Supporting Information

2-Iodoxybenzoic acid organosulfonates: preparation, X-ray structure and reactivity of new, powerful hypervalent iodine(V) oxidants

Mekhman S. Yusubov,*[a,b] Dmitrii Yu. Svitich,[a] Akira Yoshimura,[c]
Victor N. Nemykin,*[c] and Viktor V. Zhdankin*[c]

[a] *The Tomsk Polytechnic University, 634050 Tomsk, Russia;*
E-mail: yusubov@mail.ru

[b] *The Siberian State Medical University 634050 Tomsk, Russia*

[c] *Department of Chemistry and Biochemistry, University of Minnesota Duluth, Duluth, Minnesota, 55812, USA. E-mail: vzhdanki@d.umn.edu, vnemykin@d.umn.edu*

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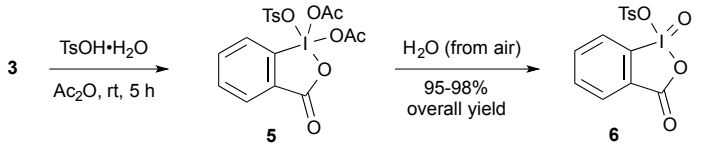
General experimental remarks

2-Iodobenzoic acid, organosulfonic acids, alcohols, and other common reagents and solvents were from commercial sources and used without further purification from freshly opened containers. Melting points were determined in an open capillary tube with a Mel-temp II melting point apparatus. NMR spectra were recorded on a Varian Inova 500 MHz NMR spectrometer at 500 MHz (^{1}H NMR) and 125 MHz (^{13}C NMR). Chemical shifts are reported in parts per million (ppm). ^{1}H and ^{13}C chemical shifts are referenced relative to tetramethylsilane.

Preparation of IBX, 1-hydroxy-1,2-benziodoxol-3(1*H*)-one 1-oxide. 2-Iodobenzoic acid (5.21 g, 21 mmol) was added to a solution of Oxone ($2KHSO_5$-$KHSO_4$-K_2SO_4) (16.78 g, 27.3 mmol) in water (65 mL) and stirred at 70-75°C for 4 h. The suspension was cooled to 2-5°C under slow stirring. The mixture was filtered and the white precipitate was washed with water (6 x 10 ml) and acetone (2 x 10 ml) and then dried under high vacuum to yield a colorless powder of IBX **3** (4.82 g, 82%). Mp: 232-233 °C (expl) (lit.[1] mp 232-233 °C). ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.14 (d, J = 8.0 Hz, 1 H), 8.03 (dd, J = 1.0, 7.5 Hz, 1 H), 8.00 (td, J = 1.5, 8.5 Hz, 1 H), 7.84 (t, J = 7.5 Hz, 1 H).

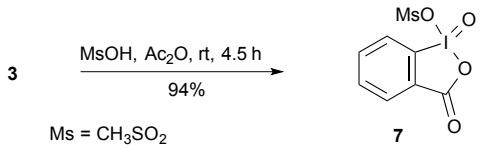
Synthesis of IBX organosulfonates



1-Tosyloxy-1-oxo-1*H*-1λ^5-benzo[*d*][1,2]iodoxol-3-one (IBX-OTs, 6). A mixture of IBX **3** (2.865 g, 10.2 mmol), *p*-TsOH•H_2O (5.81 g, 30.6 mmol, 3.0 equiv), and acetic anhydride (30-35 mL) was magnetically stirred at room temperature. The formation of a clear, colorless solution was observed after 30-40 min of stirring and then a white, microcrystalline precipitate started to form. After stirring the mixture for additional 4 h, the precipitate was filtered and washed on filter with ether (3 x 10 mL) and dried in

vacuum at room temperature to give 4.38-4.52 g (95-98%) of IBX-OTs **6** monohydrate, as a white, microcrystalline solid. Mp: 118-119 °C (dec.). Anal. Calcd for $C_{14}H_{13}IO_7S$: C, 37.18; H, 2.90; S, 7.09. Found: C, 37.08; H, 2.96; S, 7.04. IR (NaCl): 1637, 1188, 1130, 1042, 749, 695 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6, TMS): δ 8.17 (d, J = 8.0 Hz, 1H), 8.04 (dd, J = 1.0, 7.5 Hz, 1H), 8.02 (td, J = 1.5, 8.5 Hz, 1H), 7.85 (t, J = 7.5 Hz, 1 H), 7.48 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 2.29 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 167.6, 146.5, 145.1, 137.8, 133.4, 132.9, 131.00, 130.0, 128.0, 125.4, 124.8, 20.7 ppm.

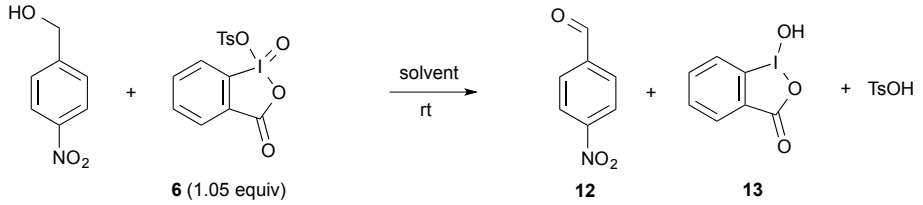
Single crystals of the diacetoxy derivative **5** suitable for X-ray crystallographic analysis were obtained by slow evaporation of the solution of IBX-OTs **6** in dichloromethane-acetic anhydride during 10 days at room temperature under anhydrous conditions. X-ray diffraction data were collected on IPDS Rigaku Rapid II diffractometrer using graphite-monochromated MoKα radiation (λ = 0.71073 Å) at 123 K. Multi-scan absorption corrections were applied to the data using CrystalClear 2.0 program. The structure was solved by direct methods (SIR-92) and refined by full-matrix least-squares refinement on F^2 using Crystals for Windows program. Crystal data for **5**. $C_{18}H_{17}ISO_9$: M = 536.30, monoclinic, space group $P2_1/c$, a = 7.5396(3), b = 33.1120(9), c = 7.9405(6) Å, a = 90.00°, β = 91.215(6)°, γ = 90.00°, V = 1981.92(17) $Å^3$, Z = 4, T = 123 K, 14171 reflections measured, 4530 unique; final R_1 = 0.0281 ($I \geq 2\sigma(I)$); R_w = 0.0596 (all); R_{int} = 0.0315. CCDC959250 contains the supplementary crystallographic data for compound **5**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ UK; fax: (+44) 1223-336-033, or deposit@ccdc.cam.ac.uk).



1-Methanesulfonyloxy-1-oxo-1*H*-1λ^5-benzo[*d*][1,2]iodoxol-3-one (IBX-OMs, 7). A mixture of IBX (280 mg, 1.0 mmol), methanesulfonic acid (288 g, 3.0 mmol, 3.0 equiv) and acetic anhydride (3.0 mL) was magnetically stirred at room temperature. A formation

of clear, colorless solution was observed after 30 min of stirring, and after additional 5 min of stirring a white, microcrystalline precipitate started to form. After stirring the mixture for additional 4 h, the mixture was concentrated under reduced pressure, and the precipitate was filtered and washed on filter with ether (3 x 1.0 mL). After drying of the solid in vacuum at room temperature, 353 mg (94%) of analytically pure IBX-OMs monohydrate was obtained in the form of a white, microcrystalline solid. Mp: 148-150 °C (dec). Anal. Calcd for $C_8H_9IO_7S$: C, 25.55; H, 2.41; S, 8.53. Found: C, 25.10; H, 2.57; S, 8.25. ^{1}H NMR (500 MHz, $CDCl_3$-CF_3COOH 10:1): δ 8.43 (d, J = 8.0 Hz, 1H), 8.31 (d, J = 7.5 Hz, 1H), 8.20 (t, J = 8.0 Hz, 1H), 7.98 (t, J = 7.5 Hz, 1H), 2.88 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$-CF_3COOH 10:1): δ 173.3, 144.9, 137.8, 135.7, 133.0, 126.1, 126.0, 39.5.

Optimization studies for oxidation of 4-nitrobenzyl alcohol by IBX-OTs 6.



6 (1.05 equiv) **12** **13**

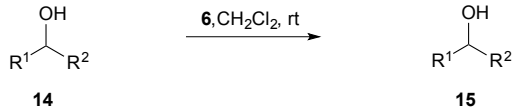
Table 1. Effect of solvent on the oxidation of 4-nitrobenzyl alcohol with reagent **6**.[a]

Entry	Solvent	Time, min	Conversion (by GC-MS), %	Yield[b] of **12**, %	Yield[b] of **13**, %
1	CH_2Cl_2	3	100	96	96
2	DMSO	7	100	94	92.5
3	CH_3CN	30	100	94	94
4	EtOAc	90	86	74	92
5	MeOH	60	-[c]	-[c]	96

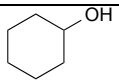
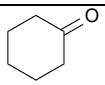
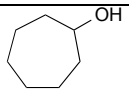
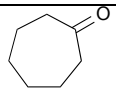
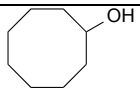
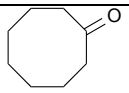
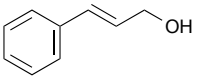
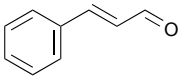
[a] Typical procedure: To a solution of 4-nitrobenzyl alcohol (46 mg, 0.3 mmol) in 1.5 mL CH_2Cl_2 IBX-OTs **6** (142 mg, 0.315 mmol) was added under stirring at rt. The conversion of alcohol was controlled by GC-MS every 1.5 min. The reaction was complete in 3 min. The precipitate of IBA and TsOH was filtered and washed with ether to afford 80 mg (96%) of IBA **13**, mp 252-253 °C (lit.[2] mp 256 °C), see page 10 of ESI for NMR spectrum of IBA. Evaporation of organic solvents from the filtrate afforded crude product **12**, which was purification by flash chromatography (hexane-EtOAc 5:1) to give 44 mg (96%) of analytically pure 4-nitrobenzaldehyde (see page 18 of ESI for NMR).
[b] Yields of isolated products.
[c] IBX-OTs **6** oxidizes MeOH under reaction conditions (see page 17 of ESI for NMR).

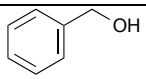
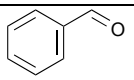
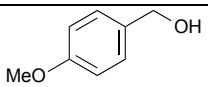
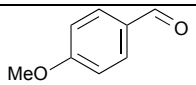
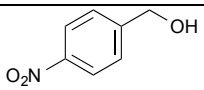
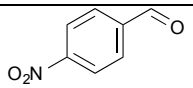
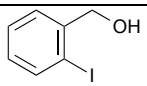
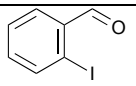
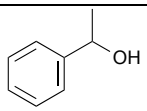
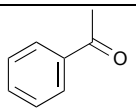
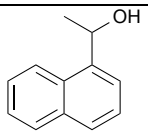
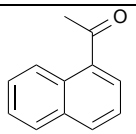
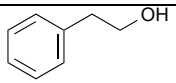
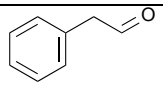
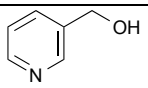
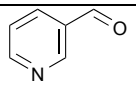
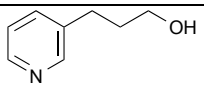
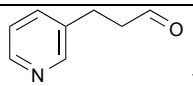
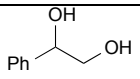
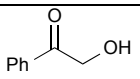
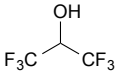
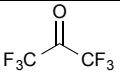
General procedure for oxidation of alcohols using IBX-OTs 6 (Tables 2 and 3). To a solution of alcohol (0.2-0.5 mmol) in 1-2 mL of appropriate solvent, IBX-OTs **6** (1.05 equiv or 3.0 equiv, see Tables 2 and 3) was added under stirring at room temperature. Reaction mixtures were monitored by GC-MS; the reaction times are listed in Tables 1 and 2. Carbonyl products **15a-d,f,j,l** and **17a** were isolated from reaction mixture as 2,4-dinitrophenylhydrazones after addition 2–5 mL of the standard solution of 2,4-dinitrophenylhydrazine [standard solution was prepared from 2,4-dinitrophenylhydrazine (3 g), concd H_2SO_4 (15 mL), ethanol (70 mL), and water (20 mL)]. The precipitate of 2,4-dinitrophenylhydrazone was filtered, washed with water, dried, and recrystallized from 95% ethanol. Carbonyl products **15e,g-i,k,m-o** and **17b-d** were isolated by preparative column chromatography of silica gel using hexane-Et_2OAc 5:1 or 3:1 as the eluent.

