Electrophilic Monoiodination of Terminal Alkenes

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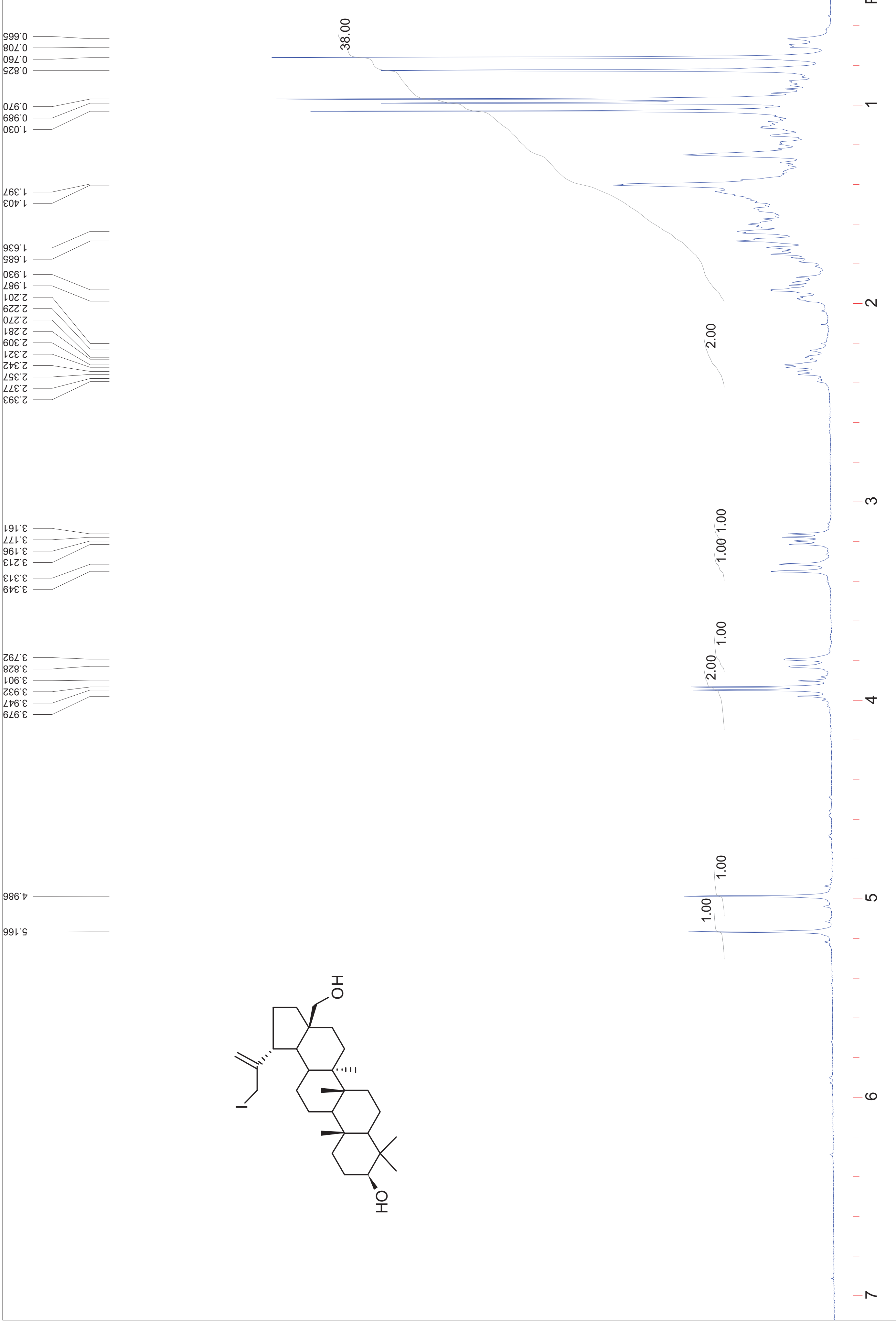
Supplementary Information

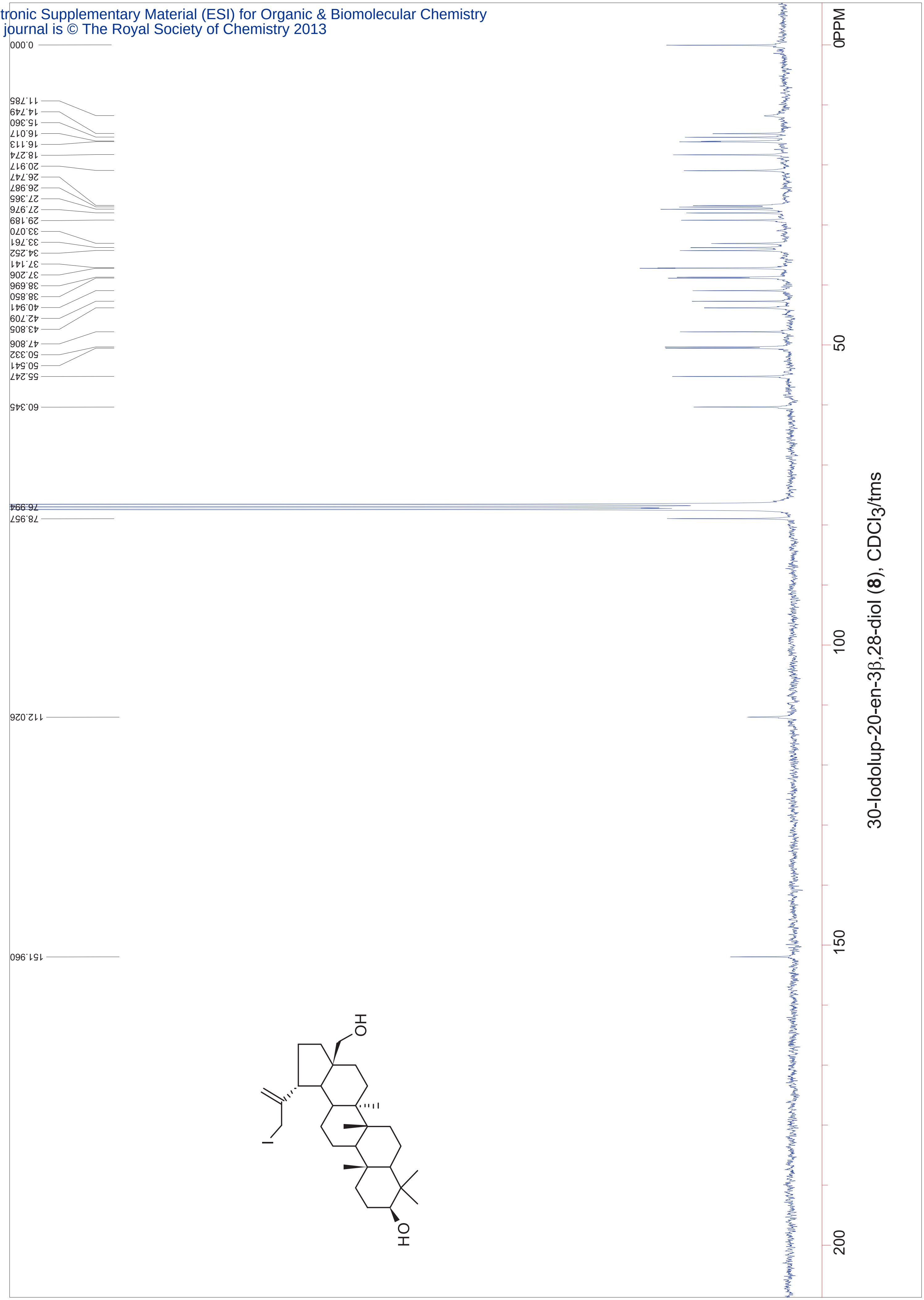
1. ^{1}H and ^{13}C NMR spectra

NMR spectra for all synthesized compounds (300 MHz ^{1}H NMR and 75 MHz ^{13}C NMR) were recorded using Varian Unity Inova 300. ^{1}H and ^{13}C NMR chemical shifts are referenced to tetramethylsilane as internal standard and reported in parts per million (ppm).

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry



30-Iodolup-20-en-3β,28-diol (**8**), $CDCl_3$/tms



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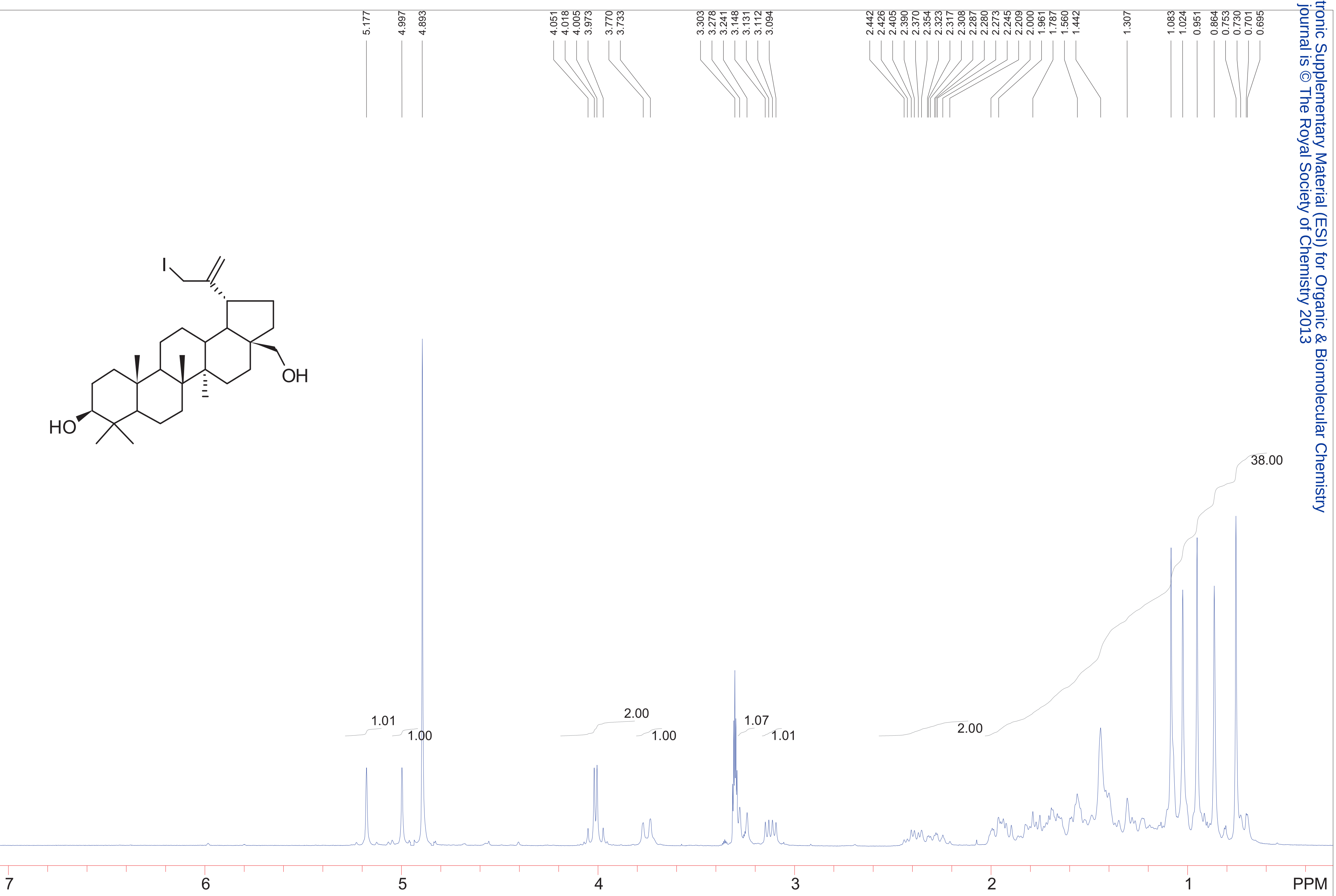
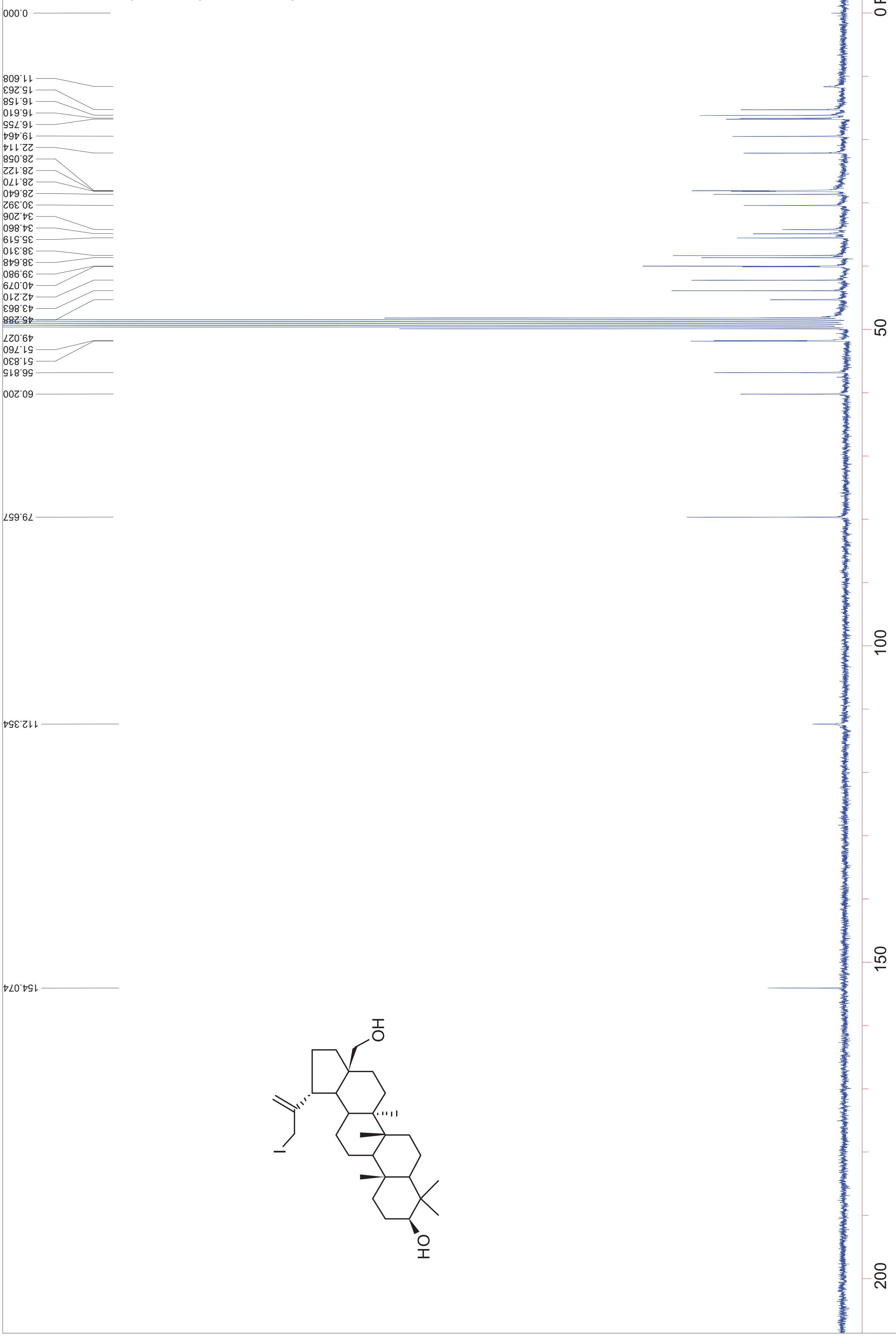


30-Iodolup-20-en-3β,28-diol (**8**), CD_3OD/tms



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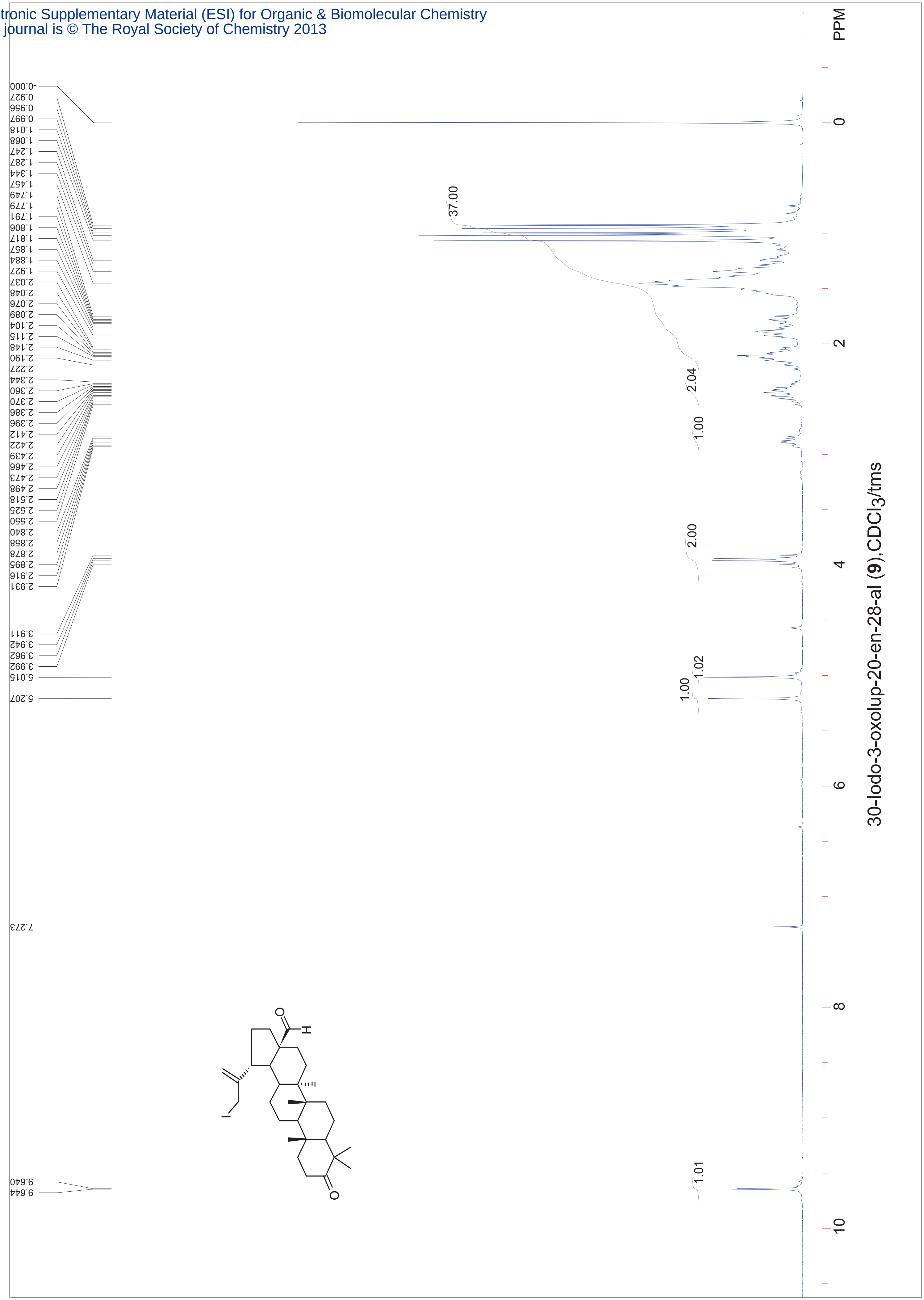

