Copper-Catalyzed Desymmetrization of Prochiral 4,4-Disubstituted Cyclopentenes *via* a Site-Selective Allylic Oxidation: A Concise Total Synthesis of Untenone A

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Contents of Supporting Information:

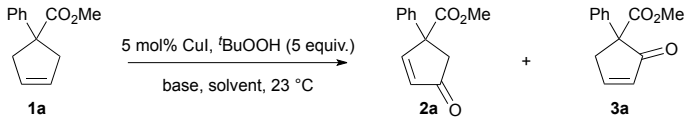
1. General Information

All reactions were carried out in anhydrous solvent using commercially available reagents that were used as received unless stated to the contrary. Grubbs second-generation catalyst was purchased from Aldrich. Tetrahydrofuran was distilled from sodium-benzophenone ketal or obtained from a Grubbs solvent purification system. Analytical thin layer chromatography (TLC) was performed on precoated aluminum-backed silica gel 60 F_{254} plates (EMD Millipore, 200 μm thickness). TLC plates were visualized with ultraviolet light and treatment with $KMnO_4$ or vanillin stain followed by heating. All compounds were purified by flash chromatography using silica gel 60 (40-63 μm, SiliCycle) and gave spectroscopic data consistent with ≥95% the assigned structure. Melting points (uncorrected) were obtained from a Büchi M-560 melting point instrument. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance DRX-500 spectrometer; chemical shifts (δ) are given in ppm and calibrated using the signal of residual undeuterated solvent as internal reference ($CHCl_3$: δ_H = 7.26 ppm and δ_C = 77.16 ppm). ^1H NMR data are reported as follows: chemical shift (multiplicity, 1st order spin system if available, coupling constant, integration). Coupling constants (*J*) are reported in Hz and splitting

patterns are designated using the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br. (broad), app. (apparent) and combinations thereof. ^{13}C NMR data with complete proton decoupling were described with the aid of an APT sequence, separating methylene and quaternary carbons (e, even) from methyl and methine (o, odd). IR spectra were recorded on an Agilent Cary 630 FTIR spectrometer; wavenumbers (ν) are given in cm^{-1}; and the abbreviations w (weak, <33%), m (medium, 33-66%), s (strong, 66-95%), vs (very strong, ≥95%) and br (broad) are used to describe the relative intensities of the IR absorbance bands. Mass spectra were obtained through the Chemistry Department Mass Spectrometry Service at Queen's University and the EPSRC National Mass Spectrometry Service Centre (Swansea, UK).

2. Reaction Optimization Experiments

Table S1. Optimization of the site-selective copper(I)-catalyzed allylic oxidation of prochiral 4,4-disubstituted cyclopentene **1a**.



Entry[a]	Base	Solvent	Ratio of **2a**:**3a**[b]	Yield of **2a**[c]
1	K_2CO_3	CH_3CN	99:1	26
2	$KHCO_3$	″	33:1	50
3	Na_2CO_3	″	26:1	38
4	NaOAc	″	21:1	20
5	K_3PO_4	″	99:1	17
6	piperidine	″	86:1	15
7	TEA	″	–	trace
8	Cs_2CO_3	″	55:1	trace
9	$NaHCO_3$	EtOAc	37:1	19
10	″	DMF	–	trace
11	″	toluene	–	trace
12	″	1,4-dioxane	–	trace
13	″	DCE	31:1	40
14	″	THF	–	trace
15	″	cyclohexane	32:1	19
16	$NaHCO_3$ (0.5 equiv.)	CH_3CN	31:1	49
17	$NaHCO_3$ (2.0 equiv.)	″	23:1	36
18[d]	$NaHCO_3$	″	21:1	34

[a] All reactions were carried out on a 0.25 mmol reaction scale using 5 equiv. of TBHP (5.5 M in decane) and 1 equiv. of the base unless otherwise stated. [b] Regioselectivity was determined by HPLC analysis of the crude reaction mixtures. [c] HPLC yields relative to the internal standard (*m*-cresol). [d] 10 mol% CuI was employed.

3. General Experimental Procedures for Preparing Cyclopentenes 1a-r

*Experimental Procedure for **1a, 1d** and **1g***: *n*-Butyllithium (6.0 mL, 15 mmol, 2.5 M in hexanes,) was added to a stirred solution of diisopropylamine (2.1 mL, 15 mmol) in anhydrous tetrahydrofuran (100 ml) at 0 °C and stirred for *ca*. 30 minutes under an atmosphere of argon. The requisite aryl acetate (10 mmol) was then added dropwise to the LDA solution at –78 °C, and stirred for an additional *ca*. 1 hour. Allyl bromide (1.3 mL, 15 mmol) was then added *via* syringe, and the reaction mixture slowly warmed to room temperature over *ca*. 4 hours and stirred overnight. The reaction was quenched with the addition of a saturated aqueous ammonium chloride solution (100 mL) and partitioned with diethyl ether. The combined organic phases were washed with saturated aqueous sodium chloride solution, dried (anhyd. $MgSO_4$), filtered and concentrated *in vacuo* to afford the monoalkylated ester. The aforementioned alkylation procedure was repeated to afford the dialkylated ester, which was added to a solution of Grubbs second-generation catalyst (2.5 mol%) in anhydrous dichloromethane (0.1 M) under an atmosphere of argon. The reaction mixture stirred for *ca*. 2 hours (t.l.c. control) before being concentrated *in vacuo* to afford the crude product. Purification by flash column chromatography (silica gel, eluting with 2-10% ethyl acetate/hexanes) furnished the *cyclopentenes* **1a, 1d** and **1g**.

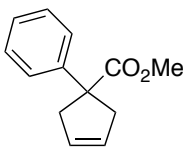
*Experimental Procedure for **1j, 1m** and **1p***: *n*-Butyllithium (6.0 mL, 15 mmol, 2.5 M in hexanes) was added to a stirred solution of diisopropylamine (2.1 mL, 15 mmol) in anhydrous tetrahydrofuran (50 ml) at 0 °C and stirred for *ca*. 30 minutes under an atmosphere of argon. Methyl cyclopent-3-ene carboxylate (0.63 g, 5.0 mmol) was then added at –78 °C and the reaction was maintained at this temperature for *ca*. 1 hour. The requisite alkyl halide (7.5 mmol) was then added, and the reaction mixture was slowly warmed to room temperature over *ca*. 4 hours and stirred overnight. The reaction was quenched with a saturated aqueous ammonium chloride solution and partitioned with diethyl ether, and the combined organic phases were washed with saturated aqueous sodium chloride solution, dried (anhyd. $MgSO_4$), filtered and concentrated *in vacuo* to afford a crude oil. Purification by flash column chromatography (silica gel, eluting with 5-10% ethyl acetate/hexanes) furnished the *cyclopentenes* **1j, 1m** and **1p**.

*Experimental Procedure for **1b, 1e, 1h, 1k, 1n** and **1q***: The requisite ester (e.g., methyl benzoate for **1b**) (10 mmol) was added dropwise to a stirred solution of allylmagnesium bromide (25 mL, 25 mmol, 1.0 M in diethyl ether) in anhydrous tetrahydrofuran (50 ml) at 0 °C under an atmosphere of argon. The reaction was allowed to warm slowly to room temperature over *ca*. 4 hours, before being carefully quenched with water (50 mL). The mixture was partitioned with diethyl ether, and the combined organic phases were washed with saturated aqueous sodium chloride solution, dried (anhyd. $MgSO_4$), filtered and concentrated *in vacuo* to afford a crude oil. The crude alcohol was then added to a solution of Grubbs second-generation catalyst (2.5 mol %) in anhydrous dichloromethane (0.1 M) and stirred for *ca*. 2 hours (t.l.c. control) under an atmosphere of argon. Dimethylsulfoxide (2.5 equiv.),

was then added and the mixture was stirred for an additional *ca*. 12 hours. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (silica gel, eluting with 10-30% ethyl acetate, hexanes) to furnish the cyclopentenol. The cyclopentenol was added to a stirred solution of diisopropylethylamine (2.0 equiv.) in anhydrous dichloromethane (0.5 M) at 0 °C under an atmosphere of argon. *tert*-Butyldimethylsilyl trifluoromethanesulfonate (1.5 equiv.) was added dropwise, and the resulting mixture was stirred at 0 °C for *ca*. 2 hours (t.l.c. control). The reaction was quenched with water and partitioned with diethyl ether, and the combined organic phases were washed with saturated aqueous sodium chloride solution, dried (anhyd. $MgSO_4$), filtered and concentrated *in vacuo* to afford a crude oil. Purification by flash column chromatography (silica gel, eluting with hexanes) furnished the *cyclopentenes* **1b, 1e, 1h, 1k, 1n** and **1q**.

*Experimental Procedure for **1c, 1f, 1i, 1l, 1o** and **1r***: The requisite cyclopent-3-enecarboxylate (e.g., **1a** for **1c**, **1d** for **1f**, *etc*.) (10 mmol) was added dropwise to a suspension of lithium aluminium hydride (0.57 g, 15.0 mmol) in anhydrous diethyl ether (100 mL) at 0 °C under an atmosphere of argon. The resulting reaction mixture was stirred for *ca*. 1 hour (t.l.c. control) at this temperature, before being carefully quenched by the addition of saturated aqueous potassium sodium tartrate solution (100 mL). The reaction was partitioned with diethyl ether, and the combined organic phases were dried (anhyd. $MgSO_4$), filtered and concentrated *in vacuo* to yield the crude alcohol. The crude alcohol was added to a stirred solution of DMAP (10 mol%) and triethylamine (1.5 equiv.) in anhydrous dichloromethane (0.2 M) at 0 °C under an atmosphere of argon. Trimethylacetyl chloride (1.5 equiv.) was added slowly *via* syringe, and the resulting mixture was allowed to warm to room temperature over *ca*. 2 hours (t.l.c. control). The reaction was quenched with saturated aqueous ammonium chloride solution and partitioned with diethyl ether, and the combined organic phases were washed with saturated aqueous sodium chloride solution, dried (anhyd. $MgSO_4$) filtered and concentrated *in vacuo* to afford a crude oil. Purification by flash column chromatography (silica gel, eluting with 5-15% ethyl acetate, hexanes) furnished the *cyclopentenes* **1c, 1f, 1i, 1l, 1o** and **1r**.

4. Spectral Data for 1a-r



Methyl 1-phenylcyclopent-3-enecarboxylate (1a)

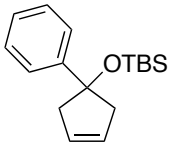
Color and state: Colorless solid; **mp** = 28-30 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.30 (m, 4H), 7.26-7.22 (m, 1H), 5.77 (s, 2H), 3.65 (s, 3H), 3.42 (d, A of AB, J_{AB} = 15.2 Hz, 2H), 2.77 (d, B of AB, J_{AB} = 15.7 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.72 (e), 143.86 (e), 129.25 (o), 128.52 (o), 126.87 (o), 126.67 (o), 58.50 (e), 52.61 (o), 42.97 (e).

IR (Neat) 3059 (w), 2951 (w), 2852 (w), 1728 (s), 1598 (w), 1433 (m), 1260 (m), 1221 (s), 1161 (s), 1050 (m), 696 (s), 671 (m) cm^{-1}.

HRMS (EI, M^+) calcd for $C_{13}H_{14}O_2$ 202.0994, found 202.0988.



***tert*-Butyl((1-butylcyclopent-3-en-1-yl)oxy)dimethylsilane (1b)**

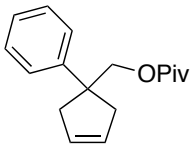
Color and state: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ7.47-7.45 (m, 2H), 7.32-7.28 (m, 2H), 7.23-7.19 (m, 1H), 5.77 (s, 2H), 2.88-2.84 (m, 2H), 2.83-2.78 (m, 2H), 0.91 (s, 9H), –0.02 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 149.50 (e), 128.82 (o), 127.96 (o), 126.45 (o), 125.25 (o), 84.44 (e), 50.57 (e), 26.15 (o), 18.55 (e), –2.88 (o).

IR (Neat) 3058 (w), 2953 (w), 2928 (m), 2855 (w), 1472 (w), 1447 (w), 1253 (m), 1090 (m), 1071 (s), 994 (m), 830 (s), 772 (s), 698 (s) cm^{-1}.

HRMS (ESI, $[M+Na]^+$) calcd for $C_{17}H_{26}NaOSi$ 297.1645, found 297.1647.



(1-Phenylcyclopent-3-en-1-yl)methyl pivalate (1c)

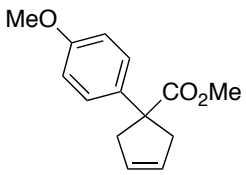
Color and state: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.29 (m, 4H), 7.24-7.20 (m, 1H), 5.78 (s, 2H), 4.13 (s, 2H), 2.82-2.77 (m, 2H), 2.76-2.71 (m, 2H), 1.13 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 178.33 (e), 146.81 (e), 129.17 (o), 128.09 (o), 127.13 (o), 126.11 (o), 71.27 (e), 49.98 (e), 42.67 (e), 38.84 (e), 27.16 (o).

IR (Neat) 3058 (w), 2971 (w), 2907 (w), 1726 (s), 1601 (w), 1479 (m), 1282 (m), 1148 (s), 1033 (m), 762 (m), 699 (s), 682 (s) cm^{-1}.

HRMS (ESI, $[M+Na]^+$) calcd for $C_{17}H_{22}NaO_2$ 281.1512, found 281.1501.



Methyl 1-(4-methoxyphenyl)cyclopent-3-enecarboxylate (1d)

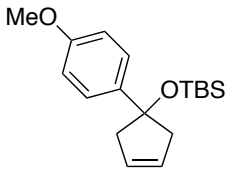
Color and state: Colorless solid; **mp** = 31-33 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30-7.27 (m, 2H), 6.89-6.86 (m, 2H), 5.79 (s, 2H), 3.79 (s, 3H), 3.65 (s, 3H), 3.47-3.42 (m, 2H), 2.78-2.74 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.59 (e), 158.33 (e), 135.71 (e), 129.14 (o), 127.58 (o), 113.66 (o), 57.65 (e), 55.03 (o), 52.26 (o), 42.76 (e).

IR (Neat) 3059 (w), 2951 (w), 2837 (w), 1726 (s), 1610 (m), 1511 (s), 1457 (m), 1441 (m), 1247 (s), 1162 (s), 1035 (s), 830 (s), 702 (m) cm^{-1}.

HRMS (EI, M^+) calcd for $C_{14}H_{16}O_3$ 232.1099, found 232.1095.



***tert*-Butyl((1-(4-methoxyphenyl)cyclopent-3-en-1-yl)oxy)dimethyl-silane (1e)**

Color and state: Colorless oil.

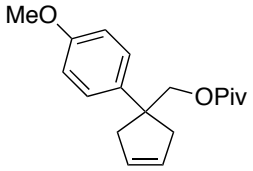
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.36 (m, 2H), 6.86-6.83 (m, 2H), 5.75 (s, 2H), 3.80 (s, 3H), 2.84-2.76 (m, 4H), 0.89 (s, 9H), –0.05 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 158.25 (e), 141.46 (e), 128.84 (o), 126.54 (o), 113.23 (o), 84.27 (e), 55.29 (o), 50.15 (e), 26.11 (o), 18.49 (e), –2.91 (o).

IR (Neat) 3058 (w), 2952 (w), 2929 (m), 2855 (w), 1612 (w), 1511 (m), 1462 (m), 1244 (s), 1178 (m),

1083 (m), 1040 (m), 994 (m), 829 (s), 799 (s), 771 (s), 671 (m) cm^{-1}.

HRMS (EI, $M]^+$) calcd for $C_{18}H_{28}O_2Si$ 304.1859, found 304.1849.



(1-(4-Methoxyphenyl)cyclopent-3-en-1-yl)methyl pivalate (1f)

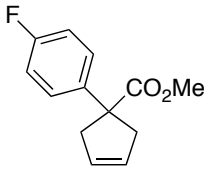
Color and state: Colorless solid; **mp** = 36-38 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21-7.19 (m, 2H), 6.86-6.84 (m, 2H), 5.75 (s, 2H), 4.07 (s, 2H), 3.79 (s, 3H), 2.73 (d, A of AB, J_{AB} = 15.0 Hz, 2H), 2.68 (d, B of AB, J_{AB} = 15.1 Hz, 2H), 1.12 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 178.47 (e), 157.87 (e), 138.99 (e), 129.21 (o), 128.12 (o), 113.45 (o), 71.40 (e), 55.26 (o), 49.35 (e), 42.58 (e), 38.86 (e), 27.19 (o).

IR (Neat) 3056 (w), 2907 (w), 1724 (s), 1611 (w), 1513 (s), 1282 (m), 1246 (s), 1150 (vs), 1032 (s), 829 (s), 676 (s) cm^{-1}.

HRMS (ESI, $[M+Na]^+$) calcd for $C_{18}H_{24}NaO_3$ 311.1618, found 311.1616.



Methyl 1-(4-fluorophenyl)cyclopent-3-enecarboxylate (1g)

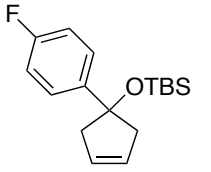
Color and state: Colorless solid; **mp** = 30-32 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.28 (m, 2H), 7.01-6.96 (m, 2H), 5.76 (s, 2H), 3.63 (s, 3H), 3.45-3.40 (m, 2H), 2.75-2.71 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.23 (e), 161.65 (e, d, $^1J_{C\text{-}F}$ = 245.6 Hz), 139.46 (e, d, $^4J_{C\text{-}F}$ = 3.8 Hz), 129.12 (o), 128.22 (o, d, $^3J_{C\text{-}F}$ = 8.2 Hz), 115.11 (o, d, $^2J_{C\text{-}F}$ = 21.1 Hz), 57.82 (e), 52.41 (o), 42.87 (e).

IR (Neat) 3062 (w), 2953 (w), 2853 (w), 1731 (s), 1606 (w), 1510 (s), 1435 (w), 1262 (m), 1225 (s), 1159 (s), 835 (m), 700 (m) cm^{-1}.

HRMS (ESI, $[M+H]^+$) calcd for $C_{13}H_{14}FO_2$ 221.0972, found 221.0972.



***tert*-Butyl((1-(4-fluorophenyl)cyclopent-3-en-1-yl)oxy)dimethylsilane (1h)**

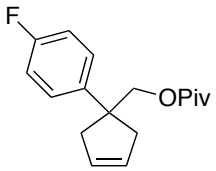
Color and state: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47-7.44 (m, 2H), 7.04-6.99 (m, 2H), 5.80 (s, 2H), 2.85 (s, 4H), 0.96 (s, 9H), 0.03 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 161.65 (e, d, $^1J_{C\text{-}F}$ = 244.5 Hz), 145.31 (e, d, $^4J_{C\text{-}F}$ = 3.4 Hz), 128.84 (o), 126.85 (o, d, $^3J_{C\text{-}F}$ = 7.6 Hz), 114.61 (o, d, $^2J_{C\text{-}F}$ = 21.2 Hz), 84.13 (e), 50.43 (e), 26.10 (o), 18.51 (e), –2.90 (o).

IR (Neat) 3062 (w), 2954 (w), 2929 (w), 2856 (w), 1602 (w), 1508 (s), 1463 (w), 1252 (m), 1231 (m), 1157 (m), 1084 (s), 994 (m), 831 (s), 772 (s), 671 (m) cm^{-1}.

HRMS (EI, M^+) calcd for $C_{17}H_{25}FOSi$ 292.1659, found 297.1663.



(1-(4-Fluorophenyl)cyclopent-3-en-1-yl)methyl pivalate (1i)

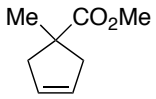
Color and state: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26-7.23 (m, 2H), 7.01-6.98 (m, 2H), 5.76 (s, 2H), 4.08 (s, 2H), 2.72 (s, 4H), 1.11 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 178.36 (e), 161.36 (e, d, $^1J_{C\text{-}F}$ = 243.6 Hz), 142.57 (e, d, $^4J_{C\text{-}F}$ = 2.7 Hz), 129.21 (o), 128.69 (o, $^3J_{C\text{-}F}$ = 7.7 Hz), 114.82 (o, d, $^2J_{C\text{-}F}$ = 21.3 Hz), 71.22 (e), 49.64 (e), 42.54 (e), 38.89 (e), 27.19 (o).

IR (Neat) 3056 (w), 2974 (w), 2907 (w), 1727 (s), 1604 (w), 1512 (s), 1480 (m), 1283 (m), 1233 (m), 1152 (s), 834 (m), 677 (m) cm^{-1}.

HRMS (ESI, $[M+Na]^+$) calcd for $C_{17}H_{21}FNaO_2$ 299.1418, found 299.1415.



Methyl 1-methylcyclopent-3-enecarboxylate (1j)

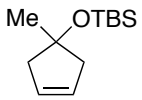
Color and state: Pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.46 (s, 2H), 3.55 (s, 3H), 2.77 (d, A of AB, J_{AB} = 14.8 Hz, 2H), 2.08 (d, B of AB, J_{AB} = 14.7 Hz, 2H), 1.16 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 178.26 (e), 128.03 (o), 51.59 (o), 47.58 (e), 44.38 (e), 25.76 (o).

IR (Neat) 3059 (w), 2952 (w), 2927 (w), 2854 (w), 1730 (s), 1620 (w), 1434 (m), 1273 (m), 1202 (s), 1118 (s), 982 (w), 669 (s) cm^{-1}.

HRMS (ESI, $[M+H]^+$) calcd for $C_8H_{13}O_2$ 141.0910, found 141.0904.



***tert*-Butyldimethyl((1-methylcyclopent-3-en-1-yl)oxy)silane (1k)**

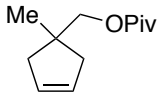
Color and state: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.63 (s, 2H), 2.51 (d, A of AB, J_{AB} = 15.4 Hz, 2H), 2.34 (d, B of AB, J_{AB} = 15.4 Hz, 2H), 1.39 (s, 3H), 0.87 (s, 9H), 0.08 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 128.96 (o), 81.42 (e), 49.10 (e), 30.21 (o), 25.94 (o), 18.09 (e), –2.45 (o).

IR (Neat) 3061 (w), 2956 (w), 2929 (m), 2857 (w), 1615 (w), 1473 (w), 1249 (m), 1154 (m), 1084 (m), 1026 (s), 832 (s), 771 (s), 668 (s) cm^{-1}.

HRMS (ESI, $[M+H]^+$) calcd for $C_{12}H_{25}OSi$ 213.1669, found 213.1659.



(1-Methylcyclopent-3-en-1-yl)methyl pivalate (1l)

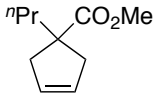
Color and state: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.57 (s, 2H), 3.88 (s, 2H), 2.30 (d, A of AB, J_{AB} = 15.2 Hz, 2H), 2.06 (d, B of AB, J_{AB} = 15.0 Hz, 2H), 1.18 (s, 9H), 1.10 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 178.65 (e), 128.96 (o), 71.74 (e), 43.41 (e), 41.65 (e), 39.01 (e), 27.30 (o), 25.34 (o).

IR (Neat) 3058 (w), 2960 (m), 2931 (w), 2873 (w), 1730 (s), 1480 (w), 1282 (m), 1151 (s), 1034 (w), 770 (w), 676 (m) cm^{-1}.

HRMS (CI, $[M+H]^+$) calcd for $C_{12}H_{21}O_2$ 197.1536, found 197.1531.



Methyl 1-propylcyclopent-3-enecarboxylate (1m)

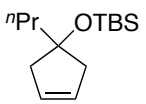
Color and state: Pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.49 (s, 2H), 3.58 (s, 3H), 2.79 (d, A of AB, J_{AB} = 15.3 Hz, 2H), 2.19 (d, B of AB, J_{AB} = 16.1 Hz, 2H), 1.57-1.54 (m, 2H), 1.18-1.10 (m, 2H), 0.79 (t, J = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 177.85 (e), 128.36 (o), 52.51 (e), 51.61 (o), 42.25 (e), 41.91 (e), 18.58 (e), 14.35 (o).

IR (Neat) 3059 (w), 2957 (m), 2932 (w), 2873 (w), 1730 (s), 1622 (w), 1433 (m), 1297 (w), 1268 (w), 1202 (s), 1025 (w), 943 (w), 735 (m), 671 (s) cm^{-1}.

HRMS (ESI, $[M+H]^+$) calcd for $C_{10}H_{17}O_2$ 169.1223, found 169.1221.



***tert*-Butyldimethyl((1-propylcyclopent-3-en-1-yl)oxy)silane (1n)**

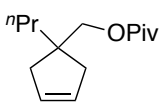
Color and state: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.63 (s, 2H), 2.43-2.35 (m, 4H), 1.59-1.55 (m, 2H), 1.45-1.37 (m, 2H), 0.91 (t, J = 7.4 Hz, 3H), 0.85 (s, 9H), 0.03 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 128.95 (o), 83.88 (e), 47.08 (e), 45.94 (e), 26.03 (o), 18.38 (e), 18.08 (e), 14.87 (o), –2.72 (o).

IR (Neat) 3057 (w), 2955 (m), 2929 (m), 2855 (m), 1462 (w), 1251 (m), 1091 (m), 1061 (s), 974 (m), 831 (s), 770 (s), 668 (s) cm^{-1}.

HRMS (ESI, $[M+Na]^+$) calcd for $C_{14}H_{28}NaOSi$ 263.1802, found 263.1809.



(1-Propylcyclopent-3-en-1-yl)methyl pivalate (1o)

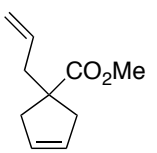
Color and state: Pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.57 (s, 2H), 3.89 (s, 2H), 2.24-2.20 (m, 2H), 2.17-2.13 (m, 2H), 1.46-1.42 (m, 2H), 1.29-1.21 (m, 2H), 1.19 (s, 9H), 0.89 (t, J = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 178.76 (e), 129.06 (o), 69.90 (e), 44.72 (e), 41.79 (e), 40.63 (e), 39.06 (e), 27.32 (o) 17.96 (e), 15.05 (o).

IR (Neat) 3056 (w), 2958 (m), 2873 (w), 2849 (w), 1729 (s), 1480 (m), 1458 (w), 1281 (m), 1149 (s), 1034 (m), 770 (w), 679 (m) cm^{-1}.

HRMS (ESI, $[M+Na]^+$) calcd for $C_{14}H_{24}NaO_2$ 247.1669, found 247.1680.



Methyl 1-allylcyclopent-3-encarboxylate (1p)

Color and state: Pale yellow oil.

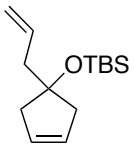
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.61-5.52 (m, 1H), 5.45 (s, 2H), 4.92-4.89 (m, 2H), 3.54 (s, 3H), 2.72 (d, A of AB, J_{AB} = 15.6 Hz, 2H), 2.27 (d, J = 7.1 Hz, 2H), 2.20 (d, B of AB, J_{AB} = 15.7 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.85 (e), 134.03 (o), 128.04 (o), 117.49 (e), 51.55 (e), 51.44 (o),

43.12 (e), 41.70 (e).

IR (Neat) 3060 (w), 2951 (w), 2924 (w), 2853 (w), 1730 (s), 1640 (w), 1434 (m), 1200 (s), 1135 (m), 992 (m), 915 (m), 678 (s) cm^{-1}.

HRMS (ESI, $[M+H]^+$) calcd for $C_{10}H_{15}O_2$ 167.1067, found 167.1065.



((1-Allylcyclopent-3-en-1-yl)oxy)(*tert*-butyl)dimethylsilane (1q)

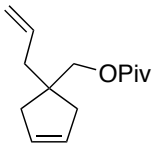
Color and state: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.93-5.83 (m, 1H), 5.62 (s, 2H), 5.06-5.02 (m, 2H), 2.45-2.38 (m, 4H), 2.37-2.34 (m, 2H), 0.86 (s, 9H), 0.05 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 135.69 (o), 128.87 (o), 116.98 (e), 83.21 (e), 47.77 (e), 46.61 (e), 25.98 (o), 18.31 (e), –2.66 (o).

IR (Neat) 3059 (w), 2956 (w), 2929 (m), 2857 (w), 1641 (w), 1471 (w), 1251 (m), 1081 (m), 1061 (m), 999 (m), 913 (m), 833 (s), 771 (s), 671 (m) cm^{-1}.

HRMS (ESI, $[M+H]^+$) calcd for $C_{14}H_{27}OSi$ 239.1826, found 239.1815.



(1-Allylcyclopent-3-en-1-yl)methyl pivalate (1r)

Color and state: Pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.77-5.69 (m, 1H), 5.55 (s, 2H), 5.04-4.99 (m, 2H), 3.88 (s, 2H), 2.22-2.19 (m, 2H), 2.19 (s, 4H), 1.17 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 178.43 (e), 134.77 (o), 128.88 (o), 117.62 (e), 69.68 (e), 44.55 (e), 42.17 (e), 41.23 (e), 38.95 (e), 27.26 (o).

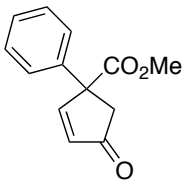
IR (Neat) 3058 (w), 2974 (w), 2906 (w), 2848 (w), 1729 (s), 1480 (m), 1281 (m), 1150 (s), 1033 (w), 990 (m), 673 (m) cm^{-1}.

HRMS (ESI, $[M+H]^+$) calcd for $C_{14}H_{23}O_2$ 223.1693, found 223.1684.

5. Representative Experimental Procedure for the Allylic Oxidation of 1a-r

Copper(I) iodide (2.38 mg, 0.013 mmol) and sodium bicarbonate (21.0 mg, 0.25 mmol) were suspended in anhydrous acetonitrile (1.25 ml) in a 10 mL vial and stirred at room temperature. The requisite cyclopentene **1a-r** (0.25 mmol) was added *via* a tared syringe or in a single portion, and the resulting mixture was stirred for *ca.* 10 minutes before *tert*-butyl hydroperoxide (0.23 mL, 1.25 mmol, 5.5 M in decane) was added over *ca*. 5 minutes. The reaction mixture was heated at 40 °C for *ca*. 36 hours (t.l.c. control). The solution was filtered through a short plug of silica gel with ethyl acetate and concentrated *in vacuo* to afford the crude product. Purification by flash chromatography (silica gel, eluting with ethyl acetate/hexanes) afforded the title *cyclopentenones* **2a-r**.

6. Spectral Data for α,β-Unsaturated Cyclopentenones 2a-r



Methyl 4-oxo-1-phenylcyclopent-2-enecarboxylate (2a)

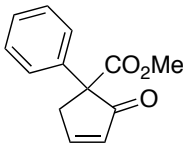
Color and state: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 5.6 Hz, 1H), 7.38-7.35 (m, 2H), 7.32-7.29 (m, 1H), 7.22-7.20 (m, 2H), 6.34 (d, J = 5.6 Hz, 1H), 3.76 (s, 3H), 3.51 (d, A of AB, J_{AB} = 18.9 Hz, 1H), 2.60 (d, B of AB, J_{AB} = 18.8 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 206.57 (e), 172.10 (e), 162.79 (o), 140.75 (e), 133.88 (o), 128.91 (o), 127.62 (o), 125.74 (o), 59.74 (e), 52.88 (o), 46.60 (e).

IR (Neat) 3062 (w), 3028 (w), 2953 (w), 1716 (s), 1591 (w), 1496 (w), 1434 (m), 1242 (s), 1148 (m), 1035 (m), 819 (m), 697 (s) cm^{-1}.

HRMS (ESI, $[M+H]^+$) calcd for $C_{13}H_{13}O_3$ 217.0859, found 217.0862.



Methyl 2-oxo-1-phenylcyclopent-3-ene-1-carboxylate (3a)

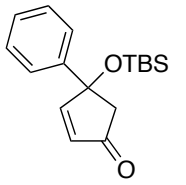
Color and state: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (dt, J = 5.7, 2.8 Hz, 1H), 7.35-7.27 (m, 5H), 6.25 (dt, J = 5.7, 2.2 Hz, 1H), 3.82 (app. dt, J = 19.3, 2.5 Hz, 1H), 3.74 (s, 3H), 3.07 (app. dt, J = 19.3, 2.4 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 203.40 (e), 170.71 (e), 163.24 (o), 138.75 (e), 132.24 (o), 128.83 (o), 127.64 (o), 127.31 (o), 62.84 (e), 53.39 (o), 43.76 (e).

IR (Neat) 3021 (w), 2953 (w), 1708 (m), 1594 (w), 1497 (w), 1433 (w), 1342 (w), 1214 (m), 1152 (m), 909 (w), 744 (vs), 667 (s) cm^{-1}.

HRMS (EI, M^+) calcd for $C_{13}H_{12}O_3$ 216.0786, found 216.0781.



4-((*tert*-Butyldimethylsilyl)oxy)-4-phenylcyclopent-2-enone (2b)

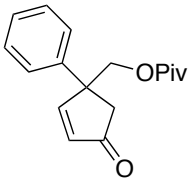
Color and state: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, J = 5.6 Hz, 1H), 7.39-7.32 (m, 4H), 7.29-7.25 (m, 1H), 6.28 (d, J = 5.5 Hz, 1H), 2.85 (d, A of AB, J_{AB} = 18.8 Hz, 1H), 2.80 (d, B of AB, J_{AB} = 18.7 Hz, 1H), 0.96 (s, 9H), 0.07 (s, 3H), 0.04 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 207.40 (e), 166.04 (o), 144.70 (e), 133.05 (o), 128.64 (o), 127.58 (o), 124.91 (o), 82.04 (e), 53.33 (e), 25.91 (o), 18.40 (e), –2.24 (o), –2.42 (o).

IR (Neat) 2954 (w), 2930 (m), 2857 (w), 1721 (s), 1589 (w), 1472 (w), 1447 (w), 1253 (m), 1153 (m), 1089 (m), 1069 (m), 934 (m), 834 (s), 807 (s), 775 (s), 699 (s) cm^{-1}.

HRMS (EI, M^+) calcd for $C_{17}H_{24}O_2Si$ 288.1546, found 288.1540.



(4-Oxo-1-phenylcyclopent-2-en-1-yl)methyl pivalate (2c)

Color and state: Colorless oil.

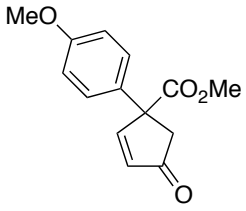
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, J = 5.7 Hz, 1H), 7.39-7.36 (m, 2H), 7.31-7.26 (m, 3H), 6.33 (d, J = 5.7 Hz, 1H), 4.52 (d, A of AB, J_{AB} = 11.0 Hz, 1H), 4.26 (d, B of

AB, J_{AB} = 11.0 Hz, 1H), 2.78 (d, A of AB, J_{AB} = 18.3 Hz, 1H), 2.64 (d, B of AB, J_{AB} = 18.4 Hz, 1H), 1.12 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 207.71 (e), 178.08 (e), 165.57 (o), 141.44 (e), 134.53 (o), 129.06 (o), 127.63 (o), 126.40 (o), 68.28 (e), 52.91 (e), 46.58 (e), 38.95 (e), 27.13 (o).

IR (Neat) 2971 (w), 2873 (w), 1718 (s), 1593 (w), 1480 (w), 1280 (m), 1141 (s), 700 (m) cm^{-1}.

HRMS (ESI, $[M+H]^+$) calcd for $C_{17}H_{21}O_3$ 273.1485, found 273.1478.



Methyl 1-(4-methoxyphenyl)-4-oxocyclopent-2-enecarboxylate (2d)

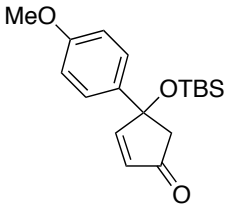
Color and state: Colorless solid; **mp** = 47-49 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, J = 5.6 Hz, 1H), 7.14-7.11 (m, 2H), 6.88-6.84 (m, 2H), 6.29 (d, J = 5.7 Hz, 1H), 3.78 (s, 3H), 3.73 (s, 3H), 3.46 (d, A of AB, J_{AB} = 18.9 Hz, 1H), 2.57 (d, B of AB, J_{AB} = 18.8 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 207.18 (e), 172.63 (e), 163.27 (o), 159.14 (e), 133.88 (o), 132.95 (e), 127.15 (o), 114.50 (o), 59.30 (e), 55.39 (o), 53.14 (o), 46.96 (e).

IR (Neat) 2954 (w), 2840 (w), 1720 (s), 1610 (w), 1512 (m), 1251 (s), 1184 (m), 1034 (m), 833 (w) cm^{-1}.

HRMS (EI, M^+) calcd for $C_{14}H_{14}O_4$ 246.0892, found 246.0898.



4-((*tert*-Butyldimethylsilyl)oxy)-4-(4-methoxyphenyl)cyclopent-2-enone (2e)

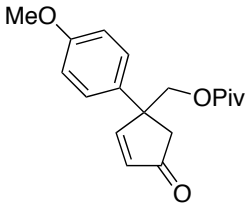
Color and state: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, J = 5.6 Hz, 1H), 7.30-7.27 (m, 2H), 6.90-6.87 (m, 2H), 6.24 (d, J = 5.5 Hz, 1H), 3.80 (s, 3H), 2.84 (d, A of AB, J_{AB} = 18.7 Hz, 1H), 2.79 (d, B of AB, J_{AB} = 18.6 Hz, 1H), 0.95 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 207.39 (e), 166.12 (o), 159.01 (e), 136.66 (e), 132.60 (o), 126.14 (o), 113.90 (o), 81.69 (e), 55.34 (o), 53.23 (e), 25.86 (o), 18.32 (e), –2.33 (o), –2.49 (o).

IR (Neat) 2954 (w), 2930 (w), 2856 (w), 1719 (s), 1609 (w), 1510 (s), 1463 (m), 1248 (s), 1175 (m), 1059 (s), 1035 (m), 932 (m), 829 (s), 805 (s), 773 (s), 750 (s), 667 (m) cm^{-1}.

HRMS (EI, M^+) calcd for $C_{18}H_{26}O_3Si$ 318.1651, found 318.1658.



(1-(4-Methoxyphenyl)-4-oxocyclopent-2-en-1-yl)methyl pivalate (2f)

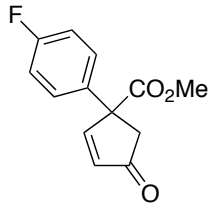
Color and state: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, J = 5.6 Hz, 1H), 7.19-7.15 (m, 2H), 6.91-6.87 (m, 2H), 6.30 (d, J = 5.6 Hz, 1H), 4.47 (d, A of AB, J_{AB} = 11.0 Hz, 1H), 4.22 (d, B of AB, J_{AB} = 10.9 Hz, 1H), 3.80 (s, 3H), 2.74 (d, A of AB, J_{AB} = 18.3 Hz, 1H), 2.59 (d, B of AB, J_{AB} = 18.3 Hz, 1H), 1.11 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 207.99 (e), 178.18 (e), 165.86 (o), 158.94 (e), 134.35 (o), 133.43 (e), 127.52 (o), 114.44 (o), 68.33 (e), 55.44 (o), 52.34 (e), 46.75 (e), 39.00 (e), 27.18 (o).

IR (Neat) 2974 (w), 2939 (w), 1720 (vs), 1610 (w), 1514 (m), 1252 (m), 1142 (s), 1035 (m), 969 (w), 831 (m) cm^{-1}.

HRMS (EI, M^+) calcd for $C_{18}H_{22}O_4$ 302.1518, found 302.1511.



Methyl 1-(4-fluorophenyl)-4-oxocyclopent-2-enecarboxylate (2g)

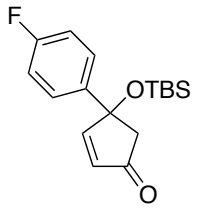
Color and state: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, J = 5.6 Hz, 1H), 7.16 (dd, J = 8.1, 5.3 Hz, 2H), 7.00 (app. t, J = 8.5 Hz, 2H), 6.30 (d, J = 5.6 Hz, 1H), 3.70 (s, 3H), 3.46 (d, A of AB, J_{AB} = 18.8 Hz, 1H), 2.51 (d, B of AB, J_{AB} = 18.8 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 206.57 (e), 172.18 (e), 162.56 (o), 162.09 (e, d, $^1J_{C\text{-}F}$ = 247.6 Hz), 136.74 (e, d, $^4J_{C\text{-}F}$ = 3.3 Hz), 134.28 (o), 127.75 (o, d, $^3J_{C\text{-}F}$ = 8.0 Hz), 115.98 (o, d, $^2J_{C\text{-}F}$ = 21.5 Hz), 59.30 (e), 53.19 (o), 46.85 (e).

IR (Neat) 3078 (w), 2956 (w), 1716 (s), 1600 (w), 1508 (s), 1435 (m), 1224 (s), 1149 (s), 1038 (m), 835 (s), 819 (s), 787 (s), 751 (m), 673 (w) cm^{-1}.

HRMS (EI, M^+) calcd for $C_{13}H_{11}FO_3$ 234.0692, found 234.0690.



4-((*tert*-Butyldimethylsilyl)oxy)-4-(4-fluorophenyl)cyclopent-2-enone (2h)

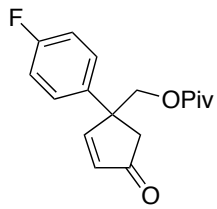
Color and state: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, J = 5.6 Hz, 1H), 7.34-7.31 (m, 2H), 7.04-6.99 (m, 2H), 6.27 (d, J = 5.6 Hz, 1H), 2.83 (d, A of AB, J_{AB} = 18.7 Hz, 1H), 2.74 (d, B of AB, J_{AB} = 18.7 Hz, 1H), 0.93 (s, 9H), 0.05 (s, 3H), 0.03 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 206.94 (e), 165.58 (o), 162.16 (e, d, $^1J_{C\text{-}F}$ = 246.7 Hz), 140.58 (e, d, $^4J_{C\text{-}F}$ = 2.8 Hz), 133.22 (o), 126.63 (o, d, $^3J_{C\text{-}F}$ = 8.1 Hz), 115.42 (o, d, $^2J_{C\text{-}F}$ = 21.4 Hz), 81.69 (e), 53.29 (e), 25.86 (o), 18.34 (e), –2.28 (o), –2.47 (o).

IR (Neat) 2955 (w), 2930 (m), 2858 (w), 1723 (s), 1603 (w), 1508 (s), 1472 (w), 1254 (m), 1228 (m), 1156 (m), 1081 (m), 932 (m), 836 (s), 808 (m), 777 (m) cm^{-1}.

HRMS (ESI, $[M+Na]^+$) calcd for $C_{17}H_{23}FNaO_2Si$ 329.1344, found 329.1346.



(1-(4-Fluorophenyl)-4-oxocyclopent-2-en-1-yl)methyl pivalate (2i)

Color and state: Colorless oil.

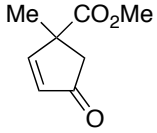
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, J = 5.7 Hz, 1H), 7.23-7.21 (m, 2H), 7.06-7.03 (m, 2H), 6.32 (d, J = 5.7 Hz, 1H), 4.48 (d, A of AB, J_{AB} = 11.0 Hz, 1H), 4.20 (d, B of AB, J_{AB} = 11.0 Hz, 1H), 2.74 (d, A of AB, J_{AB} = 18.4 Hz, 1H), 2.56 (d, B of AB, J_{AB} = 18.4 Hz, 1H), 1.10 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 207.36 (e), 178.05 (e), 165.20 (o), 162.02 (e, d, $^1J_{C\text{-}F}$ = 247.6 Hz), 137.30 (e, d, $^4J_{C\text{-}F}$ = 3.8 Hz), 134.70 (o), 128.10 (o, d, $^3J_{C\text{-}F}$ = 7.7 Hz), 115.97 (o, d, $^2J_{C\text{-}F}$ = 21.9 Hz), 68.27 (e), 52.40 (e), 46.68 (e), 38.96 (e), 27.12 (o).

IR (Neat) 2972 (w), 2873 (w), 1716 (s), 1603 (w), 1511 (s), 1480 (m), 1279 (m), 1230 (m), 1135 (s),

1035 (m), 970 (m), 834 (s), 819 (m) cm^{-1}.

HRMS (ESI, $[M+Na]^+$) calcd for $C_{17}H_{19}FNaO_3$ 313.1210, found 313.1197.



1-Methyl-4-oxocyclopent-2-enecarboxylate (2j)

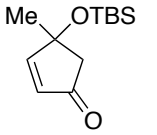
Color and state: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, J = 5.6 Hz, 1H), 6.11 (d, J = 5.6 Hz, 1H), 3.70 (s, 3H), 2.95 (d, A of AB, J_{AB} = 18.7 Hz, 1H), 2.22 (d, B of AB, J_{AB} = 18.7 Hz, 1H), 1.48 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 207.63 (e), 174.05 (e), 165.93 (o), 133.12 (o), 52.82 (o), 51.47 (e), 45.76 (e), 24.76 (o).

IR (Neat) 2956 (w), 2875 (w), 1714 (s), 1591 (w), 1457 (w), 1435 (w), 1278 (m), 1194 (m), 1169 (s), 1120 (m), 1083 (m), 868 (m), 807 (m), 760 (m) cm^{-1}.

HRMS (EI, M^+) calcd for $C_8H_{10}O_3$ 154.0630, found 154.0626.



4-((*tert*-Butyldimethylsilyl)oxy)-4-methylcyclopent-2-enone (2k)

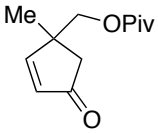
Color and state: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, J = 5.6 Hz, 1H), 6.02 (d, J = 5.6 Hz, 1H), 2.52 (d, A of AB, J_{AB} = 18.2 Hz, 1H), 2.45 (d, B of AB, J_{AB} = 18.2 Hz, 1H), 1.47 (s, 3H), 0.83 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 207.16 (e), 167.79 (o), 131.98 (o), 78.40 (e), 51.58 (e), 29.10 (o), 25.66 (o), 17.95 (e), –2.31 (o), –2.38 (o).

IR (Neat) 2956 (w), 2930 (m), 2857 (w), 1721 (s), 1592 (w), 1471 (w), 1252 (m), 1201 (m), 1134 (m), 1076 (s), 1016 (m), 832 (s), 805 (s), 773 (s), 679 (m) cm^{-1}.

HRMS (ESI, $[M+H]^+$) calcd for $C_{12}H_{23}O_2Si$ 227.1462, found 227.1463.



(1-Methyl-4-oxocyclopent-2-en-1-yl)methyl pivalate (2l)

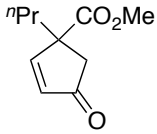
Color and state: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, J = 5.6 Hz, 1H), 6.10 (d, J = 5.6 Hz, 1H), 4.13 (d, A of AB, J_{AB} = 10.9 Hz, 1H), 3.91 (d, B of AB, J_{AB} = 10.9 Hz, 1H), 2.40 (d, A of AB, J_{AB} = 18.4 Hz, 1H), 2.13 (d, B of AB, J_{AB} = 18.4 Hz, 1H), 1.25 (s, 3H), 1.13 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 208.49 (e), 178.19 (e), 168.61 (o), 133.71 (o), 68.72 (e), 45.65 (e), 45.39 (e), 38.98 (e), 27.19 (o), 23.01 (o).

IR (Neat) 2963 (w), 2934 (w), 2875 (w), 1714 (s), 1588 (w), 1480 (w), 1459 (w), 1281 (m), 1140 (s), 1035 (m), 797 (m), 769 (w) cm^{-1}.

HRMS (ESI, $[M+H]^+$) calcd for $C_{12}H_{19}O_3$ 211.1329, found 211.1318.



Methyl 4-oxo-1-propylcyclopent-2-enecarboxylate (2m)

Color and state: Colorless oil.

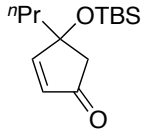
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, J = 5.6 Hz, 1H), 6.11 (d, J = 5.7 Hz, 1H), 3.70

(s, 3H), 2.92 (d, A of AB, J_{AB} = 18.8 Hz, 1H), 2.27 (d, B of AB, J_{AB} = 18.8 Hz, 1H), 1.85 (ddd, A of ABXY, J_{AB} = 13.4 Hz, J_{AX} = 9.9 Hz, J_{AY} = 7.0 Hz, 1H), 1.67 (ddd, B of ABXY, J_{AB} = 13.5 Hz, J_{BX} = 10.0 Hz, J_{BY} = 6.8 Hz, 1H), 1.29-1.21 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 207.52 (e), 173.52 (e), 165.14 (o), 133.36 (o), 56.04 (e), 52.66 (o), 43.54 (e), 40.55 (e), 18.72 (e), 14.24 (o).

