Electronic Supplementary Information:

From Simple Organobromides or Olefins to Highly Value-added Bromohydrins: A Versatile Performance of Dimethyl Sulfoxide

Song Song,[a] Xiaoqiang Huang,[a] Yu-Feng Liang,[a] Conghui Tang,[a] Xinwei Li[a] and Ning Jiao*[a,b]

[a]State Key Laboratory of Natural and Biomimetic Drugs, Peking University, Xue Yuan Rd. 38, Beijing 100191, China

[b] Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, Shanghai 200062, China

Tables of Contents:

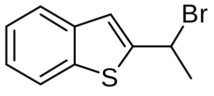
(A) General Remarks

All commercially available compounds were purchased from Sigma-Aldrich, Alfa-Aesar, Acros, Beijing Ouhe and Beijing Chemical Works, Ltd. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Analysis of crude reaction mixture was done on an Agilent 7890 GC System with an Agilent 5975 Mass Selective Detector. Products were purified by flash chromatography on silica gel. ^{1}H-NMR spectra were recorded on Bruker AVANCE III-400 spectrometers. Chemical shifts (in ppm) were referenced TMS in $CDCl_3$ (0 ppm). ^{13}C-NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.00 ppm). Mass spectra were recorded using a PE SCLEX QSTAR spectrometer. High resolution mass spectra were obtained with a Bruker APEX IV Fourier transform ion cyclotron resonance mass spectrometer.

(B) Preparation and Analytical Data of Starting Materials

Organobromides **1** were prepared according reported procedure from the corresponding alcohols in the presence of PBr_3 in CH_2Cl_2. [1]

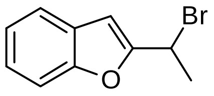
2-(1-Bromoethyl)benzo[b]thiophene (1k)



1k

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.76 (m, 1H), 7.72–7.69 (m, 1H), 7.35–7.30 (m, 3H), 5.54 (q, *J* = 6.8 Hz, 1H), 2.16 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 139.7, 139.0, 124.9, 124.6, 123.9, 122.4, 121.6, 43.5, 27.5.

2-(1-Bromoethyl)benzofuran (1l)

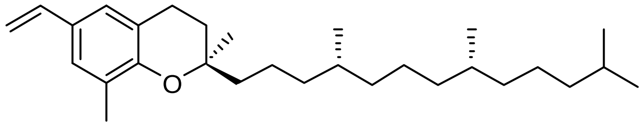


1l

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.2 Hz, 1H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.33–7.29 (m, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 6.70 (s, 1H), 5.32 (q, *J* = 6.8 Hz, 1H), 2.12 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 154.8, 127.9, 125.0, 123.1, 121.3, 111.4, 103.5, 39.6, 23.7.

Alkenes **3y** and **3z** were prepared according reported procedure from the coupling of potassium vinyltrifluoroborate and the corresponding triflate in the presence of $PdCl_2$, PPh_3 and Cs_2CO_3.[2]

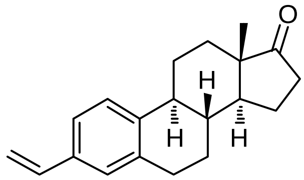
(*R*)-2,8-Dimethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)-6-vinylchroman (3y)



3y

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (s, 1H), 6.99 (s, 1H), 6.63 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.59 (d, *J* = 17.6 Hz, 1H), 5.08 (d, *J* = 10.9 Hz, 1H), 2.78 (t, *J* = 6.3 Hz, 2H), 2.21 (s, 3H), 1.86–1.78 (m, 2H), 1.64–1.10 (m, 24H), 0.93–0.87 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 136.8, 128.5, 126.3, 126.2, 125.0, 120.3, 110.4, 76.2, 40.1, 39.4, 37.5, 37.45, 37.43, 37.3, 32.8, 32.7, 31.3, 28.0, 24.8, 24.5, 24.3, 22.7, 22.6, 22.3, 21.0, 19.8, 19.7, 16.0. HRMS (ESI) Calcd for $[C_{29}H_{49}O, M + H]^+$: 413.3778, Found: 413.3781.

(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-vinyl-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one (3z)

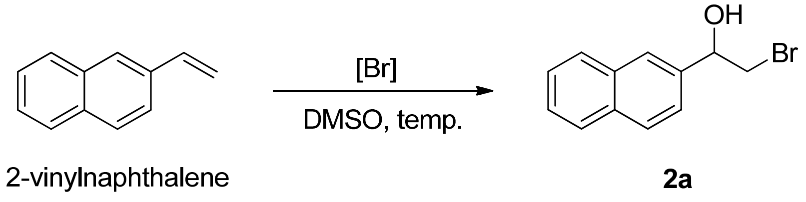


3z

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.23 (m, 2H), 7.18 (s, 1H), 6.70 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.74 (d, *J* = 17.6 Hz, 1H), 5.23 (d, *J* = 10.8 Hz, 1H), 2.95 (dd, *J* = 8.6, 3.4 Hz, 2H), 2.54 (dd, *J* = 18.4, 8.8 Hz, 1H), 2.47–2.44 (m, 1H), 2.35–2.31 (m, 1H), 2.20–1.97 (m, 4H), 1.69–1.45 (m, 6H), 0.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 220.7, 139.4, 136.49, 136.47, 135.1, 126.8, 125.5, 123.5, 113.1, 50.4, 47.9, 44.3, 38.1, 35.8, 31.5, 29.3, 26.4, 25.6, 21.5, 13.8.

(C) Optimization of the Reaction Conditions

Table S1. Hydroxybromination of 2-vinylnaphthalene.[a]



entry	[Br]	temp.	time (h)	yield (%)[b]
1	2.0 equiv Br_2	60 °C	24	22
2	2.0 equiv NBS	60 °C	24	23
3	2.0 equiv $CuBr_2$	60 °C	24	25
4	2.0 equiv NH_4Br	60 °C	24	0
5	2.0 equiv NaBr	60 °C	24	0
6	2.0 equiv HBr (33% in AcOH)	60 °C	24	80
7	2.0 equiv HBr (48% in H_2O)	60 °C	24	82
8	1.2 equiv HBr (48% in H_2O)	60 °C	24	82

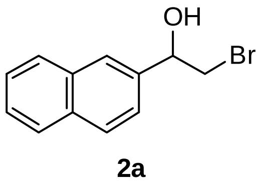
9	1.2 equiv HBr (48% in H_2O)	60 °C	12	84
10	1.2 equiv HBr (48% in H_2O)	60 °C	6	76
11	1.2 equiv HBr (20% in H_2O)	60 °C	12	84
12	1.2 equiv HBr (10% in H_2O)	60 °C	12	79
13	1.2 equiv HBr (48% in H_2O)	40 °C	12	66
14	1.2 equiv HBr (48% in H_2O)	70 °C	12	80
15	1.2 equiv HBr (48% in H_2O)	90 °C	12	48
16	1.2 equiv NaBr+1.2 equiv H_2SO_4	60 °C	12	75

[a] Reaction conditions: The mixture of 2-vinylnaphthalene (77.1 mg, 0.5 mmol) and [Br] in DMSO (2 mL) were stirred under air. [b] Isolated yield.

(D) Experimental Procedure and Characterization Data of Products

Typical procedure for hydroxybromination of secondary benzyl bromides 1: The mixture of bromide **1** (0.5 mmol) and DMSO (2 mL) were stirred at 60 °C for 18 hours under argon atmosphere. After cooling down to room temperature, the mixture was diluted with water (10 mL) and extracted with EA (3 × 10 mL). The combined extracts were washed with a saturated solution of NaCl (15 mL), dried over $MgSO_4$, and evaporated *in vacuo*. The residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate) to afford the bromohydrin **2**.

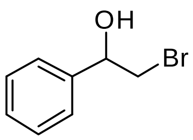
2-Bromo-1-(2-naphthyl)ethanol (2a)[3]



2a

The reaction of 2-(1-bromoethyl)naphthalene **1a** (117.6 mg, 0.5 mmol) in DMSO (2 mL) at 60 °C for 12 h, affords 89.1 mg (71%) of **2a** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.81 (m, 4H), 7.51–7.43 (m, 3H), 5.07 (dd, *J* = 8.9, 3.3 Hz, 1H), 3.70 (dd, *J* = 10.5, 3.4 Hz, 1H), 3.60 (dd, *J* = 10.5, 8.9 Hz, 1H), 2.78 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 133.3, 133.2, 128.5, 128.0, 127.7, 126.4, 126.3, 125.2, 123.5, 73.9, 40.0.

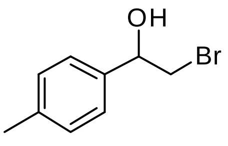
2-Bromo-(1-phenyl)ethanol (2b)[4]



2b

The reaction of 1-(1-bromoethyl)-benzene **1b** (92.5 mg, 0.5 mmol) in DMSO (2 mL) at 60 °C for 18 h, affords 61.9 mg (62%) of **2b** as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.31 (m, 5H), 4.92 (dt, *J* = 8.9, 3.1 Hz, 1H), 3.63 (dd, *J* = 10.5, 3.3 Hz, 1H), 3.56–3.51 (m, 1H), 2.68 (d, *J* = 3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 128.7, 128.4, 125.9, 73.8, 40.2.

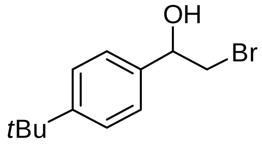
2-Bromo-1-(*p*-tolyl)ethanol (2c)[4]



2c

The reaction of 1-(1-bromoethyl)-4-methylbenzene **1c** (99.5 mg, 0.5 mmol) in DMSO (2 mL) at 60 °C for 18 h, affords 83.0 mg (77%) of **2c** as a white solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.25 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 4.88–4.86 (m, 1H), 3.60 (dd, *J* = 10.4, 3.4 Hz, 1H), 3.52 (dd, *J* = 10.4, 3.4 Hz, 1H), 2.64 (d, *J* = 3.0 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 138.2, 137.3, 129.3, 125.9, 73.6, 40.2, 21.1.

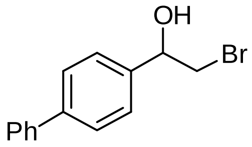
2-Bromo-1-(4-(*tert*-butyl)phenyl)ethanol (2d)[4]



2d

The reaction of 1-(1-bromoethyl)-4-(*tert*-butyl)benzene **1d** (120.6 mg, 0.5 mmol) in DMSO (2 mL) at 60 °C for 18 h, affords 101.2 mg (79%) of **2d** as a white solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 4.89 (dt, *J* = 9.0, 3.0 Hz, 1H), 3.62 (dd, *J* = 10.4, 3.3 Hz, 1H), 3.56–3.52 (m, 1H), 2.65 (d, *J* = 3.0 Hz, 1H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 151.5, 137.2, 125.7, 125.6, 73.6, 40.2, 34.6, 31.3.

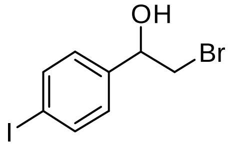
1-([1,1'-Biphenyl]-4-yl)-2-bromoethanol (2e)



2e

The reaction of 4-(1-bromoethyl)-1,1'-biphenyl **1e** (130.6 mg, 0.5 mmol) in DMSO (2 mL) at 60 °C for 18 h, affords 109.5 mg (79%) of **2e** as a white solid. 1H NMR (400 MHz, CDCl$_3$) δ 7.63–7.60 (m, 4H), 7.49–7.45 (m, 4H), 7.38 (t, *J* = 7.3 Hz, 1H), 4.98 (dd, *J* = 8.9, 3.3 Hz, 1H), 3.69 (dd, *J* = 10.5, 3.4 Hz, 1H), 3.62–3.57 (m, 1H), 2.77 (s, 1H). 13C NMR (100 MHz, CDCl$_3$) δ 141.3, 140.5, 139.2, 128.8, 127.4, 127.3, 127.0, 126.4, 73.5, 40.0. HRMS (ESI) Calcd for [$C_{14}H_{13}BrNaO$, M + Na]$^+$: 299.0042, Found: 299.0046.

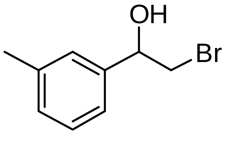
2-Bromo-1-(4-iodopheny)ethanol (2f)



2f

The reaction of 1-(1-bromoethyl)-4-iodobenzene **1f** (130.6 mg, 0.5 mmol) in DMSO (2 mL) at 60 °C for 18 h, affords 58.2 mg (36%) of **2f** as a white solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), 4.87 (d, *J* = 8.6 Hz, 1H), 3.60 (dd, *J* = 10.5, 3.4 Hz, 1H), 3.49 (dd, *J* = 10.4, 8.9 Hz, 1H), 2.67 (s, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 139.9, 137.8, 127.9, 94.0, 73.1, 39.8. HRMS (ESI) Calcd for [$C_8H_8BrINaO$, M + Na]$^+$: 348.8695, Found: 348.8711.

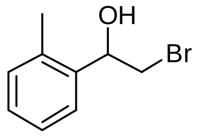
2-Bromo-1-(*m*-tolyl)ethanol (2g)[5]



2g

The reaction of 1-(1-bromoethyl)-3-methylbenzene **1g** (99.5 mg, 0.5 mmol) in DMSO (2 mL) at 60 °C for 12 h, affords 72.0 mg (67%) of **2g** as a white solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.25 (t, *J* = 6.5 Hz, 1H), 7.19 (s, 1H), 7.16–7.12 (m, 2H), 4.87 (dt, *J* = 8.8, 3.0 Hz, 1H), 3.61 (dd, *J* = 10.4, 3.3 Hz, 1H), 3.54–3.50 (m, 1H), 2.68 (d, *J* = 3.2 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 140.2, 138.4, 129.2, 128.5, 126.6, 123.0, 73.8, 40.2, 21.4.

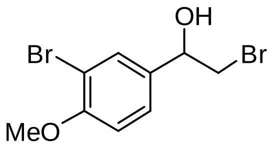
2-Bromo-1-(*o*-tolyl)ethanol (2h)[6]



2h

The reaction of 1-(1-bromoethyl)-4-methylbenzene **1h** (99.5 mg, 0.5 mmol) in DMSO (2 mL) at 60 °C for 18 h, affords 77.4 mg (72%) of **2h** as pale yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.52–7.50 (m, 1H), 7.26–7.20 (m, 2H), 7.16–7.14 (m, 1H), 5.12 (d, *J* = 9.4 Hz, 1H), 3.57 (dd, *J* = 10.6, 3.0 Hz, 1H), 3.47 (dd, *J* = 10.6, 3.0 Hz, 1H), 2.68 (d, *J* = 2.1 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 138.3, 134.7, 130.6, 128.2, 126.5, 125.3, 70.7, 39.0, 19.0.

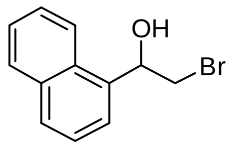
2-Bromo-1-(3-bromo-4-methoxyphenyl)ethanol (2i)



2i

The reaction of 1-(1-bromoethyl)-(3-bromo-4-methoxy)-benzene **1i** (147.0 mg, 0.5 mmol) in DMSO (2 mL) at 60 °C for 18 h, affords 94.6 mg (61%) of **2i** as a white solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.58 (d, *J* = 2.0 Hz, 1H), 7.29 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.89 (d, *J* = 8.5 Hz, 1H), 4.85 (dt, *J* = 8.7, 3.2 Hz, 1H), 3.90 (s, 3H), 3.59 (dd, *J* = 10.5, 3.4 Hz, 1H), 3.50 (dd, *J* = 10.4, 8.9 Hz, 1H), 2.68 (d, *J* = 3.2 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 155.8, 133.8, 131.0, 126.2, 111.8, 72.7, 56.3, 40.0. HRMS (ESI) Calcd for [$C_9H_{10}Br_2NaO_2$, M + Na]$^+$: 330.8940, Found: 330.8941.

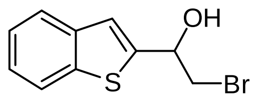
2-Bromo-1-(naphthyl)ethanol (2j)



2j

The reaction of 1-(1-bromoethyl)naphthalene **1j** (117.6 mg, 0.5 mmol) in DMSO (2 mL) at 60 °C for 18 h, affords 95.3 mg (76%) of **2j** as colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.96 (d, *J* = 8.3 Hz, 1H), 7.89–7.86 (m, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 7.2 Hz, 1H), 7.56–7.46 (m, 3H), 5.68 (dd, *J* = 9.4, 2.3 Hz, 1H), 3.82 (dd, *J* = 10.7, 2.7 Hz, 1H), 3.61 (dd, *J* = 10.7, 9.4 Hz, 1H), 2.86 (s, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 135.7, 133.7, 130.0, 129.1, 128.9, 126.5, 125.7, 125.5, 123.5, 122.3, 71.0, 39.7. HRMS (ESI) Calcd for [$C_{12}H_{11}BrONa$, M + Na]$^+$: 272.9886, Found: 272.9896.

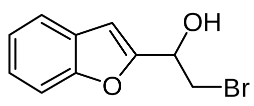
1-(Benzo[*b*]thiophenyl)-2-bromoethanol (2k)



2k

The reaction of 2-(1-bromoethyl)benzothiophene **1k** (120.6 mg, 0.5 mmol) in DMSO (2 mL) at 60 °C for 18 h, affords 87.4 mg (68%) of **2k** as a white solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.81 (d, *J* = 7.3 Hz, 1H), 7.74–7.71 (m, 1H), 7.37–7.30 (m, 2H), 7.25 (s, 1H), 5.22 (dt, *J* = 7.8, 3.9 Hz, 1H), 3.75 (dd, *J* = 10.5, 3.8 Hz, 1H), 3.68 (dd, *J* = 10.5, 8.0 Hz, 1H), 2.93 (d, *J* = 4.3 Hz, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 144.2, 139.2, 124.6, 124.5, 123.7, 122.5, 121.3, 70.3, 39.1. HRMS (ESI) Calcd for [$C_{10}H_9BrNaOS$, M + Na]$^+$: 278.9450, Found: 278.9447.

1-(Benzofuran-2-yl)-2-bromoethanol (2l)

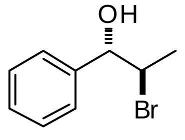


2l

The reaction of 2-(1-bromoethyl)benzofuran **1l** (112.5 mg, 0.5 mmol) in DMSO (2 mL) at 60 °C for 18 h, affords 100.9 mg

(71%) of **2l** as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.27 (t, *J* = 7.4 Hz, 1H), 7.22 (dd, *J* = 9.0, 5.7 Hz, 1H), 6.72 (s, 1H), 5.07–5.03 (m, 1H), 3.81 (dd, *J* = 10.5, 4.4 Hz, 1H), 3.75 (dd, *J* = 10.5, 6.8 Hz, 1H), 2.98 (d, *J* = 5.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 154.7, 127.7, 124.5, 123.0, 121.2, 111.2, 104.2, 68.0, 36.3. HRMS (ESI) Calcd for [$C_{10}H_9BrNaO_2$, M + Na]$^+$: 262.9678, Found: 262.9678.

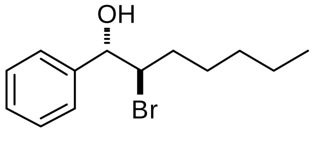
2-Bromo-1-phenylpropan-1-ol (2m)[7]



2m

The reaction of (1-bromopropyl)benzene **1m** (99.5 mg, 0.5 mmol) in DMSO (2 mL) at 60 °C for 18 h, affords 80.0 mg (65%) of **2m** as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.29 (m, 5H), 4.99 (t, *J* = 3.4 Hz, 1H), 4.41 (qd, *J* = 6.8, 3.6 Hz, 1H), 2.57 (d, *J* = 3.3 Hz, 1H), 1.54 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 128.3, 128.0, 126.3, 77.2, 56.1, 18.8.

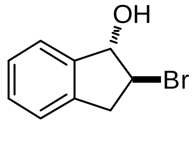
2-Bromo-1-phenylheptan-1-ol (2n)



2n

The reaction of (1-bromoheptyl)benzene **1n** (127.6 mg, 0.5 mmol) in DMSO (2 mL) at 60 °C for 18 h, affords 84.8 mg (62%) of **2n** as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.28 (m, 5H), 5.01 (t, *J* = 3.7 Hz, 1H), 4.33–4.28 (m, 1H), 2.57 (d, *J* = 3.5 Hz, 1H), 1.80–1.54 (m, 3H), 1.32–1.13 (m, 5H), 0.84 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9, 128.5, 128.3, 128.0, 126.5, 77.2, 63.7, 31.5, 31.0, 27.5, 22.4, 13.9. HRMS (ESI) Calcd for [$C_{13}H_{19}BrONa$, M + Na]$^+$: 293.0512, Found: 293.0517.

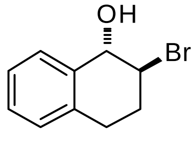
2-Bromo-2,3-dihydro-1*H*-inden-1-ol (2o)[8]



2o

The reaction of 1-bromo-2,3-dihydro-1*H*-indene **1o** (98.5 mg, 0.5 mmol) in DMSO (2 mL) at 60 °C for 18 h, affords 76.9 mg (72%) of **2o** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.39 (m, 1H), 7.32–7.21 (m, 3H), 5.30 (d, *J* = 3.8 Hz, 1H), 4.26 (dd, *J* = 13.2, 7.3 Hz, 1H), 3.56 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.21 (dd, *J* = 16.2, 7.4 Hz, 1H), 2.56 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 139.7, 129.0, 127.6, 124.5, 124.1, 83.4, 54.5, 40.4, 40.2.

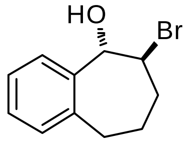
2-Bromo-1,2,3,4-tetrahydronaphthalen-1-ol (2p)[4]



2p

The reaction of 1-bromo-1,2,3,4-tetrahydronaphthalene **1p** (98.5 mg, 0.5 mmol) in DMSO (2 mL) at 60 °C for 18 h, affords 88.0 mg (78%) of **2p** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.49 (m, 1H), 7.26–7.21 (m, 2H), 7.11–7.09 (m, 1H), 4.88 (d, *J* = 6.7 Hz, 1H), 4.34 (ddd, *J* = 9.8, 7.0, 3.2 Hz, 1H), 3.00–2.86 (m, 2H), 2.64 (s, 1H), 2.53–2.46 (m, 1H), 2.31–2.21 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.4, 134.9, 128.5, 128.3, 128.0, 126.6, 74.0, 56.1, 29.6, 28.0.

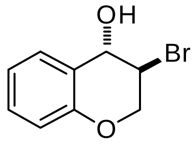
6-Bromo-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-ol (2q)



2q

The reaction of 5-bromo-6,7,8,9-tetrahydro-5*H*-benzo[7]annulene **1q** (112.6 mg, 0.5 mmol) in DMSO (2 mL) at 60 °C for 18 h, affords 60.0 mg (50%) of **2q** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 3.8 Hz, 1H), 7.25–7.18 (m, 2H), 7.11–7.09 (m, 1H), 4.96 (d, *J* = 8.3 Hz, 1H), 4.37–4.34 (m, 1H), 2.94–2.89 (m, 1H), 2.79–2.72 (m, 1H), 2.69 (s, 1H), 2.51–2.45 (m, 1H), 2.25–2.16 (m, 1H), 2.00–1.91 (m, 1H), 1.61–1.54 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 138.3, 129.3, 128.1, 127.0, 126.3, 76.3, 60.4, 36.6, 33.9, 24.5. HRMS (ESI) Calcd for $[C_{11}H_{13}BrONa, M + Na]^+$: 263.0042, Found: 263.0040.

3-Bromochroman-4-ol (2r)

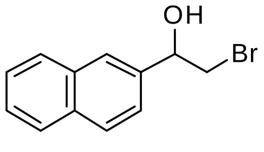


2r

The reaction of 4-bromochroman **1r** (106.5 mg, 0.5 mmol) in DMSO (2 mL) at 60 °C for 18 h, affords 101.9 mg (89%) of **2r** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.7 Hz, 1H), 7.28–7.24 (m, 1H), 7.00 (td, *J* = 7.6, 1.0 Hz, 1H), 6.89 (dd, *J* = 8.3 Hz, 0.4 Hz, 1H), 4.89 (t, *J* = 4.6 Hz, 1H), 4.52–4.47 (m, 1H), 4.32–4.27 (m, 2H), 2.52 (d, *J* = 4.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 130.2, 129.3, 121.6, 121.3, 116.9, 69.8, 66.2, 48.1. HRMS (ESI) Calcd for $[C_9H_9BrNaO_2, M + Na]^+$: 250.9678, Found: 250.9674.

Typical procedure for hydroxybromination of alkenes 3: Alkene **3** (0.5 mmol) and aqueous hydrobromic acid (48%, 0.6 mmol, 101.1 mg) were dissolved in DMSO (2 mL). The mixture were stirred at 60 °C for 12 hours under air. After cooling down to room temperature, the mixture was diluted with water (10 mL) and extracted with EA (3 × 10 mL). The combined extracts were washed with a saturated solution of NaCl (15 mL), dried over $MgSO_4$, and evaporated *in vacuo*. The residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate) to afford the bromohydrin **2**.

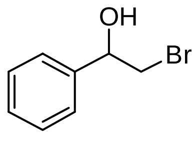
2-Bromo-1-(2-naphthyl)ethanol (2a)[3]



2a

The reaction of 2-vinylnaphthalene **3a** (77.1 mg, 0.5 mmol) and aqueous hydrobromic acid (48%, 101.1 mg, 0.6 mmol) in DMSO (2 mL) at 60 °C for 12 h, affords 105.0 mg (84%) of **2a** as a white solid.

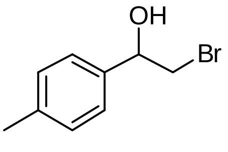
2-Bromo-1-phenylethanol (2b)[4]



2b

The reaction of styrene **3b** (52.1 mg, 0.5 mmol) and aqueous hydrobromic acid (48%, 101.1 mg, 0.6 mmol) in DMSO (2 mL) at 60 °C for 12 h, affords 71.5 mg (71%) of **2b** as colorless oil.

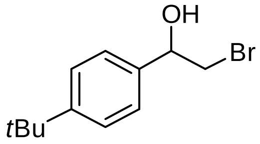
2-Bromo-1-(*p*-tolyl)ethanol (2c)[4]



2c

The reaction of 4-methylstyrene **3c** (59.1 mg, 0.5 mmol) and aqueous hydrobromic acid (48%, 101.1 mg, 0.6 mmol) in DMSO (2 mL) at 60 °C for 12 h, affords 97.4 mg (91%) of **2c** as a white solid.

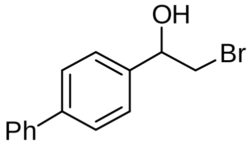
2-Bromo-1-(4-(*tert*-butyl)phenyl)ethanol (2d)[4]



2d

The reaction of 1-(*tert*-butyl)-4-vinylbenzene **3d** (80.1 mg, 0.5 mmol) and aqueous hydrobromic acid (48%, 101.1 mg, 0.6 mmol) in DMSO (2 mL) at 60 °C for 12 h, affords 110.2 mg (86%) of **2d** as a white solid.

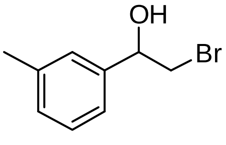
2-Bromo-1-(4-phenyl-phenyl)ethanol (2e)



2e

The reaction of 4-vinyl-1,1'-biphenyl **3e** (90.1 mg, 0.5 mmol) and aqueous hydrobromic acid (48%, 101.1 mg, 0.6 mmol) in DMSO (2 mL) at 60 °C for 12 h, affords 126.1 mg (91%) of **2e** as a white solid.

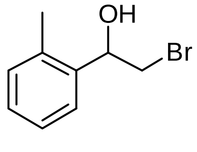
2-Bromo-1-(*m*-tolyl)ethanol (2g)[5]



2g

The reaction of 3-methyl-styrene **3g** (59.1 mg, 0.5 mmol) and aqueous hydrobromic acid (48%, 101.1 mg, 0.6 mmol) in DMSO (2 mL) at 60 °C for 12 h, affords 86.8 mg (81%) of **2g** as a white solid.

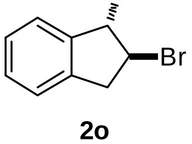
2-Bromo-1-(*o*-tolyl)ethanol (2h)[6]



2h

The reaction of 2-methylstyrene **3h** (59.1 mg, 0.5 mmol) and aqueous hydrobromic acid (48%, 101.1 mg, 0.6 mmol) in DMSO (2 mL) at 60 °C for 12 h, affords 97.2 mg (90%) of **2h** as pale yellow oil.

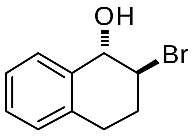
2-Bromo-2,3-dihydro-1*H*-inden-1-ol (2o)[8]



2o

The reaction of indene **3o** (58.1 mg, 0.5 mmol) and aqueous hydrobromic acid (48%, 101.1 mg, 0.6 mmol) in DMSO (2 mL) at 60 °C for 12 h, affords 74.0 mg (69%) of **2o** as a white solid.

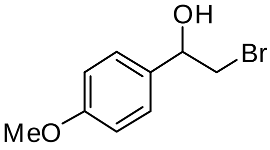
2-Bromo-1,2,3,4-tetrahydronaphthalen-1-ol (2p)[4]



2p

The reaction of 1,2-dihydronaphthalene **3p** (65.1 mg, 0.5 mmol) and aqueous hydrobromic acid (48%, 101.1 mg, 0.6 mmol) in DMSO (2 mL) at 60 °C for 12 h, affords 92.1 mg (81%) of **2p** as a white solid.

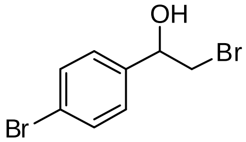
2-Bromo-1-(4-methoxyphenyl)ethanol (2s)[4]



2s

The reaction of 4-methoxystyrene **3s** (67.1 mg, 0.5 mmol) and aqueous hydrobromic acid (48%, 101.1 mg, 0.6 mmol) in DMSO (2 mL) at 60 °C for 12 h, affords 107.5 mg (93%) of **2s** as a white solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.27 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 4.84 (dd, *J* = 8.7, 3.6 Hz, 1H), 3.78 (s, 3H), 3.56 (dd, *J* = 10.4, 3.7 Hz, 1H), 3.50 (dd, *J* = 10.4, 8.8 Hz, 1H), 2.77 (s, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 159.5, 132.4, 127.2, 114.0, 73.3, 55.2, 40.0.

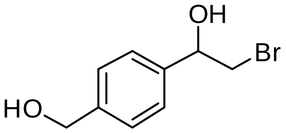
2-Bromo-1-(4-bromophenyl)ethanol (2t)[9]



2t

The reaction of 4-bromostyrene **3t** (91.5 mg, 0.5 mmol) and aqueous hydrobromic acid (48%, 101.1 mg, 0.6 mmol) in DMSO (2 mL) at 60 °C for 12 h, affords 86.0 mg (61%) of **2t** as a white solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.49 (d, *J* = 8.6 Hz, 2H), 7.25 (d, *J* = 8.6 Hz, 2H), 4.87 (dt, *J* = 8.8, 3.2 Hz, 1H), 3.59 (dd, *J* = 10.6, 3.2 Hz, 1H), 3.48 (dd, *J* = 10.6, 8.8 Hz, 1H), 2.76 (d, *J* = 3.2 Hz, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 139.2, 131.7, 127.6, 122.3, 73.0, 39.7.

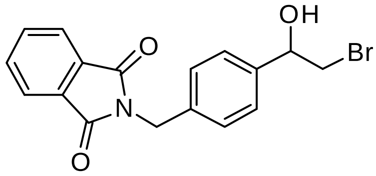
2-Bromo-1-(4-(hydroxymethyl)phenyl)ethanol (2u)



2u

The reaction of (4-vinylphenyl)methanol **3u** (67.1 mg, 0.5 mmol) and aqueous hydrobromic acid (48%, 101.1 mg, 0.6 mmol) in DMSO (2 mL) at 60 °C for 12 h, affords 95.8 mg (83%) of **2u** as a white solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.37–7.32 (m, 4H), 4.88 (dd, *J* = 8.6, 3.4 Hz, 1H), 4.62 (s, 2H), 3.58 (dd, *J* = 10.4, 3.4 Hz, 1H), 3.50 (dd, *J* = 10.3, 8.6 Hz, 1H), 3.03 (brs, 1H), 2.37 (brs, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 141.0, 139.7, 127.2, 126.1, 73.5, 64.7, 39.9. HRMS (ESI) Calcd for [$C_9H_{11}BrNaO_2$, M + Na]$^+$: 252.9835, Found: 252.9842.

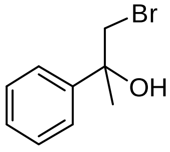
2-(4-(2-Bromo-1-hydroxyethyl)benzyl)isoindoline-1,3-dione (2v)



2v

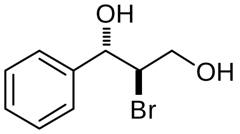
The reaction of 2-(4-vinylbenzyl)isoindoline-1,3-dione **3v** (131.6 mg, 0.5 mmol) and aqueous hydrobromic acid (48%, 101.1 mg, 0.6 mmol) in DMSO (2 mL) at 60 °C for 12 h, affords 131.5 mg (73%) of **2v** as a white solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.83 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.70 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 4.88 (dd, *J* = 8.8, 3.4 Hz, 1H), 4.83 (s, 2H), 3.58 (dd, *J* = 10.5, 3.4 Hz, 1H), 3.48 (dd, *J* = 10.5, 8.8 Hz, 1H), 2.75 (brs, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 168.0, 140.0, 136.5, 134.0, 132.0, 128.9, 126.3, 123.3, 73.4, 41.2, 39.9. HRMS (ESI) Calcd for [$C_{17}H_{14}BrNNaO_3$, M + Na]$^+$: 382.0049, Found: 382.0053.

1-Bromo-2-phenylpropan-2-ol (2w)[7]


2w

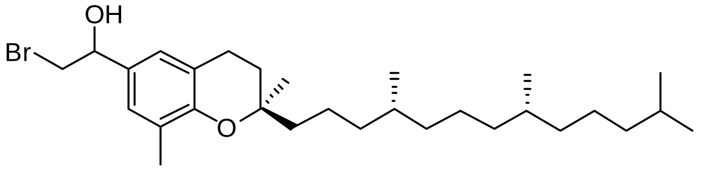
The reaction of α-methylstyrene **3w** (59.1 mg, 0.5 mmol) and aqueous hydrobromic acid (48%, 101.1 mg, 0.6 mmol) in DMSO (2 mL) at 60 °C for 12 h, affords 45.0 mg (42%) of **2w** as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.45 (m, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.31–7.27 (m, 1H), 3.76 (d, *J* = 10.6 Hz, 1H), 3.70 (d, *J* = 10.6 Hz, 1H), 2.59 (s, 1H), 1.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 128.4, 127.5, 124.8, 73.1, 46.3, 28.0.

2-Bromo-1-phenylpropane-1,3-diol (2x)[10]


2x

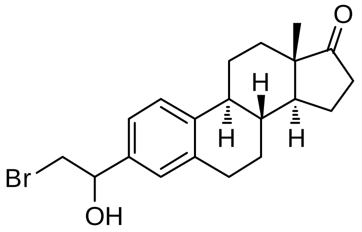
The reaction of (*E*)-cinnamyl alcohol **3x** (67.1 mg, 0.5 mmol) and aqueous hydrobromic acid (48%, 101.1 mg, 0.6 mmol) in DMSO (2 mL) at 60 °C for 12 h, affords 61.2 mg (53%) of **2x** as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.30 (m, 5H), 5.01 (dd, *J* = 6.1, 4.0 Hz, 1H), 4.26 (dd, *J* = 10.9, 4.9 Hz, 1H), 3.99 (dt, *J* = 11.4, 5.6 Hz, 1H), 3.88–3.82 (m, 1H), 3.40 (d, *J* = 4.1 Hz, 1H), 2.83 (t, *J* = 6.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 128.5, 128.4, 126.5, 76.8, 64.1, 59.4.

2-Bromo-1-((*S*)-2,8-dimethyl-2-((4*S*,8*S*)-4,8,12-trimethyltridecyl)chroman-6-yl)ethanol (2y)


2y

The reaction of (*S*)-2,8-dimethyl-2-((4*S*,8*S*)-4,8,12-trimethyltridecyl)-6-vinylchroman **3y** (206.3 mg, 0.5 mmol) and aqueous hydrobromic acid (48%, 101.1 mg, 0.6 mmol) in DMSO (2 mL) at 60 °C for 5 h, affords 172.0 mg (86%) of **2y** as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (s, 1H), 6.92 (s, 1H), 4.79 (dd, *J* = 9.1, 3.3 Hz, 1H), 3.60 (dd, *J* = 10.4, 3.5 Hz, 1H), 3.54 (dd, *J* = 10.4, 8.8 Hz, 1H), 2.75 (t, *J* = 7.1 Hz, 2H), 2.55 (brs, 1H), 2.17 (s, 2H), 1.82–1.73 (m, 2H), 1.60–1.04 (m, 24H), 0.89–0.84 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 130.3, 126.6, 126.00 (125.98), 124.57 (124.53), 120.6, 73.9, 40.4, 40.2, 40.1, 39.4, 37.43, 37.41, 32.8, 32.7, 31.1, 28.0, 24.8, 24.3, 24.2, 22.7, 22.6, 22.3, 21.0, 19.7, 19.6, 16.1. HRMS (ESI) Calcd for [$C_{29}H_{49}BrNaO_2$, M + Na]$^+$: 531.2808, Found: 531.2817.

3-(Bromoethanol)estrone (2z)

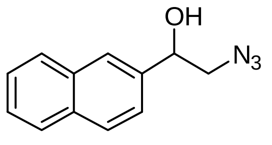

2z

The reaction of 3- vinylestrone **3z** (140.2 mg, 0.5 mmol) and aqueous hydrobromic acid (48%, 101.1 mg, 0.6 mmol) in DMSO (2 mL) at 60 °C for 3 h, affords 142.0 mg (75%) of **2z** as a white solid. ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.30 (d, *J* = 8.2 Hz, 1H), 7.15 (d, *J* = 8.2 Hz, 1H), 7.13 (s, 1H), 4.87 (d, *J* = 8.8 Hz, 1H), 3.63 (dd, *J* = 10.4, 3.2 Hz, 1H), 3.54 (dd, *J* = 10.0, 9.2 Hz, 1H), 2.93 (dd, *J* = 8.4, 4.4 Hz, 1H), 2.69 (s, 1H), 2.54–2.41 (m, 2H), 2.29–2.26 (m, 1H), 2.19–1.95 (m, 4H), 1.68–1.42 (m, 6H), 0.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.8, 140.1, 137.8, 136.9, 126.50 (126.48), 125.7, 123.39 (123.37), 73.6 (73.5), 50.4, 47.9, 44.3, 40.1, 38.0, 35.8, 31.5, 29.38 (29.35), 26.4, 25.6, 21.5, 13.8. HRMS (ESI) Calcd for $[C_{20}H_{26}BrO_2, M + H]^+$: 377.1111, Found: 377.1112.

One-pot procedure for the transformation of bromides 1 to azidoalcohols 4: Bromide **1** (0.5 mmol) was stirred in DMSO (2 mL) at 60 °C for 18 hours under argon atmosphere. Then sodium azide (65.0 mg, 1.0 mmol) was added to the mixture and the mixture was stirred for another 12 hours at 60 °C. After cooling down to room temperature, the mixture were diluted with water (10 mL) and extracted with EA (3 × 10 mL). The combined extracts were washed with a saturated solution of NaCl (15 mL), dried over $MgSO_4$, and evaporated *in vacuo*. The residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate) to afford the azidoalcohol **4**.

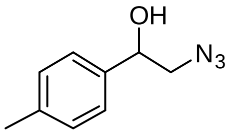
2-Azido-1-(2-naphthyl)ethanol (4a)[11]



4a

The hydroxybromination of 2-(1-bromoethyl)naphthalene **1a** (117.5 mg, 0.5 mmol) in DMSO (2 mL) at 60 °C for 18 hours under argon atmosphere, followed by the addition of NaN_3 (65 mg, 1 mmol), affords 74.1 mg (69%) of **4a** as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.87–7.83 (m, 4H), 7.52–7.45 (m, 3H), 5.05 (dd, *J* = 7.8, 4.1 Hz, 1H), 3.57 (dd, *J* = 12.4, 8.0 Hz, 1H), 3.52 (dd, *J* = 12.4, 4.8 Hz, 1H), 2.48 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 133.2, 133.1, 128.5, 127.9, 127.7, 126.4, 126.2, 124.9, 123.5, 73.5, 57.9.

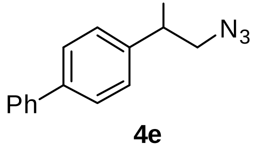
2-Azido-1-(*p*-tolyl)ethanol (4c)[11]



4c

The hydroxybromination of 1-(1-Bromoethyl)-4-methylbenzene **1c** (99.5 mg, 0.5 mmol) in DMSO (2 mL) at 60 °C for 18 hours under argon atmosphere, followed by the addition of NaN_3 (65 mg, 1 mmol), affords 65.5 mg (74%) of **4c** as colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 4.78 (dd, *J* = 8.1, 3.9 Hz, 1H), 3.42 (dd, *J* = 12.6, 8.2 Hz, 1H), 3.35 (dd, *J* = 12.6, 3.9 Hz, 1H), 2.62 (brs, 1H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 137.6, 129.3, 125.8, 73.1, 57.9, 21.0.

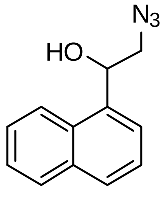
2-Azido-1-(4-phenyl-phenyl)ethanol (4e)



4e

The hydroxybromination of 1-(1-bromoethyl)-4-methylbenzene **1e** (130.6 mg, 0.5 mmol) in DMSO (2 mL) at 60 °C for 18 hours under argon atmosphere, followed by the addition of NaN_3 (65 mg, 1 mmol), affords 81.7 mg (68%) of **4e** as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.61–7.57 (m, 4H), 7.46–7.42 (m, 4H), 7.38–7.33 (m, 1H), 4.91 (dt, *J* = 7.5, 3.6 Hz, 1H), 3.52 (dd, *J* = 12.6, 7.9 Hz, 1H), 3.47 (dd, *J* = 12.6, 4.1 Hz, 1H), 2.45 (d, *J* = 3.2 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 141.3, 140.5, 139.5, 128.8, 127.5, 127.4, 127.1, 126.3, 73.2, 58.0. HRMS (ESI) Calcd for [$C_{14}H_{13}N_3NaO$, M + Na]$^+$: 262.0951, Found: 262.0955.

2-Azido-1-(1-naphthyl)ethanol (4j)[12]

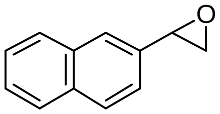


4j

The hydroxybromination of 1-(1-bromoethyl)naphthalene **1j** (117.5 mg, 0.5 mmol) in DMSO (2 mL) at 60 °C for 18 hours under argon atmosphere, followed by the addition of NaN$_3$ (65 mg, 1 mmol), affords 71.8 mg (67%) of **4j** as colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.90–7.87 (m, 1H), 7.83–7.80 (m, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.62 (d, *J* = 7.1 Hz, 1H), 7.49–7.39 (m, 3H), 5.54–5.51 (m, 1H), 3.51–3.44 (m, 2H), 2.82 (d, *J* = 3.2 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 135.9, 133. 6, 129.9, 129.0, 128.6, 126.4, 125.7, 125.3, 123.4, 122.2, 70.3, 57.2.

One-pot procedure for the transformation of bromides 1 to epoxides 5: Bromide **1** (0.5 mmol) was stirred in DMSO (2 mL) at 60 °C for 18 hours under argon atmosphere. After cooling down to room temperature, THF (1 mL) was added to the solution. At 0 °C, aqueous NaOH solution (10%, 0.5 mL) was added dropwise to the mixture. Then the mixture was stirred for another 0.5 h, diluted with water (10 mL) and extracted with EA (3 × 10 mL). The combined extracts were washed with a saturated solution of NaCl (15 mL), dried over MgSO$_4$, and evaporated *in vacuo*. The residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate) to afford the epoxide **5**.

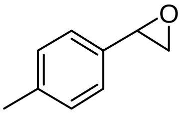
2-(2-Naphthyl)oxirane (**5a**)[13]



5a

The hydroxybromination of 2-(1-bromoethyl)naphthalene **1a** (117.5 mg, 0.5 mmol) in DMSO (2 mL) at 60 °C for 18 hours under argon atmosphere, followed by the addition of THF (1 mL) and aqueous NaOH solution (10%, 0.75 mL) at 0 °C, affords 56.0 mg (66%) of **5a** as a white solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.84–7.80 (m, 4H), 7.51–7.45 (m, 2H), 7.32 (dd, *J* = 8.5, 1.7 Hz, 1H), 4.03 (dd, *J* = 3.9, 2.6 Hz, 1H), 3.22 (dd, *J* = 5.4, 4.1 Hz, 1H), 2.90 (dd, *J* = 5.4, 2.6 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 135.0, 133.2, 133.1, 128.3, 127.7, 126.3, 126.0, 125.1, 122.6, 52.5, 51.2.

2-(*p*-Tolyl)oxirane (**5c**)[14]

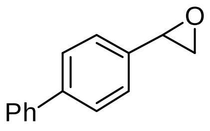


5c

The hydroxybromination of 1-(1-bromoethyl)-4-methylbenzene **1c** (99.5 mg, 0.5 mmol) in DMSO (2 mL) at 60 °C for 18 hours under argon atmosphere, followed by the addition of THF (1 mL) and aqueous NaOH solution (10%, 0.75 mL) at 0 °C, affords 41.0 mg (61%) of **5c** as colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.18–7.12

(m, 4H), 3.82 (dd, *J* = 3.9, 2.7 Hz, 1H), 3.11 (dd, *J* = 5.4, 4.1 Hz, 1H), 2.78 (dd, *J* = 5.5, 2.6 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.9, 134.5, 129.1, 125.4, 52.3, 51.0, 21.1.

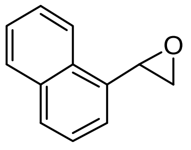
2-(*p*-Phenyl-phenyl)oxirane (5e)[14]



5e

The hydroxybromination of 4-(1-bromoethyl)-1,1'-biphenyl **1e** (130.6 mg, 0.5 mmol) in DMSO (2 mL) at 60 °C for 18 hours under argon atmosphere, followed by the addition of THF (1 mL) and aqueous NaOH solution (10%, 0.5 mL) at 0 °C, affords 68.4 mg (70%) of **5e** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.56 (m, 4H), 7.44–7.41 (m, 2H), 7.35–7.31 (m, 3H), 3.89 (dd, *J* = 3.9, 2.6 Hz, 1H), 3.16 (dd, *J* = 5.4, 4.1 Hz, 1H), 2.83 (dd, *J* = 5.4, 2.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 140.6, 136.6, 128.7, 127.4, 127.2, 127.0, 125.9, 52.2, 51.2.

2-(1-Naphthyl)oxirane (5j)[15]

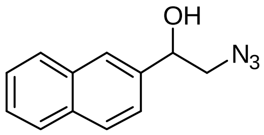


5j

The hydroxybromination of 1-(1-bromoethyl)naphthalene **1j** (117.5 mg, 0.5 mmol) in DMSO (2 mL) at 60 °C for 18 hours under argon atmosphere, followed by the addition of THF (1 mL) and aqueous NaOH solution (10%, 0.75 mL) at 0 °C, affords 60.6 mg (71%) of **5j** as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.87–7.84 (m, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.55–7.40 (m, 4H), 4.46–4.45 (m, 1H), 3.25 (dd, *J* = 5.8, 4.1 Hz, 1H), 2.77 (dd, *J* = 5.8, 2.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.6, 133.2, 131.4, 128.7, 128.1, 126.3, 125.8, 125.5, 122.8, 122.2, 50.7, 50.6.

