Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

Enzymatic kinetic resolution of primary allenic alcohols. Application to the total synthesis and stereochemical assignment of striatisporolide A.

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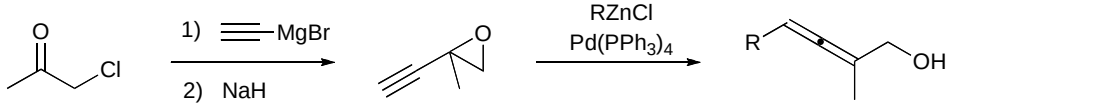
General Remarks

^{1}H- and ^{13}-NMR-spectra were recorded on with a *Bruker Avance II 400* spectrometer at 400 respectively 100 MHz. Chemical shifts are reported in ppm, using residual $CHCl_3$ (7.26 ppm and 77.1 ppm respectively) as internal standard. HPLC was performed on a *Waters 2695* with a *Waters 996* UV-detector using *Chiralcel* columns (specifications see below) at a flowrate of 0.5 ml/min Optical rotations were measured with a *Perkin-Elmer 241* polarimeter equipped with a Na-lamp. High resolution mass spectrometry was performed on a *Bruker micrOTOF/ESI*.

All moisture or air sensitive reactions were performed und argon atmosphere in oven-dried glassware. Dry tetrahydrofuran, diethyl ether, toluene and dimethylformamide were obtained from a VAC solvent purifier, dry dichloromethane was freshly distilled from calcium hydride, methanol was freshly distilled from magnesium. All commercially available reagents were used without further purification. Merck silica gel 60 (240-400 mesh) was used for flash chromatography and analytical thin-layer chromatography was performed on Merck precoated silica gel 60-F_{254} plates.

Synthesis and analytical data of the compounds

General procedure for the synthesis of allenols 1a and 1d-1j.



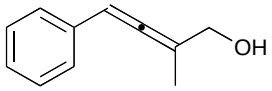
R = Aryl, Alkenyl

A solution of ethynylmagnesium bromide (ca. 1M in THF, 120 ml, ca. 120 mmol, in situ generated from EtMgBr and gaseous acetylene) was added dropwise at 0°C to a to a solution of chloroacetone (9.25 g, 100 mmol) in dry THF (150 ml) and the reaction mixture was stirred for 3 h at 0°C, followed by careful hydrolysis with sat. NH_4Cl and dilution with diethyl ether. The aqueous layer was extracted with diethyl ether (3x), the combined organic layers washed with sat. NaCl and dried over $MgSO_4$. After removal of the solvent in vacuo, the crude chlorohydrine was dissolved in dry THF (70 ml) and NaH (60 wt% in parafin, 4.0 g, 100 mmol) was added in small portions at 0°C and the suspension was stirred for 30 min at room temperature. The reaction flask was equipped with a destillation bridge and the destillate was collected between bp 60°C and 100°C at atmospheric pressure, containing THF and the desired propargylic epoxide. An approx. 0.9 M solution of 2-ethynyl-2-methyloxirane in THF was obtained (ca. 54 mmol, ca. 54% yield) and could be stored at -18°C over several months until further use.

Anhydrous $ZnCl_2$ (6.5 mmol) was carefully dried in vacuo at 100°C, allowed to cool down to room temperature and dissolved in dry THF (12 ml). The solution was cooled to 0°C at which

a 1 M solution of the respective aryl- or alkenylmagnesium bromide (6 ml, 6.0 mmol) was added dropwise. The resulting white suspension was stirred at 0°C for 30 min. $Pd(PPh_3)_4$ (23 mg, 0.02 mmol) was dissolved in dry THF (0.5 ml) and added to the organozinc solution, followed by the dropwise addition of 2-ethynyl-2-methyloxirane (0.9 M in THF, 2.2 ml, 2.0 mmol). After 2 h the reaction mixture was hydrolyzed by the addition of sat. NH_4Cl and diluted with diethyl ether. The aqueous layer was extracted with diethyl ether, the combined organic layers were dried over $MgSO_4$, concentrated in vacuo and the crude allenol was purified by column chromatography (SiO_2, pentane-diethyl ether 9:1 to 7:3).

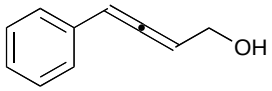
2-Methyl-4-phenylbuta-2,3-dienol (1a)



1a

Following the general procedure using phenylmagnesium bromide, **1a** (304 mg, 1.90 mmol, 95%) was obtained as a pale yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.69 (bs, 1H), 1.84 (d, *J* = 2.9 Hz, 3H), 4.10-4.18 (m, 2H), 6.28 (tq, *J* = 3.0 Hz, 1H), 7.17-7.32 (m, 5H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 15.4, 63.8, 97.0, 106.7, 126.8, 127.0, 128.6, 134.7, 200.8. HRMS (ESI) calcd for $C_{11}H_{12}NaO$ $[M+Na]^+$: 183.0785, found: 183.0780. HPLC (*Chiralcel OB*, isohexane-isopropanol gradient: [99:1 (30min)]-[99:1 to 90:10 (30min)]-[90:10 (30min)], 0.5 mL/min, 249 nm): t_R(*R*) = 54.6 min, t_R(*S*) = 57.8 min.

4-Phenylbuta-2,3-dienol (1b).

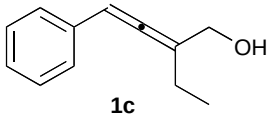


1b

To a solution of ethyl bromoacetate (1.67 g, 10 mmol) in dry toluene (10 ml) at -78°C diisobutylaluminium hydride (1 M in toluene, 12 ml, 12 mmol) was added dropwise and the reaction mixture was stirred at -78°C for 1h. Ethynylmagnesium bromide (0.5 M in THF, 30 ml, 15 mmol) was added, the mixture was allowed to warm up to room temperature and after 2 h hydrolyzed by addition of sat. NH_4Cl. The aqueous layer was extracted with diethyl ether, the combined organic layers dried over $MgSO_4$ and concentrated in vacuo. Purification by flash chromatography (SiO_2, pentane-diethyl ether 8:2) delivered 1-bromobut-3-yn-2-ol (712 mg, 4.78 mmol, 48%). The bromohydrine (500 mg, 3.6 mmol) was dissolved in dry THF (4 ml) and treated with solid NaH (60 wt%, 172 mg, 4.3 mmol) at 0°C and kept at this temperature for 30 min. Meanwhile $ZnCl_2$ (1.02 g, 7.5 mmol) was dried in vacuo at 100°C, cooled down and dissolved in dry THF (15 ml). At 0°C phenylmagnesium chloride (2 M in THF, 3.6 ml, 7.2 mmol) was added dropwise, the mixture was stirred for 20 min after which the preformed ethynyloxiran-solution and a solution of $Pd(PPh_3)_4$ (42 mg, 0.036 mmol in 0.5 ml dry THF) were added. Stirring at 0°C was continued for 2 h, sat. NH_4Cl and diethyl ether

were added, the aqueous phase was extracted with diethyl ether and the combined organic phases were dried over $MgSO_4$. After evaporation of the solvent column chromatography (SiO_2, pentane-diethyl ether 7:3) yielded **1b** (321 mg, 2.20 mmol, 61%) as a yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.72 (bs, 1H), 4.26 (m, 2H), 5.79 (dt, *J* = 6.0 Hz, 1H), 6.33 (dt, *J* = 3.0, 6.2 Hz, 1H), 7.23 (m, 1H), 7.30-7.36 (m, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 60.3, 95.8, 97.1, 126.8, 127.2, 128.6, 133.7, 204.2. HRMS (ESI) calcd for $C_{10}H_{10}NaO$ $[M+Na]^+$: 169.0624, found: 169.0604. No separation on HPLC.

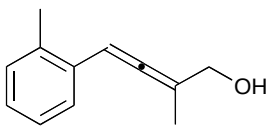
2-Ethyl-4-phenylbuta-2,3-dienol (1c).



1c

To a solution of 1-bromobutanone (225 mg, 1.5 mmol) in dry THF (5 ml) was added ethynylmagnesium bromide (0.5 M in THF, 4 ml, 2.0 mmol) at 0°C under stirring. The reaction mixture was stirred at 0°C for 3 h and then hydrolyzed with sat NH_4Cl and diluted with diethyl ether. The aqueous layer was extracted with diethyl ether and the combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The remaining crude bromohydrine was dissolved in THF (2ml), cooled to 0°C and treated with NaH (60 wt%, 60 mg, 1.5 mmol) to yield epoxide. While strirring at 0°C for 30 min, a phenylzinc chloride solution (7.8 mmol) was prepared as described for **1b**. At 0°C the epoxide solution and a solution of $Pd(PPh_3)_4$ (15 mg, 0.013 mmol in 0.3 ml dry THF) were added. After stirring at 0°C for 2 h, the reaction was hydrolyzed with sat. NH_4Cl and diluted with diethyl ether. The aqueous layer was extracted with diethyl ether, the combined organic layers were dried over $MgSO_4$, the solvents were removed in vacuo and the crude allenol was purified by column chromatography (SiO_2, pentane-diethyl ether 9:1 to 7:3) to yield **1c** (108 mg, 0.62 mmol, 41%) as a yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.11 (t, *J* = 7.4 Hz, 3H), 1.58 (bs, 1H), 2.14-2.20 (m, 2H), 4.14-4.23 (m, 2H), 6.36 (tt, *J* = 3.1 Hz, 1H), 7.18-7.23 (m, 1H), 7.29-7.33 (m, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 12.9, 22.7, 63.0, 98.9, 111.7, 126.6, 127.0, 128.6, 134.9, 200.2. HRMS (ESI) calcd for $C_{12}H_{14}NaO$ $[M+Na]^+$: 197.0937, found: 197.0936. HPLC (*Chiralcel OD-H*, isohexane-isopropanol gradient: [100:0 (30min)]-[100:0 to 90:10 (30min)]-[90:10 (30min)], 0.5 mL/min, 249 nm): t_R(*S*) = 63.7 min, t_R(*R*) = 73.7 min.

2-Methyl-4-(2-methylphenyl)buta-2,3-dienol (1d).

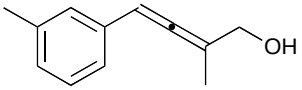


1d

Following the general procedure using 2-methylphenylmagnesium bromide, **1d** (202 mg, 1.16 mmol, 58%) was obtained as a yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.73

(bs, 1H), 1.88 (d, *J* = 3.0 Hz, 3H), 2.40 (s, 3H), 4.13-4.22 (m, 2H), 6.49 (tq, *J* = 3.0 Hz, 1H), 7.12-7.20 (m, 3H), 7.35-7.38 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 15.5, 19.9, 63.9, 94.4, 103.5, 126.1, 126.9, 127.3, 130.5, 132.9, 135.1, 201.7. HRMS (ESI) calcd for $C_{12}H_{14}NaO$ $[M+Na]^+$: 197.0937, found: 197.0932. HPLC (*Chiralcel OJ*, isohexane-isopropanol gradient: [100:0 (30min)]-[100:0 to 90:10 (30min)]-[90:10 (30min)], 0.5 mL/min, 248 nm): t_R(*R*) = 63.6 min, t_R(*S*) = 65.8 min.

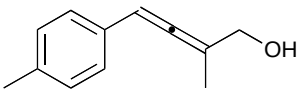
2-Methyl-4-(3-methylphenyl)buta-2,3-dienol (1e).



1e

Following the general procedure using 3-methylphenylmagnesium bromide, **1e** (291 mg, 1.67 mmol, 83%) was obtained as a yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.01 (d, *J* = 3.0 Hz, 3H), 2.24 (bs, 1H), 2.49 (s, 3H), 4.25-4.35 (m, 2H), 6.40 (tq, *J* = 2.9 Hz, 1H), 7.17-7.28 (m, 3H), 7.36 (d, *J* = 7.3 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 15.3, 21.3, 63.8, 96.8, 104.3, 123.2, 127.3, 127.8, 128.4, 134.6, 138.1, 200.7. HRMS (ESI) calcd for $C_{12}H_{14}NaO$ $[M+Na]^+$: 197.0937, found: 197.0934. HPLC (*Chiralcel OD-H*, isohexane-isopropanol gradient: [100:0 (30min)]-[100:0 to 90:10 (30min)]-[90:10 (30min)], 0.5 mL/min, 249 nm): t_R(*S*) = 61.9 min, t_R(*R*) = 73.9 min.

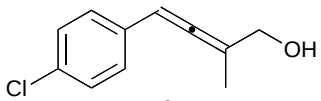
2-Methyl-4-(4-methylphenyl)buta-2,3-dienol (1f).



1f

Following the general procedure using 4-methylphenylmagnesium bromide, **1f** (317 mg, 1.82 mmol, 91%) was obtained as a yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.58 (bs, 1H), 1.85 (d, *J* = 2.9 Hz, 3H), 2.23 (s, 3H), 4.09-4.19 (m, 2H), 6.26 (dt, *J* = 3.0 Hz, 1H), 7.10-7.12 (m, 2H), 7.17-7.20 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 15.5, 21.2, 63.9, 97.1, 104.6, 126.7, 129.3, 131.7, 136.9, 200.4. HRMS (ESI) calcd for $C_{12}H_{14}NaO$ $[M+Na]^+$: 197.0937, found: 197.0934. HPLC (*Chiralcel OB*, isohexane-isopropanol gradient: [100:0 (30min)]-[100:0 to 90:10 (30min)]-[90:10 (30min)], 0.5 mL/min, 251 nm): t_R(*R*) = 59.6 min, t_R(*S*) = 66.2 min.

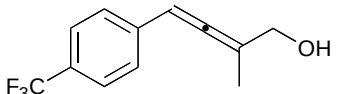
2-Methyl-4-(4-chlorophenyl)buta-2,3-dienol (1g).



1g

Following the general procedure using 4-chlorophenylmagnesium bromide, **1g** (347 mg, 1.78 mmol, 89%) was obtained as a colorless solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.77 (bs, 1H), 1.84 (d, *J* = 2.9 Hz, 3H), 4.10-4.19 (m, 2H), 6.22 (tq, *J* = 2.9 Hz, 1H), 7.18-7.21 (m, 2H), 7.24-7.27 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 15.3, 63.7, 96.0, 105.1, 127.9, 128.7, 132.5, 133.3, 201.0. HRMS (ESI) calcd for $C_{11}H_{11}ClNaO$ $[M+Na]^+$: 217.0391, found: 217.0387. HPLC (*Chiralcel OB*, isohexane-isopropanol gradient: [100:0 (30min)]-[100:0 to 90:10 (30min)]-[90:10 (30min)], 0.5 mL/min, 256 nm): t_R(*R*) = 60.4 min, t_R(*S*) = 64.9 min.

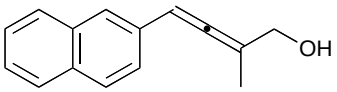
2-Methyl-4-(4-trifluoromethylphenyl)buta-2,3-dienol (1h).



1h

Following the general procedure using 4-(trifluoromethyl)phenylmagnesium bromide, **1h** (382 mg, 1.68 mmol, 84%) was obtained as a colorless solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.86 (d, *J* = 3.2 Hz, 3H), 2.17 (bs, 1H), 4.12-4.21 (m, 2H), 6.26 (tq, *J* = 3.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 15.1, 63.6, 95.7, 105.2, 124.1 (q, *J* = 265 Hz), 125.4 (q, *J* = 3.7 Hz), 126.8, 128.8 (q, *J* = 32.2 Hz), 138.7, 202.1. HRMS (ESI) calcd for $C_{12}H_{12}F_3O$ $[M+H]^+$: 229.0835, found: 229.0835. HPLC (*Chiralcel OB*, isohexane-isopropanol gradient: [100:0 (30min)]-[100:0 to 90:10 (30min)]-[90:10 (30min)], 0.5 mL/min, 251 nm): t_R(*R*) = 53.2 min, t_R(*S*) = 56.4 min.

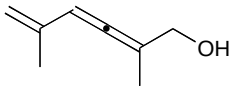
2-Methyl-4-(2-naphtyl)-buta-2,3-dienol (1i).



1i

Following the general procedure using 2-naphtylmagnesium bromide, **1i** (397 mg, 1.89 mmol, 94%) was obtained as a colourless solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.61 (bs, 1H), 1.93 (d, *J* = 3.0 Hz, 3H), 4.18-4.27 (m, 2H), 6.48 (tq, *J* = 3.0 Hz, 1H), 7.43-7.50 (m, 3H), 7.68 (s, 1H), 7.77-7.83 (m, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 15.5, 63.9, 97.5, 105.0, 124.7, 125.6, 125.7, 126.3, 127.7, 127.8, 128.3, 132.3, 132.7, 133.7, 201.4. HRMS (ESI) calcd for $C_{15}H_{14}NaO$ $[M+Na]^+$: 233.0942, found: 233.0937. HPLC (*Chiralcel OD-H*, isohexane-isopropanol gradient: [100:0 (30min)]-[100:0 to 90:10 (30min)]-[90:10 (30min)], 0.5 mL/min, 252 nm): t_R(*R*) = 71.4 min, t_R(*S*) = 82.5 min.

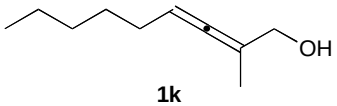
2,5-Dimethylhexa-2,3,5-trienol (1j).



1j

Following the general procedure using isopropenylmagnesium bromide, **1j** (176 mg, 1.42 mmol, 71%) was obtained as a yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.57 (bs, 1H), 1.75 (dd, *J* = 0.8, 1.4 Hz 3H), 1.77 (d, *J* = 2.9 Hz, 3H), 4.01-4.09 (m, 2H), 64.85 (m, 1H), 4.93 (m, 1H), 6.02 (tq, *J* = 2.8 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 15.6, 19.6, 63.9, 100.4, 103.6, 114.0, 139.5, 201.4. HRMS (ESI) calcd for $C_8H_{12}NaO$ $[M+Na]^+$: 147.0780, found: 147.0803. No separation on HPLC.

2-Methylnona-2,3-dienol (1k).



1k

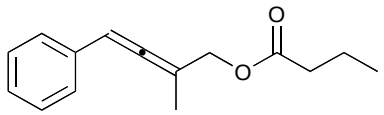
1-Bromopentane (4.5 g, 30 mmol, in 30 ml dry THF) was added dropwise to magnesium turnings (0.78 g, 32 mmol) in dry THF (15 ml) in a manner that the mixture was gently boiling. After complete addition the reaction mixture was refluxed for 30 min, allowed to cool down to room temperature and slowly added to a solution of vaccum-dried CuBr (4.3 g, 30 mmol) and LiBr (2.6 g, 30 mmol) in dry THF (45 ml) at -78°C. The deep violet solution was allowed to warm up to -30°C at which point 2-ethynyl-2-methyloxirane (0.9 M in THF, 16.7 ml, 15 mmol) was added. The reaction mixture was stirred at room temperature for 5 h, hydrolyzed with 0.5 M HCl and diluted with diethyl ether. The combined organic layers were dried over $MgSO_4$, concentrated in vacuo and the crude allenol was purified by column chromatography (SiO_2, pentane-diethyl ether 75:25) yielding **1k** (1.03 g, 6.68 mmol, 45%) as a colourless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.91 (t, *J* = 7.0 Hz, 3H), 1.28-1.45 (m, 6H), 1.55 (bs, 1H), 1.74 (d, *J* = 2.9 Hz, 3H), 2.02 (dt, *J* = 6.9 Hz, 2H), 3.96-4.05 (m, 2H), 5.30 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 14.1, 15.8, 22.5, 28.9, 29.1, 31.3, 63.9, 94.4, 100.5, 199.1. HRMS (ESI) calcd for $C_{16}H_{20}NaO_2$ $[M+Na]^+$: 267.1356, found: 267.1345. HPLC: **1k** was converted to the corresponding 4-nitrobenzoate (4-nitrobenzoyl chloride, DMAP) which was then analzed by HPLC (*Chiralcel OB*, isohexane-isopropanol gradient: [100:0 (30min)]-[100:0 to 90:10 (30min)]-[90:10 (30min)], 0.5 mL/min, 255 nm): t_R(*S*) = 49.5 min, t_R(*R*) = 50.8 min.

General procedure for the PPL-catalyzed kinetic resolution.

Allenic alcohol **1a-k** (0.1 mmol) was dissolved in diisopropyl ether (2 ml). At room temperature vinyl butyrate (63 µl, 0.5 mmol) and *Porcine pancreatic* lipase (5 mg) were added and the mixture was stirred at room temperature, following the reaction by TLC (reaction times indicated in the main document, table 2). The solution was filtered through a

plug of silica, concentrated in vacuo and subjected to HPLC analysis without further purification .

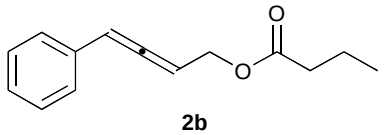
2-Methyl-4-phenylbuta-2,3-dienyl butyrate (2a)



2a

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.90 (t. *J* = 7.4 Hz, 3H), 1.61 (tq, *J* = 7.4 Hz, 2H), 1.83 (d, *J* = 2.8 Hz, 3H), 2.28 (t, *J* = 7.3 Hz, 2H), 4.58-4.67 (m, 2H), 6.17 (tq, *J* = 2.8 Hz, 1H), 7.18-7.30 (m, 5H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 13.6, 15.9, 18.4, 36.1, 64.8, 95.7, 99.9, 126.9, 127.0, 128.5, 134.4, 173.3, 203.2. HRMS (ESI) calcd for $C_{15}H_{18}NaO_2$ $[M+Na]^+$: 253.1199, found: 253.1199. HPLC (*Chiralcel OB*, isohexane-isopropanol gradient: [99:1 (30min)]-[99:1 to 90:10 (30min)]-[90:10 (30min)], 0.5 mL/min, 249 nm): t_R(*R*) = 30.8 min, t_R(*S*) = 47.4 min.

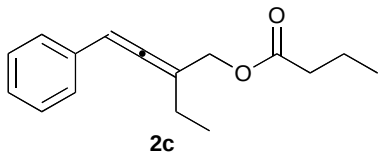
4-Phenylbuta-2,3-dienyl butyrate (2b)



2b

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.94 (t. *J* = 7.6 Hz, 3H), 1.65 (tq, *J* = 7.6 Hz, 2H), 2.29 (t, *J* = 7.6 Hz, 2H), 4.69 (dd, *J* = 2.5, 6.5 Hz, 2H), 5.72 (dt, *J* = 6.5 Hz, 1H), 6.30 (dt, *J* = 2.5, 6.4 Hz, 2H), 7.20-7.24 (m, 1H), 7.27-7.34 (m, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 13.6, 16.4, 36.1, 61.5, 91.2, 96.5, 126.9, 127.2, 128.6, 133.3, 173.3, 206.3. HRMS (ESI) calcd for $C_{14}H_{16}NaO_2$ $[M+Na]^+$: 239.1043, found: 239.1041. HPLC (*Chiralcel OB*, isohexane-isopropanol gradient: [100:0 (25min)]-[100:0 to 90:10 (20min)]-[90:10 (30min)], 0.5 mL/min, 249 nm): t_R(*R*) = 43.6 min, t_R(*R*) = 58.8 min.

2-Ethyl-4-phenylbuta-2,3-dienyl butyrate (2c)

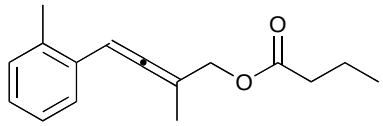


2c

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.92 (t. *J* = 7.2 Hz, 3H), 1.09 (t. *J* = 7.4 Hz, 3H), 1.61 (tq, *J* = 7.4 Hz, 2H), 2.10-2.19 (m, 2H), 2.29 (t, *J* = 7.2 Hz, 2H), 4.63-4.71 (m, 2H), 6.20-6.24

(m, 1H), 7.17-7.22 (m, 1H), 7.26-7.32 (m, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 12.0, 13.6, 18.4, 22.9, 36.1, 64.1, 97.5, 106.6, 126.7, 127.0, 128.5, 134.6, 173.3, 202.6. HRMS (ESI) calcd for $C_{16}H_{20}NaO_2$ $[M+Na]^+$: 267.1356, found: 267.1349. HPLC (*Chiralcel OD-H*, isohexane-isopropanol gradient: [100:0 (30min)]-[100:0 to 90:10 (30min)]-[90:10 (30min)], 0.5 mL/min, 249 nm): t_R(*S*) = 28.3 min, t_R(*R*) = 40.1 min.

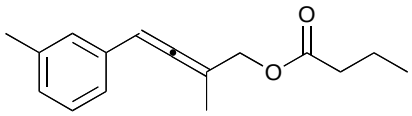
2-Methyl-4-(2-methylphenyl)buta-2,3-dienyl butyrate (2d).



2d

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.94 (t, *J* = 7.4 Hz, 3H), 1.65 (tq, *J* = 7.4 Hz, 2H), 1.85 (d, *J* = 2.9 Hz, 3H), 2.31 (t, *J* = 7.4 Hz, 2H), 2.36 (s, 3H), 4.65 (d, *J* = 2.5 Hz, 2H), 6.39 (tq, *J* = 2.8 Hz, 1H), 7.11-7.18 (m, 3H), 7.31 (dd, *J* = 1.2, 7.2 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 13.6, 16.0, 18.4, 19.9, 36.1, 65.0, 93.0, 98.6, 126.0, 126.9, 127.6, 130.4, 132.6, 135.1, 173.3, 204.1. HRMS (ESI) calcd for $C_{16}H_{20}NaO_2$ $[M+Na]^+$: 267.1356, found: 267.1345. HPLC (*Chiralcel OJ*, isohexane-isopropanol gradient: [100:0 (30min)]-[100:0 to 90:10 (30min)]-[90:10 (30min)], 0.5 mL/min, 248 nm): t_R(*S*) = 50.9 min, t_R(*R*) = 53.1 min.

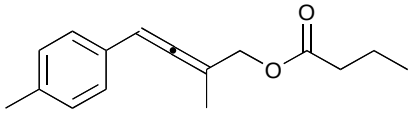
2-Methyl-4-(3-methylphenyl)buta-2,3-dienyl butyrate (2e)



2e

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.94 (t, *J* = 7.4 Hz, 3H), 1.65 (tq, *J* = 7.3 Hz, 2H), 1.85 (d, *J* = 2.8 Hz, 3H), 2.31 (t, *J* = 7.0 Hz, 2H), 2.35 (s, 3H), 4.62-4.69 (m, 2H), 6.17 (tq, *J* = 2.7 Hz, 1H), 7.01-7.09 (m, 3H), 7.18-7.22 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 13.6, 15.9, 18.4, 21.3, 36.1, 64.9, 95.6, 99.7, 123.9, 127.5, 127.7, 128.4, 134.3, 138.1, 173.2, 203.2. HRMS (ESI) calcd for $C_{16}H_{20}NaO_2$ $[M+Na]^+$: 267.1356, found: 267.1344. HPLC (*Chiralcel OD-H*, isohexane-isopropanol gradient: [100:0 (30min)]-[100:0 to 90:10 (30min)]-[90:10 (30min)], 0.5 mL/min, 249 nm): t_R(*S*) = 28.1 min, t_R(*R*) = 36.9 min.