IR (Neat) 2959 (w), 2934 (w), 2874 (w), 1716 (s), 1590 (w), 1435 (w), 1223 (m), 1191 (m), 1162 (s), 1118 (m), 1016 (w), 804 (m) cm^{-1}.

HRMS (EI, M^+) calcd for $C_{10}H_{14}O_3$ 182.0943, found 182.0941.



4-((*tert*-Butyldimethylsilyl)oxy)-4-propylcyclopent-2-enone (2n)

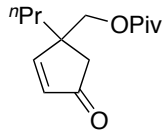
Color and state: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, J = 5.7 Hz, 1H), 6.09 (d, J = 5.7 Hz, 1H), 2.50 (d, A of AB, J_{AB} = 18.3 Hz, 1H), 2.43 (d, B of AB, J_{AB} = 18.3 Hz, 1H), 1.68 (ddd, A of ABXY, J_{AB} = 13.3 Hz, J_{AX} = 11.4 Hz, J_{AY} = 5.4 Hz, 1H), 1.61 (ddd, B of ABXY, J_{AB} = 13.3 Hz, J_{BX} = 11.1 Hz, J_{BY} = 5.3 Hz, 1H), 1.44-1.31 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H), 0.85 (s, 9H), 0.04 (s, 3H), 0.03 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 207.10 (e), 167.14 (o), 132.89 (o), 81.12 (e), 49.64 (e), 44.49 (e), 25.75 (o), 18.16 (e), 17.80 (e), 14.54 (o), –2.23 (o), –2.48 (o).

IR (Neat) 2956 (m), 2930 (m), 2856 (w), 1721 (s), 1590 (w), 1463 (w), 1253 (m), 1192 (m), 1075 (s), 1046 (s), 938 (m), 832 (s), 803 (s), 772 (vs), 680 (m) cm^{-1}.

HRMS (ESI, $[M+H]^+$) calcd for $C_{14}H_{27}O_2Si$ 255.1775, found 255.1768.



(4-Oxo-1-propylcyclopent-2-en-1-yl)methyl pivalate (2o)

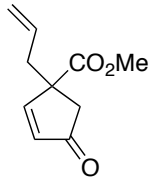
Color and state: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, J = 5.6 Hz, 1H), 6.09 (d, J = 5.6 Hz, 1H), 4.14 (d, A of AB J_{AB} = 10.9 Hz, 1H), 3.91 (d, B of AB J_{AB} = 10.9 Hz, 1H), 2.26 (d, A of AB, J_{AB} = 18.5 Hz, 1H), 2.18 (d, B of AB, J_{AB} = 18.5 Hz, 1H), 1.57-1.44 (m, 2H), 1.28-1.17 (m, 2H), 1.10 (s, 9H), 0.88 (t, J = 7.3 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 208.44 (e), 178.13 (e), 167.85 (o), 134.16 (o), 67.72 (e), 49.27 (e), 43.21 (e), 38.92 (e), 37.94 (e), 27.13 (o), 17.66 (e), 14.60 (o).

IR (Neat) 3081 (w), 2972 (w), 2934 (w), 2873 (w), 1714 (s), 1589 (w), 1480 (m), 1280 (m), 1142 (s), 1035 (w), 992 (w), 920 (m), 796 (m) cm^{-1}.

HRMS (EI, M^+) calcd for $C_{14}H_{22}O_3$ 238.1569, found 238.1561.



Methyl 1-allyl-4-oxocyclopent-2-enecarboxylate (2p)

Color and state: Colorless oil.

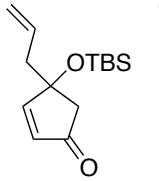
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, J = 5.6 Hz, 1H), 6.15 (d, J = 5.6 Hz, 1H), 5.61 (dddd, J = 16.8, 10.3, 7.7, 6.7 Hz, 1H), 5.13-5.08 (m, 2H), 3.71 (s, 3H), 2.88 (d, A of AB,

J_{AB} = 18.8 Hz, 1H), 2.60 (dd, A of ABX J_{AB} = 13.7 Hz, J_{AX} = 7.8 Hz, 1H), 2.51 (ddt, B of $ABXY_2$, J_{AB} = 13.8 Hz, J_{BX} = 6.9 Hz, J_{BY} = 1.2 Hz, 1H), 2.32 (d, B of AB, J_{AB} = 18.8 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 207.16 (e), 173.06 (e), 164.27 (o), 134.05 (o), 131.91 (o), 120.06 (e), 55.56 (e), 52.78 (o), 42.90 (e), 42.09 (e).

IR (Neat) 3080 (w), 2954 (w), 2855 (w), 1716 (s), 1590 (w), 1437 (m), 1217 (m), 1191 (m), 1159 (m), 994 (m), 924 (m), 805 (m) cm^{-1}.

HRMS (ESI, $[M+H]^+$) calcd for $C_{10}H_{13}O_3$ 181.0859, found 181.0858.



4-Allyl-4-((*tert*-butyldimethylsilyl)oxy)cyclopent-2-enone (2q)

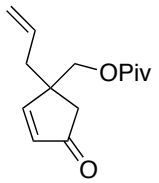
Color and state: Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, J = 5.6 Hz, 1H), 6.10 (d, J = 5.6 Hz, 1H), 5.76 (ddt, J = 17.2, 10.0, 7.2 Hz, 1H), 5.10 (d, J = 10.0 Hz, 1H), 5.07 (d, J = 17.2 Hz, 1H), 2.53 (d, A of AB, J_{AB} = 18.4 Hz, 1H), 2.47-2.38 (m, 2H), 2.40 (d, B of AB, J_{AB} = 18.6 Hz, 1H), 0.85 (s, 9H), 0.04 (s, 3H), 0.03 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 206.61 (e), 166.38 (o), 133.35 (o), 132.92 (o), 119.13 (e), 80.62 (e), 48.88 (e), 46.54 (e), 25.69 (o), 18.12 (e), –2.24 (o), –2.52 (o).

IR (Neat) 3080 (w), 2954 (w), 2930 (m), 2857 (w), 1723 (s), 1641 (w), 1591 (w), 1475 (w), 1252 (m), 1188 (m), 1074 (s), 918 (m), 832 (s), 804 (s), 773 (s), 671 (m) cm^{-1}.

HRMS (ESI, $[M+H]^+$) calcd for $C_{14}H_{25}O_2Si$ 253.1618, found 253.1609.



(1-Allyl-4-oxocyclopent-2-en-1-yl)methyl pivalate (2r)

Color and state: Colorless oil.

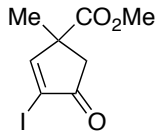
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, J = 5.6 Hz, 1H), 6.14 (d, J = 5.6 Hz, 1H), 5.64 (ddt, J = 17.1, 9.9, 7.3 Hz, 1H), 5.13-5.08 (m, 2H), 4.17 (d, A of AB, J_{AB} = 10.9 Hz, 1H), 3.95 (d, B of AB, J_{AB} = 10.9 Hz, 1H), 2.35-2.25 (m, 4H), 1.13 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 208.00 (e), 178.12 (e), 167.00 (o), 134.75 (o), 132.04 (o), 119.96 (e), 67.58 (e), 48.97 (e), 42.80 (e), 40.16 (e), 38.97 (e), 27.17 (o).

IR (Neat) 2960 (w), 2934 (w), 2874 (w), 1714 (s), 1589 (w), 1480 (m), 1280 (m), 1141 (s), 1035 (m), 796 (m) cm^{-1}.

HRMS (ESI, $[M+H]^+$) calcd for $C_{14}H_{21}O_3$ 237.1485, found 237.1480.

7. Experimental Procedures and Spectral Data for the Cyclopentenones 6, S1 and 7



Methyl 3-iodo-1-methyl-4-oxocyclopent-2-enecarboxylate (6)

A solution of iodine (254 mg, 1.0 mmol) in a mixture of anhydrous carbon tetrachloride (1.0 mL) and pyridine (1.0 mL) was added dropwise to a solution of methyl 1-methylcyclopent-3-enecarboxylate **2j** (38.5 mg, 0.25 mmol) in anhydrous carbon tetrachloride (1.0 mL) and pyridine (1.0 mL) at 0 °C under an atmosphere of argon. The mixture was allowed to warm to room temperature and stirred for *ca*. 24 hours (t.l.c. control) before being diluted

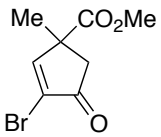
with ether (50 mL) and washed successively with water, aqueous hydrochloric acid solution (1 N), water and 20% aqueous sodium thiosulfate solution. The combined organics were dried (anhyd. $MgSO_4$), filtered and concentrated *in vacuo* to afford a crude oil. Purification by flash column chromatography (silica gel, eluting with 10-20% ethyl acetate/hexanes) furnished *vinyl iodide* **6** (64.4 mg, 92%) as a pale-yellow solid; **mp** = 57-59 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (s, 1H), 3.74 (s, 3H), 3.12 (d, A of AB, J_{AB} = 18.8 Hz, 1H), 2.37 (d, B of AB, J_{AB} = 18.8 Hz, 1H), 1.52 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 201.59 (e), 173.03 (e), 170.18 (o), 102.67 (e), 53.63 (e), 53.13 (o), 42.97 (e), 24.77 (o).

IR (Neat) 2953 (w), 2935 (w), 1722 (s), 1579 (w), 1456 (w), 1435 (w), 1272 (m), 1165 (m), 1102 (w), 907 (w), 867 (w) cm^{-1}.

HRMS (EI, M^+) calcd for $C_8H_9{}^{127}IO_3$ 279.9596, found 279.9589.



Methyl 3-iodo-1-methyl-4-oxocyclopent-2-enecarboxylate (S1)

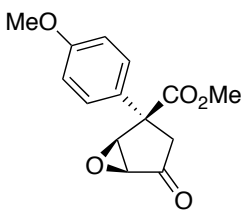
A solution of bromine (39.9 mg, 0.25 mmol) in anhydrous dichloromethane (1.0 mL) was added to a stirred solution of methyl 1-methylcyclopent-3-enecarboxylate **2j** (38.5 mg, 0.25 mmol) in anhydrous dichloromethane (2.0 mL) at 0 °C under an atmosphere of argon. After stirring for *ca*. 5 minutes, a solution of triethylamine (37.9 mg, 0.38 mmol) in anhydrous dichloromethane (2.0 mL) was added, and the reaction was allowed to warm to room temperature and stirred for *ca*. 2 hours (t.l.c. control). The reaction mixture was filtered through celite and concentrated *in vacuo* to afford the crude product. Purification by flash column chromatography (silica gel, eluting with 10-20 ethyl acetate/hexanes) furnished *vinyl bromide* **S1** (52.3 mg, 90%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (s, 1H), 3.72 (s, 3H), 3.10 (d, A of AB, J_{AB} = 18.8 Hz, 1H), 2.36 (d, J = 18.8 Hz, 1H), 1.51 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 199.24 (e), 172.98 (e), 162.68 (o), 125.78 (e), 53.08 (o), 50.62 (e), 44.20 (e), 24.71 (o).

IR (Neat) 3070 (w), 2955 (w), 1721 (s), 1592 (m), 1456 (w), 1435 (m), 1271 (s), 1193 (m), 1164 (s), 1100 (m), 925 (m), 865 (m), 696 (m) cm^{-1}.

HRMS (ESI, $[M+H]^+$) calcd for $C_8H_{10}{}^{79}BrO_3$ 232.9808, found 232.9800.



(1*S,2*R**,5*S**)-Methyl-2-(4-methoxyphenyl)-4-oxo-6-oxabicyclo[3.1.0]hexane-2-carboxylate (7).**

Hydrogen peroxide (0.35 ml, 0.75 mmol, 30% aq. soln.) was added dropwise to a stirred solution of methyl 1-(4-methoxyphenyl)-4-oxocyclopent-2-enecarboxylate **2d** (61.5 mg, 0.25 mmol) in methanol (3.0 mL) at 0 °C over *ca*. 1 minute. Sodium hydroxide (0.12 mL, 0.25 mmol, 6.0 M aq. soln.) was then added dropwise, and

the mixture was allowed to warm to room temperature and stirred for an additional *ca*. 3 hours (t.l.c. control). The reaction was partitioned between water and ethyl acetate, and the combined organic phases were dried (anhyd. $MgSO_4$), filtered and concentrated *in vacuo* to afford the crude product. Purification by flash column chromatography (silica gel, eluting with 10-30% ethyl acetate/hexanes) furnished *epoxide* **7** (53.7 mg, 82% yield) as a colorless crystalline solid; **mp** = 83-85 ºC.

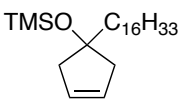
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 4.31 (d, J = 1.9 Hz, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 3.50 (d, J = 2.0 Hz, 1H), 3.09 (d, A of AB, J_{AB} = 18.1 Hz, 1H), 2.51 (d, B of AB, J_{AB} = 18.1 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 206.15 (e), 172.66 (e), 159.57 (e), 129.99 (e), 126.85 (o), 114.84 (o), 61.89 (o), 55.57 (o), 55.36 (o), 53.56 (e), 52.91 (o), 41.83 (e).

IR (Neat) 2954 (w), 2923 (m), 2850 (w), 1737 (s), 1610 (w), 1514 (s), 1439 (w), 1254 (s), 1234 (s), 1185 (m), 1031 (m), 869 (m), 832 (m) cm^{-1}.

HRMS (EI, M^+) calcd for $C_{14}H_{14}O_5$ 262.0841, found 262.0845.

8. Experimental Procedures and Spectral Data for the Synthesis of (±)-Untenone (4).



(1-Heptadecylcyclopent-3-enyloxy)trimethylsilane (9).

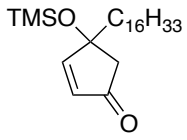
A solution of Hoveyda-Grubbs second-generation catalyst (0.16 g, 2.5 mol%) in anhydrous dichloromethane (100 mL) was added dropwise to the diene **8** (3.37 g, 10 mmol) and the resulting mixture stirred at ambient temperature for *ca*. 16 hours (t.l.c. control). The reaction mixture was then cooled with stirring to 0 °C and diisopropylethylamine (2.6 mL, 15 mmol) followed by trimethylsilyl trifluoromethanesulfonate (2.17 mL, 12.0 mmol) were sequentially added and the resulting reaction mixture stirred at 0 °C for *ca*. 1 hour (t.l.c. control). The reaction mixture was then partitioned between water and diethyl ether, and the combined organic phases washed with saturated aqueous ammonium chloride solution, saturated aqueous sodium chloride solution, dried (anhyd. $MgSO_4$), filtered and concentrated *in vacuo* to afford a crude oil. Purification by flash column chromatography (silica gel, eluting with hexanes) furnished the *cyclopentene* **9** (3.43 g, 90%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.64 (s, 2H), 2.45 (d, A of AB, J_{AB} = 16.1 Hz, 1H), 2.38 (d, B of AB, J_{AB} = 16.1 Hz, 1H), 1.60-1.57 (m, 2H), 1.39-1.33 (m, 2H), 1.30-1.26 (br. m, 28H), 0.89 (t, J = 7.0 Hz, 3H), 0.09 (s, 9H).

^{1}C NMR (125 MHz, $CDCl_3$) δ 128.95 (o), 84.29 (e), 47.06 (e), 43.22 (e), 32.13 (e), 30.37 (e), 29.91 (e), 29.87 (e), 29.57 (e), 24.81 (e), 22.89 (e), 14.28 (o), 2.22 (o).

IR (Neat) 3059 (w), 2923 (s), 2853 (s), 1467 (w), 1316 (w), 1250 (m), 1065 (m), 839 (s), 754 (w), 670 (w) cm^{-1}.

HRMS (EI, M^+) calcd for $C_{24}H_{48}OSi$ 380.3474, found 380.3470.



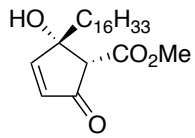
4-Heptadecyl-4-(trimethylsilyloxy)cyclopent-2-enone (10). Prepared in accordance with the general procedure for the copper(I) iodide catalyzed allylic oxidation of cyclopentenes, using the cyclopentene **9** (1.0 g, 2.6 mmol). Purification by flash column chromatography (silica gel, eluting with 5% ethyl acetate/hexanes) furnished the *cyclopentenone* **10** (726 mg, 70%) as a colorless oil with ≥19:1 site-selectivity.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, J = 5.7 Hz, 1H), 6.07 (d, J = 5.8 Hz, 1H), 2.48 (d, A of AB, J_{AB} = 18.3 Hz, 1H), 2.44 (d, B of AB, J_{AB} = 18.5 Hz, 1H), 2.40-2.34 (m, 1H), 1.70-1.63 (m, 1H), 1.58-1.51 (m, 1H), 1.28-1.20 (br. m, 27H), 0.85 (t, J = 6.8 Hz, 3H), 0.08 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 206.81 (e), 166.86 (o), 132.94 (o), 81.36 (e), 49.65 (e), 42.03 (e), 32.03 (e), 29.97 (e), 29.79 (e), 29.76 (e), 29.72 (e), 29.66 (e), 29.61 (e), 29.46 (e), 24.40 (e), 22.78 (e), 14.20 (o), 2.23 (o).

IR (Neat) 2923 (s), 2853 (m), 1724 (s), 1465 (w), 1251 (m), 1075 (m), 839 (s), 754 (m) cm^{-1}.

HRMS (EI, M^+) calcd for $C_{24}H_{46}O_2Si$ 394.3267, found 394.3262.



(±)-Untenone (4). *n*-Butyllithium (0.28 mL, 0.70 mmol, 2.5 M in hexane) was added to a stirred solution of diisopropylamine (0.09 mL, 0.70 mmol) in anhydrous tetrahydrofuran (2.50 mL) at 0 °C. The reaction was cooled to –78 °C and a solution of cyclopentenone **10** (0.099 g, 0.25 mmol) in tetrahydrofuran (1.0 mL) was added. The mixture was stirred at –78 °C for *ca*. 1 hour before a solution of methyl cyanoformate (0.05 mL, 0.60 mmol) in HMPA (0.25 mL) was added dropwise, and the reaction stirred for an hour and warmed slowly to room temperature. The reaction was carefully quenched with methanol (5 mL) at 0 °C and stirred vigorously for *ca*. 1 hour followed by the addition concentrated hydrochloric acid (1 drop). The mixture was then partitioned between water and ethyl acetate, and the combined organic phases were dried (anhyd. $MgSO_4$), filtered and concentrated *in vacuo* to afford a crude oil. Purification by flash column chromatography (silica gel, eluting with 15-25% ethyl acetate/hexanes) afforded (±)-untenone (**4**) (62.0 mg, 65%) as a white crystalline solid; **mp** = 63-65 °C (Lit. **mp** = 62-64 °C).[1]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, J = 5.7 Hz, 1H), 6.18 (d, J = 5.6 Hz, 1H), 3.78 (s, 3H), 3.62 (br. s, 1H), 3.45 (s, 1H), 1.83-1.77 (m, 1H), 1.73-1.66 (m, 1H), 1.27-1.22 (br. m, 28H), 0.87 (t, J = 6.9 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 200.10 (e), 169.19 (e), 167.20 (o), 132.49 (o), 80.03 (e), 60.99 (o), 53.04 (o), 40.52 (e), 32.06 (e), 29.89 (e), 29.82 (e), 29.81 (e), 29.79 (e), 29.77 (e), 29.74 (e), 29.66 (e), 29.57 (e), 29.49 (e), 23.99 (e), 22.82 (e), 14.25 (o).

IR (Neat) 3600-3200 (br. w), 2922 (s), 2853 (s), 1736 (s), 1713 (s), 1464 (m), 1436 (m), 1312 (m), 1153 (m), 1032 (m), 813 (w), 721 (w) cm^{-1}.

HRMS (ESI, $[M+Na]^+$) calcd for $C_{23}H_{40}NaO_4$ 403.2819, found 403.2812.

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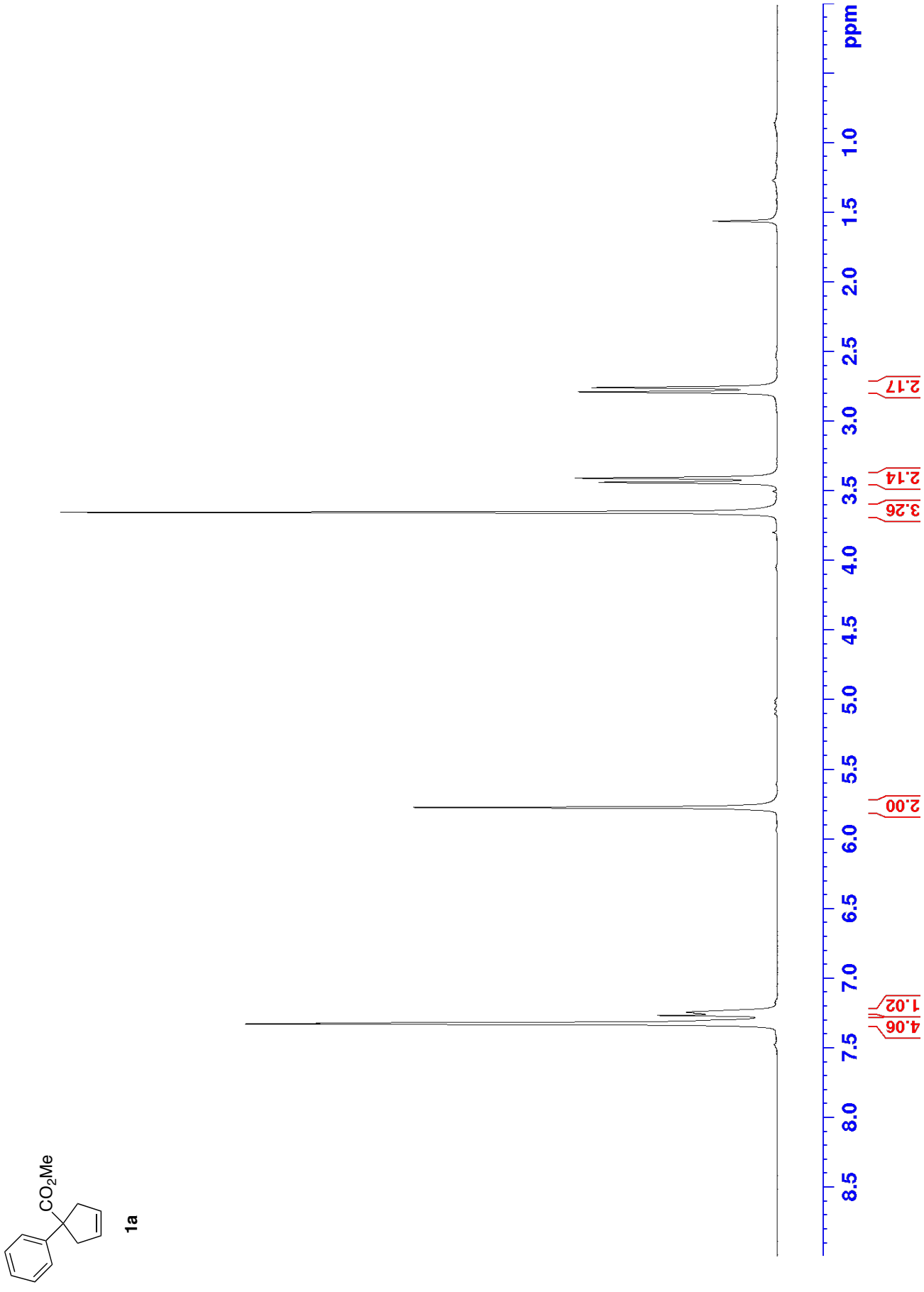
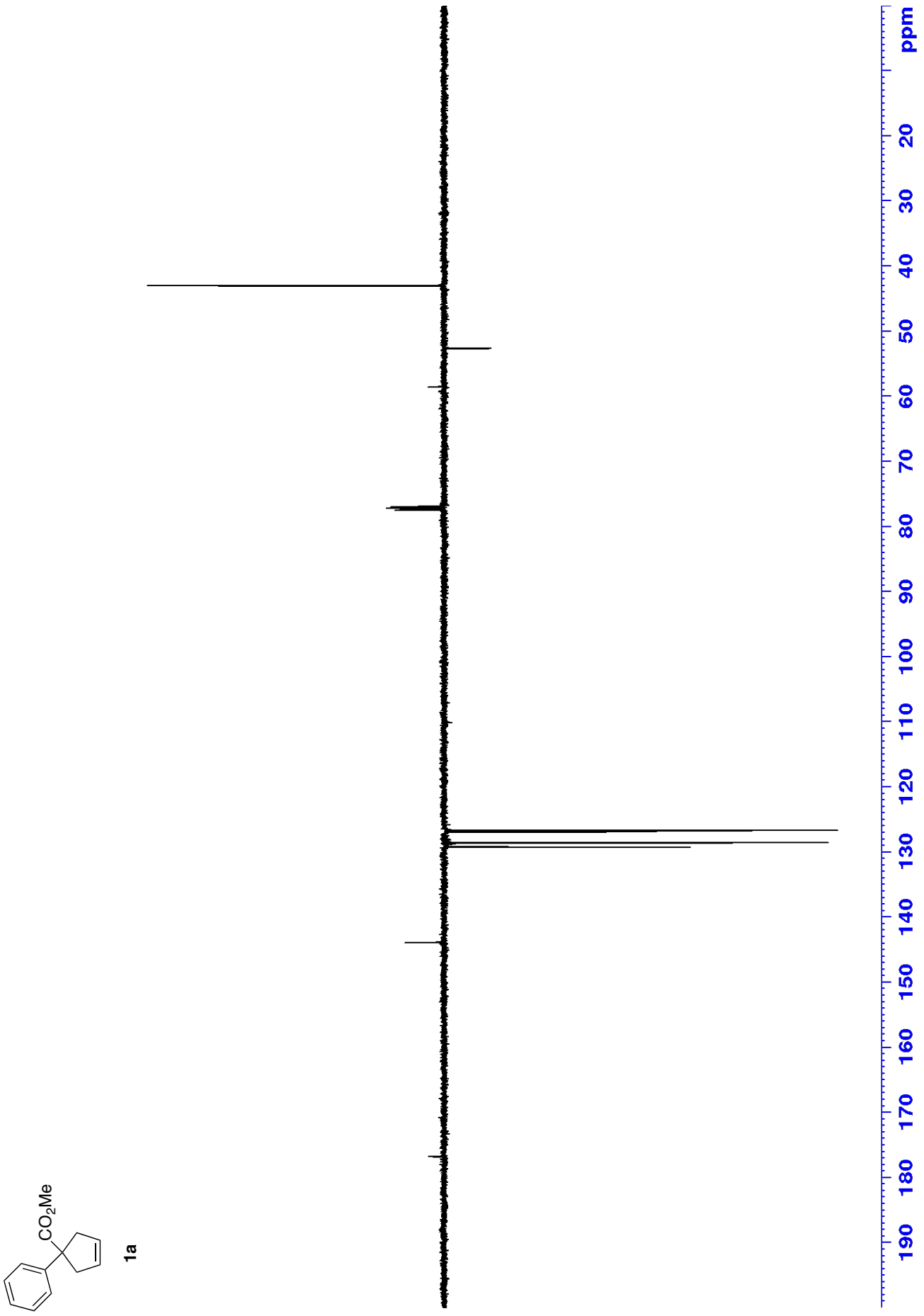
[1] M. Asami, T. Ishizaki and S. Inoue, *Tetrahedron Lett*., 1995, **36**, 1893.