One-pot procedure for the transformation of alkenes 3 to azidoalcohols 4: Alkene **6** (0.5 mmol) and aqueous hydrobromic acid (48%, 101.1 mg, 0.6 mmol) were dissolved in DMSO (2 mL). The mixture were stirred at 60 °C for 12 hours under air. Then sodium azide (65.0 mg, 1.0 mmol) was added to the mixture and the mixture was stirred for another 12 hours at 60 °C. After cooling down to room temperature, the mixture were diluted with water (10 mL) and extracted with EA (3 × 10 mL). The combined extracts were washed with a saturated solution of NaCl (15 mL), dried over $MgSO_4$, and evaporated *in vacuo*. The residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate) to afford the azidoalcohol **4**.

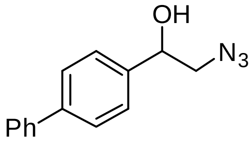
2-Azido-1-(2-naphthyl)ethanol (4a)[11]



4a

The hydroxybromination of 4-vinylnaphthalene **3a** (77.1 mg, 0.5 mmol) and aqueous hydrobromic acid (48%, 101.1 mg, 0.6 mmol) in DMSO (2 mL) at 60 °C for 12 hours, followed by the addition of NaN_3 (65 mg, 1 mmol), affords 78.9 mg (74%) of **4a** as a white solid.

1-([1,1'-Biphenyl]-4-yl)-2-azidoethanol (4e)

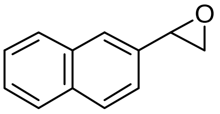


4e

The hydroxybromination of 4-vinyl-1,1'-biphenyl **3e** (90.1 mg, 0.5 mmol) and aqueous hydrobromic acid (48%, 101.1 mg, 0.6 mmol) in DMSO (2 mL) at 60 °C for 12 hours, followed by the addition of NaN_3 (65 mg, 1 mmol), affords 96.1 mg (80%) of **4e** as a white solid.

One-pot procedure for the transformation of alkenes 3 to epoxides 5: Alkene **3** (0.5 mmol) and aqueous hydrobromic acid (48%, 101.1 mg, 0.6 mmol) were dissolved in DMSO (2 mL). The mixture were stirred at 60 °C for 12 hours under air. After cooling down to room temperature, THF (1 mL) was added to the solution. At 0 °C, aqueous NaOH solution (10%, 0.5 mL) was added dropwise to the mixture. Then the mixture was stirred for another 0.5 h, diluted with water (10 mL) and extracted with EA (3 × 10 mL). The combined extracts were washed with a saturated solution of NaCl (15 mL), dried over $MgSO_4$, and evaporated *in vacuo*. The residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate) to afford the epoxide **5**.

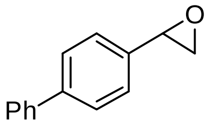
2-(2-Naphthyl)oxirane (5a)[13]



5a

The hydroxybromination of 4-vinylnaphthalene **3a** (77.1 mg, 0.5 mmol) and aqueous hydrobromic acid (48%, 101.1 mg, 0.6 mmol) in DMSO (2 mL) at 60 °C for 12 hours, followed by the addition of THF (1 mL) and aqueous NaOH solution (10%, 0.5 mL) at 0 °C, affords 64.6 mg (76%) of **5a** as a white solid.

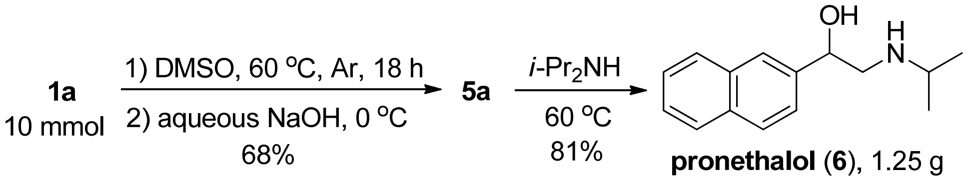
2-([1,1'-Biphenyl]-4-yl)oxirane (5e)[14]



5e

The hydroxybromination of 4-vinyl-1,1'-biphenyl **3e** (90.1 mg, 0.5 mmol) and aqueous hydrobromic acid (48%, 101.1 mg, 0.6 mmol) in DMSO (2 mL) at 60 °C for 12 hours, followed by the addition of THF (1 mL) and aqueous NaOH solution (10%, 0.5 mL) at 0 °C, affords 82.4 mg (84%) of **5e** as a white solid.

The synthesis of pronethalol 6

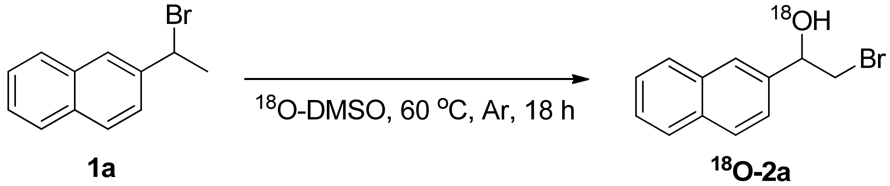


2-(2-Naphthyl)oxirane (**5a**): 2-(1-Bromoethyl)naphthalene **1a** (2.35 g, 10.0 mmol) was stirred in DMSO (20 mL) at 60 °C for 18 hours under argon atmosphere. After cooling down to room temperature, the solution was diluted with THF (15 mL). Then aqueous NaOH solution (10%, 7 mL) was added to the mixture at 0 °C and the mixture was stirred for another 0.5 h at 0 °C. The mixture was diluted with water (80 mL) and extracted with ether (3 × 50 mL). The combined extracts were dried over $MgSO_4$, and evaporated *in vacuo*. The residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate) to afford the 2-(2-naphthyl)oxirane **5a** (1.15 g, 68%) as a white solid.

Pronethalol (5)[16]: 2-(2-Naphthyl)oxirane **5a** (1.15 g, 6.8 mmol) was reacted with diisopropylamine (20 mL) and water (0.75 mL) at 55 °C for 12 h. After cooling down to room temperature, the diisopropylamine was evaporated *in vacuo*. The residue was purified by recystallization from petroleum ether/ethyl acetate to afford pronethalol **6** (1.25 g, 81%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.81 (m, 4H), 7.49–7.43 (m, 3H), 4.83 (dd, *J* = 8.8, 4.0 Hz, 1H), 3.02 (dd, *J* = 12.0, 3.6 Hz, 1H), 2.88–2.82 (m, 1H), 4.74 (dd, *J* = 12.0, 8.8 Hz, 1H), 1.09 (d, *J* = 3.2 Hz, 3H), 1.07 (d, *J* = 3.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3, 133.3, 132.9, 128.1, 127.9, 127.7, 126.0, 125.6, 124.5, 124.0, 72.1, 54.5, 48.7, 23.3, 23.0.

(E) Mechanistic Studies

(1) ^{18}O labeling experiment



The mixture of 2-(1-bromoethyl)naphthalene **1a** (58.8 mg, 0.25 mmol) and **^{18}**O-DMSO (1 mL) were stirred at 60 °C for 18 hours under argon atmosphere. After cooling down to room temperature, the mixture was diluted with water (10 mL) and extracted with EA (3 × 10 mL). The combined extracts were washed with a saturated solution of NaCl (15 mL), dried over $MgSO_4$, and evaporated *in vacuo*. The residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate) to afford the bromohydrin **2a** as a white solid. EI-MS analysis of **2a** clearly show that the ^{18}O-**2a** was the main product. The ratio of ^{18}O-**2a:**^{16}O-**2a** > **5:1**.

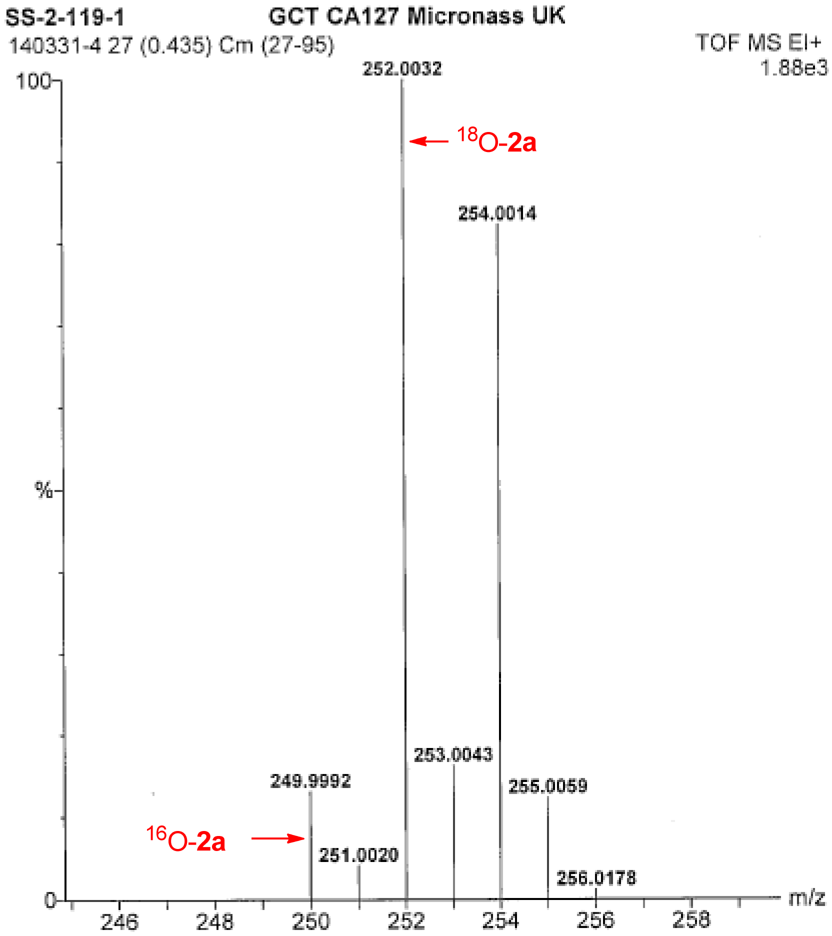
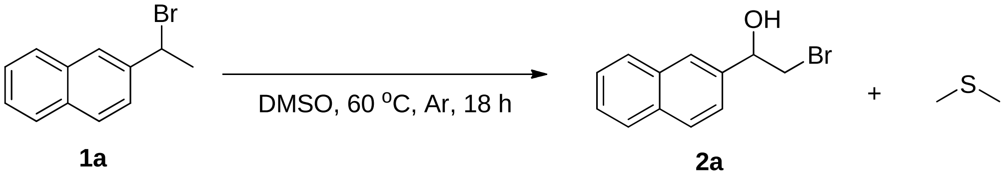


Figure S1. HR-MS of ^{18}O-2a.

(2) The isolation and determination of dimethyl sulfide



2-(1-Bromoethyl)naphthalene **1a** (2.35 g, 10.0 mmol) was stirred in DMSO (20 mL) at 60 ^{o}C for 18 hours under argon atmosphere. After cooling down to room temperature, the atmospheric distillation of the solution affords 0.3 mL of colorless oil which was determinated as dimethyl sulfide. ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.07. ^{13}C NMR (100 MHz, CDCl$_3$) δ 17.9.

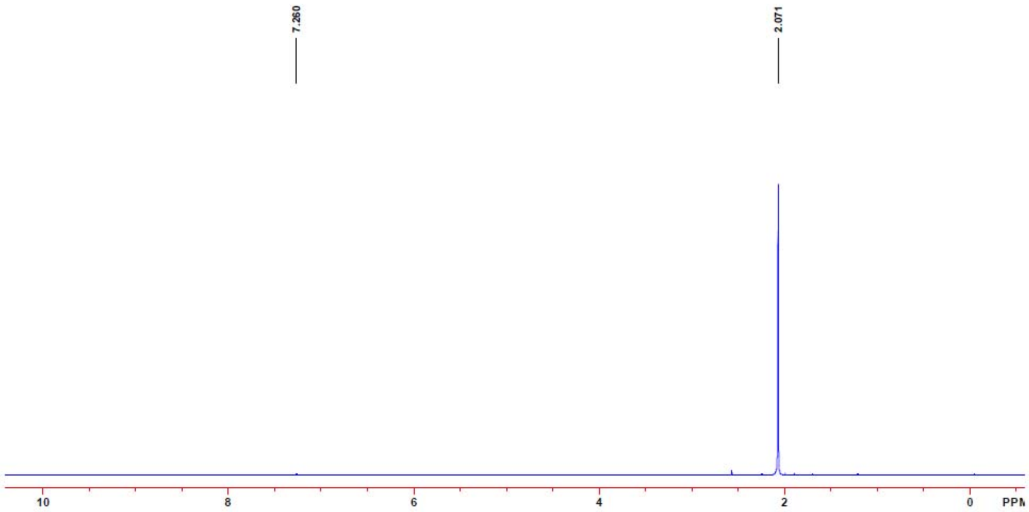


Figure S2. ^{1}H NMR of dimethyl sulfide.

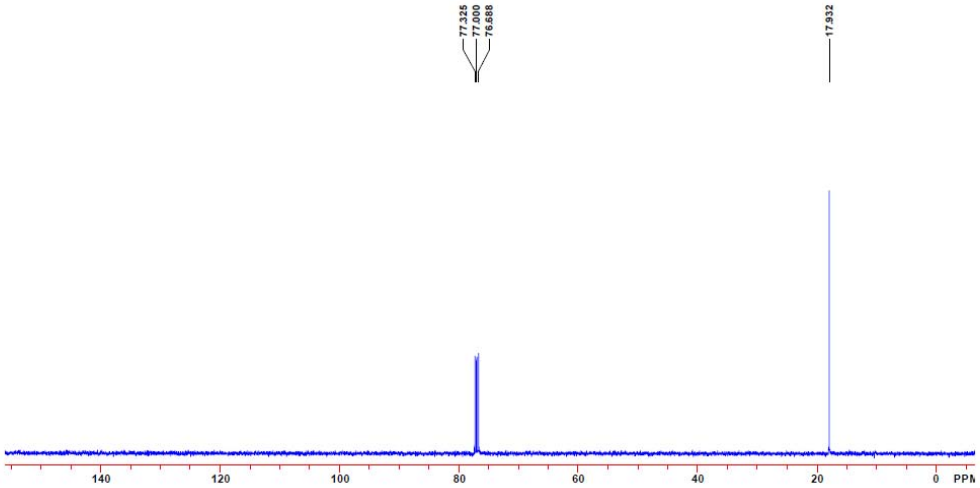


Figure S3. ^{13}C NMR of dimethyl sulfide.

(F) References

[1] Arp, F. O.; Fu, G. C. *J. Am. Chem. Soc.* **2005**, *127*, 10482.

[2] Huang C.-Y.; Doyle, A. G. *J. Am. Chem. Soc.* **2012**, *134*, 9541.

[3] Wang, Y.; Wang, J.; Xiong, Y.; Liu, Z.-Q. *Tetrahedron Lett.* **2014**, *55*, 2734.

[4] Zhang, J.; Wang, J.; Qiu, Z.; Wang, Y. *Tetrahedron* **2011**, *67*, 6859.

[5] Qaseer, H. A. *Pol. J. Chem.* **2007**, *81*, 31.

[6] Reimann, E.; Renz, H. *Arch. Pharm.* **1993**, *326*, 253.

[7] Kikushima, K.; Moriuchi, T.; Hirao, T. *Chem. Asian J.* **2009**, *4*, 1213.

[8] Sels, B. F.; De Vos, D. E.; Jacobs, P. A. *J. Am. Chem. Soc.* **2001**, *123*, 8350.

[9] Dewkar, G. K.; Narina, S. V.; Sudalai, A. *Org. Lett.* **2003**, *5*, 4501.

[10] Pandit, P.; Gayen, K. S.; Khamarui, S.; Chatterjee, N.; Maiti, D. K. *Chem. Commun.* **2011**, *47*, 6933.

[11] Mesas-Sanchez, L.; Diaz-Alvarez, A. E.; Diner, P. *Tetrahedron*, **2013**, *69*, 753.

[12] Sayyed, I. A.; Kumar, N.S.C.; Ramesh S. *Indian J. Chem.* - Section B *Org. and Med. Chem.* **2005**, *44*, 1533.

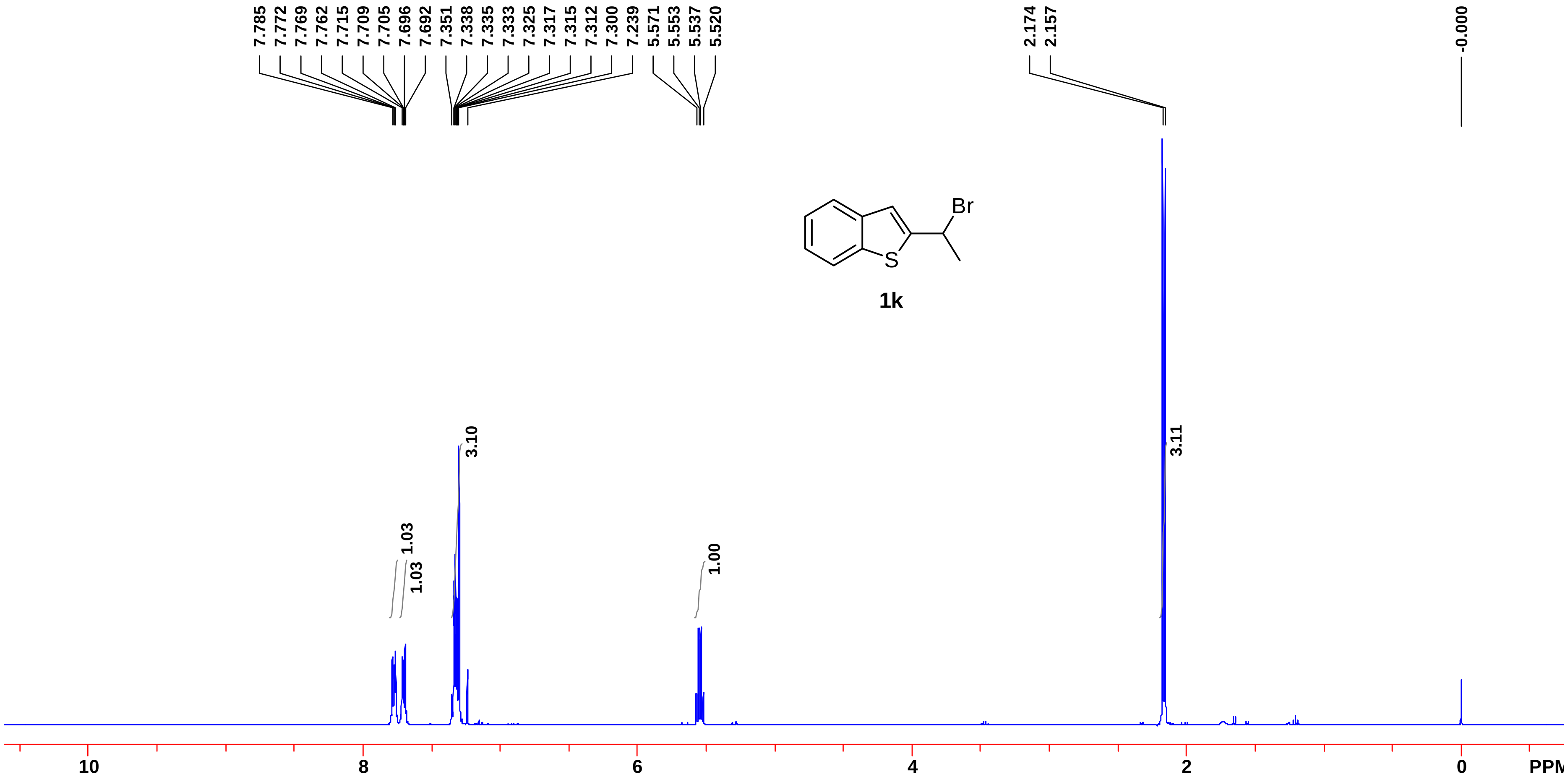
[13] Robinson, M. W. C.; Davies, A. M.; Buckle, R.; Mabbett, I.; Taylor, S. H.; Graham, A. E. *Org. Biomol. Chem.* **2009**, *7*, 2559.

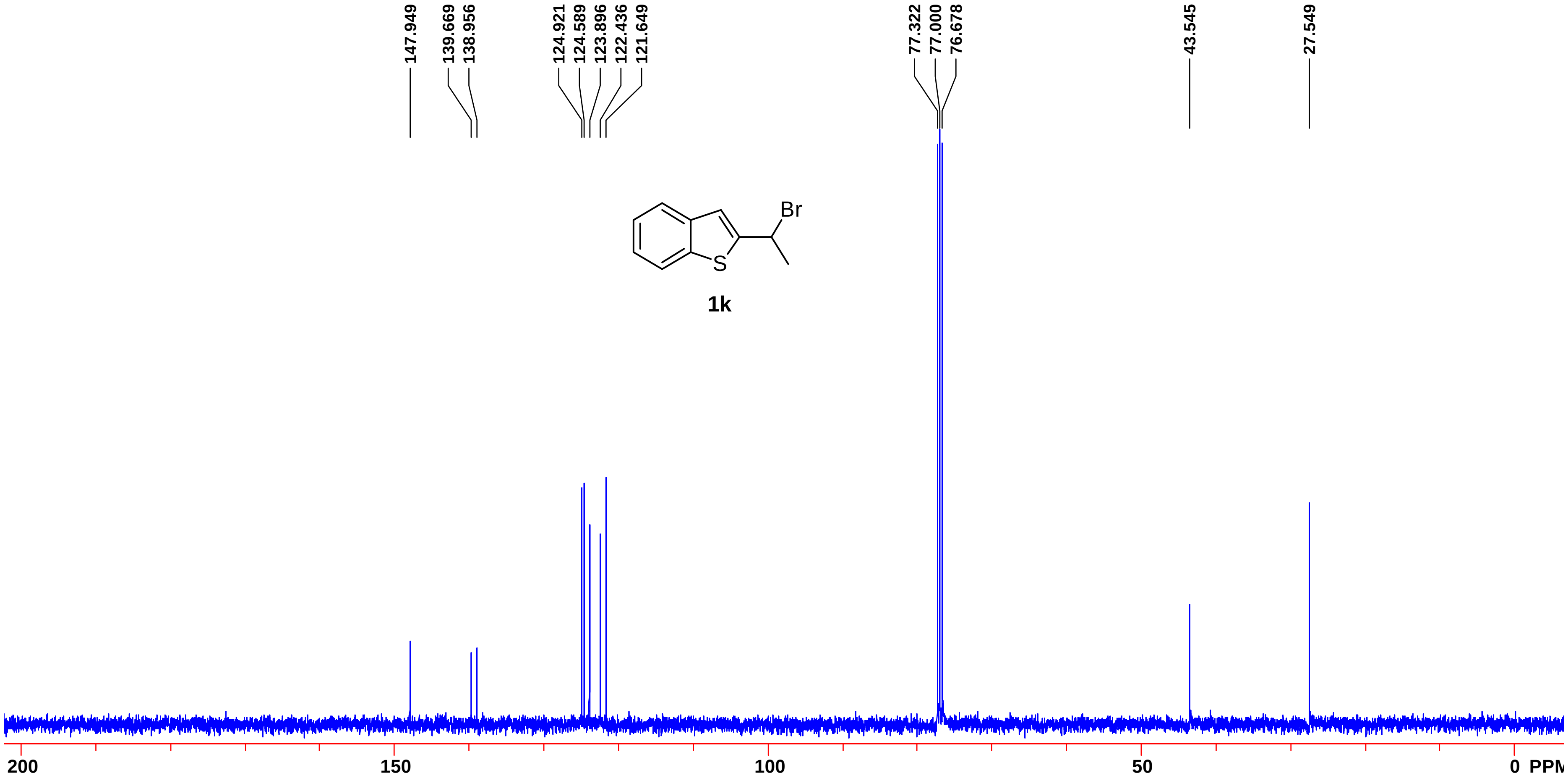
[14] Chishiro, T.; Kon, Y.; Nakashima, T.; Goto, M.; Sato, K. *Adv. Synth. Catal.* **2014**, *356*, 623.

[15] Matsumoto, K.; Kubo, T.; Katsuki, T. *Chem. Eur. J.* **2009**, *15*, 6573.

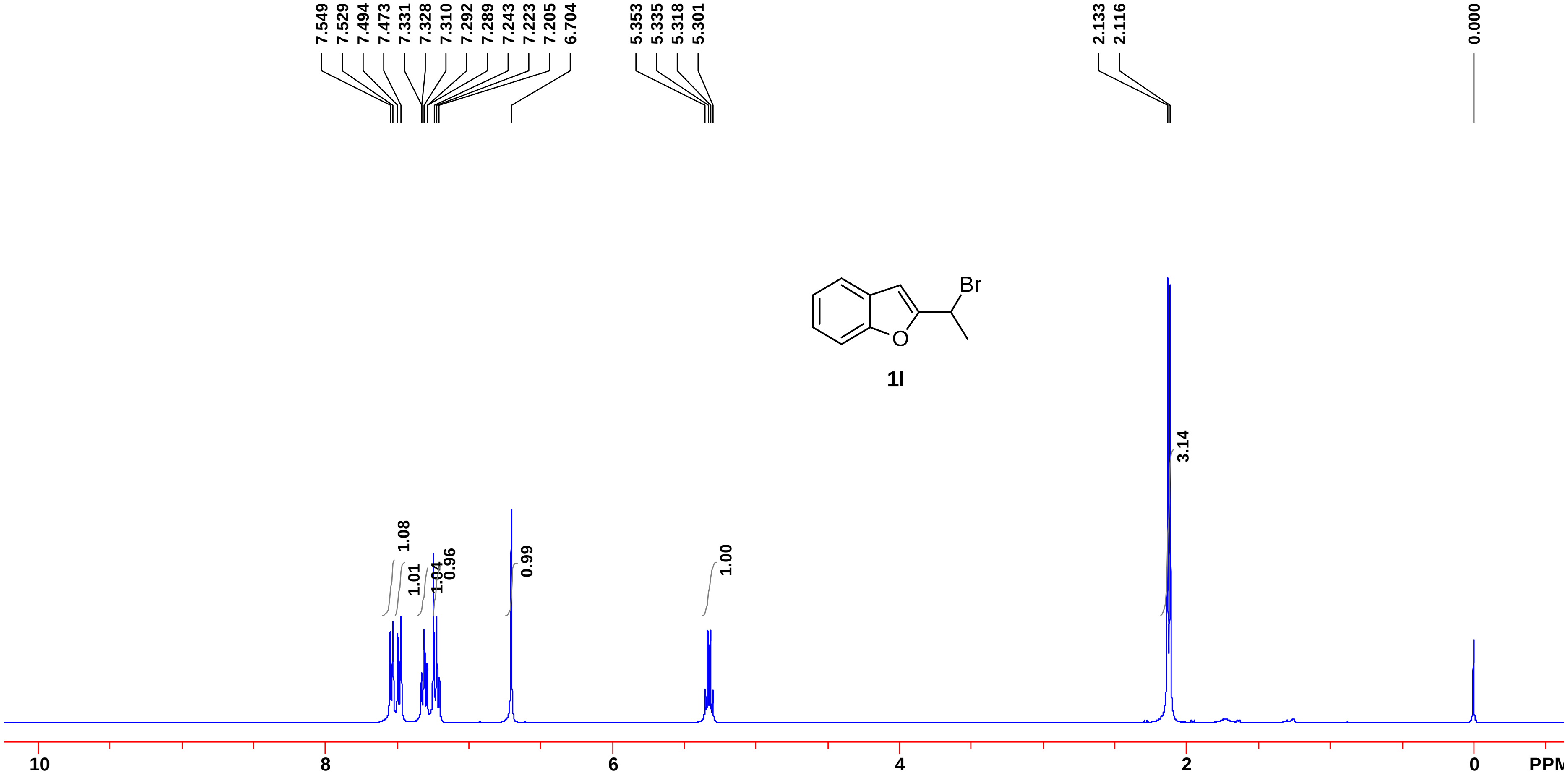
[16] Howe, R.; Crowther, A. F.; Stephenson, J. S.; Rao, B. S.; Smith, L. H. *J. Med. Chem.* **1968**, *11*, 1000.

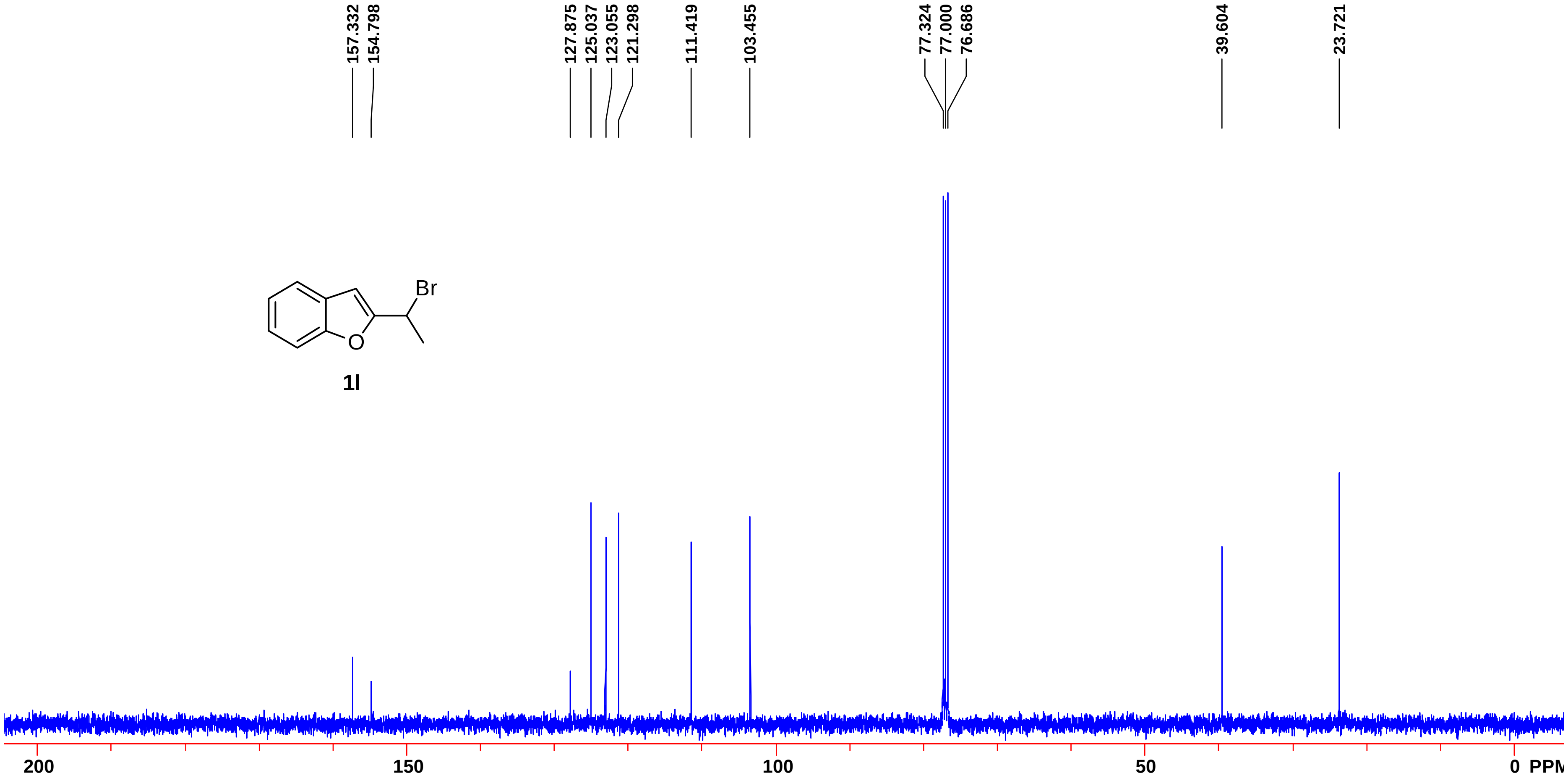
(G) ^{1}H NMR and ^{13}C NMR Spectra of Starting Materials

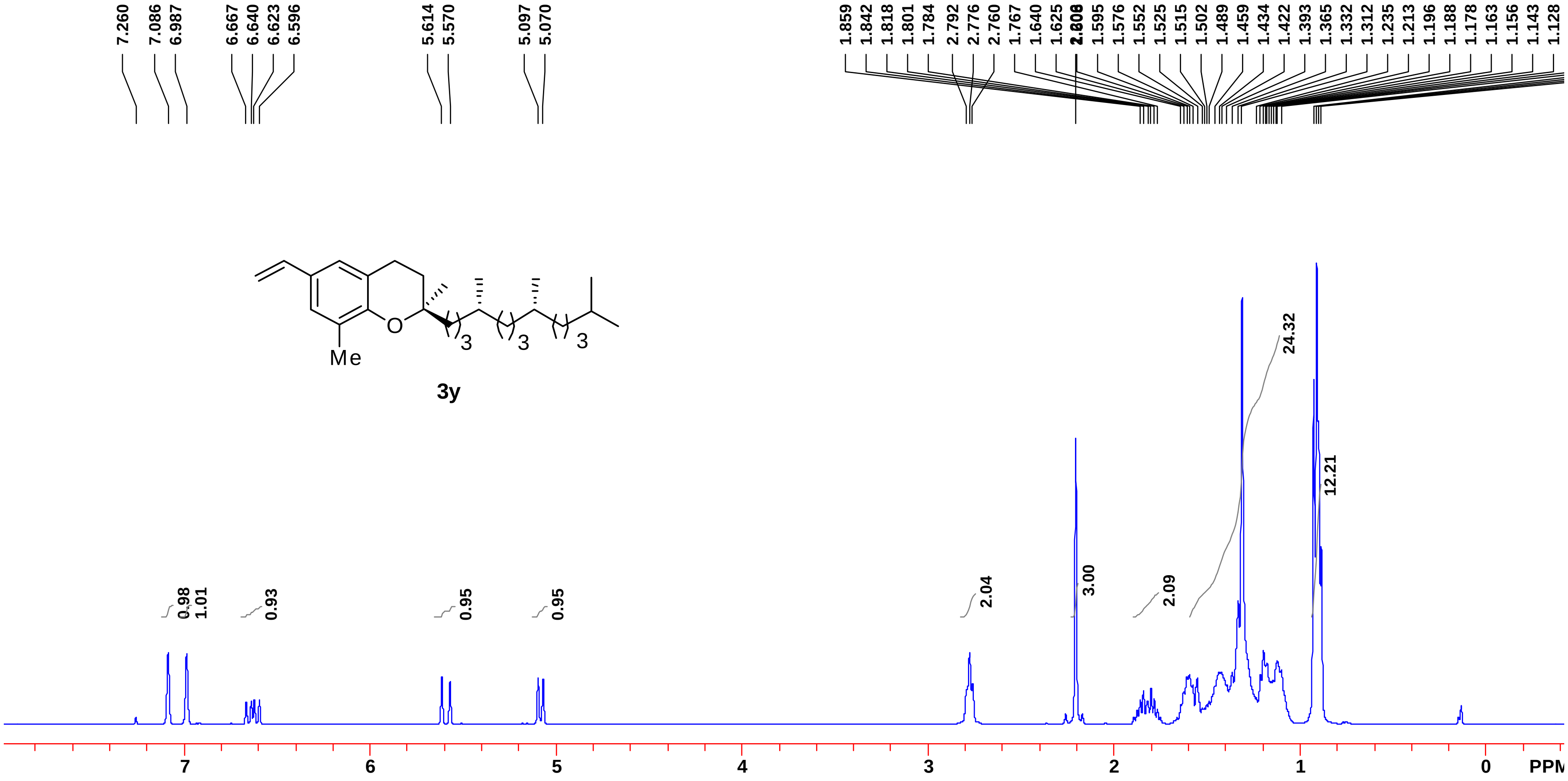



147.949
139.669
138.956
124.921
124.589
123.896
122.436
121.649
77.322
77.000
76.678
43.545
27.549
Br
S
200
150
100
50
0 PPM

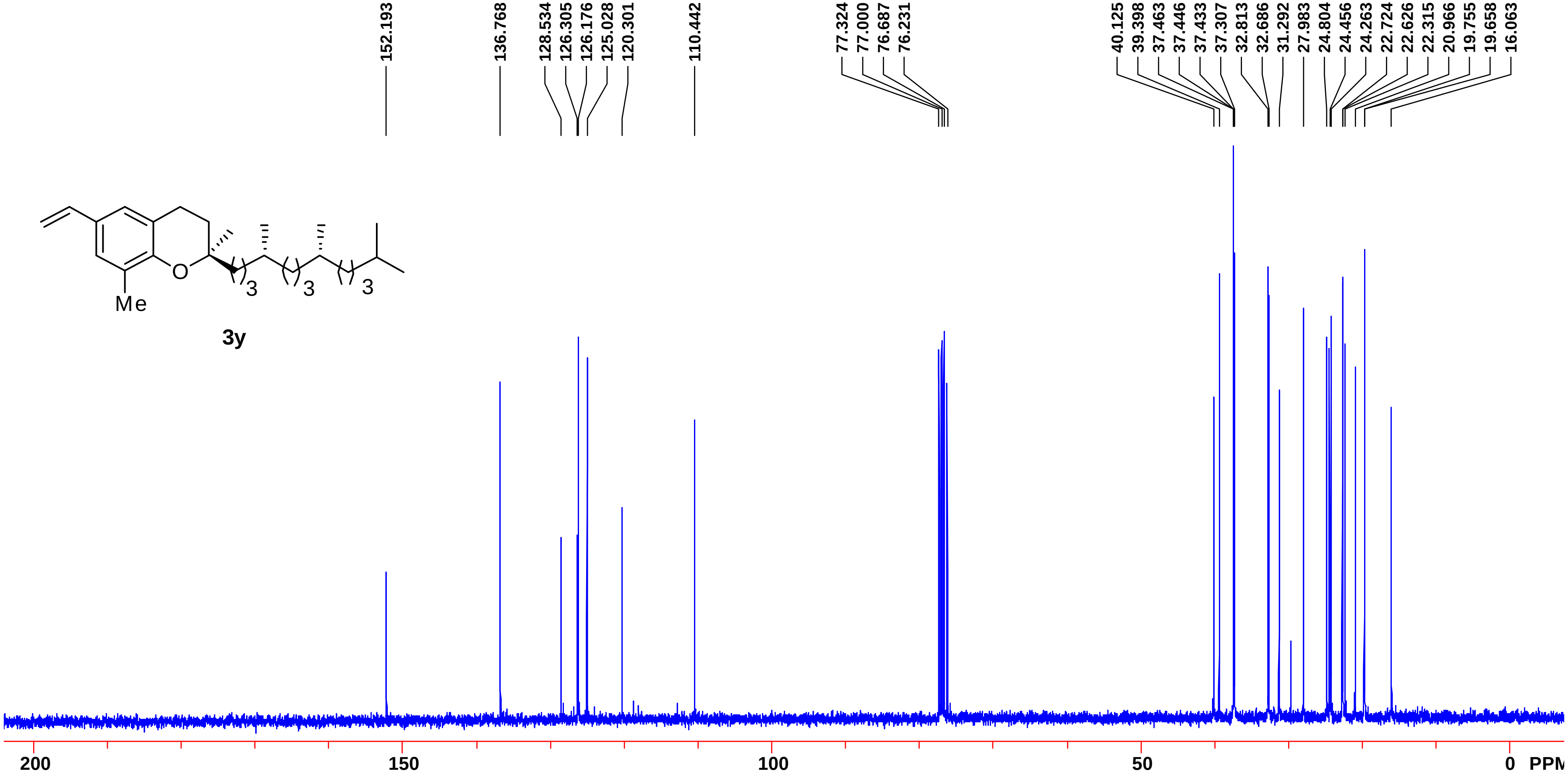
1k


7.549
7.529
7.494
7.473
7.331
7.328
7.310
7.292
7.289
7.243
7.223
7.205
6.704
5.353
5.335
5.318
5.301
2.133
2.116
0.000
Br
O
1l
3.14
1.08
1.01
1.04
0.96
0.99
1.00
10
8
6
4
2
0
PPM

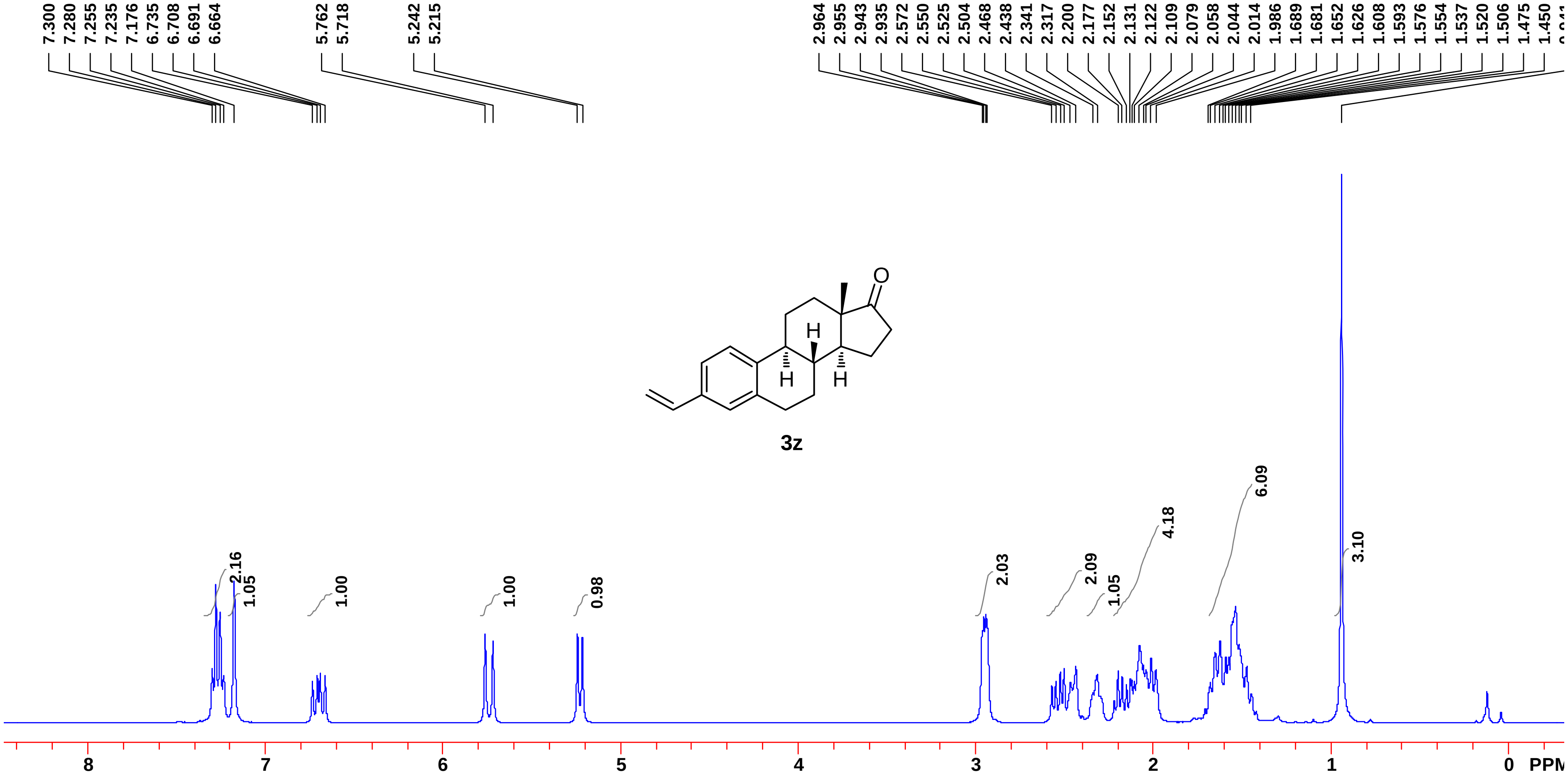

157.332
154.798
127.875
125.037
123.055
121.298
111.419
103.455
77.324
77.000
76.686
39.604
23.721
Br
O
1l
200
150
100
50
0 PPM

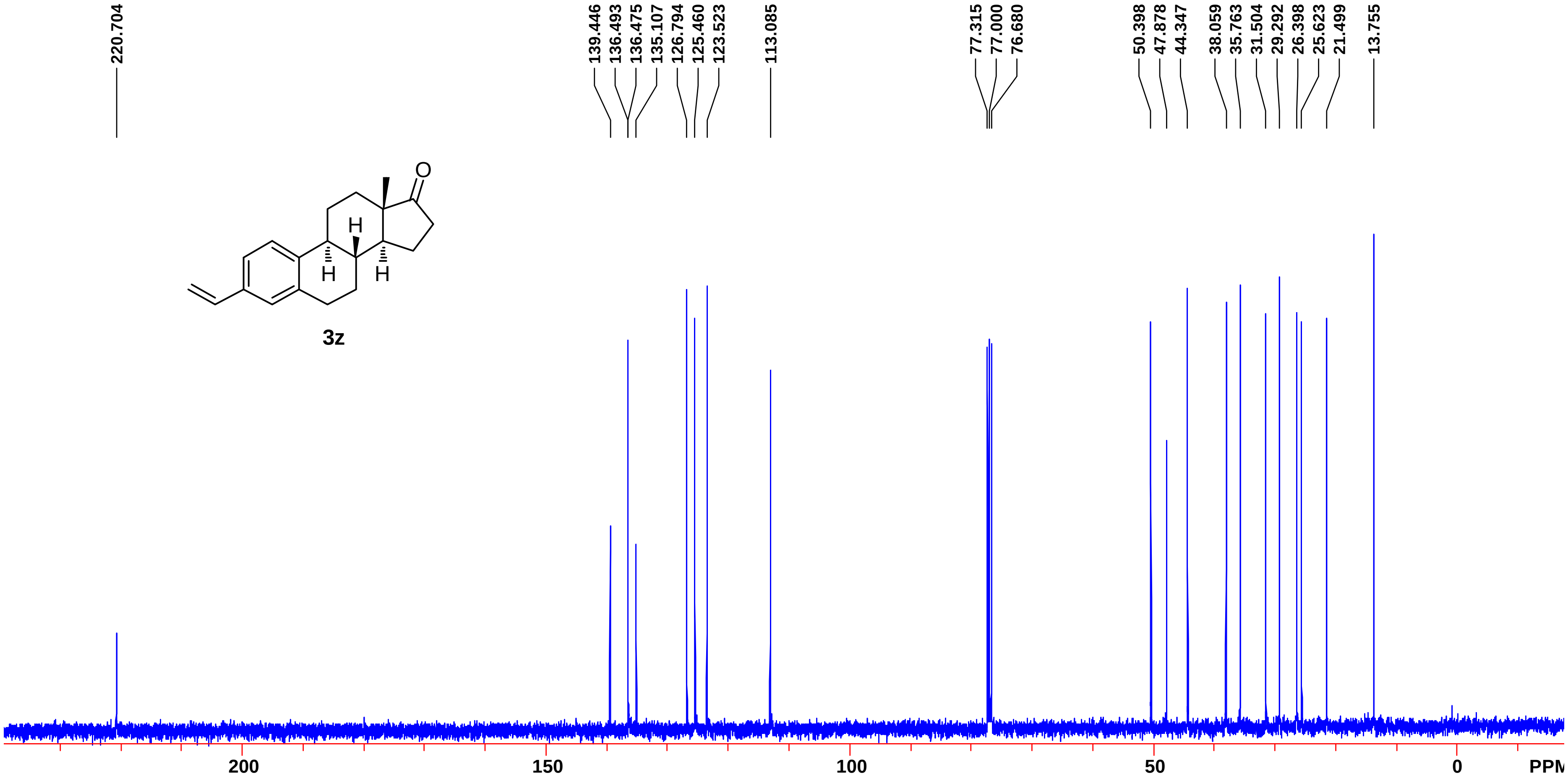

7.260
7.086
6.987
6.667
6.640
6.623
6.596
5.614
5.570
5.097
5.070
1.859
1.842
1.818
1.801
1.784
2.792
2.776
2.760
1.767
1.640
1.625
2.208
1.595
1.576
1.552
1.525
1.515
1.502
1.489
1.459
1.434
1.422
1.393
1.365
1.332
1.312
1.235
1.213
1.196
1.188
1.178
1.163
1.156
1.143
1.128
O
Me
3
3
3
0.98
1.01
0.93
0.95
0.95
2.04
3.00
2.09
24.32
12.21
7
6
5
4
3
2
1
0
PPM

