Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Efficient ruthenium(IV)-catalyzed synthesis of [3]dendralenes from 1,3-dienic allylic carbonates

Kassem Beydoun, Hui-Jun Zhang, Basker Sundararaju, Bernard Demerseman, Mathieu Achard and Christian Bruneau*

email : christian.bruneau@univ-rennes1.fr

General:

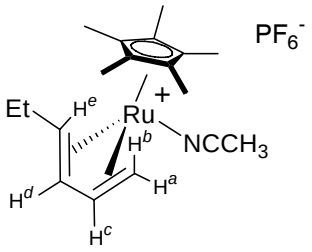
All reactions were carried out under argon atmosphere. HPLC grade solvent (Acetone and Acetonitrile) were stored under nitrogen and used as received. Dichloromethane (CH_2Cl_2) was distilled under conventional method and stored under a nitrogen atmosphere. ^1H NMR spectra were recorded on a Bruker GPX (200.131 MHz) spectrometer. ^1H NMR assignment abbreviations are the following: singlet (s), doublet (d), triplet (t), quartet (q), broad singlet (bs), doublet of doublets (dd),doublet of triplets (dt), and multiplet (m). ^{13}C NMR spectra were recorded at 50 MHz on the same spectrometer and reported in ppm. HRMS were recorded on Waters Q-Tof-2.

Part I : Synthesis and Analysis of the ruthenium complexes

Synthesis of [Ru(C_5Me_5)(η^4-CH_2=CH-CH=CHEt)(MeCN)][X] (X= PF_6^- and BF_4^-) complexes

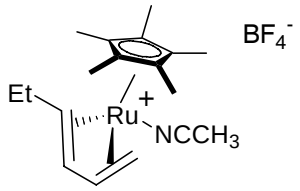
To a solution of [Ru(Cp*)($CH_3CN)_3$][X] (1.0 mmol) in acetone or in dichloromethane (20 mL), the appropriate allylic carbonate (1.0 mmol) was added. The mixture was stirred overnight at room temperature and then evaporated under vacuum to leave a pale-yellow solid.

[Ru(C_5Me_5)(η^4-CH_2=CH-CH=CHEt)(MeCN)][PF_6]



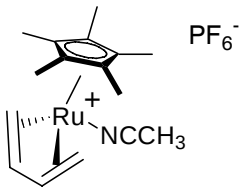
^{1}H NMR (CD_2Cl_2, 200 MHz): δ 4.83 (dd, ^3J = 9.7 and 5.7 Hz, 1H, H^d), 4.62–4.50 (m, 1H, H^c), 3.20 (d, ^3J = 8.0 Hz, 1H, H^a), 2.64 (s, 3H, MeCN), 2.13–1.64 (very broad resonances, 3H, H^e and CH_2CH_3), 1.72 (s, 15H, C_5Me_5), 1.37 (d, ^3J = 11.7 Hz, 1H, H^b), 1.10 (t, ^3J = 7.2 Hz, 3H, CH_2CH_3).

[Ru(C_5Me_5)(η^4-CH_2=CH-CH=CHEt)(MeCN)][BF_4]



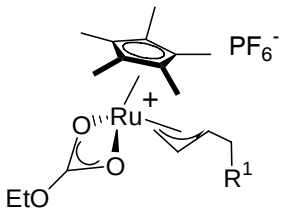
^{1}H NMR (CD_2Cl_2, 200 MHz): δ 4.85 (dd, ^3J = 10.3 and 5.5 Hz, 1H, H^d), 4.63–4.51 (m, 1H, H^c), 3.13 (dd, ^3J = 7.7, ^2J = 1.2 Hz, 1H, H^a), 2.61 (s, 3H, MeCN), 2.18–1.72 (very broad resonances, 3H, H^e and CH_2CH$_3$), 1.69 (s, 15H, C_5Me_5), 1.37 (broad d, ^3J = 10.4 Hz, 1H, H^b), 1.05 (t, ^3J = 7.3 Hz, 3H, CH$_2$CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 50 MHz): δ 132.08 (Me*C*N), 96.40 (C_5Me$_5$), 94.92 (CH=), 89.97 (CH=), 80.55 (CH=), 51.85 (=CH$_2$), 25.52 (*C*H$_2$CH$_3$), 15.68 (CH$_2$*C*H$_3$), 9.54 (C$_5$*Me*$_5$), 4.65 (*Me*CN).

[Ru(C_5Me_5)(η^4-CH_2=CH-CH=CH_2)(MeCN)][PF_6]



^{1}H NMR (CD_2Cl_2, 200 MHz): δ 4.86–4.73 (m, 2H, C*H*=CH$_2$), 3.41 (d, ^3J = 7.4 Hz, 2H, =CH$_2$, syn), 2.60 (s, 3H, MeCN), 1.73 (s, 15H, C_5Me_5), 1.40 (dd, ^3J = 10.2, ^4J = 1.2 Hz, 2H, =CH$_2$, anti). ^{13}C{^{1}H} NMR (CD_2Cl_2, 50 MHz): δ 131.99 (Me*C*N), 97.42 (C_5Me$_5$), 94.00 (*C*H=CH$_2$), 53.34 (CH=*C*H$_2$), 9.44 (C$_5$*Me*$_5$), 4.69 (*Me*CN).

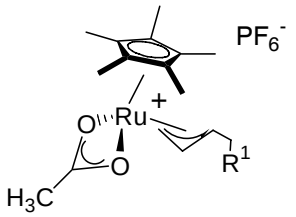
Detection of the $[Ru(C_5Me_5)(\eta^3\text{-}CH_2CHCHPr^n)(\eta^2\text{-}O_2COEt)]^+$ *intermediate*



To a solution of $[Ru(Cp^*)(CH_3CN)_3][PF_6]$ (0.50 g, 1.0 mmol) in acetone or in dichloromethane (20 mL), $Pr^nCH(OCO_2Et)CH=CH_2$ (or $Pr^nCH=CHCH_2(OCO_2Et)$ (0.17 g, 1.0 mmol) was added. The solution was stirred at room temperature for 30 min and then evaporated under vacuum. A sample of the resulting solid was dissolved in CD_2Cl_2 and immediately examined by ^1H NMR spectroscopy.

^1H NMR (CD_2Cl_2, 200 MHz): δ 5.11–4.97 (m, 1H, CH, medium), 4.45 (d, ^3J = 6.7 Hz, 1H, CH*H*, syn), 4.25 (q, ^3J = 7.1 Hz, 2H, OCH_2), 3.80–3.71 (m, 1H, Pr^nCH), 3.04 (d, ^3J = 10.2 Hz, 1H, =CH*H*, anti), 1.65 (s, 15H, C_5Me_5), other resonances overlapped with resonances from the **$[Ru(C_5Me_5)(\eta^4\text{-}CH_2=CH\text{-}CH=CHEt)(MeCN)][PF_6]$**

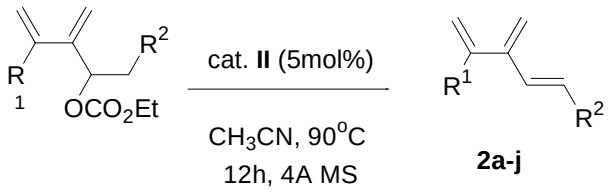
Synthesis of **[Ru(C_5Me_5)(η^3-$CH_2CHCHPr^n$)(η^2-O_2CMe)][PF_6]**



To a stirred solution of [Ru(Cp*)($CH_3CN)_3$][PF_6] (0.50 g, 1.0 mmol) in dichloromethane (15 mL), acetic acid (0.06 g, 1.0 mmol) then $Pr^nCH{=}CHCH_2(OCO_2Et)$ (0.17 g, 1.0 mmol) were added. The mixture was stirred overnight at room temperature and then evaporated under vacuum to leave a pale-brown solid.

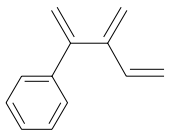
^{1}H NMR (CD_2Cl_2, 200 MHz): δ 5.35–5.21 (m, 1H, CH, medium), 4.39 (d, ^3J = 6.4 Hz, 1H, CH*H*, syn), 3.77–3.66 (m, 1H, Pr^nCH), 3.00 (d, ^3J = 10.3 Hz, 1H, =CH*H*, anti), 1.94 (s, 3H, $MeCO_2$), 1.80–1.31 (very broad resonances, 4H, 2 CH_2, Pr^n), 1.65 (s, 15H, C_5Me_5), 1.05 (t, ^3J = 7.1 Hz, 3H, Me, Pr^n). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 50 MHz): δ 194.22 (CO_2), 106.95 (C_5Me_5), 105.79 (CH, allyl), 92.11 (CH, allyl), 67.13 (CH_2, allyl), 33.18 (CH_2, Pr^n), 25.52 ($MeCO_2$), 23.46 (CH_2, Pr^n), 14.03 (Me, Pr^n), 9.18 (C_5Me_5).

Part II. Synthesis of [3]Dendralenes



A Schlenk containing powdered 4Å molecular sieves (200 mg) was flame-dried under vacuum. After cooling at room temperature, acetonitrile (3 mL) and [Ru(Cp*)(4,4'-di-Bu^t-2,2'-bipyridine)(CH_3CN)]PF_6 **II** (0.020 mmol, 5% mol) were successively added under an argon atmosphere and the resulting mixture was stirred for one minute. The appropriate diene carbonate **1** (0.40 mmol) was added directly via a microsyringe and the system was stirred at 90°C for 12h. Extraction of the acetonitrile layer with pure pentane (4*3mL) followed by direct chromatography using *n*-pentane as solvent affords the expected triene **2** after ***careful concentration at room temperature*** of the fractions.

[1,2-bis(methylene)but-3-en-1-yl]benzene **2a**

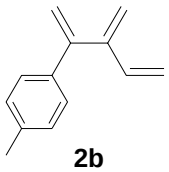


2a

Prepared from ethyl 1-methyl-2-methylene-3-phenylbut-3-en-1-yl carbonate **1a** (100 mg, 0.40 mmol). Chromatography afforded compound **2a** as a colourless oil, 48 mg (75%) and spectral data are in accordance with literature[1]: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.44-7.25 (m, 5H), 6.46 (dd, *J*= 10.3 Hz, 17.6 Hz, 1H), 5.55 (d, *J*= 1.5 Hz, 1H), 5.33 (d, *J*= 1.5 Hz, 1H), 5.26 (d, *J*= 1.5 Hz, 1H), 5.20 (s, 1H), 5.11-5.03 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 148.2, 147.9, 139.9, 137.3, 128.2, 127.5, 126.7, 118.4, 117.5, 114.8.

(1) T. N. Bradford, A. D. Payne, A. C. Willis, M. N. Paddon-Row and M. S. Sherburn, *Org. Lett.* 2007, **9**, 4861.

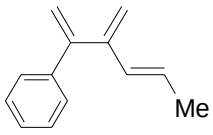
1-[1,2-bis(methylene)but-3-en-1-yl]-4-methylbenzene **2b**



2b

Prepared from ethyl 1-methyl-2-methylene-3-(4-methylphenyl)but-3-en-1-yl carbonate **1b** (100 mg, 0.38 mmol). Chromatography afforded compound **2b** as a colourless oil, 41 mg (63%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.32-7.26 (m, 3H), 7.13-7.09 (m, 2H), 6.46 (dd, *J*= 10.0, 17.5 Hz, 1H), 5.50 (d, *J*= 1.0 Hz, 1H), 5.30 (d, J= 1.8 Hz, 1H), 5.20-5.00 (m, 4H), 2.33 (bs, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 148.4, 147.8, 137.4, 137.3, 137.0, 128.9, 126.6, 118.2, 117.4, 114.0, 21.1.

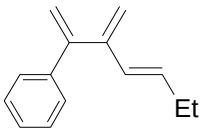
[(3*E*)-1,2-bis(methylene)pent-3-en-1-yl]benzene **2c**



2c

Prepared from ethyl 1-ethyl-2-methylene-3-phenylbut-3-en-1-yl carbonate **1c** (100 mg, 0.38 mmol). Chromatography afforded compound **2c** as a colourless oil, 47 mg (72%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.46-7.30 (m, 5H), 6.19 (d, *J*= 15.5 Hz, 1H), 5.66-5.48 (m, 2H), 5.25 (bs, 1H), 5.21 (bs, 1H), 5.07 (bs, 1H), 1.70 (d, *J*= 6.5 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 148.7, 148.0, 139.7, 131.8, 129.4, 128.2, 127.5, 126.6, 115.8, 114.4, 18.3.

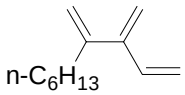
[(3*E*)-1,2-bis(methylene)hex-3-en-1-yl]benzene **2d**



2d

Prepared from ethyl 2-methylene-3-phenyl-1-propylbut-3-en-1-yl carbonate **1d** (100 mg, 0.36 mmol). Chromatography afforded compound **2d** as a colourless oil, 44 mg (66%): ^{1}H NMR (200 MHz, CD_2Cl_2) δ 7.43-7.23 (m, 5H), 6.12 (d, *J*= 15.7 Hz, 1H), 5.56 (dt, *J*= 15.7, 6.6 Hz, 1H), 5.49 (d, *J*= 1.4 Hz, 1H), 5.22 (d, *J*= 1.5 Hz, 1H), 5.20 (d, *J*= 2.2 Hz, 1H), 5.03 (d, *J*= 2.2 Hz, 1H), 2.08 (qu, *J*= 6.5 Hz, 2H), 0.90 (t, *J*= 7.0 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 148.7, 148.0, 140.0, 136.2, 129.4, 128.1, 127.4, 126.7, 115.9, 114.3, 25.7, 13.2.

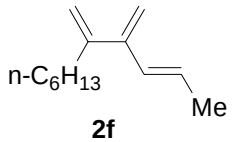
3,4-bis(methylene)dec-1-ene **2e**



2e

Prepared from ethyl 1-methyl-2,3-bis(methylene)nonyl carbonate **1e** (100 mg, 0.39 mmol). Chromatography afforded compound **2e** as a colourless oil, 42 mg (65%): ^{1}H NMR (200 MHz, CDCl3) δ 6.41 (dd, *J*= 9.8, 17.5 Hz, 1H), 5.29 (dd, J= 1.8, 17.5 Hz, 1H), 5.14-4.96 (m, 5H), 2.21 (t, *J*= 6.9 Hz, 2H), 1.49-1.23 (m, 8H), 0.88 (t, *J*= 6.9 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 148.9, 148.3, 137.9, 116.4, 114.5, 113.6, 35.7, 32.3, 29.4, 28.5, 23.0, 14.5

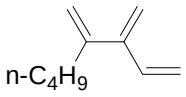
(2*E*)-4,5-bis(methylene)undec-2-ene **2f**



2f

Prepared from ethyl 1-ethyl-2,3-bis(methylene)nonyl carbonate **1f** (100 mg, 0.37 mmol). Chromatography afforded compound **2f** as a colourless oil, 50 mg (75%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.09 (d, *J*= 15.4 Hz, 1H), 5.75 (dt, *J*= 6.6, 15.4 Hz, 1H), 4.97-4.94 (m, 3H), 4.88 (d, *J*= 1.8 Hz, 1H), 2.19 (t, *J*= 6.9 Hz, 2H), 1.76 (dd, *J*= 1.4, 6.6 Hz, 3H), 1.44-1.20 (m, 8H), 0.87 (t, *J*= 6.6 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 148.8, 148.3, 131.6, 127.7, 112.7, 112.0, 35.4, 31.7, 29.0, 28.1, 22.6, 18.2, 14.0.