Table 2. Oxidation of alcohols to aldehydes or ketones with reagent **6**.[a]



14 **15**

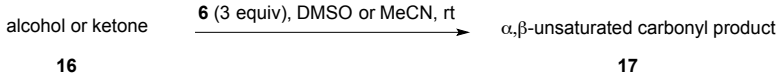
Entry	Alcohol **14**	Product **15**	Time, min	Conversion, %	Yield,[b] %
1		 **15a**	10	100	92
2		 **15b**	10	100	95
3		 **15c**	10	100	94
4	*n*-$C_7H_{15}CH_2OH$	*n*-$C_7H_{15}CHO$ **15d**	10	100	90
5		 **15e**	10	100	91

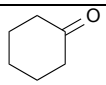
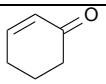
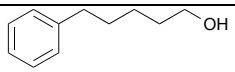
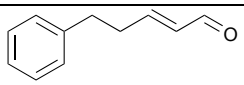
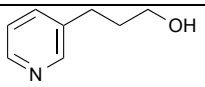
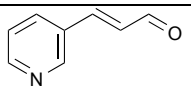
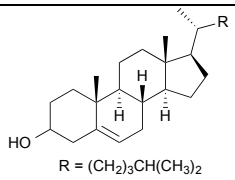
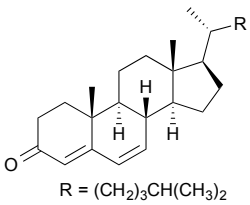
6		 **15f**	3	100	96
7		 **15g**	3	100	93
8		 **15h**	3	100	96
9		 **15i**	40	100	91
10		 **15j**	3	100	98
11[c]		 **15k**	Over night	100	83
12		 **15l**	10	100	90
13[c,d]		 **15m**	Over night	100	87
14[c,d]		 **15n**	Over night	100	74
15[e]		 **15o**	40	100	89
16[f]		 **15p**	420	60	60[g]

[a] All reactions were performed at rt in CH_2Cl_2 using 1.05 equiv of reagent **6**, unless noted otherwise.
[b] Yields of isolated products **15**.
[c] MeCN was used as a solvent, because reaction in CH_2Cl_2 was less selective.
[d] In the reactions of pyridine derivatives, 1.2 equiv of regent **6** was used and additional work-up with

aqueous $NaHCO_3$ was applied.
[e] DMSO was used as a solvent in order to improve selectivity.
[f] To a mixture of 1,1,1,3,3,3-hexafluoro-2-propanol (15 mg, 0.089 mmol) in $CDCl_3$ (0.6 mL) in sealed NMR tube was added reagent **6** (16 mg, 0.035 mmol) and $CFCl_3$ as internal standard at reflux. The progress of oxidation and conversion was monitored by ^{19}F NMR.
[g] Conversion and yield of hexafluoroacetone in this reaction were estimated from ^{19}F NMR by comparison of integral intensity of signals of hexafluoro-2-propanol and hexafluoroacetone.

Table 3. Preparation of α,β-unsaturated carbonyl compounds using reagent **6**.[a]



Entry	Substrate **16**	Product **17**	Time, h	Conversion, %	Yield,[b] %
1		 **17a**	24	100	84
2		 **17b**	14	100	81
3[c]		 **17c**	14	100	71
4		 **17d**	20	40	30

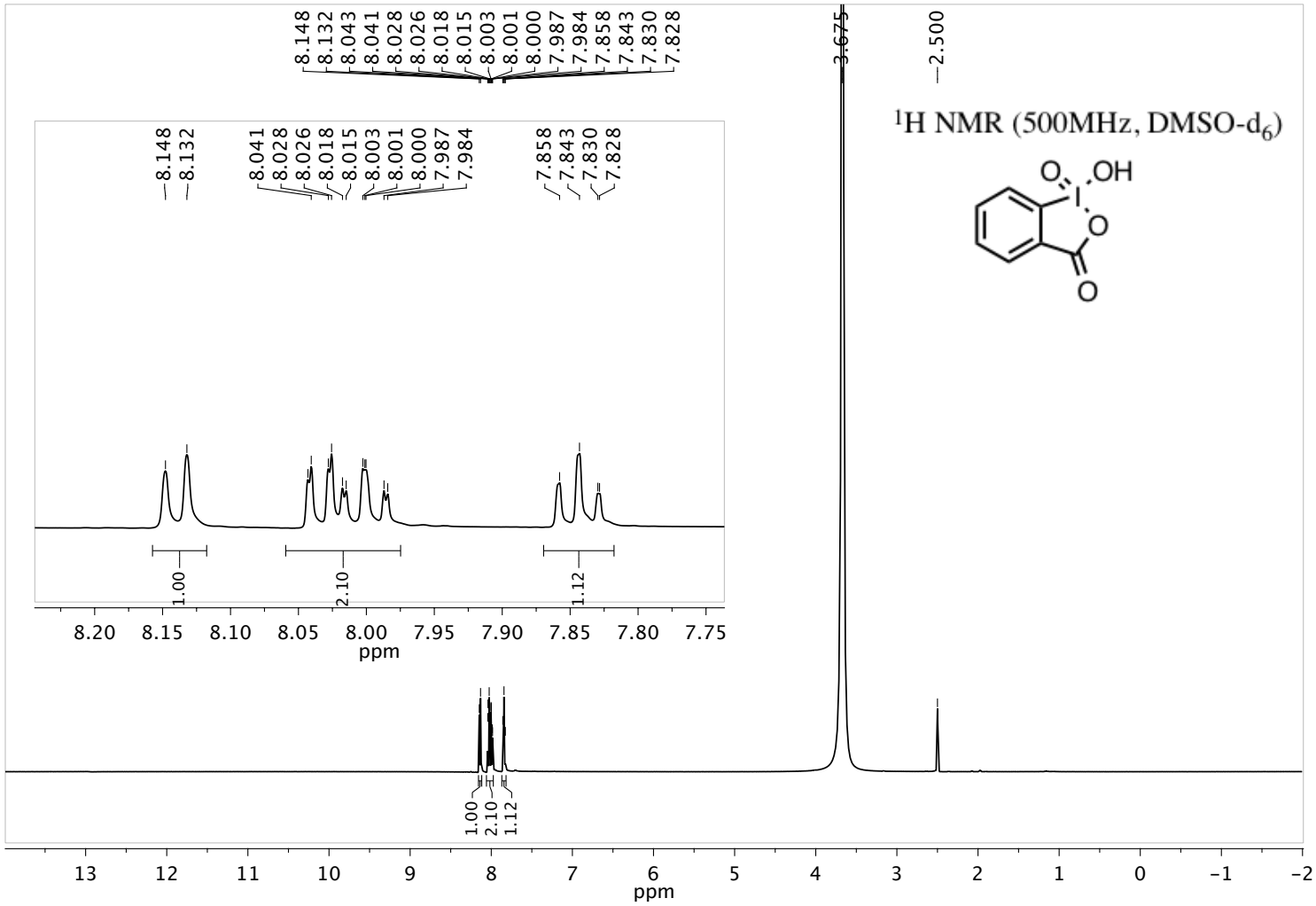
[a] All reactions were performed at rt with 3.0 equiv of reagent **6** in DMSO, unless noted otherwise.
[b] Yields of isolated products **17**.
[c] MeCN was used as a solvent.
[d] In the reactions of pyridine derivatives, 3.0 equiv of reagent **6** was used and additional work-up with aqueous $NaHCO_3$ was applied.

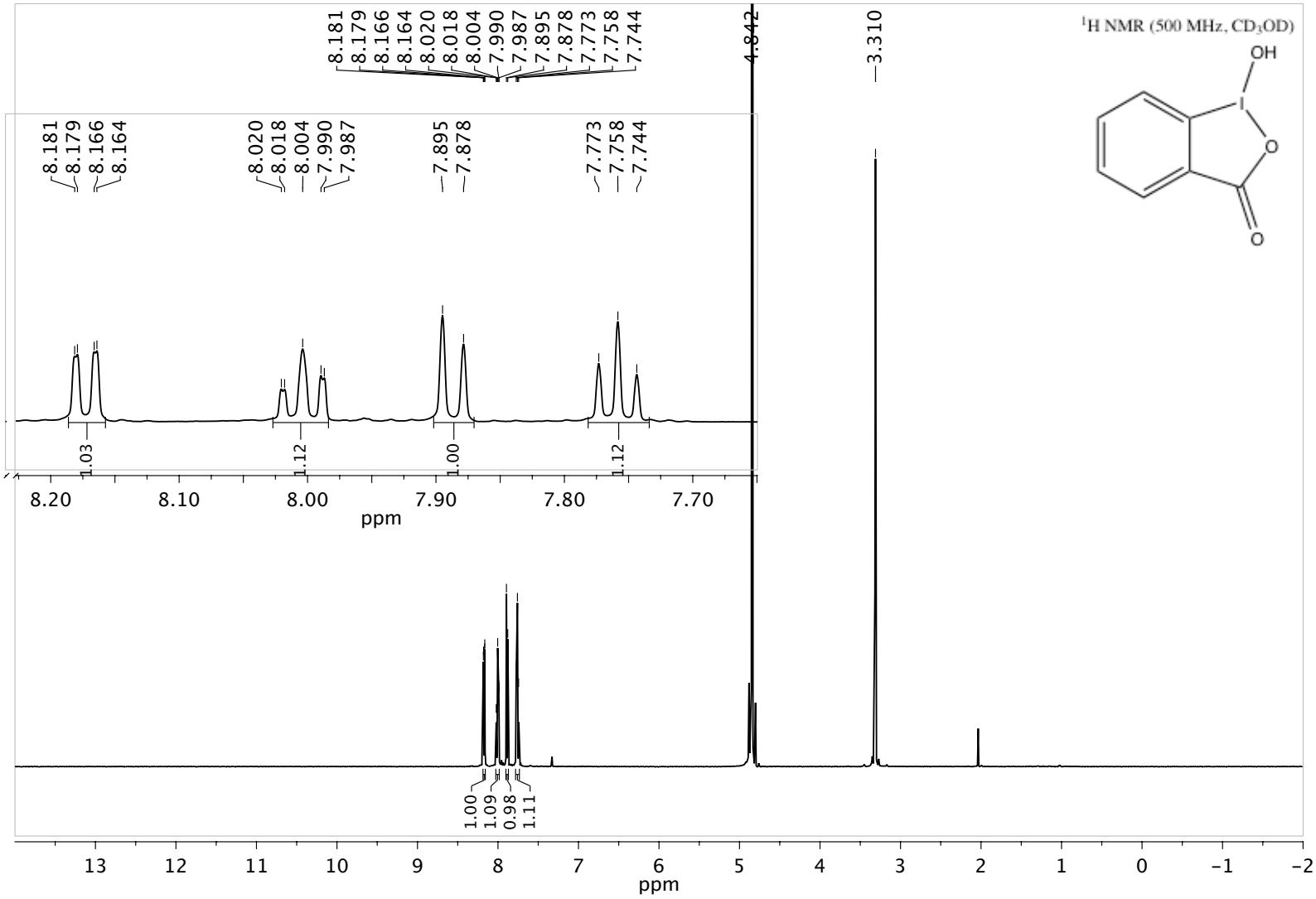
References:

