Brucine N-Oxide Catalyzed Morita-Baylis-Hillman Reaction of Vinyl Ketones: A Mechanistic Implication of Dual Catalyst System with Proline

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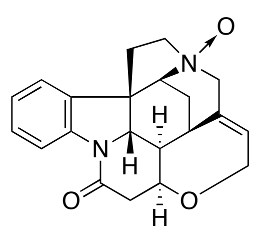
General Experimental Section: All reactions were performed under argon in an oven-dried flask. All chemicals were purchased commercially and used as received except brucine *N*-oxide and MBH products. Benzene, diethyl ether, toluene, acetonitrile, dichloromethane, and THF were purified using a commercially available Grubbs apparatus. Anhydrous MeOH, DME, DCE, and 1,4-dioxane were purchased commercially. Column chromatography was carried out with silica gel (25-63m). IR spectra were recorded on a FT-IR spectrophotometer. Mass Spectra were measured on an EI instrument. Stated otherwise, ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a 500 MHz spectrometer. Chemical shifts are reported in ppm using either residual $CHCl_3$ or TMS as internal references.

Data of Products

<u>Preparation of Amine *N*-Oxides</u>

The synthesis of N-oxides was adopted from the method of Resnati el al.[1] To a stirred solution of brucine dihydrate (20.0 g, 46 mmol) in dry methanol (120 ml) at ambient temperature, was added a solution of H_2O_2 (30% in water, 10.53 ml, 93 mmol) dropwise. The resulting mixture was stirred at 40 °C for 4 hours, after which solvent was removed under reduced pressure to give a product as a white solid. The product was further purified using flash column chromatography on silica gel (eluent ethyl acetate then methanol) to the brucine *N*-oxide **2b** (18.0 g, >95%) as a white solid.

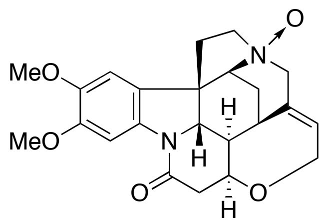


2a

The spectroscopic data were consistent with those reported in the literature.[2]
^{1}H NMR (500 MHz, DMSO): δ8.12 (1H, app. d, 8.0 Hz), 7.67 (1H, app. d, 7.5 Hz), 7.48 (1H, app. t, 7.5 Hz), 7.34 (1H, app. t, 7.5 Hz), 6.46 (1H, br. s), 4.52-4.50 (1H, m), 4.40 (1H, app. s), 4.36-4.26 (2H, m), 4.19 (1H, app. d, 10.5 Hz), 4.13 (1H, app. d, 13.0 Hz), 4.04-3.99 (2H, m), 3.63-3.59 (1H, m), 3.41 (1H, app. s), 3.13 (1H, app. dd, 16.7, 8.5 Hz), 2.83-2.70 (3H, m), 2.23-2.20 (1H, m), 1.69 (1H, app. d, 14.5 Hz), 1.57 (1H, app. d, 11Hz);

[1] Arnone, A.; Metrangolo, P.; Novo, B.; Resnati, G. *Tetrahedron* **1998**, *54*, 7831.

^{13}C NMR (125MHz, DMSO): δ 169.8, 142.5, 136.9, 133.5, 131.6, 129.9, 125.0, 123.6, 116.1, 83.4, 77.0, 71.7, 68.7, 64.3, 58.9, 53.4, 47.7, 42.3, 39.6, 30.4, 25.3.

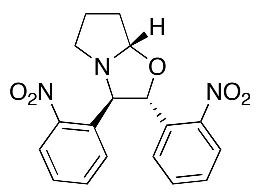


2b

The spectroscopic data were consistent with those reported in the literature (in $CDCl_3$).[1]
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (1H, app. s), 6.91 (1H, app. s), 6.25 (1H, app. s), 4.33 (1H, app. s), 4.27 (1H, app. d, 8.5 Hz), 4.19 (1H, app. dd, 14.0, 7.0 Hz), 4.10 (1H, app. d, 13.0 Hz), 4.05-4.01(1H, m), 3.91-3.80 (2H, m), 3.85 (3H, s), 3.82 (3H, s), 3.68-3.65 (1H, m), 3.20 (1H, app. s), 3.09-3.05 (2H, m), 2.73 (1H, app. d, 15.0 Hz), 2.68-2.58 (2H, m), 1.96-1.92 (1H, m), 1.63 (1H, app. d, 15.0 Hz), 1.32 (1H, app. d, 10.0 Hz);
^{13}C NMR (125MHz, $CDCl_3$): δ 168.3, 150.0, 146.7, 135.4(d, 23.8 Hz), 133.7, 119.9, 105.1, 101.0, 82.6(d, 7.5 Hz), 77.5, 71.2(d, 8.7 Hz), 67.8, 64.2, 58.6, 56.3, 56.2, 53.2, 49.9(d, 12.5Hz), 47.6, 42.0, 38.8, 30.3, 25.0.
The spectroscopic data were consistent with those reported in the literature (in DMSO).[2]
^{1}H NMR (500 MHz, DMSO): δ 7.58 (1H, app. s), 7.03 (1H, app. s), 6.22 (1H, app. s), 4.25-3.76 (8H, m), 3.73 (3H, s), 3.68 (3H, s), 3.35-3.31 (1H, m), 3.13 (1H, app. s), 2.85-2.82(1H, m), 2.56-2.46 (2H, m), 2.34-2.28 (1H, m), 1.84-1.82 (1H, m), 1.46 (1H, app. d, 14.4 Hz), 1.28 (1H, app. d, 10.4 Hz);
^{13}C NMR (125MHz, DMSO): δ 169.3, 150.1, 147.0, 137.0, 136.1, 133.5, 122.3, 107.4, 101.4, 82.9, 77.3, 71.5, 68.5, 64.4, 59.2, 56.9, 56.6, 53.5, 49.4, 42.2, 39.2, 30.5, 25.3.

Preparation of 1-Oxapyrrolizidine

To a stirred solution of (*L*)-proline (50 mg, 0.434 mmol) in dry 1,4-dioxane (5 mL) at 50 °C, was added 2-nitrobenzaldehyde **7a** (132.1 mg, 0.868 mmol) in one portion. The resulting suspension was stirred at the same temperature for 24 h, after which the mixture was directly loaded to silica gel for purification to give 1-oxapyrrolizidine **10a** (10 mg, 6 %).

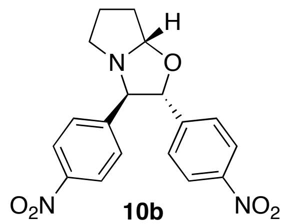


10a

2,3-bis(2-nitrophenyl)hexahydropyrrolo[2,1-*b*]oxazole (**10a**).
^{1}H NMR ($CDCl_3$, 500MHz): δ 7.90-7.83 (m, 3H), 7.76-7.73 (m, 1H), 7.69-7.62 (m, 2H), 7.48-7.40 (m, 2H), 5.52 (d, 6.5 Hz, 1H), 5.33 (dd, 4.5, 2.0 Hz, 1H), 4.68 (d, 7.0 Hz, 1H), 3.21-3.16 (m, 1H), 2.91-2.86 (m, 1H), 2.22-2.17 (m, 2H), 2.11-2.07 (m, 1H);

[2] Hadden, C. E.; Kaluzny, B. D.; Robins, R. H.; Martin G. E. *Magn. Reson. Chem.* **1999**, *37*, 325.

^{13}C NMR ($CDCl_3$, 125MHz): δ 149.2, 148.2, 136.4, 134.9, 133.4, 132.9, 129.5, 128.8, 128.1, 128.1, 124.4, 124.1, 99.2, 82.3, 73.3, 55.8, 31.4, 24.2.
IR (film, cm^{-1}): 2924, 1524, 1347, 1028.
HRMS calcd for $C_{18}H_{18}N_3O_5$ 356.1241, found 356.1238 $[M]^+$.



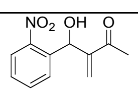
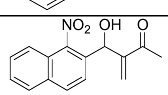
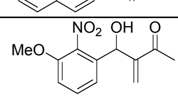
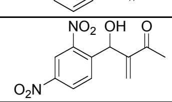
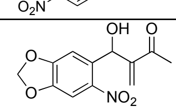
10b

2,3-bis(4-nitrophenyl)hexahydropyrrolo[2,1-*b*]oxazole **(10b)**[3]
^1H NMR ($CDCl_3$, 500MHz): δ 8.21-8.16 (m, 4H), 7.42-7.37 (m, 4H), 5.33 (dd, 5.0 2.0 Hz, 1H), 4.69 (d, 8.0 Hz, 1H), 3.84 (d, 8.0 Hz, 1H), 3.18-3.13 (m, 1H), 2.87-2.82 (m, 1H), 2.25-2.15 (m, 2H), 2.15-2.06 (m, 1H), 1.94-1.86 (m, 1H);
^{13}C NMR ($CDCl_3$, 125MHz): δ 148.1, 147.8, 147.5, 145.5, 127.9, 127.0, 123.9, 123.8, 99.3, 87.3, 78.4, 55.8, 31.5, 24.0.

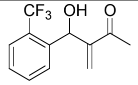
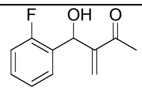
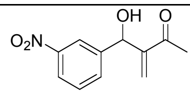
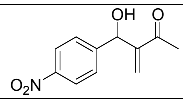
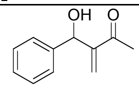
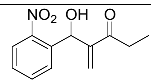
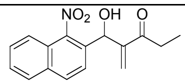
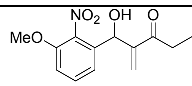
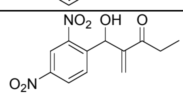
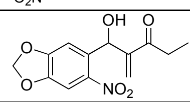
Representative Asymmetric Morita-Baylis-Hillman Reaction of Aryl Aldehydes

To a stirred solution of 2-nitroaldehyde **7a** (100 mg, 0.65 mmol), brucine *N*-oxide **2b** (404 mg, 0.98 mmol), and (*L*)-proline (37 mg, 0.32 mmol) in dry 1,4-dioxane (5.0 ml) at ambient temperature, was added methyl vinyl ketone **6a** (46 mg, 0.65 mmol) in one portion. The resulting suspension was stirred at the same temperature for 4-5 days until the aldehyde was all consumed by tlc, and the mixture was directly loaded to silica gel for flash column chromatography (eluent 33/67 diethyl ether/hexanes), to give the Morita Baylis Hillman product **8a** (61 mg, 42% with 63% ee).

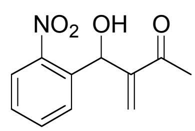
Table S1. HPLC Conditions for MBH Products of Vinyl Ketones.

8	chiral column	eluents (Hex:IPA)	flow rate (ml/min)	retention time (min) **(*S*)-8**	**(*R*)-8**	ref.
	CHIRALPAK AD-H	93:7	0.70	20.38	22.52	4
	CHIRALPAK AD-H	93:7	0.75	29.15	33.45	4
	CHIRALPAK AD-H	93:7	0.75	38.13	40.51	4
	*CHIRALPAK AD-H*	*93:7*	*0.75*	*28.90*	*32.48*	**a**
	*CHIRALPAK AD-H*	*90:10*	*0.75*	*27.57*	*33.48*	***b***

[3] Orsini, F.; Pelizzoni, F.; Forte, M.; Destro, R.; Gariboldi, P. *Tetrahedron* **1988**, *44*, 519-541.
[4] Vasbinder, M. M.; Imbriglio, J. E.; Miller, S. J. *Tetrahedron* **2006**, *62*, 11450-11459.

	CHIRALPAK AD-H	95:5	0.75	11.93	14.28	4
	CHIRALPAK AD-H	98:2	0.75	26.39	29.26	4
	CHIRALPAK AD-H	97:3	0.90	37.33	41.95	4
	CHIRALPAK OD-H	95:5	1.00	25.77	26.45	5
	CHIRALPAK AD-H	97:3	0.75	22.05	23.87	4
	*CHIRALPAK OD-H*	*95:5*	*0.75*	*23.60*	*26.21*	***b***
	*CHIRALPAK OD-H*	*95:5*	*0.75*	*25.79*	*31.24*	***b***
	*CHIRALPAK AD-H*	*93:7*	*0.75*	*31.03*	*32.52*	***b***
	*CHIRALPAK AD-H*	*93:7*	*0.75*	*23.70*	*28.16*	***b***
	*CHIRALPAK AD-H*	*90:10*	*0.75*	*24.85*	*28.56*	***b***

[*a*] The retention times are not known for our methods. [b] New compound.

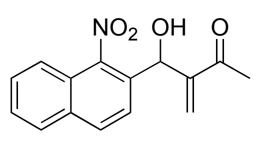


8a

The spectroscopic data were consistent with those reported in the literature.[4]

^{1}H NMR ($CDCl_3$, 500MHz): δ 7.96 (d, 8.5 Hz, 1H), 7.77 (d, 7.5 Hz, 1H), 7.64 (t, 7.7 Hz, 1H), 7.45 (t, 7.7 Hz, 1H), 6.21 (d, 4.0 Hz, 1H), 6.16 (s, 1H), 5.78 (d, 1.0 Hz, 1H), 3.51 (br s, 1H), 2.36 (s, 3H);

^{13}C NMR ($CDCl_3$, 125MHz): δ 199.8, 148.9, 148.1, 136.4, 133.4, 128.8, 128.5, 126.3, 124.6, 67.6, 25.9.

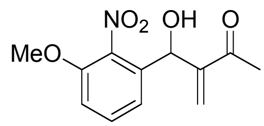


8b

The spectroscopic data were consistent with those reported in the literature.[4]

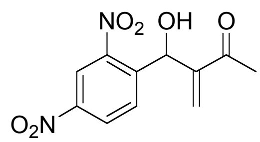
[5] (a) Hayashi, Y.; Tamura, T.; Shoji, M. *Adv. Synth. Catal.* **2004**, *346*, 1106-1110. (b) Shi, M.; Jiang J. K. *Tetrahedron: Asymmetry* **2002**, *13*, 1941-1947.

^{1}H NMR ($CDCl_3$, 500MHz): δ 7.95 (d, 8.5 Hz, 1H), 7.87 (d, 7.5 Hz, 1H), 7.74 (d, 8.5 Hz, 1H), 7.62-7.56 (m, 3H), 6.27 (s, 1H), 6.01 (d, 1.0 Hz, 1H), 5.87 (s, 1H), 3.66 (br s, 1H), 2.33 (s, 3H);
^{13}C NMR ($CDCl_3$, 125MHz): δ 199.7, 147.7, 146.5, 133.3, 131.0, 130.6, 128.6, 127.9, 127.7, 127.4, 124.3, 124.1, 121.8, 68.4, 26.0.



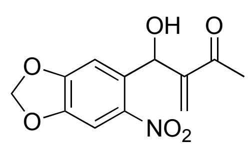
8c

The spectroscopic data were consistent with those reported in the literature.[4]
^{1}H NMR ($CDCl_3$, 500MHz): δ 7.40 (t, 8.0 Hz, 1H), 7.10 (d, 8.0 Hz, 1H), 6.97 (d, 8.5 Hz, 1H), 6.22 (s, 1H), 5.96(d, 1.0 Hz, 1H), 5.63 (s, 1H), 3.86 (s, 3H), 3.61 (br s, 1H), 2.32 (s, 3H);
^{13}C NMR ($CDCl_3$, 125MHz): δ 199.8, 150.8, 147.5, 140.2, 134.4, 131.1, 127.8, 119.4, 112.0, 68.3, 56.4, 26.0.



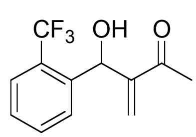
8d

The spectroscopic data were consistent with those reported in the literature.[4]
^{1}H NMR ($CDCl_3$, 500MHz): δ 8.76 (d, 2.5 Hz, 1H), 8.45 (dd, 8.7, 2.5 Hz, 1H), 8.03 (d, 8.5 Hz, 1H), 6.27 (s, 1H), 6.22(s, 1H), 5.85 (s, 1H), 3.76 (br s, 1H), 2.35 (s, 3H);
^{13}C NMR ($CDCl_3$, 125MHz): δ 199.5, 148.1, 147.8, 147.1, 143.3, 130.5, 127.2, 127.1, 120.0, 67.1, 25.8.



8e

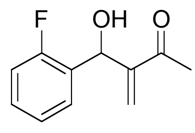
3-(Hydroxy(6-nitrobenzo[d][1,3]dioxol-5-yl)methyl)but-3-en-2-one (**8e**).
^{1}H NMR ($CDCl_3$, 500MHz): δ 7.53 (s, 1H), 7.20 (s, 1H), 6.19 (s, 1H), 6.13 (s, 1H), 6.13-6.12 (m, 2H), 5.76 (d, 1.0 Hz, 1H), 3.50 (br s, 1H), 2.38 (s, 3H);
^{13}C NMR ($CDCl_3$, 125MHz): δ 200.0, 152.3, 149.0, 147.2, 141.8, 134.1, 126.0, 107.7, 105.5, 103.0, 67.5, 26.0;
IR (film, cm^{-1}) 3424, 1675, 1519, 1261;
HRMS calcd for $C_{12}H_{11}NO_6Na$ 288.0484, found 288.0495 $[MNa]^+$.



8f

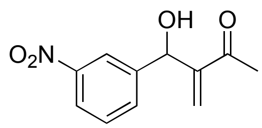
The spectroscopic data were consistent with those reported in the literature.[4]

^{1}H NMR ($CDCl_3$, 500MHz): δ 7.69 (d, 8.0 Hz 1H), 7.64 (d, 8.0 Hz, 1H), 7.58-7.55 (m, 1H), 7.42-7.39 (m, 1H), 6.17 (s, 1H), 6.04 (d, 3.0 Hz, 1H), 5.53 (d, 1.0 Hz, 1H), 3.46 (br s, 1H), 2.37 (s, 3H);
^{13}C NMR ($CDCl_3$, 125MHz): δ 200.2, 149.9, 139.3, 132.0, 128.6, 127.8, 127.7(d, 30.0Hz), 127.3, 125.8 (q, 5.0 Hz), 124.1 (d, 272.5 Hz), 67.4, 26.1.



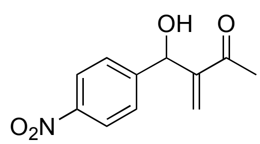
8g

The spectroscopic data were consistent with those reported in the literature.[4]
^{1}H NMR ($CDCl_3$, 500MHz): δ 7.47-7.44 (m, 1H), 7.27-7.23 (m, 1H), 7.15-7.12 (m, 1H), 7.02-6.98 (m, 1H), 6.17 (s, 1H), 5.87 (s, 1H), 5.86 (s, 1H), 3.59 (br s, 1H), 2.34 (s, 3H);
^{13}C NMR ($CDCl_3$, 125MHz): δ 200.3, 159.8 (d, 245.0 Hz), 148.7, 129.2 (d, 8.7 Hz), 128.4 (d, 11.2 Hz), 128.1 (d, 3.7 Hz), 126.8, 124.1 (d, 3.7 Hz), 115.2 (d, 21.2 Hz), 66.9 (d, 3.7 Hz), 26.3.



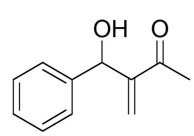
8h

The spectroscopic data were consistent with those reported in the literature.[4]
^{1}H NMR ($CDCl_3$, 500MHz): δ 8.22 (s, 1H), 8.13-8.11 (m, 1H), 7.73 (d, 7.5 Hz, 1H), 7.71 (t, 7.7 Hz, 1H), 6.28 (s, 1H), 6.07 (s, 1H), 5.66 (d, 5.5 Hz, 1H), 3.28 (d, 5.5 Hz, 1H), 2.36 (s, 3H);
^{13}C NMR ($CDCl_3$, 125MHz): δ 200.0, 149.0, 148.4, 143.9, 132.6, 129.3, 127.5, 122.6, 121.4, 72.2, 26.3.



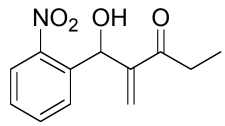
8i

The spectroscopic data were consistent with those reported in the literature.[4]
^{1}H NMR ($CDCl_3$, 500MHz): δ 8.17 (d, 9.0 Hz, 2H), 7.54 (d, 8.5 Hz, 2H), 6.26 (s, 1H), 6.03 (d, 1.0 Hz, 1H), 5.67 (d, 5.0 Hz, 1H), 3.35 (d, 5.0 Hz, 1H), 2.34 (s, 3H);
^{13}C NMR ($CDCl_3$, 125MHz): δ 199.9, 149.1, 148.9, 147.4, 127.5, 127.2, 123.5, 72.1, 26.2.



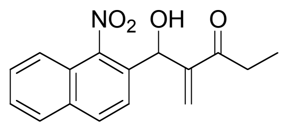
8j

The spectroscopic data were consistent with those reported in the literature. [4]
^{1}H NMR ($CDCl_3$, 500MHz): δ 7.34-7.29 (m, 4H), 7.26-7.24 (m, 1H), 6.16 (s, 1H), 5.96 (d, 1.0 Hz, 1H), 5.58 (d, 3.0 Hz, 1H), 3.21 (s, 1H), 2.30 (s, 3H);
^{13}C NMR ($CDCl_3$, 125MHz): δ 200.2, 149.9, 141.4, 128.3, 127.6, 126.5, 126.4, 72.6, 26.4.



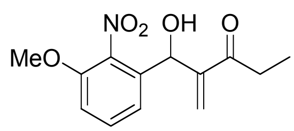
8k

2-[Hydroxy-(2-nitro-phenyl)-methyl]-pent-1-en-3-one (**8k**).[6]
^{1}H NMR ($CDCl_3$, 500MHz): δ 7.95 (dd, 8.0, 1.0 Hz, 1H), 7.77 (dd, 8.0, 1.5 Hz, 1H), 7.64 (td, 7.7, 1.0 Hz, 1H), 7.44 (td, 7.7 1.5 Hz, 1H), 6.20 (s, 1H), 6.14 (s, 1H), 5.72 (d, 1.0 Hz, 1H), 3.61 (br s, 1H), 2.77-2.71 (m, 2H), 1.07 (t, 7.5 Hz, 3H);
^{13}C NMR ($CDCl_3$, 125MHz): δ 202.7, 148.3, 147.9, 136.4, 133.4, 128.8, 128.4, 125.1, 124.6, 67.7, 31.1, 8.0;
IR (film, cm^{-1}) 3431, 1675, 1525, 1350;
HRMS calcd for $C_{12}H_{13}NO_4Na$ 258.0742, found 258.0729 $[MNa]^+$.



8l

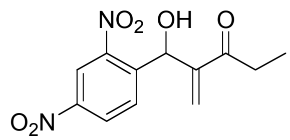
2-[Hydroxy-(1-nitro-naphthalen-2-yl)-methyl]-pent-1-en-3-one (**8l**).
^{1}H NMR ($CDCl_3$, 500MHz): δ 7.96 (d, 9.0 Hz, 1H), 7.88 (d, 8.0 Hz, 1H), 7.75 (d, 8.5 Hz, 1H), 7.63 (d, 8.5 Hz, 1H), 7.63-7.56 (m, 2H), 6.27 (s, 1H), 5.96 (d, 1.0 Hz, 1H), 5.87 (s, 1H), 3.65 (br s, 1H), 2.75-2.70 (m, 2H), 1.04 (t, 7.2 Hz, 3H);
^{13}C NMR ($CDCl_3$, 125MHz): δ 202.5, 147.0, 146.5, 133.2, 131.0, 130.6, 128.6, 127.9, 127.4, 126.6, 124.3, 124.0, 121.8, 68.8, 31.2, 7.8;
IR (film, cm^{-1}) 3432, 1676, 1526, 1356;
HRMS calcd for $C_{16}H_{15}NO_4Na$ 308.0899, found 308.0907 $[MNa]^+$.



8m

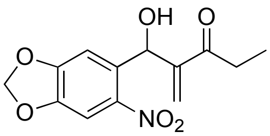
2-[Hydroxy-(3-methoxy-2-nitro-phenyl)-methyl]-pent-1-en-3-one (**8m**).
^{1}H NMR ($CDCl_3$, 500MHz): δ 7.41 (t, 8.2 Hz, 1H), 7.12 (d, 7.5 Hz, 1H), 6.97 (dd, 4.2, 1.0 Hz, 1H), 6.21 (s, 1H), 5.90 (d, 1.0 Hz, 1H), 5.64 (d, 4.5 Hz, 1H), 3.87 (s, 3H), 3.54 (d, 5.5 Hz, 1H), 2.71 (q, 7.0 Hz, 2H), 1.04 (t, 7.2 Hz, 3H);
^{13}C NMR ($CDCl_3$, 125MHz): δ 202.7, 150.8, 146.8, 140.1, 134.4, 131.1, 126.6, 119.3, 111.9, 68.8, 56.4, 31.2, 7.8;
IR (film, cm^{-1}) 3428, 1676, 1606, 1533, 1281;
HRMS calcd for $C_{13}H_{15}NO_5Na$ 288.0848, found 288.0840 $[MNa]^+$.

[6] Barrett, A. G. M.; Dozzo, P.; White, A. J. P.; Williams, D. J. *Tetrahedron* **2002**, *58*, 7303-7313.



8n

2-[(2,4-Dinitro-phenyl)-hydroxy-methyl]-pent-1-en-3-one (**8n**).
^{1}H NMR ($CDCl_3$, 500MHz): δ 8.78 (d, 2.5 Hz, 1H), 8.46 (dd, 8.7, 2.0 Hz, 1H), 8.05 (d, 8.5 Hz, 1H), 6.28 (s, 1H), 6.21 (s, 1H), 5.78 (s, 1H), 3.52 (br s, 1H), 2.77-2.72 (m, 2H), 1.08 (t, 7.2 Hz, 3H);
^{13}C NMR ($CDCl_3$, 125MHz): δ 202.3, 147.8, 147.4, 147.1, 143.3, 130.5, 127.3, 125.8, 120.0, 67.6, 31.0, 7.9;
IR (film, cm^{-1}) 3434, 1675, 1606, 1537, 1348;
HRMS calcd for $C_{12}H_{13}N_2O_6$ 281.0768, found 281.0772 $[MH]^+$.



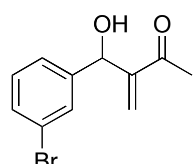
8o

2-(Hydroxy(6-nitrobenzo[d][1,3]dioxol-5-yl)methyl)pent-1-en-3-one (**8o**).
^{1}H NMR ($CDCl_3$, 500MHz): δ 7.52 (s, 1H), 7.21 (s, 1H), 6.18 (s, 1H), 6.12 (s, 2H), 6.11 (s, 1H), 5.70 (d, 1.0 Hz, 1H), 3.56 (br. s, 1H), 2.80-2.71 (m, 2H), 1.10 (t, 7.2Hz, 3H);
^{13}C NMR ($CDCl_3$, 125MHz): δ 202.8, 152.3, 148.5, 147.2, 141.8, 134.2, 124.7, 107.7, 105.5, 103.0, 67.9, 31.0, 8.0;
IR (film, cm^{-1}) 3440, 1677, 1520, 1259;
HRMS calcd for $C_{13}H_{13}NO_6$ 279.0743, found 279.0756 $[M]^+$ and $C_{13}H_{12}NO_5$ 262.0710, found 272.0707 $[M\text{-}OH]^+$

Representative BNO-Catalyzed Morita-Baylis-Hillman Reaction

To a stirred solution of 2-nitroaldehyde **7a** (100 mg, 0.65 mmol), brucine *N*-oxide **2b** (40 mg, 0.1 mmol), was added methyl vinyl ketone **6a** (138 mg, 1.95 mmol) in one portion. The resulting suspension was stirred at 23 °C for 5 days, after which the mixture was directly loaded to silica gel for flash column chromatography (eluent 33/67 diethyl ether/hexanes) to give the Morita Baylis Hillman product **8a** (130 mg, 90%).

Additional MBH Products (**8p-8u**) from Table 2.

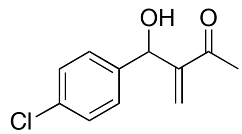


8p

The spectroscopic data were consistent with those reported in the literature.[7]
^{1}H NMR ($CDCl_3$, 500MHz): δ 7.49 (t, 1.7 Hz, 1H), 7.38 (dt, 7.8, 1.4 Hz, 1H), 7.27 (d, 7.7 Hz, 1H), 7.19 (t, 7.8 Hz, 1H), 6.21 (s, 1H), 6.00 (d, 1.0 Hz, 1H), 5.44 (d, 5.3Hz, 1H), 3.30 (d, 5.4 Hz, 1H), 2.33 (s, 3H);

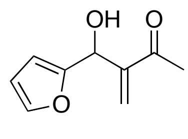
[7] Gruttadauria, M.; Giacalone, F.; Meo, P. L.; Marculescu, A. M.; Riela, S.; Noto, *Eur. J. Org. Chem.* **2008**, 1589-1596.

^{13}C NMR ($CDCl_3$, 125MHz): δ 200.1, 149.9, 143.3, 130.6, 129.9, 129.5, 127.1, 125.1, 122.5, 72.0, 26.4.



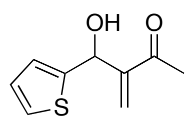
8q

The spectroscopic data were consistent with those reported in the literature.[5b]
^{1}H NMR ($CDCl_3$, 500MHz): δ 7.29 (d, 4.9 Hz, 4H), 6.19 (s, 1H), 5.97 (d, 1.1 Hz, 1H), 5.57 (d, 5.1 Hz, 1H), 3.21 (d, 5.3 Hz, 1H), 2.33 (s, 3H);
^{13}C NMR ($CDCl_3$, 125MHz): δ 200.2, 149.6, 140.0, 133.4, 128.5, 127.9, 126.9, 72.2, 26.4.



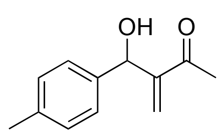
8r

The spectroscopic data were consistent with those reported in the literature.[4]
^{1}H NMR ($CDCl_3$, 500MHz): δ 7.31 (dd, 1.8, 0.7 Hz, 1H), 6.28 (dd, 3.2, 1.8 Hz, 1H), 6.21 (s, 1H), 6.18 (d, 3.3 Hz, 1H), 6.09 (d, 1.2 Hz, 1H), 5.59 (d, 6.0 Hz, 1H), 3.56 (d, 6.1 Hz, 1H), 2.32 (s, 3H);
^{13}C NMR ($CDCl_3$, 125MHz): δ 199.7, 154.2, 147.3, 142.0, 127.0, 110.2, 107.0, 66.5, 26.1.



8s

3-(Hydroxy(thiophen-2-yl)methyl)but-3-en-2-one (**8s**).[8]
^{1}H NMR ($CDCl_3$, 500MHz): δ 7.23 (dd, 4.5, 1.8 Hz, 1H), 6.95 (t, 3.2 Hz, 1H), 6.94 (d, 1.7 Hz, 1H), 6.22 (s, 1H), 6.11 (d, 1.0 Hz, 1H), 5.81 (d, 6.0 Hz, 1H), 3.45 (d, 6.1 Hz, 1H), 2.37 (s, 3H);
^{13}C NMR ($CDCl_3$, 125MHz): δ 200.2, 149.1, 145.8, 126.8, 126.7, 125.1, 124.6, 69.6, 16.5.
HRMS calcd for $C_9H_{10}O_2NS$ 182.0396, found 182.0396 $[M]^+$.

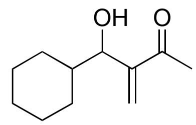


8t

3-(Hydroxy(p-tolyl)methyl)but-3-en-2-one (**8t**).[9]
^{1}H NMR ($CDCl_3$, 500MHz): δ 7.24 (d, 8.0 Hz, 2H), 7.14 (d, 7.9 Hz, 2H), 6.18 (s, 1H), 5.99 (d, 1.2 Hz, 1H), 5.58 (d, 4.6 Hz, 1H), 3.03 (d, 5.1 Hz, 1H), 2.33 (s, 6H);

[8] Nikpassand, M.; Mamaghani, M.; Tabatabaeian, K.; Abiazi, M. K. *Mol Divers* **2009**, *13*, 389-393.
[9] Huang, J. –W.; Shi, M. *Adv. Synth. Catal.* **2003**, *345*, 953-958.

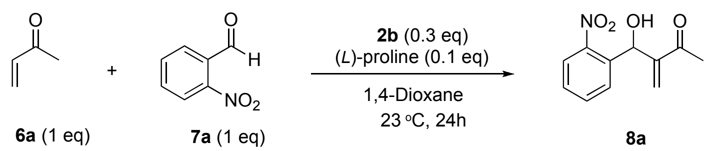
^{13}C NMR ($CDCl_3$, 125MHz): δ 200.3, 150.0, 138.6, 137.3, 129.1, 126.4, 126.4, 72.7, 26.5, 21.1.



8u

The spectroscopic data were consistent with those reported in the literature.[10]
^1H NMR ($CDCl_3$, 500MHz): δ 6.12 (s, 1H), 5.91 (s, 1H), 4.06 (t, 7.5 Hz, 1H), 2.68 (d, 7.9 Hz, 1H), 2.35 (s, 3H), 1.92 (m, 1H), 1.76-1.16 (m, 3H), 1. 53 (m, 1H), 1.43 (m, 1H), 1.24-1.06 (m, 3H), 0.98-0.89 (m, 2H);
^{13}C NMR ($CDCl_3$, 125MHz): δ 201.0, 148.8, 126.8, 77.4, 42.4, 30.1, 28.4, 26.6, 26.3, 26.1, 25.9.

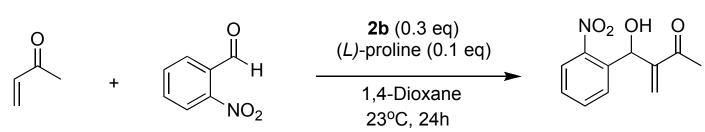
Table S2. Solvent Effect.[a]



entry	solvents	yield (%)	ee (%)
1	*t*-BuOH : H_2O = 1 : 1	-	46 (R)
2	NMP	-	10 (R)
3	$CHCl_3$	-	45 (R)
4	THF	9	67 (R)
5	$CHCl_3$: THF = 4: 1	-	62 (R)
6	MeCN	-	16 (R)
7	PrCN	-	16 (R)
8	PhCN	-	38 (R)
9	1,4-Dioxane	11	82 (R)
10	1,4-Dioxane : H_2O = 1 : 1	-	46 (R)
11	DMF	-	8 (R)
12	DMSO	-	8 (R)
13	DME	9	77 (R)
14	*N*-Methylforamide	-	19 (R)

[a] The reaction mixture was directly loaded to silica gel for flash column chromatography to give the MBH product **8a**.

Table S3. Solvent Effect with Varied Amounts of Aldehyde.[a]



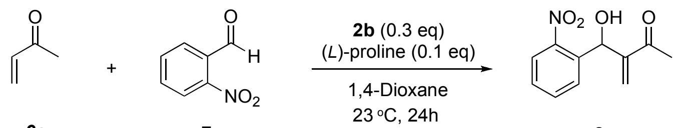
entry	solvents	yield (%)	ee (%)
1	NMP	-	10 (R)
2	$CHCl_3$	-	05 (R)
3	THF	-	52 (R)
4	$CHCl_3$: THF = 4: 1	-	18 (R)
5	MeCN	-	12 (R)
6	1,4-Dioxane	13	60 (R)

[10] Bailey, M.; Staton, I.; Ashton, P. R.; Marko, I. E.; Ollis, W. D. *Tetrahedron: Asymmetry* **1991**, *2*, 495-509.