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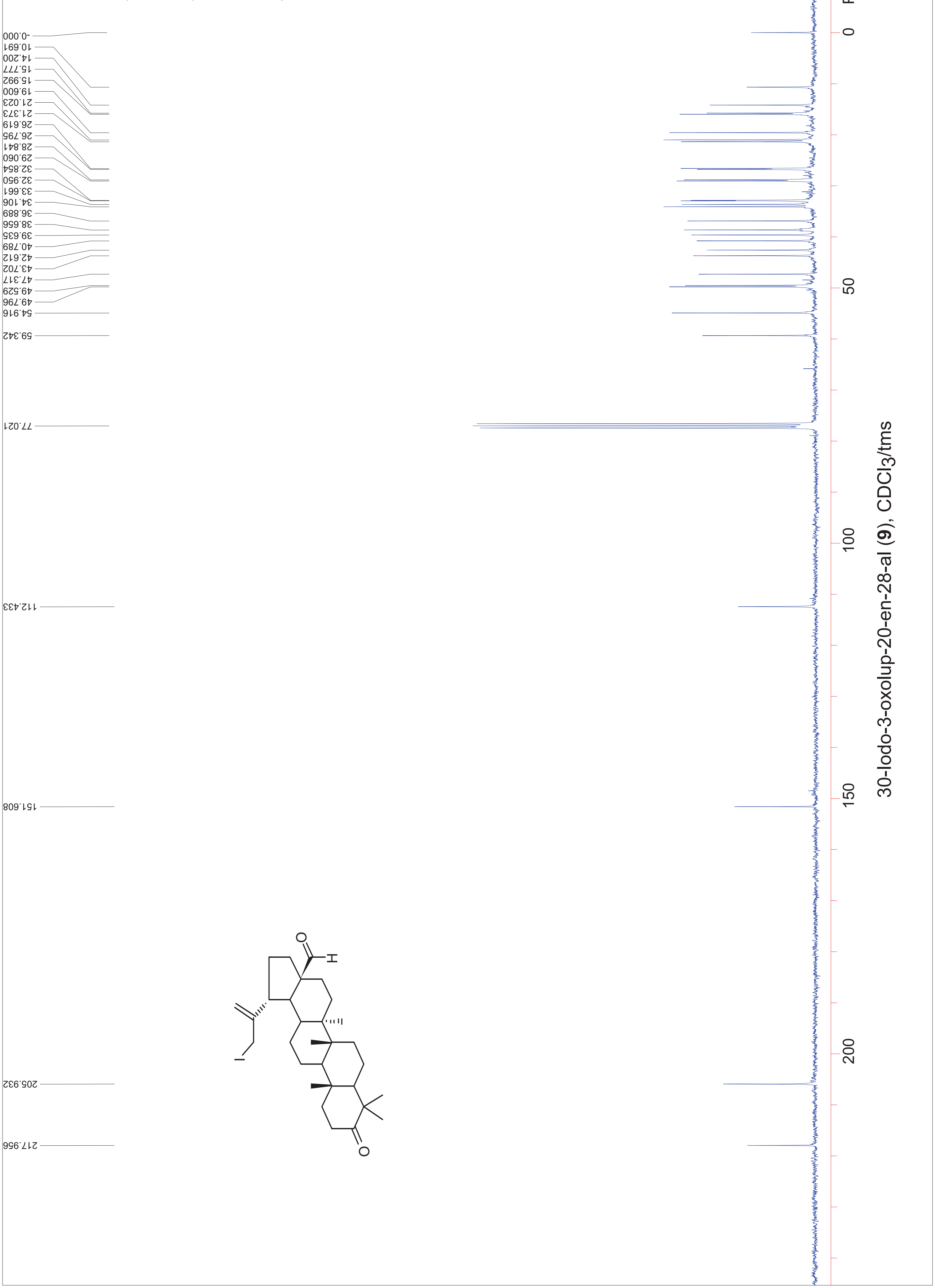

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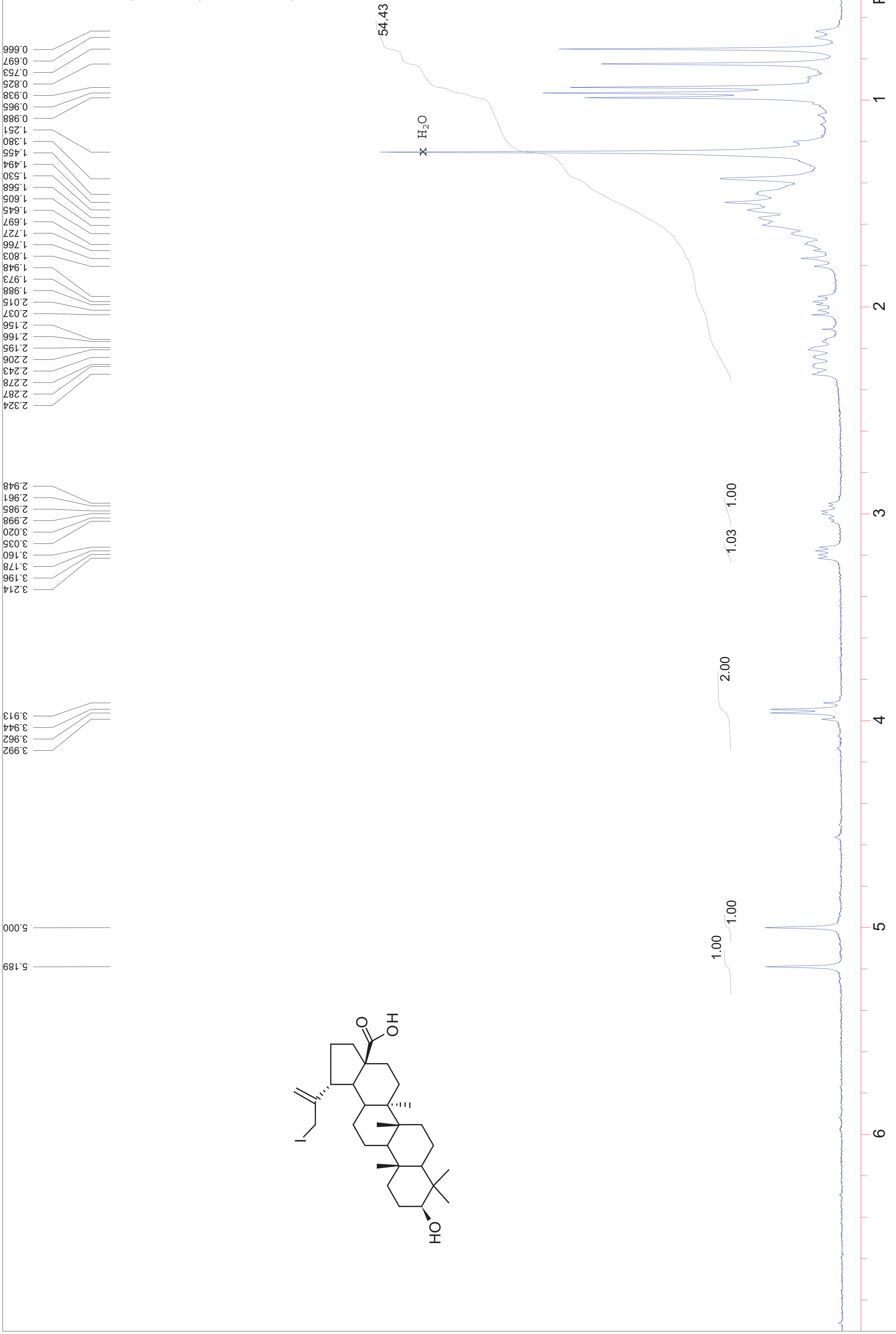

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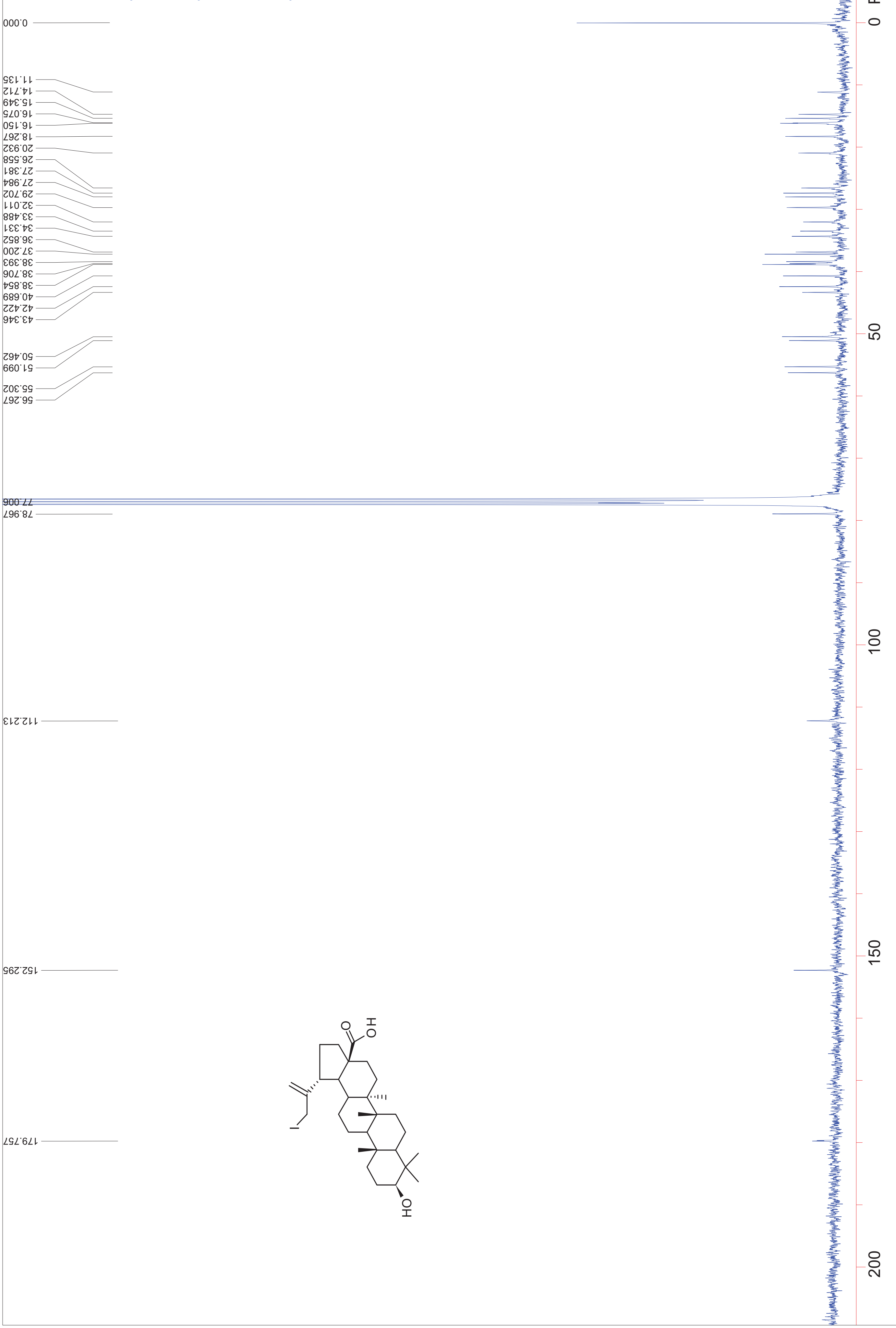

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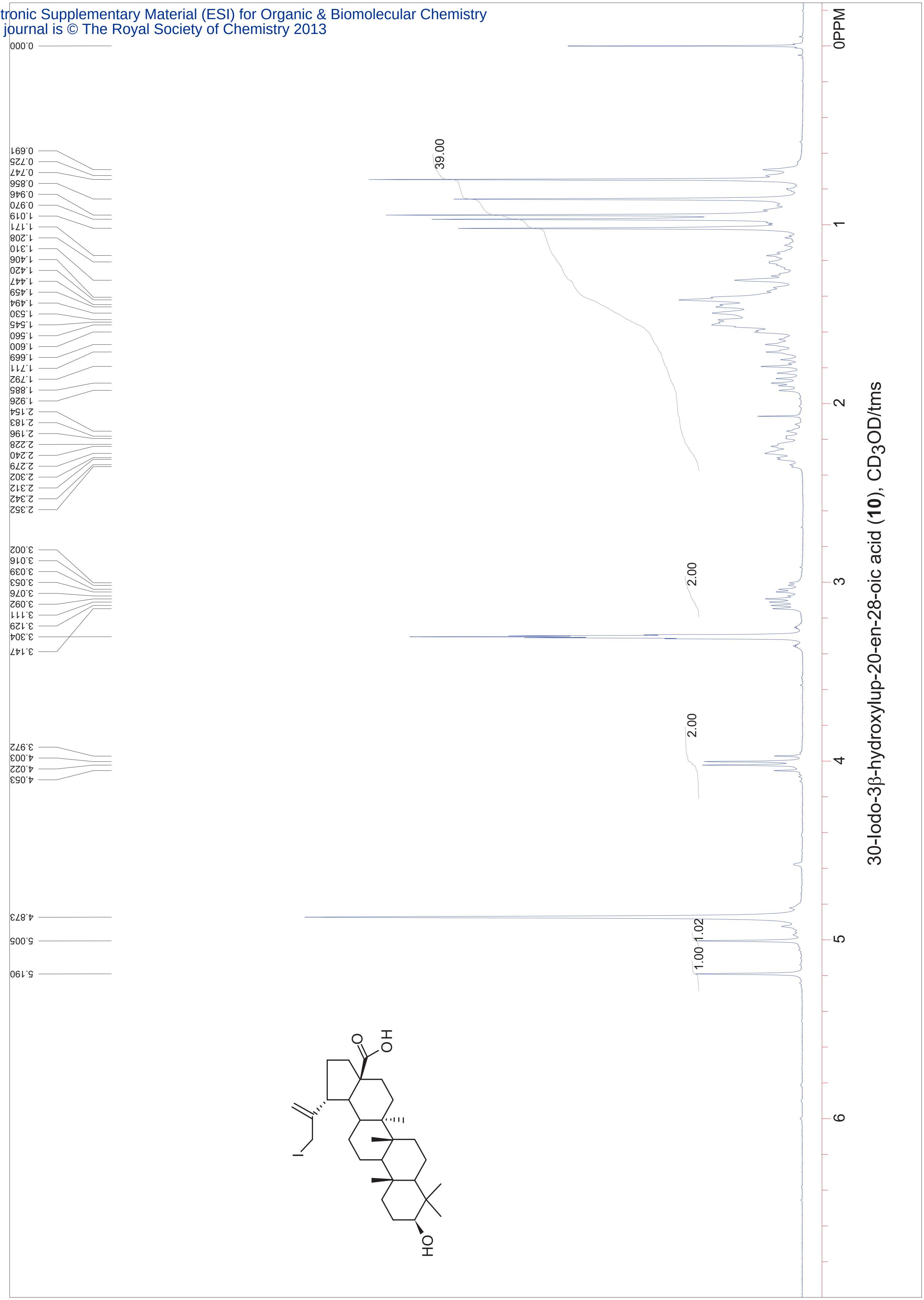

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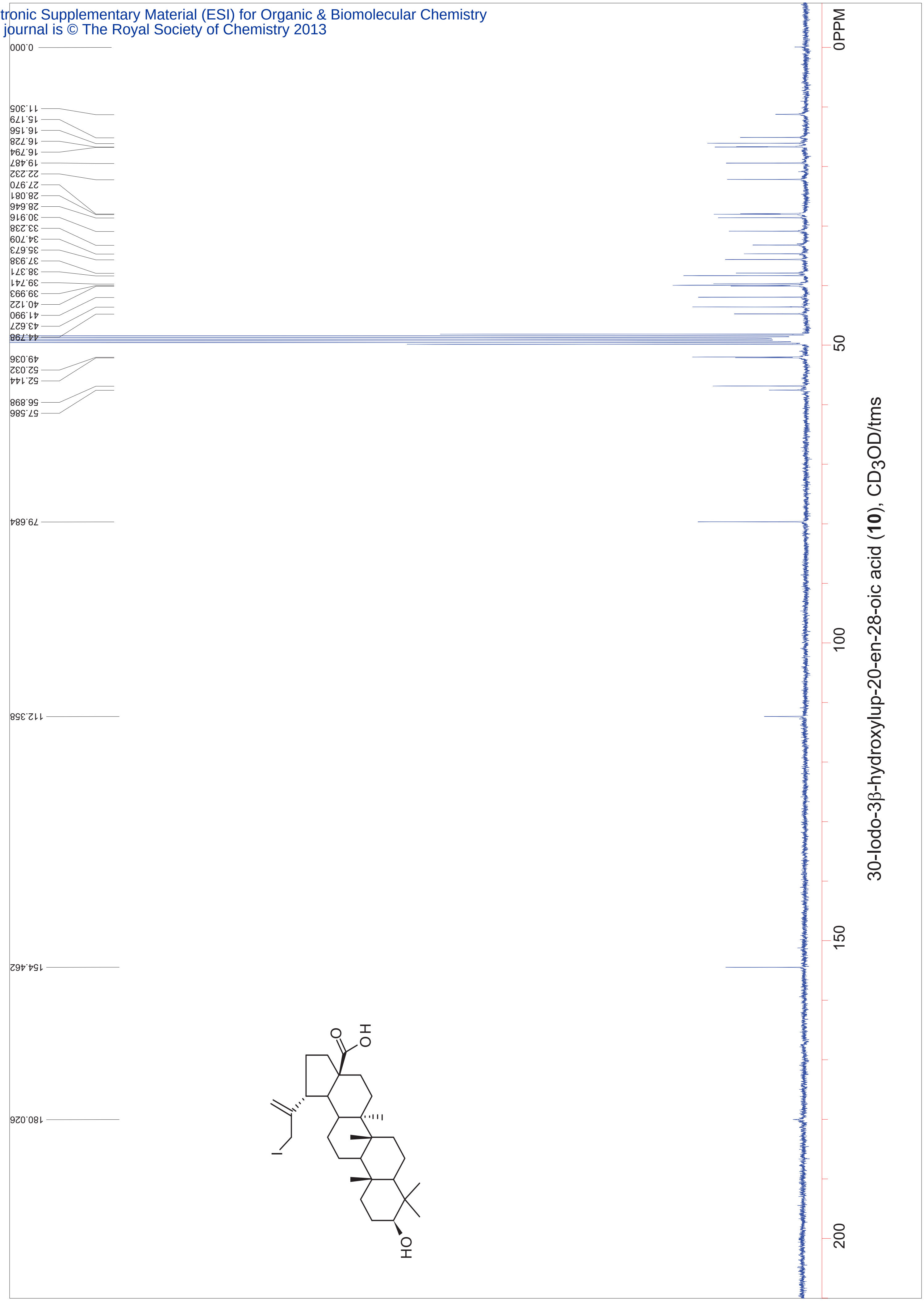