2-Methyl-4-(4-methylphenyl)buta-2,3-dienyl butyrate (2f)

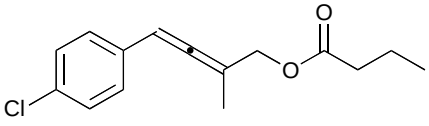


2f

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.92 (t, *J* = 7.6 Hz, 3H), 1.62 (tq, *J* = 7.5 Hz, 2H),

1.83 (d, *J* = 2.9 Hz, 3H), 2.29 (t, *J* = 7.4 Hz, 2H), 2.33 (s, 3H), 4.58-4.67 (m, 2H), 6.16 (tq, *J* = 2.7 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 13.7, 15.9, 18.4, 21.2, 36.1, 65.0, 95.5, 99.7, 126.8, 129.3, 131.5, 136.8, 173.3, 202.9. HRMS (ESI) calcd for $C_{16}H_{20}NaO_2$ $[M+Na]^+$: 267.1356, found: 267.1349. HPLC (*Chiralcel OB*, isohexane-isopropanol gradient: [100:0 (30min)]-[100:0 to 90:10 (30min)]-[90:10 (30min)], 0.5 mL/min, 251 nm): t_R(*R*) = 49.2 min, t_R(*S*) = 55.3 min.

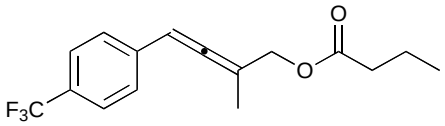
2-Methyl-4-(4-methylphenyl)buta-2,3-dienyl butyrate (2g)



2g

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.91 (t. *J* = 7.4 Hz, 3H), 1.61 (tq, *J* = 7.4 Hz, 2H), 1.83 (d, *J* = 2.9 Hz, 3H), 2.27 (t, *J* = 7.6 Hz, 2H), 4.58-4.66 (m, 2H), 6.14 (tq, *J* = 2.8 Hz, 1H), 7.15-7.19 (m, 2H), 7.24-7.27 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 13.6, 15.8, 18.4, 36.1, 64.5, 94.9, 100.4, 128.0, 128.7, 132.5, 133.0, 173.2, 203.1. HRMS (ESI) calcd for $C_{15}H_{17}ClNaO_2$ $[M+Na]^+$: 287.0809, found: 287.0806. HPLC (*Chiralcel OB*, isohexane-isopropanol gradient: [100:0 (30min)]-[100:0 to 90:10 (30min)]-[90:10 (30min)], 0.5 mL/min, 256 nm): t_R(*R*) = 51.2 min, t_R(*S*) = 59.0 min.

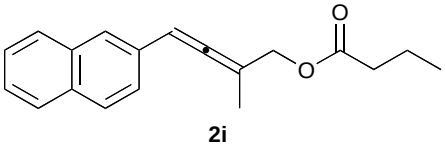
2-Methyl-4-(4-trifluoromethylphenyl)buta-2,3-dienyl butyrate (2h)



2h

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.91 (t. *J* = 7.4 Hz, 3H), 1.61 (tq, *J* = 7.4 Hz, 2H), 1.85 (d, *J* = 2.9 Hz, 3H), 2.28 (t, *J* = 7.6 Hz, 2H), 4.60-4.69 (m, 2H), 6.22 (tq, *J* = 2.8 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 13.6, 15.6, 18.4, 36.1, 64.4, 94.9, 100.7, 124.2 (q, *J* = 269 Hz), 125.5 (q, *J* = 3.7 Hz), 127.0, 128.8 (q, *J* = 32.1 Hz), 138.4, 173.2, 203.9. HRMS (ESI) calcd for $C_{16}H_{18}F_3O$ $[M+H]^+$: 299.1253, found: 299.1209. HPLC (*Chiralcel OD-H*, isohexane-isopropanol gradient: [100:0 (30min)]-[100:0 to 90:10 (30min)]-[90:10 (30min)], 0.5 mL/min, 251 nm): t_R(*R*) = 33.2 min, t_R(*S*) = 41.3 min.

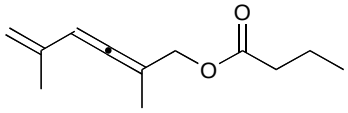
2-Methyl-4-(2-naphtyl)buta-2,3-dienyl butyrate (2i)



2i

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.93 (t. *J* = 7.6 Hz, 3H), 1.65 (tq, *J* = 7.5 Hz, 2H), 1.91 (d, *J* = 2.8 Hz, 3H), 2.3 (t, *J* = 7.6 Hz, 2H), 4.67-4.75 (m, 2H), 6.40 (tq, *J* = 2.8 Hz, 1H), 7.42-7.48 (m, 3H), 7.66 (bs, 1H), 7.77-7.82 (m, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 13.6, 15.9, 18.4, 36.1, 64.8, 96.1, 100.2, 124.7, 125.5, 125.7, 126.1, 127.6, 128.1, 131.9, 132.6, 133.6, 173.2, 203.9. HRMS (ESI) calcd for $C_{19}H_{20}NaO_2$ $[M+Na]^+$: 303.1356, found: 303.1347. HPLC (*Chiralcel OD-H*, isohexane-isopropanol gradient: [100:0 (30min)]-[100:0 to 90:10 (30min)]-[90:10 (30min)], 0.5 mL/min, 252 nm): t_R(*R*) = 56.1 min, t_R(*S*) = 65.7 min.

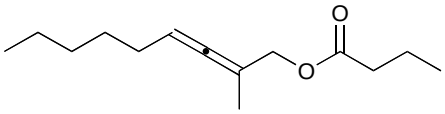
2,5-Dimethylhexa-2,3,5-trienyl butyrate (2j)



2j

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.95 (t. *J* = 7.6 Hz, 3H), 1.63 (tq, *J* = 7.6 Hz, 2H), 1.74 (m, 3H), 1.77 (d, *J* = 3.0 Hz, 3H), 2.30 (t, *J* = 7.6 Hz, 2H), 4.55 (d, *J* = 2.4 Hz, 2H), 4.87 (m, 1H), 4.91 (m, 1H), 5.94 (tq, *J* = 2.7 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 13.7, 16.1, 18.4, 19.5, 36.2, 65.0, 98.6, 113.9, 139.3, 173.3, 203.7. HRMS (ESI) calcd for $C_{12}H_{18}NaO_2$ $[M+Na]^+$: 217.1199, found: 217.1194. HPLC (*Chiralcel OB*, isohexane (100%), 0.5 mL/min, 217 nm): t_R(*S*) = 22.5 min, t_R(*R*) = 29.2 min.

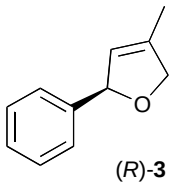
2-Methylnona-2,3-dienyl butyrate (2k)



2k

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.88 (t, *J* = 7.2 Hz, 3H), 0.94 (t. *J* = 7.4 Hz, 3H), 1.27-1.39 (m, 6H), 1.66 (tq, *J* = 7.4 Hz, 2H), 1.69 (d, *J* = 2.6 Hz, 3H), 1.96 (dd, *J* = 7.2 Hz, 2H), 2.30 (t, *J* = 7.4 Hz, 2H), 4.50 (d, *J* = 2.3 Hz, 2H), 5.14 (ttq, *J* = 2.8, 7.2 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 13.7, 14.0, 16.3, 18.5, 22.5, 28.7, 31.2, 65.9, 91.9, 95.3, 173.4, 202.3. HRMS (ESI) calcd for $C_{14}H_{24}NaO_2$ $[M+Na]^+$: 247.1669, found: 247.1670. No separation on HPLC.

(*R*)-4-Methyl-2-phenyl-2,5-dihydrofuran ((*R*)-3)

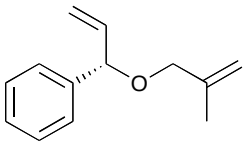


(*R*)-**3**

(*S*)-**1a** (32 mg, 200 µmol, 97% ee) was dissolved in hot pentane (2 ml). At room temperature $AgNO_3$ (10 wt% on SiO_2, 34 mg, 20 µmol) was added and the slurry was stirred in the dark

for 4 h. After filtration through a plug of silica, washing with diethyl ether and concentration in vacuo, (*R*)-**3** (31 mg, 193 µmol, 97%) was obtained as a colourless oil; 97% ee, $[\alpha]^{20}_D$ = +154° (*c* 0.3, $CHCl_3$). ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.81 (m, 3H), 4.59-4.75 (m, 2H), 5.49-5.52 (m, 1H), 5.75 (dq, *J* = 1.9, 7.5 Hz, 1H), 7.23-7.34 (m, 5H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 12.2, 78.4, 88.4, 123.9, 126.3, 127.6, 128.4, 136.4, 142.6. HRMS (ESI) calcd for $C_{11}H_{13}O$ $[M+H]^+$: 161.0961, found: 161.0962. HPLC (*Chiralcel OJ*, isohexane-isopropanol gradient: [100:0 (30min)]-[100:0 to 90:10 (30min)]-[90:10 (30min)], 0.5 mL/min, 213 nm): t_R (*R*) = 55.9 min, t_R (*S*) = 59.2 min.

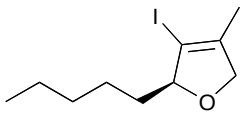
(*S*)-3-Phenylpropen-3-yl-2-methylallyl ether ((*S*)-6)



(*S*)-**6**

To a solution of (*S*)-**4** (204 mg, 1.5 mol, 99% ee) in dry DMF (2 ml) was added NaH (60 wt%, 72 mg, 1.8 mmol) at 0°C. After 30 min 3-bromo-2-methylpropene (243 mg, 1.8 mmol) was added, stirring was continued at room temperature for 3 h. Sat. NH_4Cl and diethyl ether was added, the aqueous phase was extracted with diethyl ether, the combined organic phases were dried over $MgSO_4$ and concentrated in vacuo. Column chromatography (SiO_2, pentane-diethyl ether 97:3) yielded (*S*)-**6** (234 mg, 1.24 mmol, 83%) as a colourless liquid; 99% ee, $[\alpha]^{20}_D$ = +16.3° (*c* 0.3, $CHCl_3$). ^{1}H-NMR (400MHz, $CDCl_3$): δ [ppm] = 1.79 (s, 3H), 3.92 (s, 2H), 4.80 (dd, *J* = 2.3, 7.0 Hz, 1H), 4.94 (m, 1H), 5.02 (m, 1H), 5.23 (ddd, *J* = 2.3, 2.6, 10.3 Hz, 1H), 5.31 (ddd, *J* = 2.3, 2.6, 17.1 Hz, 1H), 5.98 (ddd, *J* = 6.9, 10.3, 17.1 Hz, 1H), 7-32-7.40 (m, 5H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 19.6, 72.0, 81.7, 112.0, 116.2, 126.9, 127.5, 128.4, 138.9, 141.1, 142.2. HRMS (ESI) calcd for $C_{13}H_{16}NaO$ $[M+Na]^+$: 211.1093, found: 211.1087.

(*S*)-3-Iodo-4-methyl-2-pentyl-2,5-dihydrofuran ((*S*)-9)

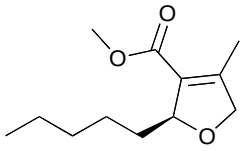


(*S*)-**9**

(*S*)-**1k** (182 mg, 1.18 mol) was dissolved in dichloromethane (5 ml) and *N*-iodosuccinimide (318 mg, 1.41 mmol) was added in small portions at room temperature. The reaction mixture was stirred for 2 h, then sat. $Na_2S_2O_3$ and dichloromethane was added, the organic phase was washed with sat. $Na_2S_2O_3$ and brine and dried over $MgSO_4$. The solvent was evaporated and the crude iododihydrofuran was purified by column chromatography (SiO_2, pentane-diethyl ether, 95:5), yielding (*S*)-**9** (274 mg, 0.98 mmol, 83%) as a yellow oil; 97% ee, $[\alpha]^{20}_D$ = –2.3° (*c* 1.0, $CHCl_3$). ^{1}H-NMR (400MHz, $CDCl_3$): δ [ppm] = 0.89 (t, *J* = 6.9 Hz, 3H), 1.25-1.38 (m,

6H), 1.48-1.54 (m, 1H), 1.74-1.80 (m, 1H), 1.77 (dt, *J* = 1.2, 1.6 Hz, 3H), 4.50-4.53 (m, 2H), 4.69-4.72 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 14.0, 14.5, 22.6, 23.7, 31.8, 34.3, 77.5, 90.1, 90.2, 140.2. HRMS (ESI) calcd for $C_{10}H_{17}INaO$ $[M+Na]^+$: 303.0216, found: 303.0219. HPLC (*Chiralcel OB*, isohexane (100%), 0.5 mL/min, 216 nm): t_R (*R*) = 11.6 min, t_R (*S*) = 12.8 min.

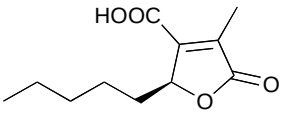
(*S*)-3-Methoxycarbonyl-4-methyl-2-pentyl-2,5-dihydrofuran ((*S*)-10)



(*S*)-**10**

In a pressure tube (30 ml) (*S*)-**9** (100 mg, 0.36 mmol) and triethylamine (148 µl, 1.07 mmol) were dissolved in dry methanol (4 ml) and CO was bubbled through the solution for 30 min. $Pd(PPh_3)_4$ (21 mg, 0.018 mmol) was added and the tube was sealed and heated to 85°C for 20 h. After cooling down to room temperature, the reaction mixture was concentrated in vacuo and the residue purified by column chromatography (SiO_2, pentane-diethyl ether, 95:5) to yield (*S*)-**10** (71.4 mg, 0.33 mmol, 92%) as a yellow oil; 97% ee, $[\alpha]^{20}_D$ = –7.2° (*c* 0.5, $CHCl_3$). ^{1}H-NMR (400MHz, $CDCl_3$): δ [ppm] = 0.87 (t, *J* = 6.8 Hz, 3H), 1.24-1.37 (m, 6H), 1.51-1.58 (m, 1H), 1.73-1.79 (m, 1H), 2.05 (dt, *J* = 1.2, 1.6 Hz, 3H), 4.54-4.68 (m, 2H), 5.03 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 11.9, 14.0, 22.6, 24.7, 31.8, 34.7, 51.1, 78.9, 86.9, 126.7, 150.6, 164.2. HRMS (ESI) calcd for $C_{12}H_{21}O_3$ $[M+H]^+$: 213.1485, found: 213.1492.

(*S*)-Striatisporolide A ((*S*)-7).

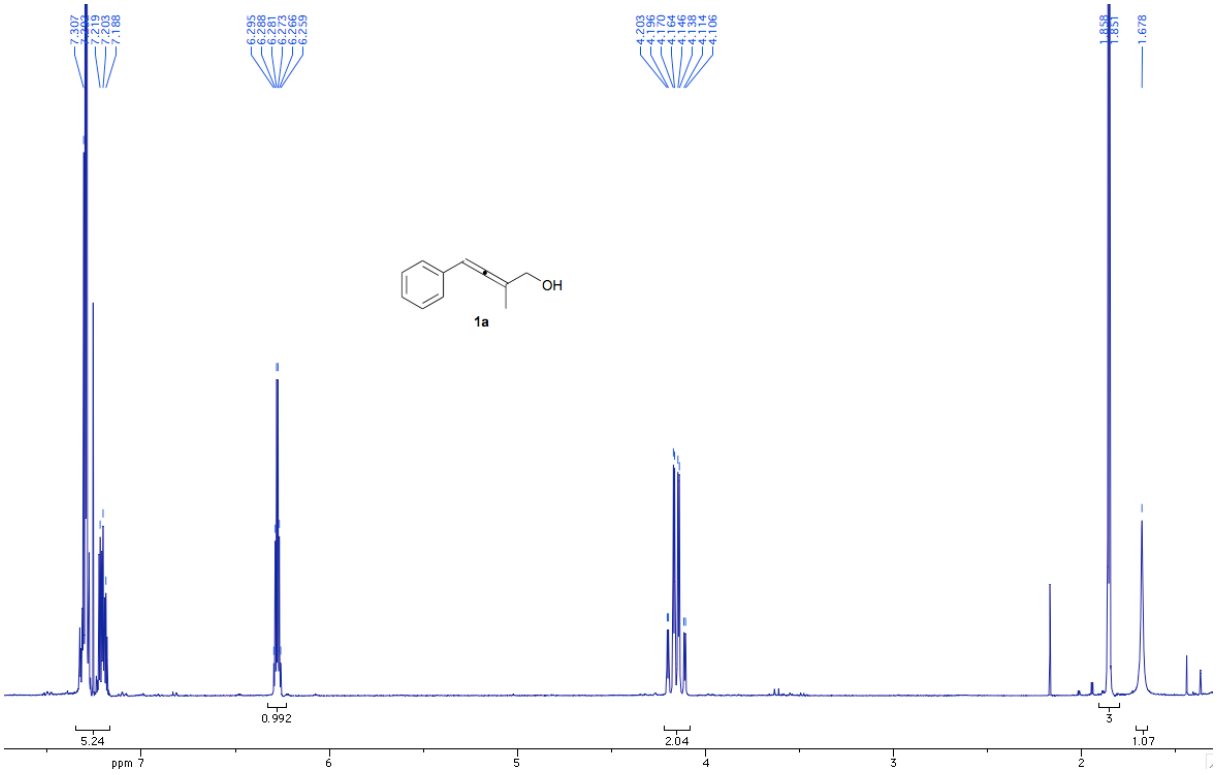


(*S*)-**7**

Powdered CrO_3 (90 mg, 0.90 mmol) was suspended in dry dichloromethane (2 ml), at -20°C solid 3,5-dimethylpyrazole (87 mg, 0.90 mmol) was added and the mixture was stirred at this temperature for 30 min, forming a dark orange solution. (*S*)-**10** (31.8 mg, 0.15 mmol) was added and stirring was continued for 6 h at -20°C. After filtration through a plug of silica, the solution was concentrated in vacuo, the residue was redissolved in THF/H_2O (1 ml, 4:1) and the solution was treated with LiOH monohydrate (19 mg, 0.45 mmol) at 0°C. After 1 h water and diethyl ether were added and the phases were separated. The aqueous layer was acidified with 1 M HCl, extracted three times with diethyl ether, the ethereal phase was dried over $MgSO_4$ and concentrated in vacuo. After purification by column chromatography (SiO_2, pentane-diethyl ether 1:1 to 2:8) (*S*)-**7** (21.4 mg, 0.10 mmol) was obtained as a pale yellow waxy solid; 97% ee, $[\alpha]^{20}_D$ = 25.2° (*c* 0.4, MeOH). ^{1}H-NMR (400MHz, $CDCl_3$): δ [ppm] =

0.84 (t, *J* = 7.0 Hz, 3H), 1.22-1.30 (m, 4H), 1.36-1.39 (m, 2H), 1.53-1.59 (m, 1H), 2.05-2.14 (m, 1H), 2.21 (d, *J* = 2.2 Hz, 3H), 5.09 (dt, *J* = 2.3, 5.4 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 11.1, 13.9, 22.4, 24.4, 31.3, 32.7, 81.4, 140.1, 146.6, 166.8, 172.6. HRMS (ESI) calcd for $C_{11}H_{17}O_4$ $[M+H]^+$: 213.1121, found: 213.2118. HPLC analysis was performed with the methylester of **7,** which was obtained after esterfication with trimethylsilyldiazomethane in MeOH: (*Chiralcel OD-H*, isohexane-isopropanol gradient: [100:0 (30min)]-[100:0 to 90:10 (30min)]-[90:10 (30min)], 0.5 mL/min, 227 nm): t_R (*S*-**7-OMe**) = 55.6 min, t_R (*R*-**7-OMe**) = 56.2 min.