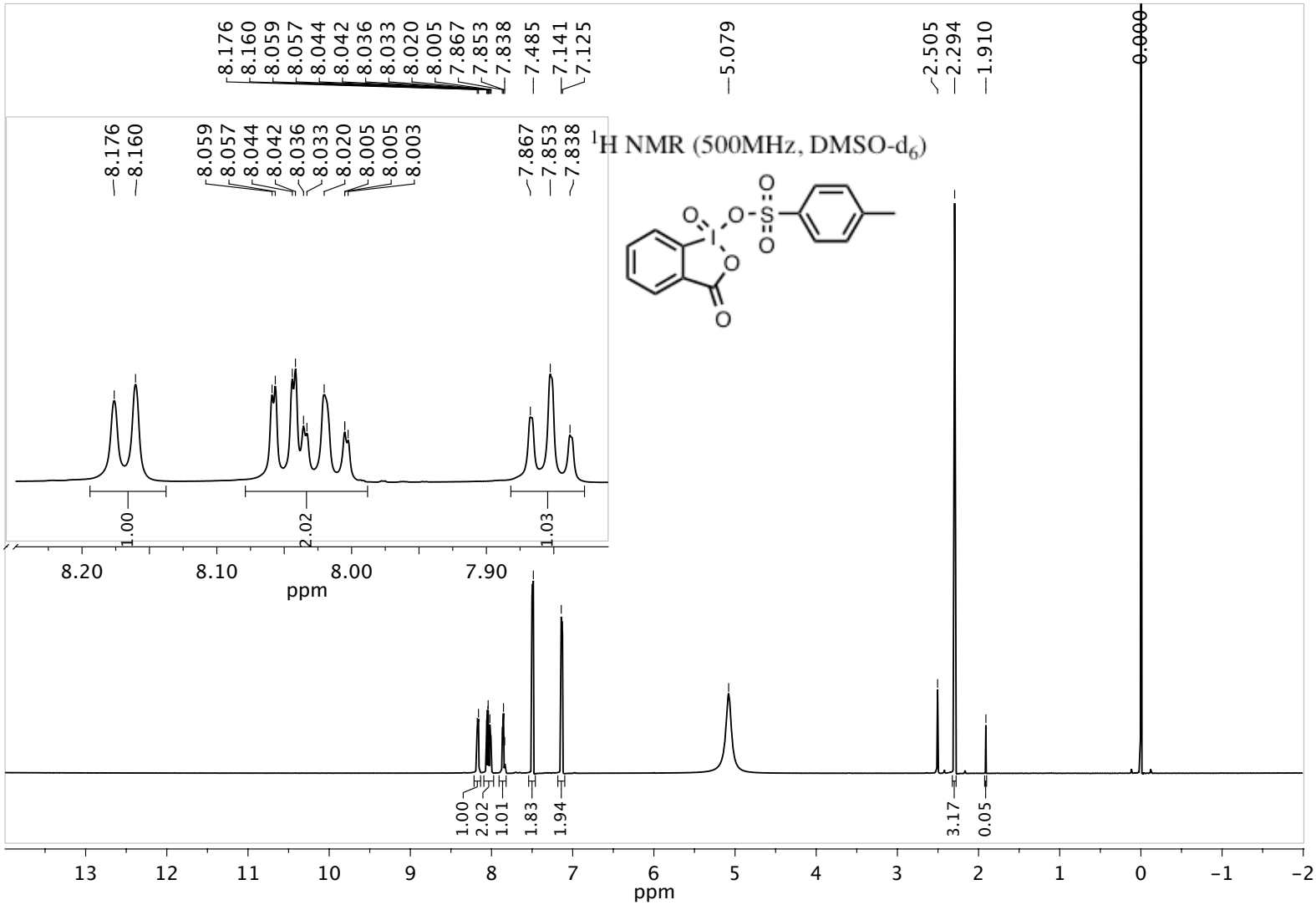
1 M. Frigerio, M. Santagostino and S. Sputore, *J. Org. Chem.*, 1999, **64**, 4537.

