Copper-Catalyzed Enantioselective 1,2-Borylation of 1,3-Dienes

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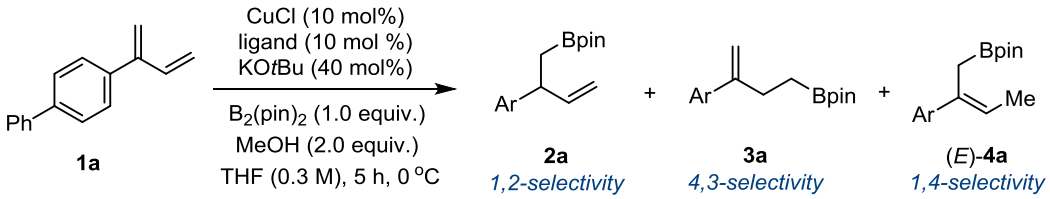
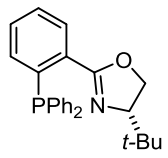
1. General information

All reactions were carried out under an inert atmosphere of nitrogen using either two-manifold vacuum/inert nitrogen lines or a M.Braun glove-box. Solvents were dried over activated alumina columns and further degassed by three successive "freeze-pump-thaw" cycles if necessary. NMR spectra were recorded on AMX–300, AMX–400 and AMX–500 Bruker Avance spectrometers at 298 K. ^{1}H and ^{13}C{^{1}H} NMR chemical shifts are given in ppm relative to $SiMe_4$, with the solvent resonance used as internal reference. ^{1}H NMR spectra were referenced to $CDCl_3$ (7.26 ppm) and ^{13}C{^{1}H} NMR spectra were referenced to $CDCl_3$ (77.16 ppm). Infrared spectra were obtained on a Perkin–Elmer 1650 FT-IR spectrometer using neat samples on a diamond ATR Golden Gate sampler. The mass spectrometric data were obtained at the mass spectrometry facility of the University of Geneva (http://www.unige.ch/sciences/sms/). GC-MS analyses were performed on GC–HP 6890, column Agilent–HP1 (30 m–ID 0.32 mm, Film 0.25 µm) coupled with MS–HP 5973.
The enantiomeric excesses (*ee*'s) were determined by HPLC, SFC and GC analyses.
HPLC analyses performed on a *Shimadzu* CTO-20AA with column DAICEL OD-H, OJ-H, AD-H and IC. GC analyses were performed on HP–6890, column HYDRODEX DiMOM and HYDRODEX TBDM, 50 m. SFC analyses were performed on a Waters Acquity UPC2 with columns OD-3, OJ-3, OZ-3, OB-H, AZ-3, AD, AS-3, AY-H. Retention times (t_R) are given in minutes. Thin layer chromatography (TLC) was performed on plates of silica precoated with 0.25 mm Kieselgel 60 F_{254} from *Merck*. Flash chromatography was performed using silica gel SiliaFlash® P60 (230-400 mesh) from *Silicycle*. Commercial reagents, precatalysts and ligands were purchased from Aldrich, Fluka, Acros or Strem and used without purification unless otherwise noted. Liquid reagents were transferred with stainless steel syringes or cannula. All the dienes were prepared following reports from the literature.[1] Copper complexes and ligands were stored and weighted inside a M. Braun glove-box. CuO*t*Bu was prepared as described in the literature.[2] Simplephos ligands **L8-9** were prepared following reports from the literature.[3]

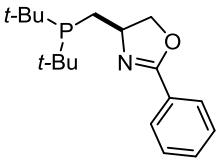
2. Reaction optimization

Table S1: Ligand screening

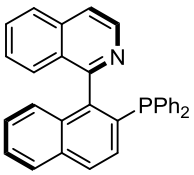




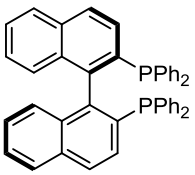
conv. 80%
2a : **3a** : **4a** = 2 : 1 : 1
–7% *ee*



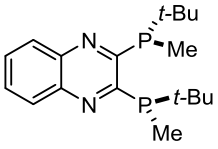
conv. 87%
2a : **3a** : **4a** = 6.5 : 1.2 : 1
0% *ee*



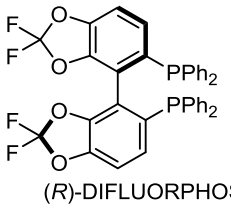
(*R*)-QUINAP
conv. 74%
2a : **3a** : **4a** = 6 : 1 : 2
–43% *ee*



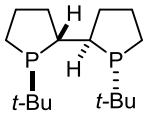
(*R*)-BINAP
conv. 86%
2a : **3a** : **4a** = 1 : 15 : -



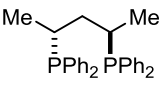
(*R,R*)-QuinoxP*
conv. 74%
2a : **3a** : **4a** = 1 : 3 : -
+5% *ee*



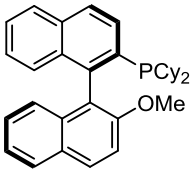
(*R*)-DIFLUORPHOS
conv. 81%
2a : **3a** : **4a** = 1 : 1.7 : -
–17% *ee*



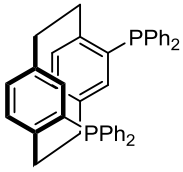
(*S,S,R,R*)-TANGPHOS
conv. 82%
2a : **3a** : **4a** = 1 : 2 : -
+14% *ee*



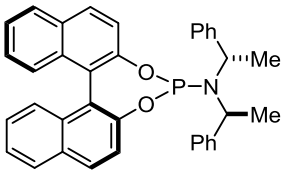
(*R,R*)-BDPP
conv. 81%
2a : **3a** : **4a** = 1 : 1.5 : -
–24% *ee*



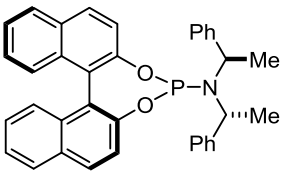
(*R*)-MOP[b]
conv. 67%
2a : **3a** : **4a** = 1 : 7 : -
–21% *ee*



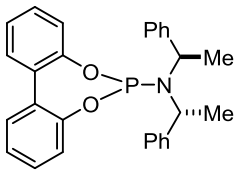
(*S*)-Phanephos
conv. 70%
2a : **3a** : **4a** = 6 : 1 : -
–40% *ee*



(S,S,S_a)[b]
conv. 80%
2a : **3a** : **4a** = 4 : 1 : 1
–20% *ee*

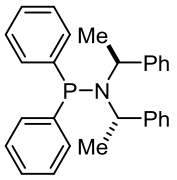


(R,R,S_a)[b]
conv. 66%
2a : **3a** : **4a** = 4.6 : 1.3 : 1
–4% *ee*



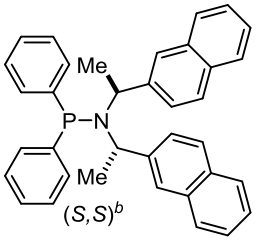
(*R*,*R*)[b]

conv. 72%
2a : **3a** : **4a** = 9 : 2 : 1
+5% *ee*



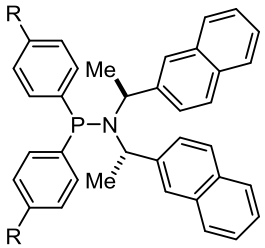
(*S*,*S*)-**L8**[b]

conv. 87%
2a : **3a** : **4a** = 8 : 2 : 1
–48% *ee*



(*S*,*S*)[b]

conv. 92%
2a : **3a** : **4a** = 6 : 2.2 : 1
–62% *ee*

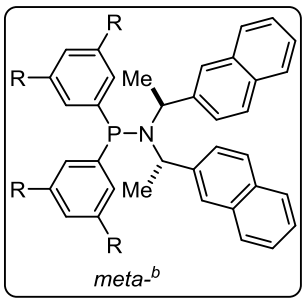


para-[b]

R = OMe
conv. 90%
2a : **3a** : **4a** = 10 : 2 : 1
–36% *ee*

R = *t*-Bu
conv. 87%
2a : **3a** : **4a** = 11 : 2.7 : 1
–54% *ee*

R = F
conv. 61%
2a : **3a** : **4a** = 4 : 1.8 : 1
–63% *ee*



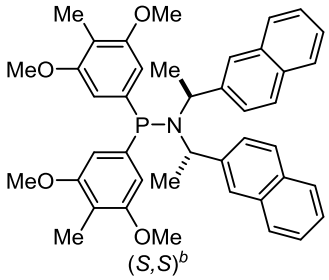
meta-[b]

R = OMe
conv. 92%
2a : **3a** : **4a** =
14 : 3.5 : 1
–41% *ee*

R = *t*-Bu
conv. 91%
2a : **3a** : **4a** =
27 : 2.7 : 1
–67% *ee*
(*S*,*S*)-**L9**

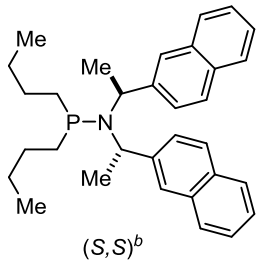
R = Me
conv. 88%
2a : **3a** : **4a** =
14 : 2.5 : 1
–43% *ee*

R = CF_3
conv. 52%
2a : **3a** : **4a** =
4 : 1.5 : 1
+60% *ee*



(*S*,*S*)[b]

conv. 87%
2a : **3a** : **4a** = 18 : 2.5 : 1
–34% *ee*

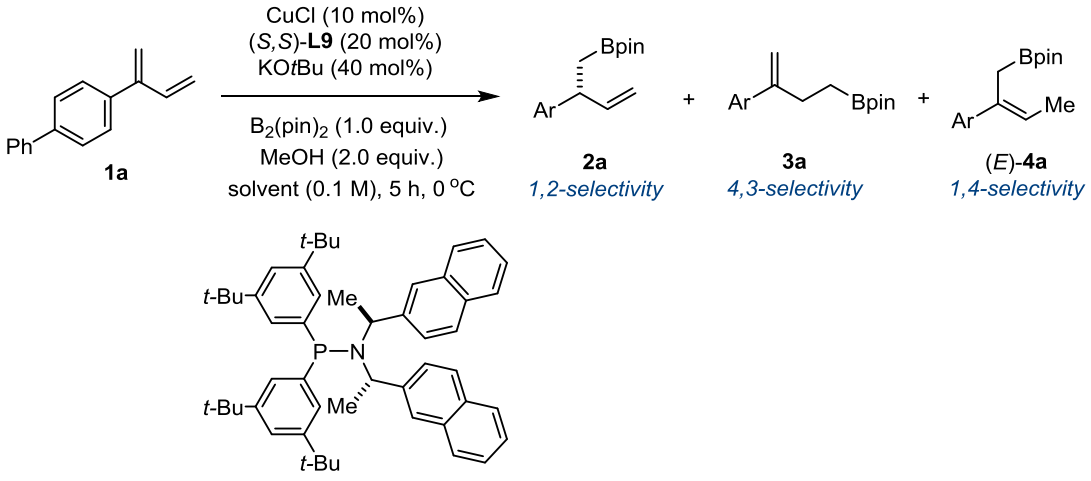


(*S*,*S*)[b]

conv. 46%
2a : **3a** : **4a** = 4.5 : 2.5 : 1
–50% *ee*

[a] Reaction conditions: Unless otherwise noted, all reactions were performed with diene (0.12 mmol), ligand/CuCl (1:1, 10 mol%), B_2pin_2 (0.1 mmol), KO*t*Bu (40 mol%), MeOH (0.2 mmol) in THF (0.3 mL) at 0 °C. Conversion and regioselectivity are for the boronic ester detected by ^{1}H NMR. Enantioselectivity determined by HPLC analysis on a chiral stationary phase after oxidation to the alcohol. [b] CuCl (10 mol%), ligand (20 mol%).

Table S2: Solvent optimization[a]

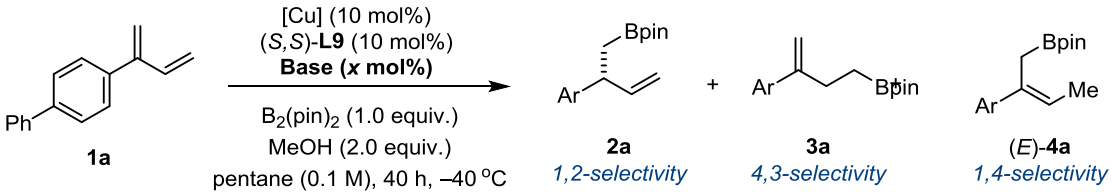


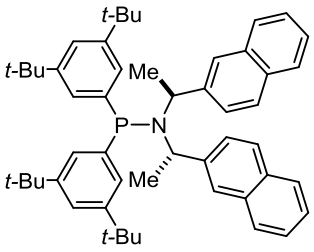
L9
(*S,S*)-Simplephos-naph

Entry	solvent	conv. (%)	**2a** : **3a** : **4a**	*ee* **2a** (%)
1	THF	29	11 : 1 : 3	64
2	toluene	83	13 : 1 : -	70
3	Et_2O	51	12 : 1 : -	72
4	CH_2Cl_2	66	15 : 1 : -	73
5	2-Me-THF	44	9 : 1 : 1	67
6[b]	1,4-dioxane	68	11 : 1.6 : 1	59
7	*i*-Pr_2O	78	12 : 1 : -	67
8	*n*-pentane	79	17 : 1 : 1	73
9	*n*-hexane	88	16 : 1 : -	71
10	cyclohexane	85	13 : 1 : -	66
11	$PhCF_3$	85	11 : 1 : -	74
12	PhCl	85	12 : 1 : -	70
13[c]	*n*-pentane	88	17 : 1 : -	70
14[c,d]	*n*-pentane	77	20 : 1 : -	85

[a] Reaction conditions: all reactions were performed with diene (0.12 mmol), (*S,S*)-**L9**/CuCl (2:1, 10 mol%), B_2pin_2 (0.1 mmol), KO*t*Bu (40 mol%), MeOH (0.2 mmol) in THF (1.0 mL) at 0 °C. [b] At room temperature. [c] Ligand/CuCl (1:1, 10 mol%). [d] At –40 °C for 40 h.

Table S3: Base survey[a]



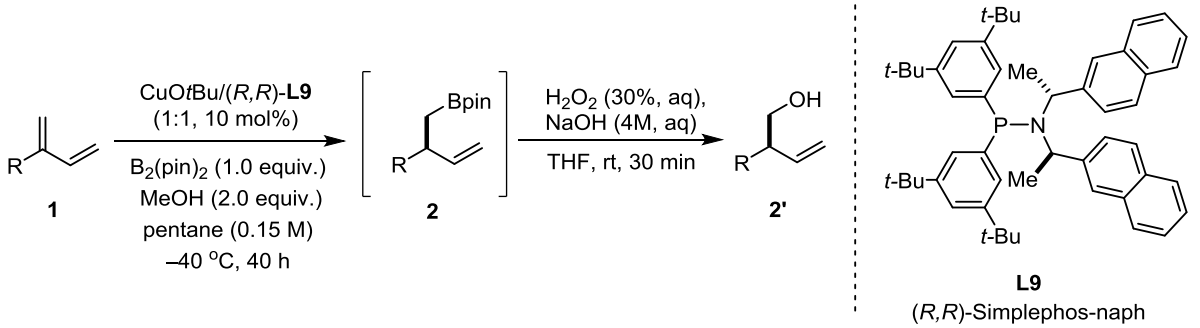


L9
(*S,S*)-Simplephos-naph

Entry	[Cu]	base	amount of base	conv. (%)	**2a** : **3a** : **4a**	*ee* **2a** (%)
1	CuCl	LiO*t*Bu	40 mol%	-	-	-
2	CuCl	NaO*t*Bu	40 mol%	-	-	-
3	CuCl	KO*t*Bu	40 mol%	77	20 : 1 : -	85
4	CuCl	KO*t*Bu	10 mol%	74	20 : 1 : -	90
5[b]	CuO*t*Bu	-	-	89	20 : 1 : -	90

[a] Reaction conditions: all reactions were performed with diene (0.12 mmol), (*S*,*S*)-**L9**/CuCl (1:1, 10 mol%), B_2pin_2 (0.1 mmol), Base (x mol%), MeOH (0.2 mmol) in *n*-pentane (1.0 mL) at –40 °C. [b] CuO*t*Bu (10 mol%) was used without extra base, 0.15 M.

3. General procedure for the borylation/oxidation sequence

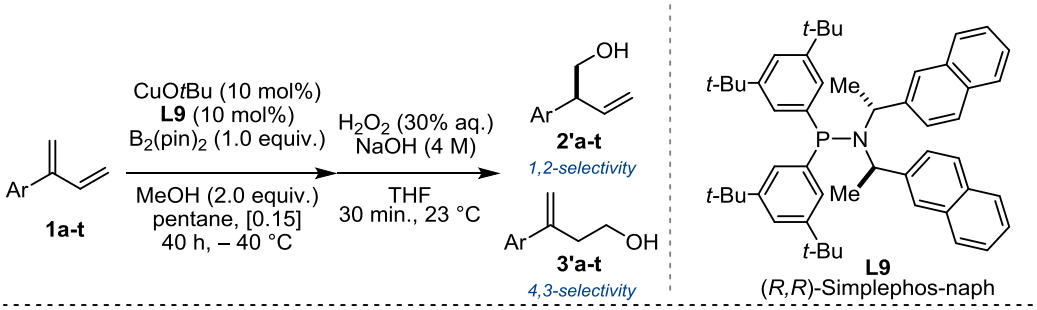


CuO*t*Bu (0.03 mmol, 10 mol%), (*R*,*R*)-Simplephos-naph **L9** (0.03 mmol, 10 mol%) and B_2pin_2 (0.3 mmol, 1.0 equiv.) were introduced into a Schlenk tube in a glove-box and dissolved in anhydrous and degassed *n*-pentane (2.0 mL, 0.15 M). After stirring at room temperature for 20 min, the reaction mixture was cooled to –40 °C. Diene **1** (0.36 mmol, 1.2 equiv.) and MeOH (0.6 mmol, 2.0 equiv.) were added next. After stirring at –40 °C for 40 h, the reaction was filtered through a short pad of Celite®, washed with diethyl ether (10 mL) and the solvent was removed under vacuum. The conversion and isomeric ratio of boronic ester were determined by ^{1}H NMR analysis of the crude reaction mixture.

To a solution of boronic ester in THF (3.0 mL) was added 30% H_2O_2 (1.5 mL) and 4 M NaOH (1.5 mL). The reaction mixture was stirred vigorously for 30 min at room temperature. The mixture was diluted with water and extracted with diethyl ether (3 x 10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography (pentane/ethyl acetate 6:1 to 3:1) to afford the corresponding alcohol **2'**. This compound was used for determination of the enantiomeric excess.

*Note: All racemates were prepared according to a similar procedure using DrewPhos (**L10**) as ligand (THF, rt, 24 h).*

4. Substrate scope



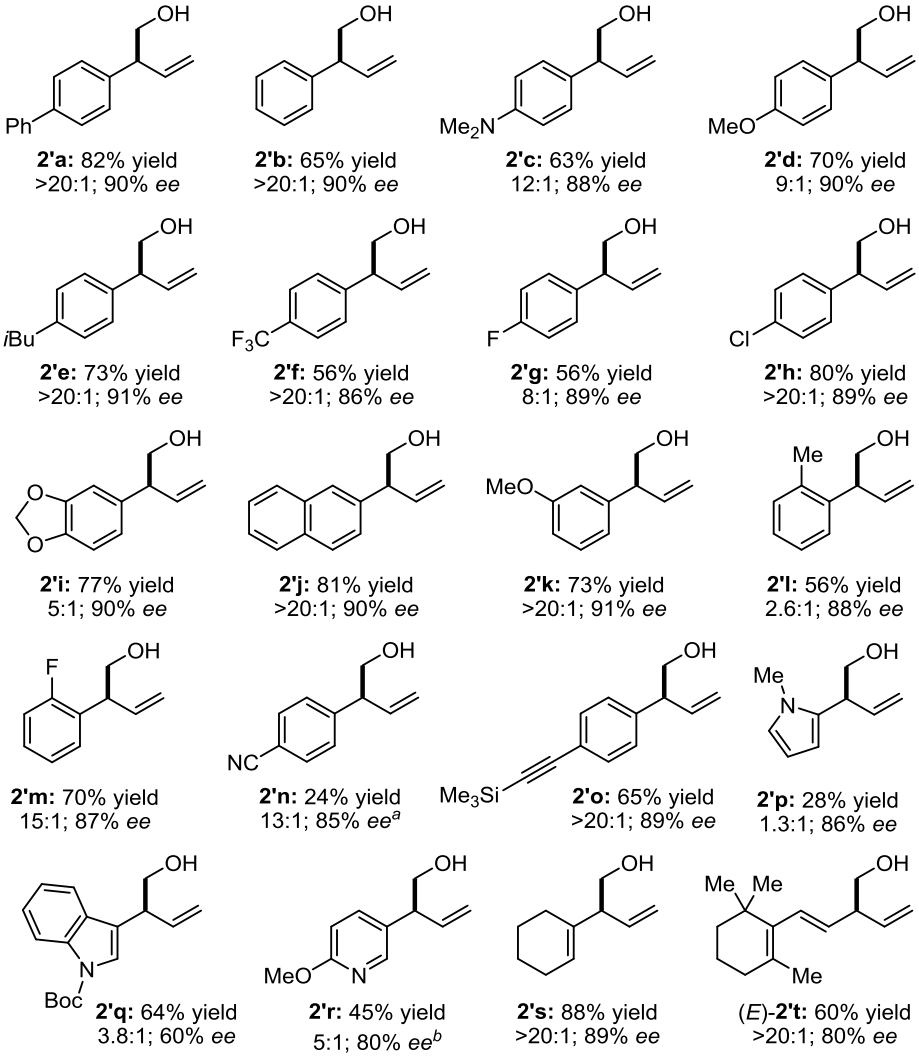


Figure S1. Sequential borylation/oxidation of 2-(hetero)aryl substituted 1,3-dienes. Reaction conditions: **1** (0.36 mmol), $B_2(pin)_2$ (0.30 mmol). Chemoselectivity assessed by ^{1}H NMR after borylation. Yields of isolated alcohols **2'**. Enantioselectivity determined by HPLC, GC or SFC using a chiral stationary phase after oxidation. [a] The minor isomer is **4'n**. [b] Isolated as a 5:1 mixture.

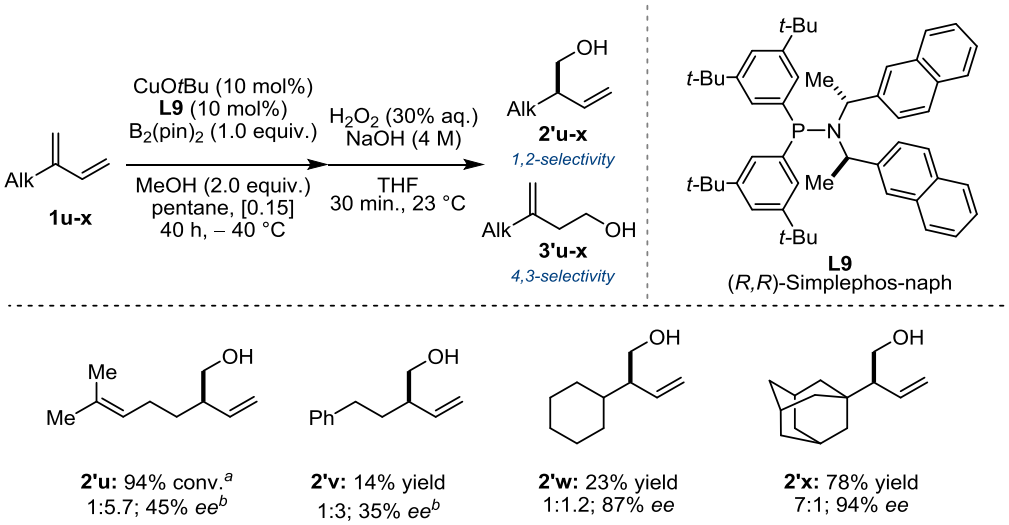


Figure S2. Sequential borylation/oxidation of 2-alkyl substituted 1,3-dienes. Reaction conditions: **1u-x** (0.18-0.36 mmol), $B_2(pin)_2$ (0.15-0.30 mmol). Chemoselectivity assessed by ^{1}H NMR after borylation. Isolated yields for alcohols **2'v-x**. Enantioselectivity determined by HPLC, GC, SFC using a chiral stationary phase after oxidation. [a] Conversion determined by ^{1}H NMR. [b] At 0 °C for 24 h.

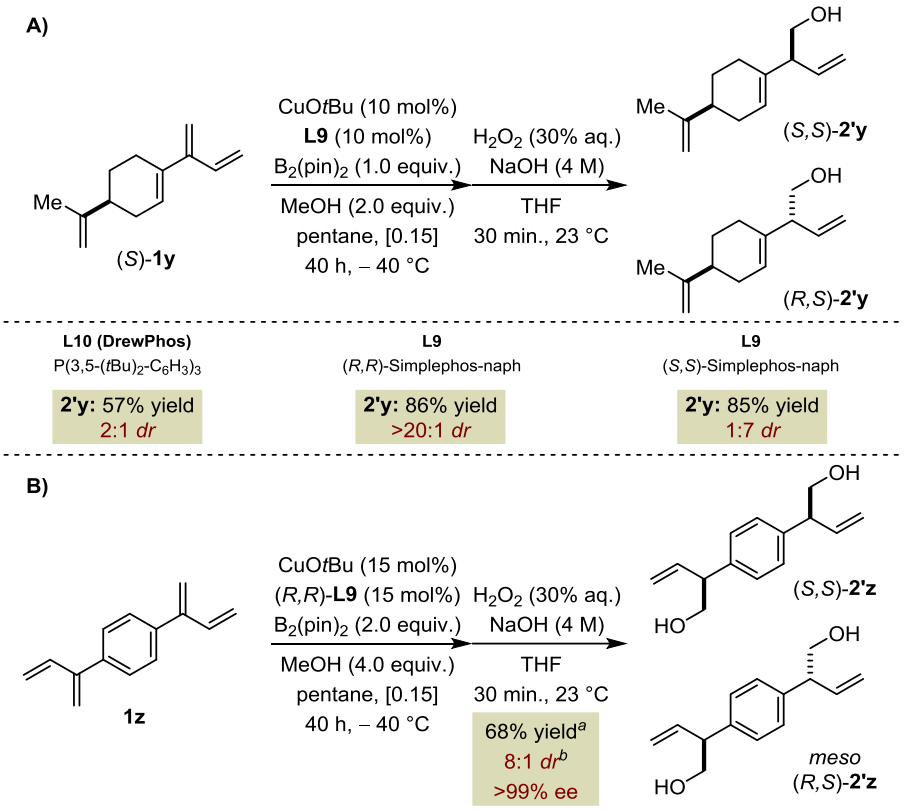


Figure S3. Catalyst-controlled diastereoselective borylation of (*S*)-**1y**. Reaction conditions: (*S*)-**1y** (0.24 mmol), $B_2(pin)_2$ (0.20 mmol). Chemoselectivity >20:1 in all cases was assessed by ^{1}H NMR after borylation. Diastereoselectivity assessed by ^{1}H and $^{13}C\{^1H\}$ NMR after borylation and oxidation. Isolated yields after oxidation. (B) borylation of bis-diene **1z** (0.36 mmol scale). [a] 1,2-/4,3-selectivity = 10:1. [b] Inseparable mixture.

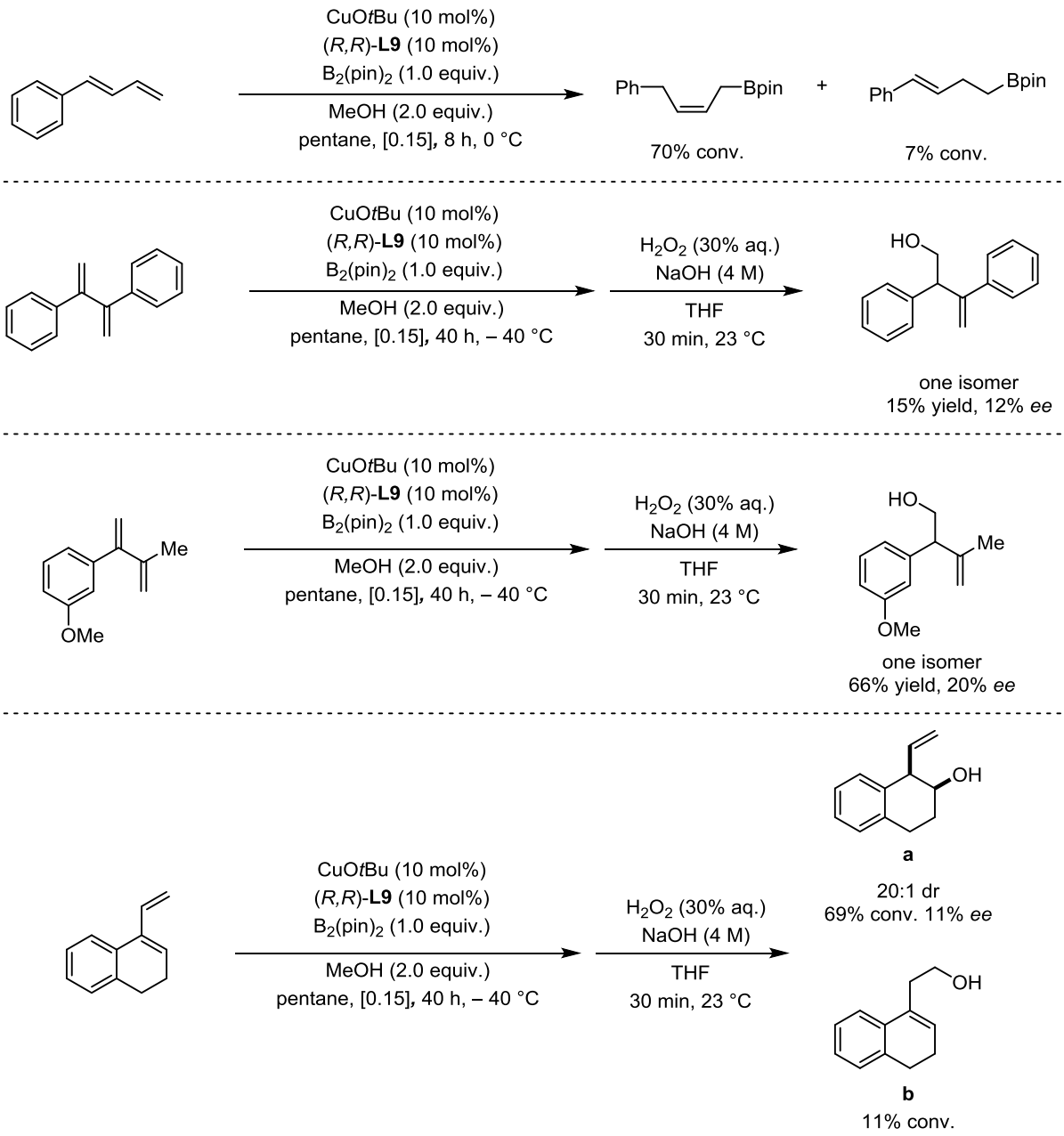
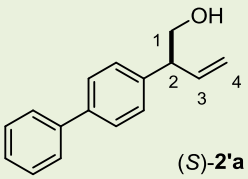


Figure S4. Sequential borylation/oxidation of other substituted 1,3-dienes.

(*S*)-2-([1,1'-biphenyl]-4-yl)but-3-en-1-ol 2'a



(*S*)-**2'a**

Following the general procedure using 4-(buta-1,3-dien-2-yl)-1,1'-biphenyl **1a** (74 mg, 0.36 mmol, 1.2 equiv.), Cu*O*t*Bu (4.1 mg, 0.03 mmol, 10 mol%), (*R,R*)-**L9** (22 mg, 0.03 mmol, 10 mol%), B_2pin_2 (76.2 mg, 0.3 mmol, 1.0 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.). Conversion: 89%, **2a**:**3a** > 20:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (*S*)-**2'a** as a colorless oil (55 mg, 82% yield, **2'a**:**3'a** > 20:1, 90% *ee*).

TLC: R_f = 0.5 (pentane/ethyl acetate 2:1).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.54 – 7.44 (m, 4H), 7.40 – 7.30 (m, 2H), 7.29 – 7.18 (m, 3H), 5.95 (ddd, $^3J_{HH}$ = 16.8, 10.7, 7.3 Hz, 1H, ***H*-3**), 5.23 – 5.05 (m, 2H, ***H*-4**), 3.77 (dd, $^3J_{HH}$ = 7.4, $^2J_{HH}$ = 3.1 Hz, 2H, ***H*-1**), 3.49 (dt, $^3J_{HH}$ = 7.3 , 7.2 Hz, 1H, ***H*-2**), 1.52 (s, 1H, **O*H***).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ (ppm) = 140.8 (***C*-Ar**), 139.9 (***C*-Ar**), 139.7 (***C*-Ar**), 138.2 (***C*H-3**), 128.8 (***C*H-Ar**), 128.4 (***C*H-Ar**), 127.5 (***C*H-Ar**), 127.3 (***C*H-Ar**), 127.1 (***C*H-Ar**), 117.2 (***C*H$_2$-4**), 66.1 (***C*H$_2$-1**), 52.2 (***C*H-2**).

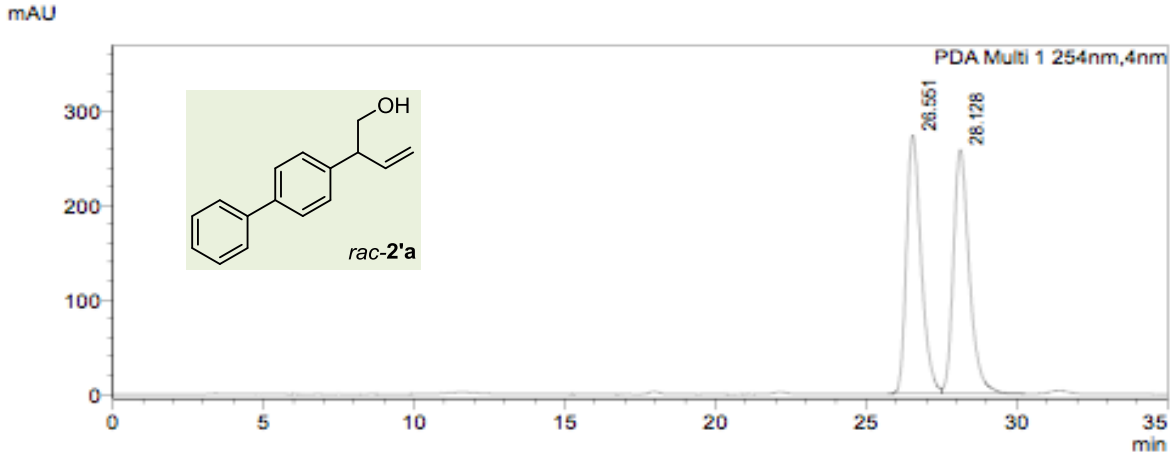
LRMS (ESI +): calculated for $C_{16}H_{16}O$ $[M]^+$: 224.12; found: 242.25 $[M+NH_4]^+$; 247.15 $[M+Na]^+$.

IR (neat) ν (cm^{-1}): 3354, 3029, 2923, 2855, 1637, 1601, 1519, 1486, 1463, 1407, 1261, 1181, 1027, 917, 836, 763, 696.

HPLC: 90% *ee*, chiral stationary column: IC, mobile phase: hexane/*i*PrOH = 99/1, 1.0 mL/min, 254 nm, 30 °C, t_R (major) = 28.1 min, t_R (minor) = 26.5 min.

[α]$^{25}_D$ = +69.2 (*c* 1.03, CH_2Cl_2).

<Chromatogram>



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	26.551	9348150	49.489
2	28.128	9541217	50.511
Total		18889367	100.000

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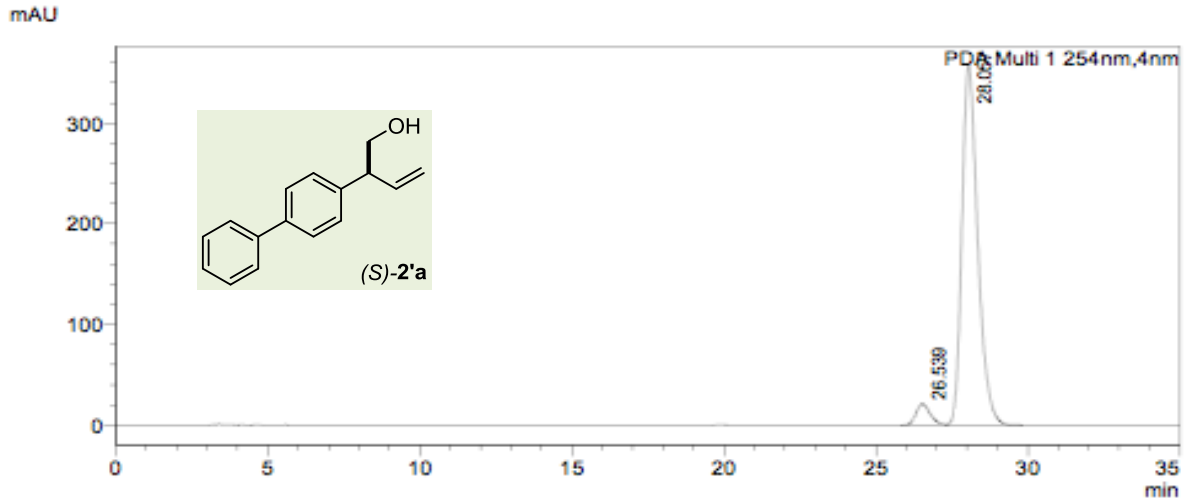
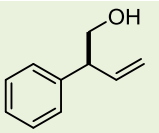


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	26.539	700527	5.140
2	28.057	12928996	94.860
Total		13629523	100.000

(*S*)-2-phenylbut-3-en-1-ol 2'b



(*S*)-**2'b**

Following the general procedure using buta-1,3-dien-2-ylbenzene **1b** (47 mg, 0.36 mmol, 1.2 equiv.), CuO*t*Bu (4.1 mg, 0.03 mmol, 10 mol%), (*R,R*)-**L9** (22 mg, 0.03 mmol, 10 mol%), B_2pin_2 (76.2 mg, 0.3 mmol, 1.0 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.). Conversions: 84%, **2b**:**3b** = 20:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (*S*)-**2'b** as a colorless oil (29 mg, 65% yield, **2'b**:**3'b** > 20:1, 90% *ee*). All spectroscopic and spectrometric analyses were in agreement with the literature.[4]

HPLC: 90% *ee*, chiral stationary column: AD-H, mobile phase: hexane/*i*PrOH = 99.5/0.5, 1.0 mL/min, 220 nm, 30 °C, t_R (major) = 33.2 min, t_R (minor) = 39.1 min.

