Supporting Information

Enantioselective Carbonyl Allylation, Crotylation and *tert*-Prenylation of Furan Methanols and Furfurals *via* Iridium Catalyzed Transfer Hydrogenation

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General Experimental Details. All reactions were run under an atmosphere of argon, unless otherwise indicated. Anhydrous solvents were transferred *via* oven-dried syringe. Reaction tubes were flame-dried and cooled under a stream of argon. Commercially available metal salts, ligands and alcohols were used as received. Commercially available aldehydes were purified *via* distillation or recrystallization prior to use. Reactions were monitored by thin-layer chromatography and products were visualized with anisaldehyde stain. Analytical thin-layer chromatography (TLC) was carried out using 0.2-mm commercial silica gel plates. Preparative column chromatography employing silica gel was performed according to the method of Still.[1] Solvents for chromatography are listed as volume/volume ratios. High-resolution mass spectra (HRMS) are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion $[M+H]^+$ or a suitable fragment ion. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with on a 400 MHz spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) relative to residual $CHCl_3$ at 7.24 ppm. Coupling constants are reported in Hertz (Hz). Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a 100 MHz spectrometer. Chemical shifts are reported in delta (δ) units, ppm relative to the center of the triplet at 77.0 ppm for deuteriochloroform. ^{13}C NMR spectra were routinely run with broadband decoupling. Compound numbers used in the experimental section correspond to those employed in the main paper.

[1] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923-2925.

General Experimental Procedures for Adducts 3a-3c

General Procedure A for the Preparation of Adducts 3a-3c from Furan Methanols 1a-1c: To a flame dried re-sealable reaction tube purged with argon and containing a magnetic stirrer, was added $[Ir(cod)Cl]_2$ (6.7 mg, 0.010 mmol, 2.5 mol%), (*R*)-Cl,MeO-BIPHEP (13.0 mg, 0.020 mmol, 5 mol%), 3-nitro-4-chlorobenzoic acid (8.1 mg, 0.040 mmol 10 mol%), Cs_2CO_3 (26.1 mg, 0.080 mmol, 20 mol%) and the furan methanol (0.40 mmol, 100 mol%). THF (2.0 mL, 0.2 M concentration with respect to the furan methanol) and allyl acetate (86 μL, 0.80 mmol, 200 mol%) were added and the reaction mixture was allowed to stir at 100 ^oC for 24 hours. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) to furnish the corresponding products of allylation **3a-3c**.

General Procedure B for the Preparation of Adducts 3a-3c from Furfurals 2a-2c: To a flame dried re-sealable reaction tube purged with argon and containing a magnetic stirrer, was added $[Ir(cod)Cl]_2$ (6.7 mg, 0.010 mmol, 2.5 mol%), (*R*)-Cl,MeO-BIPHEP (13.0 mg, 0.020 mmol, 5 mol%), 3-nitro-4-chlorobenzoic acid (8.1 mg, 0.040 mmol 10 mol%), Cs_2CO_3 (26.1 mg, 0.080 mmol, 20 mol%) and the furfural (0.40 mmol, 100 mol%). THF (2.0 mL, 0.2 M concentration with respect to the furfural), *i*-PrOH (61 μL, 0.80 mmol, 200 mol%) and allyl acetate (86 μL, 0.80 mmol, 200 mol%) were added and the reaction mixture was allowed to stir at 100 ^oC for 24 hours. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) to furnish the corresponding products of allylation **3a-3c**.

General Experimental Procedures for Adducts 4a-4c

General Procedure C for the Preparation of Adducts 4a-4c from Furan Methanols 1a-1c: To a flame dried re-sealable reaction tube purged with argon and containing a magnetic stirrer, was added (*R*)-Ir-complex I (20.4 mg, 0.020 mmol, 5 mol%), K_3PO_4 (84.9 mg, 0.40 mmol, 100 mol%), and the corresponding furan methanol (0.40 mmol, 100 mol%). THF (0.2 mL, 2 M concentration with respect to the alcohol), H_2O (36 μL, 2.0 mmol, 500 mol%) and α-methyl allyl acetate (86 μL, 0.80 mmol, 200 mol%) were added and the reaction mixture was allowed to stir at 70 ^oC for 48 hours. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) to furnish the corresponding products of crotylation **4a-4c**.

General Procedure D for the Preparation of Adducts 4a-4c from Furfurals 2a-2c: To a flame dried re-sealable reaction tube purged with argon and containing a magnetic stirrer, was added (*R*)-Ir-complex I (20.4 mg, 0.020 mmol, 5 mol%), K_3PO_4 (84.9 mg, 0.400 mmol, 100 mol%), and the corresponding furfural (0.40 mmol, 100 mol%). THF (0.2 mL, 2 M concentration with respect to the aldehyde), H_2O (36 μL, 2.0 mmol, 500 mol%), *i*-PrOH (61 μL, 0.80 mmol, 200 mol%) and α-methyl allyl acetate (86 μL, 0.80 mmol, 200 mol%) were added and the reaction mixture was allowed to stir at 70 ^oC for 48 hours. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2), under the conditions noted, to furnish the corresponding products of crotylation **4a-4c**.

General Experimental Procedures for Adducts 5a-5c

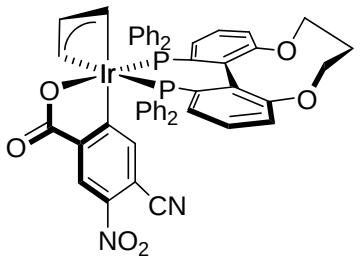
General Procedure E for the Preparation of Adducts 5a-5c from Furan Methanols 1a-1c: To a flame dried re-sealable reaction tube purged with nitrogen and containing a magnetic stirrer, was added (*R*)-Ir-complex II (5 mol%) and the corresponding furan methanol (100 mol%). Toluene (1 M concentration with respect to the alcohol), 1,1-dimethylallene (200 mol%), and propionaldehyde (5 mol%) were added and the reaction mixture was allowed to stir at 40 ^{o}C for 72 hours. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) to furnish the corresponding products of *tert*-prenylation **5a**-**5c**.

General Procedure F for the Preparation of Adducts 5a-5c from Furfurals 2a-2c: To a flame dried re-sealable reaction tube purged with nitrogen and containing a magnetic stirrer, was added (*R*)-Ir-complex II (5 mol%) and the corresponding furfural (100 mol%). Toluene (1 M concentration with respect to the aldehyde), 1,1-dimethylallene (200 mol%), and *i*-PrOH (200 mol%) were added and the reaction mixture was allowed to stir at 40 ^{o}C for 72 hours. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) to furnish the corresponding products of *tert*-prenylation **5a**-**5c**.

General Experimental Procedure for Rearrangement Products 6a-6c

General Procedure for the Achmatowicz Rearrangement of Adducts 3b, 4b, and 5b: Alcohols **3b**, **4b** or **5b** (100 mol%) were dissolved in aqueous THF (THF:H_2O, 4:1, 0.1 M) and the solution was cooled to 0 °C. N-bromosuccinimide (100 mol%) was added portion-wise while maintaining a temperature of 0 °C. After the reaction had gone to completion as determined by TLC analysis, the reaction mixture was diluted with dichloromethane and washed with KI (10% aqueous solution), $Na_2S_2O_4$ (15% aqueous solution), and $NaHCO_3$ (10% aqueous solution), and brine. The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (SiO_2) to furnish the corresponding pyrones **6a**, **6b** or **6c**, respectively.

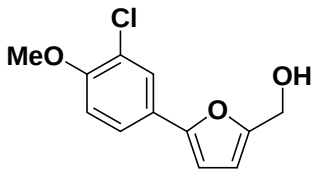
(*R*)-Ir-catalyst-I [(R)-I]



To a flame dried sealed tube, purged with argon and containing a magnetic stirrer was added $[Ir(cod)Cl]_2$ (50.4 mg, 0.075 mmol, 100 mol%), (*R*)-C_3-Tunephos (89.2 mg, 0.150 mmol, 200 mol%), Cs_2CO_3 (97.7 mg, 0.300 mmol, 400 mol%), 3-NO_2-4-CN-BzOH (57.6 mg, 0.300 mmol, 400 mol%), allyl acetate (40 μL, 0.375 mmol, 500 mol%). THF (1.5 mL, 0.05M with respect to $[Ir(cod)Cl]_2$) was added and the reaction mixture was stirred at room temperature for 30 min at which point the reaction mixture was heated to 80 °C and allowed to stir for an additional 120 min. The reaction mixture was filtered and washed with THF (~15mL) until all yellow residue was dissolved. The filtrate was concentrated *in vacuo* (~5 mL) and hexanes (~50 mL) was added. A yellow precipitate formed, which was collected by filtration and dried under vacuum to furnish the title compound (110 mg, 72% yield) as a light yellow powder.[2]

[2] S. B. Han, I. S. Kim, H. Han, M. J. Krische, *J. Amer. Chem. Soc.* **2009**, *131*, 6916–6917.

[5-(3-chloro-4-methoxyphenyl)furan-2-yl]methanol (1c)



To a solution of 5-(3-chloro-4-methoxyphenyl)furfural (1.00 g, 4.22 mmol, 100 mol%), in neat methanol (40 mL) at 0 ^{o}C, was added sodium borohydride (176 mg, 4.65 mmol, 1.1eq.) in small portions with stirring. After evolution of hydrogen ceased, the reaction mixture was a saturated solution of aqueous NH_4Cl was added. The resulting mixture was extracted with dichloromethane and the combined organic extracts were washed with brine, dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2: hexane:EtOAc, 3:1) to furnish the title compound (945 mg, 94% yield) as a colorless solid.[3]

Mp = 86 °C.

TLC (SiO_2): R_f (Hexane:Et_2O, 3:1) = 0.13.

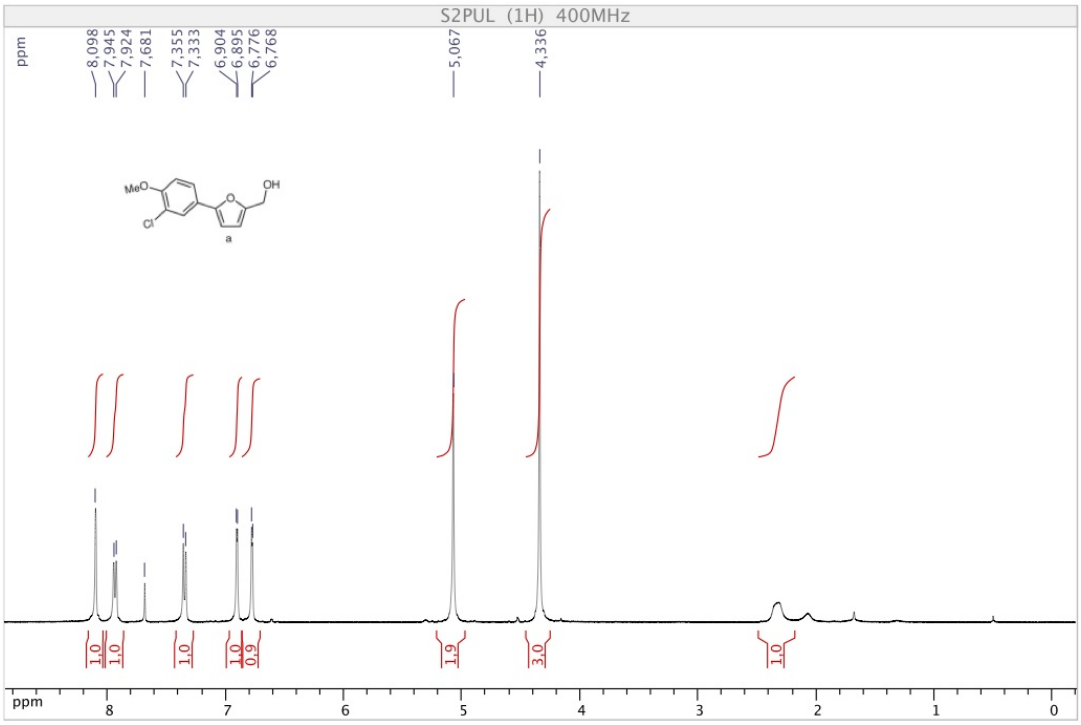
^{1}H NMR (400 MHz, $CDCl_3$): 7.66 (s, 1H), 7.49 (d, *J* = 8.7 Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 1H), 6.46 (d, *J* = 3.3 Hz, 1H), 6.33 (d, *J* = 3.1 Hz, 1H), 4.63 (s, 2H), 3.90 (s, 3H), 1.88 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): = 56.4, 57.7, 105.2, 110.2, 112.3, 123.0, 123.4, 124.7, 126.0, 152.8, 153.6, 154.5. 154.5, 153.6, 152.9, 126.0, 124.7, 123.5, 123.0, 112.4, 110.3, 105.2, 57.8, 56.4.

HRMS (CI): Calcd. for $C_{12}H_{11}O_3{}^{35}Cl$ $(M)^+$: 238.0397, Found: 238.0398.

FTIR (neat): 3359, 2940, 2839, 1548, 1489, 1461, 1440, 1267, 1062, 1006, 811, 731, 707 cm^{-1}.

[3] K. Ziach, J. Jurczak, *Org. Lett.* **2008**, 10, 5159–5162.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Cl
OH
O
a
1,0
1,0
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0,9
1,9
3,0
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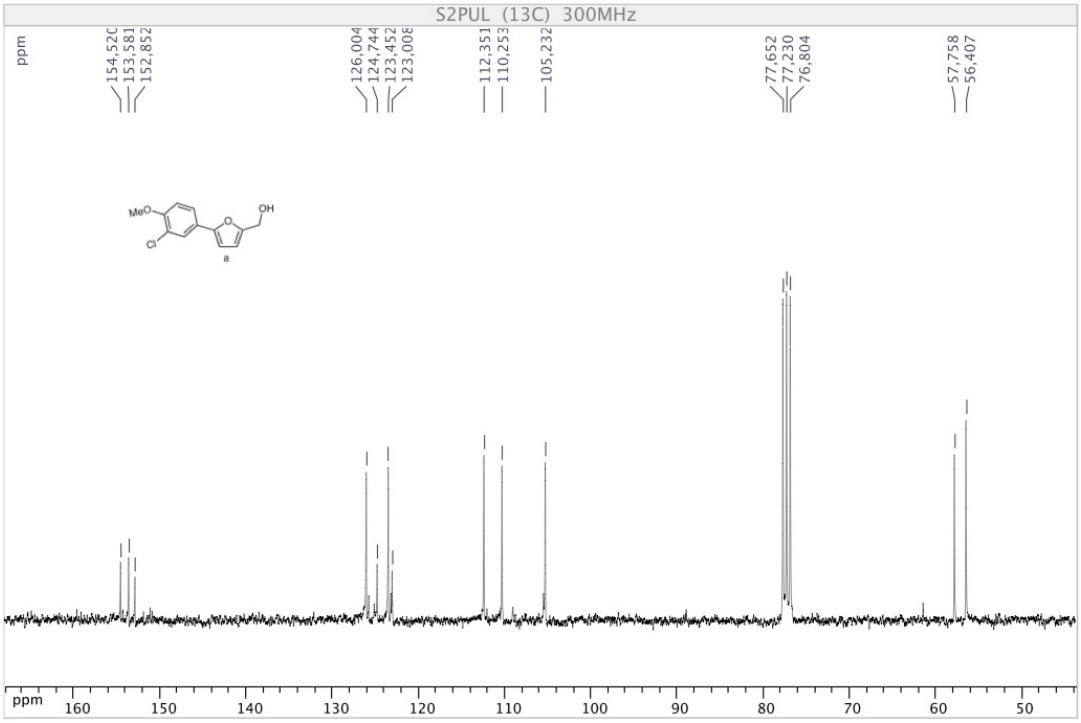
7
6
5
4
3
2
1
0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OH
O
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ppm
160
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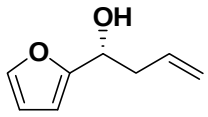
(*R*)-1-(furan-2-yl)but-3-en-1-ol (3a)



Procedure A (*via* alcohol 1a): The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2: pentane:Et_2O, 5:1) to furnish the title compound (37.5 mg, 68% yield, 94% ee) as a colorless oil.

Procedure B (*via* aldehyde 2a): The mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2: pentane:Et_2O, 5:1) to furnish the title compound (45.7 mg, 83% yield, 96% ee) as a colorless oil.

TLC (SiO_2): R_f (Hexane: Et_2O, 5:1) = 0.17.

^{1}H NMR (400 MHz, $CDCl_3$): 7.35 (d, J = 1.8 Hz, 1H), 6.31 (dd, J = 3.2, 1.8 Hz, 1H), 6.23 (d, J = 3.3 Hz, 1H), 5.78 (tdd, J = 17.1, 10.2, 7.1 Hz, 1H), 5.14 (m, 2H), 4.72 (t, J = 6.2 Hz, 1H), 2.60 (m, 2H), 2.16 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): 156.2, 142.2, 133.9, 118.8, 110.3, 106.3, 67.1, 40.3.

HRMS (CI): Calcd. for $C_8H_9O_2$ $(M-H)^+$: 138.0603, Found: 138.0604.

