Supporting Information

Uniting Anion Relay Chemistry with Pd-Mediated Cross Coupling: Design, Synthesis and Evaluation of Bifunctional Aryl and Vinyl Silane Linchpins.

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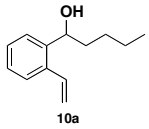
Experimental

I. Materials and Methods

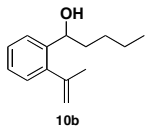
Except as otherwise indicated, reactions were run out under an argon atmosphere in flame- or oven-dried glassware. After aqueous work-up, all organic extracts were dried over sodium or magnesium sulfate, and filtered prior to concentration. Diethyl ether and THF were obtained from a Pure Solve™ PS-400. Hexamethylphosphoramide (HMPA) was freshly distilled from calcium hydride under vacuum. *n*-BuLi (2.5M in THF), Copper (I) iodide (99.999% metals basis) and $Pd(PPh_3)_4$ (99%) were purchased from Aldrich, and used without purification. Reactions were monitored by thin layer chromatography (TLC) with 0.25-mm E. Merck pre-coated silica gel plates (Kieselgel $60F_{254}$, Merck). Spots were detected by viewing under a UV light, colorizing with charring after dipping in anisaldehyde solution composed of acetic acid, sulfuric acid, and MeOH or in $KMnO_4$ solution composed of potassium carbonate, sodium hydroxide, and water. Silica gel for flash chromatography (particle size 0.040-0.063 mm) was supplied by Silicycle and Sorbent technologies. Yields refer to chromatographically and spectroscopically pure compounds unless otherwise noted. ^1H and ^{13}C spectra were recorded on a Bruker AM-500 spectrometer. Chemical shifts are reported as δ values relative to internal chloroform (δ 7.26 for ^1H and δ 77.0 for ^{13}C) and benzene (δ 7.16 for ^1H and δ 128.0 for ^{13}C). IR spectra were measured as neat oils on a Perkin-Elmer Model 1600 FTIR. Optical rotations were measured on a Jasco polarimeter. High resolution mass spectra were obtained at the University of Pennsylvania Mass Spectrometry Service Center.

II. Experiment Section:



10a

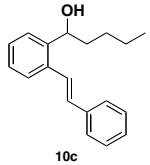
Compound 10a. To a solution of *o*-TMS benzaldehyde **10** (116.4 mg, 0.65 mmol, 1.0 equiv.) in Et_2O (1 mL) at –78 °C was added *n*-BuLi (2.5M in hexane, 0.31 mL, 0.78 mmol, 1.2 equiv.) dropwise. After stirring for 30 min, the resulting solution was added to a mixture of CuI (148.5 mg, 0.78 mmol, 1.2 equiv.) in HMPA/THF (1 mL/1 mL) via cannula at 0 °C. The resulting solution was warmed to room temperature. After being stirred for 30 min, vinyl bromide (1.3 mL, 1.3 mmol, 2.0 equiv.) and $Pd(PPh_3)_4$ (22.5 mg, 0.02 mmol, 0.03 equiv.) in THF (1 mL) were added. After being stirred for 6 h at room temperature, 3 mL of 1N HCl was added. After 10 min, a saturated aqueous NH_4Cl (3 mL) solution was added, and the resulting mixture extracted with Et_2O (10 mL x 3). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Flash chromatography (ethyl acetate/hexane = 1/15) afforded **10a** (83.2 mg, 0.44 mmol, 67% yield) as a pale yellow oil. R_f 0.4 (hexane/diethyl ether = 5/1); IR (film) 3365 (m), 3063 (w), 2956 (s), 2860 (s), 1452 (m), 1043 (m), 760 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.49-7.46 (m, 2H), 7.32-7.29 (m, 1H), 7.27-7.24 (m, 1H), 7.06 (dd, *J* = 17.0 and 11.0 Hz, 1H), 5.62 (dd, *J* = 17.0 and 1.0 Hz, 1H), 5.32 (dd, *J* = 11.0 and 1.5 Hz, 1H), 5.02-4.99 (m, 1H), 1.88 (br, 1H), 1.79-1.70 (m, 2H), 1.48-1.23 (m, 4H), 0.91 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.0, 135.6, 134.2, 128.0, 127.3, 126.1, 125.4, 116.4, 70.8, 38.1, 28.1, 22.6, 14.0; high resolution mass spectrum (CI^+) *m/z* 190.1354 [$(M)^+$; calcd for $C_{13}H_{18}O$: 190.1358].



10b

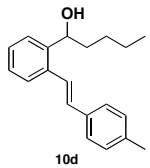
Compound 10b. Using conditions similar to those used for **10a**, *o*-TMS benzaldehyde **10** (116.3 mg, 0.65 mmol, 1.0 equiv.) affored **10b** (73.4 mg, 0.36 mmol, 55% yield) as a colorless oil after flash chromatography (ethyl acetate/hexane = 1/10), and preparative thin layer chromatography (ethyl acetate/benzene = 1/30). R_f 0.41 (hexane/diethyl ether = 5/1); IR (film) 3361 (m), 3073 (w),

3023 (w), 2957 (s), 2932 (s), 2860 (m), 1640 (w), 1451 (m), 1046 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.0 Hz, 1H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 7.5 Hz, 1H), 5.22 (s, 1H), 4.91 (dd, *J* = 8.2 and 5.0 Hz, 1H), 4.83 (s, 1H), 2.07 (s, 3H), 1.84-1.76 (m, 2H), 1.73-1.66 (m, 1H), 1.48-1.39 (m, 1H), 1.38-1.24 (m, 3H), 0.89 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 142.5, 141.4, 128.0, 127.4, 127.1, 125.6, 115.5, 70.6, 38.6, 28.4, 25.7, 22.6, 14.0; high resolution mass spectrum (ES^+) *m/z* 203.1437 [$(M-H)^+$; calcd for $C_{14}H_{19}O$: 203.1436].



10c

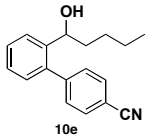
Compound 10c. Using conditions similar to those used for **10a**, *o*-TMS benzaldehyde **10** (77 mg, 0.43 mmol, 1.0 equiv.) afforded **10c** (74.6 mg, 0.28 mmol, 65% yield) as a colorless oil after flash chromatography (ethyl acetate/hexane = 1/10), and preparative thin layer chromatography (ethyl acetate/benzene = 1/20). R_f 0.45 (hexane/ethyl acetate = 4/1); IR (film) 3365 (m), 3026 (m), 2954 (s), 2930 (s), 2858 (m), 1599 (w), 1494 (m), 1449 (m), 1032 (m), 960 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.0 and 1.5 Hz, 1H), 7.52-7.49 (m, 3H), 7.47 (d, *J* = 16.0 Hz, 1H), 7.39-7.36 (m, 2H), 7.34-7.27 (m, 3H), 6.97 (d, *J* = 16.0 Hz, 1H), 5.13-5.10 (m, 1H), 1.82-1.75 (m, 3H), 1.44-1.42 (m, 1H), 1.41-1.30 (m, 3H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.4, 139.1, 137.6, 135.4, 131.3, 128.9, 128.0, 127.9, 127.7, 126.7, 126.4, 125.9, 71.3, 38.3, 28.3, 22.7, 14.2; high resolution mass spectrum (ES^-) *m/z* 301.1373 [$(M+Cl)^-$; calcd for $C_{19}H_{22}OCl$: 301.1359].



10d

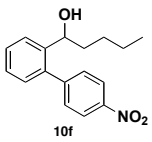
Compound 10d. Using conditions similar to those used for **10a**, *o*-TMS benzaldehyde **10** (78.3 mg, 0.44 mmol, 1.0 equiv.) afforded **10d** (70.1 mg, 0.25 mmol, 57% yield) as a colorless oil after flash chromatography (diethyl ether/hexane = 1/10), and preparative thin layer chromatography

(ethyl acetate/benzene = 1/25). R_f 0.42 (hexane/ethyl acetate = 4/1); IR (film) 3359 (m), 3024 (m), 2929 (s), 2859 (m), 1513 (m), 1451 (m), 1038 (w), 962 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.43-7.40 (m, 3H), 7.32-7.27 (m, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 6.94 (d, *J* = 16.0 Hz, 1H), 5.27-5.09 (m, 1H), 2.37 (s, 3H), 1.81-1.77 (m, 3H), 1.49-1.42 (m, 1H), 1.39-1.29 (m, 3H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.3, 137.8, 135.5, 134.9, 131.2, 129.6, 127.8, 127.6, 126.6, 126.3, 125.8, 124.8, 71.2, 38.3, 28.3, 22.7, 21.4, 14.2; high resolution mass spectrum (ES^+) *m/z* 281.1909 [$(M+H)^+$; calcd for $C_{20}H_{25}O$: 281.1905].



10e

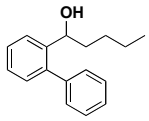
Compound 10e. Using conditions similar to those used for **10a**, *o*-TMS benzaldehyde **10** (86.1 mg, 0.48 mmol, 1.0 equiv.) afforded **10e** (76.9 mg, 0.29 mmol, 60% yield) as a pale yellow oil after flash chromatography (ethyl acetate/hexane = 1/15). R_f 0.31 (hexane/ethyl acetate = 4/1); IR (film) 3435 (m), 3072 (m), 2957 (s), 2930 (s), 2859 (m), 2229 (s), 1607 (m), 1481 (m), 1399 (m), 1005 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 6.5 and 1.5 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.48-7.43 (m, 3H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 4.67-4.64 (m, 1H), 1.77-1.70 (m, 2H), 1.65-1.58 (m, 1H), 1.25-1.08 (m. 4H), 0.80 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.1, 142.0, 139.1, 132.1, 130.3, 129.7, 129.1, 127.6, 126.2, 118.9, 111.2, 70.4, 38.6, 28.2, 22.5, 14.0; high resolution mass spectrum (ES^+) *m/z* 288.1375 [$(M+Na)^+$; calcd for $C_{18}H_{19}NONa$: 288.1364].



10f

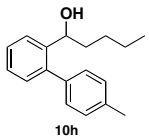
Compound 10f. Using conditions similar to those used for **10a**, *o*-TMS benzaldehyde **10** (124.1 mg, 0.69 mmol, 1.0 equiv.) afforded **10f** (115.7 mg, 0.40 mmol, 58% yield) as a pale yellow oil after flash chromatography (diethyl ether/hexane = 1/10). R_f 0.23 (hexane/ethyl acetate = 5/1); IR (film) 3389 (m), 3063 (w), 2955 (s), 2929 (s), 2858 (s), 1596 (s), 1519 (s), 1347 (s), 1311 (m),

1006 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.50-7.46 (m, 3H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 4.66 (dd, *J* = 8.0 and 5.0 Hz, 1H), 1.89 (br, 1H), 1.75-1.71 (m, 1H), 1.66-1.60 (m, 1H), 1.27-1.09 (m, 4H), 0.80 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.0, 147.0, 141.8, 138.5, 130.3, 129.4, 129.0, 127.4, 126.1, 123.3, 70.2, 38.5, 28.0, 22.3, 13.8; high resolution mass spectrum (ES^-) *m/z* 320.1049 [$(M+Cl)^-$; calcd for $C_{17}H_{19}NO_3Cl$: 320.1053].



10g

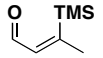
Compound 10g. Using conditions similar to those used for **10a**, *o*-TMS benzaldehyde **10** (123.1 mg, 0.69 mmol, 1.0 equiv.) afforded **10g** (96.1 mg, 0.40 mmol, 58% yield) as a colorless oil after flash chromatography (diethyl ether/hexane = 1/10), and preparative thin layer chromatography (ethyl acetate/benzene = 1/30). R_f 0.32 (hexane/diethyl ether = 5/1); IR (film) 3360 (s), 3059 (m), 3024 (m), 2955 (s), 2931 (s), 2860 (m), 1953 (w), 1817 (w), 1598 (w), 1476 (s), 1463 (s), 1453 (s), 1190 (w), 1045 (s), 1006 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 3H), 7.38-7.35 (m, 1H), 7.34-7.30 (m, 3H), 7.22 (dd, *J* = 7.5 and 1.0 Hz, 1H), 4.87 (dd, *J* = 8.0 and 5.0 Hz, 1H), 1.75-1.65 (m, 3H), 1.30-1.13 (m, 4H), 0.81 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.2, 141.0, 140.8, 129.9, 129.3, 128.1, 127.9, 127.03, 127.02, 125.7, 70.3, 38.4, 28.1, 22.3, 13.9; high resolution mass spectrum (ES^+) *m/z* 263.1401 [$(M+Na)^+$; calcd for $C_{17}H_{20}ONa$: 263.1412].



10h

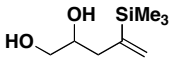
Compound 10h. Using conditions similar to those used for **10a**, *o*-TMS benzaldehyde **10** (115.5 mg, 0.65 mmol, 1.0 equiv.) afforded **10h** (83.9 mg, 0.33 mmol, 50% yield) as a colorless oil after flash chromatography (diethyl ether/hexane = 1/10), and preparative thin layer chromatography (ethyl acetate/benzene = 1/30). R_f 0.3 (hexane/diethyl ether = 5/1); IR (film) 3361 (m), 3056 (w), 3023 (w), 2955 (s), 2929 (s), 2861 (m), 1515 (w), 1480 (m), 1448 (m), 1188 (w), 1004 (m) cm^{-1};

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 8.0 and 1.5 Hz, 1H), 7.40 (ddd, *J* = 7.5, 7.5 and 1.5 Hz, 1H), 7.31 (ddd, *J* = 7.5, 7.5 and 1.5 Hz, 1H), 7.24-7.19 (m, 5H), 4.80 (dd, *J* = 8.0 and 5.5 Hz, 1H), 2.42 (s, 3H), 1.79 (br, 1H), 1.78-1.64 (m, 2H), 1.32-1.14 (m, 4H), 0.83 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.3, 140.7, 138.0, 136.6, 130.0, 129.2, 128.8, 127.7, 127.0, 125.7, 70.3, 38.4, 28.1, 22.4, 21.1, 13.9; high resolution mass spectrum (ES^+) *m/z* 277.1571 [$(M+Na)^+$; calcd for $C_{18}H_{22}ONa$: 277.1568].



11

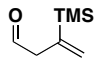
Compound 11. To a solution of (Z)-3-(trimethylsilyl)but-2-en-1-ol **17** (1.02 g, 7.07 mmol, 1.0 equiv.) in Et_2O (141 mL, 0.05 M) was added MnO_2 (6.15 g, 70.7 mmol, 10 equiv.). After being stirred for 14 h at room temperature, the solids were filtered through celite, and rinsed with a small quantity of Et_2O. The filtrates were concentrated *in vacuo* at 0 ºC for 4 h to provide **11** (0.86 g, 6.08 mmol, 86% yield, *Z:E* = >97:<3 by ^{1}H NMR) as a pale yellow liquid. Without further purification, **11** was used in ARC reactions. R_f 0.7 (hexane/diethyl ether = 5/1); IR (film) 2958 (s), 2856 (m), 2738 (w), 1728 (m), 1684 (s), 1582 (w), 1253 (s), 1075 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.84 (d, *J* = 8.5 Hz, 1H), 6.43 (ddd, *J* = 8.5, 3.0 and 1.5 Hz, 1H), 2.04 (d, *J* = 1.5 Hz, 3H), 0.25 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.5, 169.4, 142.1, 26.2, 0.2; high resolution mass spectrum (CI^+) *m/z* 127.0581 [$(M-CH_3)^+$; calcd for $C_6H_{11}OSi$: 127.0579].



20

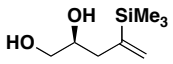
Compound 20. To a solution of Mg turnings (0.54 g, 22.4 mmol, 3.0 equiv.) in THF (100 mL) was added few drops of 1,2-dibromoethane as initiator. A solution of α-bromovinylsilane (2.30 mL, 14.9 mmol, 2.0 equiv.) in THF (10 mL) was slowly added at room temperature over 30 min. After the addition was complete, the reaction mixture was vigorously stirred at room temperature for 1 h. The resulted solution was then cooled to –35 ºC, and then CuI (0.142 g, 0.746 mmol, 0.1 equiv.) was added. After stirring for 30 min at –35 ºC, a solution of epoxide 1**8** (2.36 g, 7.46 mmol, 1.0 equiv.) in THF (20 mL) was added over 10 min. The reaction mixture was then warmed to 0

ºC over 2 h. A saturated aqueous NH_4Cl solution was added, and the resulting mixture was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was then dissolved in MeOH (10 mL) and treated with TsOH (0.142 g, 0.746 mmol, 0.1 equiv.) at room temperature. After being stirred for 5 h, K_2CO_3 (0.103 g, 0.746 mmol, 0.1 equiv.) was added to neutralize the acid. After stirring for 30 min, the reaction mixture was filtered through celite and concentrated *in vacuo*. Flash chromatography (ethyl acetate/hexane = 1/2) afforded **20** (1.05 g, 6.04 mmol, 81% yield, 2 steps) as a pale yellow oil. R_f 0.15 (hexane/ethyl acetate = 2/1); Data is consistent with that reported in the literature.[1]



12

Compound 12. To a solution of 4-(trimethylsilyl)pent-4-ene-1,2-diol **20** (1.90 g, 10.9 mmol, 1.0 equiv.) in EtOH (13 mL) was added $NaIO_4$ (4.66 g, 21.8 mmol, 2.0 equiv.) in H_2O (19 mL) at 0 ºC. After being stirred for 1 h at room temperature, H_2O (20 mL) was added. The resulting mixture was then extracted with Et_2O (10 mL x 3), and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo* at 0 ºC for 4 h to provide **12** (1.41 g, 9.91 mmol, 91% yield) as a pale yellow liquid. Without further purification, **12** was used in ARC reactions. R_f 0.7 (hexane/diethyl ether = 5/1); IR (film) 3053 (w), 2956 (s), 2898 (w), 2814 (w), 2718 (w), 1724 (s), 1417 (m), 1251 (s), 841 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.59 (t, J = 2.5 Hz, 1H), 5.72 (d, J = 2.5 Hz, 1H), 5.63 (d, J = 2.5 Hz, 1H), 3.20-3.19 (m, 2H), 0.10 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.6, 143.0, 129.9, 50.7, –1.9; high resolution mass spectrum (CI^+) *m/z* 143.0885 [$(M+H)^+$; calcd for $C_7H_{15}OSi$: 143.0892].

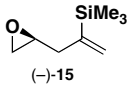


(–)-**29**

Compound (–)-**29**. To a solution of Mg turnings (1.3 g, 54.1 mmol, 4.0 equiv.) in THF (100 mL) was added few drops of 1,2-dibromoethane as initiator. A solution of α-bromovinylsilane (4.16

[1] Landais, Y.; Planchenault. *Tetrahedron* **1995**, *51*, 12097.

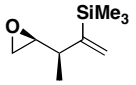
mL, 27.0 mmol, 2.0 equiv.) in THF (10 mL) was slowly added at room temperature over 30 min. After the addition was complete, the reaction mixture was vigorously stirred at room temperature for 1 h. The resulted solution was then cooled to –40 ºC, and then CuI (0.257 g, 1.35 mmol, 0.1 equiv.) was added. After stirring for 30 min at –40 ºC, a solution of epoxide (+)-**28** (2.54 g, 13.5 mmol, 1.0 equiv.) in THF (20 mL) was added over 10 min. The reaction mixture was then warmed to 0 ºC over 5 h, before being allowed to further warm to room temperature and stir overnight. A saturated aqueous NH_4Cl solution was added, and the resulting mixture was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was then dissolved in MeOH (10 mL) and treated with TsOH (0.256 g, 0.135 mmol, 0.1 equiv.) at room temperature. After being stirred for 1 h, K_2CO_3 (0.186 g, 0.135 mmol, 0.1 equiv.) was added to neutralize the acid. After stirring for 30 min, the reaction mixture was filtered through celite and concentrated *in vacuo*. Flash chromatography (ethyl acetate/hexane = 1/2) afforded (–)-**29** (1.96 g, 11.2 mmol, 83% yield, 2 steps) as a pale yellow oil. R_f 0.15 (hexane/ethyl acetate = 2/1); $[\alpha]^{18}_D$ –2.02 (*c* 1.0, $CHCl_3$); IR (film) 3375 (s), 3049 (w), 2954 (s), 1651 (w), 1409 (m), 1249 (s), 1031 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.68 (d, *J* = 3.0 Hz, 1H), 5.49 (d, *J* = 3.0 Hz, 1H), 3.83-3.78 (m, 1H), 3.67 (dd, *J* = 11.0 and 3.0 Hz, 1H), 3.46 (dd, *J* = 11.0 and 7.0 Hz, 1H), 2.39 (br, 2H), 2.35 (dd, *J* = 14.5 and 4.5 Hz, 1H), 2.27 (dd, *J* = 14.0 and 8.5 Hz, 1H), 0.11 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.5, 127.8, 70.3, 66.4, 40.2, -1.4; high resolution mass spectrum (ES^+) *m/z* 197.0973 [$(M+Na)^+$; calcd for $C_8H_{18}O_2NaSi$: 197.0974].



(–)-**15**

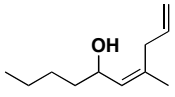
Compound (–)-**15**. To a stirred suspension of NaH (0.75 g, 31.4 mmol, 3.3 equiv.) in THF (20 mL) at 0 ºC was added a solution of diol (–)-**29** (1.83 g, 10.5 mmol, 1.1 equiv.) in THF (10 mL) via cannula, followed by THF rinse (3 mL). After being stirred for 1 h at 0 ºC, a solution of trisylimidazole (3.18 g, 9.5 mmol, 1.0 equiv.) in THF (20 mL) to the white suspension via syringe pump over 2 h. After an additional 1 h, the white slurry was carefully quenched with sat. NH_4Cl

and then diluted with H_2O. The aqueous phase was washed with Et_2O (30 mL x 3), and the combined organic layers were washed with sat. $NaHCO_3$, dried over $MgSO_4$, and concentrated *in vacuo*. Flash chromatography (diethyl ether/hexane = 1/10) afforded (–)-**15** (1.44 g, 9.21 mmol, 97% yield) as a pale yellow liquid. R_f 0.75 (hexane/diethyl ether = 5/1); $[\alpha]^{18}_D$ –5.95 (*c* 1.0, $CHCl_3$); IR (film) 3048 (w), 2955 (s), 2925 (s), 2855 (s), 1601 (w), 1461 (m), 1249 (s), 1180 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.71 (d, *J* = 2.5 Hz, 1H), 5.43 (d, *J* = 2.5 Hz, 1H), 2.99-2.96 (m, 1H), 2.76 (t, *J* = 4.5 Hz, 1H), 2.47 (dd, *J* = 5.0 and 2.5 Hz, 1H), 2.40 (dd, *J* = 15.5 and 6.0 Hz, 1H), 2.28 (dd, *J* = 15.5 and 6.0 Hz, 1H), 0.09 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.9, 126.4, 51.6, 47.1, 38.8, -1.8; high resolution mass spectrum (CI^+) *m/z* 141.0732 [$(M\text{-}CH_3)^+$; calcd for $C_7H_{13}OSi$: 141.0736].



(+)-**16**

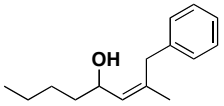
Compound (+)-**16**. Using conditions similar to those used for (–)-**15**, trisylimidazole (0.43 g, 1.28 mmol, 1.0 equiv.) afforded (+)-**16** (200.9 mg, 1.18 mmol, 92% yield) as a pale yellow liquid after flash chromatography (diethyl ether/pentane = 1/10). R_f 0.45 (pentane/diethyl ehter = 10/1) ; $[\alpha]^{18}_D$ +16.6 (*c* 1.2, $CDCl_3$); IR (film) 3050 (w), 2959 (s), 2926 (m), 2900 (m), 1599 (w), 1456 (m), 1408 (s), 1249 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.74 (d, *J* = 2.0 Hz, 1H), 5.48 (d, *J* = 2.5 Hz, 1H), 2.87 (ddd, *J* = 7.5, 3.5 and 3.0 Hz, 1H), 2.75 (dd, *J* = 5.0 and 4.0 Hz, 1H), 2.50 (dd, *J* = 5.0 and 2.0 Hz, 1H), 2.06 (m, 1H), 1.19 (d, *J* = 7.0 Hz, 3H), 0.11 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.0, 125.3, 56.8, 47.4, 41.7, 18.4, -1.0; high resolution mass spectrum (ES^+) *m/z* 171.1206 [$(M+H)^+$; calcd for $C_9H_{19}OSi$: 171.1206].



21a

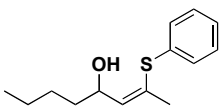
Compound 21a. To a solution of linchpin **11** (65.9 mg, 0.46 mmol, 1.0 equiv.) in Et_2O (1 mL) at –78 °C was added *n*-BuLi (2.2M in hexane, 0.25 mL, 0.55 mmol, 1.2 equiv.) dropwise. After being stirred for 30 min, the resulting solution was added to a mixture of CuI (105.8 mg, 0.55 mmol, 1.2 equiv.) in HMPA/THF (1 mL/1 mL) via cannula at 0 °C. The resulting solution was warmed to

room temperature. After stirring for 30 min at room temperature, allyl bromide (0.08 mL, 0.93 mmol, 2.0 equiv.) was added. After 2 h at room temperature, 3 mL of 1N HCl was added. After 10 min, a saturated aqueous NH_4Cl (3 mL) solution was added, and the resulting mixture was extracted with Et_2O (10 mL x 2) and CH_2Cl_2 (10 mL x 2). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Flash chromatography (diethyl ether/hexane = 1/15) afforded **21a** (50.3 mg, 0.30 mmol, 65% yield) as a colorless oil. R_f 0.2 (hexane/diethyl ether = 5/1); IR (film) 3346 (m), 3063 (w), 2957 (s), 2929 (s), 2858 (s), 1670 (w), 1636 (m), 1029 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.80-5.72 (m, 1H), 5.24 (d, J = 9.0 Hz, 1H), 5.07-5.00 (m, 2H), 4.33 (ddd, J = 8.5, 6.5 and 6.5 Hz, 1H), 2.83 (ddd, J = 25.5, 15.0 and 6.5 Hz, 2H), 1.71 (d, J = 1.5 Hz, 3H), 1.61-1.54 (m, 1H), 1.47 (br, 1H), 1.45-1.38 (m, 1H), 1.35-1.25 (m, 4H), 0.89 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.5, 135.9, 129.6, 115.6, 68.3, 37.3, 36.7, 27.6, 23.4, 22.6, 14.0; high resolution mass spectrum (CI^+) *m/z* 151.1491 [$(M\text{-}OH)^+$; calcd for $C_{11}H_{19}$: 151.1487].



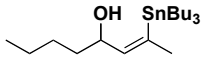
21b

Compound 21b. Using conditions similar to those used for **21a**, linchpin **11** (68.2 mg, 0.48 mmol, 1.0 equiv.) afforded **21b** (68.8 mg, 0.32 mmol, 66% yield) as a colorless oil after flash chromatography (diethyl ether/hexane = 1/10). R_f 0.22 (hexane/diethyl ether = 5/1); IR (film) 3437 (m), 3027 (w), 2956 (s), 2928 (s), 1666 (w), 1601 (w), 1495 (m), 1452 (m), 1031 (m), 1003 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.31-7.28 (m, 2H), 7.22-7.18 (m, 3H), 5.36 (d, J = 9.0 Hz, 1H), 4.51 (ddd, J = 8.5, 6.5 and 6.5 Hz, 1H), 3.45 (s, 2H), 1.67 (d, J = 1.0 Hz, 3H), 1.66-1.61 (m, 1H), 1.59-1.48 (m, 2H), 1.41-1.30 (m, 4H), 0.92 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.4, 137.2, 130.0, 128.5, 128.4, 126.0, 68.4, 38.2, 37.6, 27.7, 23.4, 22.6, 14.0; high resolution mass spectrum (ES^+) *m/z* 241.1558 [$(M+Na)^+$; calcd for $C_{15}H_{22}ONa$: 241.1568].



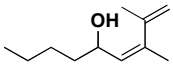
21c

Compound 21c. Using conditions similar to those used for **21a**, linchpin **11** (65.9 mg, 0.46 mmol, 1.0 equiv.) afforded **21c** (74.7 mg, 0.31 mmol, 68% yield) as a colorless oil after flash chromatography (diethyl ether/hexane = 1/10). R_f 0.18 (hexane/diethyl ether = 5/1); IR (film) 3347 (m), 3026 (w), 2956 (s), 2927 (s), 2858 (s), 1633 (w), 1584 (m), 1478 (m), 1439 (m), 1080 (m), 1024 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.35-7.33 (m, 2H), 7.31-7.28 (m, 2H), 7.25-7.22 (m, 1H), 5.78 (dd, J = 4.0 and 1.0 Hz, 1H), 4.76 (app dd, J = 14.5 and 7.0 Hz, 1H), 1.90 (d, J = 1.2 Hz, 3H), 1.85 (br, 1H), 1.69-1.62 (m, 1H), 1.56-1.49 (m, 1H), 1.41-1.29 (m, 4H), 0.92 (t, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.9, 133.6, 131.8, 131.1, 128.9, 126.9, 69.7, 36.8, 27.5, 24.1, 22.6, 14.0; high resolution mass spectrum (ES^-) *m/z* 235.1154 [$(M-H)^-$; calcd for $C_{14}H_{19}OS$: 235.1157].



21d

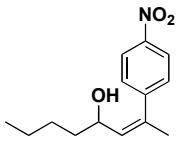
Compound 21d. Using conditions similar to those used for **21a**, linchpin **11** (66.9 mg, 0.47 mmol, 1.0 equiv.) afforded **21d** (124.2 mg, 0.30 mmol, 63% yield) as a colorless oil after flash chromatography (diethyl ether/hexane = 1/40). R_f 0.7 (hexane/diethyl ether = 5/1); IR (film) 3389 (m), 2956 (s), 2927 (s), 2855 (s), 1461 (m), 1377 (m), 1073 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.05 (dd, J_{H-H} = 8.5 and 1.5 Hz, J_{H-Sn} = 126.6 Hz, 1H), 3.87-3.82 (m, 1H), 1.92 (d, J_{H-H} = 1.5 Hz, J_{H-Sn} = 19.8 Hz, 3H), 1.61-1.43 (m, 8H), 1.38-1.26 (m, 11H), 0.95-0.91 (m, 3H), 0.89 (t, J = 7.0 Hz, 15H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.6, 143.1, 74.9, 37.3, 29.3 (t, J = 9.8 Hz), 28.0, 27.6 (t, J = 29.0 Hz), 27.1, 22.9, 14.2, 13.8, 10.5 (t, J = 157.7 Hz); high resolution mass spectrum (ES^+) *m/z* 441.2156 [$(M+Na)^+$; calcd for $C_{20}H_{42}OSnNa$: 441.2155].



21e

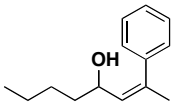
Compound 21e. Using conditions similar to those used for **10a**, linchpin **11** (69.3 mg, 0.49 mmol, 1.0 equiv.) afforded **21e** (43.3 mg, 0.26 mmol, 53% yield) as a pale yellow oil after flash chromatography (diethyl ether/hexane = 1/10). R_f 0.24 (hexane/diethyl ether = 5/1); IR (film) 3347 (m), 3080 (w), 2958 (s), 2930 (s), 2859 (s), 1634 (m), 1445 (m), 1028 (m) cm^{-1}; ^1H NMR (500

MHz, $CDCl_3$) δ 5.16 (dd, *J* = 9.0 and 1.5 Hz, 1H), 4.90 (dd, *J* = 2.5 and 1.5 Hz, 1H), 4.70 (dd, *J* = 2.5 and 1.0 Hz, 1H), 4.30 (ddd, *J* = 8.5, 6.5 and 6.5 Hz, 1H), 1.80 (t, *J* = 1.5 Hz, 3H), 1.79 (d, *J* = 1.5 Hz, 3H), 1.59-1.52 (m, 1H), 1.48 (br, 1H), 1.45-1.39 (m, 1H), 1.33-1.24 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 141.5, 128.7, 112.8, 69.1, 37.3, 27.7, 23.0, 22.6, 22.2, 14.0; high resolution mass spectrum (CI^+) *m/z* 168.1514 [$(M)^+$; calcd for $C_{11}H_{20}O$: 168.1514].



21f

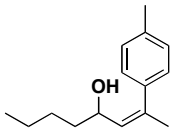
Compound 21f. Using conditions similar to those used for **10a**, linchpin **11** (69.7 mg, 0.49 mmol, 1.0 equiv.) afforded **21f** (63.9 mg, 0.26 mmol, 52% yield) as a pale yellow oil after flash chromatography (ethyl acetate/hexane = 1/9). R_f 0.15 (hexane/ethyl acetate = 5/1); IR (film) 3365 (m), 2956 (s), 2930 (s), 2858 (m), 1597 (m), 1520 (s), 1346 (s), 1031 (w), 1013 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.22-8.19 (m, 2H), 7.40-7.37 (m, 2H), 5.58 (dd, *J* = 9.5 and 1.5 Hz, 1H), 3.96 (ddd, *J* = 8.5, 6.5 and 6.5 Hz, 1H), 2.08 (d, *J* = 1.5 Hz, 3H), 1.63 (br, 1H), 1.60-1.54 (m, 1H), 1.50-1.43 (m, 1H), 1.28-1.20 (m, 4H), 0.86 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.2, 146.9, 137.6, 132.1, 128.7, 123.5, 69.1, 37.5, 27.5, 25.2, 22.5, 14.0; high resolution mass spectrum (ES^-) *m/z* 248.1298 [$(M-H)^-$; calcd for $C_{14}H_{18}NO_3$: 248.1287].



21g

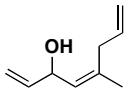
Compound 21g. Using conditions similar to those used for **10a**, linchpin **11** (67.8 mg, 0.48 mmol, 1.0 equiv.) afforded **21g** (52.5 mg, 0.26 mmol, 54% yield) as a pale yellow oil after flash chromatography (ethyl acetate/hexane = 1/9). R_f 0.28 (hexane/ethyl acetate = 5/1); IR (film) 3347 (m), 3023 (w), 2959 (s), 2929 (s), 2858 (s), 1658 (w), 1600 (w), 1464 (m), 1442 (m), 1261 (s), 1026 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37-7.34 (m, 2H), 7.30-7.26 (m, 1H), 7.22-7.21 (m, 2H), 5.49 (dd, *J* = 9.0 and 1.0 Hz, 1H), 4.08 (ddd, *J* = 8.5, 6.5 and 6.5 Hz, 1H), 2.07 (d, *J* = 1.0

Hz, 3H), 1.61-1.54 (m, 2H), 1.51-1.45 (m, 1H), 1.34-1.21 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.3, 139.5, 130.2, 128.1, 127.7, 126.9, 69.1, 37.3, 27.5, 25.7, 22.6, 14.0; high resolution mass spectrum (CI^+) *m/z* 204.1513 [$(M)^+$; calcd for $C_{14}H_{20}O$: 204.1514].



21h

Compound 21h. Using conditions similar to those used for **10a**, linchpin **11** (63.3 mg, 0.44 mmol, 1.0 equiv.) afforded **21h** (59.5 mg, 0.27 mmol, 61% yield) as a pale yellow oil after flash chromatography (diethyl ether/hexane = 1/10). R_f 0.28 (hexane/diethyl ether = 5/1); IR (film) 3345 (m), 3023 (w), 2957 (s), 2928 (s), 2858 (s), 1657 (w), 1568 (w), 1511 (m), 1444 (m), 1031(m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 5.45 (dd, *J* = 9.5 and 1.5 Hz, 1H), 4.09 (ddd, *J* = 9.0, 6.5 and 6.5 Hz, 1H), 2.36 (s, 3H), 2.04 (d, *J* = 1.5 Hz, 3H), 1.59-1.52 (m, 1H), 1.49-1.46 (m, 1H), 1.41 (br, 1H), 1.31-1.22 (m, 4H), 0.87 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.5, 138.3, 136.6, 129.9, 128.8, 127.5, 69.2, 37.4, 27.6, 25.8, 22.6, 21.1, 14.0; high resolution mass spectrum (CI^+) *m/z* 218.1663 [$(M)^+$; calcd for $C_{15}H_{22}O$: 218.1670].

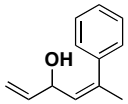


22a

Compound 22a. To a solution of linchpin **11** (67.9 mg, 0.48 mmol, 1.0 equiv.) in Et_2O (1 mL) at –78 °C was added vinyl lithium[2] (1.12 M in THF, 0.51 mL, 0.57 mmol, 1.2 equiv.) dropwise. After stirring for 30 min, the resulting solution was added to a mixture of CuI (108.5 mg, 0.57 mmol, 1.2 equiv.) in HMPA/THF (1 mL/1 mL) via cannula at 0 °C. The resulting solution was warmed to room temperature. After being stirred for 30 min at room temperature, allyl bromide (0.08 mL, 0.96 mmol, 2.0 equiv.) was added. After being stirred for 2 h at room temperature, TBAF (1.92 mL, 1.92 mmol, 4.0 equiv.) was added. After 1 h, the resulting mixture was filtered through

[2] Uozumi, Y.; Tsuji, H.; Hayashi, T. *J. Org. Chem.* **1998**, *63*, 6137.

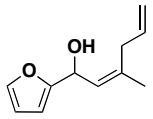
triethylamine-buffered silica gel (2.5 v/v). Flash chromatography on triethylamine-buffered silica gel (diethyl ether/hexane = 1/10), afforded **22a** (41.2 mg, 0.30 mmol, 62% yield) as a pale yellow oil. R_f 0.24 (hexane/diethyl ether = 5/1); IR (film) 3362 (s), 3080 (m), 2925 (s), 1638 (m), 1442 (m), 1250 (m), 1110 (m) cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 5.89-5.82 (m, 1H), 5.68-5.60 (m, 1H), 5.25-5.20 (m, 2H), 4.99-4.93 (m, 3H), 4.74 (dd, J = 8.5 and 5.5 Hz, 1H), 2.65 (ddd, J = 36.5, 14.5 and 6.5 Hz, 2H), 1.56 (d, J = 1.5 Hz, 3H), 1.30 (br, 1H); ^{13}C NMR (125 MHz, C_6D_6) δ 140.9, 135.9, 128.6, 127.8, 115.8, 113.5, 69.5, 36.9, 23.4; high resolution mass spectrum (CI^+) *m/z* 120.1020 [$(M\text{-}OH)^+$; calcd for C_9H_{13}: 121.1017].



22b

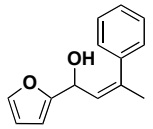
Compound 22b. To a solution of linchpin **11** (68.4 mg, 0.48 mmol, 1.0 equiv.) in Et_2O (1 mL) at –78 °C was added vinyl lithium[1] (1.12 M in THF, 0.52 mL, 0.58 mmol, 1.2 equiv.) dropwise. After stirring for 30 min, the resulting solution was added to a mixture of CuI (109.8 mg, 0.58 mmol, 1.2 equiv.) in HMPA/THF (1 mL/1 mL) via cannula at 0 °C. The resulting solution was warmed to room temperature. After being stirred for 30 min at room temperature, phenyl iodide (0.11 mL, 0.96 mmol, 2.0 equiv.) and $Pd(PPh_3)_4$ (16.7 mg, 0.014 mmol, 0.03 equiv.) in THF (1 mL) were added. After being stirred for 6 h at room temperature, TBAF (1.92 mL, 1.92 mmol, 4.0 equiv.) was added. After 1 h, the resulting mixture was filtered through triethylamine-buffered silica gel (2.5 v/v). Flash chromatography on triethylamine-buffered silica gel (diethyl ether/hexane = 1/10) afforded **22b** (37.8 mg, 0.22 mmol, 45% yield) as a pale yellow oil. R_f 0.28 (hexane/diethyl ether = 5/1); IR (film) 3340 (s), 3079 (w), 3057 (w), 3023 (w), 2970 (s), 2916 (s), 1643 (w), 1493 (w), 1438 (m), 1115 (w), 987 (s) cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 7.29-7.22 (m, 4H), 7.18-7.15 (m, 1H), 6.01-5.94 (m, 1H), 5.55 (dd, J = 9.5 and 1.5 Hz, 1H), 5.25 (ddd, J = 3.0, 1.5 and 1.5 Hz, 1H), 5.05 (ddd, J = 3.0, 1.5 and 1.5 Hz, 1H), 4.75 (dd, J = 9.0 and 5.5 Hz, 1H), 1.98 (d, J = 1.5 Hz, 3H), 1.53 (br, 1H); ^{13}C NMR (125 MHz, C_6D_6) δ 141.5, 140.9, 139.1, 129.1, 128.4, 127.8, 127.3, 113.9,

70.3, 25.5; high resolution mass spectrum (ES^+) *m/z* 197.0941 [$(M+Na)^+$; calcd for $C_{12}H_{14}ONa$: 197.0942].



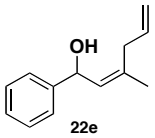
22c

Compound 22c. Using conditions similar to those used for **22a**, linchpin **11** (68.2 mg, 0.47 mmol, 1.0 equiv.) afforded **22c** (55.9 mg, 0.31 mmol, 65% yield) as a pale yellow oil after flash chromatography (diethyl ether/hexane = 1/10). R_f 0.23 (hexane/diethyl ether = 5/1); IR (film) 3362 (s), 3078 (w), 2973 (s), 2917 (s), 2854 (m), 1721 (w), 1669 (w), 1636 (m), 1442 (m), 1146 (m), 1005 (s) cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 7.09 (dd, *J* = 1.5 and 1.0 Hz, 1H), 6.13 (d, *J* = 3.0 Hz, 1H), 6.07 (dd, *J* = 3.0 and 2.0 Hz, 1H), 5.68-5.59 (m, 2H), 5.37 (d, *J* = 8.5 Hz, 1H), 4.98-4.91 (m, 2H), 2.69 (ddd, *J* = 26.0, 14.5 and 6.5 Hz, 2H), 2.08 (br, 1H), 1.57 (d, *J* = 1.5 Hz, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 157.3, 142.0, 137.2, 135.8, 126.6, 115.9, 110.4, 105.9, 64.7, 36.9, 23.3; high resolution mass spectrum (CI^+) *m/z* 161.0962 [$(M-OH)^+$; calcd for $C_{11}H_{13}O$: 161.0966].



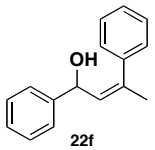
22d

Compound 22d. Using conditions similar to those used for **22b**, linchpin **11** (67 mg, 0.47 mmol, 1.0 equiv.) afforded **22d** (50.4 mg, 0.24 mmol, 50% yield) as a pale yellow oil after flash chromatography (diethyl ether/hexane = 1/10). R_f 0.23 (hexane/diethyl ether = 5/1); IR (film) 3393 (s), 3146 (w), 3056 (w), 3025 (w), 2916 (s), 1956 (w), 1892 (w), 1723 (w), 1656 (m), 1438 (s), 1146 (s), 999 (s) cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 7.22 (d, *J* = 7.0 Hz, 2H), 7.12 (t, *J* = 7.0 Hz, 2H), 7.07-7.05 (m, 2H), 6.05 (dd, *J* = 11.0 and 3.0 Hz, 2H), 5.83 (d, *J* = 9.5 Hz, 1H), 5.25 (d, *J* = 9.5 Hz, 1H), 1.88 (d, *J* = 1.5 Hz, 3H), 1.71 (br, 1H); ^{13}C NMR (125 MHz, C_6D_6) δ 157.2, 142.0, 141.1, 140.2, 128.5, 128.2, 127.5, 127.1, 110.4, 106.1, 65.6, 25.4; high resolution mass spectrum (ES^+) *m/z* 237.0893 [$(M+Na)^+$; calcd for $C_{14}H_{14}O_2Na$: 237.0891].



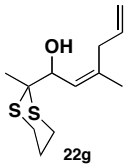
22e

Compound 22e. Using conditions similar to those used for **22a**, linchpin **11** (68.5 mg, 0.48 mmol, 1.0 equiv.) afforded **22e** (60.1 mg, 0.32 mmol, 66% yield) as a pale yellow oil after flash chromatography (diethyl ether/hexane = 1/10). R_f 0.24 (hexane/diethyl ether = 5/1); IR (film) 3341 (s), 3062 (m), 3029 (m), 2972 (s), 2914 (s), 1667 (w), 1636 (m), 1447 (s), 1068 (m), 997 (s) cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 7.39 (d, *J* = 7.5 Hz, 2H), 7.21-7.18 (m, 2H), 7.09 (t, *J* = 7.0 Hz, 1H), 5.70-5.62 (m, 1H), 5.44 (d, *J* = 8.0 Hz, 1H), 5.32 (d, *J* = 8.5 Hz, 1H), 4.99-4.94 (m, 2H), 2.73 (ddd, *J* = 32.0, 15.0 and 6.5 Hz, 2H), 1.78 (br, 1H), 1.55 (d, *J* = 1.5 Hz, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 145.4, 136.3, 136.0, 130.6, 128.9, 127.7, 126.7, 116.3, 70.8, 37.3, 23.7; high resolution mass spectrum (ES^+) *m/z* 211.1100 [$(M+Na)^+$; calcd for $C_{13}H_{16}ONa$: 211.1099].



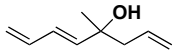
22f

Compound 22f. Using conditions similar to those used for **22b**, linchpin **11** (68.5 mg, 0.48 mmol, 1.0 equiv.) afforded **22f** (54.9 mg, 0.25 mmol, 51% yield) as a pale yellow oil after flash chromatography (diethyl ether/hexane = 1/10). R_f 0.28 (hexane/diethyl ether = 5/1); IR (film) 3328 (s), 3058 (s), 3027 (s), 2970 (s), 2912 (s), 1952 (w), 1884 (w), 1810 (w), 1653 (m), 1492 (s), 1447 (s), 998 (s) cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 7.34 (d, *J* = 7.5 Hz, 2H), 7.22-7.20 (m, 2H), 7.19-7.14 (m, 4H), 7.11-7.06 (m, 2H), 5.68 (dd, *J* = 9.0 and 1.0 Hz, 1H), 5.22 (d, *J* = 9.5 Hz, 1H), 1.87 (d, *J* = 1.0 Hz, 3H), 1.76 (br, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 141.0, 139.7, 129.1, 128.5, 128.2, 127.8, 127.4, 127.2, 126.0, 71.3, 25.7; high resolution mass spectrum (ES^+) *m/z* 247.1107 [$(M+Na)^+$; calcd for $C_{16}H_{16}ONa$: 247.1099].



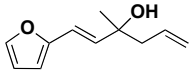
22g

Compound 22g. Using conditions similar to those used for **21a**, linchpin **11** (66.5 mg, 0.46 mmol, 1.0 equiv.) afforded **22g** (66.1 mg, 0.27 mmol, 58% yield) as a pale yellow oil after flash chromatography (ethyl acetate/hexane = 1/15). R_f 0.25 (hexane/diethyl ether = 5/1); IR (film) 3447 (s), 3051 (w), 2956 (s), 2915 (s), 1636 (m), 1442 (s), 1376 (s), 1276 (m), 1066 (s), 1013 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.86-5.78 (m, 1H), 5.14 (dd, *J* = 3.5 and 1.5 Hz, 1H), 5.10 (dd, *J* = 3.0 and 1.5 Hz, 1H), 5.06 (dd, *J* = 3.0 and 1.5 Hz, 1H), 4.68 (dd, *J* = 3.5 and 1.5 Hz, 1H), 3.03-2.90 (m, 4H), 2.71-2.65 (m, 2H), 2.58 (d, *J* = 2.0 Hz, 1H), 2.10-2.04 (m, 1H), 1.94-1.86 (m, 1H), 1.78 (d, *J* = 1.0 Hz, 3H), 1.49 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.5, 135.7, 122.5, 116.2, 69.7, 53.6, 37.2, 26.8, 25.9, 24.5, 23.8, 22.7; high resolution mass spectrum (ES^+) *m/z* 267.0848 [$(M+Na)^+$; calcd for $C_{17}H_{15}OS$: 267.0848].



22h

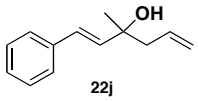
Compound 22h. Using conditions similar to those used for **21a**, linchpin **11** (69.9 mg, 0.49 mmol, 1.0 equiv.) afforded **22h** (43.3 mg, 0.31 mmol, 64% yield) as a pale yellow oil after flash chromatography (diethyl ether/hexane = 1/10). R_f 0.24 (hexane/diethyl ether = 5/1); IR (film) 3405 (m), 3079 (w), 2925 (s), 2854 (s), 1734 (m), 1641 (m), 1461 (m), 1378 (m), 1255 (m), 1078 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.37-6.29 (m, 1H), 6.26-6.21 (m, 1H), 5.82-5.74 (m, 2H), 5.20 (dd, *J* = 16.5 and 1.0 Hz, 1H), 5.16-5.10 (m, 2H), 5.07 (dd, *J* = 10.0 and 1.5 Hz, 1H), 2.31 (ddd, *J* = 37.0, 13.5 and 6.5 Hz, 2H), 1.76 (br, 1H), 1.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.3, 136.4, 133.5, 128.3, 119.2, 117.0, 72.0, 47.1, 27.7; high resolution mass spectrum (CI^+) *m/z* 121.1012 [$(M-OH)^+$; calcd for C_9H_{13}: 121.1017].



22i

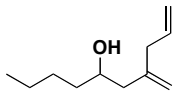
Compound 22i. Using conditions similar to those used for **21a**, linchpin **11** (67.2 mg, 0.47 mmol, 1.0 equiv.) afforded **22i** (47.0 mg, 0.26 mmol, 56% yield) as a pale yellow oil after flash chromatography (diethyl ether/hexane = 1/10). R_f 0.23 (hexane/diethyl ether = 5/1); IR (film) 3404 (s), 3076 (w), 2974 (s), 2925 (s), 1640 (m), 1489 (m), 1373 (m), 1275 (m), 1149 (s), 1013 (s) cm^{-1};

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 1.5 Hz, 1H), 6.43 (d, *J* = 16.0 Hz, 1H), 6.36 (dd, *J* = 3.5 and 2.0 Hz, 1H), 6.25 (d, *J* = 16.0 Hz, 1H), 6.21 (d, *J* = 3.5 Hz, 1H), 5.87-5.79 (m, 1H), 5.19-5.13 (m, 2H), 2.38 (ddd, *J* = 43.5, 13.5 and 6.5 Hz, 2H), 1.76 (br, 1H), 1.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.6, 141.7, 134.9, 133.5, 119.4, 116.2, 111.3, 107.7, 72.1, 47.3, 28.0; high resolution mass spectrum (CI^+) *m/z* 161.0973 [$(M\text{-}OH)^+$; calcd for $C_{11}H_{13}O$: 161.0966].



22j

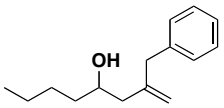
Compound 22j. Using conditions similar to those used for **21a**, linchpin **11** (67.5 mg, 0.47 mmol, 1.0 equiv.) afforded **22j** (54.5 mg, 0.29 mmol, 61% yield) as a pale yellow oil after flash chromatography (diethyl ether/hexane = 1/10). R_f 0.24 (hexane/diethyl ether = 5/1); IR (film) 3397 (s), 3077 (m), 3026 (m), 2976 (s), 2928 (m), 1947 (w), 1813 (w), 1640 (m), 1493 (m), 1448 (m), 1053 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.38 (m, 2H), 7.34-7.31 (m, 2H), 7.25-7.22 (m, 1H), 6.61 (d, *J* = 16.0 Hz, 1H), 6.31 (d, *J* = 16.0 Hz, 1H), 5.89-5.81 (m, 1H), 5.19-5.15 (m, 2H), 2.42 (ddd, *J* = 40.5, 13.5 and 6.5 Hz, 2H), 1.86 (br, 1H), 1.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.9, 136.2, 133.5, 128.5, 127.39, 127.38, 126.4, 119.3, 72.3, 47.3, 27.9; high resolution mass spectrum (ES^+) *m/z* 211.1093 [$(M+Na)^+$; calcd for $C_{13}H_{16}ONa$: 211.1099].



23a

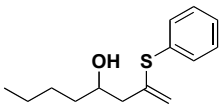
Compound 23a. To a solution of *n*-BuLi (2.2 M in hexane, 0.41 mL, 0.89 mmol, 2.0 equiv.) in Et_2O (0.5 mL) at –78 °C was added linchpin **12** (63.5 mg, 0.446 mmol, 1.0 equiv.) in Et_2O (0.5 mL) dropwise. After being stirred for 30 min, the resulting solution was added to a mixture of CuI (169.9 mg, 0.89 mmol, 2.0 equiv.) in HMPA/THF (1 mL/1 mL) via cannula at 0 °C. The resulting solution was warmed to room temperature. After stirring for 2 h at room temperature, allyl bromide (0.08 mL, 0.89 mmol, 2.0 equiv.) was added. After being stirred for 12 h at room temperature, 3 mL of 1N HCl was added. After 10 min, a saturated aqueous NH_4Cl (3 mL) solution was added, and the resulting mixture extracted with Et_2O (10 mL x 2) and CH_2Cl_2 (10 mL x 2). The combined

organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Flash chromatography (diethyl ether/hexane = 1/20), afforded **23a** (36.9 mg, 0.22 mmol, 49% yield) as a colorless oil. R_f 0.3 (hexane/diethyl ether = 5/1); IR (film) 3402 (m), 3078 (m), 2957 (s), 2929 (s), 2860 (s), 1641 (m), 1434 (m), 1035 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.83-5.78 (m, 1H), 5.09-5.05 (m, 2H), 4.92 (d, *J* = 1.0 Hz, 1H), 4.88 (d, *J* = 1.0 Hz, 1H), 3.73-3.69 (m, 1H), 2.79 (ddd, *J* = 23.0, 16.0 and 7.2 Hz, 2H), 2.26 (dd, *J* = 17.0 and 3.5 Hz, 1H), 2.07 (dd, *J* = 14.0 and 9.5 Hz, 1H), 1.71 (br, 1H), 1.49-1.41 (m, 3H), 1.38-1.31 (m, 3H), 0.91 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.1, 135.9, 116.6, 113.5, 68.8, 44.3, 40.5, 36.8, 27.9, 22.7, 14.0; high resolution mass spectrum (CI^+) *m/z* 151.1490 [$(M\text{-}OH)^+$; calcd for $C_{11}H_{19}$: 151.1487].



23b

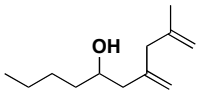
Compound 23b. Using conditions similar to those used for **23a**, linchpin **12** (64.1 mg, 0.45 mmol, 1.0 equiv.) afforded **23b** (41.5 mg, 0.19 mmol, 42% yield) as a colorless oil after flash chromatography (diethyl ether/hexane = 1/10). R_f 0.24 (hexane/diethyl ether = 5/1); IR (film) 3422 (m), 3065 (m), 2955 (s), 2930 (s), 2860 (s), 1715 (w), 1643 (m), 1602 (w), 1494 (m), 1453 (m), 1032 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.33-7.30 (m, 2H), 7.25-7.20 (m, 3H), 4.97 (s, 1H), 4.93 (s, 1H), 3.74-3.72 (m, 1H), 3.39 (dd, *J* = 26.5 and 15 Hz, 2H), 2.21 (dd, *J* = 14.0 and 3.5 Hz, 1H), 2.05 (dd, *J* = 14.0 and 9.5 Hz, 1H), 1.69 (br, 1H), 1.48-1.39 (m, 3H), 1.37-1.26 (m, 3H), 0.90 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.0, 139.2, 129.0, 128.4, 126.2, 114.5, 68.9, 43.8, 42.8, 36.8, 27.8, 22.7, 14.0; high resolution mass spectrum (ES^+) *m/z* 219.1745 [$(M+H)^+$; calcd for $C_{15}H_{23}O$: 219.1749].



23c

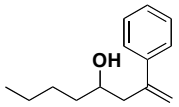
Compound 23c. Using conditions similar to those used for **23a**, linchpin **12** (62.1 mg, 0.44 mmol, 1.0 equiv.) afforded **23c** (53.6 mg, 0.23 mmol, 52% yield) as a colorless oil after flash chromatography (diethyl ether/hexane = 1/10). R_f 0.24 (hexane/diethyl ether = 5/1); IR (film) 3403

(m), 3060 (w), 2955 (s), 2930 (s), 2860 (m), 1608 (m), 1583 (w), 1473 (m), 1438 (m), 1148 (w), 1027 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.0 Hz, 2H), 7.44-7.32 (m, 3H), 5.22 (s, 1H), 4.95 (s, 1H), 3.89-3.86 (m, 1H), 2.42 (dd, *J* = 14.0 and 3.5 Hz, 1H), 2.31 (dd, *J* = 14.0 and 3.5 Hz, 1H), 1.88 (br, 1H). 1.49- 1.41 (m, 2H), 1.40-1.26 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.0, 133.6, 132.3, 129.2, 128.2, 114.6, 69.7, 44.7, 36.3, 27.8, 22.6, 14.0; high resolution mass spectrum (ES^+) *m/z* 259.1127 [$(M+Na)^+$; calcd for $C_{14}H_{20}OSNa$: 259.1133].



23d

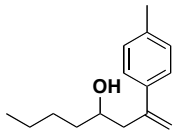
Compound 23d. Using conditions similar to those used for **23a**, linchpin **12** (60.3 mg, 0.42 mmol, 1.0 equiv.) afforded **23d** (39.2 mg, 0.22 mmol, 51% yield) as a colorless oil after flash chromatography (diethyl ether/hexane = 1/20). R_f 0.35 (hexane/diethyl ether = 5/1); IR (film) 3405 (m), 3075 (m), 2957 (s), 2930 (s), 2860 (s), 1640 (m), 1439 (m), 1035 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.93 (d, *J* = 6.0 Hz, 2H), 4.82 (d, *J* = 1.0 Hz, 1H), 4.74 (d, *J* = 1.0 Hz, 1H), 3.71-3.69 (m, 1H), 2.76 (dd, *J* = 22.0 and 14.5 Hz, 2H), 2.23 (dd, *J* = 14.0 and 3.0 Hz, 1H), 2.01 (dd, *J* = 14.0 and 9.5 Hz, 1H), 1.72 (br, 1H), 1.68 (s, 3H), 1.49-1.42 (m, 3H), 1.35-1.29 (m, 3H), 0.90 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 143.1, 114.5, 112.6, 68.8, 45.2, 43.5, 36.8, 27.9, 22.7, 21.8, 14.0; high resolution mass spectrum (CI^+) *m/z* 165.1637 [$(M-OH)^+$; calcd for $C_{12}H_{21}$: 165.1643].



23e

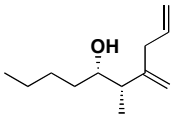
Compound 23e. To a solution of *n*-BuLi (2.2 M in hexane, 0.41 mL, 0.89 mmol, 2.0 equiv.) in Et_2O (0.5 mL) at –78 °C was added linchpin **12** (63.4 mg, 0.45 mmol, 1.0 equiv.) in Et_2O (0.5 mL) dropwise. After being stirred for 30 min, the resulting solution was added to a mixture of CuI (169.6 mg, 0.89 mmol, 2.0 equiv.) in HMPA/THF (1 mL/1 mL) via cannula at 0 °C. The resulting solution was warmed to room temperature. After stirring for 2 h at room temperature, phenyl

iodide (0.1 mL, 0.89 mmol, 2.0 equiv.) and $Pd(PPh_3)_4$ (15.5 mg, 0.013 mmol, 0.03 equiv.) in THF (1 mL) were added. After being stirred for 12 h at room temperature, 3 mL of 1N HCl was added. After 10 min, a saturated aqueous NH_4Cl (3 mL) solution was added, and the resulting mixture extracted with Et_2O (10 mL x 2) and CH_2Cl_2 (10 mL x 2). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Flash chromatography (diethyl ether/hexane = 1/10), afforded **23e** (40.7 mg, 0.20 mmol, 45% yield) as a pale yellow oil. R_f 0.21 (hexane/diethyl ether = 5/1); IR (film) 3386 (m), 3082 (w), 2955 (s), 2930 (s), 2861 (s), 1626 (w), 1494 (w), 1448 (m), 1030 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.42-7.40 (m, 2H), 7.36-7.33 (m, 2H), 7.30-7.29 (m, 1H), 5.41 (d, J = 1.5 Hz, 1H), 5.17 (d, J = 1.0 Hz, 1H), 3.67-3.62 (m, 1H), 2.81 (dd, J = 14.5 and 4.0 Hz, 1H), 2.51 (dd, J = 14.0 and 9.0 Hz, 1H), 1.67 (br, 1H), 1.51-1.48 (m, 2H), 1.46-1.40 (m, 1H), 1.35-1.27 (m, 3H), 0.89 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.5, 140.5, 128.4, 127.7, 126.2, 115.2, 69.4, 43.8, 36.7, 27.8, 22.7, 14.0; high resolution mass spectrum (CI^+) *m/z* 204.1514 [$(M)^+$; calcd for $C_{14}H_{20}O$: 204.1514].



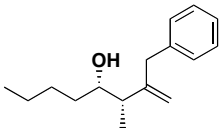
23f

Compound 23f. Using conditions similar to those used for **23e**, linchpin **12** (69.2 mg, 0.48 mmol, 1.0 equiv.) afforded **23f** (46.3 mg, 0.21 mmol, 44% yield) as a pale yellow oil after flash chromatography (diethyl ether/hexane = 1/10). R_f 0.21 (hexane/diethyl ether = 5/1); IR (film) 3389 (m), 3083 (w), 3024 (w), 2955 (s), 2930 (s), 2862 (s), 1902 (w), 1703 (w), 1624 (m), 1512 (m), 1455 (m), 1032 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, J = 8.5 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 5.39 (d, J = 1.5 Hz, 1H), 5.13 (d, J = 1.5 Hz, 1H), 3.68-3.63 (m, 1H), 2.80 (dd, J = 14.0 and 3.5 Hz, 1H), 2.49 (dd, J = 14.0 and 9.0 Hz, 1H), 2.36 (s, 3H), 1.52-1.48 (m, 2H), 1.45-1.43 (m, 1H), 1.35-1.27 (m, 4H), 0.90 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.3, 137.6, 137.4, 129.0, 126.0, 114.4, 69.4, 43.8, 36.6, 27.8, 22.7, 21.0, 14.0; high resolution mass spectrum (CI^+) *m/z* 219.1739 [$(M+H)^+$; calcd for $C_{15}H_{23}O$: 219.1749].



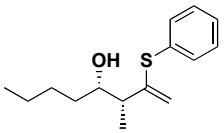
(–)-24a

Compound (–)-24a. Using conditions similar to those used for **23b**, linchpin (+)-**13** (63.0 mg, 0.40 mmol, 1.0 equiv.) afforded (–)-**24a** (47.3 mg, 0.26 mmol, 65% yield) as a colorless oil after flash chromatography (ethyl acetate/hexane = 1/15). R_f 0.55 (hexane/ethyl acetate = 10/1); $[\alpha]^{25}_D$ –73.4 (*c* 0.64, $CHCl_3$); IR (film) 3367 (m), 3079 (w), 2958 (s), 2932 (s), 2873 (m), 1641 (m), 1459 (m), 997 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.81 (m, 1H), 5.08 (d, *J* = 1.5 Hz, 1H), 5.05 (m, 1H), 4.94 (dd, *J* = 3.0 and 1.5 Hz, 1H), 4.89 (s, 1H), 3.59 (m, 1H), 2.84 (dd, *J* = 16.0 and 6.5 Hz, 1H), 2.76 (dd, *J* = 16.0 and 7.5 Hz, 1H), 2.21 (m, 1H), 1.62 (br, 1H), 1.50-1.20 (m, 6H), 1.03 (d, *J* = 7.0 Hz, 3H), 0.92 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.1, 136.5, 116.7, 111.6, 72.2, 44.3, 40.4, 34.4, 28.7, 22.9, 14.3, 12.8; high resolution mass spectrum (ES^+) *m/z* 205.1574 [$(M+Na)^+$; calcd for $C_{12}H_{22}ONa$: 205.1568].



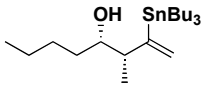
(–)-24b

Compound (–)-24b. Using conditions similar to those used for **23b**, linchpin (+)-**13** (63.0 mg, 0.40 mmol, 1.0 equiv.) afforded (–)-**24b** (61.2 mg, 0.26 mmol, 66% yield) as a colorless oil after flash chromatography (ethyl acetate/hexane = 1/10). R_f 0.46 (hexane/ethyl acetate = 10/1); $[\alpha]^{25}_D$ –59.4 (*c* 0.72, $CHCl_3$); IR (film) 3376 (m), 3084 (w), 3027 (w), 2953 (s), 2931 (s), 2872 (m), 1639 (w), 1495 (w), 1454 (m), 1109 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.30 (m, 2H), 7.23 (m, 1H), 7.20 (m, 2H), 4.96 (s, 1H), 4.88 (s, 1H), 3.61 (m, 1H), 3.44 (d, *J* = 15.0 Hz, 1H), 3.35 (d, *J* = 15.5 Hz, 1H), 2.18 (m, 1H), 1.55 (br, 1H), 1.50-1.20 (m, 6H), 1.02 (d, *J* = 7.0 Hz, 3H), 0.91 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.1, 139.5, 129.3, 128.6, 126.4, 112.7, 72.2, 43.6, 42.9, 34.3, 28.7, 22.9, 14.3, 13.0; high resolution mass spectrum (CI^+) *m/z* 232.1827 [$(M)^+$; calcd for $C_{16}H_{24}O$: 232.1827].



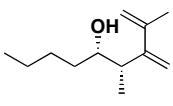
(–)-24c

Compound (–)-24c. Using conditions similar to those used for **23b**, linchpin (+)-**13** (63.0 mg, 0.40 mmol, 1.0 equiv.) afforded (–)-**24c** (56.0 mg, 0.22 mmol, 56% yield) as a pale yellow oil after flash chromatography (ethyl acetate/hexane = 1/15). R_f 0.41 (hexane/ethyl acetate = 10/1); $[\alpha]^{25}_D$ –92.0 (*c* 0.68, $CHCl_3$); IR (film) 3390 (m), 3074 (w), 2956 (s), 2932 (s), 2872 (m), 1605 (w), 1583 (m), 1476 (m), 1457 (m), 1440 (m), 748 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.46 (m, 2H), 7.34 (m, 3H), 5.20 (s, 1H), 4.87 (s, 1H), 3.85 (m, 1H), 2.38 (m, 1H), 1.65 (d, *J* = 2.5 Hz, 1H), 1.51-1.30 (m, 6H), 1.16 (d, *J* = 7.0 Hz, 3H), 0.91 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.8, 134.0, 132.7, 129.5, 128.4, 111.9, 73.0, 45.6, 34.3, 28.6, 22.9, 14.3, 13.4; high resolution mass spectrum (ES^+) *m/z* 233.1365 [$(M\text{-}OH)^+$; calcd for $C_{15}H_{21}S$: 233.1364].



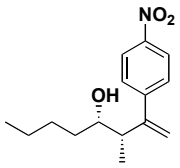
(–)-24d

Compound (–)-24d. Using conditions similar to those used for **23b**, linchpin (+)-**13** (63.0 mg, 0.40 mmol, 1.0 equiv.) afforded (–)-**24d** (114.0 mg, 0.26 mmol, 66% yield) as a colorless oil after flash chromatography (ethyl acetate/hexane = 1/20). R_f 0.53 (hexane/ethyl acetate = 20/1); $[\alpha]^{25}_D$ –7.2 (*c* 1.05, $CHCl_3$); IR (film) 3566 (m), 2957 (s), 2927 (s), 2872 (m), 2855 (m), 1463 (w), 1417 (w), 1377 (w), 916 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.77 (s, $J_{H\text{-}Sn}$ = 69.5 Hz, 1H), 5.25 (d, $J_{H\text{-}H}$ = 2.5 Hz, $J_{H\text{-}Sn}$ = 33.0 Hz, 1H), 3.45 (m, 1H), 2.43 (m, 1H), 1.70-1.20 (m, 25H), 1.04 (d, *J* = 7.0 Hz, 3H), 0.89 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.1, 125.7, 73.8, 49.4, 34.8, 29.3 (t, *J* = 9.8 Hz), 28.5, 28.1 (t, *J* = 11.0 Hz), 27.6 (t, *J* = 28.3 Hz), 27.1 (t, *J* = 61.9 Hz), 23.0, 17.7 (t, *J* = 167.0 Hz), 14.3, 14.1, 13.9, 13.8, 10.4 (t, *J* = 157.6 Hz); high resolution mass spectrum (ES^+) *m/z* 455.2309 [$(M+Na)^+$; calcd for $C_{21}H_{44}OSnNa$: 455.2312].



