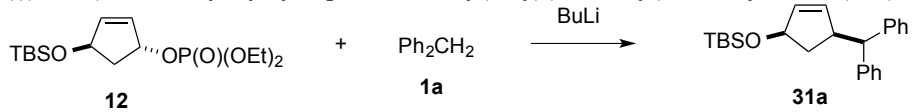
***trans*-4-((4-((*tert*-Butyldimethylsilyl)oxy)cyclopent-2-en-1-yl)(phenyl)methyl)pyridine (30e)**



11 **1e** **30e**

According to GP3 using phosphate **11** (49 mg, 0.14 mmol) in THF (0.5 mL), **1e** (76 mg, 0.45 mmol), *i*-Pr_2NH (0.061 mL, 0.44 mmol) and BuLi (1.55 M in hexane, 0.27 mL, 0.42 mmol) in THF (1.5 mL) at –15 °C for 15 min afforded a mixture of **30e**, cis isomer **31e** and the regioisomer **32e** in a ratio of 91:4:5 by ^{1}H NMR (76 mg, 86% yield). The major product **30e**: diastereomeric ratio 53:47 by ^{1}H NMR; R_f 0.65 and 0.70 (hexane/EtOAc 1:1); IR (neat) 1593, 1254, 1068, 1046 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.034 and 0.038 (2s, 6 H), 0.86 (s, 9 x 0.47 H), 0.87 (s, 9 x 0.53 H), 1.71–1.91 (m, 2 H), 3.51 and 3.52 (2d, J = 11.2 and 11.1 Hz, 1 H), 3.73–3.84 (m, 1 H), 4.81–4.88 (m, 1 H), 5.63 and 5.64 (2dm, J = 6.3 and 6.4 Hz, 1 H), 5.73–5.79 (m, 1 H), 7.15–7.34 (m, 7 H), 8.49 and 8.50 (2d, J = 6.2 and 6.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ –4.55 and –4.53 (+), 18.37 and 18.38 (–), 26.0 (+), 39.8 and 39.9 (–), 48.2 (+), 57.49 and 57.52 (+), 123.4 and 123.5 (+), 126.9 (+), 128.08 and 128.11 (+), 128.8 (+), 134.8 and 135.0 (+), 136.3 and 136.5 (+), 142.4 and 142.7 (–), 149.96 and 150.01 (+), 153.0 and 153.2 (–); HRMS (FAB): m/z calcd for $C_{23}H_{32}NOSi$ [(M+H)$^+$] 366.2253, found 366.2258.

(((1*R*,4*S*)-4-Benzhydrylcyclopent-2-en-1-yl)oxy)(*tert*-butyl)dimethylsilane (31a)

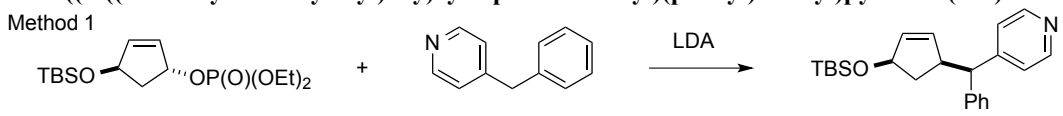


12 **1a** **31a**

According to GP2 using phosphate **12** (48 mg, 0.137 mmol) in THF (1 mL), **1a** (75 mg, 0.446 mmol) and BuLi (1.55 M in hexane, 0.27 mL, 0.42 mmol) in THF (1 mL) at –15 °C for 1 h afforded a mixture of **31a**, trans isomer **30a** and the regioisomer **32a** in a ratio of 97:2:1 by ^{1}H NMR (35 mg, 70% yield). The major product **31a**: R_f 0.92 (hexane/EtOAc 1:1); IR (neat) 1252, 1089, 836, 701 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.03 (s, 3 H), 0.05 (s, 3 H), 0.88 (s, 9 H), 1.32 (dt, J = 13.4, 6.0 Hz, 1 H), 2.27 (dt, J = 13.4, 7.2 Hz, 1 H), 3.32–3.44 (m, 1 H), 3.73 (d, J = 11.4 Hz, 1 H), 4.78–4.86 (m, 1 H), 5.60 (dt, J = 5.7, 1.5 Hz, 1 H), 5.71 (dt, J = 5.7, 2.1 Hz, 1 H), 7.10–7.32 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –4.6 (+), –4.5 (+), 18.3 (–), 26.0 (+), 40.6 (–), 48.7 (+), 58.8 (+), 77.5 (+), 126.2 (+), 126.06 (+), 128.11 (+), 128.51 (+), 128.55 (+), 134.9 (+), 135.8 (+), 144.2 (–), 144.4 (–); HRMS (FAB): m/z calcd for $C_{24}H_{31}OSi$ [(M–H)$^+$] 363.2144, found 363.2147.

***cis*-4-((4-((*tert*-Butyldimethylsilyl)oxy)cyclopent-2-en-1-yl)(phenyl)methyl)pyridine (31e)**

Method 1



12 **1e** **31e**

Method 2

11

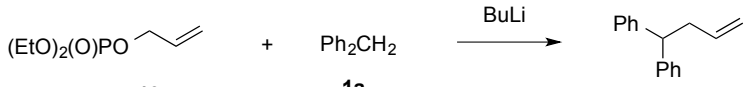
Method 1: According to GP3 using phosphate **12** (48 mg, 0.137 mmol) in THF (0.5 mL), **1e** (76 mg, 0.45 mmol), *i*-Pr_2NH (0.061 mL, 0.44 mmol) and BuLi (1.55 M in hexane, 0.27 mL, 0.42 mmol) in THF (1.5 mL) at –15 °C for 1 h afforded a mixture of **31e** and the regioisomer **32e** in a ratio of 99:1 by ^{1}H NMR (45 mg, 89% yield,

56:44 dr).

Method 2: A solution of LDA in THF (1 mL) was prepared from *i*-Pr_2NH (0.061 mL, 0.435 mmol) and BuLi (1.55 M in hexane, 0.27 mL, 0.419 mmol) (0 °C, 1 h). To this solution was added **1e** (75 mg, 0.443 mmol) in THF (0.5 mL). The solution was stirred at 0 °C for 15 min and cooled to –15 °C. $Pd(PPh_3)_4$ (8 mg, 0.007 mmol) and a THF solution (0.5 mL) of phosphate **11** (49 mg, 0.140 mmol) were added to the solution. The solution was stirred at –15 °C for 15 min and diluted with saturated NH_4Cl. The resulting mixture was extracted with hexane three times. The combined extracts were washed with brine, dried over $MgSO_4$ and concentrated. The residual oil was purified by chromatography on silica gel (hexane/EtOAc) to afford a mixture of **31e** and the regioisomer **32e** in a ratio of >99:1 by ^1H NMR (41 mg, 78% yield, 57:43 dr).

The product **31e** obtained by Methods 1 and 2 were combined and purified again by chromatography for characterization: diastereomeric ratio, 61:39 by ^1H NMR; R_f 0.53 and 0.64 (hexane/EtOAc 2:1); IR (neat) 1594, 1368, 1256, 1092 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.030 (s, 3 x 0.61 H), 0.035 (s, 3 x 0.39 H), 0.055 (s, 3 H), 0.88 (s, 9 H), 1.22–1.38 (m, 1 H), 2.24–2.33 (m, 1 H), 3.33–3.43 (m, 1 H), 3.73 (d, *J* = 11.5 Hz, 1 H), 4.78–4.87 (m, 1 H), 5.55–5.61 (m, 1 H), 5.73–5.80 (m, 1 H), 7.18–7.34 (m, 7 H), 8.45–8.52 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ –4.6 (+), 18.3 (–), 26.0 (+), 40.2 and 40.3 (–), 48.00 and 48.02 (+), 58.1 and 58.2 (+), 77.3 (+), 123.45 and 123.52 (+), 126.9 (+), 128.0 and 128.1 (+), 128.79 and 128.82 (+), 134.8 and 135.1 (+), 135.4 and 135.7 (+), 142.4 and 142.6 (–), 149.97 and 150.02 (+), 152.9 and 153.1 (–); HRMS (FAB): m/z calcd for $C_{23}H_{32}NOSi$ [$(M+H)^+$] 366.2253, found 366.2254.

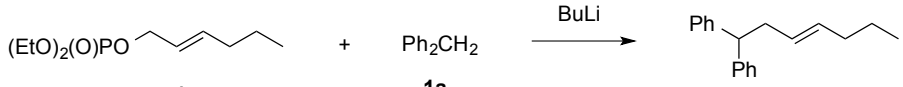
But-3-ene-1,1-diyldibenzene (33)



13 **1a** **33**

According to GP2 using phosphate **13** (39 mg, 0.201 mmol) in THF (1 mL), **1a** (118 mg, 0.701 mmol) and BuLi (1.60 M in hexane, 0.38 mL, 0.608 mmol) in THF (1 mL) at –15 °C for 15 min afforded **33** (34 mg, 81% yield): R_f 0.90 (hexane/EtOAc 1:2); ^1H NMR (300 MHz, $CDCl_3$) δ 2.82 (dt, *J* = 8.1, 6.7 Hz, 2 H), 4.01 (t, *J* = 8.1 Hz, 1 H), 4.94 (d, *J* = 11.1 Hz, 1 H), 5.01 (d, *J* = 17.1 Hz, 1 H), 5.54 (ddt, *J* = 17.1, 11.1, 6.7 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 40.0 (–), 51.3 (+), 116.4 (–), 126.3 (+), 128.0 (+), 128.5 (+), 136.9 (+), 144.6 (–). The ^1H and ^{13}C NMR spectra were consistent with those reported.[S14–S16]

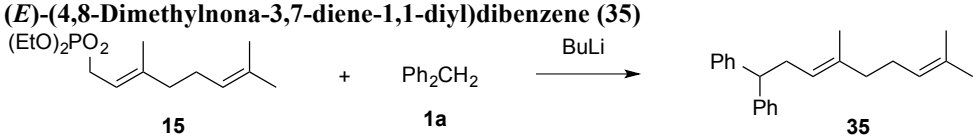
(*E*)-Hept-3-ene-1,1-diyldibenzene (34)



14 **1a** **34**

According to GP2 using phosphate **14** (15 mg, 0.065 mmol) in THF (0.5 mL), **1a** (35.3 mg, 0.210 mmol) and BuLi (1.60 M in hexane, 0.12 mL, 0.192 mmol) in THF (0.5 mL) at –15 °C for 15 min afforded **34** (14 mg, 86% yield, >99% rs by ^1H NMR): R_f 0.93 and 0.45 (hexane/EtOAc 1:1 and 20:1, respectively); IR (neat) 1494, 1450, 968, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.77 (t, *J* = 7.4 Hz, 3 H), 1.26 (tq, *J* = 7.2, 7.4 Hz, 2 H), 1.87 (dt, *J* = 6.6, 7.2 Hz, 2 H), 2.74 (dd, *J* = 7.8, 6.6 Hz, 2 H), 3.95 (t, *J* = 7.8 Hz, 1 H), 5.30 (dt, *J* = 15.2, 6.6 Hz, 1 H), 5.40 (dt, *J* = 15.2, 6.6 Hz, 1 H), 7.13–7.29 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6 (+), 22.6 (–), 34.7 (–), 38.9 (–), 51.8 (+), 126.1 (+), 128.1 (+), 128.3 (+), 128.4 (+), 132.4 (+), 144.9 (–); HRMS (EI): m/z calcd for $C_{19}H_{22}$ [M^+] 250.1722, found 250.1721.

(*E*)-(4,8-Dimethylnona-3,7-diene-1,1-diyl)dibenzene (35)

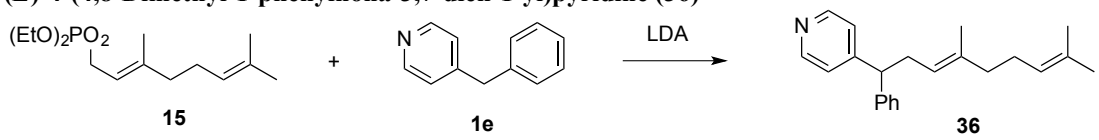


15 **1a** **35**

According to GP2 using phosphate **15** (491 mg, 1.69 mmol) in THF (1 mL), **1a** (910 mg, 5.41 mmol) and BuLi (1.63 M in hexane, 3.11 mL, 5.07 mmol) in THF (11 mL) at –15 °C for 15 min afforded **35** (409 mg, 80% yield, >99% rs and 98% *E* olefin by ^1H and ^{13}C NMR): R_f 0.90 (hexane/EtOAc 2:1); IR (neat) 1600, 1494, 1449, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.54 (s, 3 H), 1.55 (s, 3 H), 1.64 (s, 3 H), 1.86–2.03 (m, 4 H), 2.73 (t, *J* = 7.5 Hz, 2 H), 3.94 (t, *J* = 7.8 Hz, 1 H), 4.99 (t, *J* = 6.2 Hz, 1 H), 5.07 (t, *J* = 7.0 Hz, 1 H), 7.12–7.30 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.2 (+), 17.7 (+), 25.8 (+), 26.6 (–), 34.3 (–), 39.8 (–), 51.5 (+), 122.7 (+), 124.3 (+), 126.1

(+), 128.1 (+), 128.3 (+), 131.3 (–), 136.3 (–), 145.0 (–). The ^{1}H NMR spectrum is corrected as presented above, while the ^{13}C NMR spectrum is consistent with that reported.[S17]

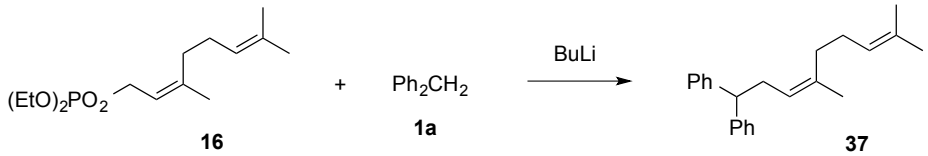
(*E*)-4-(4,8-Dimethyl-1-phenylnona-3,7-dien-1-yl)pyridine (36)



15 **1e** **36**

According to GP3 using phosphate **15** (484 mg, 1.67 mmol) in THF (1 mL), **1e** (903 mg, 5.34 mmol), *i*-Pr_2NH (0.73 mL, 5.21 mmol) and BuLi (1.63 M in hexane, 3.07 mL, 5.00 mmol) in THF (10 mL) at –15 °C for 15 min afforded **36** (383 mg, 75% yield, >99% rs and 98% *E* olefin by ^{1}H and ^{13}C NMR): R_f 0.57 (hexane/EtOAc 2:1); IR (neat) 1596, 1451, 1414, 739, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53 (s, 3 H), 1.55 (s, 3 H), 1.64 (d, *J* = 0.8 Hz, 3 H), 1.88–2.10 (m, 4 H), 2.73 (t, *J* = 7.6 Hz, 2 H), 3.92 (t, *J* = 7.6 Hz, 1 H), 4.96–5.07 (m, 2 H), 7.12–7.33 (m, 7 H), 8.48 (dd, *J* = 4.4 Hz, 1.2 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.2 (+), 17.7 (+), 25.7 (+), 26.5 (–), 33.6 (–), 39.7 (–), 51.0 (+), 121.6 (+), 123.6 (+) (br s), 124.1 (+), 126.7 (+), 128.0 (+), 128.6 (+), 131.4 (–), 137.2 (–), 143.1 (–), 149.7 (+), 153.8 (–); HRMS (EI): m/z calcd for $C_{22}H_{27}N$ (M^+) 305.2144, found 305.2144. The ^{1}H and ^{13}C NMR spectra in the lit.[S14] are corrected as presented above.

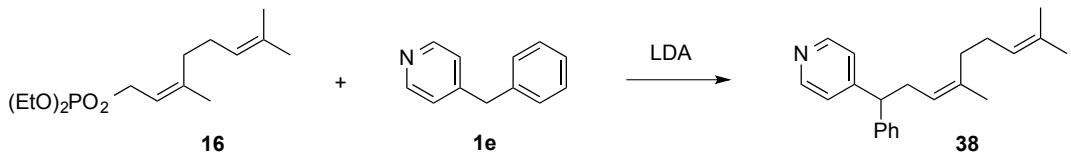
(*Z*)-(4,8-Dimethylnona-3,7-diene-1,1-diyl)dibenzene (37)



16 **1a** **37**

According to GP2 using phosphate **16** (41 mg, 0.141 mmol) in THF (1 mL), **1a** (75 mg, 0.446 mmol) and BuLi (1.55 M in hexane, 0.27 mL, 0.42 mmol) in THF (1 mL) at –15 °C for 15 min afforded **37** (34 mg, 80% yield, >99% rs and 98% *Z* olefin by ^{1}H and ^{13}C NMR): R_f 0.83 (hexane/EtOAc 2:1); IR (neat) 1600, 1495, 1449, 1376, 699 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.60 (s, 3 H), 1.61 (d, *J* = 1.5 Hz, 3 H), 1.69 (s, 3 H), 1.97–2.08 (m, 4 H), 2.74 (t, *J* = 7.6 Hz, 2 H), 3.92 (t, *J* = 7.8 Hz, 1 H), 5.02–5.16 (m, 2 H), 7.12–7.32 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.8 (+), 23.4 (+), 25.8 (+), 26.5 (–), 32.2 (–), 34.1 (–), 51.8 (+), 123.3 (+), 124.4 (+), 126.1 (+), 128.1 (+), 128.4 (+), 131.7 (–), 136.5 (–), 145.0 (–); HRMS (EI): m/z calcd for $C_{23}H_{28}$ (M^+) 304.2191, found 304.2191

(*Z*)-4-(4,8-Dimethyl-1-phenylnona-3,7-dien-1-yl)pyridine (38)

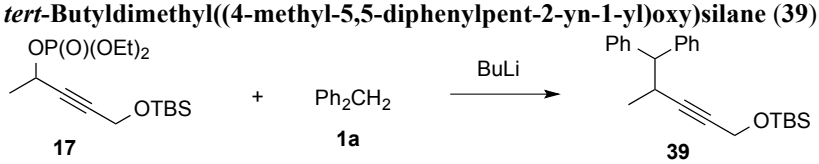


16 **1e** **38**

According to GP3 using phosphate **16** (40 mg, 0.138 mmol) in THF (0.5 mL), **1e** (74 mg, 0.437 mmol), *i*-Pr_2NH (0.061 mL, 0.43 mmol) and BuLi (1.55 M in hexane, 0.27 mL, 0.42 mmol) in THF (1.5 mL) at –15 °C for 15 min afforded **38** (33 mg, 79% yield, >99% rs and 98% *Z* olefin by ^{1}H and ^{13}C NMR): R_f 0.47 (hexane/EtOAc 3:1); IR (neat) 1596, 1495, 1451, 1415, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.60 (s, 3 H), 1.62 (d, *J* = 1.2 Hz, 3 H), 1.69 (s, 3 H), 1.97–2.03 (m, 4 H), 2.73 (t, *J* = 7.2 Hz, 2 H), 3.90 (t, *J* = 8.0 Hz, 1 H), 5.01 (t, *J* = 6.8 Hz, 1 H), 5.05–5.14 (m, 1 H), 7.12–7.33 (m, 7 H), 8.48 (br d, *J* = 3.2 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.7 (+), 23.4 (+), 25.8 (+), 26.4 (–), 32.1 (–), 33.3 (–), 51.2 (+), 122.3 (+), 123.5 (+) (br s), 124.2 (+), 126.7 (+), 128.0 (+), 128.6 (+), 131.8 (–), 137.3 (–), 143.1 (–), 149.8 (+), 153.8 (–); HRMS (FAB): m/z calcd for $C_{22}H_{28}N$ [($M+H^+$)] 306.2222, found 306.2225.

Propargylic Products

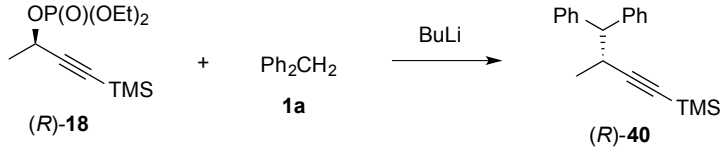
***tert*-Butyldimethyl((4-methyl-5,5-diphenylpent-2-yn-1-yl)oxy)silane (39)**



17 **1a** **39**

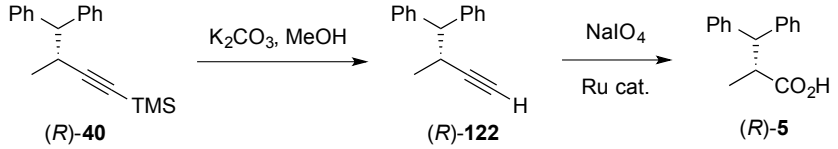
According to GP2 using phosphate **17** (31 mg, 0.087 mmol) in THF (0.5 mL), **1a** (52.5 mg, 0.312 mmol) and BuLi (1.60 M in hexane, 0.16 mL, 0.256 mmol) in THF (0.5 mL) at –15 °C for 15 min afforded **39** (33 mg, 87% yield, >99% rs by ^{1}H NMR): R_f 0.87 (hexane/EtOAc 1:1); IR (neat) 1598, 1494, 1450, 1263, 1083 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.01 (s, 6 H), 0.86 (s, 9 H), 1.15 (d, J = 6.8 Hz, 3 H), 3.31 (dtq, J = 9.4, 2.0, 6.8 Hz, 1 H), 3.85 (d, J = 9.4 Hz, 1 H), 4.18 (d, J = 2.0 Hz, 2 H), 7.14–7.37 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ –5.1 (+), 18.3 (–), 20.4 (+), 25.9 (+), 30.6 (+), 52.0 (–), 57.5 (+), 81.0 (–), 88.2 (–), 126.4 (+), 126.5 (+), 128.2 (+), 128.5 (+), 128.6 (+), 143.1 (–), 143.2 (–); HRMS (FAB): m/z calcd for $C_{24}H_{31}OSi$ [$(M–H)^+$] 363.2144, found 363.2138.

(*R*)-Trimethyl(3-methyl-4,4-diphenylbut-1-yn-1-yl)silane ((*R*)-40)



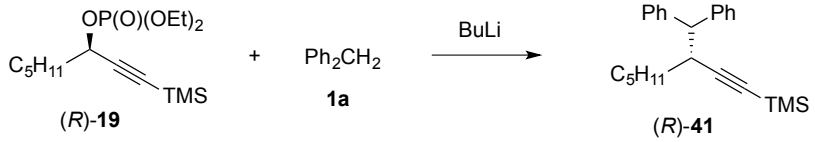
According to GP2 using phosphate (*R*)-**18** (98%% ee, 39 mg, 0.141 mmol) in THF (1 mL), **1a** (75 mg, 0.446 mmol) and BuLi (1.60 M in hexane, 0.26 mL, 0.416 mmol) in THF (1 mL) at –15 °C for 15 min afforded (*R*)-**40** (29 mg, 70% yield, >99% rs by ^{1}H NMR): >98% ee as determined by HPLC analysis of the derived acid (see below); $[\alpha]_D^{21}$ –4 (*c* 0.86, $CHCl_3$); mp 47–48 °C; R_f 0.91 (hexane/EtOAc 1:1); IR (nujol) 1451, 1250, 842, 702 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.00 (s, 9 H), 1.15 (t, J = 6.6 Hz, 3 H), 3.27 (dq, J = 9.0, 6.6 Hz, 1 H), 3.84 (d, J = 9.0 Hz, 1 H), 7.11–7.38 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.0 (+), 20.1 (+), 31.8 (+), 57.6 (+), 87.0 (–), 110.6 (–), 126.3 (+), 126.5 (+), 128.0 (+), 128.2 (+), 128.5 (+), 128.8 (+), 142.95 (–), 143.04 (–); HRMS (EI): m/z calcd for $C_{20}H_{24}Si$ (M^+) 292.1647, found 292.1647.

Determination of enantiomeric purity and the absolute configuration of (*R*)-**40**.



A mixture of the above product (*R*)-**40** (29 mg, 0.099 mmol) and K_2CO_3 (20 mg, 0.145 mmol) in MeOH (5 mL) was stirred at rt for 2 h and diluted with H_2O. The resulting mixture was extracted with hexane twice. The combined extracts were dried over $MgSO_4$ and concentrated to afford acetylene (*R*)-**122**, which was dissolved in CCl_4 (1 mL), MeCN (1 mL) and H_2O (0.5 mL). To the solution were added $NaIO_4$ (63 mg, 0.295 mmol) and $RuCl_3 \cdot nH_2O$ (ca. 1 mg). The mixture was stirred at rt for 1 h and filtered through a pad of Celite. The filtrate was concentrated to leave an oil, which was purified by chromatography on silica gel to afford acid (*R*)-**5** (21 mg, 89% from (*R*)-**40**): R_f 0.13 (hexane/EtOAc 4:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.12 (d, J = 6.9 Hz, 3 H), 3.31 (dq, J = 11.7, 6.6 Hz, 1 H), 4.05 (d, J = 11.7 Hz, 1 H), 7.10–7.33 (m, 10 H), ca. 8–11 (br s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.2 (+), 44.3 (+), 54.7 (+), 126.6 (+), 126.7 (+), 127.6 (+), 128.2 (+), 128.6 (+), 128.8 (+), 142.1 (–), 142.9 (–), 181.6 (–). These ^{1}H NMR and ^{13}C–APT NMR spectra were consistent with the spectra (400 MHz and 100 MHz, respectively) of the same acid obtained from (*S*)-**4**. Comparison of specific rotations: $[\alpha]_D^{22}$ +58 (*c* 0.42, $CHCl_3$) for (*R*)-**5** from (*R*)-**40**; $[\alpha]_D^{21}$ +57 (*c* 1.25, $CHCl_3$) for (*R*)-**5** from (*S*)-**4** (vide supra); $[\alpha]_D^{26.5}$ –52.6 ±1.7 (*c* 1.578, $CHCl_3$) for the (*S*)-isomer in lit.,[S12] confirming the (*R*)-configuration of (*R*)-**5**. HPLC analysis of (*R*)-**5**: >98% ee (Chiralcel AS-H; hexane/*i*-PrOH = 99/1, 1 mL/min, 40 °C): t_R (min) = 14.1 (minor (*S*)-isomer), 15.2 (major (*R*)-isomer)).

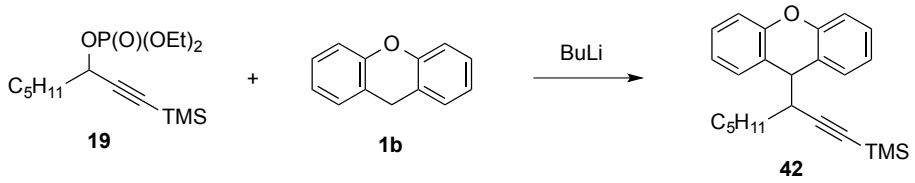
(*R*)-(3-Benzhydryloct-1-yn-1-yl)trimethylsilane ((*R*)-41)



According to GP2 using phosphate (*R*)-**19** (93% ee, 46 mg, 0.138 mmol) in THF (1 mL), **1a** (74 mg, 0.44 mmol) and BuLi (1.60 M in hexane, 0.26 mL, 0.416 mmol) in THF (1 mL) at –15 °C for 15 min afforded (*R*)-**41** (37 mg, 77% yield, >99% rs by ^{1}H NMR): 92% ee as determined by HPLC analysis (Chiralcel OD-H, hexane/*i*-PrOH = 99.9/0.1, 0.5 mL/min, 35 °C, t_R (min) = 11.8 (minor (*S*)-isomer), 12.1 (major (*R*)-isomer)); $[\alpha]_D^{21}$ +16 (*c* 0.71, $CHCl_3$); R_f 0.73 (hexane/EtOAc 3:1); IR (neat) 2169, 1496, 1451, 1249, 842, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.01 (s, 9 H), 0.85 (t, J = 7.2 Hz, 3 H), 1.12–1.31 (m, 4 H), 1.31–1.47 (m, 3 H), 1.48–1.63 (m, 1 H),

3.16 (ddd, J = 8.6, 8.6, 4.0 Hz, 1 H), 3.91 (d, J = 8.6 Hz, 1 H), 7.13–7.20 (m, 2 H), 7.21–7.38 (m, 8 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.0 (+), 14.1 (+), 22.6 (–), 27.0 (–), 31.6 (–), 33.3 (–), 37.8 (+), 55.9 (+), 88.2 (–), 109.4 (–), 126.3 (+), 126.4 (+), 128.0 (+), 128.3 (+), 128.5 (+), 129.0 (+), 143.1 (–), 143.2 (–); HRMS (EI): m/z calcd for $C_{24}H_{32}Si$ (M^+) 348.2273, found 348.2274.

(3-(9*H*-Xanthen-9-yl)oct-1-yn-1-yl)trimethylsilane (42)



According to GP2 using phosphate **19** (47 mg, 0.141 mmol) in THF (1 mL), xanthene (**1b**) (82 mg, 0.45 mmol) and BuLi (1.60 M in hexane, 0.26 mL, 0.416 mmol) in THF (1 mL) at –15 °C for 15 min afforded **42** (44 mg, 87% yield, >99% rs by ^{1}H NMR): R_f 0.83 (hexane/EtOAc 2:1); IR (neat) 2169, 1479, 1458, 1255, 842, 754 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.14 (s, 9 H), 0.80 (t, J = 6.8 Hz, 3 H), 1.04–1.30 (m, 7 H), 1.38–1.48 (m, 1 H), 2.57–2.68 (m, 1 H), 4.15 (d, J = 3.6 Hz, 1 H), 7.02–7.11 (m, 4 H), 7.20–7.28 (m, 3 H), 7.44 (d, J = 7.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.0 (+), 14.1 (+), 22.6 (–), 27.2 (–), 29.7 (–), 31.5 (–), 43.0 (+), 43.3 (+), 88.0 (–), 108.4 (–), 116.1 (+), 116.3 (+), 122.5 (–), 122.7 (+), 123.0 (+), 123.2 (–), 128.0 (+), 129.2 (+), 129.8 (+), 152.9 (–), 153.0 (–); HRMS (EI): m/z calcd for $C_{24}H_{30}OSi$ (M^+) 362.2066, found 362.2060.

Part 2: References

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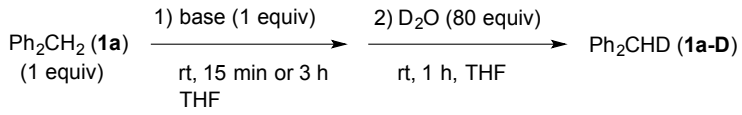
Part 3: D-Incorporation Experiments of Ph_2CH_2 (1a) (Table S1)

Table S1. D-Incorporation Experiments of Reactant 1a[a]



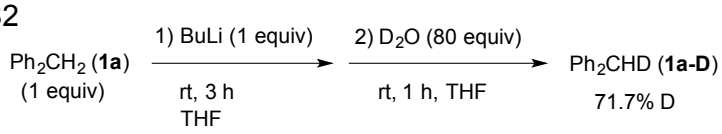
entry	base (equiv)	reaction time	D-incorporation (%)[b]
S1	BuLi (1)	15 min	70.2
S2	BuLi (1)	3 h	71.7
S3	BuLi (3)	15 min	84.2
S4	LDA (1)	15 min	72.5
S5	LDA (1)	3 h	71.9
S6	LiHMDS (1)	15 min	0%
S7	LiHMDS (1)	3 h	0%
S8	NaHMDS (1)	15 min	0%
S9	NaHMDS (1)	3 h	0%
S10	KHMDS (1)	15 min	0%
S11	KHMDS (1)	3 h	0%
S12	NaH (1)	15 min	0%

[a]Reactant **1a** was exposed to given bases in THF at rt for 15 min or 3 h and excess D_2O was added to the solution (see below for further details). [b]Calculated as described in the next page.

An Entry using BuLi (Table S1, entry S2): To a solution **1a** (35 mg, 0.208 mmol) in THF (0.5 mL) was added BuLi (1.60 M in hexane, 0.13 mL, 0.208 mmol) at rt. The resulting dark red solution was stirred at rt for 3 h, and D_2O (0.30 mL from a freshly opened ampule, 99.96% D, 16.6 mmol, 80 equiv) was added to the solution, which turned to colorless immediately. After 1 h of stirring at rt, the product was extracted with EtOAc. The extract was dried over $MgSO_4$ and concentrated to afford **1a-D** (34 mg, 97% yield). D-incorporation was 71.7% by ^1H NMR spectroscopy.

Other Entries using given Bases: D-incorporation was carried out at rt for 15 min or 3 h according to the method mentioned above using a base (1 equiv). In entry S3, three equiv of BuLi was used to generate the anion **1a**/BuLi.

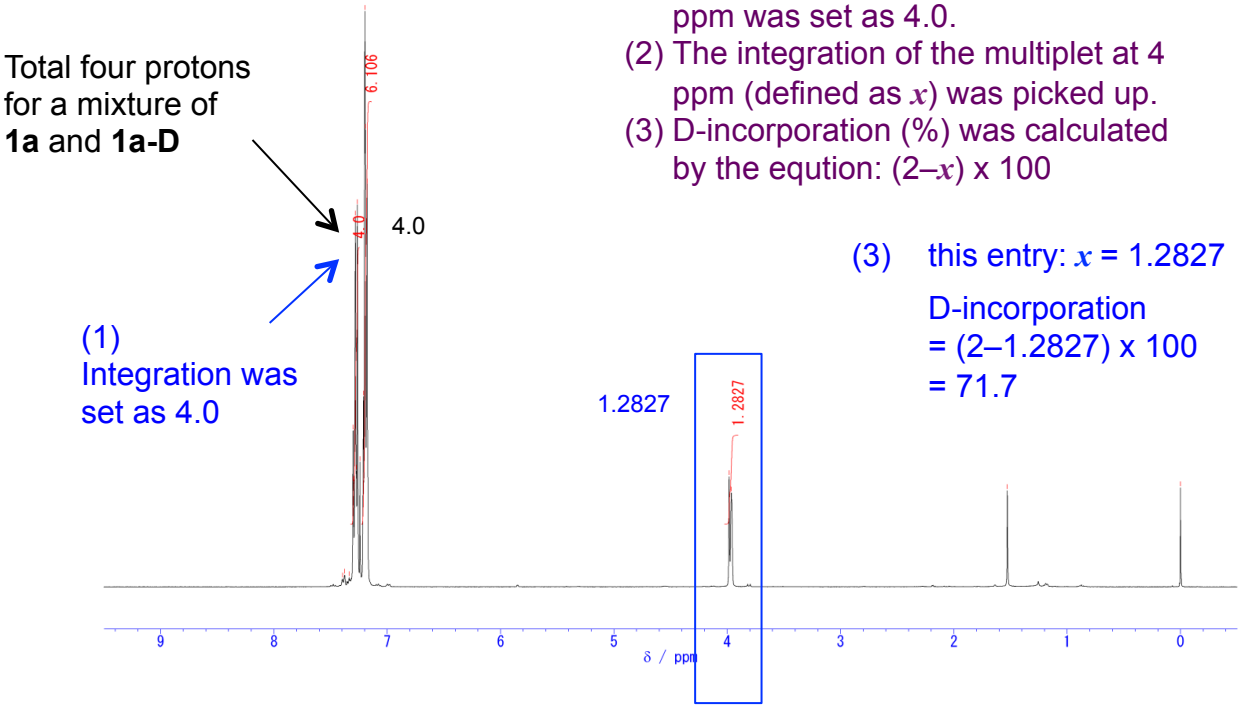
Table S1, entry S2

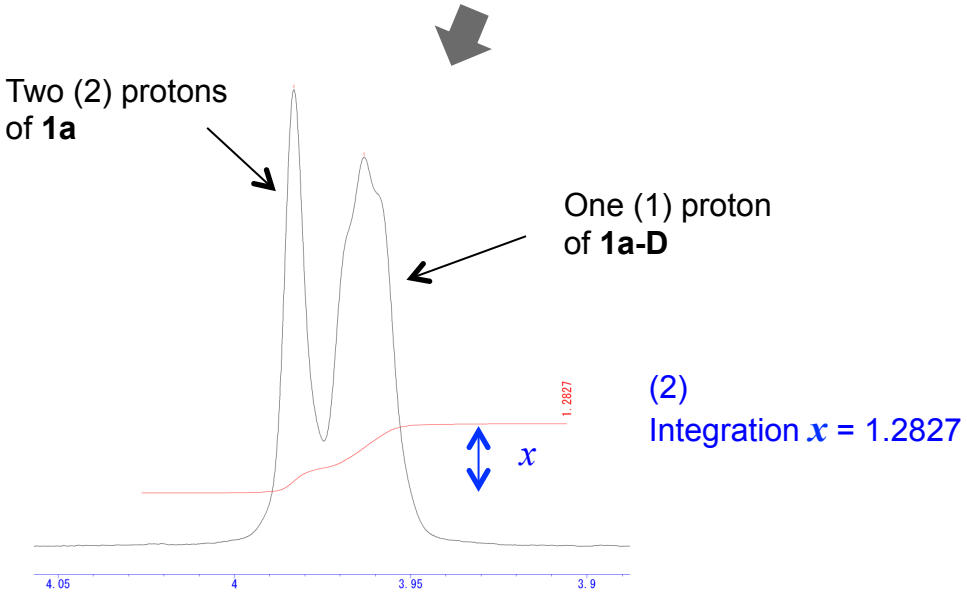


Calculation of D-incorporation (%)

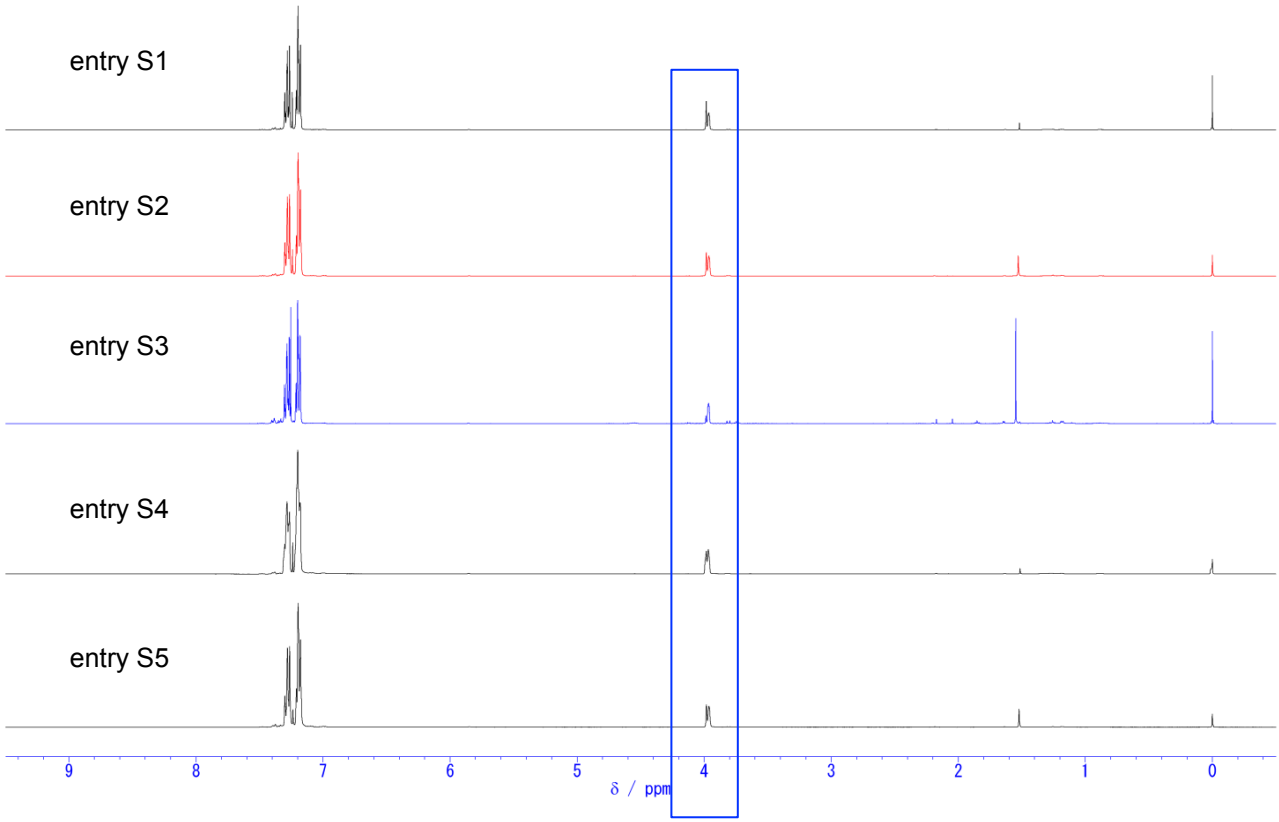
(1) Integration of the multiplet at 7.3 ppm was set as 4.0.
(2) The integration of the multiplet at 4 ppm (defined as x) was picked up.
(3) D-incorporation (%) was calculated by the eqution: (2–x) x 100

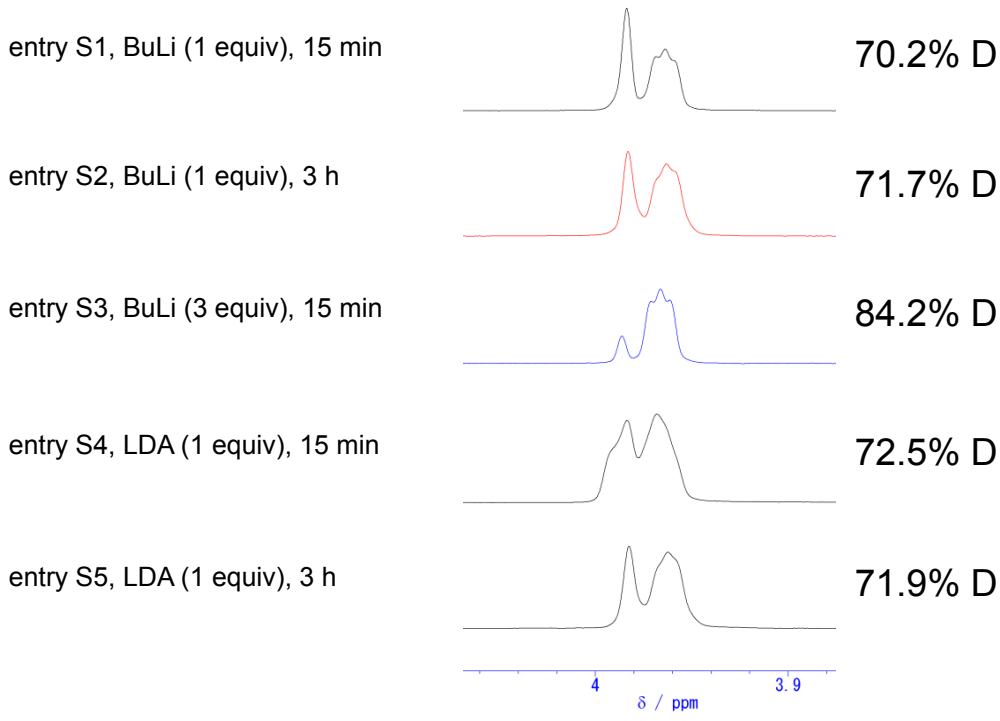
^{1}H NMR (400 MHz, $CDCl_3$)





^{1}H NMR (400 MHz, $CDCl_3$)





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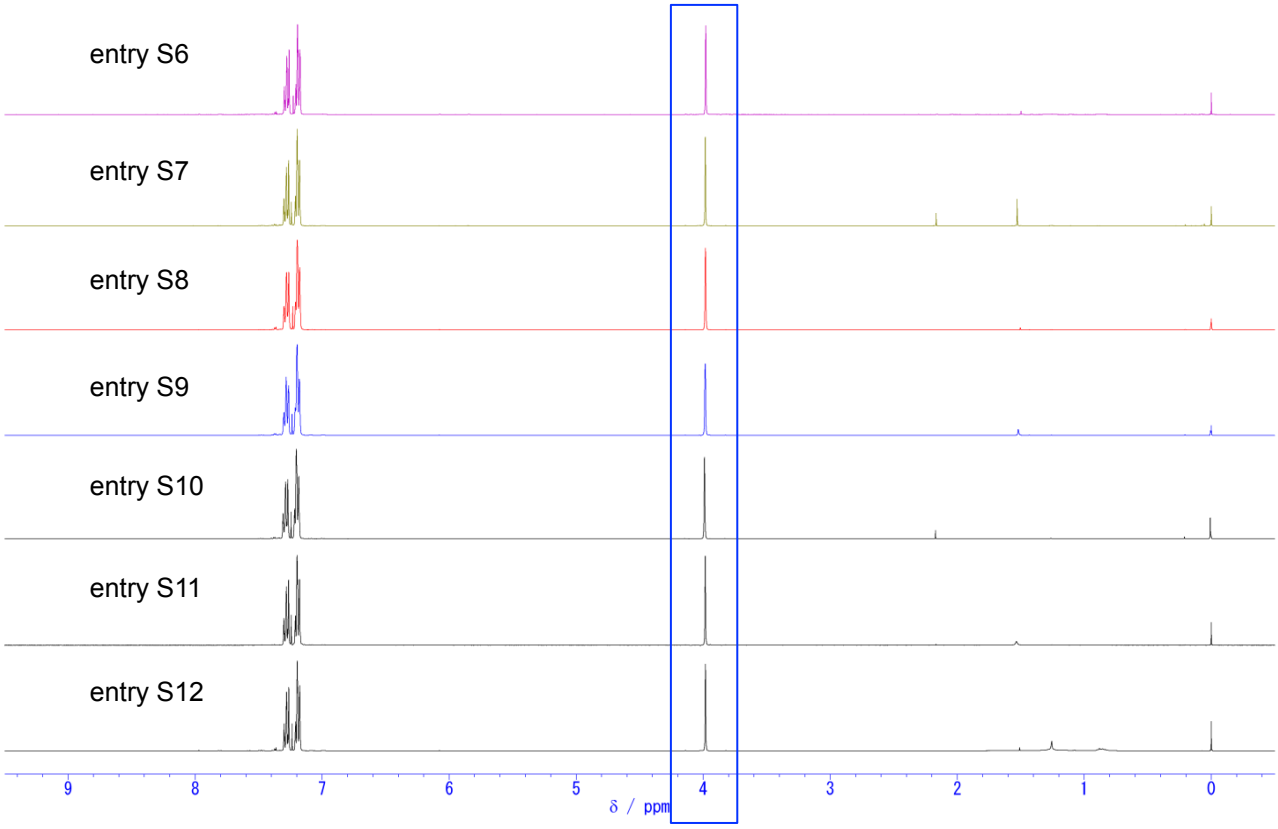
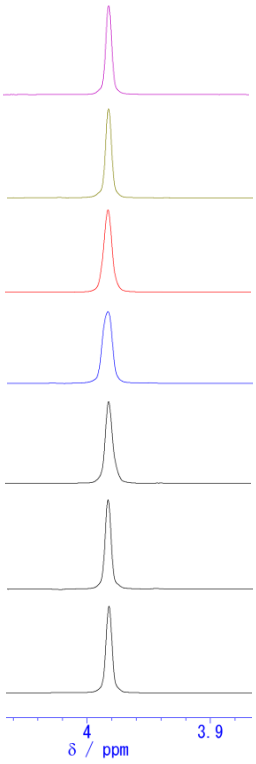
^{1}H NMR (400 MHz, $CDCl_3$)





entry S6, LiHMDS (1 equiv), 15 min — 0% D

entry S7, LiHMDS (1 equiv), 3 h — 0% D

entry S8, NaHMDS (1 equiv), 15 min — 0% D

entry S9, NaHMDS (1 equiv), 3 h — 0% D

entry S10, KHMDS (1 equiv), 15 min — 0% D

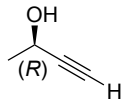
entry S11, KHMDS (1 equiv), 3 h — 0% D

entry S12, NaH (1 equiv), 15 min — 0% D

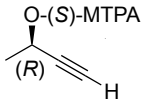
Part 4: Determination of Enantiomeric, Diastereomeric, Regioisomeric Ratios

Determination of the enantiomeric purity of (*R*)-**117** by ^{1}H NMR

(This alcohol (*R*)-**117** was used for the synthesis of (*R*)-**2**, (*R*)-**3**, and (*R*)-**18**)

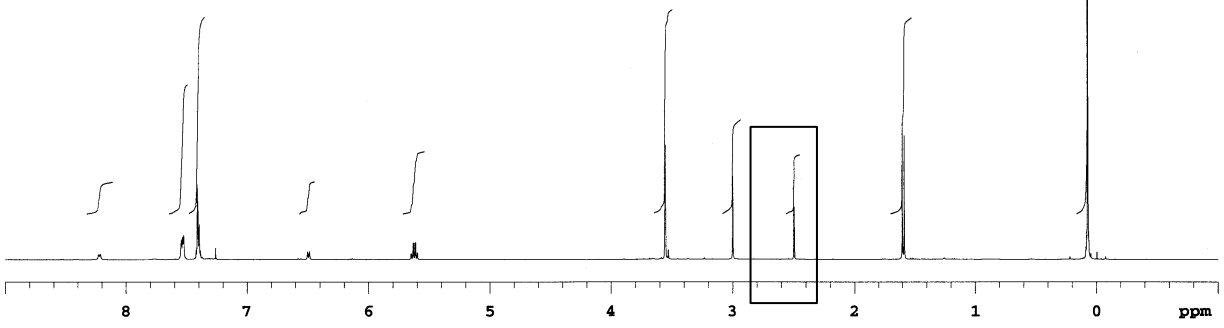


(*R*)-**117**

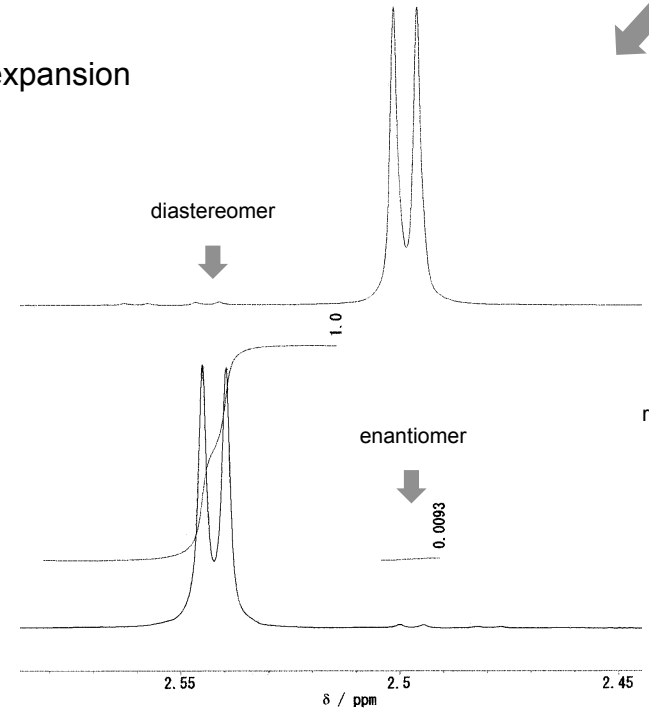


(*S*)-MTPA ester of (*R*)-**117**

^{1}H NMR (400 MHz, $CDCl_3$)