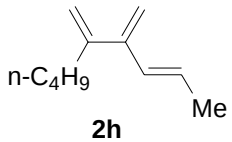
3,4-bis(methylene)oct-1-ene **2g**



2g

Prepared from ethyl 1-methyl-2,3-bis(methylene)heptyl carbonate **1g** (100 mg, 0.44 mmol). Chromatography afforded compound **2g** as a colourless oil, 47 mg (78%): ^{1}H NMR (200 MHz, CD_2Cl_2) δ 6.40 (dd, *J*= 10.0, 17.0 Hz, 1H), 5.29 (d, *J*= 17.0 Hz, 1H), 5.14-4.97 (m, 5H), 2.22 (t, *J*= 6.9 Hz, 2H), 1.46-1.25 (m, 4H), 0.89 (t, *J*= 6.5 Hz, 3H); ^{13}C NMR (50 MHz, CD_2Cl_2) δ 150.9, 150.4, 137.9, 116.4, 114.5, 113.6, 35.5, 30.9, 22.9, 14.2.

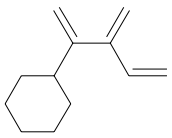
(2*E*)-4,5-bis(methylene)non-2-ene **2h**



2h

Prepared from ethyl 1-ethyl-2,3-bis(methylene)heptyl carbonate **1h** (100 mg, 0.41 mmol). Chromatography afforded compound **2h** as a colourless oil, 46 mg (73%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.06 (d, *J*= 15.7 Hz, 1H), 5.74 (dqu, *J*= 6.9, 15.7 Hz, 1H), 4.97-4.89 (m, 4H), 2.20 (t, *J*= 6.9 Hz, 2H), 1.76 (d, *J*= 6.5 Hz, 3H), 1.47-1.22 (m, 4H), 0.89 (t, *J*= 6.9 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 148.8, 148.3, 131.6, 127.7, 112.7, 112.0, 35.0, 30.4, 22.4, 18.2, 13.9.

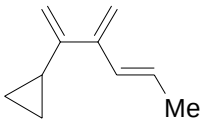
[1,2-bis(methylene)but-3-en-1-yl]cyclohexane **2i**



2i

Prepared from 3-cyclohexyl-1-methyl-2-methylenebut-3-en-1-yl ethyl carbonate **1i** (100 mg, 0.39 mmol). Chromatography afforded compound **2i** as a colourless oil, 53 mg (82%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.39 (dd, *J*= 10.2, 17.2 Hz, 1H), 5.21 (dd, *J*= 1.5, 17.2 Hz, 1H), 5.12-5.06 (m, 2H), 4.98-4.94 (m, 2H), 4.87 (d, *J*= 1.8 Hz, 1H), 2.12-2.00 (m, 1H), 1.85-1.64 (m, 4H), 1.37-1.00 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 153.4, 149.5, 138.2, 116.0, 114.8, 111.0, 42.4, 32.3, 26.7, 26.4.

[(3*E*)-1,2-bis(methylene)pent-3-en-1-yl]cyclopropane **2j**

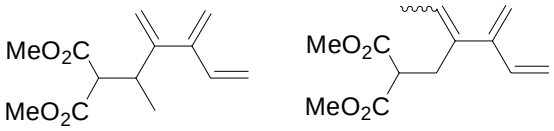


2j

Prepared from 3-cyclopropyl-1-ethyl-2-methylenebut-3-en-1-yl ethyl carbonate **1j** (100 mg, 0.44 mmol). Chromatography afforded compound **2j** as a colourless oil, 41 mg (68%) which dimerized rapidly. Spectral analysis were performed on diluted sample in n-pentane: ^{1}H NMR (200 MHz, CD_2Cl_2) δ 6.17 (d, *J*= 15.3 Hz, 1H), 5.84 (dqu, *J*= 6.5, 15.3 Hz, 1H), 5.05 (bs, 2H), 4.92-4.89 (m, 2H), 1.80 (d, *J*= 6.5 Hz, 3H), 1.56-1.46 (m, 1H), 0.76-0.67 (m, 2H), 0.52-0.44 (m, 2H); ^{13}C NMR (50 MHz, CD_2Cl_2) δ 152.15, 150.3, 134.0, 130.3, 114.6, 112.0, 20.3, 17.6, 8.9.

Concurrent Catalysis: Allylation/Elimination sequence

Compounds **2k**



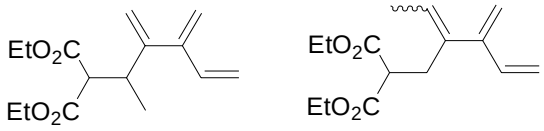
Branched:Linear
83 : 17

2k

A Schlenk containing powdered 4Å molecular sieves (200 mg) and potassium carbonate (62 mg, 0,44 mmol) was flame-dried under vacuum. After cooling at room temperature, acetonitrile (4 mL), dimethyl malonate (39 mg, 0,29 mmol) and diene dicarbonate **1k** (100 mg, 0,38 mmol) were successively added under an argon atmosphere and the resulting mixture was stirred for two minutes. Then, [Ru(Cp*)(4,4'-di-Bu^{t}-2,2'-bipyridine)(CH_3CN)]PF_6 **II** (15 mg, 0.02 mmol, 7.5 mol%) was added and the system

was stirred at 100°C for 24h. Chromatography (silica gel, n-pentane/diethyl ether : 90/10) of the crude (silica cake) affords 39 mg of the expected triene **2k** (55 %) in a 83:17 Branched:Linear ratio (*only the branched compound is described*): ^{1}H NMR (200 MHz, C_6D_6) δ 6.30 (ddd, *J*= 0.7, 10.7, 17.4 Hz, 1H), 5.36 (dd, *J*= 1.5, 17.4 Hz, 1H), 5.03-4.97 (m, 4H), 3.75 (d, *J*= 8.8 Hz, 1H), 3.55-3.40 (m, 1H), 3.26 (s, 3H), 3.24 (s, 3H), 1.19 (d, *J*= 6.9 Hz, 3H); ^{13}C NMR (50 MHz, C_6D_6) δ 168.7, 168.6, 149.8, 148.7, 137.9, 116.8, 116.2, 113.8, 56.5, 51.9, 51.7, 38.3, 17.4; HRMS calculated for $[C_{13}H_{18}NaO_4]^+$, $[M+Na]^+$: 261.1097 found 261.1103.

Compounds **2l**

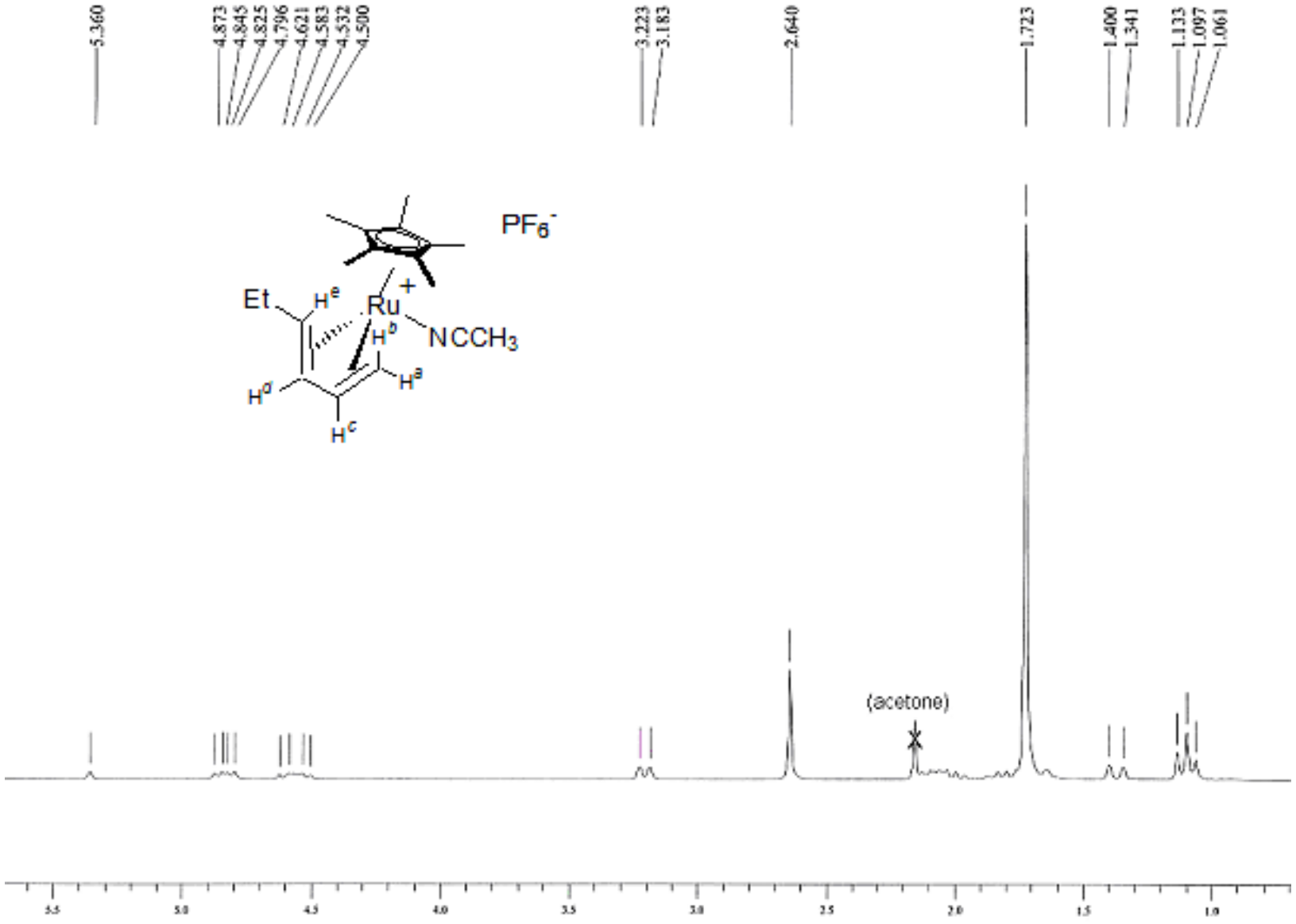


Branched:Linear
75 : 25

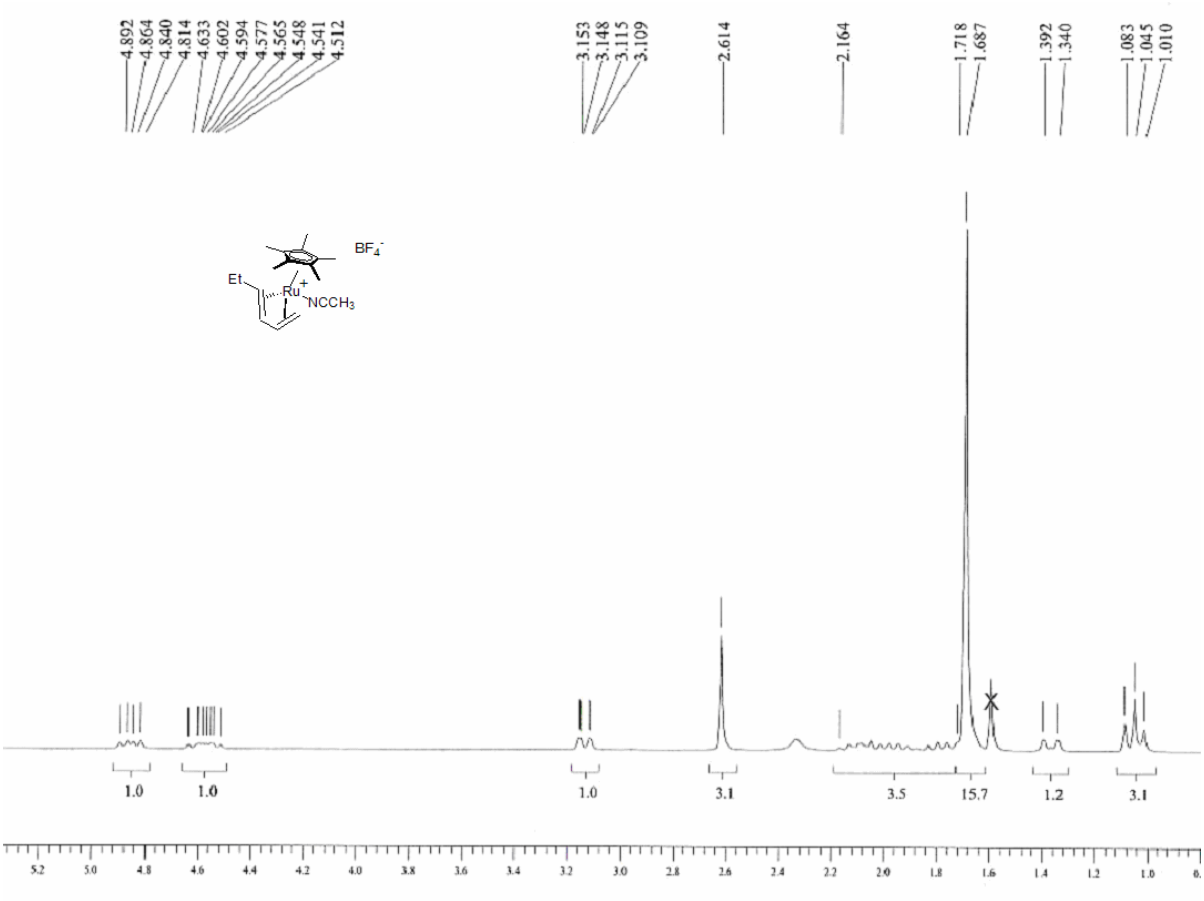
2l

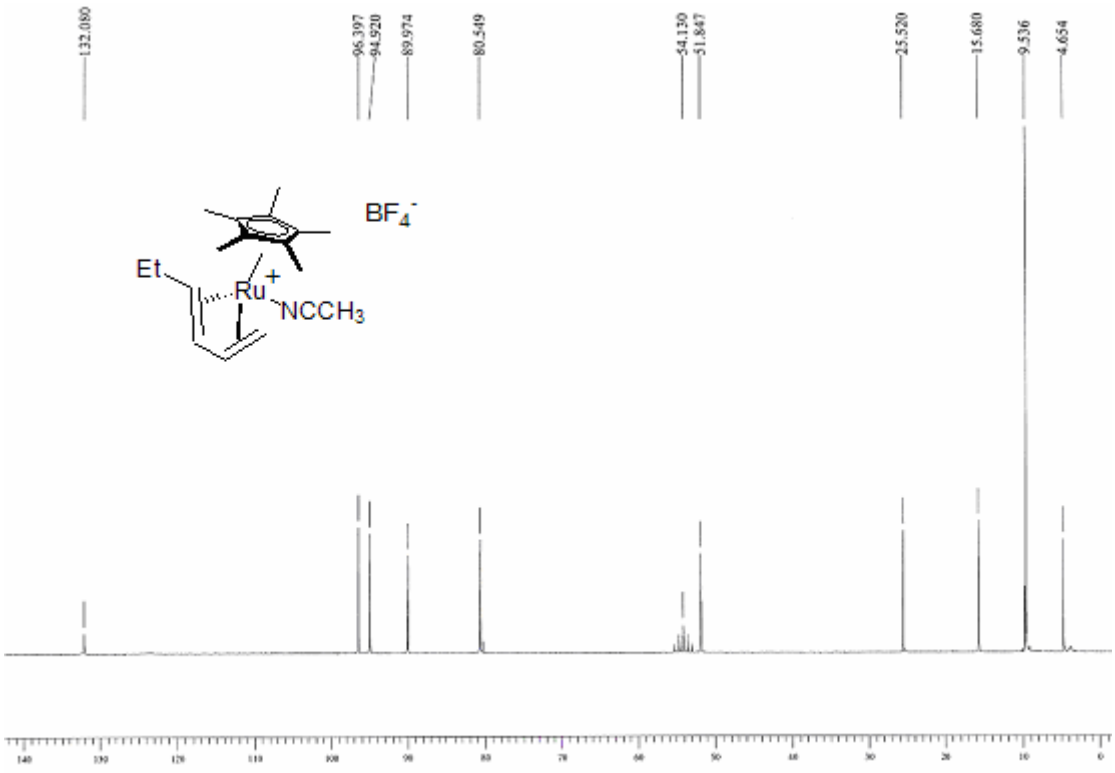
Compounds **2l** were obtained in 75:25 Branched:Linear ratio using the above protocol (*only the branched compound is described*): ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.37 (dd, *J*= 10.3, 17.6 Hz, 1H), 5.30 (ddd, *J*= 1.0, 1.6, 17.6 Hz, 1H), 5.16-5.01 (m, 5H), 4.24-4.10 (m, 4H), 3.55 (d, *J*= 9.01 Hz, 1H), 3.27-3.12 (m, 1H), 1.30-1.19 (m, 6H), 1.12 (d, J= 6.9 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 168.5, 168.4, 149.1, 148.0, 137.6, 116.6, 115.9, 113.7, 61.3, 61.2, 56.3, 37.8, 17.2, 14.1, 14.0.