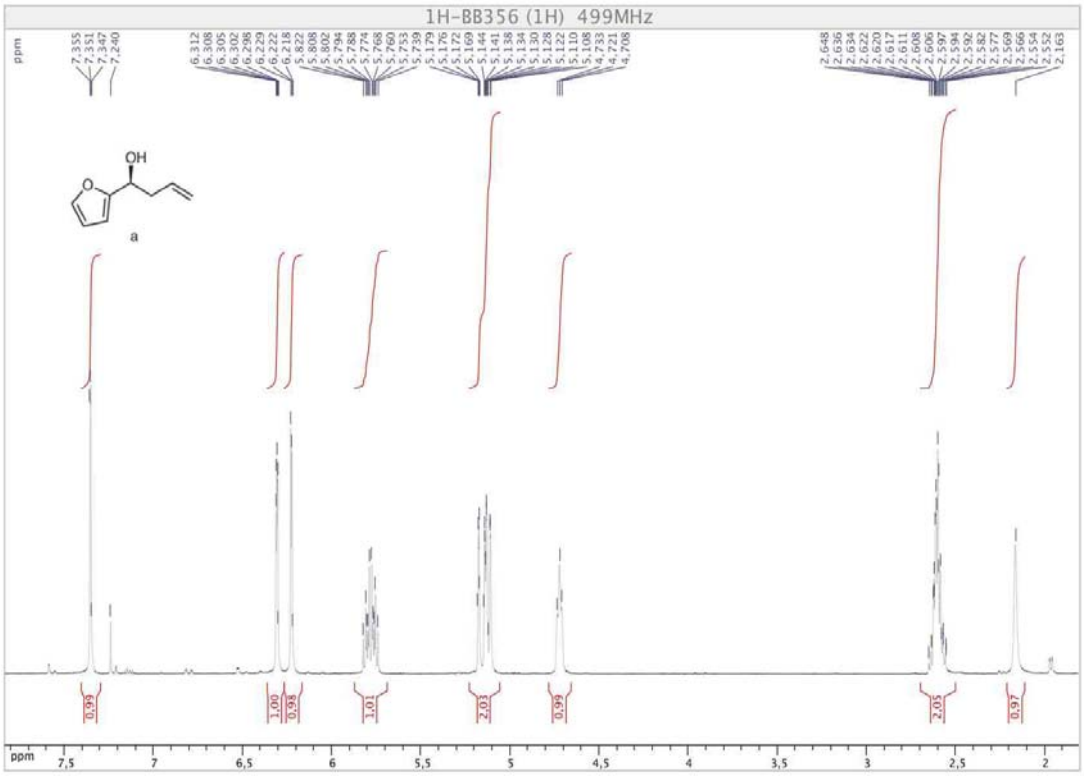
FTIR (neat): 3363, 3078, 2913, 1150, 1010, 918 cm^{-1}.

Opt. Rot. $[\alpha]_D^{26}$ = +30.5 (c = 0.688, in $CHCl_3$) for 93% ee (*R*)-**3a**, Lit.[4] $[\alpha]_D^{26}$ +24.9 (c = 1.0, $CHCl_3$) for 83% ee (*R*)-**3a**.

HPLC (Chiralcel AD-H column, Hexane:*i*-PrOH, 99.5:0.5, 0.5 mL/min, 210 nm): t_{minor} = 52.1 min, t_{major} = 55.0 min.

The spectroscopic properties of this compound are consistent with the data available in the literature.[4]

[4] S. E. Denmark, J. Fu, M. J. Lawler, *J. Org. Chem.* **2006**, *71*, 1523–1536.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5.169
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5.134
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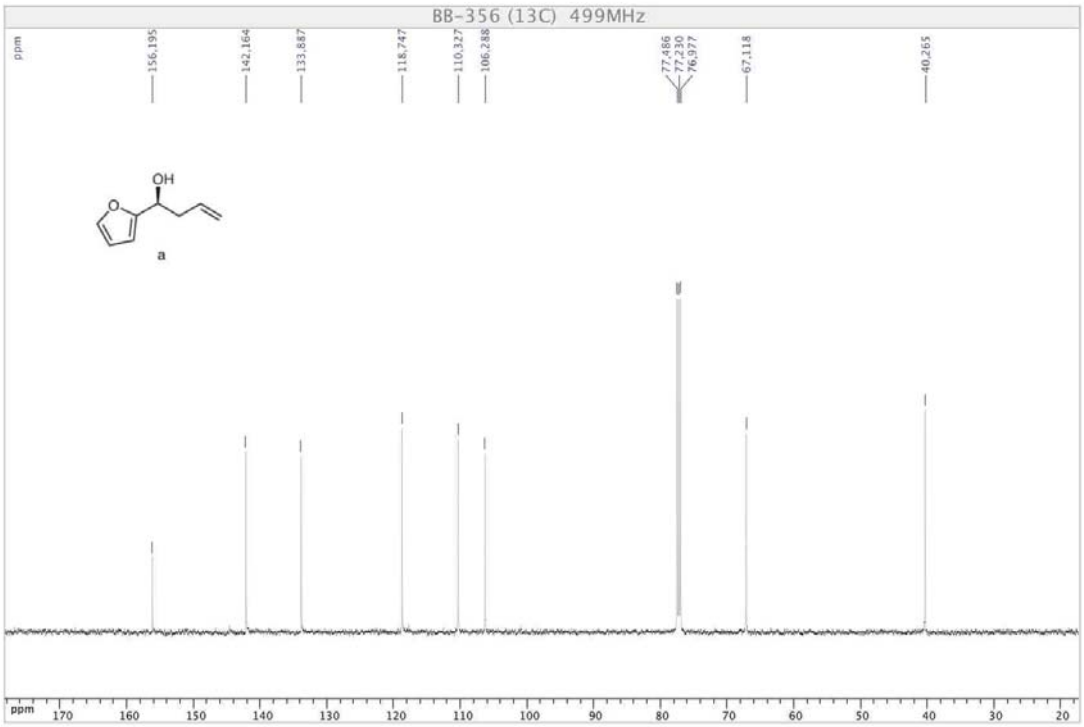
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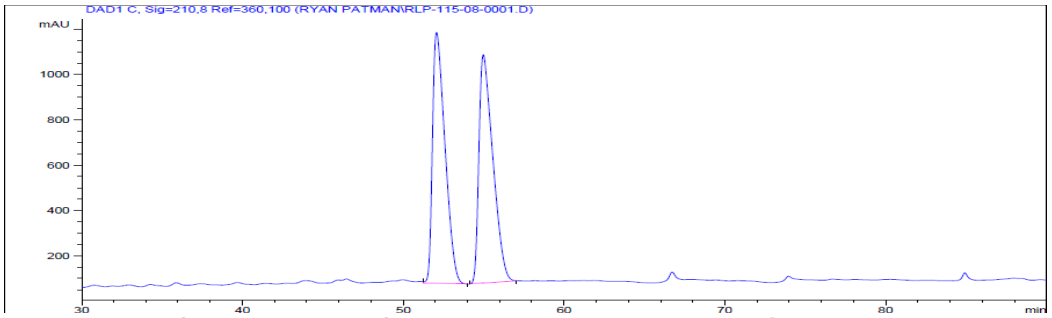

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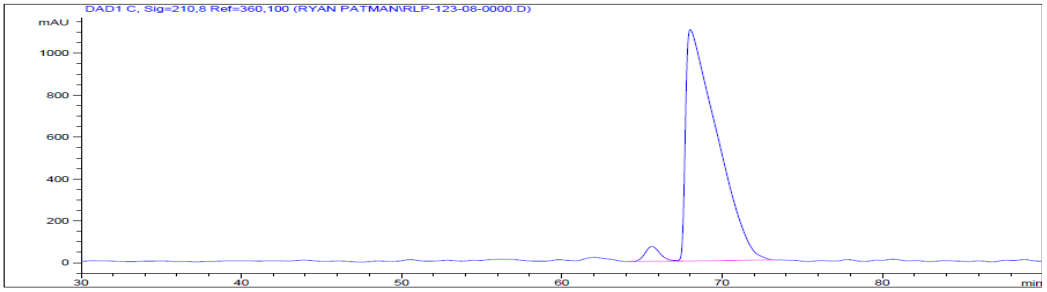

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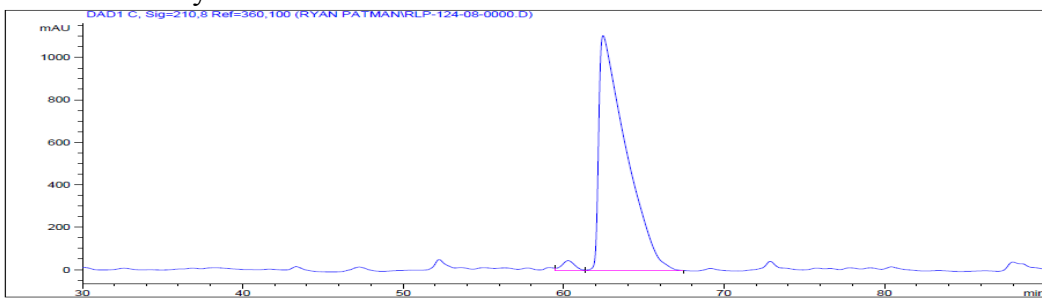
From the aldehyde oxidation level:



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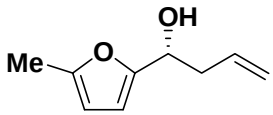
2	62.445	VB	1.5466	1.29634e5	1106.68933	98.0410

(*R*)-1-(5-methylfuran-2-yl)but-3-en-1-ol (3b)



Procedure A (*via* alcohol 1b): The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2: pentane:Et_2O, 5:1) to furnish the title compound (42.8 mg, 70% yield, 91% ee) as a colorless oil.

Procedure B (*via* aldehyde 2b): The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2: pentane:Et_2O, 5:1) to furnish the title compound (56.2 mg, 92% yield, 94% ee) as a colorless oil.

TLC (SiO_2): R_f (Hexane:Et_2O, 10:1) = 0.07.

^{1}H NMR (400 MHz, $CDCl_3$): 6.09 (d, J = 3.1 Hz, 1H), 5.87 (d, J = 2.9 Hz, 1H), 5.79 (dddd, J = 17.2, 10.2, 7.2, 6.9 Hz, 1H), 5.12 (m, 2H), 4.65 (t, J = 6.8 Hz, 1H), 2.58 (m, 2H), 2.25 (s, 3H), 2.10 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): 154.3, 151.9, 134.2, 118.5, 107.1, 106.2, 67.1, 40.2, 13.7.

HRMS (CI): Calcd. for $C_9H_{11}O_2$ $(M-H)^+$: 151.0759, Found: 151.0756.

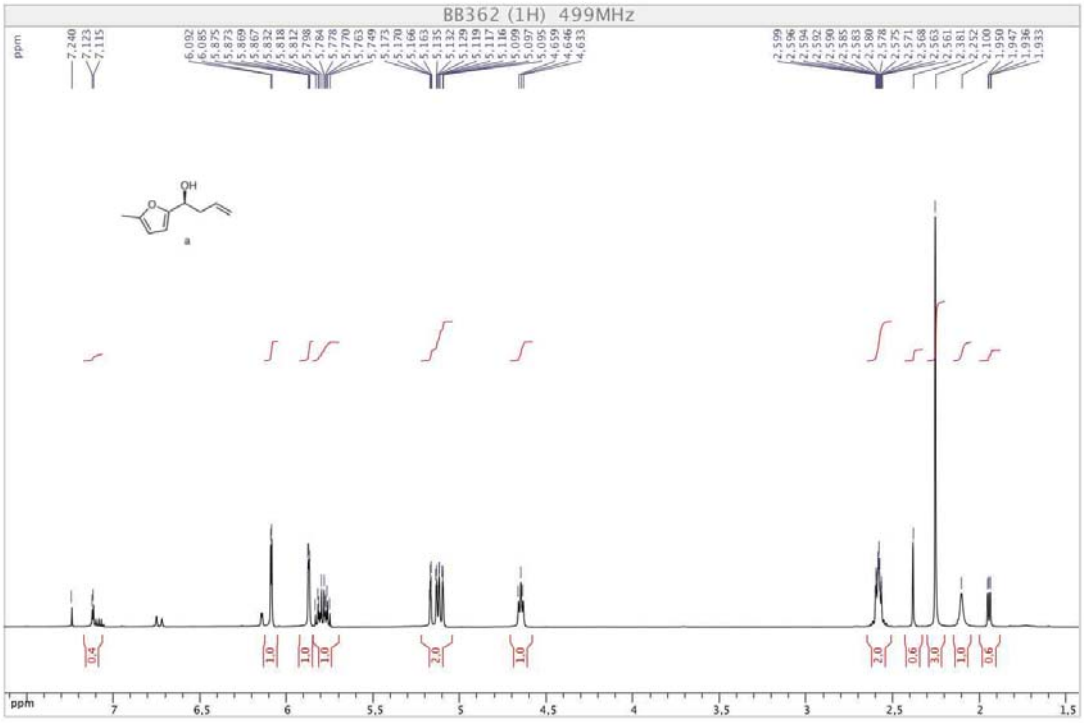
FTIR (neat): 3392, 3078, 2922, 1663, 1513, 1219, 914, 783 cm^{-1}.

Opt. Rot. $[\alpha]_D^{26}$ = -30.0 (c = 0.81, in CH_2Cl_2) for 95% ee (*R*)-**3b**, Lit.[5] $[\alpha]_D^{26}$ = -24.8 (c = 0.98, CH_2Cl_2) for 94% ee (*R*)-**3b**.

HPLC (Chiralcel OD-H column, Hexane:*i*-PrOH, 98:2, 0.5 mL/min, 210 nm): t_{major} = 17.2 min, t_{minor} = 18.2 min.

The spectroscopic properties of this compound are consistent with the data available in the literature.[5]

[5] J. Lu, S.-J. Ji, Y.-C. Teo, T.-P. Loh, *Org. Lett.* **2005**, *7*, 159–161.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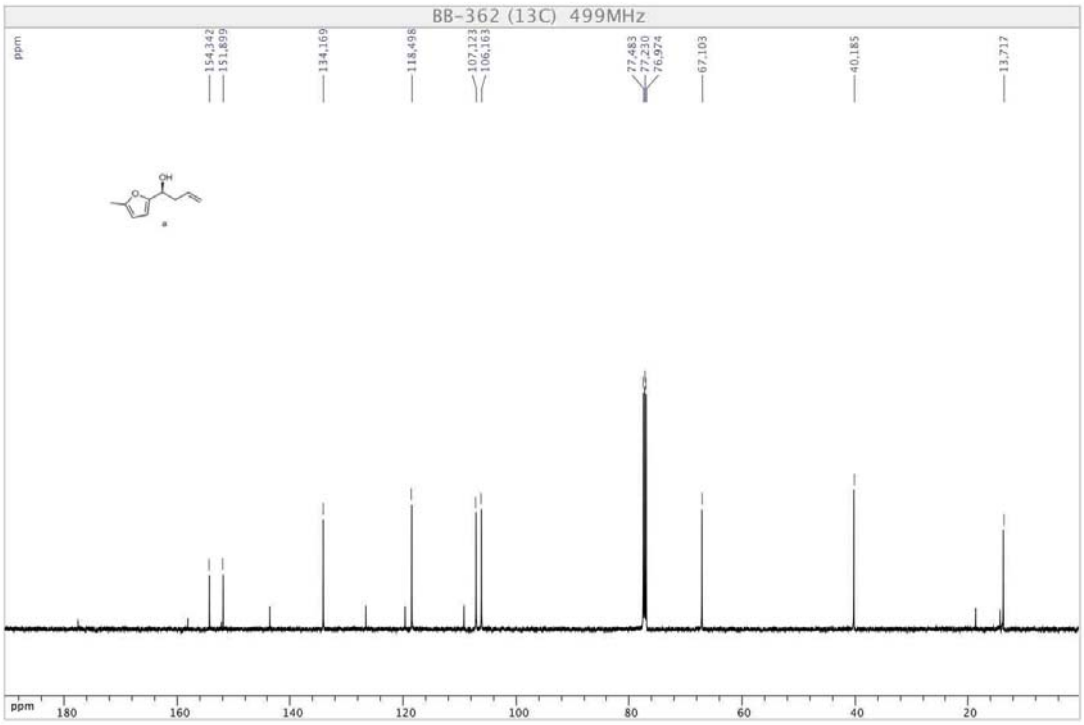
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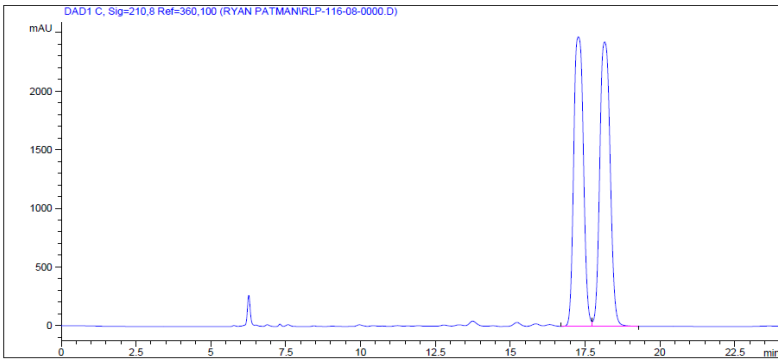

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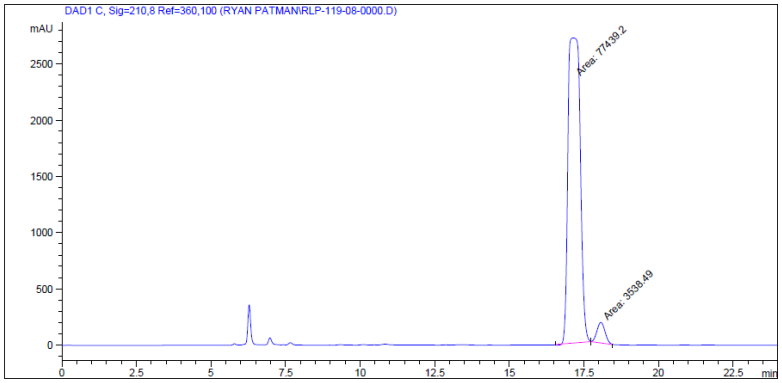

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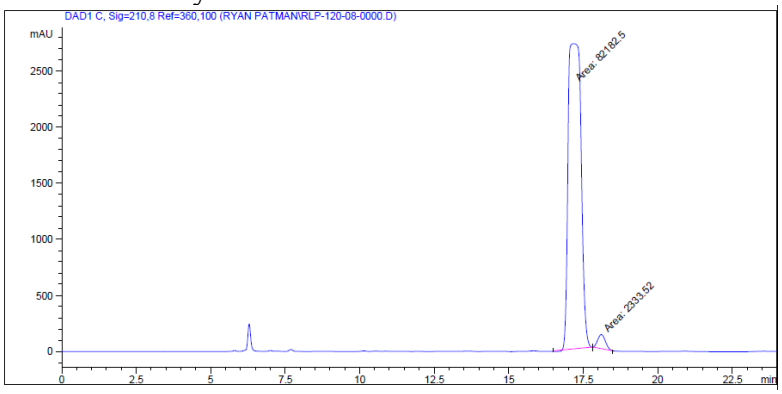
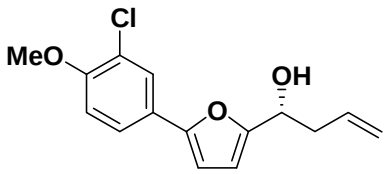


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.157	MM	0.5025	8.21825e4	2725.66284	97.2390
2	18.110	MM	0.3037	2333.51880	128.04263	2.7610

(*R*)-1-[5-(3-chloro-4-methoxyphenyl)furan-2-yl]but-3-en-1-ol (3c)



Procedure A (*via* alcohol 1c): The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2: hexane:Et_2O, 4:1) to furnish the title compound (94.9 mg, 85% yield, 96% ee) as a viscous yellow oil.