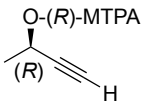


expansion



major : minor = 1.0 : 0.0093

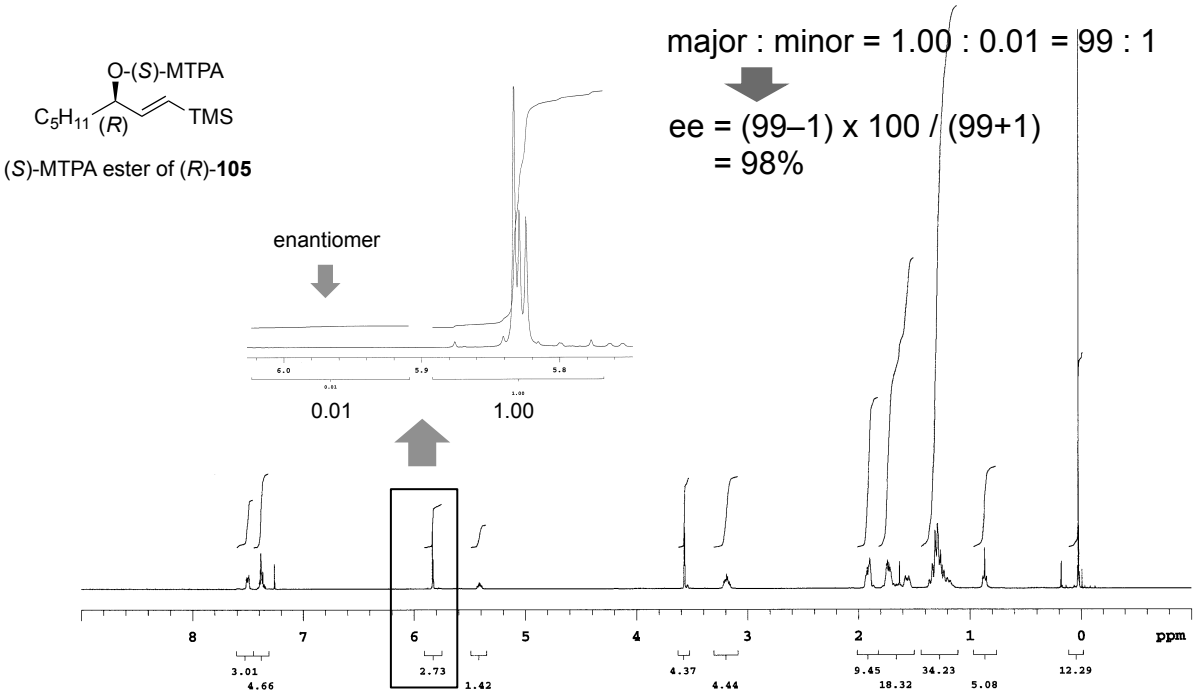
ee = (1.0–0.0093) x 100 / (1.0+0.0093)
= 98.2%

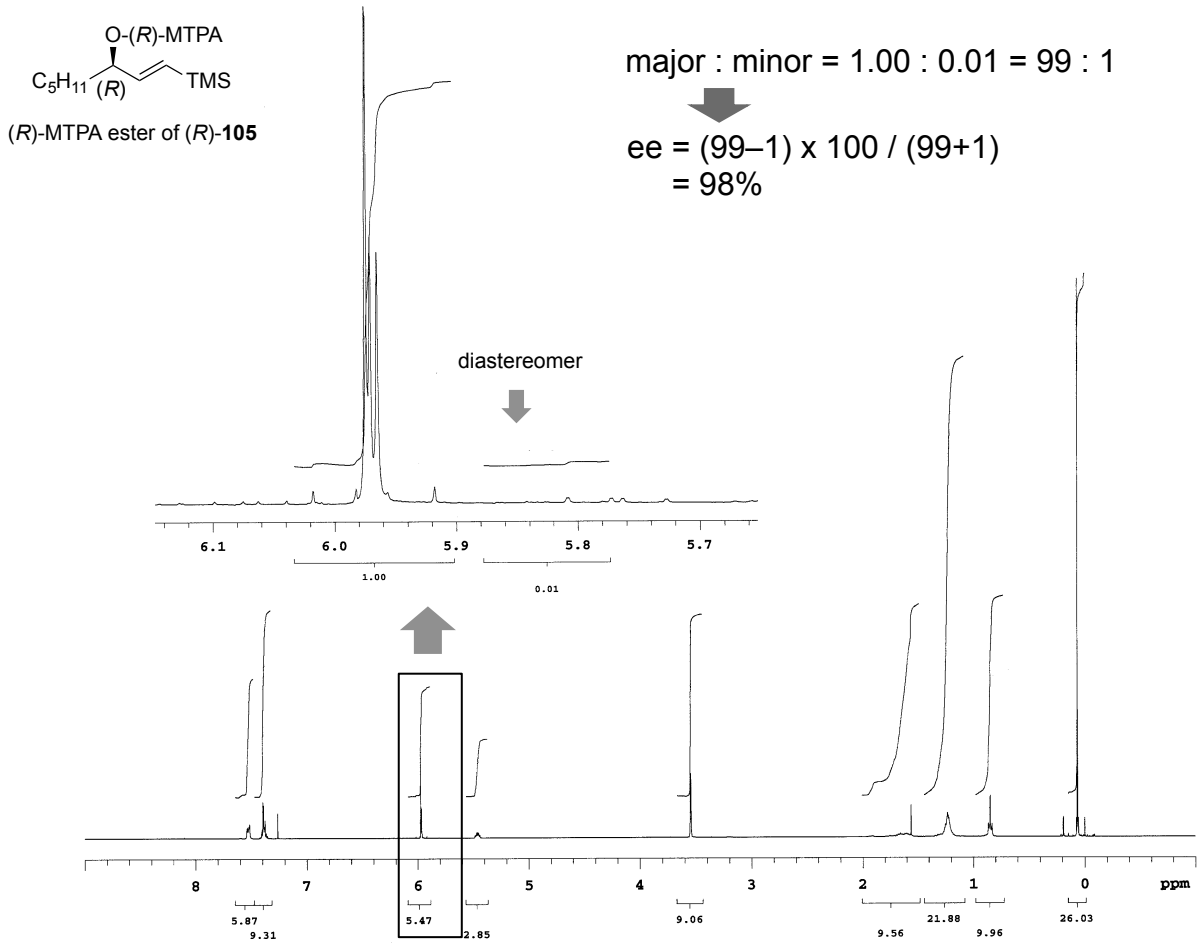


(*R*)-MTPA ester of (*R*)-**117**

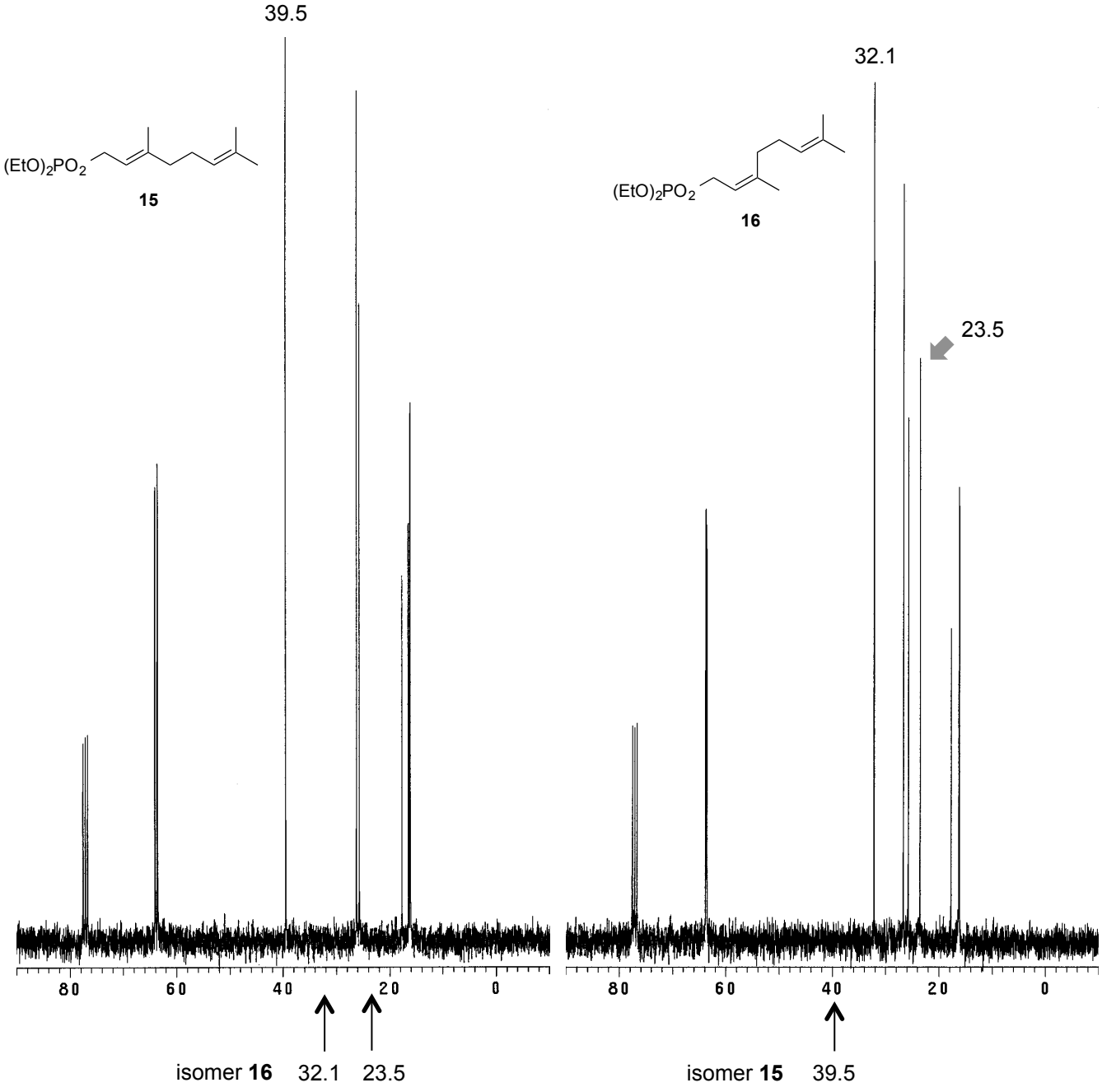
^{1}H NMR (400 MHz, $CDCl_3$)

Determination of the enantiomeric purity of (*R*)-**105** by ^{1}H NMR (400 MHz, $CDCl_3$)





Determination of the olefinic purity of **15** and **16**, respectively, by ^{13}C NMR (75 MHz, $CDCl_3$)
(The full specta of **15** and **16** are attached to part 5 of the supporting info.)

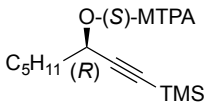


15 : **16** by height ratio of signal (39.5 ppm) and noise
= 17.3 : 0.4 (cm)
= 97.7 : 2.3 = >97 : 3

16 : **15** by height ratio of signal (39.5 ppm) and noise
= 16.3 : 0.4 (cm)
= 97.6 : 2.4 = >97 : 3

Determination of the enantiomeric purity of (*R*)-**119** by ^{1}H NMR (400 MHz, $CDCl_3$)

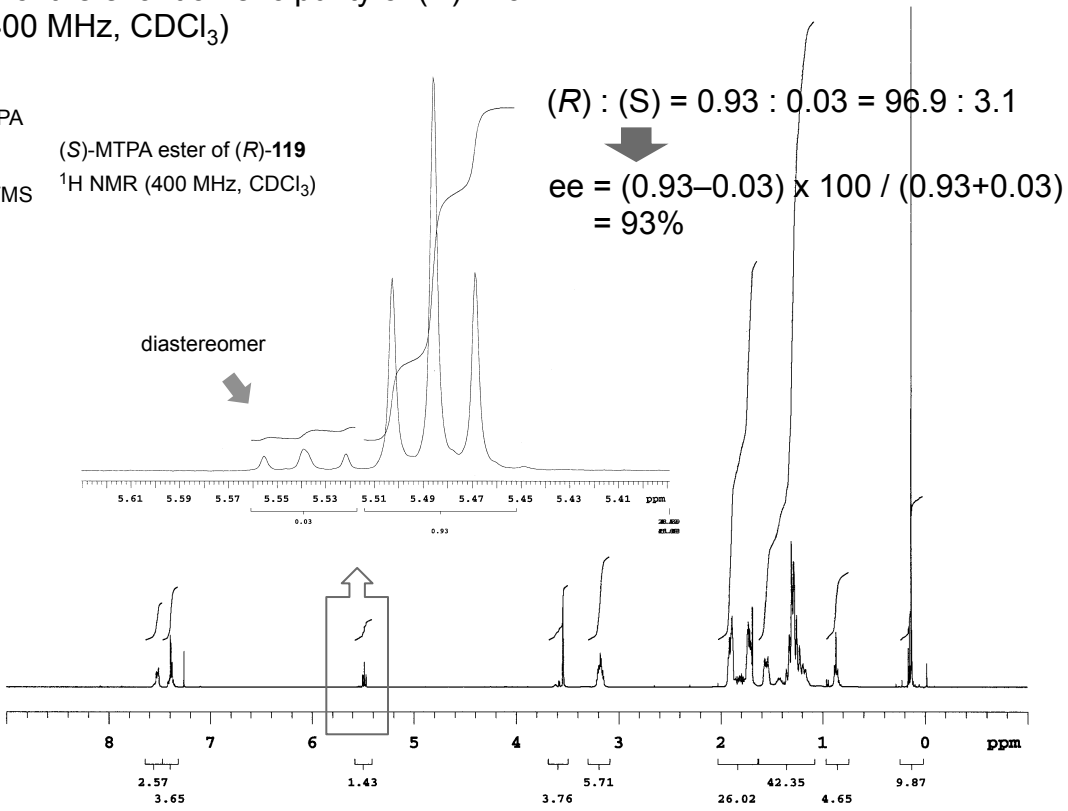
ratio calculated using two sets of the signals

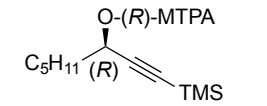


(*S*)-MTPA ester of (*R*)-**119**
^{1}H NMR (400 MHz, $CDCl_3$)

(*R*) : (S) = 0.93 : 0.03 = 96.9 : 3.1

ee = (0.93–0.03) x 100 / (0.93+0.03)
= 93%

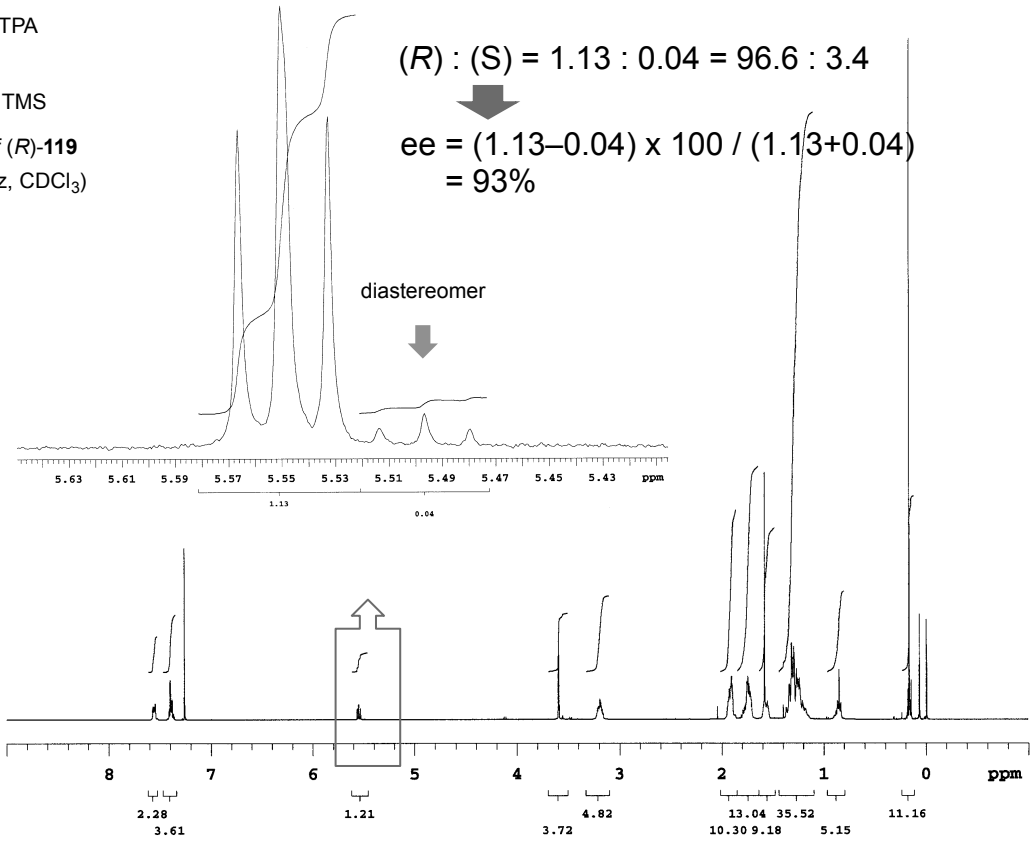




(*R*)-MTPA ester of (*R*)-**119**
^{1}H NMR (400 MHz, $CDCl_3$)

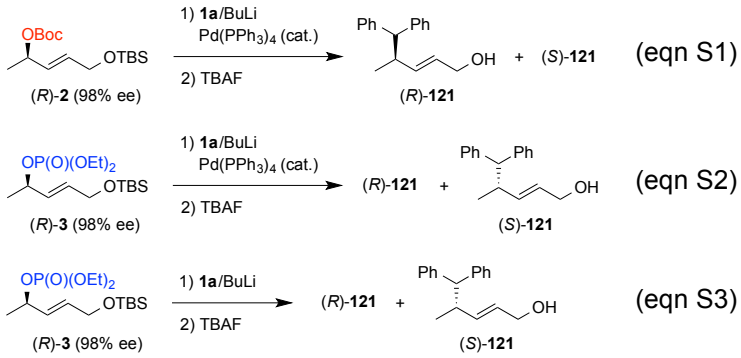
(*R*) : (S) = 1.13 : 0.04 = 96.6 : 3.4

ee = (1.13–0.04) x 100 / (1.13+0.04)
= 93%



Determination of the enantiomeric purity of the products obtained by Scheme 1 in the text and eqns S1–S3 below by chiral HPLC

conditions: Chiralcel AS-H, hexane/*i*-PrOH = 99/1, 0.5 mL/min, 33 °C



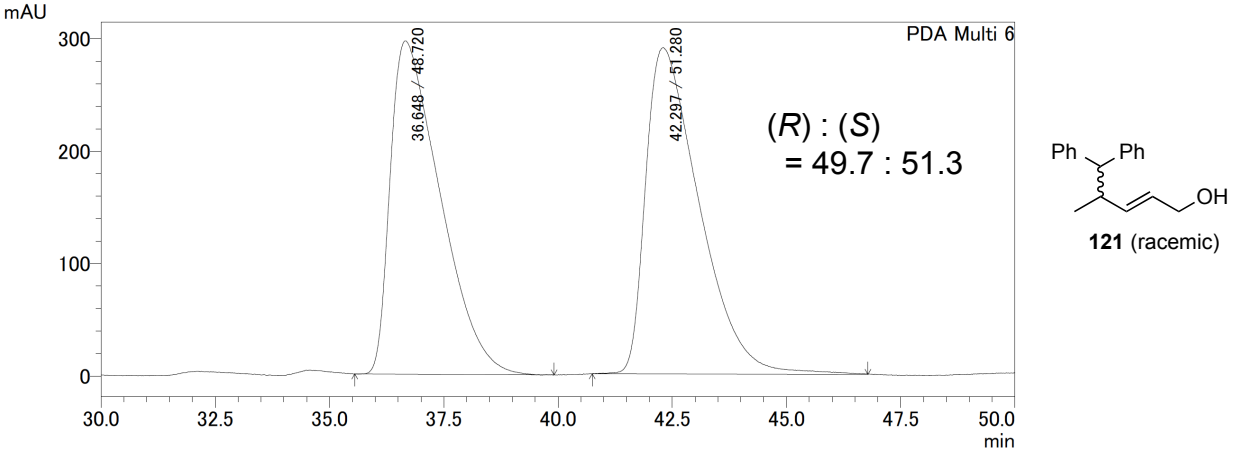


Figure S1. Racemic alcohol **121**

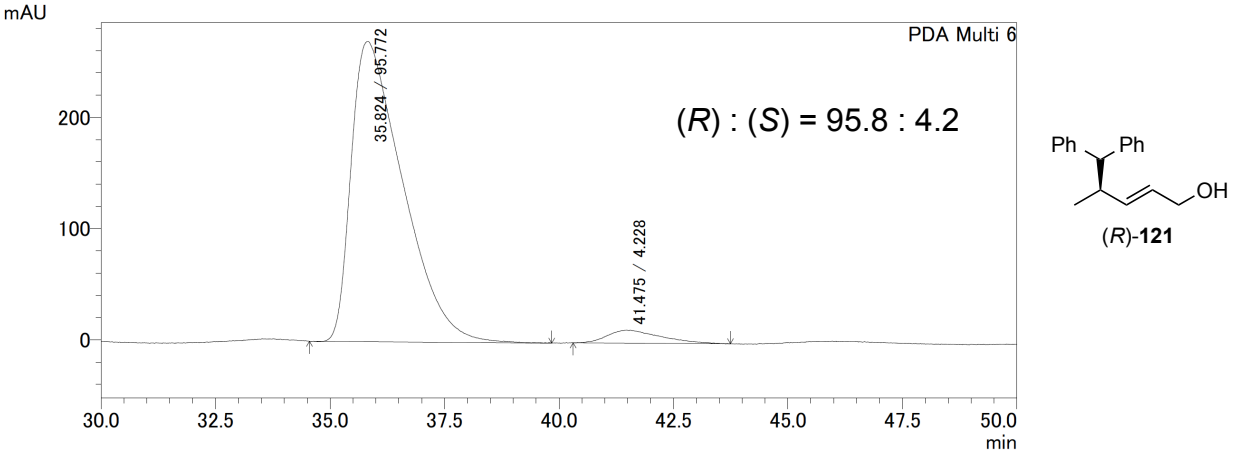


Figure S2. The product of eq S1

continued to the next page

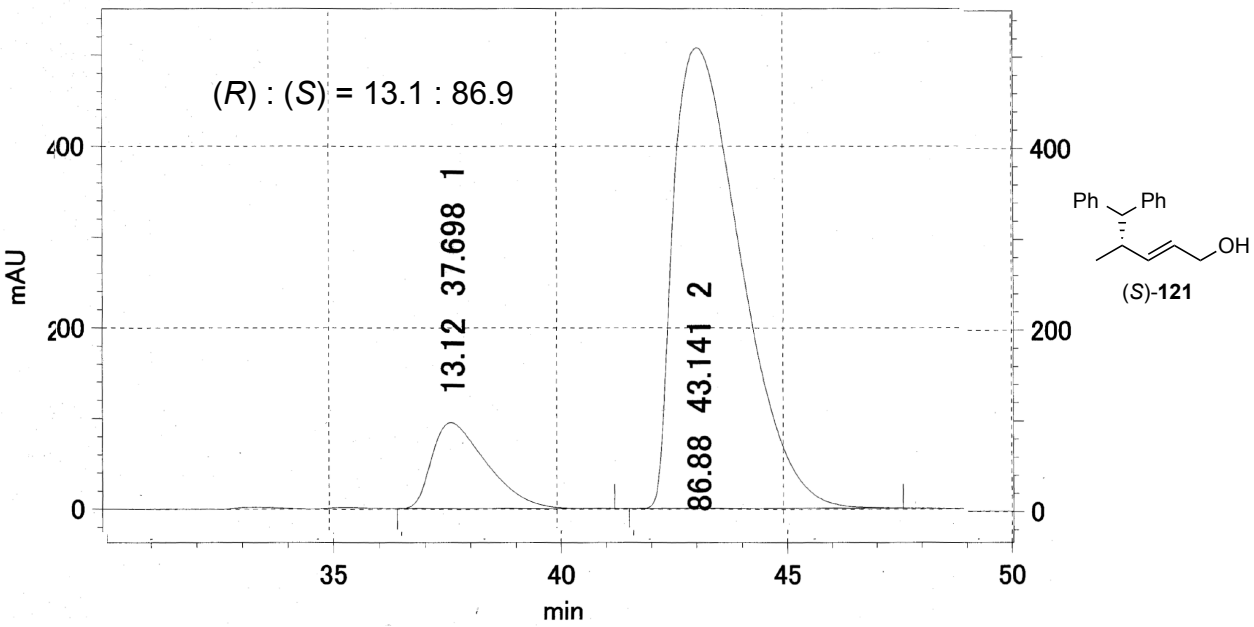


Figure S3. The product of eq S2

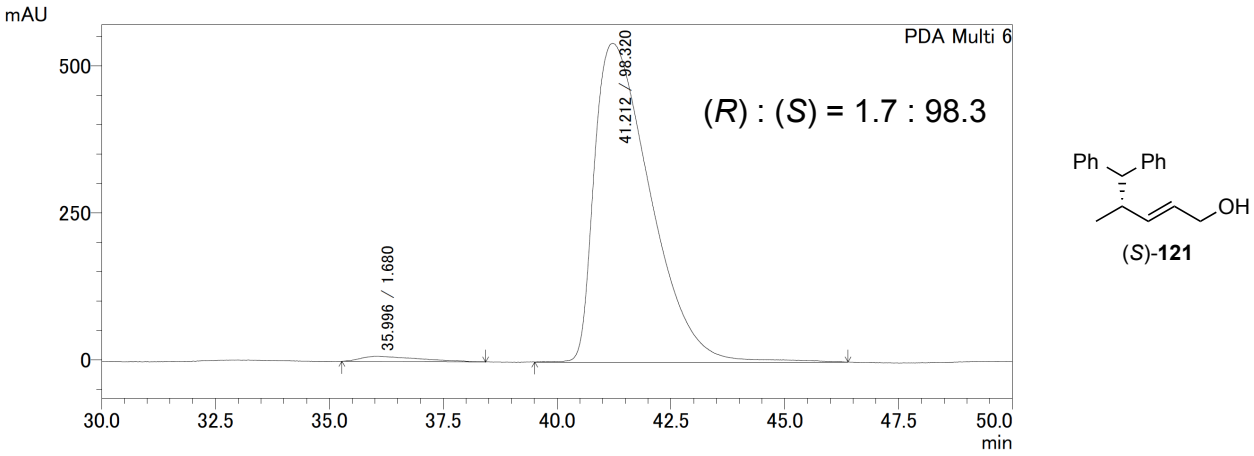
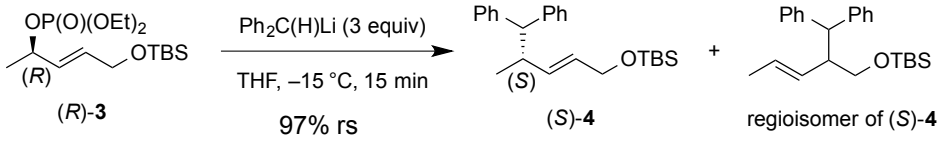
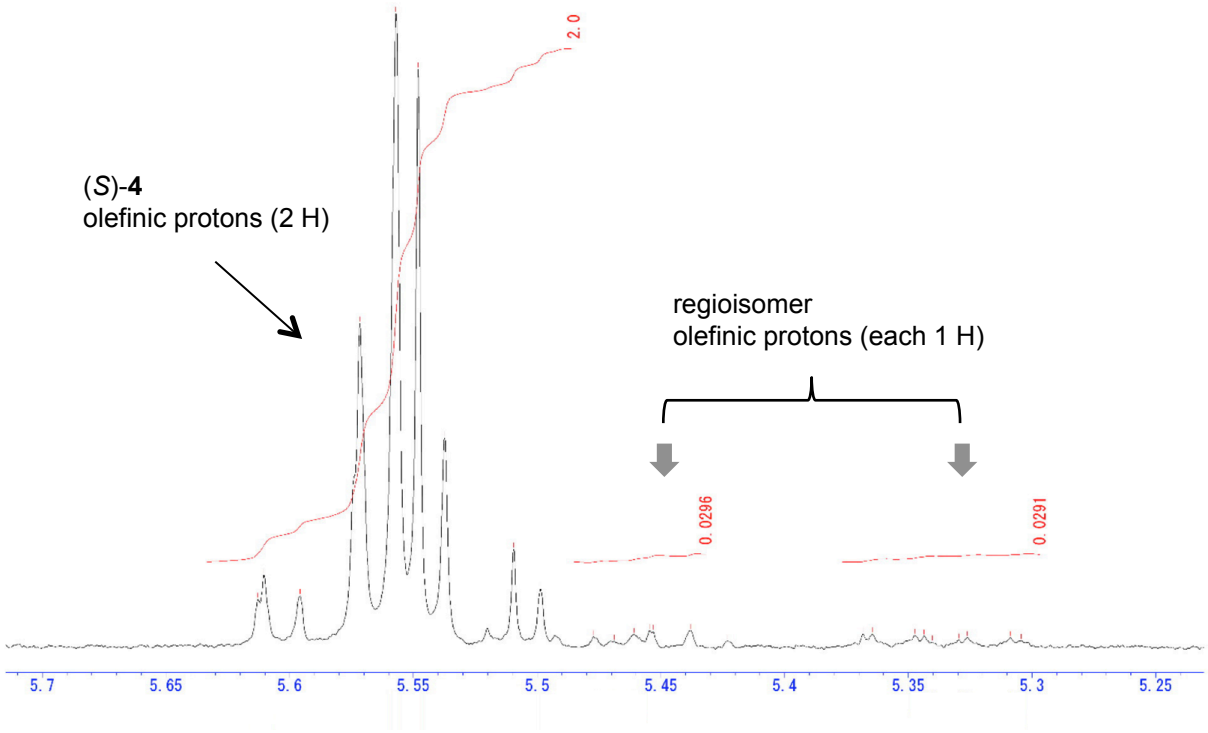


Figure S4. The product of eq S3

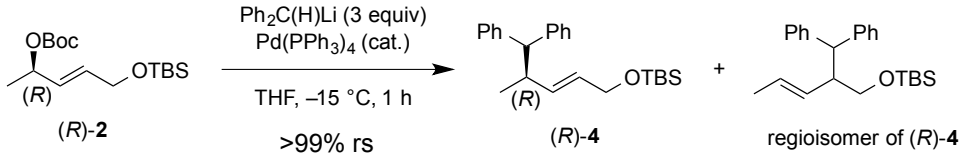
Determination of the ratio of (*S*)-**4** and the regioisomer by ^{1}H NMR (400 MHz, $CDCl_3$)
(The full spectrum of (*S*)-**4** is attached to part 5 of this ESI)



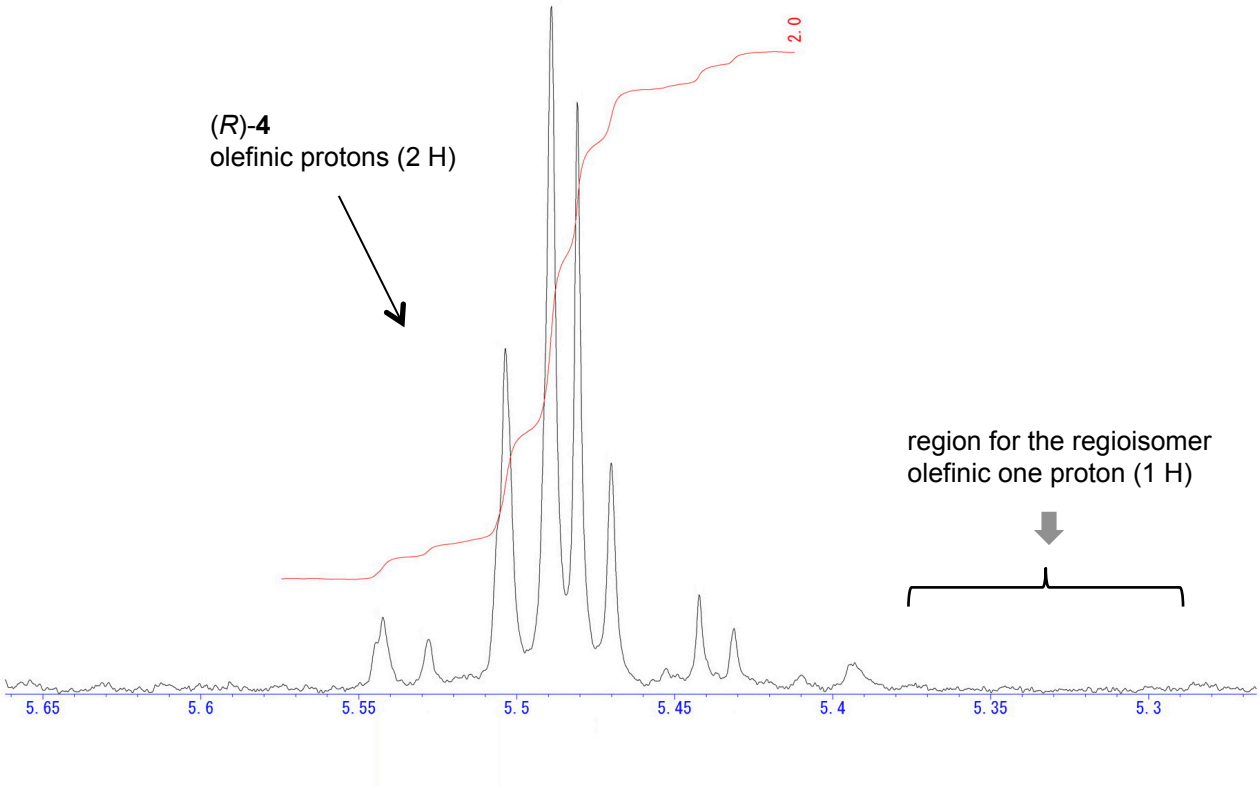
(*S*)-**4** : regioisomer = 2.0/2 : (0.0291 + 0.0296/2)
= 97 : 3



Determination of the ratio of (*R*)-**4** and the regioisomer by ^{1}H NMR (400 MHz, $CDCl_3$)
(The full spectrum of (*R*)-**4** is attached to part 5 of this ESI)



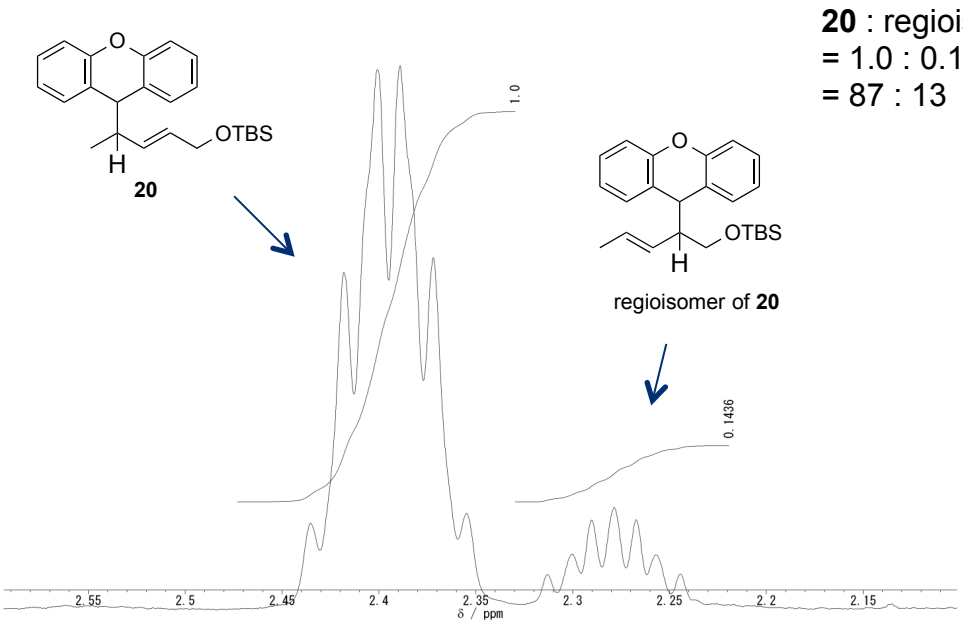
(*R*)-**4** : regioisomer = >99 : 1



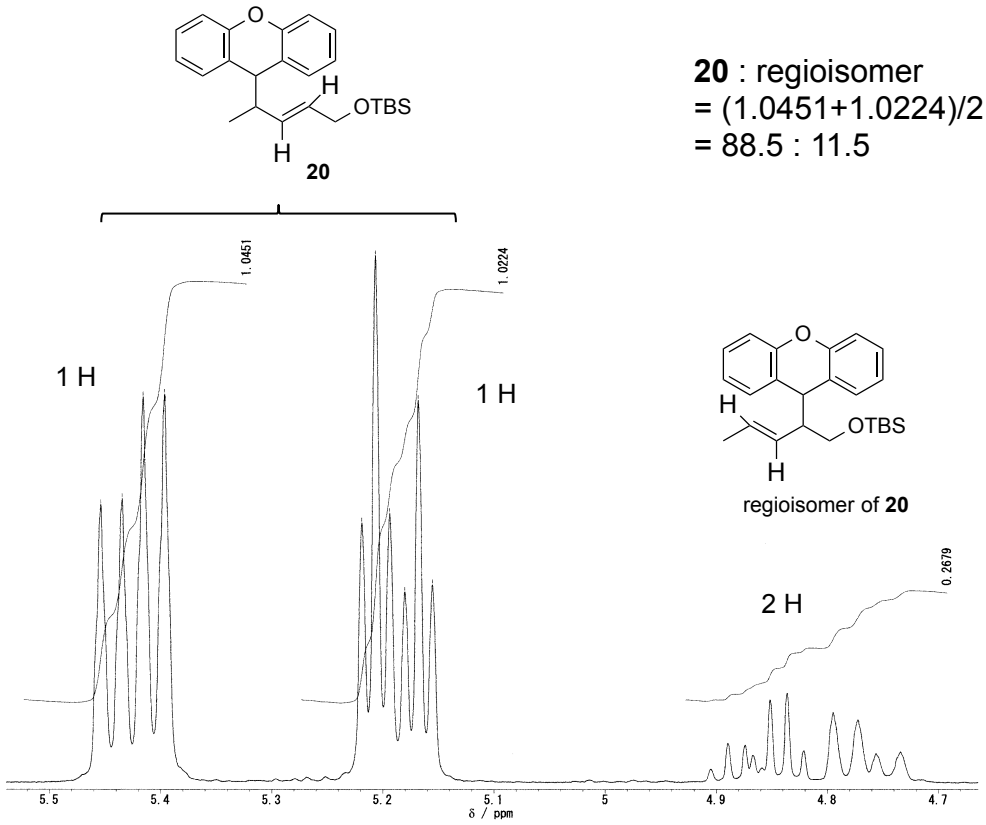
^{1}H NMR (400 MHz, $CDCl_3$)

Determination of the ratio of **20** and the regioisomer by ^{1}H NMR (400 MHz, $CDCl_3$)
(The full spectrum of **20** is attached to part 5 of this ESI)

ratio calculated using two sets of the signals



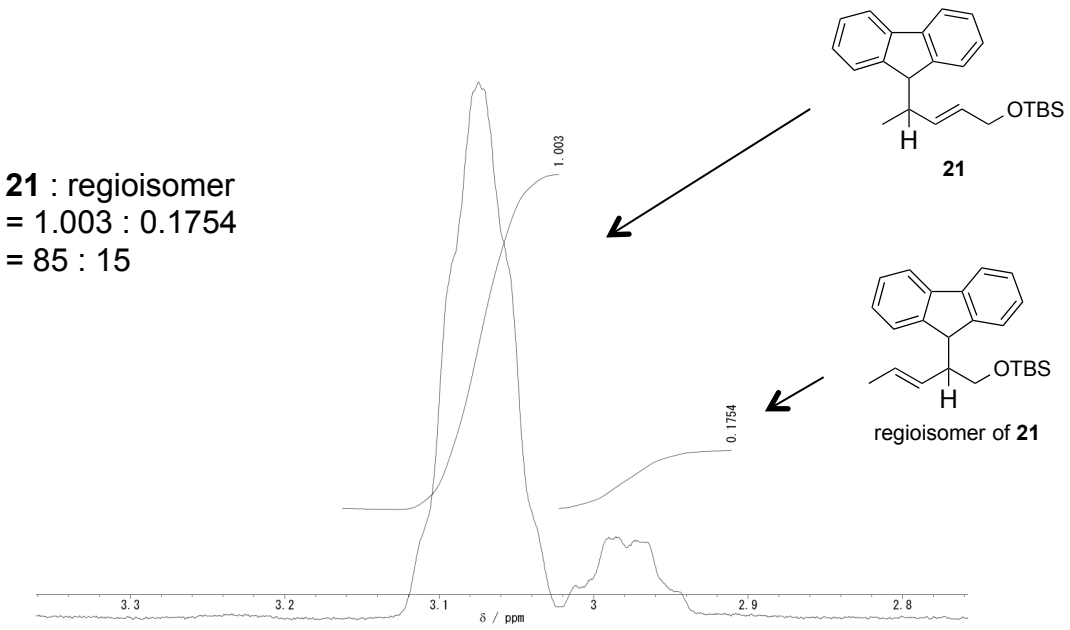
20 : regioisomer
= 1.0 : 0.1436
= 87 : 13



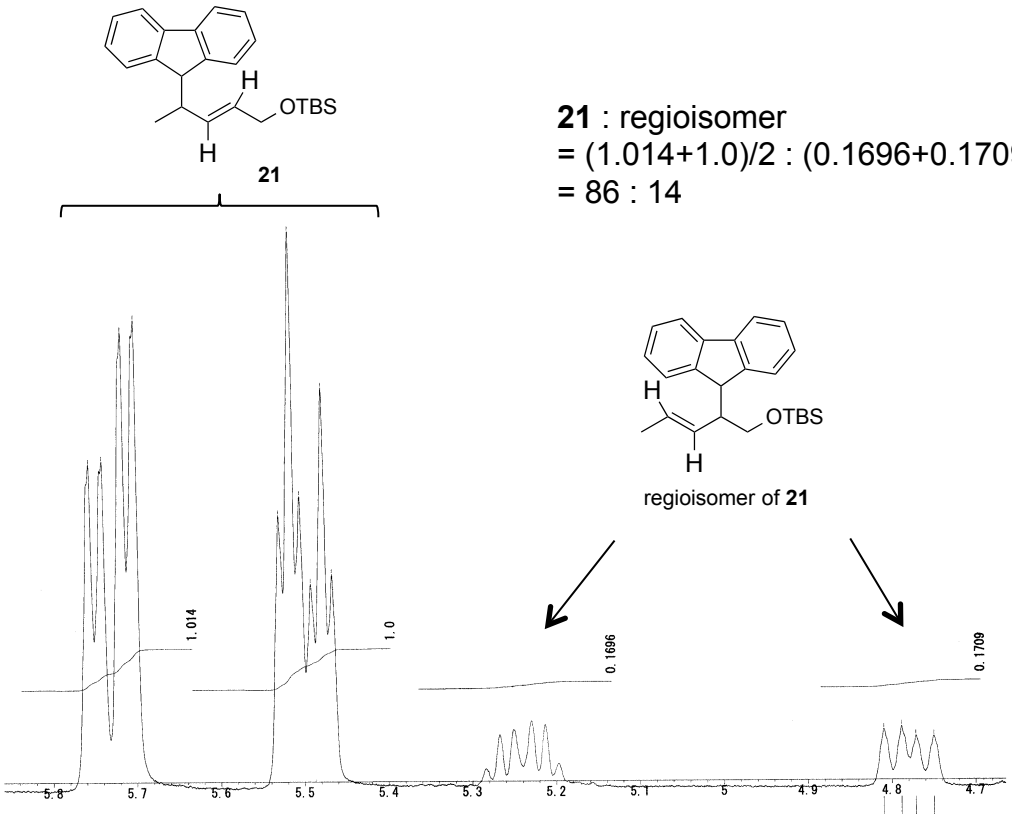
20 : regioisomer
= (1.0451+1.0224)/2 : 0.2679/2
= 88.5 : 11.5

Determination of the ratio of **21** and the regioisomer by ^{1}H NMR (400 MHz, $CDCl_3$)
(The full spectrum of **21** is attached to part 5 of this ESI)

ratio calculated using two sets of the signals



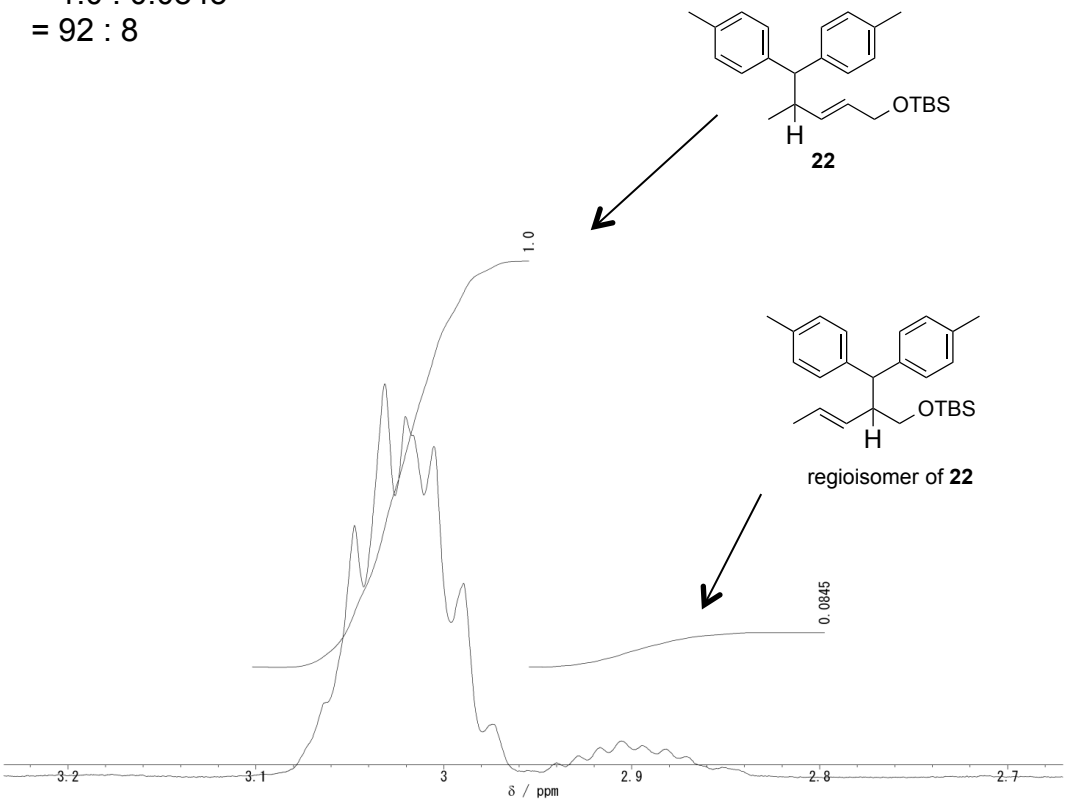
21 : regioisomer
= 1.003 : 0.1754
= 85 : 15



21 : regioisomer
= (1.014+1.0)/2 : (0.1696+0.1709)/2
= 86 : 14

Determination of the ratio of **22** and the regioisomer by ^{1}H NMR (400 MHz, $CDCl_3$)
(The full spectrum of **22** is attached to part 5 of this ESI)

22 : regioisomer
= 1.0 : 0.0845
= 92 : 8

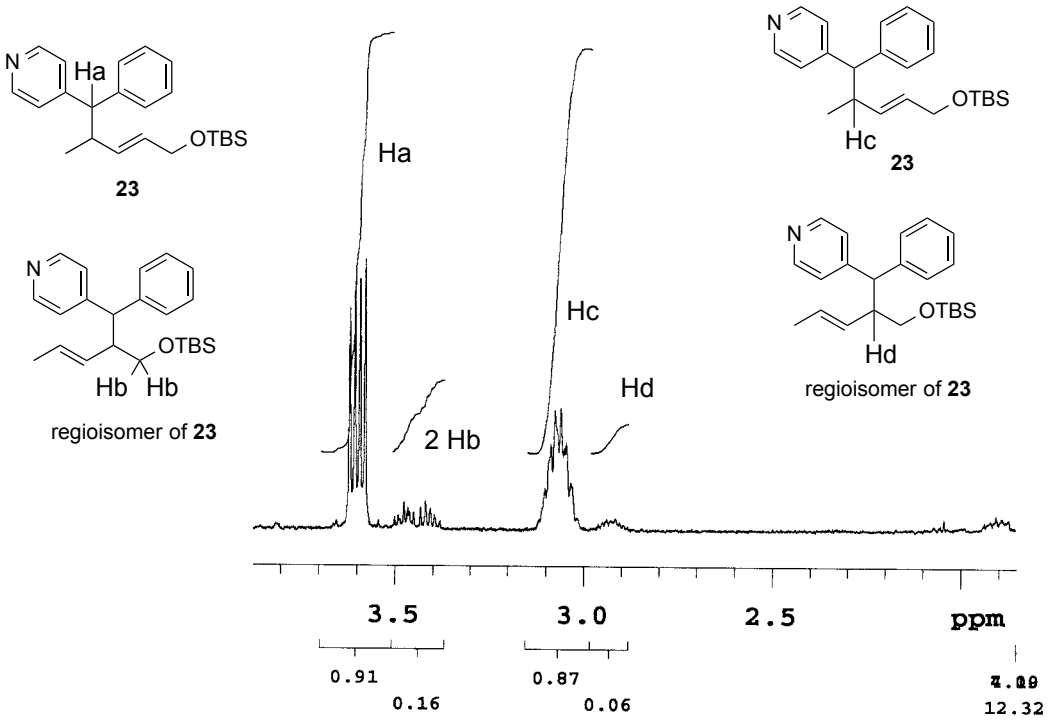


Determination of the ratio of **23** and the regioisomer by ^{1}H NMR (400 MHz, $CDCl_3$)
(The full spectrum of **23** is attached to part 5 of this ESI)

ratio calculated using two sets of the signals

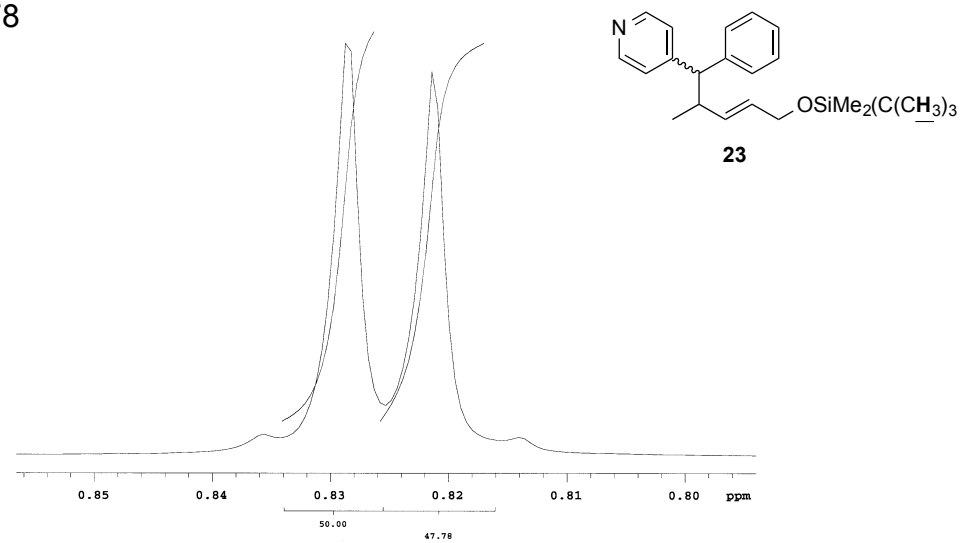
23 : regioisomer
= 0.91/1 : 0.16/2
= 92 : 8

23 : regioisomer
= 0.87 : 0.06
= 94 : 6

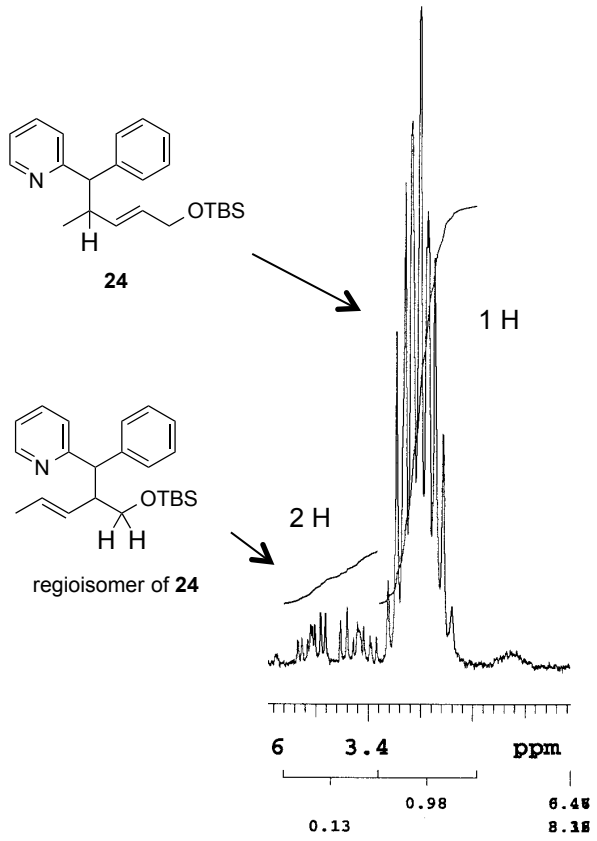


Determination of the diastereomeric ratio of **23**

= 50.00 : 47.78
= 51 : 49



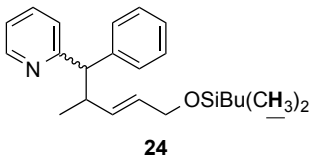
Determination of the ratio of **24** and the regioisomer by ^{1}H NMR (400 MHz, $CDCl_3$)
(The full spectrum of **24** is attached to part 5 of this ESI)



