# Stereoselective Borylative Ketone–Diene Coupling

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## Supporting Information

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## General Information

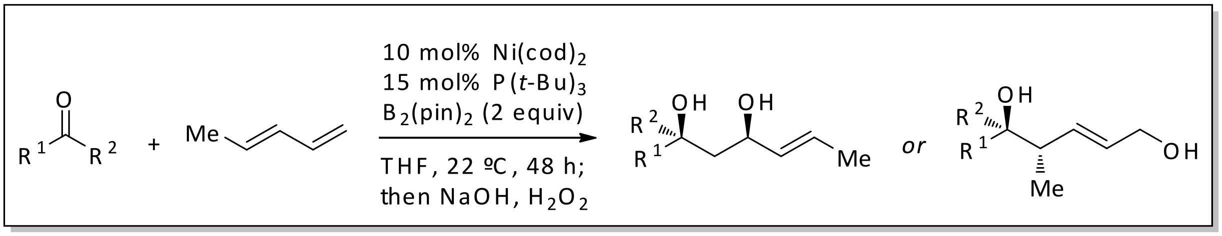
$^1$H NMR spectra were recorded on either a Varian Gemini-400 (400 MHz), or a Varian Inova-500 (500 MHz) spectrometer. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm, $C_6D_6$: 7.16 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, br = broad, and m = multiplet), coupling constants (Hz), and assignment. $^{13}$C NMR spectra were recorded on either a Varian Gemini-400 (100 MHz), or a Varian Inova-500 (125 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 77.16 ppm). Infrared (IR) spectra were recorded on a Bruker alpha spectrophotometer, $\nu_{max}$ cm$^{-1}$. Bands are characterized as broad (br), strong (s), medium (m), and weak (w). High resolution mass spectrometry was performed at the Mass Spectrometry Facility, Boston College.

Liquid Chromatography was performed using forced flow (flash chromatography) on silica gel ($SiO_2$, 40-63 μm) purchased from Silicycle. Thin Layer Chromatography was performed on 25 μm silica gel plates purchased from Silicycle. Visualization was performed using ultraviolet light (254 nm), phosphomolybdic acid (PMA) in ethanol, potassium permanganate ($KMnO_4$) in water, or cerium(IV) sulfate and ammonium molybdate in sulfuric acid.

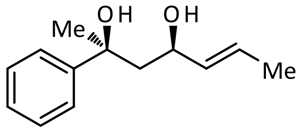
All reactions were conducted in oven- or flame-dried glassware under an inert atmosphere of nitrogen or argon. Tetrahydrofuran (THF), dichloromethane, and diethyl ether were purified using a Pure Solv MD-4 solvent purification system from Innovative Technology Inc. Bis(pinacolato)diboron [$B_2$(pin)$_2$] was obtained from AllyChem Co., Ltd. and recrystallized from pentane prior to use. Ketones were purchased from Aldrich and distilled/recrystallized prior to use. Bis(1,5-cyclooctadiene)nickel(0) [Ni(cod)$_2$] and phosphine ligands were purchased from Strem Chemicals, Inc. and used without further purification. Piperylene (1,3-pentadiene) was purchased from ChemSampCo and distilled prior to use. All other reagents were purchased from either Fisher or Aldrich and used without further purification.

## Experimental Procedures

### General Procedure for Borylative Ketone–Diene Coupling (Scheme 3 & Table 1).



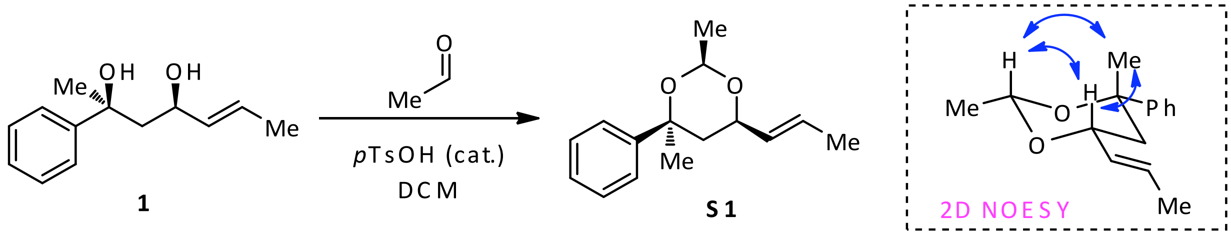
An oven-dried 20 mL scintillation vial, equipped with a magnetic stir-bar, was charged with Ni(cod)$_2$ (0.05 mmol, 0.10 equiv), P(*t*-Bu)$_3$ (0.075 mmol, 0.15 equiv), and THF (2.5 mL, 0.2 M) in a dry box under an argon atmosphere. After stirring for 5 min, the ketone (0.5 mmol. 1.0 equiv), *trans*-1,3-pentadiene (1.0 mmol, 2.0 equiv), and B$_2$(pin)$_2$ (1.0 mmol, 2.0 equiv) were added sequentially. The vial was sealed with a polypropylene cap and removed from the dry box. The reaction mixture was then allowed to stir at ambient temperature for 48 h. After this time, the mixture was cooled to 0 $^o$C (ice-water bath), and 2 mL of 3 M NaOH and 1.5 mL of 30% H$_2$O$_2$ were added dropwise with caution. The mixture was then allowed to stir at ambient temperature for 10 h. The resulting solution was cooled to 0 $^o$C and quenched by the addition of 2 mL of saturated aqueous Na$_2$S$_2$O$_3$. The two-phase mixture was extracted with ethyl acetate (3 × 20 mL), and the combined organic layers were dried over anhydrous Na$_2$SO$_4$. The drying agent was removed by filtration and the solvent was evaporated *in vacuo*. The crude material was purified by silica gel chromatography (hexanes/EtOAc) to afford the title compounds.



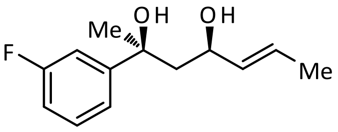
**1**

**(2*S**,4*R**,*E*)-2-phenylhept-5-ene-2,4-diol (1)**. The reaction was performed according to the general procedure with 13.8 mg (0.05 mmol) of Ni(cod)$_2$, 15.2 mg (0.075 mmol) of P(*t*-Bu)$_3$, 60.1 mg (0.5 mmol) of acetophenone, 68.1 mg (1.0 mmol) of *trans*-1,3-pentadiene, and 253.9 mg (1.0 mmol) of B$_2$(pin)$_2$ in THF (2.5 mL) for 48 h, followed by oxidation, to afford the title compound (**1**) as a colorless oil (78.2 mg, 76% yield). R$_f$ = 0.32 (1:1 hexanes:Et$_2$O); $^1$H NMR (500 MHz, CDCl$_3$): δ 7.46 (2H, d, *J* = 7.5 Hz, aromatic), 7.34 (2H, t, *J* = 7.0 Hz, aromatic), 7.23 (1H, t, *J* = 7.0 Hz, aromatic), 5.68 (1H, dq, *J* = 15.5 Hz, 6.5 Hz, CH$_3$C**H**CH), 5.47 (1H, dd, *J* = 15.5 Hz, 7.0 Hz, CH$_3$CHC**H**), 4.52 (1H, br t, *J* = 7.5 Hz, CH$_3$CHCHC**H**), 3.66 (1H, br s, O**H**), 2.89 (1H, br s, O**H**), 1.97 (1H, dd, *J* = 15.0 Hz, 10.0 Hz, ArCC**H$_a$**H$_b$), 1.85 (1H, dd, *J* = 15.0 Hz, 3.0 Hz, ArCCH$_a$**H$_b$**), 1.67 (3H, s, ArCC**H$_3$**), 1.66 (3H, d, *J* = 6.0 Hz, CHCHC**H$_3$**); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 149.2, 133.9, 128.4, 127.1, 126.8, 124.5, 74.8, 71.0, 49.5, 28.3, 17.7; IR (neat): 3328 (br), 2973 (w), 2915 (w), 1446 (m), 1375 (m), 1211 (m), 1099 (m), 1065 (s), 964 (s), 842 (m), 761 (s), 698 (s), 565 (m) cm$^{-1}$; HRMS (ESI+) calculated for $C_{13}H_{15}$ $[M–2H_2O+H]^+$: 171.1174, found: 171.1182.

***Proof of Stereochemistry***. The relative configuration was assigned as *syn* ($C_2$-$C_4$) by analysis of the spectral data, after conversion of the title compound (**1**) into **S1** as shown below.



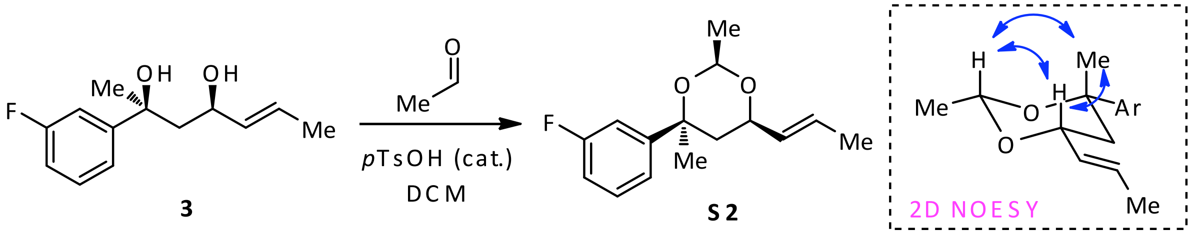
**(2*S**,4*S**,6*R**)-2,4-dimethyl-4-phenyl-6-((*E*)-prop-1-en-1-yl)-1,3-dioxane (S1)**. A flame-dried 10 mL round-bottom flask, equipped with a magnetic stir-bar, was charged with diol **1** (59.8 mg, 0.29 mmol, 1 equiv), acetaldehyde (25.5 mg, 0.58 mmol, 2 equiv), *p*-toluenesulfonic acid (2.9 mg, 0.015 mmol, 0.05 equiv), and dichloromethane (1.5 mL, 0.2 M). After stirring at ambient temperature for 6 h, a saturated aqueous $NaHCO_3$ solution was added. The reaction mixture was extracted with diethyl ether (3 × 10 mL) and the organic layer was washed with brine. The combined organic layers were dried over anhydrous $Na_2SO_4$. The drying agent was removed by filtration and the solvent was evaporated *in vacuo*. The crude product was purified by silica gel chromatography to afford **S1** as a colorless oil. $R_f$ = 0.23 (9:1 hexanes:$Et_2O$); $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.46 (2H, d, *J* = 8.5 Hz, aromatic), 7.34 (2H, t, *J* = 8.5 Hz, aromatic), 7.24 (1H, t, *J* = 8.5 Hz, aromatic), 5.79 (1H, dq, *J* = 15.5 Hz, 6.5 Hz, $CH_3C\mathbf{H}CH$), 5.49 (1H, dd, *J* = 15.5 Hz, 7.0 Hz, $CH_3CHC\mathbf{H}$), 5.25 (1H, q, *J* = 5.0 Hz, $CH_3C\mathbf{H}O$), 4.37-4.33 (1H, m, $CH_3CHCHC\mathbf{H}O$), 1.83 (1H, dd, *J* = 13.5 Hz, 3.0 Hz, $ArCC\mathbf{H_a}H_b$), 1.77 (1H, dd, *J* = 14.0 Hz, *J* = 11.5 Hz, $ArCCH_a\mathbf{H_b}$), 1.71 (3H, d, *J* = 6.0 Hz, $CHCHC\mathbf{H_3}$), 1.63 (3H, s, $ArCC\mathbf{H_3}$), 1.44 (3H, d, *J* = 5.0 Hz, $OCHC\mathbf{H_3}$); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 148.9, 131.2, 128.5, 128.3, 126.8, 124.1, 92.3, 74.6, 73.6, 42.0, 23.2, 21.8, 17.9; IR (neat): 2980 (w), 2934 (w), 2852 (w), 1495 (w), 1447 (m), 1405 (w), 1378 (w), 1173 (m), 1121 (s), 1042 (w), 969 (s), 937 (w), 763 (m), 676 (s), 544 (w) cm$^{-1}$; HRMS (ESI+) calculated for $C_{15}H_{24}NO_2$ $[M+NH_4]^+$: 250.1807, found: 250.1806.



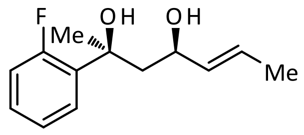
**3**

**(2*S**,4*R**,*E*)-2-(3-fluorophenyl)hept-5-ene-2,4-diol (3)**. The reaction was performed according to the general procedure with 13.8 mg (0.05 mmol) of $Ni(cod)_2$, 15.2 mg (0.075 mmol) of $P(t\text{-}Bu)_3$, 69.1 mg (0.5 mmol) of 3′-fluoroacetophenone, 68.1 mg (1.0 mmol) of *trans*-1,3-pentadiene, and 253.9 mg (1.0 mmol) of $B_2(pin)_2$ in THF (2.5 mL) for 48 h, followed by oxidation, to afford the title compound (**3**) as a colorless oil (81.8 mg, 73% yield). $R_f$ = 0.27 (1:1 hexanes:$Et_2O$); $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.31-7.26 (1H, m, aromatic), 7.22-7.19 (2H, m, aromatic), 6.94-6.89 (1H, m, aromatic), 5.69 (1H, dq, *J* = 15.5 Hz, 6.5 Hz, $CH_3C\mathbf{H}CH$), 5.46 (1H, dd, *J* = 15.0 Hz, 7.0 Hz, $CH_3CHC\mathbf{H}$), 4.53 (1H, br t, *J* = 8.0 Hz, $CH_3CHCHC\mathbf{H}$), 3.93 (1H, br s, O**H**), 2.58 (1H, br s, O**H**), 1.93 (1H, dd, *J* = 14.0 Hz, 9.5 Hz, $ArCC\mathbf{H_a}H_b$), 1.83 (1H, dd, *J* = 14.5 Hz, 3.0 Hz, $ArCCH_a\mathbf{H_b}$), 1.67 (3H, d, *J* = 6.5 Hz, $CHCHC\mathbf{H_3}$), 1.65 (3H, s, $ArCC\mathbf{H_3}$); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 163.0 (d, $^1J_{CF}$ = 244.4 Hz), 152.1, 133.7, 129.7, 127.4, 120.2, 113.5 (d, $^2J_{CF}$ = 20.7 Hz), 111.9 (d, $^2J_{CF}$ = 22.5 Hz), 74.4, 71.2, 49.2, 28.3, 17.7; IR (neat): 3239 (br), 2940 (m), 2879 (m), 1614 (m), 1589 (s), 1485 (m), 1439 (s), 1377 (m), 1272 (m), 1252 (m), 1178 (m), 966 (s), 786 (m), 699 (s) cm$^{-1}$; HRMS (ESI+) calculated for $C_{13}H_{21}FNO_2$ $[M+NH_4]^+$: 242.1556, found: 242.1565.

***Proof of Stereochemistry***. The relative configuration was assigned as *syn* ($C_2$-$C_4$) by analysis of the spectral data, after conversion of the title compound (**3**) into **S2** as shown below.



**(2*S**,4*S**,6*R**)-4-(3-fluorophenyl)-2,4-dimethyl-6-((*E*)-prop-1-en-1-yl)-1,3-dioxane (S2)**. The acetonide (**S2**) was prepared in the same method as described for acetonide **S1**. $R_f$ = 0.23 (9:1 hexanes:$Et_2O$); $^1$H NMR (500 MHz, $CDCl_3$): δ 7.31-7.27 (1H, m, aromatic), 7.22-7.17 (2H, m, aromatic), 6.94-6.90 (1H, m, aromatic), 5.79 (1H, dq, *J* = 15.5 Hz, 6.0 Hz, $CH_3C\mathbf{H}CH$), 5.36 (1H, dd, *J* = 15.5 Hz, 8.5 Hz, $CH_3CHC\mathbf{H}$), 5.33 (1H, q, *J* = 5.0 Hz, $CH_3C\mathbf{H}O$), 4.36-4.32 (1H, m, $CH_3CHCHC\mathbf{H}O$), 1.81 (1H, dd, *J* = 13.0 Hz, 2.5 Hz, $ArCC\mathbf{H_a}H_b$), 1.74 (1H, dd, overlapped $ArCCH_a\mathbf{H_b}$), 1.71 (3H, d, *J* = 6.5 Hz, $CHCHC\mathbf{H_3}$), 1.61 (3H, s, $ArCC\mathbf{H_3}$), 1.44 (3H, d, *J* = 5.0 Hz, $OCHC\mathbf{H_3}$); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 163.0 (d, $^1J_{CF}$ = 244.4 Hz), 151.7, 131.0, 129.7, 128.7, 119.6, 113.6 (d, $^2J_{CF}$ = 21.1 Hz), 111.5 (d, $^2J_{CF}$ = 23.1 Hz), 92.4, 74.4, 73.5, 41.9, 23.2, 21.7, 17.9; IR (neat): 2989 (w), 2939 (w), 2873 (w), 1618 (w), 1589 (m), 1484 (w), 1437 (w), 1271 (m), 1156 (s), 1109 (s), 1040 (w), 968 (s), 899 (m), 864 (m), 784 (s), 744 (s), 482 (w) cm$^{-1}$; HRMS (ESI+) calculated for $C_{15}H_{23}FNO_2$ $[M+NH_4]^+$: 268.1713, found: 268.1708.

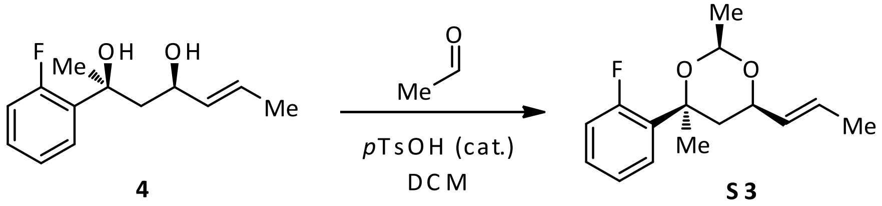


4

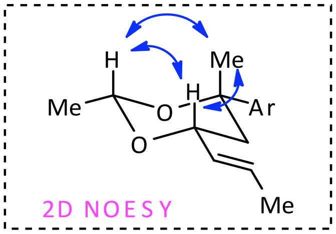
**(2*S**,4*R**,*E*)-2-(2-fluorophenyl)hept-5-ene-2,4-diol (4)**. The reaction was performed according to the general procedure with 13.8 mg (0.05 mmol) of $Ni(cod)_2$, 15.2 mg (0.075 mmol) of $P(t\text{-}Bu)_3$, 69.1 mg (0.5 mmol) of 2′-fluoroacetophenone, 68.1 mg (1.0 mmol) of *trans*-1,3-pentadiene, and 253.9 mg (1.0 mmol) of $B_2(pin)_2$ in THF (2.5 mL) for 48 h, followed by oxidation, to afford the title compound (**4**) as a colorless oil (70.9 mg, 63% yield).

$R_f$ = 0.31 (1:1 hexanes:$Et_2O$); $^1$H NMR (500 MHz, $CDCl_3$): δ 7.67 (1H, t, *J* = 8.0 Hz, aromatic), 7.24-7.20 (1H, m, aromatic), 7.14 (1H, t, *J* = 8.0 Hz, aromatic), 7.00 (1H, dd, *J* = 12.0 Hz, 8.0 Hz, aromatic), 5.68 (1H, dq, *J* = 15.5 Hz, 7.0 Hz, CH$_3$C**H**CH), 5.45 (1H, dd, *J* = 15.0 Hz, 7.0 Hz, CH$_3$CHC**H**), 4.55 (1H, br t, *J* = 7.5 Hz, CH$_3$CHCHC**H**), 3.99 (1H, br s, O**H**), 2.47 (1H, br s, O**H**), 2.17 (1H, dd, *J* = 14.5 Hz, 3.0 Hz, ArCC$\mathbf{H_a}$H$_b$), 1.99 (1H, dd, *J* = 15.0 Hz, 10.0 Hz, ArCCH$_a$$\mathbf{H_b}$), 1.70 (3H, s, ArCC$\mathbf{H_3}$), 1.65 (3H, d, *J* = 6.5 Hz, CHCHC$\mathbf{H_3}$); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 159.5 (d, $^1J_{CF}$ = 243.7 Hz), 135.6, 135.5, 133.7, 128.6, 127.1 (d, $^2J_{CF}$ = 21.6 Hz), 124.2, 116.0 (d, $^2J_{CF}$ = 24.0 Hz), 73.6, 71.1, 46.5, 27.5, 17.7; IR (neat): 3340 (br), 2972 (w), 2917 (w), 1614 (w), 1485 (m), 1448 (s), 1376 (w), 1214 (s), 1066 (m), 1037 (w), 965 (m), 818 (m), 757 (s), 447 (w) cm$^{-1}$; HRMS (ESI+) calculated for $C_{13}H_{14}F$ $[M–2H_2O+H]^+$: 189.1079, found: 189.1074.

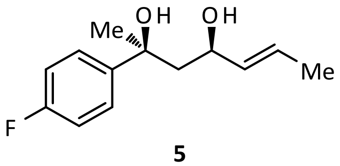
***Proof of Stereochemistry***. The relative configuration was assigned as *syn* ($C_2$-$C_4$) by analysis of the spectral data, after conversion of the title compound (**4**) into **S3** as shown below.



**4** **S3**



**(2*S**,4*S**,6*R**)-4-(2-fluorophenyl)-2,4-dimethyl-6-((*E*)-prop-1-en-1-yl)-1,3-dioxane (S3)**. The acetonide (**S3**) was prepared in the same method as described for acetonide **S1**. $R_f$ = 0.33 (9:1 hexanes:$Et_2O$); $^1$H NMR (500 MHz, $CDCl_3$): δ 7.69 (1H, t, *J* = 8.0 Hz, aromatic), 7.23-7.19 (1H, m, aromatic), 7.13 (1H, t, *J* = 7.5 Hz, aromatic), 6.98 (1H, dd, *J* = 12.0 Hz, 8.0 Hz, aromatic), 5.78 (1H, dq, *J* = 15.0 Hz, 6.5 Hz, CH$_3$C**H**CH), 5.46 (1H, dd, *J* = 15.5 Hz, 7.0 Hz, CH$_3$CHC**H**), 5.26 (1H, q, *J* = 5.0 Hz, CH$_3$C**H**O), 4.37-4.33 (1H, m, CH$_3$CHCHC**H**O), 2.21 (1H, dd, *J* = 13.5 Hz, 2.5 Hz, ArCC$\mathbf{H_a}$H$_b$), 1.71 (1H, dd, overlapped, ArCCH$_a$$\mathbf{H_b}$), 1.69 (3H, d, *J* = 6.5 Hz, CHCHC$\mathbf{H_3}$), 1.69 (3H, s, ArCC$\mathbf{H_3}$), 1.45 (3H, d, *J* = 5.0 Hz, OCHC$\mathbf{H_3}$); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 159.4 (d, $^1J_{CF}$ = 245.5 Hz), 135.5, 135.4, 131.1, 128.4 (d, $^2J_{CF}$ = 22.2 Hz), 126.4, 124.1, 115.9 (d, $^2J_{CF}$ = 23.2 Hz), 91.9, 73.5, 73.2, 40.0, 21.8, 21.7, 17.9; IR (neat): 3089 (w), 2991 (w), 2876 (w), 1678 (w), 1616 (w), 1581 (m), 1488 (s), 1449 (w), 1125 (s), 1110 (s), 1069 (w), 1037 (m), 971 (s), 879 (w), 804 (m), 758 (s), 498 (w) cm$^{-1}$; HRMS (ESI+) calculated for $C_{15}H_{23}FNO_2$ $[M+NH_4]^+$: 268.1713, found: 268.1722.

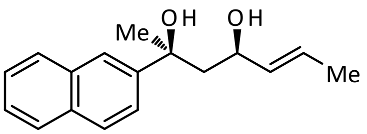


**5**

**(2*S**,4*R**,*E*)-2-(4-fluorophenyl)hept-5-ene-2,4-diol (5)**. The reaction was performed according to the general procedure with 13.8 mg (0.05 mmol) of Ni(cod)$_2$, 15.2 mg (0.075 mmol) of P(*t*-Bu)$_3$, 69.1 mg (0.5 mmol) of 4′-fluoroacetophenone, 68.1 mg (1.0 mmol) of *trans*-1,3-pentadiene, and 253.9 mg (1.0 mmol) of $B_2(pin)_2$ in THF

(2.5 mL) for 48 h, followed by oxidation, to afford the title compound (**5**) as a colorless oil (79.3 mg, 71% yield). $R_f$ = 0.23 (1:1 hexanes:$Et_2O$); $^1$H NMR (500 MHz, $CDCl_3$): δ 7.43-7.41 (2H, m, aromatic), 7.02-6.98 (2H, m, aromatic), 5.68 (1H, dq, *J* = 15.0 Hz, 6.5 Hz, $CH_3C\mathbf{H}CH$), 5.46 (1H, dd, *J* = 15.5 Hz, 7.0 Hz, $CH_3CHC\mathbf{H}$), 4.52 (1H, br t, *J* = 7.5 Hz, $CH_3CHCHC\mathbf{H}$), 3.88 (1H, br s, O**H**), 2.71 (1H, br s, O**H**), 1.92 (1H, dd, *J* = 15.0 Hz, 10.5 Hz, $ArCC\mathbf{H_a}H_b$), 1.81 (1H, dd, *J* = 14.5 Hz, 2.5 Hz, $ArCCH_a\mathbf{H_b}$), 1.66 (3H, d, *J* = 6.0 Hz, $CHCHC\mathbf{H_3}$), 1.65 (3H, s, $ArCC\mathbf{H_3}$); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 161.7 (d, $^1J_{CF}$ = 244.4 Hz), 145.0, 133.8, 127.3, 126.3, 114.9 (d, $^2J_{CF}$ = 21.2 Hz), 74.4, 71.2, 49.5, 28.3, 17.7; IR (neat): 3324 (br), 2941 (m), 2876 (m), 1602 (w), 1510 (s), 1420 (w), 1375 (w), 1223 (s), 1160 (m), 1090 (m), 1074 (w), 967 (m), 849 (m), 836 (s), 814 (w), 563 (w) cm$^{-1}$; HRMS (ESI+) calculated for $C_{13}H_{14}F$ $[M–2H_2O+H]^+$: 189.1080, found: 180.1083.

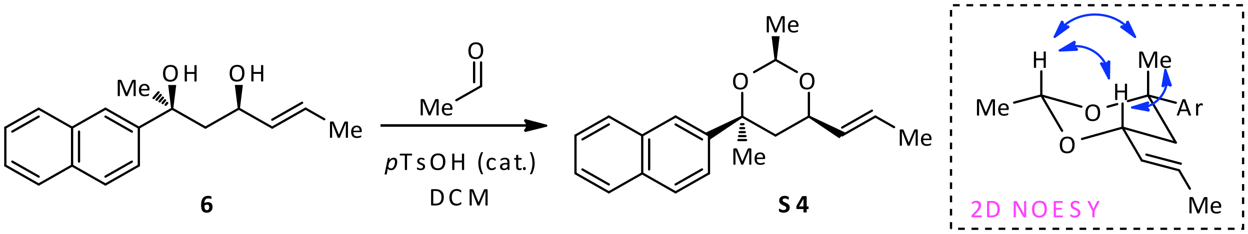
***Stereochemistry***. The relative configuration was assigned as *syn* ($C_2$-$C_4$) by analogy.



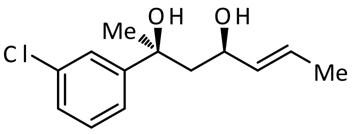
**6**

**(2*S**,4*R**,*E*)-2-(naphthalen-2-yl)hept-5-ene-2,4-diol (6)**. The reaction was performed according to the general procedure with 13.8 mg (0.05 mmol) of $Ni(cod)_2$, 15.2 mg (0.075 mmol) of P(*t*-Bu)$_3$, 85.1 mg (0.5 mmol) of 2′-acetonaphthone, 68.1 mg (1.0 mmol) of *trans*-1,3-pentadiene, and 253.9 mg (1.0 mmol) of $B_2(pin)_2$ in THF (2.5 mL) for 48 h, followed by oxidation, to afford **6** (92.4 mg, 72% yield). $R_f$ = 0.24 (1:1 hexanes:$Et_2O$); $^1$H NMR (500 MHz, $CDCl_3$): δ 7.95 (1H, s, aromatic), 7.85-7.81 (3H, m, aromatic), 7.56 (1H, dd, *J* = 8.5 Hz, 2.0 Hz, aromatic), 7.49-7.44 (2H, m, aromatic), 5.70 (1H, dq, *J* = 15.5 Hz, 6.5 Hz, $CH_3C\mathbf{H}CH$), 5.50 (1H, dd, *J* = 15.5 Hz, 7.0 Hz, $CH_3CHC\mathbf{H}$), 4.58 (1H, br t, *J* = 9.0 Hz, $CH_3CHCHC\mathbf{H}$), 3.71 (1H, br s, O**H**), 2.64 (1H, br s, O**H**), 2.06 (1H, dd, *J* = 14.5 Hz, 10.0 Hz, $ArCC\mathbf{H_a}H_b$), 1.97 (1H, dd, *J* = 15.0 Hz, 3.5 Hz, $ArCCH_a\mathbf{H_b}$), 1.76 (3H, s, $ArCC\mathbf{H_3}$), 1.67 (3H, d, *J* = 6.5 Hz, $CHCHC\mathbf{H_3}$); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 146.5, 133.9, 133.4, 132.4, 128.4, 128.1, 127.6, 127.3, 126.2, 125.8, 123.5, 122.8, 74.9, 71.2, 49.3, 28.5, 17.7; IR (neat): 3325 (br), 3022 (w), 2938 (w), 2853 (w), 1600 (w), 1506 (w), 1450 (m), 1435 (m), 1420 (m), 1376 (m), 1186 (m), 1128 (s), 965 (m), 922 (w), 902 (w), 860 (s), 820 (s), 747 (s), 479 (m) cm$^{-1}$; HRMS (ESI+) calculated for $C_{17}H_{17}O$ $[M–2H_2O+H]^+$: 237.1279, found: 237.1283.

***Proof of Stereochemistry***. The relative configuration was assigned as *syn* ($C_2$-$C_4$) by analysis of the spectral data, after conversion of the title compound (**6**) into **S4** as shown below.



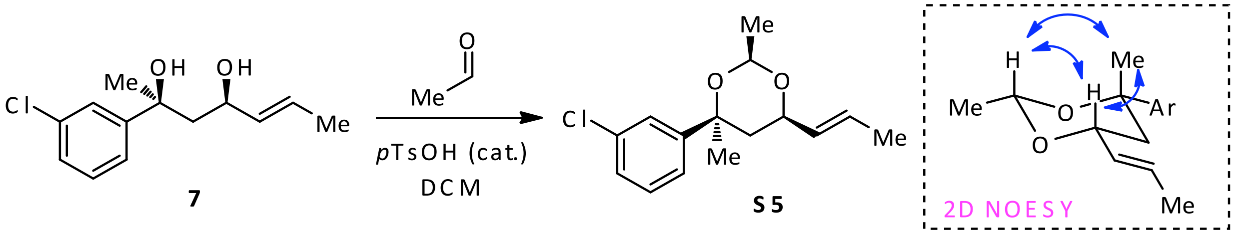
**(2*S**,4*S**,6*R**)-2,4-dimethyl-4-(naphthalen-2-yl)-6-((*E*)-prop-1-en-1-yl)-1,3-dioxane (S4).** The acetonide (**S4**) was prepared in the same method as described for acetonide **S1**. $R_f$ = 0.22 (9:1 hexanes:$Et_2O$); $^1$H NMR (500 MHz, $CDCl_3$): δ 7.93 (1H, s, aromatic), 7.86-7.82 (3H, m, aromatic), 7.59 (1H, dd, *J* = 8.5 Hz, 2.0 Hz, aromatic), 7.49-7.44 (2H, m, aromatic), 5.83 (1H, dq, *J* = 15.0 Hz, 6.5 Hz, $CH_3C\mathbf{H}CH$), 5.52 (1H, dd, *J* = 15.5 Hz, 7.0 Hz, $CH_3CHC\mathbf{H}$), 5.32 (1H, q, *J* = 5.0 Hz, $CH_3C\mathbf{H}O$), 4.44-4.40 (1H, m, $CH_3CHCHC\mathbf{H}O$), 1.94 (1H, dd, *J* = 13.5 Hz, 2.5 Hz, $ArCC\mathbf{H_a}H_b$), 1.86 (1H, dd, *J* = 13.0 Hz, *J* = 11.5 Hz, $ArCCH_a\mathbf{H_b}$), 1.73 (3H, d, overlapped, $CHCHC\mathbf{H_3}$), 1.72 (3H, s, $ArCC\mathbf{H_3}$), 1.51 (3H, d, *J* = 5.0 Hz, $OCHC\mathbf{H_3}$); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 146.2, 133.3, 132.5, 131.2, 128.6, 128.4, 128.0, 127.6, 126.0, 125.8, 123.0, 122.4, 92.4, 74.8, 73.6, 42.0, 23.2, 21.8, 18.0; IR (neat): 2987 (w), 2936 (w), 2917 (w), 2869 (w), 1405 (m), 1378 (m), 1163 (m), 1128 (s), 1108 (s), 1040 (w), 966 (s), 935 (m), 856 (m), 817 (m), 746 (s), 663 (w), 652 (w), 478 (s) $cm^{-1}$; HRMS (ESI+) calculated for $C_{19}H_{26}NO_2$ $[M+NH_4]^+$: 300.1963, found: 300.1953.