[α]$^{20}_{D}$ = +51.2 (*c* 0.24, CH_2Cl_2).

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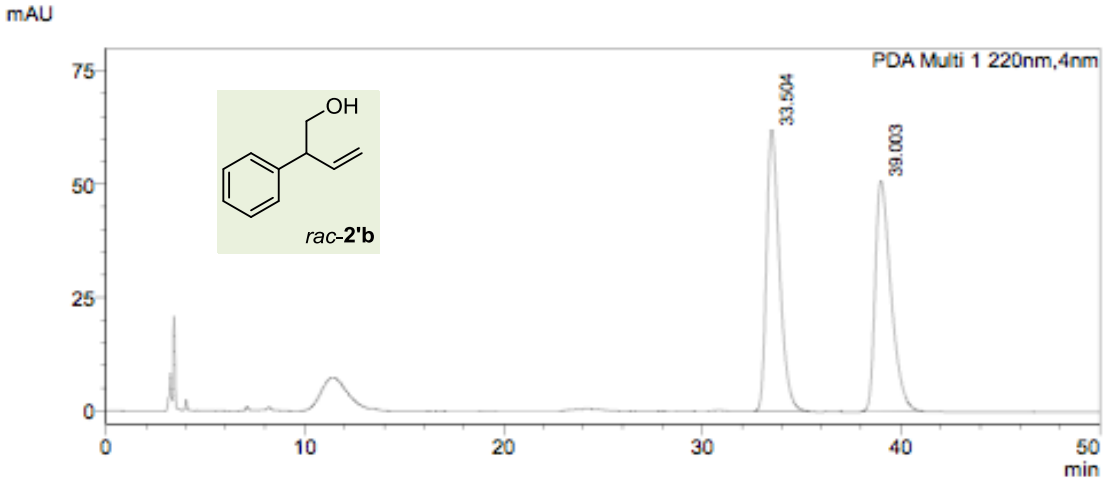
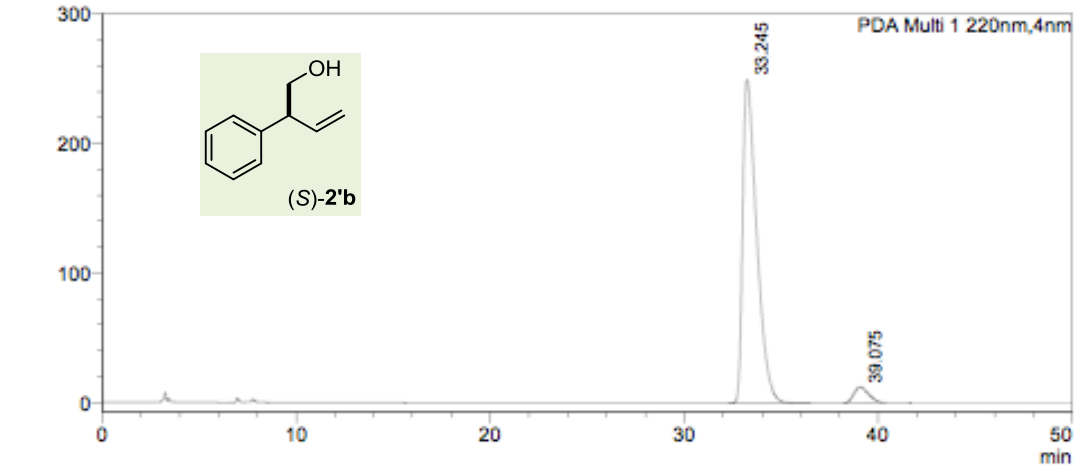


<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	33.504	2833436	50.147
2	39.003	2816818	49.853
Total		5650254	100.000

<Chromatogram>

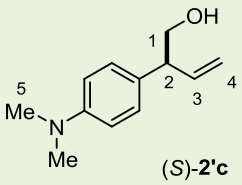


<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	33.245	12593524	95.021
2	39.075	659954	4.979
Total		13253478	100.000

(*S*)-2-(4-(dimethylamino)phenyl)but-3-en-1-ol 2'c



(*S*)-**2'c**

Following the general procedure using 4-(buta-1,3-dien-2-yl)-*N,N*-dimethylaniline **1c** (62 mg, 0.36 mmol, 1.2 equiv.), Cu*O*t*B*u (4.1 mg, 0.03 mmol, 10 mol%), (*R,R*)-**L9** (22 mg, 0.03 mmol, 10 mol%), B_2pin_2 (76.2 mg, 0.3 mmol, 1.0 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.). Conversions: 70%, **2c**:**3c** = 12:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (*S*)-**2'c** as a colorless oil (36 mg, 63% yield, **2'c**:**3'c** = 14:1, 88% *ee*).

TLC: R_f = 0.3 (pentane/ethyl acetate 2:1).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.16 – 7.06 (m, 2H), 6.78 – 6.68 (m, 2H), 5.98 (ddd, $^3J_{HH}$ = 16.6, 10.8, 7.6 Hz, 1H, ***H*-3**), 5.24 – 5.08 (m, 2H, ***H*-4**), 3.78 (d, $^3J_{HH}$ = 7.2 Hz, 2H, ***H*-1**), 3.44 (dt, $^3J_{HH}$ = 7.3, 7.2 Hz, 1H, ***H*-2**), 2.94 (s, 6H, ***H*-5**), 1.59 (s, 1H, **O-*H***).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ (ppm) = 149.7 (***C*-Ar**), 138.9 (***C*H-3**), 128.6 (***C*H-Ar**), 128.2 (***C*-Ar**), 116.3 (***C*H$_2$-4**), 113.1 (***C*H-Ar**), 66.2 (***C*H$_2$-1**), 51.5 (***C*H-2**), 40.7 (***C*H$_3$-5**).

LRMS (ESI +): calculated for $C_{12}H_{17}NO$ $[M]^+$: 191.13; found: 192.14 $[M+H]^+$.

IR (neat) ν (cm^{-1}): 3366, 3077, 2922, 2875, 2800, 1613, 1565, 1519, 1478, 1445, 1345, 1223, 1163, 1134, 1055, 1027, 946, 913, 814, 745, 646.

HPLC: 88% *ee*, chiral stationary column: AD-H, mobile phase: hexane/*i*PrOH = 97/3, 1.0 mL/min, 254 nm, 30 °C, t_R (major) = 20.4 min, t_R (minor) = 17.9 min.

[α]$^{20}_D$ = +63.2 (*c* 0.65, CH_2Cl_2).

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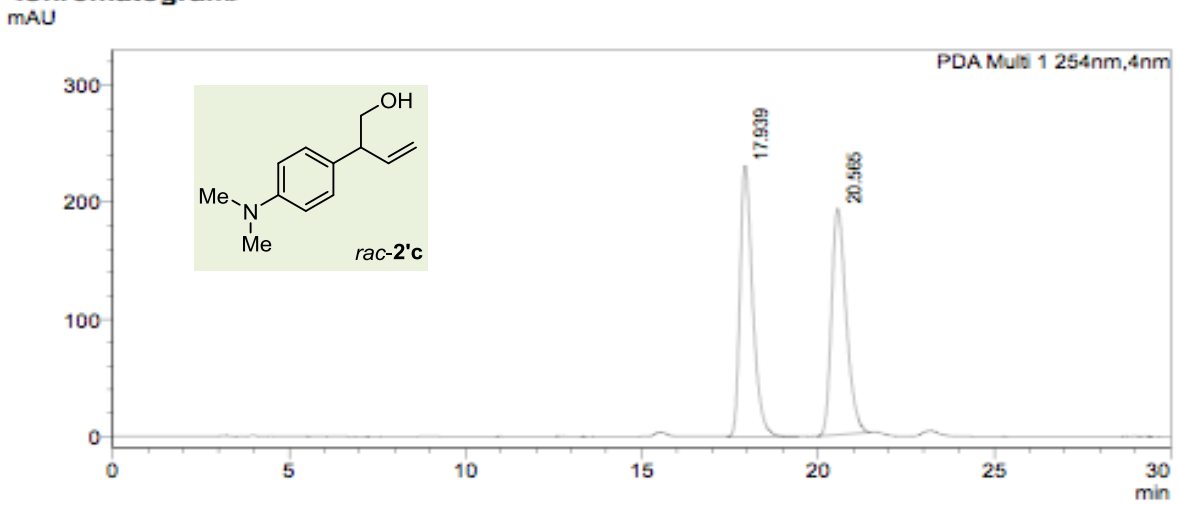
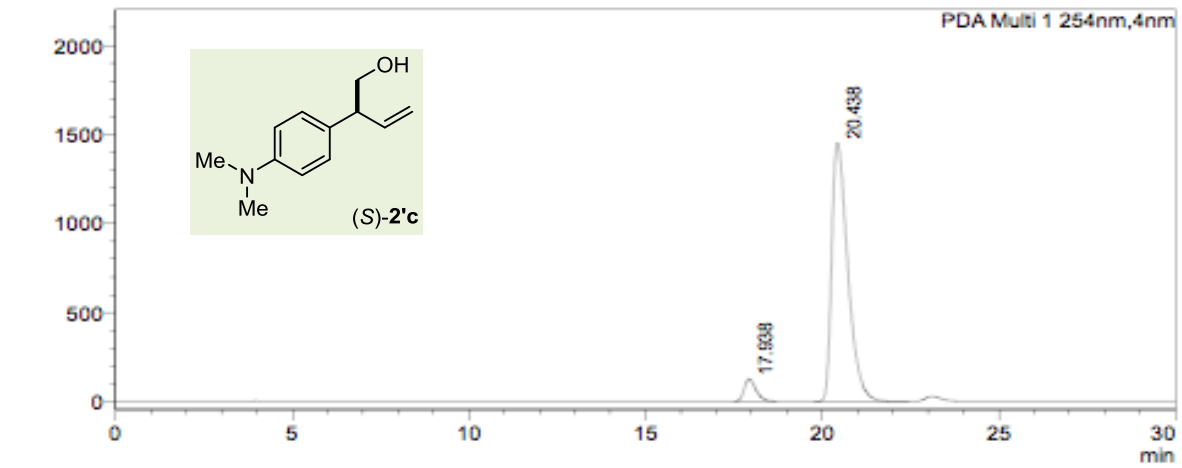


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	17.939	5761392	50.783
2	20.565	5583755	49.217
Total		11345147	100.000

<Chromatogram>

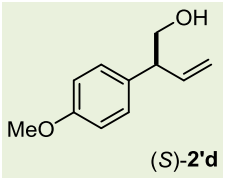


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	17.938	2972545	6.061
2	20.438	46074039	93.939
Total		49046584	100.000

(*S*)-2-(4-methoxyphenyl)but-3-en-1-ol 2'd



(*S*)-**2'd**

Following the general procedure using 1-(buta-1,3-dien-2-yl)-4-methoxybenzene **1d** (58 mg, 0.36 mmol, 1.2 equiv.), CuO*t*Bu (4.1 mg, 0.03 mmol, 10 mol%), (*R,R*)-**L9** (22 mg, 0.03 mmol, 10 mol%), B_2pin_2 (76.2 mg, 0.3 mmol, 1.0 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.). Conversions: 87%, **2d**:**3d** = 9:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (*S*)-**2'd** as a colorless oil (37 mg, 70% yield, **2'd**:**3'd** > 20:1, 90% *ee*). All spectroscopic and spectrometric analyses were in agreement with the literature.[4]

HPLC: 90% *ee*, chiral stationary column: AD-H, mobile phase: hexane/*i*PrOH = 98/2, 1.0 mL/min, 220 nm, 30 °C, t_R (major) = 26.3 min, t_R (minor) = 23.6 min.

[α]$^{25}_{D}$ = +68.2 (*c* 0.56, CH_2Cl_2).

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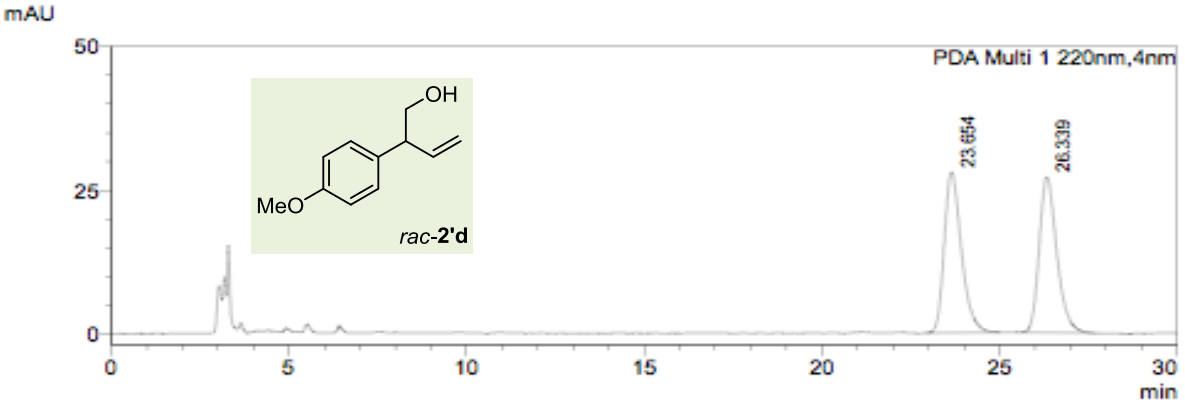
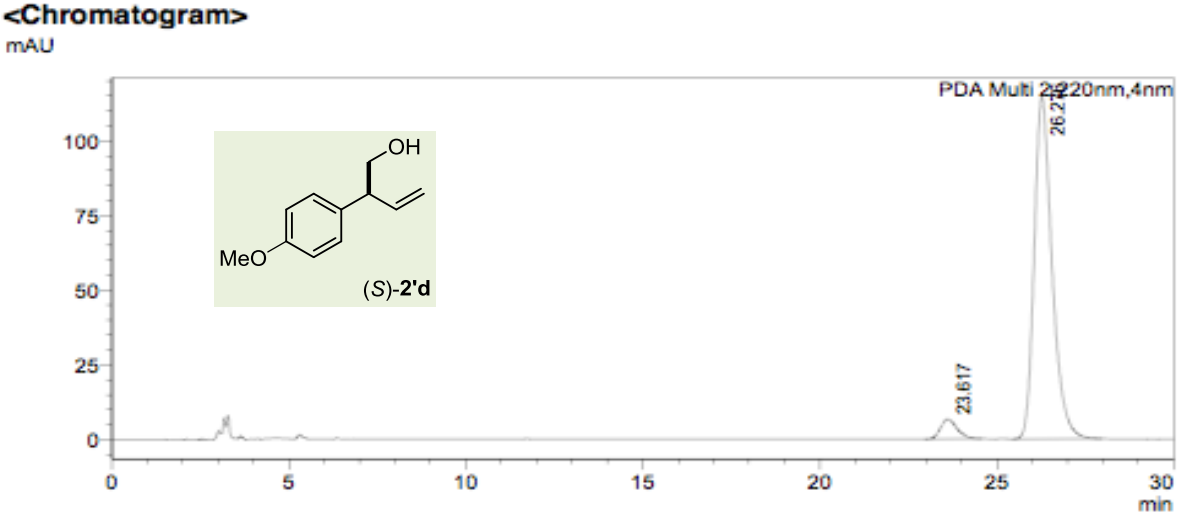


<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	23.654	942439	50.231
2	26.339	933774	49.769
Total		1876213	100.000

<Chromatogram>

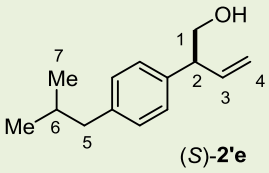


<Peak Table>

PDA Ch2 220nm

Peak#	Ret. Time	Area	Area%
1	23.617	217264	5.139
2	26.276	4010678	94.861
Total		4227941	100.000

(*S*)-2-(4-isobutylphenyl)but-3-en-1-ol 2'e



Following the general procedure using 1-(buta-1,3-dien-2-yl)-4-isobutylbenzene **1e** (74 mg, 0.3 mmol, 1.0 equiv.), CuO*t*Bu (4.1 mg, 0.03 mmol, 10 mol%), (*R,R*)-**L9** (22 mg, 0.03 mmol, 10 mol%), B_2pin_2 (91 mg, 0.36 mmol, 1.2 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.). Conversions: 84%, **2e**:**3e** = 20:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (*S*)-**2'e** as a colorless oil (45 mg, 73% yield, **2'e**:**3'e** > 20:1, 91% *ee*).

TLC: R_f = 0.6 (pentane/ethyl acetate 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.18 – 7.10 (m, 4H), 6.01 (ddd, $^3J_{HH}$ = 16.8, 10.6, 7.7 Hz, 1H, ***H*-3**), 5.23 – 5.16 (m, 2H, ***H*-4**), 3.85 – 3.77 (m, 2H, ***H*-1**), 3.51 (dt, $^3J_{HH}$ = 7.3, 7.2 Hz, 1H, ***H*-2**), 2.46 (d, $^3J_{HH}$ = 7.1 Hz, 2H, ***H*-5**), 1.85 (dt, $^3J_{HH}$ = 13.5, 6.8 Hz, 1H, ***H*-6**), 1.50 (s, 1H, ***H*-O**), 0.90 (d, $^3J_{HH}$ = 6.6 Hz, 6H, ***H*-7**).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 140.4 (***C*-Ar**), 138.4 (***C*H-3**), 137.7 (***C*-Ar**), 129.5 (***C*H-Ar**), 127.6 (***C*H-Ar**), 116.9 (***C*H_2-4**), 66.1 (***C*H_2-1**), 52.2 (***C*H-2**), 45.0 (***C*H_2-5**), 30.2 (***C*H-6**), 22.4 (***C*H_3-7**).

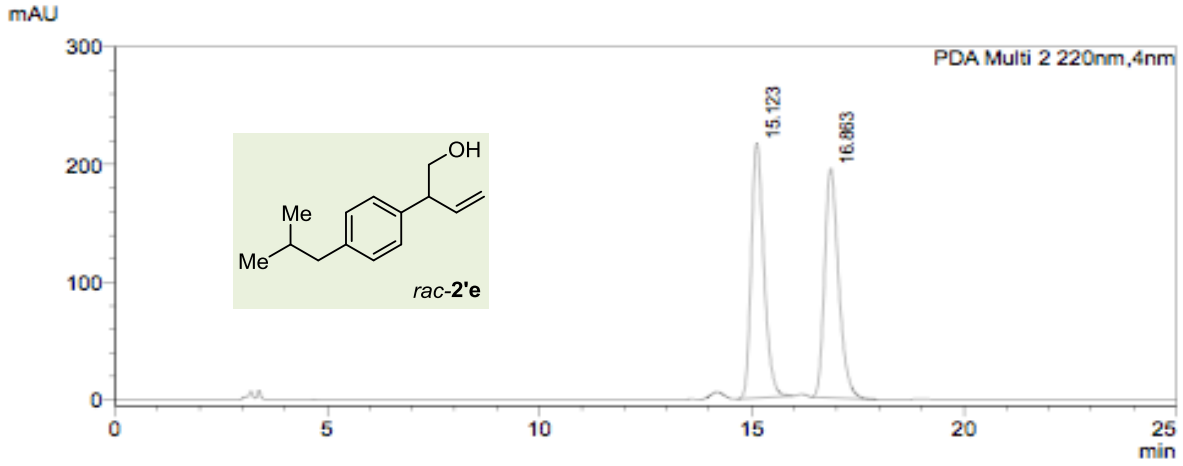
LRMS (ESI+): calculated for $C_{14}H_{20}O$ $[M]^+$: 204.15; found: 222.25 $[M+NH_4]^+$; 227.25 $[M+Na]^+$.

IR (neat) ν (cm^{-1}): 3351, 3082, 2954, 2923, 2869, 1638, 1512, 1465, 1415, 1383, 1367, 1168, 1117, 1054, 1031, 917, 844, 794.

HPLC: 91% *ee*, chiral stationary column: AD-H, mobile phase: hexane/*i*PrOH = 99/1, 1.0 mL/min, 220 nm, 30 °C, t_R (major) = 16.9 min, t_R (minor) = 15.2 min.

[α]$^{25}_D$ = +55.5 (*c* 0.84, CH_2Cl_2).

<Chromatogram>

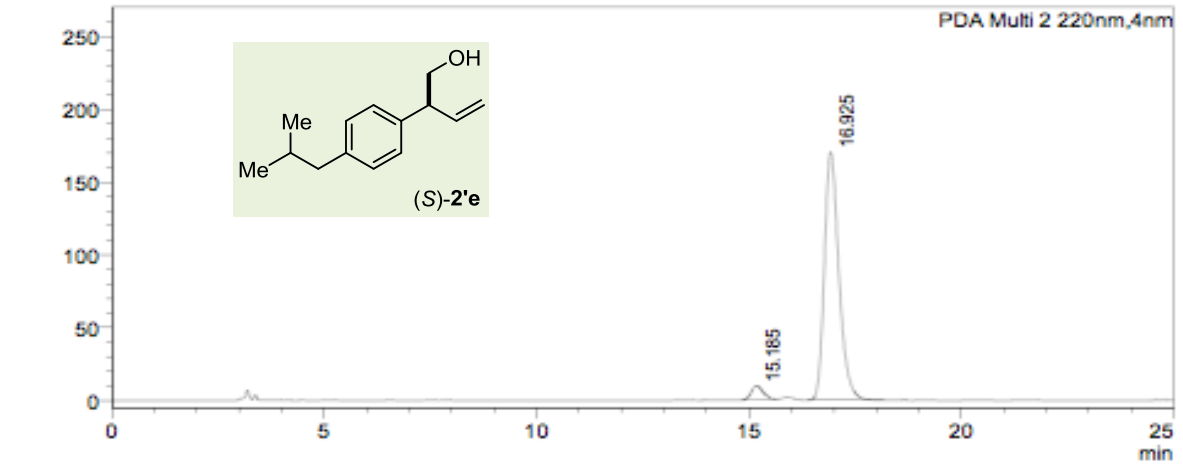


<Peak Table>

PDA Ch2 220nm

Peak#	Ret. Time	Area	Area%
1	15.123	4485654	49.959
2	16.863	4493067	50.041
Total		8978722	100.000

<Chromatogram>

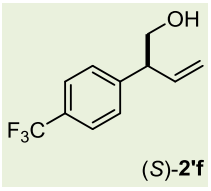


<Peak Table>

PDA Ch2 220nm

Peak#	Ret. Time	Area	Area%
1	15.185	187992	4.430
2	16.925	4055665	95.570
Total		4243657	100.000

(*S*)-2-(4-(trifluoromethyl)phenyl)but-3-en-1-ol 2'f

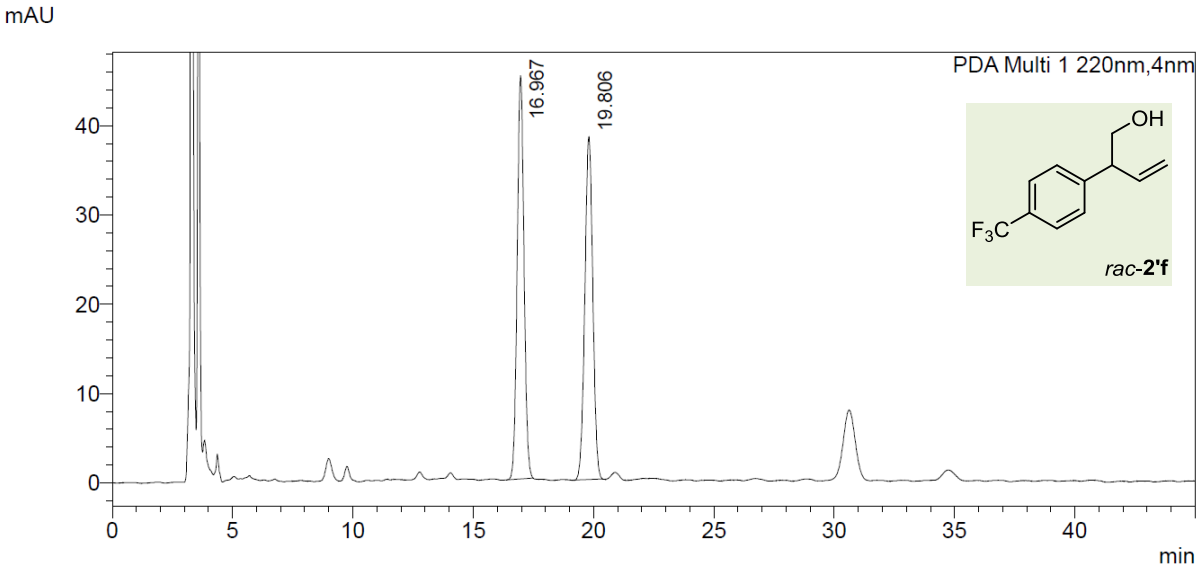


Following the general procedure using 1-(buta-1,3-dien-2-yl)-4-(trifluoromethyl)benzene **1f** (48 mg, 0.24 mmol, 1.2 equiv.), Cu*O*t*Bu (2.7 mg, 0.02 mmol, 10 mol%), (*R,R*)-**L9** (15 mg, 0.02 mmol, 10 mol%), B_2pin_2 (51 mg, 0.2 mmol, 1.0 equiv.) and MeOH (16 µL, 0.4 mmol, 2.0 equiv.). Conversions: 70%, **2f**:**3f** = 50:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (*S*)-**2'f** as a colorless oil (24 mg, 56% yield, **2'f**:**3'f** > 50:1, 86% *ee*). All spectroscopic and spectrometric analyses were in agreement with the literature.[4]

HPLC: 86% *ee*, chiral stationary column: OJ-H, mobile phase: hexane/^{i}PrOH = 99/1, 1.0 mL/min, 220 nm, 30 °C, t_R (major) = 16.5 min, t_R (minor) = 19.7 min.

[α]$^{20}_{D}$ = +34.6 (*c* 0.80, $CHCl_3$).

<Chromatogram>

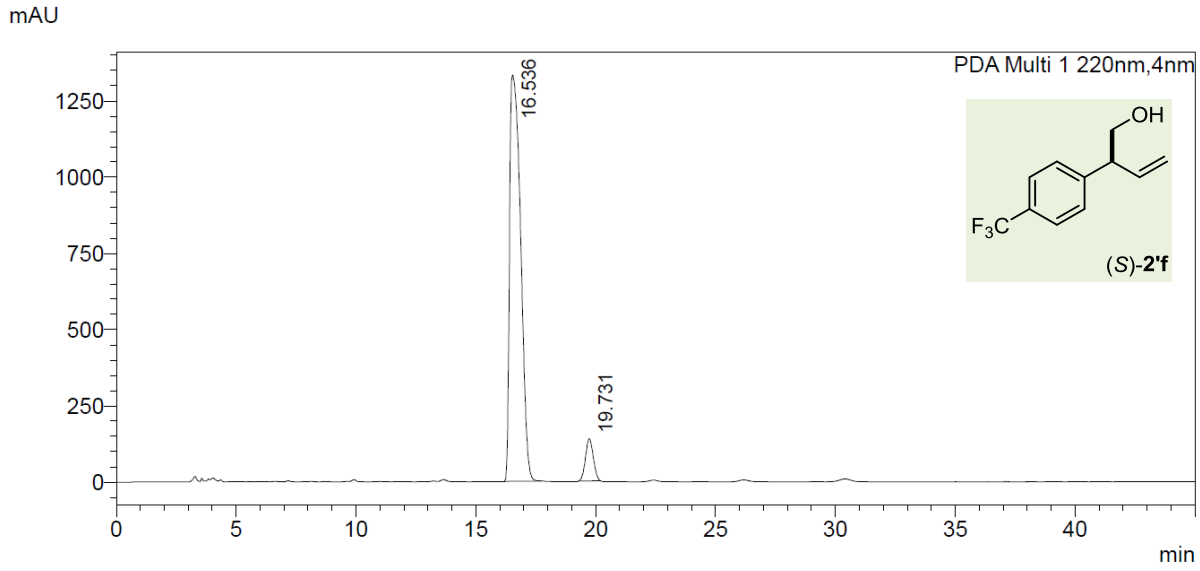


<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area%
1	16.967	50.075
2	19.806	49.925
Total		100.000

<Chromatogram>

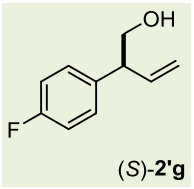


<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area%
1	16.536	93.207
2	19.731	6.793
Total		100.000

(*S*)-2-(4-fluorophenyl)but-3-en-1-ol 2'g



(*S*)-**2'g**

Following the general procedure using 1-(buta-1,3-dien-2-yl)-4-fluorobenzene **1g** (54 mg, 0.36 mmol, 1.2 equiv.), CuO*t*Bu (4.1 mg, 0.03 mmol, 10 mol%), (*R,R*)-**L9** (22 mg, 0.03 mmol, 10 mol%), B_2pin_2 (76.2 mg, 0.3 mmol, 1.0 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.). Conversions: 76%, **2g**:**3g** = 8:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (*S*)-**2'g** as a colorless oil (28 mg, 56% yield, **2'g**:**3'g** > 20:1, 89% *ee*). All spectroscopic and spectrometric analyses were in agreement with the literature.[4]

HPLC: 89% *ee*, chiral stationary column: AD-H, mobile phase: hexane/*i*PrOH = 99/1, 1.0 mL/min, 220 nm, 30 °C, t_R (major) = 26.6 min, t_R (minor) = 24.6 min.

[α]$^{20}_{D}$ = +61.0 (*c* 0.26, CH_2Cl_2).

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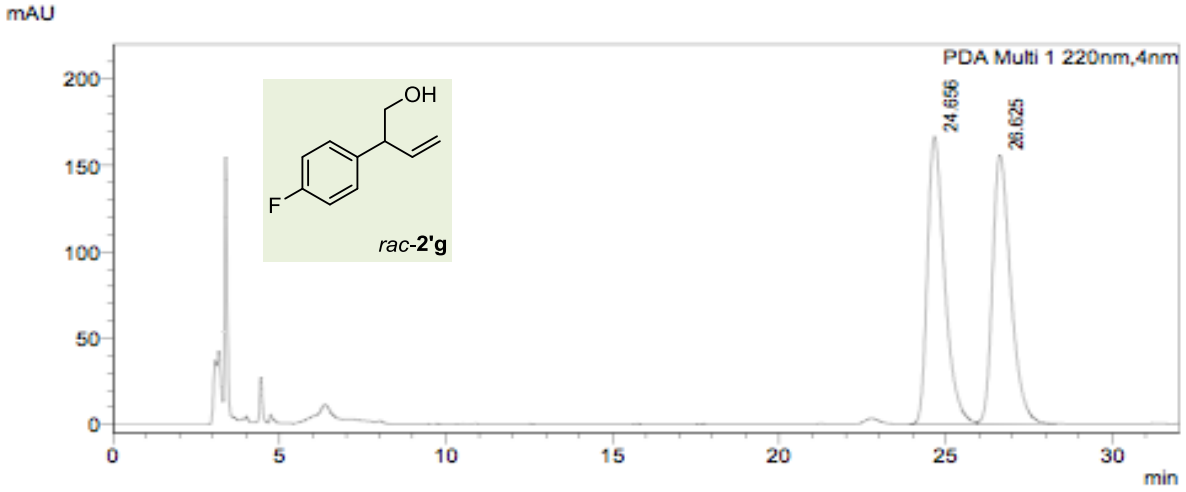
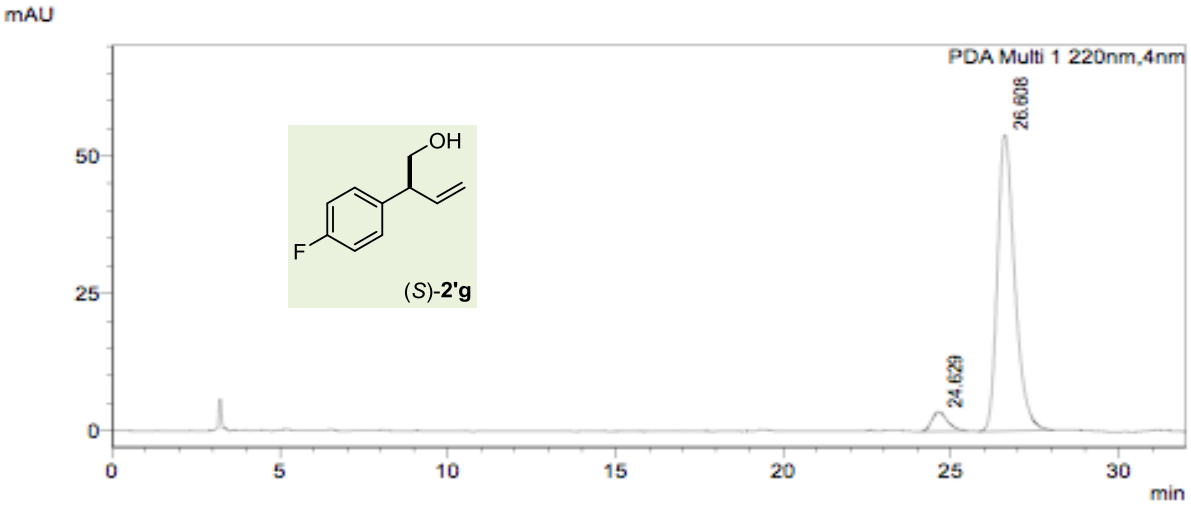


<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	24.656	5967707	50.270
2	26.625	5903490	49.730
Total		11871198	100.000

<Chromatogram>

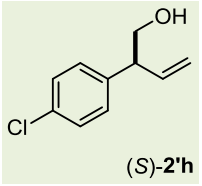


<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	24.629	114074	5.594
2	26.608	1925015	94.406
Total		2039089	100.000

(*S*)-2-(4-chlorophenyl)but-3-en-1-ol 2'h



(*S*)-**2'h**

Following the general procedure using 1-(buta-1,3-dien-2-yl)-4-chlorobenzene **1h** (60 mg, 0.36 mmol, 1.2 equiv.), Cu*O*t*B*u (4.1 mg, 0.03 mmol, 10 mol%), (*R,R*)-**L9** (22 mg, 0.03 mmol, 10 mol%), B_2pin_2 (76.2 mg, 0.3 mmol, 1.0 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.). Conversions: 95%, **2h**:**3h** = 20:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (*S*)-**2'h** as a colorless oil (44 mg, 80% yield, **2'h**:**3'h** > 50:1, 89% *ee*). All spectroscopic and spectrometric analyses were in agreement with the literature.[4]

HPLC: 89% *ee*, chiral stationary column: AD-H, mobile phase: hexane/*i*PrOH = 99/1, 1.0 mL/min, 221 nm, 30 °C, t_R (major) = 30.8 min, t_R (minor) = 28.1 min.

[α]$^{20}_{D}$ = +55.9 (*c* 0.60, $CHCl_3$).