NMR-Spectra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6.259
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4.170
4.164
4.146
4.138
4.114
4.106
1.858
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1.07
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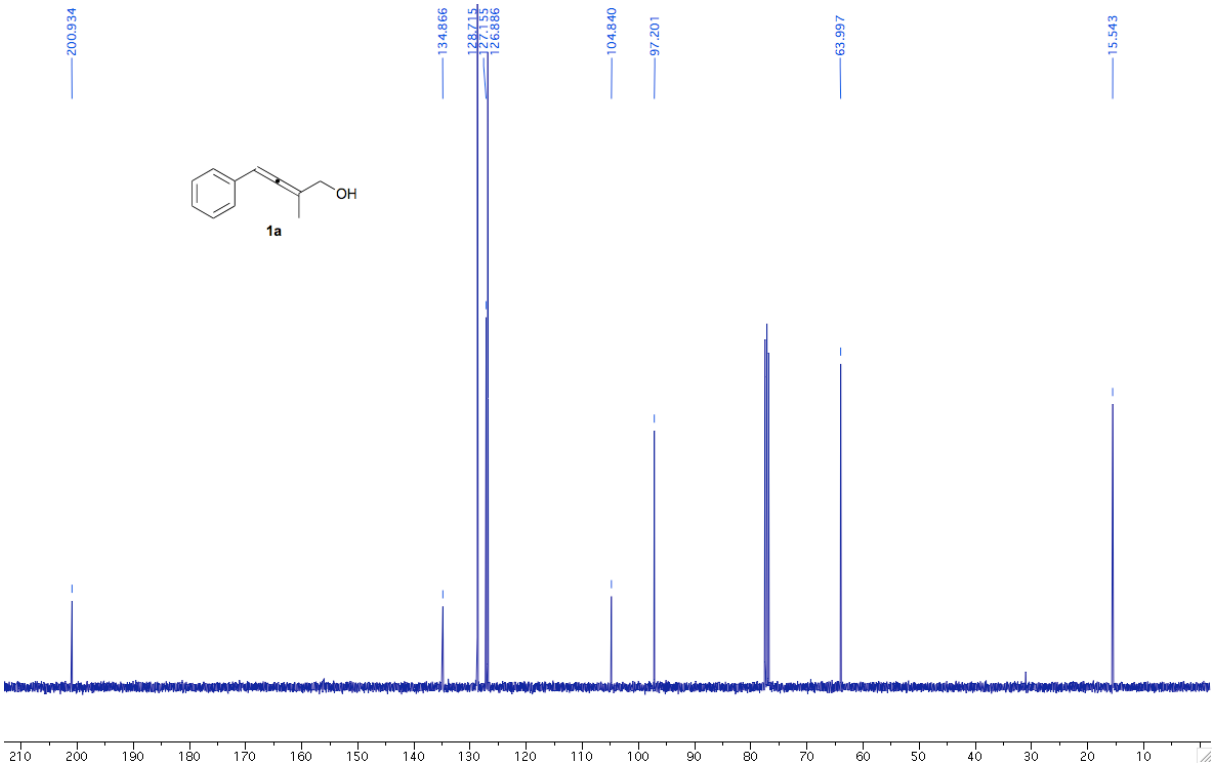
4
3
2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100
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80
70
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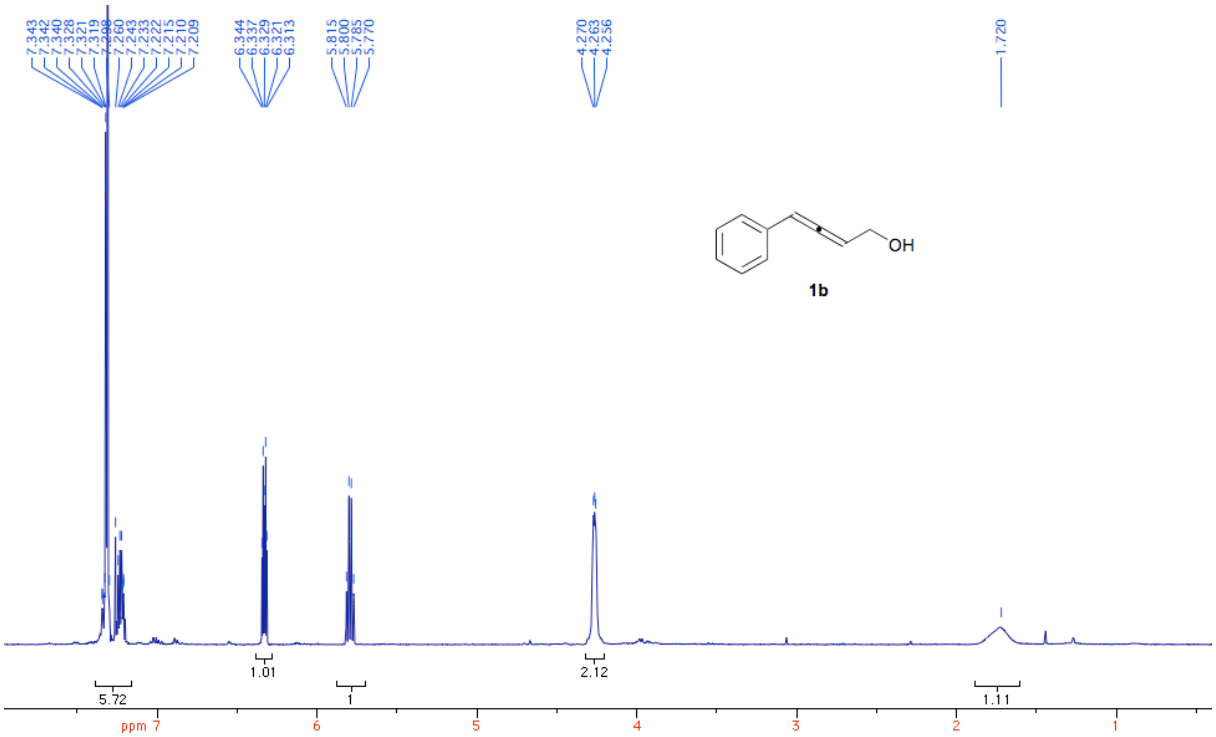
50
40
30
20
10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7.209
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6.329
6.321
6.313
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5.800
5.785
5.770
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4.263
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3
2
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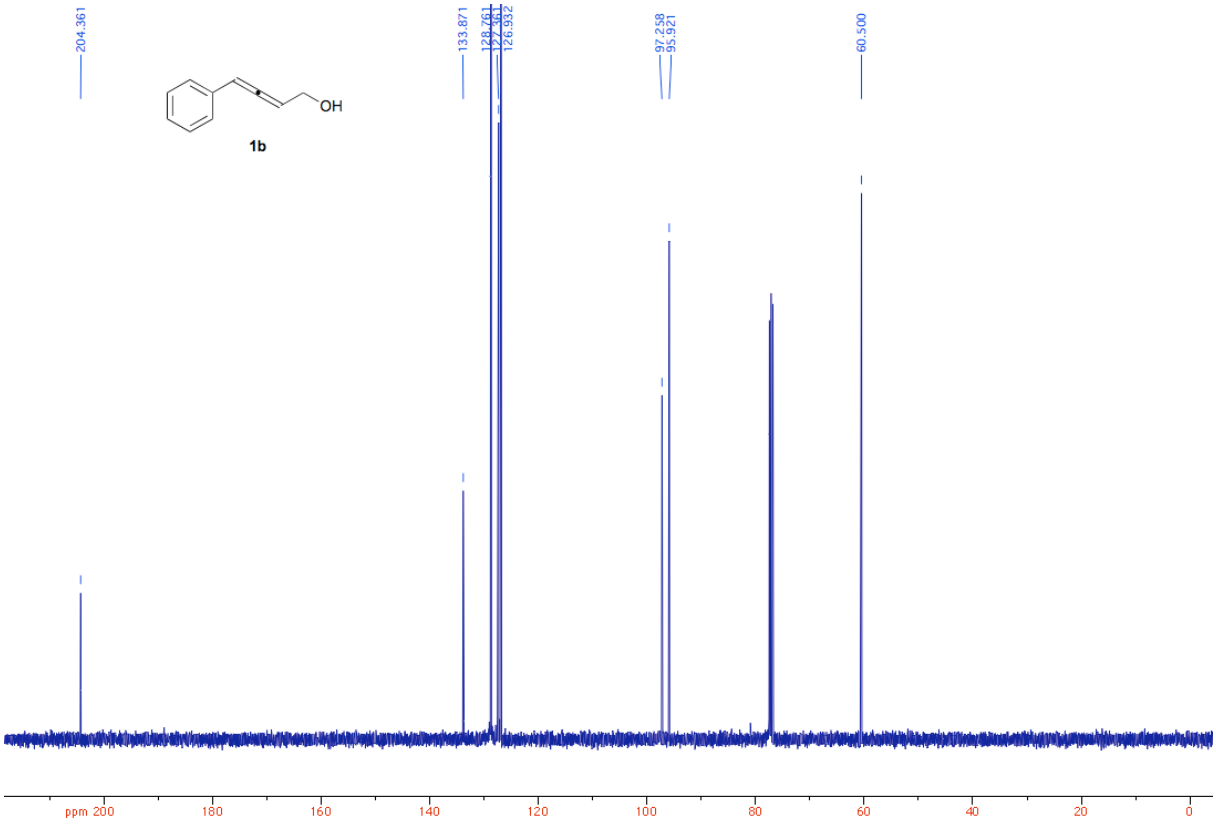
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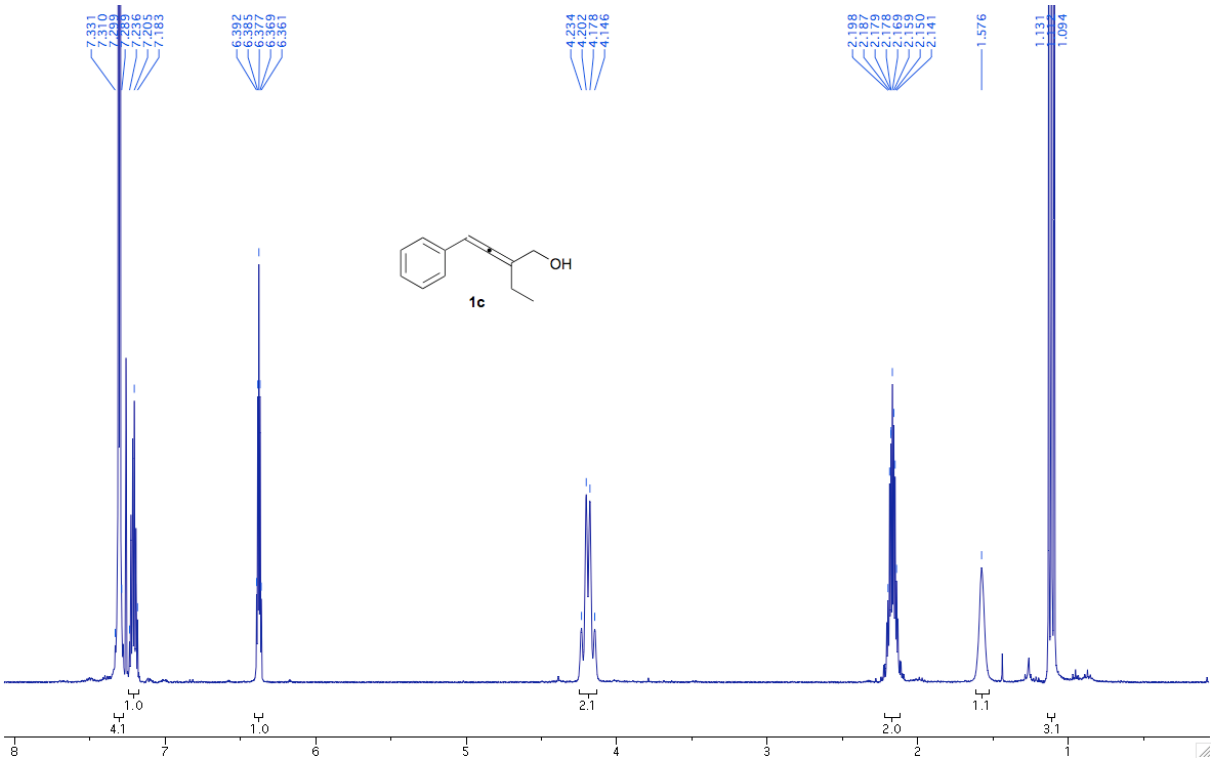
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6.369
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4.222
4.178
4.146
2.198
2.187
2.178
2.169
2.159
2.150
2.141
1.576
1.131
1.094
OH
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8
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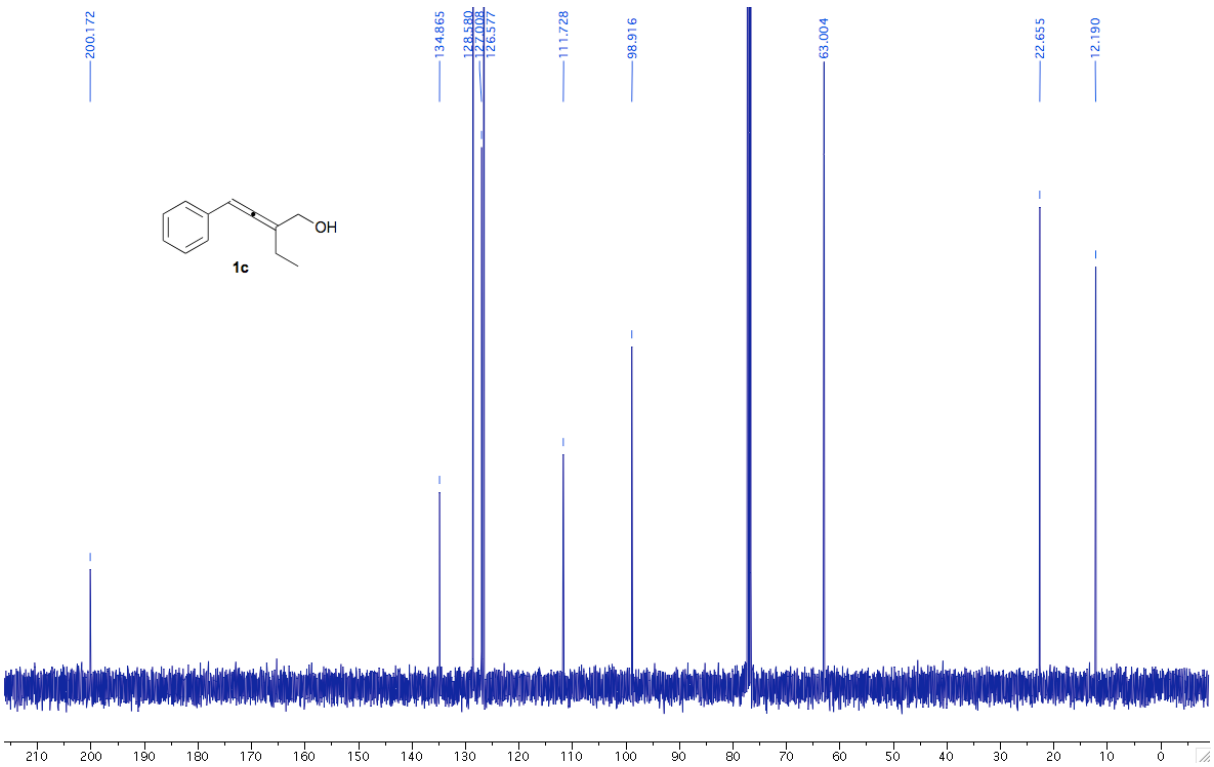
4
3
2
1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10
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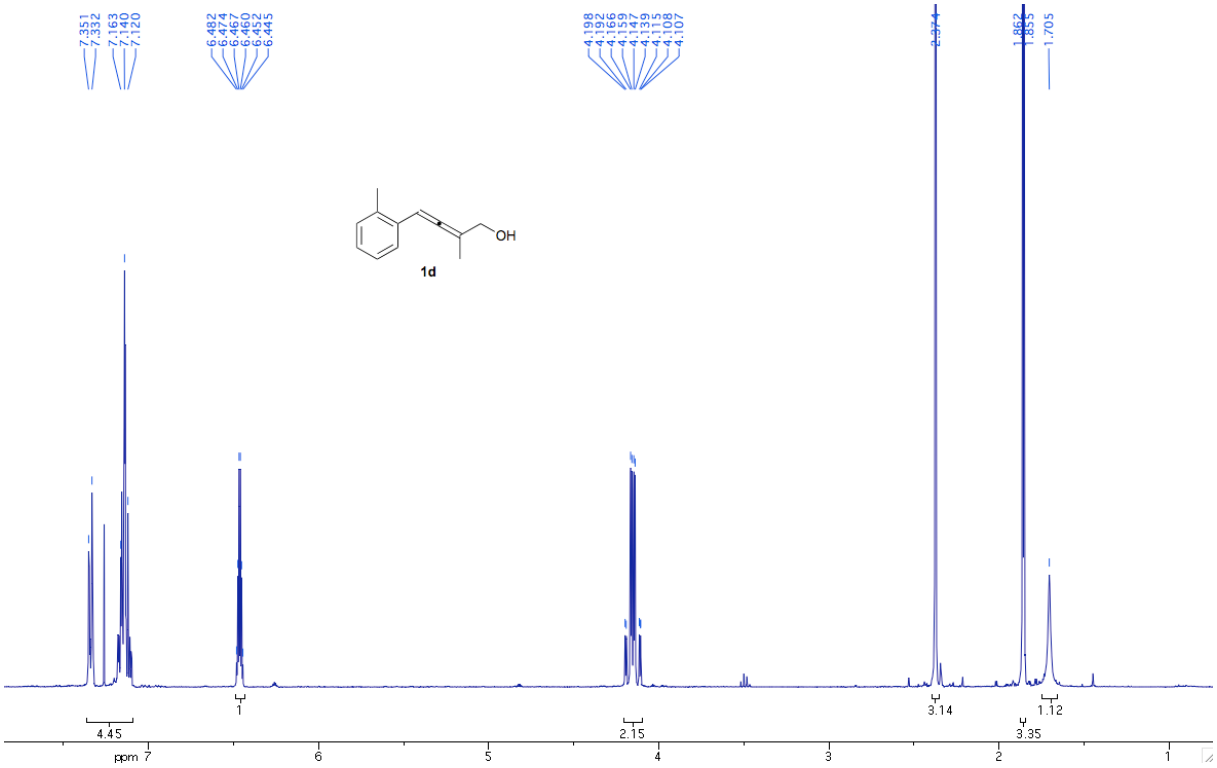
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4.159
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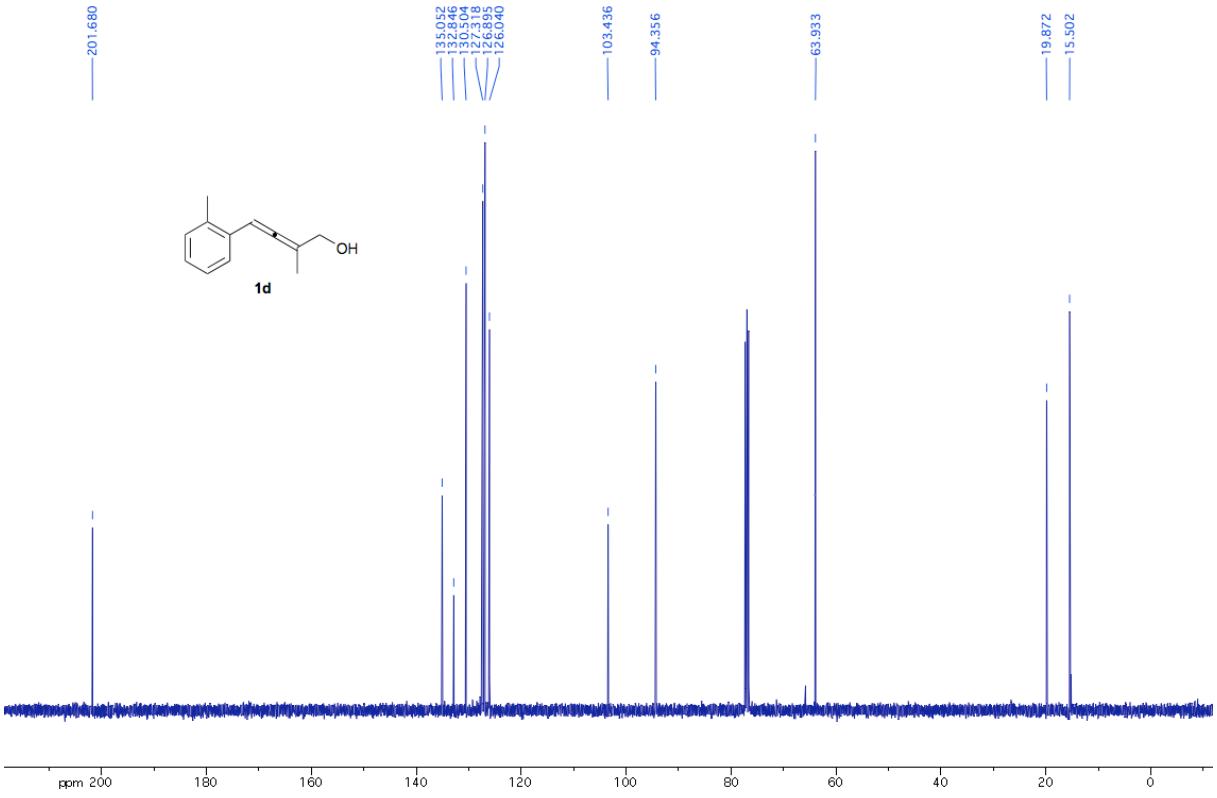
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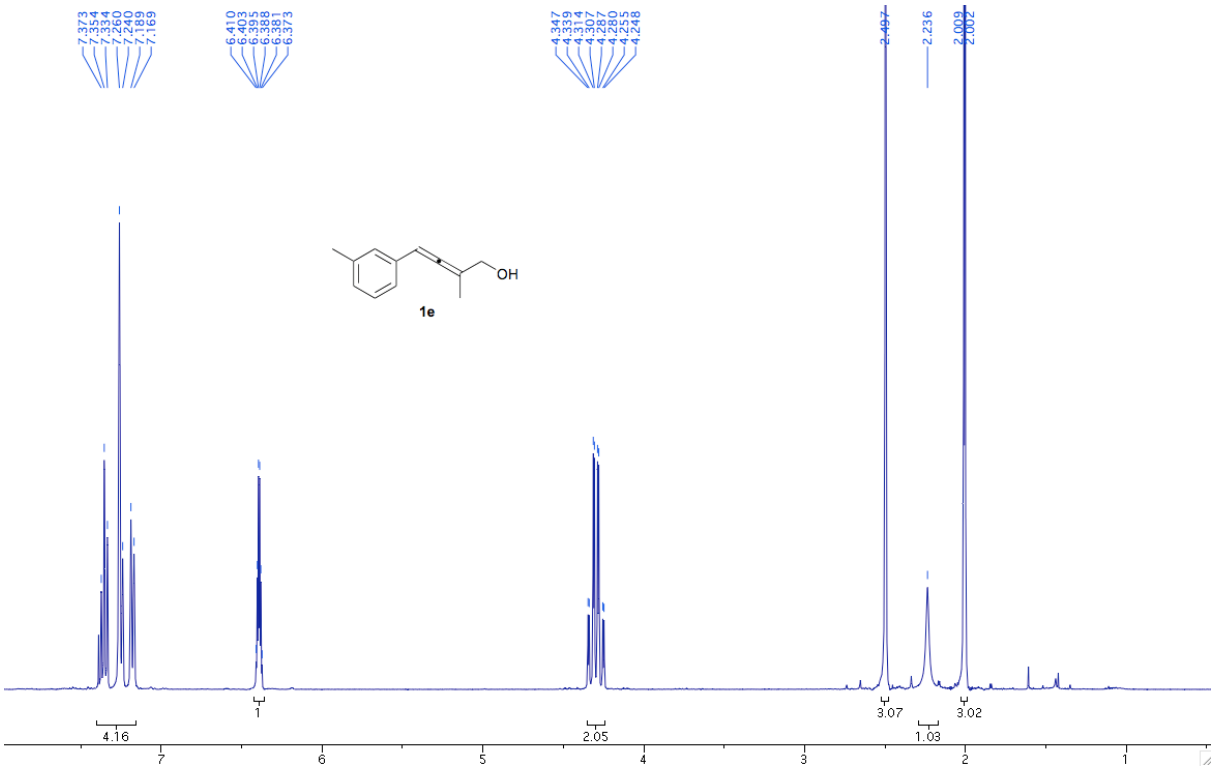
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6.373
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4.339
4.314
4.307
4.287
4.280
4.255
4.248
2.497
2.236
2.009
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OH
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1
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3.02
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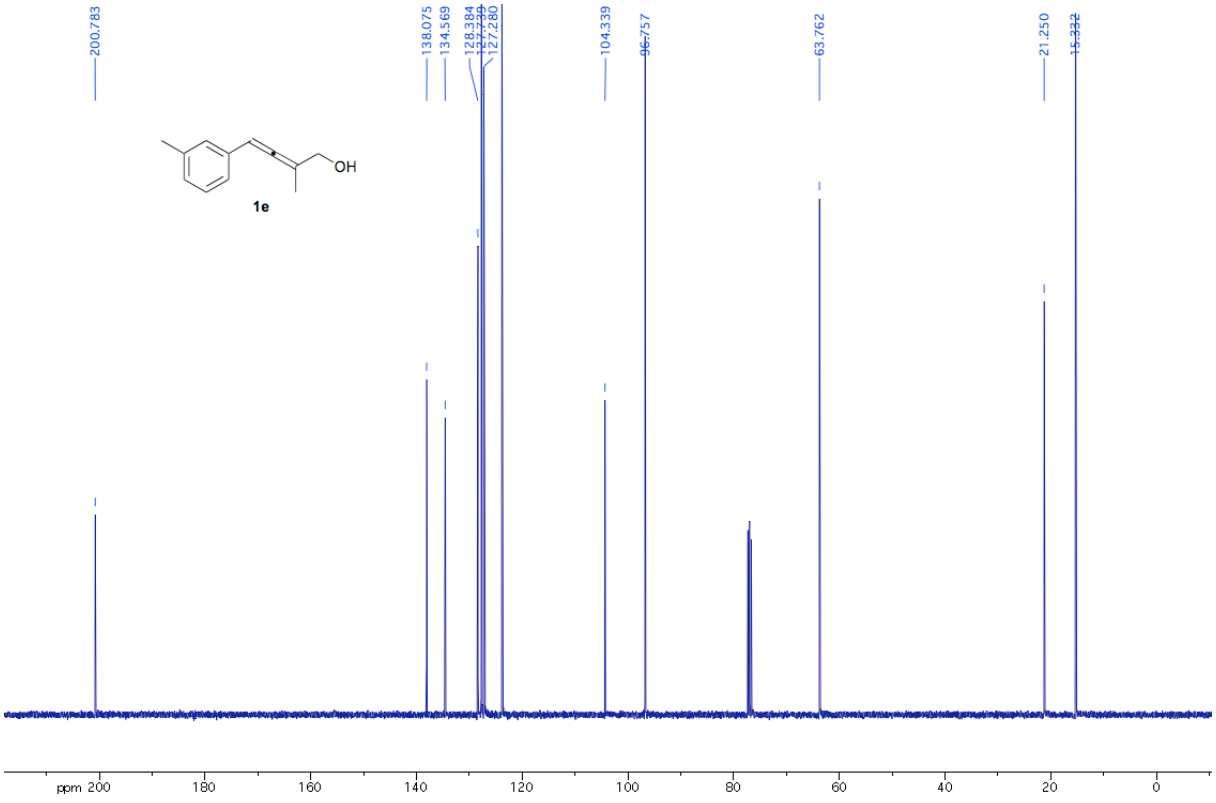
4
3
2
1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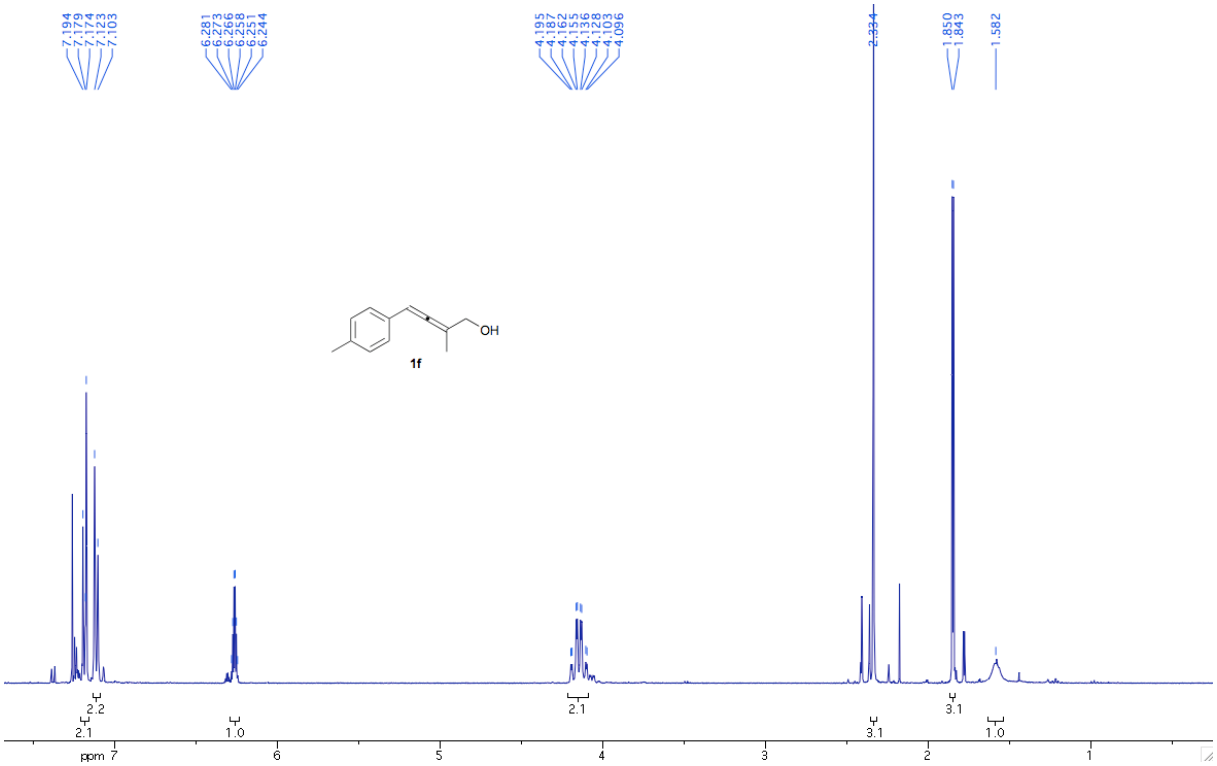
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4.128
4.103
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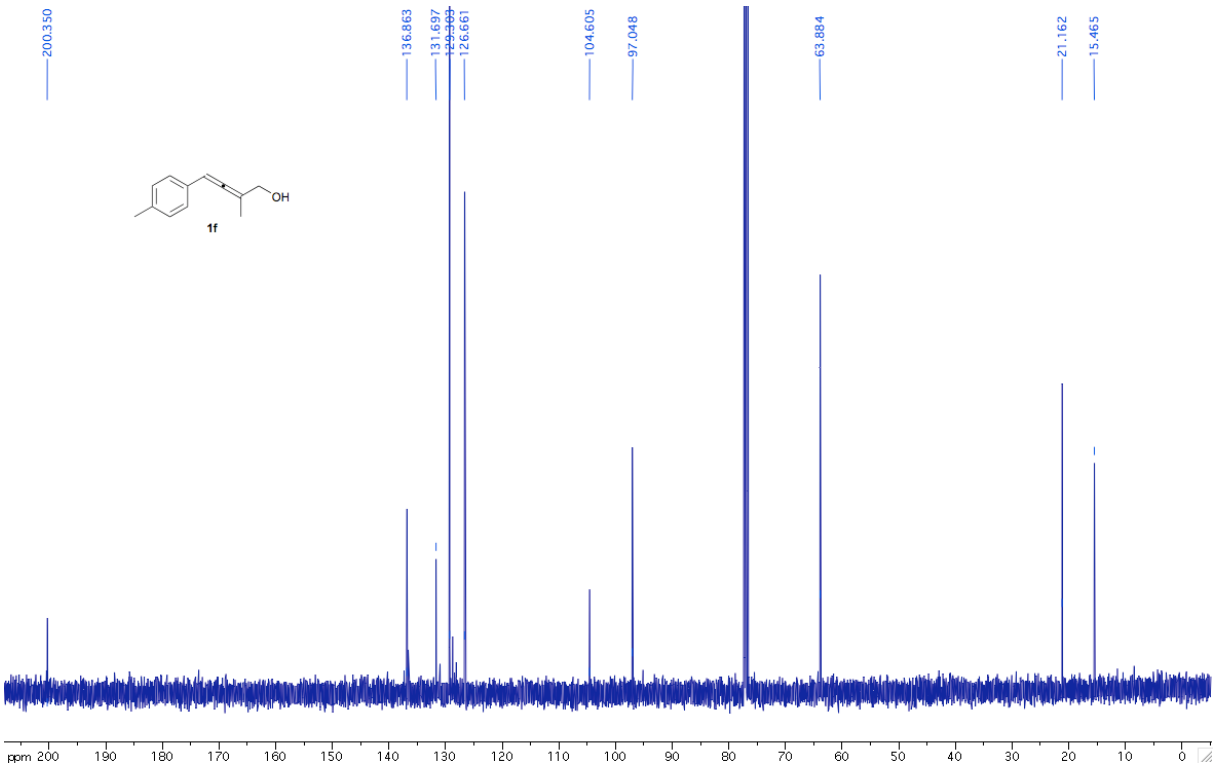
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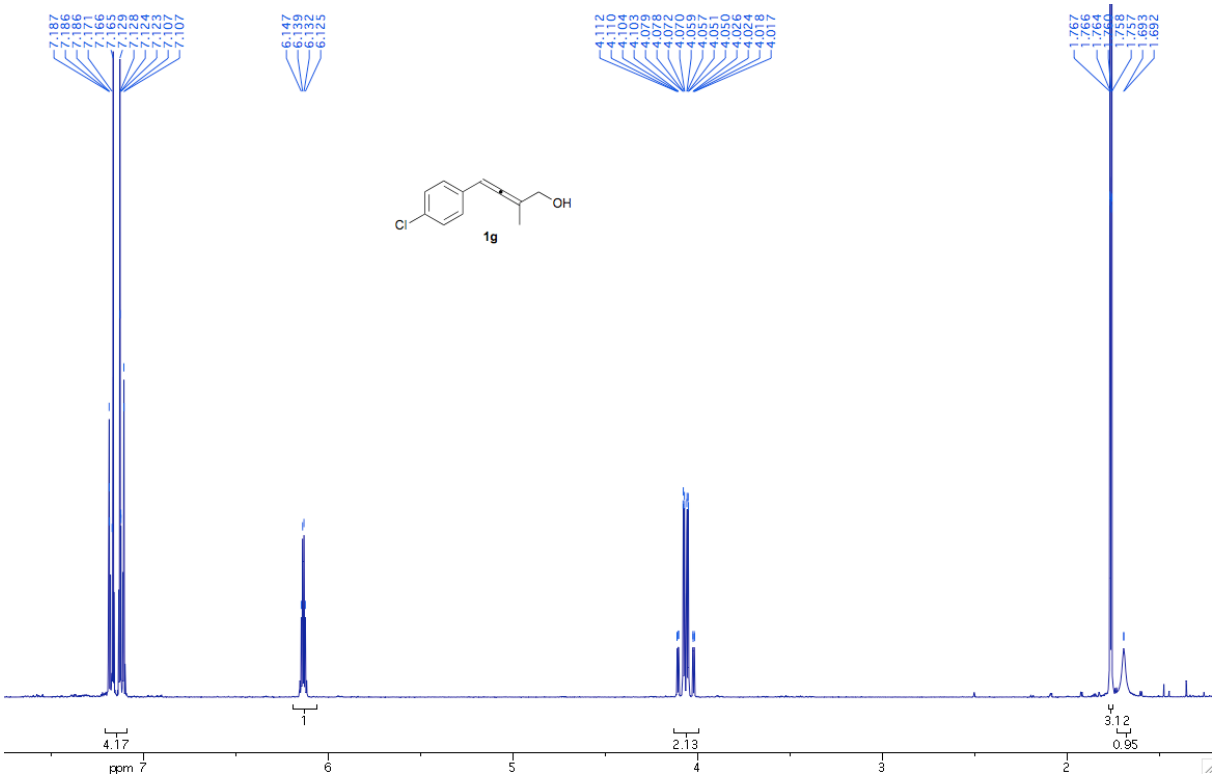
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6.132
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4.103
