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Experimental Section

General. All reactions were performed in flame dried glassware under an argon atmosphere with magnetic stirring. Reactions were monitored by gas chromatography (GLC) on an Alltech Econocap column (15 m, 0.54 mm id) with temperature programming and by thin layer chromatography (TLC). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 250 or 300 MHz spectrometer and referenced to an internal protic standard. ^{51}V NMR spectra were recorded on a Bruker 250 MHz spectrometer and referenced to $^{51}VOCl_3$. Coupling constants (J) are reported in Hz. Infrared spectra were recorded on a Bruker ISF 25 spectrometer. Flash column chromatography was performed with silica gel 60. Solvents for chromatography and work-up were reagent grade and not distilled.

Chemicals. Copper(I) iodide was purchased from Aldrich chemical company and purified according to the published procedure.[1] Hexane was distilled from calcium hydride immediately before use. Tetrahydrofuran (THF) was distilled from sodium-benzophenone ketyl immediately before use. Methylene chloride (CH_2Cl_2) was distilled from P_2O_5 prior to use. Solutions of *n*-butyllithium (*n*-BuLi) in hexanes were titrated with 2-butanol (2.00 M in ethylbenzene) in ether at 0 °C with 2,2-dipyridal as an indicator. Tetramethylethylenediamine (TMEDA) was distilled from and stored over KOH. Chlorotrimethylsilane (TMSCl) was distilled from and stored over sodium. 2-(trimethylsilylmethyl)-2-methylselenoprop-1-ene, (**3**), was prepared according to the published procedure.[2] All starting materials were distilled or recrystallized prior to use.

Preparation of Dichloro(2,2,2-trifluoroethoxy)oxovanadium (V) (1a):[3] A 250 mL round-bottomed flask equipped with a reflux condenser, magnetic stirring bar and septum was flame dried under a stream of argon. Hexane (120 mL) was added followed by trichlorooxovanadium (V) (17.3 g, 9.4 ml, 0.1 mol). The solution was stirred at room temperature while 2,2,2-trifluoroethanol (7.3 mL, 0.1 mol) was added dropwise via syringe with a constant flow of argon to remove HCl evolved from the reaction. Upon completion of the addition, the mixture was heated to reflux for 30 min and

was then allowed to cool to room temperature. The reflux condenser was then quickly replaced with a distillation head, which had previously been flame dried under a stream of argon, and the solvent was removed at atmospheric pressure. The product was distilled at atmospheric pressure to give dichloro(2,2,2-trifluoroethoxy)oxovanadium (V) (**1a**, (TFEO)VCl_2) as a yellow/orange liquid which was stored under argon (19.4 g, 82%, bp 140 - 145 °C). ^{1}H NMR (C_6D_6, 300 MHz) δ 4.4 (br s); ^{13}C NMR (C_6D_6, 300 MHz) δ 121.7 (d, J = 925 Hz), 84.1-83.2 (m); ^{51}V NMR (C_6D_6, 250 MHz) δ -281.6 (s) from $^{51}VOCl_3$.

General Procedure for the Homo-Coupling of Silyl Enol Ethers. Preparation of Diketone 14: A 100 mL round-bottomed flask equipped with a magnetic stirring bar and septum was flame dried under a stream of argon. The flask was charged with CH_2Cl_2 (30 mL), (TFEO)$VOCl_2$ (2.84 g, 12 mmol) and cooled to –78 °C. A solution of silyl enol ether, **11a** (1.020 g, 6 mmol), in CH_2Cl_2 (5 mL) was then added dropwise by syringe over 30 min. The resulting mixture was stirred at –78 °C for 10 min and then poured into a seperatory funnel containing aqueous HCl (1.5 M, 5 mL) and ether (30 mL). The layers were mixed, separated and the aqueous layer was extracted with ether (20 mL). The combined organic layers were washed with saturated aqueous sodium bicarbonate (10 mL), brine (10 mL), dried ($MgSO_4$) and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (10% Et_2O/Hexanes for elution) to give a diastereomeric mixture of the 1,4-diketone **14** as a white solid (1.083 g, 93%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.89-2.81 (m, 1H), 2.63-2.57 (m, 1H), 2.42-2.32 (m, 3H), 2.29-2.18 (m, 1H), 2.09-1.93 (m, 3H), 1.91-1.82 (m, 3H), 1.75-1.50 (m, 5H), 1.34-1.20 (m, 1H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 211.6 (C), 210.6 (C), 50.2 (CH), 48.9 (CH), 42.2 (CH_2), 41.7 (CH_2), 30.0 (CH_2), 29.0 (CH_2), 28.0 (CH_2), 26.4 (CH_2), 25.4 (CH_2), 24.9 (CH_2); GCMS, e/m (%) M^+ 194 (13), 148 (11), 137 (22), 109 (12), 98 (100).[4]