2 L. Kraszkiewicz and L. Skulski, *ARKIVOC*, 2003, **(vi)**, 120.

Spectra of products



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8.057
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8.042
8.036
8.033
8.020
8.005
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7.853
7.838
7.485
7.141
7.125
5.079
2.505
2.294
1.910
0.000
^{1}H NMR (500MHz, DMSO-d$_6$)
1.00
2.02
1.03
8.20
8.10
8.00
7.90
ppm
1.00
2.02
1.01
1.83
1.94
3.17
0.05
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12
11
10
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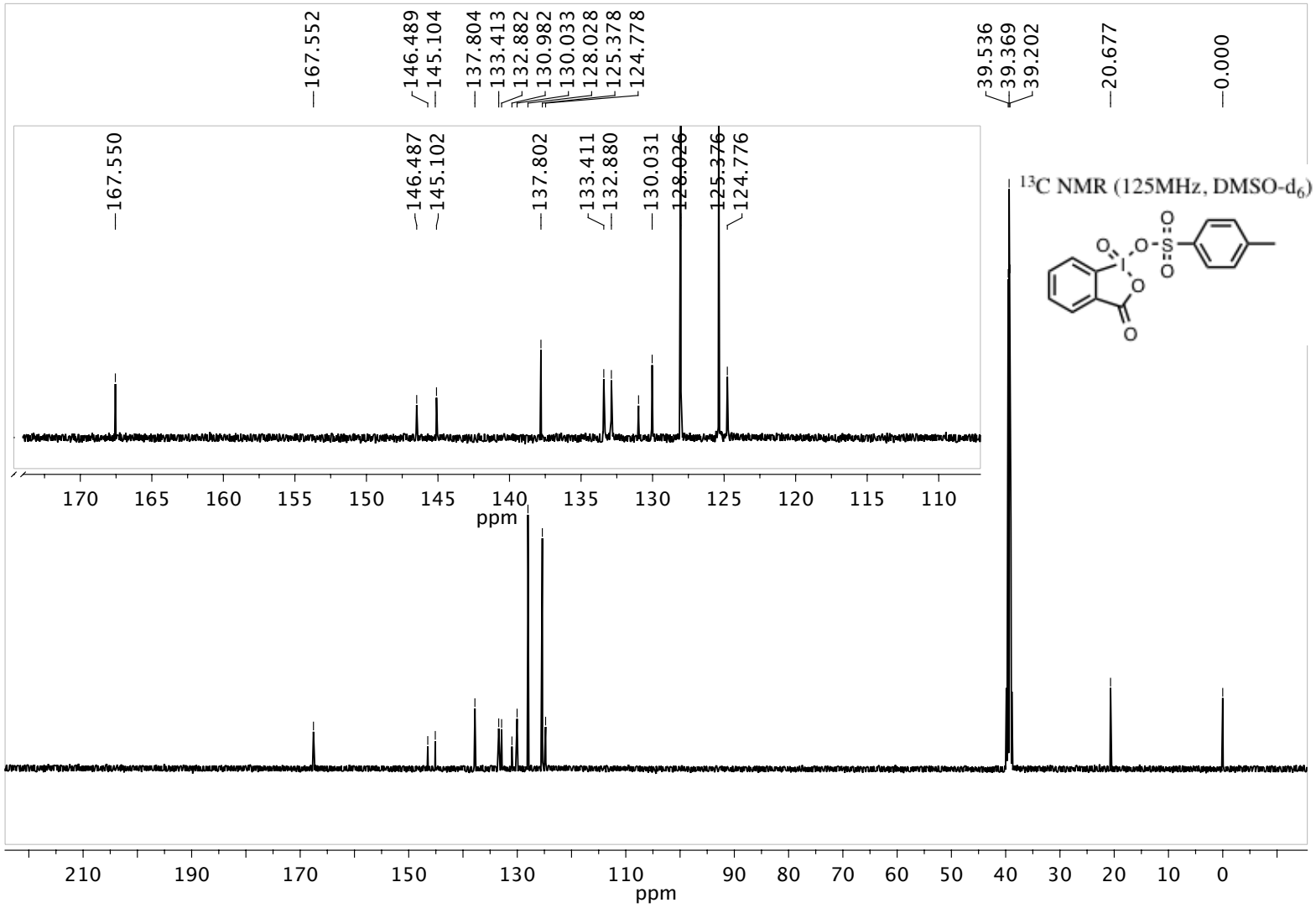
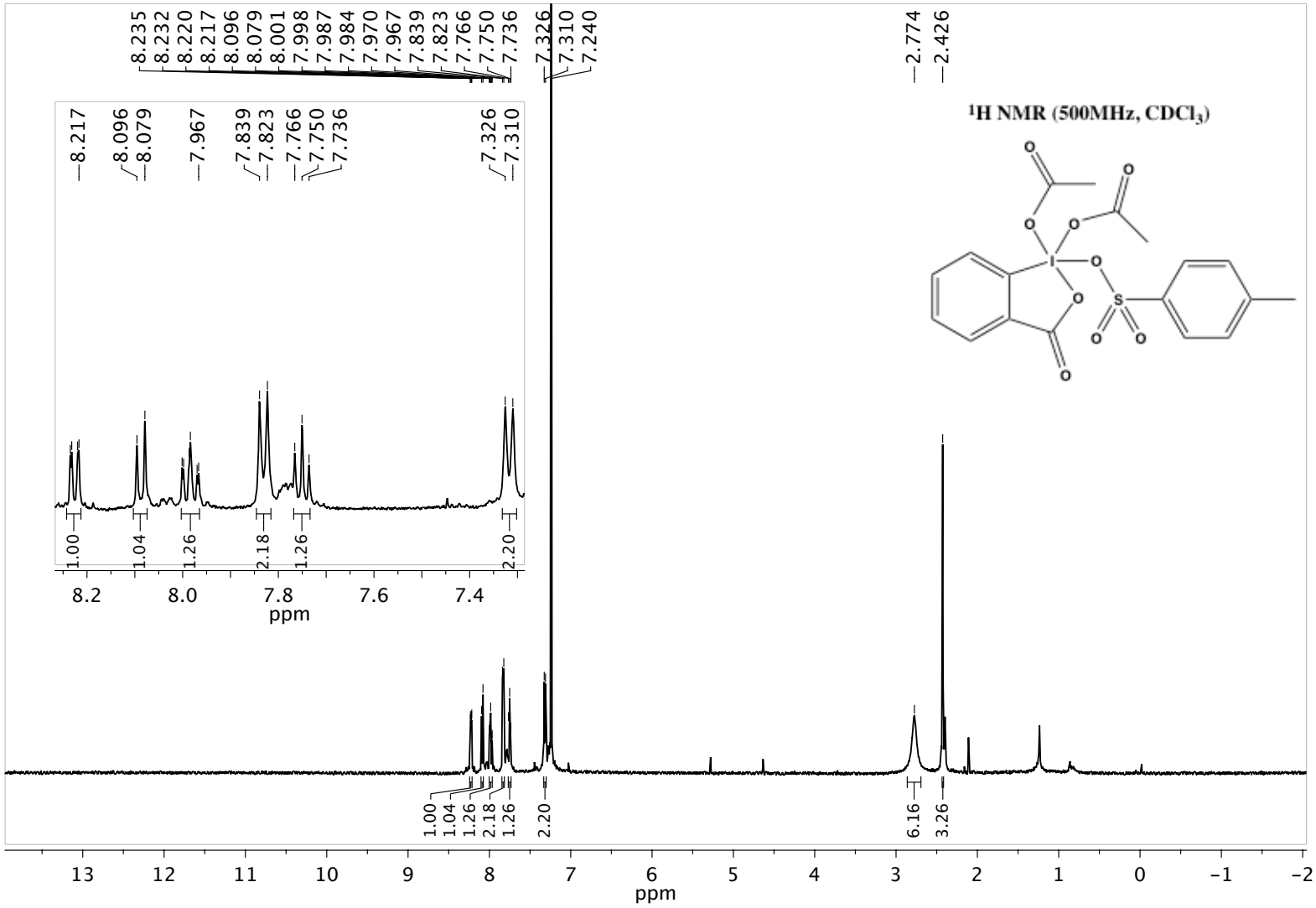
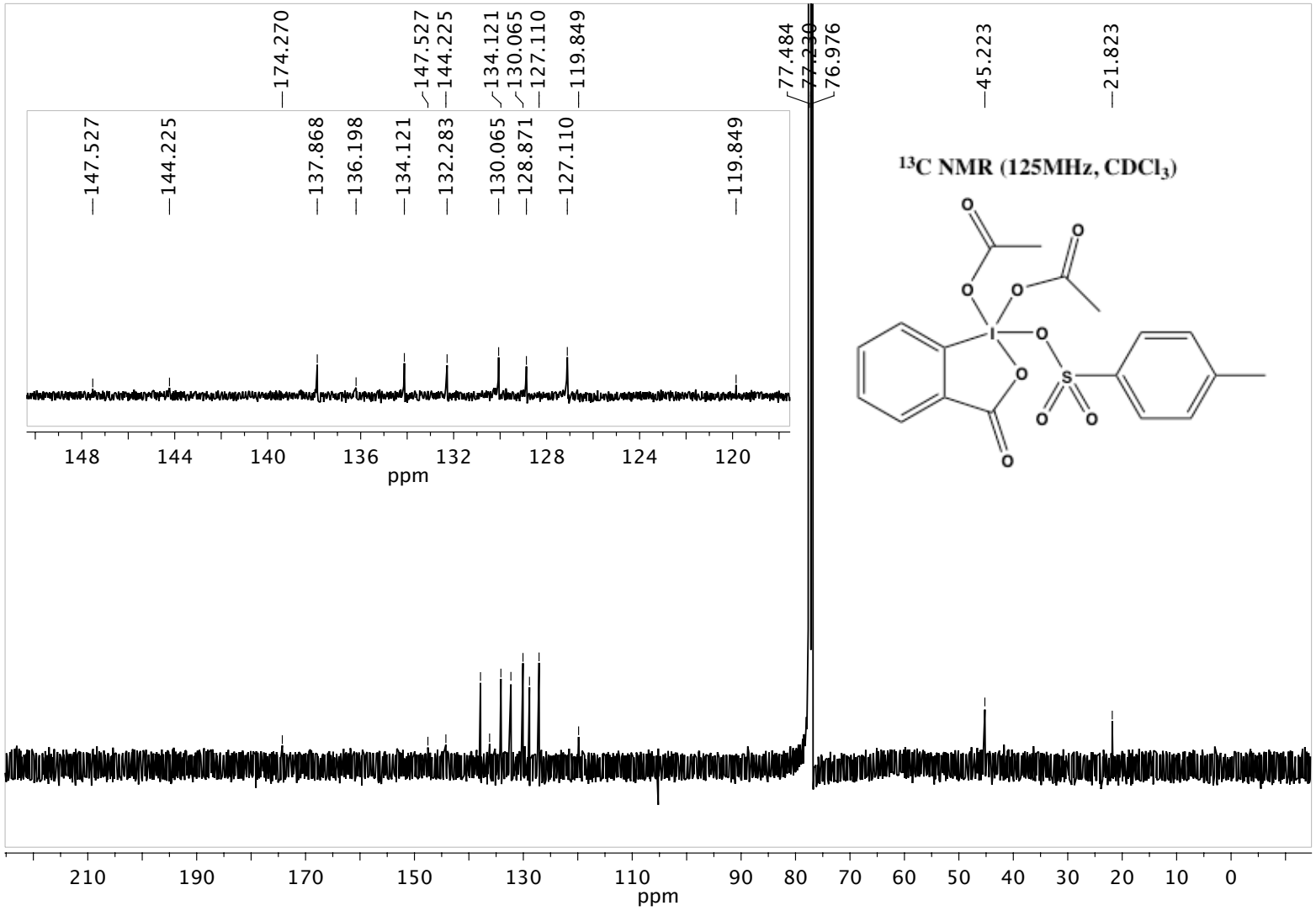
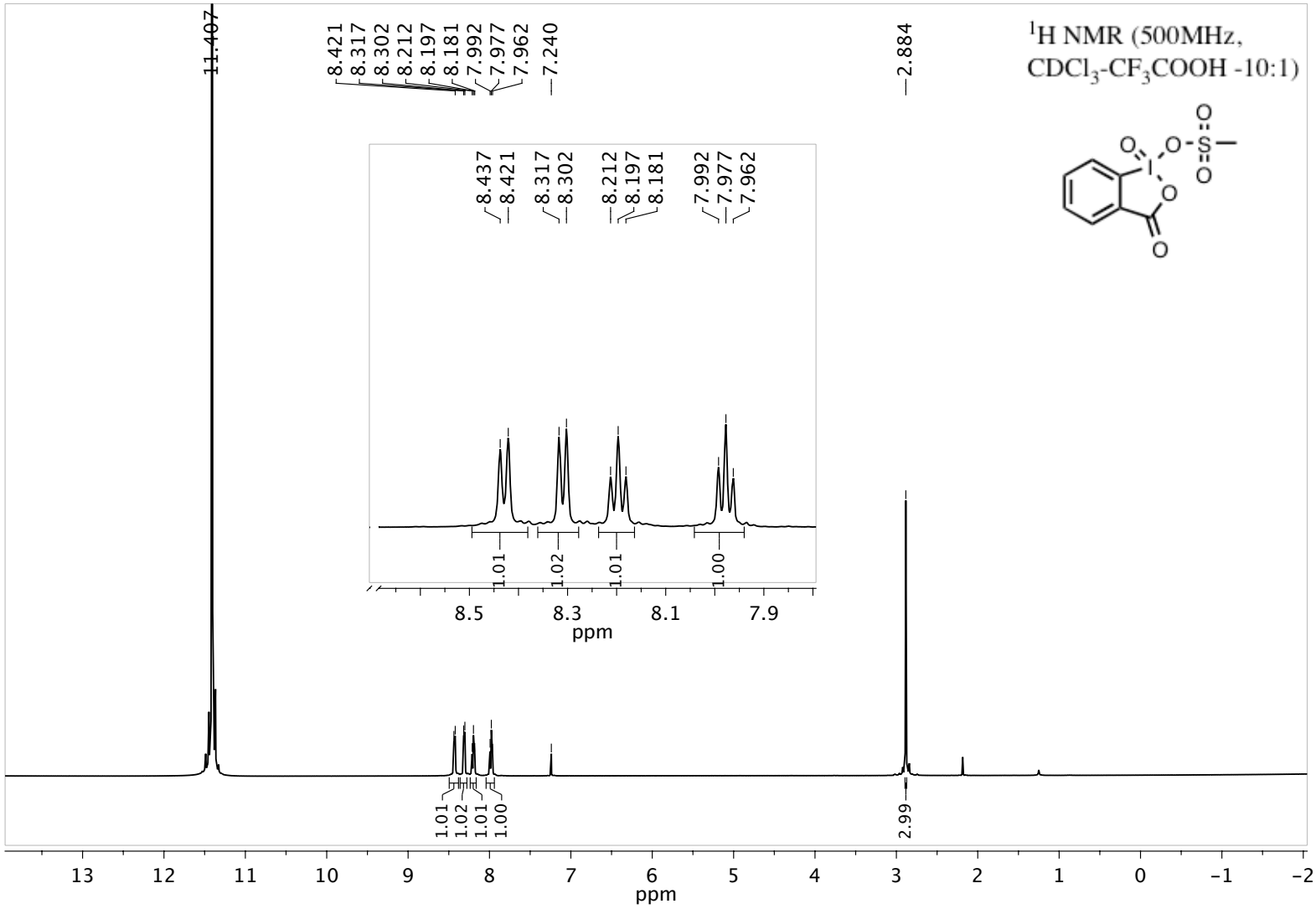
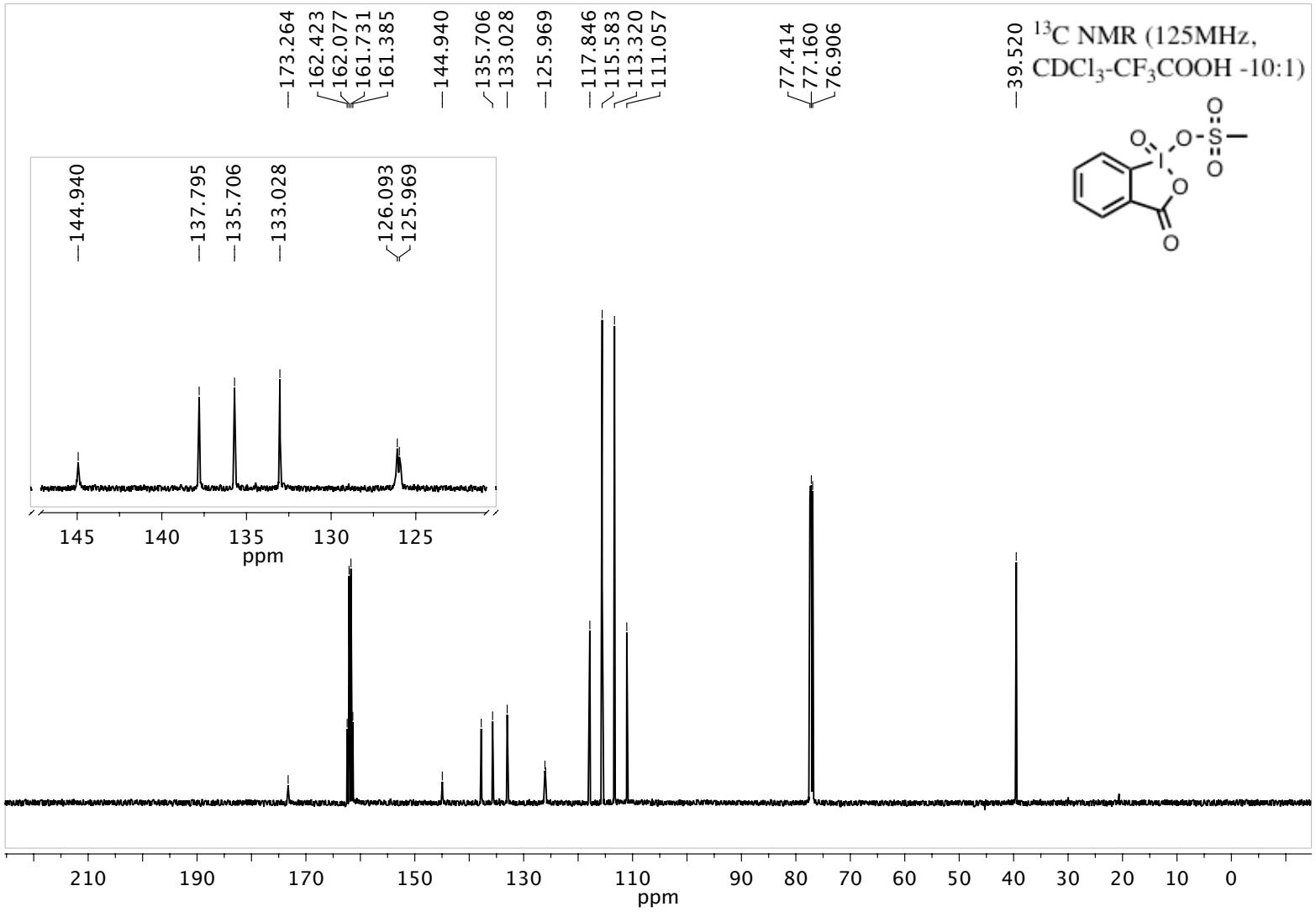
8
7
6
5
4
3
2
1
0
−1
−2
ppm