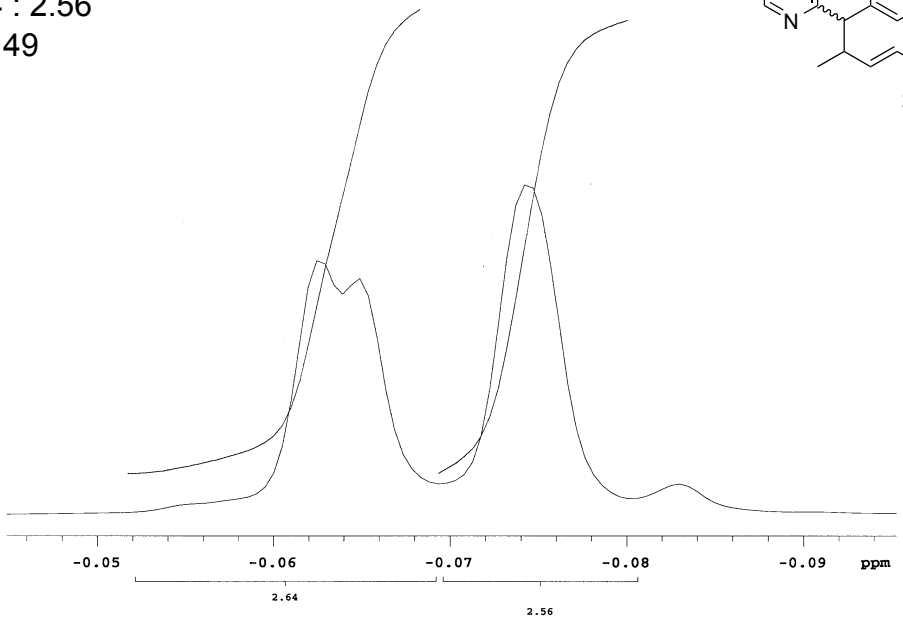
24 : regioisomer
= 0.99 : 0.13/2
= 94 : 6

Determination of the diastereomeric ratio of **24**

= 2.64 : 2.56
= 51 : 49

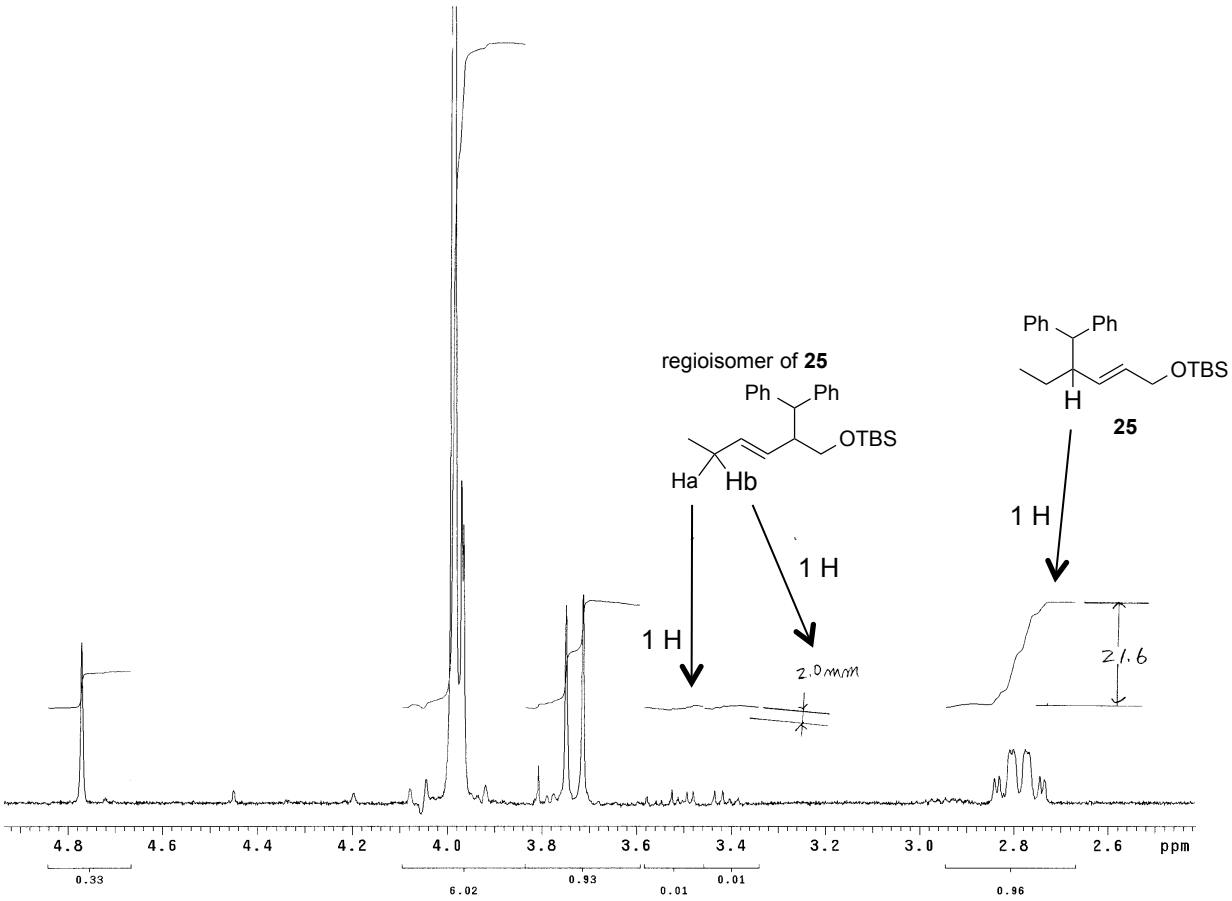


24

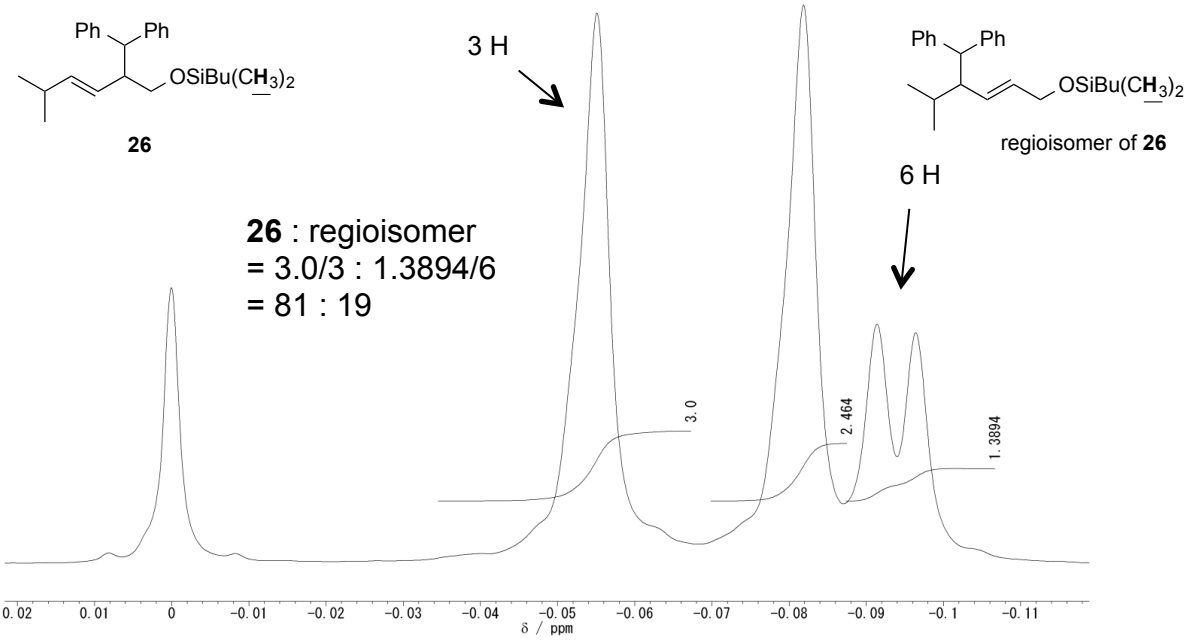


Determination of the ratio of **25** and the regioisomer by ^{1}H NMR (400 MHz, $CDCl_3$)
(The full spectrum of **25** is attached to part 5 of this ESI)

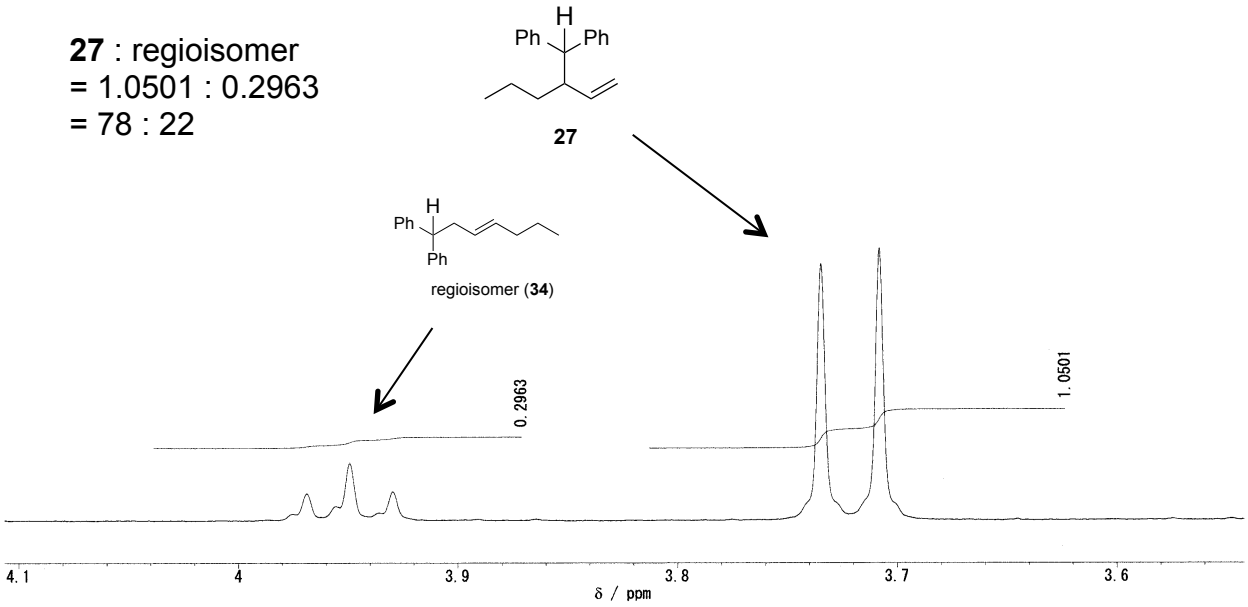
25 : regioisomer
= 21.6 : 2.0
= 91 : 9



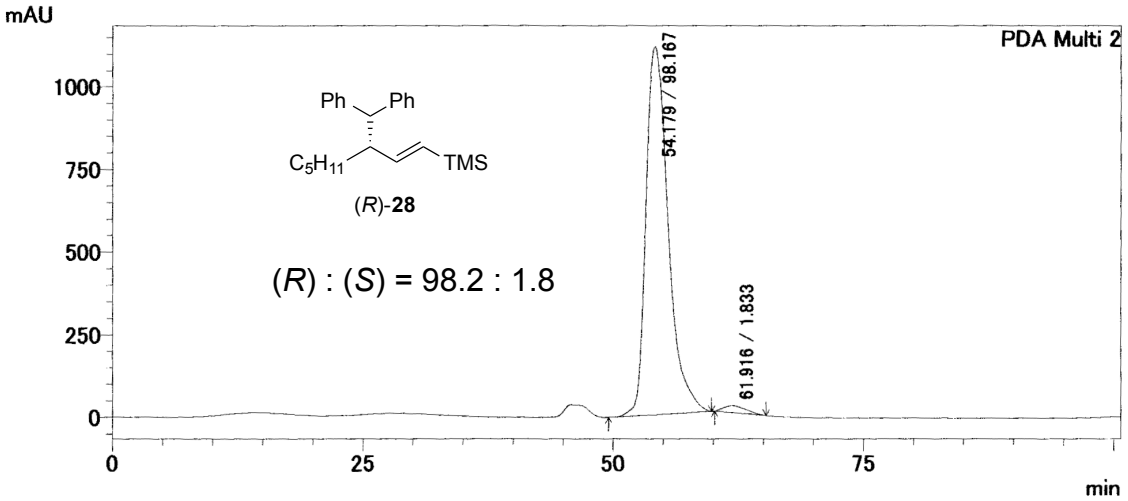
Determination of the ratio of **26** and the regioisomer by ^{1}H NMR (400 MHz, $CDCl_3$)
(The full spectrum of **26** is attached to part 5 of this ESI)

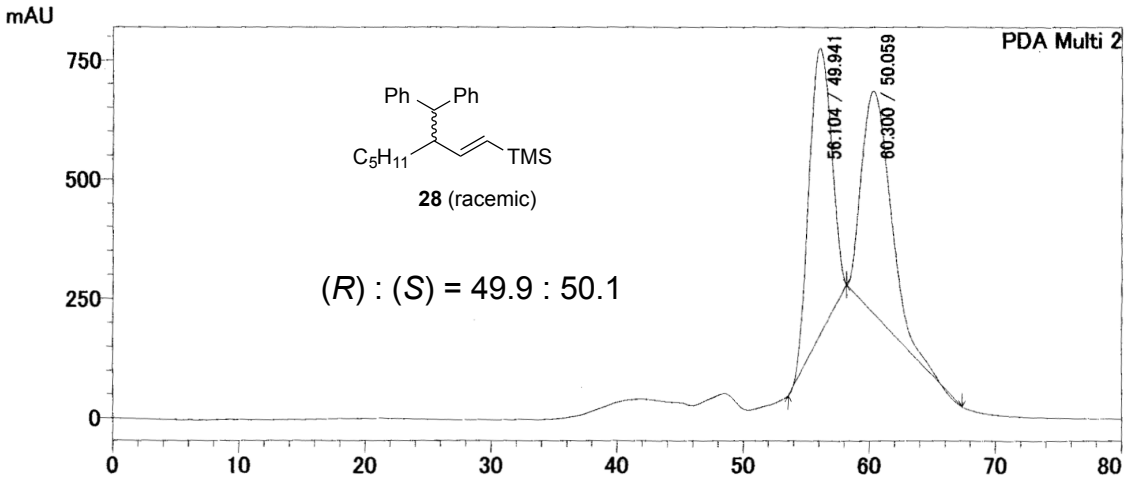


Determination of the ratio of **27** and the regioisomer by ^{1}H NMR (400 MHz, $CDCl_3$)
(The full spectrum of **27** is attached to part 5 of this ESI)



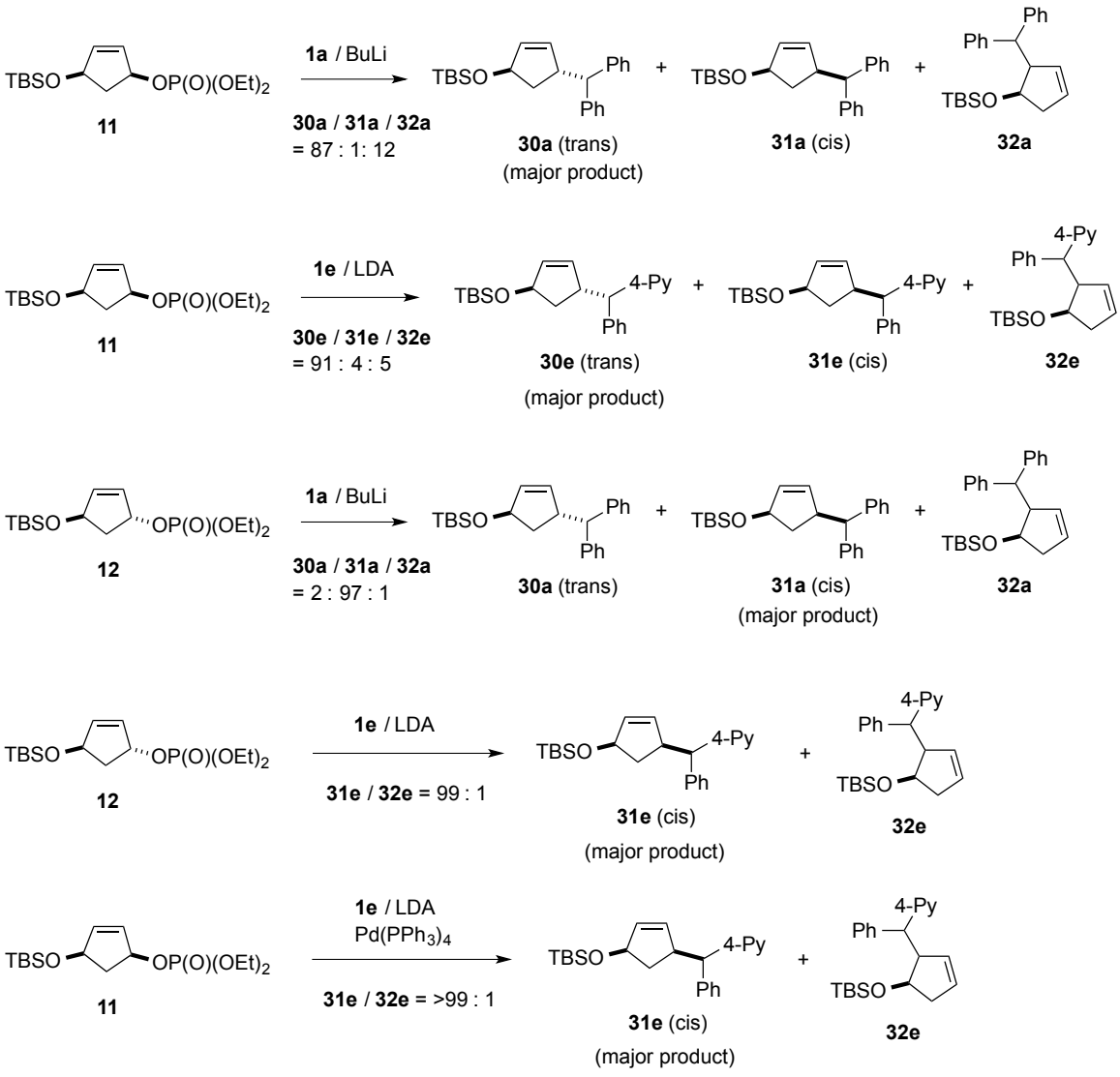
Determination of the enantiomeric purity of (*R*)-**28** by chiral HPLC analysis
conditions: Chiralcel OJ-H, hexane/*i*-PrOH = 99.5/0.5, 0.1 mL/min, 35 °C



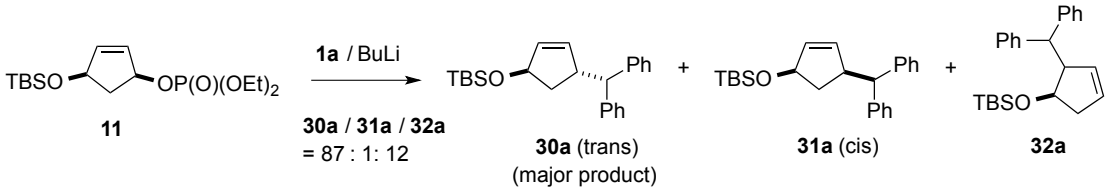


Determination of the product ratios of **30a**,**e** and **31a**,**e** by ^{1}H NMR for calculation of the regioselectivity, stereoselectivity, and diastereselectivity (for **30e** and **31e**)
(spectra are shown on the next pages)

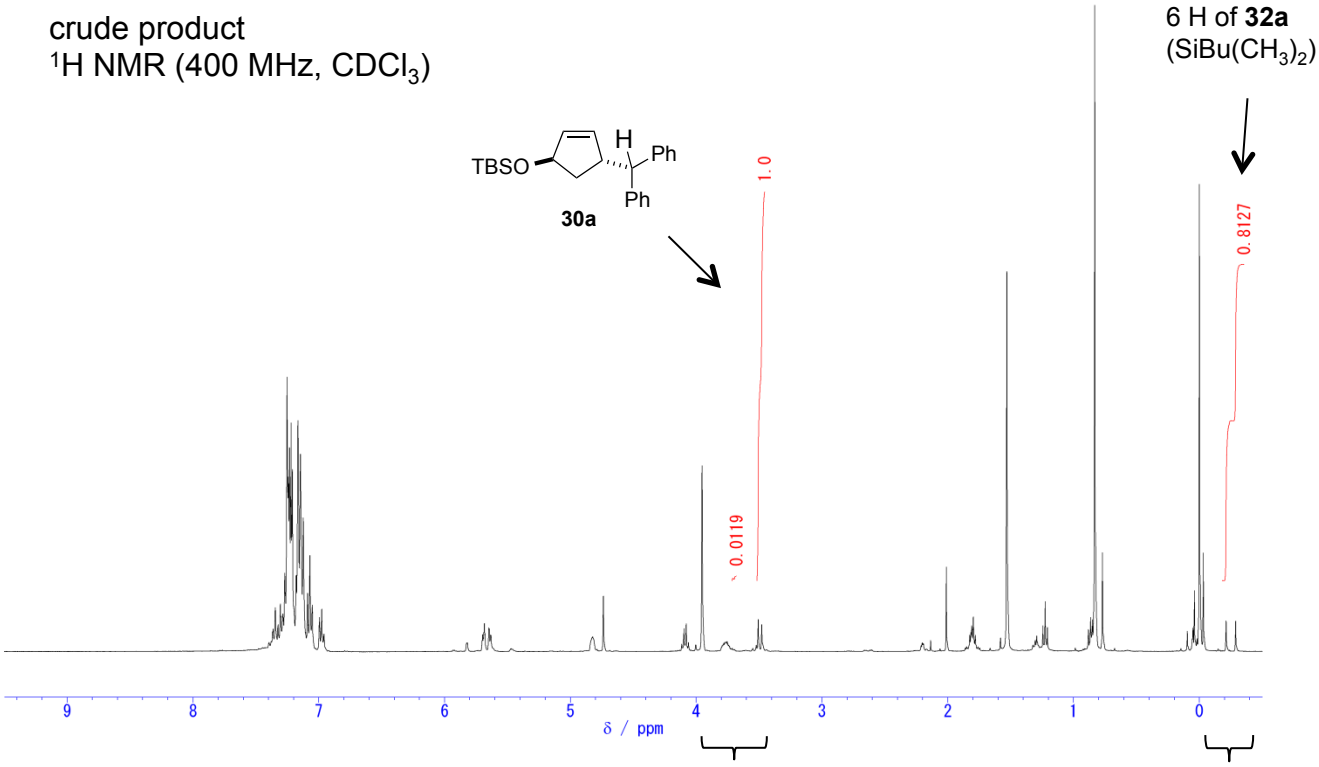
Note: The ^{1}H NMR signals of the Si(CH_3)$_2$Bu appeared at higher position were referred to the regioisomer on the basis of the fact that the signals for **26** (derived from **8** and **1a**) were observed at a higher position than that of the S_N2 product. The cis stereochemistry for **31a** and **31e** was confirmed on the basis of the large difference (Δδ ca. 1 ppm) between the methylene protons on the cyclopentene ring.



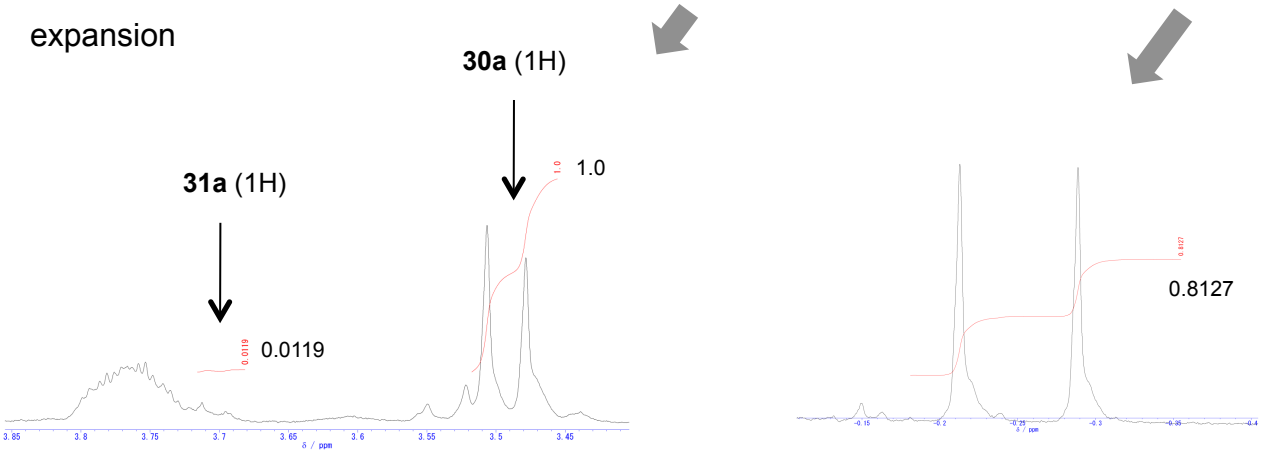
Determination of the product ratio by ^{1}H NMR



crude product
^{1}H NMR (400 MHz, $CDCl_3$)

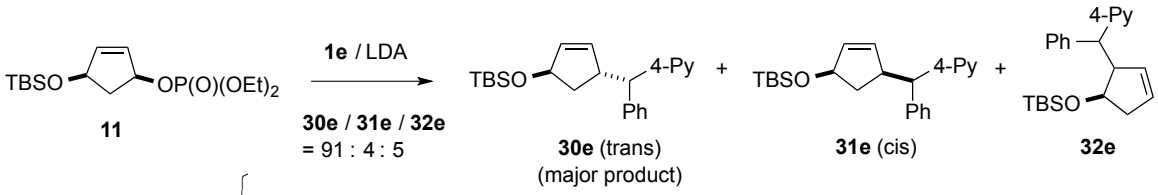


expansion

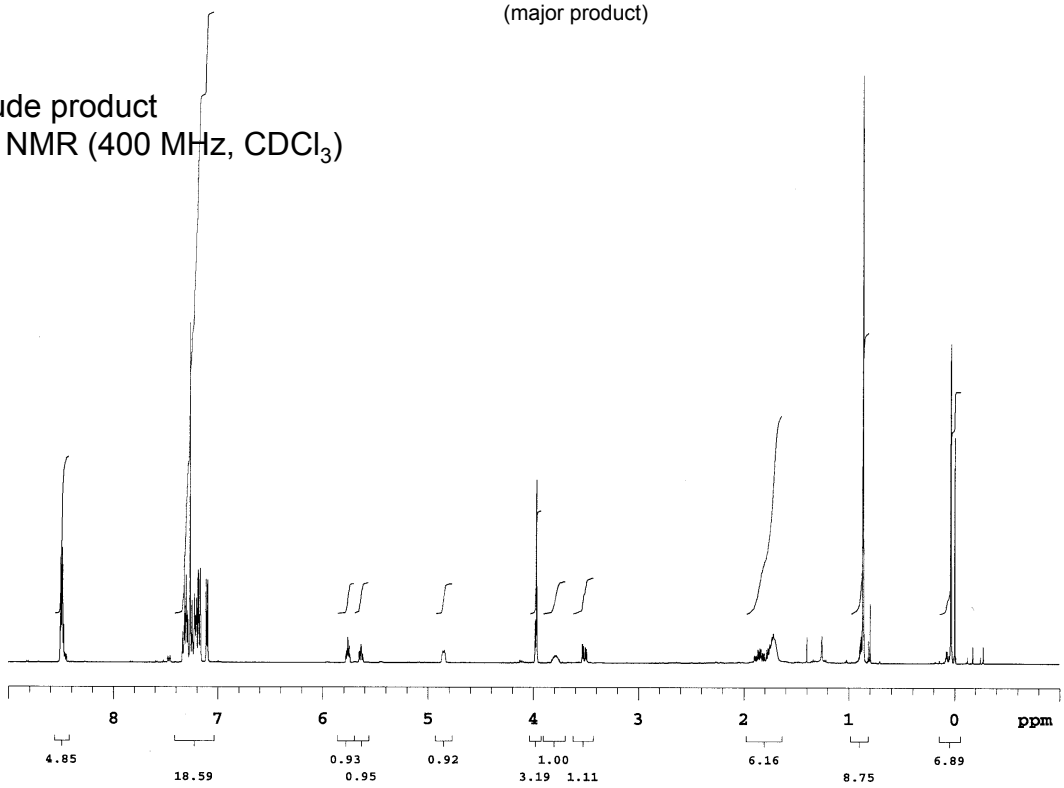


30a : **31a** : **32a** = 1.0/1 : 0.0119/1 : 0.8127/6 = 87 : 1 : 12
(**30a**+**31a**) : **32a** = (87+1) : 12 = 88 : 12 (regioselectivity)
30a : 31a = 87 : 1 = 99 : 1 (stereoselectivity)

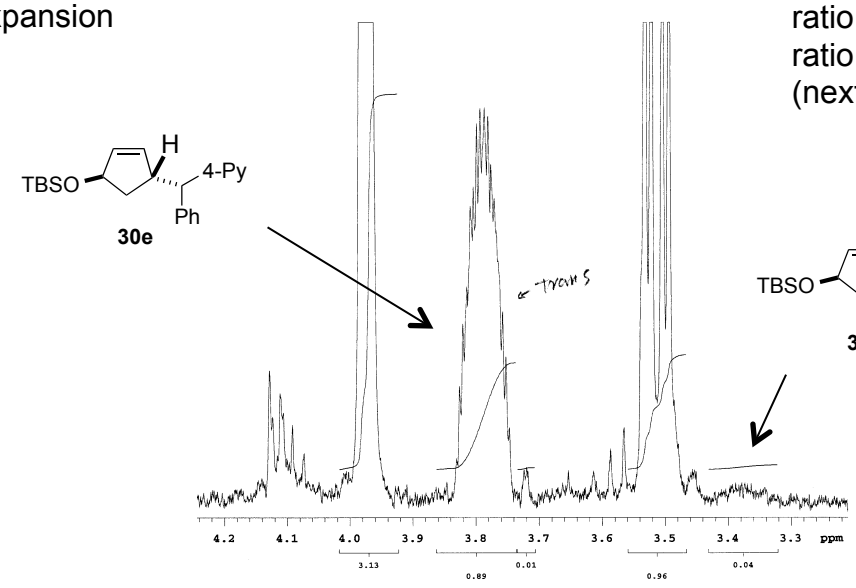
Determination of the product ratio by ^{1}H NMR



crude product
^{1}H NMR (400 MHz, $CDCl_3$)

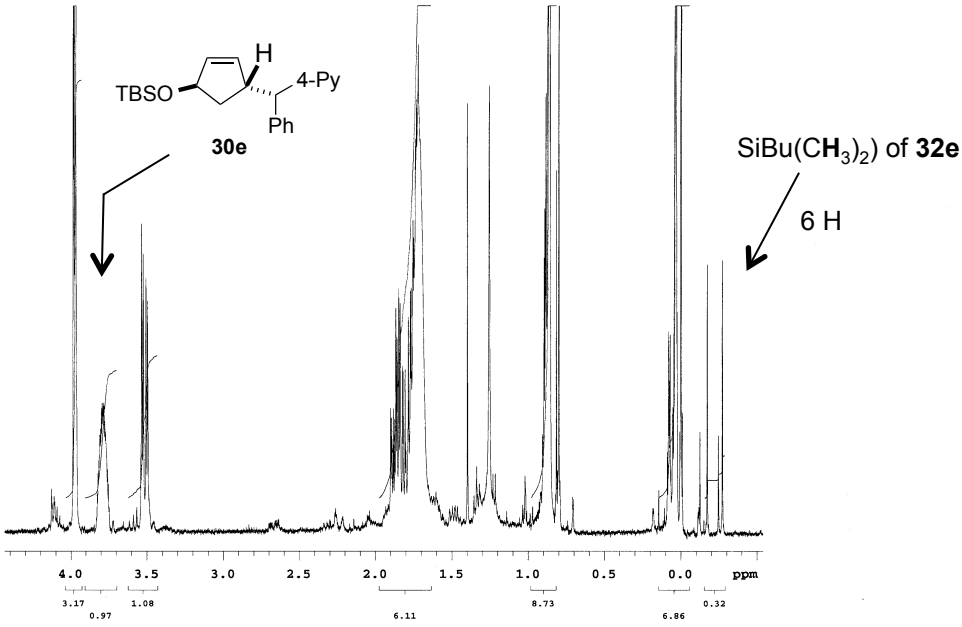


expansion



ratio of **30e**, **31e**, **32e**
ratio of diastereomers of **30e**
(next page)

continued to the next page

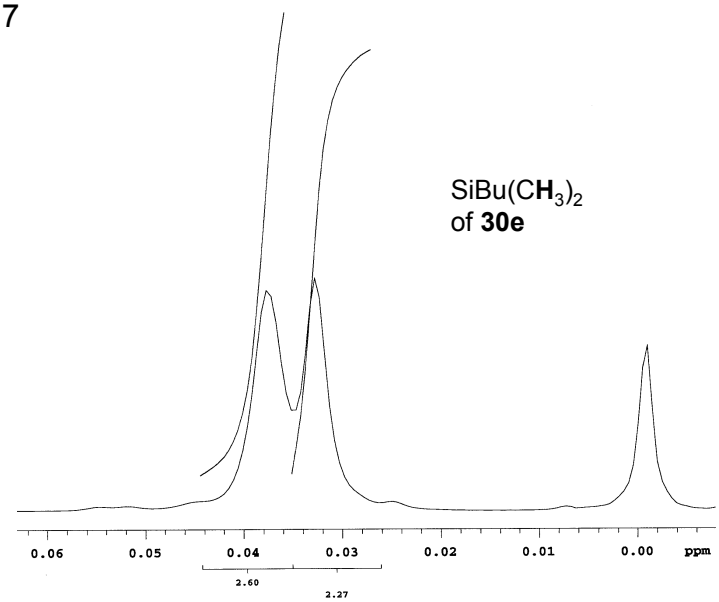


30e : **31e** = 0.89 : 0.04
30e : **32e** = 0.97/1 : 0.32/6

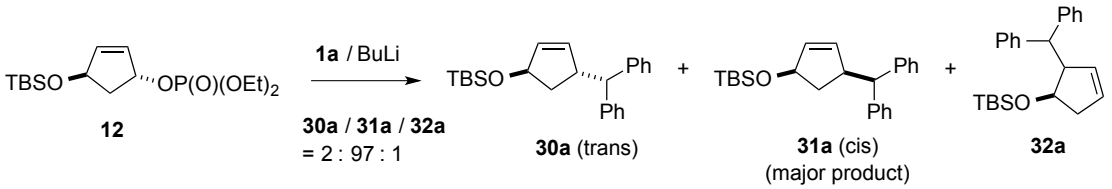
➡ **30e** : **31e** : **32e** = 91 : 4 : 5
(**30e**+**31e**) : **32a** = (91+4) : 5 = 95 : 5
(regioselectivity)
30e : **31e** = 91 : 4 = 96 : 4
(stereoselectivity)

Determination of the diastereomeric ratio of **30e**

= 2.60 : 2.27
= 53 : 47



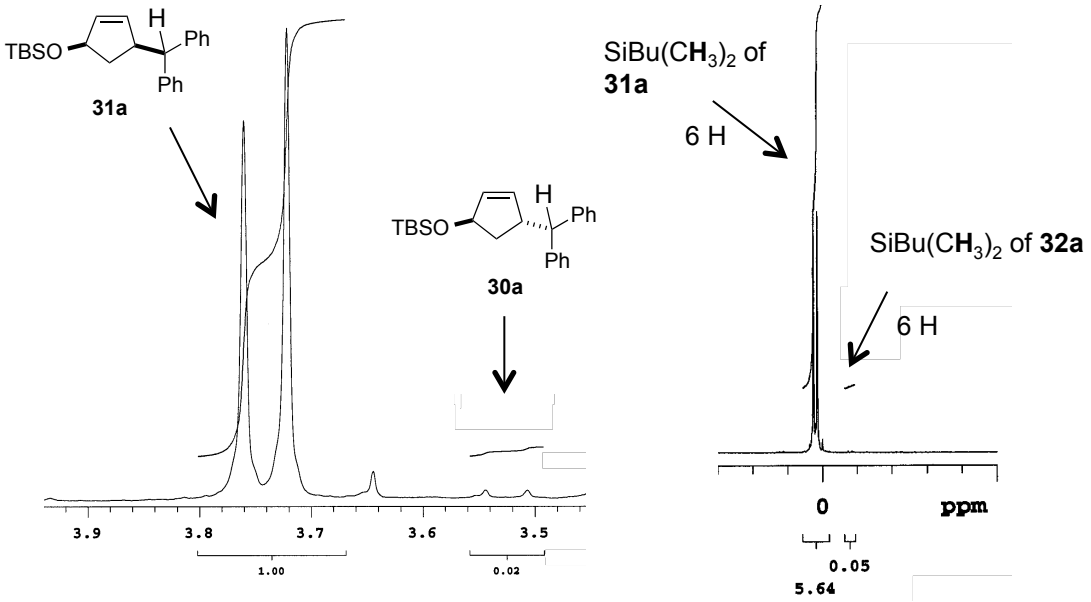
Determination of the product ratio by ^{1}H NMR



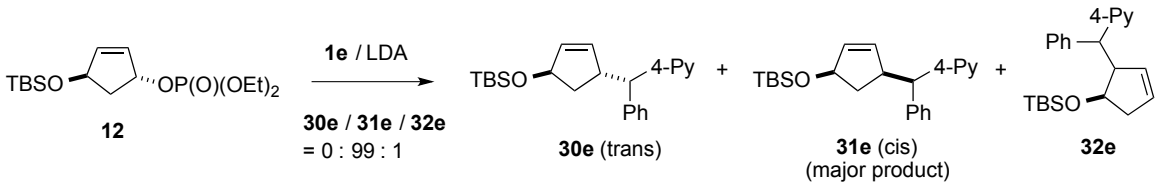
30a : **31a** = 0.02 : 1.00
31a : **32a** = 5.64/6 : 0.05/6

➡ **30a** : **31a** : **32a** = 2 : 97 : 1
(**30a**+**31a**) : **32a** = (2+97) : 1 = 99 : 1
(regioselectivity)
30a : **31a** = 2 : 97 = 2 : 98
(stereoselectivity)

expanded ^{1}H NMR (300 MHz, $CDCl_3$)
(The full spectrum of **31a** is attached to part 5 of this ESI)



Determination of the product ratio by ^{1}H NMR

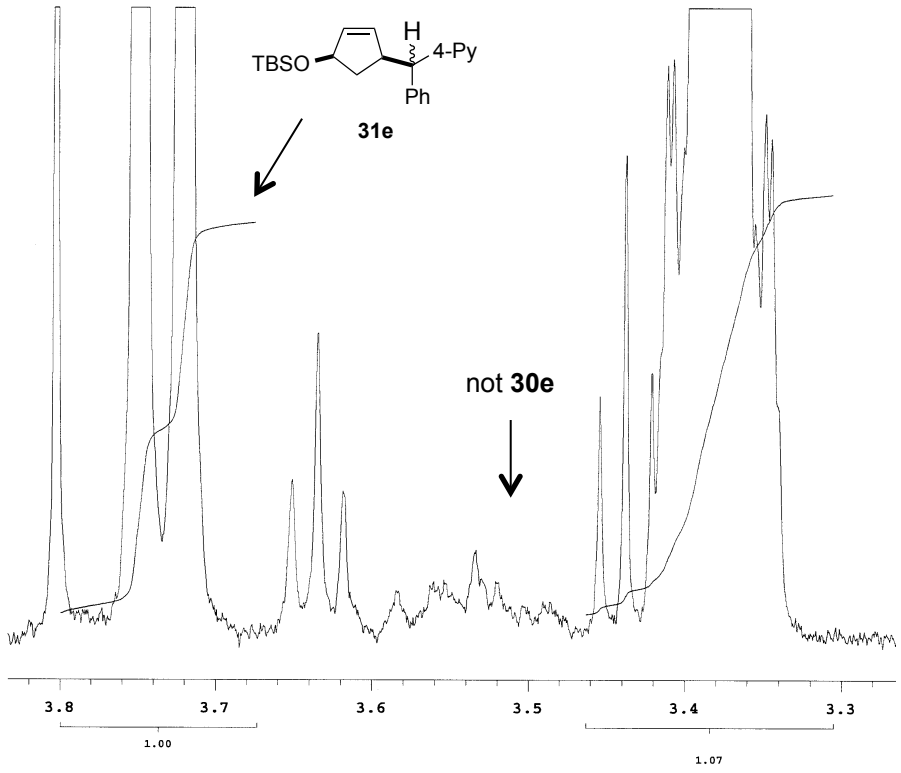


30e : **31e** = 0 : 1.00 (below)
31e : **32e** = 99 : 1 (next page)

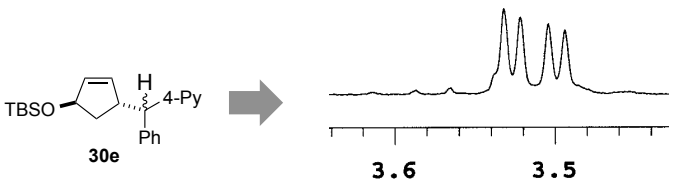
➡ **30e** : **31e** : **32e** = 0 : 99 : 1
31e : **32e** = 99 : 1 (regioselectivity)
30e : 31e= 0 : 100 (stereoselectivity)

ratio of diastereomers of **31e**
= 56 : 44 (next page)

expanded ^{1}H NMR (400 MHz, $CDCl_3$)
(The full spectrum of **31e** is attached to part 5 of this ESI)



cf.



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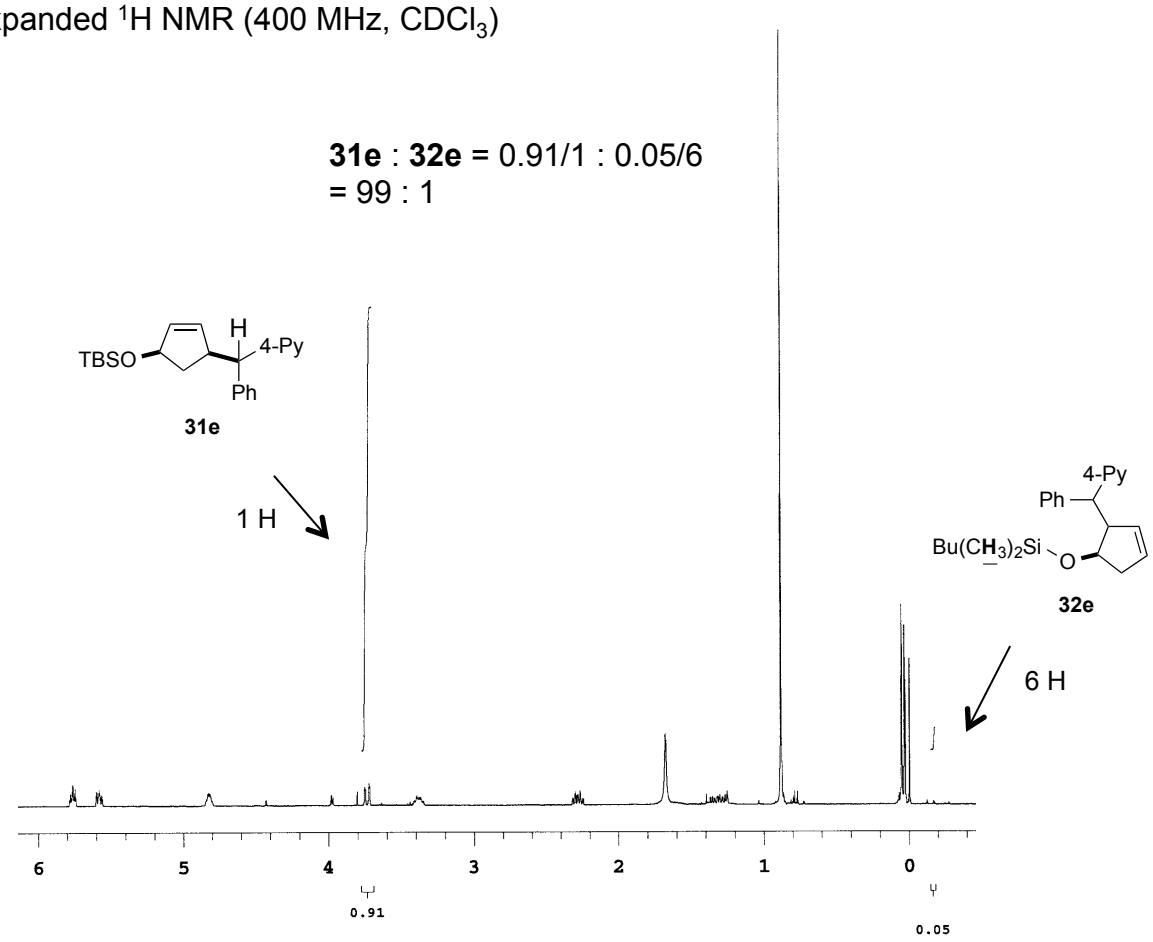
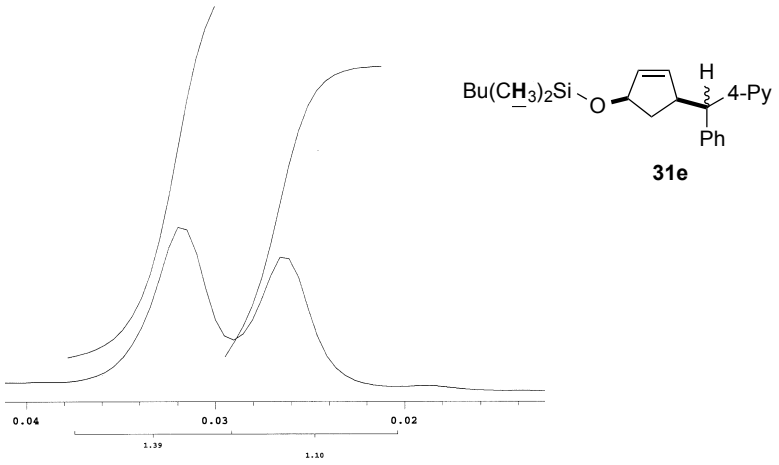
expanded ^{1}H NMR (400 MHz, $CDCl_3$)

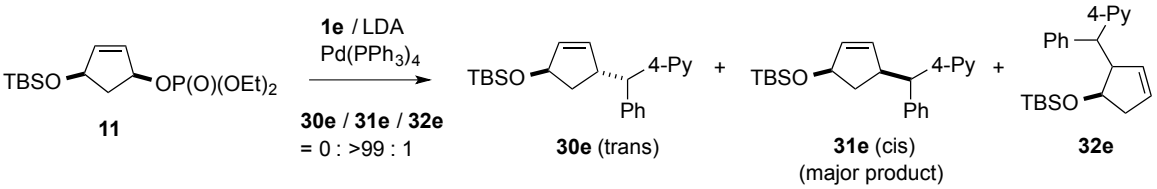


Determination of the diastereomeric ratio of **31e**

= 1.39 : 1.10
= 56 : 44



Determination of the product ratio by ^{1}H NMR

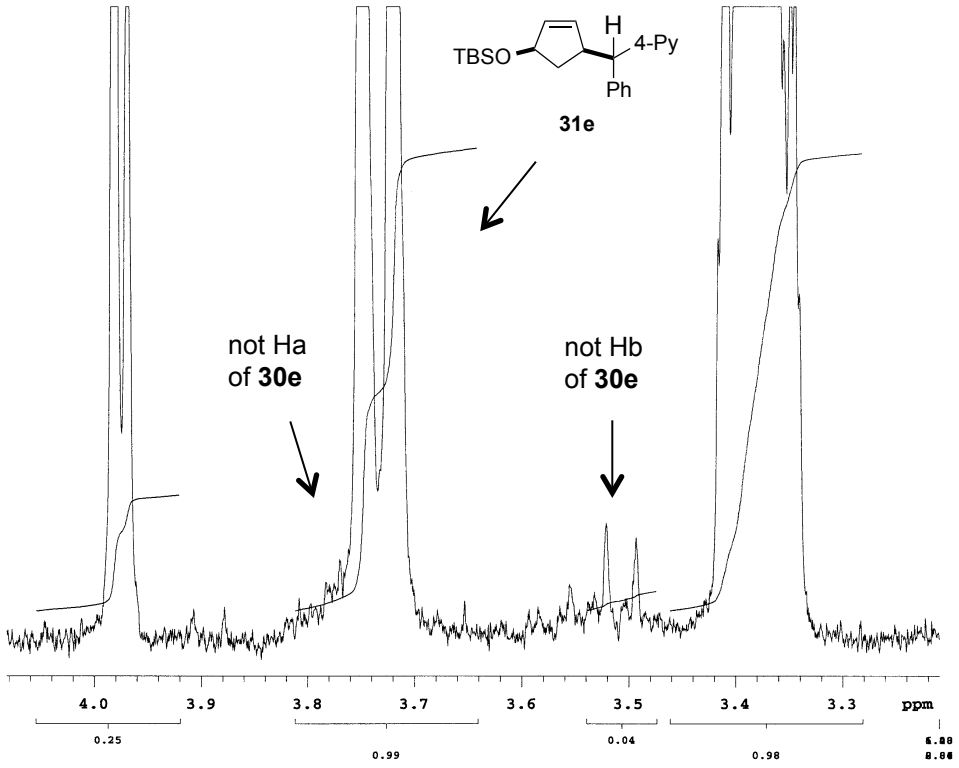


30e : **31e** = 0 : 0.99 (below)
31e : **32e** = 99.8 : 0.2 (next page)

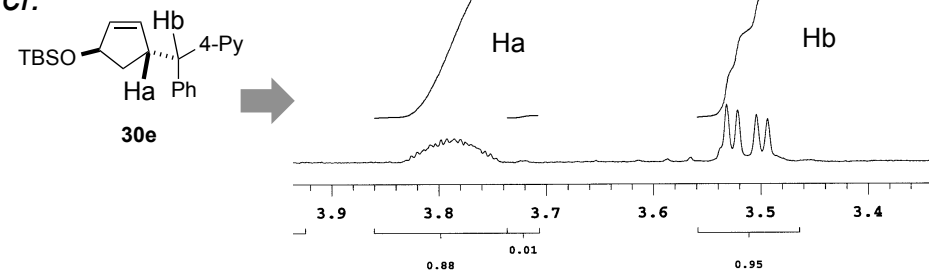
➡ **30e** : **31e** : **32e** = 0 : >99 : 1
31e : **32a** = >99 : 1 (regioselectivity)
30e : **31e** = 0 : 100 (stereoselectivity)

ratio of diastereoisomers of **31e**
= 57 : 43 (next page)

expanded ^{1}H NMR (400 MHz, $CDCl_3$)
(The full spectrum of **31e** is attached to part 5 of this ESI)



cf.