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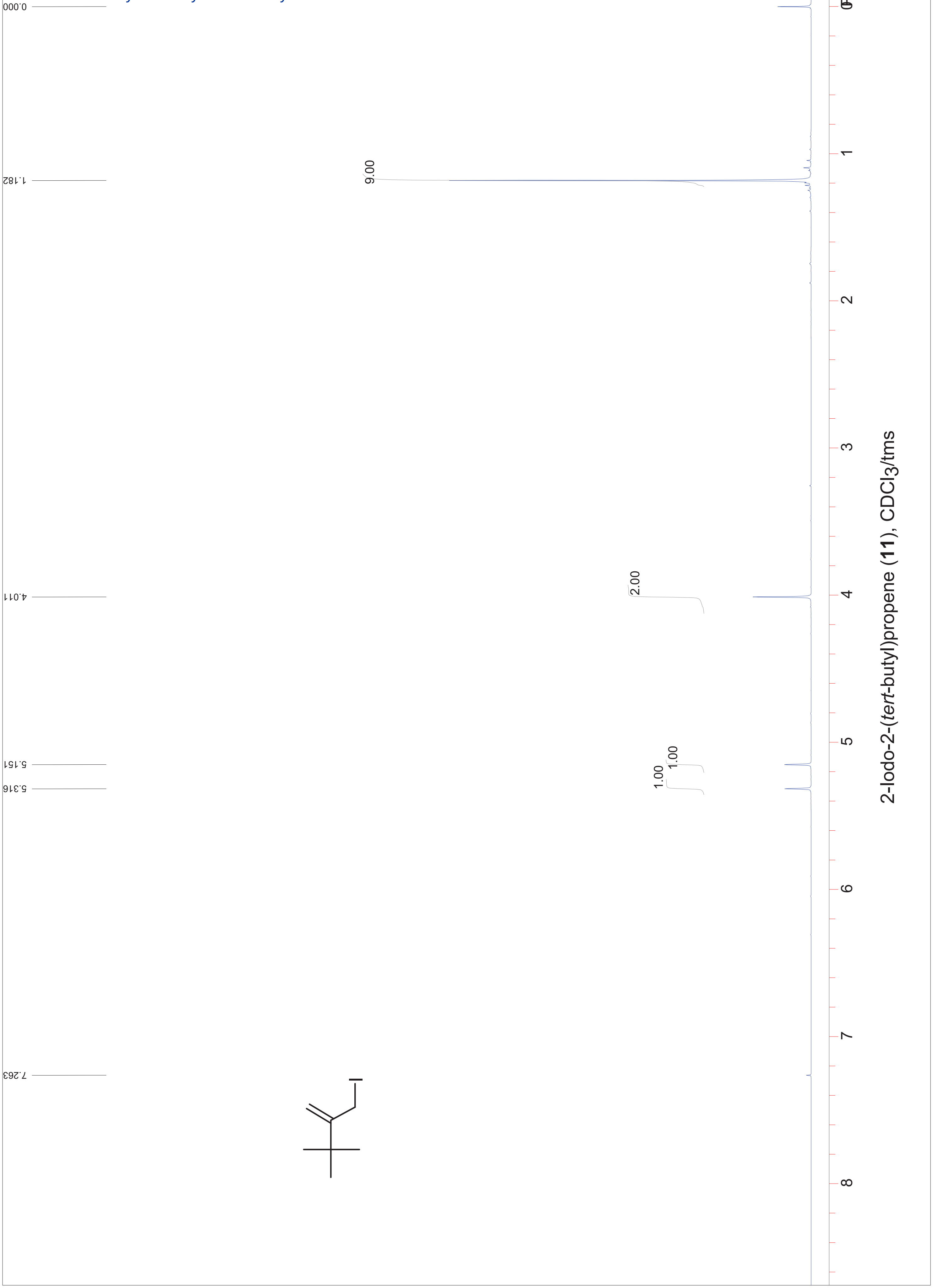
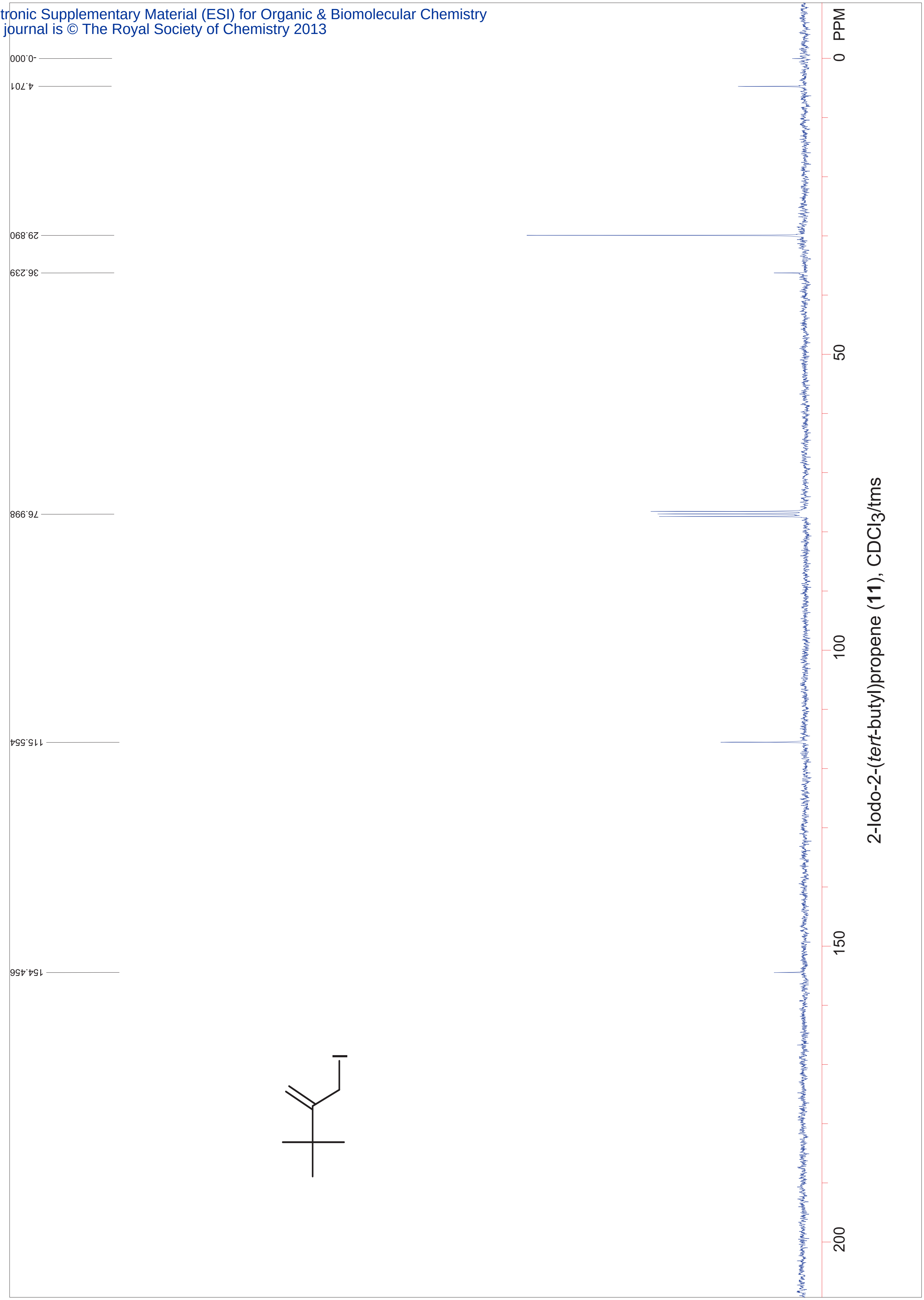
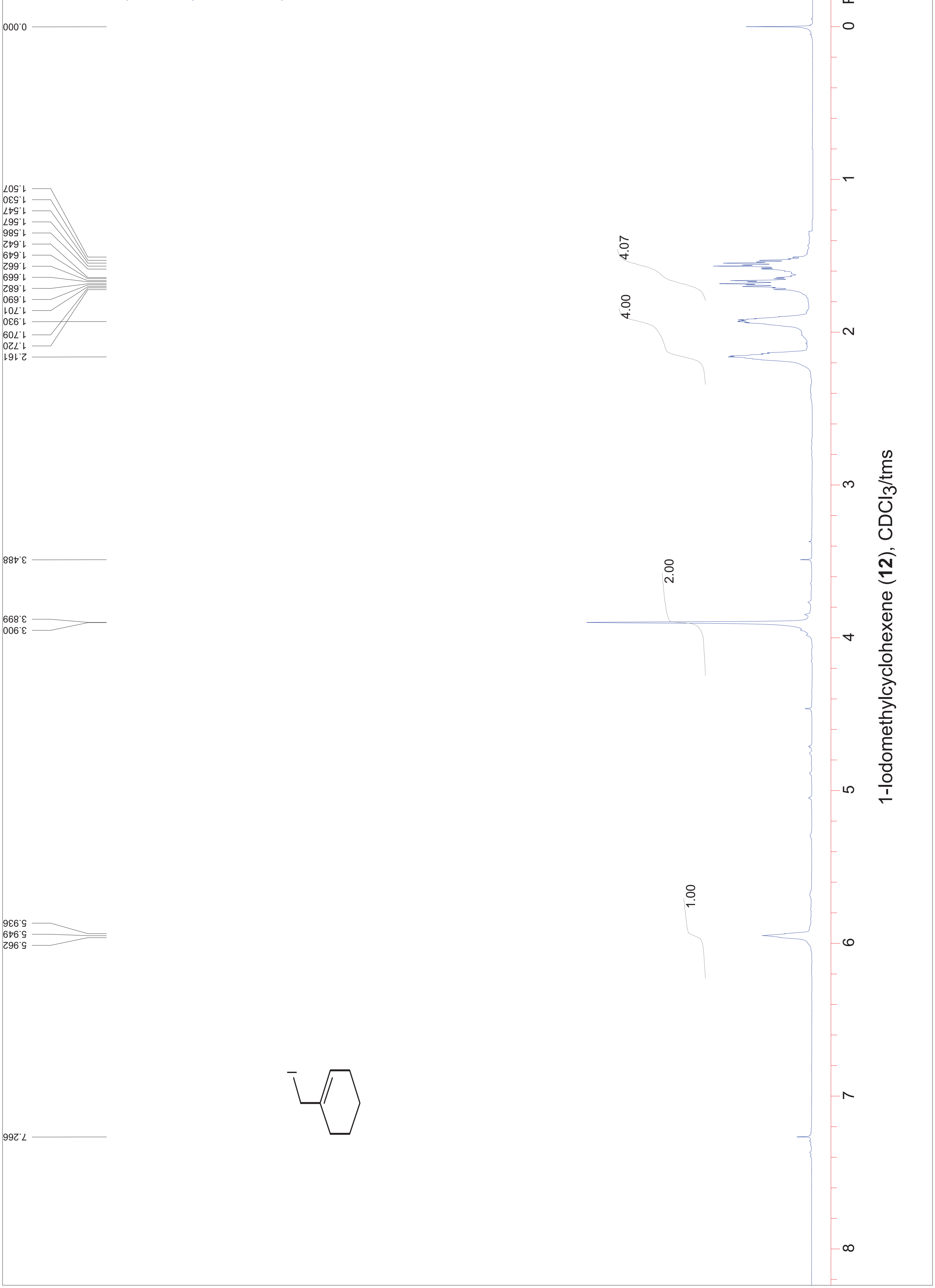


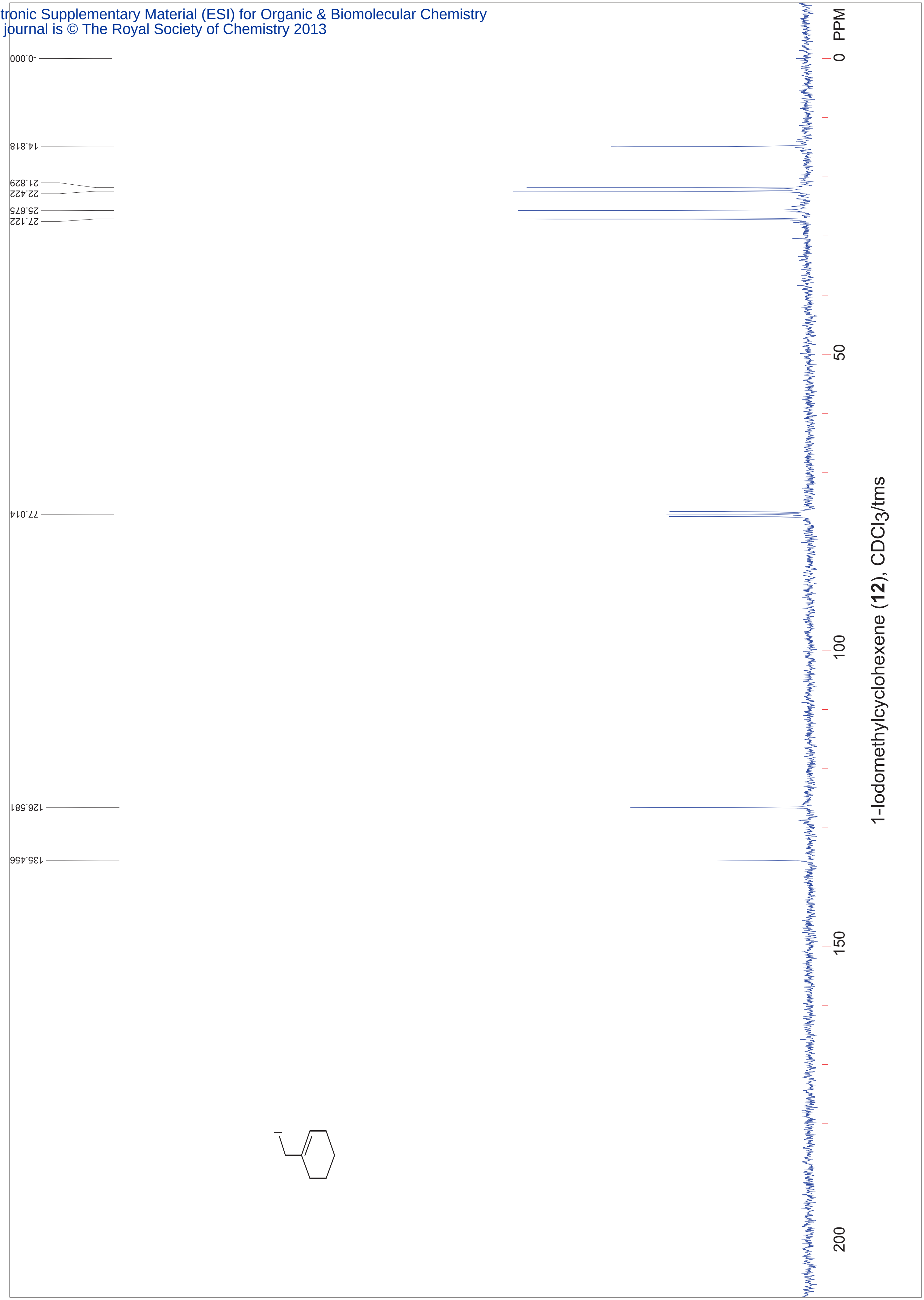
2-Iodo-2-(*tert*-butyl)propene (**11**), $CDCl_3$/tms



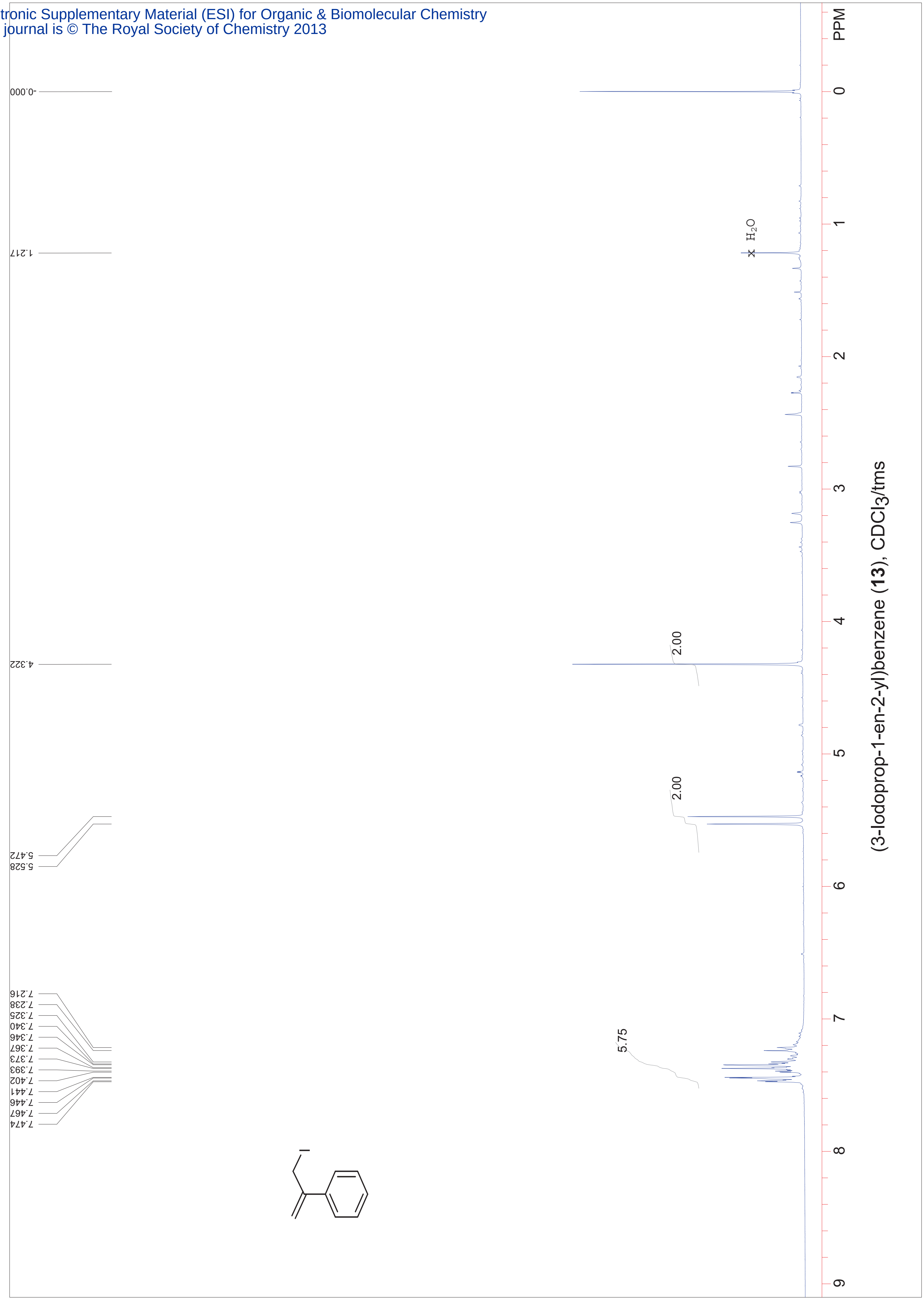
2-Iodo-2-(*tert*-butyl)propene (**11**), $CDCl_3$/tms