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4.051
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4.024
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4.017
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1.764
1.760
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1.757
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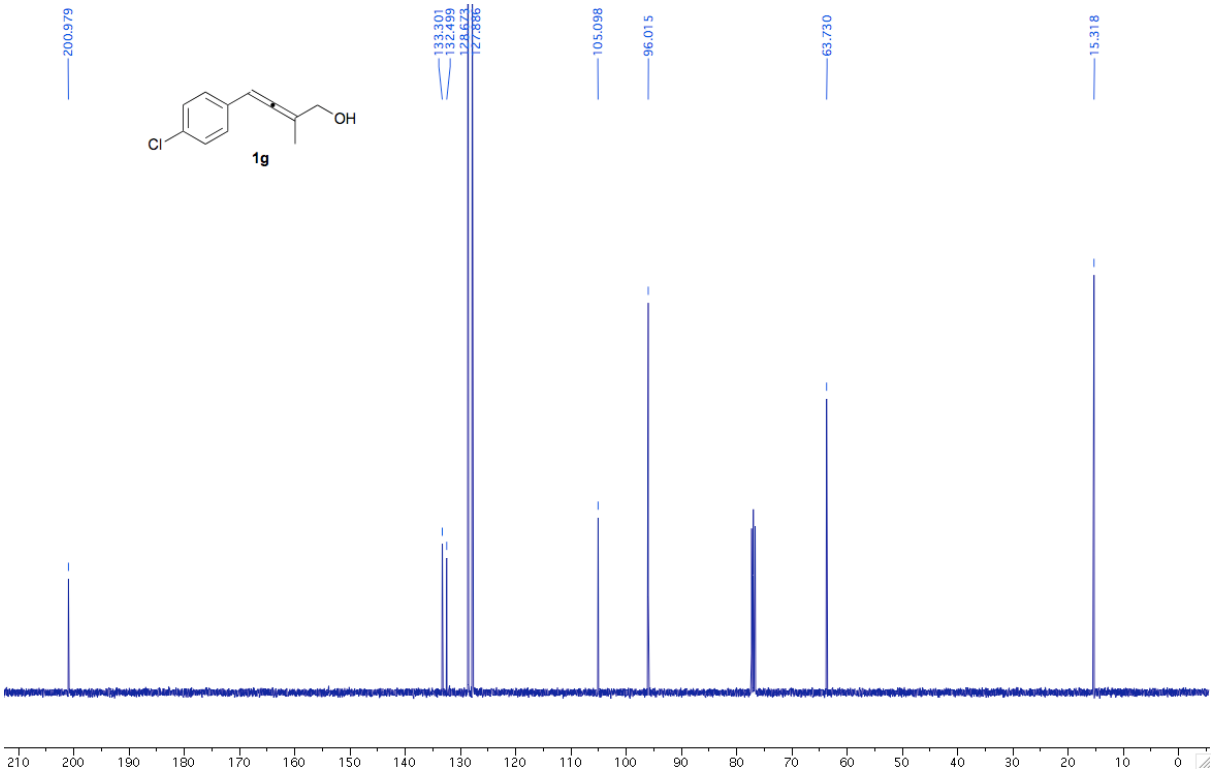
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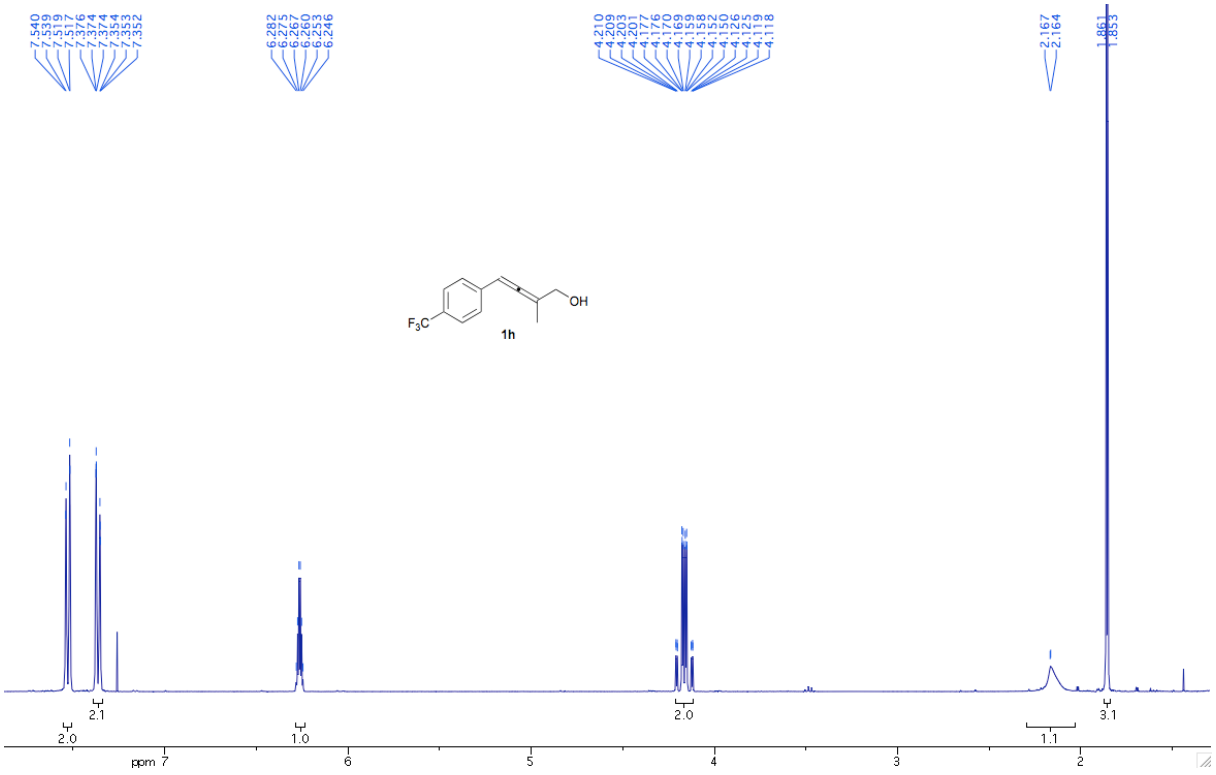
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4.201
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4.176
4.170
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4.159
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4.150
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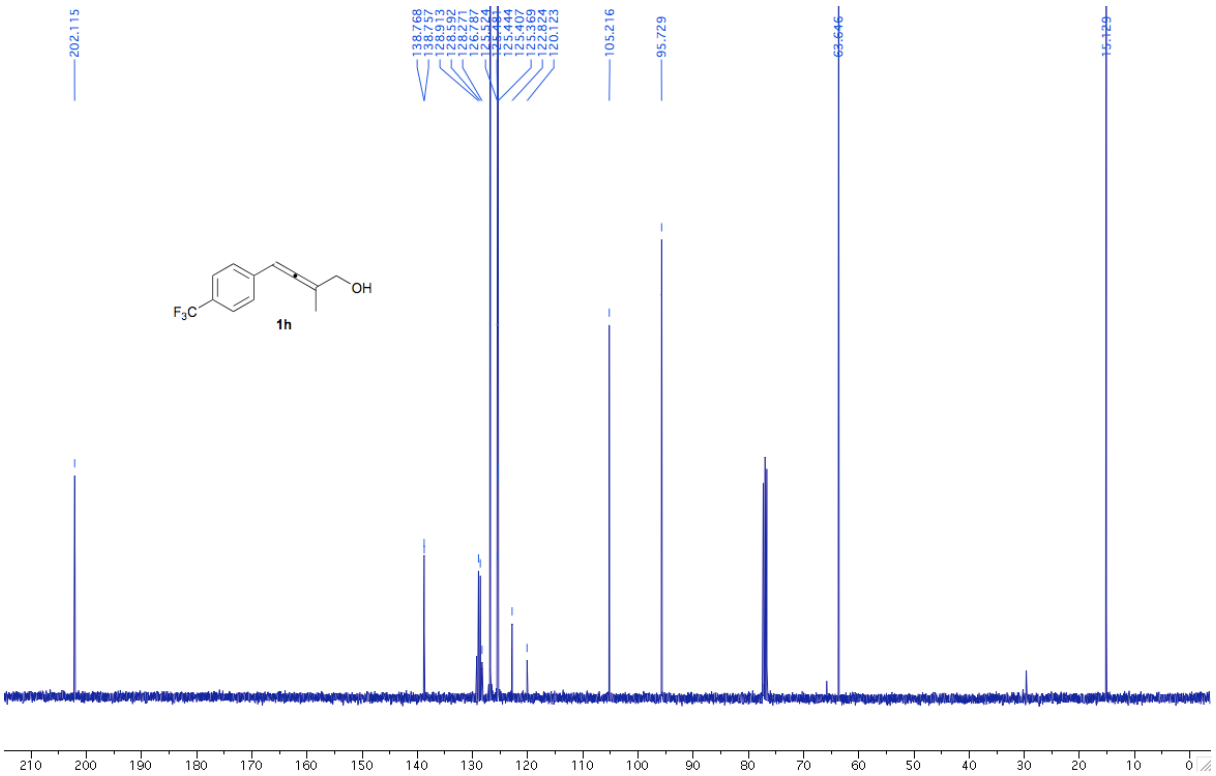
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63.646
15.129
F3C
OH
1h
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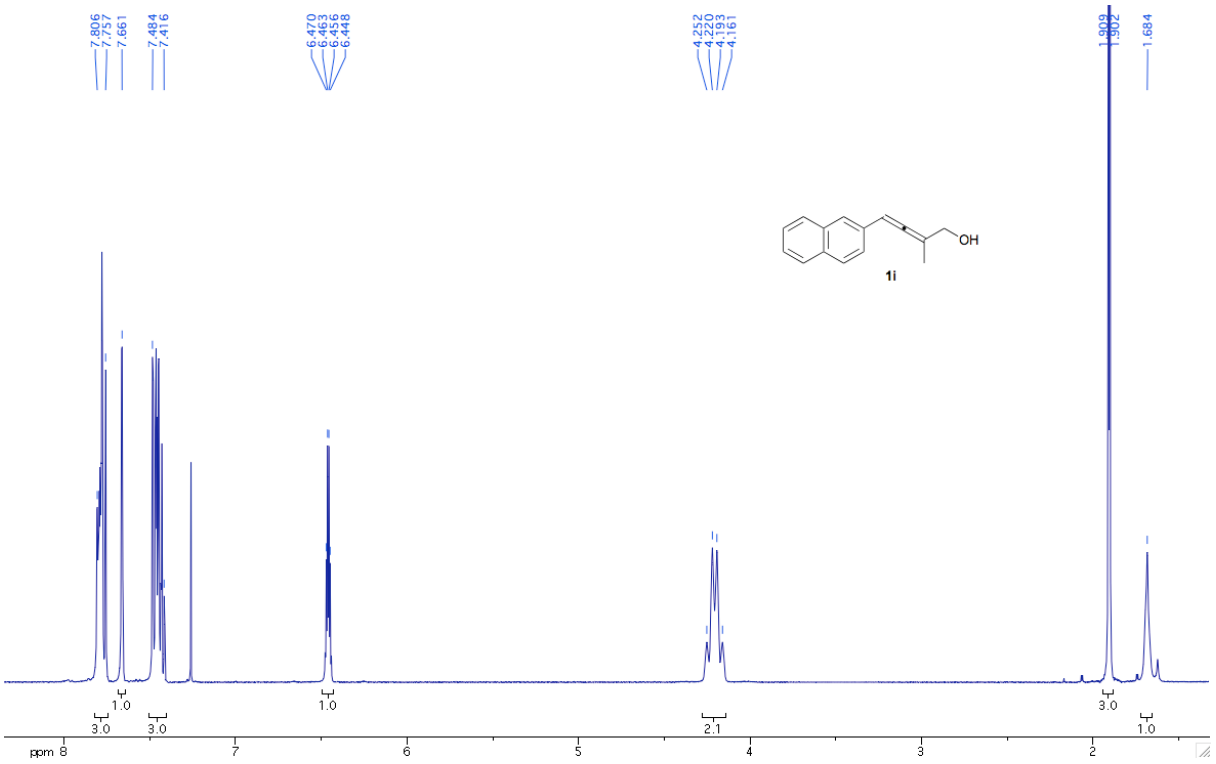
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5
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3
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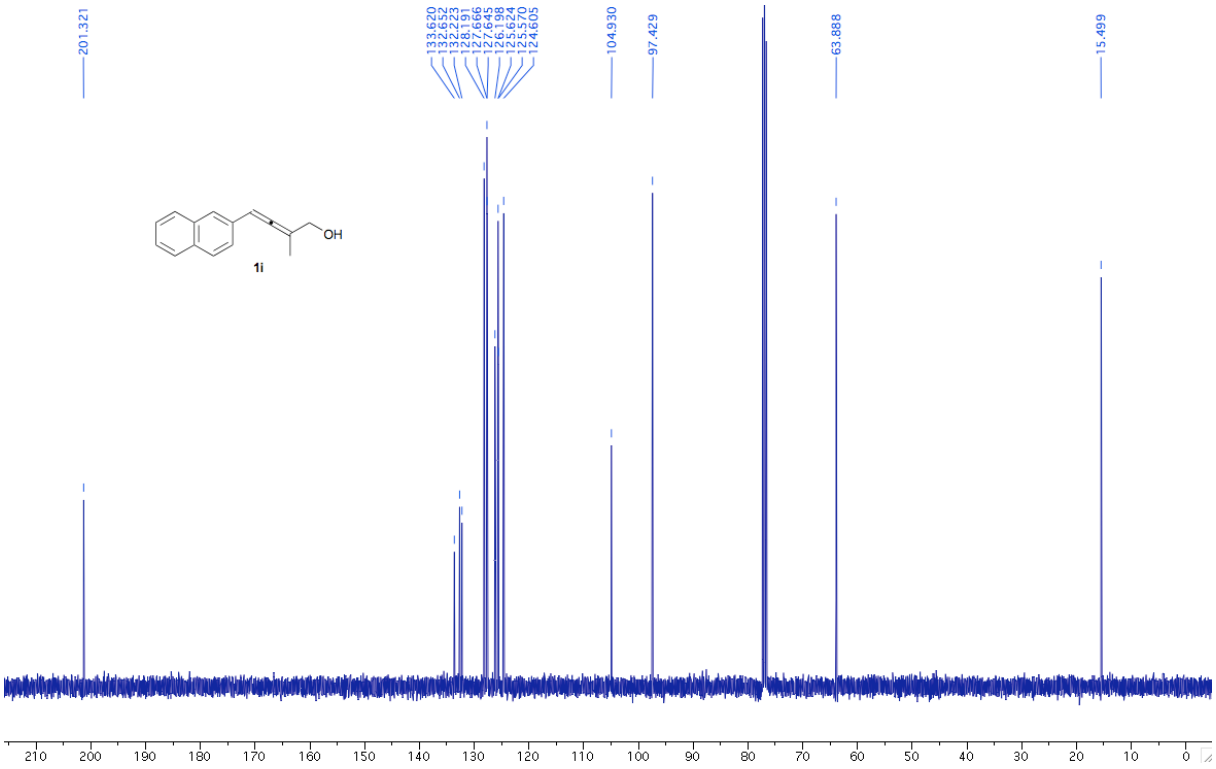
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1i
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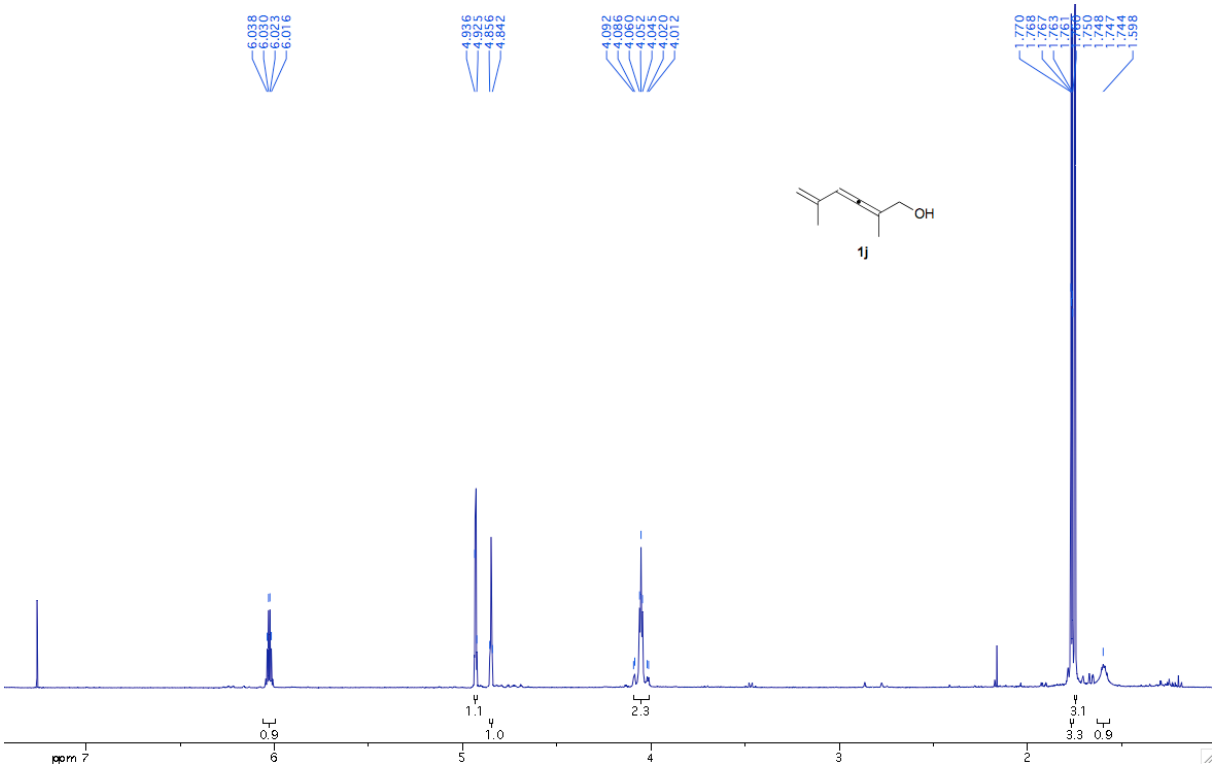
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4.045
4.020
4.012
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1.768
1.767
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1.761
1.750
1.748
1.747
1.744
1.598
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0.9
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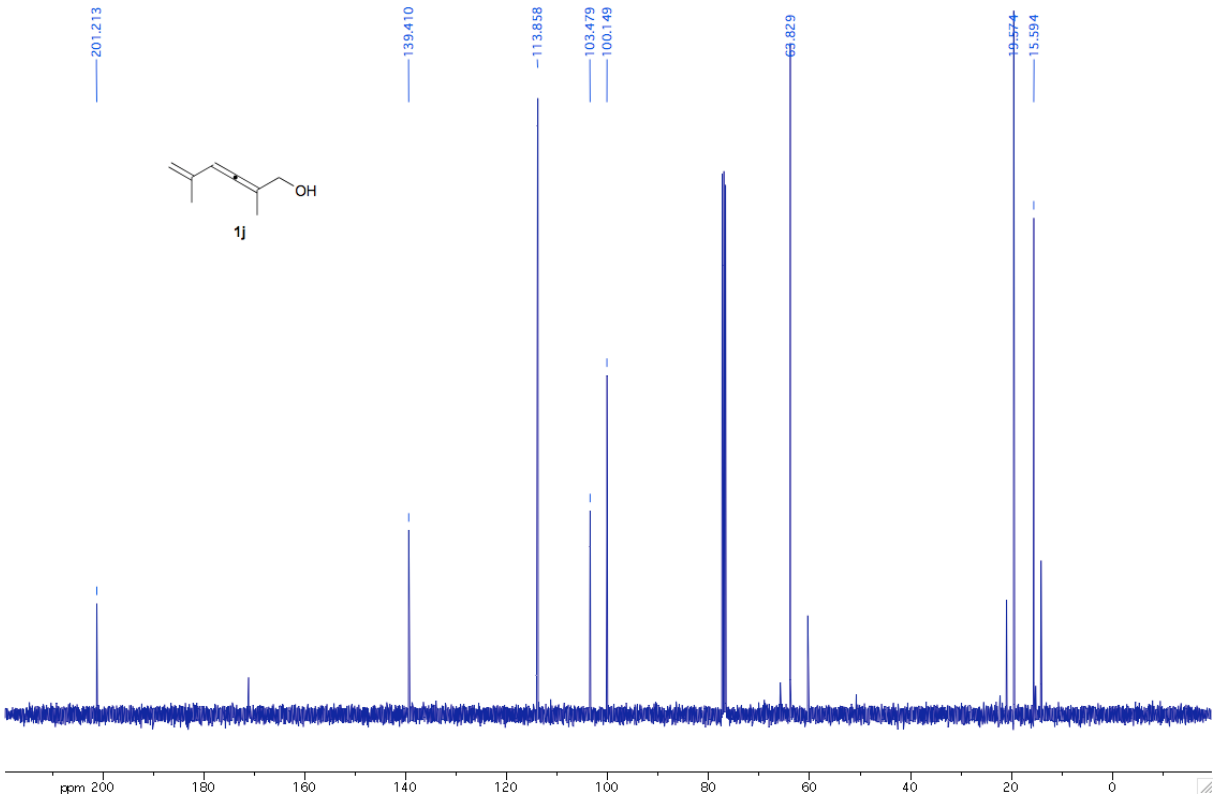
5
4
3
2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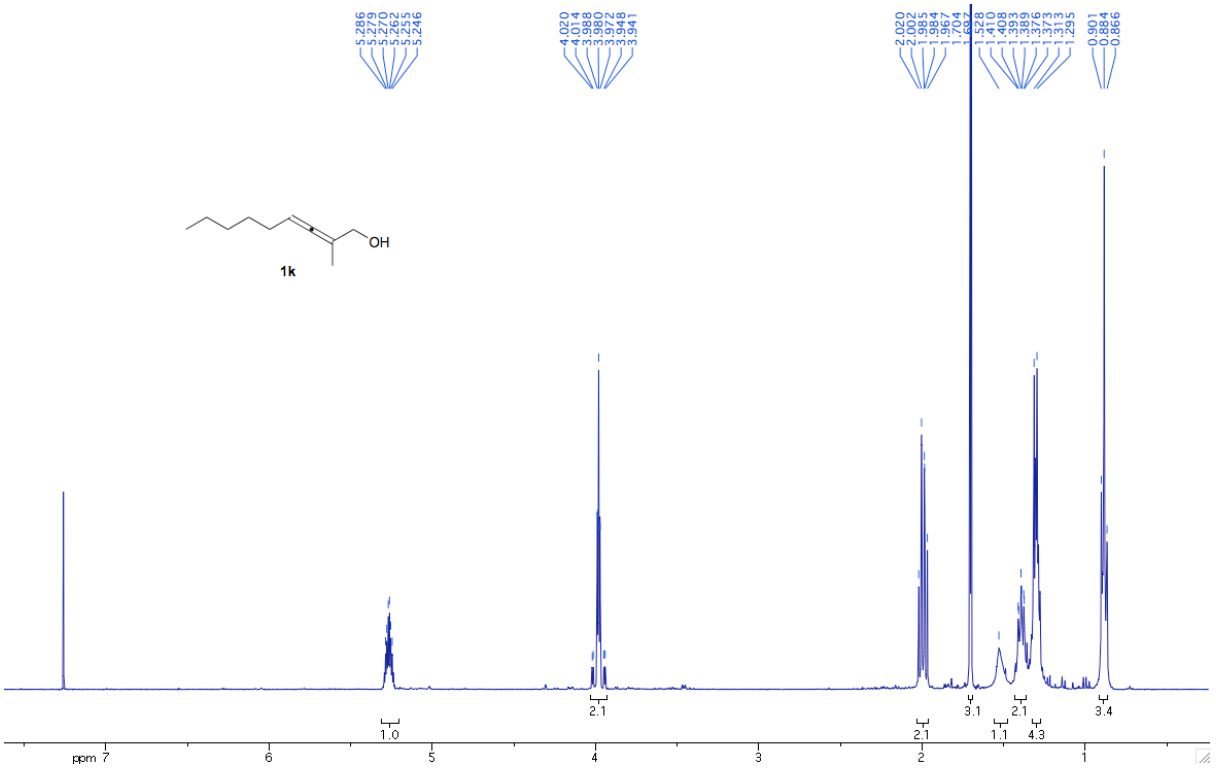
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3.972
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3.941
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2.002
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1.984
1.967
1.704
1.632
1.528
1.410
1.408
1.393
1.389
1.376
1.313
1.295
0.901
0.884
0.866
OH
1k
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3.1
2.1
1.1
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ppm 7
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4
3
2
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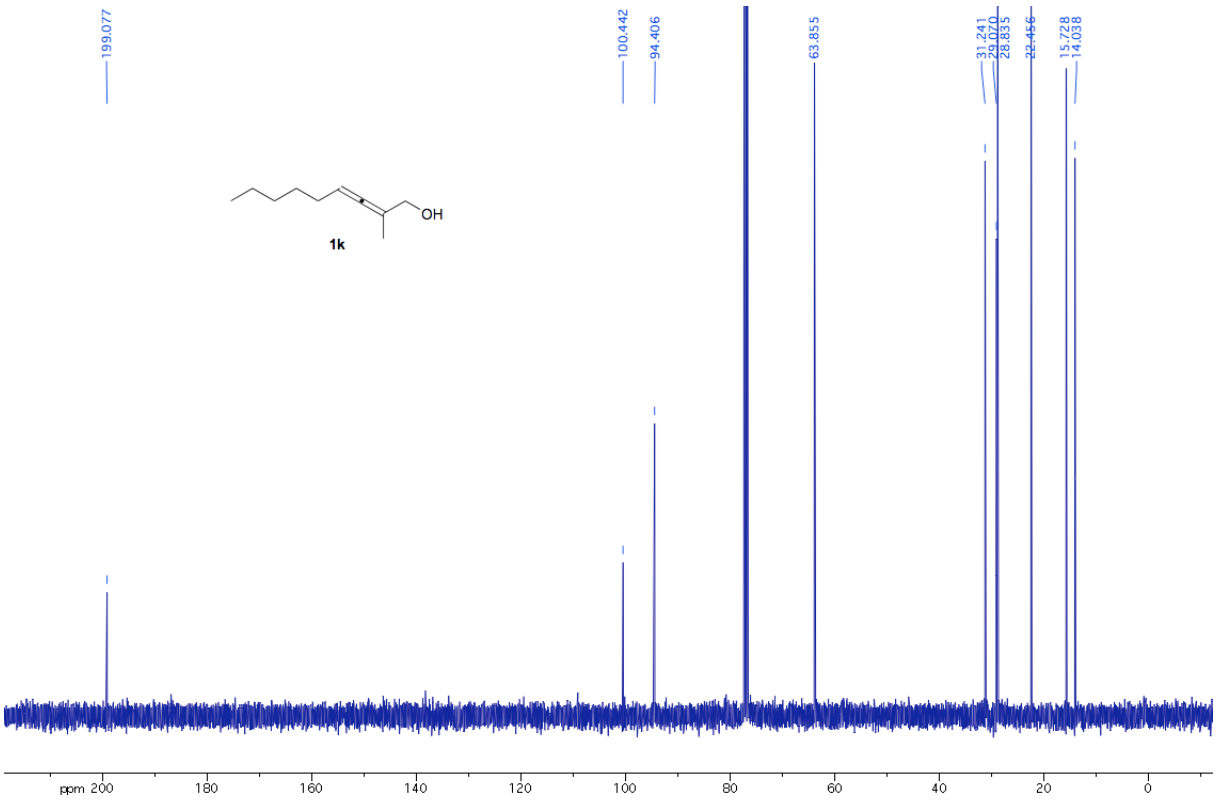
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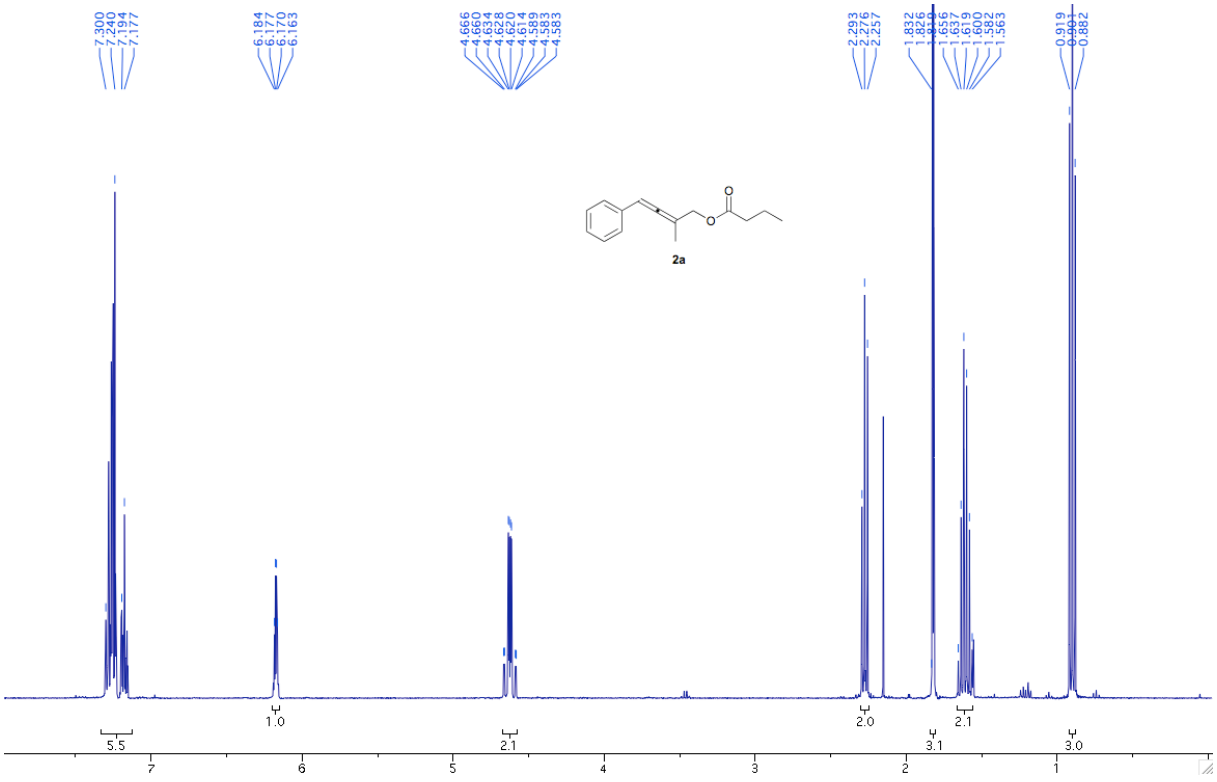
60
40
20
0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4.660
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4.620
4.614
4.589
4.583
4.583
2.293
2.276