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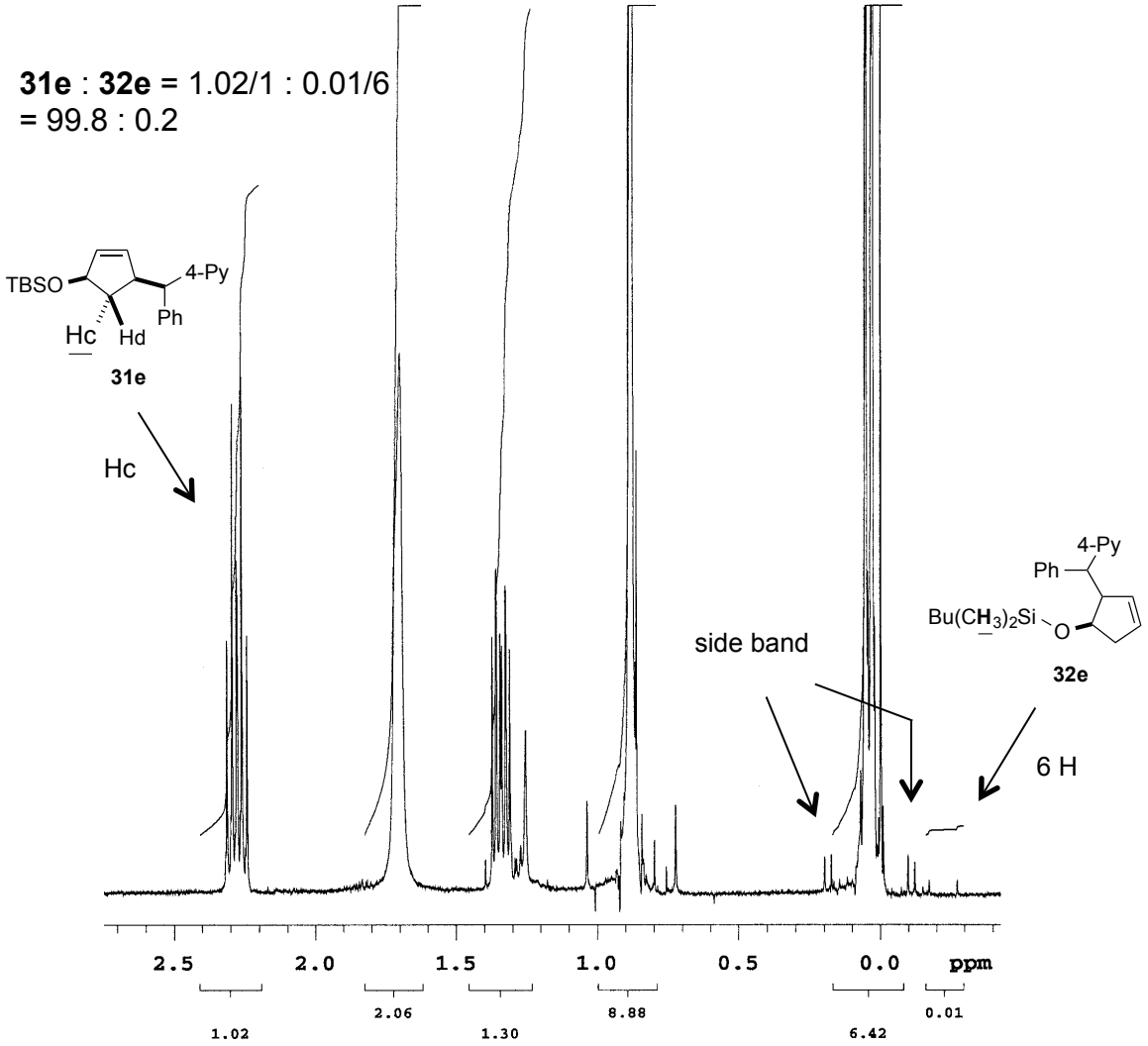
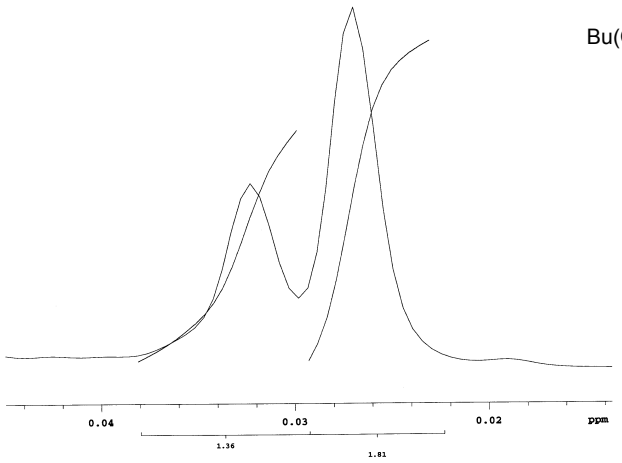
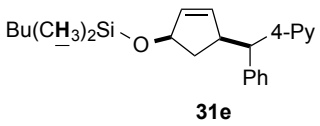


Determination of the diastereomeric ratio of **31e**

= 1.36 : 1.81
= 43 : 57





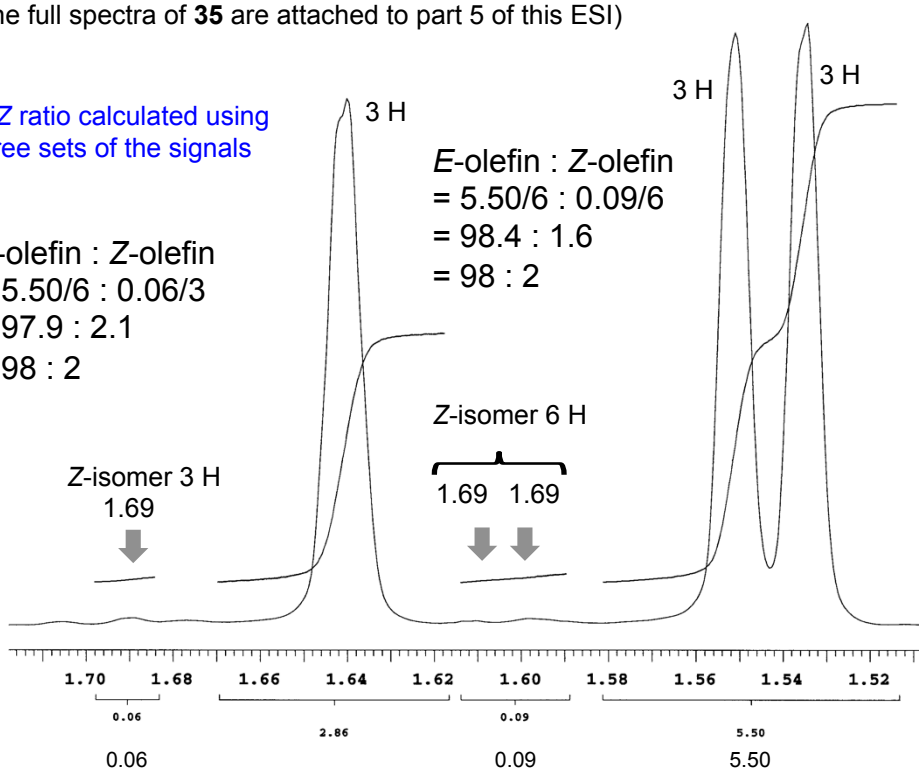
31e

Determination of the olefinic purity of **35** by ^{1}H and ^{13}C NMR
(The full spectra of **35** are attached to part 5 of this ESI)

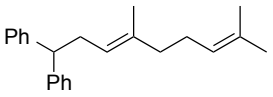
E/*Z* ratio calculated using three sets of the signals

E-olefin : *Z*-olefin
= 5.50/6 : 0.06/3
= 97.9 : 2.1
= 98 : 2

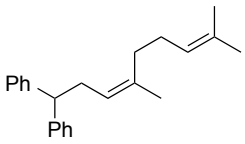
E-olefin : *Z*-olefin
= 5.50/6 : 0.09/6
= 98.4 : 1.6
= 98 : 2



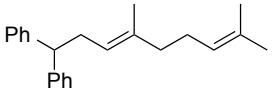
E-product 3 H x 2



E-product **35**
^{1}H NMR (400 MHz, $CDCl_3$)



Z-isomer **37**

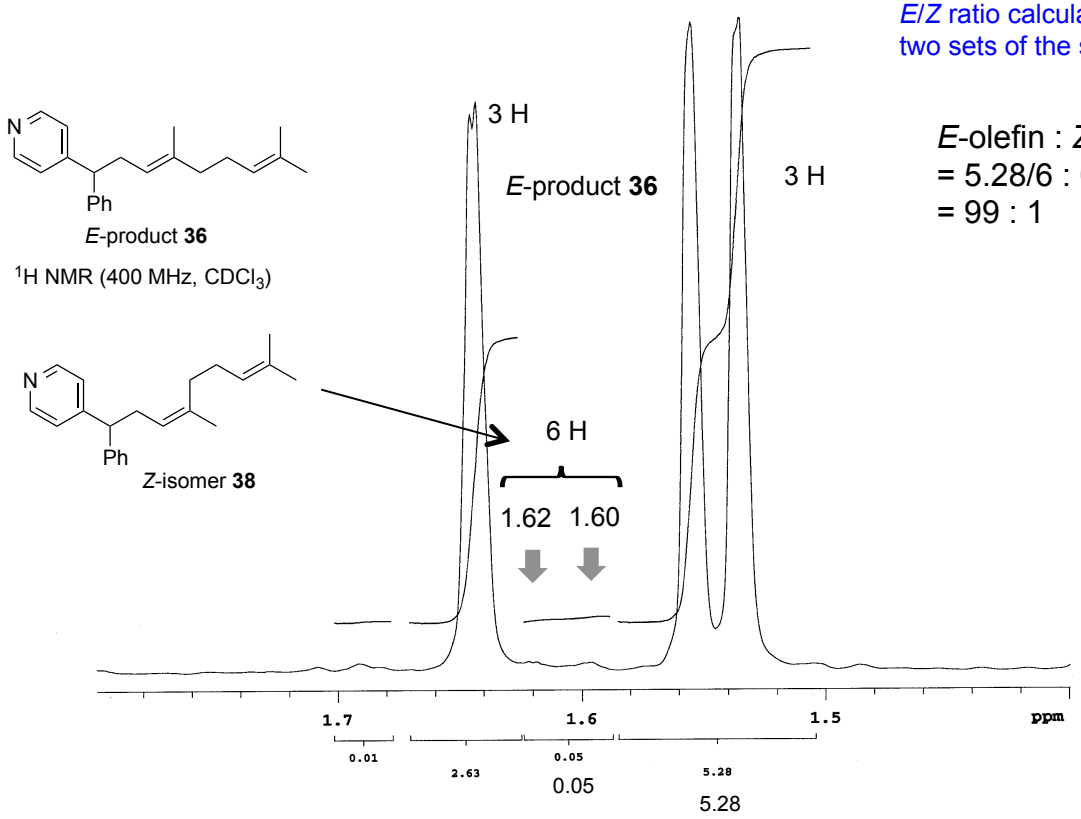


E-product **35**
^{13}C NMR (75 MHz, $CDCl_3$)

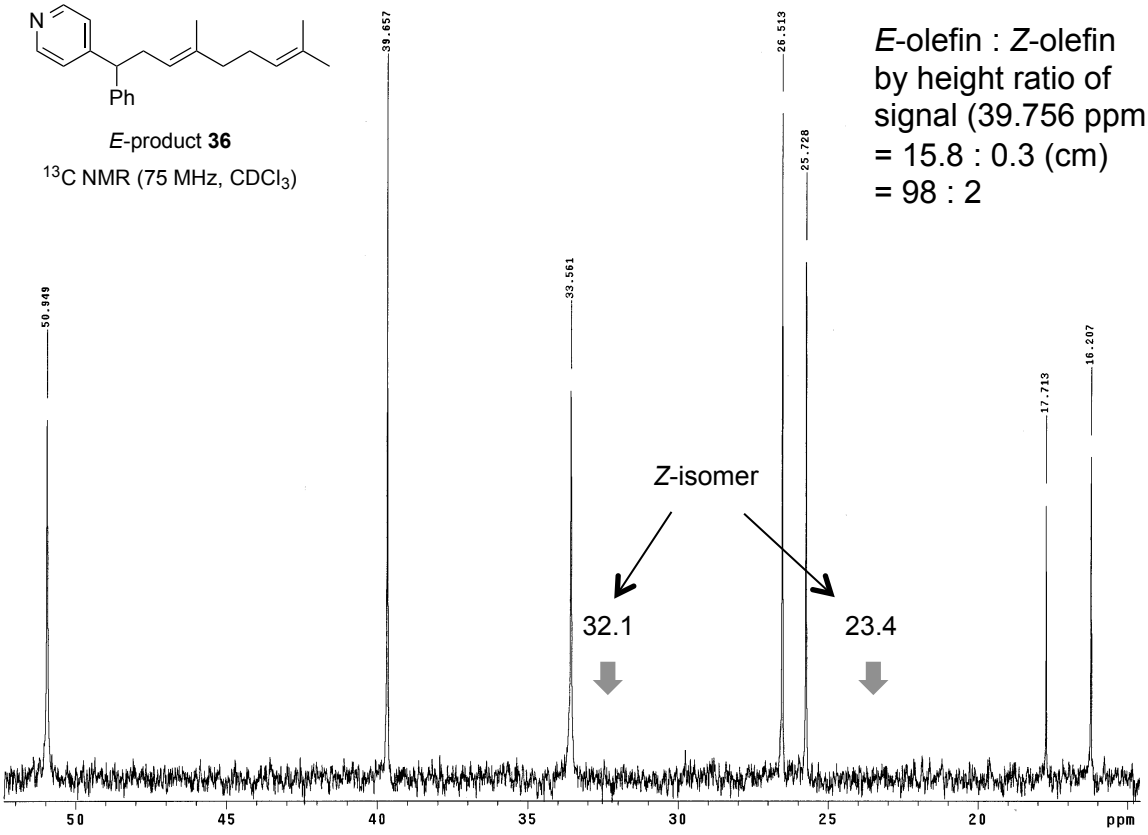
E-olefin : *Z*-olefin by height ratio of signal (39.756 ppm) : noise
= 16.0 : 0.3 (cm)
= 98 : 2

Determination of the olefinic purity of **36** by ^{1}H and ^{13}C NMR
(The full spectra of **36** are attached to part 5 of this ESI)

E/*Z* ratio calculated using two sets of the signals



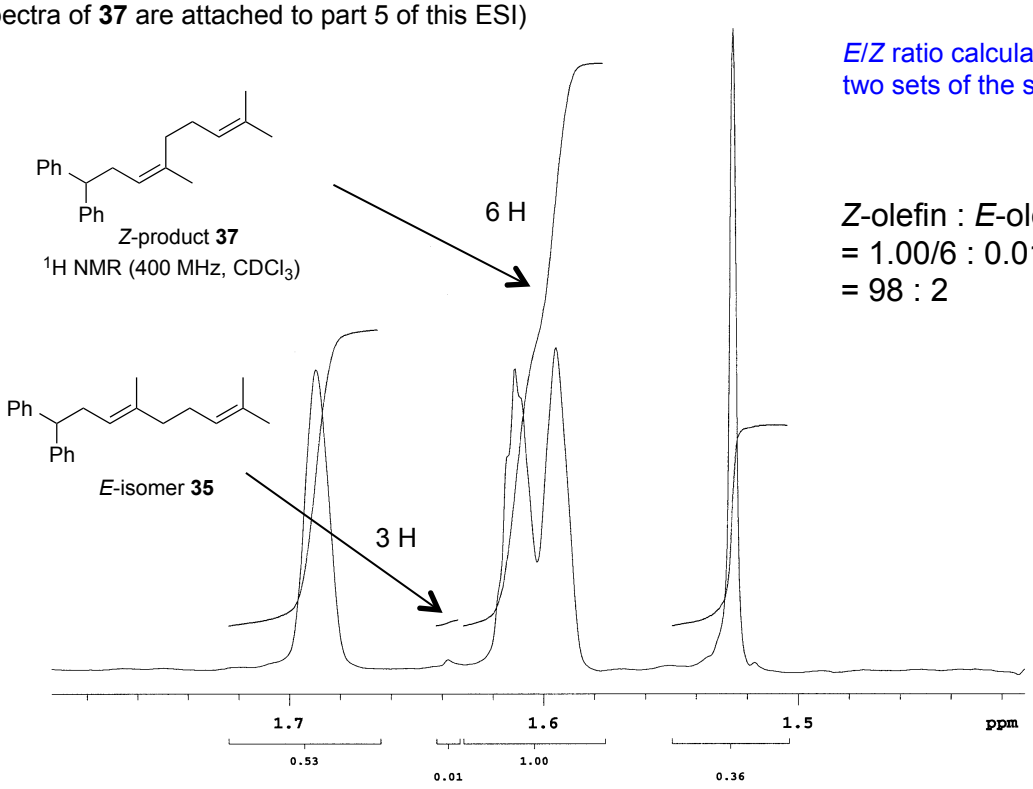
E-olefin : *Z*-olefin
= 5.28/6 : 0.05/6
= 99 : 1



E-olefin : *Z*-olefin
by height ratio of
signal (39.756 ppm) : noise
= 15.8 : 0.3 (cm)
= 98 : 2

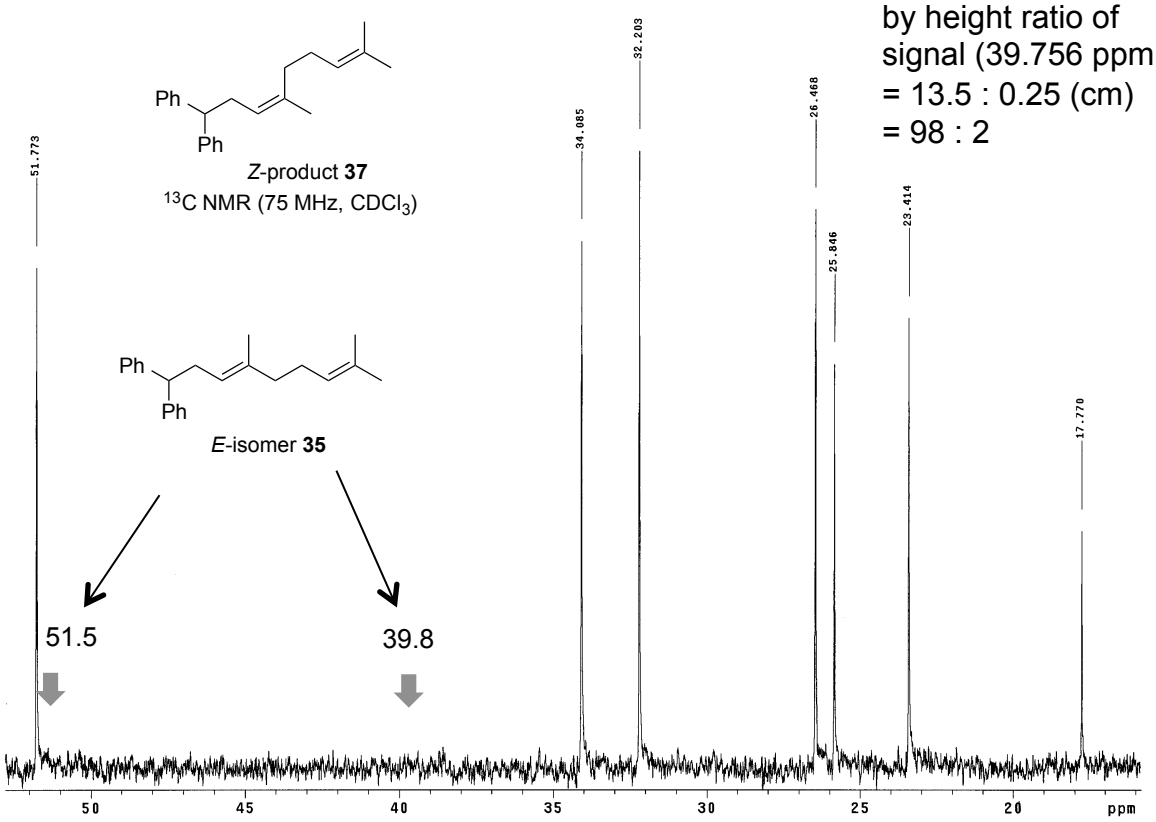
Determination of the olefinic purity of **37** by ^{1}H and ^{13}C NMR
(The full spectra of **37** are attached to part 5 of this ESI)

E/*Z* ratio calculated using two sets of the signals

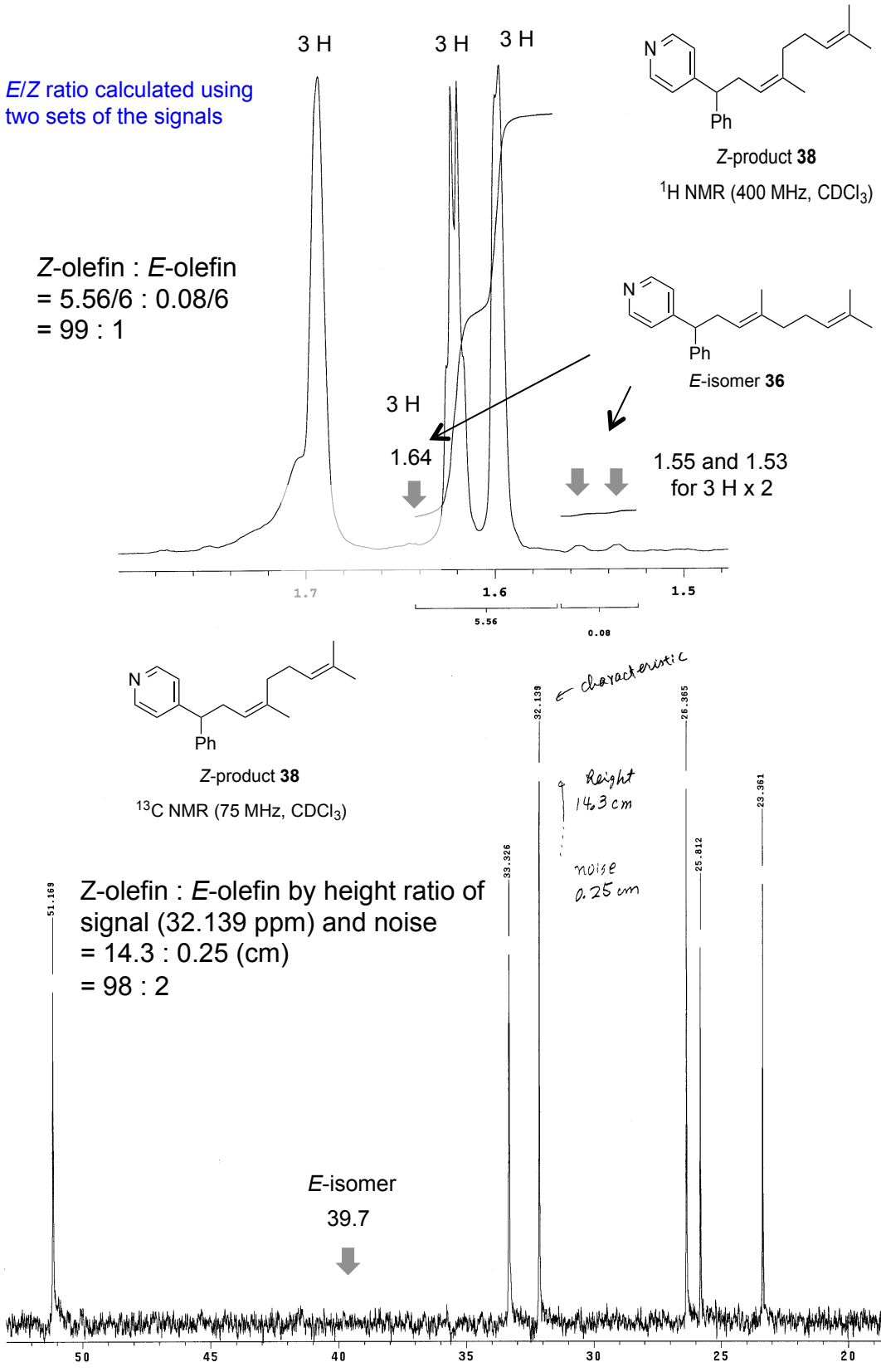


Z-olefin : *E*-olefin
= 1.00/6 : 0.01/3
= 98 : 2

Z-olefin : *E*-olefin
by height ratio of
signal (39.756 ppm) : noise
= 13.5 : 0.25 (cm)
= 98 : 2

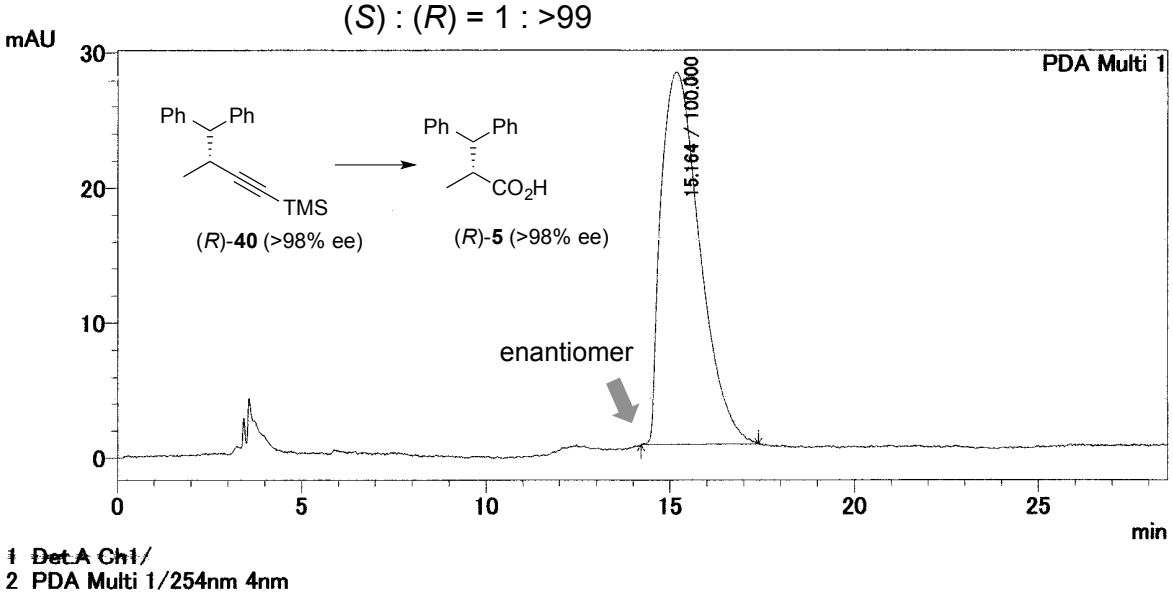


Determination of the olefinic purity of **38** by ^{1}H and ^{13}C NMR
(The full spectra of **38** are attached to part 5 of this ESI)

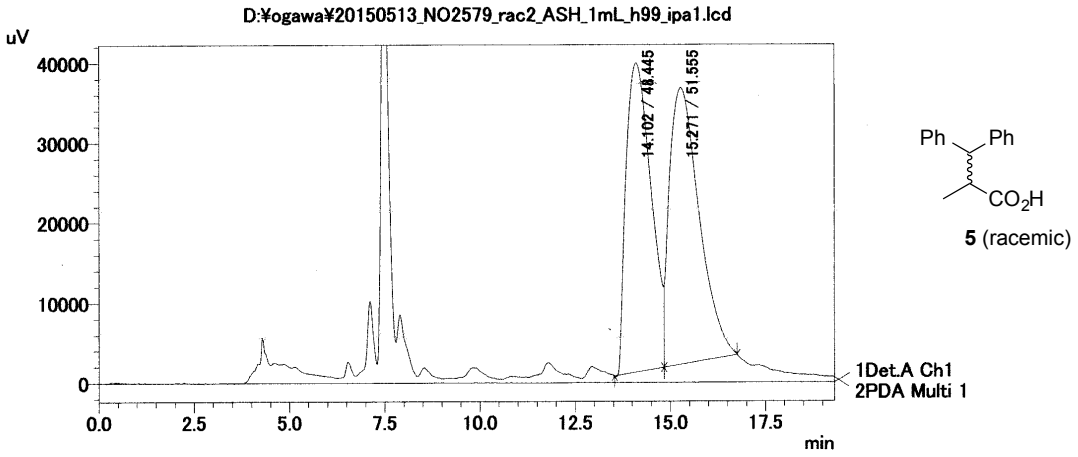


Determination of the enantiomeric purity of the acid (*R*)-**5** by chiral HPLC analysis
conditions: Chiralcel AS-H, hexane/*i*-PrOH = 99/1, 1 mL/min, 40 °C

(*S*) : (*R*) = 1 : >99



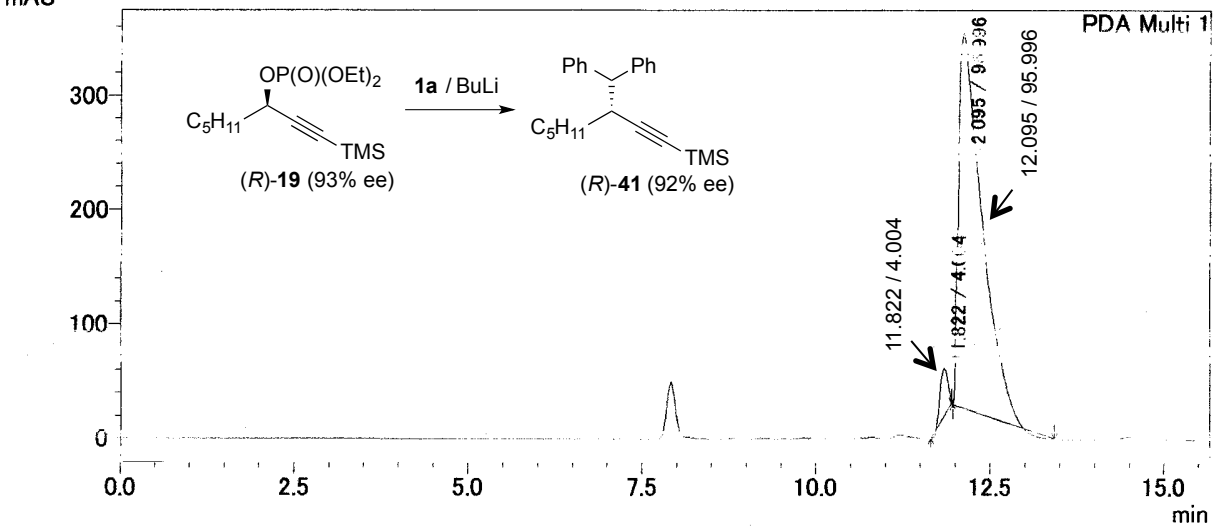
(*S*) : (*R*) = 48.445 : 51.555 = 48.4 : 51.6



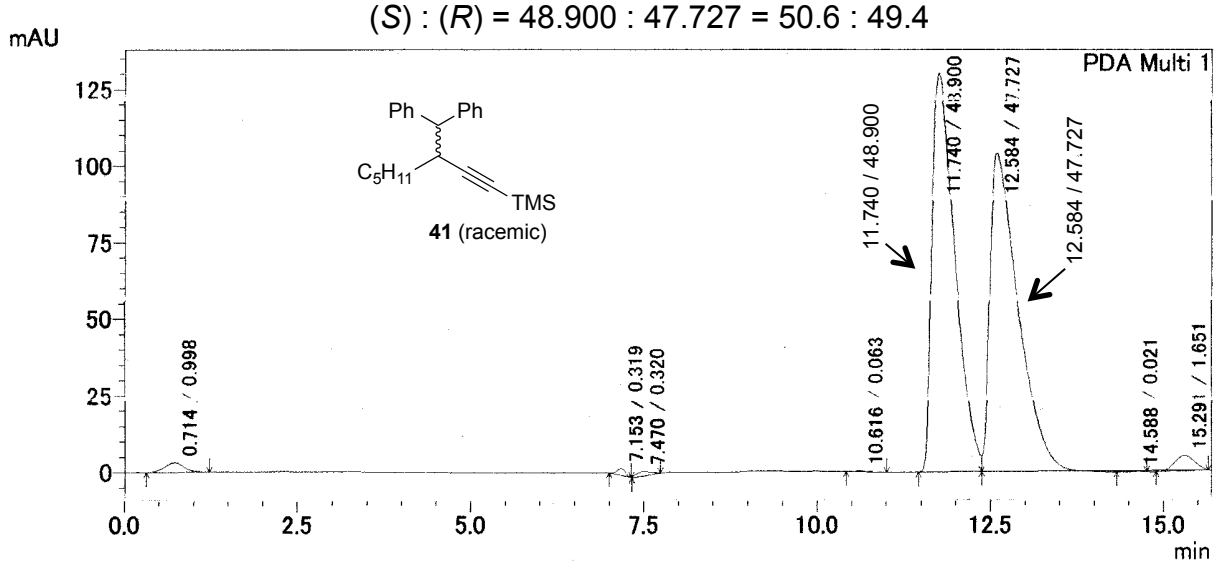
Ph
Ph
CO2H
5 (racemic)

Determination of the enantiomeric purity of (*R*)-**41** by chiral HPLC analysis
conditions: Chiralcel OD-H, hexane/*i*-PrOH = 99.9/0.1, 0.5 mL/min, 35 °C

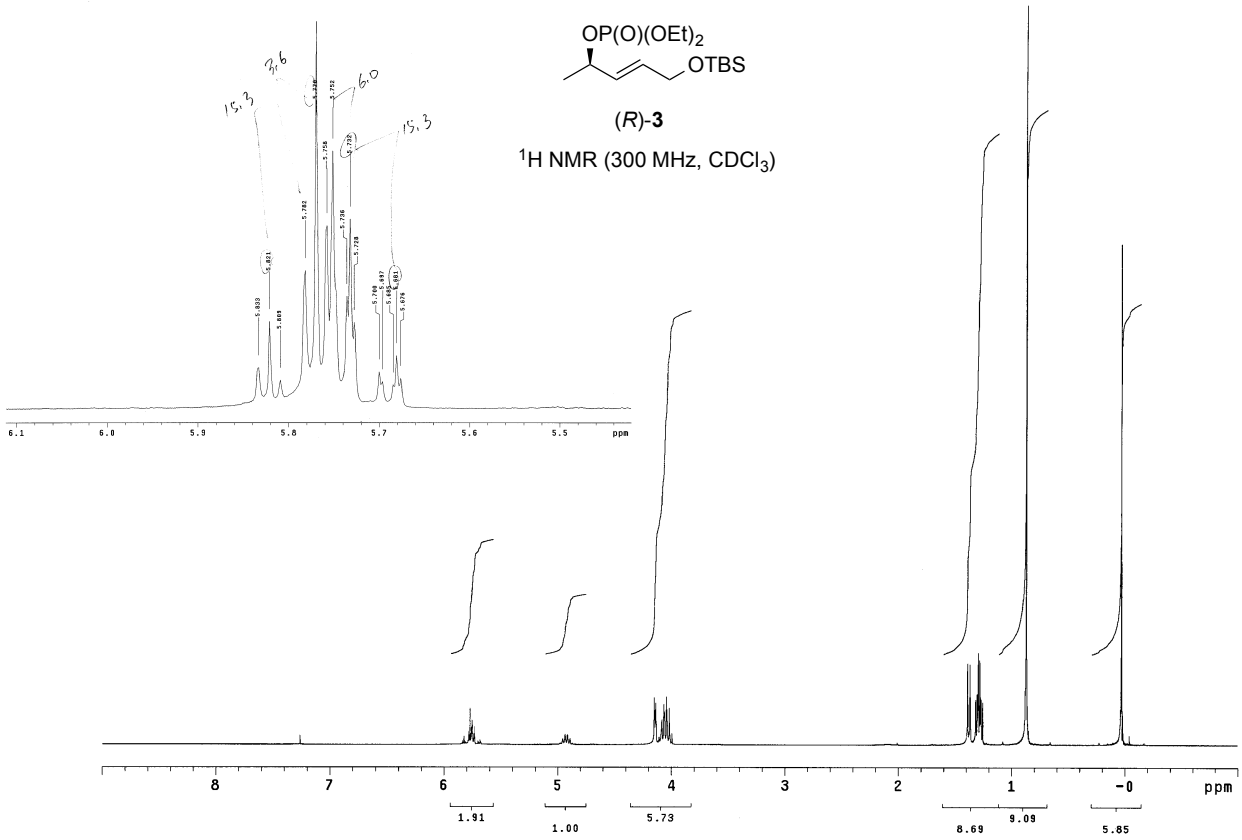
(*S*) : (*R*) = 95.996 : 4.004 = 96.0 : 4.0

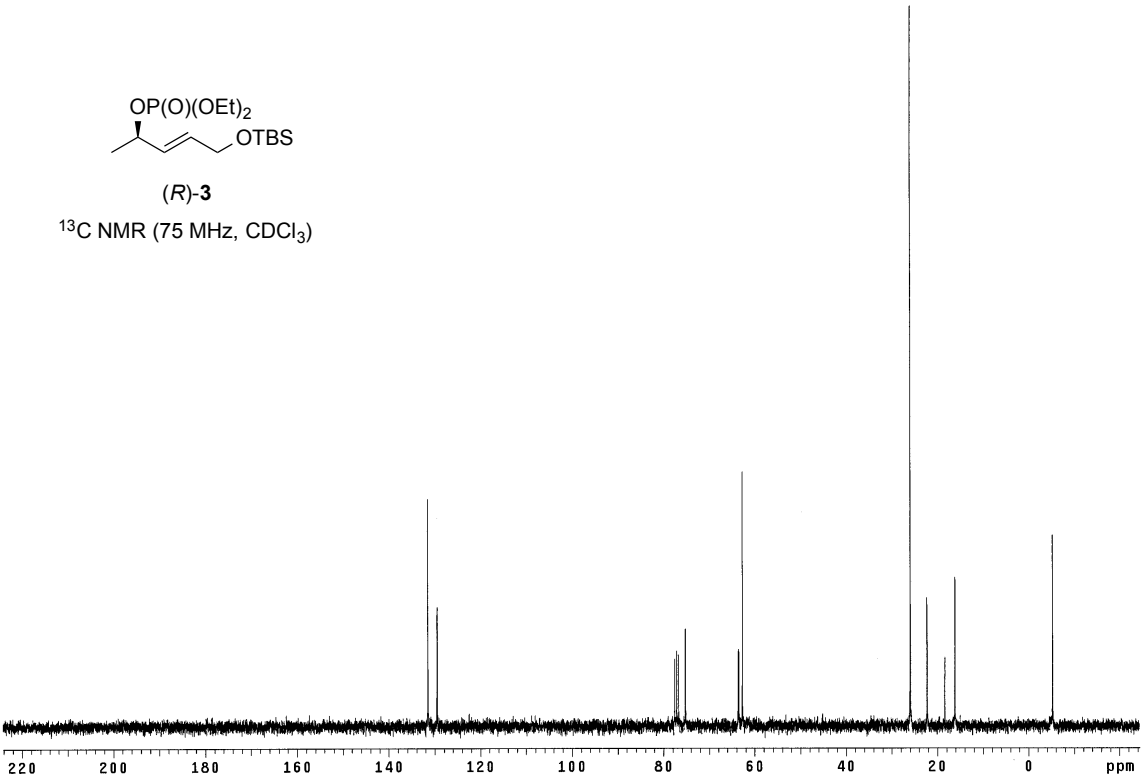


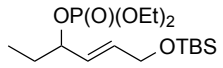
(*S*) : (*R*) = 48.900 : 47.727 = 50.6 : 49.4



Part 5: ^{1}H and ^{13}C NMR Spectra to Establish Identity and Purity

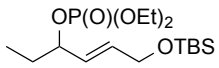

OP(O)(OEt)2
OTBS
(R)-3
1H NMR (300 MHz, CDCl3)
8
7
6
5
4
3
2
1
-0
ppm
1.91
1.00
5.73
8.69
9.09
5.85


OP(O)(OEt)2
OTBS
(R)-3
13C NMR (75 MHz, CDCl3)
220
200
180
160
140
120
100
80
60
40
20
0
ppm



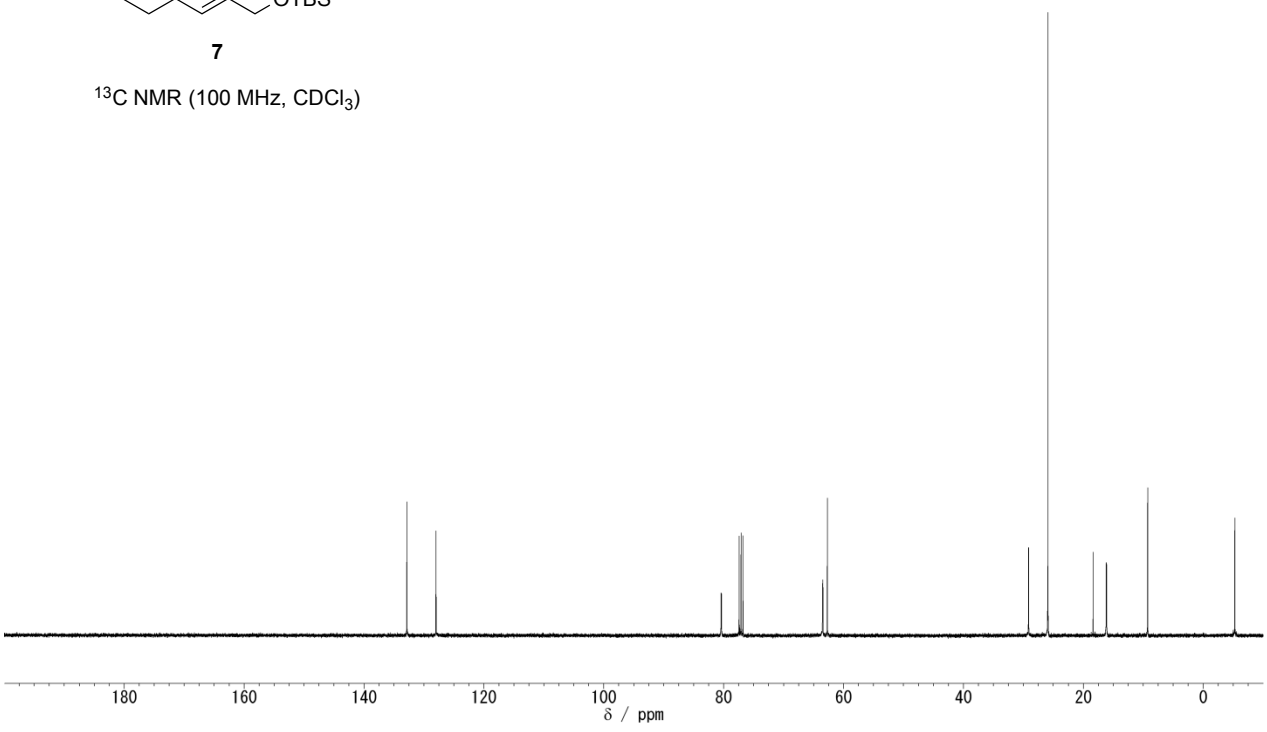
7

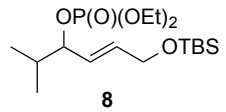
^{1}H NMR (400 MHz, $CDCl_3$)



7

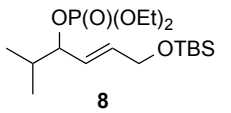
^{13}C NMR (100 MHz, $CDCl_3$)





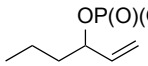
8

^{1}H NMR (400 MHz, $CDCl_3$)



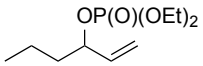
8

^{13}C NMR (100 MHz, $CDCl_3$)



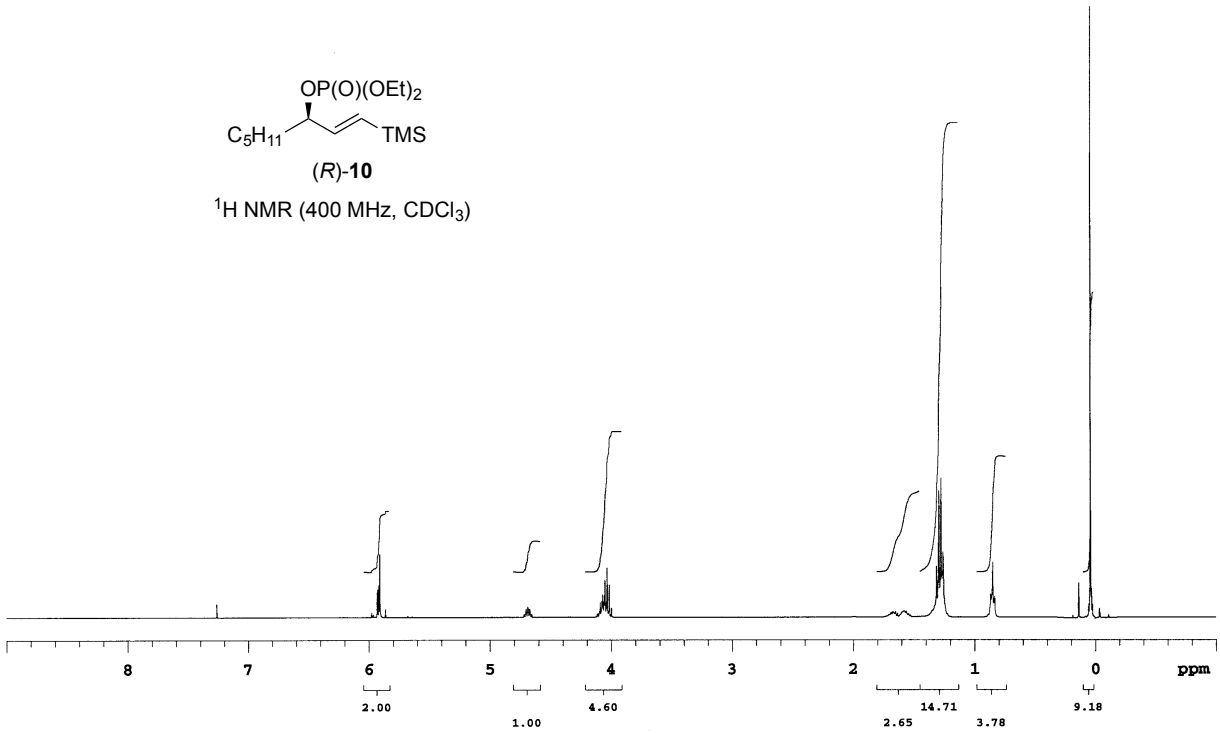
9

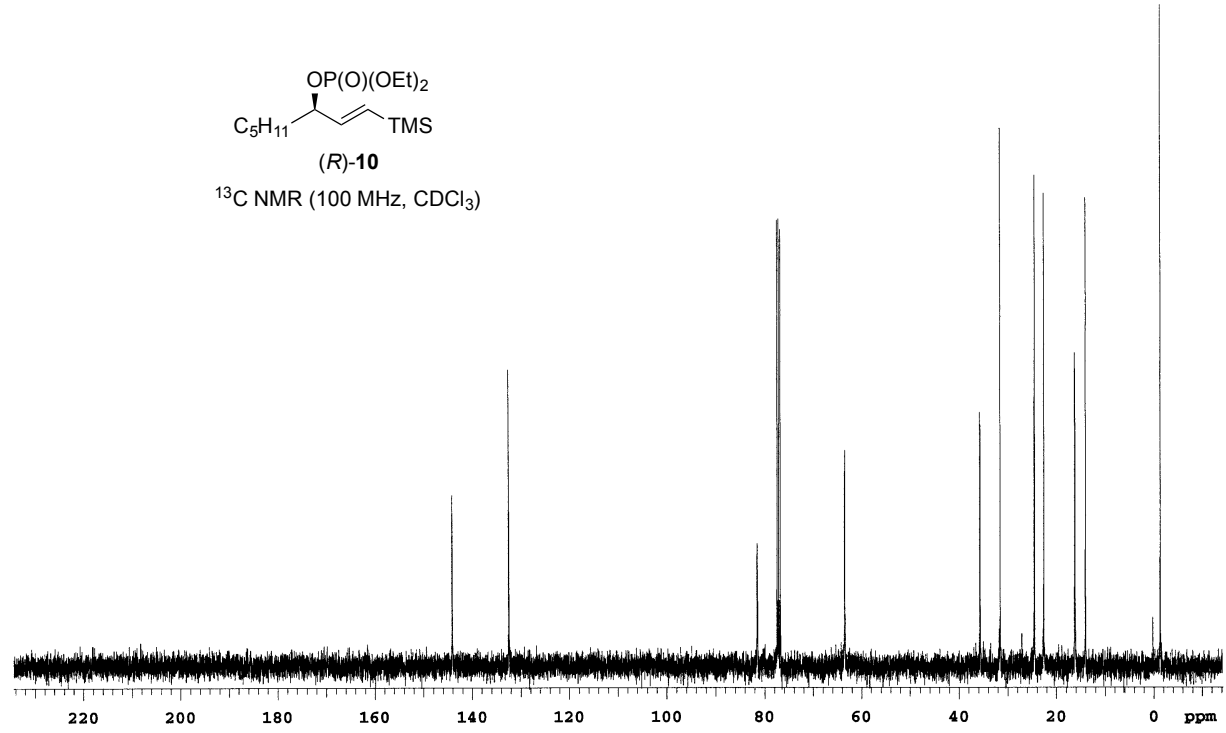
^{1}H NMR (400 MHz, $CDCl_3$)

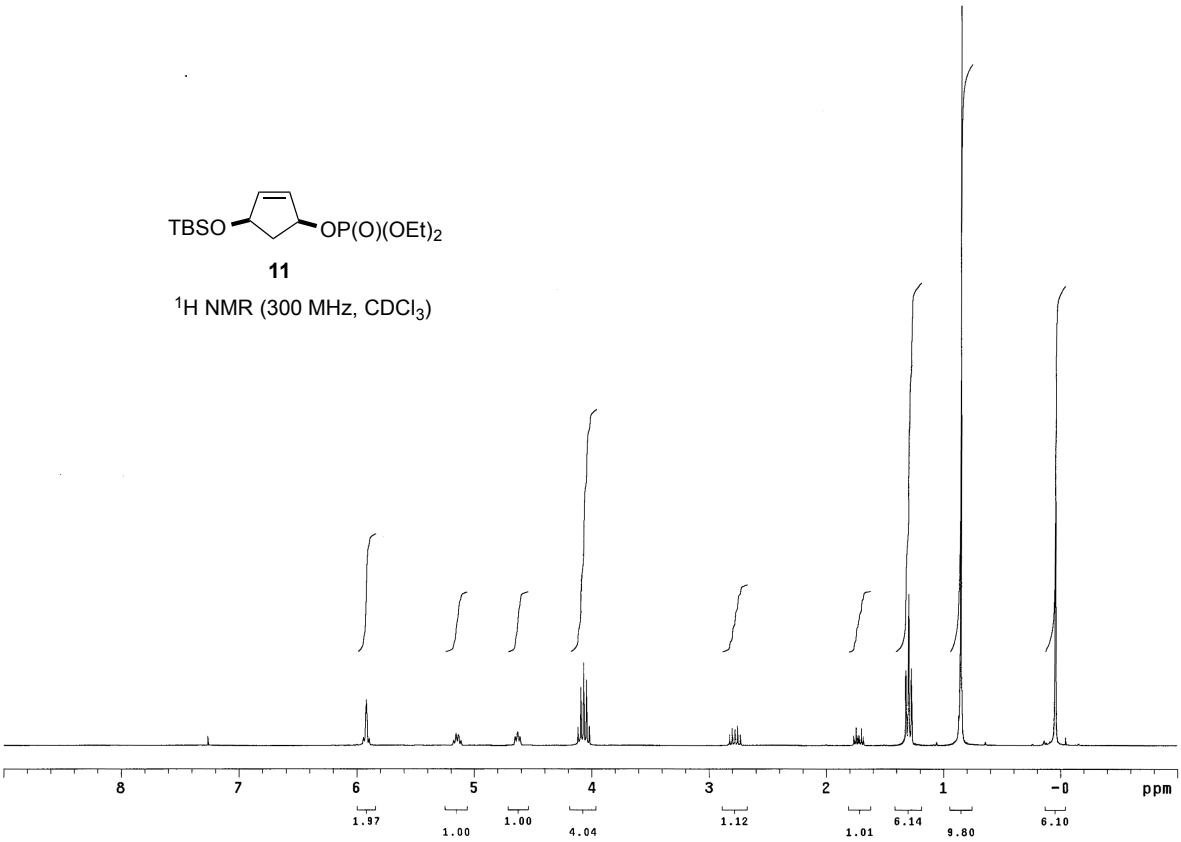


9

^{13}C NMR (100 MHz, $CDCl_3$)