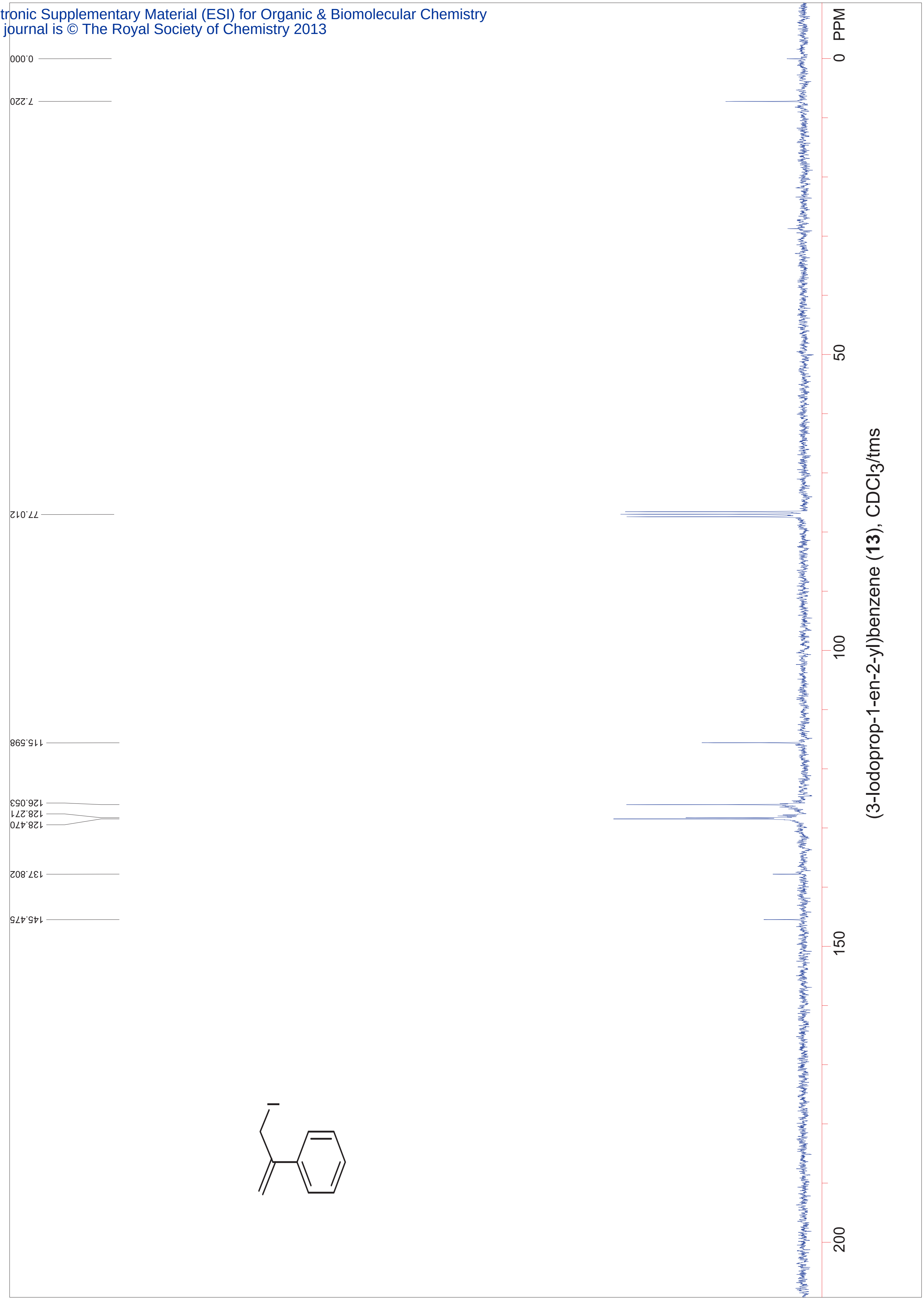
1-Iodomethylcyclohexene (**12**), $CDCl_3$/tms



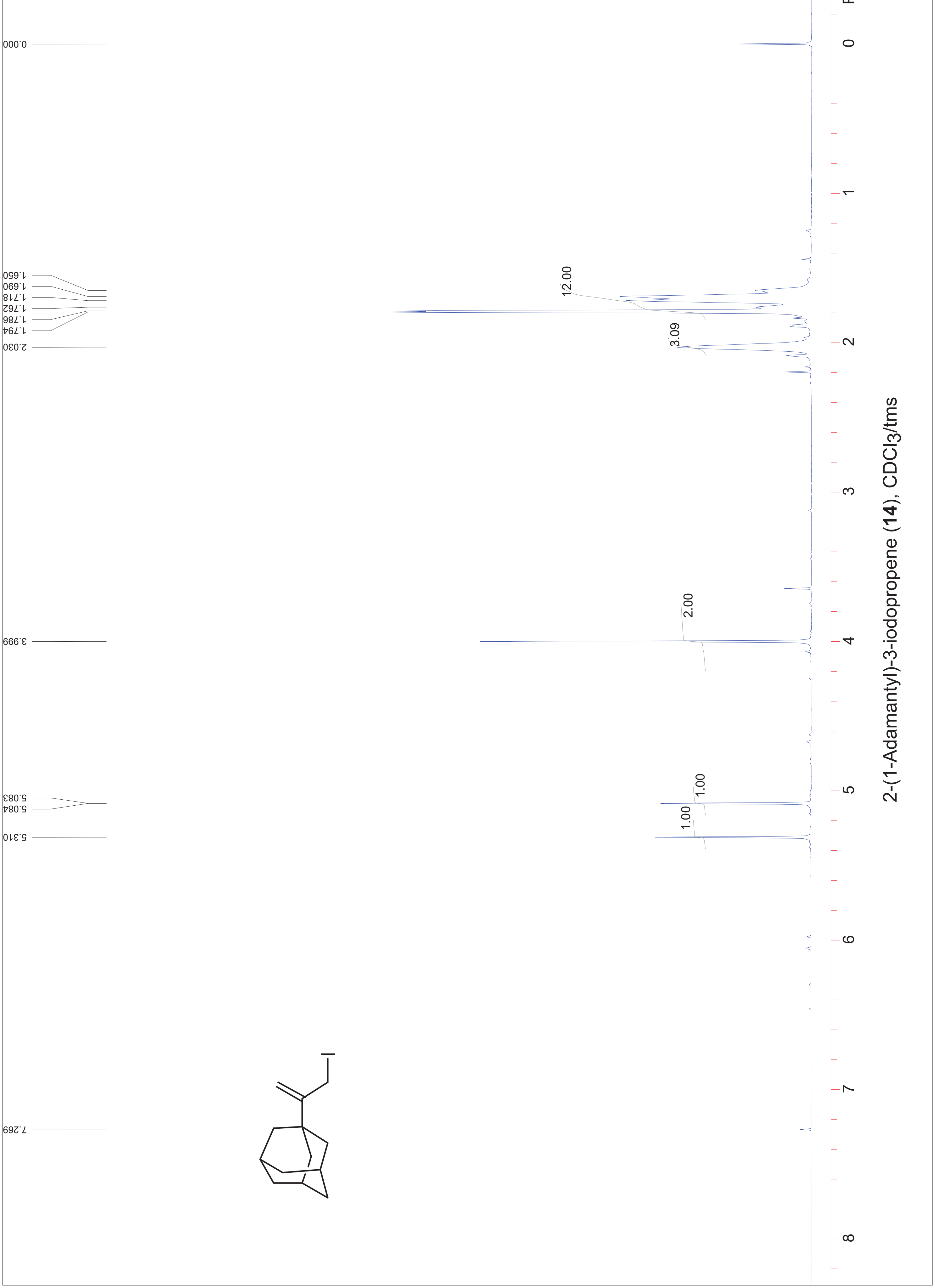
1-Iodomethylcyclohexene (**12**), $CDCl_3$/tms



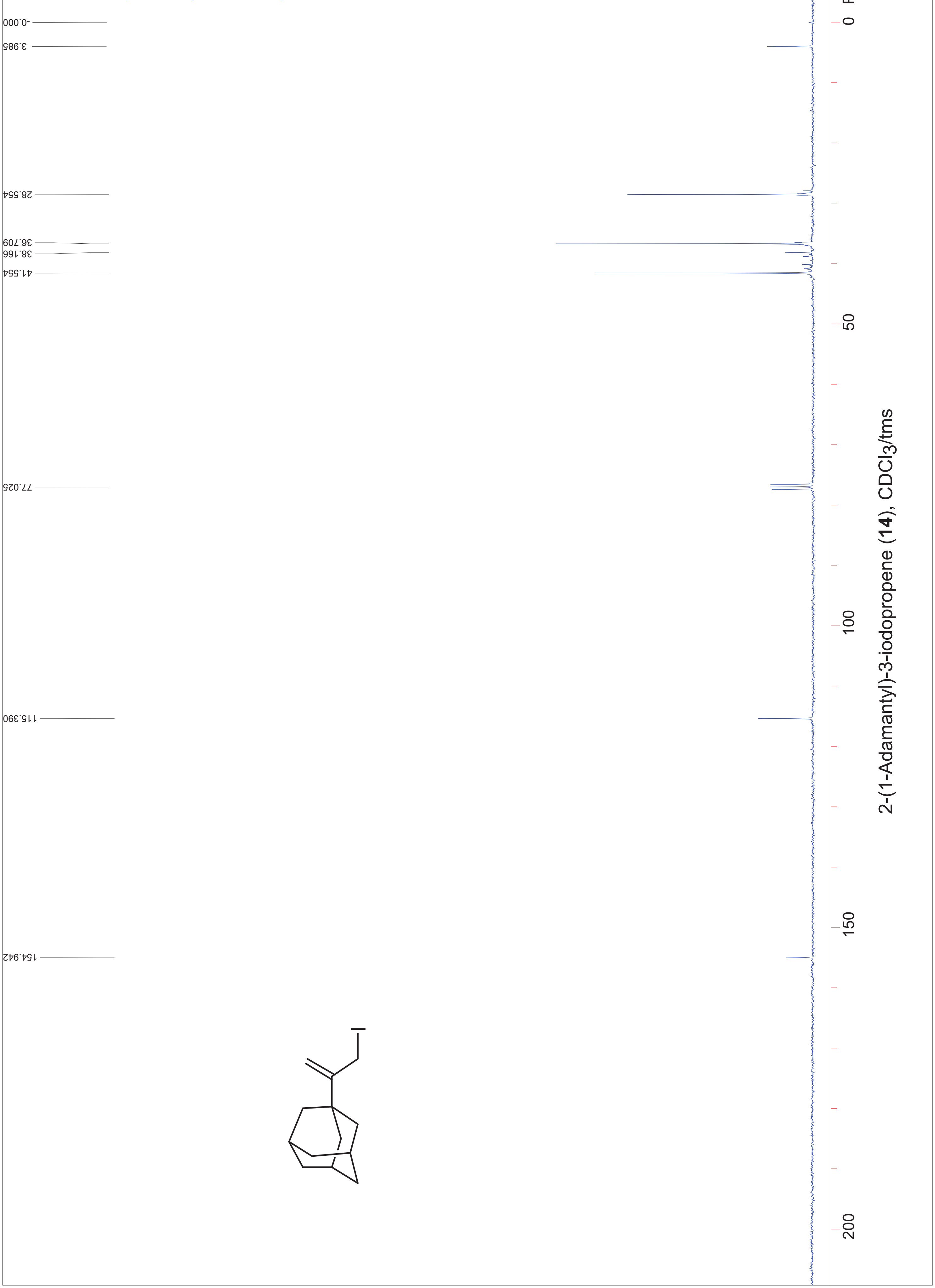
(3-Iodoprop-1-en-2-yl)benzene (**13**), CDCl$_3$/tms



(3-Iodoprop-1-en-2-yl)benzene (**13**), $CDCl_3$/tms



2-(1-Adamantyl)-3-iodopropene (**14**), $CDCl_3$/tms



2-(1-Adamantyl)-3-iodopropene (**14**), $CDCl_3$/tms

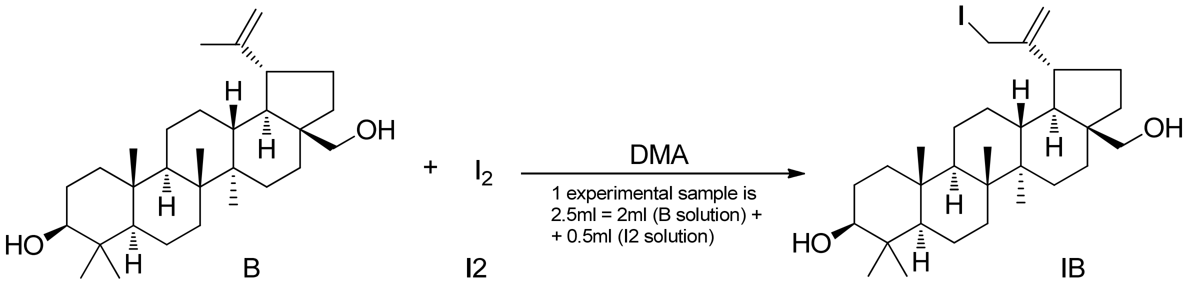
2. Kinetic measurement data

2.1. Experimental part

^{1}H NMR spectra for all samples from kinetic experiments (500 MHz, $CDCl_3$) were recorded using Varian 500 with Auto-Tuner. ^{1}H NMR chemical shifts are referenced to tetramethylsilane as internal standard and reported in parts per million (ppm). *N,N*-Dimethylacetamide 99+% (DMA) was purchased from Acros. Betulin (B) was obtained using previously developed procedures.[1] The other reagents were purchased from Aldrich. The quenching and analyzing technique was used to obtain reagent concentration/time data. The reaction time intervals were chosen for a betulin conversion less than 15% when no inhibition (related to the hydrogen iodide accumulation in the reaction media) was observed (up to 25-90 sec); several sets of experiments (**A-G**) were performed. Betulin (B) and iodine (I2) were dissolved separately in DMA to form solutions containing a precisely known concentration of the reagents for each set of experiments. Determined volumes of the solutions were mixed (1:1, 1:1.2 and 1.2:1 betulin to iodine molar ratios) at a specified temperature (25, 35, 45, 55 and 65 °C) and stirred for a fixed period of time for each experiment. The mixture was immediately treated with aqueous sodium bisulfite solution to neutralize iodine and terminate the reaction. The precipitate was filtered, washed with water and dried. The solid samples from these experiments are mixtures of 30-iodolup-20-en-3β,28-diol (IB) and starting betulin (B). They were dissolved in $CDCl_3$ and analyzed by ^{1}H NMR to determine the content of IB in the mixture. This value was used to determine the concentration of betulin (B) and iodine (I2) at the moment of reaction termination. Kinetic data was analyzed by the least squares linear regression to find corresponding functional correlations. The reaction order, rate constants, activation energy E_A, enthalpy $\Delta H^{\ddagger}_{298}$, entropy $\Delta S^{\ddagger}_{298}$ and Gibbs free energy $\Delta G^{\ddagger}_{298}$ were calculated using standard kinetic and thermodynamic equations.

2.1.1. Experiments A

Betulin (B) (Scheme 1) (0.6226 g) was dissolved in DMA in a volumetric flask (25 ml total volume). Iodine (I2) crystals (0.5711 g) were dissolved in DMA in a volumetric flask (10 ml total volume). The reaction vessels were filled with the betulin solution (2 ml each, volumetric pipette). The sample of betulin solution was stirred at 25±0.1 °C. The iodine solution (0.5 ml, volumetric pipette) was added and reaction mixture was intensively stirred at 25±0.1 °C for a fixed period of time (Table 1). The mixture was immediately treated with aqueous sodium bisulfite solution (5 ml) (3.3 g sodium bisulfite in 200 ml of the solution). The white suspensions were left for 1 hr at room temperature. Each precipitate was filtered, washed with water (5x10 ml) and dried to give a set of **A** samples for ^{1}H NMR analysis (Table 1).



M	442.72	442.72	253.81	253.81	568.61	g/mol
m		0.6226		0.5711		g
V						ml
ν	0.1125	1.4063	0.1125	2.2500		mmol
	x1	x12.5 (25/2)	x1	x20 (10/0.5)		

Scheme 1 Experiments **A** and **D-G**, calculated reagent ratio

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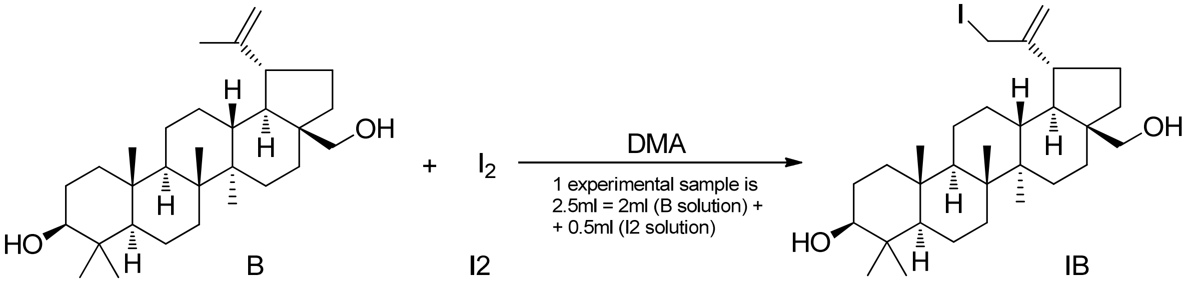
[1] *US Pat.* 6815553, 2004.

2.1.2. Experiments B

The reaction conditions are identical to the experiments **A**, except the concentration of iodine is 1.2 times higher (Scheme 2).