Procedure for the Cross-Coupling of Silyl Enol Ethers. Preparation of Diketone 13b: A 100 mL round-bottomed flask equipped with a magnetic stirring bar and septum was flame dried under a stream of argon. The flask was charged with CH_2Cl_2 (30 mL), (TFEO)$VOCl_2$ (2.84 g, 12.0 mmol) and cooled to –78 °C. Silyl enol ether **11b** (0.94 g, 6.0 mmol) and **12** (1.03 g, 6.0 mmol) were combined, diluted with CH_2Cl_2 (10 mL) and added dropwise via syringe over 30 min. The resulting mixture was stirred at –78 °C for 10 min and then poured into a seperatory funnel containing a solution of aqueous HCl (10 mL, 1.5 M) and ether (20 mL). The layers were mixed, separated and the aqueous layer was extracted with ether (20 mL). The combined organic layers were washed with saturated aqueous sodium bicarbonate (10 mL), brine (10 mL), dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (10% Et_2O/Hexanes for elution) to give the 1,4 diketone, **13b**, as a colorless oil (819 mg, 75%). ^1H NMR (C_6D_6, 300 MHz) δ 2.73 (d, 1H, J = 14.4 Hz), 2.34 (dd, 1H, J = 7.5, 14.7 Hz), 2.32-2.25 (m, 1H), 1.99-1.86 (m, 3H), 1.57-1.48 (m, 1H), 1.32-1.11 (m, 2H), 0.95 (s, 9H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 212.5 (C), 45.0 (CH), 43.8 (CH), 37.4 (CH_2), 36.9 (CH_2), 29.6 (CH_2), 26.5 (CH_3), 20.9 (CH_2); GCMS, m/e (%) M^+ 182 (6), 149 (7), 125 (100), 97 (40), 69 (47).[4]

General Procedure for Conjugate Additions. Preparation of 1-(Trimethylsilyloxy)-3-(2-(trimethylsilylmethyl)prop-1-enyl)cyclopent-1-ene (5a): A 100 mL round-bottomed flask equipped with a magnetic stirring bar and septum was flame dried under a stream of argon. THF (4 mL) was introduced and the flask was cooled to –78 °C. *n*-BuLi (2.45 M, 2.45 mL, 6.0 mmol) was then added followed by the dropwise addition of 2-(trimethylsilylmethyl)-2-methylselenoprop-1-ene, (**3**) (1.33 g, 1.26 mL, 6.0 mmol) via syringe. The resulting solution was stirred at –78 °C for 30 min. A second 50 mL round-bottomed flask equipped with a magnetic stirring bar and septum was flame dried under a stream of argon and CuI (1.143 g, 6.0 mmol) was then added. The flask was purged with argon and TMEDA (2.09 g, 2.71 mL, 18.0 mmol)

was added by syringe followed by THF (25 mL). The resulting suspension was stirred at room temperature until homogeneous. The solution containing the CuI·TMEDA complex was then transferred via cannula, with THF wash (2.5 mL), into the first flask containing the allyllithium solution. The reaction mixture was stirred at –78 °C for 6 min, placed in an ice-water bath for 6 min and recooled to –78 °C. After stirring at –78 °C for 6 min, TMSCl (1.64 g, 1.91 mL, 15 mmol) was added in one portion via syringe followed by the immediate addition of cyclopent-2-en-1-one (0.492 g, 0.502 mL, 6.0 mmol) via syringe. The reaction mixture was stirred for 30 min at –78 °C and poured into a seperatory funnel containing an aqueous solution of HCl (30 mL, 0.1 M) and pentane (25 mL). The layers were mixed, separated and the aqueous layer was extracted with pentane (2 x 20 mL). The combined organic extracts were washed with saturated aqueous sodium bicarbonate (15 mL), dried (Na_2SO_4) and filtered through a pad of celite. The solvent was removed in vacuo and the residue was added to DMSO (5 mL) to complex copper salts. The DMSO mixture was extracted with pentane (3 x 25 mL) and the combined organic phases were washed with saturated aqueous sodium bicarbonate (20 mL), dried (Na_2SO_4), filtered and concentrated in vacuo. The crude product was then placed under high vacuum (1 - 0.5 mm Hg) for 30 min (to remove the butyl methyl selenide byproduct) to afford the crude silyl enol ether, **5a**, as a colorless oil in a high state of purity (>90% by NMR). The silyl enol ether was used immediately in the next reaction.

