Supporting Information

Efficient, Selective and Green: Catalyst Tuning for Highly Enantioselective Reactions of Ethylene

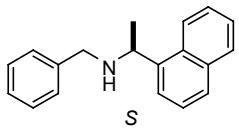
Craig R. Smith and T. V. RajanBabu*

Department of Chemistry, The Ohio State University, 100 W. 18th Avenue, Columbus, OH 43210

Page

General methods: Reactions requiring air–sensitive manipulations were conducted under an inert atmosphere of nitrogen by using Schlenk techniques or a Vacuum Atmospheres glovebox. Tetrahydrofuran was distilled under nitrogen from sodium/benzophenone ketyl. All olefins were made from Wittig reactions of the corresponding aldehydes or ketones with triphenylphosphonium bromide in the presence of *n*-BuLi in THF at reflux. Methylene chloride was freshly distilled under a dry atmosphere from calcium hydride. $Na^+[[3,5\text{-}(CF_3)_2C_6H_3]_4B]^-$ (NaBARF) and ligands $\mathbf{L_1}$ - $\mathbf{L_{10}}$ were prepared according to the literature. Ethylene (99.5%) was purchased from Matheson Inc., and passed through Drierite before use. Analytical TLC was performed on E. Merck precoated (0.25 mm) silica gel 60 F254 plates. Flash column chromatography was carried out on silica gel 40 (Scientific Adsorbents Incorporated, Microns Flash). Enantiomeric excesses of chiral compounds **3**, **4**, **6**, **7**, **8**, and **9** were determined by chiral gas chromatographic analyses, which were performed on a Hewlett-Packard 5890 equipped with Cyclodex B (25 m x 0.25 mm, 0.12 mm film thickness) capillary GC column purchased from Chrompack and a FID detector connected to a HP 3396 integrator. The enantiomeric excess of compound **10** was determined by chiral gas chromatographic analysis, which was performed on a Hewlett-Packard 5890 equipped with Cyclodex β-Ph (25 m x 0.25 mm, 0.025 mm film thickness) capillary GC column purchased from Chrompack and a FID detector connected to a HP 3396 integrator. Helium was used as the carrier gas. Enantiomeric excesses of compound **5** was determined by HPLC using a Daicel Chiralcel OJ-H column with hexane/isopropanol as the eluent where base-line separation was obtained. Optical rotations were recorded on a Perkin-Elmer Model 241 polarimeter at the sodium D line in chloroform.

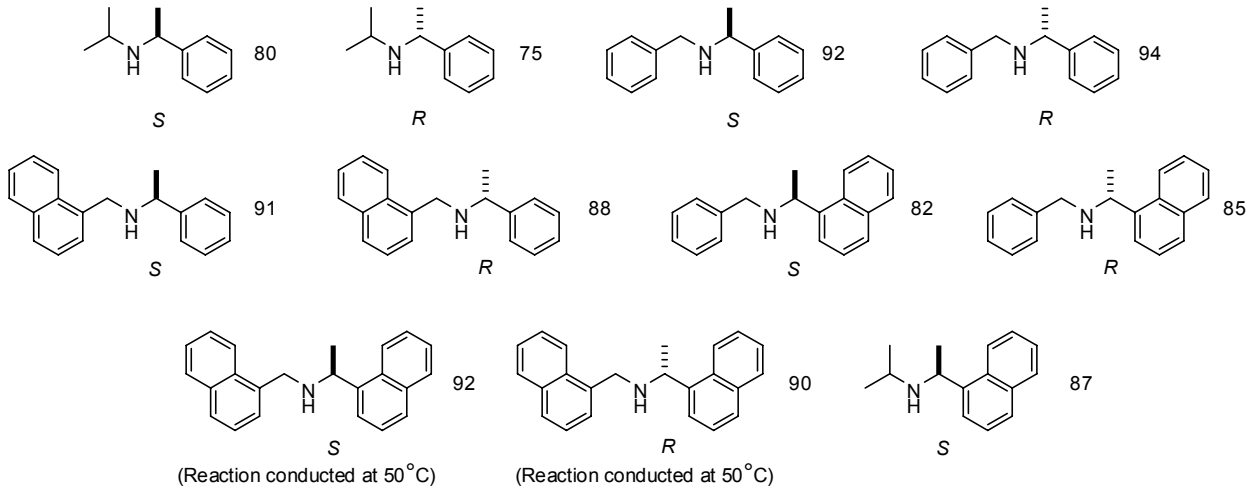
Typical procedure for the synthesis of α-chiral amines: A 50 mL three-necked round bottomed flask was equipped with a magnetic stirring bar, a rubber septum, a nitrogen inlet, and a digital thermometer probe was evacuated, flame-dried, and purged with nitrogen (all ground-glass joints were greased during apparatus setup). The flask was then charged with sodium borohydride (0.17 g, 4.50 mmol) and 1,2-dichloroethane (10 mL), then was cooled to 0°C. Glacial acetic acid (0.78 mL, 13.50 mmol) was added dropwise over a 10 minute period maintaining the internal temperature of the flask below 5°C and upon completion of acid addition was allowed to further react at 0°C for 45 minutes to ensure completion of formation of sodium triacetoxyborohydride (as noted by the halt in H_2 gas evolution). The flask was then brought to ambient temperature (25°C) over the course of 30 minutes. (*S*)-α-methyl-1-naphthylamine (0.48 mL, 3.00 mmol) and glacial acetic acid (0.26 mL, 4.50 mmol) were added to the flask and allowed to stir for five minutes, then benzaldehyde (0.33 mL, 3.00 mmol) was added to the flask dropwise over the course of two minutes. The reaction mixture was further agitated at ambient temperature for a period of 4 h or until reaction completion was complete by TLC. Upon completion, the reaction was quenched by the slow addition of saturated $NaHCO_3$ (10 mL) and extraction into ethyl acetate (4 x 10 mL). The resulting organic layers were combined, dried over anhydrous $MgSO_4$ (3.00 g), filtered through a sintered glass funnel, and dried *in vacuo* by rotary evaporation. The resulting yellow oil was diluted into 40 mL of ethyl acetate and a solution of oxalic acid (0.38 g, 3.00 mmol) in hot (70°C) ethyl acetate (5 mL) was added dropwise to the desired amine. The salt was allowed to precipitate overnight before filtration through a Büchner funnel. The ammonium salt was washed with cold (0°C) ethyl acetate (2 x 15 mL). The oxalate salt was then dried in vacuo for 12 h to afford 0.97 g (92%) of the pure salt as a white crystalline solid. To obtain free amine, the oxalate salt was stirred in a biphasic solution of 6N KOH and ether (1:1) for 6 h (resulted in quantitative recovery of the free amine).



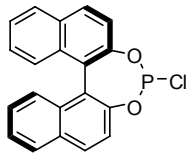
S

***N*-benzyl-(*S*)-*N*-[1-(1-naphthylethyl)]amine**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J = 9.60 Hz, 1H), 7.85 (d, J = 9.60 Hz, 1H), 7.74 (dd, J_1 = 7.60 Hz, J_2 = 2.80 Hz, 2H), 7.50-7.43 (m, 3H), 7.32-7.18 (m, 5H), 4.67 (q, J = 6.67 Hz, 1H), 3.77-3.65 (AB quartet, ν_A = 3.78, ν_B = 3.64, J_{AB} = 13.00 Hz, 2H), 1.76 (br s, 1H), 1.50 (d, J = 6.80 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.0, 140.7, 134.0, 131.4, 128.9, 128.3, 128.2, 127.2, 126.8, 125.7, 125.6, 125.3, 123.0, 122.9, 53.0, 51.9, 23.6. IR (neat) cm^{-1}: 3380, 3060, 2965, 1452, 1174, 1125, 778, 699. $[\alpha]_D^{22}$ = +5.2 ± 0.2 (*c* 0.98, $CHCl_3$). GC (achiral) conditions: 10 min at 150°C, 5°C/min, 20 min at 250°C; retention time (min): 30.67. HRMS (ESI); m/z 284.1405 ([M + Na]; exact mass calculated for $C_{19}H_{18}NNa$, 284.1415).