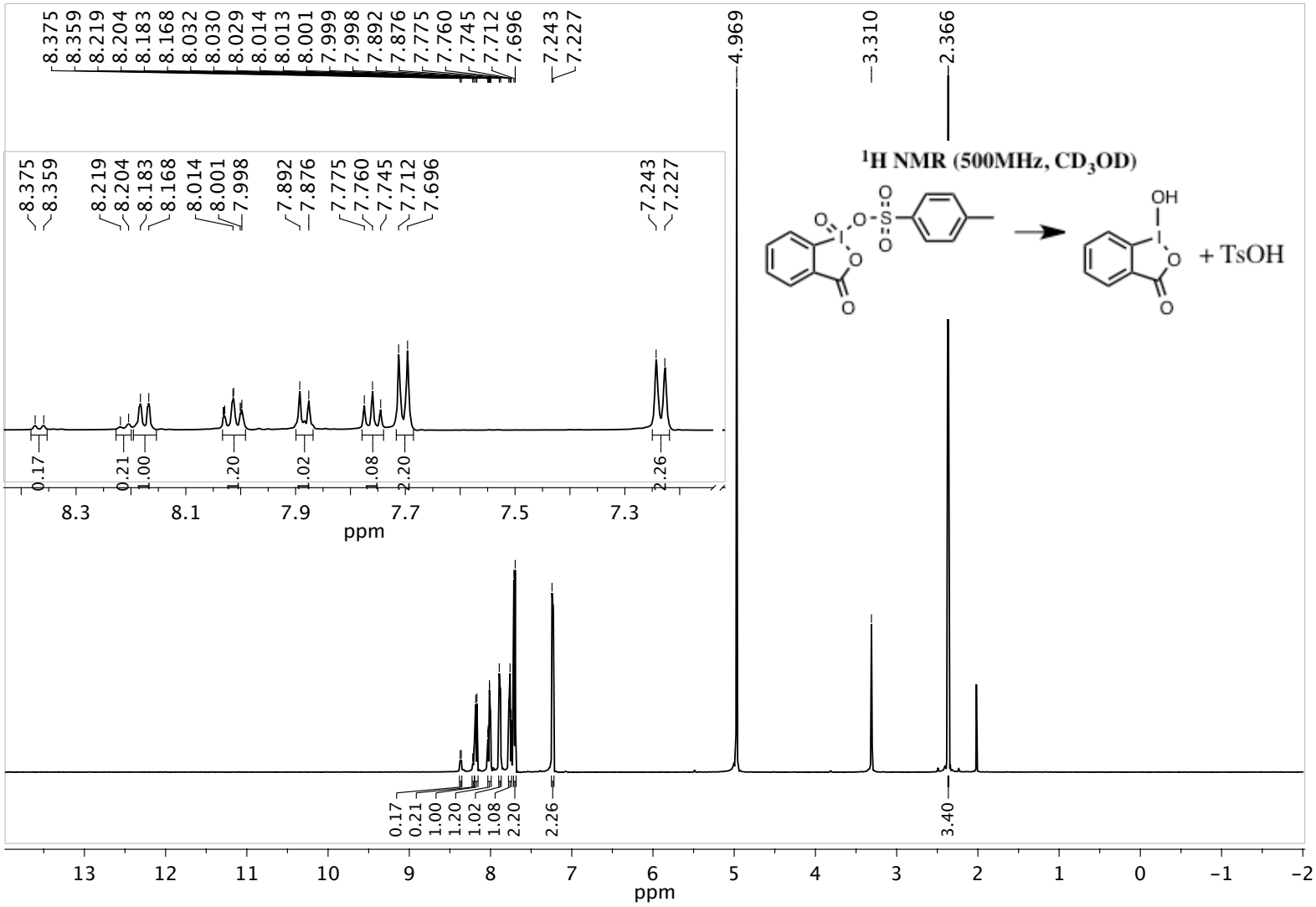


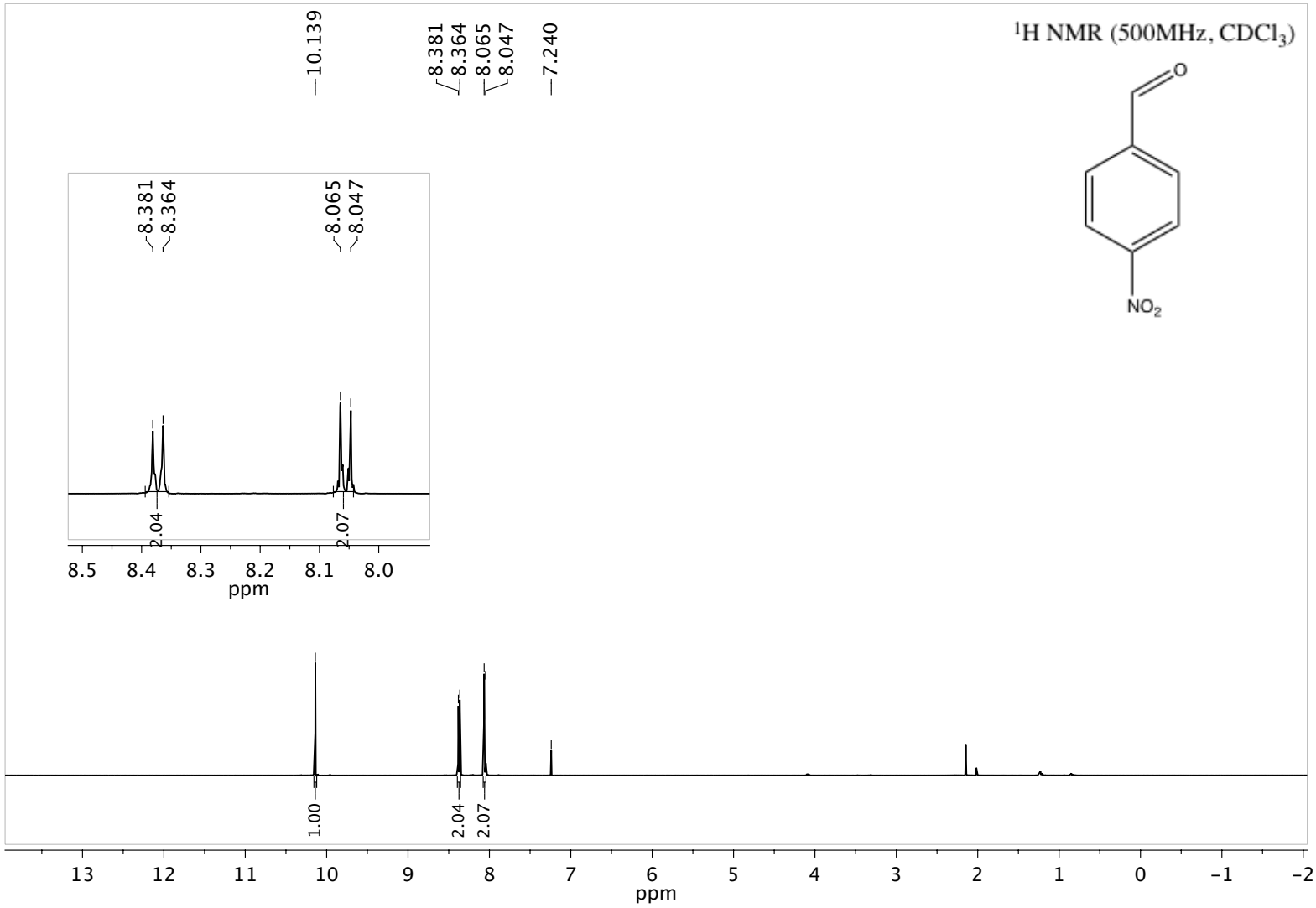


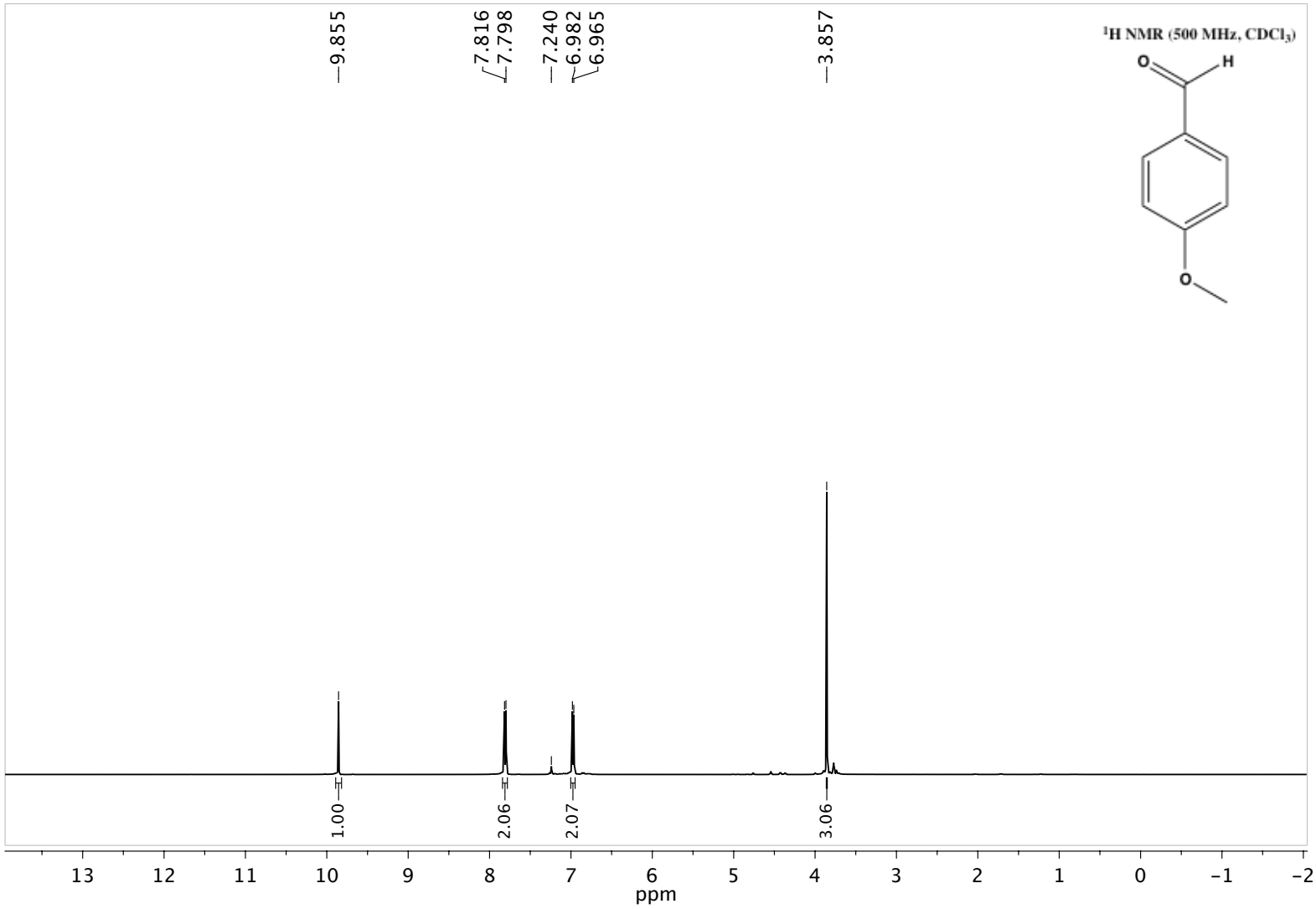


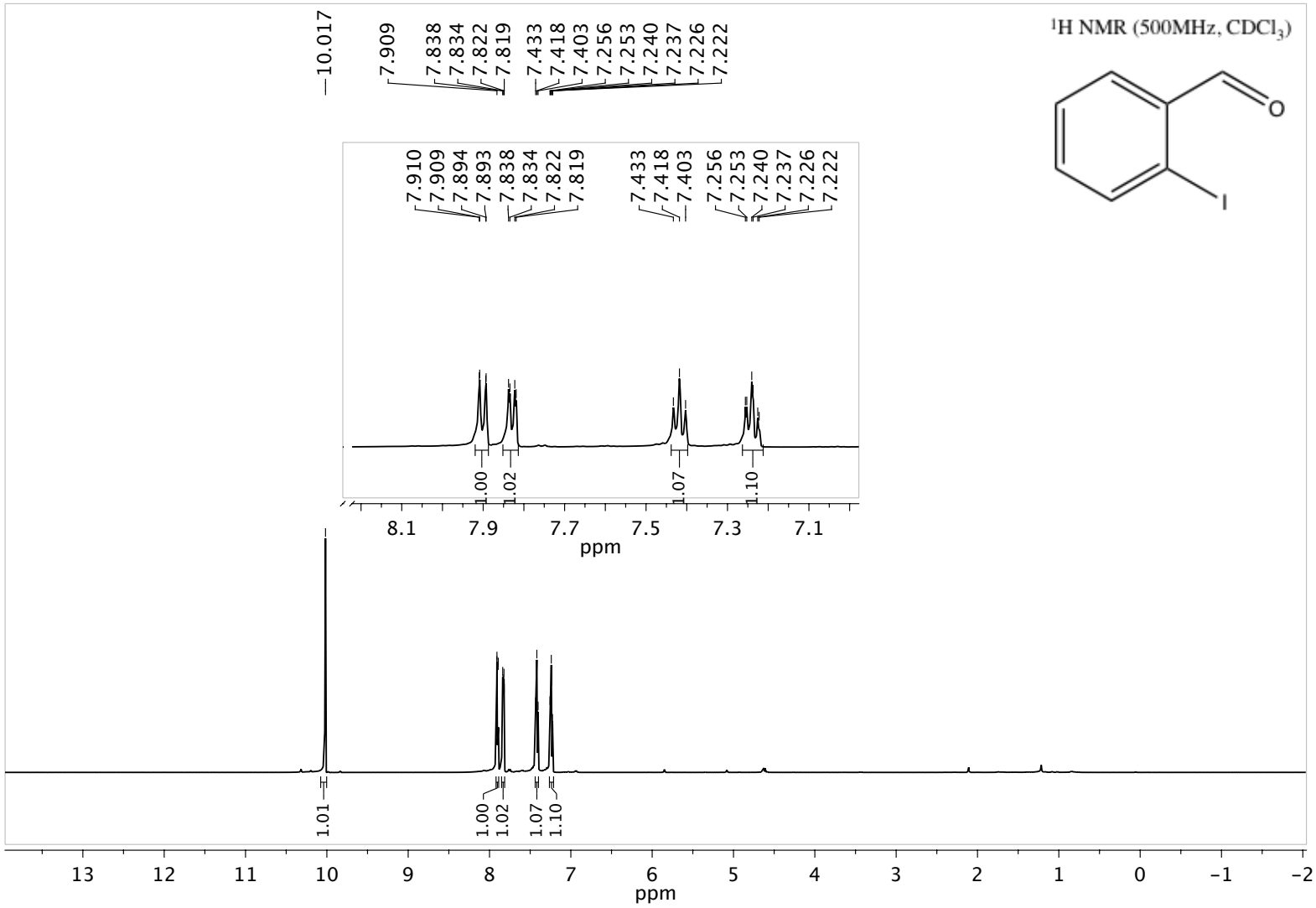