$[Ru(C_5Me_5)(\eta^4\text{-}CH_2{=}CH\text{-}CH{=}CHEt)(MeCN)][PF_6]$

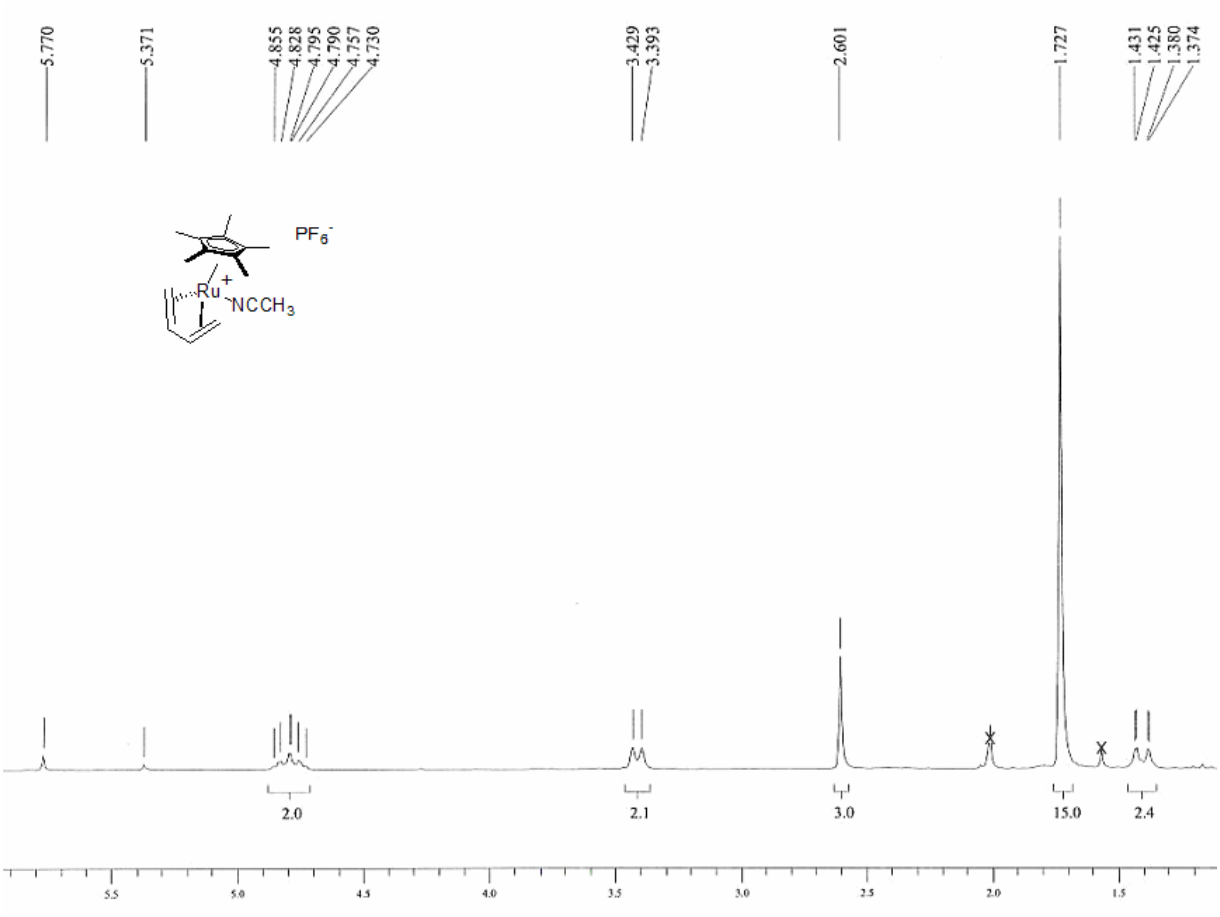


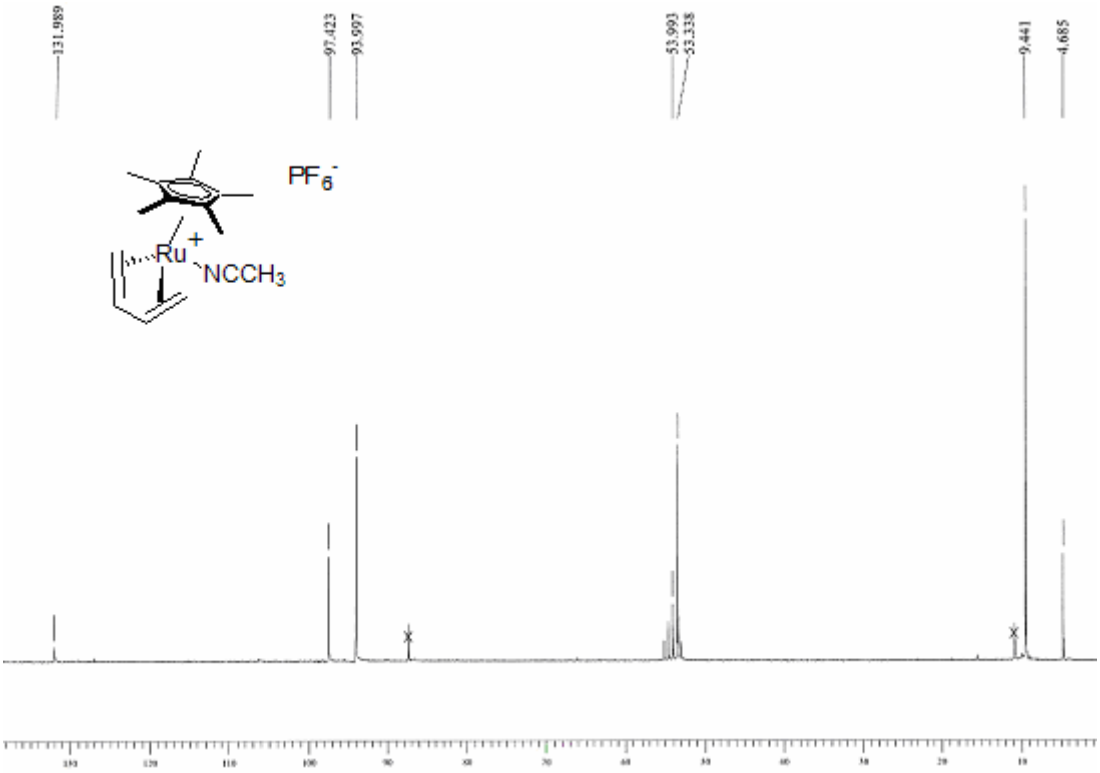
[Ru(C$_5$Me$_5$)(η^4-CH$_2$=CH-CH=CHEt)(MeCN)][BF$_4$]



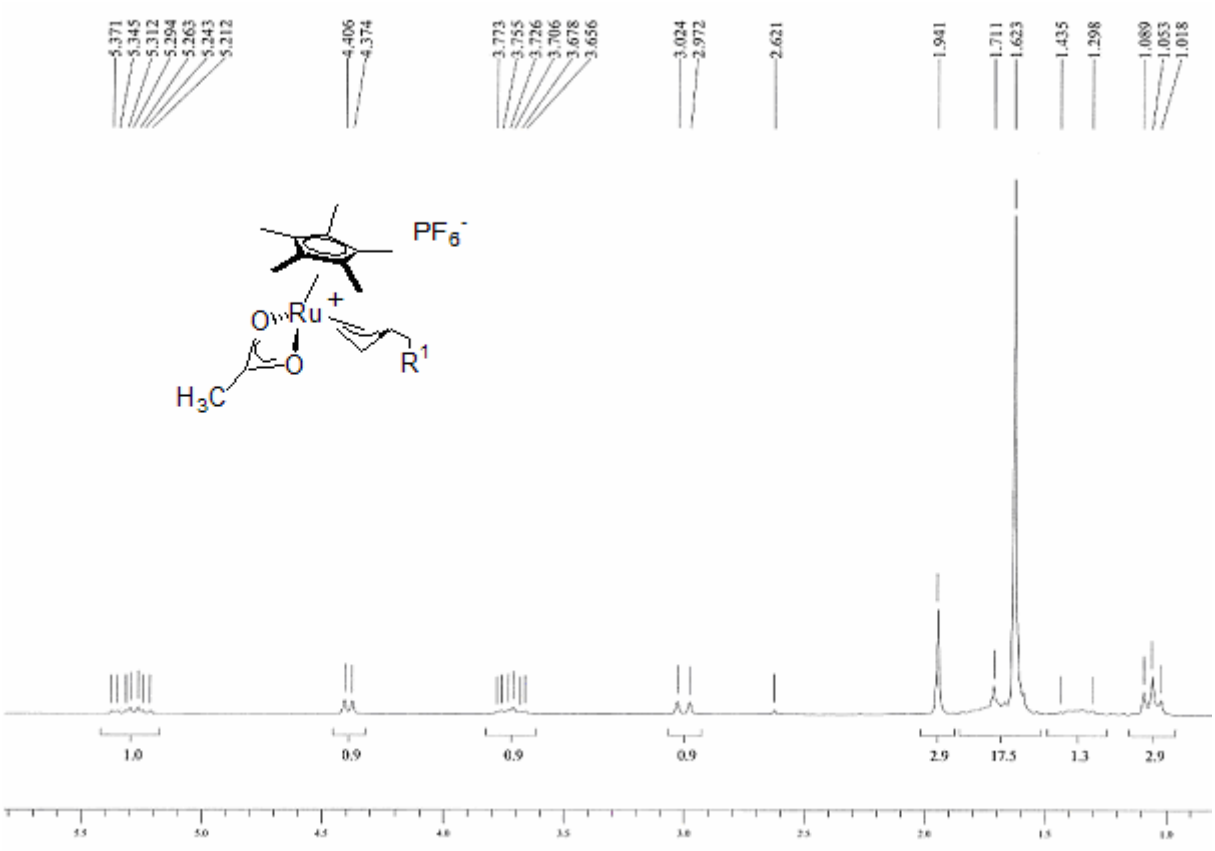


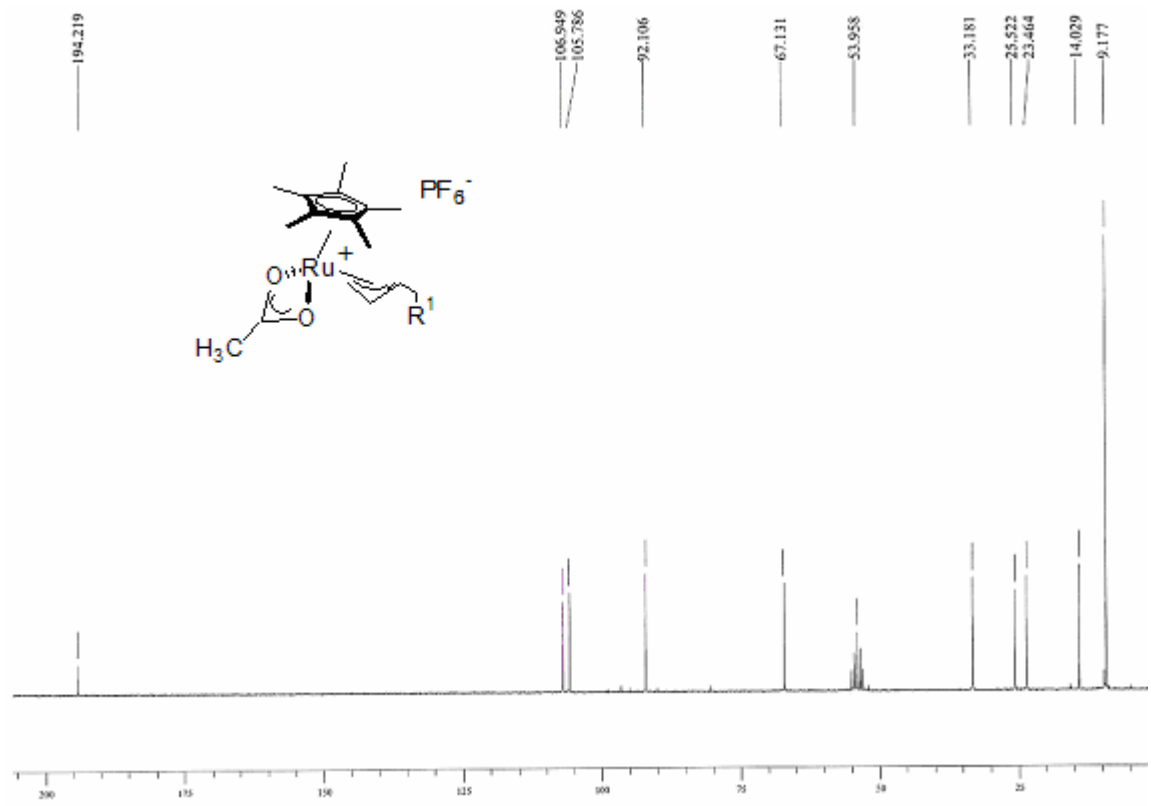
$[Ru(C_5Me_5)(\eta^4\text{-}CH_2{=}CH\text{-}CH{=}CH_2)(MeCN)][PF_6]$