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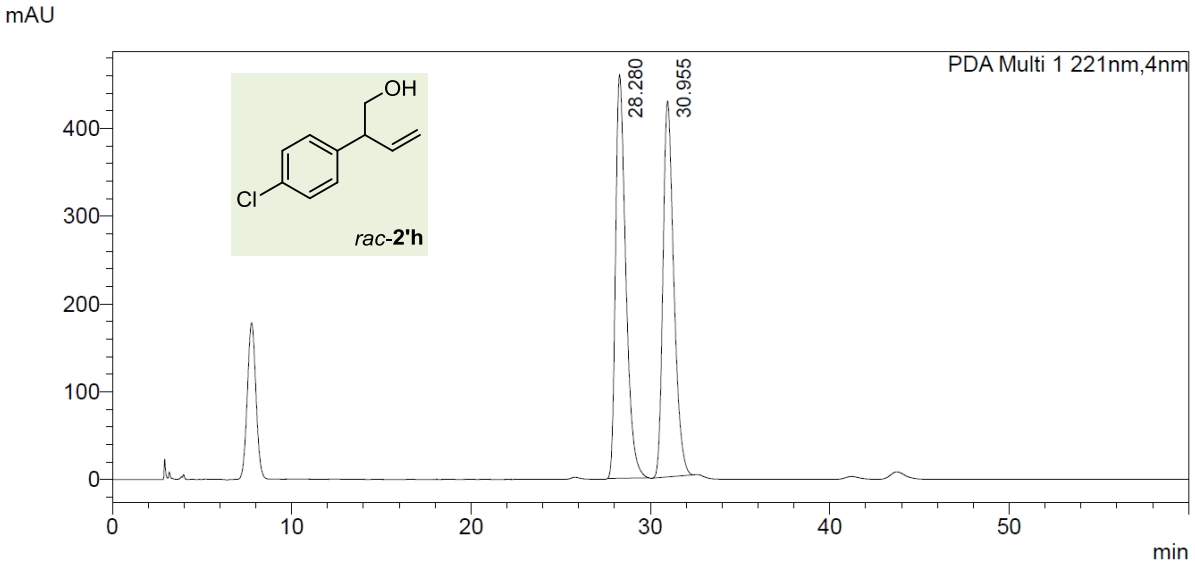
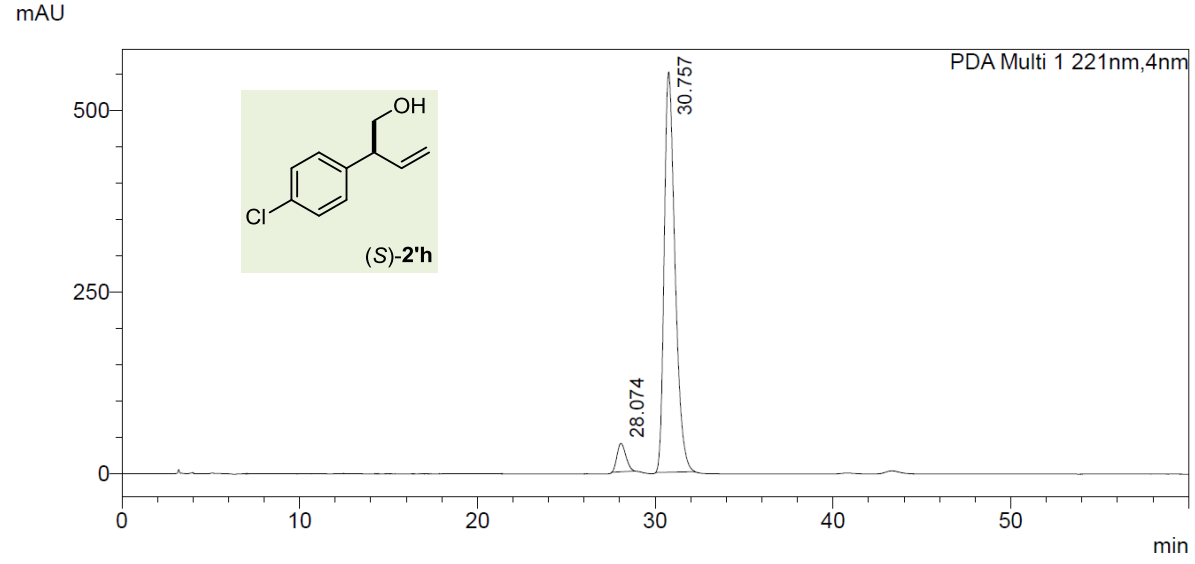


<Peak Table>

PDA Ch1 221nm

Peak#	Ret. Time	Area%
1	28.280	50.400
2	30.955	49.600
Total		100.000

<Chromatogram>

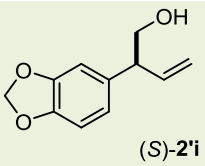


<Peak Table>

PDA Ch1 221nm

Peak#	Ret. Time	Area%
1	28.074	5.497
2	30.757	94.503
Total		100.000

(*S*)-2-(benzo[d][1,3]dioxol-5-yl)but-3-en-1-ol 2'i



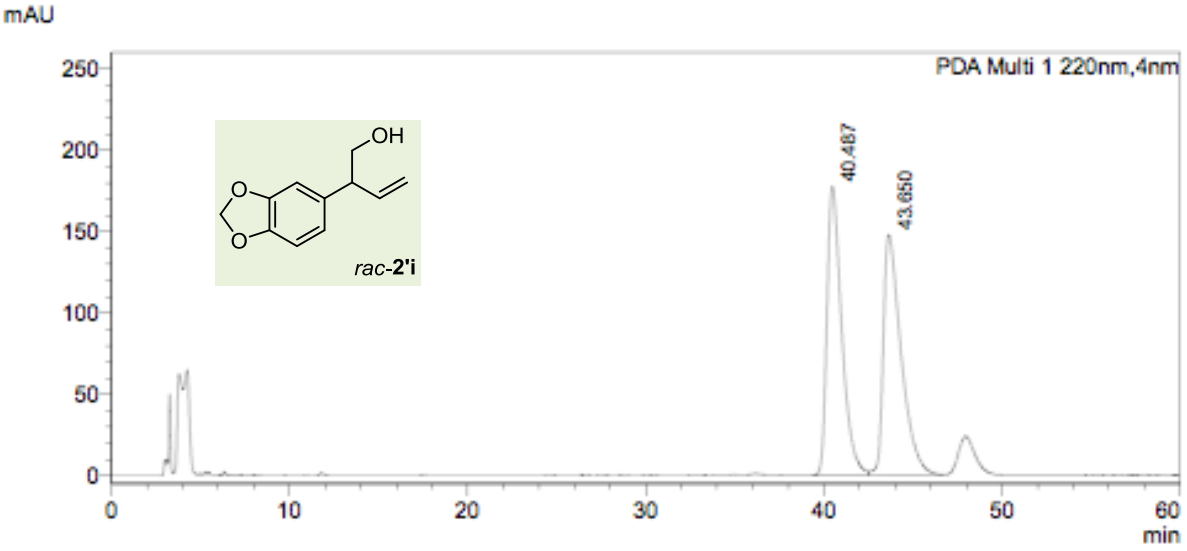
(*S*)-**2'i**

Following the general procedure using 5-(buta-1,3-dien-2-yl)benzo[d][1,3]dioxole **1i** (63 mg, 0.36 mmol, 1.2 equiv.), CuO*t*Bu (4.1 mg, 0.03 mmol, 10 mol%), (*R,R*)-**L9** (22 mg, 0.03 mmol, 10 mol%), B_2pin_2 (76.2 mg, 0.3 mmol, 1.0 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.). Conversions: 93%, **2i**:**3i**:**4i** = 20:4:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (*S*)-**2'i** as a colorless oil (45 mg, 77% yield, **2'i**:**3'i**:**4'i** = 50:1:1.6, 90% *ee*). All spectroscopic and spectrometric analyses were in agreement with the literature.[5]

HPLC: 90% *ee*, chiral stationary column: AD-H, mobile phase: hexane/*i*PrOH = 98/2, 1.0 mL/min, 220 nm, 30 °C, t_R (major) = 40.6 min, t_R (minor) = 44.1 min.

[α]$^{20}_{D}$ = +52.8 (*c* 0.72, CH_2Cl_2).

<Chromatogram>

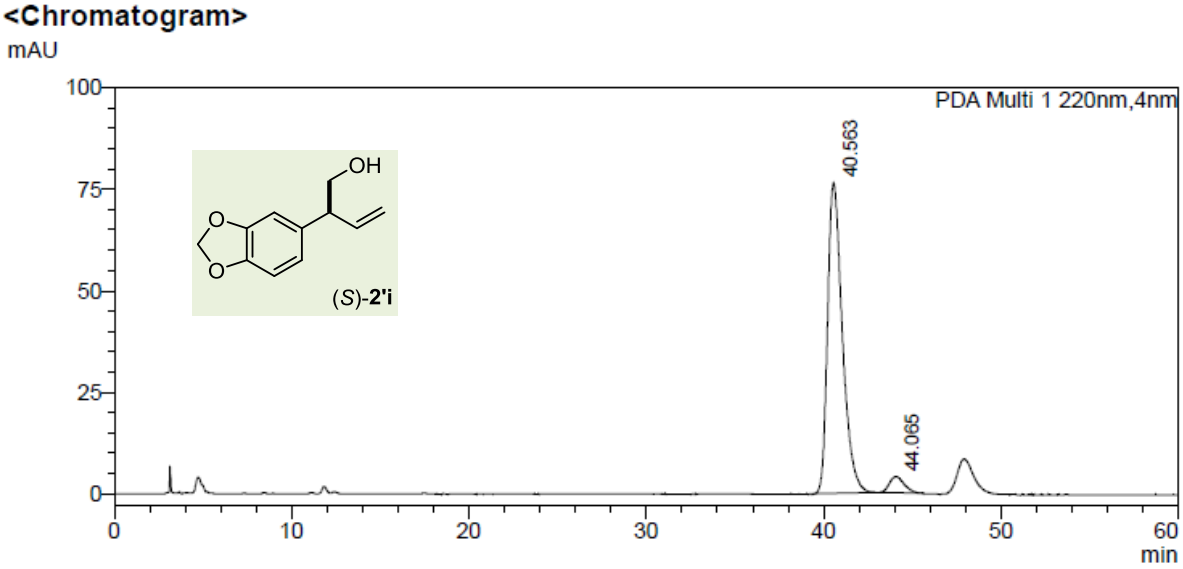


<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	40.487	10219687	49.862
2	43.650	10276089	50.138
Total		20495777	100.000

<Chromatogram>

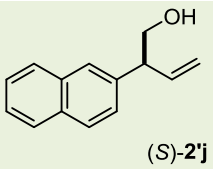


<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	40.563	4424592	95.102
2	44.065	227866	4.898
Total		4652457	100.000

(*S*)-2-(naphthalen-2-yl)but-3-en-1-ol 2'j



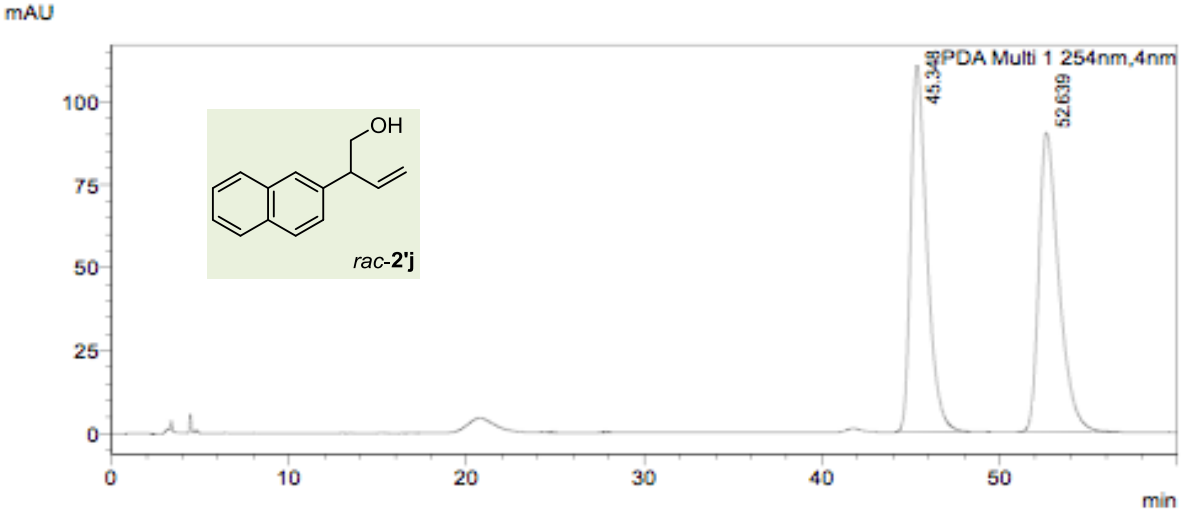
(*S*)-**2'j**

Following the general procedure using 2-(buta-1,3-dien-2-yl)naphthalene **1j** (65 mg, 0.36 mmol, 1.2 equiv.), CuO*t*Bu (4.1 mg, 0.03 mmol, 10 mol%), (*R,R*)-**L9** (22 mg, 0.03 mmol, 10 mol%), B_2pin_2 (76.2 mg, 0.3 mmol, 1.0 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.). Conversions: 90%, **2j**:**3j** > 20:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (*S*)-**2'j** as a colorless oil (48 mg, 81% yield, **2'j**:**3'j** > 20:1, 90% *ee*). All spectroscopic and spectrometric analyses were in agreement with the literature.[4]

HPLC: 90% *ee*, chiral stationary column: AD-H, mobile phase: hexane/^{i}PrOH = 99/1, 1.0 mL/min, 254 nm, 30 °C, t_R (major) = 52.9 min, t_R (minor) = 45.7 min.

[α]$^{20}_{D}$ = +73.4 (*c* 0.96, CH_2Cl_2).

<Chromatogram>

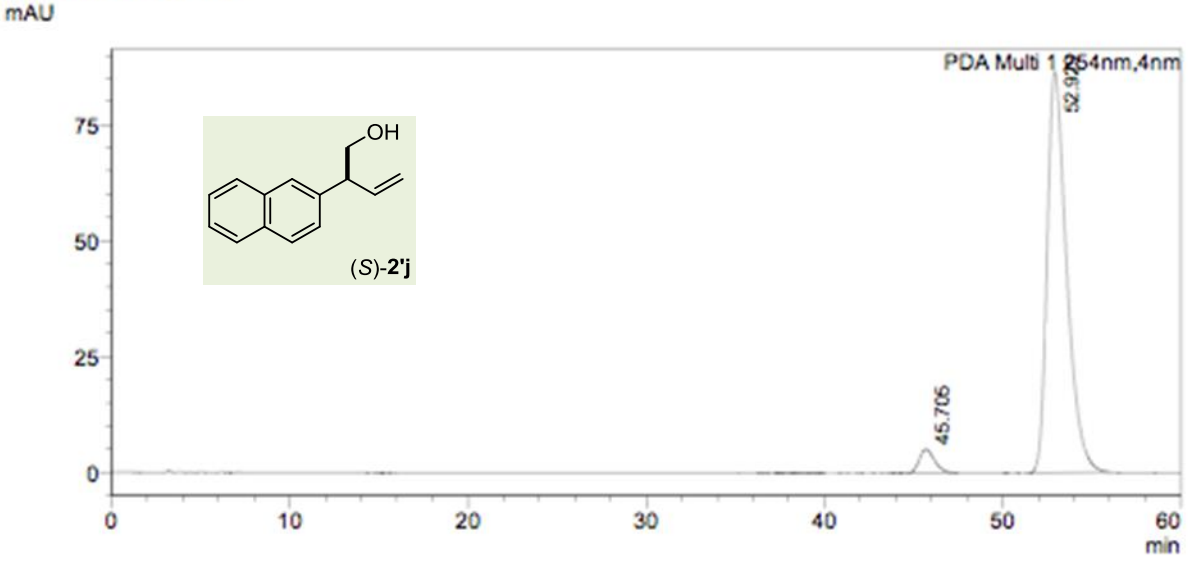


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	45.348	7018620	49.709
2	52.639	7100816	50.291
Total		14119437	100.000

<Chromatogram>

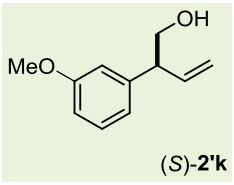


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	45.705	316990	4.591
2	52.929	6587496	95.409
Total		6904485	100.000

(*S*)-2-(3-methoxyphenyl)but-3-en-1-ol 2'k



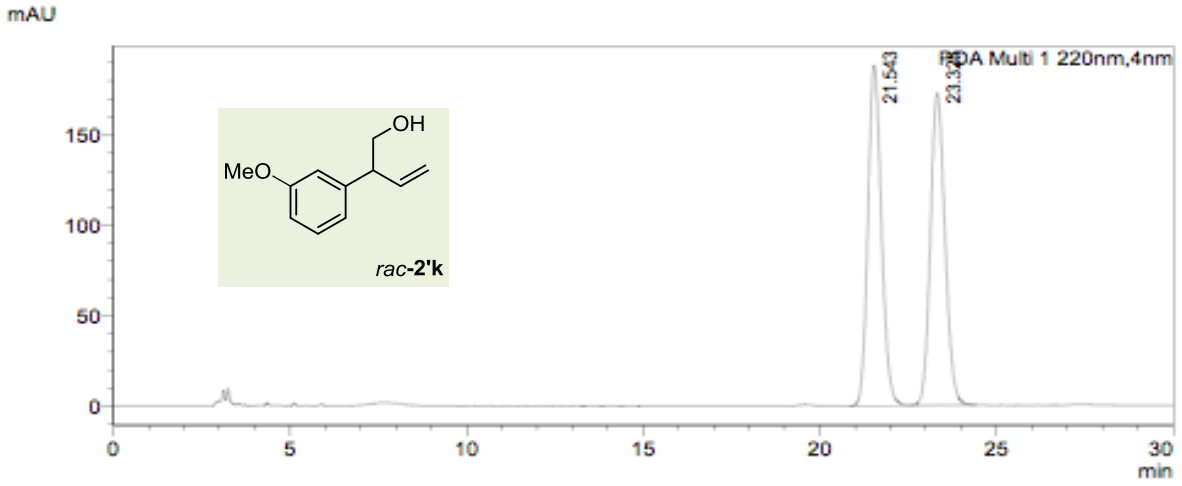
(*S*)-**2'k**

Following the general procedure using 1-(buta-1,3-dien-2-yl)-3-methoxybenzene **1k** (49 mg, 0.3 mmol, 1.0 equiv.), Cu*O*t*Bu* (4.1 mg, 0.03 mmol, 10 mol%), (*R,R*)-**L9** (22 mg, 0.03 mmol, 10 mol%), B_2pin_2 (91 mg, 0.36 mmol, 1.2 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.). Conversions: 85%, **2k**:**3k** = 20:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (*S*)-**2'k** as a colorless oil (43 mg, 73% yield, **2'k**:**3'k** > 20:1, 91% *ee*). All spectroscopic and spectrometric analyses were in agreement with the literature.[6]

HPLC: 91% *ee*, chiral stationary column: OD-H, mobile phase: hexane/*i*PrOH = 98/2, 1.0 mL/min, 220 nm, 30 °C, t_R (major) = 23.3 min, t_R (minor) = 21.6 min.

[α]$^{25}_{D}$ = +56.2 (*c* 0.70, CH_2Cl_2).

<Chromatogram>

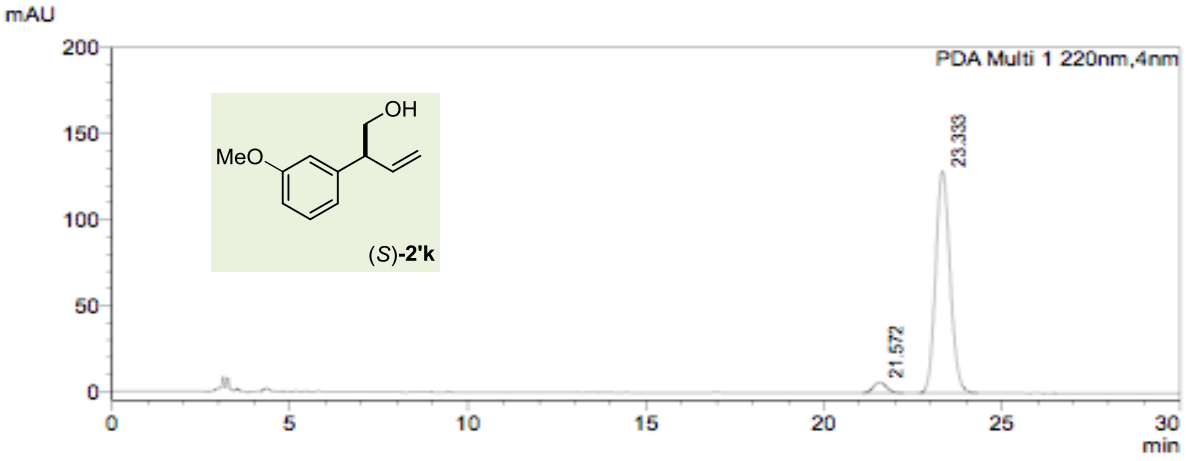


<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	21.543	5005627	50.197
2	23.325	4966432	49.803
Total		9972059	100.000

<Chromatogram>

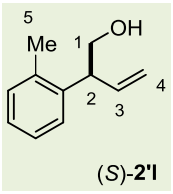


<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	21.572	162269	4.256
2	23.333	3650231	95.744
Total		3812501	100.000

(S)-2-(*o*-tolyl)but-3-en-1-ol 2'l



Following the general procedure using 1-(buta-1,3-dien-2-yl)-2-methylbenzene **1l** (35 mg, 0.24 mmol, 1.2 equiv.), CuO*t*Bu (2.7 mg, 0.02 mmol, 10 mol%), (*R,R*)-**L9** (14.7 mg, 0.02 mmol, 10 mol%), B_2pin_2 (50.8 mg, 0.2 mmol, 1.0 equiv.) and MeOH (18 µL, 0.4 mmol, 2.0 equiv.) at –40 °C for 60 h. Conversions: 90%, **2l**:**3l** = 2.6:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (*S*)-**2'l** as a colorless oil (18 mg, 56% yield, **2'l**:**3'l** > 20:1, 88% *ee*).

TLC: R_f = 0.6 (pentane/ethyl acetate 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.22 – 7.12 (m, 4H), 5.96 (ddd, $^3J_{HH}$ = 17.1, 10.3, 6.8 Hz, 1H, ***H*-3**), 5.26 – 5.06 (m, 2H, ***H*-4**), 3.88 – 3.74 (m, 3H, ***H*-1** and ***H*-2**), 2.37 (s, 3H, ***H*-5**), 1.56 (s, 1H, ***H*-O**).

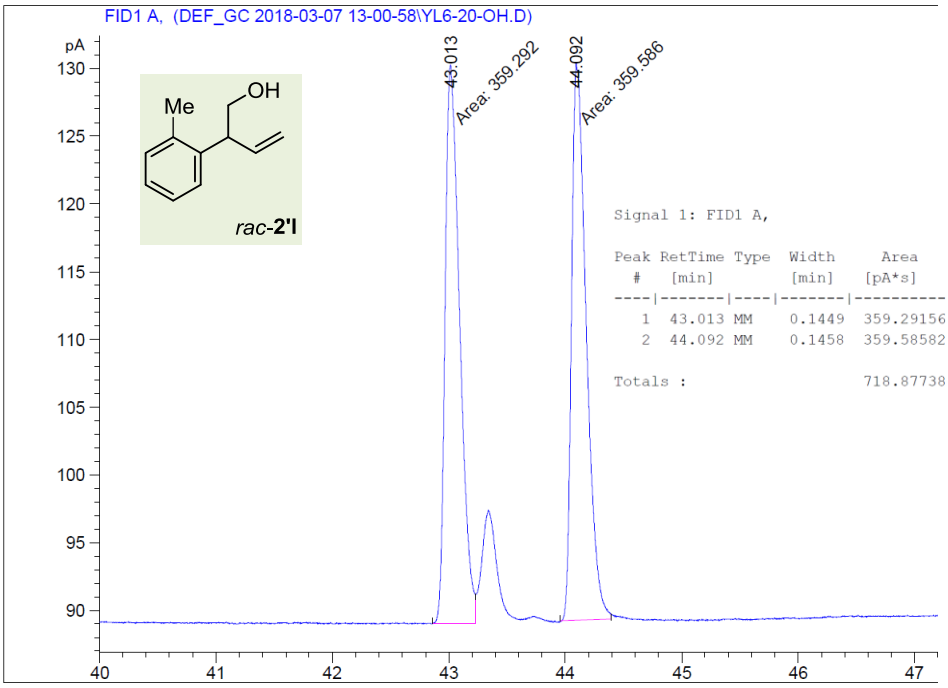
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 138.6 (***C*-Ar**), 138.2 (***C*H-3**), 136.7 (***C*-Ar**), 130.8 (***C*H-Ar**), 126.7 (***C*H-Ar**), 126.4 (***C*H-Ar**), 126.3 (***C*H-Ar**), 117.0 (***C*H_2-4**), 65.3 (***C*H_2-1**), 47.9 (***C*H-2**), 19.6 (***C*H_3-5**).

LRMS (ESI+): calculated for $C_{14}H_{20}O$ $[M]^+$: 162.10; found: 185.09 $[M+Na]^+$.

IR (neat) ν (cm^{-1}): 3355, 3075, 3020, 2927, 2876, 1726, 1637, 1604, 1490, 1462, 1413, 1380, 1295, 1261, 1028, 994, 916, 869, 753, 726, 665.

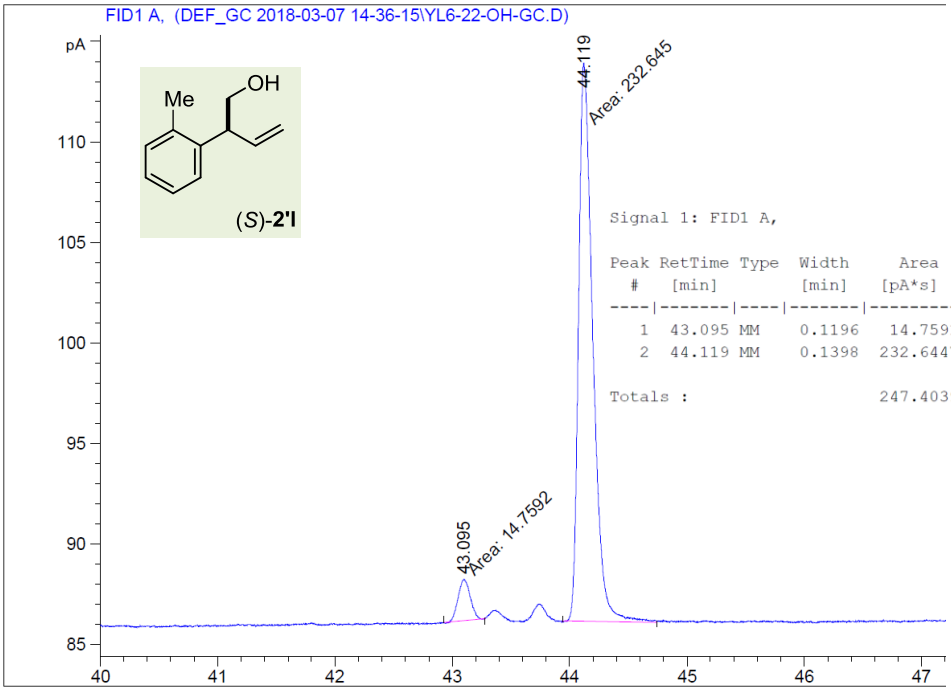
GC: 88% *ee*, HYDRODEX G-DiMOM, 100°C-1°C/min-170°C, 45 cm/s, H_2, t_R (major) = 44.1 min, t_R (minor) = 43.1 min.

[α]$^{20}_D$ = +52.4 (*c* 0.25, CH_2Cl_2).



Signal 1: FID1 A,

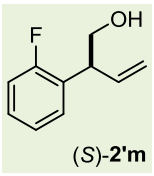
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	43.013	MM	0.1449	359.29156	41.31588	49.97953
2	44.092	MM	0.1458	359.58582	41.10785	50.02047
Totals :				718.87738	82.42373	



Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	43.095	MM	0.1196	14.75919	2.05757	5.96562
2	44.119	MM	0.1398	232.64479	27.74338	94.03438
Totals :				247.40398	29.80095	

(*S*)-2-(2-fluorophenyl)but-3-en-1-ol 2'm

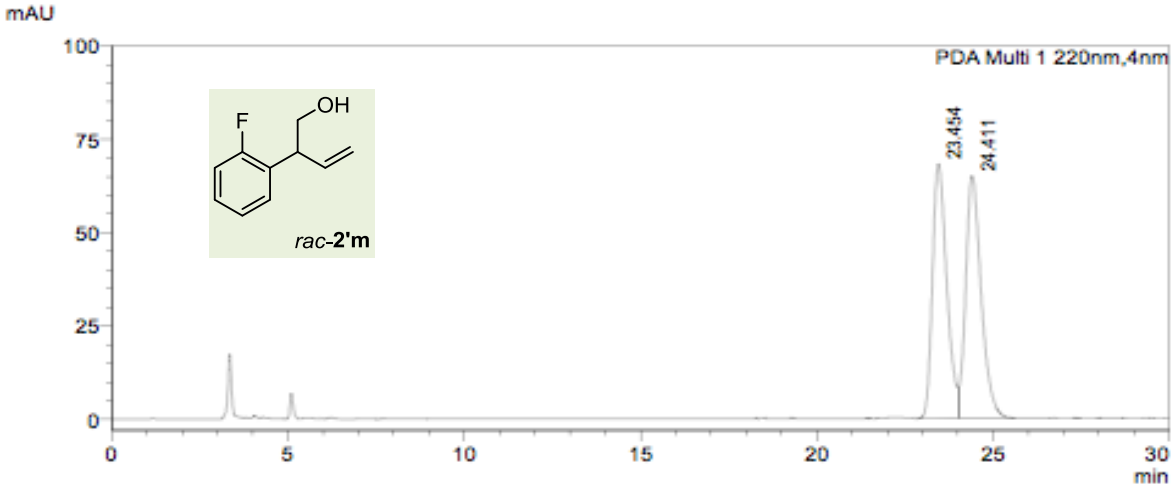


Following the general procedure using 1-(buta-1,3-dien-2-yl)-2-fluorobenzene **1m** (54 mg, 0.36 mmol, 1.2 equiv.), Cu*O*t*Bu (4.1 mg, 0.03 mmol, 10 mol%), (*R,R*)-**L9** (22 mg, 0.03 mmol, 10 mol%), B_2pin_2 (76.2 mg, 0.3 mmol, 1.0 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.). Conversions: 81%, **2m**:**3m** = 15:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (*S*)-**2'm** as a colorless oil (35 mg, 70% yield, **2'ml**:**3'm** > 20:1, 87% *ee*). All spectroscopic and spectrometric analyses were in agreement with the literature.[7]

HPLC: 87% *ee*, chiral stationary column: IC, mobile phase: hexane/*i*PrOH = 99.5/0.5, 1.0 mL/min, 220 nm, 30 °C, t_R (major) = 24.5 min, t_R (minor) = 23.6 min.

[α]$^{25}_{D}$ = +55.8 (*c* 0.45, CH_2Cl_2).

<Chromatogram>

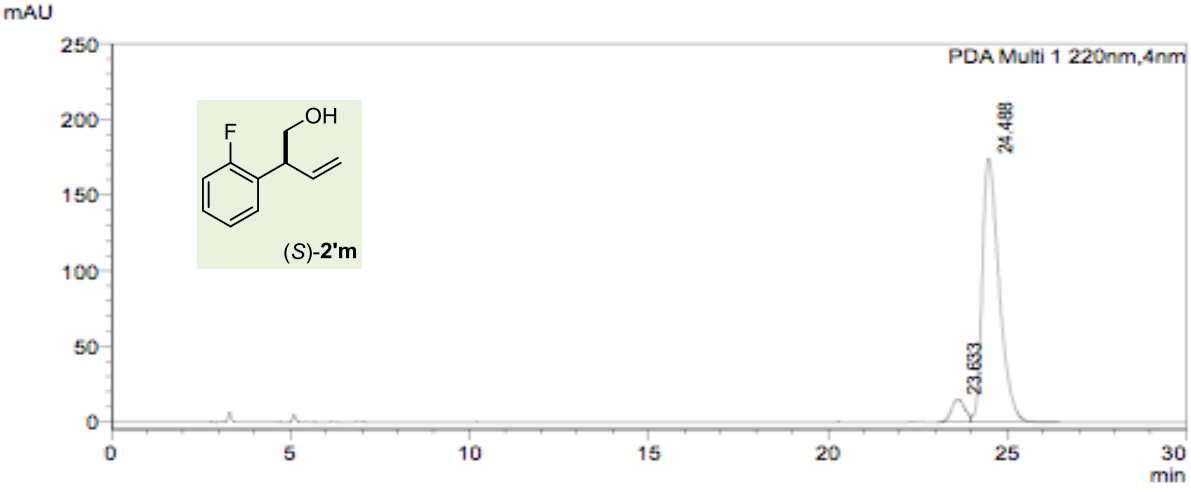


<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	23.454	1918228	49.077
2	24.411	1990388	50.923
Total		3908616	100.000

<Chromatogram>

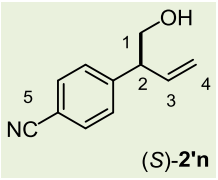


<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	23.633	404657	6.652
2	24.488	5678593	93.348
Total		6083250	100.000

(*S*)-4-(1-hydroxybut-3-en-2-yl)benzonitrile 2'n



(*S*)-**2'n**

Following the general procedure using 4-(buta-1,3-dien-2-yl)benzonitrile **1n** (56 mg, 0.36 mmol, 1.2 equiv.), CuO*t*Bu (4.1 mg, 0.03 mmol, 10 mol%), (*R,R*)-**L9** (22 mg, 0.03 mmol, 10 mol%), B_2pin_2 (76.2 mg, 0.3 mmol, 1.0 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.). Conversions: 26%, **2n**:**4n** = 13:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (*S*)-**2'n** as a colorless oil (13 mg, 24% yield, **2'n**:**4'n** = 18:1, 85% *ee*).

TLC: R_f = 0.3 (pentane/ethyl acetate 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.66 – 7.58 (m, 2H), 7.40 – 7.30 (m, 2H), 5.97 (ddd, $^3J_{HH}$ = 17.2, 10.4, 7.6 Hz, 1H, ***H*-3**), 5.33 – 5.11 (m, 2H, ***H*-4**), 3.86 (d, $^3J_{HH}$ = 6.8 Hz, 2H, ***H*-1**), 3.60 (dt, $^3J_{HH}$ = 7.1 , 7.0 Hz, 1H, ***H*-2**), 1.55 (br, 1H, ***H*-O**).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ (ppm) = 146.5 (***C*-Ar**), 136.8 (***C*H-3**), 132.5 (***C*H-Ar**), 128.9 (***C*H-Ar**), 118.8 (***C*-5**), 118.3 (***C*H$_2$-4**), 110.8 (***C*-Ar**), 65.6 (***C*H$_2$-1**), 52.4 (***C*H-2**).

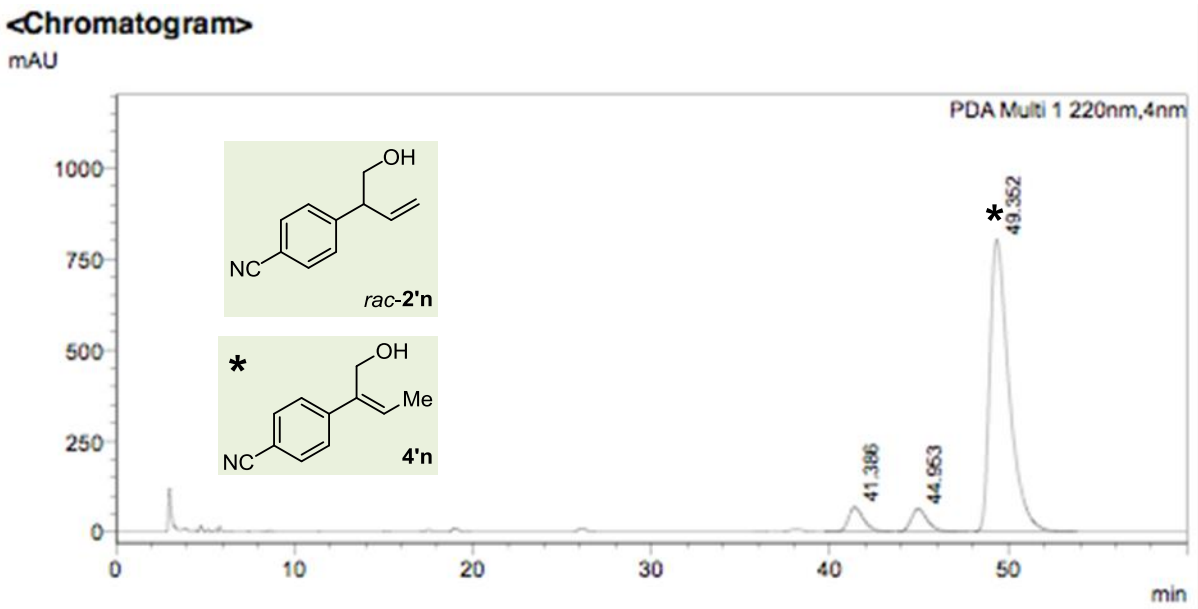
LRMS (ESI +): calculated for $C_{11}H_{11}NO$ $[M]^+$: 173.08; found: 191.12 $[M+NH_4]^+$.

IR (neat) ν (cm^{-1}): 3437, 2926, 2228,1741, 1643, 1604, 1504, 1377, 1266, 1022, 984, 825, 733.

HPLC: 85% *ee*, chiral stationary column: AD-H, mobile phase: hexane/^{i}PrOH = 97/3, 1.0 mL/min, 220 nm, 30 °C, t_R (major) = 44.9 min, t_R (minor) = 41.5 min.

[α]$^{20}_D$ = +71.9 (*c* 0.15, CH_2Cl_2).

<Chromatogram>

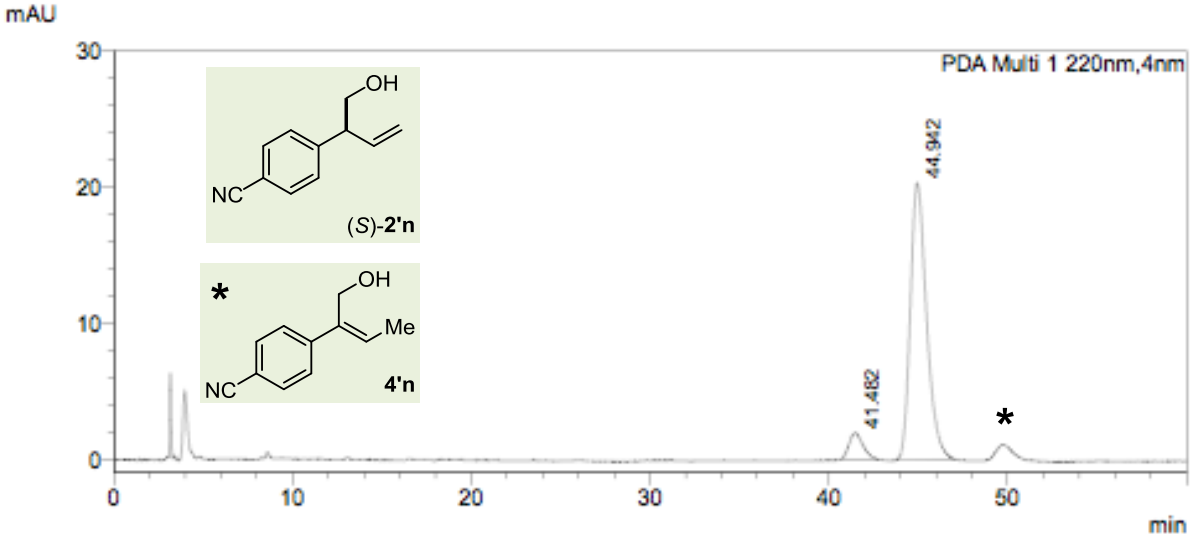


<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	41.386	4019518	5.917
2	44.953	4007721	5.899
3	49.352	59908782	88.184
Total		67936021	100.000

<Chromatogram>

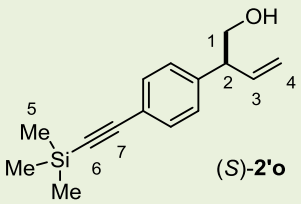


<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	41.482	105826	7.596
2	44.942	1287277	92.404
Total		1393103	100.000

(*S*)-2-(4-((trimethylsilyl)ethynyl)phenyl)but-3-en-1-ol 2'o



Following the general procedure using ((4-(buta-1,3-dien-2-yl)phenyl)ethynyl)-trimethylsilane **1o** (82 mg, 0.36 mmol, 1.2 equiv.), CuO*t*Bu (4.1 mg, 0.03 mmol, 10 mol%), (*R,R*)-**L9** (22 mg, 0.03 mmol, 10 mol%), B_2pin_2 (76.2 mg, 0.3 mmol, 1.0 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.). Conversions: 75%, **2o**:**3o** > 20:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (*S*)-**2'o** as a colorless oil (47 mg, 65% yield, **2'o**:**3'o** > 20:1, 89% *ee*).