7	DMF	-	08 (R)
8	DMSO	-	06 (R)
9	DME	13	49 (R)

[a] The reaction mixture was directly loaded to silica gel for flash column chromatography to give the MBH product **8a**.

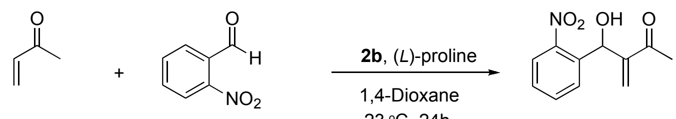
Table S4. Molar Ratio of Substrates.[a]



entry	**6a** (eq)	**7a** (eq)	yield (%)	ee (%)
1	1.0	1.0	11	82 (R)
2	1.0	2.0	16	74 (R)
3	1.0	3.0	16	75 (R)
4	2.0	1.0	12	73 (R)
5	3.0	1.0	14	71 (R)

[a] The reaction mixture was directly loaded to silica gel for flash column chromatography to give the MBH product **8a**.

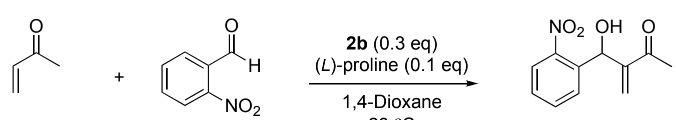
Table S5. Amounts of Catalysts Loading Effect.[a]



entry[b]	**2b** (eq)	**(*L*)-proline** (eq)	yield (%)	ee (%)
1	0.3	0.1	12	76
2	0.6	0.2	18	66
3	0.9	0.3	21	71
4	1.5	0.5	28	74
5	3.0	1.0	33	66

[a] The reaction mixture was directly loaded to silica gel for flash column chromatography to give the MBH product **8a**. [b] Due to the experimental delay on purifications, slightly higher reaction conversion/yields were observed on this particular experimental set, subsequently lower ee's were obtained.

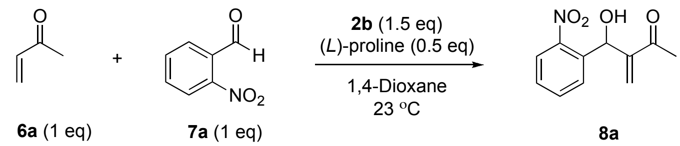
Table S6. Reaction Conversion with BNO (0.3 eq) & (*L*)-Proline (0.1 eq).[a]



entry[b]	time (h)	conversion (%)	ee (%)
1	4	2	77 (R)
2	8	4	76 (R)
3	12	6	70 (R)
4	24	12	64 (R)
5	36	18	61 (R)
6	48	23	59 (R)
7	60	28	56 (R)
8	72	32	50 (R)

[a] The reaction was performed using methyl vinyl ketone **6** (1 mmol) and aldehyde **7a** (1 mmol) in 1,4-dioxane (2.3 mL) in the presence of *N*-oxide **2b** (0.3 mmol) and (*L*)-proline (0.1 mmol). The aliquots were taken out at intervals and filtered using a short pad of silica gel. After removal of solvents, the ^{1}H NMR was taken in $CDCl_3$ to work out the reaction conversion. Subsequently, the mixture was further purified using flash column chromatography to give the MBH products for HPLC analysis. [b] Due to the removal of aliquots from the reaction at frequent intervals, the observed reaction conversion and ee's were somewhat different from that of our normal experimental set, this is in part due to the uneven removal of *N*-oxide and proline upon taking out aliquots.

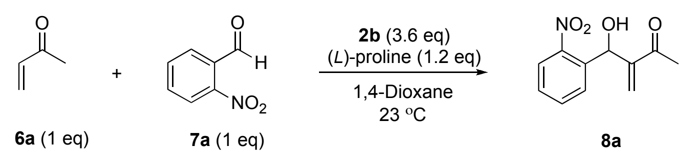
Table S7. Reaction Conversion with BNO (1.5 eq) & (*L*)-Proline (0.5 eq).[a]



entry[b]	time (h)	conversion (%)	ee (%)
1	4	4	80 (R)
2	8	8	75 (R)
3	12	12	76 (R)
4	24	27	69 (R)
5	36	36	65 (R)
6	48	49	58 (R)
7	60	58	58 (R)
8	72	74	54 (R)

[a] The reaction was performed using methyl vinyl ketone **6** (1 mmol) and aldehyde **7a** (1 mmol) in 1,4-dioxane (11.6 mL) in the presence of *N*-oxide **2b** (1.5 mmol) and (*L*)-proline (0.5 mmol). The aliquots were taken out at intervals and filtered using a short pad of silica gel. After removal of solvents, the ^1H NMR was taken in $CDCl_3$ to work out the reaction conversion. Subsequently, the mixture was further purified using flash column chromatography to give the MBH products for HPLC analysis. [b] Due to the removal of aliquots from the reaction at frequent intervals, the observed ee's were somewhat lower than expected, this is in part due to the uneven removal of solid components, *N*-oxides and proline, upon taking out aliquots.

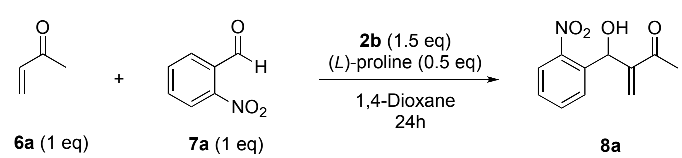
Table S8. Reaction Conversion with BNO (3.6 eq) & (*L*)-Proline (1.2 eq).[a]



entry[b]	time (h)	conversion (%)	ee (%)
1	4	7	82 (R)
2	8	12	80 (R)
3	12	18	64 (R)
4	24	35	55 (R)
5	36	46	46 (R)
6	48	52	44 (R)
7	60	60	35 (R)
8	72	68	35 (R)

[a] The reaction was performed using methyl vinyl ketone **6** (1 mmol) and aldehyde **7a** (1 mmol) in 1,4-dioxane (27.7 mL) in the presence of *N*-oxide **2b** (3.6 mmol) and (*L*)-proline (1.2 mmol). The aliquots were taken out at intervals and filtered using a short pad of silica gel. After removal of solvents, the ^1H NMR was taken in $CDCl_3$ to work out the reaction conversion. Subsequently, the mixture was further purified using flash column chromatography to give the MBH products for HPLC analysis. [b] Due to the removal of aliquots from the reaction at frequent intervals, the observed ee's were somewhat lower than expected, this is in part due to the uneven removal of solid components, *N*-oxides and proline, upon taking out aliquots.

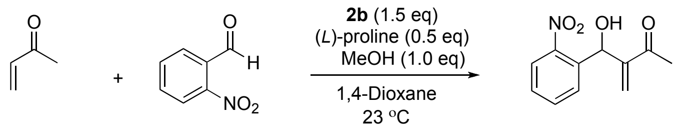
Table S9. Temperature Effect.[a]



entry	°C	conversion (%)	isolated yield (%) (based on the SM)	ee (%)
1	25	26	83	74 (R)
2	30	29	84	77 (R)
3	35	44	82	68 (R)

[a] The reaction was stopped after 24h by filtering the mixture using a short pad of silica gel. After removal of solvents, the ^{1}H NMR was taken in $CDCl_3$ to work out the reaction conversion. Subsequently, the mixture was further purified using flash column chromatography to give the MBH products for HPLC analysis.

Table S10. Reaction in the Presence of MeOH (1 eq).[a]

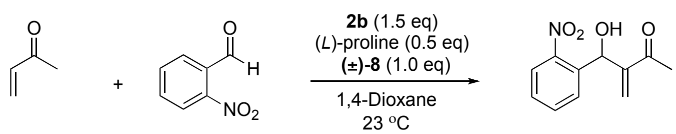


6a (1 eq) **7a** (1 eq) **8a**

entry[b]	time (h)	conversion (%)	ee (%)
1	4	5	68 (R)
2	8	8	69 (R)
3	12	11	64 (R)
4	24	23	51 (R)
5	36	34	51 (R)
6	48	41	50 (R)
7	60	54	49 (R)
8	72	61	46 (R)

[a] The reaction was performed using methyl vinyl ketone **6** (1 mmol) and aldehyde **7a** (1 mmol) in 1,4-dioxane (11.6 mL) in the presence of *N*-oxide **2b** (1.5 mmol) and (*L*)-proline (0.5 mmol). The aliquots were taken out at intervals and filtered using a short pad of silica gel. After removal of solvents, the ^{1}H NMR was taken in $CDCl_3$ to work out the reaction conversion. Subsequently, the mixture was further purified using flash column chromatography to give the MBH products for HPLC analysis. [b] Due to the removal of aliquots from the reaction at frequent intervals, the observed ee values might be lower than expected, this is in part due to the uneven removal of solid components, *N*-oxides and proline, upon taking out aliquots.

Table S11. Reaction in the Presence of (±)-8 (1 eq).[a]

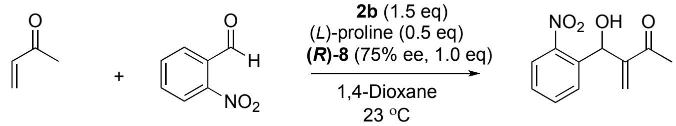


6a (1 eq) **7a** (1 eq) **8a**

entry[b]	time (h)	conversion (%)	ee (%)[c]
1	4	3	8 (R)-99[d]
2	8	8	7 (R)-98[d]
3	12	15	9 (R)-64[d]
4	24	28	11 (R)-50[d]
5	36	37	12 (R)-44[d]
6	48	49	14 (R)-43[d]
7	60	54	14 (R)-40[d]
8	72	58	16 (R)-43[d]

[a] The reaction was performed using methyl vinyl ketone **6** (1 mmol) and aldehyde **7a** (1 mmol) in 1,4-dioxane (11.6 mL) in the presence of *N*-oxide **2b** (1.5 mmol) and (*L*)-proline (0.5 mmol). The aliquots were taken out at intervals and filtered using a short pad of silica gel. After removal of solvents, the ^{1}H NMR was taken in $CDCl_3$ to work out the reaction conversion. Subsequently, the mixture was further purified using flash column chromatography to give the MBH products for HPLC analysis. [b] Due to the removal of aliquots from the reaction at frequent intervals, the observed ee values might be lower than expected, this is in part due to the uneven removal of solid components, *N*-oxides and proline, upon taking out aliquots. [c] Observed ee's in the presence of (±)-**8** (1 eq). [d] Corrected ee's based on the reaction conversion by subtracting the amount of (±)-**8** (1 eq).

Table S12. Reaction in the Presence of (*R*)-8 (1 eq).[a]

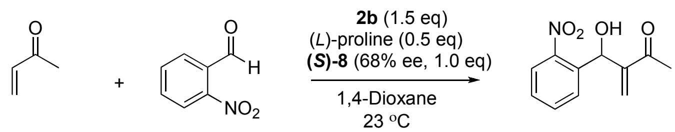


6a (1 eq) **7a** (1 eq) **8a**

Entry[b]	time (h)	conversion (%)	ee (%)[c]
1	4	4	75 (R)-98[d]
2	8	9	74 (R)-96[d]
3	12	16	71 (R)-91[d]
4	24	22	75 (R)-94[d]
5	36	29	69 (R)-87[d]
6	48	32	71 (R)-86[d]
7	60	39	64 (R)-78[d]
8	72	43	67 (R)-81[d]

[a] The reaction was performed using methyl vinyl ketone **6** (1 mmol) and aldehyde **7a** (1 mmol) in 1,4-dioxane (11.6 mL) in the presence of *N*-oxide **2b** (1.5 mmol) and (*L*)-proline (0.5 mmol). The aliquots were taken out at intervals and filtered using a short pad of silica gel. After removal of solvents, the ^{1}H NMR was taken in $CDCl_3$ to work out the reaction conversion. Subsequently, the mixture was further purified using flash column chromatography to give the MBH products for HPLC analysis. [b] Due to the removal of aliquots from the reaction at frequent intervals, the observed ee values might be lower than expected, this is in part due to the uneven removal of solid components, *N*-oxides and proline, upon taking out aliquots. [c] Observed ee's in the presence of 1 equivalent mixture of (*R*)-**8** (87.5%) and (*S*)-**8** (12.5%). [d] Corrected ee's based on the reaction conversion by subtracting the amount of 1 equivalent mixture of (*R*)-**8** (87.5%) and (*S*)-**8** (12.5%).

Table S13. Reaction in the Presence of (*S*)-8 (1 eq).[a]

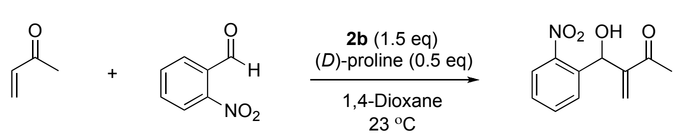


6a (1 eq) **7a** (1 eq) **8a**

entry[b]	time (h)	conversion (%)	ee (%)[c]
1	4	0	64 (S)
2	8	0	63 (S)
3	12	0	61 (S)
4	24	0	61 (S)
5	36	1	60 (S)
6	48	1	57 (S)
7	60	13	54 (S)-75[d]
8	72	16	54 (S)-75[d]

[a] The reaction was performed using methyl vinyl ketone **6** (1 mmol) and aldehyde **7a** (1 mmol) in 1,4-dioxane (11.6 mL) in the presence of *N*-oxide **2b** (1.5 mmol) and (*L*)-proline (0.5 mmol). The aliquots were taken out at intervals and filtered using a short pad of silica gel. After removal of solvents, the ^{1}H NMR was taken in $CDCl_3$ to work out the reaction conversion. Subsequently, the mixture was further purified using flash column chromatography to give the MBH products for HPLC analysis. [b] Due to the removal of aliquots from the reaction at frequent intervals, the observed ee values might be lower than expected, this is in part due to the uneven removal of solid components, *N*-oxides and proline, upon taking out aliquots. [c] Observed ee's in the presence of 1 equivalent mixture of (*R*)-**8** (16%) and (*S*)-**8** (84%). [d] Corrected ee's based on the reaction conversion by subtracting the amount of 1 equivalent mixture of (*R*)-**8** (16%) and (*S*)-**8** (84%).

Table S14. (*D*)-Proline-Catalyzed Reaction.[a]



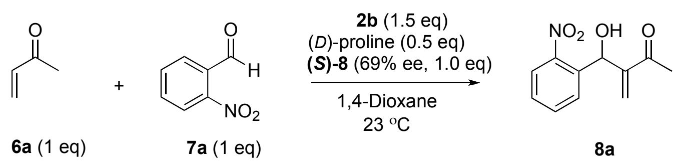
6a (1 eq) **7a** (1 eq) **8a**

entry[b]	time (h)	conversion (%)	ee (%)
1	4	4	65 (S)
2	8	8	60 (S)

3	12	12	58 (S)
4	24	21	57 (S)
5	36	27	56 (S)
6	48	38	43 (S)
7	60	45	40 (S)
8	72	51	36 (S)

[a] The reaction was performed using methyl vinyl ketone **6** (1 mmol) and aldehyde **7a** (1 mmol) in 1,4-dioxane (11.6 mL) in the presence of *N*-oxide **2b** (1.5 mmol) and (*D*)-proline (0.5 mmol). The aliquots were taken out at intervals and filtered using a short pad of silica gel. After removal of solvents, the ^{1}H NMR was taken in $CDCl_3$ to work out the reaction conversion. Subsequently, the mixture was further purified using flash column chromatography to give the MBH products for HPLC analysis. [b] Due to the removal of aliquots from the reaction at frequent intervals, the observed ee values might be lower than expected, this is in part due to the uneven removal of solid components, *N*-oxides and proline, upon taking out aliquots.

Table S15. (*D*)-Proline-Catalyzed Reaction in the Presence of (*S*)-8 (1 eq).[a]

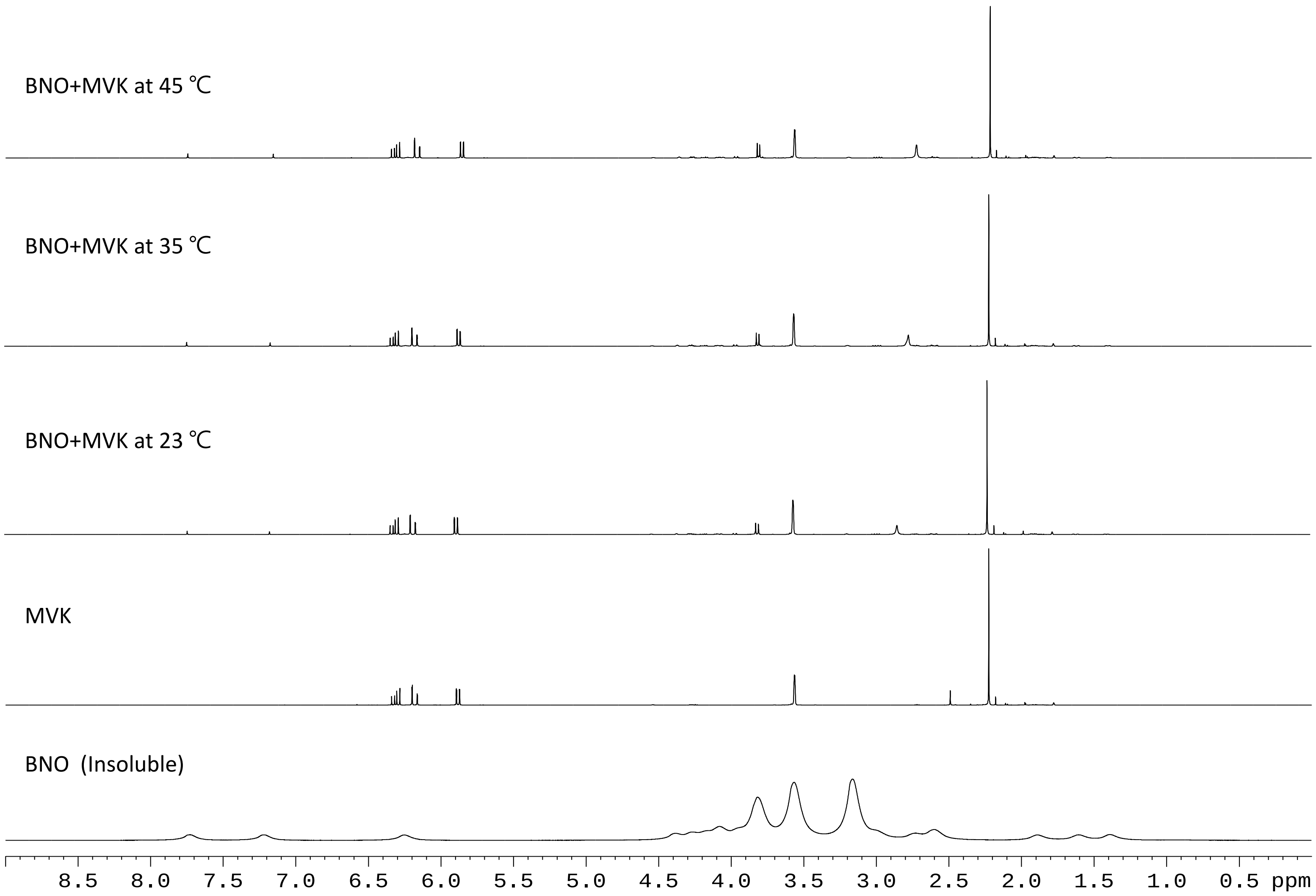


entry[b]	time (h)	conversion (%)	ee (%)[c]
1	4	7	64 (S)-90[d]
2	8	12	65 (R)-90[d]
3	12	18	66 (R)-90[d]
4	24	21	62 (R)-83[d]
5	36	29	61 (R)-80[d]
6	48	36	72 (R)-80[d]
7	60	41	61 (R)-78[d]
8	72	44	57 (R)-73[d]

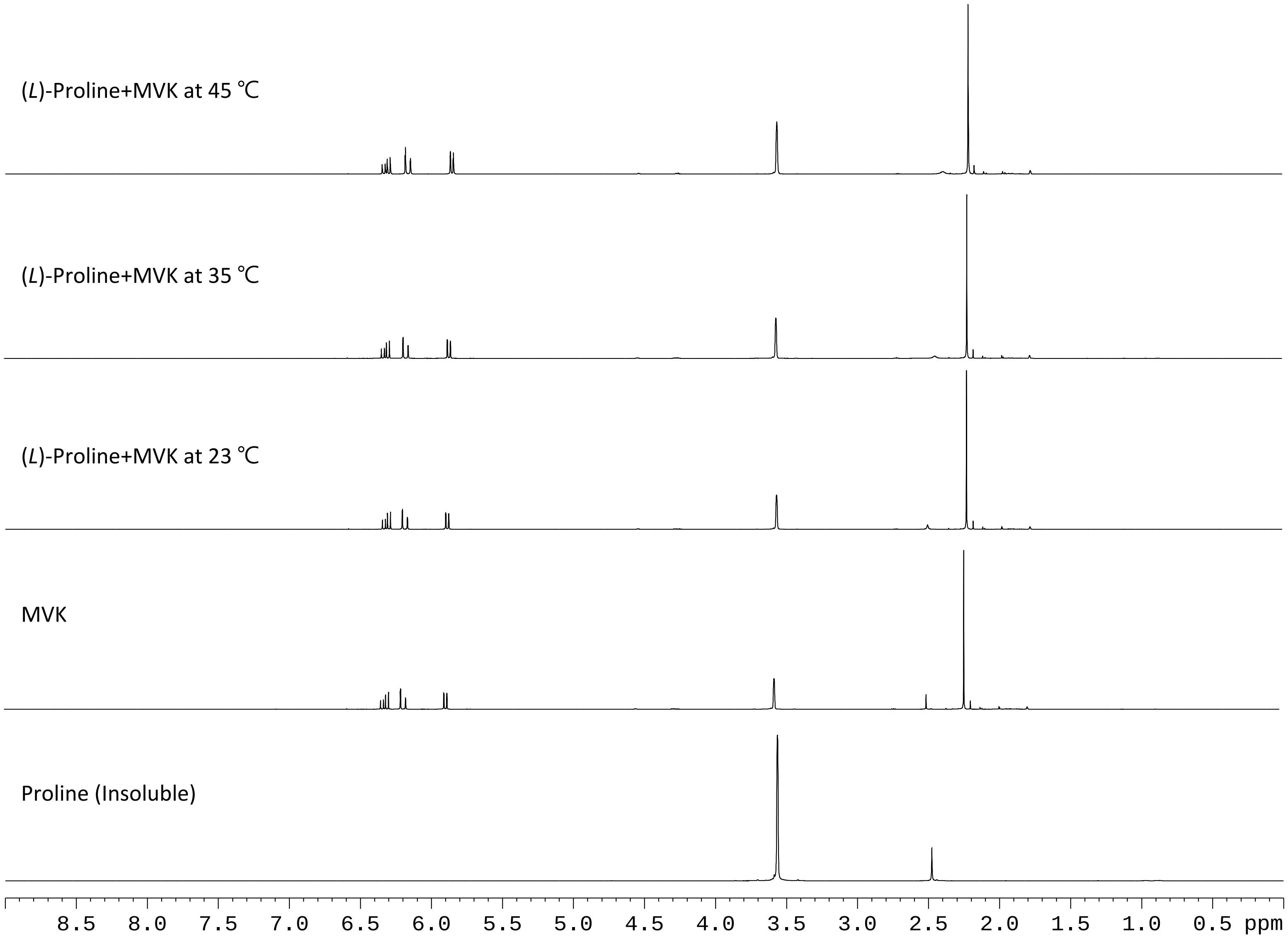
[a] The reaction was performed using methyl vinyl ketone **6** (1 mmol) and aldehyde **7a** (1 mmol) in 1,4-dioxane (11.6 mL) in the presence of *N*-oxide **2b** (1.5 mmol) and (*D*)-proline (0.5 mmol). The aliquots were taken out at intervals and filtered using a short pad of silica gel. After removal of solvents, the ^{1}H NMR was taken in $CDCl_3$ to work out the reaction conversion. Subsequently, the mixture was further purified using flash column chromatography to give the MBH products for HPLC analysis. [b] Due to the removal of aliquots from the reaction at frequent intervals, the observed ee values might be lower than expected, this is in part due to the uneven removal of solid components, *N*-oxides and proline, upon taking out aliquots. [c] Observed ee's in the presence of 1 equivalent mixture of (*R*)-**8** (15.5%) and (*S*)-**8** (84.5%). [d] Corrected ee's based on the reaction conversion by subtracting the amount of 1 equivalent mixture of (*R*)-**8** (15.5%) and (*S*)-**8** (84.5%).

^{1}H NMR Studies in 1,4-Dioxane-D_8

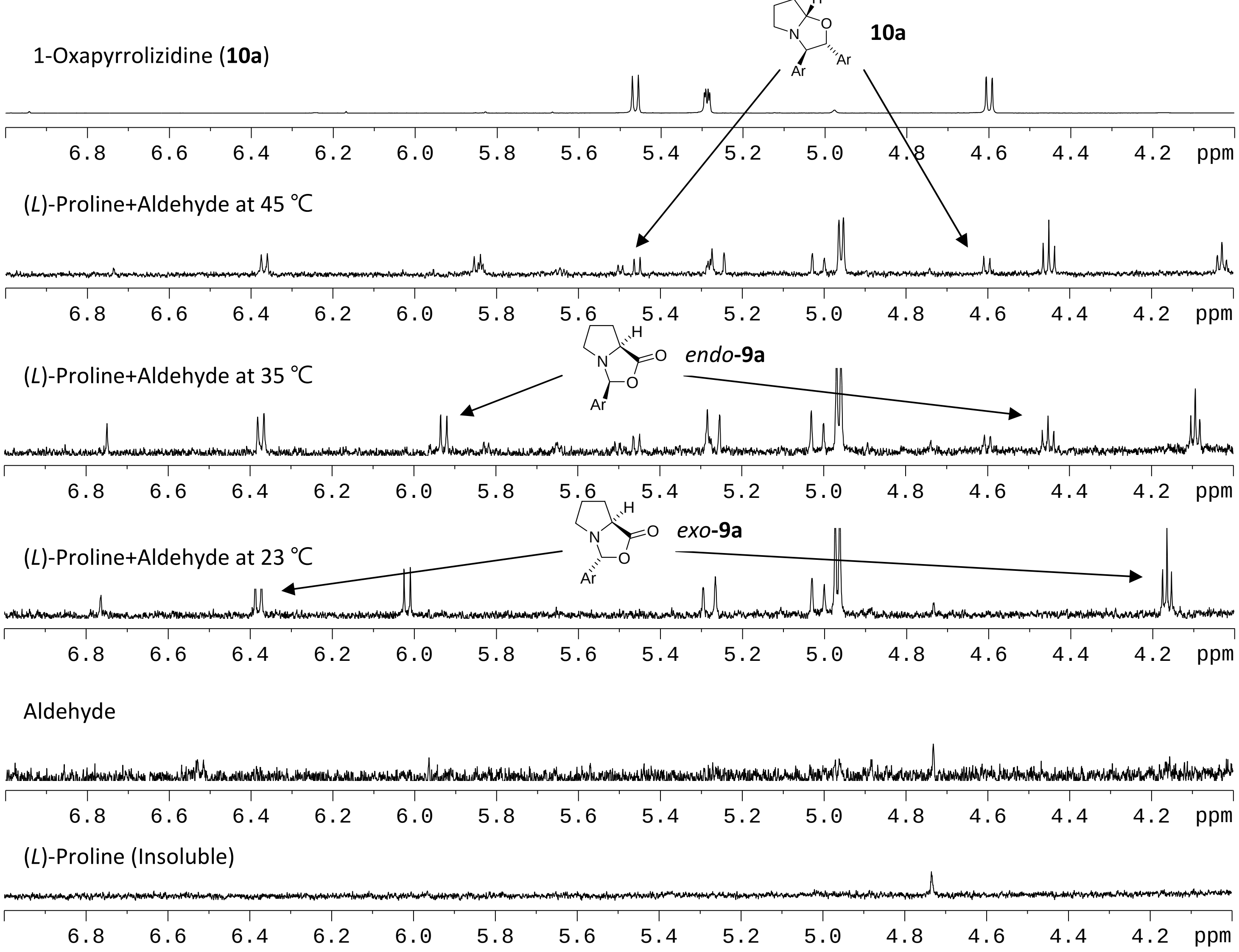
1. NMR Study of BNO+MVK in 1,4-Dioxane-D_8



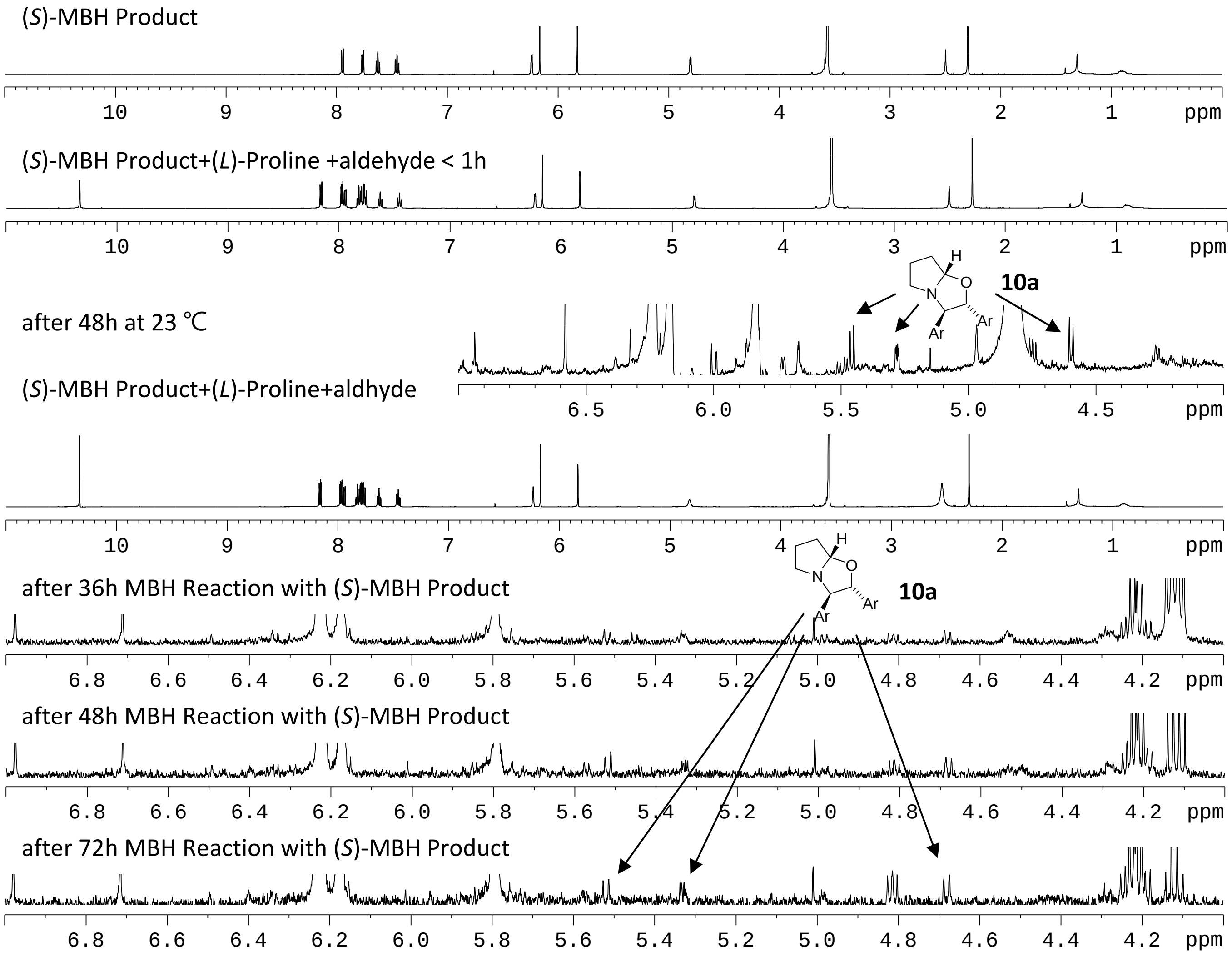
2. NMR Study of (*L*)-Proline+MVK in 1,4-Dioxane-D_8



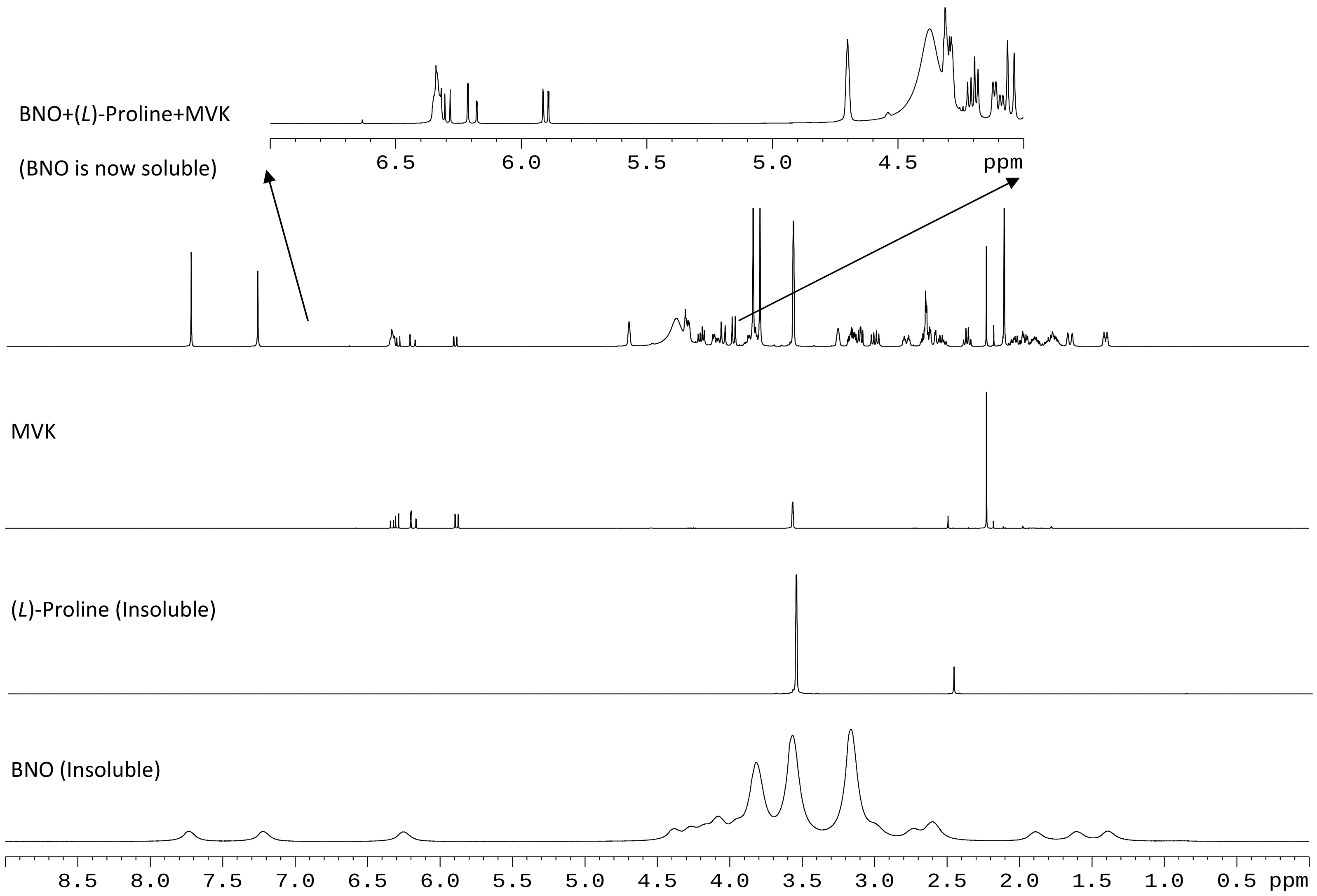
3. NMR Study of (*L*)-Proline +2-Nitrobenzaldehyde in 1,4-Dioxane-D_8