Betulin (B) (0.6226 g) was dissolved in DMA in a volumetric flask (25 ml total volume). Iodine (I2) crystals (0.6853 g) were dissolved in DMA in a volumetric flask (10 ml total volume). The reaction vessels were filled with the betulin solution (2 ml each, volumetric pipette). The sample of betulin solution was stirred at 25±0.1 °C. The iodine solution (0.5 ml, volumetric pipette) was added and reaction mixture was intensively stirred at 25±0.1 °C for a fixed period of time (Table 2). The mixture was immediately treated with aqueous sodium bisulfite solution (5 ml) (3.3 g sodium bisulfite in 200 ml of the solution). The white suspensions were left for 1 hr at room temperature. Each precipitate was filtered, washed with water (5x10 ml) and dried to give a set of **B** samples for ^{1}H NMR analysis (Table 2).



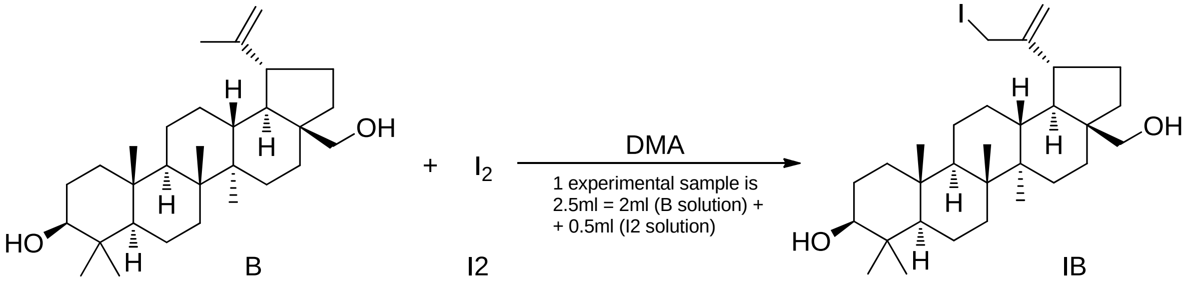
M	442.72	442.72	253.81	253.81	568.61	g/mol
m		0.6226		0.6853		g
V						ml
ν	0.1125	1.4063	0.1350	2.7000		mmol
	x1	x12.5 (25/2)	x1.2	x24 (1.2x10/0.5)		

Scheme 2 Experiments **B**, calculated reagent ratio

2.1.3. Experiments C

The reaction conditions are identical to the experiments **A**, except the concentration of betulin is 1.2 times higher (Scheme 3).

Betulin (B) (0.7471 g) was dissolved in DMA in a volumetric flask (25 ml total volume). Iodine (I2) crystals (0.5710 g) were dissolved in DMA in a volumetric flask (10 ml total volume). The reaction vessels were filled with the betulin solution (2 ml each, volumetric pipette). The sample of the betulin solution was stirred at 25±0.1 °C. The iodine solution (0.5 ml, volumetric pipette) was added and reaction mixture was intensively stirred at 25±0.1 °C for a fixed period of time (Table 3). The mixture was immediately treated with aqueous sodium bisulfite solution (5 ml) (3.3 g sodium bisulfite in 200 ml of the solution). The white suspensions were left for 1 hr at room temperature. Each precipitate was filtered, washed with water (5x10 ml) and dried to give a set of **C** samples for ^{1}H NMR analysis (Table 3).



M	442.72	442.72	253.81	253.81	568.61	g/mol
m		0.7471		0.5710		g
V						ml
ν	0.1350	1.6875	0.1125	2.2500		mmol
	x1.2	x15 (1.2x25/2)	x1	x20 (10/0.5)		

Scheme 3 Experiments **C**, calculated reagent ratio

2.1.4. Experiments D

The reaction conditions are identical to the experiments **A** (Scheme 1), except the reaction temperature is 35 ^{o}C.

Betulin (B) (0.6226 g) was dissolved in DMA in a volumetric flask (25 ml total volume). Iodine (I2) crystals (0.5711 g) were dissolved in DMA in a volumetric flask (10 ml total volume). The reaction vessels were filled with the betulin solution (2 ml each, volumetric pipette). The smaller vessel (thin glass) was filled with the iodine solution (0.5 ml, volumetric pipette) and immersed into the betulin solution in the reaction vessel (the solutions did not mix). The system was thermostabilized at 35±0.1 ^{o}C. Then the smaller vessel was broken (to start the reaction) and reaction mixture was intensively stirred at 35±0.1 ^{o}C for a fixed period of time (Table 4). The mixture was immediately treated with aqueous sodium bisulfite solution (5 ml) (3.3 g sodium bisulfite in 200 ml of the solution). The white suspensions were left for 1 hr at room temperature. Each precipitate was filtered, washed with water (5x10 ml) and dried to give a set of **D** samples for ^{1}H NMR analysis (Table 4).

2.1.5. Experiments E

The reaction conditions are identical to the experiments **A** (Scheme 1), except the reaction temperature is 45 ^{o}C.

Betulin (B) (0.6226 g) was dissolved in DMA in a volumetric flask (25 ml total volume). Iodine (I2) crystals (0.5711 g) were dissolved in DMA in a volumetric flask (10 ml total volume). The reaction vessels were filled with the betulin solution (2 ml each, volumetric pipette). The smaller vessel (thin glass) was filled with the iodine solution (0.5 ml, volumetric pipette) and immersed into the betulin solution in the reaction vessel (the solutions did not mix). The system was thermostabilized at 45±0.1 ^{o}C. Then the smaller vessel was broken (to start the reaction) and reaction mixture was intensively stirred at 45±0.1 ^{o}C for a fixed period of time (Table 5). The mixture was immediately treated with aqueous sodium bisulfite solution (5 ml) (3.3 g sodium bisulfite in 200 ml of the solution). The white suspensions were left for 1 hr at room temperature. Each precipitate was filtered, washed with water (5x10 ml) and dried to give a set of **E** samples for ^{1}H NMR analysis (Table 5).

2.1.6. Experiments F

The reaction conditions are identical to the experiments **A** (Scheme 1), except the reaction temperature is 55 ^{o}C.

Betulin (B) (0.6226 g) was dissolved in DMA in a volumetric flask (25 ml total volume). Iodine (I2) crystals (0.5711 g) were dissolved in DMA in a volumetric flask (10 ml total volume). The reaction vessels were filled with the betulin solution (2 ml each, volumetric pipette). The smaller vessel (thin glass) was filled with the iodine solution (0.5 ml, volumetric pipette) and immersed into the betulin solution in the reaction vessel (the solutions did not mix). The system was thermostabilized at 55±0.1 ^{o}C. Then the smaller vessel was broken (to start the reaction) and reaction mixture was intensively stirred at 55±0.1 ^{o}C for a fixed period of time (Table 6). The mixture was immediately treated with aqueous sodium bisulfite solution (5 ml) (3.3 g sodium bisulfite in 200 ml of the solution). The white suspensions were left for 1 hr at room temperature. Each precipitate was filtered, washed with water (5x10 ml) and dried to give a set of **F** samples for ^{1}H NMR analysis (Table 6).

2.1.7. Experiments G

The reaction conditions are identical to the experiments **A** (Scheme 1), except the reaction temperature is 65 °C.

Betulin (B) (0.6226 g) was dissolved in DMA in a volumetric flask (25 ml total volume). Iodine (I2) crystals (0.5711 g) were dissolved in DMA in a volumetric flask (10 ml total volume). The reaction vessels were filled with the betulin solution (2 ml each, volumetric pipette). The smaller vessel (thin glass) was filled with the iodine solution (0.5 ml, volumetric pipette) and immersed into the betulin solution in the reaction vessel (the solutions did not mix). The system was thermostabilized at 65±0.1 °C. Then the smaller vessel was broken (to start the reaction) and reaction mixture was intensively stirred at 65±0.1 °C for a fixed period of time (Table 7). The mixture was immediately treated with aqueous sodium bisulfite solution (5 ml) (3.3 g sodium bisulfite in 200 ml of the solution). The white suspensions were left for 1 hr at room temperature. Each precipitate was filtered, washed with water (5x10 ml) and dried to give a set of **G** samples for ^{1}H NMR analysis (Table 7).

2.2. Kinetic parameters of the iodination reaction

The data from experiments **A**, **B** and **C** was used. **A**, **B** and **C** samples are the mixtures of 30-iodolup-20-en-3β,28-diol (IB) product and starting betulin (B) (Schemes 1-3). They were analyzed by ^{1}H NMR to determine the content of IB (mol%) in the mixture. It could be determined as a ratio of total integral intensity of IB 29-CH$_2$ signals (5.17 ppm (s) and 5.00 ppm (s)) to total integral intensity of IB 29-CH$_2$ and B 29-CH$_2$ (4.68 ppm (s) and 4.58 ppm (s)) signals. This value was used to determine the current (at the moment of reaction termination with sodium bisulfite) concentration (mmol/l) of betulin ($[B]$) and iodine ($[I2]$): $[B] = B_0 - B_0\frac{IB\%}{100}$ and $[I2] = I2_0 - I2_0\frac{IB\%}{100}$, where $IB\%$ is the content of IB (mol%) in the reaction sample, B_0 and $I2_0$ are starting concentrations of betulin and iodine (mmol/l) respectively (Tables 1-3).

Table 1 Experiments **A** data (25 °C)

A sample #	Time t, sec	$IB\%$, mol%, ^{1}H NMR	$[B] = [I2]$, mmol/l	$\frac{1}{[I2]}$, l/mol
0	0.00	0.0	45.000	22.22222
1	12.21	2.7	43.785	22.83887
2	20.28	3.9	43.245	23.12406
3	30.07	5.9	42.345	23.61554
4	40.32	7.7	41.535	24.07608
5	50.11	8.8	41.040	24.36647
6	60.06	9.8	40.590	24.63661
7	70.23	10.9	40.095	24.94077
8	80.33	12.3	39.465	25.33891
9	90.00	13.1	39.105	25.57218

Table 2 Experiments **B** data (25 °C)

B sample #	Time *t*, sec	*IB%*, mol%, ^{1}H NMR	[*B*], mmol/l	[*I2*], mmol/l	$\frac{1}{(I2_0-B_0)} ln\frac{B_0\cdot[I2]}{I2_0\cdot[B]}$, l/mol
0	0.00	0.0	45.000	54.000	0.000000
1	12.65	3.3	43.515	52.515	0.630176
2	21.09	4.5	42.975	51.975	0.869192
3	30.25	7.2	41.760	50.760	1.427571
4	41.17	8.8	41.040	50.040	1.772659
5	49.81	10.6	40.230	49.230	2.174295
6	61.44	12.5	39.375	48.375	2.614500
7	70.20	13.6	38.880	47.880	2.877372
8	79.75	14.4	38.520	47.520	3.072392
9	89.91	15.6	37.980	46.980	3.371191

Table 3 Experiments **C** data (25 °C)

C sample #	Time *t*, sec	*IB%*, mol% ^{1}H NMR	[*B*], mmol/l	[*I2*], mmol/l	$\frac{1}{(I2_0-B_0)} ln\frac{B_0\cdot[I2]}{I2_0\cdot[B]}$, l/mol
0	0.00	0.0	54.000	45.000	0.000000
1	11.43	2.1	52.866	43.866	0.477702
2	20.89	4.4	51.624	42.624	1.027517
3	31.04	6.1	50.706	41.706	1.453076
4	41.08	7.4	50.004	41.004	1.790203
5	49.94	8.6	49.356	40.356	2.110856
6	60.45	10.0	48.600	39.600	2.496984
7	70.34	11.2	47.952	38.952	2.838759
8	80.23	12.1	47.466	38.466	3.101930
9	90.07	12.8	47.088	38.088	3.310818

The functional relation between the current iodine concentration ([*I2*]) and reaction time (*t*) is shown in Figures 1-3.

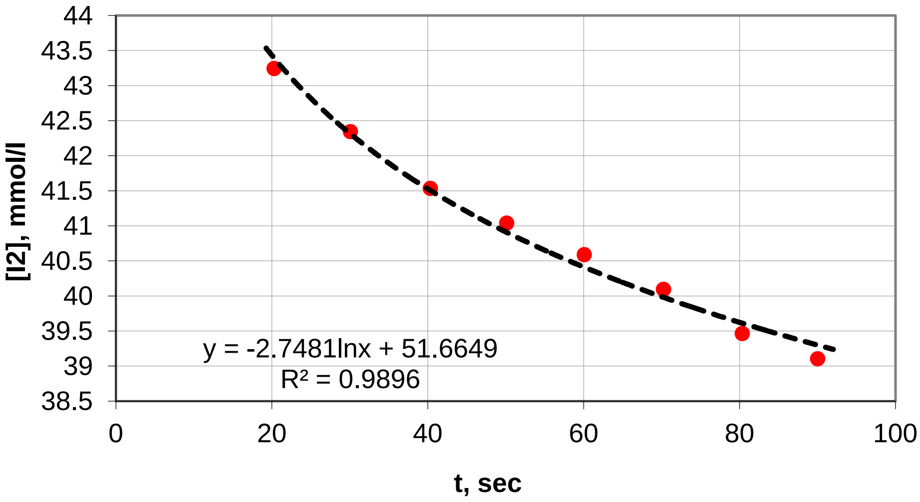


Figure 1 Experiments **A**, a plot of [*I2*] against reaction time (*t*)

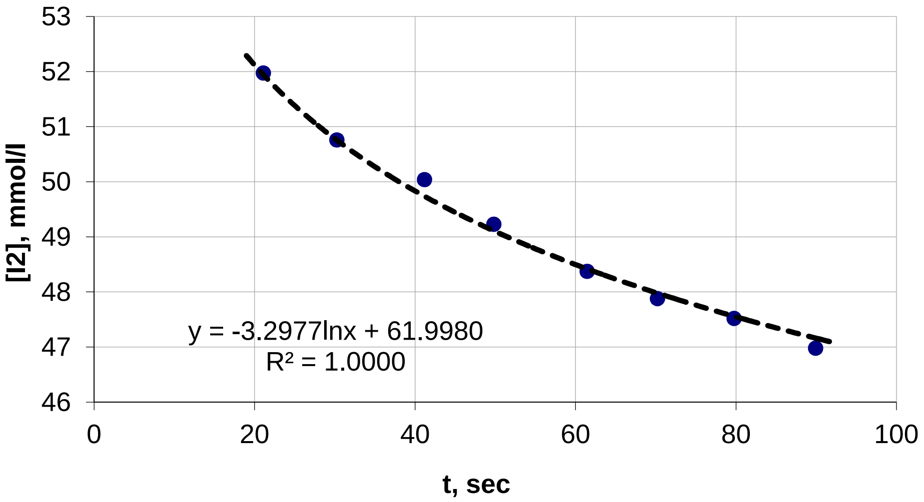


Figure 2 Experiments **B**, a plot of [*I2*] against reaction time (*t*)

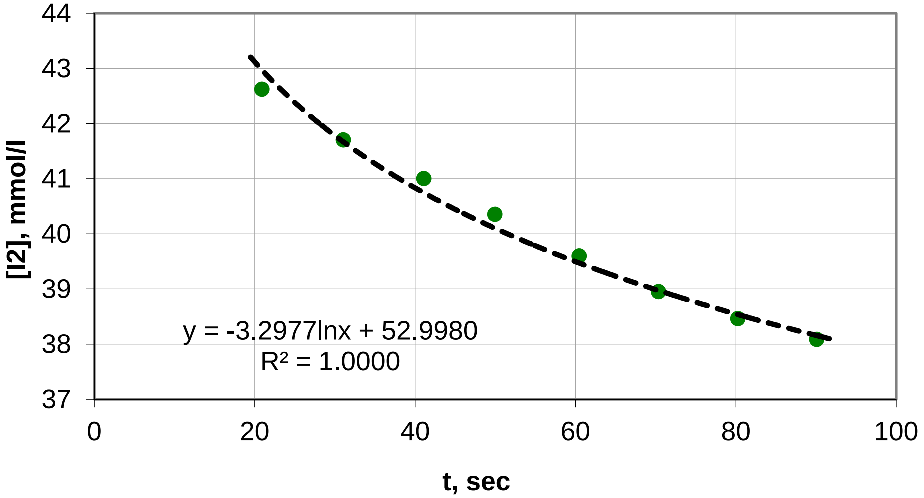


Figure 3 Experiments **C**, a plot of [*I2*] against reaction time (*t*)

The equations for iodine concentration and reaction rate for each case are[2]

$[I2] = -2.7481lnt + 51.6649$, $r_{\boldsymbol{A}} = -\frac{d[I2]}{dt} = \frac{2.7481}{t}$, where $20 \leq t \leq 90$ sec (experiments **A**);

$[I2] = -3.2977lnt + 61.9980$, $r_{\boldsymbol{B}} = -\frac{d[I2]}{dt} = \frac{3.2977}{t}$, where $20 \leq t \leq 90$ sec (experiments **B**);

$[I2] = -3.2977lnt + 52.9980$, $r_C = -\frac{d[I2]}{dt} = \frac{3.2977}{t}$, where $20 \leq t \leq 90$ sec (experiments **C**).

The reaction order in iodine is $n_{I2} = log_m \frac{r_{\boldsymbol{B}}}{r_{\boldsymbol{A}}} = 1$, where $m = \frac{I2_{0B}}{I2_{0A}} = 1.2$.

The reaction order in betulin is $n_B = log_m \frac{r_C}{r_A} = 1$, where $m = \frac{B_{0C}}{B_{0A}} = 1.2$.

The iodination reaction is second order overall, first order in iodine and first order in betulin. The equation for the reaction rate is $r = k \cdot [I2] \cdot [B]$. Then the following equations must be correct and can be used to calculate the rate

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[2] *March's Advanced Organic Chemistry*, eds. M. B. Smith, J. March, John Willey & Sons, New York, 2001, 290.

constant (k) at 25 ^{o}C: $\frac{1}{[I2]} = kt + \frac{1}{I2_0}$ (when $[B] = [I2]$, experiments **A**) and $\frac{1}{(I2_0 - B_0)} ln \frac{B_0 \cdot [I2]}{I2_0 \cdot [B]} = kt$ (when $[B] \neq [I2]$, experiments **B** and **C**) (Figures 4-6).