TLC: R_f = 0.5 (pentane/ethyl acetate 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.43 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 7.17 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 5.97 (ddd, $^3J_{HH}$ = 17.6, 10.4, 7.6 Hz, 1H, ***H*-3**), 5.27 – 5.11 (m, 2H, ***H*-4**), 3.80 (d, $^3J_{HH}$ = 7.0 Hz, 2H, ***H*-1**), 3.51 (dt, $^3J_{HH}$ = 7.2 Hz, 7.2 Hz, 1H, ***H*-2**), 1.51 (br, 1H, ***H*-O**), 0.24 (s, 9H, ***H*-5**).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 141.2 (***C*-Ar**), 137.7 (***C*H-3**), 132.3 (***C*H-Ar**), 127.9 (***C*H-Ar**), 121.8 (***C*-Ar**), 117.4 (***C*H$_2$-4**), 104.9 (***C*-7**), 94.2 (***C*-6**), 65.9 (***C*H$_2$-1**), 52.3 (***C*H-2**), 0.0 (***C*H$_3$-5**).

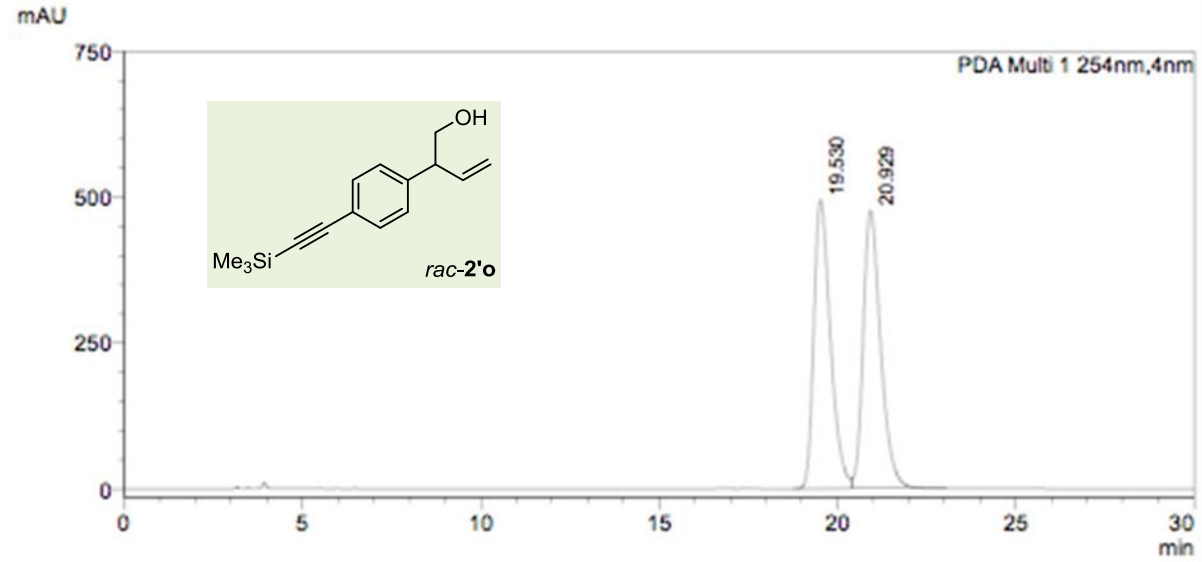
LRMS (ESI +): calculated for $C_{15}H_{20}OSi$ $[M]^+$: 244.13; found: 262.15 $[M+NH_4]^+$.

IR (neat) ν (cm^{-1}): 3347, 3081, 2959, 2926, 2158, 1639, 1503, 1409, 1249, 1223, 1107, 1057, 1020, 995, 912, 861, 837, 758, 667.

HPLC: 89% *ee*, chiral stationary column: AD-H, mobile phase: hexane/*i*PrOH = 99.5/0.5, 1.0 mL/min, 254 nm, 30 °C, t_R (major) = 20.9 min, t_R (minor) = 19.5 min.

[α]$^{20}_D$ = +66.3 (*c* 0.54, CH_2Cl_2).

<Chromatogram>

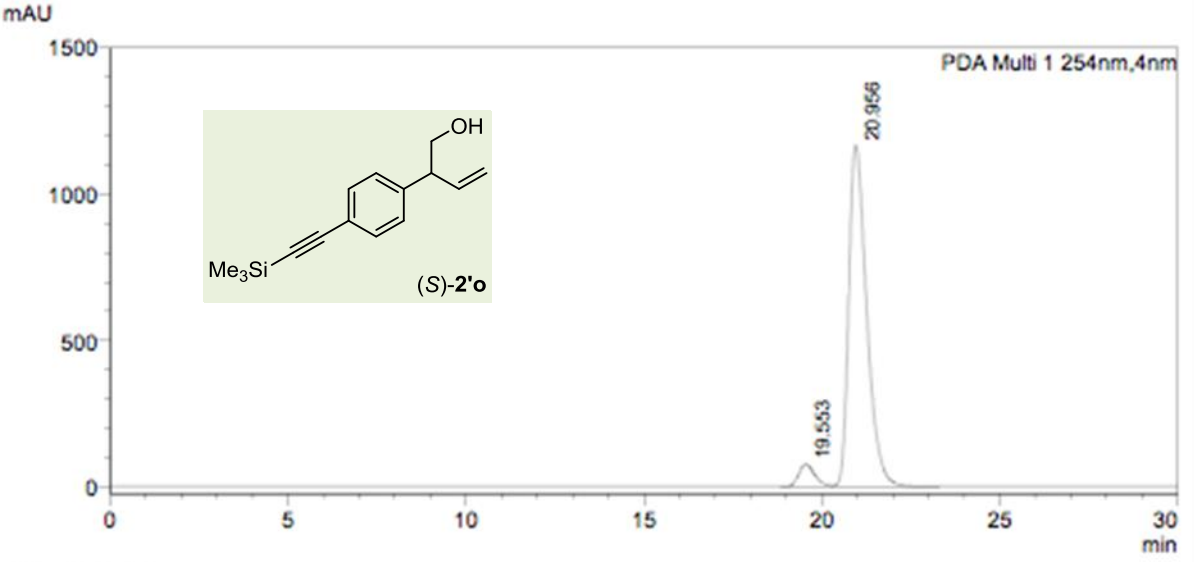


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	19.530	16066825	49.569
2	20.929	16346307	50.431
Total		32413132	100.000

<Chromatogram>

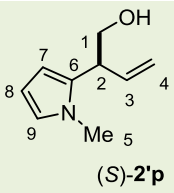


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	19.553	2408679	5.558
2	20.956	40931323	94.442
Total		43340002	100.000

(*S*)-2-(1-methyl-1*H*-pyrrol-2-yl)but-3-en-1-ol 2'p



(*S*)-**2'p**

Following the general procedure using 2-(buta-1,3-dien-2-yl)-1-methyl-1*H*-pyrrole **1p** (48 mg, 0.36 mmol, 1.2 equiv.), CuO*t*Bu (4.1 mg, 0.03 mmol, 10 mol%), (*R,R*)-**L9** (22 mg, 0.03 mmol, 10 mol%), B_2pin_2 (76.2 mg, 0.3 mmol, 1.0 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.). Conversions: 60%, **2p**:**3p** = 1.3:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (*S*)-**2'p** as a colorless oil (13 mg, 28% yield).

TLC: R_f = 0.4 (pentane/ethyl acetate 2:1).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 6.59 (dd, $^3J_{HH}$ = 2.7, 1.8 Hz, 1H, ***H*-8**), 6.11 (dd, $^3J_{HH}$ = 3.6, 2.7 Hz, 1H, ***H*-9**), 5.97 (dd, $^3J_{HH}$ = 3.6, 1.8 Hz, 1H, ***H*-7**), 5.82 (ddd, $^3J_{HH}$ = 17.1, 10.2, 7.5 Hz, 1H, ***H*-3**), 5.21 – 5.15 (m, 1H, ***H*-4**), 5.13 – 5.05 (m, 1H, ***H*-4**), 3.89 – 3.74 (m, 2H, ***H*-1**), 3.60 (t, $^3J_{HH}$ = 7.2 Hz, 1H, ***H*-2**), 3.55 (s, 3H, ***H*-5**), 1.69 (br, 1H, ***H*-O**).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 137.5 (***C*H-3**), 131.0 (***C*-6**), 122.3 (***C*H-8**), 117.2 (***C*H$_2$-4**), 107.0 (***C*H-9**), 105.1 (***C*H-7**) , 64.6 (***C*H$_2$-1**), 44.5 (***C*H-2**), 33.7 (***C*H$_3$-5**).

LRMS (ESI+): calculated for $C_9H_{13}NO$ $[M]^+$: 151.10; found: 134.45 $[M\text{-}OH]^+$.

IR (neat) ν (cm^{-1}): 3358, 2958, 2925, 2864, 1731, 1637, 1592, 1464, 1422, 1395, 1364, 1300, 1248, 1176, 1148, 1057, 1032, 996, 917, 870, 792, 608.

HPLC: 86% *ee*, chiral stationary column: OD-H, mobile phase: hexane/*i*PrOH = 99/1, 1.0 mL/min, 220 nm, 30 °C, t_R (major) = 28.3 min, t_R (minor) = 37.2 min.

[α]$^{20}_D$ = +74.7 (*c* 0.12, CH_2Cl_2).

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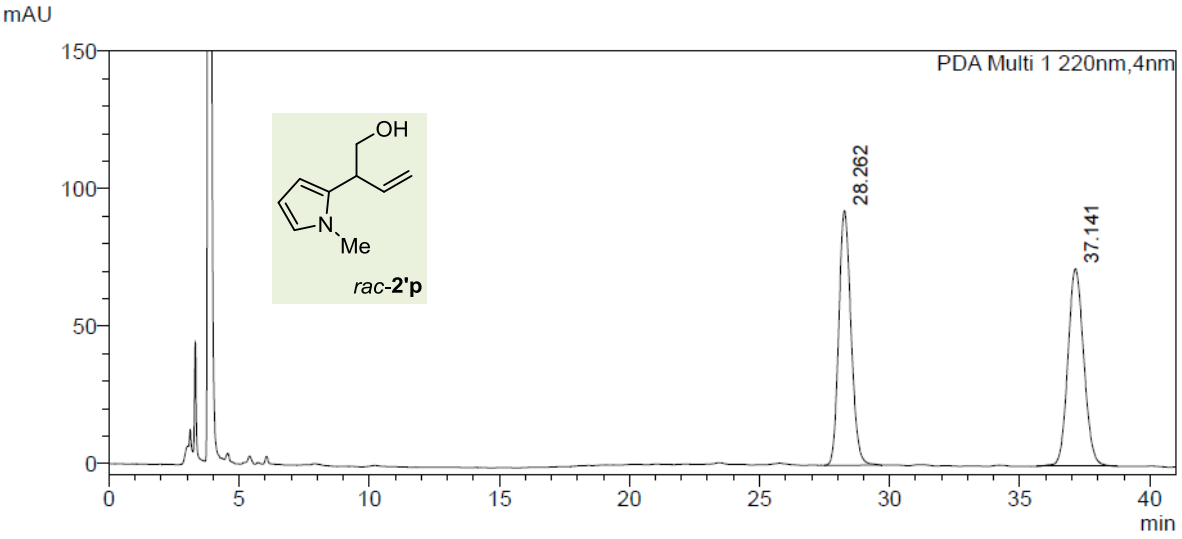
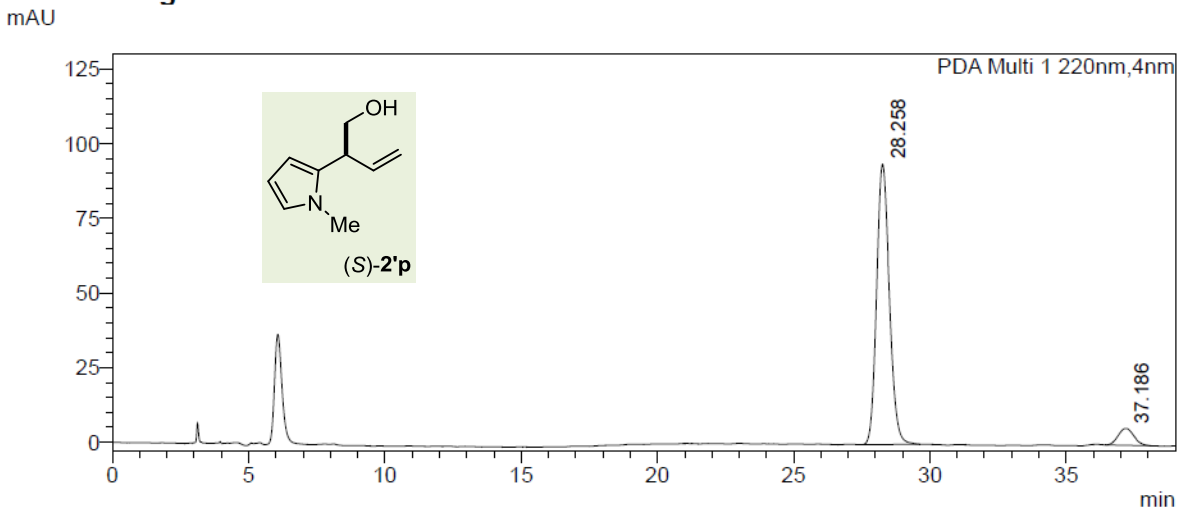


<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	28.262	3026412	49.673
2	37.141	3066280	50.327
Total		6092692	100.000

<Chromatogram>

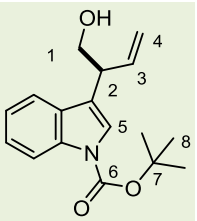


<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	28.258	3066306	93.144
2	37.186	225684	6.856
Total		3291990	100.000

***tert*-butyl (*S*)-3-(1-hydroxybut-3-en-2-yl)-1*H*-indole-1-carboxylate 2'q**



(*S*)-**2'q**

Following the general procedure using *tert*-butyl 3-(buta-1,3-dien-2-yl)-1*H*-indole-1-carboxylate **1q** (97 mg, 0.36 mmol, 1.2 equiv.), CuO*t*Bu (4.1 mg, 0.03 mmol, 10 mol%), (*R,R*)-**L9** (22 mg, 0.03 mmol, 10 mol%), B_2pin_2 (76.2 mg, 0.3 mmol, 1.0 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.). Conversions: 84%, **2q**:**3q** = 3.8:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (*S*)-**2'q** as a colorless oil (55 mg, 64% yield, **2'q**:**4'q** = 20:1, 60% *ee*).

TLC: R_f = 0.4 (pentane/ethyl acetate 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.15 (d, $^3J_{HH}$ = 8.4 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.47 (s, 1H, ***H*-5**), 7.36 – 7.30 (m, 1H), 7.25 – 7.19 (m, 1H), 6.06 (ddd, $^3J_{HH}$ = 17.4, 10.3, 7.3 Hz, 1H, ***H*-3**), 5.31 – 5.25 (m, 2H, ***H*-4**), 4.02 – 3.94 (m, 1H, ***H*-1**), 3.80 (td, $^3J_{HH}$ = 7.1, 6.1, Hz, 1H, ***H*-2**), 3.83 – 3.73 (m, 1H, ***H*-1**), 1.68 (br, 10H, ***H*-O and *H*-8**).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 149.7 (***C*-6**), 137.1 (***C*H-3**), 135.6 (***C*-Ar**), 129.7 (***C*-Ar**), 124.5 (***C*H-Ar**), 122.8 (***C*H-Ar**), 122.4 (***C*H-Ar**), 119.5 (***C*-Ar**), 119.4 (***C*H-5**), 117.5 (***C*H$_2$-4**), 115.4 (***C*H-Ar**), 83.7 (***C*-7**), 64.8 (***C*H$_2$-1**), 43.7 (***C*H-2**), 28.2 (***C*H$_3$-8**).

LRMS (ESI +): calculated for $C_{17}H_{21}NO_3$ $[M]^+$: 287.15; found: 288.05 $[M+H]^+$; 305.35 $[M+NH_4]^+$.

IR (neat) ν (cm^{-1}): 3405, 3055, 2978, 2930, 1728, 1639, 1608, 1567, 1452, 1369, 1308, 1255, 1068, 1020, 919, 856, 765, 739, 704, 636.

HPLC: 60% *ee*, chiral stationary column: OD-H, mobile phase: hexane/*i*PrOH = 98/2, 1.0 mL/min, 254 nm, 30 °C, t_R (major) = 16.1 min, t_R (minor) = 21.3 min.

[α]$^{20}_D$ = +36.6 (*c* 0.96, CH_2Cl_2).

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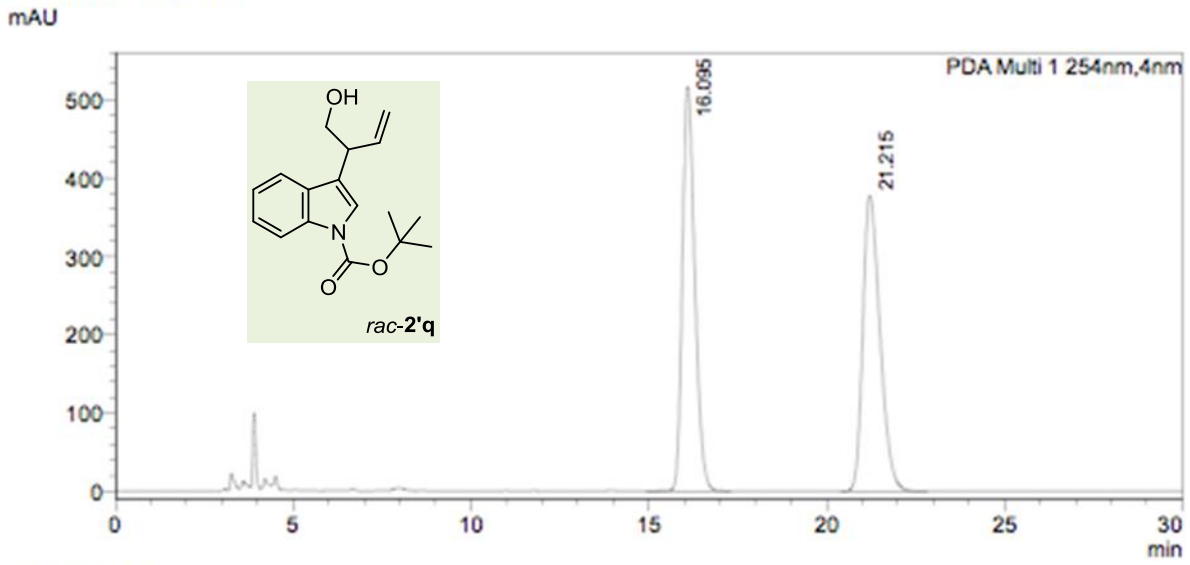
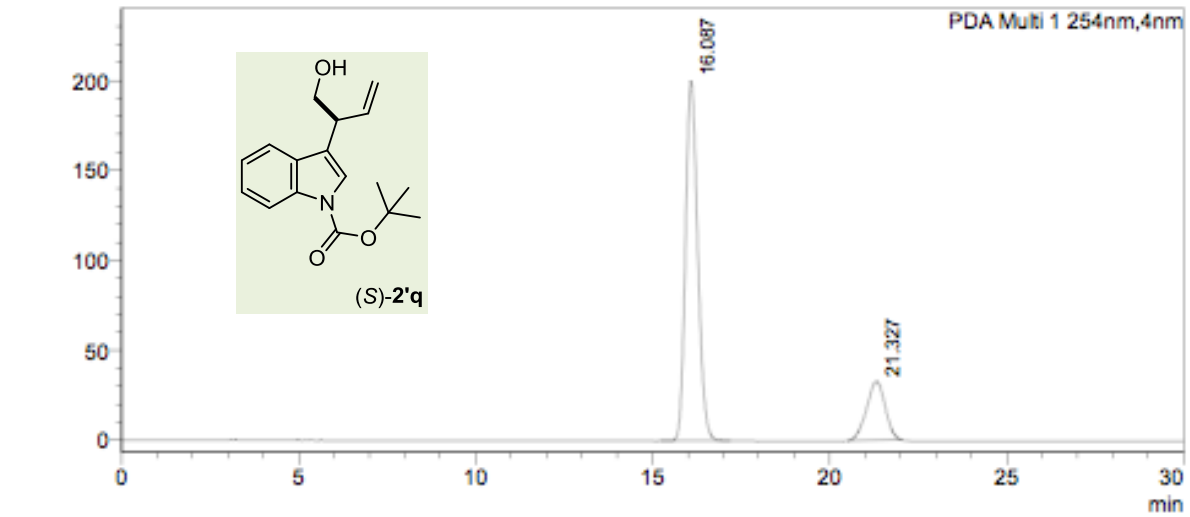


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	16.095	12539360	49.724
2	21.215	12678451	50.276
Total		25217811	100.000

<Chromatogram>

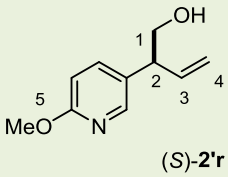


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	16.087	4799842	79.999
2	21.327	1200007	20.001
Total		5999849	100.000

(*S*)-2-(6-methoxypyridin-3-yl)but-3-en-1-ol 2'r



(*S*)-**2'r**

Following the general procedure using 5-(buta-1,3-dien-2-yl)-2-methoxypyridine **1r** (65 mg, 0.36 mmol, 1.2 equiv.), CuO*t*Bu (4.1 mg, 0.03 mmol, 10 mol%), (*R,R*)-**L9** (22 mg, 0.03 mmol, 10 mol%), B_2pin_2 (76.2 mg, 0.3 mmol, 1.0 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.). Conversions: 46%, **2r**:**3r**:**4r** = 50:10:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (*S*)-**2'r** as a colorless oil (24 mg, 45% yield, **2'r**:**3'r**:**4'r** = 50:10:1, 80% *ee*).

TLC: R_f = 0.2 (pentane/acetone 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.02 (d, $^3J_{HH}$ = 2.4 Hz, 1H), 7.45 (dd, $^3J_{HH}$ = 8.5, 2.5 Hz, 1H), 6.72 (dd, $^3J_{HH}$ = 8.5, 0.7 Hz, 1H), 5.96 (ddd, $^3J_{HH}$ = 17.5, 10.4, 7.4 Hz, 1H, ***H*-3**), 5.26 – 5.11 (m, 2H, ***H*-4**), 3.91 (s, 3H, ***H*-5**), 3.83 – 3.77 (m, 2H, ***H*-1**), 3.48 (dt, $^3J_{HH}$ = 7.1 Hz, 7.1 Hz, 1H, ***H*-2**), 1.70 – 1.64 (m, 1H, ***H*-O**).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 163.3 (***C*-Ar**), 146.2 (***C*H-Ar**), 138.2 (***C*H-Ar**), 137.6 (***C*H-3**), 128.8 (***C*-Ar**), 117.5 (***C*H_2-4**), 110.9 (***C*H-Ar**), 65.8 (***C*H_2-1**), 53.4 (***C*H_3-5**), 48.9 (***C*H-2**).

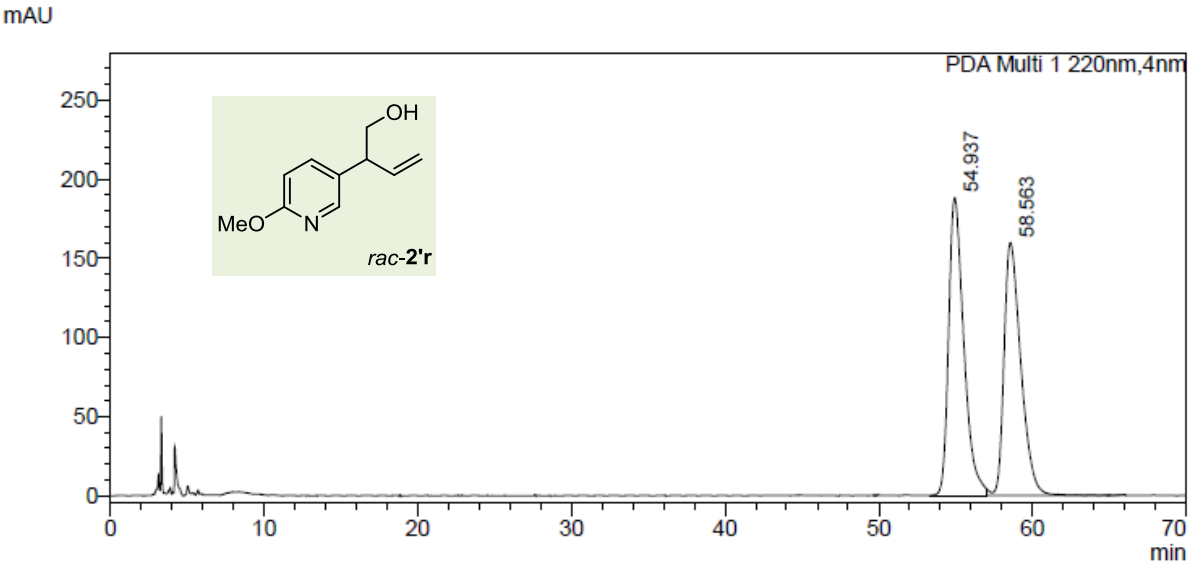
LRMS (ESI +): calculated for $C_{10}H_{13}NO_2$ $[M]^+$: 179.09; found: 180.05 $[M+H]^+$; 162.25 $[M-OH]^+$.

IR (neat) ν (cm^{-1}): 3328, 3080, 2980, 2946, 2871, 2816, 1844, 1639, 1605, 1572, 1492, 1391, 1312, 1286, 1130, 1055, 1023, 996, 919, 878, 827, 762, 662.

HPLC: 80% *ee*, chiral stationary column: OD-H, mobile phase: hexane/*i*PrOH = 99/1, 1.0 mL/min, 220 nm, 30 °C, t_R (major) = 55.2 min, t_R (minor) = 59.3 min.

$[\alpha]^{20}_D$ = +44.8 (*c* 0.36, CH_2Cl_2).

<Chromatogram>

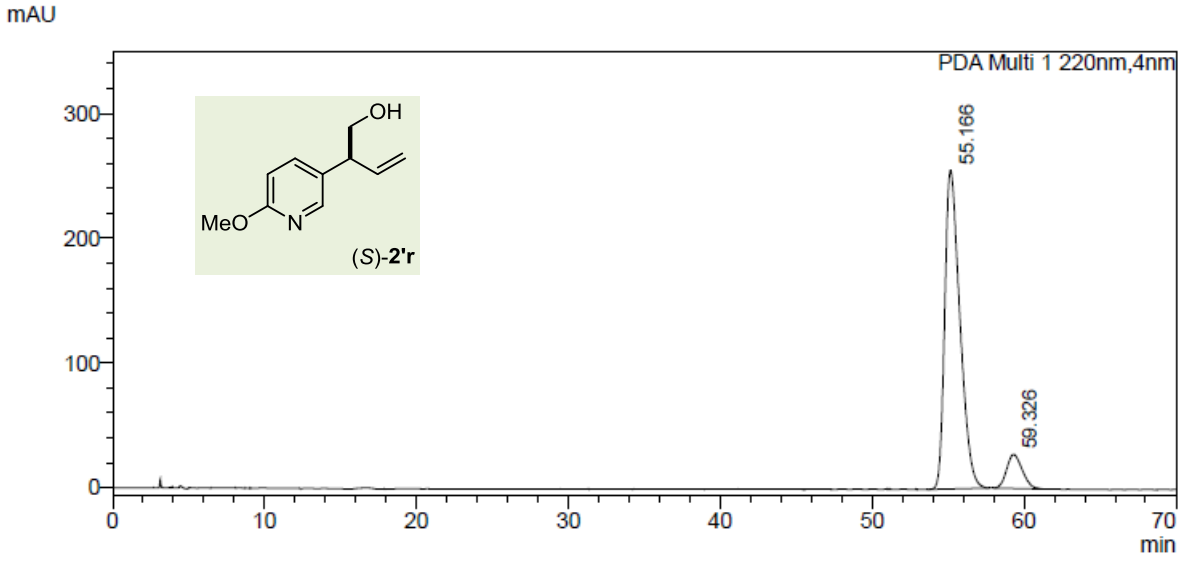


<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	54.937	12925541	51.547
2	58.563	12149586	48.453
Total		25075128	100.000

<Chromatogram>

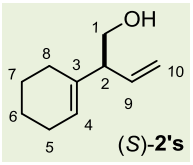


<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	55.166	17718140	90.002
2	59.326	1968260	9.998
Total		19686400	100.000

(*S*)-2-(cyclohex-1-en-1-yl)but-3-en-1-ol **2's**



(*S*)-**2's**

Following the general procedure using 1-(buta-1,3-dien-2-yl)cyclohex-1-ene **1s** (48 mg, 0.36 mmol, 1.2 equiv.), Cu*O*t*B*u (4 mg, 0.03 mmol, 10 mol%), (*R*,*R*)-**L9** (22 mg, 0.03 mmol, 10 mol%), B_2pin_2 (76 mg, 0.3 mmol, 1.0 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.). Conversions: 99%, **2s**:**4s** = 25:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (*S*)-**2's** as a colorless oil (40 mg, 88% yield, **2's**:**4's** = 25:1, 89% *ee*).

TLC: R_f = 0.2 (pentane/ diethyl ether 9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 5.75 (m, 1H, ***H*-9**), 5.55 (m, 1H, ***H*-4**), 5.12 (d, $^3J_{HH}$ = 10.9 Hz, 1H, ***H*-10**), 5.11 (d, $^3J_{HH}$ = 16.4 Hz, 1H, ***H*-10**), 3.60 (m, 2H, ***H*-1**) 2.81 (m, 1H, ***H*-2**), 2.03 (m, 2H, ***H*-5**), 1.94 (m, 2H, ***H*-8**), 1.58 (m, 4H, ***H*-6** + ***H*-7**), 1.45 (t, $^3J_{HH}$ = 6.1 Hz, 1H, **O*H***).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 137.8 (***C*H-9**), 136.5 (***C*-3**), 124.1 (***C*H-4**), 116.7 (***C*H$_2$-10**), 63.4 (***C*H$_2$-1**), 54.2 (***C*H-2**), 26.6 (***C*H$_2$-8**), 25.4 (***C*H$_2$-5**), 23.0 (***C*H$_2$-6** or ***C*H$_2$-7**), 22.6 (***C*H$_2$-6** or ***C*H$_2$-7**).

GC-MS (EI) ($C_{10}H_{16}O$): 152.1 (3, M^+), 134.1 (5, M^+–18), 121.1 (53, M^+–31), 105.1 (53, M^+–47), 105.1 (12, M^+–47), 93.1 (49, M^+–49), 91.1 (63, M^+–61), 79.1 (100, M^+–73), 77.1 (48, M^+–75), 67.1 (39, M^+–85).

IR (neat) ν (cm^{-1}): 3347, 2925, 2858, 2837, 1635, 1438, 1341, 1207, 1138, 1054, 102, 994, 913, 838, 801.

HPLC: 89% *ee*, chiral stationary column: AD-H, mobile phase: hexane/^{i}PrOH = 99/1, 1.0 mL/min, 208 nm, 30 °C, t_R (major) = 14.5 min, t_R (minor) = 16.1 min.

[α]$^{25}_D$ = +38.3 (*c* 0.30, CH_2Cl_2).

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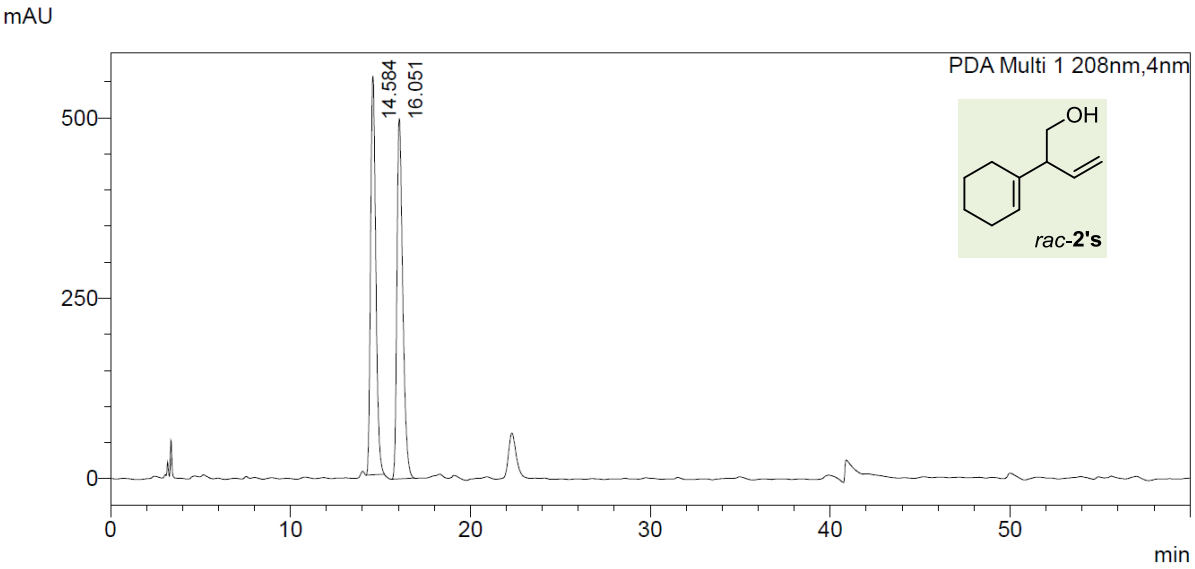
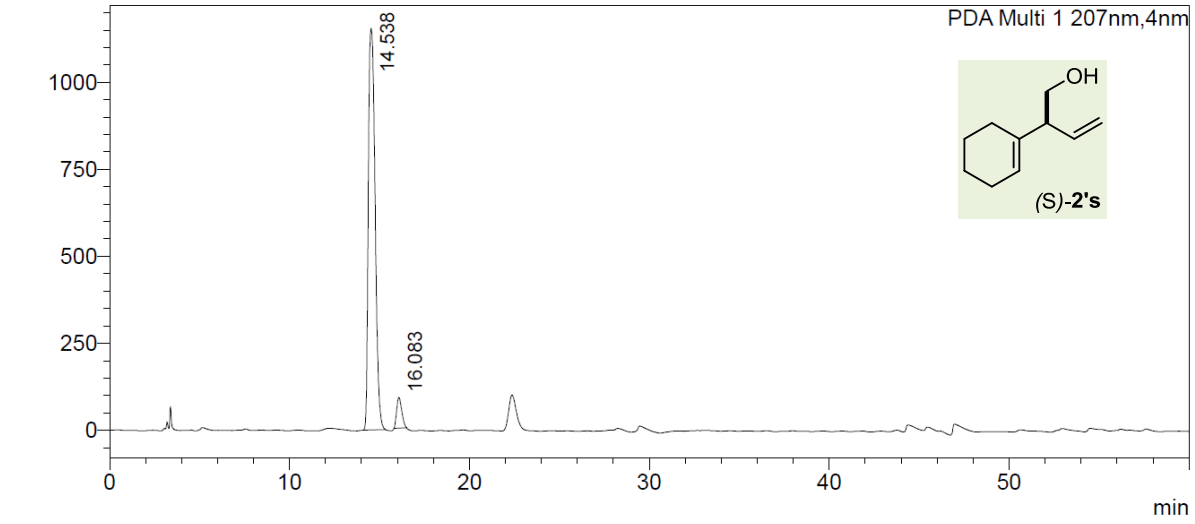


<Peak Table>

PDA Ch1 208nm

Peak#	Ret. Time	Area	Area%
1	14.584	11121471	49.635
2	16.051	11284970	50.365
Total		22406441	100.000

<Chromatogram>

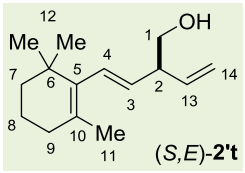


<Peak Table>

PDA Ch1 207nm

Peak#	Ret. Time	Area	Area%
1	14.538	29971109	94.521
2	16.083	1737448	5.479
Total		31708556	100.000

(*S*,*E*)-4-(2,6,6-trimethylcyclohex-1-en-1-yl)-2-vinylbut-3-en-1-ol 2't



Following the general procedure using (*E*)-1,3,3-trimethyl-2-(3-methylenepenta-1,4-dien-1-yl)cyclohex-1-ene **1t** (73 mg, 0.36 mmol, 1.2 equiv.), CuO*t*Bu (4 mg, 0.03 mmol, 10 mol%), (*R,R*)-**L9** (22 mg, 0.03 mmol, 10 mol%), B_2pin_2 (76 mg, 0.3 mmol, 1.0 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.). Conversions: 99%, **2t**:**3t** = 50:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (*S*,*E*)-**2't** as a colorless oil (40 mg, 60% yield, **2't**:**3't** = 50:1, 80% *ee*).

TLC: R_f = 0.3 (pentane/ diethyl ether 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 5.98 (d, $^3J_{HH}$ = 16.0 Hz, 1H, ***H*-4**), 5.80 (ddd, $^3J_{HH}$ = 17.4, 10.5, 7.1 Hz, 1H, ***H*-13**), 5.29 (dd, $^3J_{HH}$ = 16.0, 7.9 Hz, 1H, ***H*-3**), 5.18 (m, 2H, ***H*-14**), 3.58 (m, 2H, ***H*-1**), 3.03 (m, 1H, ***H*-2**), 1.97 (m, 2H, ***H*-9**), 1.67 (s, 3H, ***H*-11**), 1.60 (s, 1H, ***H*-8**), 1.46 (m, 1H, ***H*-7**), 0.99 (s, 3H, ***H*-12**), 0.98 (s, 3H, ***H*-12**).