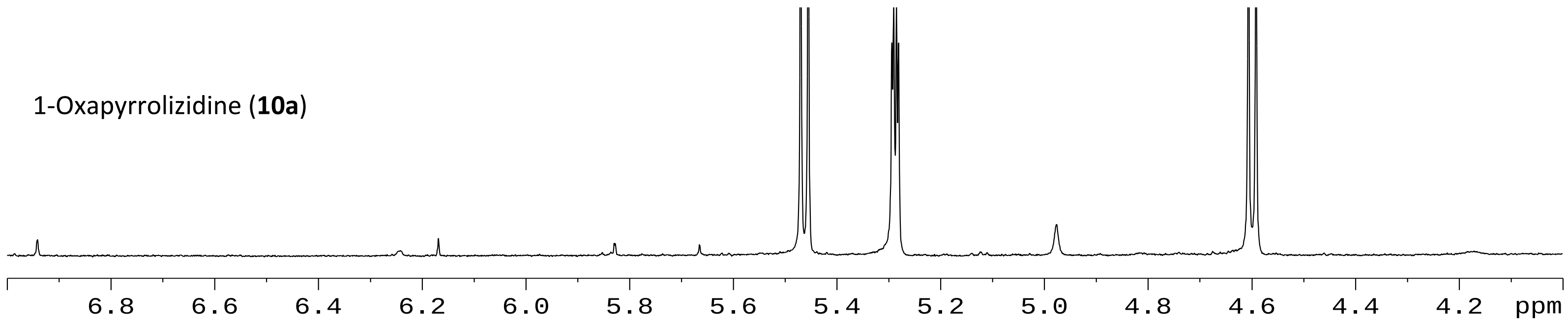
4. NMR Study of (*S*)-MBH Product+(*L*)-Proline+2-Nitrobenzaldehyde in 1,4-Dioxane-D_8

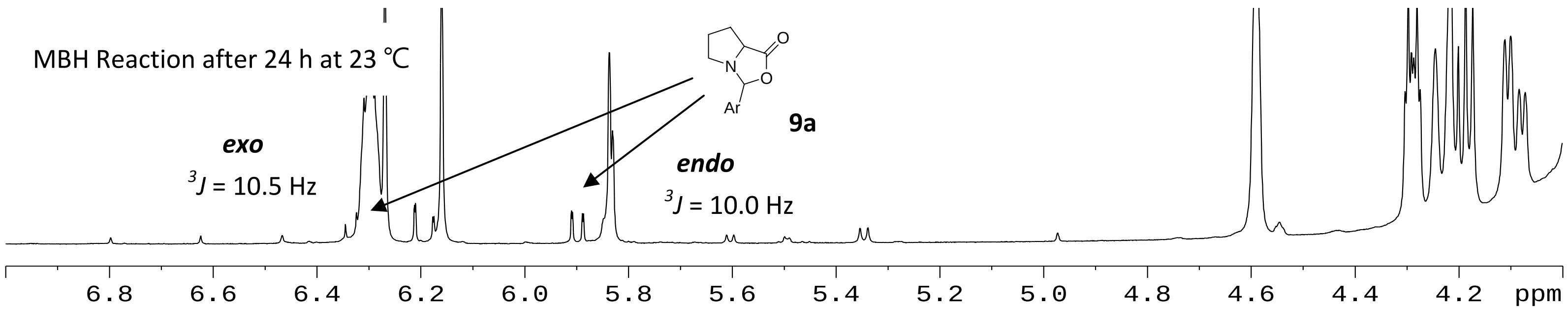


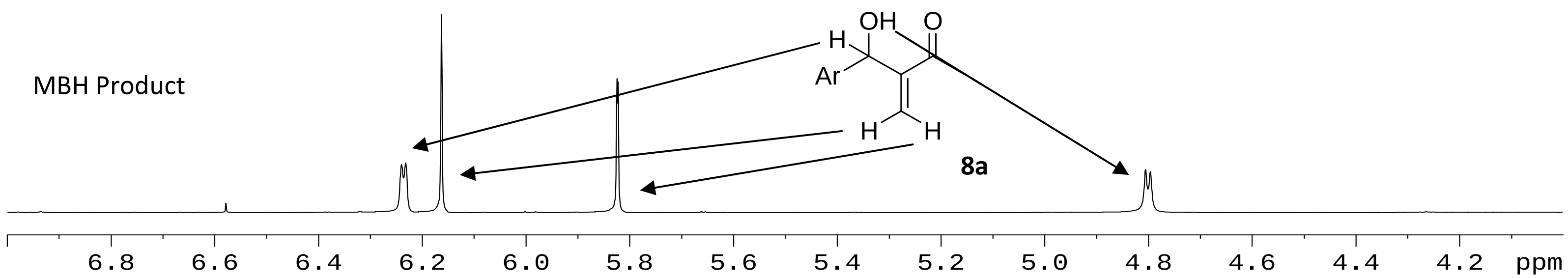
5. NMR Study of BNO+(*L*)-Proline+MVK in 1,4-Dioxane-D_8



6. NMR Study of the MBH Reaction in 1,4-Dioxane-D_8







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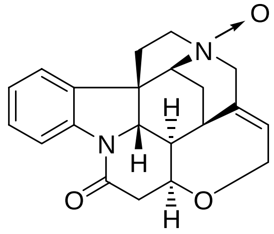
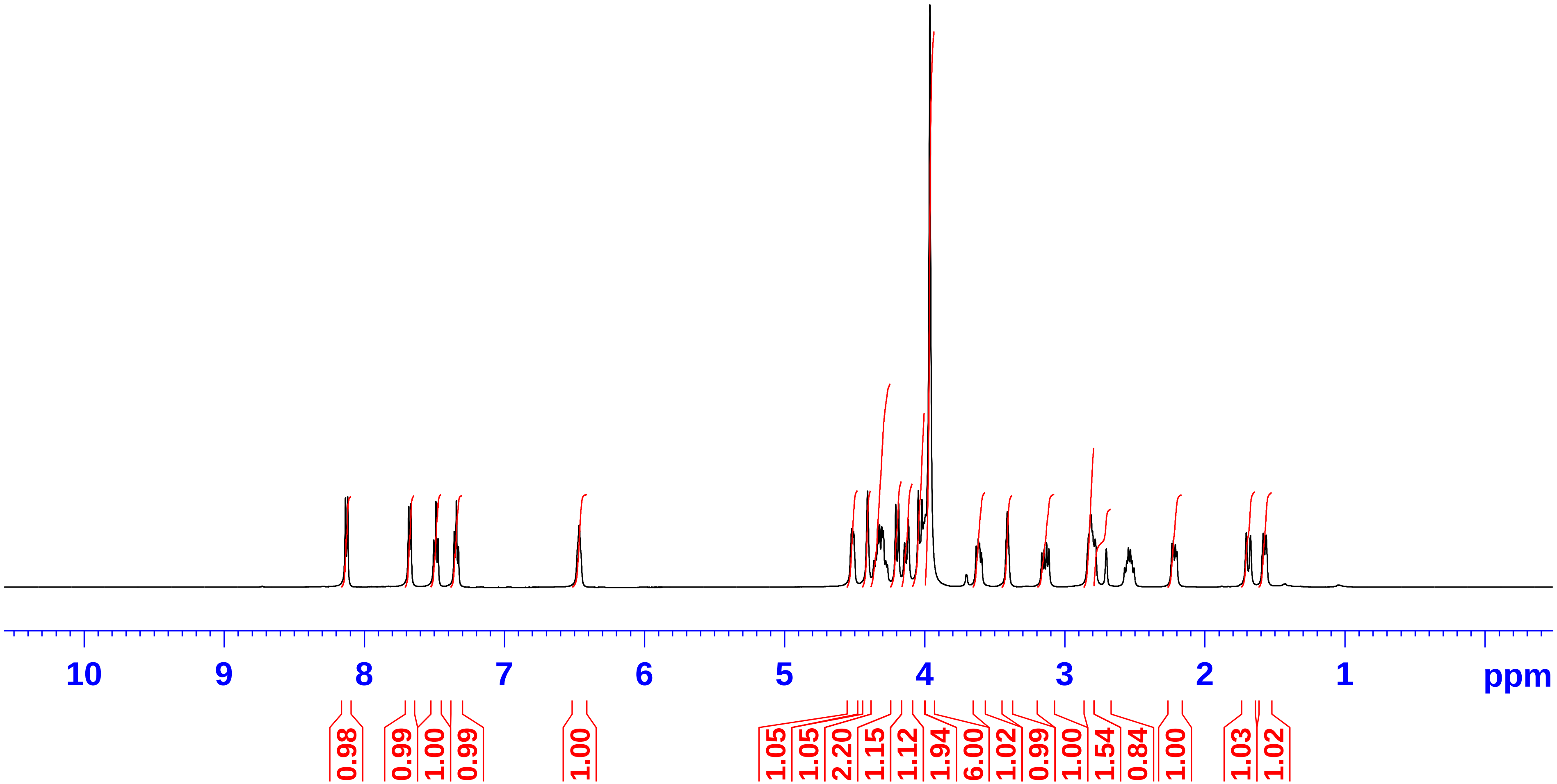
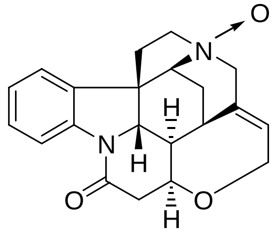
^{1}H NMR Spectrum of **2a** in DMSO



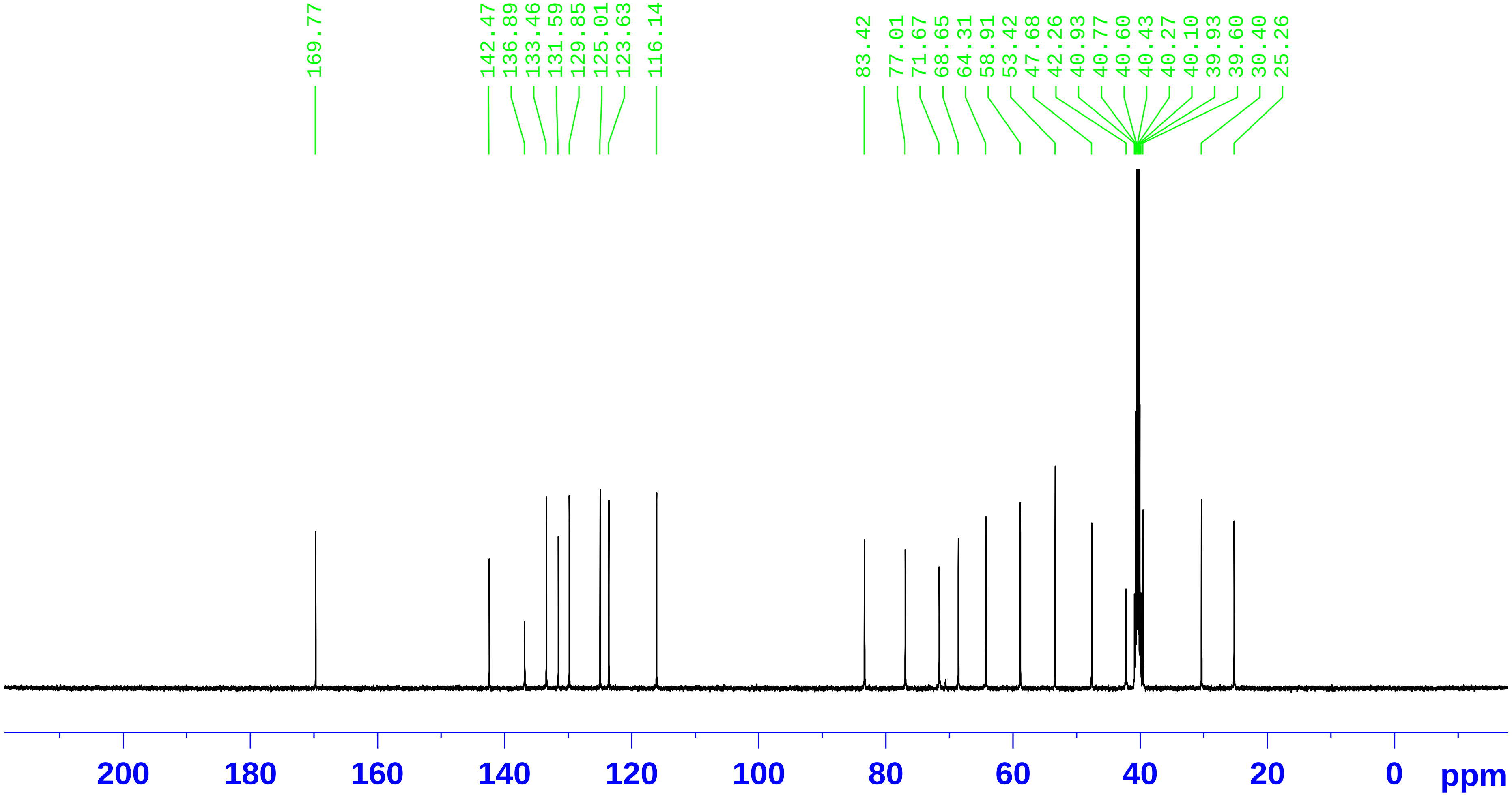
Strichnine N-Oxide (**2a**)



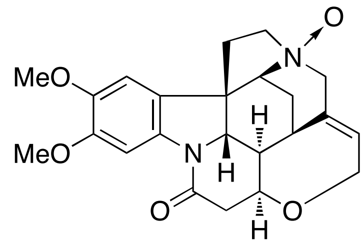
^{13}C NMR Spectrum of **2a** in DMSO



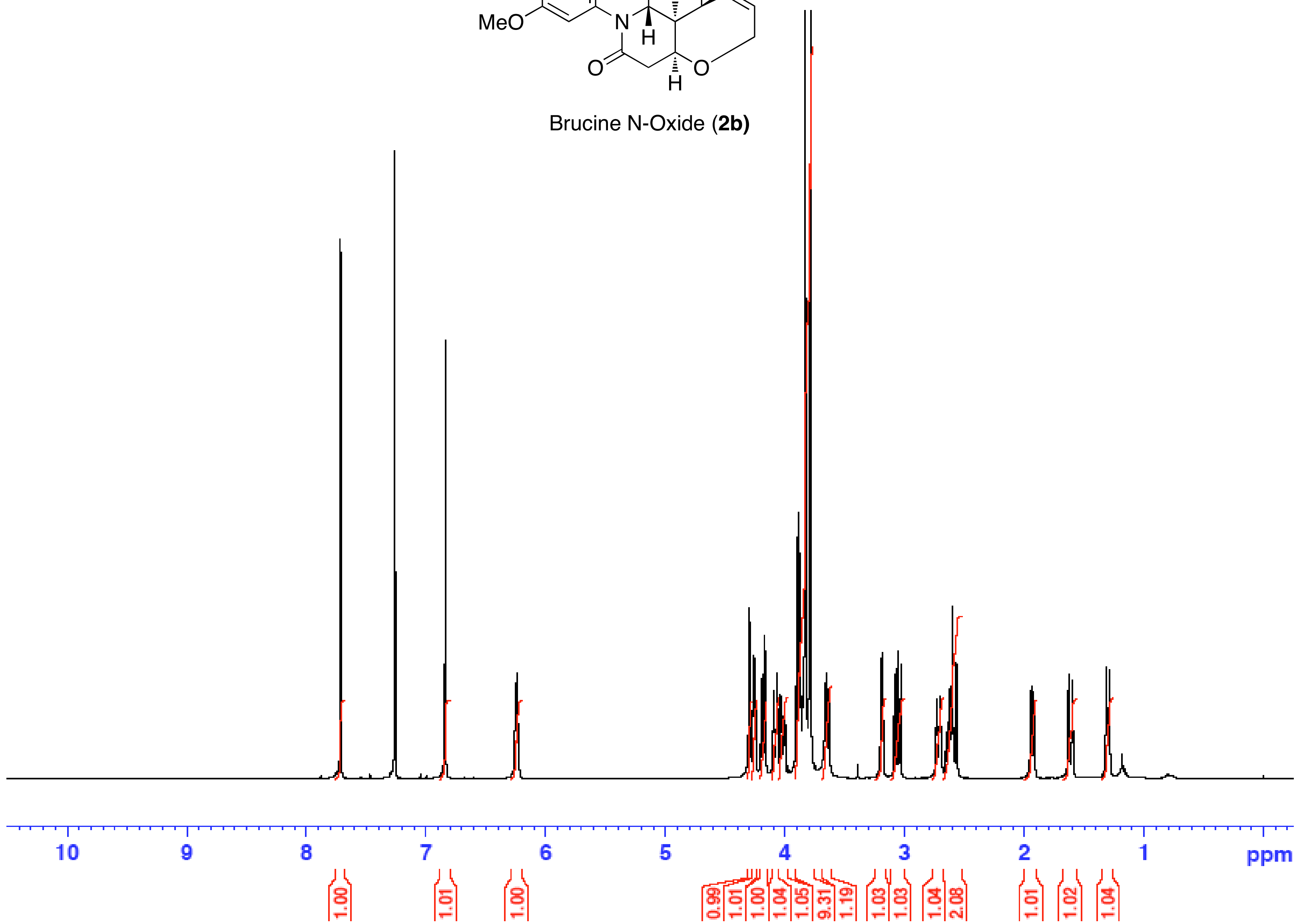
Strichnine N-Oxide (**2a**)



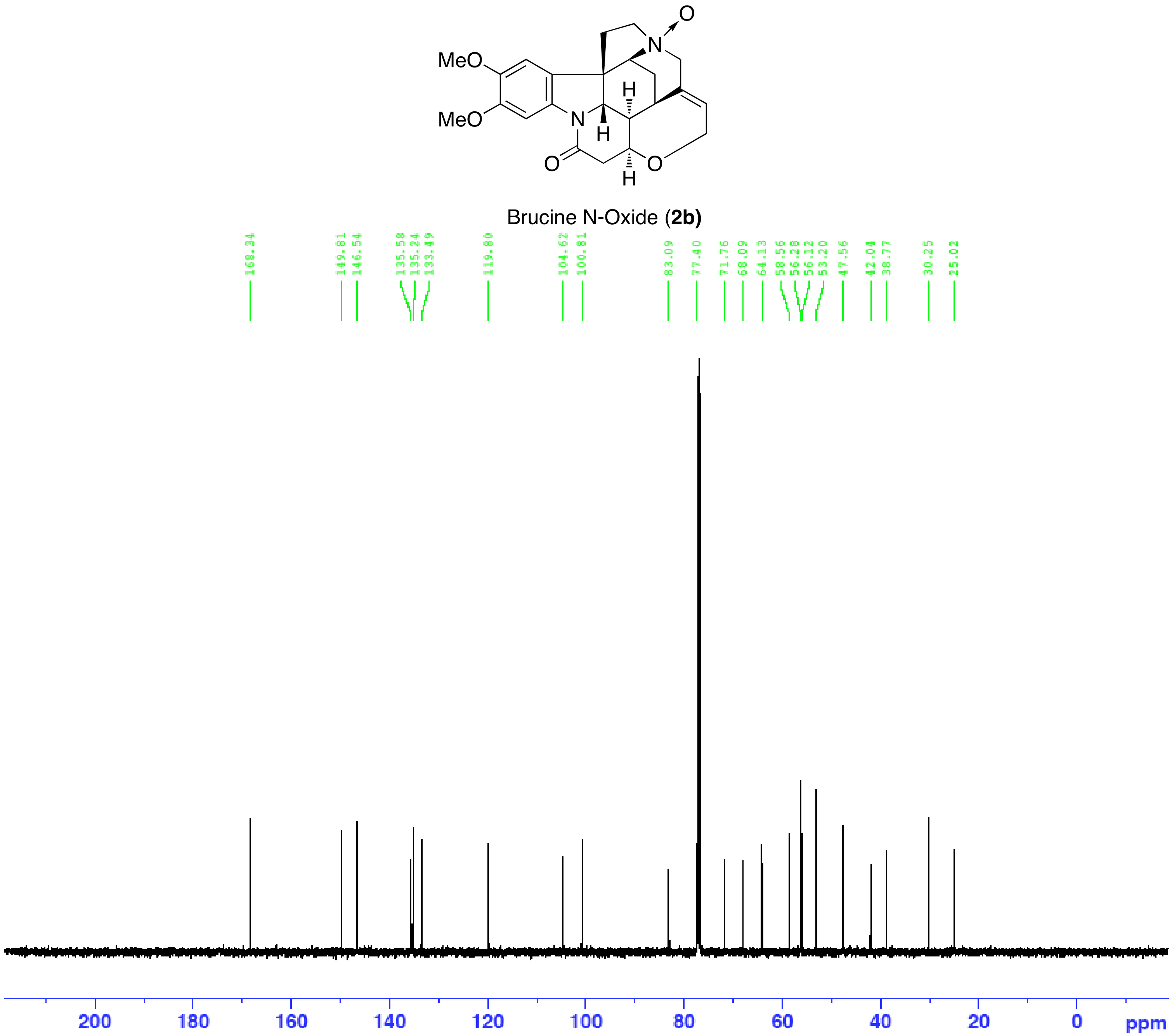
^{1}H NMR Spectrum of **2b** in $CDCl_3$



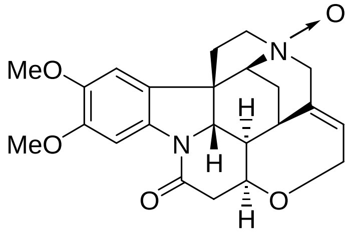
Brucine N-Oxide (**2b)**



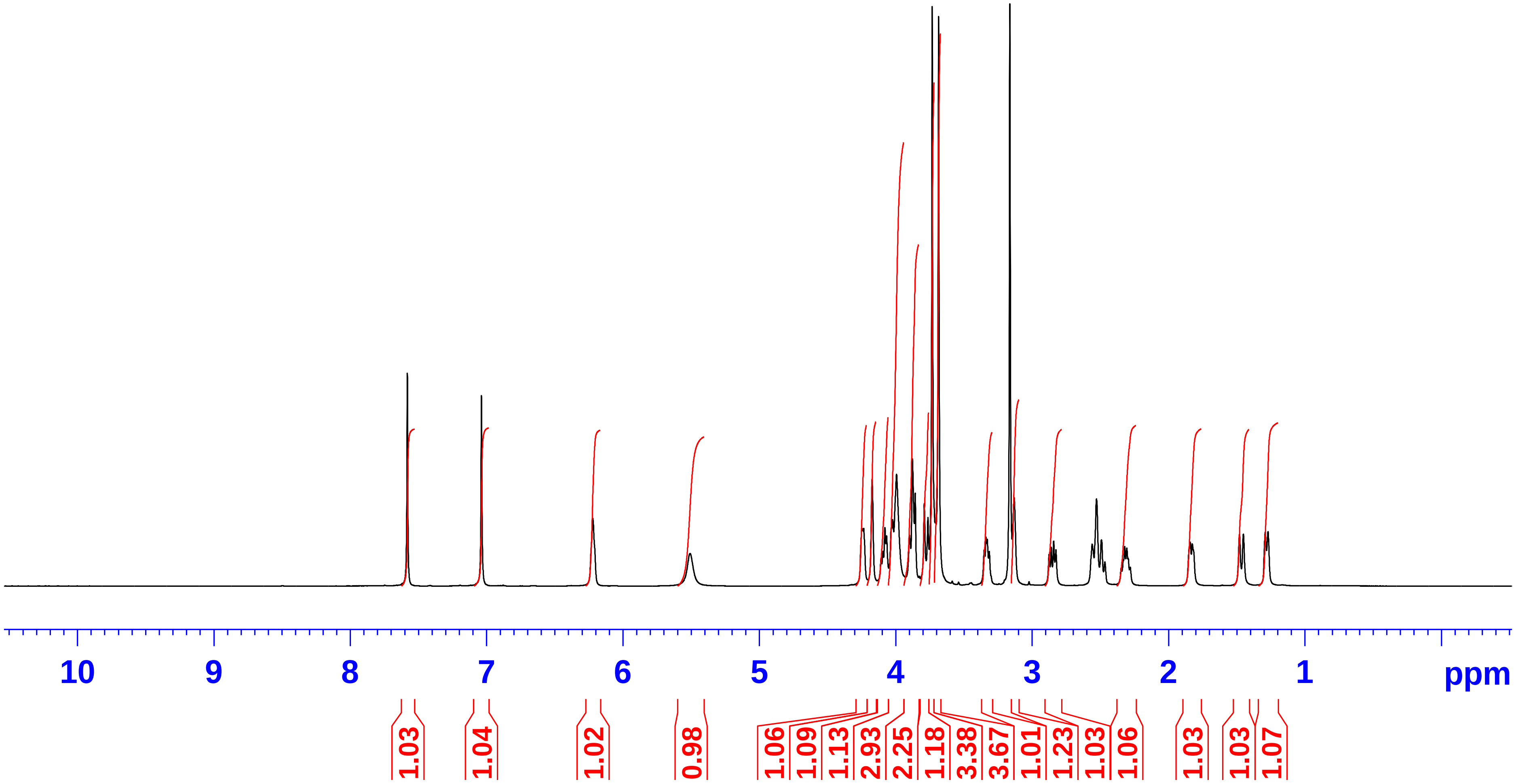
^{13}C NMR Spectrum of **2b** in $CDCl_3$



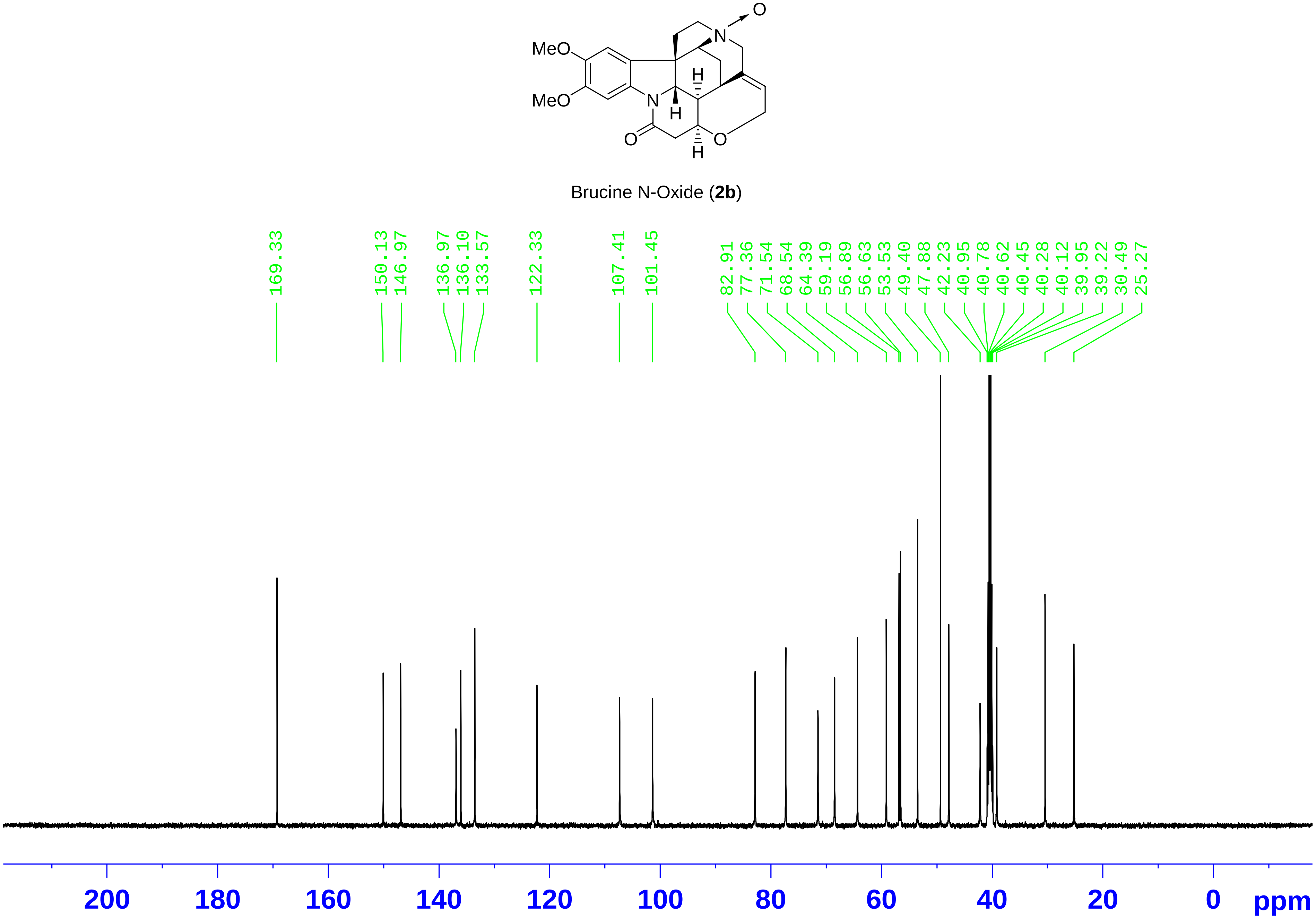
^{1}H NMR Spectrum of **2b** in DMSO



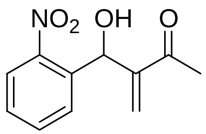
Brucine N-Oxide (**2b**)



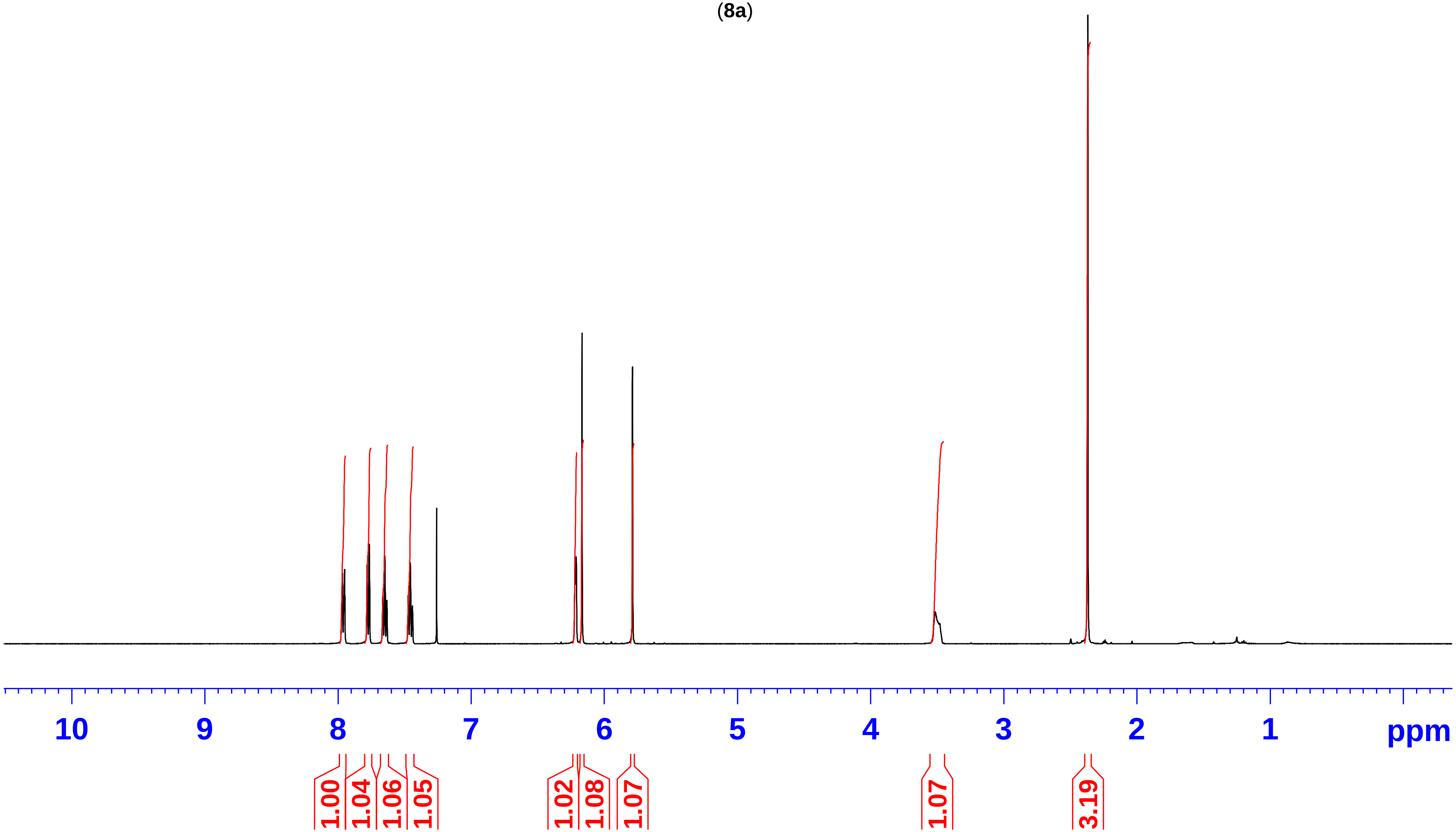
^{13}C NMR Spectrum of **2b** in DMSO



^{1}H NMR Spectrum of **8a**



3-[Hydroxy-(2-nitro-phenyl)-methyl]-but-3-en-2-one
(**8a**)



