Supplementary Material (ESI) for Chemical Communications

Supporting information for

Synthesis and structural analysis of a novel iodinated cyclopentadienone via ring-contraction iodination and its application in synthesis of alkyne-functionlized cyclopentadienones

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1. Tables

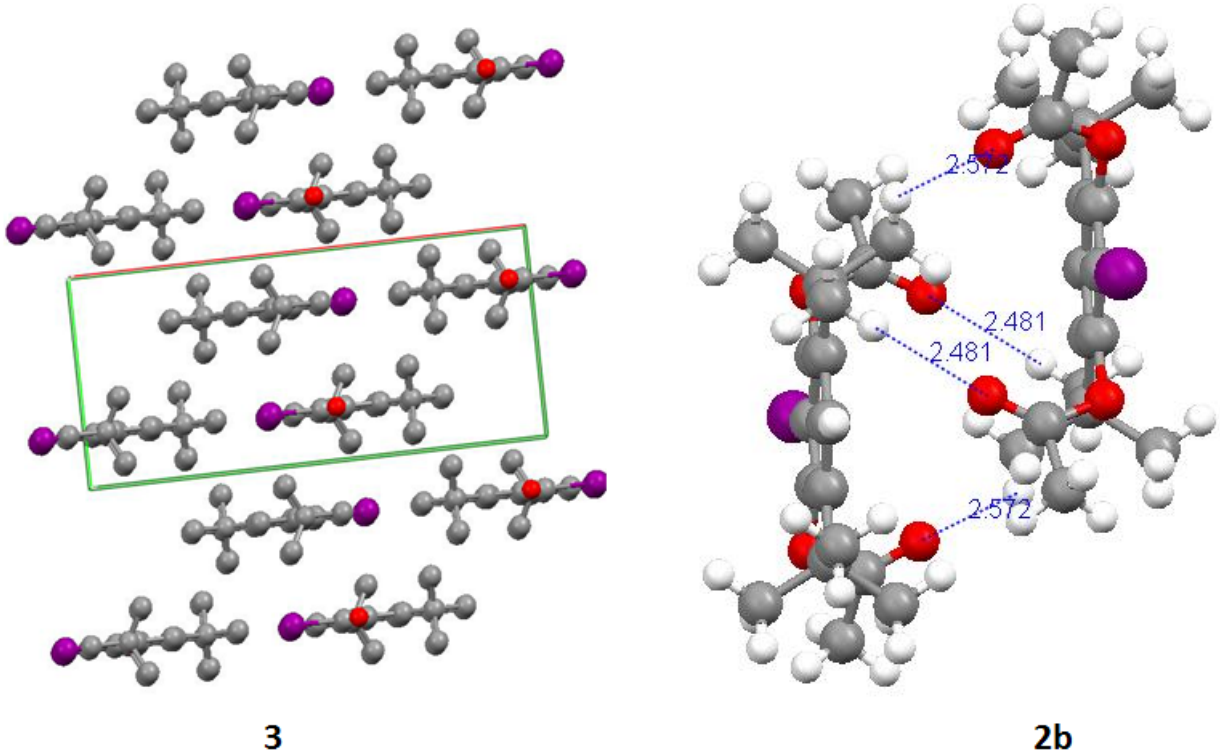
Table 1 Spectral characteristics of cyclopentadienones in chloroform

Compound	λ_{max}^{*}(nm)	ε($cm^{-1}M^{-1}$)	Compound	λ_{max}^{*} (nm)	ε ($cm^{-1}M^{-1}$)
3	448	305	**4m**	478	1423
4a	462	434	**4f**	480	395
4b	460	457	**4l**	482	1623
4e	466	398	**4i**	490	2204
4c	468	370	**4k**	490	1635
4d	468	384	**4g**	492	1598
4s	468	374	**4h**	492	1996
			4j	522	1751

Table2 UV-Visible absorption maxima of substituted cyclopentadienone in different solvents (nm)

	Hexane	Ether	EtOAc	Methanol	Acetone	CCl_4	CH_2Cl_2	$CHCl_3$
4l	473	475.5	476	479	478	478.5	480	481
4e	448	454.5	460	463	464	457	464.5	467
4h	479	480.5	483	485	485.5	485	486	488
3	437	439	441.5	445	444	442.5	446	445
4j	503	506	510	511	512	511	513	517
4s	446	452	457	462	461	456	463	464

2. Figures



3 **2b**

Fig. 1 Packing of **3** in its single crystal and the short O···H contact of **2b** in its crystal lattice

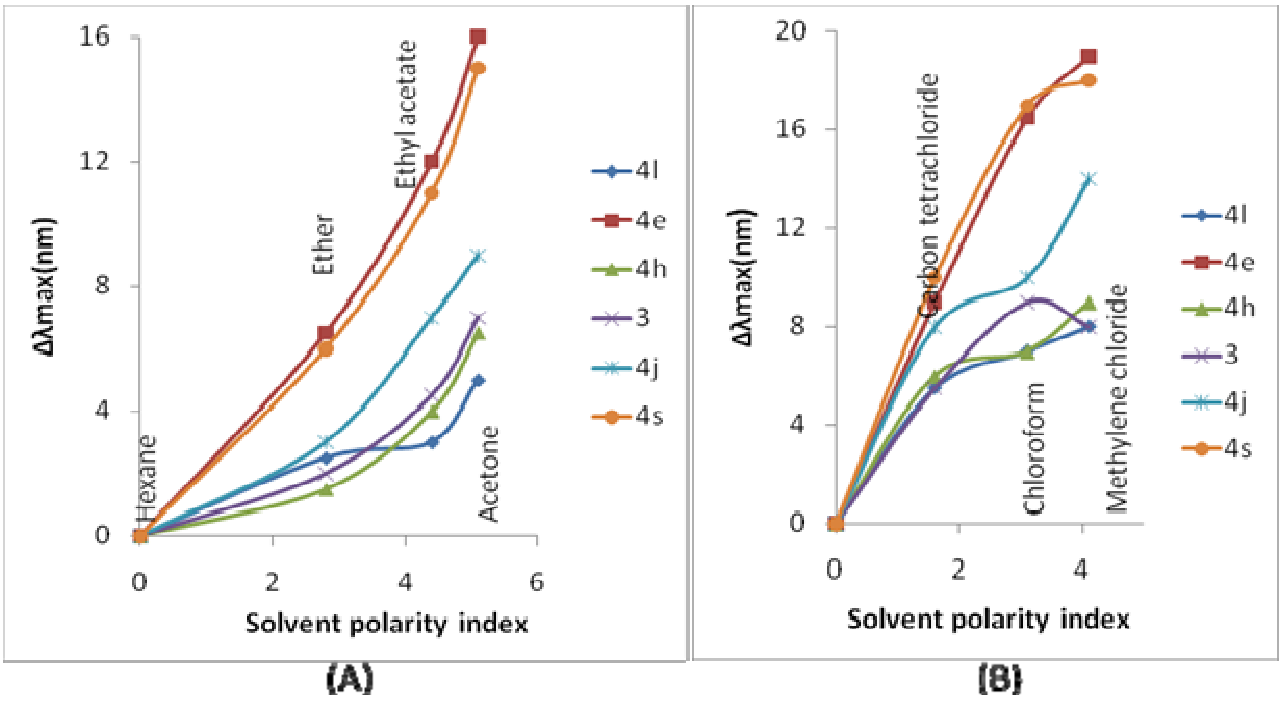


Fig. 2. The visible absorption maxima shift ($\Delta\lambda_{max}$) of substituted cyclopentadienones in solvents with different polarities. ($\Delta\lambda_{max} = \lambda_{max}^{solvent} - \lambda_{max}^{hexane}$); (A) in non-halogenated solvent, (B) in chlorinated solvents; Solvent polarity index values from Phenomenex technical resources.

3. Experiment Section

- **Materials:**

All the chemicals and reagents were purchased from Acros Organics. Tetrahydrofuran was freshly distilled from sodium-potassium alloy. Triethylamine was freshly distilled from sodium hydride. ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively, using a Varian ANOVA spectrometer. X-ray data were collected on an Bruker SMART 1000 CCD diffractometer. UV−vis absorption spectra were measured on a Hewlett-Packard 8452A diode array spectrophotometer. GCMS analyses were performed with an Agilent 6890 gas chromatograph and Agilent 5937 mass-spectrometer instrument equipped with an Agilent HP-5MS column (30 m x 0.25 mm), using helium (99.9995 %) as a carrier gas, a split ratio of 30:1, and an injection volume of 1-3 µL. In the standard GC program,.the oven temperature was kept at 50 °C for 2 min, then raised to 200 °C at a rate of 25 °C per minute, and kept at 200 for 20 min. The solvent delay for MS acquisition was 5 min.

- **General procedures:**

Compound **2a** and compound **3**

(1) Oxygen free conditions: 50 mL of a degased aqueous solution of 0.840 g sodium bicarbonate (10 mmol) were slowly added, with stirring, to 50 mL of a degased methanol solution of 2.223 g compound **1** and 2.538 g iodine (10 mmol). Reaction mixtures were allowed to react for 1 hour under nitrogen protection, followed by extraction of products with methylene chloride. The resulting red methylene chloride solution was washed 3 times with 10 mL saturated sodium thiosulfate solution and 3 times with water. This solution was dried overnight over anhydrous sodium sulfate. A mixture of compound **2** and compound **3** were obtained by vacuum evaporation, following which 2.611g pure compound **2** and 0.637g pure compound **3** were obtained by column chromatography using hexanes/ethyl acetate solvent pair as eluent.

(2) Oxygen rich conditions: 50 mL of an aqueous solution of 0.840 g sodium bicarbonate (10 mmol) were slowly added, with stirring, to a 50 mL methanol solution of 2.223 g compound **1** and 2.538 g iodine (10 mmol) in the presence of bubbled oxygen. Reaction mixtures were allowed to react for 1 hour, followed by same work up procedures as above. 2.437g pure compound **2** and 0.254g pure compound **3** were obtained.

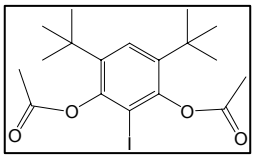
Compound **2b**

0.75 mL of acetyl chloride was slowly added to a 20 mL THF solution of 1.74 g compound **2a** at -5°C with rapid stirring, followed by dropwise addition of 5.6 mL triethylamine. The reaction mixture was then allowed to warm to room temperature and to stir for 30 minutes. Following quenching of the reaction by addition of ice, the product was extracted into ether which was then dried overnight over anhydrous sodium sulfate. After evaporation of solvent from the crude product, 2.118 g pure compound **2b** were obtianed by column chromatography using hexanes/ethyl acetate solvent pair as eluent.

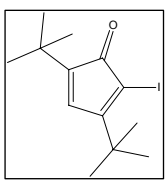
Compound **4a-m, 4s**

Detailed procedures are described in our previous work [10]

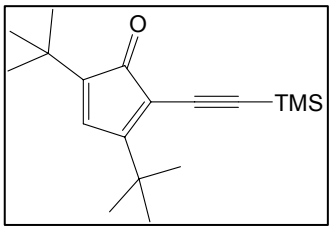
- Physical properties of products:



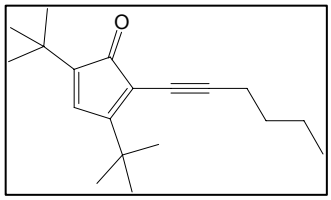
4,6-di-*tert*-butyl-2-iodo-1,3-phenylene diacetate (2b): ^{1}H NMR (400MHz, $CDCl_3$) δ 7.46 (s, 1H), 2.376 (s, 6H), 1.329 (s, 18H); ^{13}C NMR (100MHz, $CDCl_3$) δ 168.8 (2C), 148.7 (2C), 139.7 (2C), 126.8 (1C), 95.8 (1C), 35.1 (2C), 30.5 (6C), 22.4 (2C).



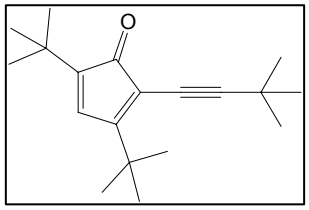
3,5-di-*tert*-butyl-2-iodocyclopenta-2,4-dienone (3): ^{1}H NMR (400MHz, $CDCl_3$) δ 6.74 (s, 1H), 1.317 (s, 9H), 1.165 (s, 9H); ^{13}C NMR (100MHz, $CDCl_3$) δ 196.3 (1C), 167.3 (1C), 142.1 (1C), 139.9 (1C), 80.0 (1C), 32.3 (1C), 29.7 (1C), 28.9 (3C), 28.1 (3C). HRMS (ESI) Calcd for $C_{13}H_{19}IO$ [MNa^+] 341.0378, found 341.0376.



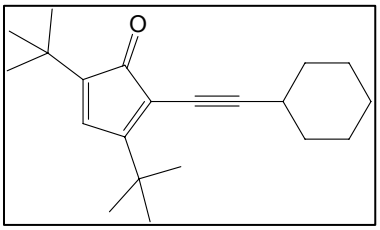
3,5-di-*tert*-butyl-2-((trimethylsilyl)ethynyl)cyclopenta-2,4-dienone (4a): ^{1}H NMR (400MHz, $CDCl_3$) δ 6.64 (s, 1H), 1.29 (s, 9H), 1.16 (s, 9H), 0.20 (s, 9H); ^{13}C NMR (100MHz, $CDCl_3$) δ 198.6 (1C), 170.4 (1C), 142.4 (1C), 137.7 (1C), 107.6 (1C), 104.7 (1C), 97.9 (1C), 34.8(1C), 32.1(1C), 29.0 (3C), 28.0 (3C), 0.2(3C). HRMS (ESI) Calcd for $C_{18}H_{28}OSi$ [MNa^+] 311.1807, found 311.1785.



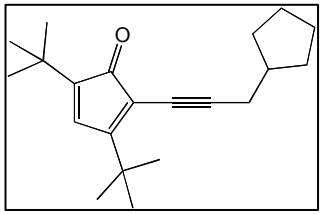
3,5-di-*tert*-butyl-2-(hex-1-yn-1-yl)cyclopenta-2,4-dienone (4b): ^{1}H NMR (400MHz, $CDCl_3$) δ 6.63 (s, 1H), 2.42 (t, 2H, J=7.0 Hz), 1.55 (m, 2H), 1.45 (m, 2H), 0.91 (t, 3H, J=7.2 Hz); ^{13}C NMR (100MHz, $CDCl_3$) δ 199.4 (1C), 166.9 (1C), 141.5 (1C), 138.1 (1C), 108.1 (1C), 100.3 (1C), 73.5 (1C), 34.4 (1C), 31.9 (1C), 30.7 (1C), 29.1 (3C), 28.1 (3C), 22.1 (1C), 19.7 (1C), 13.6 (1C). HRMS (ESI) Calcd for $C_{19}H_{28}O$ [MNa^+] 295.2038, found 295.2013.