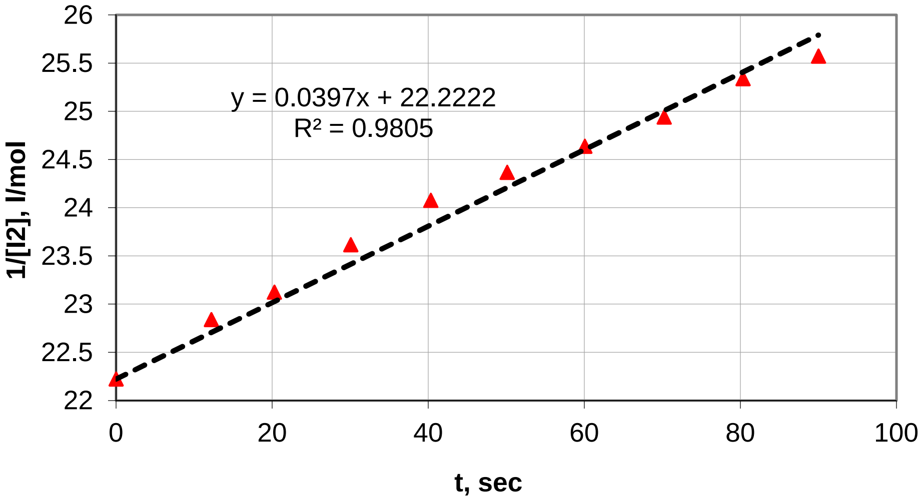

Figure 4 Experiments **A**, a plot of $\frac{1}{[I2]}$ against reaction time (*t*)

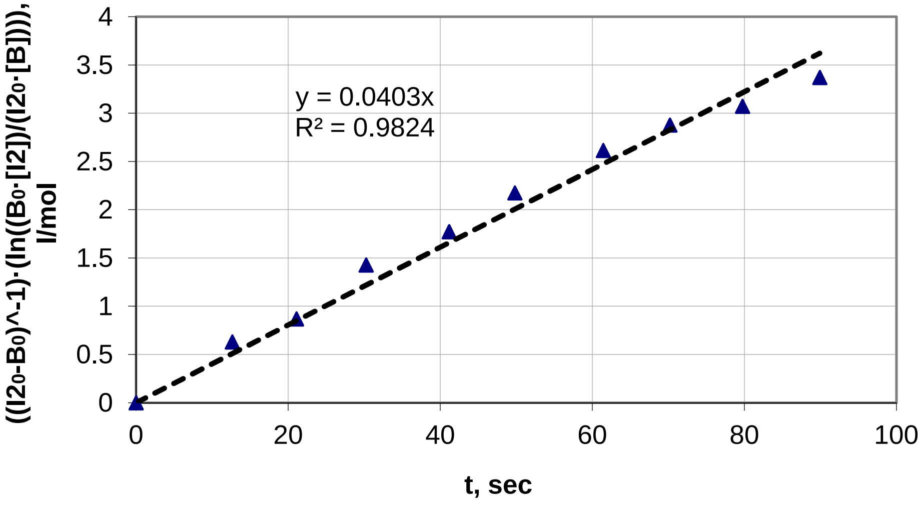

Figure 5 Experiments **B**, a plot of $\frac{1}{(I2_0 - B_0)} ln \frac{B_0 \cdot [I2]}{I2_0 \cdot [B]}$ against reaction time (*t*)

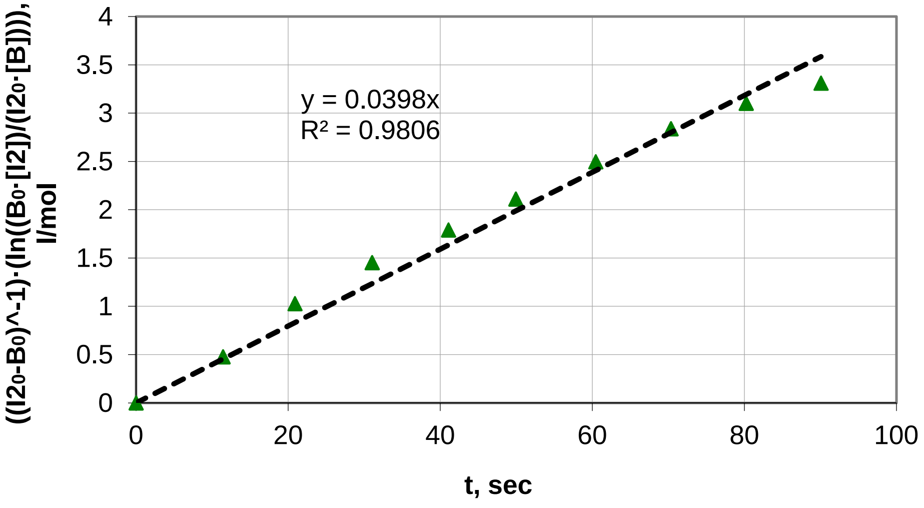

Figure 6 Experiments **C**, a plot of $\frac{1}{(I2_0-B_0)} ln \frac{B_0 \cdot [I2]}{I2_0 \cdot [B]}$ against reaction time (t)

The plots of $\frac{1}{[I2]}$ and $\frac{1}{(I2_0-B_0)} ln \frac{B_0 \cdot [I2]}{I2_0 \cdot [B]}$ against t are linear (if $0 \le t \le 90$ sec). This corresponds to reaction second order overall (first order in each reagent) and rate constant k is a slope of these lines. The following rate constant values were obtained:

$k_1 = 0.0397$ l/(mol·sec) (experiments **A**);
$k_2 = 0.0403$ l/(mol·sec) (experiments **B**);
$k_3 = 0.0398$ l/(mol·sec) (experiments **C**).

Average $k = \frac{\sum_{i=1}^{n} k_i}{n} = 0.0399$ l/(mol·sec).

Standard deviation $s_k = \sqrt{\frac{\sum_{i=1}^{n}(k_i-k)^2}{n-1}} = 0.0003$ l/(mol·sec).

Rate constant for the reaction at 25 °C is

k = (3.99±0.03)·10^{-2} l/(mol·sec).

2.3. Thermodynamic parameters of the iodination reaction

The data from experiments **A** and **D-G** was used. **A** and **D-G** samples are the mixtures of 30-iodolup-20-en-3β,28-diol (IB) product and starting betulin (B) (Scheme 1). They were analyzed by ^{1}H NMR to determine the content of IB (mol%) in the mixture. It could be determined as a ratio of total integral intensity of IB 29-CH_2 signals (5.17 ppm (s) and 5.00 ppm (s)) to total integral intensity of IB 29-CH_2 and B 29-CH_2 (4.68 ppm (s) and 4.58 ppm (s)) signals. This value was used to determine the current (at the moment of reaction termination with sodium bisulfite) concentration (mmol/l) of betulin ([*B*]) and iodine ([*I2*]): $[B] = B_0 - B_0 \frac{IB\%}{100}$ and $[I2] = I2_0 - I2_0 \frac{IB\%}{100}$, where *IB%* is the content of IB (mol%) in the reaction sample, B_0 and $I2_0$ are starting concentrations of betulin and iodine (mmol/l) respectively (Tables 1, 4-7).

Table 4 Experiments **D** data (35 ^{o}C)

D sample #	Time t, sec	$IB\%$, mol%, ^{1}H NMR	$[B] = [I2]$, mmol/l	$\frac{1}{[I2]}$, l/mol
0	0.00	0.0	45.000	22.22222
1	10.21	3.6	43.380	23.05210
2	20.02	5.7	42.435	23.56545
3	30.21	7.8	41.490	24.10219
4	40.21	9.2	40.860	24.47381
5	50.06	11.2	39.960	25.02503
6	60.46	12.3	39.465	25.33891
7	70.08	14.0	38.700	25.83979
8	79.56	14.9	38.295	26.11307

Table 5 Experiments **E** data (45 ^{o}C)

E sample #	Time t, sec	$IB\%$, mol%, ^{1}H NMR	$[B] = [I2]$, mmol/l	$\frac{1}{[I2]}$, l/mol
0	0.00	0.0	45.000	22.22222
1	8.93	3.4	43.470	23.00437
2	16.14	6.1	42.255	23.66584
3	22.22	7.6	41.580	24.05002
4	28.66	8.7	41.085	24.33978
5	35.45	10.4	40.320	24.80159
6	42.93	11.5	39.825	25.10986
7	49.38	13.0	39.150	25.54278
8	56.65	14.9	38.295	26.11307

Table 6 Experiments **F** data (55 ^{o}C)

F sample #	Time t, sec	$IB\%$, mol%, ^{1}H NMR	$[B] = [I2]$, mmol/l	$\frac{1}{[I2]}$, l/mol
0	0.00	0.0	45.000	22.22222
1	7.58	4.7	42.885	23.31818
2	13.61	7.2	41.760	23.94636
3	19.28	8.8	41.040	24.36647
4	23.36	10.0	40.500	24.69136
5	30.38	11.9	39.645	25.22386
6	35.38	13.5	38.925	25.69043

Table 7 Experiments **G** data (65 ^{o}C)

G sample #	Time t, sec	$IB\%$, mol%, ^{1}H NMR	$[B] = [I2]$, mmol/l	$\frac{1}{[I2]}$, l/mol
0	0.00	0.0	45.000	22.22222
1	7.09	5.3	42.615	23.46592
2	11.99	8.3	41.265	24.23361
3	16.22	10.0	40.500	24.69136
4	19.69	11.5	39.825	25.10986
5	25.12	14.0	38.700	25.83979

This reaction is second order overall, first order in iodine and first order in betulin. The rate of the reaction is $r = k \cdot [I2] \cdot [B]$. Then the equation $\frac{1}{[I2]} = kt + \frac{1}{I2_0}$ (when $[B] = [I2]$, experiments **A** and **D-G**) must be correct and can be used to calculate the rate constant at different temperatures (Figures 4, 7-10).

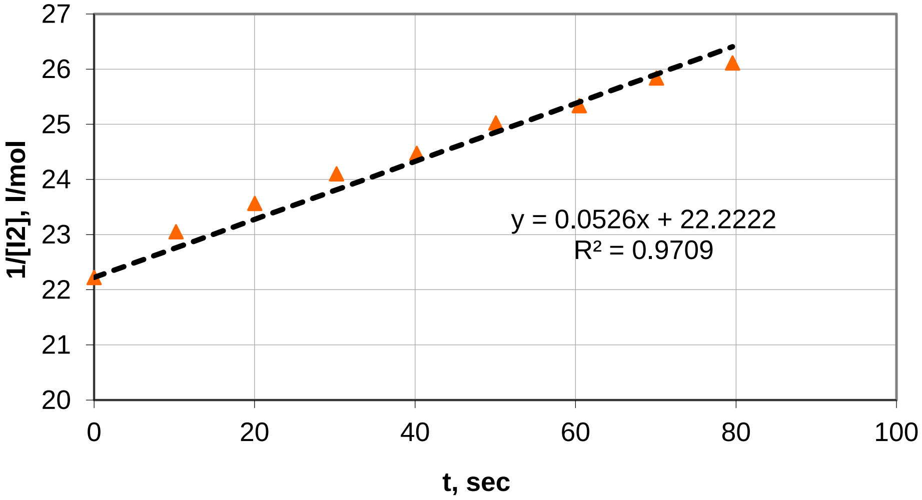

Figure 7 Experiments **D**, a plot of $\frac{1}{[I2]}$ against reaction time (t)

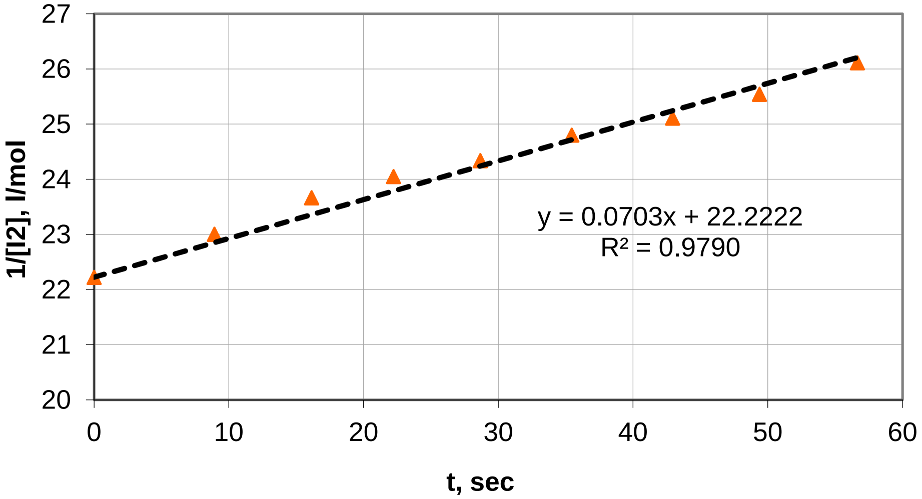

Figure 8 Experiments **E**, a plot of $\frac{1}{[I2]}$ against reaction time (t)

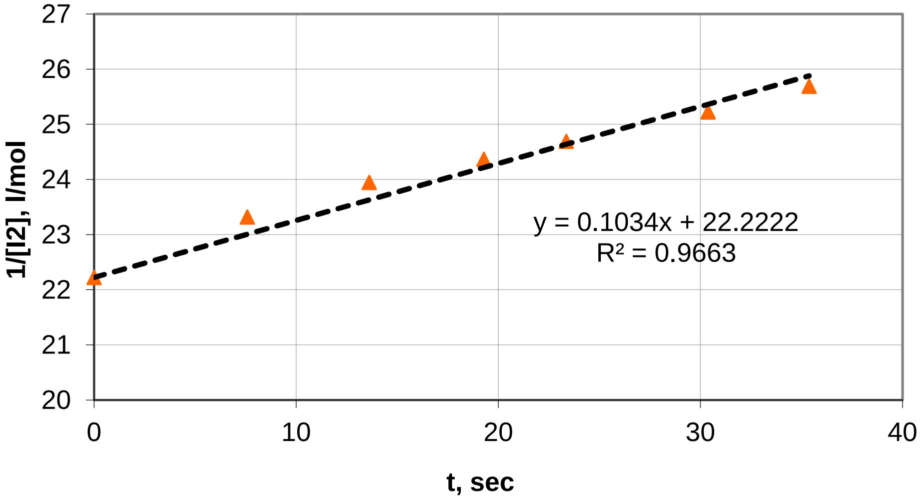

Figure 9 Experiments **F**, a plot of $\frac{1}{[I2]}$ against reaction time (t)

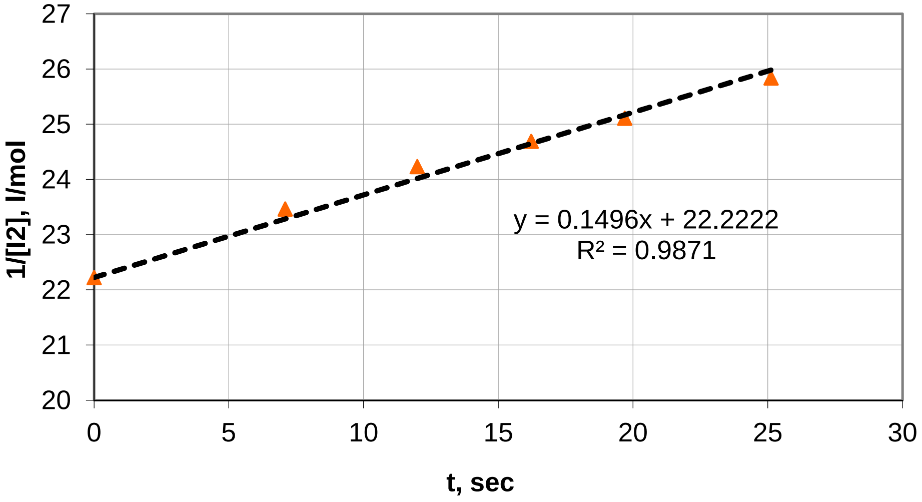

Figure 10 Experiments **G**, a plot of $\frac{1}{[I2]}$ against reaction time (t)

The plots of $\frac{1}{[I2]}$ against t are linear (if $0 \leq t \leq 90$ sec). This corresponds to reaction second order overall (first order in each reagent) and rate constant k is a slope of these lines (Table 8).

Table 8 Rate constants at different reaction temperatures

Experiments	Reaction temperature, °C	Reaction temperature, K	$-\frac{1}{RT}$, −mol/cal	k, l/(mol·sec)	lnk
A	25	298.15	−0.00169	0.0397	−3.22640
D	35	308.15	−0.00163	0.0526	−2.94504
E	45	318.15	−0.00158	0.0703	−2.65498
F	55	328.15	−0.00153	0.1034	−2.26915
G	65	338.15	−0.00149	0.1496	−1.89979

The set of rate constants at different reaction temperatures (Table 8) is used to determine the activation energy via Arrhenius equation $k = Ae^{\frac{-E_A}{RT}}$ or $lnk = -\frac{E_A}{RT} + lnA$, where E_A is activation energy (cal/mol); k is rate constant (l/(mol·sec) for second order reaction); universal gas constant $R = 1.987$ cal/(mol·K); A is pre-exponential factor (l/(mol·sec) for second order reaction); T stands for absolute temperature (K). A plot of experimental $y = lnk$ against $x = -\frac{1}{RT}$ is linear with high coefficient of determination (the least squares linear regression analysis, $y = 6646.7018x + 7.9360$, $R^2 = 0.9882$) (Figure 11).

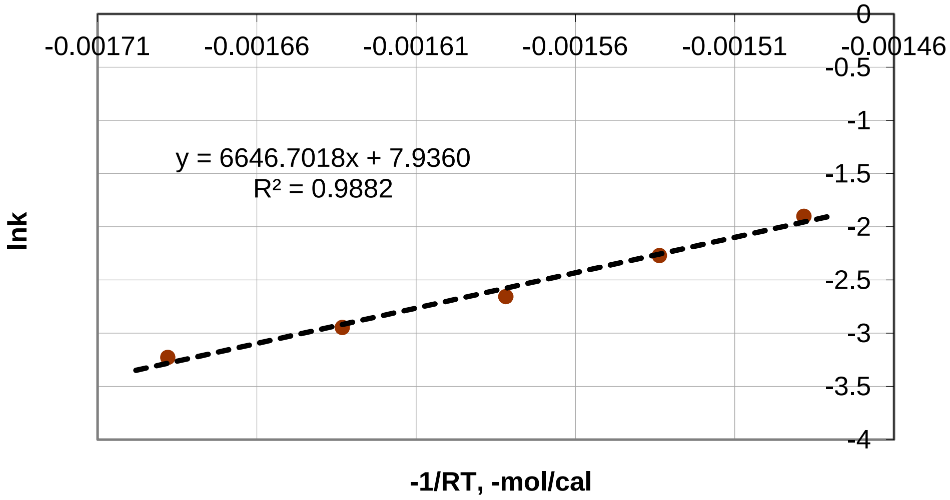

Figure 11 A plot of lnk against $-\frac{1}{RT}$

Activation energy was found for every combination of four experiments (Table 8) to determine average E_A and its deviation value. The following equations were obtained (the least squares linear regression analysis, $y = lnk$, $x = -\frac{1}{RT}$):

$y = 6130.0678x + 7.0905$ ($R^2 = 0.9889$, experiments **A**, **D**, **E**, **F**), $E_{A1} = 6130.1$cal/mol;
$y = 6576.6383x + 7.8322$ ($R^2 = 0.9873$, experiments **A**, **E**, **F**, **G**), $E_{A2} = 6576.6$ cal/mol;
$y = 6658.7807x + 7.9743$ ($R^2 = 0.9948$, experiments **A**, **D**, **F**, **G**), $E_{A3} = 6658.8$ cal/mol;
$y = 6680.3227x + 7.9925$ ($R^2 = 0.9868$, experiments **A**, **D**, **E**, **G**), $E_{A4} = 6680.3$ cal/mol;
$y = 7276.8468x + 8.9043$ ($R^2 = 0.9929$, experiments **D**, **E**, **F**, **G**), $E_{A5} = 7276.8$ cal/mol.