Procedure B (*via* aldehyde 2c): The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2: hexane:Et_2O, 4:1) to furnish the title compound (105 mg, 95% yield, 96% ee) as a viscous yellow oil.

TLC (SiO_2): R_f (Hexane:Et_2O, 3:1) = 0.20.

^{1}H NMR (400 MHz, $CDCl_3$): 7.65 (d, J = 2.2 Hz, 1H), 7.49 (dd, J = 8.6, 2.2 Hz, 1H), 6.91 (d, J = 8.6 Hz, 1H) 6.46 (d, J = 3.4 Hz, 1H), 6.30 (d, J = 3.4 Hz, 1H), 5.83 (tdd, J = 17.1, 10.2, 7.0, Hz, 1H), 5.18 (m, 2H), 4.77 (dd, J = 7.0, 5.8 Hz, 1H), 3.90 (s, 3H), 2.67 (m, 2H), 2.07 (s, 1H).

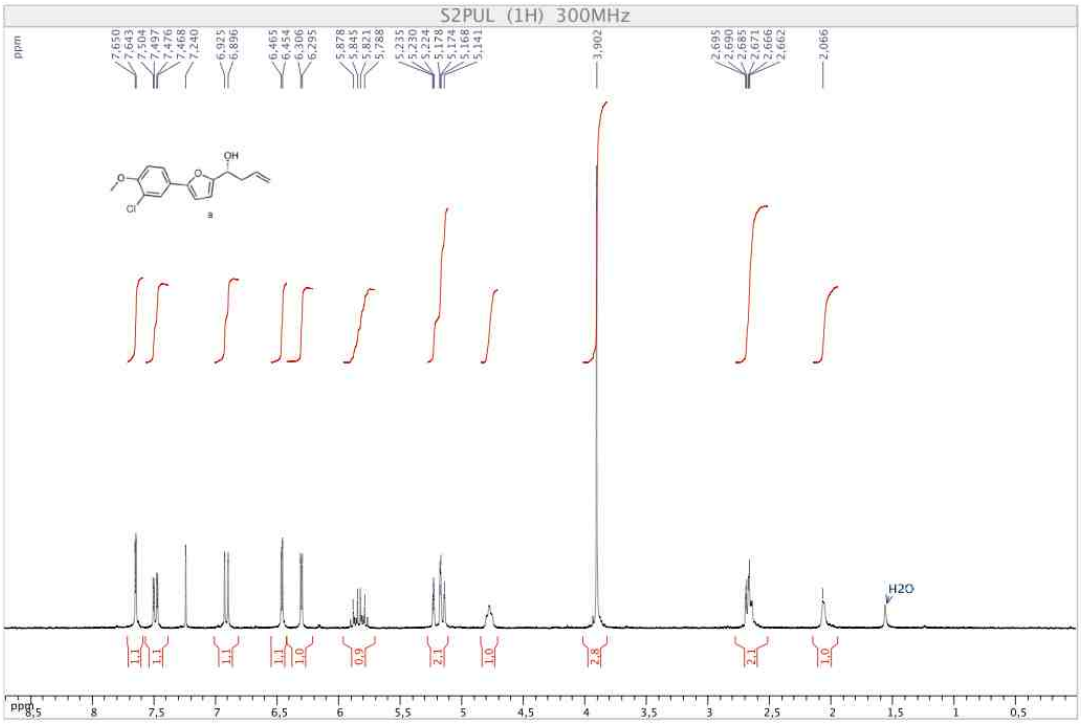
^{13}C NMR (100 MHz, $CDCl_3$): 155.6, 154.5, 152.3, 133.8, 126.0, 124.9, 123.4, 123.0, 119.0, 112.4, 108.6, 105.1, 67.2, 56.5, 40.4.

HRMS (CI): Calcd. for $C_{15}H_{14}O_3{}^{35}Cl$ $(M-H)^+$: 277.0631, Found: 277.0629.

FTIR (neat): 3383, 2940, 1658, 1613, 1490, 1475, 1266, 1062, 1019, 786, 736, 708 cm^{-1}.

Opt. Rot. $[\alpha]_D^{26}$ = +18.8 (c = 0.75, in $CHCl_3$) for 97% ee (*R*)-**3c**.

HPLC (Chiralcel AS-H column, Hexane:*i*-PrOH, 95:5, 0.5 mL/min, 210 nm): t_{minor} = 26.9 min, t_{major} = 34.0 min.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6,306
6,295
5,878
5,845
5,821
5,788
5,235
5,230
5,224
5,178
5,174
5,168
5,141
3,902
2,695
2,690
2,685
2,671
2,666
2,662
2,066
OH
O
O
Cl
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H2O
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1,0
0,9
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1,0
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2,1
1,0
ppm
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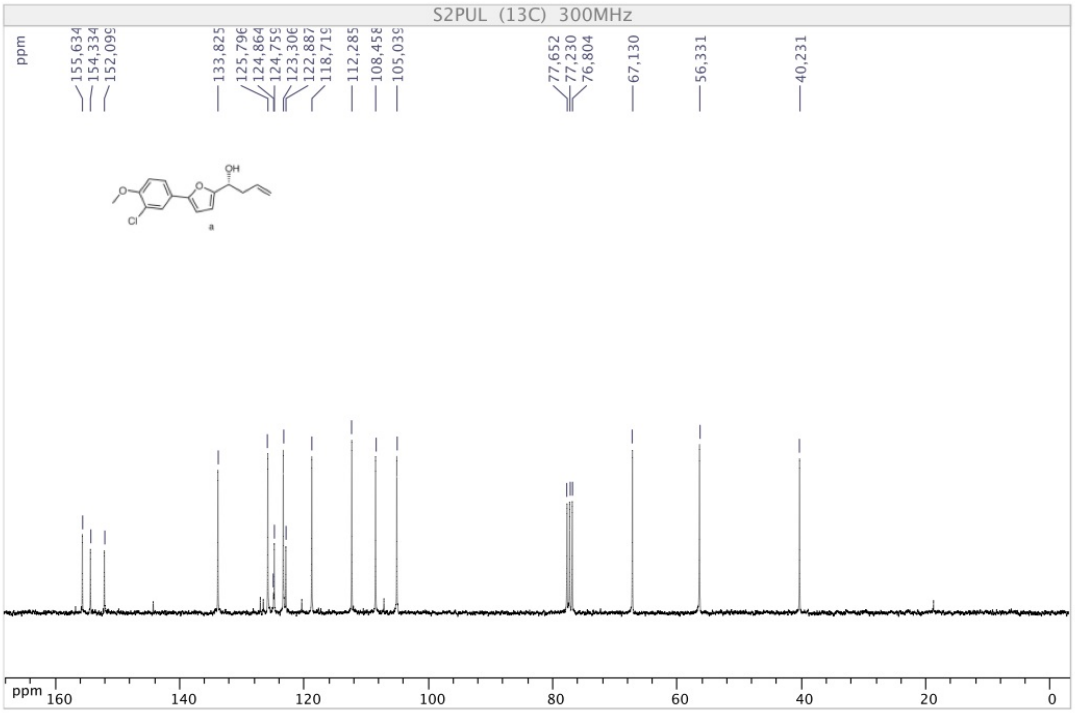
1
0,5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76,804
67,130
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40,231
OH
O
O
Cl
a
ppm
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140
120
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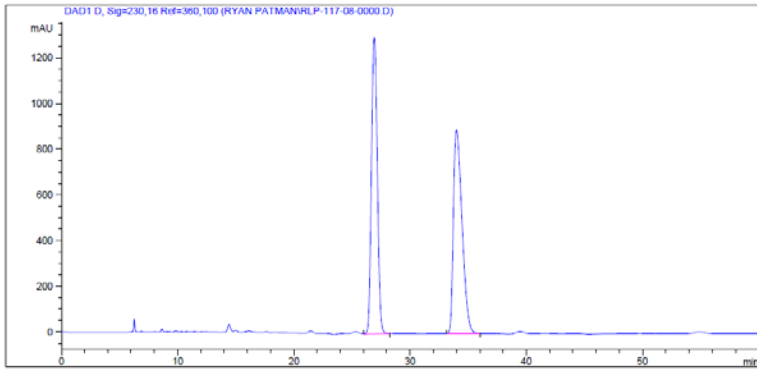
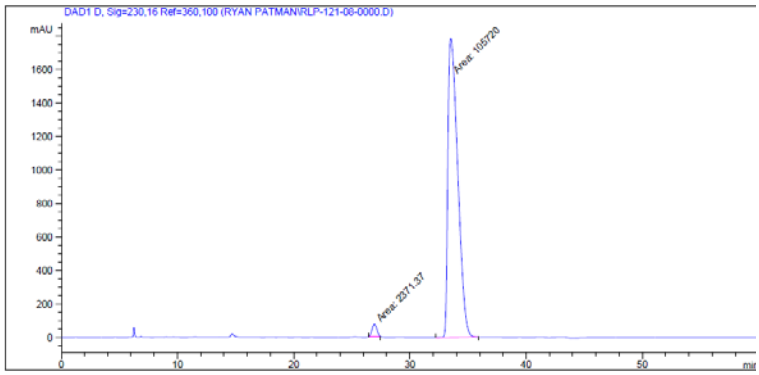
80
60
40
20
0



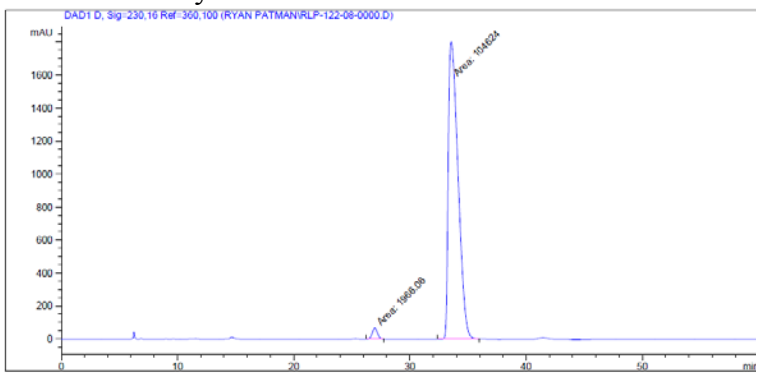
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.904	VB	0.5572	4.55784e4	1299.35779	49.6921
2	33.980	BB	0.8111	4.61432e4	892.63361	50.3079

From the alcohol oxidation level:



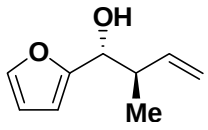
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.937	MM	0.5005	2371.36646	78.95996	2.1938
2	33.511	MM	0.9844	1.05720e5	1789.92944	97.8062

From the aldehyde oxidation level:



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.967	MM	0.4926	1966.05969	66.52432	1.8445
2	33.541	MM	0.9687	1.04624e5	1800.02209	98.1555

(1*R*,2*R*)-1-(furan-2-yl)-2-methylbut-3-en-1-ol (4a)



Procedure C (*via* alcohol 1a): The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2: pentane:Et_2O, 5:1) to furnish the title compound (47.1 mg, 77% yield, 10:1 dr, 92% ee) as a colorless oil.

Procedure D (*via* aldehyde 2a): The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2: pentane:Et_2O, 5:1) to furnish the title compound (43.9 mg, 72% yield, >20:1 dr, 97% ee) as a colorless oil.

TLC (SiO_2): R_f (Hexane:Et_2O, 5:1) = 0.09.

^{1}H NMR (400 MHz, $CDCl_3$): 7.36 (d, J = 1.8 Hz, 1H), 6.31 (dd, J = 3.3, 1.9 Hz, 1H), 6.25 (d, J = 3.2 Hz, 1H), 5.78 (ddd, J = 17.2, 10.3, 8.1 Hz, 1H), 4.40 (d, J = 7.8 Hz, 1H), 2.68 (sext, J = 7.3 Hz, 1H), 2.13 (s, 1H), 0.92 (d, J = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 155.2, 142.2, 140.2, 117.2, 110.3, 107.5, 71.6, 43.8, 16.4.

HRMS (CI): Calcd. for $C_9H_{11}O_2$ $(M-H)^+$: 151.0759, Found: 151.0757.

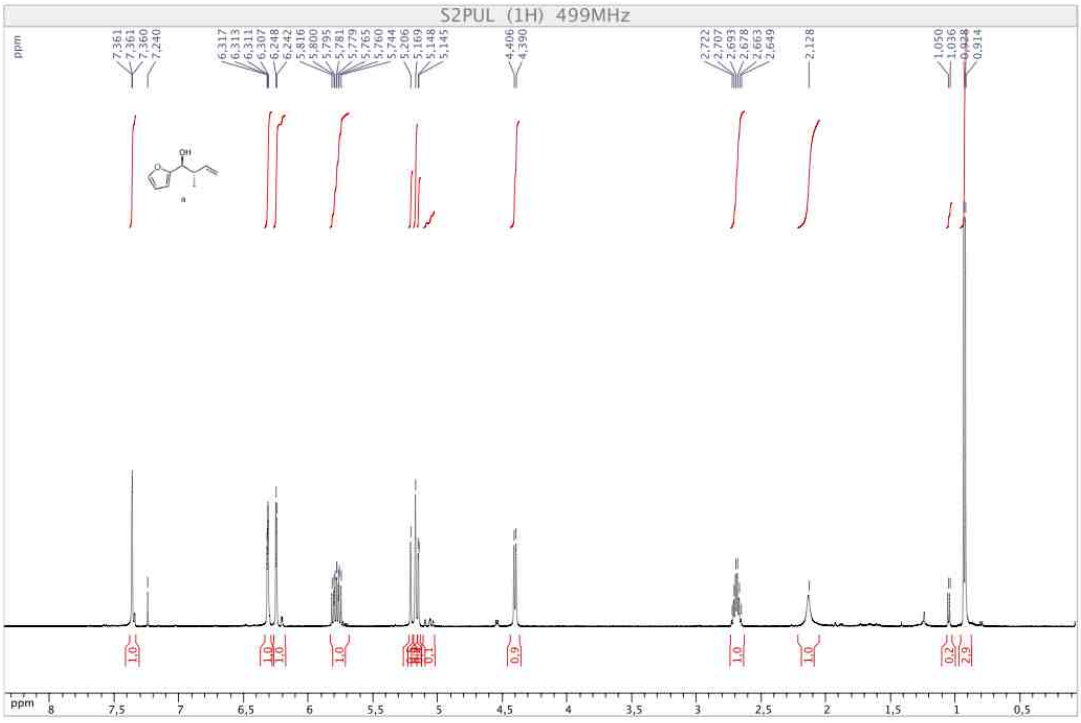
FTIR (neat): 3398, 2973, 2931, 1073, 1007, 913 cm^{-1}.

Opt. Rot. $[\alpha]_D^{26}$ = +126.5 (c = 0.15, in $CHCl_3$) for 95% ee

HPLC (Chiralcel AS-H column, Hexane:*i*-PrOH, 99:1, 0.5 mL/min, 210 nm): t_{major} = 21.4 min, t_{minor} = 22.9 min.