9. Copies of all NMR Spectra

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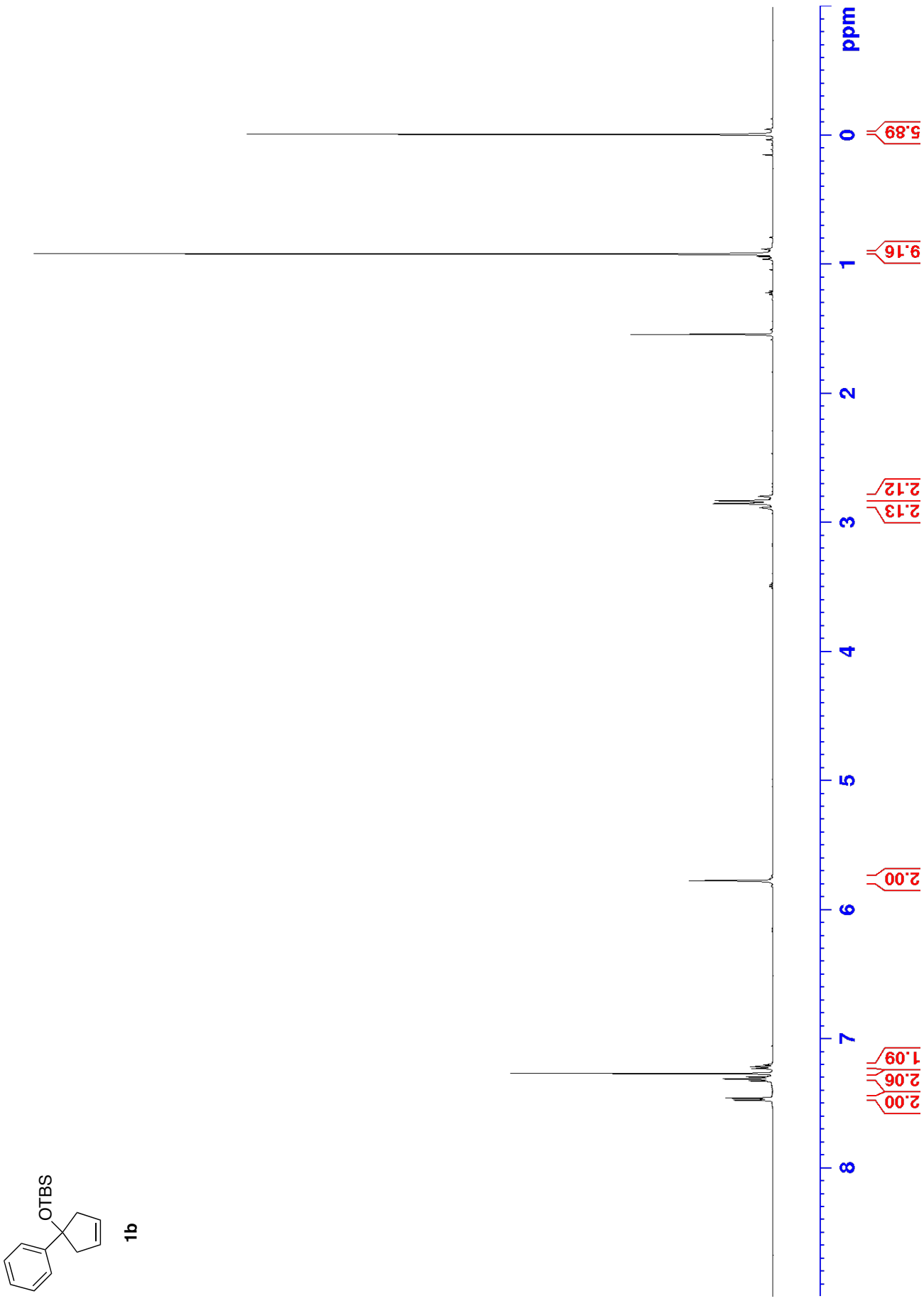
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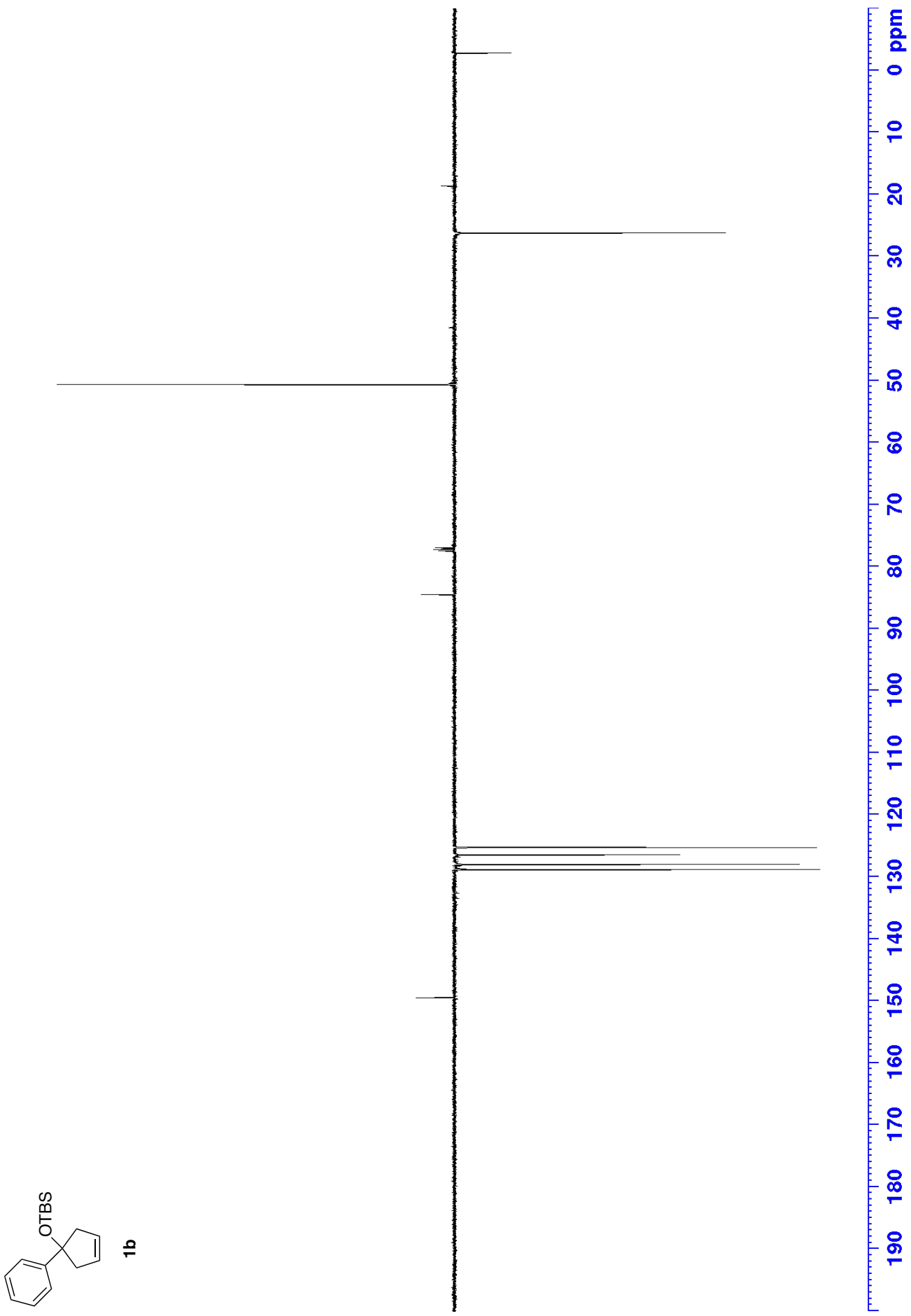
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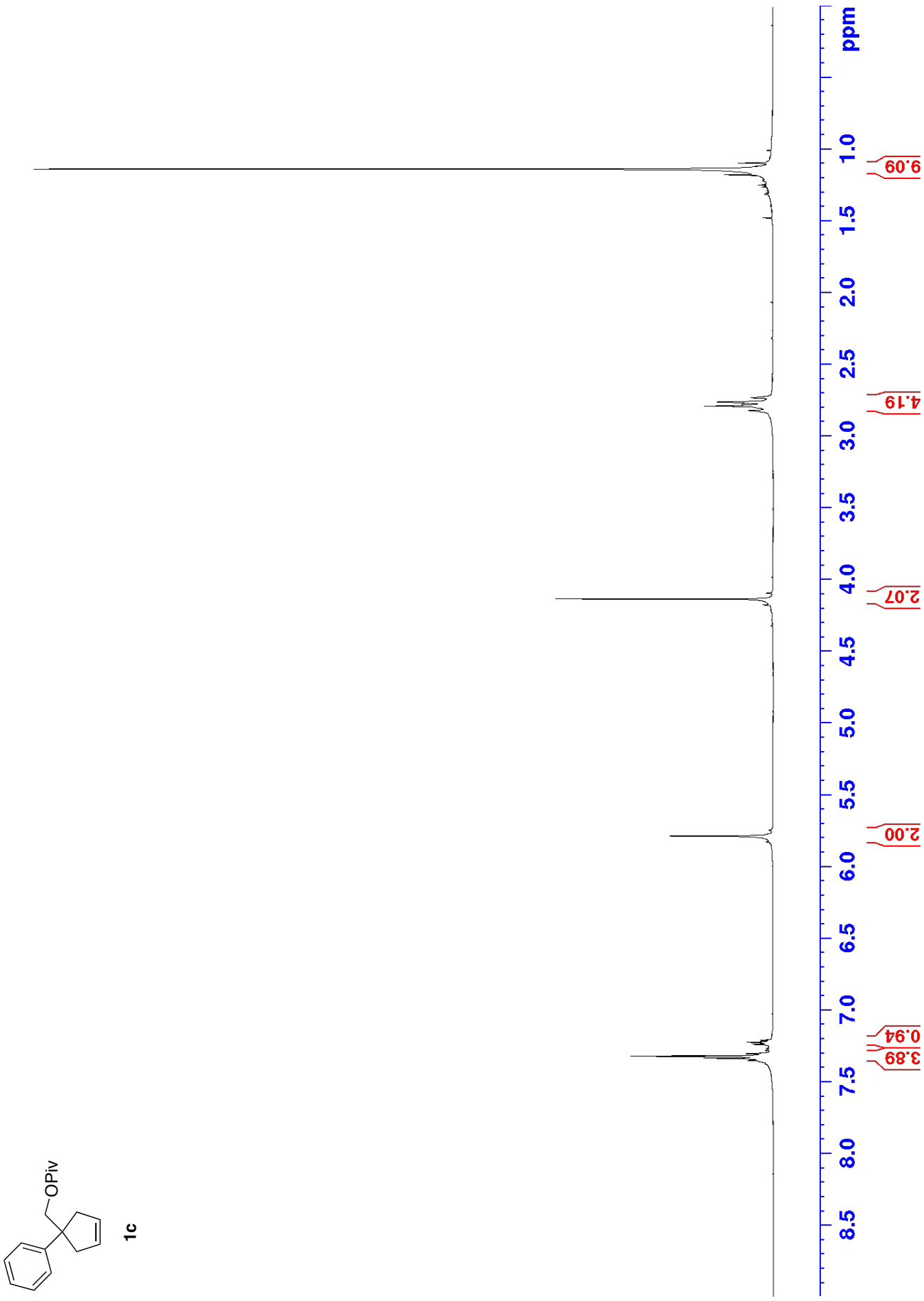
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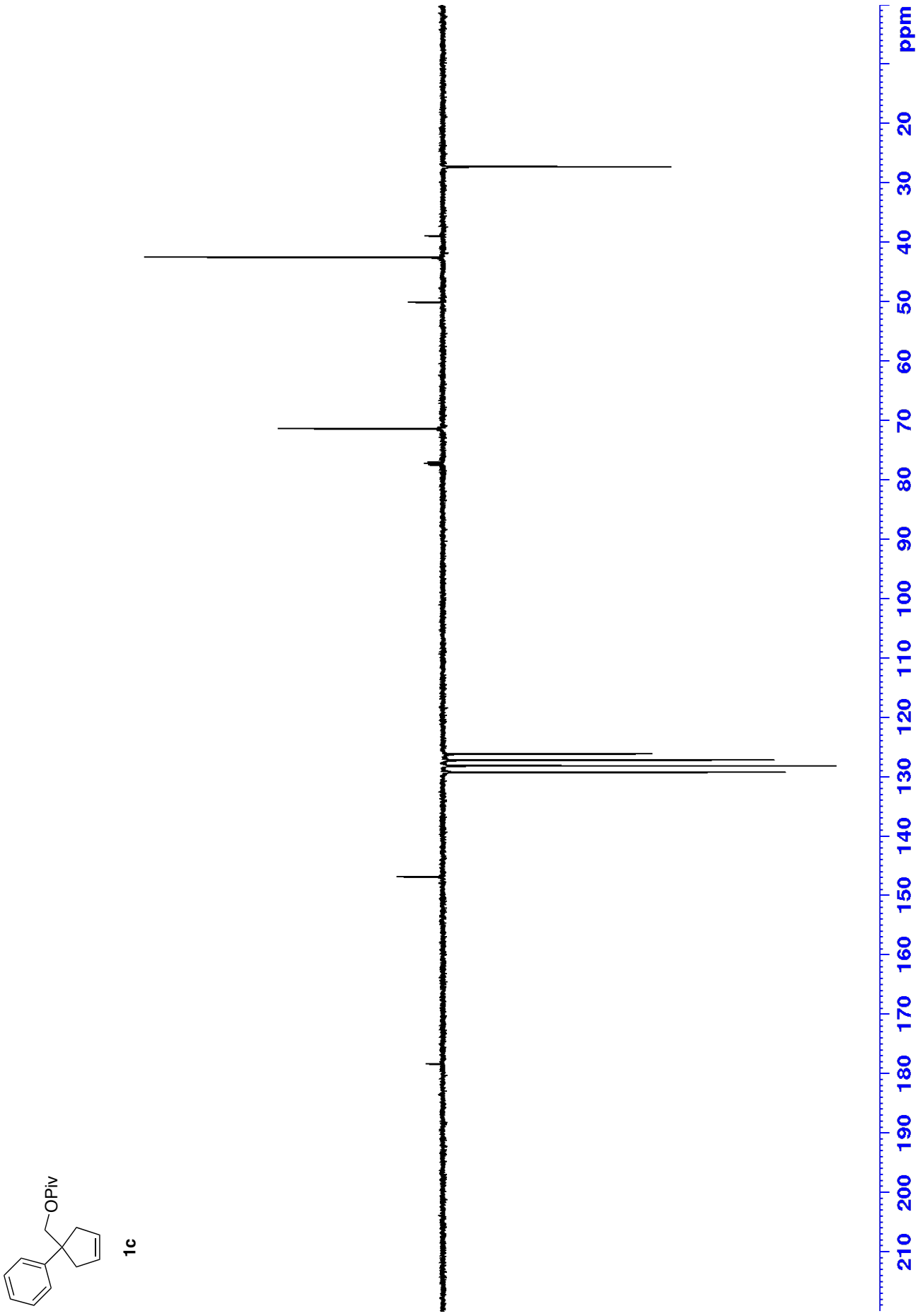
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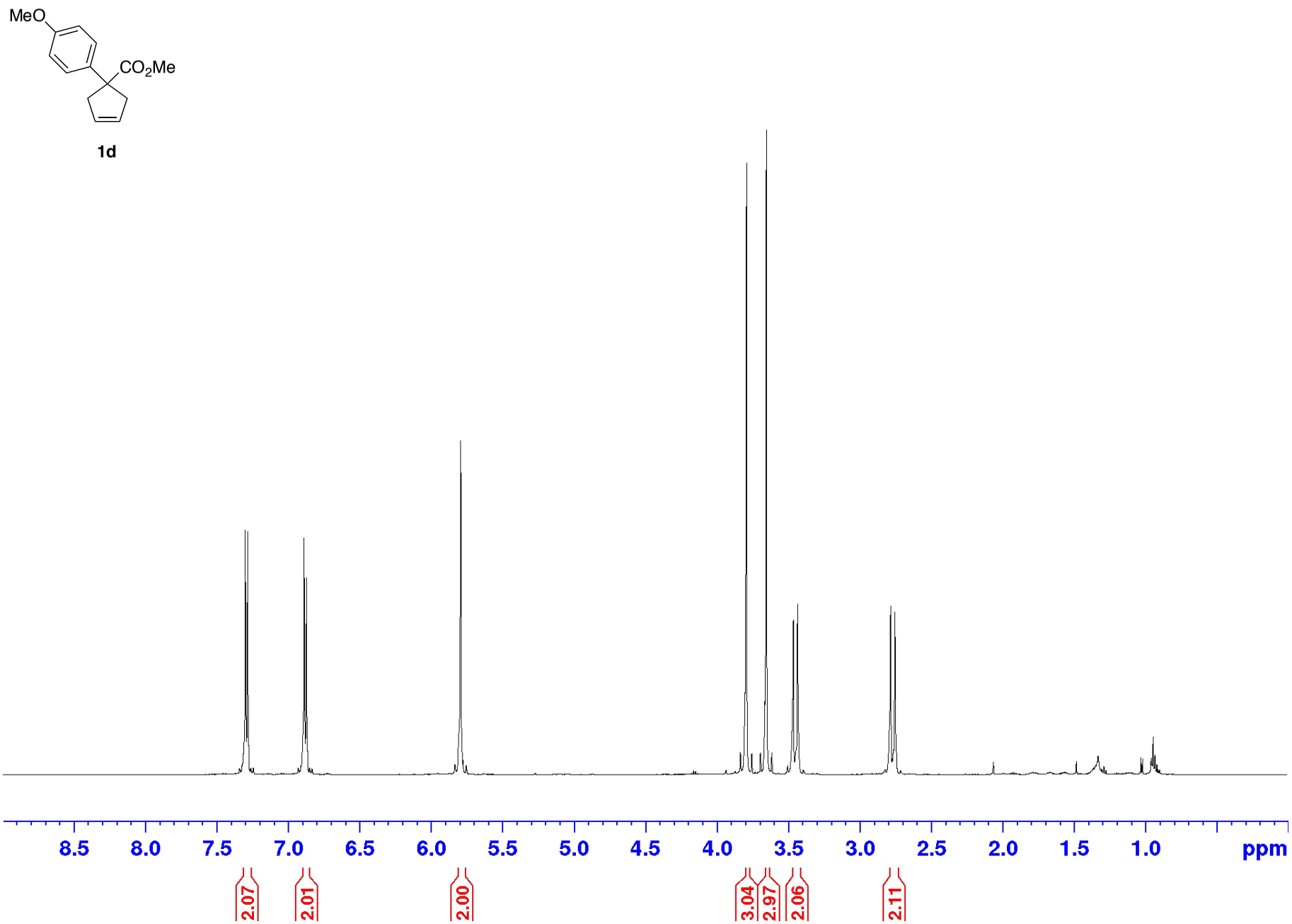
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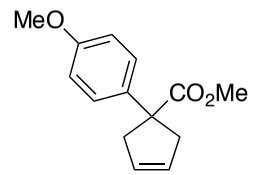
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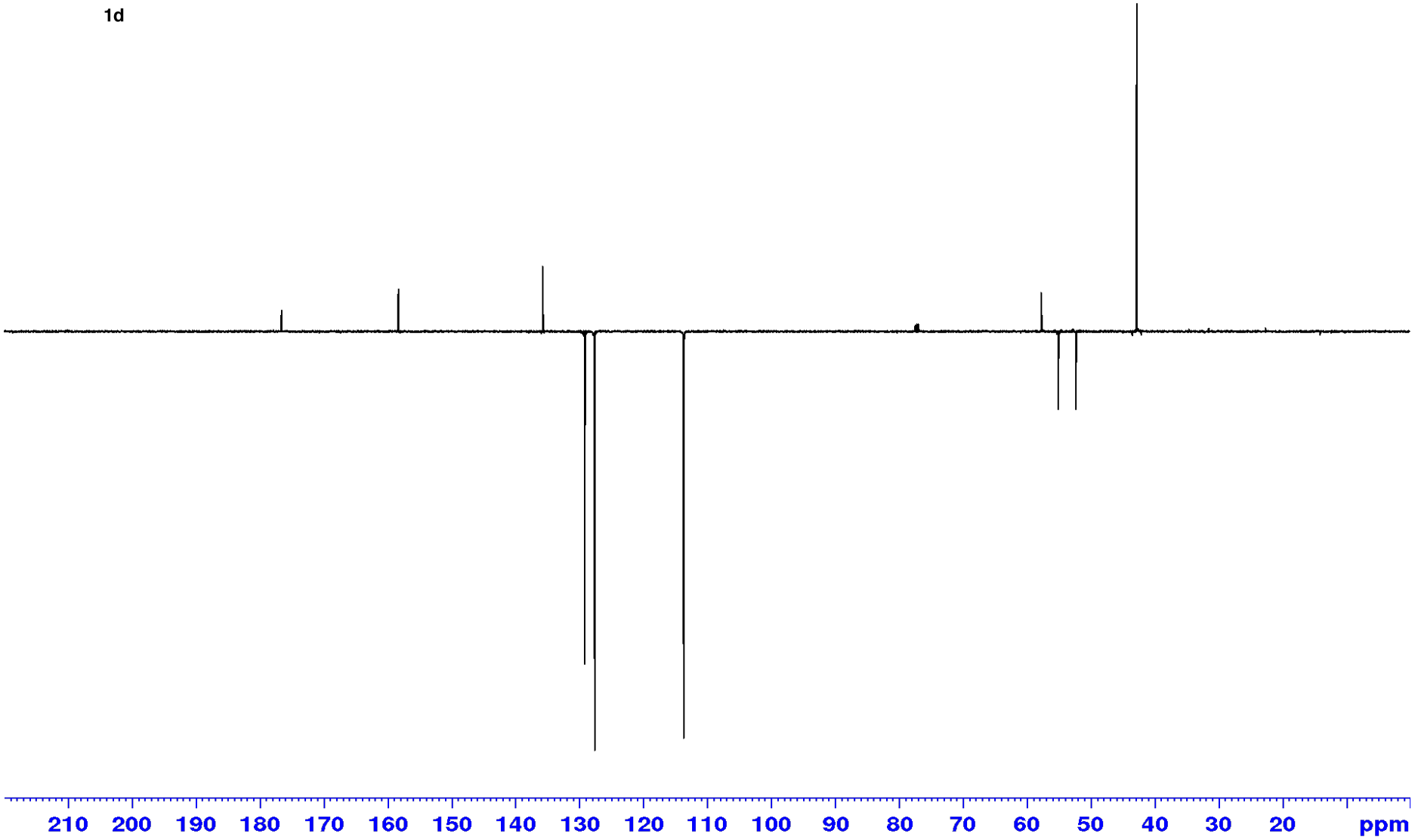
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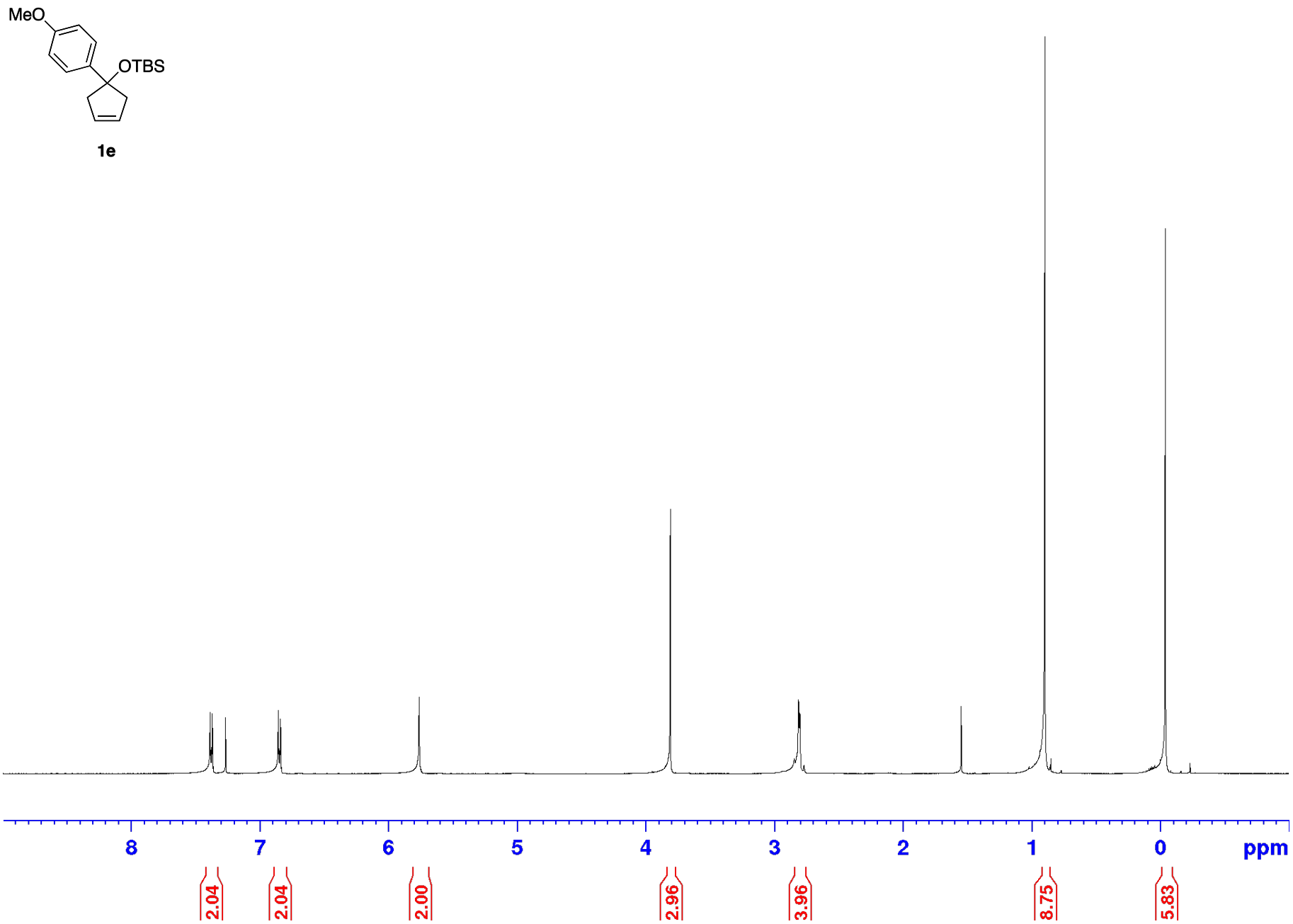
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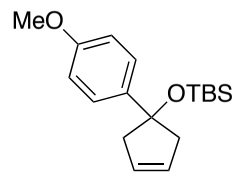
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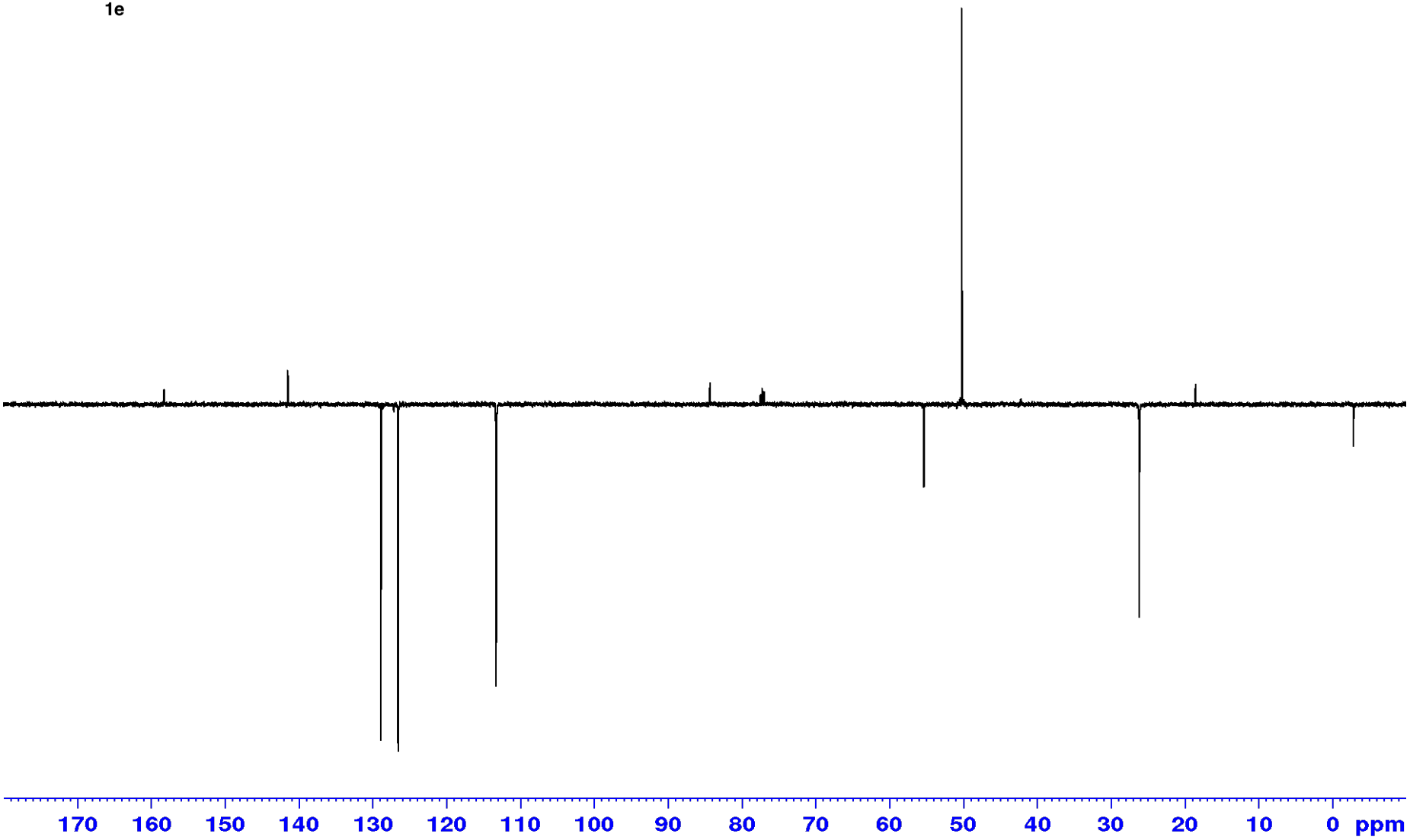
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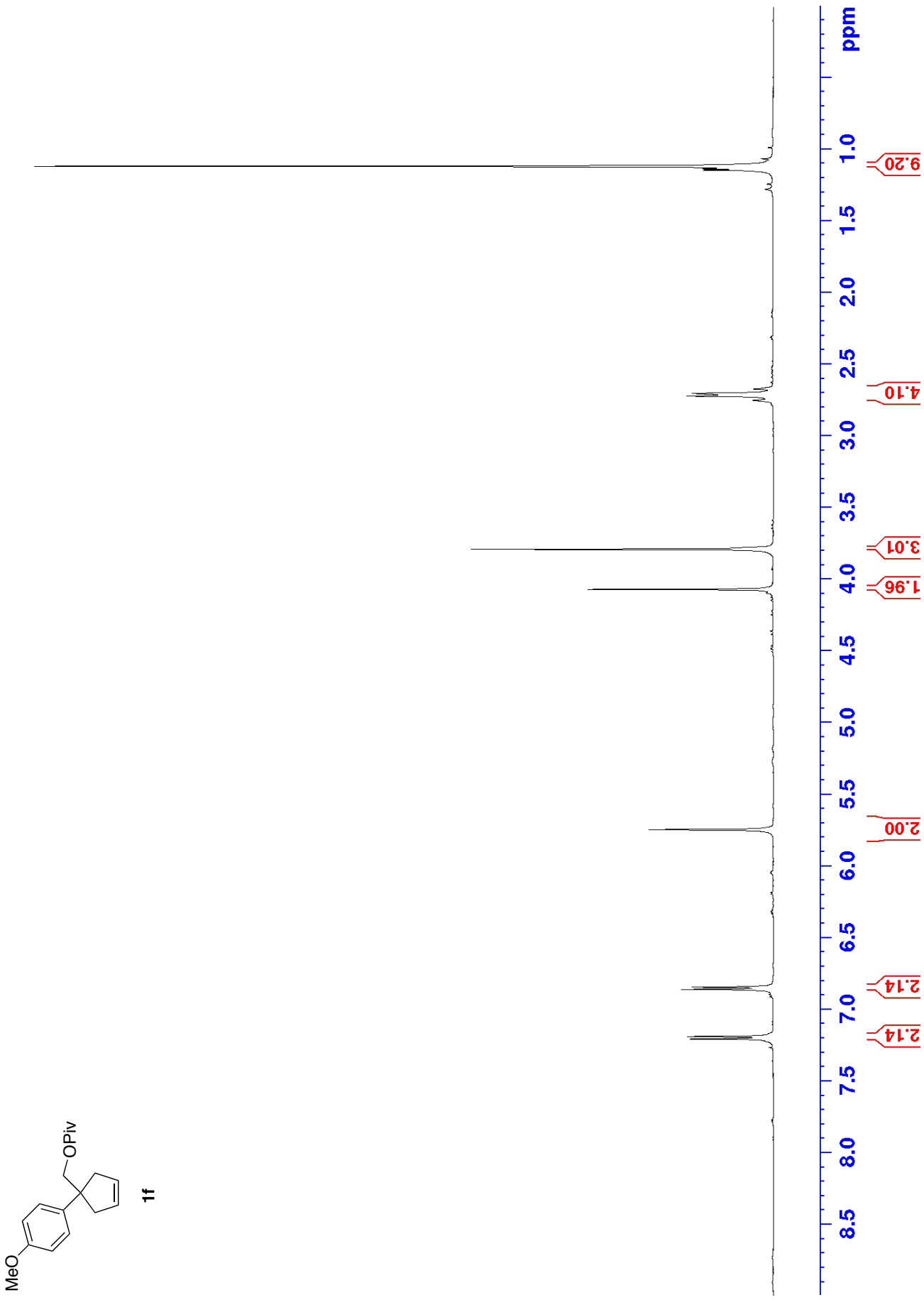
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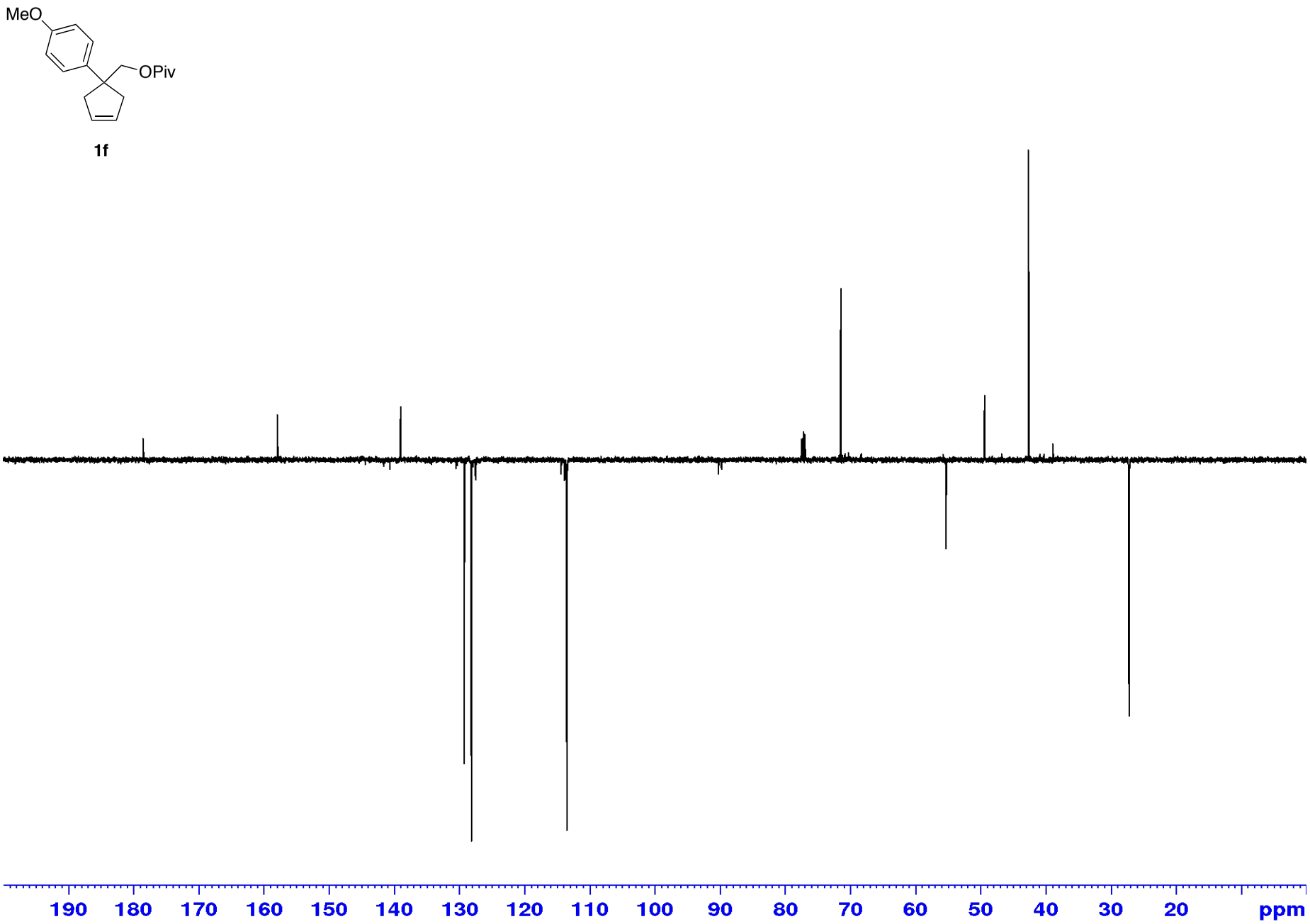
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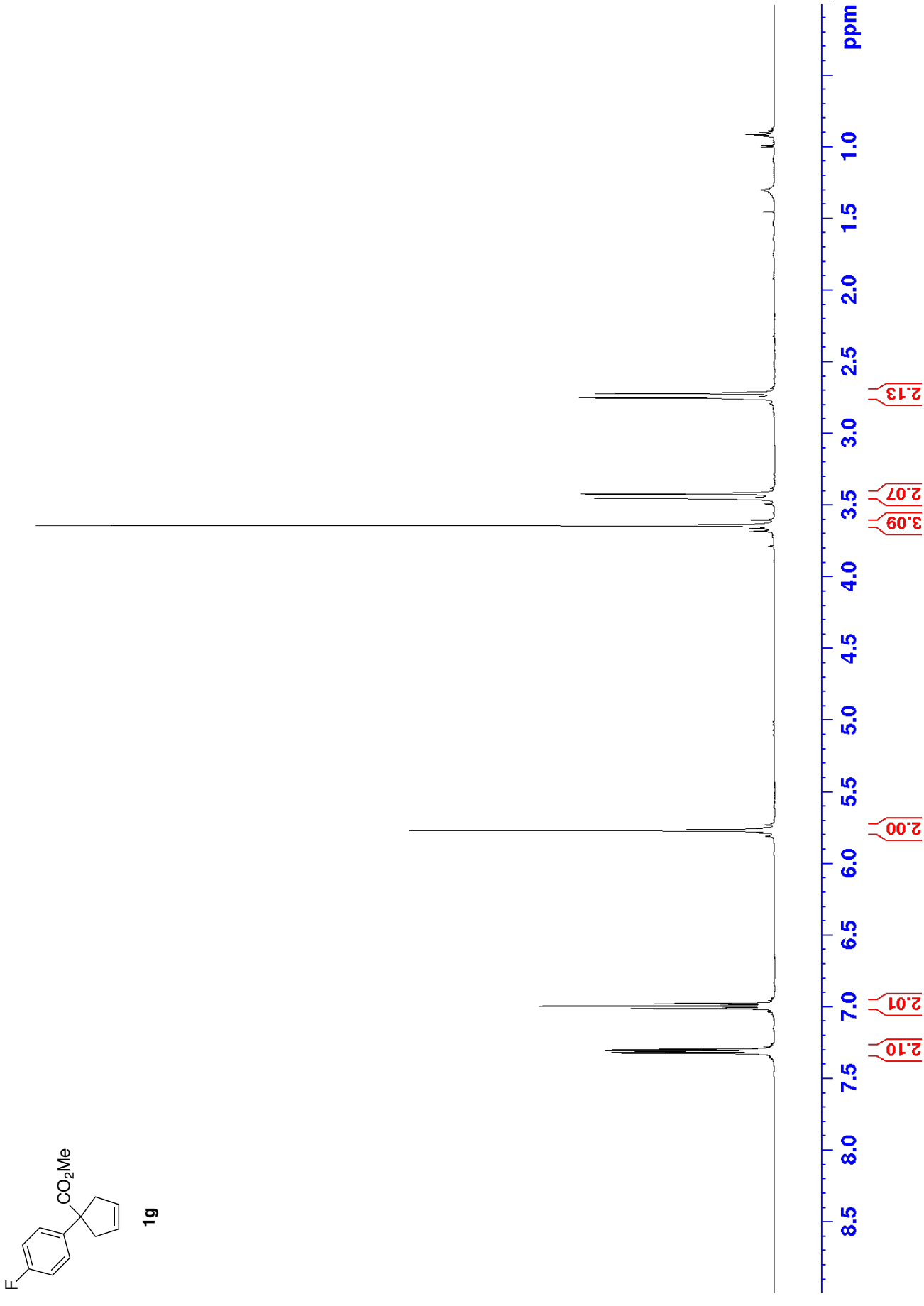
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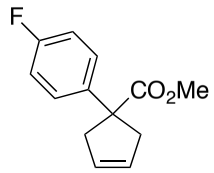
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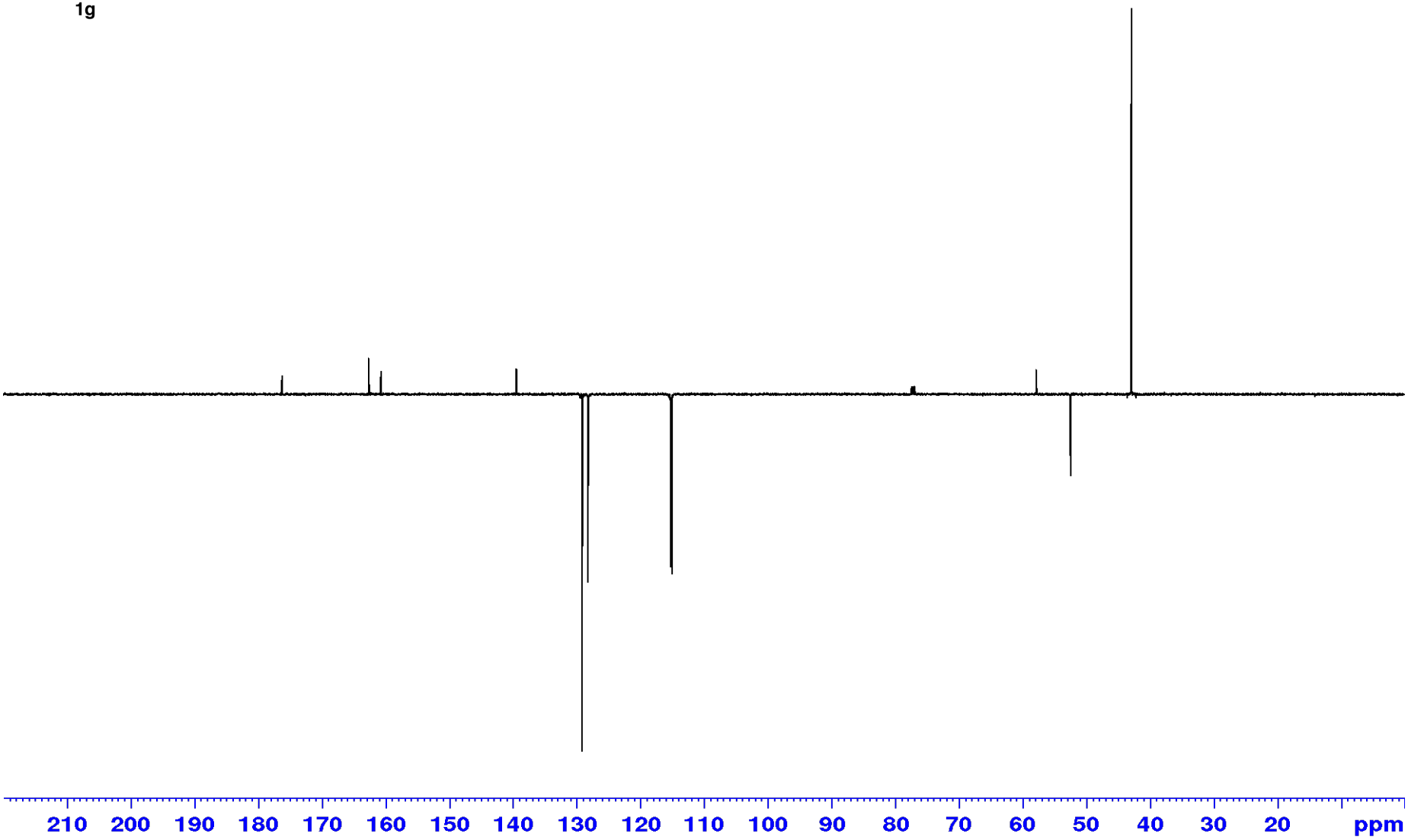
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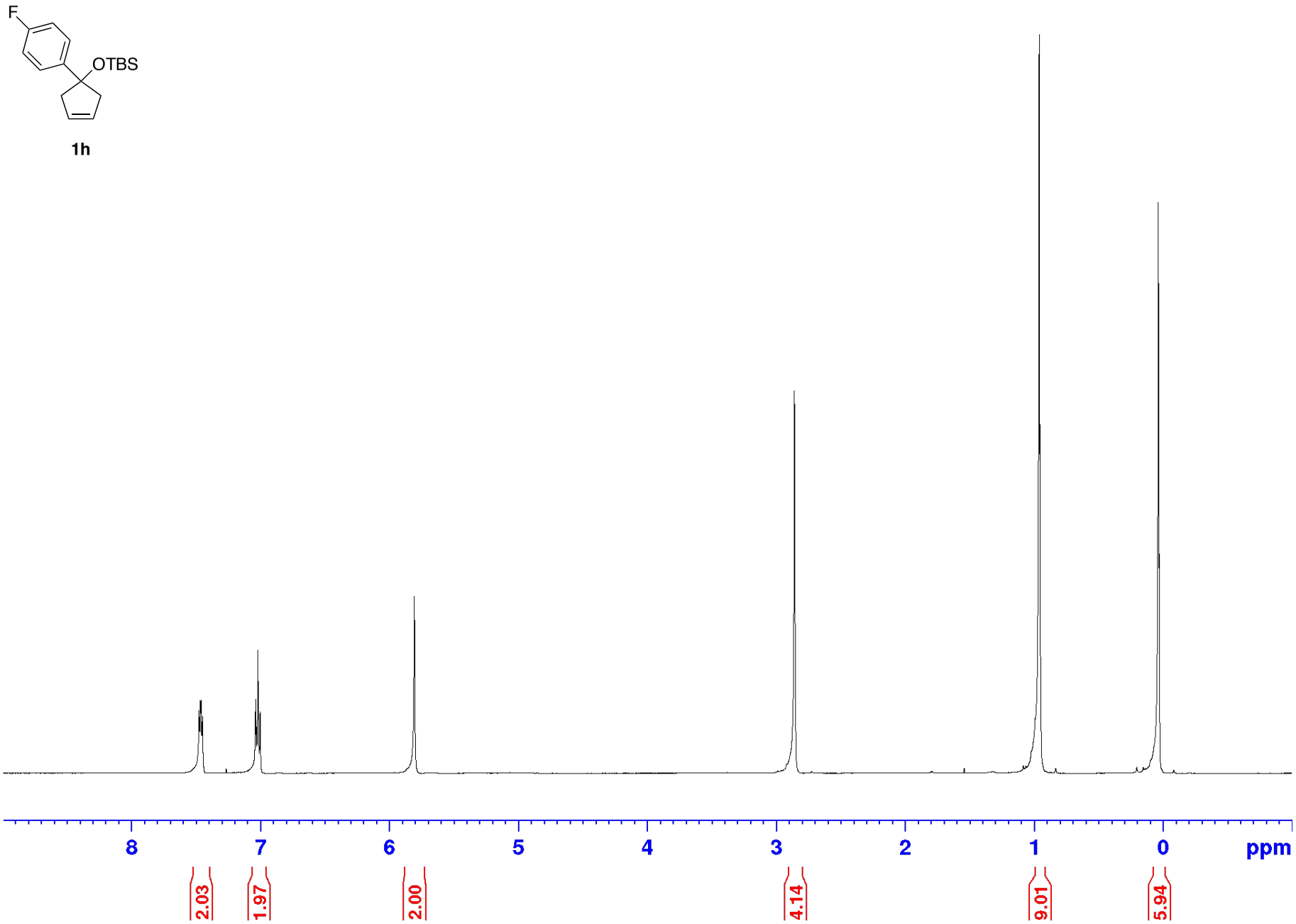
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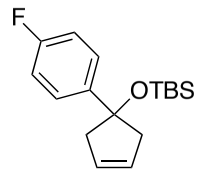
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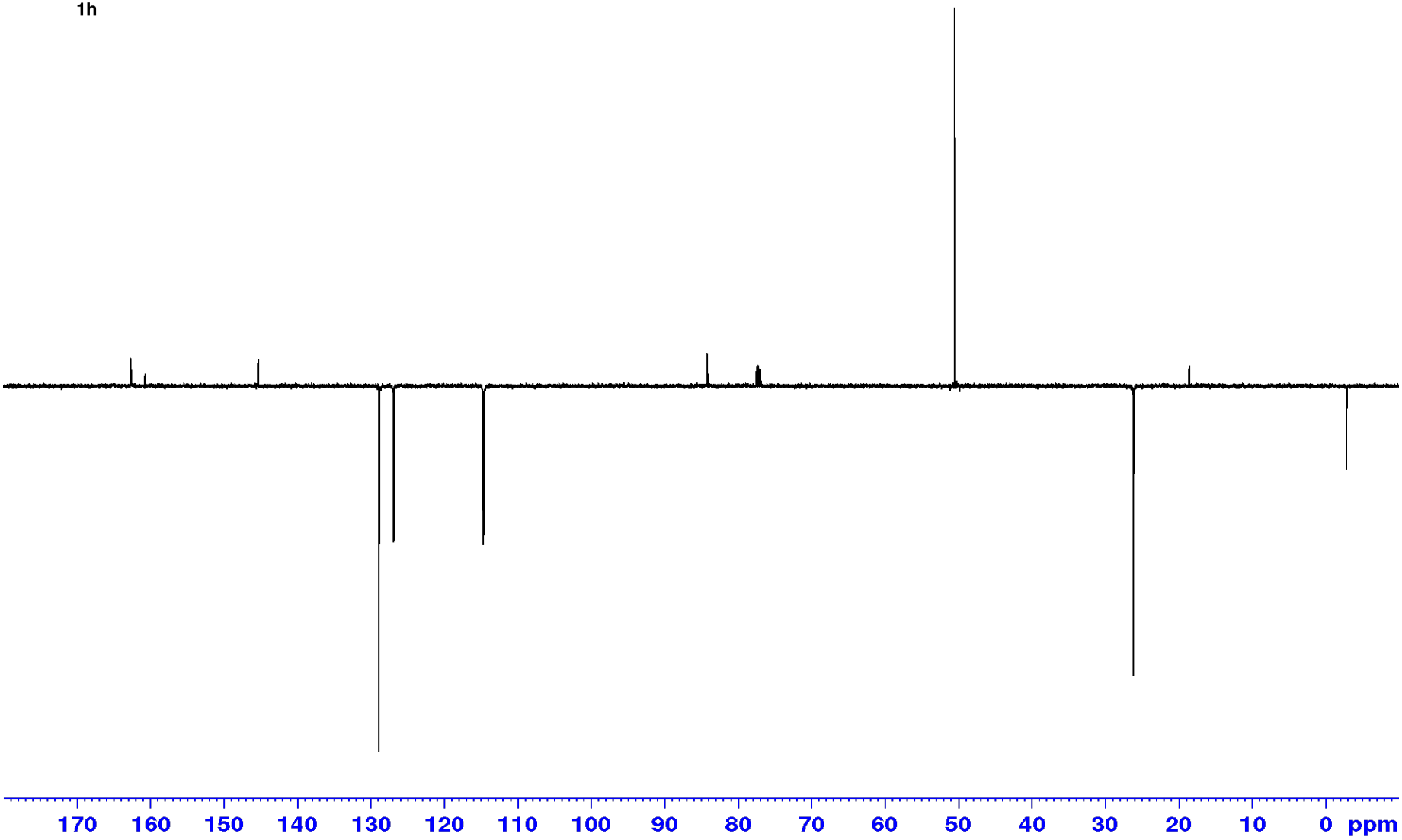
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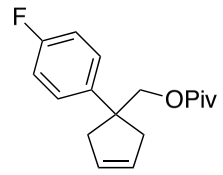
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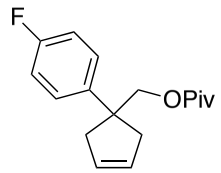
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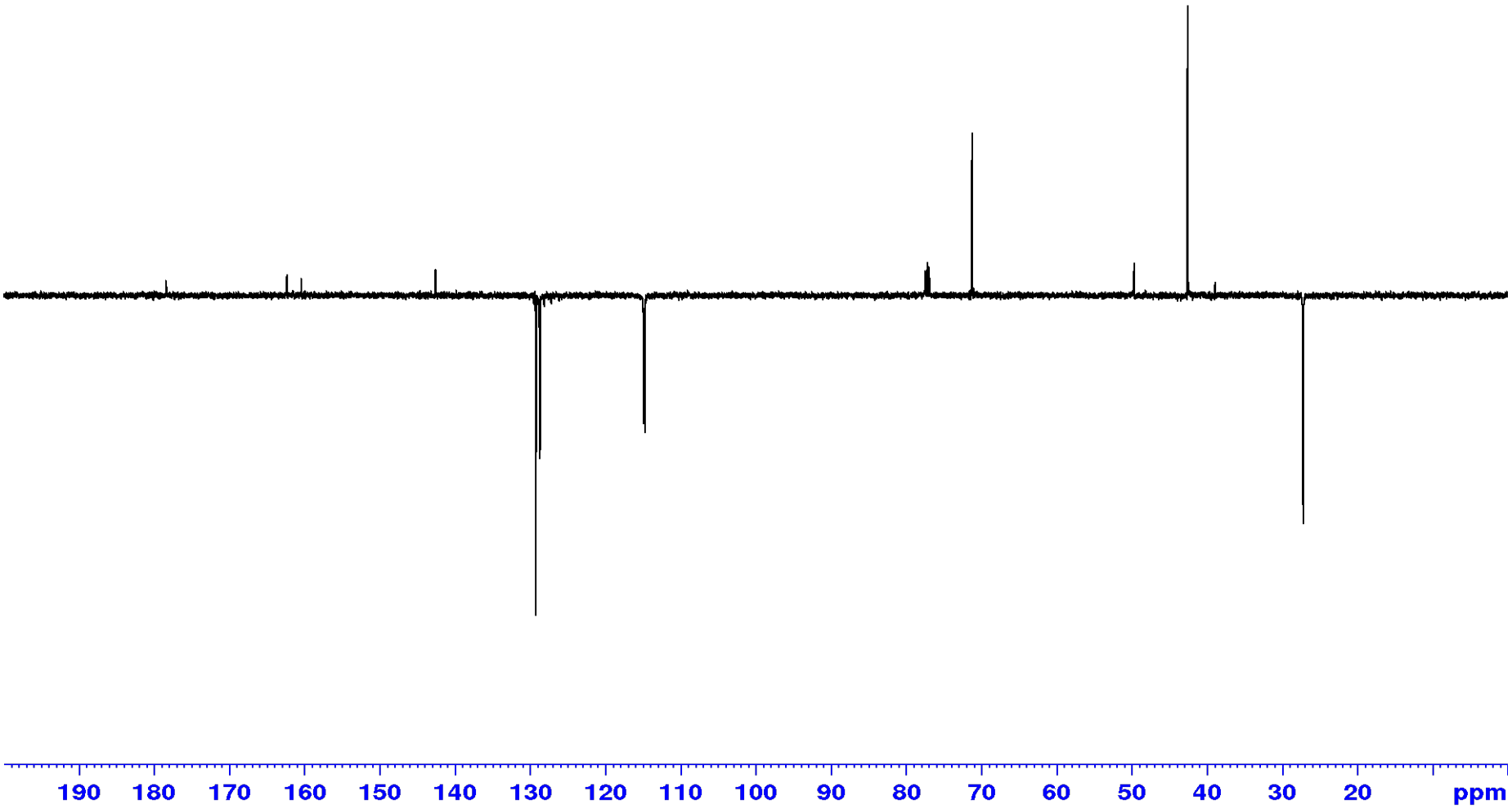
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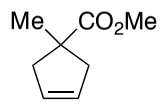
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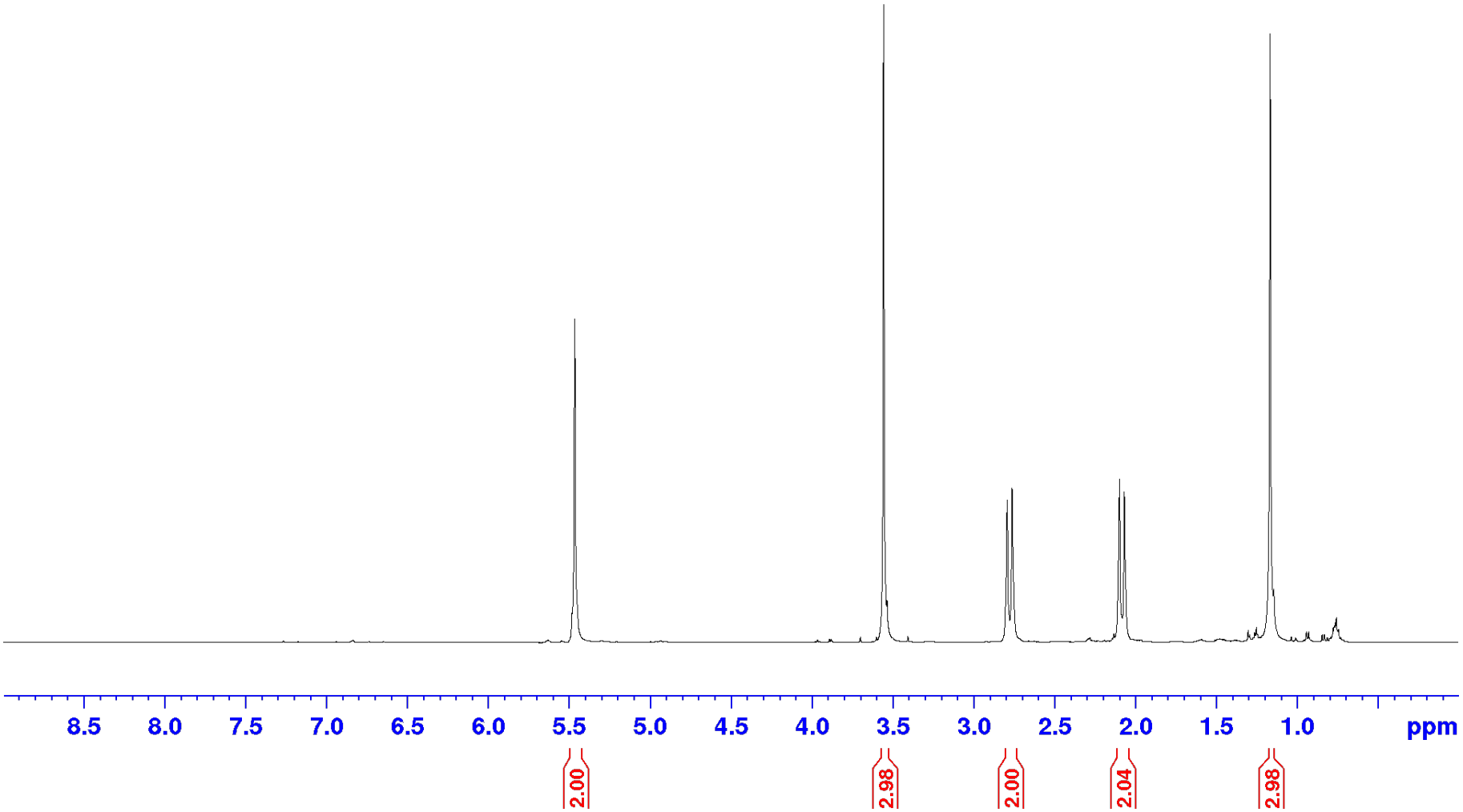
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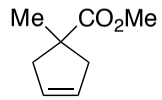

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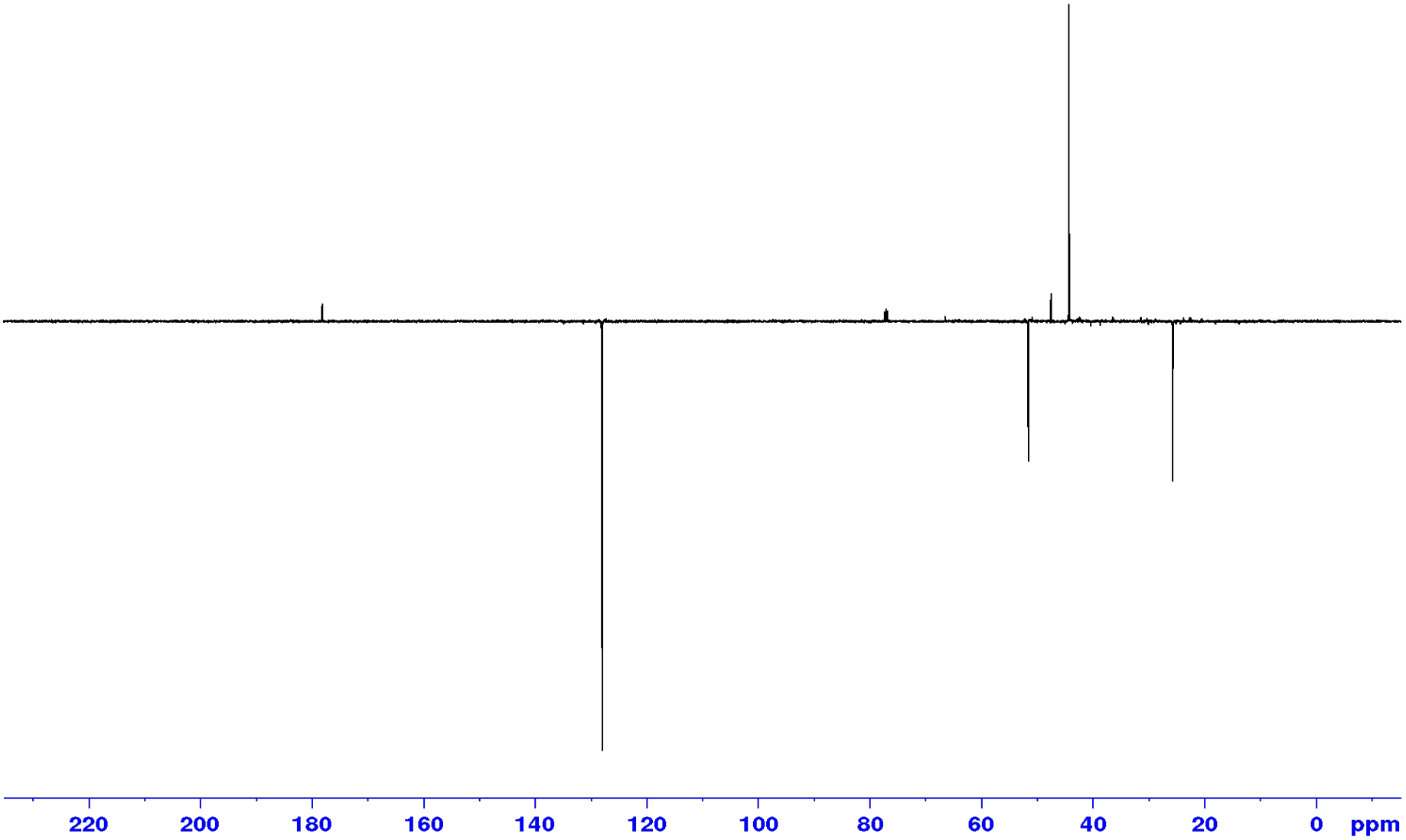

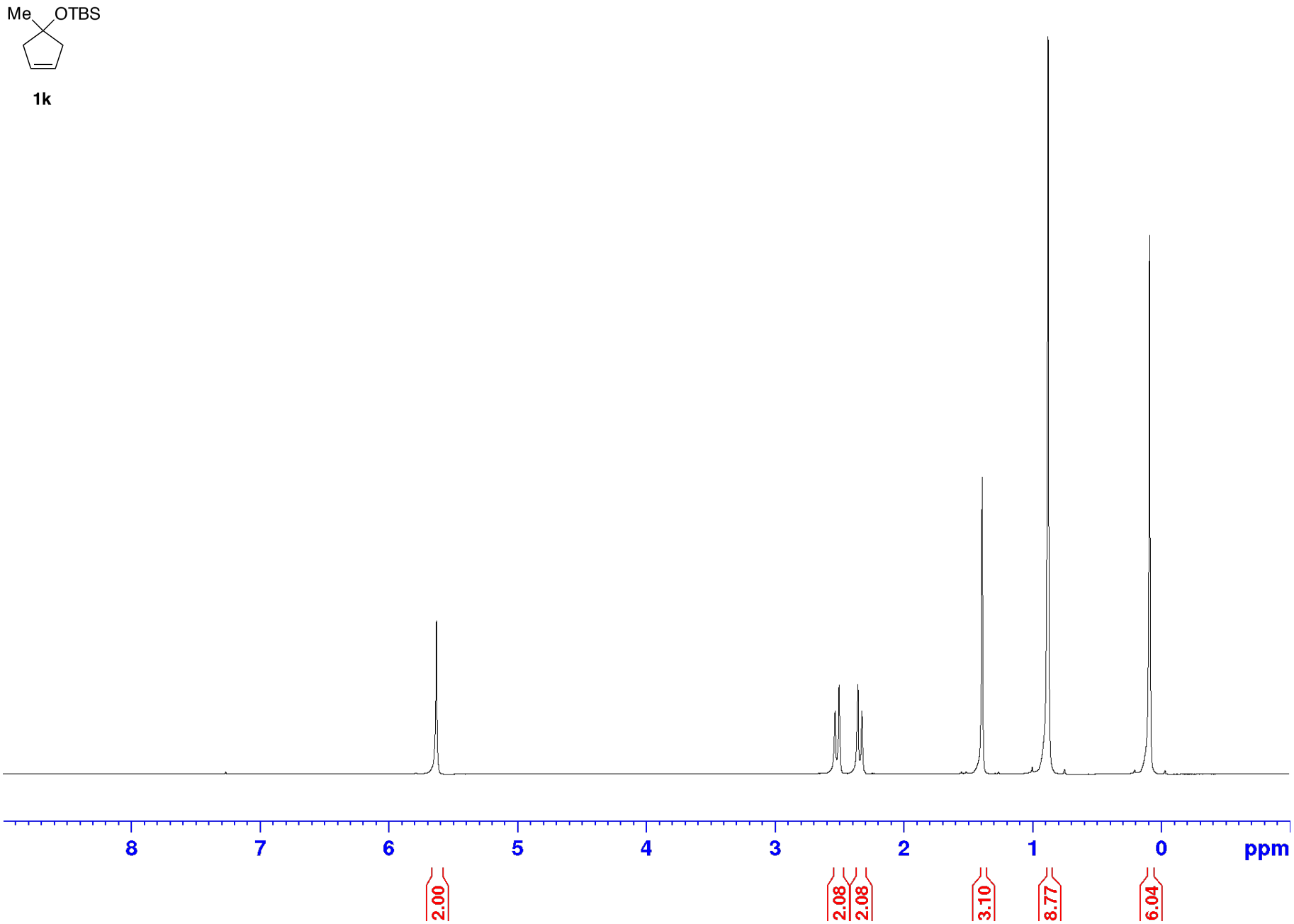
Me
OTBS
1k
8
7
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4
3
2
1
0
ppm
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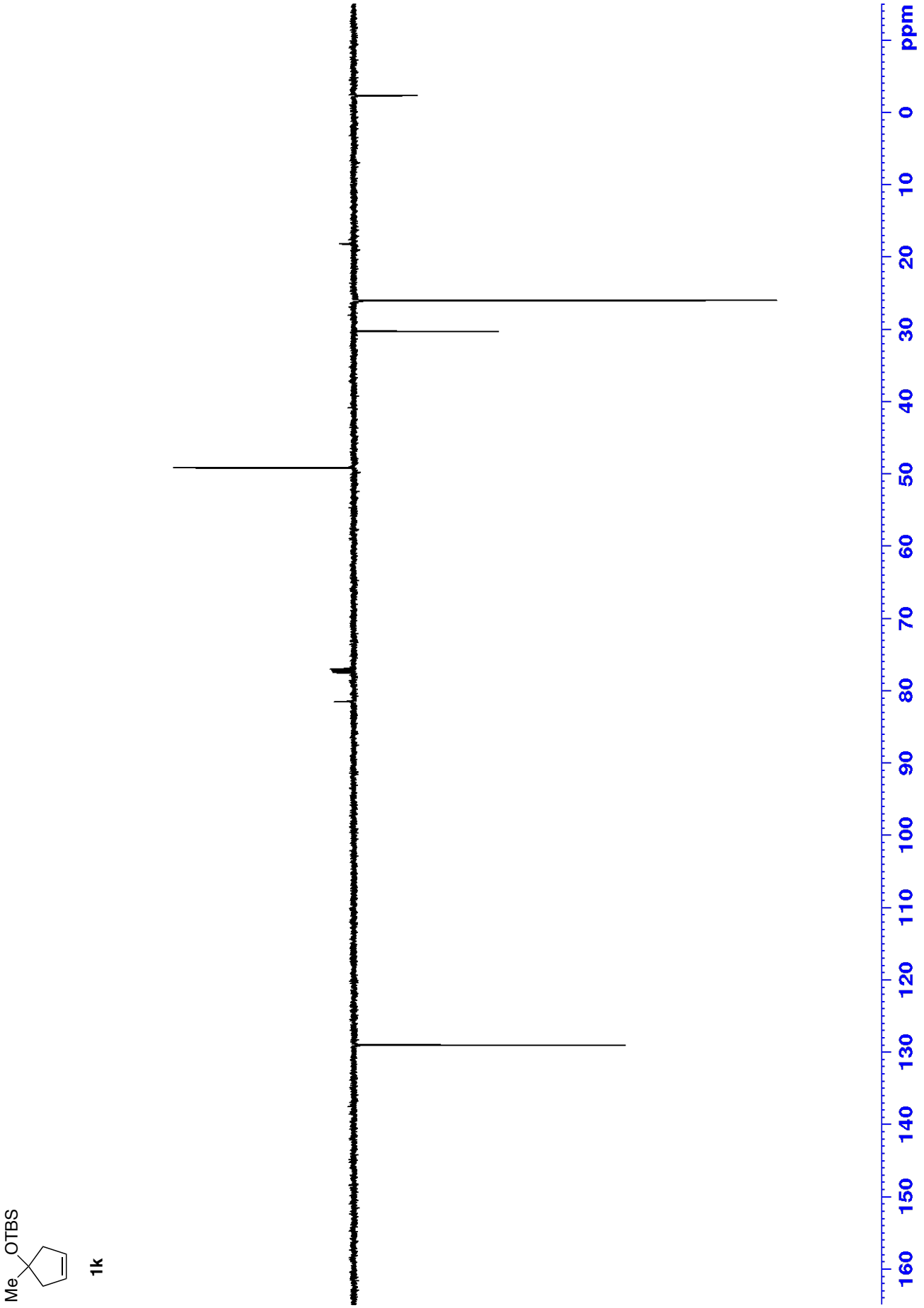
2.08
2.08
3.10
8.77
6.04