3y

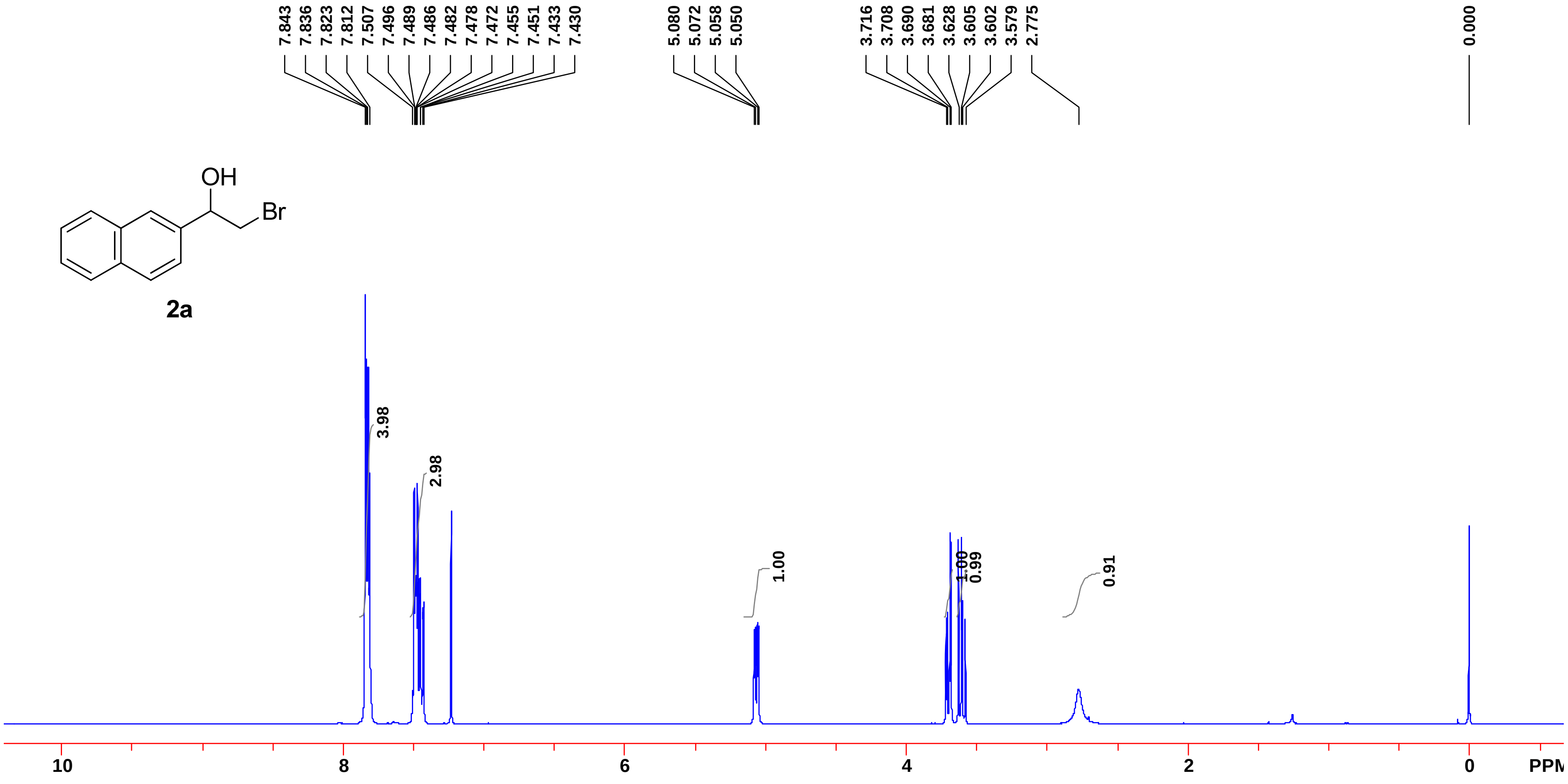

152.193
136.768
128.534
126.305
126.176
125.028
120.301
110.442
77.324
77.000
76.687
76.231
40.125
39.398
37.463
37.446
37.433
37.307
32.813
32.686
31.292
27.983
24.804
24.456
24.263
22.724
22.626
22.315
20.966
19.755
19.658
16.063
O
Me
3
3
3
200
150
100
50
0
PPM

3y


7.300
7.280
7.255
7.235
7.176
6.735
6.708
6.691
6.664
5.762
5.718
5.242
5.215
2.964
2.955
2.943
2.935
2.572
2.550
2.525
2.504
2.468
2.438
2.341
2.317
2.200
2.177
2.152
2.131
2.122
2.109
2.079
2.058
2.044
2.014
1.986
1.689
1.681
1.652
1.626
1.608
1.593
1.576
1.554
1.537
1.520
1.506
1.475
1.450
O
H
H
H
3z
2.16
1.05
1.00
1.00
0.98
2.03
2.09
1.05
4.18
6.09
3.10
8
7
6
5
4
3
2
1
0
PPM


220.704
139.446
136.493
136.475
135.107
126.794
125.460
123.523
113.085
77.315
77.000
76.680
50.398
47.878
44.347
38.059
35.763
31.504
29.292
26.398
25.623
21.499
13.755
O
H
H
H
3z
200
150
100
50
0
PPM

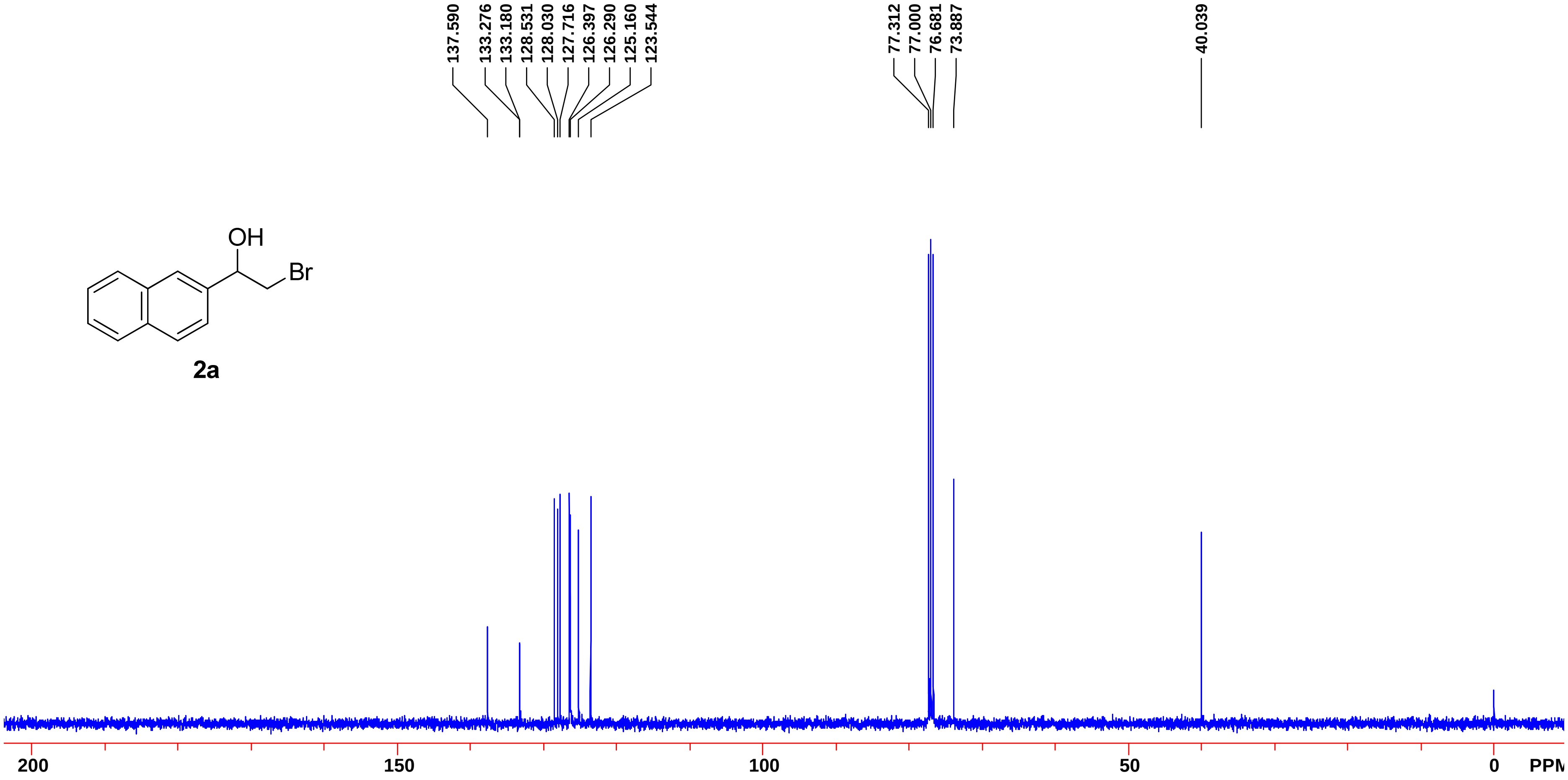
(H) ^{1}H NMR and ^{13}C NMR Spectra of Products

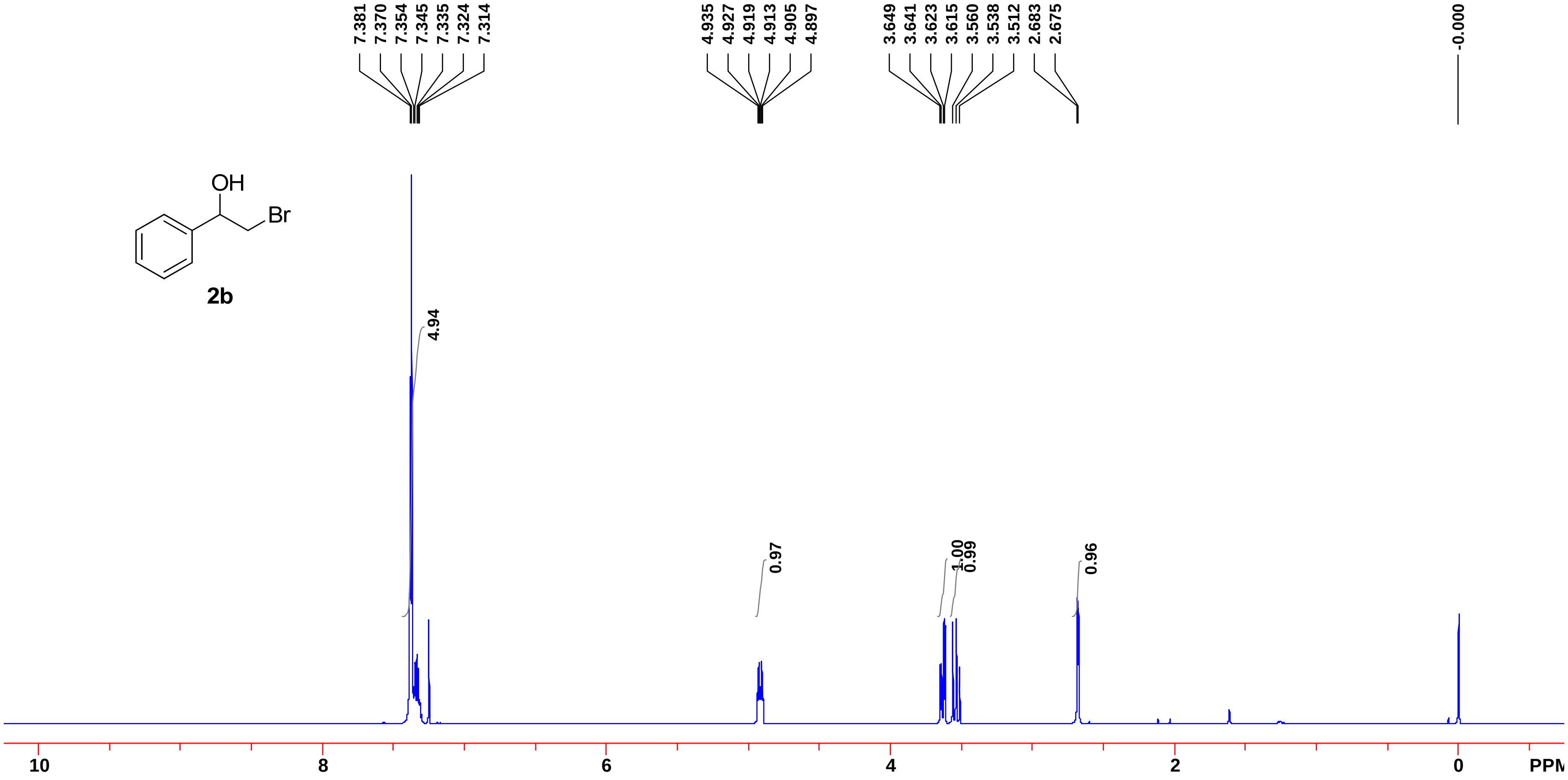


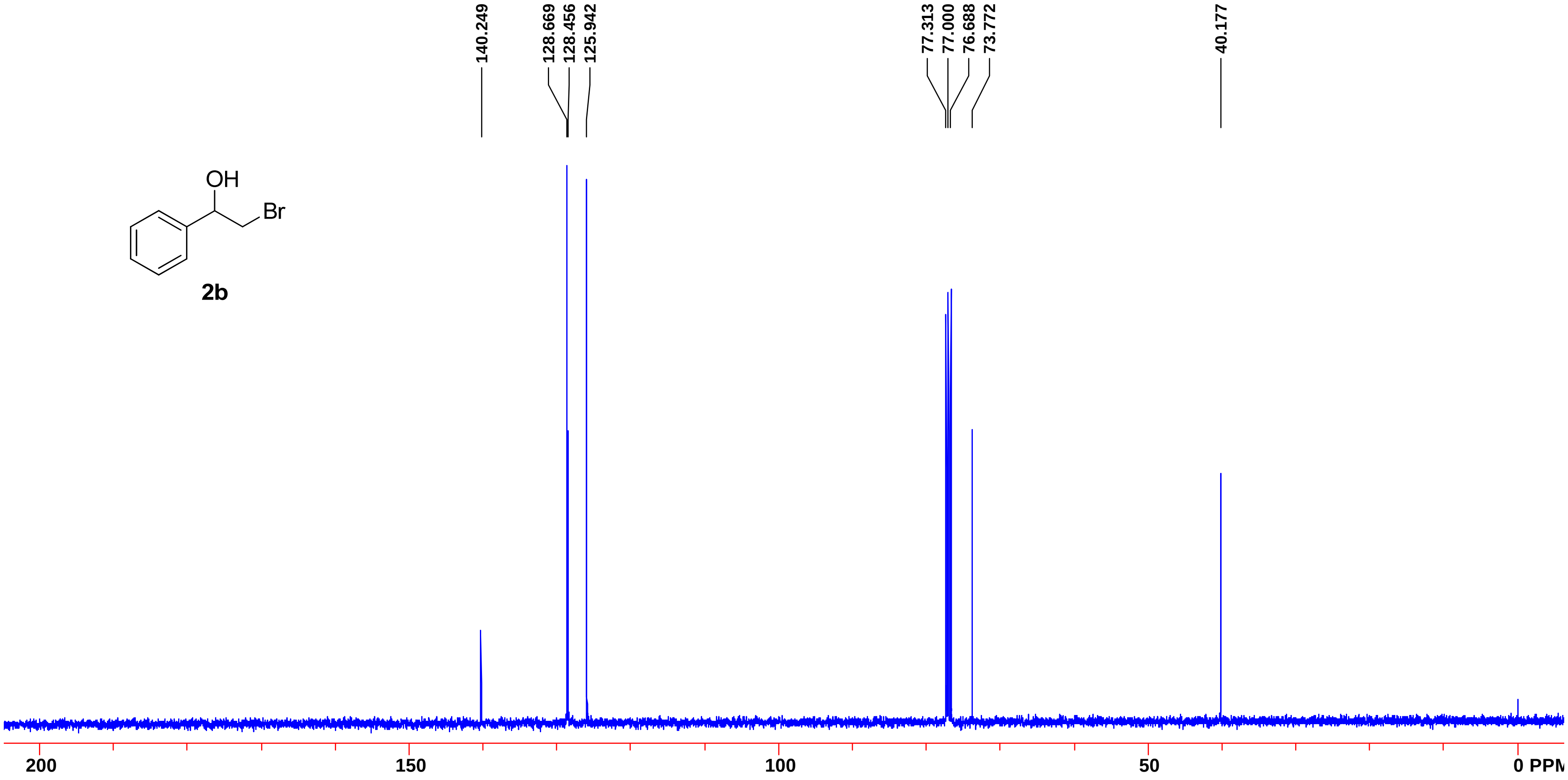
2a

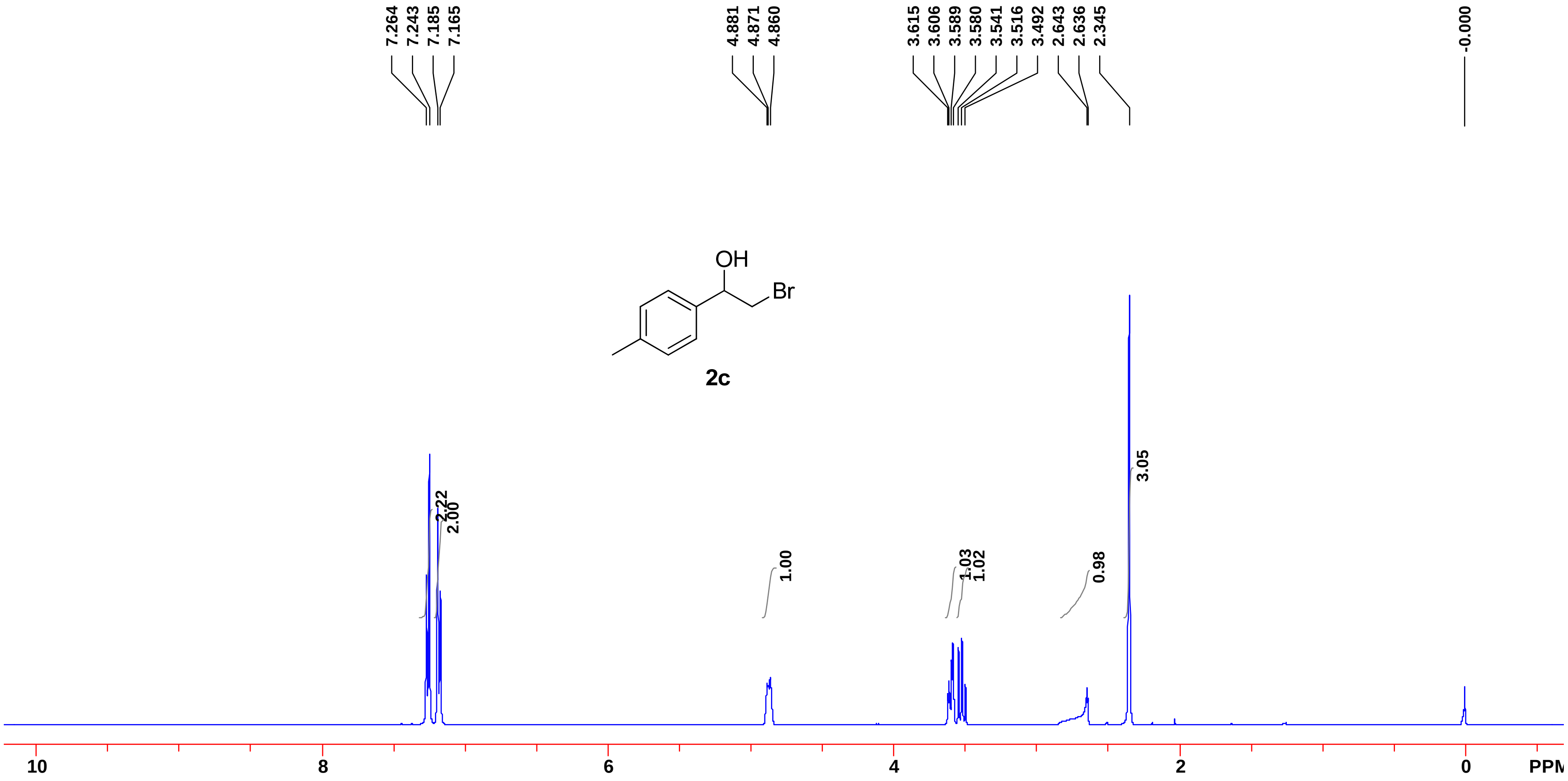
OH
Br

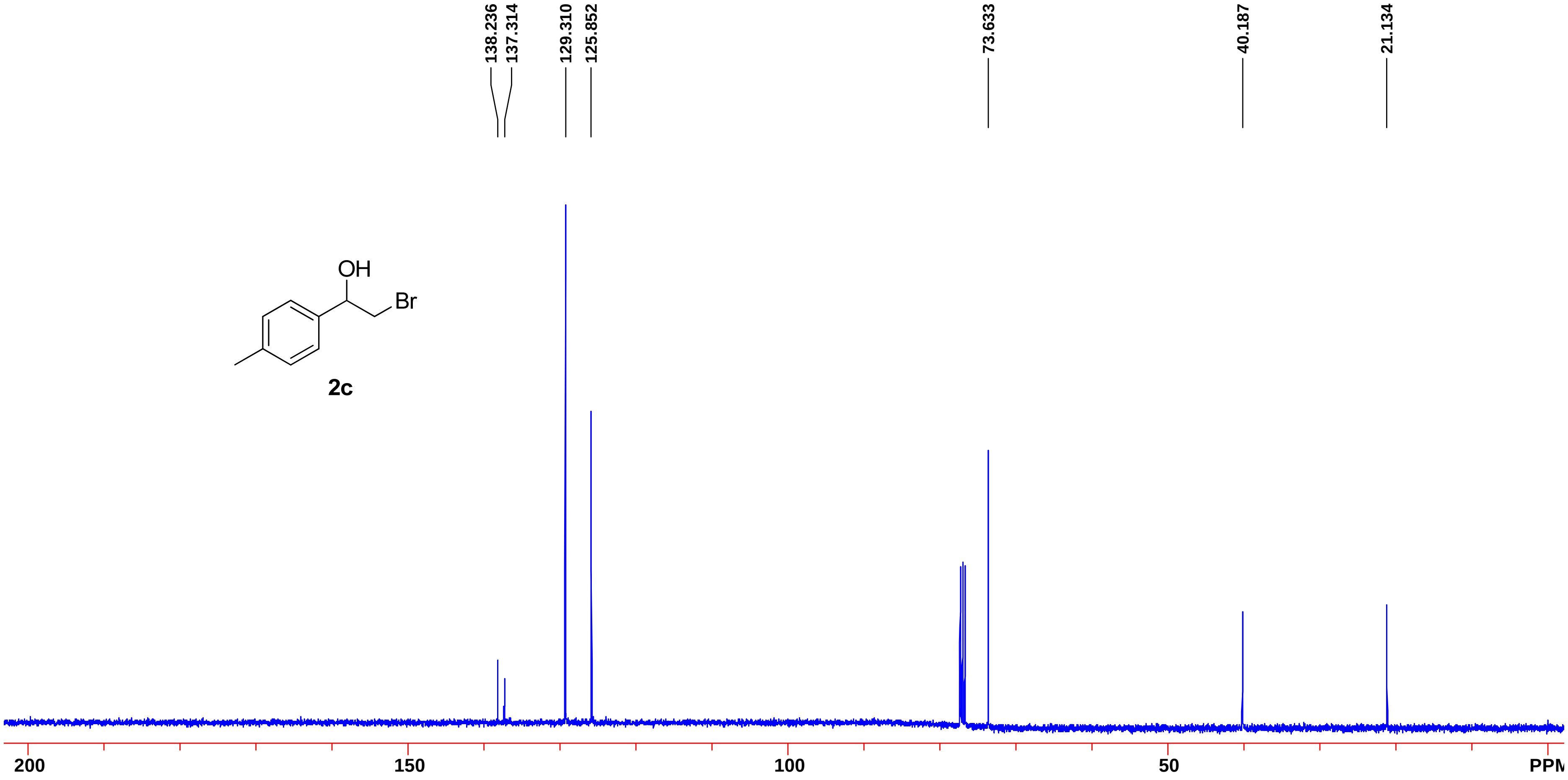
2a

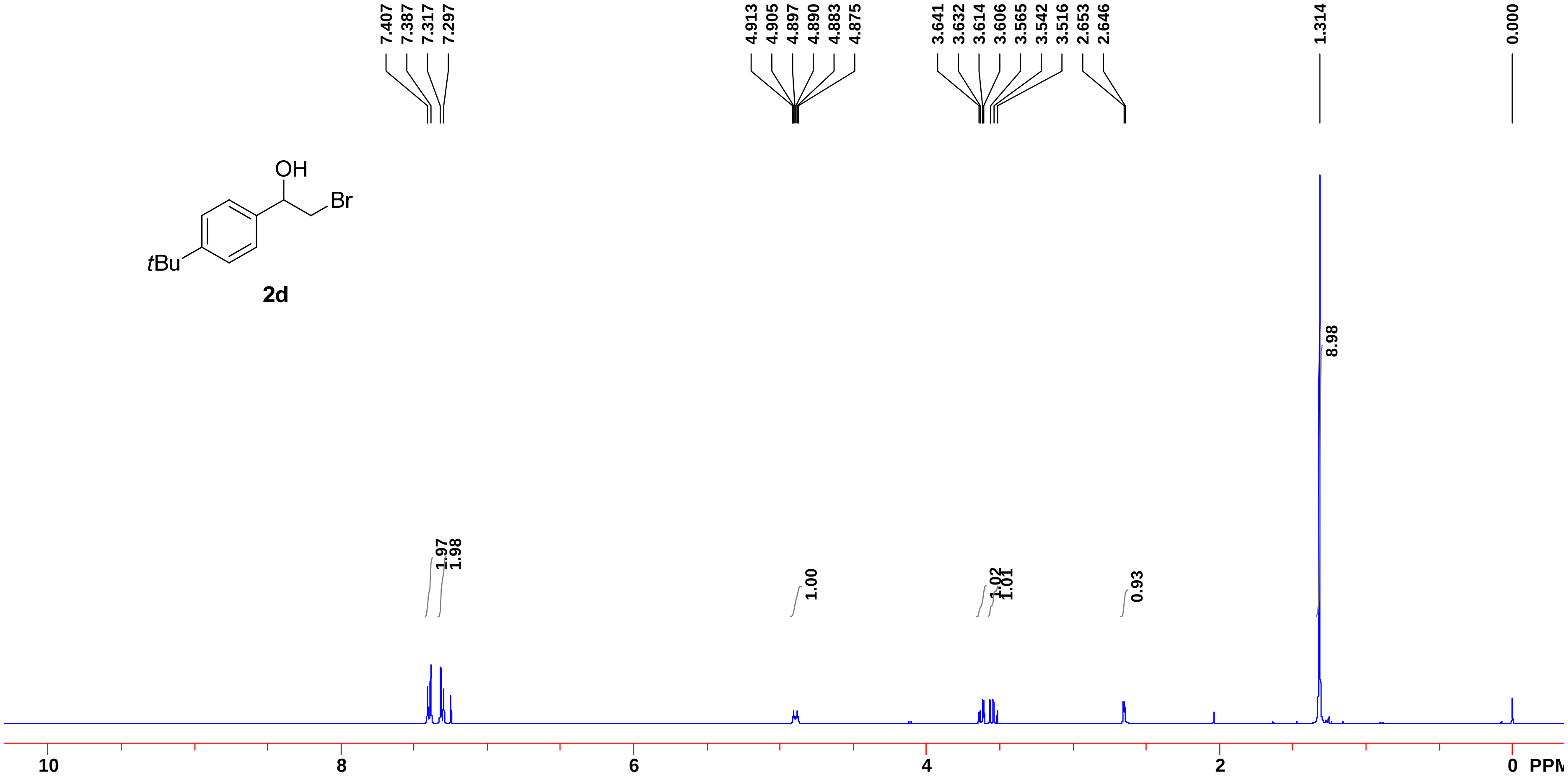

137.590
133.276
133.180
128.531
128.030
127.716
126.397
126.290
125.160
123.544
77.312
77.000
76.681
73.887
40.039
200
150
100
50
0
PPM


7.381
7.370
7.354
7.345
7.335
7.324
7.314
4.935
4.927
4.919
4.913
4.905
4.897
3.649
3.641
3.623
3.615
3.560
3.538
3.512
2.683
2.675
-0.000
OH
Br
2b
4.94
0.97
1.00
0.99
0.96
10
8
6
4
2
0
PPM

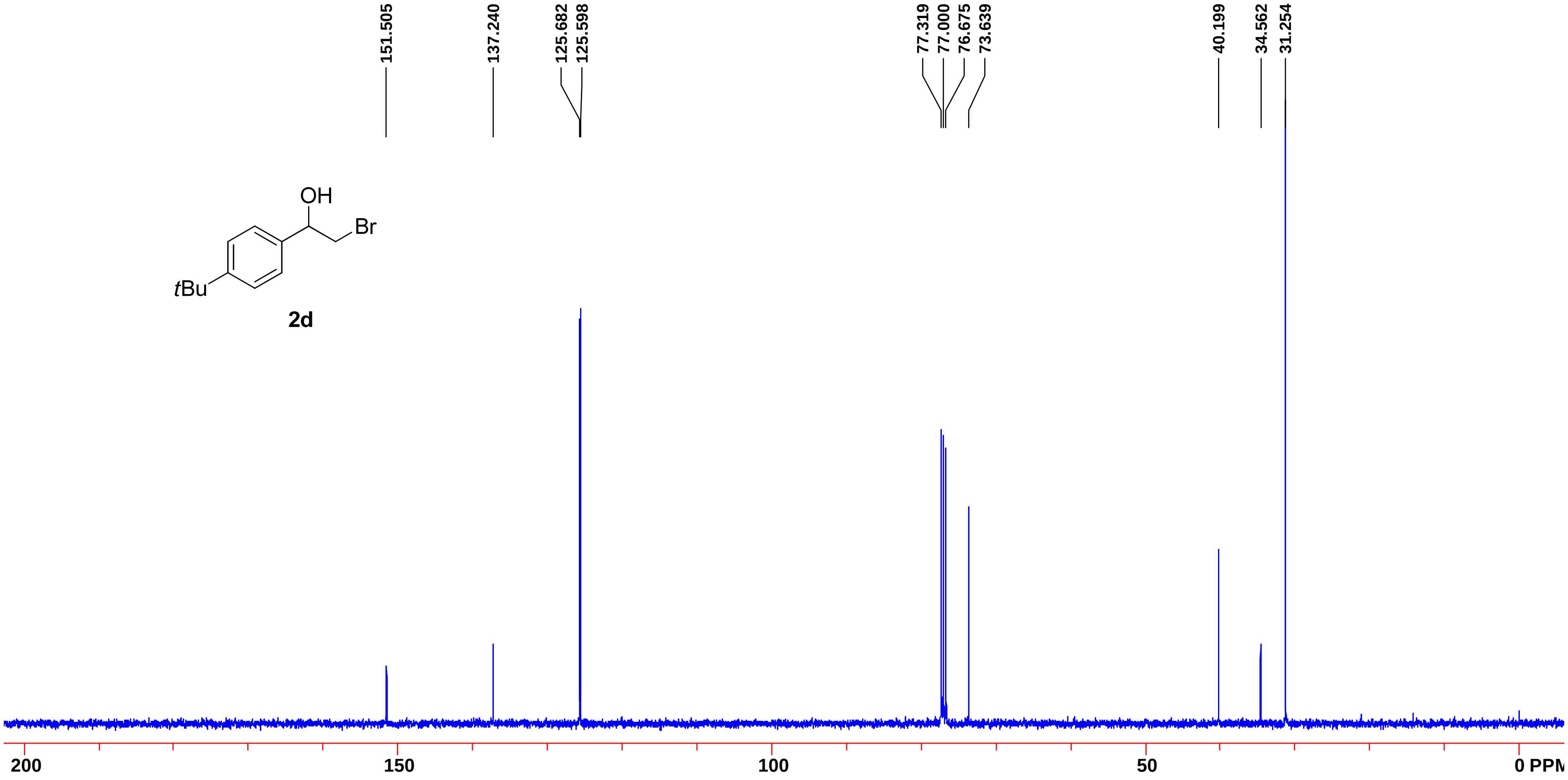

140.249
128.669
128.456
125.942
77.313
77.000
76.688
73.772
40.177
OH
Br
2b
200
150
100
50
0 PPM


7.264
7.243
7.185
7.165
4.881
4.871
4.860
3.615
3.606
3.589
3.580
3.541
3.516
3.492
2.643
2.636
2.345
-0.000
OH
Br
2c
2.22
2.00
1.00
1.03
1.02
0.98
3.05
10
8
6
4
2
0
PPM

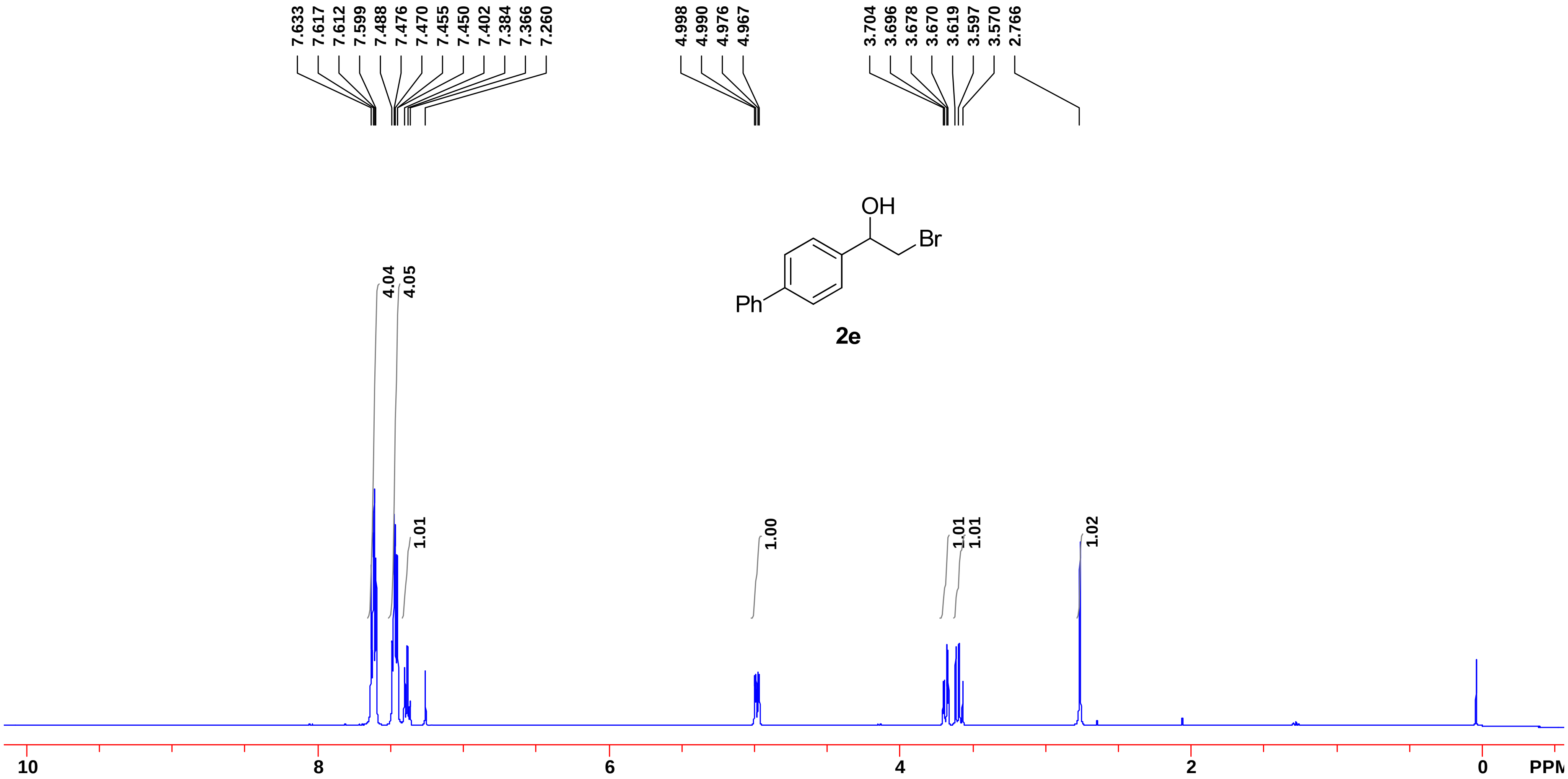

138.236
137.314
129.310
125.852
73.633
40.187
21.134
OH
Br
2c
200
150
100
50
PPM


7.407
7.387
7.317
7.297
4.913
4.905
4.897
4.890
4.883
4.875
3.641
3.632
3.614
3.606
3.565
3.542
3.516
2.653
2.646
1.314
0.000
OH
Br
tBu
1.97
1.98
1.00
1.02
1.01
0.93
8.98
10
8
6
4
2
0
PPM

2d

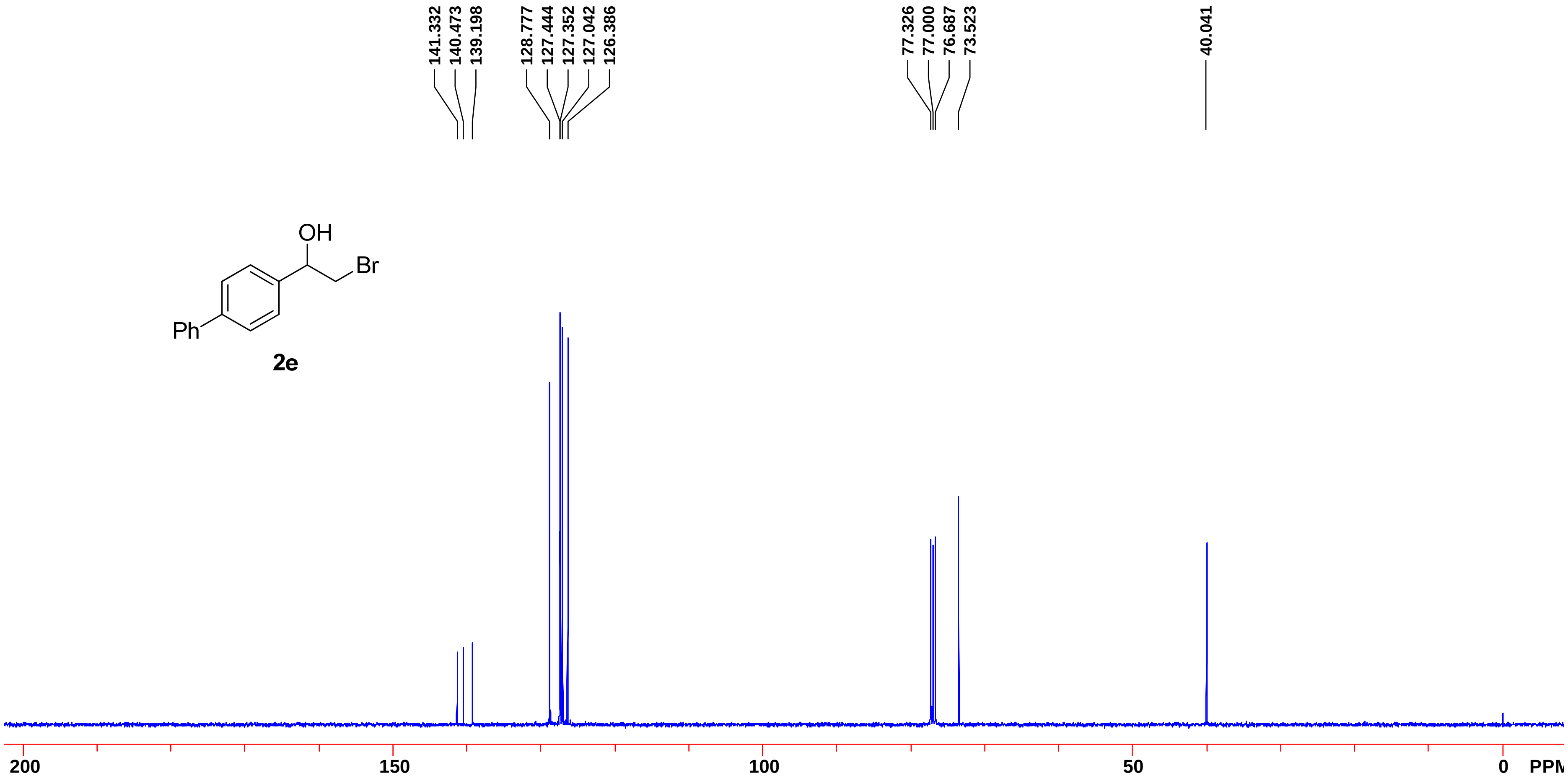

151.505
137.240
125.682
125.598
77.319
77.000
76.675
73.639
40.199
34.562
31.254
OH
Br
tBu
200
150
100
50
0 PPM

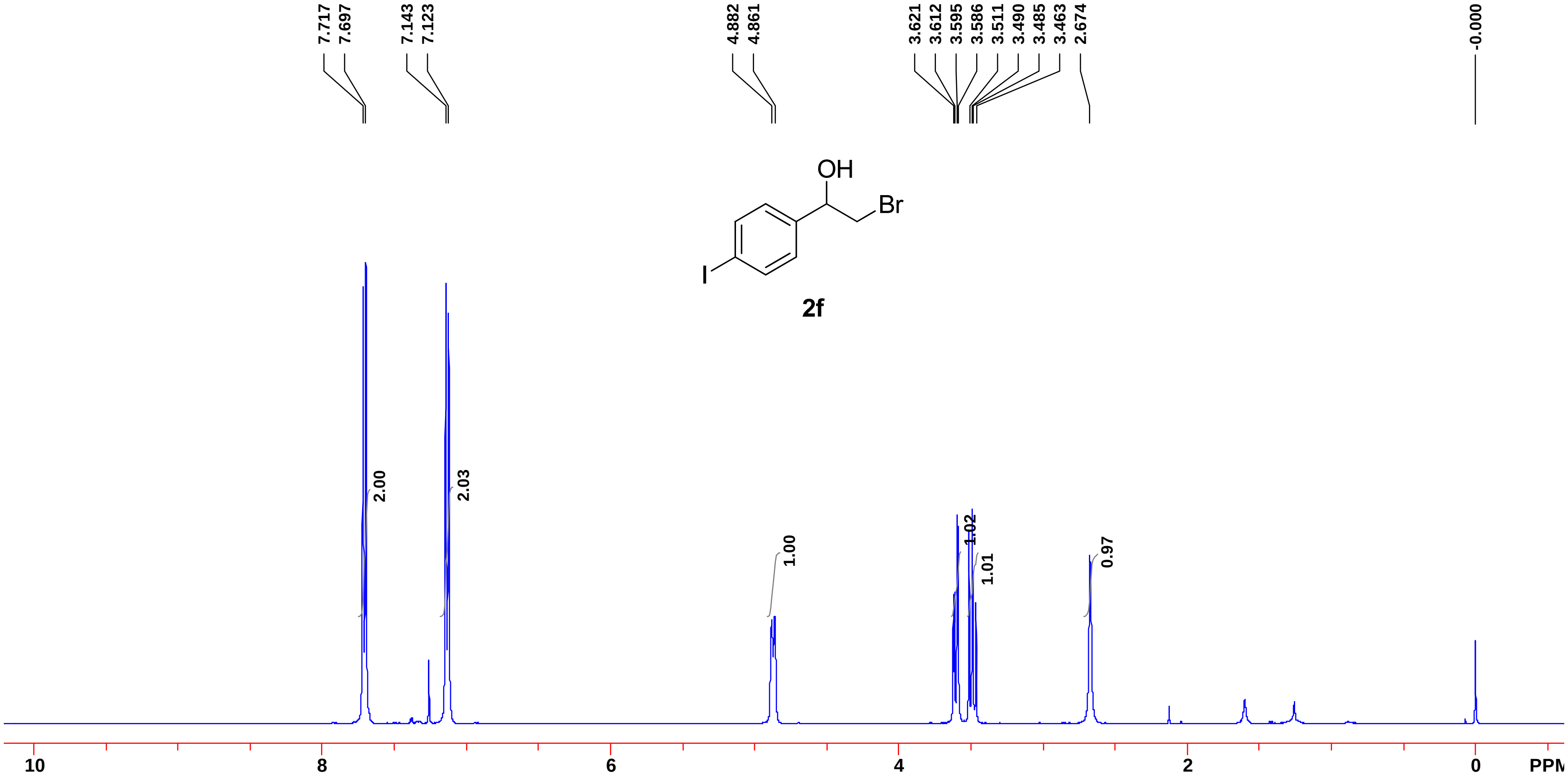
2d



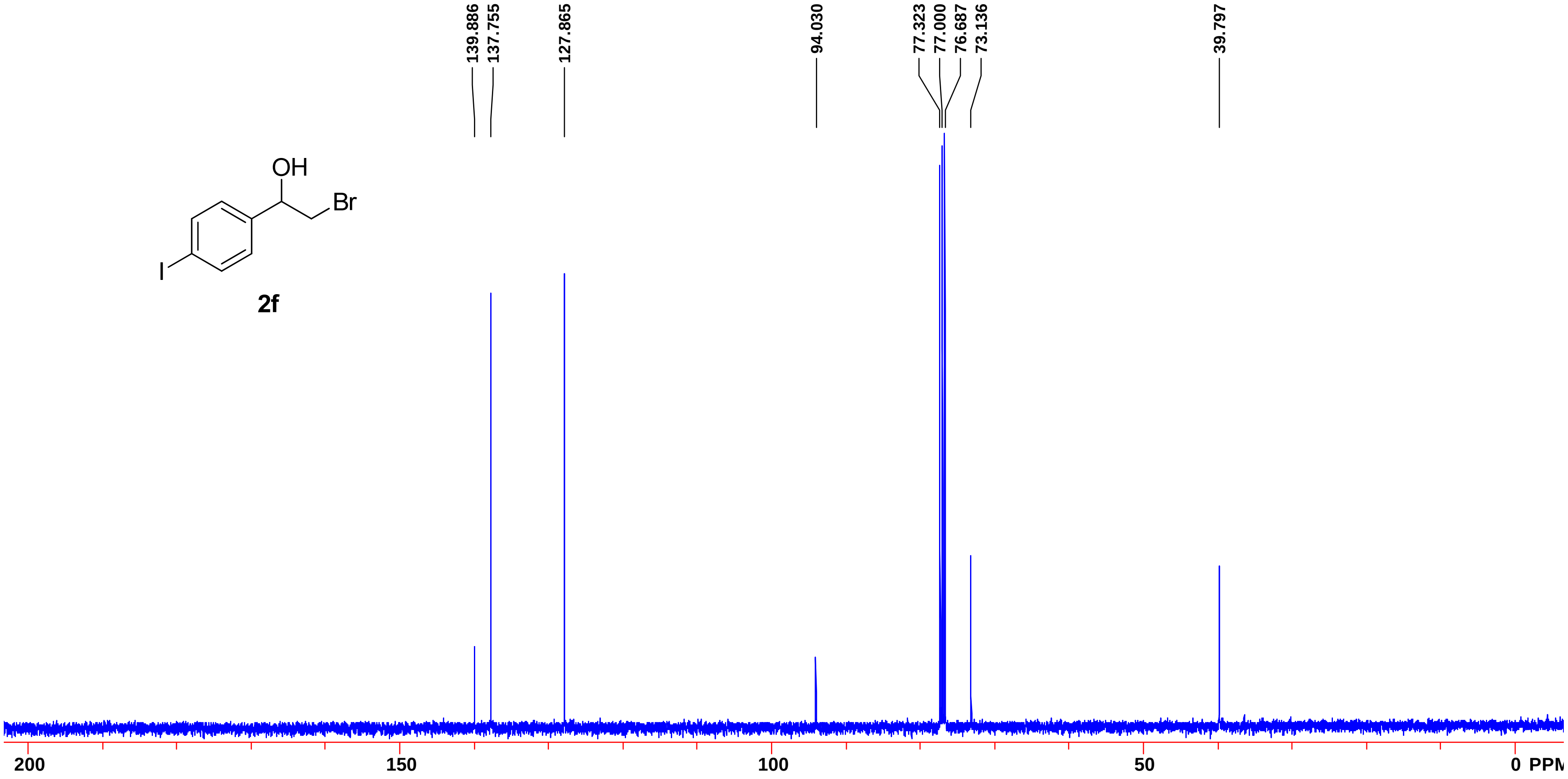
2e

7.633
7.617
7.612
7.599
7.488
7.476
7.470
7.455
7.450
7.402
7.384
7.366
7.260
4.998
4.990
4.976
4.967
3.704
3.696
3.678
3.670
3.619
3.597
3.570
2.766
OH
Br
Ph
4.04
4.05
1.01
1.00
1.01
1.01
1.02
10
8
6
4
2
0
PPM