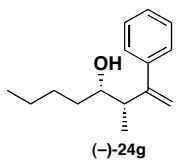
(–)-24e

Compound (–)-24e. Using conditions similar to those used for **23f**, linchpin (+)-**13** (63.0 mg, 0.40 mmol, 1.0 equiv.) afforded (–)-**24e** (51.0 mg, 0.28 mmol, 70% yield) as a colorless oil after flash chromatography (ethyl acetate/hexane = 1/15). R_f 0.55 (hexane/ethyl acetate = 10/1); $[\alpha]^{25}_D$ –53.0 (*c* 0.91, $CHCl_3$); IR (film) 3353 (m), 3096 (w), 2957 (s), 2932 (s), 2870 (m), 2857 (m), 1701 (w), 1597 (w), 1458 (w), 1100 (m), 890 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.28 (s, 1H), 5.08 (s, 1H), 5.01 (s, 1H), 4.99 (d, *J* = 1.0 Hz, 1H), 3.57 (m, 1H), 2.73 (m, 1H), 1.92 (d, *J* = 1.0 Hz, 3H), 1.52-1.45 (m, 7H), 1.08 (d, *J* = 7.0 Hz, 3H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.6, 143.4, 112.8, 112.2, 72.9, 39.7, 34.4, 28.8, 22.9, 21.9, 14.3, 12.9; high resolution mass spectrum (ES^+) *m/z* 205.1582 [$(M+Na)^+$; calcd for $C_{12}H_{22}ONa$: 205.1568].



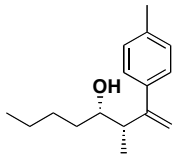
(–)-24f

Compound (–)-24f. Using conditions similar to those used for **23f**, linchpin (+)-**13** (63.0 mg, 0.40 mmol, 1.0 equiv.) afforded (–)-**24f** (65.1 mg, 0.25 mmol, 62% yield) as a pale yellow oil after flash chromatography (ethyl acetate/hexane = 1/10). R_f 0.32 (hexane/ethyl acetate = 10/1); $[\alpha]^{26}_D$ –92.4 (*c* 1.58, $CHCl_3$); IR (film) 3435 (m), 3080 (w), 2956 (s), 2931 (s), 2860 (m), 1596 (m), 1518 (s), 1345 (s), 1111 (w), 859 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.20 (ddd, *J* = 9.5, 2.5 and 1.0 Hz, 2H), 7.50 (ddd, *J* = 9.0, 2.5 and 1.5 Hz, 2H), 5.47 (s, 1H), 5.31 (s, 1H), 3.48 (m, 1H), 2.82 (m, 1H), 1.59 (br, 1H), 1.85 (m, 2H), 1.40-1.20 (m, 4H), 1.20 (d, *J* = 7.0 Hz, 3H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.0, 149.4, 147.3, 127.7, 123.9, 116.7, 72.8, 43.1, 34.7, 28.6, 22.9, 14.2, 13.1; high resolution mass spectrum (ES^-) *m/z* 298.1221 [$(M+Cl)^-$; calcd for $C_{15}H_{21}NO_3Cl$: 298.1210].



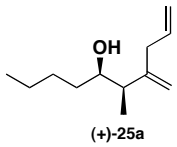
(–)-24g

Compound (–)-24g. Using conditions similar to those used for **23f**, linchpin (+)-**13** (63.0 mg, 0.40 mmol, 1.0 equiv.) afforded (–)-**24g** (54.1 mg, 0.28 mmol, 71% yield) as a pale yellow oil after flash chromatography (ethyl acetate/hexane = 1/10). R_f 0.44 (hexane/ethyl acetate = 10/1); $[\alpha]^{26}_D$ –70.6 (*c* 1.99, $CHCl_3$); IR (film) 3403 (m), 3080 (w), 3055 (w), 2957 (s), 2930 (s), 2873 (m), 2857 (m), 1626 (w), 1491 (m), 1464 (w), 1096 (m), 1027 (m), 899 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37-7.28 (m, 5H), 5.37 (d, *J* = 1.0 Hz, 1H), 5.14 (d, *J* = 1.0 Hz, 1H), 3.50 (m, 1H), 2.85 (m, 1H), 1.86 (br, 1H), 1.51-1.20 (m, 6H), 1.04 (d, *J* = 6.5 Hz, 3H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.6, 142.5, 128.6, 127.7, 126.8, 113.7, 72.4, 43.0, 34.5, 28.7, 22.9, 14.2, 12.7; high resolution mass spectrum (ES^+) *m/z* 241.1569 [$(M+Na)^+$; calcd for $C_{15}H_{22}ONa$: 241.1568].



(–)-24h

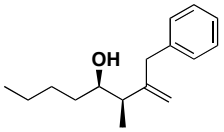
Compound (–)-24h. Using conditions similar to those used for **23f**, linchpin (+)-**13** (63.0 mg, 0.40 mmol, 1.0 equiv.) afforded (–)-**24h** (69.6 mg, 0.30 mmol, 75% yield) as a pale yellow oil after flash chromatography (ethyl acetate/hexane = 1/10). R_f 0.45 (hexane/ethyl acetate = 10/1); $[\alpha]^{25}_D$ –81.5 (*c* 1.38, $CHCl_3$); IR (film) 3408 (m), 3084 (w), 3024 (w), 2957 (s), 2931 (s), 2872 (m), 1623 (w), 1511 (m), 1457 (m), 1119 (m), 898 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 5.38 (s, 1H), 5.12 (s, 1H), 3.52 (m, 1H), 2.87 (m, 1H), 2.38 (s, 3H), 1.52-1.33 (m, 7H), 1.20 (d, *J* = 7.0 Hz, 3H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.4, 139.5, 137.4, 129.3, 126.7, 112.9, 72.4, 42.9, 34.4, 28.7, 22.9, 21.3, 14.2, 12.6; high resolution mass spectrum (ES^+) *m/z* 255.1761 [$(M+Na)^+$; calcd for $C_{16}H_{24}ONa$: 255.1725].



(+)-25a

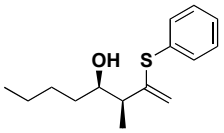
Compound (+)-25a. Using conditions similar to those used for **23b**, linchpin (–)-**14** (63.0 mg, 0.40 mmol, 1.0 equiv.) afforded (+)-**25a** (49.5 mg, 0.27 mmol, 68% yield) as a colorless oil after flash chromatography (ethyl acetate/hexane = 1/15). R_f 0.55 (hexane/ethyl acetate = 10/1); $[\alpha]^{25}_D$ +72.0

(*c* 0.19, $CHCl_3$); IR (film) 3343 (m), 3079 (w), 2958 (s), 2932 (s), 2873 (m), 1641 (m), 1459 (m), 997 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.81 (m, 1H), 5.08 (d, *J* = 1.5 Hz, 1H), 5.05 (m, 1H), 4.94 (dd, *J* = 3.0 and 1.5 Hz, 1H), 4.89 (s, 1H), 3.59 (m, 1H), 2.84 (dd, *J* = 16.0 and 6.5 Hz, 1H), 2.76 (dd, *J* = 16.0 and 7.5 Hz, 1H), 2.21 (m, 1H), 1.62 (br, 1H), 1.50-1.20 (m, 6H), 1.03 (d, *J* = 7.0 Hz, 3H), 0.92 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.1, 136.5, 116.7, 111.6, 72.2, 44.3, 40.4, 34.4, 28.7, 22.9, 14.3, 12.8; high resolution mass spectrum (ES^+) *m/z* 205.1579 [$(M+Na)^+$; calcd for $C_{12}H_{22}ONa$: 205.1568].



(+)-25b

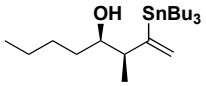
Compound (+)-25b. Using conditions similar to those used for **23b**, linchpin (–)-**14** (63.0 mg, 0.40 mmol, 1.0 equiv.) afforded (+)-**25b** (63.1 mg, 0.27 mmol, 68% yield) as a colorless oil after flash chromatography (ethyl acetate/hexane = 1/10). R_f 0.46 (hexane/ethyl acetate = 10/1); $[\alpha]^{23}_D$ +54.8 (*c* 0.88, $CHCl_3$); IR (film) 3364 (m), 3084 (w), 3027 (w), 2956 (s), 2931 (s), 2872 (m), 1639 (w), 1495 (w), 1454 (m), 1109 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.30 (m, 2H), 7.23 (m, 1H), 7.20 (m, 2H), 4.96 (s, 1H), 4.88 (s, 1H), 3.61 (m, 1H), 3.44 (d, *J* = 15.0 Hz, 1H), 3.35 (d, *J* = 15.5 Hz, 1H), 2.18 (m, 1H), 1.55 (br, 1H), 1.50-1.20 (m, 6H), 1.02 (d, *J* = 7.0 Hz, 3H), 0.91 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.1, 139.5, 129.3, 128.6, 126.4, 112.7, 72.2, 43.6, 42.9, 34.3, 28.7, 22.9, 14.3, 13.0; high resolution mass spectrum (CI^+) *m/z* 232.1827 [$(M)^+$; calcd for $C_{16}H_{24}O$: 232.1827].



(+)-25c

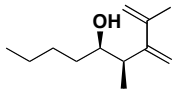
Compound (+)-25c. Using conditions similar to those used for **23b**, linchpin (–)-**14** (63.0 mg, 0.40 mmol, 1.0 equiv.) afforded (+)-**25c** (57.0 mg, 0.23 mmol, 57% yield) as a pale yellow oil after flash chromatography (ethyl acetate/hexane = 1/15). R_f 0.41 (hexane/ethyl acetate = 10/1); $[\alpha]^{25}_D$ +96.0 (*c* 0.57, $CHCl_3$); IR (film) 3390 (m), 3074 (w), 2956 (s), 2932 (s), 2872 (m), 1605 (w), 1583 (m),

1476 (m), 1457 (m), 1440 (m), 748 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.46 (m, 2H), 7.34 (m, 3H), 5.20 (s, 1H), 4.87 (s, 1H), 3.85 (m, 1H), 2.38 (m, 1H), 1.65 (d, *J* = 2.5 Hz, 1H), 1.51-1.30 (m, 6H), 1.16 (d, *J* = 7.0 Hz, 3H), 0.91 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.8, 134.0, 132.7, 129.5, 128.4, 111.9, 73.0, 45.6, 34.3, 28.6, 22.9, 14.3, 13.4; high resolution mass spectrum (ES^+) *m/z* 233.1354 [$(M\text{-}OH)^+$; calcd for $C_{15}H_{21}S$: 233.1364].



(+)-25d

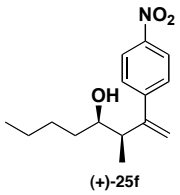
Compound (+)-25d. Using conditions similar to those used for **23b**, linchpin (–)-**14** (63.0 mg, 0.40 mmol, 1.0 equiv) afforded (+)-**25d** (116.0 mg, 0.27 mmol, 67% yield) as a colorless oil after flash chromatography (ethyl acetate/hexane = 1/20). R_f 0.53 (hexane/ethyl acetate = 20/1); $[\alpha]^{26}_D$ +8.9 (*c* 1.23, $CHCl_3$); IR (film) 3358 (m), 2956 (s), 2928 (s), 2872 (m), 2855 (m), 1463 (w), 1417 (w), 1377 (w), 916 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.77 (s, $J_{H\text{-}Sn}$ = 69.5 Hz, 1H), 5.25 (d, $J_{H\text{-}H}$ = 2.5 Hz, $J_{H\text{-}Sn}$ = 33.0 Hz, 1H), 3.45 (m, 1H), 2.43 (m, 1H), 1.70-1.20 (m, 25H), 1.04 (d, *J* = 7.0 Hz, 3H), 0.89 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.1, 125.7, 73.8, 49.4, 34.8, 29.3 (t, *J* = 9.8 Hz), 28.5, 28.1 (t, *J* = 11.0 Hz), 27.6 (t, *J* = 28.3 Hz), 27.1 (t, *J* = 61.9 Hz), 23.0, 17.7 (t, *J* = 167.0 Hz), 14.3, 14.1, 13.9, 13.8, 10.4 (t, *J* = 157.6 Hz); high resolution mass spectrum (ES^+) *m/z* 455.2314 [$(M+Na)^+$; calcd for $C_{21}H_{44}OSnNa$: 455.2312].



(+)-25e

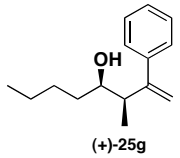
Compound (+)-25e. Using conditions similar to those used for **23f**, linchpin (–)-**14** (63.0 mg, 0.40 mmol, 1.0 equiv.) afforded (+)-**25e** (50.0 mg, 0.28 mmol, 69% yield) as a colorless oil after flash chromatography (ethyl acetate/hexane = 1/15). R_f 0.55 (hexane/ethyl acetate = 10/1); $[\alpha]^{25}_D$ +57.0 (*c* 0.97, $CHCl_3$); IR (film) 3361 (m), 3096 (w), 2957 (s), 2932 (s), 2870 (m), 2857 (m), 1701 (w), 1597 (w), 1458 (w), 1100 (m), 890 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.28 (s, 1H), 5.08 (s, 1H), 5.01 (s, 1H), 4.99 (d, *J* = 1.0 Hz, 1H), 3.57 (m, 1H), 2.73 (m, 1H), 1.92 (d, *J* = 1.0 Hz, 3H), 1.52-1.45 (m, 7H), 1.08 (d, *J* = 7.0 Hz, 3H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$)

δ 151.6, 143.4, 112.8, 112.2, 72.9, 39.7, 34.4, 28.8, 22.9, 21.9, 14.3, 12.9; high resolution mass spectrum (ES^+) *m/z* 205.1579 [$(M+Na)^+$; calcd for $C_{12}H_{22}ONa$: 205.1568].



(+)-25f

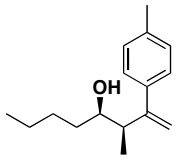
Compound (+)-25f. Using conditions similar to those used for **23f**, linchpin (–)-**14** (63.0 mg, 0.40 mmol, 1.0 equiv.) afforded (+)-**25f** (63.0 mg, 0.24 mmol, 60% yield) as a pale yellow oil after flash chromatography (ethyl acetate/hexane = 1/10). R_f 0.32 (hexane/ethyl acetate = 10/1); $[\alpha]^{26}_D$ +96.3 (*c* 1.2, $CHCl_3$); IR (film) 3434 (m), 3080 (w), 2956 (s), 2931 (s), 2859 (m), 1596 (m), 1518 (s), 1345 (s), 1111 (w), 859 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.20 (ddd, *J* = 9.5, 2.5 and 1.0 Hz, 2H), 7.50 (ddd, *J* = 9.0, 2.5 and 1.5 Hz, 2H), 5.47 (s, 1H), 5.31 (s, 1H), 3.48 (m, 1H), 2.82 (m, 1H), 1.59 (br, 1H), 1.85 (m, 2H), 1.40-1.20 (m, 4H), 1.20 (d, *J* = 7.0 Hz, 3H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.0, 149.4, 147.3, 127.7, 123.9, 116.7, 72.8, 43.1, 34.7, 28.6, 22.9, 14.2, 13.1; high resolution mass spectrum (ES^-) *m/z* 298.0811 [$(M+Cl)^-$; calcd for $C_{15}H_{21}NO_3Cl$: 298.1210].



(+)-25g

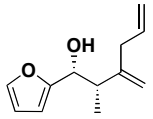
Compound (+)-25g. Using conditions similar to those used for **23f**, linchpin (–)-**14** (63.0 mg, 0.40 mmol, 1.0 equiv.) afforded (+)-**25g** (62.8 mg, 0.29 mmol, 72% yield) as a pale yellow oil after flash chromatography (ethyl acetate/hexane = 1/10). R_f 0.44 (hexane/ethyl acetate = 10/1); $[\alpha]^{25}_D$ +65.6 (*c* 1.09, $CHCl_3$); IR (film) 3420 (m), 3084 (w), 3059 (w), 3030 (w), 2957 (s), 2930 (s), 2873 (m), 2857 (m), 1626 (w), 1491 (m), 1464 (w), 1096 (m), 1027 (m), 899 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37-7.28 (m, 5H), 5.37 (d, *J* = 1.0 Hz, 1H), 5.14 (d, *J* = 1.0 Hz, 1H), 3.50 (m, 1H), 2.85 (m, 1H), 1.86 (br, 1H), 1.51-1.20 (m, 6H), 1.04 (d, *J* = 6.5 Hz, 3H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.6, 142.5, 128.6, 127.7, 126.8, 113.7, 72.4, 43.0, 34.5, 28.7, 22.9,

14.2, 12.7; high resolution mass spectrum (ES$^+$) *m/z* 241.1556 [(M+Na)$^+$; calcd for $C_{15}H_{22}ONa$: 241.1568].



(+)-25h

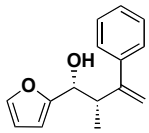
Compound (+)-25h. Using conditions similar to those used for **23f**, linchpin (–)-**14** (63.0 mg, 0.40 mmol, 1.0 equiv.) afforded (+)-**25h** (68.7 mg, 0.30 mmol, 74% yield) as a pale yellow oil after flash chromatography (ethyl acetate/hexane = 1/10). R_f 0.45 (hexane/ethyl acetate = 10/1); $[\alpha]^{25}_D$ +79.8 (*c* 1.30, $CHCl_3$); IR (film) 3406 (m), 3084 (w), 3024 (w), 2957 (s), 2931 (s), 2872 (m), 1623 (w), 1511 (m), 1457 (m), 1119 (m), 898 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 5.38 (s, 1H), 5.12 (s, 1H), 3.52 (m, 1H), 2.87 (m, 1H), 2.38 (s, 3H), 1.52-1.33 (m, 7H), 1.20 (d, *J* = 7.0 Hz, 3H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.4, 139.5, 137.4, 129.3, 126.7, 112.9, 72.4, 42.9, 34.4, 28.7, 22.9, 21.3, 14.2, 12.6; high resolution mass spectrum (ES$^+$) *m/z* 255.1768 [(M+Na)$^+$; calcd for $C_{16}H_{24}ONa$: 255.1725].



(–)-26a

Compound (–)-26a. To a solution of furan (58.2 μL, 0.81 mmol, 2.0 equiv.) in THF (0.5 mL) was added *n*-BuLi (2.2 M in hexane, 0.36 mL, 0.81 mmol, 2.0 equiv.) at –15 ºC. After the addition was complete, the reaction mixture was stirred for an additional 30 min. The resulting solution was warmed to 0 ºC, and stirred for 1.5 h. After cooling to –78 ºC, linchpin (+)-**13** (63 mg, 0.40 mmol, 1.0 equiv.) dissolved in Et_2O (0.5 mL) was added dropwise to the reaction mixture. After being stirred for 30 min, the resulting solution was added to a mixture of CuI (152.3 mg, 0.81 mmol, 2.0 equiv.) in HMPA/THF (1 mL/1 mL) via cannula at 0 ºC, and allowed to warm to room temperature. After stirring for 2 h at room temperature, allyl bromide (0.07 mL, 0.81 mmol, 2.0 equiv.) was added. After 12 h, TBAF (1.62 mL, 1.62 mmol, 4.0 equiv.) was added. After 1 h, a saturated aqueous NH_4Cl (3 mL) solution was added, and the resulting mixture was extracted with Et_2O (10

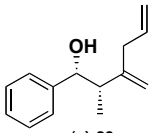
mL x 2) and CH_2Cl_2 (10 mL x 2). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Flash chromatography (ethyl acetate/hexane = 1/10), afforded (–)-**26a** (44.5 mg, 0.23 mmol, 58% yield) as a colorless oil. R_f 0.41 (hexane/ethyl acetate = 10/1); $[\alpha]^{18}_D$ –14.1 (*c* 1.5, $CHCl_3$); IR (film) 3420 (s), 3078 (w), 2978 (s), 2917 (s), 1642 (w), 1505 (m), 1149 (m), 1009 (s), 914 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 1.0 and 0.5 Hz, 1H), 6.33 (dd, *J* = 3.0 and 2.0 Hz, 1H), 6.23 (dd, *J* = 3.0 and 0.5 Hz, 1H), 5.77 (m, 1H), 5.07 (s, 1H), 5.04 (d, *J* = 8.0 Hz, 1H), 4.92 (d, *J* = 6.0 Hz, 2H), 4.71 (d, *J* = 6.0 Hz, 1H), 3.27 (m, 3H), 1.80 (br, 1H), 1.12 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.8, 149.8, 141.7, 136.4, 116.7, 112.3, 110.4, 106.5, 70.5, 44.4, 40.1, 14.6; high resolution mass spectrum (ES^+) *m/z* 215.1046 [$(M+Na)^+$; calcd for $C_{12}H_{16}ONa$: 215.1048].



(–)-26b

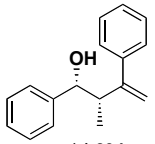
Compound (–)-26b. To a solution of furan (58.2 μL, 0.81 mmol, 2.0 equiv.) in THF (0.5 mL) was added *n*-BuLi (2.2 M in hexane, 0.36 mL, 0.81 mmol, 2.0 equiv.) at –15 ºC. After the addition was complete, the reaction mixture was stirred for an additional 30 min. The resulting solution was warmed to 0 ºC, and stirred for 1.5 h. After cooling to –78 ºC, linchpin (+)-**13** (63 mg, 0.40 mmol, 1.0 equiv.) dissolved in Et_2O (0.5 mL) was added dropwise to the reaction mixture. After being stirred for 30 min, the resulting solution was added to a mixture of CuI (152.3 mg, 0.81 mmol, 2.0 equiv.) in HMPA/THF (1 mL/1 mL) via cannula at 0 ºC, and allowed to warm to room temperature. After stirring for 2 h at room temperature, phenyl iodide (0.09 mL, 0.81 mmol, 2.0 equiv.) and $Pd(PPh_3)_4$ (13.9 mg, 0.012 mmol, 0.03 equiv.) in THF (1 mL) were added. After 12 h, TBAF (1.62 mL, 1.62 mmol, 4.0 equiv.) was added. After 1 h, a saturated aqueous NH_4Cl (3 mL) solution was added, and the resulting mixture was extracted with Et_2O (10 mL x 2) and CH_2Cl_2 (10 mL x 2). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Flash chromatography (ethyl acetate/hexane = 1/10), afforded (–)-**26b** (52.9 mg, 0.23 mmol, 58% yield) as a colorless oil. R_f 0.22 (hexane/ethyl acetate = 10/1); $[\alpha]^{18}_D$ –

12.3 (*c* 0.81, C_6D_6); IR (film) 3412 (m), 3081 (w), 3054 (w), 3025 (w), 2974 (s), 2927 (s), 1627 (w), 1403 (s), 1147 (w), 1010 (s), 903 (m) cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 7.33 (m, 2H), 7.25-7.10 (m, 4H), 6.20 (dd, *J* = 3.0 and 0.5 Hz, 1H), 6.12 (dd, *J* = 3.0 and 2.0 Hz, 1H), 5.32 (d, *J* = 1.0 Hz, 1H), 5.12 (d, *J* = 1.0 Hz, 1H), 4.70 (d, *J* = 4.0 Hz, 1H), 3.38 (m, 1H), 1.43 (br, 1H), 1.30 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 156.8, 151.6, 142.6, 141.3, 128.5, 127.6, 127.0, 113.9, 110.4, 106.4, 70.3, 43.2, 14.2; high resolution mass spectrum (ES^+) *m/z* 251.1040 [$(M+Na)^+$; calcd for $C_{15}H_{16}ONa$: 251.1048].



(–)-26c

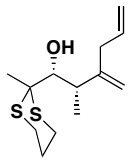
Compound (–)-26c. Using conditions similar to those used for (–)-**26a**, linchpin (+)-**13** (63.0 mg, 0.40 mmol, 1.0 equiv.) afforded (–)-**26c** (50.9 mg, 0.25 mmol, 63% yield) as a colorless oil after flash chromatography (ethyl acetate/hexane = 1/10). R_f 0.25 (hexane/ethyl acetate = 10/1); $[\alpha]^{18}_D$ –34.1 (*c* 0.7, $CHCl_3$); IR (film) 3426 (s), 3077 (w), 3030 (w), 2977 (s), 2916 (s), 1642 (m), 1452 (m), 1017 (m), 998 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.40-7.20 (m, 5H), 5.78 (m, 1H), 5.09 (d, *J* = 1.0 Hz, 1H), 5.06 (d, *J* = 6.0 Hz, 1H), 4.97 (d, *J* = 8.5 Hz, 2H), 4.77 (d, *J* = 5.0 Hz, 1H), 2.80 (dd, *J* = 15.5 and 7.0 Hz, 1H), 2.74 (dd, *J* = 15.5 and 7.0 Hz, 1H), 2.53 (q, *J* = 7.0 Hz, 1H), 1.95 (br, 1H), 1.01 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.3, 143.1, 136.4, 128.3, 127.3, 126.8, 116.8, 112.3, 74.9, 46.4, 40.9, 13.2; high resolution mass spectrum (ES^+) *m/z* 225.1250 [$(M+Na)^+$; calcd for $C_{14}H_{18}ONa$: 225.1255].



(–)-26d

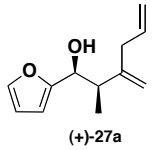
Compound (–)-26d. Using conditions similar to those used for (–)-**26b**, linchpin (+)-**13** (63.0 mg, 0.40 mmol, 1.0 equiv.) afforded (–)-**26d** (56.2 mg, 0.24 mmol, 59% yield) as a pale yellow oil after flash chromatography (ethyl acetate/hexane = 1/10). R_f 0.24 (hexane/ethyl acetate = 10/1); $[\alpha]^{18}_D$ –39.9 (*c* 1.5, C_6D_6); IR (film) 3427 (m), 3083 (w), 3028 (w), 2975 (s), 2929 (s), 1623 (w), 1494

(m), 1451 (m), 1059 (m), 1028 (m) cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 7.38 (d, J = 8.5 Hz, 2H), 7.30-7.10 (m, 8H), 5.33 (d, J = 1.0 Hz, 1H), 5.15 (d, J = 1.0 Hz, 1H), 4.69 (d, J = 3.5 Hz, 1H), 3.12 (m, 1H), 1.50 (br, 1H), 1.20 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.0, 143.0, 142.4, 128.7, 128.3, 127.8, 127.2, 126.9, 126.1, 114.4, 74.2, 45.6, 12.3; high resolution mass spectrum (ES^+) *m/z* 261.1247 [$(M+Na)^+$; calcd for $C_{17}H_{18}ONa$: 261.1255].



(+)-26e

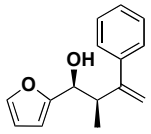
Compound (+)-26e. Using conditions similar to those used for (–)-**26a**, linchpin (+)-**13** (63.0 mg, 0.40 mmol, 1.0 equiv.) afforded (+)-**26e** (54.7 mg, 0.21 mmol, 53% yield) as a pale yellow oil after flash chromatography (ethyl acetate/hexane = 1/10). R_f 0.43 (hexane/ethyl acetate = 10/1); $[\alpha]^{18}_D$ +7.6 (*c* 0.4, $CHCl_3$); IR (film) 3481 (m), 3075 (w), 2975 (s), 2931 (s), 2911 (s), 1640 (m), 1424 (m), 1240 (m), 1031 (m), 908 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.88 (m, 1H), 5.10 (dd, J = 19.0 and 2.0 Hz, 1H), 5.07 (dd, J = 10.0 and 1.0 Hz, 1H), 5.00 (s, 1H), 4.82 (s, 1H), 4.00 (s, 1H), 3.00-2.85 (m, 5H), 2.67-2.59 (m, 3H), 2.08 (m, 1H), 1.85 (m, 1H), 1.47 (s, 3H), 1.20 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.9, 136.9, 116.4, 110.5, 72.6, 55.2, 39.6, 39.2, 26.7, 26.1, 24.5, 22.8, 15.2; high resolution mass spectrum (ES^+) *m/z* 281.1002 [$(M+Na)^+$; calcd for $C_{13}H_{22}ONaS_2$: 281.1010].



(+)-27a

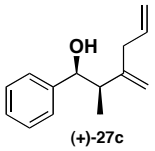
Compound (+)-27a. Using conditions similar to those used for (–)-**26a**, linchpin (–)-**14** (63.0 mg, 0.40 mmol, 1.0 equiv.) afforded (+)-**27a** (45.3 mg, 0.24 mmol, 59% yield) as a colorless oil after flash chromatography (ethyl acetate/hexane = 1/10). R_f 0.41 (hexane/ethyl acetate = 10/1); $[\alpha]^{18}_D$ +15.6 (*c* 1.6, $CHCl_3$); IR (film) 3420 (m), 3078 (w), 2978 (s), 2915 (s), 1642 (w), 1506 (m), 1149 (m), 1010 (s), 914 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 (dd, J = 1.0 and 0.5 Hz, 1H), 6.33 (dd, J = 3.0 and 2.0 Hz, 1H), 6.23 (dd, J = 3.0 and 0.5 Hz, 1H), 5.77 (m, 1H), 5.07 (s, 1H), 5.04

(d, J = 8.0 Hz, 1H), 4.92 (d, J = 6.0 Hz, 2H), 4.71 (d, J = 6.0 Hz, 1H), 3.27 (m, 3H), 1.95 (br, 1H), 1.12 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.8, 149.8, 141.7, 136.4, 116.7, 112.3, 110.4, 106.5, 70.5, 44.4, 40.1, 14.6; high resolution mass spectrum (ES^+) *m/z* 215.1042 [$(M+Na)^+$; calcd for $C_{12}H_{16}ONa$: 215.1048].



(+)-27b

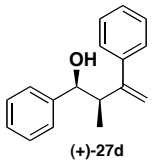
Compound (+)-27b. Using conditions similar to those used for (–)-**26b**, linchpin (–)-**14** (63.0 mg, 0.40 mmol, 1.0 equiv.) afforded (+)-**27b** (50.2 mg, 0.22 mmol, 55% yield) as a pale yellow oil after flash chromatography (ethyl acetate/hexane = 1/10). R_f 0.22 (hexane/ethyl acetate = 10/1); $[\alpha]^{18}_D$ +12.1 (*c* 0.82, C_6D_6); IR (film) 3420 (m), 3054 (w), 3025 (w), 2974 (s), 2928 (s), 1623 (w), 1404 (s), 1147 (w), 1009 (s), 903 (m) cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6) δ 7.33 (m, 2H), 7.25-7.10 (m, 4H), 6.20 (dd, J = 3.0 and 0.5 Hz, 1H), 6.12 (dd, J = 3.0 and 2.0 Hz, 1H), 5.32 (d, J = 1.0 Hz, 1H), 5.12 (d, J = 1.0 Hz, 1H), 4.70 (d, J = 4.0 Hz, 1H), 3.38 (m, 1H), 1.47 (br, 1H), 1.30 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 156.8, 151.6, 142.6, 141.3, 128.5, 127.6, 127.0, 113.9, 110.4, 106.4, 70.3, 43.2, 14.2; high resolution mass spectrum (ES^+) *m/z* 251.1046 [$(M+Na)^+$; calcd for $C_{15}H_{16}ONa$: 251.1048].



(+)-27c

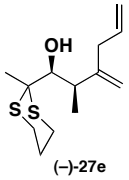
Compound (+)-27c. Using conditions similar to those used for (–)-**26a**, linchpin (–)-**14** (63.0 mg, 0.40 mmol, 1.0 equiv.) afforded (+)-**27c** (49.3 mg, 0.24 mmol, 61% yield) as a colorless oil after flash chromatography (ethyl acetate/hexane = 1/10). R_f 0.25 (hexane/ethyl acetate = 10/1); $[\alpha]^{18}_D$ +30.0 (*c* 0.9, $CHCl_3$); IR (film) 3422 (s), 3077 (w), 3030 (w), 2977 (s), 2915 (s), 1641 (m), 1452 (m), 1015 (m), 998 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.20 (m, 5H), 5.78 (m, 1H), 5.09 (d, J = 1.0 Hz, 1H), 5.06 (d, J = 6.0 Hz, 1H), 4.97 (d, J = 8.5 Hz, 2H), 4.77 (d, J = 5.0 Hz, 1H), 2.80 (dd, J = 15.5 and 7.0 Hz, 1H), 2.74 (dd, J = 15.5 and 7.0 Hz, 1H), 2.53 (q, J = 7.0 Hz, 1H),

1.95 (br, 1H), 1.01 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.3, 143.1, 136.4, 128.3, 127.3, 126.8, 116.8, 112.3, 74.9, 46.4, 40.9, 13.2; high resolution mass spectrum (ES^+) *m/z* 225.1262 [$(M+Na)^+$; calcd for $C_{14}H_{18}ONa$: 225.1255].



(+)-27d

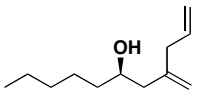
Compound (+)-27d. Using conditions similar to those used for (–)-**26b**, linchpin (–)-**14** (63.0 mg, 0.40 mmol, 1.0 equiv.) afforded (+)-**27d** (54.3 mg, 0.23 mmol, 57% yield) as a pale yellow oil after flash chromatography (ethyl acetate/hexane = 1/10). R_f 0.24 (hexane/ethyl acetate = 10/1); $[\alpha]^{18}_D$ +45.0 (*c* 2.0, C_6D_6); IR (film) 3437 (m), 3080 (w), 3028 (w), 2975 (s), 2929 (s), 1624 (w), 1494 (m), 1451 (m), 1059 (m), 1028 (m) cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6) δ 7.38 (d, J = 8.5 Hz, 2H), 7.30-7.10 (m, 8H), 5.33 (d, J = 1.0 Hz, 1H), 5.15 (d, J = 1.0 Hz, 1H), 4.69 (d, J = 3.5 Hz, 1H), 3.12 (m, 1H), 1.51 (br, 1H), 1.20 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.0, 143.0, 142.4, 128.7, 128.3, 127.8, 127.2, 126.9, 126.1, 114.4, 74.2, 45.6, 12.3; high resolution mass spectrum (ES^+) *m/z* 261.1245 [$(M+Na)^+$; calcd for $C_{17}H_{18}ONa$: 261.1255].



(–)-27e

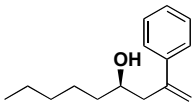
Compound (–)-27e. Using conditions similar to those used for (–)-**26a**, linchpin (–)-**14** (63.0 mg, 0.40 mmol, 1.0 equiv.) afforded (–)-**27e** (51.6 mg, 0.20 mmol, 50% yield) as a pale yellow oil after flash chromatography (ethyl acetate/hexane = 1/10). R_f 0.43 (hexane/ethyl acetate = 10/1); $[\alpha]^{18}_D$ –14.6 (*c* 0.48, $CHCl_3$); IR (film) 3479 (m), 3075 (w), 2975 (s), 2931 (s), 2912 (s), 1640 (m), 1425 (m), 1240 (m), 1031 (m), 908 (s) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.88 (m, 1H), 5.10 (dd, J = 19.0 and 2.0 Hz, 1H), 5.07 (dd, J = 10.0 and 1.0 Hz, 1H), 5.00 (s, 1H), 4.82 (s, 1H), 3.99 (d, J = 2.0 Hz, 1H), 3.00-2.85 (m, 5H), 2.67-2.59 (m, 3H), 2.08 (m, 1H), 1.85 (m, 1H), 1.47 (s, 3H), 1.20 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.9, 136.9, 116.4, 110.5, 72.6, 55.1, 39.6,

39.2, 26.7, 26.1, 24.5, 22.8, 15.2; high resolution mass spectrum (ES^+) *m/z* 281.0999 [$(M+Na)^+$; calcd for $C_{13}H_{22}ONaS_2$: 281.1010].



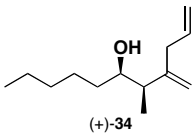
(+)-**32**

Compound (+)-**32**. To a suspension of CuI (0.1 g, 0.52 mmol, 1.2 equiv.) in Et_2O (1.5 mL) at –40 ºC was added *n*-BuLi (2.5 in hexane, 0.42 mL, 1.05 mmol, 2.4 equiv.) dropwise. The reaction mixture was then allowed to warm to 0 ºC over 1 h. The resulting solution was cooled to –70 ºC and a solution of epoxide (–)-**15** (68.5 mg, 0.44 mmol, 1.0 equiv.) in THF (1 mL) was added. The reaction mixture was allowed to warm to 0 ºC over 1 h. After being stirred for 1 h, the resulting solution was added to a mixture of CuI (0.1 g, 0.52 mmol, 1.2 equiv.) in HMPA/THF (1 mL/1 mL) via cannula at 0 ºC. The resulting solution was then warmed to room temperature. After stirring for 2 h at room temperature, allyl bromide (0.08 mL, 0.88 mmol, 2.0 equiv.) was added. After being stirred for 12 h at room temperature, 3 mL of 1N HCl was added. After 10 min, a saturated aqueous NH_4Cl (3 mL) solution was added, and the resulting mixture was extracted with Et_2O (10 mL x 2) and CH_2Cl_2 (10 mL x 2). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Flash chromatography (diethyl ether/hexane = 1/10) afforded (+)-**32** (38.4 mg, 0.21 mmol, 48% yield) as a pale yellow oil. R_f 0.3 (hexane/diethyl ether = 5/1); $[\alpha]^{20}_D$ +4.61 (*c* 0.42, $CHCl_3$); IR (film) 3387 (m), 3078 (m), 2956 (s), 2930 (s), 2858 (s), 1642 (m), 1434 (m), 1125 (m), 1041 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.85-5.77 (m, 1H), 5.09-5.07 (m, 1H), 5.05 (d, *J* = 1.0 Hz, 1H), 4.92 (d, *J* = 1.5 Hz, 1H), 4.89 (s, 1H), 3.74-3.69 (m, 1H), 2.79 (ddd, *J* = 22.0, 15.5 and 6.5 Hz, 2H), 2.26 (dd, *J* = 14.0 and 3.5 Hz, 1H), 2.07 (dd, *J* = 14.0 and 9.5 Hz, 1H), 1.68 (br, 1H), 1.49-1.43 (m, 3H), 1.36-1.27 (m, 5H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.1, 135.9, 116.6, 113.5, 68.8, 44.4, 40.6, 37.1, 31.9, 25.4, 22.6, 14.0; high resolution mass spectrum (ES^+) *m/z* 205.1577 [$(M+Na)^+$; calcd for $C_{12}H_{22}ONa$: 205.1568].



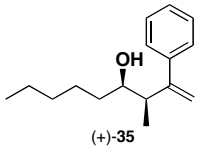
(+)-**33**

Compound (+)-**33**. To a suspension of CuI (98.2 mg, 0.51 mmol, 1.2 equiv.) in Et_2O (1.5 mL) at –40 ºC was added *n*-BuLi (2.5 in hexane, 0.41 mL, 1.02 mmol, 2.4 equiv.) dropwise. The reaction mixture was then allowed to warm to 0 ºC over 1 h. The resulting solution was cooled to –70 ºC and a solution of epoxide (–)-**15** (67.2 mg, 0.43 mmol, 1.0 equiv.) in THF (1 mL) was added. The reaction mixture was then warmed to 0 ºC over 1 h. After stirring for 1 h, the resulting solution was added to a mixture of CuI (98.2 g, 0.51 mmol, 1.2 equiv.) in HMPA/THF (1 mL/1 mL) via cannula at 0 ºC. The resulting solution was warmed to room temperature. After stirring for 2 h at room temperature, phenyl iodide (0.98 mL, 0.86 mmol, 2.0 equiv.) and $Pd(PPh_3)_4$ (15.0 mg, 0.013 mmol, 0.03 equiv.) in THF (1 mL) were added. After being stirred for 12 h at room temperature, 3 mL of 1N HCl was added. After 10 min, a saturated aqueous NH_4Cl (3 mL) solution was added, and the resulting mixture extracted with Et_2O (10 mL x 2) and CH_2Cl_2 (10 mL x 2). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Flash chromatography (diethyl ether/hexane = 1/10) afforded (+)-**33** (39.5 mg, 0.19 mmol, 45% yield) as a pale yellow oil. R_f 0.23 (hexane/diethyl ether = 5/1); $[\alpha]^{18}_D$ +23.1 (*c* 1.0, $CHCl_3$); IR (film) 3392 (m), 3082 (w), 3057 (w), 3026 (w), 2930 (s), 2858 (s), 1705 (w), 1626 (m), 1448 (m), 1031 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.42-7.40 (m, 2H), 7.36-7.33 (m, 2H), 7.30-7.29 (m, 1H), 5.41 (d, *J* = 1.5 Hz, 1H), 5.17 (d, *J* = 1.0 Hz, 1H), 3.67-3.62 (m, 1H), 2.81 (dd, *J* = 14.0 and 4.0 Hz, 1H), 2.51 (dd, *J* = 14.0 and 9.0 Hz, 1H), 1.64 (br, 1H), 1.51-1.42 (m, 3H), 1.35-1.24 (m, 5H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.5, 140.5, 128.4, 127.7, 126.2, 115.2, 69.4, 43.8, 36.9, 31.8, 25.3, 22.6, 14.0; high resolution mass spectrum (ES^+) *m/z* 241.1559 [$(M+Na)^+$; calcd for $C_{15}H_{22}ONa$: 241.1568].



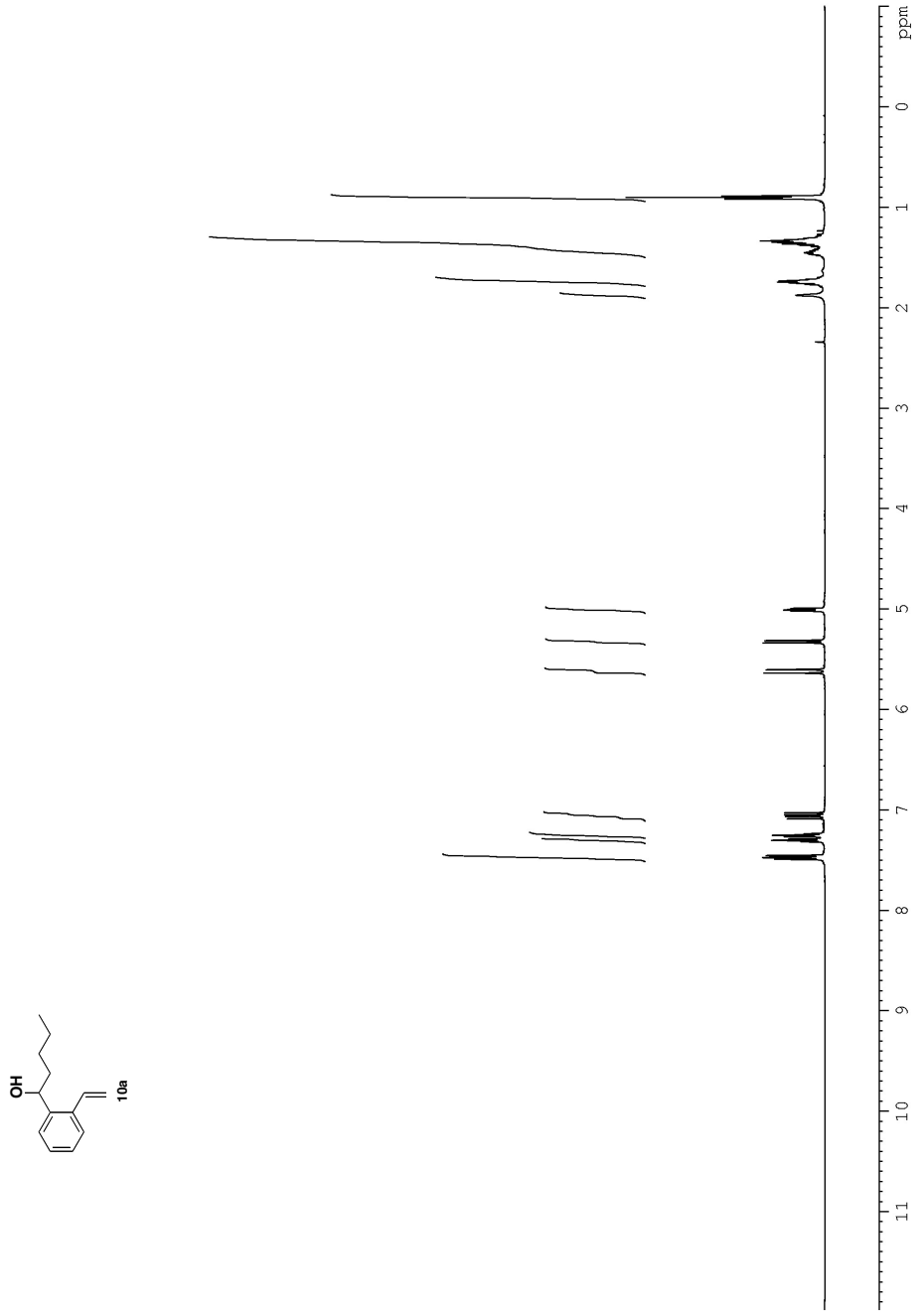
(+)-**34**

Compound (+)-34. Using conditions similar to those used for (+)-**32**, linchpin (+)-**16** (68.0 mg, 0.40 mmol, 1.0 equiv.) afforded (+)-**34** (53.3 mg, 0.27 mmol, 68% yield) as a colorless oil after flash chromatography (ethyl acetate/hexane = 1/10). R_f 0.32 (hexane/ethyl acetate = 10/1); $[\alpha]^{18}_D$ +40.5 (*c* 3.2, C_6D_6); IR (film) 3391 (m), 3082 (w), 2962 (s), 2930 (s), 2851 (m), 1640 (m), 1463 (m), 1403 (s), 1022 (w), 912 (w) cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 5.79-5.71 (m, 1H), 5.02 (d, *J* = 1.0 Hz, 1H), 4.99 (ddd, *J* = 7.0, 2.0 and 1.0 Hz, 1H), 4.86 (dd, *J* = 2.5 and 1.0 Hz, 1H), 4.84 (s, 1H), 3.46-3.42 (m, 1H), 2.66 (ddd, *J* = 37.2, 15.9 and 6.5 Hz, 2H), 2.62 (dd, *J* = 16.0 and 7.5 Hz, 1H), 1.52-1.37 (m, 3H), 1.32-1.22 (m, 5H), 1.15 (br, 1H), 1.05 (d, *J* = 7.0 Hz, 3H), 0.90 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 151.6, 137.0, 116.8, 111.7, 72.9, 45.6, 40.7, 35.6, 32.6, 26.7, 23.5, 14.7, 14.1; high resolution mass spectrum (ES^+) *m/z* 219.1719 [$(M+Na)^+$; calcd for $C_{13}H_{24}ONa$: 219.1725].