General Procedure for Oxovanadium (V) Induced Cyclizations; Preparation of *cis*-Hexahydro-5-methylene-1(2*H*)-pentalenone (6a): A 100 mL round bottomed flask equipped with a magnetic stirring bar and septum was flame dried under a stream of argon, charged with CH_2Cl_2 (40 mL), $(TFEO)VOCl_2$ (2.84 g, 12.0 mmol) and cooled to –78 °C. The silyl enol ether, **5a**, was diluted in CH_2Cl_2 (5 mL) and added to the reaction vessel via syringe pump over 30 min. The reaction mixture was stirred another 10 min. at –78 °C and poured into a seperatory funnel containing an aqueous solution of HCl (10 mL, 1.5 M) and ether (30 mL). The layers were mixed,

separated and the aqueous layer extracted with ether (2 x 20 mL). The combined organic extracts were washed with saturated aqueous sodium bicarbonate (10 mL), brine (10 mL), dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (2.5% Et_2O/pentane with 0.01% Et_3N for elution) to give the pentalenone, **6a**, as a colorless oil (669 mg, 82% from 2-cyclopentenone). Spectral data were consistent with those reported in the literature.[5] ^1H NMR (C_6D_6, 300 MHz) δ 4.85 (app s, 1H), 4.82 (app s, 1H), 2.57 (d, 1H, J = 18.3 Hz), 2.46-2.36 (m, 1H), 2.27-2.22 (m, 3H), 2.01-1.88 (m, 2H), 1.84-1.73 (m, 1H), 1.53 (m, 1H), 1.20 (ddd, 1H, J = 15.9, 8.7, 3.9); ^{13}C NMR (C_6D_6, 300 MHz) δ 150.9 (C), 107.0 (CH_2), 51.8 (CH), 40.7 (CH), 39.4 (CH_2), 37.1 (CH_2), 35.3 (CH_2), 26.2 (CH_2).

Preparation of 2-Methyl-1-((trimethylsilyl)oxy)-3-(2-(trimethylsilylmethyl)prop-1-enyl)cyclopent-1-ene (5b), and *cis*-Hexahydro-5-methylene-6a-methyl-1(2*H*)-pentalen-1-one (6b): 2-Methylcyclopent-2-en-1-one (576 mg, 6.0 mmol) was subjected to the experimental protocol described above for conjugate addition and cyclization. The crude cyclization product was purified by flash chromatography on silica gel (2.5% Et_2O/pentane with 0.01% Et_3N for elution) to give the pentalenone, **6b**, as a colorless oil (639 mg, 71%). ^1H NMR (C_6D_6, 300 MHz) δ 4.88 (app s, 1H), 4.84 (app s, 1H), 2.52 (d, 1H, J = 16.8 Hz), 2.47-2.38 (m, 1H), 2.13-1.86 (m, 4H), 1.63-1.51 (m, 1H), 1.36-1.27 (m, 1H), 1.22-1.12 (m, 1H), 1.00 (s, 3H); ^{13}C NMR (C_6D_6, 300 MHz) δ 210.5 (C), 150.4 (C), 107.5 (CH_2), 56.3 (C), 48.1 (CH), 42.7 (CH_2), 38.9 (CH_2), 36.6 (CH_2), 25.2 (CH_2), 21.6 (CH_3); FTIR (neat) 2928, 1739, 1647, 1406, 1065 cm^{-1}; HRMS (EI) calcd. for $C_{10}H_{14}O$ (M^+) 150.1045, found 150.1039.

Preparation of 1-((Trimethylsilyl)oxy)-3-(2-(trimethylsilylmethyl)prop-1-enyl)cyclohex-1-ene (5c), and *cis*-Hexahydro-2-methylene-4*H*-inden-4-one (6c): Cyclohex-2-en-1-one (576 mg, 6.0 mmol) was subjected to the experimental protocol described above for conjugate

addition and cyclization. The crude cyclization product was purified by flash chromatography on silica gel (2.5% Et_2O/pentane with 0.01% Et_3N for elution) to give the indenone, **6c**, as a colorless oil (702 mg, 78%). Spectral data were consistent with those reported in the literature.[5] ^1H NMR (C_6D_6, 300 MHz) δ 4.99 (m, 2H), 2.91 (ddd, 1H, *J* = 6.5, 5.7, 2.1 Hz), 2.46-2.39 (m, 1H), 2.27-2.15 (m, 1H), 2.13-1.88 (m, 5H), 1.47 (ddd, 1H, *J* = 17.7, 9.0, 5.4 Hz), 1.39-1.27 (m, 2H), 1.15 (ddd, 1H, *J* = 16.2, 6.0, 1.8 Hz); ^{13}C NMR (C_6D_6, 300 MHz) δ 209.9 (C), 149.8 (C), 107.2 (CH_2), 52.9 (CH), 42.8 (CH), 39.7 (CH_2), 38.1 (CH_2), 33.4 (CH_2), 26.6 (CH_2), 23.8 (CH_2).