The spectroscopic properties of this compound are consistent with the data available in the literature.[6]

[6] M. Tsubuki, T. Kamata, M. Nakatani, K. Yamazaki, T. Matsui, T. Honda, *Tetrahedron: Asymmetry* **2000**, *11*, 4725-4736.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6.311
6.307
6.248
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5.779
5.765
5.760
5.744
5.206
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5.148
5.145
4.406
4.390
2.722
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2.663
2.649
2.128
1.050
1.036
0.928
0.914
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1.0
1.0
0.1
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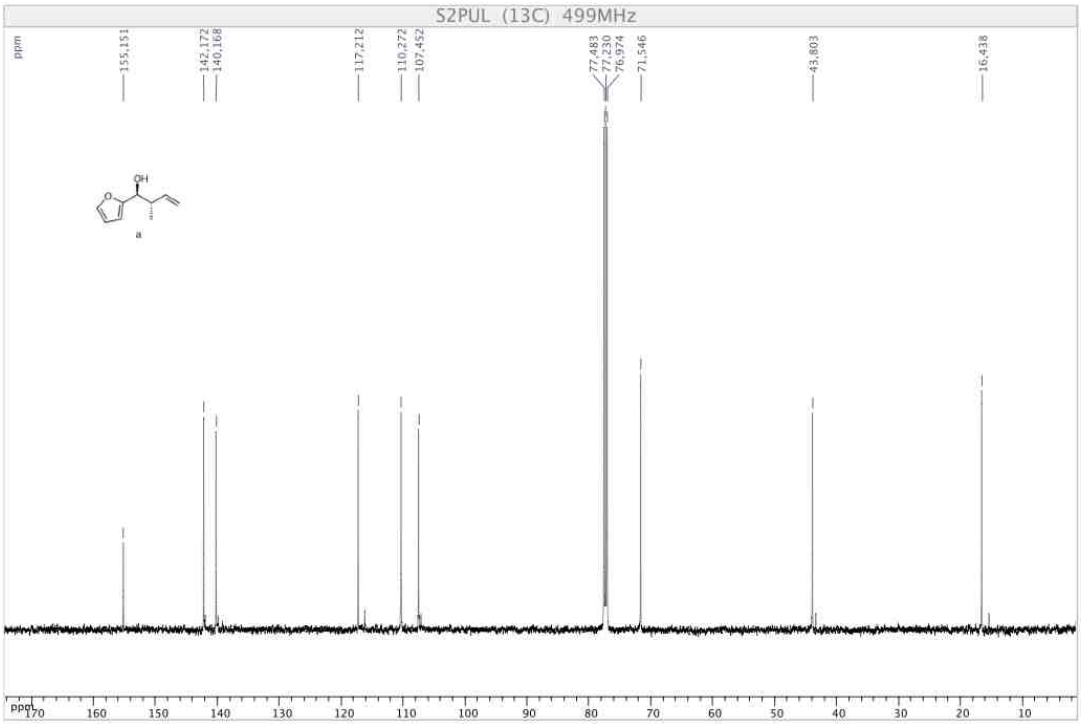
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150
140
130
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80
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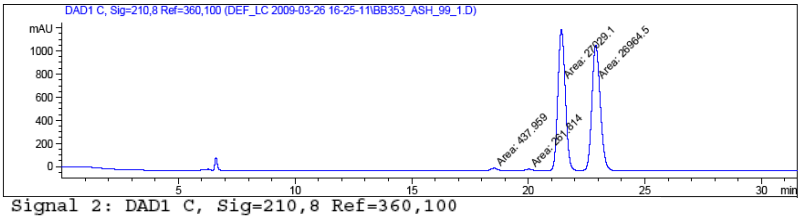
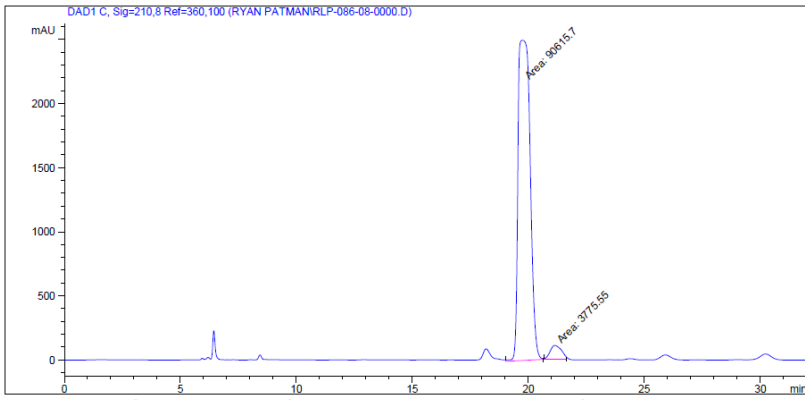
30
20
10



Signal 2: DAD1 C, Sig=210,8 Ref=360,100

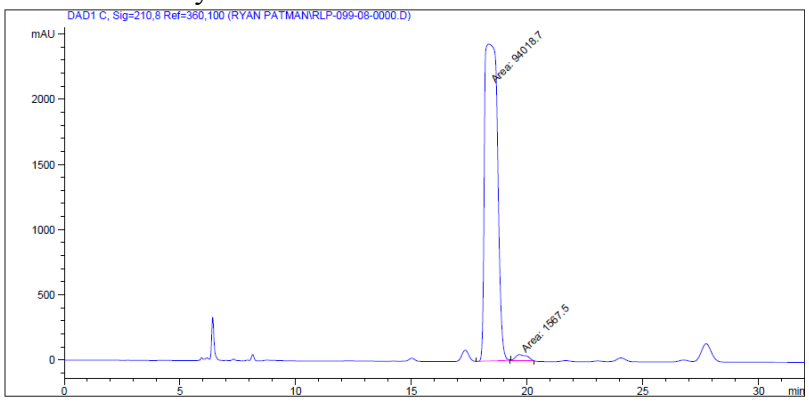
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.519	MM T	0.3414	437.95856	21.38206	0.8008
2	20.011	MM T	0.3443	261.81375	12.67479	0.4787
3	21.413	MM T	0.3703	2.70291e4	1216.39795	49.4193
4	22.886	MM T	0.4145	2.69645e4	1084.21619	49.3012
Totals :				5.46934e4	2334.67098	

From the alcohol oxidation level:



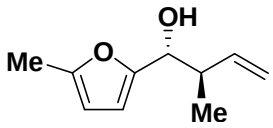
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.756	MM	0.6045	9.06157e4	2498.32495	96.0001
2	21.133	MM	0.5759	3775.55396	109.27399	3.9999

From the aldehyde oxidation level:



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.341	MM	0.6439	9.40187e4	2433.46191	98.3601
2	19.654	MM	0.5769	1567.49866	45.28896	1.6399

(1*R*,2*R*)-2-methyl-1-(5-methylfuran-2-yl)but-3-en-1-ol (4b)



Procedure C (*via* alcohol 1b): The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2: pentane:Et_2O, 5:1) to furnish the title compound (50.3 mg, 76% yield, 7:1 dr, 91% ee) as a colorless oil.

Procedure D (*via* aldehyde 2b): The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2: pentane:Et_2O, 5:1) to furnish the title compound (52.6 mg, 79% yield, >20:1 dr, 94% ee) as a colorless oil.

TLC (SiO_2): R_f (Hexane:Et_2O, 5:1) = 0.09.

^{1}H NMR (400 MHz, $CDCl_3$): 6.11 (d, J = 3.2 Hz, 1H), 5.88 (d, J = 3.2 Hz, 1H), 5.79 (ddd, J = 17.3, 10.3, 8.1 Hz, 1H), 5.17 (m, 2H), 4.31 (dd, J = 8.1, 3.8 Hz, 1H), 2.67 (sext, J = 7.3 Hz, 1H), 2.26 (s, 3H), 2.06 (d, J = 4.0 Hz, 1H), 0.92 (d, J = 6.8 Hz, 3H).

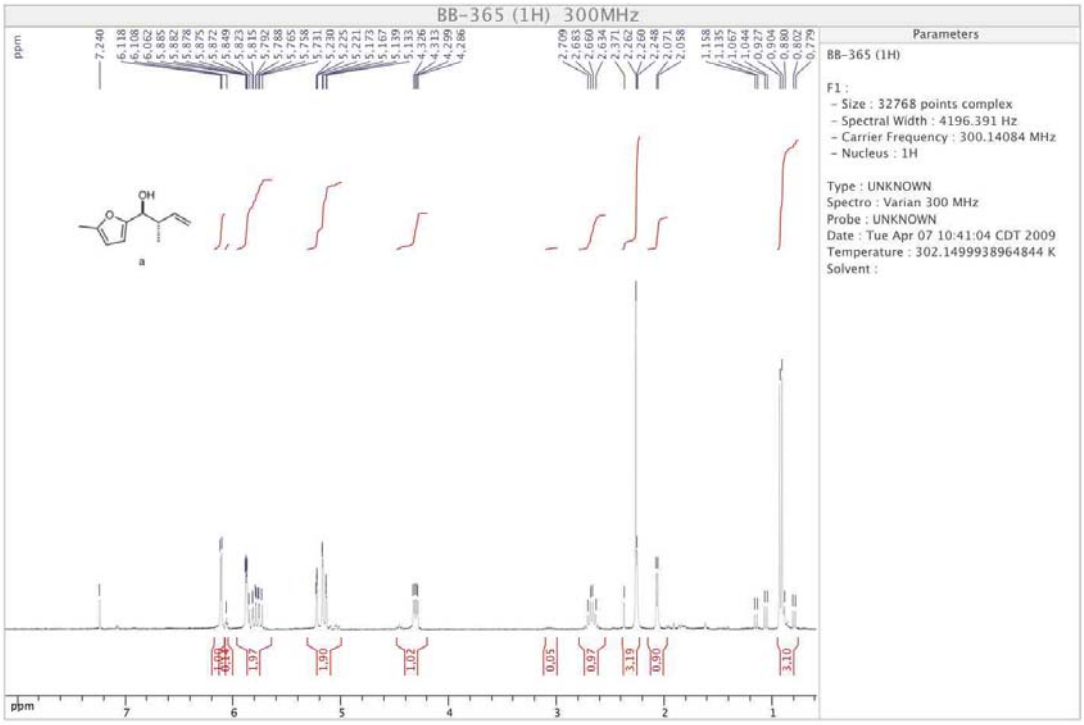
^{13}C NMR (100 MHz, $CDCl_3$): 153.2, 151.9, 140.5, 117.1, 108.4, 106.1, 71.6, 43.7, 16.7, 13.8.

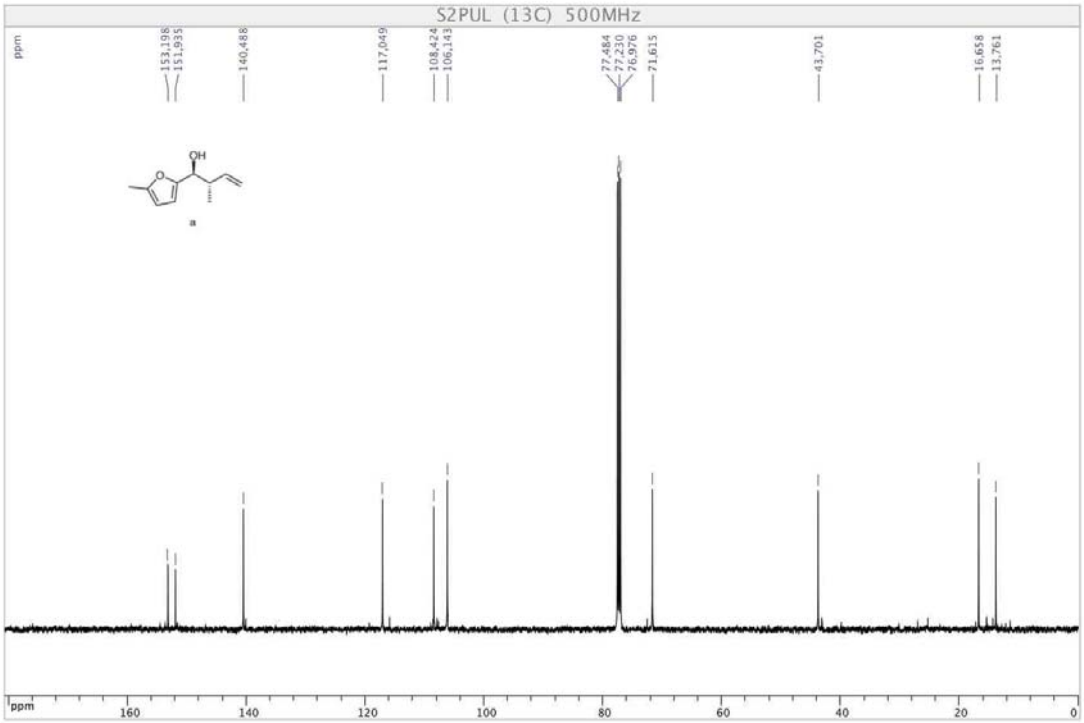
HRMS (CI): Calcd. for $C_{10}H_{13}O_2$ $(M-H)^+$: 165.0916, Found: 165.0916.

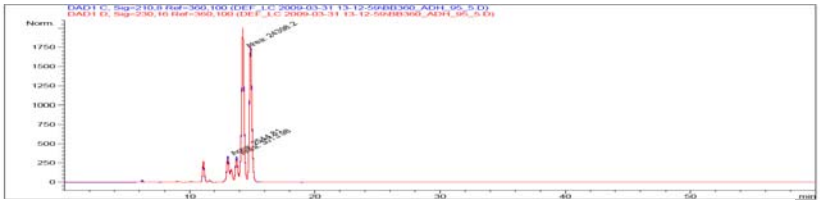
FTIR (neat): 3414, 2965, 2924, 1219, 1017, 912 cm^{-1}.

Opt. Rot. $[\alpha]_D^{26}$ = +69.1 (c = 0.58, in $CHCl_3$) for 88% ee

HPLC (Chiralcel AD-H column, hexane:*i*-PrOH, 95:5, 0.5 mL/min, 210 nm): t_{minor} = 14.2 min, t_{major} = 14.9 min


BB-365 (1H) 300MHz
Parameters
BB-365 (1H)
F1 :
- Size : 32768 points complex
- Spectral Width : 4196.391 Hz
- Carrier Frequency : 300.14084 MHz
- Nucleus : 1H
Type : UNKNOWN
Spectro : Varian 300 MHz
Probe : UNKNOWN
Date : Tue Apr 07 10:41:04 CDT 2009
Temperature : 302.1499938964844 K
Solvent :
ppm

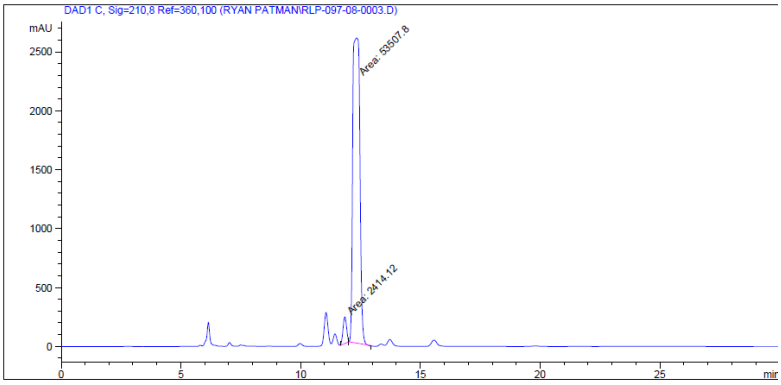

S2PUL (13C) 500MHz
ppm



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

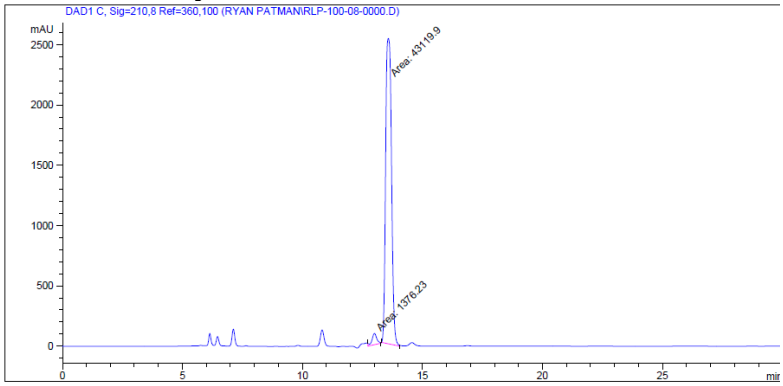
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.037	MM T	0.1679	2544.80933	252.56302	4.7655
2	13.741	MM T	0.1848	3013.97974	271.80624	5.6441
3	14.245	MM T	0.2182	2.43982e4	1863.61255	45.6893
4	14.863	MM R	0.2277	2.34432e4	1715.61096	43.9010

From the alcohol oxidation level:



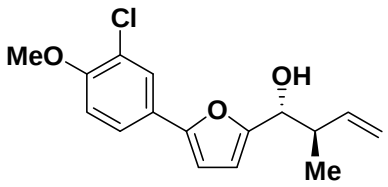
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.842	MM	0.1753	2414.11572	229.53998	4.3169
2	12.336	MM	0.3439	5.35078e4	2593.21167	95.6831

From the aldehyde oxidation level:



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.994	MM	0.2388	1376.22986	96.07098	3.0929
2	13.571	MM	0.2836	4.31199e4	2534.23608	96.9071

(1*R*,2*R*)-1-[5-(3-chloro-4-methoxyphenyl)furan-2-yl]-2-methylbut-3-en-1-ol (4c)



Procedure C (*via* alcohol 1c): The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2: hexane:Et_2O, 4:1) to furnish the title compound (111 mg, 95% yield, 10:1 dr, 95% ee) as a viscous yellow oil.