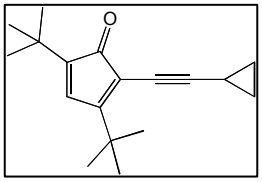
3,5-di-*tert*-butyl-2-(3,3-dimethylbut-1-yn-1-yl)cyclopenta-2,4-dienone (4c): ^{1}H NMR (400MHz, $CDCl_3$) δ 6.59 (s, 1H), 1.25 (s, 18H), 1.12 (s, 9H); ^{13}C NMR (100MHz, $CDCl_3$) δ 199.5 (1C), 167.0 (1C), 141.5 (1C), 138.0 (1C), 109.8 (1C), 108.0 (1C), 72.1 (1C), 34.4 (1C), 31.9 (1C), 30.7 (3C), 29.1 (3C), 28.5 (1C), 28.1 (3C). HRMS (ESI) Calcd for $C_{19}H_{28}O$ [MNa^+] 295.2038, found 295.2023.



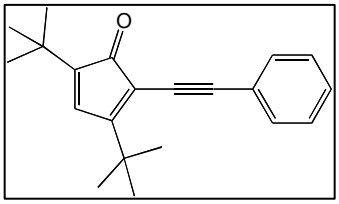
3,5-di-*tert*-butyl-2-(cyclohexylethynyl)cyclopenta-2,4-dienone (4d): ^{1}H NMR (400MHz, $CDCl_3$) δ 6.63 (s, 1H), 2.61 (m, 1H), 1.81 (m, 2H), 1.72 (m, 2H), 1.50 (m, 3H), 1.31 (m, 3H), 1.27 (s, 9H), 1.16 (s, 9H); ^{13}C NMR (100MHz, $CDCl_3$) δ 199.5 (1C), 167.0 (1C), 141.5 (1C), 138.1 (1C), 108.1 (1C), 104.3 (1C), 73.5 (1C), 34.4 (1C), 32.5 (2C), 31.9 (1C), 30.1 (1C), 29.1 (3C), 28.1 (3C), 25.9 (2C), 24.8 (1C). HRMS (ESI) Calcd for $C_{21}H_{30}O$ [MNa^+] 321.2194, found 321.2174.



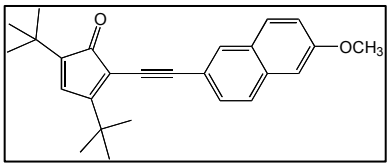
3,5-di-*tert*-butyl-2-(3-cyclopentylprop-1-yn-1-yl)cyclopenta-2,4-dienone (4e): ^{1}H NMR (400MHz, $CDCl_3$) δ 6.63 (s, 1H), 2.42 (d, 2H, J=6.8), 1.82-2.27 (m, 2H), 1.78 (m, 2H), 1.45-1.67 (m, 4H), 1.43 (s, 1H), 1.29 (s, 9H), 1.17 (s, 9H); ^{13}C NMR (100MHz, $CDCl_3$) δ 199.5 (1C), 166.8 (1C), 141.5 (1C), 138.1 (1C), 108.2 (1C), 99.9 (1C), 73.5 (1C), 39.2 (1C), 34.3 (1C), 31.9 (1C), 31.8 (2C), 29.1 (3C), 28.1 (3C), 25.9 (1C), 24.8 (2C). HRMS (ESI) Calcd for $C_{21}H_{30}O$ [MNa^+] 321.2194, found 321.2187.



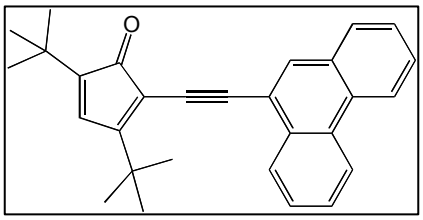
3,5-di-*tert*-butyl-2-(cyclopropylethynyl)cyclopenta-2,4-dienone(4f):
^{1}H NMR (400MHz, $CDCl_3$) δ 6.62 (s, 1H), 1.46 (m, 1H), 1.25 (s, 9H), 1.15 (s, 9H), 0.83 (m, 2H), 0.76 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 199.4 (1C), 167.0 (1C), 141.5 (1C), 138.1 (1C), 108.0 (1C), 103.3 (1C), 68.8 (1C), 34.3 (1C), 31.9 (1C), 29.1 (3C), 28.1 (3C), 8.8 (2C), 0.85 (1C). HRMS (ESI) Calcd for $C_{18}H_{24}O$ [MNa^+] 279.1725, found 279.1715.



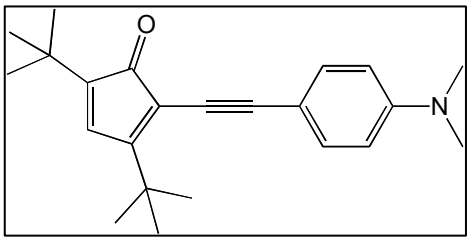
3,5-di-*tert*-butyl-2-(phenylethynyl)cyclopenta-2,4-dienone (4g): ^{1}H NMR (400MHz, $CDCl_3$) δ 7.47 (m, 2H), 7.30 (m, 3H), 6.63 (s, 1H), 1.35 (s, 9H), 1.20 (s, 9H); ^{13}C NMR (100MHz, $CDCl_3$) δ 198.8(1C), 168.8 (1C), 142.4 (1C), 138.3 (1C), 131.2 (2C), 128.2 (3C), 123.6 (1C) 107.6 (1C), 98.7 (1C), 82.9 (1C), 34.8 (1C), 32.1 (1C), 29.1 (3C), 28.2 (3C). HRMS (ESI) Calcd for $C_{21}H_{24}O$ [MNa^+] 315.1725, found 315.1718.



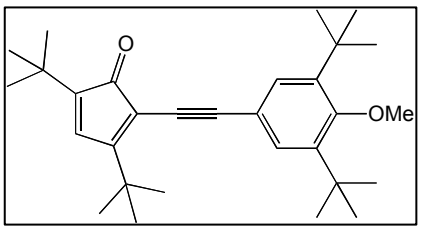
3,5-di-*tert*-butyl-2-((6-methoxynaphthalen-2-yl)ethynyl)-cyclopenta-2,4-dienone (4h): ^{1}H NMR (400MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.65 (dd, 2H, J_1=9.2Hz, 8.0 Hz), 7.45 (d, 1H, J=9.2), 7.11 (dd, 1H, J=8.8, 1.2 Hz), 7.07 (s, 1H), 6.63 (s, 1H), 3.89 (s, 3H), 1.35 (s, 9H), 1.18 (s, 9H); ^{13}C NMR (100MHz, $CDCl_3$) δ 198.8(1C), 168.8 (1C), 158.3 (1C), 142.4 (1C), 138.3 (1C), 134.1 (1C), 130.9 (1C), 129.3 (1C), 128.7 (1C), 128.5 (1C), 126.7 (1C), 119.3 (1C), 118.6 (1C), 107.8 (1C), 105.8 (1C), 99.4 (1C), 82.7 (1C), 55.3 (1C), 34.8 (1C), 32.1 (1C), 29.1 (3C), 28.3 (3C). HRMS (ESI) Calcd for $C_{26}H_{29}O_2$ [MNa^+] 395.1987, found 395.1988.



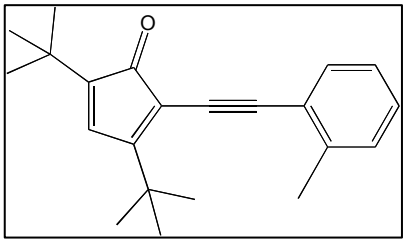
3,5-di-*tert*-butyl-2-(phenanthren-9-ylethynyl)cyclopenta-2,4-dienone (4i) ^{1}H NMR (400MHz, $CDCl_3$) δ 8.58-8.70 (m, 3H), 8.00 (s, 1H), 7.85 (dd, 2H, J=7.8, 1.2Hz), 7.58-7.74 (m, 4H), 6.78 (s, 1H), 1.44 (s, 9H), 1.24 (s, 9H); ^{13}C NMR (100MHz, $CDCl_3$) δ 198.8(1C), 168.8 (1C), 142.8 (1C), 138.3 (1C), 131.4 (1C), 131.3 (1C), 131.1 (1C), 130.2 (1C), 130.0 (1C), 128.5 (1C), 127.4 (2C), 127.3(1C), 127.0 (1C), 126.9 (1C), 122.6 (2C), 120.2 (1C), 107.8 (1C), 97.3 (1C), 87.5 (1C), 34.8 (1C), 32.2 (1C), 29.1 (3C), 28.4 (3C). HRMS (ESI) Calcd for $C_{29}H_{28}O$ [MNa^+] 415.2038, found 415.2031.



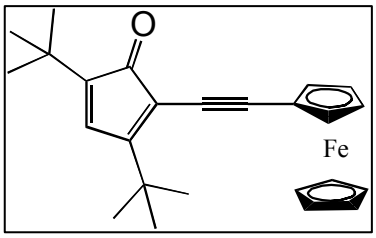
3,5-di-*tert*-butyl-2-((4-(dimethylamino)phenyl)ethynyl)-cyclopenta-2,4-dienone (4j): ^{1}H NMR (400MHz, $CDCl_3$) δ 7.31 (d, 2H, J=9.2 Hz), 6.66 (s, 1H), 6.60 (d, 2H, J=8.4 Hz), 2.95 (s, 6H,), 1.31 (s, 9H), 1.16 (s, 9H); ^{13}C NMR (100MHz, $CDCl_3$) δ 199.3 (1C), 168.8 (1C), 150.4 (1C), 141.6 (1C), 138.7 (1C), 132.4 (2C), 111.7 (2C), 110.9 (1C), 107.8 (1C), 97.3 (1C), 87.5 (1C), 40.1 (2C), 34.6 (1C), 32.0 (1C), 29.1 (3C), 28.2 (3C). HRMS (ESI) Calcd for $C_{23}H_{29}NO$ [MH^+] 336.2327, found 336.2316.



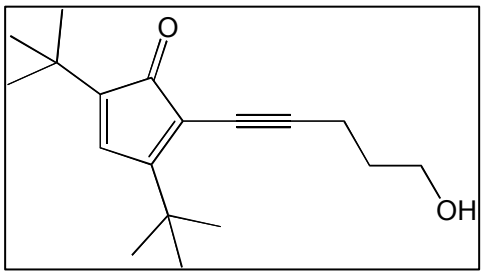
3,5-di-*tert*-butyl-2-((3,5-di-*tert*-butyl-4-methoxyphenyl)ethynyl)-cyclopenta-2,4-dienone (4k): ^{1}H NMR (400MHz, $CDCl_3$) δ 7.33 (s, 2H), 6.68 (s, 1H), 3.65 (s, 3H), 1.39 (s, 18H), 1.33 (s, 9H), 1.17 (s, 9H); ^{13}C NMR (100MHz, $CDCl_3$); δ 199.1 (1C), 167.9 (1C), 160.1 (1C), 143.9 (2C), 142.1 (1C), 138.4 (1C), 129.7 (2C), 117.9 (1C), 107.8 (1C), 99.5 (1C), 81.3 (1C), 64.3 (1C), 35.7 (1C), 34.6 (1C), 32.0 (1C), 31.9 (6C), 29.1 (3C), 28.2 (3C). HRMS (ESI) Calcd for $C_{30}H_{43}O_2$ [MH^+] 435.3263, found 435.3259.



3,5-di-*tert*-butyl-2-(*o*-tolylethynyl)cyclopenta-2,4-dienone (4l): ^{1}H NMR (400MHz, $CDCl_3$) δ 7.44 (d, 1H, J=7.6Hz), 7.20 (m, 2H), 7.14 (m, 1H), 6.71 (s, 1H), 2.50 (s, 3H), 1.34 (s, 9H), 1.19 (s, 9H) ^{13}C NMR (100MHz, $CDCl_3$); δ 199.1 (1C), 167.1 (1C), 141.7 (1C), 140.1 (1C), 138.4 (1C), 131.7 (1C), 129.4 (1C) 128.2 (1C), 125.4 (1C), 123.4 (1C), 107.8 (1C), 97.9 (1C), 86.5 (1C), 34.7 (1C), 32.1 (1C), 29.1 (3C), 28.2 (3C), 20.9 (1C). HRMS (ESI) Calcd for $C_{22}H_{26}O$ [MNa^+] 329.1881, found 329.1885.