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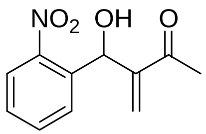
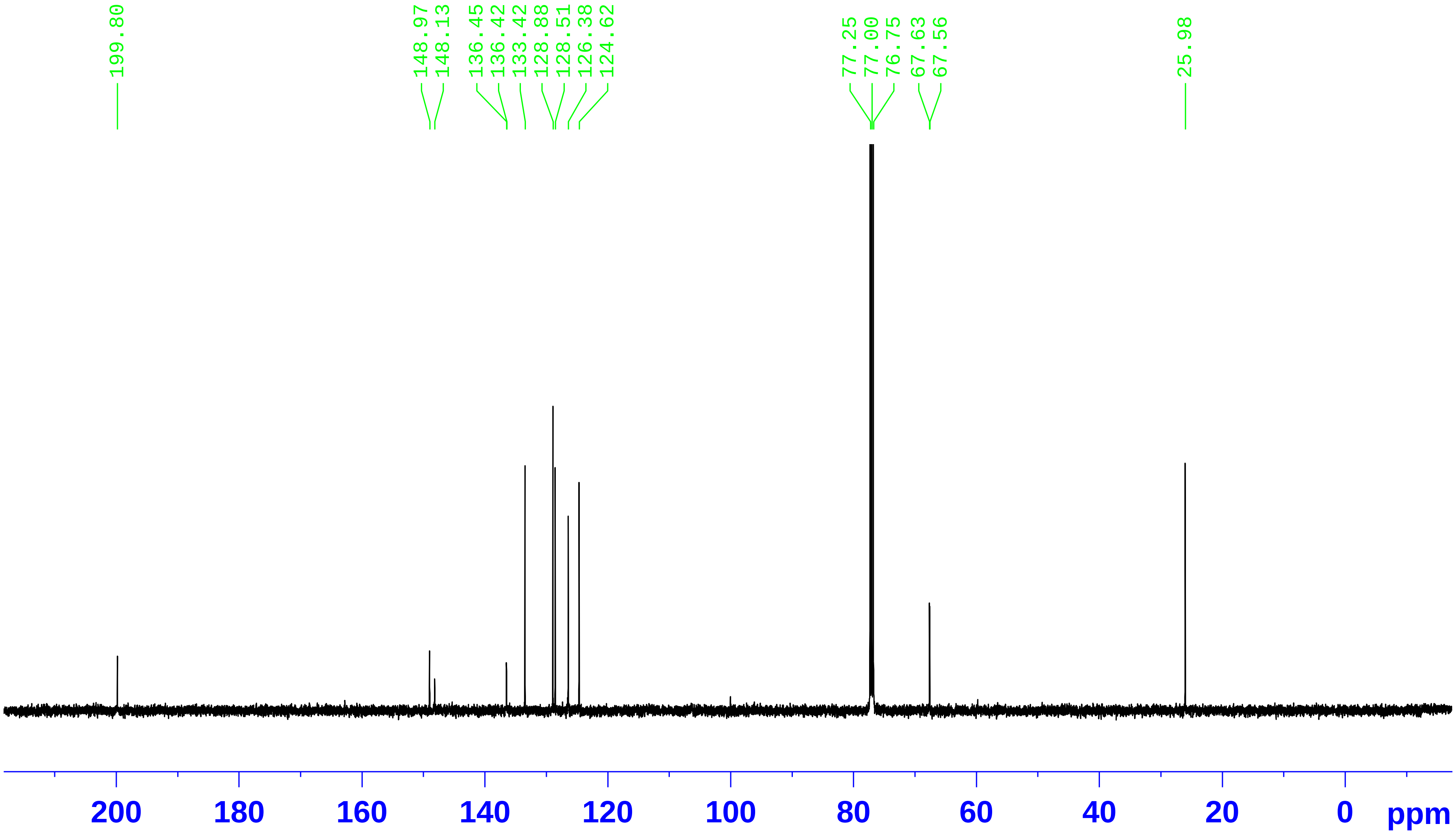
^{13}C NMR Spectrum of **8a**



3-[Hydroxy-(2-nitro-phenyl)-methyl]-but-3-en-2-one
(**8a**)



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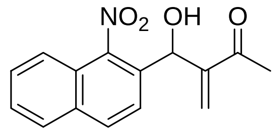
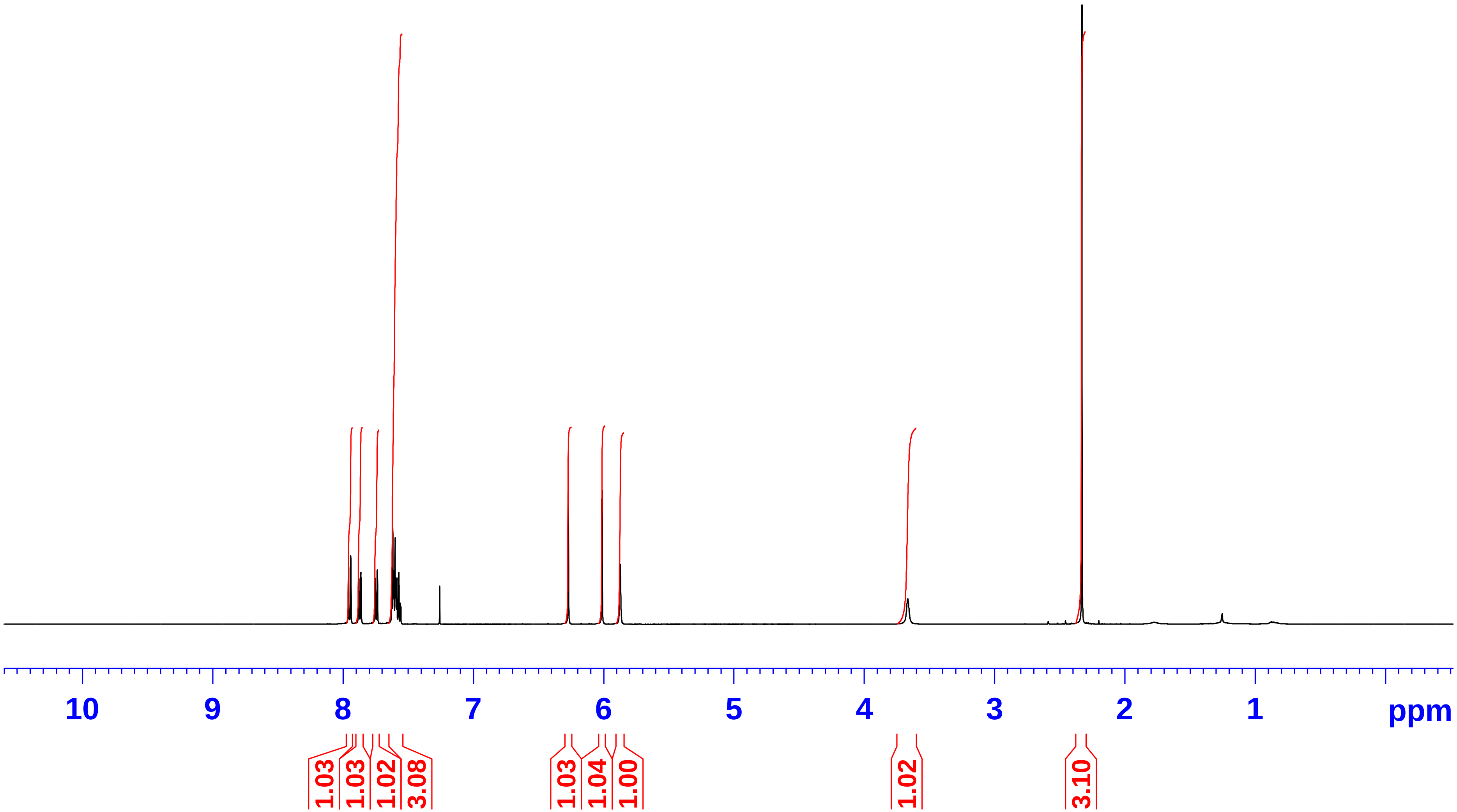
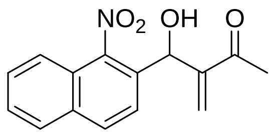
^{1}H NMR Spectrum of **8b**



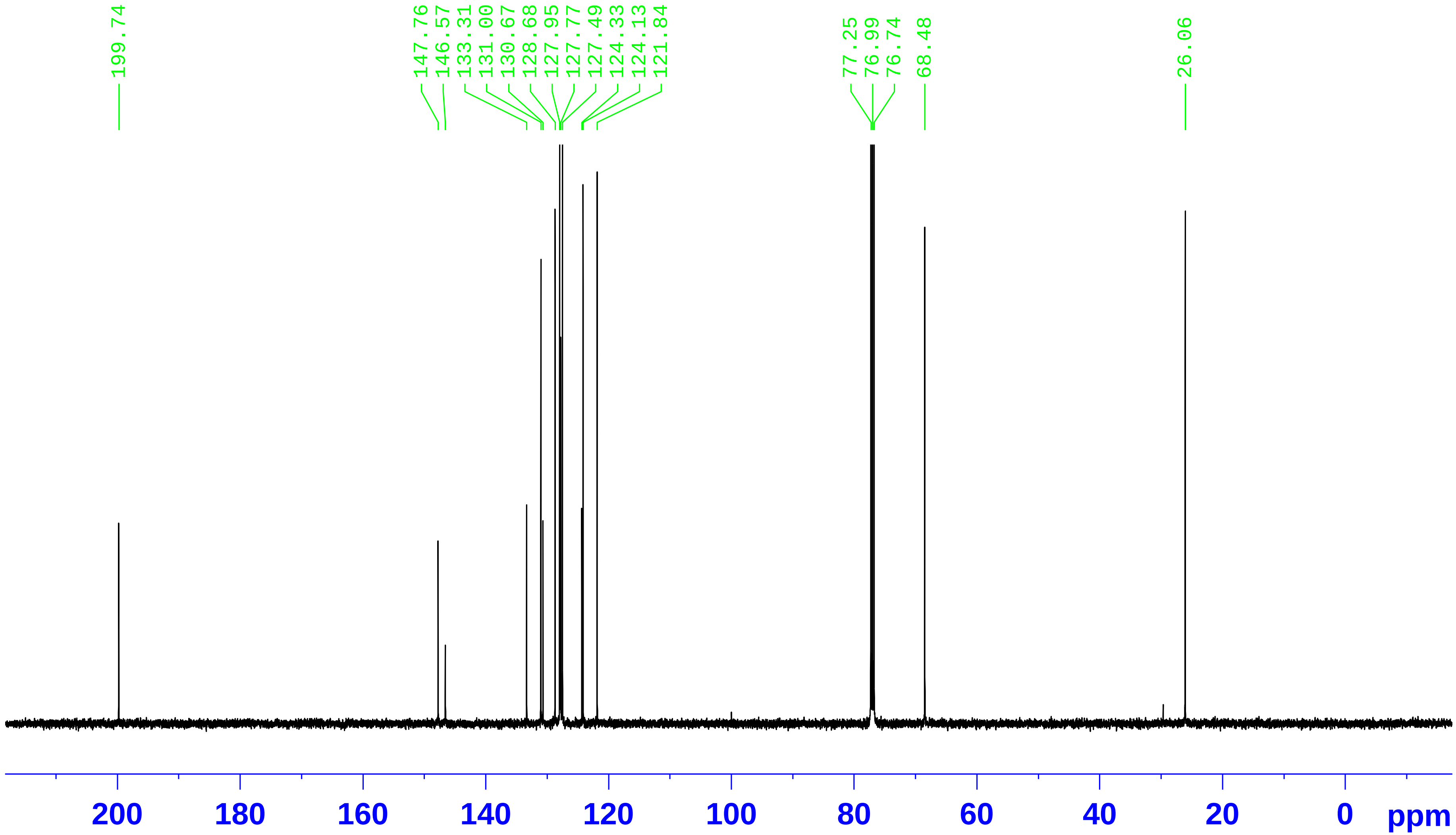
3-[Hydroxy-(1-nitro-naphthalen-2-yl)-methyl]-but-3-en-2-one (**8b**)



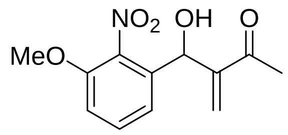
^{13}C NMR Spectrum of **8b**



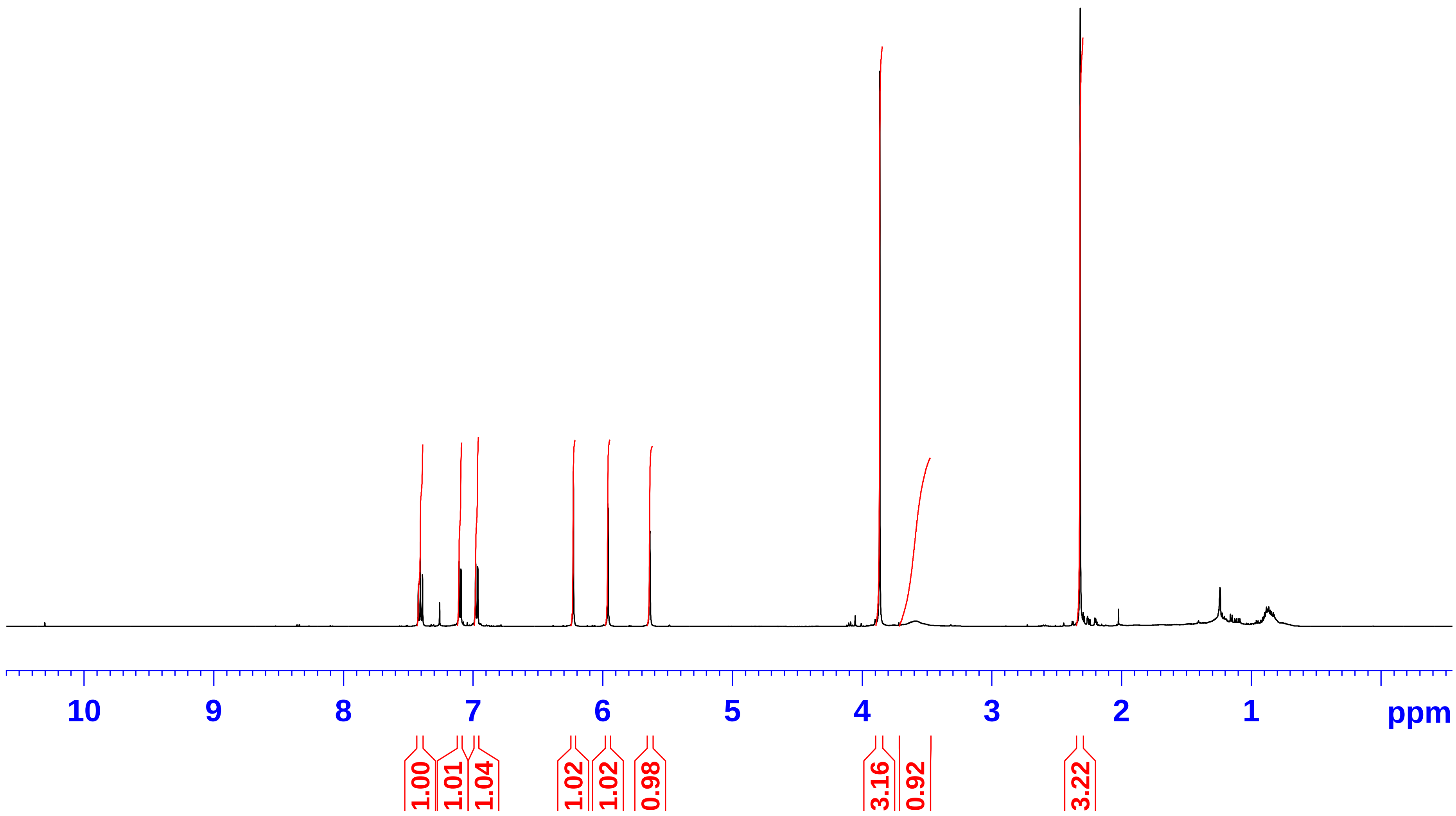
3-[Hydroxy-(1-nitro-naphthalen-2-yl)-methyl]-but-3-en-2-one (**8b**)



^{1}H NMR Spectrum of **8c**



3-[Hydroxy-(3-methoxy-2-nitro-phenyl)-methyl]-but-3-en-2-one (**8c**)



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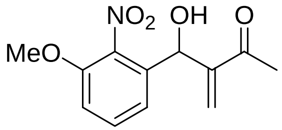
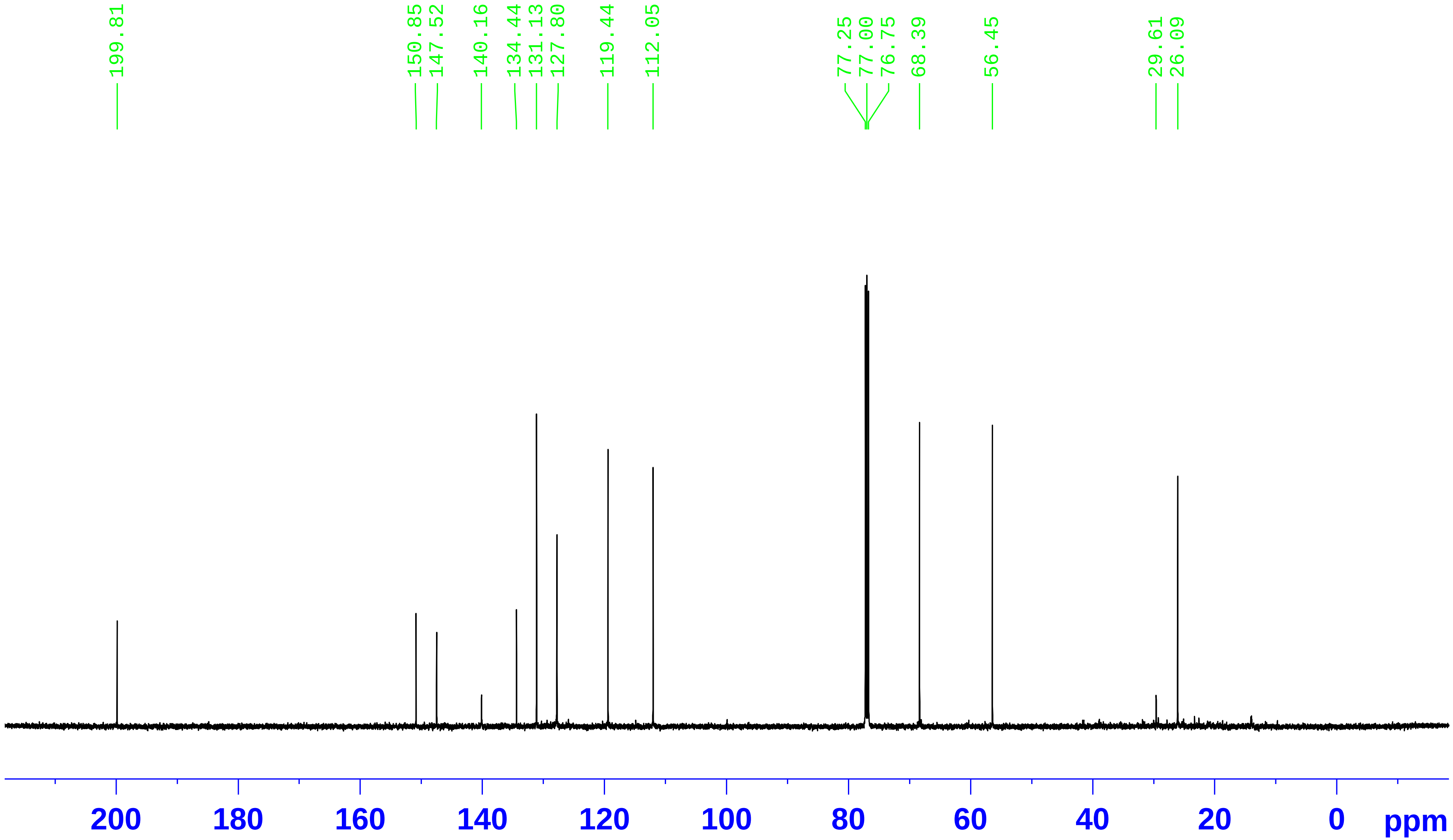
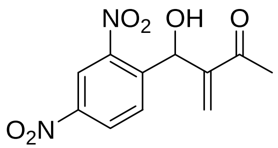
^{13}C NMR Spectrum of **8c**



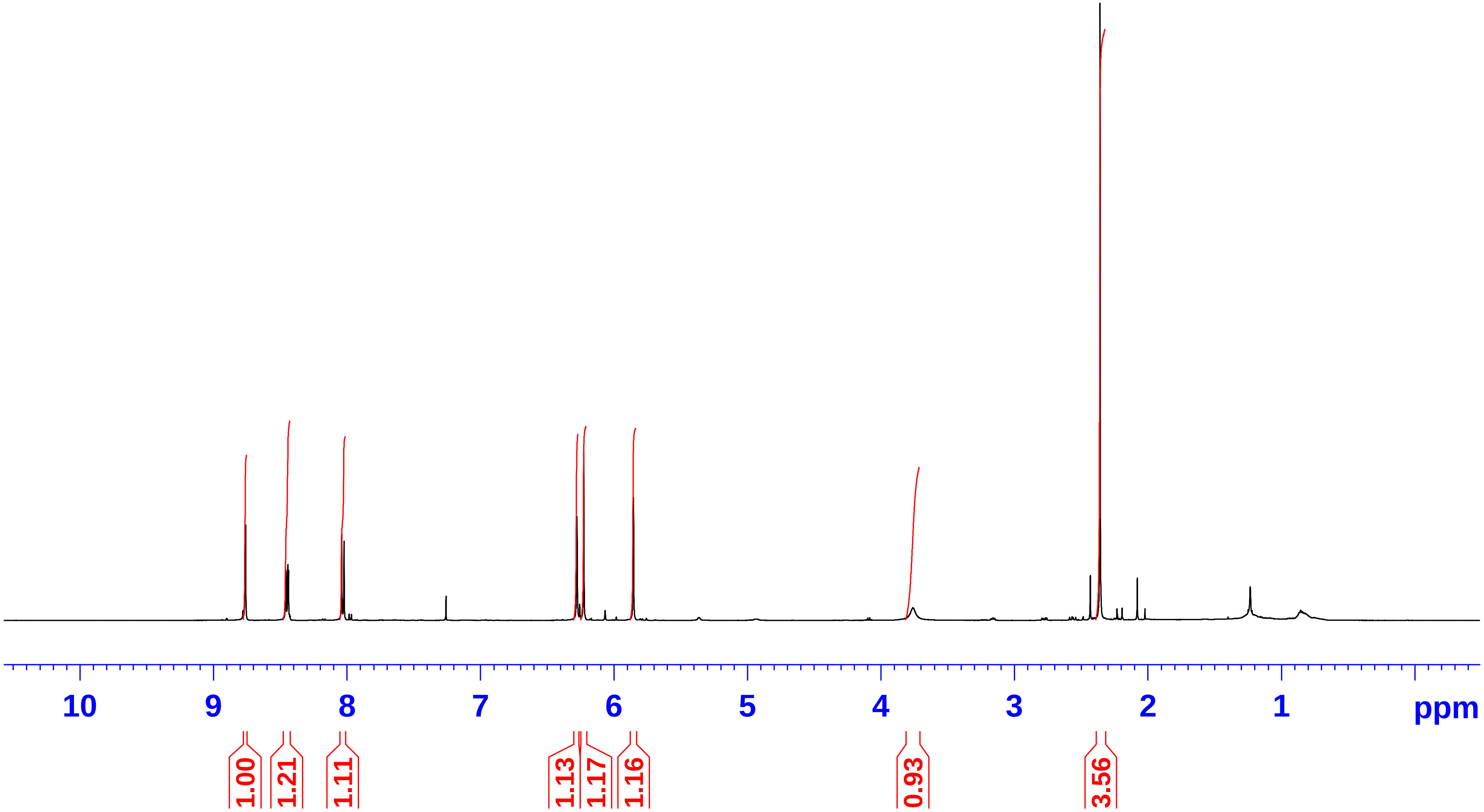
3-[Hydroxy-(3-methoxy-2-nitro-phenyl)-methyl]-but-3-en-2-one (**8c**)



^{1}H NMR Spectrum of **8d**



3-[(2,4-Dinitro-phenyl)-hydroxy-methyl]-but-3-en-2-one (**8d**)



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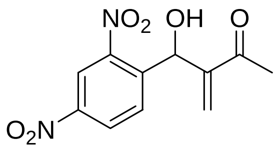
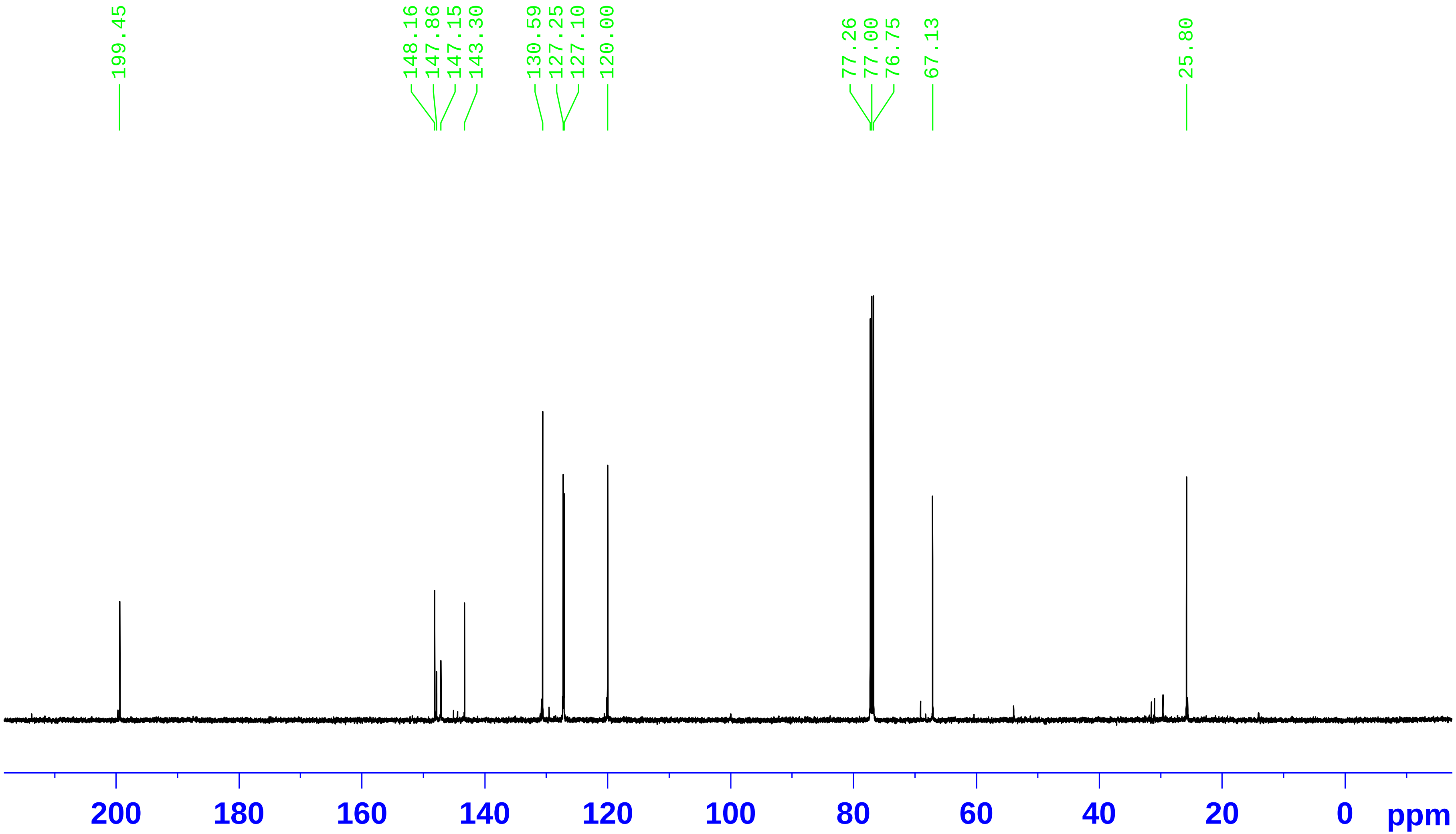
^{13}C NMR Spectrum of **8d**



3-[(2,4-Dinitro-phenyl)-hydroxy-methyl]-but-3-en-2-one (**8d**)



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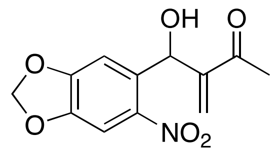
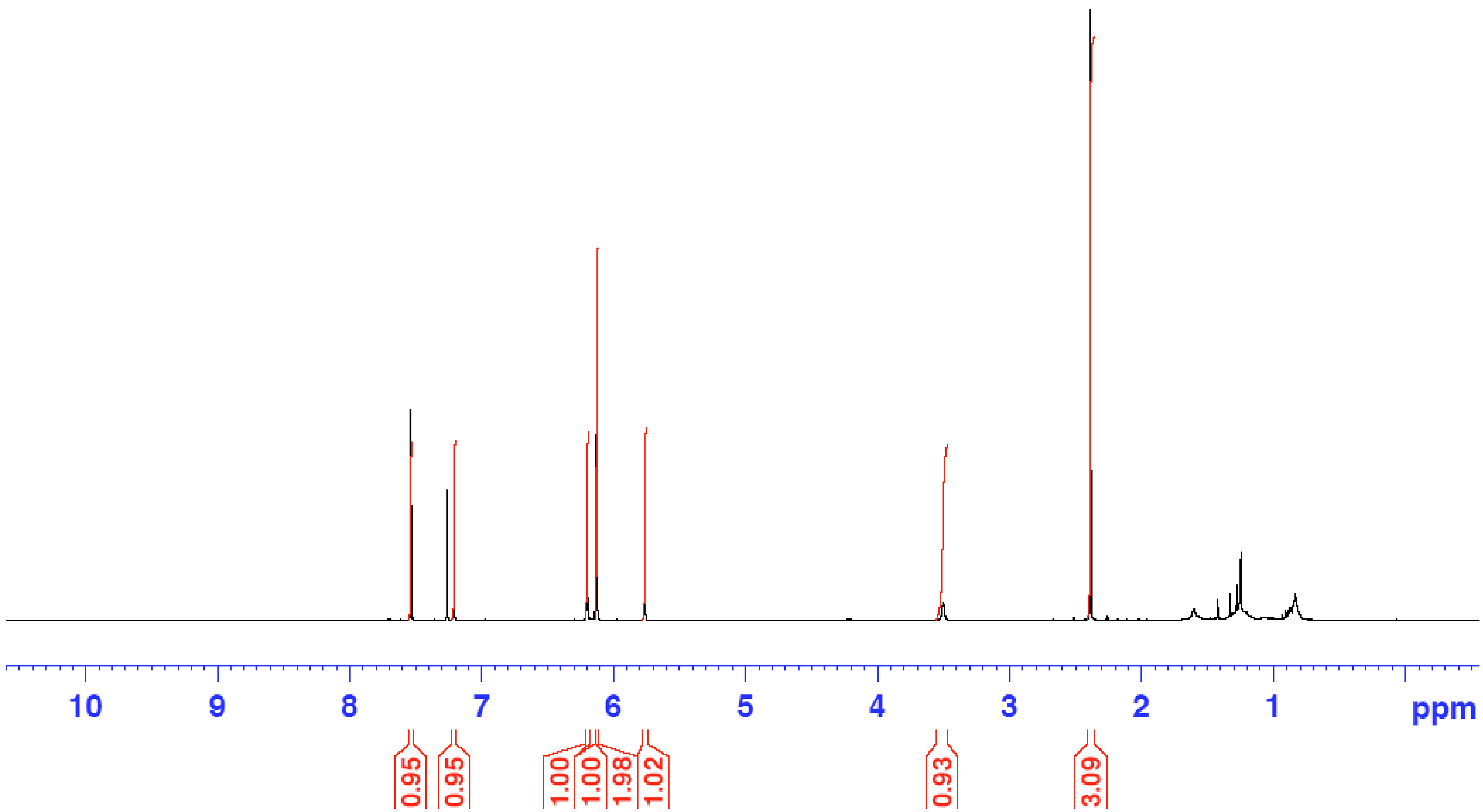
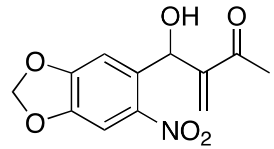
^{1}H NMR Spectrum of **8e**



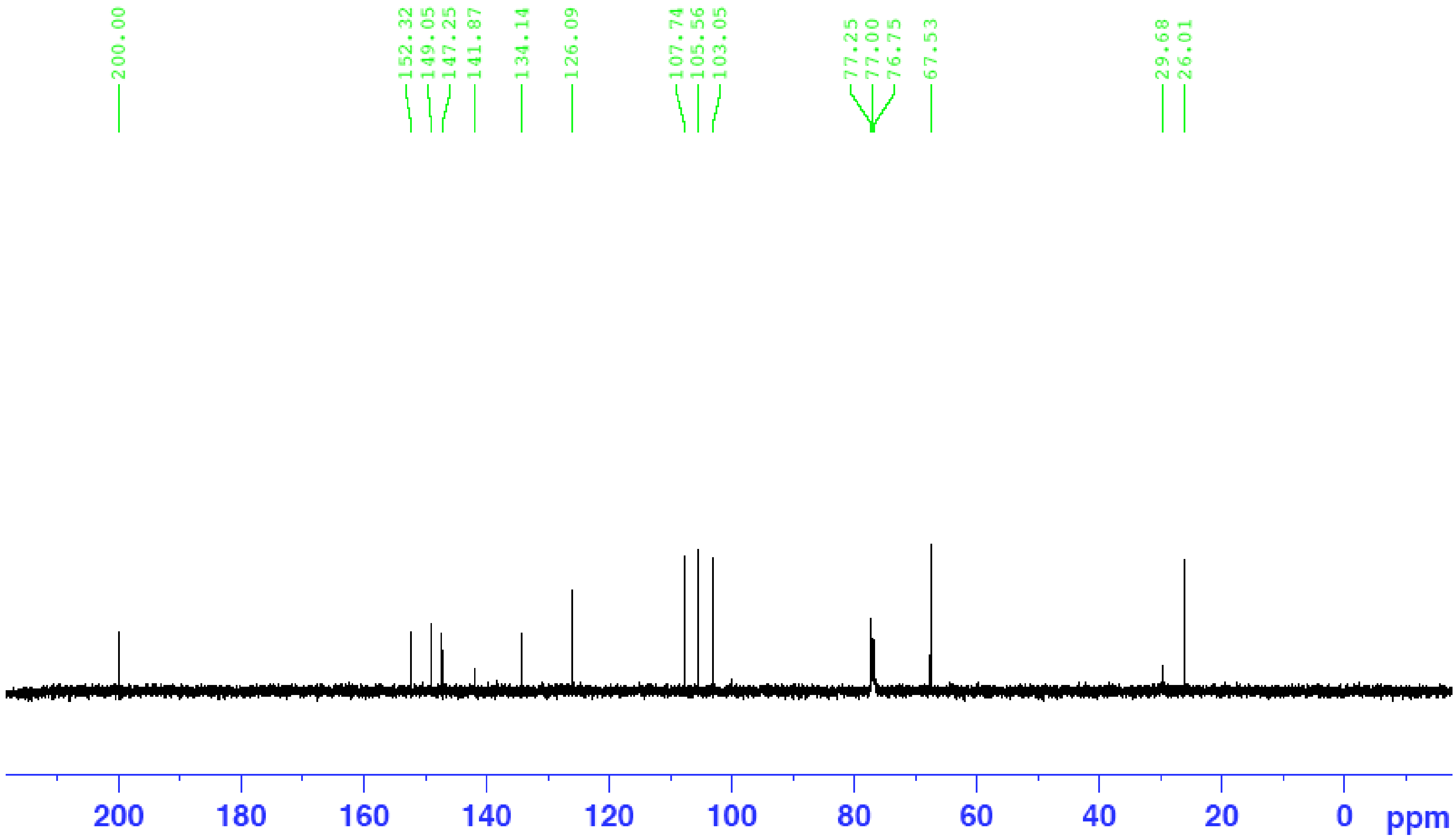
3-(Hydroxy(6-nitrobenzo[*d*][1,3]dioxol-5-yl)methyl)but-3-en-2-one (**8e**)