Average $E_A = \frac{\sum_{i=1}^{n} E_{Ai}}{n} = 6664.5$ cal/mol.

Standard deviation $s_{E_A} = \sqrt{\frac{\sum_{i=1}^{n}(E_{Ai} - E_A)^2}{n-1}} = 408.8$ cal/mol.

The activation energy of reaction is

$E_A = 6664.5 \pm 408.8$ cal/mol.

The other thermodynamic parameters of reaction were calculated as following.[3]

Activation enthalpy $\Delta H^\ddagger = E_A - RT = 6664.5 - 1.987 \cdot 298.15 = 6072.1$ cal/mol.

Standard deviation $s_{\Delta H^\ddagger} = \sqrt{\left(\frac{d\Delta H^\ddagger}{dE_A} s_{E_A}\right)^2 + \left(\frac{d\Delta H^\ddagger}{dT} s_T\right)^2} = \sqrt{{s_{E_A}}^2 + (Rs_T)^2} = \sqrt{408.8^2 + (1.987 \cdot 0.1)^2} = 408.8$ cal/mol.

$\Delta H^\ddagger_{298} = 6072.1 \pm 408.8$ cal/mol.

Activation entropy for energies in calorie units $\Delta S^\ddagger = 4.576 \cdot \left(lgk - 10.753 - lgT + \frac{E_A}{4.576 \cdot T}\right) = 4.576 \cdot \left(lg0.0399 - 10.753 - lg298.15 + \frac{6664.5}{4.576 \cdot 298.15}\right) = -44.578$ cal/(mol·K).

Standard deviation

$s_{\Delta S^\ddagger} = \sqrt{\left(\frac{d\Delta S^\ddagger}{dk} s_k\right)^2 + \left(\frac{d\Delta S^\ddagger}{dE_A} s_{E_A}\right)^2 + \left(\frac{d\Delta S^\ddagger}{dT} s_T\right)^2} = \sqrt{\left(\frac{4.576lge}{k} s_k\right)^2 + \left(\frac{s_{E_A}}{T}\right)^2 + \left(\frac{4.576lge}{T} + \frac{E_A}{T^2}\right)^2 {s_T}^2} = \sqrt{\left(\frac{4.576 \cdot 0.4343}{0.0399} 0.0003\right)^2 + \left(\frac{408.8}{298.15}\right)^2 + \left(\frac{4.576 \cdot 0.4343}{298.15} + \frac{6664.5}{298.15^2}\right)^2 0.1^2} = 1.374$ cal/(mol·K).

$\Delta S^\ddagger_{298} = -44.578 \pm 1.374$ cal/(mol·K).

Activation free energy $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger = 6072.1 + 298.15 \cdot 44.578 = 19363.0$ cal/mol.

Standard deviation $s_{\Delta G^\ddagger} = \sqrt{\left(\frac{d\Delta G^\ddagger}{d\Delta H^\ddagger} s_{\Delta H^\ddagger}\right)^2 + \left(\frac{d\Delta G^\ddagger}{d\Delta S^\ddagger} s_{\Delta S^\ddagger}\right)^2 + \left(\frac{d\Delta G^\ddagger}{dT} s_T\right)^2} = \sqrt{{s_{\Delta H^\ddagger}}^2 + (Ts_{\Delta S^\ddagger})^2 + (\Delta S^\ddagger s_T)^2} = \sqrt{408.8^2 + (298.15 \cdot 1.374)^2 + (44.578 \cdot 0.1)^2} = 578.7$ cal/mol.

$\Delta G^\ddagger_{298} = 19363.0 \pm 578.7$ cal/mol.

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[3] *Teechnique of Organic Chemistry, Volume VIII, Investigation of Rates and Mechanisms of Reaction, Part I*, eds. S. L. Friess, E. S. Lewis, A. Weissberger, Interscience Publishers, Inc., New York, 1961, 199.

3. Optimized geometries for all species

Quantum mechanics calculations of the model reaction between 2,3,3-trimethylbut-1-ene (**4**) and iodine in *N*,*N*-dimethylacetamide (DMA) were performed by using the Gaussian 03 program package.[4] Geometries of all structures were fully optimized at the PW91PW91,[5a-c] ωB97XD[6] and MP2[7a-c] levels of theory using the DZVP[8] basis set. Stationary points were confirmed to be minima or transition states (**TS**) by calculating the normal vibrations within the harmonic approximation. The reaction pathways along both directions from the transition structures were followed by the IRC[9a,b] method. All computed energies are corrected for zero-point vibrational energies (ZPVE). Additionally, single-point calculations including solvent model (COSMO, DMF as a model solvent) were done with Orca 2.6 program[10] (Table 9).

N,*N*-Dimethylacetamide (DMA)

```
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W91PW91/GEN OPT FREQ=NORAMAN NAME=TS\\DMA\\0,1\N,0.3133106538,-0.46869
83927,0.2209351628\C,-0.511342561,0.5857254055,-0.1319065359\C,-0.2028
561183,1.3165482529,-1.4364060811\O,-1.4692747064,0.9333906944,0.57794
34639\H,-0.9520527929,2.1089757137,-1.5460844881\H,0.797682464,1.77693
00688,-1.4298857083\H,-0.2641080568,0.6509873347,-2.3118169815\C,1.453
6967403,-0.9397565741,-0.5508993149\H,1.318525722,-1.9974531698,-0.841
0502195\H,1.5877855232,-0.3507806141,-1.4642923782\H,2.3829575232,-0.8
689793294,0.0429308649\C,0.0512073191,-1.1921383656,1.460108144\H,-0.1
485014199,-2.2579940289,1.2525186287\H,0.9194248215,-1.1264630275,2.13
90087376\H,-0.8249229901,-0.7437320661,1.9432004205\\Version=IA32L-G03
RevC.02\State=1-A\HF=-287.7529113\RMSD=9.173e-09\RMSF=4.039e-06\Dipole
=1.2330104,-0.7063626,-0.5831449\PG=C01 [X(C4H9N1O1)]\\@
```

ZPVE = 79.74663 kcal/mol

Iodine (I$_2$)

```
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000005336,0.0000005336\I,1.3666243272,0.0000005336,-0.0000005336\\Vers
ion=IA32L-G03RevC.02\State=1-SGG\HF=-13840.4231558\RMSD=5.260e-09\RMSF
=2.178e-05\Dipole=0.,0.,0.\PG=D*H [C*(I1.I1)]\\@
```

ZPVE = 0.29937 kcal/mol

---

[4] *Gaussian 03, Revision D.02*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT 2004.

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[8] N. Godbout, D. R. Salahub, J. Andzelm, E. Wimmer, *Can. J. Chem.*, 1992, **70**, 560.

[9] (*a*) C. Gonzalez, H. B. Schlegel, *J. Phys. Chem.*, 1990, **94**, 5523; (*b*) C. Gonzalez, H. B. Schlegel, *J. Chem. Phys.*, 1989, **90**, 2154.

[10] F. Neese, *WIREs: Comput. Mol. Sci.*, 2012, **2**, 73.

CTC1 (DMA–––I_2) (Figure 12)

```
1\1\GINC-A09\FOpt\RPW91PW91\Gen\C4H9I2N1O1\TS\20-Nov-2007\0\\#P PW91PW
91/gen OPT Freq=NoRaman Name=TS\\DMA:I2\\0,1\N,-3.3572371351,0.0812633
383,0.9341917445\C,-2.8371420291,0.946923657,0.0142398039\C,-3.7392001
124,1.471621201,-1.0925132482\O,-1.6432323617,1.3396339849,0.068858621
2\H,-3.1774024932,2.2426252849,-1.6316680918\H,-4.001227409,0.67410863
77,-1.8057789896\H,-4.6732494329,1.9084197747,-0.7085983557\I,0.604320
4324,-0.1535283816,-0.0903326795\C,-4.6865444807,-0.5160671367,0.85026
83556\H,-5.2783742436,-0.2658521702,1.7470256112\H,-5.2269595591,-0.16
17721277,-0.0331916954\H,-4.606124487,-1.6144887049,0.7862326642\C,-2.
5260203789,-0.3792296618,2.0479656922\H,-3.1494758162,-0.451155404,2.9
52583253\H,-2.0845248466,-1.3670608638,1.8369017688\H,-1.7146329161,0.
3379417191,2.2159074879\I,2.921007269,-1.670543147,-0.3592819423\\Vers
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ZPVE = 80.77651 kcal/mol

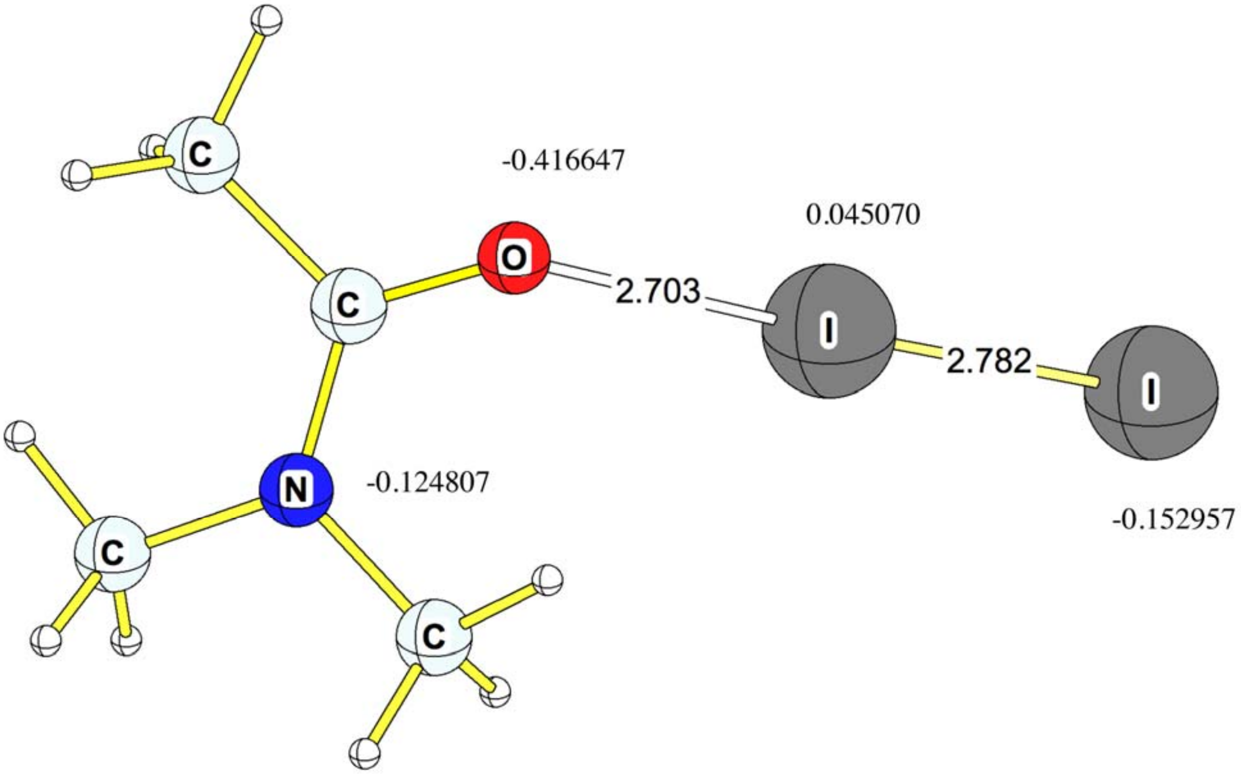

Figure 12 PW91PW91/DZVP computed structure of the DMA–––I_2 complex (**CTC1**)

2,3,3-Trimethylbut-1-ene (4)

```
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n Freq=NoRaman OPT Name=TS\\tBuallyl\\0,1\C,1.3469696793,0.3568478611,
-1.2875519989\C,0.6029247865,-0.005871725,0.0125092001\H,2.435157407,0
```

```
.3178159397,-1.1191235169\H,1.0981053351,1.3738957295,-1.6300668822\H,
1.1142215745,-0.3476263715,-2.1016401521\C,-0.9248745324,0.0535464066,
-0.1555263443\C,1.0498144522,0.9831027153,1.1184720004\C,1.0236542982,
-1.441347569,0.4208769126\C,-1.7719492306,-0.1639480769,1.0828063812\H
,0.6297889937,0.7217369448,2.1017608666\H,2.1476650796,0.9721845855,1.
2159192612\H,0.7411070357,2.0132019363,0.8777319352\H,0.5910027072,-1.
743369068,1.387140965\H,0.7084792236,-2.1746661252,-0.3382171751\H,2.1
2002456,-1.5022085882,0.5197193005\C,-1.527251344,0.2892034253,-1.3403
794177\H,-2.6186876704,0.3132546804,-1.4193715458\H,-0.9731238572,0.46
63820243,-2.2645816705\H,-2.8406559708,-0.1947322018,0.8264442879\H,-1
.522654536,-1.1067798824,1.5963555955\H,-1.6291079913,0.6449673592,1.8
182419972\\Version=IA64L-G03RevD.01\State=1-A\HF=-275.0424089\RMSD=8.5
30e-09\RMSF=4.404e-06\Thermal=0.\Dipole=0.1044207,-0.0294048,0.1689564
\PG=C01 [X(C7H14)]\\@
```

ZPVE = 118.46823 kcal/mol

CTC2 (DMA–––I$_2$–––(4)) (Figure 13)

```
1\1\GINC-A06\FOpt\RPW91PW91\Gen\C11H23I2N1O1\TS\03-Dec-2007\0\\#P PW91
PW91/gen OPT Freq=NoRaman scfcyc=300 Name=TS\\Complex with DMA...I2\\0
,1\C,1.914823834,-2.9537176426,-0.6567417496\C,2.9253333036,-2.2312206
981,0.2557894661\H,1.4547171655,-3.7947533064,-0.112698143\H,2.3984927
389,-3.3673848109,-1.5560132739\H,1.1061267358,-2.2784671972,-0.978107
4551\C,3.5784864435,-1.0260703557,-0.4422556684\C,4.0216962676,-3.2499
498176,0.6621671066\C,2.1774174114,-1.7631452893,1.5293408519\C,4.4999
694874,-0.1512992707,0.3843577066\H,4.7389100405,-2.8229437579,1.38021
05467\H,3.5629875748,-4.1314240116,1.1405102018\H,4.5865565581,-3.5947
42601,-0.2186295245\H,2.8601868309,-1.3153308656,2.2676826418\H,1.4036
062839,-1.0184995848,1.2840516435\H,1.6839095005,-2.621494561,2.015084
7218\C,3.3606882973,-0.7186748202,-1.7381220258\H,3.9493347803,0.37723
57654,1.1797902997\H,5.2978626529,-0.7315409092,0.8766638095\H,4.97908
78493,0.6128756371,-0.2443925056\N,-4.7318473885,-1.1087385762,0.19770
96185\C,-3.8583390714,-0.0625892154,0.3132459292\C,-4.3742464975,1.258
4077151,0.8545956006\O,-2.6552181007,-0.2130324945,-0.0277165035\H,-3.
5329516043,1.9589721185,0.9122839957\H,-5.1435094681,1.6918601061,0.19
70472119\H,-4.8071075859,1.1456003226,1.8599828264\I,-0.7122122932,1.5
935201615,-0.0084199272\C,-6.1434076946,-1.0577134686,0.5626318468\H,-
6.3507643308,-1.7405121653,1.4047676395\H,-6.4463850356,-0.0468245108,
0.8526380131\H,-6.7644855252,-1.3704097101,-0.2934840496\C,-4.25934437
78,-2.4016618786,-0.2983820735\H,-4.4310593019,-3.1833443989,0.4601112
173\H,-4.8028142879,-2.6778064565,-1.2171269789\H,-3.1881272271,-2.330
7475683,-0.5149771701\I,1.3833395725,3.4373258414,0.0191584006\H,3.847
312957,0.1474544609,-2.1968375276\H,2.691334505,-1.2924911854,-2.38222
87196\\Version=IA64L-G03RevD.01\State=1-A\HF=-14403.2364742\RMSD=5.523
e-09\RMSF=4.597e-05\Thermal=0.\Dipole=-3.1340193,-1.331302,0.5124309\P
G=C01 [X(C11H23I2N1O1)]\\@
```

ZPVE = 199.18801 kcal/mol

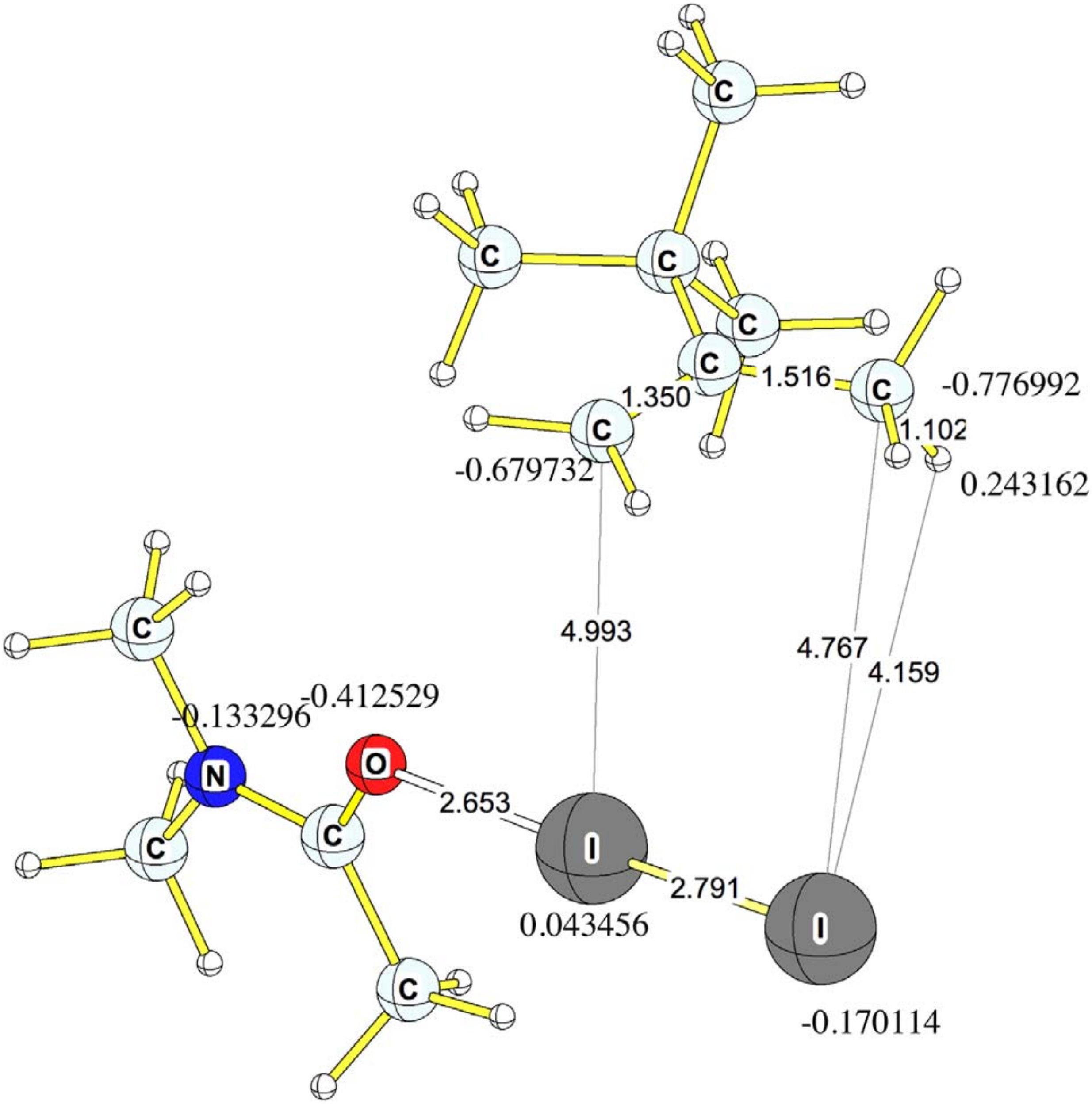

Figure 13 PW91PW91/DZVP computed structure of the DMA——I_2——(4) complex (**CTC2**)

Transition State (TS) (Figure 14)