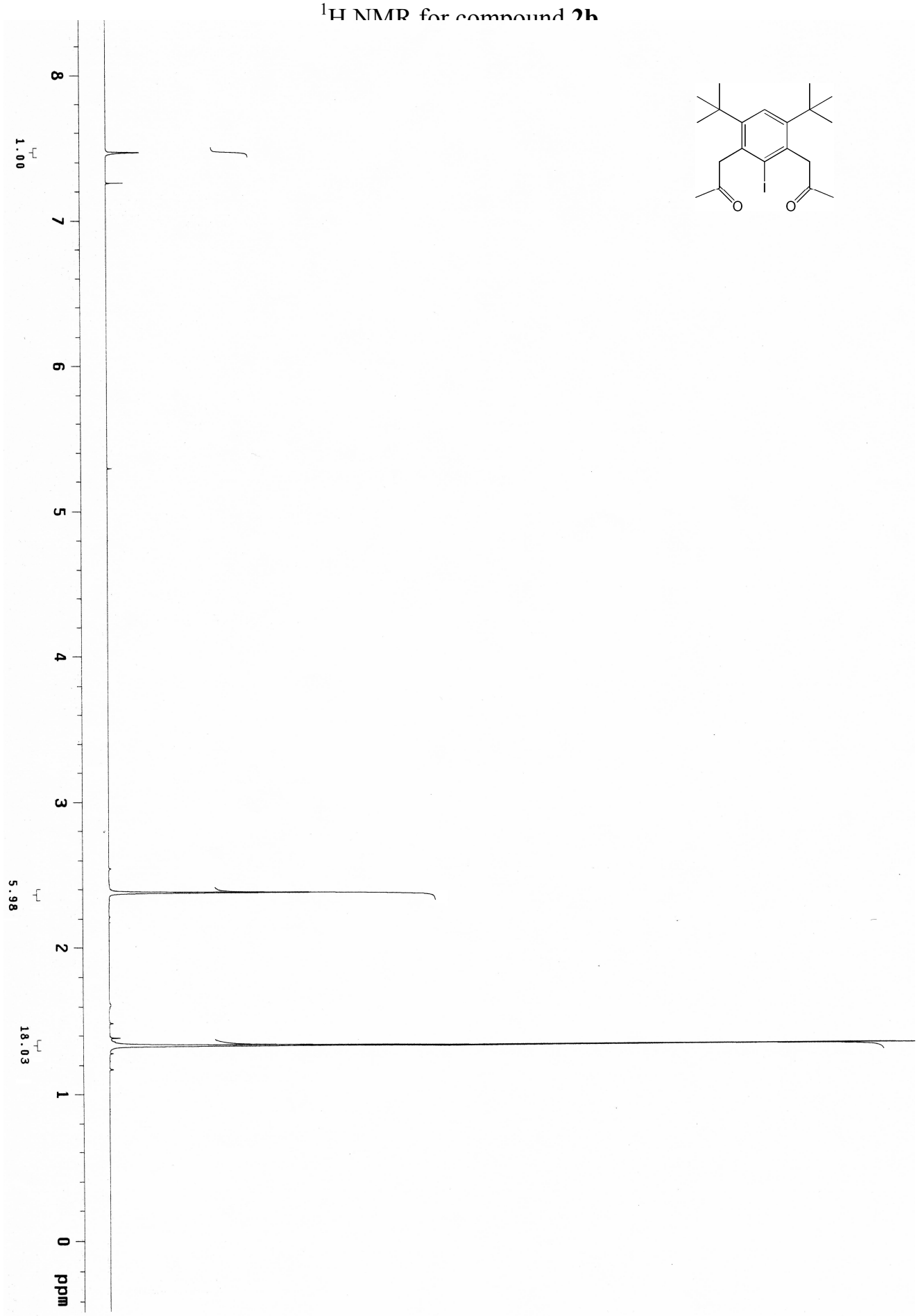


3,5-di-*tert*-butyl-2-(ferrocenyl)cyclopenta-2,4-dienone (4m): ^{1}H NMR (400MHz, $CDCl_3$) δ 6.68 (s, 1H), 4.64 (t, 2H, J=1.6 Hz), 4.24 (s, 5H), 4.22 (t, 2H, J=1.6Hz) 1.35 (s, 9H), 1.20 (s, 9H); ^{13}C NMR (100MHz, $CDCl_3$) δ 198.8 (1C), 167.1 (1C), 141.7 (1C), 138.5 (1C), 108.3 (1C), 98.1 (1C), 79.0 (1C), 71.3 (2C), 69.9 (5C), 68.8 (2C) 65.6 (1C), 34.6 (1C), 32.0 (1C), 29.1 (3C), 28.2 (3C). HRMS (ESI) Calcd for $C_{25}H_{28}FeO$ [MNa^+] 423.1387, found 423.1389.

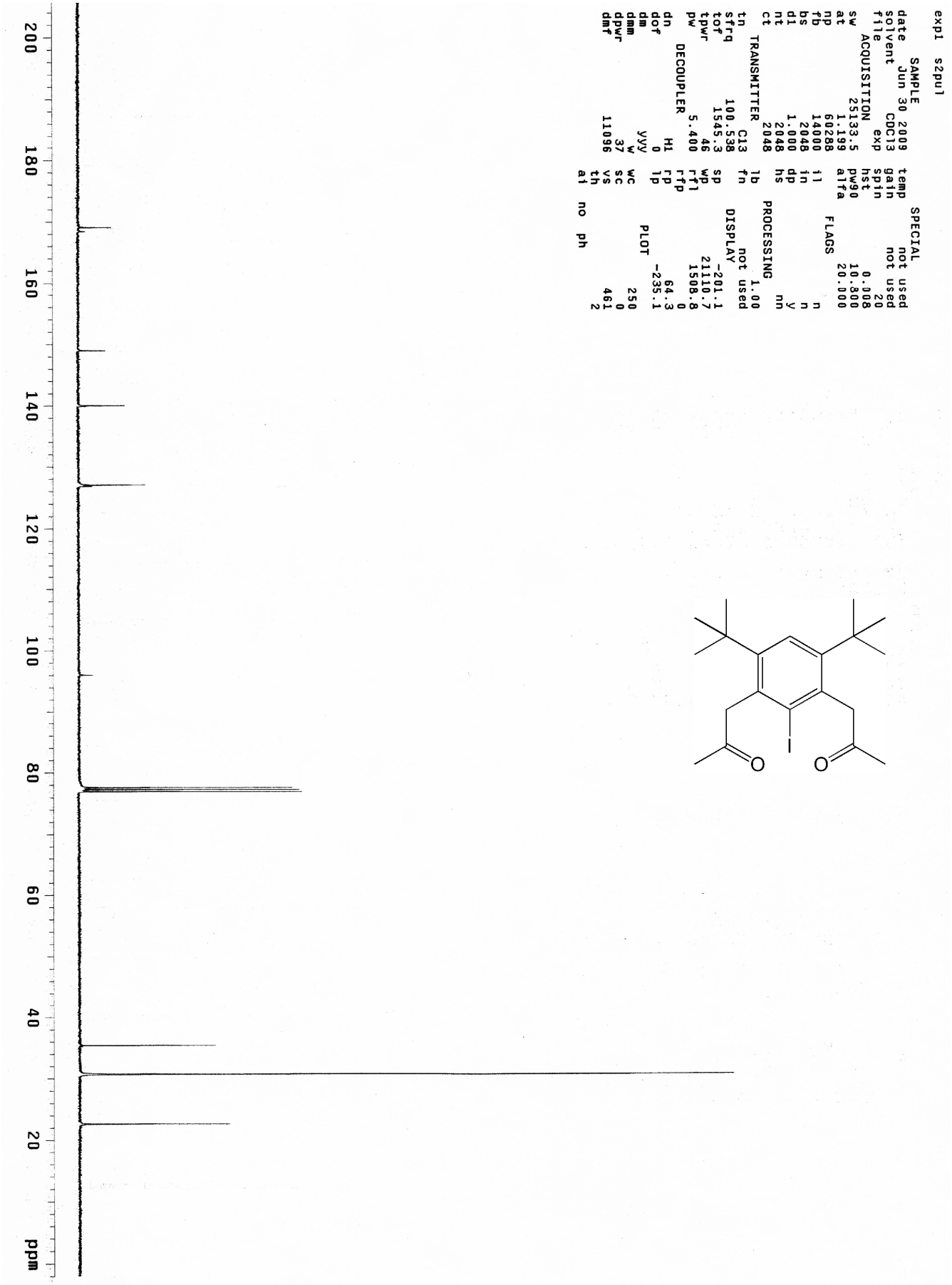


3,5-di-*tert*-butyl-2-(5-hydroxypent-1-yn-1-yl)cyclopenta-2,4-dienone (4s): ^{1}H NMR (400MHz, $CDCl_3$) δ 6.63 (s, 1H), 3.81 (t, 2H, J=6.4 Hz), 2.55 (t, 2H, J=6.8 Hz), 1.83 (p, 2H, 6.4Hz), 1.27 (s, 9H), 1.16 (s, 9H); ^{13}C NMR (100MHz, $CDCl_3$) δ 199.6 (1C), 167.1 (1C), 141.8 (1C), 138.1 (1C), 107.8 (1C), 99.1 (1C), 74.2 (1C), 62.0 (1C), 34.4 (1C), 32.0 (1C), 31.2 (1C), 29.0 (3C), 28.1 (3C), 16.8 (1C). HRMS (ESI) Calcd for $C_{18}H_{26}O_2$ [MH^+] 275.2011, found 275.1999.