Me
OTBS
1k
ppm
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130
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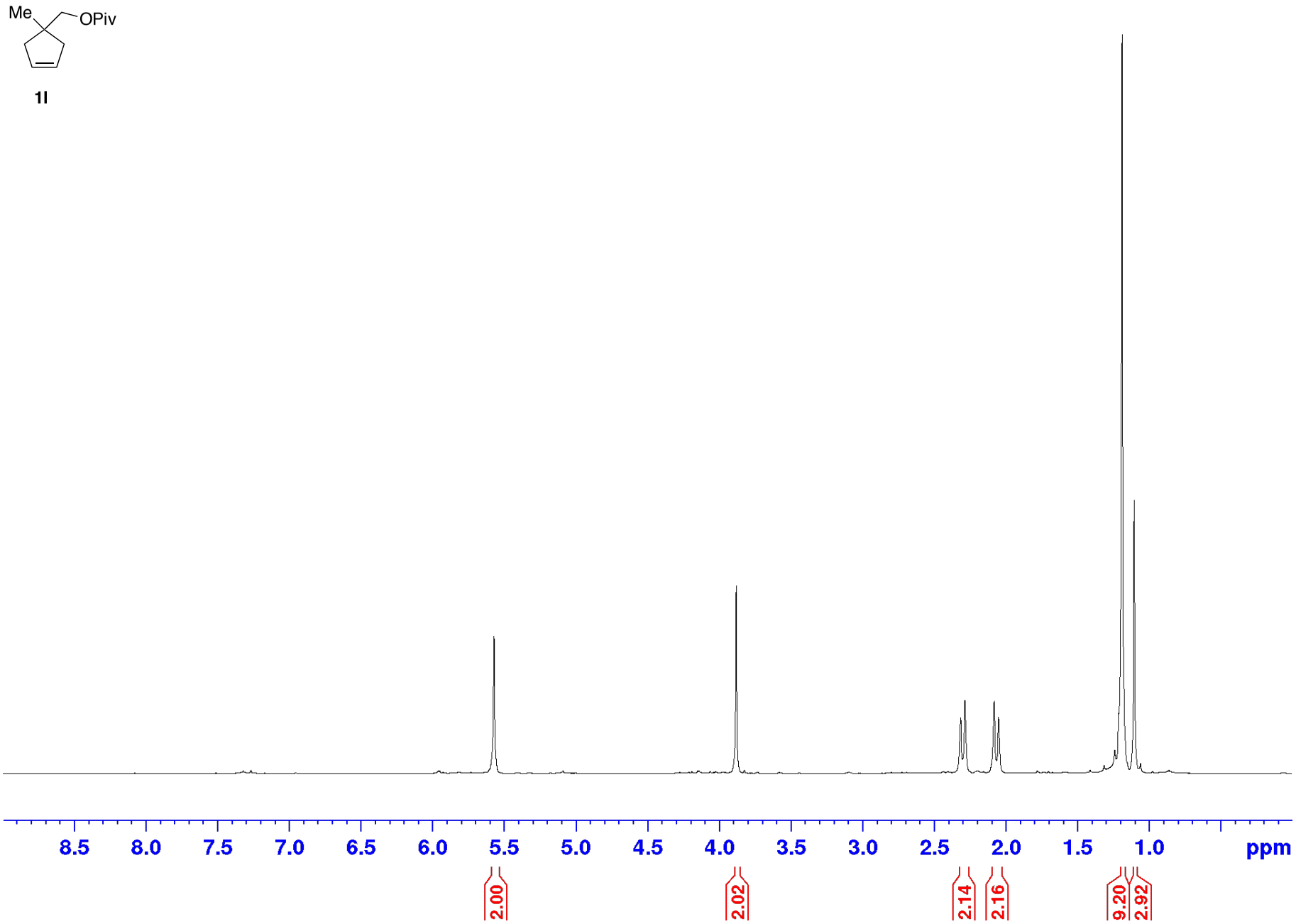
150
160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OPiv
1l
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
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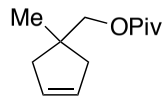
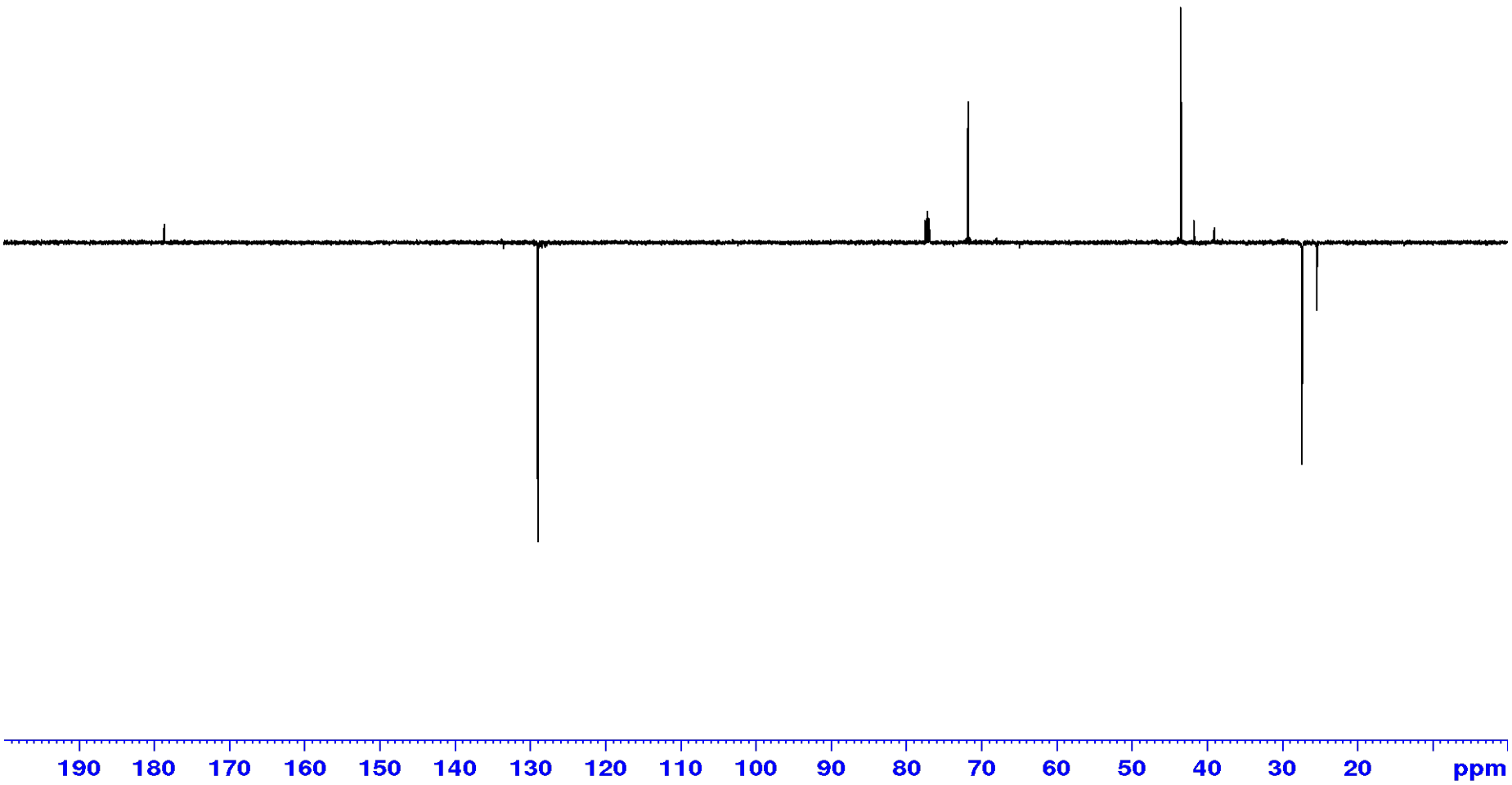
2.0
1.5
1.0
ppm
2.00
2.02
2.14
2.16
9.20
2.92


Me
OPiv

1l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120
110
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90
80
70
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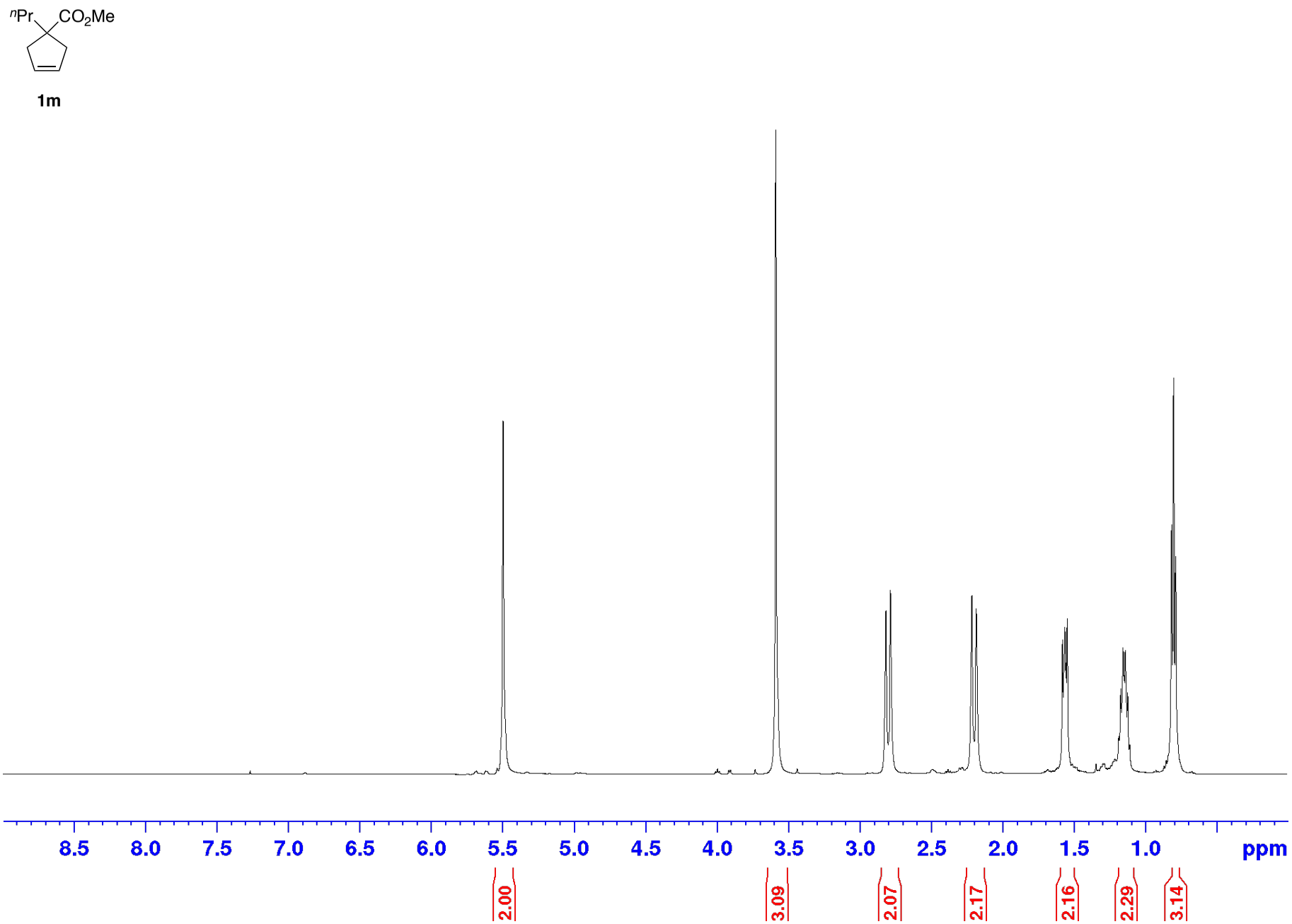
50
40
30
20
ppm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CO2Me
1m
8.5
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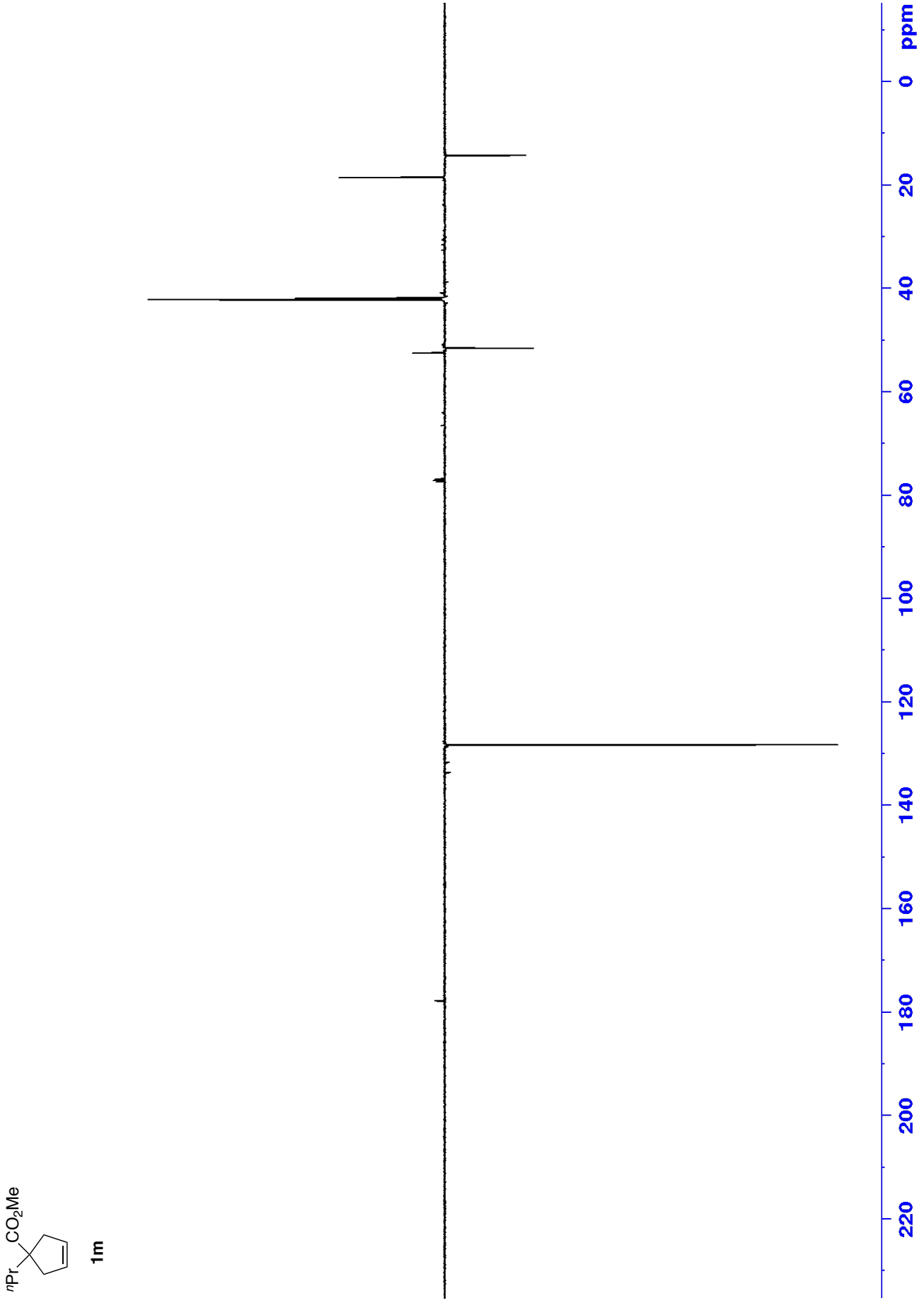
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.00
3.09
2.07
2.17
2.16
2.29
3.14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CO2Me
1m
0
20
40
60
80
100
120
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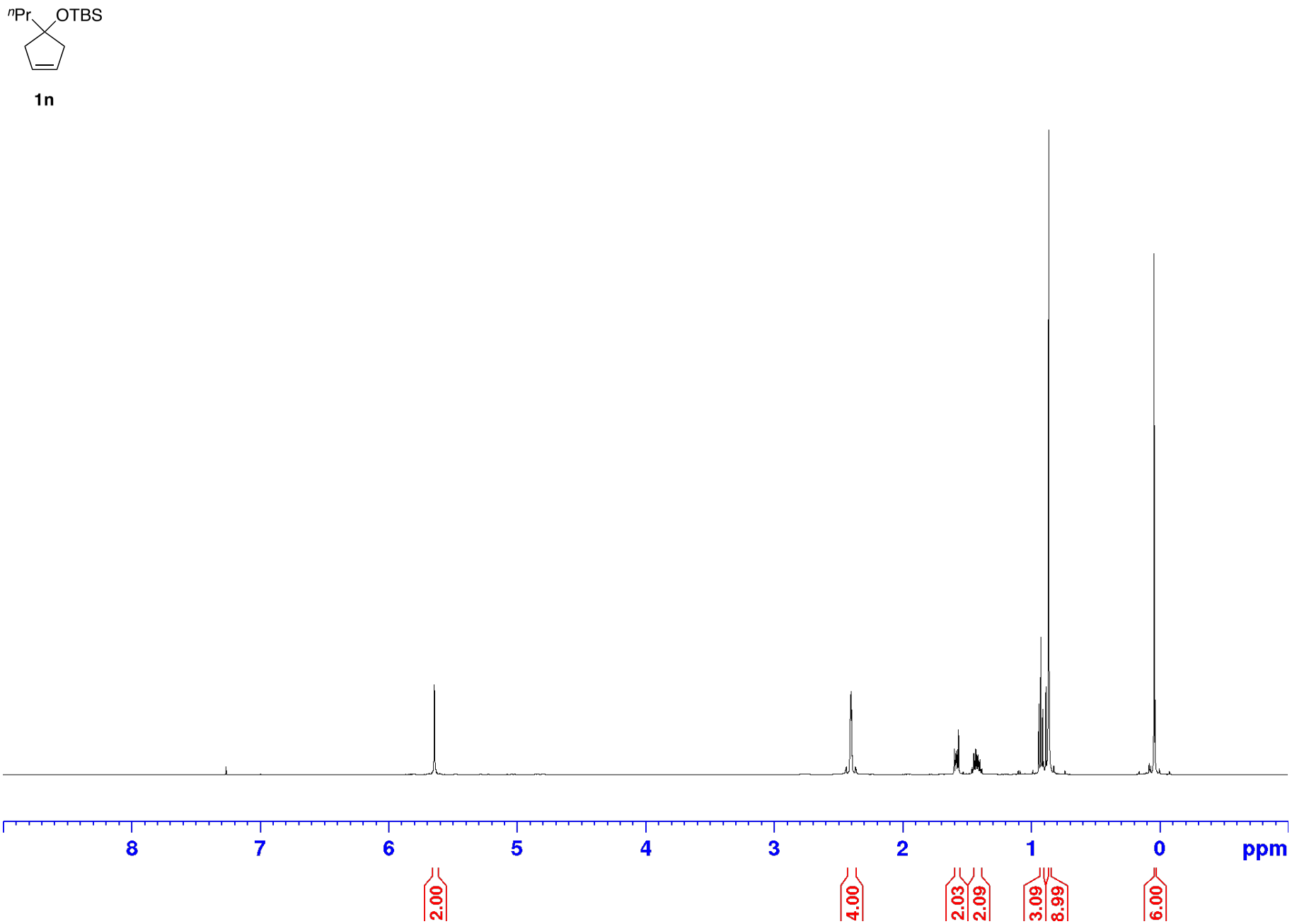
160
180
200
220
ppm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OTBS
1n
8
7
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3
2
1
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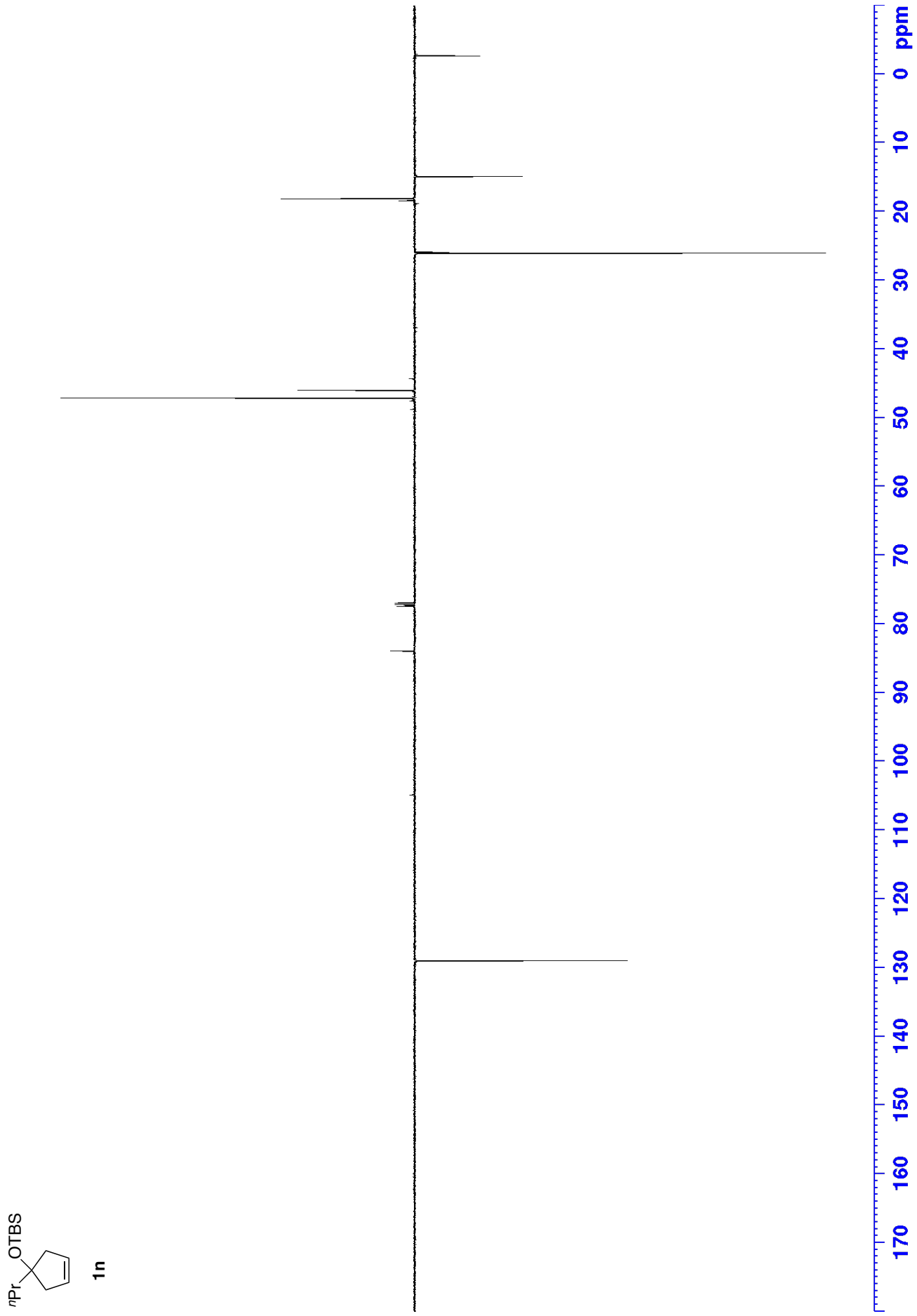
4.00
2.03
2.09
3.09
8.99
6.00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OTBS
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50
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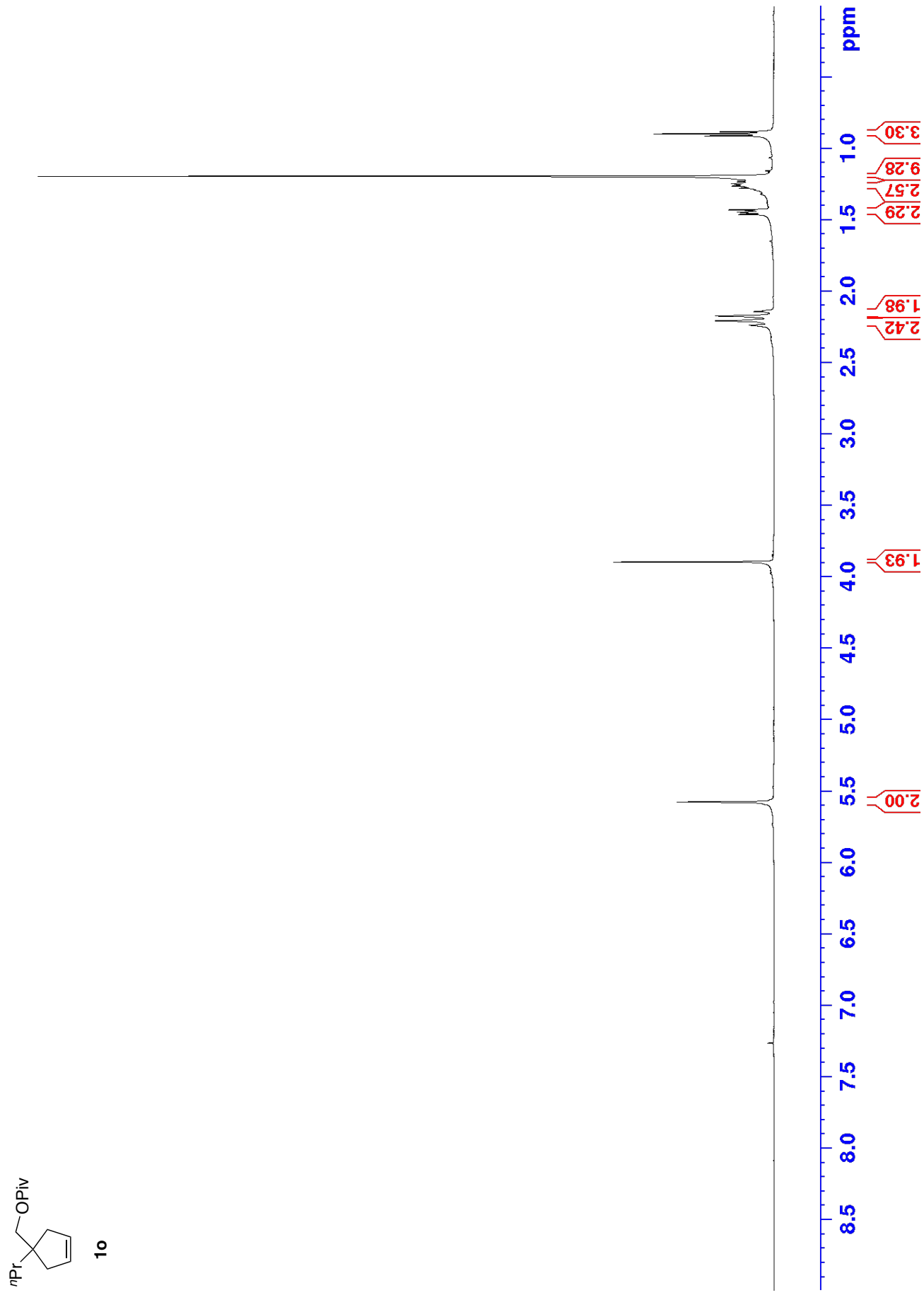
20
10
0
ppm


OPiv
nPr
1o
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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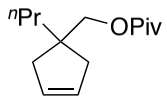
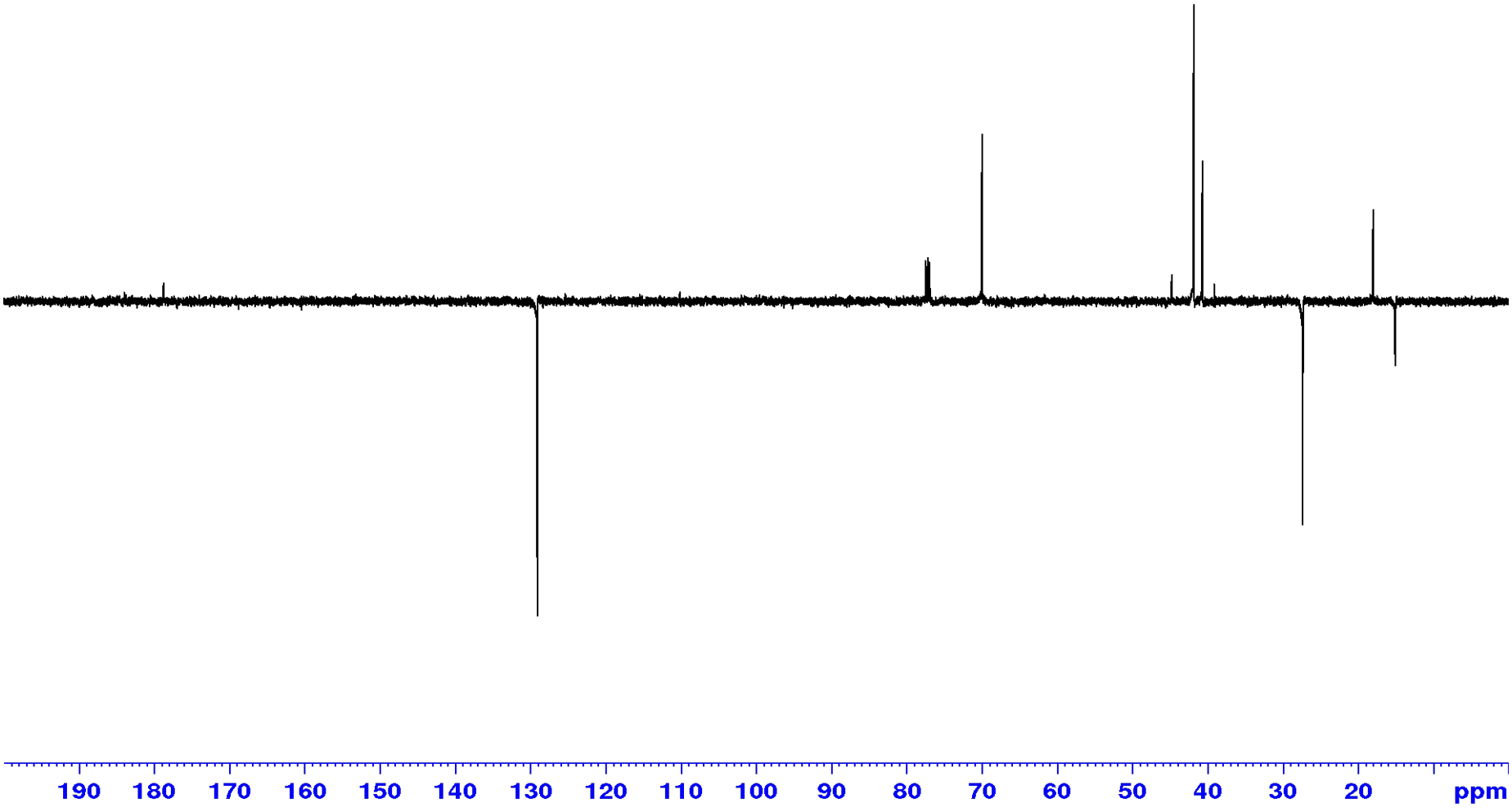
1.98
2.29
2.57
9.28
3.30


nPr
OPiv

1o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110
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70
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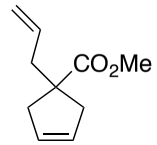
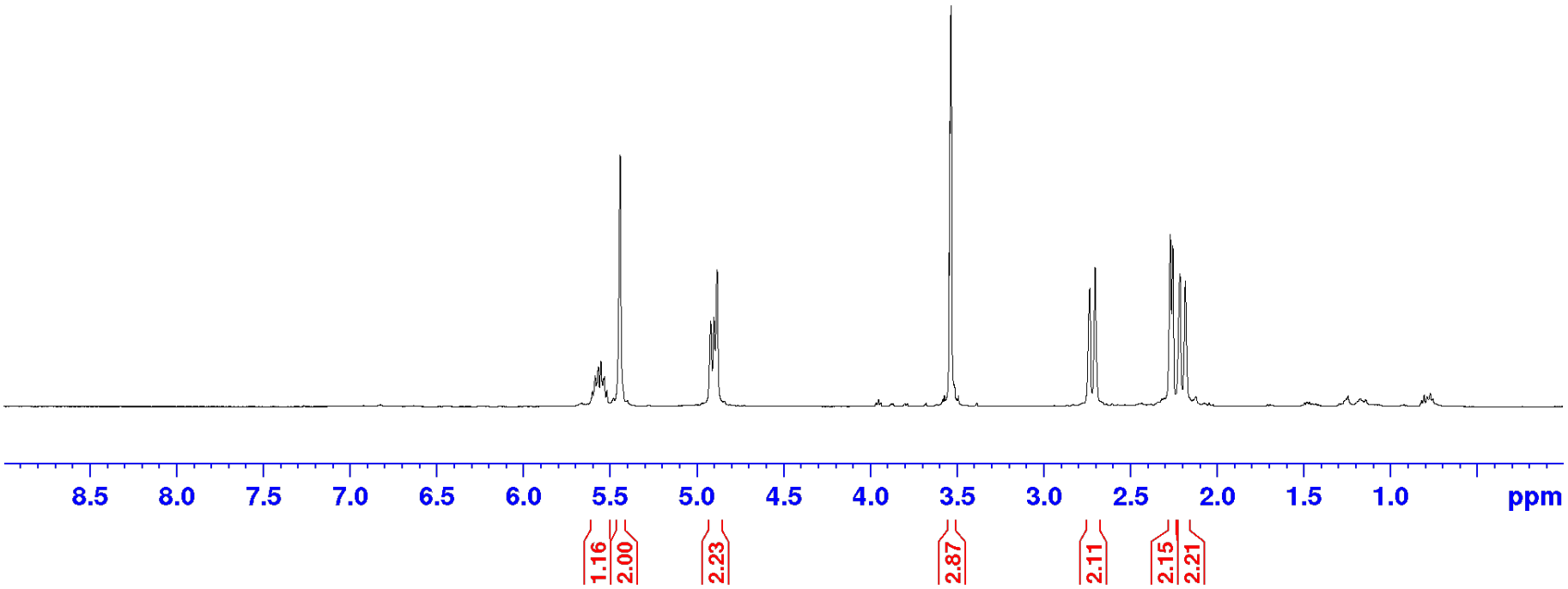
50
40
30
20
ppm


CO2Me

1p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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
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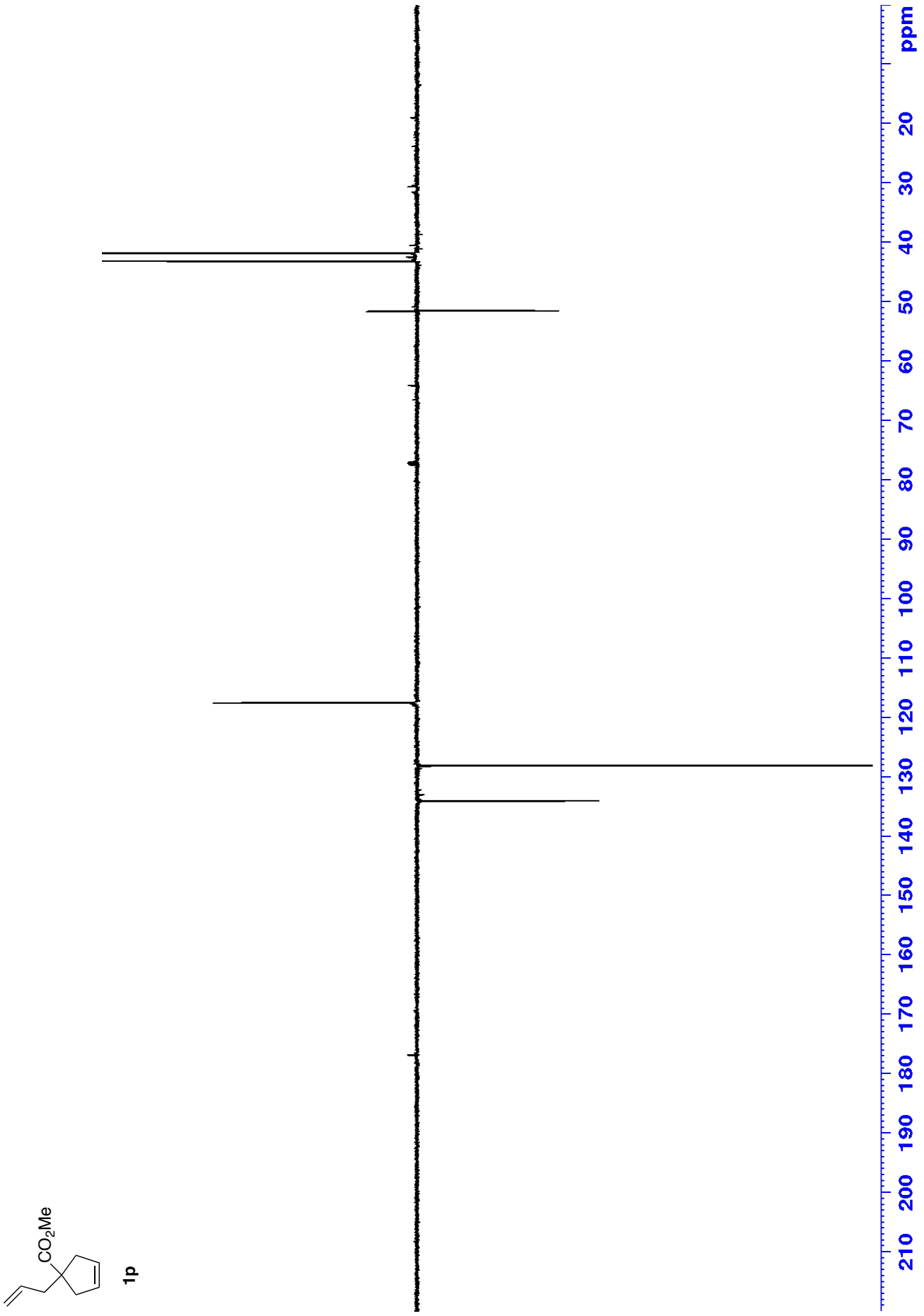
2.00
2.23
2.87
2.11
2.15
2.21


CO2Me
1p
ppm
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200
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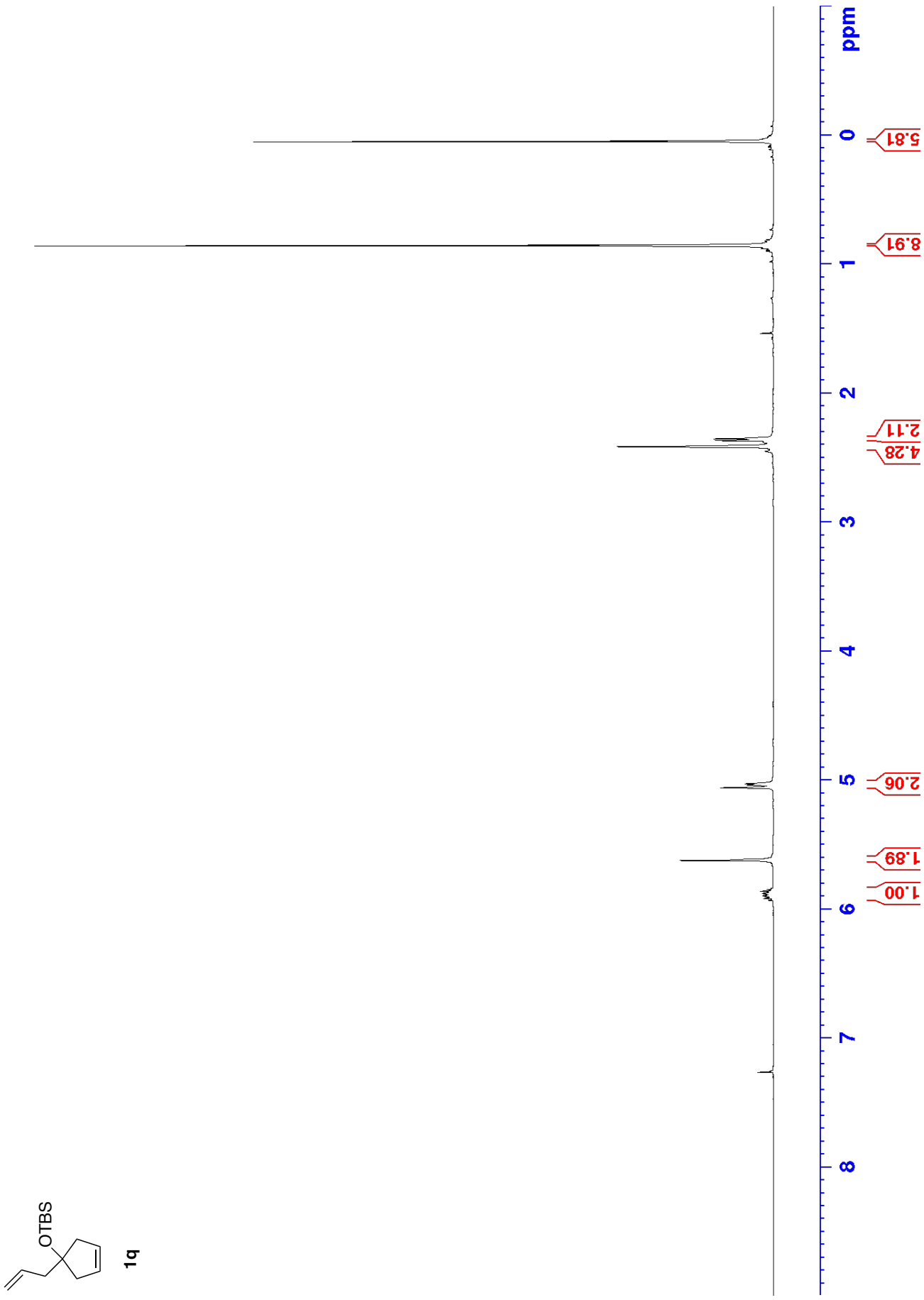
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20


OTBS
1q
ppm
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6
7
8
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2.11
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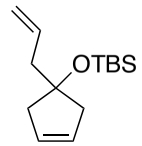
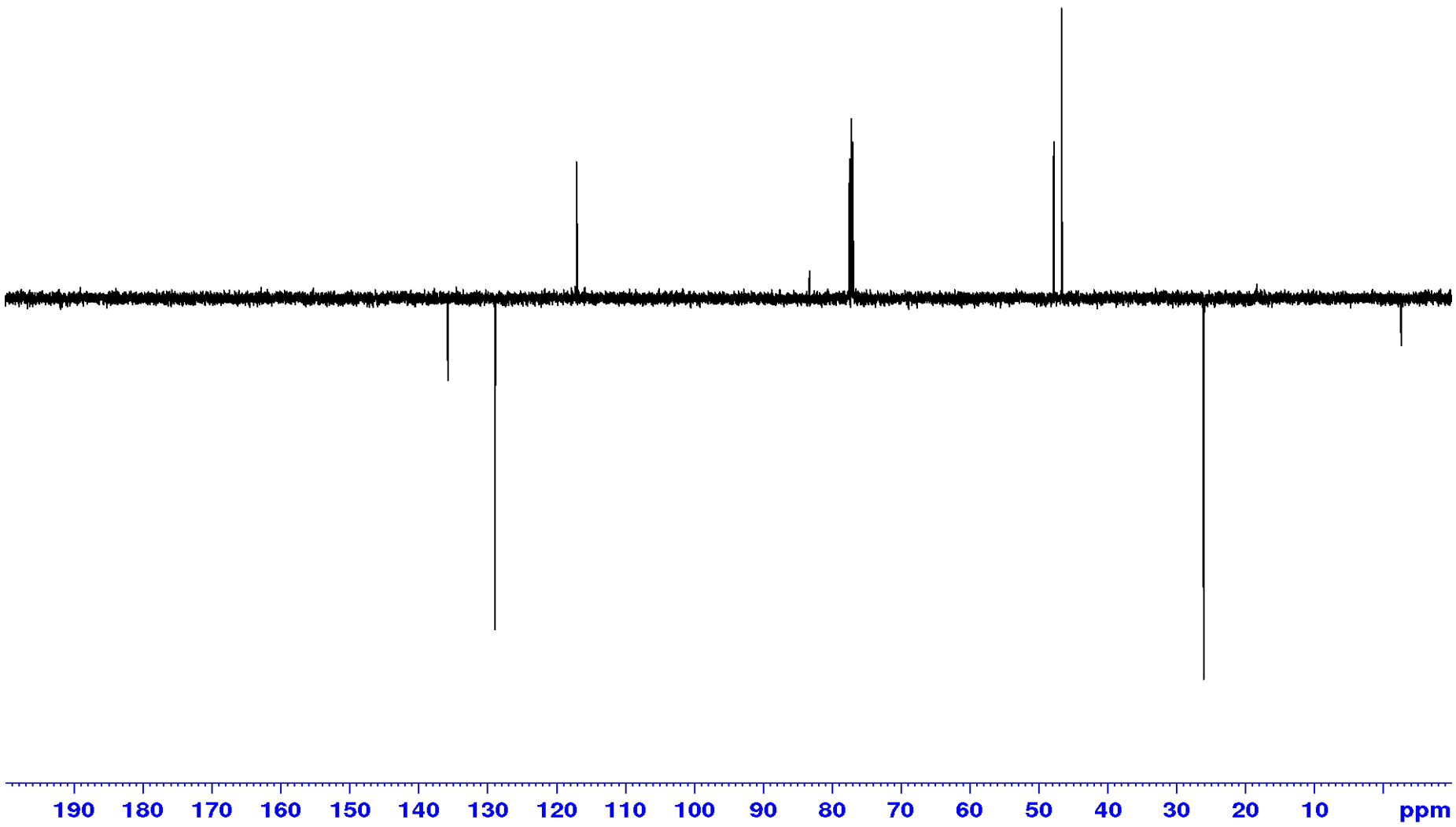
2.06
1.89
1.00