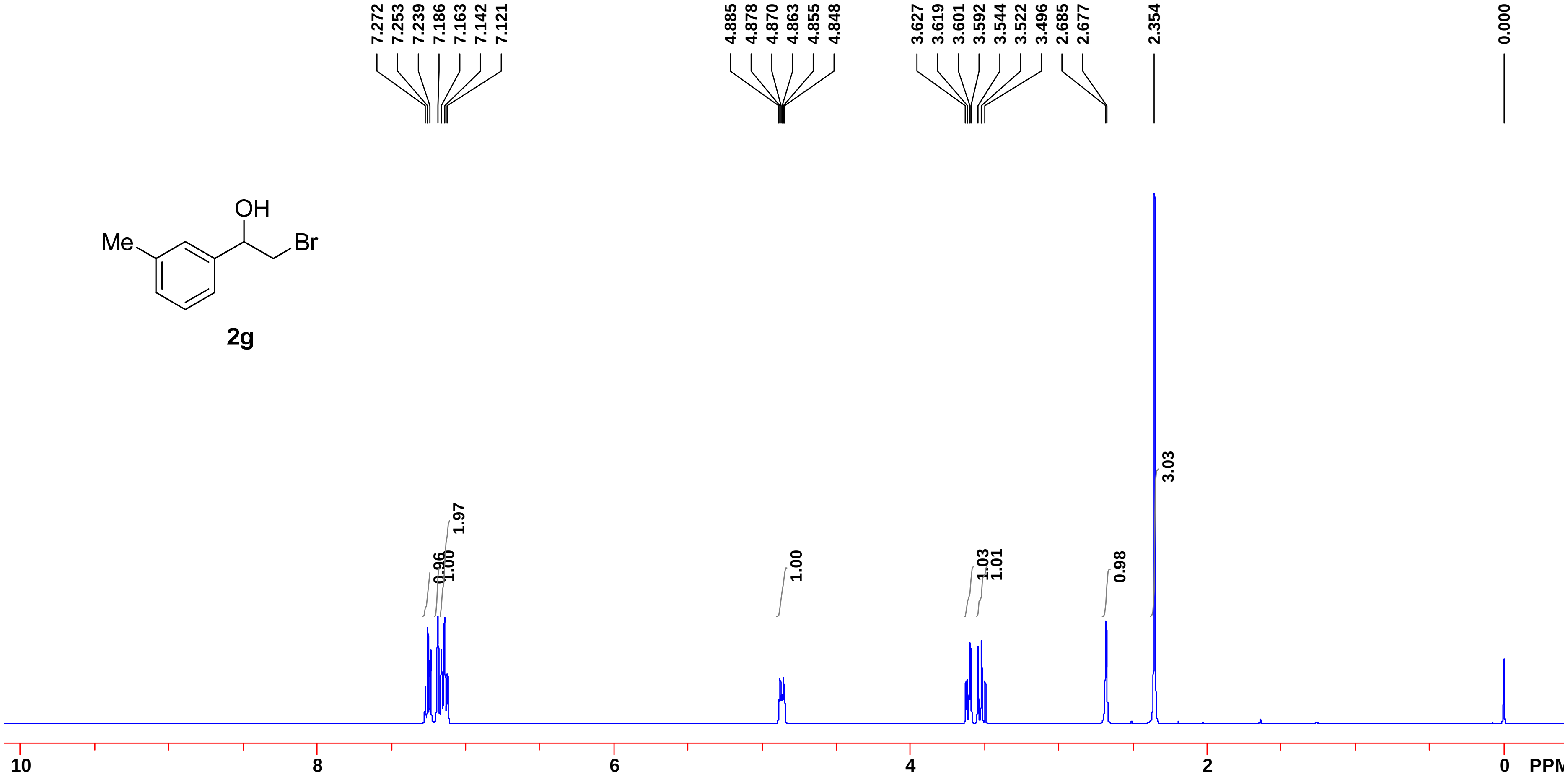

141.332
140.473
139.198
128.777
127.444
127.352
127.042
126.386
77.326
77.000
76.687
73.523
40.041
OH
Br
Ph
2e
200
150
100
50
0
PPM


7.717
7.697
7.143
7.123
4.882
4.861
3.621
3.612
3.595
3.586
3.511
3.490
3.485
3.463
2.674
-0.000
OH
Br
I
2.00
2.03
1.00
1.02
1.01
0.97
10
8
6
4
2
0
PPM

2f


139.886
137.755
127.865
94.030
77.323
77.000
76.687
73.136
39.797
OH
Br
I
200
150
100
50
0 PPM

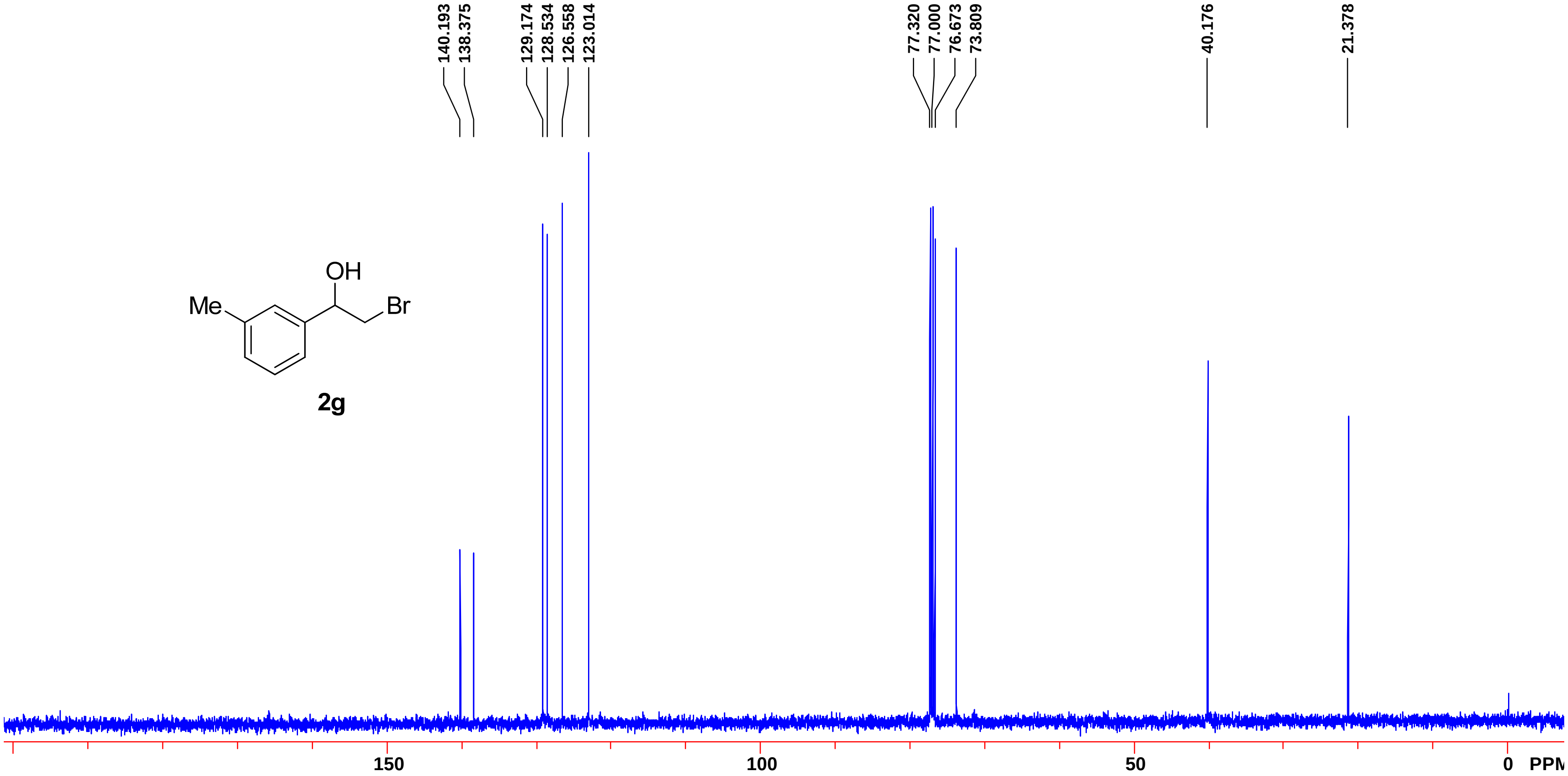
2f

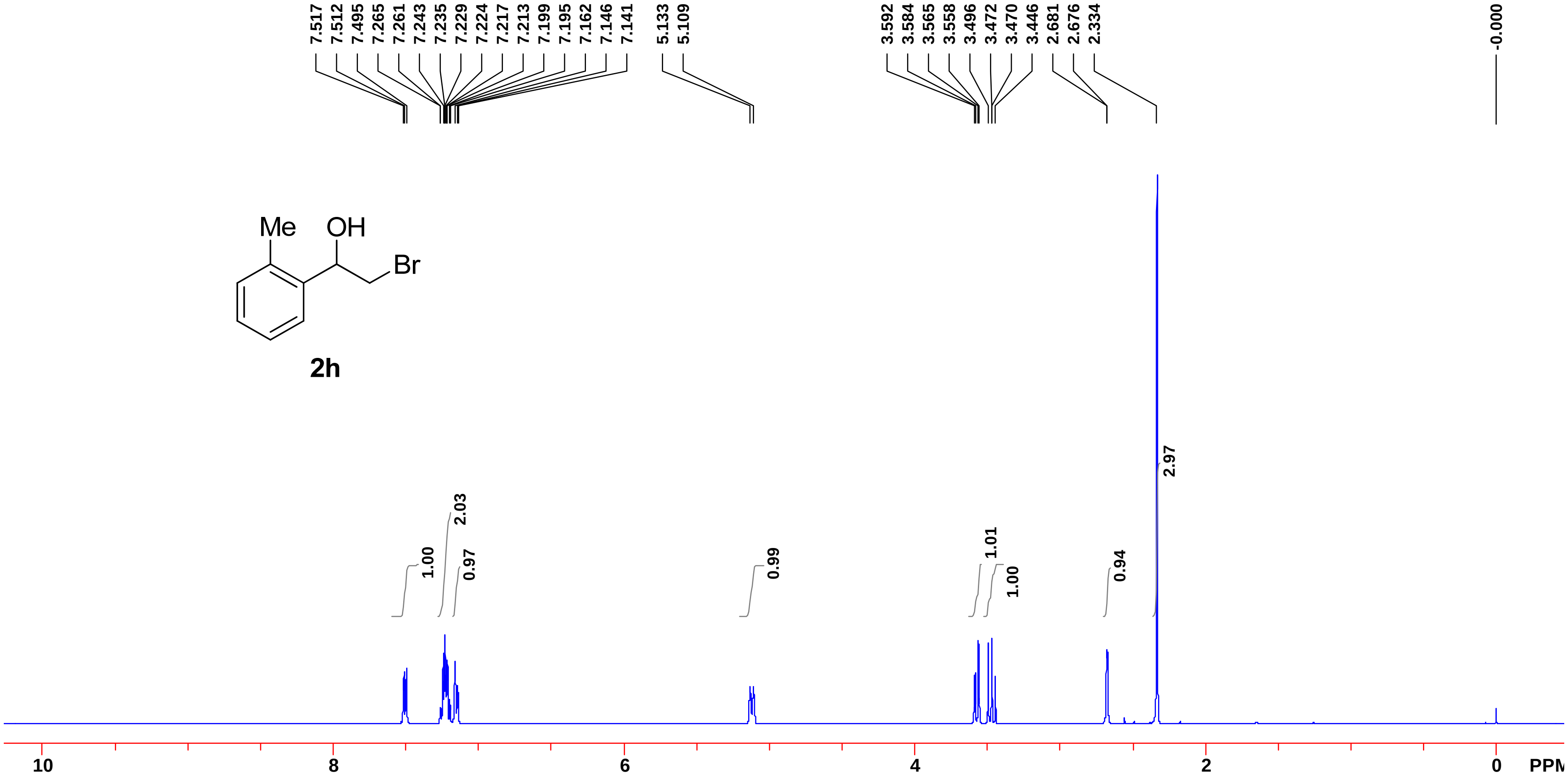


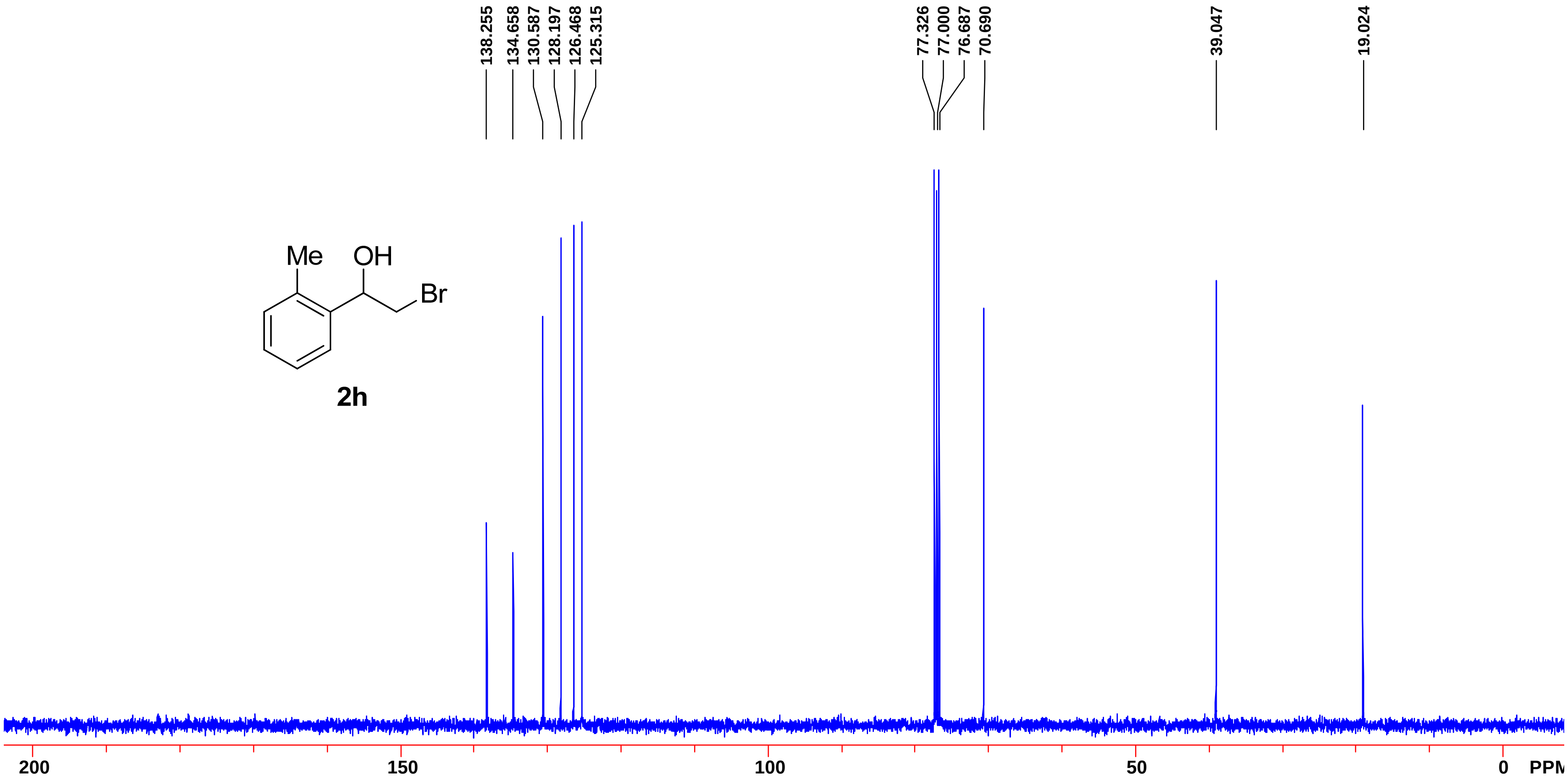
OH
Me
Br

2g

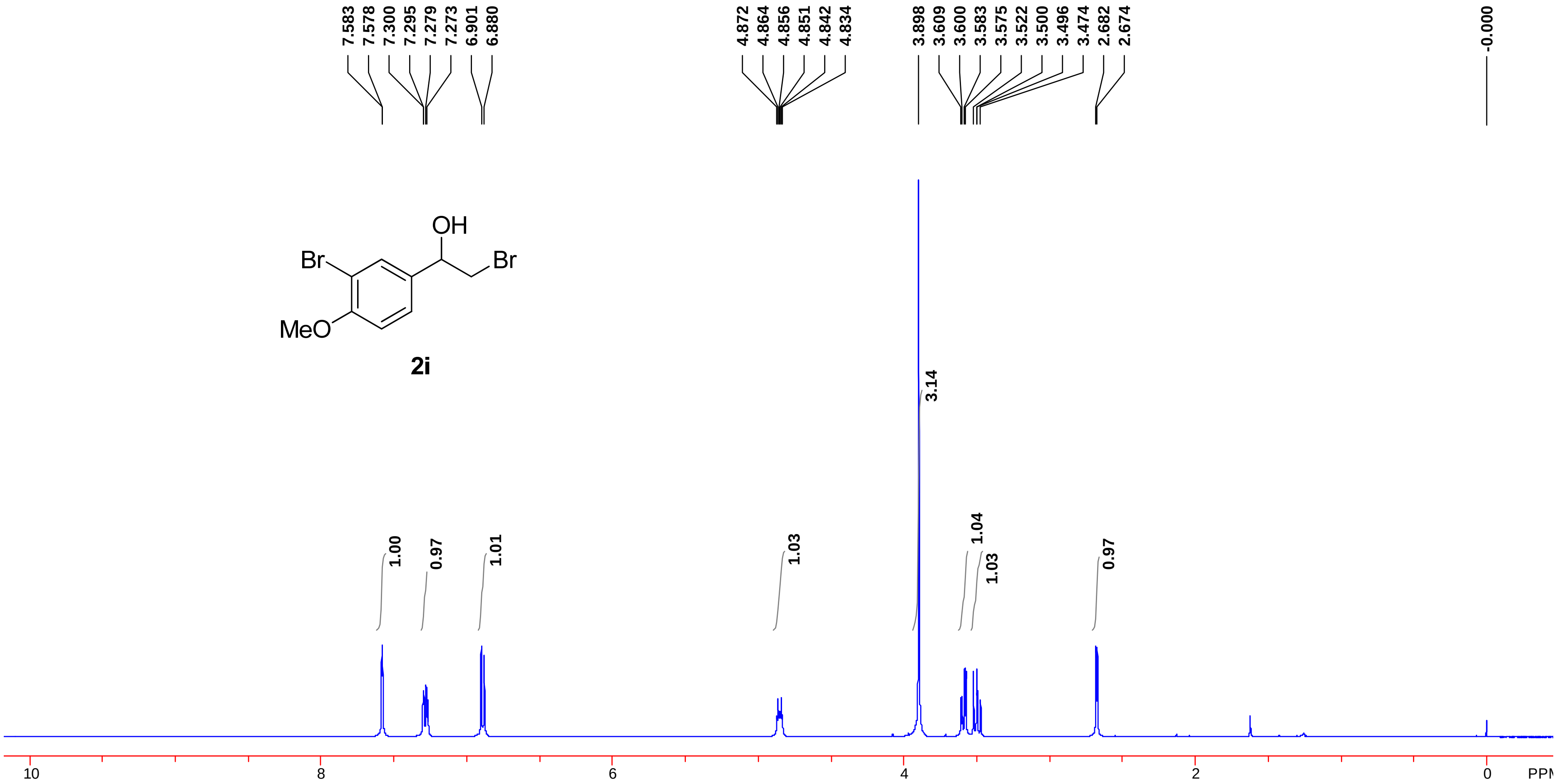
7.272
7.253
7.239
7.186
7.163
7.142
7.121
4.885
4.878
4.870
4.863
4.855
4.848
3.627
3.619
3.601
3.592
3.544
3.522
3.496
2.685
2.677
2.354
0.000
0.96
1.00
1.97
1.00
1.03
1.01
0.98
3.03
10
8
6
4
2
0
PP

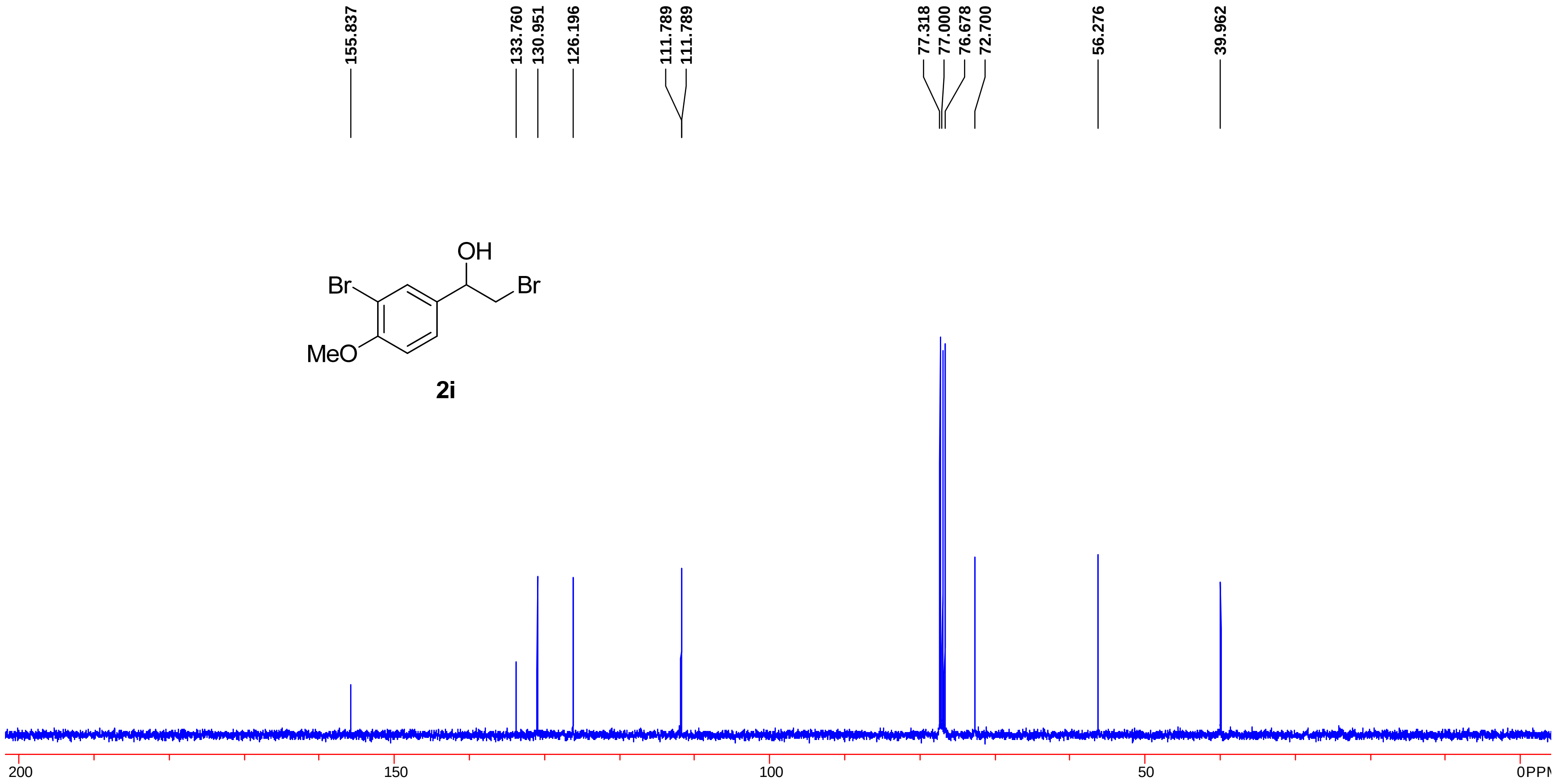

140.193
138.375
129.174
128.534
126.558
123.014
77.320
77.000
76.673
73.809
40.176
21.378
OH
Me
Br
2g
150
100
50
0
PPM


7.517
7.512
7.495
7.265
7.261
7.243
7.235
7.229
7.224
7.217
7.213
7.199
7.195
7.162
7.146
7.141
5.133
5.109
3.592
3.584
3.565
3.558
3.496
3.472
3.470
3.446
2.681
2.676
2.334
-0.000
Me
OH
Br
2h
1.00
2.03
0.97
0.99
1.01
1.00
0.94
2.97
10
8
6
4
2
0
PPM

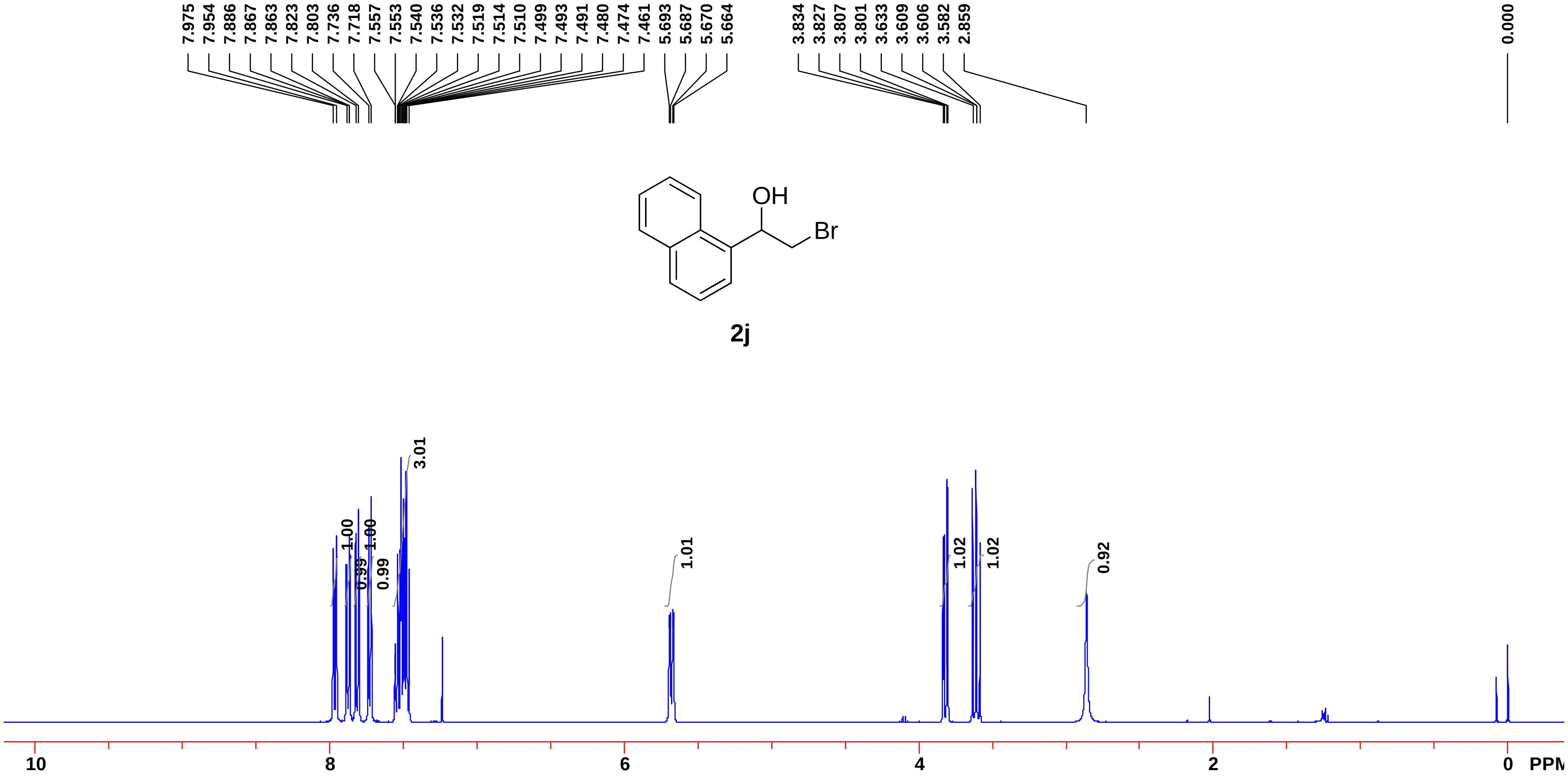

138.255
134.658
130.587
128.197
126.468
125.315
77.326
77.000
76.687
70.690
39.047
19.024
Me
OH
Br
200
150
100
50
0
PPM

2h

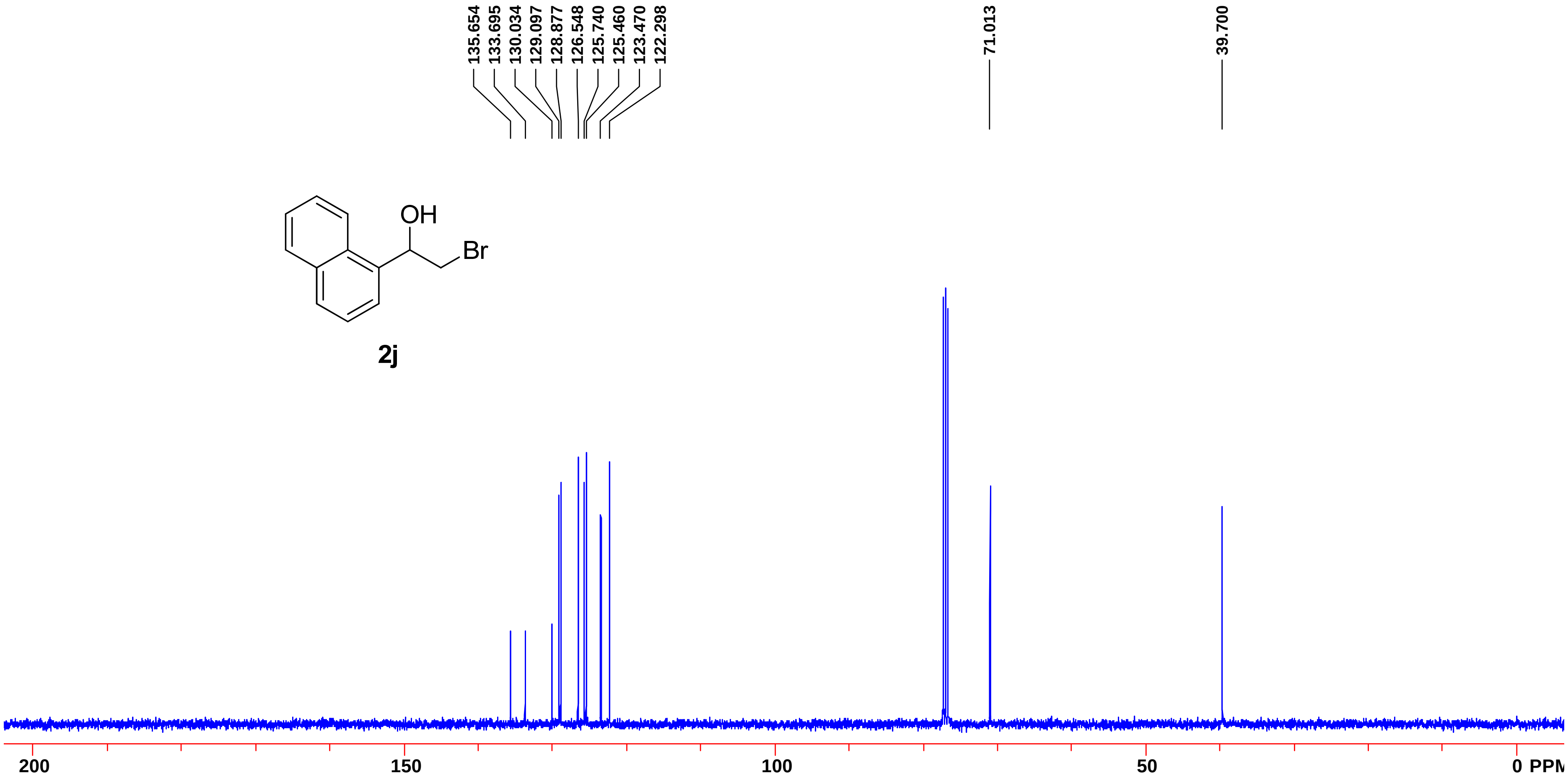

7.583
7.578
7.300
7.295
7.279
7.273
6.901
6.880
4.872
4.864
4.856
4.851
4.842
4.834
3.898
3.609
3.600
3.583
3.575
3.522
3.500
3.496
3.474
2.682
2.674
-0.000
OH
Br
Br
MeO
2i
1.00
0.97
1.01
1.03
3.14
1.04
1.03
0.97
10
8
6
4
2
0
PPM


155.837
133.760
130.951
126.196
111.789
111.789
77.318
77.000
76.678
72.700
56.276
39.962
OH
Br
Br
MeO
200
150
100
50
0PP

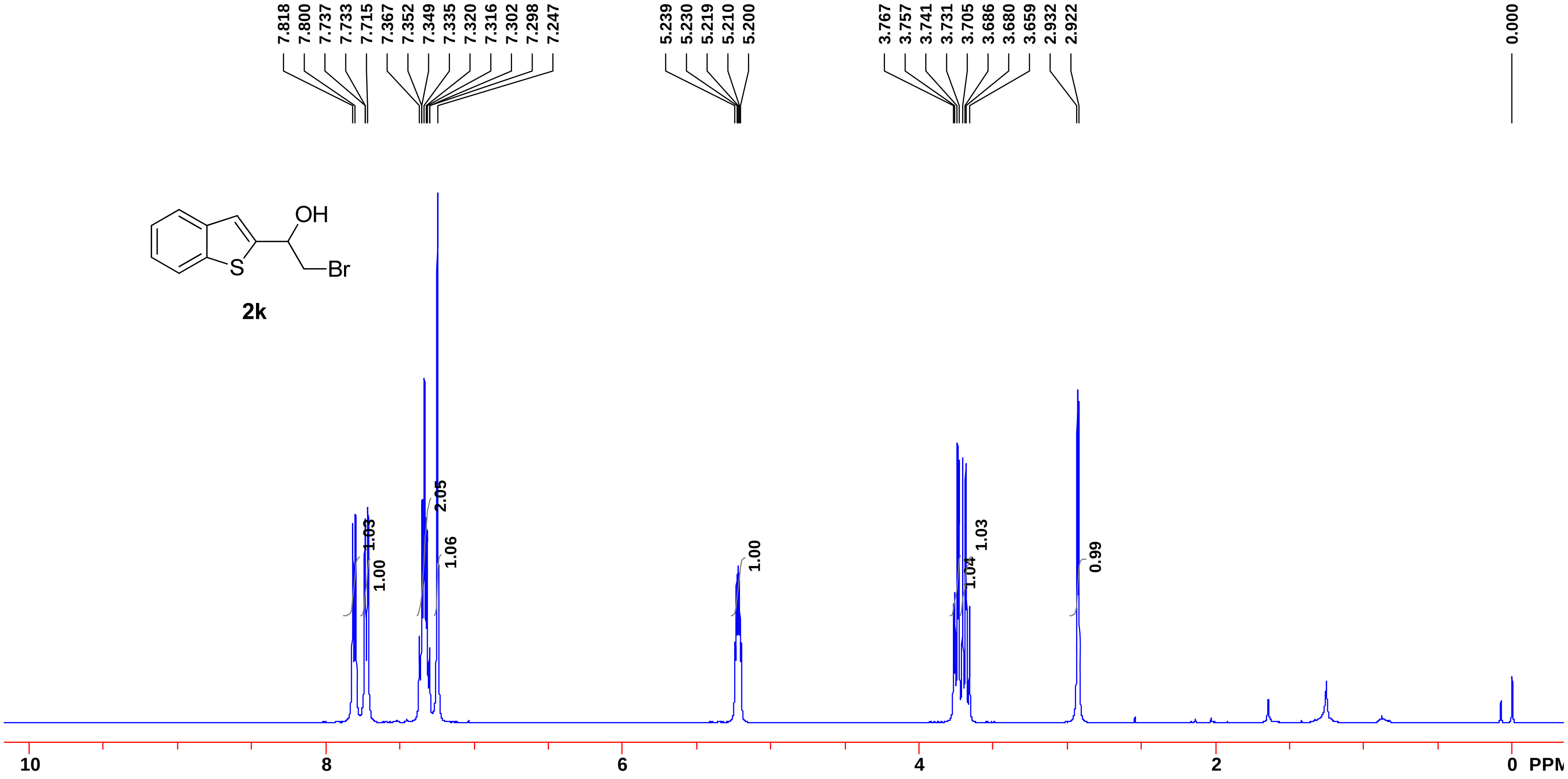
2i

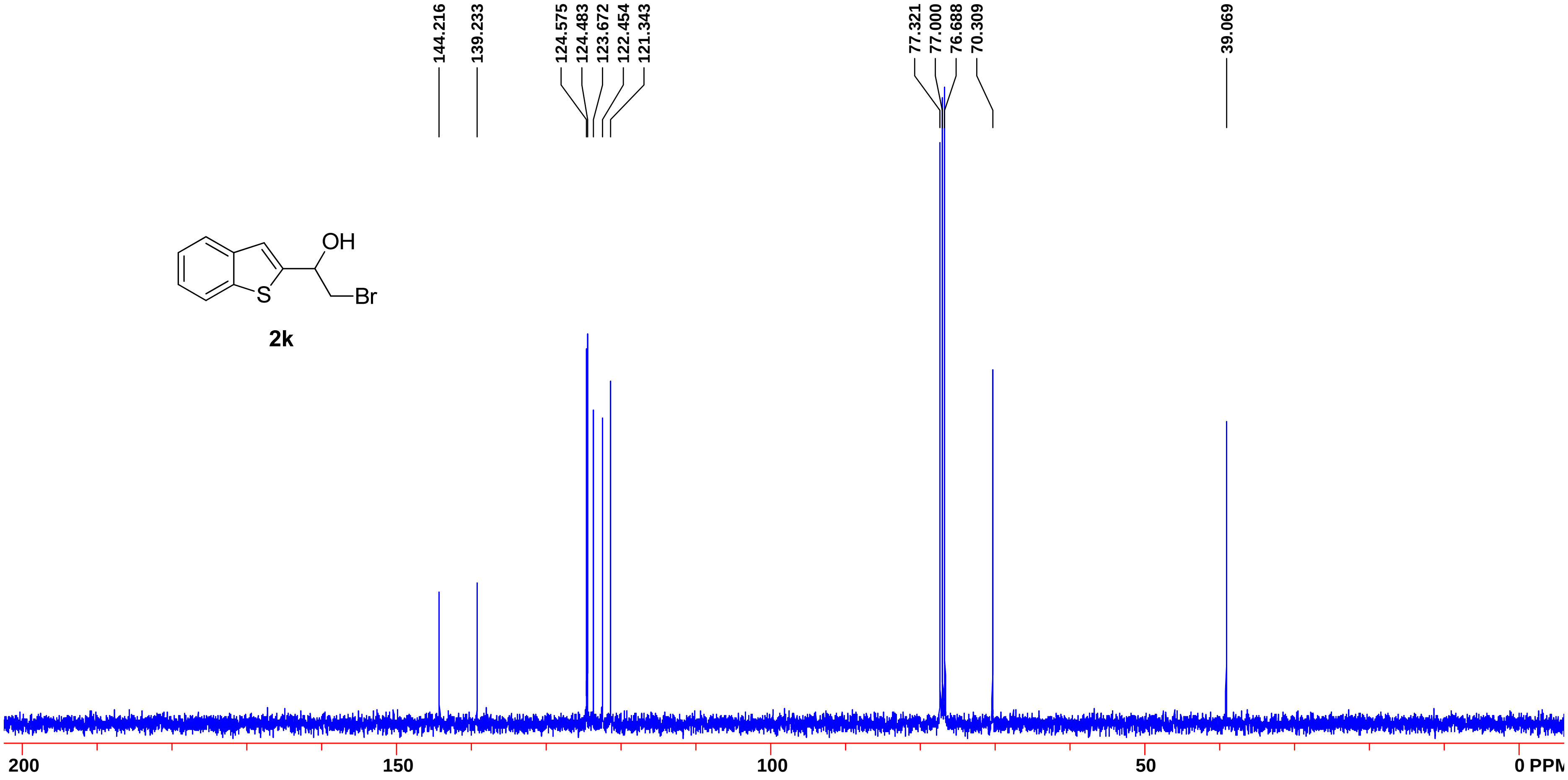

7.975
7.954
7.886
7.867
7.863
7.823
7.803
7.736
7.718
7.557
7.553
7.540
7.536
7.532
7.519
7.514
7.510
7.499
7.493
7.491
7.480
7.474
7.461
5.693
5.687
5.670
5.664
3.834
3.827
3.807
3.801
3.633
3.609
3.606
3.582
2.859
0.000
OH
Br
1.00
0.99
1.00
0.99
3.01
1.01
1.02
1.02
0.92
10
8
6
4
2
0
PPM

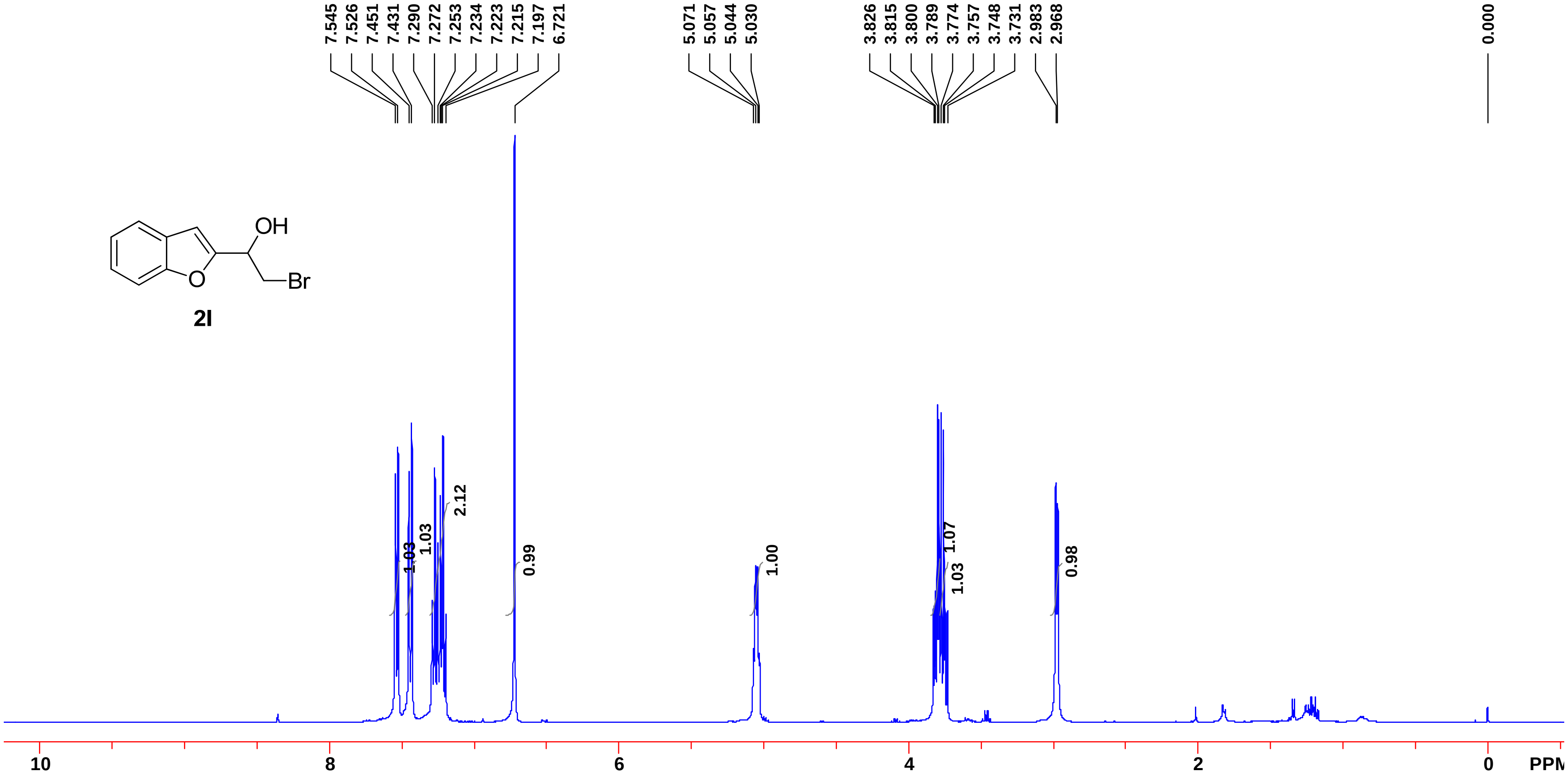
2j


135.654
133.695
130.034
129.097
128.877
126.548
125.740
125.460
123.470
122.298
71.013
39.700
OH
Br
200
150
100
50
0 PPM

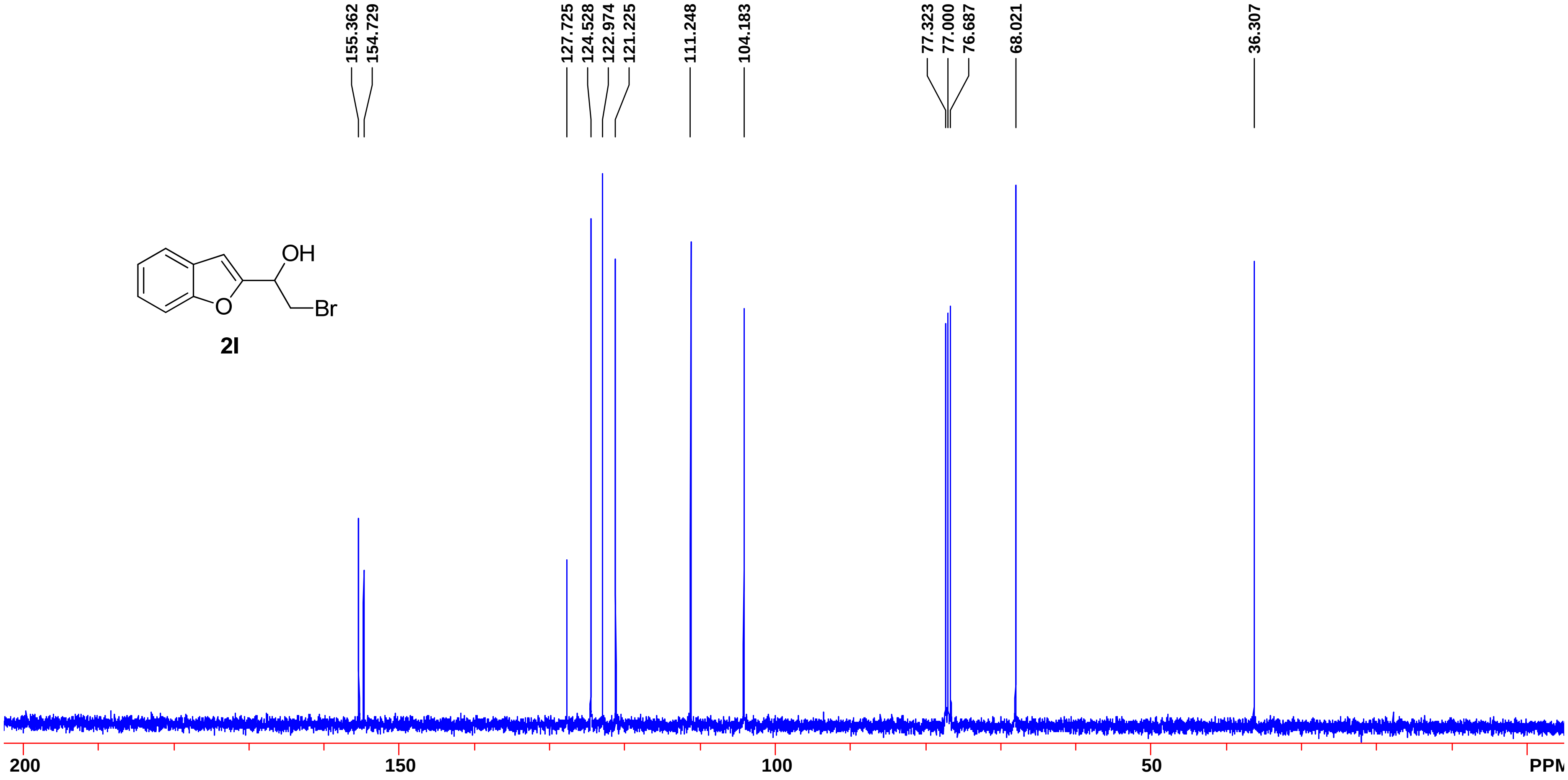
2j


2k
7.818
7.800
7.737
7.733
7.715
7.367
7.352
7.349
7.335
7.320
7.316
7.302
7.298
7.247
5.239
5.230
5.219
5.210
5.200
3.767
3.757
3.741
3.731
3.705
3.686
3.680
3.659
2.932
2.922
0.000
OH
Br
S
1.03
1.00
2.05
1.06
1.00
1.04
1.03
0.99
10
8
6
4
2
0 PPM