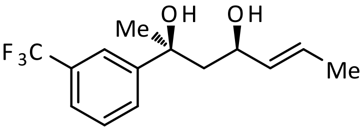
**7**

**(2*S**,4*R**,*E*)-2-(3-chlorophenyl)hept-5-ene-2,4-diol (7).** The reaction was performed according to the general procedure with 13.8 mg (0.05 mmol) of $Ni(cod)_2$, 15.2 mg (0.075 mmol) of P(*t*-Bu)$_3$, 77.3 mg (0.5 mmol) of 3′-chloroacetophenone, 68.1 mg (1.0 mmol) of *trans*-1,3-pentadiene, and 253.9 mg (1.0 mmol) of $B_2(pin)_2$ in THF (2.5 mL) for 48 h, followed by oxidation, to afford the title compound (**7**) as a colorless oil (75.5 mg, 63% yield). $R_f$ = 0.33 (1:1 hexanes:$Et_2O$); $^1$H NMR (500 MHz, $CDCl_3$): δ 7.47 (1H, t, *J* = 2.0 Hz, aromatic), 7.33 (1H, dt, *J* = 8.0 Hz, 2.0 Hz, aromatic), 7.26 (1H, t, *J* = 8.0 Hz, aromatic), 7.20 (1H, d, *J* = 8.0 Hz, aromatic), 5.69 (1H, dq, *J* = 15.5 Hz, 6.5 Hz, $CH_3C\mathbf{H}CH$), 5.46 (1H, dd, *J* = 15.5 Hz, 7.0 Hz, $CH_3CHC\mathbf{H}$), 4.53 (1H, br t, *J* = 8.5 Hz, $CH_3CHCHC\mathbf{H}$), 3.94 (1H, br s, O**H**), 2.50 (1H, br s, O**H**), 1.93 (1H, dd, *J* = 15.0 Hz, 10.0 Hz, $ArCC\mathbf{H_a}H_b$), 1.83 (1H, dd, *J* = 15.0 Hz, 3.0 Hz, $ArCCH_a\mathbf{H_b}$), 1.67 (3H, d, *J* = 6.5 Hz, $CHCHC\mathbf{H_3}$), 1.64 (3H, s, $ArCC\mathbf{H_3}$); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 151.4, 134.3, 133.7, 129.6, 127.4, 126.8, 125.1, 122.8, 74.4, 71.1, 49.1, 28.2, 17.7; IR (neat): 3320 (br), 2977 (m), 2897 (m), 1596 (w), 1571 (w), 1421 (s), 1376 (w), 1212 (m), 1142 (w), 1112 (w), 1080 (m), 965 (s), 894 (w), 850 (w), 785 (s), 699 (s), 495 (w), 406 (w) $cm^{-1}$; HRMS (ESI+) calculated for $C_{13}H_{14}Cl$ $[M–2H_2O+H]^+$: 205.0784, found: 205.0784.

***Proof of Stereochemistry***. The relative configuration was assigned as *syn* ($C_2$-$C_4$) by analysis of the spectral data, after conversion of the title compound (**7**) into **S5** as shown below.



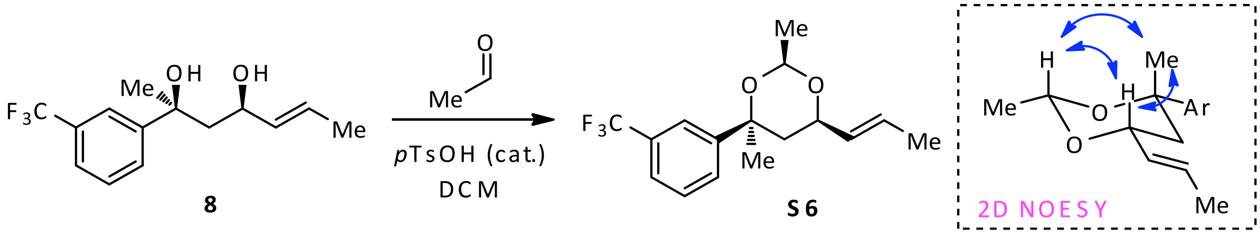
**(2*S**,4*S**,6*R**)-4-(3-chlorophenyl)-2,4-dimethyl-6-((*E*)-prop-1-en-1-yl)-1,3-dioxane (S5)**. The acetonide (**S5**) was prepared in the same method as described for acetonide **S1**. $R_f$ = 0.28 (9:1 hexanes:Et$_2$O); $^1$H NMR (500 MHz, CDCl$_3$): δ 7.46 (1H, t, *J* = 1.5 Hz, aromatic), 7.31 (1H, d, *J* = 7.5 Hz, aromatic), 7.26 (1H, t, *J* = 8.0 Hz, aromatic), 7.21 (1H, d, *J* = 7.5 Hz, aromatic), 5.79 (1H, dq, *J* = 15.5 Hz, 7.0 Hz, CH$_3$C**H**CH), 5.48 (1H, dd, *J* = 15.5 Hz, 7.0 Hz, CH$_3$CHC**H**), 5.22 (1H, q, *J* = 5.0 Hz, CH$_3$C**H**O), 4.35-4.31 (1H, m, CH$_3$CHCHC**H**O), 1.80 (1H, dd, *J* = 13.5 Hz, 2.5 Hz, ArCC**H$_a$**H$_b$), 1.71 (1H, dd, overlapped, ArCCH$_a$**H$_b$**), 1.70 (3H, d, *J* = 6.5 Hz, CHCHC**H$_3$**), 1.61 (3H, s, ArCC**H$_3$**), 1.44 (3H, d, *J* = 5.0 Hz, OCHC**H$_3$**); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 151.0, 134.3, 131.0, 129.6, 128.7, 127.0, 124.6, 122.3, 92.4, 74.4, 73.5, 41.9, 23.3, 21.7, 17.9; IR (neat): 2990 (w), 2938 (w), 2918 (w), 2876 (w), 1597 (w), 1572 (w), 1474 (w), 1419 (m), 1407 (m), 1223 (w), 1173 (s), 1124 (s), 1081 (w), 971 (s), 879 (w), 847 (w), 785 (m), 697 (s), 610 (w) cm$^{-1}$; HRMS (ESI+) calculated for C$_{15}$H$_{23}$ClNO$_2$ [M+NH$_4$]$^+$: 284.1417, found: 284.1410.



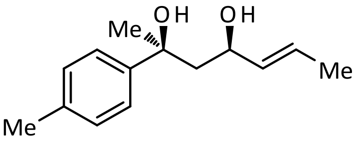
**8**

**(2*S**,4*R**,*E*)-2-(3-(trifluoromethyl)phenyl)hept-5-ene-2,4-diol (8)**. The reaction was performed according to the general procedure with 13.8 mg (0.05 mmol) of Ni(cod)$_2$, 15.2 mg (0.075 mmol) of P(*t*-Bu)$_3$, 94.1 mg (0.5 mmol) of 3′-(trifluoromethyl)-acetophenone, 68.1 mg (1.0 mmol) of *trans*-1,3-pentadiene, and 253.9 mg (1.0 mmol) of B$_2$(pin)$_2$ in THF (2.5 mL) for 48 h, followed by oxidation, to afford the title compound (**8**) as a colorless oil (96.3 mg, 70% yield). $R_f$ = 0.27 (1:1 hexanes:Et$_2$O); $^1$H NMR (500 MHz, CDCl$_3$): δ 7.75 (1H, s, aromatic), 7.64 (1H, d, *J* = 8.0 Hz, aromatic), 7.49 (1H, d, *J* = 7.5 Hz, aromatic), 7.44 (1H, t, *J* = 7.5 Hz, aromatic), 5.69 (1H, dq, *J* = 15.5 Hz, 6.5 Hz, CH$_3$C**H**CH), 5.46 (1H, dd, *J* = 15.5 Hz, 7.0 Hz, CH$_3$CHC**H**), 4.56 (1H, br t, *J* = 8.0 Hz, CH$_3$CHCHC**H**), 4.19 (1H, br s, O**H**), 2.50 (1H, br s, O**H**), 1.94 (1H, dd, *J* = 14.5 Hz, 10.0 Hz, ArCC**H$_a$**H$_b$), 1.85 (1H, dd, *J* = 15.0 Hz, 3.0 Hz, ArCCH$_a$**H$_b$**), 1.68 (3H, s, ArCC**H$_3$**), 1.66 (3H, d, *J* = 6.5 Hz, CHCHC**H$_3$**); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 150.3, 133.6, 130.6 (q, $^2J_{CF}$ = 31.8 Hz), 128.7, 128.1, 127.7, 124.0 (q, $^1J_{CF}$ = 272.1 Hz), 123.6 (q, $^3J_{CF}$ = 3.6 Hz), 121.6 (q, $^3J_{CF}$ = 3.6 Hz), 74.4, 71.3, 49.2, 28.2, 17.7; IR (neat): 3333 (br), 2976 (m), 2919 (m), 1438 (w), 1377 (w), 1328 (s), 1207 (w), 1164 (s), 1122 (s), 1072 (m), 966 (w), 899 (w), 852 (w), 804 (w), 730 (w), 704 (m), 657 (w) cm$^{-1}$; HRMS (ESI+) calculated for C$_{13}$H$_{21}$FNO$_2$ [M+NH$_4$]$^+$: 292.1524, found: 292.1525.

***Proof of Stereochemistry***. The relative configuration was assigned as *syn* ($C_2$-$C_4$) by analysis of the spectral data, after conversion of the title compound (**8**) into **S6** as shown below.



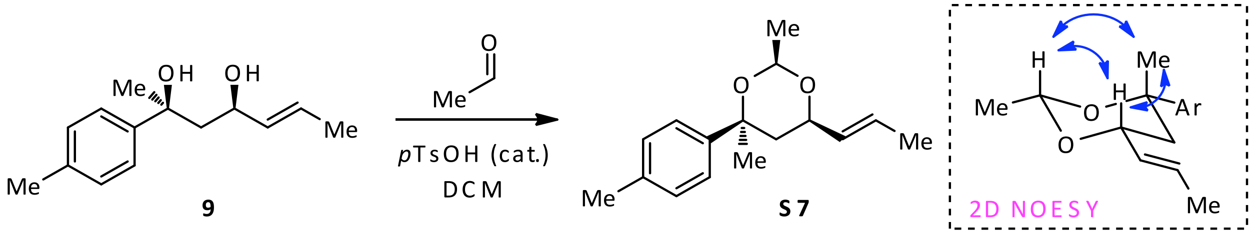
**(2*S**,4*S**,6*R**)-2,4-dimethyl-6-((*E*)-prop-1-en-1-yl)-4-(3-(trifluoromethyl)phenyl)-1,3-dioxane (S6)**. The acetonide (**S6**) was prepared in the same method as described for acetonide **S1**. $R_f$ = 0.23 (9:1 hexanes:$Et_2O$); $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.72 (1H, s, aromatic), 7.64 (1H, d, *J* = 7.5 Hz, aromatic), 7.50 (1H, d, *J* = 7.5 Hz, aromatic), 7.45 (1H, t, *J* = 7.5 Hz, aromatic), 5.80 (1H, dq, *J* = 15.0 Hz, 6.5 Hz, $CH_3C\mathbf{H}CH$), 5.48 (1H, dd, *J* = 15.5 Hz, 7.0 Hz, $CH_3CHC\mathbf{H}$), 5.25 (1H, q, *J* = 5.0 Hz, $CH_3C\mathbf{H}O$), 4.38-4.35 (1H, m, $CH_3CHCHC\mathbf{H}O$), 1.85 (1H, dd, *J* = 13.5 Hz, 2.5 Hz, $ArCC\mathbf{H_a}H_b$), 1.72 (1H, dd, overlapped, $ArCCH_a\mathbf{H_b}$), 1.71 (3H, d, *J* = 6.5 Hz, $CHCHC\mathbf{H_3}$), 1.64 (3H, s, $ArCC\mathbf{H_3}$), 1.45 (3H, d, *J* = 5.0 Hz, $OCHC\mathbf{H_3}$); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 149.9, 130.9, 130.6 (q, $^2J_{CF}$ = 31.8 Hz), 128.8 (2 C′s), 127.6, 124.4 (q, $^1J_{CF}$ = 272.5 Hz), 123.7 (q, $^3J_{CF}$ = 3.6 Hz), 121.1 (q, $^3J_{CF}$ = 3.6 Hz), 92.4, 74.4, 73.4, 41.8, 23.3, 21.7, 18.0; IR (neat): 2990 (w), 2940 (w), 2921 (w), 2878 (w), 1440 (w), 1333 (s), 1287 (w), 1220 (w), 1165 (s), 1125 (s), 1072 (m), 971 (m), 804 (w), 703 (m), 656 (w), 611 (w), 546 (w) $cm^{-1}$; HRMS (ESI+) calculated for $C_{16}H_{23}F_3NO_2$ $[M+NH_4]^+$: 318.1681, found: 318.1694.



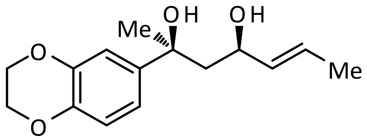
**9**

**(2*S**,4*R**,*E*)-2-(*p*-tolyl)hept-5-ene-2,4-diol (9)**. The reaction was performed according to the general procedure with 13.8 mg (0.05 mmol) of $Ni(cod)_2$, 15.2 mg (0.075 mmol) of $P(t\text{-}Bu)_3$, 67.1 mg (0.5 mmol) of 4′-methylacetophenone, 68.1 mg (1.0 mmol) of *trans*-1,3-pentadiene, and 253.9 mg (1.0 mmol) of $B_2(pin)_2$ in THF (2.5 mL) for 48 h, followed by oxidation, to afford the title compound (**9**) as a colorless oil (86.9 mg, 79% yield). $R_f$ = 0.26 (1:1 hexanes:$Et_2O$); $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.35 (2H, d, *J* = 8.5 Hz, aromatic), 7.15 (2H, d, *J* = 8.5 Hz, aromatic), 5.69 (1H, dq, *J* = 15.5 Hz, 6.5 Hz, $CH_3C\mathbf{H}CH$), 5.48 (1H, dd, *J* = 15.0 Hz, 7.0 Hz, $CH_3CHC\mathbf{H}$), 4.52 (1H, br t, *J* = 7.5 Hz, $CH_3CHCHC\mathbf{H}$), 3.32 (1H, br s, O**H**), 2.71 (1H, br s, O**H**), 2.33 (3H, s, $ArC\mathbf{H_3}$), 1.96 (1H, dd, *J* = 15.0 Hz, 10.5 Hz, $ArCC\mathbf{H_a}H_b$), 1.85 (1H, dd, *J* = 15.0 Hz, 3.0 Hz, $ArCCH_a\mathbf{H_b}$), 1.67 (3H, d, *J* = 6.0 Hz, $CHCHC\mathbf{H_3}$), 1.66 (3H, s, $ArCC\mathbf{H_3}$); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 146.3, 136.4, 134.0, 129.1, 127.0, 124.4, 74.8, 71.0, 49.6, 28.4, 21.1, 17.7; IR (neat): 3331 (br), 2973 (m), 2917 (m), 2883 (w), 1514 (w), 1450 (m), 1420 (m), 1375 (m), 1218 (m), 1207 (m), 1135 (m), 1094 (s), 1074 (s), 1043 (m), 1020 (w), 965 (s), 846 (s), 817 (s), 723 (w), 565 (s), 504 (w) $cm^{-1}$; HRMS (ESI+) calculated for $C_{14}H_{17}$ $[M–2H_2O+H]^+$: 185.1330, found: 185.1336.

***Proof of Stereochemistry***. The relative configuration was assigned as *syn* ($C_2$-$C_4$) by analysis of the spectral data, after conversion of the title compound (**9**) into **S7** as shown below.



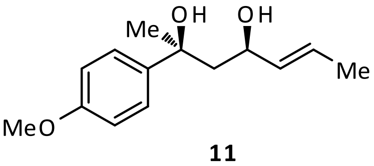
**(2*S**,4*S**,6*R**)-2,4-dimethyl-6-((*E*)-prop-1-en-1-yl)-4-(*p*-tolyl)-1,3-dioxane (S7)**. The acetonide (**S7**) was prepared in the same method as described for acetonide **S1**. $R_f$ = 0.22 (9:1 hexanes:$Et_2O$); $^1$H NMR (500 MHz, $CDCl_3$): δ 7.34 (2H, d, *J* = 8.5 Hz, aromatic), 7.15 (2H, d, *J* = 8.5 Hz, aromatic), 5.78 (1H, dq, *J* = 15.0 Hz, 6.0 Hz, $CH_3C\mathbf{H}CH$), 5.48 (1H, dd, *J* = 15.5 Hz, 7.0 Hz, $CH_3CHC\mathbf{H}$), 5.23 (1H, q, *J* = 5.0 Hz, $CH_3C\mathbf{H}O$), 4.36-4.32 (1H, m, $CH_3CHCHC\mathbf{H}O$), 2.33 (3H, s, $ArC\mathbf{H_3}$), 1.80 (1H, dd, *J* = 13.5 Hz, 3.0 Hz, $ArCC\mathbf{H_a}H_b$), 1.75 (1H, dd, overlapped, $ArCCH_a\mathbf{H_b}$), 1.70 (3H, d, *J* = 6.5 Hz, $CHCHC\mathbf{H_3}$), 1.61 (3H, s, $ArCC\mathbf{H_3}$), 1.43 (3H, d, *J* = 5.5 Hz, $OCHC\mathbf{H_3}$); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 146.1, 136.3, 131.3, 129.0, 128.5, 124.0, 92.3, 74.5, 73.6, 42.1, 23.2, 21.8, 21.1, 18.0; IR (neat): 3024 (w), 2990 (m), 2937 (m), 2919 (m), 2869 (w), 1515 (w), 1450 (w), 1406 (m), 1377 (w), 1172 (s), 1115 (s), 969 (s), 875 (w), 837 (w), 817 (m), 721 (w), 560 (w), 460 (w) cm$^{-1}$; HRMS (ESI+) calculated for $C_{16}H_{26}NO_2$ $[M+NH_4]^+$: 264.1963, found: 264.1953.



**10**

**(2*S**,4*R**,*E*)-2-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)hept-5-ene-2,4-diol (10).** The reaction was performed according to the general procedure with 13.8 mg (0.05 mmol) of $Ni(cod)_2$, 15.2 mg (0.075 mmol) of $P(t\text{-}Bu)_3$, 89.1 mg (0.5 mmol) of 1,4-benzodioxan-6-yl methyl ketone, 68.1 mg (1.0 mmol) of *trans*-1,3-pentadiene, and 253.9 mg (1.0 mmol) of $B_2(pin)_2$ in THF (2.5 mL) for 48 h, followed by oxidation, to afford the title compound (**10**) as a colorless oil (90.9 mg, 69% yield). $R_f$ = 0.28 (1:2 hexanes:$Et_2O$); $^1$H NMR (500 MHz, $CDCl_3$): δ 6.98 (1H, s, aromatic), 6.91 (1H, d, *J* = 9.0 Hz, aromatic), 6.82 (1H, d, *J* = 8.5 Hz, aromatic), 5.67 (1H, dq, *J* = 15.5 Hz, 6.5 Hz, $CH_3C\mathbf{H}CH$), 5.46 (1H, dd, *J* = 15.0 Hz, 7.0 Hz, $CH_3CHC\mathbf{H}$), 4.49 (1H, br t, *J* = 8.5 Hz, $CH_3CHCHC\mathbf{H}$), 4.25 (4H, s, $ArOC\mathbf{H_2}C\mathbf{H_2}$), 3.38 (1H, br s, **OH**), 2.80 (1H, br s, **OH**), 1.93 (1H, dd, *J* = 15.0 Hz, 10.0 Hz, $ArCC\mathbf{H_a}H_b$), 1.80 (1H, dd, *J* = 15.0 Hz, 2.5 Hz, $ArCCH_a\mathbf{H_b}$), 1.67 (3H, d, *J* = 6.0 Hz, $CHCHC\mathbf{H_3}$), 1.63 (3H, s, $ArCC\mathbf{H_3}$); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 143.2, 142.8, 142.3, 133.9, 127.0, 117.6, 117.0, 113.8, 74.5, 71.0, 64.5 (2 C′s), 49.5, 28.3, 17.8; IR (neat): 3412 (br), 2996 (m), 2930 (w), 2854 (w), 1590 (w), 1505 (s), 1460 (w), 1424 (m), 1377 (m), 1309 (m), 1285 (s), 1258 (m), 1175 (w), 1126 (m), 1100 (w), 1068 (s), 949 (w), 887 (w), 642 (w), 496 (w) cm$^{-1}$; HRMS (ESI+) calculated for $C_{15}H_{17}O_2$ [M–2$H_2O$+H]$^+$: 229.1228, found: 229.1228.

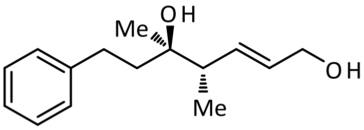
***Stereochemistry***. The relative configuration was assigned as *syn* ($C_2$-$C_4$) by analogy.



**11**

**(2*S**,4*R**,*E*)-2-(4-methoxyphenyl)hept-5-ene-2,4-diol (11).** The reaction was performed according to the general procedure with 13.8 mg (0.05 mmol) of Ni(cod)$_2$, 15.2 mg (0.075 mmol) of P(*t*-Bu)$_3$, 75.1 mg (0.5 mmol) of 4′-methoxylacetophenone, 68.1 mg (1.0 mmol) of *trans*-1,3-pentadiene, and 253.9 mg (1.0 mmol) of B$_2$(pin)$_2$ in THF (2.5 mL) for 48 h, followed by oxidation, to afford the title compound (**11**) as a colorless oil (61.3 mg, 52% yield). R$_f$ = 0.31 (1:2 hexanes:Et$_2$O); $^1$H NMR (500 MHz, CDCl$_3$): δ 7.38 (2H, d, *J* = 9.0 Hz, aromatic), 6.87 (2H, d, *J* = 9.0 Hz, aromatic), 5.69 (1H, dq, *J* = 15.0 Hz, 6.5 Hz, CH$_3$C**H**CH), 5.48 (1H, dd, *J* = 15.5 Hz, 7.0 Hz, CH$_3$CHC**H**), 4.51 (1H, br t, *J* = 7.5 Hz, CH$_3$CHCHC**H**), 3.80 (3H, s, ArOC**H$_3$**), 3.35 (1H, br s, O**H**), 2.72 (1H, br s, O**H**), 1.96 (1H, dd, *J* = 14.5 Hz, 10.0 Hz, ArCC**H$_a$**H$_b$), 1.83 (1H, dd, *J* = 15.0 Hz, 3.0 Hz, ArCCH$_a$**H$_b$**), 1.68 (3H, d, *J* = 6.5 Hz, CHCHC**H$_3$**), 1.66 (3H, s, ArCC**H$_3$**); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 158.5, 141.5, 134.0, 127.0, 125.7, 113.7, 74.6, 71.1, 55.4, 49.7, 28.4, 17.8; IR (neat): 3372 (br), 2938 (w), 2916 (w), 2854 (w), 1611 (w), 1512 (s), 1459 (w), 1442 (w), 1416 (w), 1302 (m), 1249 (s), 1215 (w), 1179 (s), 1094 (m), 1074 (w), 1035 (m), 966 (m), 847 (m), 832 (m), 802 (w), 491 (w) cm$^{-1}$; HRMS (ESI+) calculated for $C_{14}H_{19}O_2$ [M–$H_2O$+H]$^+$: 219.1385, found: 219.1386.

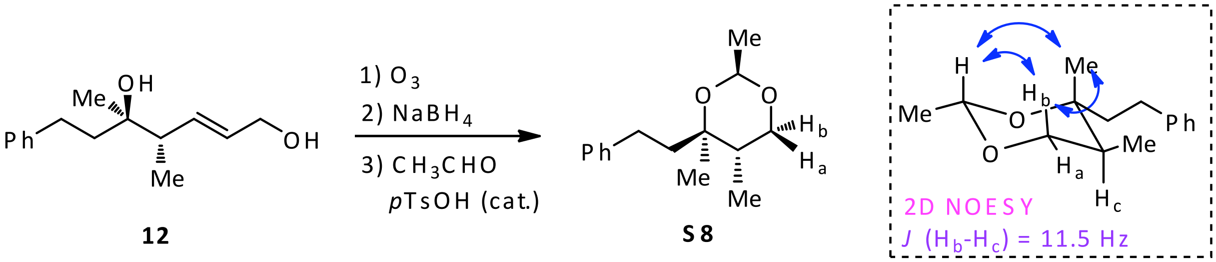
***Stereochemistry***. The relative configuration was assigned as *syn* ($C_2$-$C_4$) by analogy.



**12**

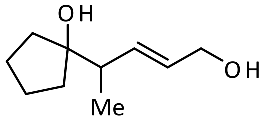
**(4*S**,5*R**,*E*)-4,5-dimethyl-7-phenylhept-2-ene-1,5-diol (12)**. The reaction was performed according to the general procedure with 13.8 mg (0.05 mmol) of Ni(cod)$_2$, 15.2 mg (0.075 mmol) of P(*t*-Bu)$_3$, 74.1 mg (0.5 mmol) of benzylacetone, 68.1 mg (1.0 mmol) of *trans*-1,3-pentadiene, and 253.9 mg (1.0 mmol) of B$_2$(pin)$_2$ in THF (2.5 mL) for 48 h, followed by oxidation, to afford the title compound (**12**) as a colorless oil (80.5 mg, 69% yield). R$_f$ = 0.59 (1:2 hexanes:EtOAc); $^1$H NMR (500 MHz, C$_6$D$_6$): δ 7.19-7.12 (4H, m, aromatic), 7.08-7.04 (1H, m, aromatic), 5.67 (1H, dd, *J* = 15.5 Hz, 8.0 Hz, C**H**CHCH$_2$), 5.58 (1H, dt, *J* = 15.0 Hz, 5.0 Hz CHC**H**CH$_2$), 3.95 (1H, dd, *J* = 9.0 Hz, 5.0 Hz, CHC**H$_a$**H$_b$), 3.92 (1H, dd, *J* = 9.0 Hz, 5.0 Hz, CHCH$_a$**H$_b$**), 2.78 (1H, br, O**H**), 2.70 (2H, t, *J* = 7.5 Hz, ArC**H$_2$**), 2.35 (1H, br, O**H**), 2.20 (1H, qn, *J* = 7.0 Hz, C**H**CH$_3$), 1.71 (2H, m, ArCH$_2$C**H$_2$**), 1.02 (3H, s, CC**H$_3$**), 0.88 (3H, d, *J* = 7.0 Hz, CHC**H$_3$**); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 142.8, 133.9, 131.2, 128.6, 128.5, 125.9, 74.1, 63.6, 46.1, 42.3, 29.9, 23.6, 15.5; IR (neat): 3356 (br), 2970 (m), 2934 (m), 1454 (m), 1378 (m), 1090 (w), 1068 (w), 999 (s), 974 (w), 754 (w), 735 (m), 698 (s) cm$^{-1}$; HRMS (ESI+) calculated for $C_{15}H_{26}NO_2$ $[M+NH_4]^+$: 252.1964, found: 252.1963.

***Proof of Stereochemistry***. The relative configuration was determined by analysis of the spectral data, after conversion of the title compound (**12**) into **S8** by ozonolysis, reduction, and acetonide synthesis as illustrated below.



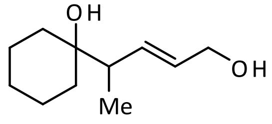
**12** **S8**

**(2*S**,4*R**,5*S**)-2,4,5-trimethyl-4-phenethyl-1,3-dioxane (S8)**. $R_f$ = 0.78 (5:1 hexanes:EtOAc); $^1$H NMR (500 MHz, CDCl$_3$): δ 7.30-7.27 (2H, t, *J* = 7.5 Hz, aromatic), 7.24-7.22 (2H, d, *J* = 7.0 Hz, aromatic), 7.19-7.16 (1H, t, *J* = 7.5 Hz, aromatic), 4.94 (1H, q, *J* = 4.5 Hz, OC**H**CH$_3$), 3.74 (1H, dd, *J* = 11.5 Hz, 5.0 Hz, CCHC**H**$_a$H$_b$), 3.55 (1H, t, *J* = 11.5 Hz, CCHCH$_a$**H**$_b$), 2.80 (1H, td, 13.5 Hz, 5.0 Hz, ArC**H**$_A$H$_B$), 2.72 (1H, td, *J* = 13.5 Hz, 5.5 Hz, ArCH$_A$**H**$_B$), 2.09-2.02 (1H, m, CC**H**$_c$CH$_3$), 1.88-1.75 (2H, m, ArCH$_2$C**H**$_2$), 1.30 (3H, d, *J* = 5.0 Hz, OCHC**H**$_3$), 1.20 (3H, s, CC**H**$_3$), 0.72 (3H, d, *J* = 6.0 Hz, CCH$_c$C**H**$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 143.2, 128.6, 128.4, 125.7, 92.5, 76.5, 68.5, 43.4, 36.2, 28.8, 21.6, 16.4, 11.9; IR (neat): 2959 (m), 2938 (m), 2857 (w), 1454 (w), 1402 (s), 1386 (w), 1374 (w), 1149 (s), 1119 (s), 1095 (m), 1038 (w), 973 (w), 947 (w), 848 (w), 754 (w), 698 (m) cm$^{-1}$; HRMS (ESI+) calculated for $C_{15}H_{23}O_2$ $[M+H]^+$: 235.1698, found: 235.1687.