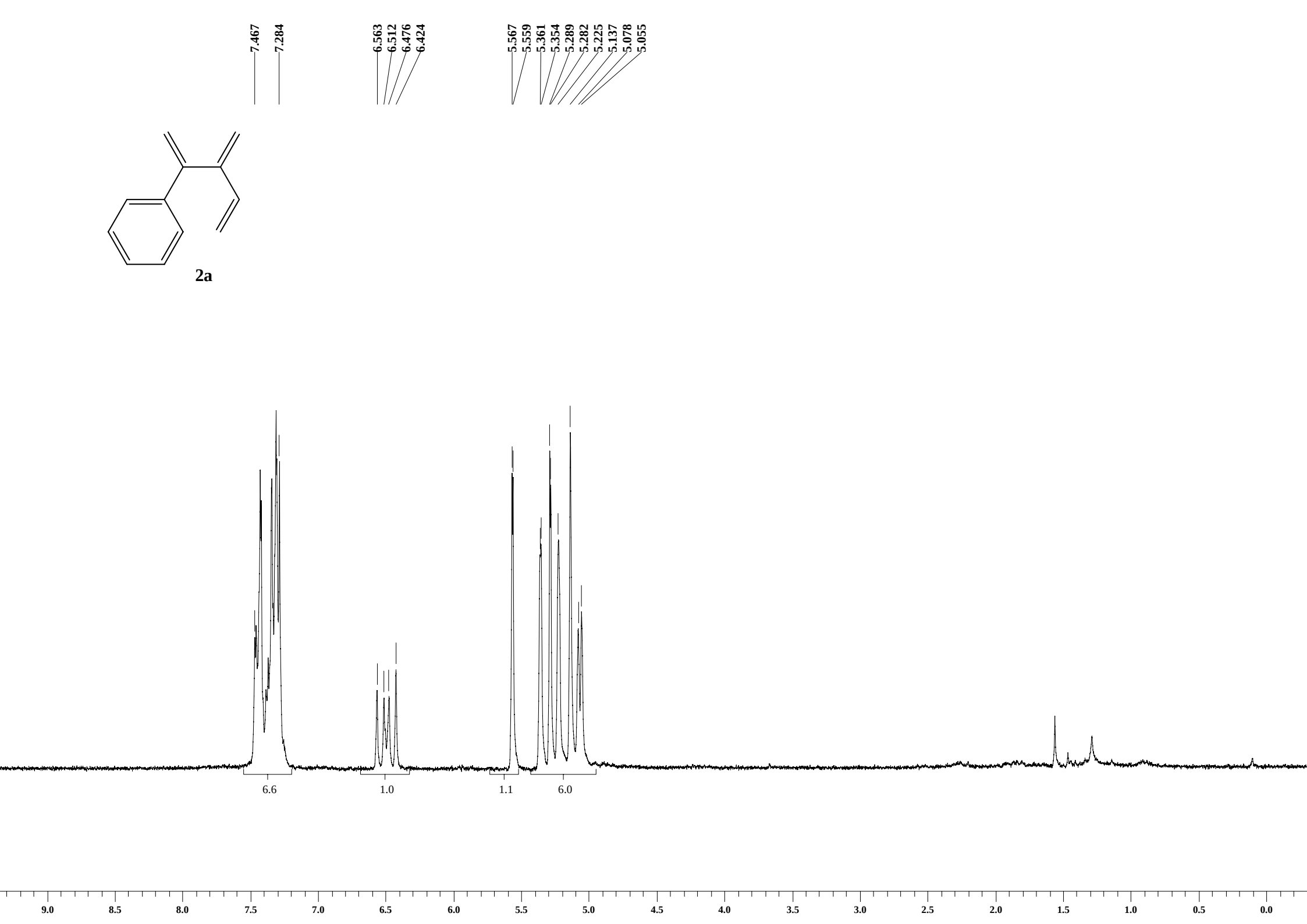


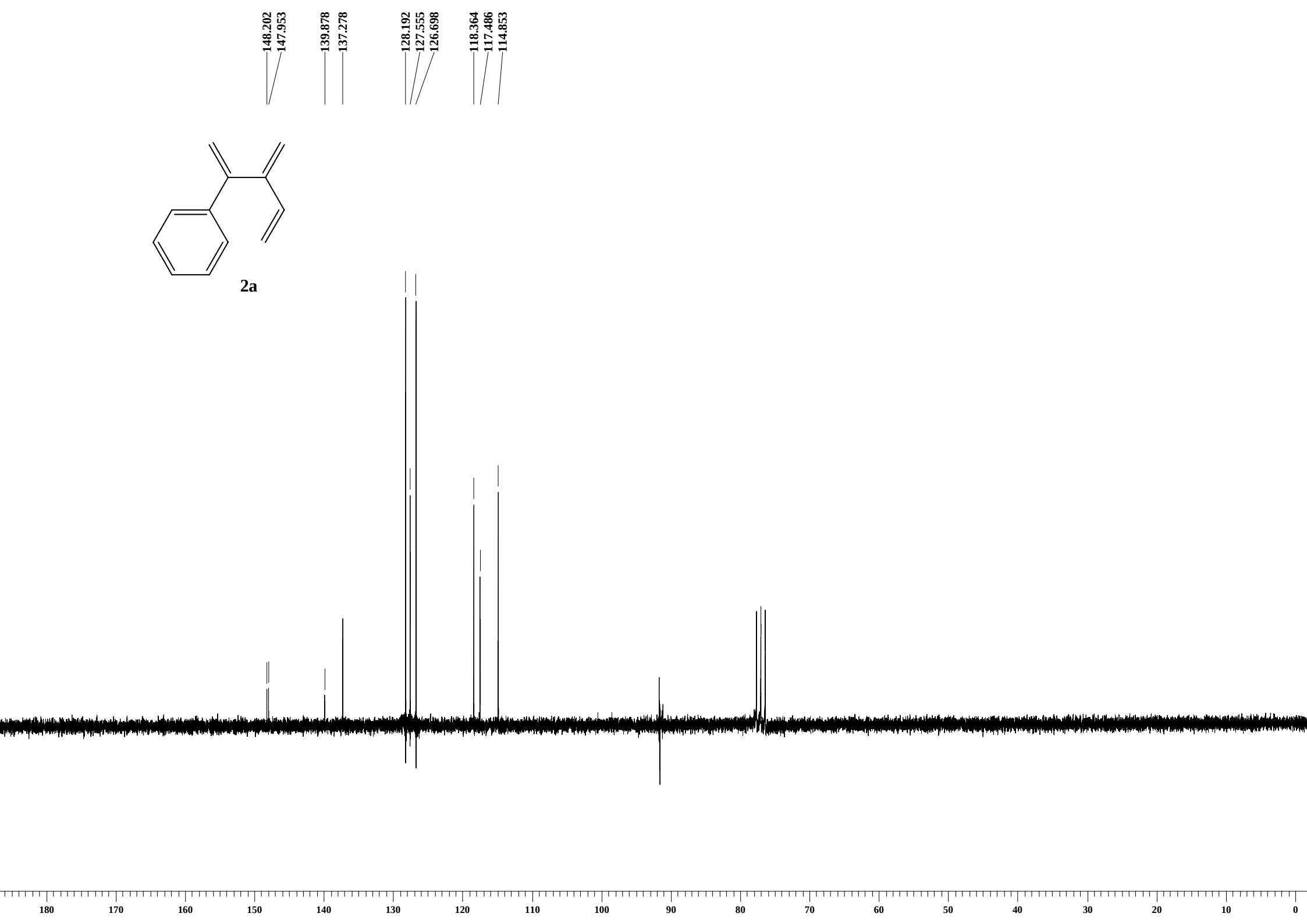


[Ru(C$_5$Me$_5$)(η^3-CH$_2$CHCHPr^n)(η^2-O$_2$CMe)][PF$_6$]



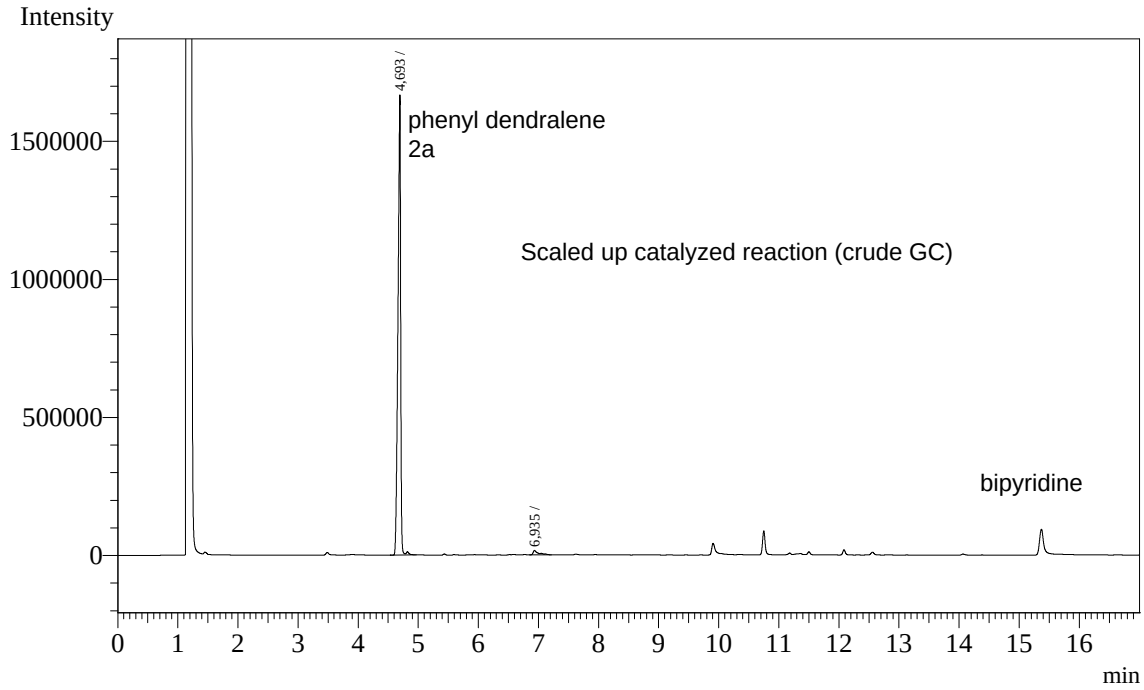



7.467
7.284
6.563
6.512
6.476
6.424
5.567
5.559
5.361
5.354
5.289
5.282
5.225
5.137
5.078
5.055
2a
6.6
1.0
1.1
6.0
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


148.202
147.953
139.878
137.278
128.192
127.555
126.698
118.364
117.486
114.853
2a
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Analysis Date & Time : 17/12/2008 09:50:20
User Name : Admin
Vial# : 12
Sample Name : MA17122008MS90ACNbip
Sample ID : MA17122008MS90ACNbip
Sample Type : Unknown
Injection Volume : 4,00
ISTD Amount :

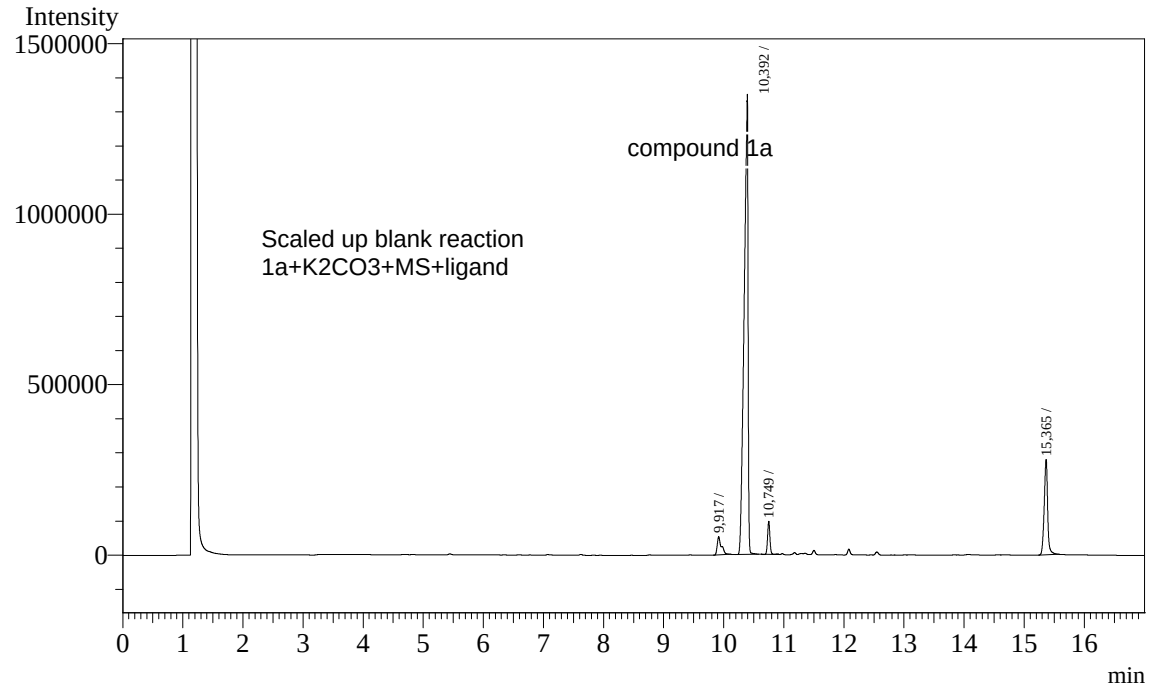
Data Name : D:\Eq. Achard\MA\MA17122008MS90ACNbip.gcd
Method Name : D:\Eq. Achard\MA\menyne.gcm



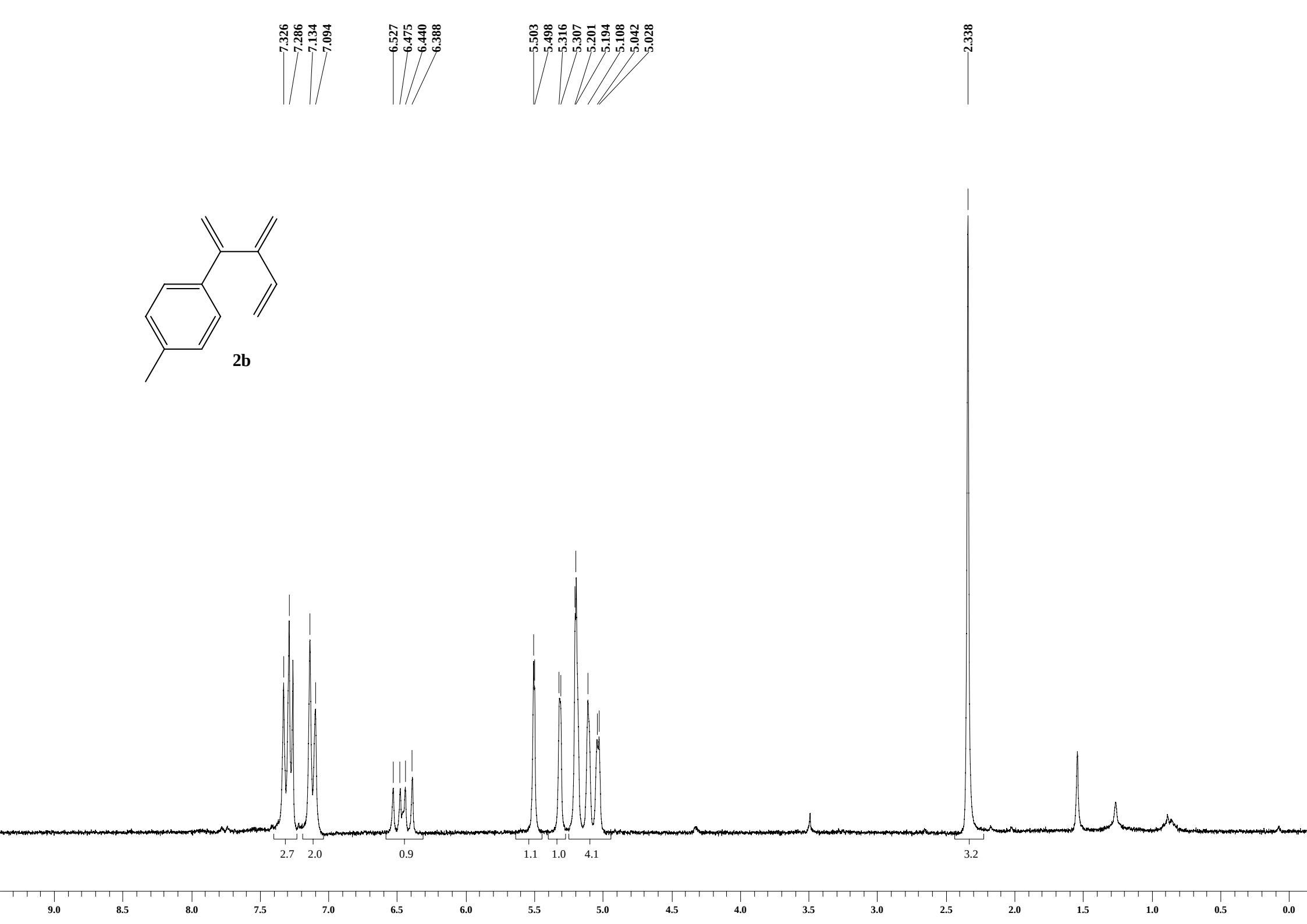
Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	4,693	5127713	1655687	98,083				
2	6,935	100241	16089	1,917				
Total		5227954	1671776					