Preparation of 2-Methyl-5-*R*-(2-methylethenyl)-1-((trimethylsilyl)oxy)-3-*S*-(2-(trimethylsilylmethyl)prop-1-enyl)cyclohex-1-ene (5d), and *cis*-Hexahydro-3a-methyl-2-methylene-6-*R*-((2-methyl)prop-1-enyl)-4*H*-inden-4-one (6d): (*l*)-Carvone (876 mg, 6.0 mmol) was subjected to the experimental protocol described above for conjugate addition and cyclization. The crude cyclization product was purified by flash chromatography on silica gel (2.5% Et_2O/pentane with 0.01% Et_3N for elution) to give the indenone, **6d**, as a colorless oil (1.016 g, 83%). ^1H NMR (C_6D_6, 300 MHz) δ 5.04 (m, 1H), 4.98 (m, 1H), 4.78 (m, 1H), 4.71 (m, 1H), 3.50 (d, 1H, *J* = 15 Hz), 2.36-2.32 (m, 3H), 2.18-2.15 (m, 1H), 2.10-2.00 (m, 1H), 1.97-1.91 (m, 1H), 1.90-1.88 (m, 1H), 1.60-1.48 (m, 2H), 1.54 (s, 3H), 1.03 (s, 3H); ^{13}C NMR (C_6D_6, 300 MHz) δ 211.7 (C), 148.9 (C), 147.7 (C), 110.4 (CH_2), 106.9 (CH_2), 54.7 (C), 47.2 (CH), 43.0 (CH_2), 42.4 (CH_2), 41.1 (CH), 37.2 (CH_2), 29.6 (CH_2), 23.6 (CH_3), 20.9 (CH_3); FTIR (neat) 2927, 1709, 1644, 1446, 1377, 1248 cm^{-1}; $[\alpha]^D_{23}$ +92 ($CHCl_3$, c = 2.3); HRMS (EI) calcd. for $C_{14}H_{20}O$ (M^+) 204.1514, found 204.1507.

Preparation of Trimethyl[(4-(2-(trimethylsilylmethyl)prop-1-enyl)-4*H*-1-benzopyran-2-yl)oxy]silane (5e), and *cis*-2, 3, 3a, 9b-Tetrahydro-2-methylene-cyclopenta[c][1]benzopyran-4*H*(1)-one (6e): Coumarin (876 mg, 6.0 mmol) was subjected to the experimental protocol described above for conjugate

addition and cyclization. The crude cyclization product was purified by flash chromatography on silica gel (2.5% Et_2O/pentane with 0.01% Et_3N for elution) to give the benzopyranone, **6e**, as a white solid (876 mg, 73%, mp 51-53 °C, 1:2 Et_2O/pentane). Spectral data were consistent with those reported in the literature.[5] ^1H NMR ($CDCl_3$, 300 MHz) δ 7.22-7.01 (m, 4H), 4.96-4.93 (m, 2H), 3.43 (dt, 1H, J = 9.3, 7.2 Hz), 3.15 (ddd, 1H, J = 7.5, 3.9, 0.9 Hz), 3.04 (br d, 1H, J = 16.5 Hz), 2.82-2.69 (m, 2H), 2.42 (ddd, 1H, J =14.4, 9.6, 1.8 Hz); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 170.2 (C), 151.3 (C), 146.8 (C), 128.9 (CH), 128.6 (CH), 125.0 (CH), 124.0 (C), 117.4 (CH), 108.4 (CH_2), 43.2 (CH), 40.8 (CH), 40.4 (CH_2), 35.5 (CH_2).

References:

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2) Ryter, K.; Livinghouse, T. *J. Org. Chem.* **1997**, *62*, 4842-4844.

3) This procedure was adapted from the preparation of $(EtO)VOCl_2$ by Hirao, T.; Mori, M.; Ohshiro, Y. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2399-2400.

4) The diketones were also prepared by Hirao, T.; Mori, M.; Ohshiro, Y.; Fujii, T. *Tetrahedron Lett.* **1992**, *33(39)*, 5823-5826.