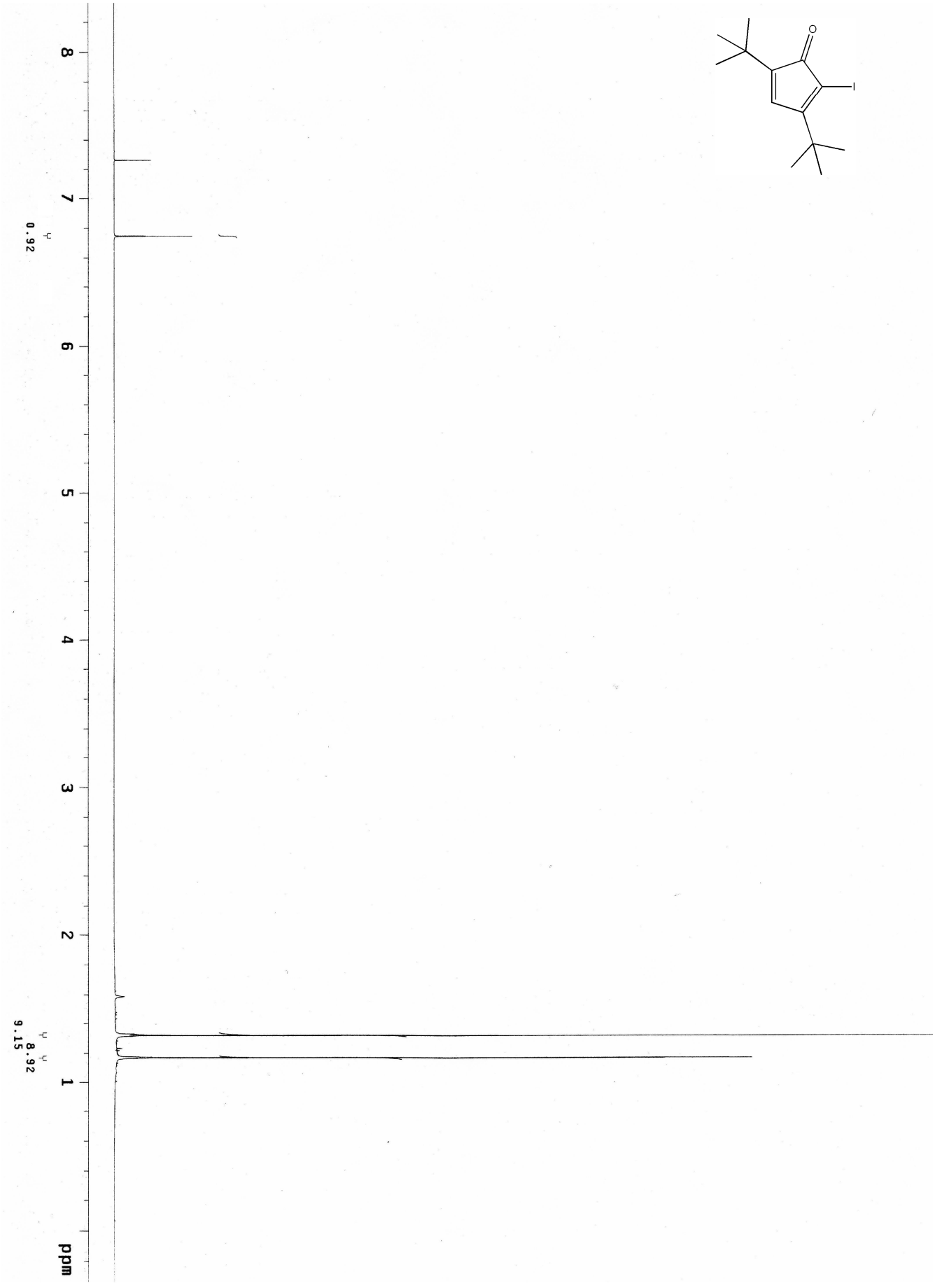
^{1}H NMR for compound **2b**



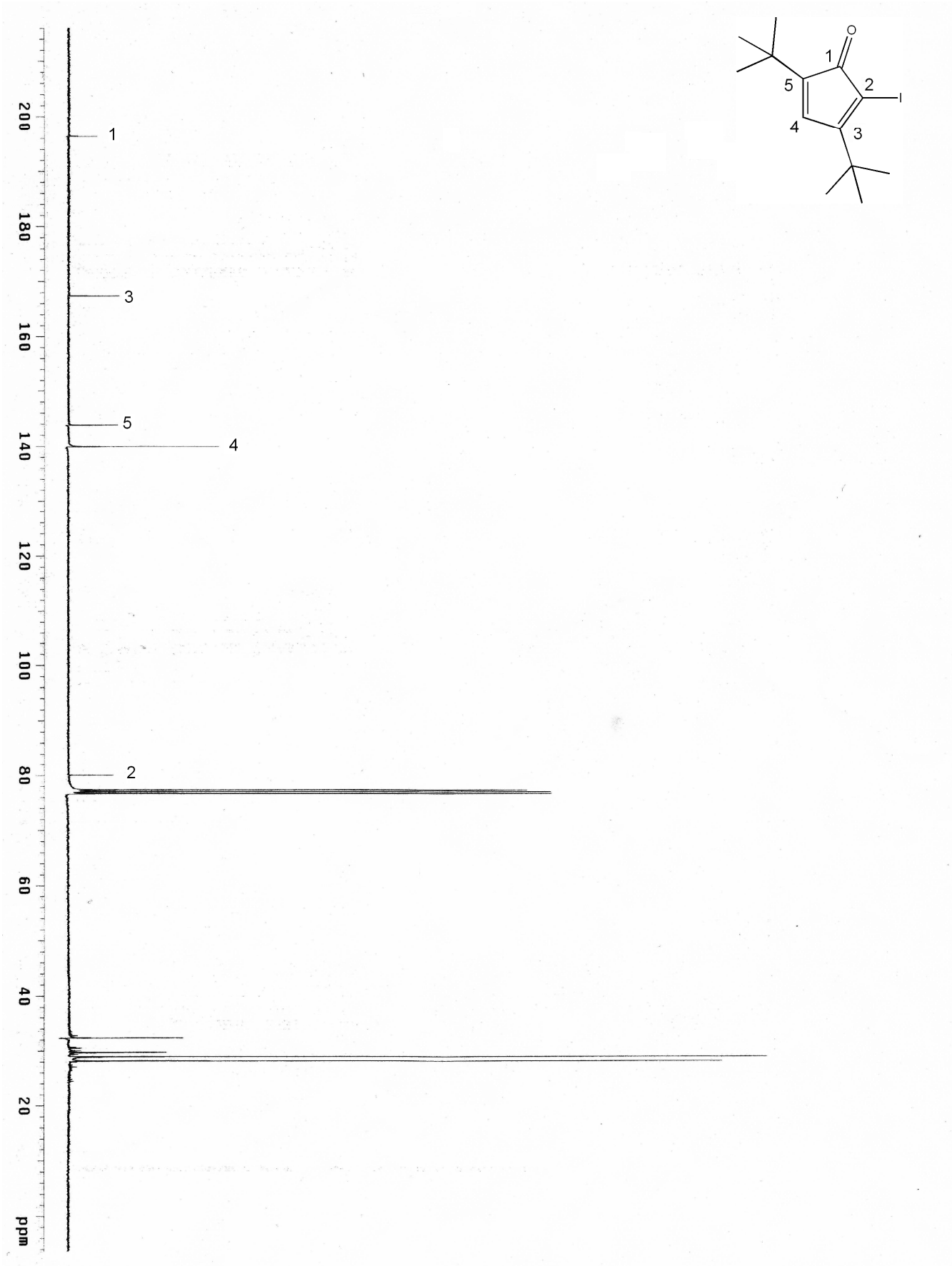
^{13}C NMR for compound **2b**



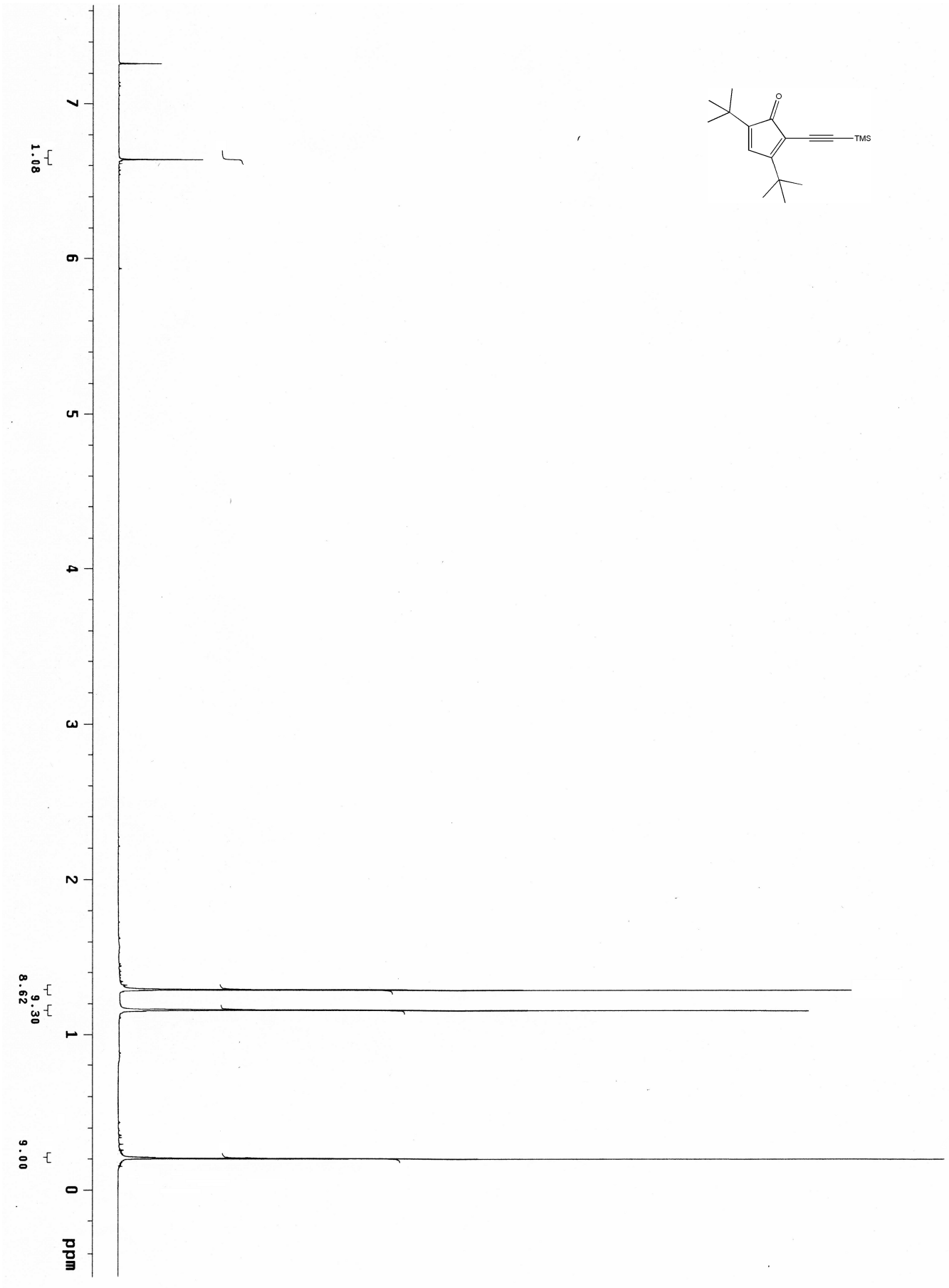
^{1}H NMR for compound **3**



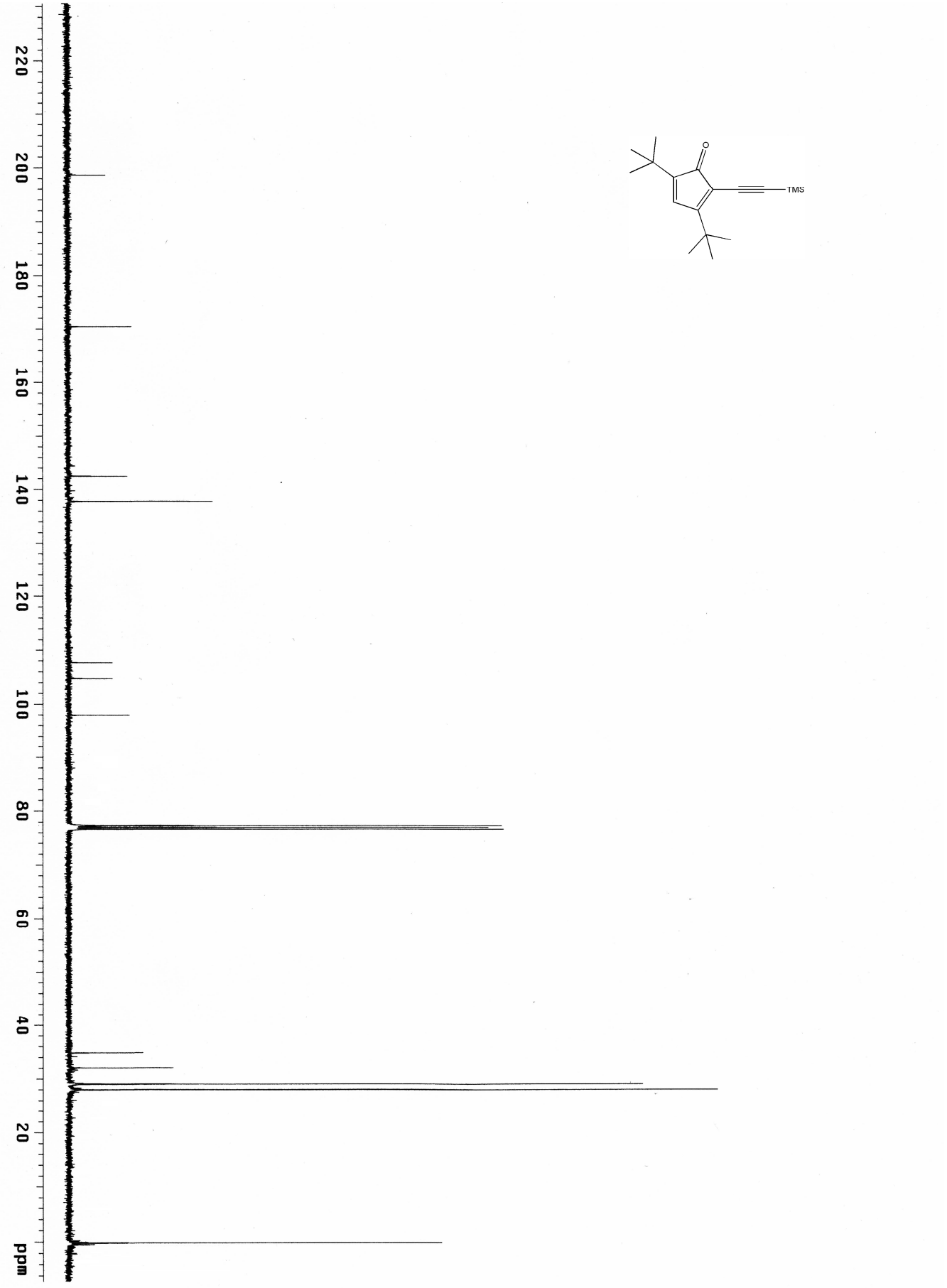
^{13}C NMR for compound **3**