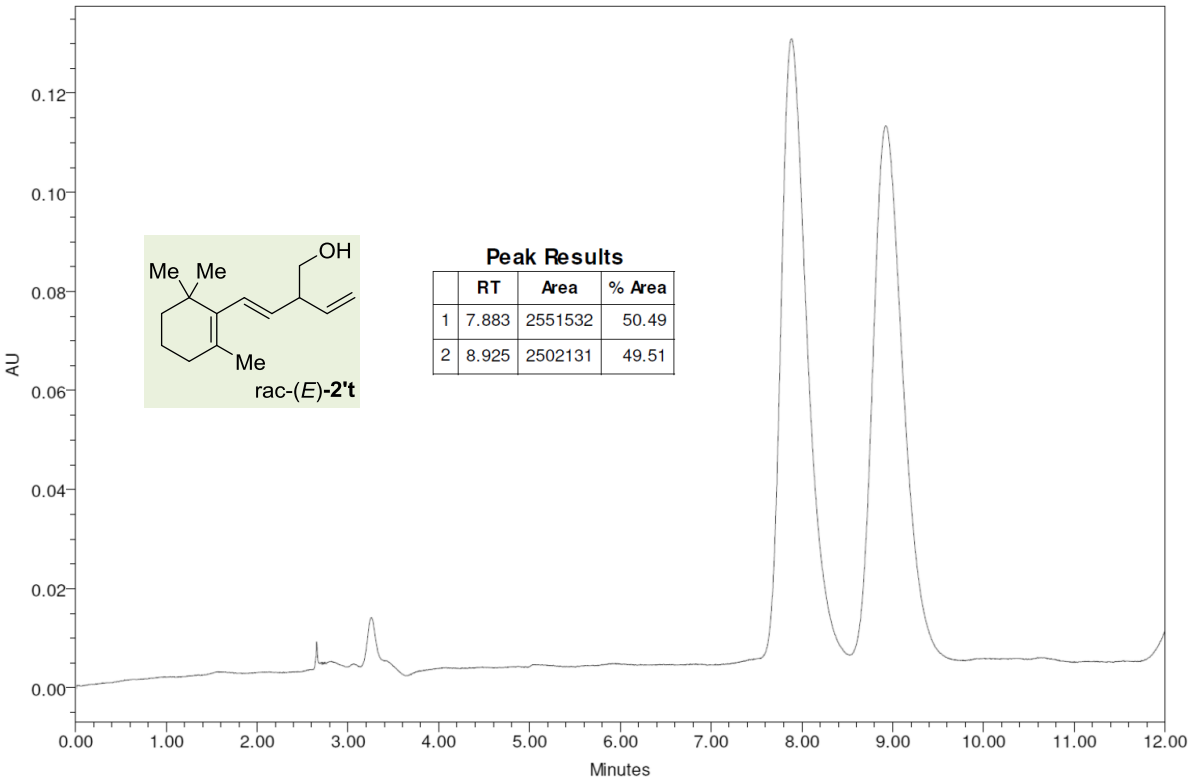
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 138.1 (***C*H-13**), 137.4 (***C*-10**), 132.3 (***C*H-3**), 130.7 (***C*H-13**), 128.7 (***C*-5**), 116.8 (***C*H$_2$-14**), 65.5 (***C*H$_2$-1**), 50.6 (***C*H-2**), 39.5 (***C*H$_2$-7**), 34.0 (***C*-6**), 32.8 (***C*H$_2$-9**), 29.0 (***C*H$_3$-12**), 28.9 (***C*H$_3$-12**), 21.7 (***C*H$_3$-11**), 19.4 (***C*H$_2$-8**).

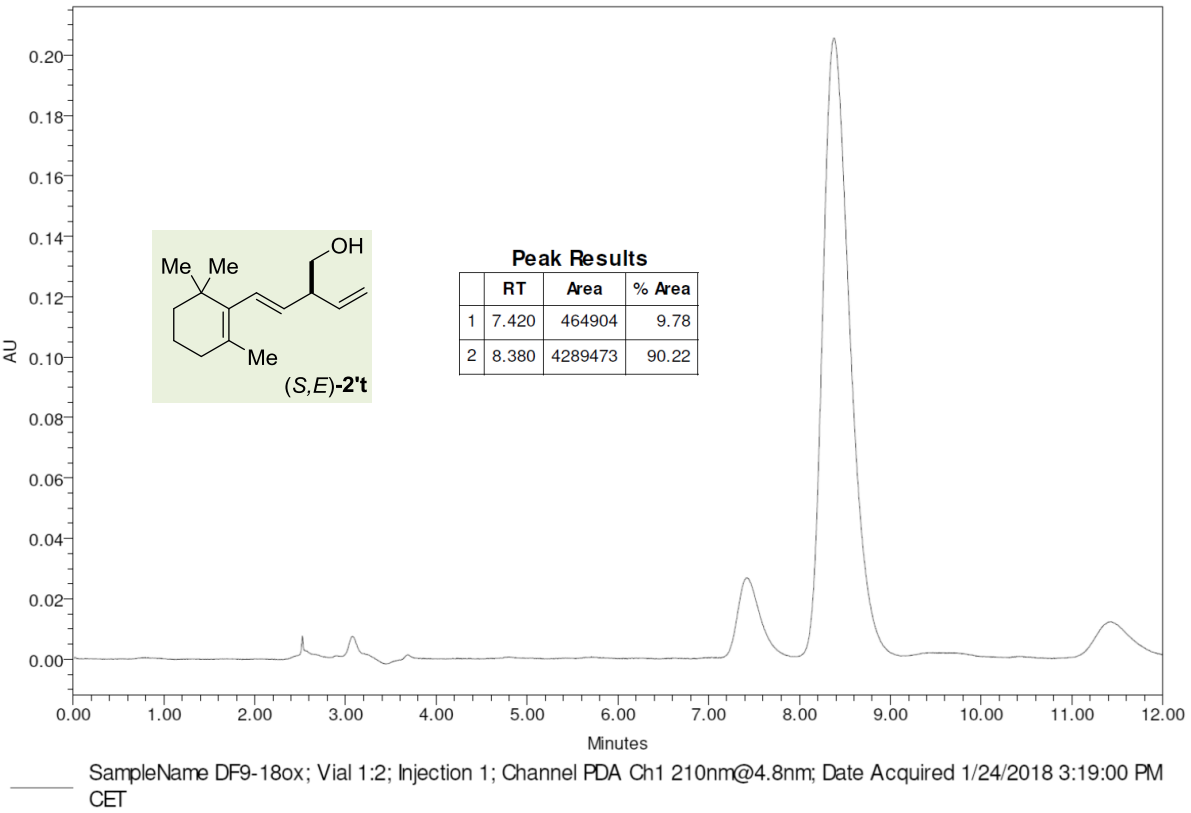
LRMS (ESI +): calculated for $C_{15}H_{24}O$ $[M]^+$: 220.18; found: 238.4 $[M+NH_4]^+$;

IR (neat) ν (cm^{-1}): 3344, 2927, 2865, 1638, 1457, 1360, 1205, 1039, 973, 916.

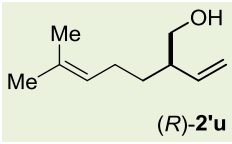
SFC: 80% *ee*; chiral stationary phase: AZ column; 2% MeOH; t_R (major) = 8.4 min, t_R (minor) = 7.4 min.

[α]$^{25}_D$ = +30.0 (*c* 0.55, CH_2Cl_2)


OH
Me Me
Me
rac-(*E*)-**2't**
Peak Results
RT Area % Area
1 7.883 2551532 50.49
2 8.925 2502131 49.51
AU
Minutes
SampleName Q61; Vial 1:1; Injection 1; Channel PDA Ch1 210nm@4.8nm; Date Acquired 1/24/2018 3:02:45 PM CET


OH
Me Me
Me
(*S*,*E*)-**2't**
Peak Results
RT Area % Area
1 7.420 464904 9.78
2 8.380 4289473 90.22
AU
Minutes
SampleName DF9-18ox; Vial 1:2; Injection 1; Channel PDA Ch1 210nm@4.8nm; Date Acquired 1/24/2018 3:19:00 PM CET

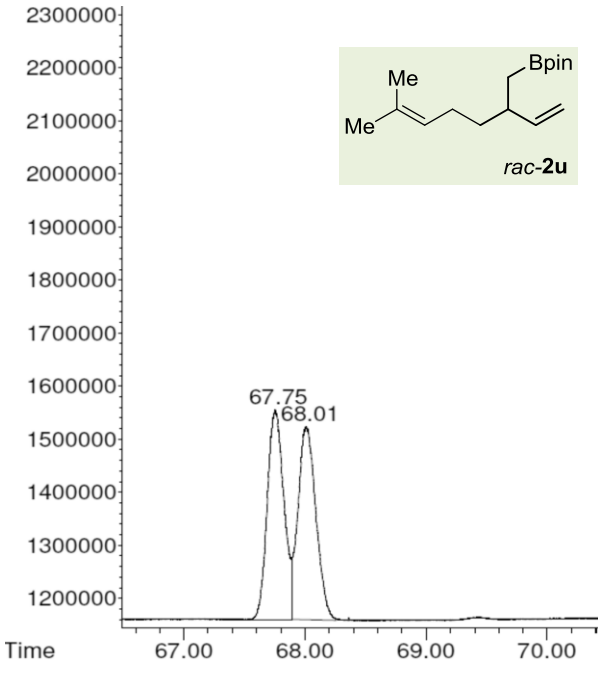
(*R*)-6-methyl-2-vinylhept-5-en-1-ol 2'u



Following the general procedure using myrcene **1u** (25 mg, 0.18 mmol, 1.2 equiv.), CuO*t*Bu (2.1 mg, 0.015 mmol, 10 mol%), (*R,R*)-**L9** (11 mg, 0.0015 mmol, 10 mol%), B_2pin_2 (38 mg, 0.15 mmol, 1.0 equiv.) and MeOH (12 µL, 0.3 mmol, 2.0 equiv.). Reaction temperature: 0°C. Reaction time: 24 h. Conversions: 94%, **2u**:**3u** = 1:5.7. Then it was oxidized under basic condition following the general procedure to afford mixture of alcohols **2'u**:**3'u**, whose ratio was determined by ^{1}H NMR **2'u**:**3'u** = 1:5.7. All spectroscopic and spectrometric analyses of **2'u** and **3'u** were in agreement with the literature.[8]

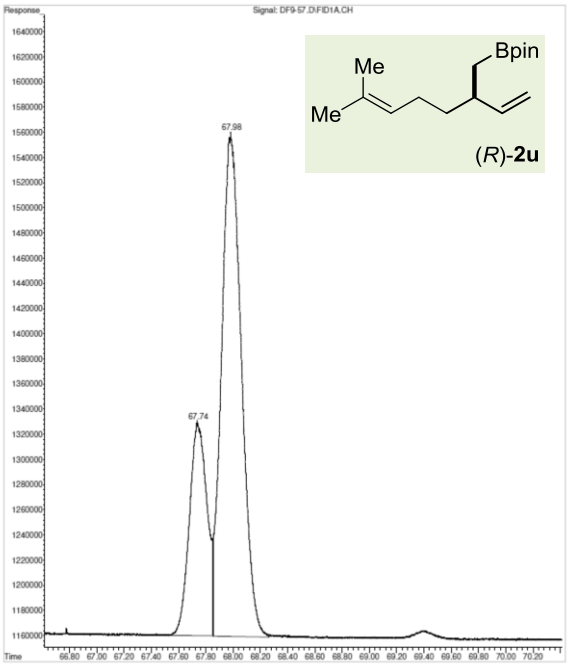
Determination of enantiomeric excess was carried out on the crude mixture of homoallylic boronates **2u** and **3u**.

GC: HYDRODEX TBDM, 160°C-1°C/min-180°C, 45 cm/s, H_2, t_R (major) = 67.98 min, t_R (minor) = 67.74 min.



Peak Results

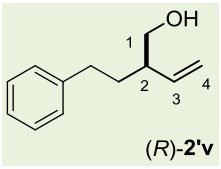
	RT	Area	% Area
1	67.75	37799025	50.17
2	68.01	37539709	49.83



Peak Results

	RT	Area	% Area
1	67.74	15118793	27.19
2	67.98	40494769	72.82

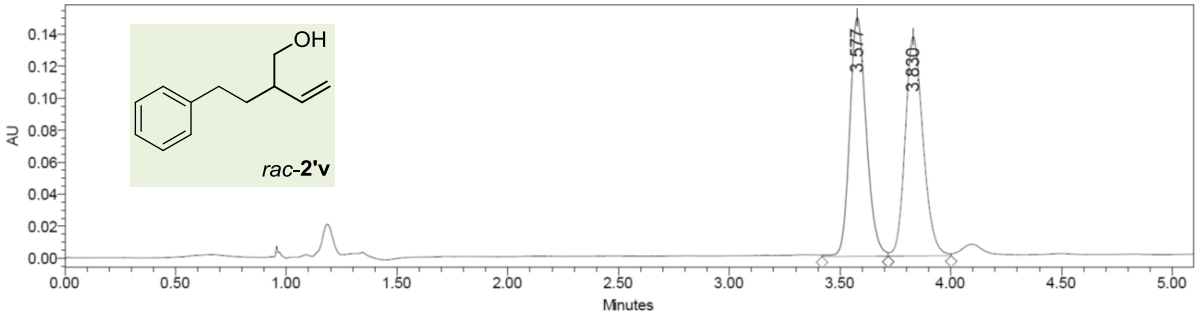
(*R*)-2-phenethylbut-3-en-1-ol 2'v



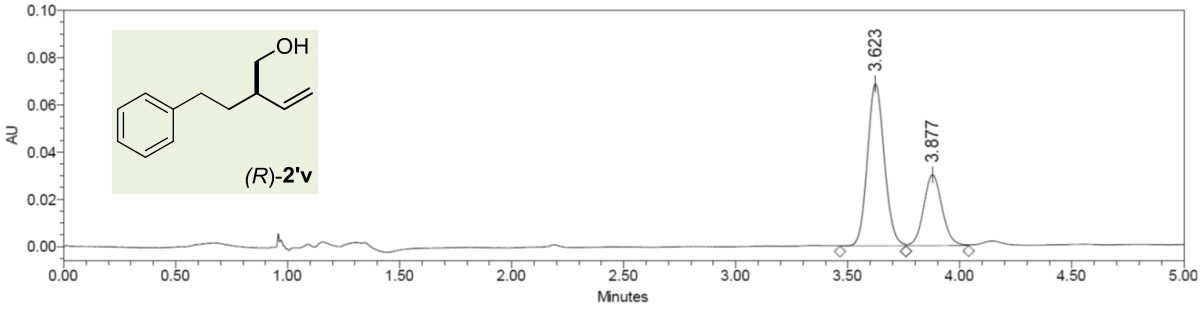
Following the general procedure using (3-methylenepent-4-en-1-yl)benzene **1v** (57 mg, 0.36 mmol, 1.2 equiv.), CuO*t*Bu (4.1 mg, 0.03 mmol, 10 mol%), (*R,R*)-**L9** (22 mg, 0.03 mmol, 10 mol%), B_2pin_2 (76.2 mg, 0.3 mmol, 1.0 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.). Reaction temperature: 0°C. Reaction time: 24 h. Conversions: 84%, **2v**:**3v** = 1:3. Then it was oxidized under basic condition following the general procedure to afford the alcohol (*R*)-**2'v** as a colorless oil (7.6 mg, 14% yield, **2'v**:**3'v** > 20:1, 35% *ee*). All spectroscopic and spectrometric analyses were in agreement with the literature.[9]

SFC: 35% *ee*; chiral stationary phase: AY column, 2% MeOH, 3 ml/min, 210 nm, t_R (major) = 3.6 min, t_R (minor) = 3.9 min.

[α]$^{20}_D$ = +3.5 (*c* 0.10, CH_2Cl_2).

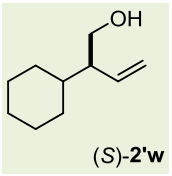


	Retention Time	Area	% Area
1	3.577	773590	50.12
2	3.830	769892	49.88



	Retention Time	Area	% Area
1	3.623	360067	67.77
2	3.877	171251	32.23

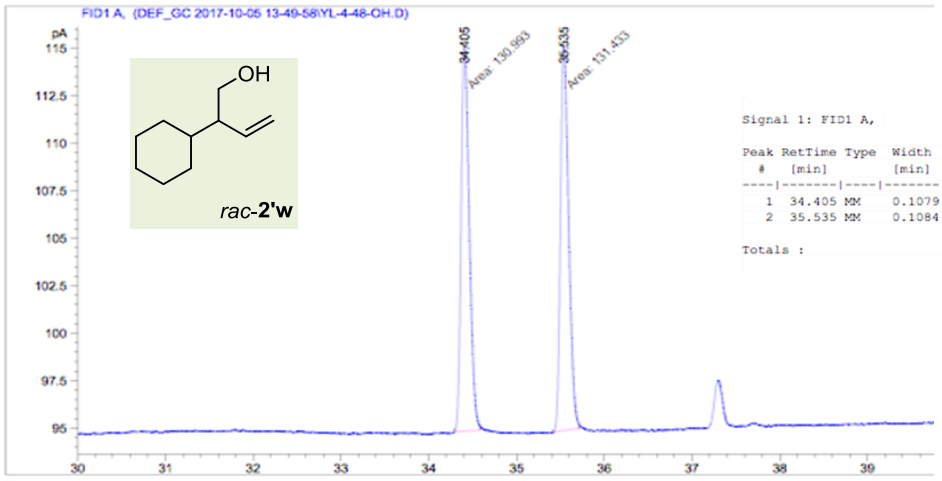
(*S*)-2-cyclohexylbut-3-en-1-ol 2'w

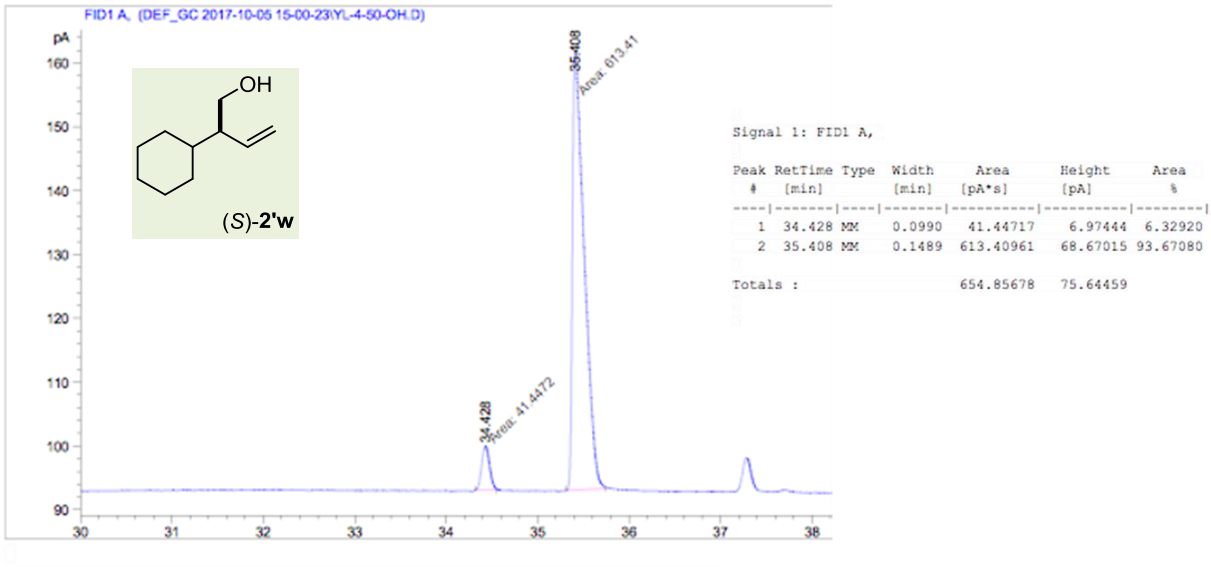


Following the general procedure using buta-1,3-dien-2-ylcyclohexane **1w** (49 mg, 0.36 mmol, 1.2 equiv.), CuO*t*Bu (4.1 mg, 0.03 mmol, 10 mol%), (*R,R*)-**L9** (22 mg, 0.03 mmol, 10 mol%), B_2pin_2 (76.2 mg, 0.3 mmol, 1.0 equiv.) and MeOH (27 µL, 0.6 mmol, 2.0 equiv.). Conversions: 77%, **2w**:**3w**:**4w** = 10:12:1. Then it was oxidized under basic condition following the general procedure to afford the alcohol (*S*)-**2'w** as a yellow oil (11 mg, 23% yield, **2'w**:**3'w**:**4'w** = 20:1:4, 87% *ee*). All spectroscopic and spectrometric analyses were in agreement with the literature.[7]

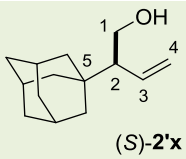
GC: HYDRODEX G-DiMOM, 100°C-1°C/min-170°C, 45 cm/s, H_2, t_R (major) = 35.4 min, t_R (minor) = 34.4 min.

[α]$^{20}_{D}$ = +11.5 (*c* 0.10, CH_2Cl_2).





(*S*)-2-((3r,5r,7r)-adamantan-1-yl)but-3-en-1-ol 2'x



(*S*)-**2'x**

Following the general procedure using (3r,5r,7r)-1-(buta-1,3-dien-2-yl)adamantine **1x** (34 mg, 0.18 mmol, 1.2 equiv.), CuO*t*Bu (2.1 mg, 0.015 mmol, 10 mol%), (*R,R*)-**L9** (11 mg, 0.015 mmol, 10 mol%), B_2pin_2 (38 mg, 0.15 mmol, 1.0 equiv.) and MeOH (13 µL, 0.3 mmol, 2.0 equiv.). Conversions: 87%, **2x**:**3x**:**4x** = 14:2:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (*S*)-**2'x** as a colorless oil (24 mg, 78% yield, **2'x**:**4'x** = 25:1, 94% *ee*).

TLC: R_f = 0.4 (pentane/ethyl acetate 9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 5.73 (ddd, $^3J_{HH}$ = 17.0, 10.1 Hz, 1H, ***H*-3**), 5.25 (dd, $^3J_{HH}$ = 10.1 Hz, $^2J_{HH}$ = 2.2 Hz, 1H, ***H*-4**), 5.12 (dd, $^3J_{HH}$ = 17.0 Hz, $^2J_{HH}$ = 2.2 Hz, 1H, ***H*-4**), 3.80 (m, 1H, ***H*-1**), 3.42 (t, $^3J_{HH}$ = 10.3 Hz, 1H, ***H*-1**), 1.95 (m, 3H, **C*H*-adamantyl**), 1.82 (dt, $^3J_{HH}$ = 10.1, 5.0 Hz, 1H, ***H*-2**), 1.71 – 1.50 (m, 12H, **C*H*$_2$-adamantyl**), 1.30 (bs, 1H, **O*H***).

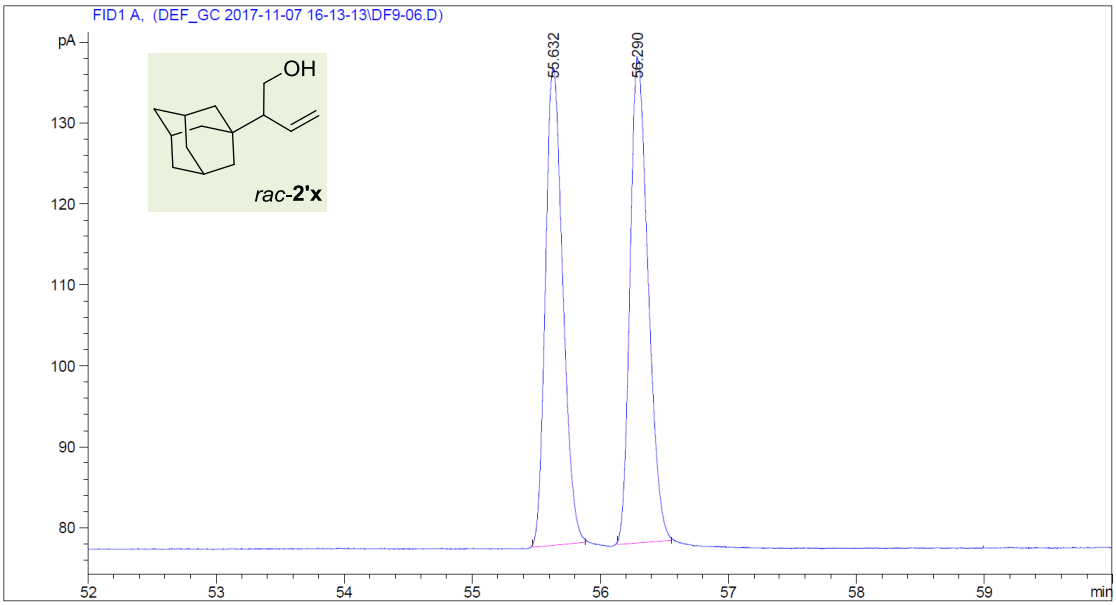
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 137.1 (***C*H-3**), 119.4 (***C*H$_2$-4**), 60.5 (***C*H$_2$-1**), 58.9 (***C*H-2**), 40.7 (***C*H$_2$-adamantyl**), 37.3 (***C*H$_2$-adamantyl**), 34.1 (***C*-5**), 28.8 (***C*H-adamantyl**).

LRMS (ESI +): calculated for $C_{14}H_{22}O$ $[M]^+$: 206.17; found: 224.6 $[M+NH_4]^+$; 229.1 $[M+Na]^+$.

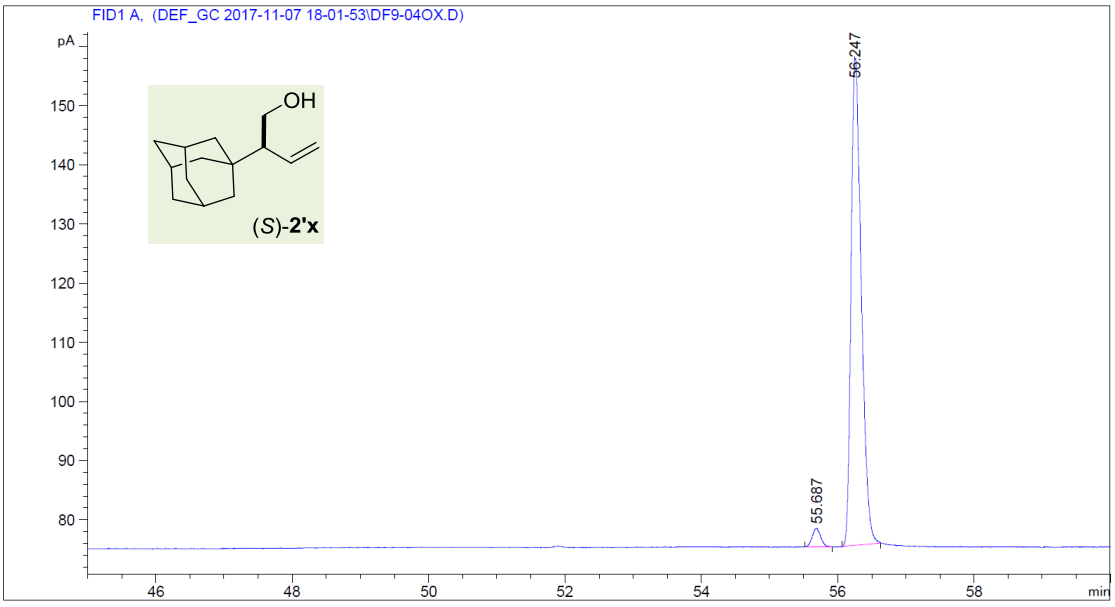
IR (neat) ν (cm^{-1}): 3338, 1902, 2849, 1447, 1344, 1260, 1024, 913, 797.

GC: 94% *ee*; chiral stationary phase: Hydrodex DiMOM, method: 100 °C for 120 minutes then 100–170 °C in 70 minutes, t_R (major) = 56.3 min, t_R (minor) = 55.7 min.

[α]$^{20}_D$ = +27.1 (*c* 0.25, CH_2Cl_2).

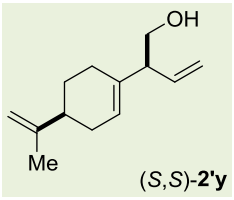


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	55.632	BB	0.1321	556.86194	58.98906	48.68336
2	56.290	BB	0.1183	586.98254	59.90941	51.31664
Totals :				1143.84448	118.89848	



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	55.687	BB	0.1005	26.95286	3.17769	3.05731
2	56.247	BB	0.1257	854.63513	82.59700	96.94269
Totals :				881.58800	85.77469	

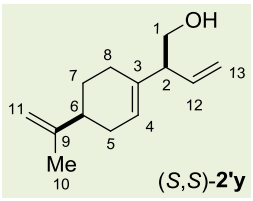
(*S*)-2-((*S*)-4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)but-3-en-1-ol 2'y



Following the general procedure using (*S*)-1-(buta-1,3-dien-2-yl)-4-(prop-1-en-2-yl)cyclohex-1-ene **1y** (41 mg, 0.24 mmol, 1.0 equiv.), CuO*t*Bu (2.8 mg, 0.020 mmol, 10 mol%), DrewPhos-**L10** (12 mg, 0.020 mmol, 10 mol%), B_2pin_2 (51 mg, 0.2 mmol, 1.0 equiv.) and MeOH (16 µL, 0.4 mmol, 2.0 equiv.). Conversions: 80%, **2y**:**4y** = 20:1, dr 1.8:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (*S*,*S*)-**2'y** as a colorless oil (22 mg, 57% yield, **2'y**:**4'y** = 20:1, *dr* 1.8:1). **TLC**: R_f = 0.3 (pentane/diethyl ether 4:1).

[α]$^{25}_{D}$ = –68.3 (*c* 0.55, CH_2Cl_2).

(*S*)-2-((*S*)-4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)but-3-en-1-ol 2'y



Following the general procedure using (*S*)-1-(buta-1,3-dien-2-yl)-4-(prop-1-en-2-yl)cyclohex-1-ene **1y** (41 mg, 0.24 mmol, 1.0 equiv.), CuO*t*Bu (2.8 mg, 0.020 mmol, 10 mol%), (*R*,*R*)-**L9** (14.6 mg, 0.020 mmol, 10 mol%), B_2pin_2 (51 mg, 0.2 mmol, 1.0 equiv.) and MeOH (16 µL, 0.4 mmol, 2.0 equiv.). Conversions: 99%, **2y**:**3y** = 50:1, dr >20:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (*S*,*S*)-**2'y** as a colorless oil (34 mg, 86% yield, **2'y**:**4'y** > 50:1, *dr* >20:1). *Diasteroisomeric ratio (dr) calculated by integration of non isochronic signals by* $^{13}C\{^1H\}$ *NMR.*

TLC: R_f = 0.3 (pentane/diethyl ether 4:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 5.75 (ddd, $^3J_{HH}$ = 16.9, 10.7, 7.8 Hz, 1H, ***H*-12**), 5.58 (m, 1H, ***H*-4**), 5.12 (m, 2H, ***H*-13**), 4.71 (m, 2H, ***H*-11**), 3.62 (m, 2H, ***H*-1**), 2.84 (m, 1H, ***H*-2**), 2.14 (m, 3H, ***H*-6** + ***H*-5**), 2.02 (m, 2H, ***H*-8**), 1.98 (m, 1H, ***H*-5**), 1.83 (m, 1H, ***H*-7**), 1.73 (s, 3H, ***H*-10**), 1.47 (m, 2H, ***H*-7** + ***H*-10**).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ (ppm) = 149.9 (***C*-9**), 137.8 (***C*H-12**), 136.3 (***C*-3**), 123.7 (***C*H-4**), 116.7 (***C*H$_2$-13**), 108.8 (***C*H$_2$-11**), 63.4 (***C*H$_2$-1**), 53.8 (***C*H-2**), 41.2 (***C*H-6**), 30.9 (***C*H$_2$-5**), 27.8 (***C*H$_2$-7**), 26.9 (***C*H$_2$-8**), 20.9 (***C*H$_3$-10**).

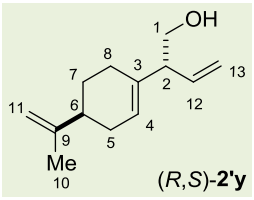
LRMS (ESI +): calculated for $C_{13}H_{20}O$ $[M]^+$: 192.15; found: 210.4 $[M+NH_4]^+$.

GC-MS (EI) ($C_{13}H_{20}O$): 161.2 (19, M^+-31), 131.1 (19, M^+-61), 121.1 (13, M^+-71), 117.1 (23, M^+-75), 105.1 (52, M^+-87), 91.1 (100, M^+-101), 79.1 (58, M^+-113), 67.1 (34, M^+-125), 53.1 (23, M^+-139).

IR (neat) ν (cm^{-1}): 3352, 3078, 2920, 1642, 1643, 1436, 1375, 1292, 1202, 1146, 1055, 1027, 994, 914, 886.

[α]$^{25}_{D}$ = –37.9 (*c* 0.80, CH_2Cl_2).

(*R*)-2-((*S*)-4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)but-3-en-1-ol 2'y



Following the general procedure using (*S*)-1-(buta-1,3-dien-2-yl)-4-(prop-1-en-2-yl)cyclohex-1-ene **1y** (41 mg, 0.24 mmol, 1.0 equiv.), CuO*t*Bu (2.8 mg, 0.020 mmol, 10 mol%), (*S*,*S*)-**L9** (14.6 mg, 0.020 mmol, 10 mol%), B_2pin_2 (51 mg, 0.2 mmol, 1.0 equiv.) and MeOH (16 µL, 0.4 mmol, 2.0 equiv.). Conversions: 99%, **2y**:**3y**:**4y** = 20:1:1, dr 1:7. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford alcohol (*R*,*S*)-**2'y** as a colorless oil (33 mg, 85% yield, **2'y**:**4'y** = 20:1, *dr* 1:7).

Diasteroisomeric ratio (dr) calculated by integration of non isochronic signals by $^{13}C\{^1H\}$ NMR.

TLC: R_f = 0.3 (pentane/diethyl ether 4:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 5.74 (m, 1H, ***H*-12**), 5.57 (m, 1H, ***H*-4**), 5.13 (m, 2H, ***H*-13**), 4.71 (m, 2H, ***H*-11**), 3.61 (m, 2H, ***H*-1**), 2.84 (m, 1H, ***H*-2**), 2.16 (m, 3H, ***H*-6** + ***H*-5**), 2.03 (m, 2H, ***H*-8**), 1.98 (m, 1H, ***H*-5**), 1.83 (m, 1H, ***H*-7**), 1.73 (s, 3H, ***H*-10**), 1.46 (m, 2H, ***H*-7** + ***H*-10**).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ (ppm) = 149.9 (***C*-9**), 137.6 (***C*H-12**), 136.2 (***C*-3**), 123.4 (***C*H-4**), 117.0 (***C*H_2-13**), 108.8 (***C*H_2-11**), 63.6 (***C*H_2-1**), 53.8 (***C*H-2**), 41.2 (***C*H-6**), 30.9 (***C*H_2-5**), 27.9 (***C*H_2-7**), 27.1 (***C*H_2-8**), 20.9 (***C*H_3-10**).

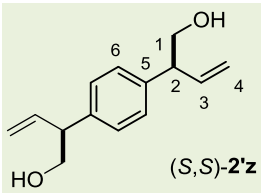
LRMS (ESI +): calculated for $C_{13}H_{20}O$ $[M]^+$: 192.15; found: 210.4 $[M+NH_4]^+$.

GC-MS (EI) ($C_{13}H_{20}O$): 161.2 (19, M^+-31), 131.1 (19, M^+-61), 121.1 (13, M^+-71), 117.1 (23, M^+-75), 105.1 (52, M^+-87), 91.1 (100, M^+-101), 79.1 (58, M^+-113), 67.1 (34, M^+-125), 53.1 (23, M^+-139).

IR (neat) ν (cm^{-1}): 3357, 3079, 2920, 1726, 1642, 1436, 1375, 1291, 1203, 1145, 1055, 1027, 994, 914, 886.

[α]$^{25}_D$ = –94.6 (*c* 0.80, CH_2Cl_2).

(2*S*,2'*S*)-2,2'-(1,4-phenylene)bis(but-3-en-1-ol) 2'z



Following the general procedure using 1,4-di(buta-1,3-dien-2-yl)benzene **1z** (65.6 mg, 0.36 mmol, 1.2 equiv.), Cu*O*t*B*u (6.2 mg, 0.045 mmol, 15 mol%), (*R,R*)-**L9** (33 mg, 0.045 mmol, 15 mol%), B_2pin_2 (152.4 mg, 0.6 mmol, 2.0 equiv.) and MeOH (54 µL, 1.2 mmol, 4.0 equiv.). Conversion: 79%, **2z**:**3z**:**4z** = 24:2:1. The reaction mixture was then oxidized under basic conditions following the general procedure and purified by column chromatography to afford the isomers of alcohol as a colorless oil (45 mg, 68% yield, **2'z**:**3'z**:**4'z** = 10:1:0.3). For the alcohol (*S*,*S*)-**2'z** (8:1 *dr*, 99% ee). *Diasteroisomeric ratio (dr) estimated by integration of the HPLC chromatogram.*

TLC: R_f = 0.4 (pentane/acetone 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.21 (s, 4H, ***H*-6**), 5.99 (ddd, $^3J_{HH}$ = 17.1, 10.4, 7.8 Hz, 2H, ***H*-3**), 5.10 – 5.26 (m, 4H, ***H*-4**), 3.81 (d, $^3J_{HH}$ = 7.1 Hz, 4H, ***H*-1**), 3.60 – 3.43 (m, 2H, ***H*-2**), 1.56 (s, 2H, ***H*-*O***).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 139.3 (***C*-5**), 138.2 (***C*H-3**), 128.3 (***C*H-6**), 117.1 (***C*H$_2$-4**), 66.0 (***C*H$_2$-1**), 52.2 (***C*H-2**).

LRMS (ESI +): calculated for $C_{14}H_{18}O_2$ $[M]^+$: 218.13; found: 236.1 $[M+NH_4]^+$.