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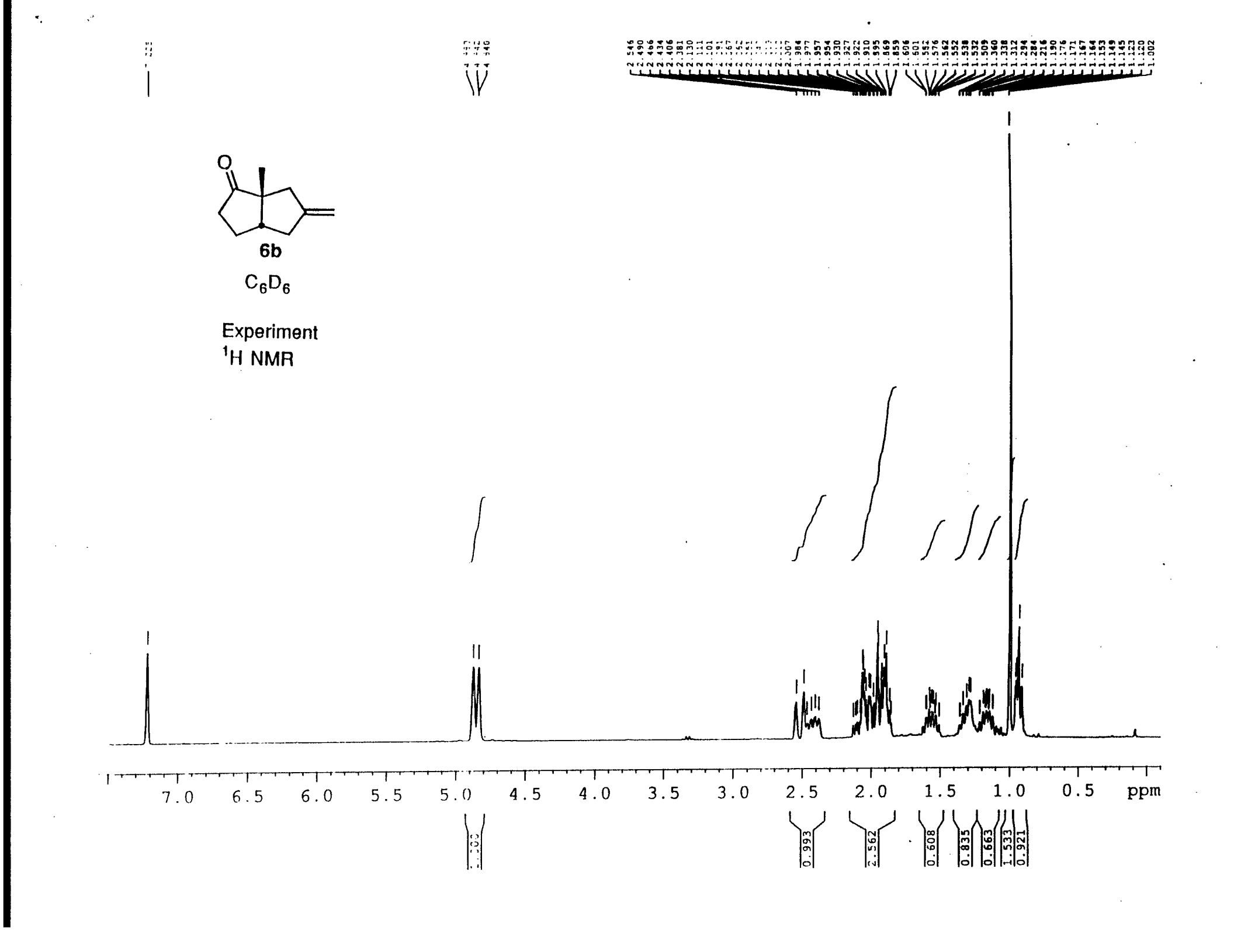
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