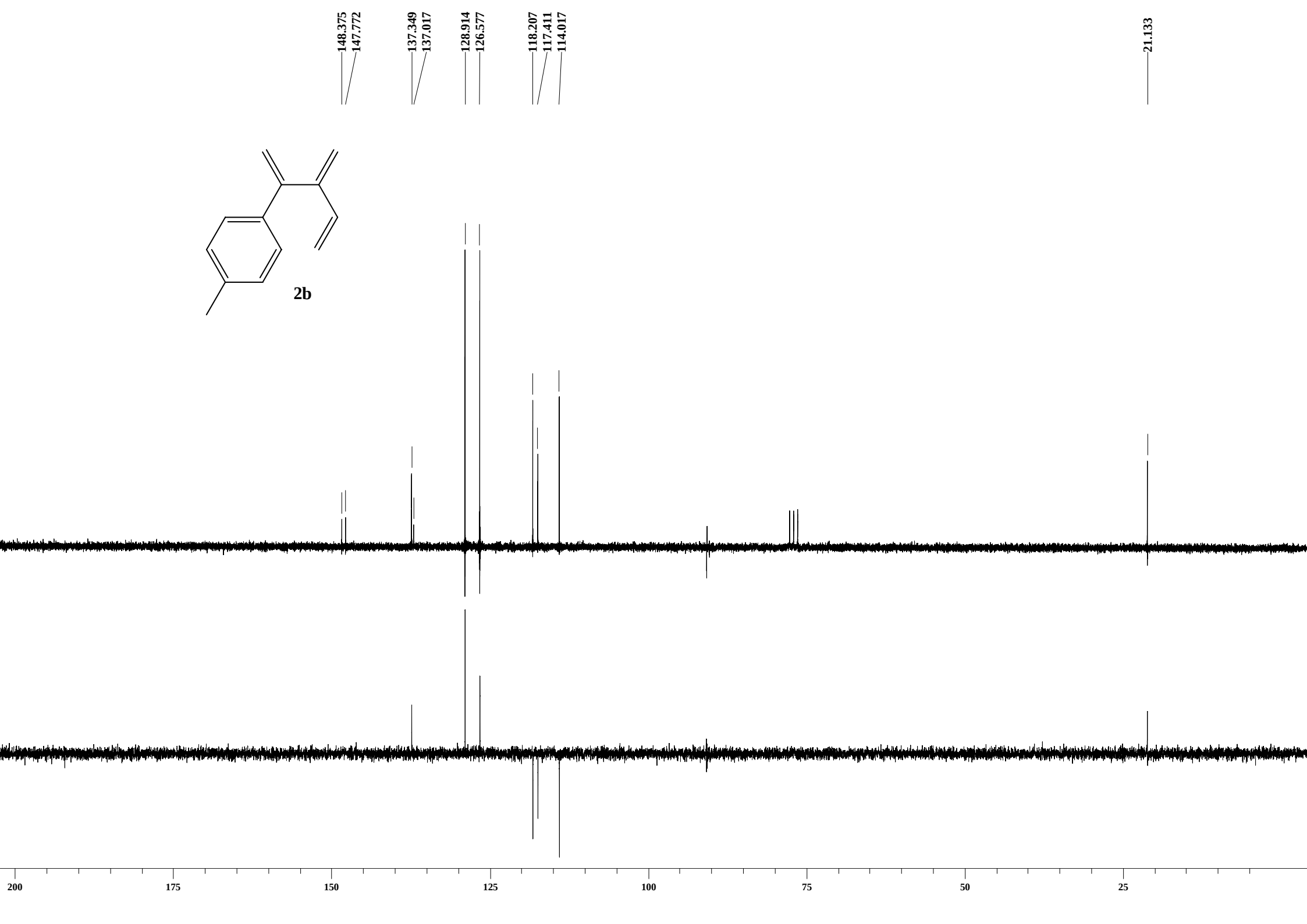
Analysis Date & Time : 18/12/2008 14:26:55
User Name : Admin
Vial# : 12
Sample Name : ma18122008BLANCms
Sample ID : ma18122008BLANCms
Sample Type : Unknown
Injection Volume : 4,00
ISTD Amount :

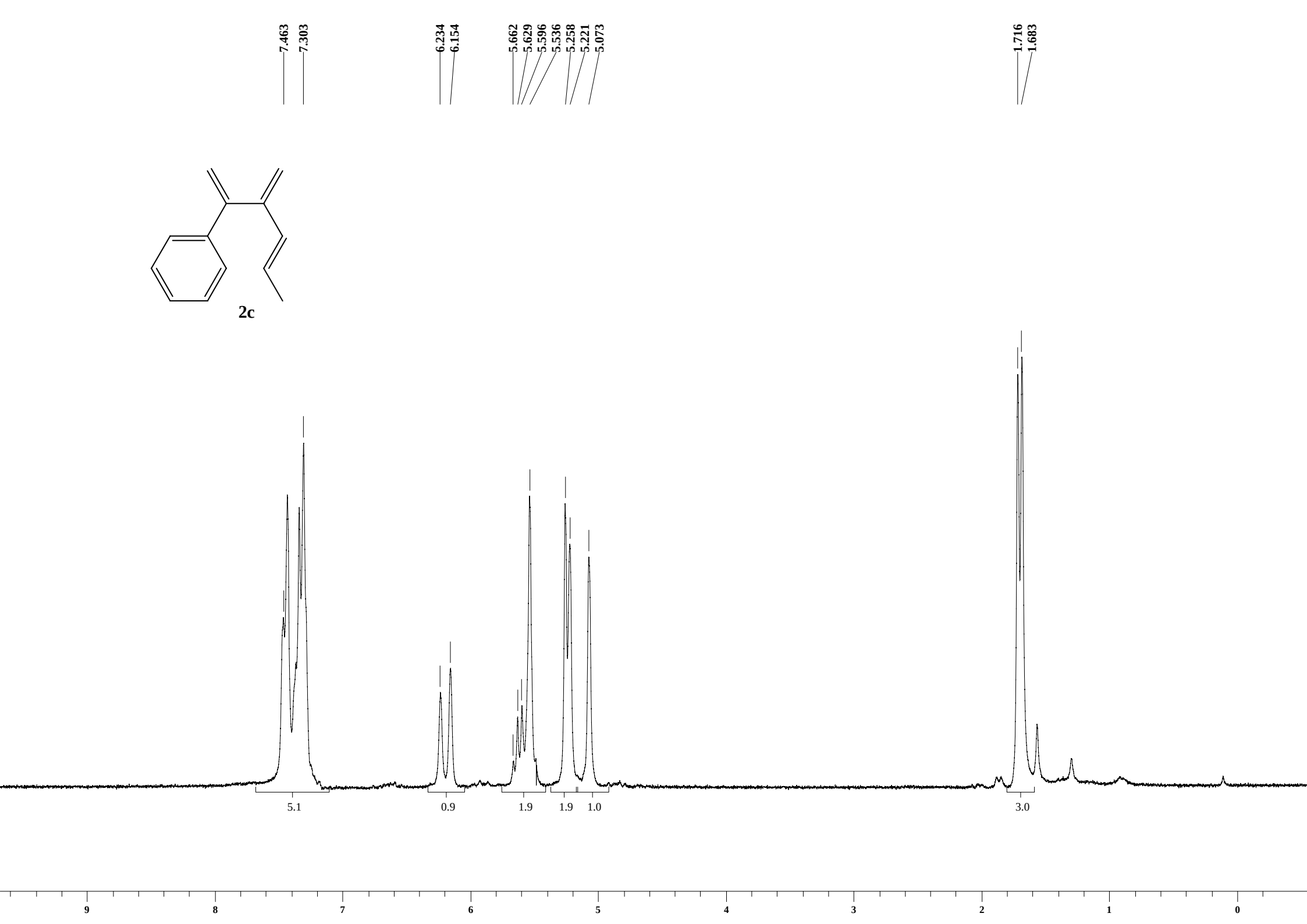
Data Name : D:\Eq. Achard\MA\ma18122008BLANCms.gcd
Method Name : D:\Eq. Achard\MA\menyne.gcm

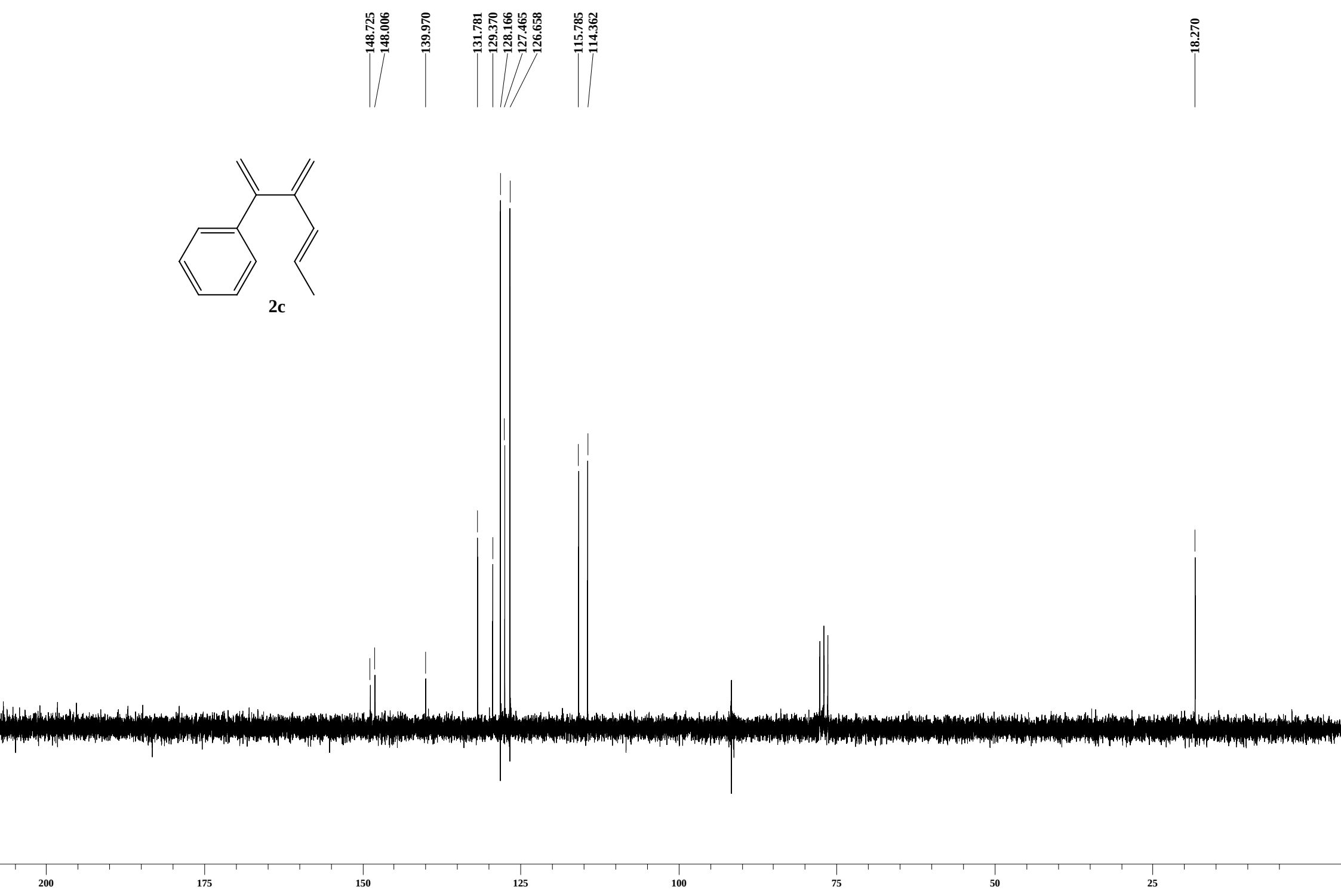


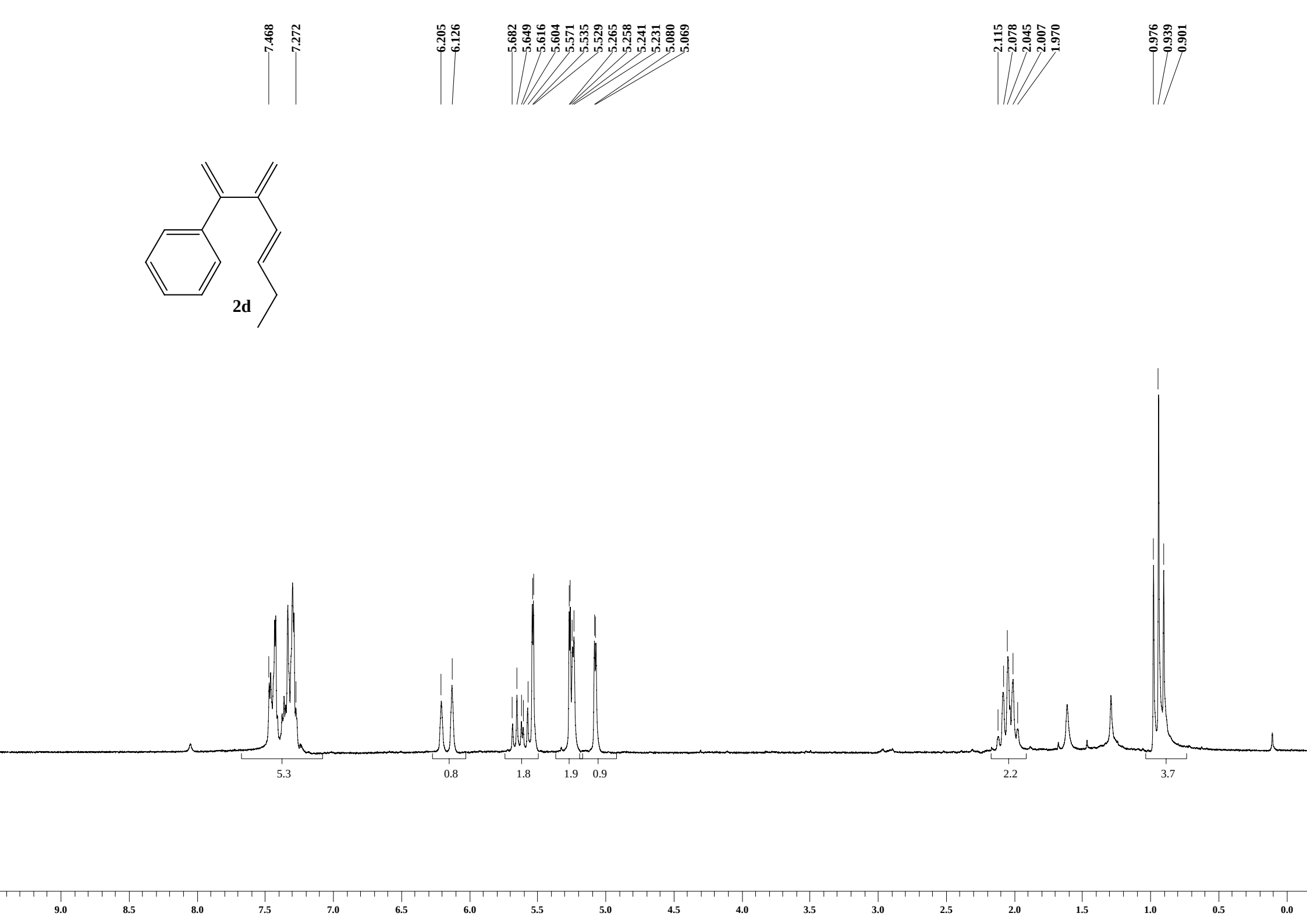
Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	9,917	257811	53204	3,372				
2	10,392	6015679	1335412	78,676				
3	10,749	258004	96084	3,374				
4	15,365	1114675	278763	14,578				
Total		7646169	1763463					