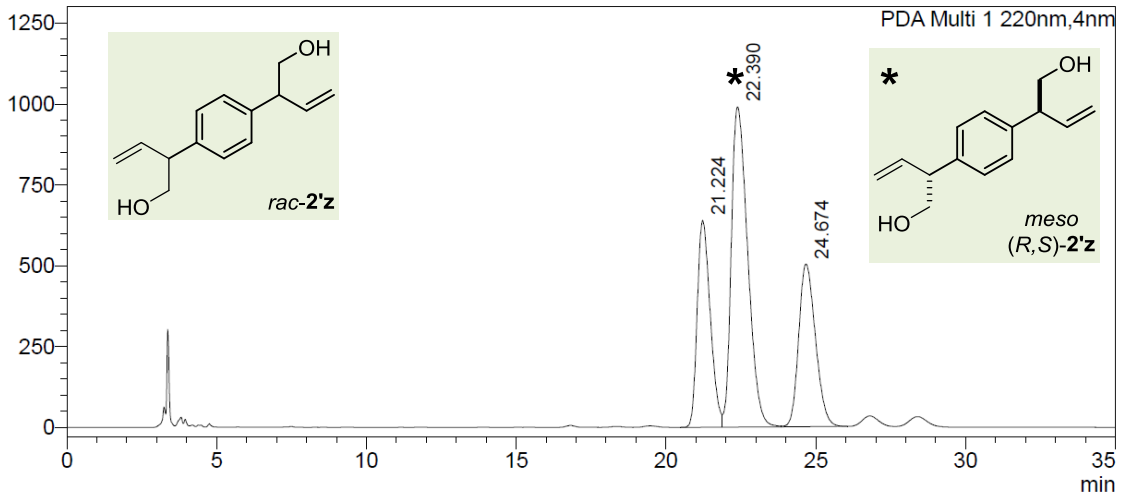
IR (neat) ν (cm^{-1}): 3334, 3080, 2928, 2878, 1638, 1511, 1412, 1300, 1189, 1111, 1051, 1025, 994, 915, 829, 732, 641.

HPLC: 99% *ee*, chiral stationary column: OD-H, mobile phase: hexane/*i*PrOH = 95/5, 1.0 mL/min, 220 nm, 30 °C, t_R (major) = 24.7 min, t_R (minor) = 21.5 min.

[α]$^{25}_D$ = +89.3 (*c* 0.90, CH_2Cl_2).

<Chromatogram>

mAU



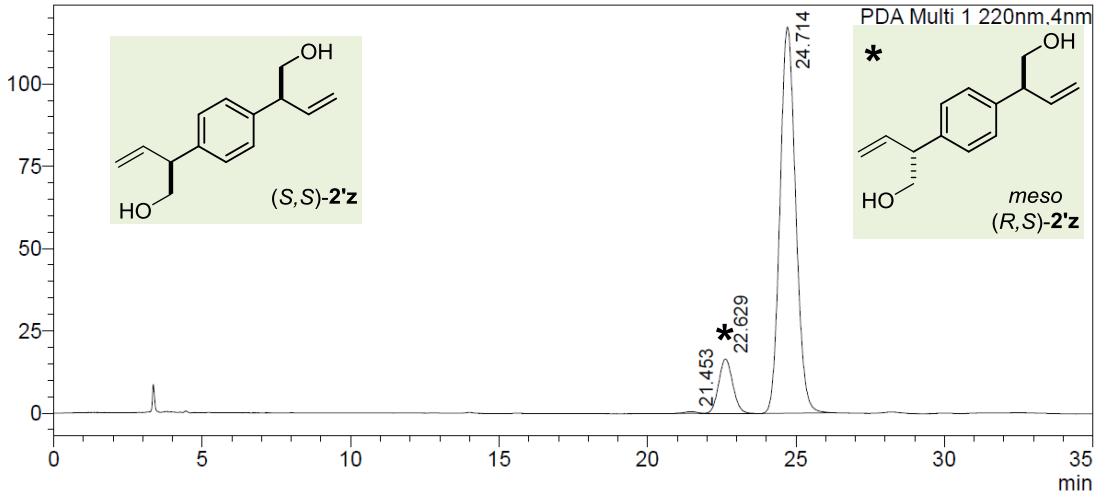
<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	21.224	19376017	25.285
2	22.390	37680591	49.173
3	24.674	19572765	25.542
Total		76629373	100.000

<Chromatogram>

mAU



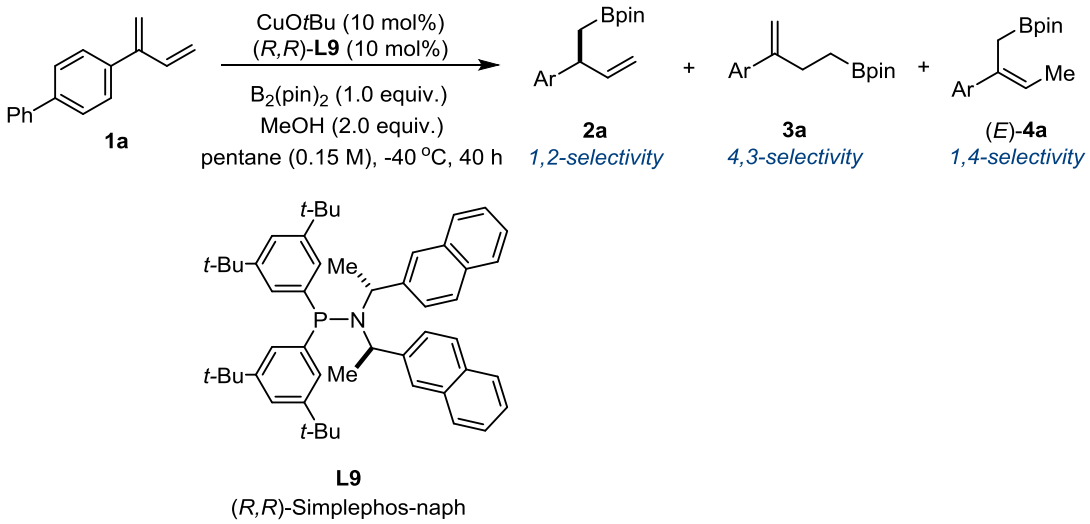
<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%
1	21.453	14923	0.306
2	22.629	545919	11.188
3	24.714	4318779	88.506
Total		4879621	100.000

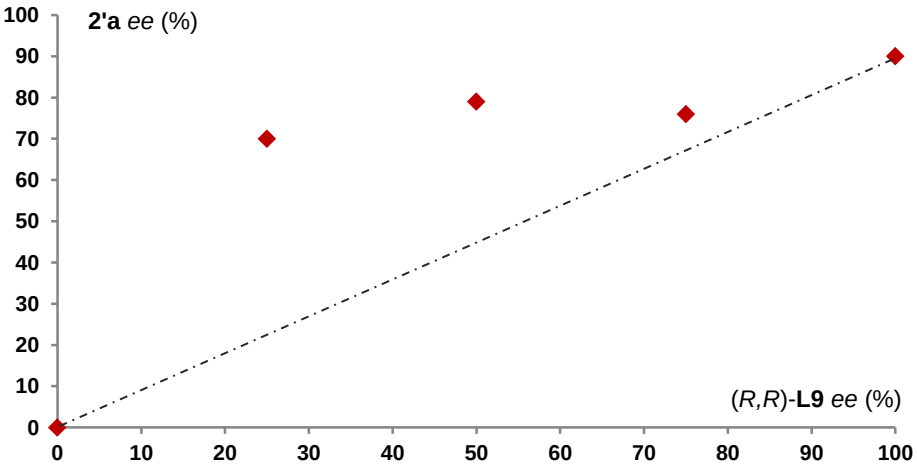
5. Non-linear effect

Table S4[a]



Entry	*ee* **L9** (%)	conv. (%)	**2a** : **3a** : **4a**	*ee* **2a** (%)
1	25	86	> 20 : 1 : -	70
2	50	82	> 20 : 1 : -	79
3	75	83	> 20 : 1 : -	76

[a] Reaction conditions: all reactions were performed with **1a** (0.12 mmol), (*R*,*R*)-**L9**/CuO*t*Bu (1:1, 10 mol%), B_2pin_2 (0.10 mmol), MeOH (0.20 mmol) in *n*-pentane (0.7 mL, 0.15 M) at –40 °C for 40 h. Average of two experiments.



6. References

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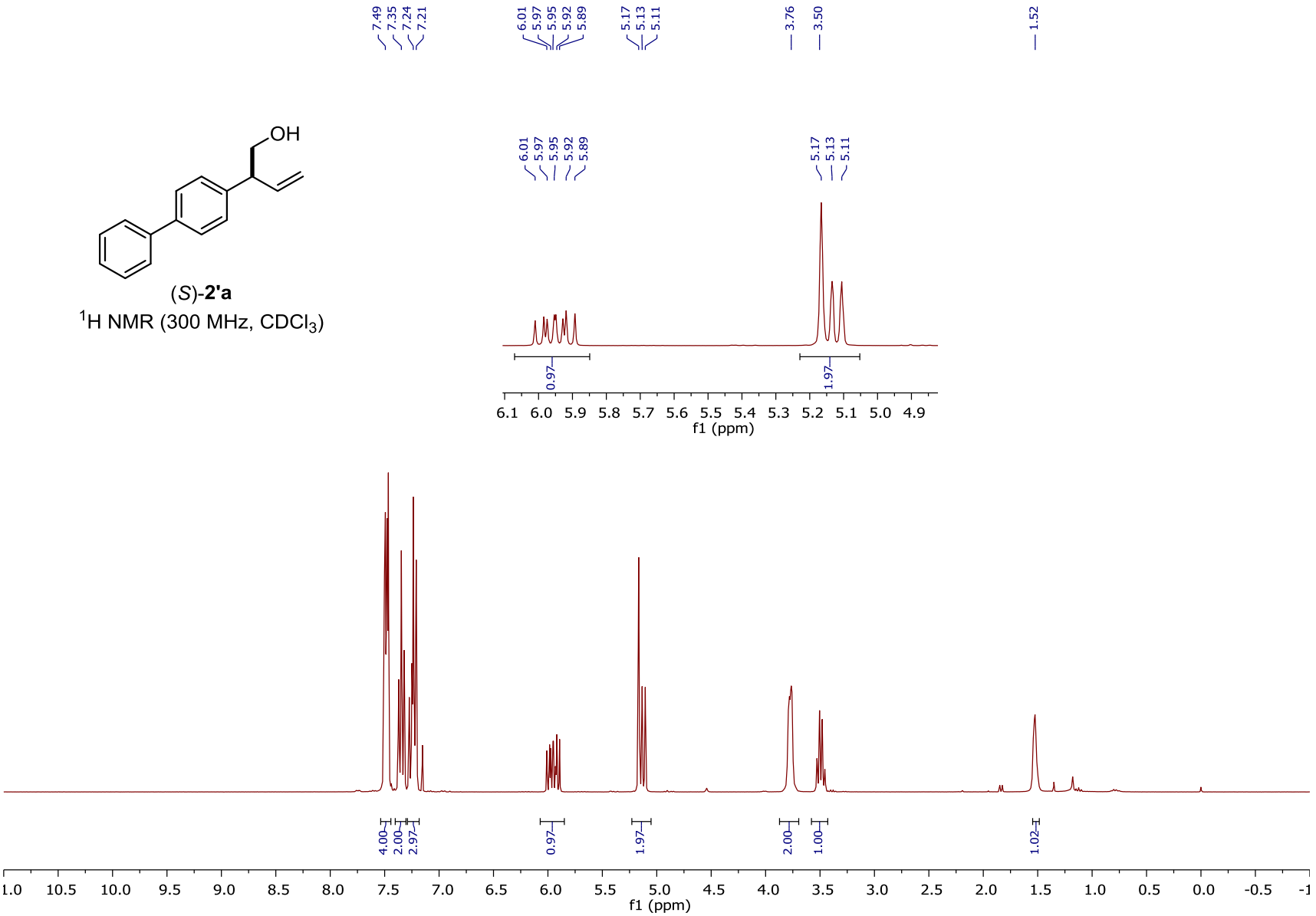
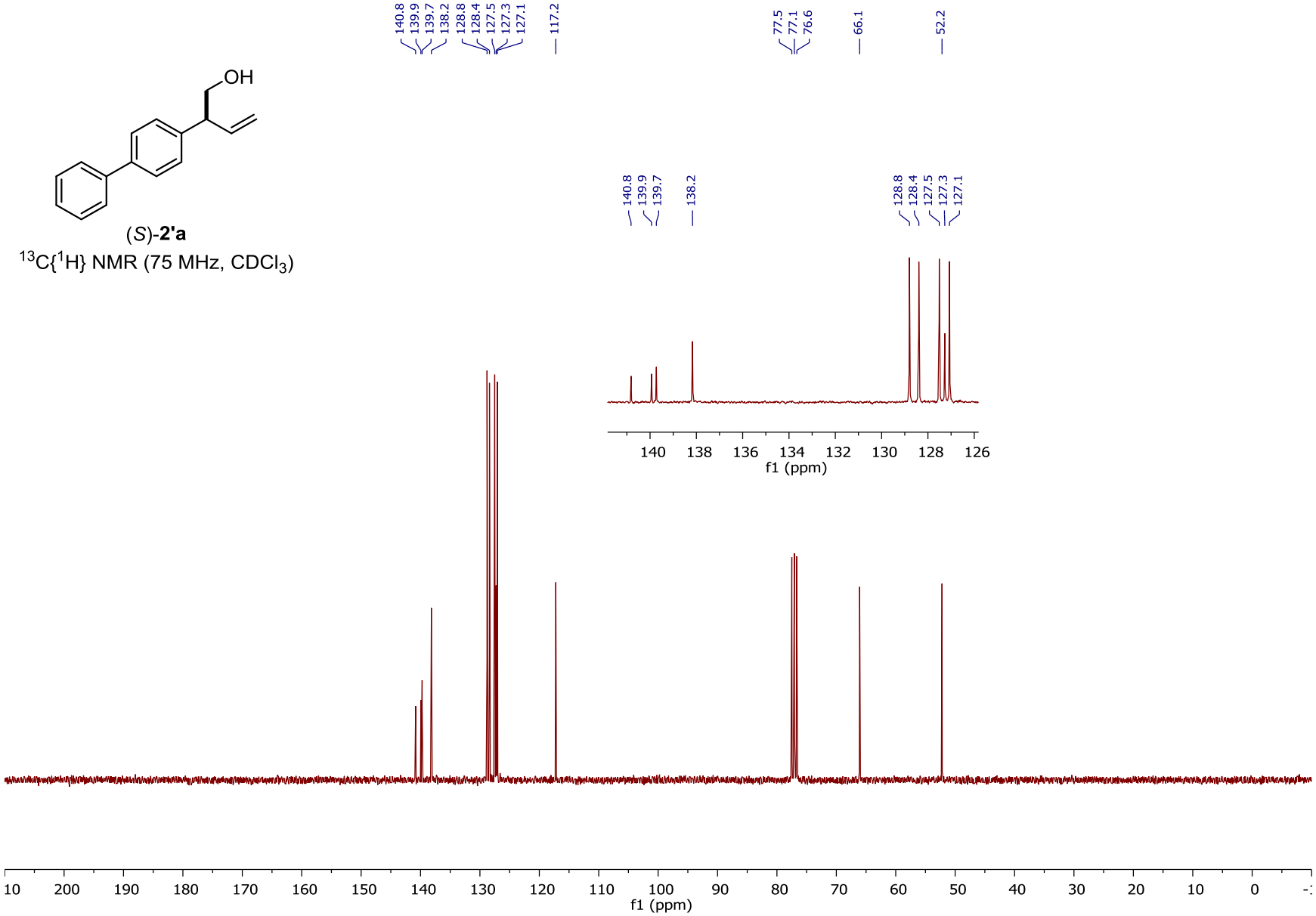
[7] Y. Shi and A. H. Hoveyda, *Angew. Chem., Int. Ed.* 2016, **55**, 3455.

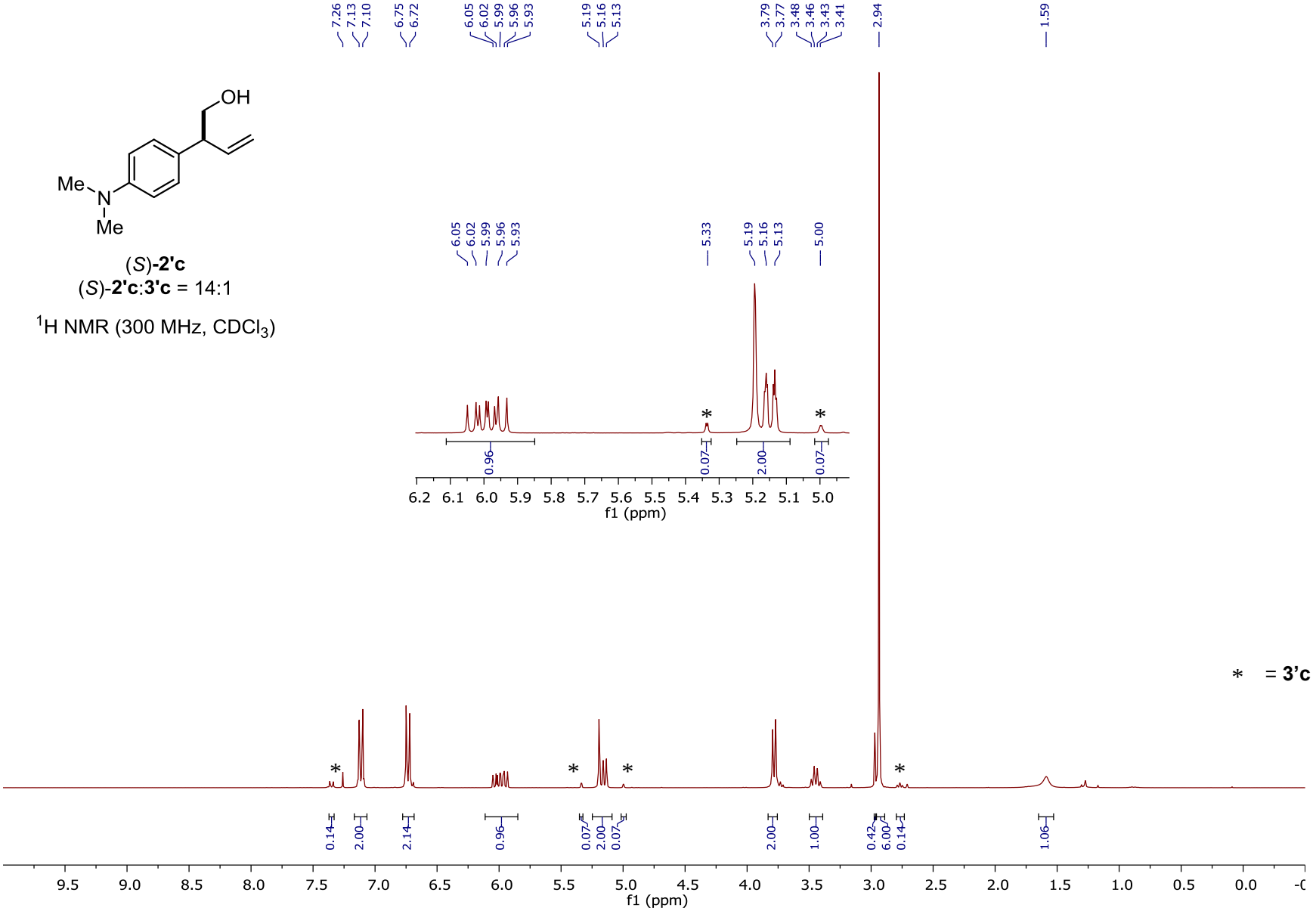
[8] M. Zaidlewicz and J. Meller, *Tetrahedron Lett.* 1997, **38**, 7279.

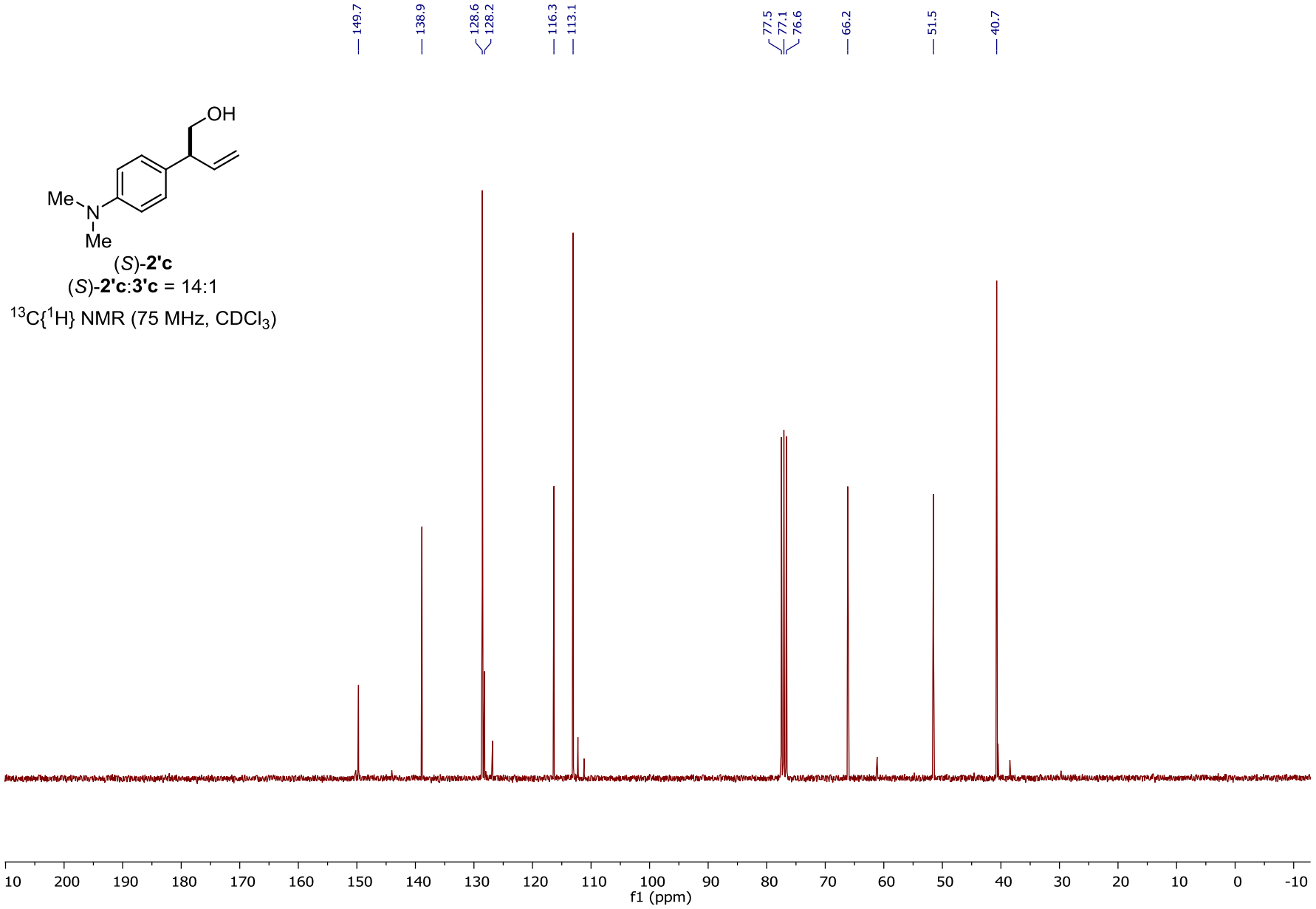
[9] J. Kim, S. Park, J. Park and S. H. Cho, *Angew. Chem., Int. Ed.* 2016, **55**, 1498.

7. NMR spectra of new compounds


7.49
7.35
7.24
7.21
6.01
5.97
5.95
5.92
5.89
5.17
5.13
5.11
3.76
3.50
1.52
OH
(S)-2'a
1H NMR (300 MHz, CDCl3)
0.97
1.97
6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9
f1 (ppm)
4.00
2.00
2.97
0.97
1.97
2.00
1.00
1.02
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


OH
(S)-2'a
13C{1H} NMR (75 MHz, CDCl3)
140.8
139.9
139.7
138.2
128.8
128.4
127.5
127.3
127.1
117.2
77.5
77.1
76.6
66.1
52.2
f1 (ppm)
f1 (ppm)

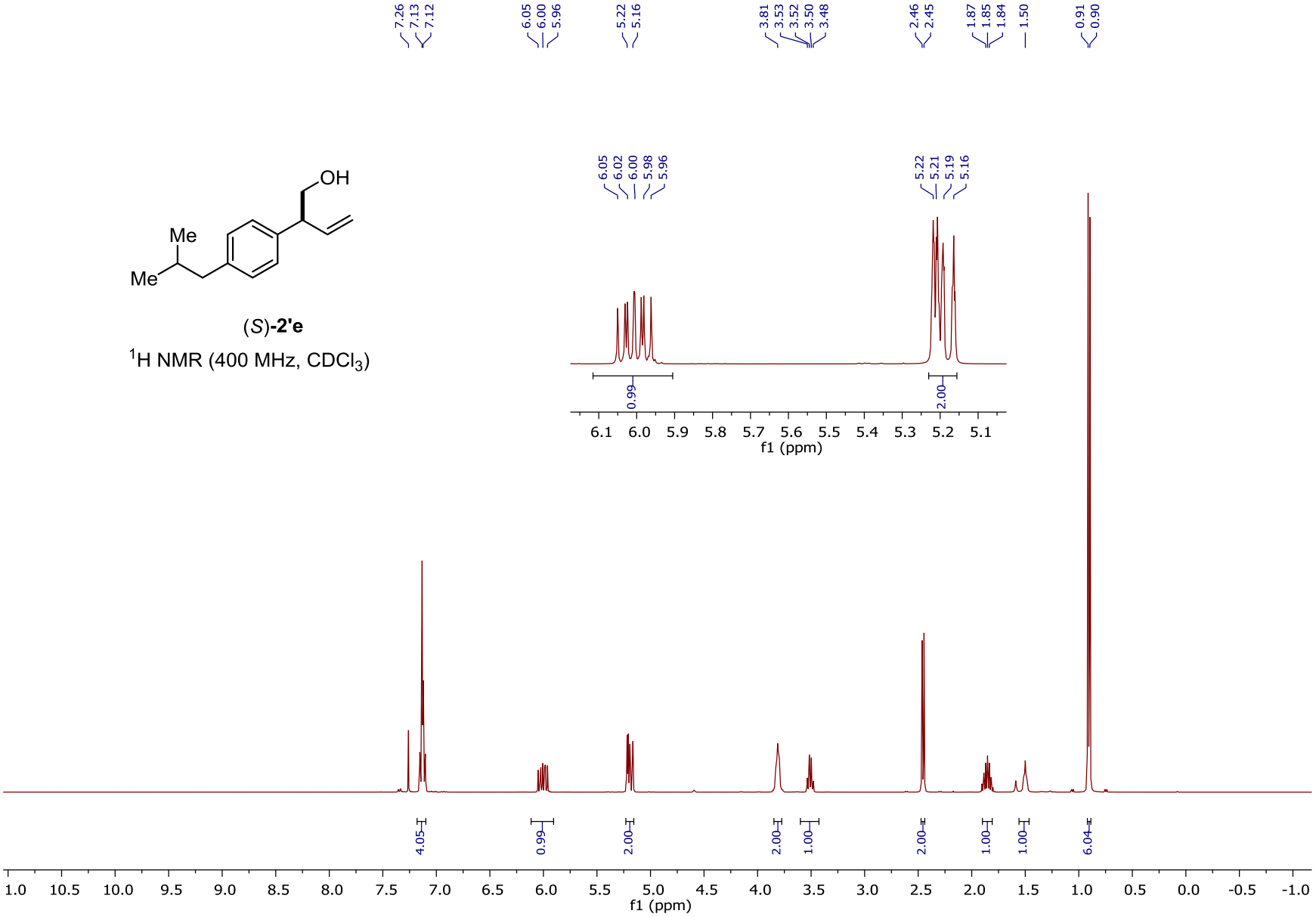

OH
Me
N
Me
(S)-2'c
(S)-2'c:3'c = 14:1
1H NMR (300 MHz, CDCl3)
* = 3'c
f1 (ppm)

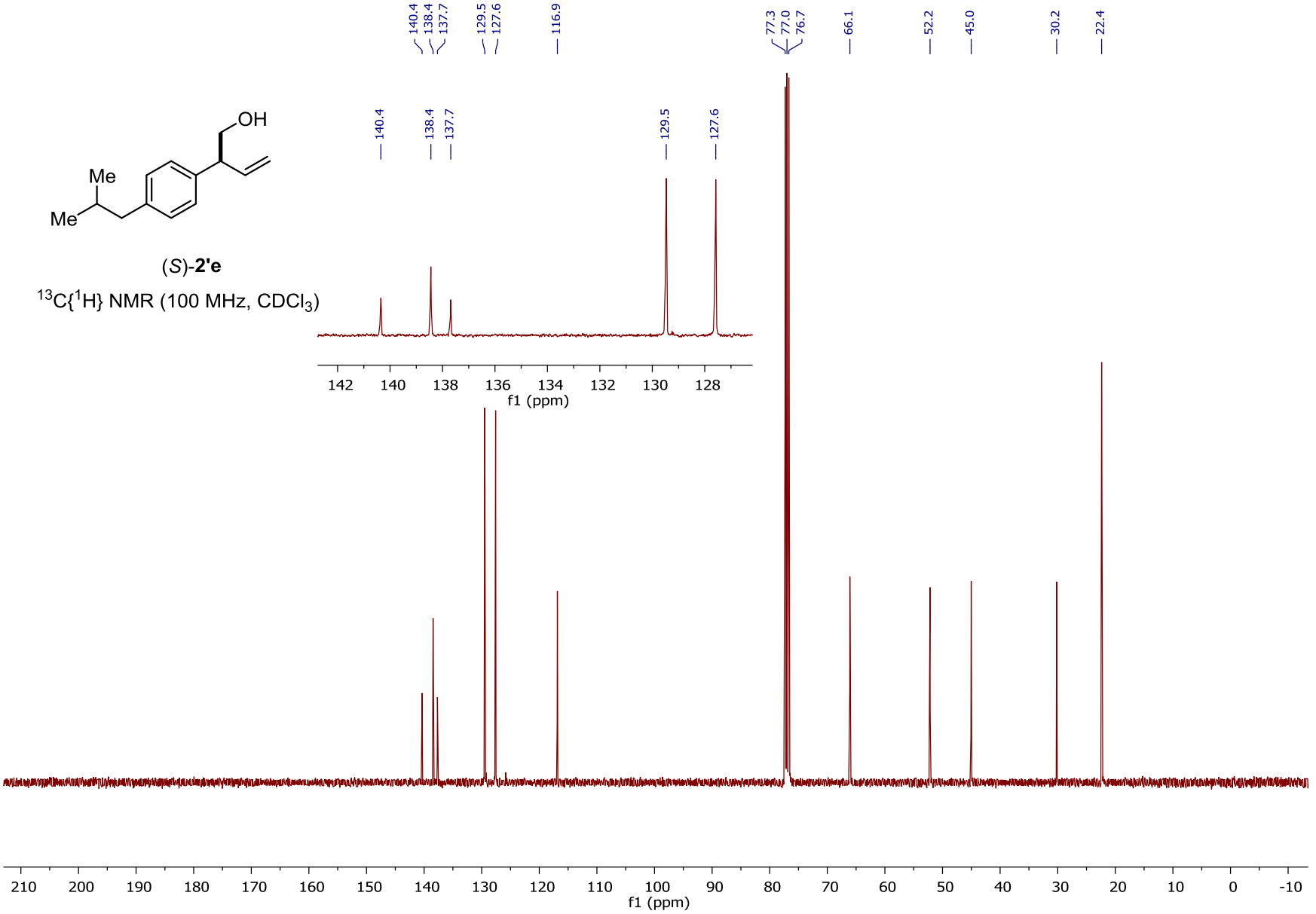


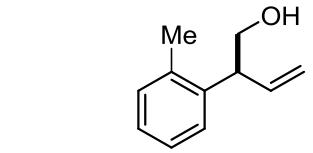
(*S*)-**2'c**

(*S*)-**2'c**:**3'c** = 14:1

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

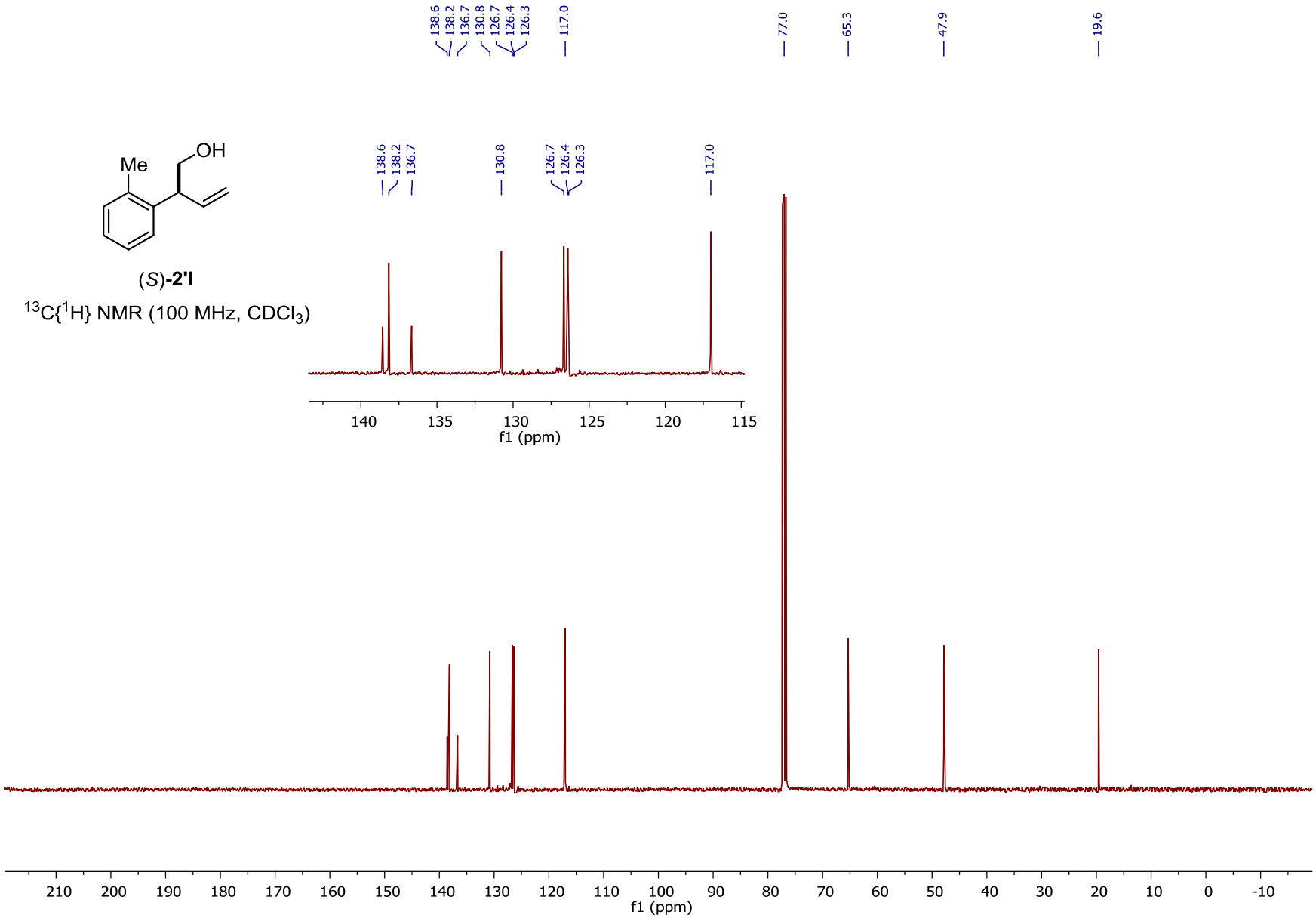

OH
Me
Me
(S)-2'e
1H NMR (400 MHz, CDCl3)
7.26
7.13
7.12
6.05
6.00
5.96
5.22
5.16
3.81
3.53
3.52
3.50
3.48
2.46
2.45
1.87
1.85
1.84
1.50
0.91
0.90
6.05
6.02
6.00
5.98
5.96
5.22
5.21
5.19
5.16
0.99
2.00
6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1
f1 (ppm)
4.05
0.99
2.00
2.00
1.00
2.00
1.00
1.00
6.04
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

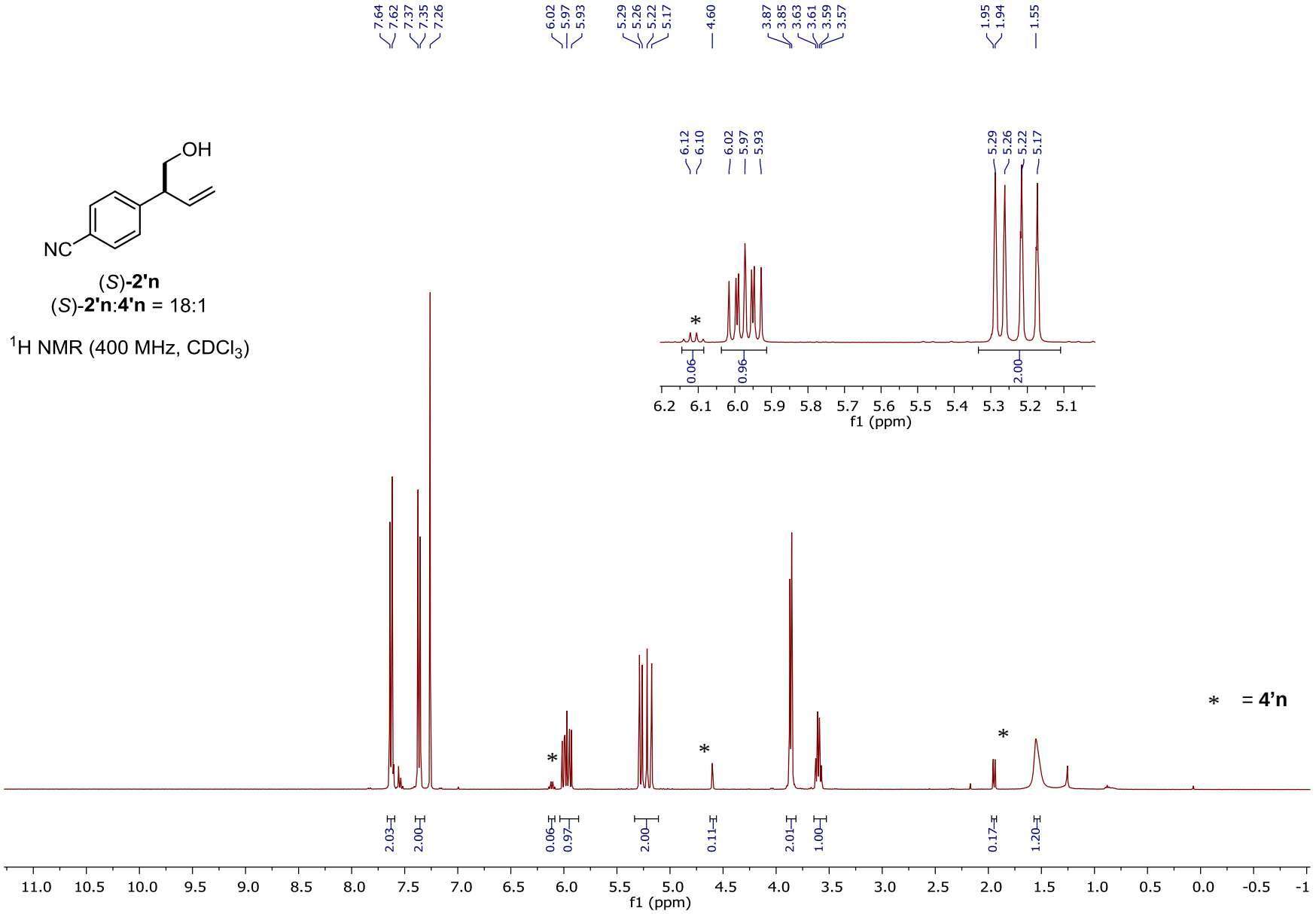

OH
Me
Me
(S)-2'e
13C{1H} NMR (100 MHz, CDCl3)
140.4
138.4
137.7
129.5
127.6
116.9
77.3
77.0
76.7
66.1
52.2
45.0
30.2
22.4
f1 (ppm)
f1 (ppm)