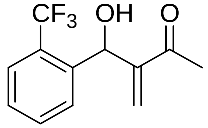
^{13}H NMR Spectrum of **8e**



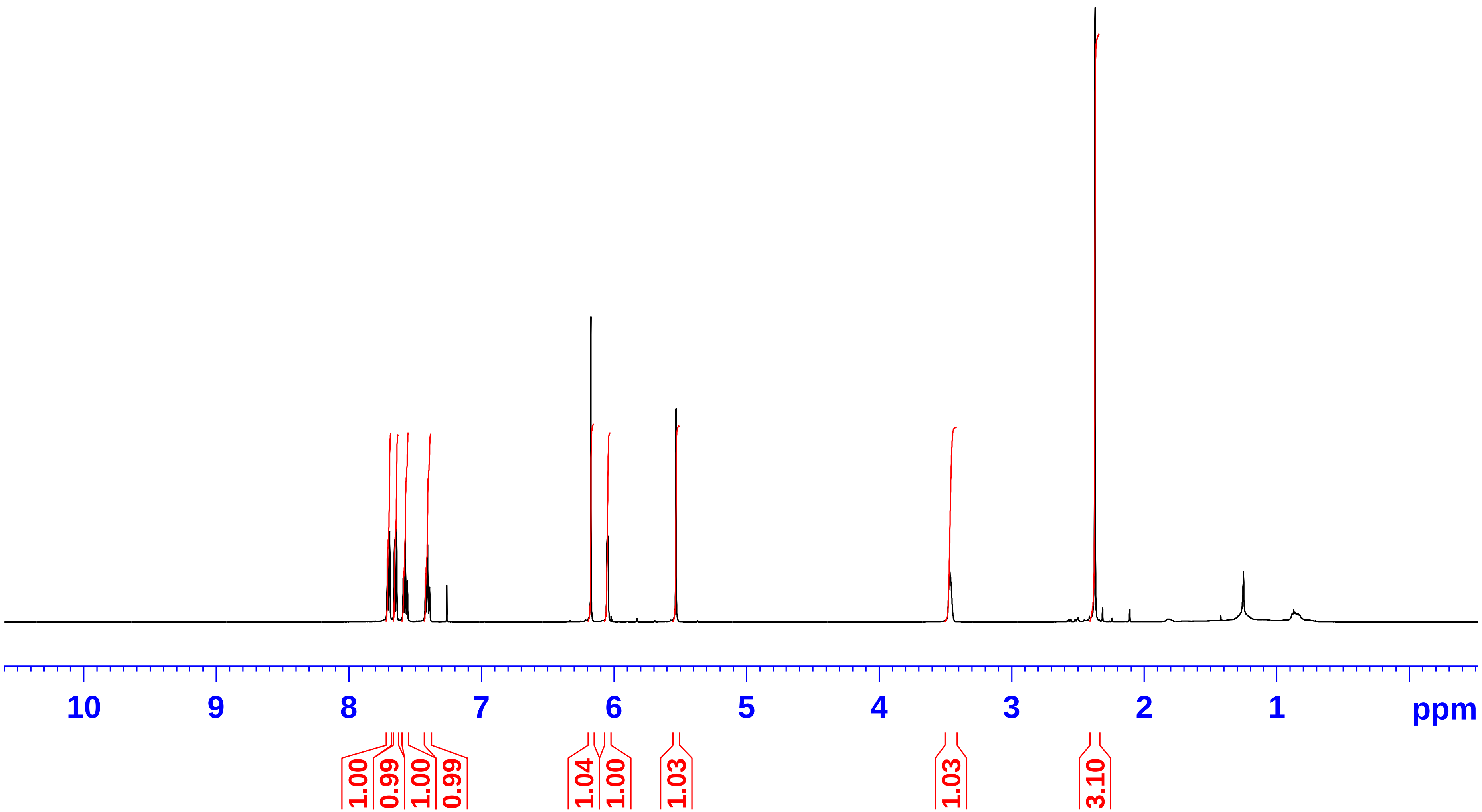
3-(Hydroxy(6-nitrobenzo[*d*][1,3]dioxol-5-yl)methyl)but-3-en-2-one (**8e**)



^{1}H NMR Spectrum of **8f**

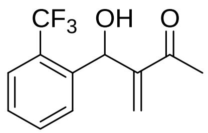


3-[Hydroxy-(2-trifluoromethyl-phenyl)-methyl]-but-3-en-2-one (**8f**)

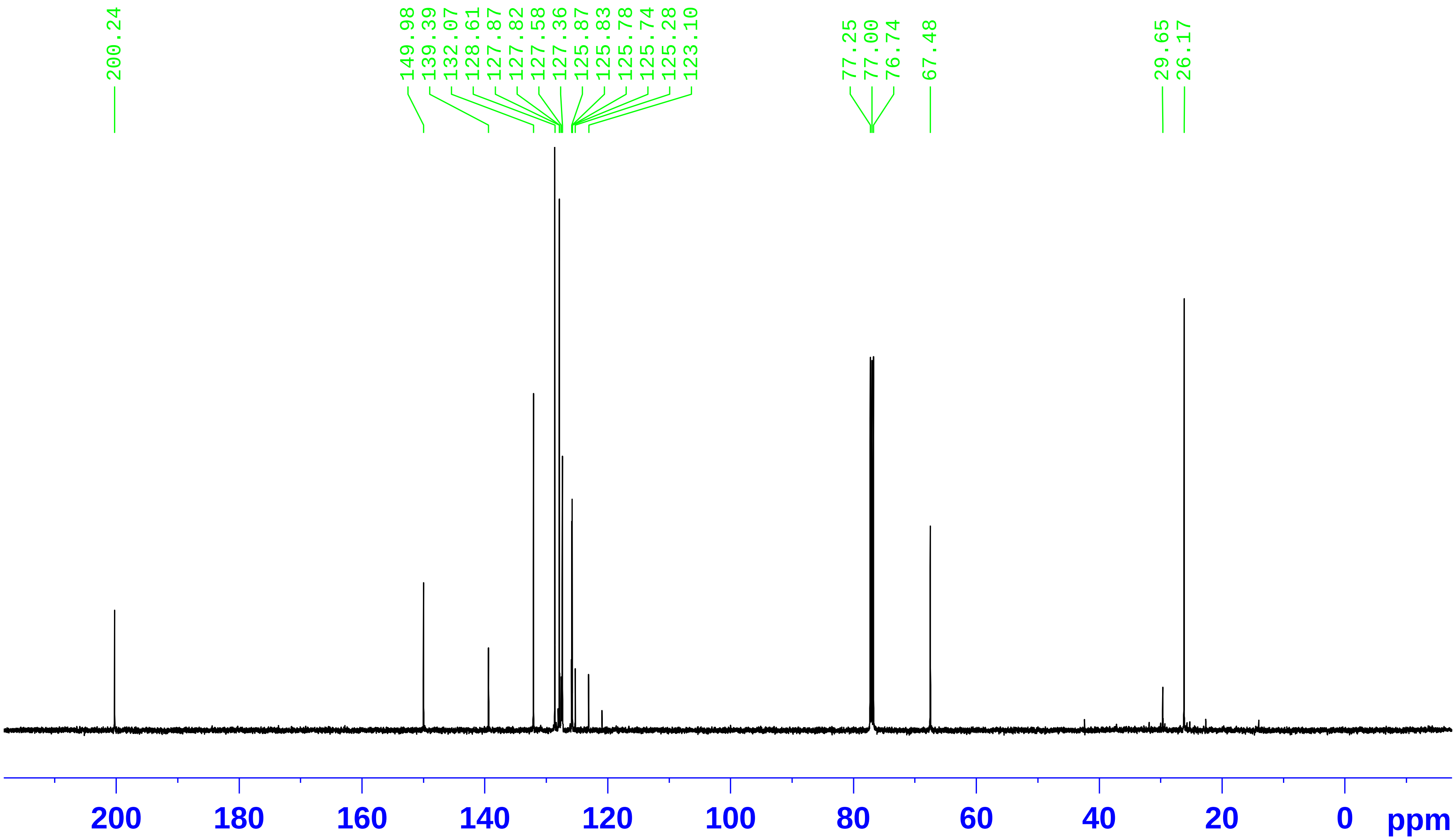


Supplementary Material (ESI) for Organic & Biomolecular Chemistry

^{13}C NMR Spectrum of **8f**

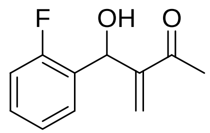


3-[Hydroxy-(2-trifluoromethyl-phenyl)-methyl]-but-3-en-2-one (**8f**)

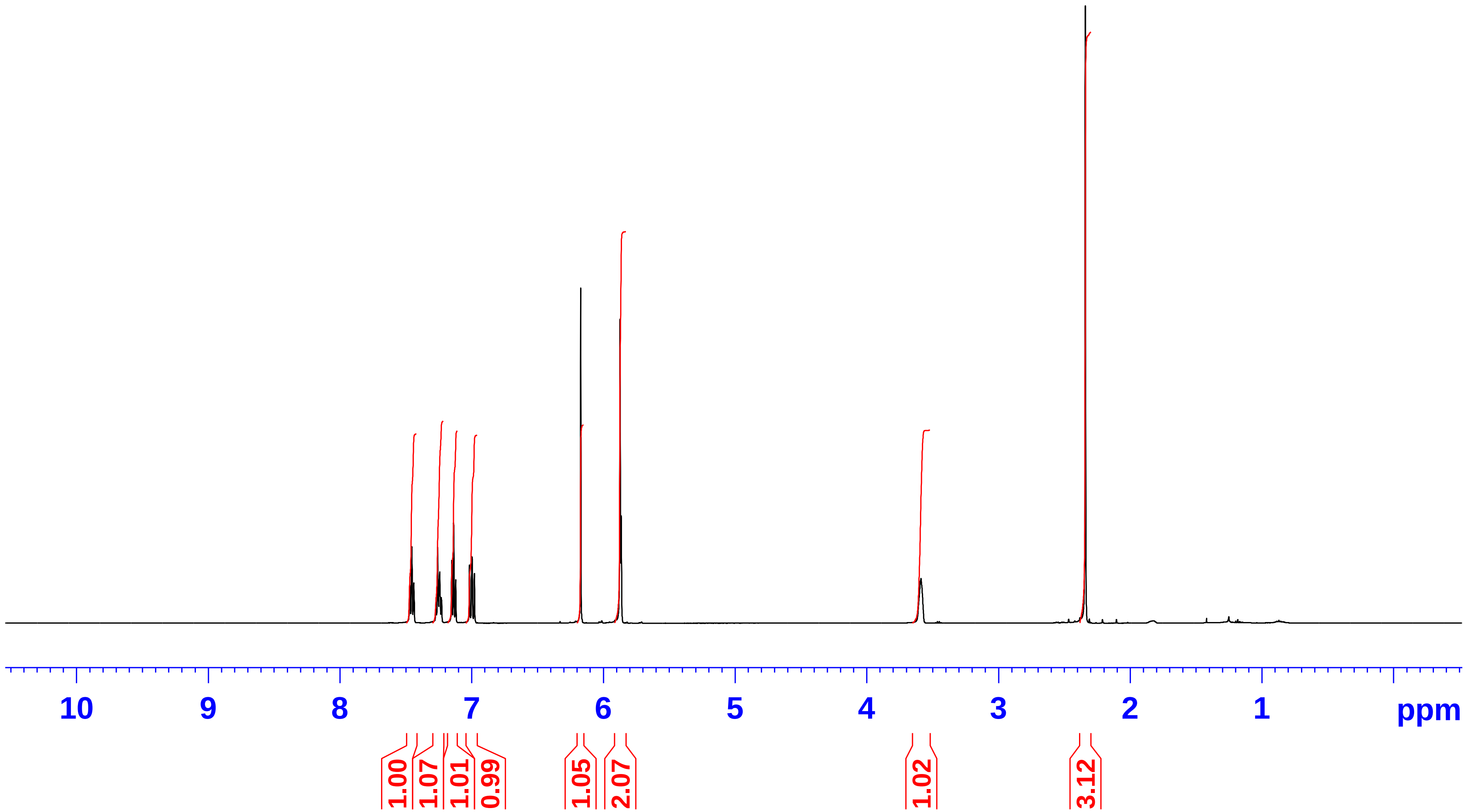


Supplementary Material (ESI) for Organic & Biomolecular Chemistry

^{1}H NMR Spectrum of **8g**

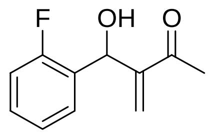


3-[(2-Fluoro-phenyl)-hydroxy-methyl]-but-3-en-2-one (**8g**)

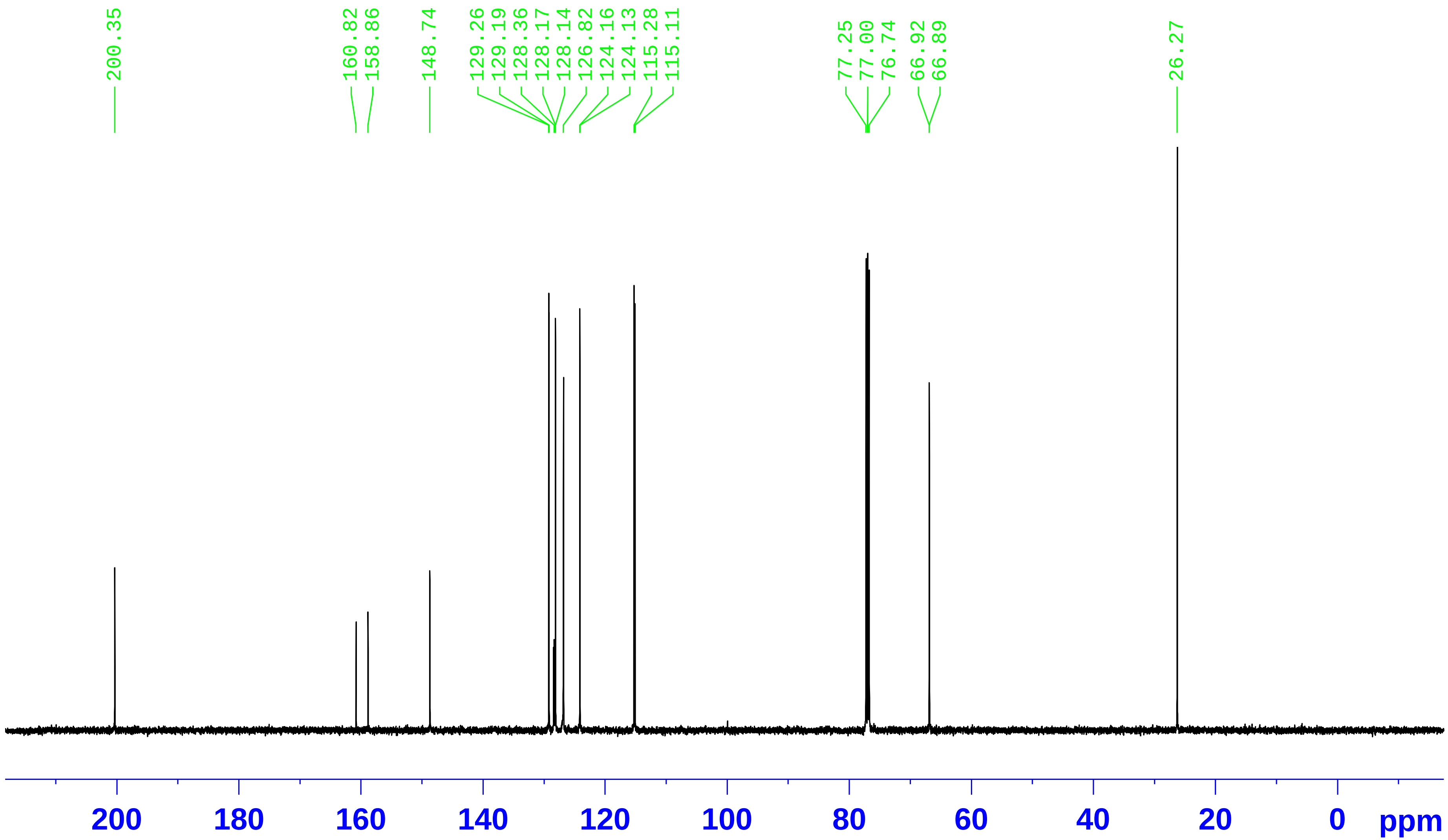


Supplementary Material (ESI) for Organic & Biomolecular Chemistry

^{13}C NMR Spectrum of **8g**

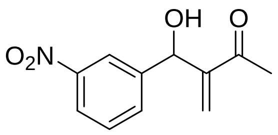


3-[(2-Fluoro-phenyl)-hydroxy-methyl]-but-3-en-2-one (**8g**)

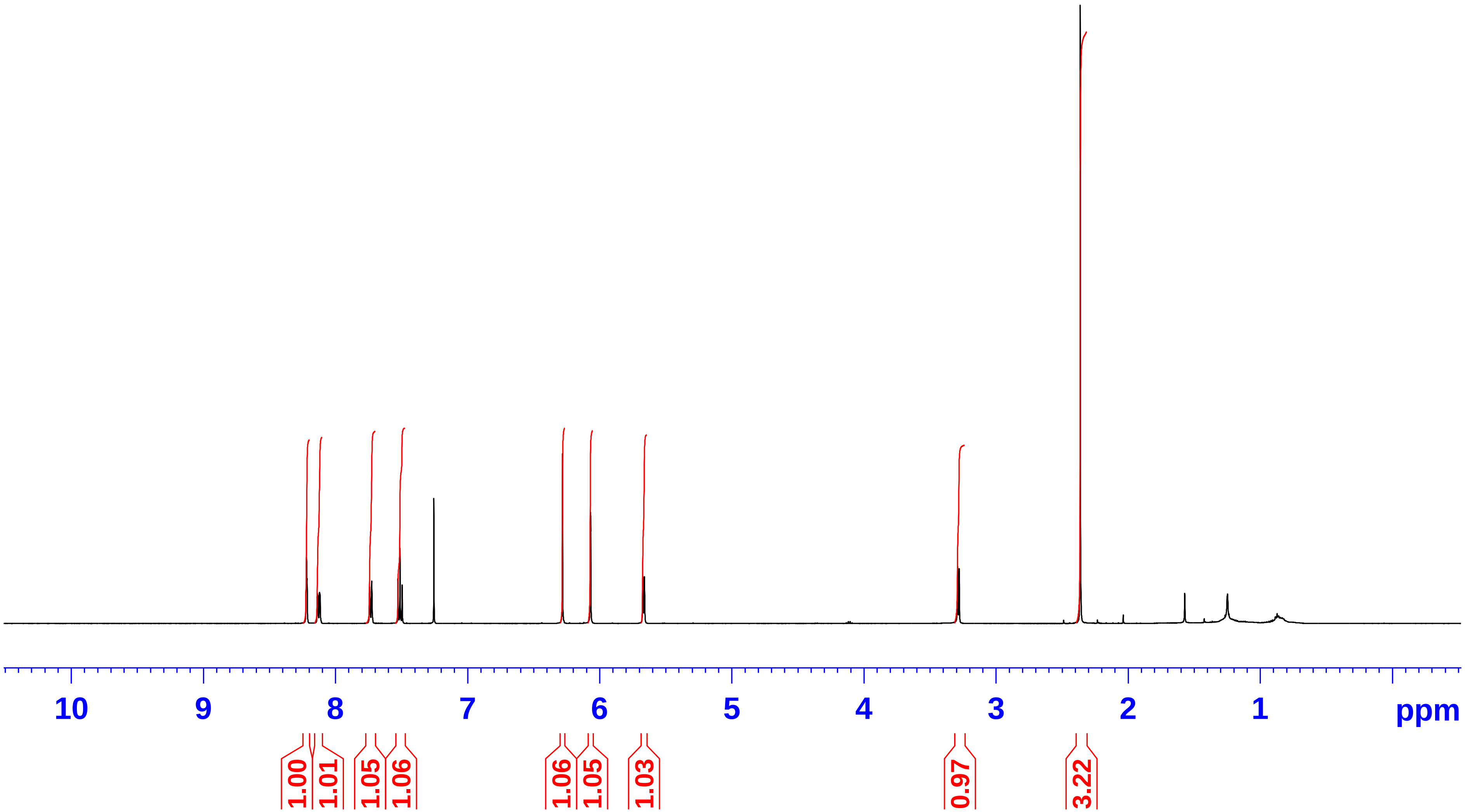


Supplementary Material (ESI) for Organic & Biomolecular Chemistry

^{1}H NMR Spectrum of **8h**

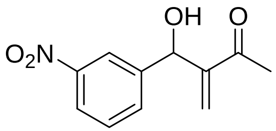


3-[Hydroxy-(3-nitro-phenyl)-methyl]-but-3-en-2-one (**8h**)

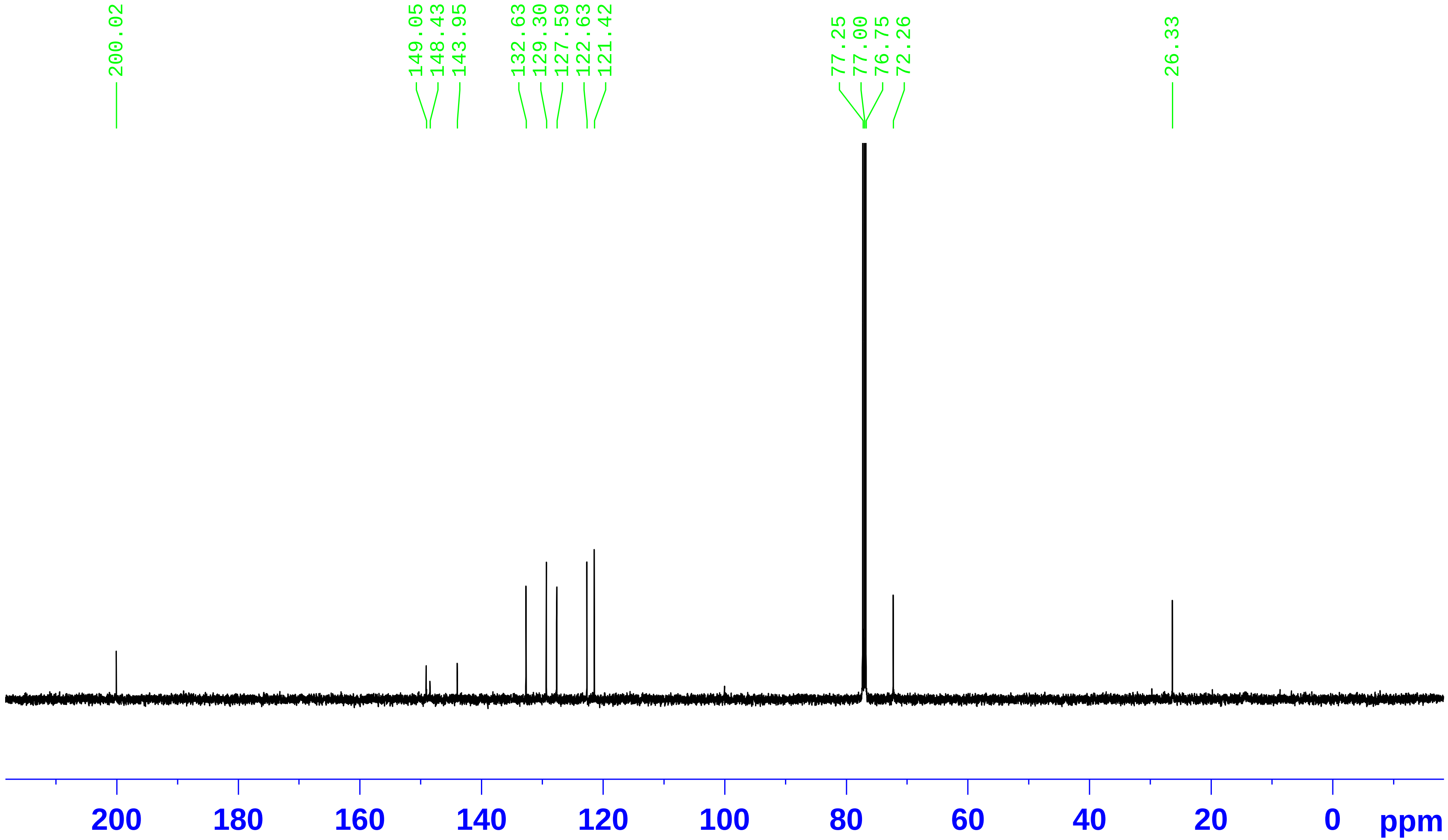


Supplementary Material (ESI) for Organic & Biomolecular Chemistry

^{13}C NMR Spectrum of **8h**

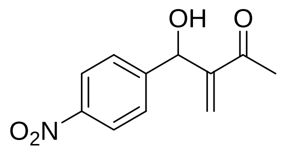


3-[Hydroxy-(3-nitro-phenyl)-methyl]-but-3-en-2-one (**8h**)

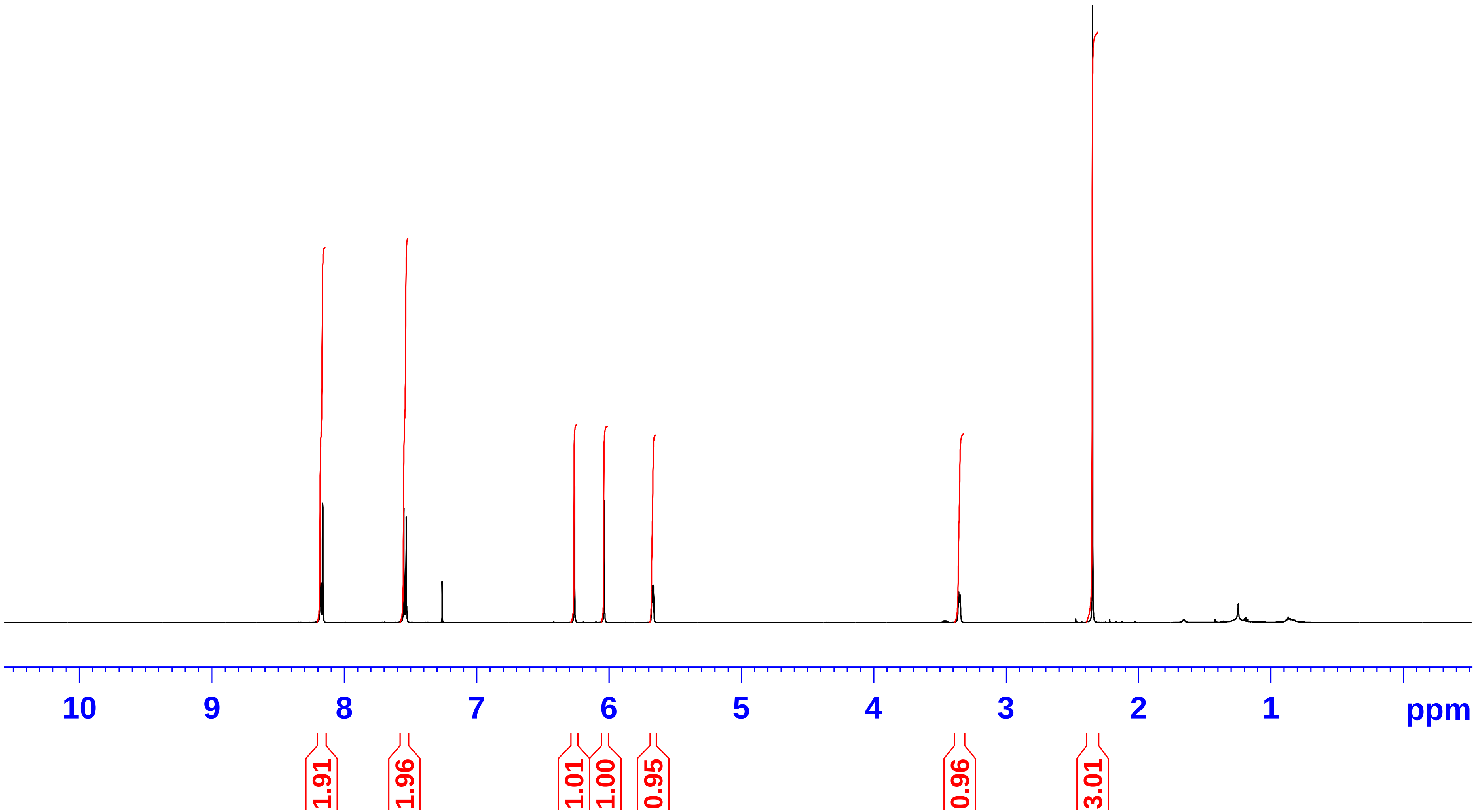


Supplementary Material (ESI) for Organic & Biomolecular Chemistry

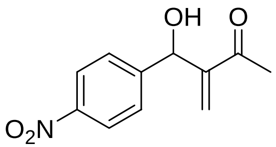
^{1}H NMR Spectrum of **8i**



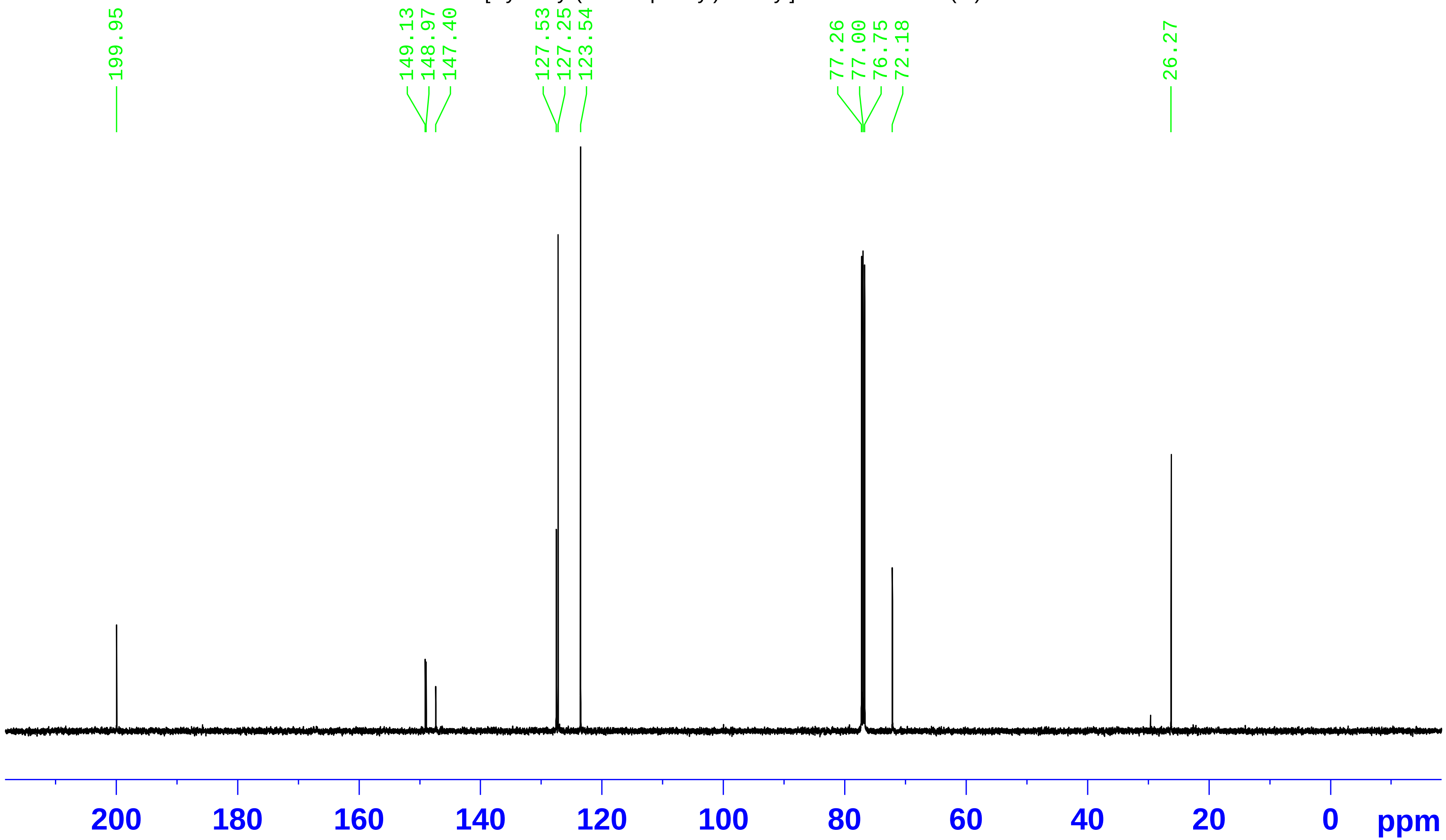
3-[Hydroxy-(4-nitro-phenyl)-methyl]-but-3-en-2-one (**8i**)



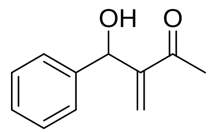
^{13}C NMR Spectrum of **8i**



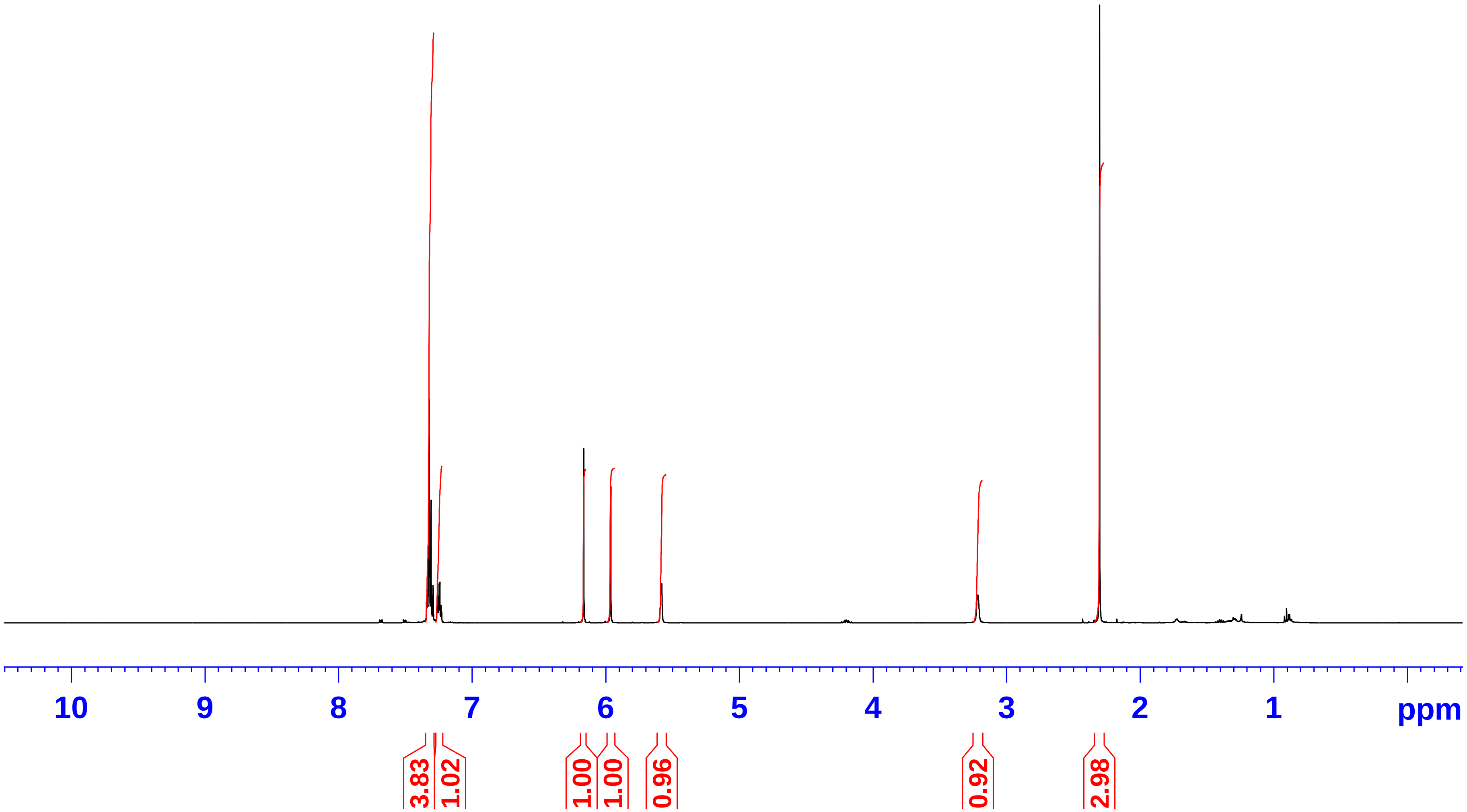
3-[Hydroxy-(4-nitro-phenyl)-methyl]-but-3-en-2-one (**8i**)