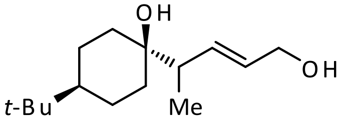
**13**

**(*E*)-1-(5-hydroxypent-3-en-2-yl)cyclopentanol (13)**. The reaction was performed according to the general procedure with 13.8 mg (0.05 mmol) of Ni(cod)$_2$, 15.2 mg (0.075 mmol) of P(*t*-Bu)$_3$, 42.0 mg (0.5 mmol) of cyclopentanone, 68.1 mg (1.0 mmol) of *trans*-1,3-pentadiene, and 253.9 mg (1.0 mmol) of B$_2$(pin)$_2$ in THF (2.5 mL) for 48 h, followed by oxidation, to afford the title compound (**13**) as a colorless oil (47.3 mg, 56% yield). $R_f$ = 0.35 (1:2 hexanes:EtOAc); $^1$H NMR (500 MHz, CDCl$_3$): δ 5.75 (1H, dd, *J* = 15.5 Hz, 7.5 Hz, C**H**CHCH$_2$), 5.68 (1H, dt, *J* = 15.5 Hz, 5.5 Hz, CHC**H**CH$_2$), 4.10 (2H, d, *J* = 5.0 Hz, CHCHC**H**$_2$), 2.25 (1H, qn, *J* = 7.0 Hz, C**H**CH$_3$), 1.90 (1H, br, **OH**) 1.83-1.74 (2H, m, aliphatic), 1.62-1.53 (6H, m, aliphatic), 1.05 (3H, d, *J* = 7.5 Hz, CHC**H**$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 134.7, 130.1, 84.4, 63.5, 45.7, 38.6, 37.7, 24.0, 23.9, 15.3; IR (neat): 3341 (br), 2960 (w), 2871 (w), 1453 (w), 1372 (w), 1326 (w), 1194 (w), 1124 (w), 1088 (m), 1051 (w), 971 (s), 809 (w), 700 (w), 638 (m), 500 (w) cm$^{-1}$; HRMS (ESI+) calculated for $C_{10}H_{22}NO_2$ $[M+NH_4]^+$: 188.1650, found: 188.1657.



**14**

**(*E*)-1-(5-hydroxypent-3-en-2-yl)cyclohexanol (14)**. The reaction was performed according to the general procedure with 13.8 mg (0.05 mmol) of Ni(cod)$_2$, 15.2 mg (0.075 mmol) of P(*t*-Bu)$_3$, 49.0 mg (0.5 mmol) of cyclohexanone, 68.1 mg (1.0 mmol) of *trans*-1,3-pentadiene, and 253.9 mg (1.0 mmol) of B$_2$(pin)$_2$ in THF (2.5 mL) for 48 h, followed by oxidation, to afford the title compound (**14**) as a colorless oil (47.8 mg, 52% yield). R$_f$ = 0.49 (1:2 hexanes:EtOAc); $^1$H NMR (500 MHz, $C_6D_6$): δ 5.59 (1H, dd, *J* = 15.5 Hz, 8.5 Hz, C**H**CHCH$_2$), 5.47 (1H, dt, *J* = 15.0 Hz, 5.5 Hz, CHC**H**CH$_2$), 3.84 (2H, d, *J* = 6.0 Hz, CHCHC**H$_2$**), 1.96 (1H, m, C**H**CH$_3$), 1.66-1.53 (3H, m, aliphatic), 1.45-1.35 (4H, m, aliphatic), 1.23-1.16 (2H, m, aliphatic), 1.15-1.01 (1H, m, aliphatic), 0.95 (3H, d, *J* = 7.0 Hz, CHC**H$_3$**); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 134.2, 130.2, 72.5, 63.6, 35.2, 34.4, 25.7, 21.7, 14.3; IR (neat): 3354 (br), 2931 (s), 2858 (m), 1448 (w), 1373 (w), 1256 (w), 1164 (w), 1139 (w), 1080 (w), 1002 (m), 972 (s), 664 (w) cm$^{-1}$; HRMS (ESI+) calculated for $C_{11}H_{24}NO_2$ $[M+NH_4]^+$: 202.1807, found: 202.1800.



**15**

**(*E*)-4-(*tert*-butyl)-1-(5-hydroxypent-3-en-2-yl)cyclohexanol (15)**. The reaction was performed according to the general procedure with 13.8 mg (0.05 mmol) of Ni(cod)$_2$, 15.2 mg (0.075 mmol) of P(*t*-Bu)$_3$, 77.0 mg (0.5 mmol) of 4-*tert*-butylcyclohexanone, 68.1 mg (1.0 mmol) of *trans*-1,3-pentadiene, and 253.9 mg (1.0 mmol) of B$_2$(pin)$_2$ in THF (2.5 mL) for 48 h, followed by oxidation, to afford the title compound (**15**) as a colorless oil (64.0 mg, 53% yield). R$_f$ = 0.56 (1:2 hexanes:EtOAc); $^1$H NMR (500 MHz, $C_6D_6$): δ 5.65 (1H, ddt, *J* = 15.0 Hz, 8.5 Hz, 1.2 Hz, C**H**CHCH$_2$), 5.54 (1H, dt, *J* = 15.0 Hz, 5.5 Hz, CHC**H**CH$_2$), 3.92 (2H, dd, *J* = 5.5 Hz, 1.2 Hz, CHCHC**H$_2$**), 1.97 (1H, m, C**H**CH$_3$), 1.62-1.40 (7H, m, aliphatic), 1.17 (2H, tt, *J* = 13.0 Hz, 4.0 Hz, aliphatic), 0.99 (3H, d, *J* = 6.8 Hz, CHCHC**H$_3$**), 0.91 (9H, s, C(C**H$_3$**)$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 134.5, 130.5, 72.3, 63.8, 48.0, 47.9, 35.2, 34.7, 32.5, 27.7, 22.6, 22.5, 14.7; IR (neat): 3346 (br), 2939 (s), 2866 (m), 1666 (w), 1461 (w), 1442 (w), 1392 (w), 1364 (m), 1316 (w), 1235 (w), 1190 (w), 1140 (w), 1118 (w), 1091 (w), 1050 (w), 1003 (m), 973 (s), 915 (w), 890 (w), 828 (w) cm$^{-1}$; HRMS (ESI+) calculated for $C_{15}H_{32}NO_2$ $[M+NH_4]^+$: 258.2433, found: 258.2437.

***Stereochemistry***. The relative configuration was assigned as *syn* (C$_1$-C$_4$) by analysis of the $^{13}$C NMR spectrum based on the NMR studies of related compounds.[1]

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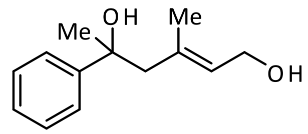
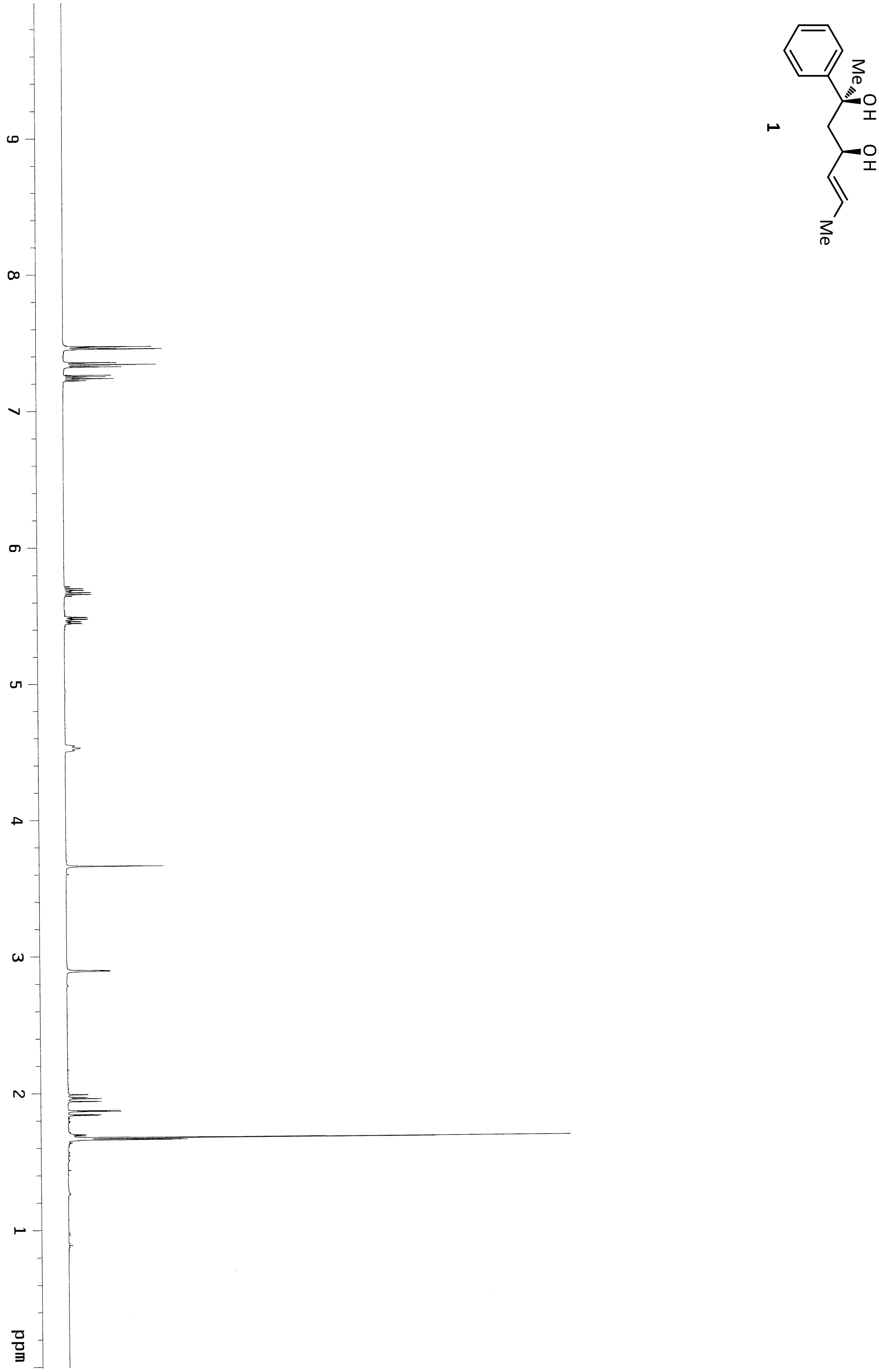
[1] (a) Trost, B. M.; Florez, J.; Jebaratnam, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 613. (b) Trost, B. M.; Florez, J.; Haller, K. J. *J. Org. Chem.* **1988**, *53*, 2394. (c) Lindsay, H, A.; Salisbury, C. L.; Cordes, W.; McIntosh, M. C. *Org. Lett.* **2001**, *3*, 4007.



**16**

**(*E*)-3-methyl-5-phenylhex-2-ene-1,5-diol (16)**. The reaction was performed according to the general procedure with 13.8 mg (0.05 mmol) of Ni(cod)$_2$, 15.2 mg (0.075 mmol) of P(*t*-Bu)$_3$, 60.1 mg (0.5 mmol) of acetophenone, 68.1 mg (1.0 mmol) of isoprene, and 253.9 mg (1.0 mmol) of B$_2$(pin)$_2$ in THF (2.5 mL) for 48 h, followed by oxidation, to afford the title compound (**16**) as a colorless oil (40.1 mg, 39% yield). R$_f$ = 0.28 (1:2 hexanes:EtOAc); $^1$H NMR (500 MHz, CDCl$_3$): δ 7.45 (2H, d, *J* = 7.0 Hz, aromatic), 7.34 (2H, d, *J* = 7.0 Hz, aromatic), 7.24 (1H, t, *J* = 7.0 Hz, aromatic), 5.34 (1H, t, *J* = 7.5 Hz, C**H**CH$_2$OH), 3.97 (2H, s, CHC**H$_2$**OH), 2.60 (2H, d, *J* = 8.0 Hz, ArCC**H$_2$**), 1.95 (1H, br s, O**H**), 1.64 (3H, s, OHCH$_2$CHCC**H$_3$**), 1.57 (3H, s, ArCC**H$_3$**); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 147.9, 139.1, 128.3, 126.8, 124.9, 120.4, 74.7, 68.8, 42.1, 30.0, 14.1; IR (neat): 3357 (br), 2965 (m), 2846 (m), 2792 (w), 1494 (w), 1446 (s), 1373 (m), 1286 (w), 1218 (w), 1068 (m), 1028 (m), 1013 (m), 950 (w), 880 (w), 764 (s), 700 (s), 623 (w), 555 (w) cm$^{-1}$; HRMS (ESI+) calculated for C$_{13}$H$_{22}$NO$_2$ [M+NH$_4$]$^+$: 224.1650, found: 224.1645.

***Stereochemistry***. The alkene configuration was assigned as (*E*) by NOESY analysis.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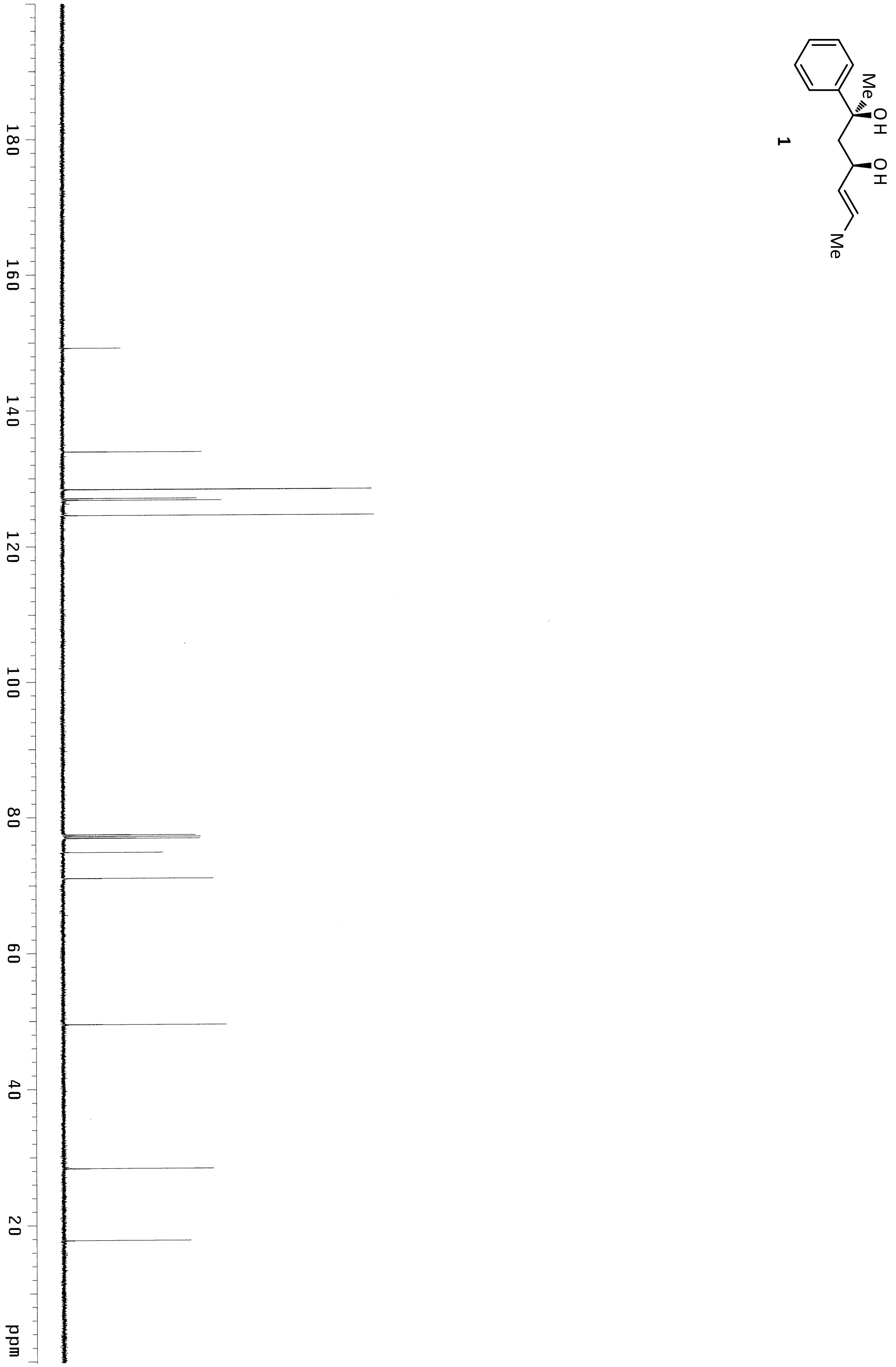

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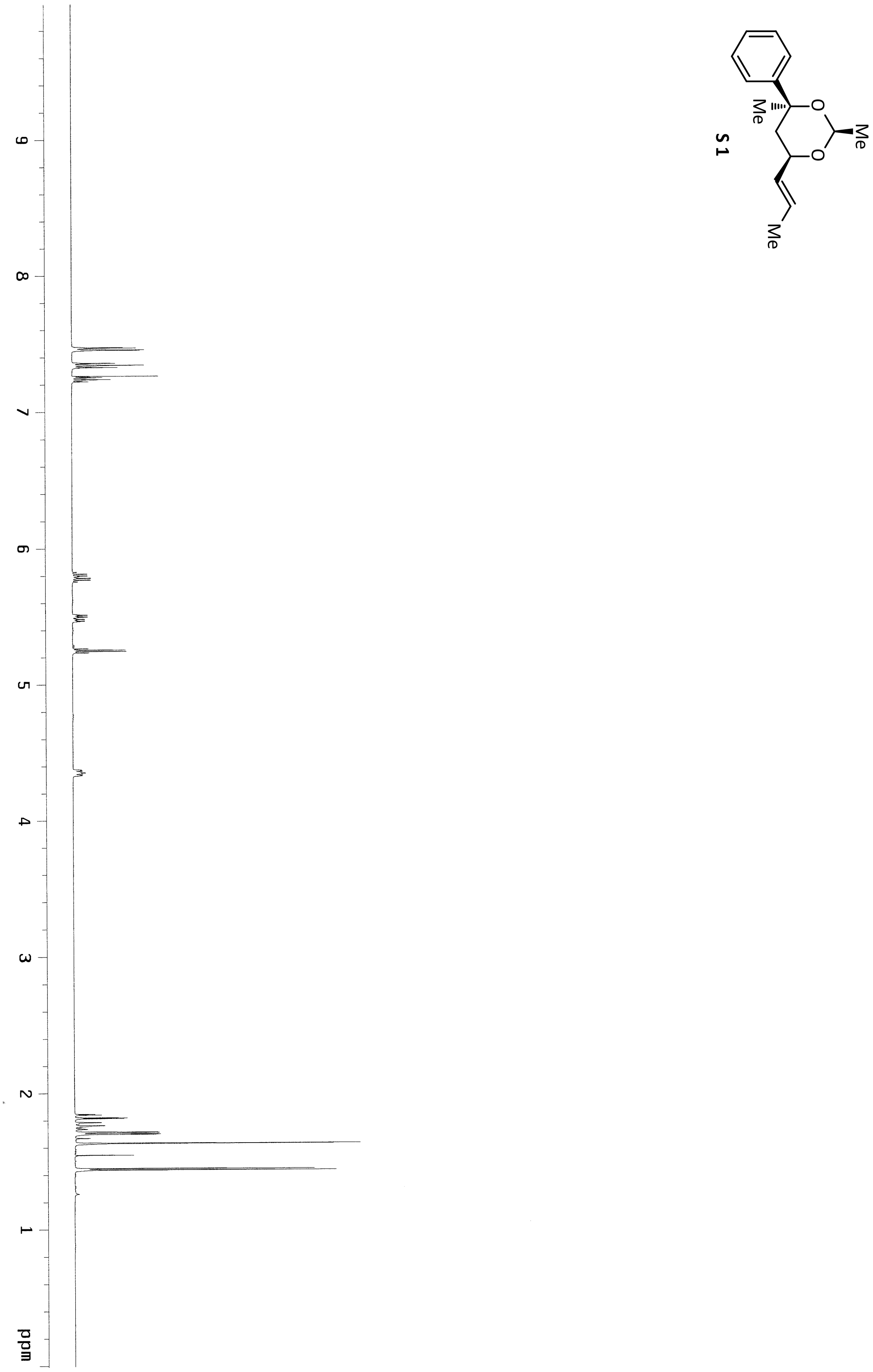

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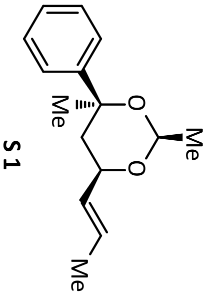

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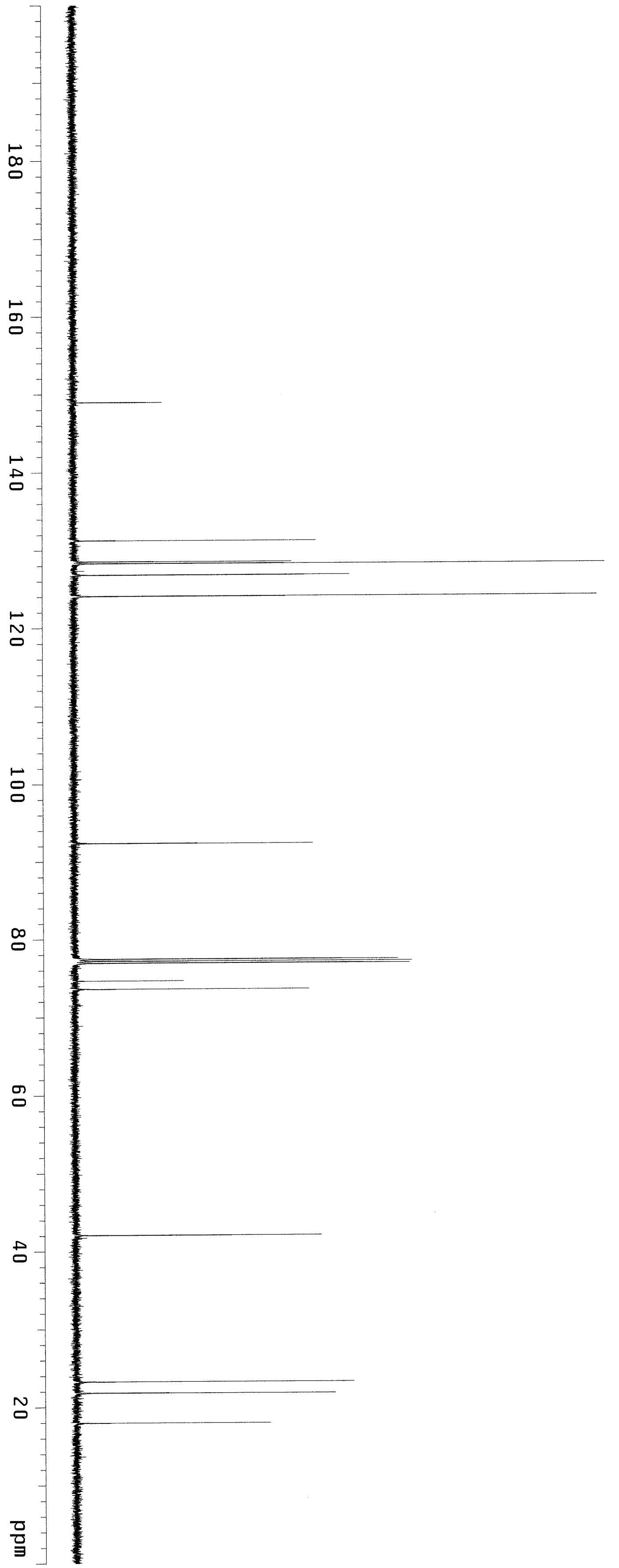

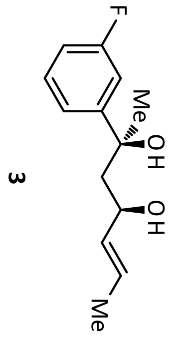

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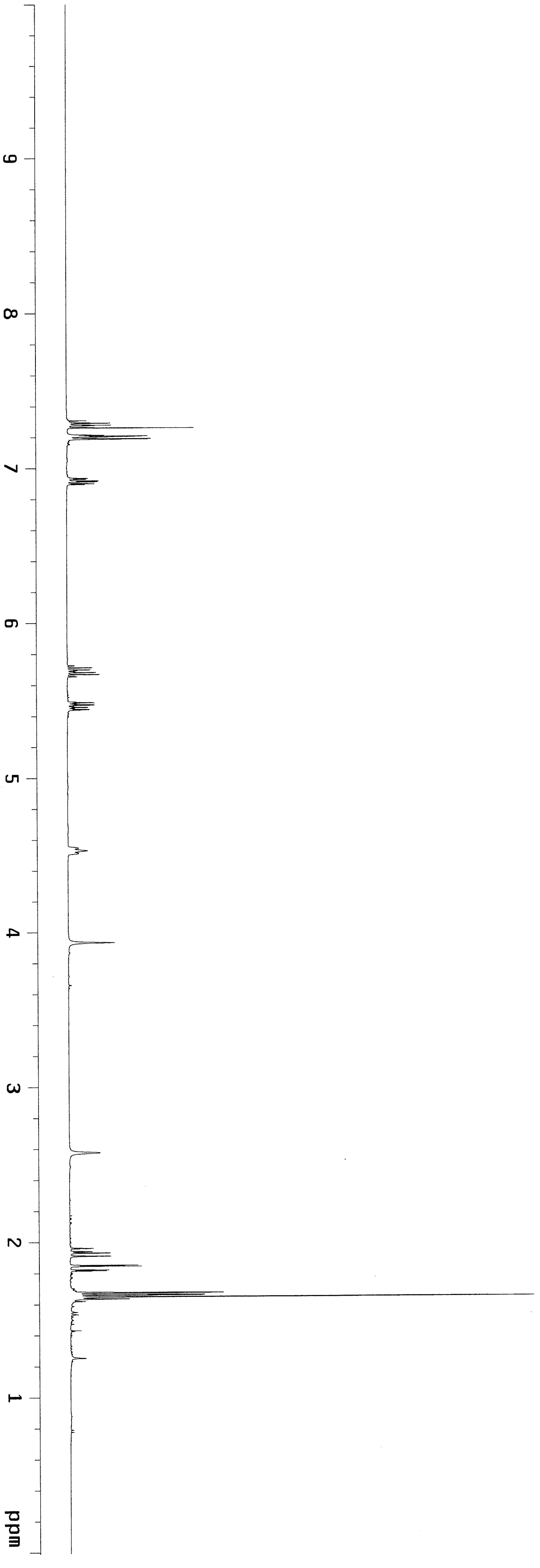

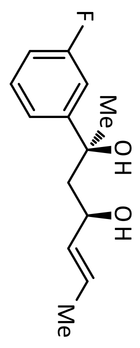

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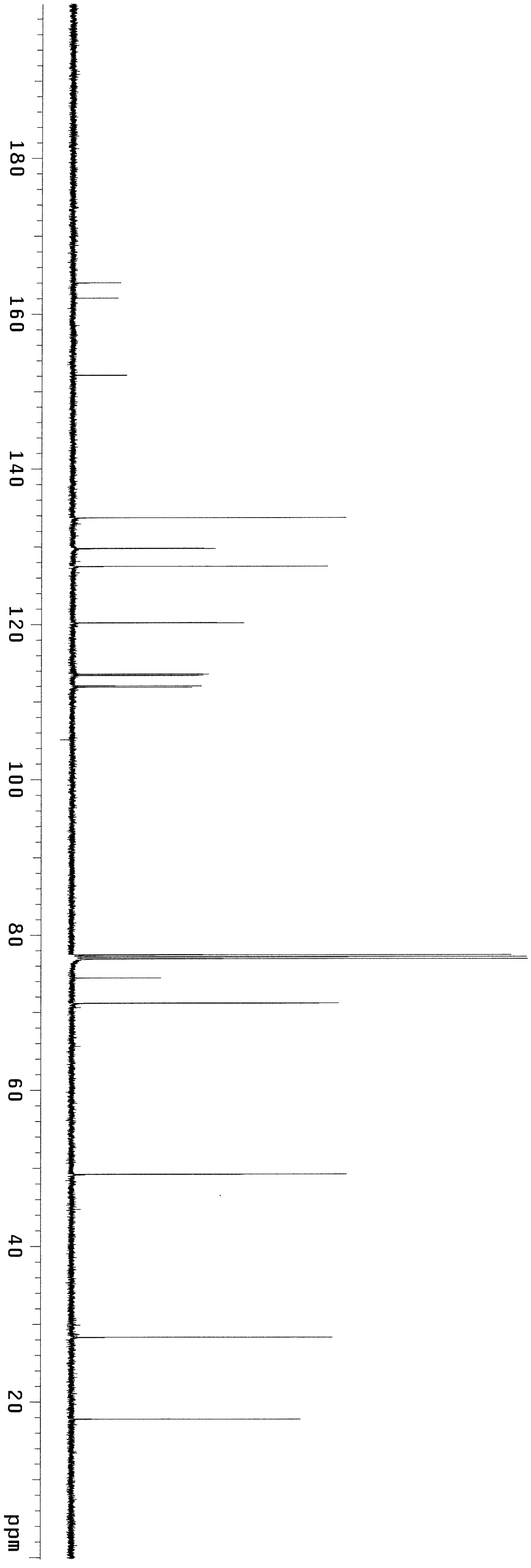

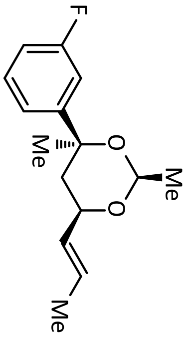

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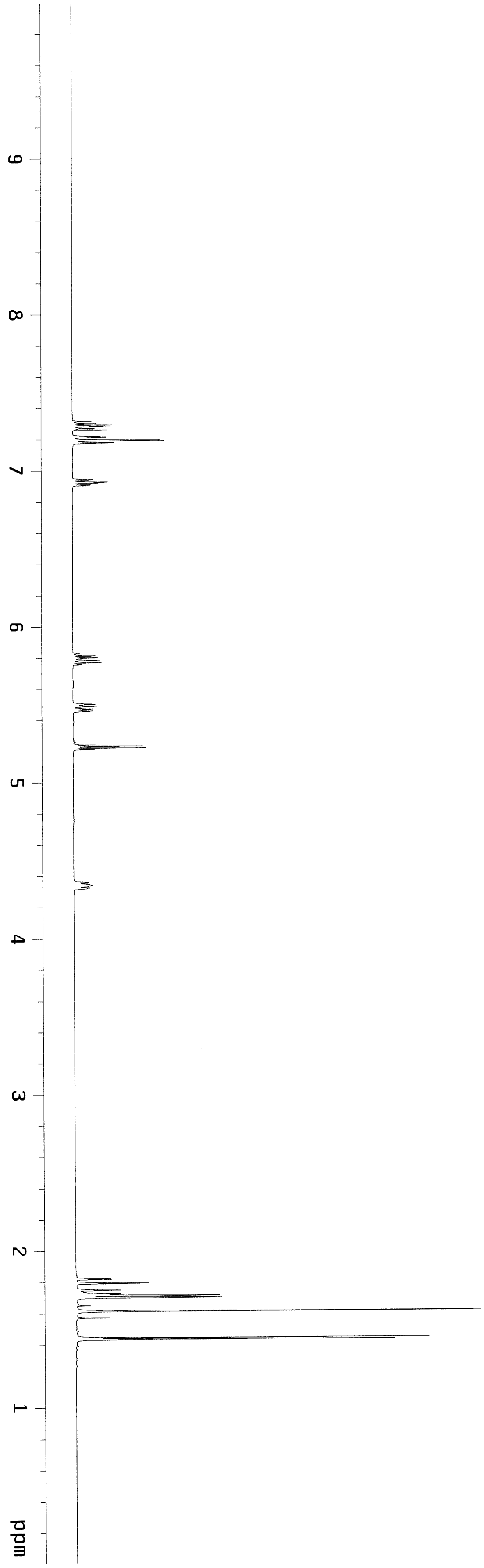