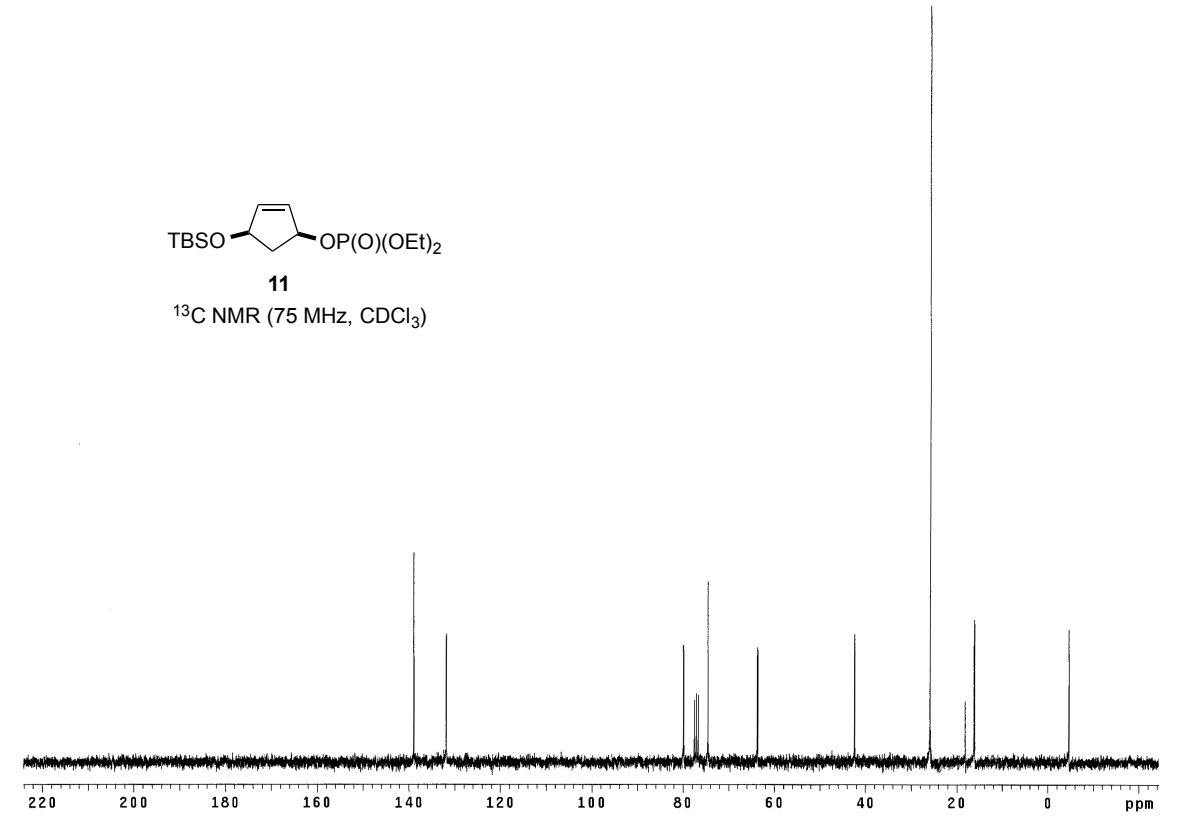

OP(O)(OEt)2
C5H11
TMS
(R)-10
1H NMR (400 MHz, CDCl3)
8
7
6
5
4
3
2
1
0
ppm
2.00
1.00
4.60
2.65
14.71
3.78
9.18


OP(O)(OEt)2
C5H11
TMS
(R)-10
13C NMR (100 MHz, CDCl3)
220
200
180
160
140
120
100
80
60
40
20
0
ppm



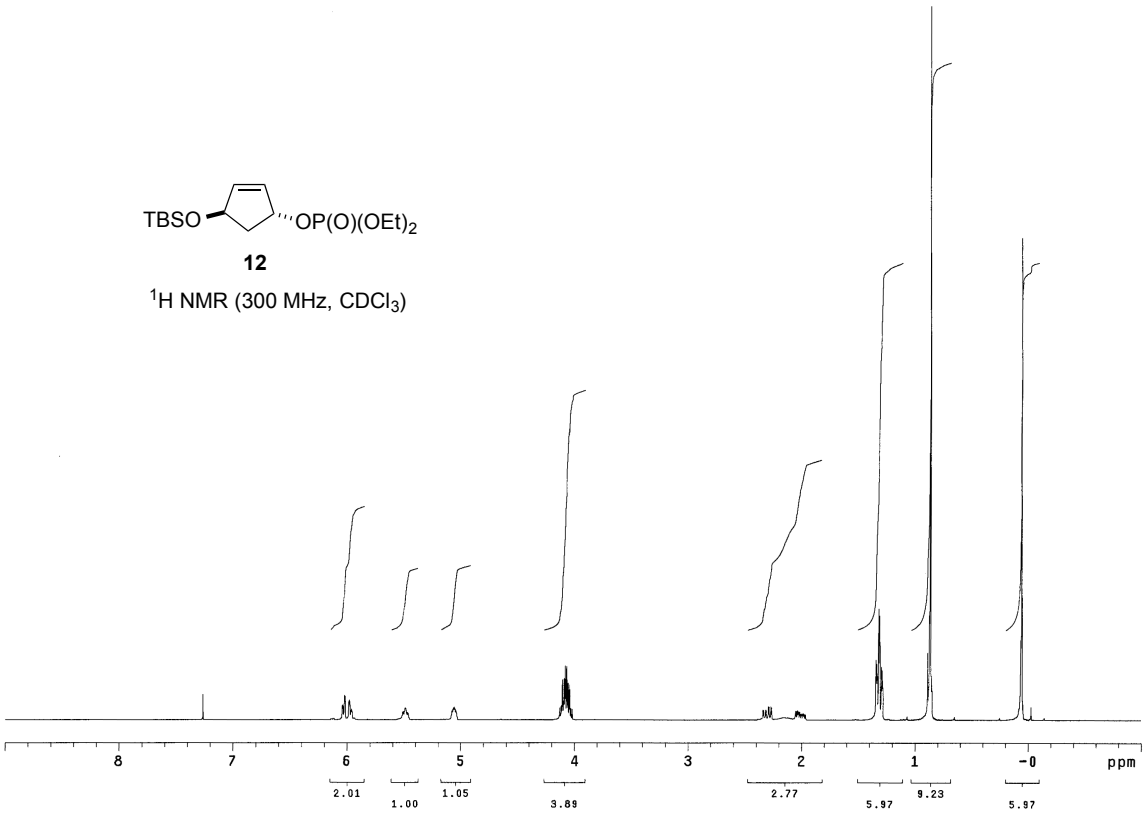
11

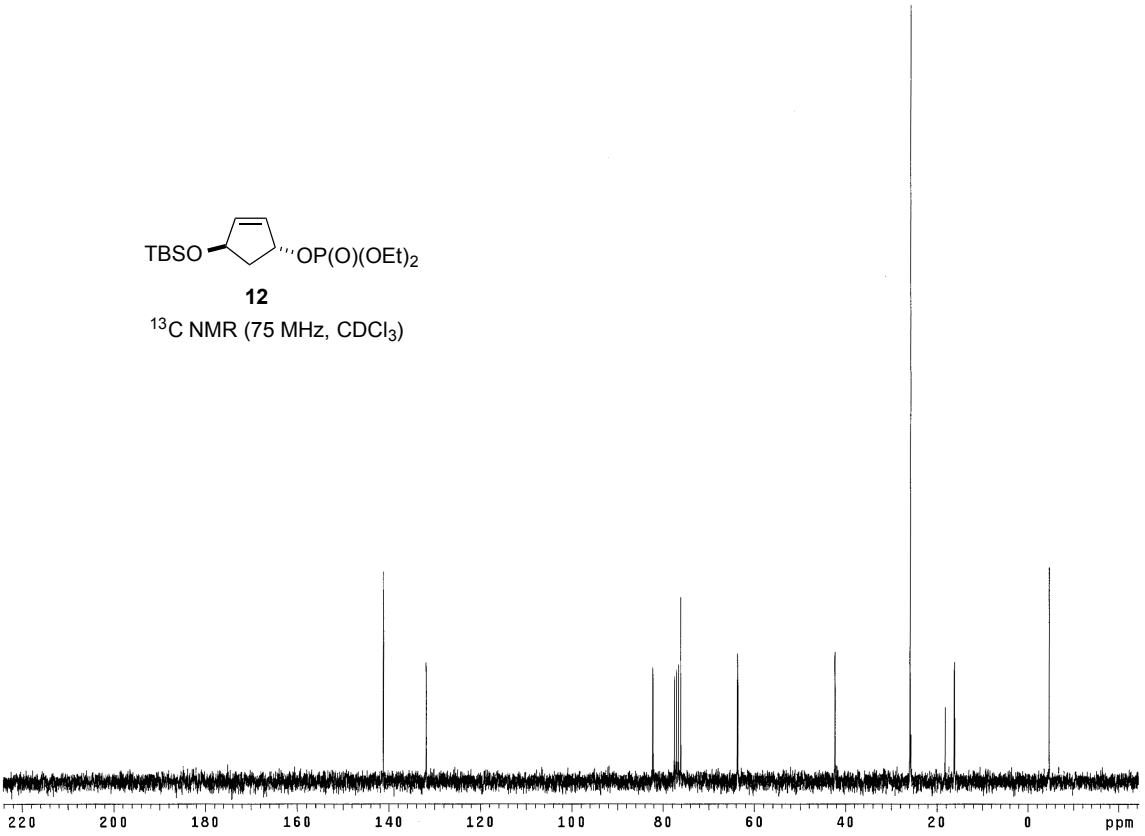
^{1}H NMR (300 MHz, $CDCl_3$)

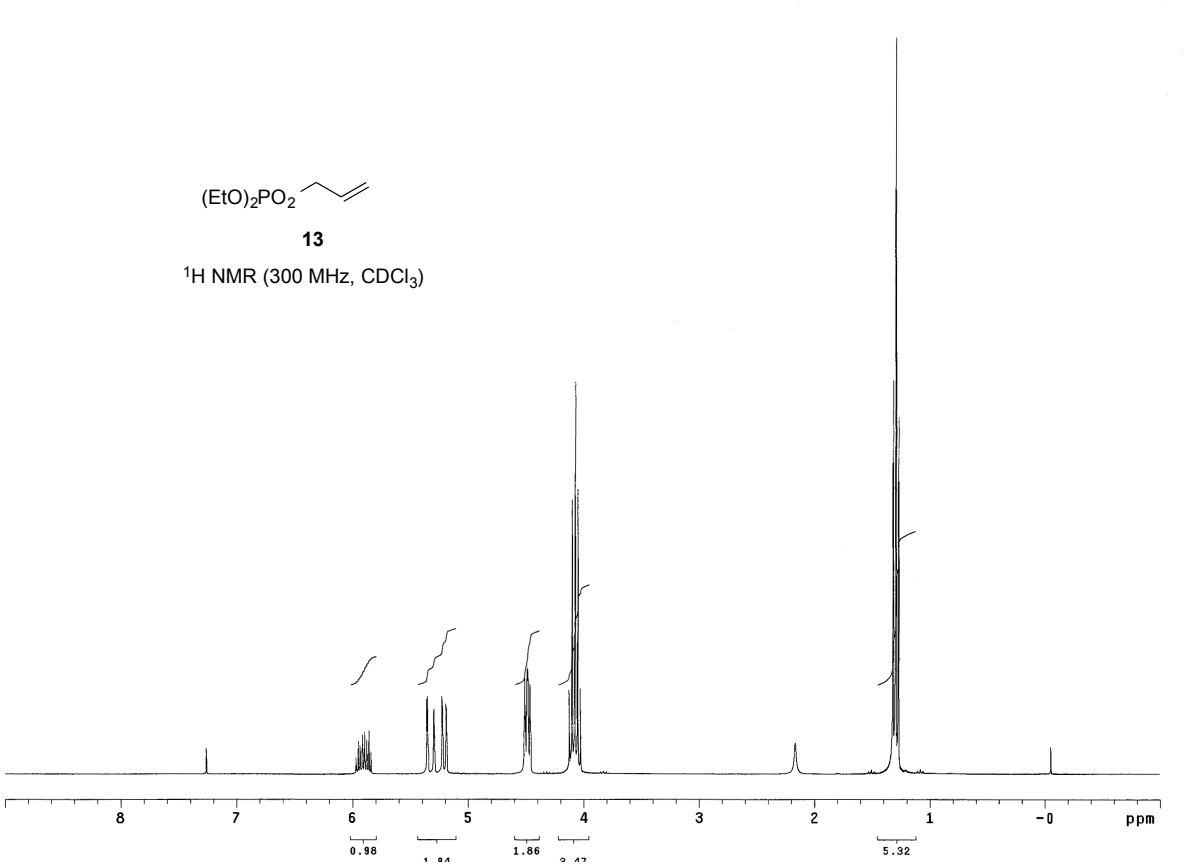


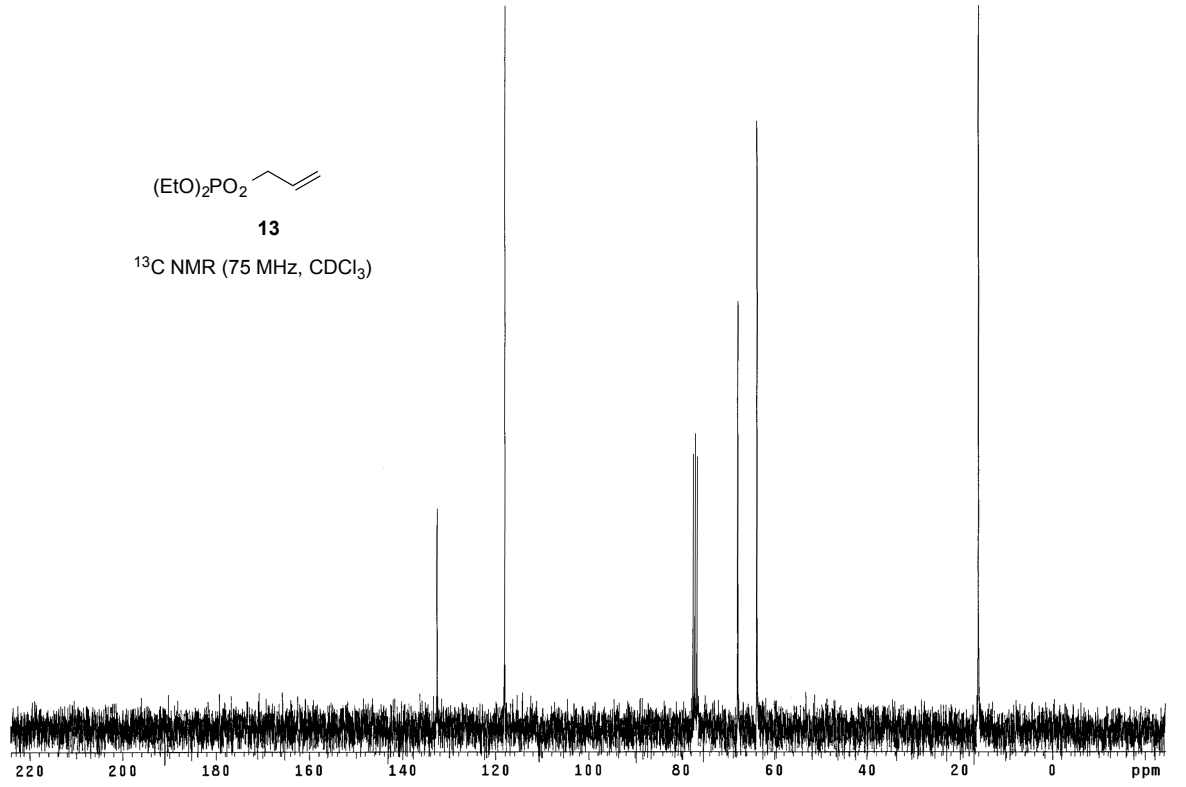
11

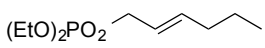
^{13}C NMR (75 MHz, $CDCl_3$)


TBSO
OP(O)(OEt)2
12
1H NMR (300 MHz, CDCl3)
8
7
6
5
4
3
2
1
-0
ppm
2.01
1.00
1.05
3.88
2.77
5.97
9.23
5.97


TBSO
OP(O)(OEt)2
12
13C NMR (75 MHz, CDCl3)
220
200
180
160
140
120
100
80
60
40
20
0
ppm

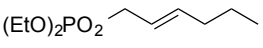

(EtO)2PO2
13
1H NMR (300 MHz, CDCl3)
8
7
6
5
4
3
2
1
-0
ppm
0.98
1.86
5.32


(EtO)2PO2
13
13C NMR (75 MHz, CDCl3)
220
200
180
160
140
120
100
80
60
40
20
0
ppm



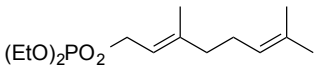
14

^{1}H NMR (400 MHz, $CDCl_3$)



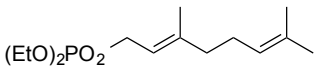
14

^{13}C NMR (100 MHz, $CDCl_3$)



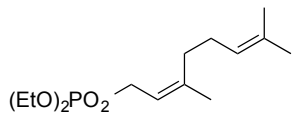
15

^{1}H NMR (300 MHz, $CDCl_3$)



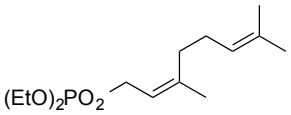
15

^{13}C NMR (75 MHz, $CDCl_3$)



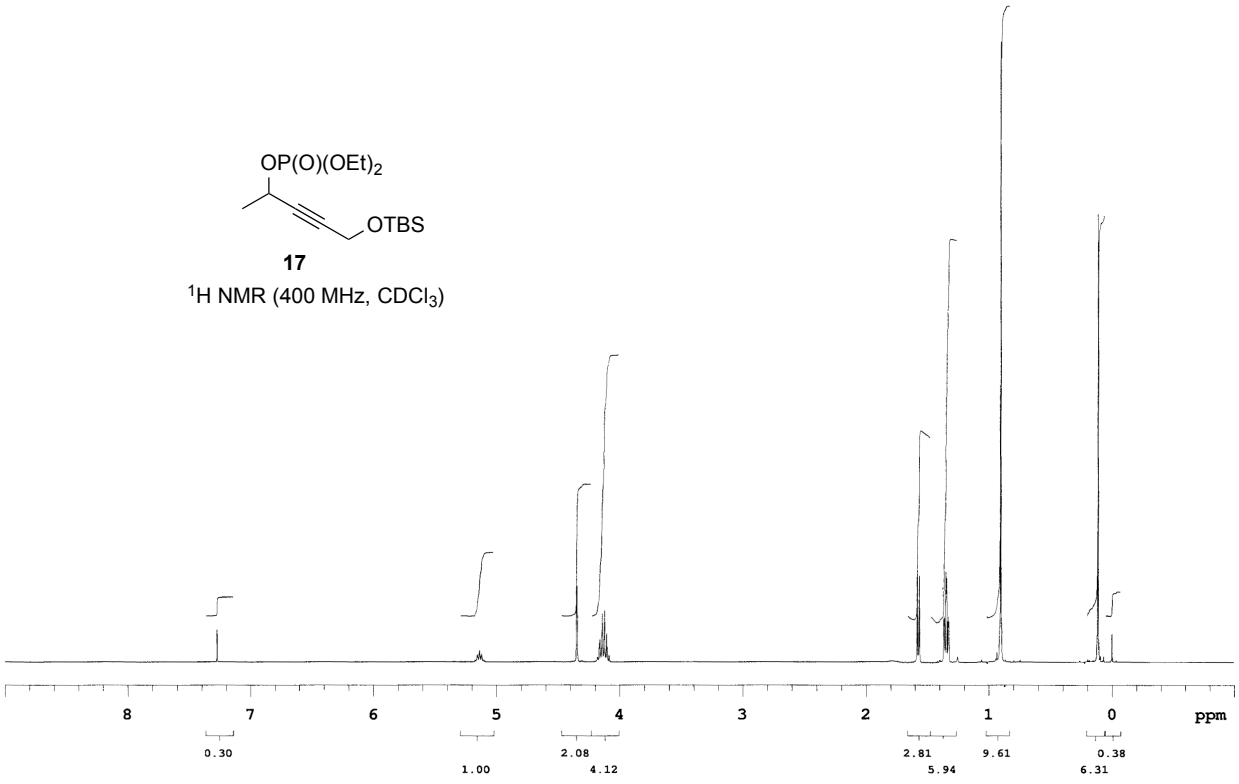
16

^{1}H NMR (300 MHz, $CDCl_3$)



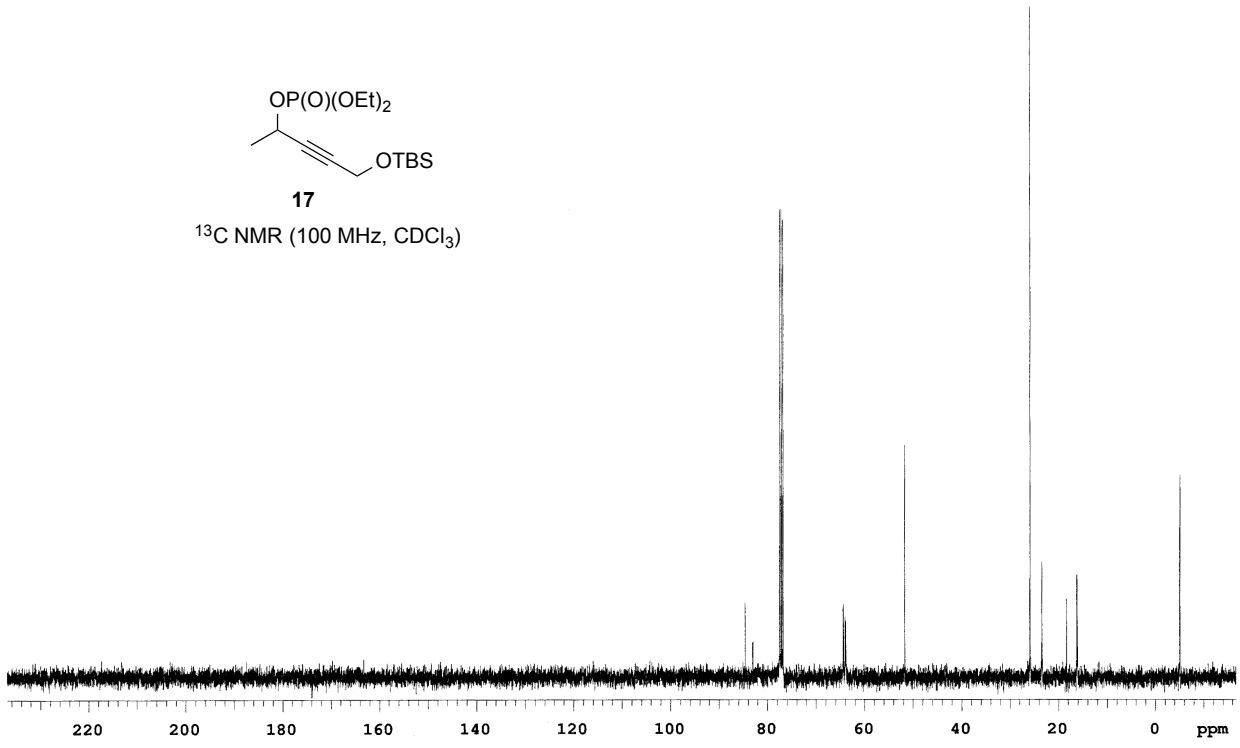
16

^{13}C NMR (75 MHz, $CDCl_3$)



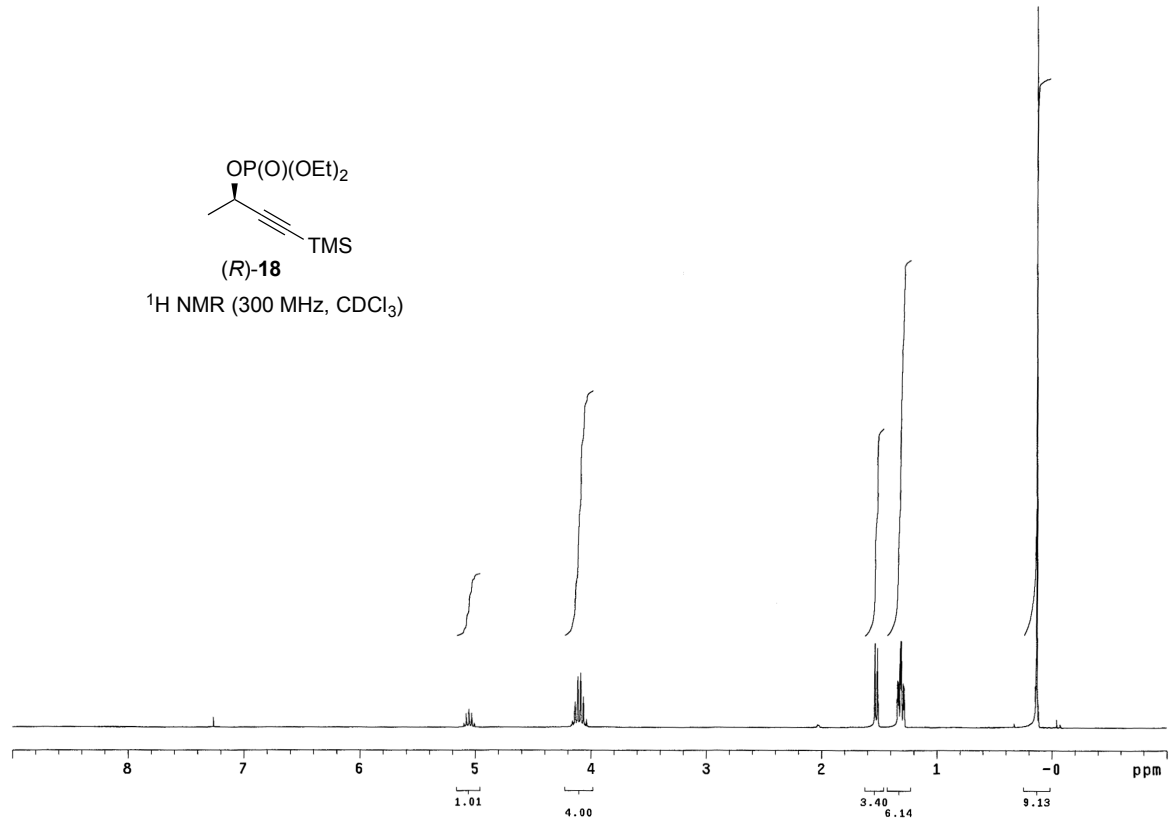
17

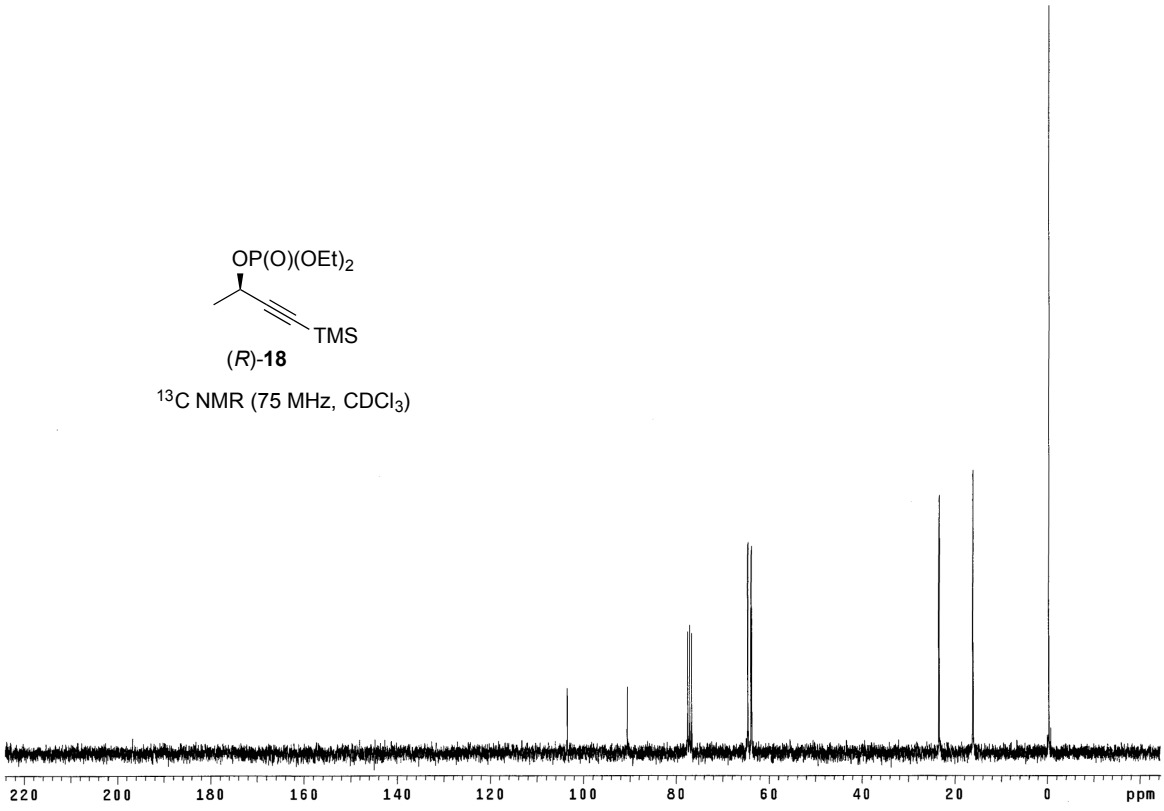
^{1}H NMR (400 MHz, $CDCl_3$)

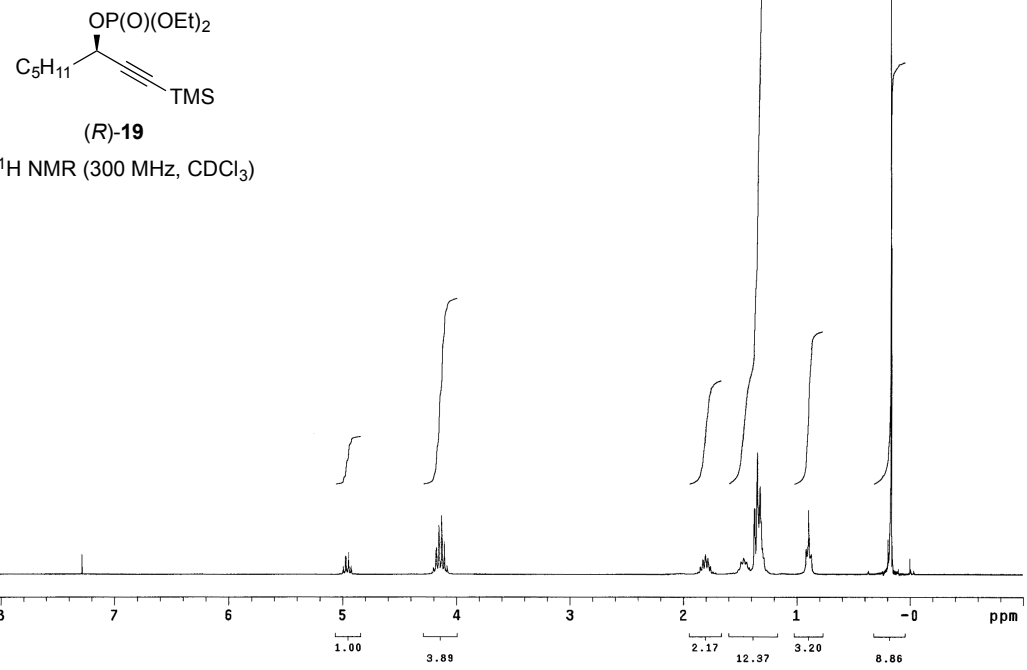


17

^{13}C NMR (100 MHz, $CDCl_3$)

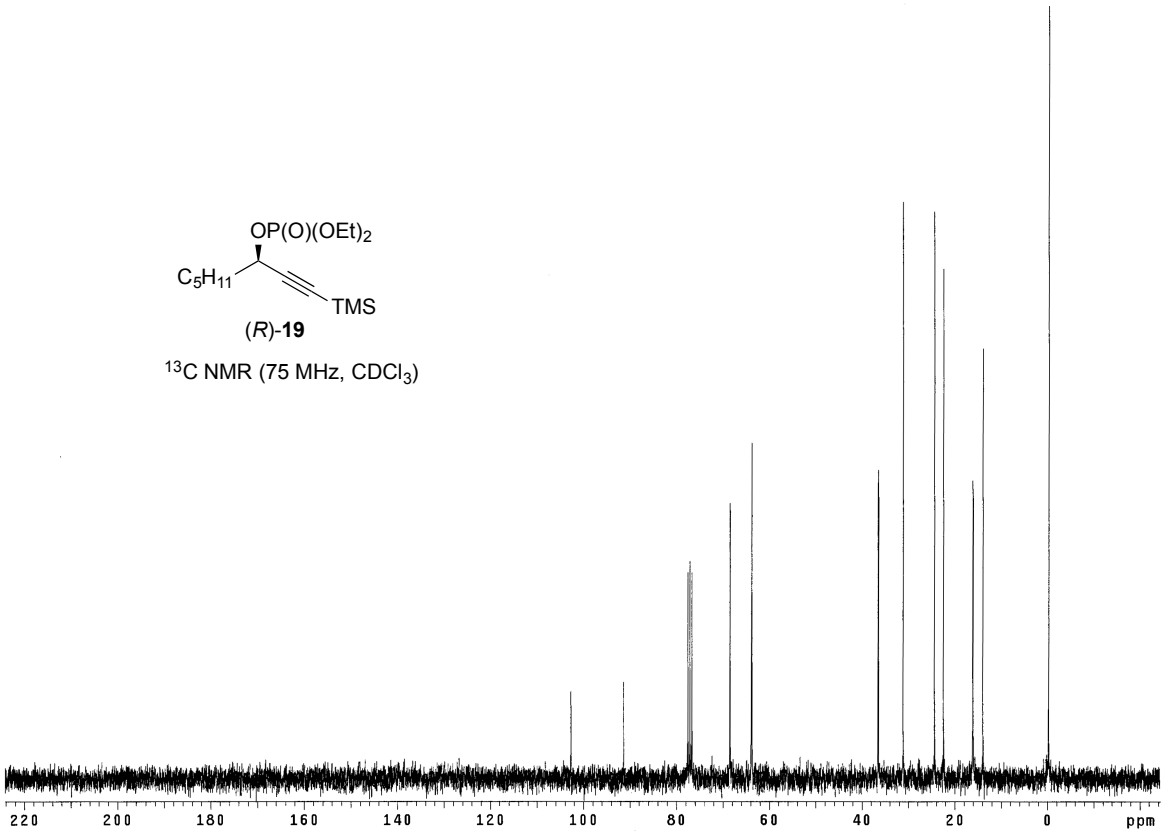

OP(O)(OEt)2
TMS
(R)-18
1H NMR (300 MHz, CDCl3)
8
7
6
5
4
3
2
1
-0
ppm
1.01
4.00
3.40
6.14
9.13


OP(O)(OEt)2
TMS
(R)-18
13C NMR (75 MHz, CDCl3)
220
200
180
160
140
120
100
80
60
40
20
0
ppm



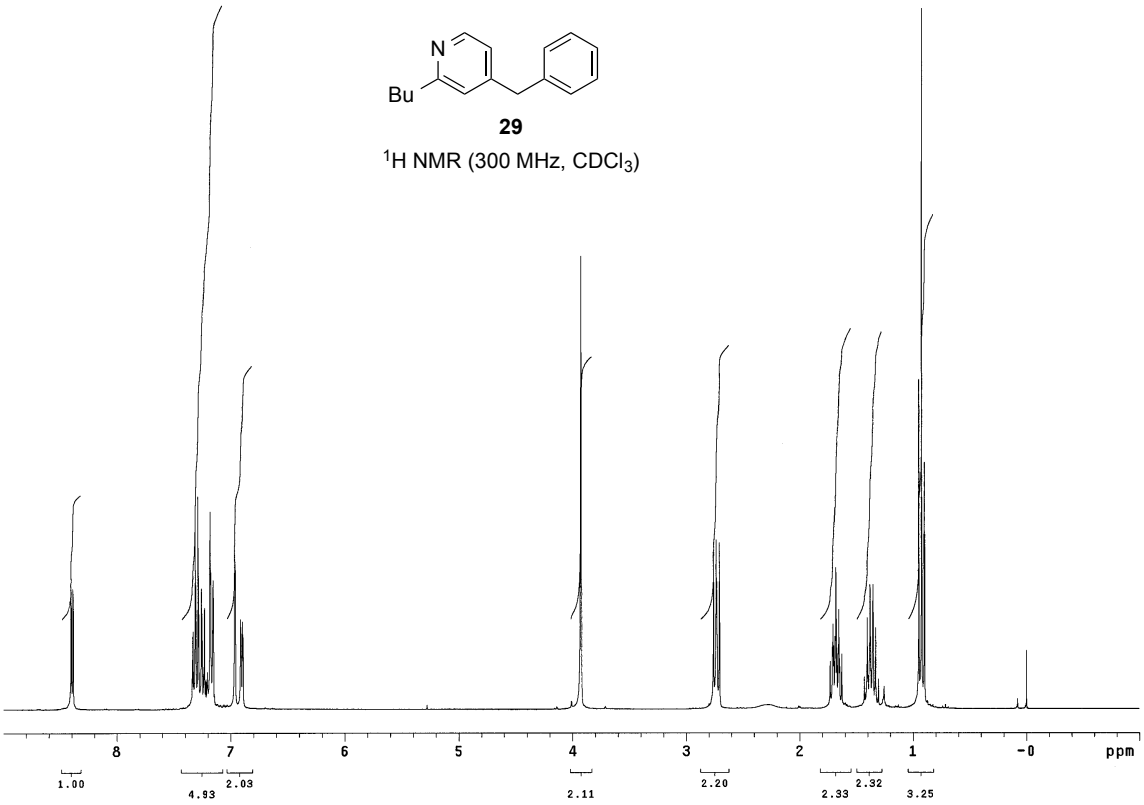
(*R*)-**19**

^{1}H NMR (300 MHz, $CDCl_3$)



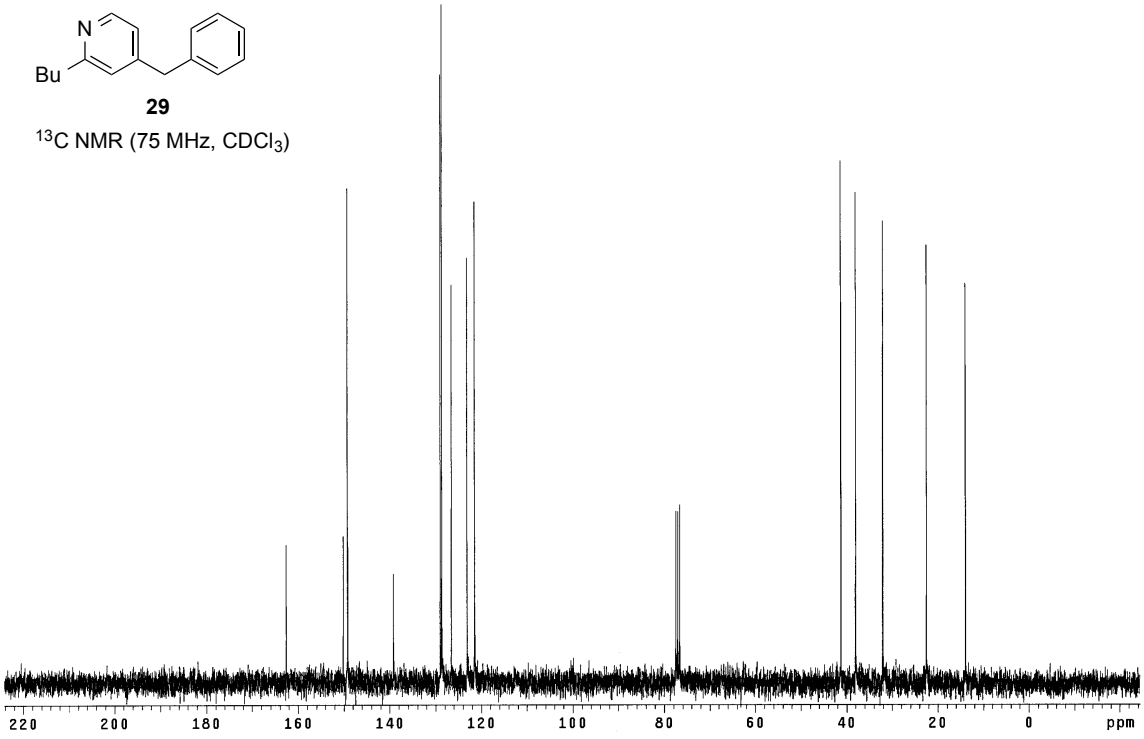
(*R*)-**19**

^{13}C NMR (75 MHz, $CDCl_3$)



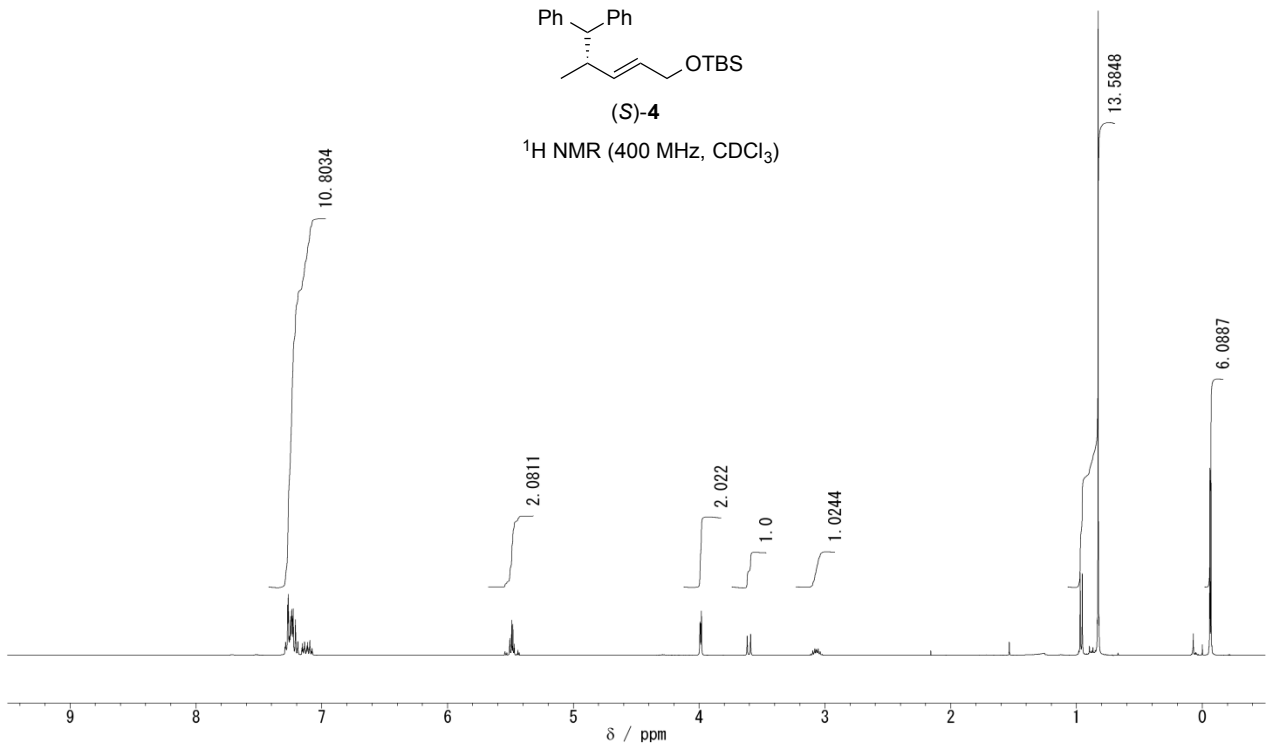
29

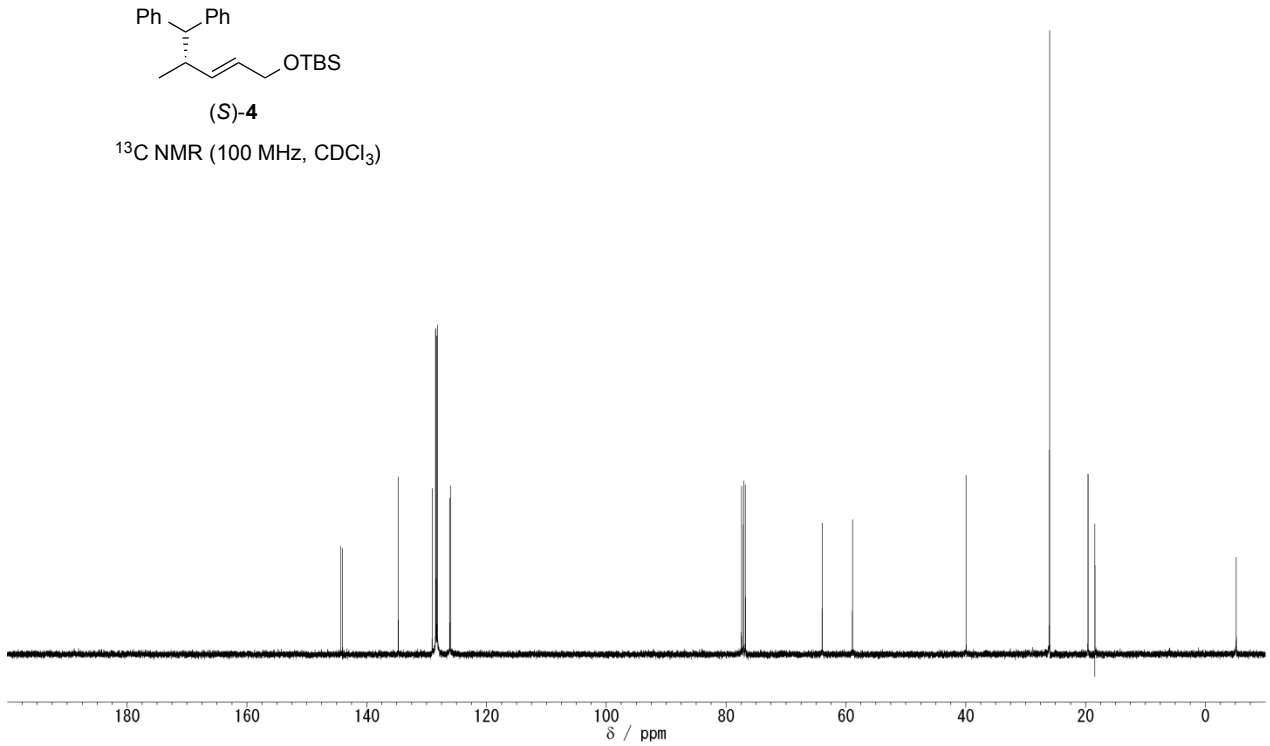
^{1}H NMR (300 MHz, $CDCl_3$)

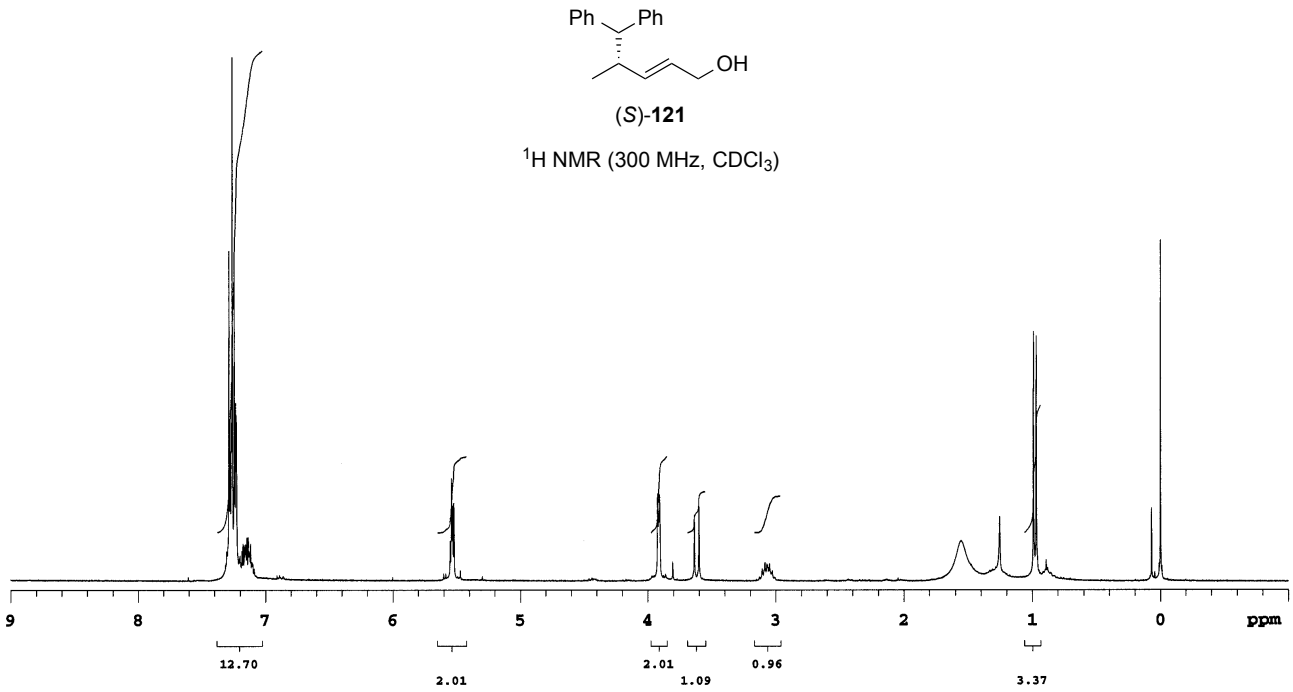


29

^{13}C NMR (75 MHz, $CDCl_3$)

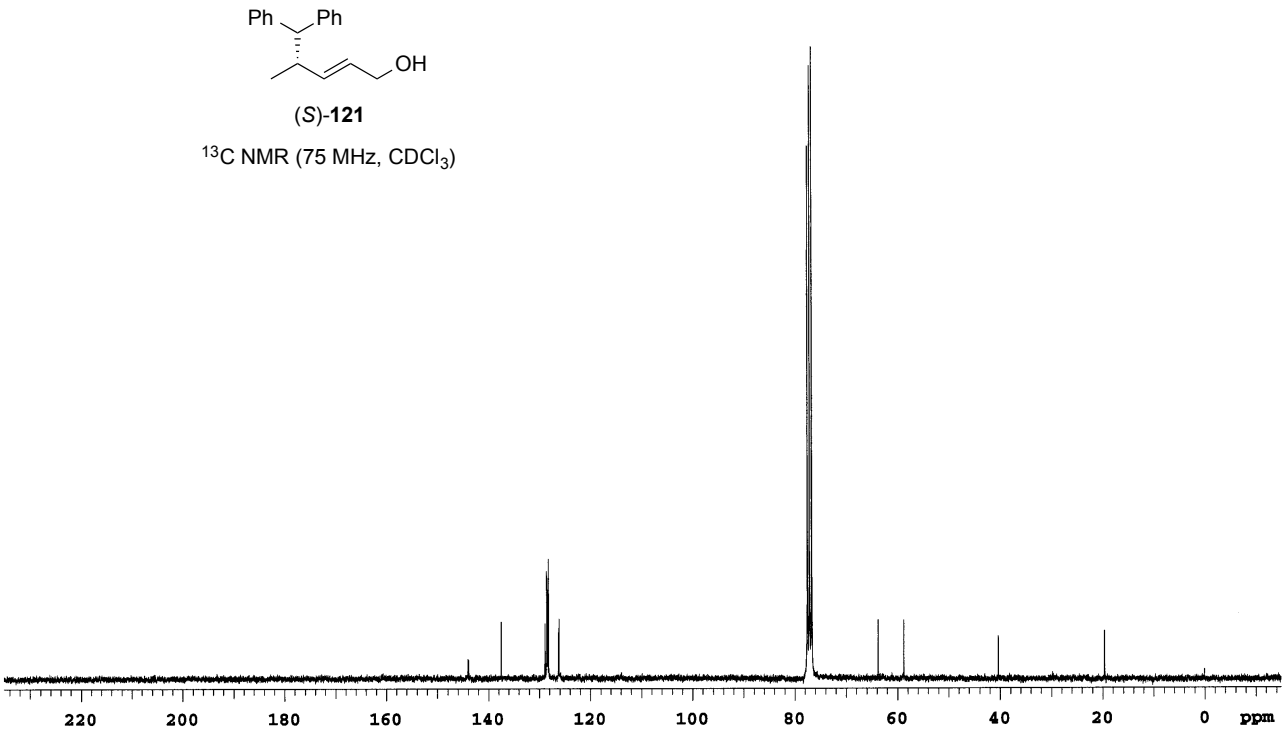

Ph
Ph
OTBS
(S)-4
1H NMR (400 MHz, CDCl3)
10.8034
2.0811
2.022
1.0
1.0244
13.5848
6.0887
9
8
7
6
5
4
3
2
1
0
δ / ppm