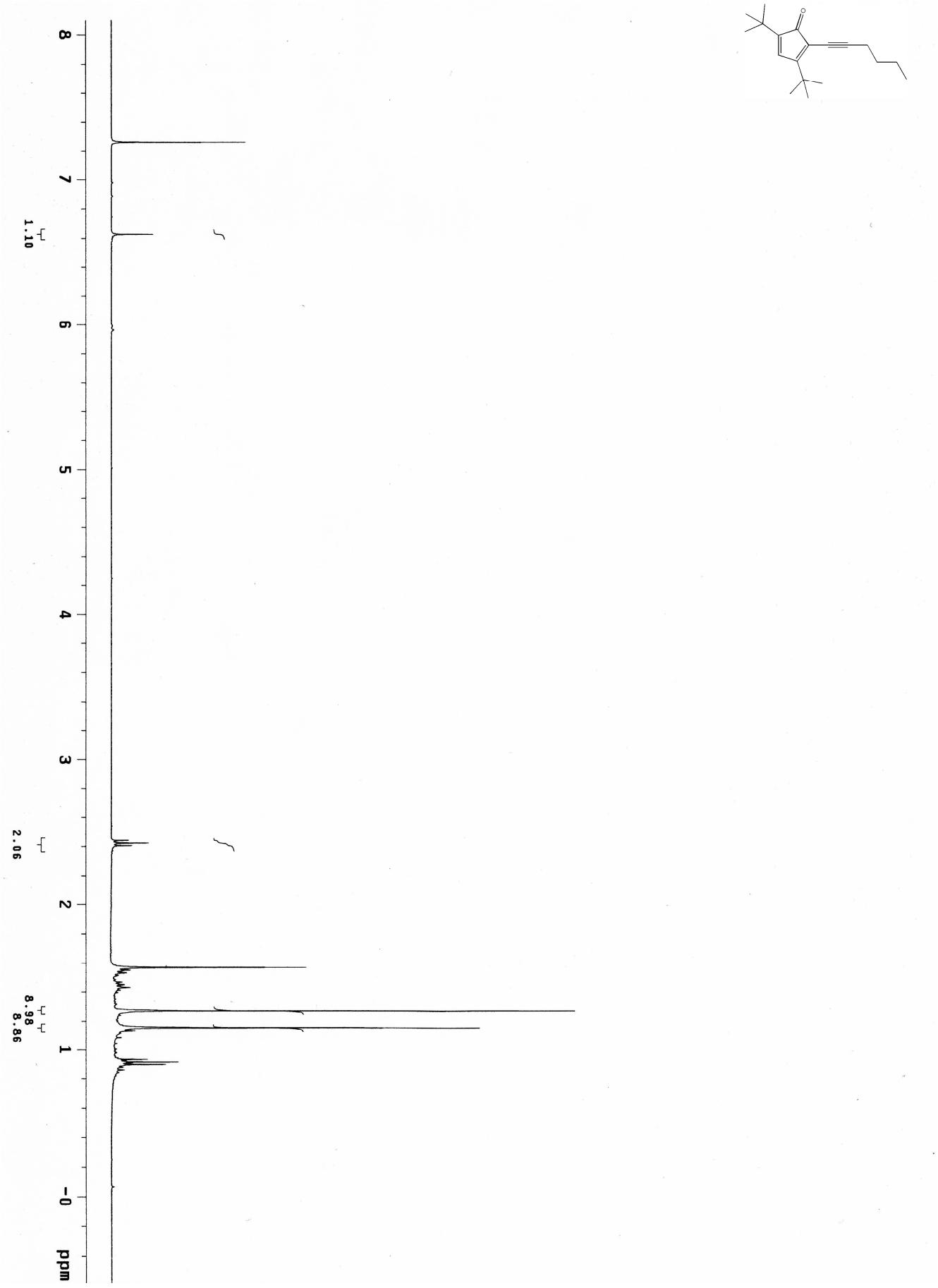
^{1}H NMR for compound **4a**



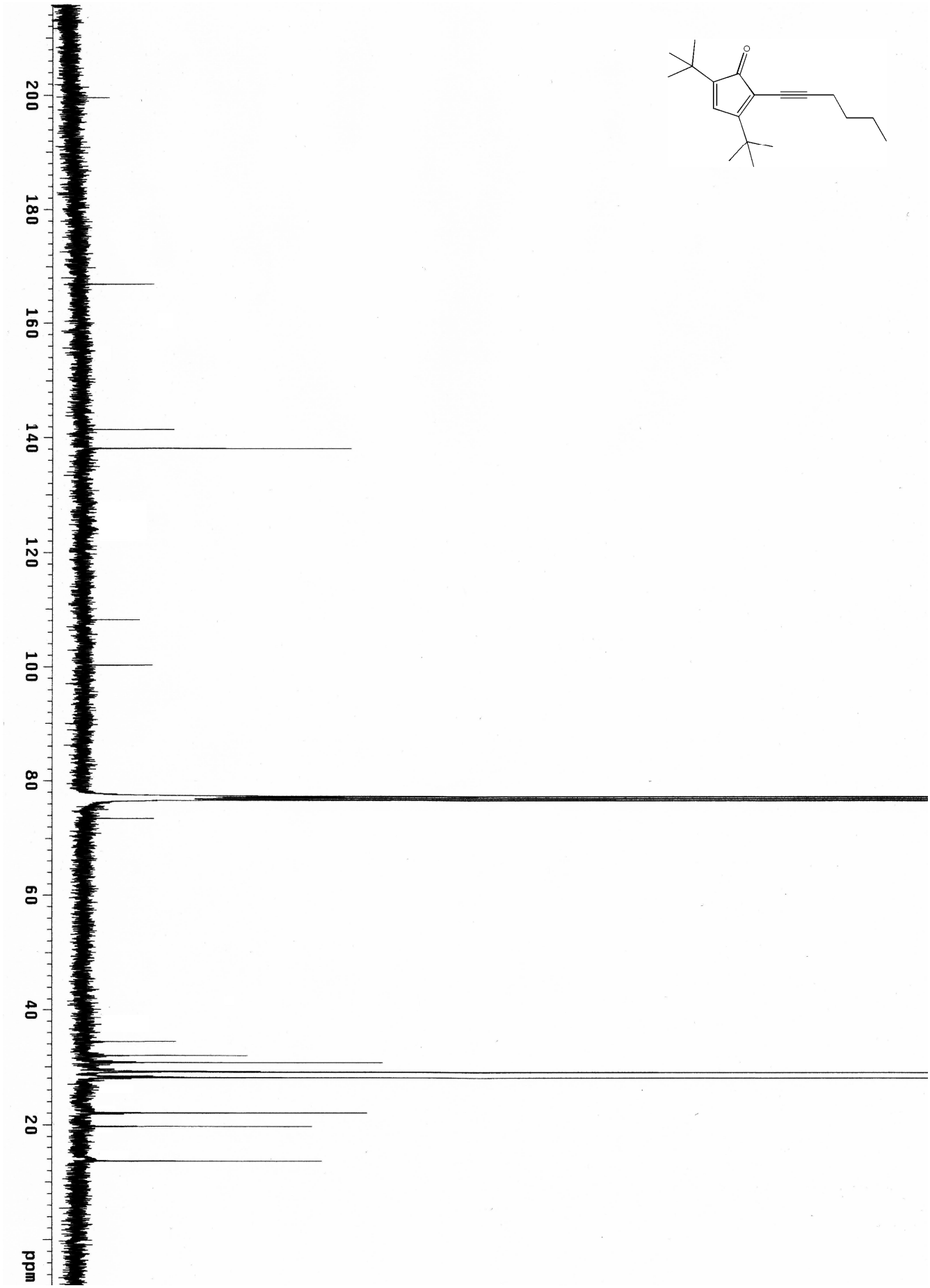
^{13}C NMR for compound **4a**



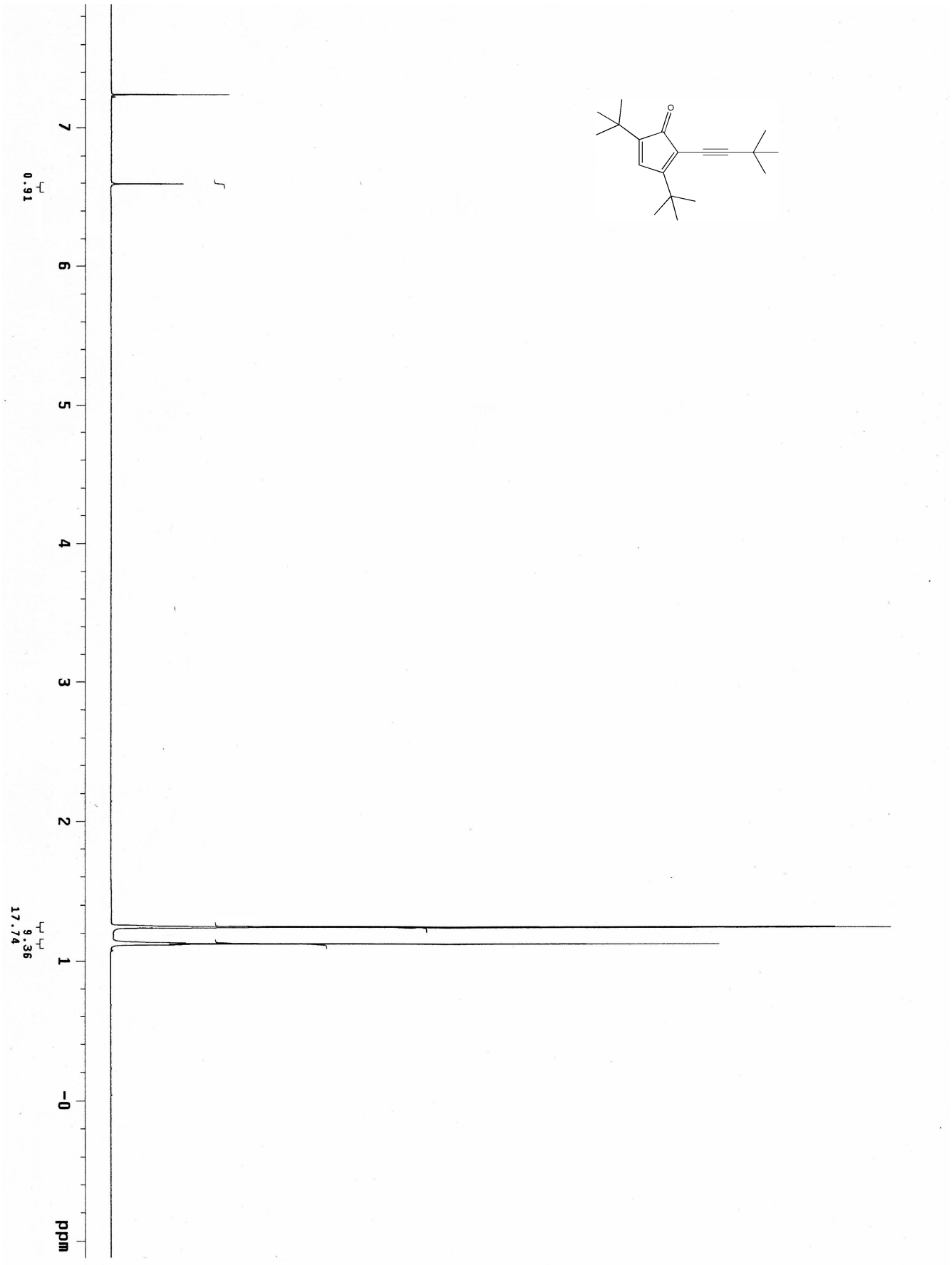
^{1}H NMR for compound **4b**



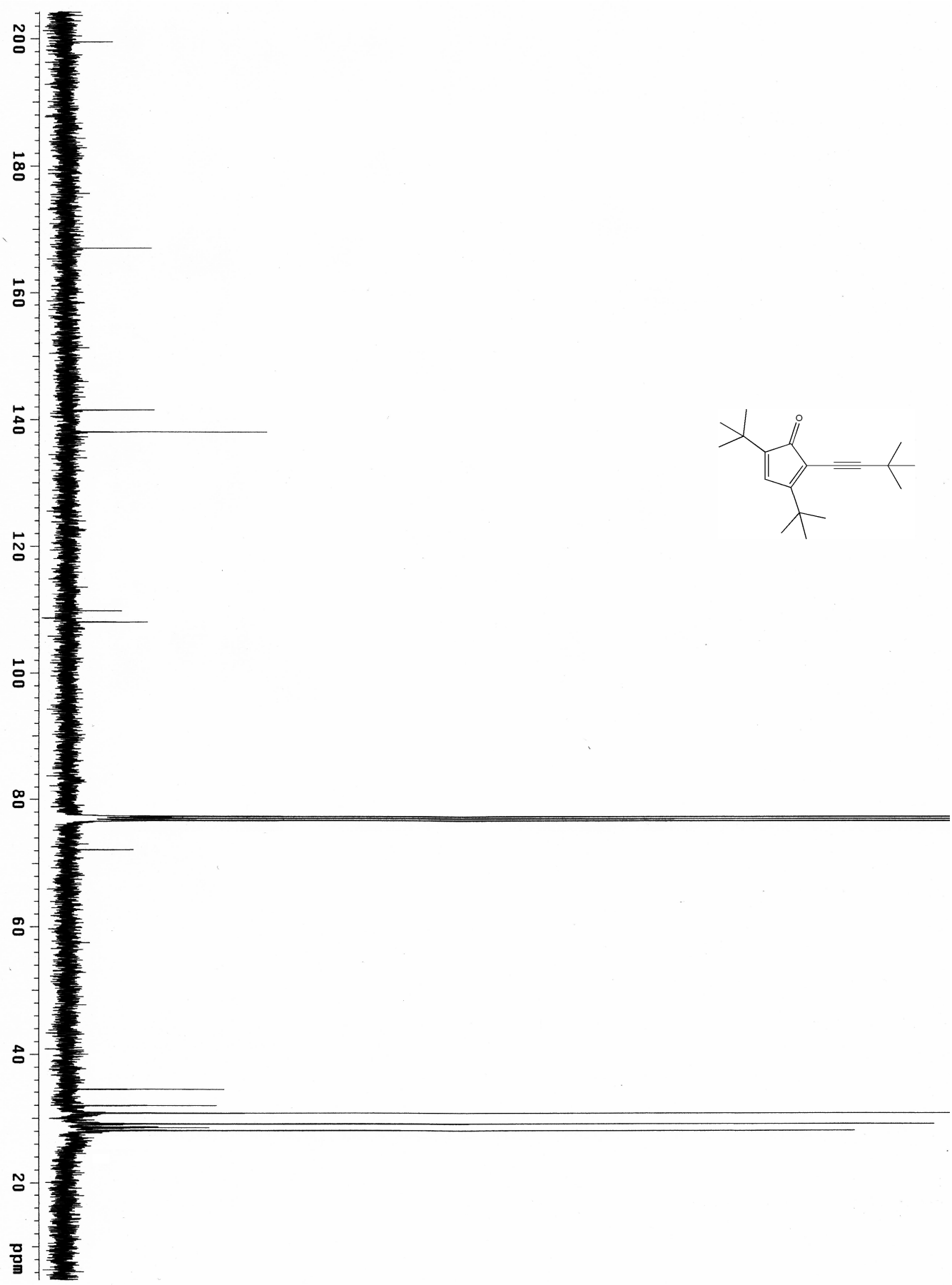
^{13}C NMR for compound **4b**



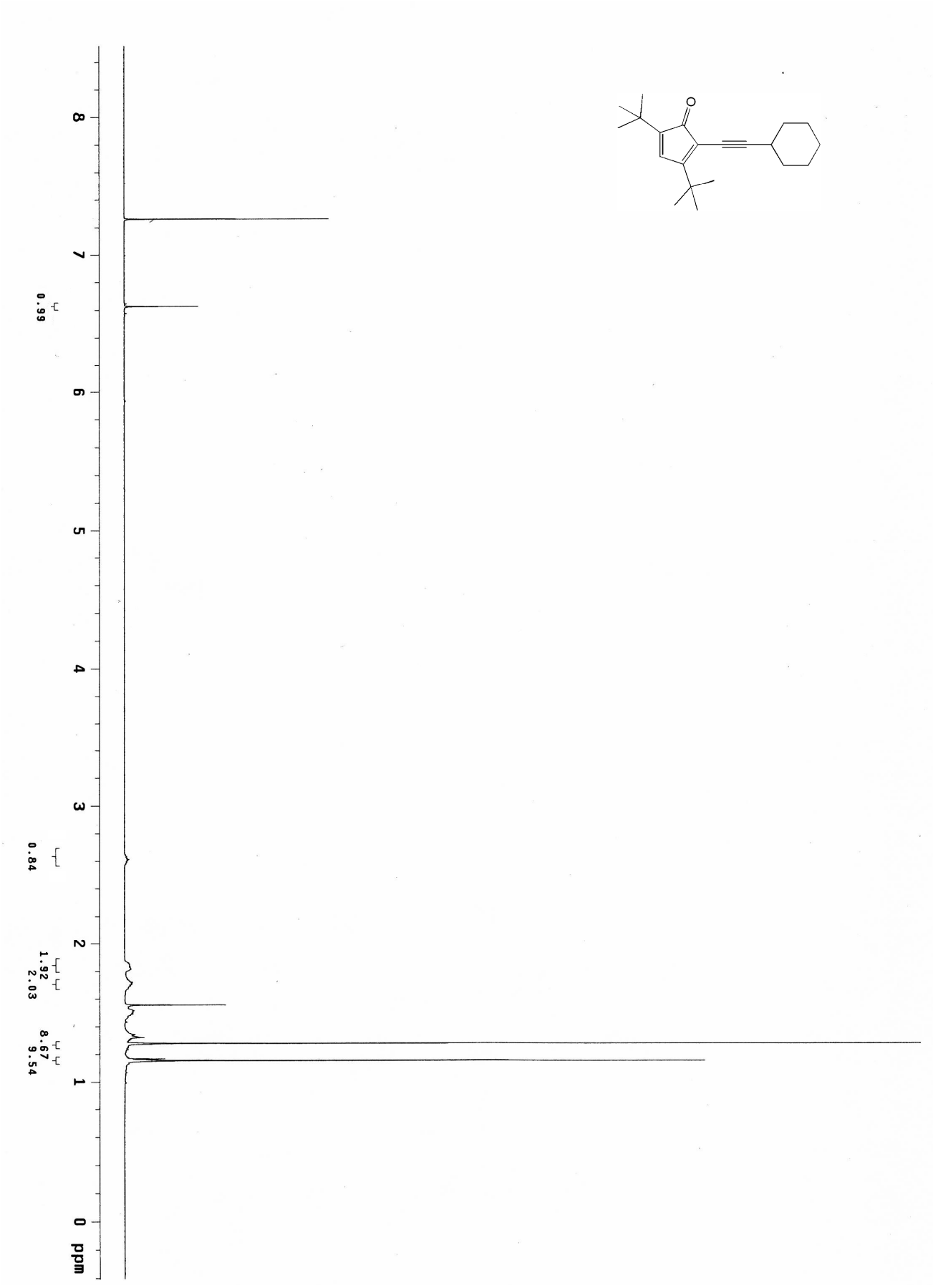