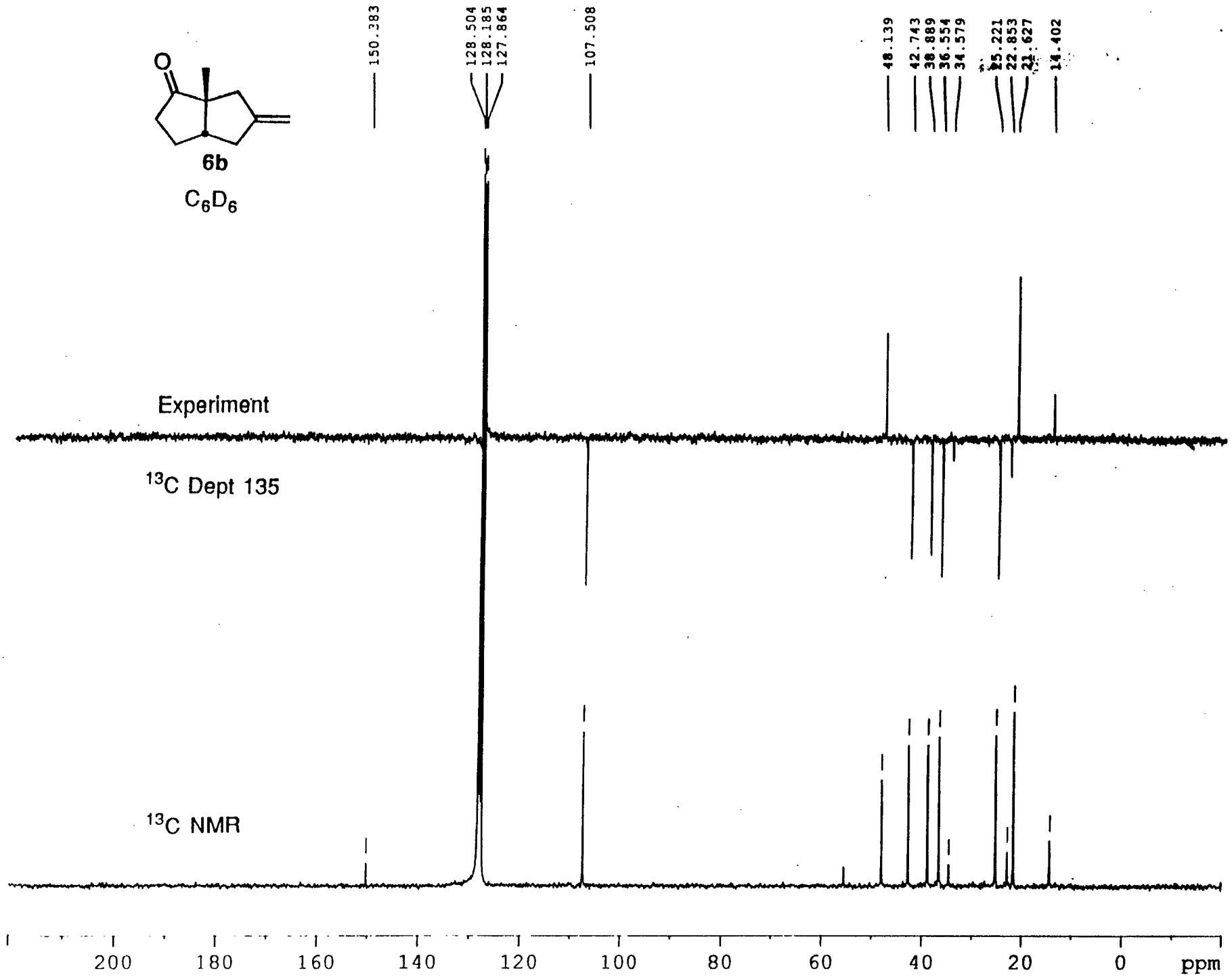
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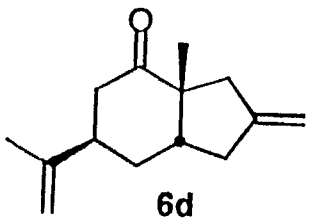
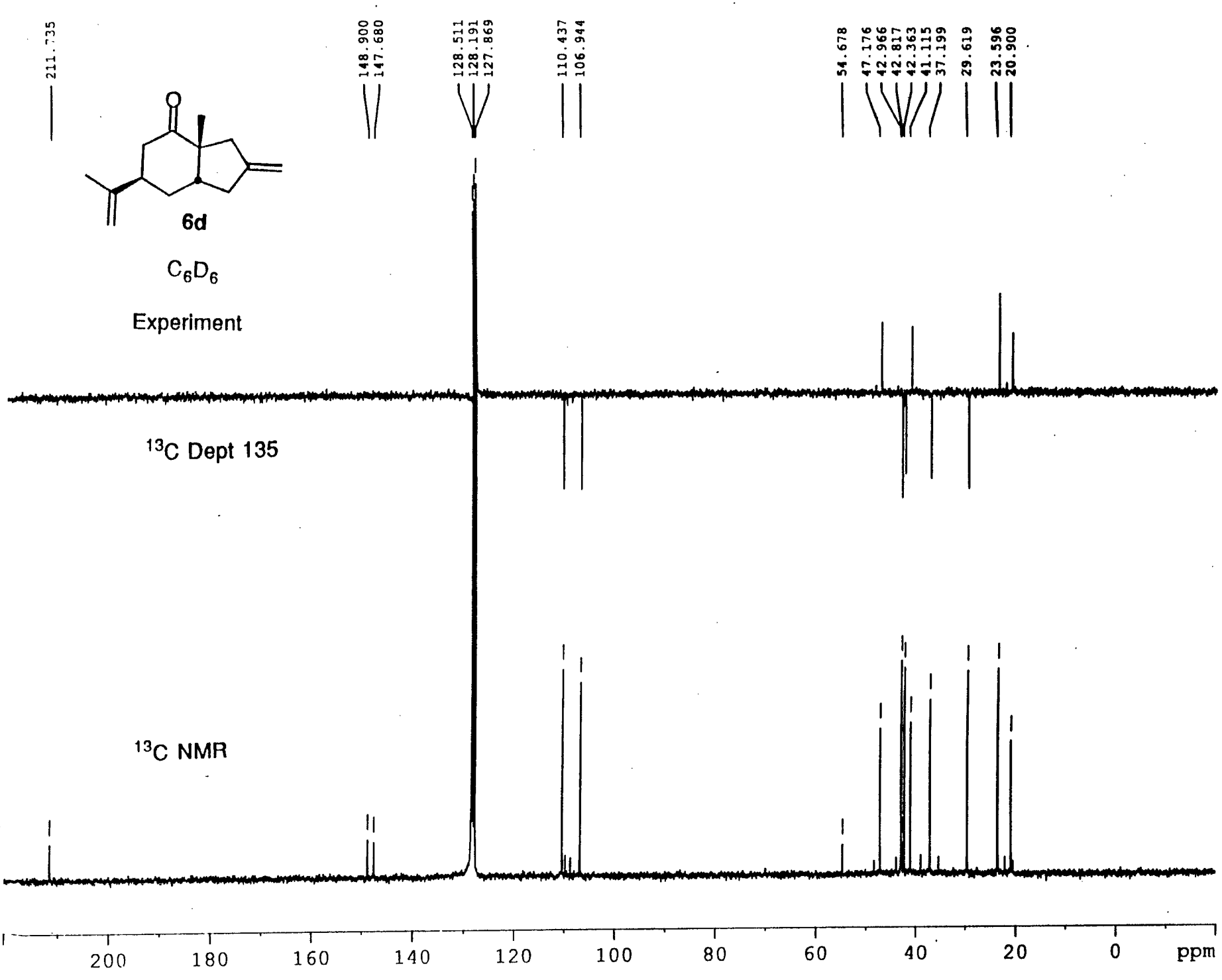