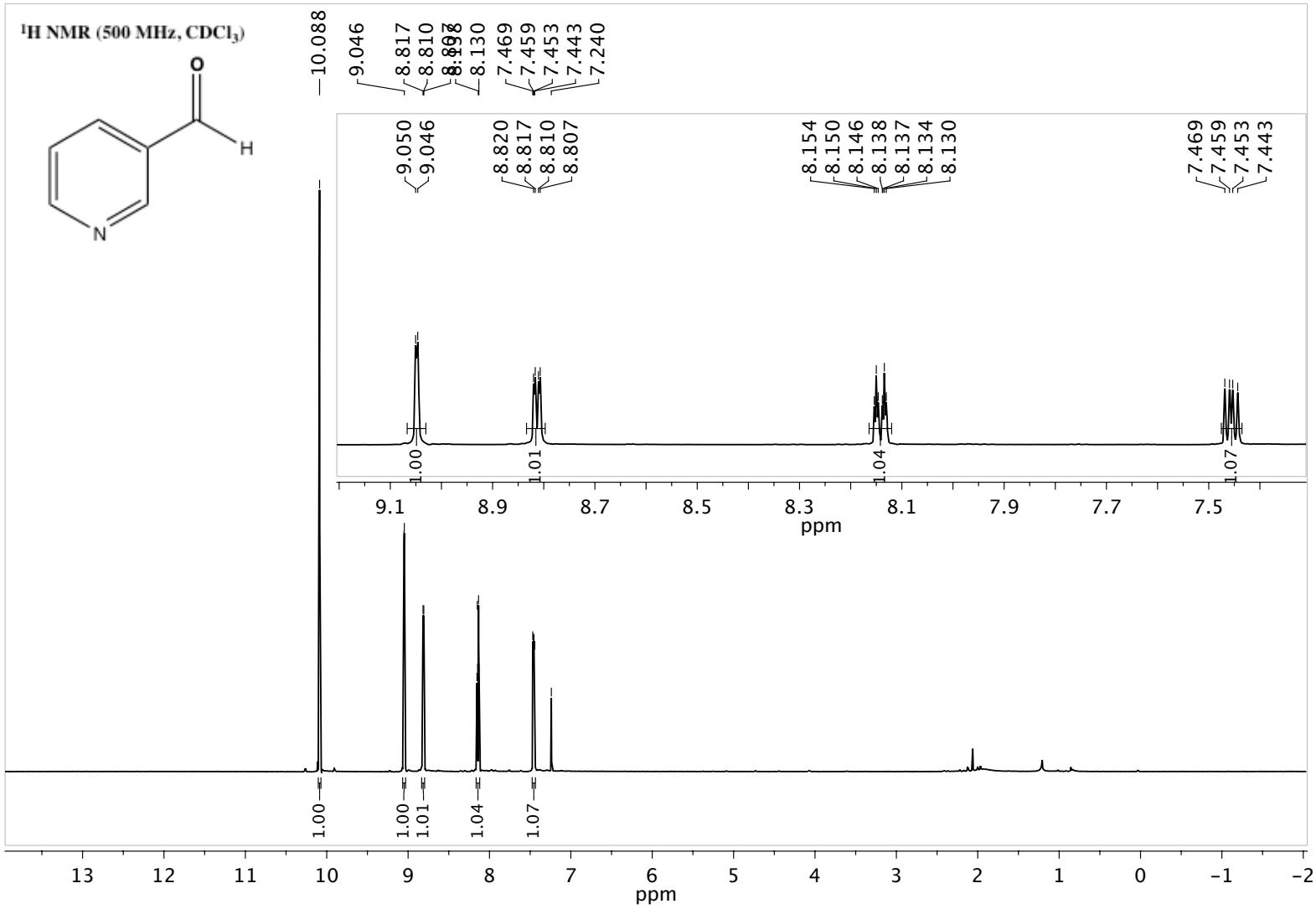


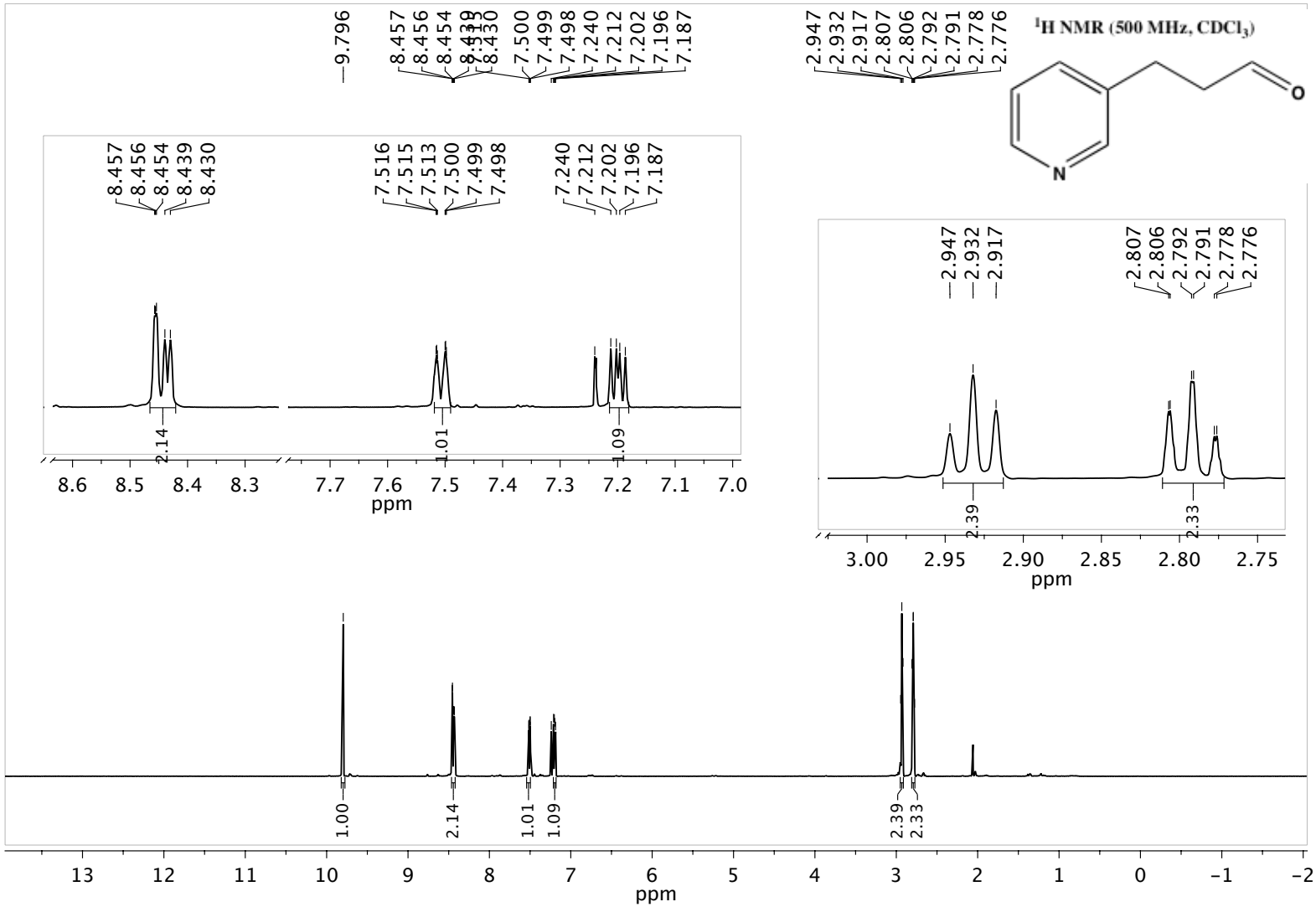


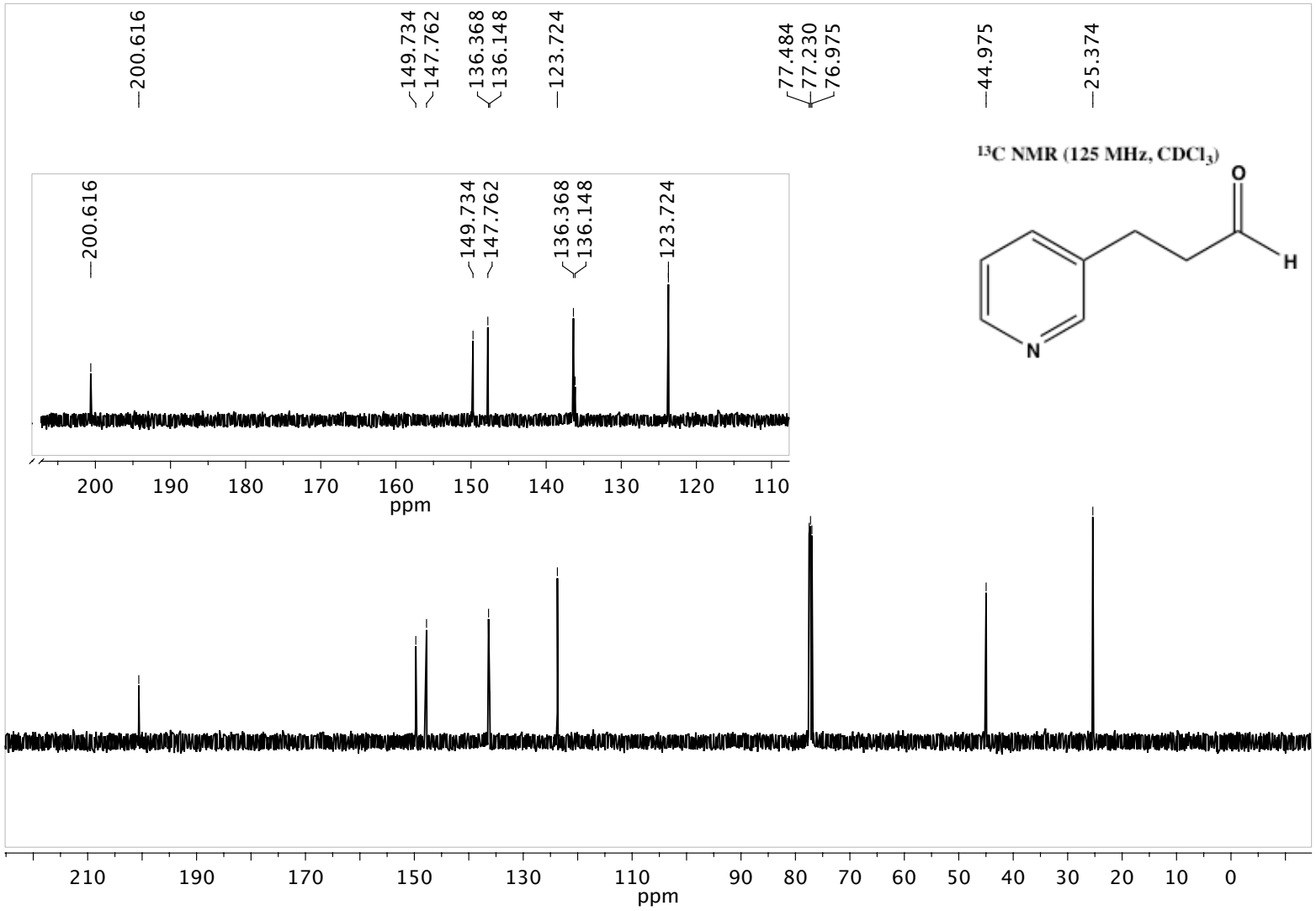