Ph
Ph
OTBS
(S)-4
13C NMR (100 MHz, CDCl3)
180
160
140
120
100
80
60
40
20
0
δ / ppm



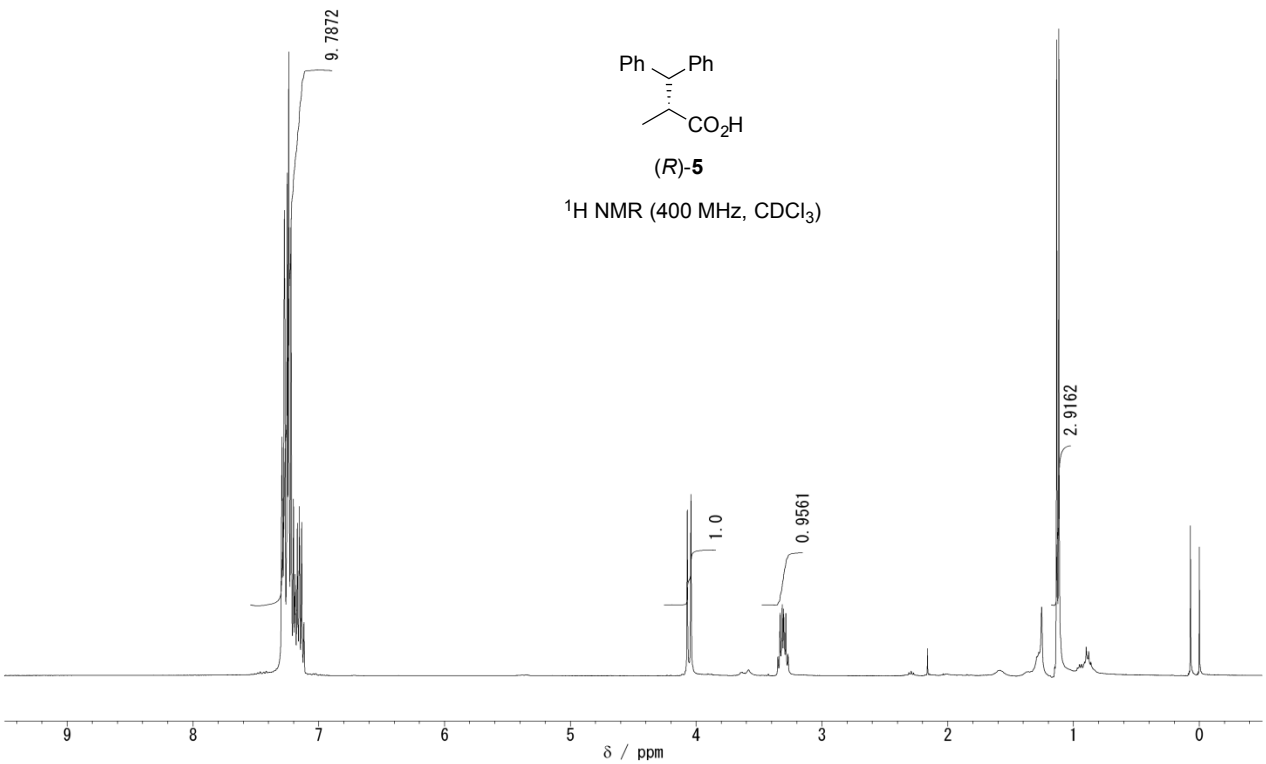
(*S*)-**121**

^{1}H NMR (300 MHz, $CDCl_3$)



(*S*)-**121**

^{13}C NMR (75 MHz, $CDCl_3$)

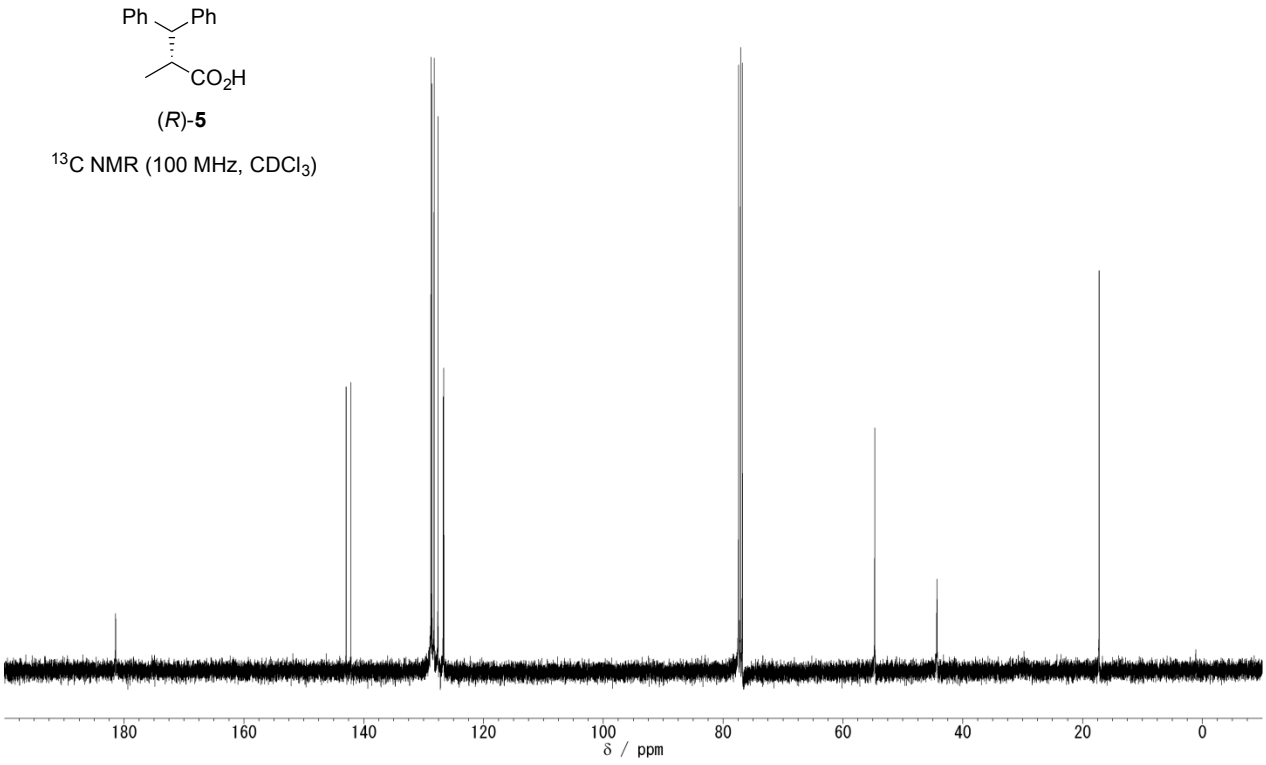


Ph Ph

CO_2H

(*R*)-**5**

^{1}H NMR (400 MHz, $CDCl_3$)

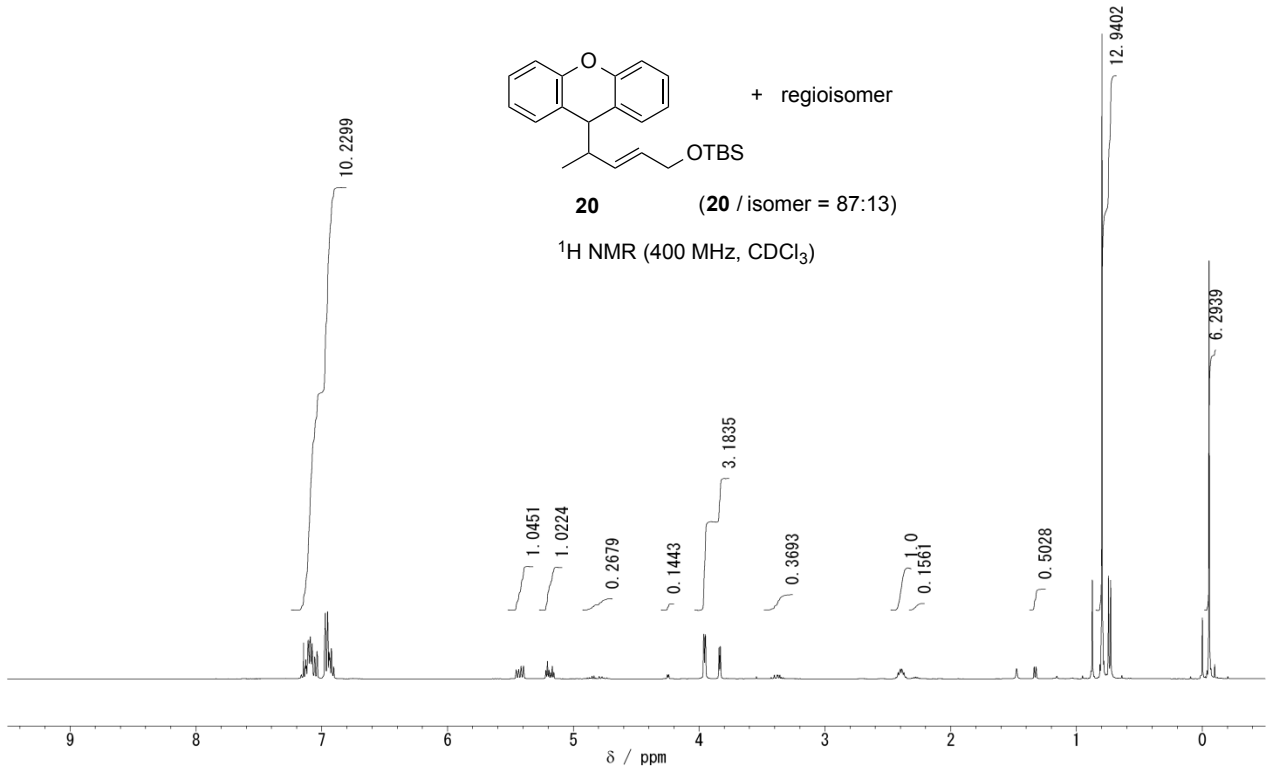


Ph Ph

CO_2H

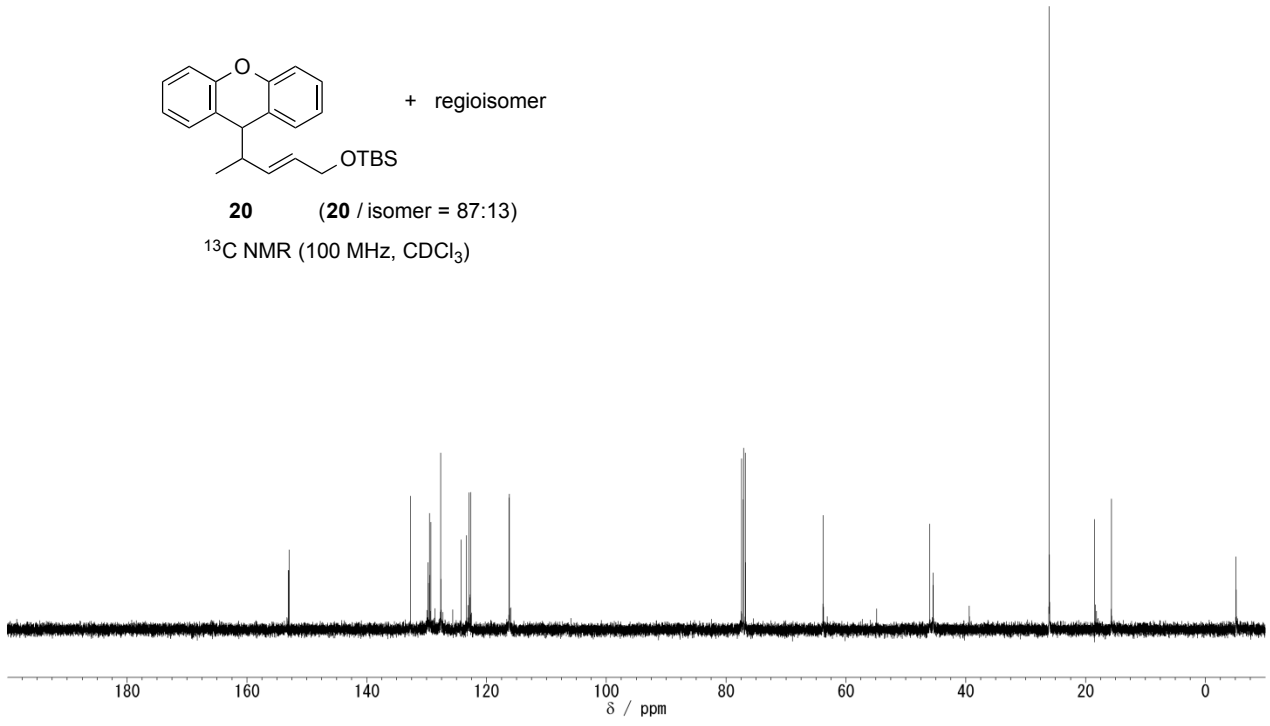
(*R*)-**5**

^{13}C NMR (100 MHz, $CDCl_3$)



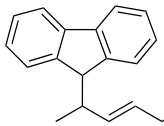
20 (**20** / isomer = 87:13)

^{1}H NMR (400 MHz, $CDCl_3$)



20 (**20** / isomer = 87:13)

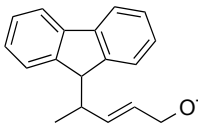
^{13}C NMR (100 MHz, $CDCl_3$)



+ regioisomer

21 (**21** / isomer = 85:15)

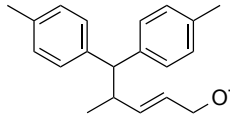
^{1}H NMR (400 MHz, $CDCl_3$)



+ regioisomer

21 (**21** / isomer = 85:15)

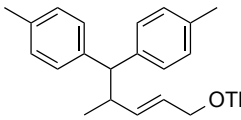
^{13}C NMR (100 MHz, $CDCl_3$)



+ regioisomer

22 (**22** / isomer = 92:8)

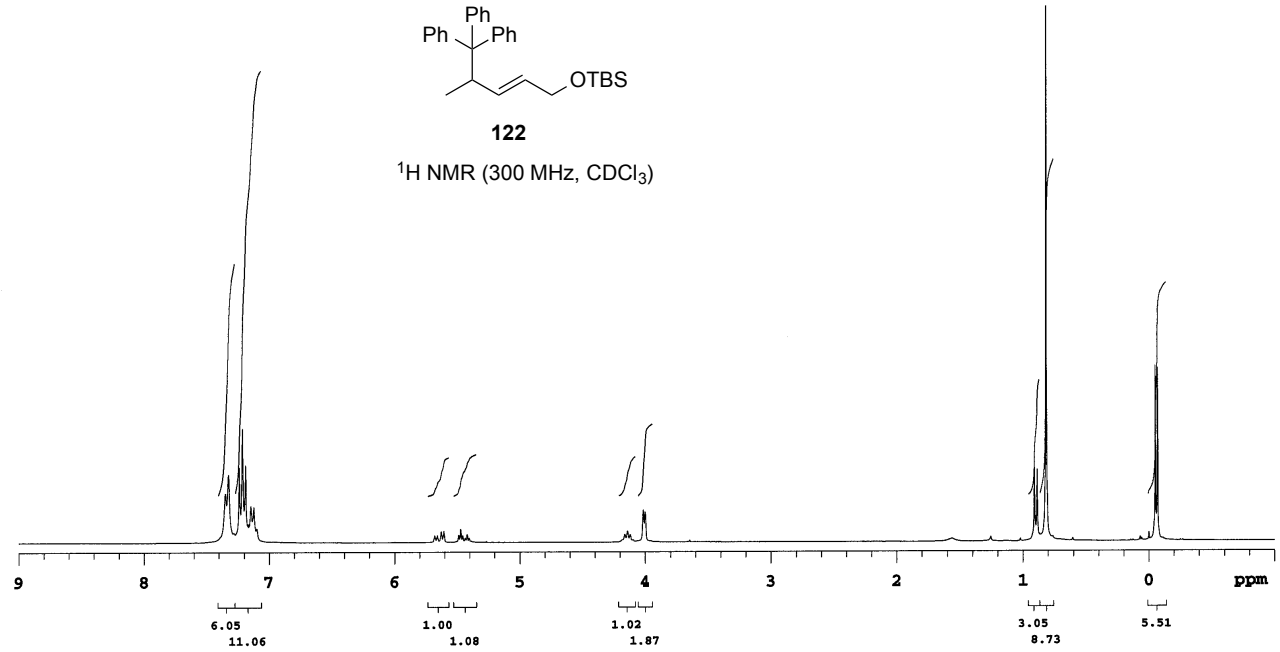
^{1}H NMR (400 MHz, $CDCl_3$)



+ regioisomer

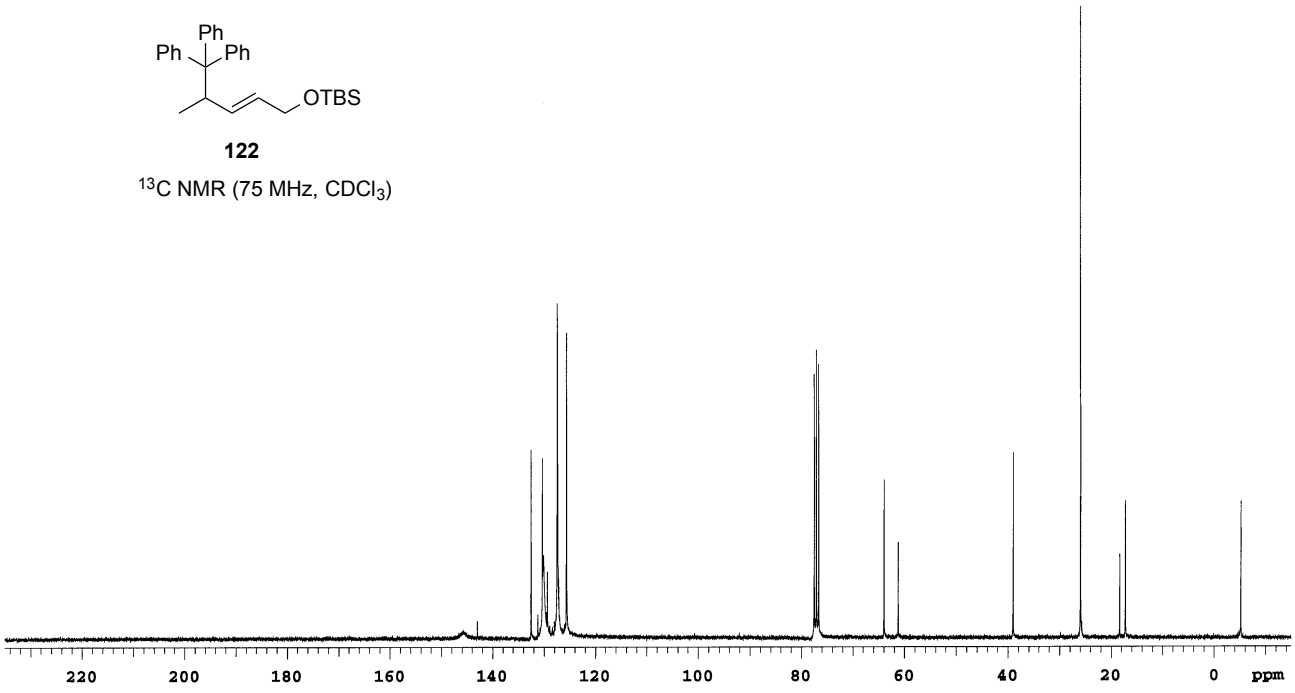
22 (**22** / isomer = 92:8)

^{13}C NMR (100 MHz, $CDCl_3$)



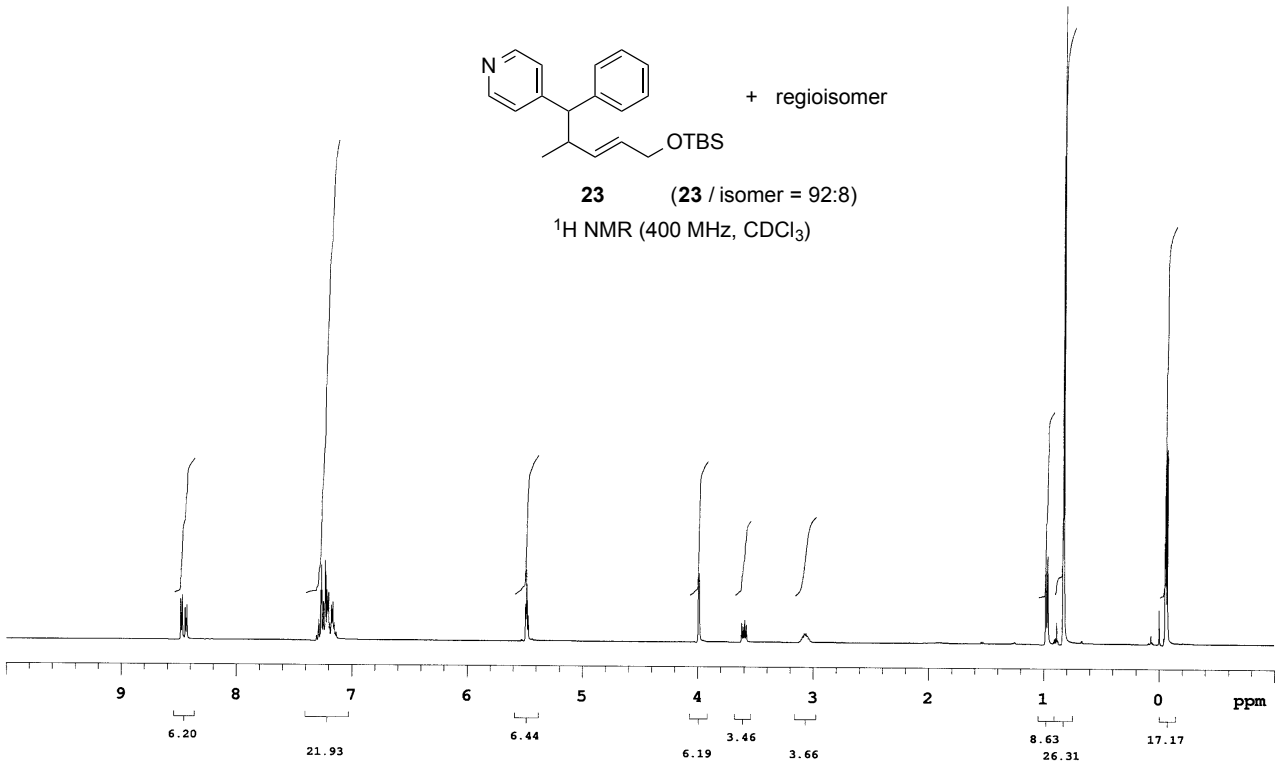
122

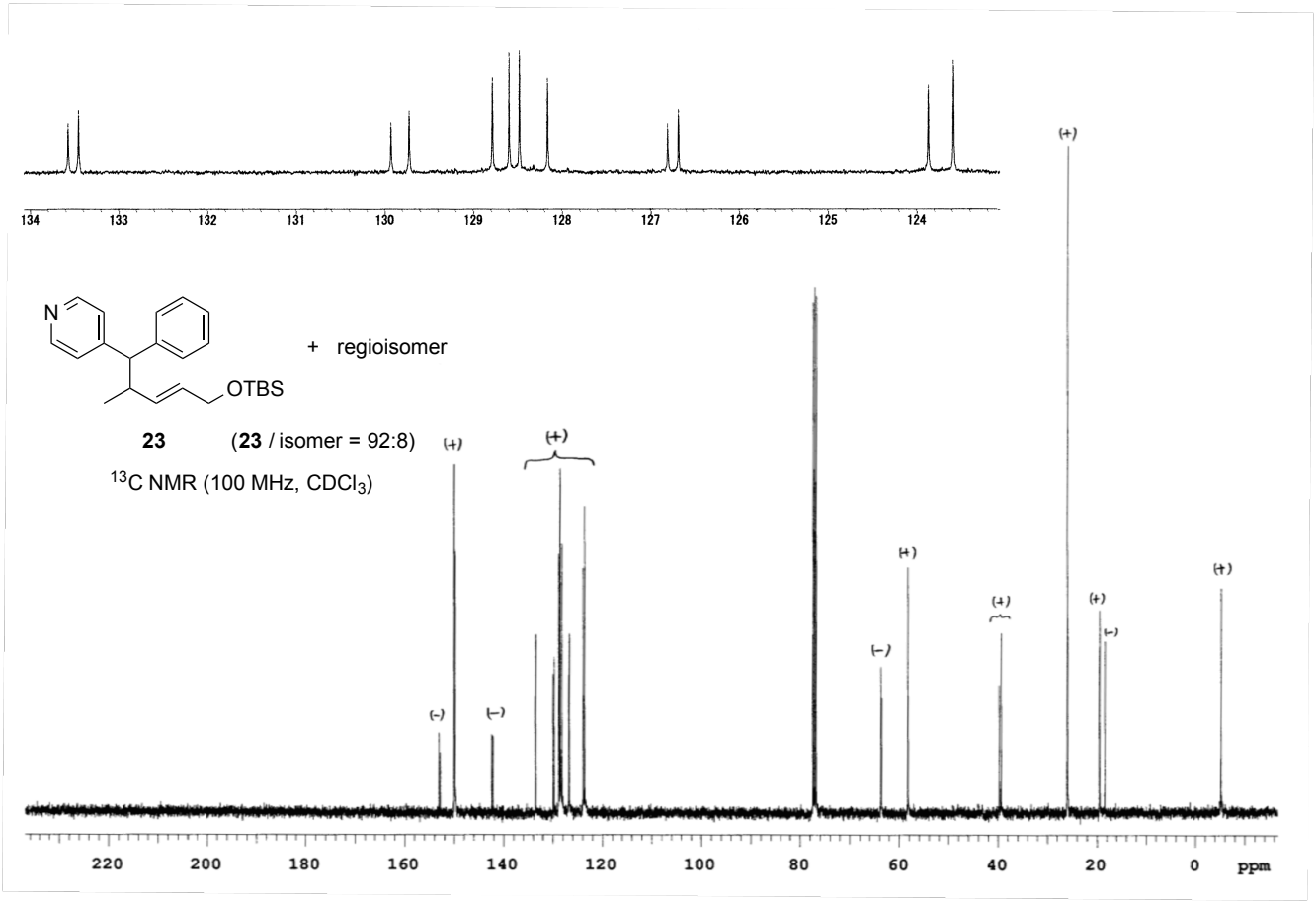
^{1}H NMR (300 MHz, $CDCl_3$)

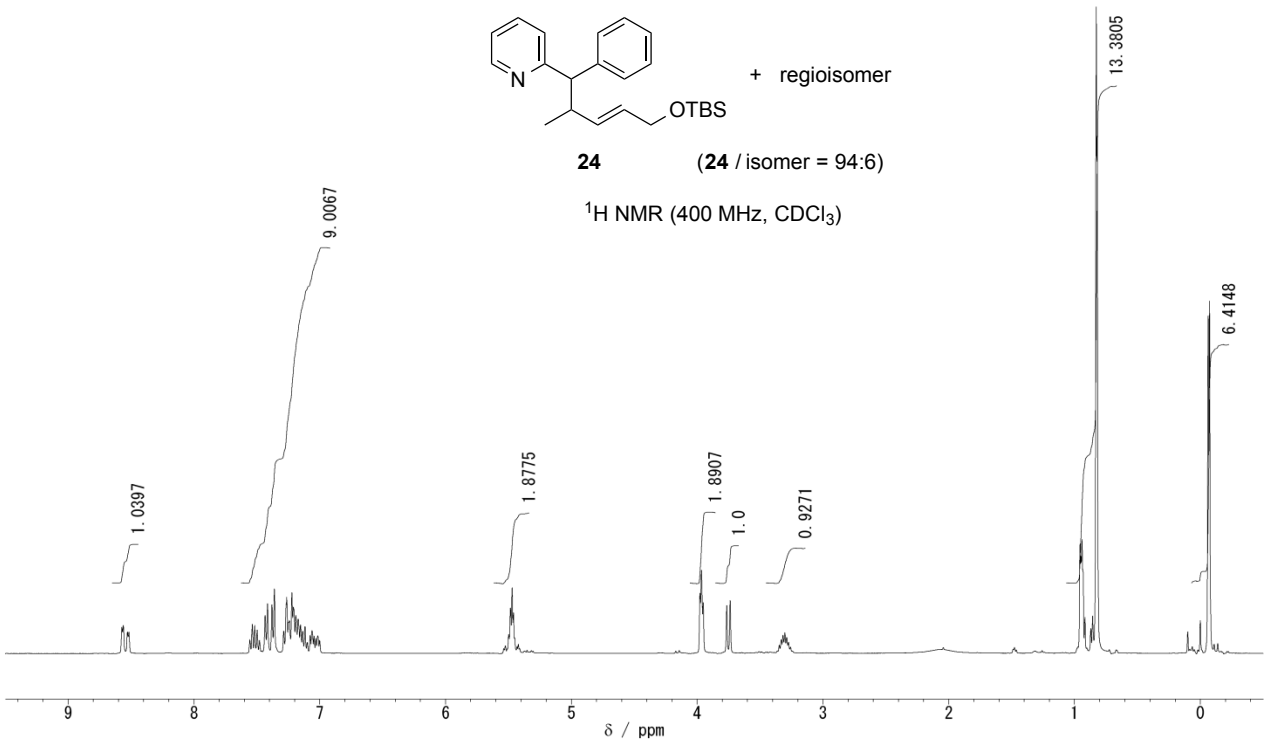


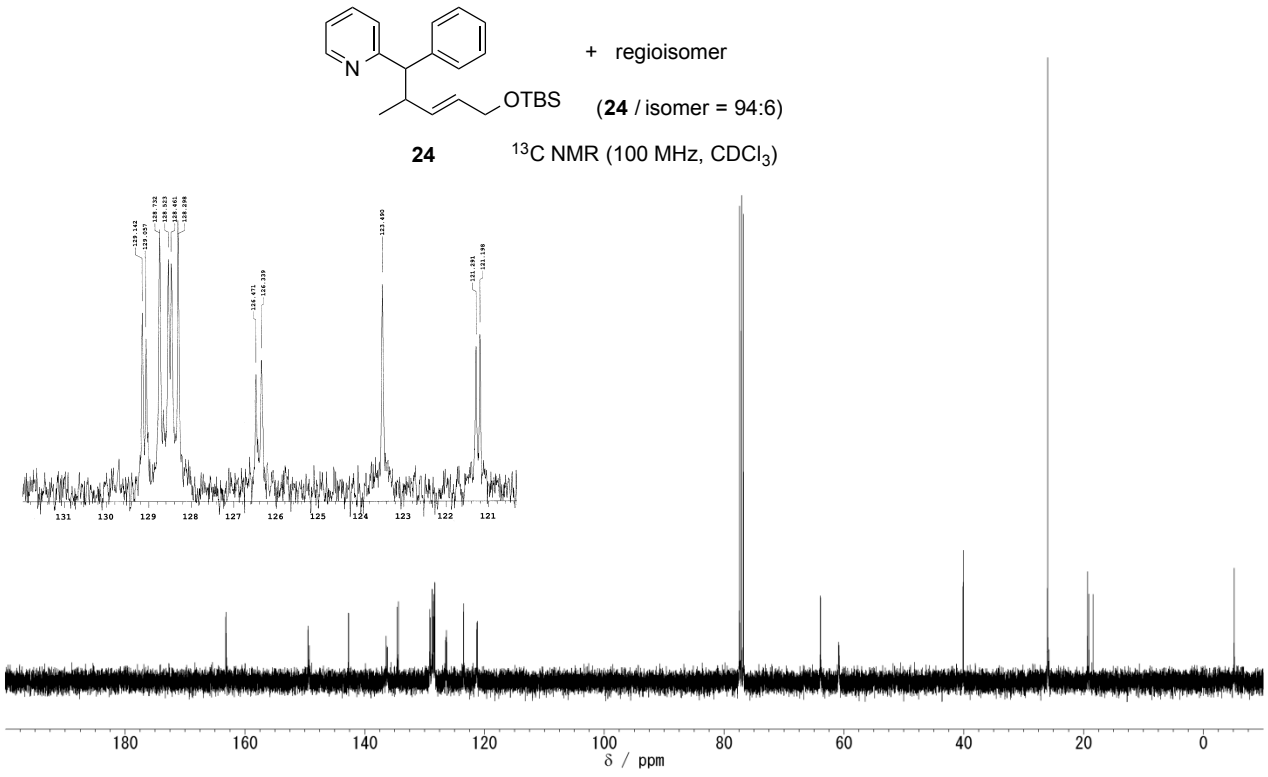
122

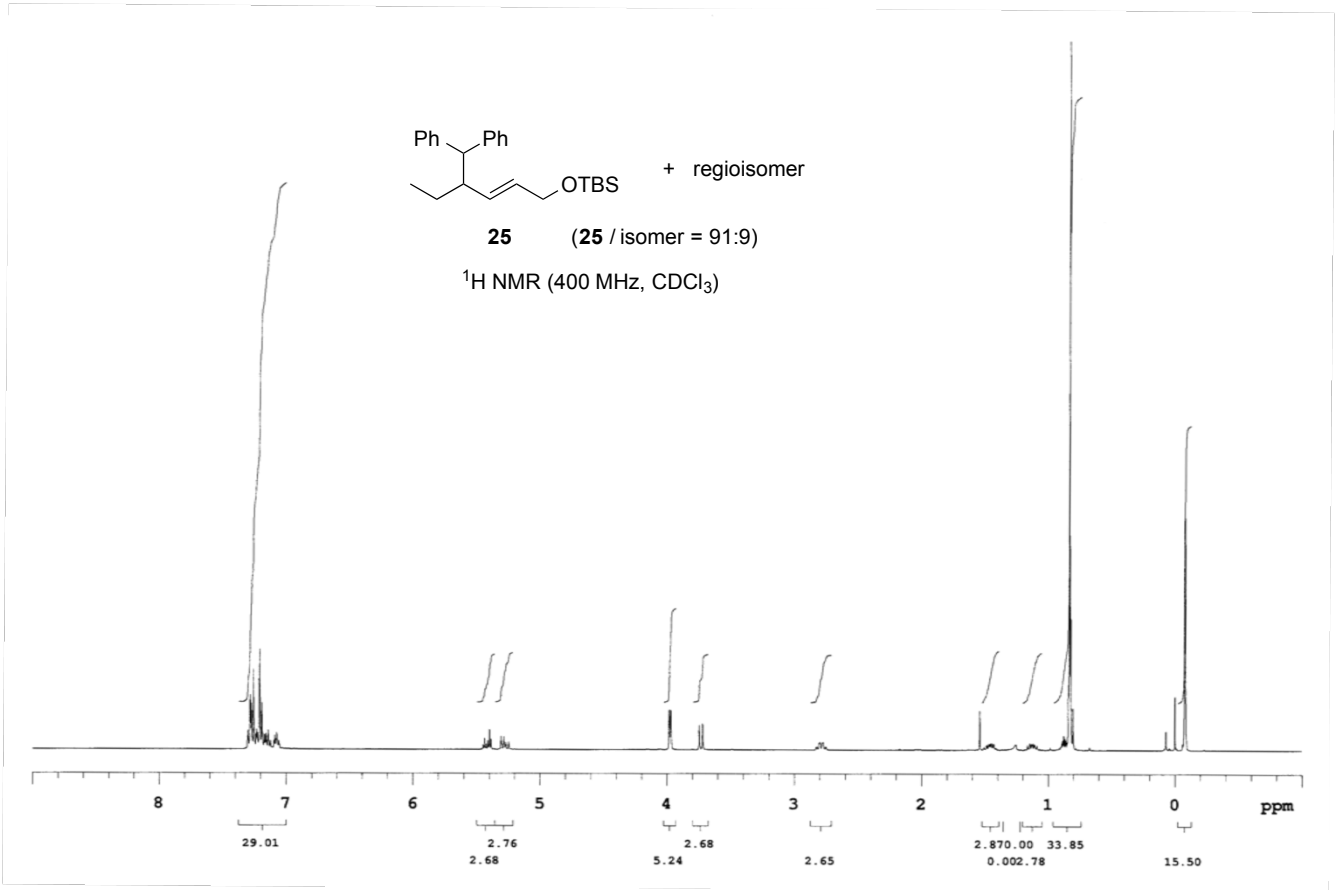
^{13}C NMR (75 MHz, $CDCl_3$)

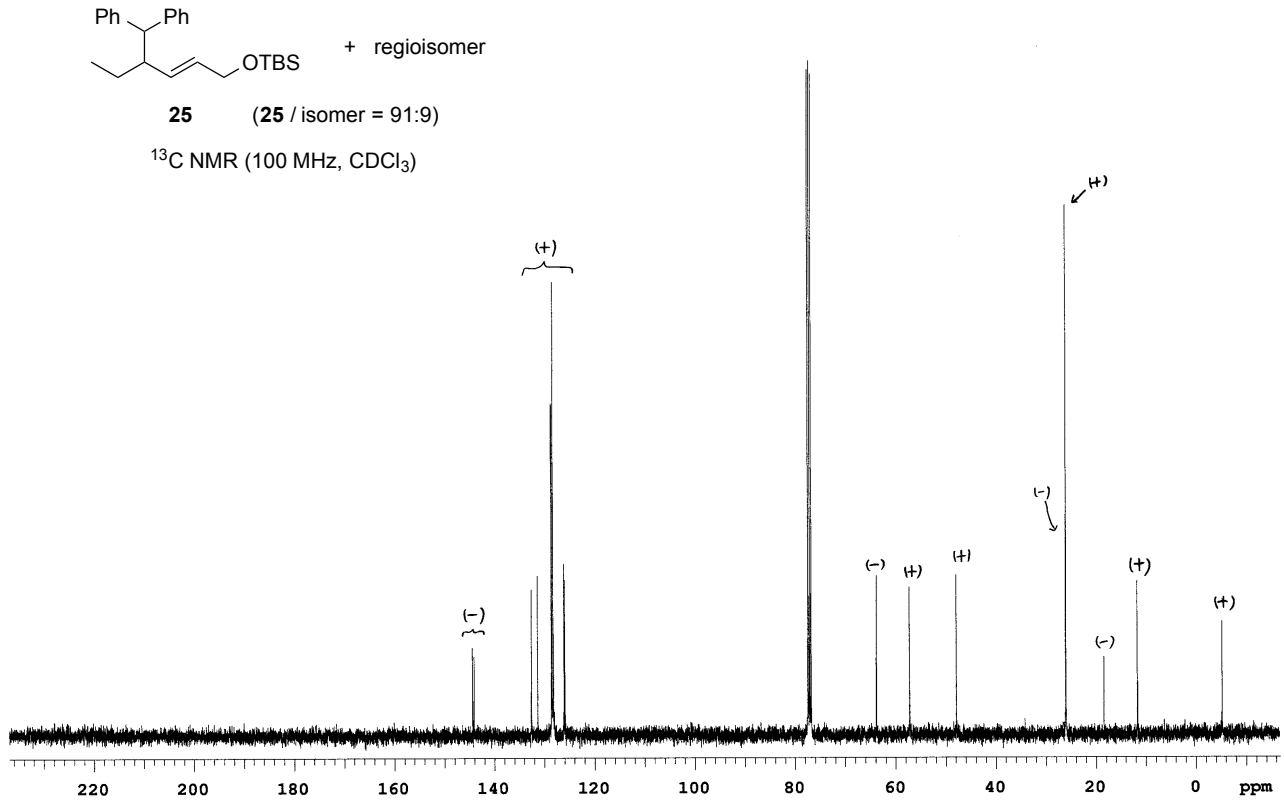

N
OTBS
+ regioisomer
23 (23 / isomer = 92:8)
1H NMR (400 MHz, CDCl3)
9 8 7 6 5 4 3 2 1 0 ppm
6.20
21.93
6.44
6.19
3.46
3.66
8.63
26.31
17.17

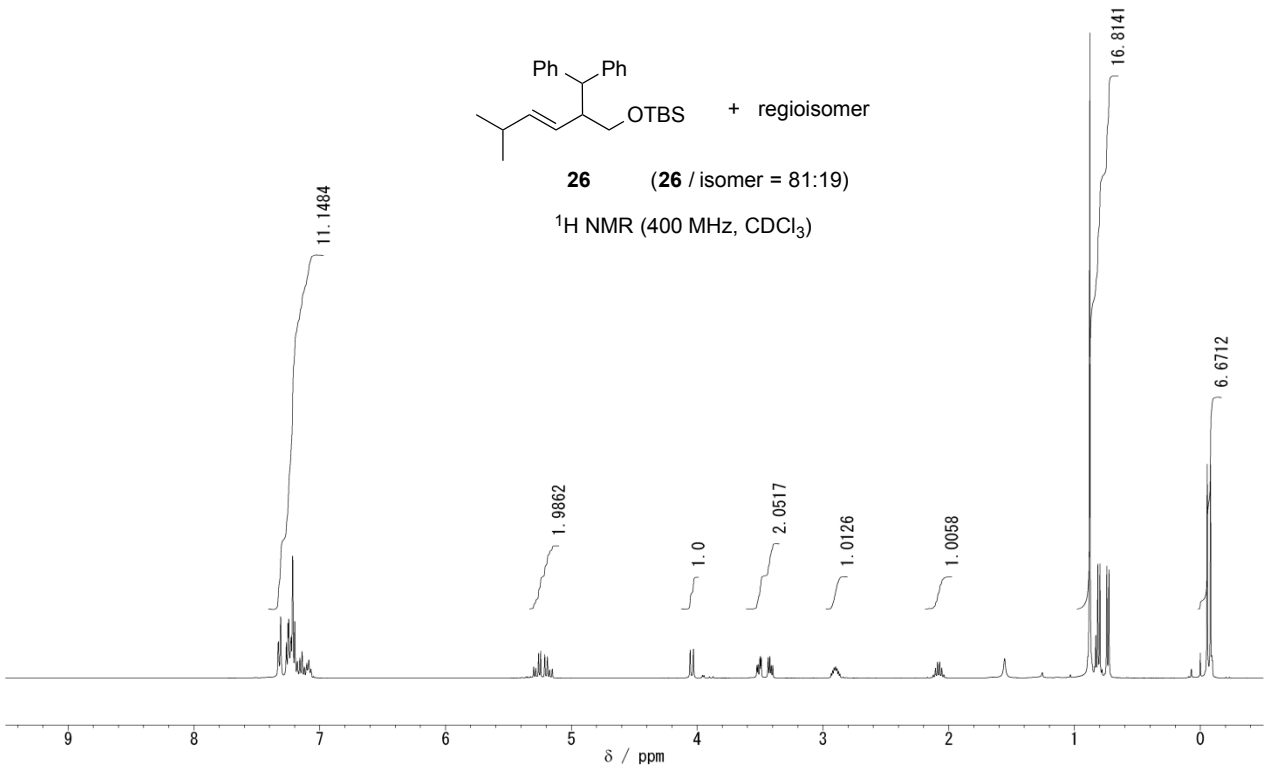

134 133 132 131 130 129 128 127 126 125 124
N
OTBS
+ regioisomer
23 (23 / isomer = 92:8)
13C NMR (100 MHz, CDCl3)
220 200 180 160 140 120 100 80 60 40 20 0 ppm

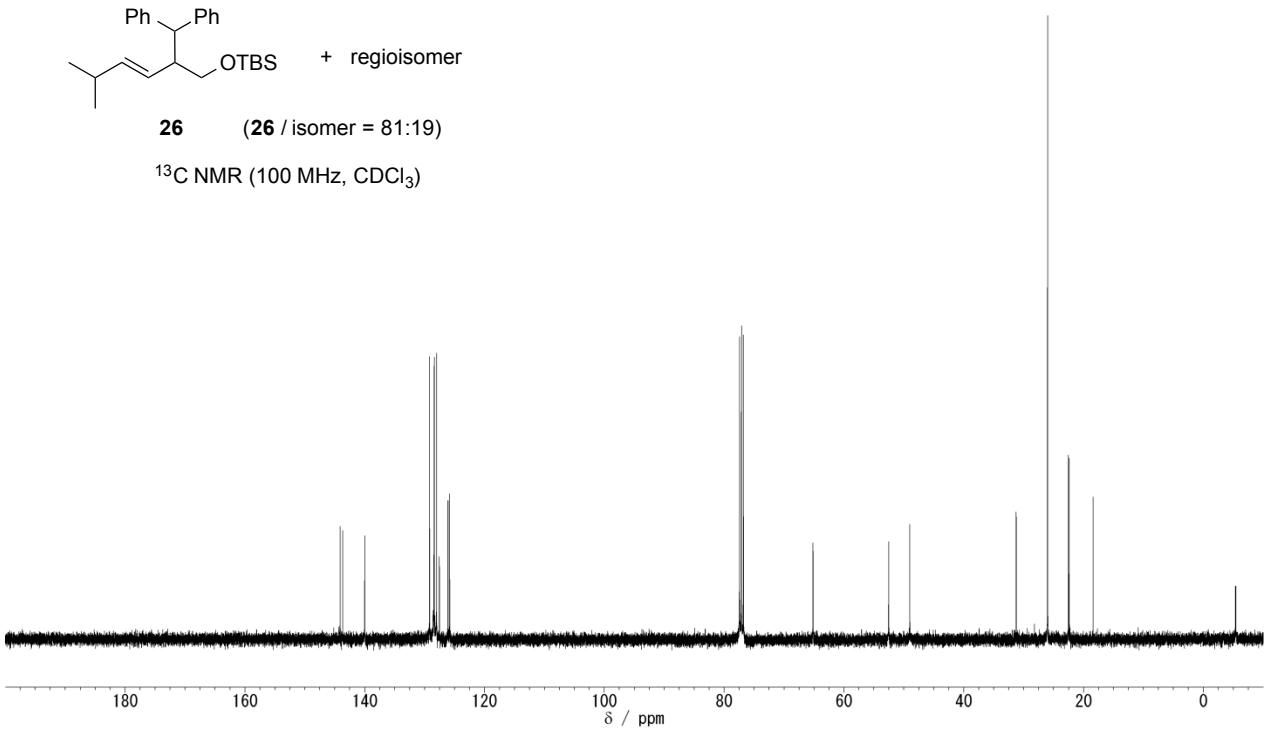

N
OTBS
+ regioisomer
24
(24 / isomer = 94:6)
1H NMR (400 MHz, CDCl3)
13.3805
9.0067
6.4148
1.8775
1.8907
1.0397
1.0
0.9271
δ / ppm

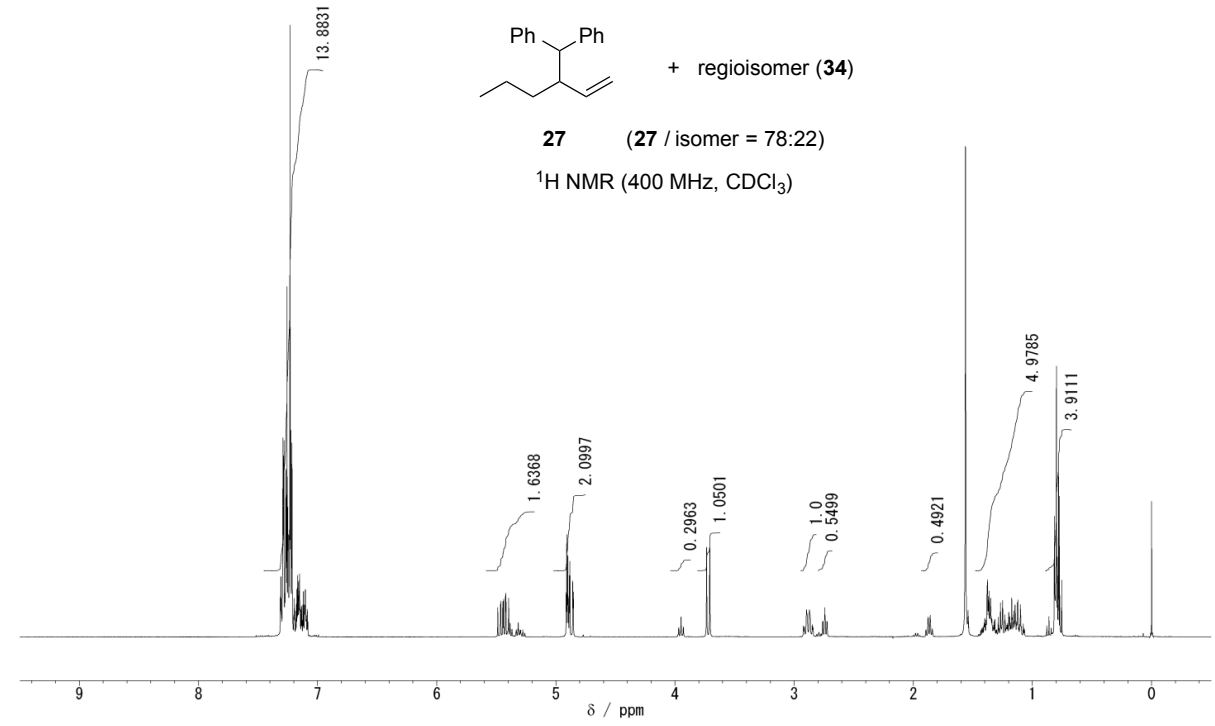

N
OTBS
+ regioisomer
(24 / isomer = 94:6)
24
13C NMR (100 MHz, CDCl3)
δ / ppm

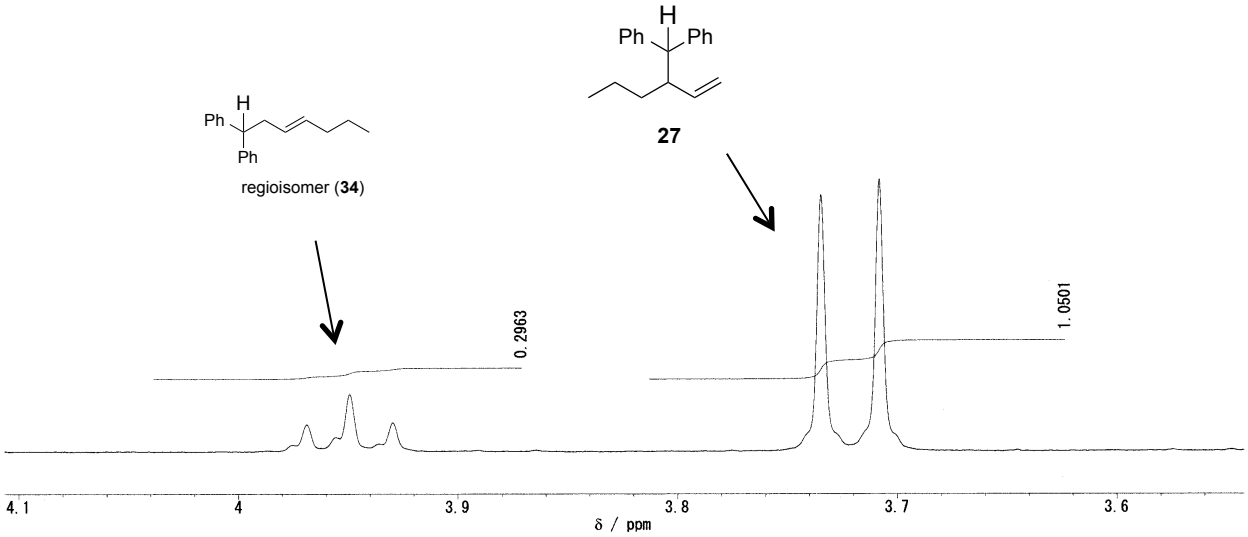

Ph
Ph
OTBS
+ regioisomer
25 (25 / isomer = 91:9)
1H NMR (400 MHz, CDCl3)
8
7
6
5
4
3
2
1
0
ppm
29.01
2.76
2.68
2.68
5.24
2.65
2.870.00
33.85
0.002.78
15.50