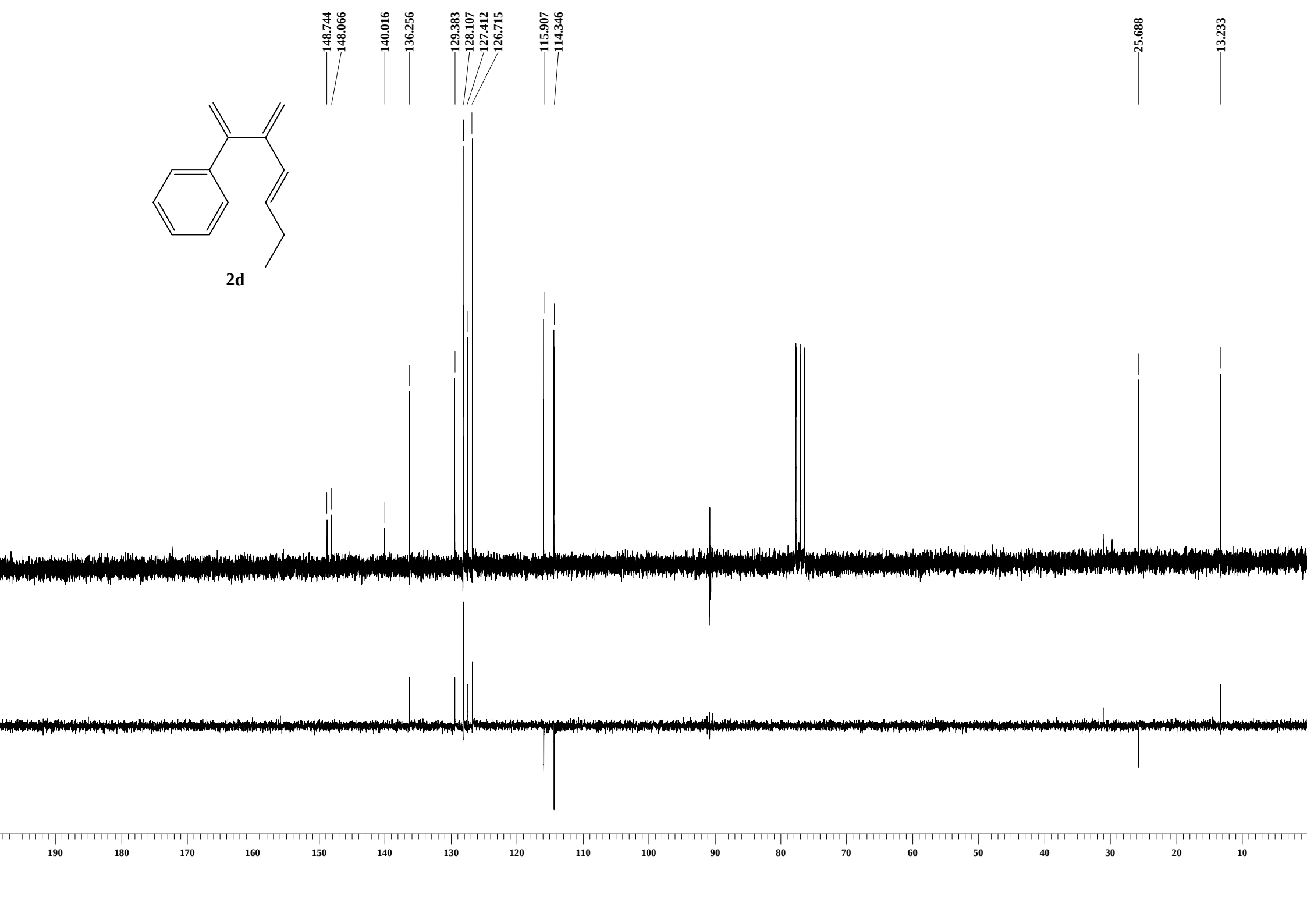

7.326
7.286
7.134
7.094
6.527
6.475
6.440
6.388
5.503
5.498
5.316
5.307
5.201
5.194
5.108
5.042
5.028
2.338
2b
2.7
2.0
0.9
1.1
1.0
4.1
3.2
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

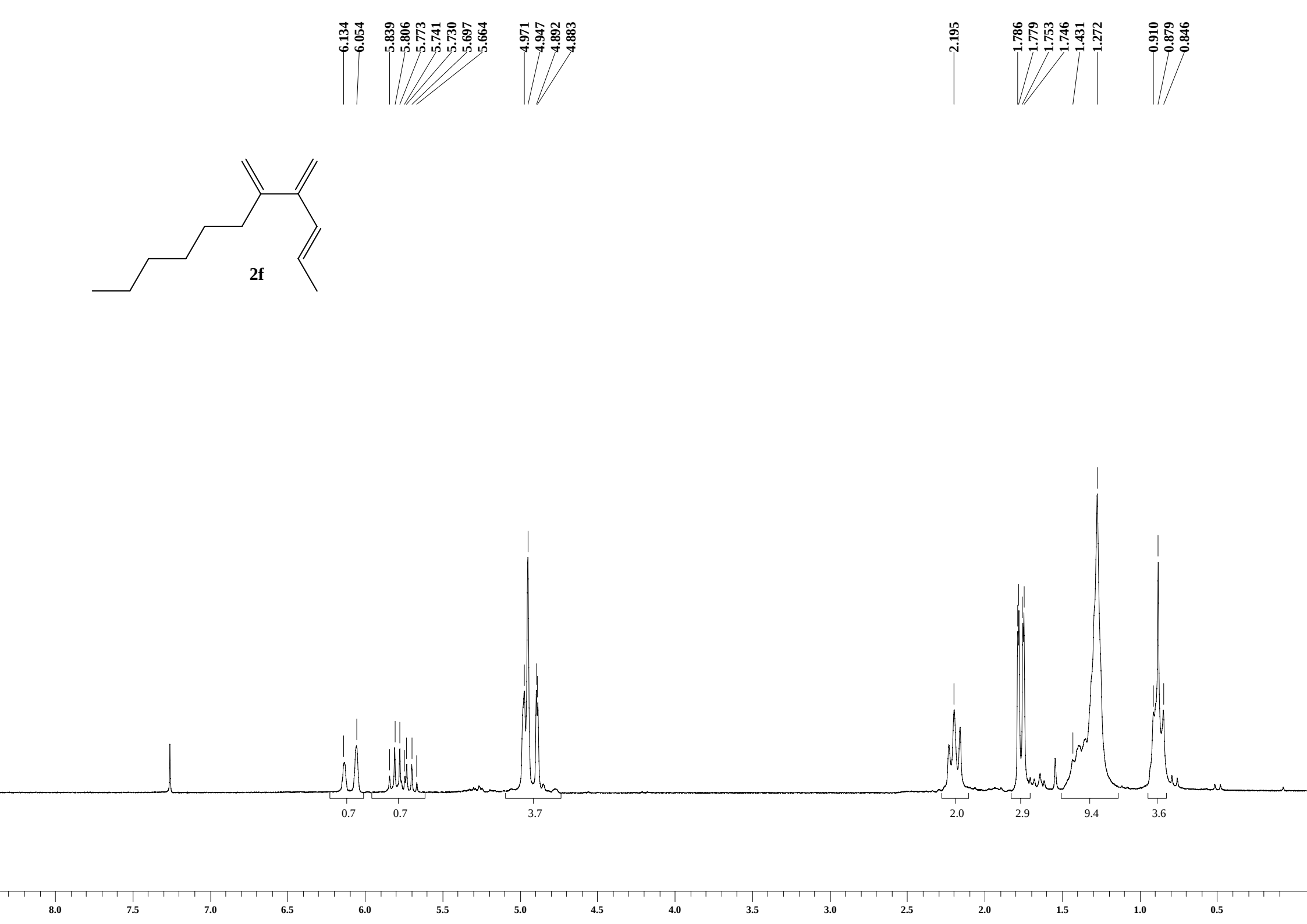

148.375
147.772
137.349
137.017
128.914
126.577
118.207
117.411
114.017
21.133
2b
200
175
150
125
100
75
50
25

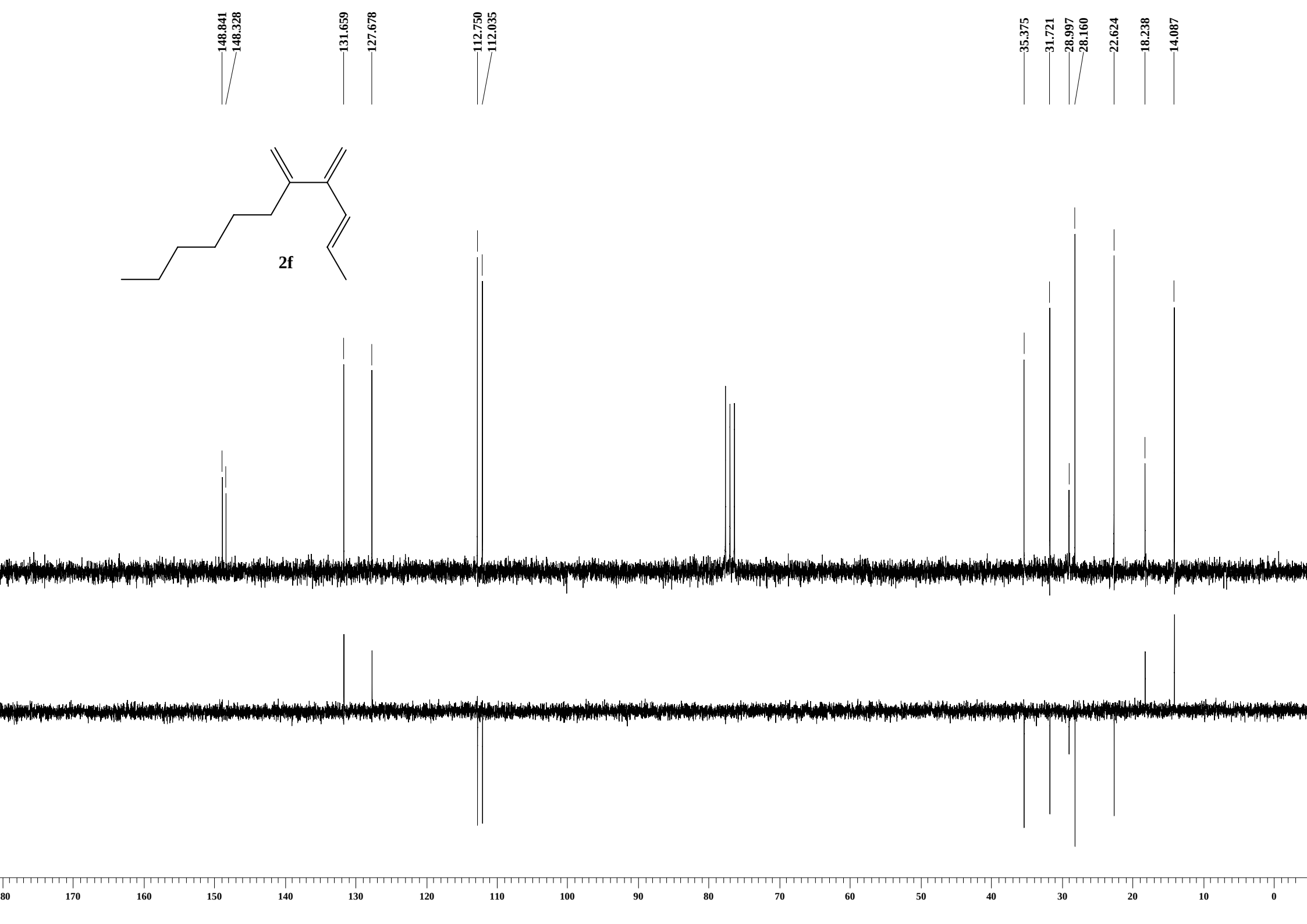

7.463
7.303
6.234
6.154
5.662
5.629
5.596
5.536
5.258
5.221
5.073
1.716
1.683
2c
5.1
0.9
1.9
1.9
1.0
3.0
9
8
7
6
5
4
3
2
1
0

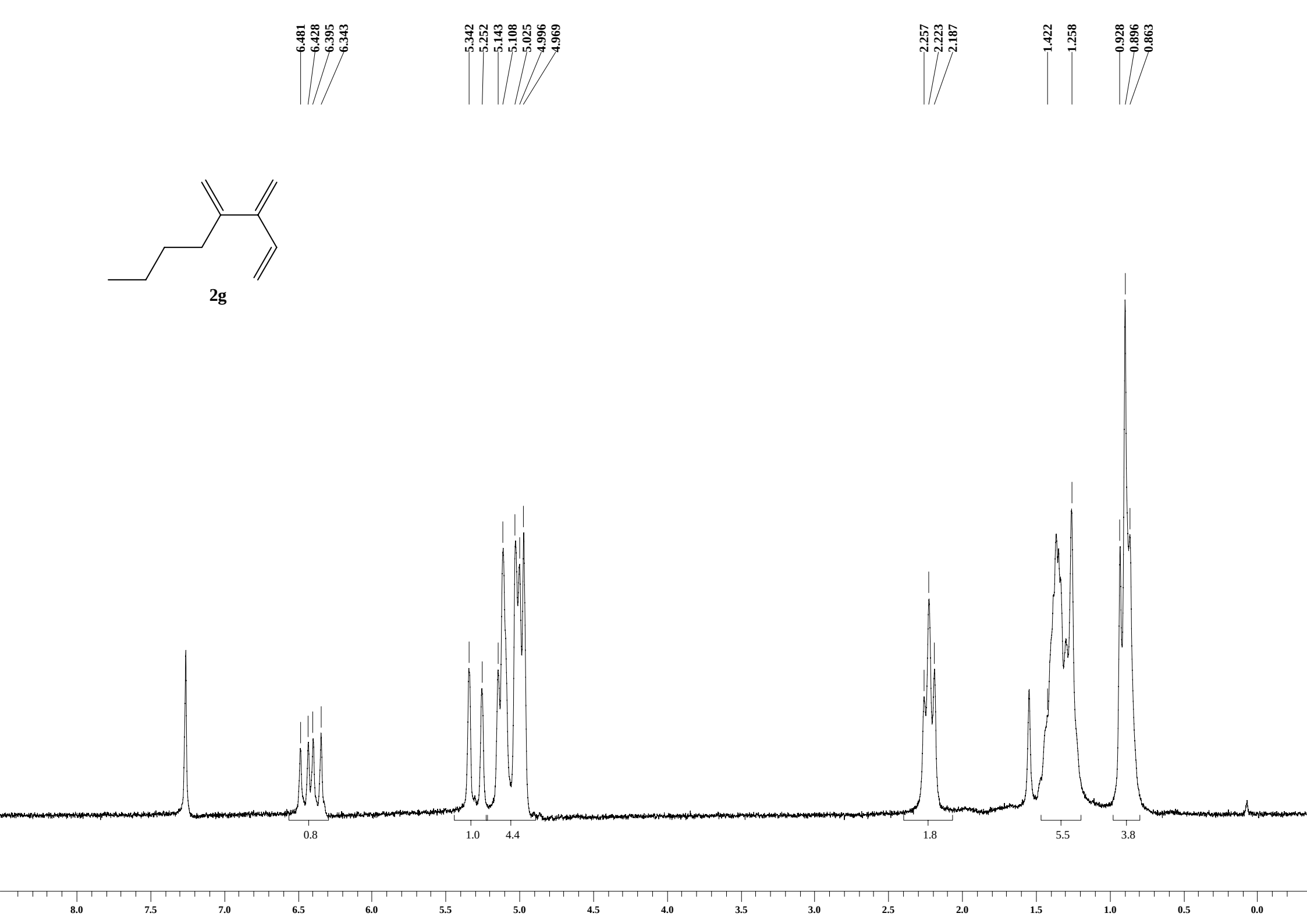

148.725
148.006
139.970
131.781
129.370
128.166
127.465
126.658
115.785
114.362
18.270
2c
200
175
150
125
100
75
50
25