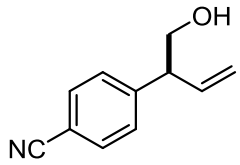


(*S*)-**2'l**

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

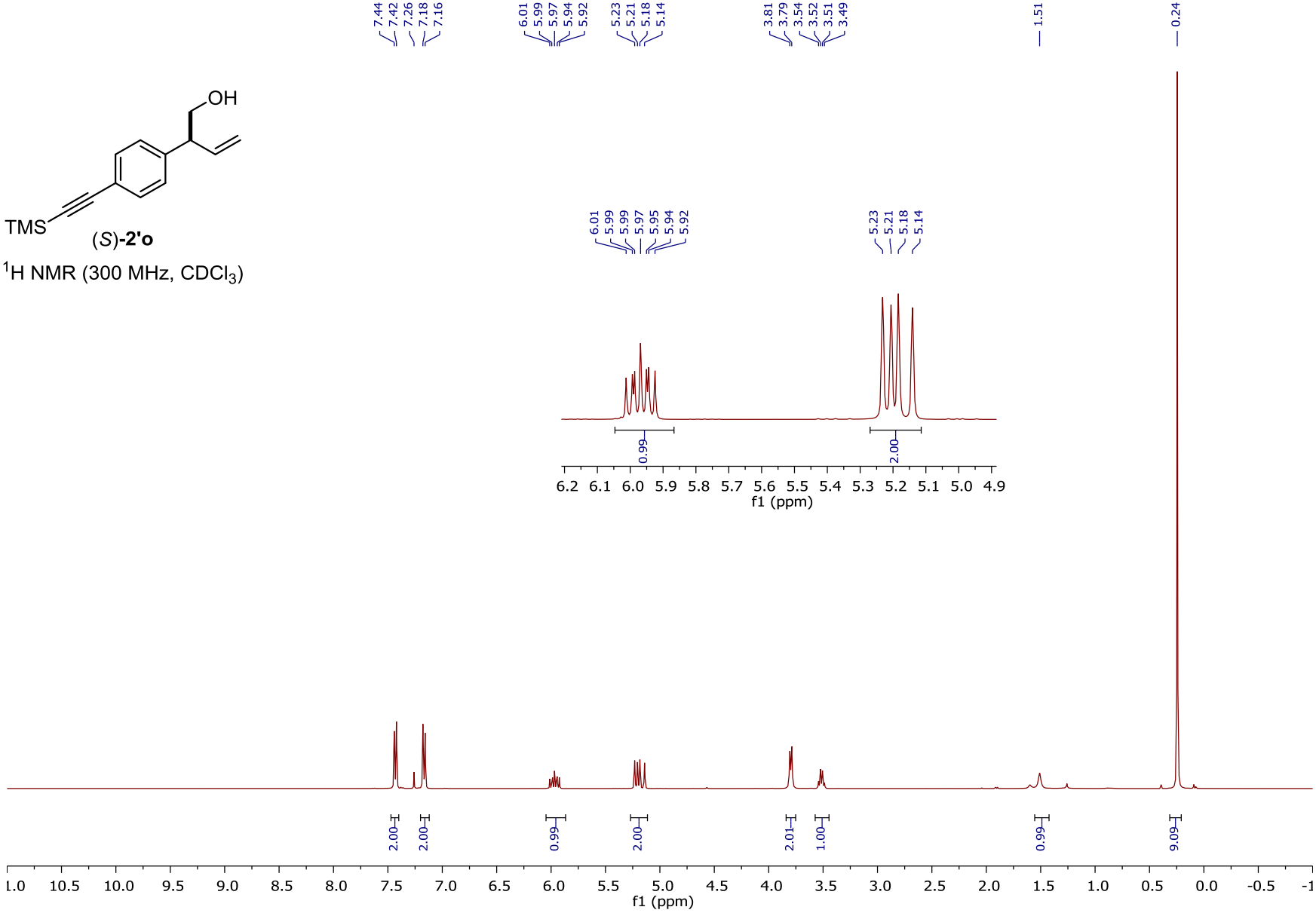

138.6
138.2
136.7
130.8
126.7
126.4
126.3
117.0
77.0
65.3
47.9
19.6
Me
OH
(S)-2'l
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)
f1 (ppm)

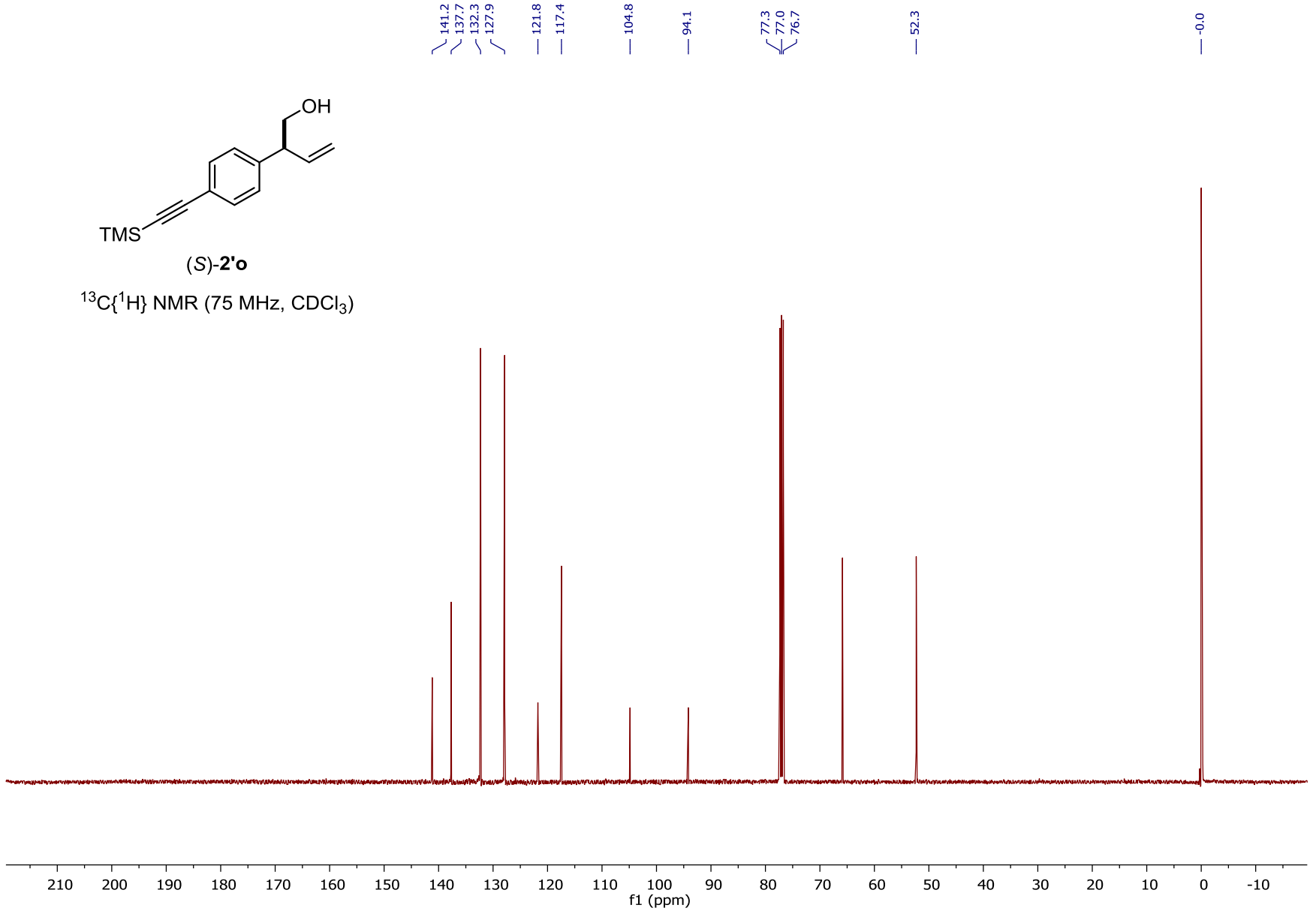

OH
NC
(S)-2'n
(S)-2'n:4'n = 18:1
1H NMR (400 MHz, CDCl3)
* = 4'n
f1 (ppm)

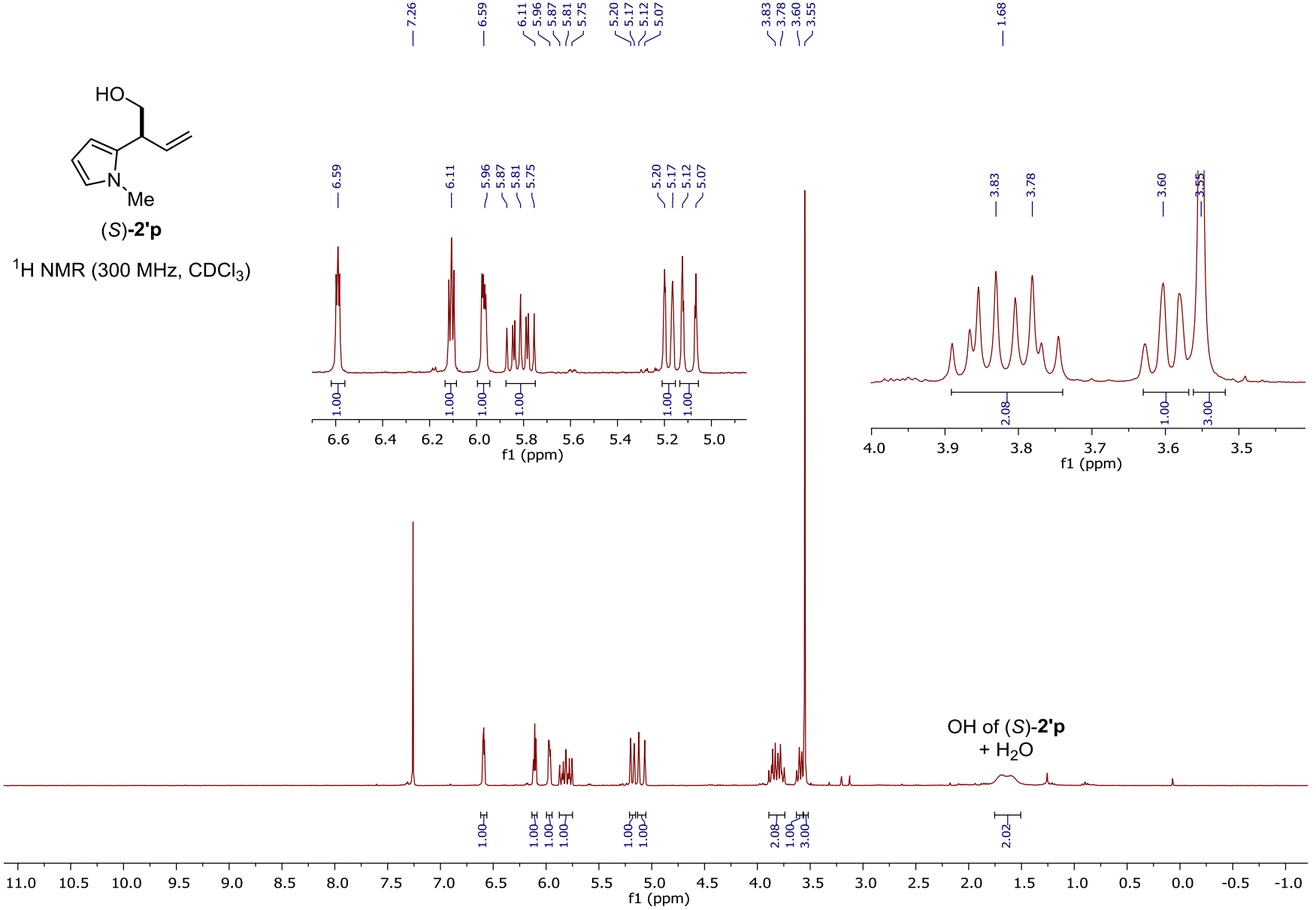


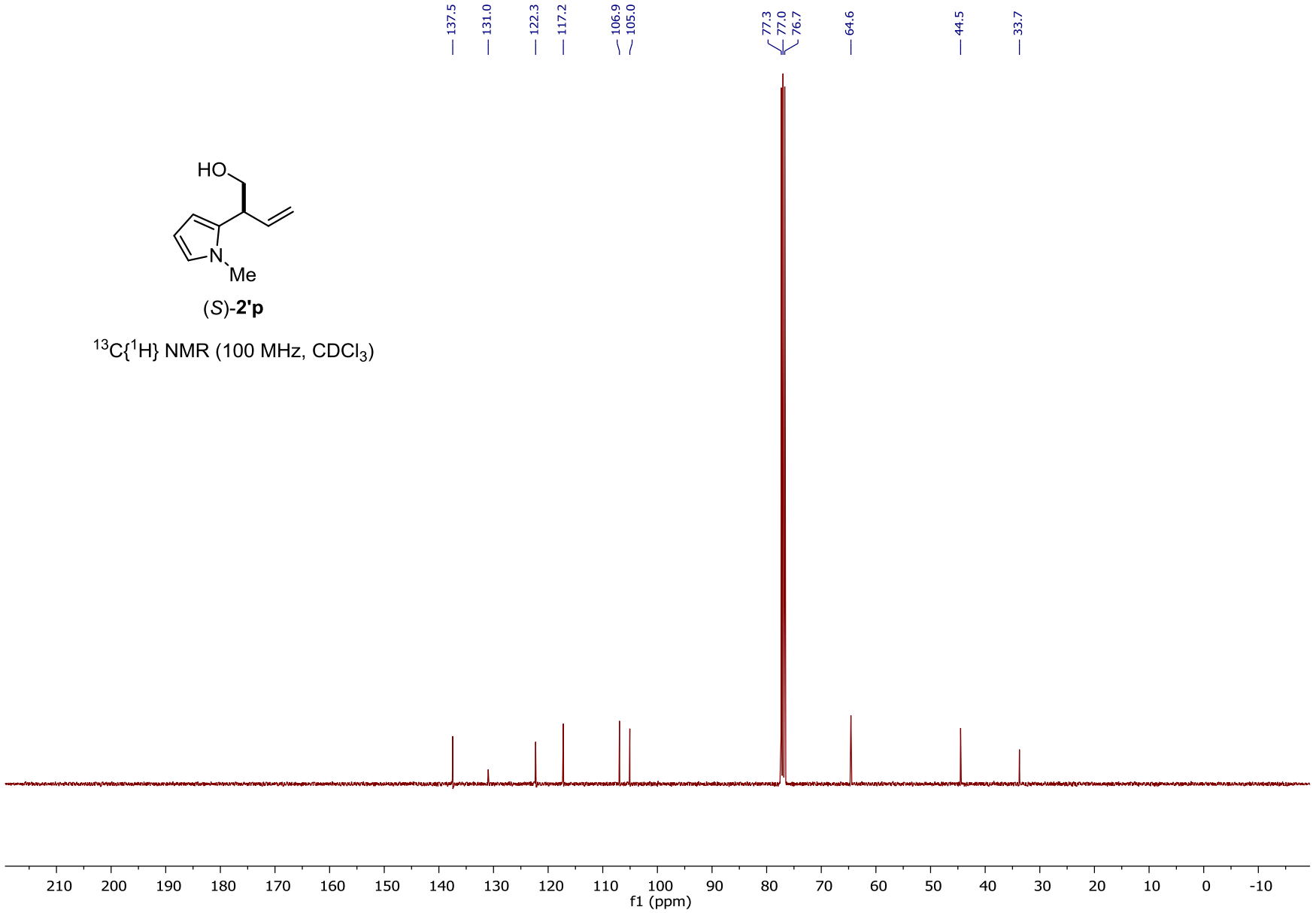
(*S*)-**2'n**
(*S*)-**2'n**:**4'n** = 18:1

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)


OH
TMS
(S)-2'o
1H NMR (300 MHz, CDCl3)
7.44
7.42
7.26
7.18
7.16
6.01
5.99
5.97
5.94
5.92
5.23
5.21
5.18
5.14
3.81
3.79
3.54
3.52
3.51
3.49
1.51
0.24
2.00
2.00
0.99
2.00
2.01
1.00
0.99
9.09
f1 (ppm)
0.99
2.00
f1 (ppm)

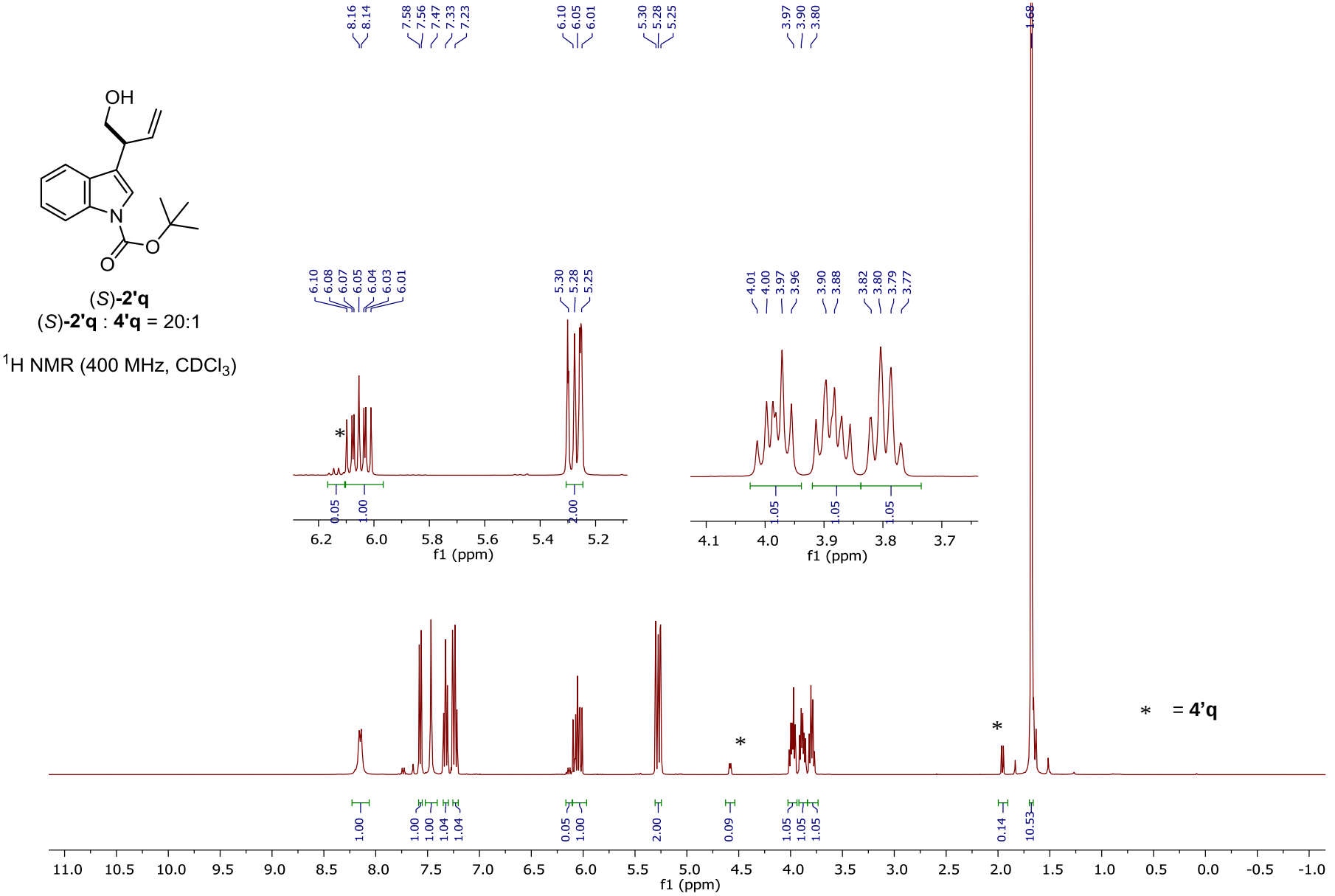

141.2
137.7
132.3
127.9
121.8
117.4
104.8
94.1
77.3
77.0
76.7
52.3
-0.0
OH
TMS
(S)-2'o
13C{1H} NMR (75 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

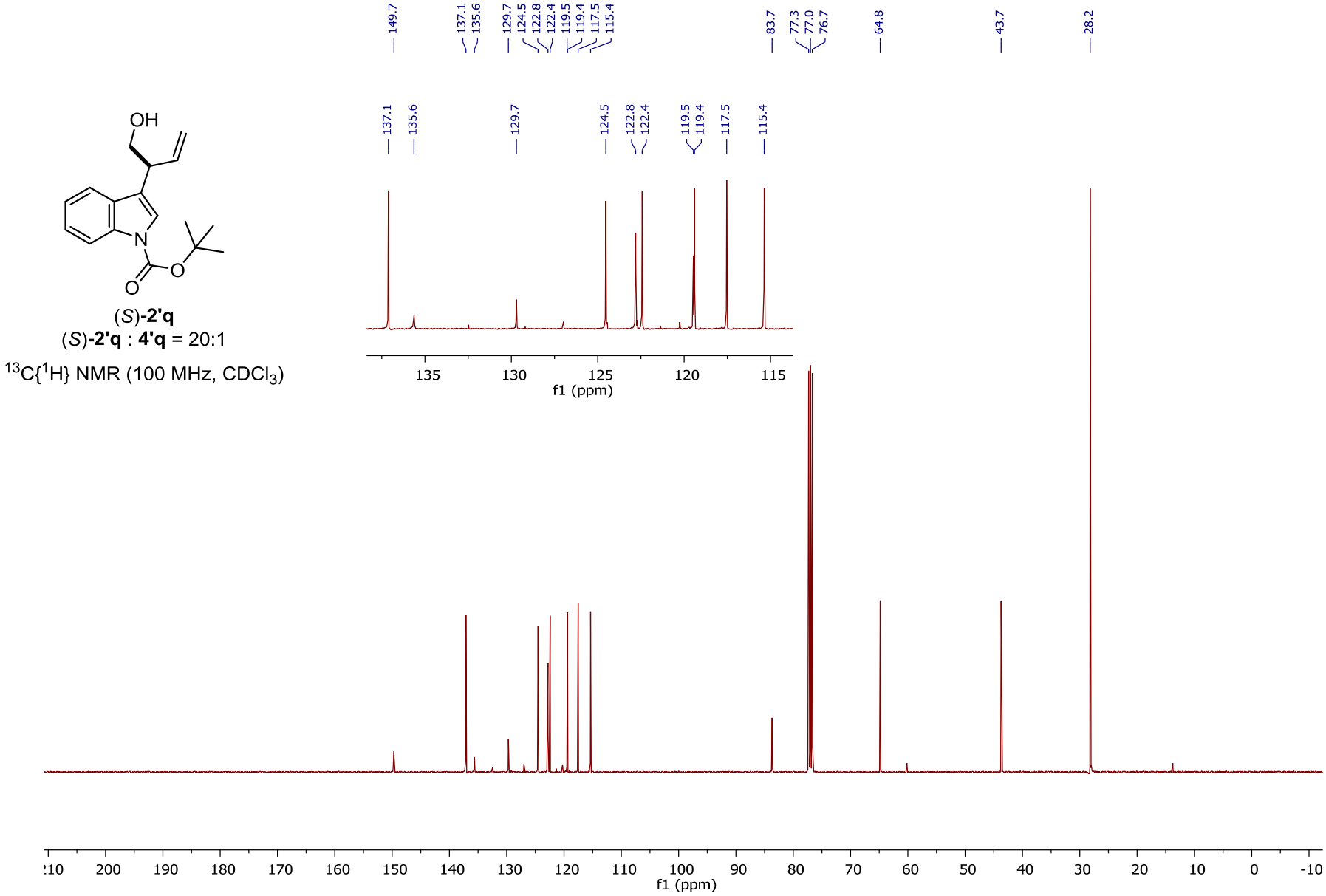

HO
N
Me
(S)-2'p
1H NMR (300 MHz, CDCl3)
7.26
6.59
6.11
5.96
5.87
5.81
5.75
5.20
5.17
5.12
5.07
3.83
3.78
3.60
3.55
1.68
OH of (S)-2'p
+ H2O
f1 (ppm)

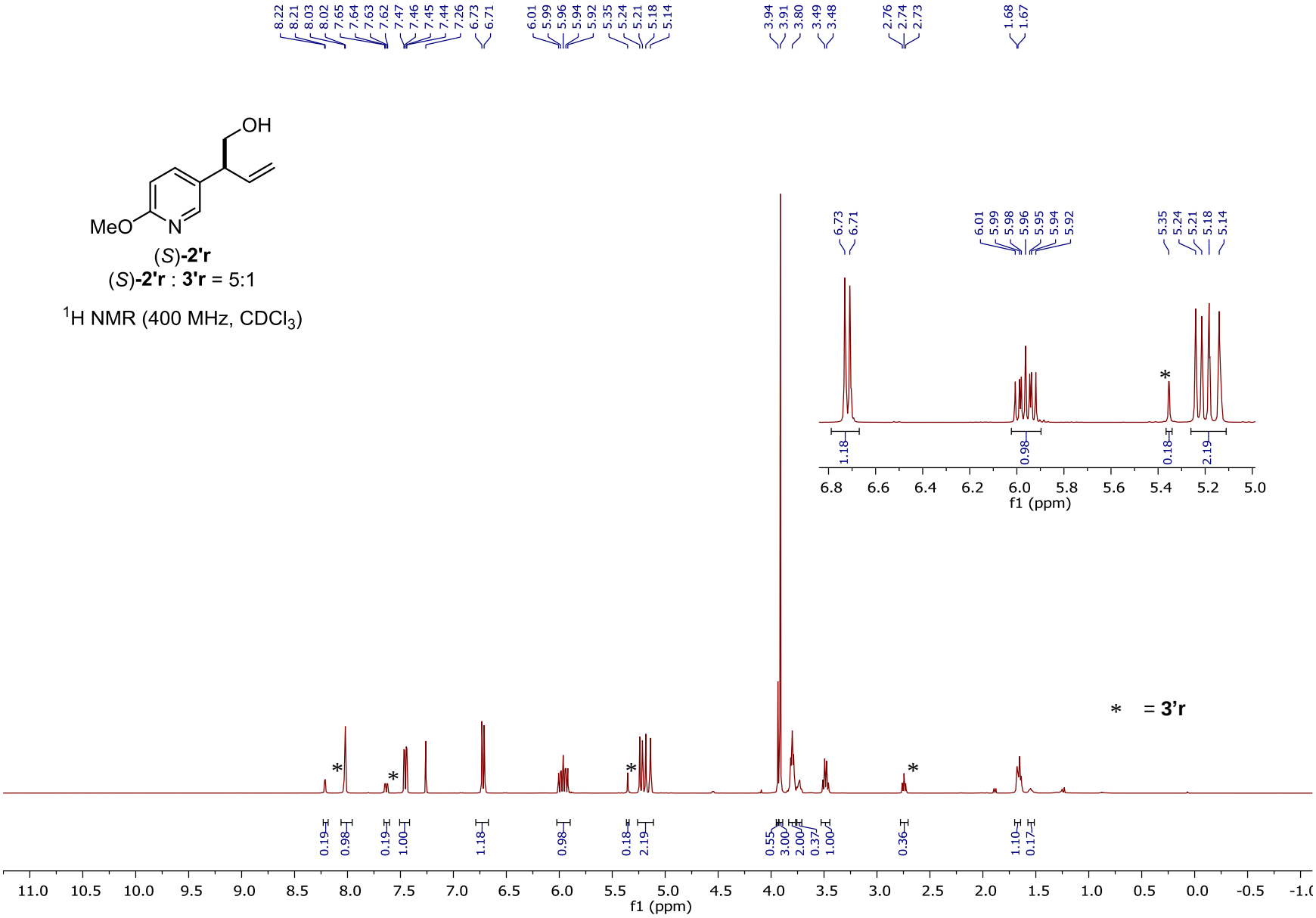


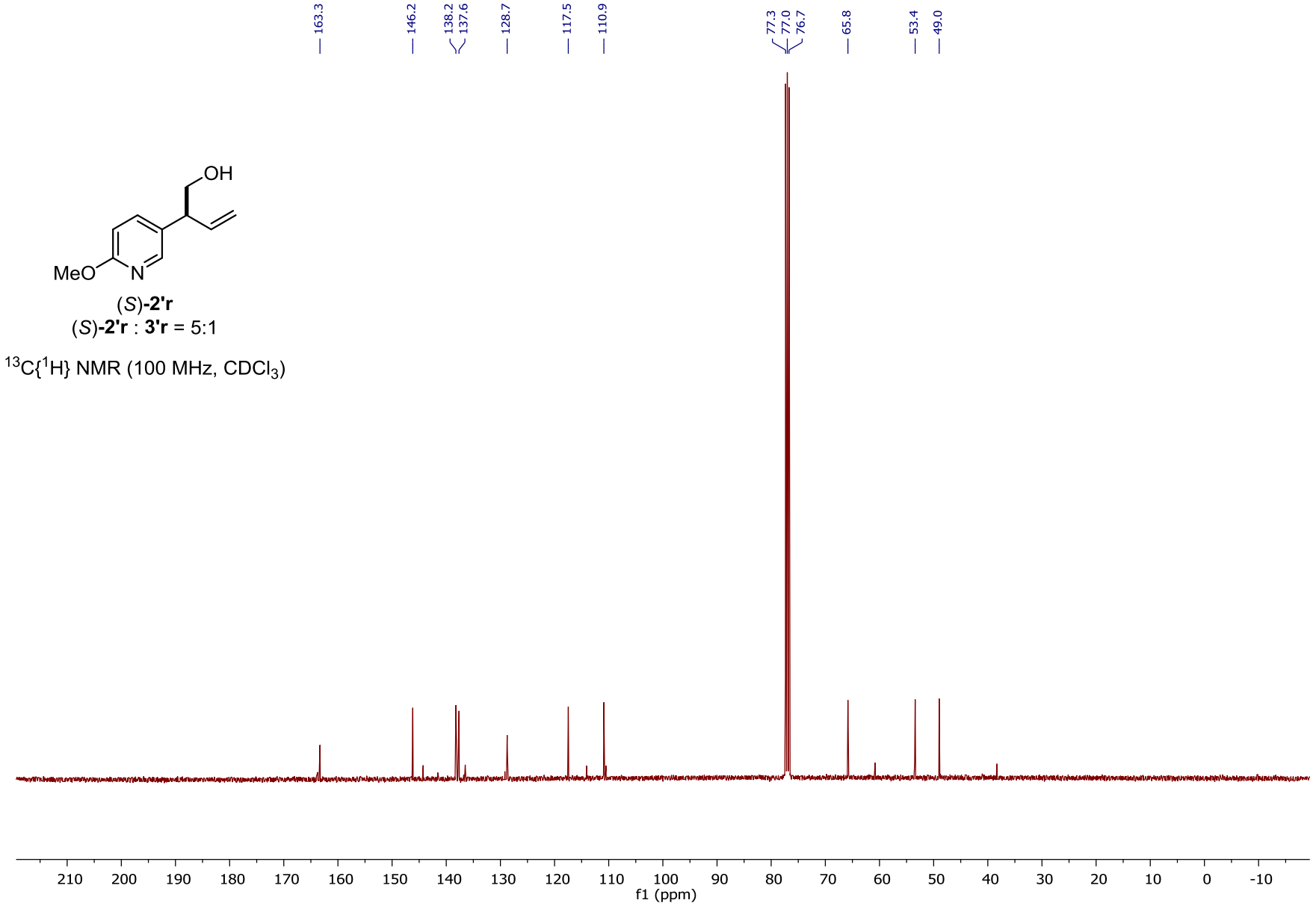
(*S*)-**2'p**

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)


OH
N
O
O
(S)-2'q
(S)-2'q : 4'q = 20:1
1H NMR (400 MHz, CDCl3)
8.16
8.14
7.58
7.56
7.47
7.33
7.23
6.10
6.05
6.01
5.30
5.28
5.25
3.97
3.90
3.80
1.68
6.10
6.08
6.07
6.05
6.04
6.03
6.01
5.30
5.28
5.25
4.01
4.00
3.97
3.96
3.90
3.88
3.82
3.80
3.79
3.77
0.05
1.00
2.00
1.05
1.05
1.05
f1 (ppm)
f1 (ppm)
1.00
1.00
1.00
1.04
1.04
0.05
1.00
2.00
0.09
1.05
1.05
1.05
0.14
10.53
f1 (ppm)
* = 4'q


OH
N
O
O
(S)-2'q
(S)-2'q : 4'q = 20:1
13C{1H} NMR (100 MHz, CDCl3)
149.7
137.1
135.6
129.7
124.5
122.8
122.4
119.5
119.4
117.5
115.4
83.7
77.3
77.0
76.7
64.8
43.7
28.2
f1 (ppm)
f1 (ppm)

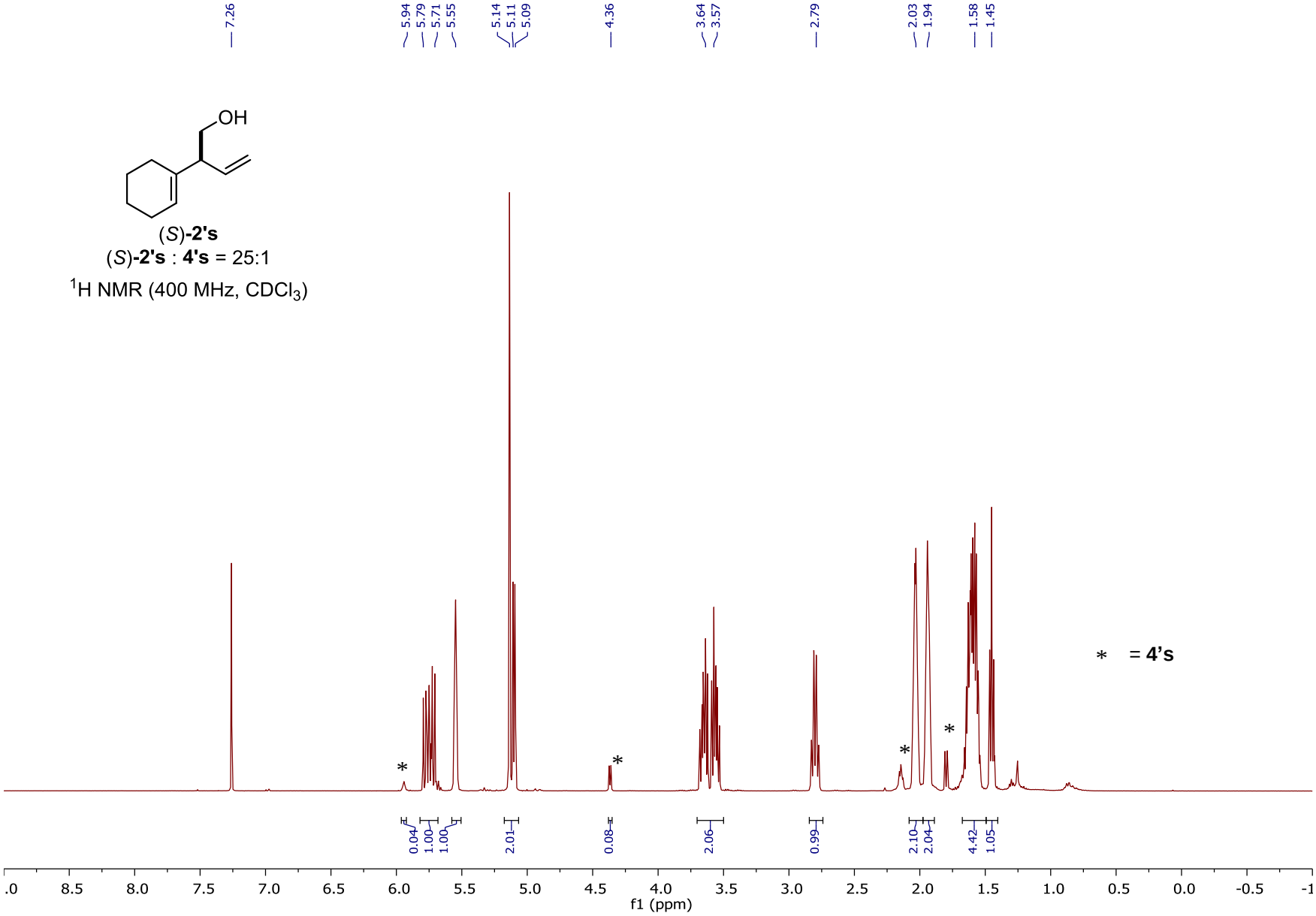

8.22
8.21
8.03
8.02
7.65
7.64
7.63
7.62
7.47
7.46
7.45
7.44
7.26
6.73
6.71
6.01
5.99
5.96
5.94
5.92
5.35
5.24
5.21
5.18
5.14
3.94
3.91
3.80
3.49
3.48
2.76
2.74
2.73
1.68
1.67
OH
MeO
N
(S)-2'r
(S)-2'r : 3'r = 5:1
1H NMR (400 MHz, CDCl3)
* = 3'r
f1 (ppm)