Figure 1: Structures and yields of free α-chiral amines after purification as the oxalate salts.

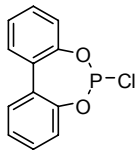


Typical procedure for the synthesis of dioxychlorophosphines: A 100 mL single-necked round bottomed flask equipped with a magnetic stirring bar, reflux condenser, and nitrogen inlet was flame-dried and purged with nitrogen. The flask was charged with (*R*)-(+)-1,1'-bi(2-naphthol) (7.0 g, 26.00 mmol) and freshly distilled phosphorus trichloride (20.5 mL, 234 mmol) under a strong stream of nitrogen. All joints were greased and the vessel was brought to reflux *via* oil bath and stirred for 16 h. The reaction was cooled to ambient temperature and the reflux condenser was quickly traded for a flame-dried, pre-assembled and greased distillation apparatus composed of a Hickman head with glass stopper, West condenser, vacuum adapter connected to a nitrogen line, and 50 mL round bottomed collection flask. The collection flask was then submerged into a liquid nitrogen bath and the excess PCl_3 was distilled away, leaving a thick, yellow oil. The pot was cooled to ambient temperature and the distillation apparatus was removed and replaced with a rubber septum. Immediately upon positioning the rubber septum, a vacuum was applied to the flask *via* needle inserted through the septum to remove any additional remaining phosphorus trichloride. The atmosphere was then replaced with nitrogen and the oil was dissolved in 20 mL dry diethyl ether and transferred *via* cannula to a 100 mL single-necked pear shaped flask equipped with a rubber septum. The initial product-containing flask was then washed with 5 mL of diethyl ether and is again transferred via cannula to the pear shaped flask. After transfer was complete, the rubber septum on the pear shaped flask was exchanged for a flame-dried flow-controlled gas inlet with stopcock. High vacuum was applied to the ethereal solution of chlorophosphine to remove the ether and any remaining trace amounts of phosphorus trichloride. The product was then dried for 3 h and transferred into a drybox, yielding 9.16 g (99-100%) of the desired product as an off-white foam.



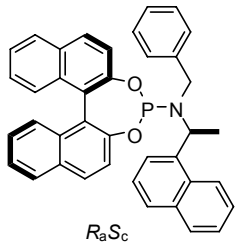
R_a

(*R*)-(+)-1,1'-binaphthyl-2,2'-dioxychlorophosphine: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 8.80 Hz, 2H), 7.97 (dd, J_1 = 8.20 Hz, J_2 = 3.40 Hz, 2H), 7.55 (dd, J_1 = 8.80 Hz, J_2 = 0.80 Hz, 1H), 7.52-7.45 (m, 3H), 7.45-7.41 (m, 2H), 7.35-7.29 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.8, 147.2, 132.7, 132.4, 132.0, 131.6, 130.9, 130.1, 128.5, 127.0, 126.9, 126.7, 126.5, 125.7, 125.5, 124.44, 124.38, 123.1, 121.6, 121.1. ^{31}P NMR (101.3 MHz, $CDCl_3$): δ 178.5.



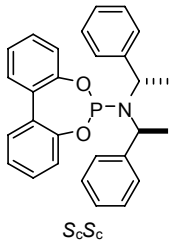
1,1'-biphenyl-2,2'-dioxychlorophosphine: The procedure was the same as above. Starting from 2,2'-biphenol (3.72 g, 20.0 mmol) to afford 4.89 g (97%) of the desired dioxychlorophosphine as a thick brown syrup. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (dd, J_1 = 7.25 Hz, J_2 = 1.75 Hz, 2H), 7.37-7.25 (m, 4H), 7.16 (d, J = 8.25 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.3, 131.0, 130.2, 129.5, 126.3, 122.2. ^{31}P NMR (101.3 MHz, $CDCl_3$): δ 179.7.

Typical procedure for the synthesis of chiral phosphoramidite ligands: A 50 mL three-necked flask equipped with a rubber septum, nitrogen inlet, and a temperature probe was flame-dried and purged with nitrogen. The flask was charged with anhydrous THF (5 mL) and *N*-benzyl-*N*-(*S*)-[1-(1-naphthylethyl)]amine (119 mg, 0.45 mmol). The solution was then cooled to -78°C in a dry ice-acetone slush bath. A 1.6 M solution of *n*-butyllithium (0.28 mL, 0.45 mmol) in hexanes was added dropwise over a five minute period maintaining the internal temperature of the vessel below -75°C until addition was complete, resulting in a pale pink homogenous solution. The contents of the flask were warmed to -30°C and immediately cooled to -78°C for an additional 1 h, which resulted in the solution becoming dark pink in color. A solution of (*R*)-(-)-1,1'-binaphthyl-2,2'-dioxychlorophosphine (0.18 g, 0.50 mmol) in dry THF (2 mL) was then introduced dropwise *via* syringe maintaining the solution temperature below -70°C. The solution was maintained at -78°C for an additional 2 h before it was warmed to ambient temperature and stirred for an additional 12 h. The resulting mixture was filtered through Celite, washed with ether, and reduced by rotary evaporation to afford 0.25 g of a pale yellow foam. The resulting foam was purified by flash column chromatography (elution with 40% dichloromethane in pentane, R_f = 0.48) to afford 238 mg (90%) of (*R*)-2,2'-binaphthoyl-benzyl-(*S*)-[1-(1-naphthylethyl)]aminoylphosphine as a white foam.



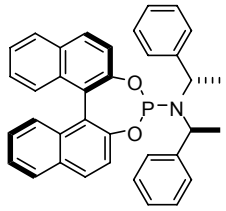
R_aS_c

(*R*)-2,2'-binaphthoyl-benzyl-(*S*)-[1-(1-naphthylethyl)]aminoylphosphine (L_{10}): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 8.80 Hz, 1H), 7.86-7.84 (m, 3H), 7.82 (d, J = 8.80 Hz, 1H), 7.76 (d, J = 8.20 Hz, 1H), 7.66 (d, J = 8.80 Hz, 1H), 7.62 (d, J = 7.20 Hz, 1H), 7.54 (d, J = 8.80 Hz, 1H), 7.48 (t, J = 7.40 Hz, 2H), 7.43-7.37 (m, 2H), 7.33-7.28 (m, 3H), 7.25-7.16 (m, 7H), 6.96 (d, J = 8.80 Hz, 1H), 5.40-5.33 (m, 1H), 3.95-3.36 (d_{AB} quartet, ν_A = 4.21, ν_B = 3.11, J_{AB} = 15.30 Hz, $J_{H\text{-}P}$ = 2.10 Hz, 2H), 1.69 (d, J = 6.80 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1, 150.0, 149.5, 139.3, 136.52, 136.46, 133.9, 123.8, 132.5, 131.5, 131.4, 130.5, 130.2, 129.9, 128.8, 128.7, 128.4, 128.3, 128.1, 128.0, 127.02, 126.96, 126.9, 126.0, 125.6, 125.4, 125.3, 124.9, 124.8, 124.4, 124.1, 124.0, 123.8, 122.3, 122.2, 121.7, 52.0, 47.2, 21.7. ^{31}P NMR (101.3 MHz, $CDCl_3$): δ 145.5. HRMS (ESI); m/z 598.1910 ([M + Na]; exact mass calculated for $C_{39}H_{30}NO_2PNa$, 598.1906).