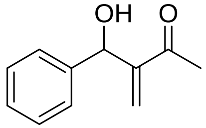
^{1}H NMR Spectrum of **8j**



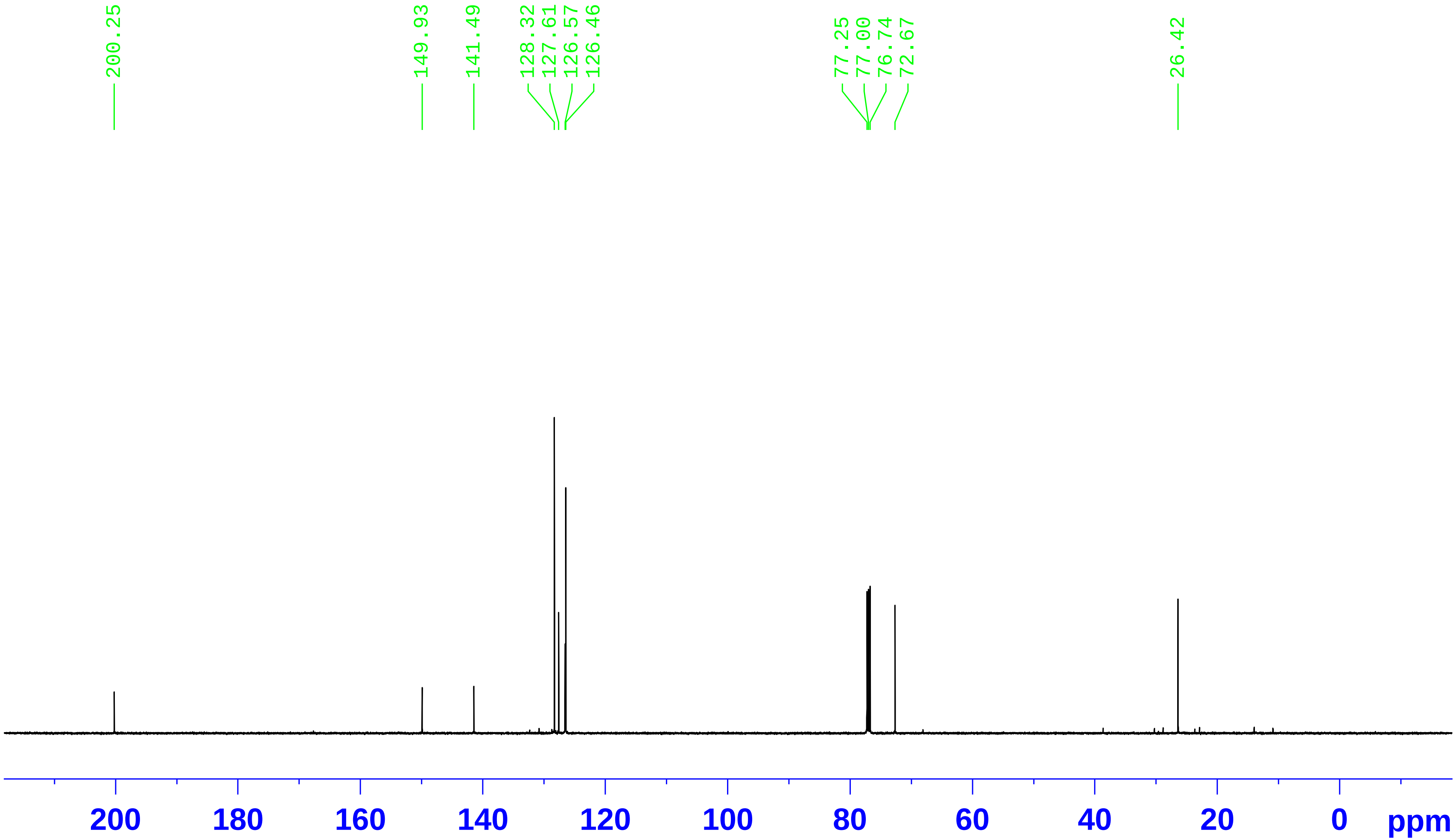
3-(Hydroxy-phenyl-methyl)-but-3-en-2-one (**8j**)



^{13}C NMR Spectrum of **8j**



3-(Hydroxy-phenyl-methyl)-but-3-en-2-one (**8j**)



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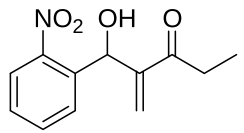
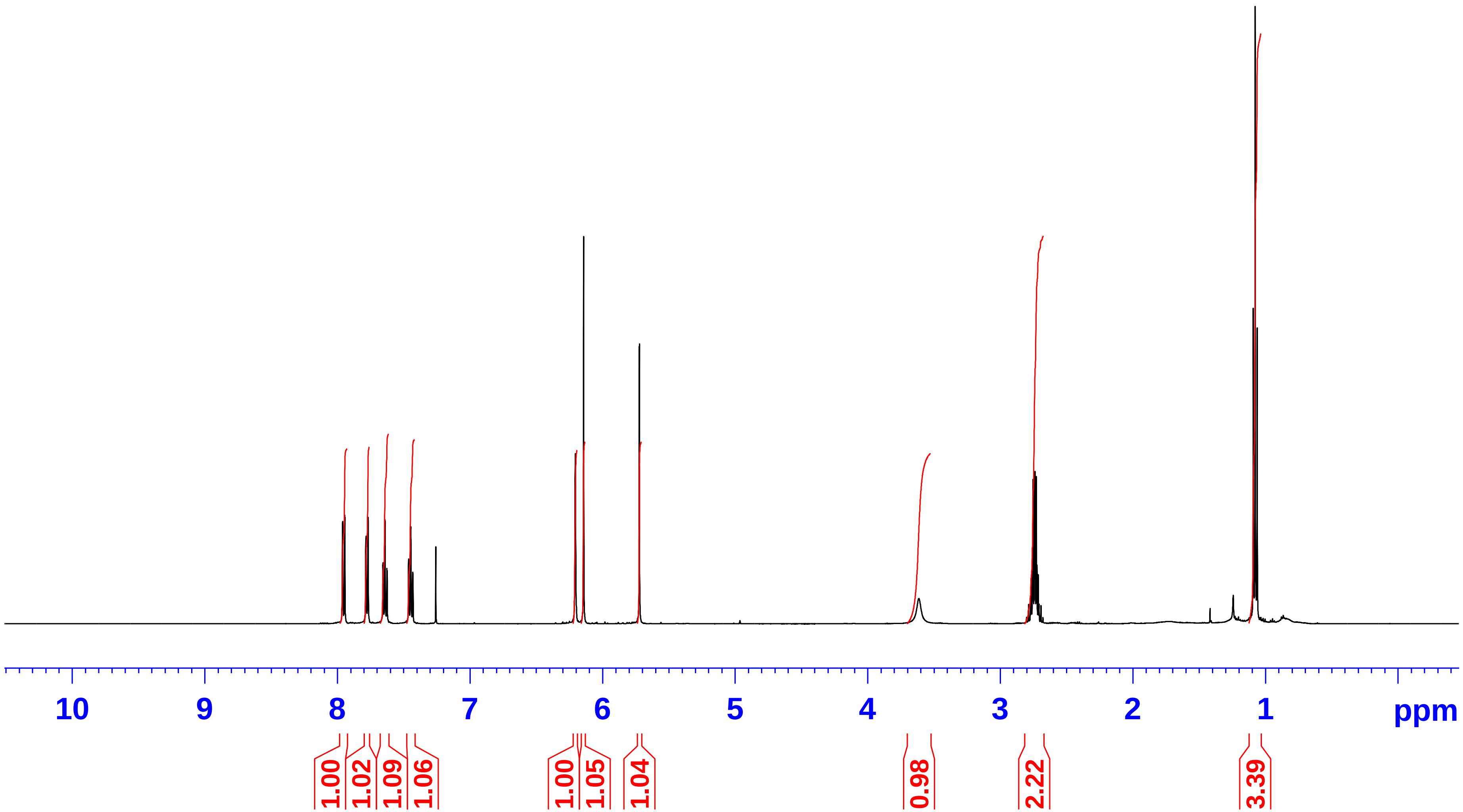
^{1}H NMR Spectrum of **8k**

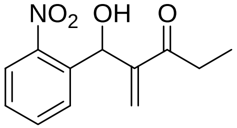


2-[Hydroxy-(2-nitro-phenyl)-methyl]-pent-1-en-3-one (**8k**)

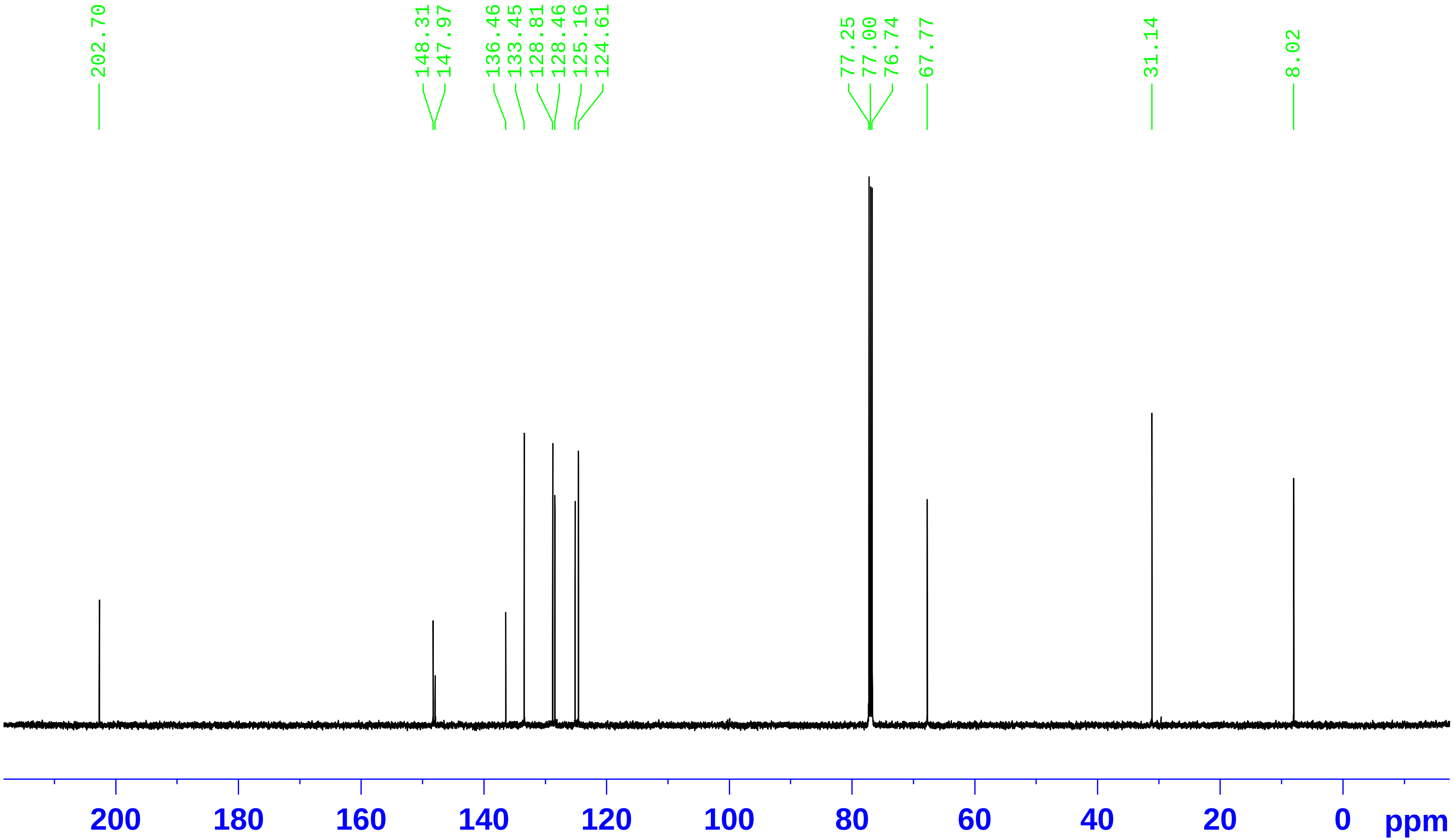


Supplementary Material (ESI) for Organic & Biomolecular Chemistry

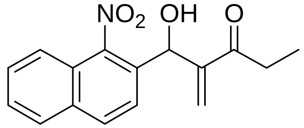
^{13}C NMR Spectrum of **8k**



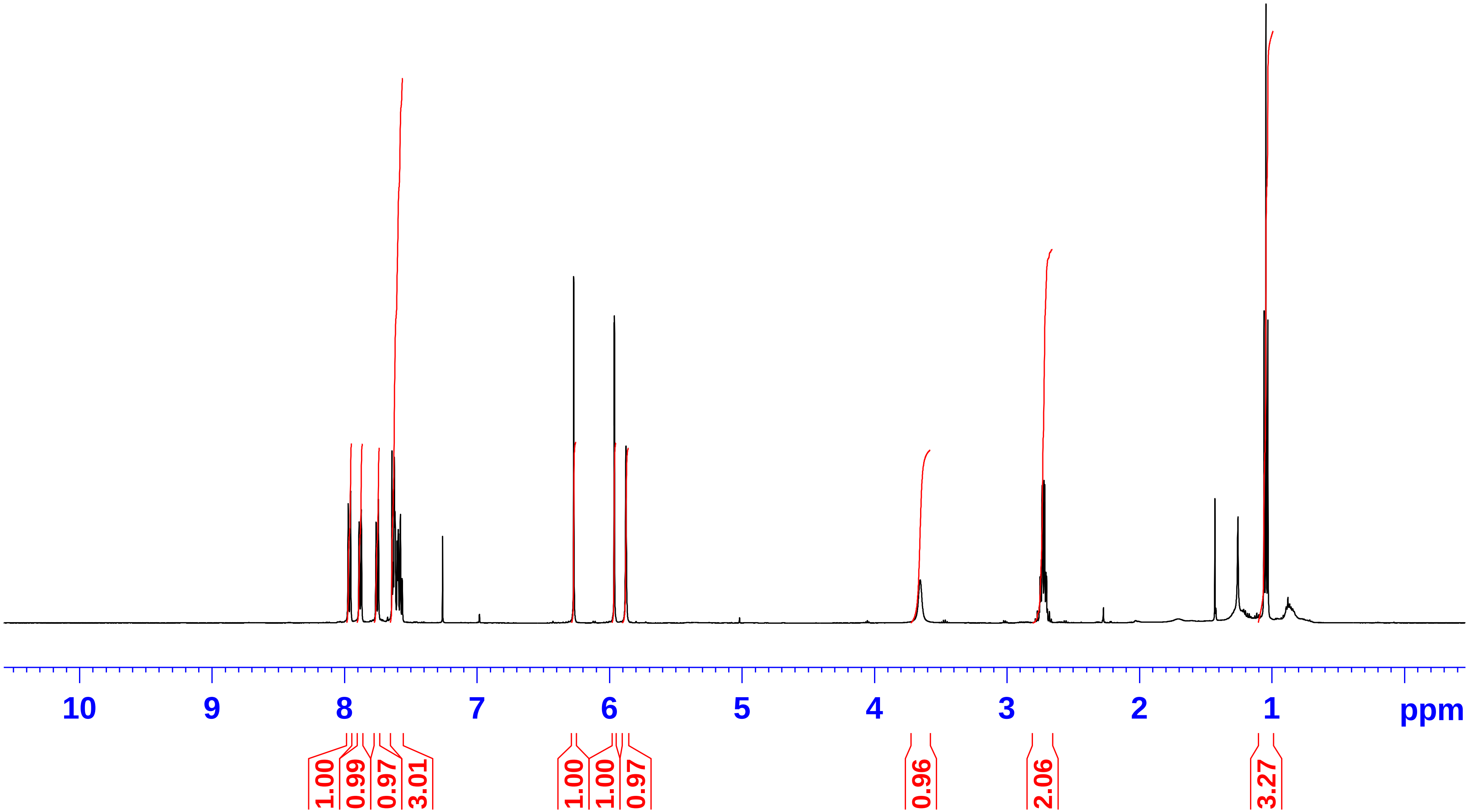
2-[Hydroxy-(2-nitro-phenyl)-methyl]-pent-1-en-3-one (**8k**)



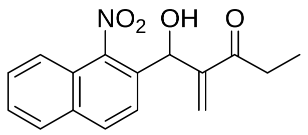
^{1}H NMR Spectrum of **8l**



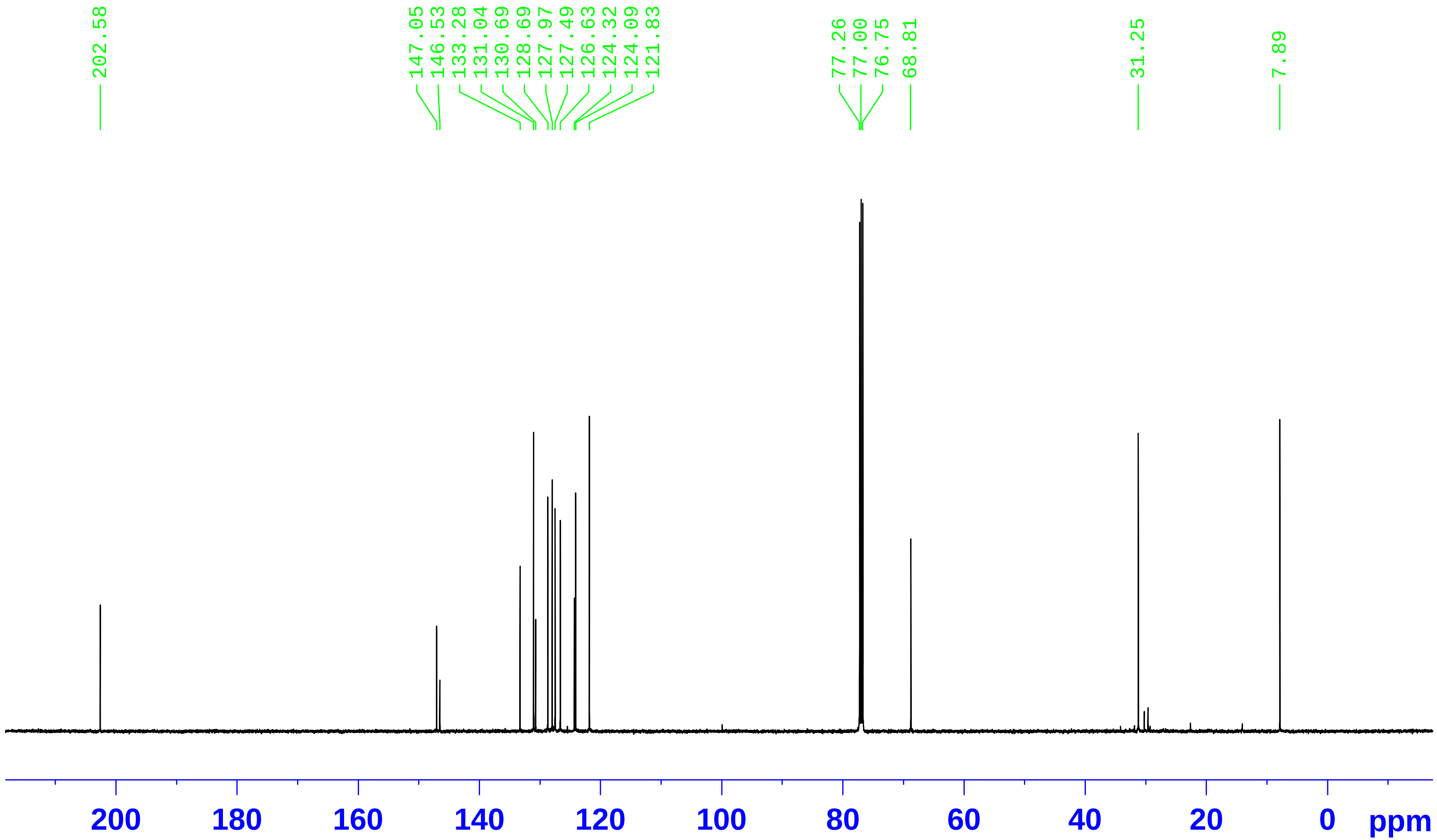
2-[Hydroxy-(1-nitro-naphthalen-2-yl)-methyl]-pent-1-en-3-one (**8l**)



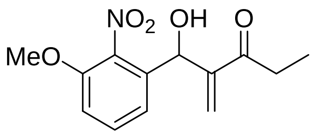
^{13}C NMR Spectrum of **8l**



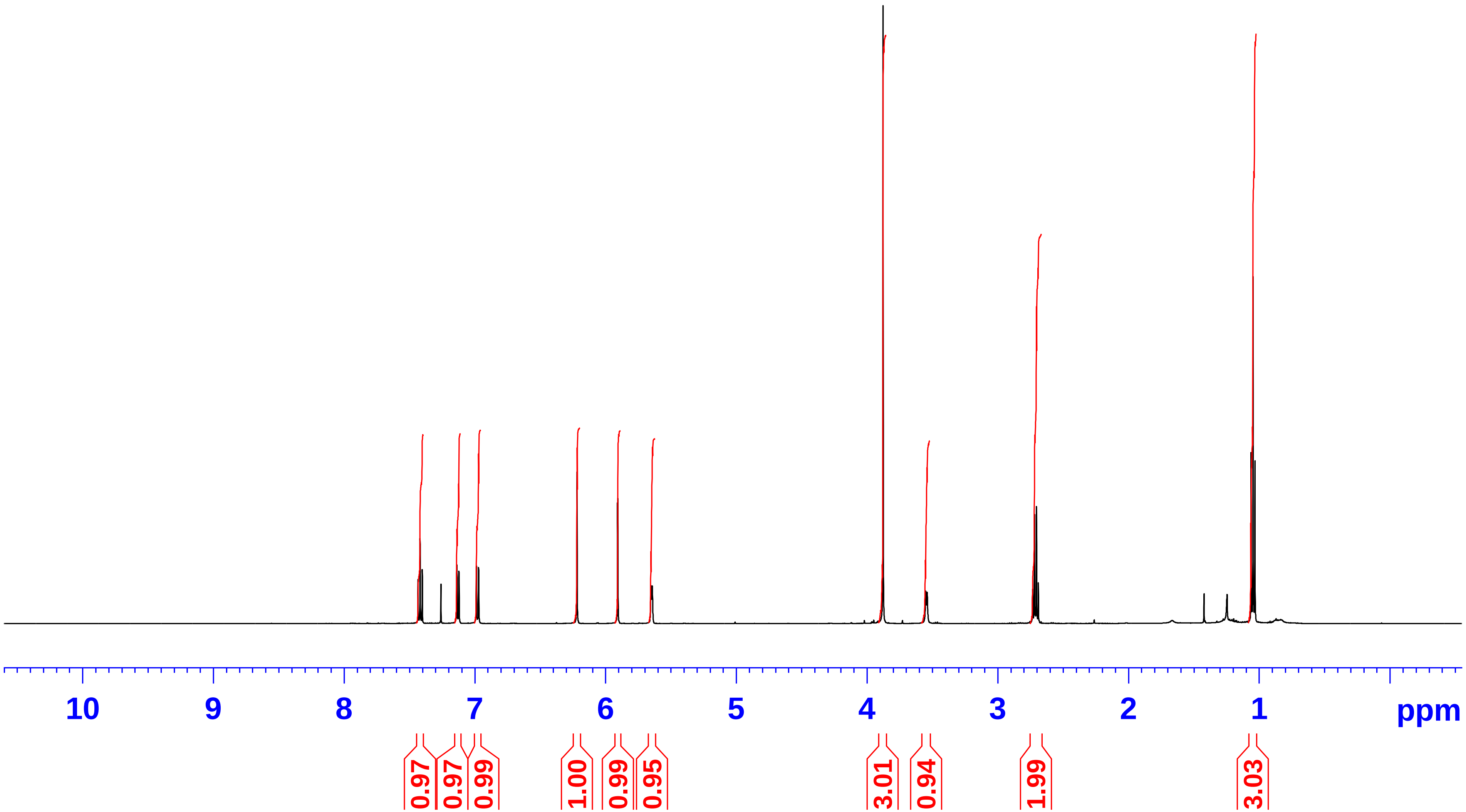
2-[Hydroxy-(1-nitro-naphthalen-2-yl)-methyl]-pent-1-en-3-one (**8l**)



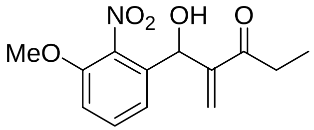
^{1}H NMR Spectrum of **8m**



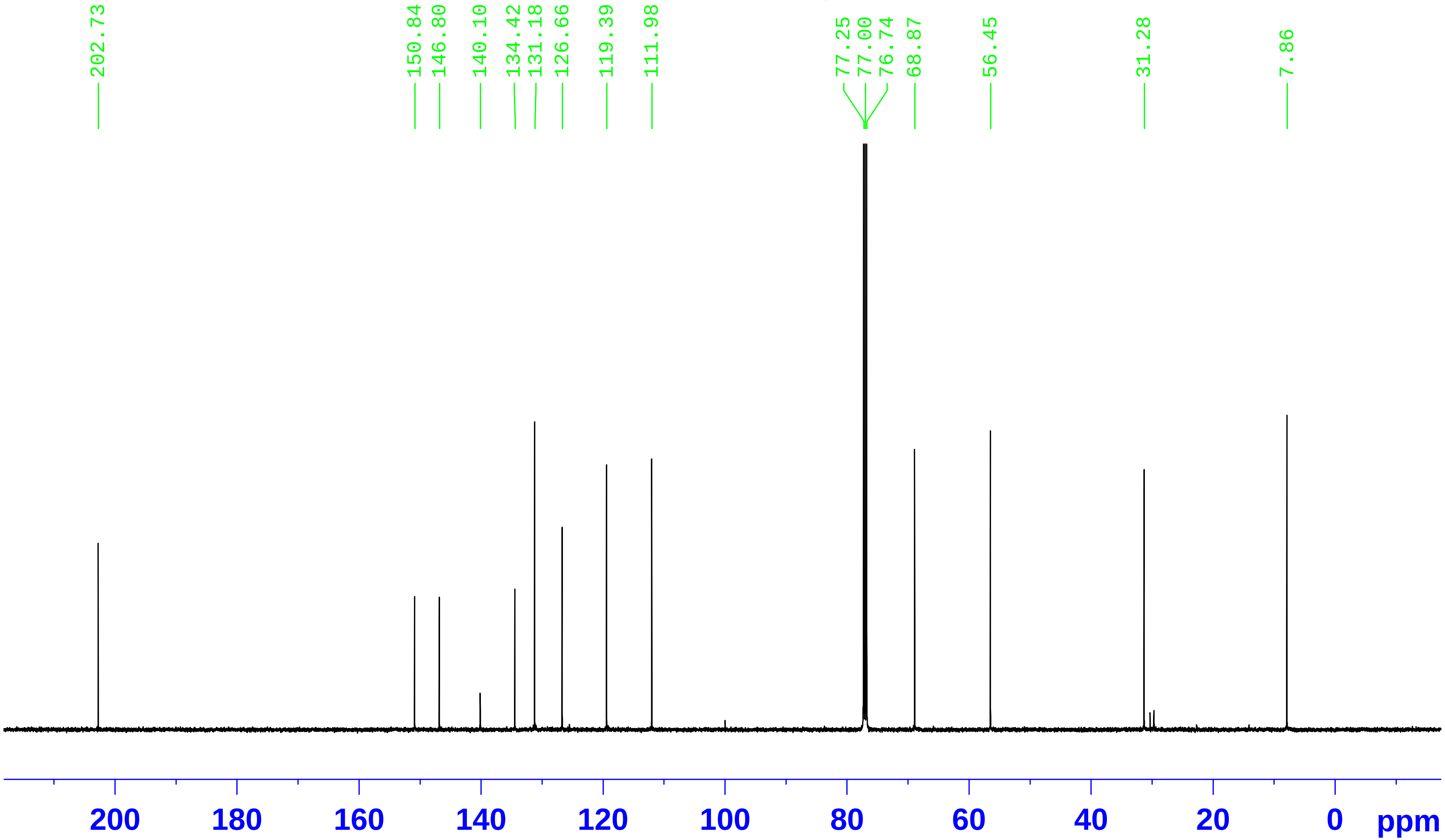
2-[Hydroxy-(3-methoxy-2-nitro-phenyl)-methyl]-pent-1-en-3-one (**8m**)



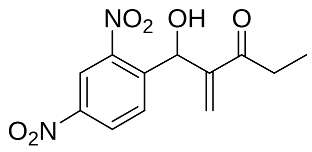
^{13}C NMR Spectrum of **8m**



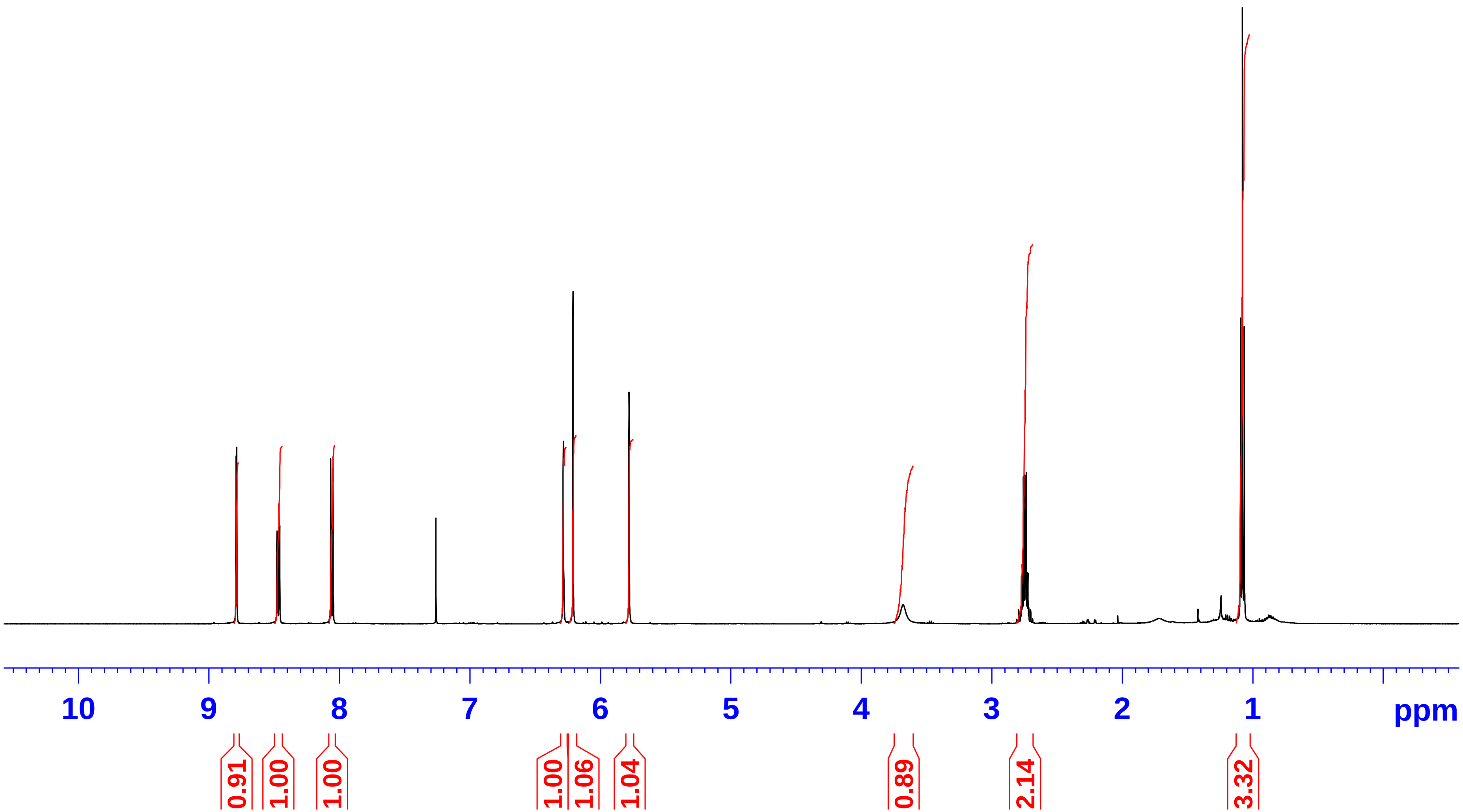
2-[Hydroxy-(3-methoxy-2-nitro-phenyl)-methyl]-pent-1-en-3-one (**8m**)



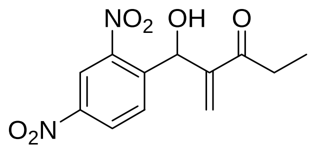
^{1}H NMR Spectrum of **8n**



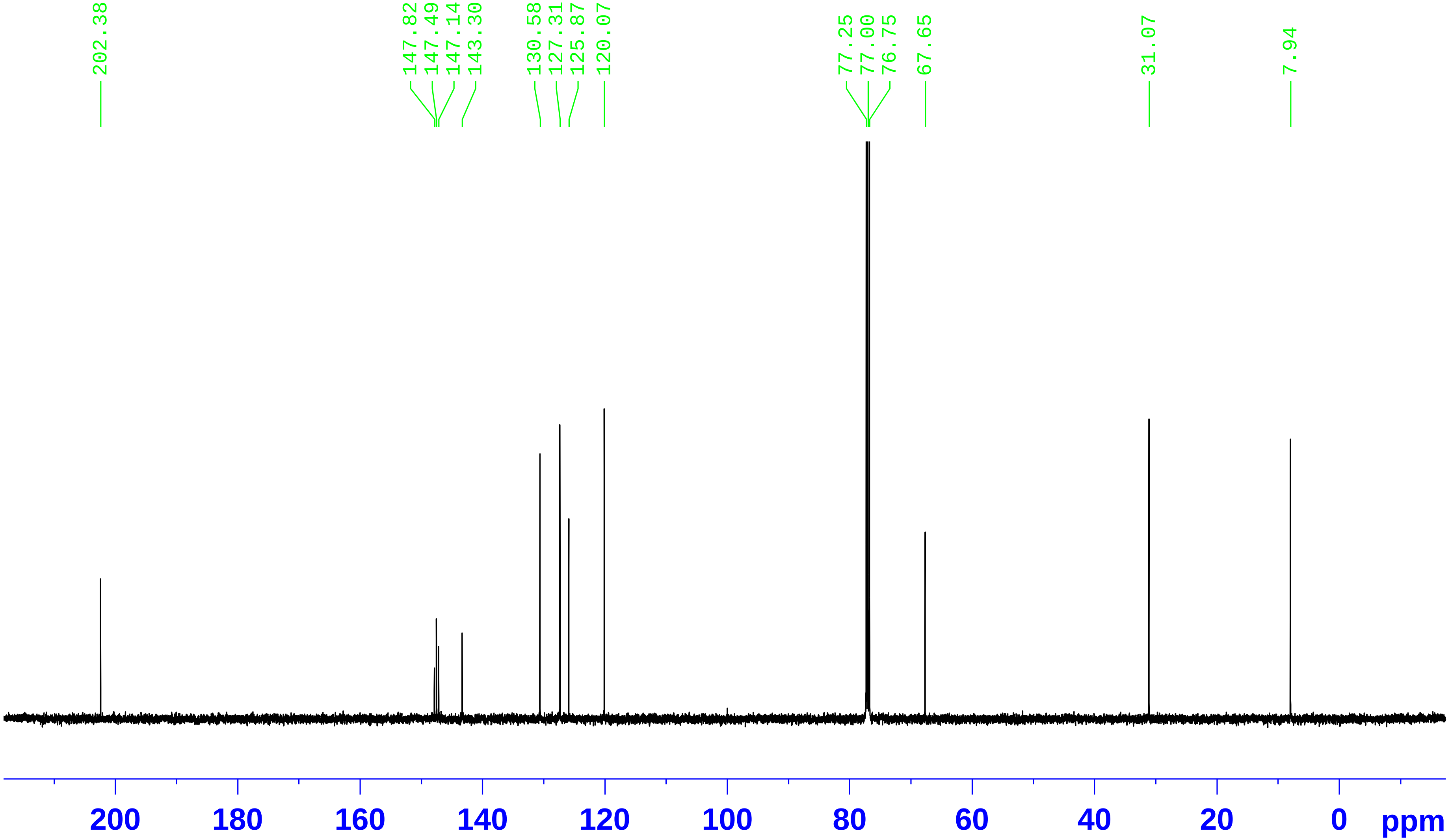
2-[(2,4-Dinitro-phenyl)-hydroxy-methyl]-pent-1-en-3-one (**8n**)