OTBS

1q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180
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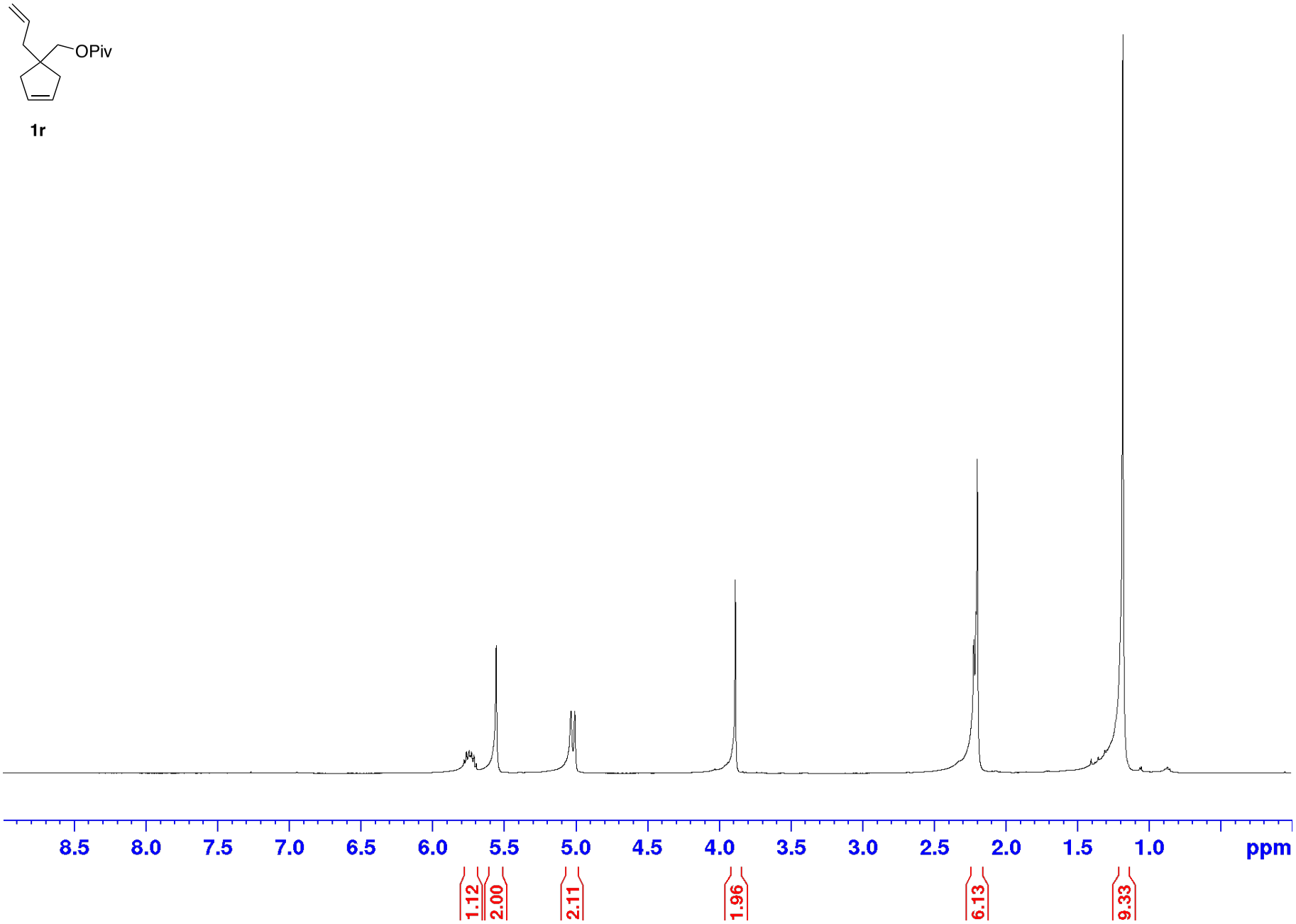
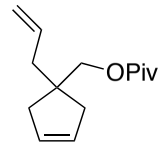
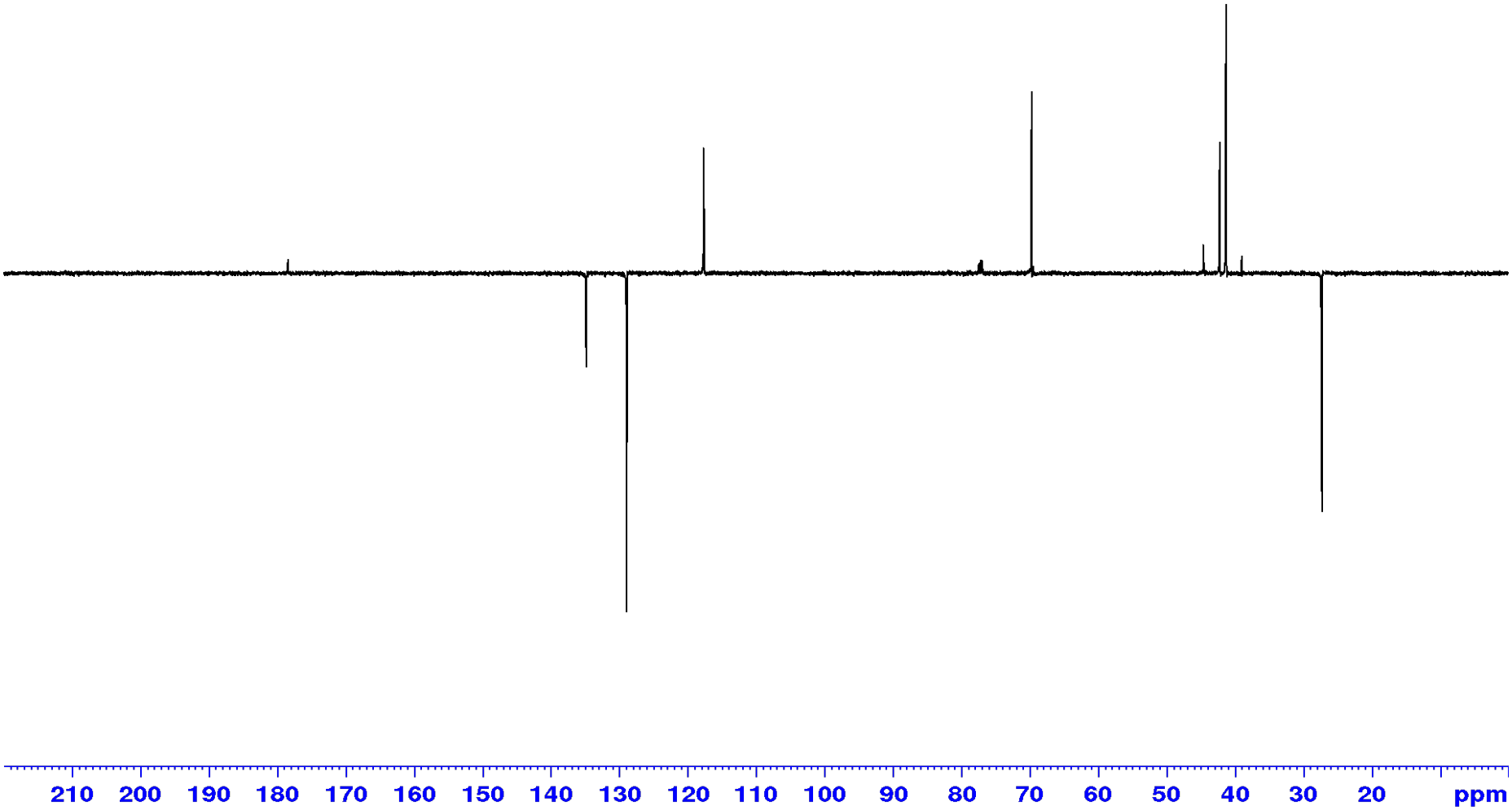
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


OPiv
1r
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.12
2.00
2.11
1.96
6.13
9.33


OPiv

1r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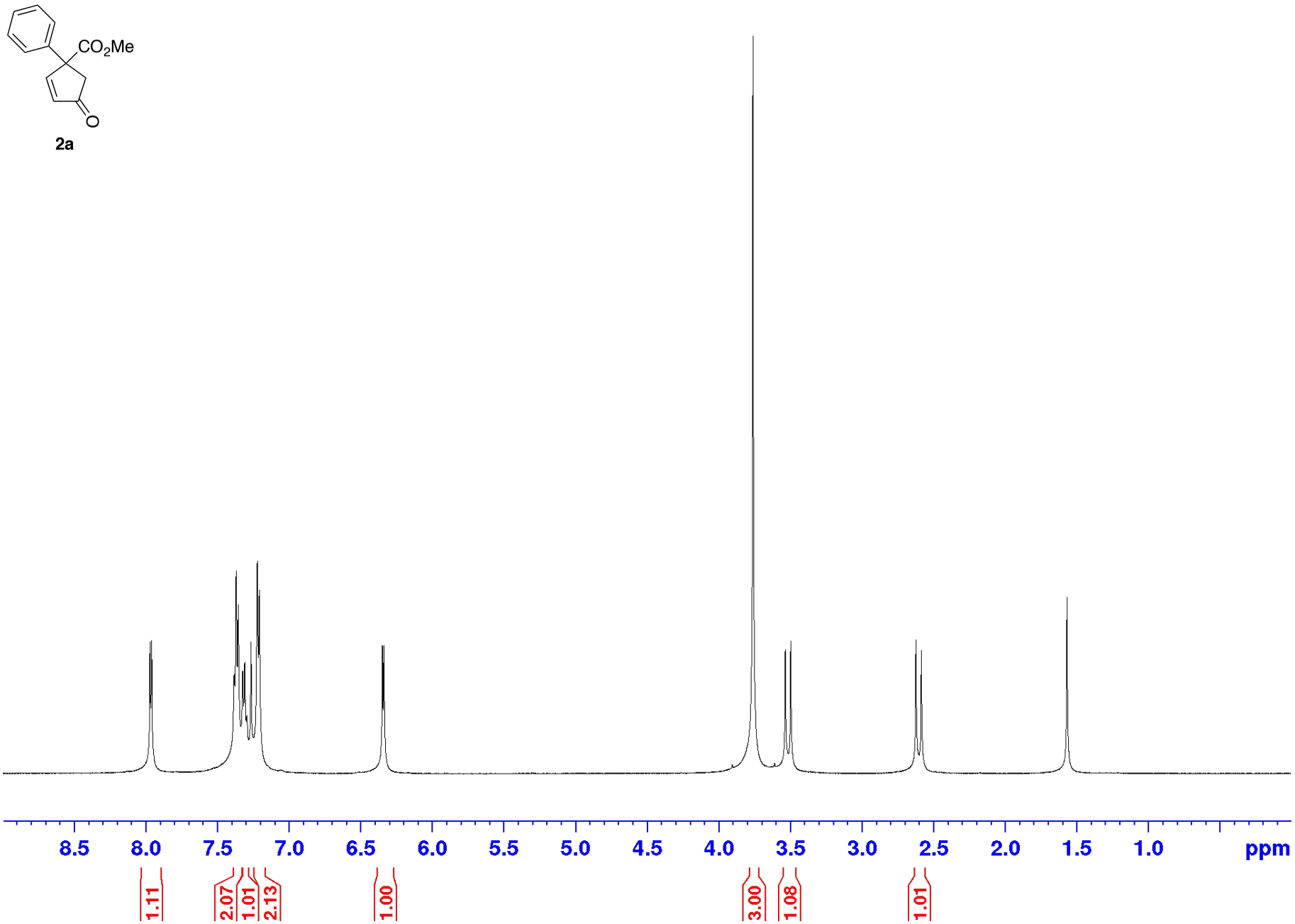
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


CO2Me
O
2a
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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1.0
ppm
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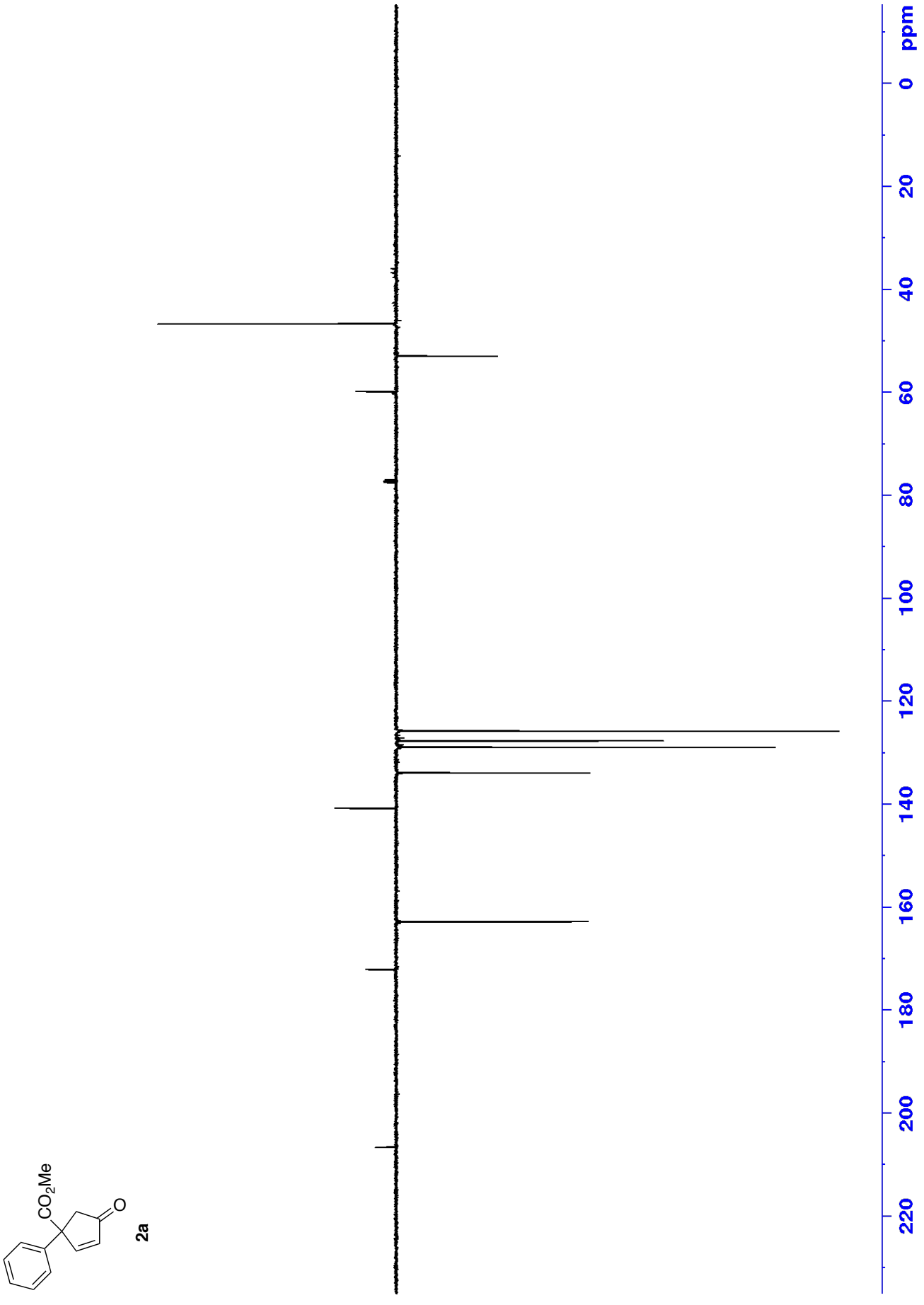
2.07
1.01
2.13
1.00
3.00
1.08
1.01


CO2Me
O
2a
ppm
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80
100
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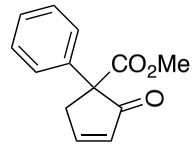
160
180
200
220


CO2Me
O

3a

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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2.0
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ppm
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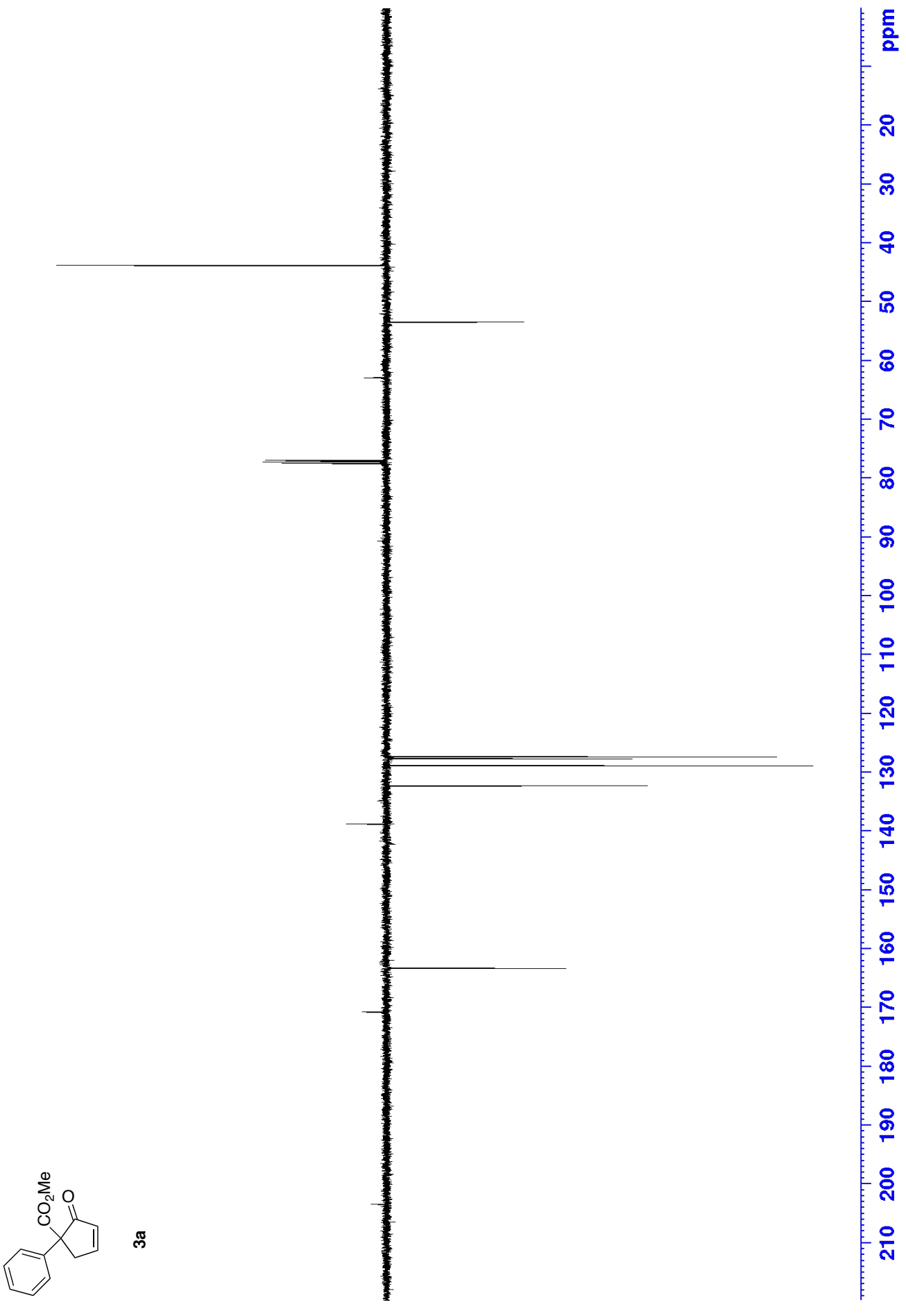
1.00
1.02
2.99
1.01


CO2Me
O
3a
ppm
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200
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90
80
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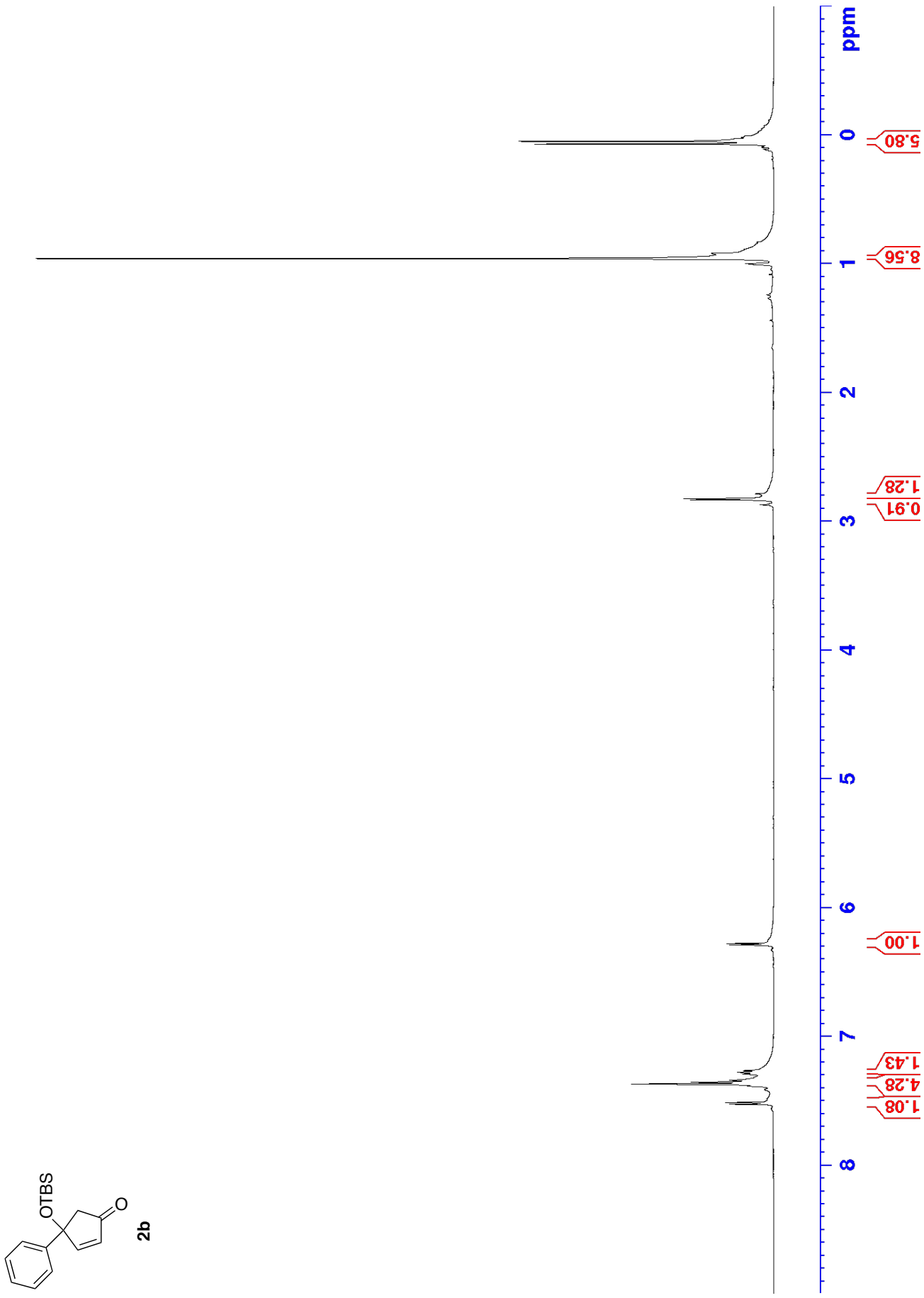
40
30
20


OTBS
O
2b
ppm
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6
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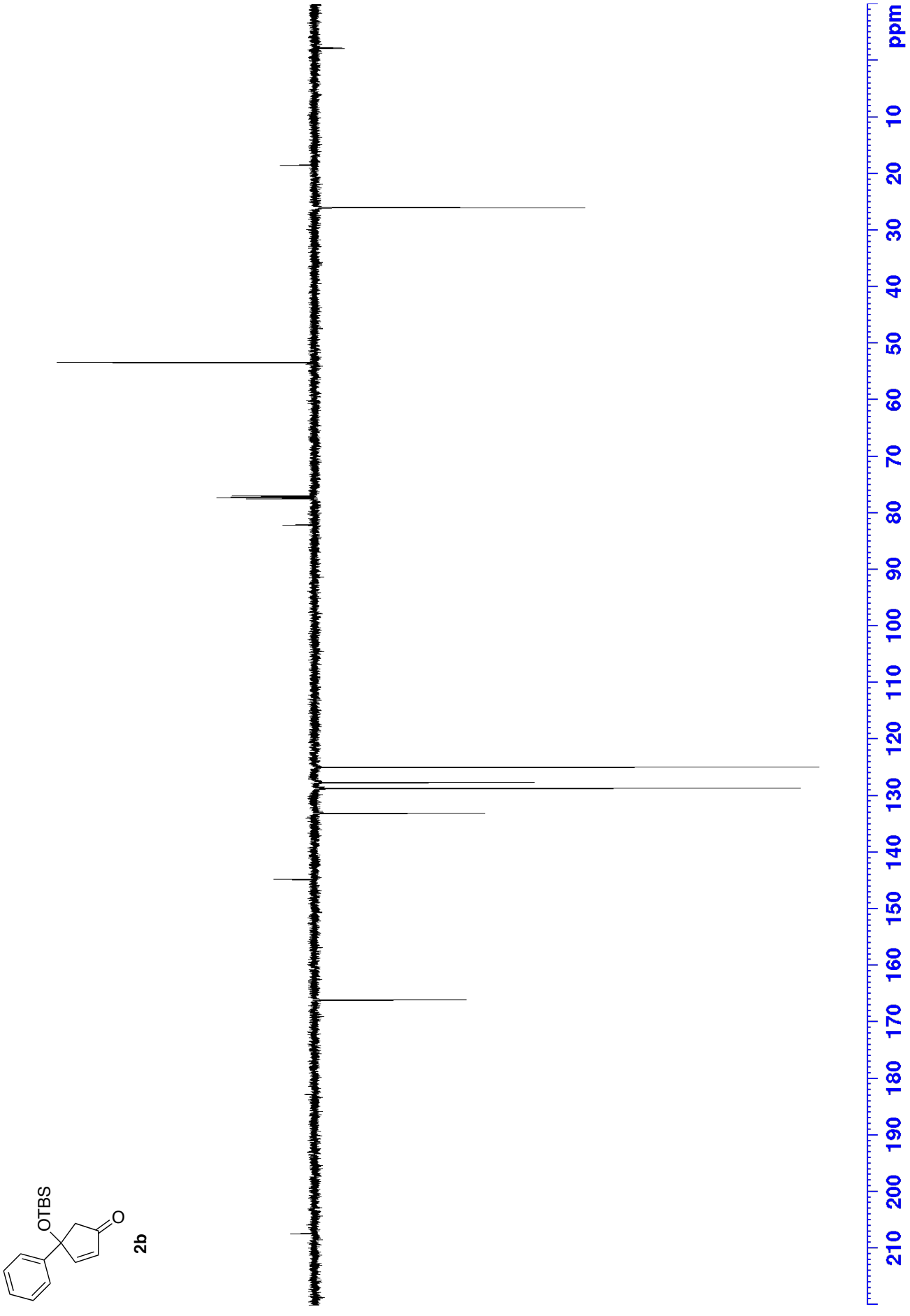
1.08


OTBS
O
2b
ppm
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70
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90
100
110
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140
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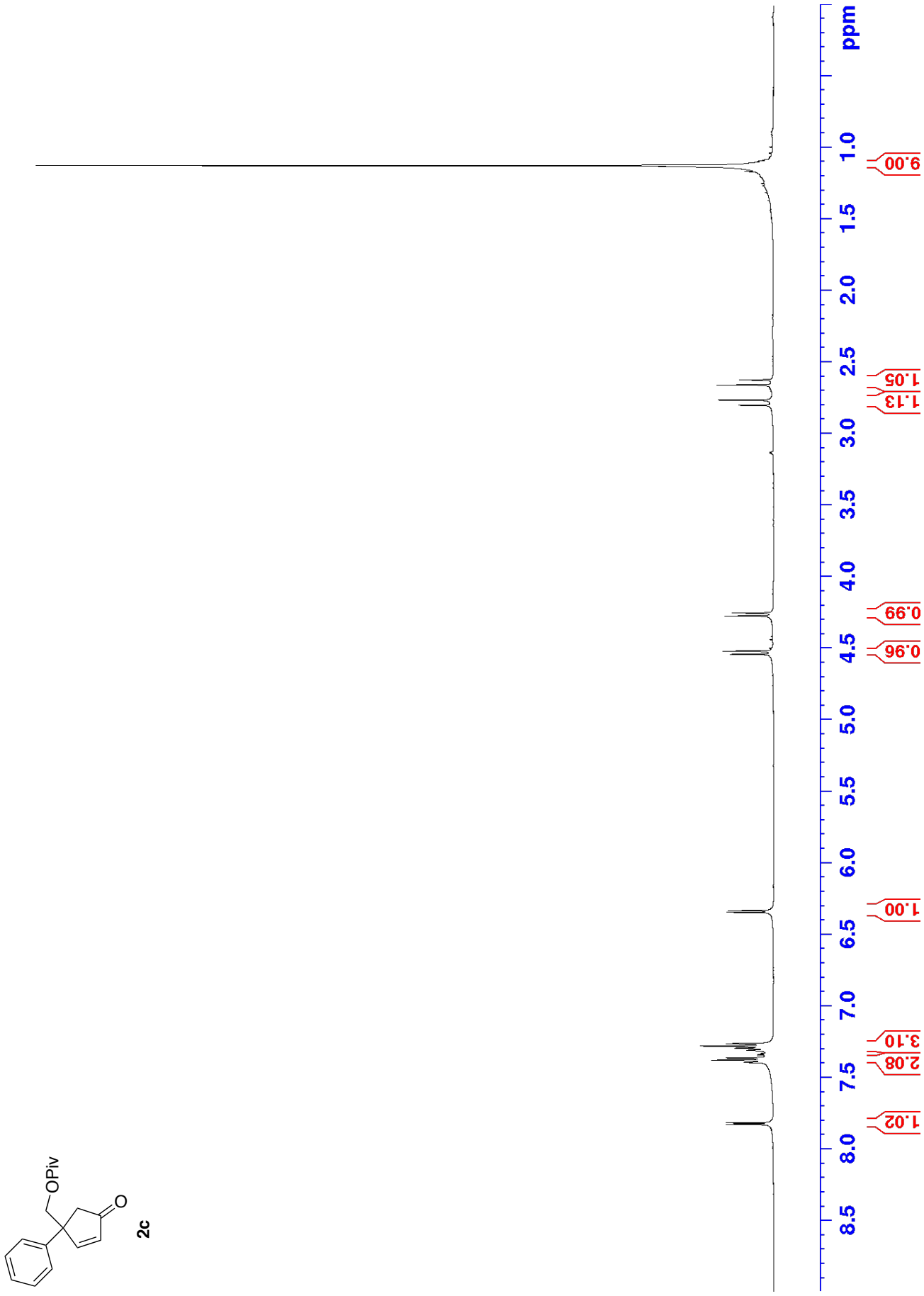
170
180
190
200
210


OPiv
O
2c
ppm
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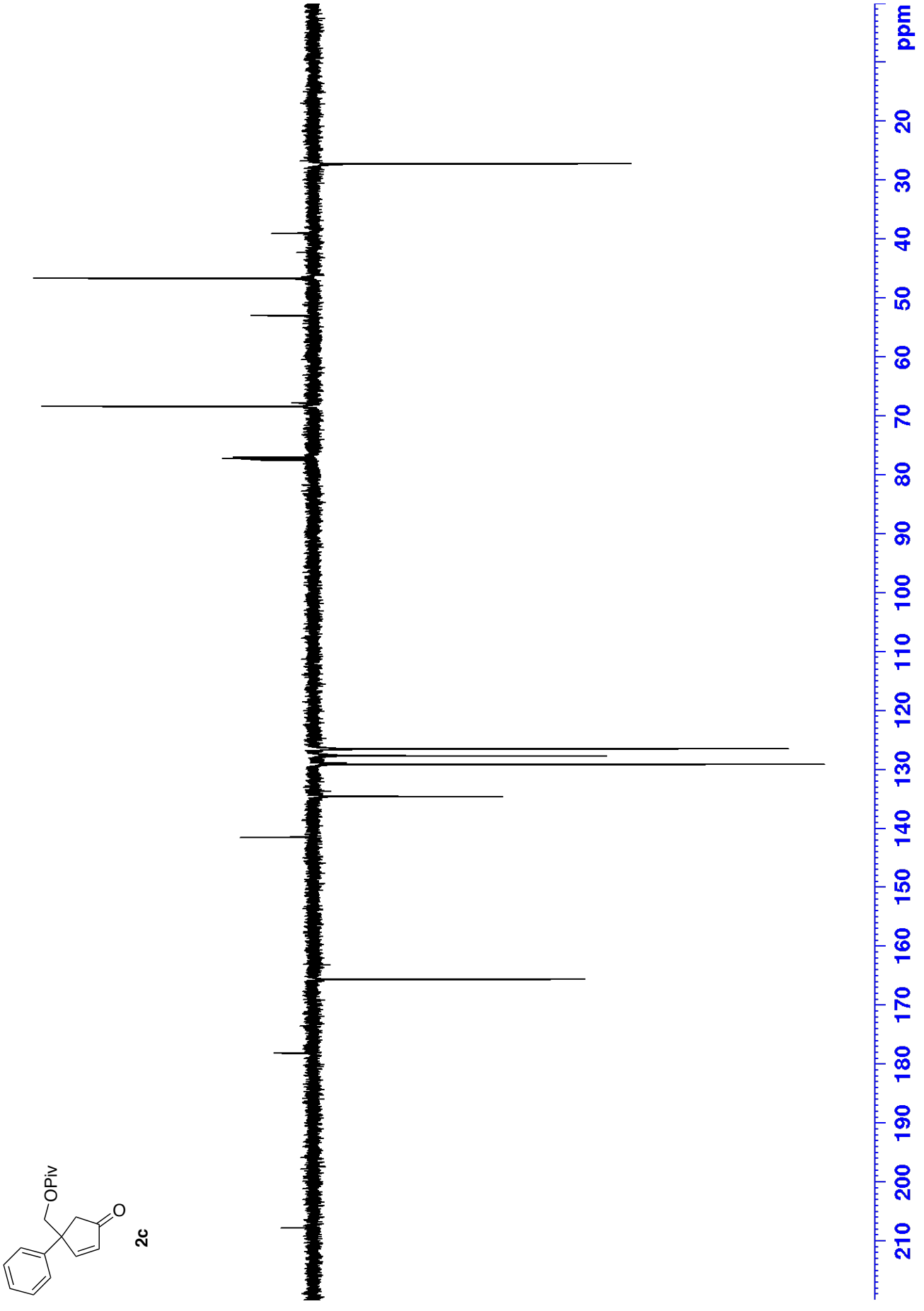
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
9.00
1.05
1.13
0.99
0.96
1.00
3.10
2.08
1.02


OPiv
O
2c
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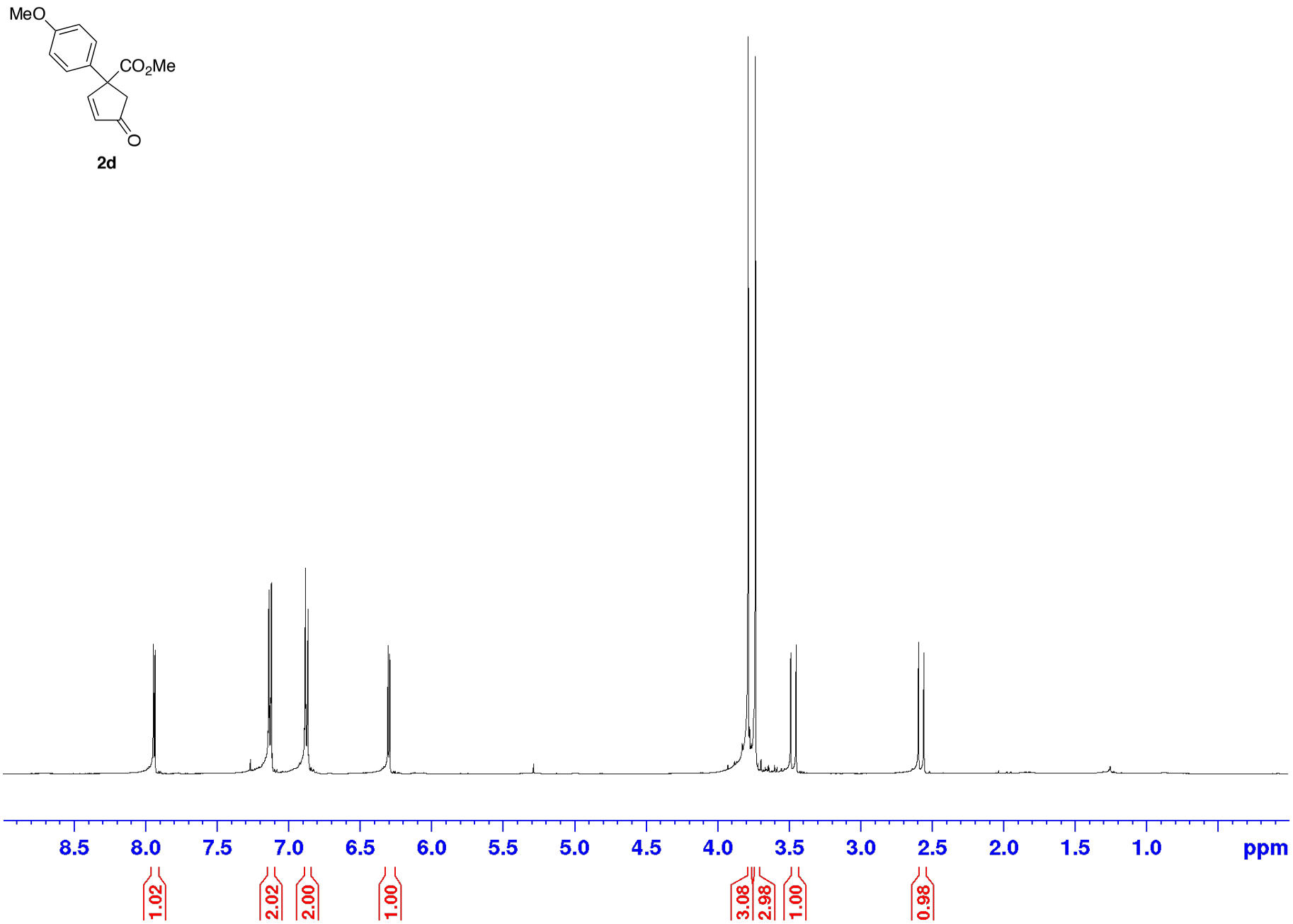
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


MeO
CO2Me
O
2d
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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1.0
ppm
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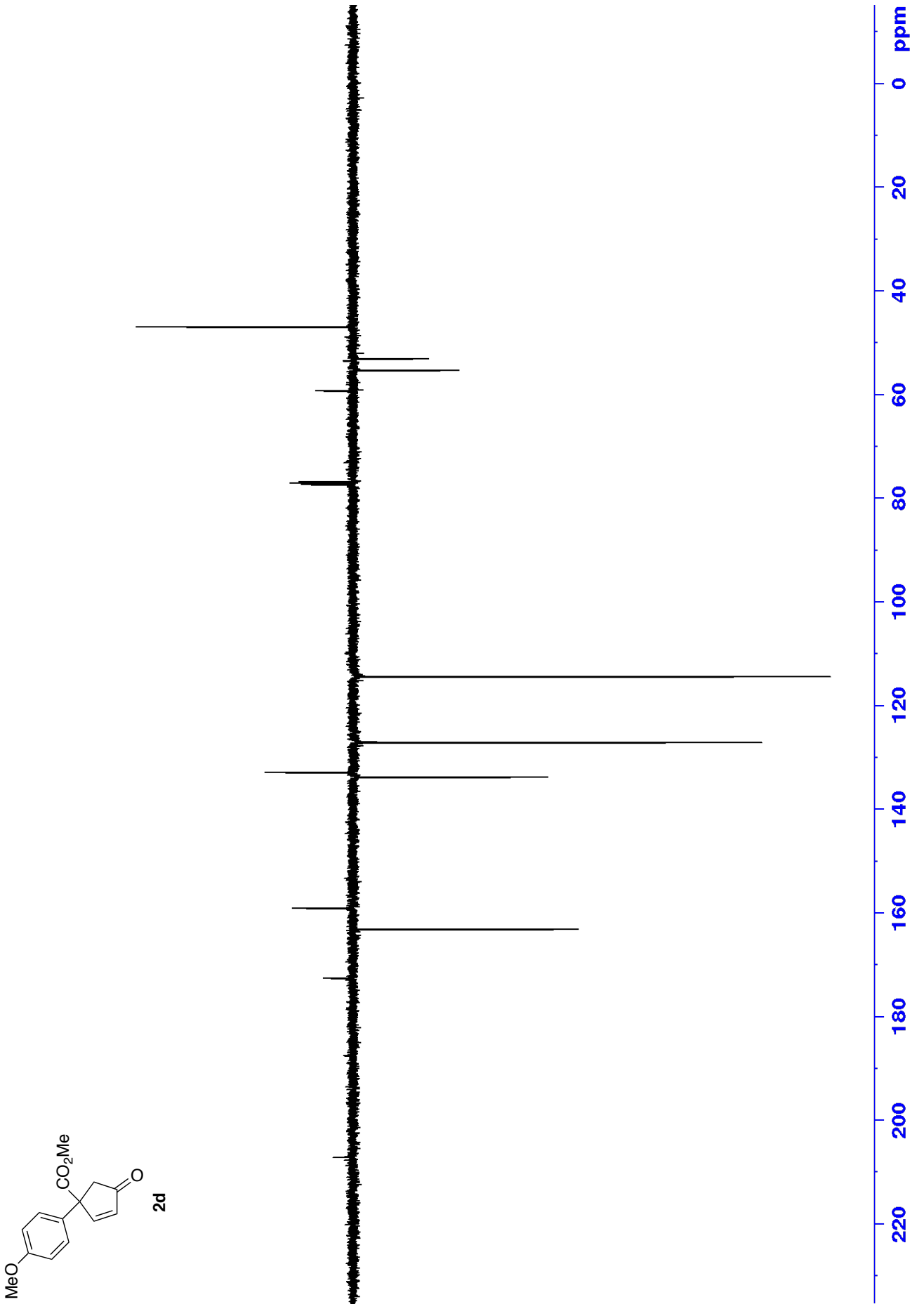
2.02
2.00
1.00
3.08
2.98
1.00
0.98


MeO
CO2Me
O
2d
ppm
0
20
40
60
80
100
120
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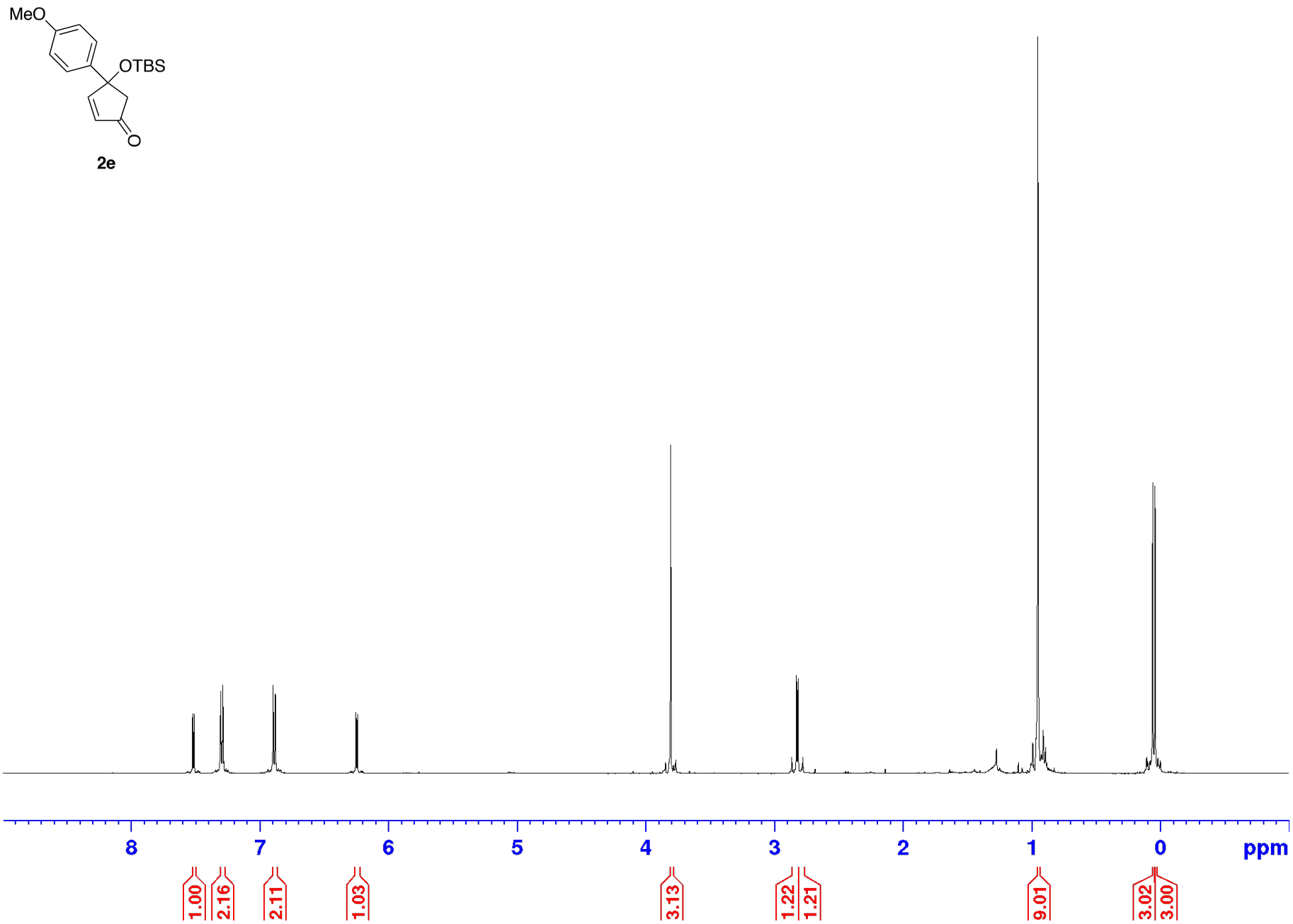
160
180
200
220


MeO
OTBS
O
2e
8
7
6
5
4
3
2
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0
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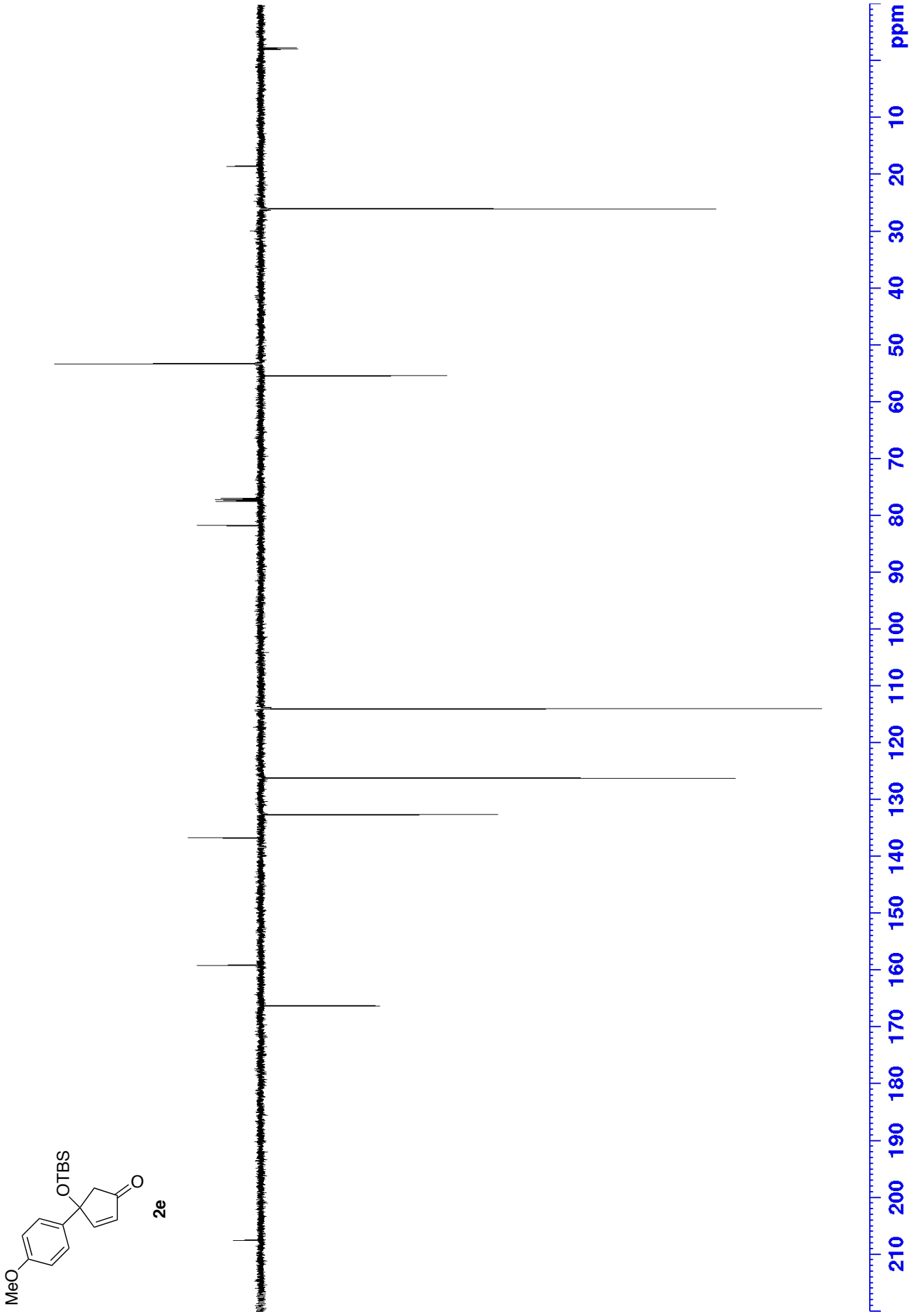
2.16
2.11
1.03
3.13
1.22
1.21
9.01
3.02
3.00