S_cS_c

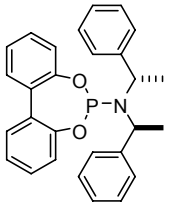
2,2'-biphenoyl-(*S*,*S*)-di(1-phenylethyl)aminoylphosphine (L_1): The reaction of 1,1'-biphenyl-2,2'-dioxychlorophosphine (125 mg, 0.5 mmol) with (-)-bis[(*S*)-1-phenylethyl]amine (102 mg, 0.454 mmol) afforded 177 mg (89%) of $\mathbf{L_1}$ as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.44 (m, 2H), 7.33-7.30 (m, 2H), 7.28-7.27 (m, 2H), 7.21-7.16 (m, 2H), 7.13-7.09 (m, 11H), 4.61-4.56 (m, 2H), 1.72 (d, J = 6.80 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.9, 151.0, 142.9, 131.2, 129.8, 128.9, 127.9, 126.6, 124.3 (d, J = 252.0 Hz), 122.2 (d, J = 188.0 Hz), 52.6, 22.2. ^{31}P NMR (101.3 MHz, $CDCl_3$): δ 146.4. HRMS (ESI); m/z 462.1590 ([M + Na]; exact mass calculated for $C_{28}H_{26}NO_2PNa$, 462.1593).



$R_aS_cS_c$

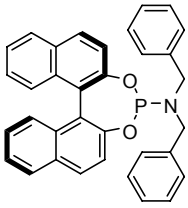
(*R*)-2,2'-binaphthoyl-(*S*,*S*)-di(1-phenylethyl)aminoylphosphine (L_3): Coupling of (-)-bis[(*S*)-1-phenylethyl]amine (1.69 mL, 7.39 mmol) and (*R*)-(-)-1,1'-binaphthyl-2,2'-dioxychlorophosphine (2.85 g, 8.13 mmol) afforded 3.70 g (93%) of $\mathbf{L_3}$ as a white foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, J = 8.80 Hz, 2H), 7.87 (dd, J_1 = 7.80 Hz, J_2 = 4.20 Hz, 2H), 7.57 (d, J = 8.80 Hz, 1H), 7.42 (d, J = 8.80 Hz, 1H), 7.40-7.34 (m, 3H), 7.27 (d, J = 8.00 Hz, 1H), 7.23-7.16 (m, 2H), 7.13-7.06 (m, 10H), 4.41-4.37 (m, 2H), 1.63 (d, J = 7.25 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1, 150.0, 149.5, 142.8, 132.8, 132.7, 131.4, 130.4, 130.2, 129.4, 128.3, 128.1, 127.9, 127.7, 127.1, 127.0, 126.6, 126.0, 125.9, 124.7, 124.4, 124.1, 124.0, 122.4, 122.3, 121.74, 121.71, 52.3, 52.2, 22.0. ^{31}P NMR (101.3 MHz, $CDCl_3$): δ 145.6. IR (KBr) cm^{-1}: 3056, 2968, 1947, 1890, 1810, 1590, 1506, 1462, 1374, 1326, 1231, 1203, 1070, 948, 924, 821, 746, 696, 626. HRMS (ESI); m/z 562.1904 ([M + Na]; exact mass calculated for $C_{36}H_{30}NO_2PNa$, 562.1906).

Figure 2: Structures and yields (from the corresponding bisphenol) of phosphoramidites synthesized by the two-step procedure.



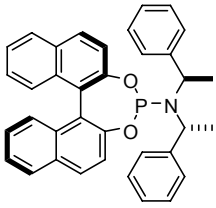
89

L1, S_cS_c



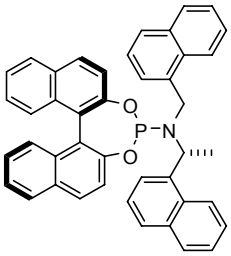
95

L7, R_aR_c



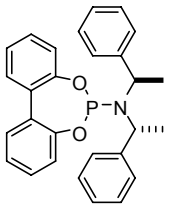
87

L13, $R_aR_cR_c$



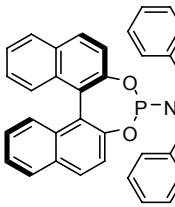
88

L19, R_aR_c



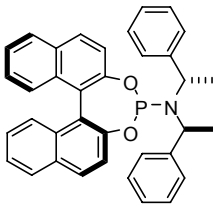
94

L2, R_cR_c



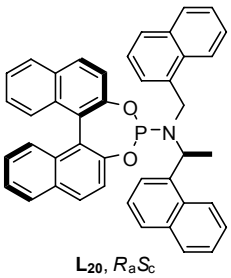
93

L8, R_aS_c



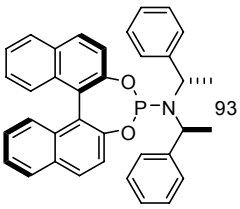
95

L14, $S_aS_cS_c$



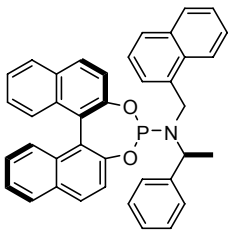
90

L20, R_aS_c



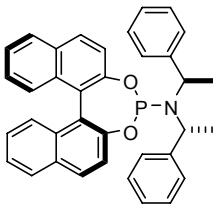
93

L3, $R_aS_cS_c$



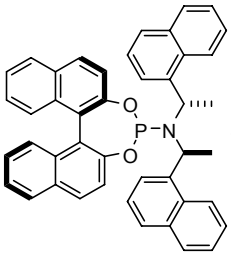
92

L9, R_aS_c



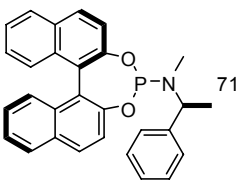
83

L15, $S_aR_cR_c$



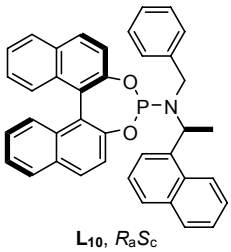
87

L21, $R_aS_cS_c$



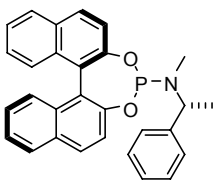
71

L4, R_aS_c



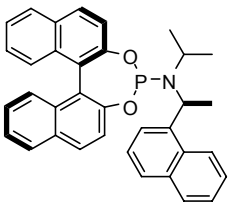
90

L10, R_aS_c



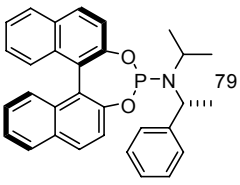
68

L16, R_aR_c



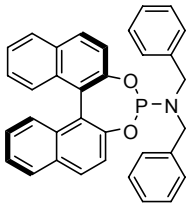
79

L22, R_aS_c



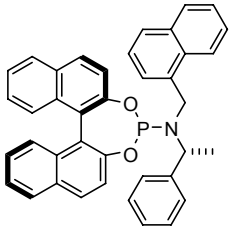
79

L5, R_aR_c



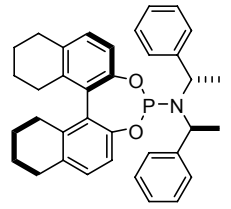
97

L11, R_a



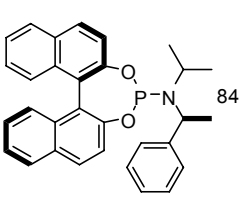
89

L17, R_aR_c



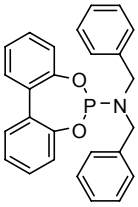
84

L23, $R_aS_cS_c$-H_8



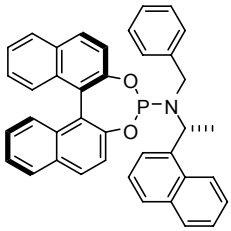
84

L6, R_aS_c



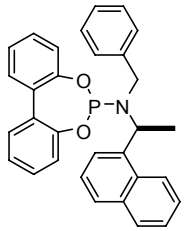
82

L12



90

L18, R_aR_c

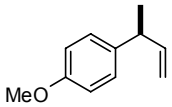


84

L24, S_c

Typical procedure for asymmetric hydrovinylation: The pre-catalyst was prepared as follows in a glovebox: To [di(μ-bromo)bis(η-allyl)nickel(II) (2.6 mg, 0.007 mmol for substrate **2**) in CH_2Cl_2 (1 mL) was added a solution of ligand (0.014 mmol for substrate **2**) in CH_2Cl_2 (1 mL) at ambient temperature. The resulting solution was added to a suspension of NaBARF (12.4 mg, 0.014 mmol for substrate **2**) dissolved in CH_2Cl_2 (1 mL) and the mixture was stirred at ambient temperature in a 10 mL pear shaped flask for 2 h affording a dark brown solution containing a small amount of fine particulate (NaBr).