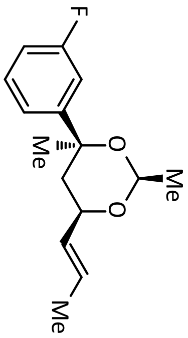

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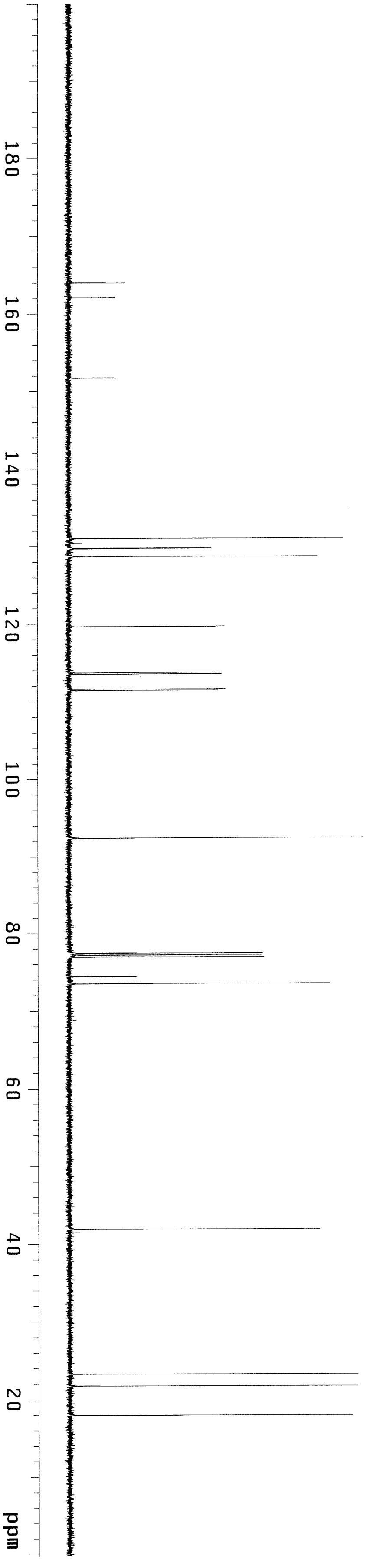

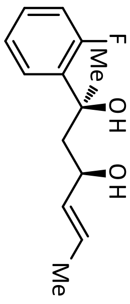

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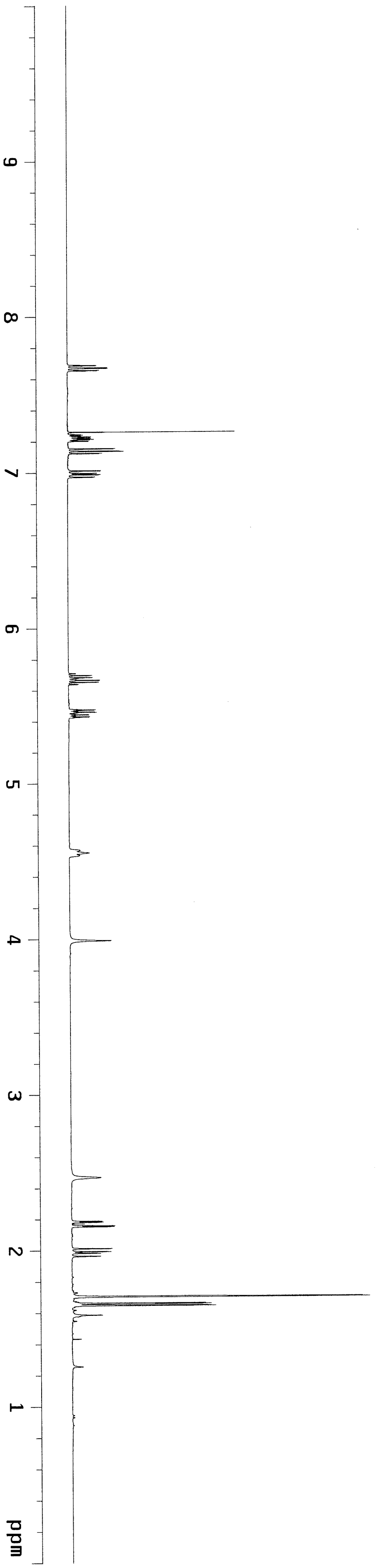

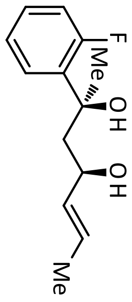

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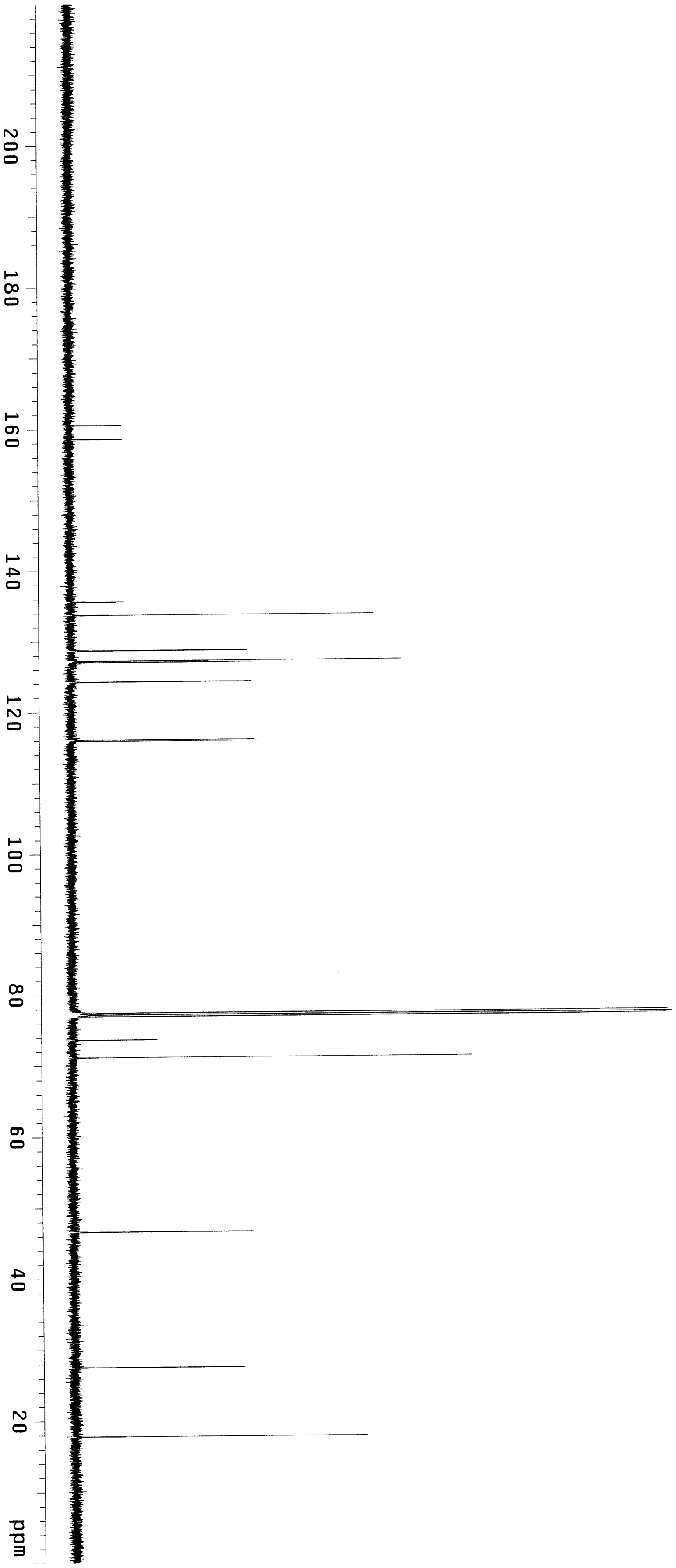

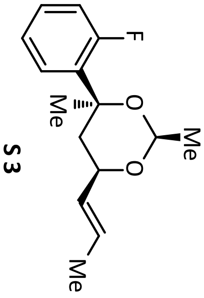

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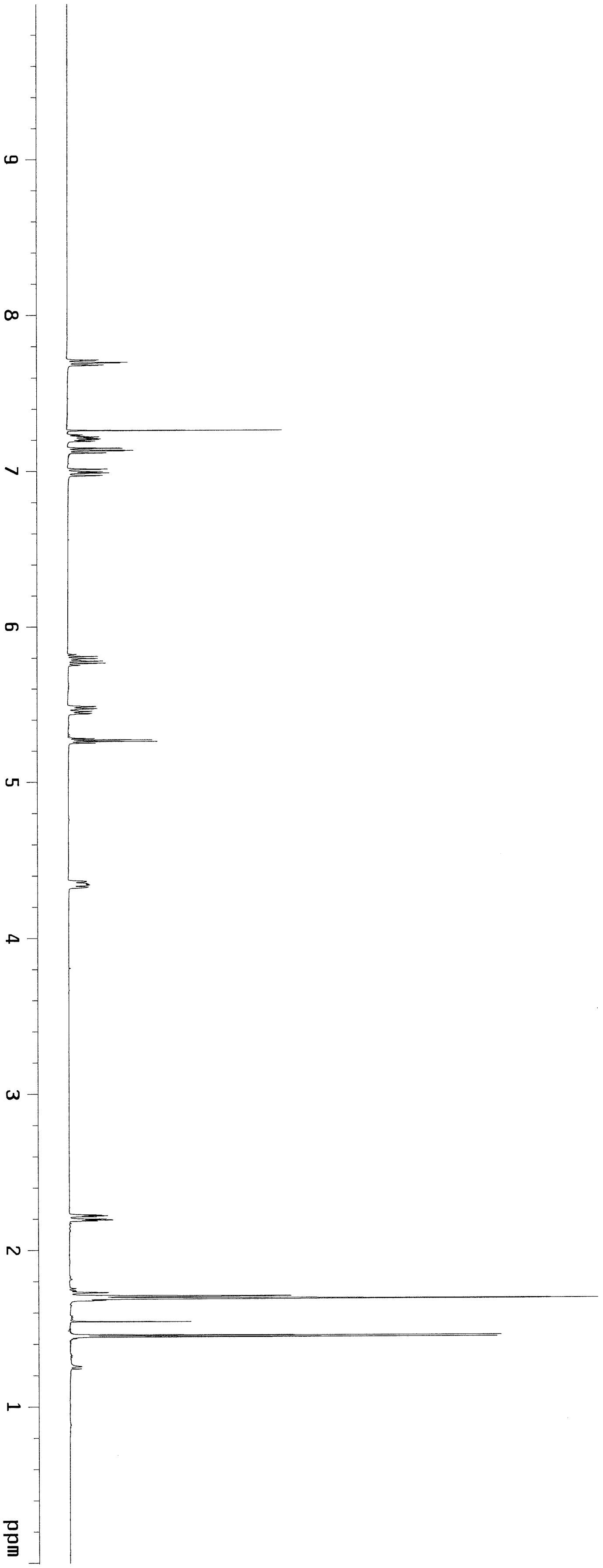
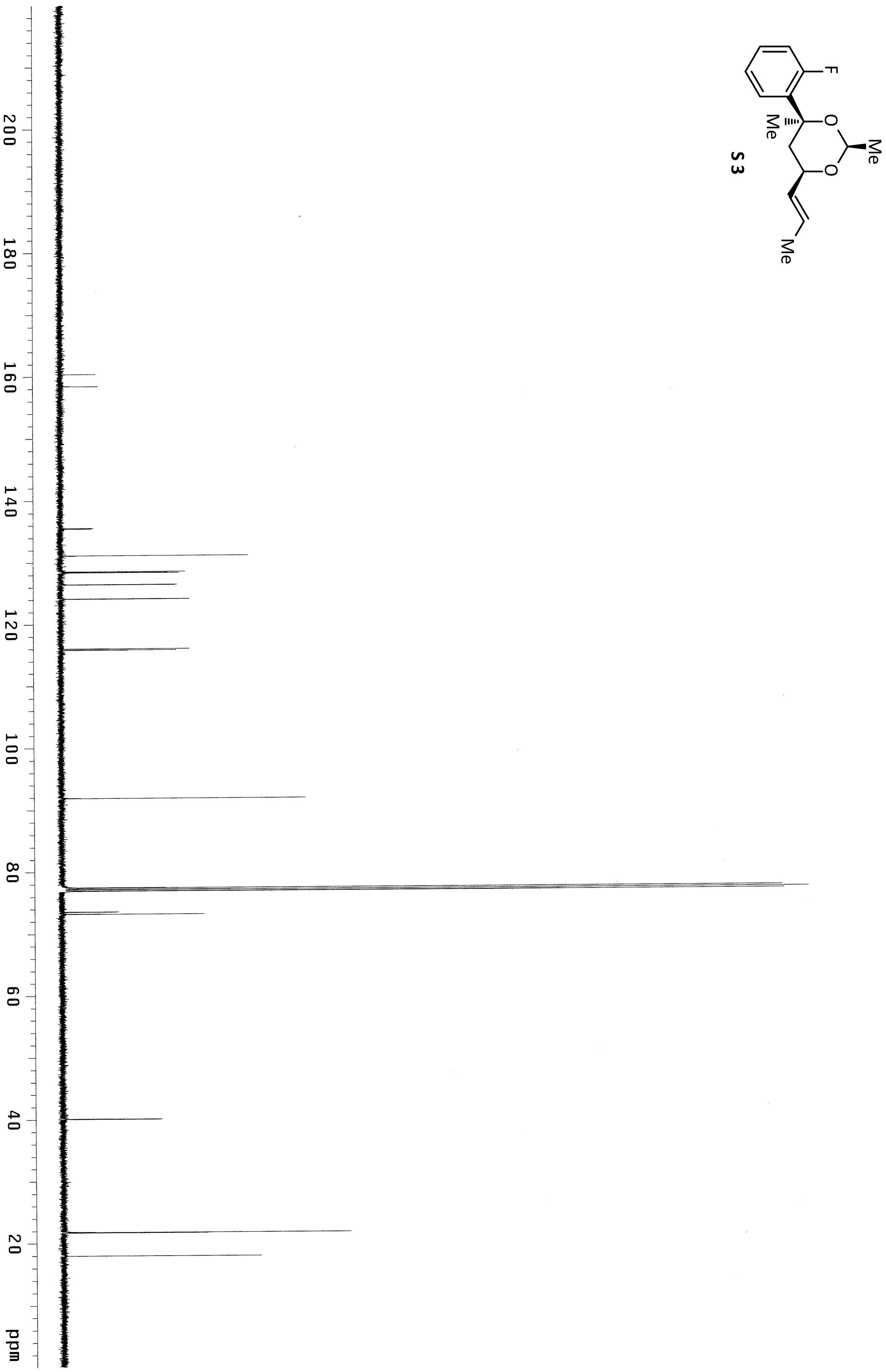
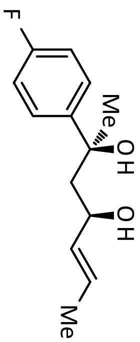




**S3**



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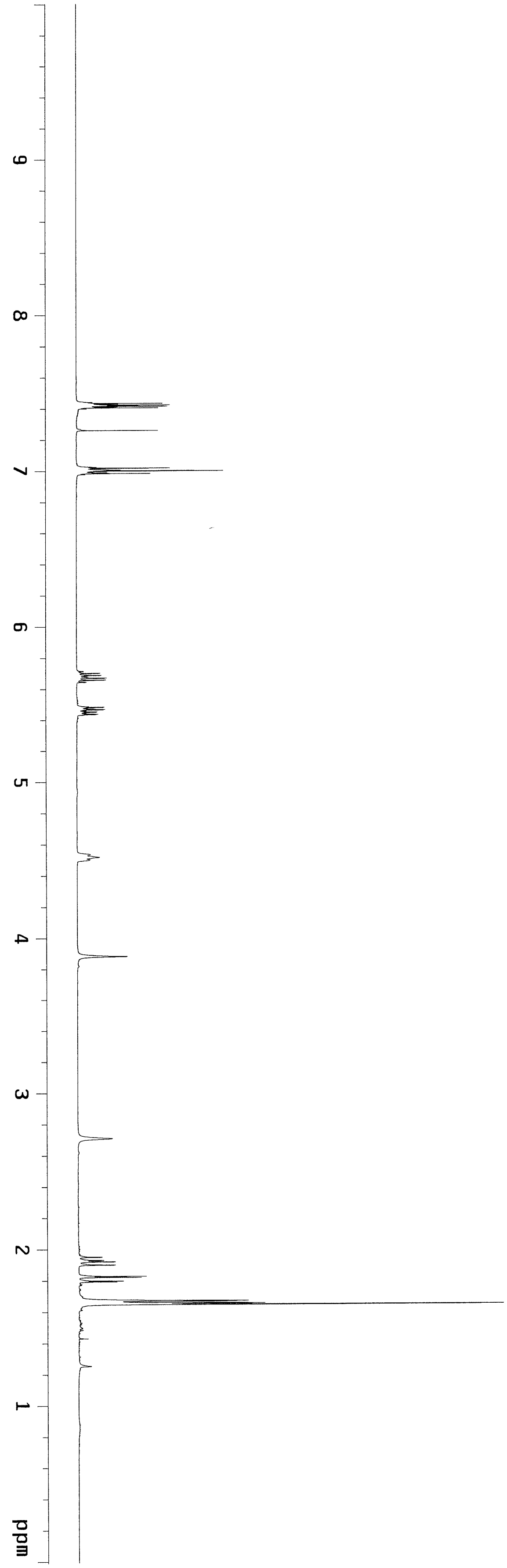

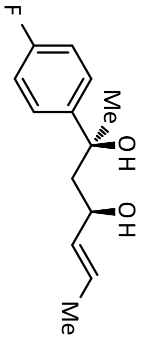

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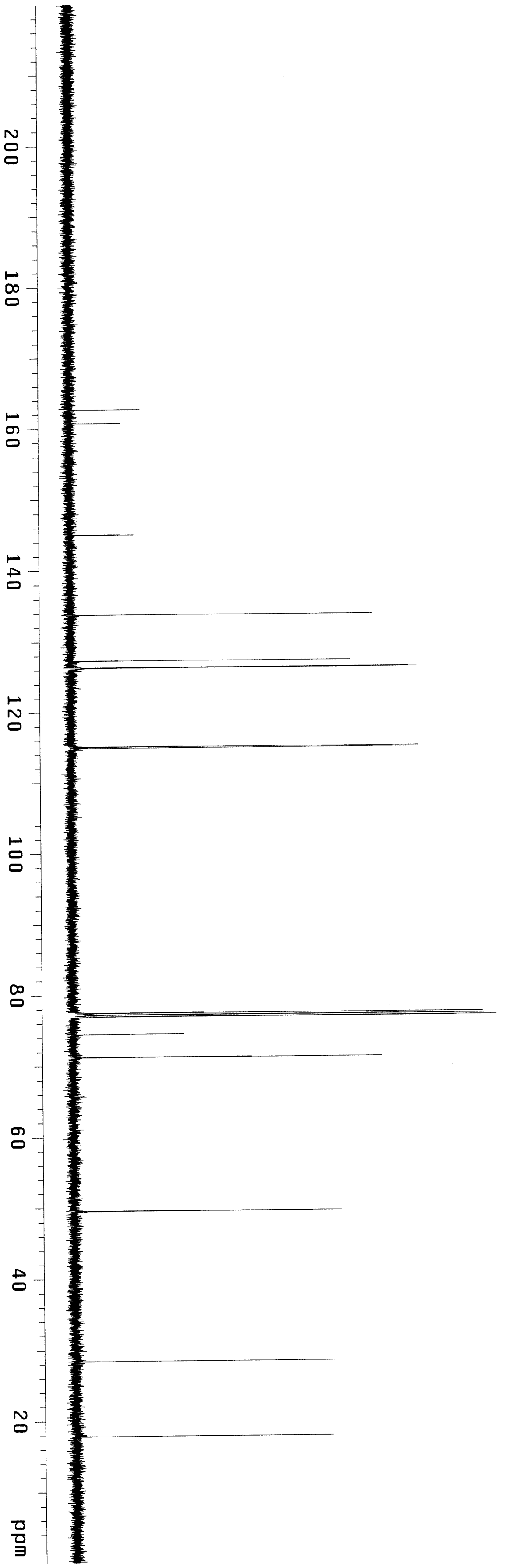

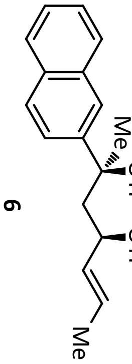

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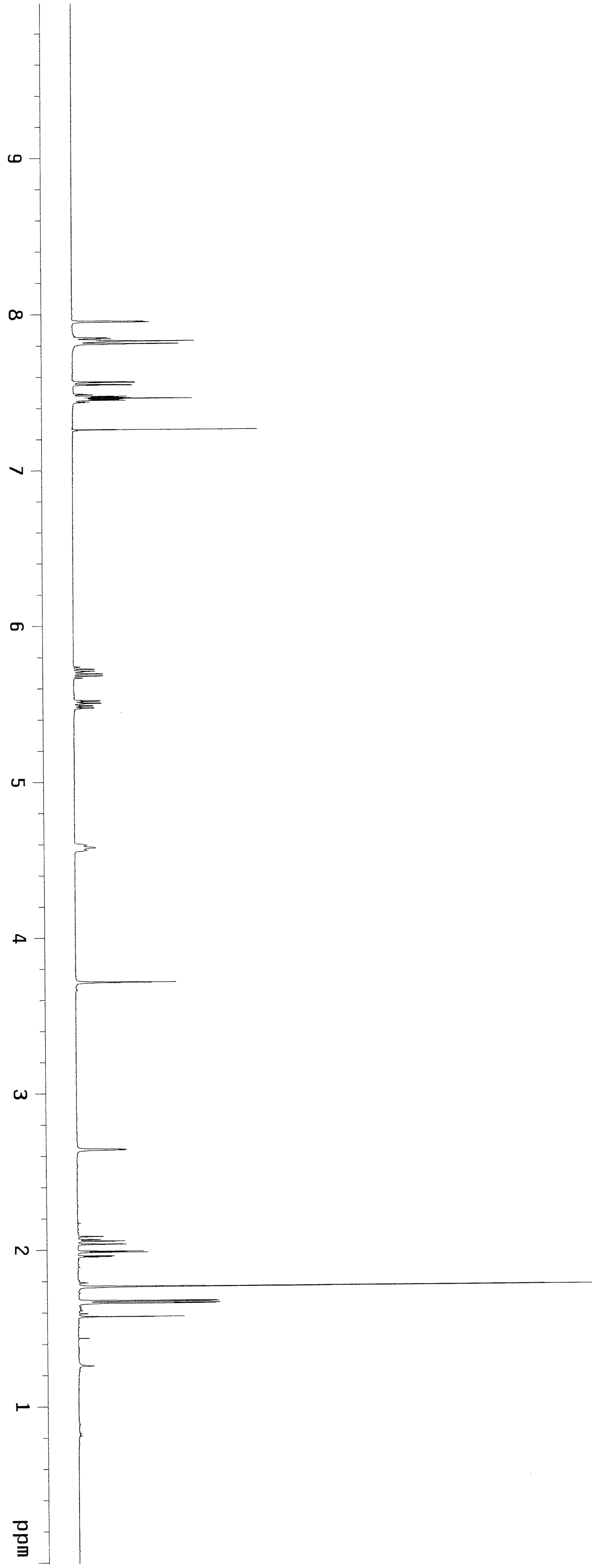

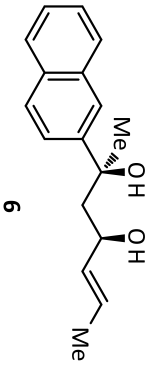

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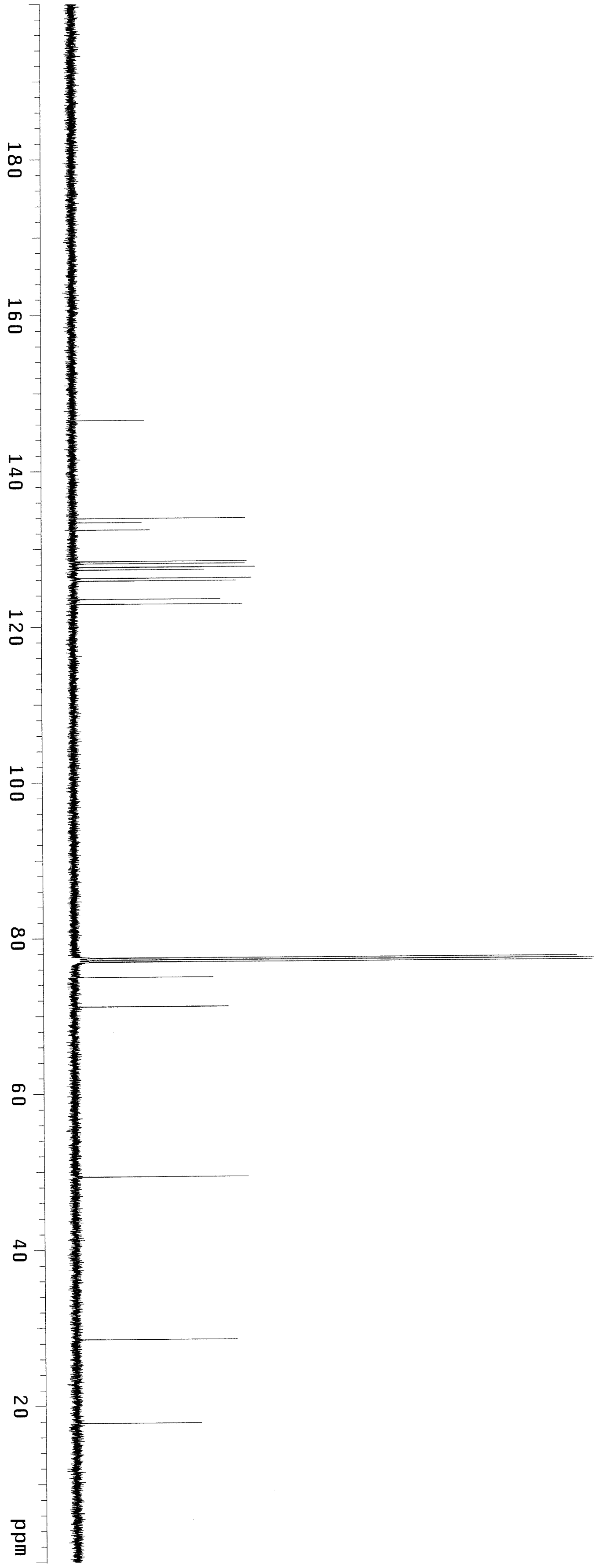

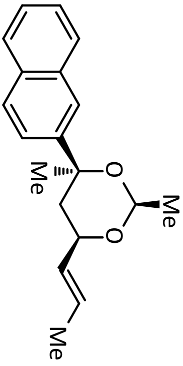

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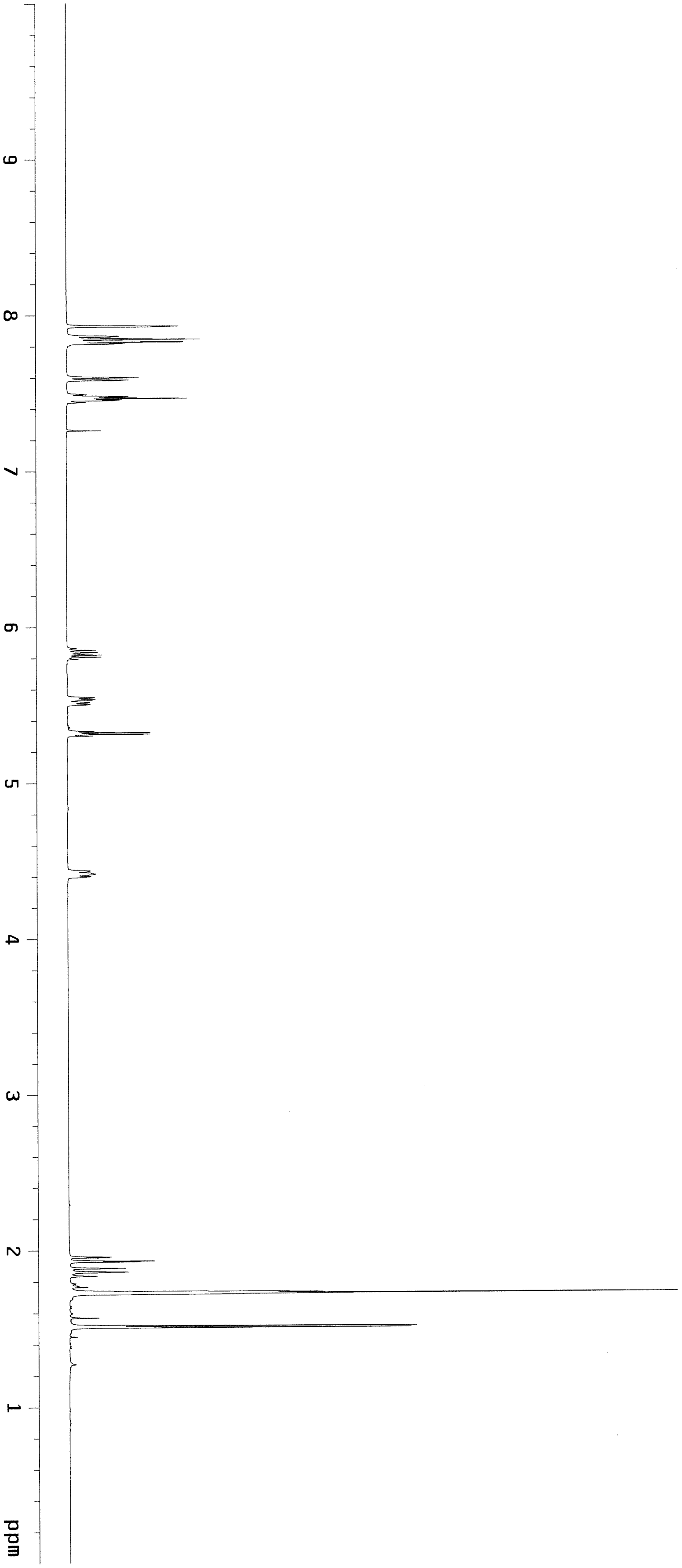

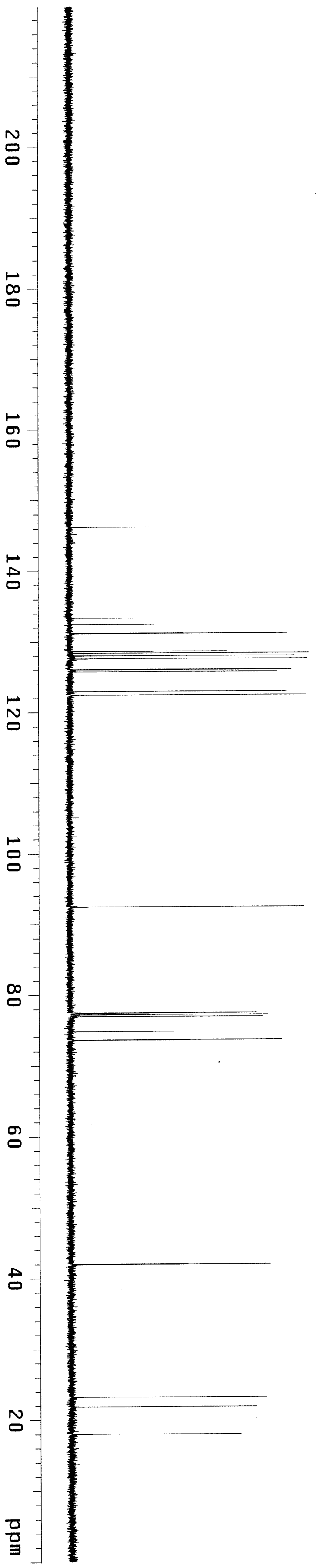

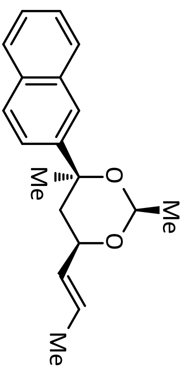

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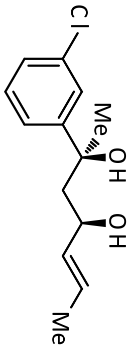