(+)-**35**

Compound (+)-35. Using conditions similar to those used for (+)-**33**, linchpin (+)-**16** (68.0 mg, 0.40 mmol, 1.0 equiv.) afforded (+)-**35** (58.5 mg, 0.25 mmol, 63% yield) as a pale yellow oil after flash chromatography (ethyl acetate/hexane = 1/10). R_f 0.30 (hexane/ethyl acetate = 10/1); $[\alpha]^{18}_D$ +24.7 (*c* 0.6, C_6D_6); IR (film) 3391 (m), 3082 (w), 3059 (w), 3025 (w), 2958 (s), 2930 (s), 1624 (w), 1460 (m), 1403 (s), 1024 (m), 900 (m) cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 7.22 (d, *J* = 6.0 Hz, 2H), 7.20-7.05 (m, 3H), 5.25 (d, *J* = 1.0 Hz, 1H), 5.02 (d, *J* = 1.0 Hz, 1H), 3.47 (m, 1H), 2.69 (m, 1H), 1.50-1.32 (m, 3H), 1.30-1.02 (m, 5H), 1.18 (d, *J* = 7.0 Hz, 3H), 0.85 (t, *J* = 7.0 Hz, 3H), 0.42 (br, 1H); ^{13}C NMR (125 MHz, C_6D_6) δ 153.5, 143.4, 129.0, 128.7, 128.3, 128.0, 127.4, 113.6, 73.0, 44.1, 35.7, 32.6, 26.7, 23.4, 14.6, 13.8; high resolution mass spectrum (ES^+) *m/z* 255.1720 [$(M+Na)^+$; calcd for $C_{16}H_{24}ONa$: 255.1725].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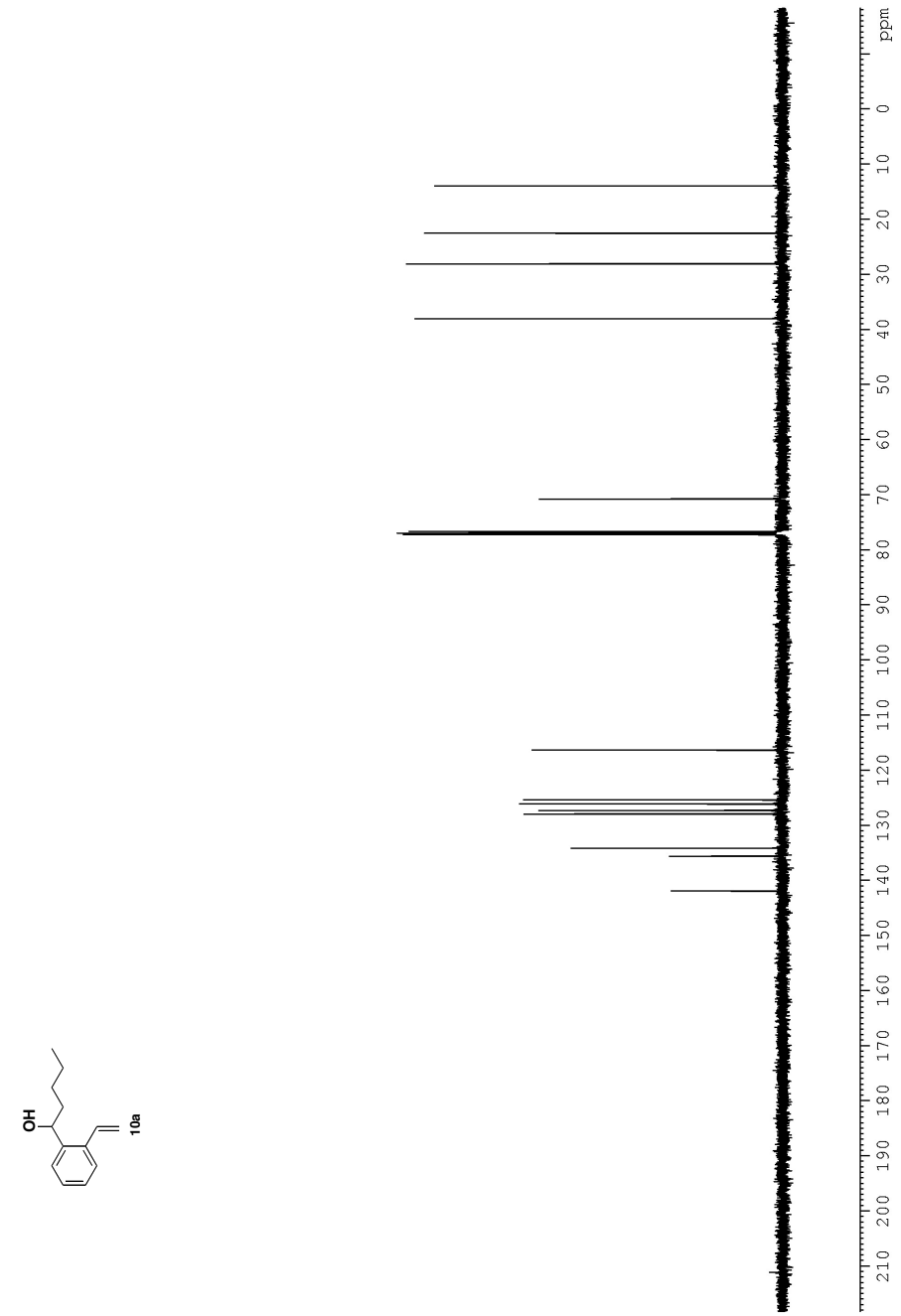
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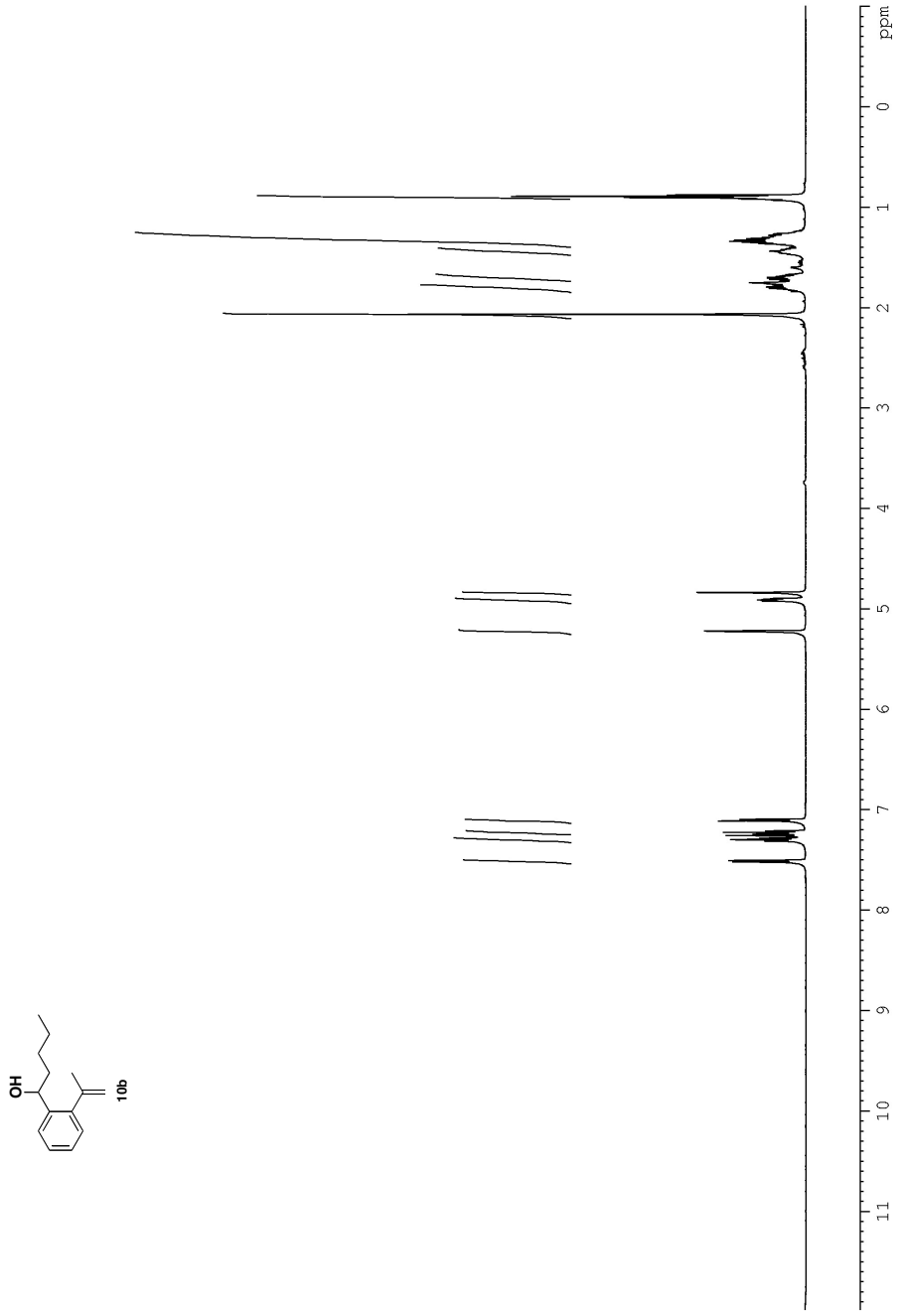
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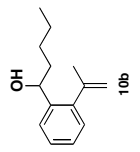
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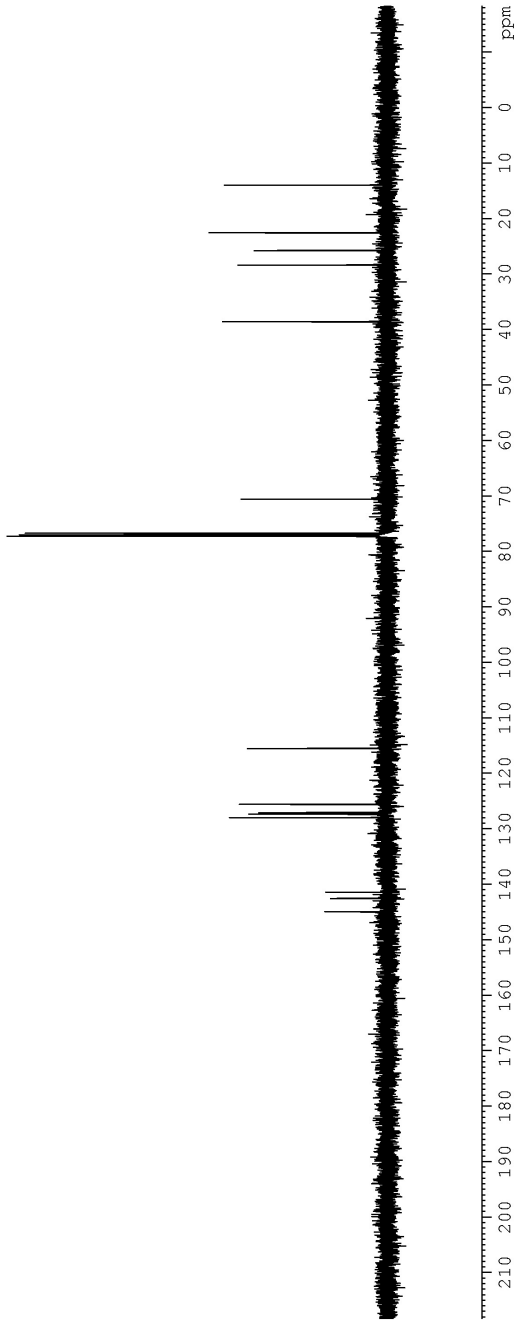
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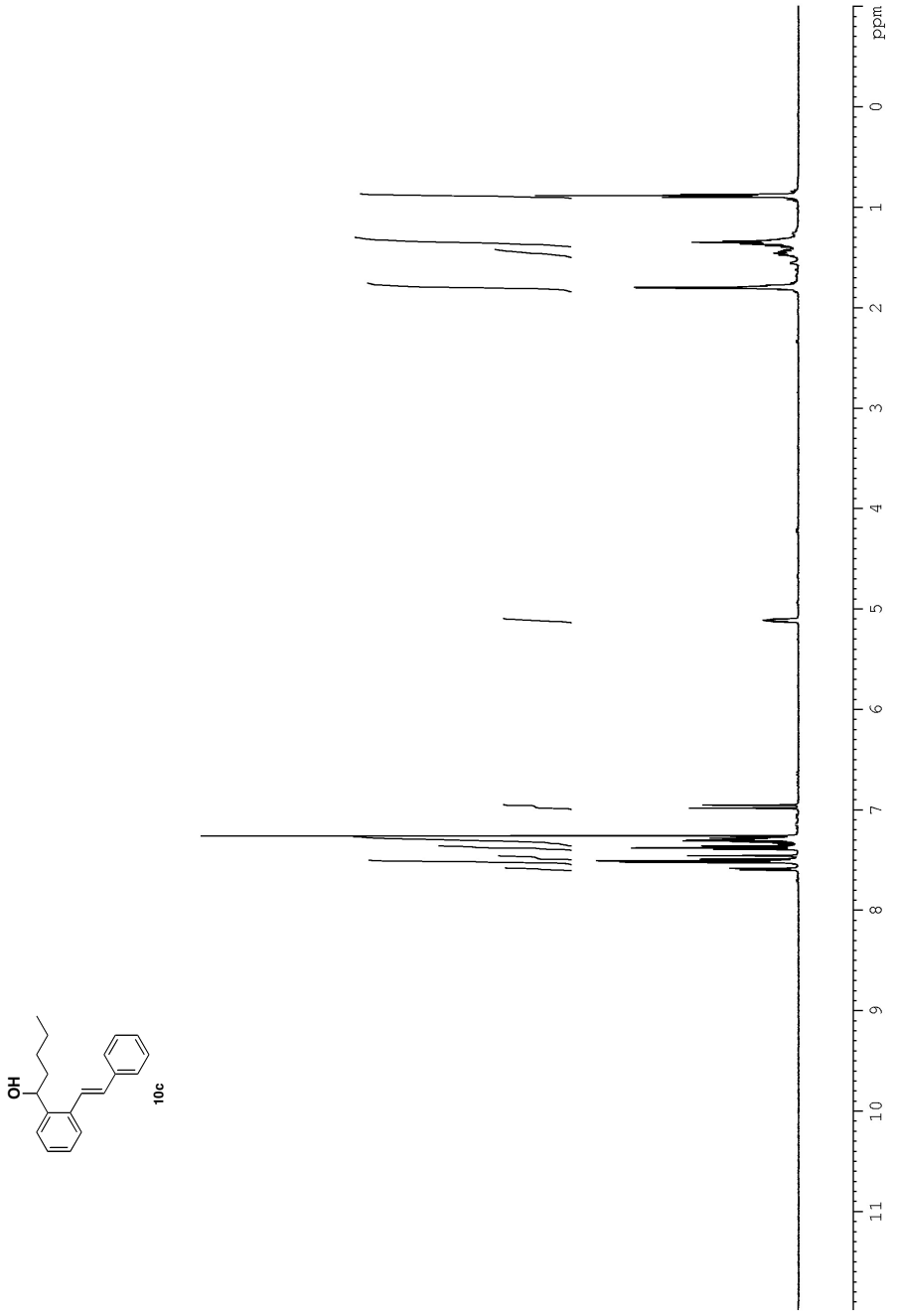
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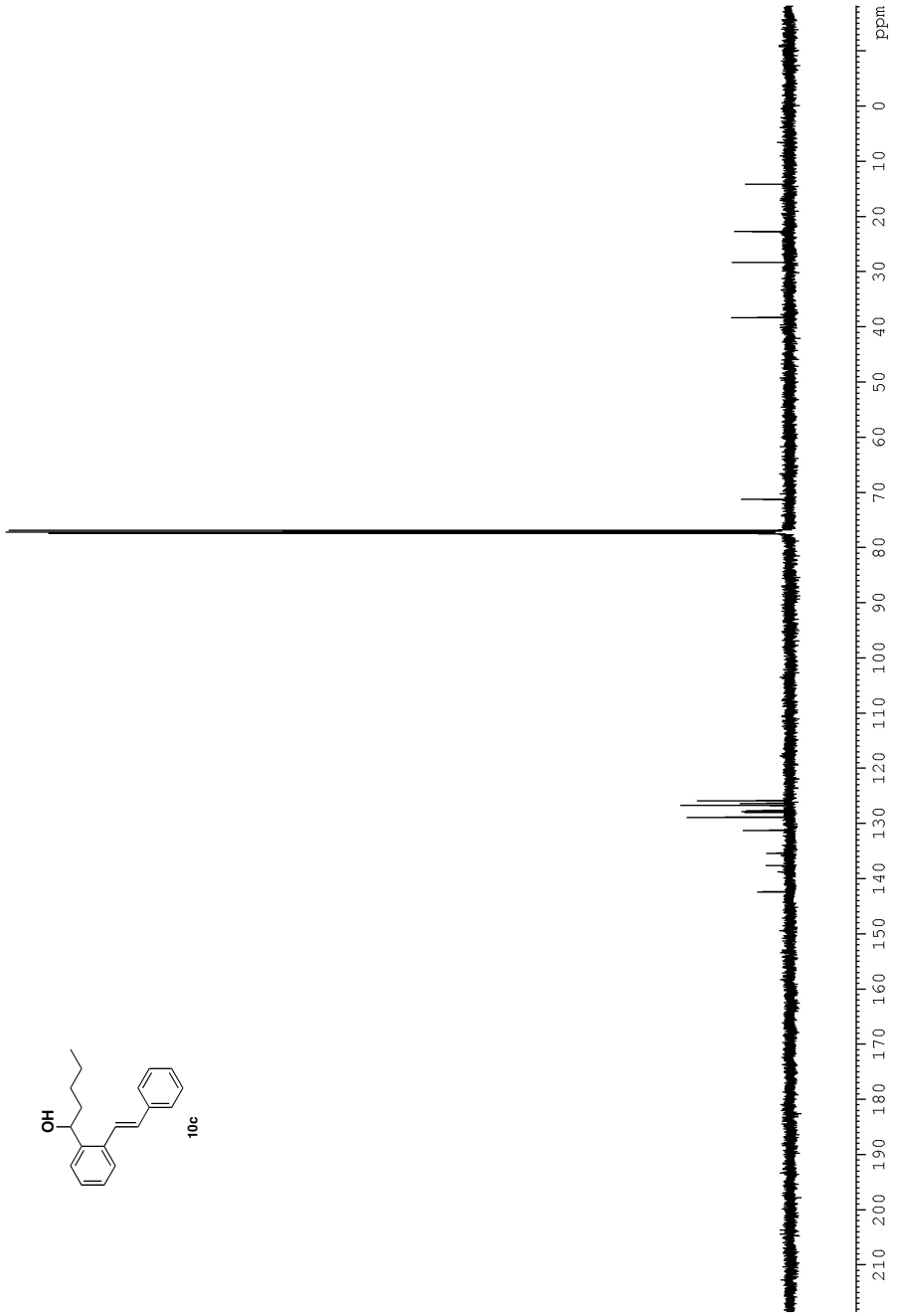
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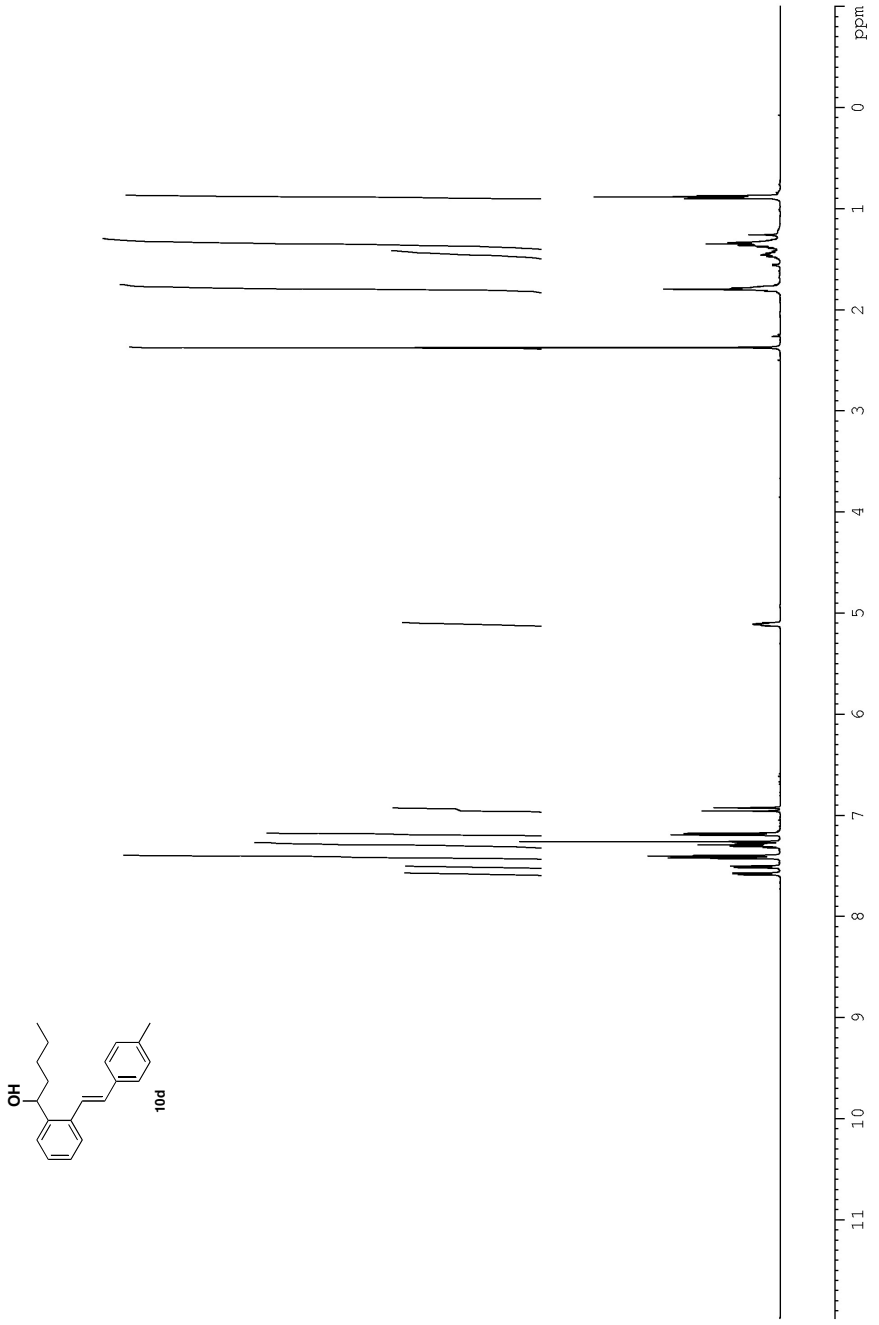
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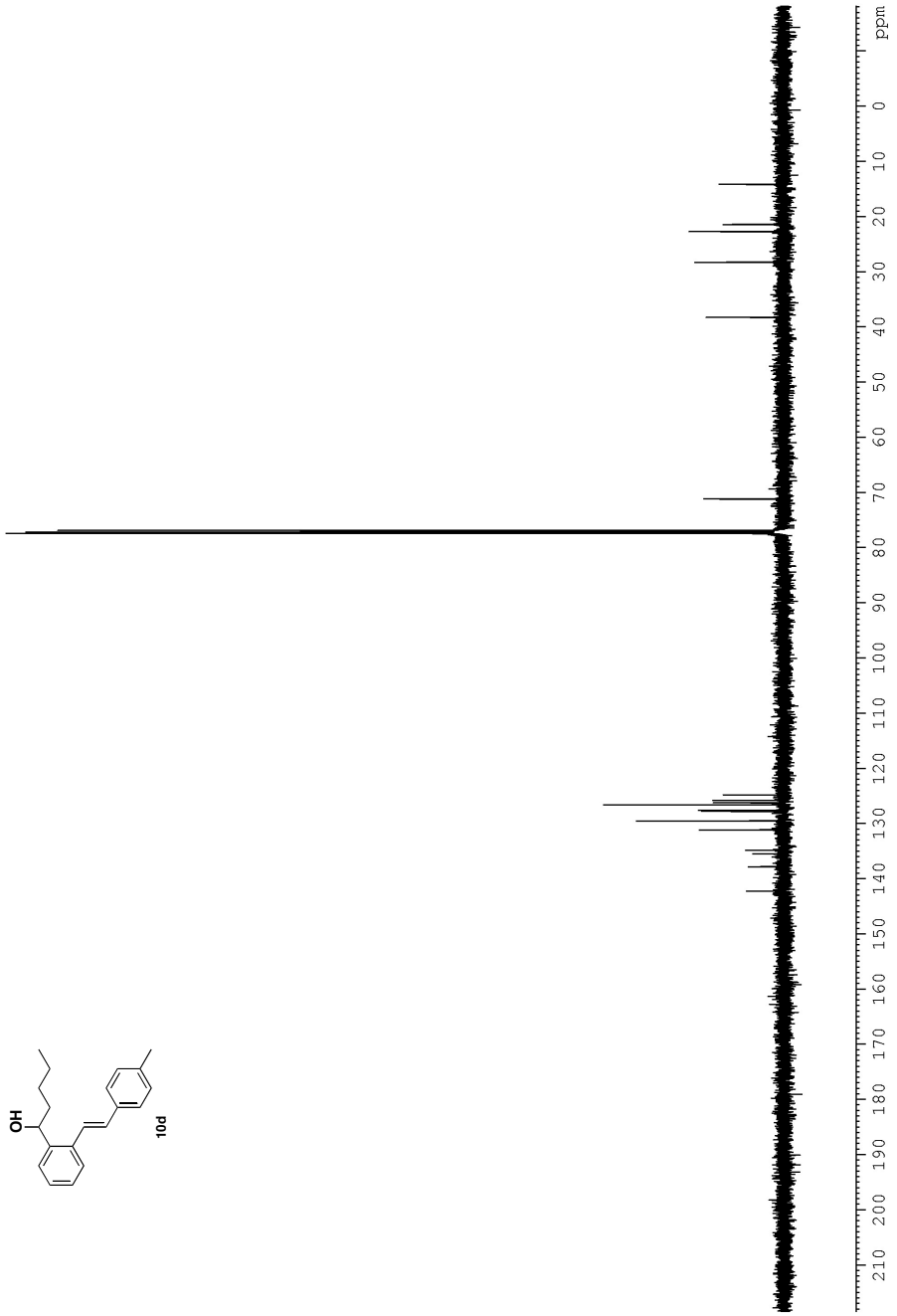
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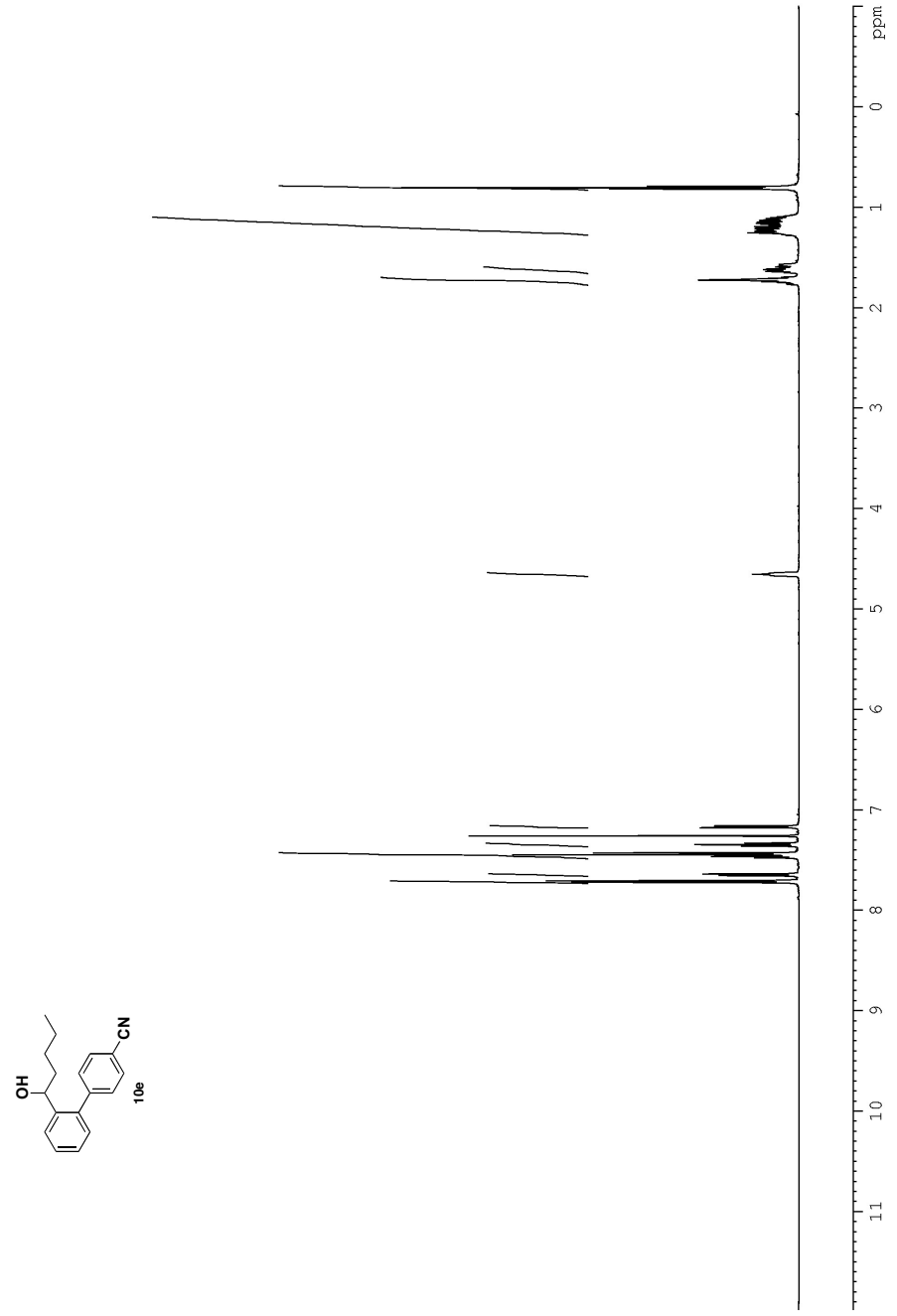
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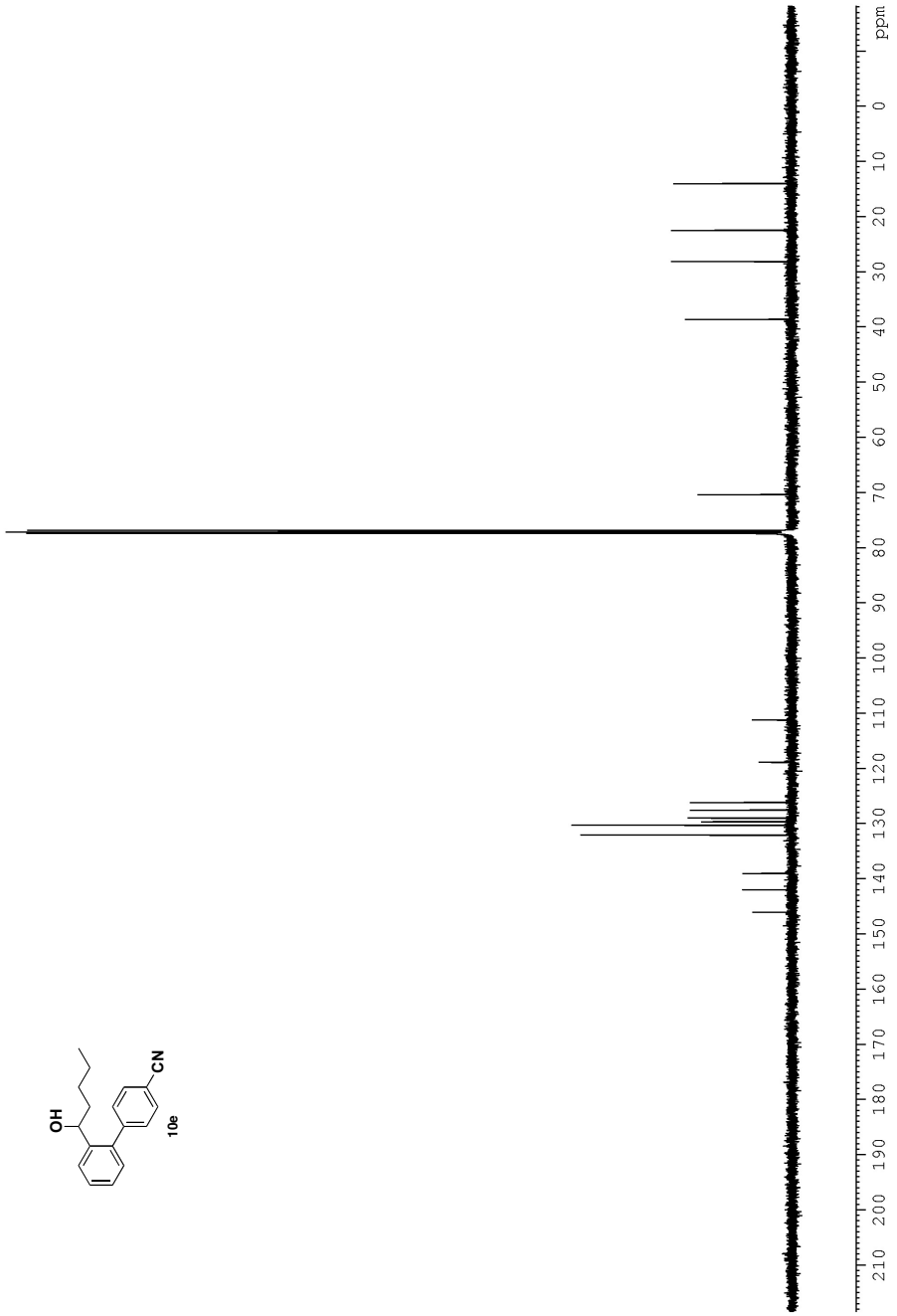
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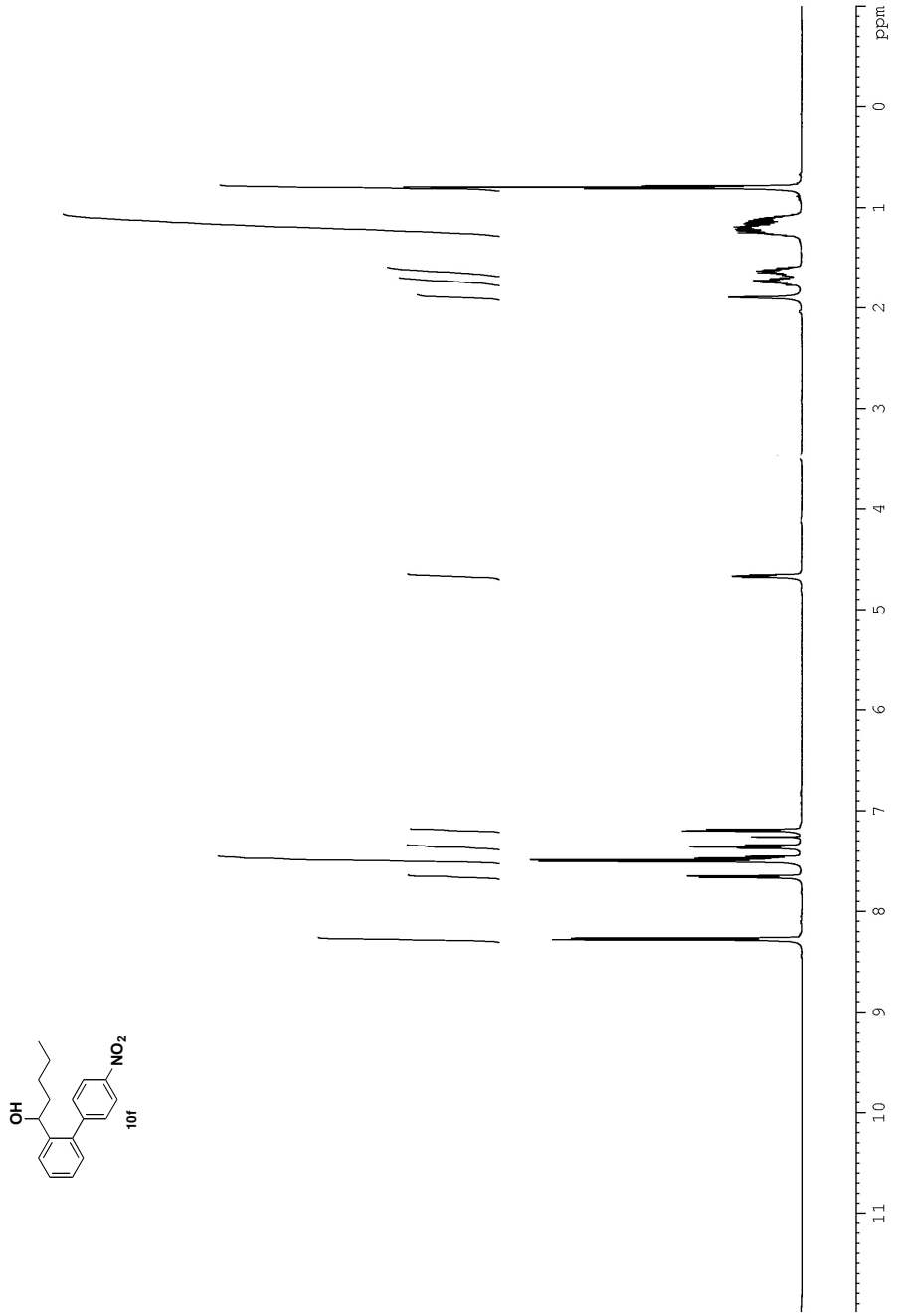
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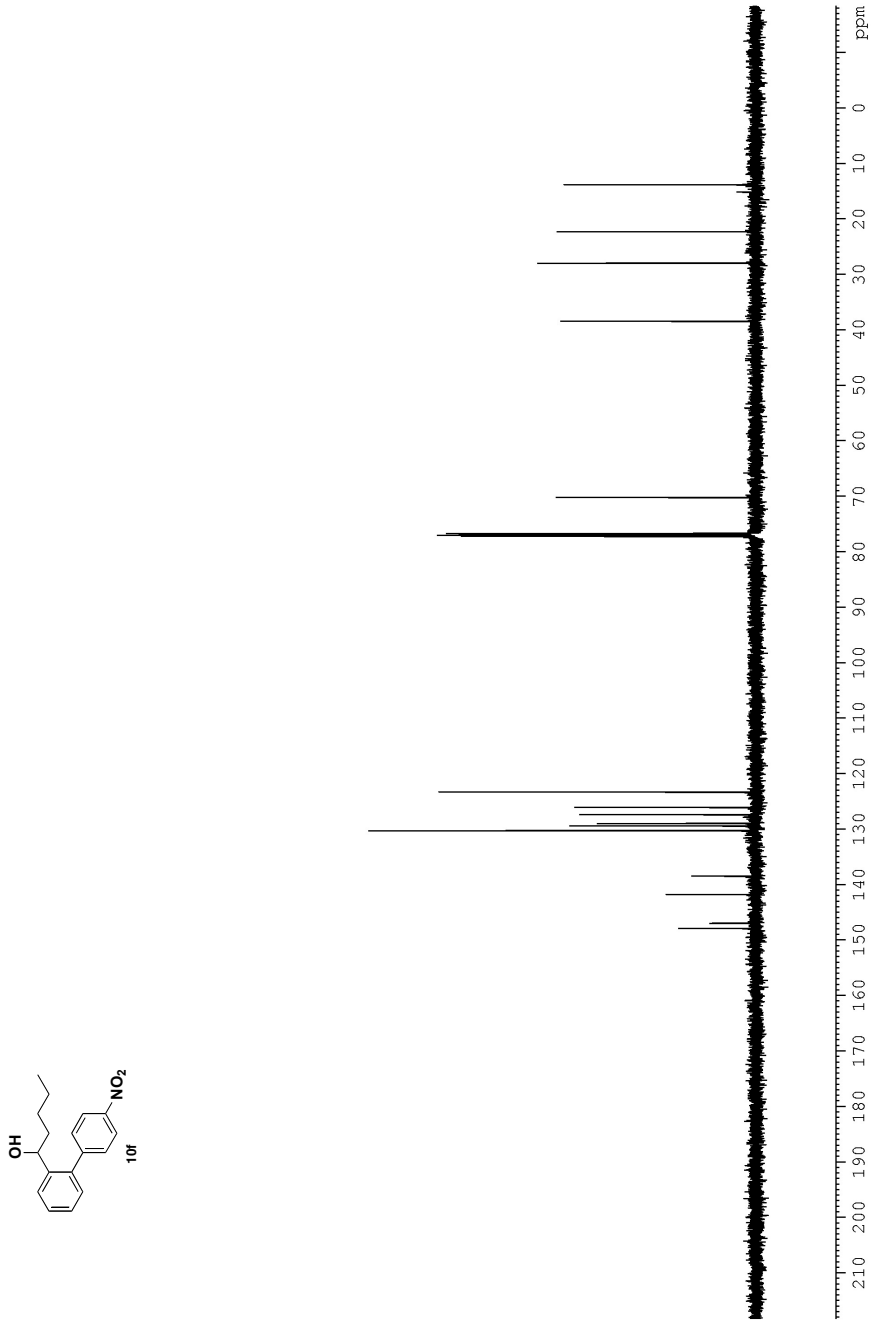
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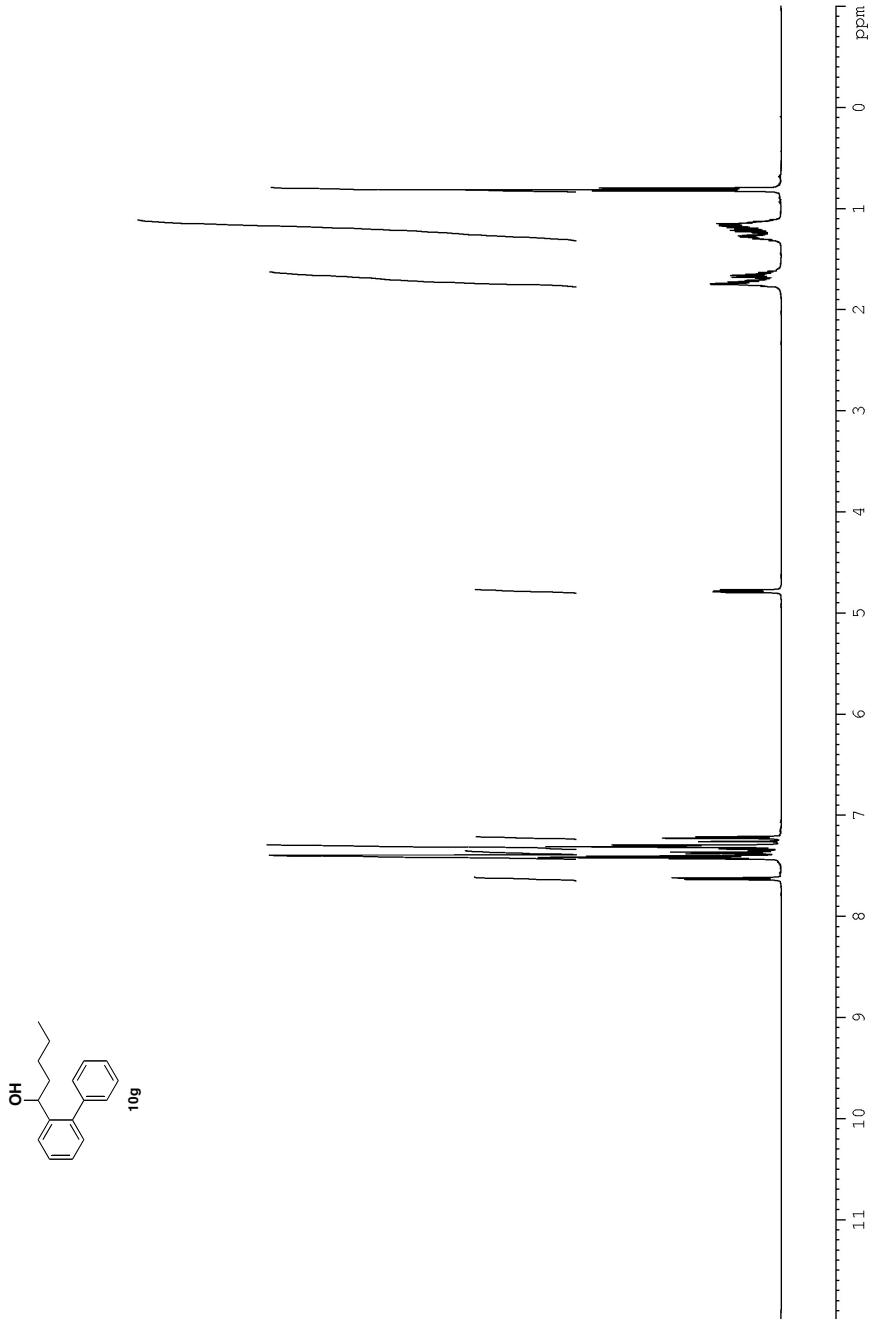
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10g
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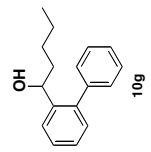
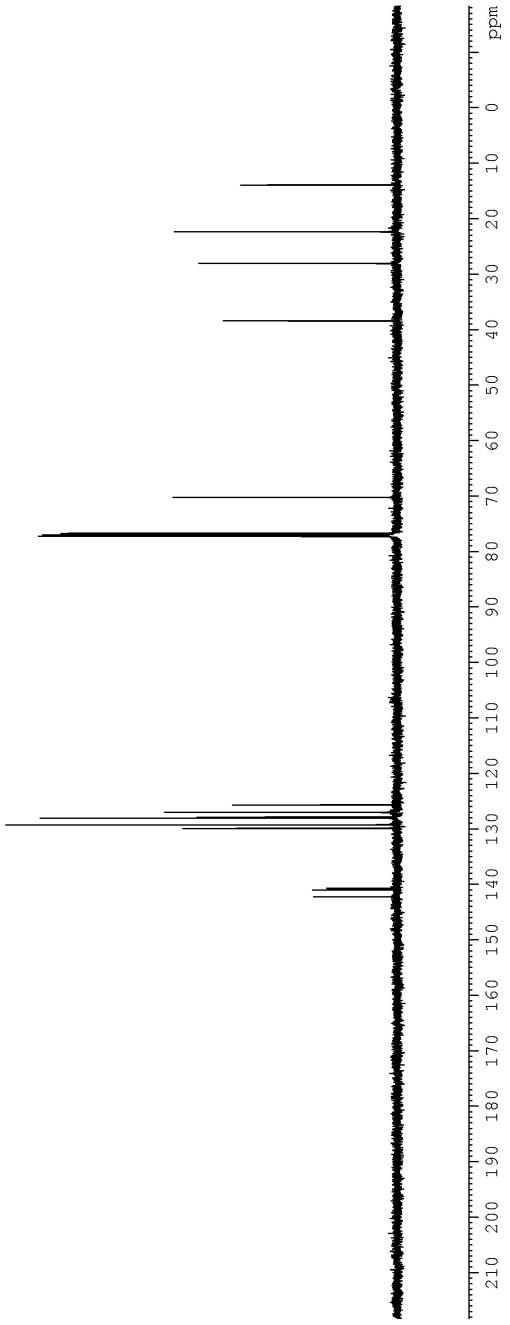

OH

10g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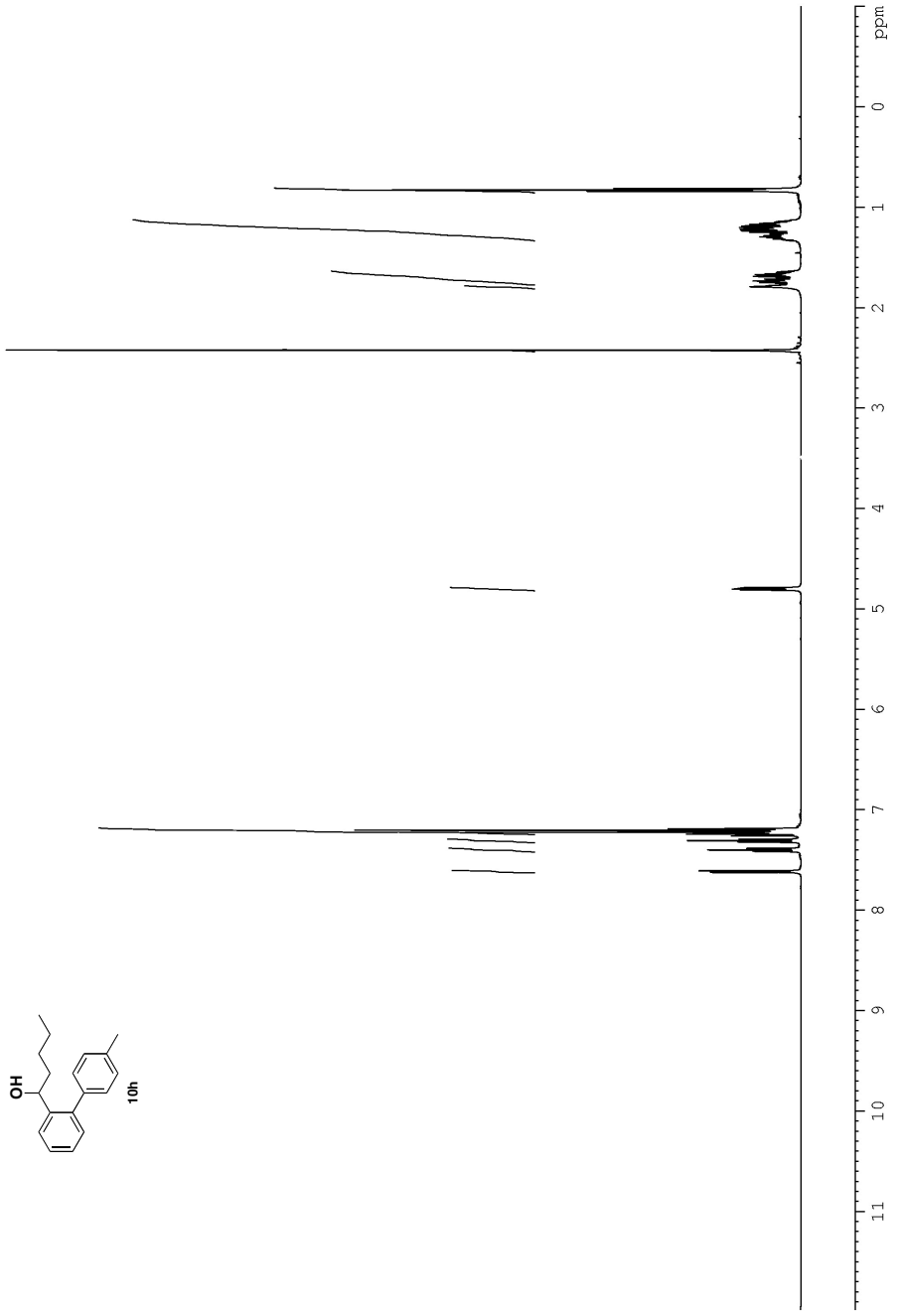
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10h
ppm
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10
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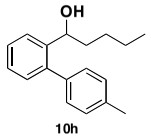
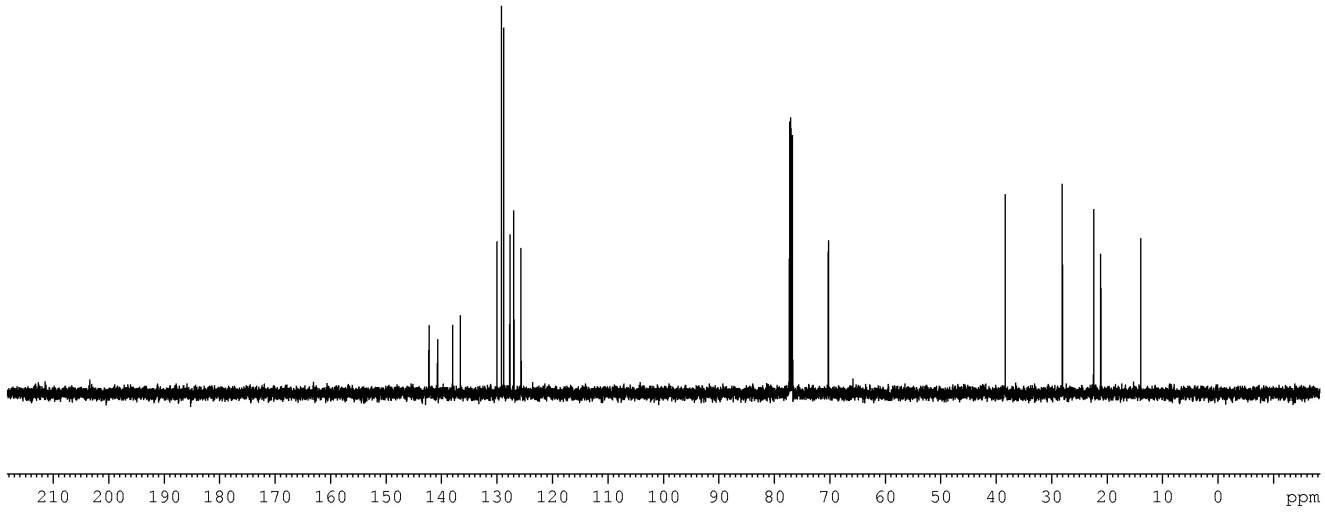

OH

10h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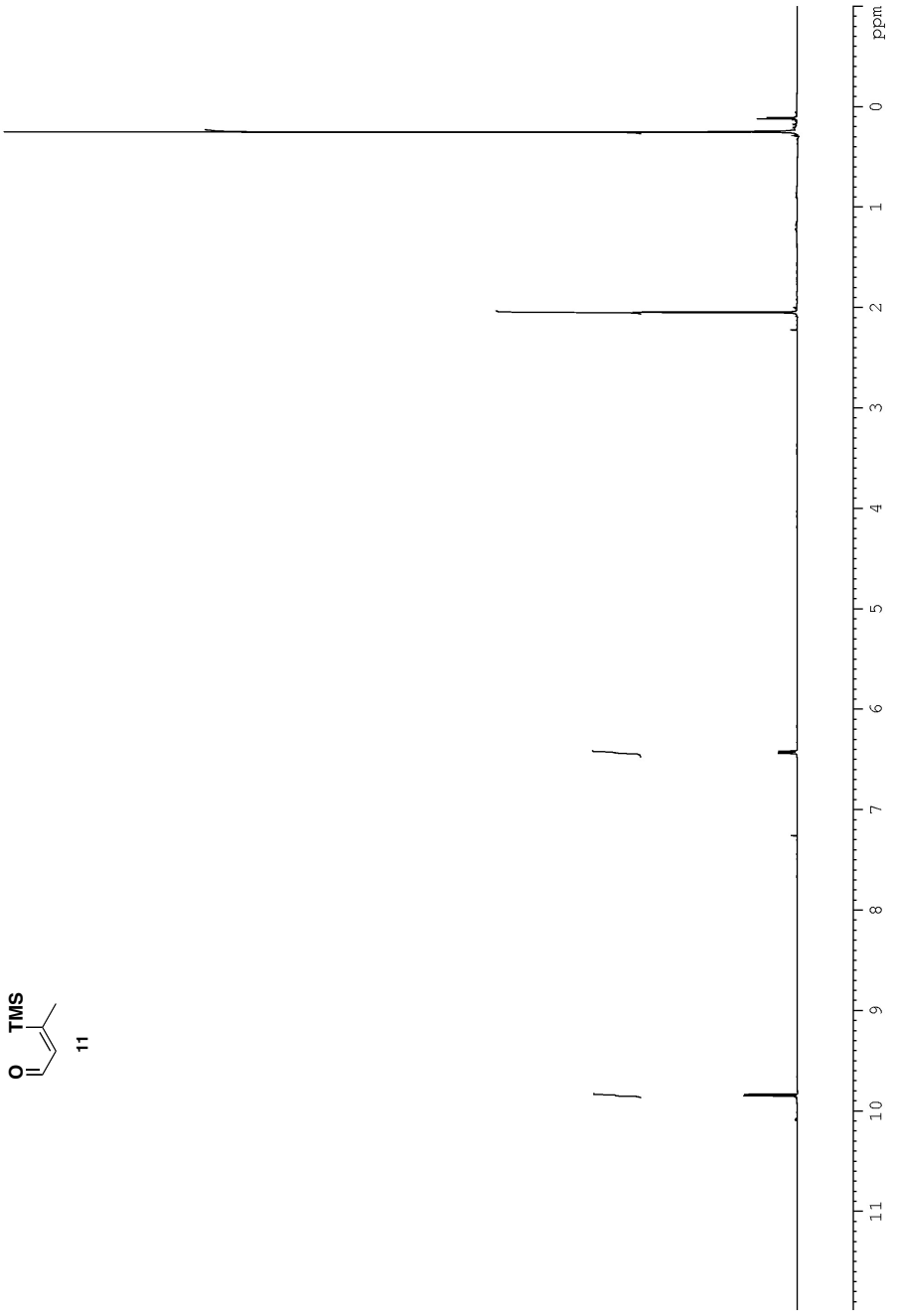
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ppm
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4
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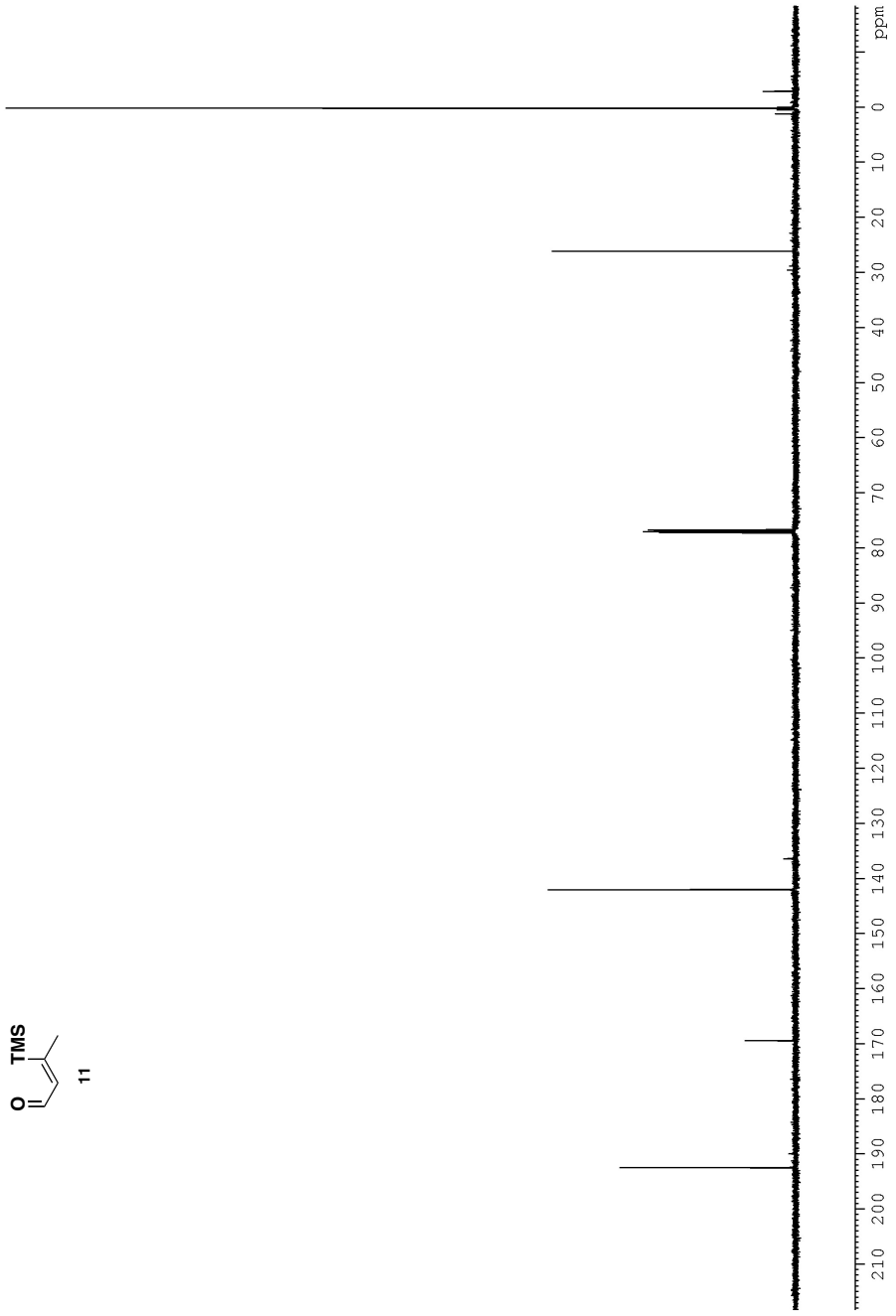
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O
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ppm
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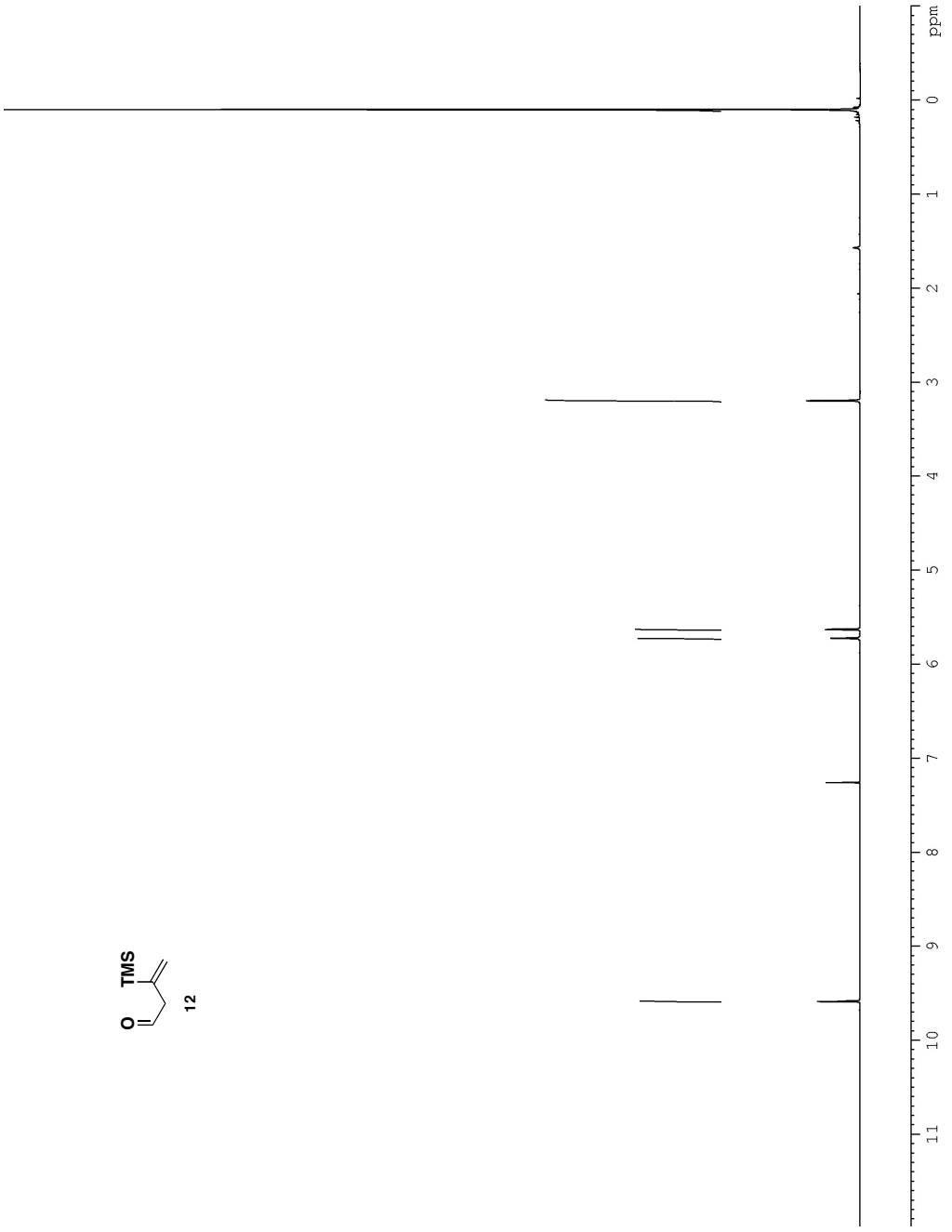
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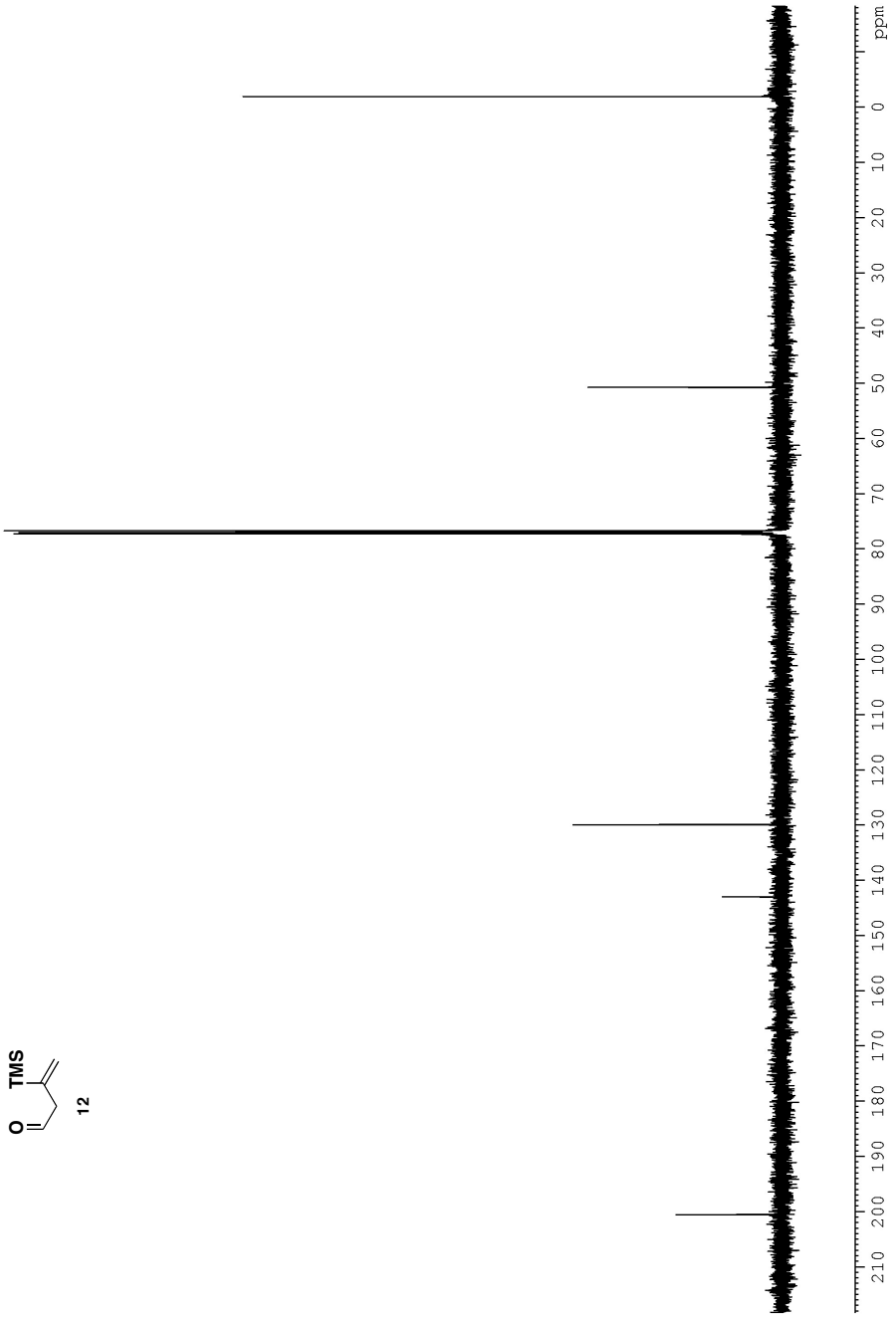
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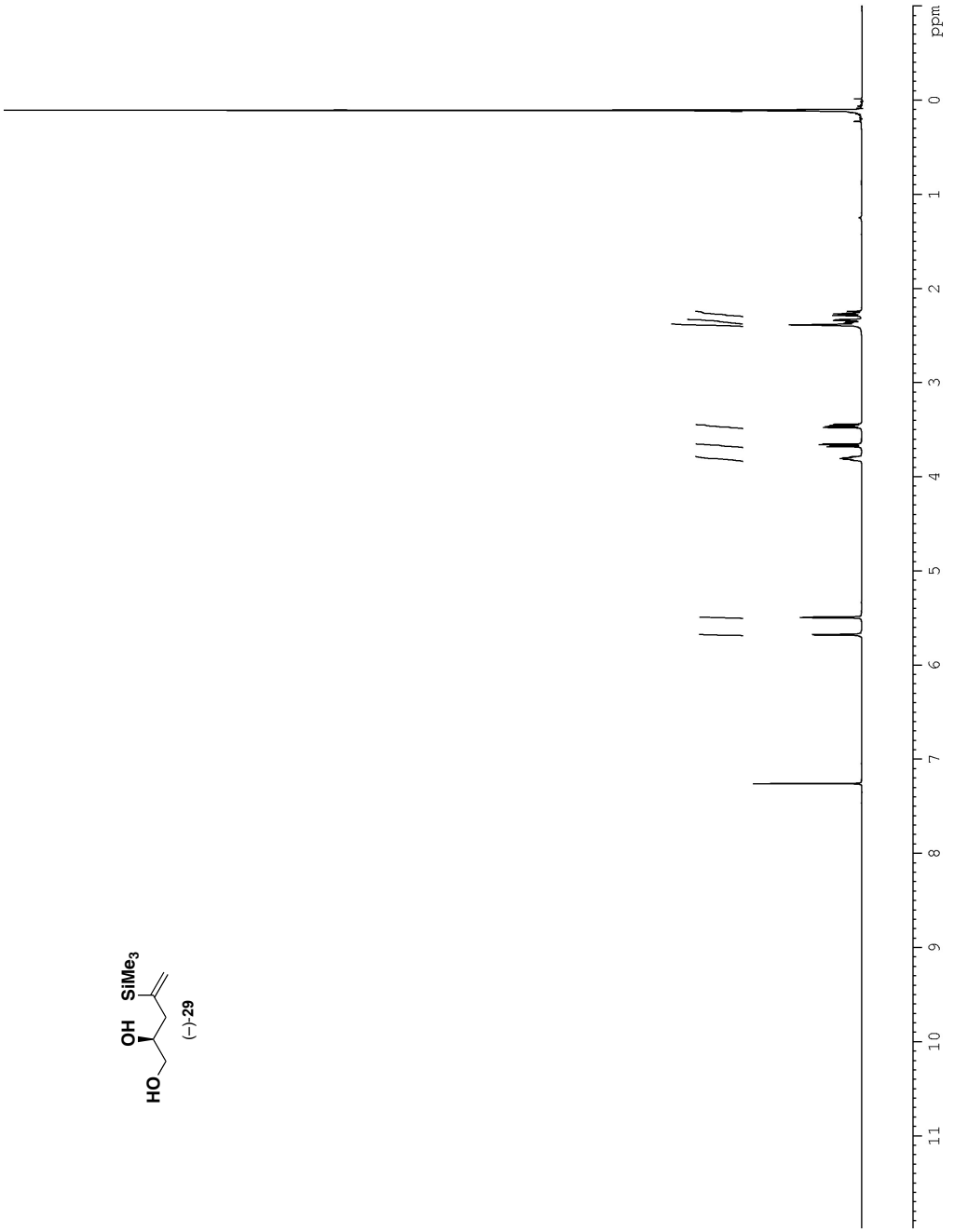
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HO
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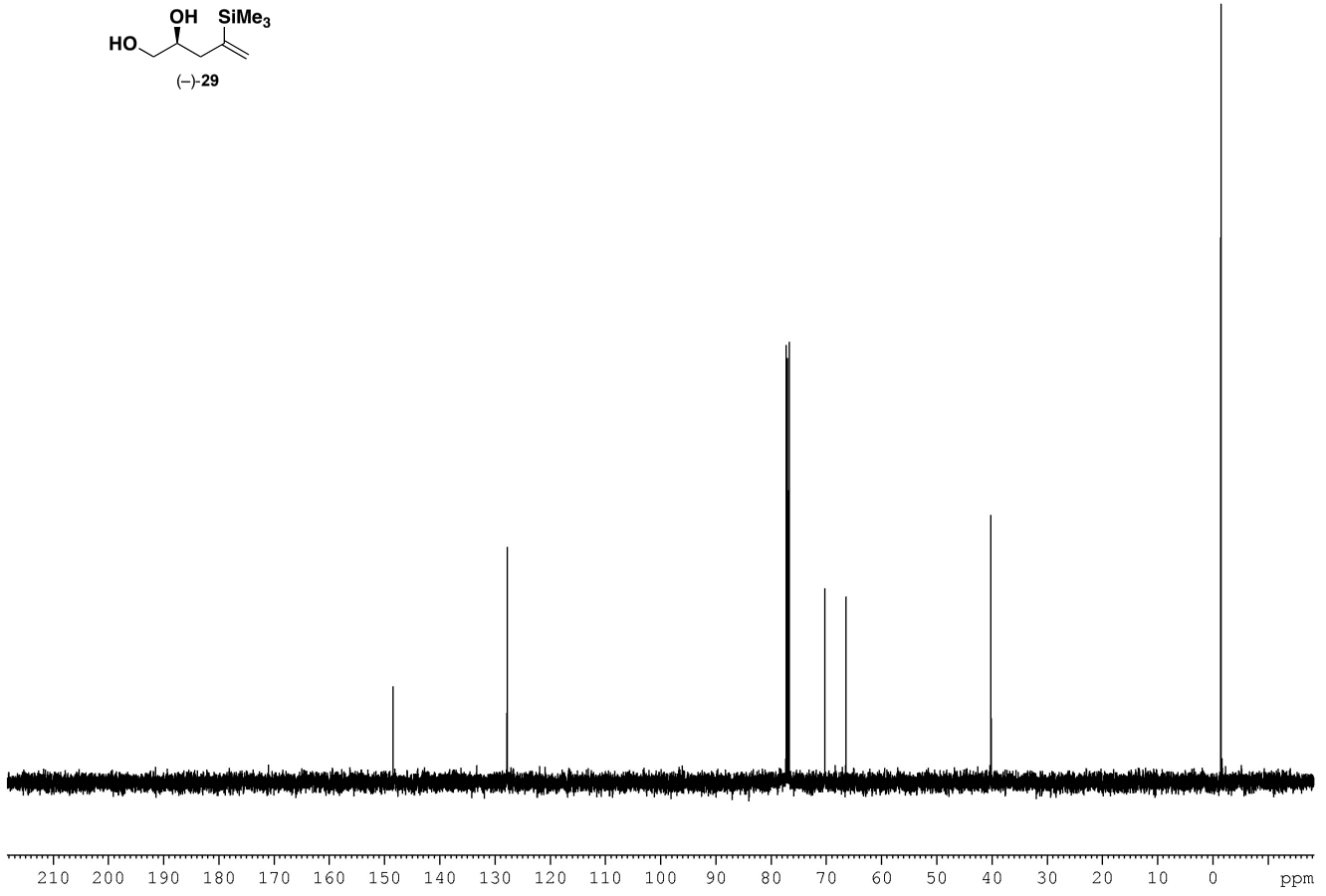
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SiMe3
HO
(–)-29
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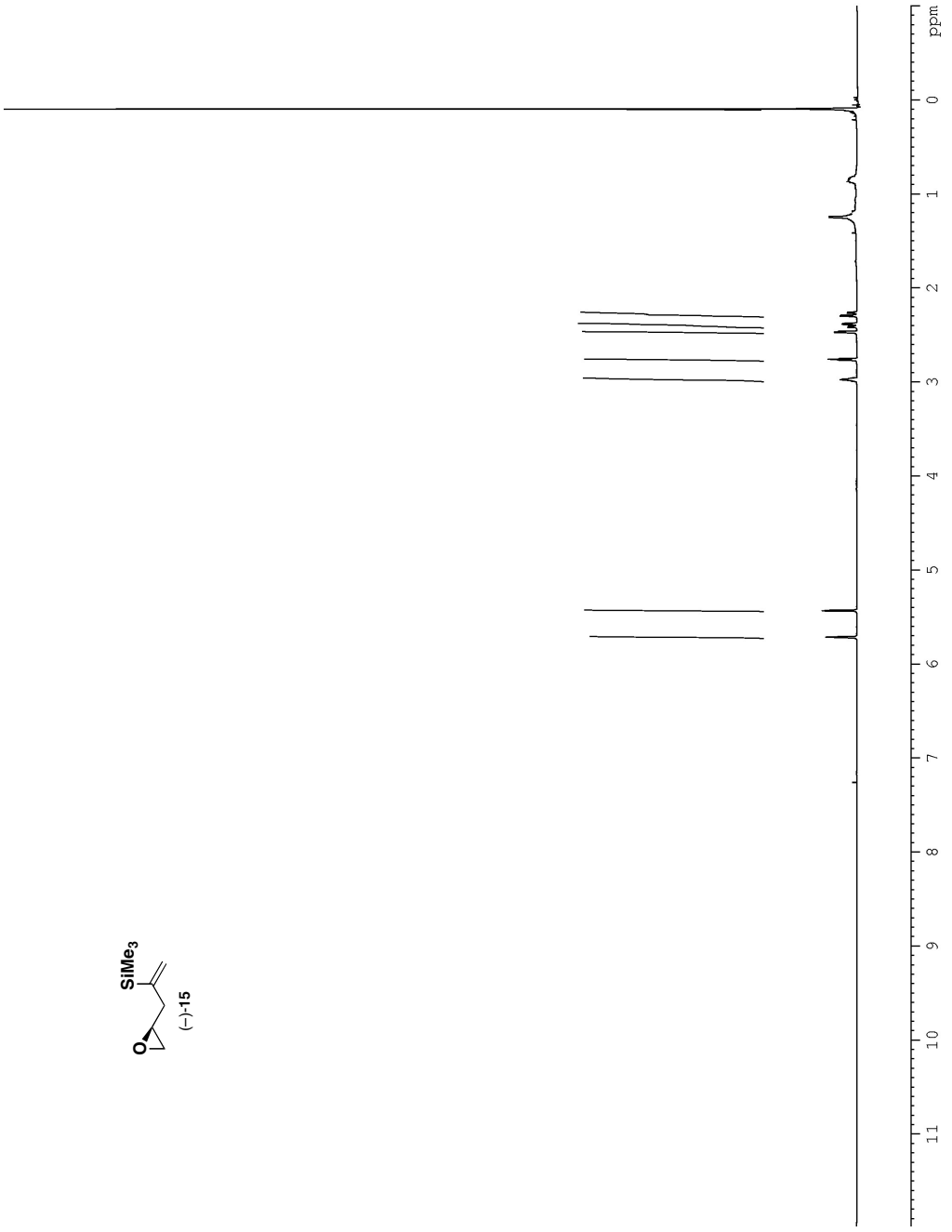
ppm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O
(–)-15
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4
5
6
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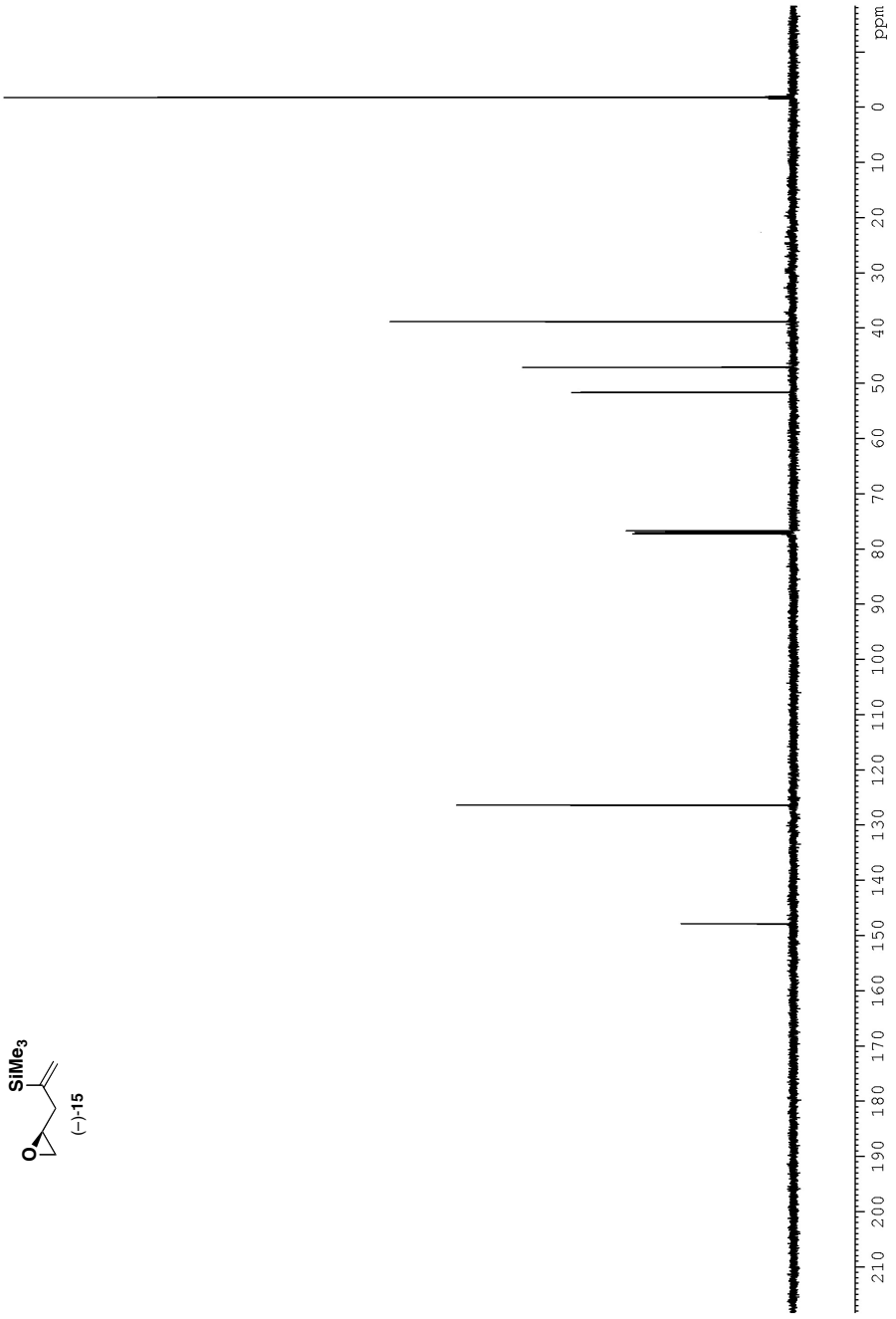
8
9
10
11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O
(−)-15
ppm
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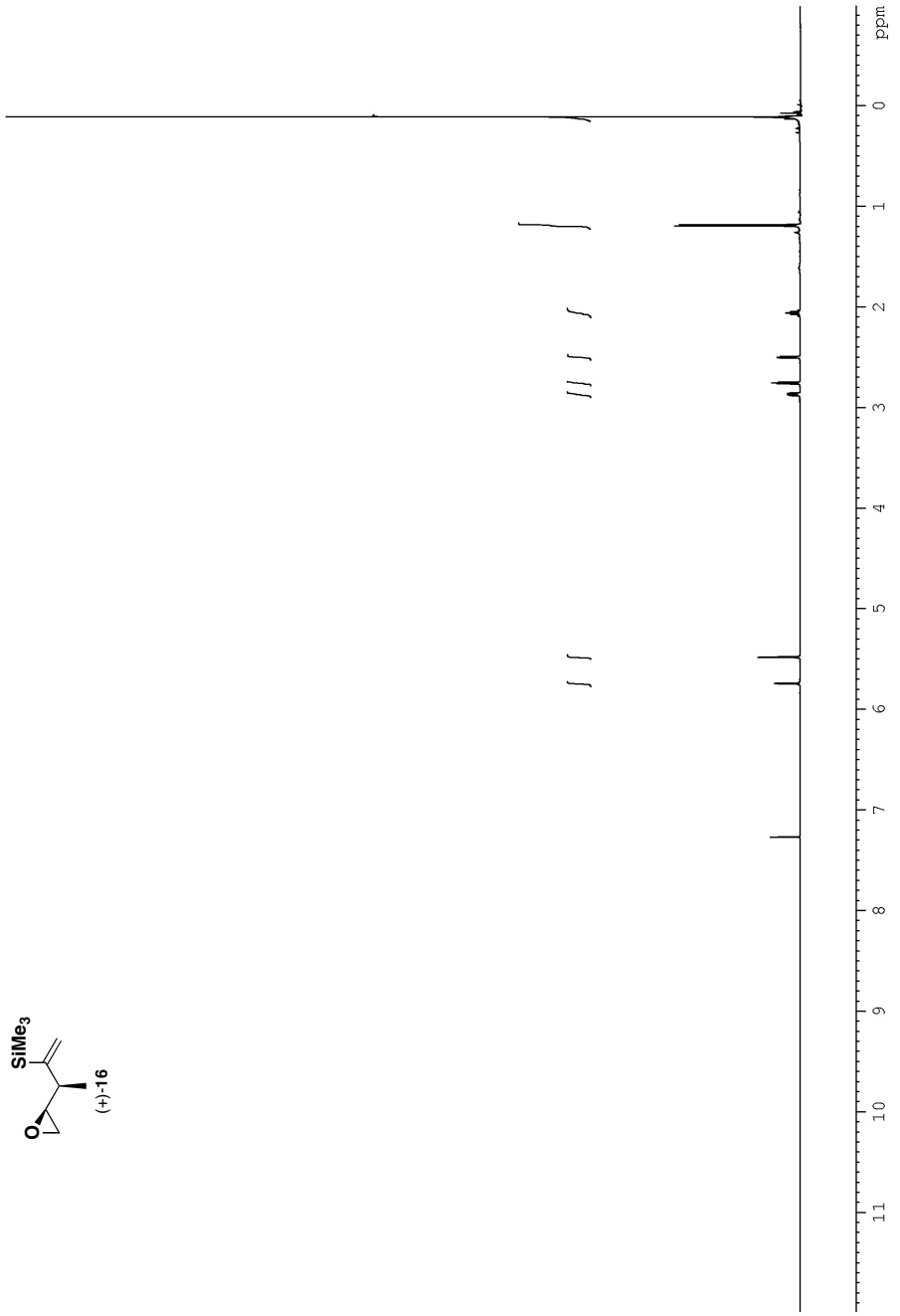
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O
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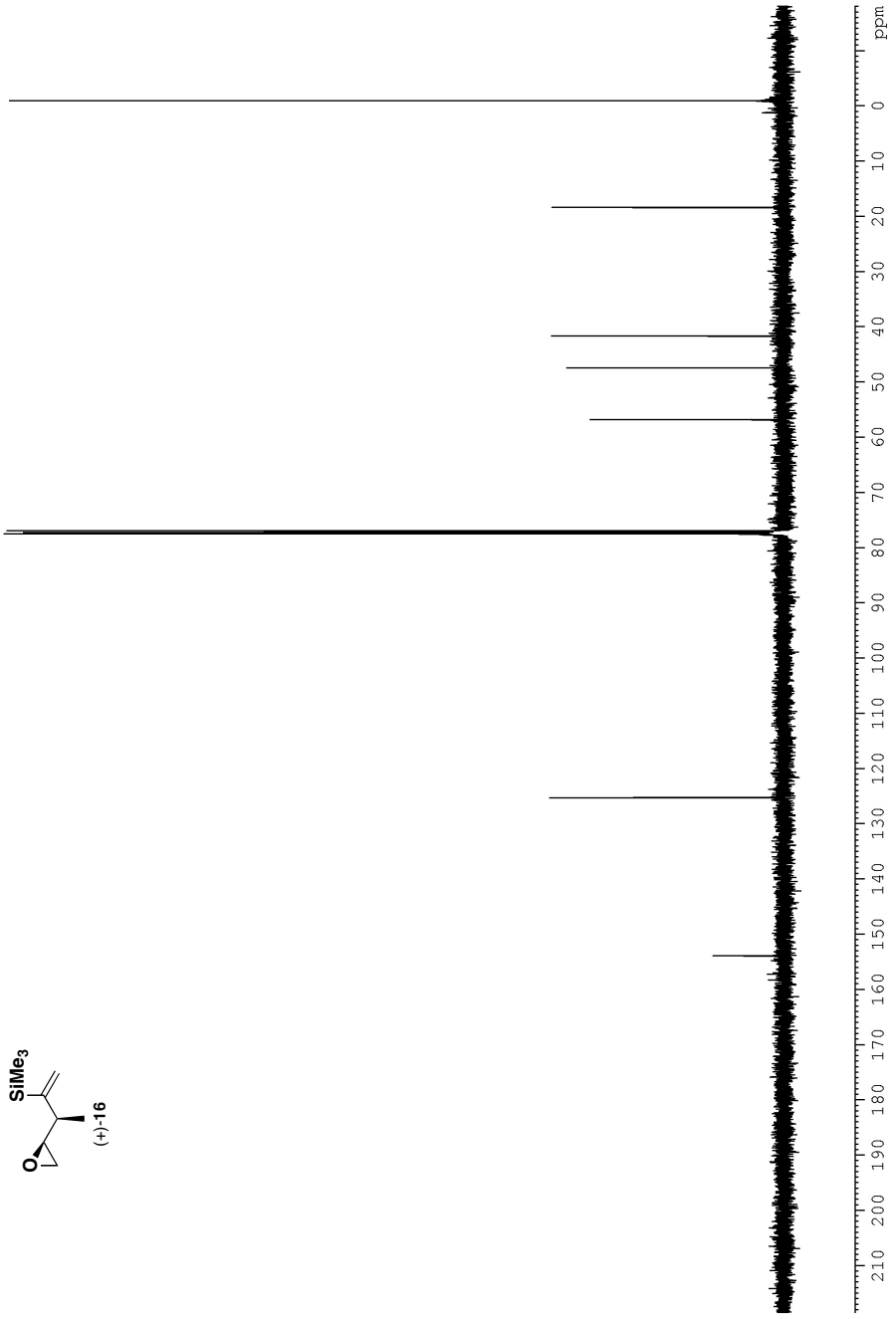
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O
(+)-16
ppm
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200
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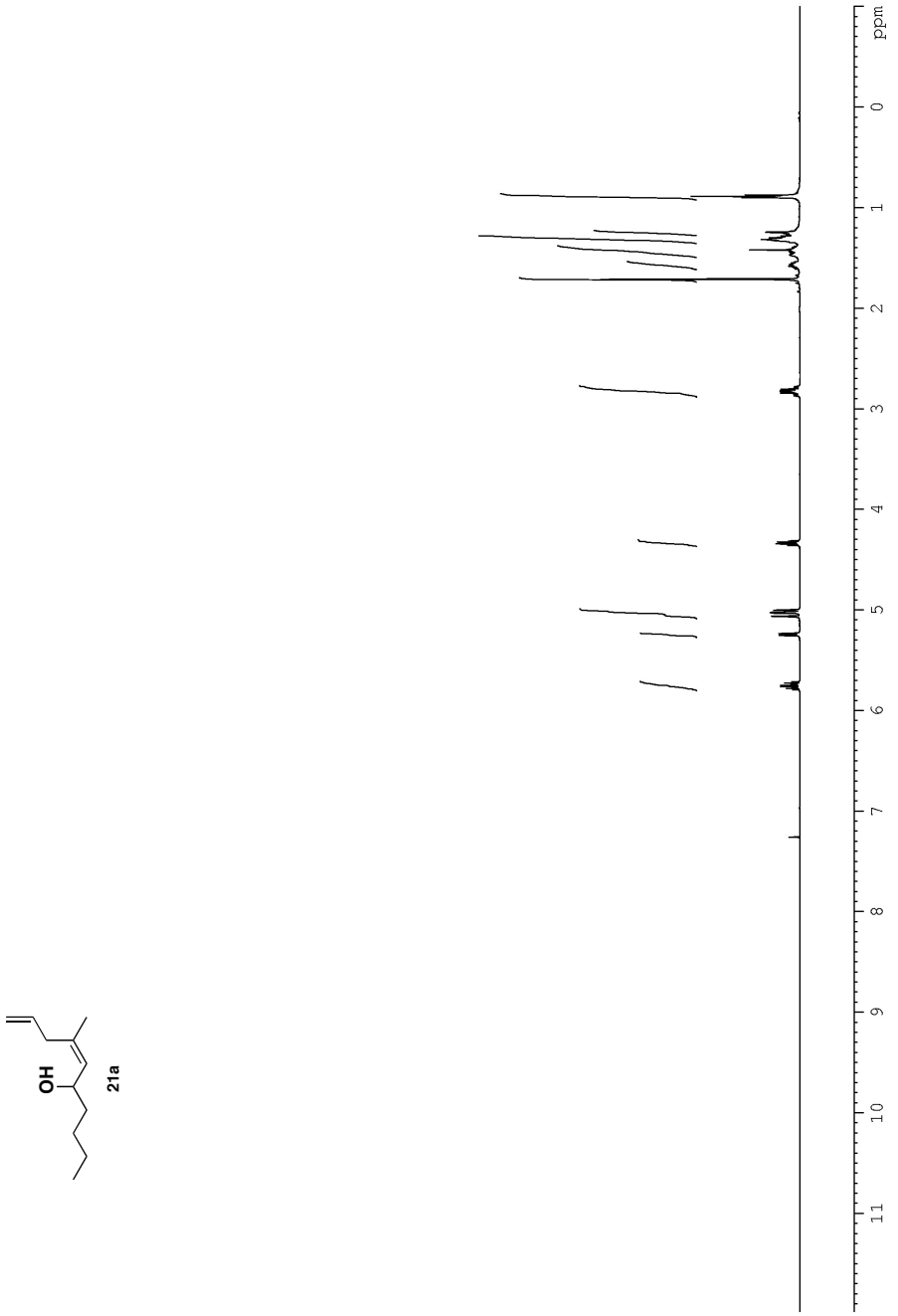
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ppm
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5
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8
9
10
11