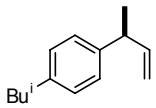
In a fumehood, a 25 mL three-necked round bottomed flask equipped with a rubber septum, flow-controlled nitrogen inlet, a temperature probe, and a magnetic stirring bar was flame-dried and purged with nitrogen. The flask was then charged with 5 mL of dry dichloromethane. The catalyst solution prepared above now removed from the drybox, was introduced to the vessel *via* cannula. The flask containing the catalyst solution was further rinsed with 2 mL CH_2Cl_2, and this solution was also transferred to the reaction mixture. Upon completion of pre-catalyst transfer, the system was closed at the flow-controlled stopcock and cooled to -78 ^oC, creating a small vacuum. Dry ethylene (passed through a 0.5" x 4" column of Drierite®) was introduced *via* needle through the serum stopper and the vessel atmosphere was slowly evacuated 3 times with a 20 mL syringe. After cooling the solution to -78^oC, a solution of *p*-methoxystyrene (**2**, 134 mg, 1.00 mmol) in 2 mL dry CH_2Cl_2 was introduced dropwise into the solution of pre-catalyst over a one minute period *via* syringe followed by a 1 mL rinse with CH_2Cl_2. The vessel was then maintained at -78°C for a period of 1 h. At the end of this period the ethylene line was removed and the system exposed to nitrogen. Deionized H_2O (1 mL) was introduced into the flask, the septum was pierced with a needle, and nitrogen was blown through the flask to remove any remaining ethylene. The biphasic solution was then poured into a 100-mL separatory funnel containing 20 mL H_2O and the CH_2Cl_2 is collected. The aqueous layer was then extracted with three 10 mL portions of methylene chloride. The organic layers were combined, dried, filtered through a sintered glass funnel and the volume was reduced by rotary evaporation, yielding a free-flowing yellow oil. The resulting oil was filtered by flash column chromatography (eluted with isocratic pentane) to afford the desired crude hydrovinylation product as a colorless oil, which was then used to acquire all analytical data without further purification.



3

1-Methoxy-4-[(*S*)-1-methylallyl]benzene: ^1H NMR (400 MHz, $CDCl_3$): δ 7.13 (d, J = 9.20 Hz, 2H), 6.84 (d, J = 9.20 Hz, 2H), 5.98 (ddd, J_1 = 17.20 Hz, J_2 = 10.40 Hz, J_3 = 6.40 Hz, 1H), 5.02 (dt, J_1 = 17.20 Hz, J_2 = 1.40 Hz, 1H), 5.00 (dt, J_1 = 10.40 Hz, J_2 = 1.40 Hz, 1H), 3.78 (s, 3H), 3.44-3.39 (m, 1H), 1.33 (d, J = 6.80 Hz, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 157.9, 143.6, 137.7, 128.1, 113.8, 112.8, 55.24, 42.3, 20.8. IR (neat) cm^{-1}: 2963, 1611, 1511, 1246, 1178, 1038, 830, 758. $[\alpha]_D^{22}$ = 8.2 ± 0.02 (*c* 0.50, $CHCl_3$). GC (achiral) conditions: 5 min at 80°C, 5°C/min, 5 min at 200°C; retention time (min): 16.71. GC (chiral) conditions: (Cyclodex-β) 70 min at 85°C (isothermal); retention time (min): 57.31 (*R*), 58.46 (*S*). HRMS (ESI); m/z 162.1040 ([M]; exact mass calculated for $C_{11}H_{14}O$, 162.1045).

ligand	mol % cat.	time (h)	temp (°C)	conv. (%)	selec. (%)	% ee, conf.
rac	0.7	1	-78	>99	>99	rac
$\mathbf{L_1}$	0.7	1	-78	>99	>99	95, *S*
$\mathbf{L_3}$	0.7	1	-78	>99	>99	>95. *S*
$\mathbf{L_{10}}$	0.7	1	-78	>99	>99	>97, *S*

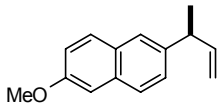


4

1-Isobutyl-4-[(*S*)-1-methylallyl]benzene: ^1H NMR (400 MHz, $CDCl_3$): δ 7.12-7.06 (m, 4H), 6.00 (ddd, J_1 = 17.00 Hz, J_2 = 10.40 Hz, J_3 = 6.40 Hz, 1H), 5.03 (dt, J_1 = 17.00 Hz, J_2 = 1.60 Hz, 1H), 5.00 (dt, J_1 = 10.40 Hz, J_2 = 1.60 Hz, 1H), 3.45-3.42 (m, 1H), 2.43 (d, J = 7.20 Hz, 2H), 1.84 (septet, J = 6.80 Hz, 1H), 1.34 (d, J = 6.80 Hz, 3H), 0.89 (d, J = 6.80 Hz, 6H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 143.6, 142.8, 139.4, 129.1, 126.9, 112.8, 45.1, 42.8, 30.2,

22.4, 20.8. IR (neat) cm^{-1}: 2957, 1637, 1511, 1465, 1018, 912, 844, 797. $[\alpha]_D^{22} = 9.0 \pm 0.02$ (*c* 0.50, $CHCl_3$). GC (achiral) conditions: 5 min at 100°C, 5°C/min, 5 min at 200°C; retention time (min): 15.23. GC (chiral) conditions: (Cyclodex-β) 45 min at 100°C (isothermal); retention time (min): 37.72 (*R*), 38.37 (*S*). HRMS (ESI); m/z 188.1567 ([M]; exact mass calculated for $C_{14}H_{20}$, 188.1565).

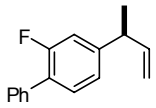
ligand	mol % cat.	time (h)	temp (°C)	conv. (%)	selec. (%)	% ee, conf.
rac	0.7	2	-78	>99	>98	rac
$\mathbf{L_1}$	0.7	2	-78	>99	98	90, *S*
$\mathbf{L_3}$	0.7	2	-78	>99	>99	90, *S*
$\mathbf{L_{10}}$	0.7	2	-78	>97	>99	96, *S*



5

2-Methoxy-6-[(*S*)-1-methylallyl]naphthalene: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, $J_1 = 8.80$ Hz, $J_2 = 1.60$ Hz, 2H), 7.61 (s, 1H), 7.36 (d, $J_1 = 8.40$ Hz, $J_2 = 1.60$ Hz, 1H), 7.18-7.15 (m, 2H), 6.12 (ddd, $J_1 = 16.80$ Hz, $J_2 = 10.00$ Hz, $J_3 = 6.40$ Hz, 1H), 5.14 (dt, $J_1 = 16.80$ Hz, $J_2 = 1.60$ Hz, 1H), 5.10 (dt, $J_1 = 10.00$ Hz, $J_2 = 1.60$ Hz, 1H), 3.95 (s, 3H), 3.64 (m, 1H), 1.48 (d, $J = 6.80$ Hz, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 157.3, 143.3, 140.7, 133.2, 129.1, 126.8, 126.7, 125.0, 118.6, 113.2, 105.7, 55.3, 43.1, 20.7. IR (neat) cm^{-1}: 2963, 1634, 1605, 1484, 1391, 1215, 1034, 852, 475. $[\alpha]_D^{22} = 18.9 \pm 0.02$ (*c* 1.00, $CHCl_3$). GC (achiral) conditions: 5 min at 100°C, 10°C/min, 10 min at 250°C; retention time (min): 18.90. HPLC (chiral) conditions: (Chiracil OJ-H) hexanes:isopropanol = 95:5, 0.50 mL/min; retention time (min): 25.52 (*R*), 26.80 (*S*). HRMS (ESI); m/z 212.1200 ([M]; exact mass calculated for $C_{15}H_{16}O$, 212.120).