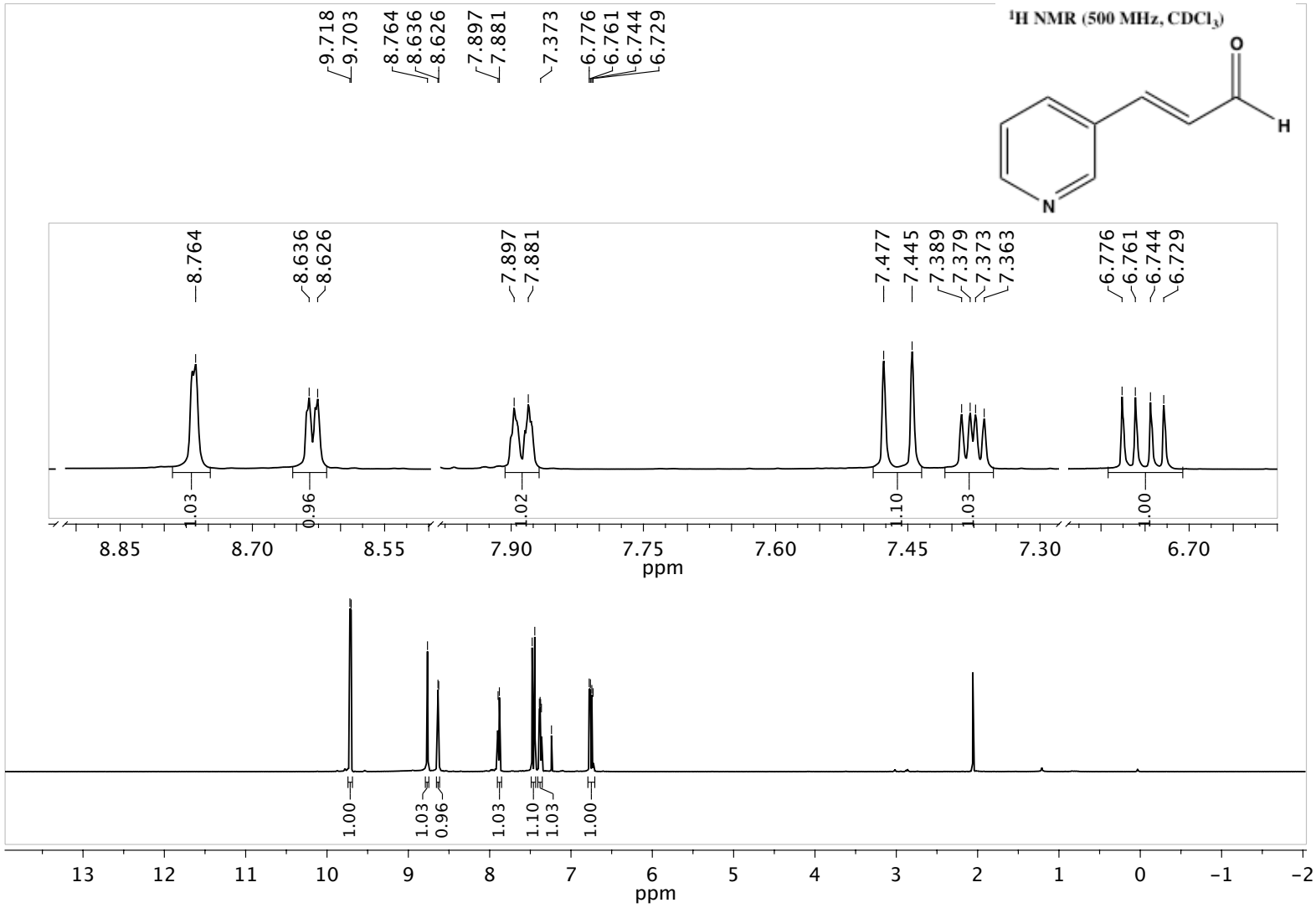


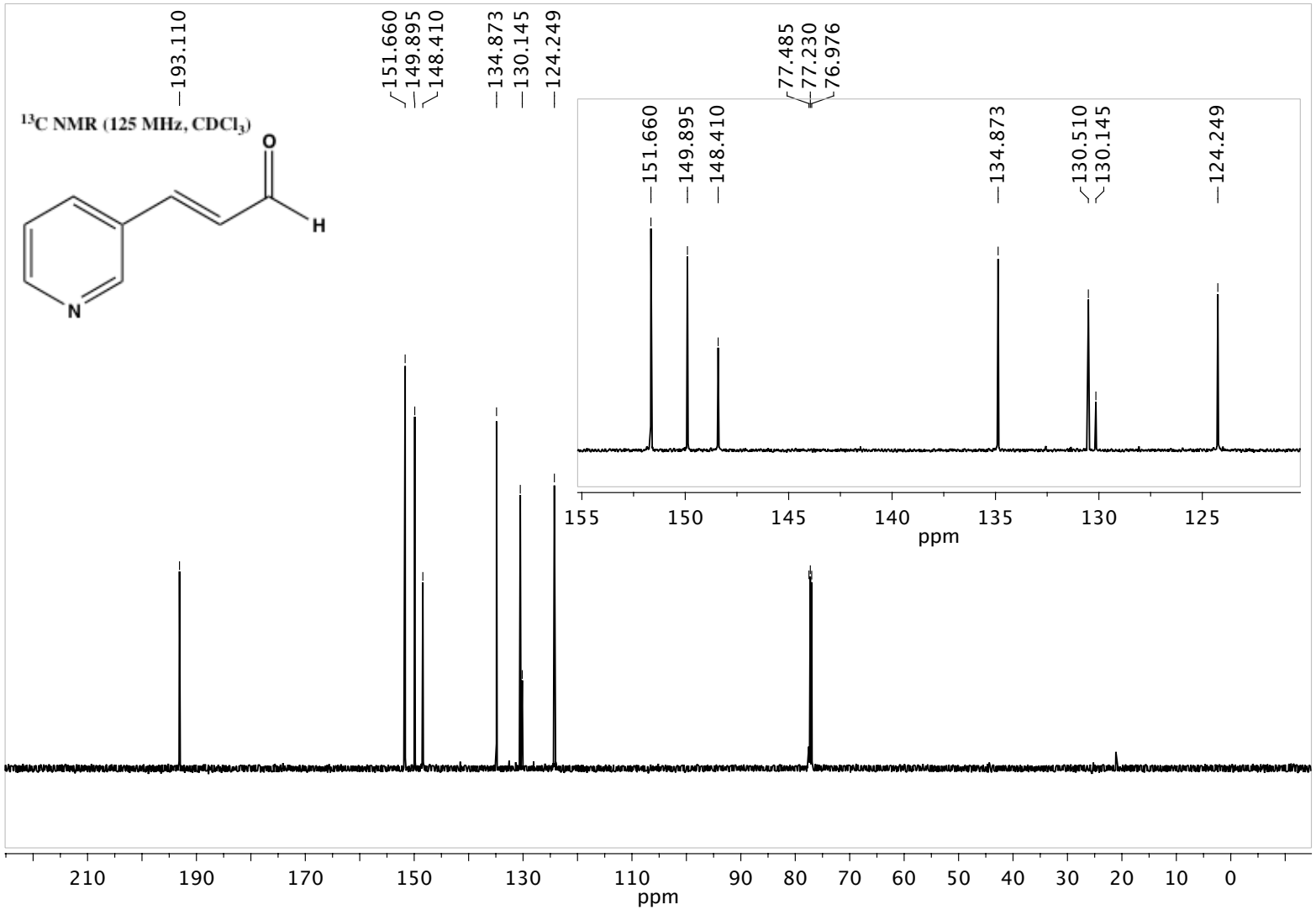


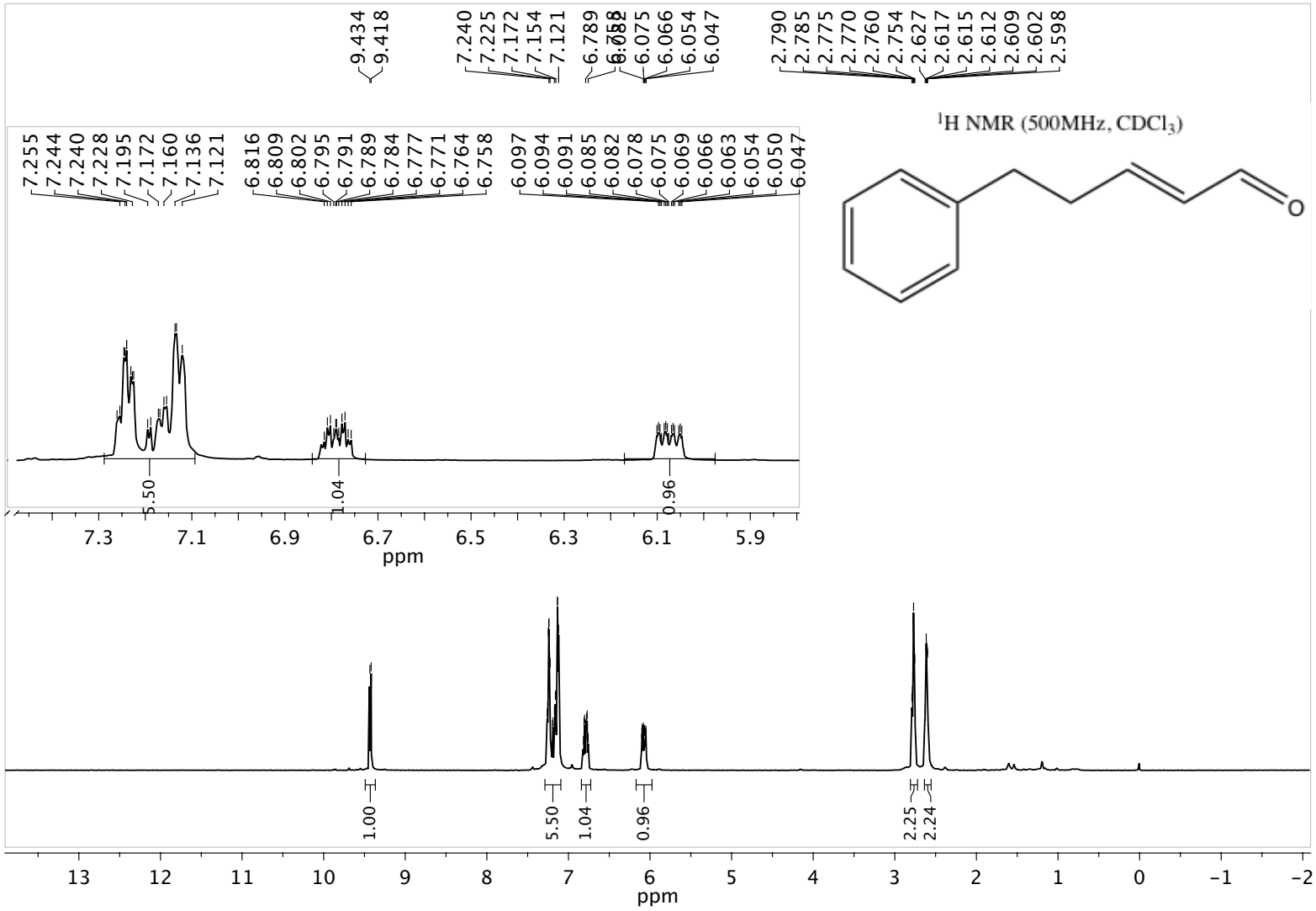


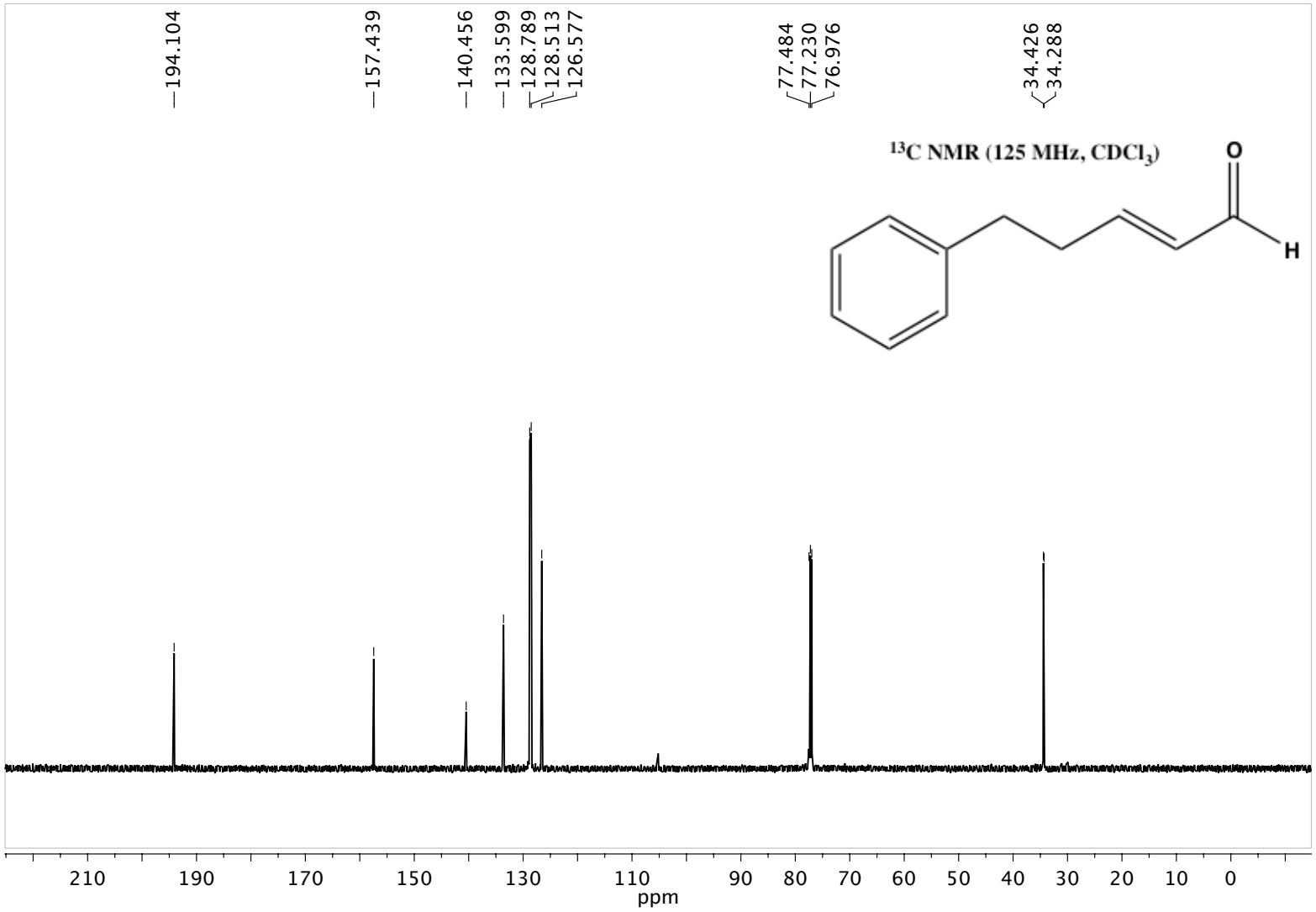