OH
21a
ppm
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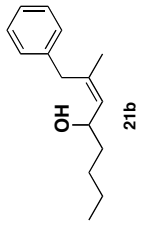
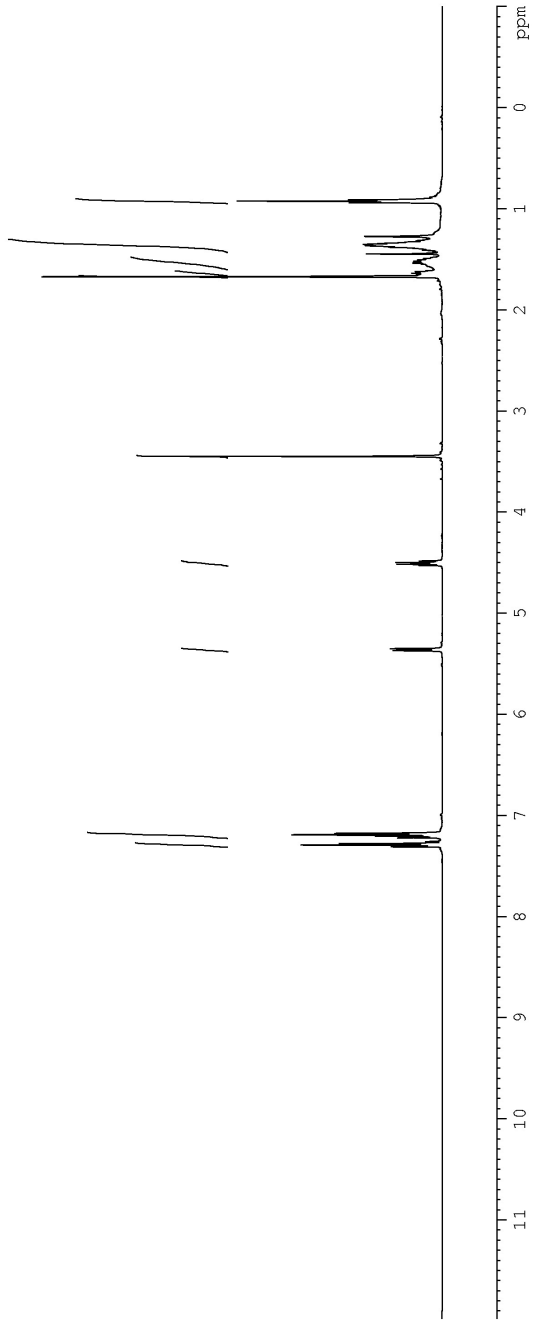
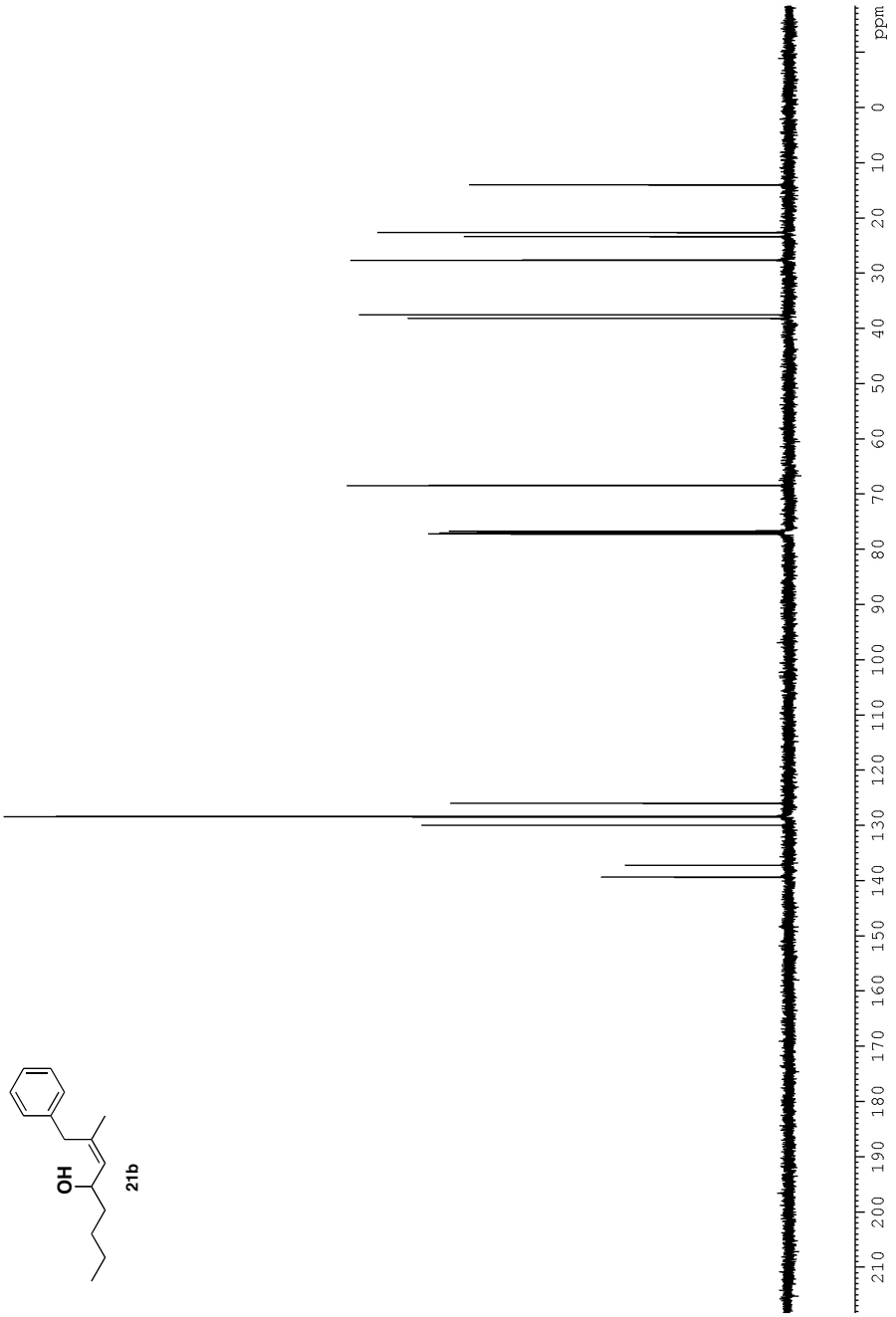


21b

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200
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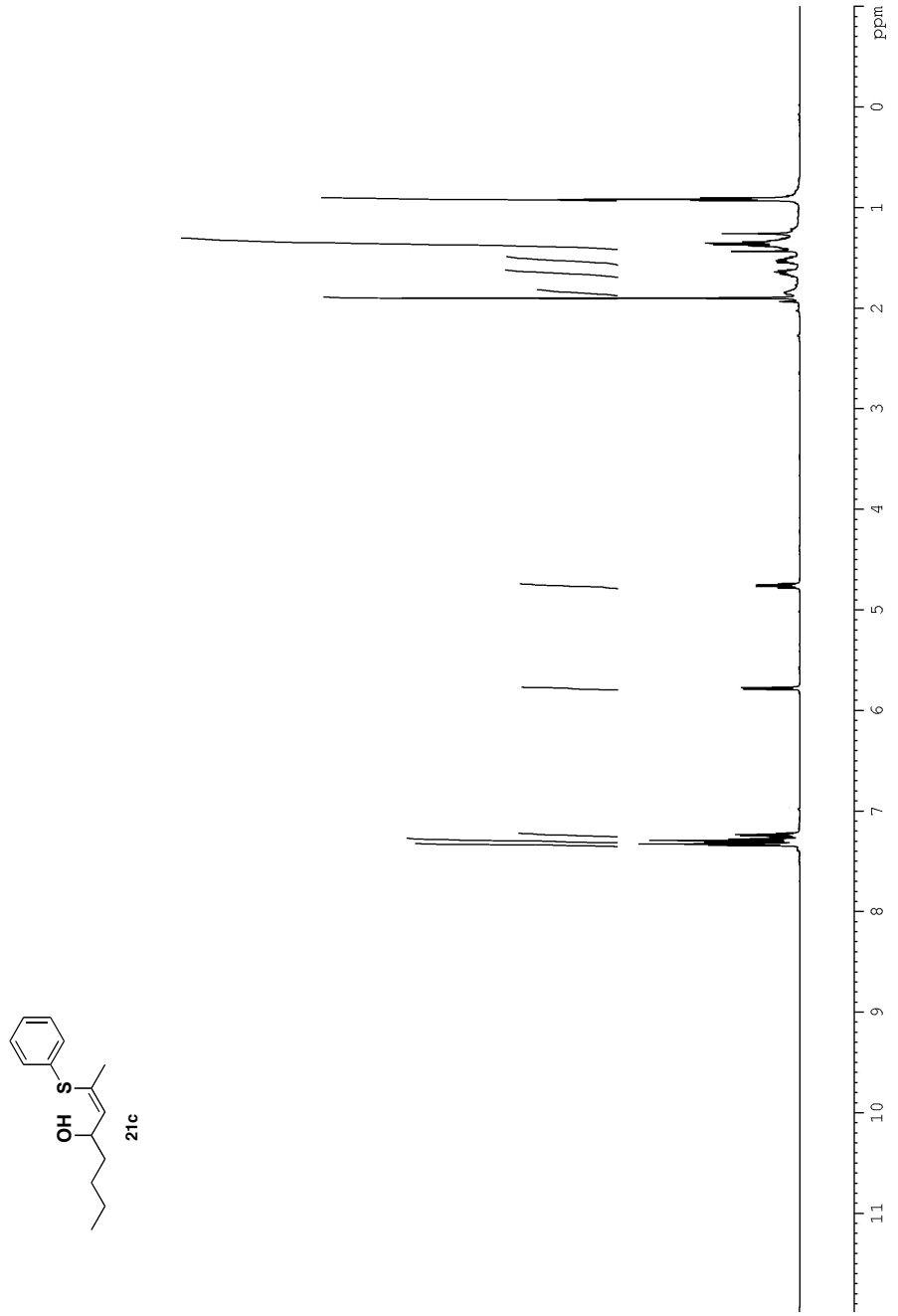
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S
21c
ppm
0
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5
6
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8
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10
11

OH
S
21c

ppm
0
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200
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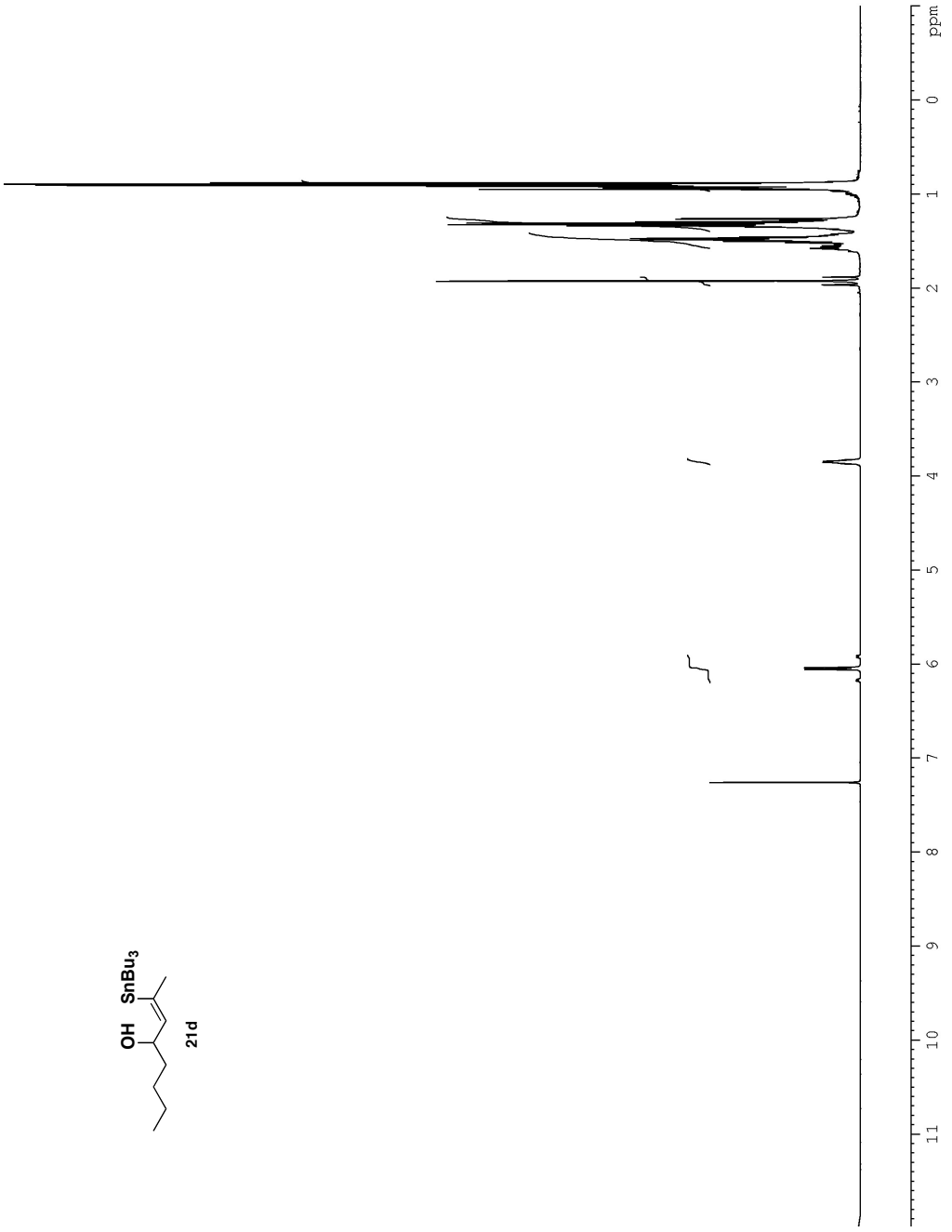
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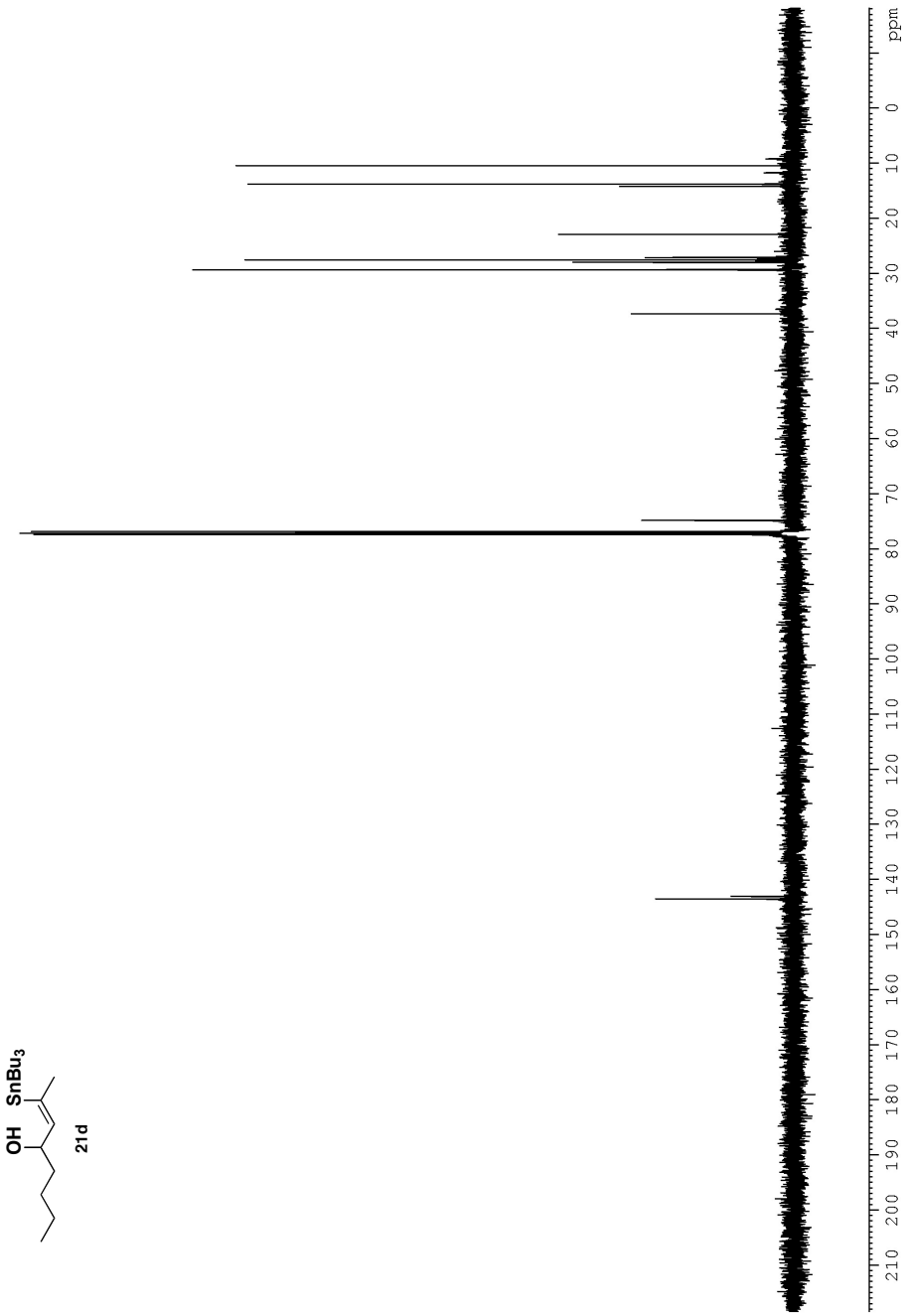
OH
SnBu3
21d
ppm
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200
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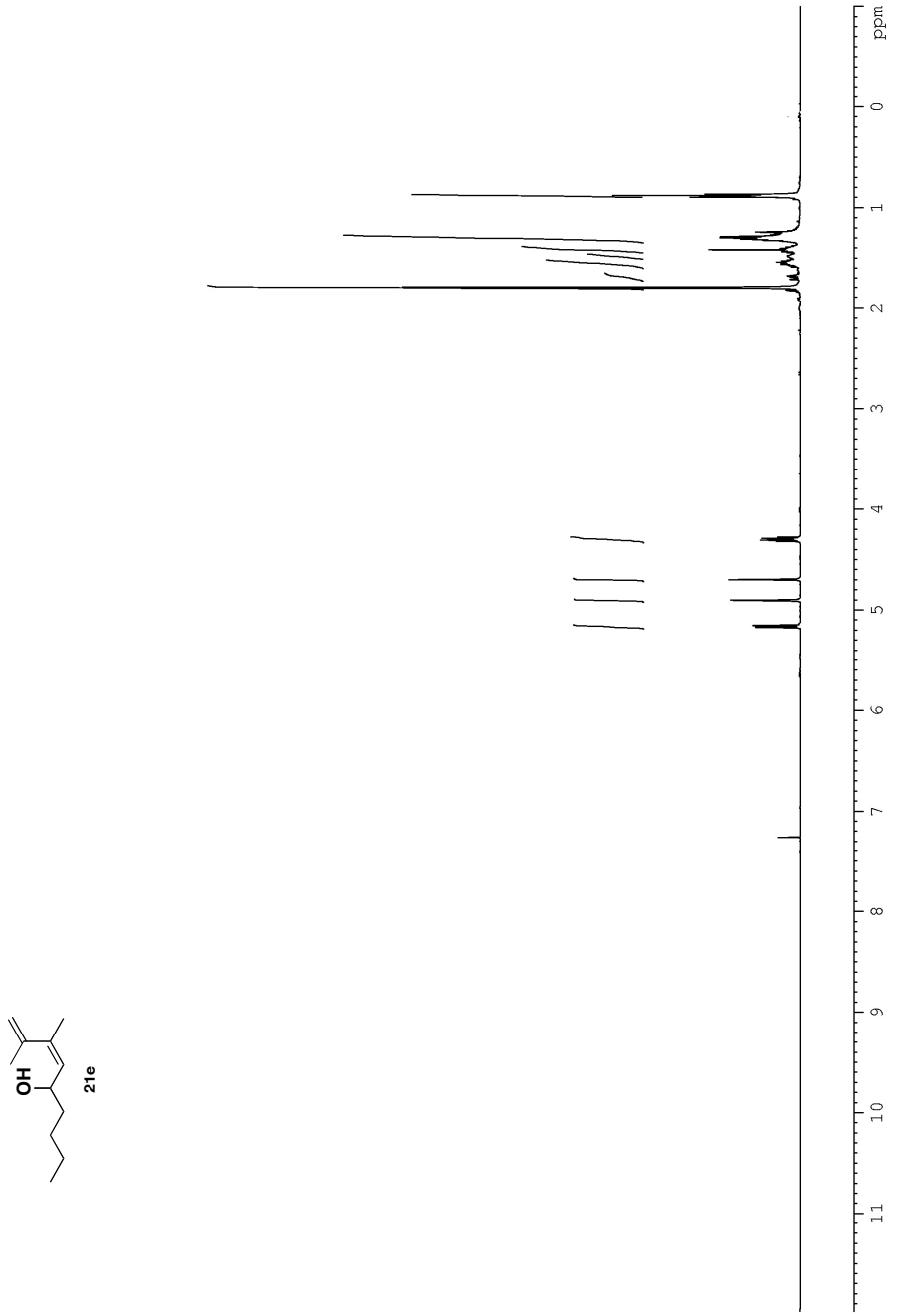
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21e
ppm
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10
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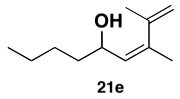
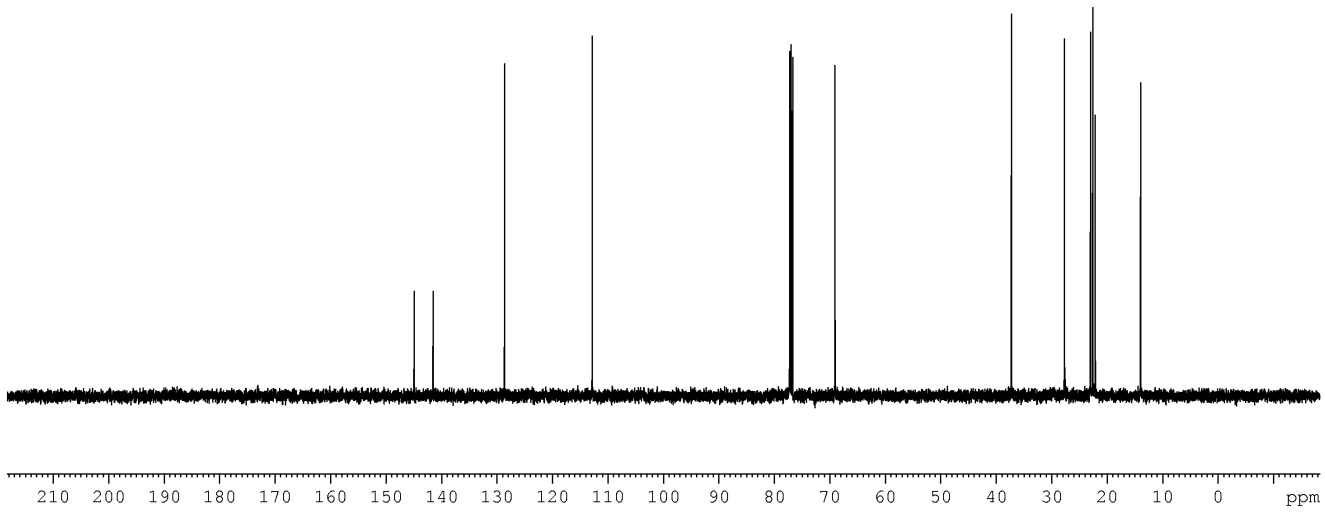

OH

21e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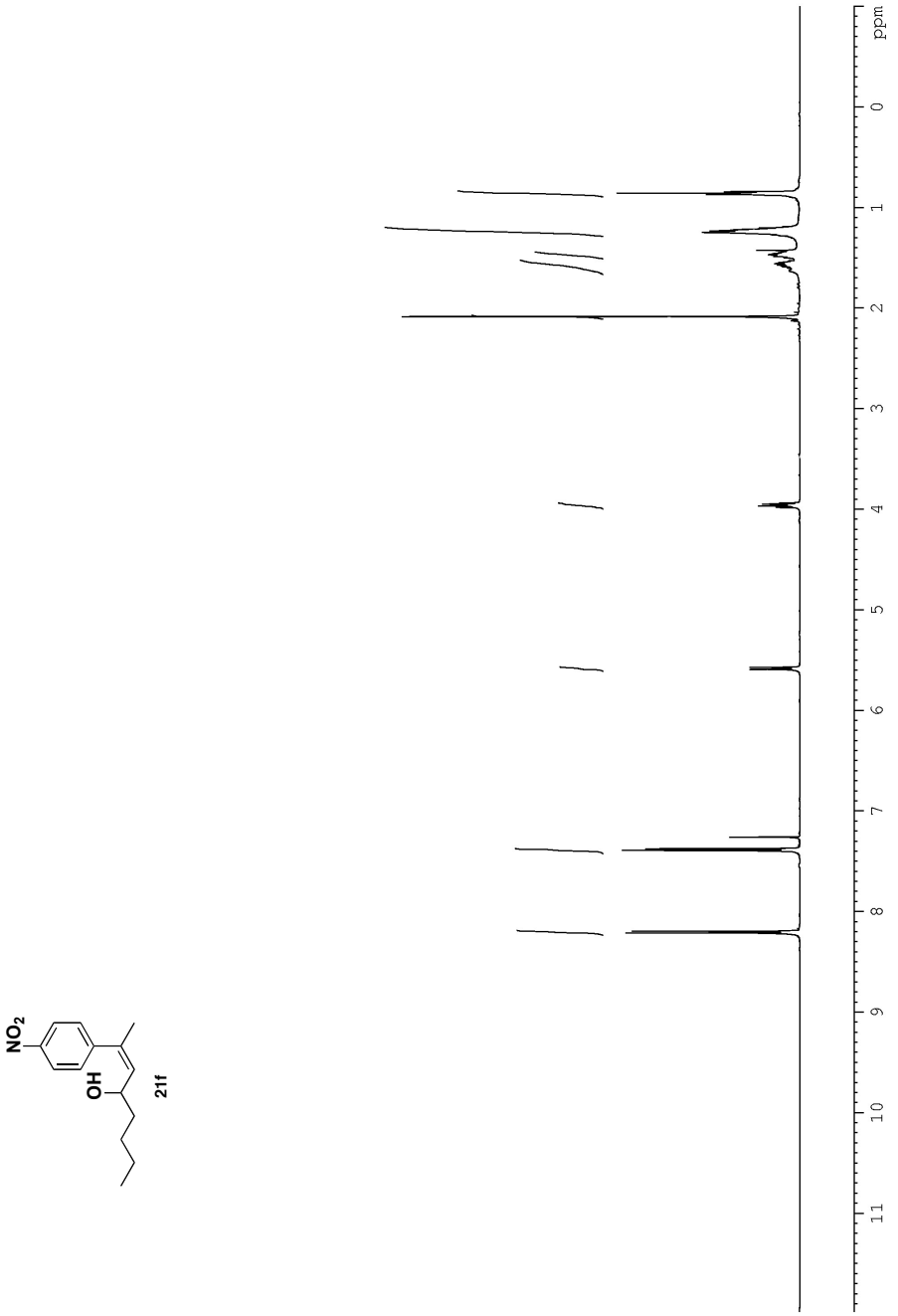
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OH
21f
ppm
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4
5
6
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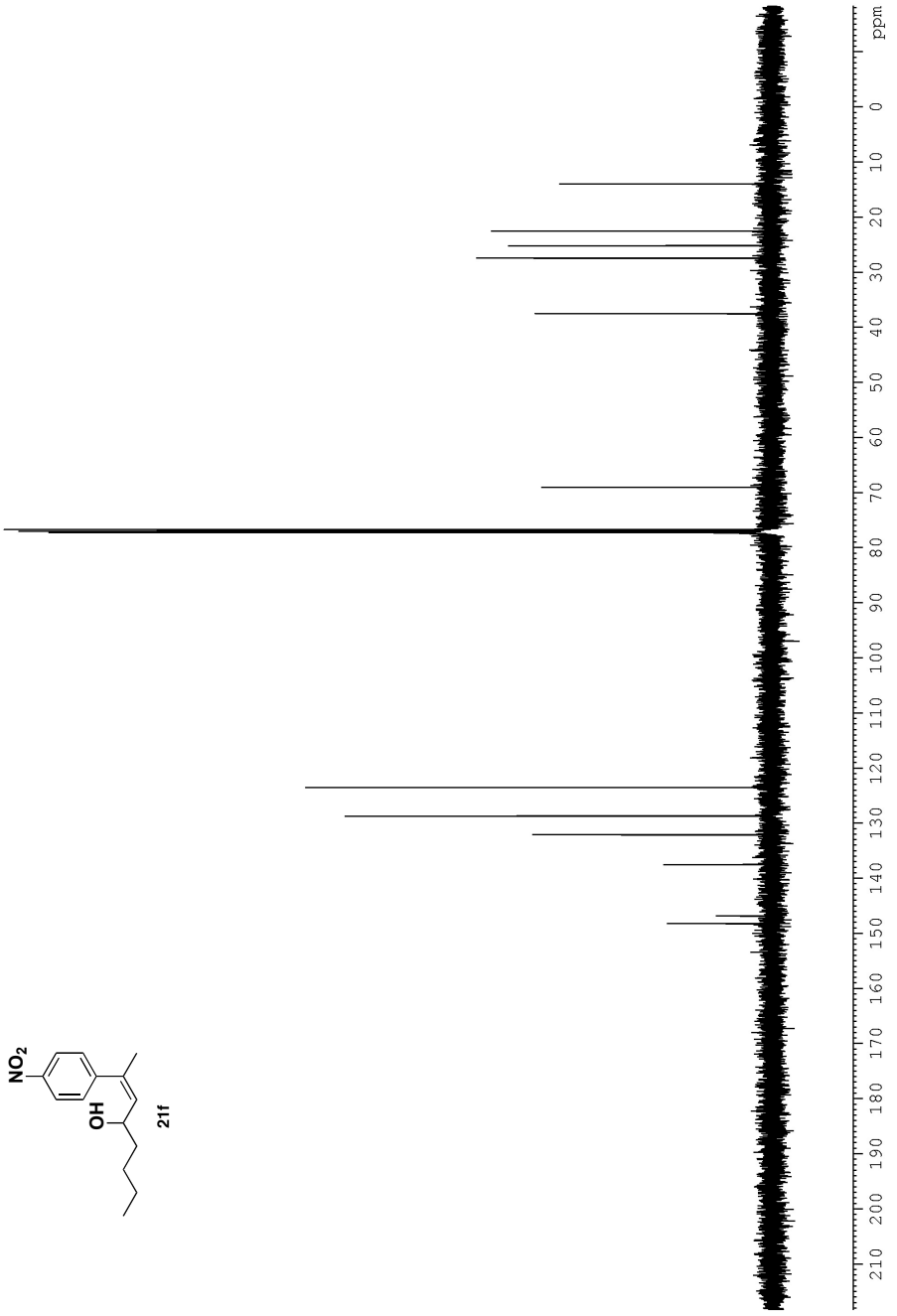
8
9
10
11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21f
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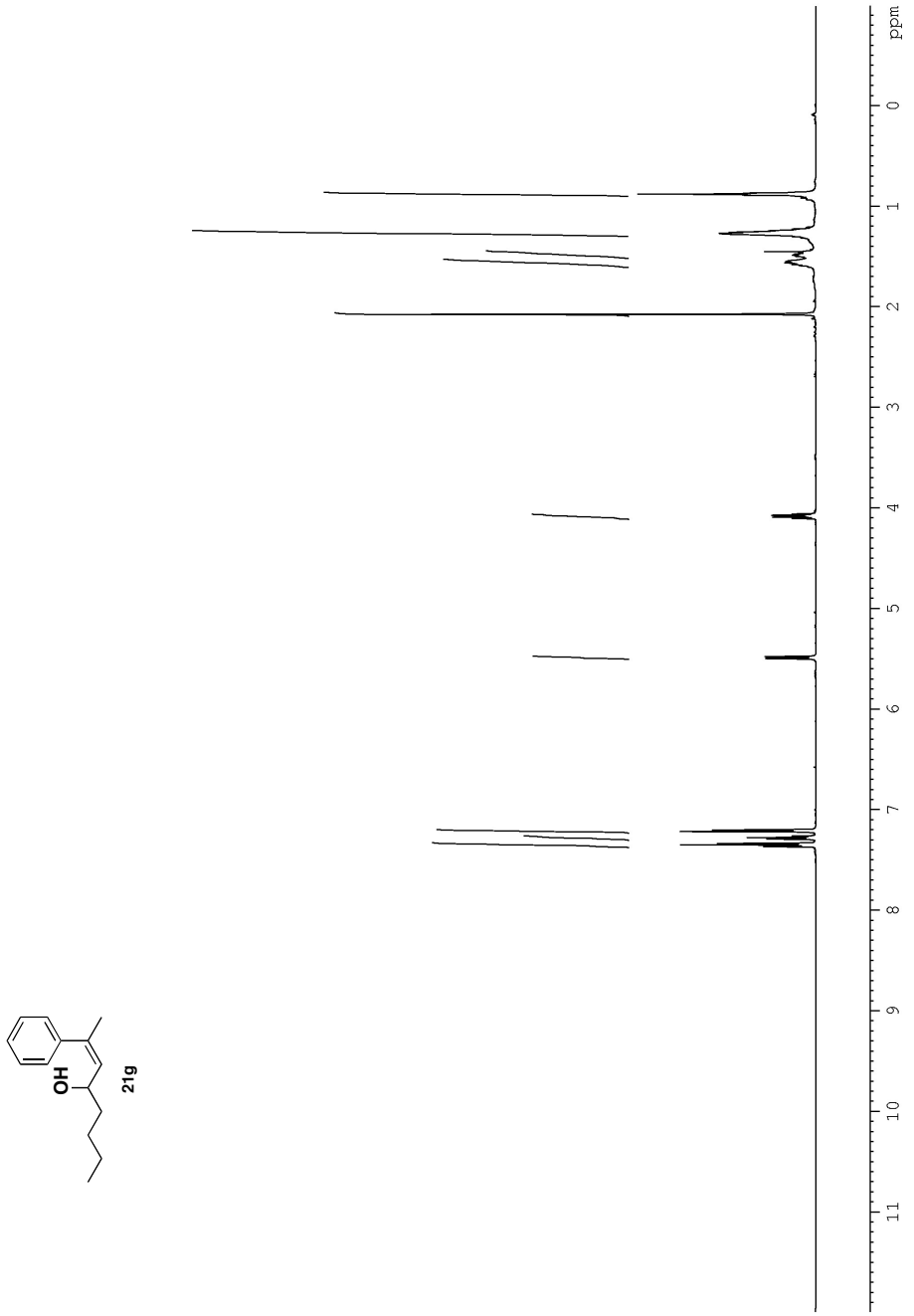
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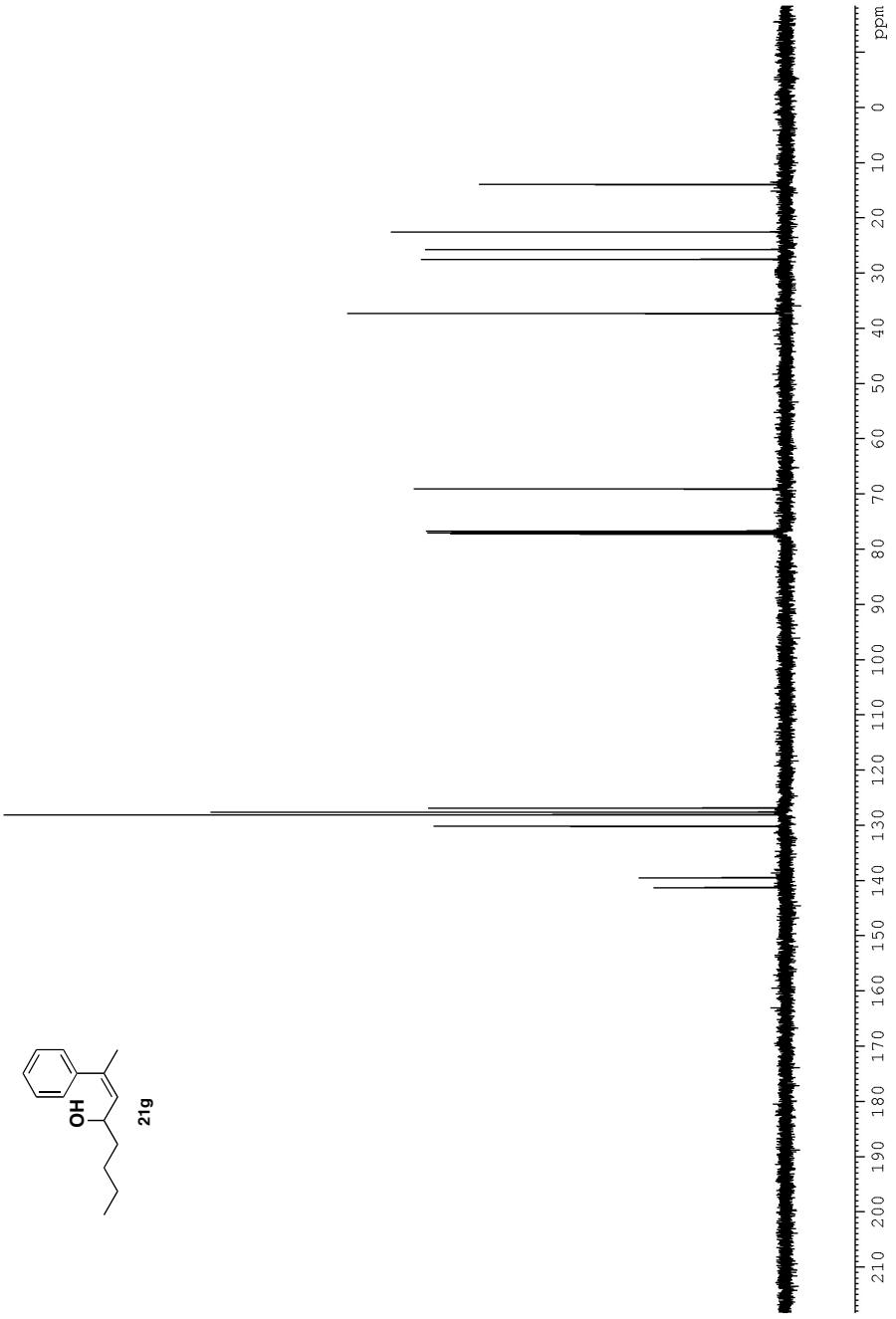
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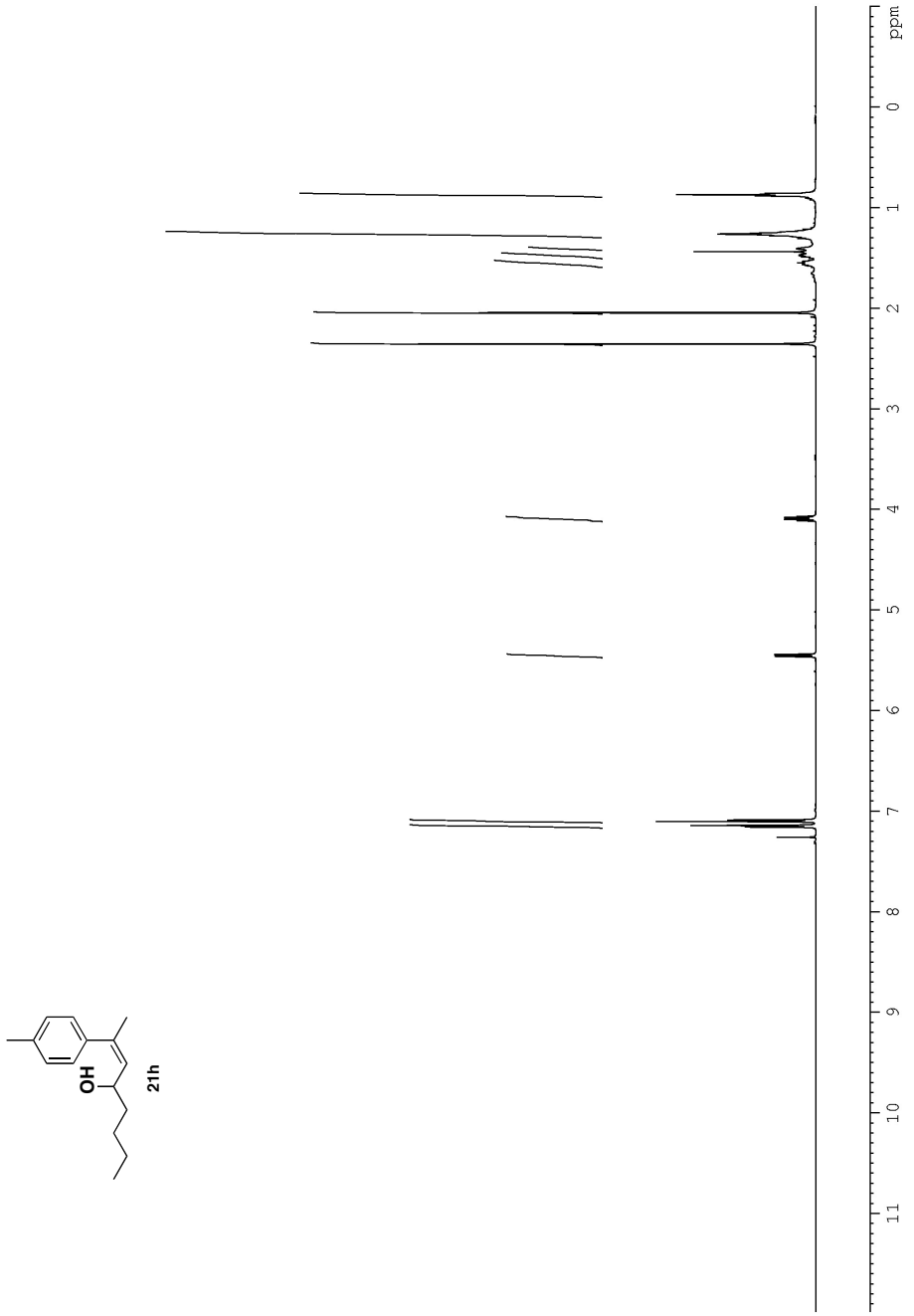
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OH
21h
ppm
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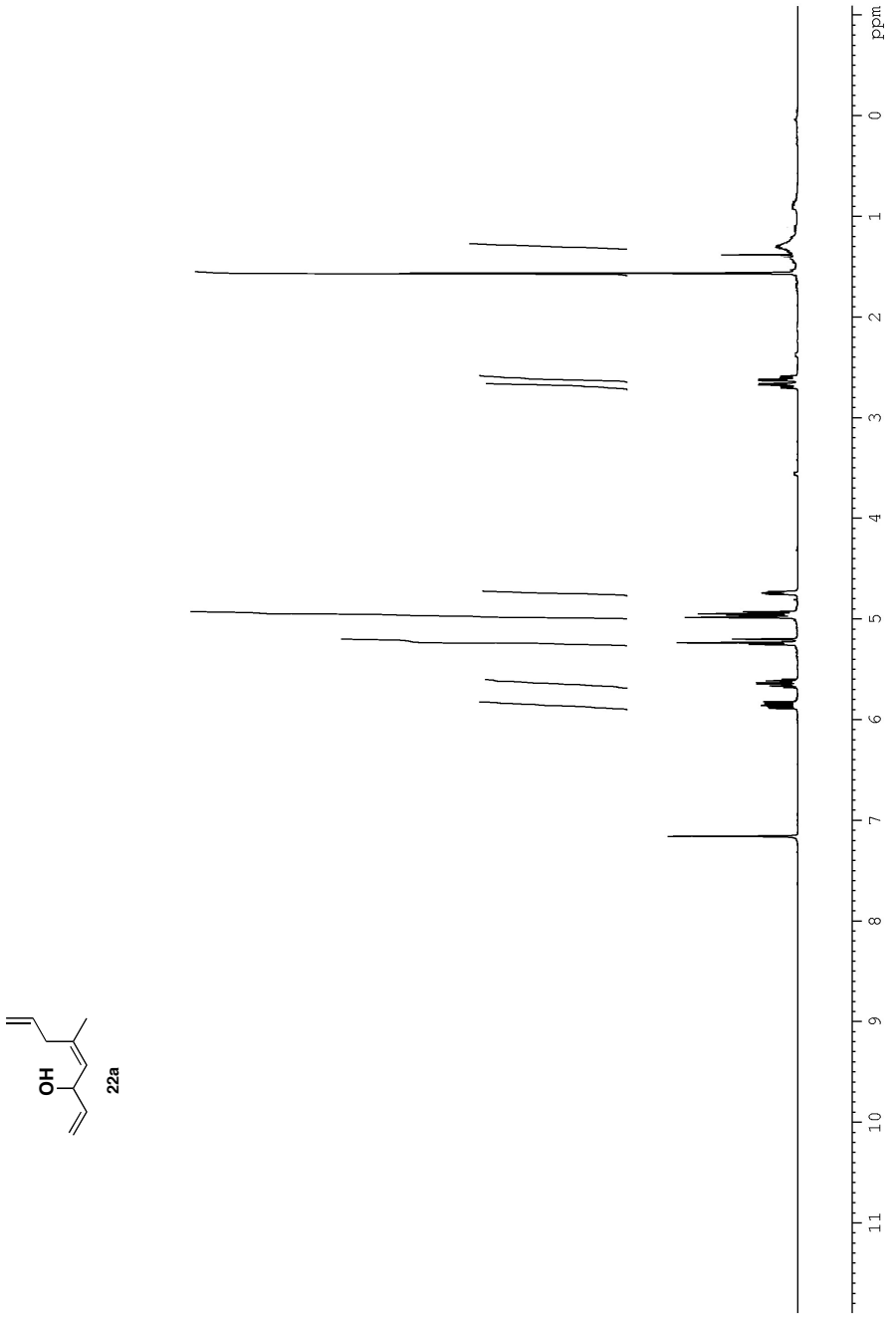
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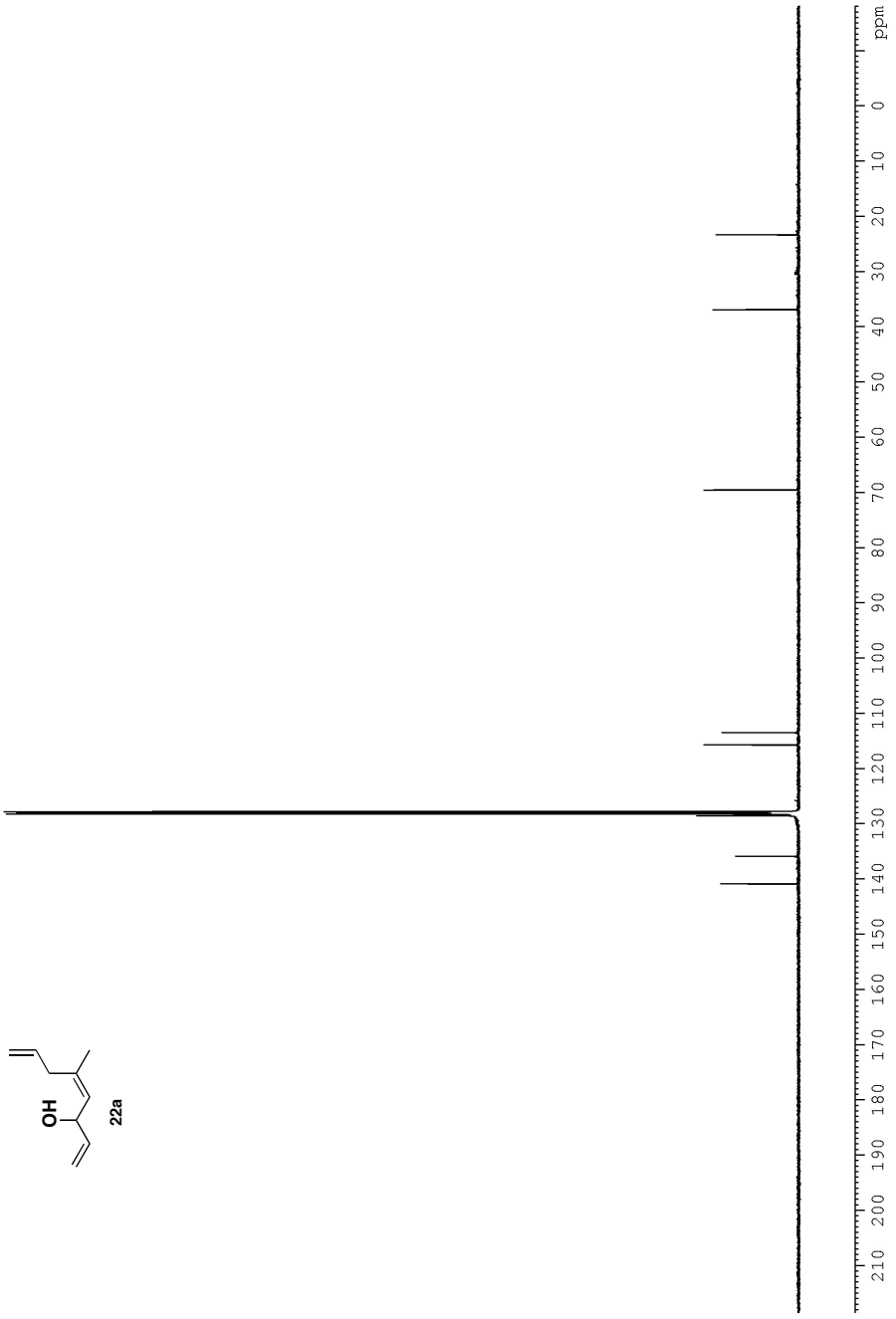
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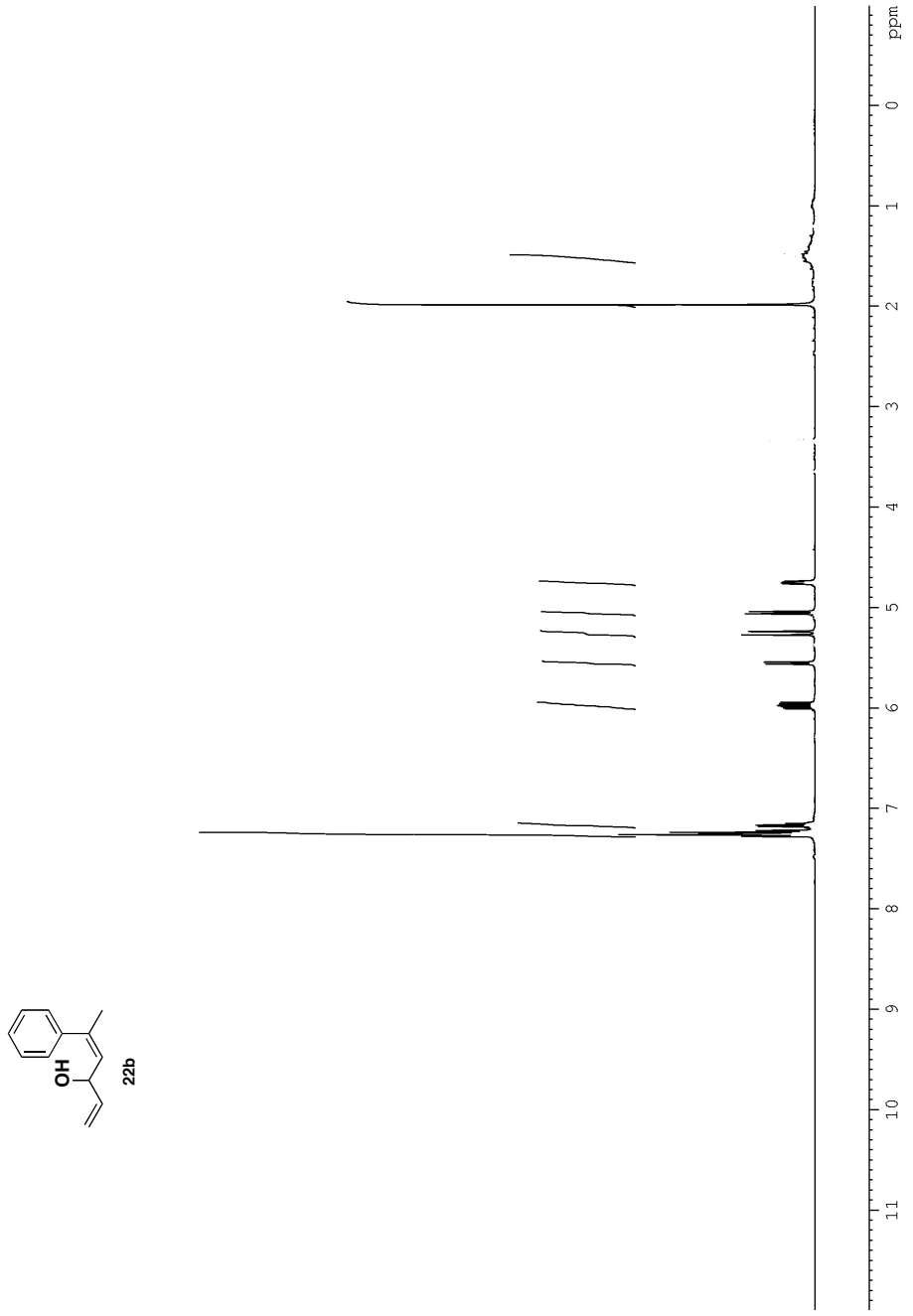
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22b
ppm
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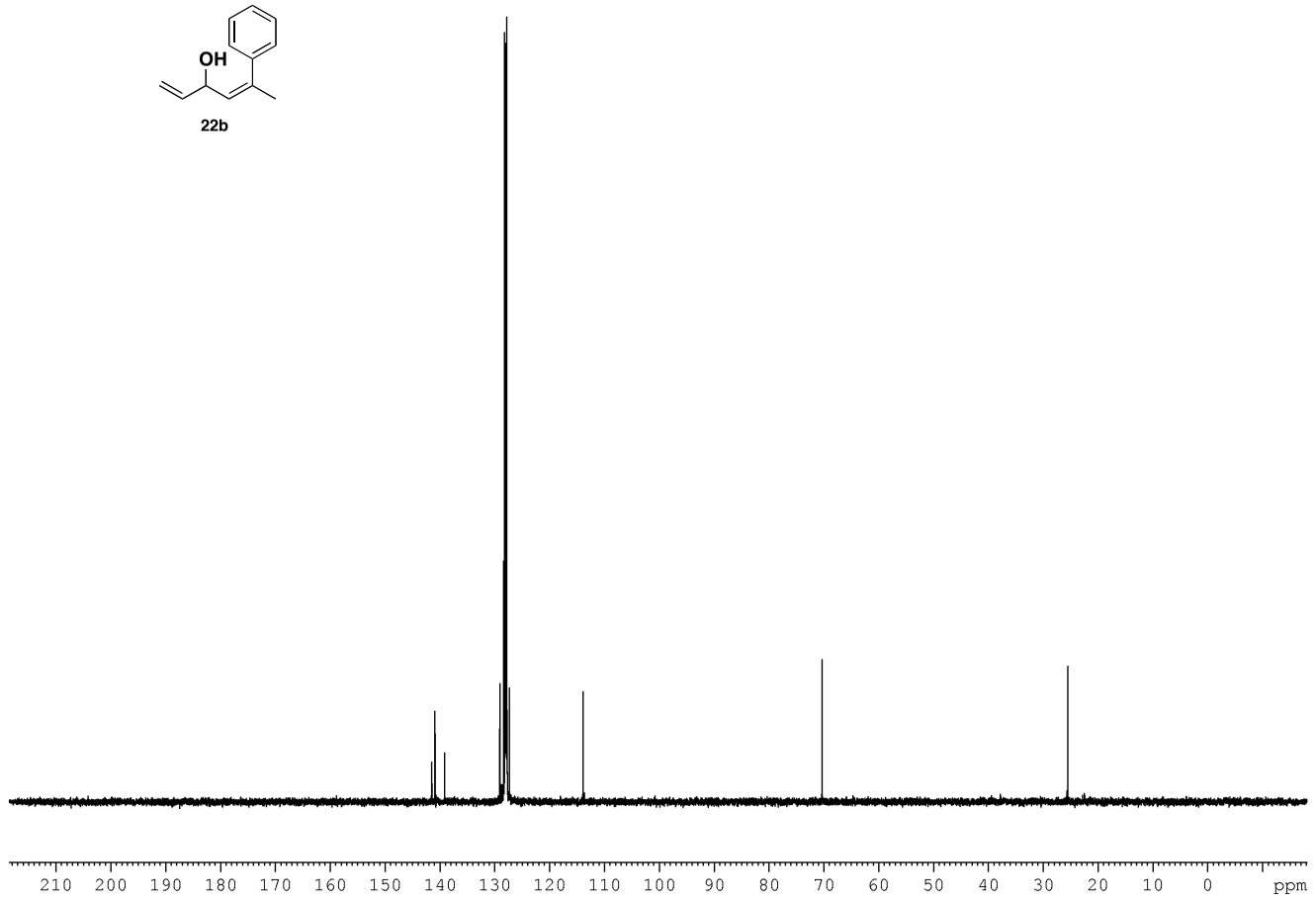
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22b
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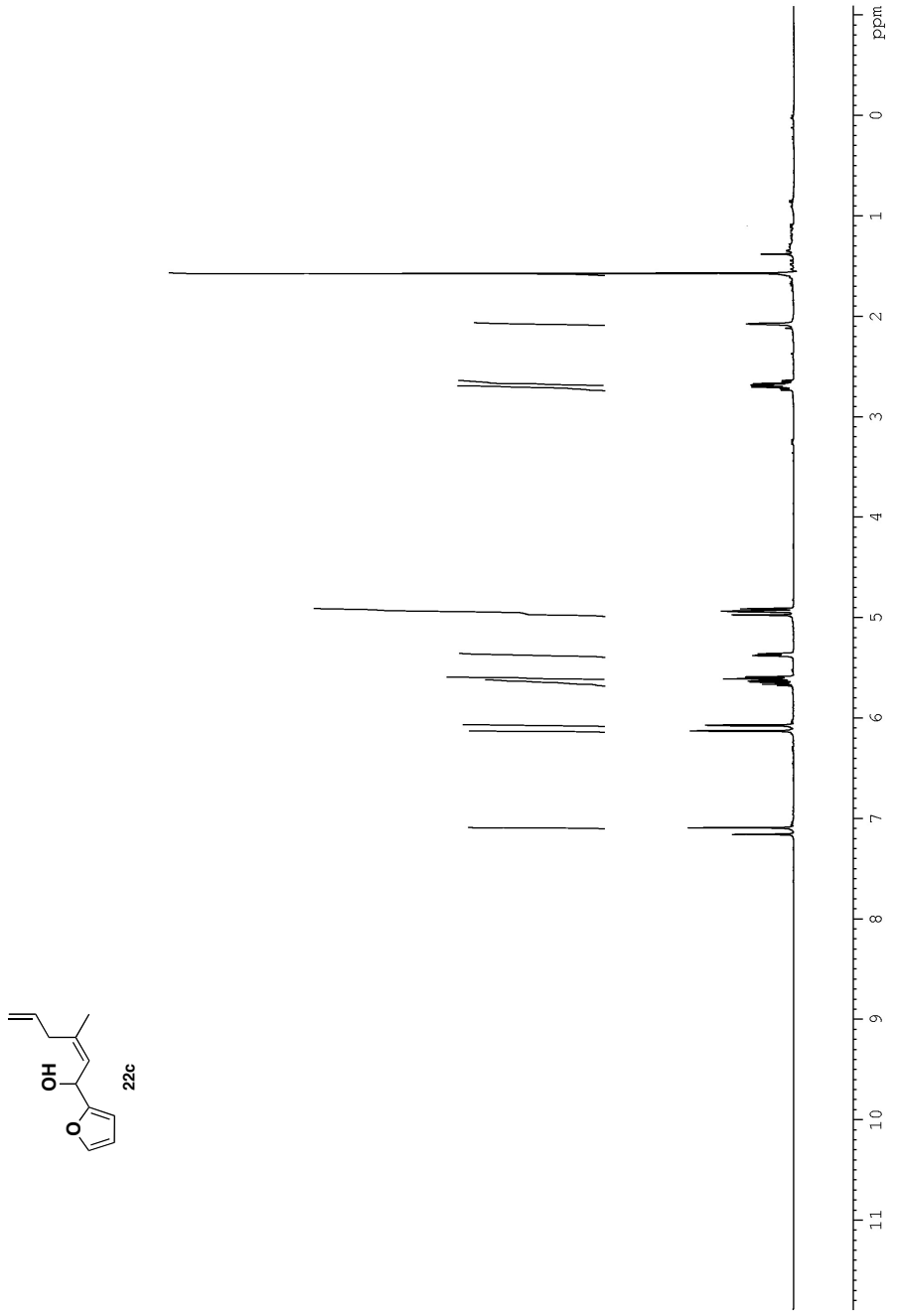
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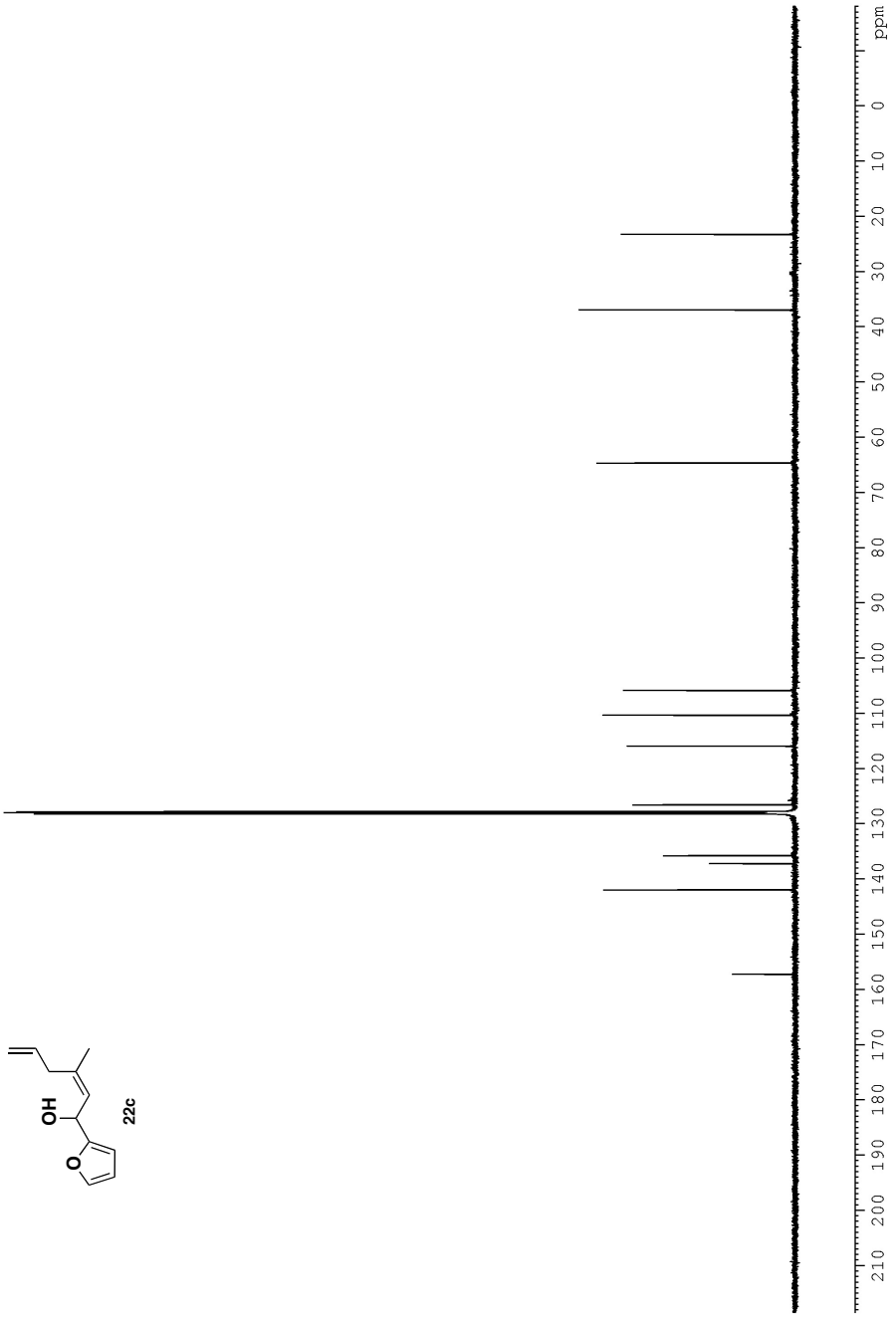
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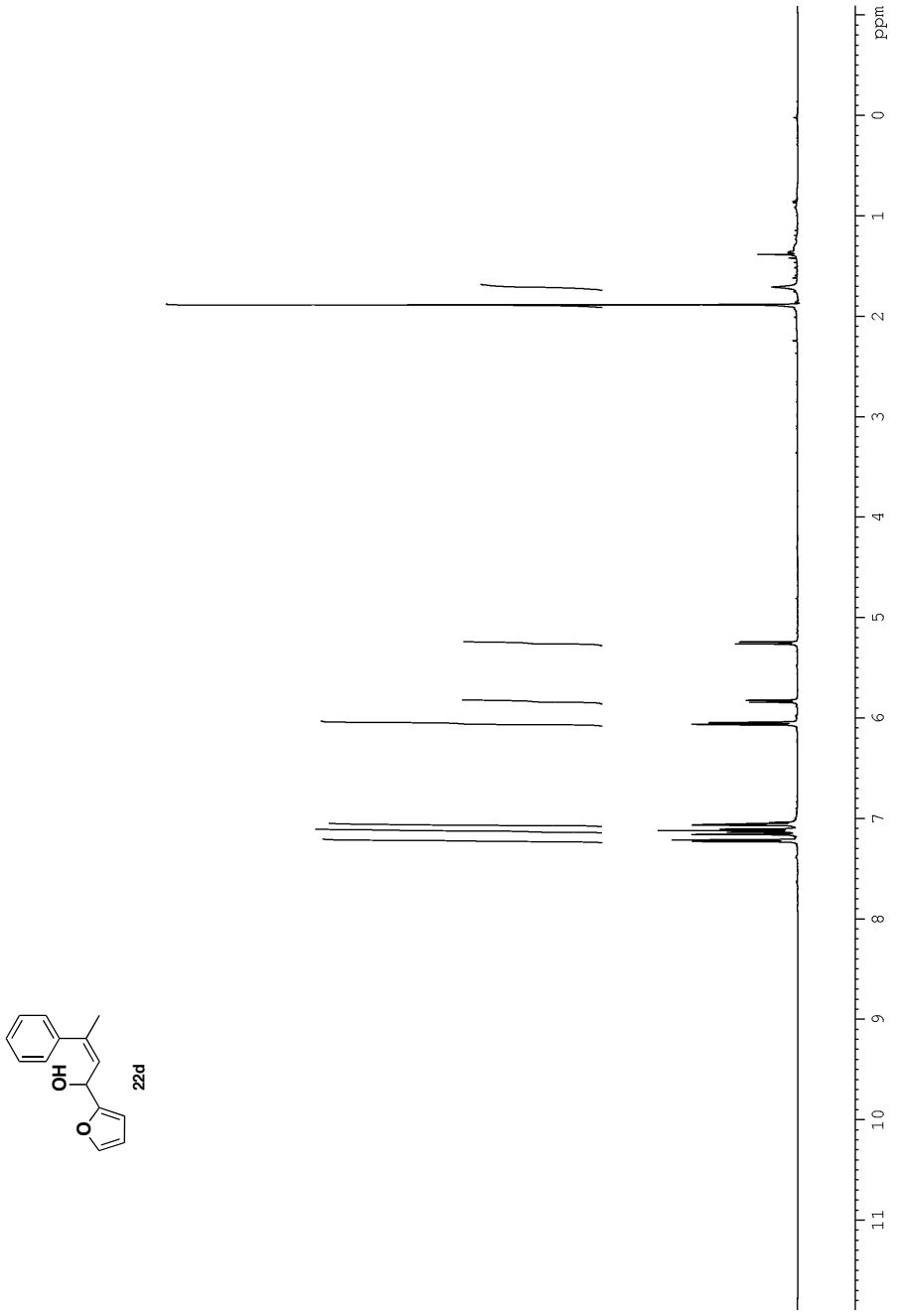
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O
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ppm
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11