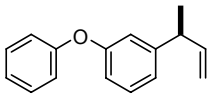
ligand	mol % cat.	time (h)	temp (°C)	conv. (%)	selec. (%)	% ee, conf.
rac	1.0	2.5	-78	>99	>99	rac
$\mathbf{L_1}$	1.0	2.5	-78	>99	>99	>90, *S*
$\mathbf{L_3}$	1.0	2.5	-78	>99	>99	>95, *S*
$\mathbf{L_{10}}$	1.0	2.5	-78	>99	>99	99, *S*



6

2-Fluoro-1-phenyl-4-[(*S*)-1-methylallyl]benzene: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.54 (m, 2H), 7.46-7.42 (m, 2H), 7.38-7.34 (m, 2H), 7.08 (dd, $J_1 = 7.60$ Hz, $J_2 = 1.60$ Hz, 1H), 7.02 (dd, $J_1 = 8.00$ Hz, $J_2 = 1.60$ Hz, 1H), 6.06-5.97 (m, 1H), 5.14-5.08 (m, 2H), 3.53-3.50 (m, 1H), 1.40 (d, $J = 6.80$ Hz, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 161.0, 147.3, 142.4, 135.8, 130.6, 130.5, 129.0, 128.9, 128.4, 127.4, 123.2, 114.9, 114.7, 113.8, 42.7, 20.6. IR (neat) cm^{-1}: 2968, 1624, 1581, 1483, 1417, 1267, 1129, 916, 767. $[\alpha]_D^{22} = 18.7 \pm 0.02$ (*c* 1.00, $CHCl_3$). GC (achiral) conditions: 5 min at 100°C, 5°C/min, 5 min at 200°C; retention time (min): 25.14. GC (chiral) conditions: (Cyclodex-β) 120 min at 130°C (isothermal); retention time (min): 91.98 (*R*), 93.24 (*S*). HRMS (ESI); m/z 226.1157 ([M]; exact mass calculated for $C_{16}H_{15}F$, 226.1158.

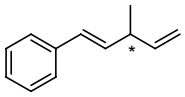
ligand	mol % cat.	time (h)	temp (°C)	conv. (%)	selec. (%)	% ee, conf.
rac	1.0	2	-78	>99	>99	rac
$\mathbf{L_1}$	1.0	2	-78	>99	>99	80, *S*
$\mathbf{L_3}$	1.0	2	-78	>99	>99	86, *S*
$\mathbf{L_{10}}$	1.0	2	-78	>99	>99	>97, *S*



7

1-Phenoxy-3--[(*S*)-1-methylallyl]benzene: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (t, J = 7.80 Hz, 2H), 7.26 (t, J = 7.80 Hz, 1H), 7.10 (t, J = 7.40 Hz, 1H), 7.01 (d, J = 7.60 Hz, 2H), 6.97 (d, J = 8.00 Hz, 1H), 6.92 (s, 1H), 6.83 (dd, J_1 = 7.80 Hz, J_2 = 2.40 Hz, 1H), 6.03-5.95 (m, 1H), 5.08-5.03 (m, 2H), 3.47-3.44 (m, 1H), 1.35 (d, J = 6.80 Hz, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 157.3, 157.2, 147.8, 142.8, 129.7, 129.6, 123.0, 122.2, 118.7, 118.0, 116.5, 113.4, 43.1, 20.7. IR (neat) cm^{-1}: 2967, 1582, 1487, 1442, 1244, 1163, 932, 755, 693. $[\alpha]_D^{22}$ = 7.8 ± 0.02 (*c* 1.00, $CHCl_3$). GC (achiral) conditions: 5 min at 100°C, 5°C/min, 5 min at 250°C; retention time (min): 24.81. GC (chiral) conditions: (Cyclodex-β) 100 min at 100°C, 0.3°C/min, 91.67 min at 125°C; retention time (min): 215.68 (*R*), 216.85 (*S*). HRMS (ESI); m/z 224.1205 ([M]; exact mass calculated for $C_{16}H_{16}O$, 224.1201).

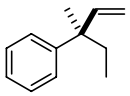
ligand	mol % cat.	time (h)	temp (°C)	conv. (%)	selec. (%)	% ee, conf.
rac	1.0	2	-78	>99	>99	rac
L_1	1.0	2	-78	>99	>99	>95
L_3	1.0	2	-78	>99	>99	>97
L_{10}	1.0	2	-78	>99	>99	>97



8

1-Phenyl-3-methyl-1,4-pentadiene: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.34 (m, 2H), 7.30-7.26 (m, 2H), 7.21-7.17 (m, 1H), 6.37 (d, J = 16.00 Hz, 1H), 6.16 (dd, J_1 = 16.00 Hz, J_2 = 7.20 Hz, 1H), 5.87 (ddd, J_1 = 16.80 Hz, J_2 = 10.00 Hz, J_3 = 6.40 Hz, 1H), 5.06 (dt, J_1 = 16.80 Hz, J_2 = 1.60 Hz, 1H), 5.01 (dt, J_1 = 10.00 Hz, J_2 = 1.60 Hz, 1H), 3.06-3.00 (m, 1H), 1.19 (d, J = 6.80 Hz, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 142.4, 137.7, 134.3, 128.7, 128.5, 127.0, 126.1, 113.3, 40.6, 19.8. IR (neat) cm^{-1}: 2965, 1636, 1496, 1448, 965, 913, 747, 693. $[\alpha]_D^{22}$ = 33.9 ± 0.02 (*c* 0.55, $CHCl_3$). GC (achiral) conditions: 5 min at 100°C, 5°C/min, 5 min at 200°C, retention time (min): 13.05. GC (chiral) conditions: (Cyclodex-β) 20 min at 80°C, 0.5°C/min to 100°C, retention time (min): 52.13 and 52.77.

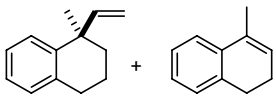
ligand	mol % cat.	time (h)	temp (°C)	conv. (%)	selec. (%)	% ee, conf.
rac	1.0	19	-20	>99	40	rac
L_1	1.0	19	-20	>99	57	84
L_3	1.0	19	-20	>99	>97	77
L_{10}	1.0	19	-20	61	>99	80



9

(*R*)-3-Methyl-3-phenyl-1-pentene: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.27 (m 4H), 7.19-7.15 (m, 1H), 6.02 (dd, J_1 = 17.60 Hz, J_2 = 10.80 Hz, 1H), 5.10 (dd, J_1 = 10.80 Hz, J_2 = 1.20 Hz, 1H), 5.03 (dd, J_1 = 17.60 Hz, J_2 = 1.20 Hz, 1H), 1.88-1.70 (ABX_3, ν_A = 1.83, ν_B = 1.75, J_{AB} = 13.80 Hz, J_{AX} = 7.40 Hz, J_{BX} = 7.40 Hz, 2H), 1.34 (s, 3H), 0.76 (t, J = 7.40 Hz, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 147.4, 146.9, 128.0, 126.7, 125.7, 111.7, 44.5, 33.4, 24.4, 8.9. IR (neat) cm^{-1}: 3083, 3058, 2966, 2877, 1636, 1600, 1493, 1446, 1030, 913, 760, 700. $[\alpha]_D^{22}$ = -14.2 ± 0.02 (*c* 1.00, $CHCl_3$). GC (achiral) conditions: 5 min at 100°C, 5°C/min, 5 min at 200°C, retention time (min): 10.61. GC (chiral) conditions: (Cyclodex-β) 40 min at 70°C, 5°C/min, 10 min at 90°C, retention time (min): 53.90 (*R*), 55.65 (*S*). HRMS (ESI); m/z 160.1257 ([M]; exact mass calculated for $C_{12}H_{16}$, 160.1252).