OTBS
O
MeO
2e
ppm
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200
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180
170
160
150
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130
120
110
100
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80
70
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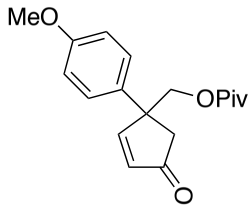
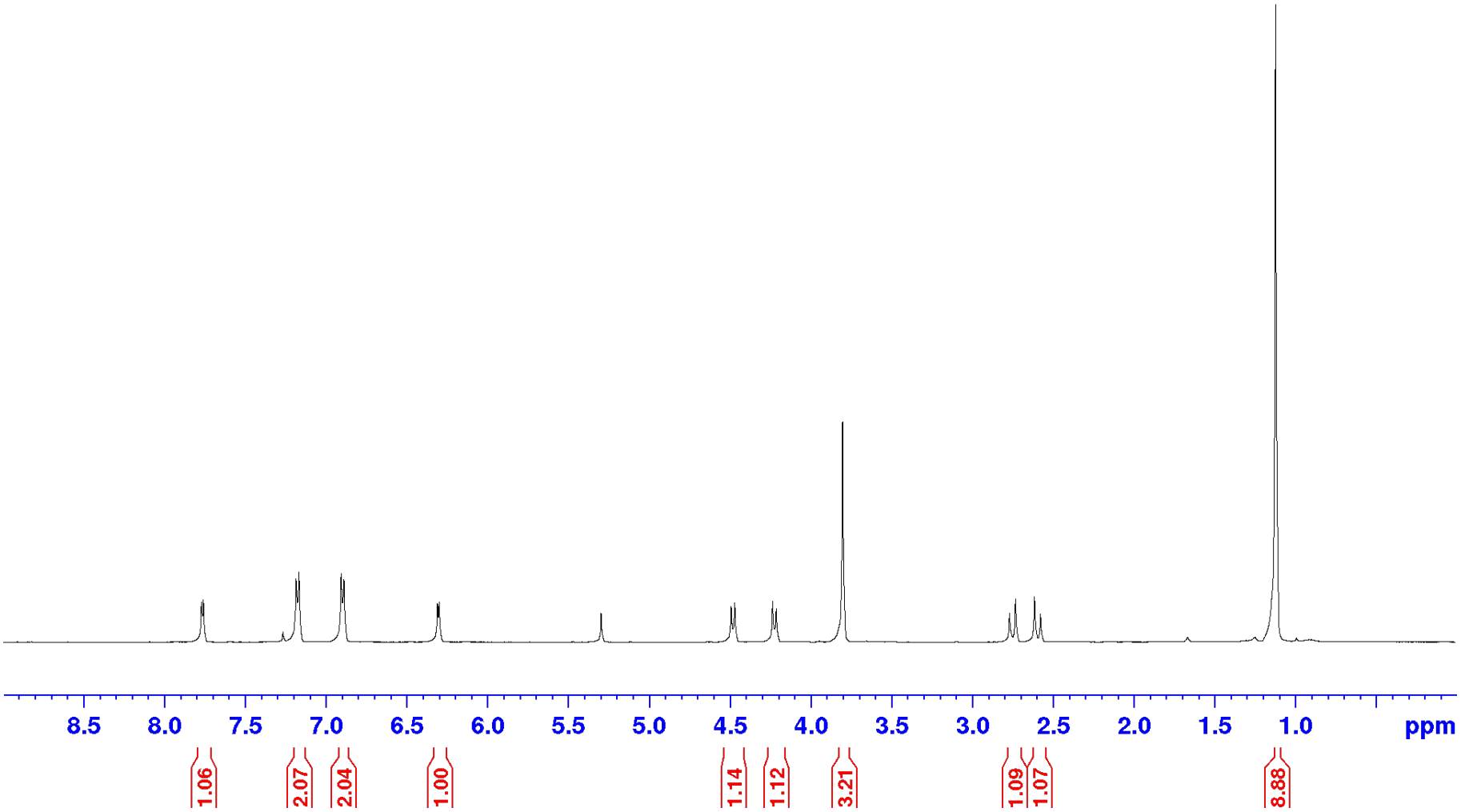
40
30
20
10


MeO
OPiv
O

2f


8.5
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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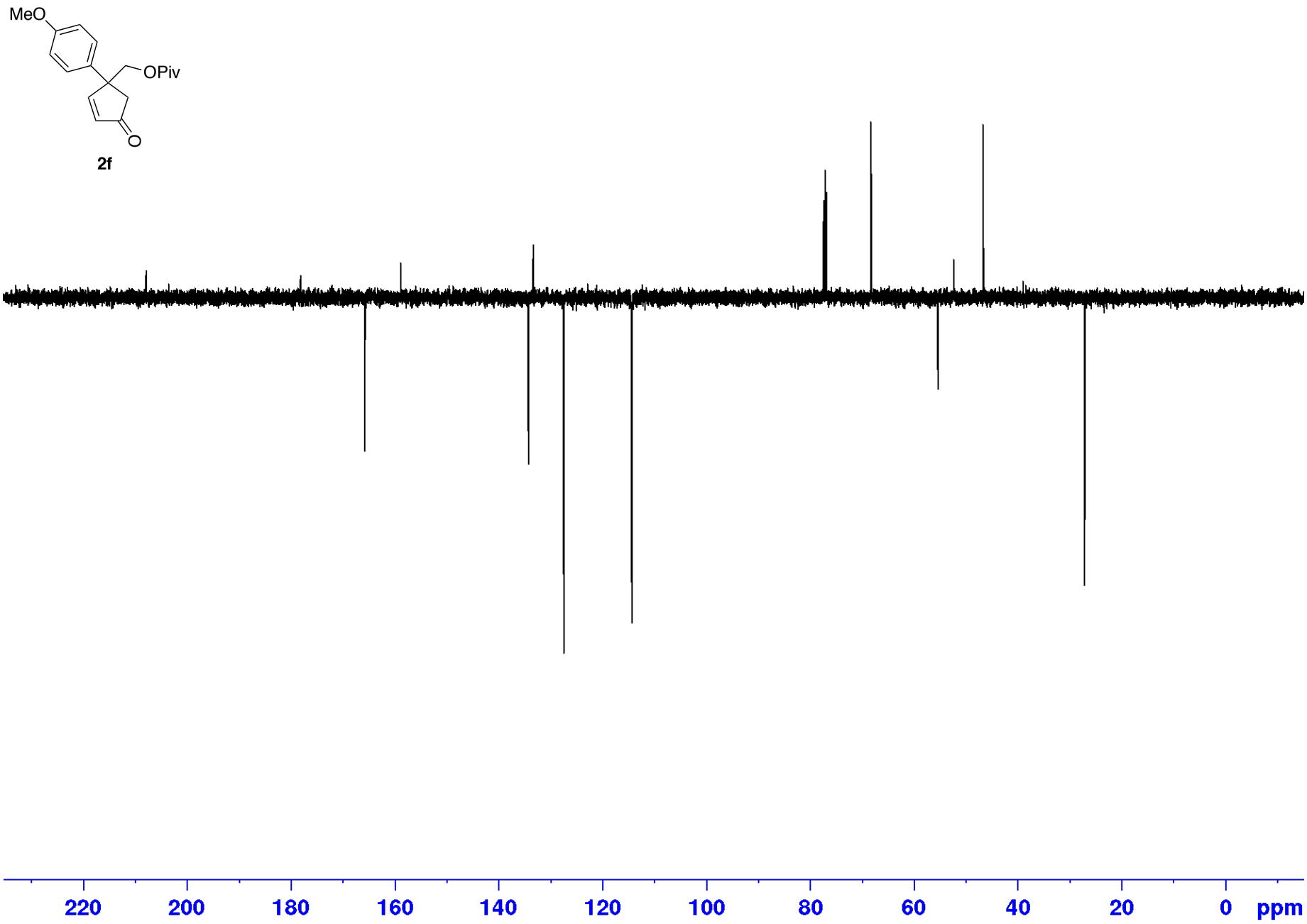
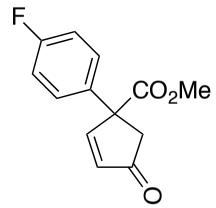
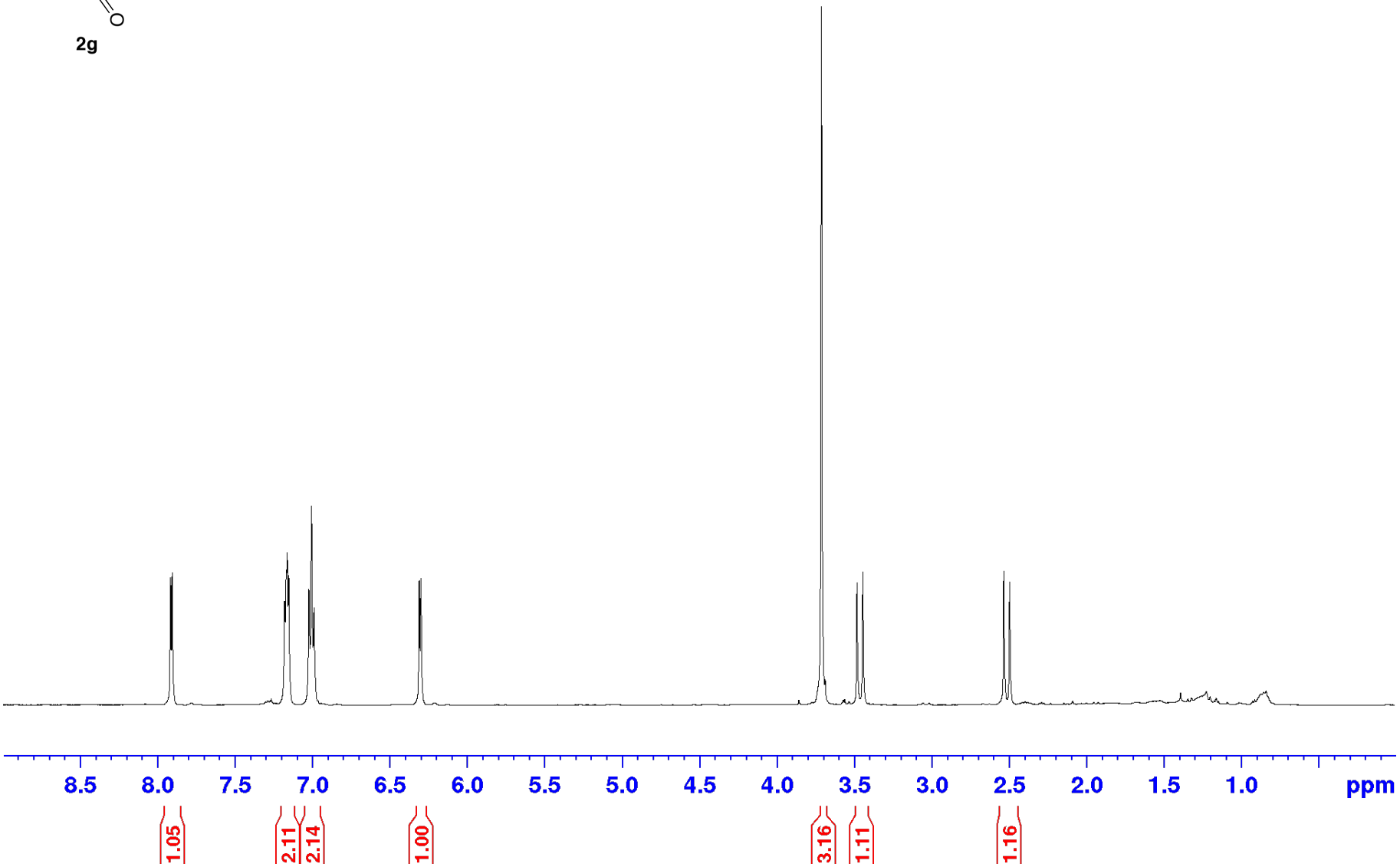
1.06
2.07
2.04
1.00
1.14
1.12
3.21
1.09
1.07
8.88


MeO
OPiv
O
2f
220
200
180
160
140
120
100
80
60
40
20
0
ppm


F
CO2Me
O

2g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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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1.5
1.0
ppm
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2.14
1.00
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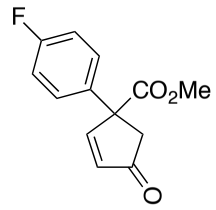
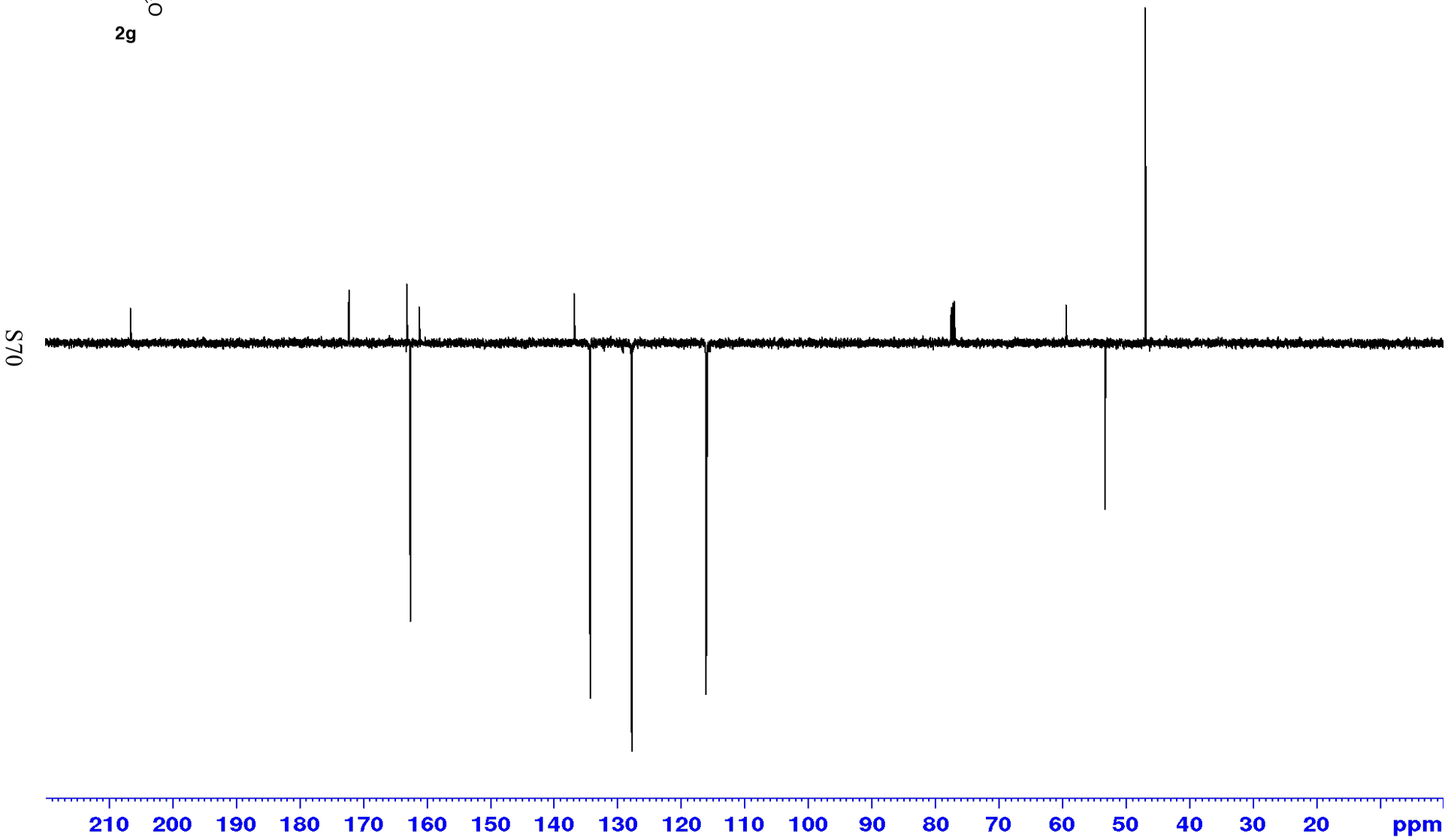
1.11
1.16


F
CO2Me
O

2g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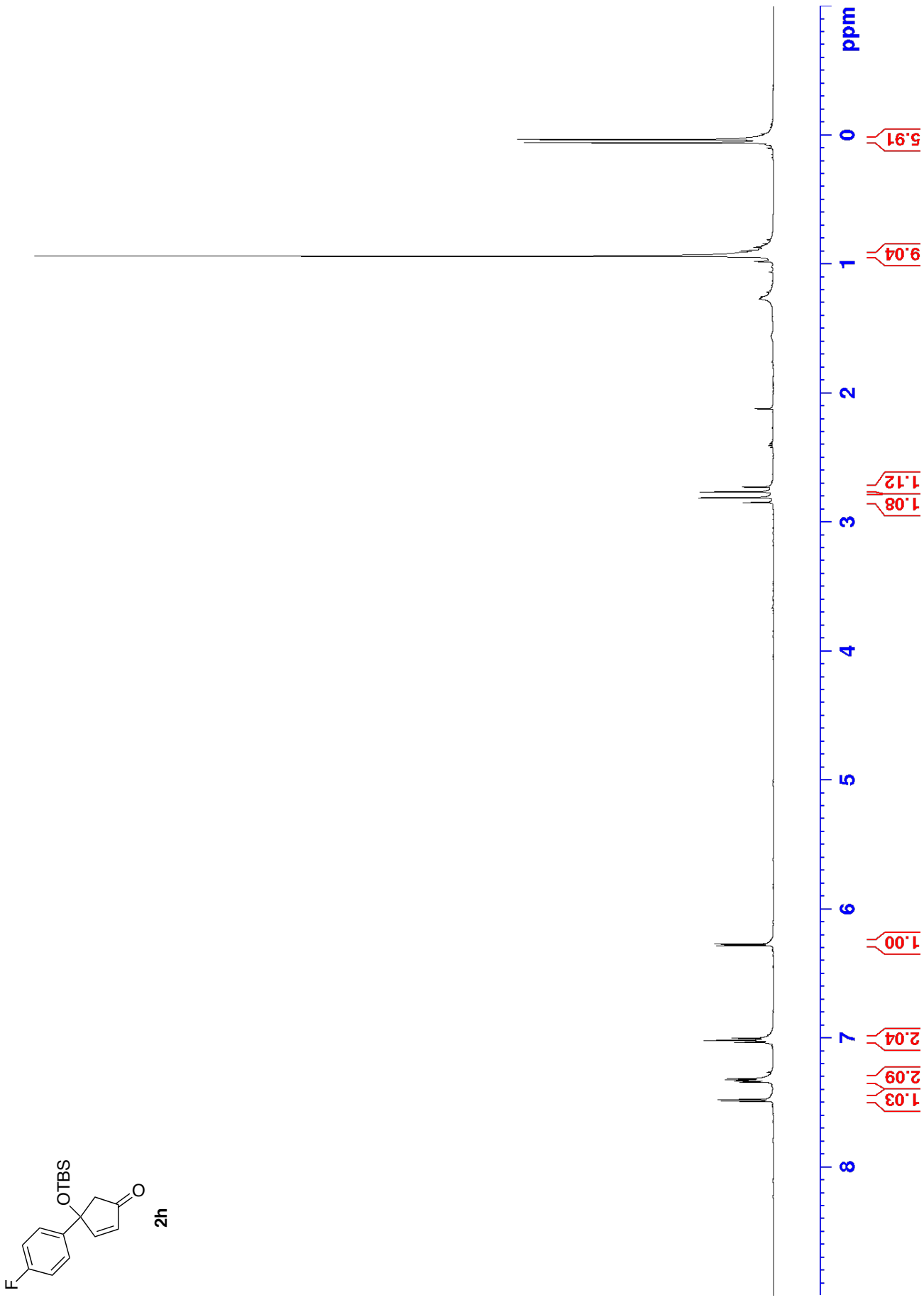
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O
F
2h
ppm
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6
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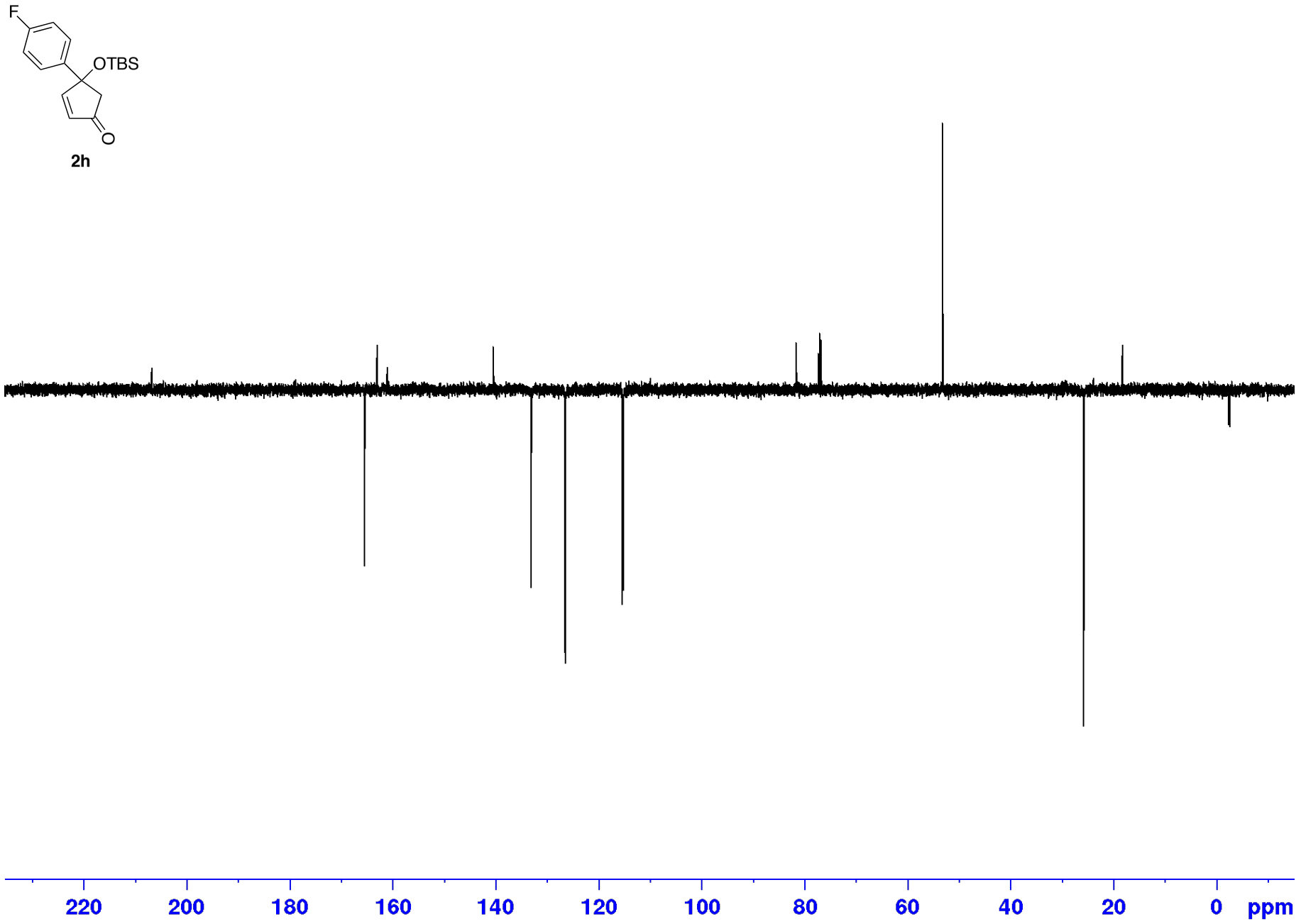
9.04
1.12
1.08
1.00
2.04
2.09
1.03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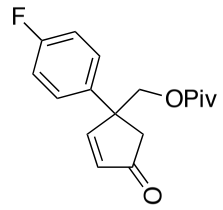
ppm


F
OPiv
O

2i

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7.0
6.5
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5.5
5.0
4.5
4.0
3.5
3.0
2.5
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1.99
1.00
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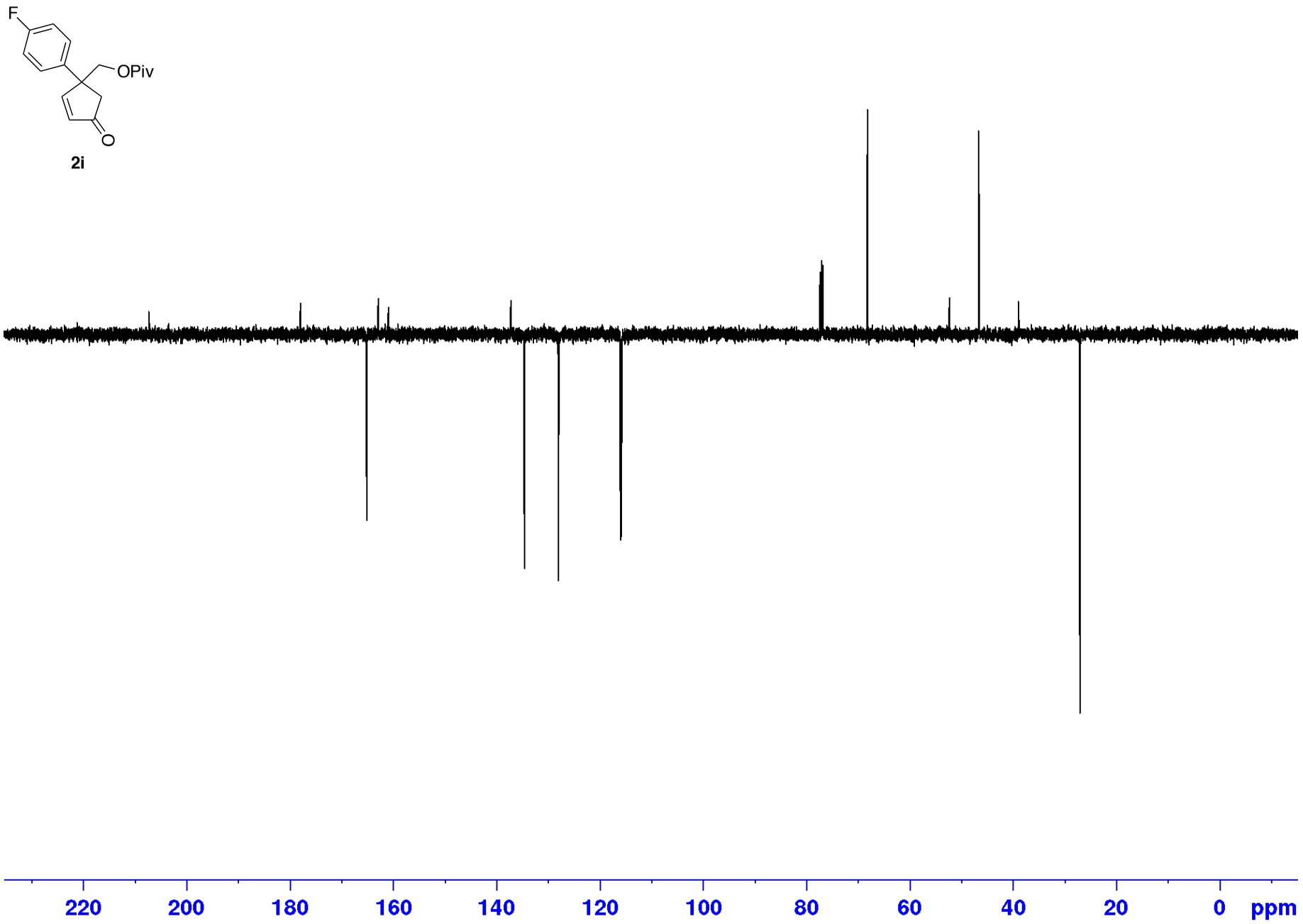
1.08
1.06
1.06
9.12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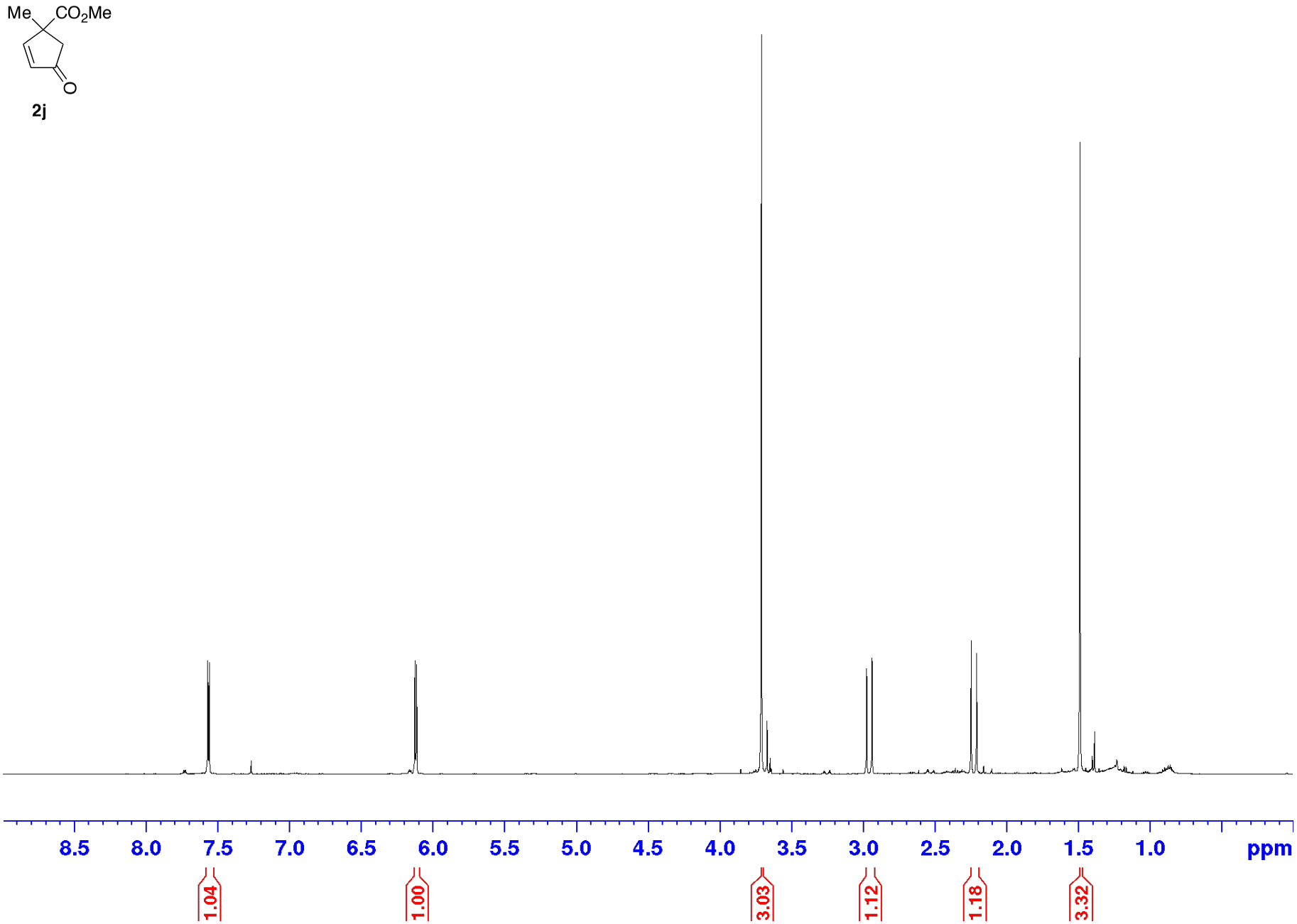
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CO2Me
O
2j
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5.5
5.0
4.5
4.0
3.5
3.0
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ppm
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1.00
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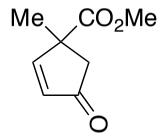
3.32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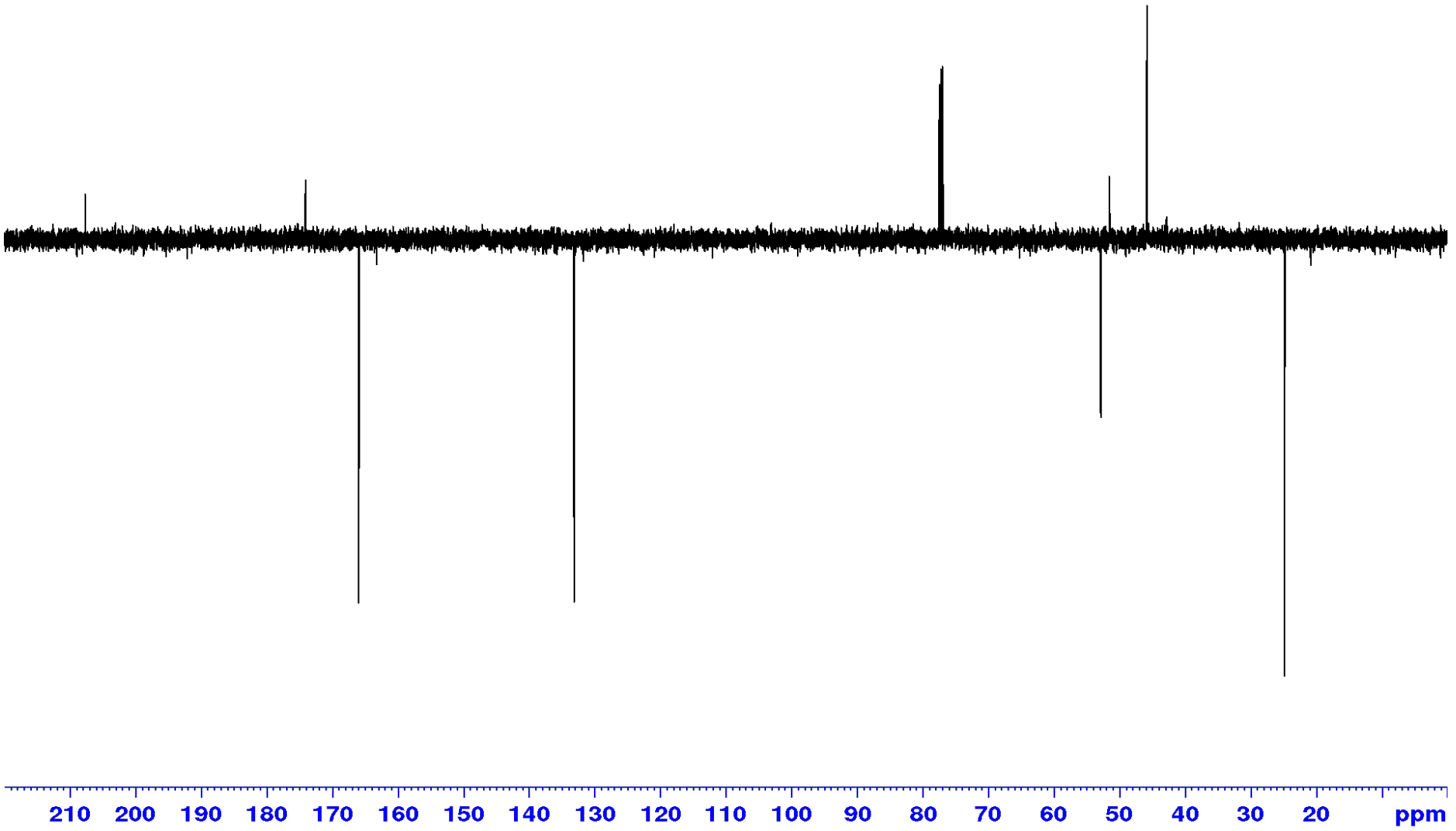
CO2Me
O

2j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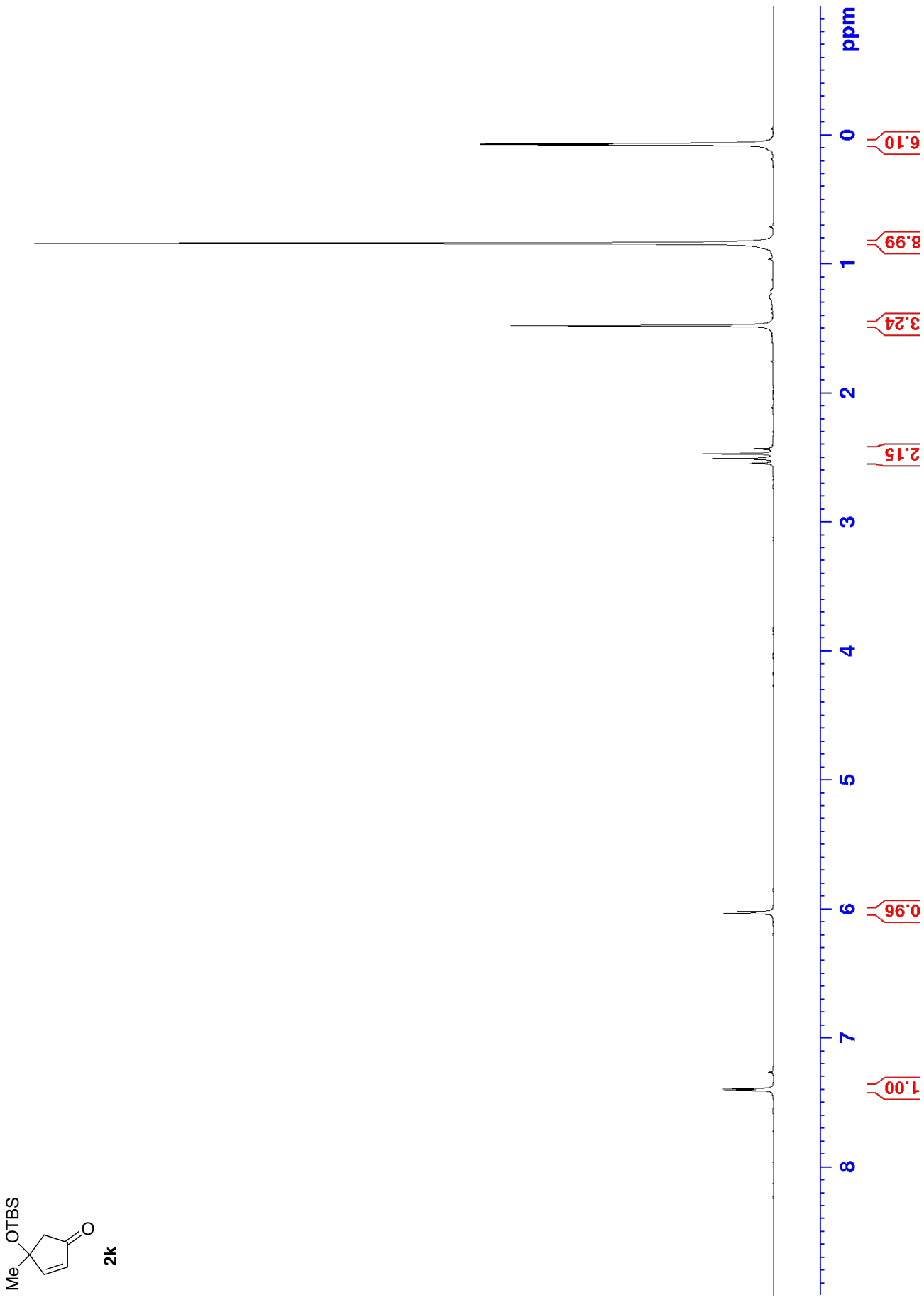
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Me
O
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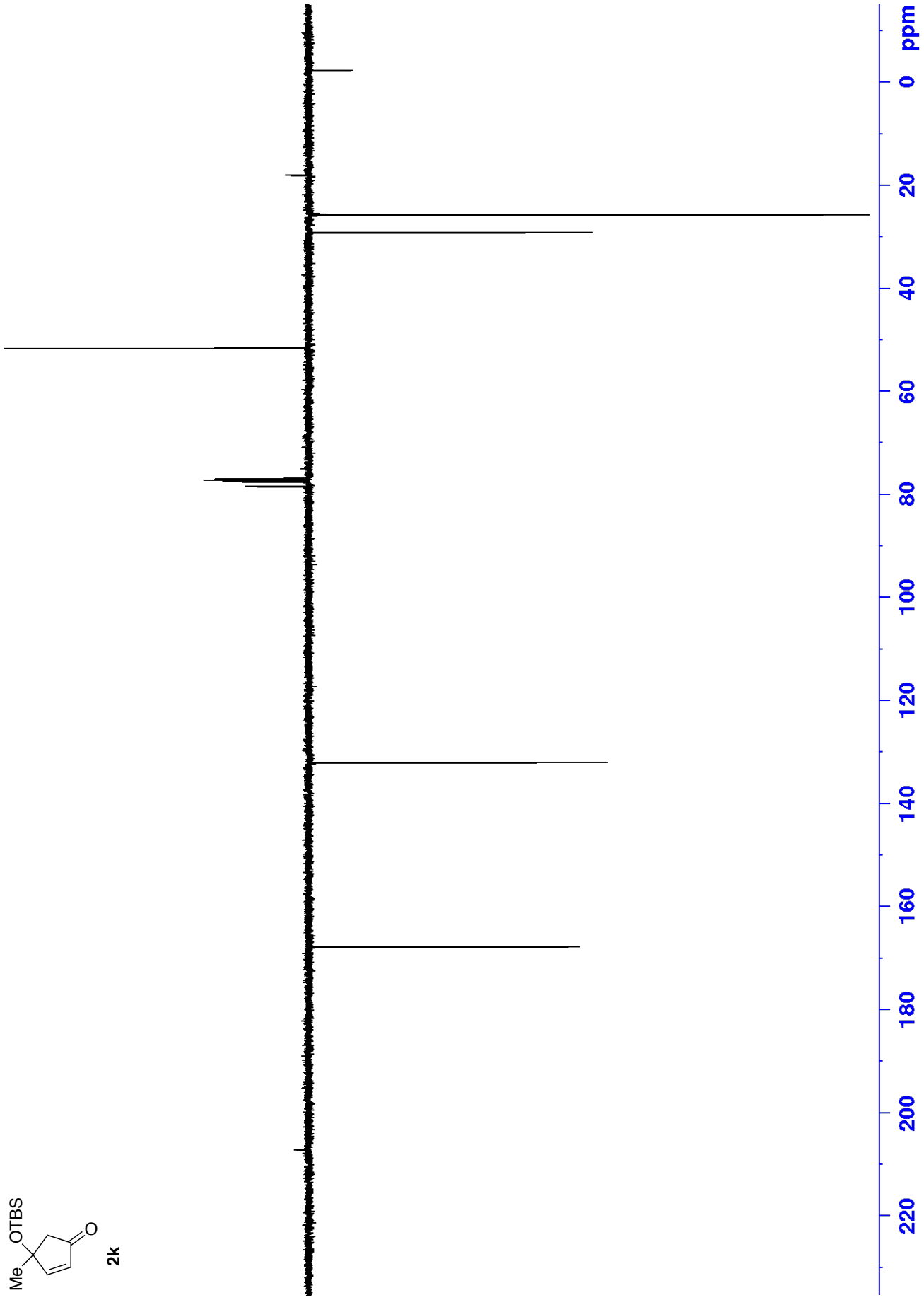
1.00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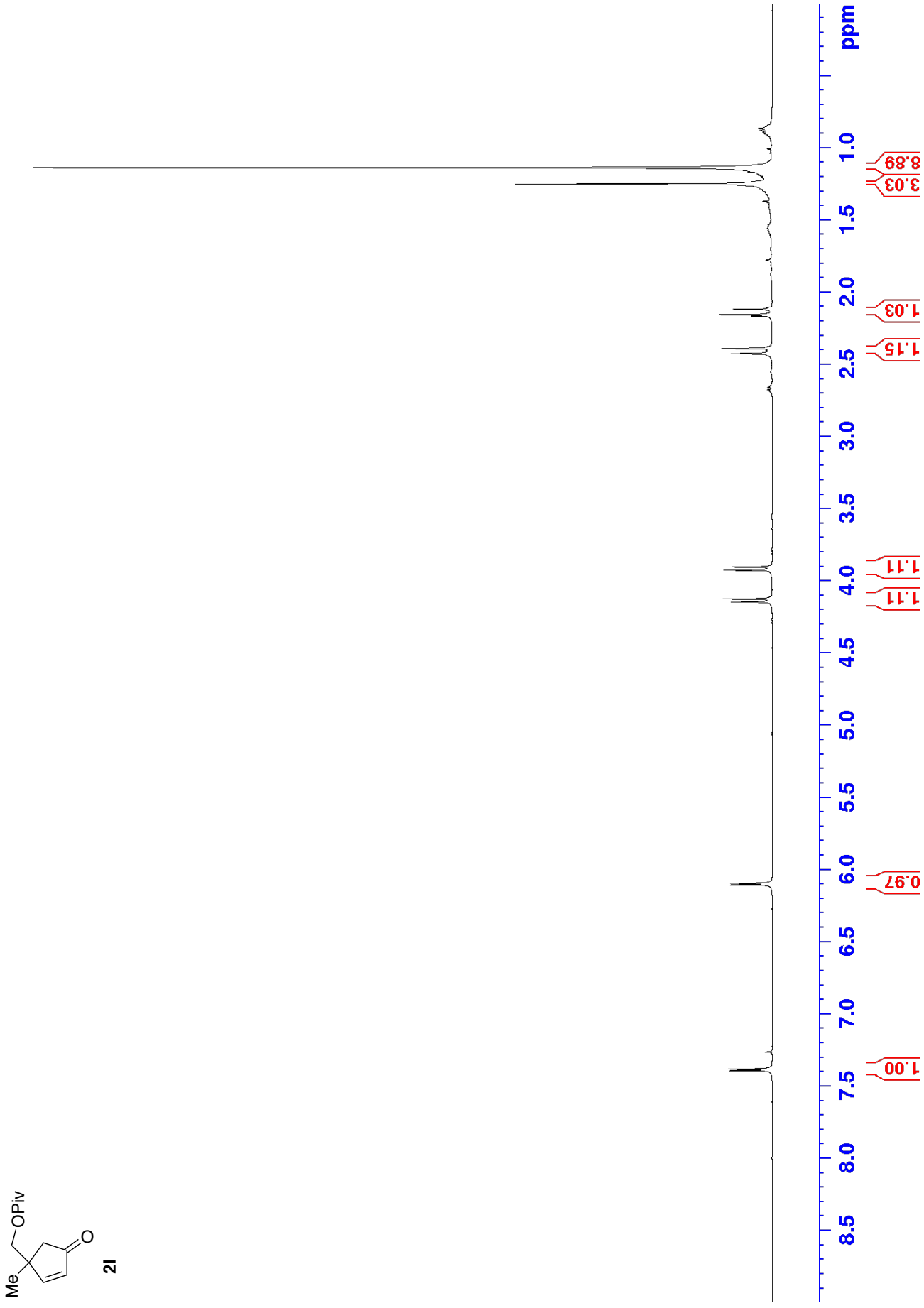
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2l
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4.5
4.0
3.5
3.0
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1.11
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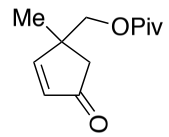
3.03
8.89