Procedure D (*via* aldehyde 2c): The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2: hexane:Et_2O, 4:1) to furnish the title compound (110 mg, 94% yield, >20:1 dr, 99% ee) as a viscous yellow oil.

TLC (SiO_2): R_f (Hexane:EtOAc, 3:1) = 0.14.

^{1}H NMR (400 MHz, $CDCl_3$): 7.64 (d, J = 2.2 Hz, 1H), 7.48 (dd, J = 8.6, 2.1 Hz, 1H), 6.90 (d, J = 8.7 Hz, 1H), 6.46 (d, J = 3.5 Hz, 1H), 6.31 (d, J = 3.3 Hz, 1H), 5.82 (ddd, J = 17.3, 10.3, 8.0 Hz, 1H), 5.19 (m, 2H), 4.44 (dd, J = 7.8, 2.7 Hz, 1H), 3.90 (s, 3H), 2.75 (m, 1H), 2.16 (d, J = 3.0 Hz, 1H), 0.98 (d, J = 6.8 Hz, 3H).

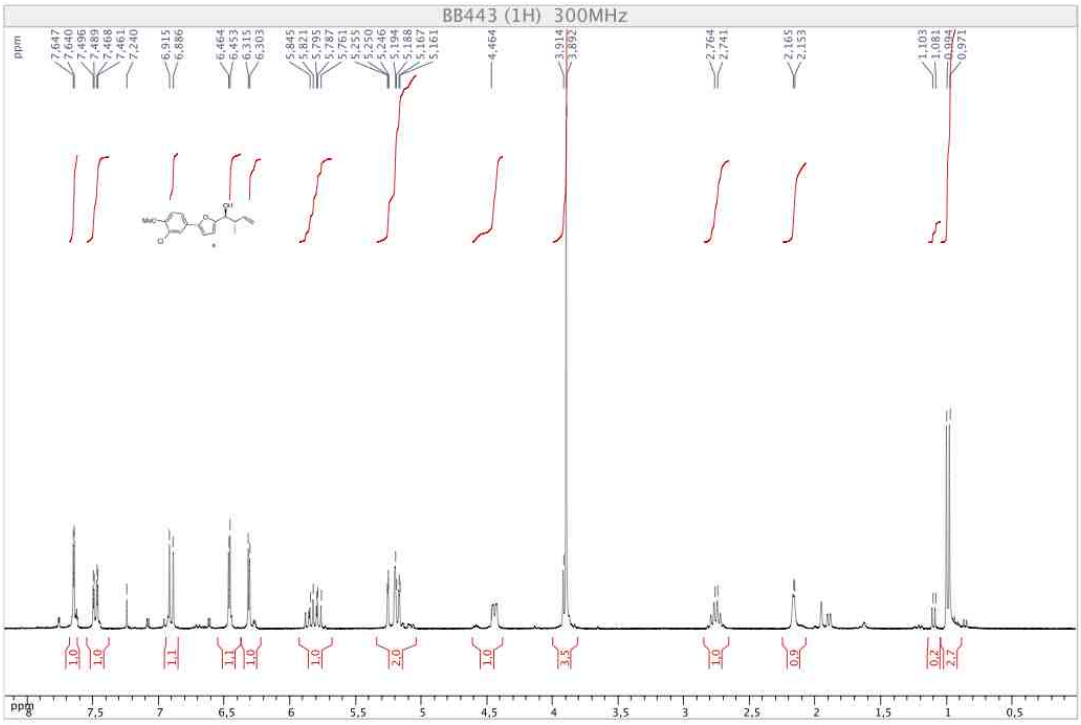
^{13}C NMR (100 MHz, $CDCl_3$): 154.7, 154.4, 152.2, 140.1, 125.9, 124.9, 123.4, 123.0, 117.3, 112.3, 109.6, 105.1, 71.7, 56.4, 43.8, 16.6.

HRMS (CI): Calcd. for $C_{16}H_{18}O_3{}^{35}Cl$ $(M+H)^+$: 293.0944, Found: 293.0946.

FTIR (neat): 3427, 2967, 1490, 1439, 1289, 1267, 1062, 1018, 909, 788, 730, 709 cm^{-1}.

Opt. Rot. $[\alpha]_D^{26}$ = +4.7 (c = 1.07, in $CHCl_3$) for 83% ee

HPLC (Chiralcel AD-H column, Hexane:*i*-PrOH, 98:2, 0.8 mL/min, 210 nm): t_{major} = 28.4 min, t_{minor} = 34.2 min.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5,167
5,161
4,464
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2,7
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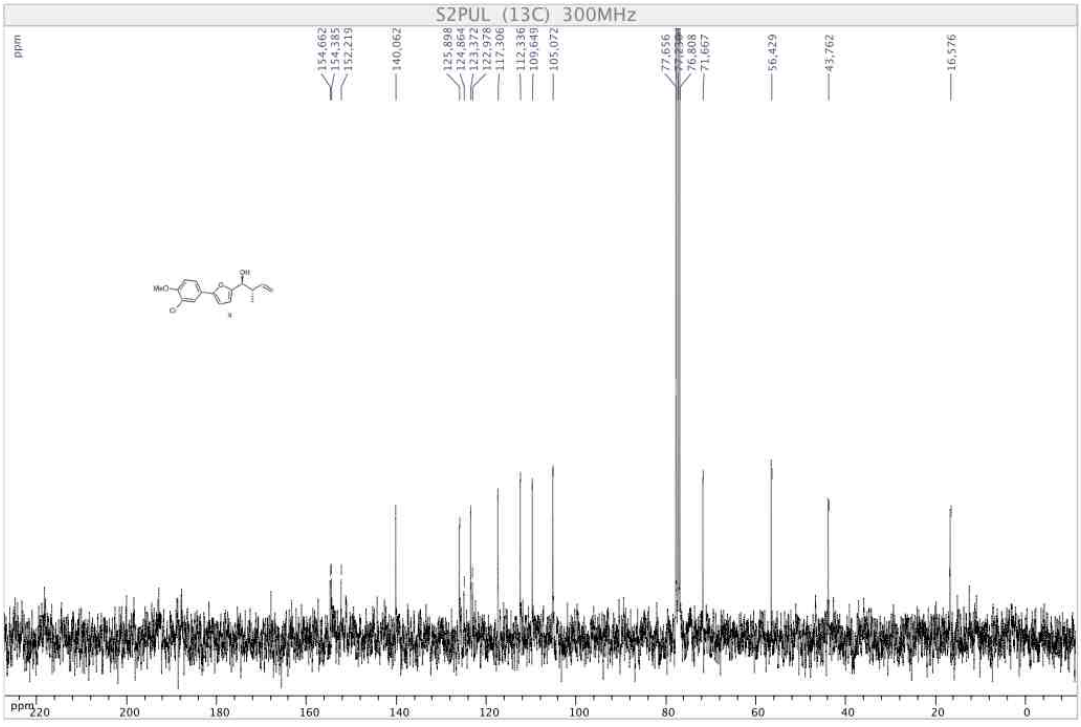
1
0,5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76,808
71,667
56,429
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16,376
ppm
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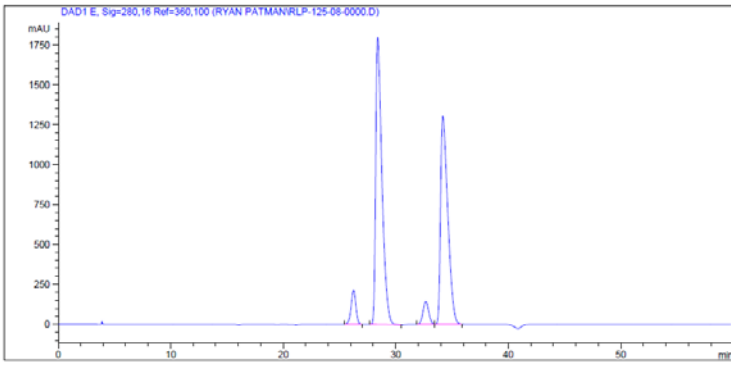
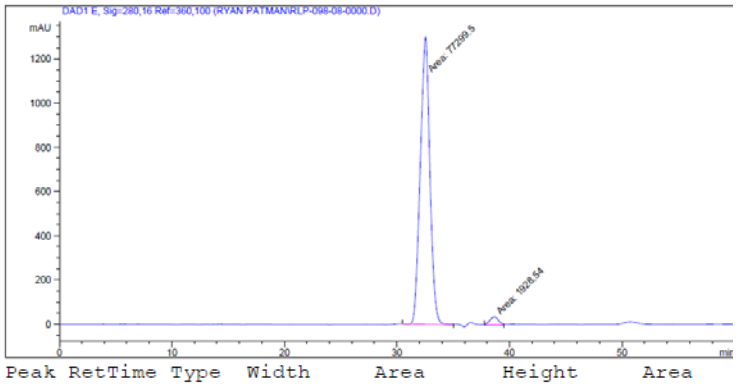
160
140
120
100
80
60
40
20
0



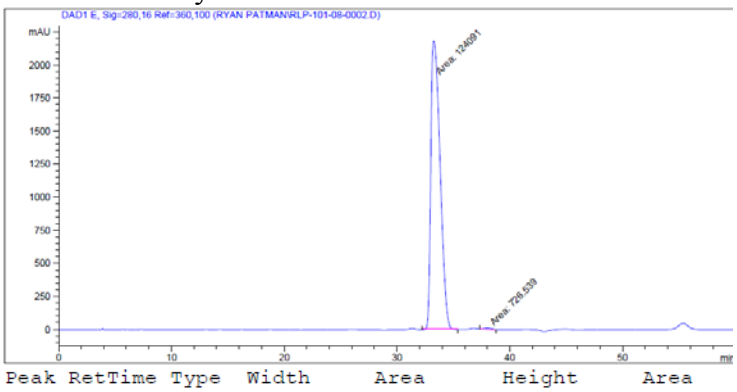
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.231	BB	0.4536	6320.72314	214.58772	4.5532
2	28.380	BB	0.5759	6.93016e4	1797.28894	49.9218
3	32.646	BV	0.5539	5061.10547	142.67514	3.6458
4	34.166	VB	0.6776	5.81370e4	1305.43762	41.8793

From the alcohol oxidation level:



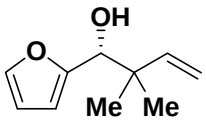
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.527	MM	0.9909	7.72995e4	1300.20459	97.5658
2	38.642	MM	0.8857	1928.54309	36.29213	2.4342

From the aldehyde oxidation level:



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.244	MM	0.9481	1.24091e5	2181.28174	99.4179
2	38.040	MM	0.9231	726.53894	13.11822	0.5821

(*R*)-1-(furan-2-yl)-2,2-dimethylbut-3-en-1-ol (5a)



Procedure E (*via* alcohol 1a): Reaction was conducted on 0.4 mmol scale with respect to alcohol. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2: hexane:EtOAc, 10:1) to furnish the title compound (54.5 mg, 82% yield, 87% ee) as a colorless oil.

Procedure F (*via* aldehyde 2a): Reaction was conducted on 0.4 mmol scale with respect to aldehyde. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2: hexane:EtOAc, 10:1) to furnish the title compound (54.5 mg, 82% yield, 88% ee) as a colorless oil.

TLC (SiO_2): R_f (Hexane:Et_2O, 10:1) = 0.18.

^{1}H NMR (400 MHz, $CDCl_3$): 7.33 (m, 1H), 6.31 (dd, J = 3.1, 1.7 Hz, 1H), 6.20 (d, J = 3.2 Hz, 1H), 5.90 (dd, J = 17.5, 10.9 Hz, 1H), 5.10 (m, 2H), 4.39 (s, 1H), 2.02 (s, 1H), 1.05 (s, 3H), 1.00 (s, 3H).

HRMS (CI): Calcd. for $C_{10}H_{15}O_2$ $(M+H)^+$: 167.1072, Found: 167.1077.

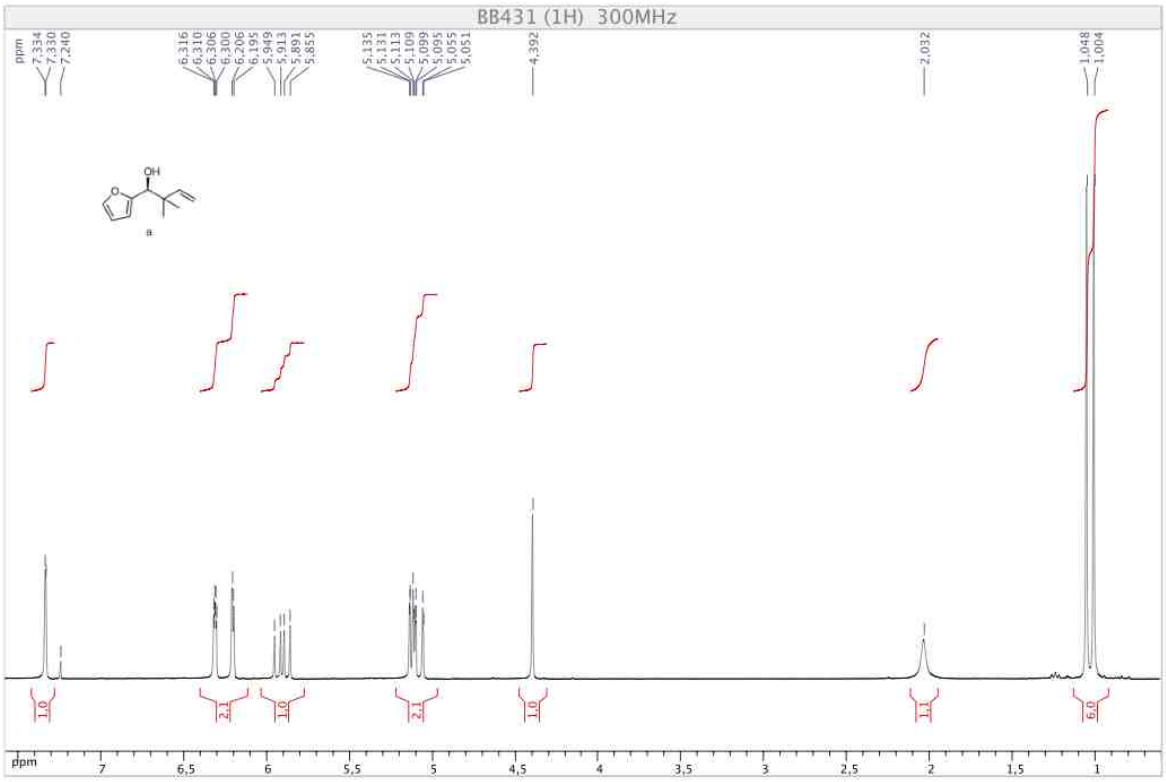
FTIR (neat): 3435, 2966, 2873, 1638, 1469, 1149, 1007, 915, 731 cm^{-1}.

Opt. Rot. $[\alpha]_D^{26}$ = +78.4 (c = 0.97, in Ethanol), Lit.[7] $[\alpha]_D^{26}$ = -15.1 (c = 1.00, in ethanol) for 95% ee (*S*)-**5a**.

HPLC (Chiralcel AD-H column, Hexane:*i*-PrOH, 98:2, 0.5 mL/min, 210 nm): t_{major} = 19.0 min, t_{minor} = 19.9 min.

The spectroscopic properties of this compound are consistent with the data available in the literature.[7]

[7] S. E. Denmark, J. Fu, M. J. Lawler, *J. Org. Chem.* **2006**, *71*, 1523–1536.


BB431 (1H) 300MHz
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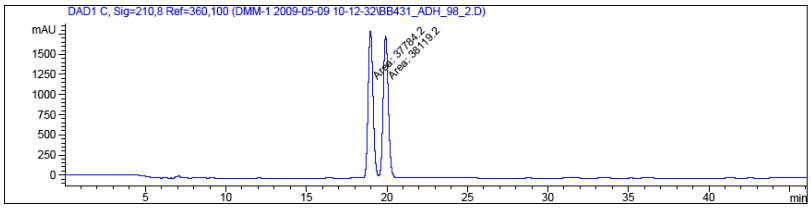
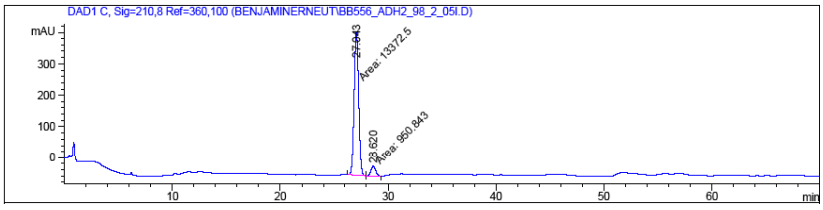
7.330
7.240
6.316
6.310
6.306
6.300
6.206
6.195
5.949
5.913
5.891
5.855
5.135
5.131
5.113
5.109
5.099
5.095
5.055
5.051
4.392
2.032
1.048
1.004
OH
a
1.0
2.1
1.0
2.1
1.0
1.1
6.0
ppm
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.977	MM T	0.3470	3.77842e4	1814.89001	49.7794
2	19.916	MM T	0.3631	3.81192e4	1749.71460	50.2206
Totals :				7.59033e4	3564.60461	

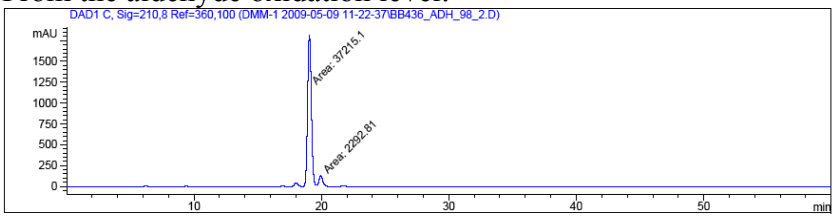
From the alcohol oxidation level:



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.043	MM T	0.4844	1.33725e4	460.13919	93.3616
2	28.620	MM T	0.4986	950.84259	31.78444	6.6384

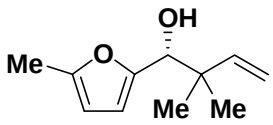
From the aldehyde oxidation level:



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.049	MM T	0.3411	3.72151e4	1818.16675	94.1966
2	19.948	MM T	0.3245	2292.80566	117.75801	5.8034
Totals :				3.95079e4	1935.92476	

(*R*)-2,2-dimethyl-1-(5-methylfuran-2-yl)but-3-en-1-ol (5b)



Procedure E (*via* alcohol 1b): The reaction was conducted on 0.6 mmol scale with respect to alcohol. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, hexane:EtOAc, 10:1) to furnish the title compound (90.7 mg, 84% yield, 84% ee) as a colorless oil.