6d

C_6D_6

Experiment
^{1}H NMR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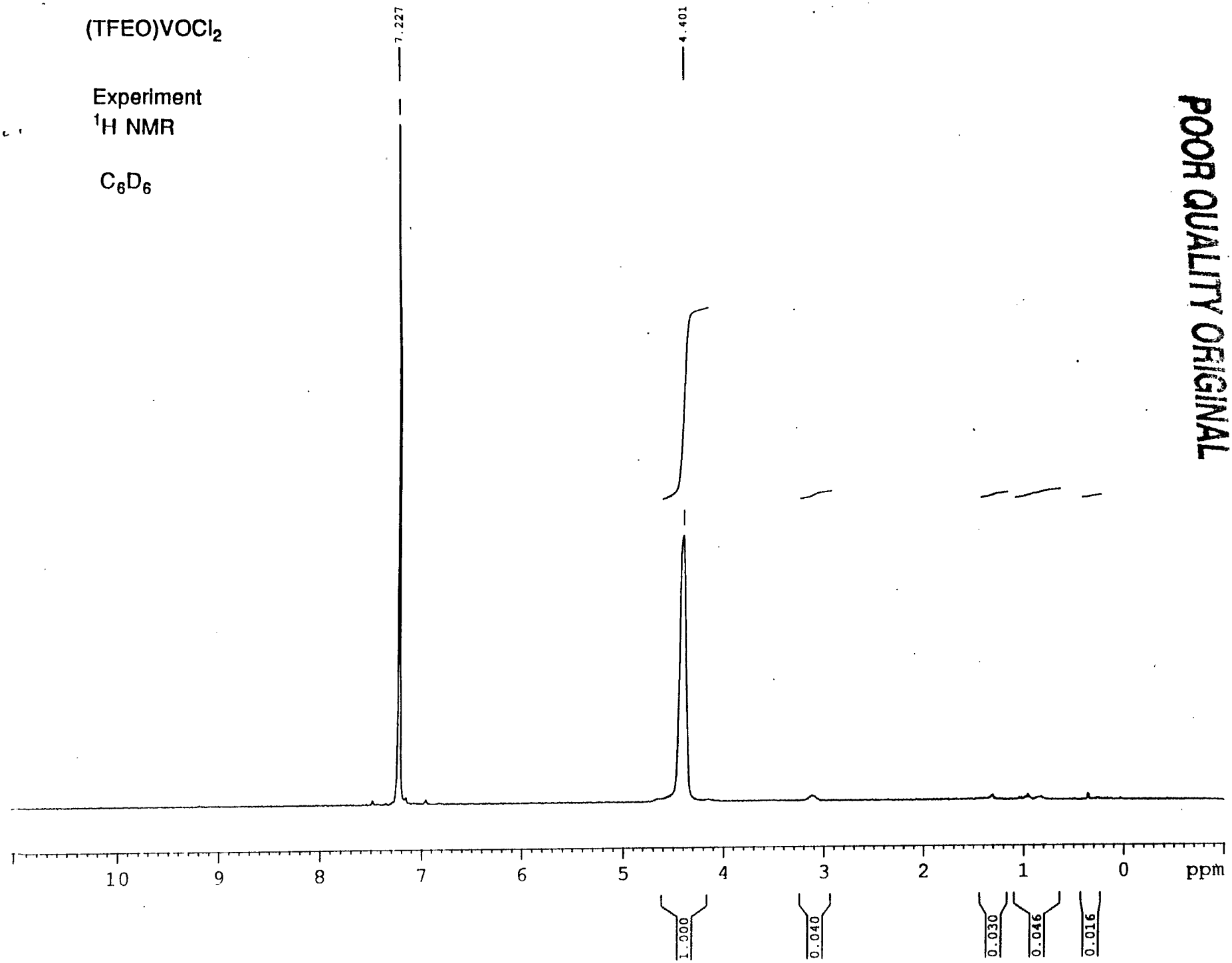