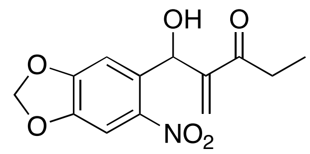
^{13}C NMR Spectrum of **8n**



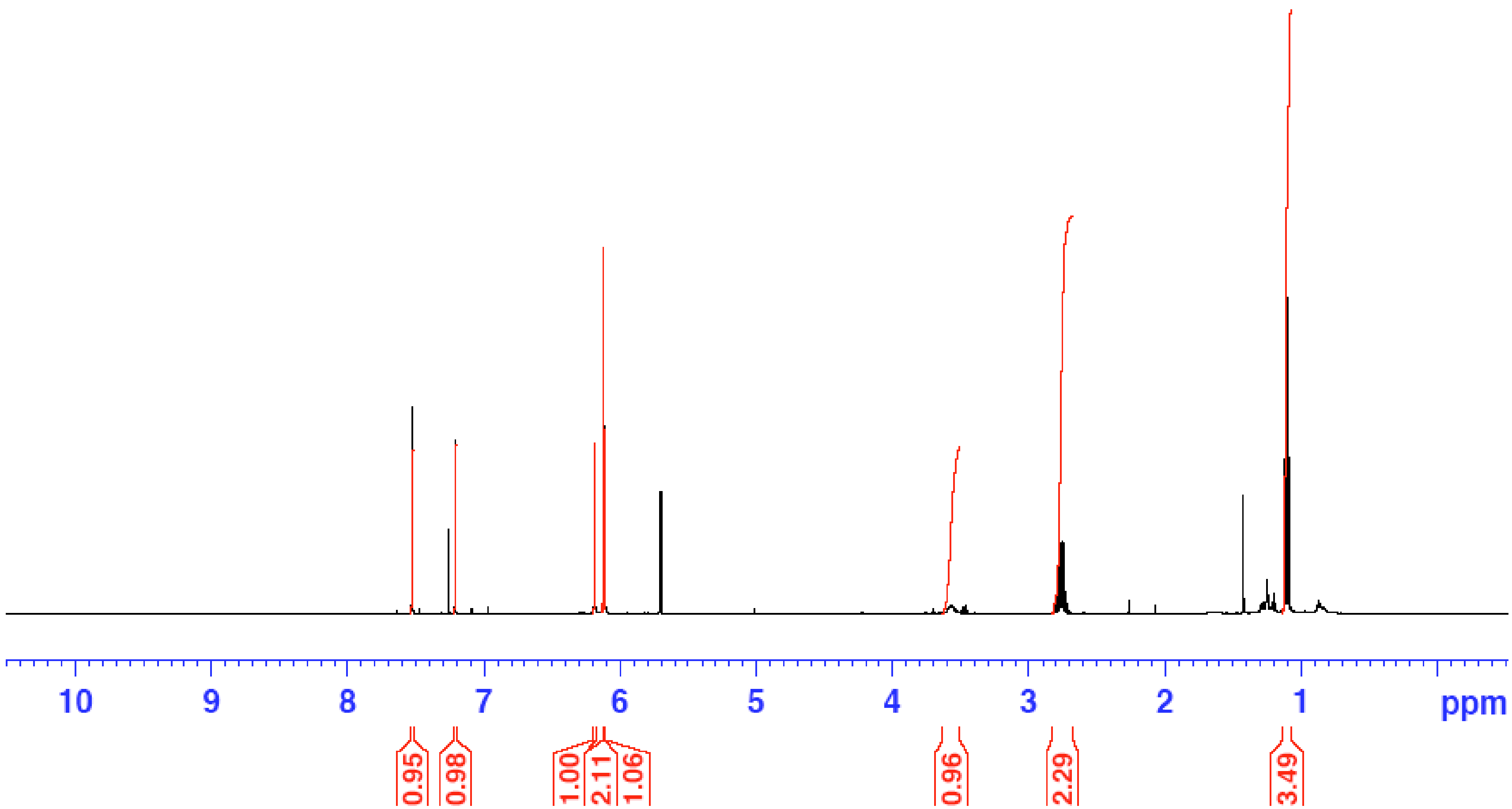
2-[(2,4-Dinitro-phenyl)-hydroxy-methyl]-pent-1-en-3-one (**8n**)



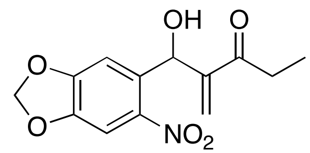
[1]H NMR Spectrum of **8o**



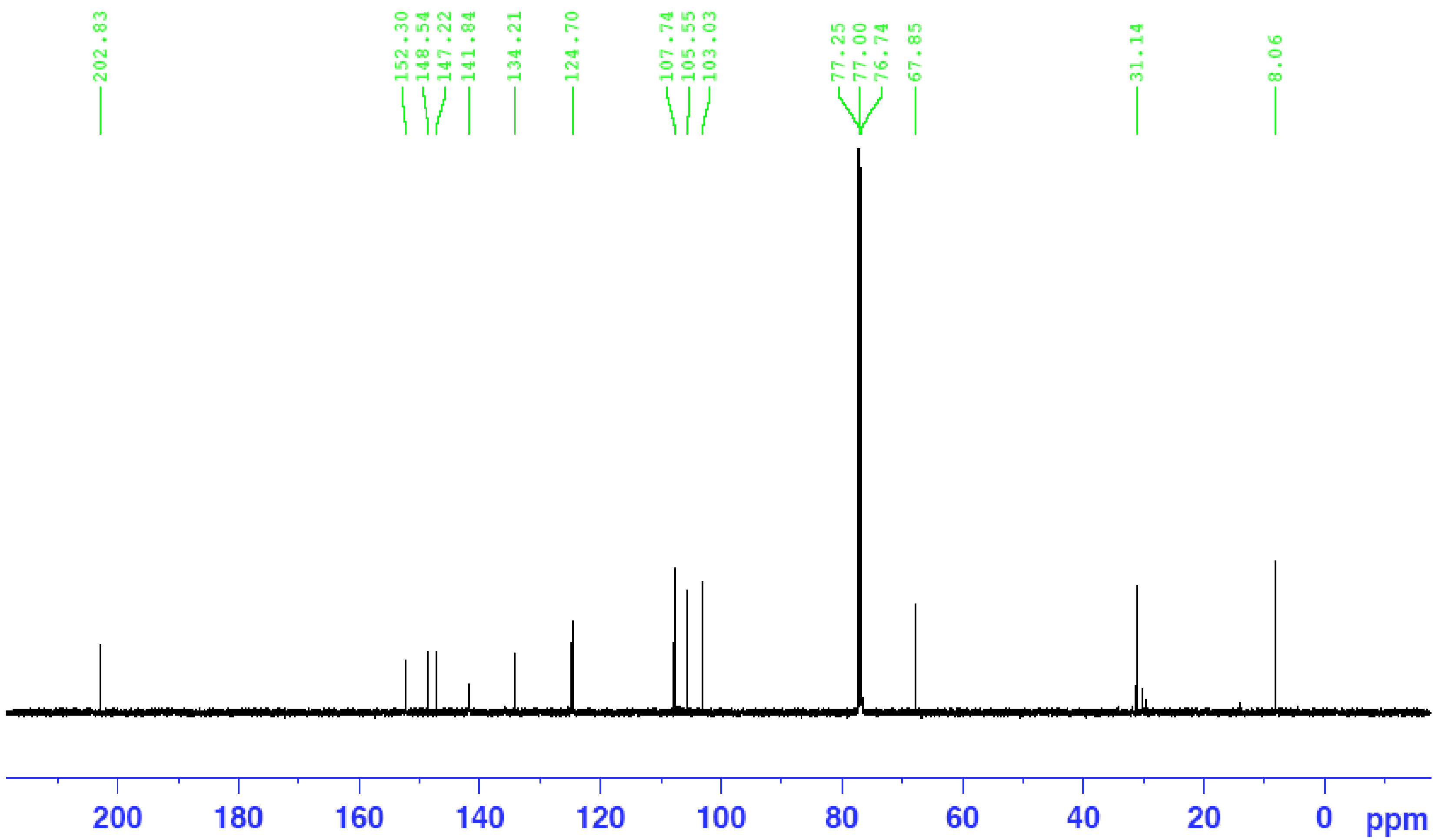
2-(Hydroxy(6-nitrobenzo[*d*][1,3]dioxol-5-yl)methyl)pent-1-en-3-one (**8o**)



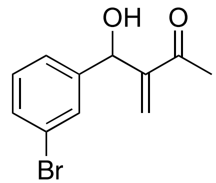
^{13}H NMR Spectrum of **8o**



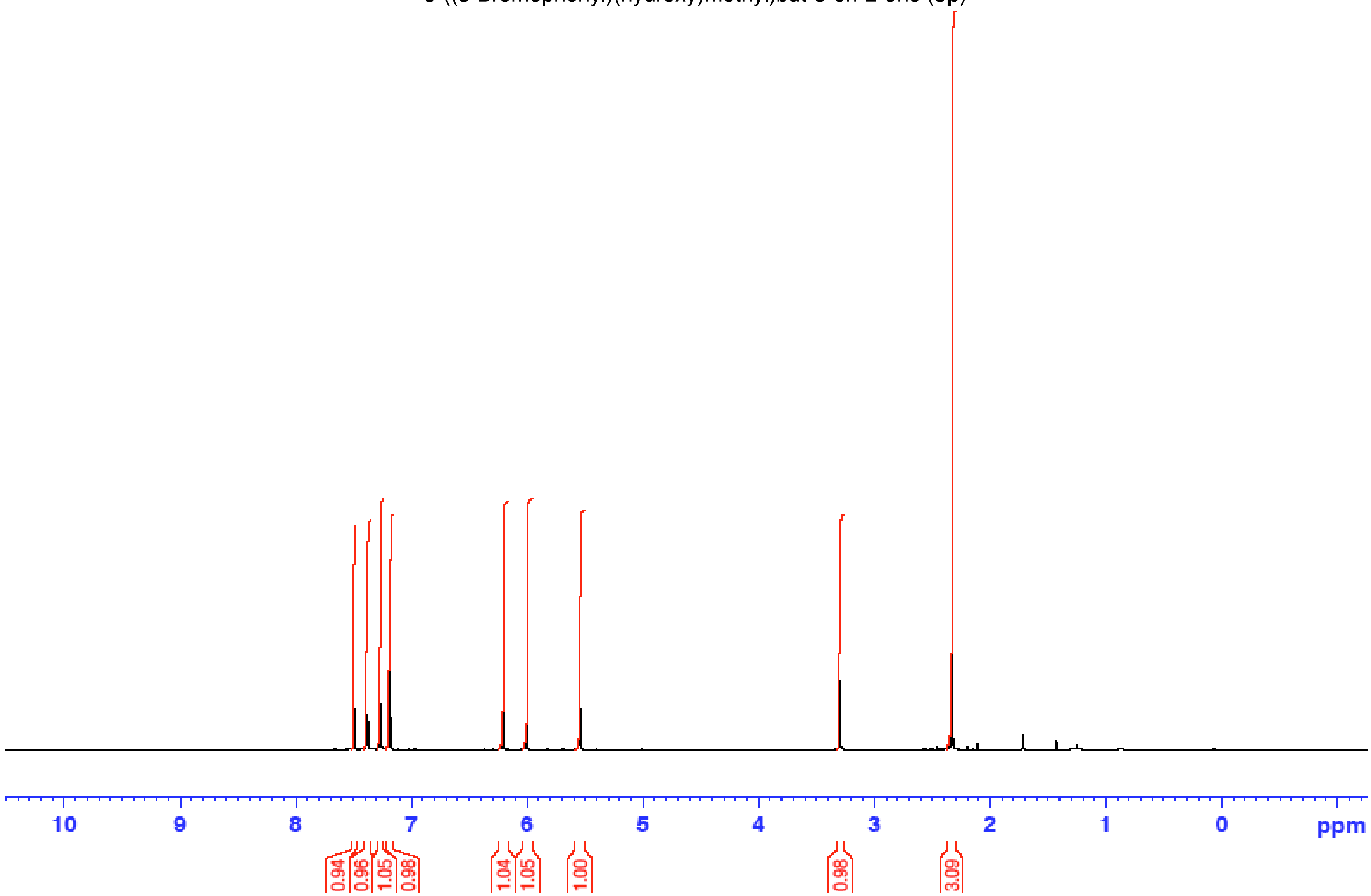
2-(Hydroxy(6-nitrobenzo[*d*][1,3]dioxol-5-yl)methyl)pent-1-en-3-one (**8o**)



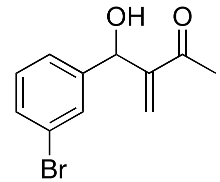
1H NMR Spectrum of **8p**



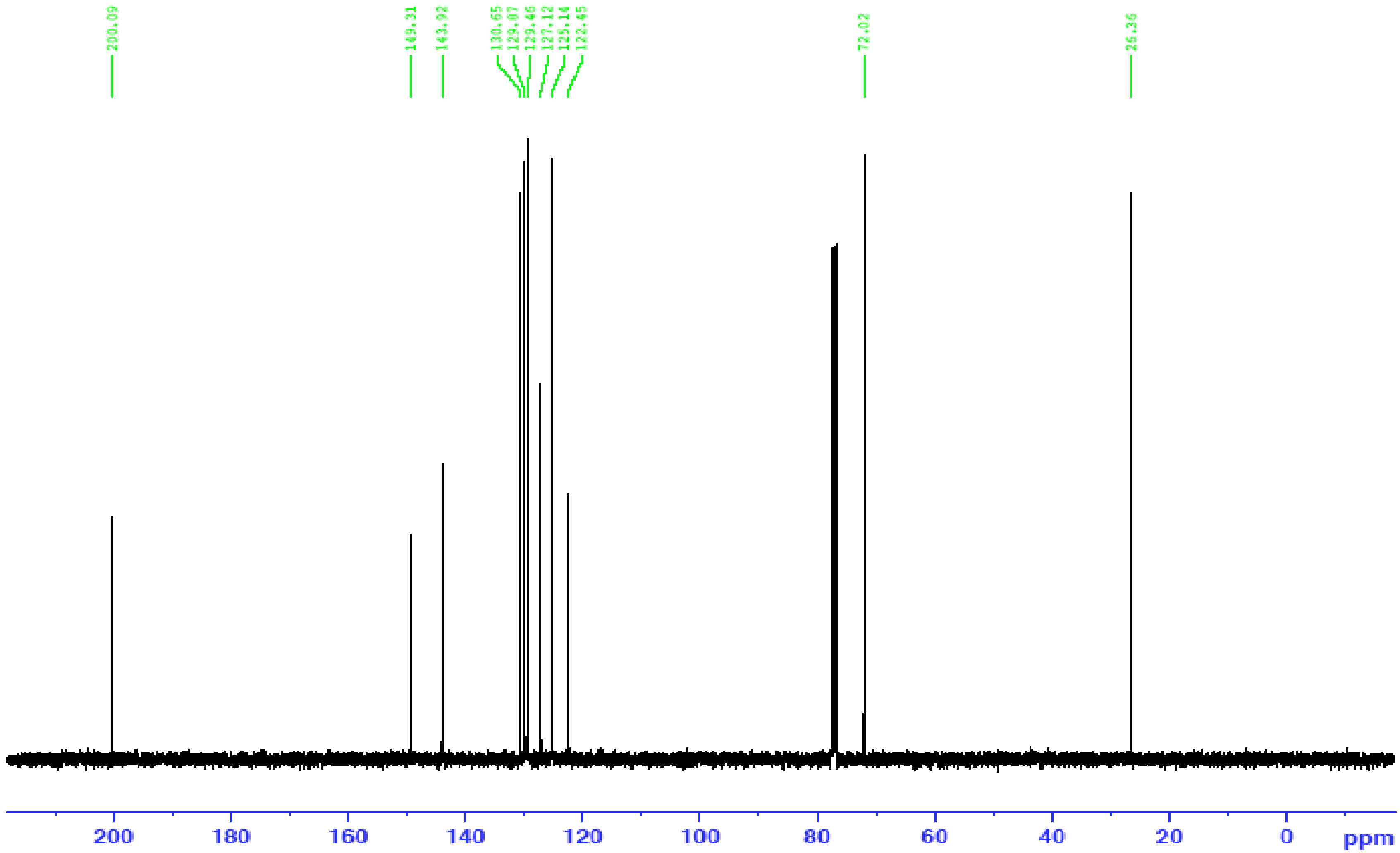
3-((3-Bromophenyl)(hydroxy)methyl)but-3-en-2-one (**8p**)



^{13}C NMR Spectrum of **8p**



3-((3-Bromophenyl)(hydroxy)methyl)but-3-en-2-one (**8p)**



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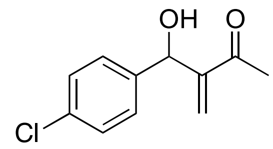
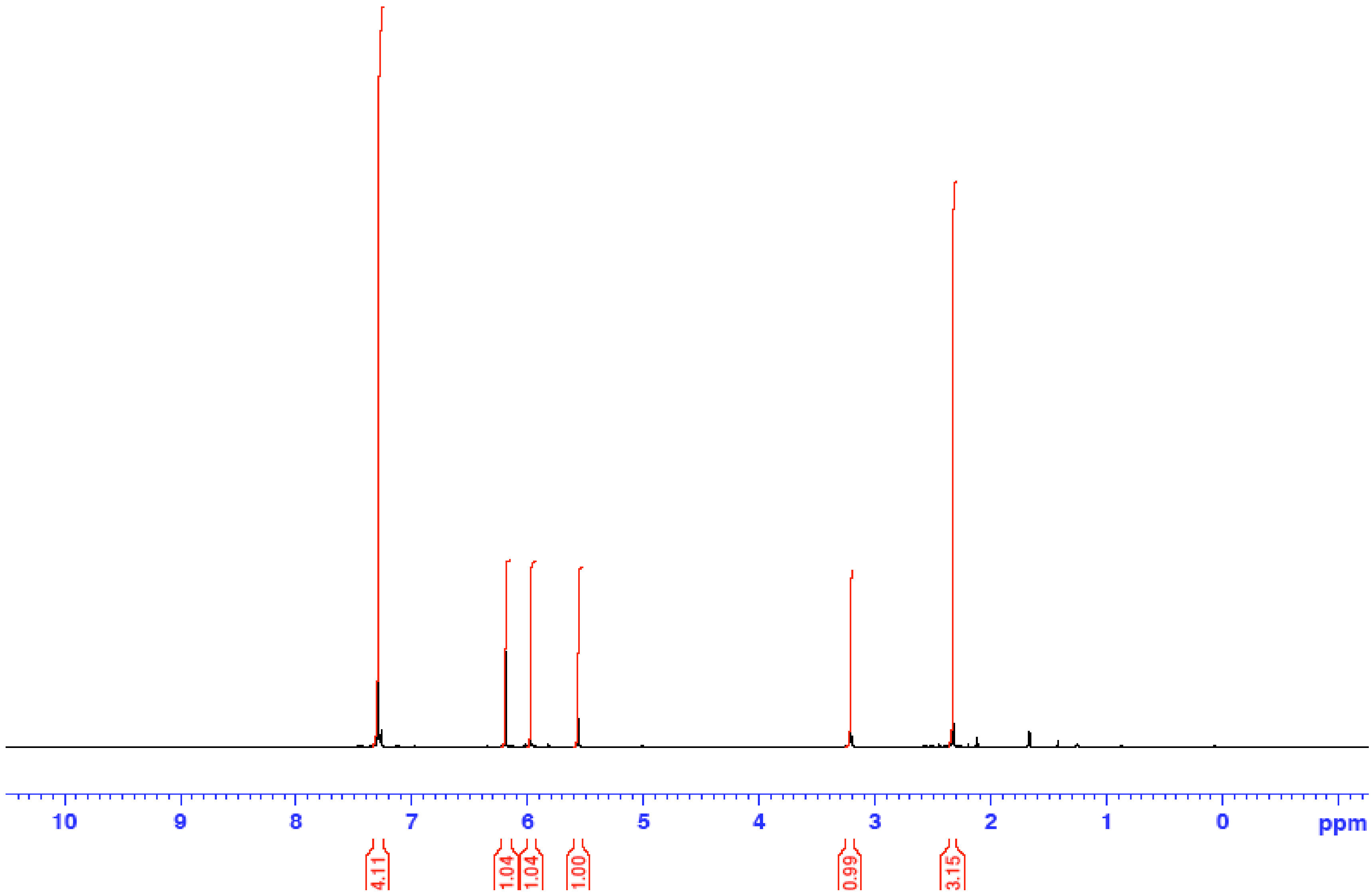
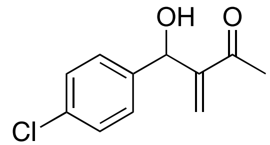
1H NMR Spectrum of **8q**



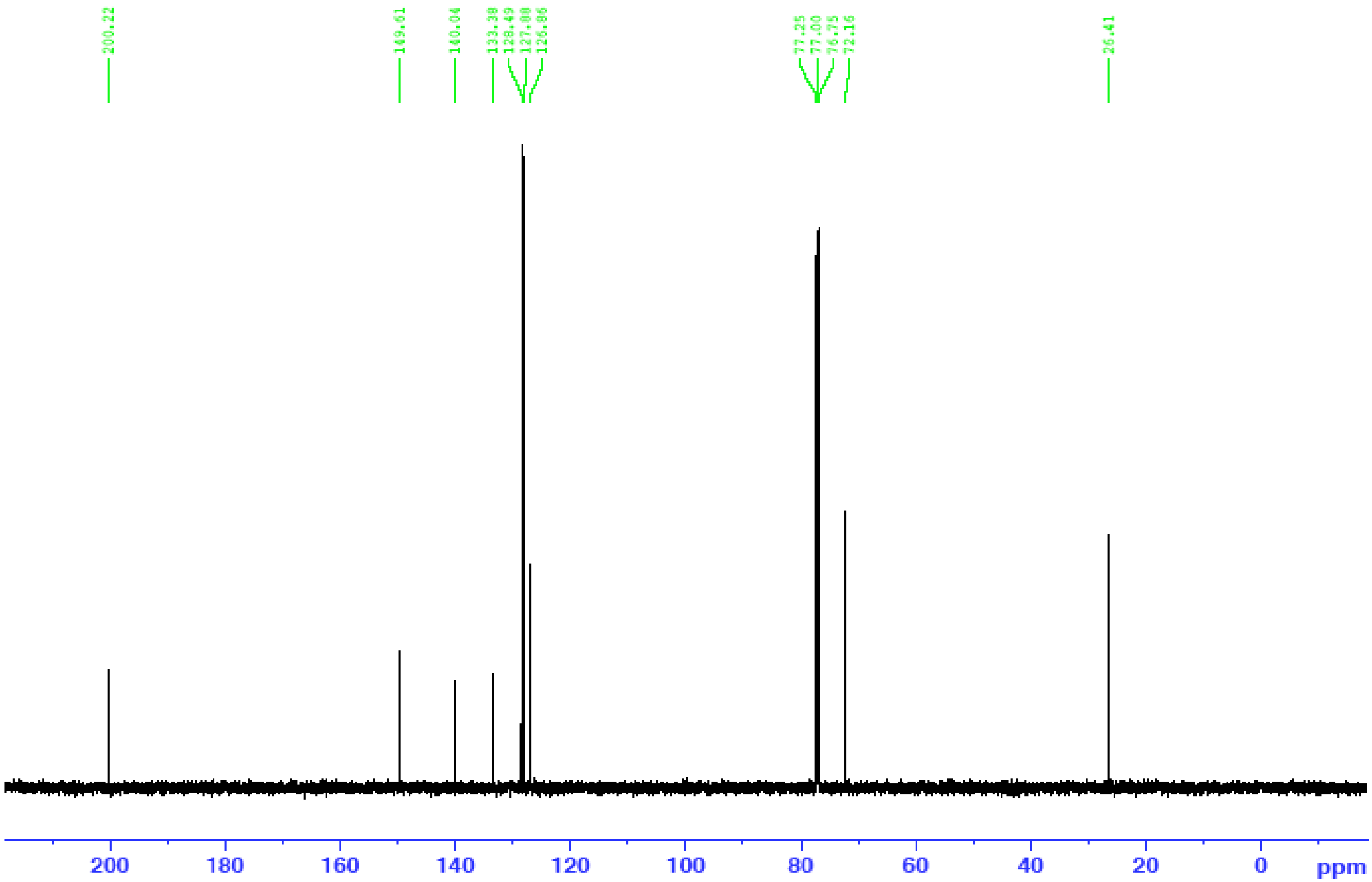
3-((4-Chlorophenyl)(hydroxy)methyl)but-3-en-2-one (**8q**)



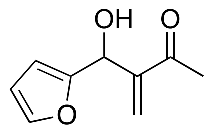
^{13}C NMR Spectrum of **8q**



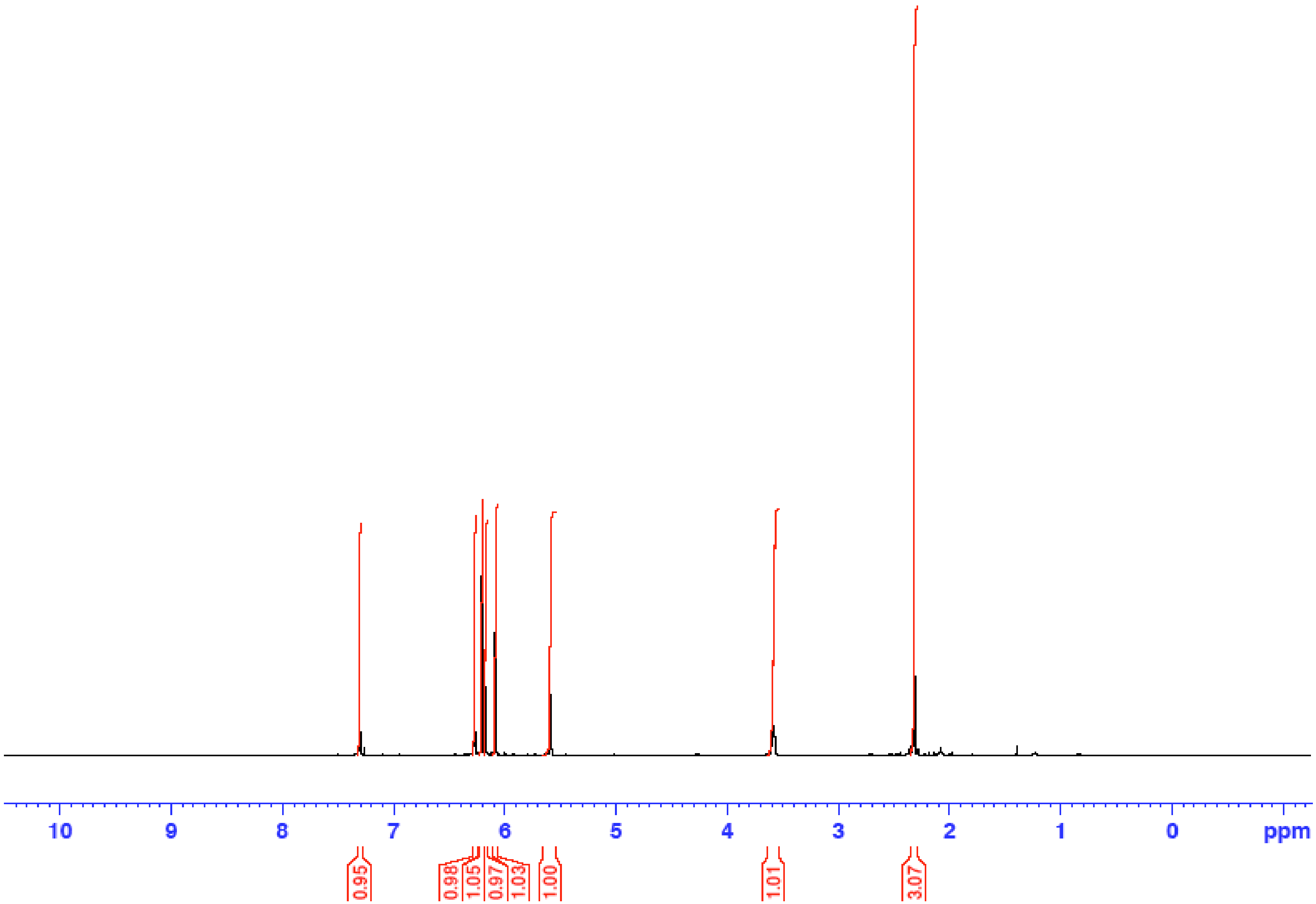
3-((4-Chlorophenyl)(hydroxy)methyl)but-3-en-2-one (**8q**)



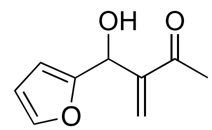
1H NMR Spectrum of **8r**



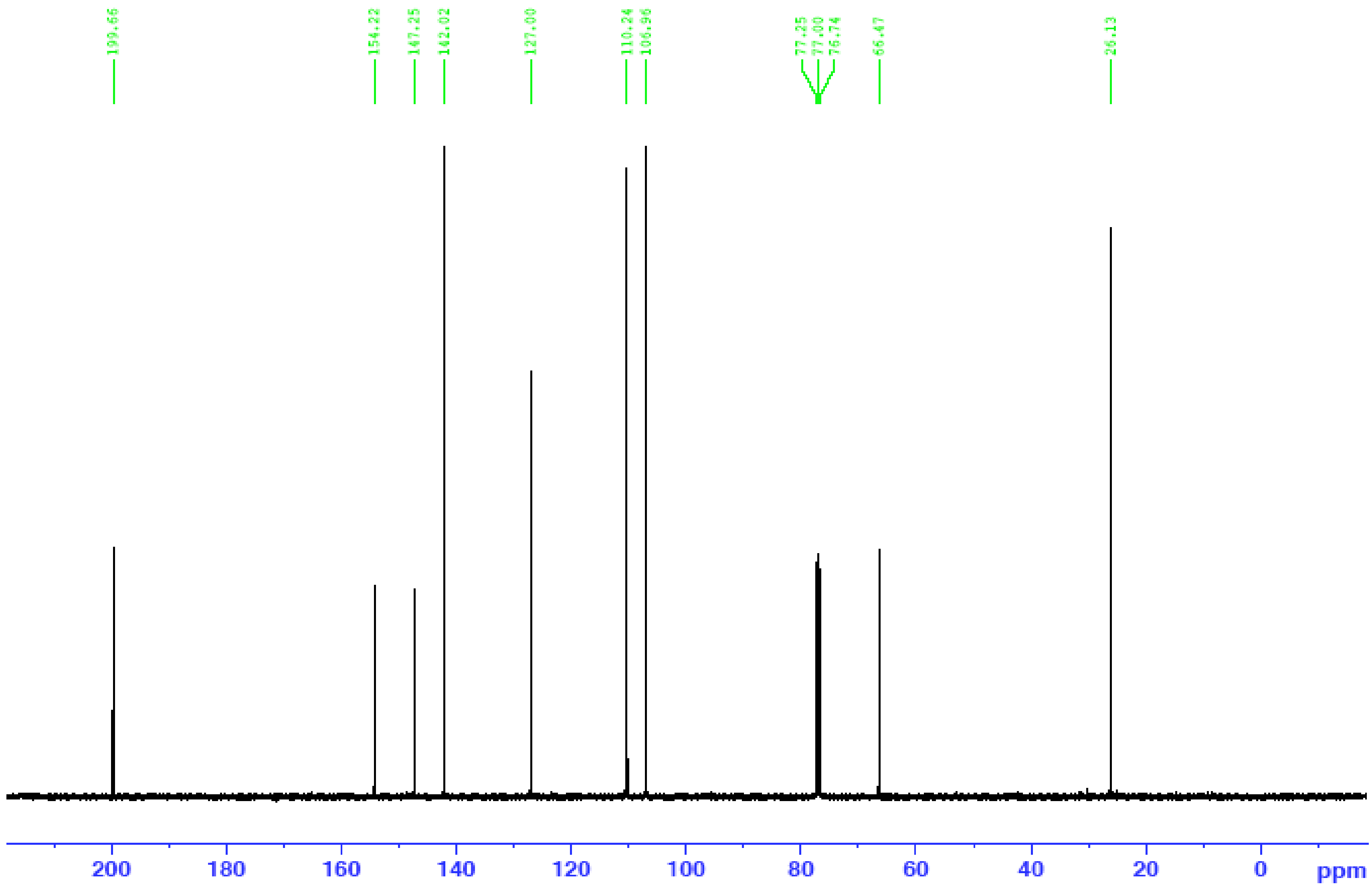
3-(Furan-2-yl(hydroxy)methyl)but-3-en-2-one (**8r**)