2.257
1.832
1.826
1.656
1.637
1.619
1.600
1.582
1.563
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0.907
0.882
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2
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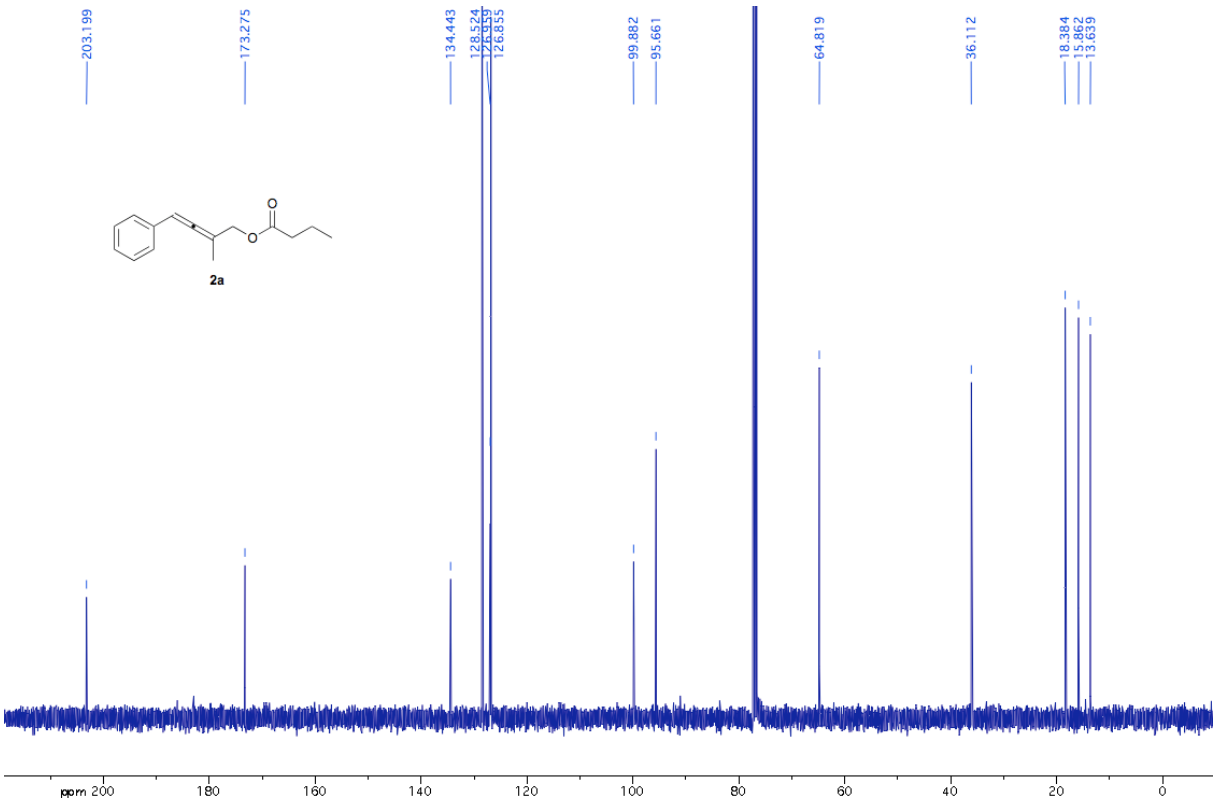
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140
120
100
80
60
40
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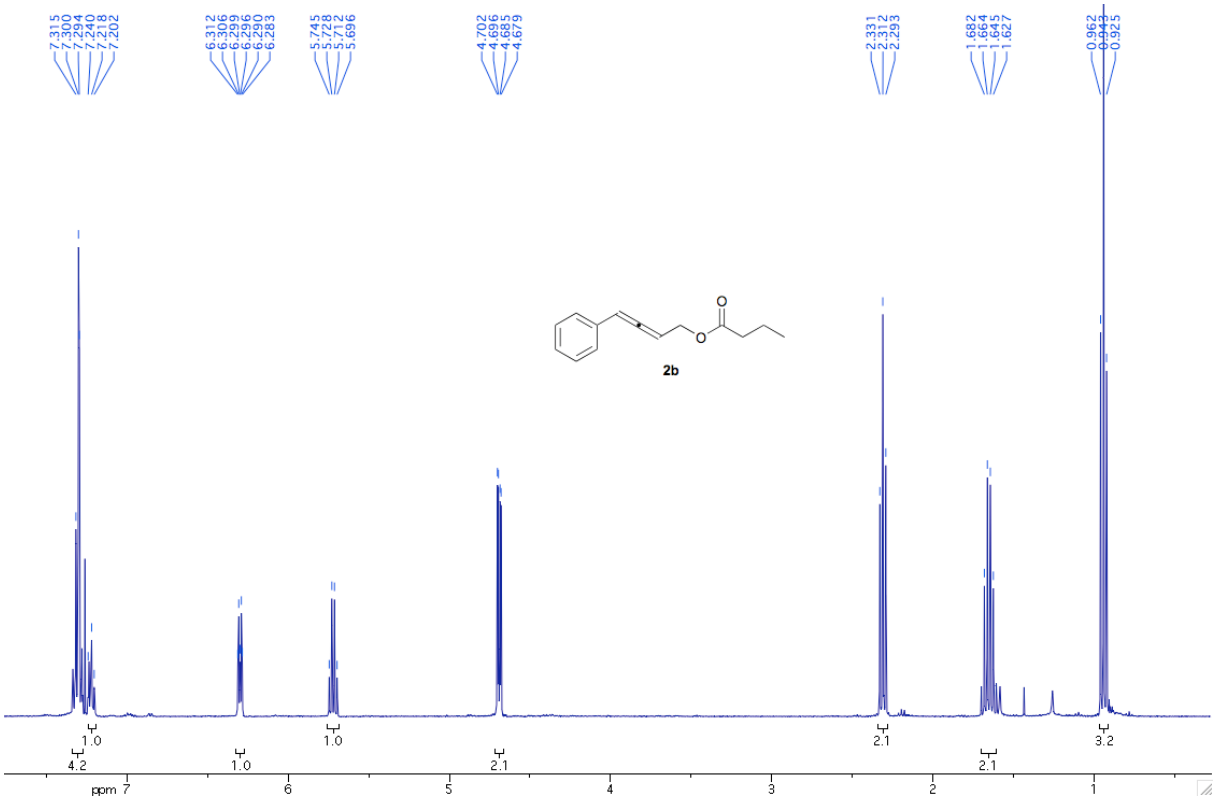
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5.728
5.712
5.696
4.702
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4.685
4.679
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0.943
0.925
2b
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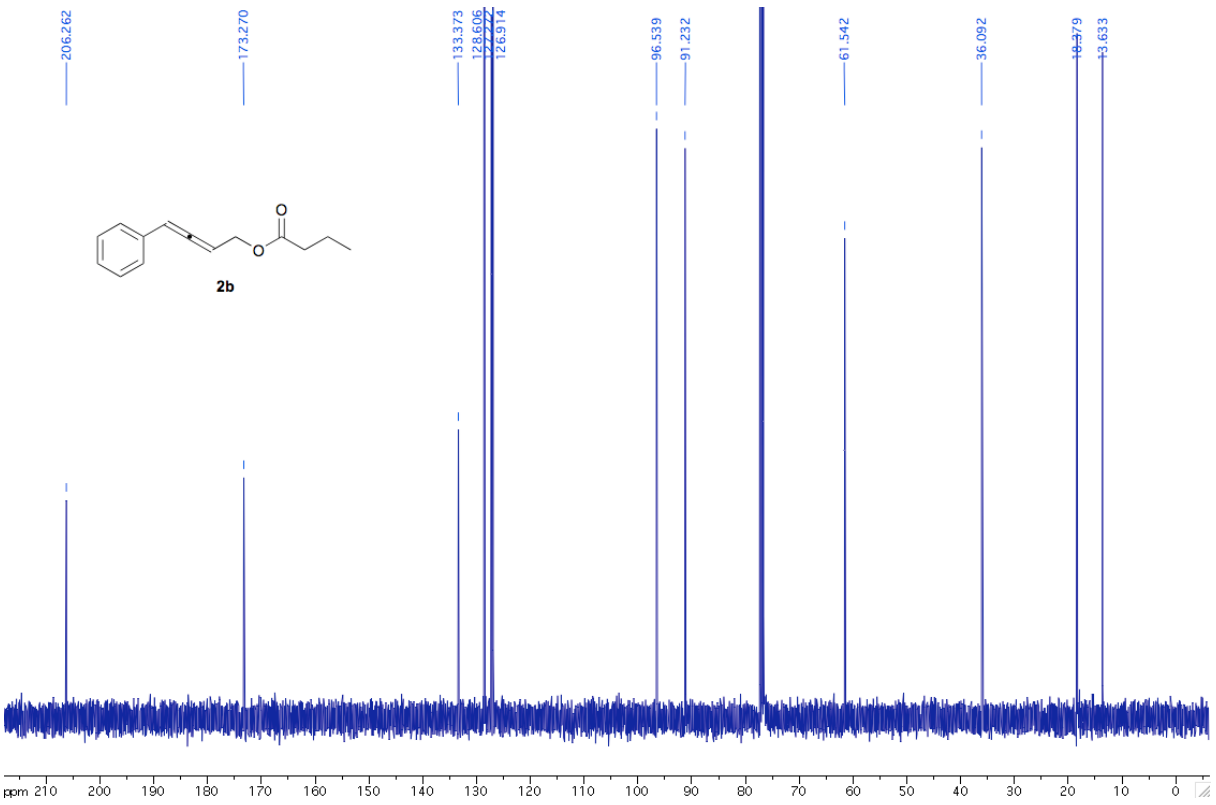
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91.232
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2b
ppm 210
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110
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70
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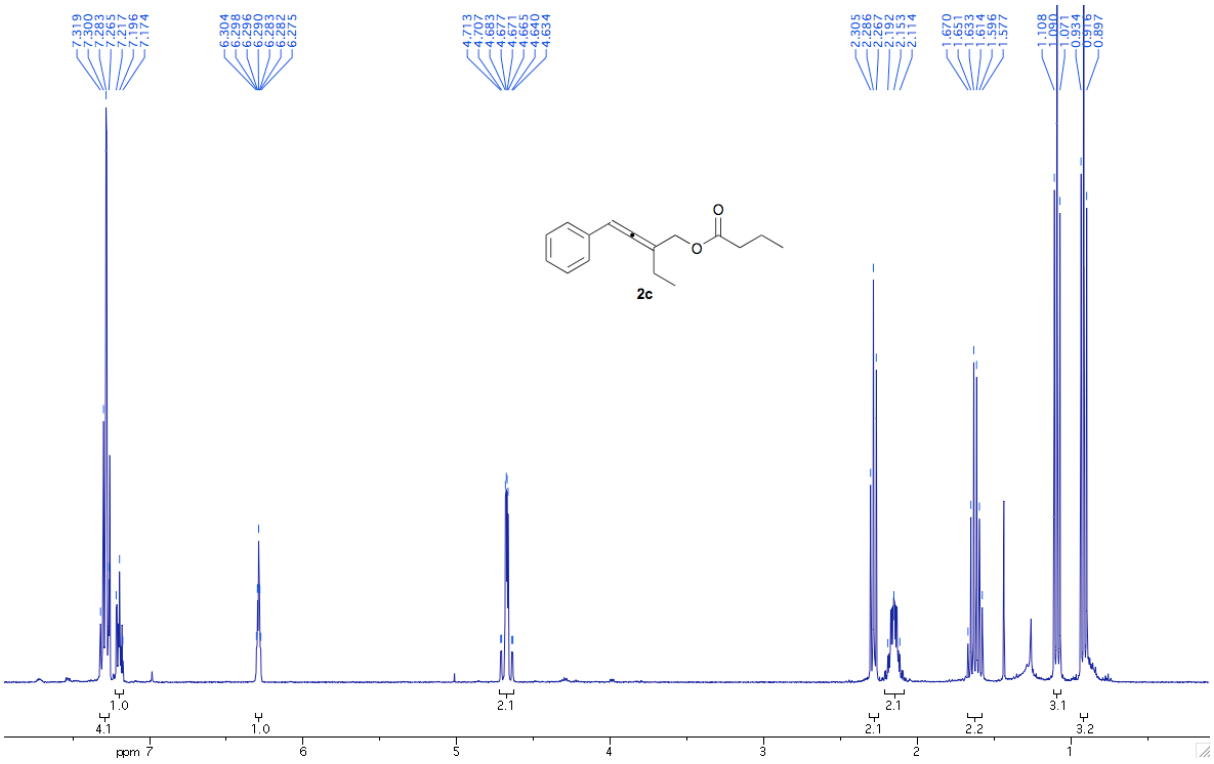
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2.153
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1.633
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1.596
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1.108
1.090
1.071
0.934
0.897
O
O
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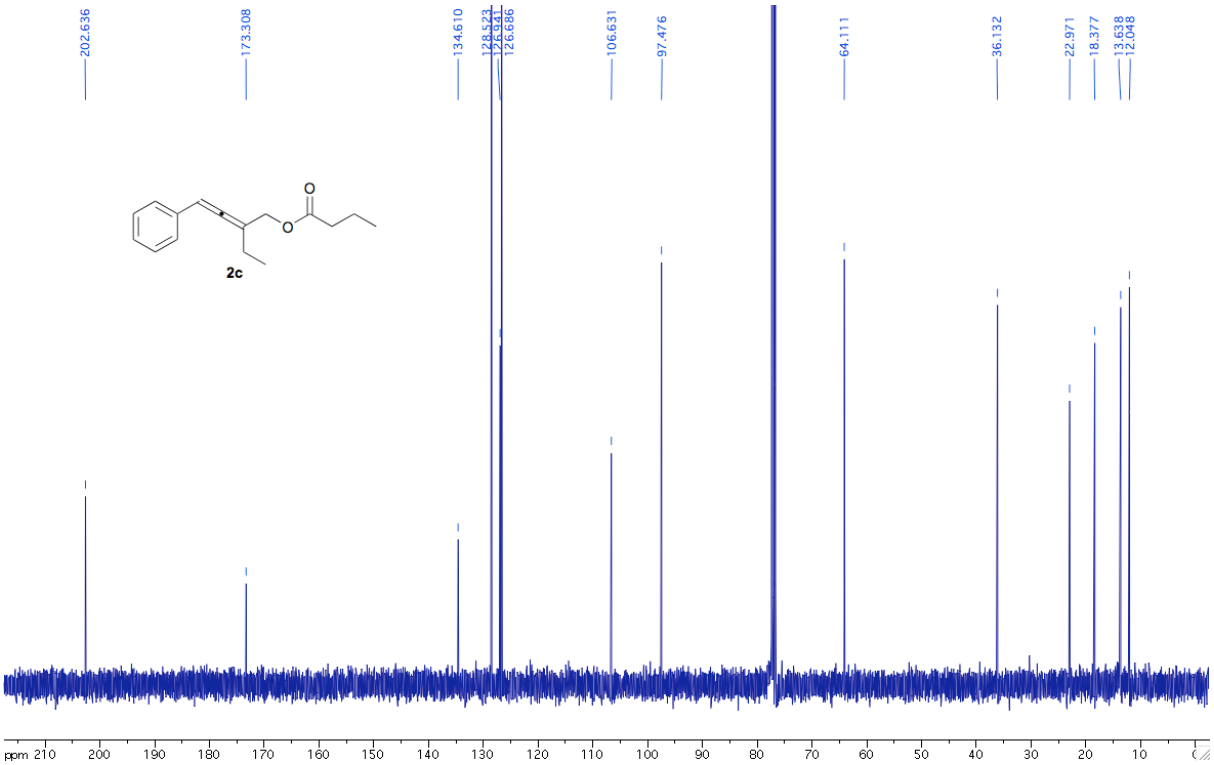
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97.476
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18.377
13.638
12.048
O
O
2c
ppm 210
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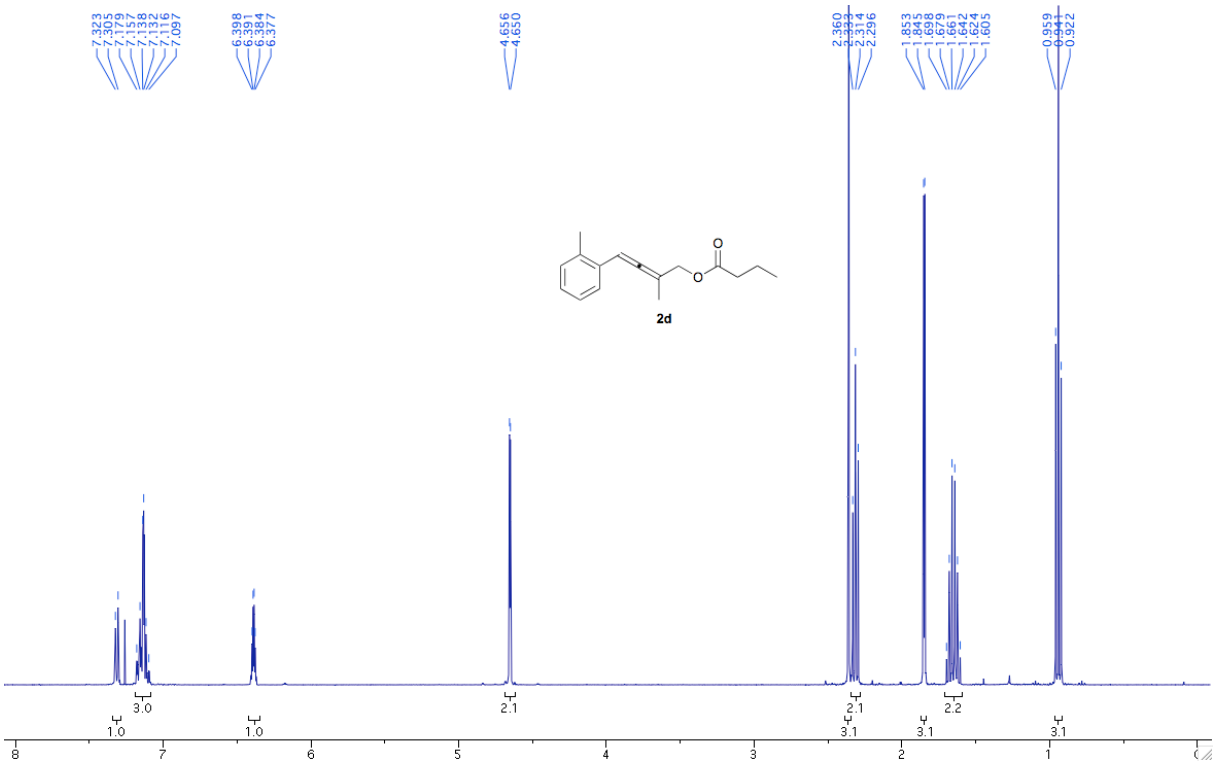
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4.650
2.360
2.339
2.314
2.296
1.853
1.845
1.698
1.679
1.661
1.642
1.624
1.605
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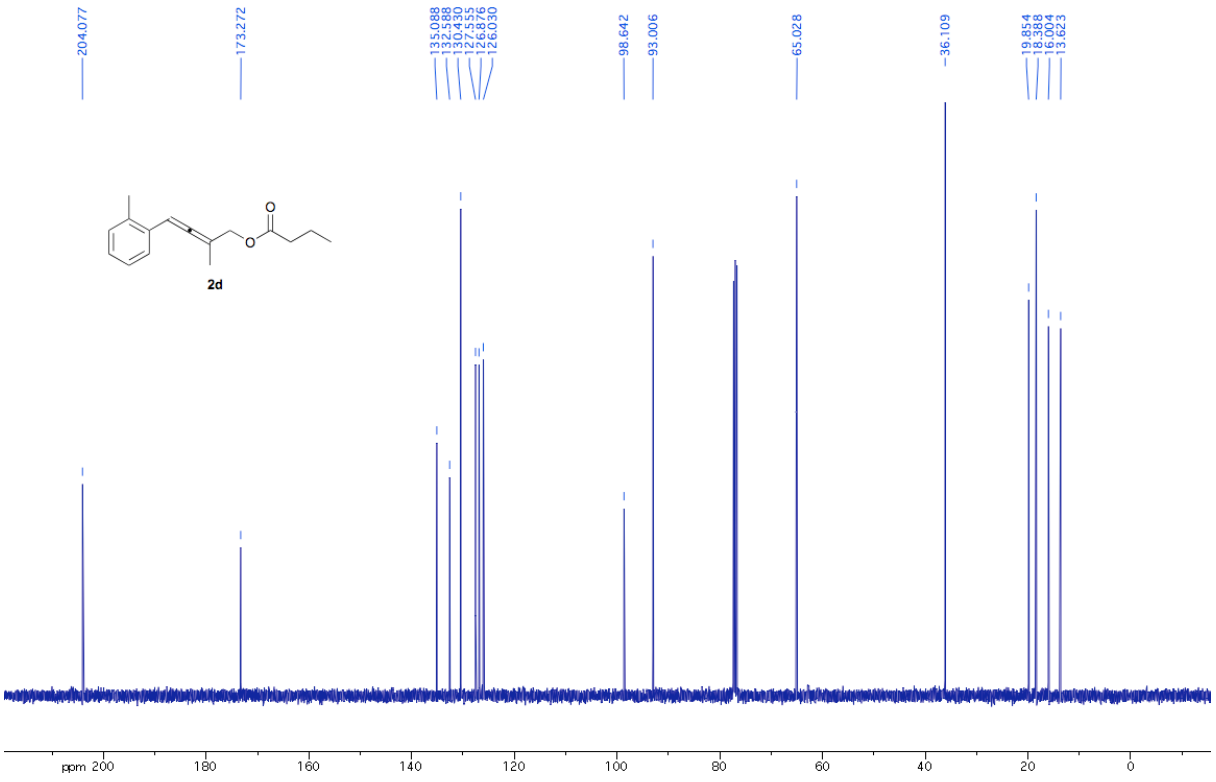
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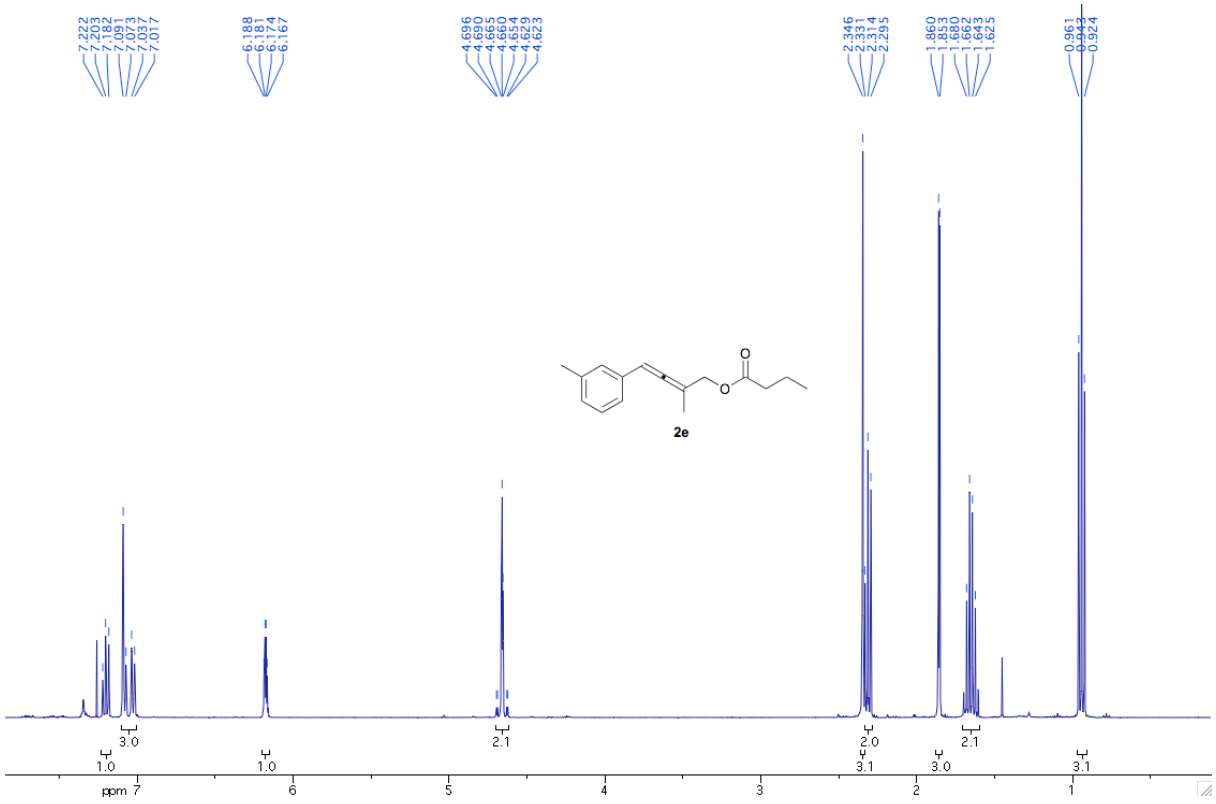
2d
ppm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4.665
4.660
4.654
4.629
4.623
2.346
2.331
2.314
2.295
1.860
1.853
1.680
1.662
1.643
1.625
0.961
0.943
0.924
2e
3.0
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2.0
3.1
3.0
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3.1
ppm 7
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4
3
2
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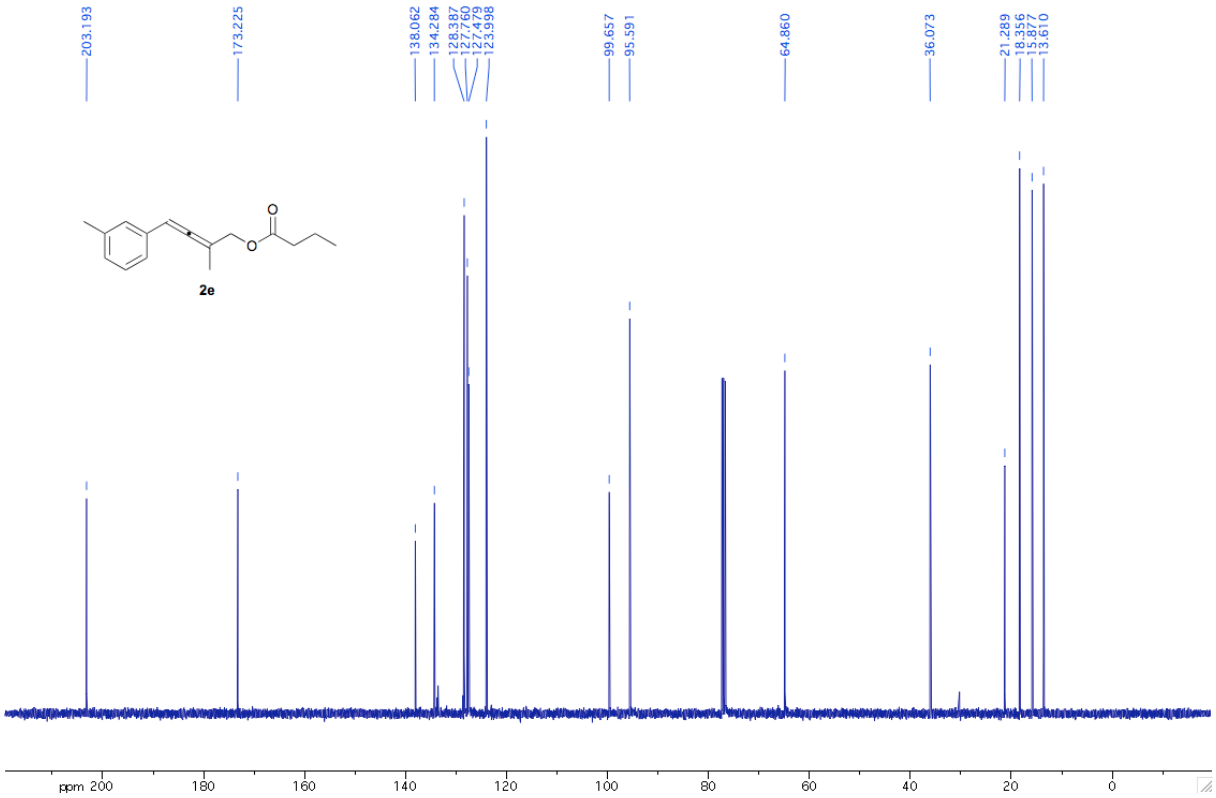
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127.760
127.479
123.998
99.657
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64.860
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18.556
18.377
13.610
2e
ppm 200