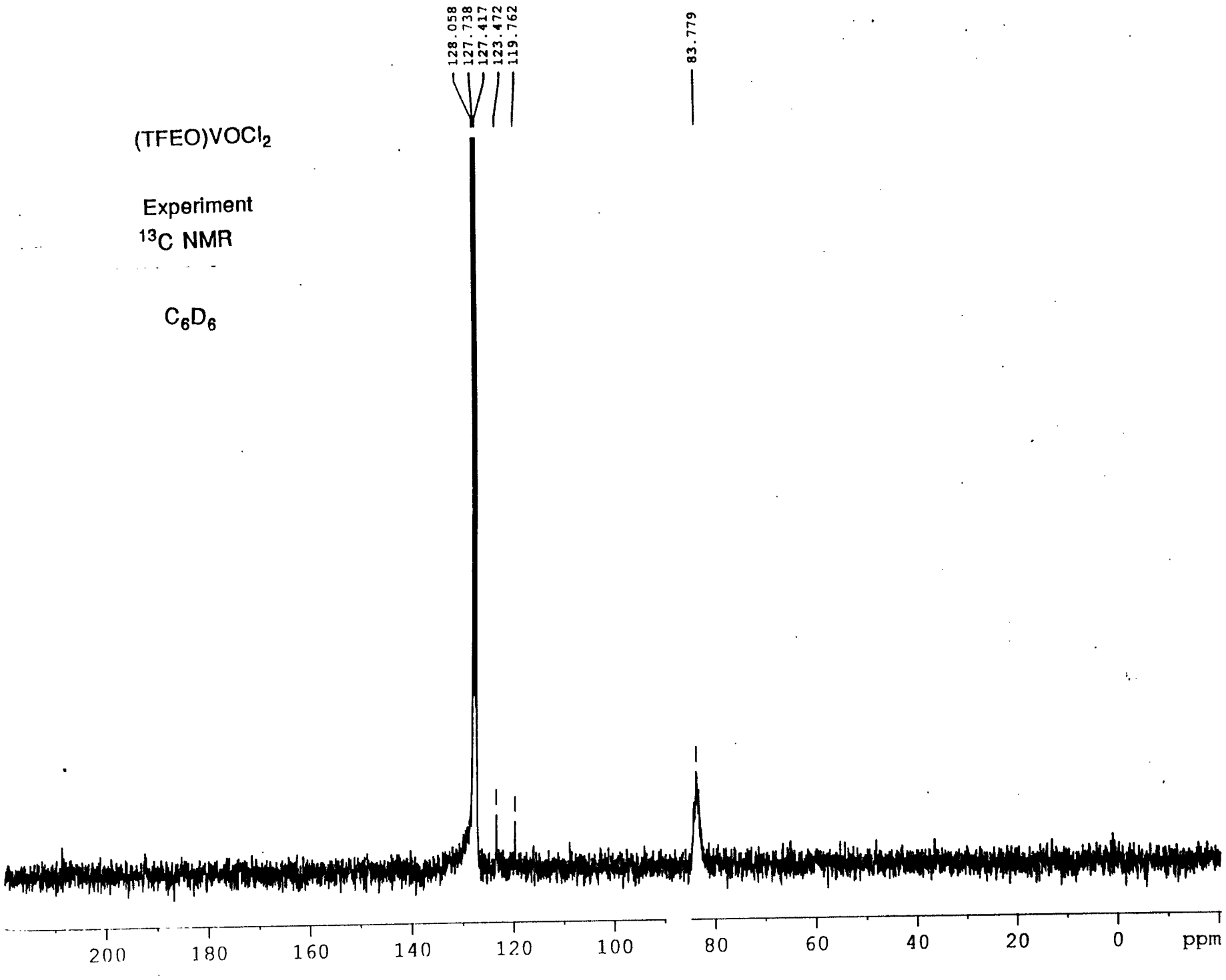
(TFEO)$VOCl_2$

Experiment
^1H NMR

C_6D_6

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