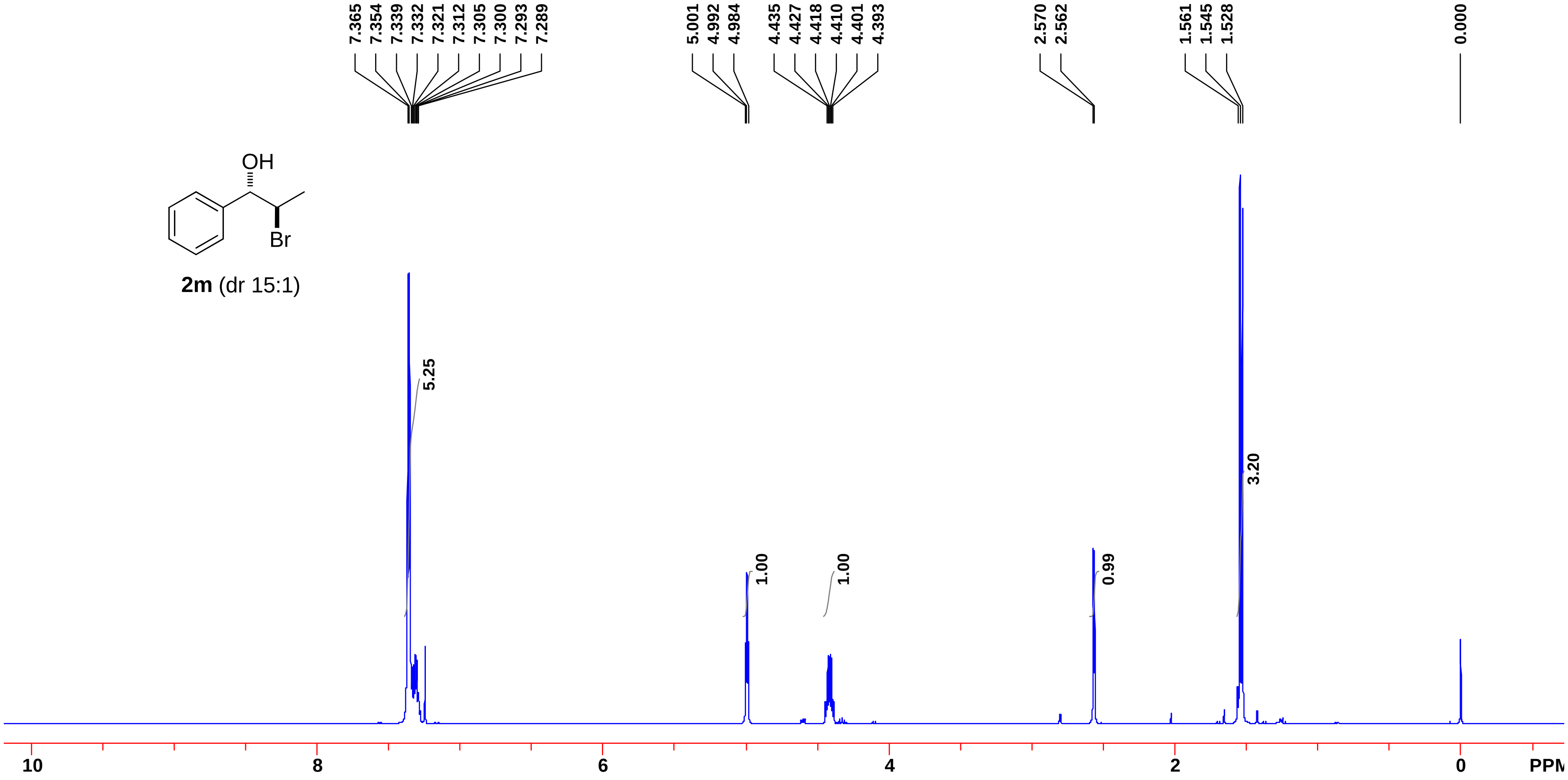

144.216
139.233
124.575
124.483
123.672
122.454
121.343
77.321
77.000
76.688
70.309
39.069
OH
S
Br
2k
200
150
100
50
0 PPM


7.545
7.526
7.451
7.431
7.290
7.272
7.253
7.234
7.223
7.215
7.197
6.721
5.071
5.057
5.044
5.030
3.826
3.815
3.800
3.789
3.774
3.757
3.748
3.731
2.983
2.968
0.000
OH
O
Br
1.03
1.03
2.12
0.99
1.00
1.07
1.03
0.98
10
8
6
4
2
0
PPM

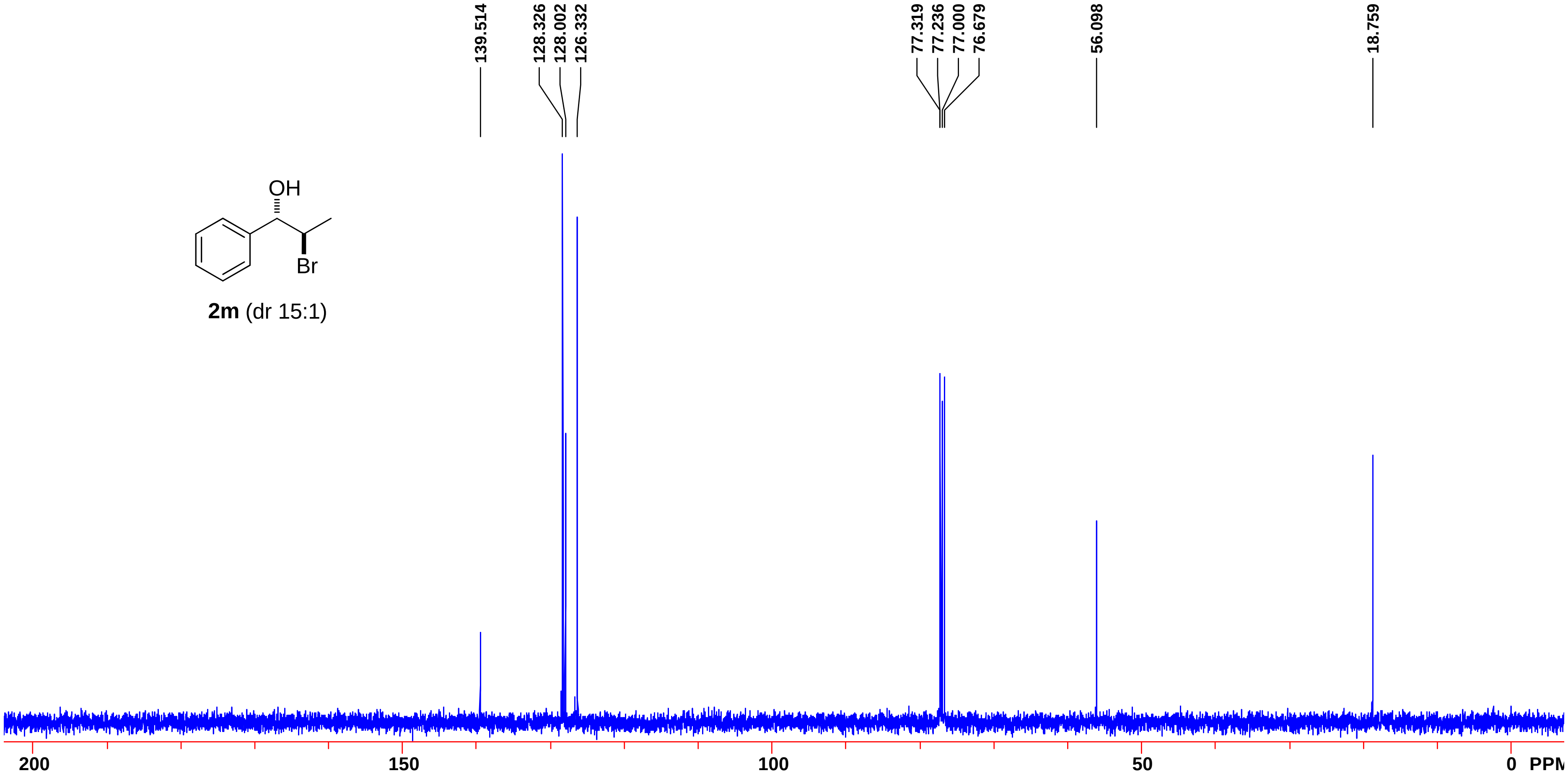
2l


155.362
154.729
127.725
124.528
122.974
121.225
111.248
104.183
77.323
77.000
76.687
68.021
36.307
OH
O
Br
200
150
100
50
PPM

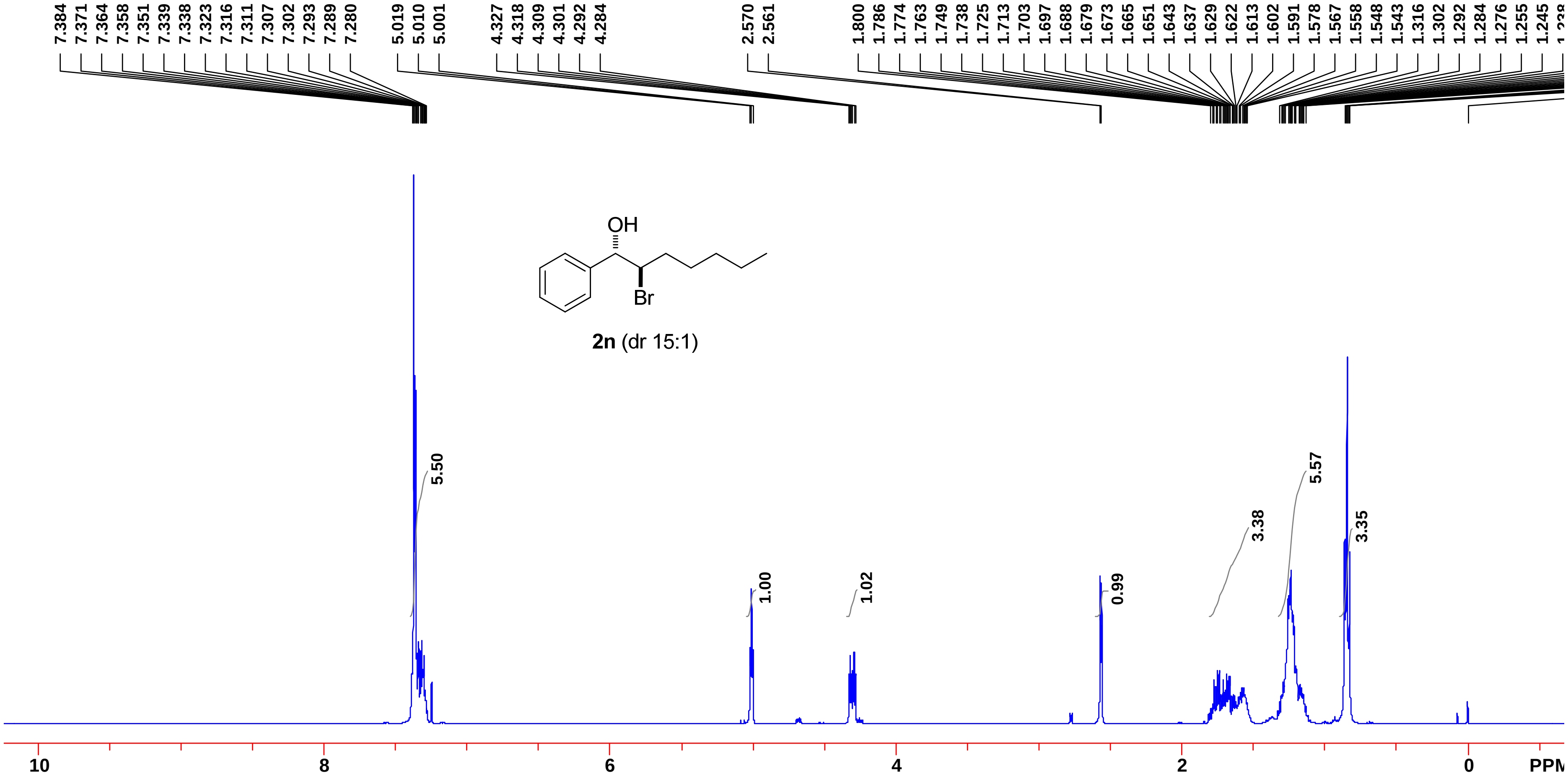
2l


7.365
7.354
7.339
7.332
7.321
7.312
7.305
7.300
7.293
7.289
5.001
4.992
4.984
4.435
4.427
4.418
4.410
4.401
4.393
2.570
2.562
1.561
1.545
1.528
0.000
OH
Br
5.25
1.00
1.00
0.99
3.20
10
8
6
4
2
0
PPM

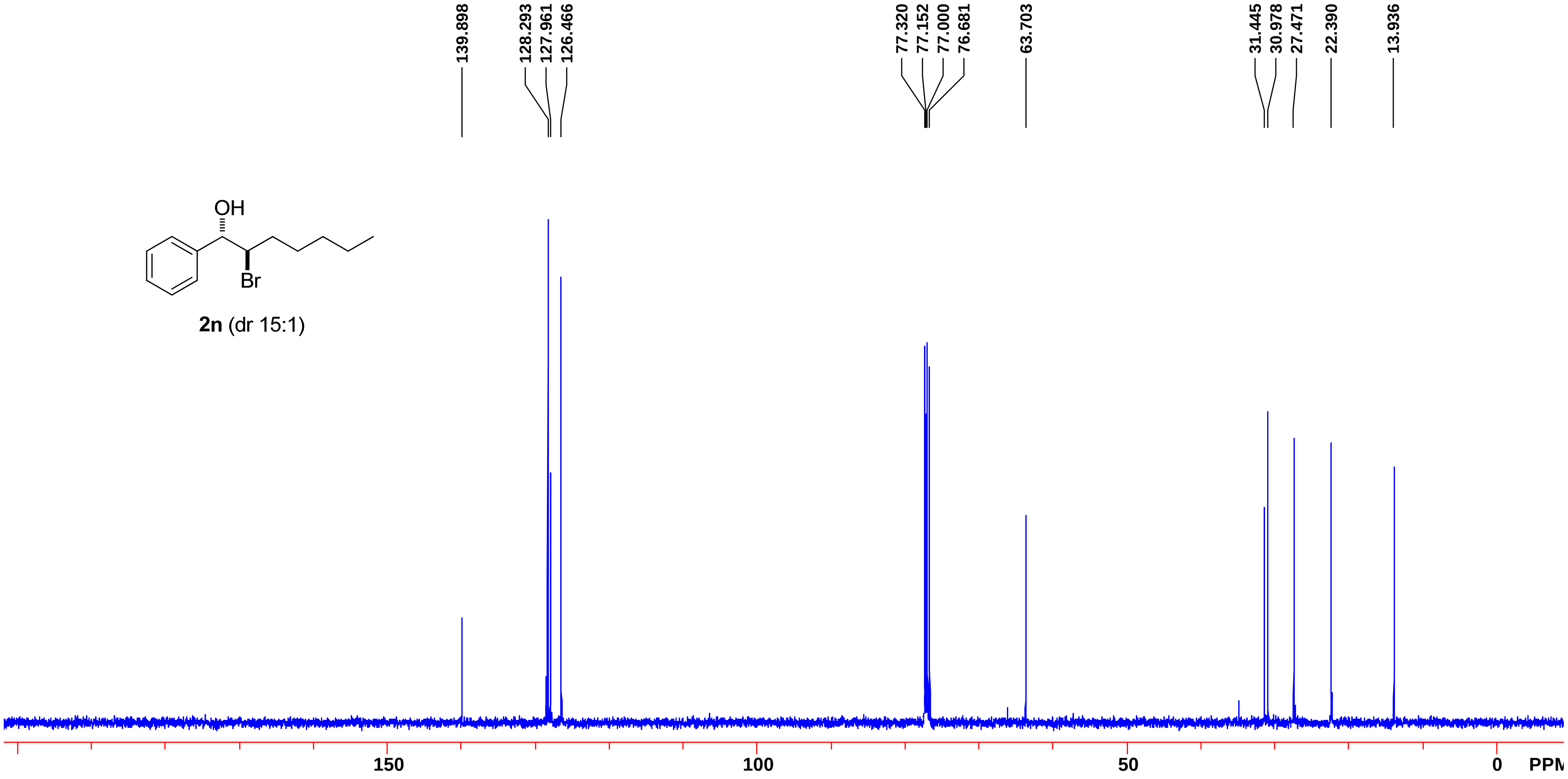
2m (dr 15:1)

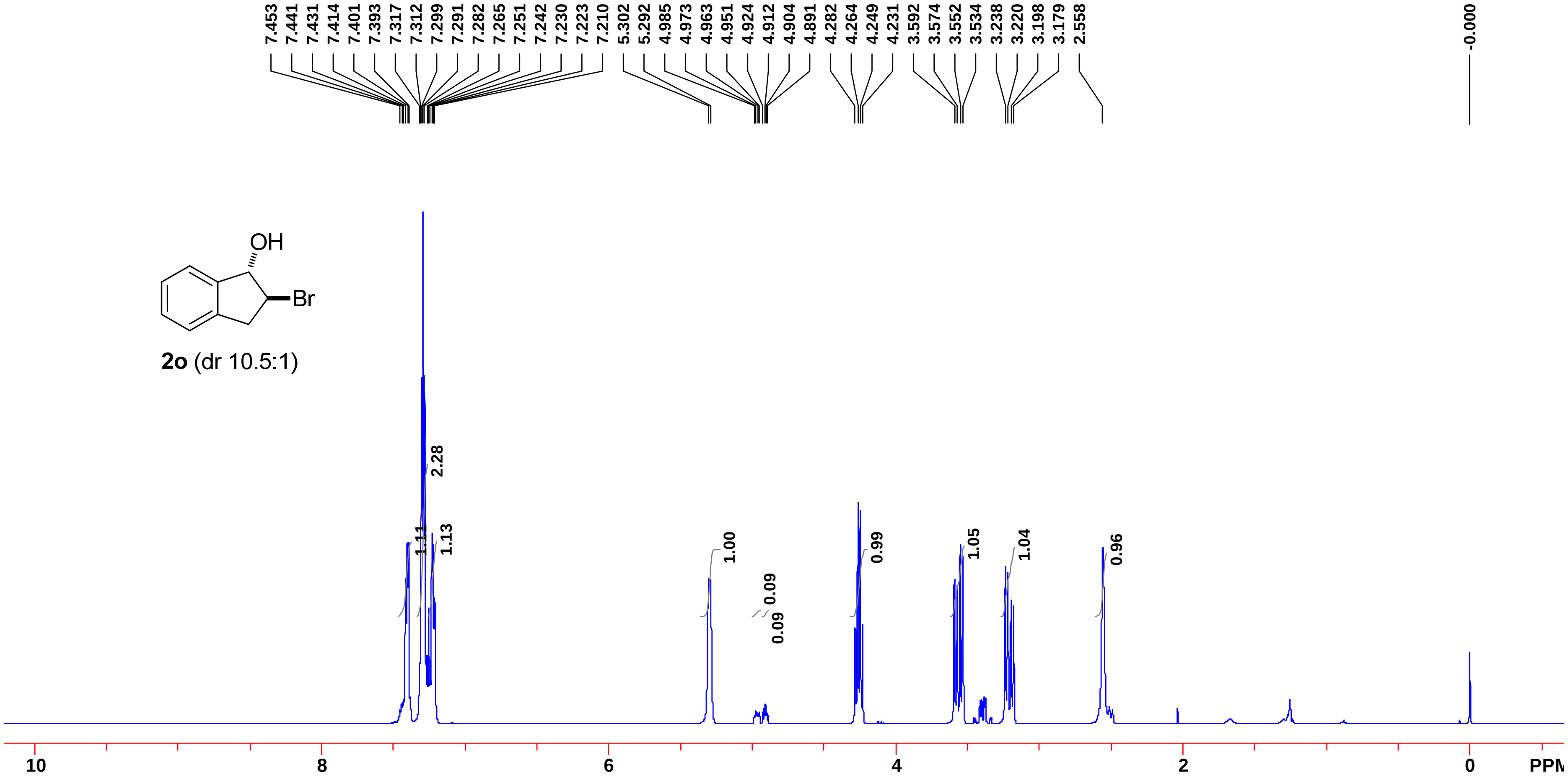

139.514
128.326
128.002
126.332
77.319
77.236
77.000
76.679
56.098
18.759
OH
Br
200
150
100
50
0
PPM

2m (dr 15:1)


7.384
7.371
7.364
7.358
7.351
7.339
7.338
7.323
7.316
7.311
7.307
7.302
7.293
7.289
7.280
5.019
5.010
5.001
4.327
4.318
4.309
4.301
4.292
4.284
2.570
2.561
1.800
1.786
1.774
1.763
1.749
1.738
1.725
1.713
1.703
1.697
1.688
1.679
1.673
1.665
1.651
1.643
1.637
1.629
1.622
1.613
1.602
1.591
1.578
1.567
1.558
1.548
1.543
1.316
1.302
1.292
1.284
1.276
1.255
1.245
OH
Br
5.50
1.00
1.02
0.99
3.38
5.57
3.35
10
8
6
4
2
0
PPM

2n (dr 15:1)

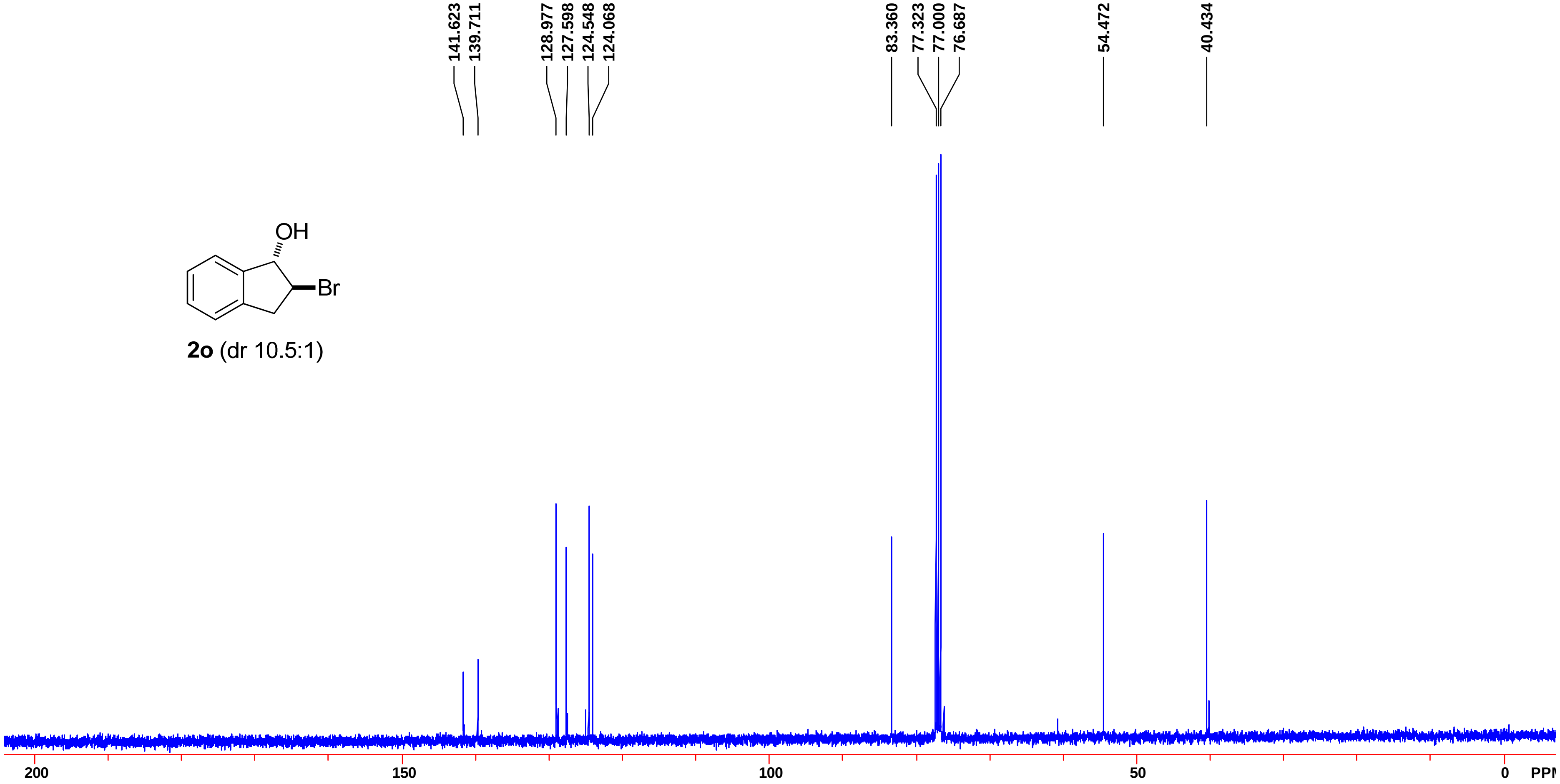

139.898
128.293
127.961
126.466
77.320
77.152
77.000
76.681
63.703
31.445
30.978
27.471
22.390
13.936
OH
Br
2n (dr 15:1)
150
100
50
0
PPM

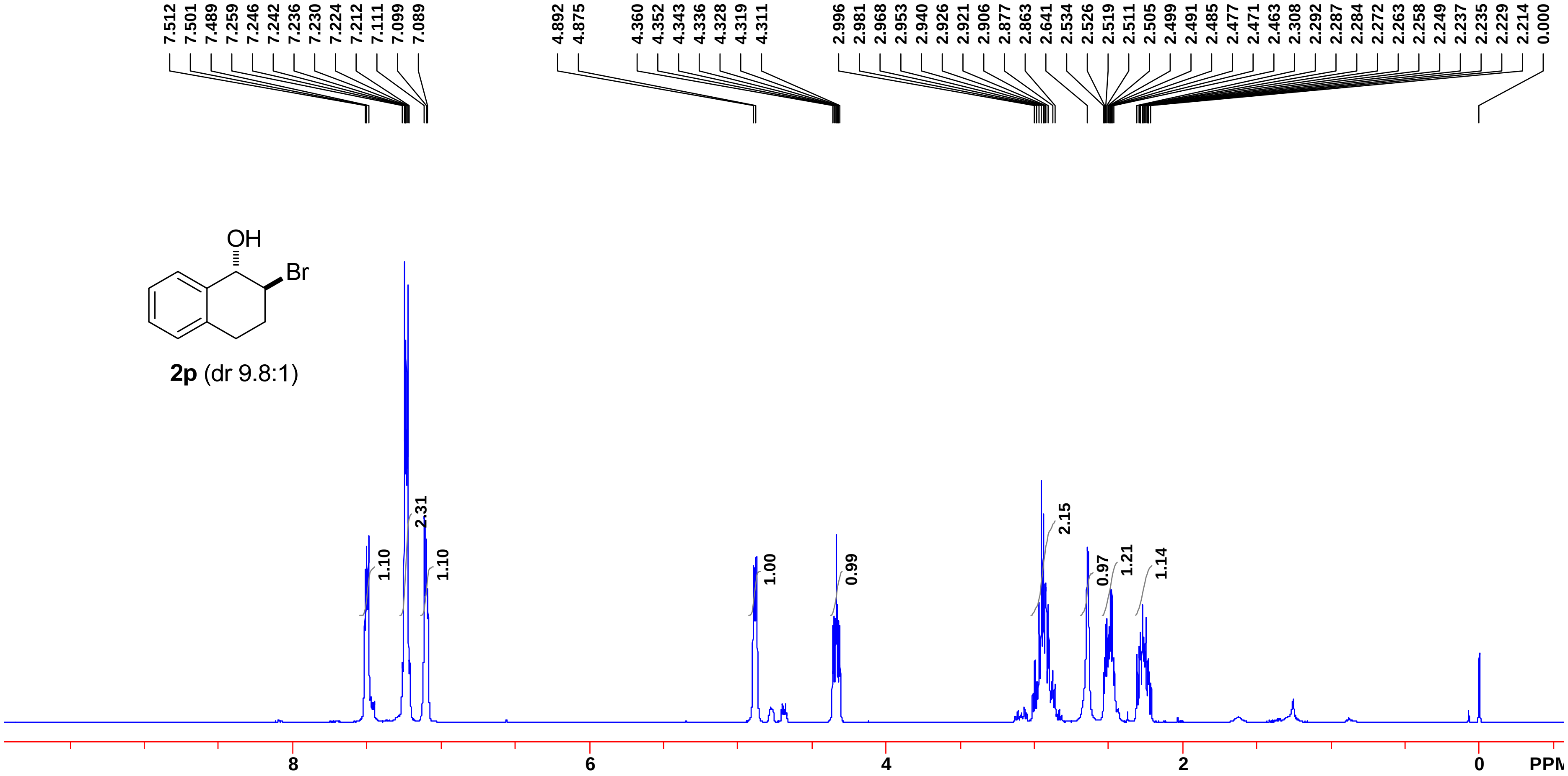

7.453
7.441
7.431
7.414
7.401
7.393
7.317
7.312
7.299
7.291
7.282
7.265
7.251
7.242
7.230
7.223
7.210
5.302
5.292
4.985
4.973
4.963
4.951
4.924
4.912
4.904
4.891
4.282
4.264
4.249
4.231
3.592
3.574
3.552
3.534
3.238
3.220
3.198
3.179
2.558
-0.000
OH
Br
2.28
1.11
1.13
1.00
0.09
0.09
0.99
1.05
1.04
0.96
10
8
6
4
2
0
PPM

2o (dr 10.5:1)

OH
Br

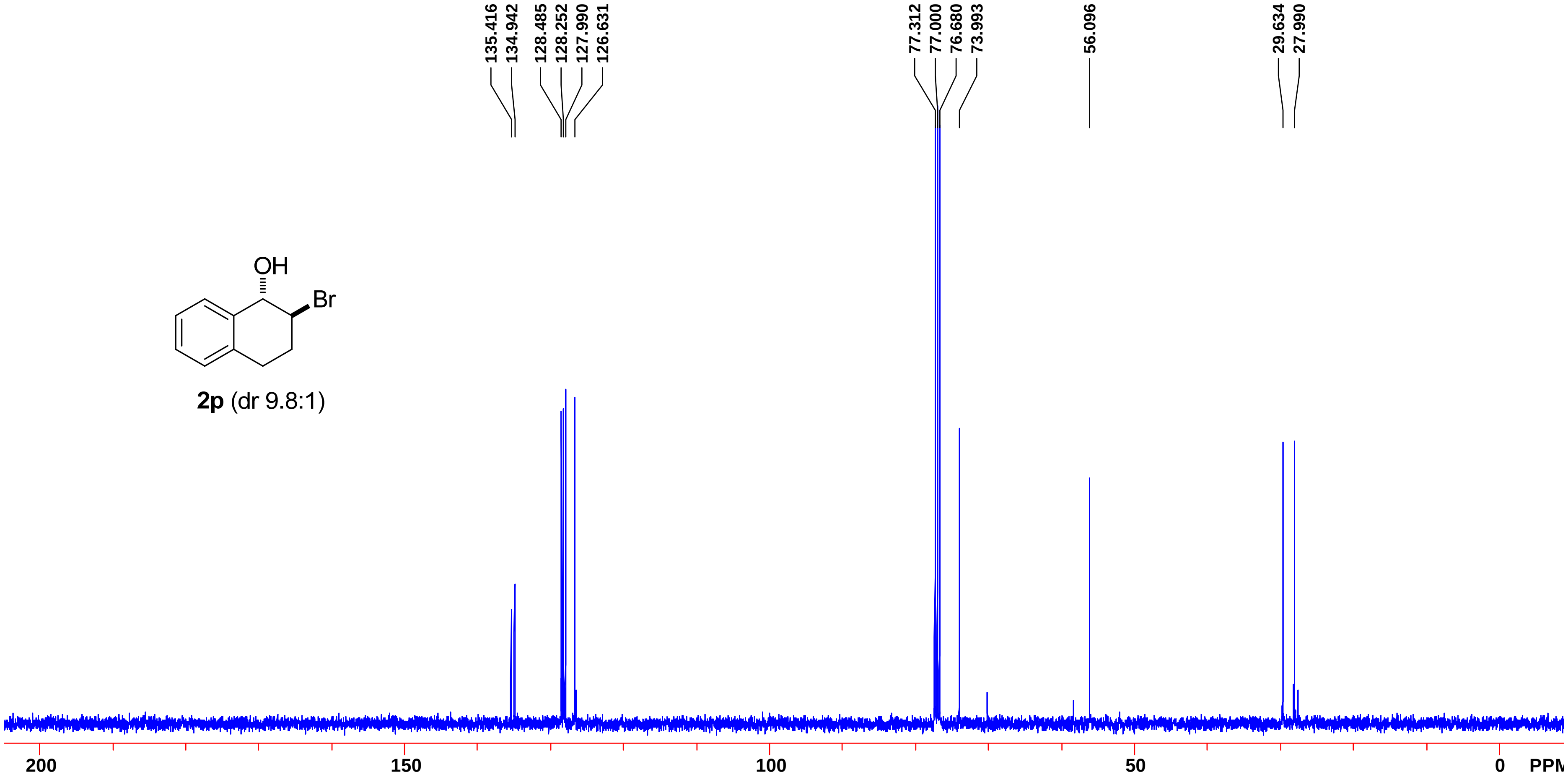
2o (dr 10.5:1)


141.623
139.711
128.977
127.598
124.548
124.068
83.360
77.323
77.000
76.687
54.472
40.434
200
150
100
50
0
PPM

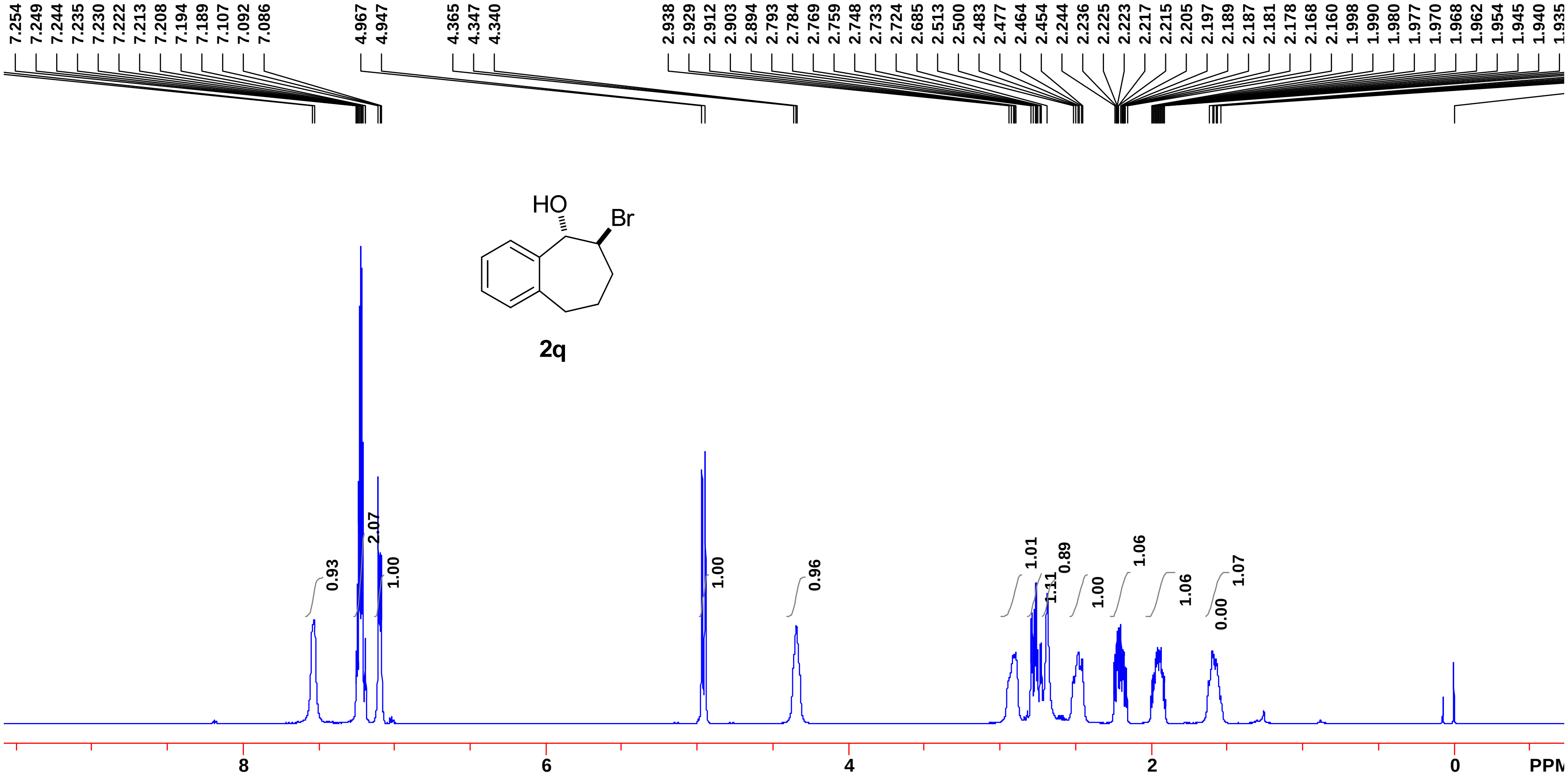


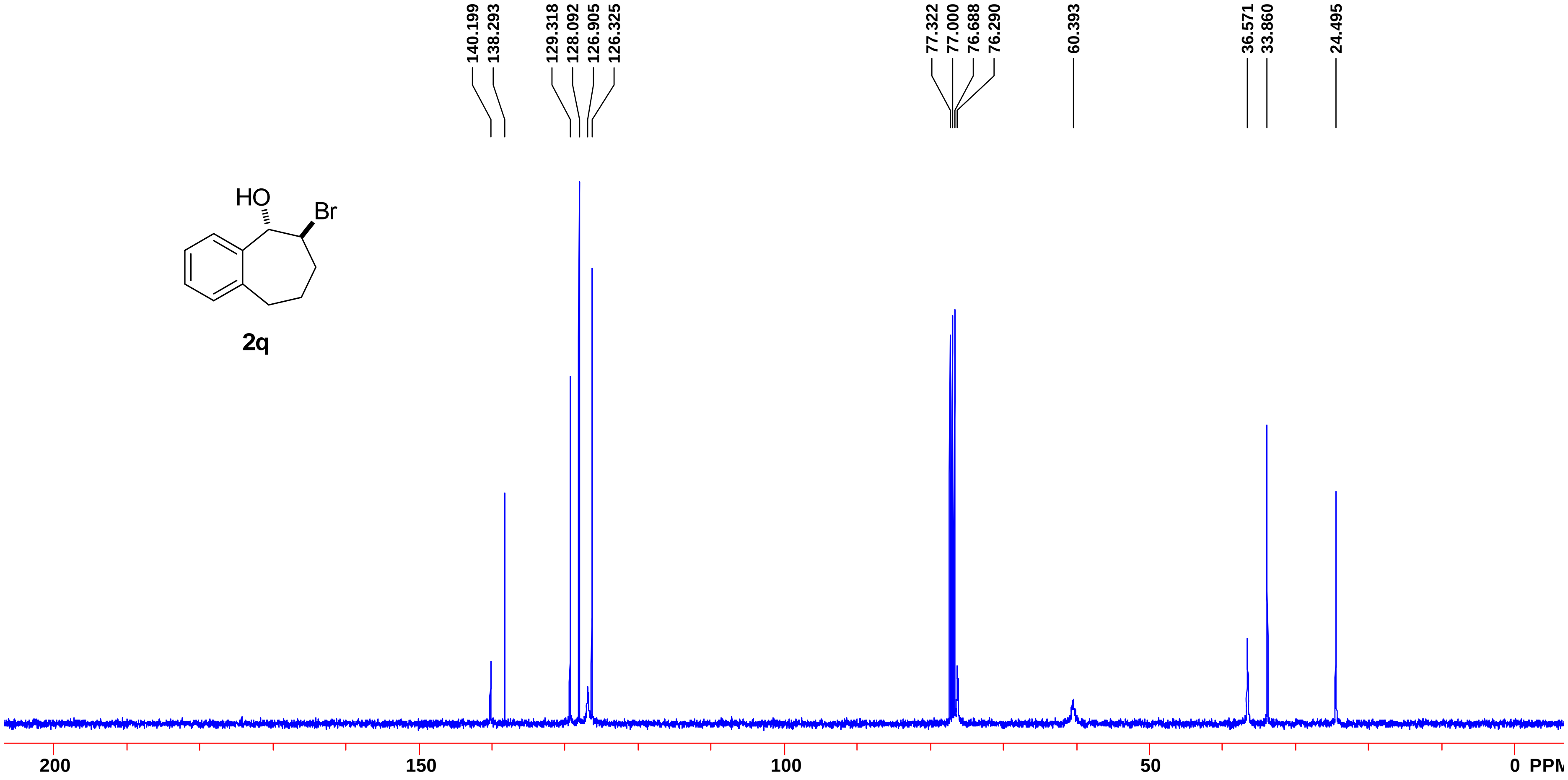
2p (dr 9.8:1)

7.512
7.501
7.489
7.259
7.246
7.242
7.236
7.230
7.224
7.212
7.111
7.099
7.089
4.892
4.875
4.360
4.352
4.343
4.336
4.328
4.319
4.311
2.996
2.981
2.968
2.953
2.940
2.926
2.921
2.906
2.877
2.863
2.641
2.534
2.526
2.519
2.511
2.505
2.499
2.491
2.485
2.477
2.471
2.463
2.308
2.292
2.287
2.284
2.272
2.263
2.258
2.249
2.237
2.235
2.229
2.214
0.000
OH
Br
1.10
2.31
1.10
1.00
0.99
2.15
0.97
1.21
1.14
8
6
4
2
0
PPM

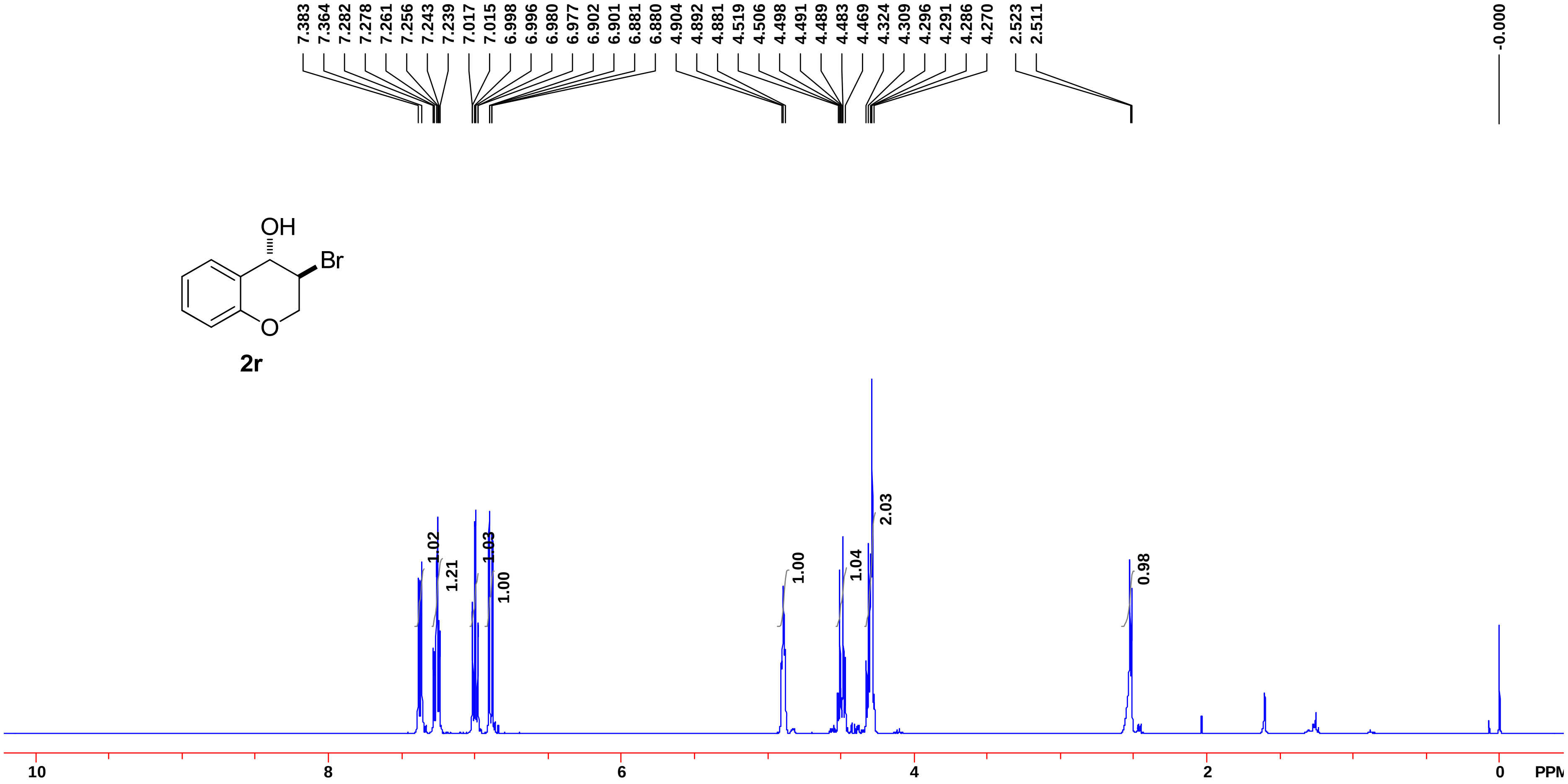

135.416
134.942
128.485
128.252
127.990
126.631
77.312
77.000
76.680
73.993
56.096
29.634
27.990
OH
Br
200
150
100
50
0
PPM

2p (dr 9.8:1)