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160
140
120
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20
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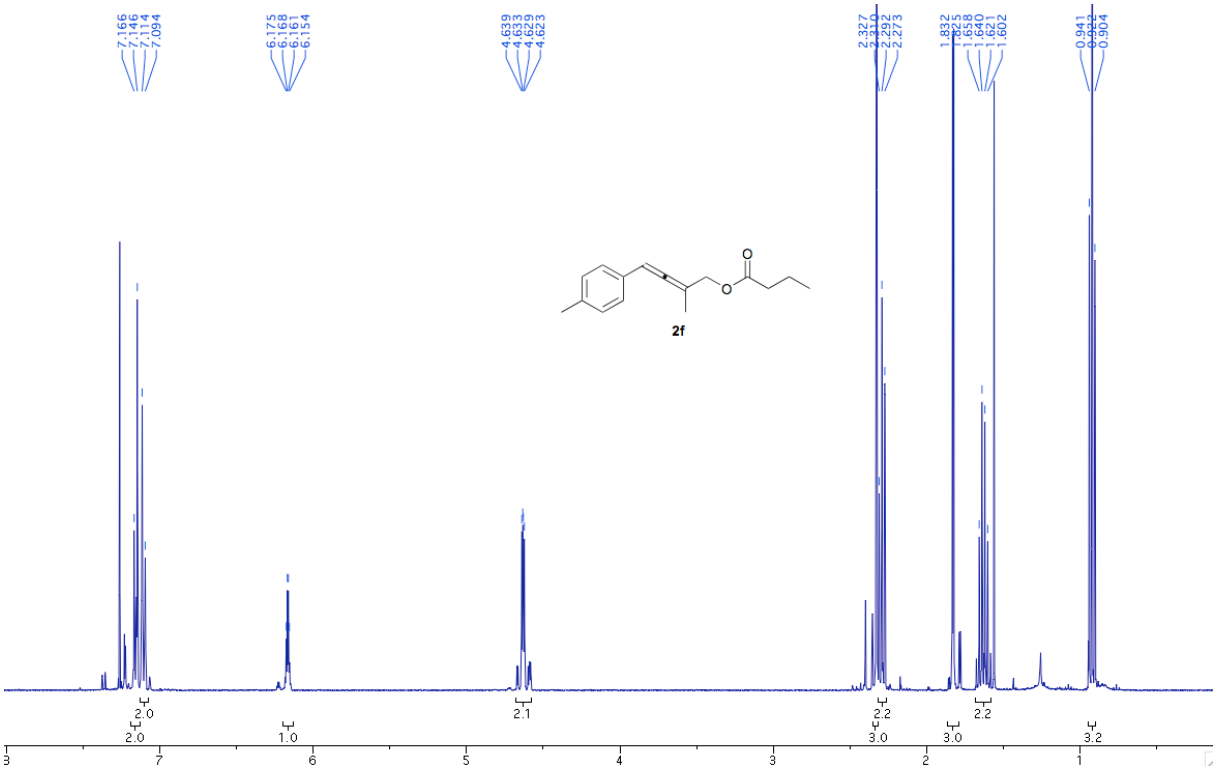
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4.629
4.623
2.327
2.310
2.292
2.273
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1.625
1.658
1.640
1.621
1.602
0.941
0.923
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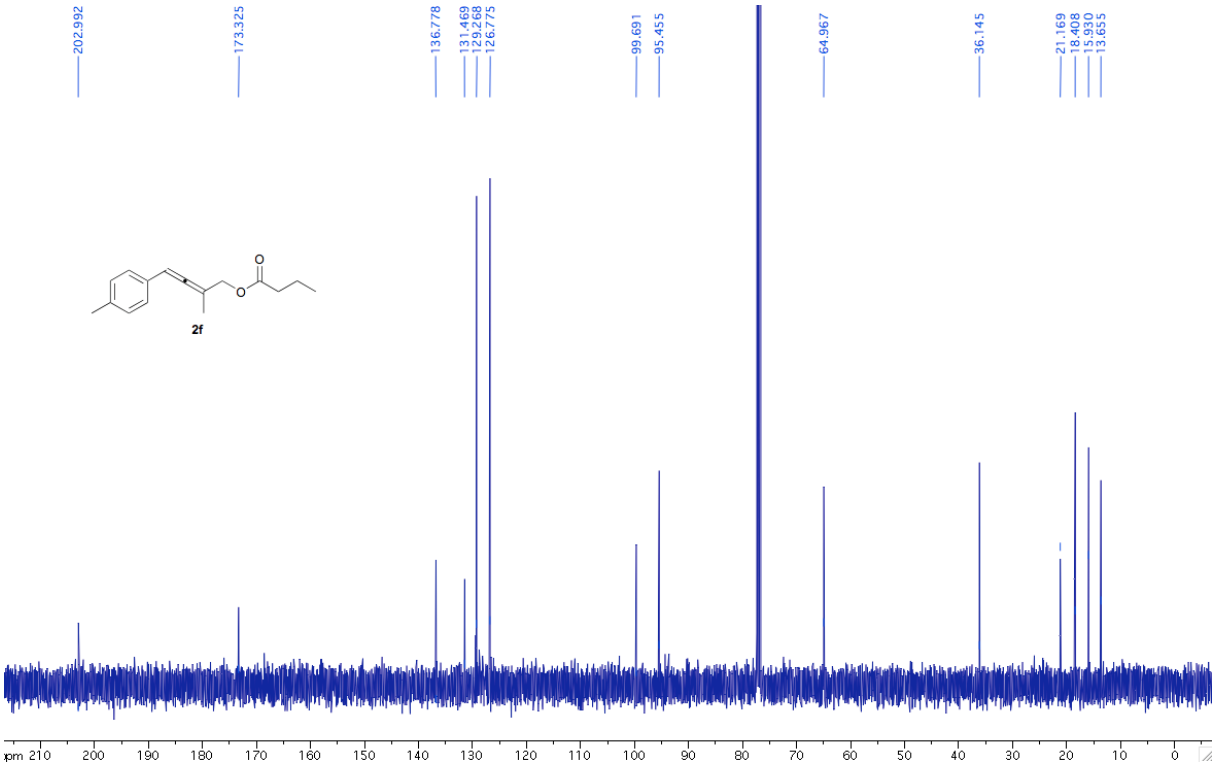
3.2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18.498
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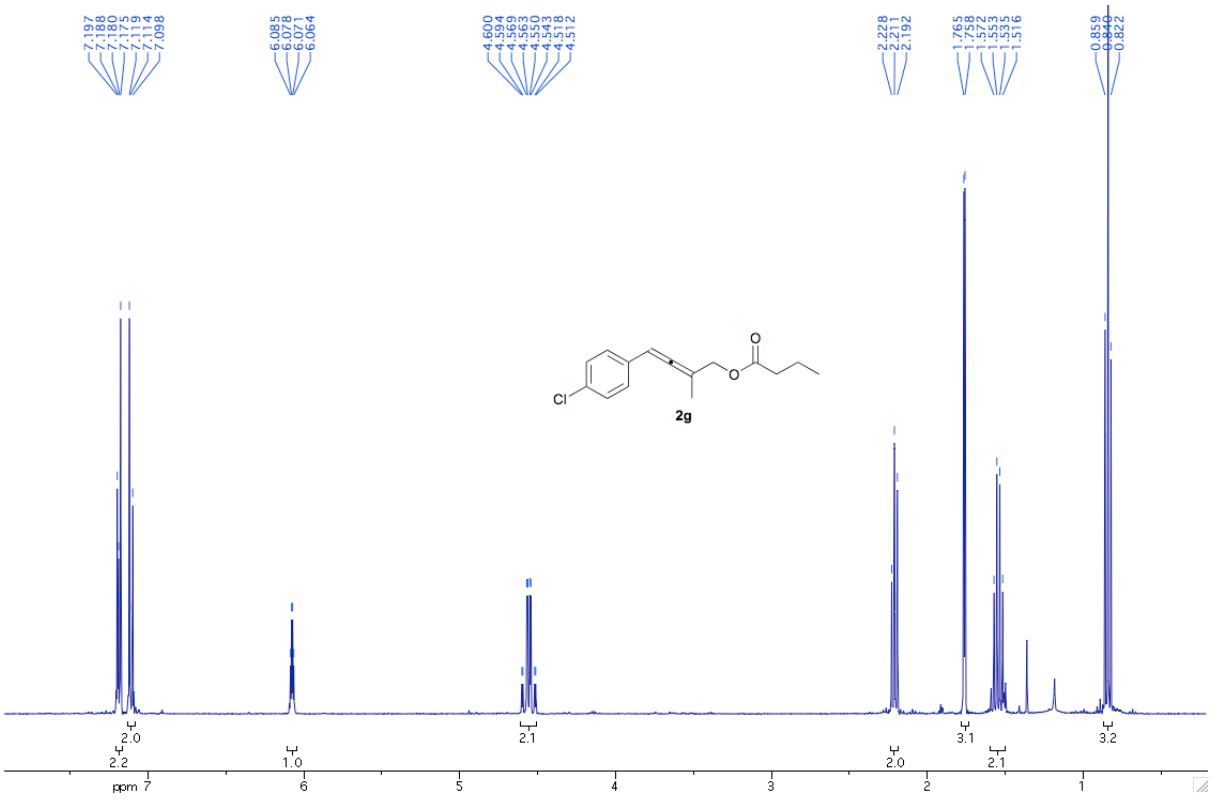
13.655
O
O
2f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7.114
7.098
6.085
6.078
6.071
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4.594
4.569
4.563
4.550
4.543
4.518
4.512
2.228
2.211
2.192
1.765
1.758
1.572
1.553
1.535
1.516
0.859
0.840
0.822
Cl
O
O
2g
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2.2
1.0
2.1
2.0
3.1
2.1
3.2
ppm 7
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4
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2
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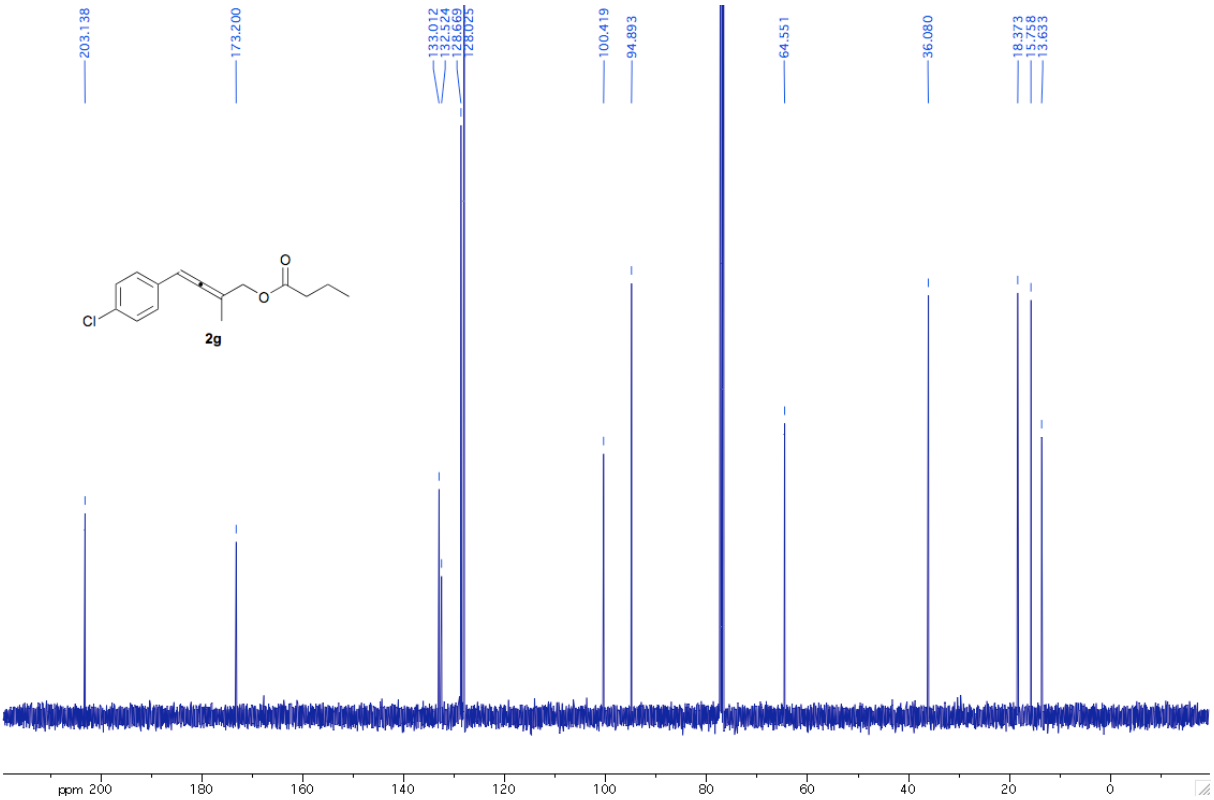
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36.080
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Cl
O
O
2g
ppm 200
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140
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60
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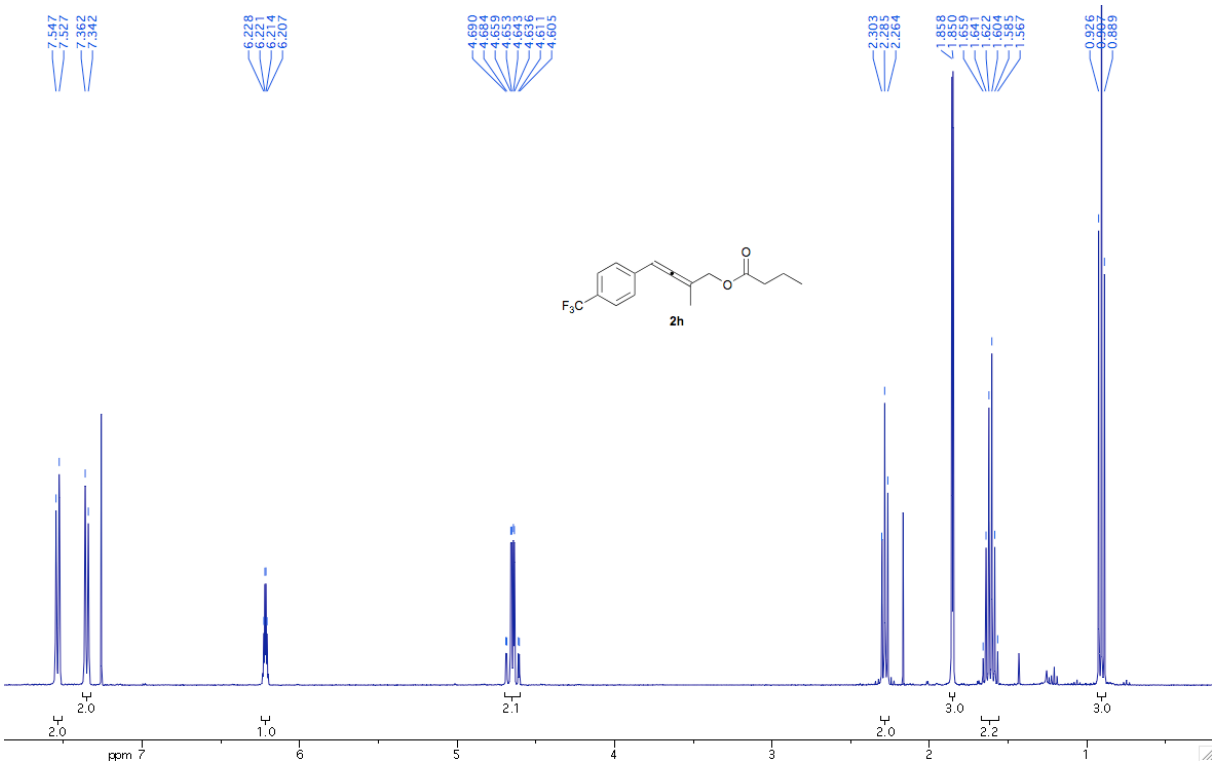
20
0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6.207
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4.659
4.653
4.643
4.636
4.611
4.605
2.303
2.285
2.264
1.858
1.850
1.641
1.622
1.604
1.585
1.567
0.926
0.907
0.889
F3C
O
O
2h
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1.0
2.1
2.0
3.0
2.2
3.0
ppm 7
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4
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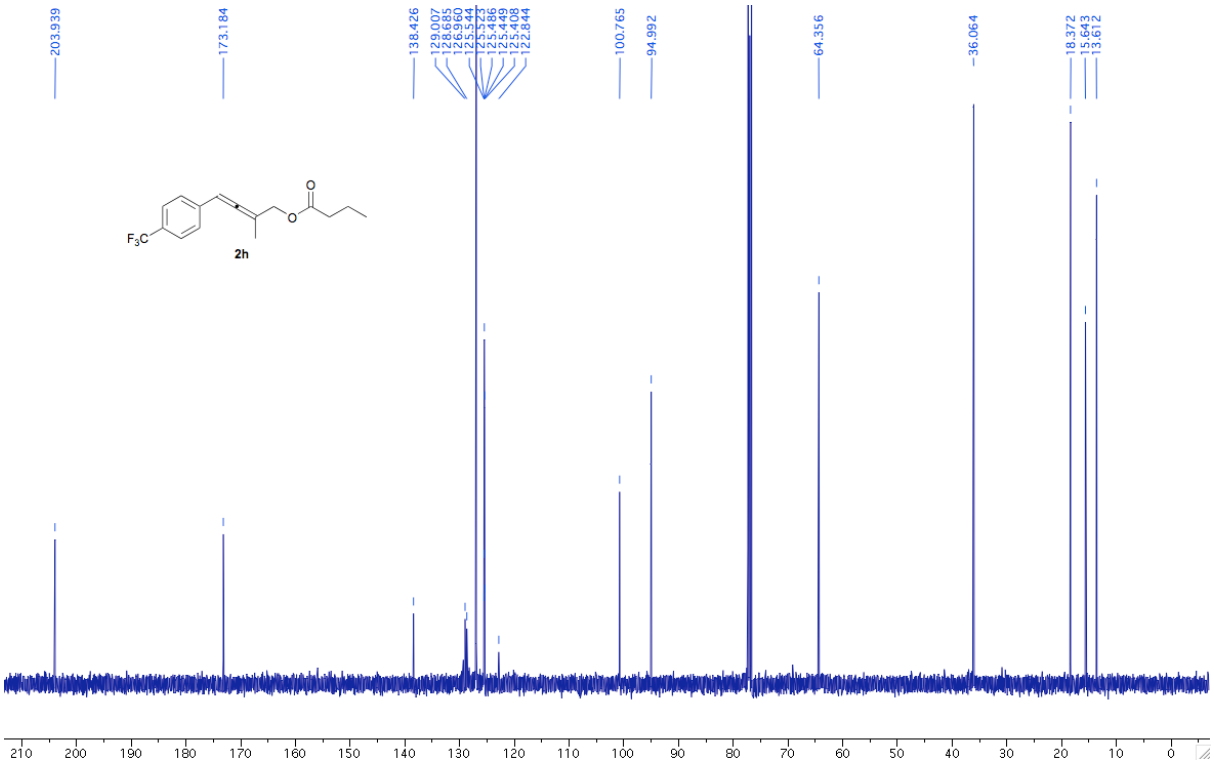
2
1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125.448
122.844
100.765
94.992
64.356
36.064
18.372
15.643
13.612
F3C
O
O
2h
210
200
190
180
170
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150
140
130
120
110
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70
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10
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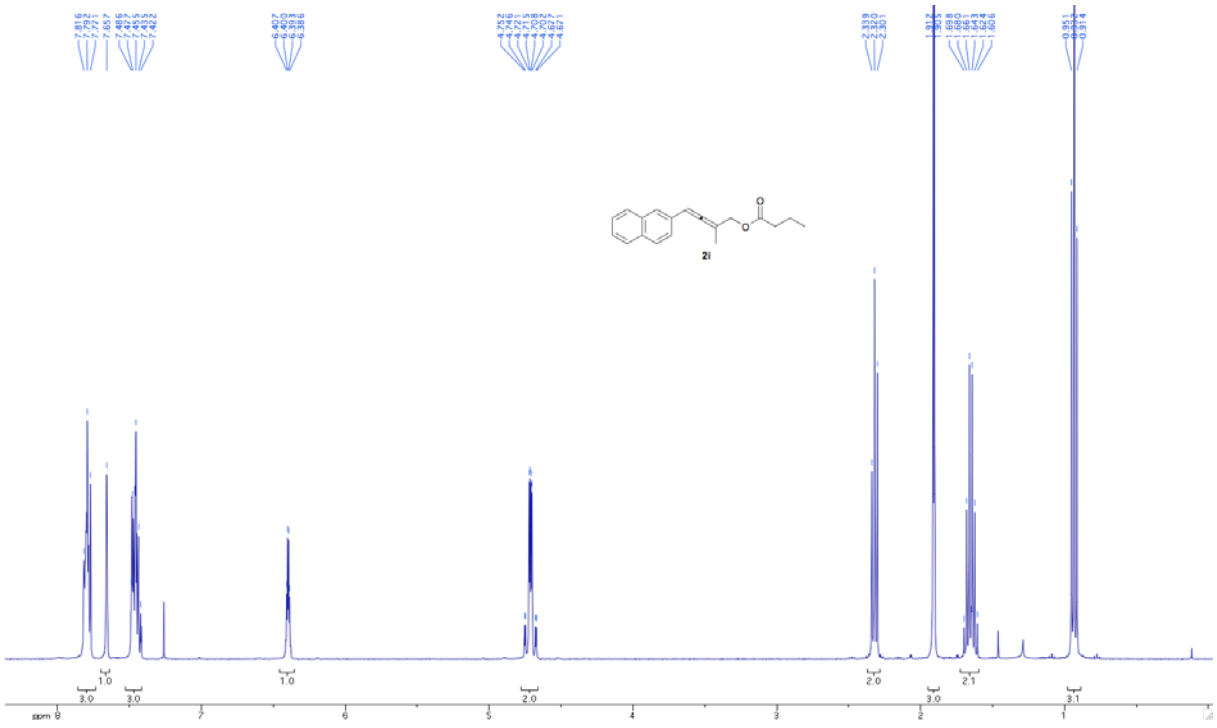
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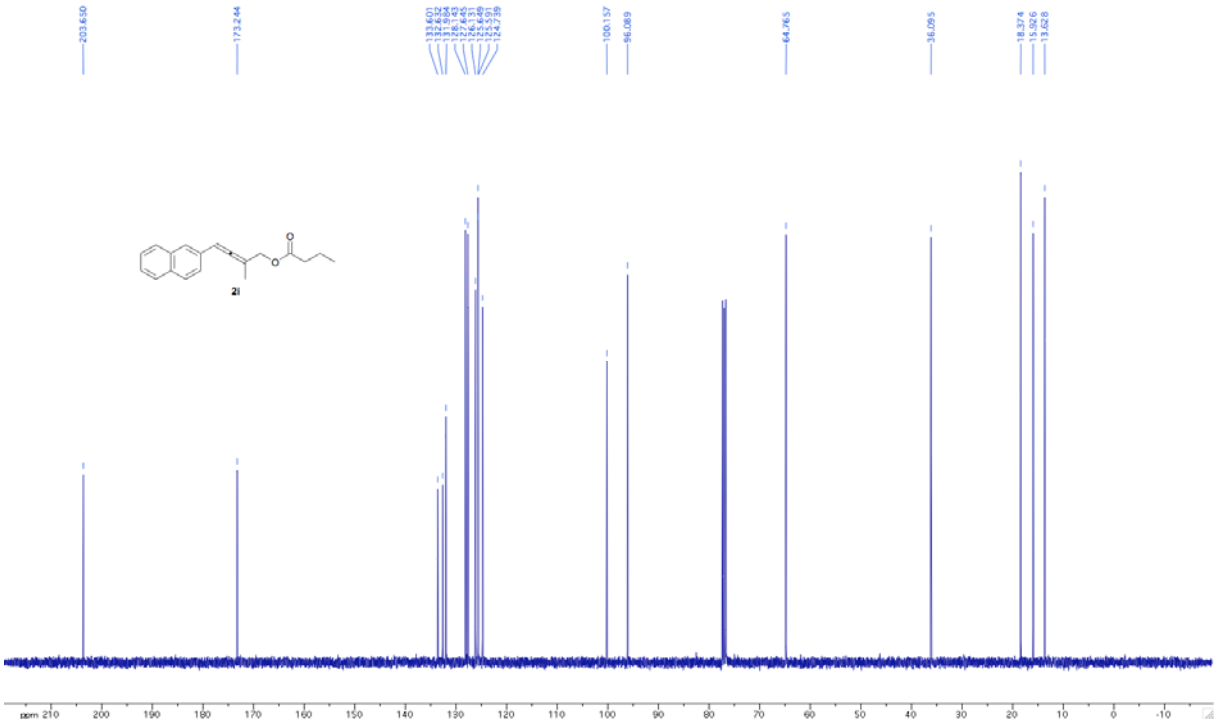
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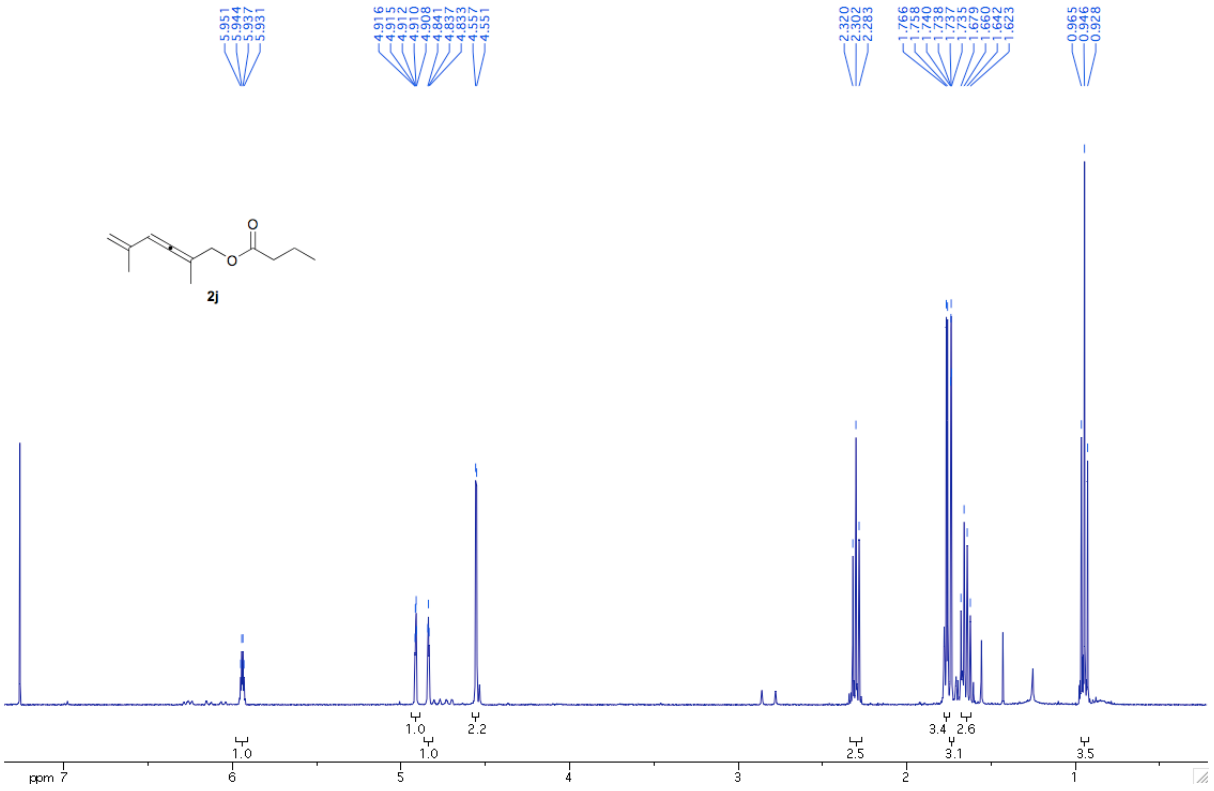
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4.908