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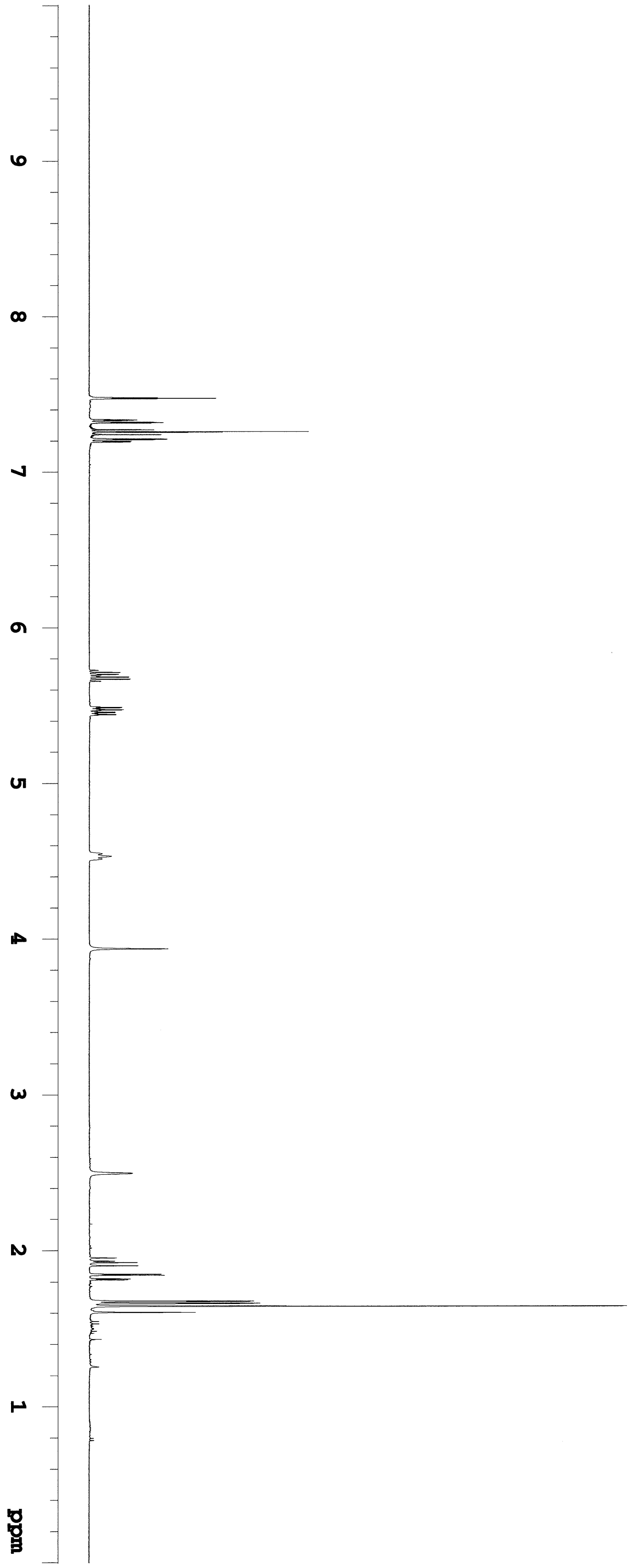

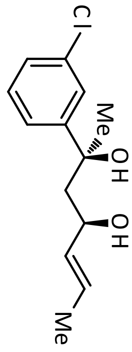

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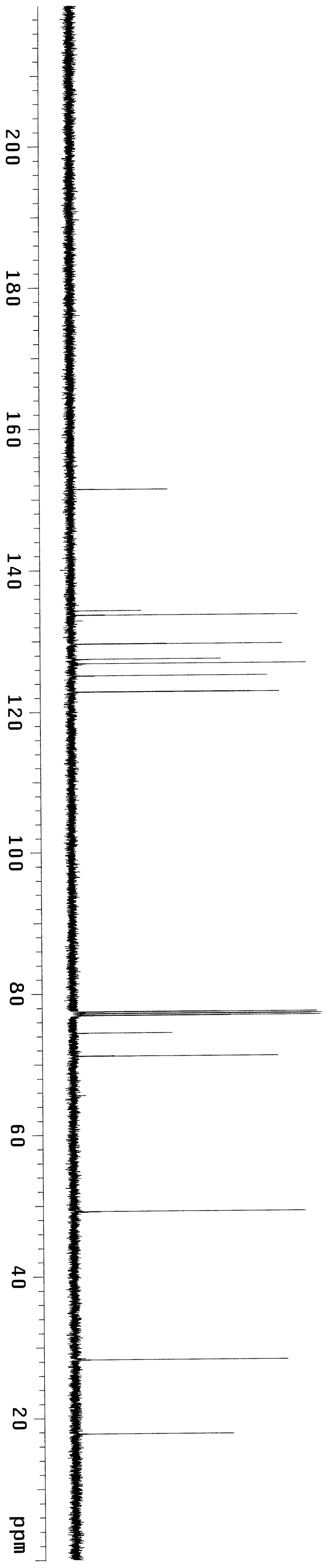

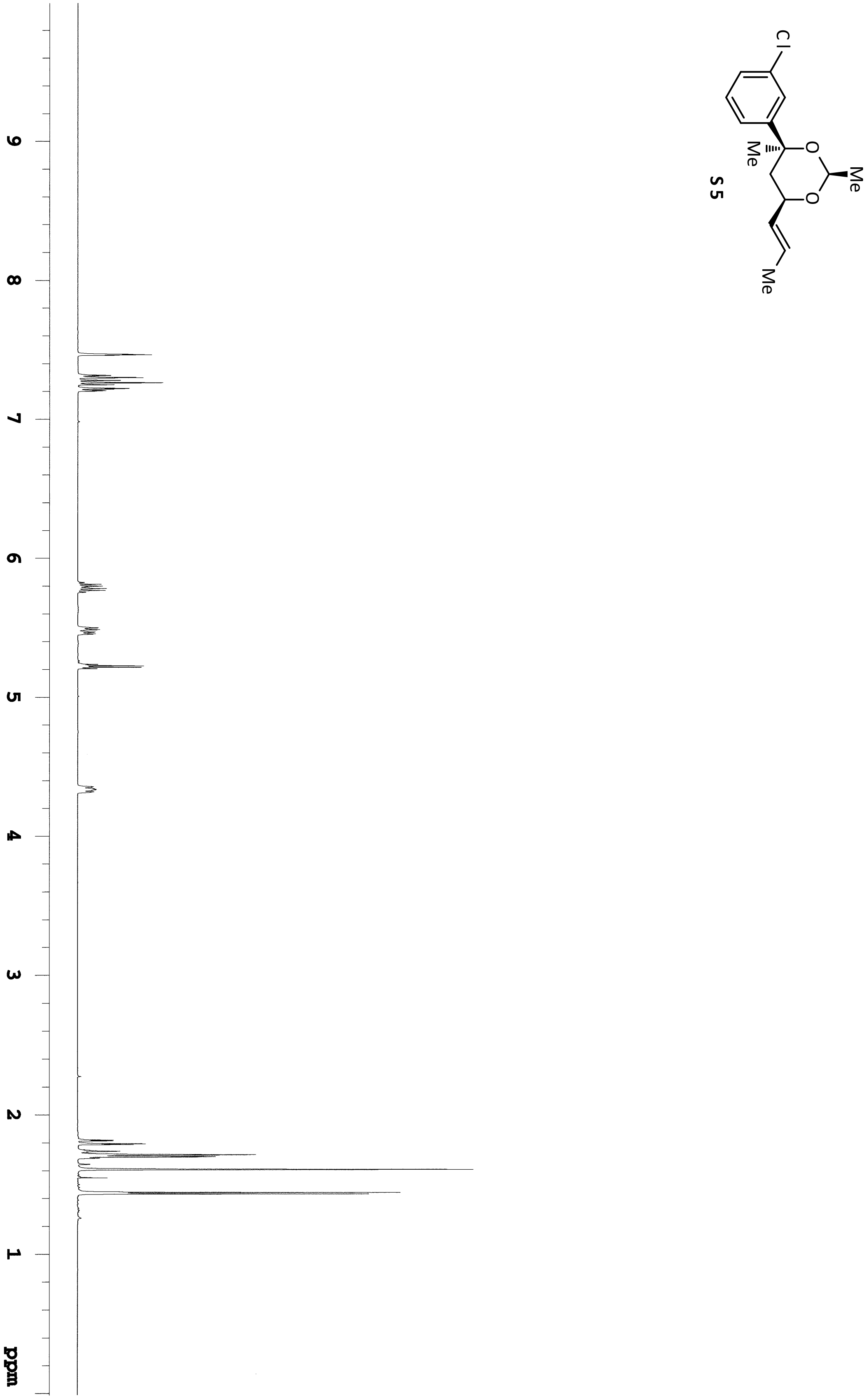

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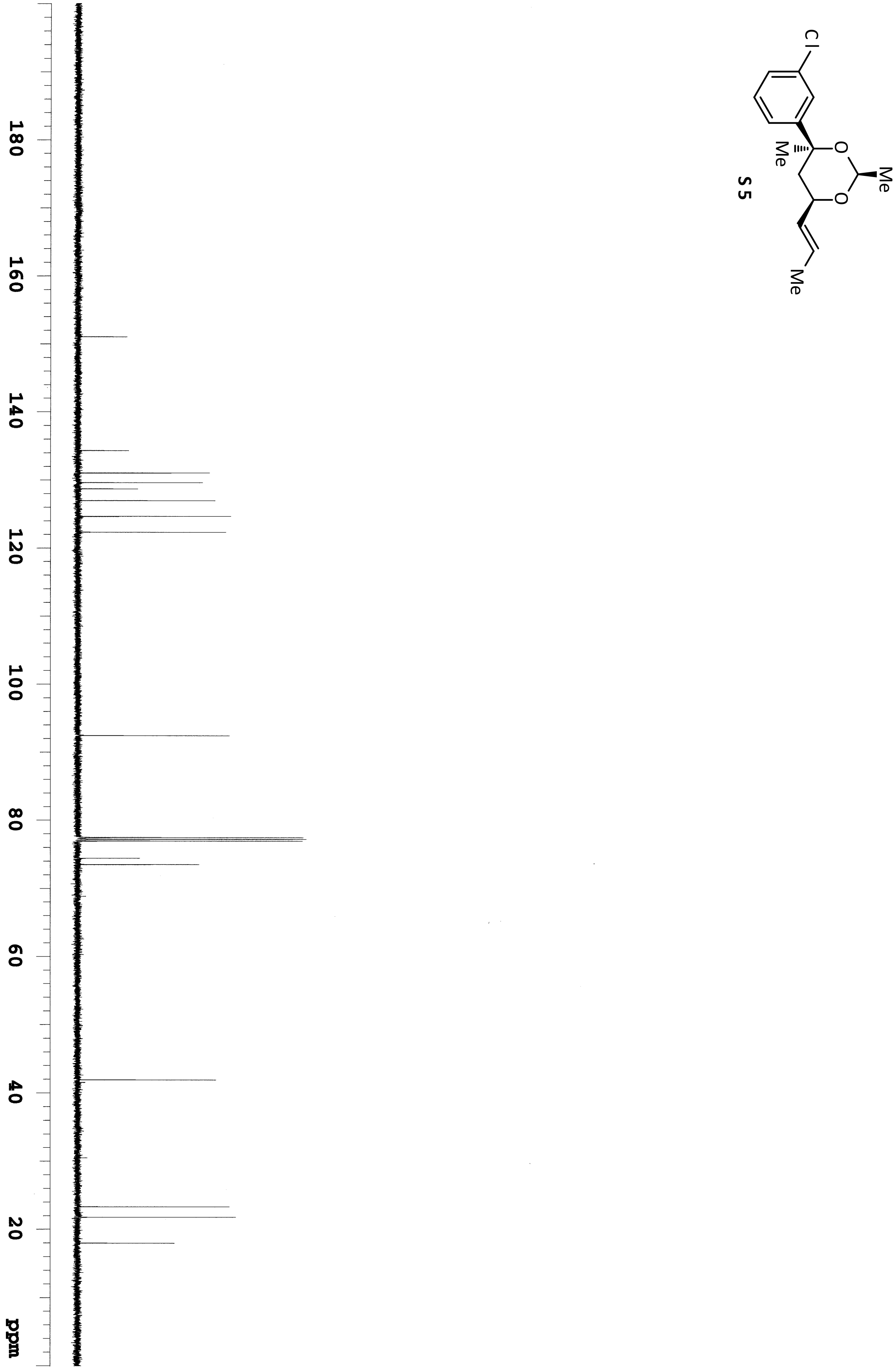

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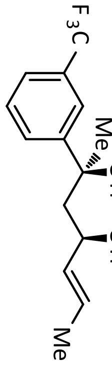

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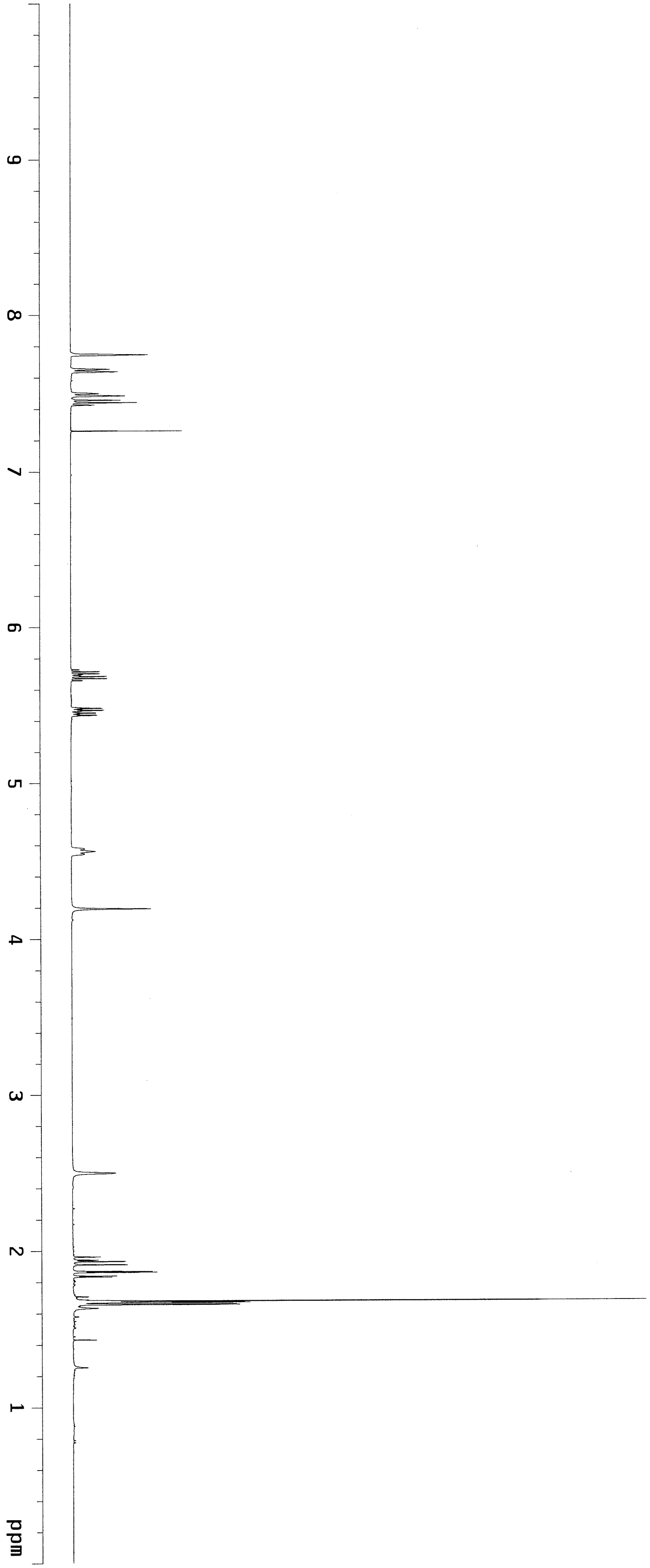

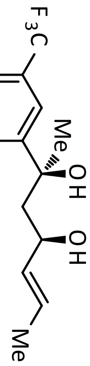

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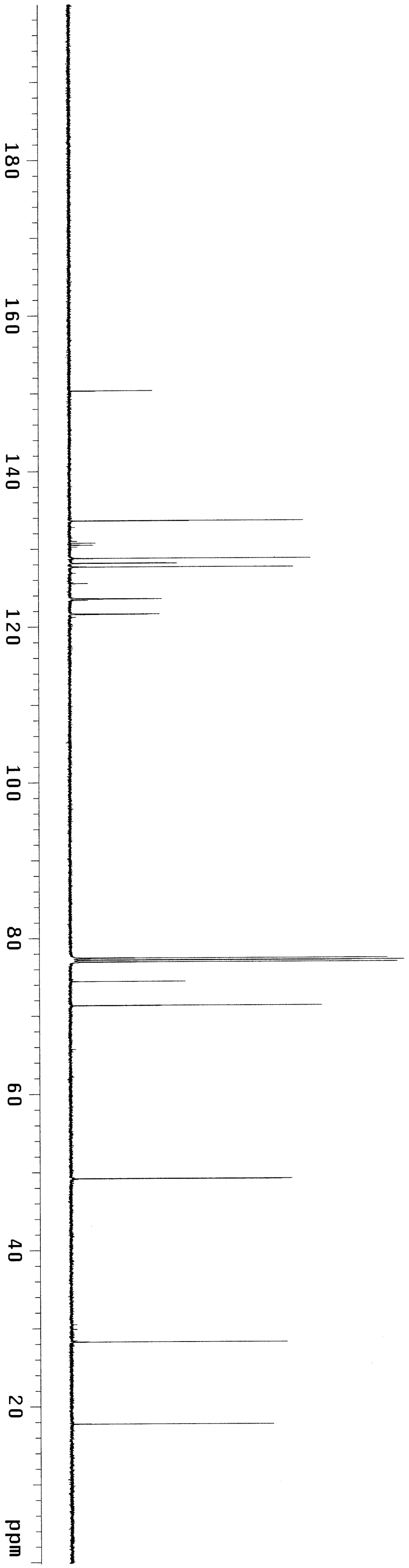

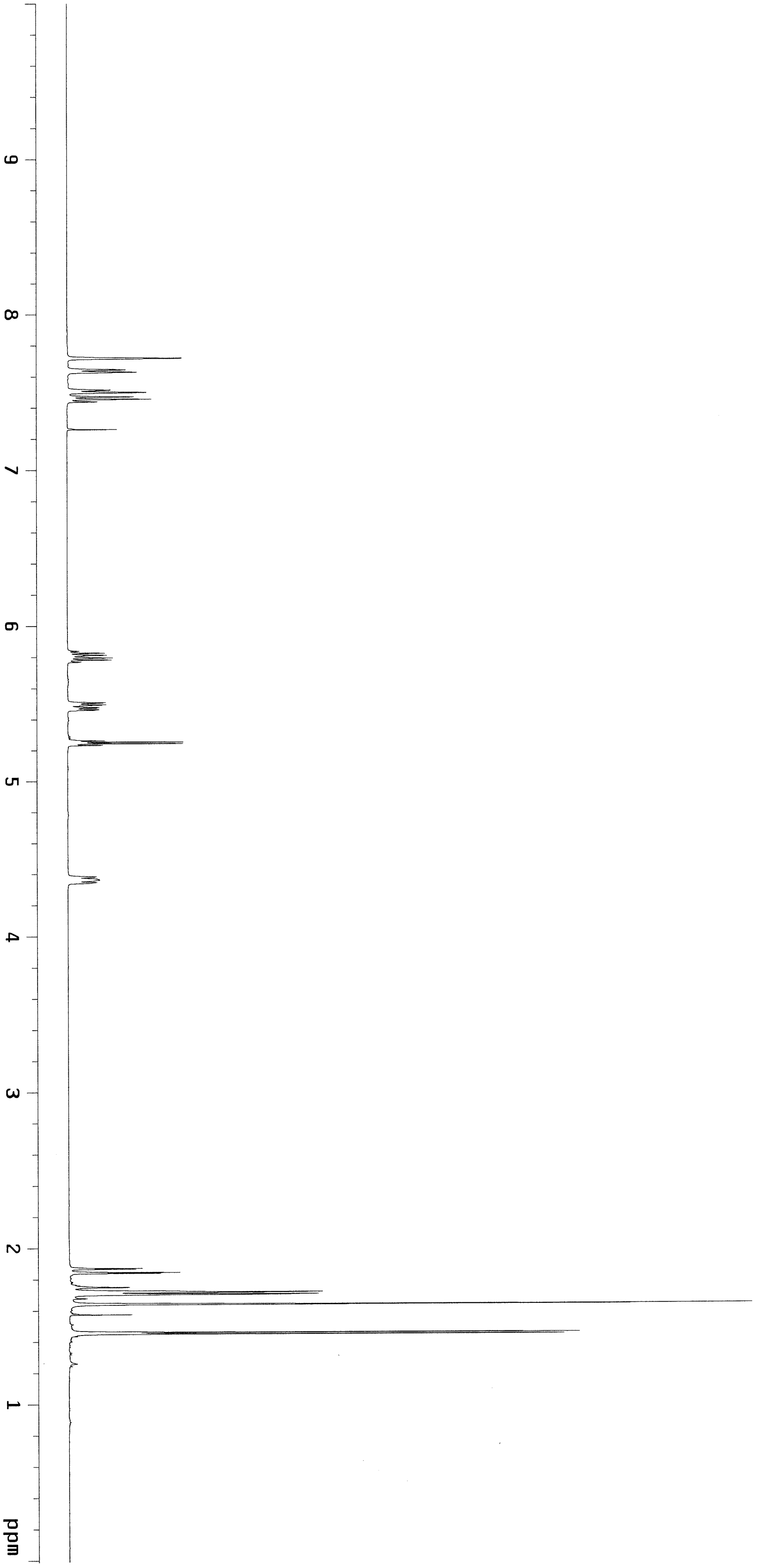

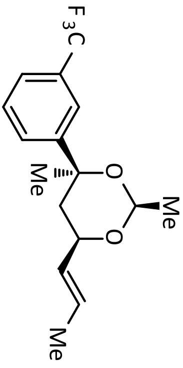

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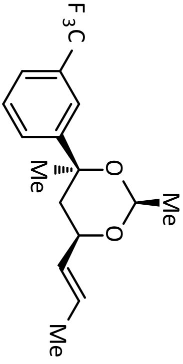

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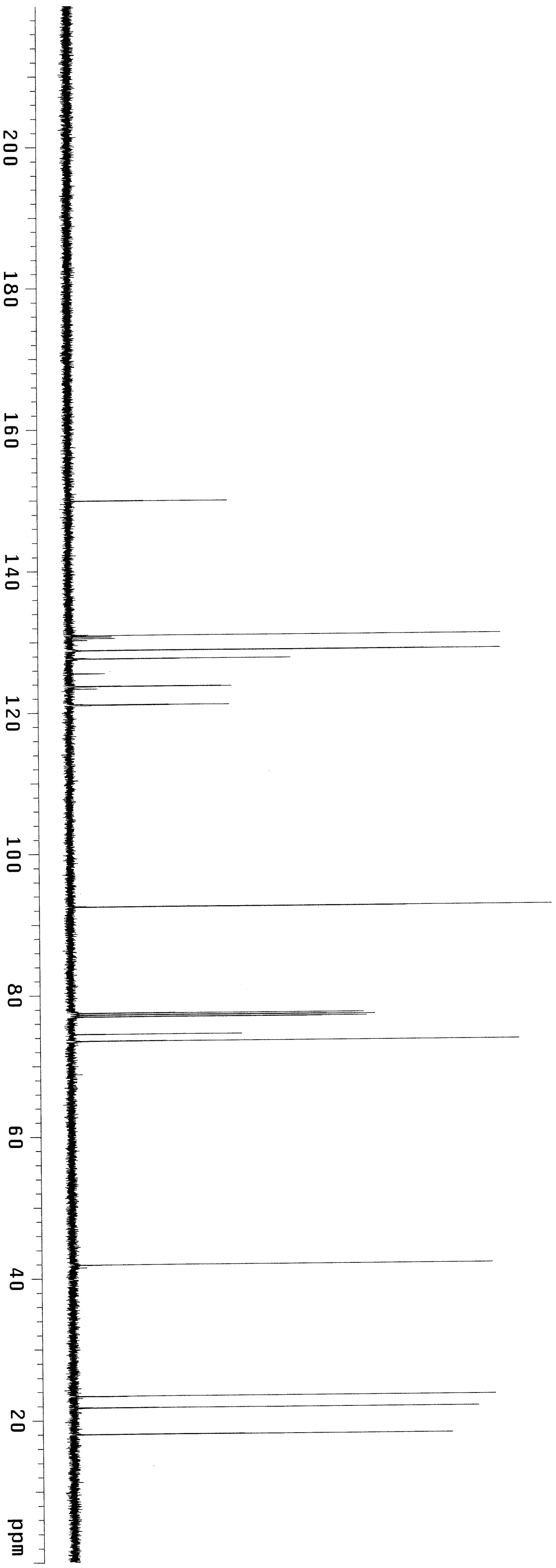

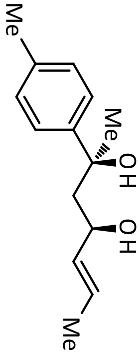

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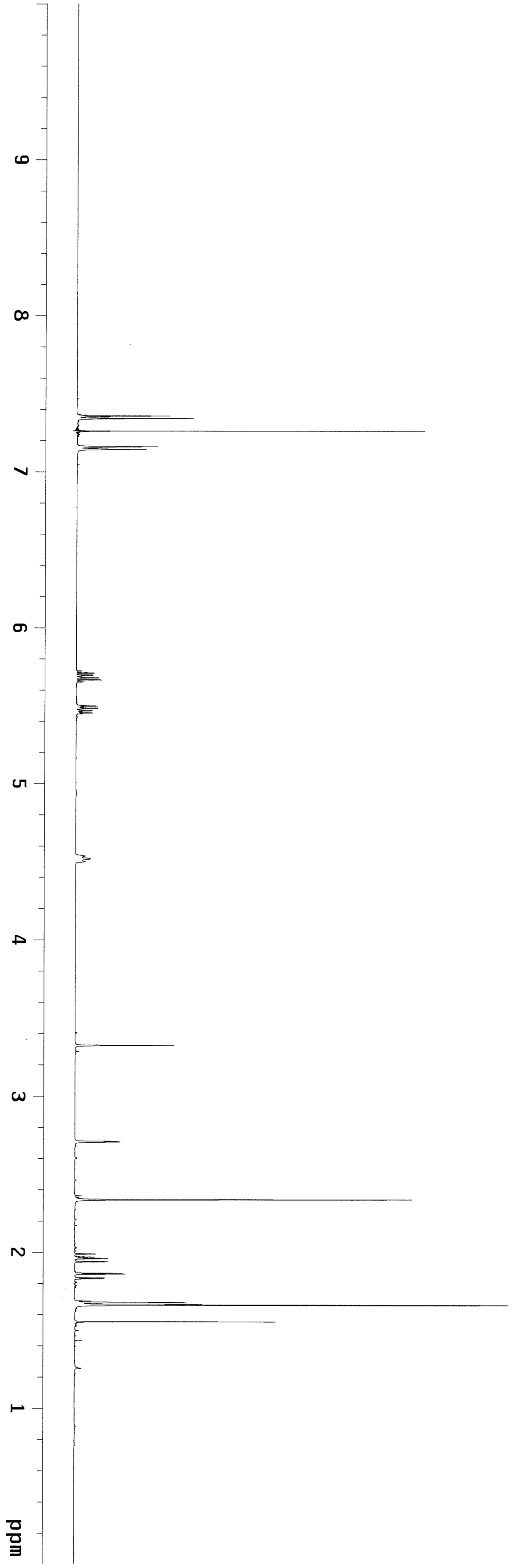

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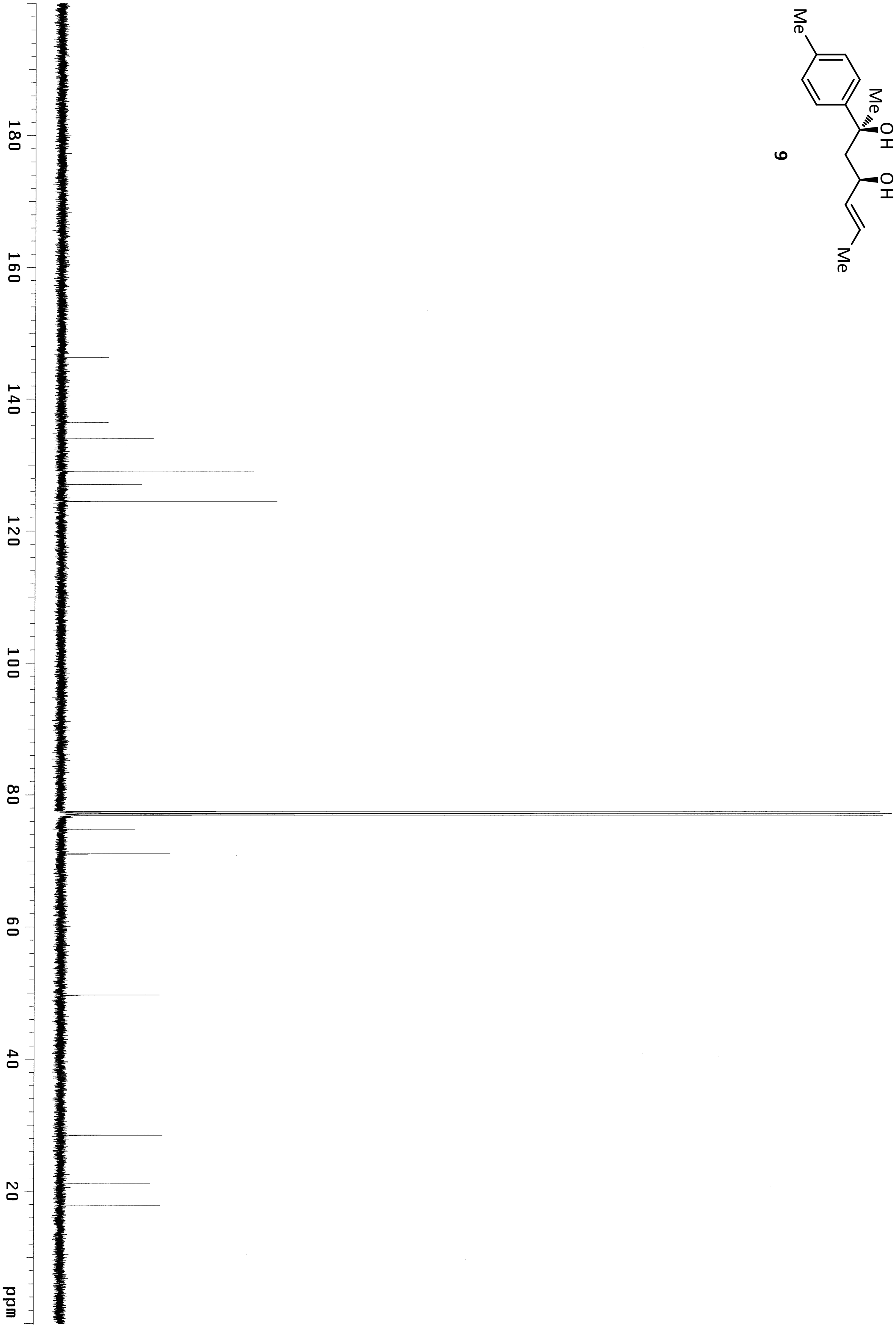