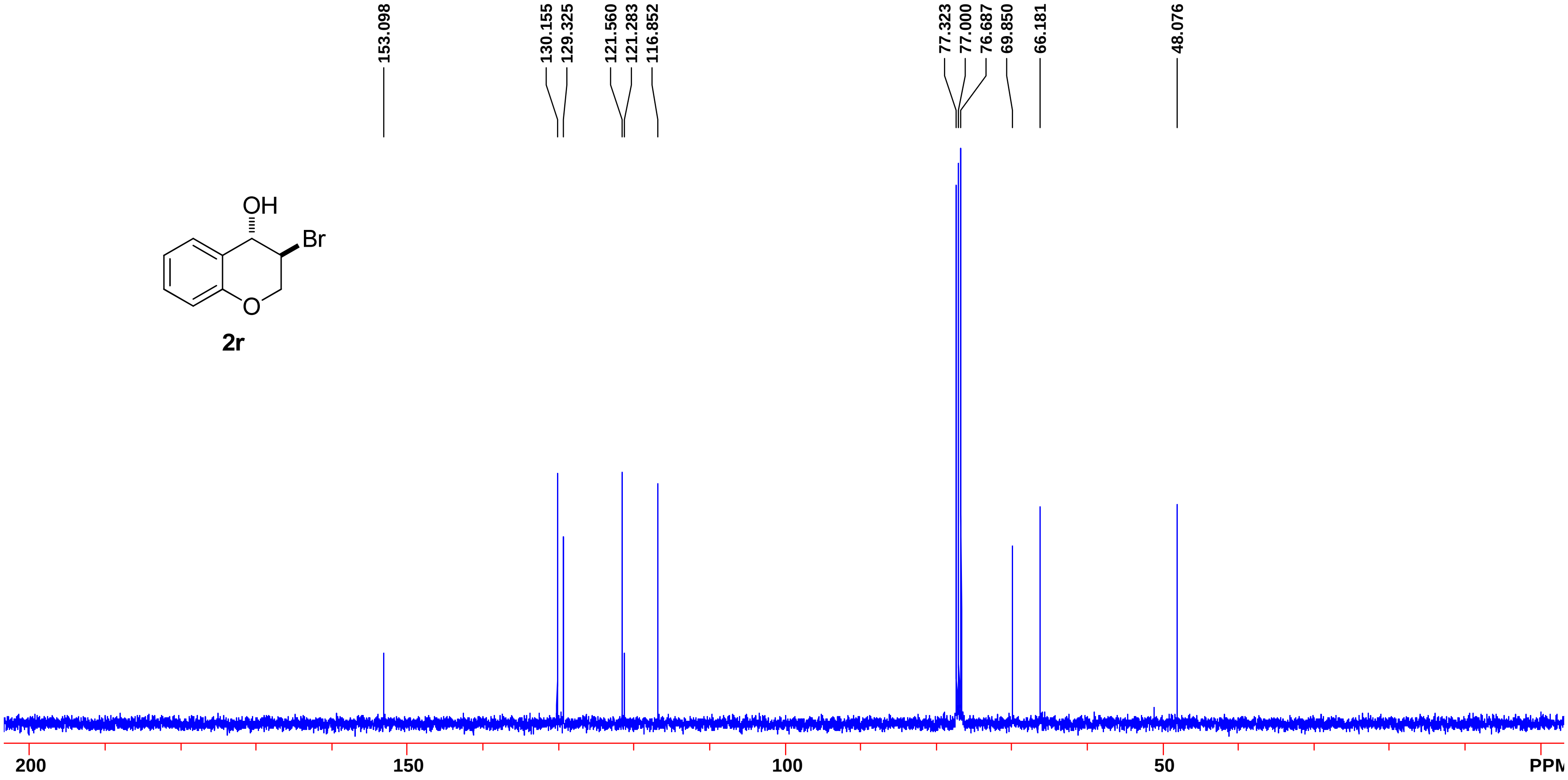

2q
7.254
7.249
7.244
7.235
7.230
7.222
7.213
7.208
7.194
7.189
7.107
7.092
7.086
4.967
4.947
4.365
4.347
4.340
2.938
2.929
2.912
2.903
2.894
2.793
2.784
2.769
2.759
2.748
2.733
2.724
2.685
2.513
2.500
2.483
2.477
2.464
2.454
2.244
2.236
2.225
2.223
2.217
2.215
2.205
2.197
2.189
2.187
2.181
2.178
2.168
2.160
1.998
1.990
1.980
1.977
1.970
1.968
1.962
1.954
1.945
1.940
1.935
HO
Br
0.93
2.07
1.00
1.00
0.96
1.01
1.11
0.89
1.00
1.06
1.06
0.00
1.07
8
6
4
2
0
PPM

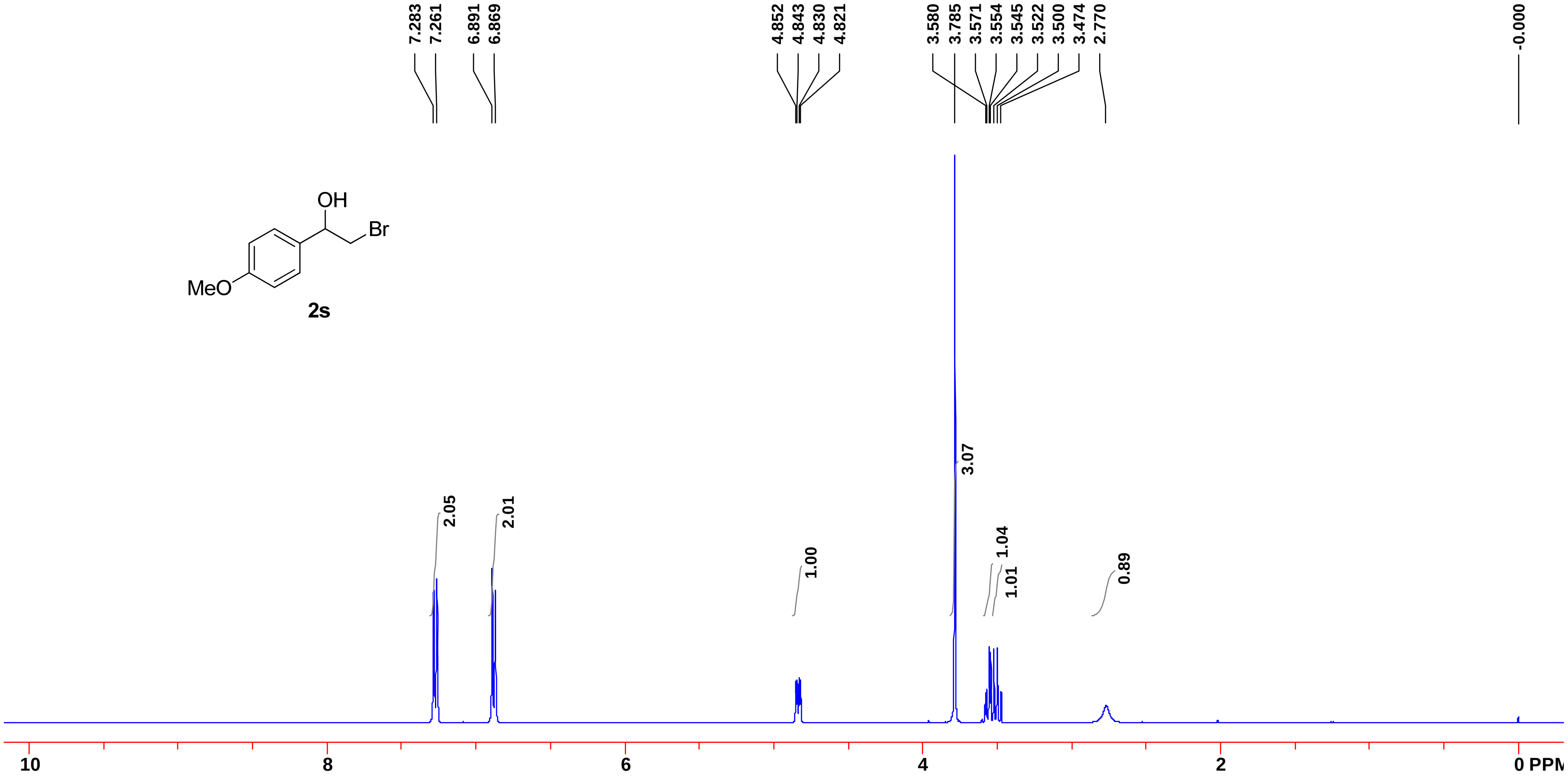

140.199
138.293
129.318
128.092
126.905
126.325
77.322
77.000
76.688
76.290
60.393
36.571
33.860
24.495
HO
Br
200
150
100
50
0 PPM

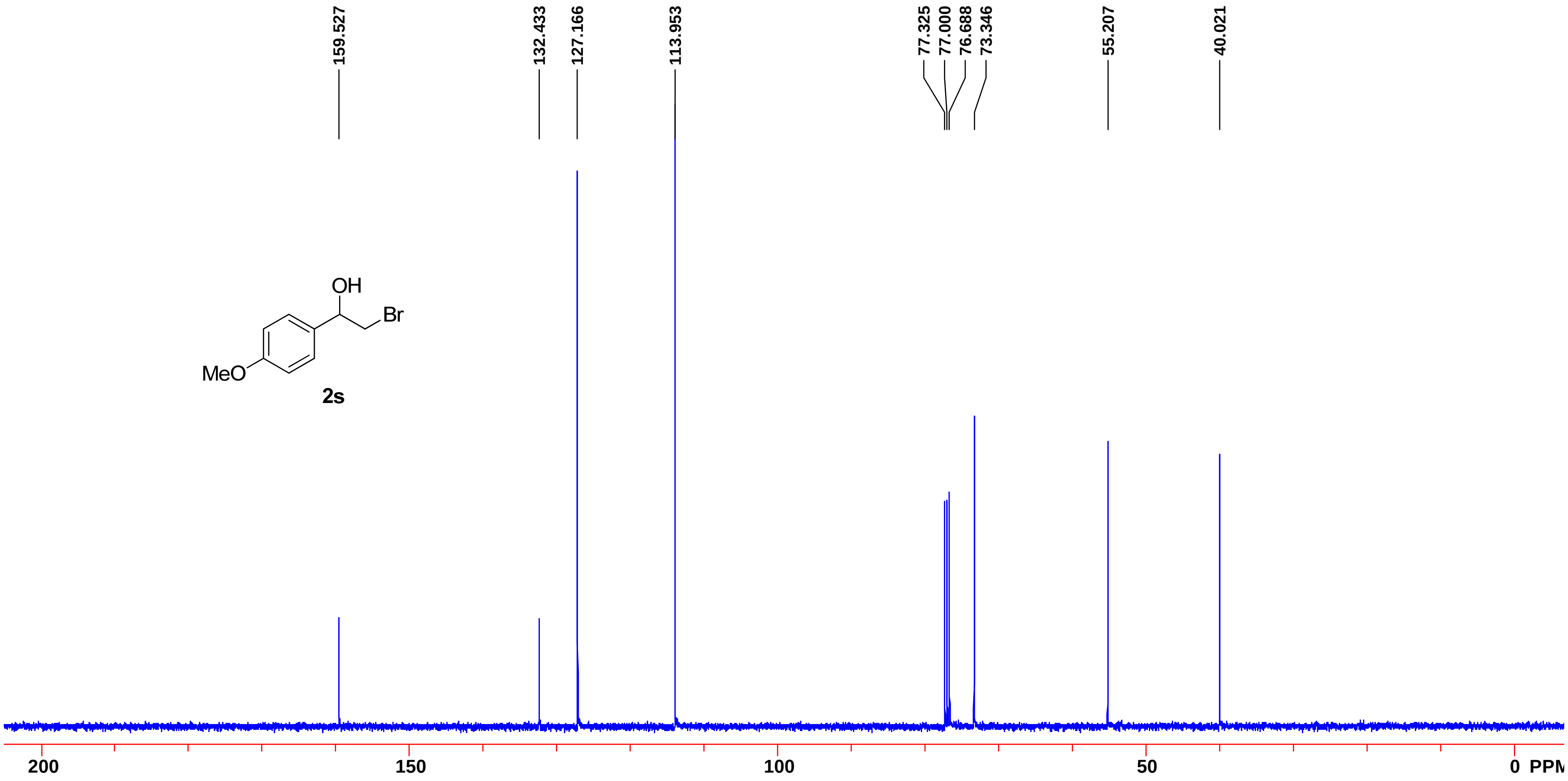
2q

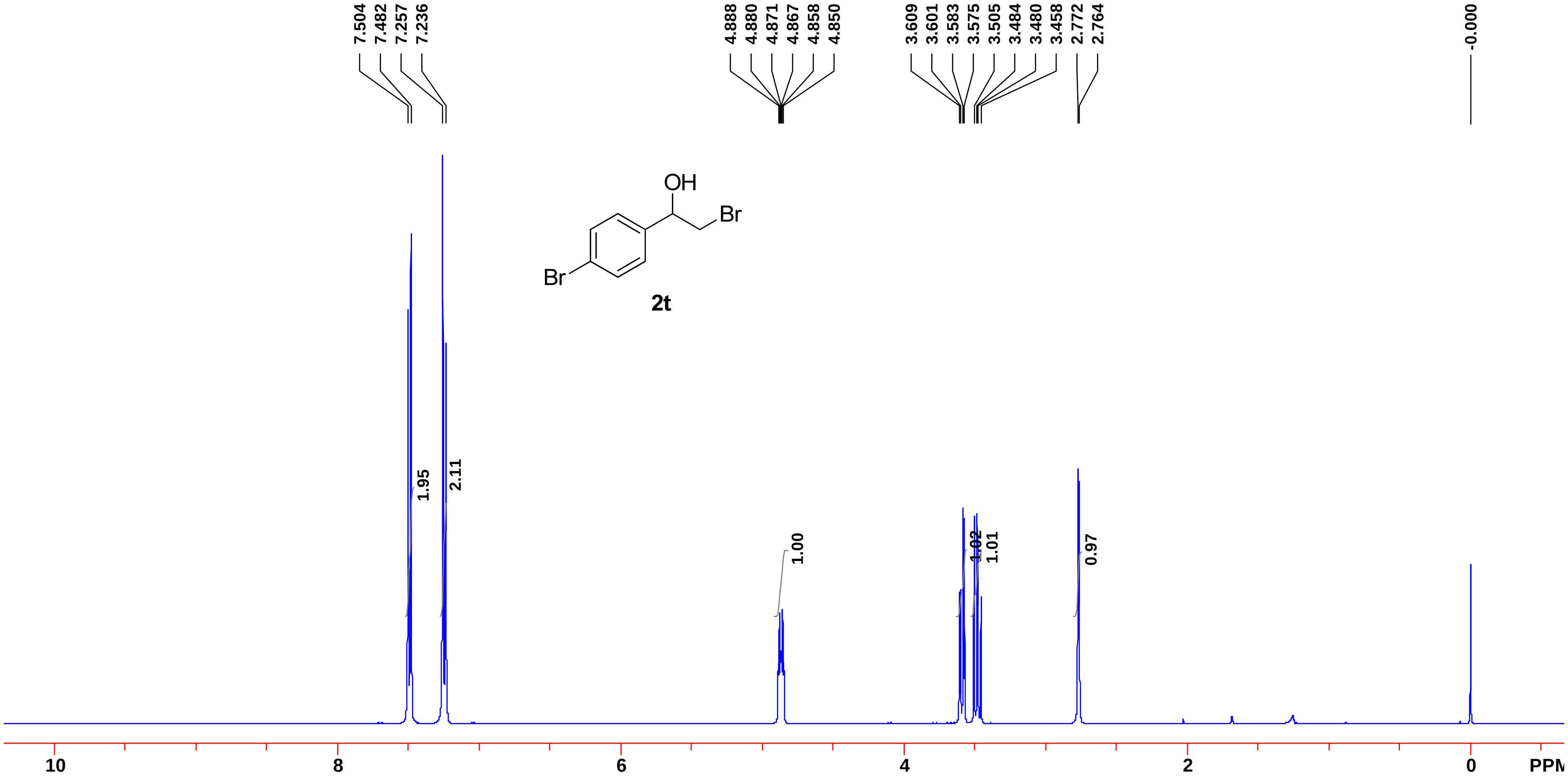

7.383
7.364
7.282
7.278
7.261
7.256
7.243
7.239
7.017
7.015
6.998
6.996
6.980
6.977
6.902
6.901
6.881
6.880
4.904
4.892
4.881
4.519
4.506
4.498
4.491
4.489
4.483
4.469
4.324
4.309
4.296
4.291
4.286
4.270
2.523
2.511
-0.000
OH
Br
O
1.02
1.21
1.03
1.00
1.00
1.04
2.03
0.98
10
8
6
4
2
0
PPM

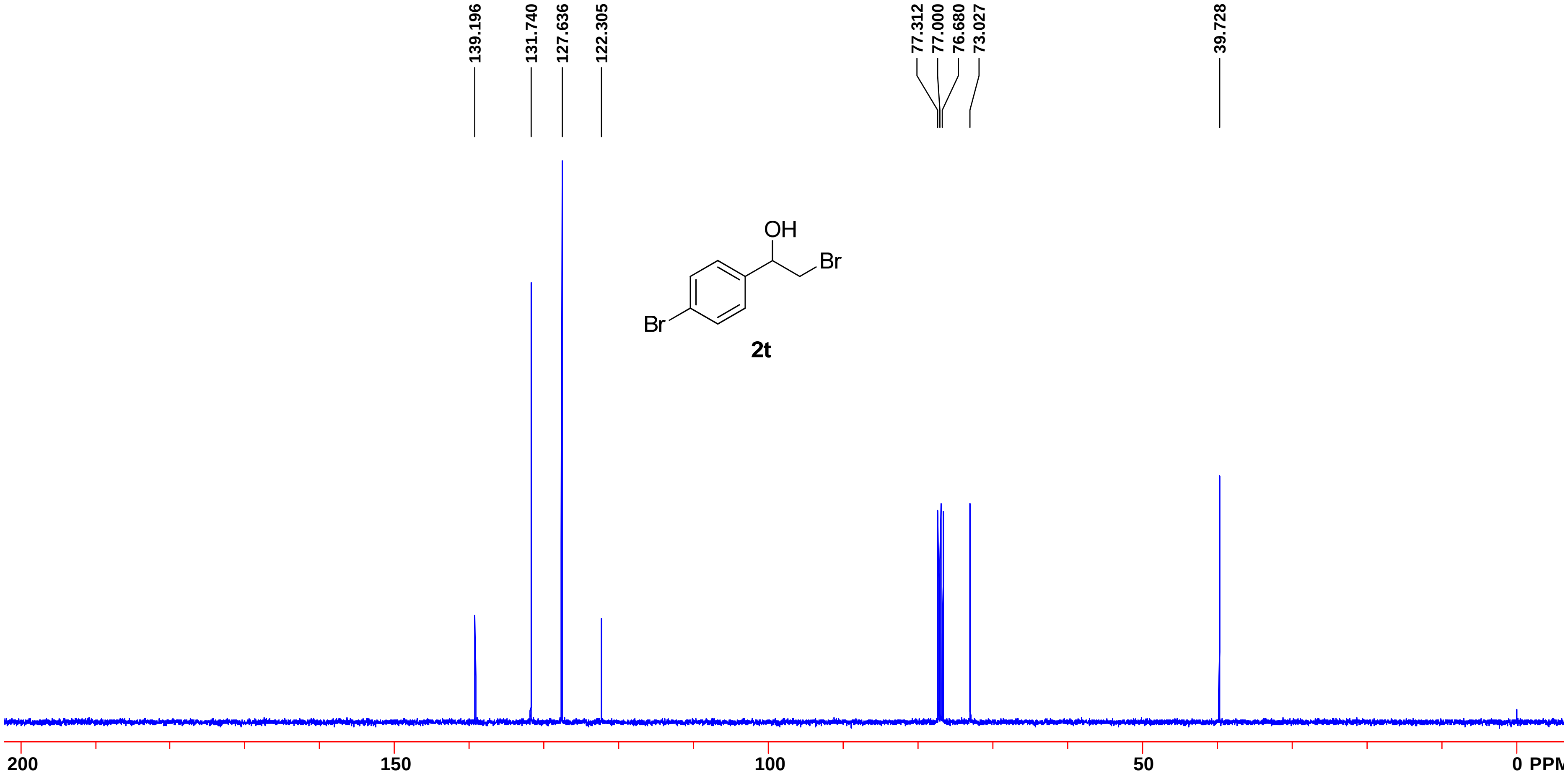
2r


153.098
130.155
129.325
121.560
121.283
116.852
77.323
77.000
76.687
69.850
66.181
48.076
OH
Br
O
2r
200
150
100
50
PPM


7.283
7.261
6.891
6.869
4.852
4.843
4.830
4.821
3.580
3.785
3.571
3.554
3.545
3.522
3.500
3.474
2.770
-0.000
OH
Br
MeO
2s
2.05
2.01
1.00
3.07
1.04
1.01
0.89
10
8
6
4
2
0 PPM

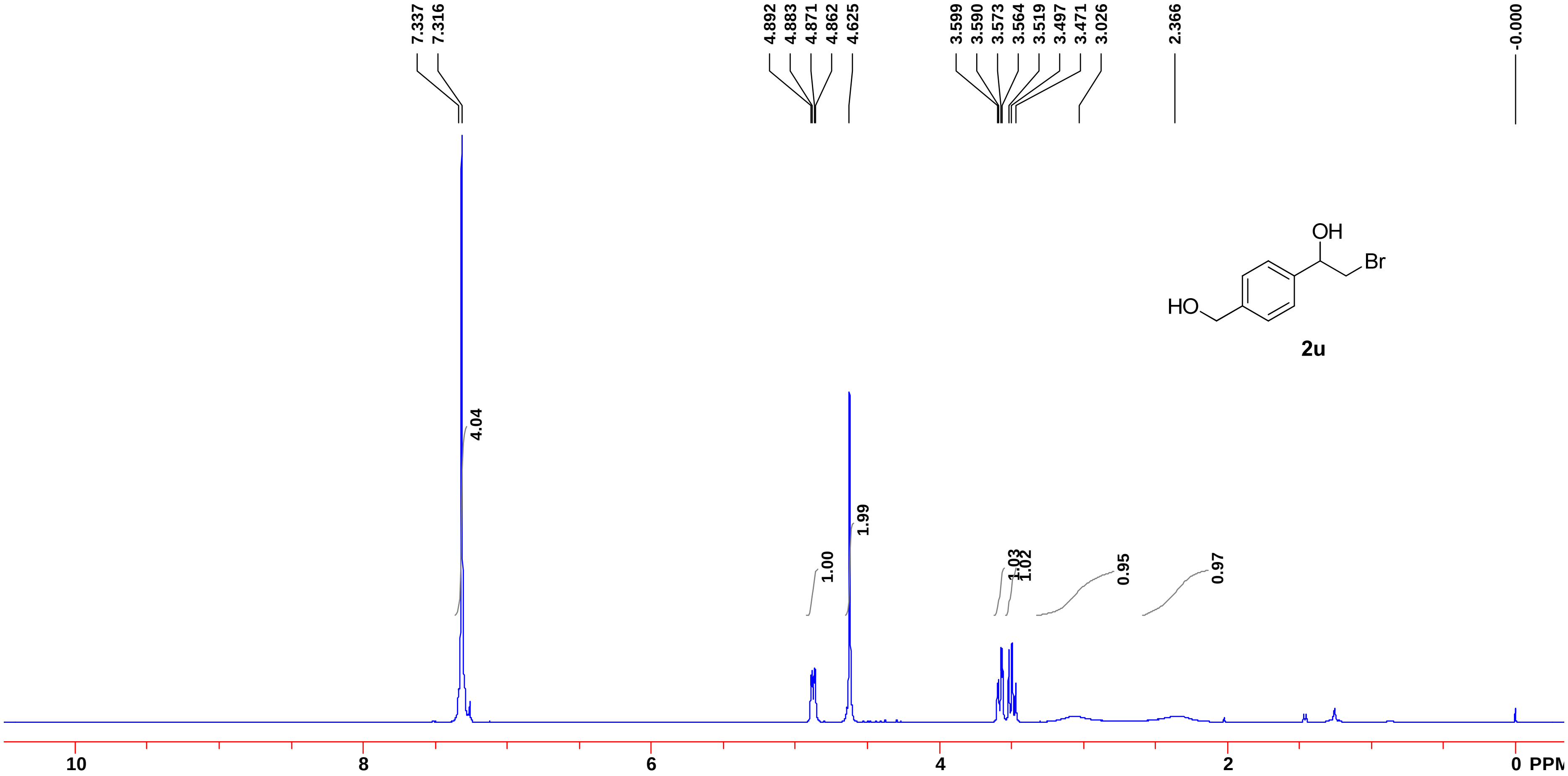

159.527
132.433
127.166
113.953
77.325
77.000
76.688
73.346
55.207
40.021
OH
Br
MeO
2s
200
150
100
50
0 PPM


7.504
7.482
7.257
7.236
4.888
4.880
4.871
4.867
4.858
4.850
3.609
3.601
3.583
3.575
3.505
3.484
3.480
3.458
2.772
2.764
-0.000
OH
Br
Br
2t
1.95
2.11
1.00
1.02
1.01
0.97
10
8
6
4
2
0
PPM

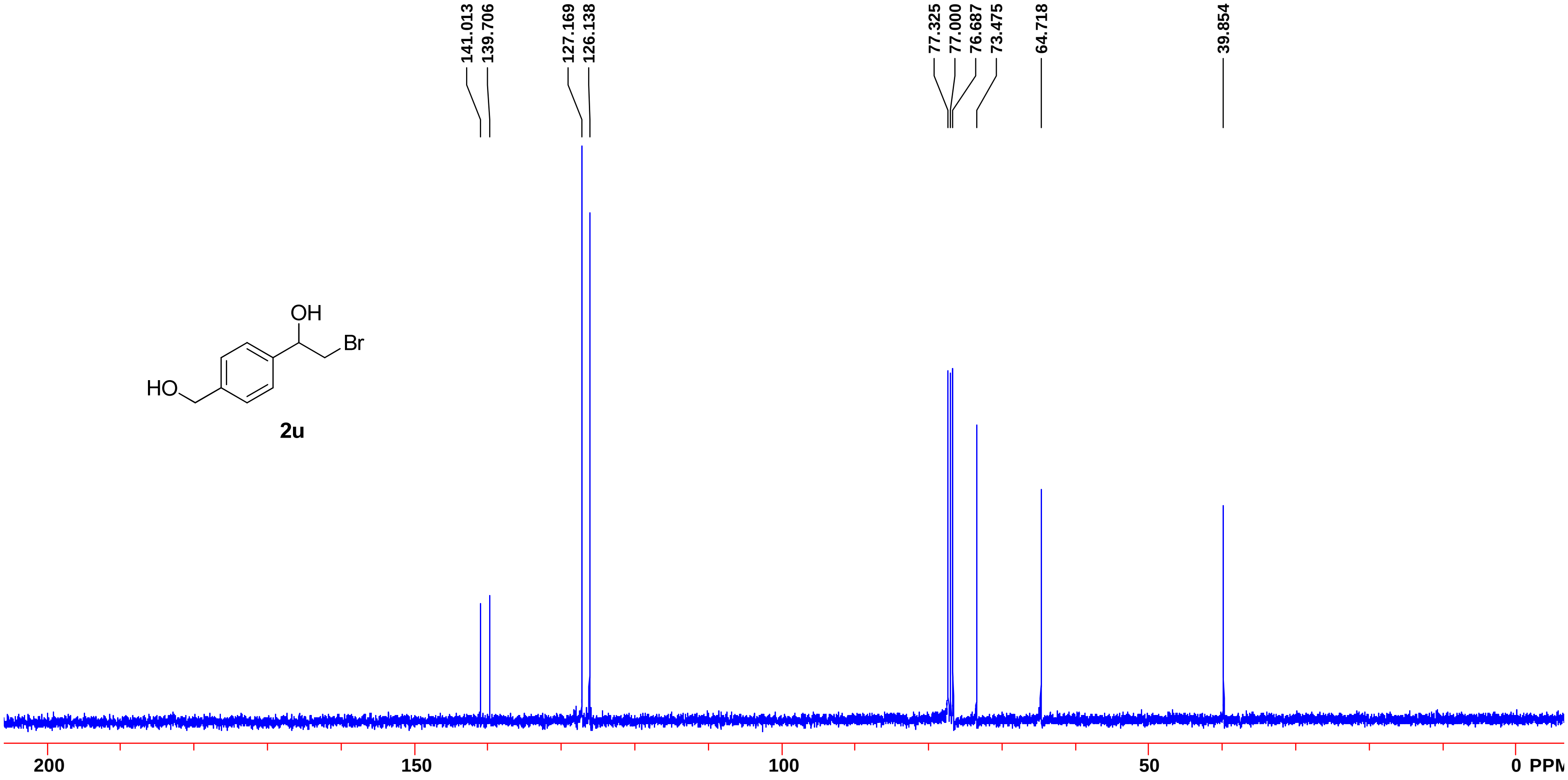


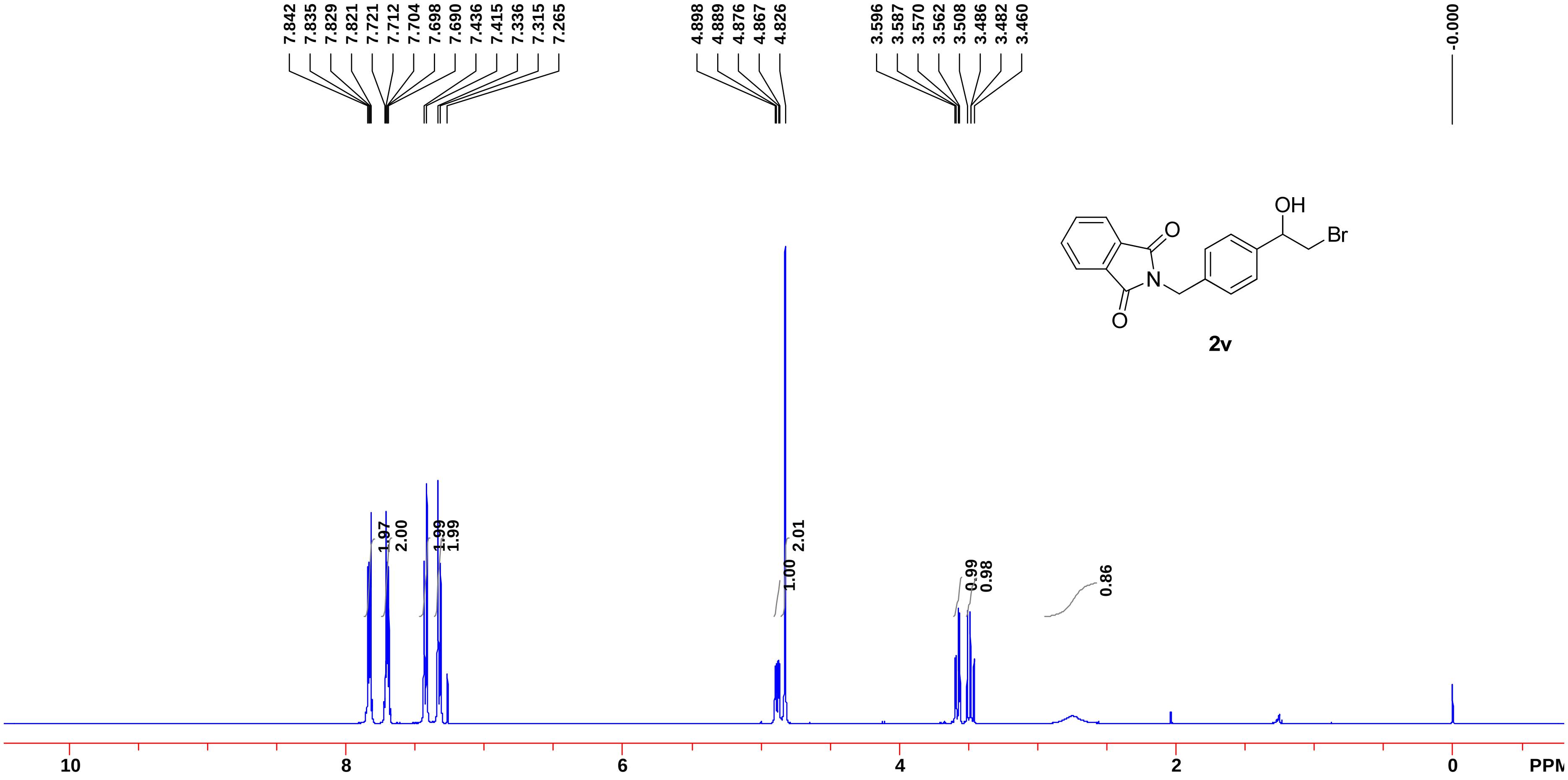
2t

139.196
131.740
127.636
122.305
77.312
77.000
76.680
73.027
39.728
OH
Br
Br
200
150
100
50
0 PPM

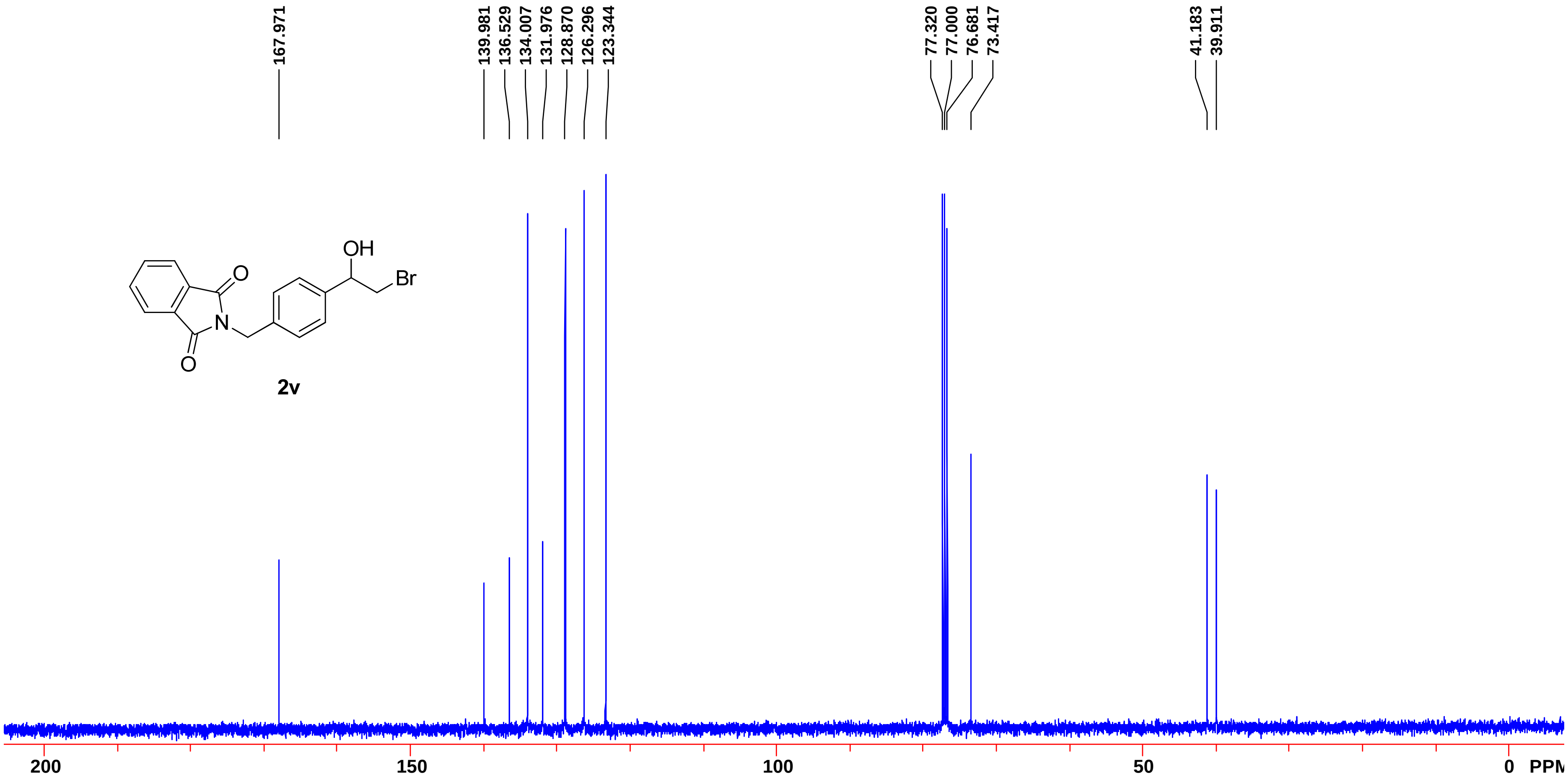

7.337
7.316
4.892
4.883
4.871
4.862
4.625
3.599
3.590
3.573
3.564
3.519
3.497
3.471
3.026
2.366
-0.000
4.04
1.99
1.00
1.03
1.02
0.95
0.97
OH
Br
HO
10
8
6
4
2
0 PPM

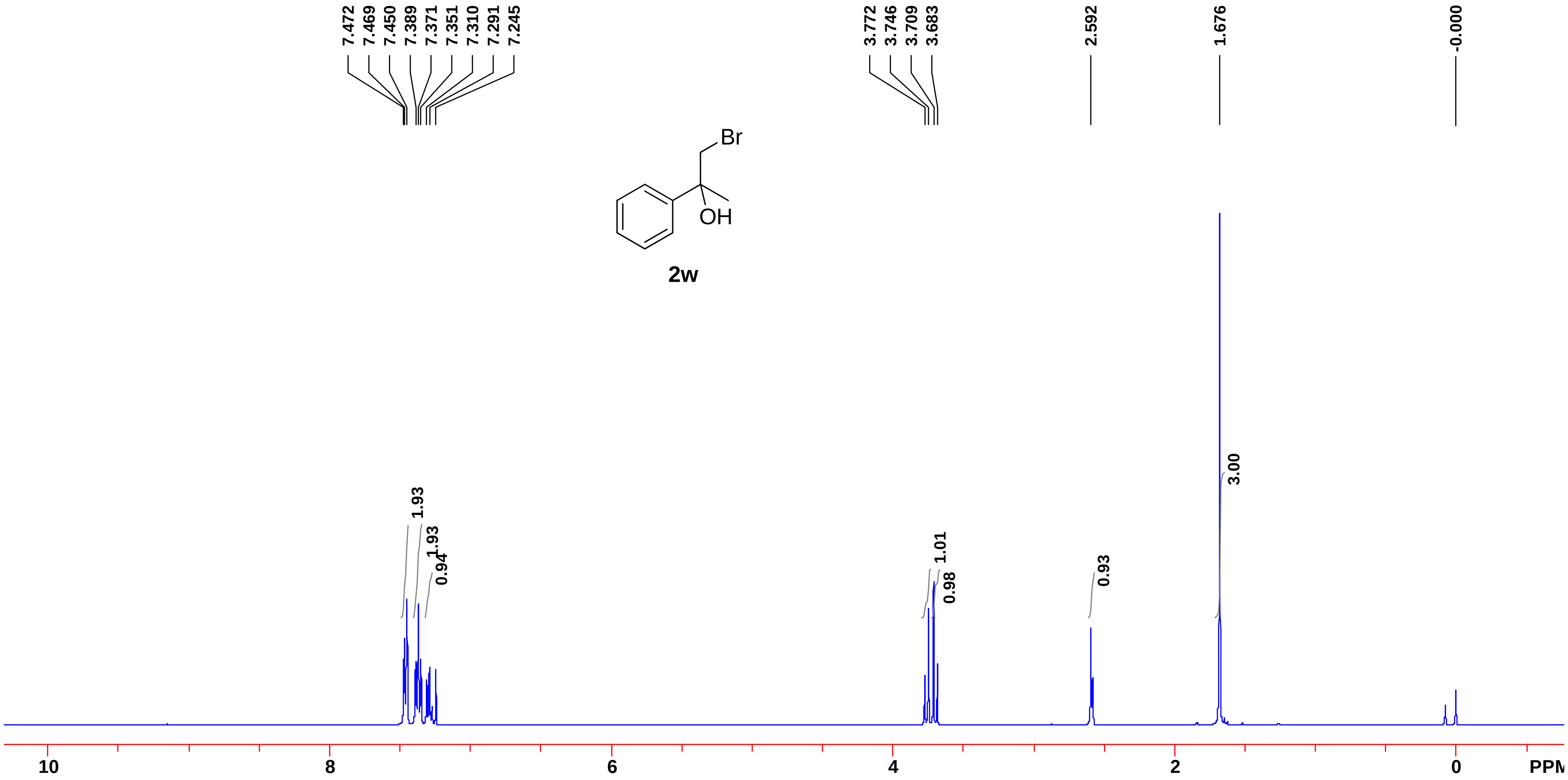
2u

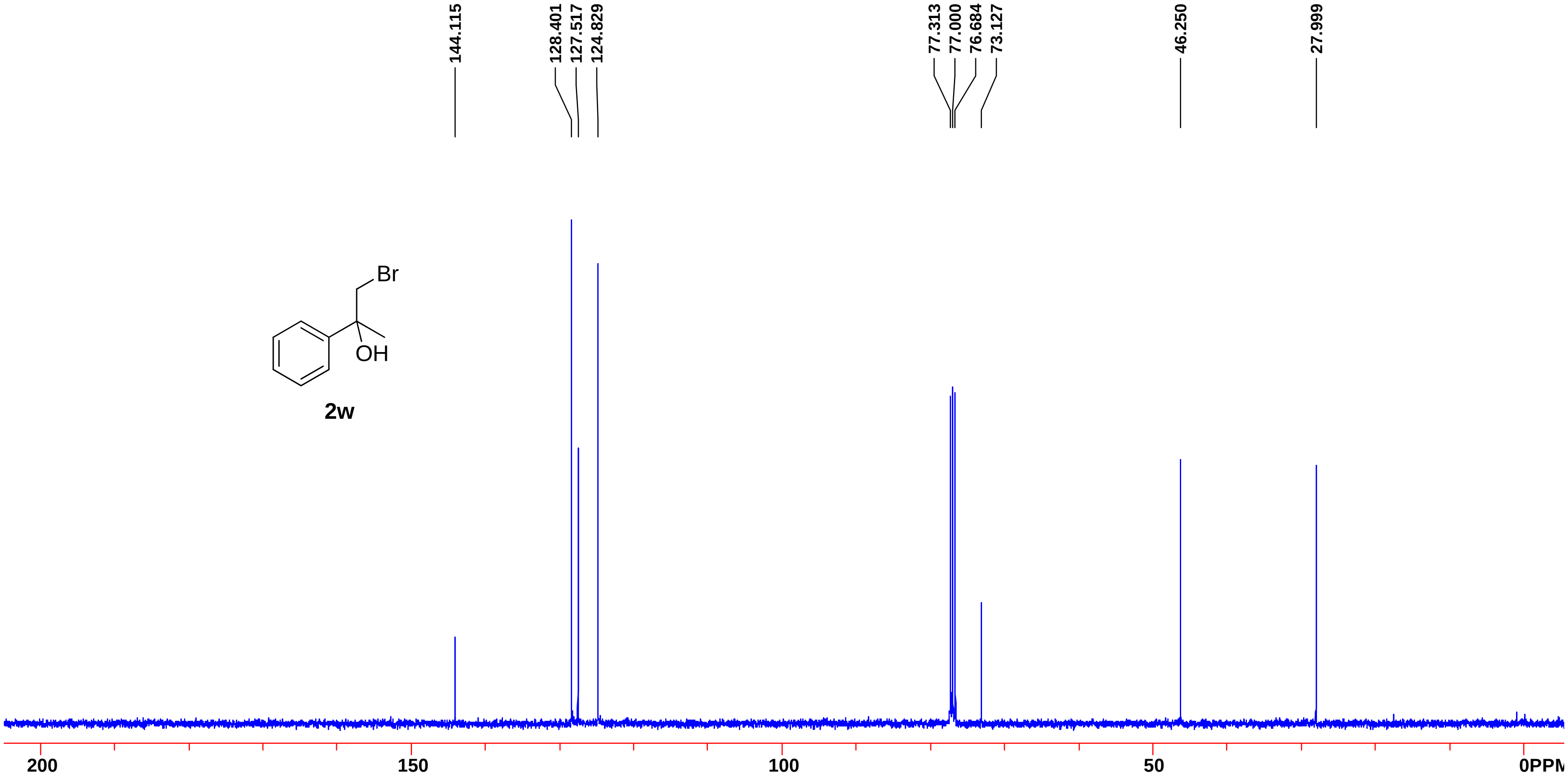

141.013
139.706
127.169
126.138
77.325
77.000
76.687
73.475
64.718
39.854
OH
Br
HO
2u
200
150
100
50
0 PPM


7.842
7.835
7.829
7.821
7.721
7.712
7.704
7.698
7.690
7.436
7.415
7.336
7.315
7.265
4.898
4.889
4.876
4.867
4.826
3.596
3.587
3.570
3.562
3.508
3.486
3.482
3.460
-0.000
1.97
2.00
1.99
1.99
1.00
2.01
0.99
0.98
0.86
OH
Br
O
N
O
10
8
6
4
2
0
PPM

2v

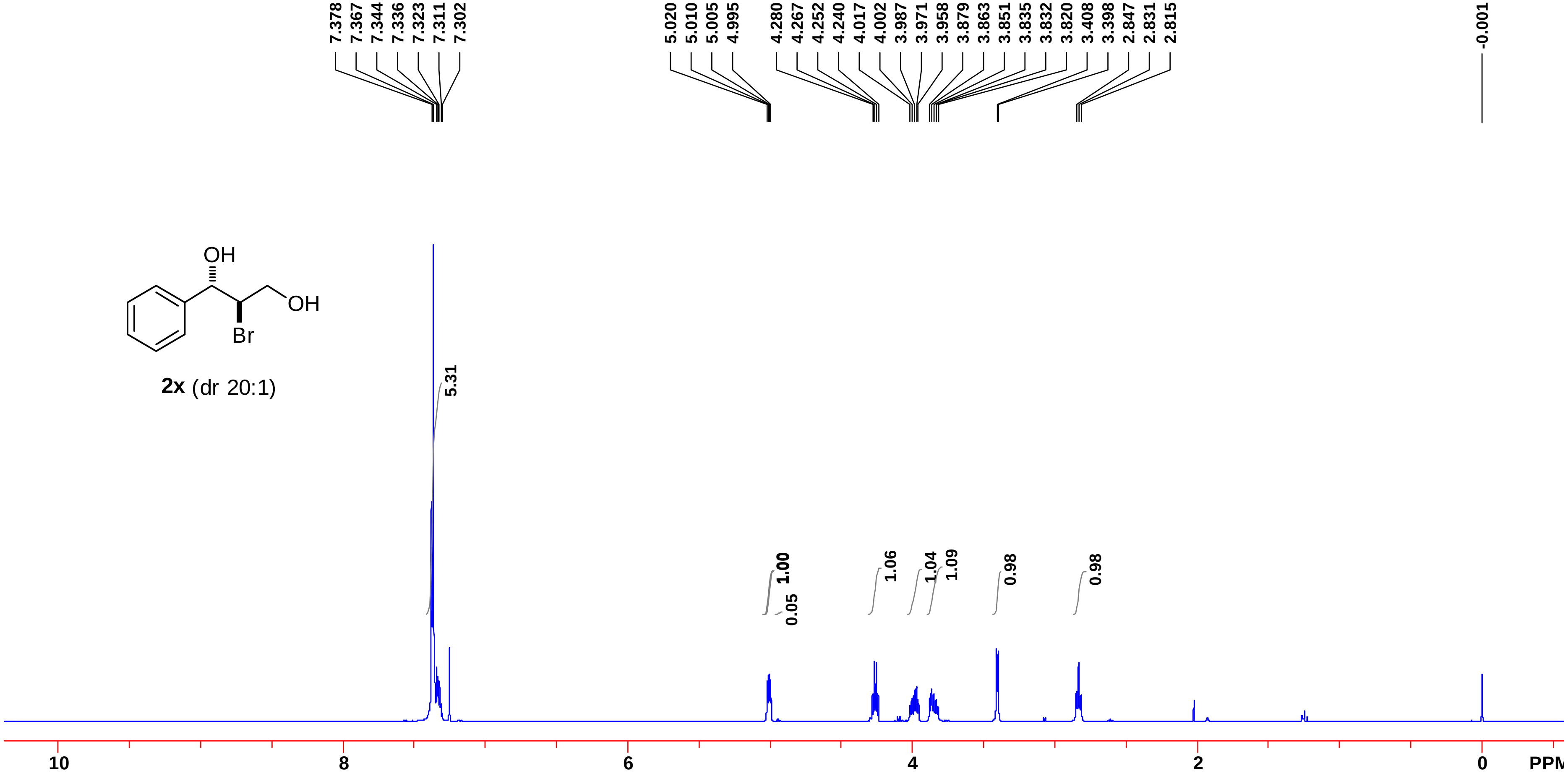

167.971
139.981
136.529
134.007
131.976
128.870
126.296
123.344
77.320
77.000
76.681
73.417
41.183
39.911
OH
Br
O
N
O
2v
200
150
100
50
0
PPM