Procedure F (*via* aldehyde 2b): The reaction was conducted on 0.6 mmol scale with respect to aldehyde. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, hexane:EtOAc, 10:1) to furnish the title compound (96.1 mg, 89% yield, 89% ee) as a colorless oil.

TLC (SiO_2): R_f (Hexane:Et_2O, 10:1) = 0.22.

^{1}H NMR (400 MHz, $CDCl_3$): 6.07 (d, J = 3.0 Hz, 1H), 5.92 (dd, J = 17.4, 10.9 Hz, 1H), 5.88 (d, J = 3.0 Hz, 1H), 5.11 (dd, J = 10.9, 1.3 Hz, 1H), 5.09 (dd, J = 17.4, 1.2 Hz, 1H), 4.32 (d, J = 5.0 Hz, 1H), 2.25 (s, 3H), 1.99 (d, J = 5.3 Hz, 1H), 1.05 (s, 3H), 1.01 (s, 3H).

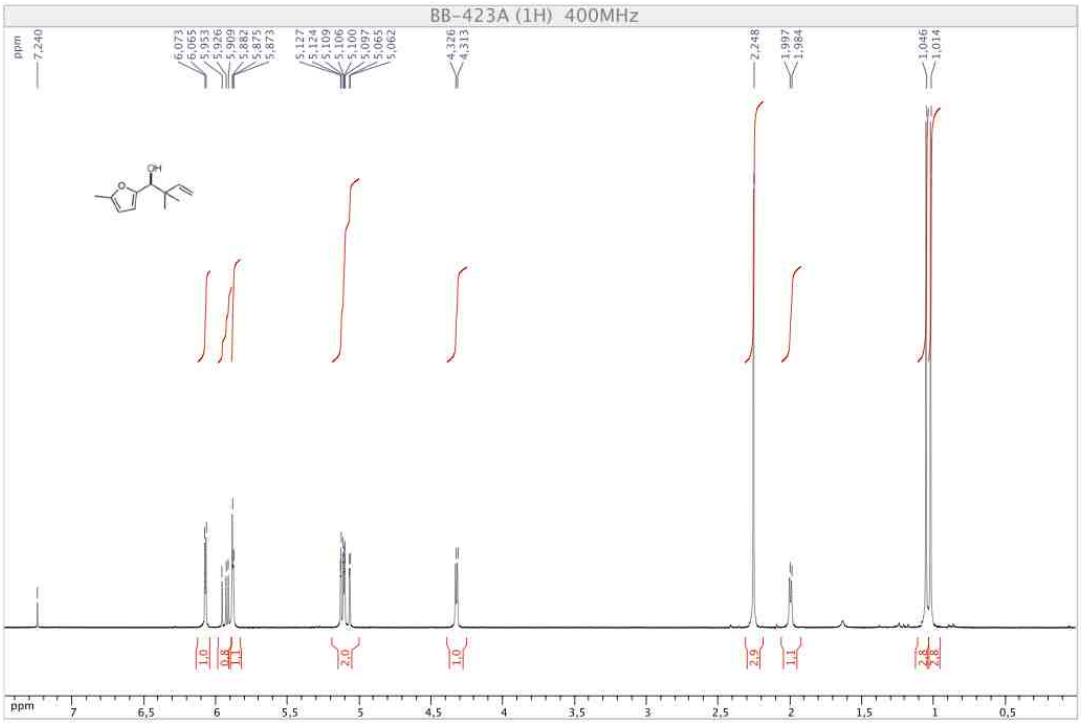
^{13}C NMR (100 MHz, $CDCl_3$): 153.0, 151.4, 144.8, 114.0, 108.5, 106.1, 75.3, 42.3, 24.1, 22.4, 13.8.

HRMS (CI): Calcd. for $C_{11}H_{16}O_2$ $(M)^+$: 180.1150, Found: 180.1147.

FTIR (neat): 3439, 2964, 2924, 2873, 1638, 1560, 1380, 1057, 1019, 913, 783 cm^{-1}.

Opt. Rot. $[\alpha]_D^{26}$ = +59.8 (c = 1.14, in $CHCl_3$).

HPLC (Chiralcel AD-H column, hexane:*i*-PrOH, 95:5, 0.5 mL/min, 210 nm): t_{major} = 12.4 min, t_{minor} = 13.4 min.


BB-423A (1H) 400MHz
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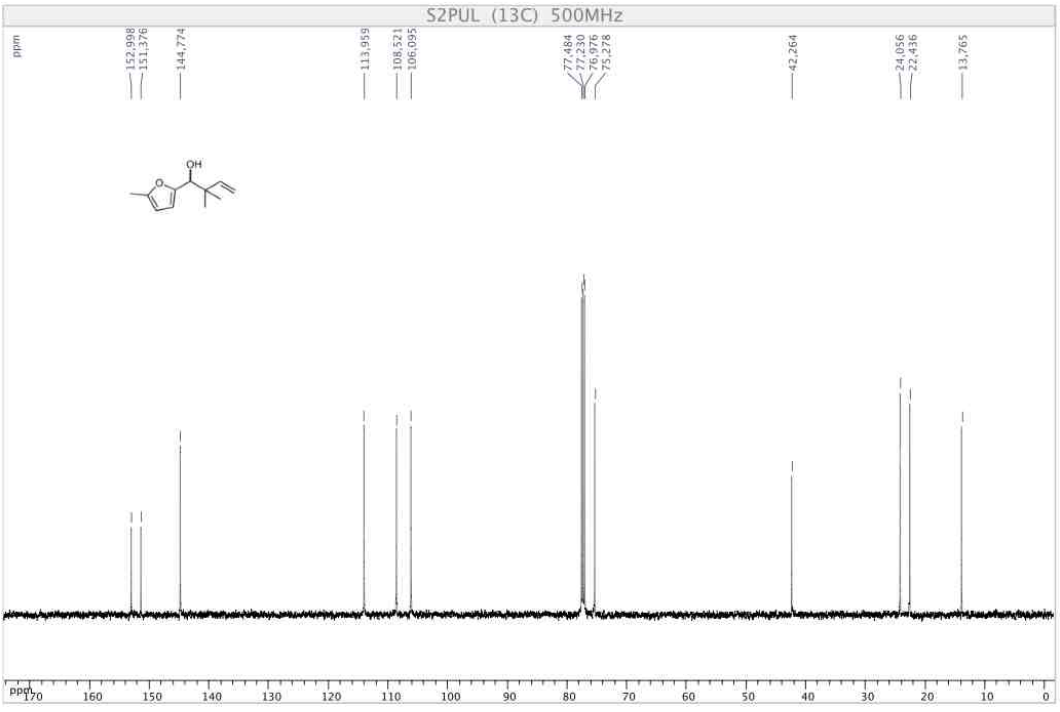
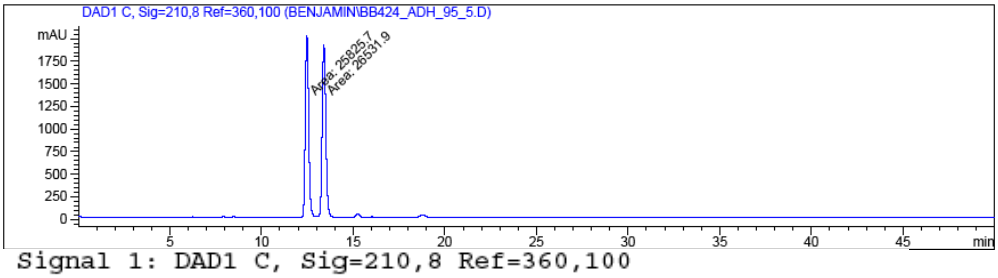
6,065
5,953
5,926
5,909
5,882
5,875
5,873
5,127
5,124
5,109
5,106
5,100
5,097
5,065
5,062
4,326
4,313
2,248
1,997
1,984
1,046
1,014
OH
1,0
0,8
1,1
2,0
1,0
2,9
1,1
2,8
2,6
ppm
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5

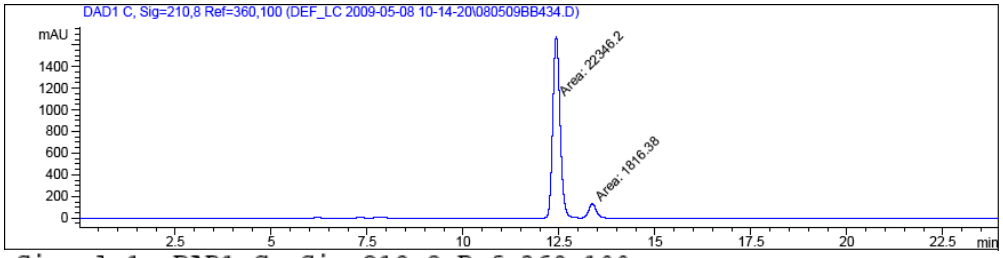

S2PUL (13C) 500MHz
ppm
152,998
151,376
144,774
113,959
108,521
106,095
77,484
77,230
76,976
75,278
42,264
24,056
22,436
13,765
OH
ppm
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.472	MM T	0.2136	2.58257e4	2015.24121	49.3256
2	13.398	MM T	0.2314	2.65319e4	1910.89221	50.6744

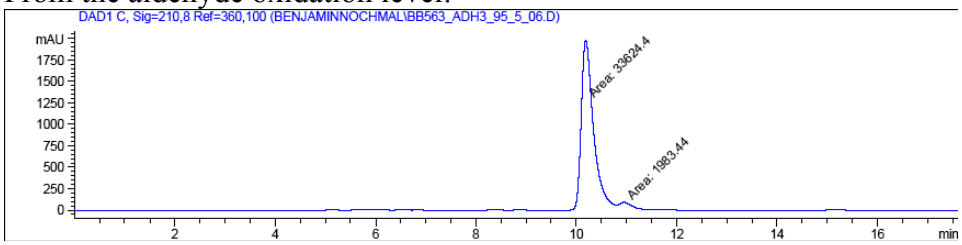
From the alcohol oxidation level:



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.425	MM T	0.2207	2.23462e4	1687.33789	92.4827
2	13.367	MM T	0.2293	1816.37939	131.99971	7.5173
Totals :				2.41626e4	1819.33760	

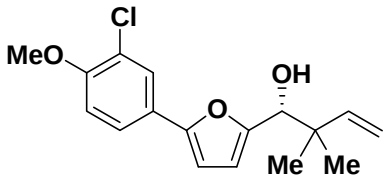
From the aldehyde oxidation level:



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.186	MM T	0.2826	3.36244e4	1982.71423	94.4298
2	10.953	MM T	0.3379	1983.43518	92.30791	5.5702

(*R*)-1-(5-(3-chloro-4-methoxyphenyl)furan-2-yl)-2,2-dimethylbut-3-en-1-ol (5c)



Procedure E (*via* alcohol 1b): The reaction was conducted on 0.2 mmol scale with respect to alcohol. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, hexane:EtOAc, 3:1) to afford the title compound (56.0 mg, 91% yield, 85% ee) as a colorless oil.

Procedure F (*via* aldehyde 2b): The reaction was conducted on 0.2 mmol scale with respect to aldehyde. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2, hexane:EtOAc, 3:1) to afford the title compound (57.7 mg, 94% yield, 93% ee) as a colorless oil.

TLC (SiO_2): R_f (Hexane:Et_2O, 3:1) = 0.25.

^{1}H NMR (400 MHz, $CDCl_3$): 7.60 (d, *J* = 2.2 Hz, 1H), 7.45 (dd, *J* = 8.6, 2.3, Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 1H), 6.46 (d, *J* = 3.3 Hz, 1H), 6.27 (d, *J* = 3.2 Hz, 1H), 5.95 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.15 (dd, *J* = 10.6, 1.2 Hz, 1H), 5.11 (dd, *J* = 17.4, 1.2 Hz, 1H), 4.43 (s, 1H), 3.89 (s, 3H), 2.10 (s, 1H), 1.10 (s, 3H), 1.06 (s, 3H).

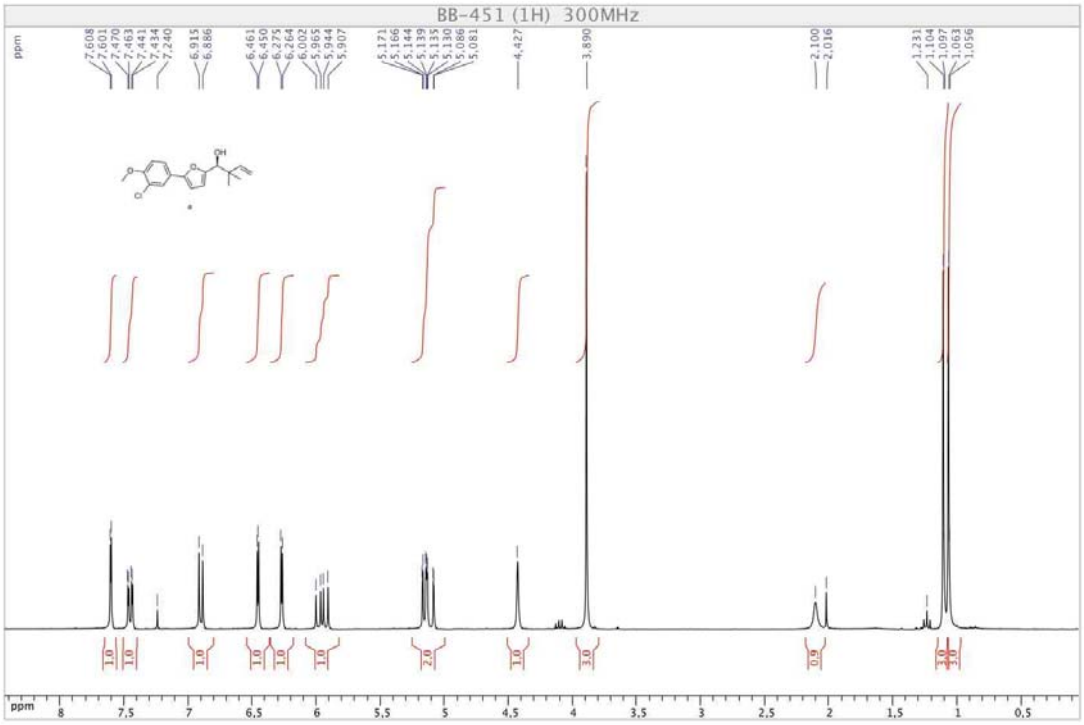
^{13}C NMR (100 MHz, $CDCl_3$): 154.4, 154.3, 151.8, 144.4, 125.8, 124.9, 123.3, 123.0, 114.3, 112.4, 109.9, 105.0, 75.2, 56.4, 42.3, 24.1, 22.4.

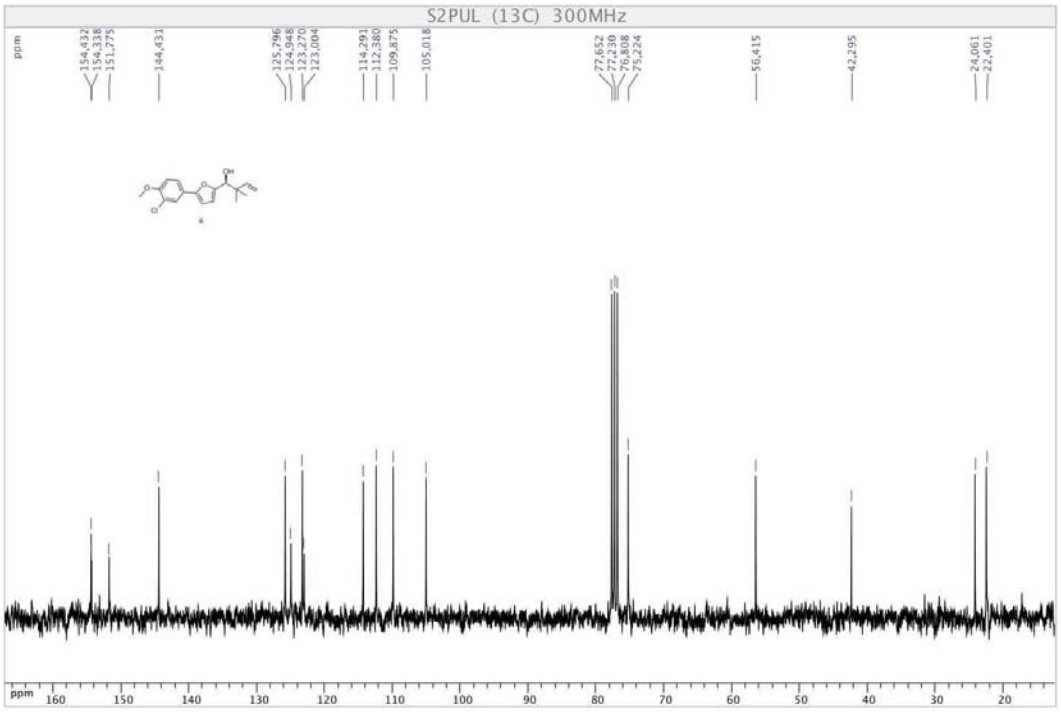
HRMS (CI): Calcd. for $C_{17}H_{18}O_2{}^{35}Cl$ $(M\text{-}OH)^+$: 289.0995, Found: 289.0999.