```
1\1\GINC-A03\Freq\RPW91PW91\Gen\C11H23I2N1O1\TS\30-Nov-2007\0\\#P PW91
PW91/gen OPT(TS,CalcAll,Noeigen,NoRaman) Name=TS\\Complex with DMA...I
2\\0,1\C,0.5477627727,1.0411967079,4.364531117\C,-0.4161053577,-0.1138
150308,4.027747722\H,1.0140709969,0.8568575633,5.3452071842\H,0.022959
3106,2.0081024651,4.4289636896\H,1.3542612705,1.1275014406,3.620132570
1\C,-1.0850070687,0.0493183582,2.6660969814\C,-1.5321652768,-0.1585295
785,5.1080382196\C,0.3791511285,-1.447620085,4.0636856265\C,-2.0619435
261,-0.9793973829,2.2009886027\H,-2.2272084781,-0.9974734041,4.9551816
622\H,-1.0725618329,-0.2795566546,6.1024309339\H,-2.1173968144,0.77471
43872,5.1155306376\H,-0.261674084,-2.3214765675,3.8748759229\H,1.18343
```

```
   63935,-1.4429439073,3.3131065639\H,0.8324575263,-1.5749091443,5.059785
   8352\C,-0.8163237798,1.1232780921,1.8173976562\H,-1.8095574237,-1.2883
   056043,1.1595739899\H,-2.1169205871,-1.8674867728,2.8430682276\H,-3.07
   32252214,-0.5470727546,2.1120871097\N,5.6628250326,-0.0513808427,-1.62
   52421541\C,4.3441323406,-0.207270904,-1.2952188411\C,3.4142635979,-0.8
   453634709,-2.3093790481\O,3.9411632568,0.18051556,-0.1636076408\H,2.40
   40522666,-0.8941386309,-1.8859631807\H,3.3697233365,-0.2596471083,-3.2
   402933114\H,3.7383233777,-1.8662269514,-2.5629054137\I,1.3487767492,0.
   2550563492,0.5118007014\C,6.2669535493,-0.5170873972,-2.8694670111\H,6
   .9781379642,-1.3380851123,-2.6721049028\H,5.5092381895,-0.8748125612,-
   3.5732216281\H,6.8195025513,0.3085690785,-3.3478574401\C,6.5920400739,
   0.5387947866,-0.6616428059\H,7.3296710335,-0.2112544426,-0.3292468174\
   H,7.1314384969,1.3788789981,-1.1284710137\H,6.0275677146,0.899527251,0
   .2047837742\I,-1.3452375341,-0.8741105605,-1.4374873633\H,-1.421228437
   2,1.2569977415,0.9168323101\H,-0.2821835081,2.0035460895,2.1758915343\
   \Version=IA64L-G03RevD.01\State=1-A\HF=-14403.1918707\RMSD=6.485e-09\R MSF=3.944e-
06\ZeroPoint=0.3178346\Thermal=0.340597\Dipole=2.8739487,0.
   2854422,0.8035669\DipoleDeriv=-0.0249076,-0.0542406,0.018131,-0.070923
```

ZPVE = 199.44420 kcal/mol

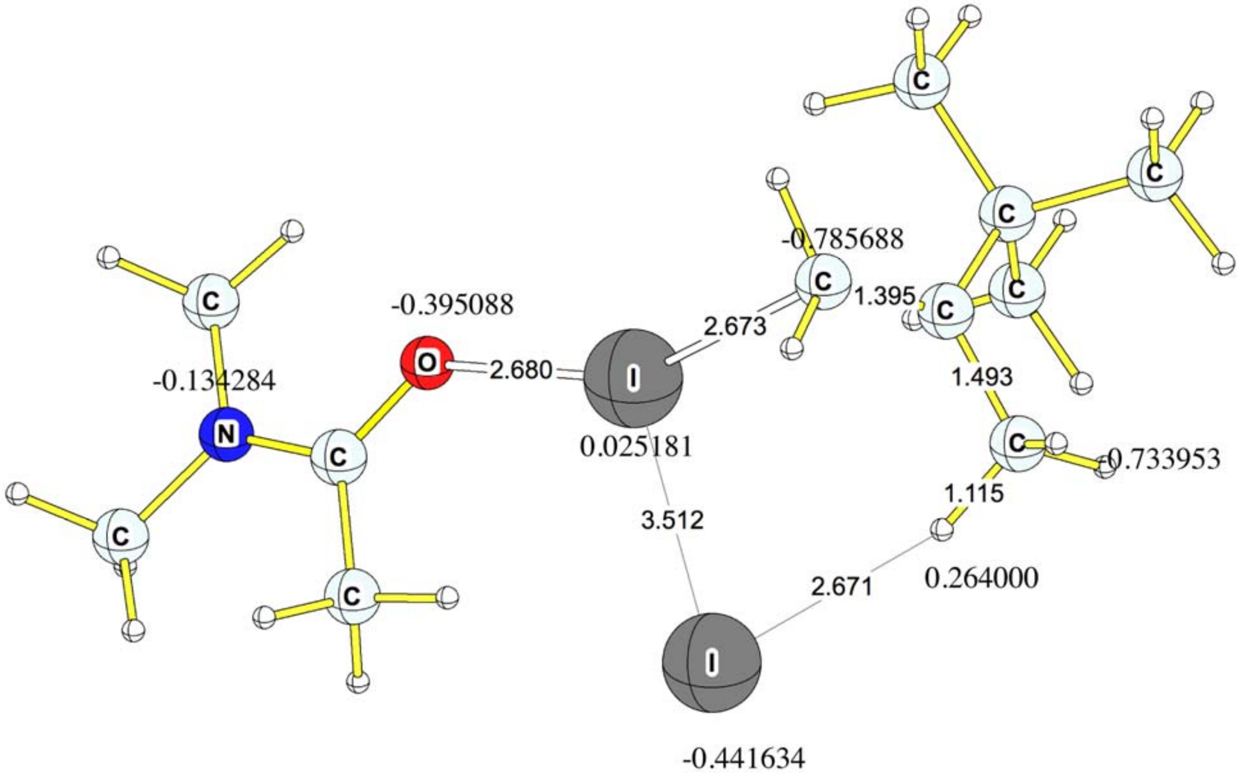

Figure 14 PW91PW91/DZVP computed structure of the transition state (**TS**)

Final Cluster FIN ((DMA−−−(11)−−−HI) (Figure 15)

```
1\1\GINC-A03\Freq\RPW91PW91\Gen\C11H23I2N1O1\TS\05-Dec-2007\0\\#P Geom
=AllCheck Guess=Read SCRF=Check GenChk RPW91PW91/ChkBas Freq\\Final Co
mplex with DMA…I2\\0,1\C,2.6908771796,-3.4607166762,0.1405744613\C,3
.1436615159,-2.0377011406,0.5284916314\H,2.9904923133,-4.162885371,0.9
```

```
337865919\H,3.1641772929,-3.8077325275,-0.7923437734\H,1.5981543306,-3
.5334858561,0.028933234\C,2.7137772253,-0.9689564256,-0.4764239021\C,4
.6977184936,-2.0328681539,0.6039107376\C,2.5643693378,-1.6922270665,1.
9269091311\C,3.0004421903,0.4069936859,-0.2232512929\H,5.0939483018,-1
.0785807699,0.9799845804\H,5.0270158582,-2.8270899337,1.2926775714\H,5
.1502940171,-2.2292574662,-0.3810466386\H,2.8558900375,-0.688558075,2.
2694176177\H,1.4652050455,-1.7338622231,1.9182353942\H,2.9357203436,-2
.4244413439,2.6617322696\C,1.9371366567,-1.3116235239,-1.6674623029\H,
2.0888181468,0.8931907693,0.4359663492\H,3.8437556484,0.6153567838,0.4
447555164\H,2.9880781524,1.0622486061,-1.1036271672\N,-5.0285693359,-0
.608549623,0.1082461445\C,-3.6595626118,-0.5110562341,0.0668347081\C,-
2.9930931782,0.6015491916,0.854276419\O,-2.9932144795,-1.3326129115,-0
.6120595774\H,-1.9062192439,0.5337831814,0.7310250389\H,-3.3113617057,
1.5957790662,0.5044916093\H,-3.2195290165,0.5339998236,1.9295282959\I,
-0.270452988,-1.3132729765,-1.0964461941\C,-5.9027739958,0.2726927675,
0.8729606021\H,-6.4413005116,-0.2958575536,1.6514886491\H,-5.336498567
7,1.0731231356,1.3591289327\H,-6.6522699227,0.7348593337,0.2076763424\
C,-5.7039638041,-1.6744304356,-0.6285380579\H,-6.2732389678,-2.3171208
466,0.064372927\H,-6.4055604109,-1.2451639998,-1.3636652426\H,-4.95101
7874,-2.275974491,-1.1495182914\I,0.8923165909,2.2016132487,1.64161752
61\H,1.985967506,-0.561783419,-2.4635194959\H,2.0870504303,-2.32596054
95,-2.0479303451\\Version=IA64L-G03RevD.01\State=1-A\HF=-14403.2072073
\RMSD=5.138e-09\RMSF=2.506e-05\ZeroPoint=0.3160266\Thermal=0.3389716\D
ipole=-0.8097282,-1.5879098,-0.6409399\DipoleDeriv=-0.0386348,-0.02241
8,-0.0331111,0.0102559,-0.0717757,0.0554105\Polar=319.5632583,-17.4453
389,250.8023609,-2.9037826,56.077429,191.1464201\PG=C01 [X(C11H23I2N1O
1)]\NImag=0\\0.55726317,-0.02985652,0.45689658,-0.00475623,-0.02204629
546,0.00963572,-0.00814965,0.09378076,0.08188338\\0.00000174,0.0000079
1940,0.00001141,-0.00001195\\\@
```

ZPVE = 198.30966 kcal/mol

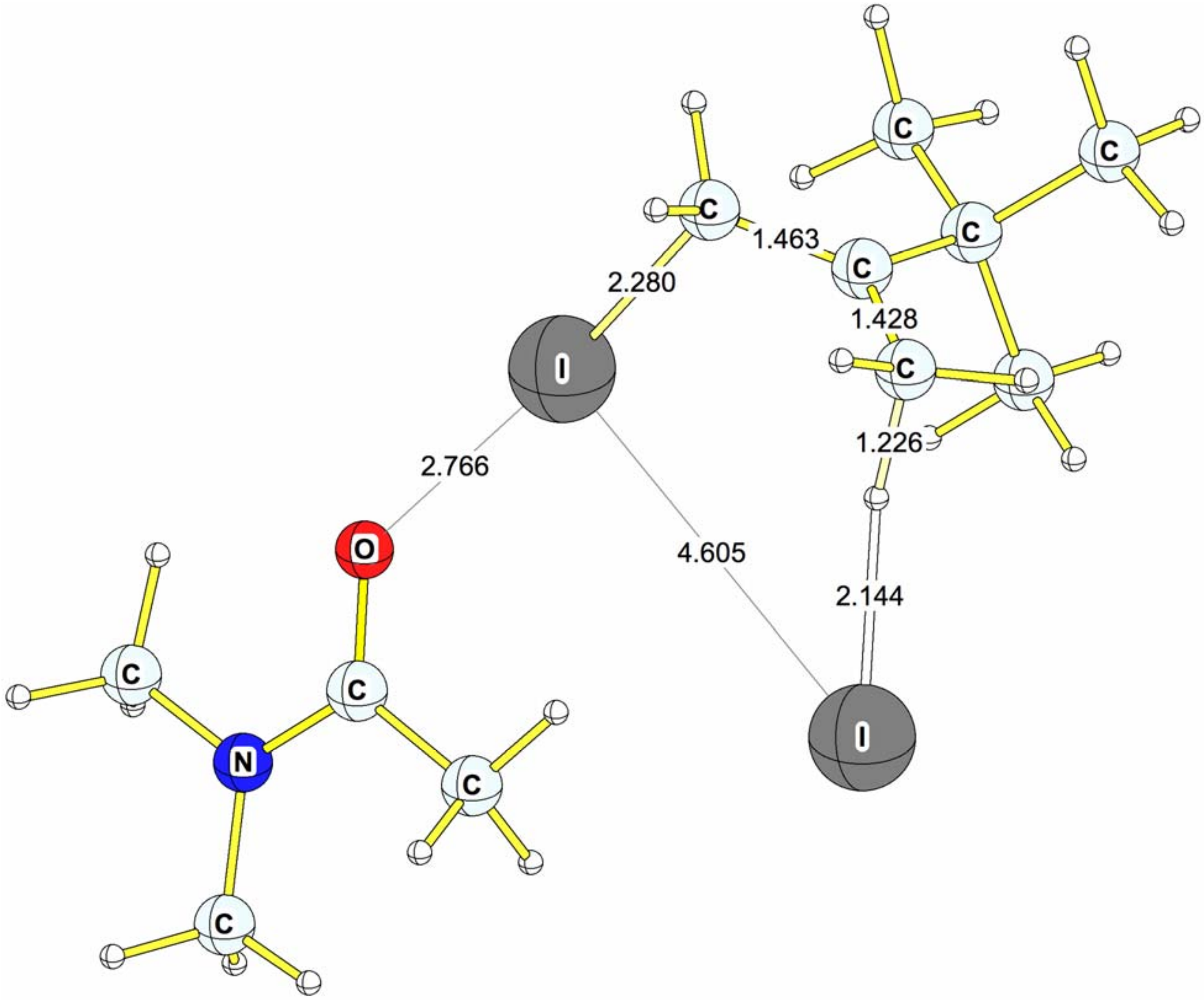

Figure 15 PW91PW91/DZVP computed structure of the DMA–––(11)–––HI final cluster (**FIN**)

2-Iodo-2-(*tert*-butyl)propene (11)

```
   1\1\GINC-A04\Freq\RPW91PW91\Gen\C7H13I1\TS\20-Nov-2007\0\\#P PW91PW91/
   gen Freq=NoRaman guess=read geom=check Name=TS\\I in
Me\\0,1\C,3.2781480392,1.2173903189,0.0713331464\C,2.3206103332,0.0360583489,0.32291415
   6\H,3.9770034439,1.3151154785,0.9170579129\H,2.7319585844,2.1692585234
   ,-0.022814909\H,3.8828507281,1.072336667,-0.8378768995\C,1.2988369194,
   -0.1198762312,-0.815251147\C,1.6081448448,0.268823468,1.6773141518\C,3
   .1680889623,-1.2607830299,0.4145317734\C,0.2224746251,-1.1566763556,-0
   .6750375329\H,0.9445592533,-0.5643522578,1.9532170073\H,2.3592787285,0
   .3724900715,2.4774513326\H,0.9994009619,1.1856342334,1.65777625\H,2.55
   42313115,-2.1460595582,0.643449826\H,3.7014087645,-1.4523451134,-0.529
   9258396\H,3.9164995697,-1.1666912659,1.2180722175\C,1.3581717835,0.573
   5576795,-1.9749574649\H,0.6162474787,0.4120943103,-2.7633177055\H,2.11
   84131005,1.3306538752,-2.1735748128\H,-0.083541615,-1.5745100292,-1.63
   91303628\H,0.459784534,-1.9673914655,0.0215094497\I,-1.7157433513,-0.3
   768196679,0.1272234505\\Version=IA64L-G03RevD.01\State=1-A\HF=-7194.64
   86433\RMSD=2.349e-09\RMSF=6.464e-06\ZeroPoint=0.1792601\Thermal=0.1896
   708\Dipole=0.9100723,-0.1414587,-0.1744733\DipoleDeriv=-0.0053971,-0.0
```

ZPVE = 112.48741 kcal/mol

Hydrogen iodide (HI)

```
1\1\FAU-CCC-CCAT072\FOpt\RPW91PW91\Gen\H1I1\SHUBINA\20-Nov-2007\0\\#P
PW91PW91/GEN OPT FREQ=NORAMAN NAME=SHUBINA\\HI\\0,1\H,-1.6186190562,-0
.0000014342,0.0000014342\I,0.0305399822,0.0000000271,-0.0000000271\\Ve
rsion=IA32L-G03RevC.02\State=1-SG\HF=-6920.7945857\RMSD=3.787e-09\RMSF
=1.449e-04\Dipole=-0.2726894,-0.0000002,0.0000002\PG=C*V [C*(H1I1)]\\@
```

ZPVE = 3.16244 kcal/mol

Table 9 PW91PW91/DZVP ZPVE corrected energies adjusted to the DMF solvent model and ωB97XD/DZVP, MP2/DZVP calculated energies

Name	PW91PW91/DZVP, DMF solvent	ωB97XD/DZVP		MP2/DZVP	
	E, Hartree	E, Hartree	ZPVE, kcal/mol	E, Hartree	ZPVE, kcal/mol
DMA	-287.76894	-287.76894	83.2	-286.86822	82.9
I_2	-13840.03568	-13840.03568	0.3	-13834.47196	0.3
CTC1	-14127.81716	-14127.81716	84.0	-14121.35381	83.8
(4)	-275.09576	-275.09576	122.8	-274.09813	122.6
CTC2	-14402.92530	-14402.92530	207.7	-14395.46313	206.9
TS	-14402.85260	-14402.85260	207.2	-14395.39328	207.1
FIN	-14402.56848	-14402.8932	205.0	-14395.43724	203.8
(11)	-7194.50488	-7194.50488	116.9	-7190.74682	116.6
HI	-6920.78289	-6920.60606	3.3	-6917.80635	3.3