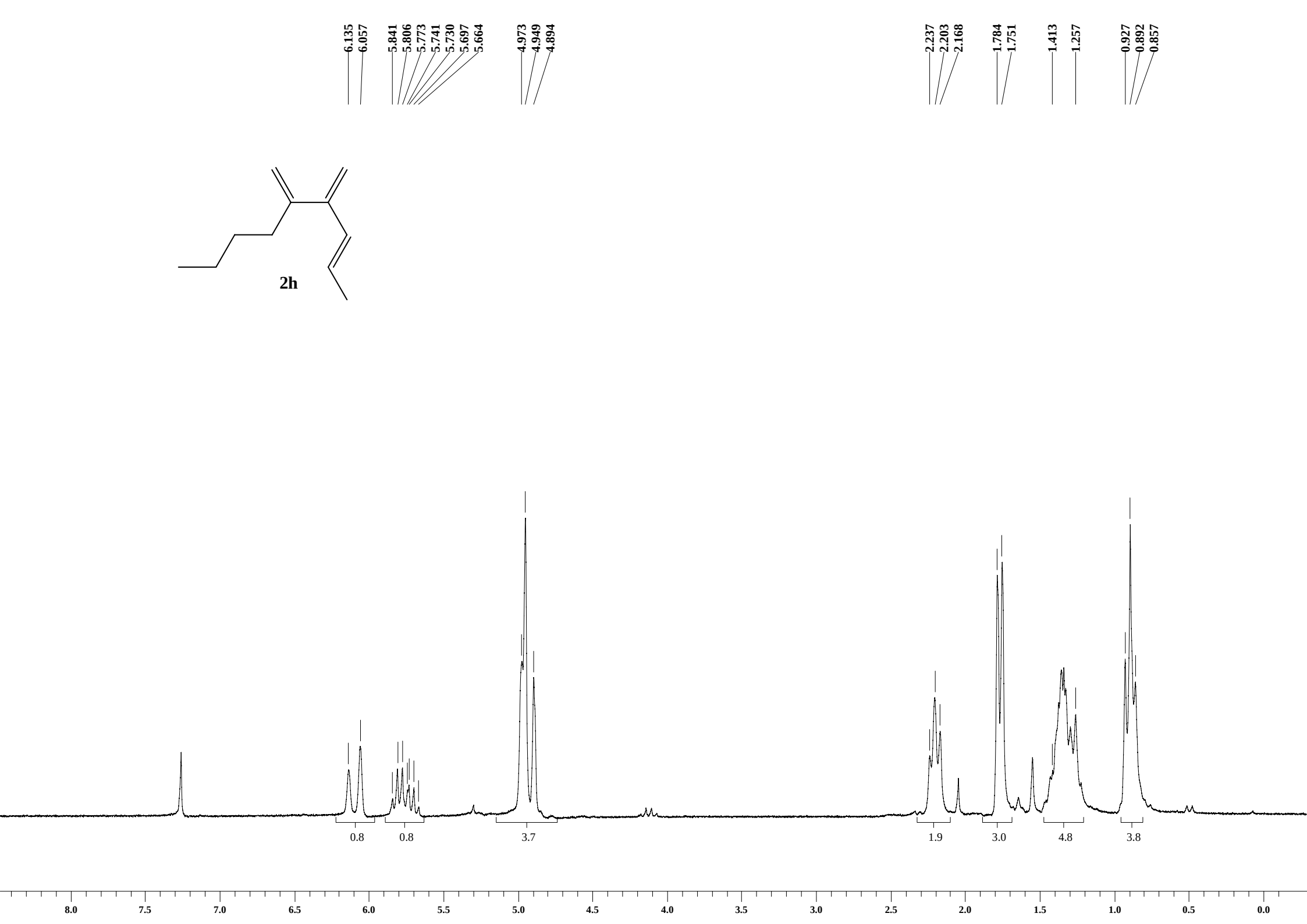

7.468
7.272
6.205
6.126
5.682
5.649
5.616
5.604
5.571
5.535
5.529
5.265
5.258
5.241
5.231
5.080
5.069
2.115
2.078
2.045
2.007
1.970
0.976
0.939
0.901
2d
5.3
0.8
1.8
1.9
0.9
2.2
3.7
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

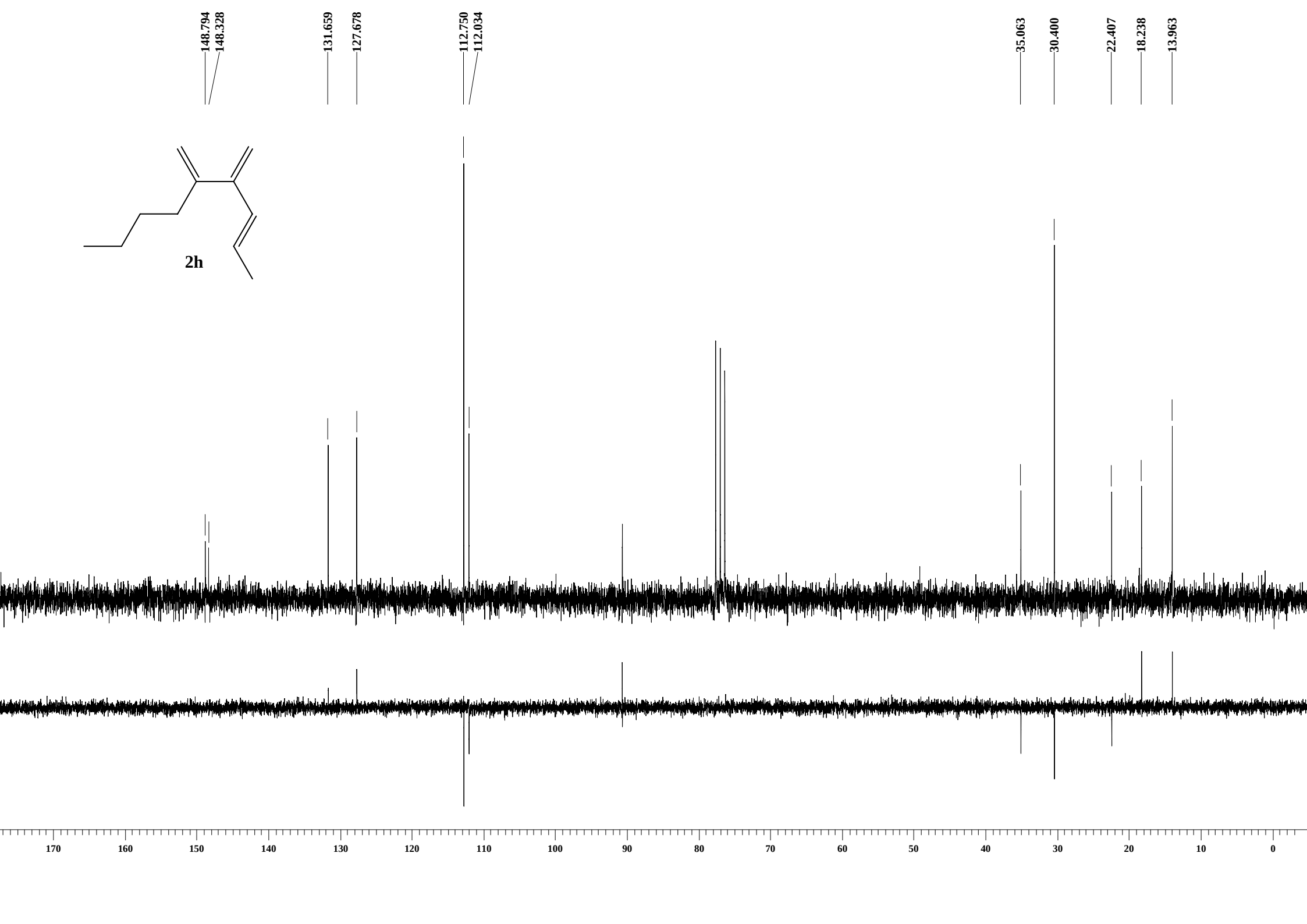

148.744
148.066
140.016
136.256
129.383
128.107
127.412
126.715
115.907
114.346
25.688
13.233
2d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

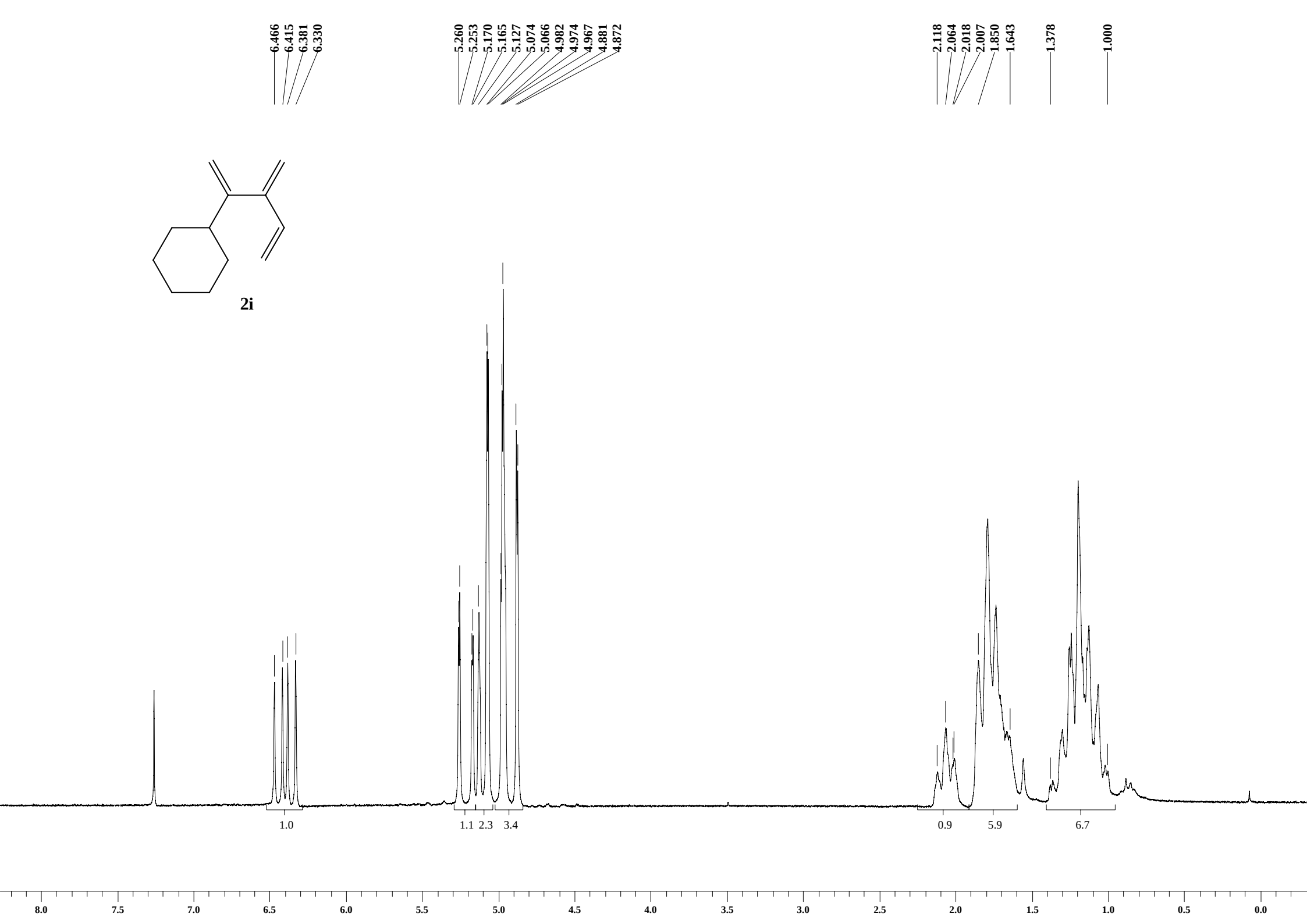

6.134
6.054
5.839
5.806
5.773
5.741
5.730
5.697
5.664
4.971
4.947
4.892
4.883
2.195
1.786
1.779
1.753
1.746
1.431
1.272
0.910
0.879
0.846
2f
0.7
0.7
3.7
2.0
2.9
9.4
3.6
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