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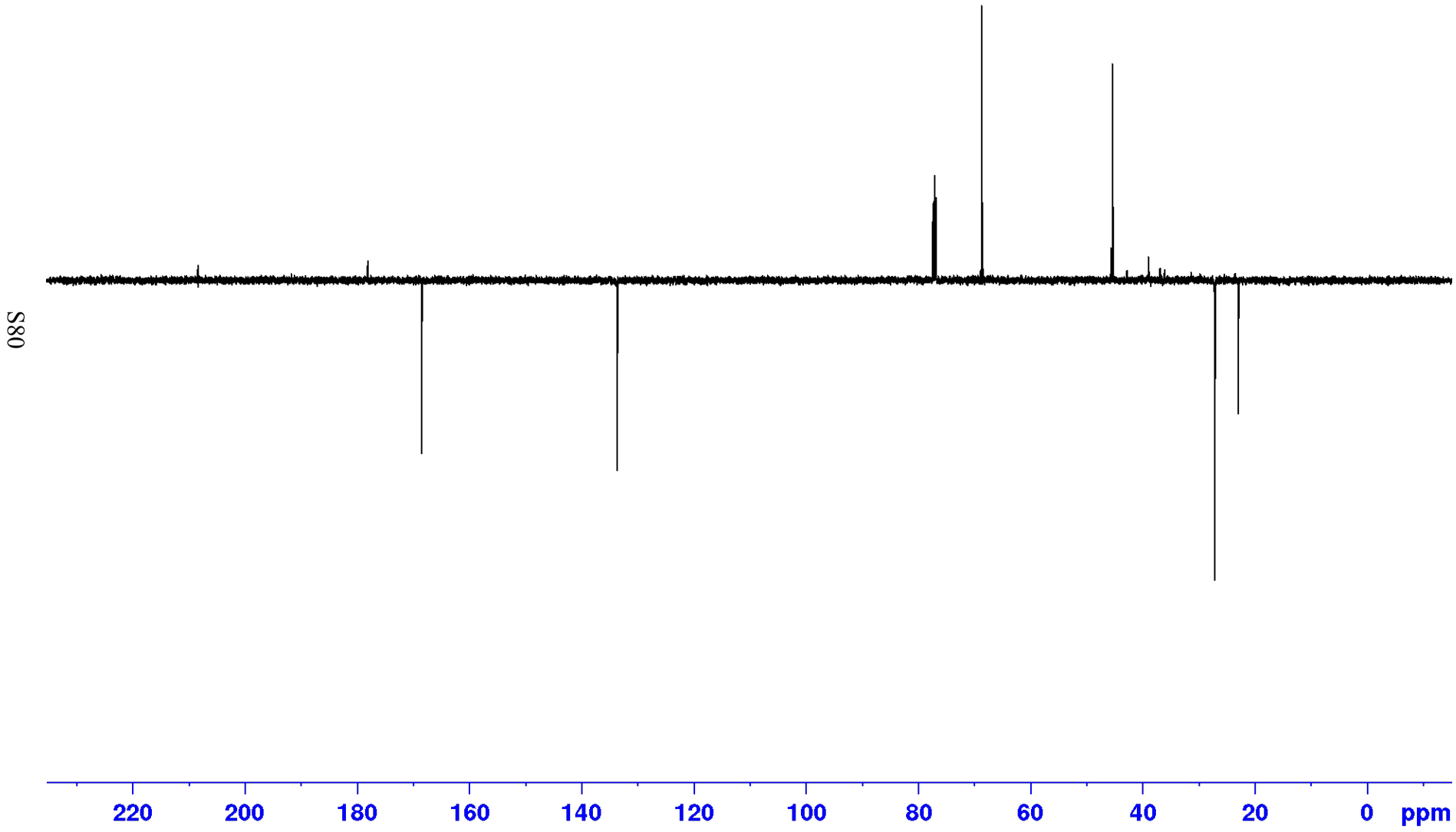

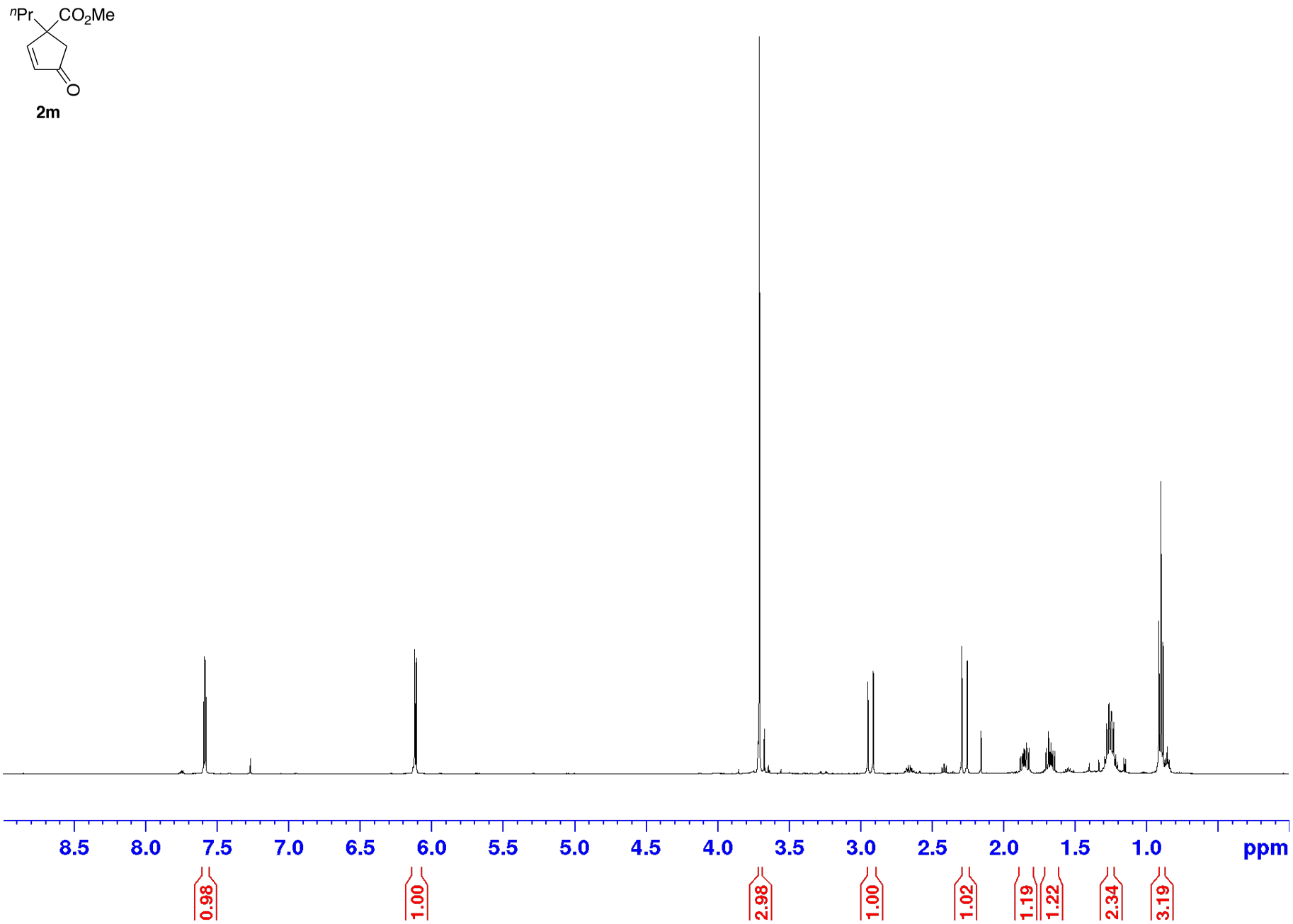
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O
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5.5
5.0
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4.0
3.5
3.0
2.5
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1.00
1.02
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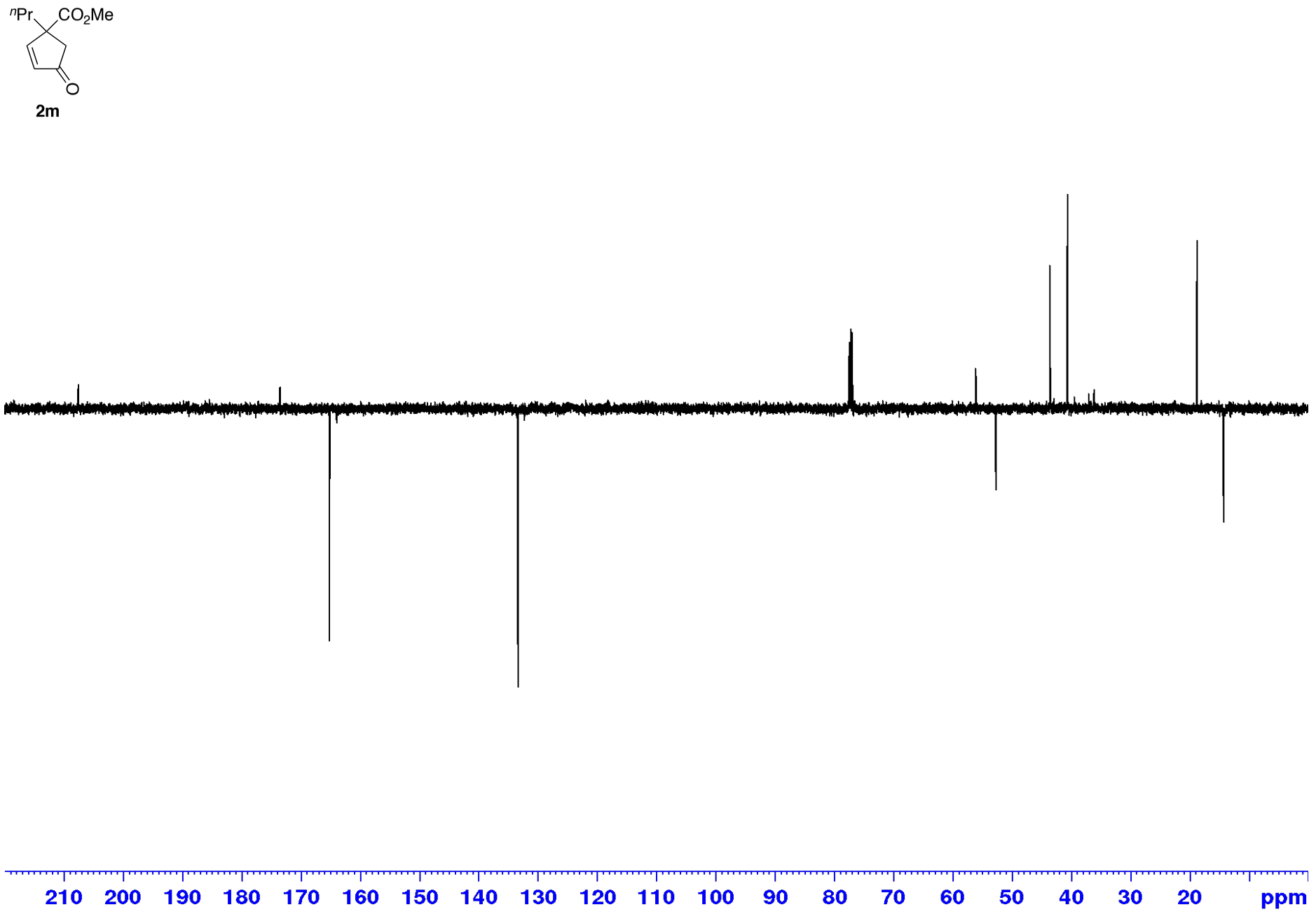
3.19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CO2Me
O
2m
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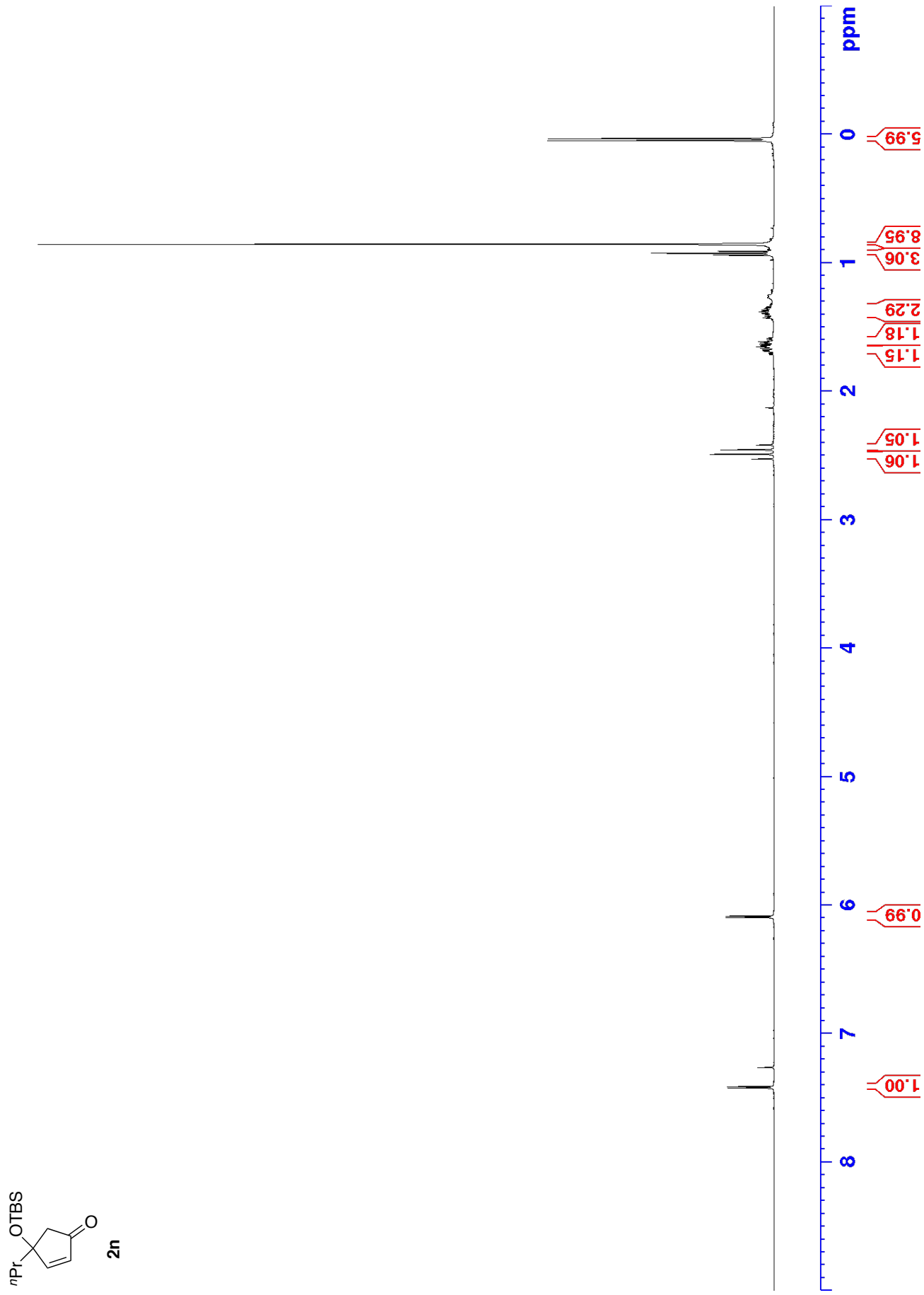
50
40
30
20
ppm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nPr
2n
ppm
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2
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8.95
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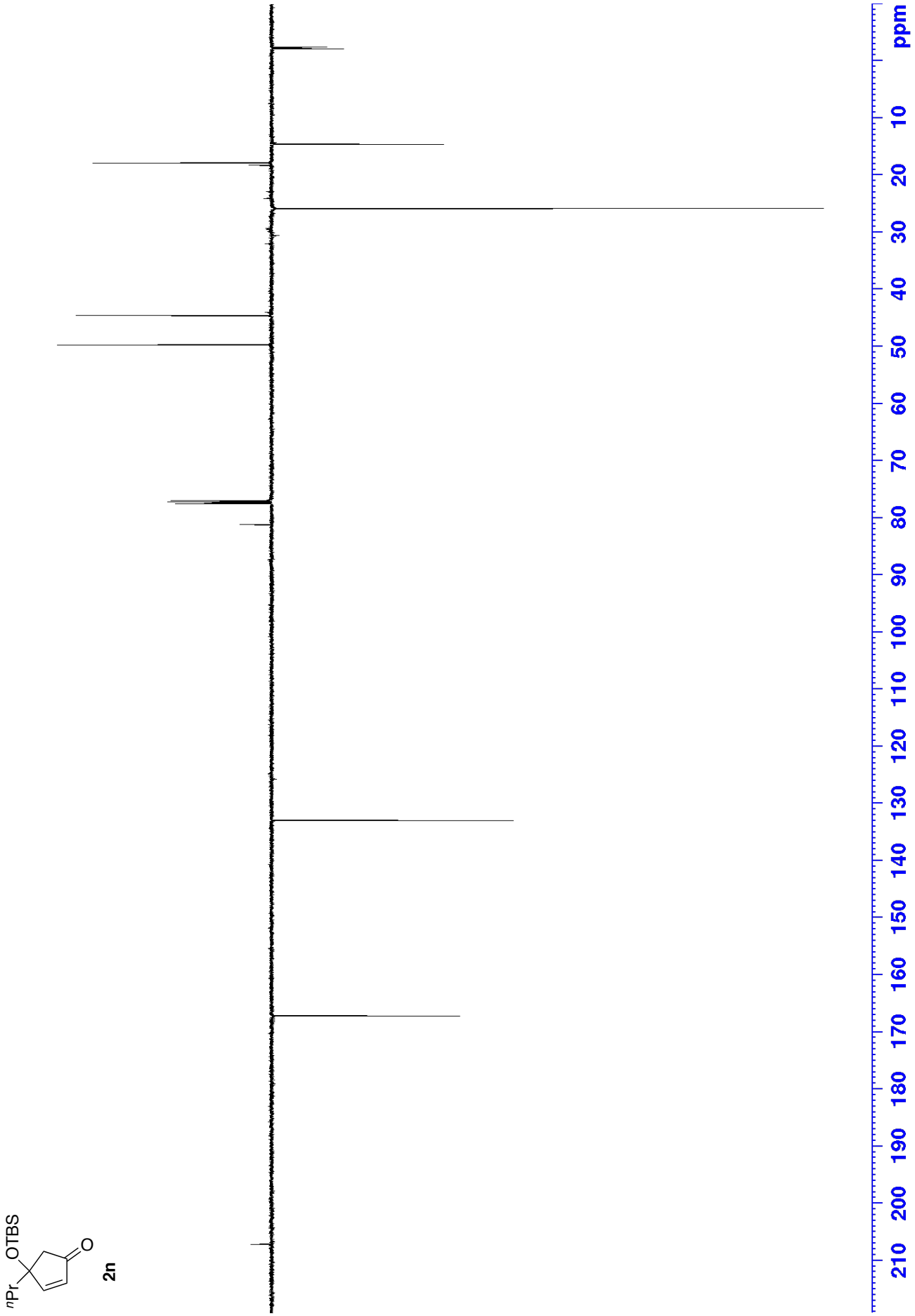
2.29
1.18
1.15
1.05
1.06
0.99
1.00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2n
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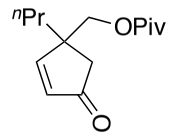
30
20
10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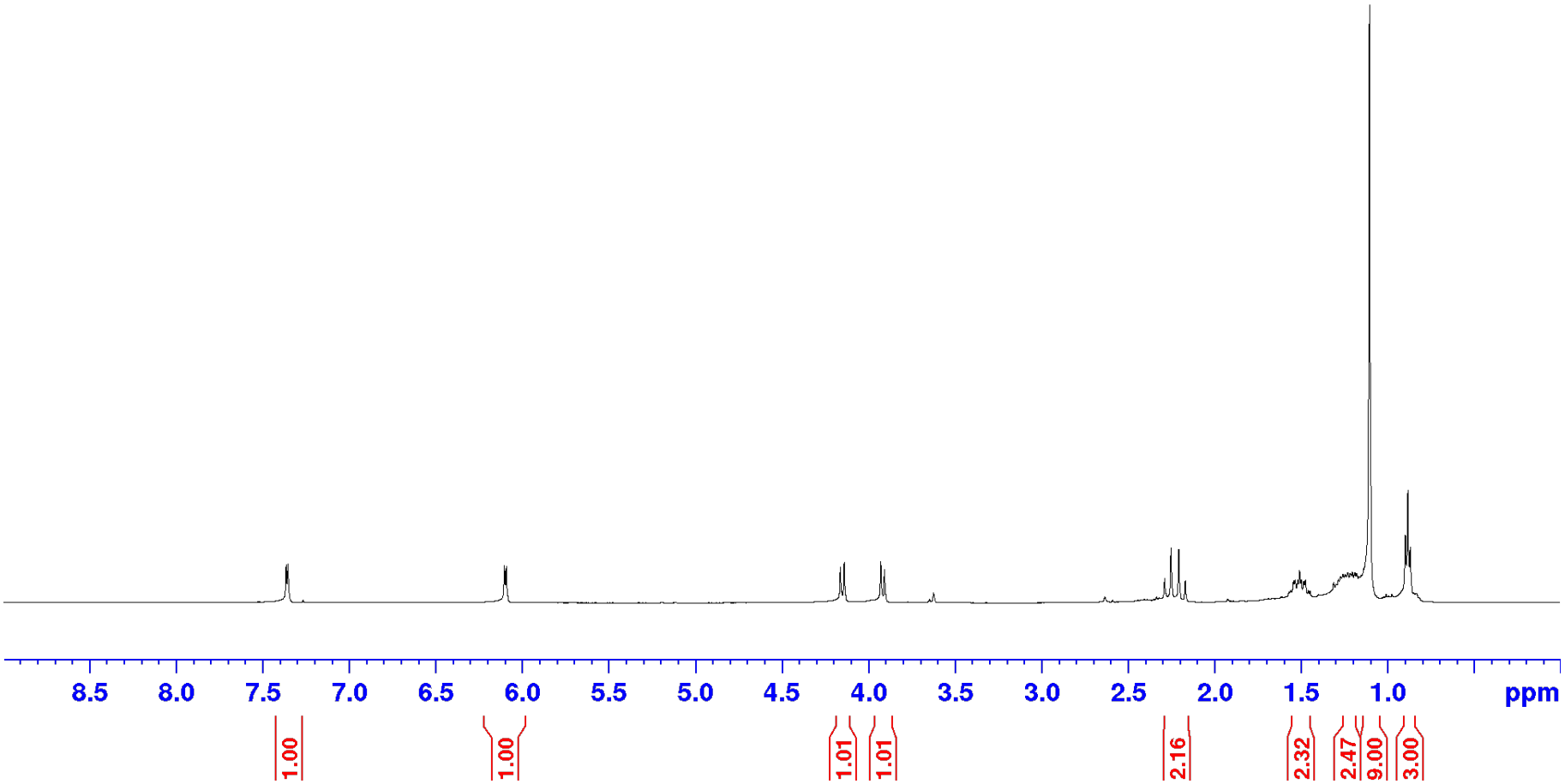
OPiv
O

2o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4.0
3.5
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2.5
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1.01
2.16
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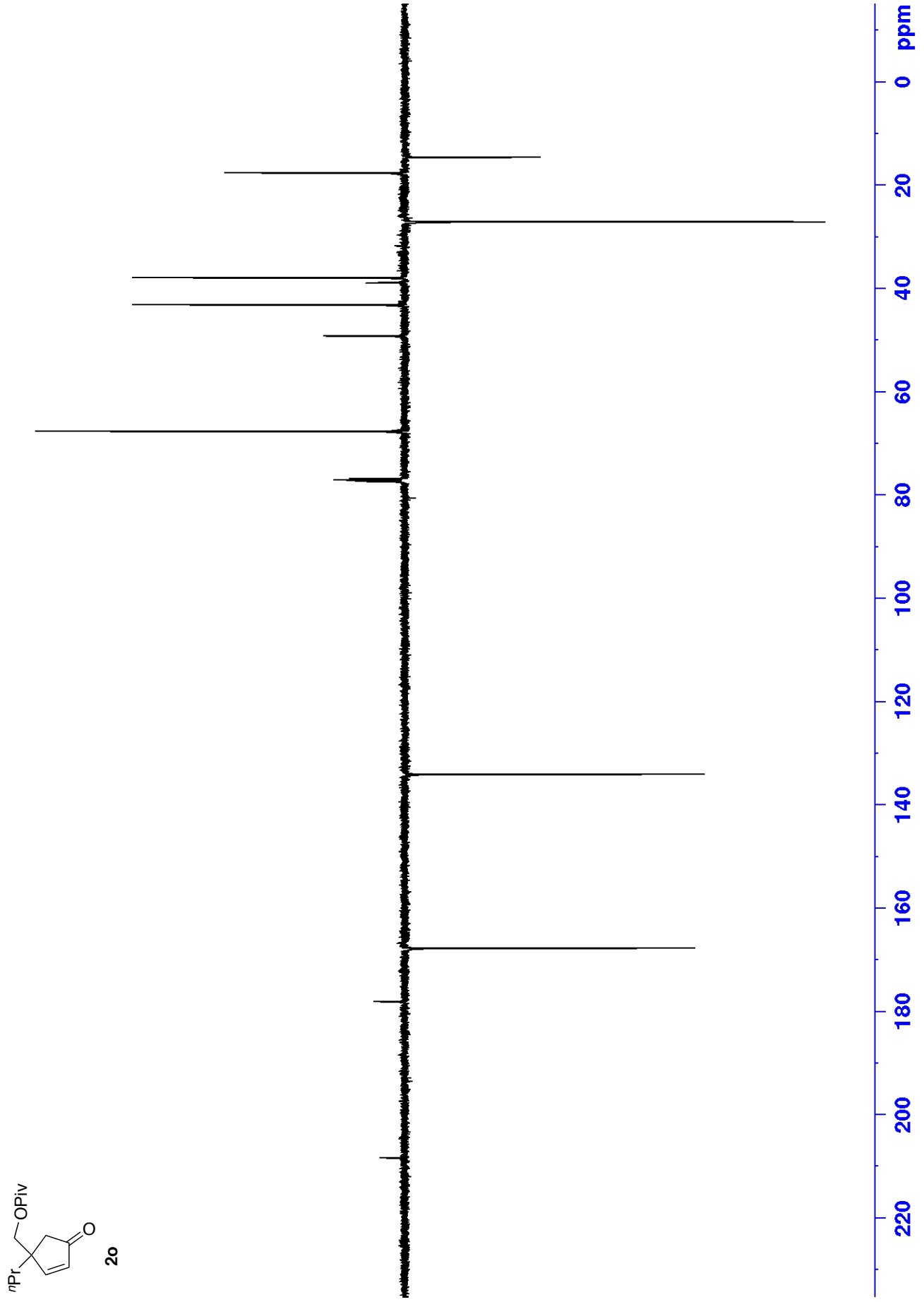
9.00
3.00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O
nPr
2o
ppm
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60
80
100
120
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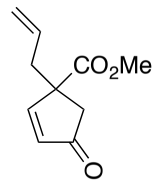
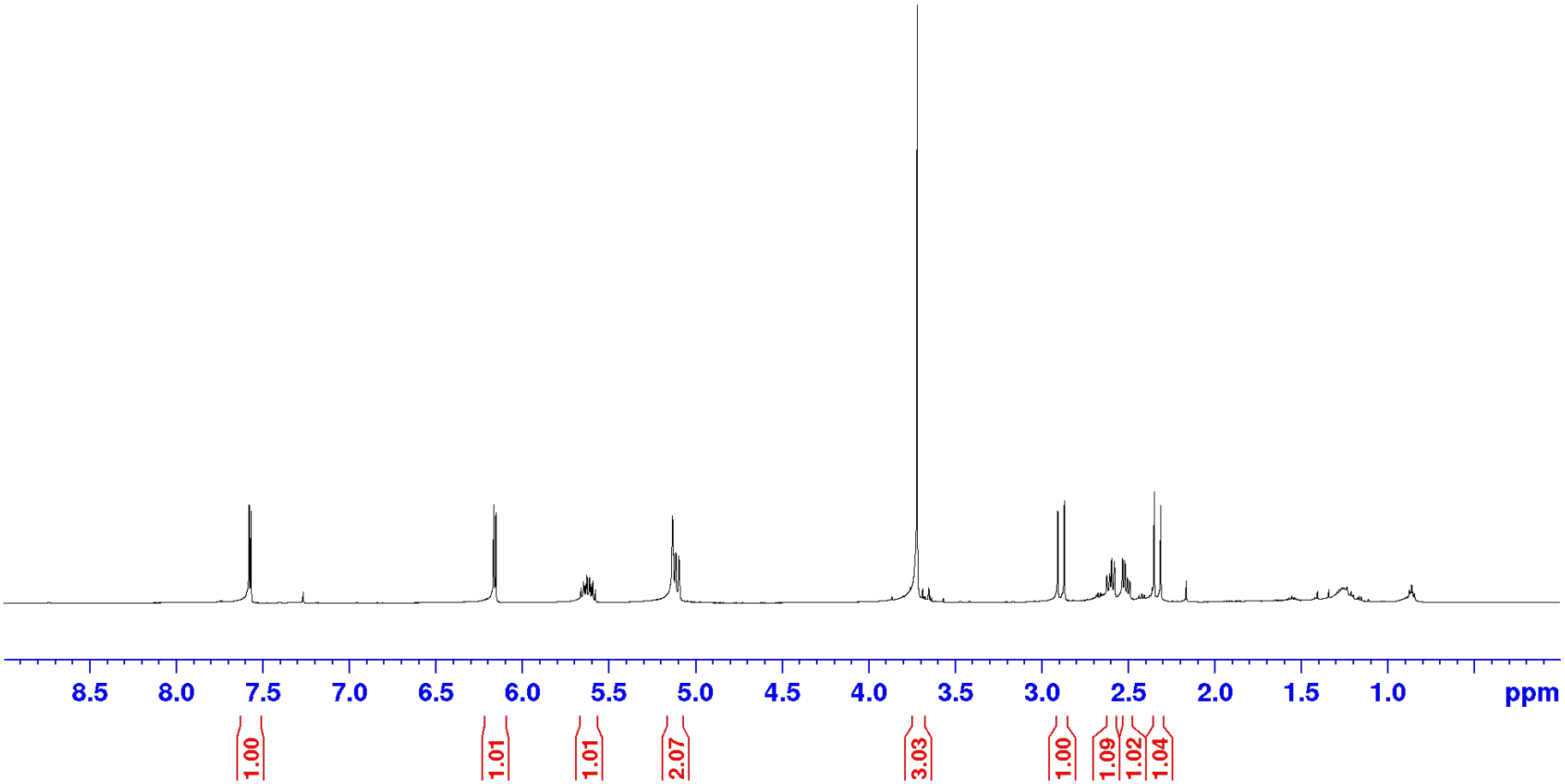
160
180
200
220


CO2Me
O

2p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4.0
3.5
3.0
2.5
2.0
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ppm
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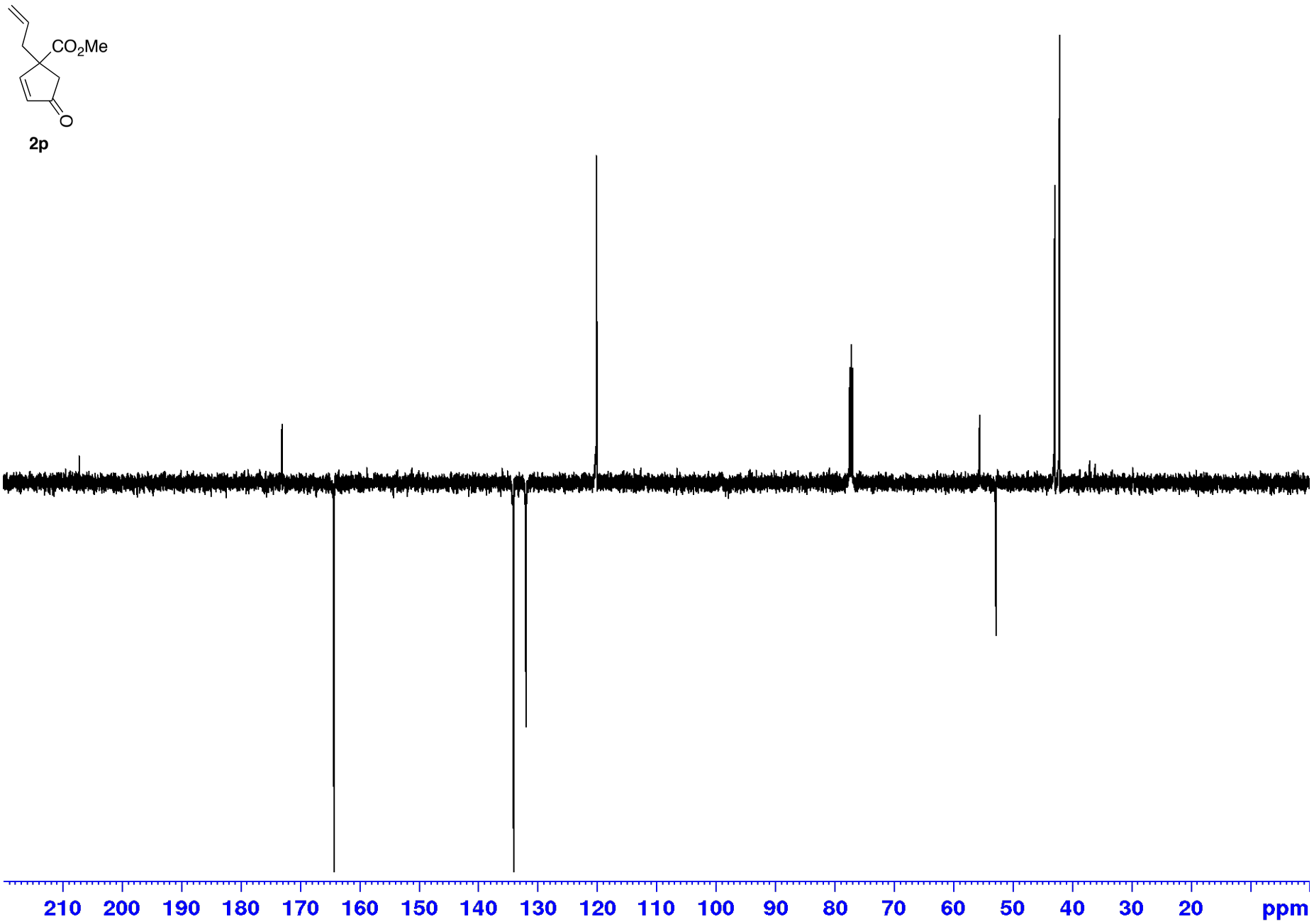
1.01
1.01
2.07
3.03
1.00
1.09
1.02
1.04


CO2Me
O
2p
S88
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150
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130
120
110
100
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80
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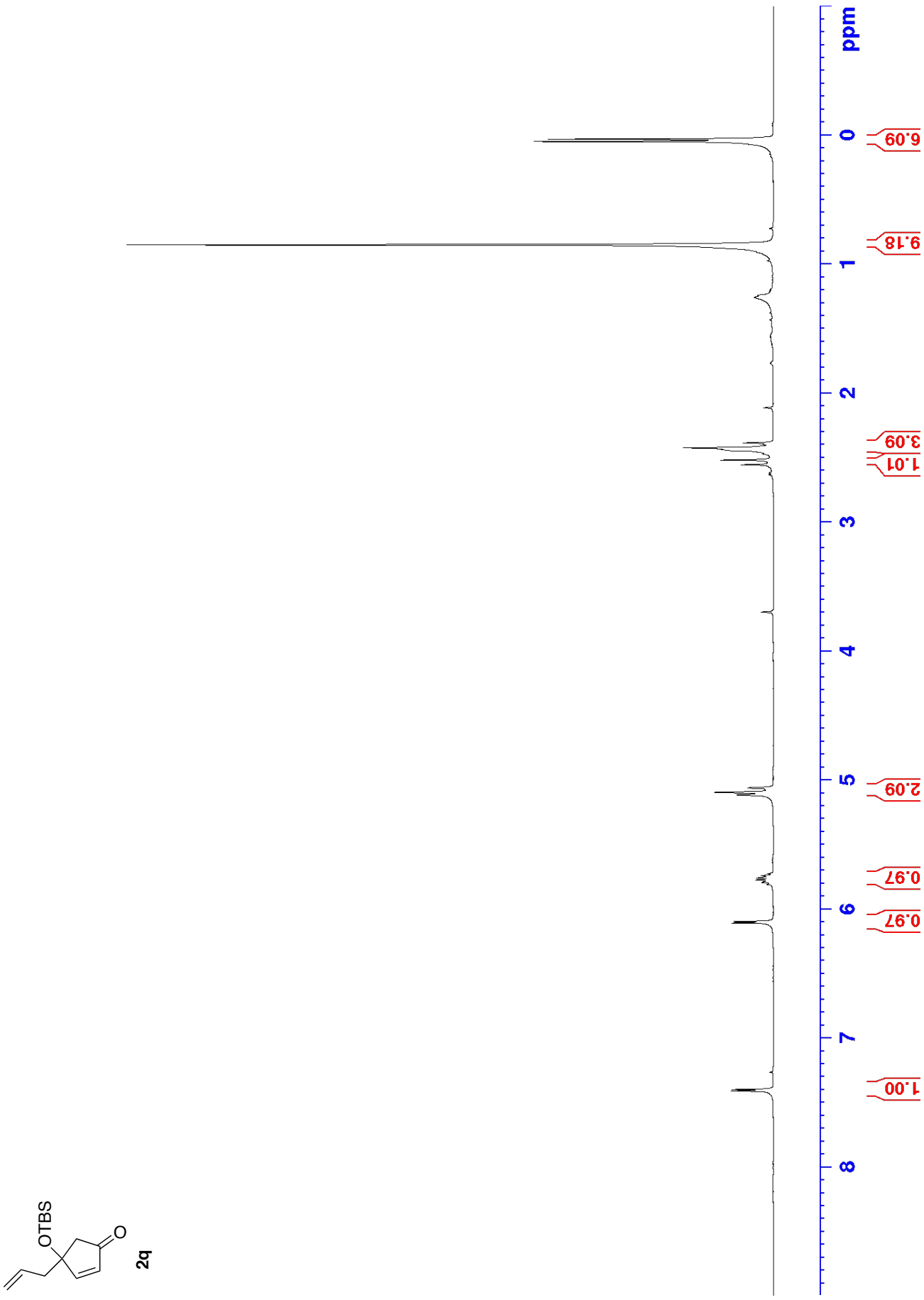
40
30
20
ppm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ppm
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9.18
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1.01
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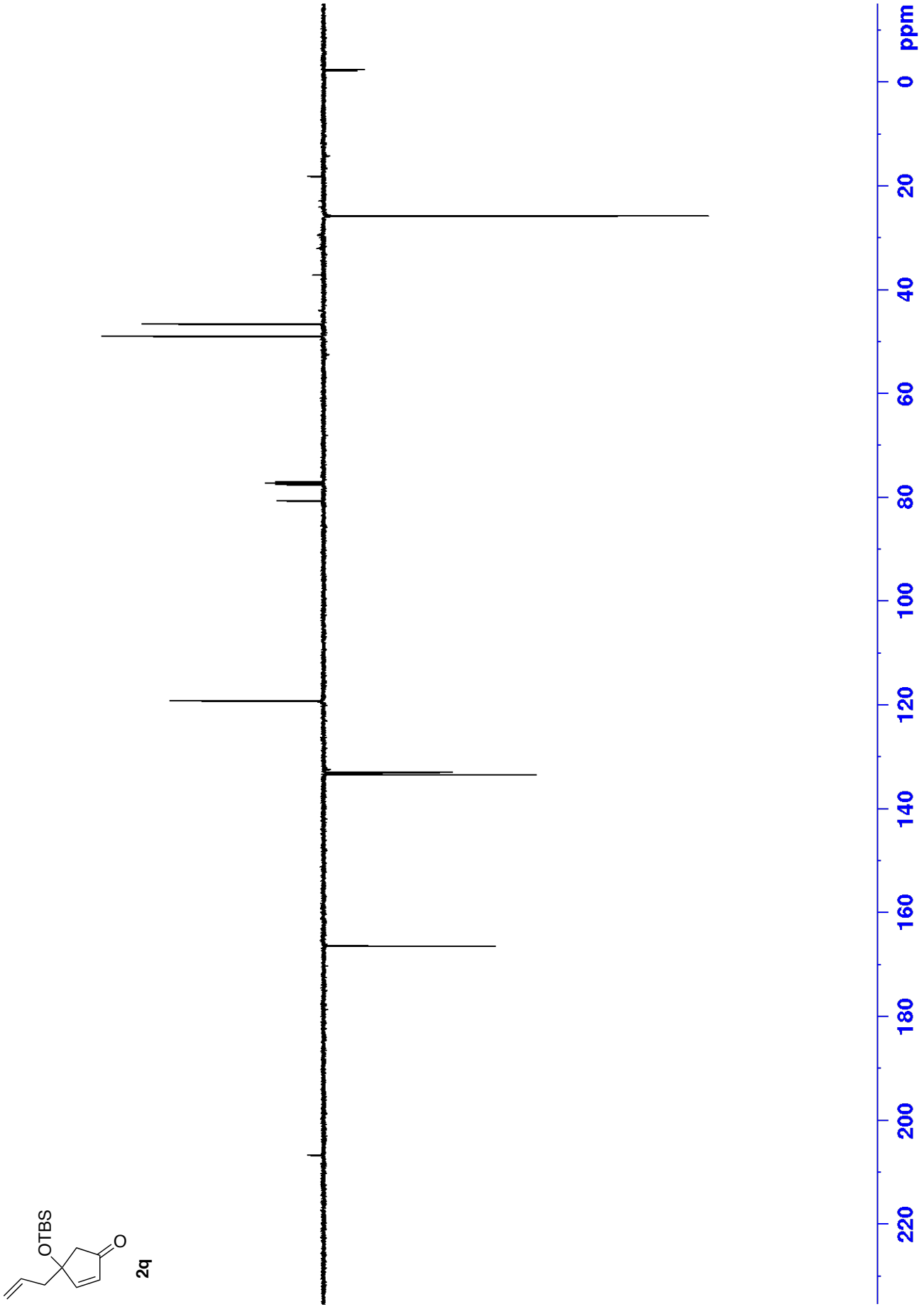
0.97
1.00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ppm
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160
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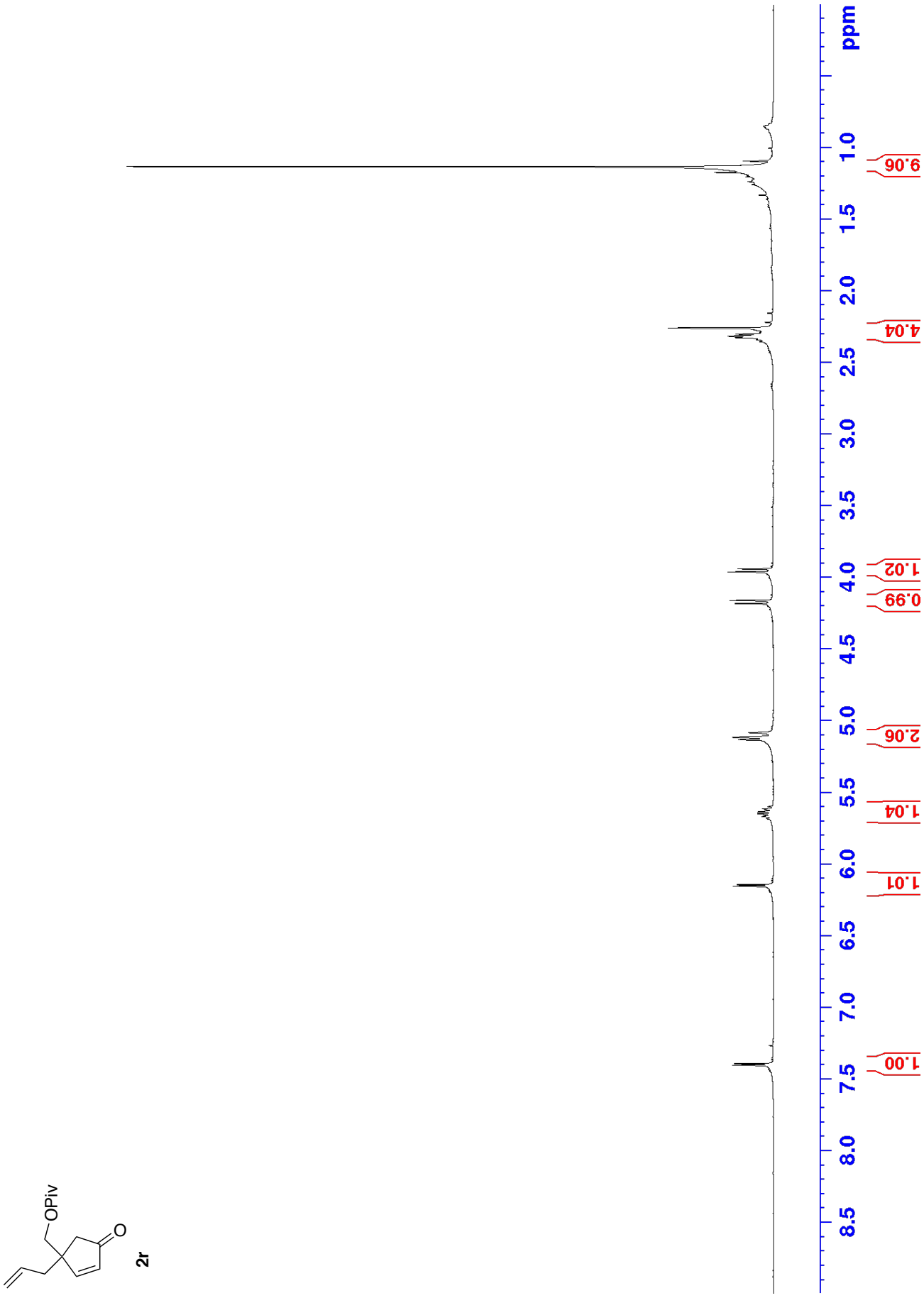
200
220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O
2r
ppm
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5.0
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6.0
6.5
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8.5
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0.99
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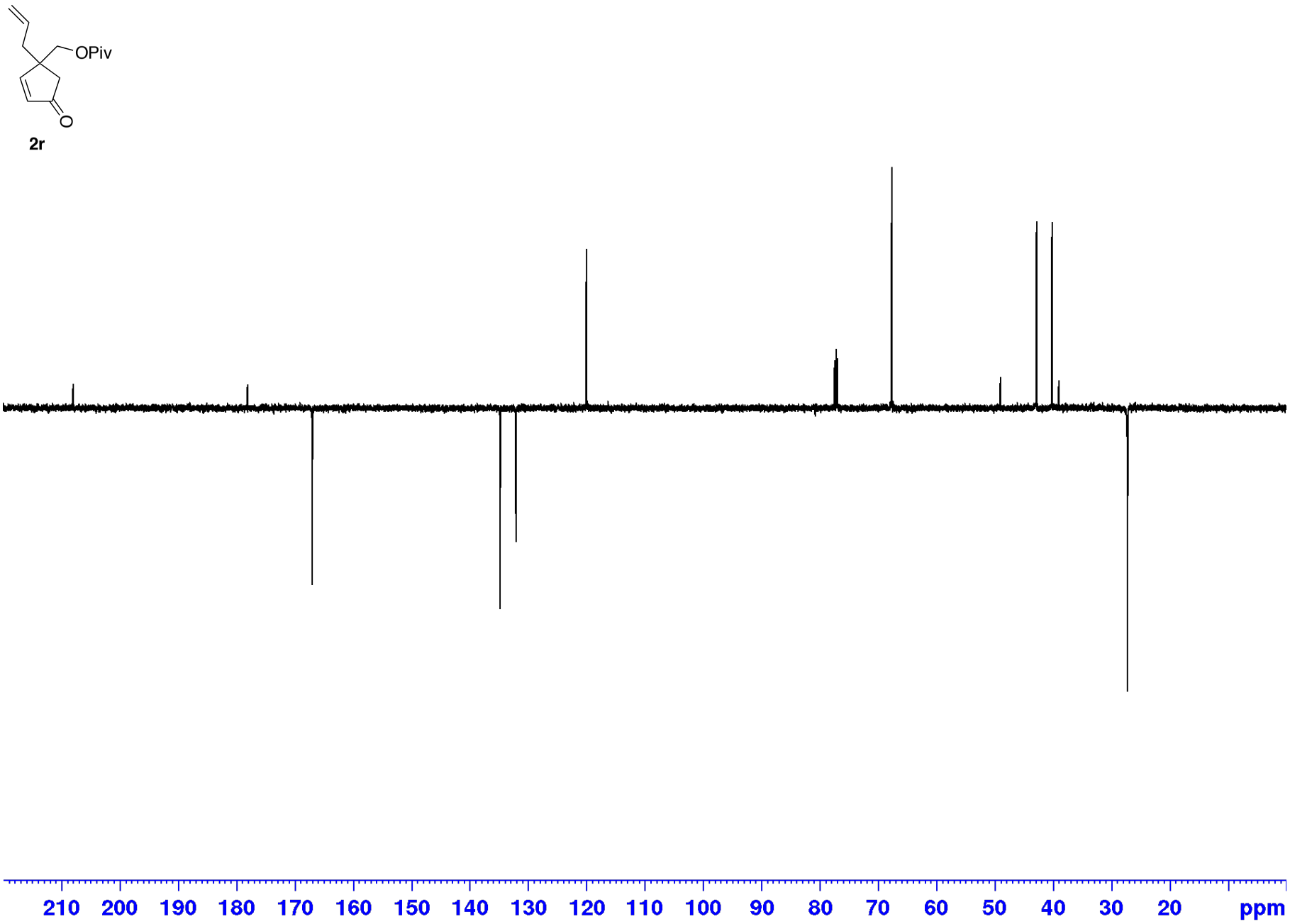
1.04
1.01
1.00