2w
7.472
7.469
7.450
7.389
7.371
7.351
7.310
7.291
7.245
3.772
3.746
3.709
3.683
2.592
1.676
-0.000
Br
OH
1.93
1.93
0.94
1.01
0.98
0.93
3.00
10
8
6
4
2
0
PPM

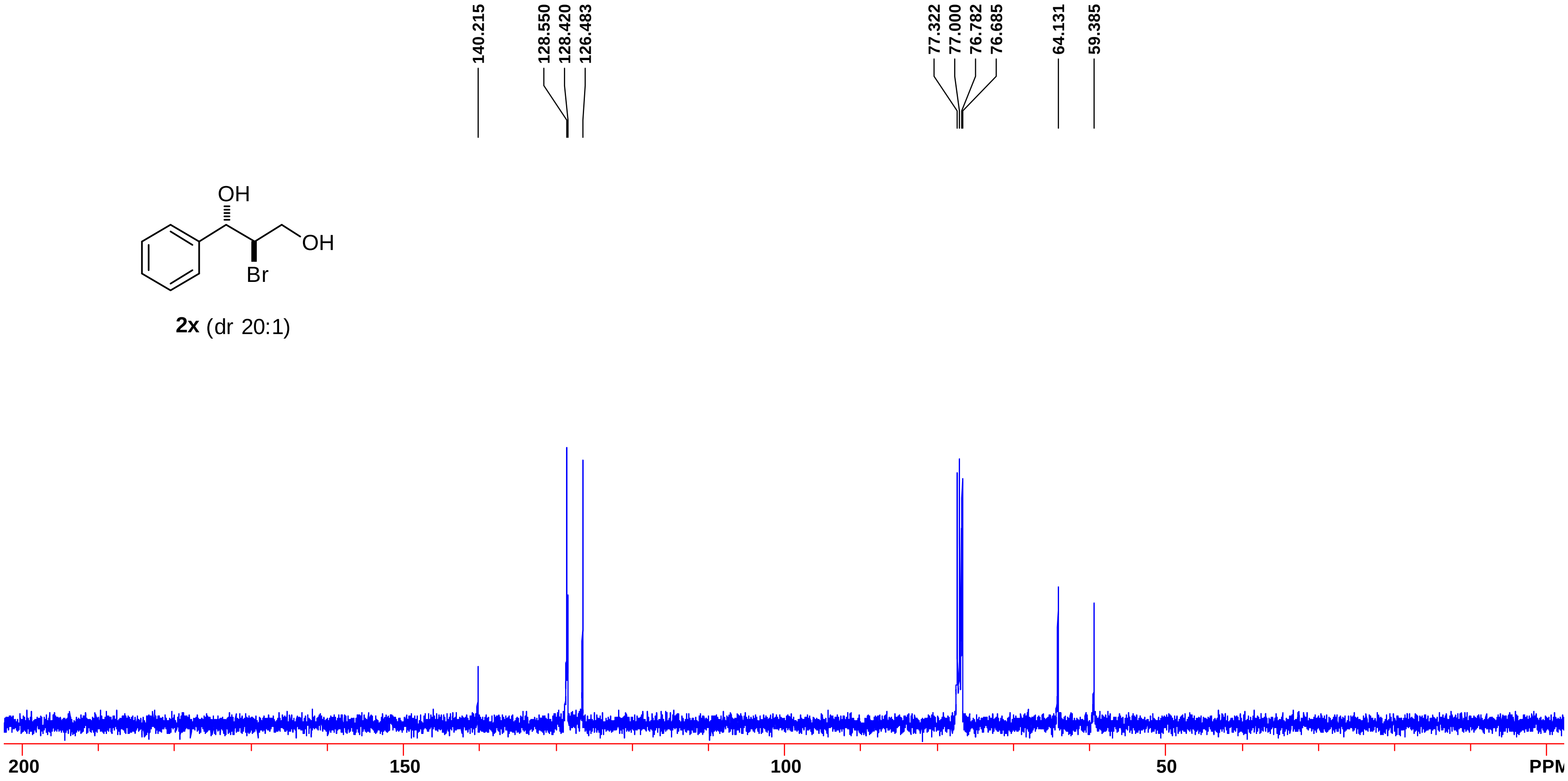


2w

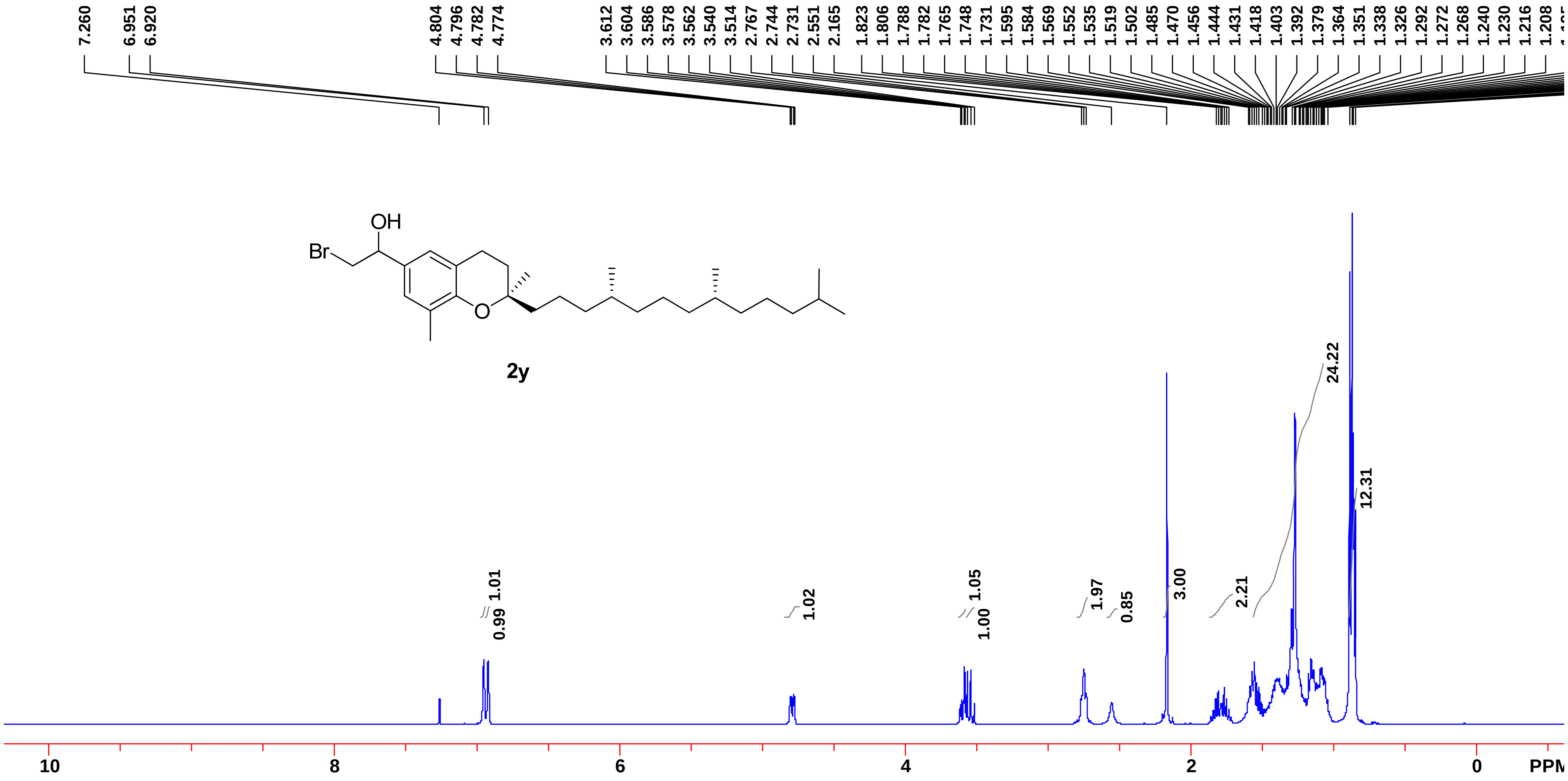
144.115
128.401
127.517
124.829
77.313
77.000
76.684
73.127
46.250
27.999
Br
OH
200
150
100
50
0PPM


7.378
7.367
7.344
7.336
7.323
7.311
7.302
5.020
5.010
5.005
4.995
4.280
4.267
4.252
4.240
4.017
4.002
3.987
3.971
3.958
3.879
3.863
3.851
3.835
3.832
3.820
3.408
3.398
2.847
2.831
2.815
-0.001
OH
OH
Br
5.31
1.00
0.05
1.06
1.04
1.09
0.98
0.98
10
8
6
4
2
0
PPM

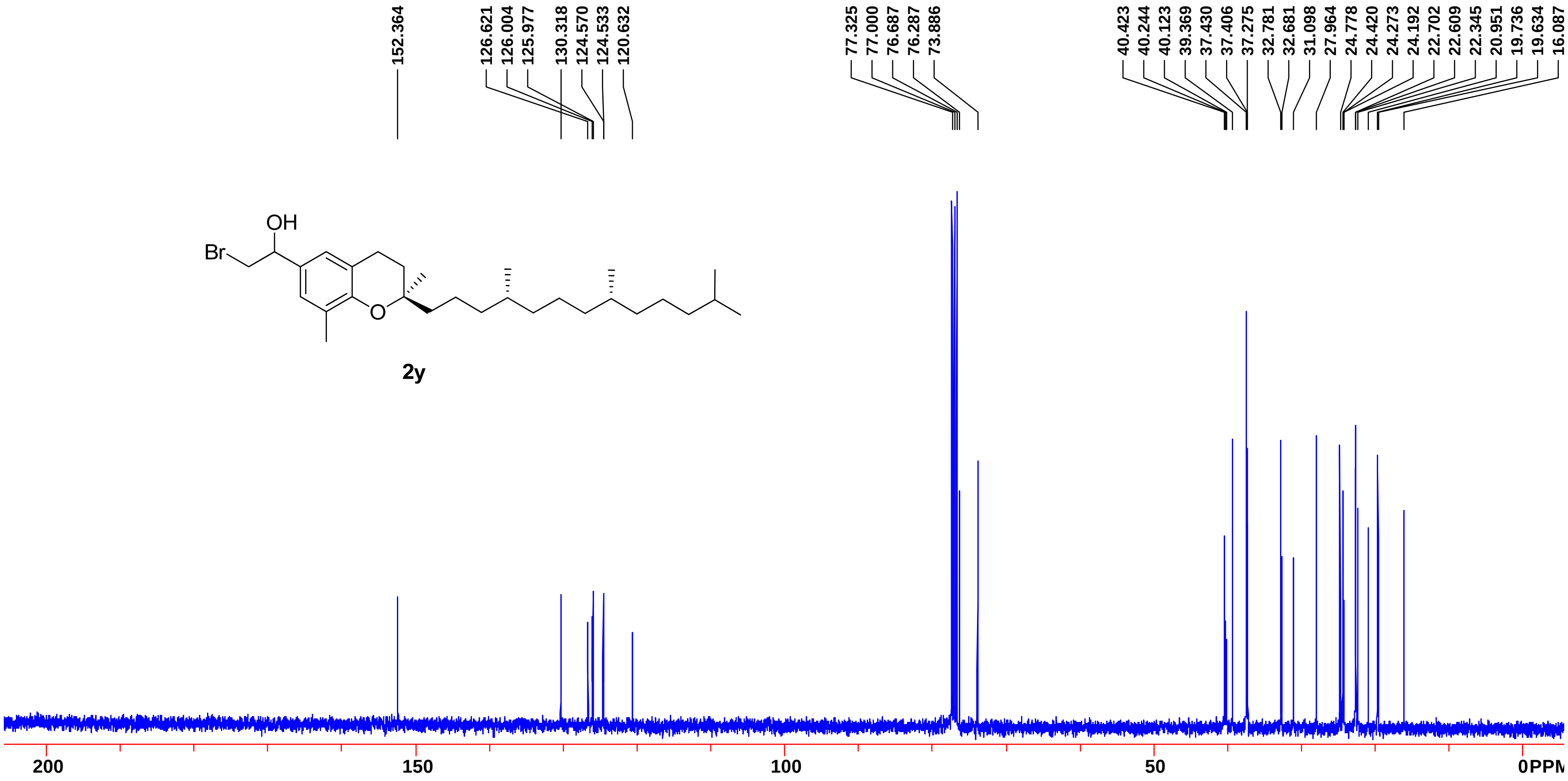
2x (dr 20:1)


2x (dr 20:1)

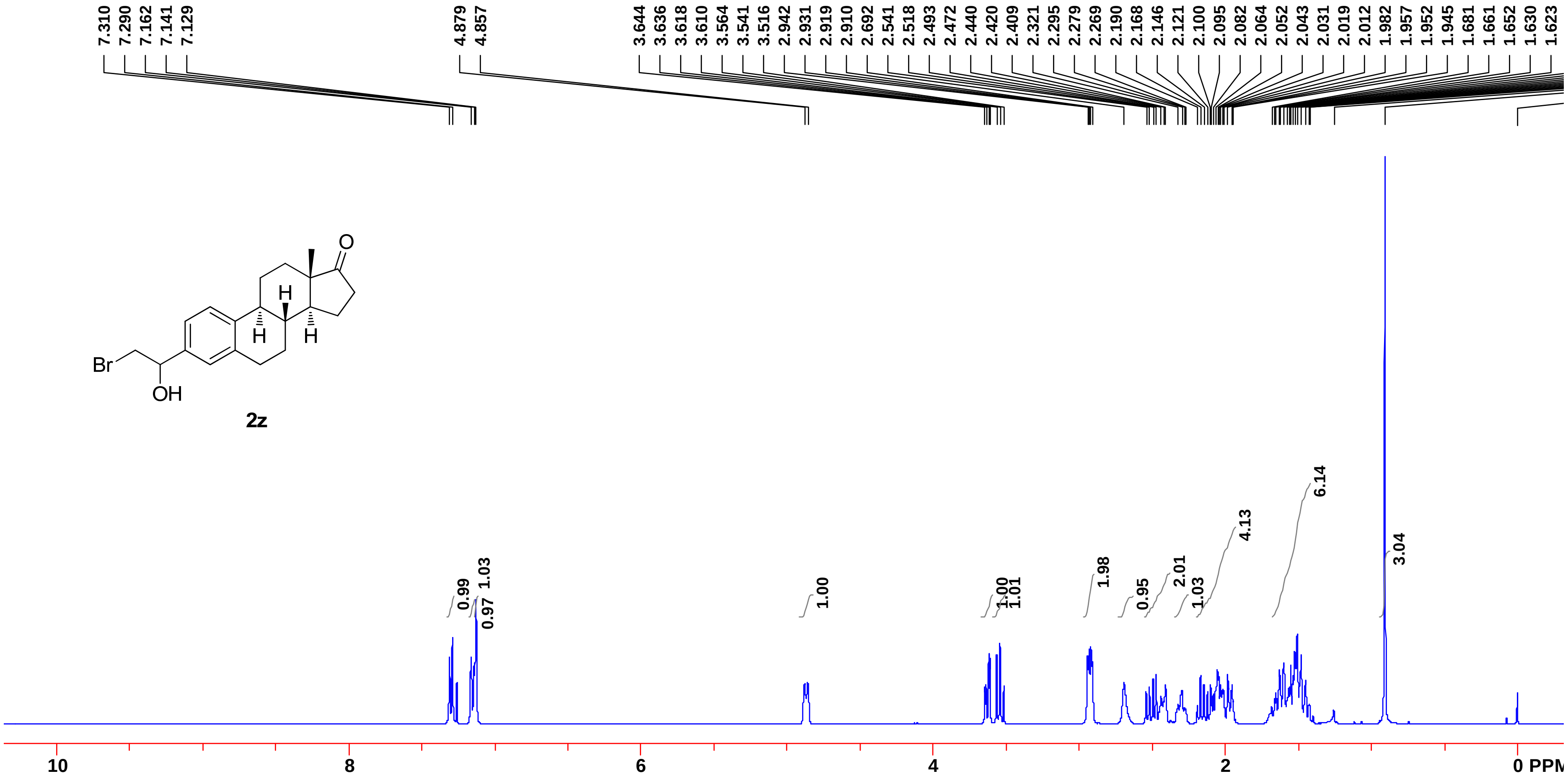
140.215
128.550
128.420
126.483
77.322
77.000
76.782
76.685
64.131
59.385
OH
OH
Br
200
150
100
50
PPM

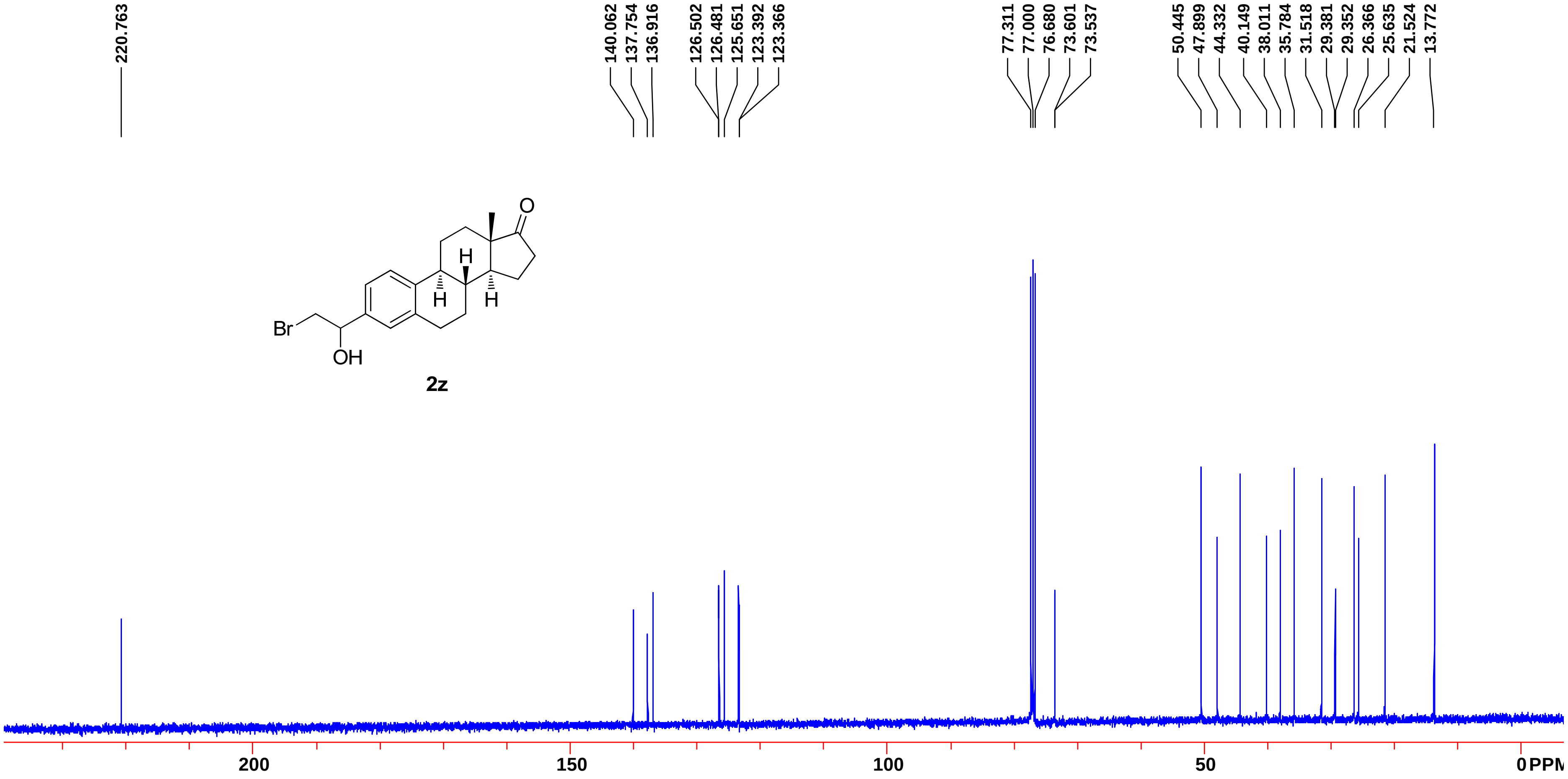
7.260
6.951
6.920
4.804
4.796
4.782
4.774
3.612
3.604
3.586
3.578
3.562
3.540
3.514
2.767
2.744
2.731
2.551
2.165
1.823
1.806
1.788
1.782
1.765
1.748
1.731
1.595
1.584
1.569
1.552
1.535
1.519
1.502
1.485
1.470
1.456
1.444
1.431
1.418
1.403
1.392
1.379
1.364
1.351
1.338
1.326
1.292
1.272
1.268
1.240
1.230
1.216
1.208
OH
Br
O
0.99
1.01
1.02
1.05
1.00
1.97
0.85
3.00
2.21
24.22
12.31
10
8
6
4
2
0
PP

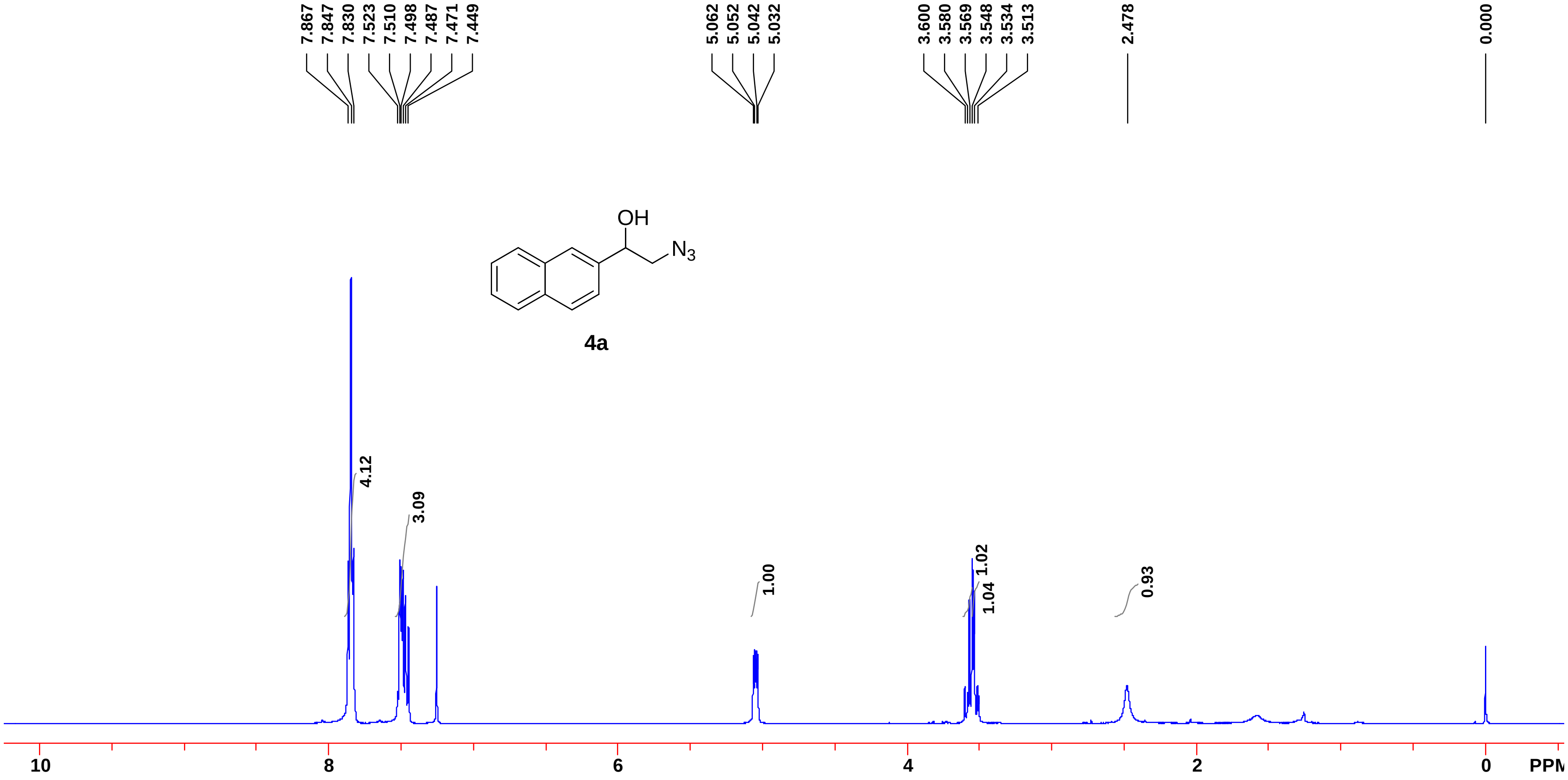
2y

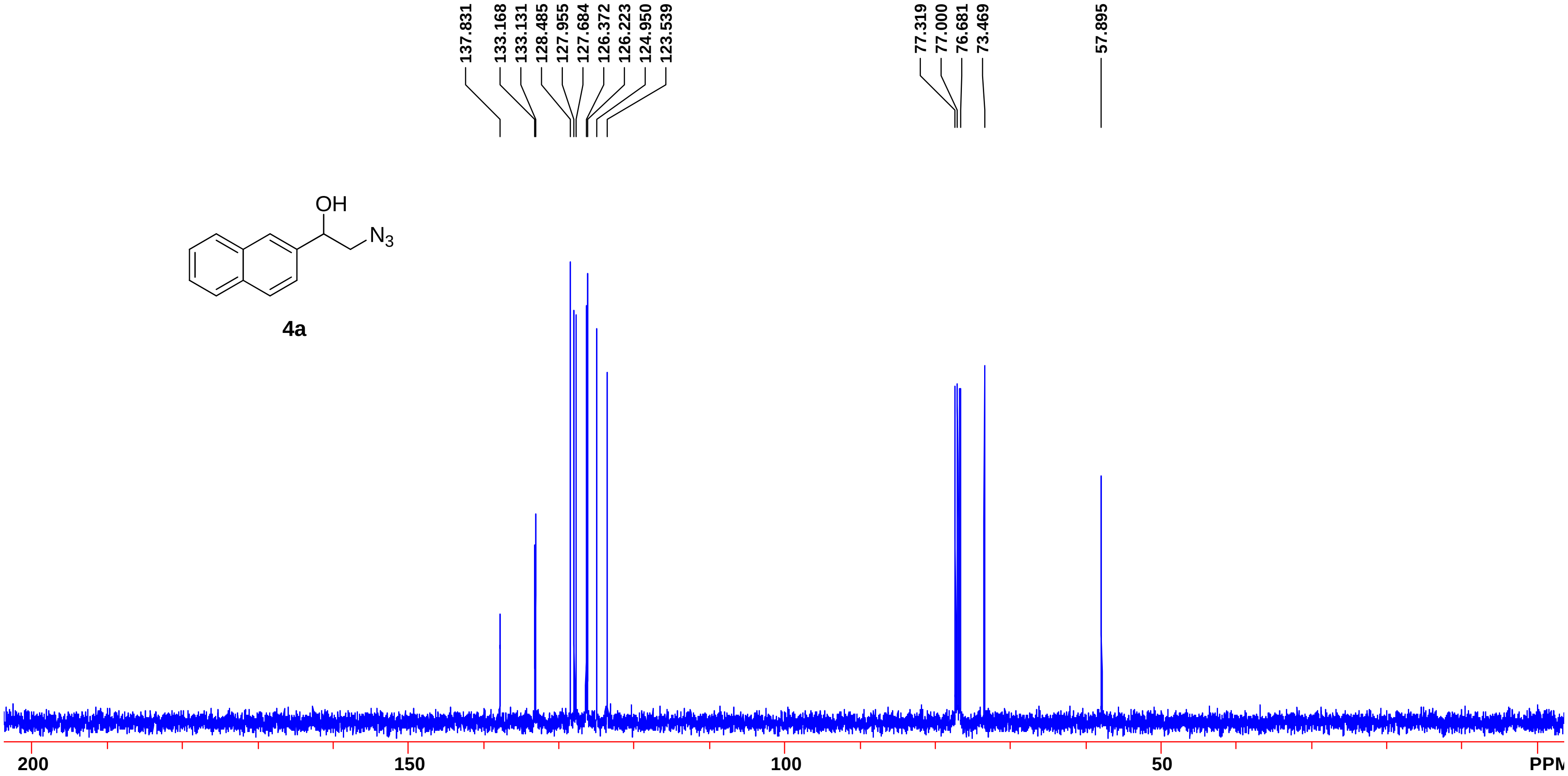

152.364
126.621
126.004
125.977
130.318
124.570
124.533
120.632
77.325
77.000
76.687
76.287
73.886
40.423
40.244
40.123
39.369
37.430
37.406
37.275
32.781
32.681
31.098
27.964
24.778
24.420
24.273
24.192
22.702
22.609
22.345
20.951
19.736
19.634
16.087
OH
Br
O
200
150
100
50
0PPM

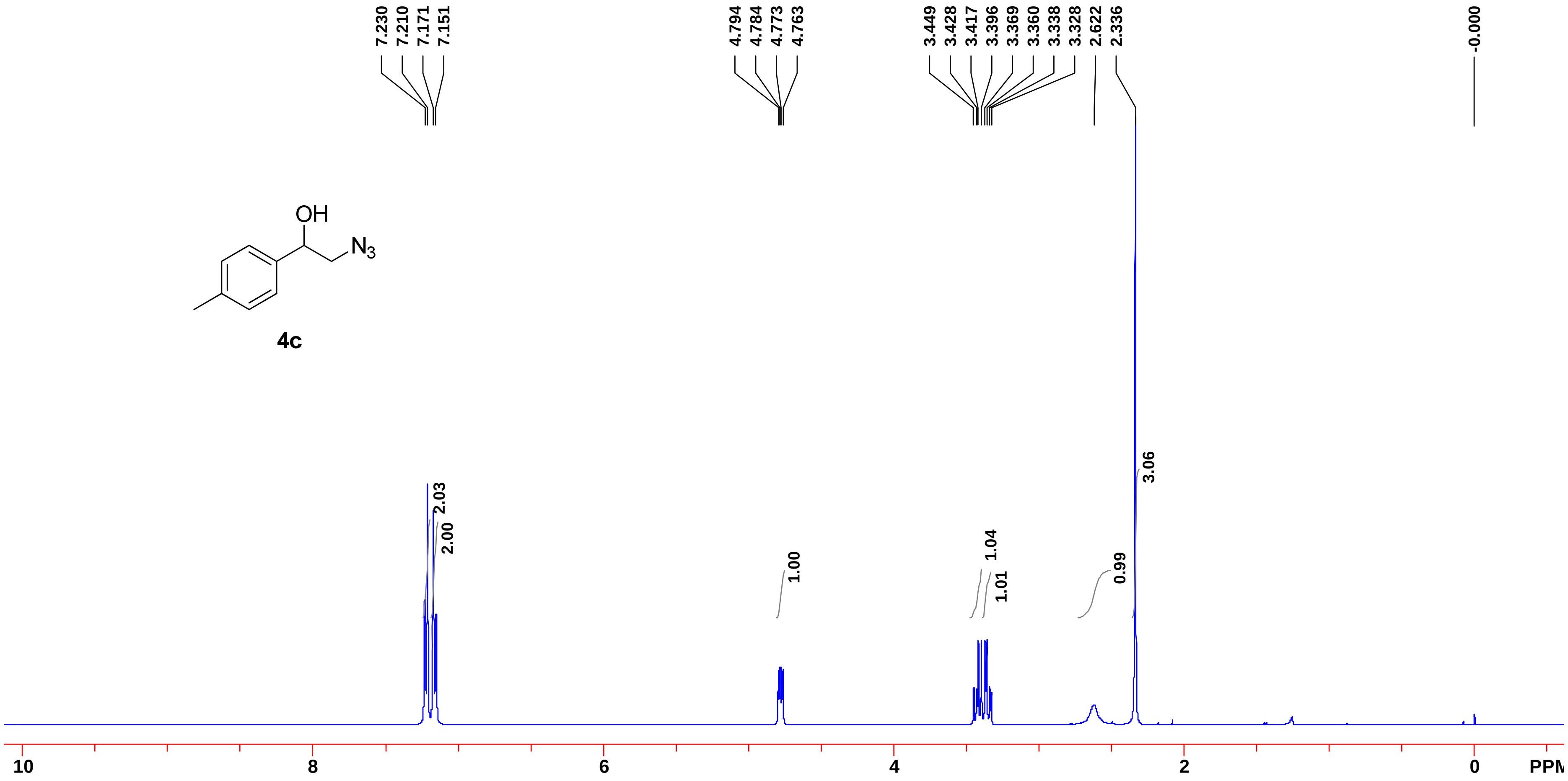
2y


7.310
7.290
7.162
7.141
7.129
4.879
4.857
3.644
3.636
3.618
3.610
3.564
3.541
3.516
2.942
2.931
2.919
2.910
2.692
2.541
2.518
2.493
2.472
2.440
2.420
2.409
2.321
2.295
2.279
2.269
2.190
2.168
2.146
2.121
2.100
2.095
2.082
2.064
2.052
2.043
2.031
2.019
2.012
1.982
1.957
1.952
1.945
1.681
1.661
1.652
1.630
1.623
O
H
H
H
Br
OH
2z
0.99
0.97
1.03
1.00
1.00
1.01
1.98
0.95
2.01
1.03
4.13
6.14
3.04
10
8
6
4
2
0 PP

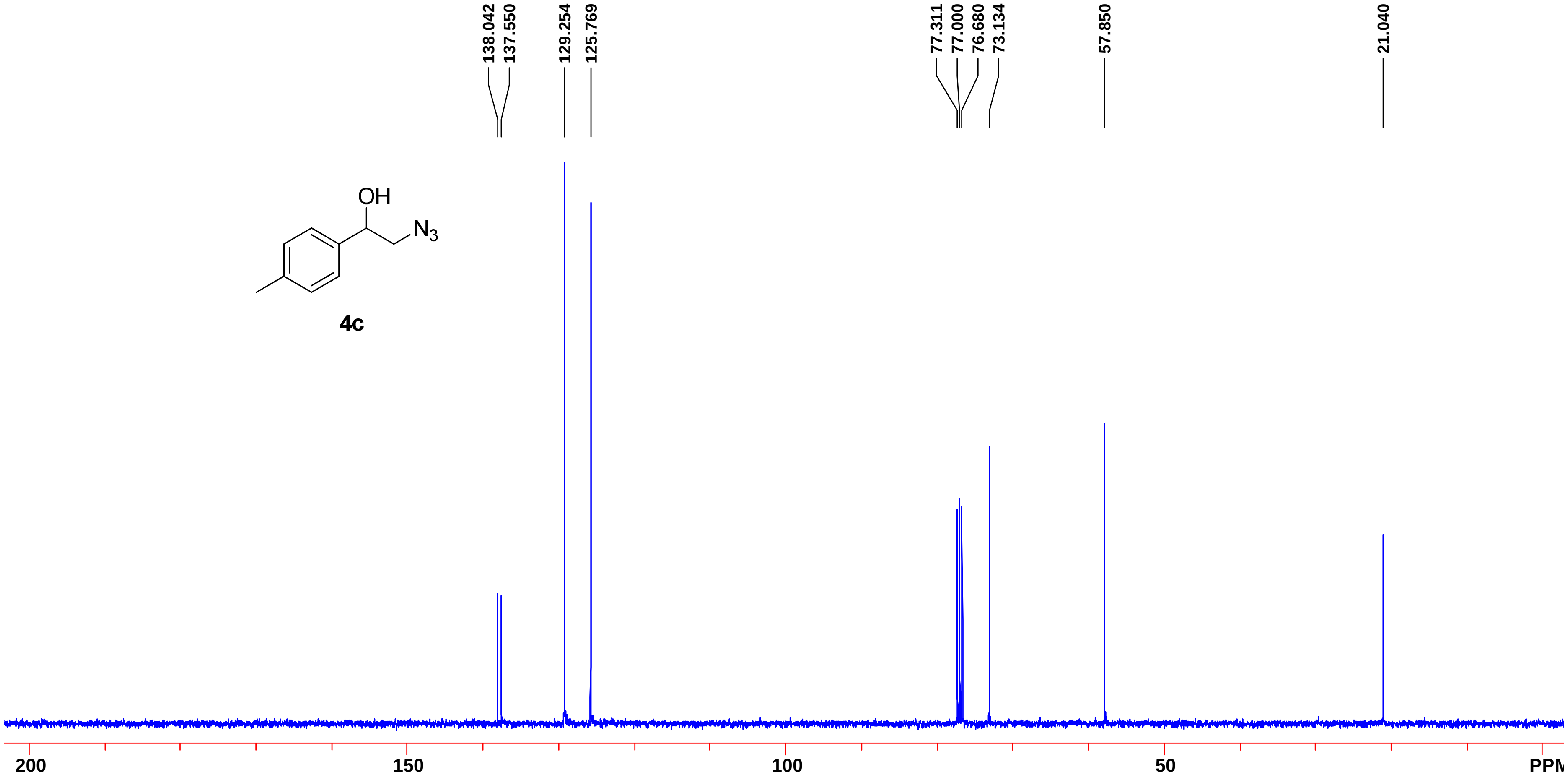

220.763
140.062
137.754
136.916
126.502
126.481
125.651
123.392
123.366
77.311
77.000
76.680
73.601
73.537
50.445
47.899
44.332
40.149
38.011
35.784
31.518
29.381
29.352
26.366
25.635
21.524
13.772
O
H
H
H
Br
OH
2z
200
150
100
50
0 PP

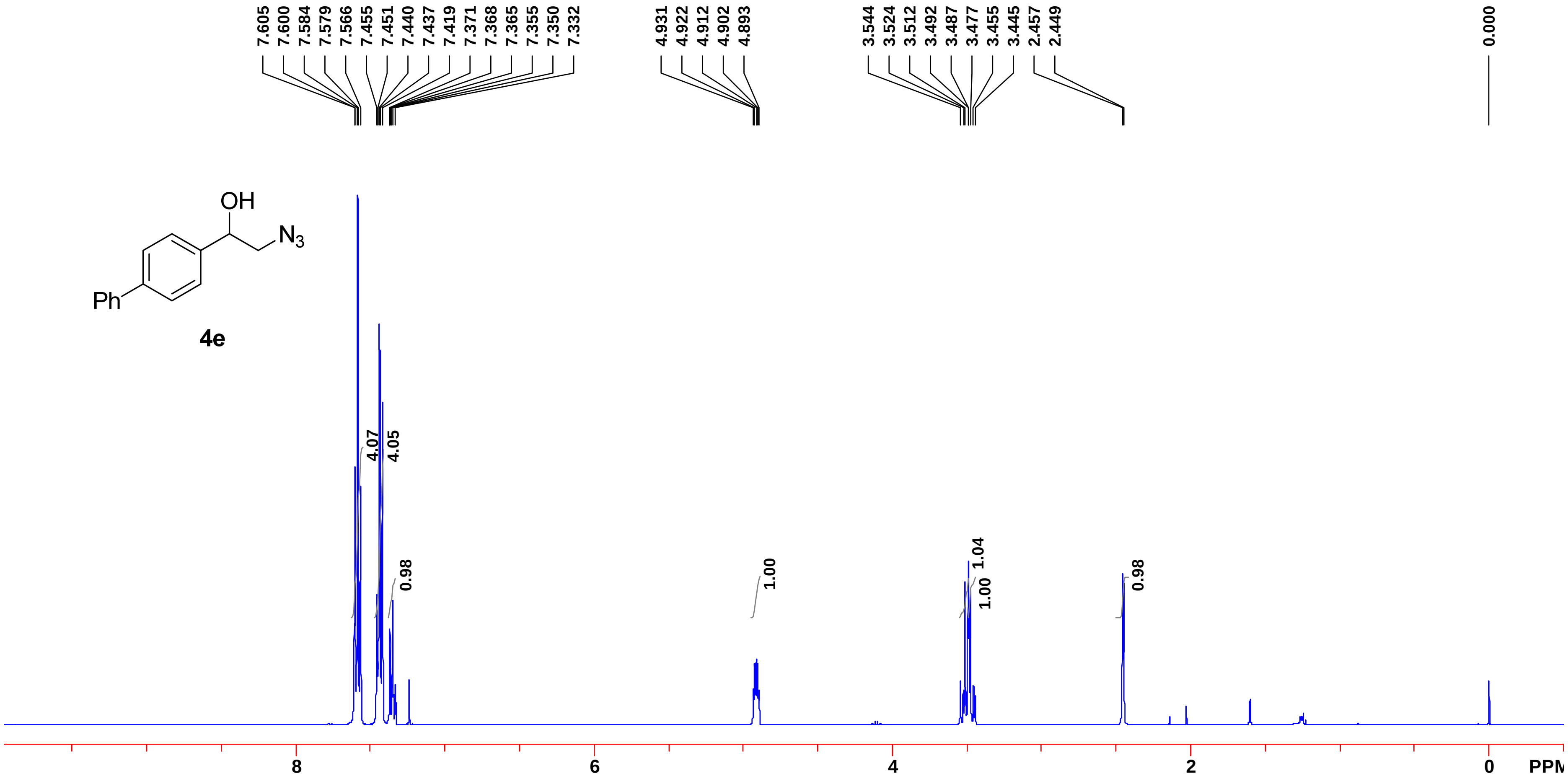

7.867
7.847
7.830
7.523
7.510
7.498
7.487
7.471
7.449
5.062
5.052
5.042
5.032
3.600
3.580
3.569
3.548
3.534
3.513
2.478
0.000
OH
N3
4a
4.12
3.09
1.00
1.02
1.04
0.93
10
8
6
4
2
0
PPM

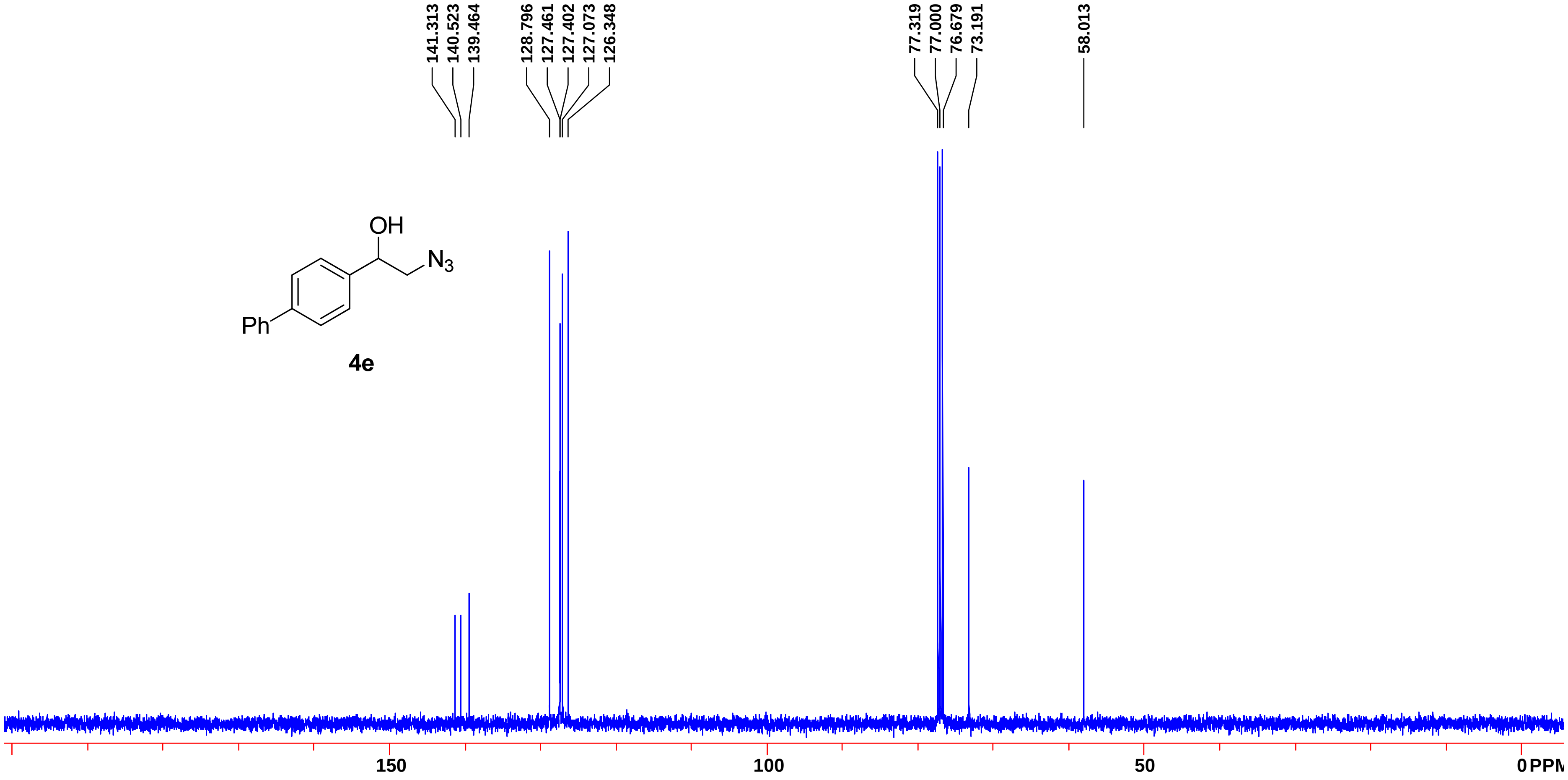

137.831
133.168
133.131
128.485
127.955
127.684
126.372
126.223
124.950
123.539
77.319
77.000
76.681
73.469
57.895
OH
N3
4a
200
150
100
50
PPM


7.230
7.210
7.171
7.151
4.794
4.784
4.773
4.763
3.449
3.428
3.417
3.396
3.369
3.360
3.338
3.328
2.622
2.336
-0.000
OH
N_3
2.03
2.00
1.00
1.04
1.01
0.99
3.06
10
8
6
4
2
0
PPM