OH
O
22d
ppm
210
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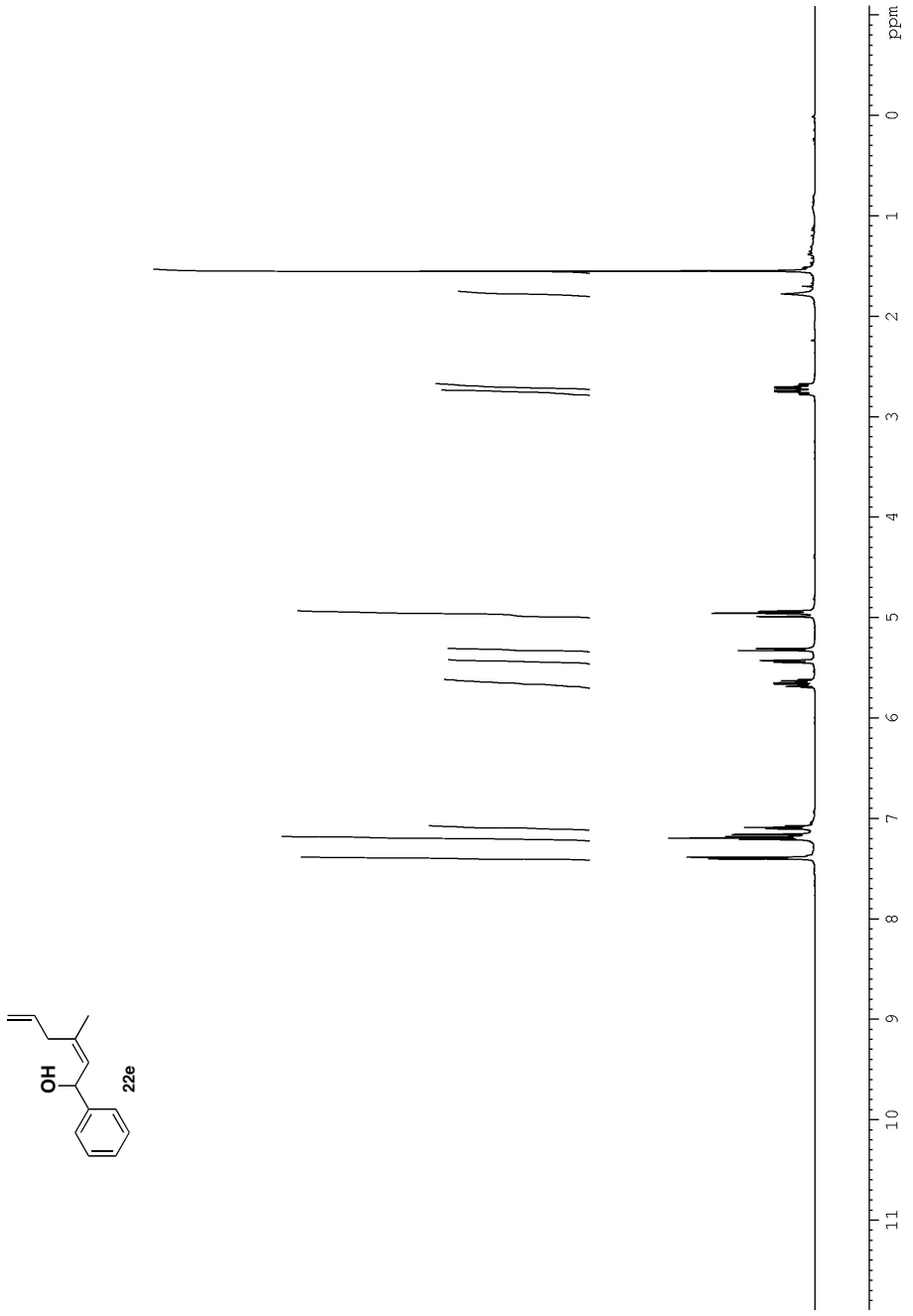
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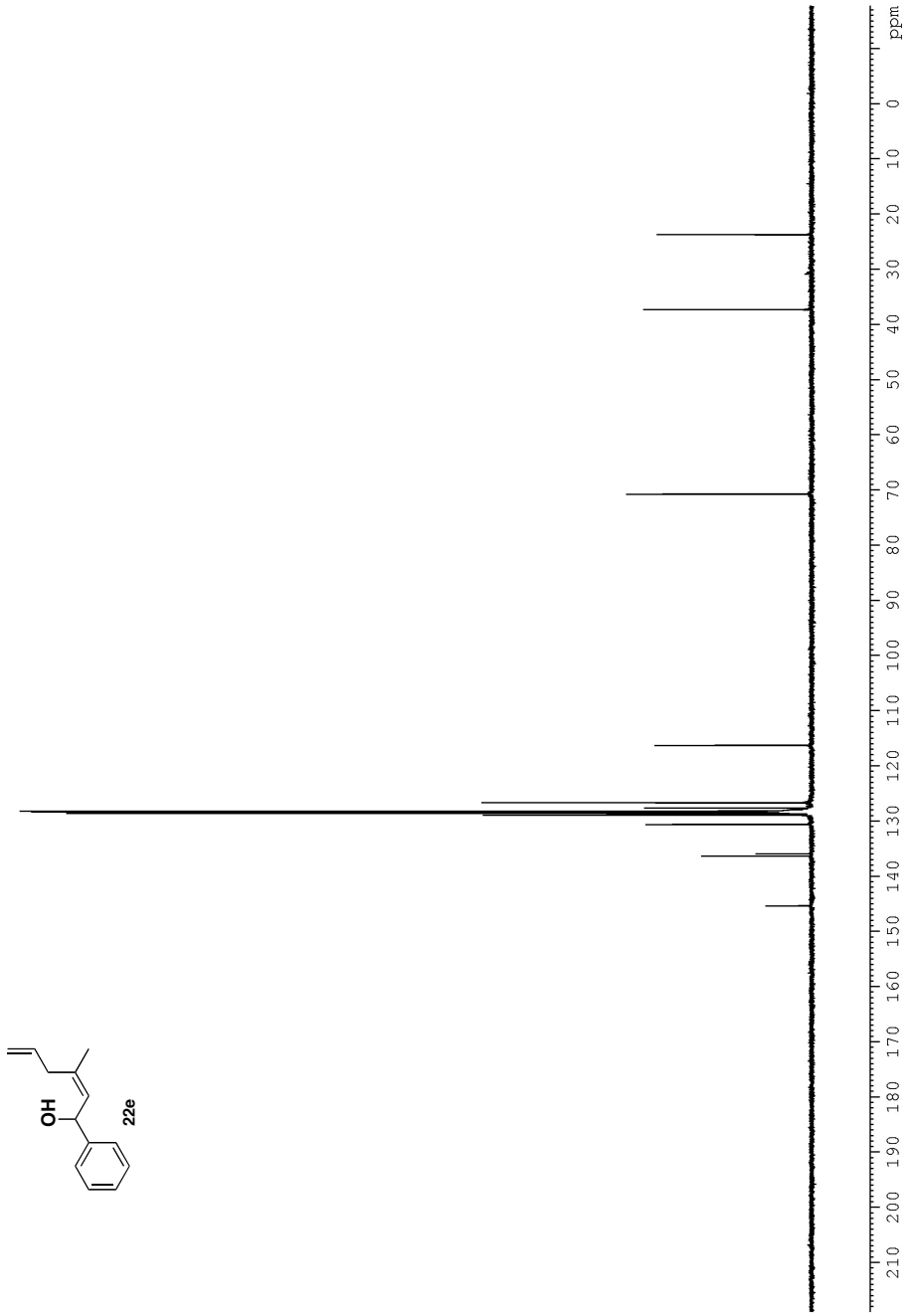
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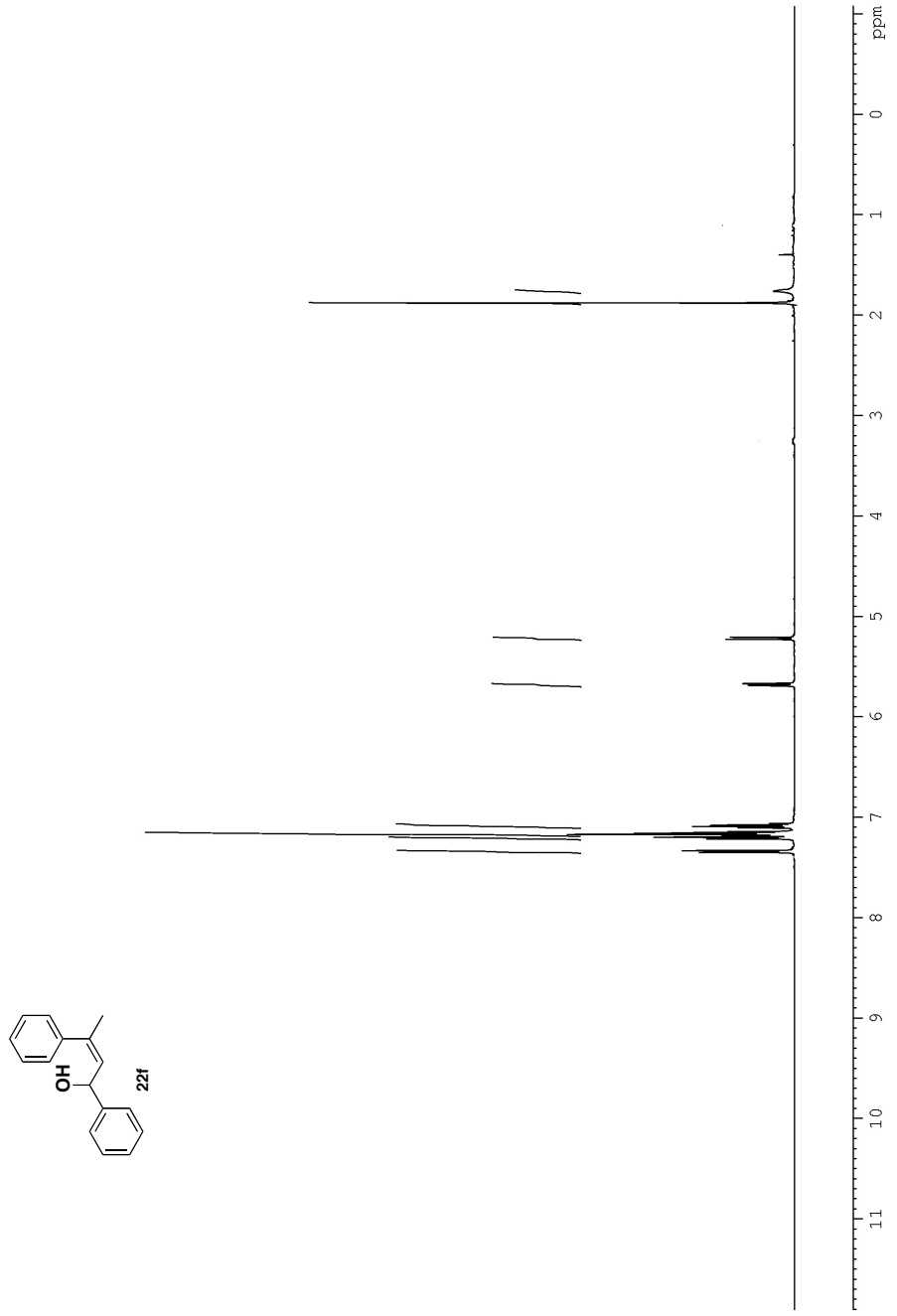
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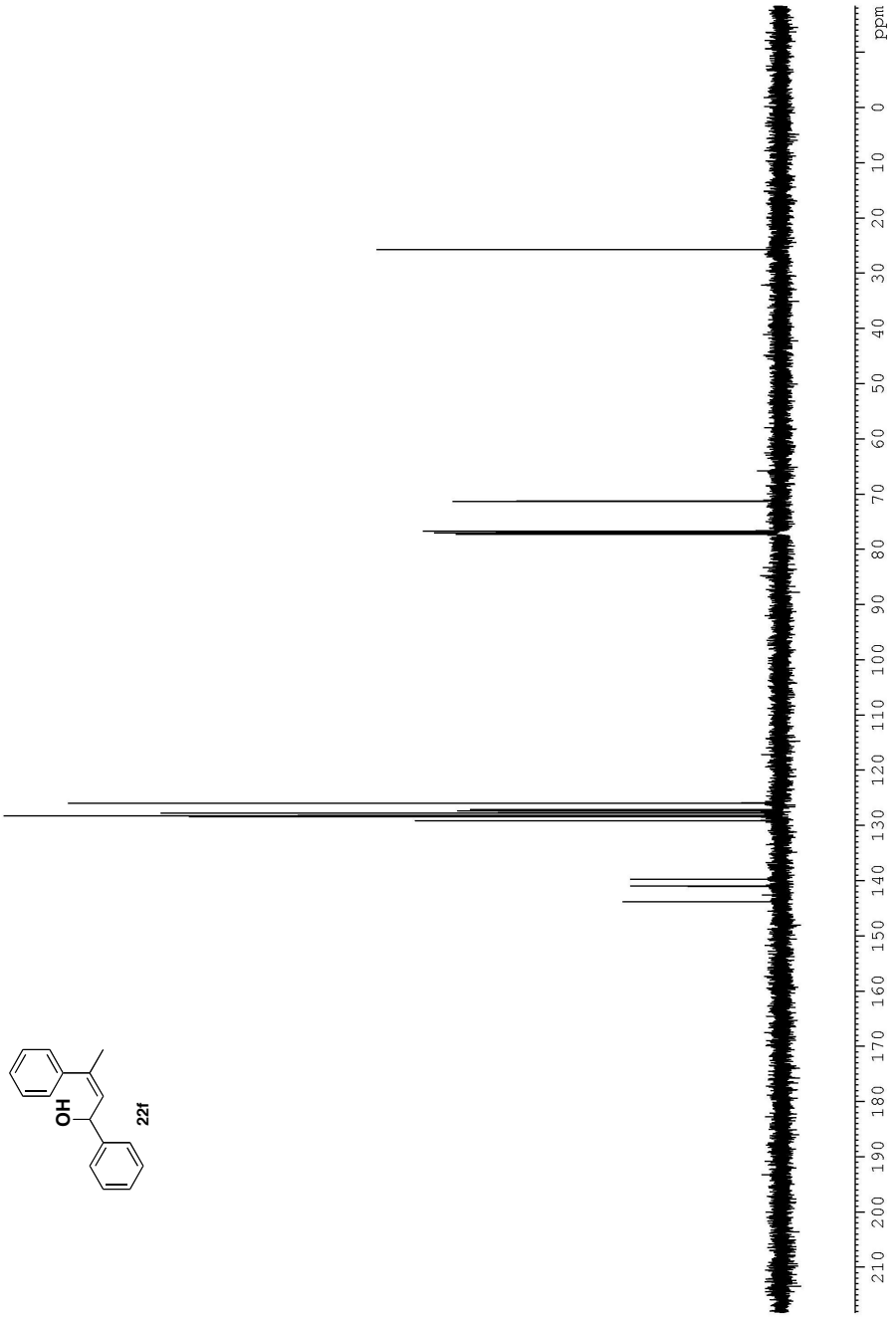
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22f
ppm
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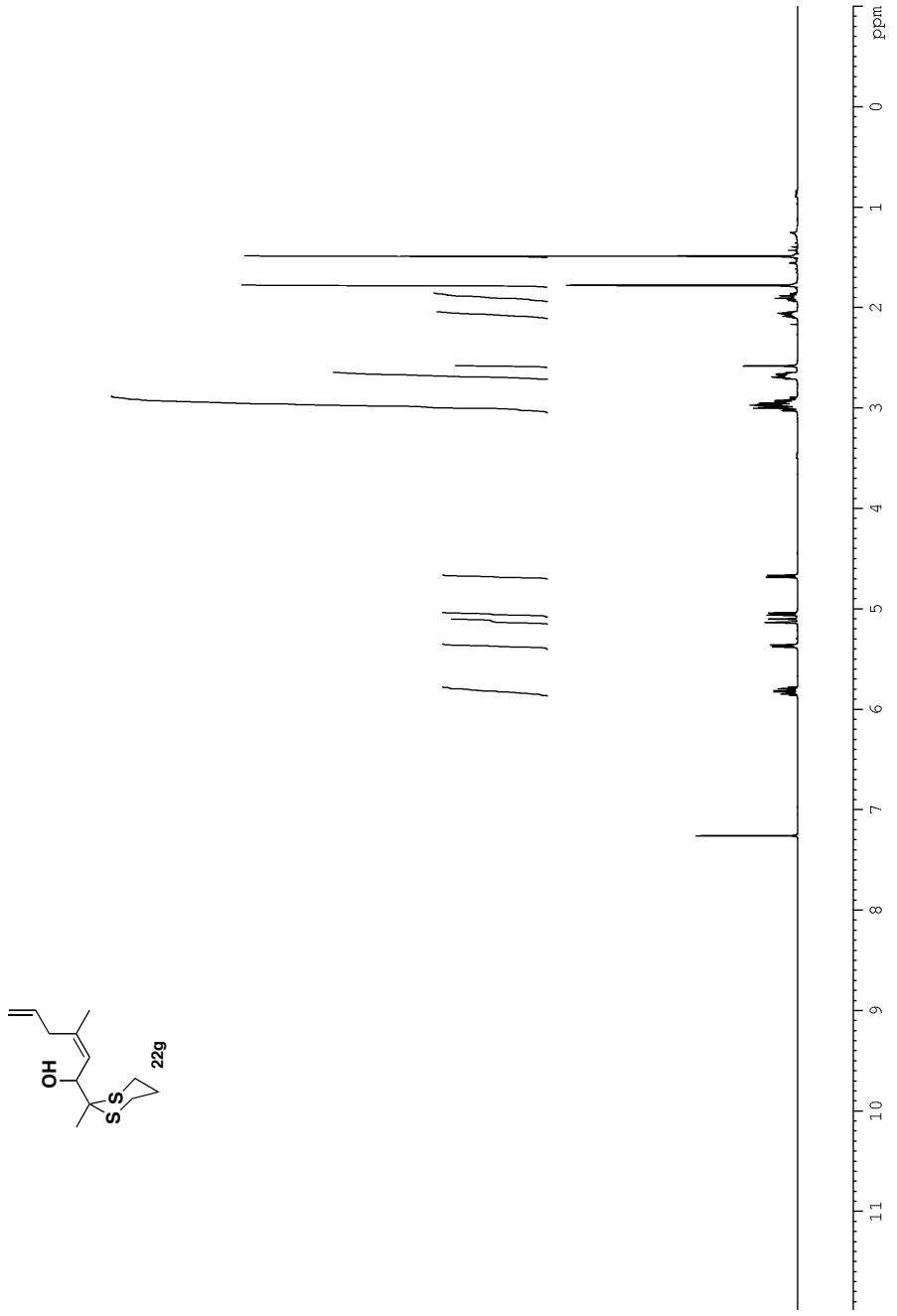
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S
S
22g
ppm
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6
7
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9
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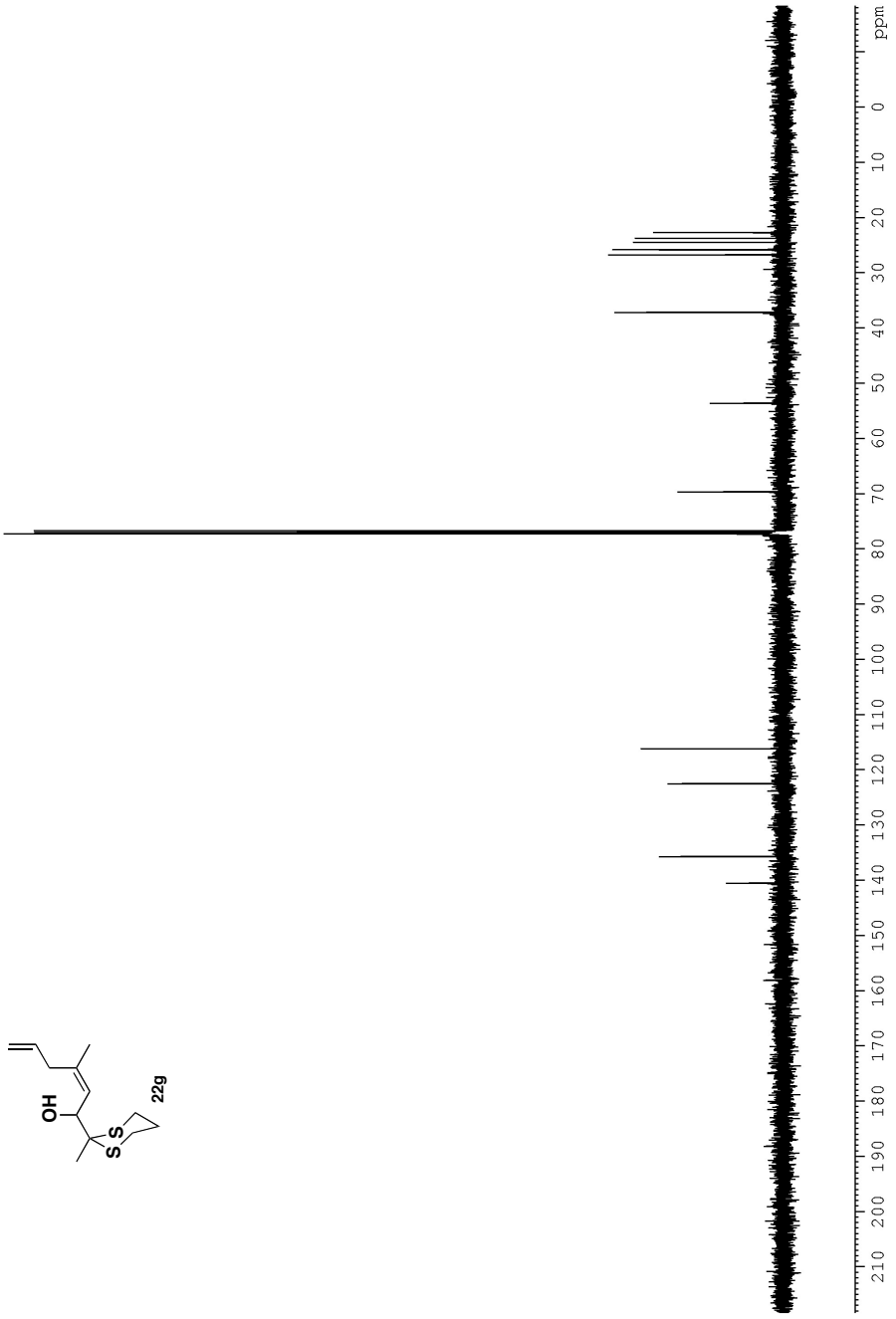
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S S
22g
ppm
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200
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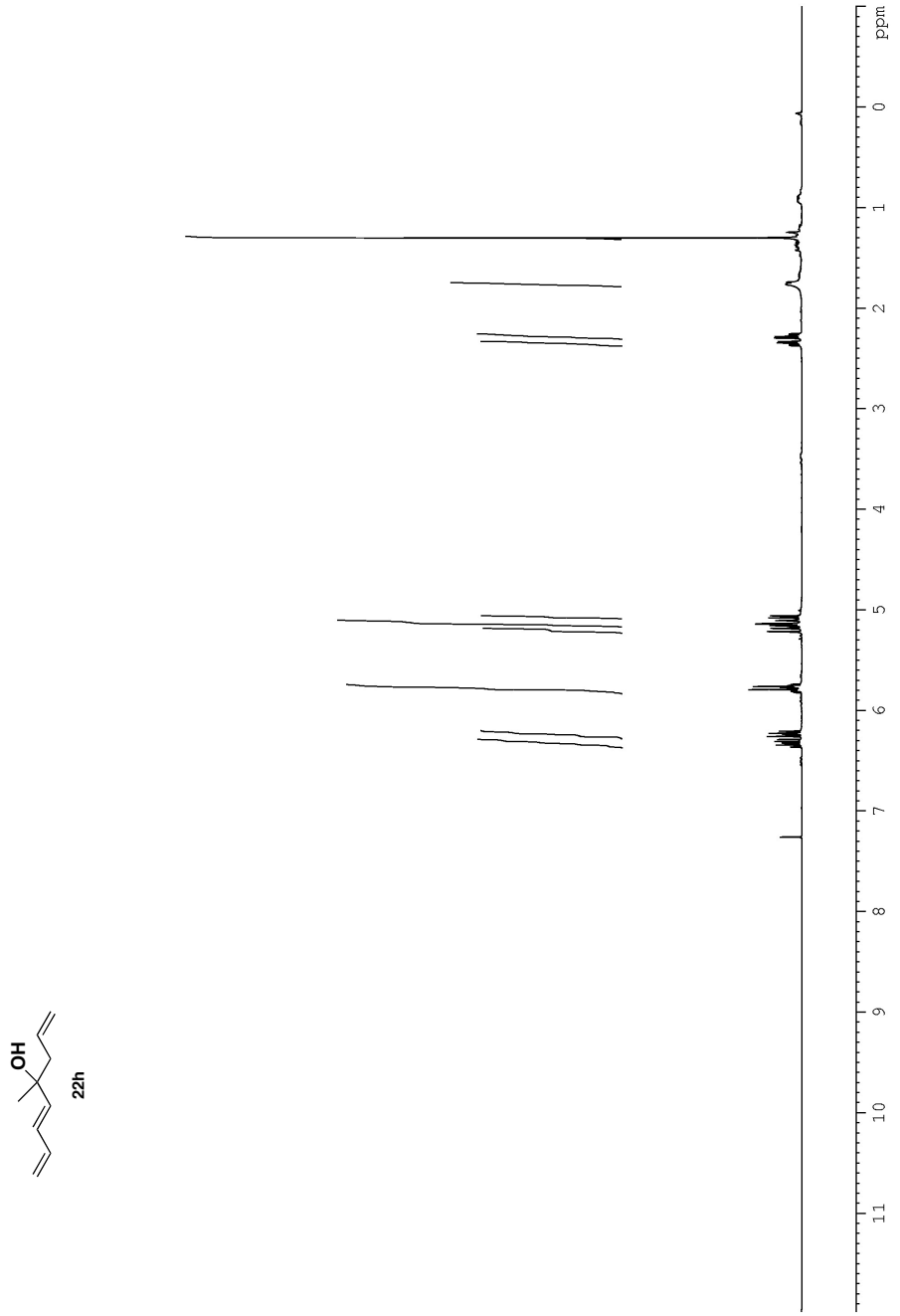
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22h
ppm
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OH
22h
ppm
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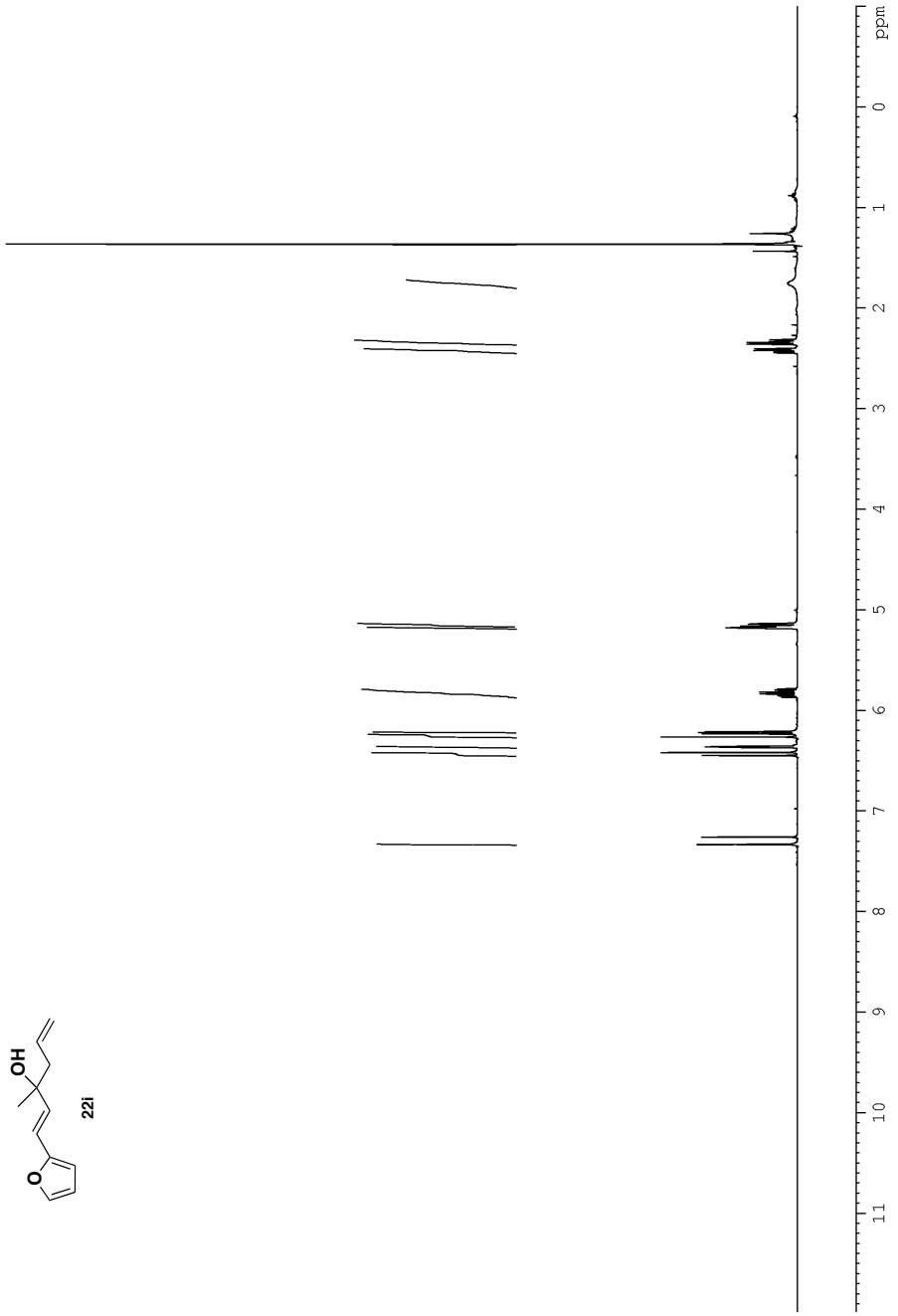
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22i
ppm
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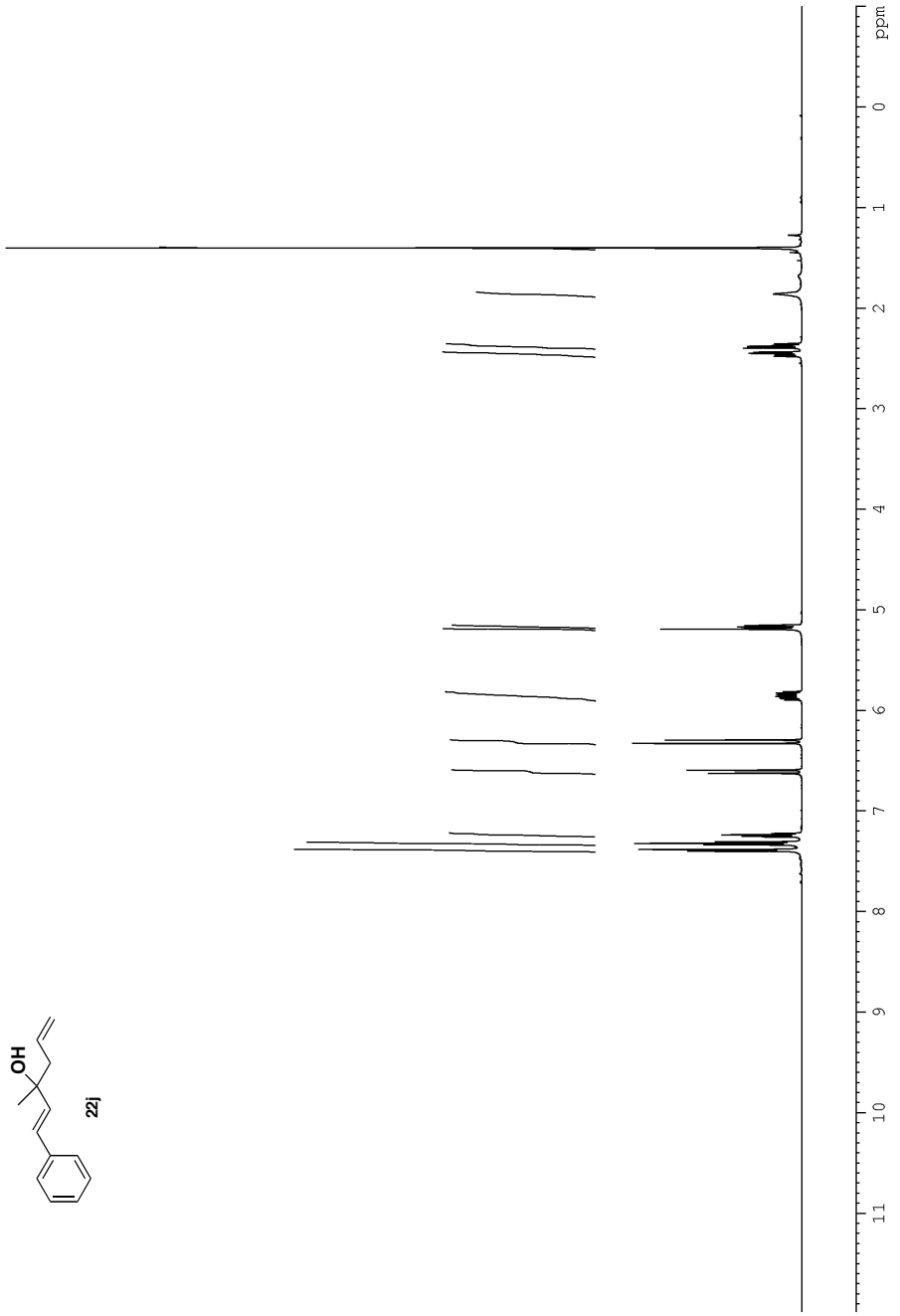
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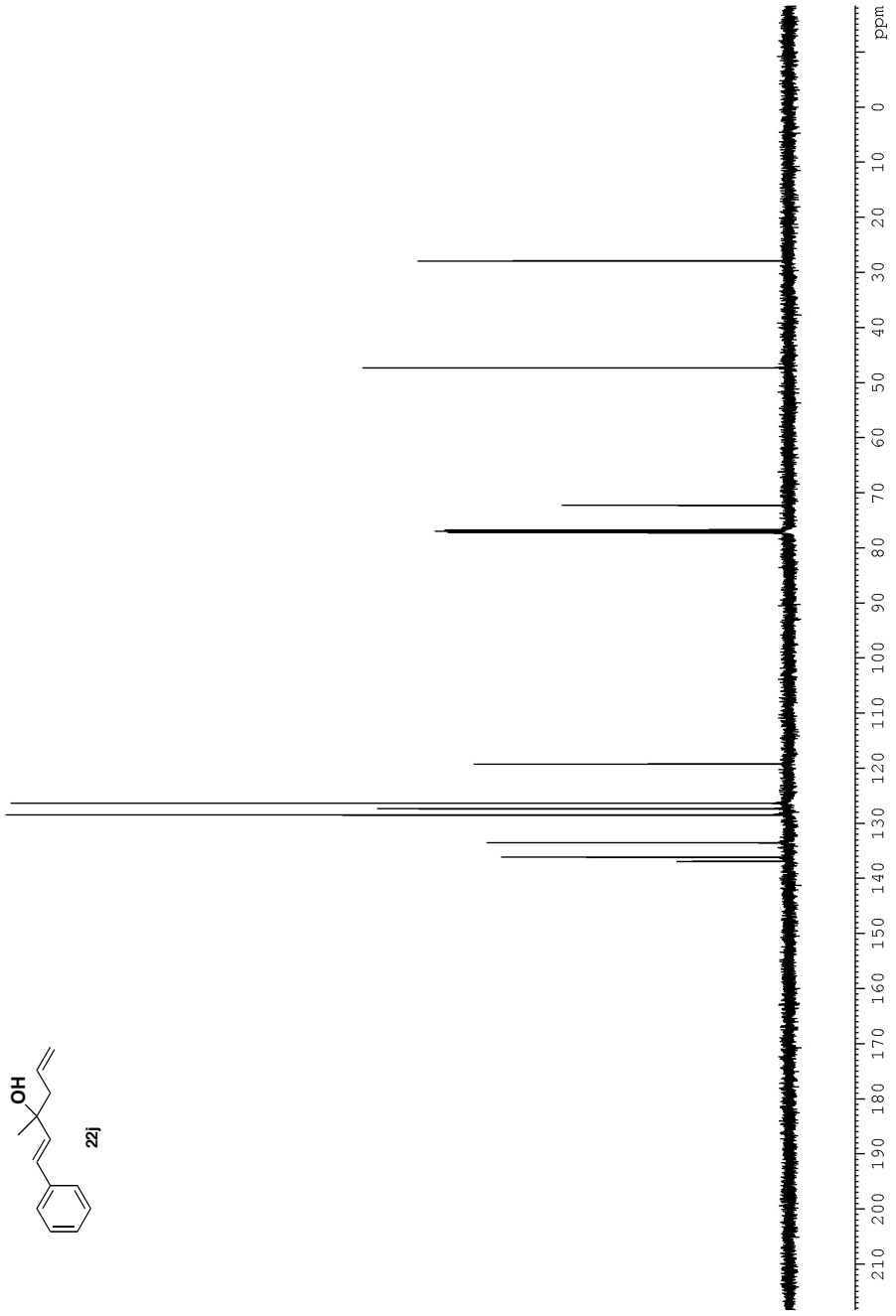
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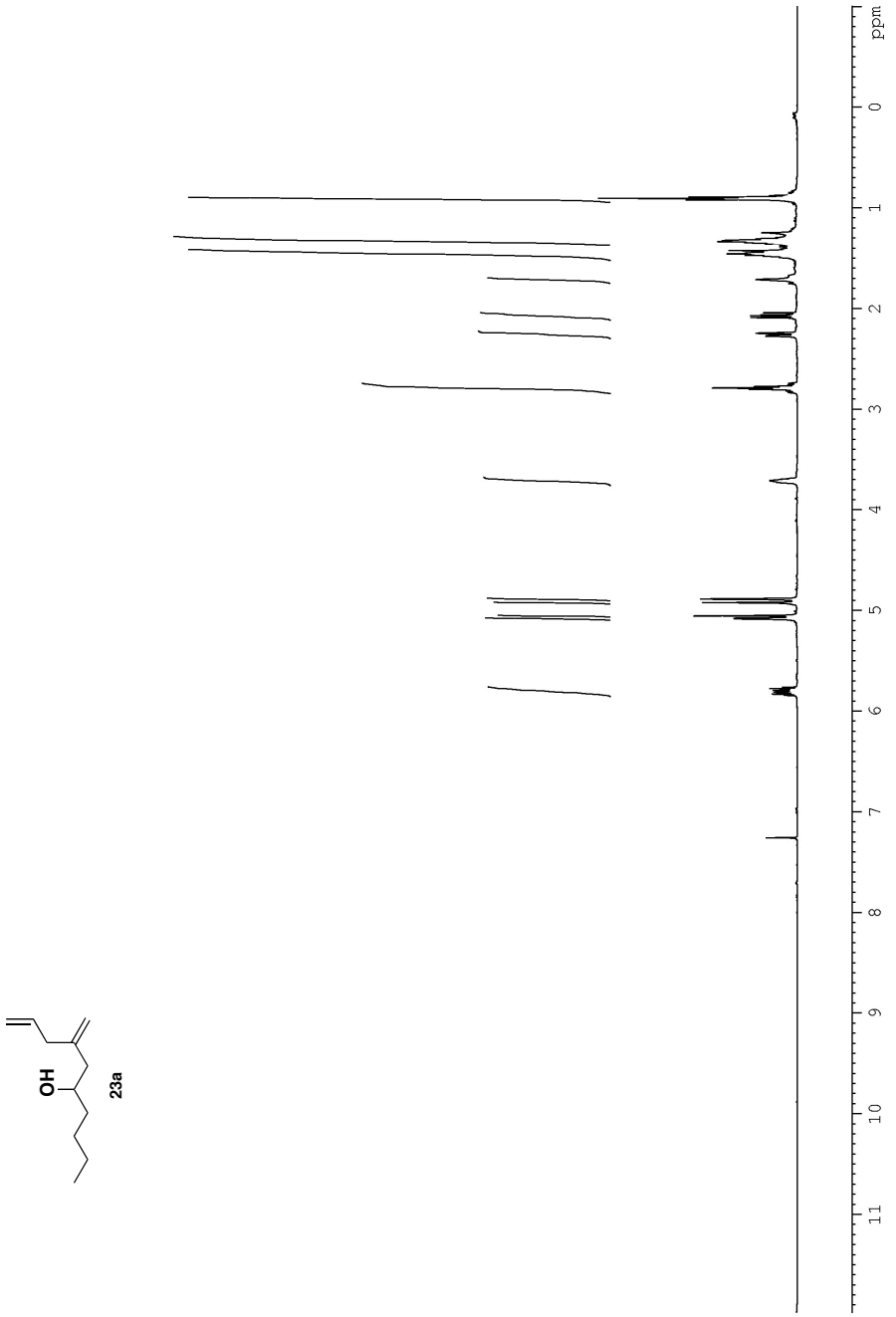
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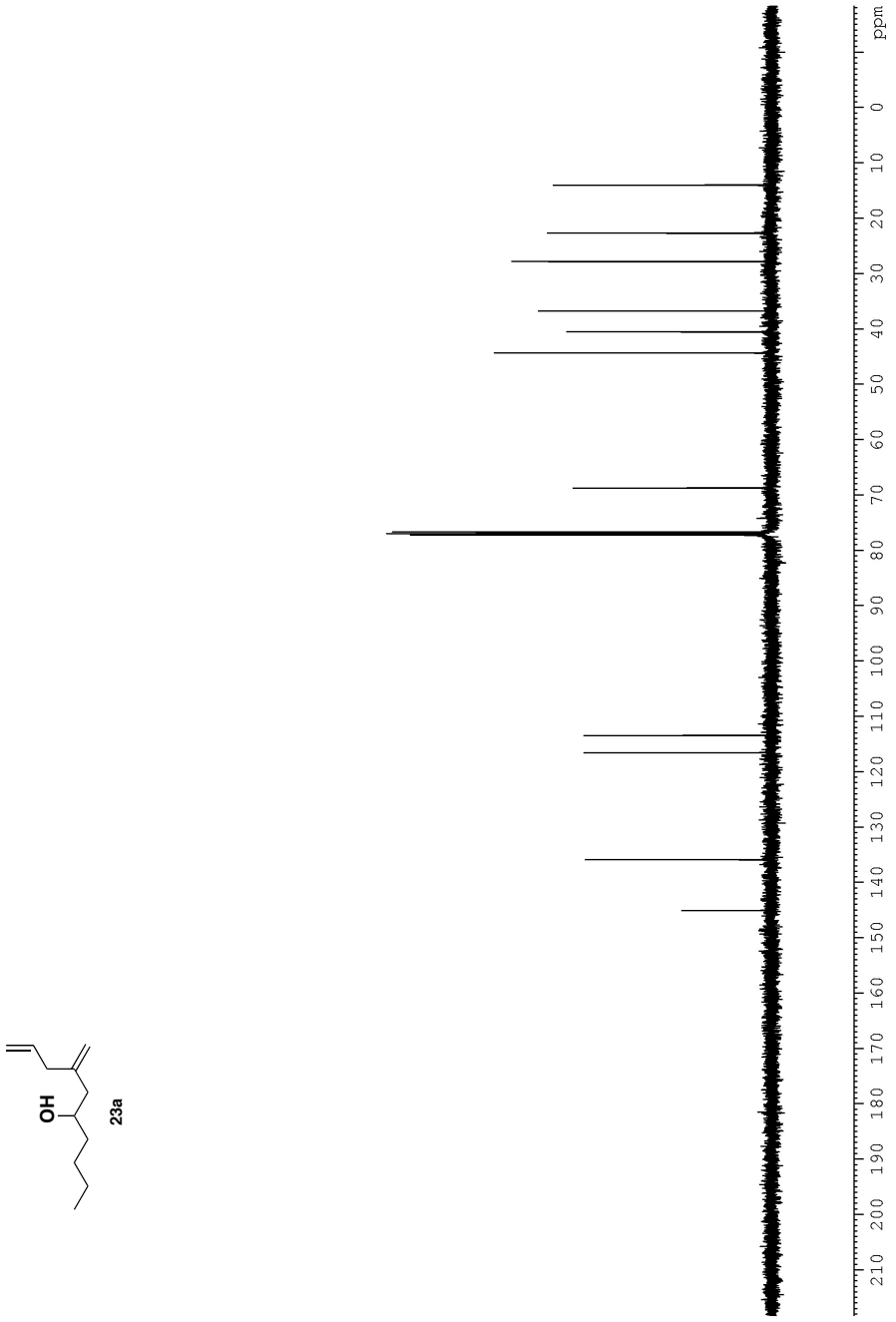
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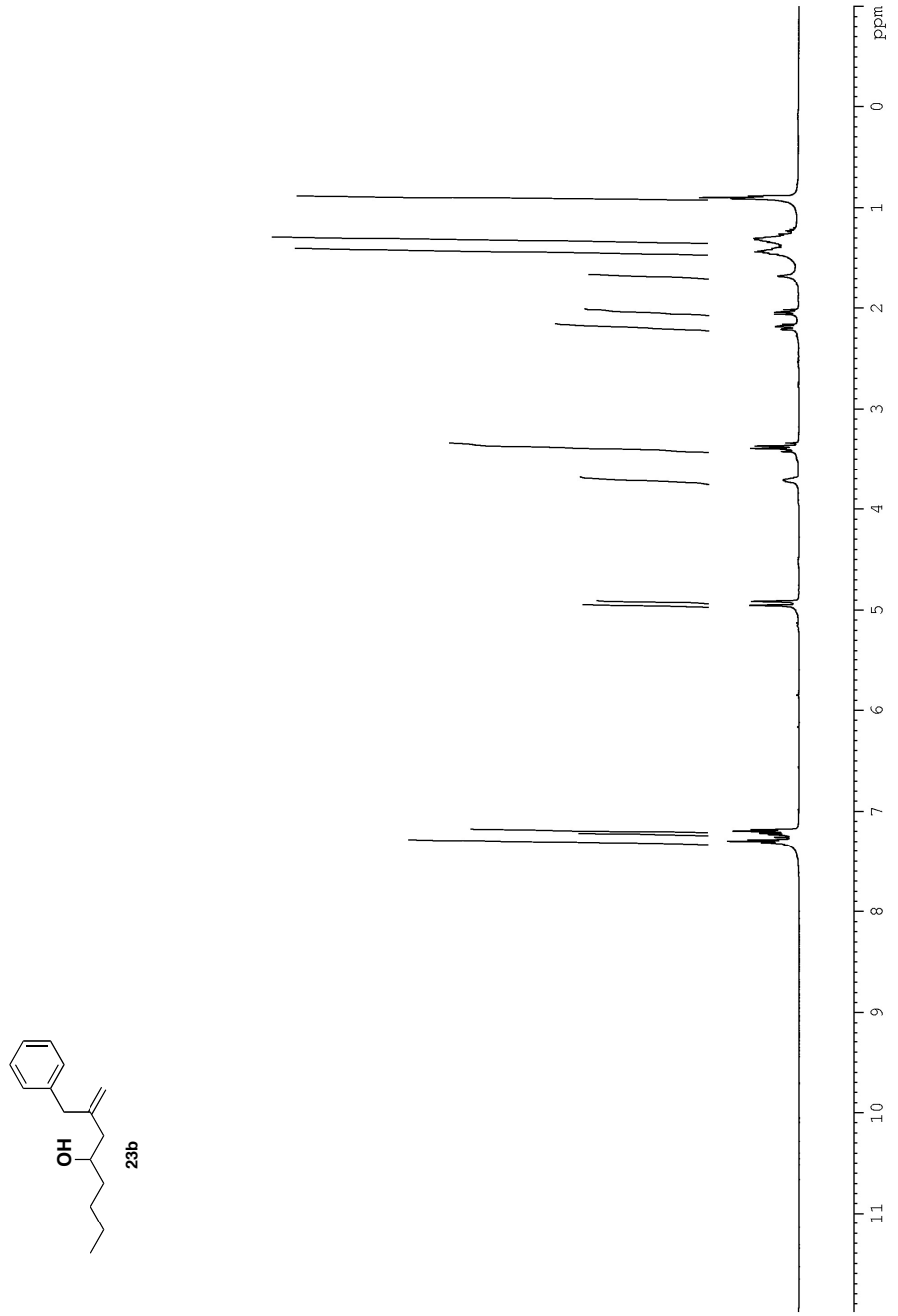
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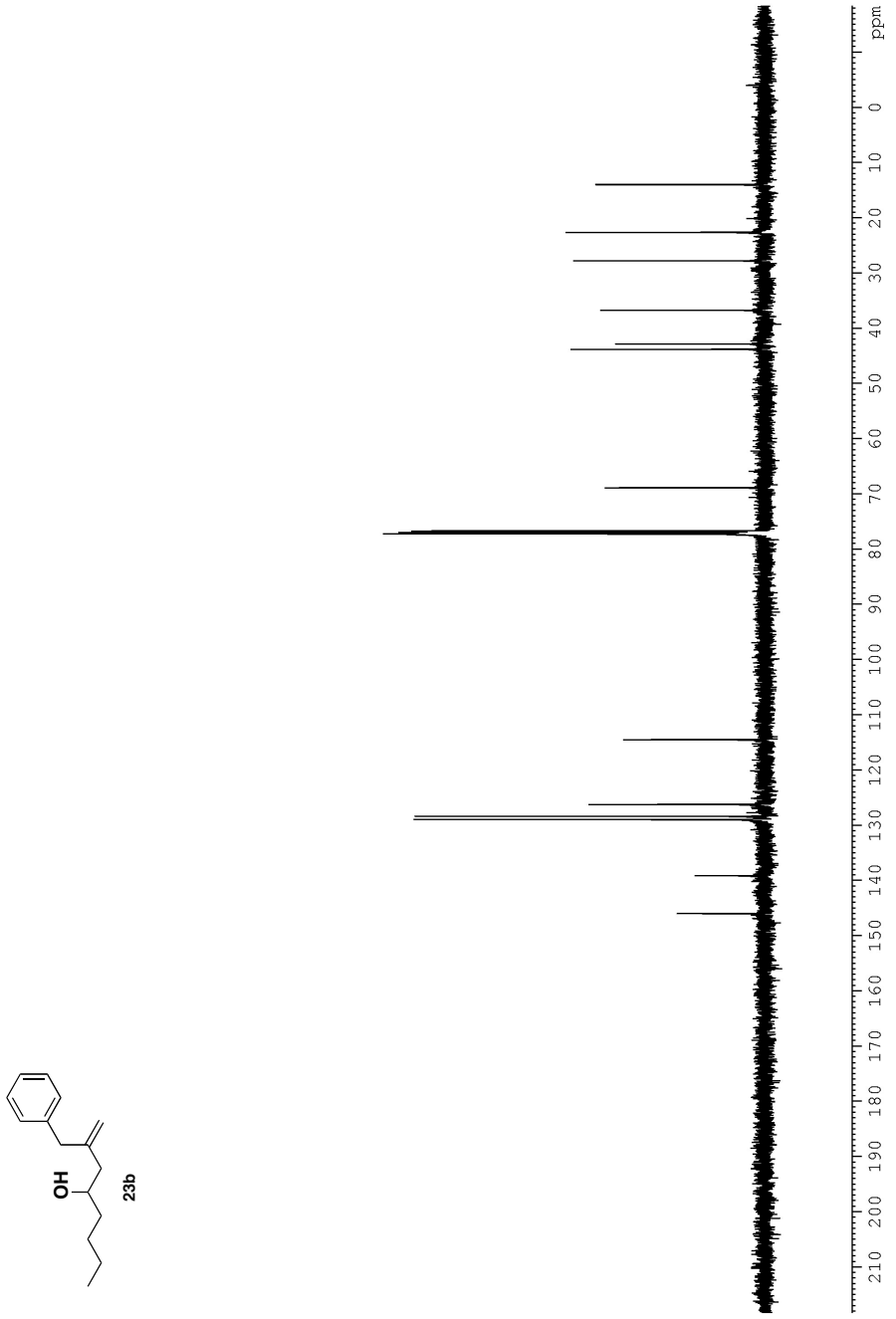
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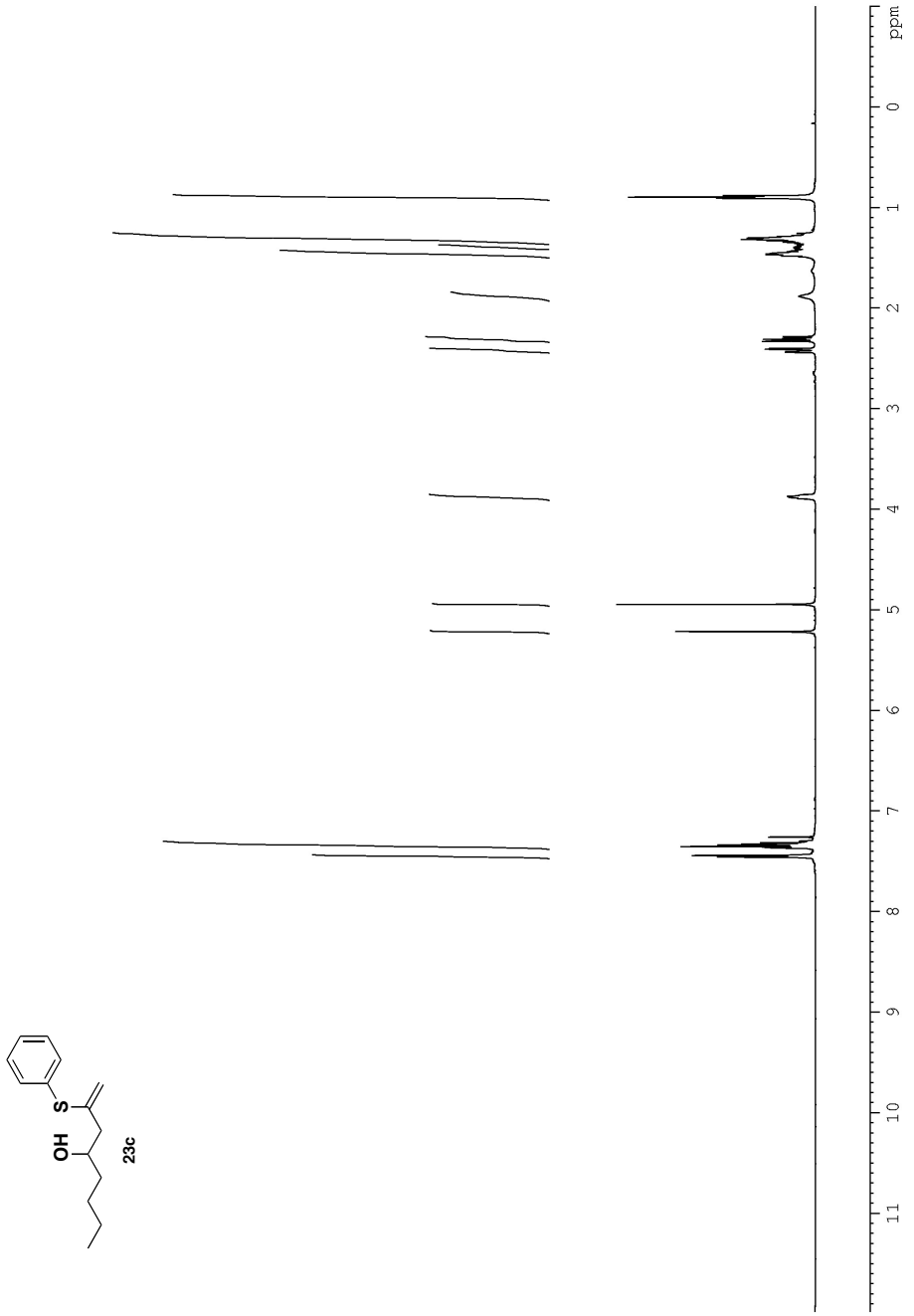
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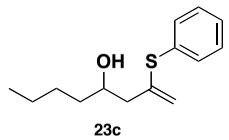
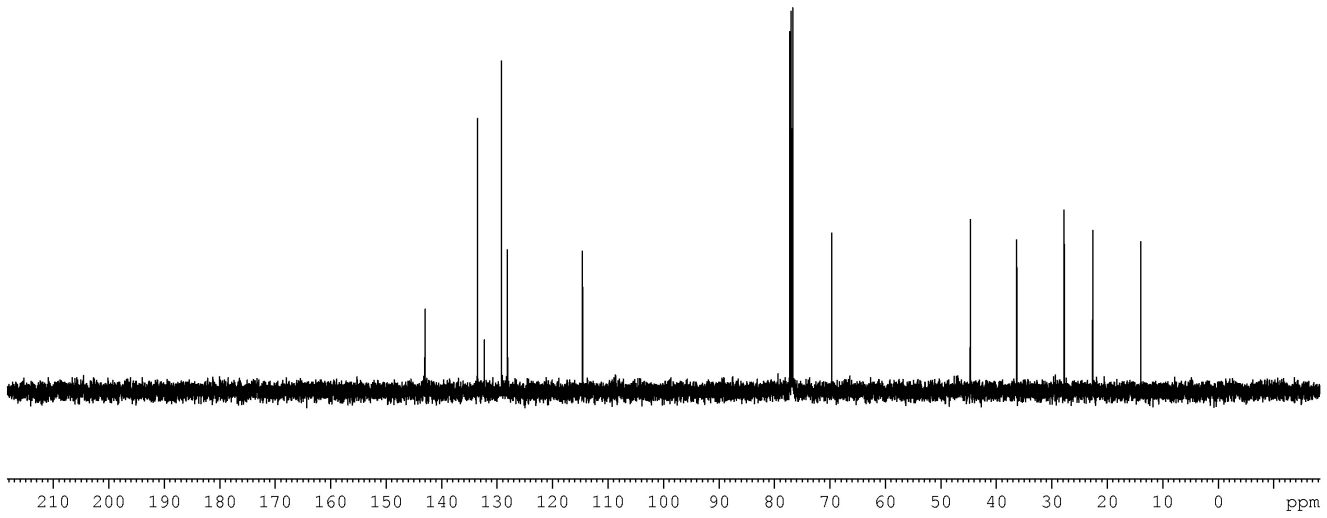