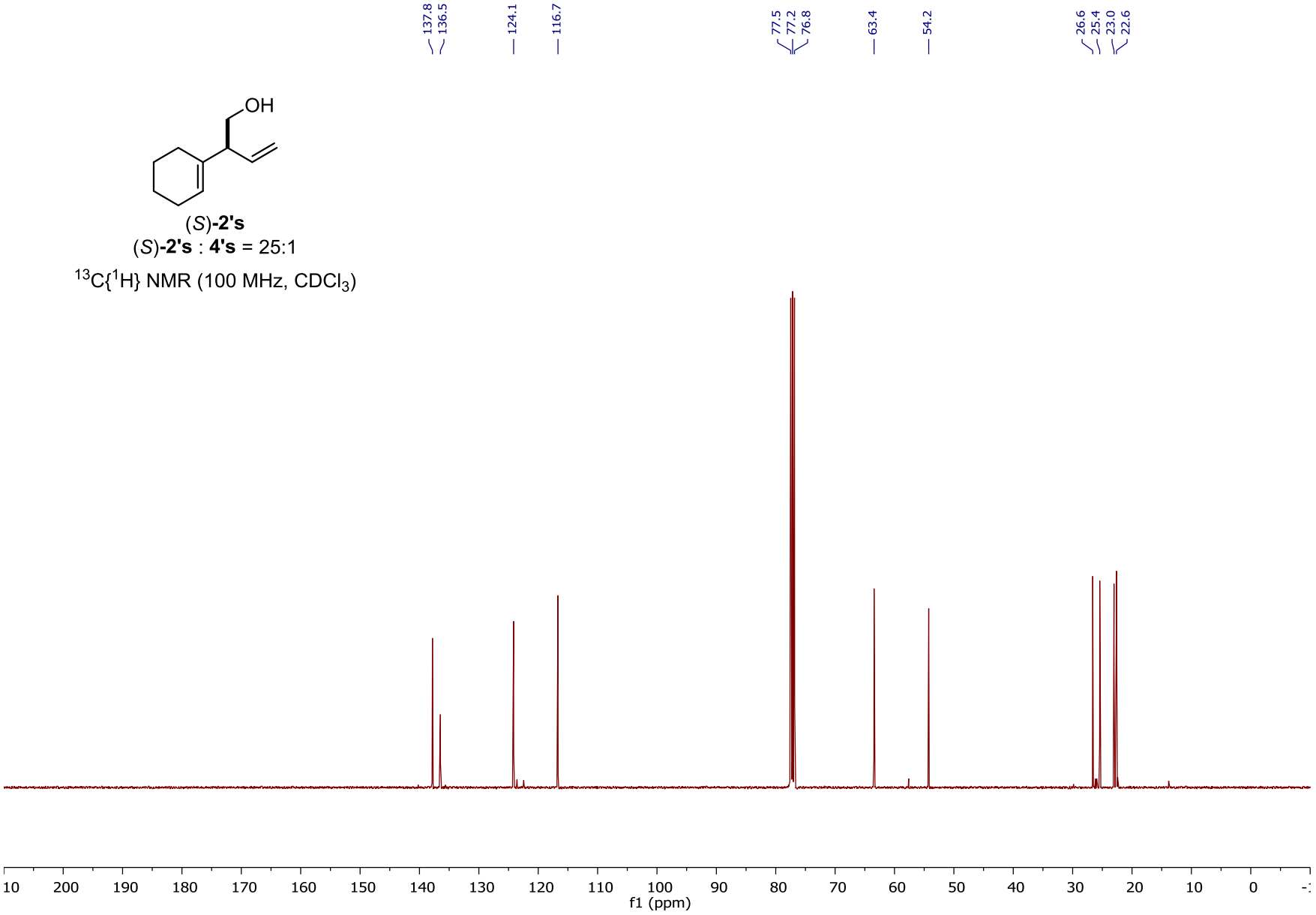


(*S*)-**2'r**

(*S*)-**2'r** : **3'r** = 5:1

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

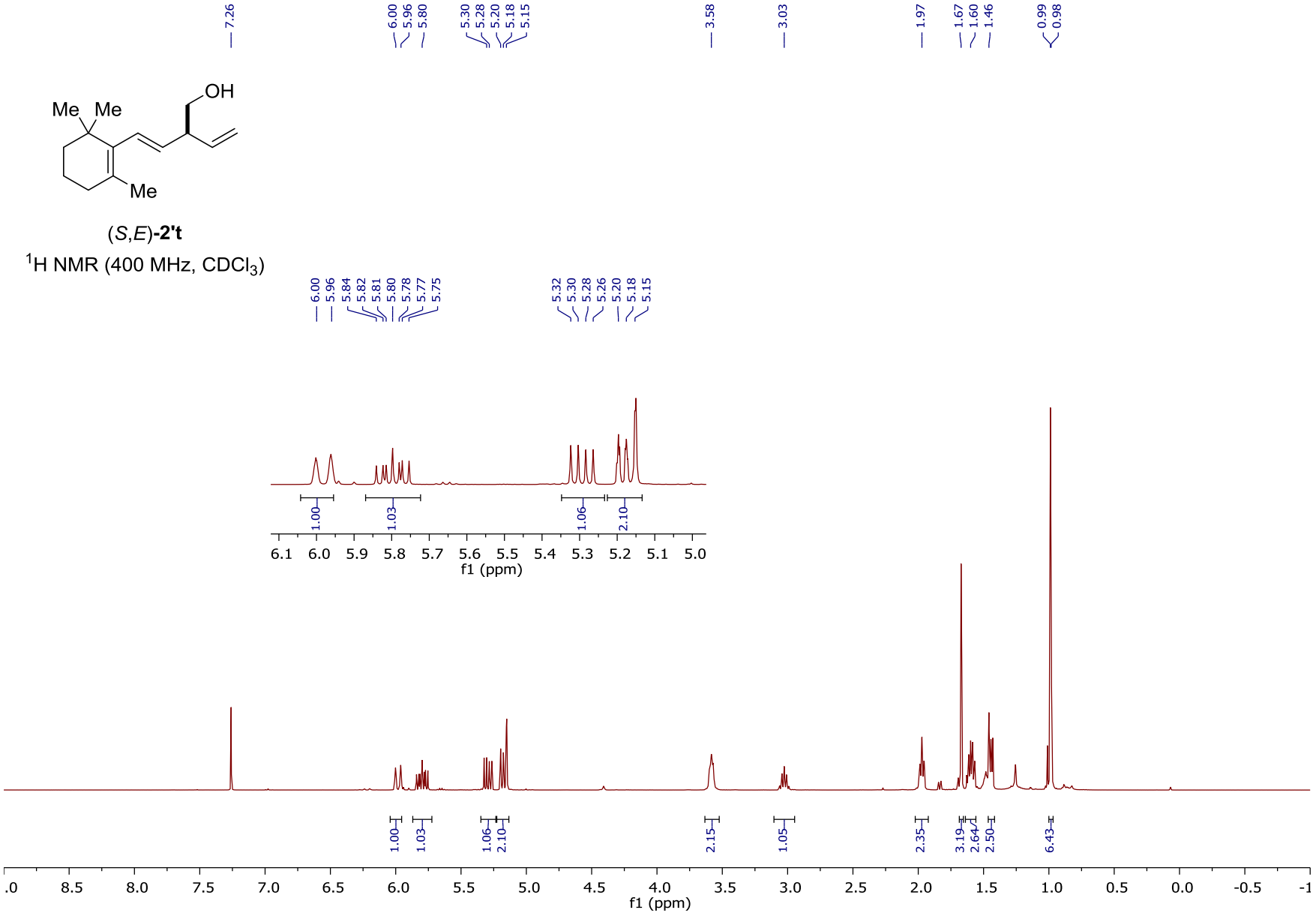

7.26
5.94
5.79
5.71
5.55
5.14
5.11
5.09
4.36
3.64
3.57
2.79
2.03
1.94
1.58
1.45
OH
(S)-2's
(S)-2's : 4's = 25:1
1H NMR (400 MHz, CDCl3)
* = 4's
0.04
1.00
1.00
2.01
0.08
2.06
0.99
2.10
2.04
4.42
1.05
f1 (ppm)



(*S*)-**2's**

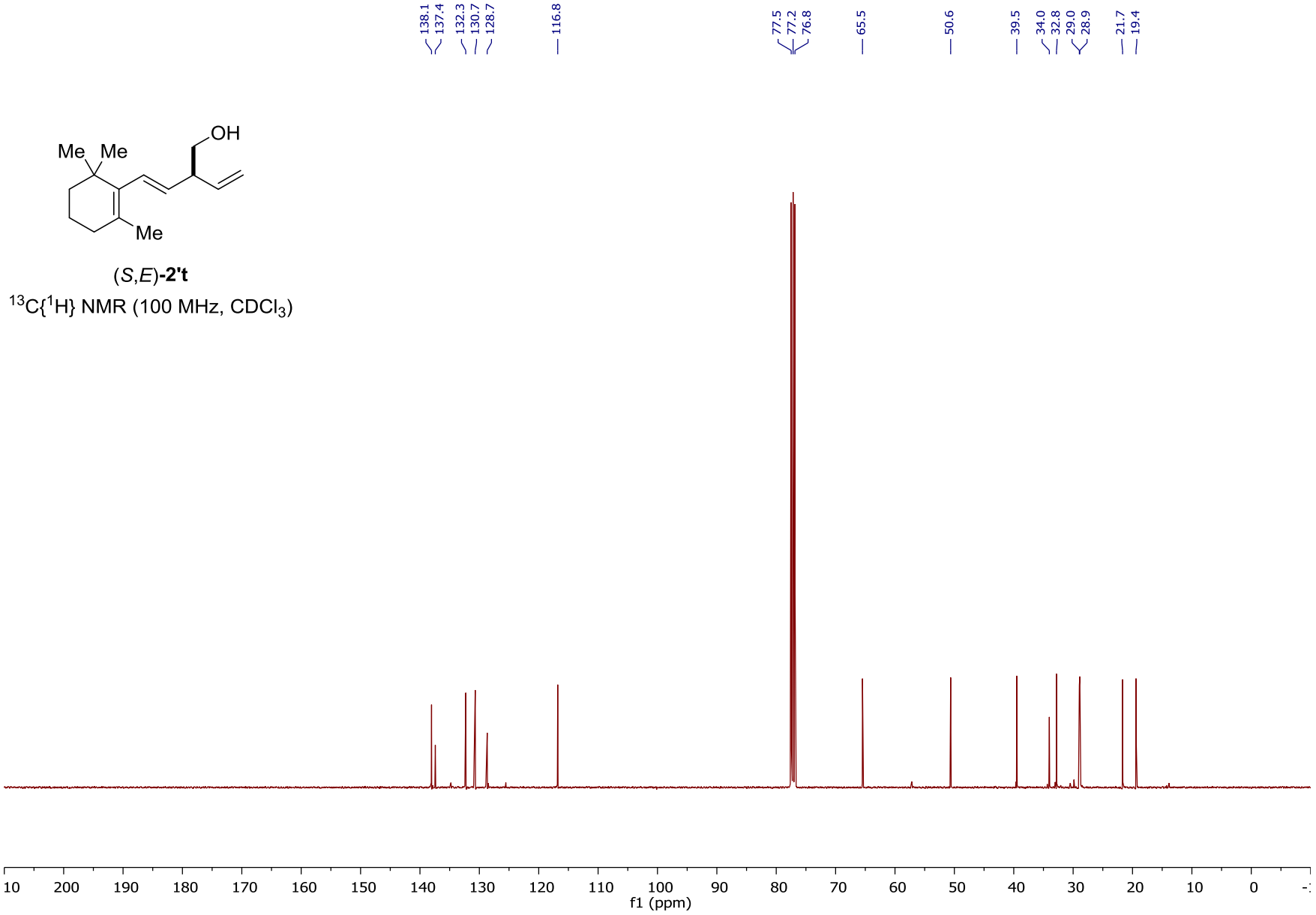
(*S*)-**2's** : **4's** = 25:1

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



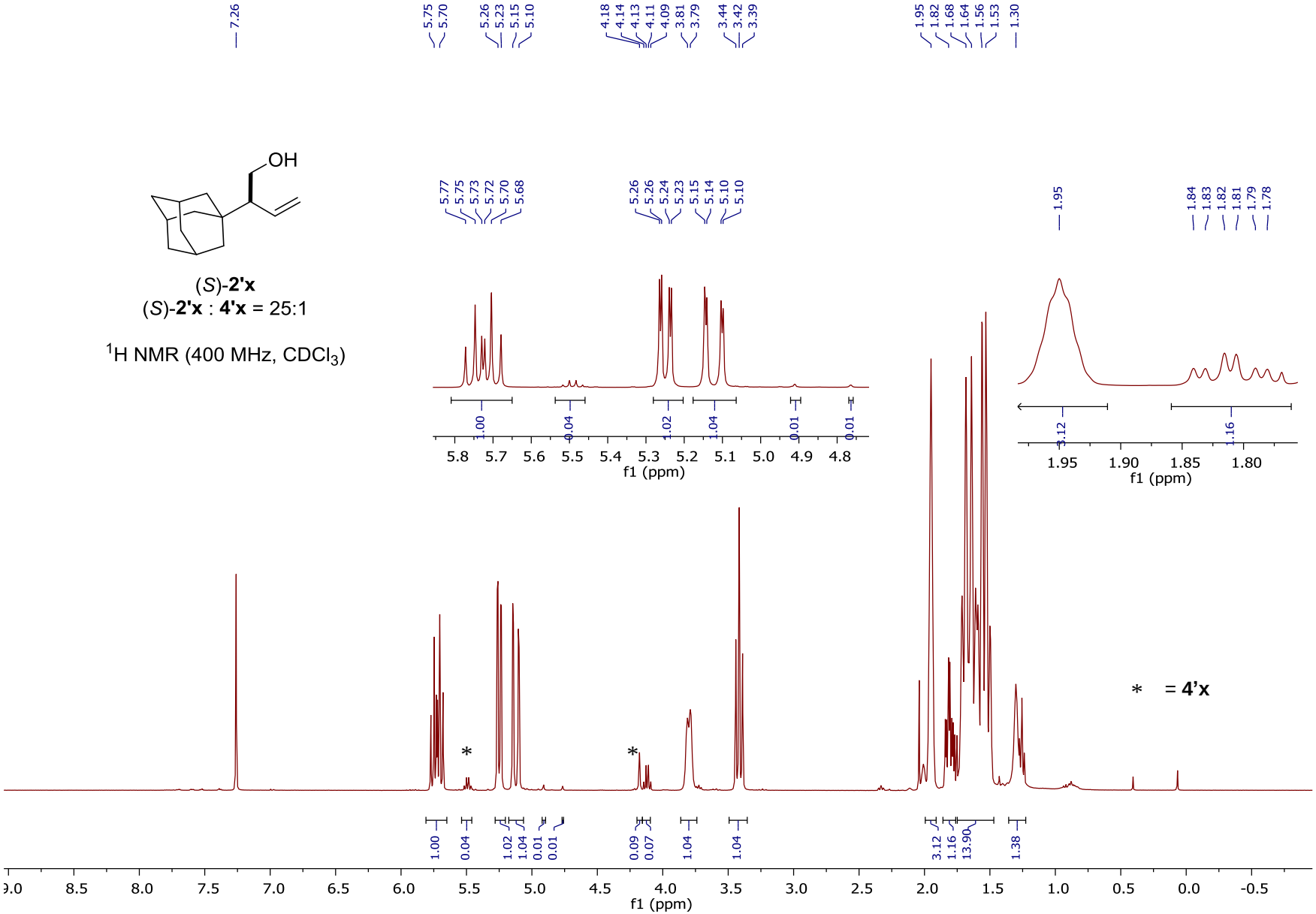
(*S*,*E*)-**2't**

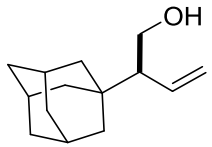
^{1}H NMR (400 MHz, $CDCl_3$)



(*S*,*E*)-**2't**

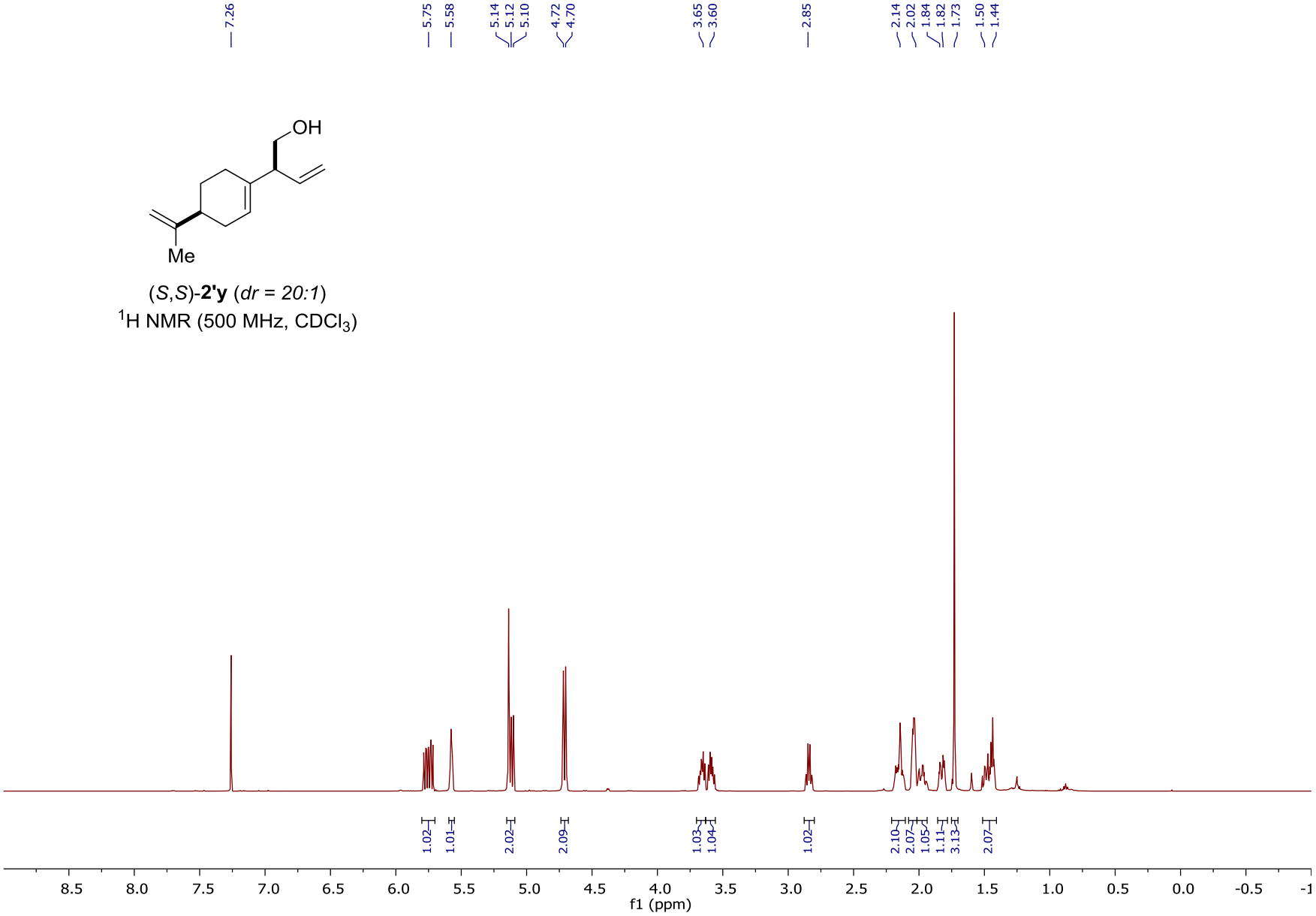
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)


OH
(S)-2'x
(S)-2'x : 4'x = 25:1
1H NMR (400 MHz, CDCl3)
* = 4'x
f1 (ppm)



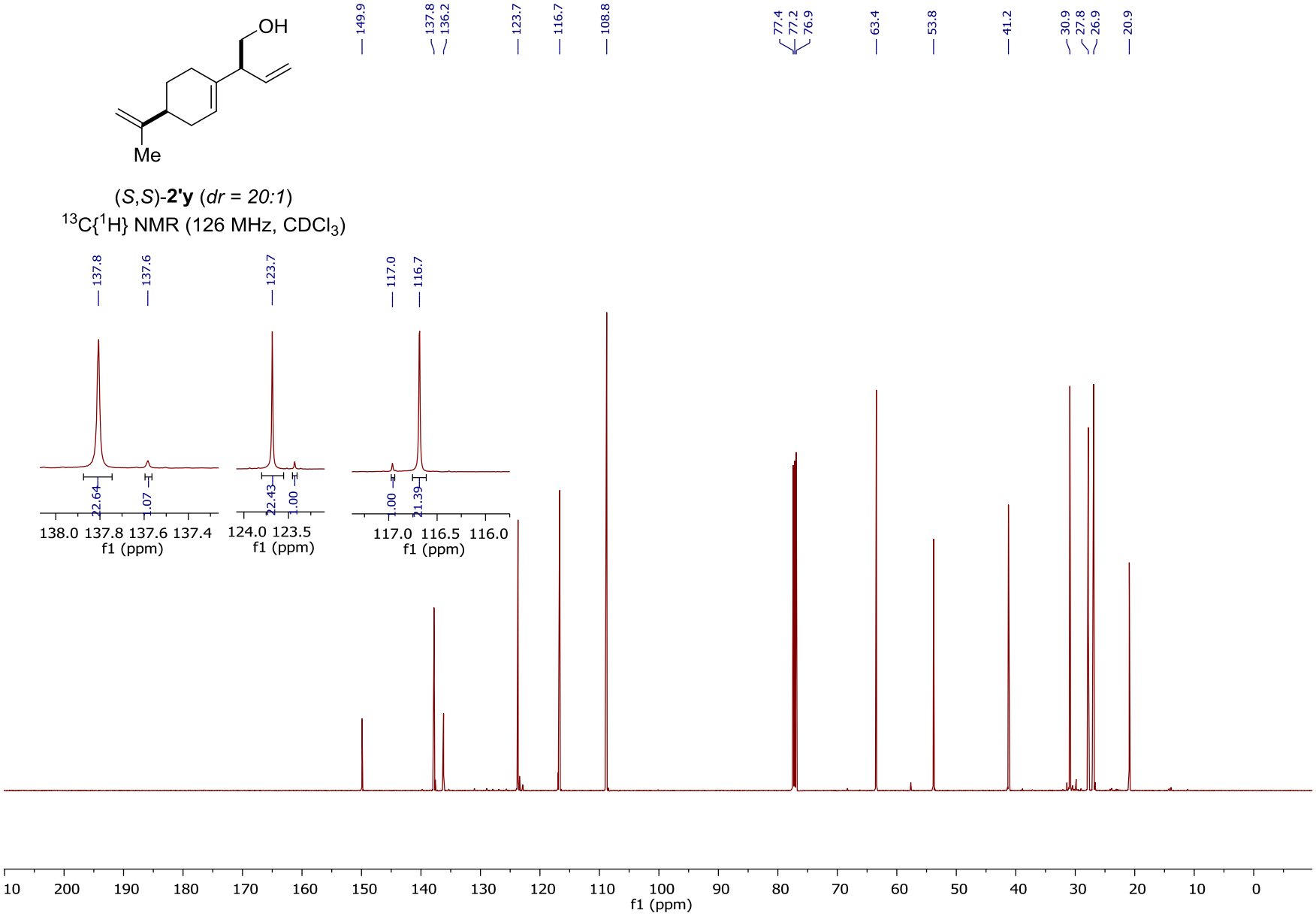
(*S*)-**2'x**
(*S*)-**2'x** : **4'x** = 25:1

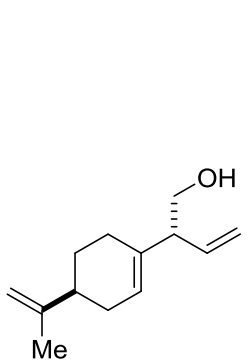
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



(*S*,*S*)-**2'y** (*dr = 20:1*)

^{1}H NMR (500 MHz, $CDCl_3$)

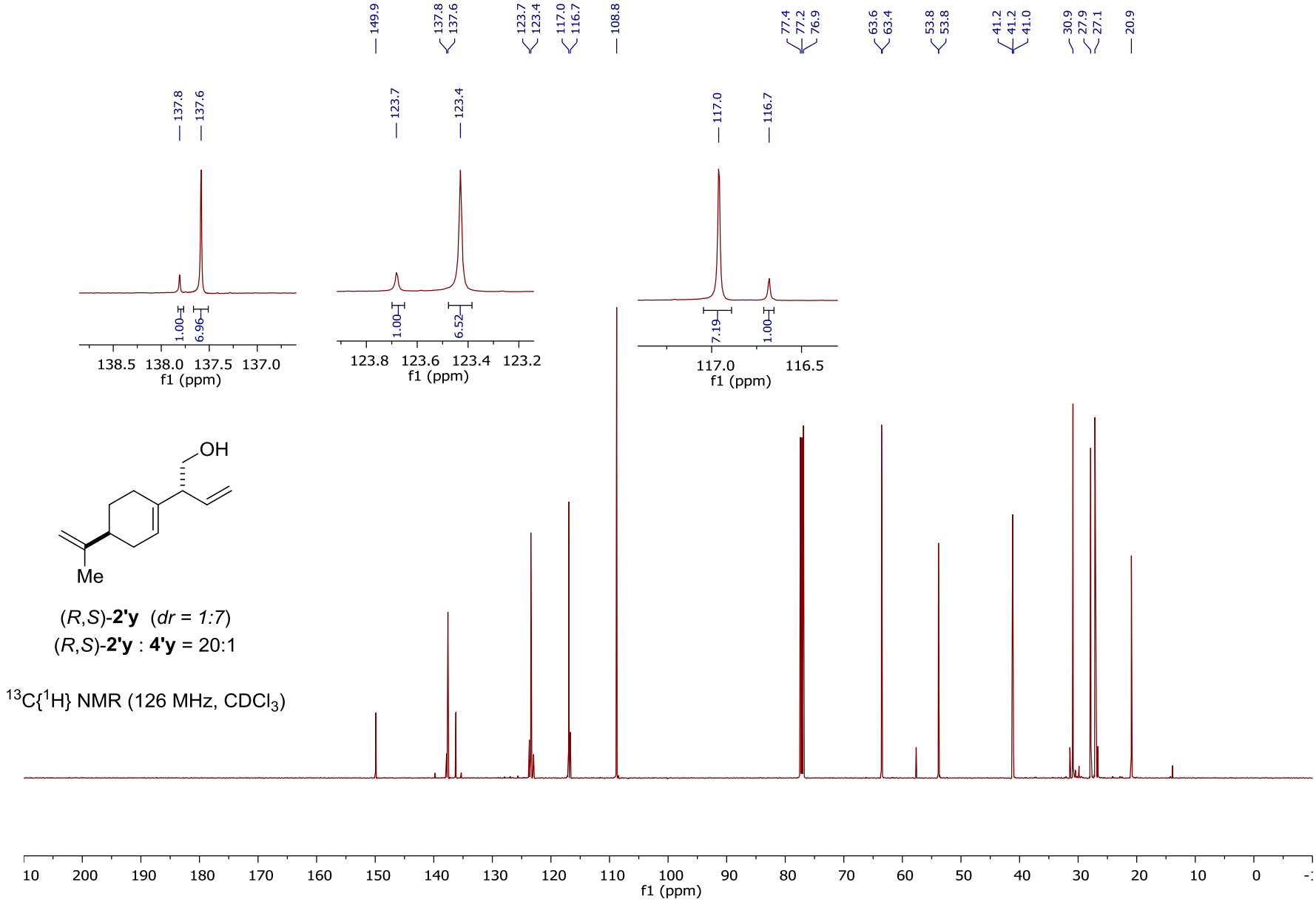

OH
Me
149.9
137.8
136.2
123.7
116.7
108.8
77.4
77.2
76.9
63.4
53.8
41.2
30.9
27.8
26.9
20.9
(S,S)-2'y (dr = 20:1)
13C{1H} NMR (126 MHz, CDCl3)
137.8
137.6
123.7
117.0
116.7
22.64
1.07
22.43
1.00
1.00
21.39
138.0 137.8 137.6 137.4
f1 (ppm)
124.0 123.5
f1 (ppm)
117.0 116.5 116.0
f1 (ppm)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

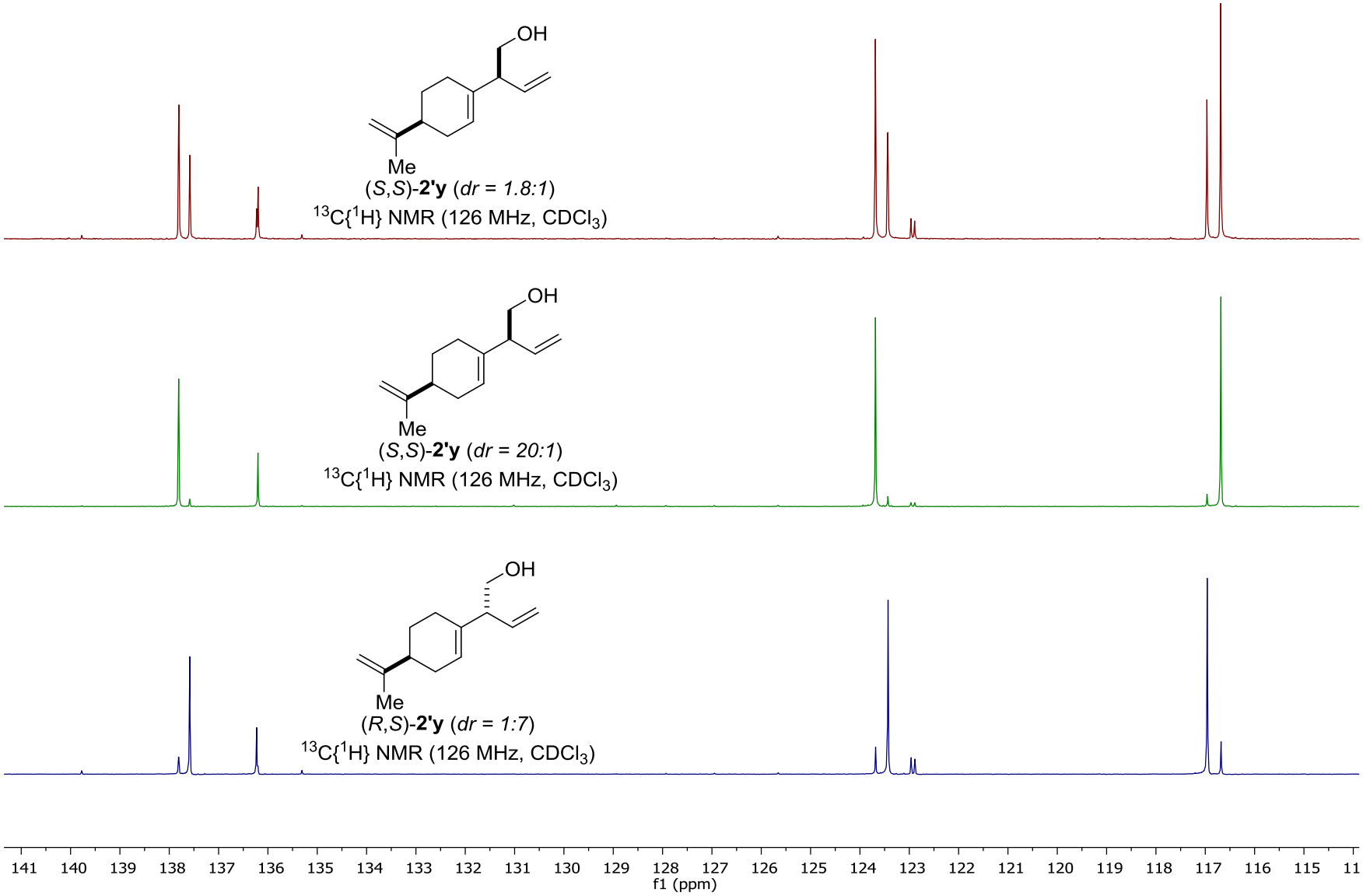


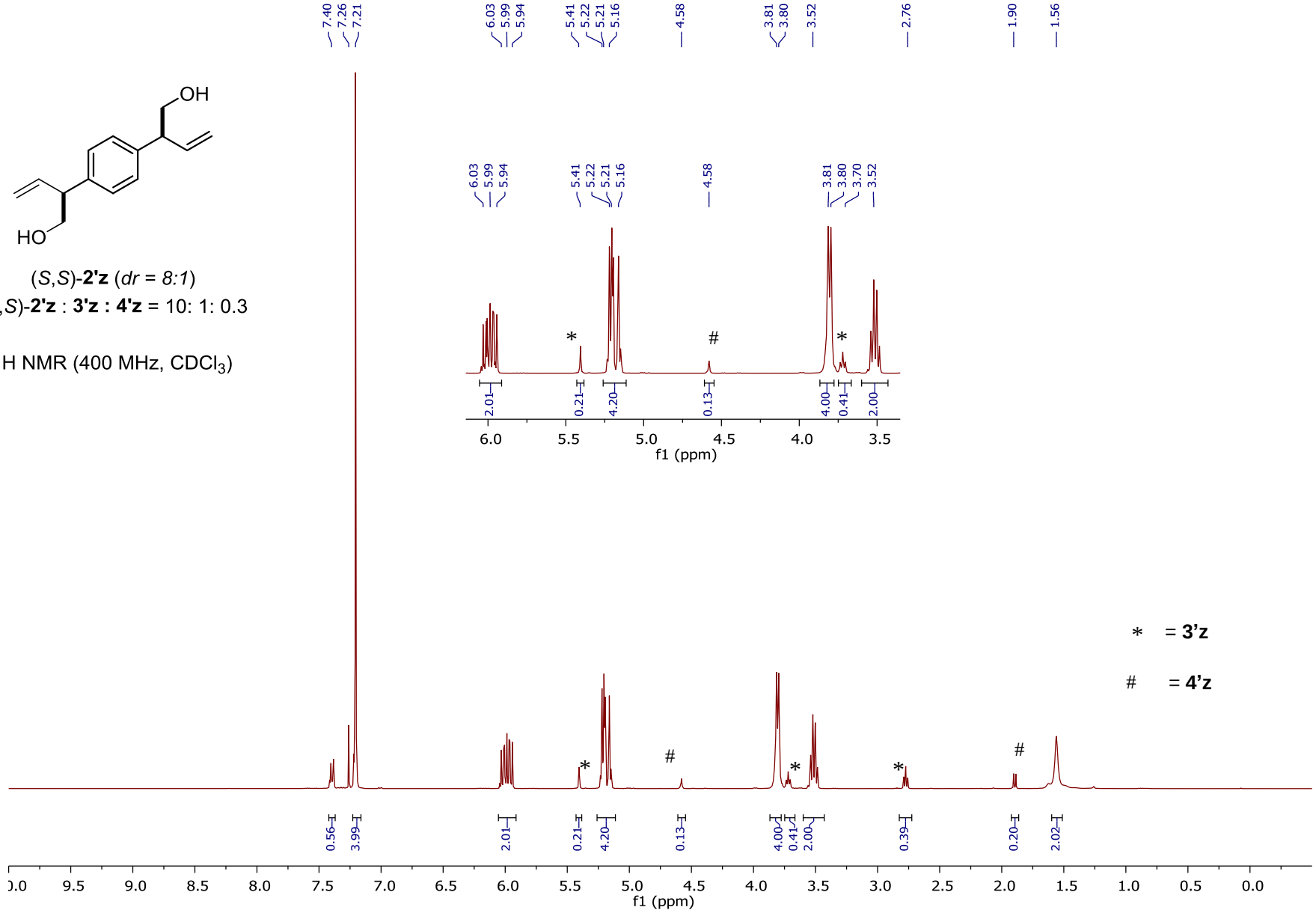
(*R*,*S*)-**2'y** (*dr* = *1:7*)

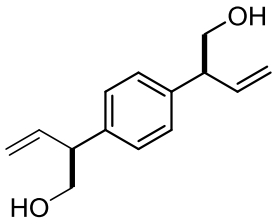
(*R*,*S*)-**2'y** : **4'y** = 20:1

^{1}H NMR (500 MHz, $CDCl_3$)


149.9
137.8
137.6
123.7
123.4
117.0
116.7
108.8
77.4
77.2
76.9
63.6
63.4
53.8
53.8
41.2
41.2
41.0
30.9
27.9
27.1
20.9
1.00
6.96
1.00
6.52
7.19
1.00
138.5 138.0 137.5 137.0
f1 (ppm)
123.8 123.6 123.4 123.2
f1 (ppm)
117.0 116.5
f1 (ppm)
OH
Me
(R,S)-2'y (dr = 1:7)
(R,S)-2'y : 4'y = 20:1
13C{1H} NMR (126 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OH
Me
(S,S)-2'y (dr = 1.8:1)
13C{1H} NMR (126 MHz, CDCl3)
OH
Me
(S,S)-2'y (dr = 20:1)
13C{1H} NMR (126 MHz, CDCl3)
OH
Me
(R,S)-2'y (dr = 1:7)
13C{1H} NMR (126 MHz, CDCl3)
141 140 139 138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119 118 117 116 115 11
f1 (ppm)


OH
HO
(S,S)-2'z (dr = 8:1)
(S,S)-2'z : 3'z : 4'z = 10: 1: 0.3
1H NMR (400 MHz, CDCl3)
7.40
7.26
7.21
6.03
5.99
5.94
5.41
5.22
5.21
5.16
4.58
3.81
3.80
3.52
2.76
1.90
1.56
3.70
2.01
0.21
4.20
0.13
4.00
0.41
2.00
0.56
3.99
0.39
0.20
2.02
f1 (ppm)
* = 3'z
# = 4'z



(*S*,*S*)-**2'z** (*dr = 8:1*)
(*S*,*S*)-**2'z** : **3'z : 4'z** = 10: 1: 0.3

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)