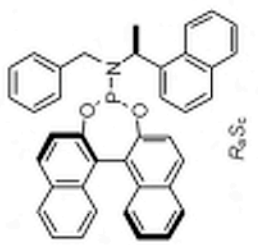
ligand	mol % cat.	time (h)	temp (°C)	conv. (%)	selec. (%)	% ee, conf.
rac	1.0	4	-78	>99	>99	Rac
$\mathbf{L_1}$	1.0	4	-78	>99	>99	92, *R*
$\mathbf{L_3}$	1.0	4	-78	>99	>99	>97, *R*
$\mathbf{L_{10}}$	1.0	4	-78	>99	>99	94, *R*



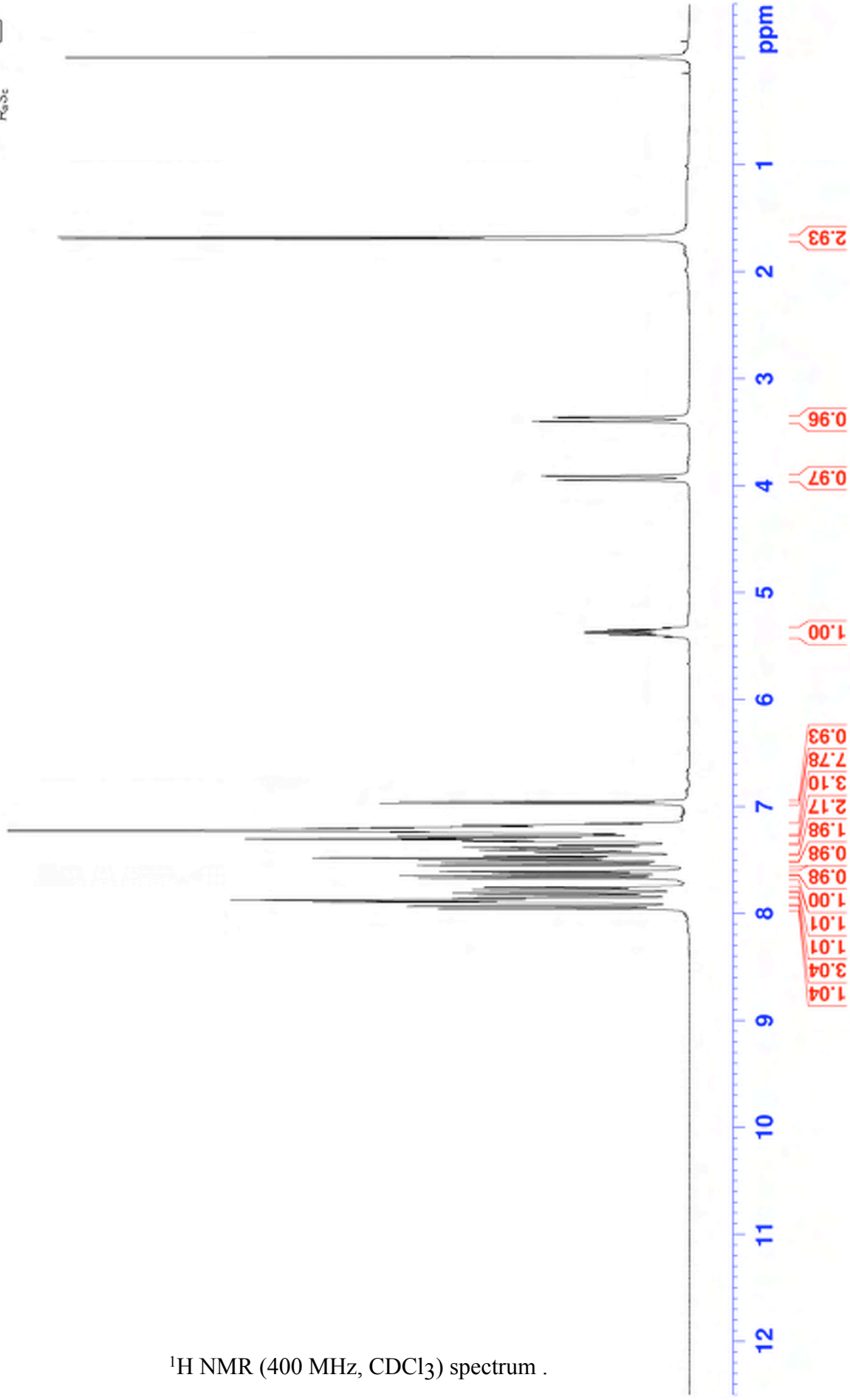
10A[g] **10B**

(*R*)-1-Methyl-1-vinyltetrahydronaphthalene (A) and 1-methyl-3,4-dihydronaphthalene (B):
A ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21-7.13 (m, 4H), 6.01 (dd, J_1 = 17.60 Hz, J_2 = 10.40 Hz, 1H), 5.10 (dd, J_1 = 10.40 Hz, J_2 = 1.20 Hz, 1H), 4.89 (dd, J_1 = 17.60 Hz, J_2 = 1.20 Hz, 1H), 1.90-1.83 (m, 3H), 1.76-1.71 (m, 1H), 1.46 (s, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 148.8, 142.3, 135.8, 129.1, 128.5, 125.7, 125.6, 112.0, 40.9, 37.6, 34.1, 28.3, 22.4. GC (achiral) conditions: 5 min at 100°C, 5°C/min, 5 min at 200°C, retention time (min): 13.10. GC (chiral) conditions: (Cyclodex β-Ph) 75 min. at 90°C, retention time (min): 70.80 (*S*) and 71.33 (*R*). (Cyclodex-β) 75 min. at 90°C, retention time (min): 62.85 (*S*) and 63.69 (*R*).
B ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.26 (m, 4H), 5.94-5.90 (m, 1H), 2.86-2.82 (m, 3H), 2.33-2.31 (m, 1H), 2.14-2.12 (m, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 136.6, 136.3, 132.2, 127.3, 126.7, 126.3, 125.4, 122.7, 30.31, 23.2, 19.3. GC (achiral) conditions: 5 min at 100°C, 5°C/min, 5 min at 200°C, retention time (min): 13.11. GC (chiral) conditions: (Cyclodex β-Ph) 75 min. at 90°C, retention time (min): 60.13. (Cyclodex-β) 75 min. at 90°C, retention time (min): 45.37.

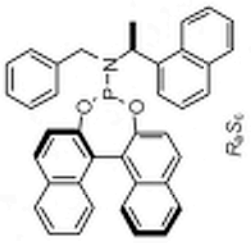
ligand	mol % cat.	time (h)	temp (°C)	conv. (%)	selec. (%)	% ee, conf.	ratio A:B
rac	5.0	6	-78	93	64	rac	64:36
$\mathbf{L_1}$	5.0	6	-78	>99	66	>95, *R*	66:34
$\mathbf{L_3}$	5.0	6	-78	>99	71	>99, *R*	71:29
$\mathbf{L_{10}}$	5.0	6	-78	79	79	>99, *R*	79:21