4c

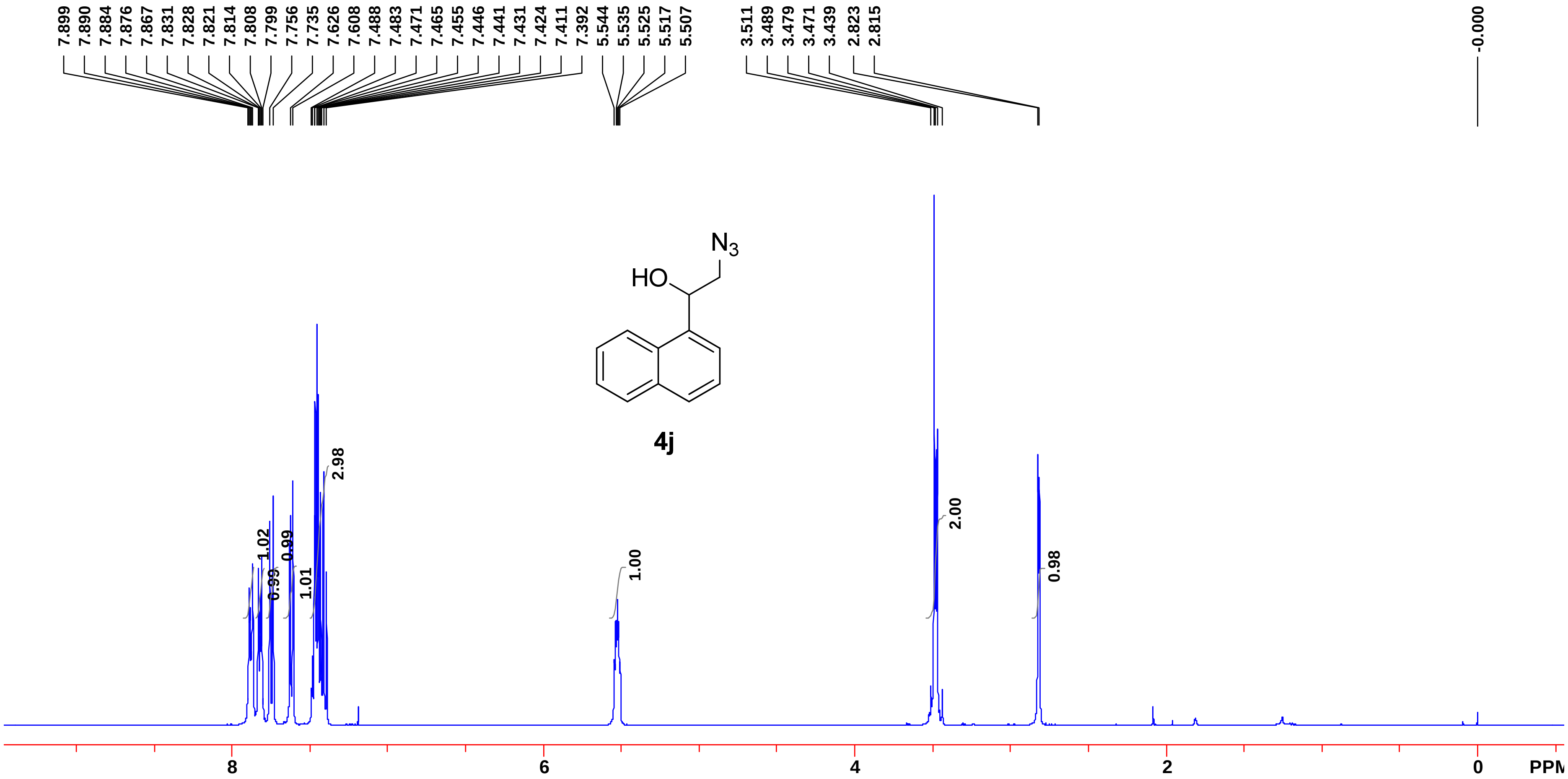

138.042
137.550
129.254
125.769
77.311
77.000
76.680
73.134
57.850
21.040
OH
N3
4c
200
150
100
50
PPM


4e
7.605
7.600
7.584
7.579
7.566
7.455
7.451
7.440
7.437
7.419
7.371
7.368
7.365
7.355
7.350
7.332
4.931
4.922
4.912
4.902
4.893
3.544
3.524
3.512
3.492
3.487
3.477
3.455
3.445
2.457
2.449
0.000
OH
N3
Ph
4.07
4.05
0.98
1.00
1.04
1.00
0.98
8
6
4
2
0
PPM

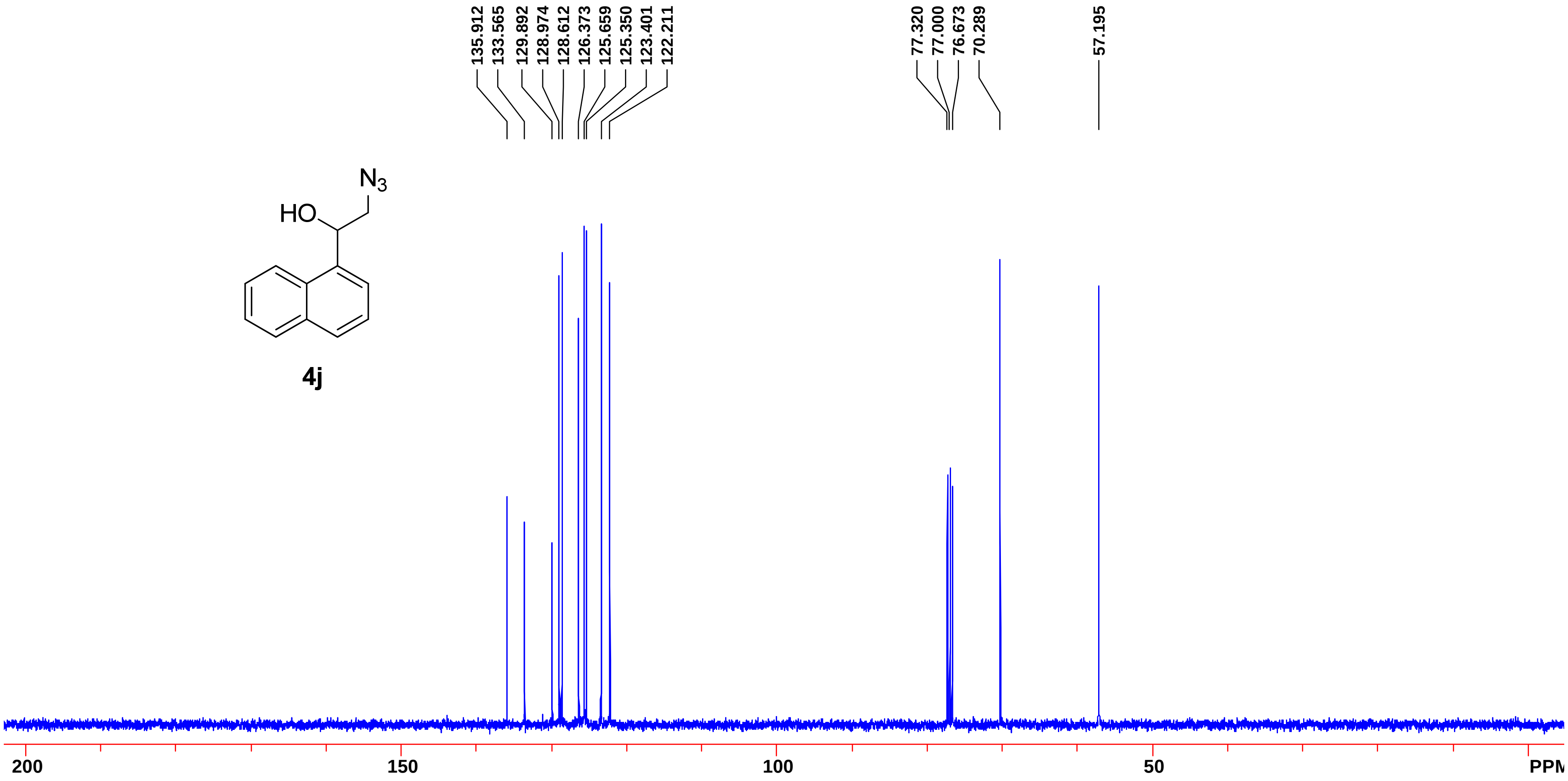


4e

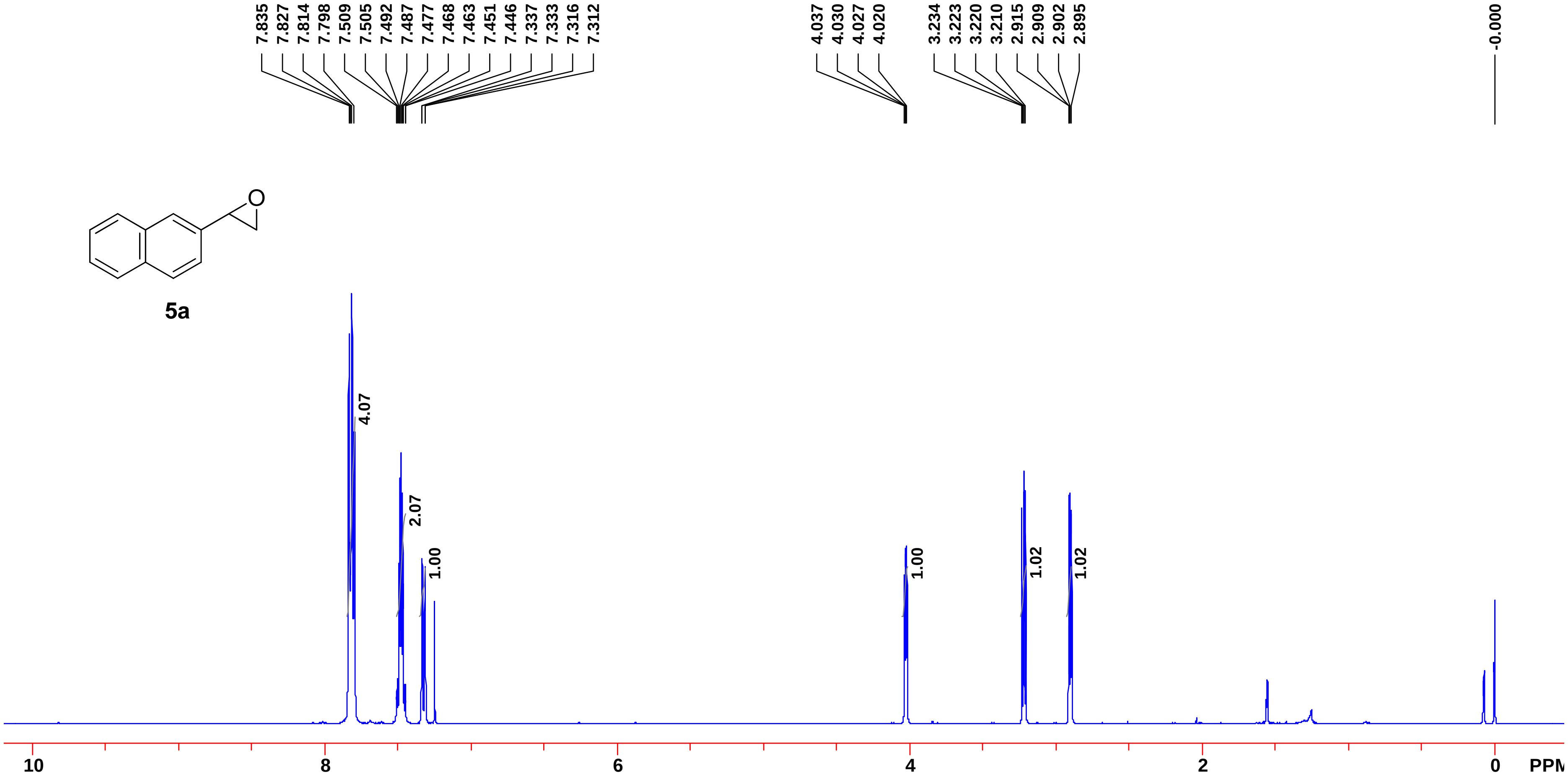
141.313
140.523
139.464
128.796
127.461
127.402
127.073
126.348
77.319
77.000
76.679
73.191
58.013
OH
N3
Ph
150
100
50
0 PPM

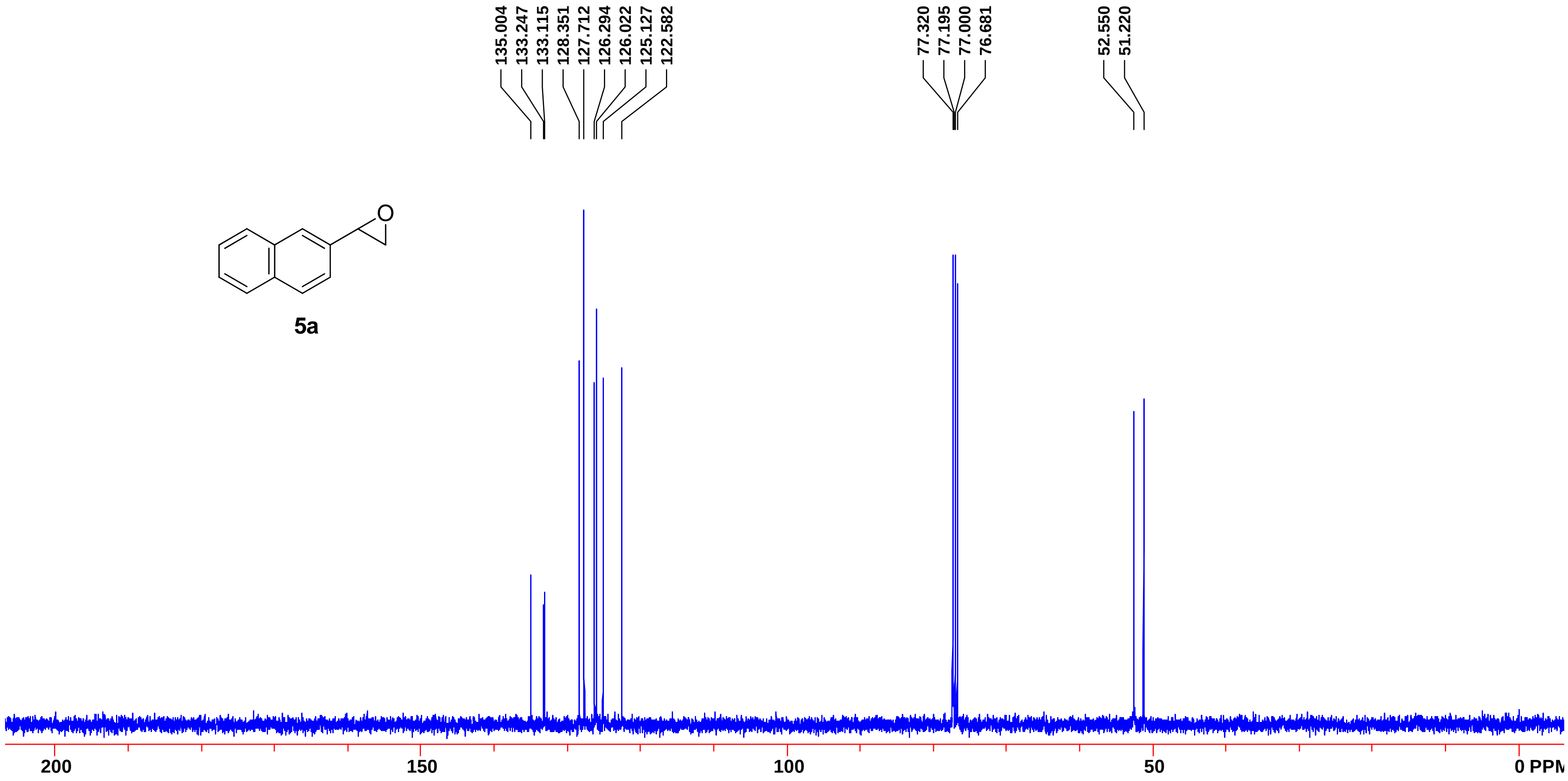

7.899
7.890
7.884
7.876
7.867
7.831
7.828
7.821
7.814
7.808
7.799
7.756
7.735
7.626
7.608
7.488
7.483
7.471
7.465
7.455
7.446
7.441
7.431
7.424
7.411
7.392
5.544
5.535
5.525
5.517
5.507
3.511
3.489
3.479
3.471
3.439
2.823
2.815
-0.000
HO
N3
1.02
0.99
0.99
1.01
2.98
1.00
2.00
0.98
8
6
4
2
0
PPM

4j


135.912
133.565
129.892
128.974
128.612
126.373
125.659
125.350
123.401
122.211
77.320
77.000
76.673
70.289
57.195
HO
N3
200
150
100
50
PPM

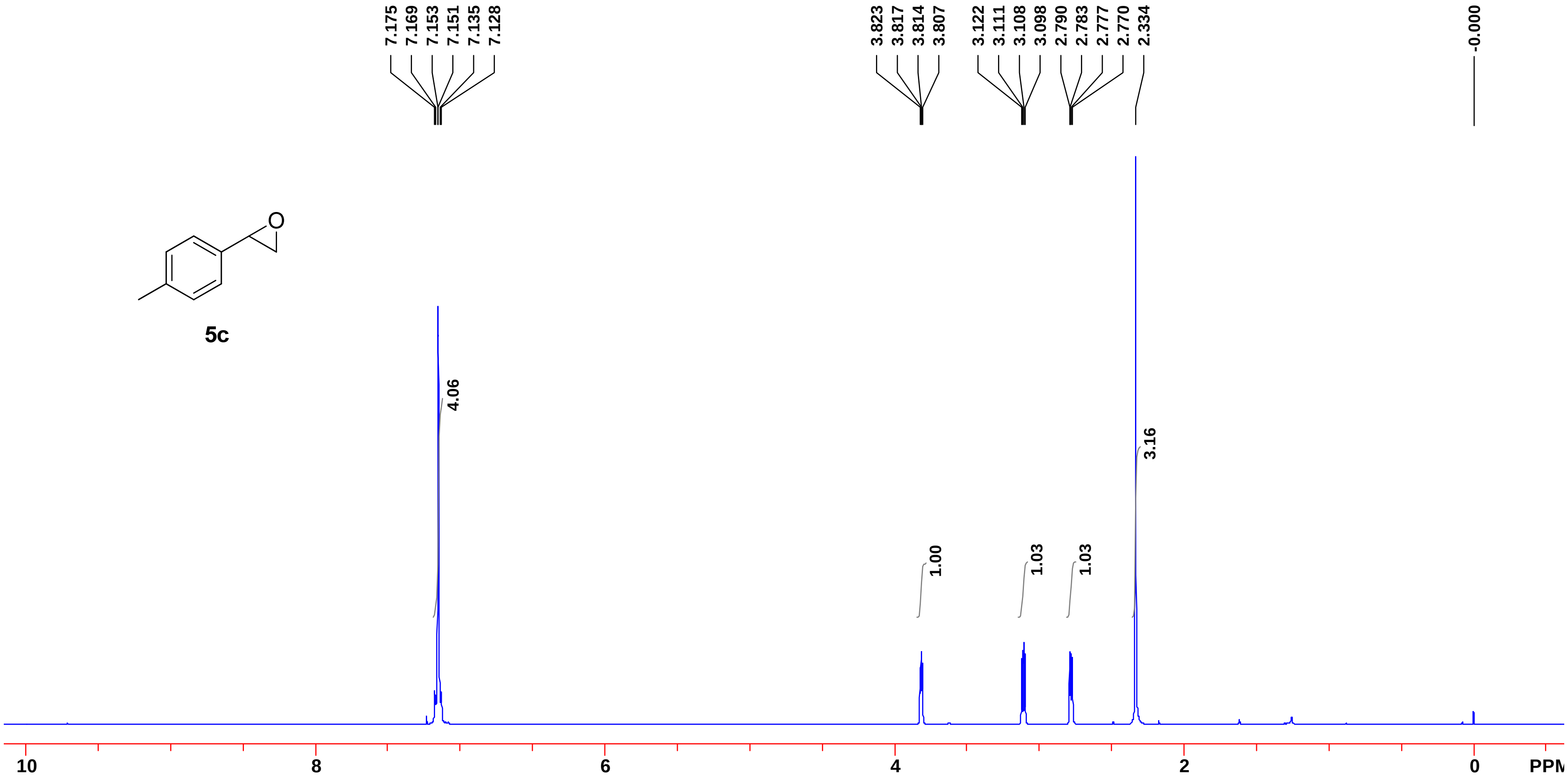
4j

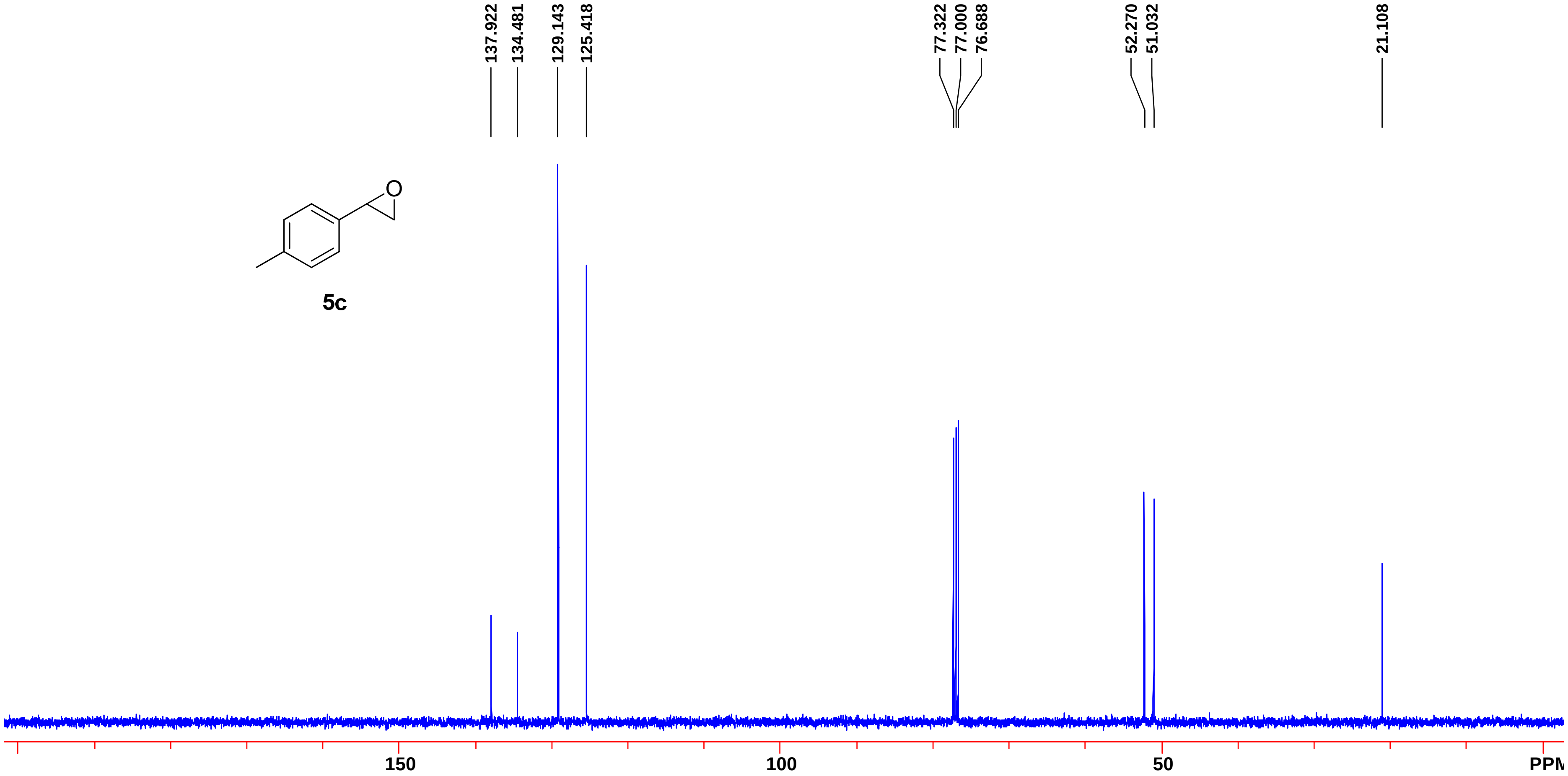

7.835
7.827
7.814
7.798
7.509
7.505
7.492
7.487
7.477
7.468
7.463
7.451
7.446
7.337
7.333
7.316
7.312
4.037
4.030
4.027
4.020
3.234
3.223
3.220
3.210
2.915
2.909
2.902
2.895
-0.000
O
5a
4.07
2.07
1.00
1.00
1.02
1.02
10
8
6
4
2
0
PPM



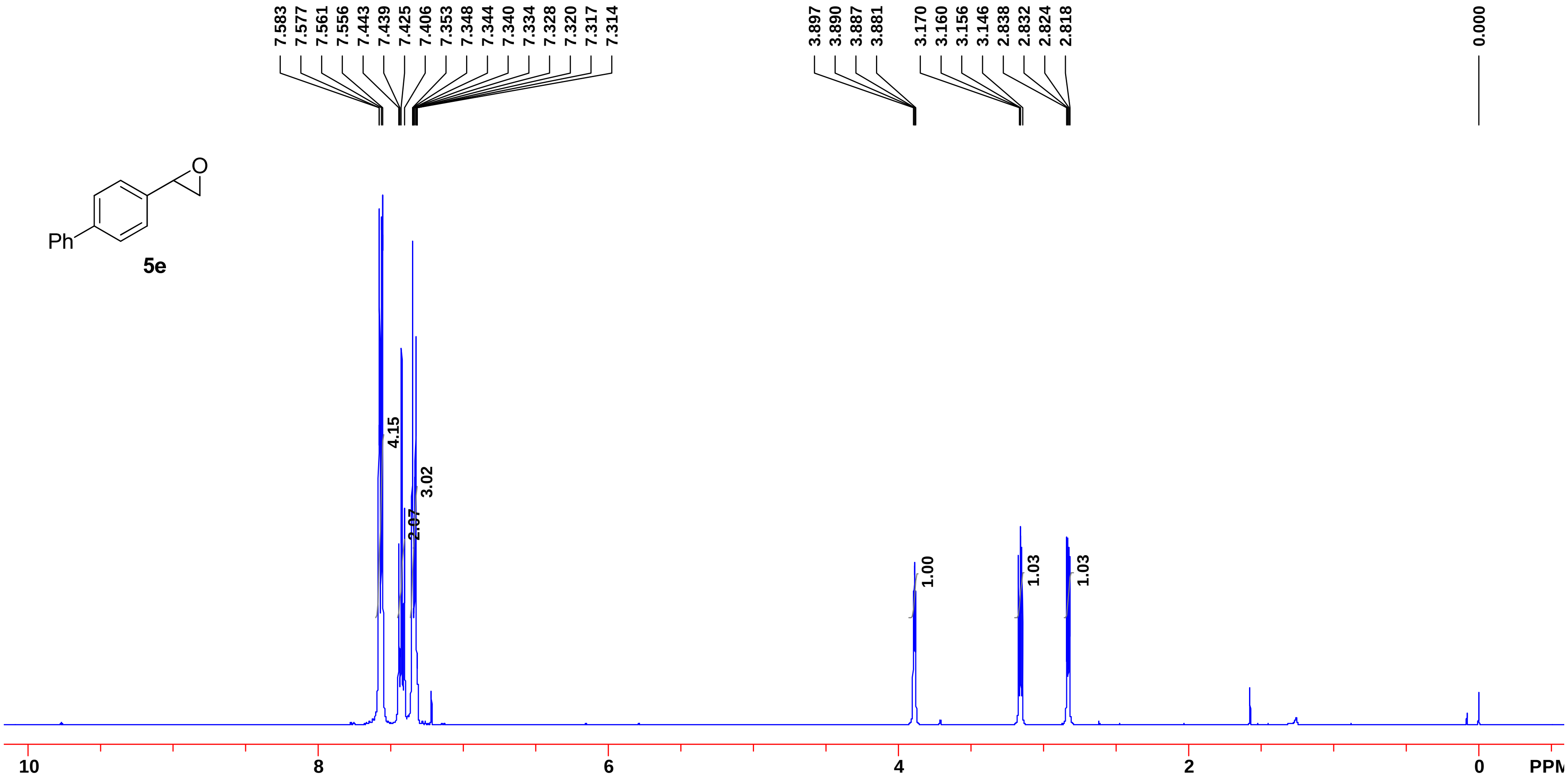
5a

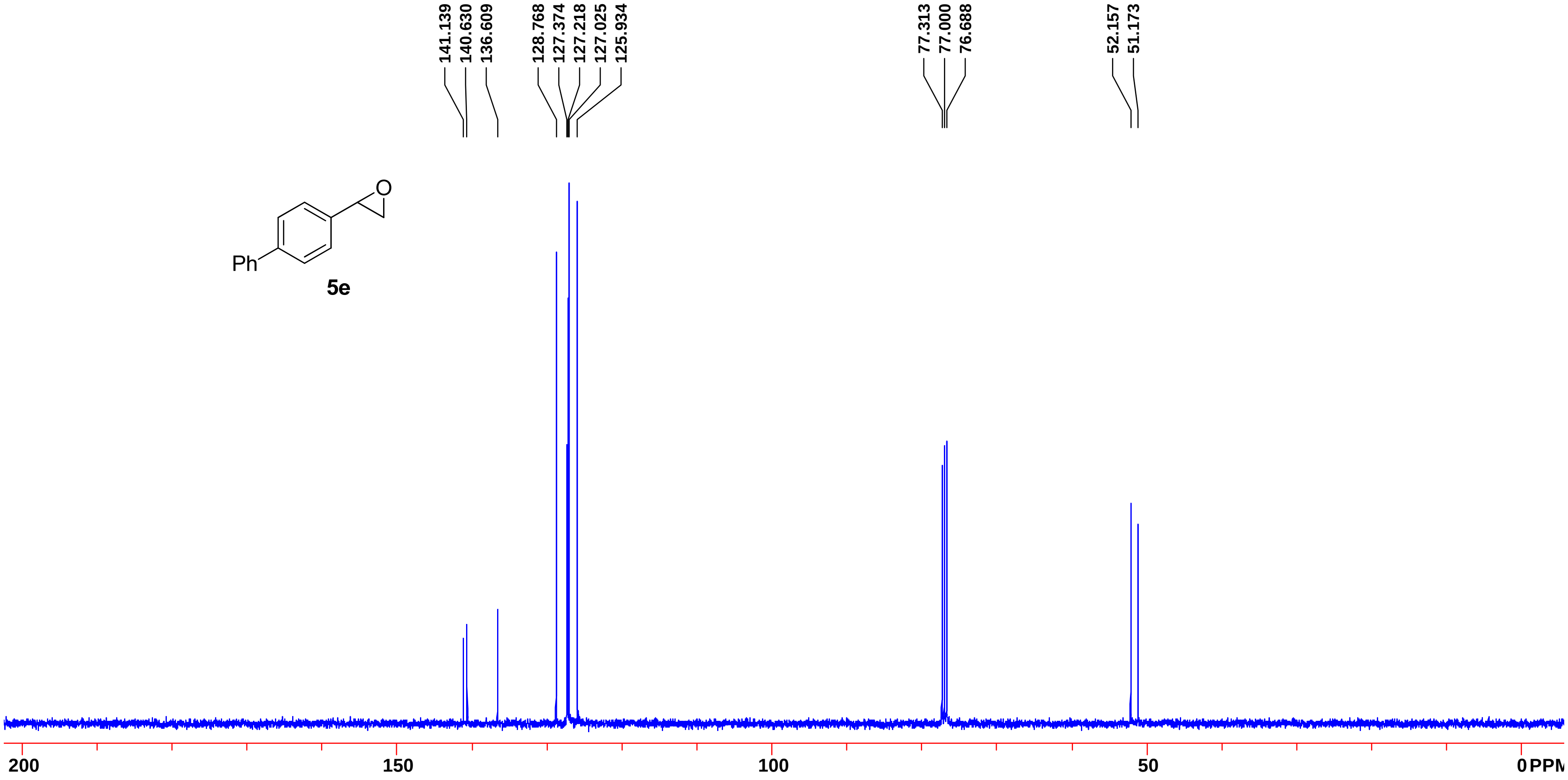
135.004
133.247
133.115
128.351
127.712
126.294
126.022
125.127
122.582
77.320
77.195
77.000
76.681
52.550
51.220
O
200
150
100
50
0 PPM

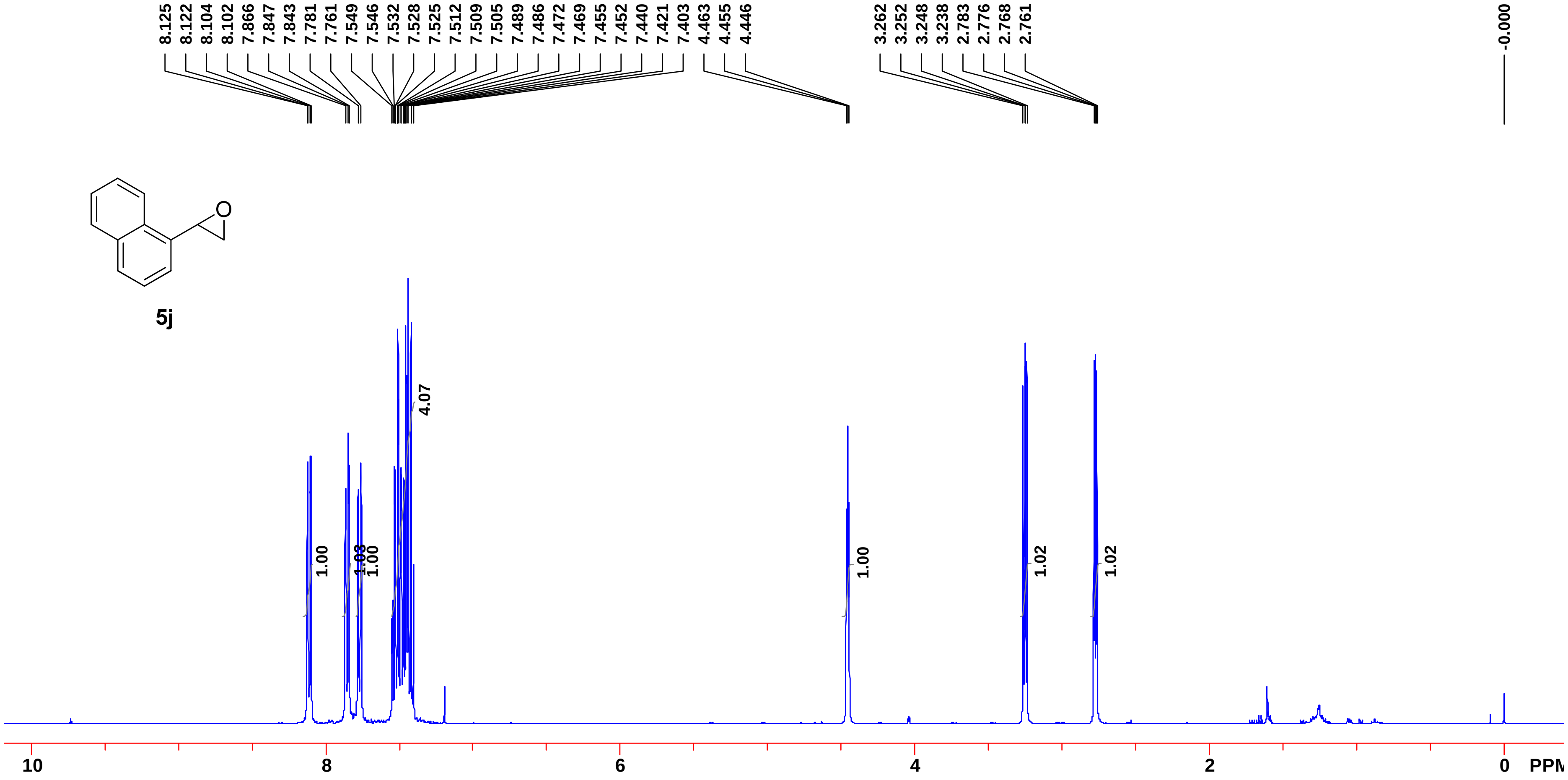

7.175
7.169
7.153
7.151
7.135
7.128
3.823
3.817
3.814
3.807
3.122
3.111
3.108
3.098
2.790
2.783
2.777
2.770
2.334
-0.000
O
5c
4.06
1.00
1.03
1.03
3.16
10
8
6
4
2
0
PPM

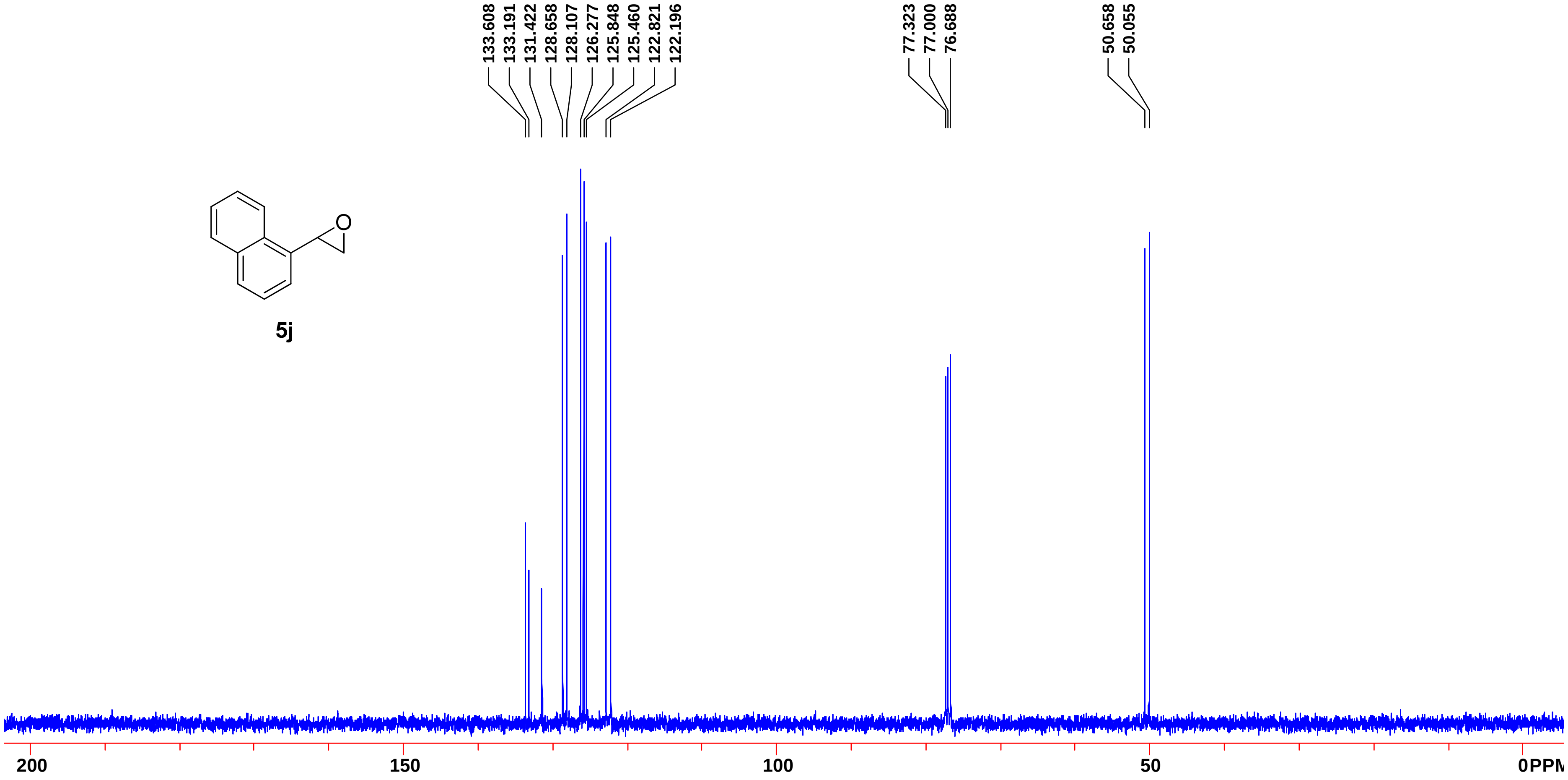

137.922
134.481
129.143
125.418
77.322
77.000
76.688
52.270
51.032
21.108
O
150
100
50
PPM

5c


7.583
7.577
7.561
7.556
7.443
7.439
7.425
7.406
7.353
7.348
7.344
7.340
7.334
7.328
7.320
7.317
7.314
3.897
3.890
3.887
3.881
3.170
3.160
3.156
3.146
2.838
2.832
2.824
2.818
0.000
Ph
O
5e
4.15
2.07
3.02
1.00
1.03
1.03
10
8
6
4
2
0
PPM

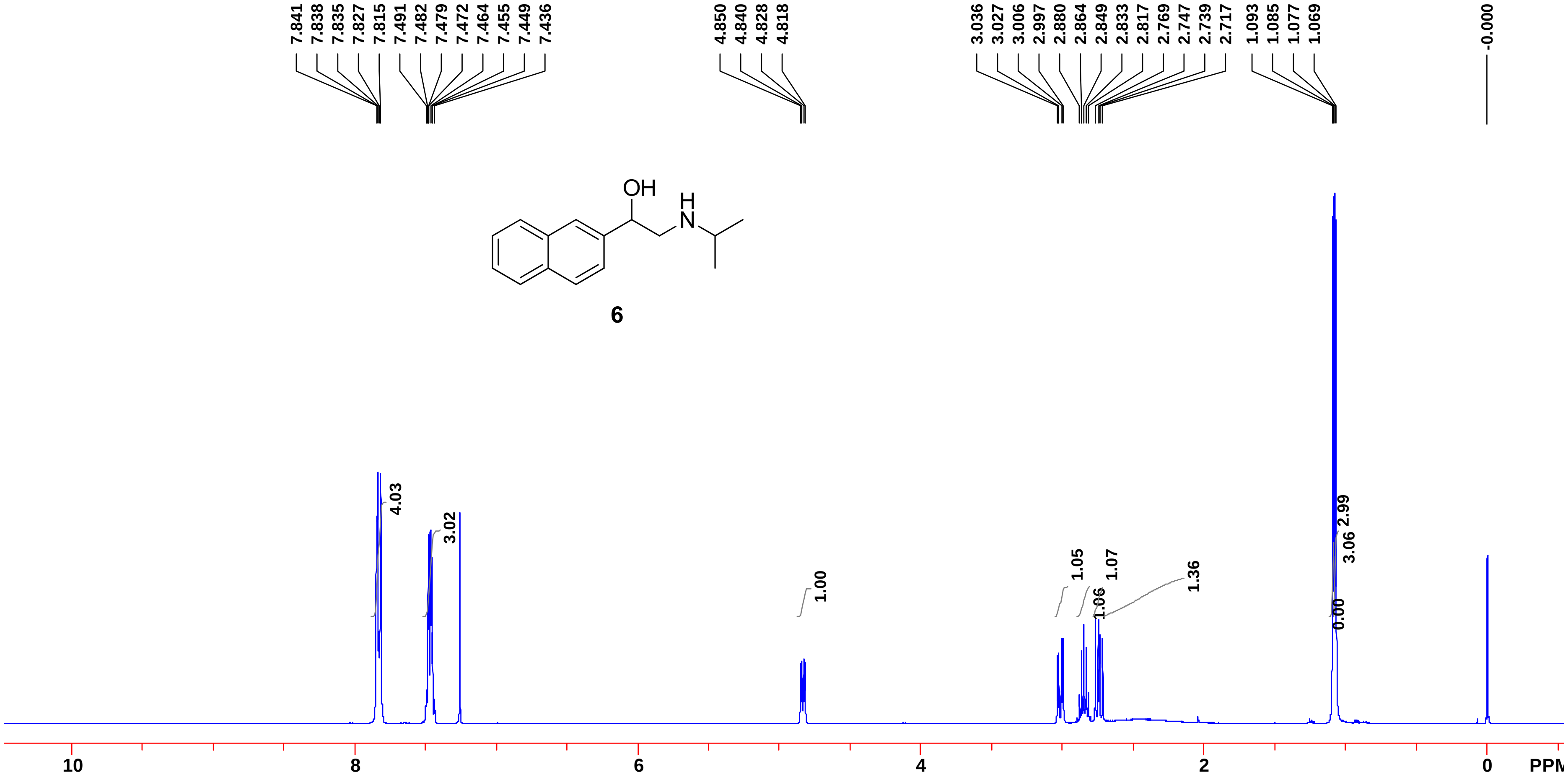

141.139
140.630
136.609
128.768
127.374
127.218
127.025
125.934
77.313
77.000
76.688
52.157
51.173
O
Ph
5e
200
150
100
50
0 PPM


8.125
8.122
8.104
8.102
7.866
7.847
7.843
7.781
7.761
7.549
7.546
7.532
7.528
7.525
7.512
7.509
7.505
7.489
7.486
7.472
7.469
7.455
7.452
7.440
7.421
7.403
4.463
4.455
4.446
3.262
3.252
3.248
3.238
2.783
2.776
2.768
2.761
-0.000
O
5j
1.00
1.03
1.00
4.07
1.00
1.02
1.02
10
8
6
4
2
0
PPM

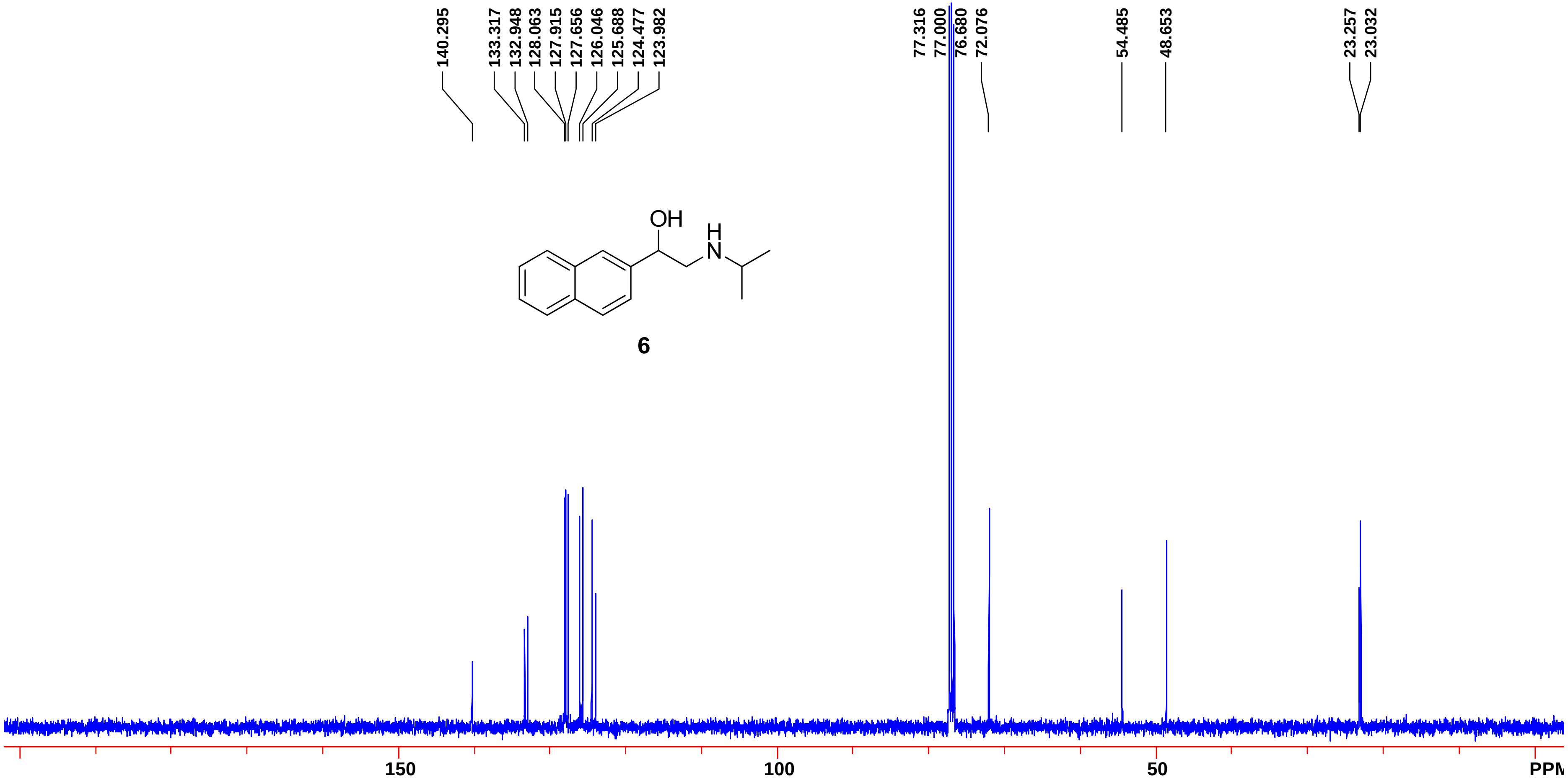


133.608
133.191
131.422
128.658
128.107
126.277
125.848
125.460
122.821
122.196
77.323
77.000
76.688
50.658
50.055
O
200
150
100
50
0PPM

5j


7.841
7.838
7.835
7.827
7.815
7.491
7.482
7.479
7.472
7.464
7.455
7.449
7.436
4.850
4.840
4.828
4.818
3.036
3.027
3.006
2.997
2.880
2.864
2.849
2.833
2.817
2.769
2.747
2.739
2.717
1.093
1.085
1.077
1.069
-0.000
OH
H
N
4.03
3.02
1.00
1.05
1.06
1.07
1.36
0.00
3.06
2.99
10
8
6
4
2
0
PPM

6


140.295
133.317
132.948
128.063
127.915
127.656
126.046
125.688
124.477
123.982
77.316
77.000
76.680
72.076
54.485
48.653
23.257
23.032
OH
H
N
6
150
100
50
PPM