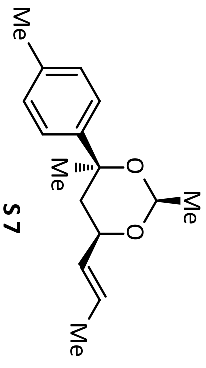

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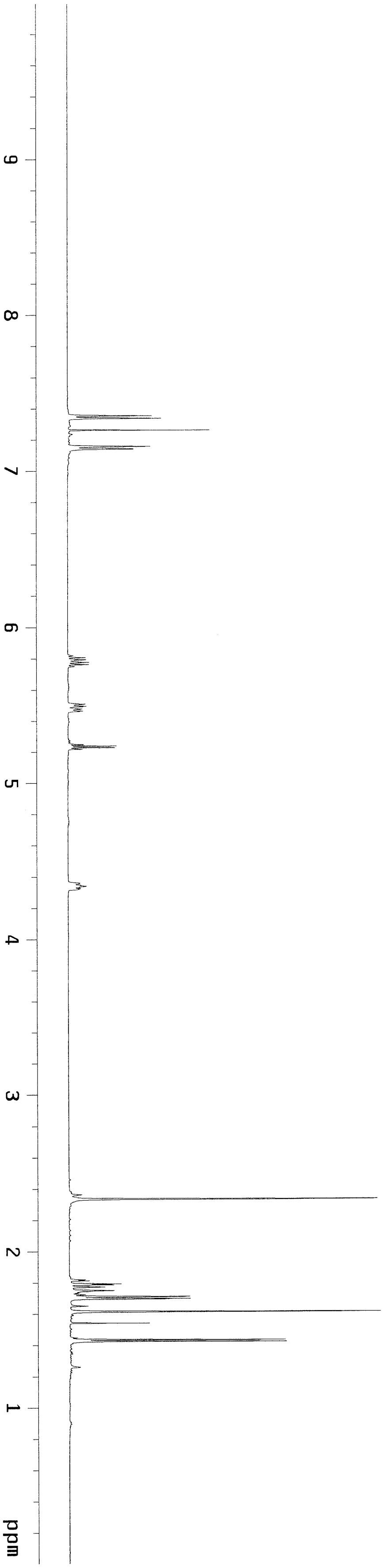

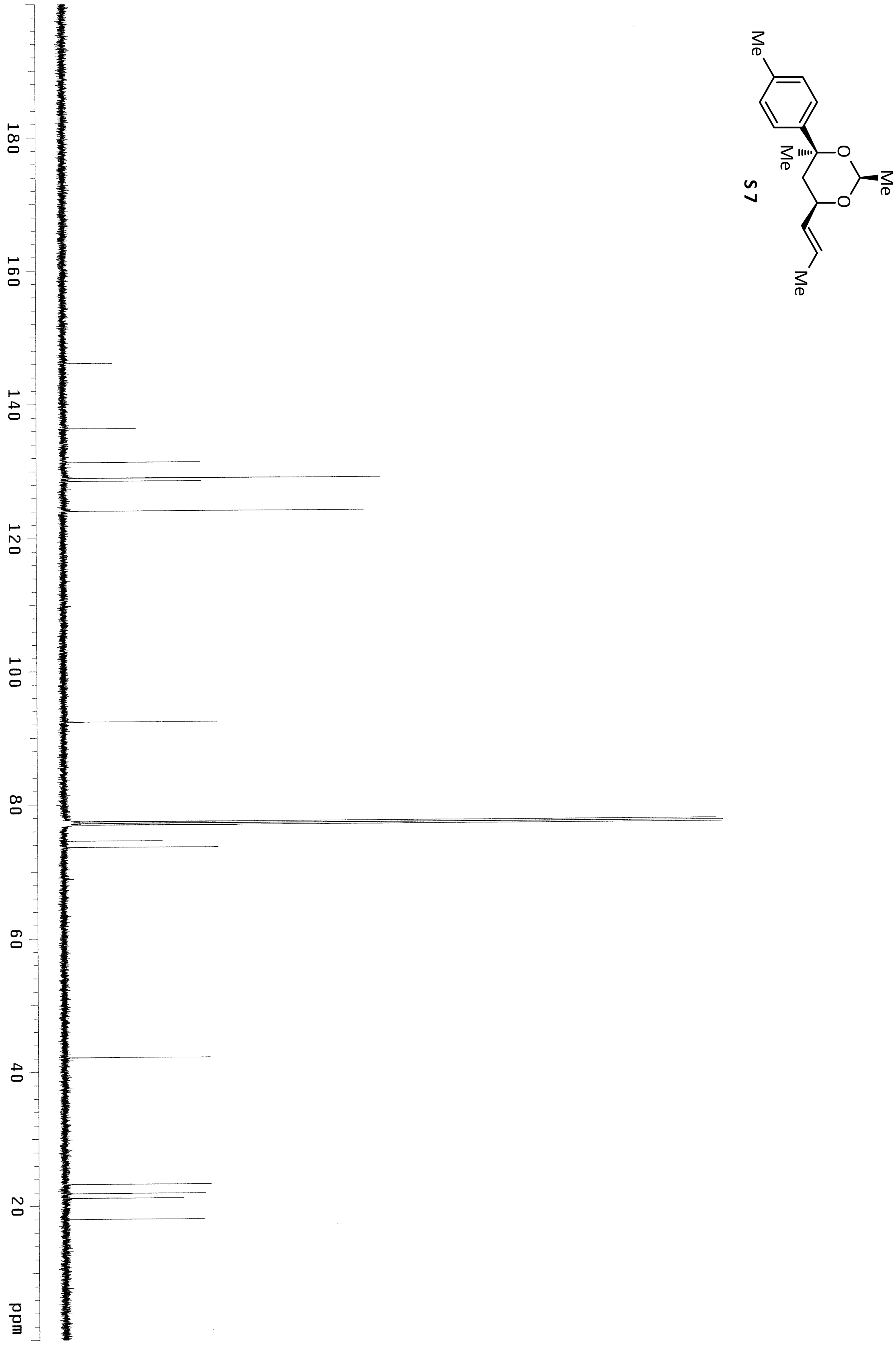

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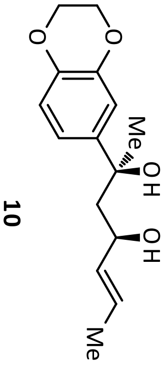

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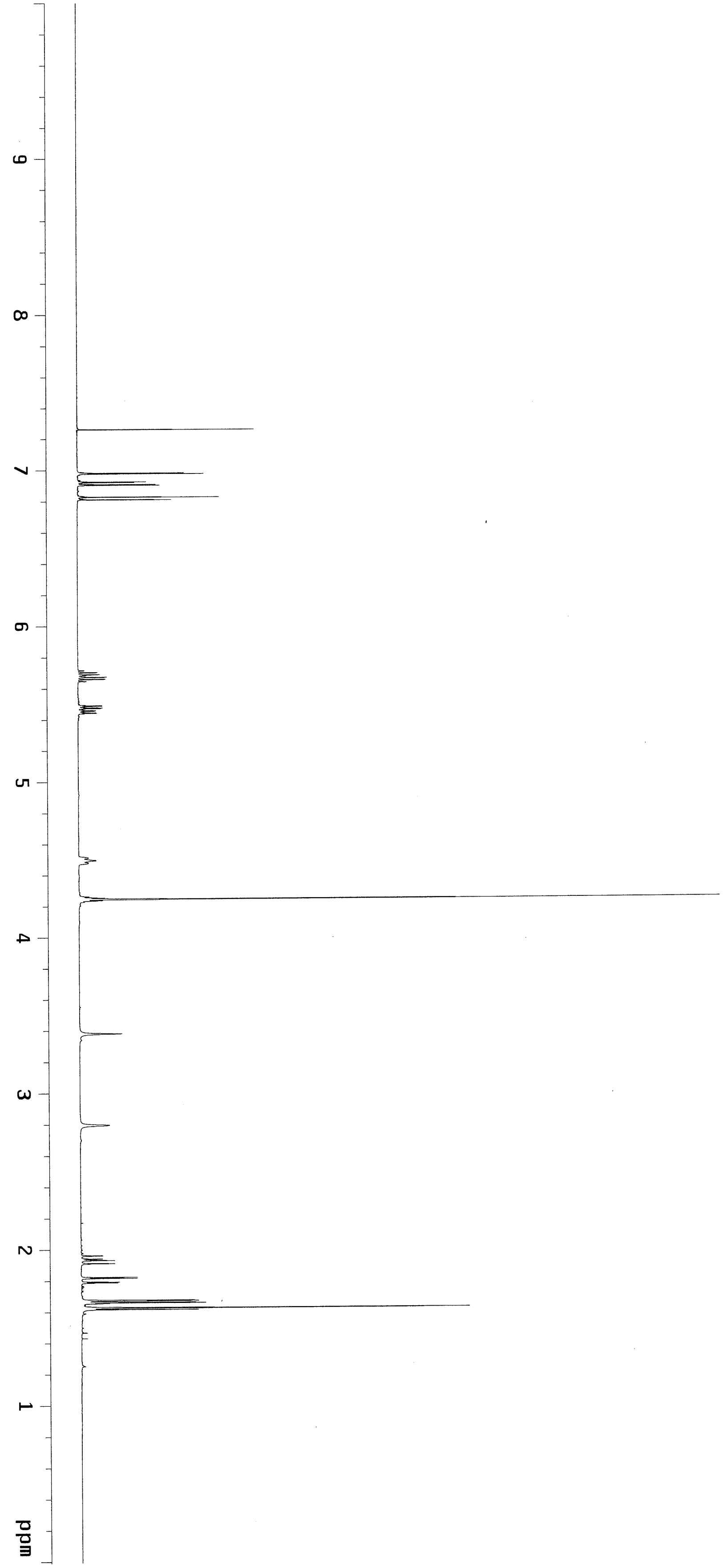

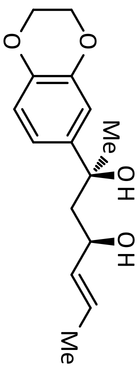

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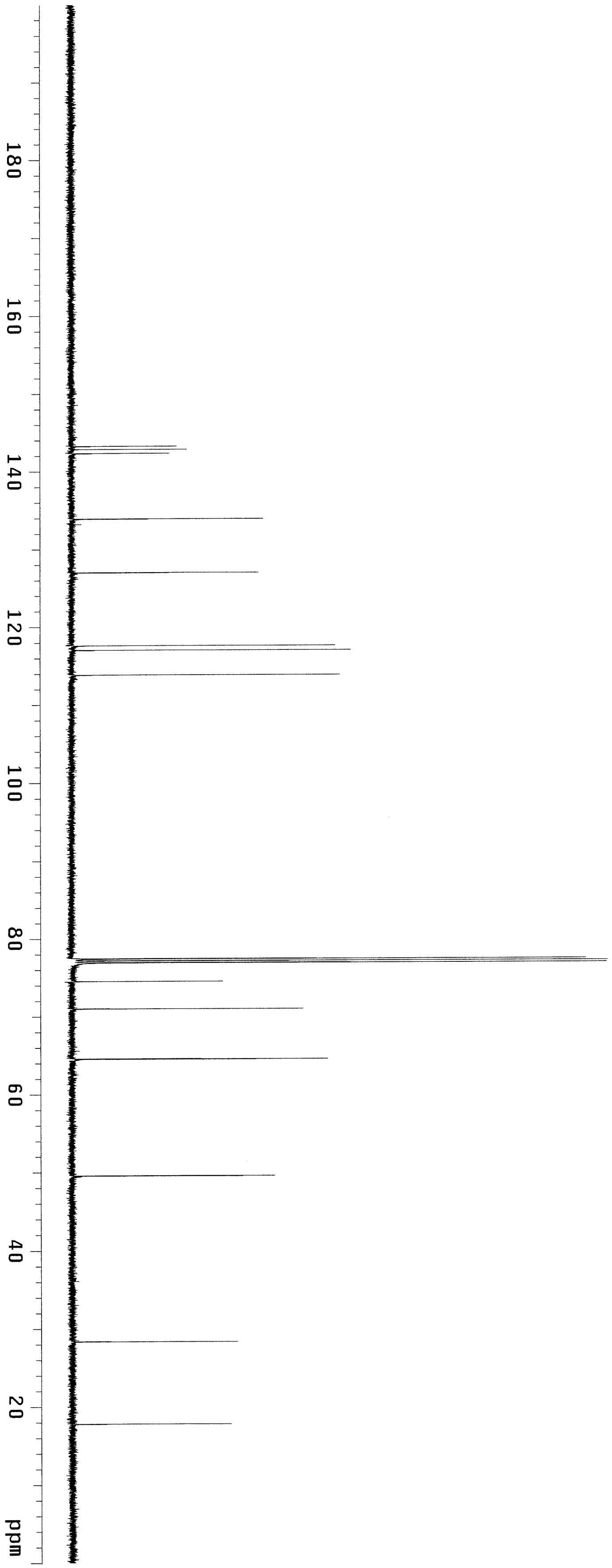

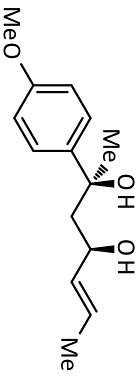

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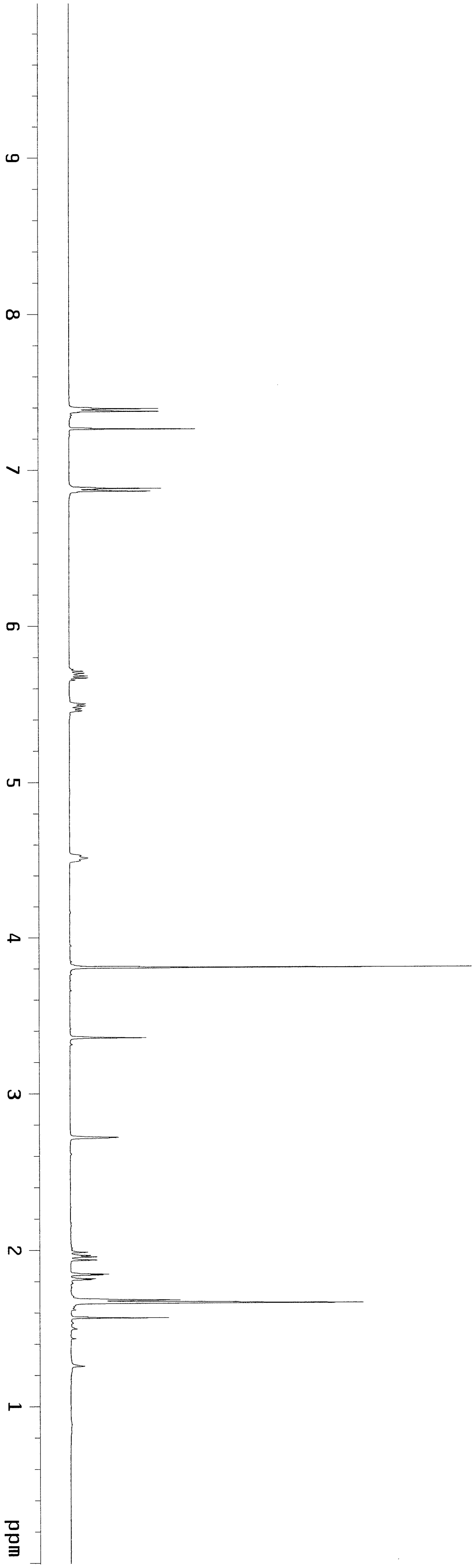

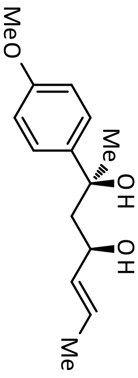

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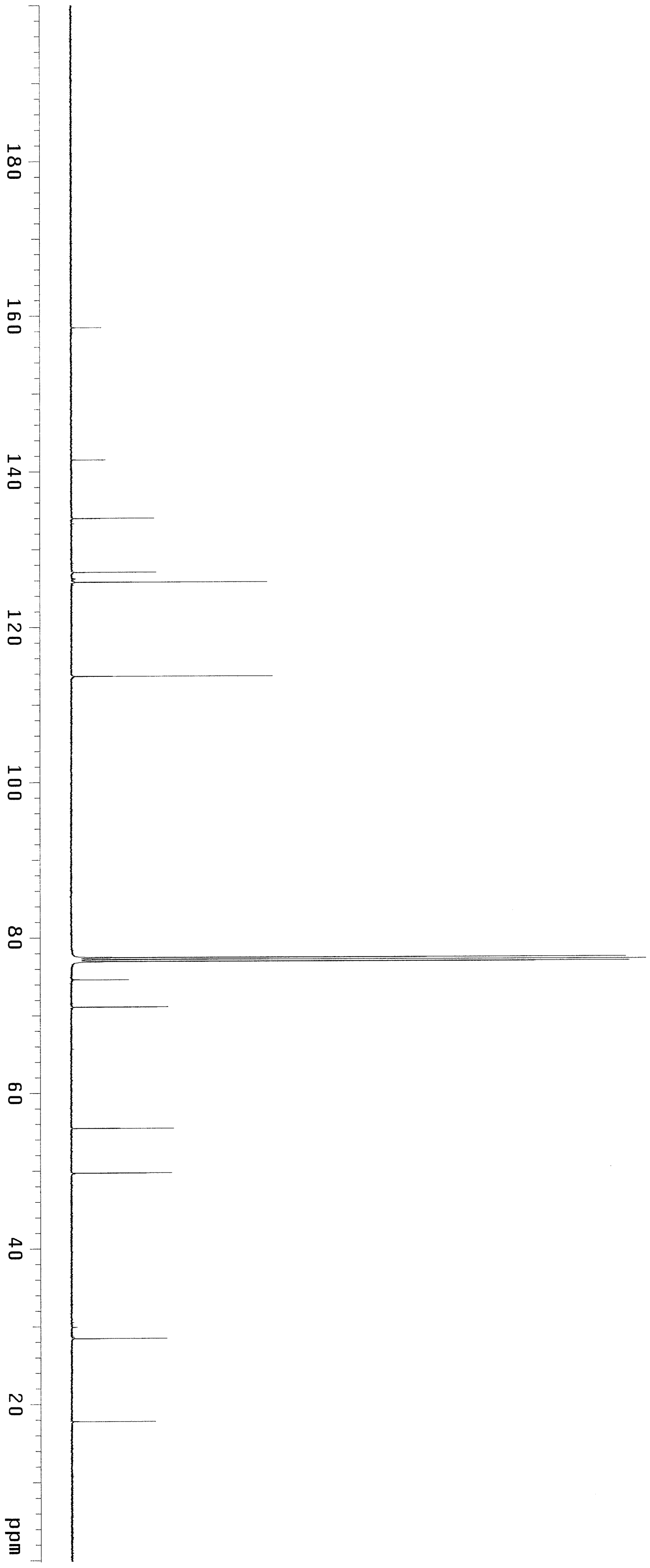

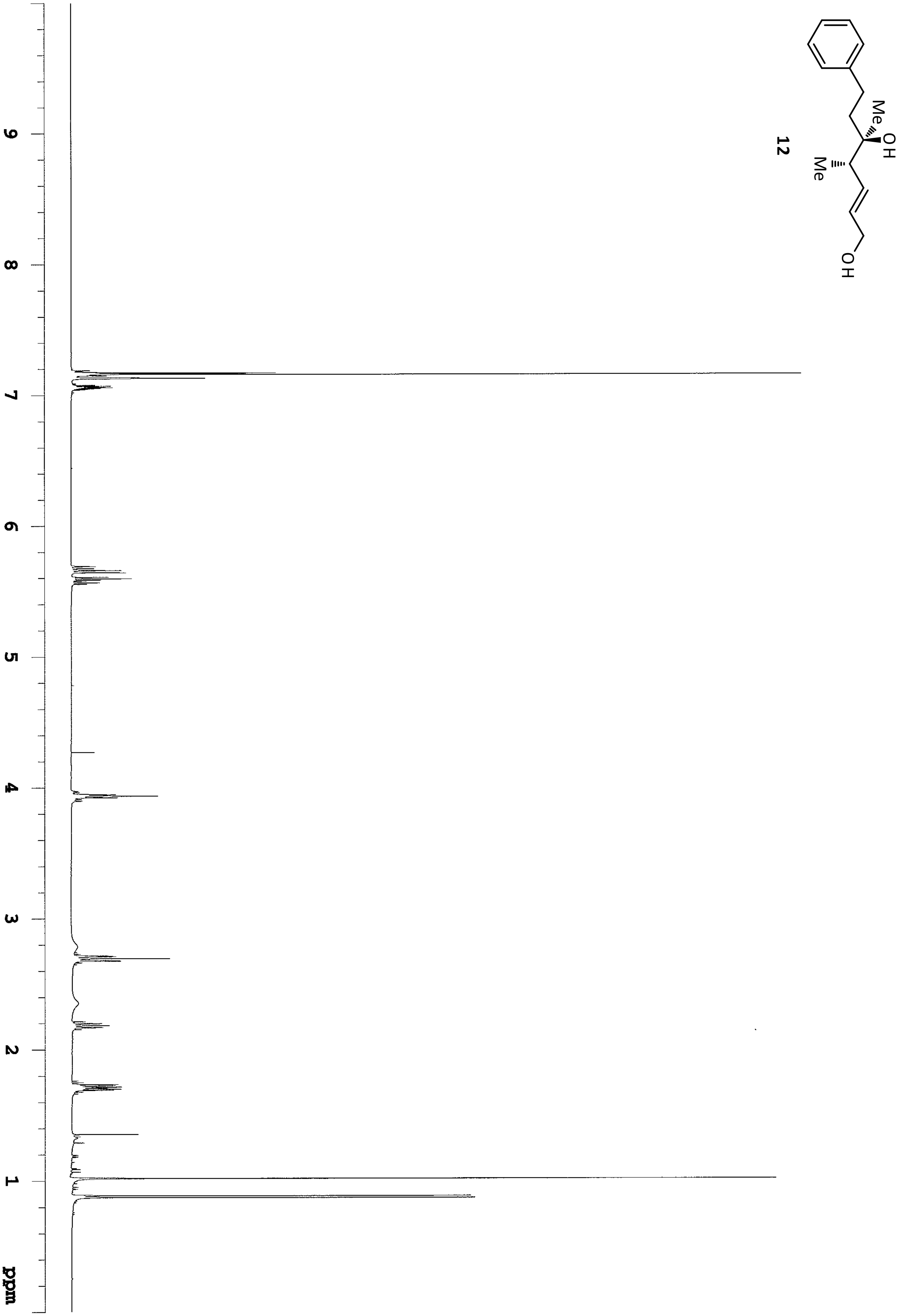

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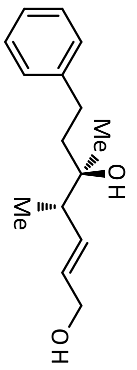

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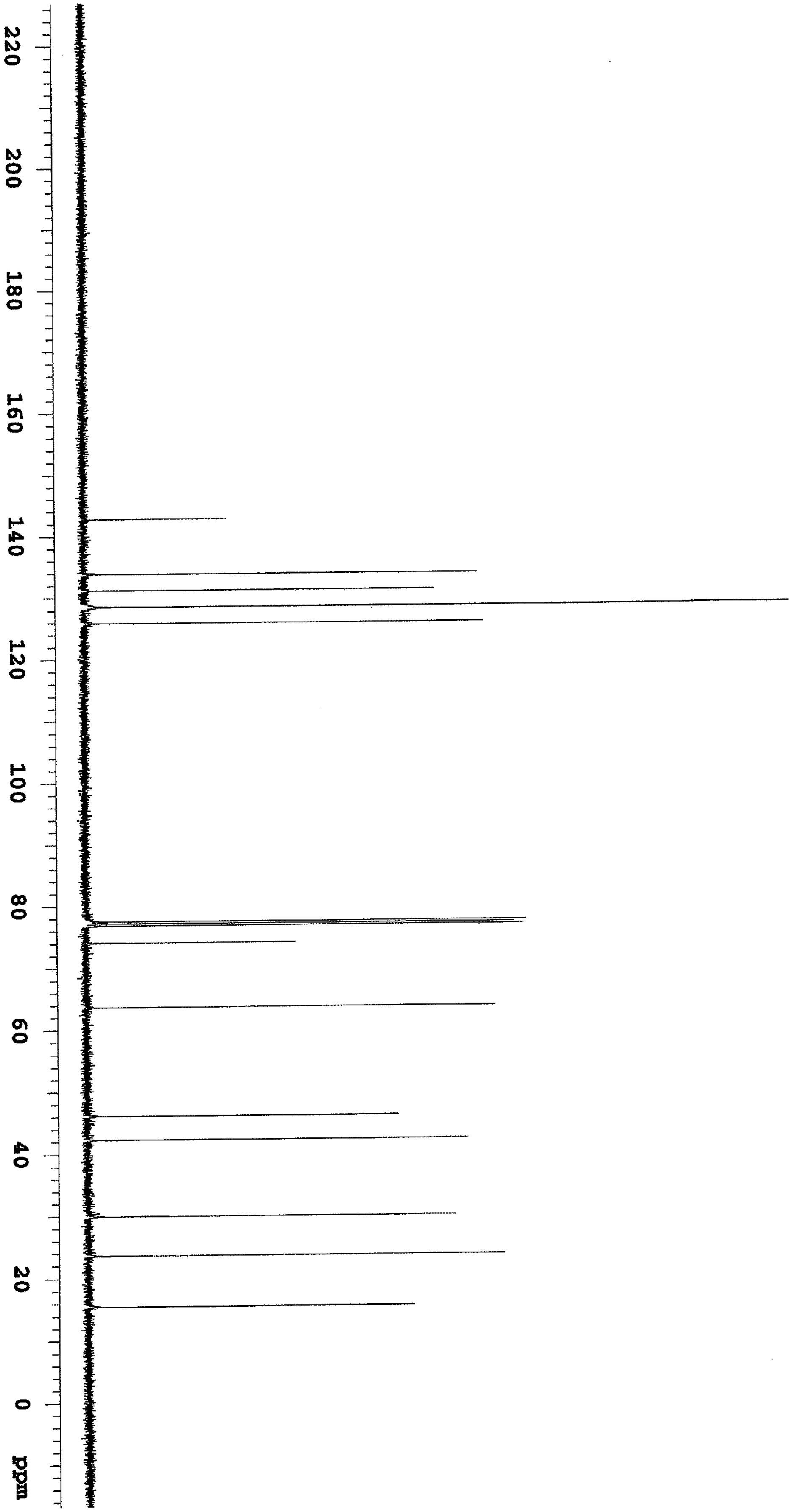