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4.833
4.557
4.551
2.320
2.302
2.283
1.766
1.758
1.740
1.738
1.737
1.735
1.679
1.660
1.642
1.623
0.965
0.946
0.928
O
O
2j
1.0
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3.4
2.6
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1.0
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4
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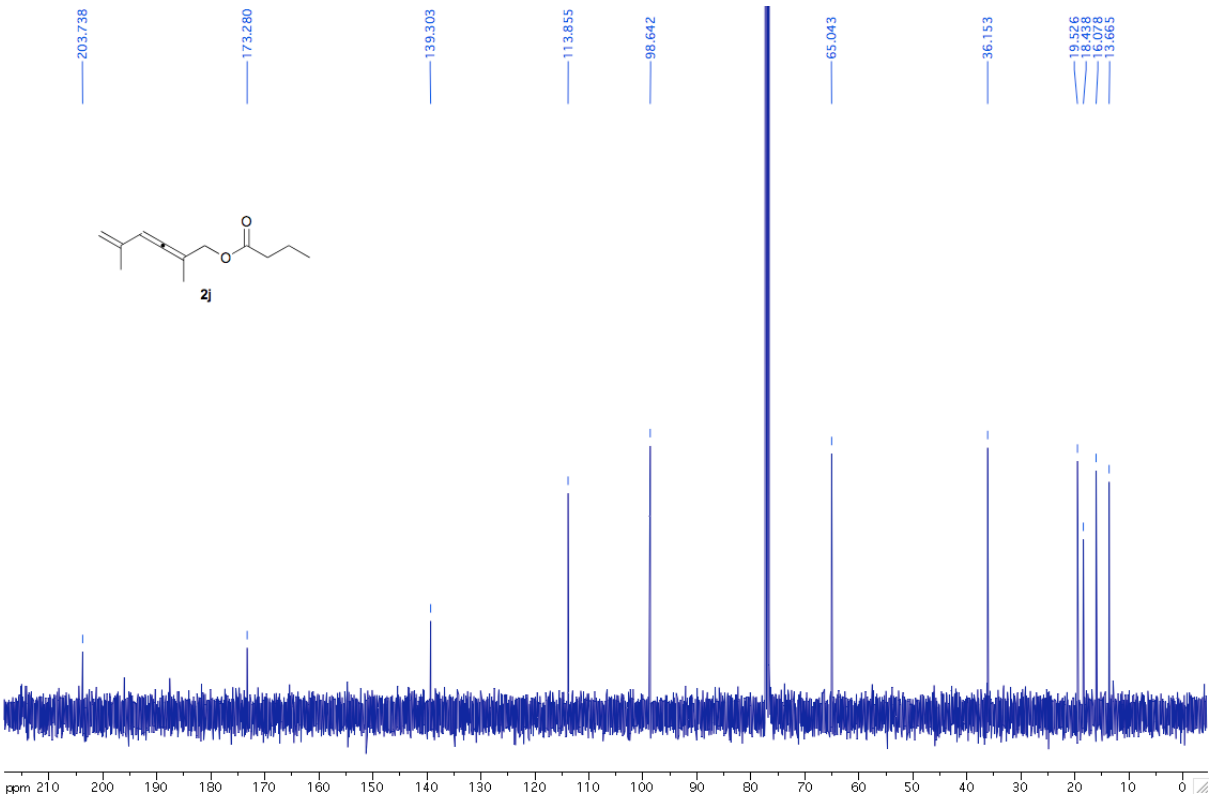
2
1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19.526
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16.078
13.665
O
O
2j
ppm 210
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150
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120
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100
90
80
70
60
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30
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10
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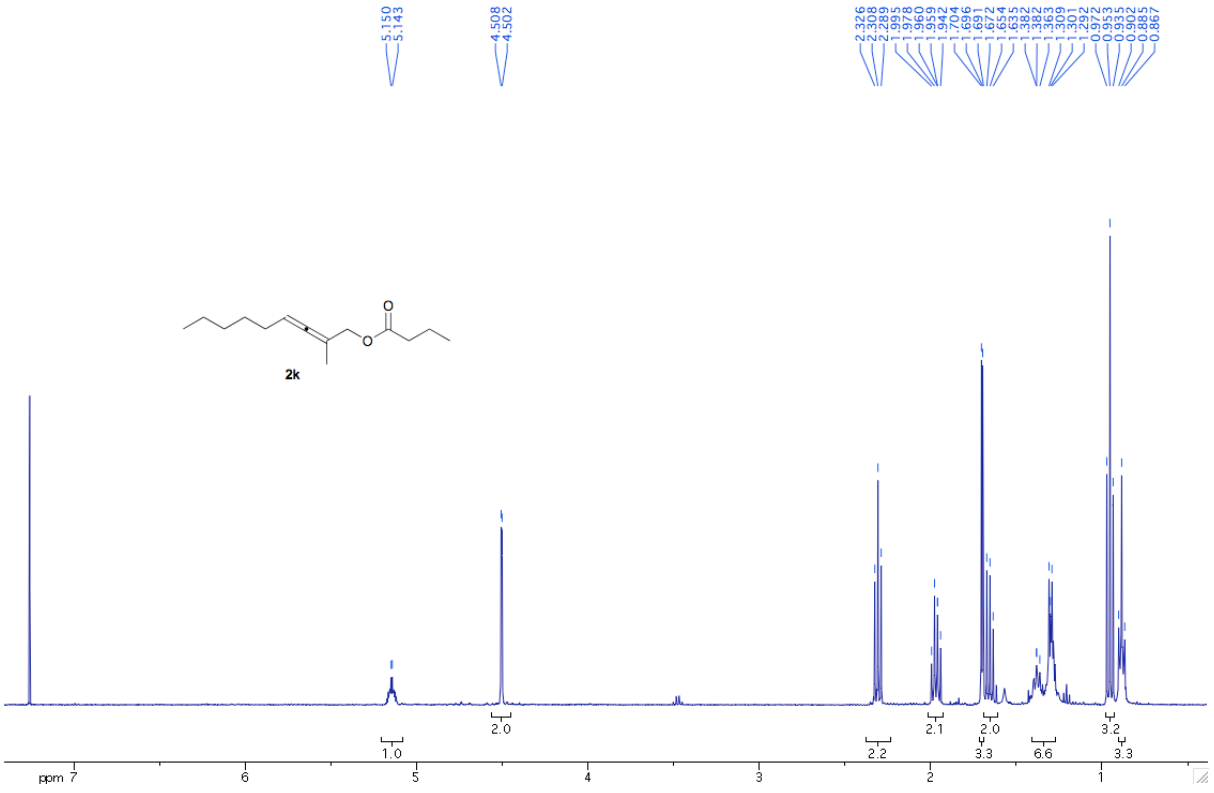
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1.942
1.704
1.696
1.691
1.672
1.654
1.635
1.382
1.382
1.363
1.309
1.301
1.292
0.972
0.953
0.935
0.902
0.885
0.867
O
O
2k
1.0
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2.0
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3.3
ppm 7
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4
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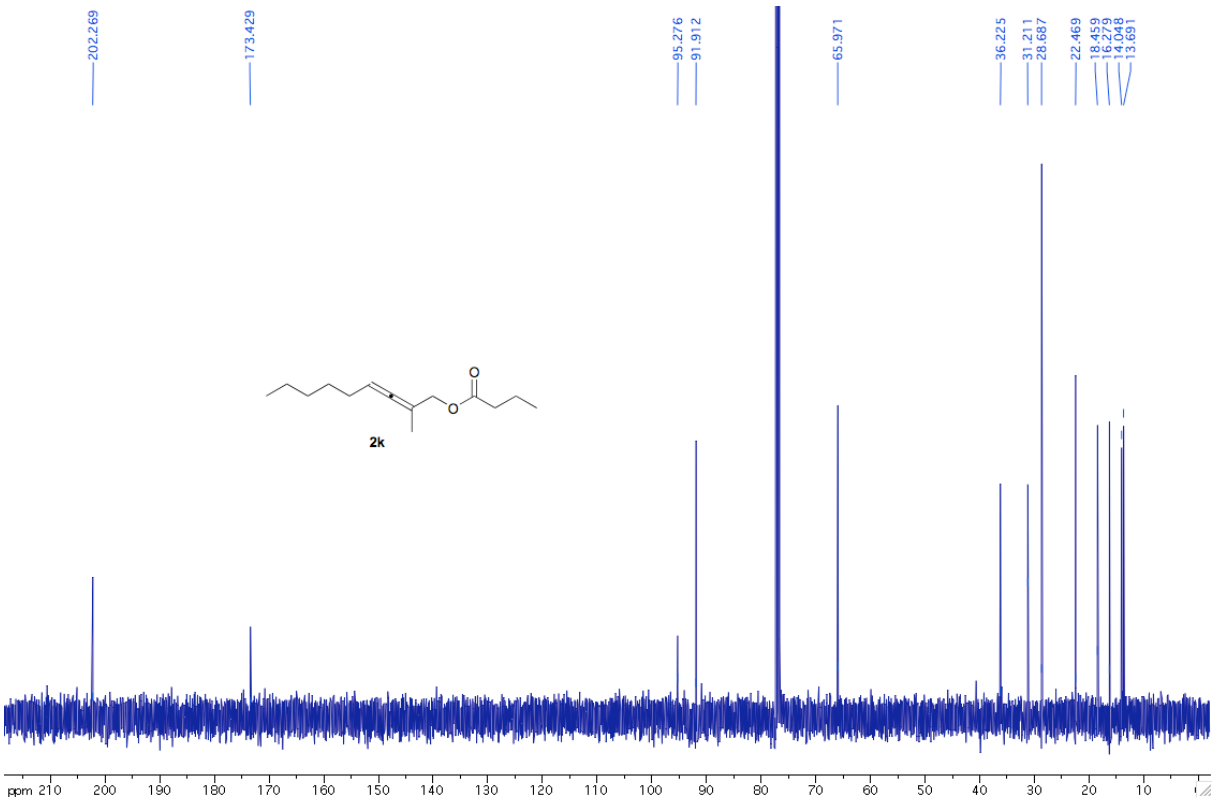
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28.687
22.469
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16.279
14.048
13.691
O
O
2k
ppm 210
200
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180
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160
150
140
130
120
110
100
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80
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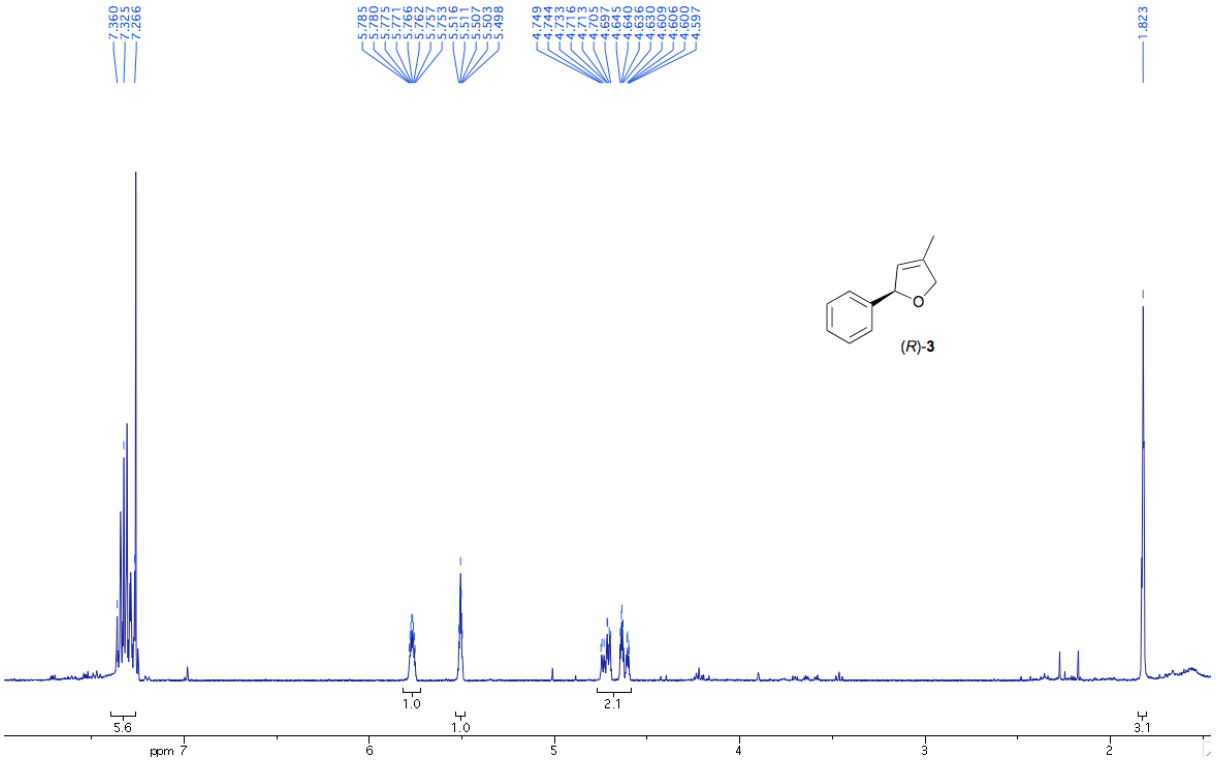
20
10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5.511
5.507
5.503
5.498
4.749
4.744
4.739
4.733
4.716
4.713
4.705
4.697
4.645
4.640
4.636
4.630
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4.606
4.600
4.597
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3.1
ppm 7
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5
4
3
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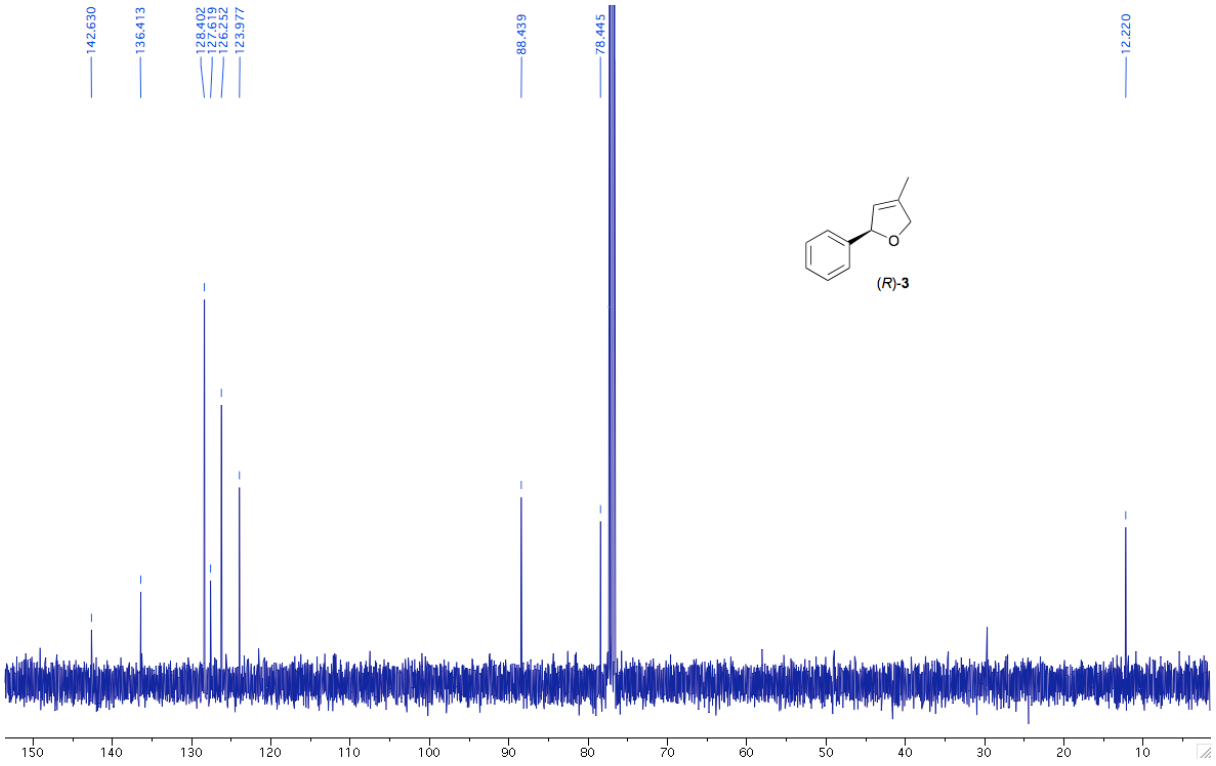
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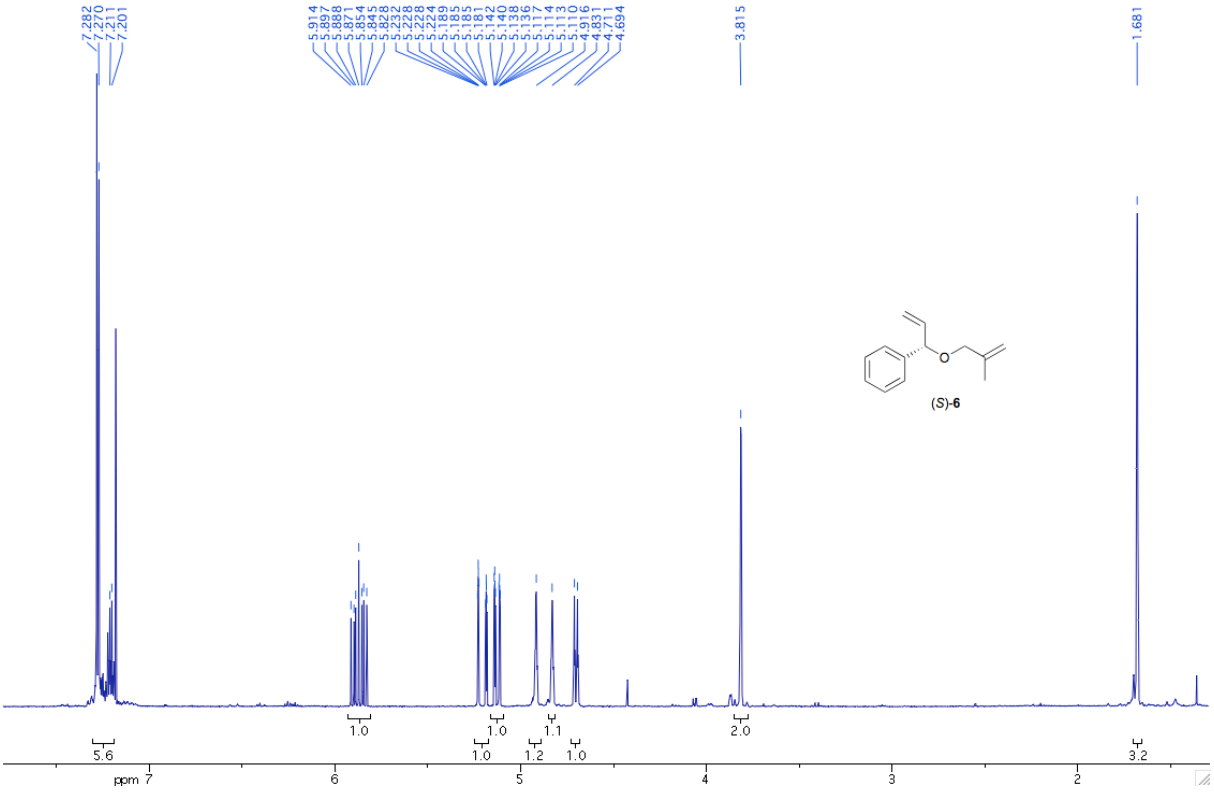
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5.871
5.854
5.845
5.828
5.232
5.228
5.228
5.224
5.189
5.185
5.181
5.142
5.140
5.138
5.136
5.117
5.114
5.113
5.110
4.931
4.931
4.711
4.694
3.815
1.681
(S)-6
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1.0