OH
S

23c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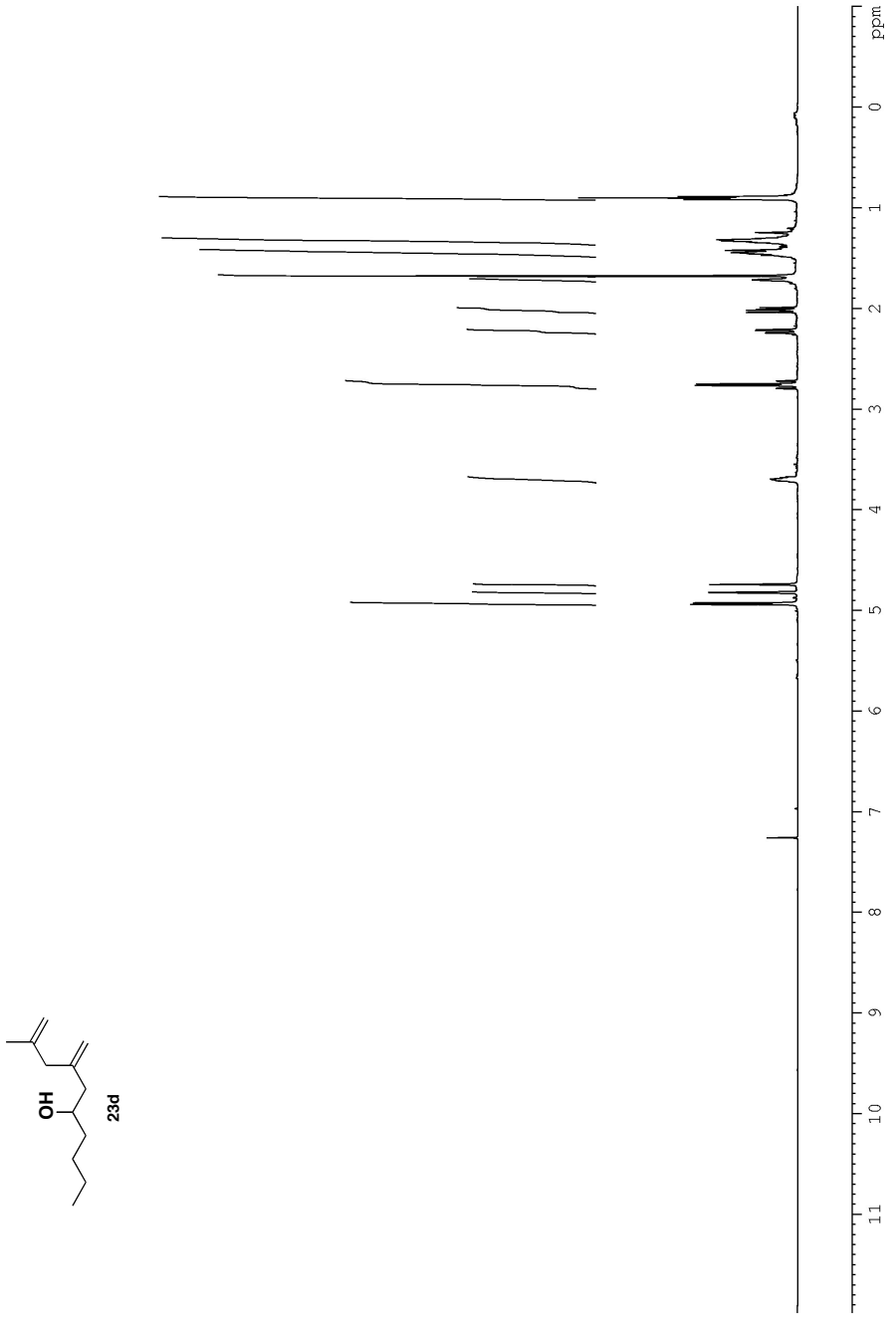
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8
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10
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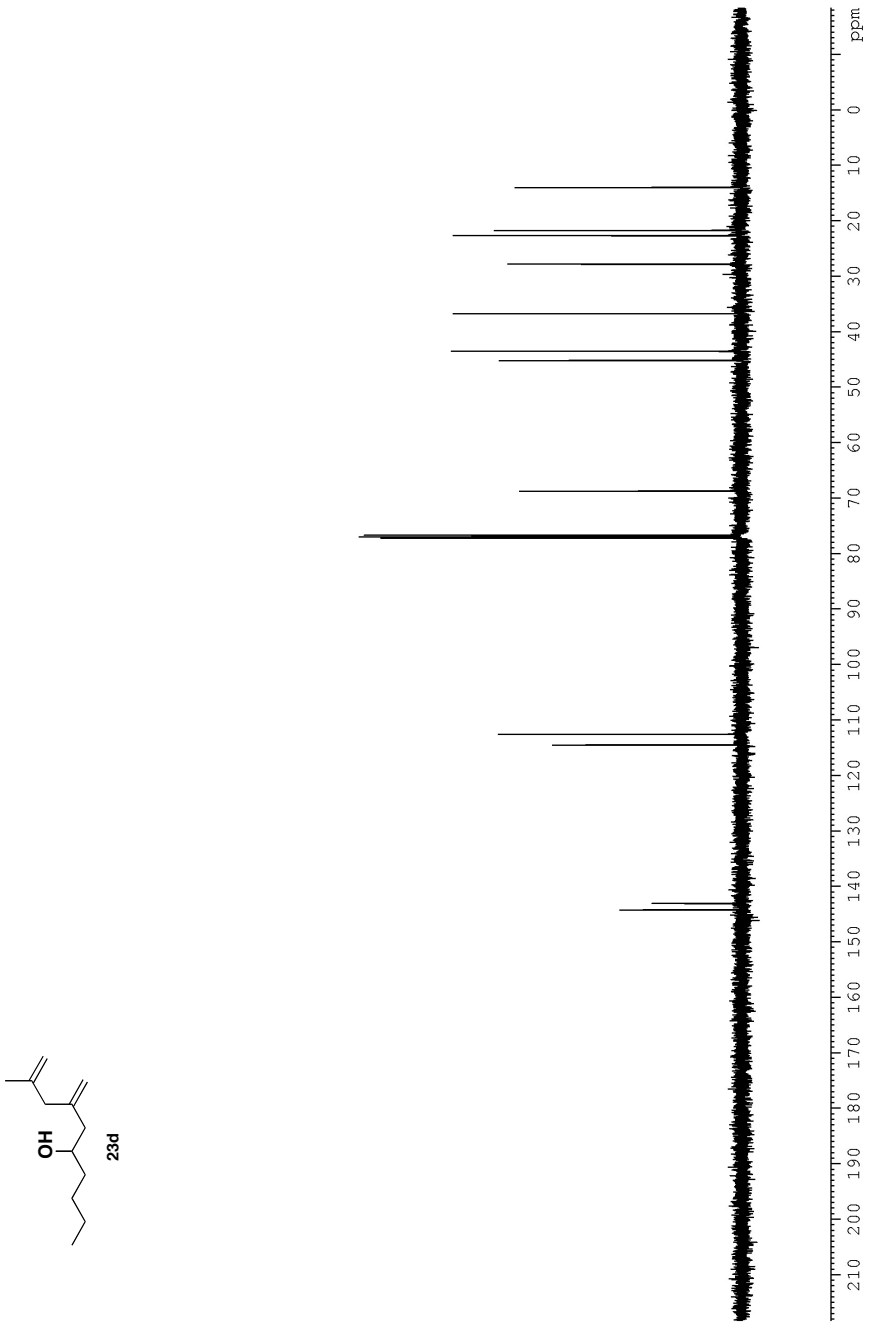
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ppm
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200
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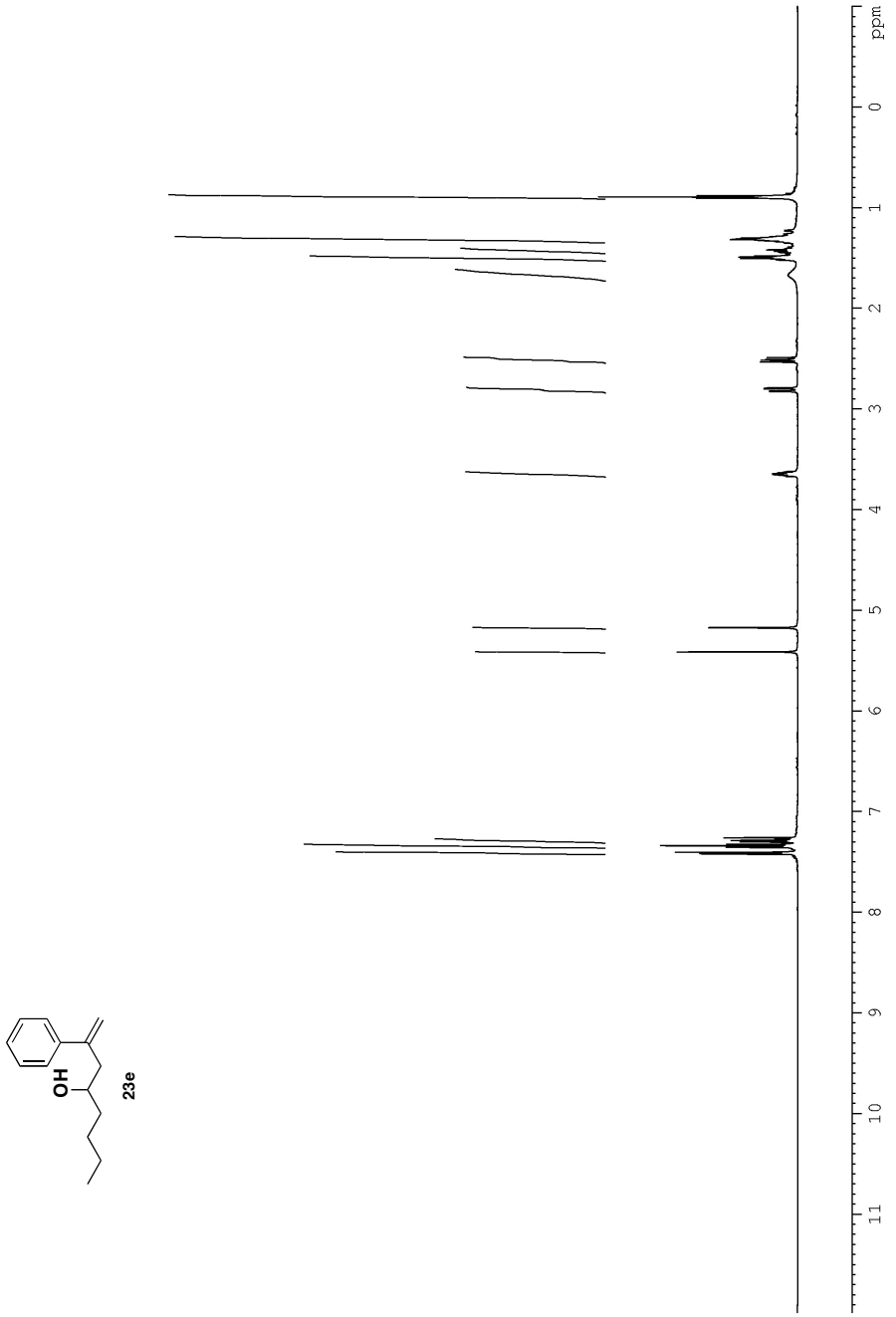
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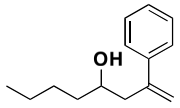
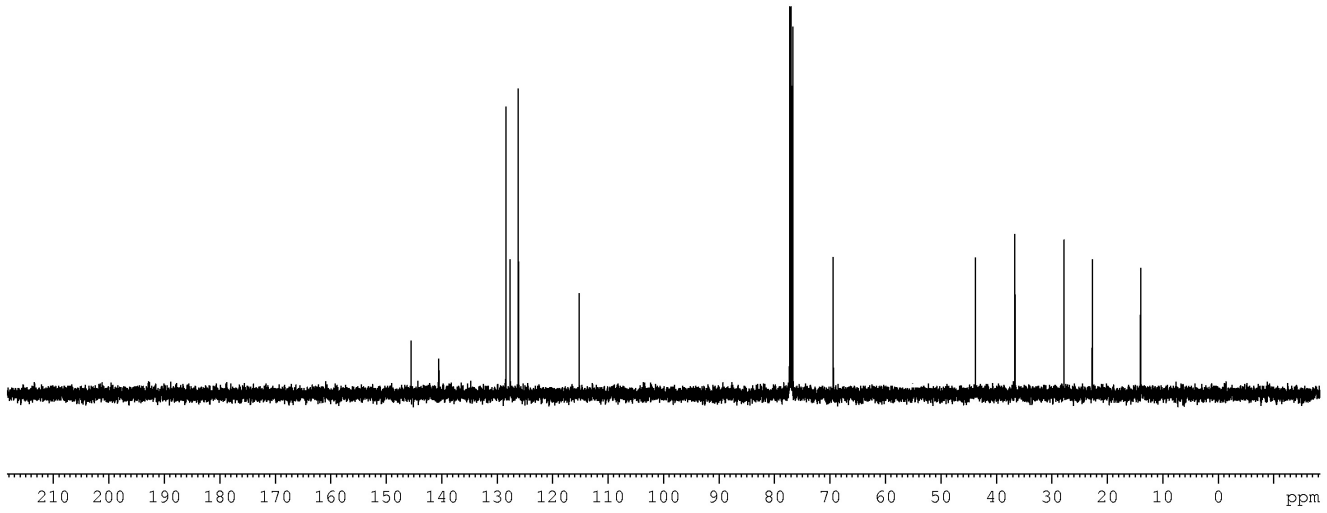

OH

23e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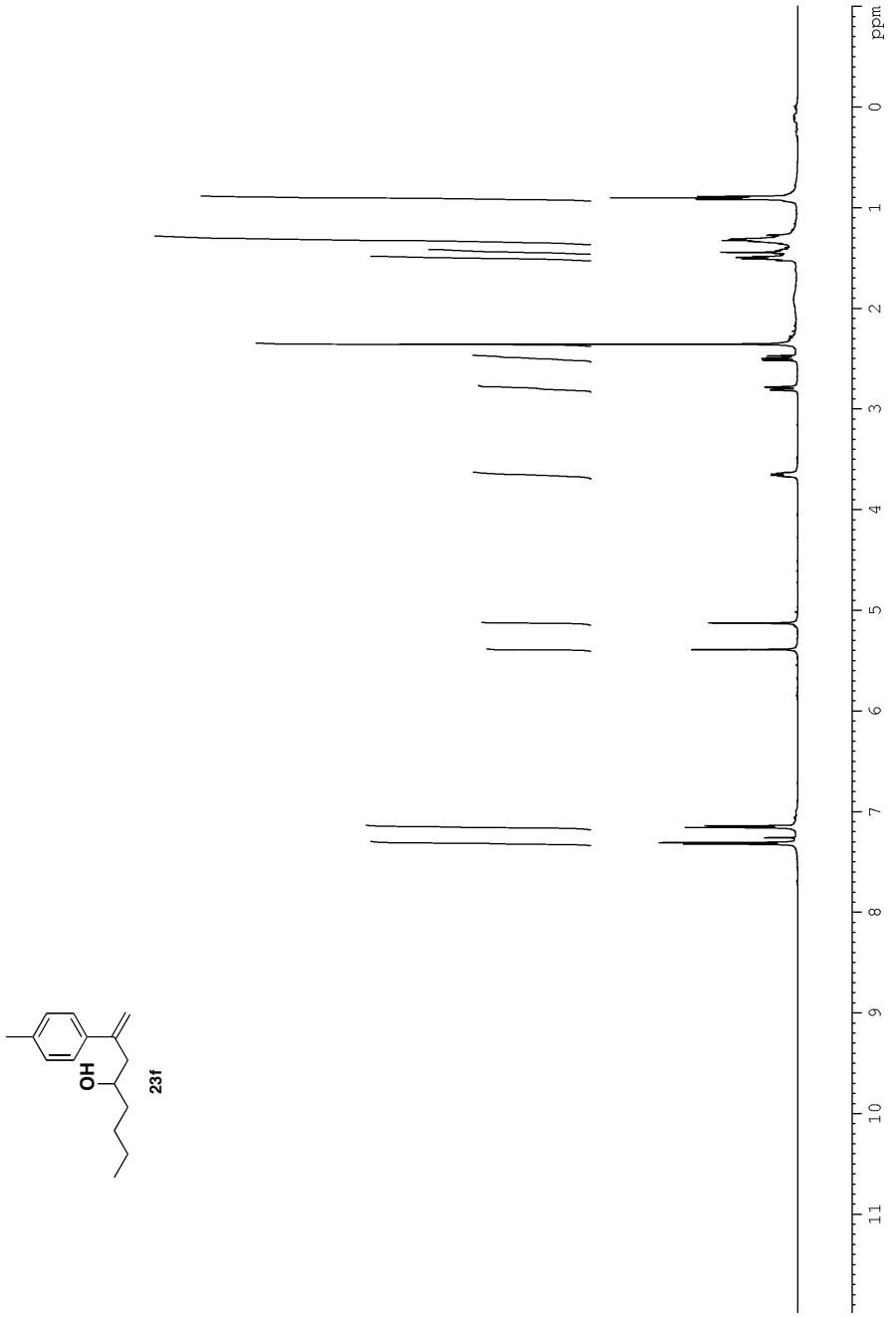
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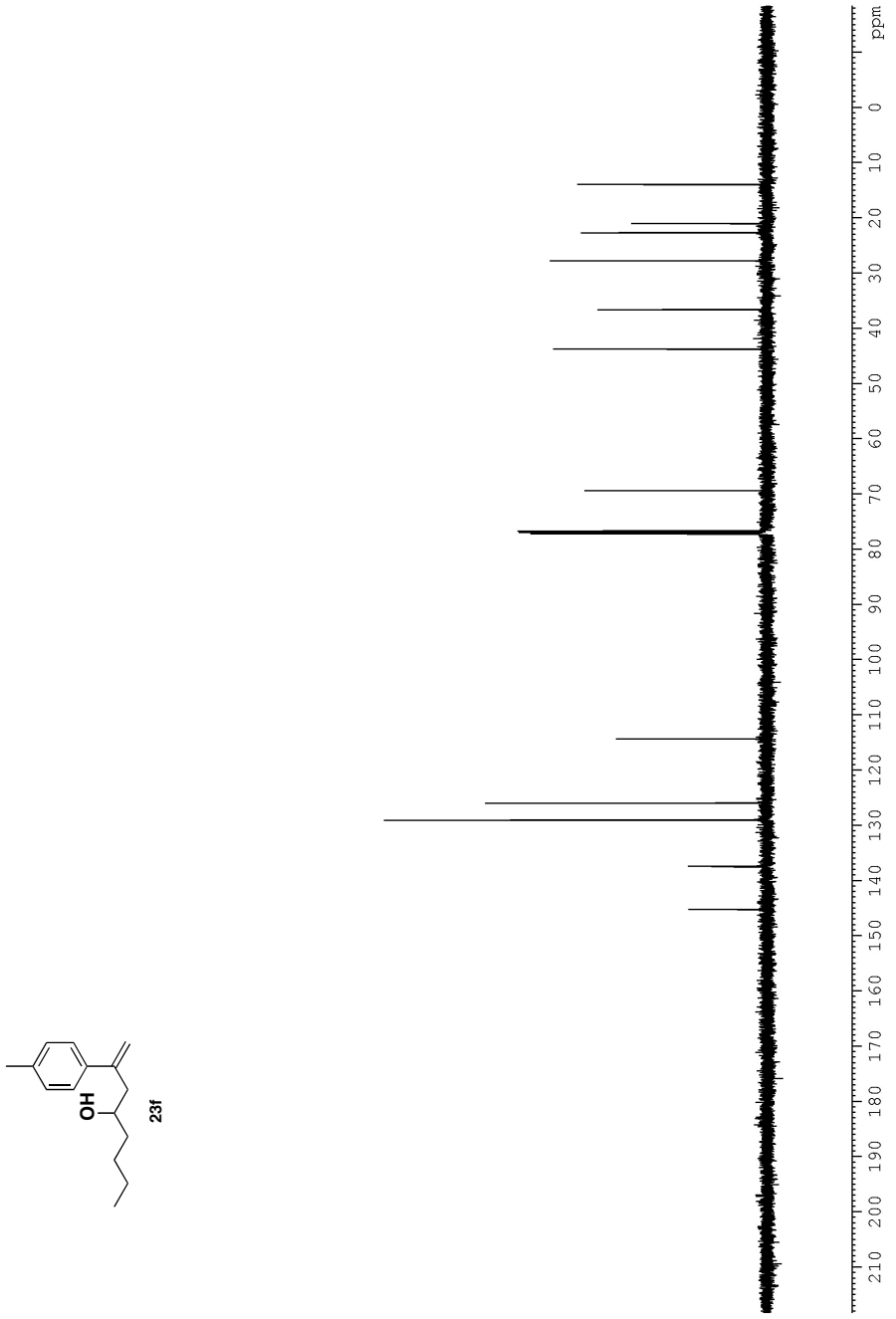
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ppm
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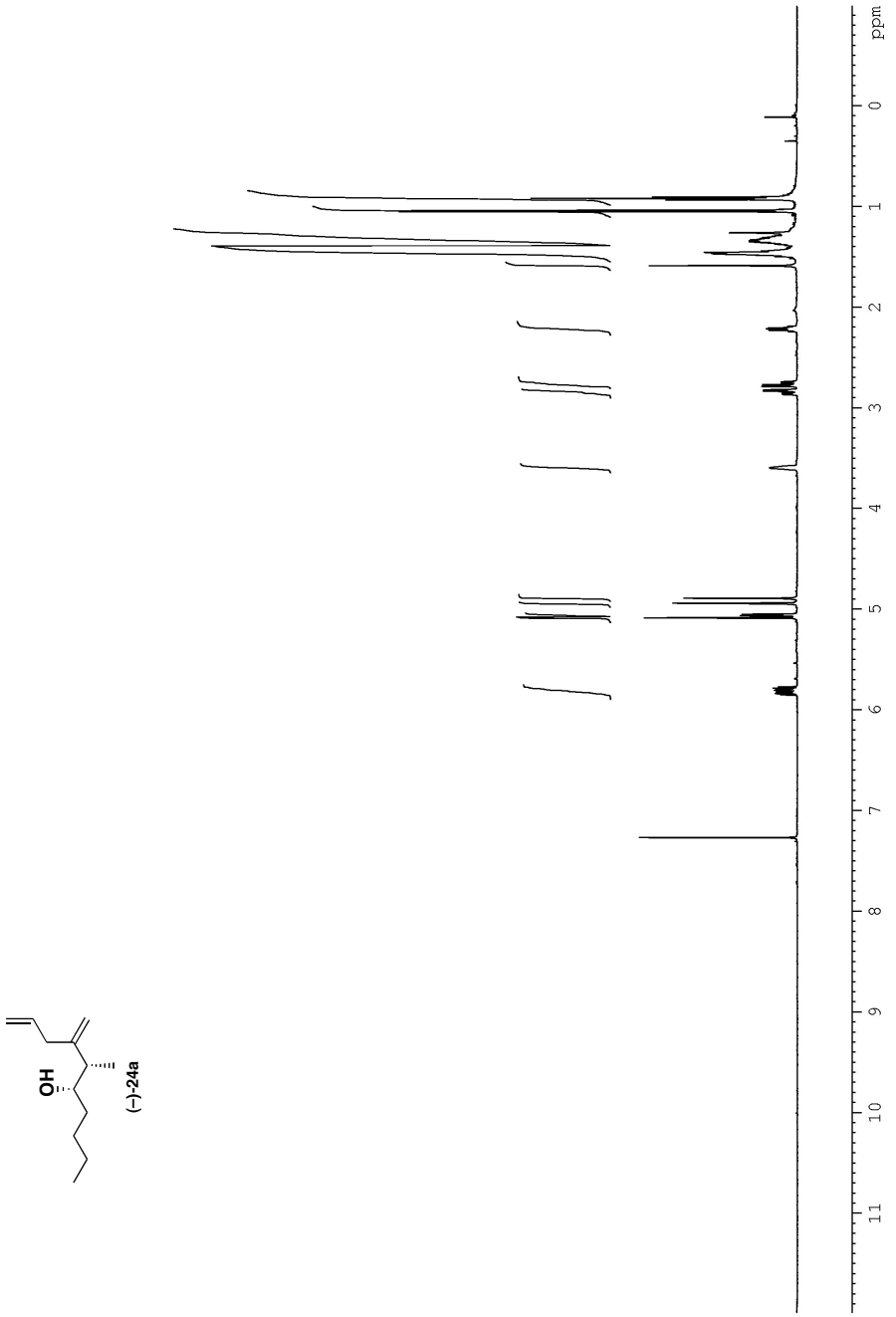
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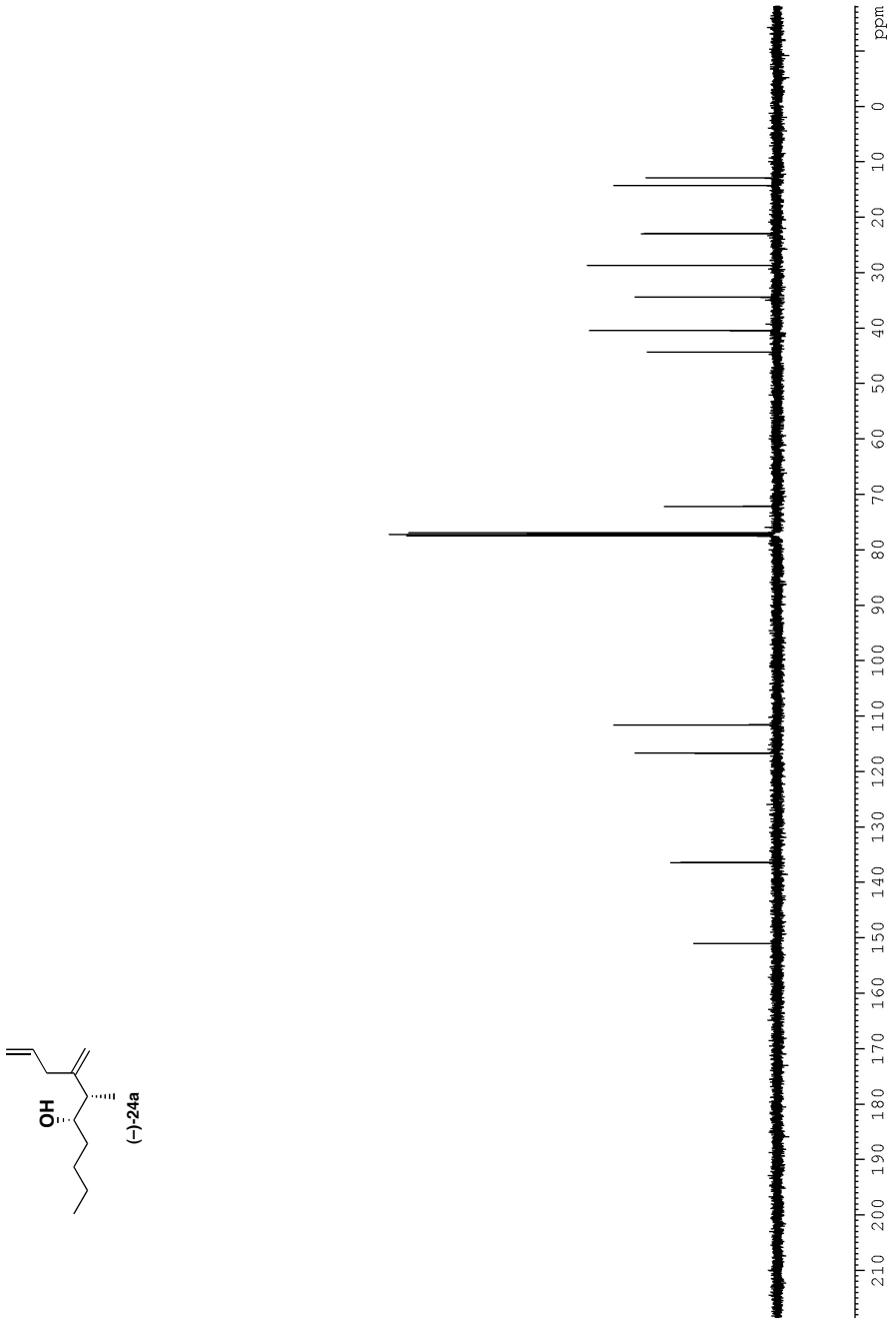
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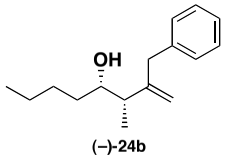
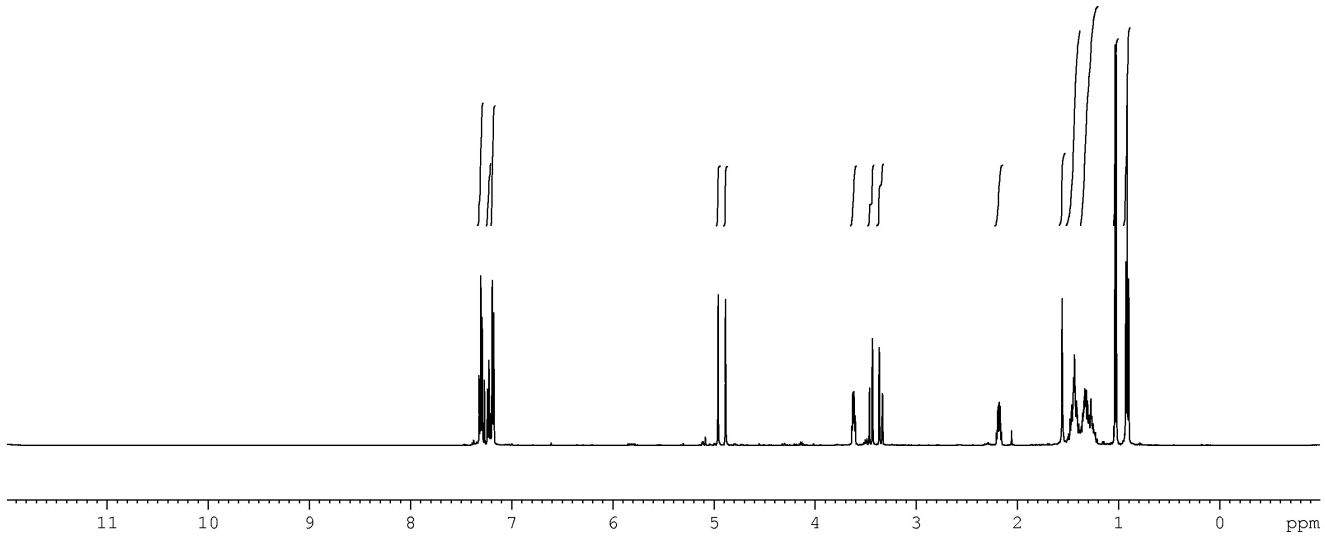
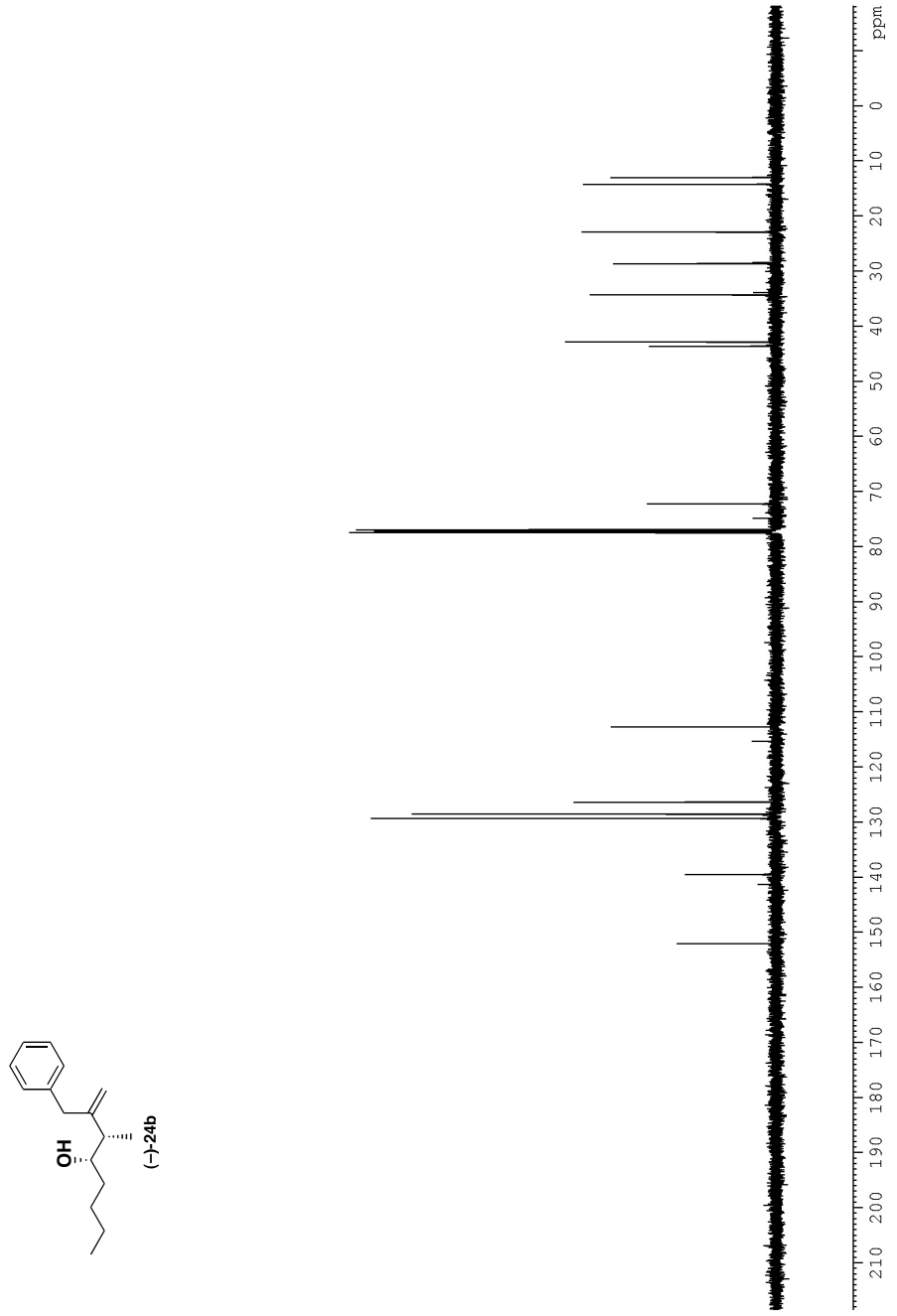


(–)-24b

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200
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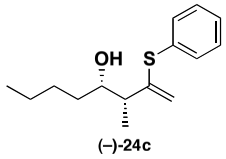
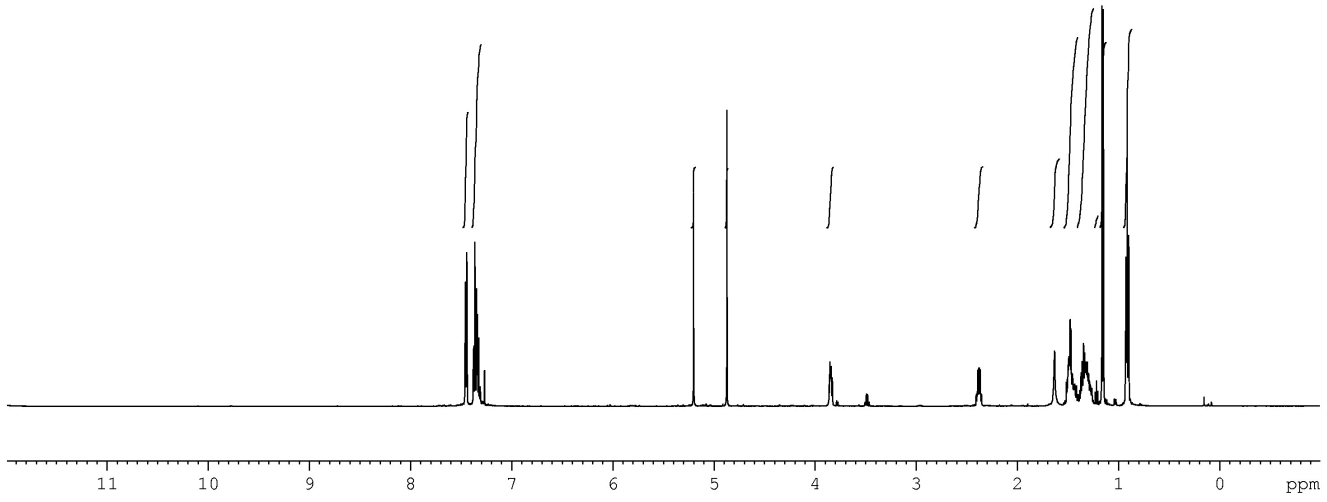
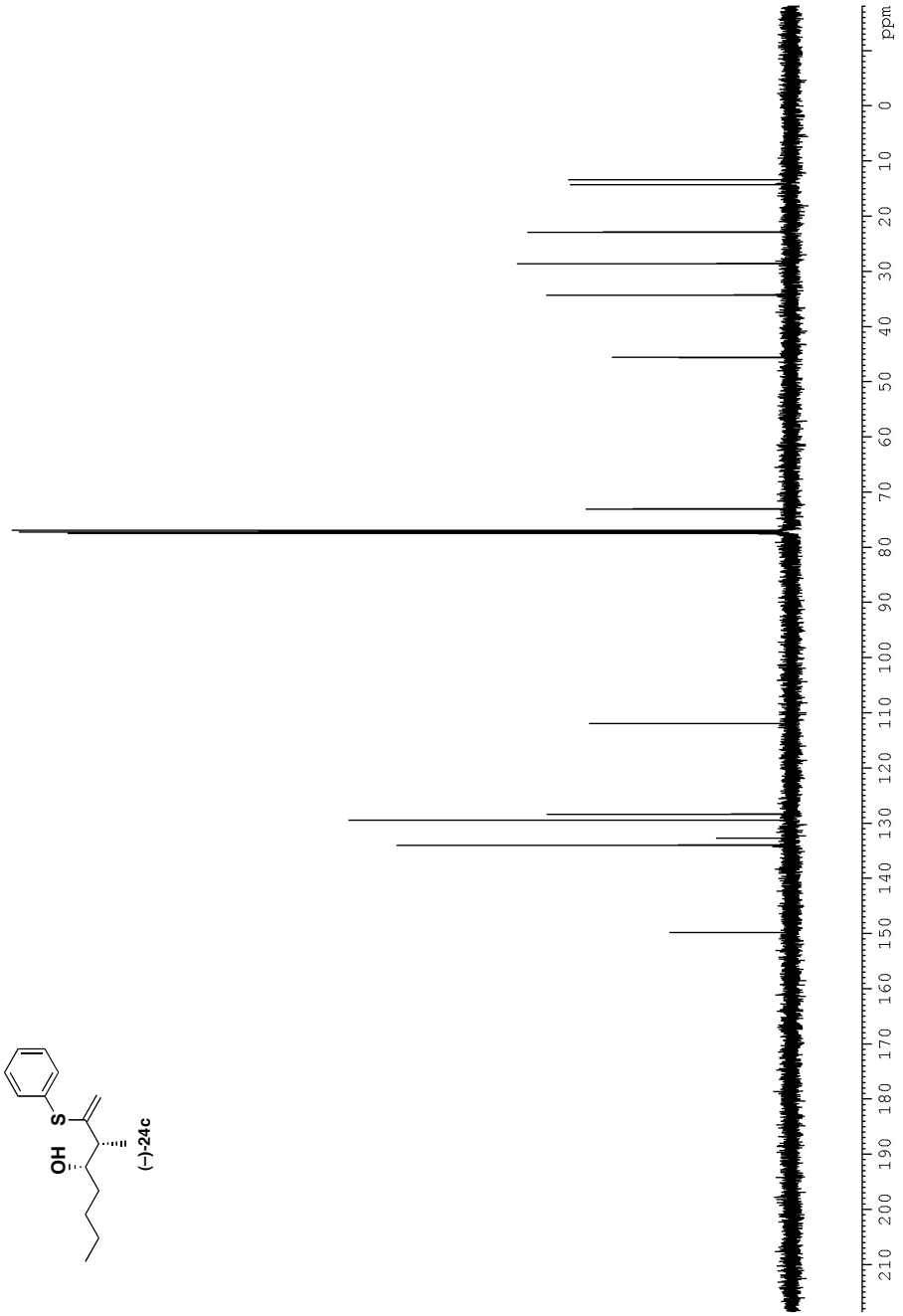


(–)-24c

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S
(–)-24c
ppm
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100
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200
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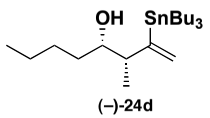
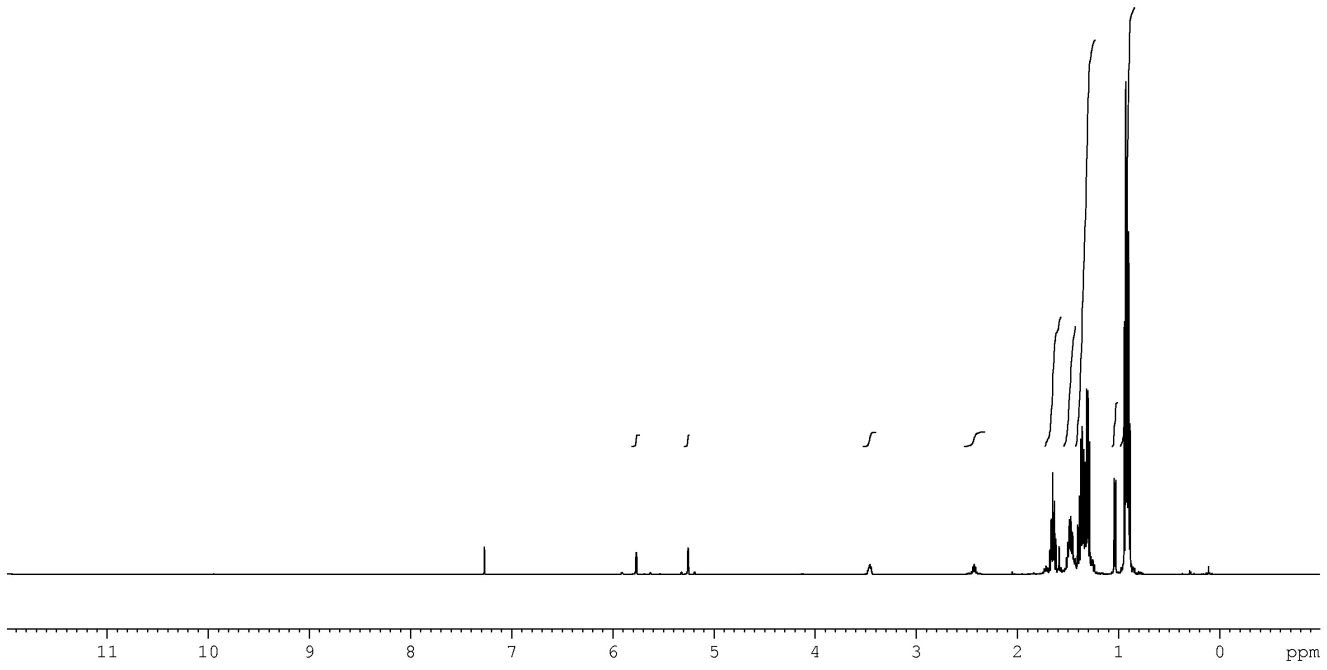
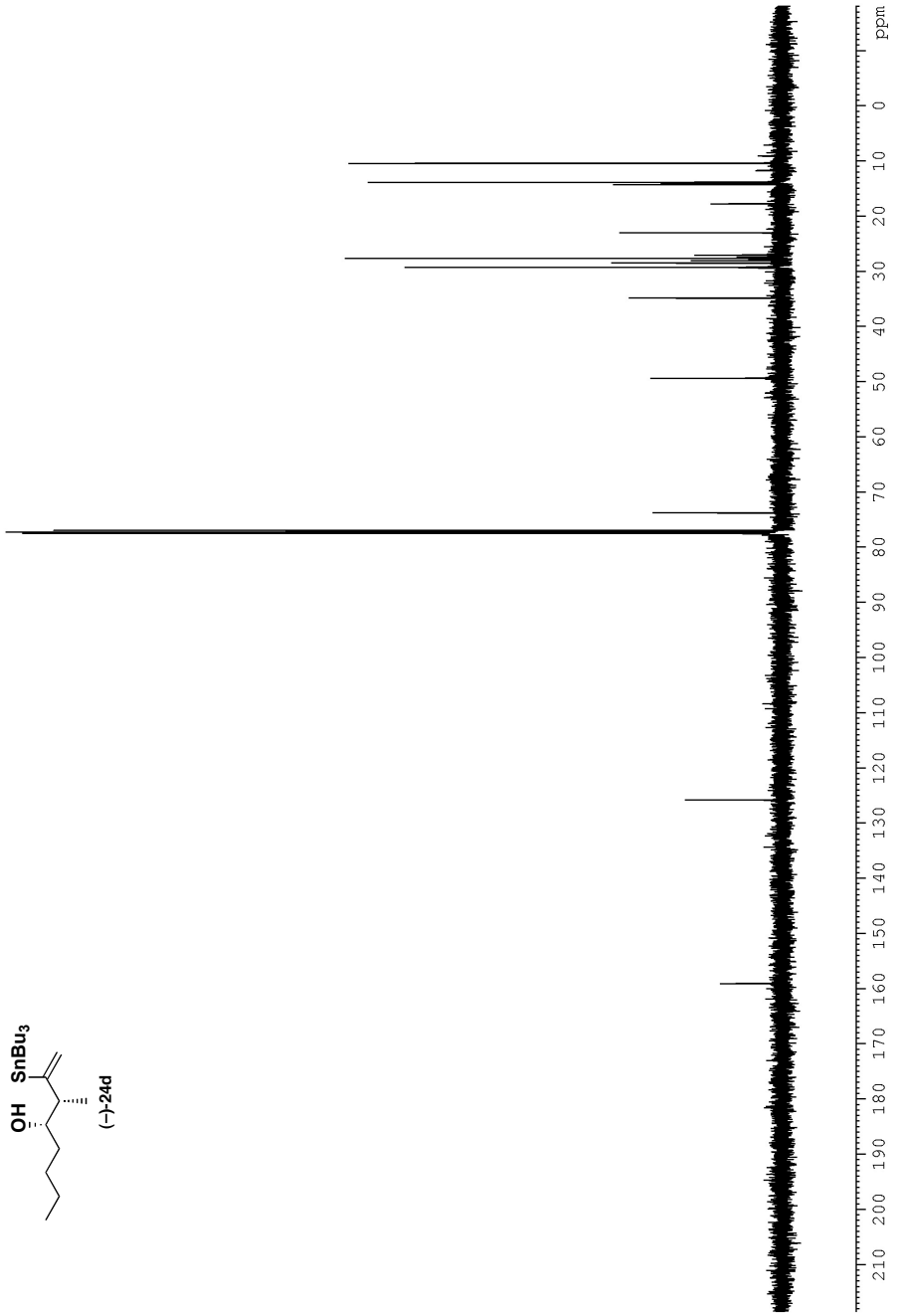


(–)-24d

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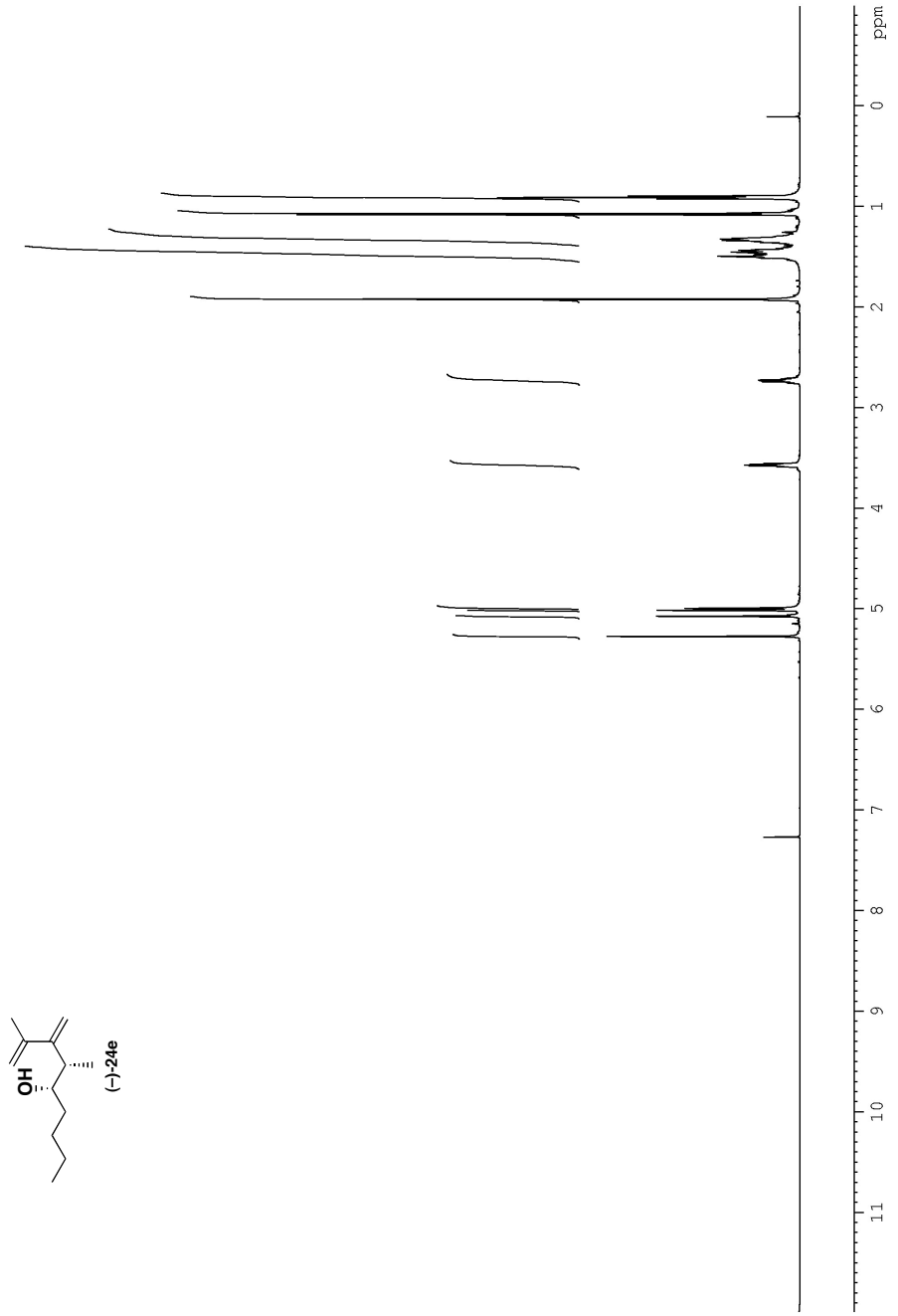
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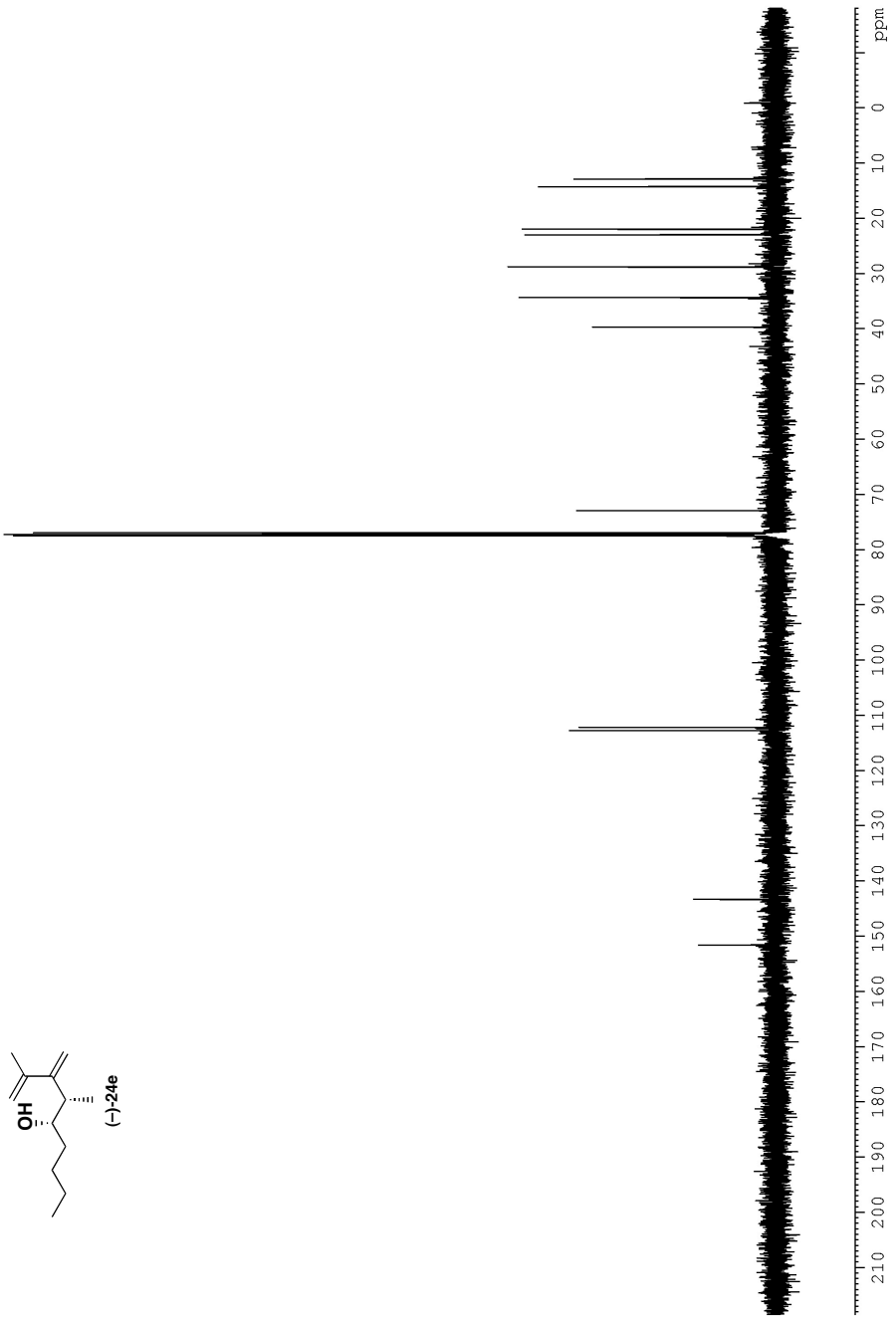
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200
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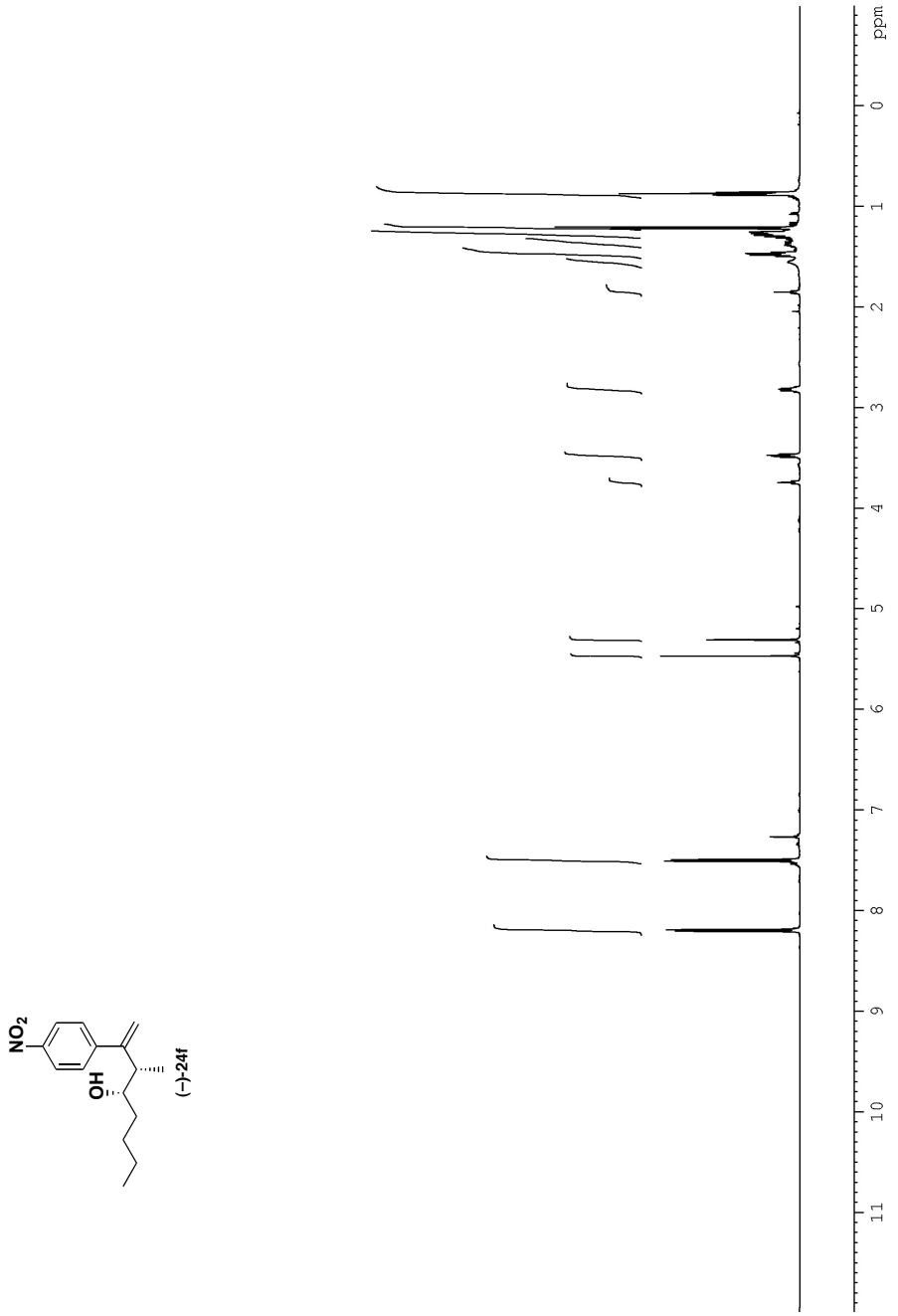
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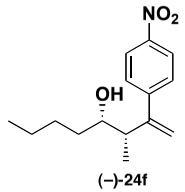
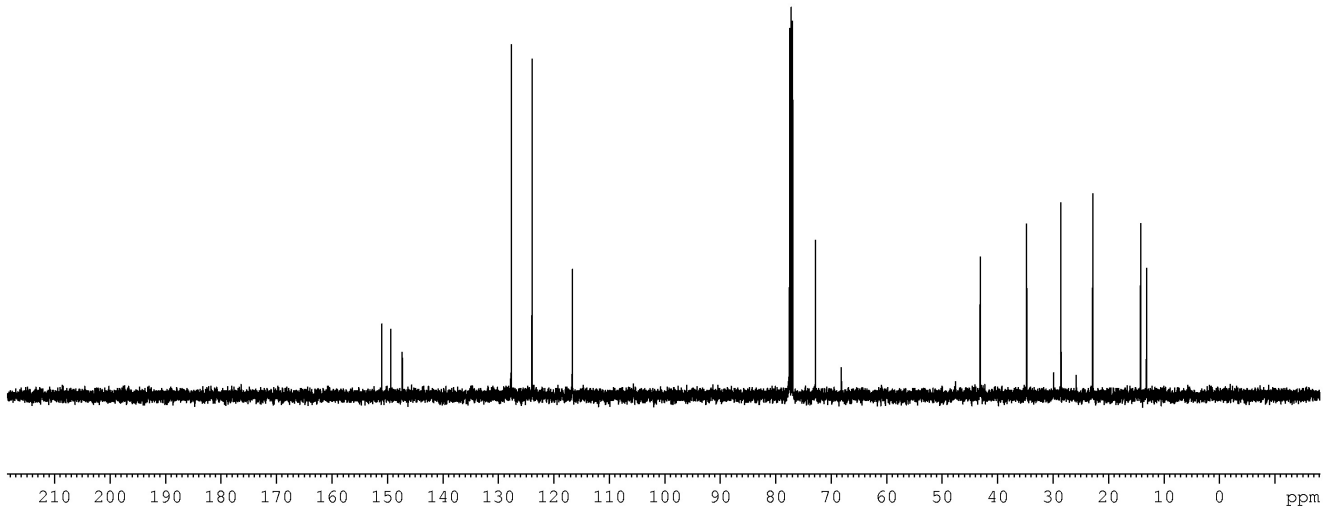

NO2
OH

(–)-24f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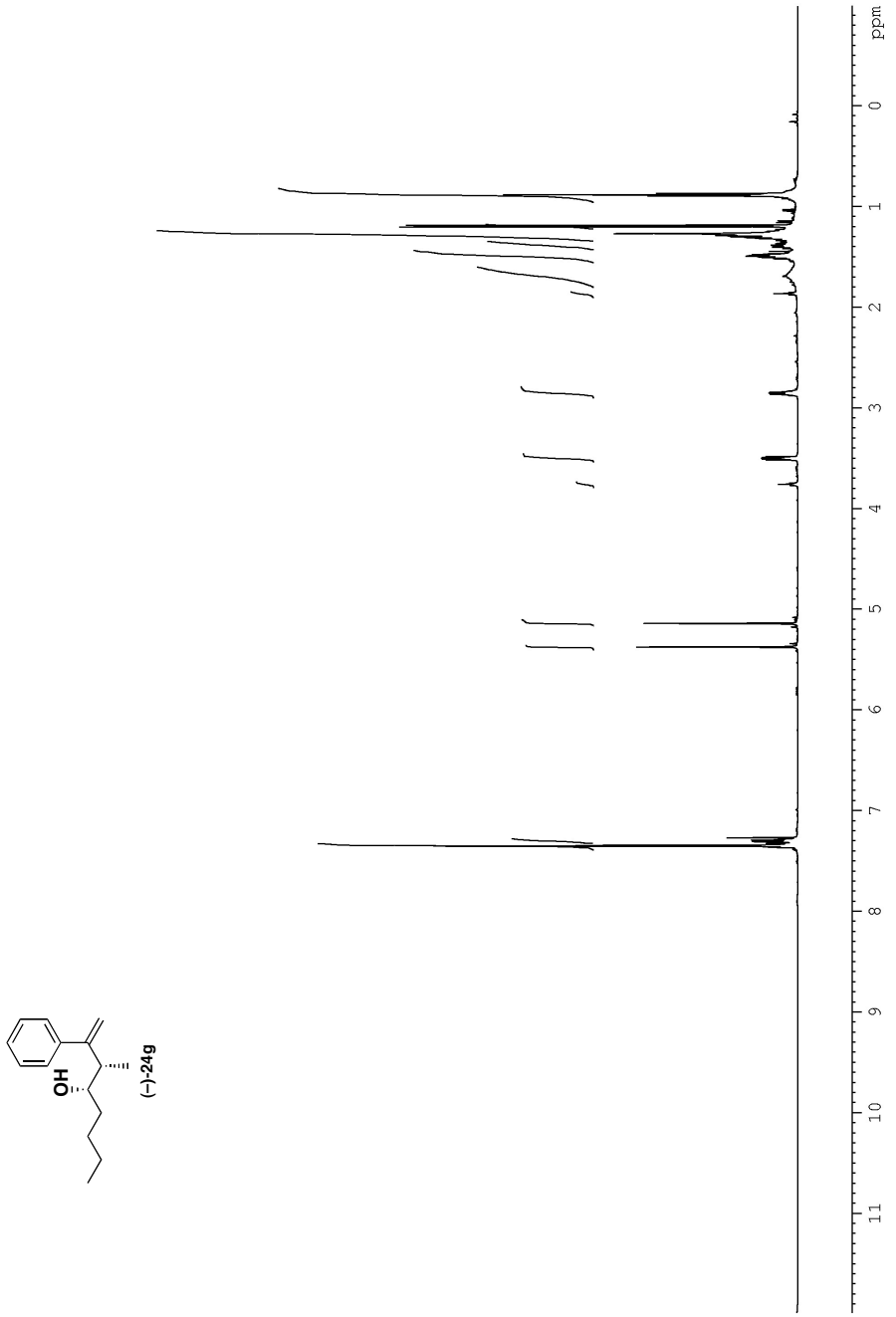
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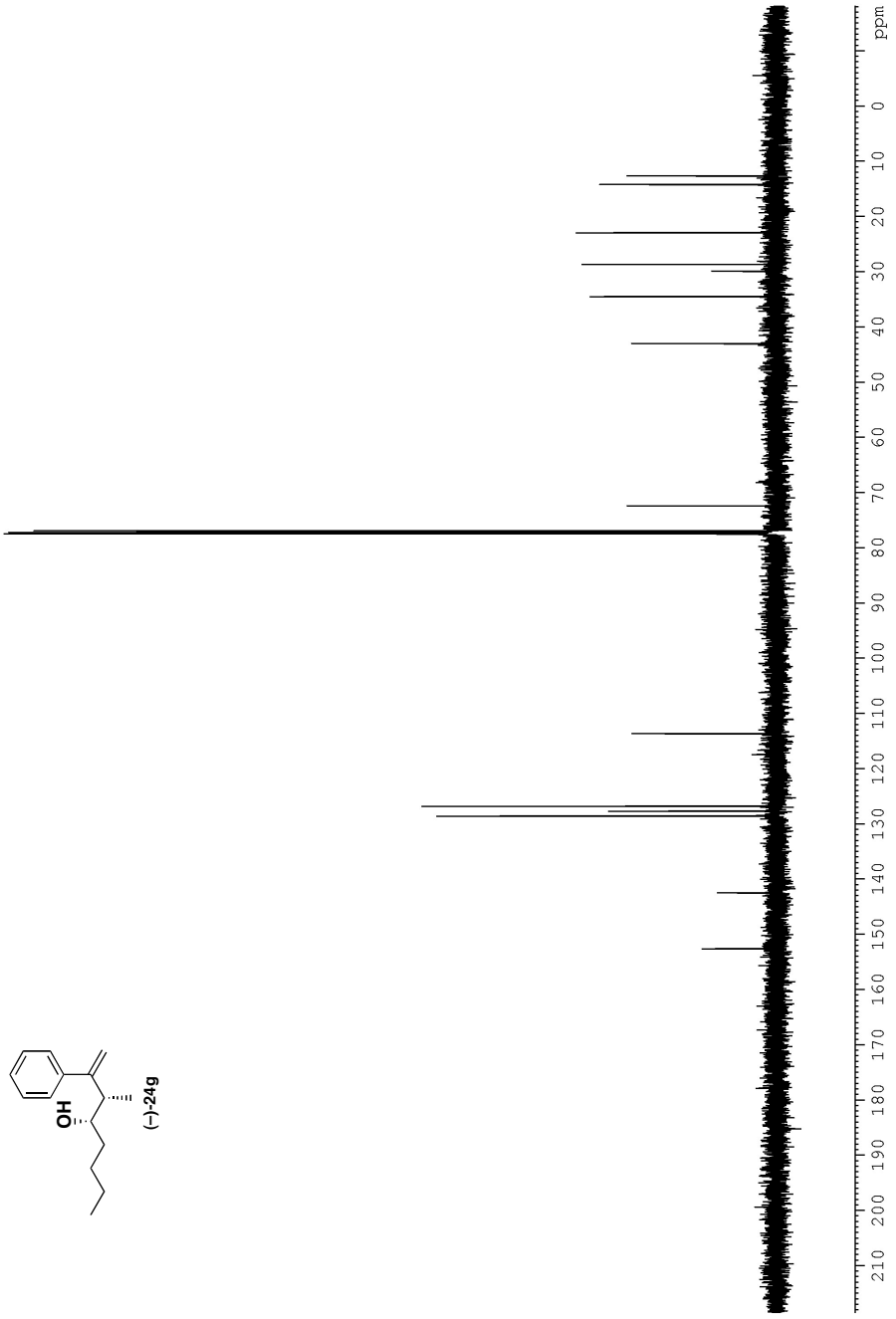
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ppm
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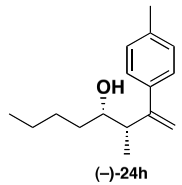
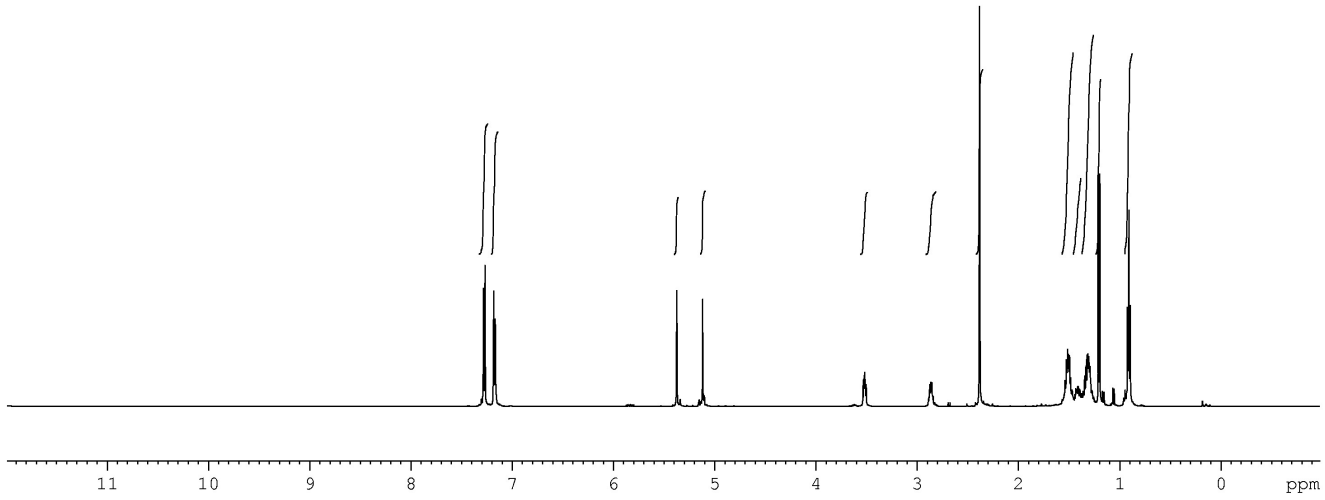
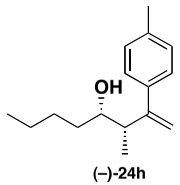
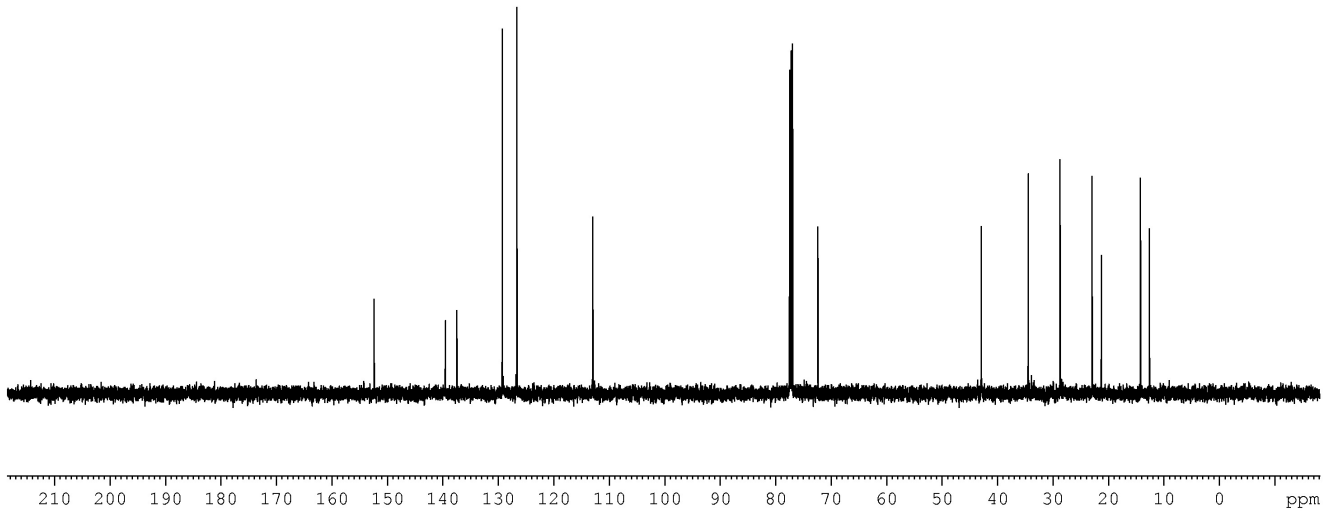