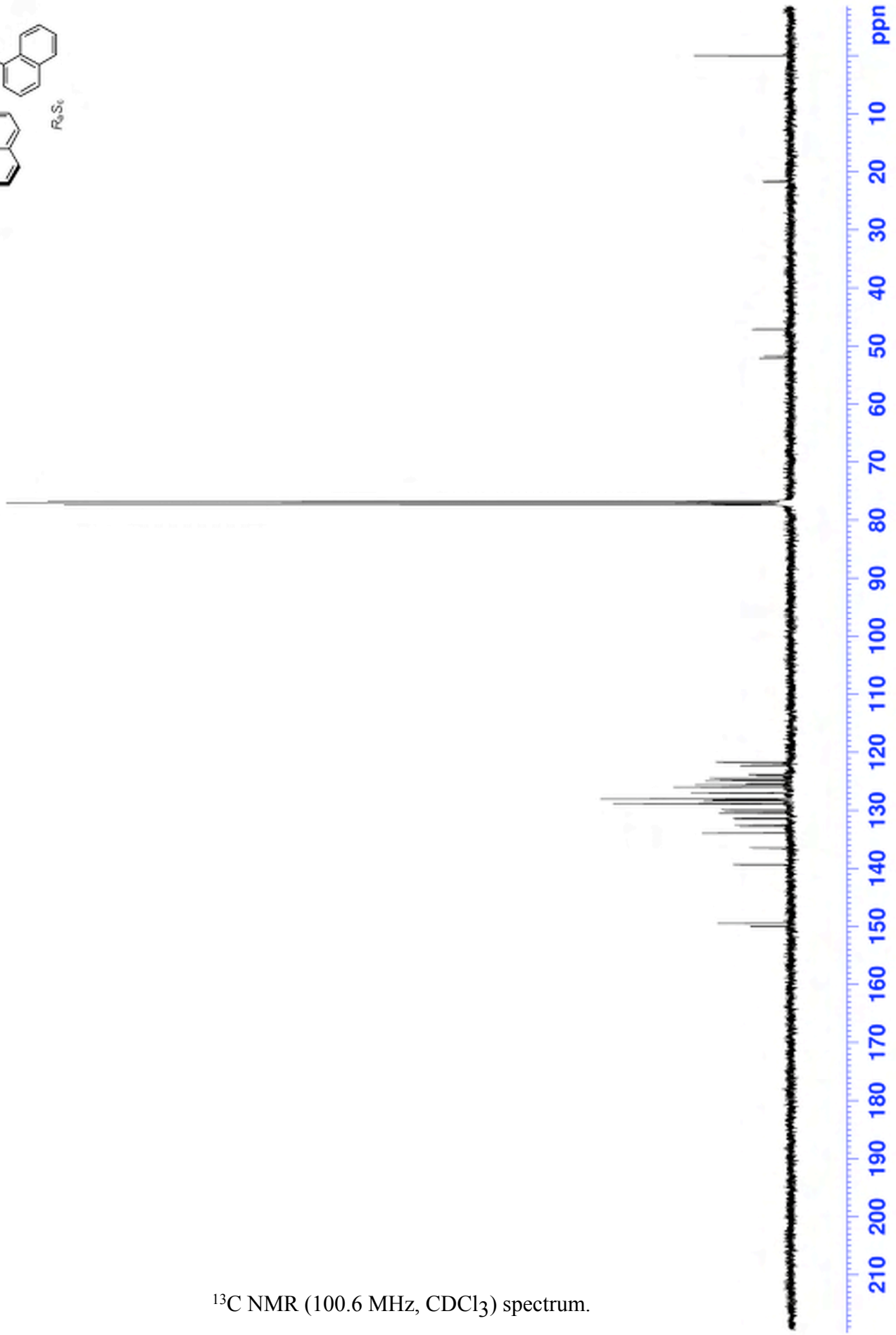
L10



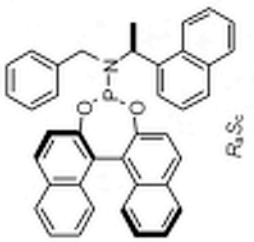
^{1}H NMR (400 MHz, $CDCl_3$) spectrum .



L10

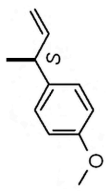


^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum.



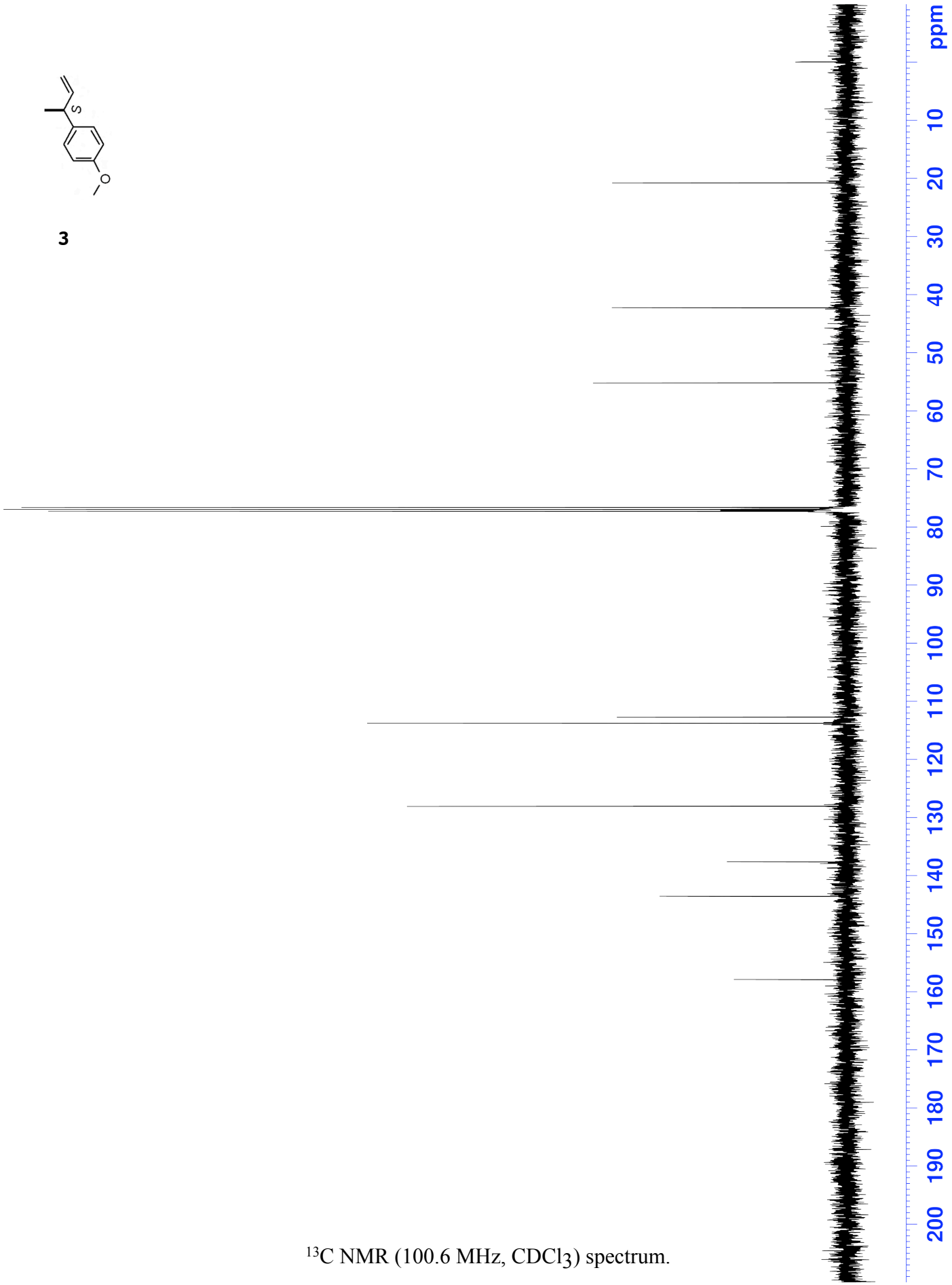
L10

^{31}P NMR (101.3 MHz, $CDCl_3$) spectrum.



3

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



^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum.

3

R_cR_c & S_cS_c (rac)

Achiral GC: 5 min at 80°C, 5°C/min, 5 min at 200°C.