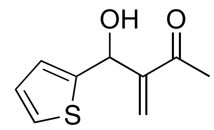
^{13}C NMR Spectrum of **8r**



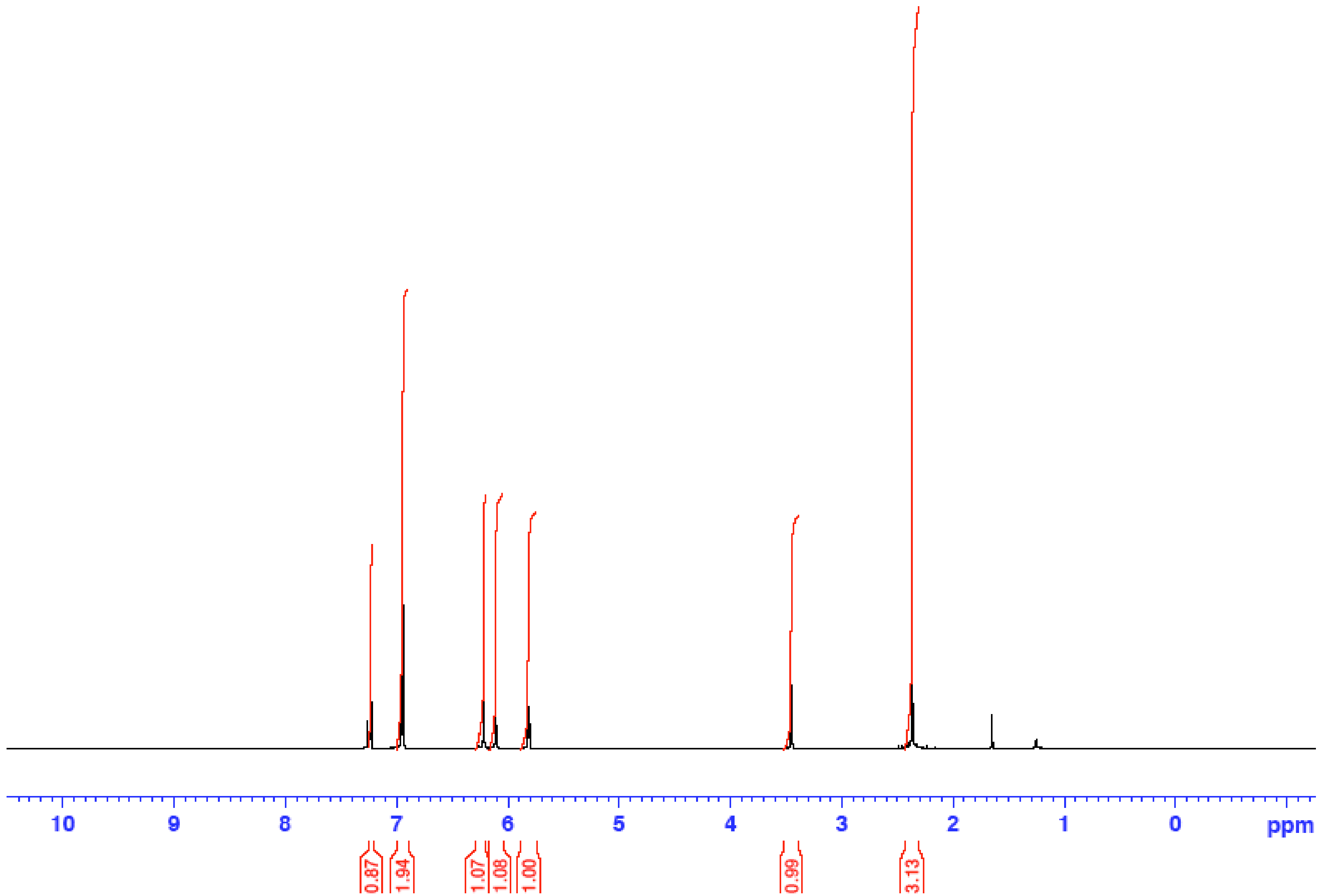
3-(Furan-2-yl(hydroxy)methyl)but-3-en-2-one (**8r**)



1H NMR Spectrum of **8s**



3-(Hydroxy(thiophen-2-yl)methyl)but-3-en-2-one (**8s**)



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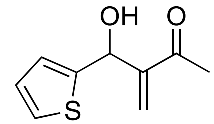
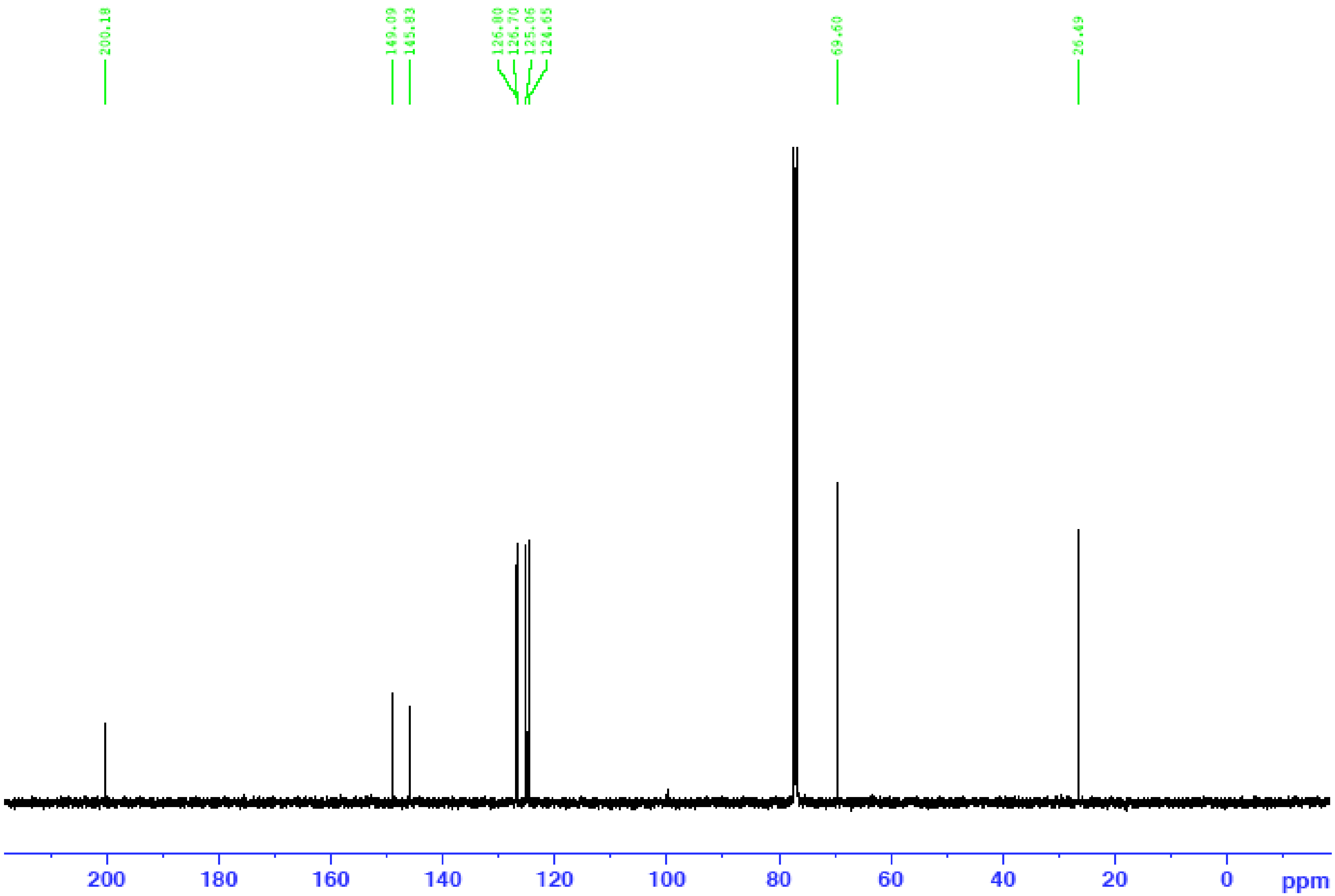
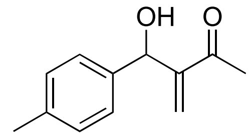
^{13}C NMR Spectrum of **8s**



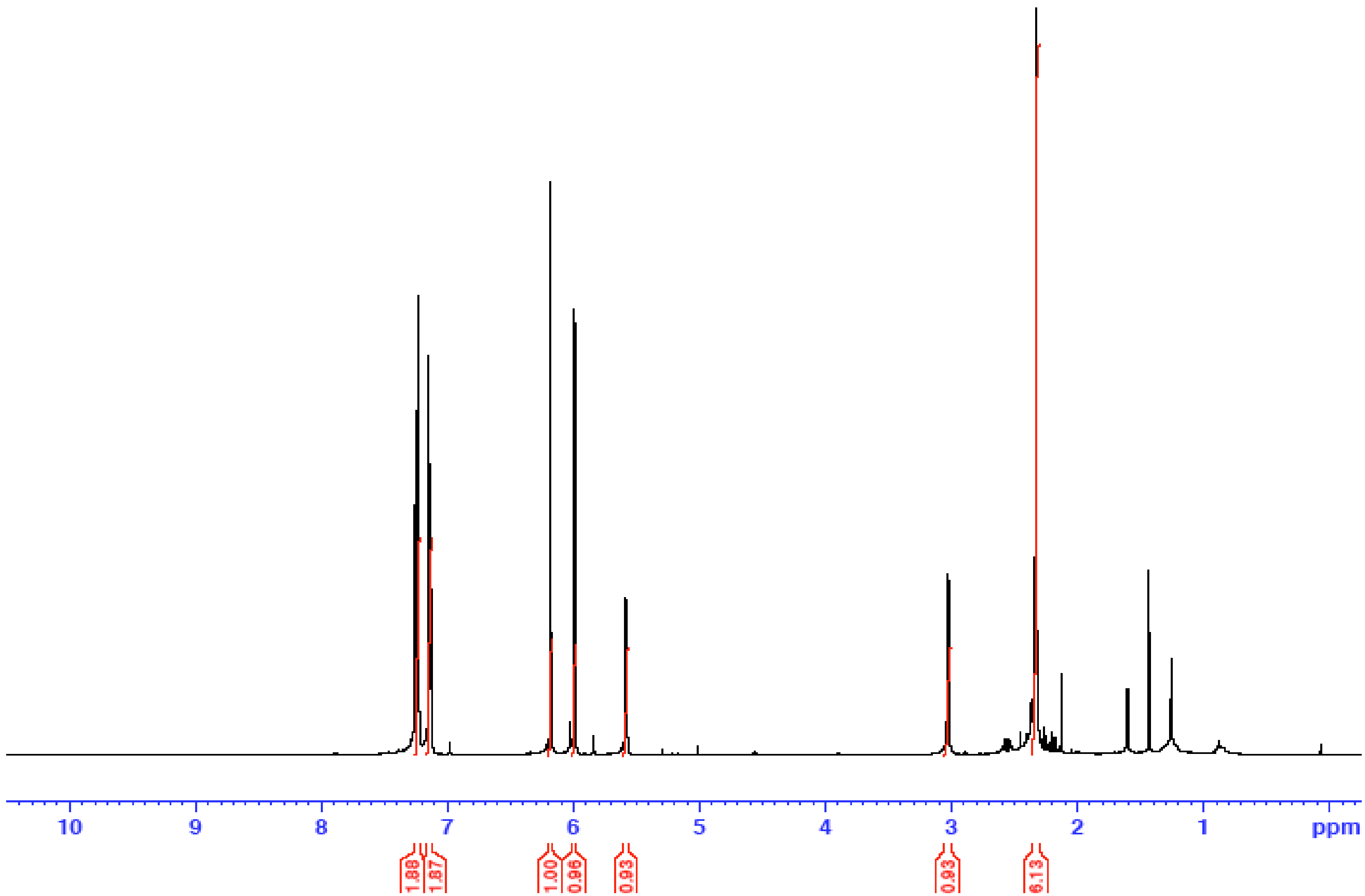
3-(Hydroxy(thiophen-2-yl)methyl)but-3-en-2-one (**8s**)



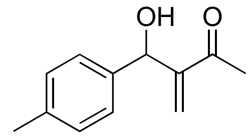
^{1}H NMR Spectrum of **8t**



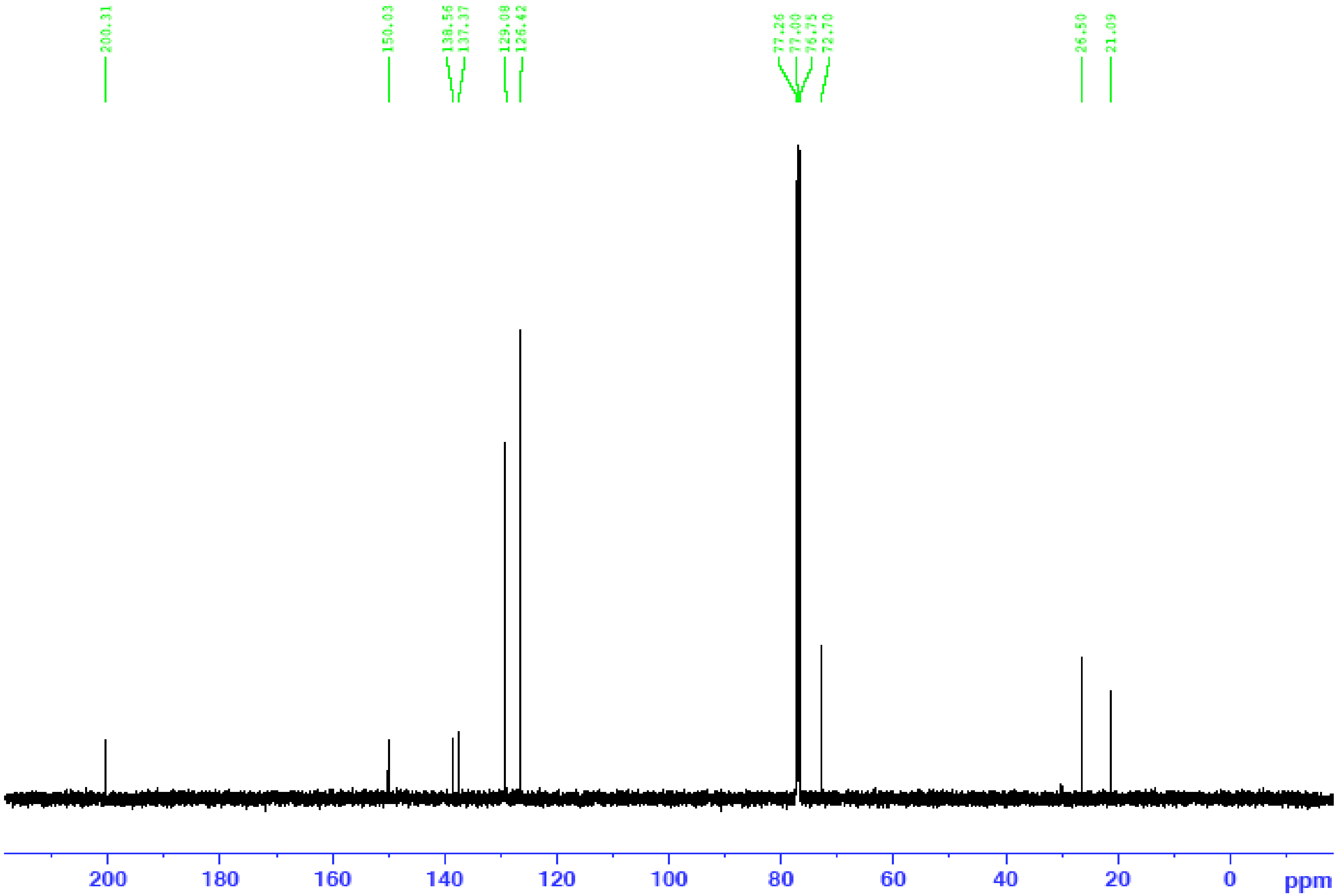
3-(Hydroxy(*p*-tolyl)methyl)but-3-en-2-one (**8t**)



^{13}C NMR Spectrum of **8t**



3-(Hydroxy(*p*-tolyl)methyl)but-3-en-2-one (**8t**)



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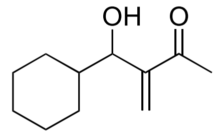
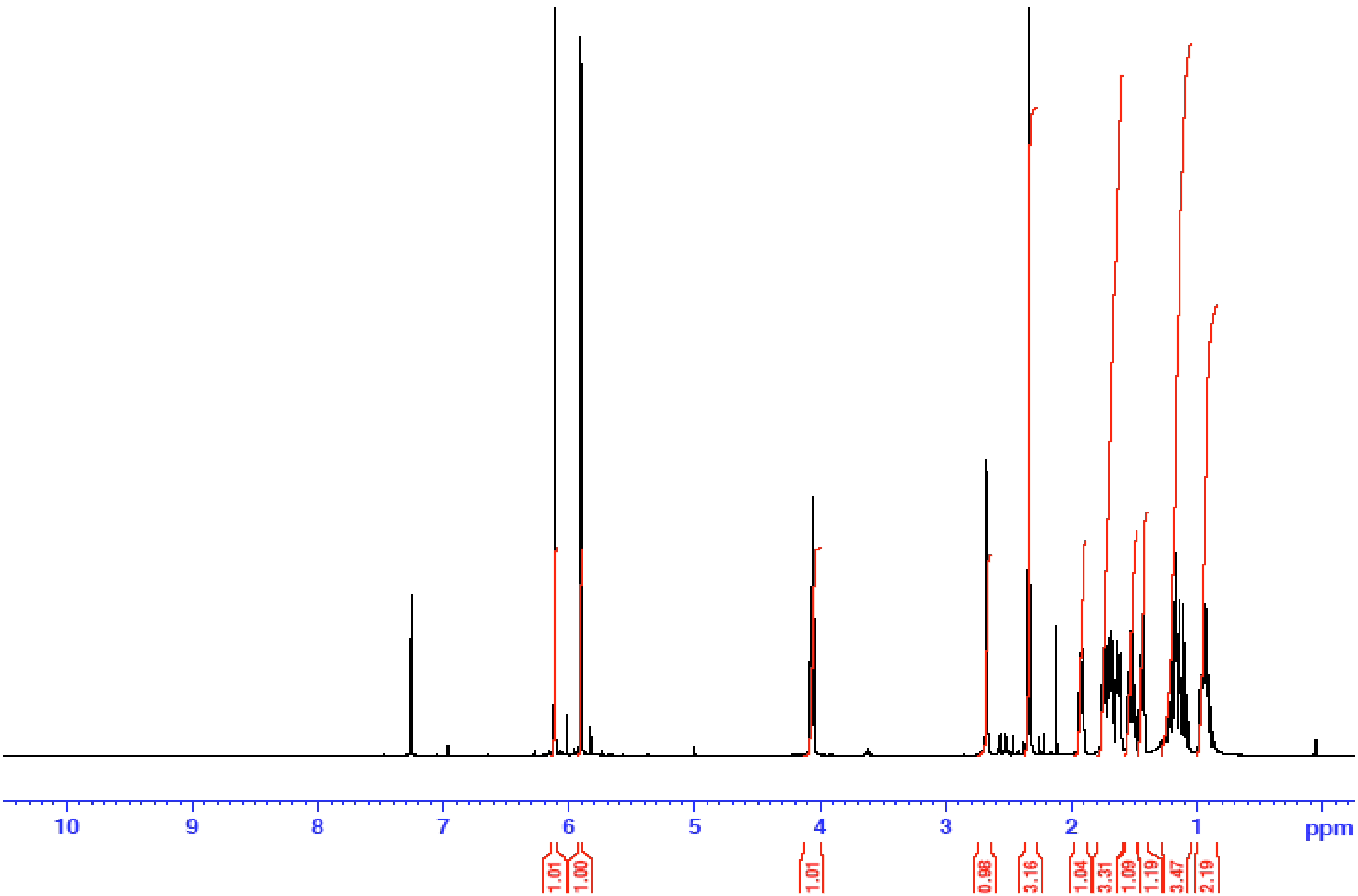
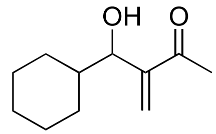
^{1}H NMR Spectrum of **8u**



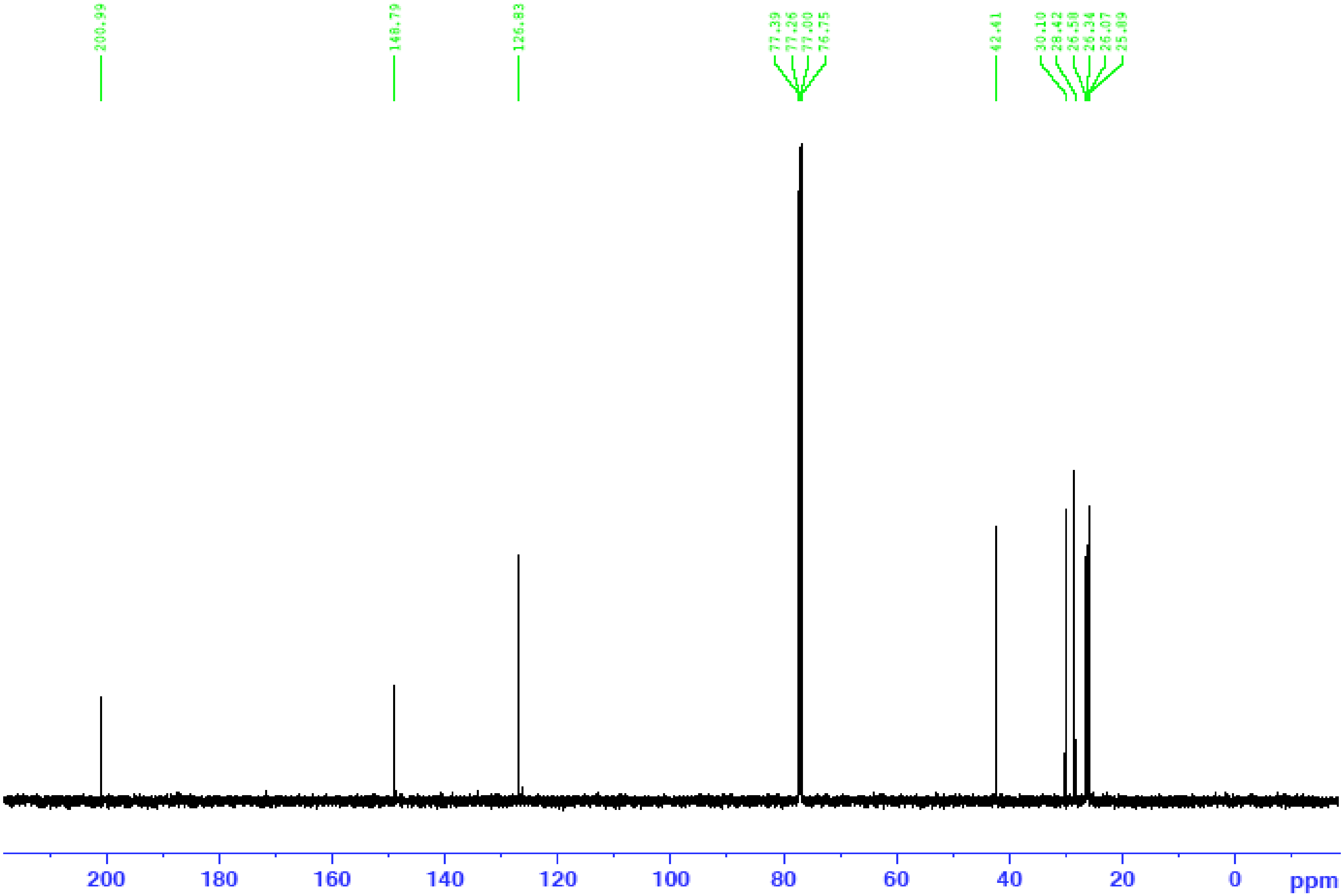
3-(Cyclohexyl(hydroxy)methyl)but-3-en-2-one (**8u**)

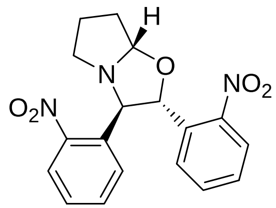


^{13}C NMR Spectrum of **8u**

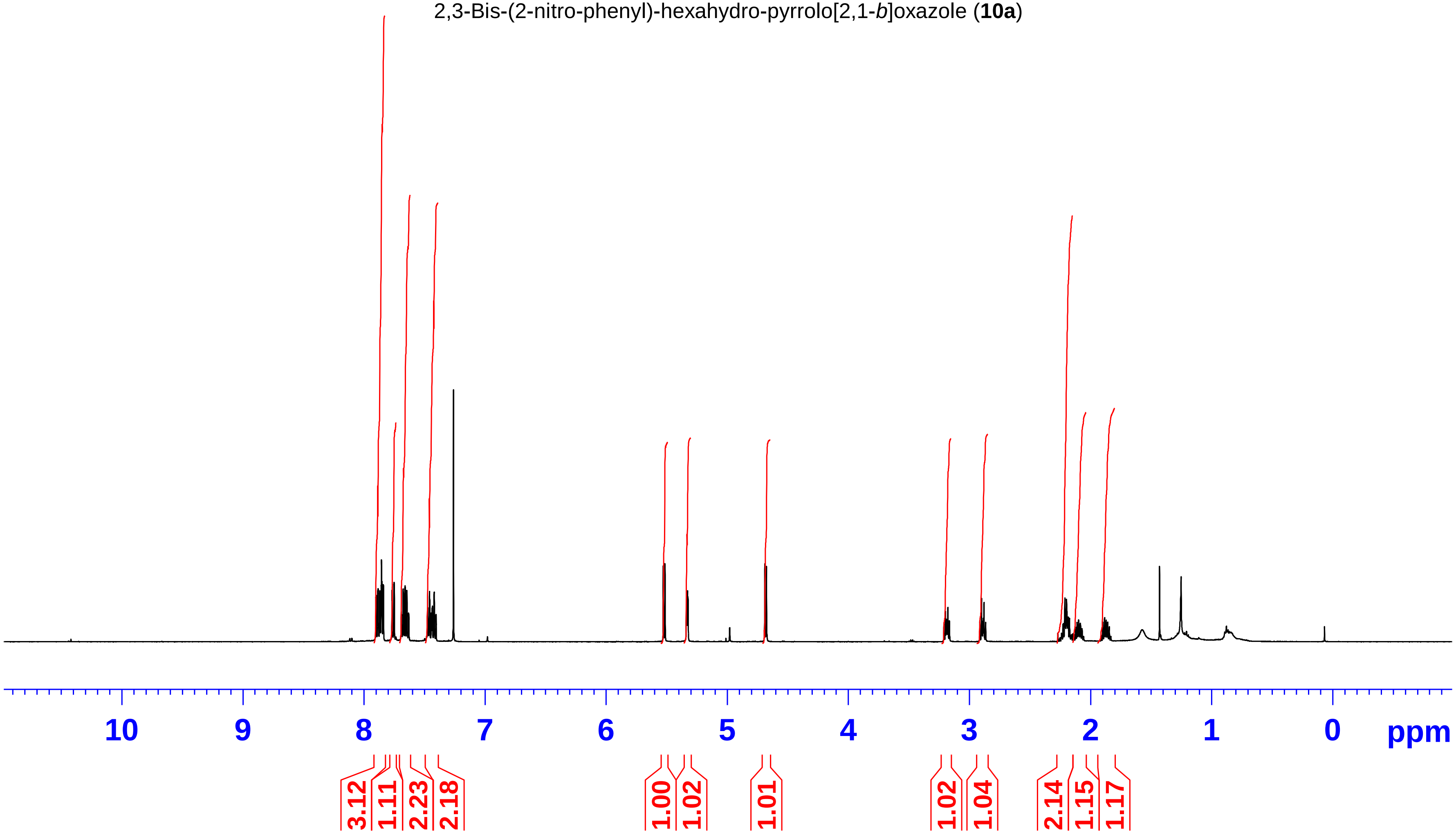


3-(Cyclohexyl(hydroxy)methyl)but-3-en-2-one (**8u**)

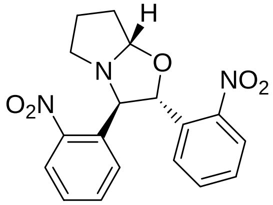




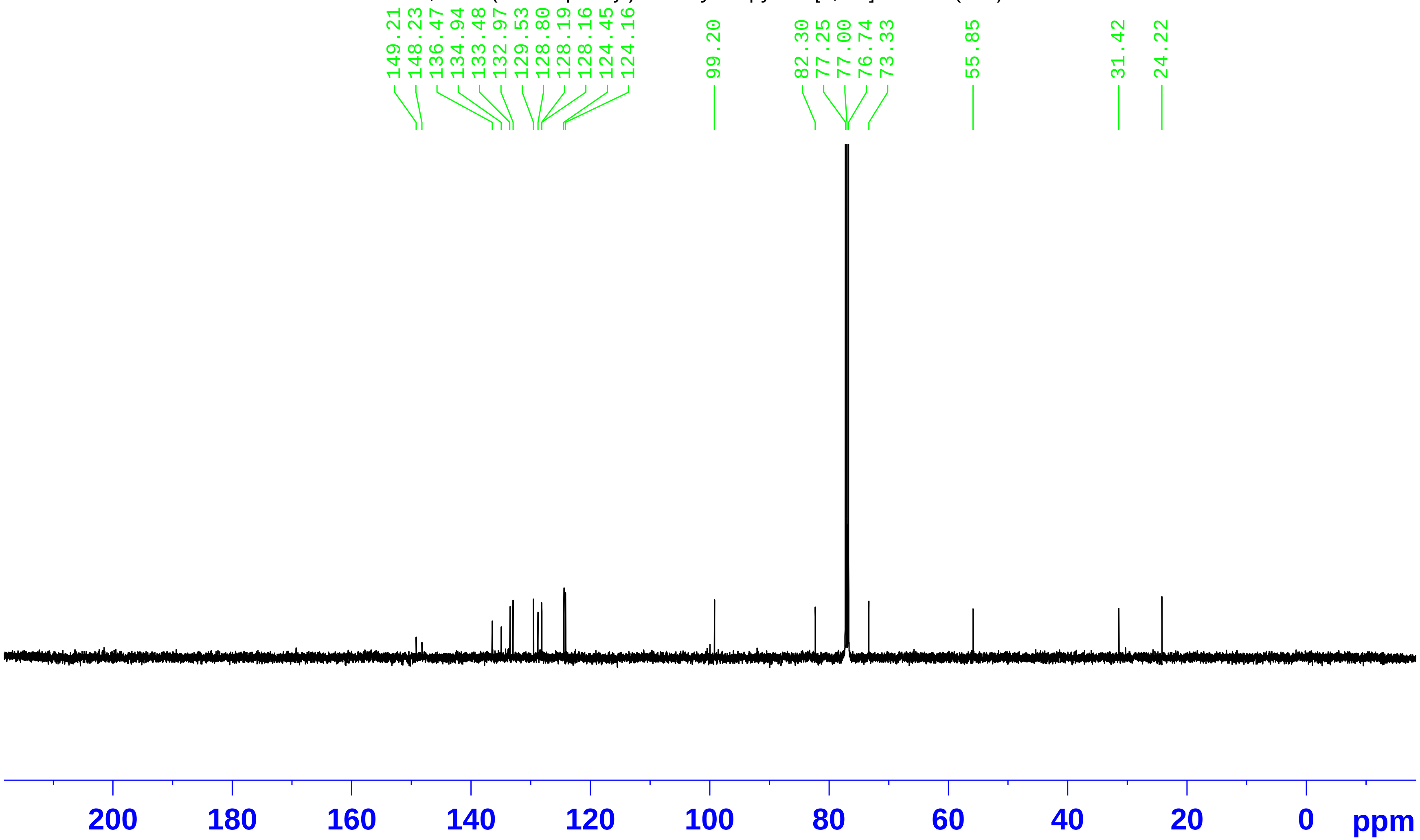
2,3-Bis-(2-nitro-phenyl)-hexahydro-pyrrolo[2,1-*b*]oxazole (**10a**)



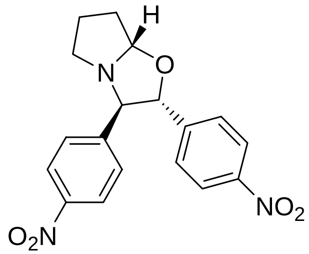
^{13}C NMR Spectrum of **10a**



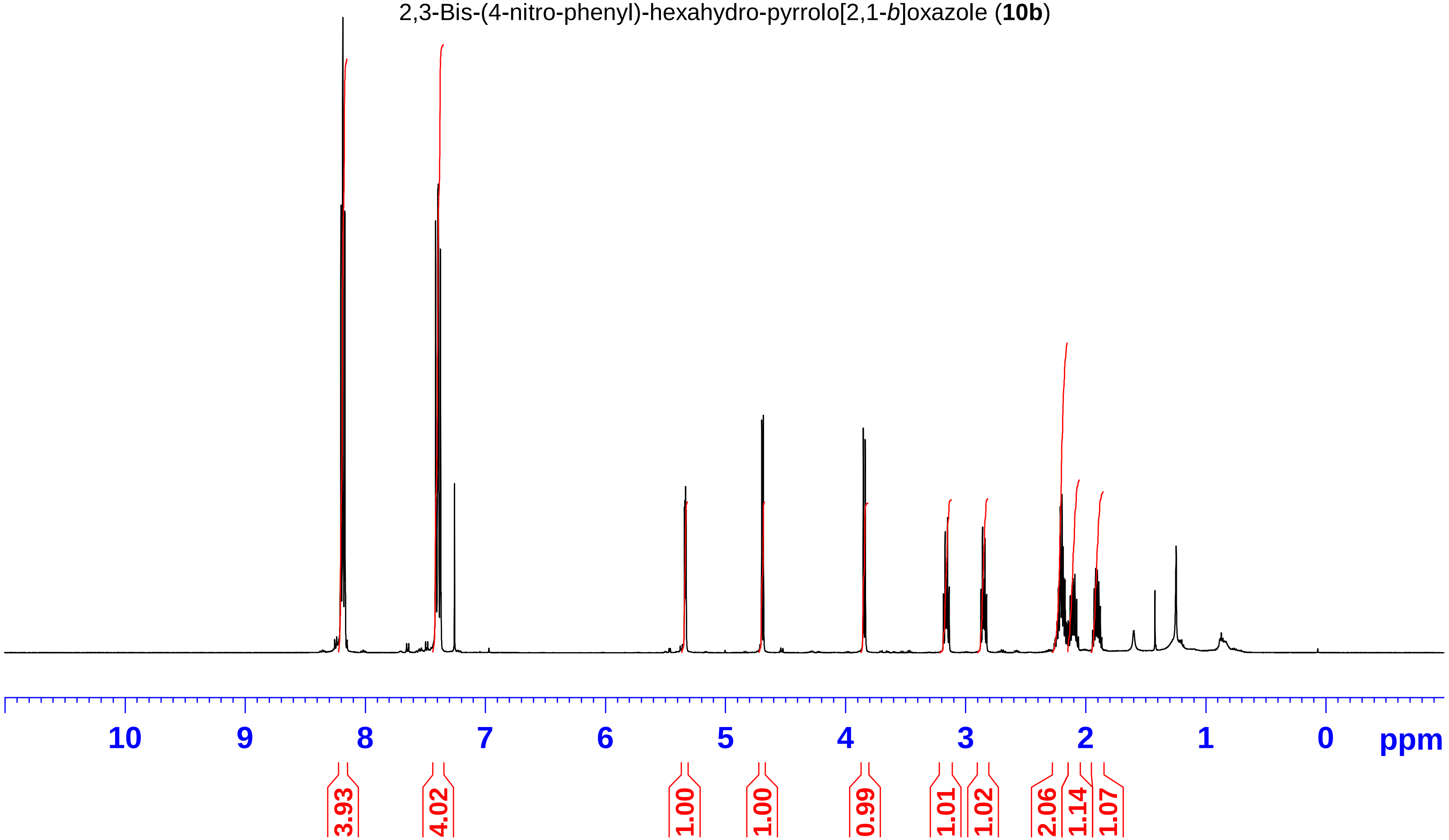
2,3-Bis-(2-nitro-phenyl)-hexahydro-pyrrolo[2,1-*b*]oxazole (**10a**)



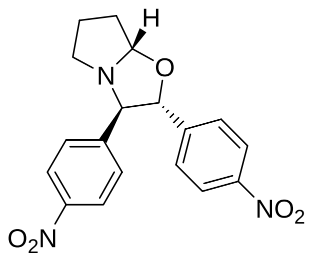
^{1}H NMR Spectrum of **10b**



2,3-Bis-(4-nitro-phenyl)-hexahydro-pyrrolo[2,1-*b*]oxazole (**10b**)



^{13}C NMR Spectrum of **10b**



2,3-Bis-(4-nitro-phenyl)-hexahydro-pyrrolo[2,1-*b*]oxazole (**10b**)