^{1}H NMR for compound **4c**



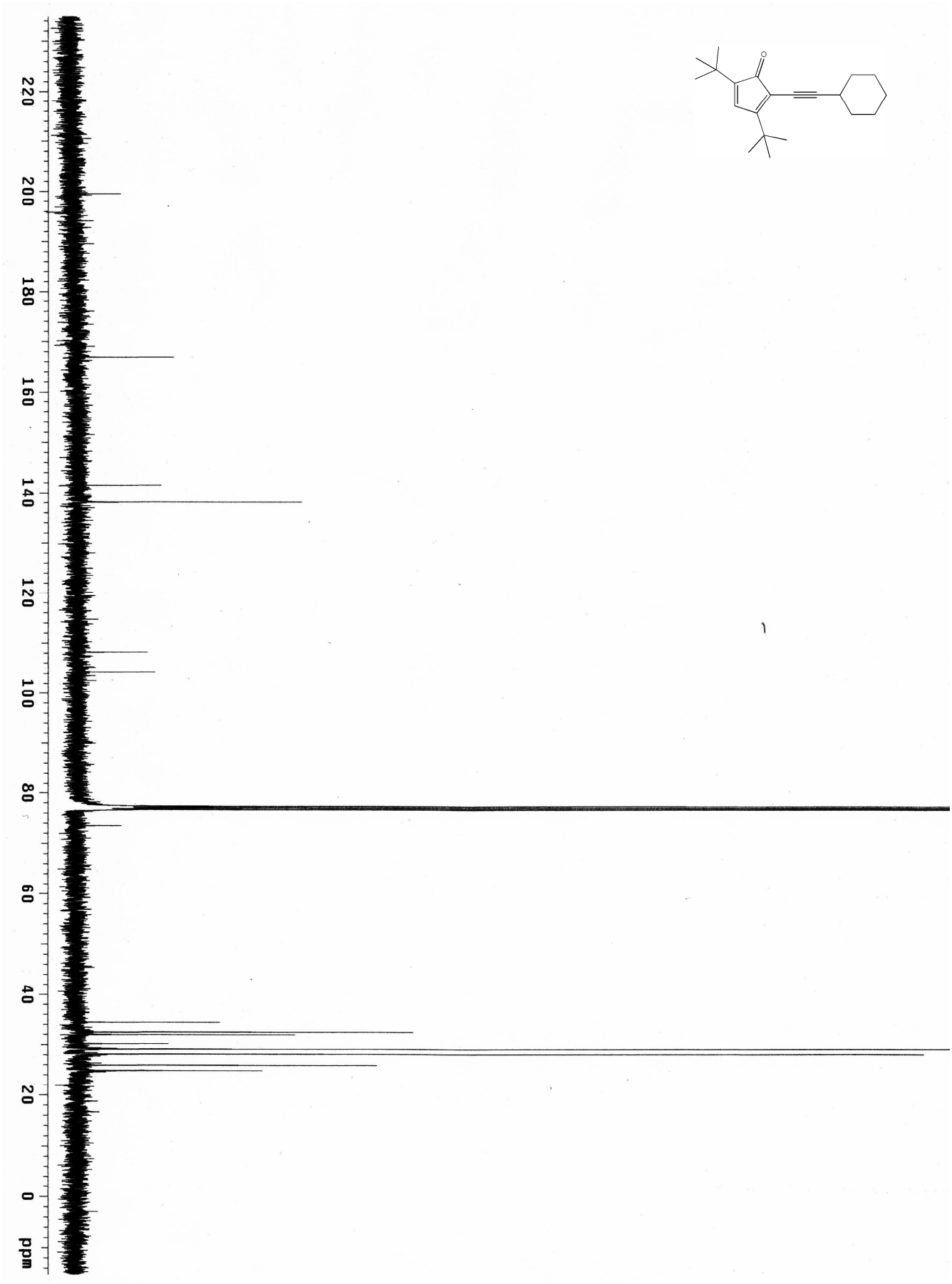
^{13}C NMR for compound **4c**



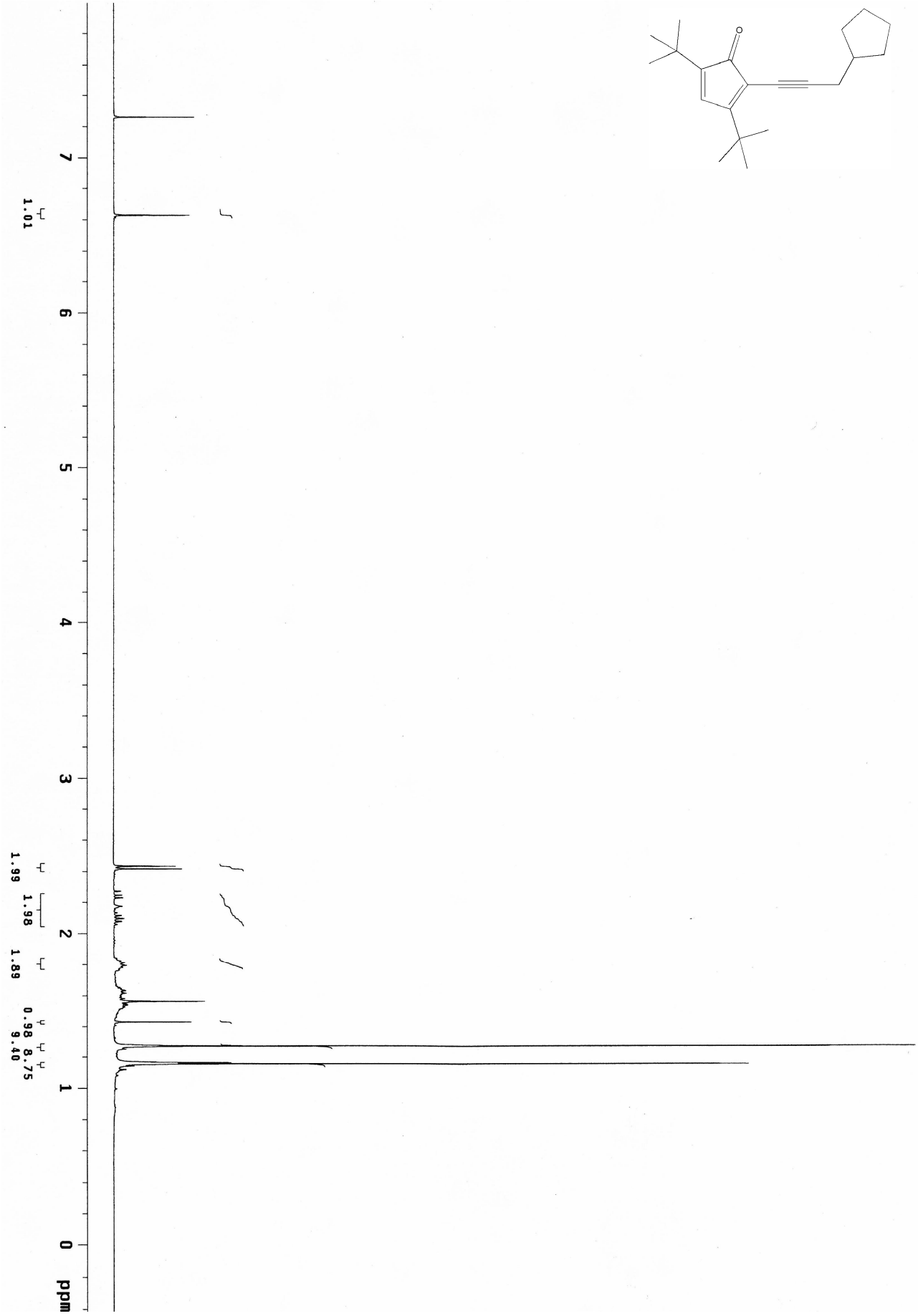
^{1}H NMR for compound **4d**



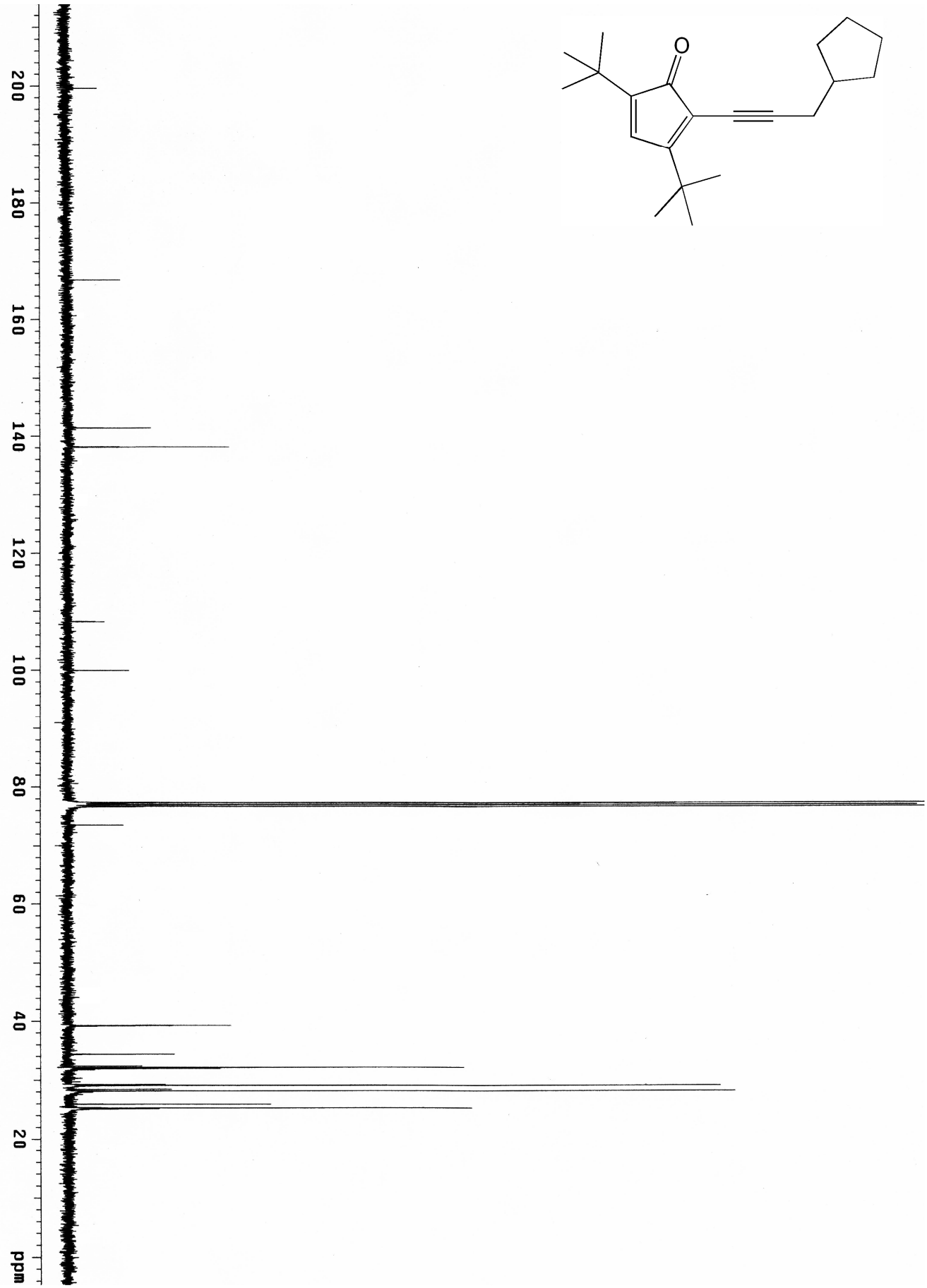
^{13}C NMR for compound **4d**



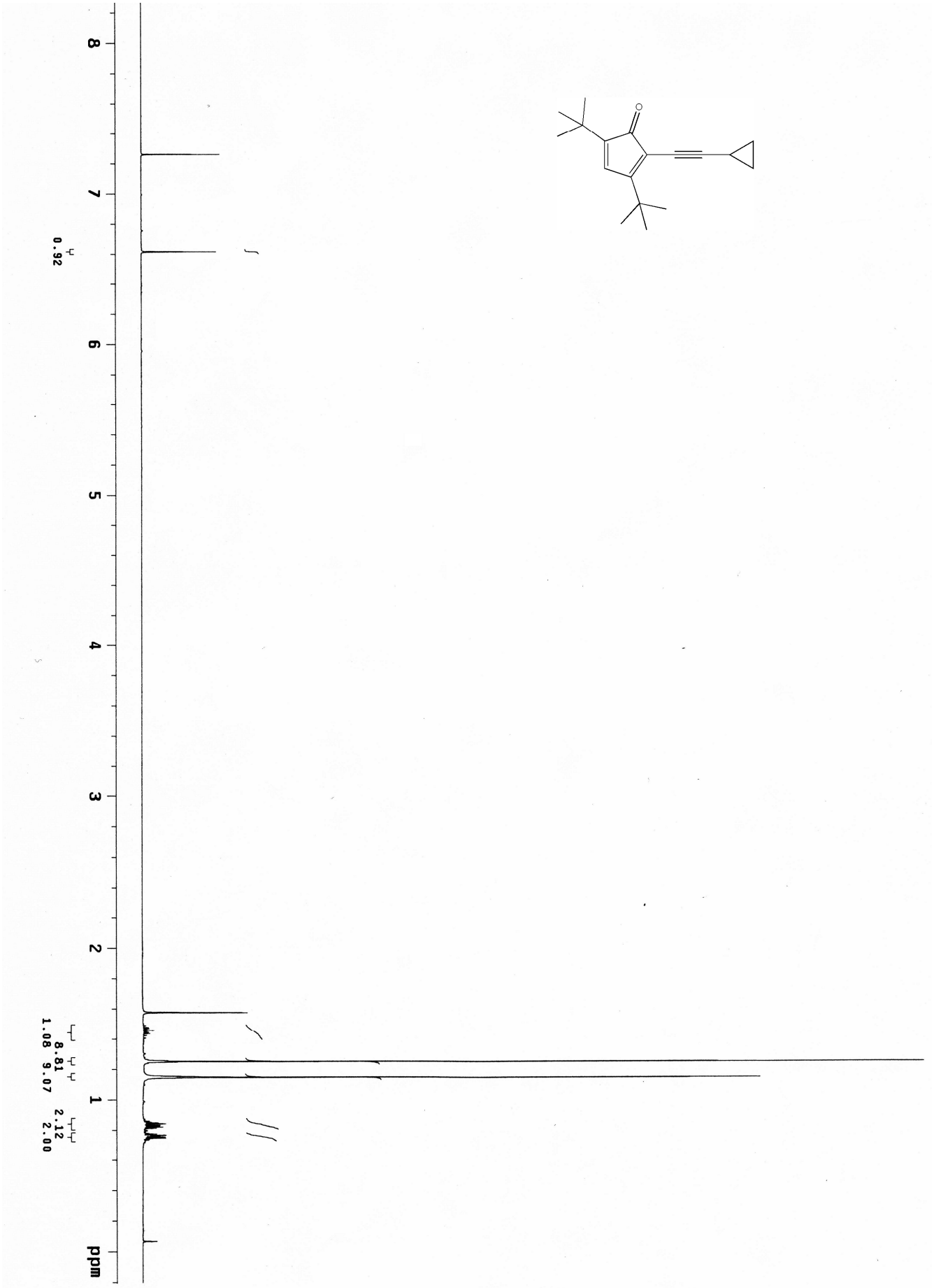