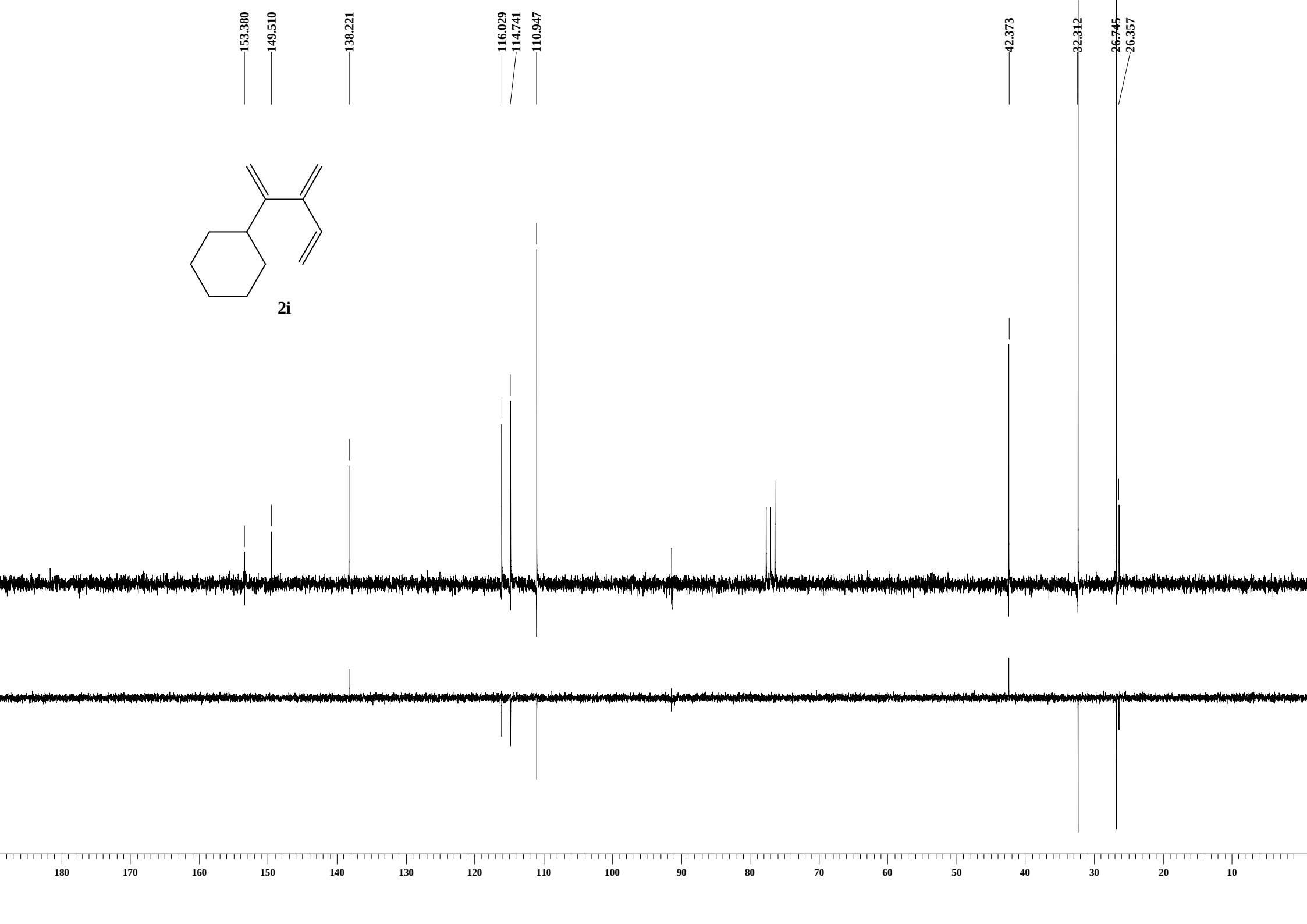

148.841
148.328
131.659
127.678
112.750
112.035
35.375
31.721
28.997
28.160
22.624
18.238
14.087
2f
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

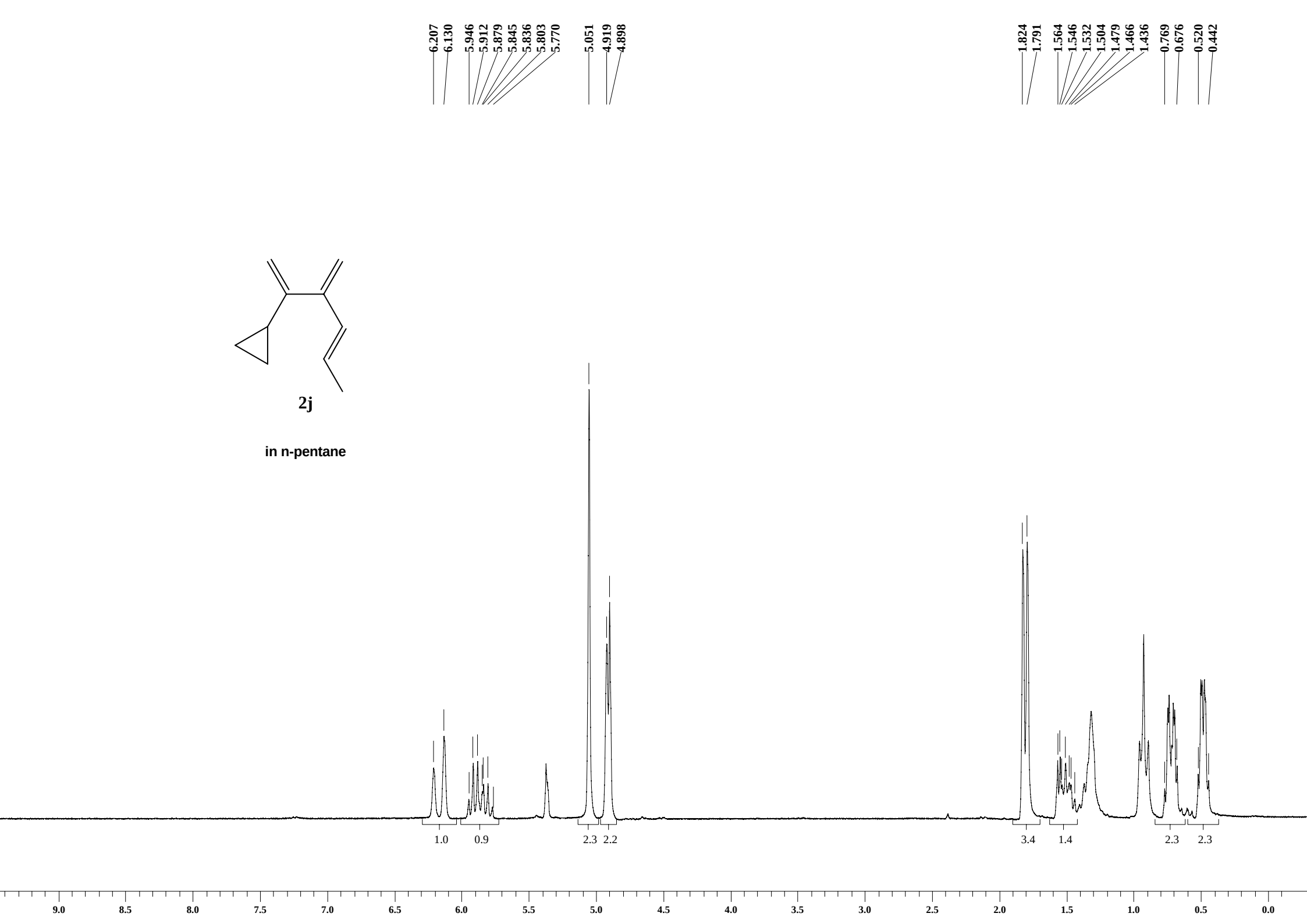

6.481
6.428
6.395
6.343
5.342
5.252
5.143
5.108
5.025
4.996
4.969
2.257
2.223
2.187
1.422
1.258
0.928
0.896
0.863
2g
0.8
1.0
4.4
1.8
5.5
3.8
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

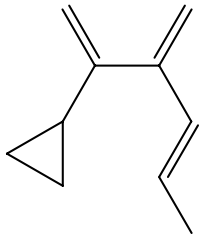

6.135
6.057
5.841
5.806
5.773
5.741
5.730
5.697
5.664
4.973
4.949
4.894
2.237
2.203
2.168
1.784
1.751
1.413
1.257
0.927
0.892
0.857
2h
0.8
0.8
3.7
1.9
3.0
4.8
3.8
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


148.794
148.328
131.659
127.678
112.750
112.034
35.063
30.400
22.407
18.238
13.963
2h
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


6.466
6.415
6.381
6.330
5.260
5.253
5.170
5.165
5.127
5.074
5.066
4.982
4.974
4.967
4.881
4.872
2.118
2.064
2.018
2.007
1.850
1.643
1.378
1.000
2i
1.0
1.1
2.3
3.4
0.9
5.9
6.7
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

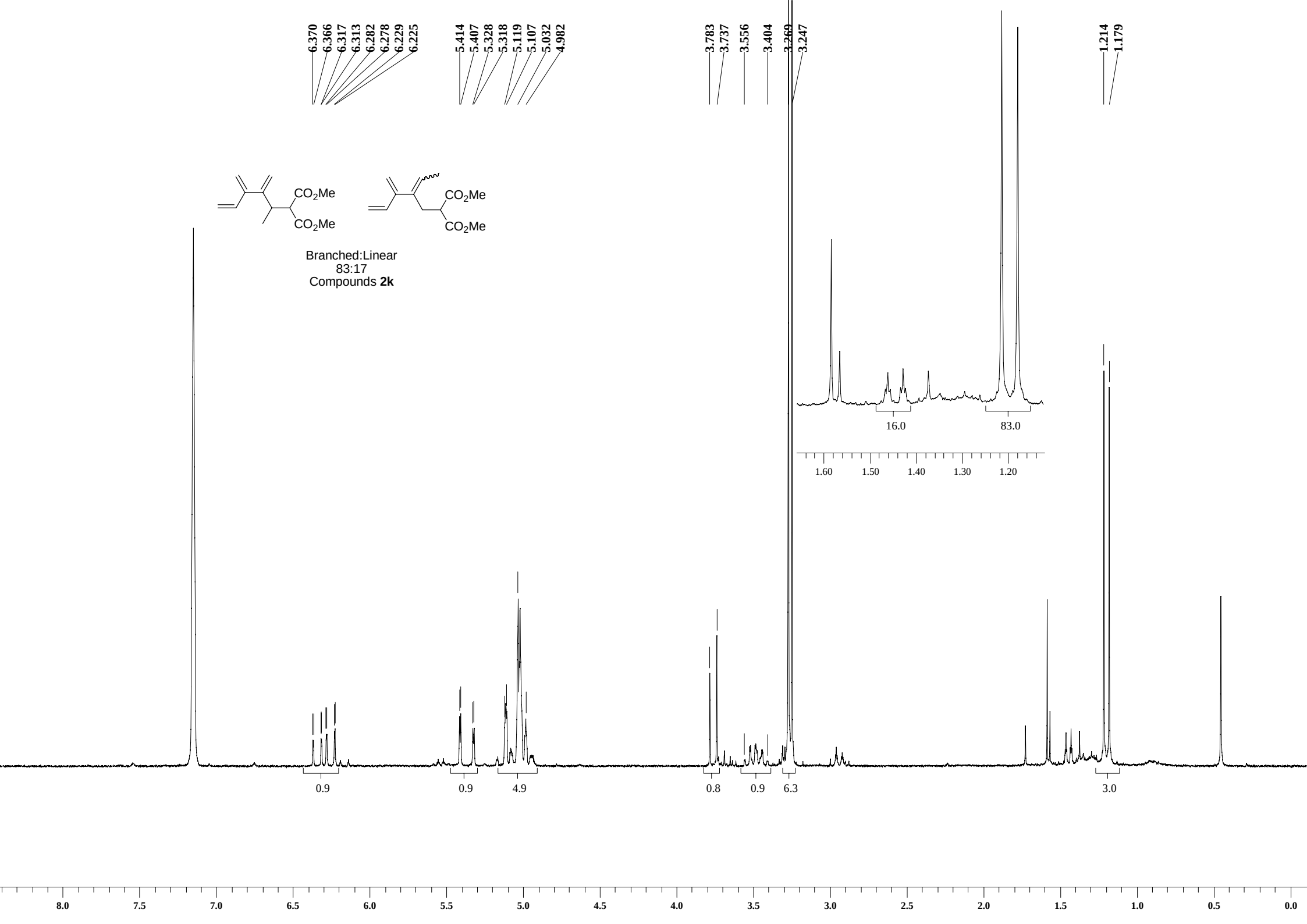

153.380
149.510
138.221
116.029
114.741
110.947
42.373
32.312
26.745
26.357
2i
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

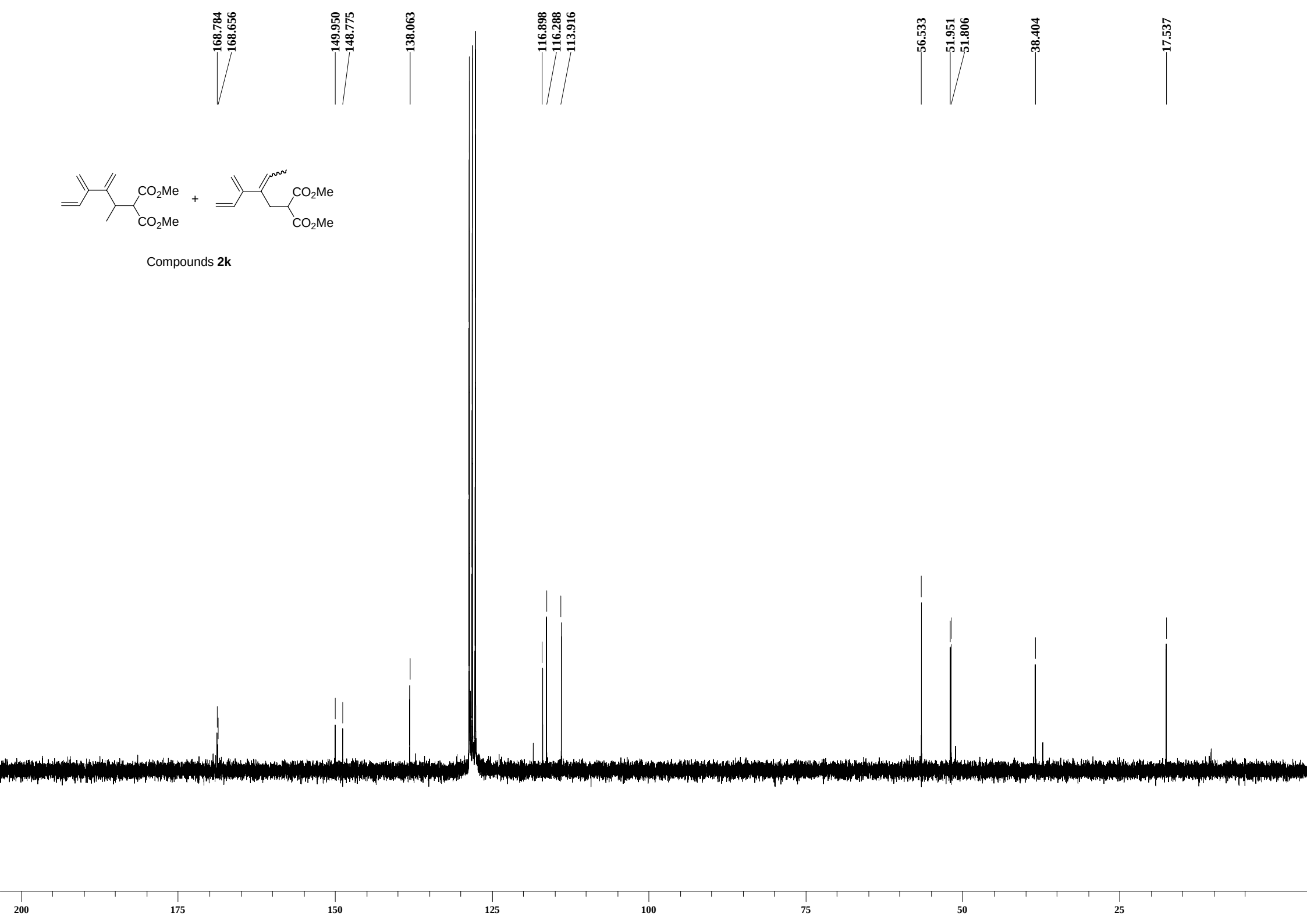

6.207
6.130
5.946
5.912
5.879
5.845
5.836
5.803
5.770
5.051
4.919
4.898
1.824
1.791
1.564
1.546
1.532
1.504
1.479
1.466
1.436
0.769
0.676
0.520
0.442
2j
in n-pentane
1.0
0.9
2.3
2.2
3.4
1.4
2.3
2.3
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0



2j

in n-pentane


6.370
6.366
6.317
6.313
6.282
6.278
6.229
6.225
5.414
5.407
5.328
5.318
5.119
5.107
5.032
4.982
3.783
3.737
3.556
3.404
3.269
3.247
1.214
1.179
CO2Me
CO2Me
CO2Me
CO2Me
Branched:Linear
83:17
Compounds 2k
16.0
83.0
1.60
1.50
1.40
1.30
1.20
0.9
0.9
4.9
0.8
0.9
6.3
3.0
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0



Compounds **2k**