Ph
Ph
OTBS
+ regioisomer
25 (25 / isomer = 91:9)
13C NMR (100 MHz, CDCl3)
(+)
(+)
(−)
(−)
(+)
(+)
(−)
(+)
(−)
(+)
(+)
220
200
180
160
140
120
100
80
60
40
20
0
ppm

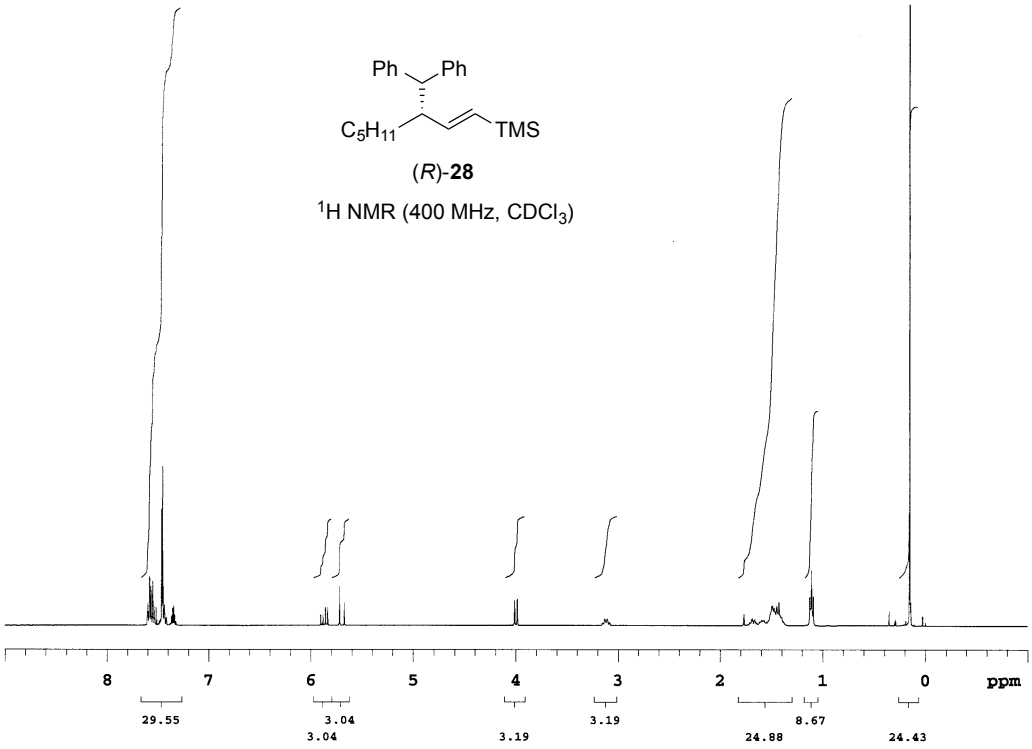

Ph
Ph
OTBS
+ regioisomer
26 (26 / isomer = 81:19)
1H NMR (400 MHz, CDCl3)
11.1484
1.9862
1.0
2.0517
1.0126
1.0058
16.8141
6.6712
9
8
7
6
5
4
3
2
1
0
δ / ppm

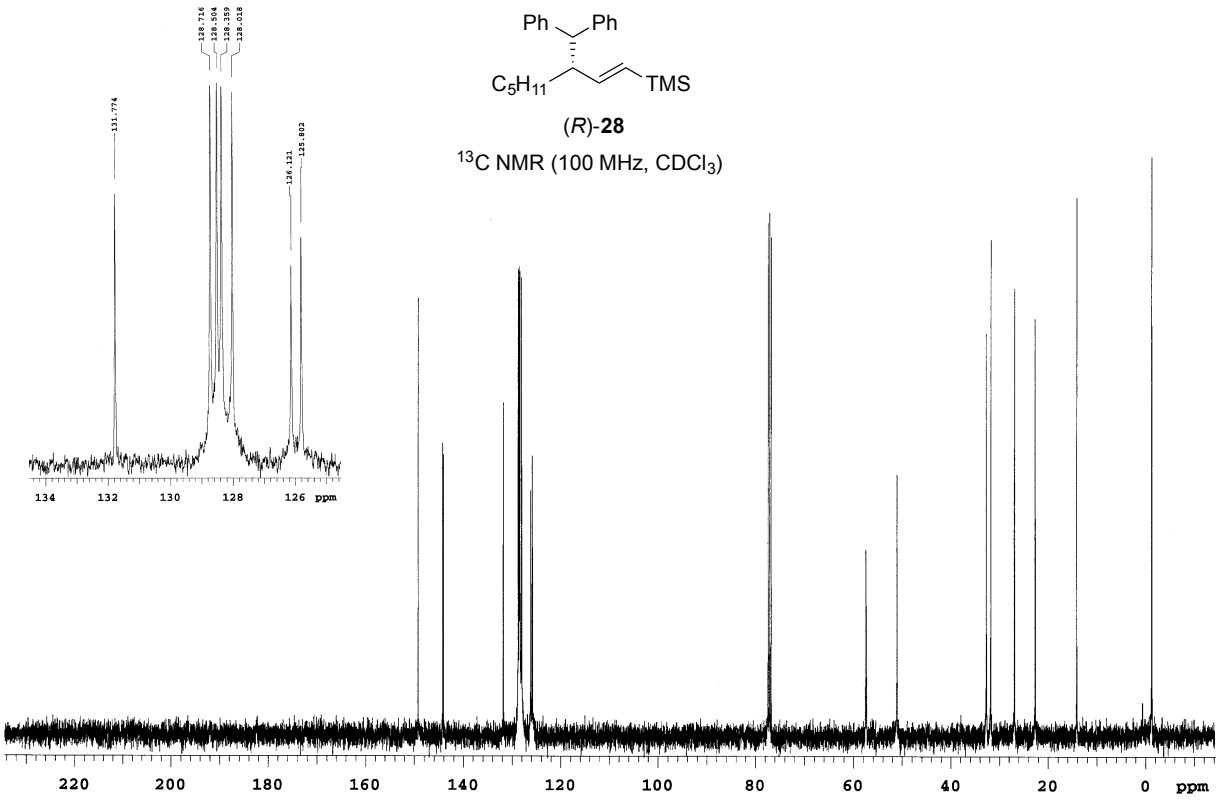

Ph
Ph
OTBS
+ regioisomer
26 (26 / isomer = 81:19)
13C NMR (100 MHz, CDCl3)
180
160
140
120
100
80
60
40
20
0
δ / ppm

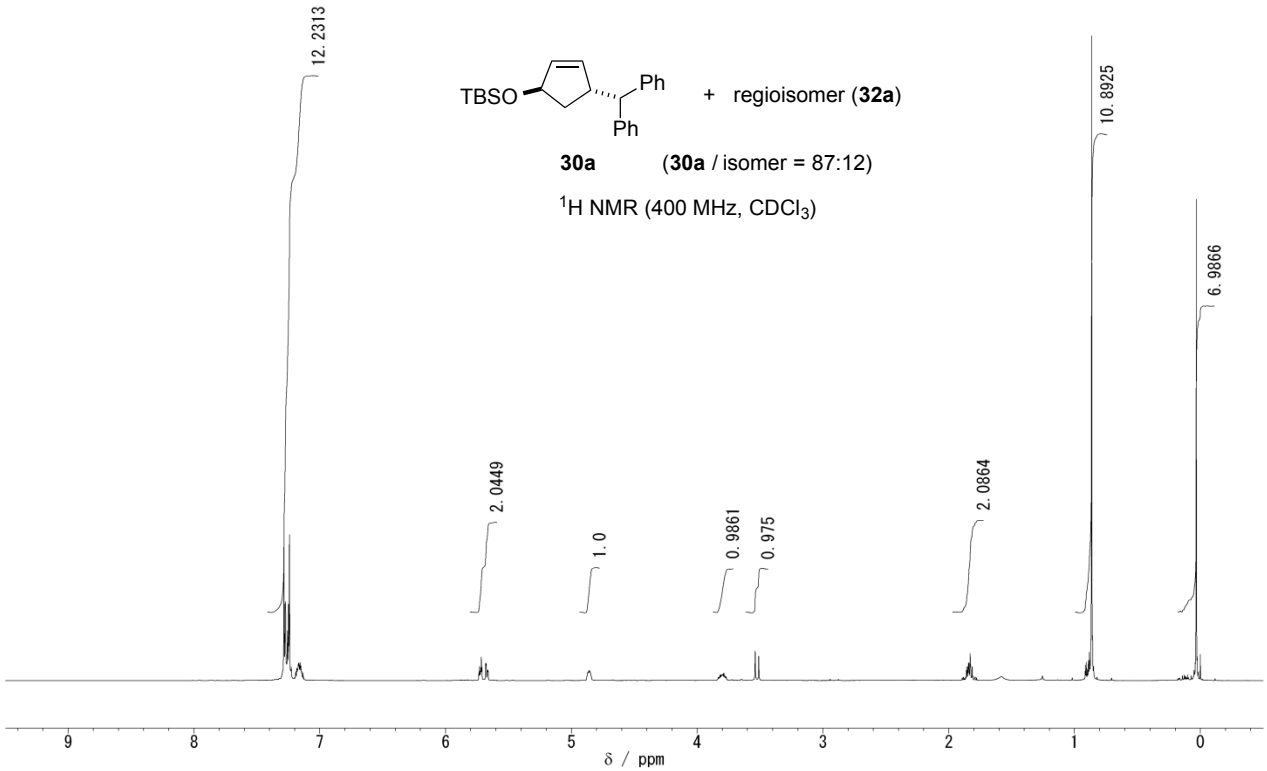


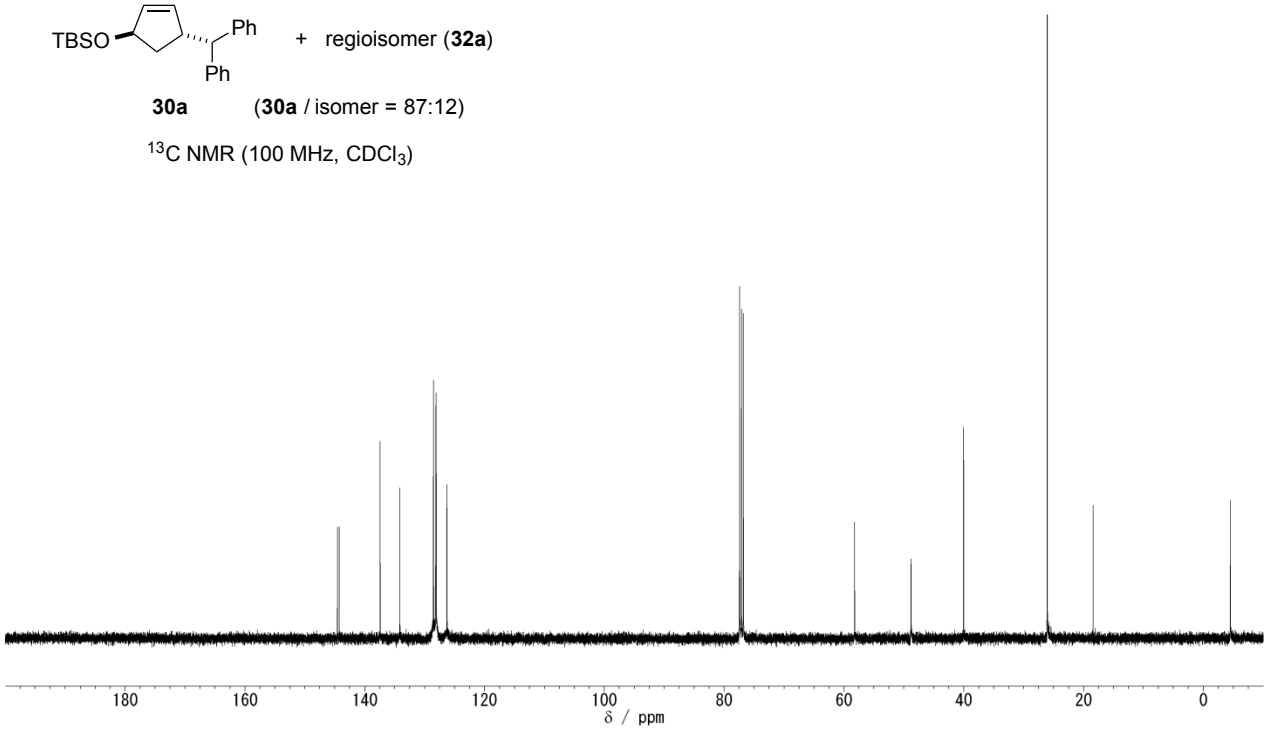


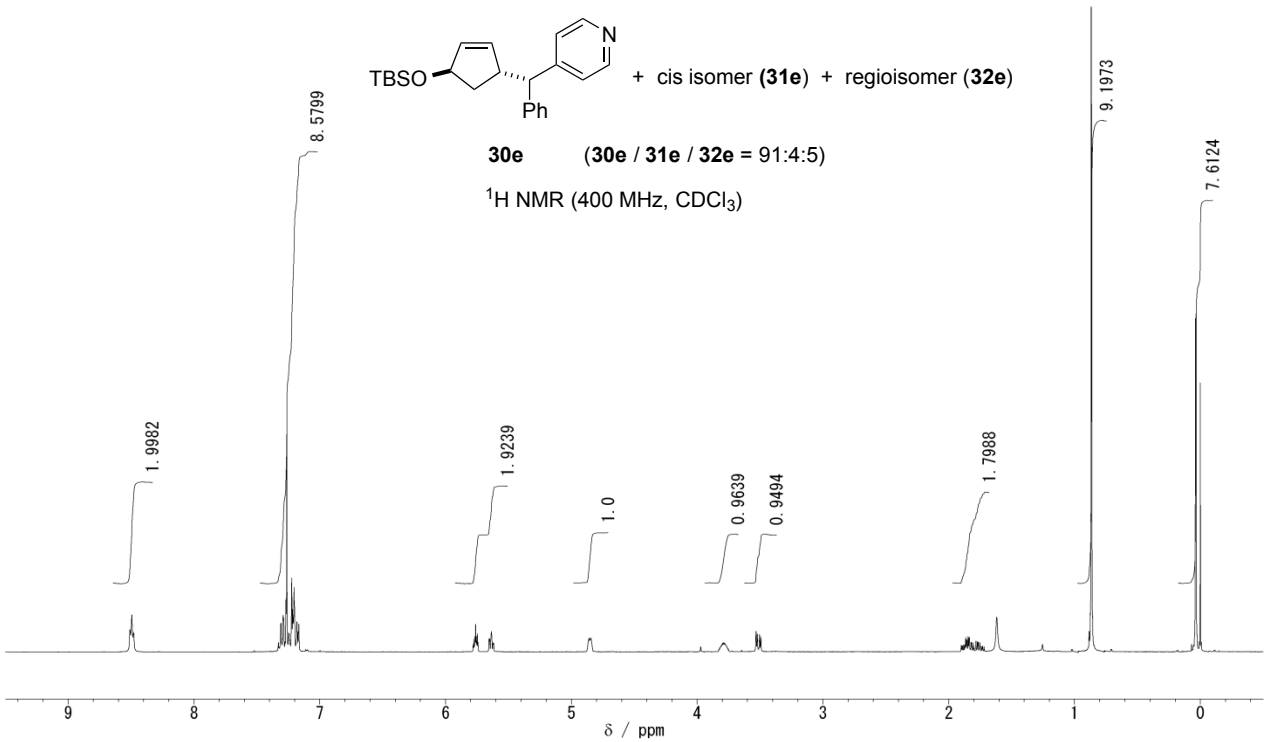
27 : regioisomer
= 1.0501 : 0.2963
= 78 : 22

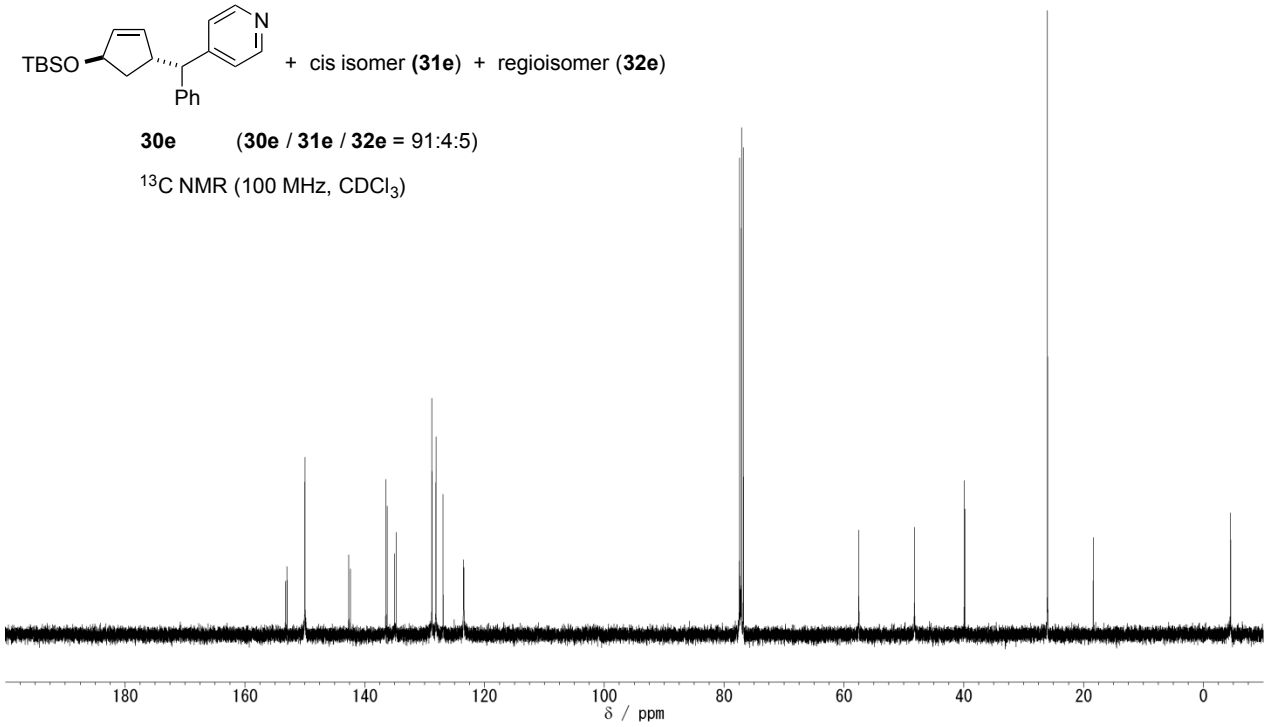

Ph
Ph
C5H11
TMS
(R)-28
1H NMR (400 MHz, CDCl3)
8
7
6
5
4
3
2
1
0
ppm
29.55
3.04
3.04
3.19
3.19
24.88
8.67
24.43

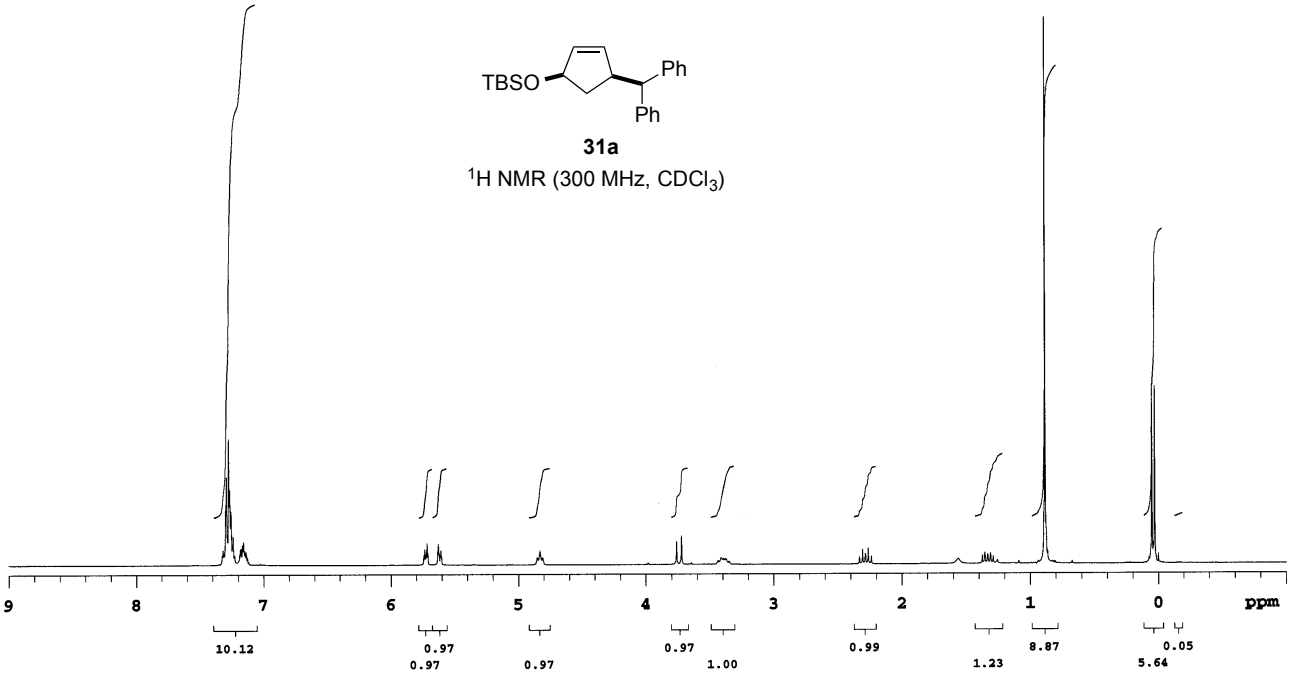

Ph
Ph
C5H11
TMS
(R)-28
13C NMR (100 MHz, CDCl3)
131.774
128.716
128.504
128.359
128.018
126.121
125.802
134
132
130
128
126
ppm
220
200
180
160
140
120
100
80
60
40
20
0
ppm


12.2313
2.0449
1.0
0.9861
0.975
2.0864
10.8925
6.9866
TBSO
Ph
Ph
+ regioisomer (32a)
30a (30a / isomer = 87:12)
1H NMR (400 MHz, CDCl3)
9
8
7
6
5
4
3
2
1
0
δ / ppm


TBSO
Ph
Ph
+ regioisomer (32a)
30a (30a / isomer = 87:12)
13C NMR (100 MHz, CDCl3)
180
160
140
120
100
80
60
40
20
0
δ / ppm

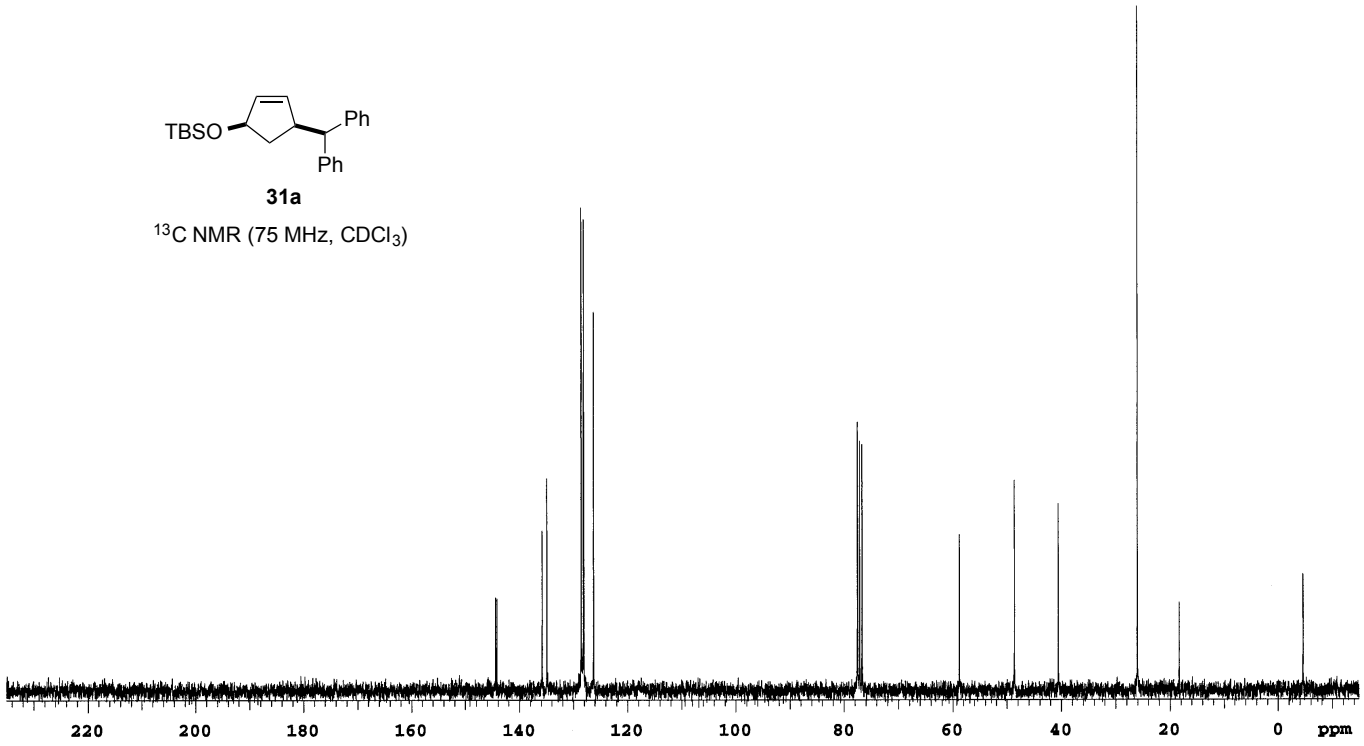

TBSO
N
Ph
+ cis isomer (31e) + regioisomer (32e)
30e (30e / 31e / 32e = 91:4:5)
1H NMR (400 MHz, CDCl3)
8.5799
9.1973
7.6124
1.9982
1.9239
1.0
0.9639
0.9494
1.7988
δ / ppm


TBSO
N
Ph
+ cis isomer (31e) + regioisomer (32e)
30e (30e / 31e / 32e = 91:4:5)
13C NMR (100 MHz, CDCl3)
δ / ppm



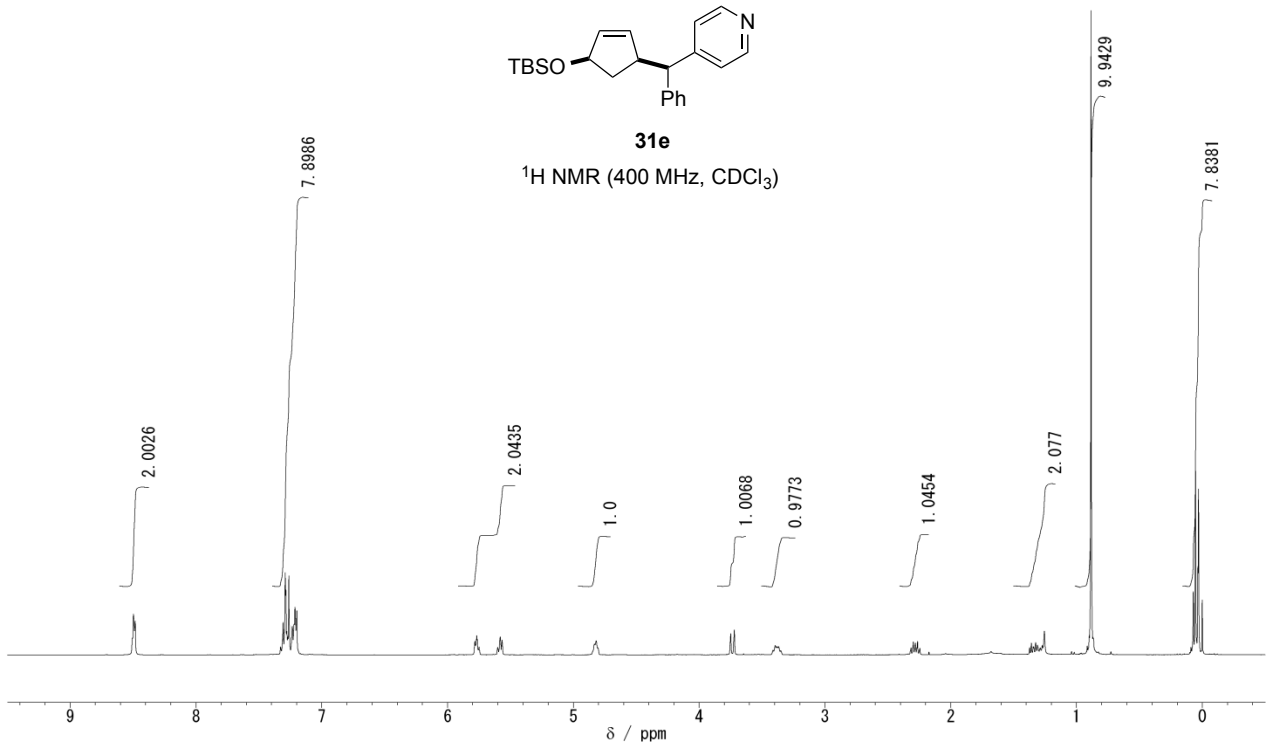
31a

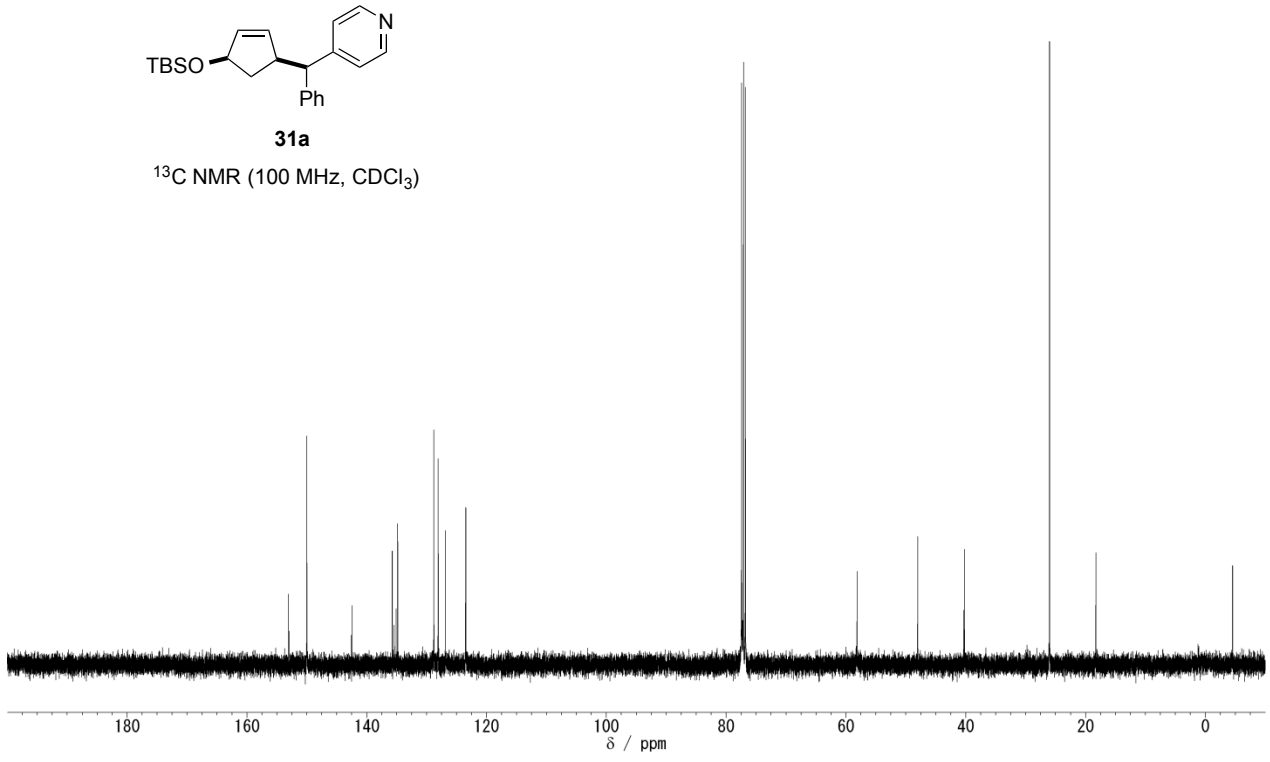
^{1}H NMR (300 MHz, $CDCl_3$)

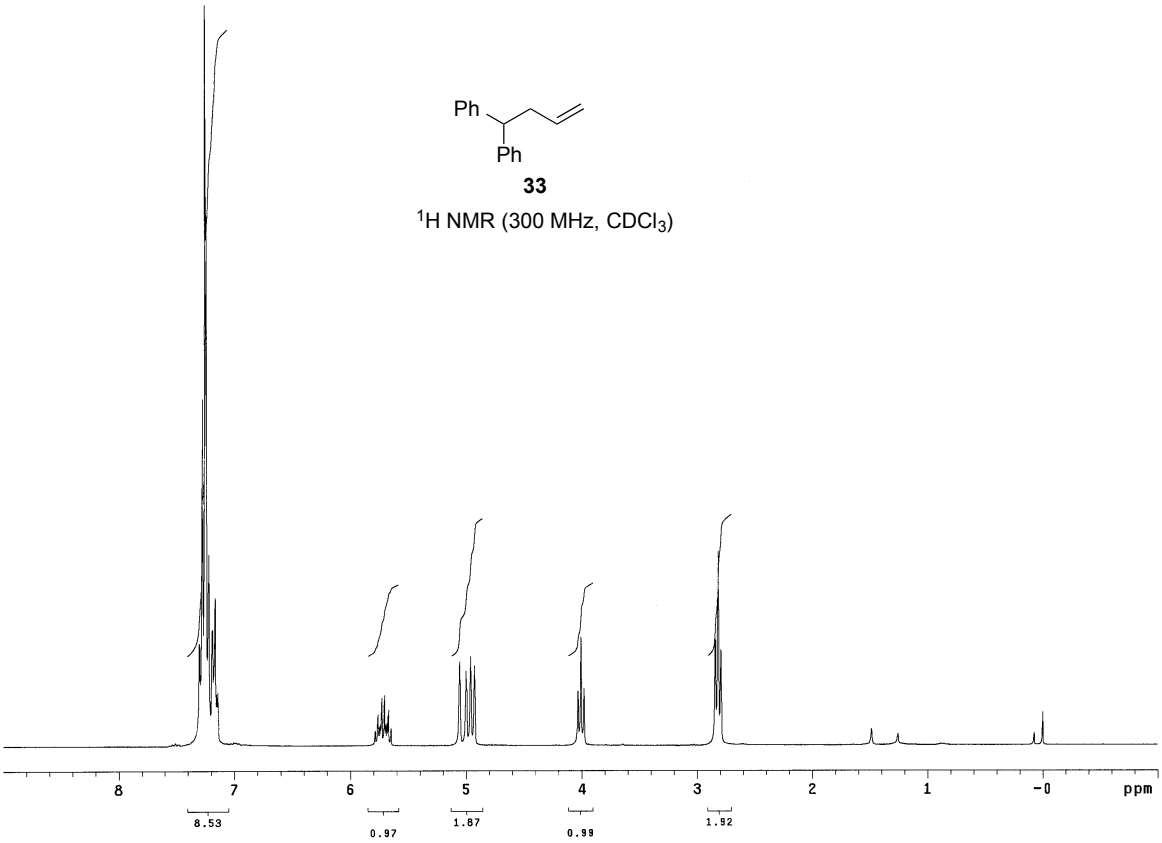


31a

^{13}C NMR (75 MHz, $CDCl_3$)

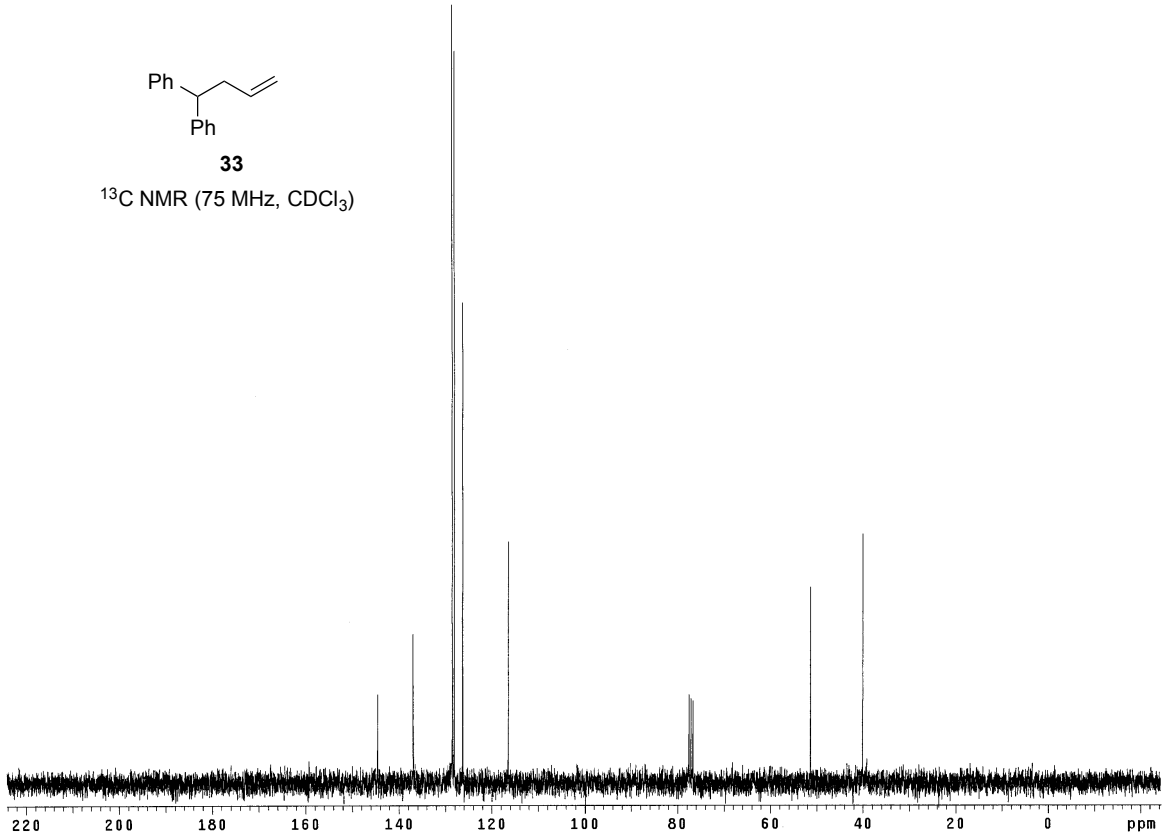

TBSO
N
Ph
31e
^{1}H NMR (400 MHz, $CDCl_3$)
2.0026
7.8986
2.0435
1.0
1.0068
0.9773
1.0454
2.077
9.9429
7.8381
9
8
7
6
5
4
3
2
1
0
δ / ppm


TBSO
N
Ph
31a
^{13}C NMR (100 MHz, $CDCl_3$)
180
160
140
120
100
80
60
40
20
0
δ / ppm



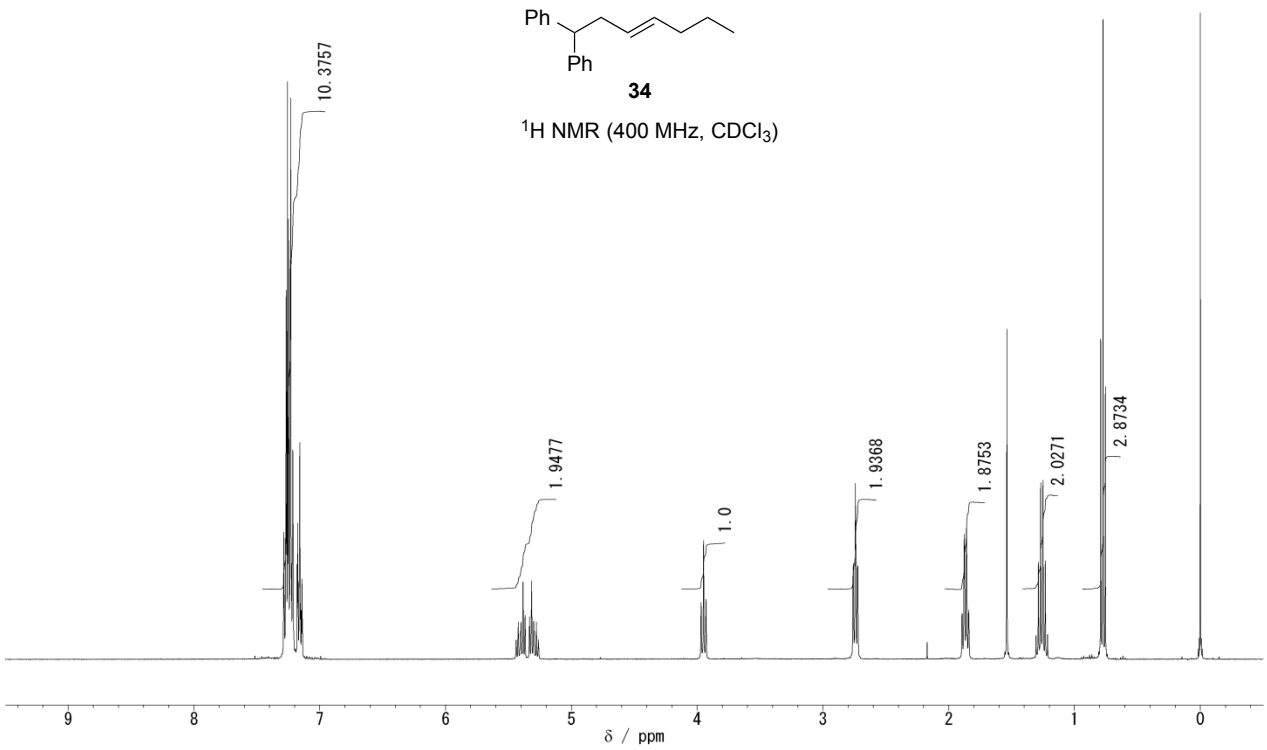
33

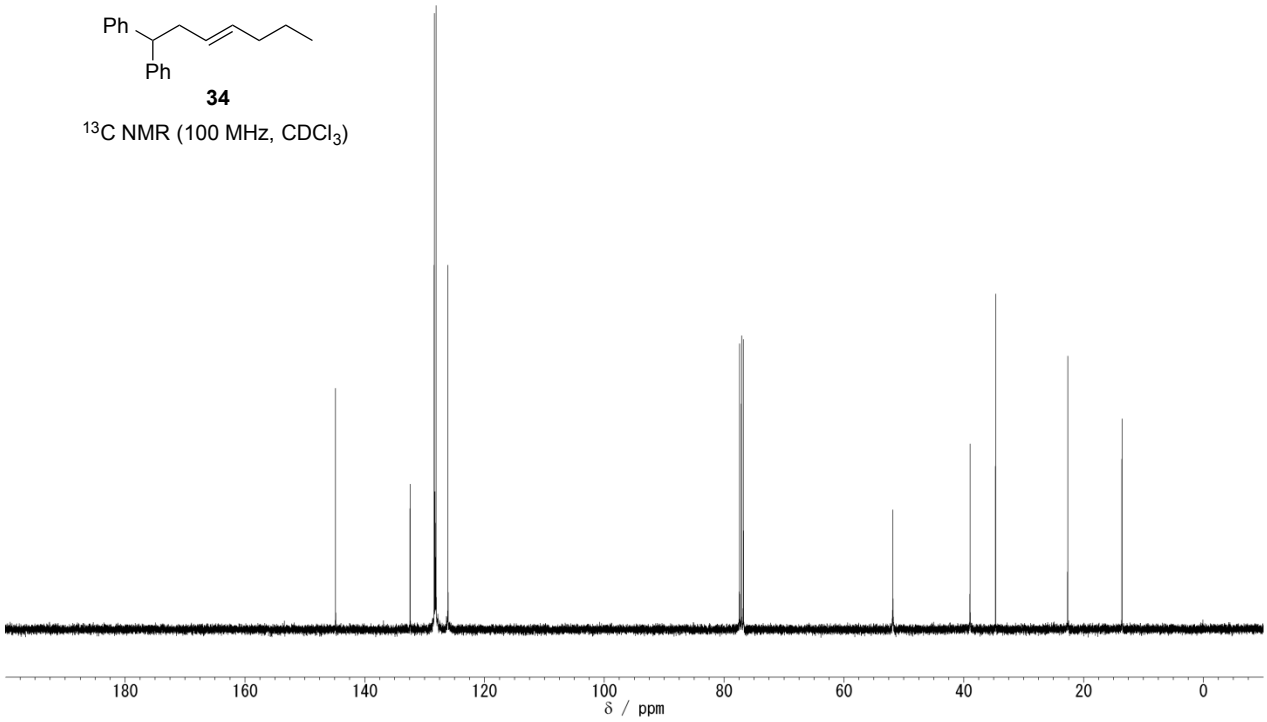
^{1}H NMR (300 MHz, $CDCl_3$)

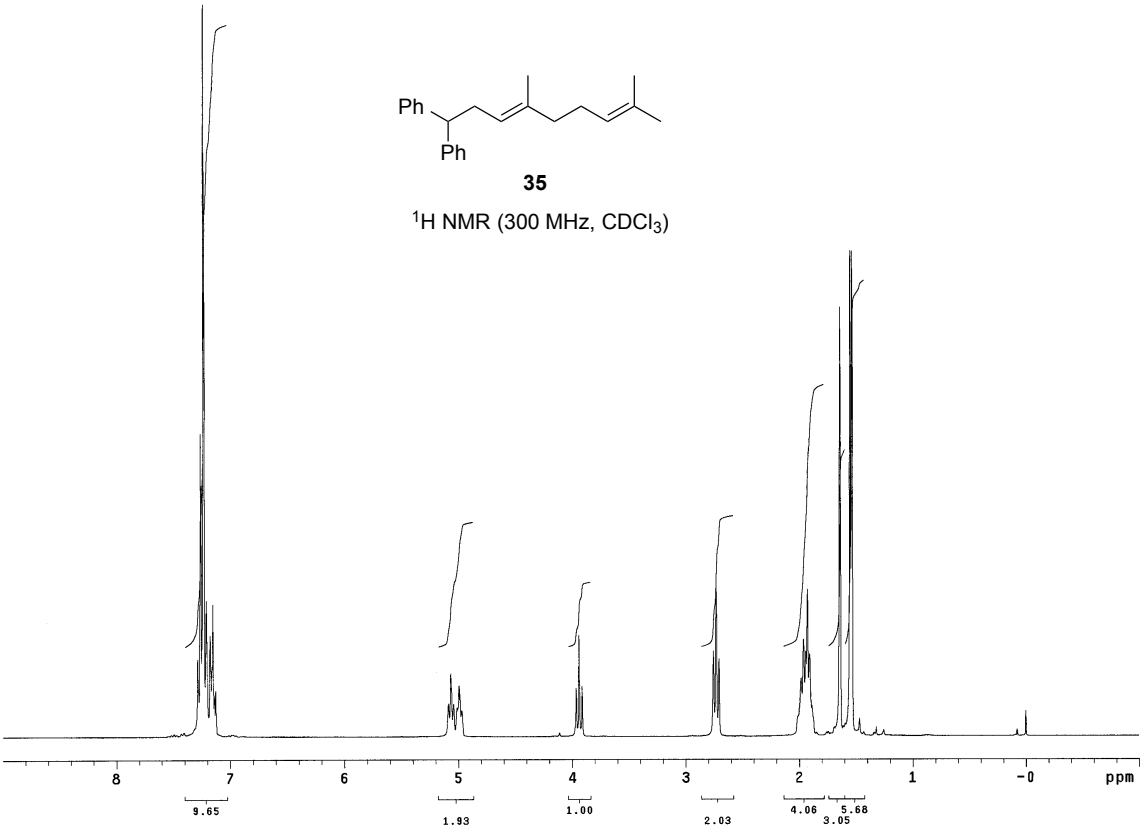


33

^{13}C NMR (75 MHz, $CDCl_3$)

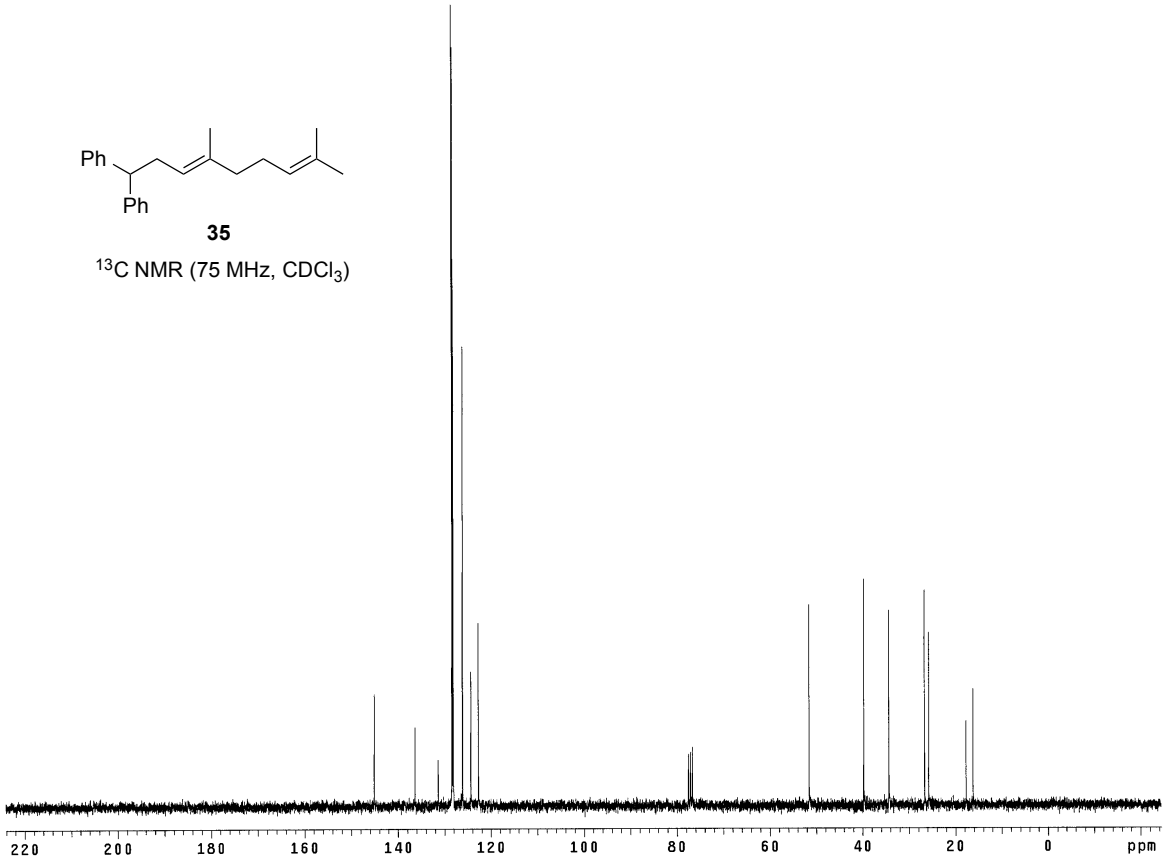

Ph
Ph
34
1H NMR (400 MHz, CDCl3)
10.3757
1.9477
1.0
1.9368
1.8753
2.0271
2.8734
9
8
7
6
5
4
3
2
1
0
δ / ppm