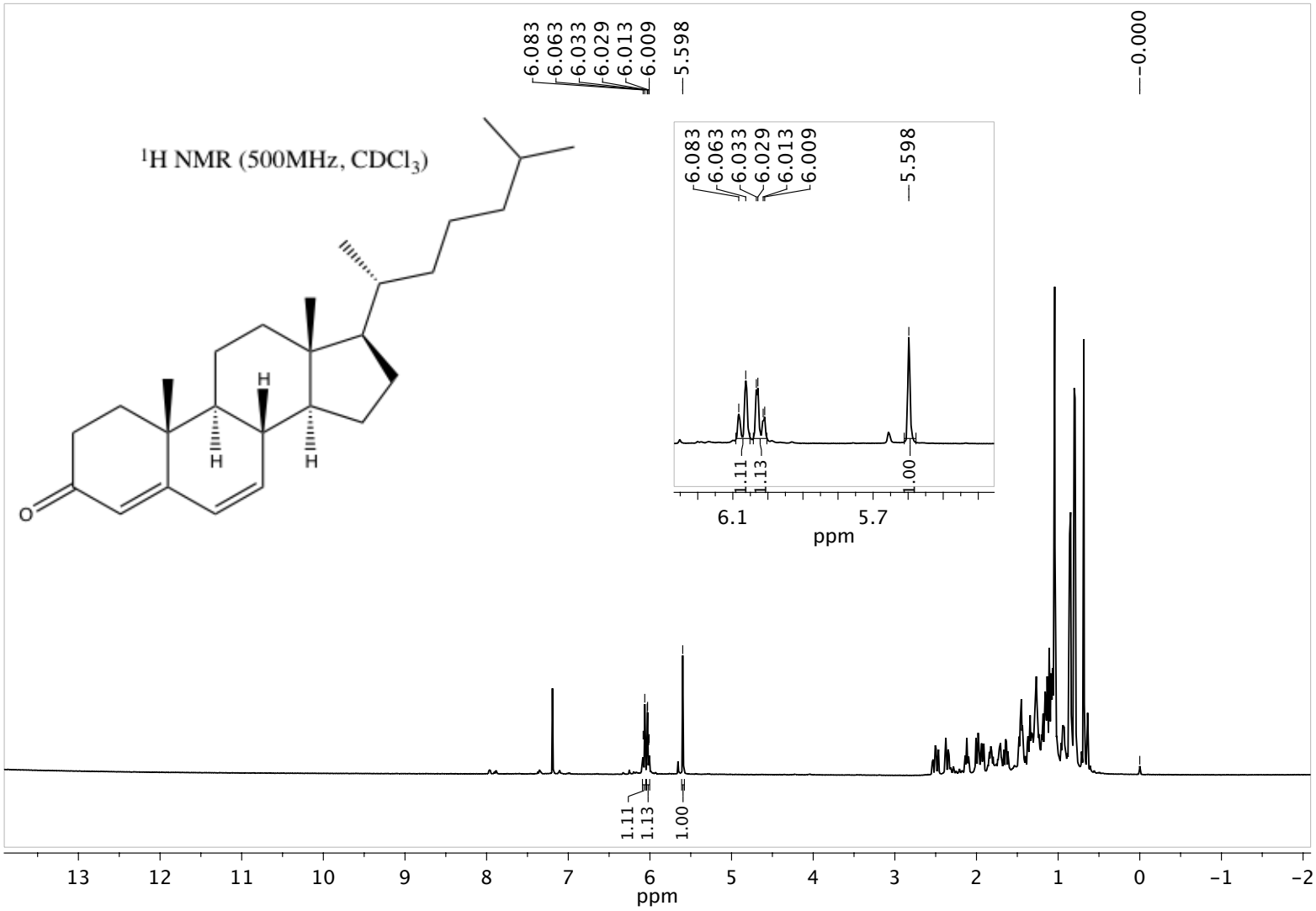


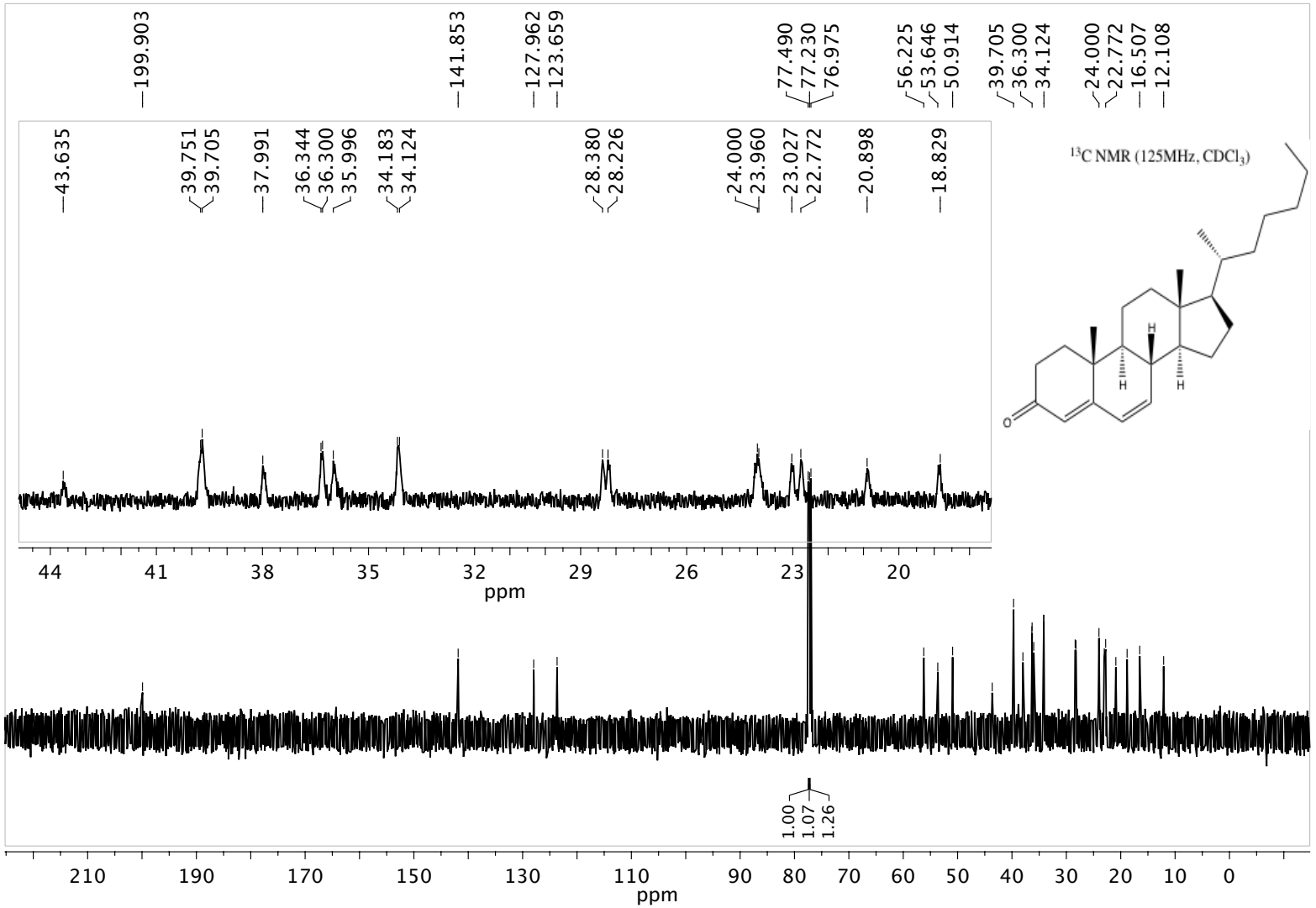








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ppm