^{1}H NMR for compound **4e**



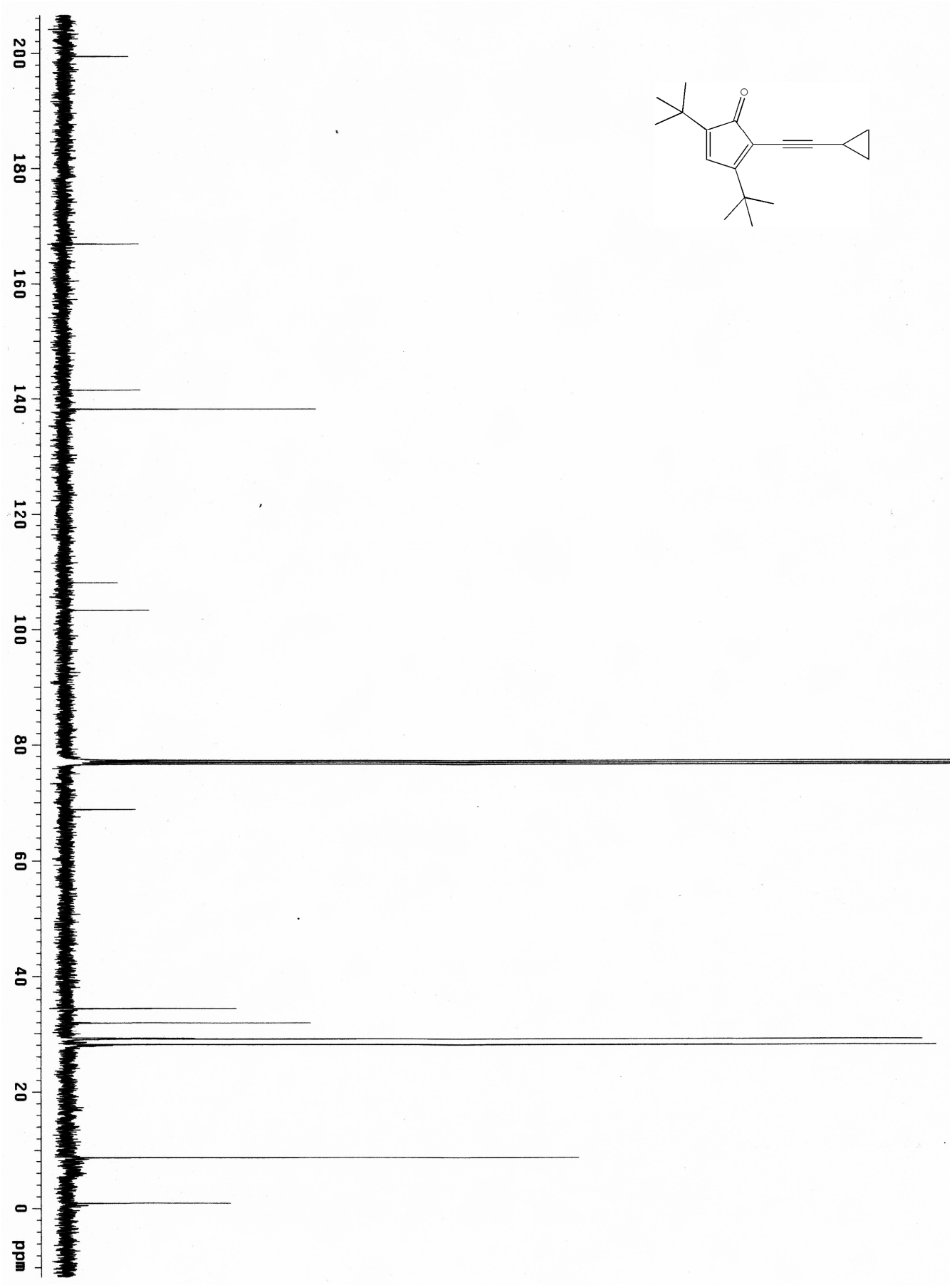
^{13}C NMR for compound **4e**



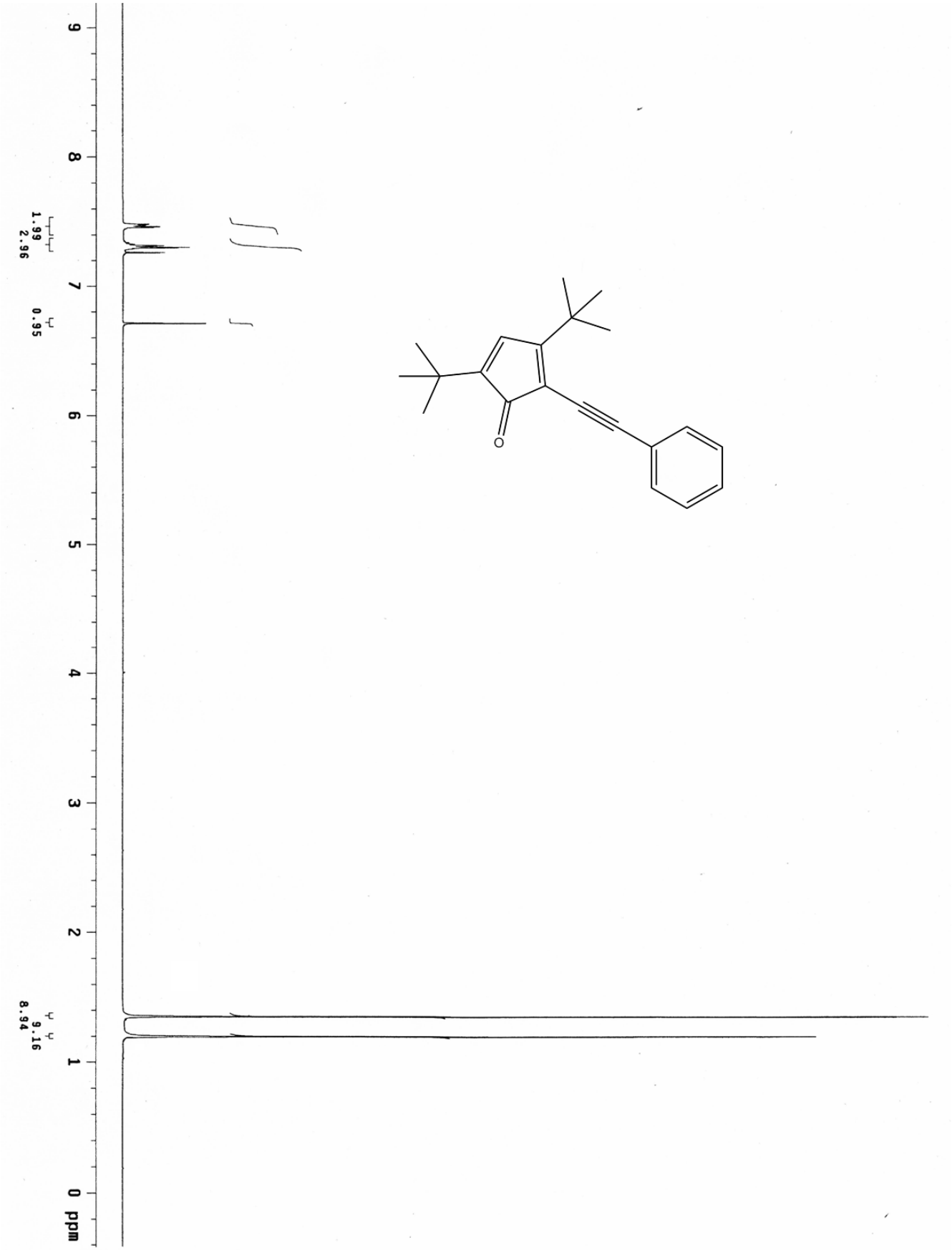
^{1}H NMR for compound **4f**



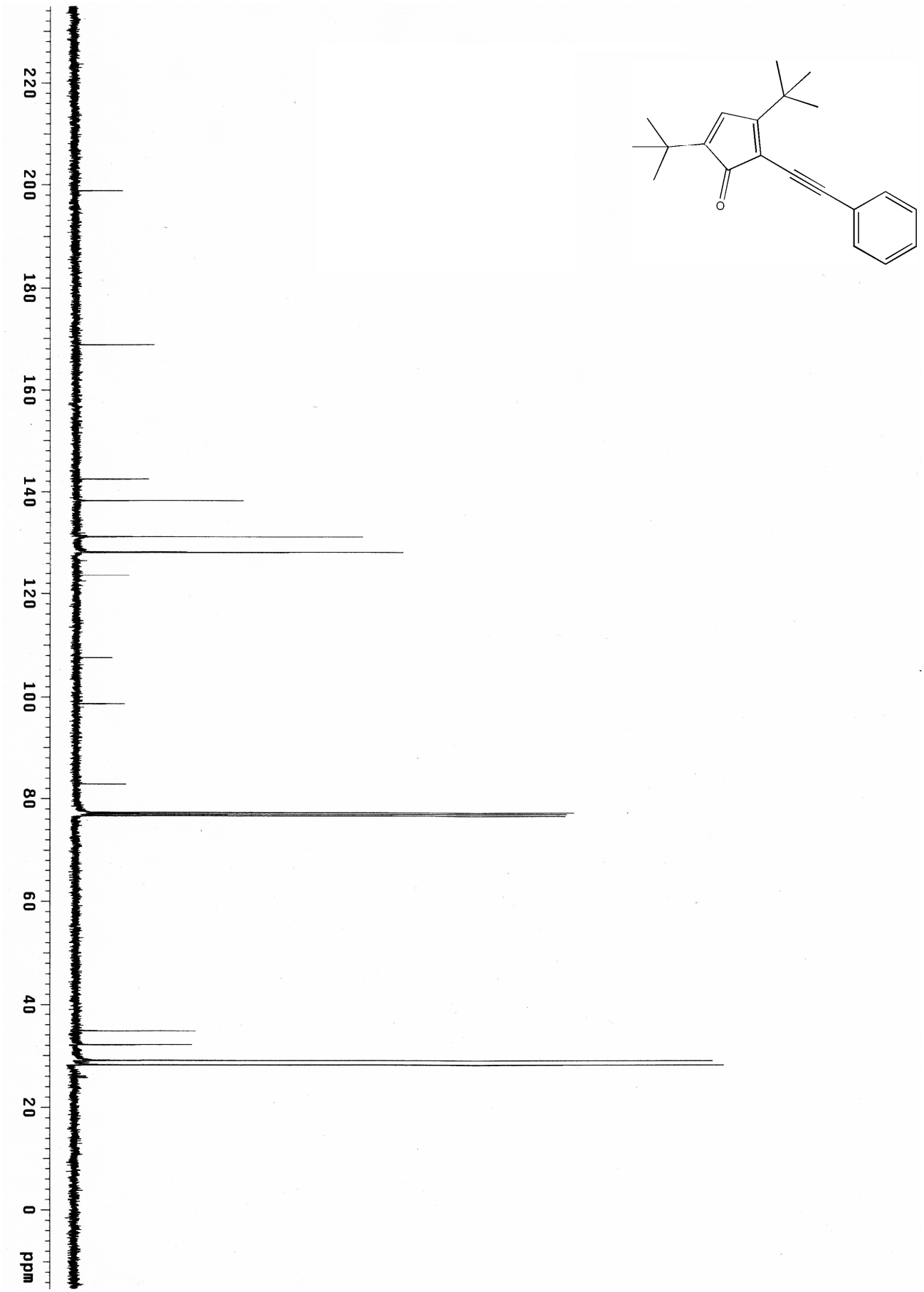
^{13}C NMR for compound **4f**



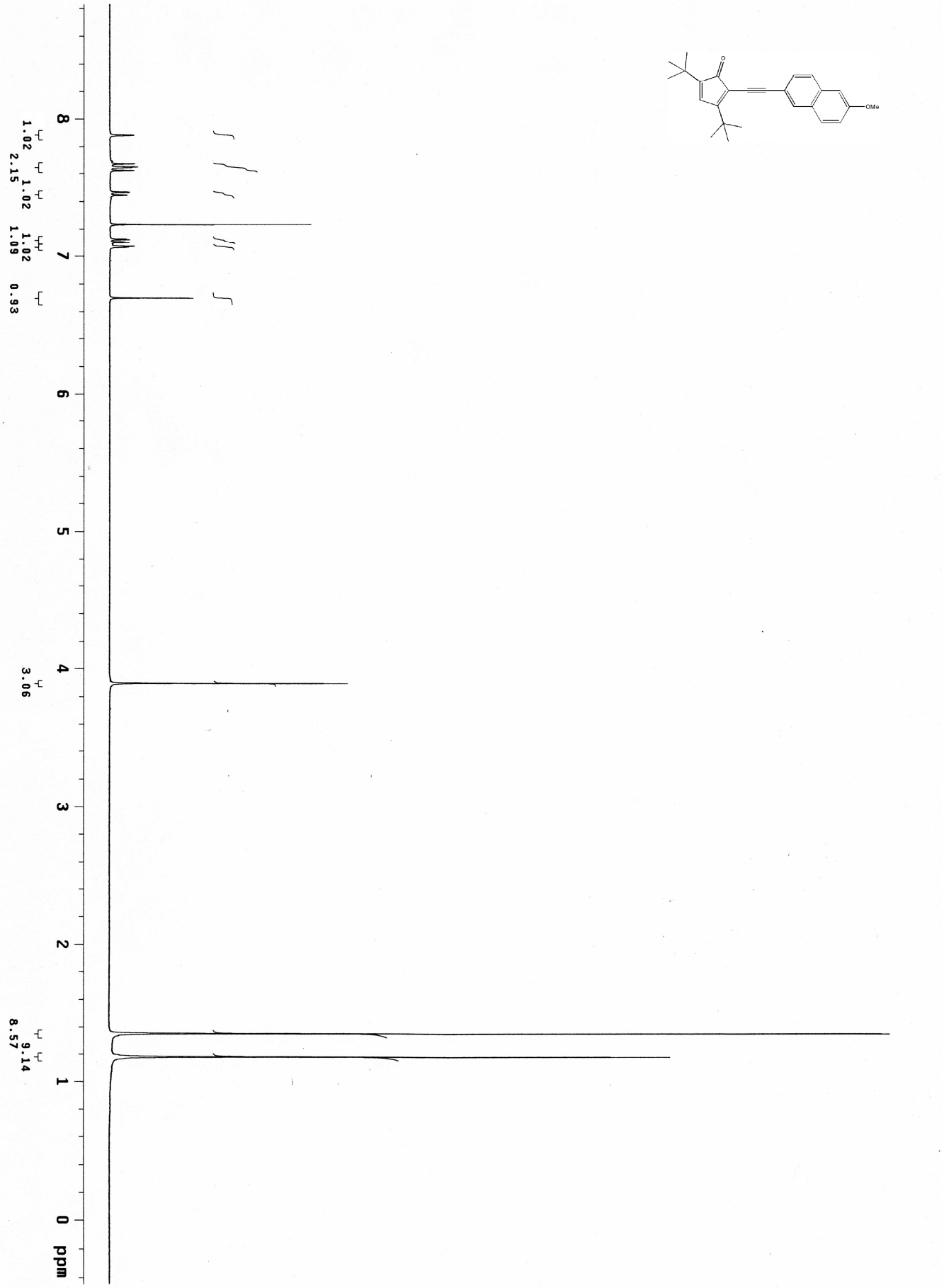
^{1}H NMR for compound **4g**