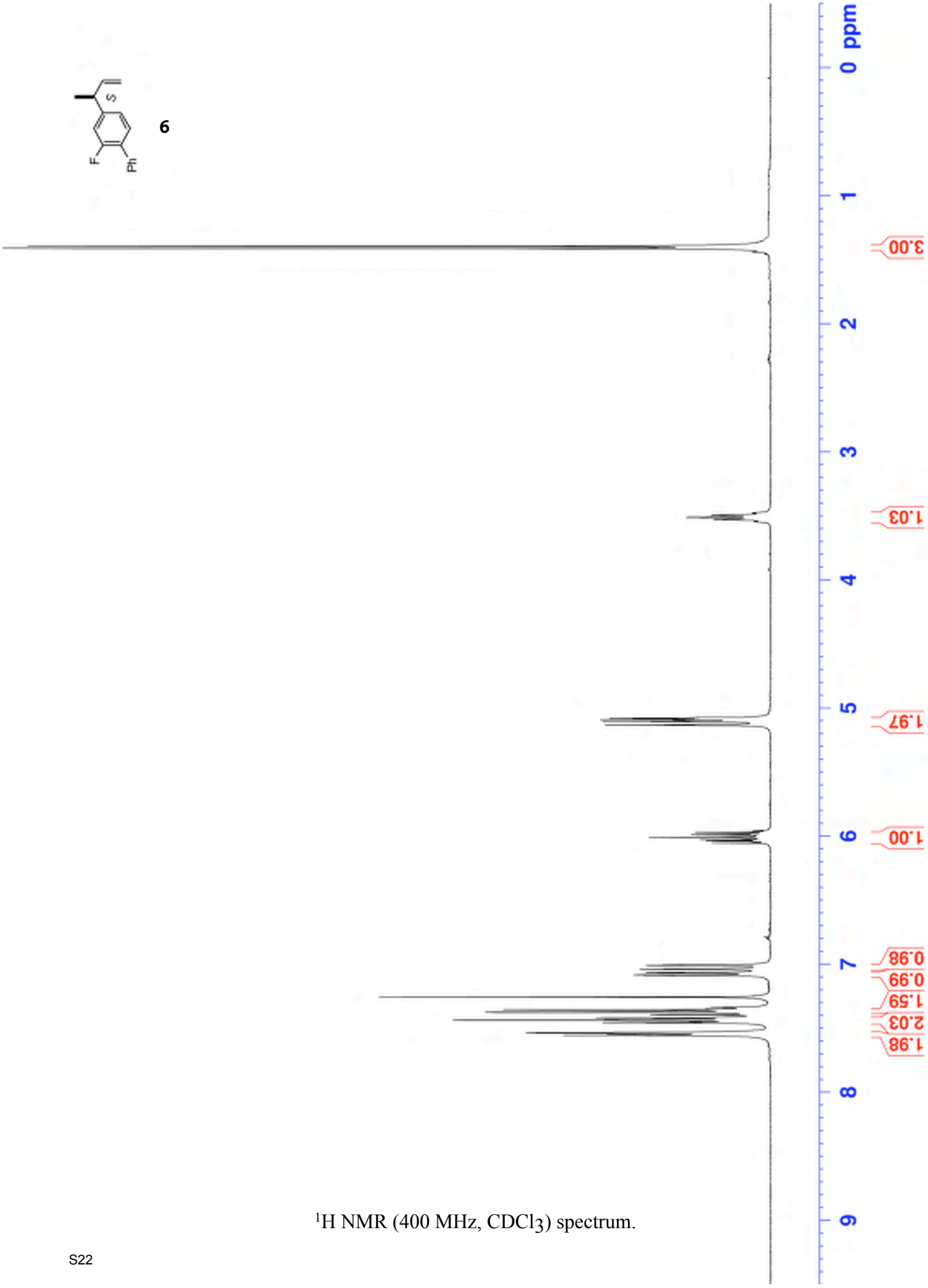
3

Chiral GC (racemic mixture): 70 min at 85°C.

Chiral GC: 70 min at 85°C.

Chiral GC: 45 min at 100°C.

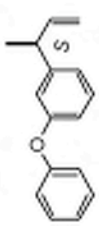
Chiral HPLC: hexanes:isopropanol (95:5), 45 min at 0.50 mL/min.



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

6

Chiral GC: 120 min at 130°C.



7

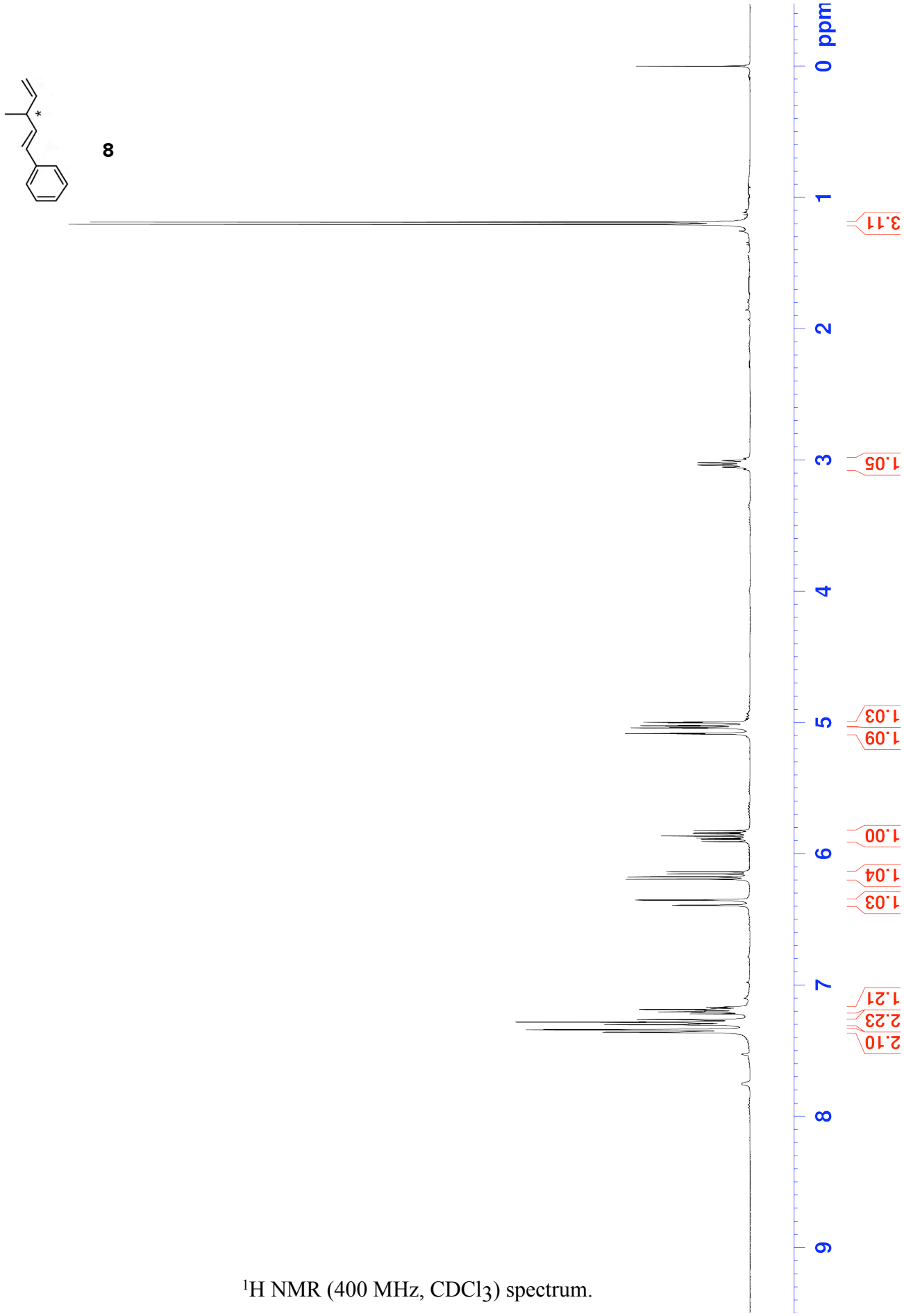
^{1}H NMR (400 MHz, $CDCl_3$) spectrum.

7

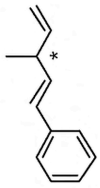
R_cR_c & S_cS_c (rac)

Chiral GC (racemic mixture): 100 min at 100°C, 0.3°C/min, 91.67 min at 125°C.

Chiral GC: 100 min at 100°C, 0.3°C/min, 91.67 min at 125°C.



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



8

^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum.

Chiral GC: 20 min at 80°C, 0.5°C/min to 100°C.