FTIR (film): 3447, 2965, 1544, 1489, 1266, 1018, 811, 708 cm^{-1}.

Opt. Rot. $[\alpha]_D{}^{26}$ = +51.0 (c = 1.00, in $CHCl_3$).

HPLC (Chiralcel AD-H column, hexane:*i*-PrOH, 98:2, 0.8 mL/min, 210 nm): t_{minor} = 40.5 min, t_{major} = 41.9 min.


BB-451 (1H) 300MHz
ppm
7.608
7.601
7.470
7.463
7.441
7.434
7.240
6.915
6.886
6.461
6.450
6.275
6.264
6.002
5.965
5.944
5.907
5.171
5.166
5.144
5.139
5.135
5.130
5.086
5.081
4.427
3.890
2.100
2.016
1.231
1.104
1.097
1.063
1.056
1.0
1.0
1.0
1.0
1.0
1.0
2.0
1.0
3.0
0.9
3.0
3.0
ppm
8
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5


S2PUL (13C) 300MHz
ppm
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154,338
151,775
144,431
125,796
124,948
123,270
123,004
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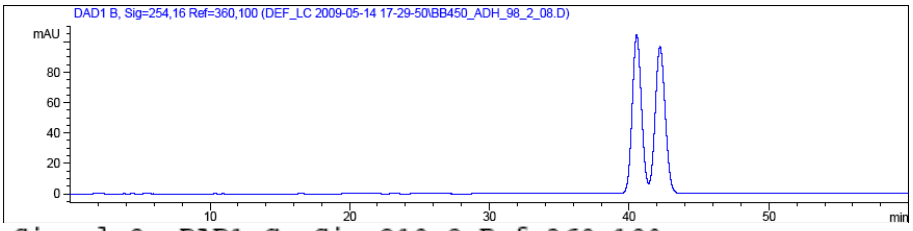
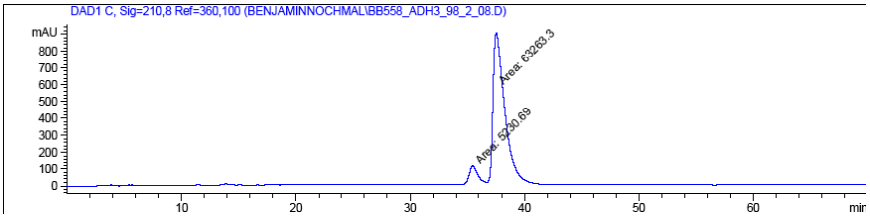
112,380
109,875
105,018
77,652
77,230
76,808
75,224
56,415
42,295
24,061
22,401
ppm
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20



Signal 2: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.520	MM T	0.9266	1.77167e4	403.86667	50.2041
2	42.193	MM T	0.7889	1.75726e4	371.23380	49.7959

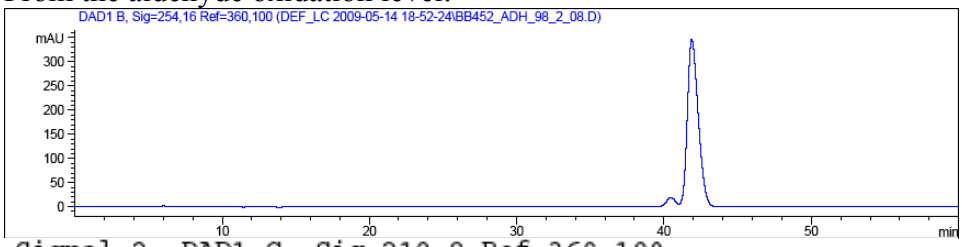
From the alcohol oxidation level:



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.450	MM T	0.9697	5230.69141	105.65318	7.6367
2	37.507	MM T	1.1860	6.32633e4	889.02063	92.3633

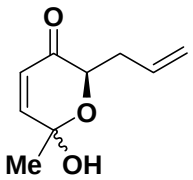
From the aldehyde oxidation level:



Signal 2: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.451	MM R	0.6332	2377.83350	62.58628	3.3579
2	41.879	MM T	0.8622	6.84343e4	1322.93689	96.6421

(*R*)-2-allyl-6-hydroxy-6-methyl-2H-pyran-3(6H)-one (6a)



Procedure G (*via* alcohol (*R*)-3b): The reaction was conducted on 0.329 mmol scale with respect to alcohol. The crude product purified by flash column chromatography (SiO_2: hexane:Et_2O, 2:1) to furnish the title compound (41.5 mg, 75% yield, 94% ee) as a colorless oil.

TLC (SiO_2): R_f (Pet. Ether:Et_2O, 2:1) = 0.10.

^{1}H NMR (400 MHz, $CDCl_3$): 6.79 (d, *J* = 10.1 Hz, 1H), 5.99 (d, *J* = 10.0 Hz, 1H), 5.81 (tdd, *J* = 17.2, 10.2, 6.8 Hz, 1H), 5.12 (dd, *J* = 17.1, 2.0 Hz, 1H), 5.05 (dd, *J* = 10.1, 1.8 Hz, 1H), 4.56 (dd, *J* = 7.7, 3.9 Hz, 1H), 2.84 (s, 1H), 2.67 (m, 1H), 2.42 (m, *J* = 7.5 Hz, 1H), 1.61 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 196.4, 148.1, 134.0, 126.6, 117.7, 93.1, 74.2, 34.1, 29.1.

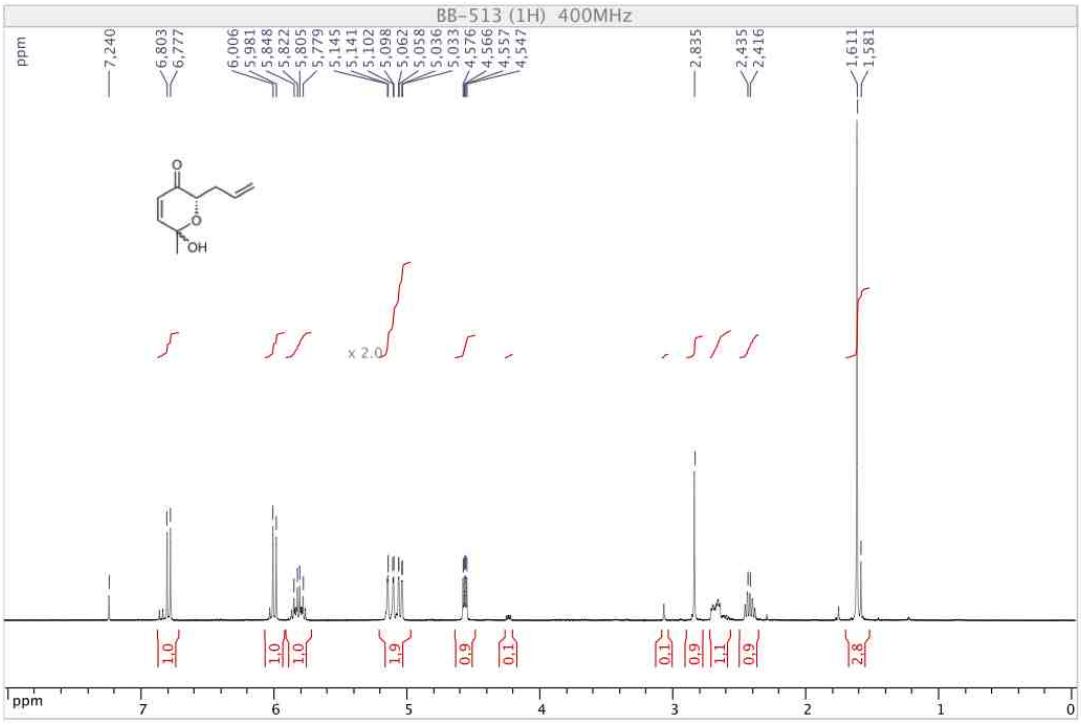
HRMS (CI): Calcd. for $C_9H_{12}O_3$ $(M+H)^+$: 169.0865, Found: 169.0868.

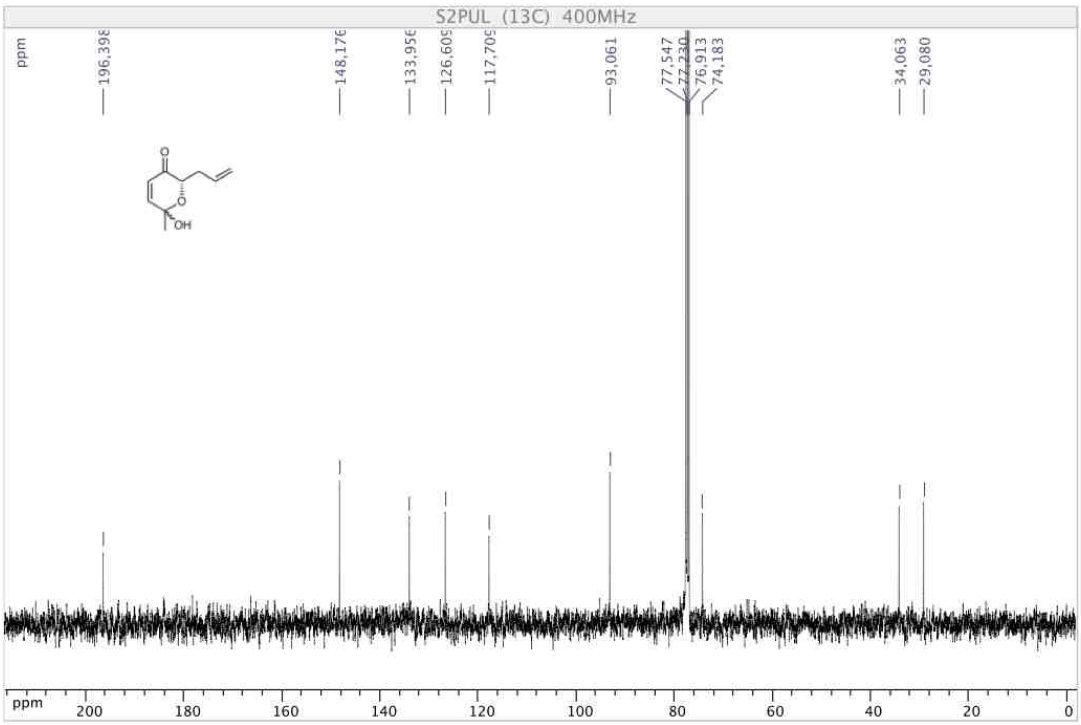
FTIR (neat): 3392, 3075, 2989, 2917, 1687, 1643, 1402, 1378, 1270, 1123, 1083, 995, 920, 736 cm^{-1}.

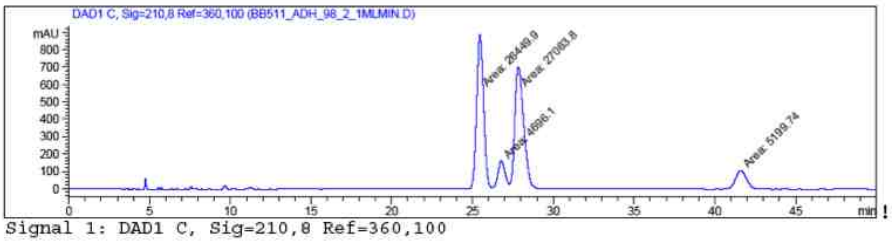
HPLC (Chiralcel AD-H column, hexane:*i*-PrOH, 98:2, 1.0 mL/min, 210 nm): t_{major}=24.7 min, t_{minor}=27.3 min.

The spectroscopic properties of this compound are consistent with the data available in the literature.[8]

[8] G. Piancatelli, A. Scettri, M. D'Auria, *Tet. Lett.* **1977**, *18*, 2199–2200.

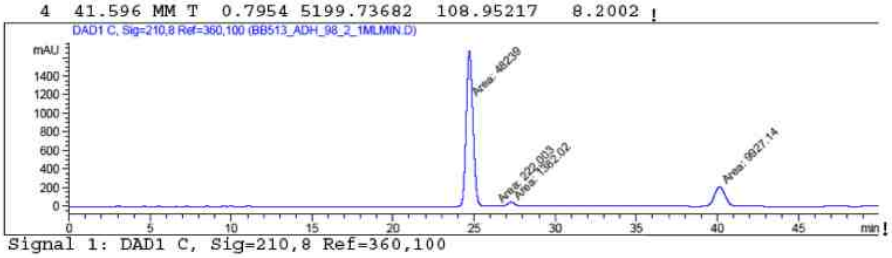

BB-513 (1H) 400MHz
ppm
7,240
6,803
6,777
6,006
5,981
5,848
5,822
5,805
5,779
5,145
5,141
5,102
5,098
5,062
5,058
5,036
5,033
4,576
4,566
4,557
4,547
2,835
2,435
2,416
1,611
1,581
x 2.0
1.0
1.0
1.0
1.9
0.9
0.1
0.1
0.9
1.1
0.9
2.8
ppm
7
6
5
4
3
2
1
0


S2PUL (13C) 400MHz
ppm
196,398
148,176
133,956
126,605
117,705
93,061
77,547
77,230
76,913
74,183
34,063
29,080
ppm
200
180
160
140
120
100
80
60
40
20
0



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

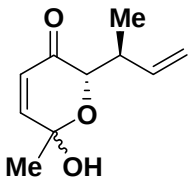
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.448	MM T	0.4958	2.64499e4	889.19482	41.7128
2	26.768	MM T	0.5013	4696.10303	156.13420	7.4060
3	27.821	MM T	0.6401	2.70638e4	704.63013	42.6809
4	41.596	MM T	0.7954	5199.73682	108.95217	8.2002



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.694	MM T	0.4810	4.82390e4	1671.64160	80.7075
2	26.279	MM T	0.5415	222.00323	8.28000	0.3714
3	27.272	MM T	0.5102	1382.02478	45.14209	2.3122
4	40.122	MM T	0.7764	9927.13965	213.09850	16.6089

(*S*)-2-((*S*)-but-3-en-2-yl)-6-hydroxy-6-methyl-2H-pyran-3(6H)-one (6b)



Procedure G (*via* alcohol (*S,S*)-4b): The reaction was conducted on 1.23 mmol scale with respect to alcohol. The crude product purified by flash column chromatography (SiO_2, hexane:Et_2O, 2:1) to afford the title compound (166 mg, 74% yield, 82% ee) as a colorless oil.

TLC (SiO_2): R_f (Pet. Ether:Et_2O, 2:1) = 0.27.

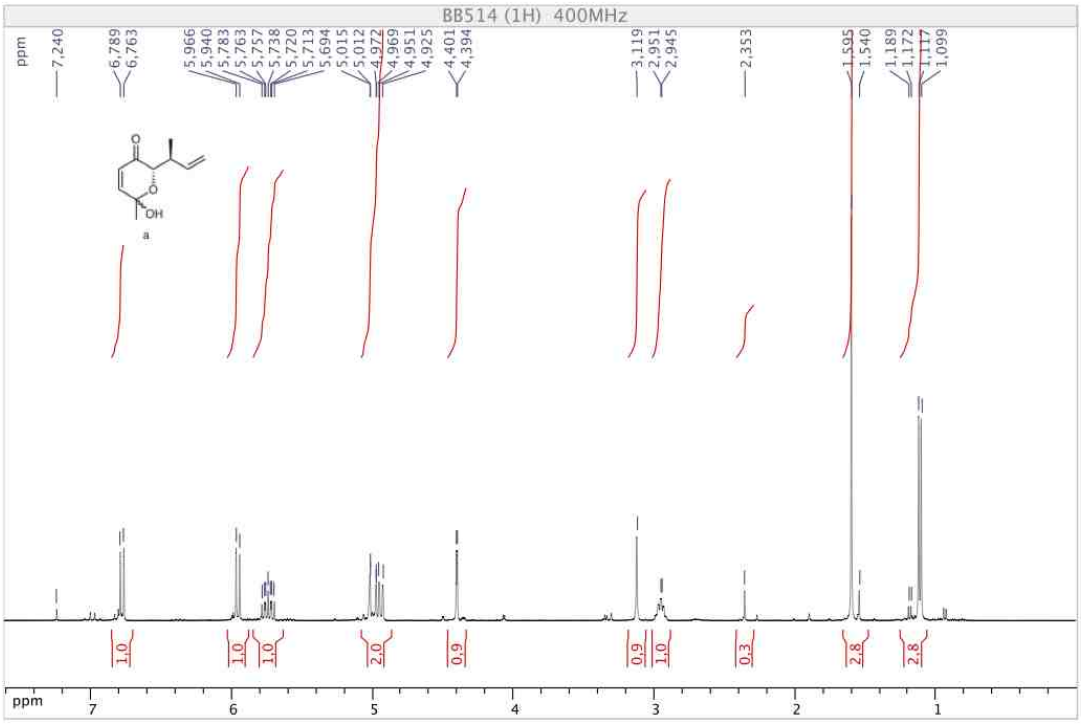
^{1}H NMR (400 MHz, $CDCl_3$): 6.78 (d, *J* = 10.1 Hz, 1H), 5.95 (d, *J* = 10.1 Hz, 1H), 5.74 (ddd, *J* = 17.4, 10.4, 7.7 Hz, 1H), 4.97 (m, 2H), 4.40 (d, *J* = 2.8 Hz, 1H), 3.12 (s, 1H), 2.95 (m, 1H), 1.60 (s, 3H), 1.11 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 196.6, 148.3, 138.7, 127.0, 116.0, 92.8, 78.3, 38.5, 28.8, 16.9.