(–)-24h




OH

(–)-24h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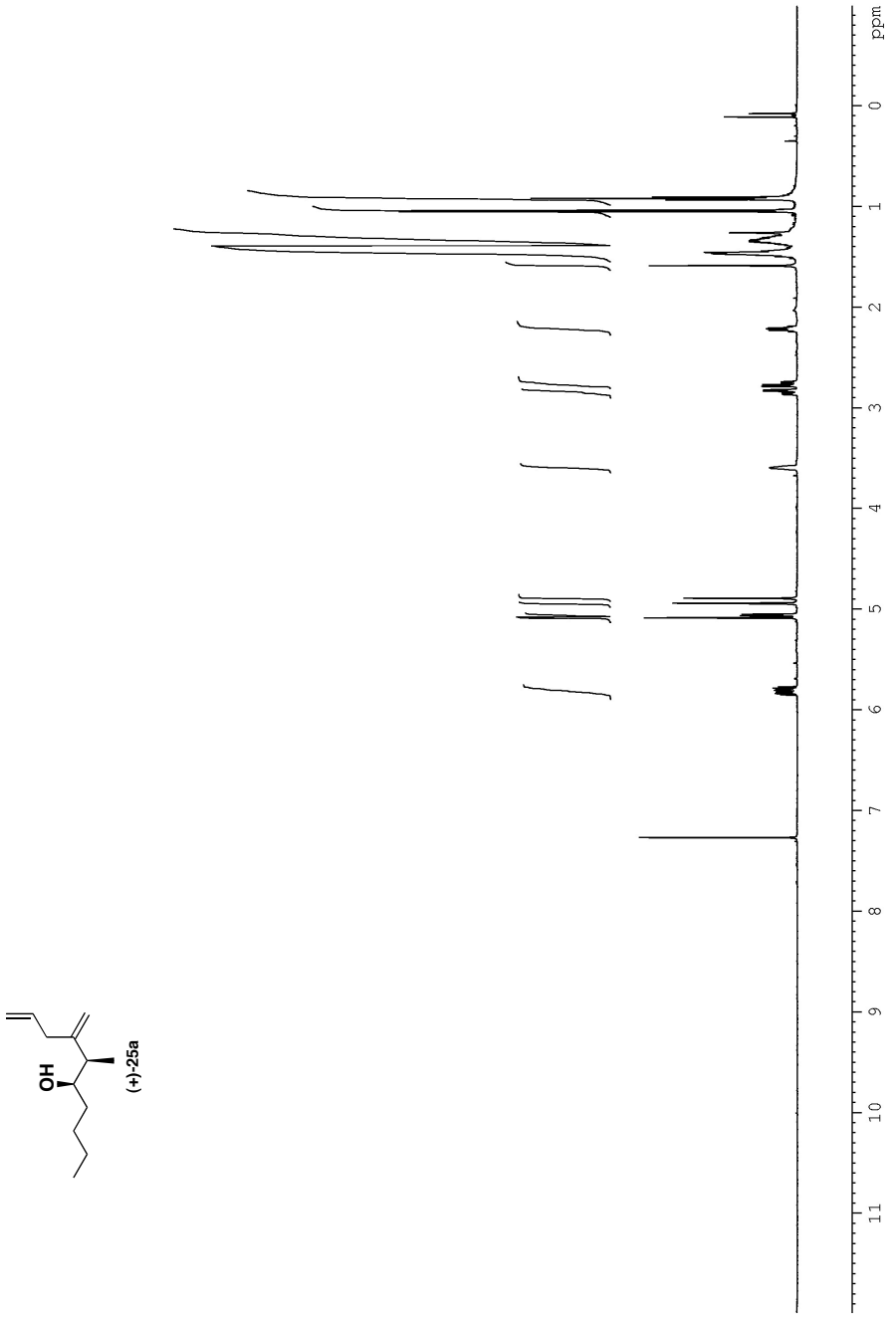
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(+)-25a
ppm
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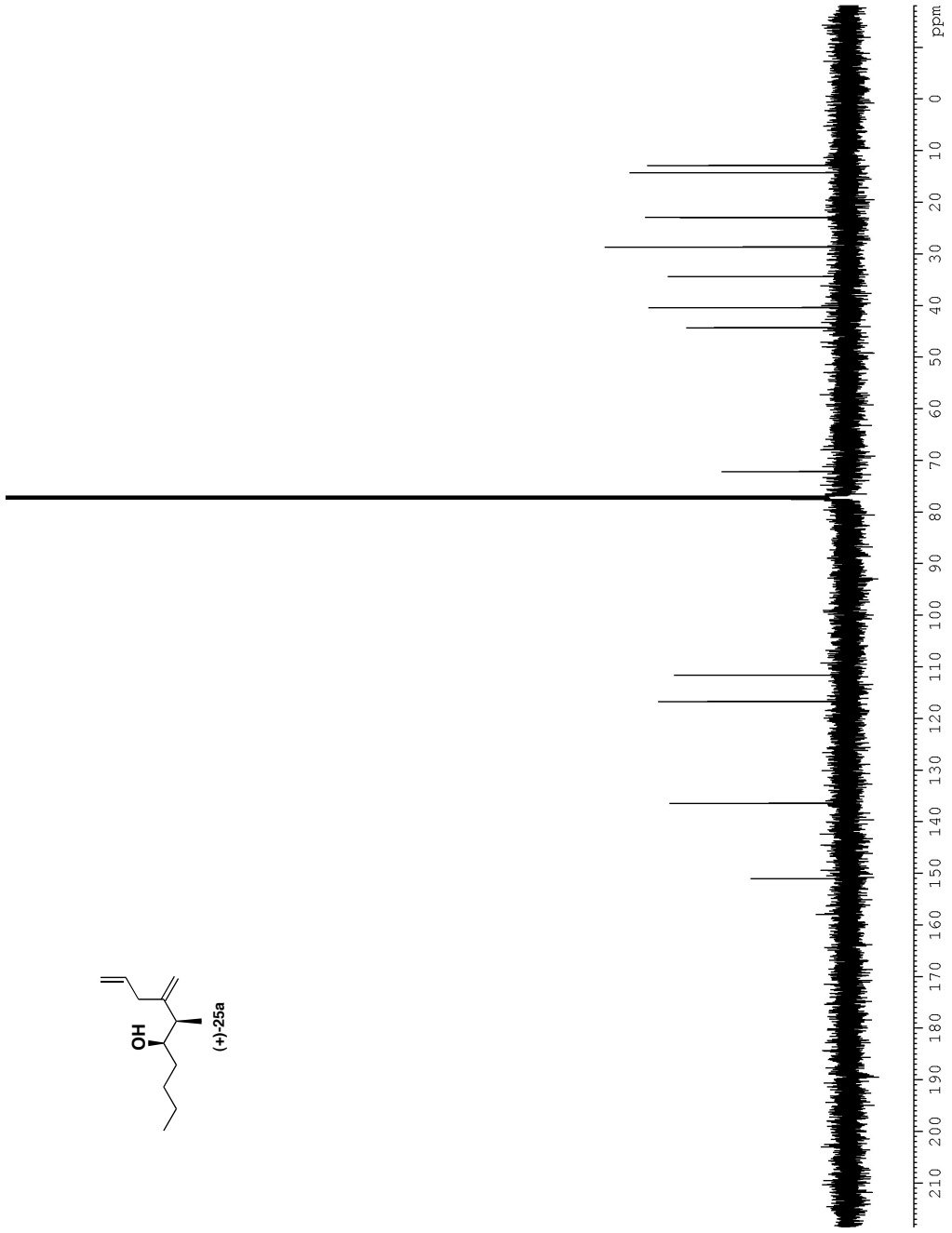
4
5
6
7
8
9
10
11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(+)-25a
ppm
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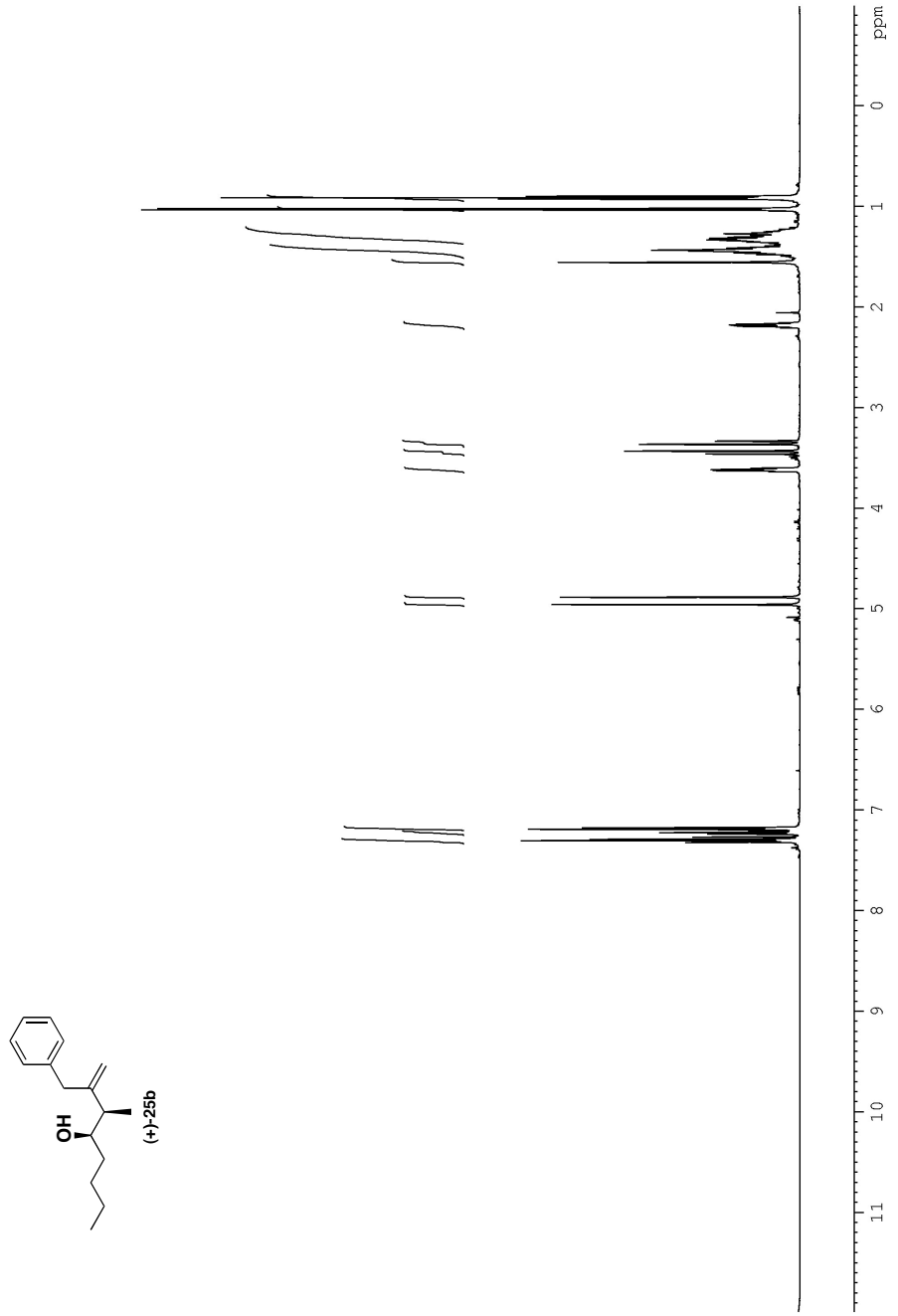
200
210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(+)-25b
ppm
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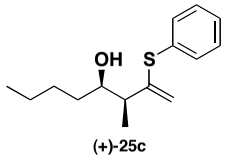
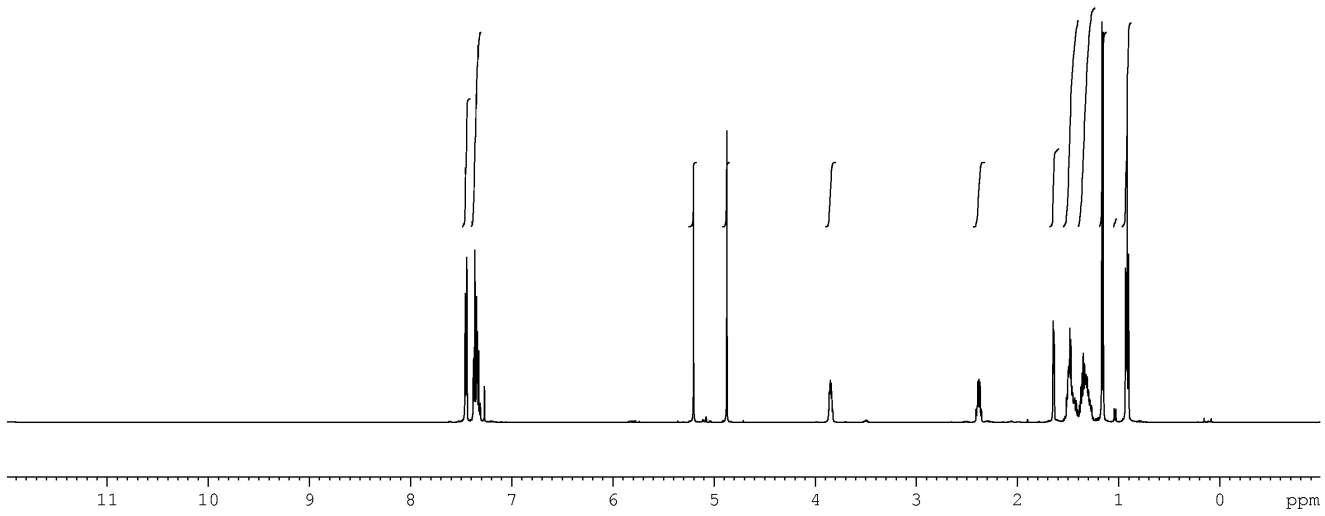
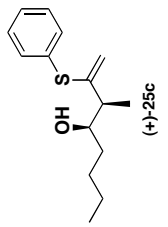
6
7
8
9
10
11

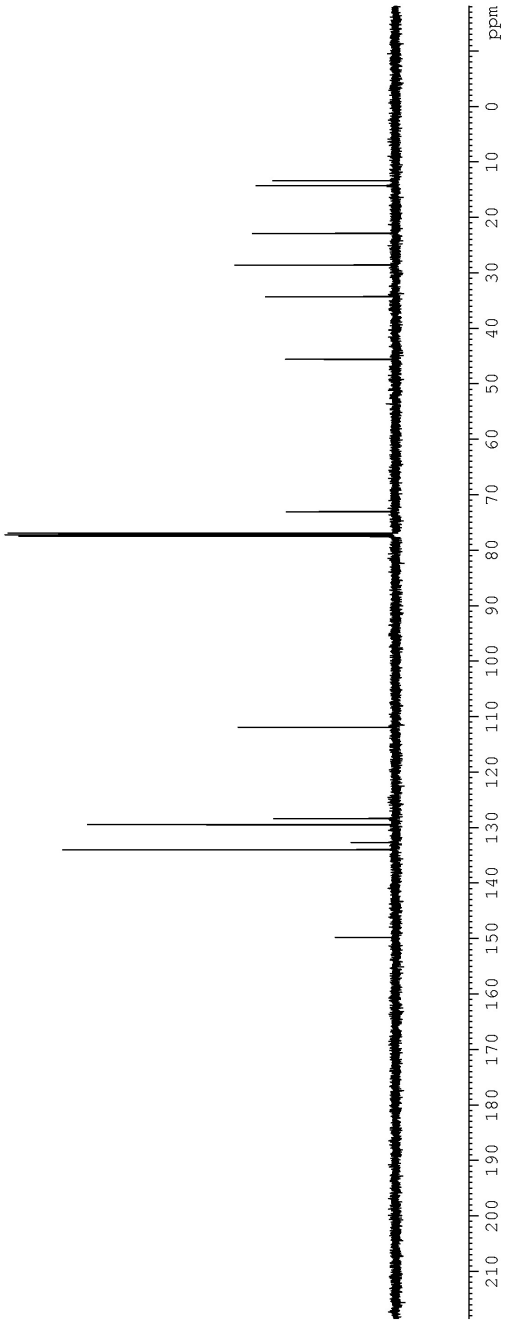
OH
(+)-25b



(+)-25c




OH
S
(+)-25c


ppm
0
10
20
30
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100
110
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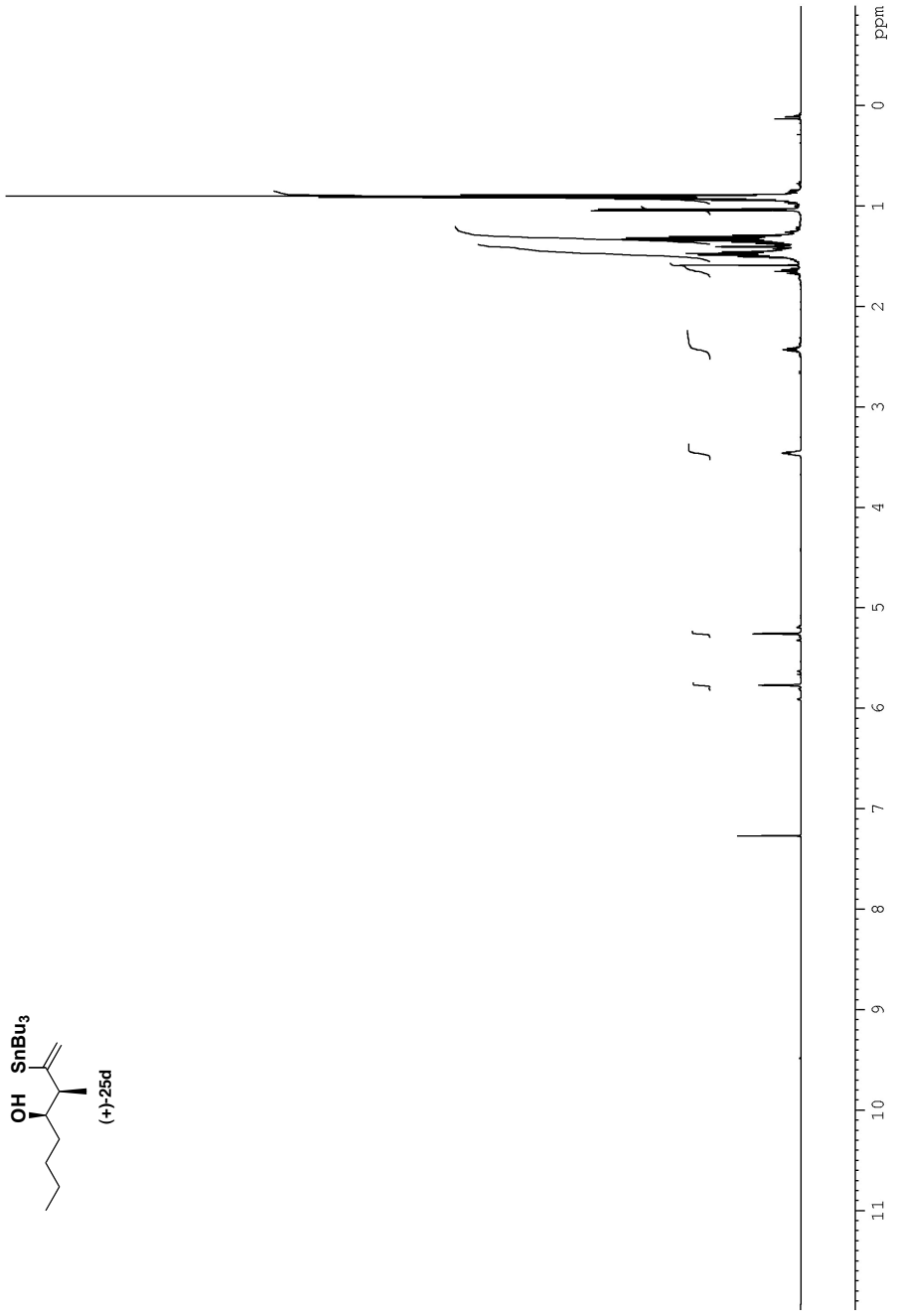
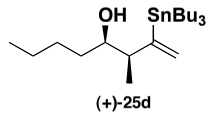
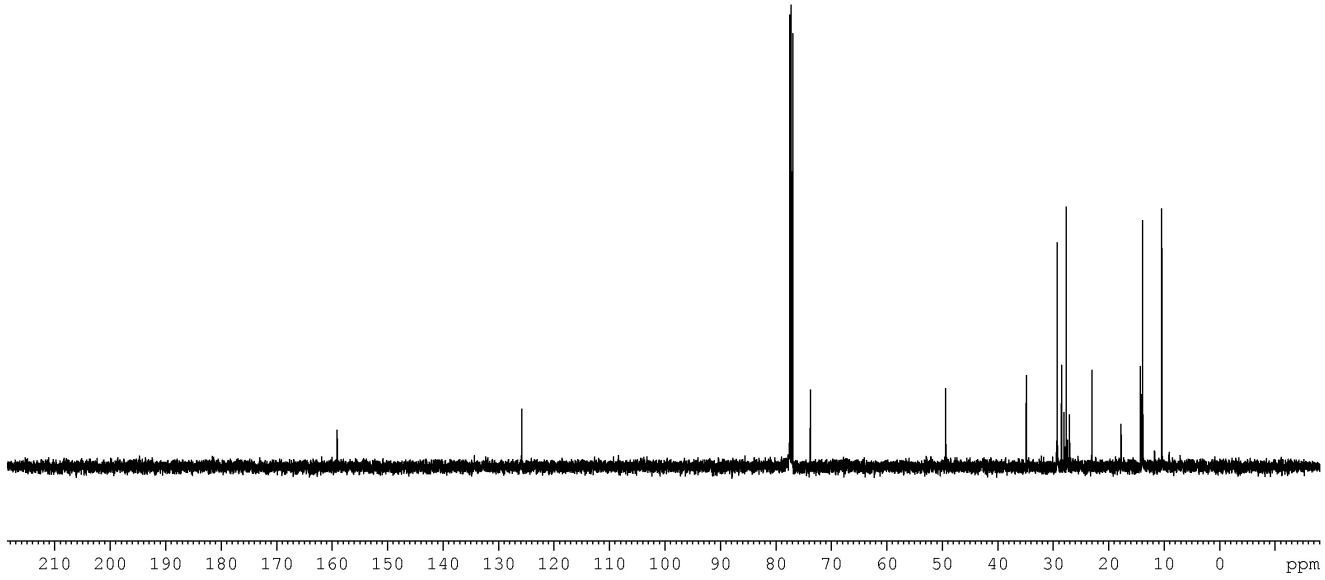
200
210


OH SnBu3
(+)-25d
ppm
0
1
2
3
4
5
6
7
8
9
10
11


OH
SnBu3

(+)-25d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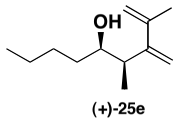
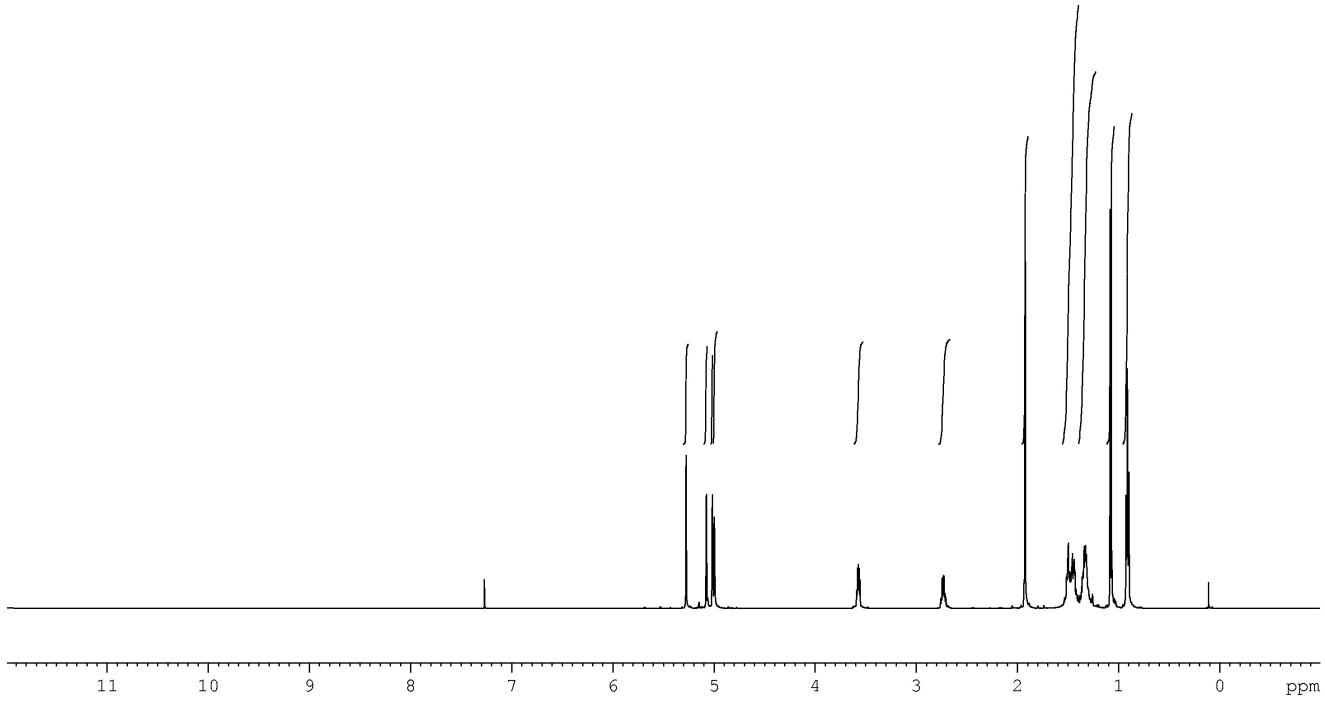
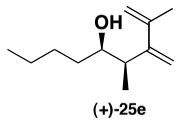
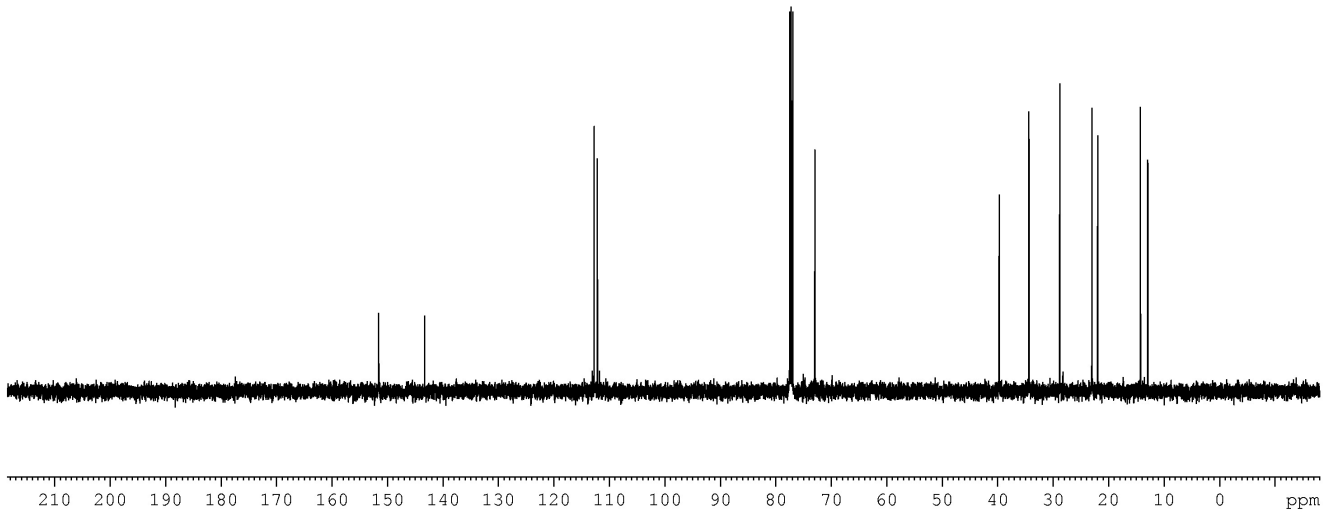


(+)-25e




OH

(+)-25e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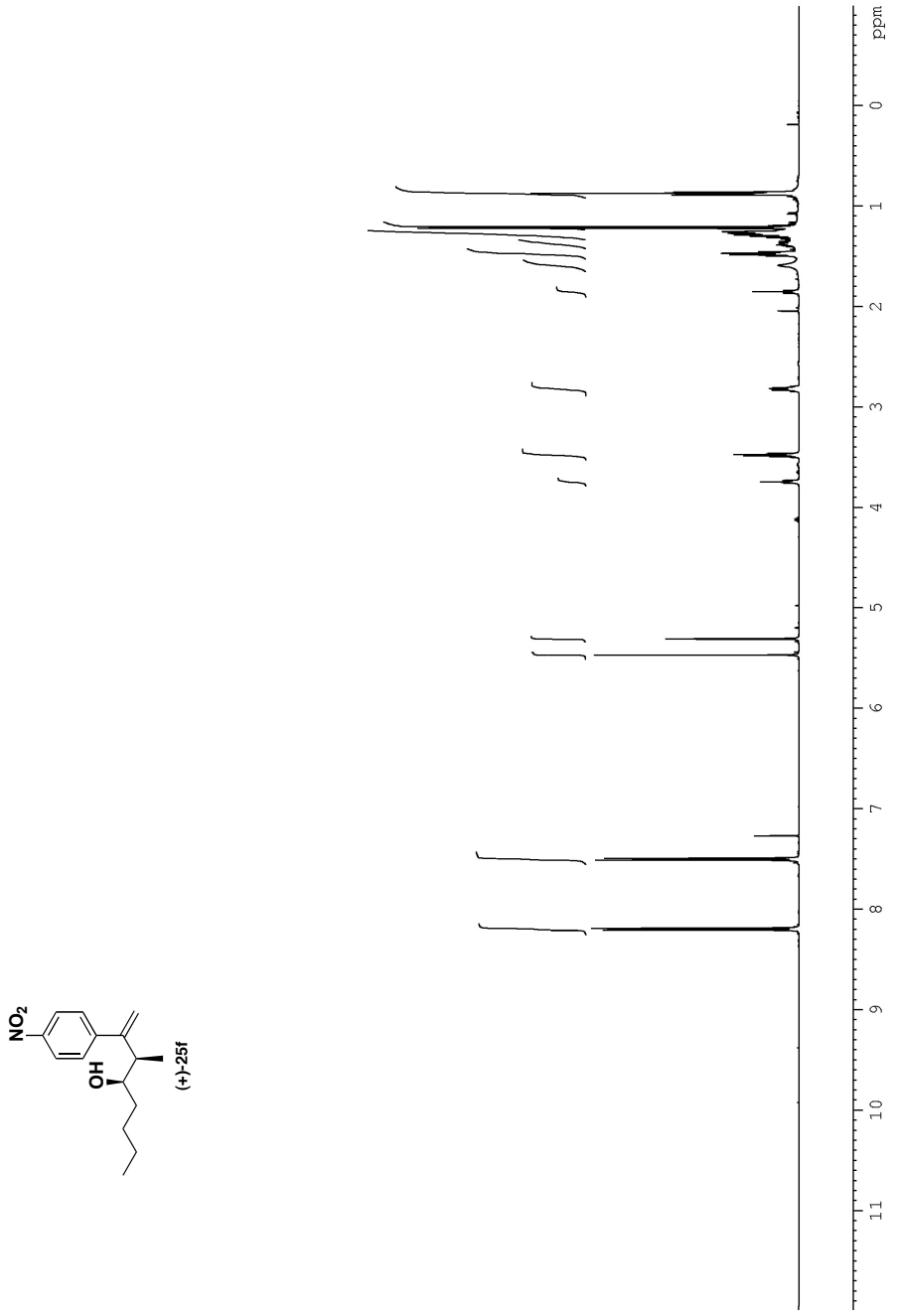
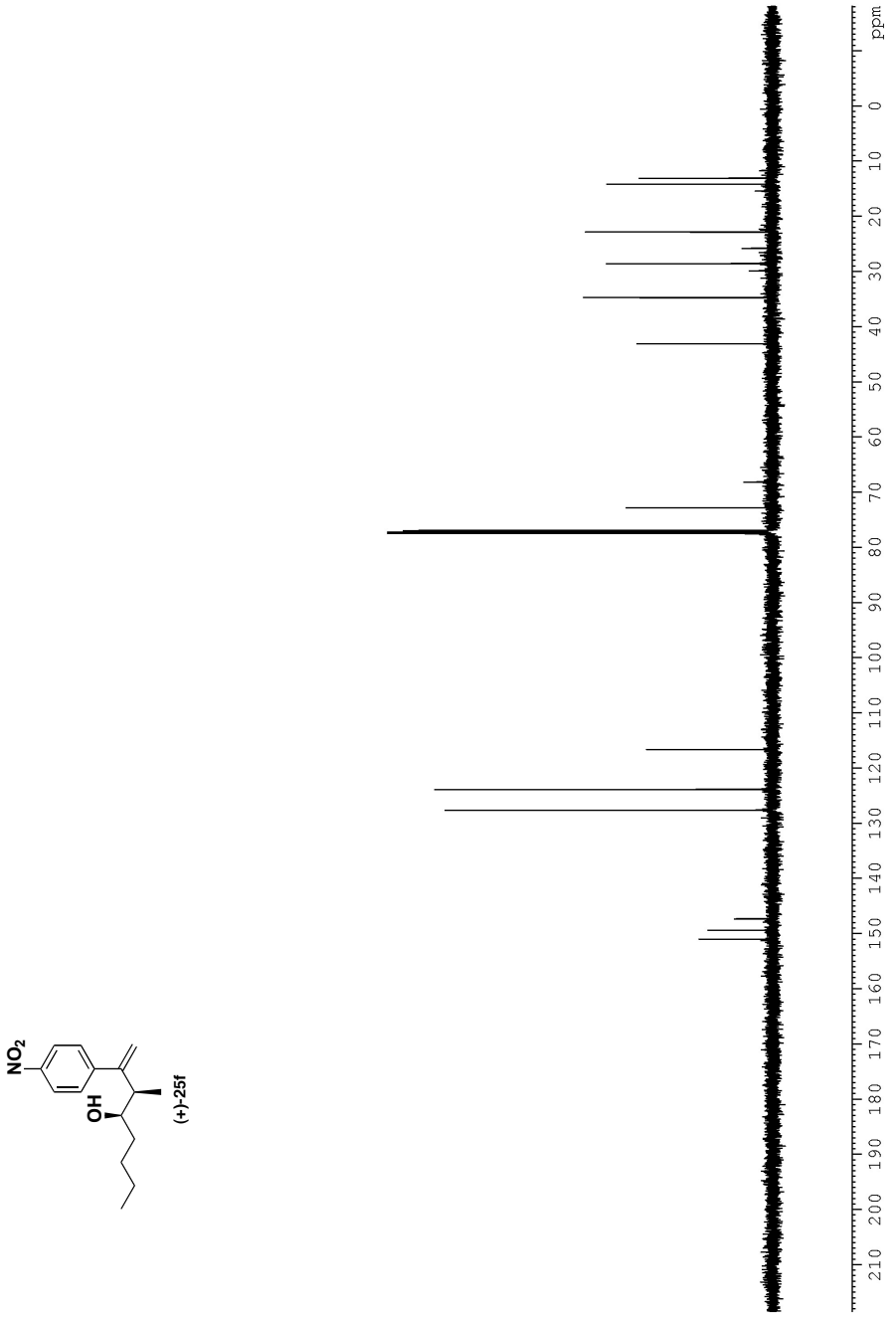

NO2
OH
(+)-25f
ppm
0
1
2
3
4
5
6
7
8
9
10
11


NO2
OH
(+)-25f
ppm
0
10
20
30
40
50
60
70
80
90
100
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150
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180
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200
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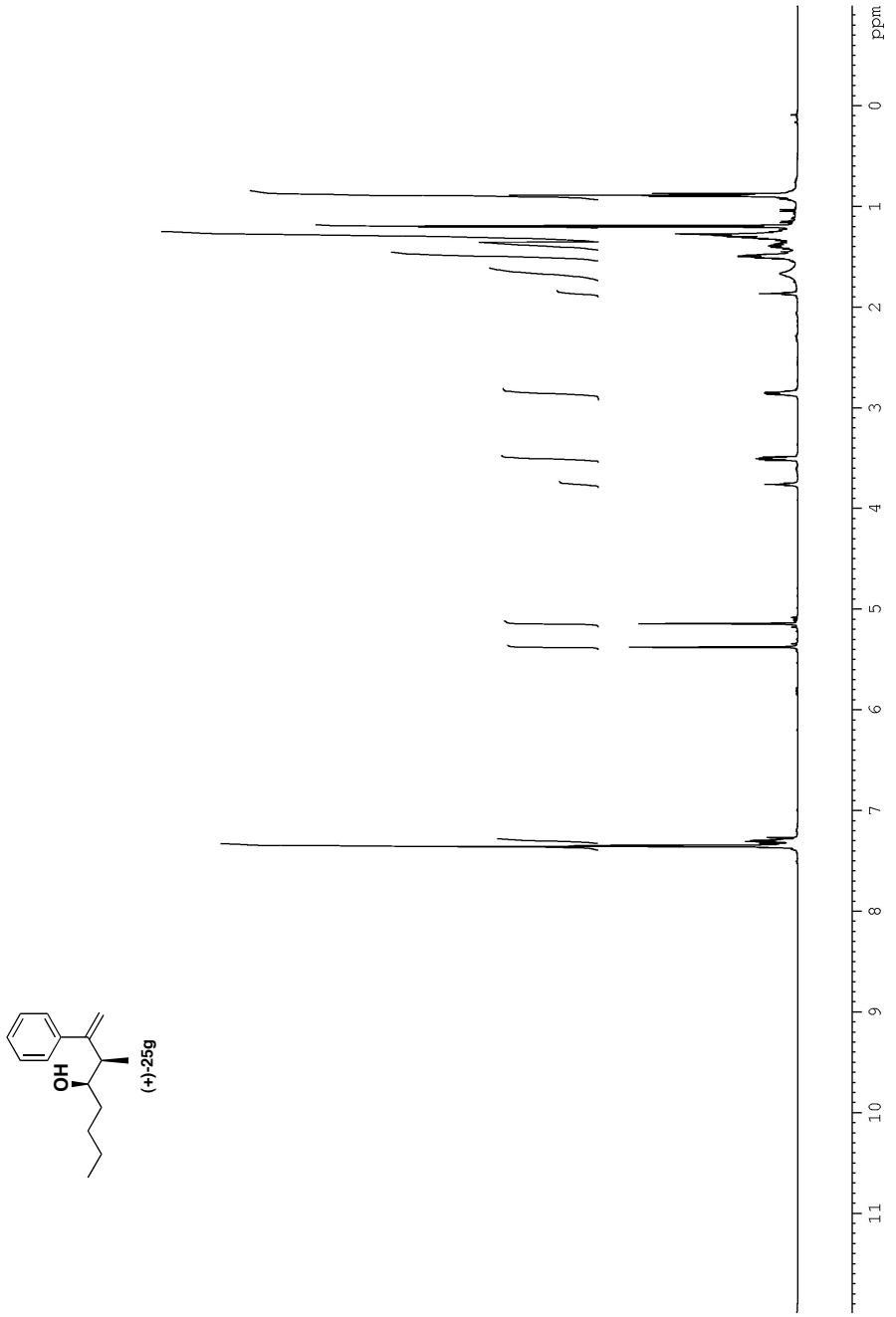
OH
(+)-25g
ppm
0
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2
3
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5
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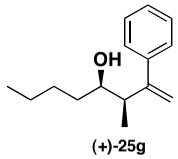
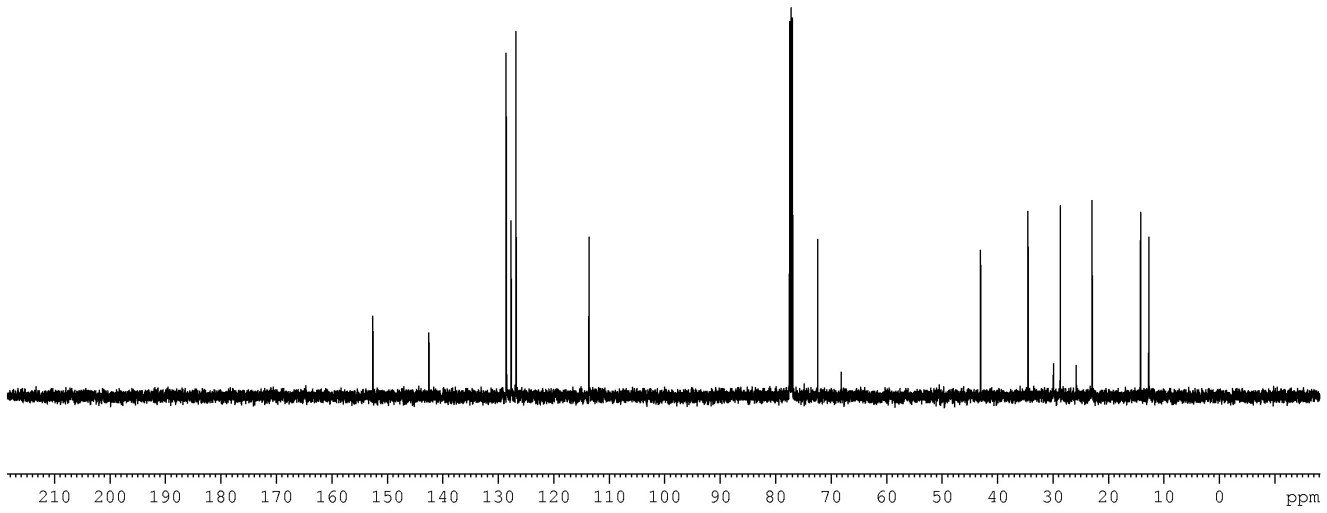
9
10
11


OH

(+)-25g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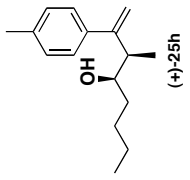
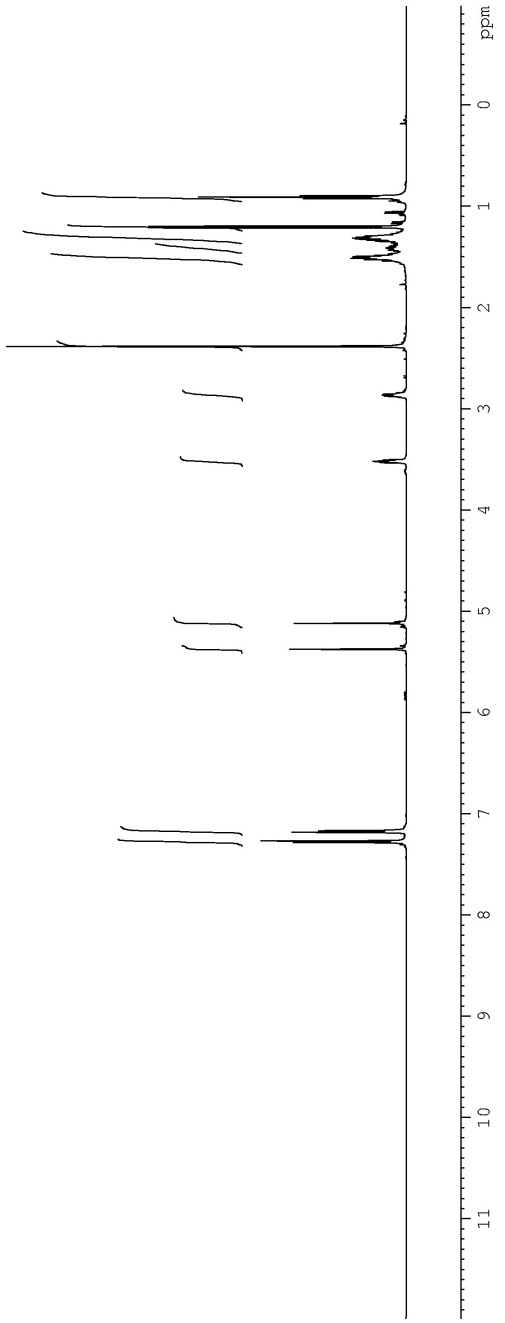

OH
(+)-25h


ppm
0
1
2
3
4
5
6
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8
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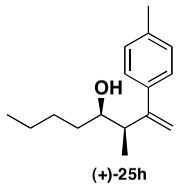
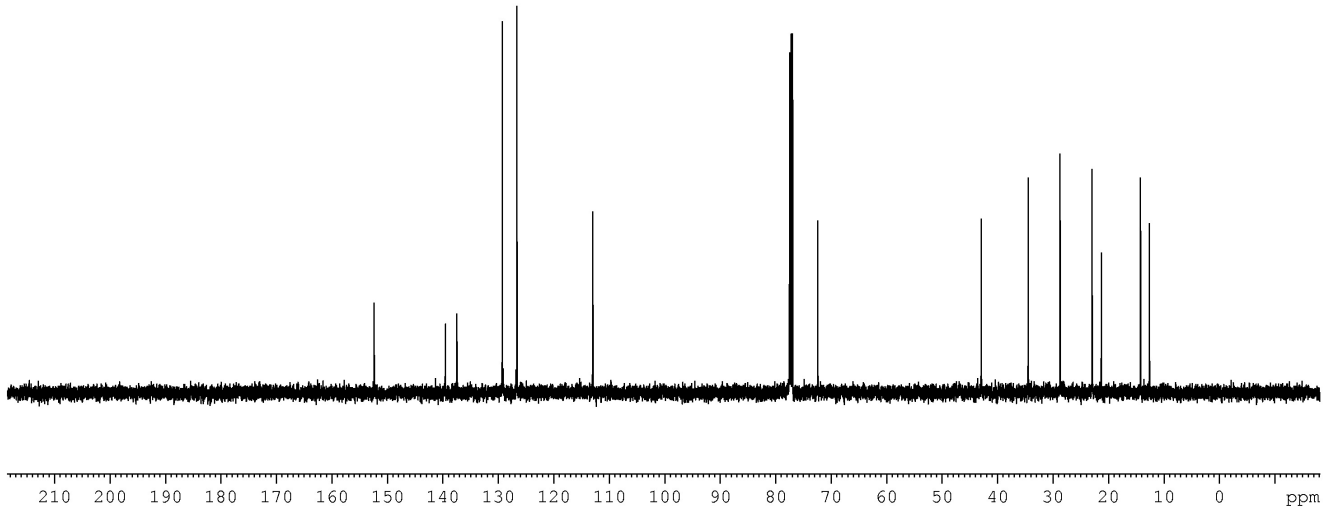
10
11


OH

(+)-25h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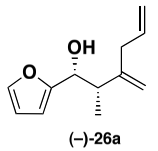
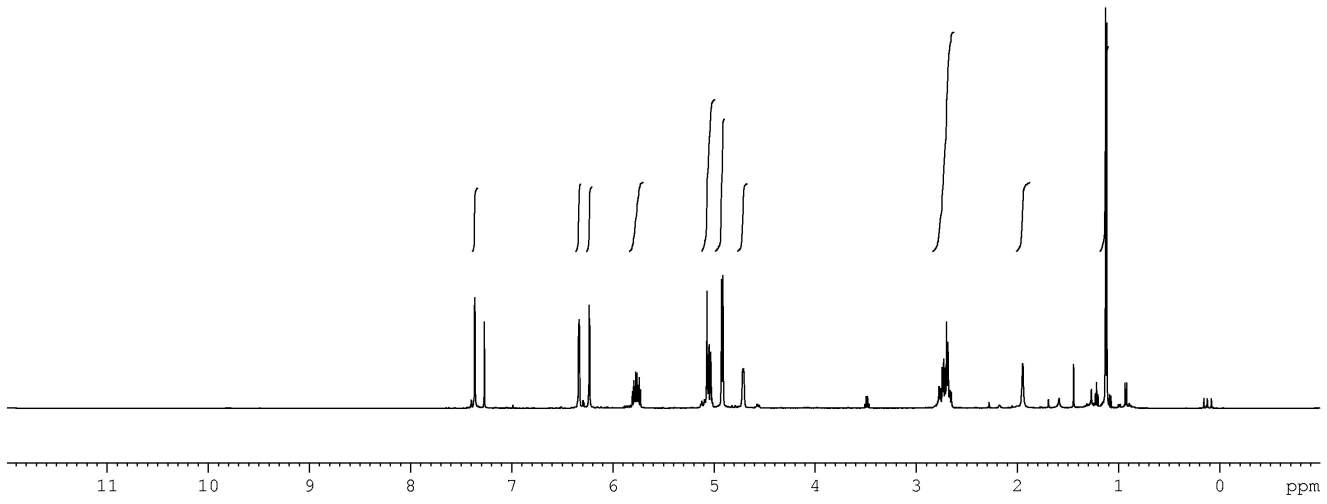
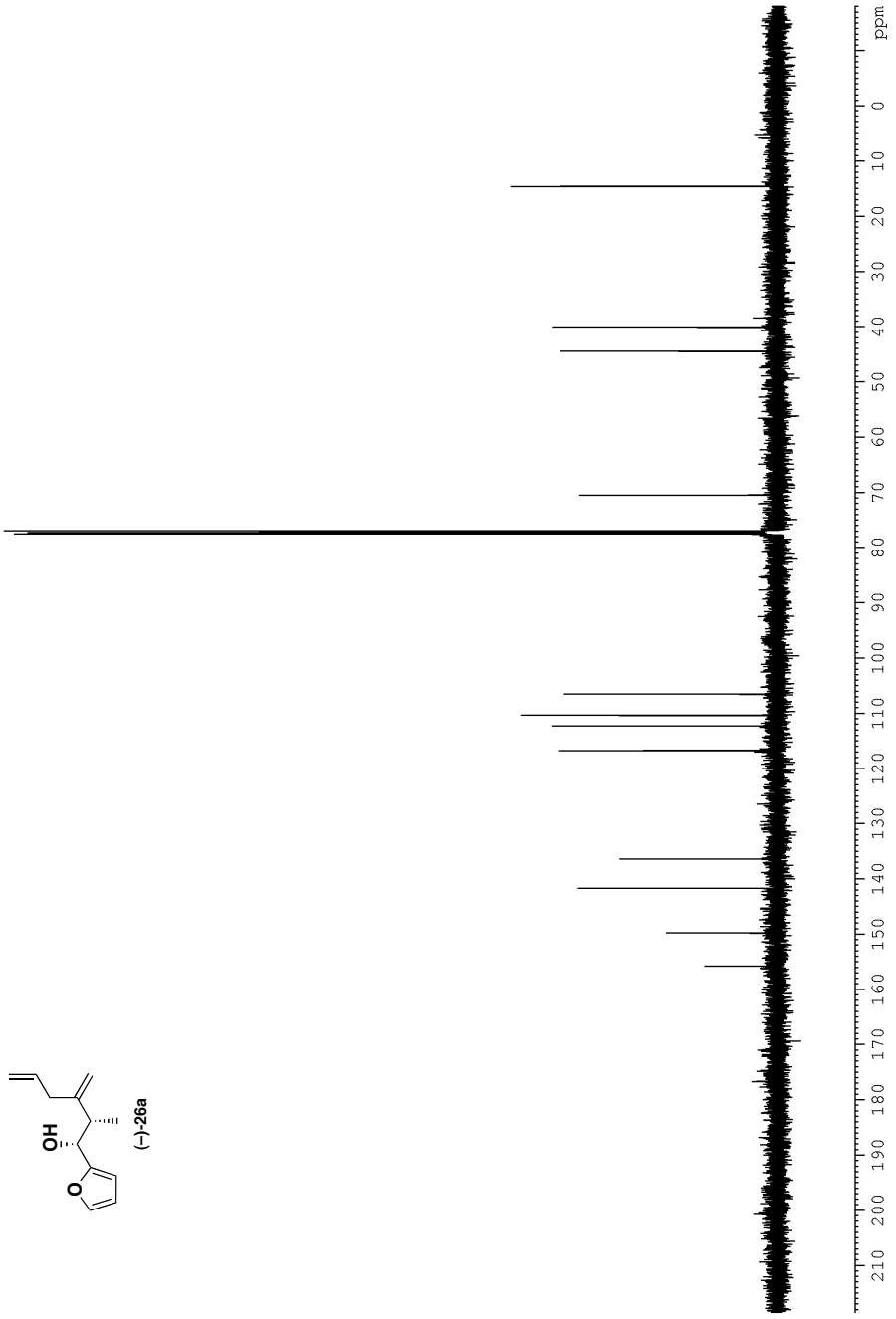


(–)-26a




OH
O
(–)-26a
ppm
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10
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30
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50
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70
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100
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130
140
150
160
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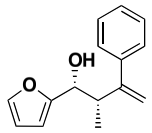
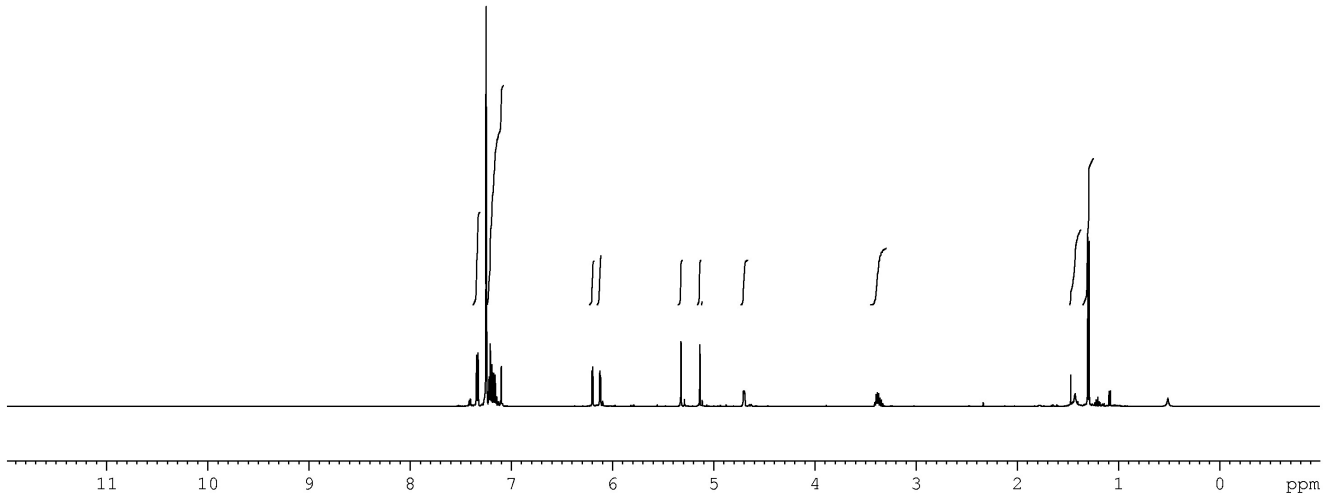
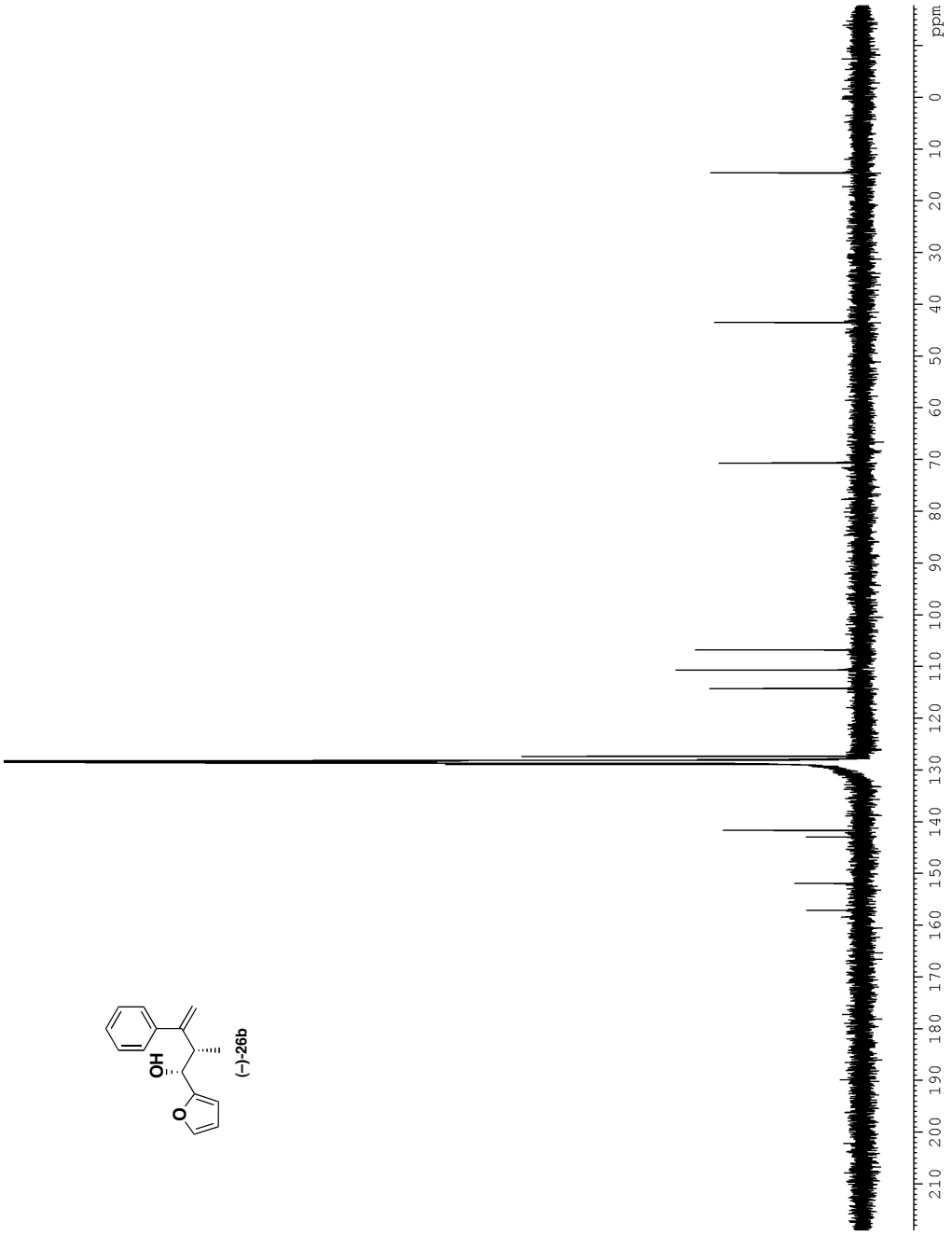
180
190
200
210



(–)-26b




OH
O
(–)-26b
ppm
0
10
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30
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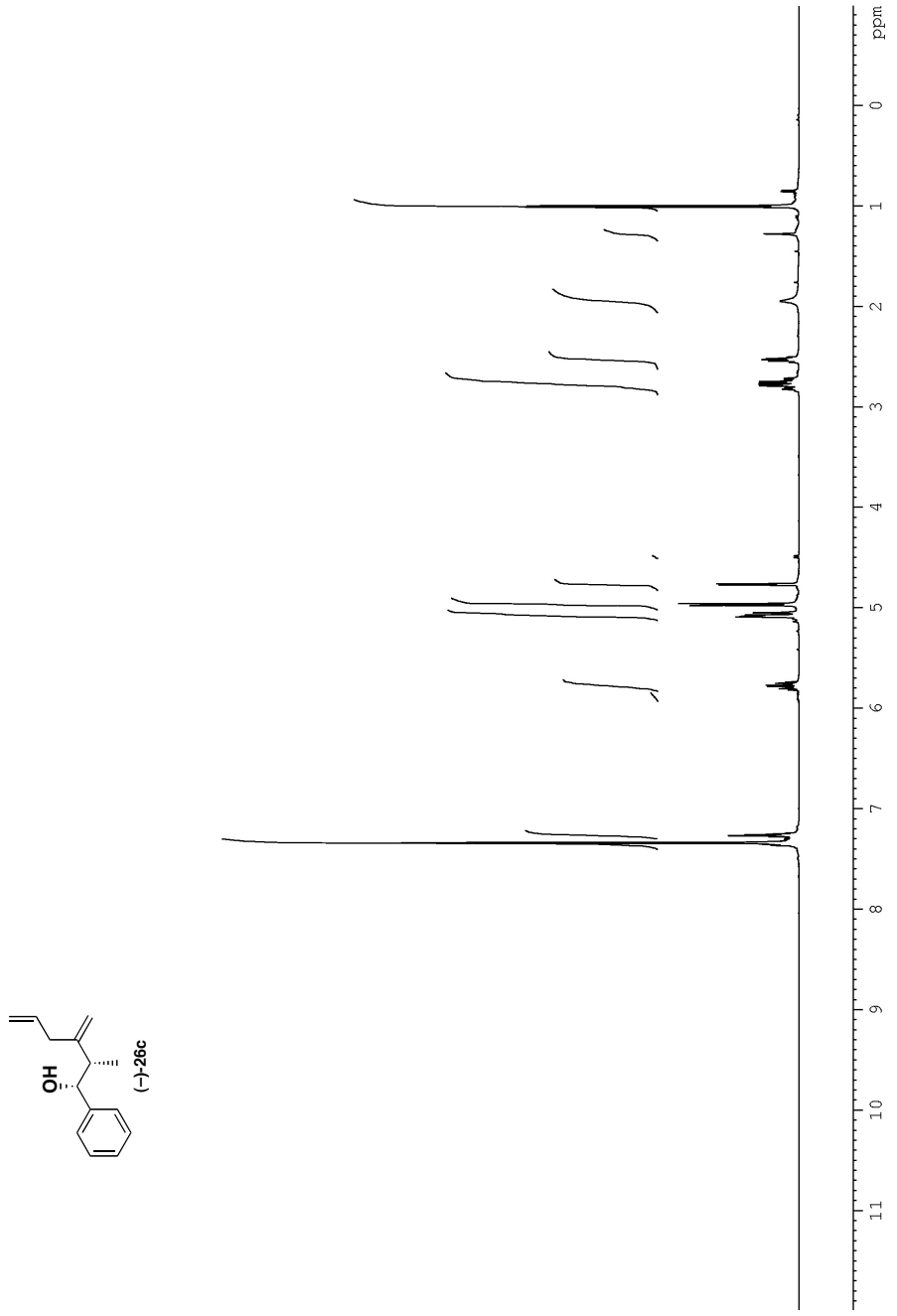
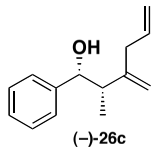
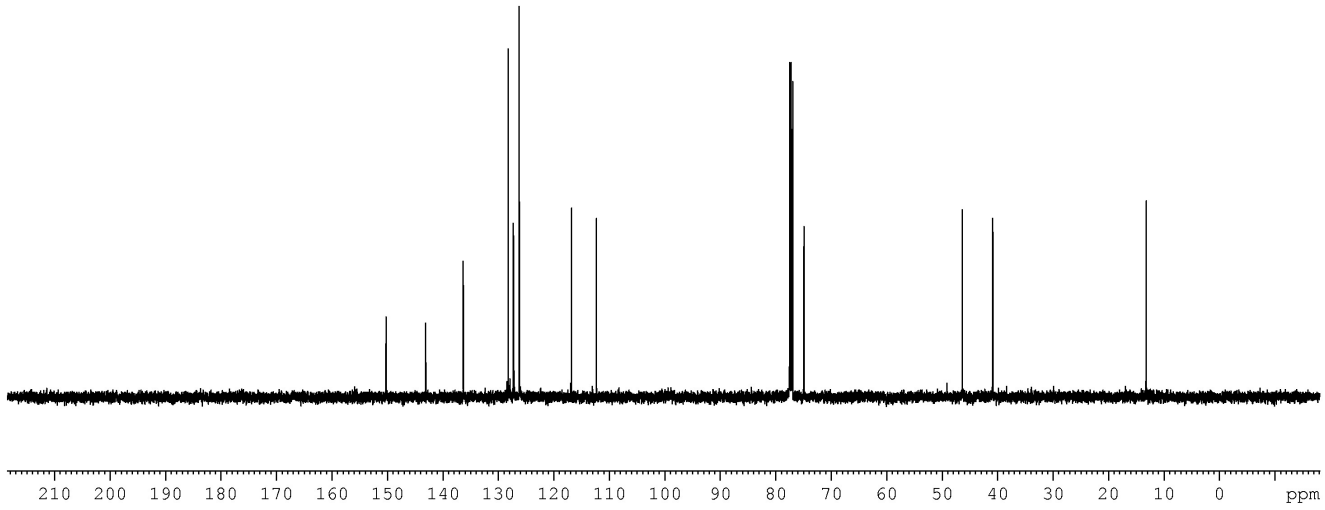
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210