OPiv
O
2r
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200
190
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150
140
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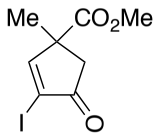
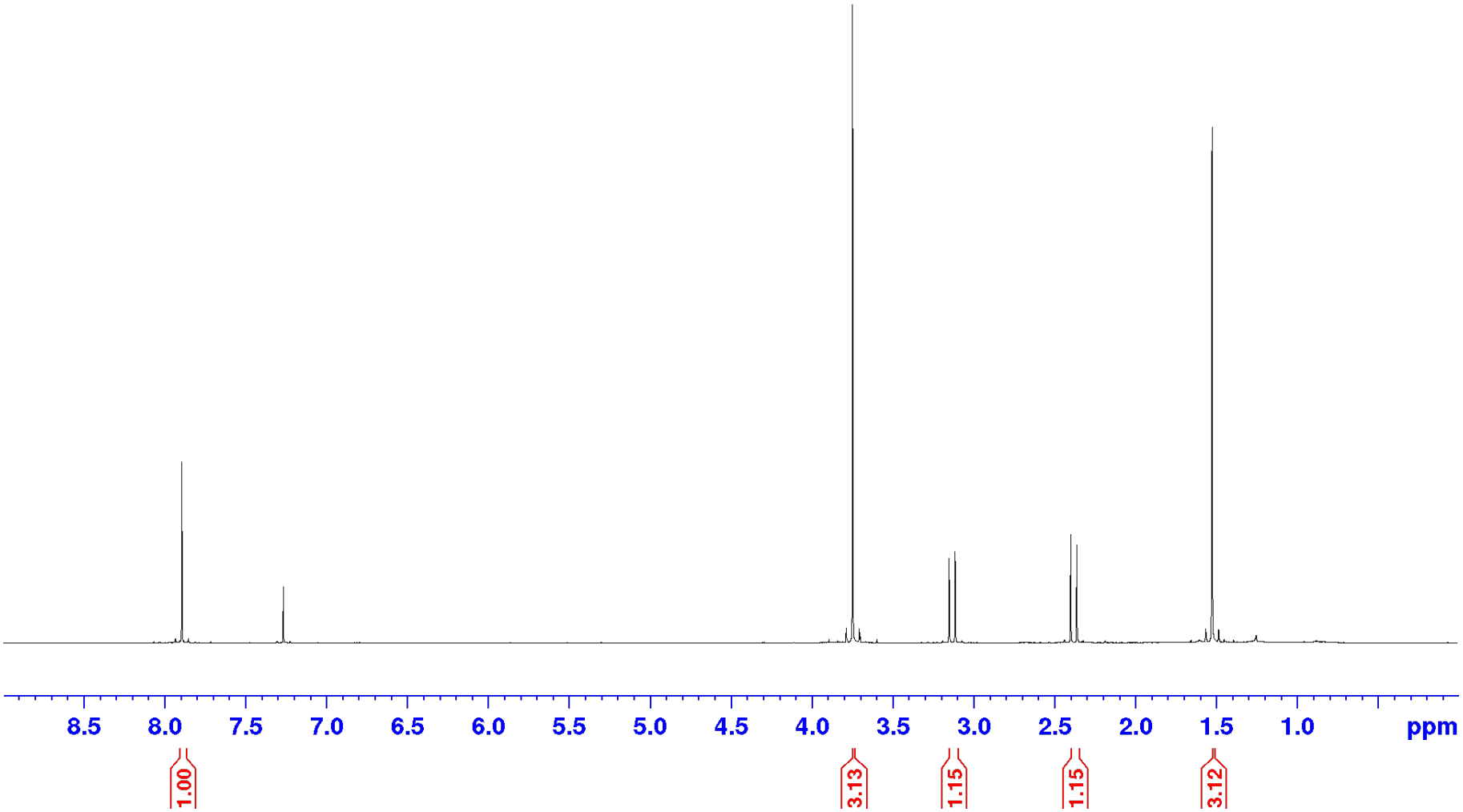
120
110
100
90
80
70
60
50
40
30
20
ppm


Me
CO2Me
I
O

6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1.00
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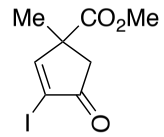
3.12



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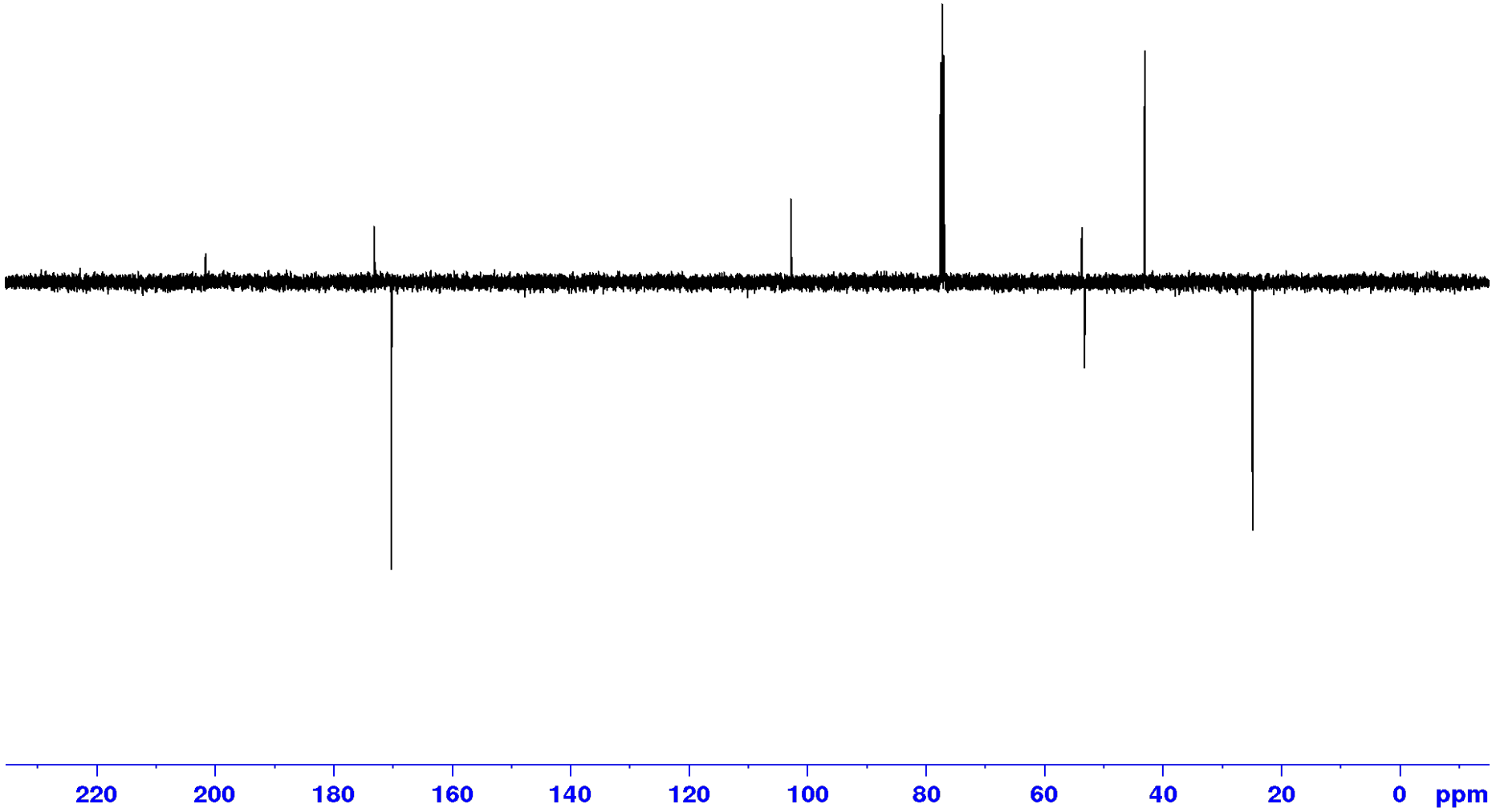
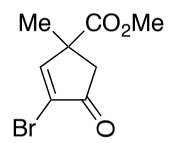
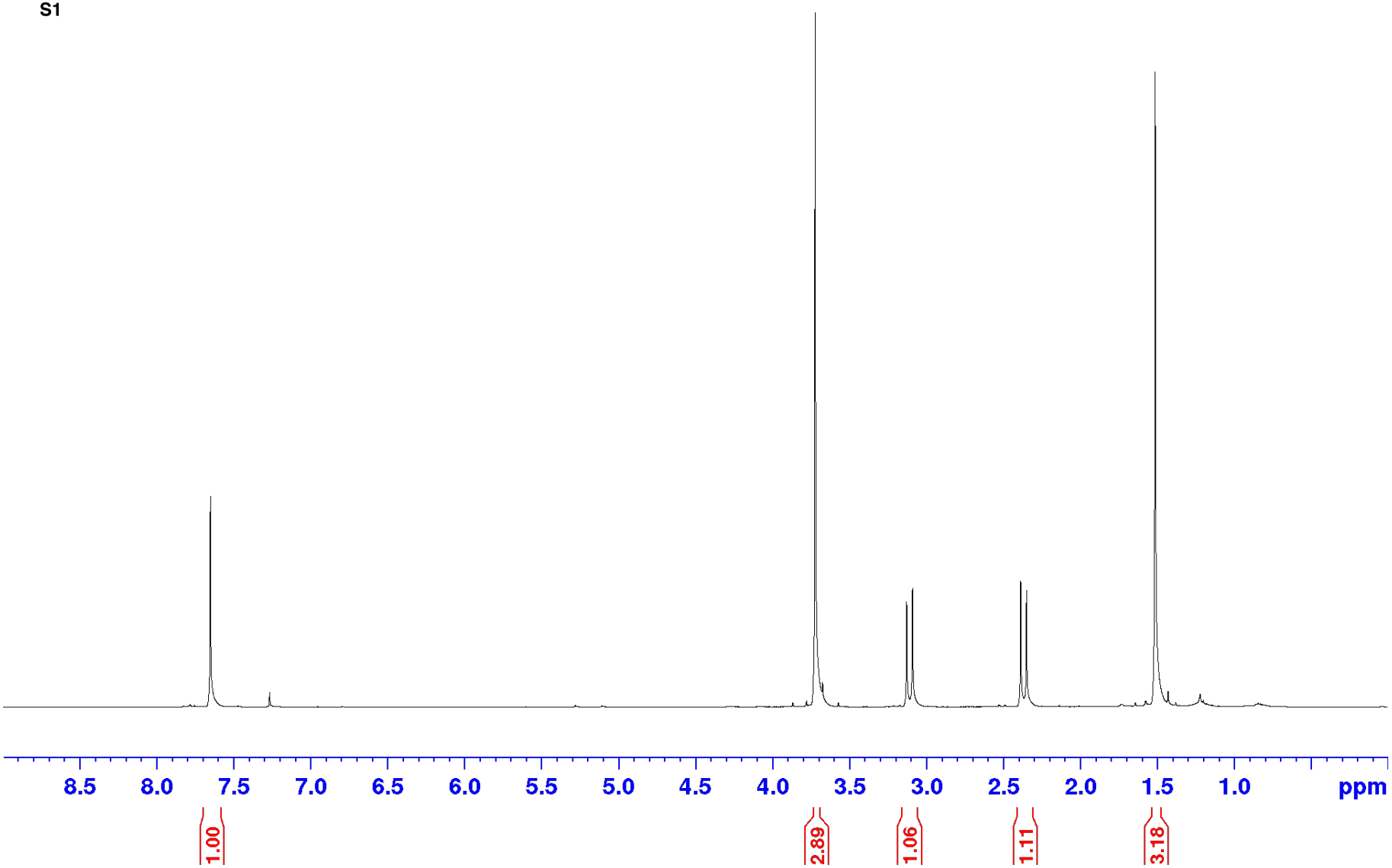



Me
CO2Me
Br
O

S1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7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.5
2.0
1.5
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ppm
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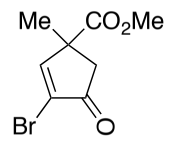
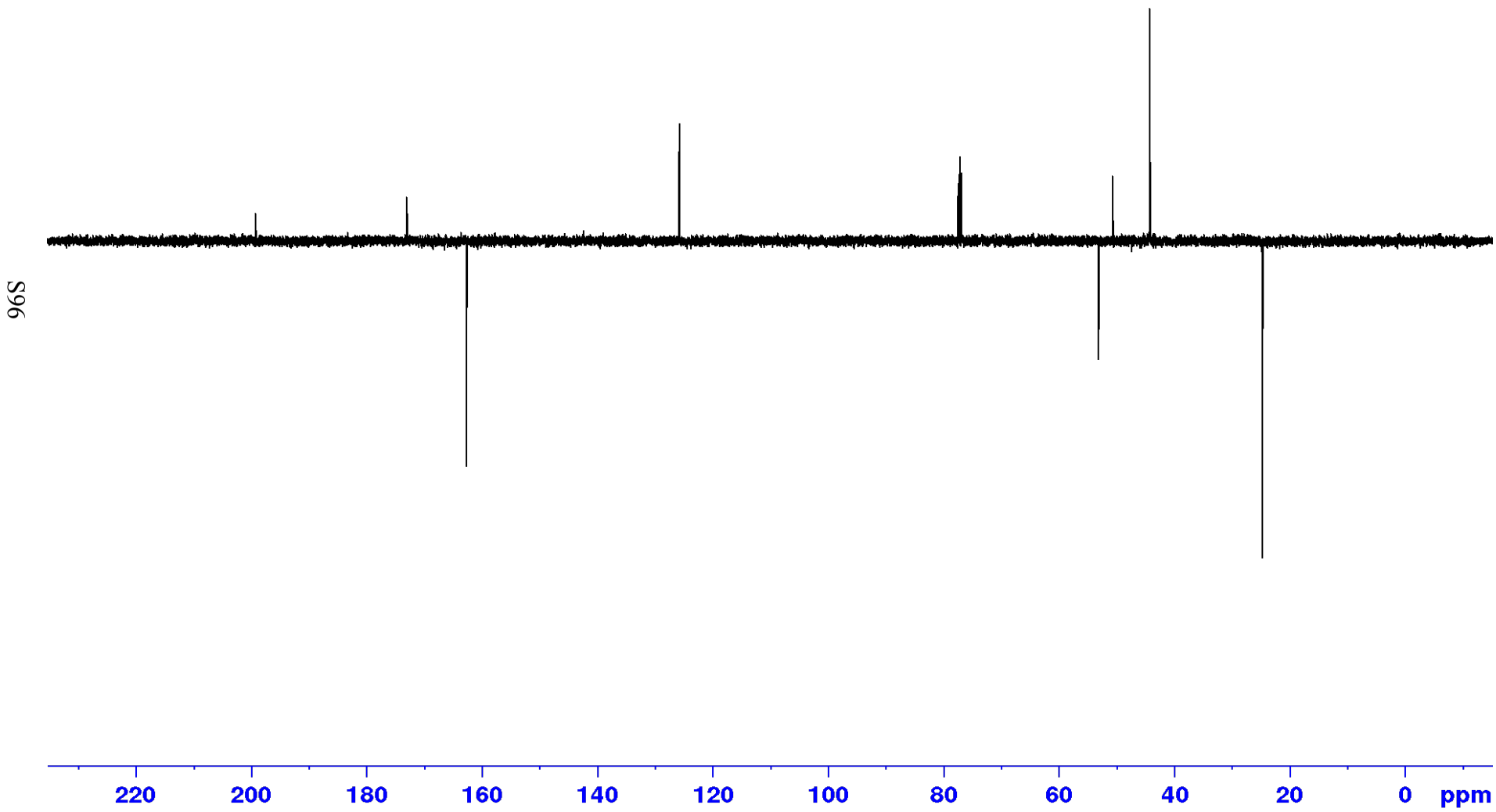
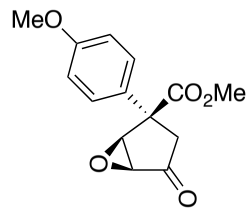
1.11
3.18

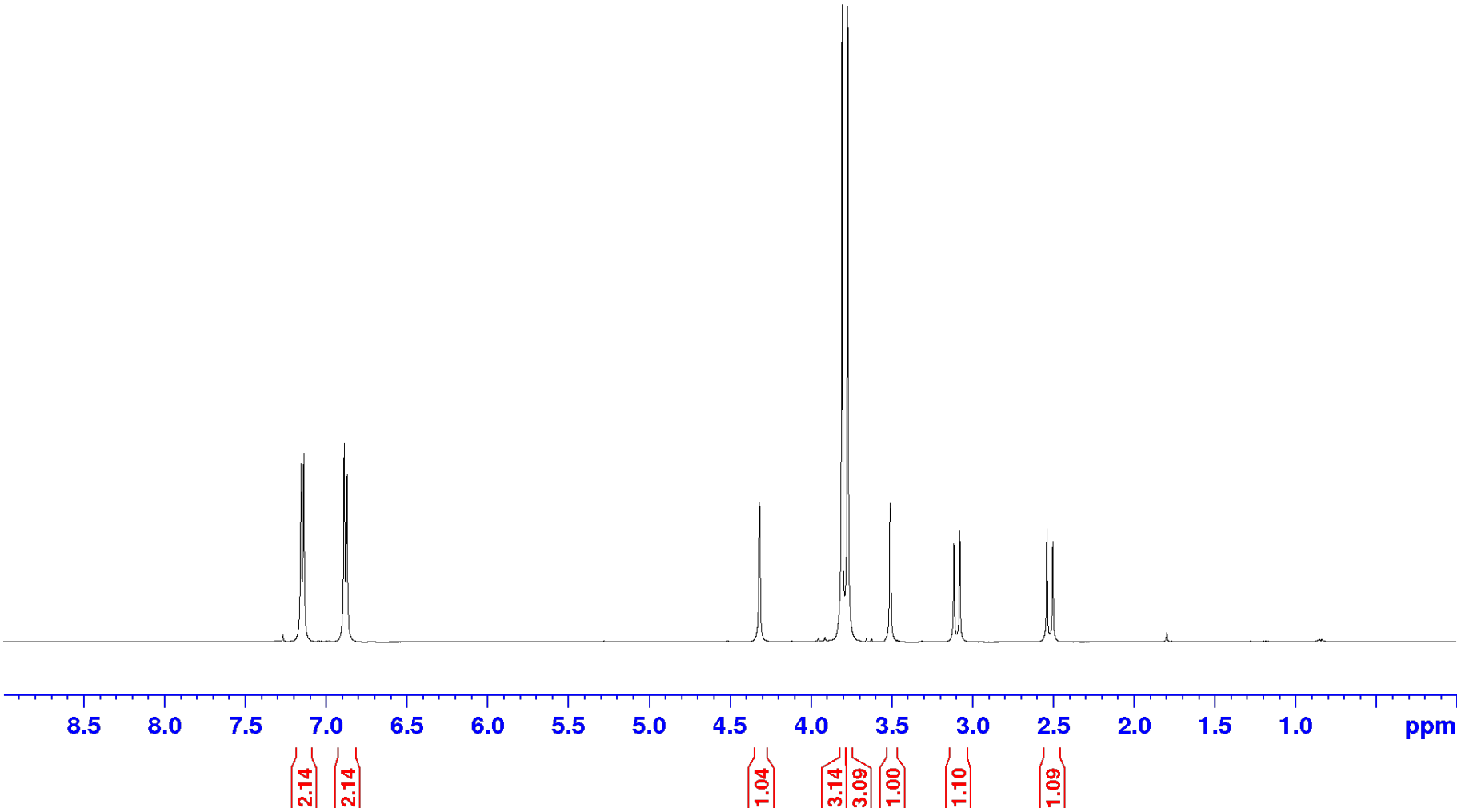


S1




MeO
CO2Me
O
O

7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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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1.0
ppm
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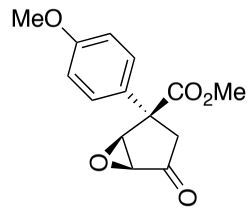
2.14
1.04
3.14
3.09
1.00
1.10
1.09


MeO
CO2Me
O
O

7

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200
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160
150
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120
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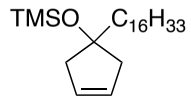
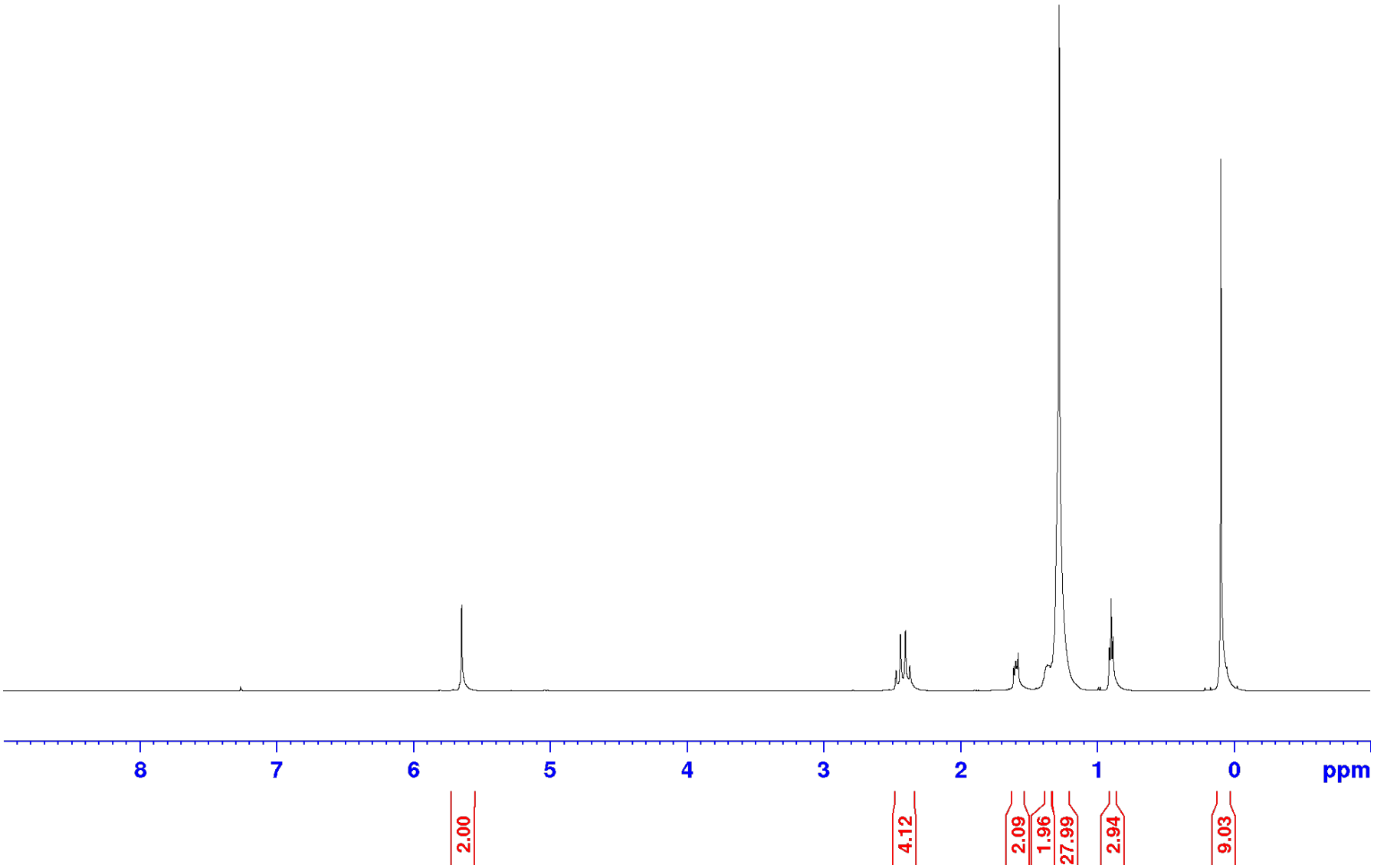
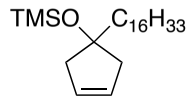
30
20
ppm

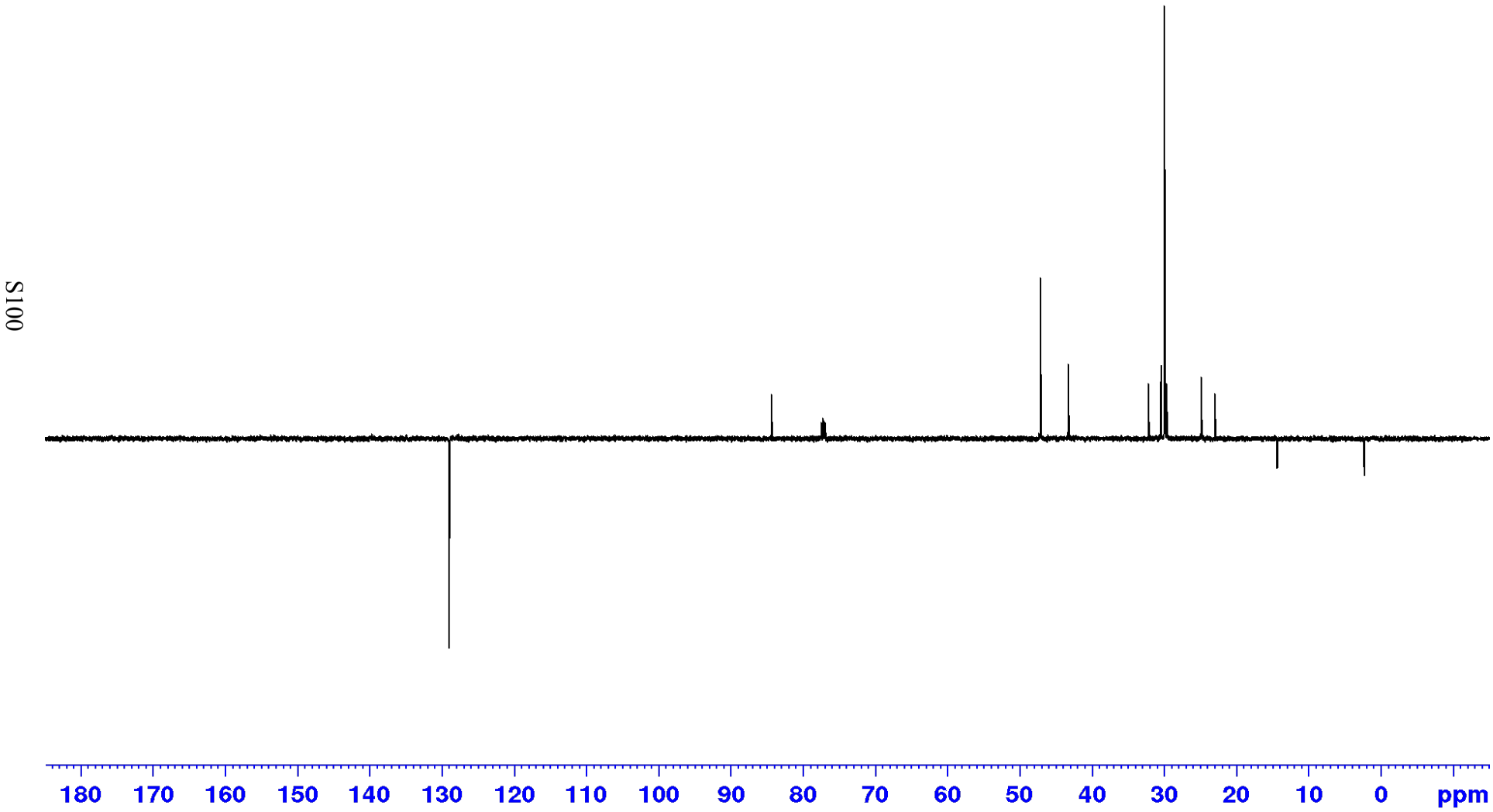


9




TMSO
$C_{16}H_{33}$

9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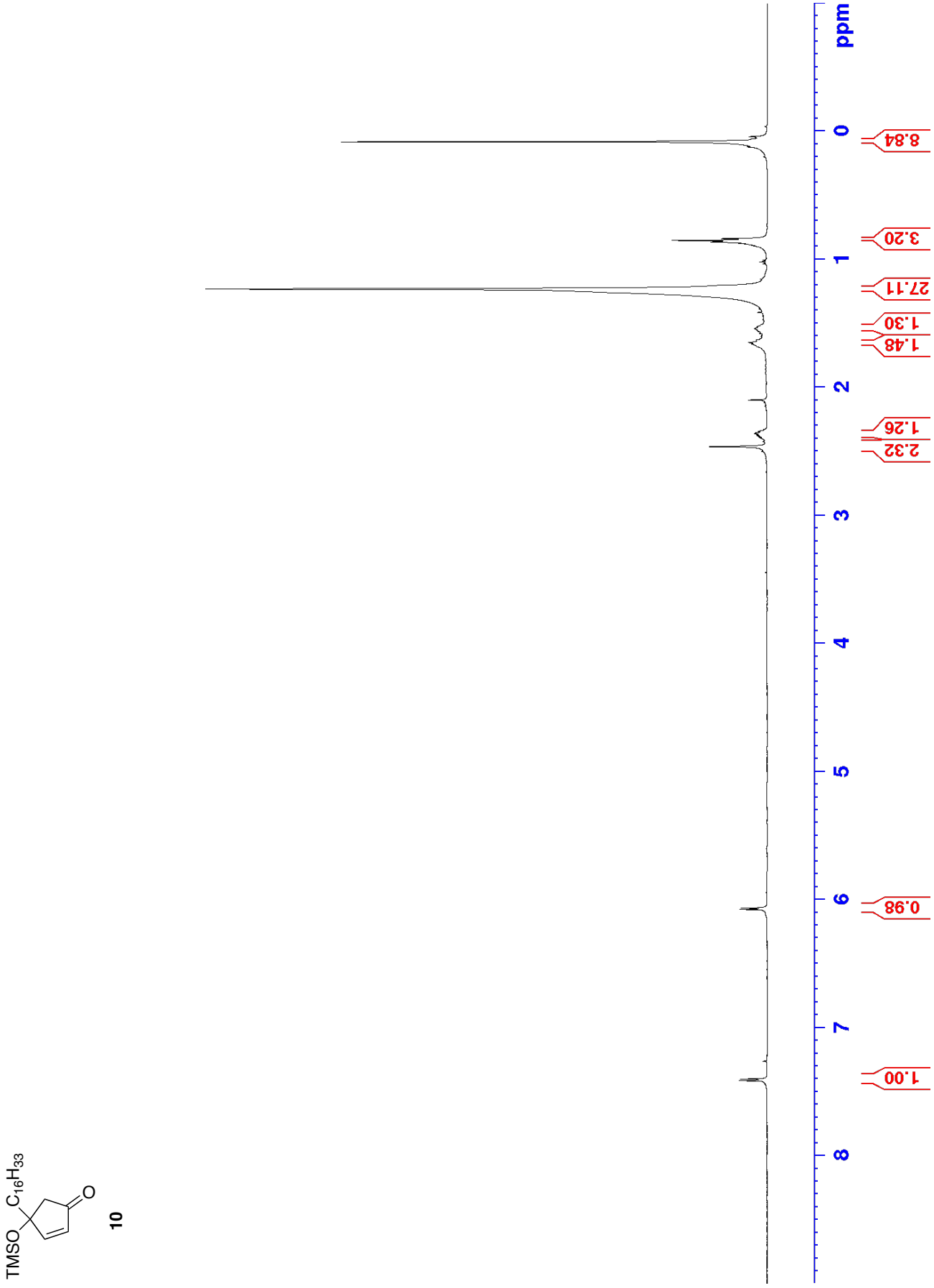
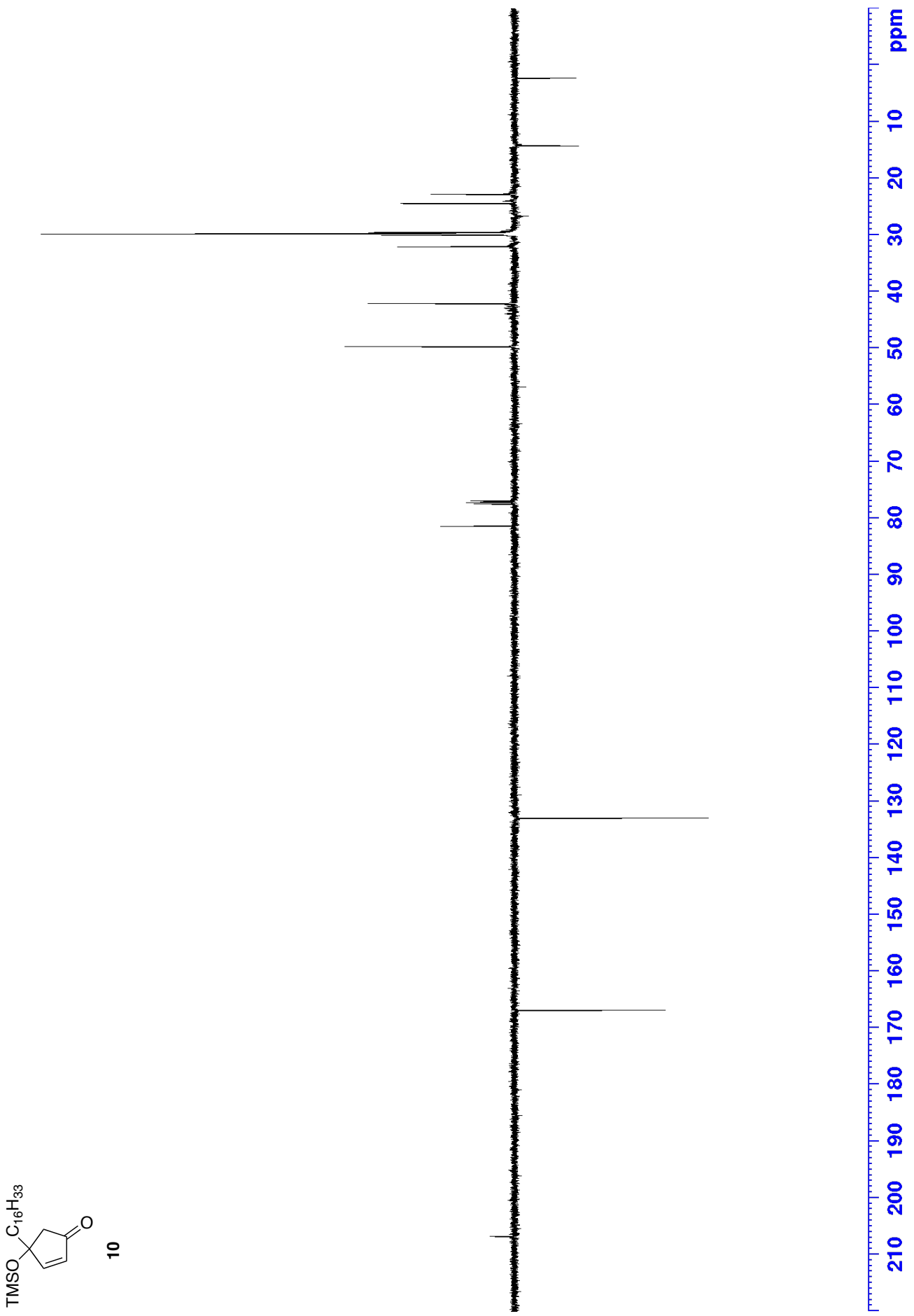
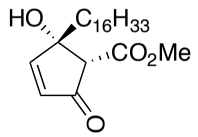
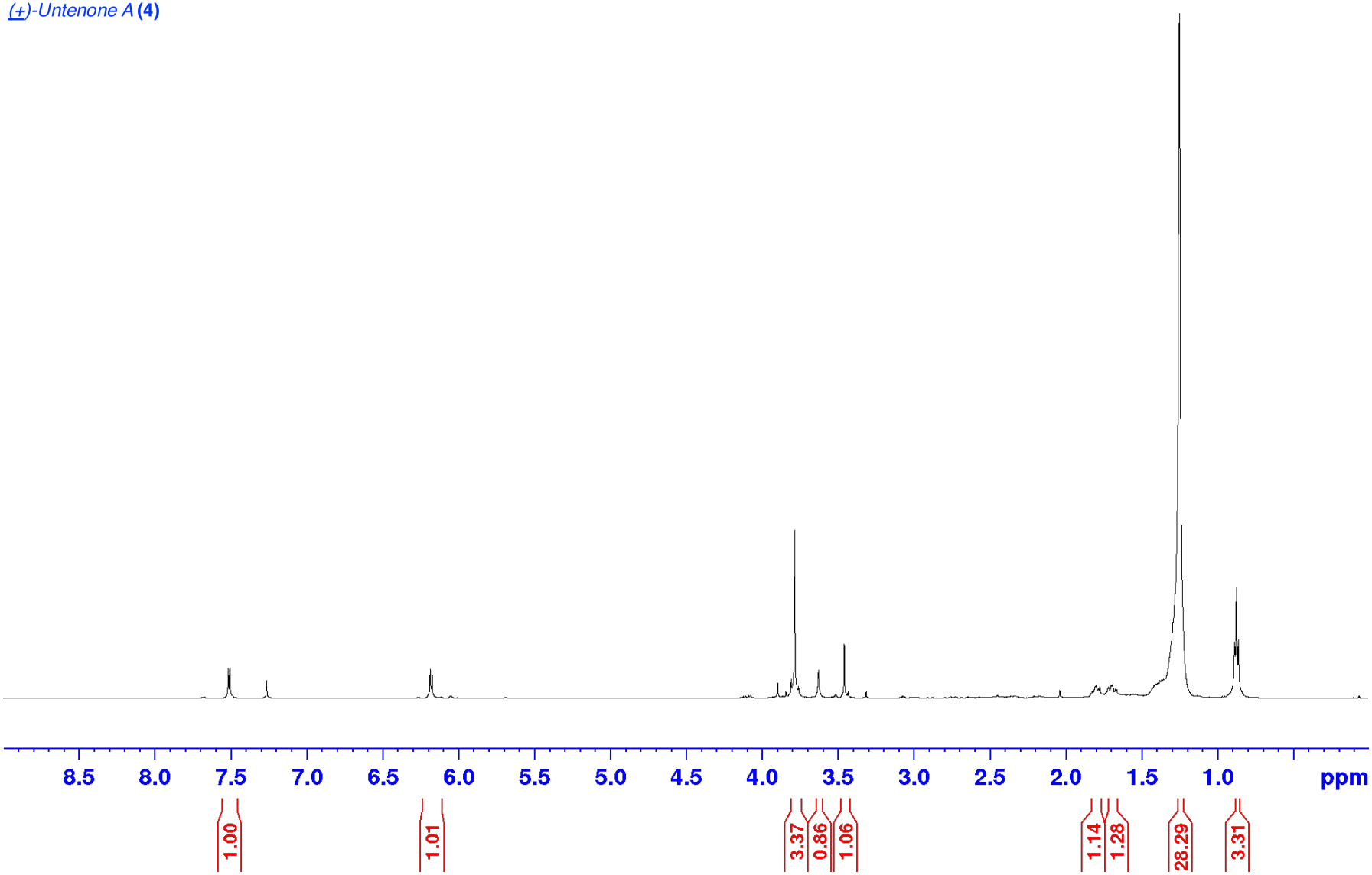
110
100
90
80
70
60
50
40
30
20
10
0
ppm

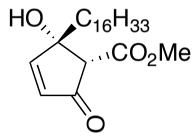

TMSO
$C_{16}H_{33}$
O
10
ppm
0
1
2
3
4
5
6
7
8
8.84
3.20
27.11
1.30
1.48
1.26
2.32
0.98
1.00


TMSO
$C_{16}H_{33}$
O
10
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

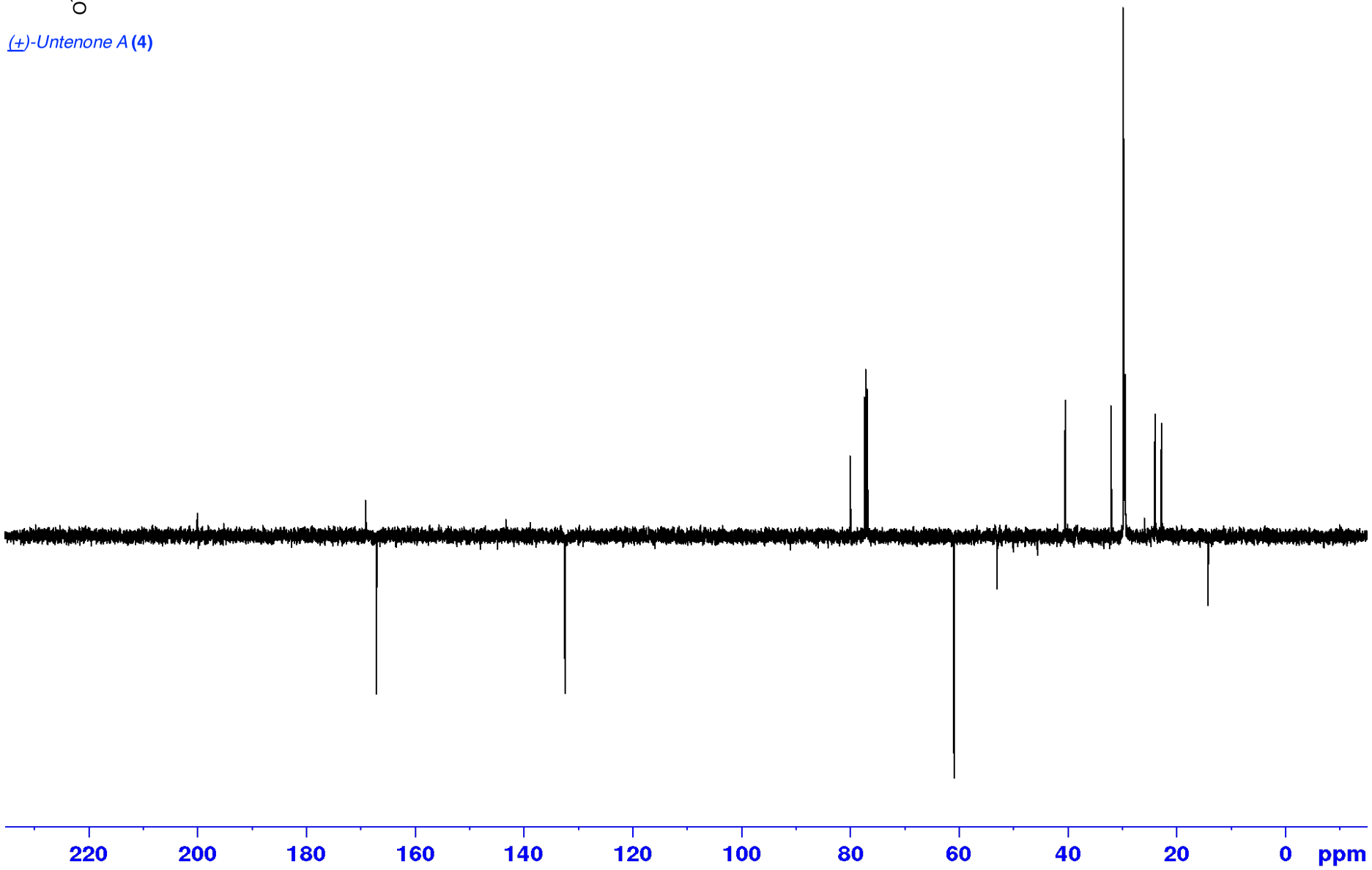

HO
$C_{16}H_{33}$
CO_2Me
O

(+)-Untenone A **(4)**


8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.01
3.37
0.86
1.06
1.14
1.28
28.29
3.31



(+)-Untenone A **(4)**

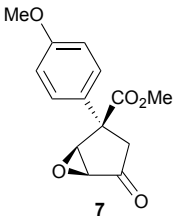


10. Structure Report for Epoxy Ketone 7

X-Ray Crystallography Laboratory (Dr. Gabriele Schatte)

Department of Chemistry, Queen's University

Structure Report for methyl (1S,5S)-2-(4-methoxyphenyl)-4-oxo-6-oxabicyclo[3.1.0]hexane- 2-carboxylate (7)

Crystal and Refinement Data	
$C_{14}H_{14}O_5$	 7
M = 262.25	
colourless, plate-like,	
0.199× 0.181× 0.120 mm^3	
μ = 0.099 mm^{-1}	
monoclinic, space group $P2_1/c$[No.14]	
a = 7.5934(2)	
b = 6.2414(2)	
c = 26.6906(7)	
$\alpha = 90°$	
β = 94.3100(10) °	
$\gamma = 90°$	
V= 1261.38(6) Å^3	
Z = 4	
D_c = 1.381 g/cm^3	
F_{000} = 552	
T = 180(2) K	
13271reflections collected, 3582 unique	
3015 reflections with I > 2σ(I)	
R_{int}= 0.0205	
Final *GooF* = 1.026	
R_1 = 0.0408, wR_2 = 0.1064	
174 parameters, 0 restraints	

Data collection, structure solution and refinement

A colorless plate-like crystal of epoxy ketone (**7**, $C_{14}H_{14}O_5$) having the approximate dimensions of 0.199× 0.181× 0.120 mm, coated with oil (Paratone 8277, Exxon), was collected onto the aperture of a mounted Micromount™ (diameter of the aperture: 100 microns; *MiTeGen* - Microtechnologies for Structural Genomics; USA) and quickly transferred to the cold stream of the Oxford Cryostream 700. The mounted Micromount™ had previously been inserted into reusable magnetic goniometer base(B3S-R, *MiTeGen* - Microtechnologies for Structural Genomics; USA).

All measurements were made on a Bruker-AXS Smart Apex II 3-Circle diffractometer using graphite-monochromated Mo K_α radiation (λ = 0.71073 Å) at –93 °C (power: 50 kV × 30 mA, Bruker-

AXSK780, diameter of the Monocap^{TM}collimator: 0.50 mm; frame size: 512 × 512).

An initial orientation matrix and cell was determined from three sets of 12 frames each using ω-scans (0.5º per frame, 10 s exposures per degree for each 6° in omega rotation at dx = 63.00 mm):Data reduction was performed with the Bruker SAINT software, which corrects for beam inhomogeneity, possible crystal decay, Lorentz and polarisation effects. The linear absorption coefficient, μ, is 0.105 mm^{-1}. A multi-scan absorption correction was applied (Bruker SADABS,). The value for $wR_2(int)$ was 0.0459 before and 0.0350 after correction. The ratio of minimum to maximum transmission is 0.9413. The resulting mean value $<E^2\text{-}1>$ for all data is 0.975[expected 0.968 for centrosymmetric and 0.736 for non-centrosymmetric structures, respectively], which corresponds to a centrosymmetric structure. A total of 1788 frames were collected. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 13271 reflections to a maximum θ angle of 30.03° (0.71 Å resolution). The final cell constants are based upon the refinement of the XYZ-centroids of 6229 reflections with $6.123° < 2\theta < 64.85°$:

The structure was solved using direct methods in the space group $P2_1/c$ [No. 14](SHELXT-2014) and refined by full-matrix least-squares method on F^2 with SHELXL-2014/7 [6] using ShelXle [8] as the graphical user interface (*GUI*). The non-hydrogen atoms were refined anisotropically.Hydrogen atoms of the phenyl-, CH_3-,CH_2- and *ipso*-CH groups were included at geometrically idealized positions (C-H bond distances 0.95/0.98/0.99/1.00 Å) and were not refined. The isotropic thermal parameters of these hydrogen atoms were fixed at 1.2 times (phenyl-, CH_2- and *ipso*-CH groups) and 1.5 times (CH_3-groups) that of the preceding carbon atom, respectively

The final cycle of full-matrix least squares refinement using F^2 (SHELXL-2014/7) was based on 3582 reflections, 0 restraints, 174 variable parameters and converged (largest parameter shift was 0.000 times its esd) with an unweighted factor of R_1 = 0.0408 for $I > 2(I)$. The standard deviation of an observation of unit weight (*goodness-of-fit*) was 1.026. The maximum and minimum peaks in the final difference Fourier map corresponded to 0.345 and -0.244 e$^-$/Å^3, respectively. Neutral atom scattering factors for non-hydrogen atoms and anomalous dispersion coefficients are contained in the SHELXTL program library. The plots for the crystal structure were generated using the program XP (part of the SHELXTL6.14 program library) and then imported into CorelDRAW^{TM} X6. If not otherwise stated, the thermal ellipsoids in the molecular plots are shown at the 30% probability level.