Ph
Ph
34
13C NMR (100 MHz, CDCl3)
180
160
140
120
100
80
60
40
20
0
δ / ppm



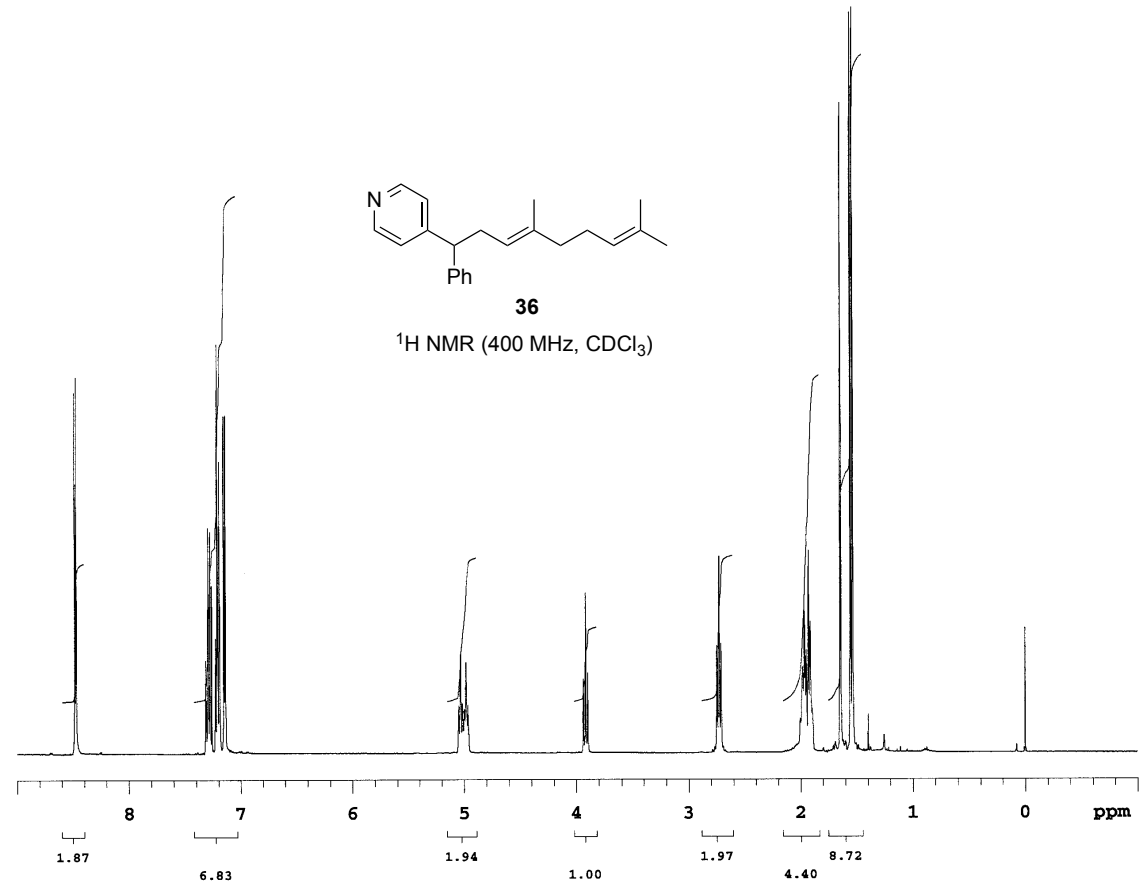
35

^{1}H NMR (300 MHz, $CDCl_3$)



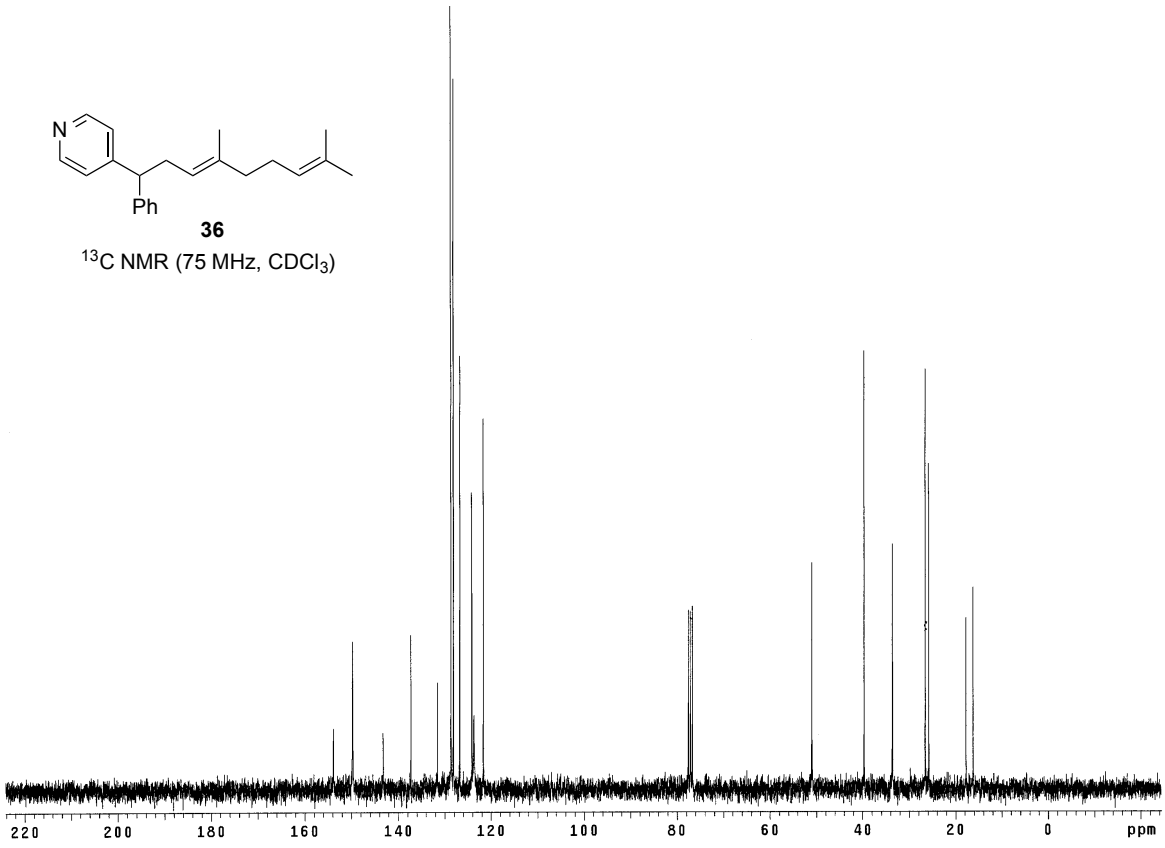
35

^{13}C NMR (75 MHz, $CDCl_3$)



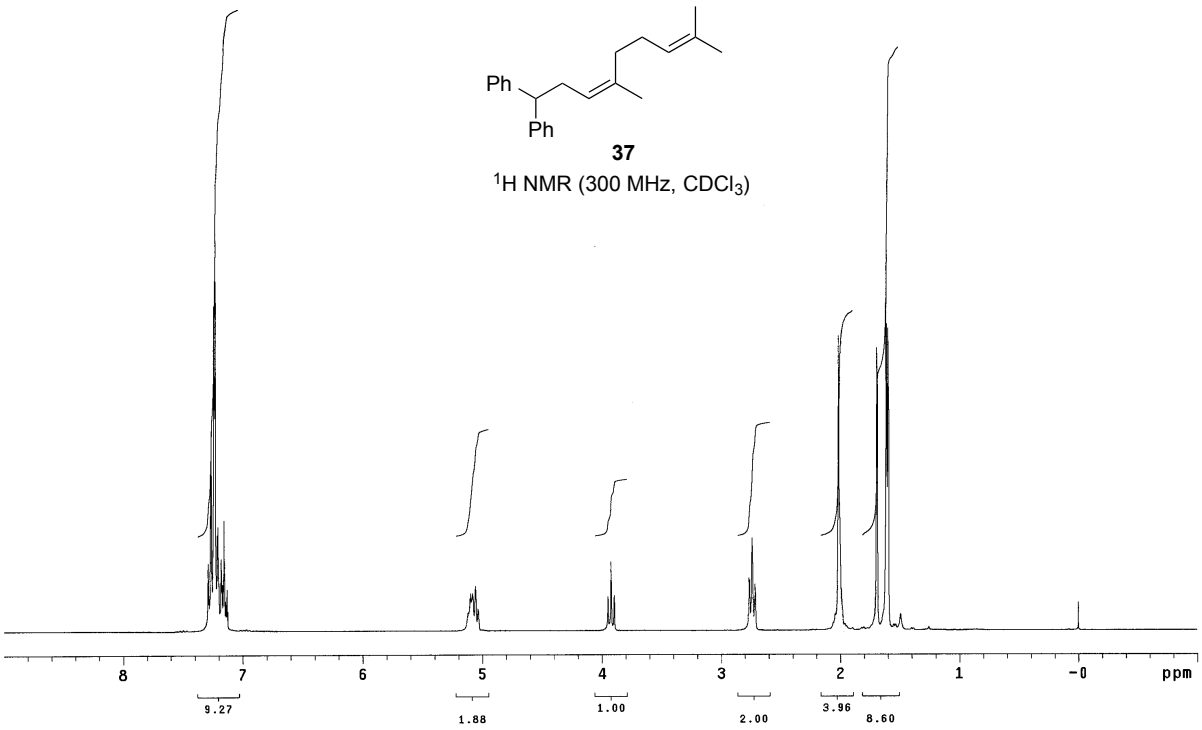
36

^{1}H NMR (400 MHz, $CDCl_3$)



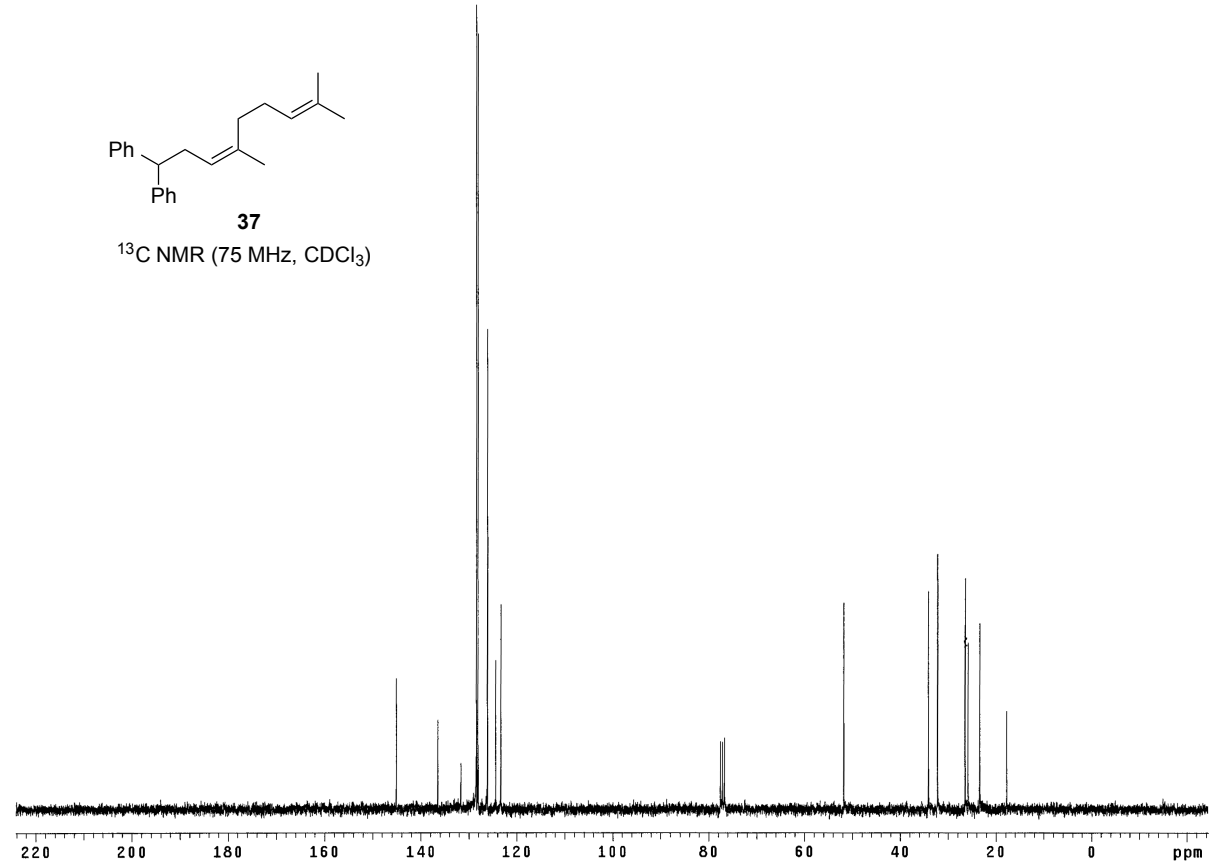
36

^{13}C NMR (75 MHz, $CDCl_3$)



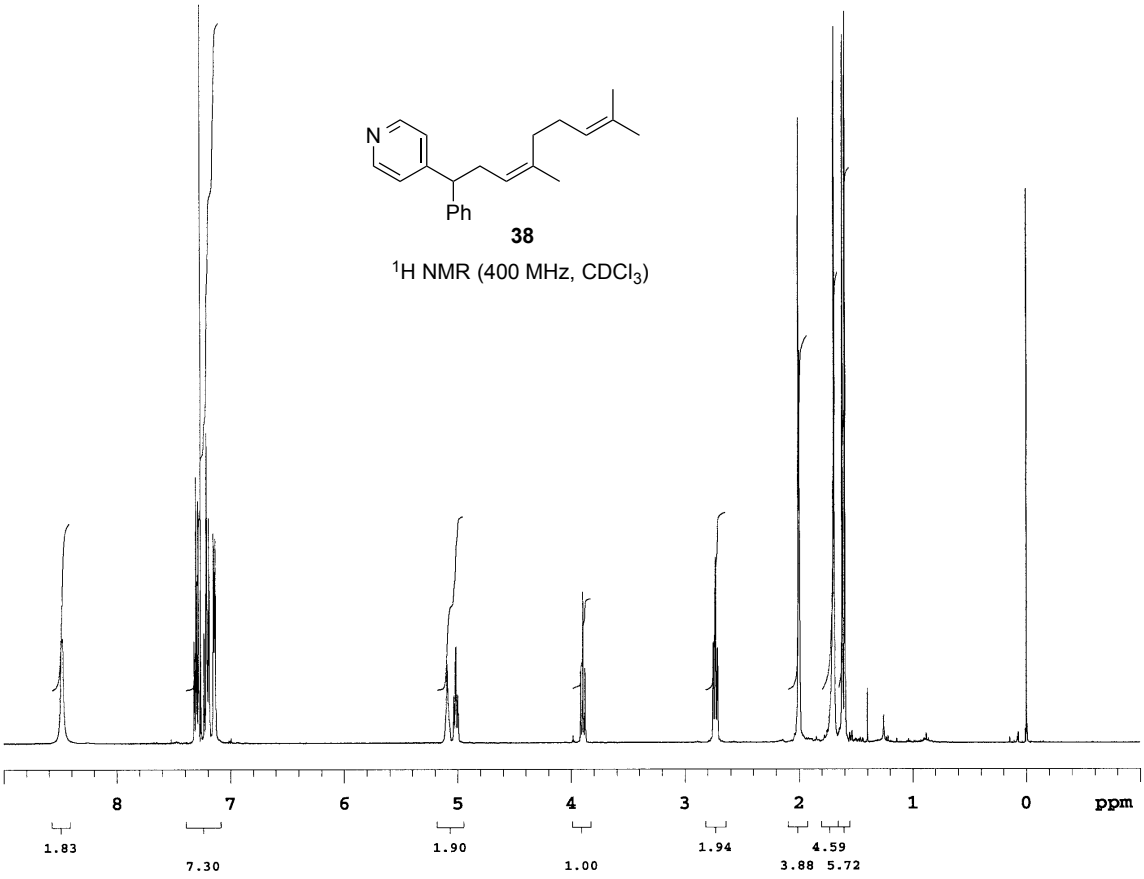
37

^{1}H NMR (300 MHz, $CDCl_3$)



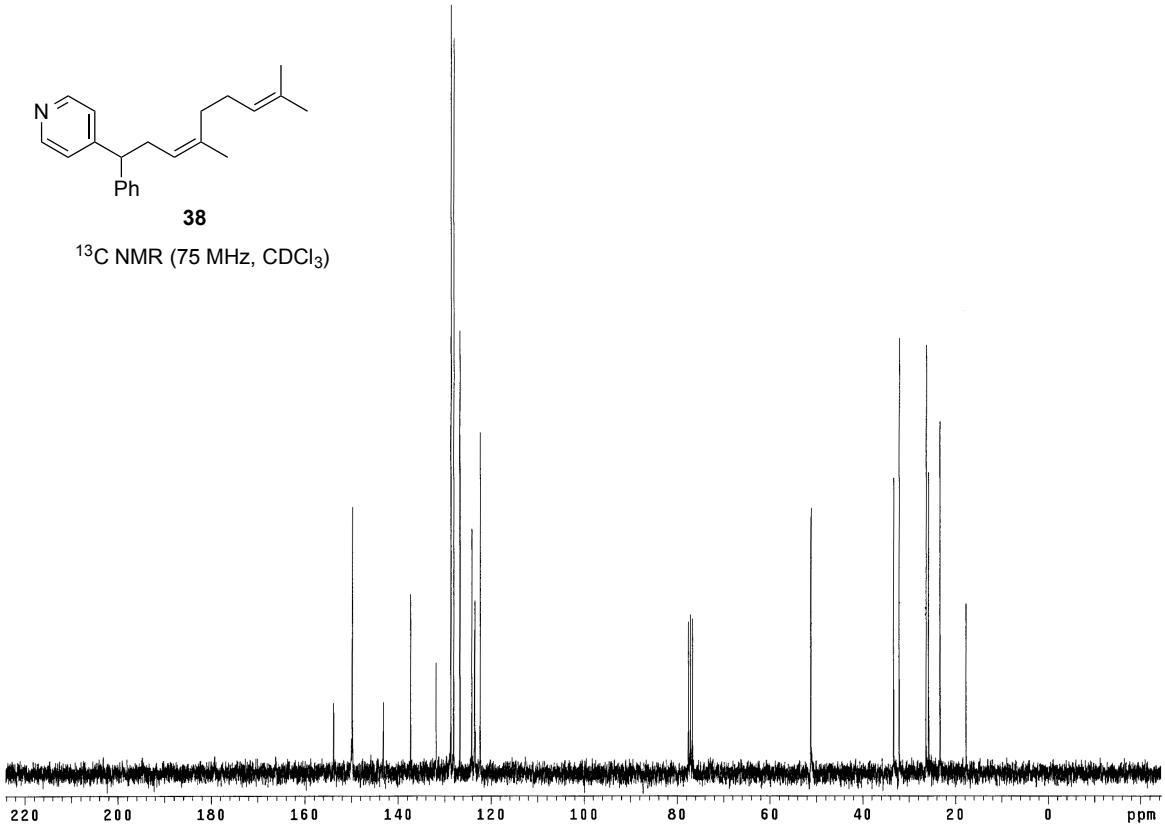
37

^{13}C NMR (75 MHz, $CDCl_3$)



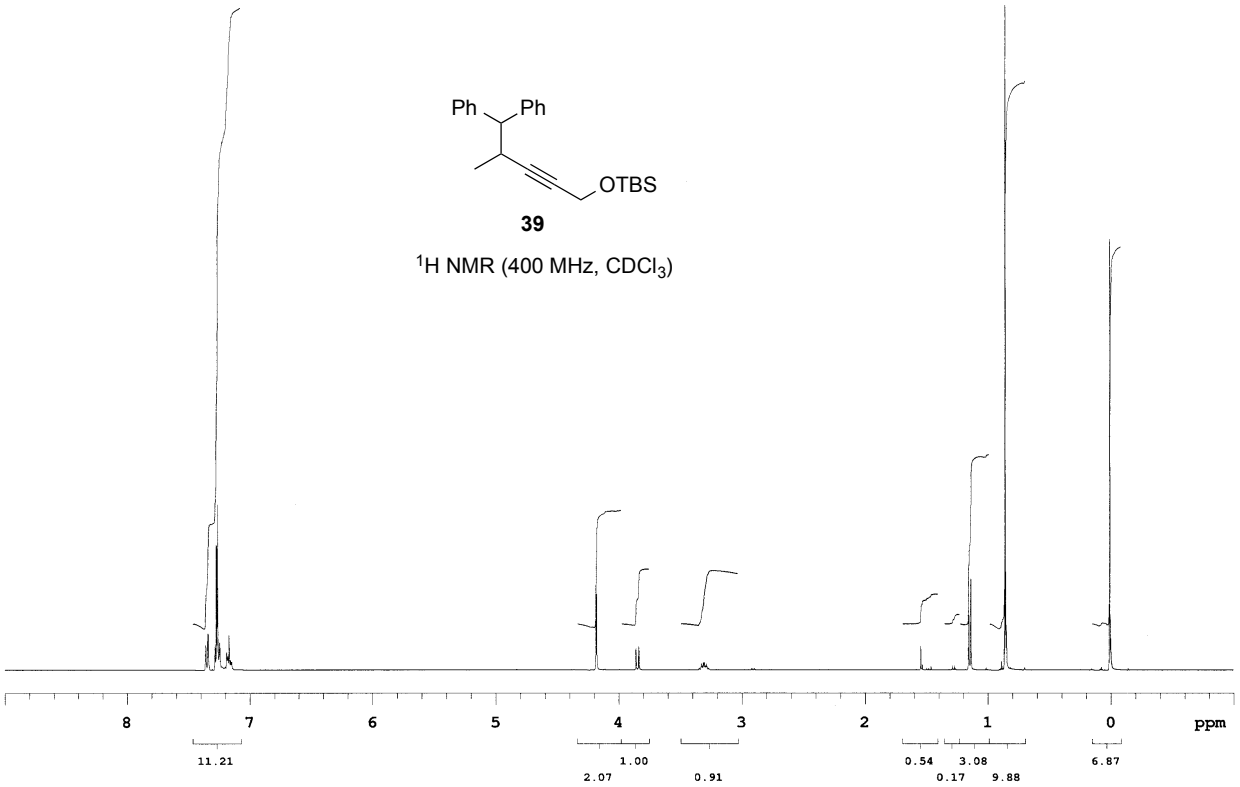
38

^{1}H NMR (400 MHz, $CDCl_3$)



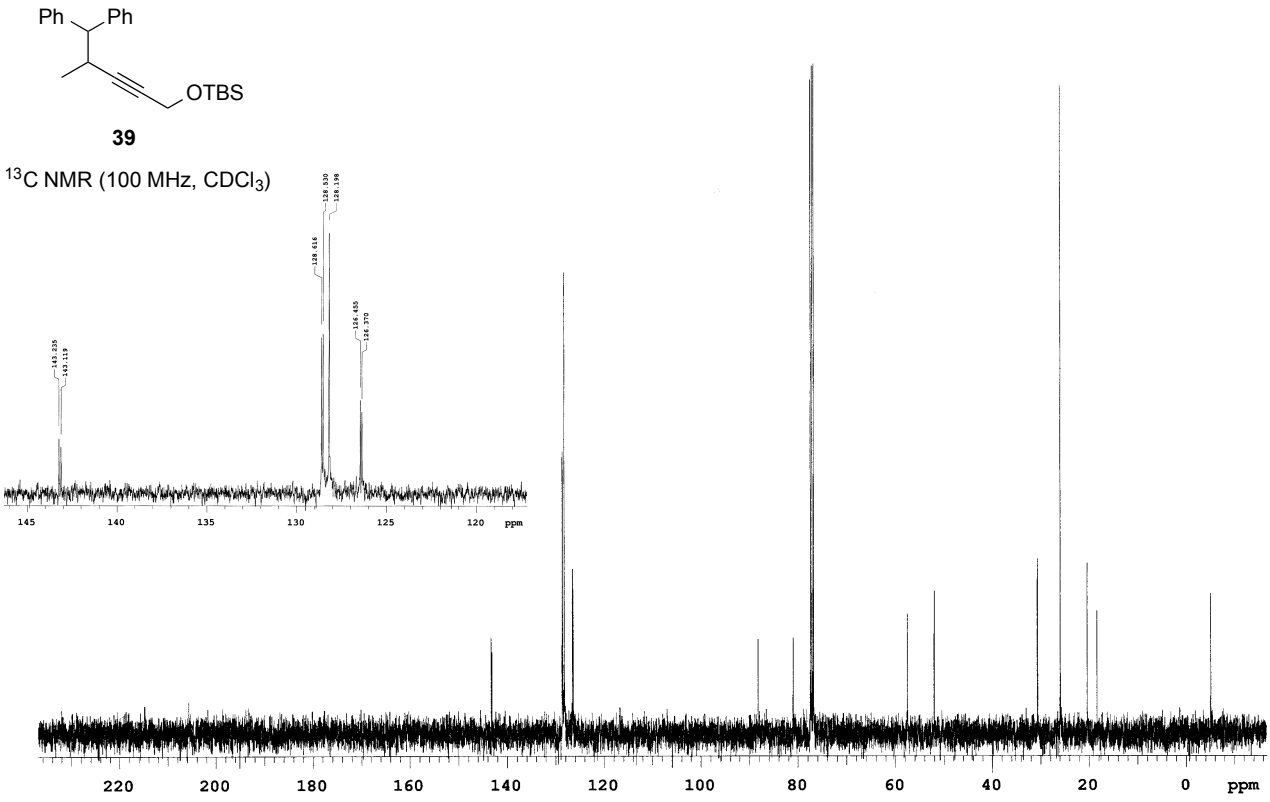
38

^{13}C NMR (75 MHz, $CDCl_3$)



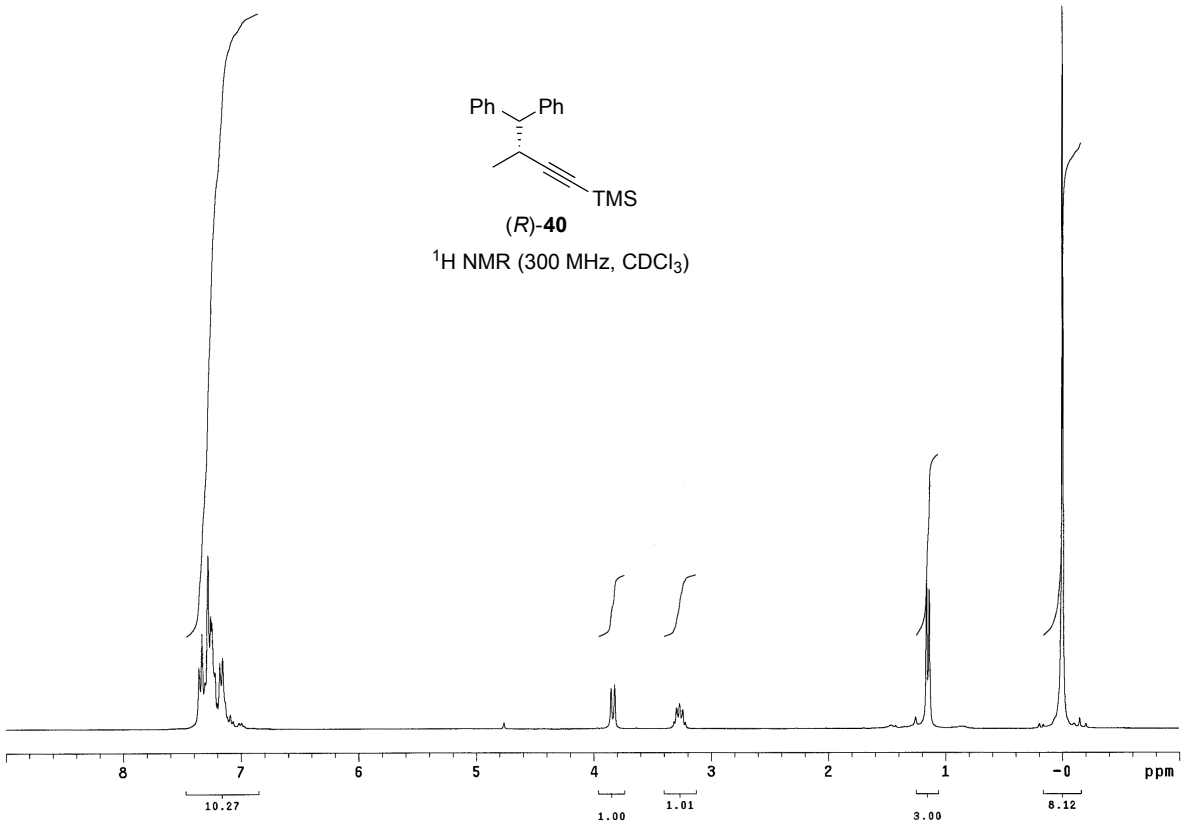
39

^{1}H NMR (400 MHz, $CDCl_3$)



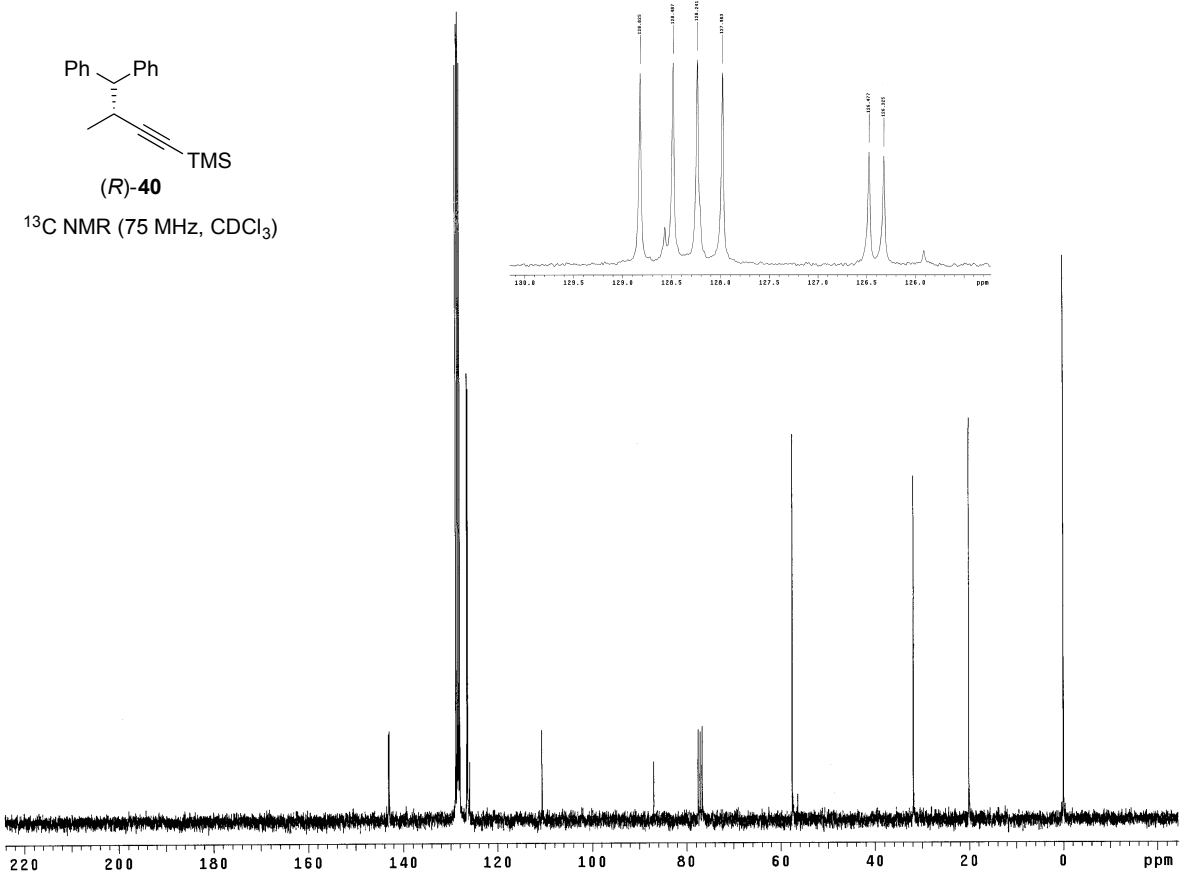
39

^{13}C NMR (100 MHz, $CDCl_3$)



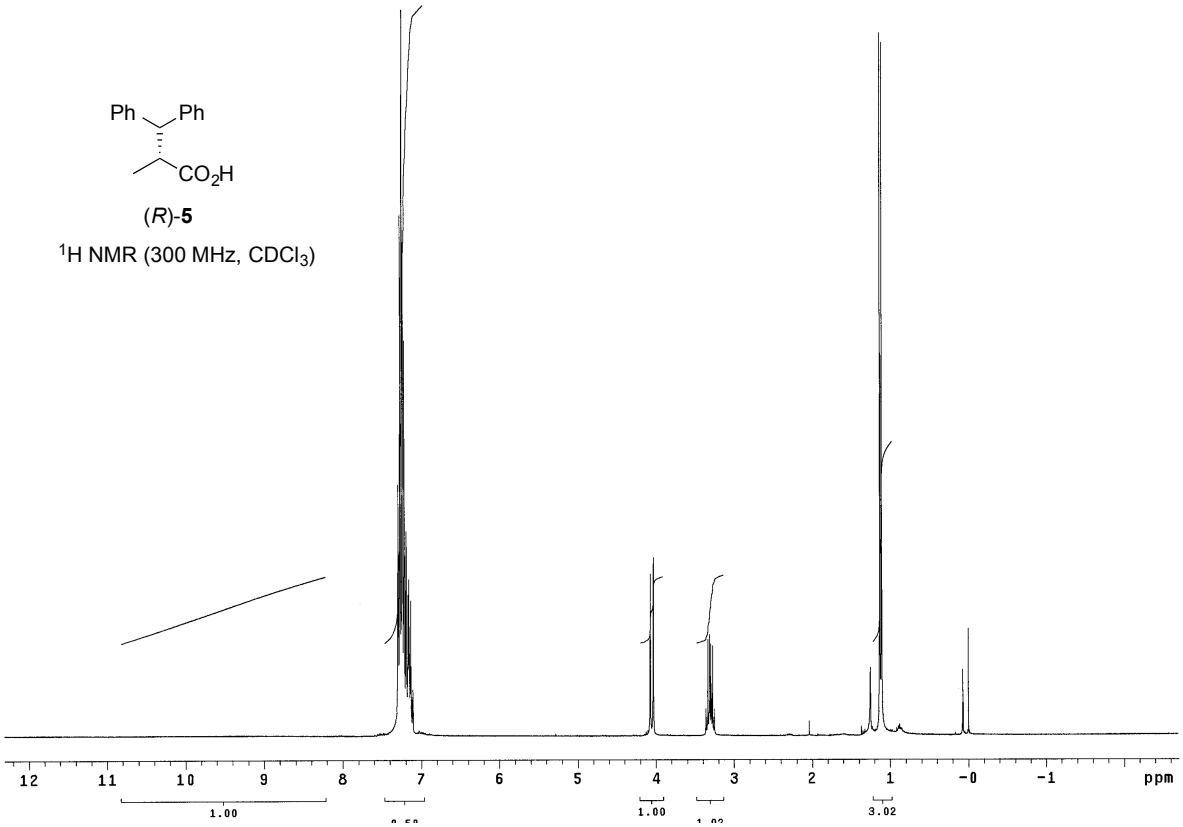
(*R*)-**40**

^{1}H NMR (300 MHz, $CDCl_3$)



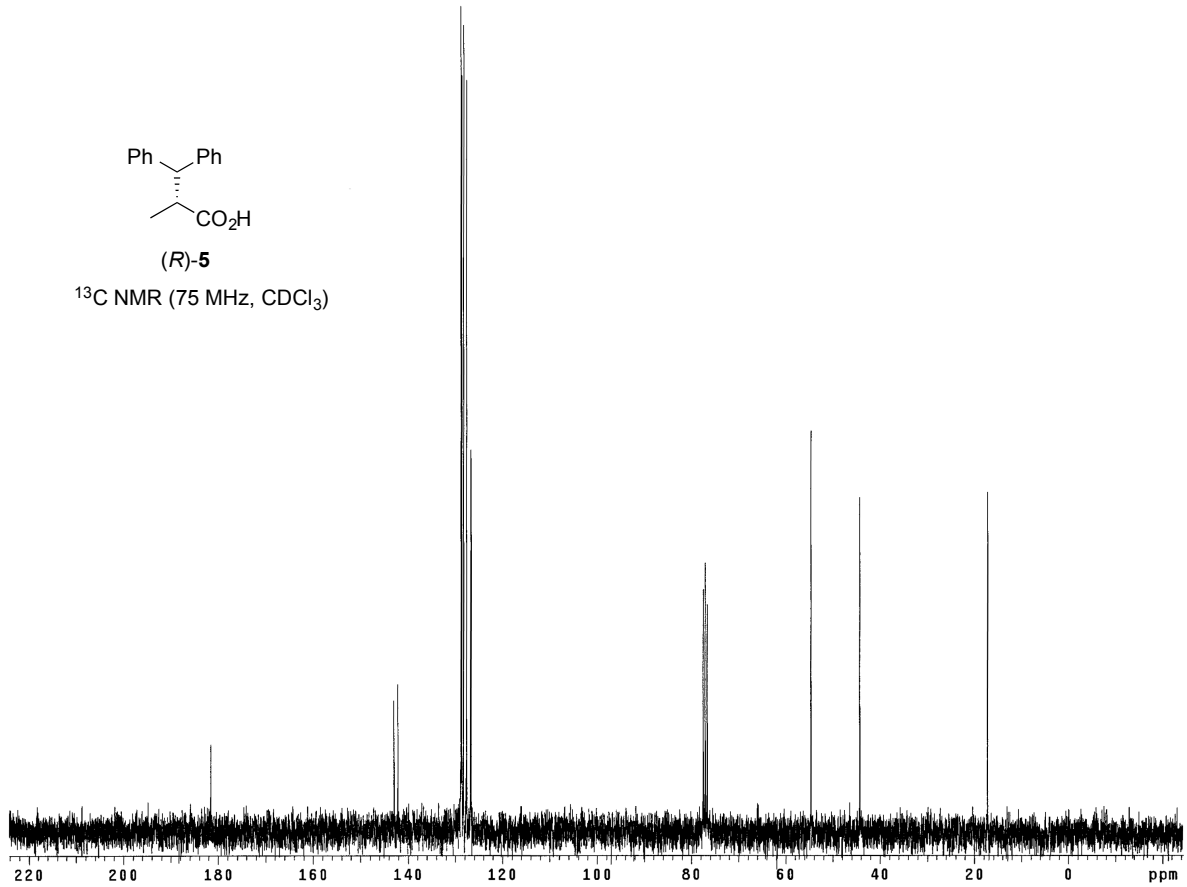
(*R*)-**40**

^{13}C NMR (75 MHz, $CDCl_3$)



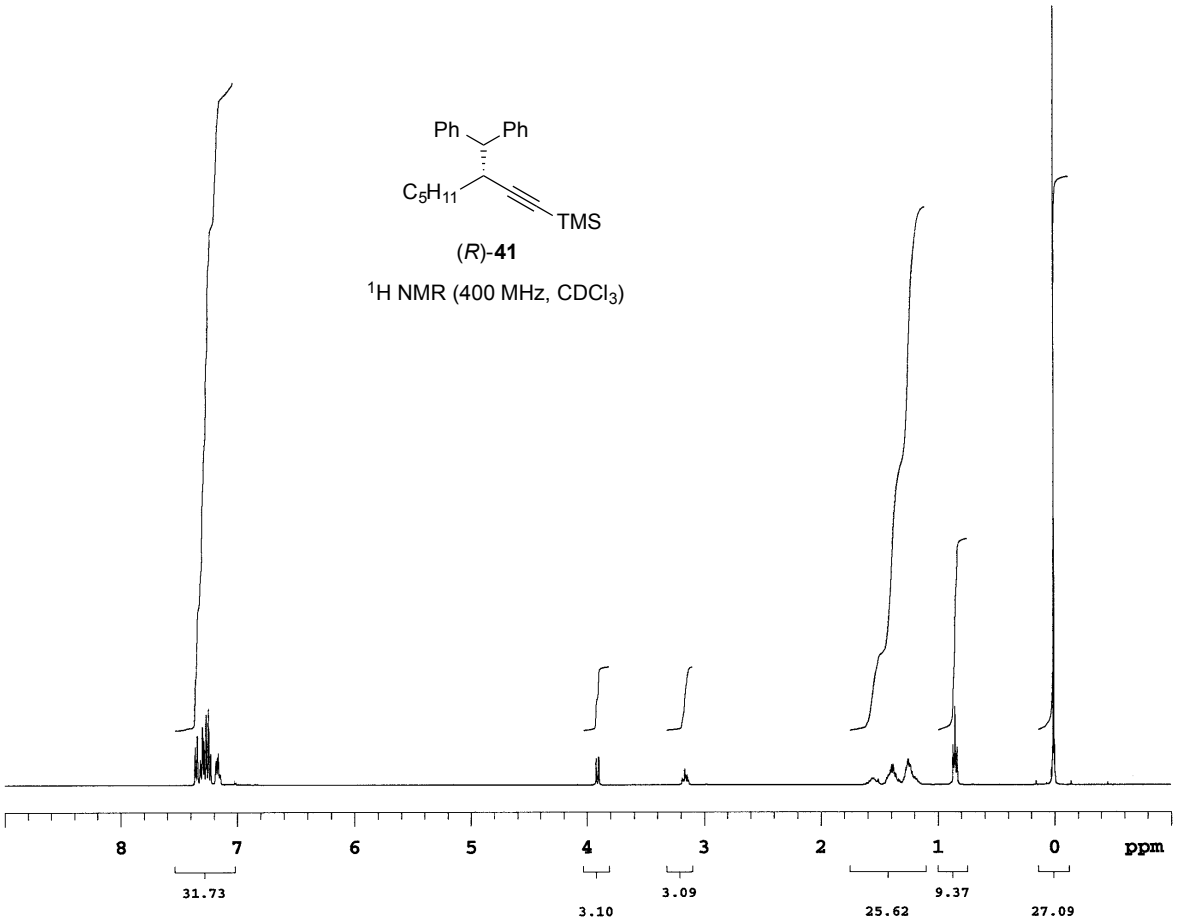
(*R*)-**5**

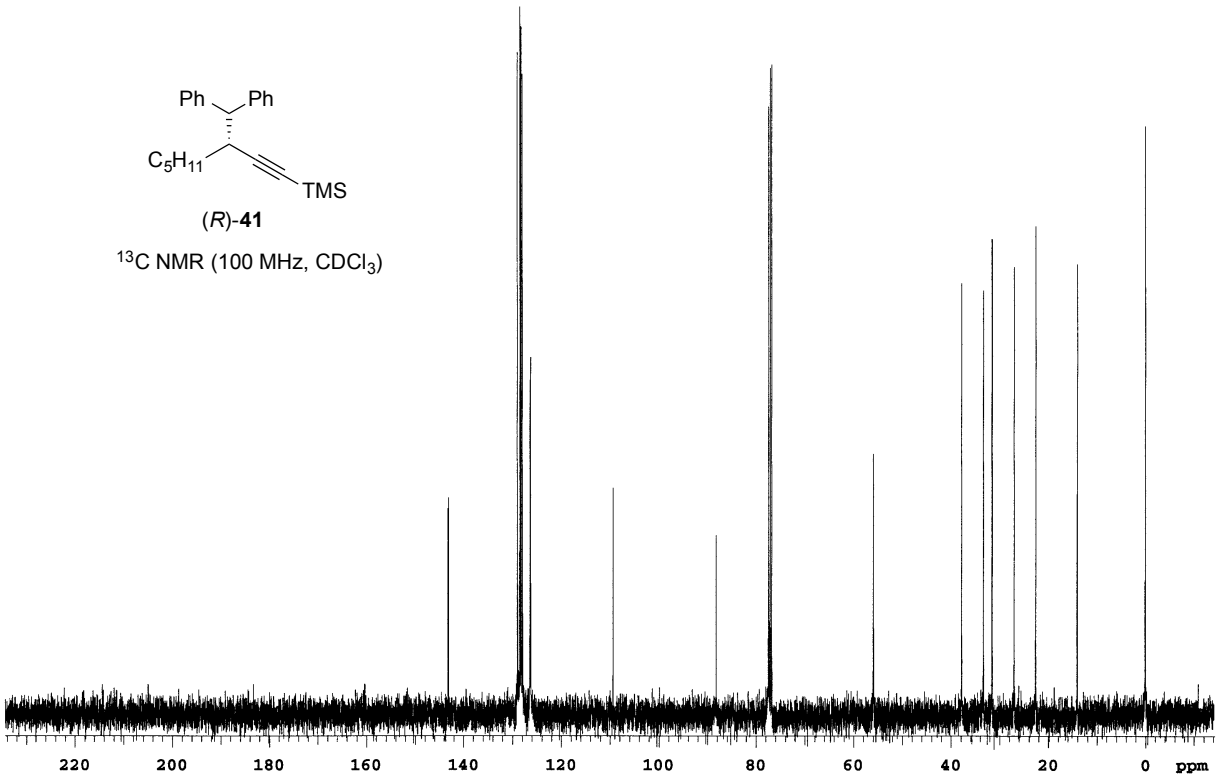
^{1}H NMR (300 MHz, $CDCl_3$)

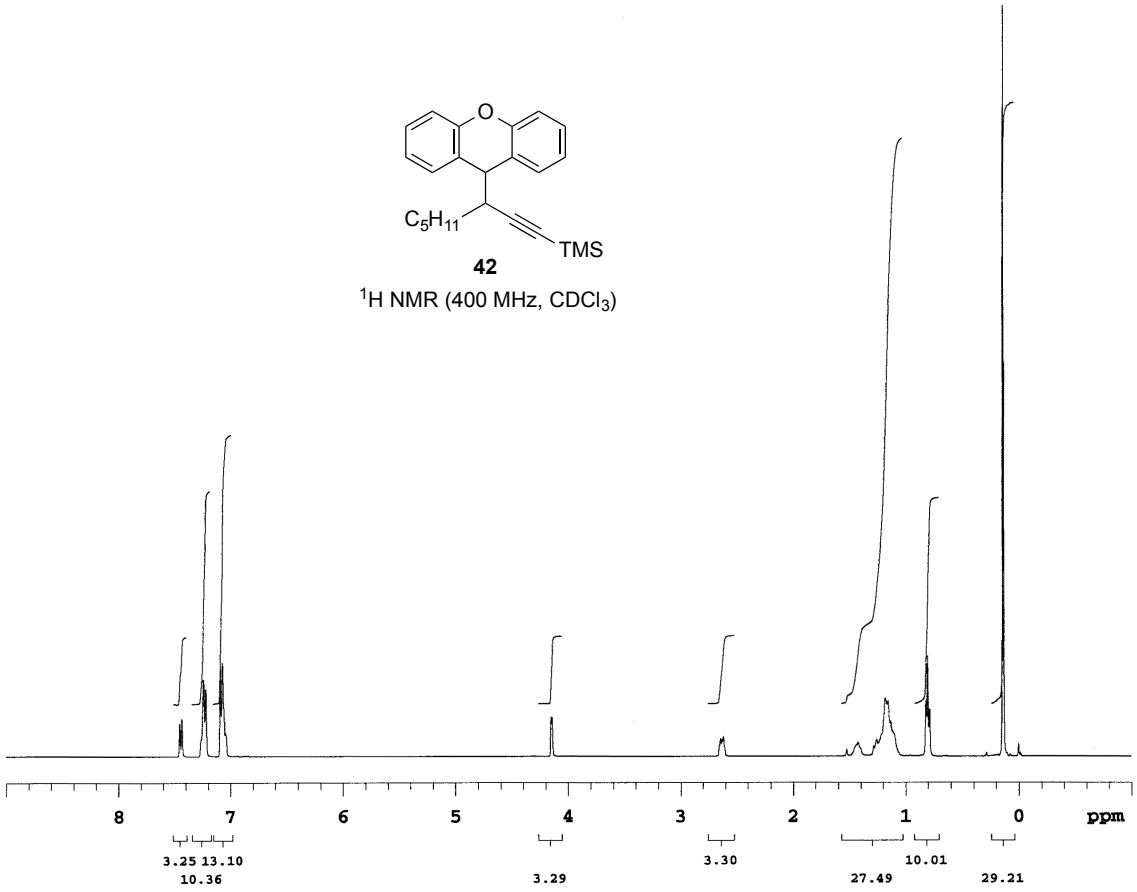


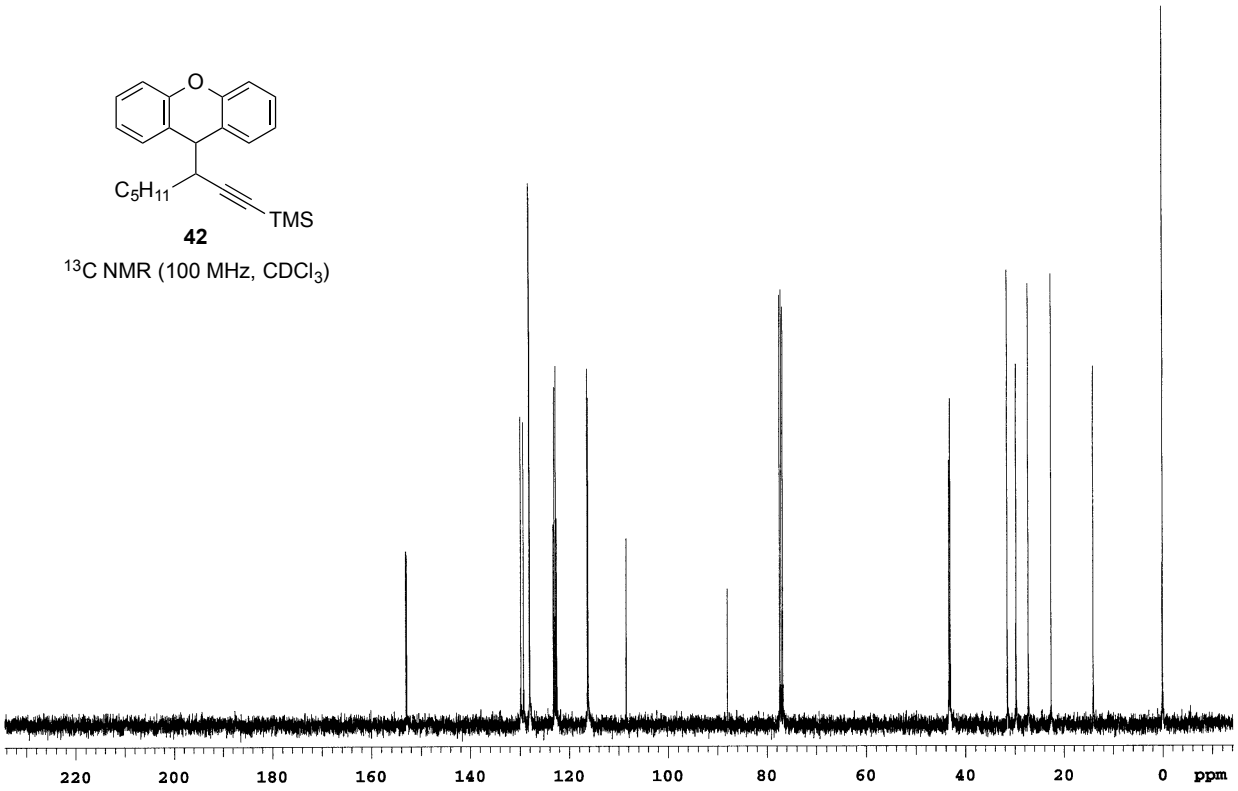
(*R*)-**5**

^{13}C NMR (75 MHz, $CDCl_3$)


Ph
Ph
C5H11
TMS
(R)-41
1H NMR (400 MHz, CDCl3)
8
7
6
5
4
3
2
1
0
ppm
31.73
3.10
3.09
25.62
9.37
27.09


Ph
Ph
C5H11
TMS
(R)-41
13C NMR (100 MHz, CDCl3)
220
200
180
160
140
120
100
80
60
40
20
0
ppm


O
C_5H_{11}
TMS
42
^{1}H NMR (400 MHz, $CDCl_3$)
8
7
6
5
4
3
2
1
0
ppm
3.25 13.10
10.36
3.29
3.30
27.49
10.01
29.21


O
C_5H_{11}
TMS
42
^{13}C NMR (100 MHz, $CDCl_3$)
220
200
180
160
140
120
100
80
60
40
20
0
ppm