OH
(–)-26c
ppm
0
1
2
3
4
5
6
7
8
9
10
11


OH

(–)-26c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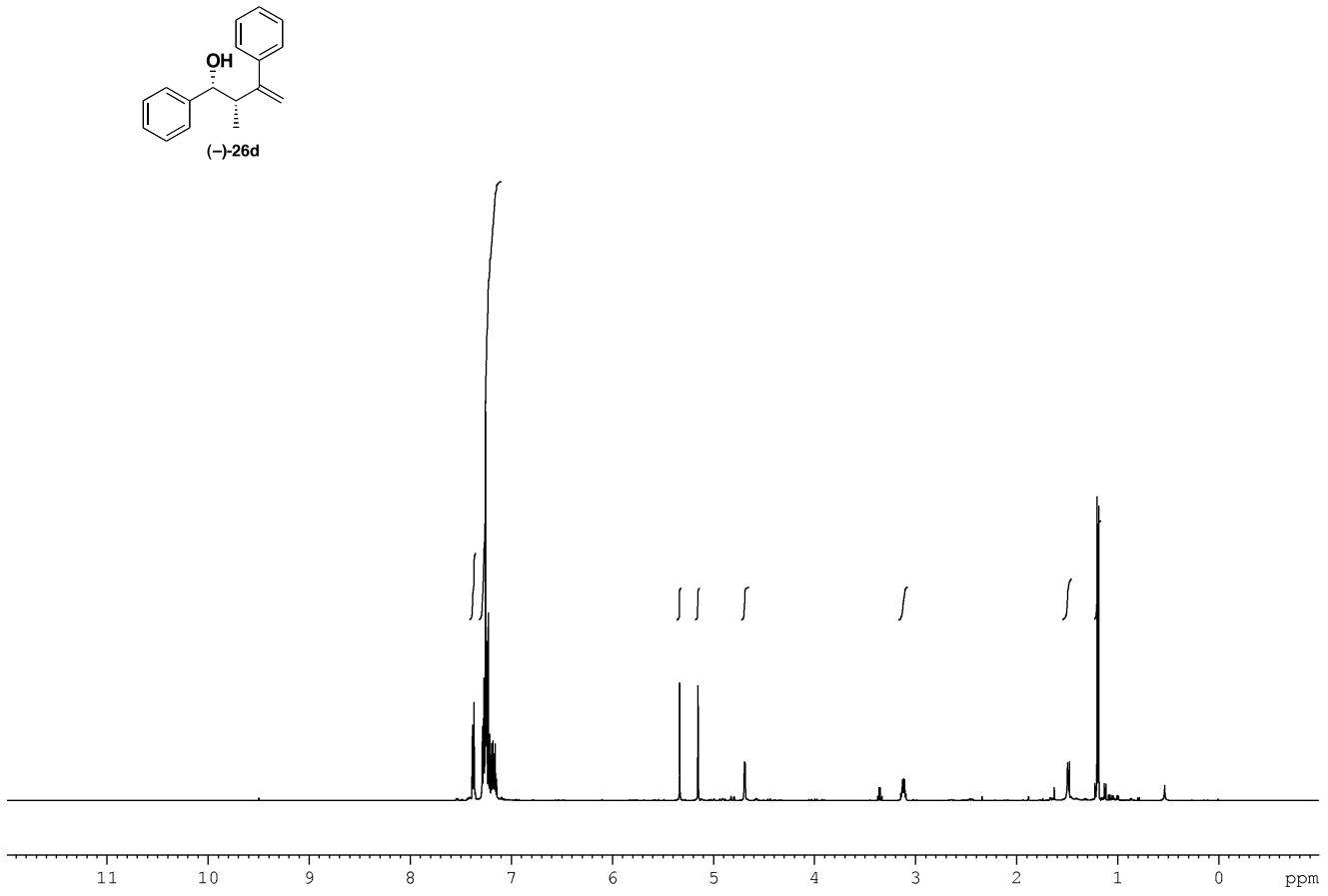
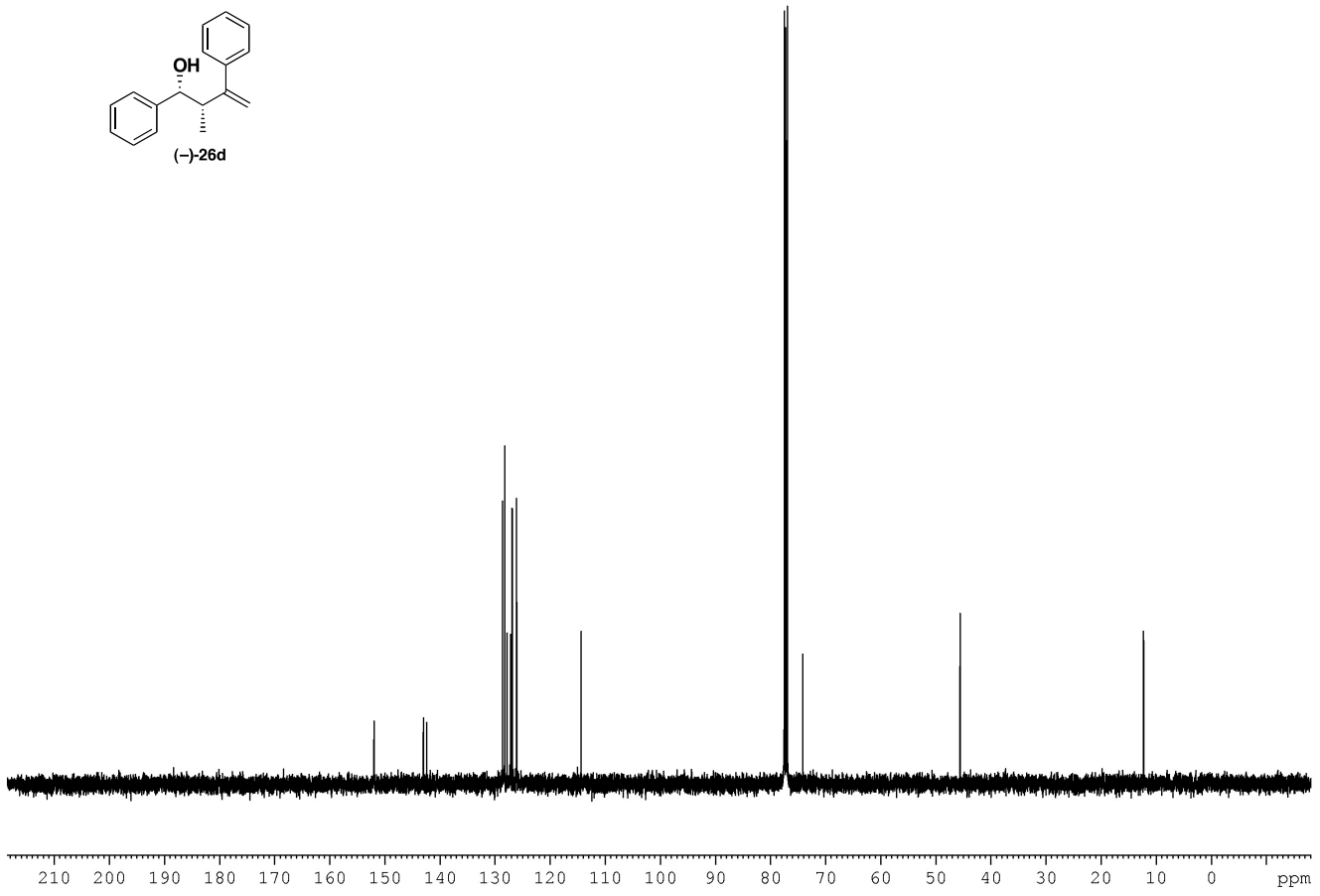
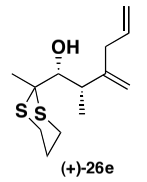
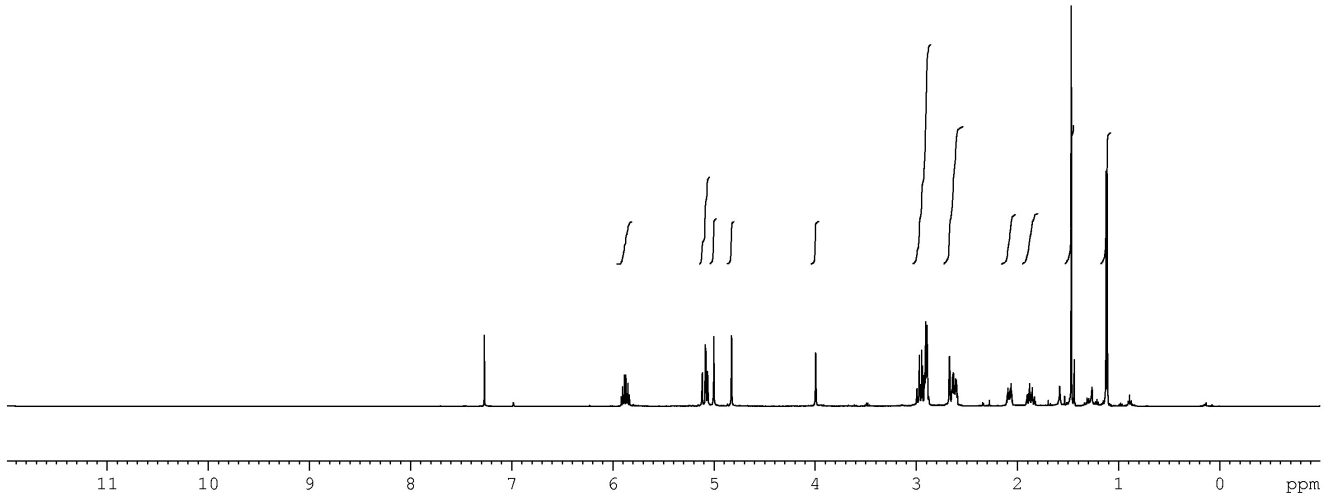
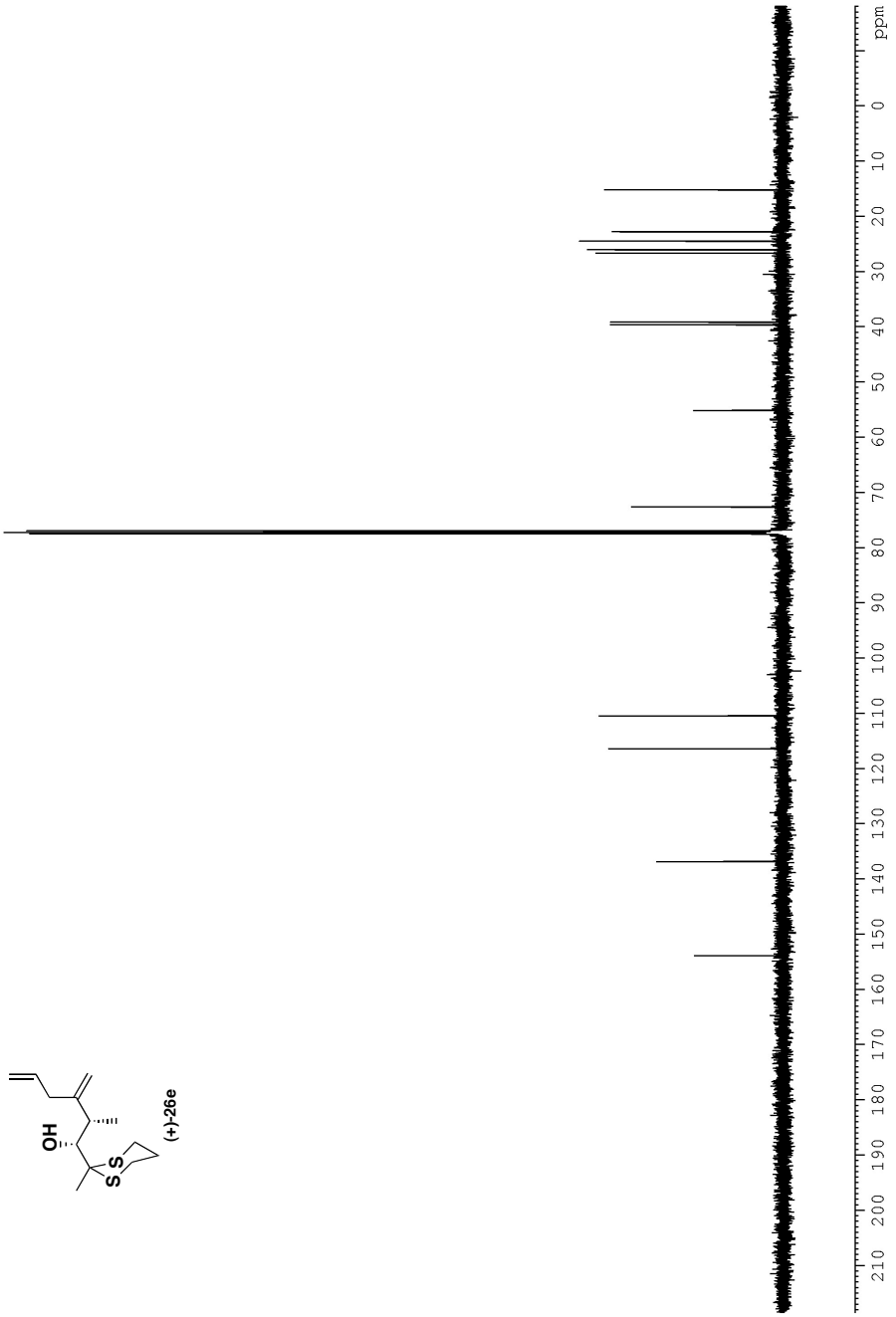

OH
(–)-26d
11
10
9
8
7
6
5
4
3
2
1
0
ppm


OH
(–)-26d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



(+)-26e




OH
S
S
(+)-26e
ppm
0
10
20
30
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50
60
70
80
90
100
110
120
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140
150
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180
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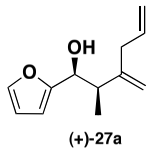
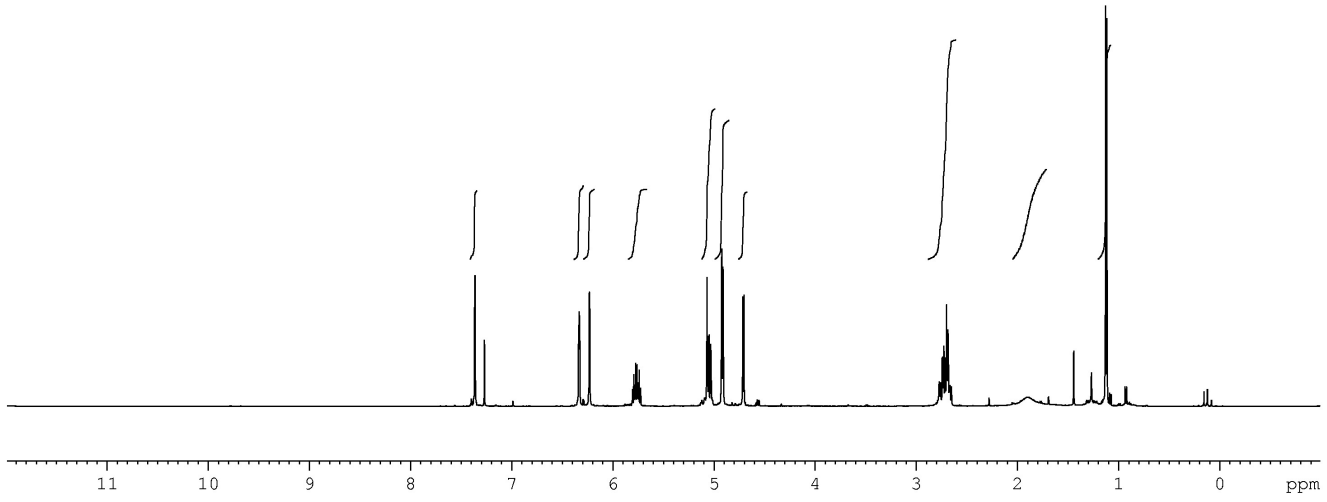
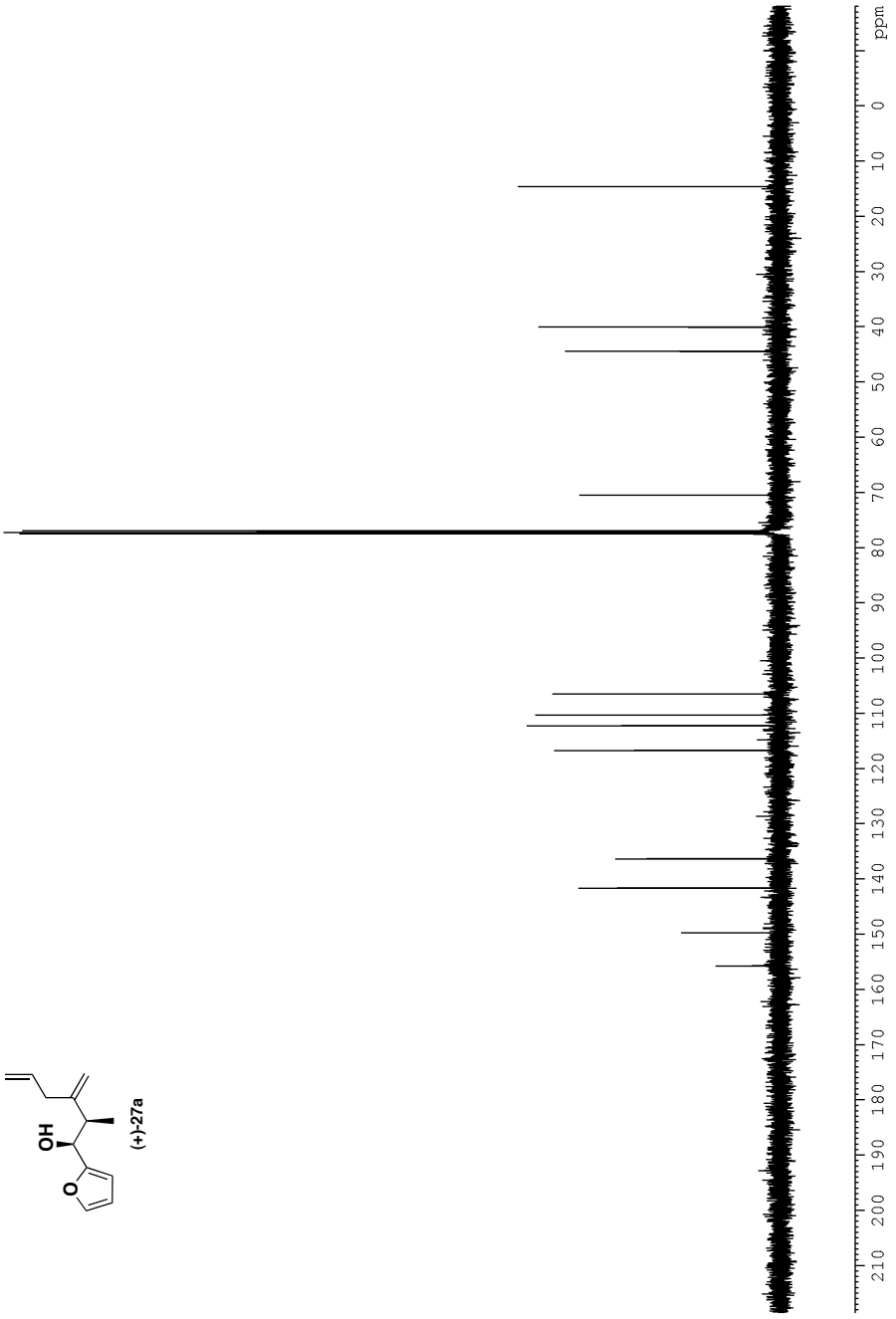
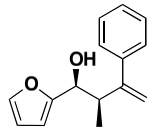
200
210



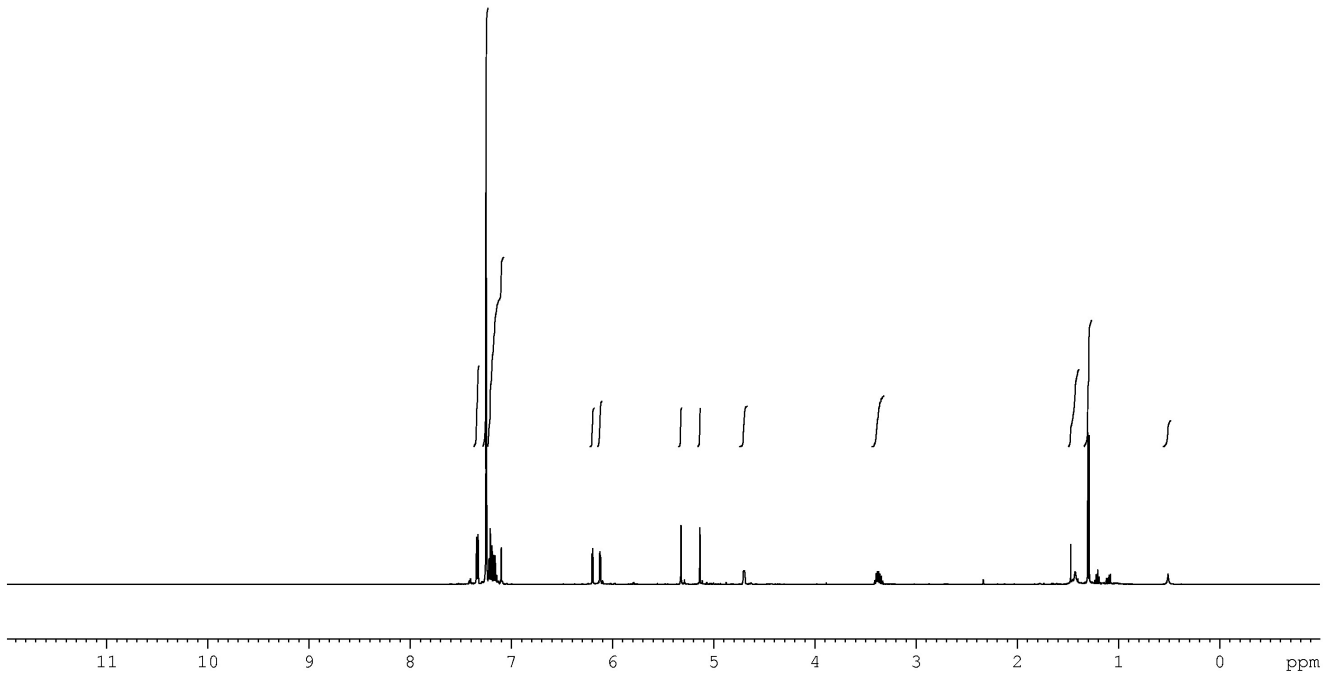
(+)-27a

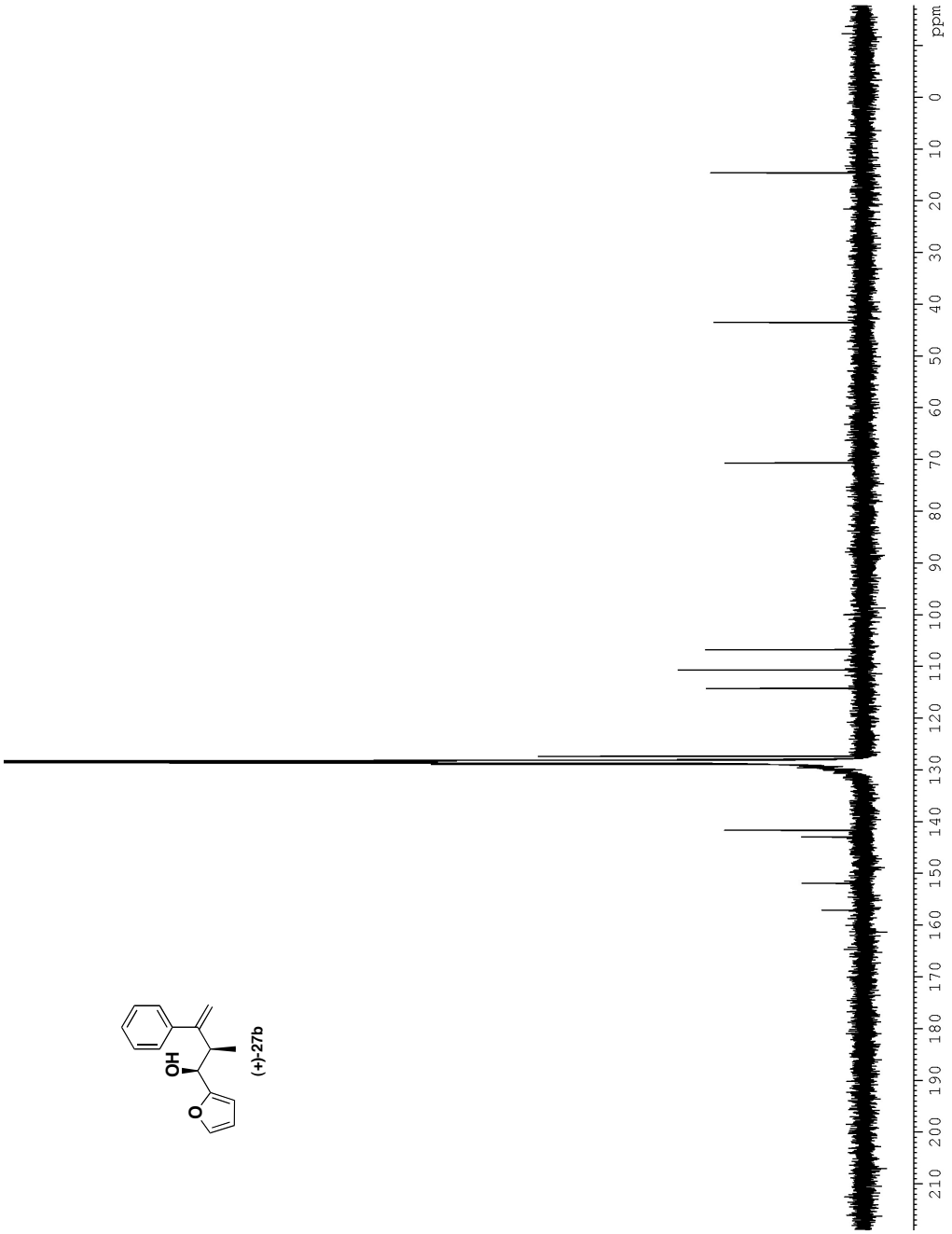


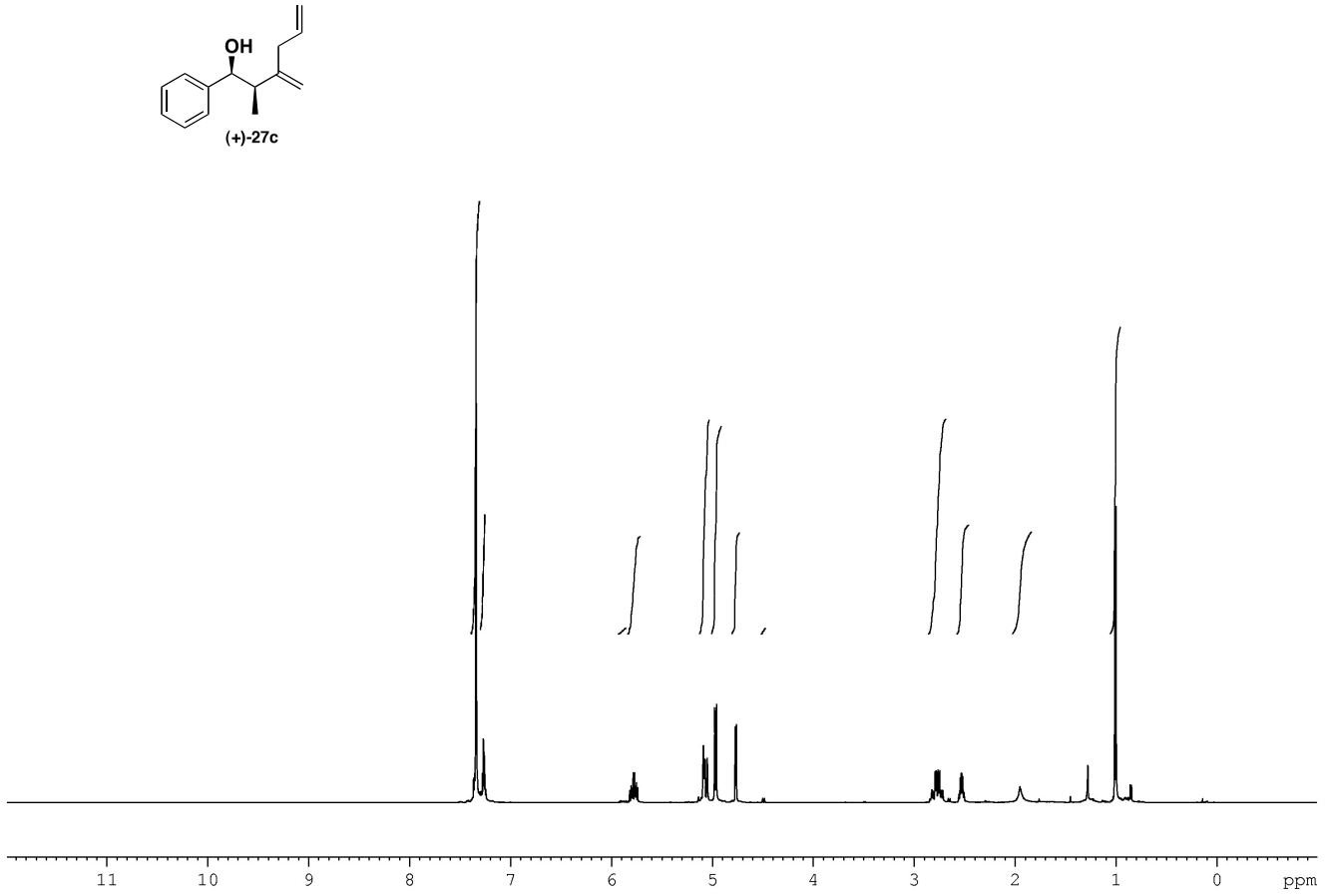

OH
O
(+)-27a
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210

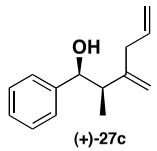


(+)-27b

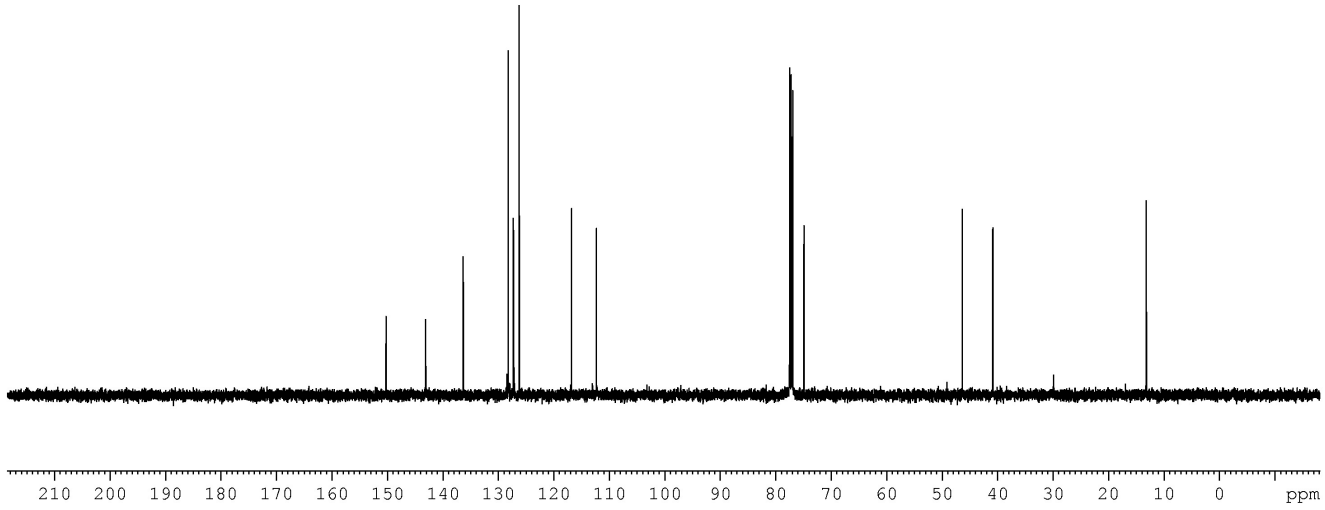



OH
O
(+)-27b
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210


OH
(+)-27c
11
10
9
8
7
6
5
4
3
2
1
0
ppm


OH

(+)-27c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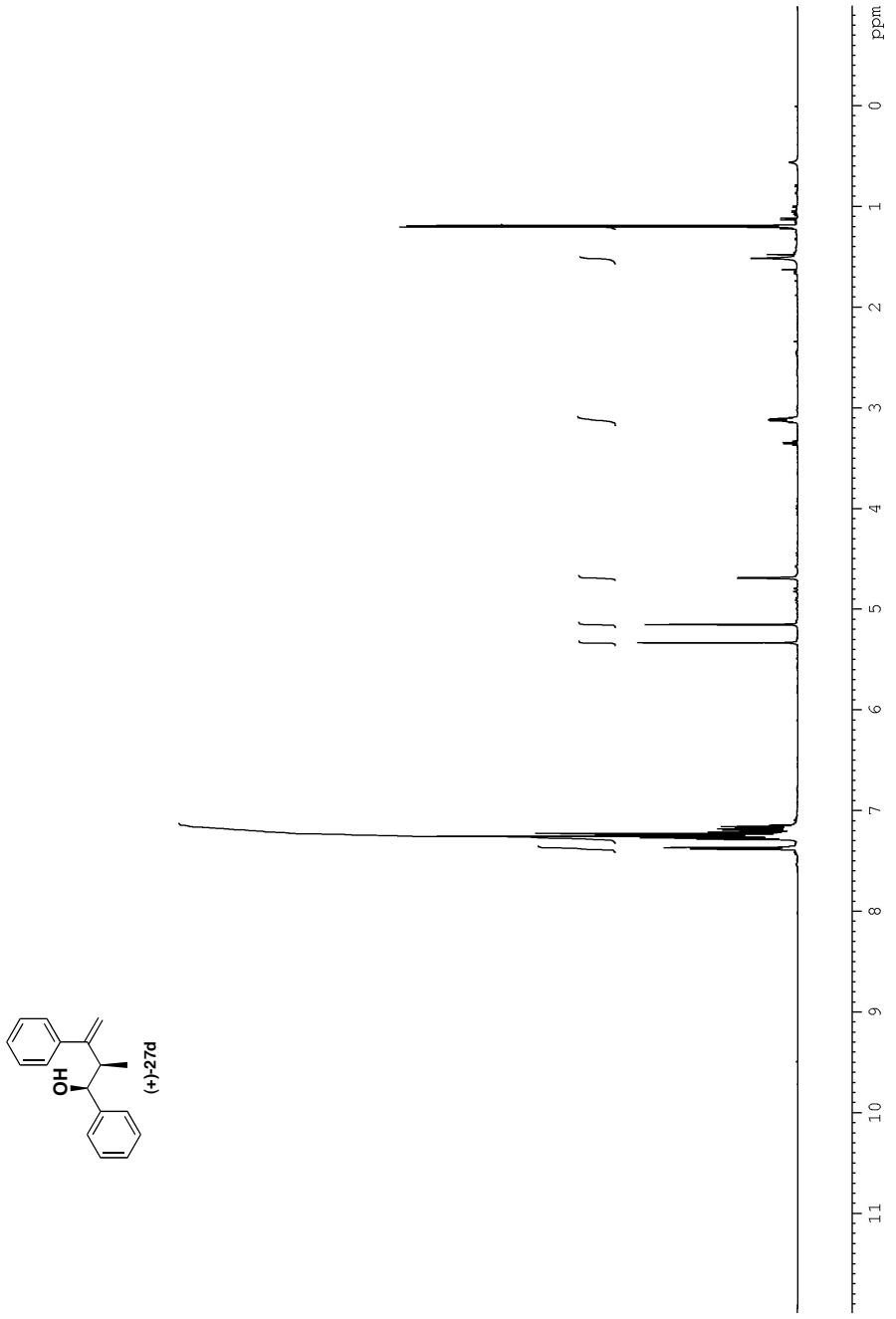
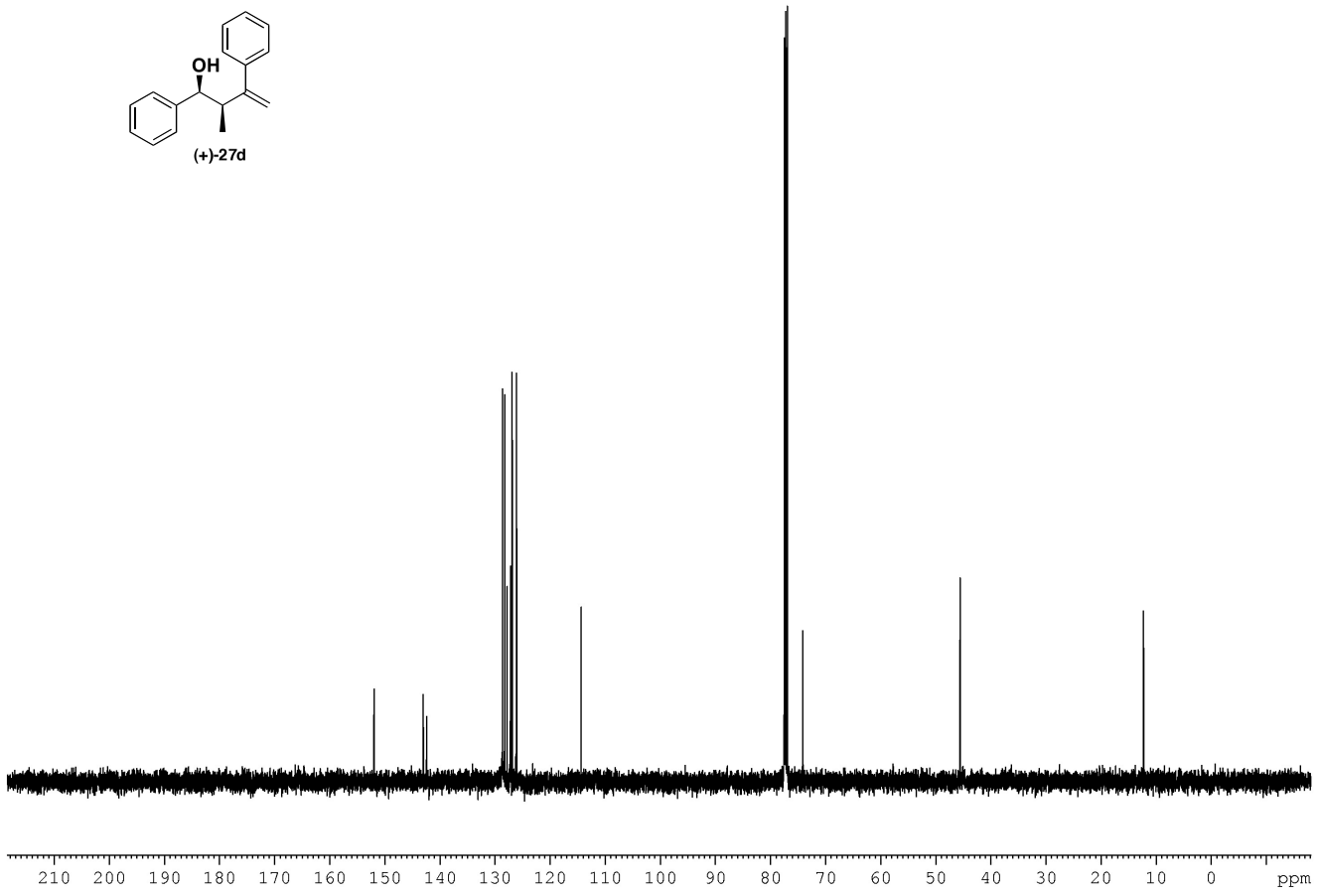
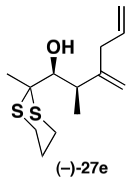
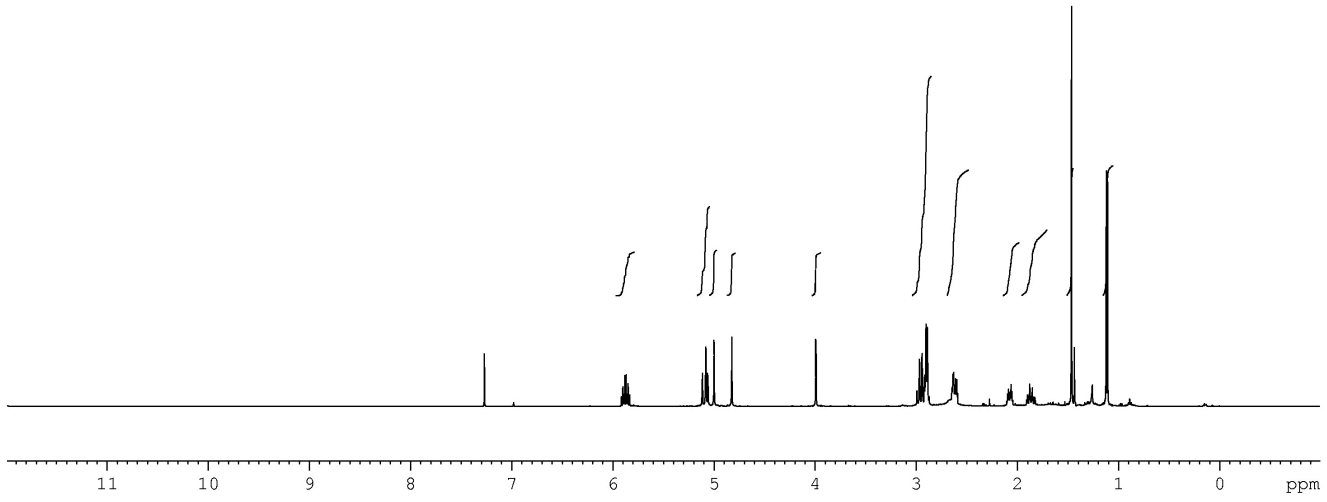
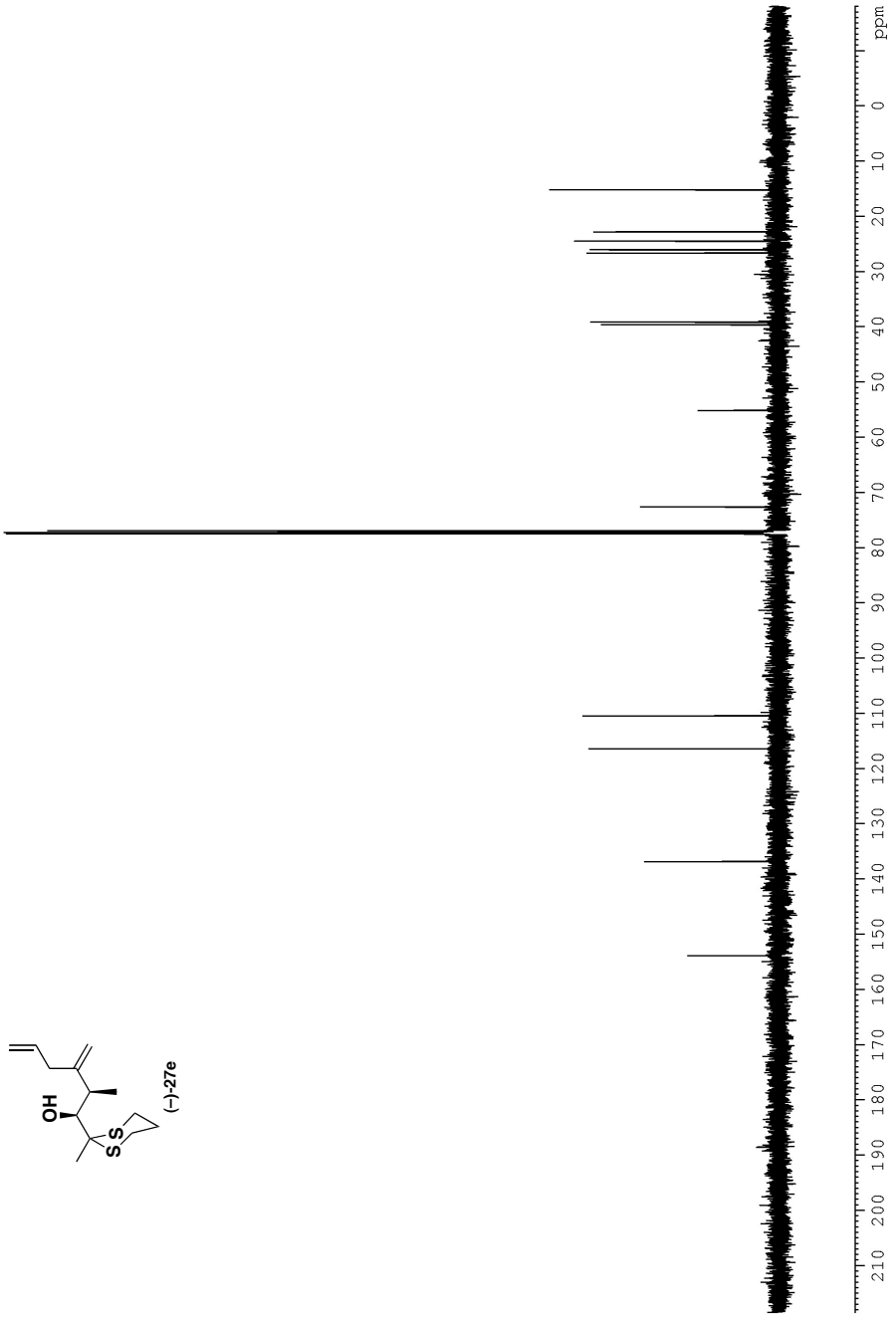

OH
(+)-27d
ppm
0
1
2
3
4
5
6
7
8
9
10
11


OH
(+)-27d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



(–)-27e




OH
S
S
(–)-27e
ppm
0
10
20
30
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50
60
70
80
90
100
110
120
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140
150
160
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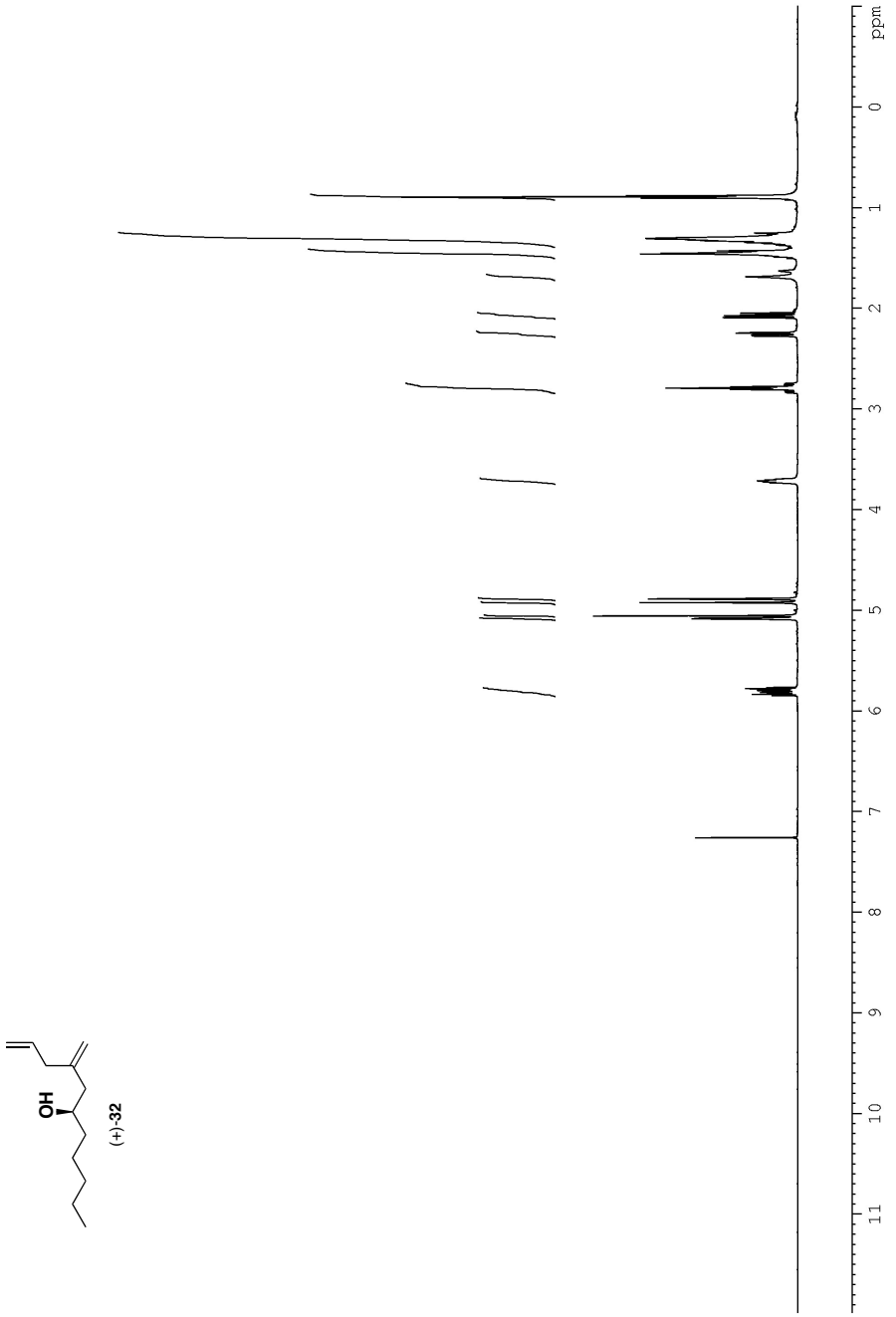
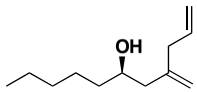
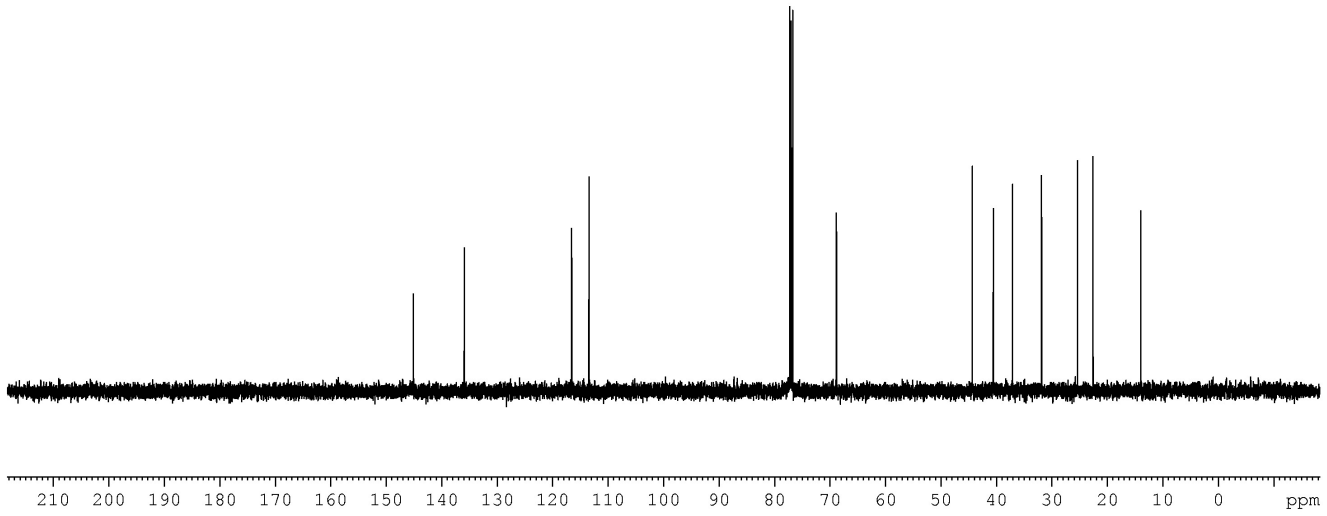
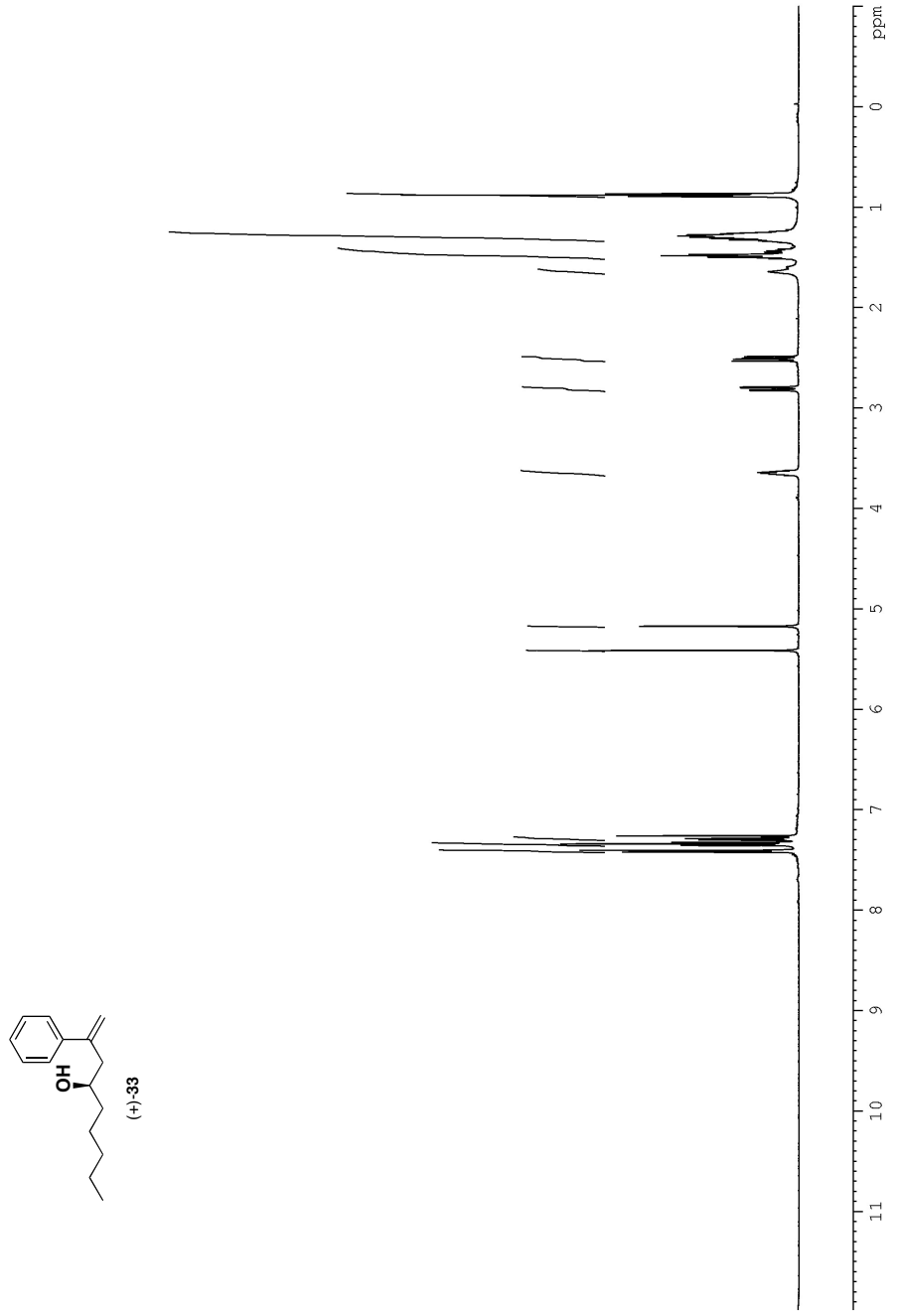
180
190
200
210


OH
(+)-32
ppm
0
1
2
3
4
5
6
7
8
9
10
11


OH

(+)-**32**


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


OH
(+)-33
ppm
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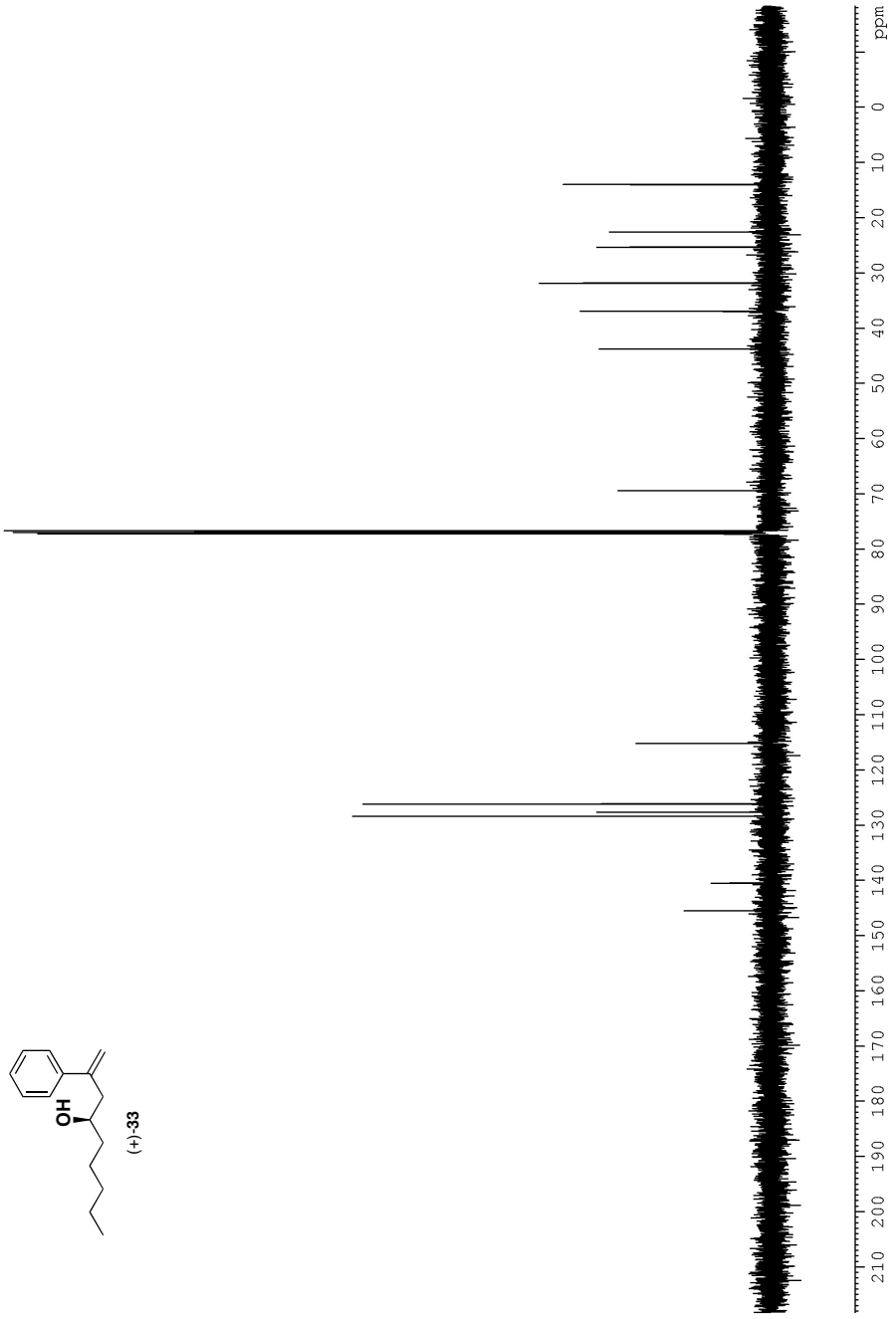
2
3
4
5
6
7
8
9
10
11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(+)-33
ppm
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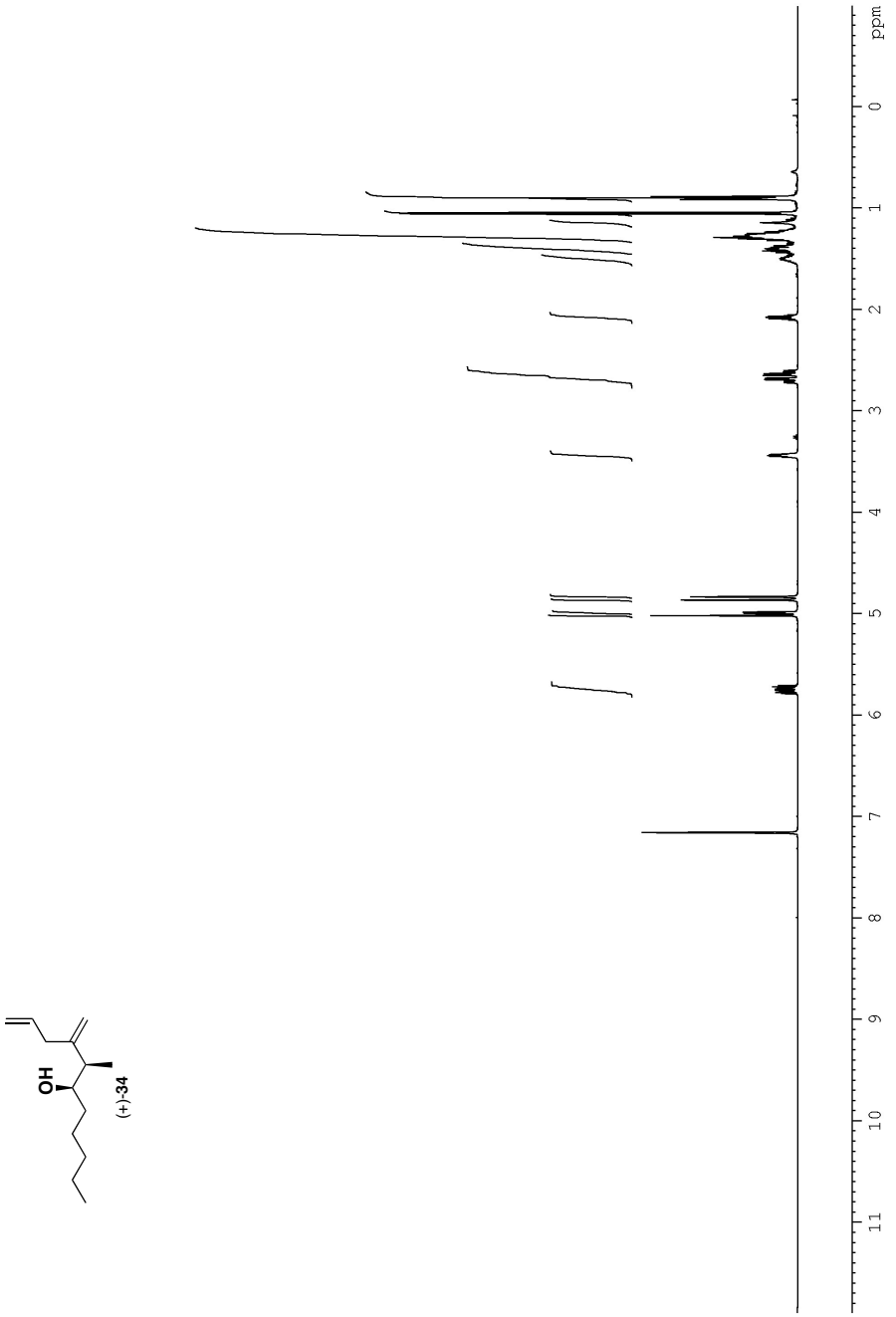
190
200
210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ppm
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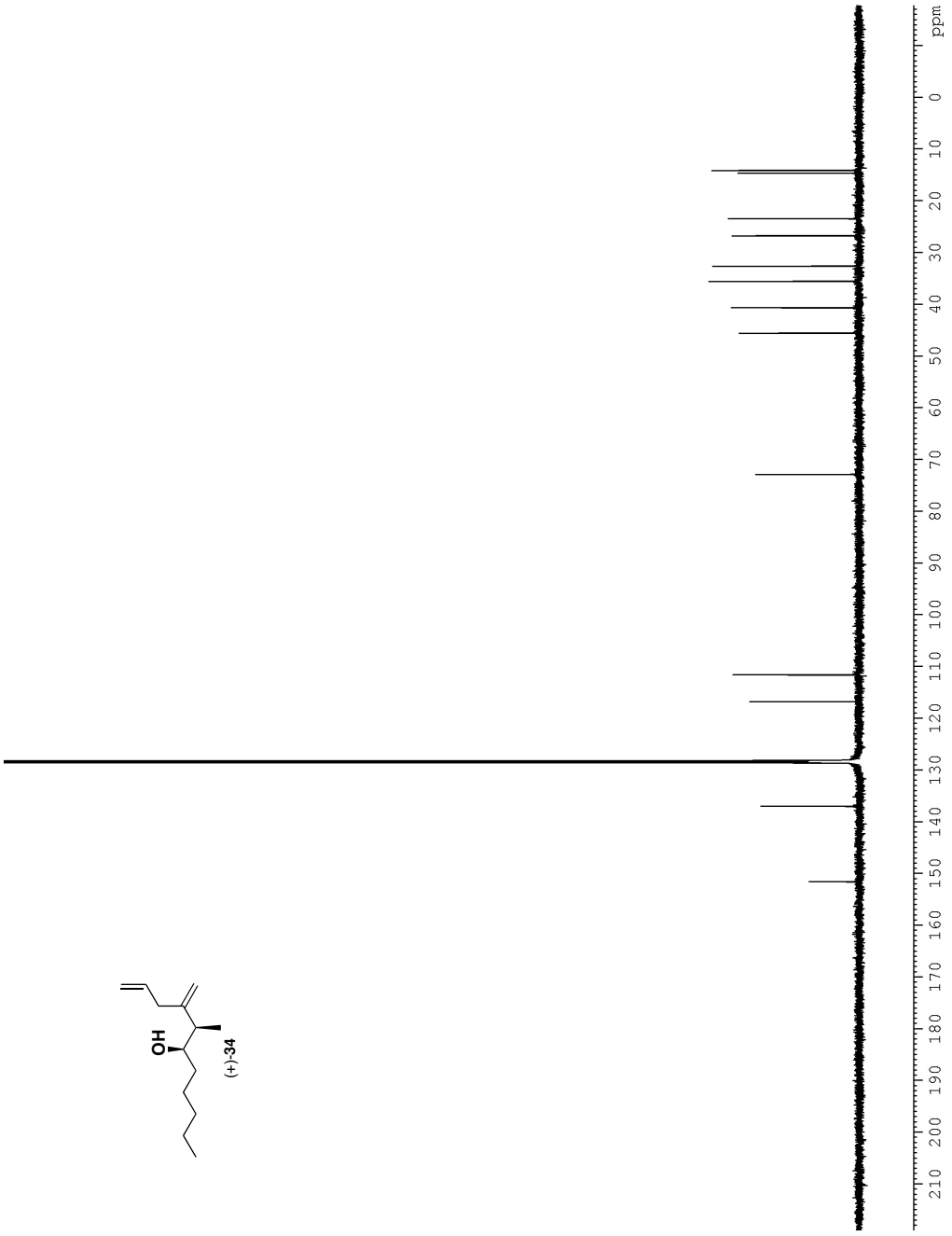
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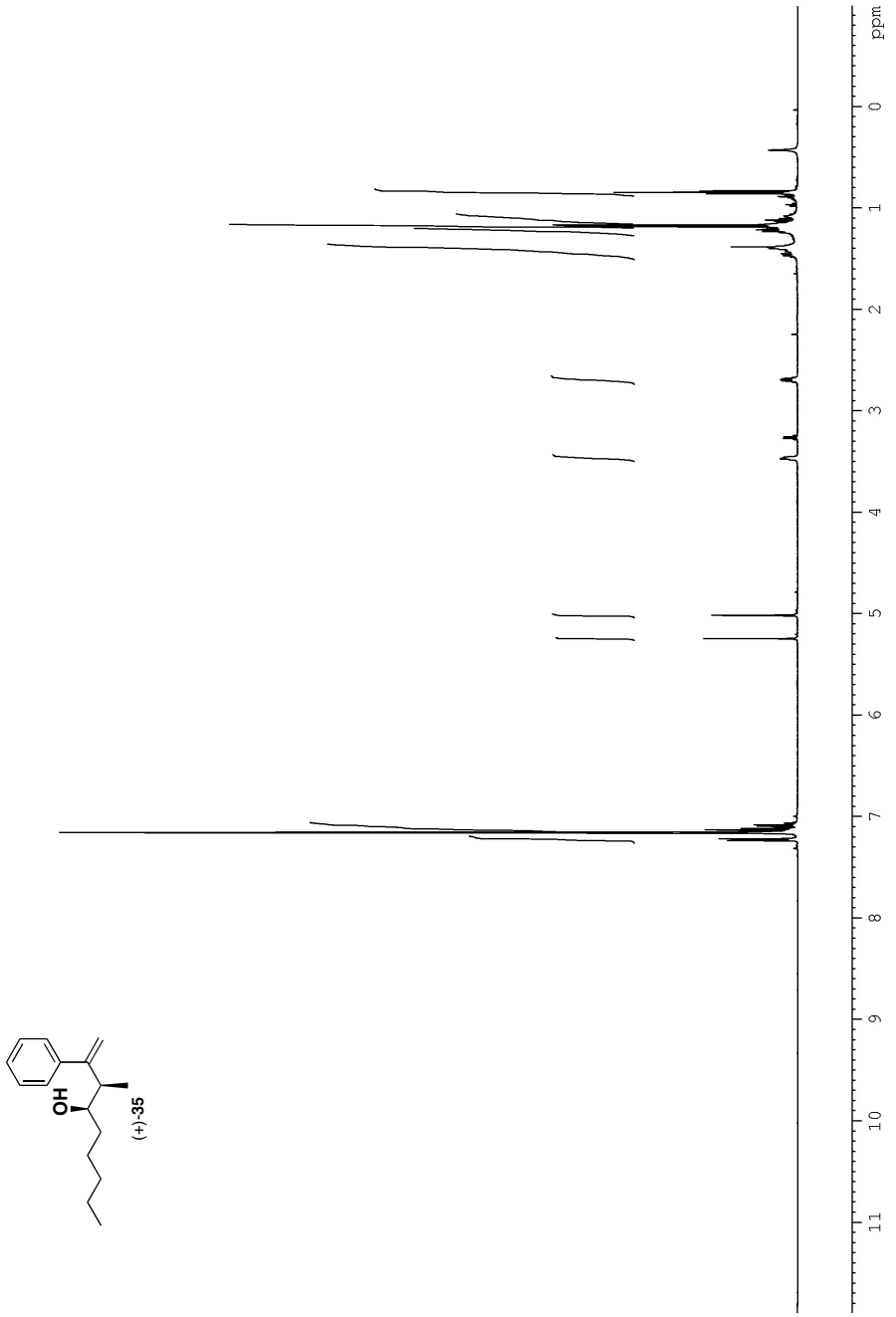
OH
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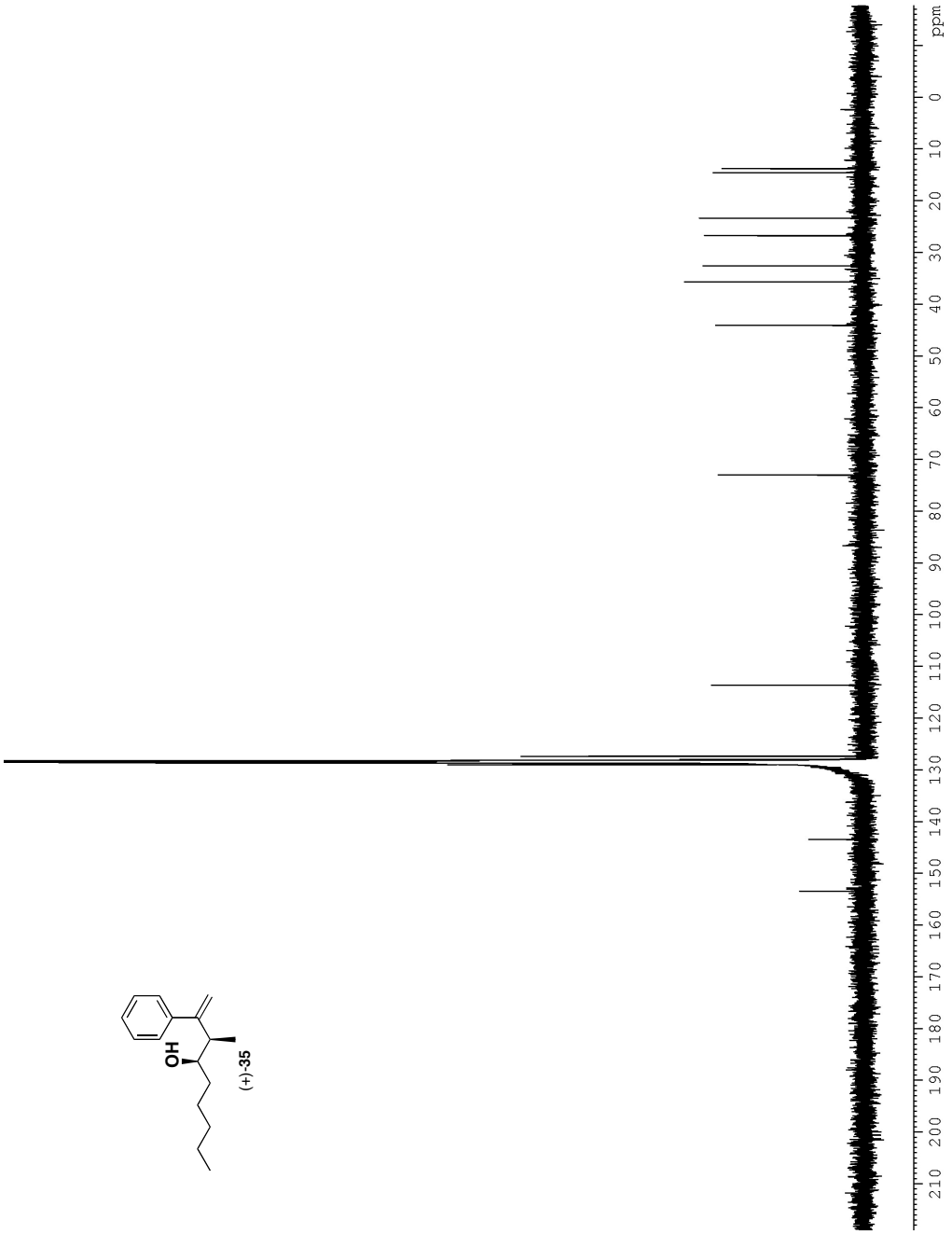
OH
(+)-35
ppm
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170
180
190
200
210