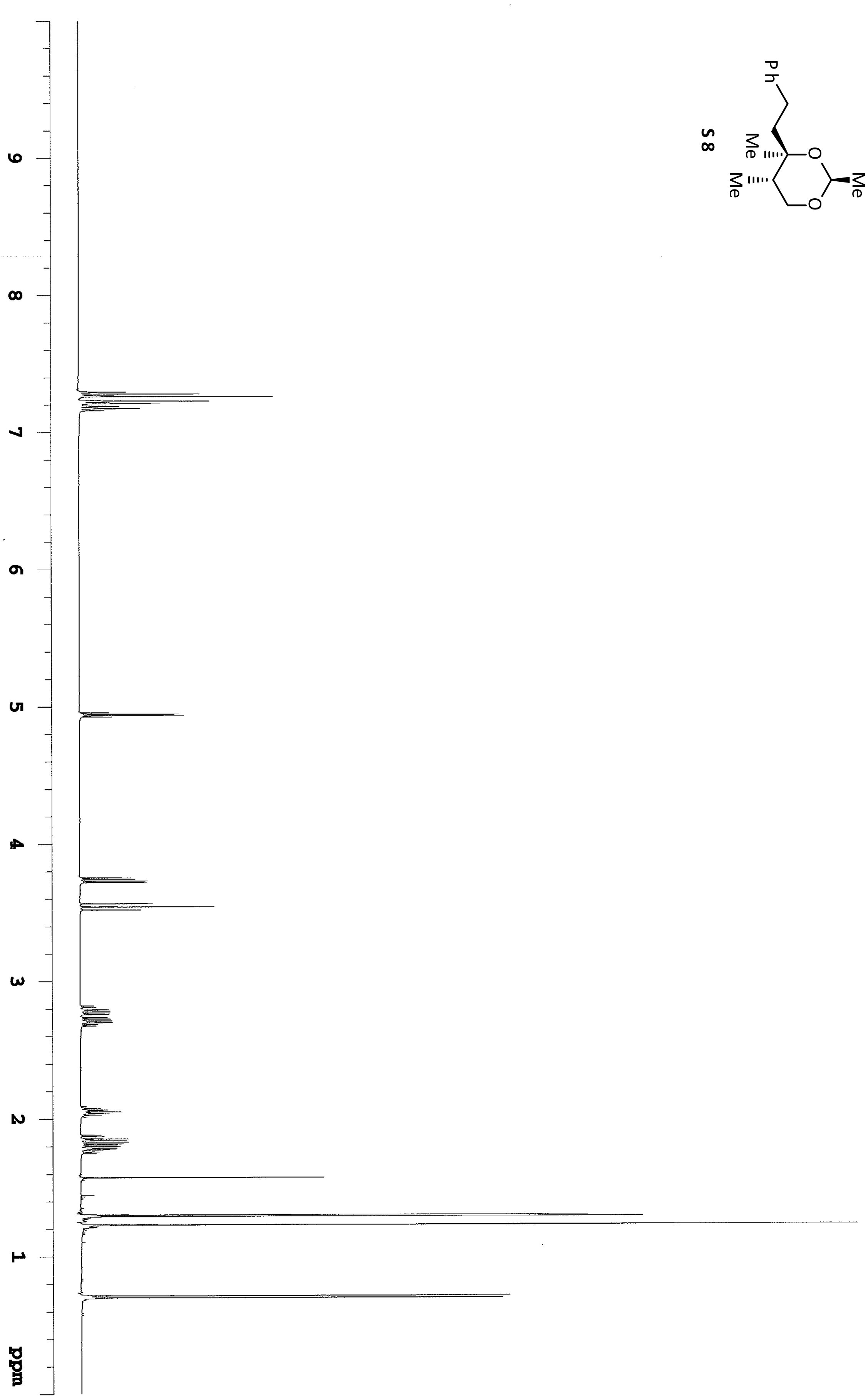

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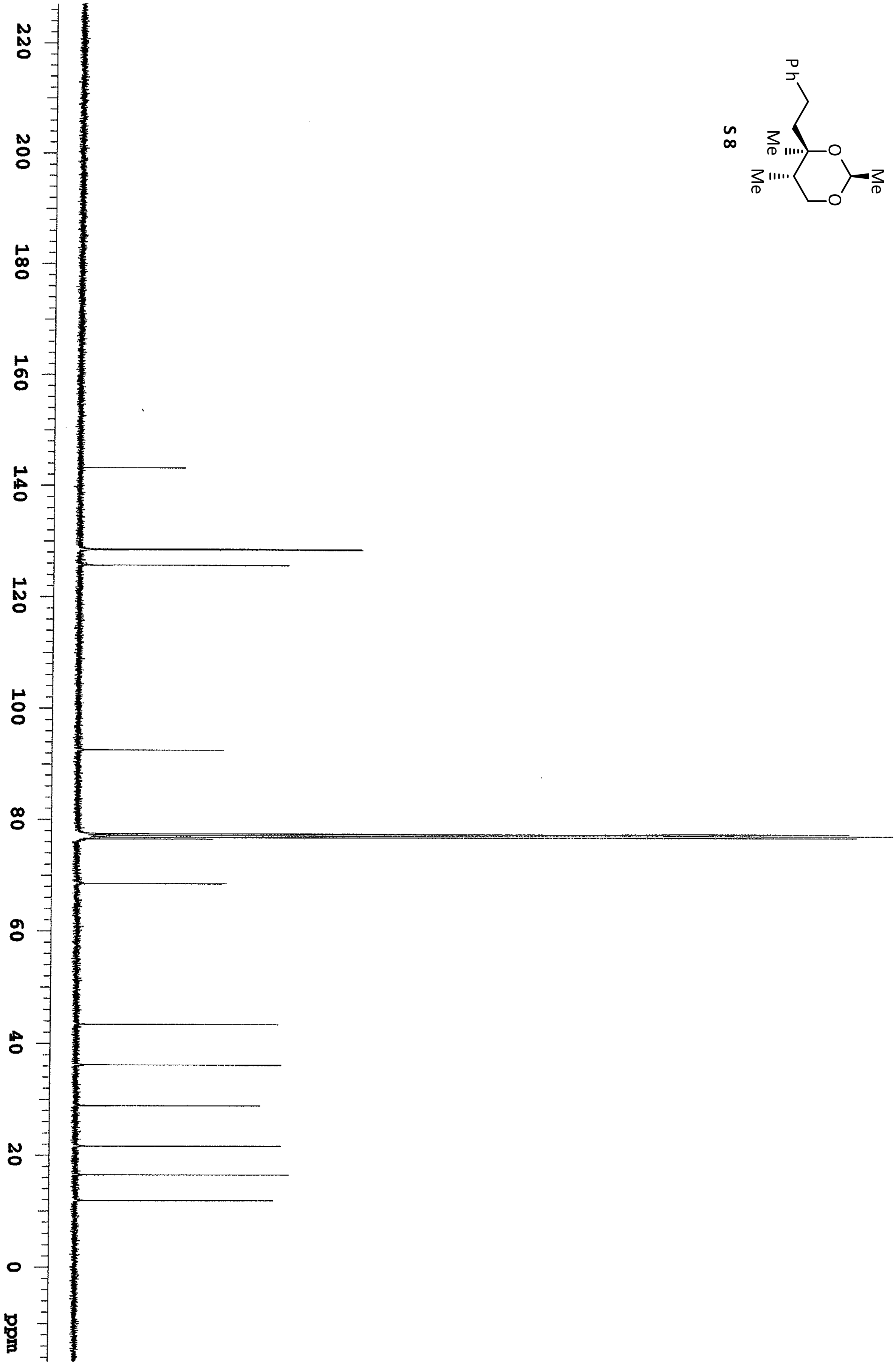
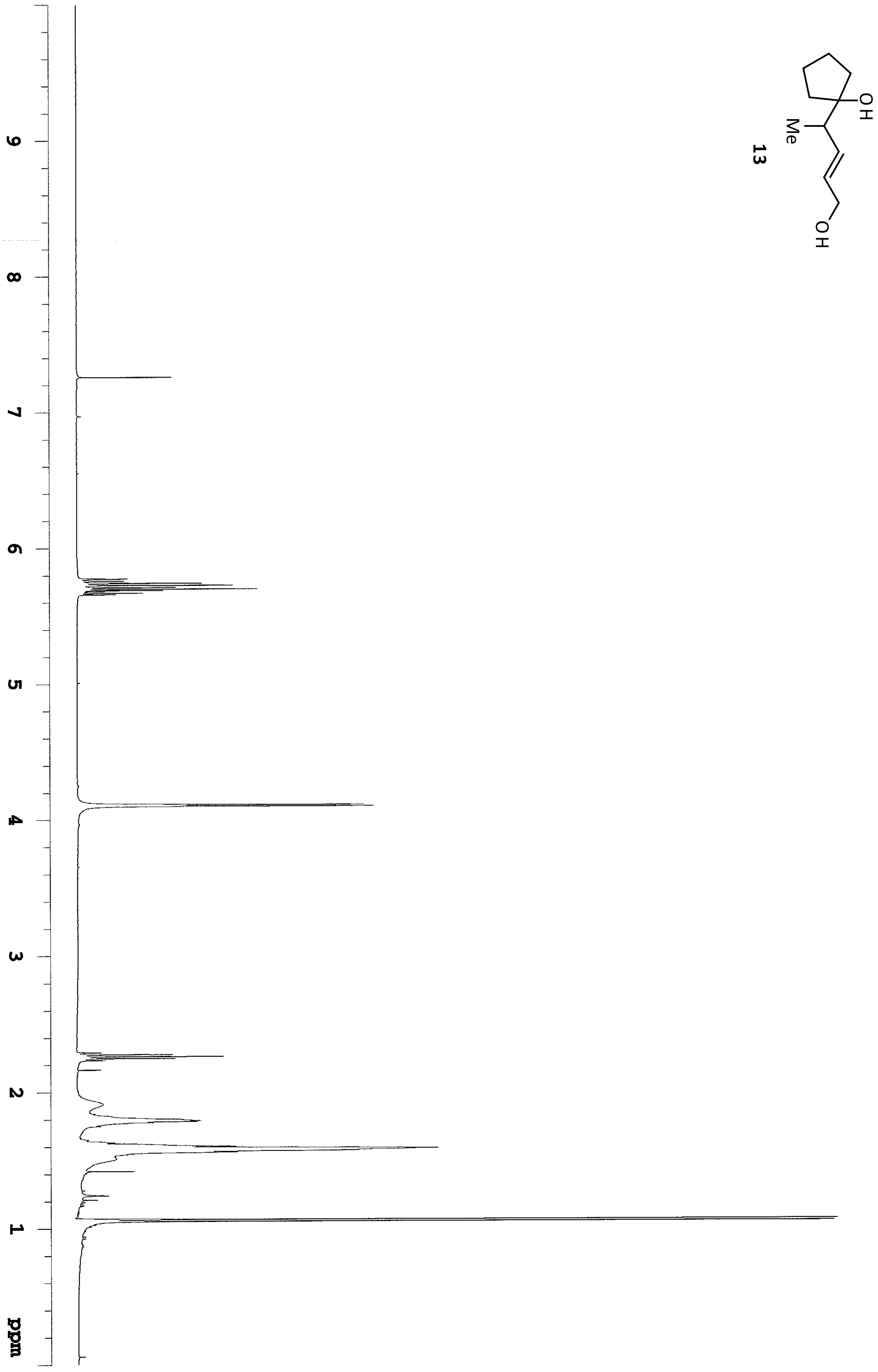
**S8**





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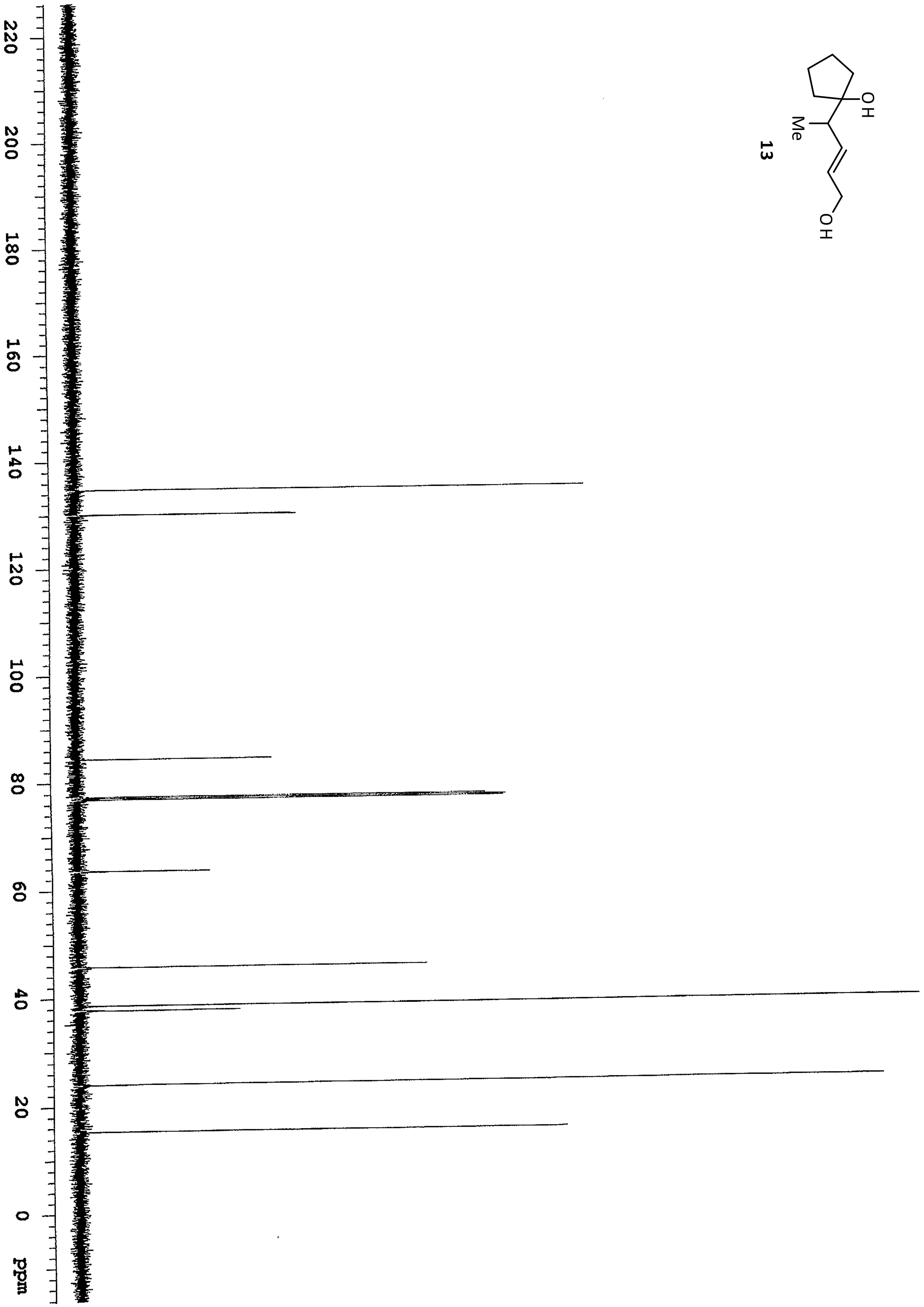

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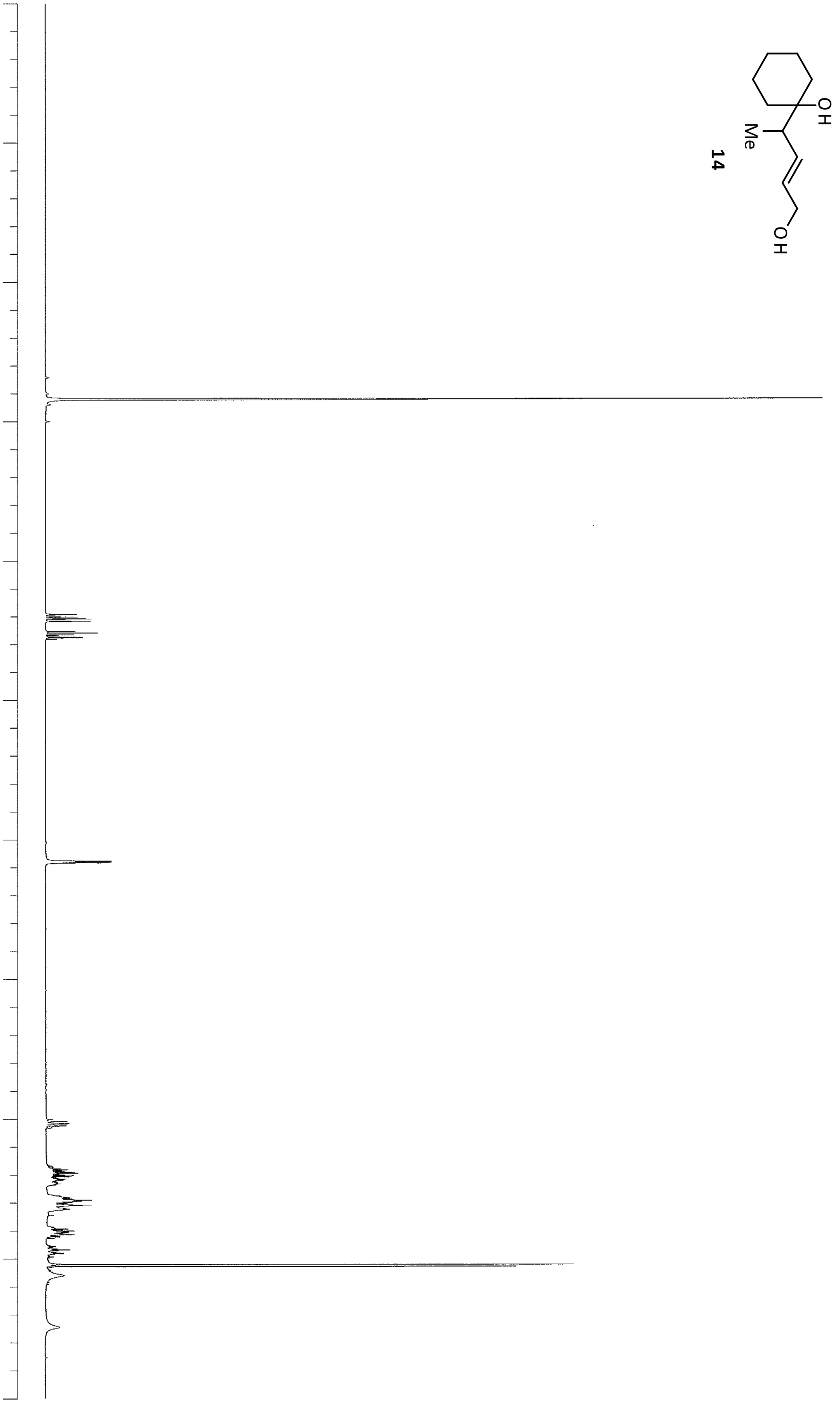

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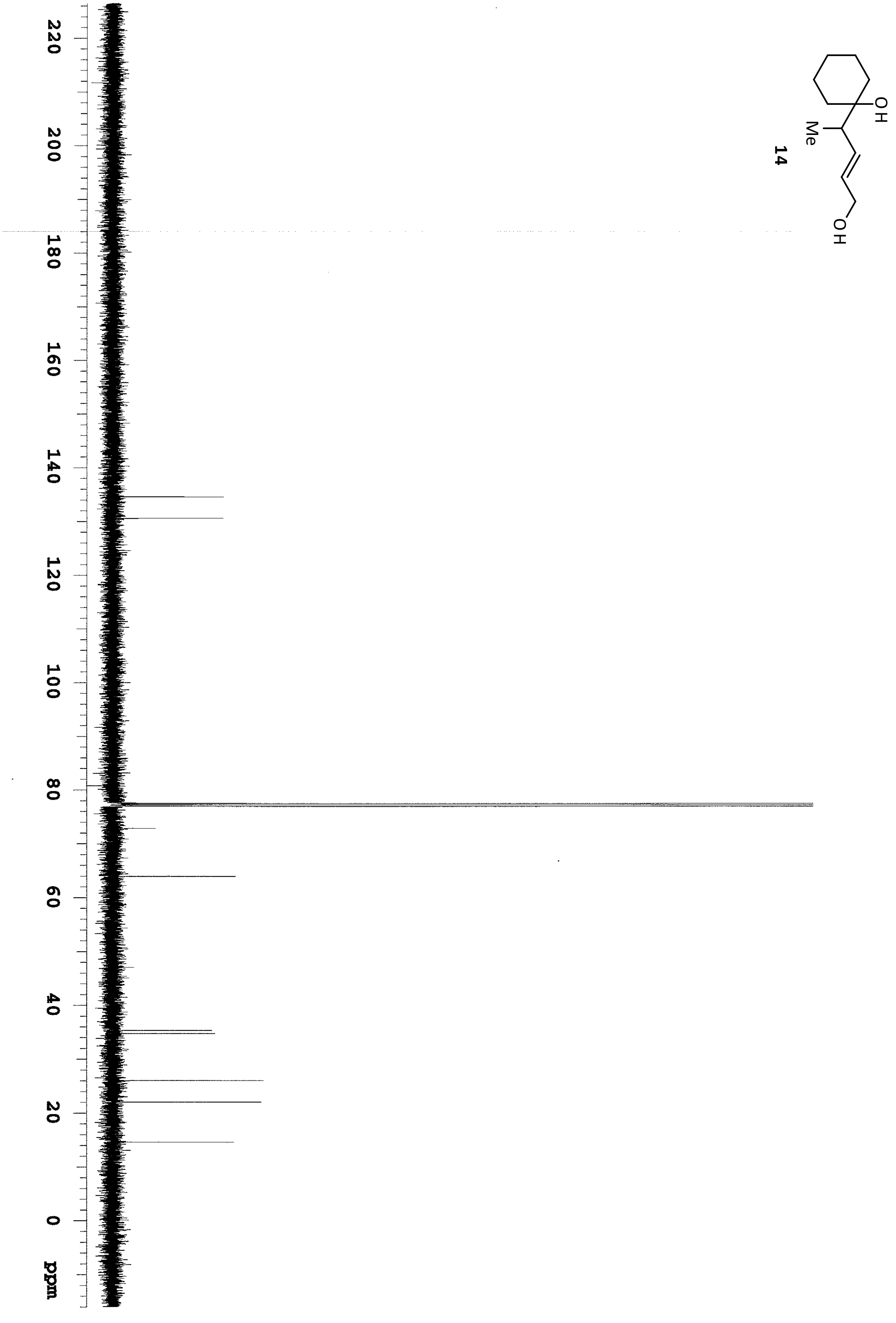

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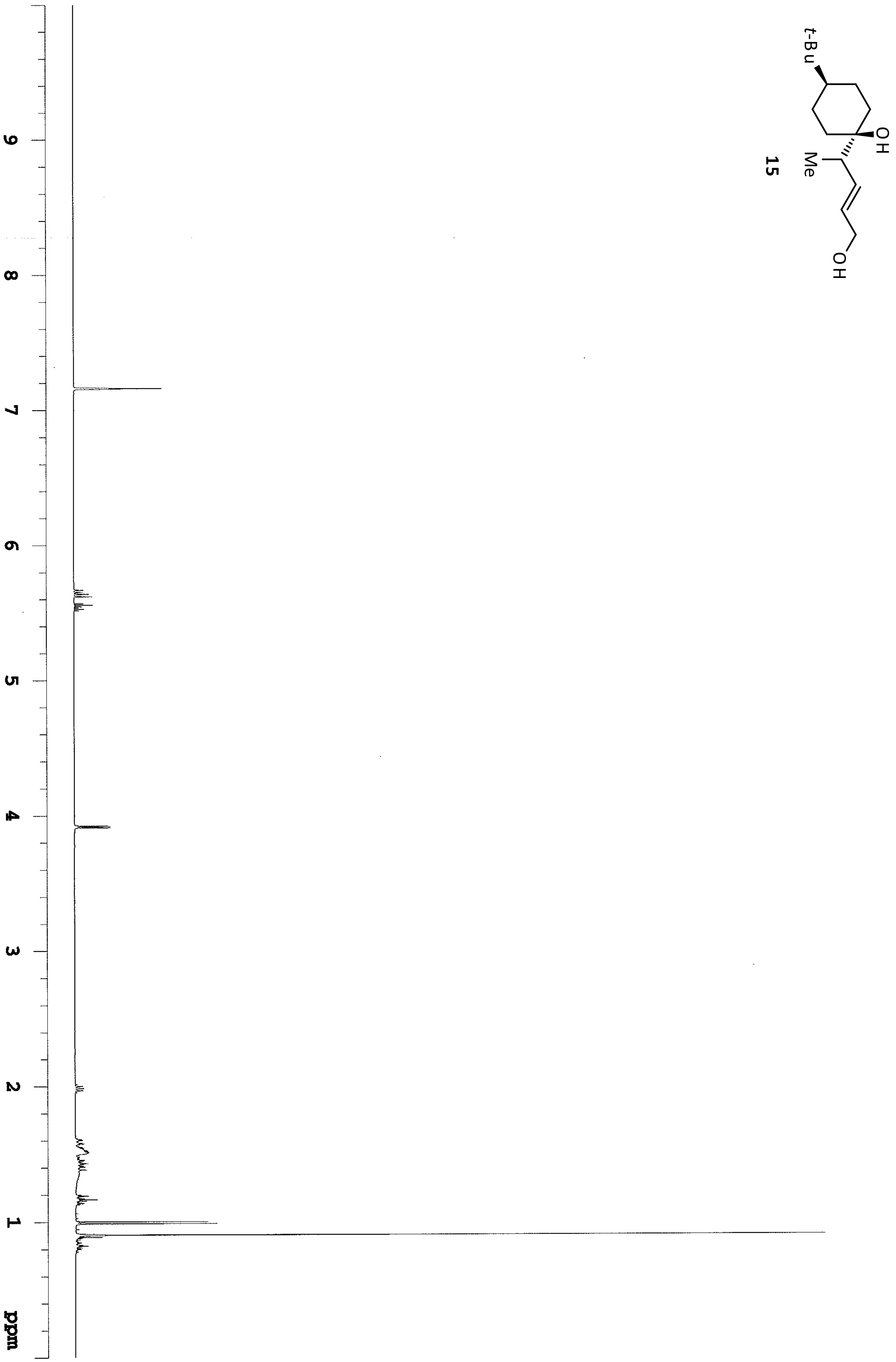

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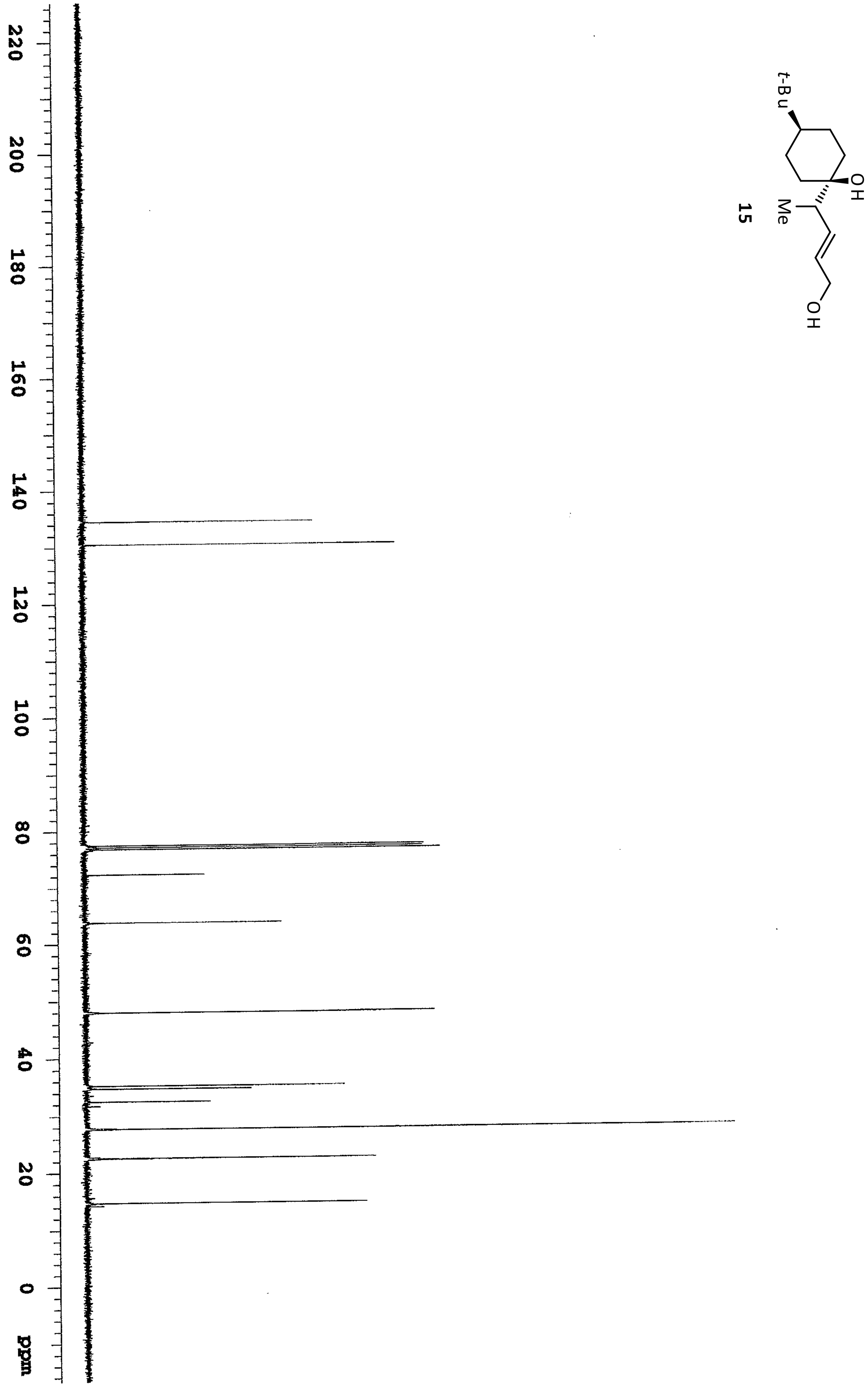
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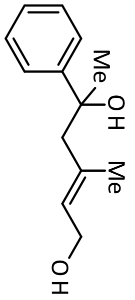

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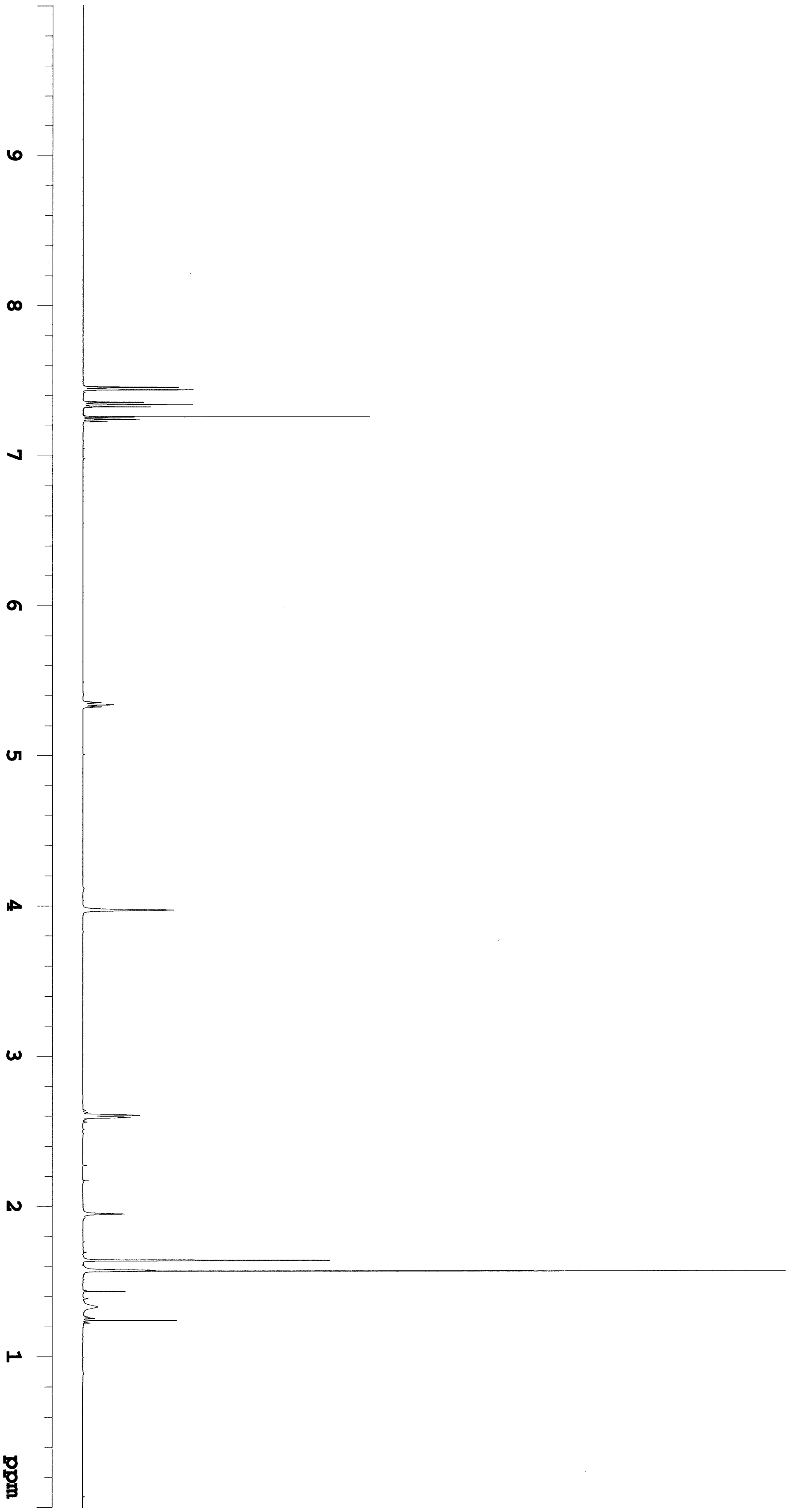

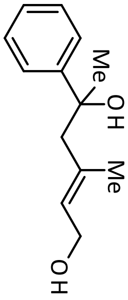

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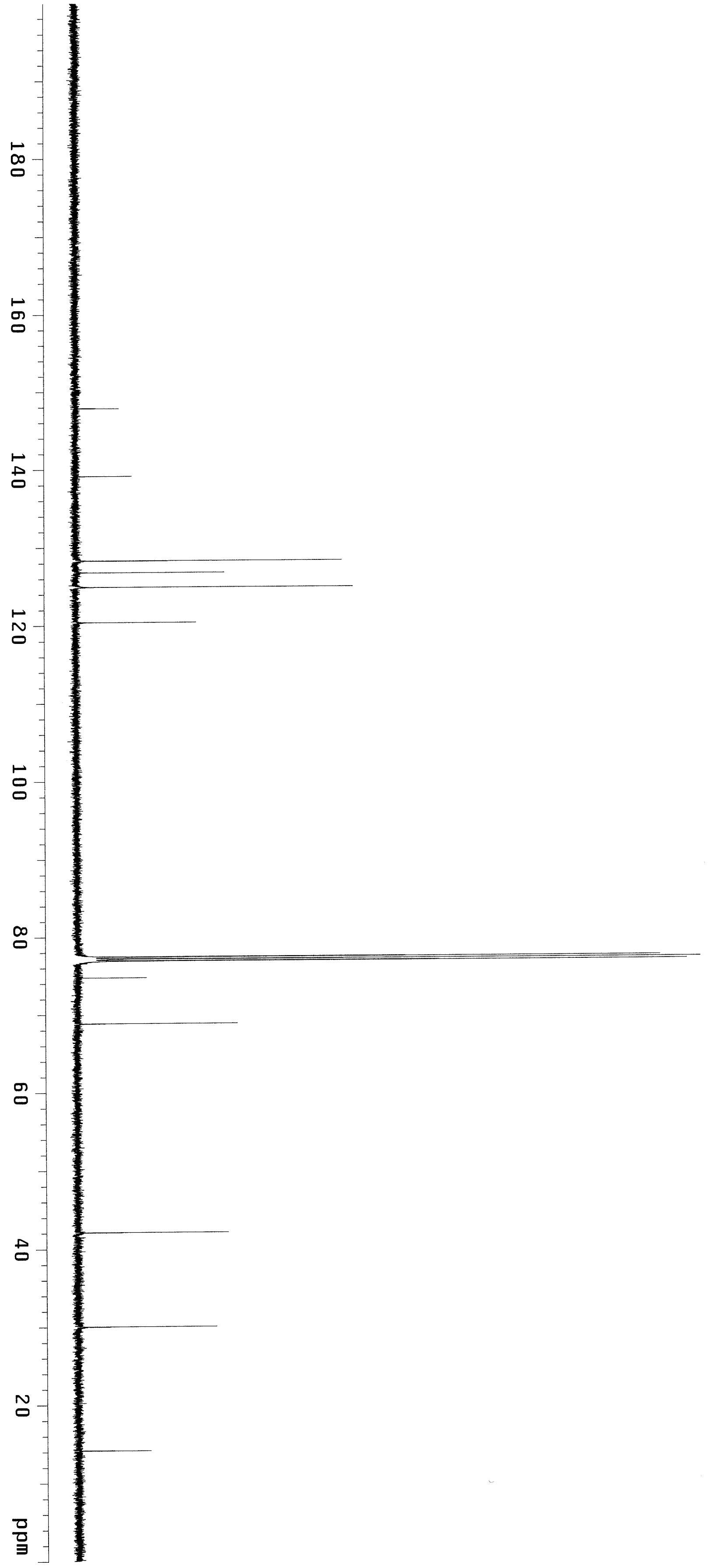