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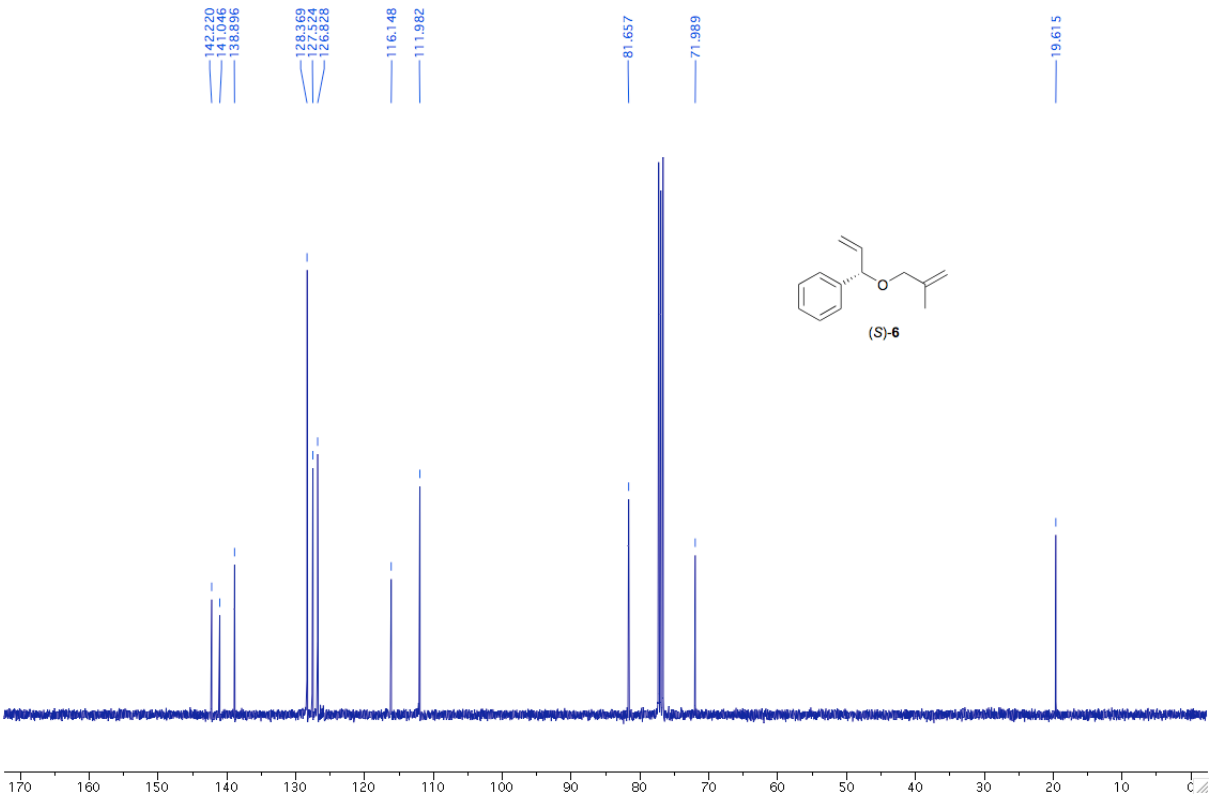
5
4
3
2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71.989
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160
150
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130
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80
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40
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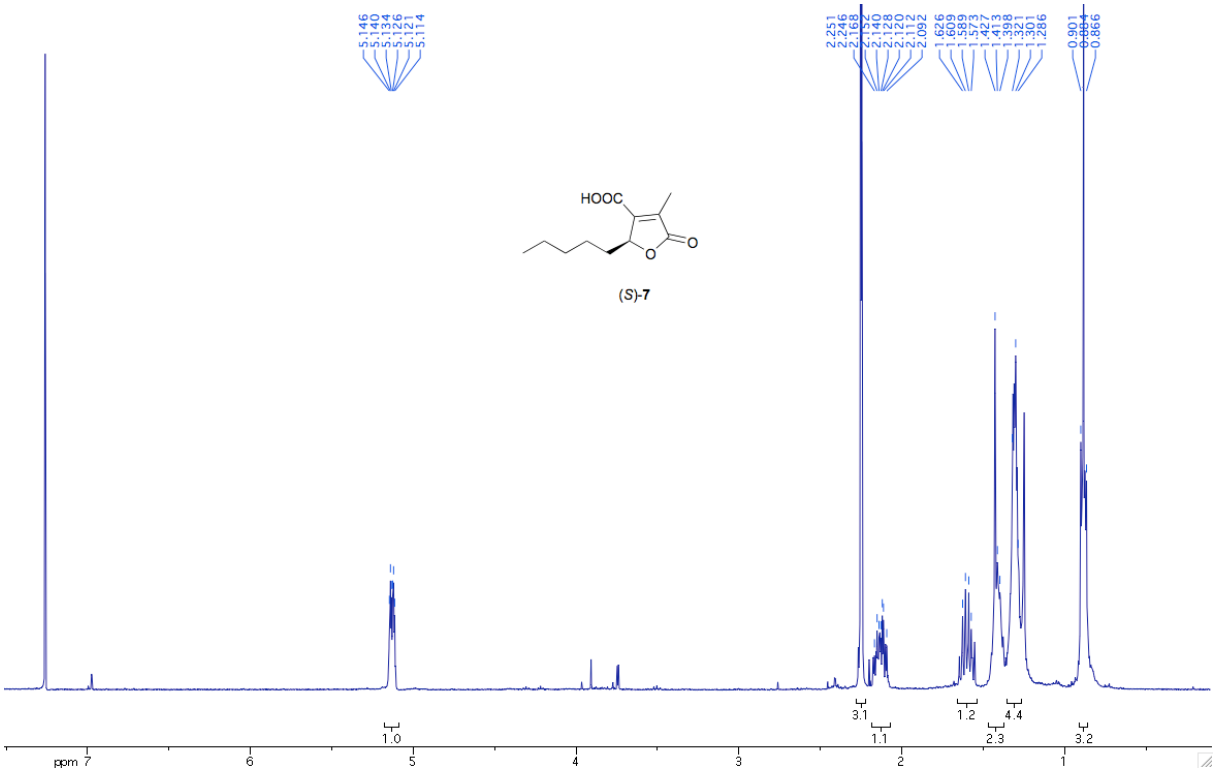
20
10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5.126
5.121
5.114
2.251
2.246
2.168
2.147
2.140
2.128
2.120
2.112
2.092
1.626
1.609
1.589
1.573
1.427
1.413
1.398
1.321
1.301
1.286
0.901
0.884
0.866
HOOC
O
O
(S)-7
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1.1
1.2
2.3
4.4
3.2
ppm 7
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4
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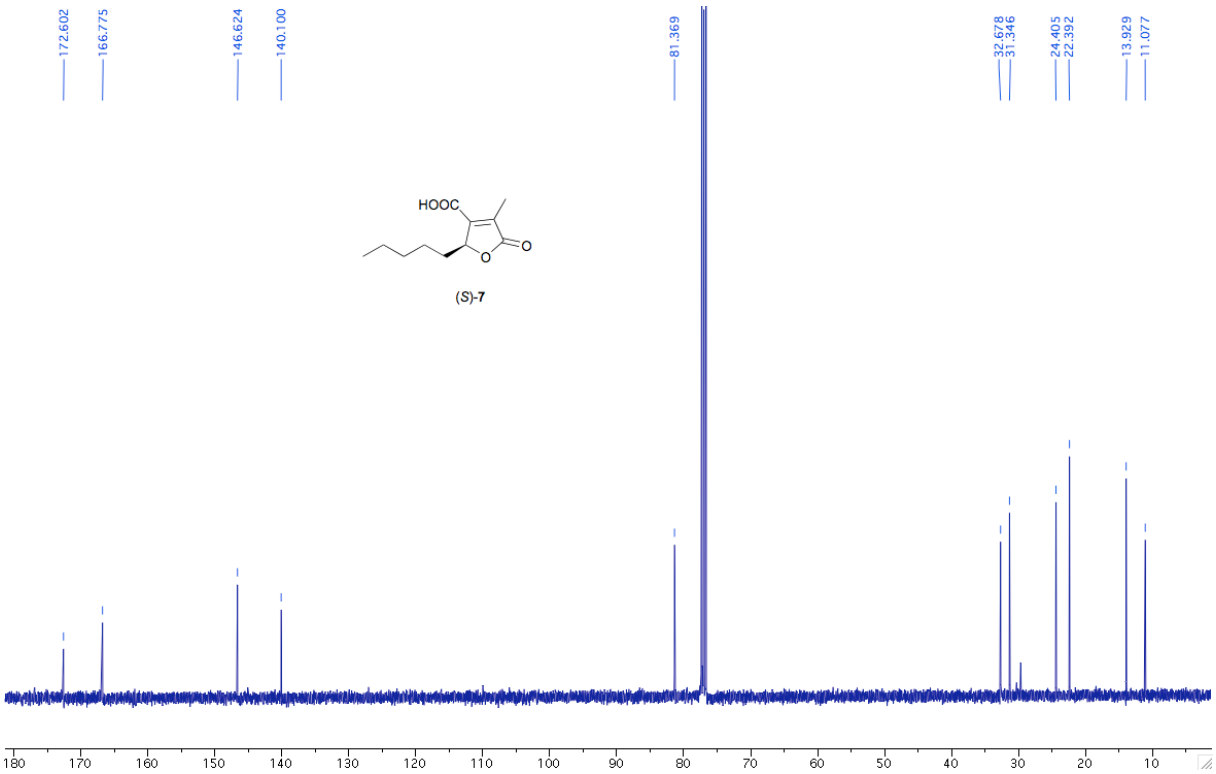
2
1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140.100
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31.346
24.405
22.392
13.929
11.077
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O
O
(S)-7
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160
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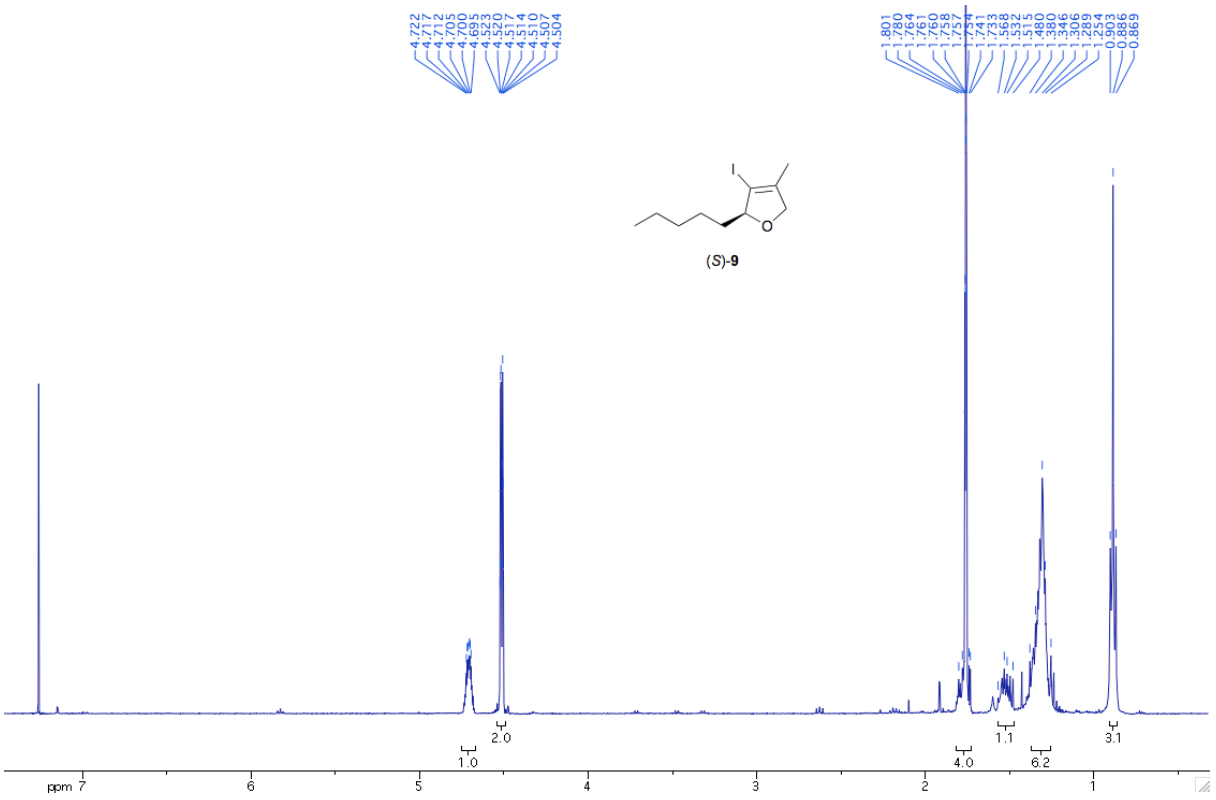
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4.517
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4.510
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4.504
1.801
1.780
1.764
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1.760
1.758
1.757
1.734
1.741
1.723
1.538
1.532
1.515
1.480
1.380
1.346
1.286
1.269
1.254
0.903
0.886
0.869
I
O
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ppm 7
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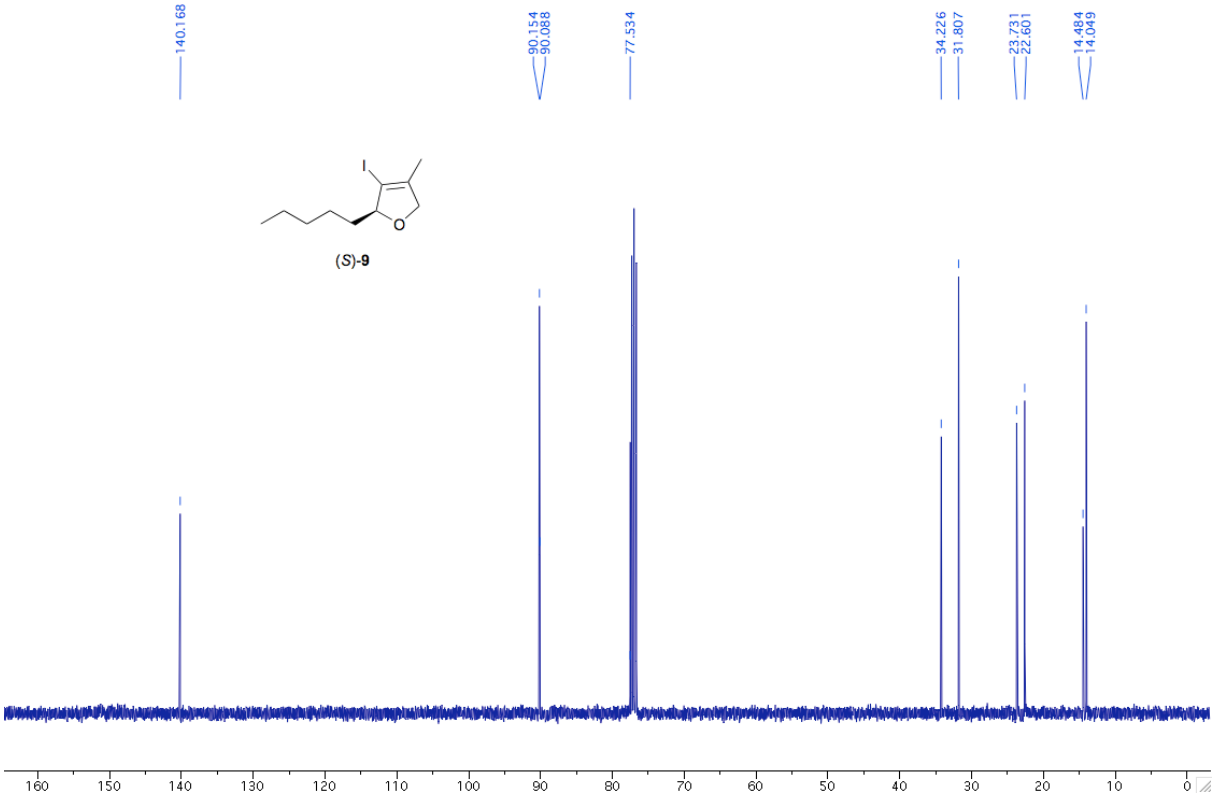
4
3
2
1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90.088
77.534
34.226
31.807
23.731
22.601
14.484
14.049
I
O
(S)-9
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
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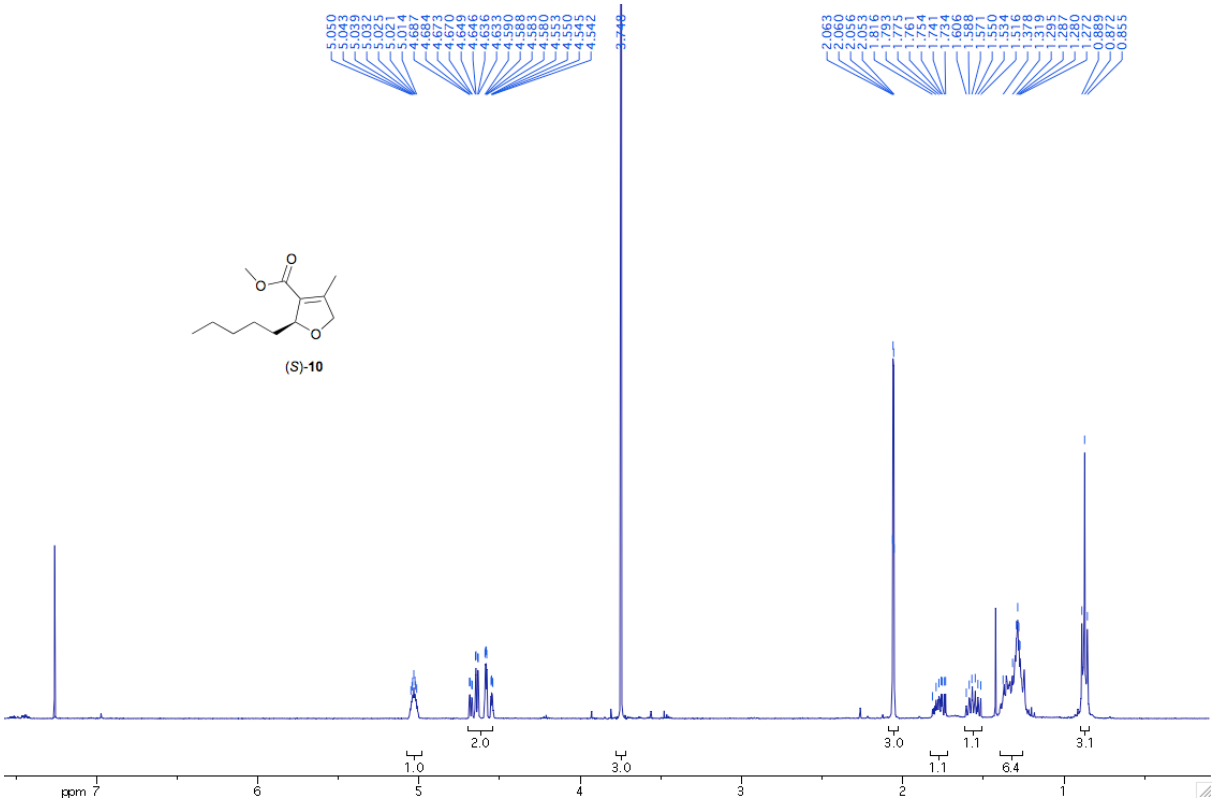
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4.588
4.583
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4.553
4.550
4.545
4.542
3.748
2.063
2.060
2.056
2.053
1.816
1.793
1.775
1.761
1.754
1.741
1.734
1.606
1.588
1.571
1.550
1.534
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1.378
1.319
1.295
1.287
1.280
1.272
0.889
0.872
0.855
(S)-10
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6.4
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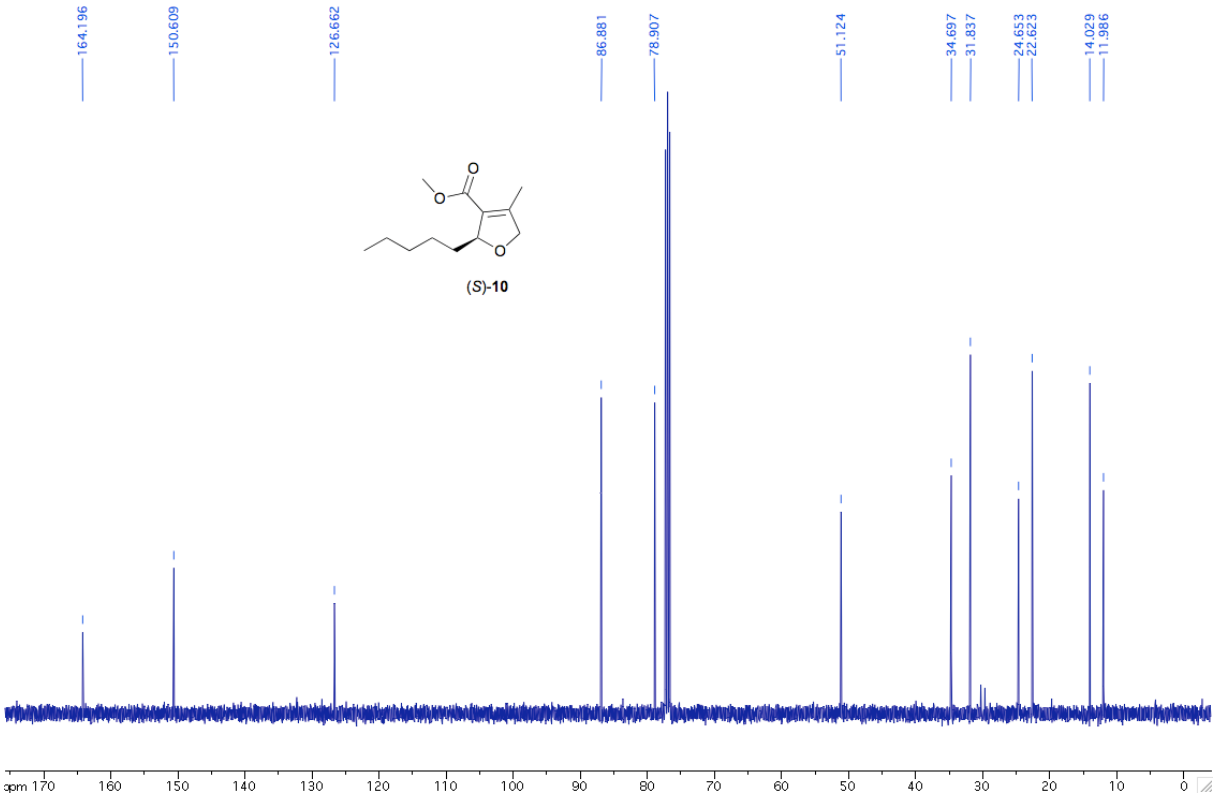
ppm 7
6
5
4
3
2
1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(S)-10
ppm 170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0