HRMS (CI): Calcd. for $C_{10}H_{15}O_3$ $(M+H)^+$: 183.1021, Found: 183.1024.

FTIR (neat): 3393, 3078, 2981, 2936, 1683, 1639, 1454, 1403, 1376, 1278, 1235, 1124, 1092, 1028, 998, 914, 778 cm^{-1}.

HPLC (Chiralcel OJ-H column, Hexane:*i*-PrOH, 97:3, 0.5 mL/min, 210 nm): t_{major} = 20.6 min, t_{minor} = 26.4 min.


BB514 (1H) 400MHz
ppm
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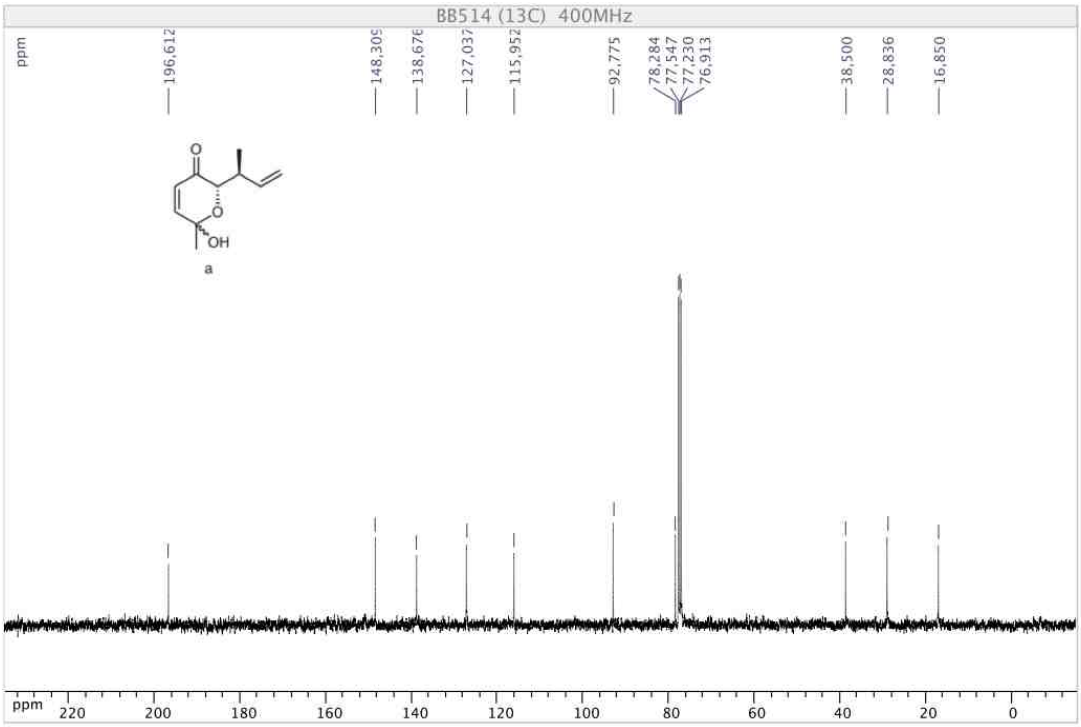
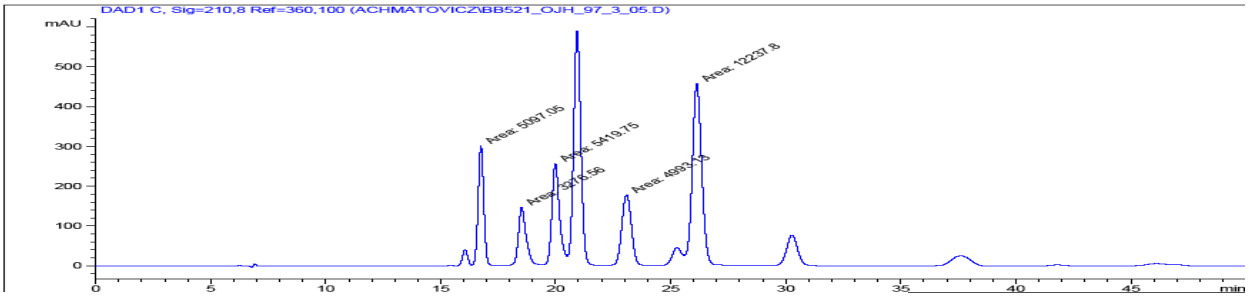
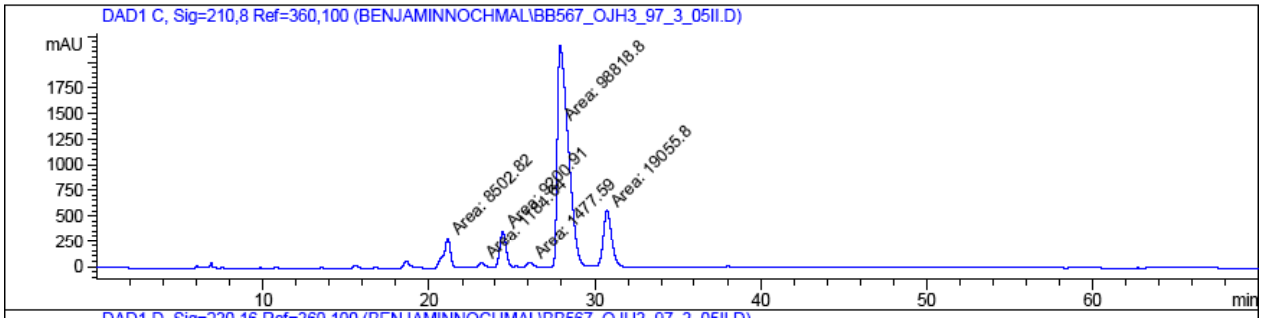
6,789
6,763
5,966
5,940
5,783
5,763
5,757
5,738
5,720
5,713
5,694
5,015
5,012
4,972
4,969
4,951
4,925
4,401
4,394
3,119
2,951
2,945
2,353
1,595
1,540
1,189
1,172
1,117
1,099
OH
a
1,0
1,0
1,0
2,0
0,9
0,9
1,0
0,3
2,8
2,8
ppm
7
6
5
4
3
2
1


BB514 (13C) 400MHz
ppm
196,612
148,305
138,676
127,037
115,952
92,775
78,284
77,547
77,230
76,913
38,500
28,836
16,850
OH
a
ppm
220
200
180
160
140
120
100
80
60
40
20
0



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

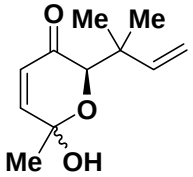
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.737	MM T	0.2816	5097.04590	301.67883	11.7546
2	18.510	MM T	0.3776	3276.55591	144.62331	7.5563
3	19.969	MM T	0.3641	5419.75342	248.08441	12.4988
4	20.918	MM R	0.3559	1.23377e4	577.78363	28.4529
5	23.069	MM T	0.4733	4993.12646	175.84109	11.5150
6	26.120	MM T	0.4612	1.22378e4	442.28876	28.2224



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.120	MM T	0.4893	8502.81934	289.62146	6.1507
2	23.189	MM T	0.4153	1184.64026	47.54165	0.8569
3	24.436	MM T	0.5486	9200.90820	355.30753	6.6557
4	26.103	MM T	0.4666	1477.59485	52.77736	1.0689
5	27.896	MM T	0.7629	9.88188e4	2158.84131	71.4832

(*R*)-6-hydroxy-6-methyl-2-(2-methylbut-3-en-2-yl)-2H-pyran-3(6H)-one (6c)



Procedure G (*via* alcohol (*R*)-5b): The reaction was conducted on 0.201 mmol scale with respect to alcohol. The crude product purified by flash column chromatography (SiO_2: hexane:Et_2O, 2:1) to furnish the title compound (16.9 mg, 43% yield, 84% ee) as a colorless oil.

TLC (SiO_2): R_f (Pet. Ether:Et_2O, 3:1) = 0.19.

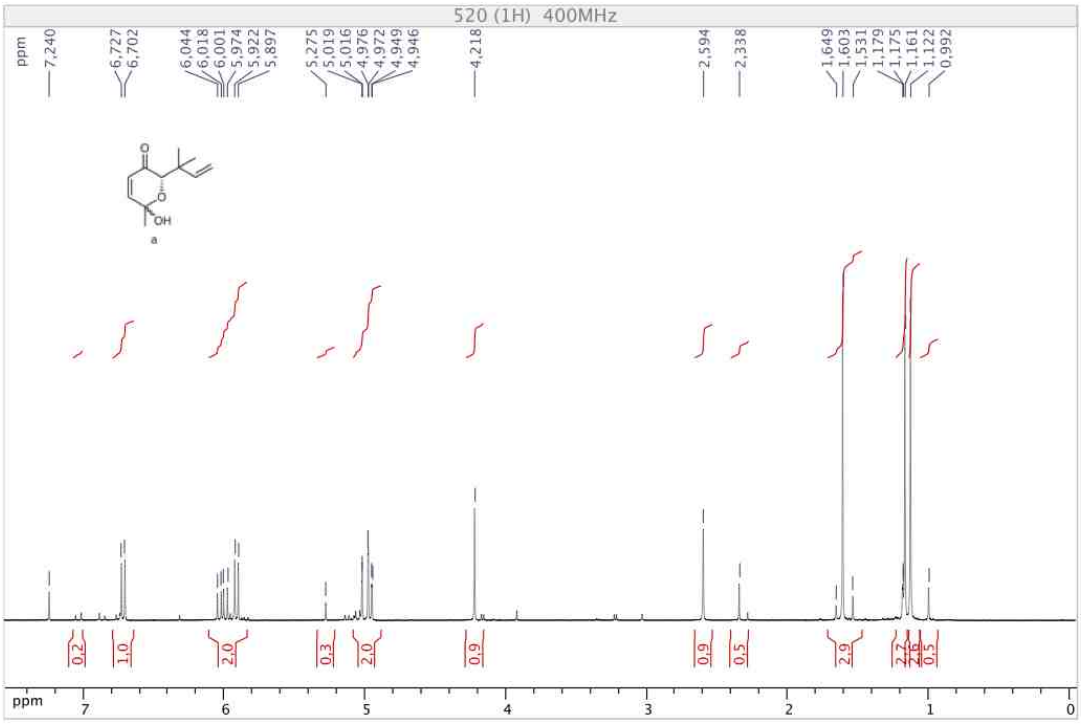
^{1}H NMR (400 MHz, $CDCl_3$): 6.71 (d, J = 10.1 Hz, 1H), 6.01 (dd, J = 17.6, 10.8 Hz, 1H), 5.91 (d, J = 10.1 Hz, 1H), 4.97 (m, 2H), 4.22 (s, 1H), 2.59 (s, 1H), 1.60 (s, 3H), 1.16 (s, 3H), 1.12 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 196.3, 146.8, 145.0, 128.2, 112.0, 93.1, 80.0, 40.4, 29.0, 24.1, 23.8.

HRMS (CI): Calcd. for $C_{11}H_{17}O_3$ $(M+H)^+$: 197.1178, Found: 197.1178.

FTIR (neat): 3396, 3084, 2986, 2967, 1684, 1638, 1465, 1414, 1378, 1362, 1256, 1127, 1093, 1067, 918 cm^{-1}.

HPLC (Chiralcel AD-H column, Hexane:*i*-PrOH, 97:3, 0.5 mL/min, 210 nm): t_{minor} = 14.8 min, t_{major} = 25.1 min.


520 (1H) 400MHz
ppm
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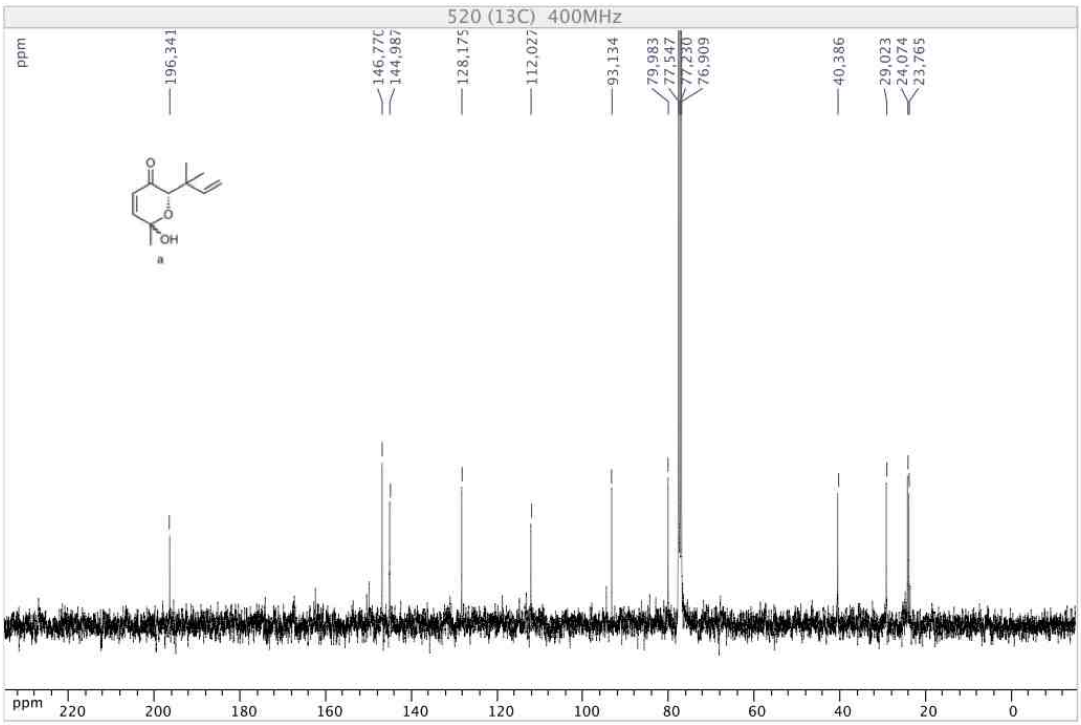
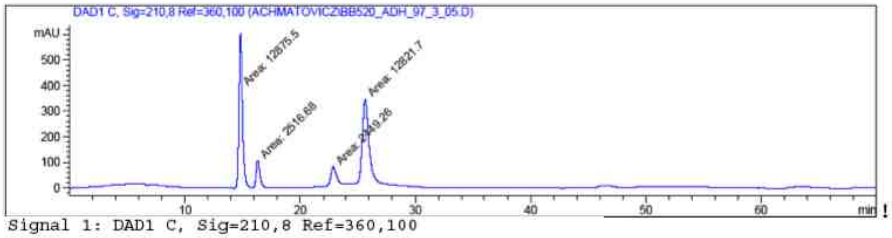
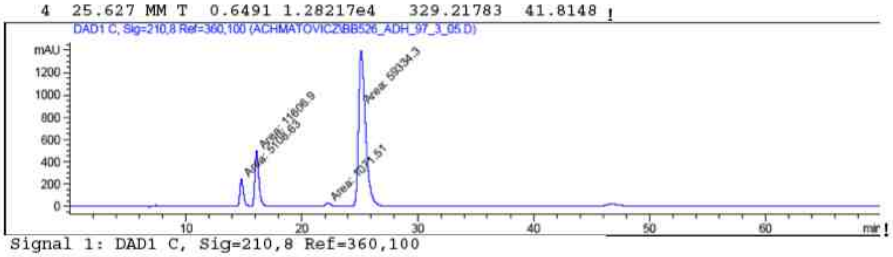
6,727
6,702
6,044
6,018
6,001
5,974
5,922
5,897
5,275
5,019
5,016
4,976
4,972
4,949
4,946
4,218
2,594
2,338
1,649
1,603
1,531
1,179
1,175
1,161
1,122
0,992
OH
a
0,2
1,0
2,0
0,3
2,0
0,9
0,9
0,5
2,9
2,7
2,6
0,5
ppm
7
6
5
4
3
2
1
0


520 (13C) 400MHz
ppm
196,341
146,770
144,987
128,175
112,027
93,134
79,983
77,547
77,230
76,909
40,386
29,023
24,074
23,765
OH
a
ppm
220
200
180
160
140
120
100
80
60
40
20
0



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.806	MM T	0.3535	1.28755e4	607.07343	41.9901
2	16.318	MM T	0.4572	2516.68359	107.54316	8.2075
3	22.864	MM T	0.5634	2449.26294	72.46011	7.9876
4	25.627	MM T	0.6491	1.28217e4	329.21783	41.8148



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.768	MM T	0.3439	5108.62598	247.56685	6.6241
2	16.068	MM T	0.4671	1.16069e4	497.61237	15.0502
3	22.238	MM T	0.6044	1071.51416	29.54573	1.3894
4	25.110	MM T	0.7077	5.93343e4	1397.38623	76.9363