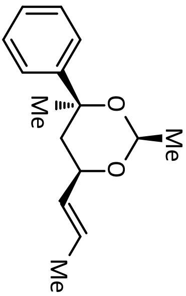

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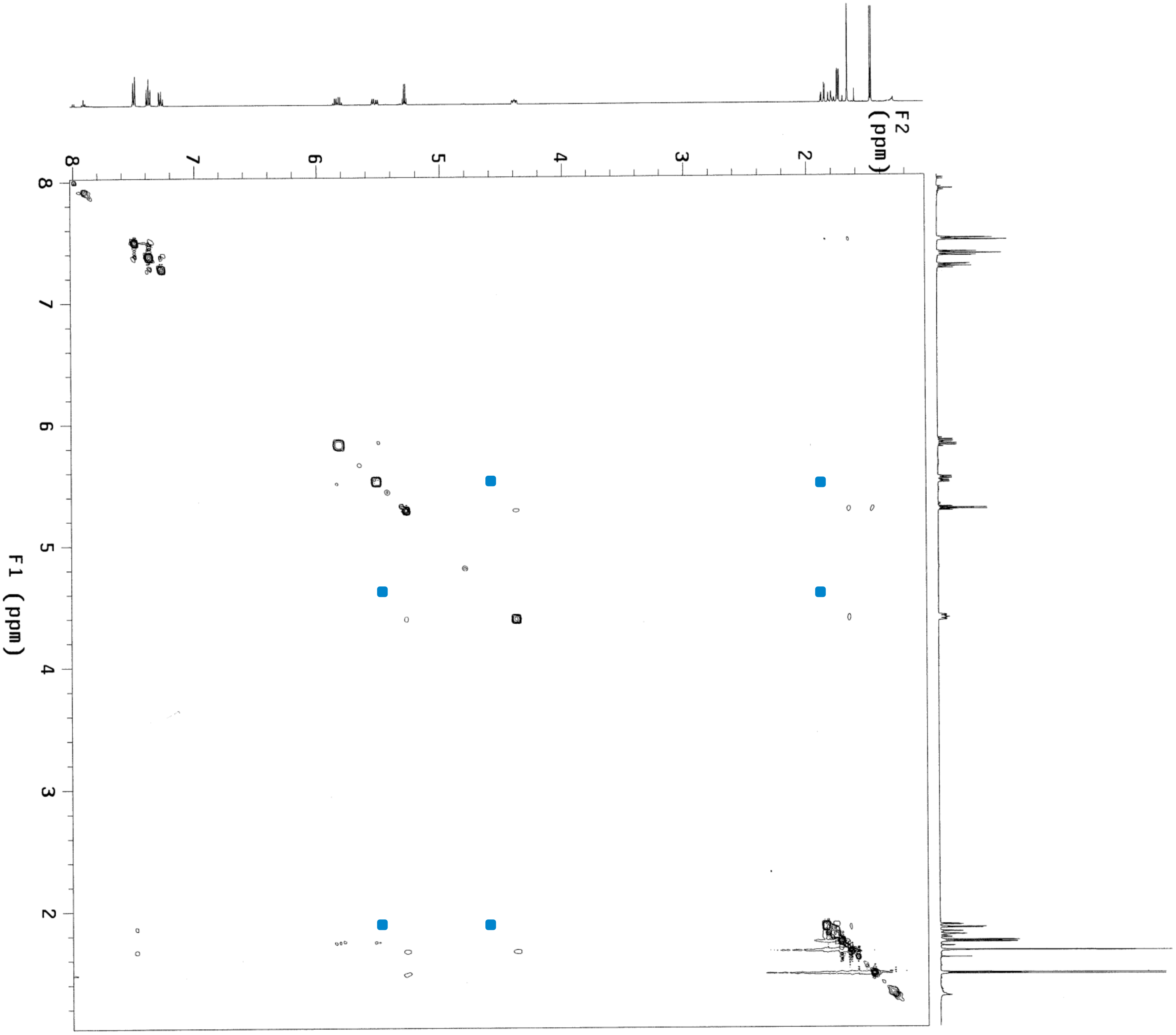

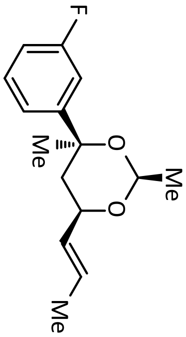

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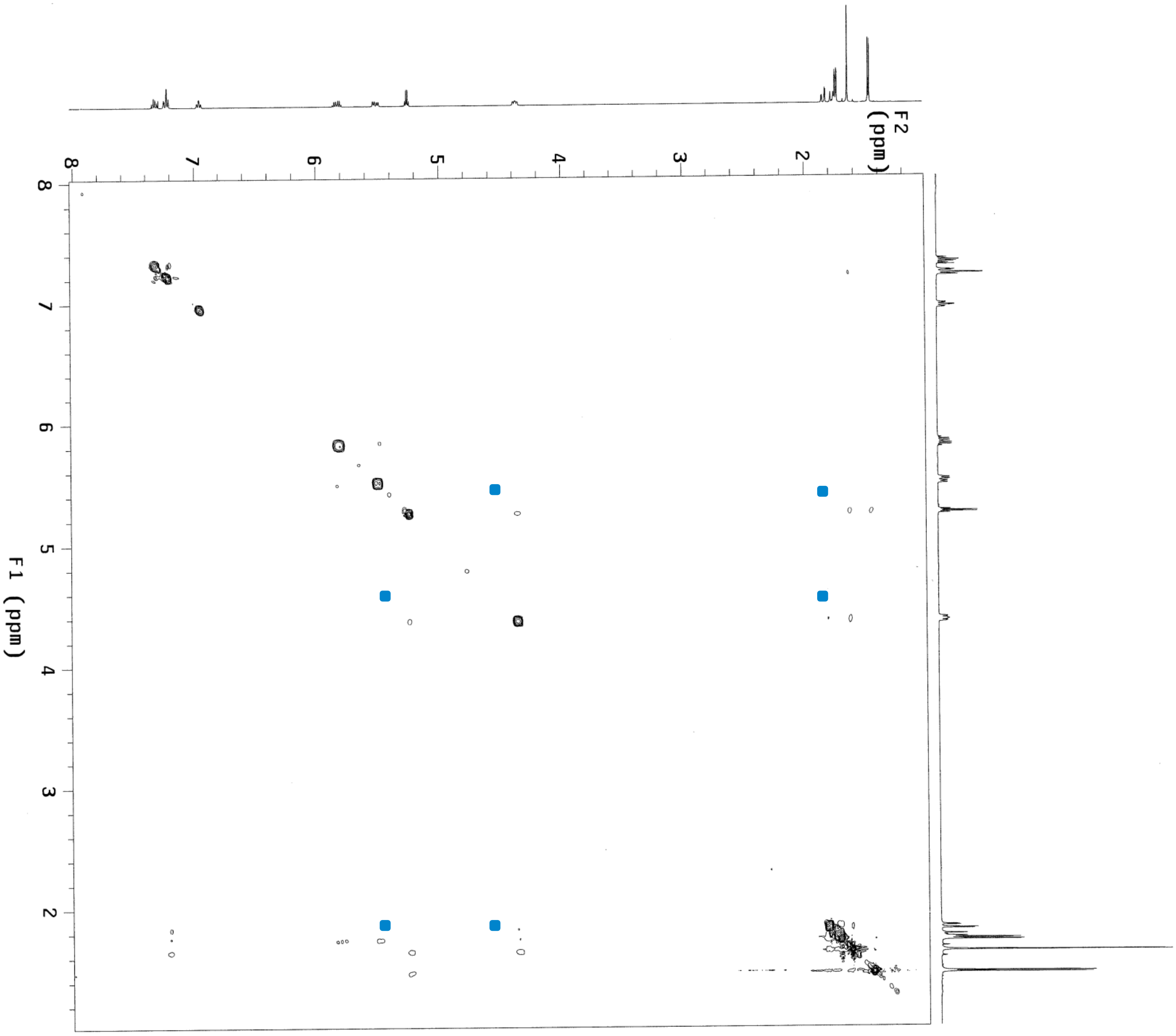

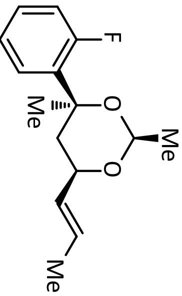

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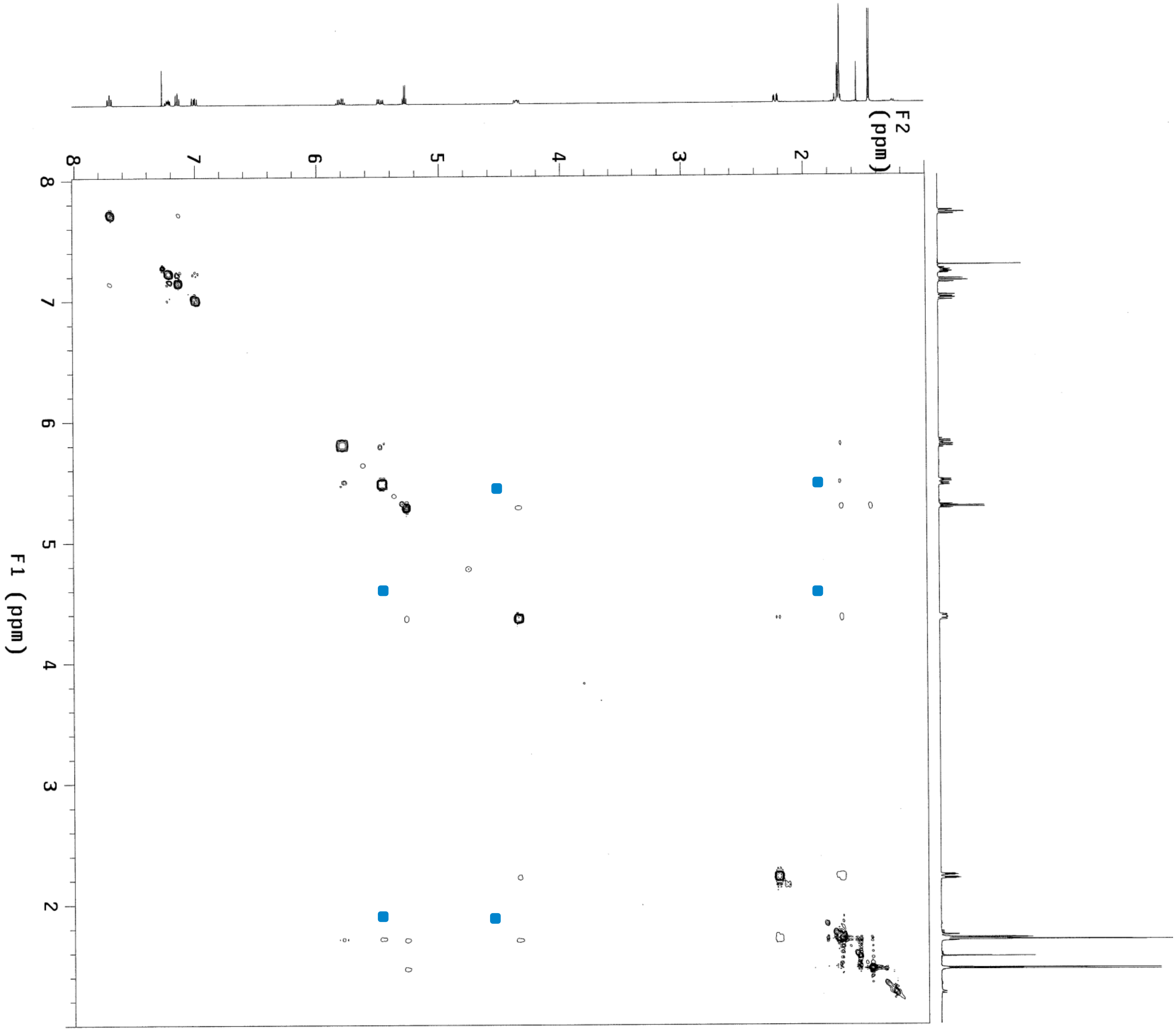

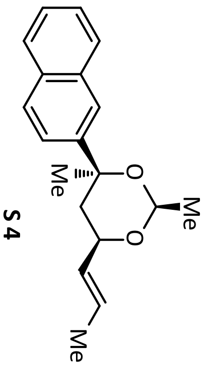

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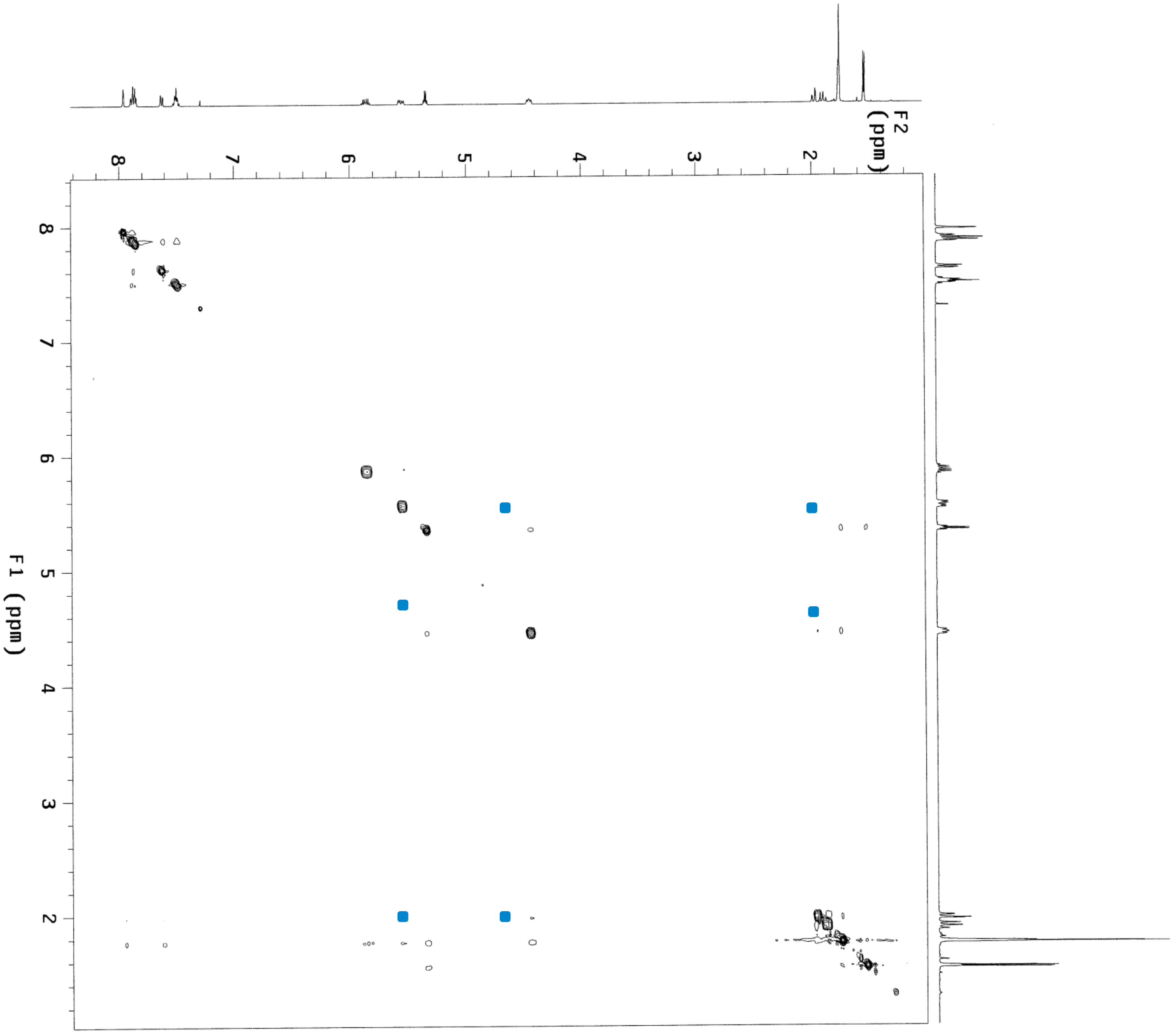

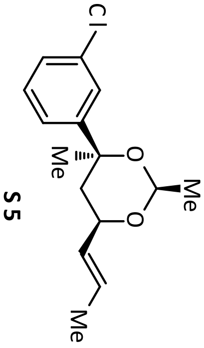

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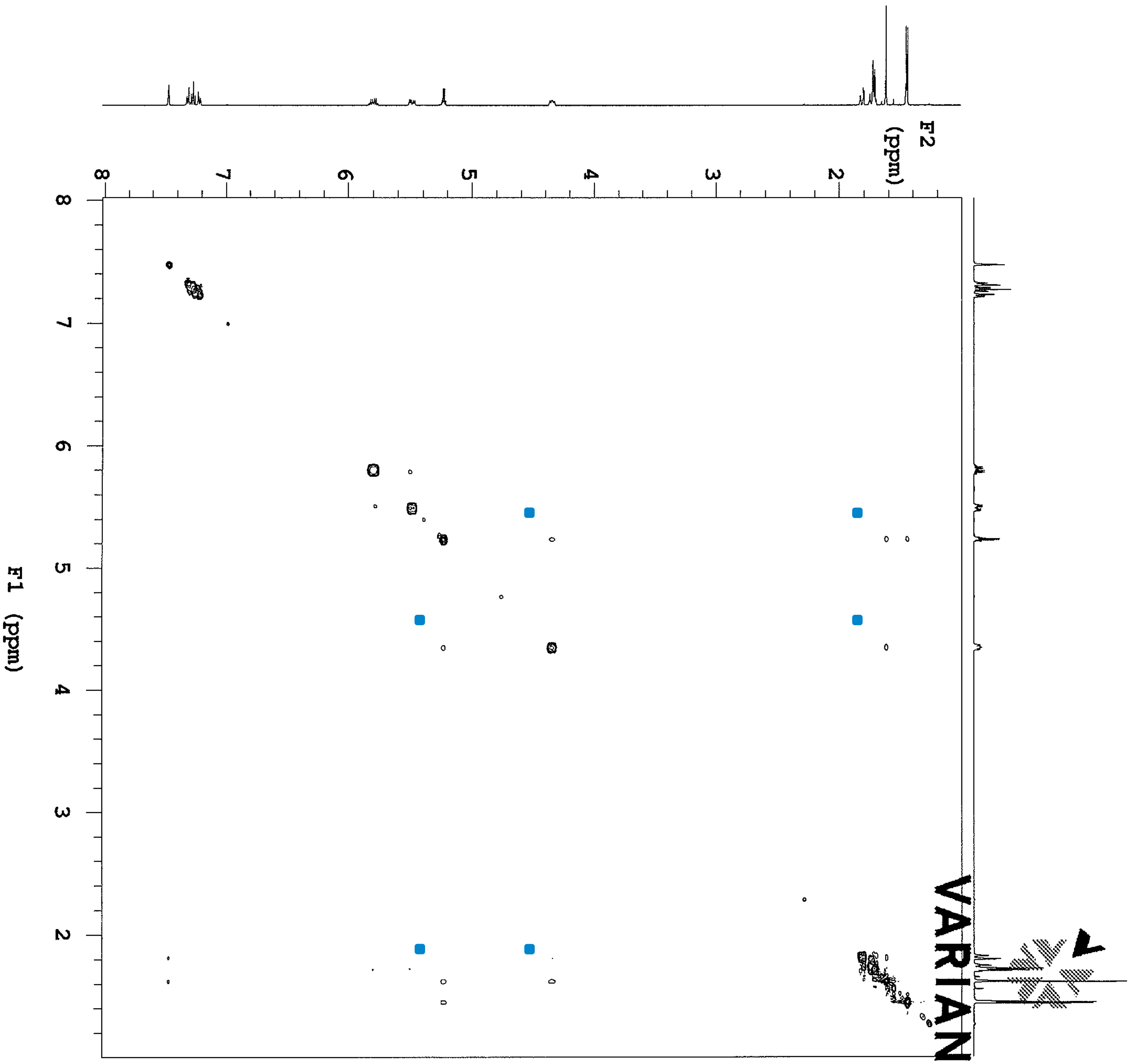

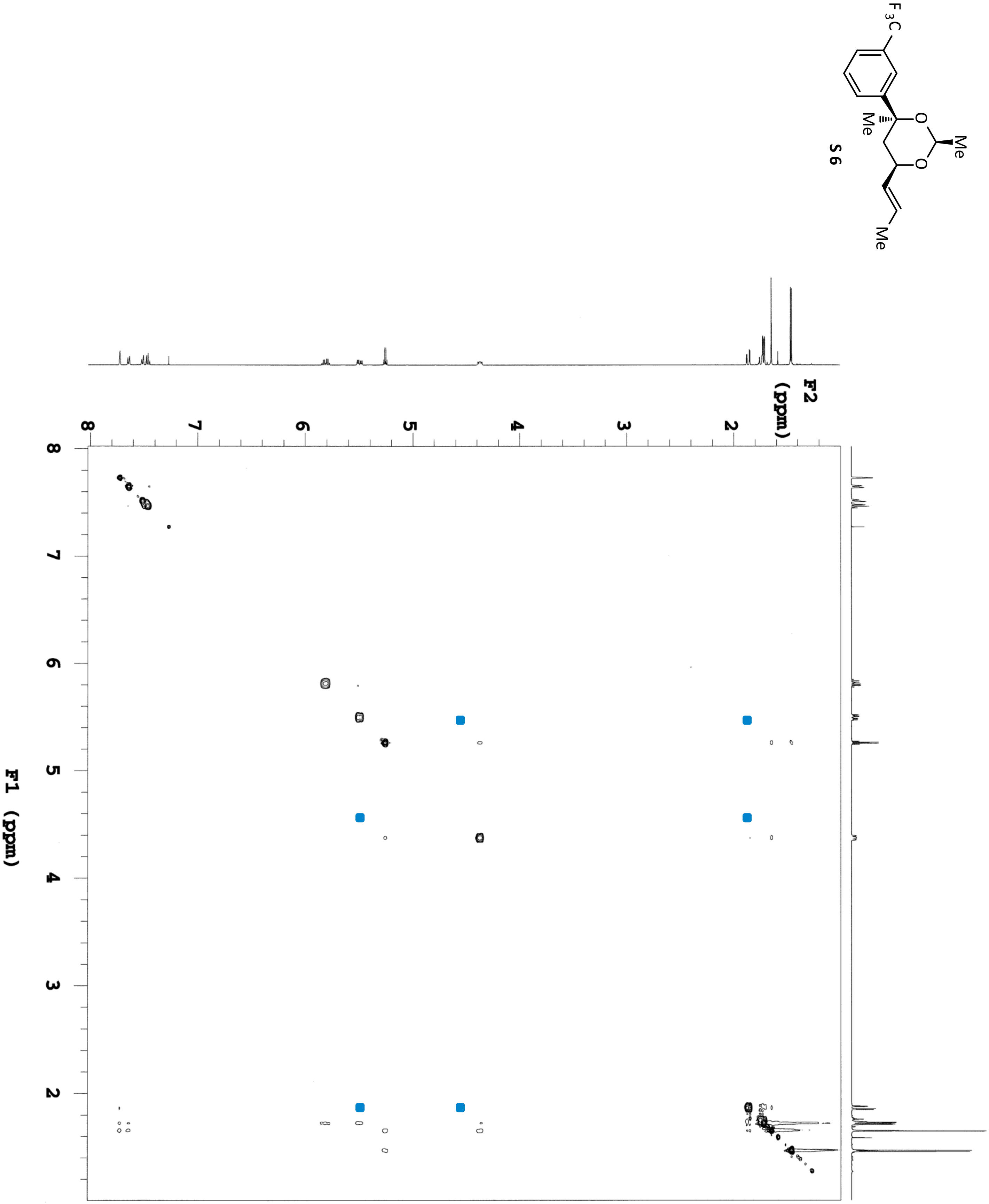

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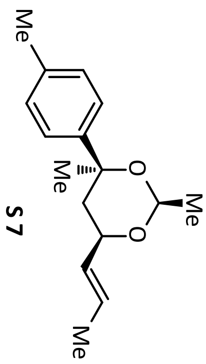
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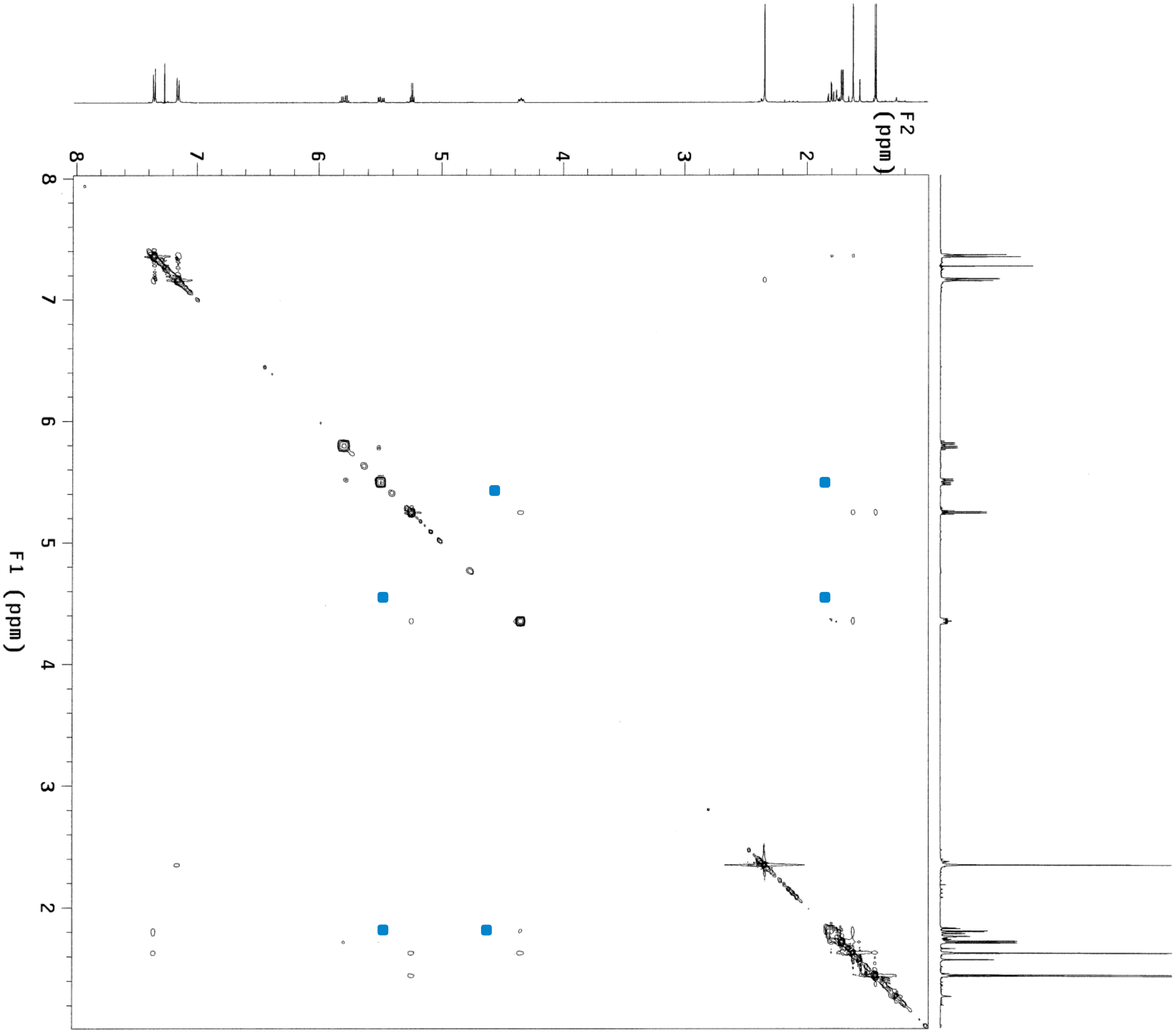
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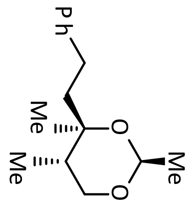

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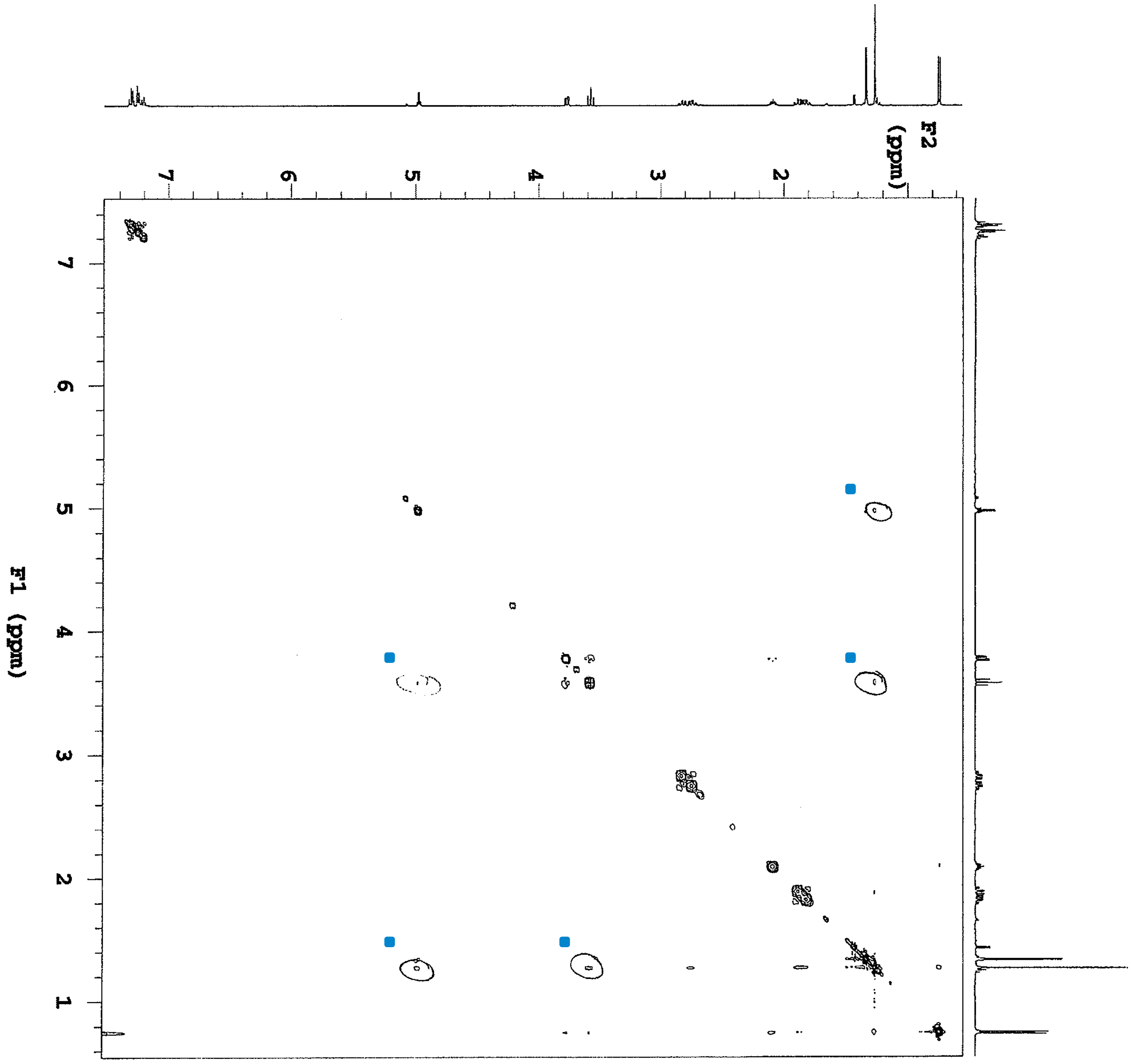

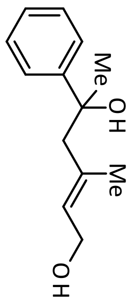

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