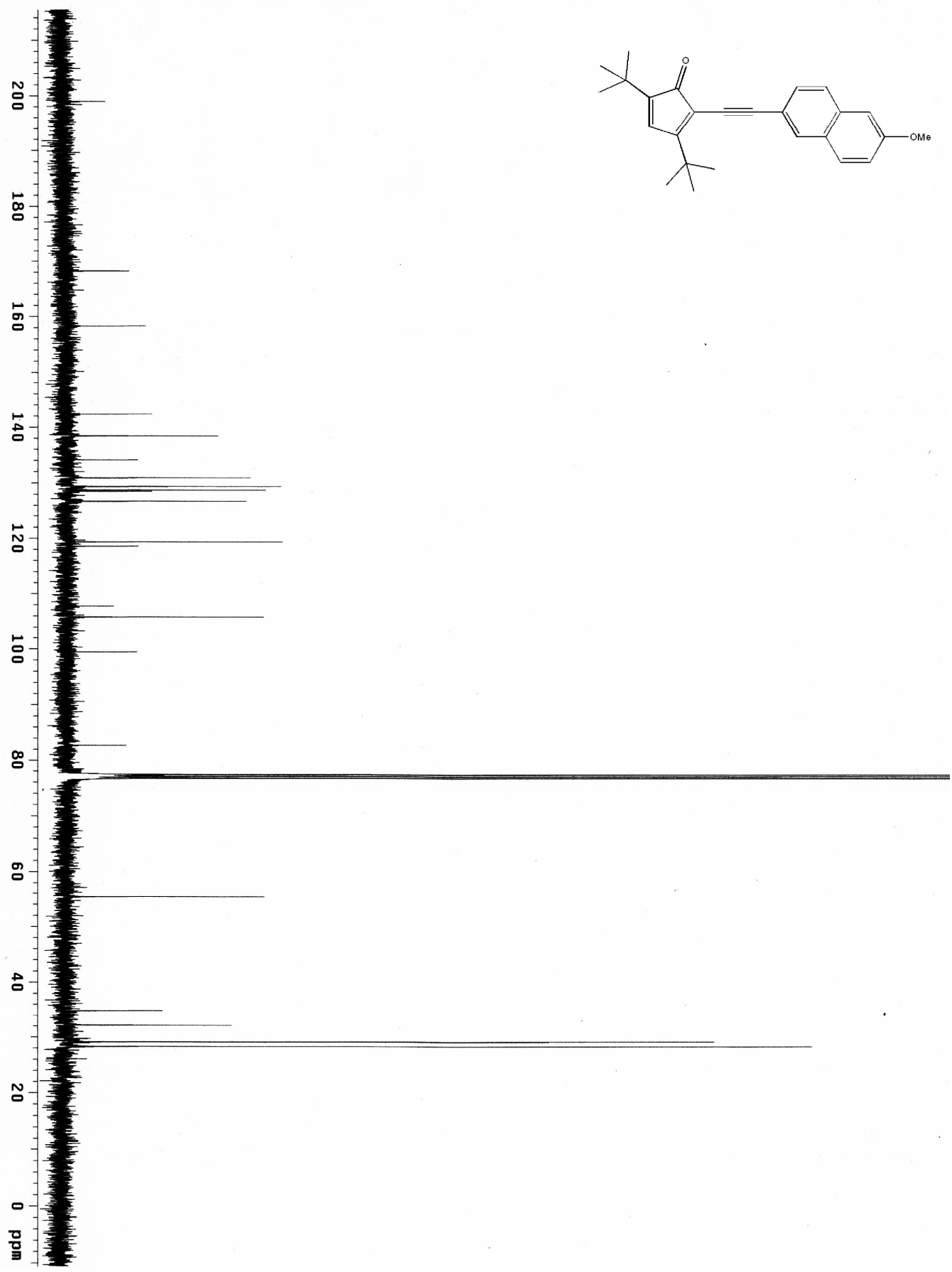
^{13}C NMR for compound **4g**



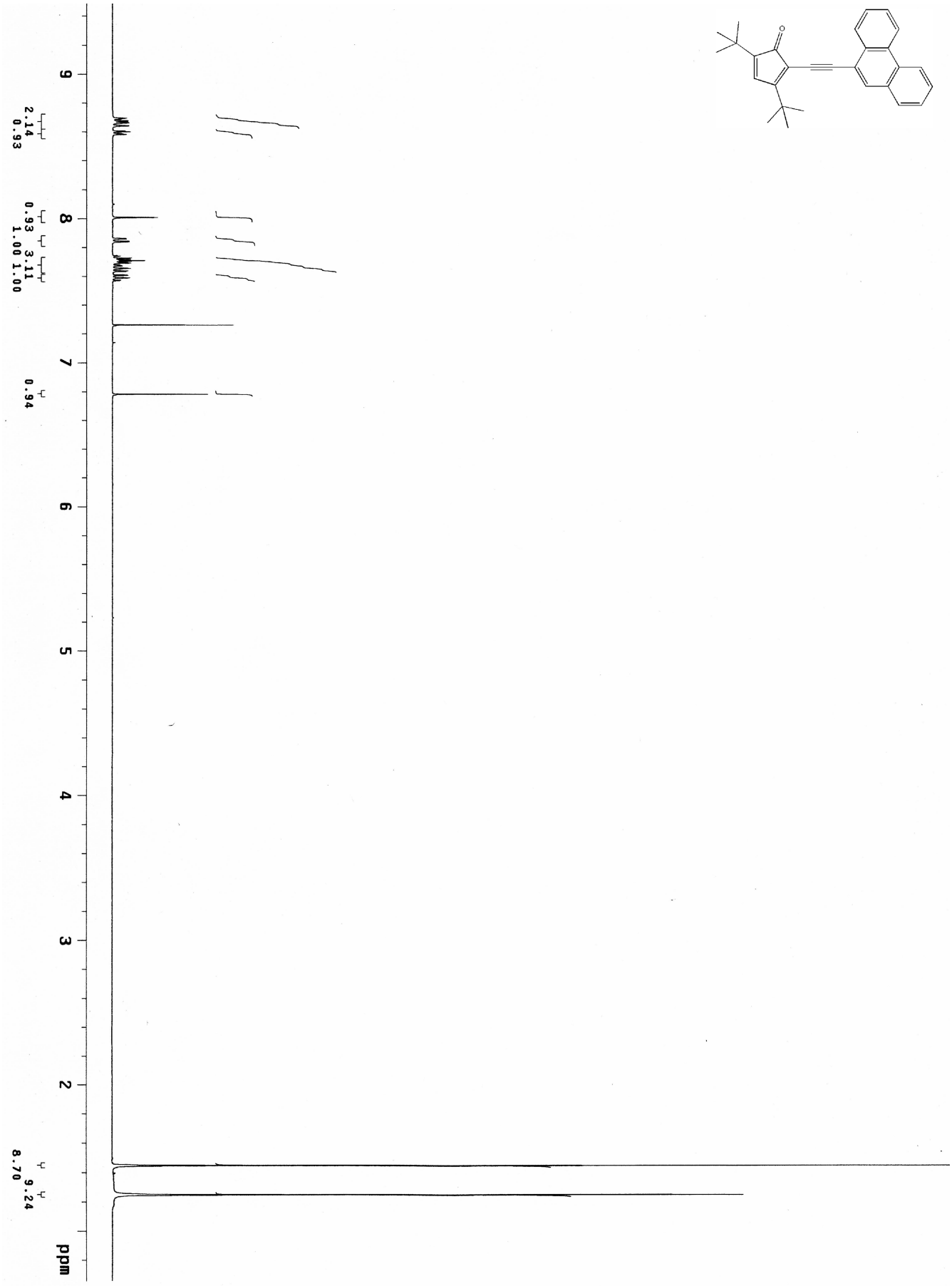
^{1}H NMR for compound **4h**



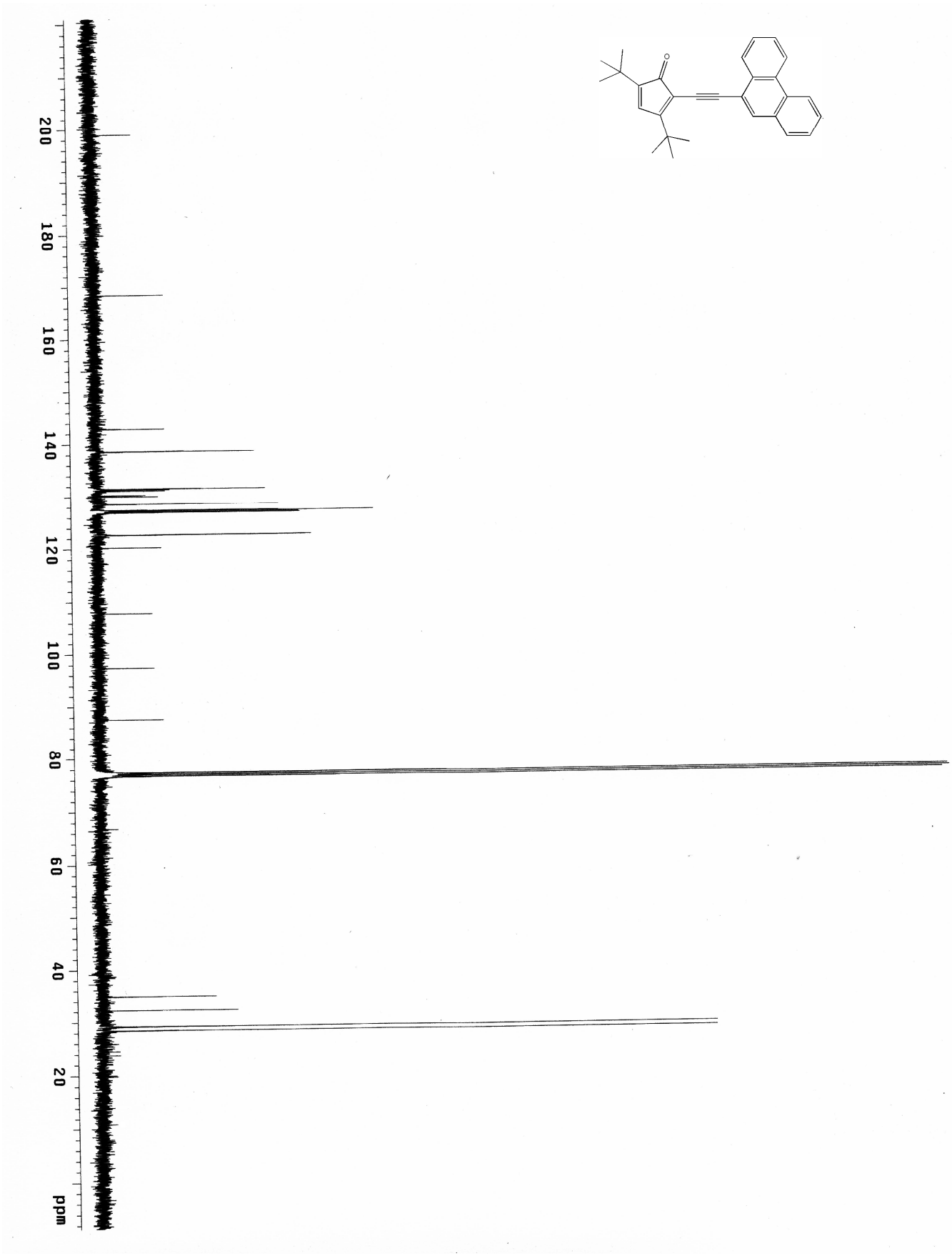
^{13}C NMR for compound **4h**



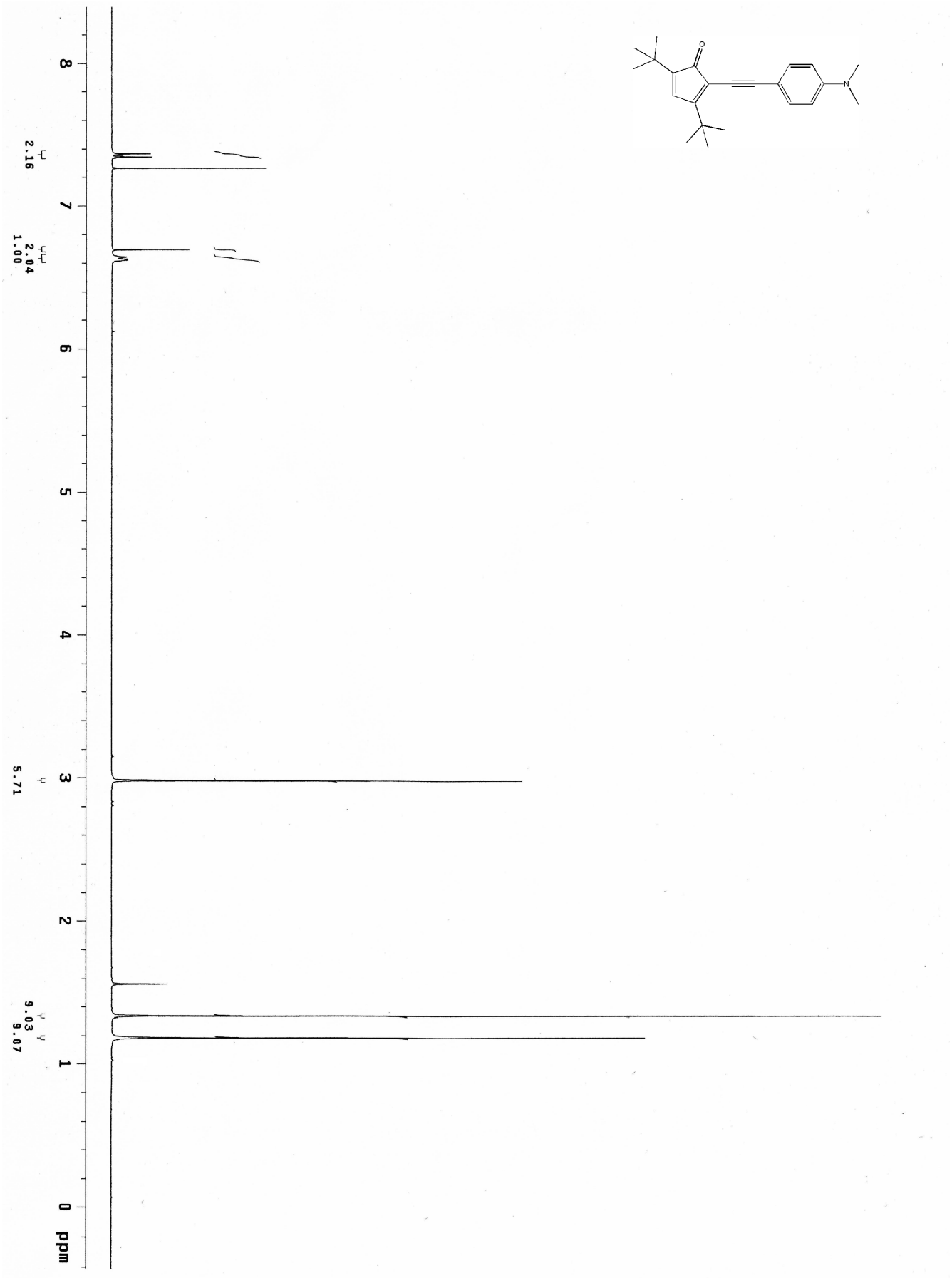
^{1}H NMR for compound **4i**



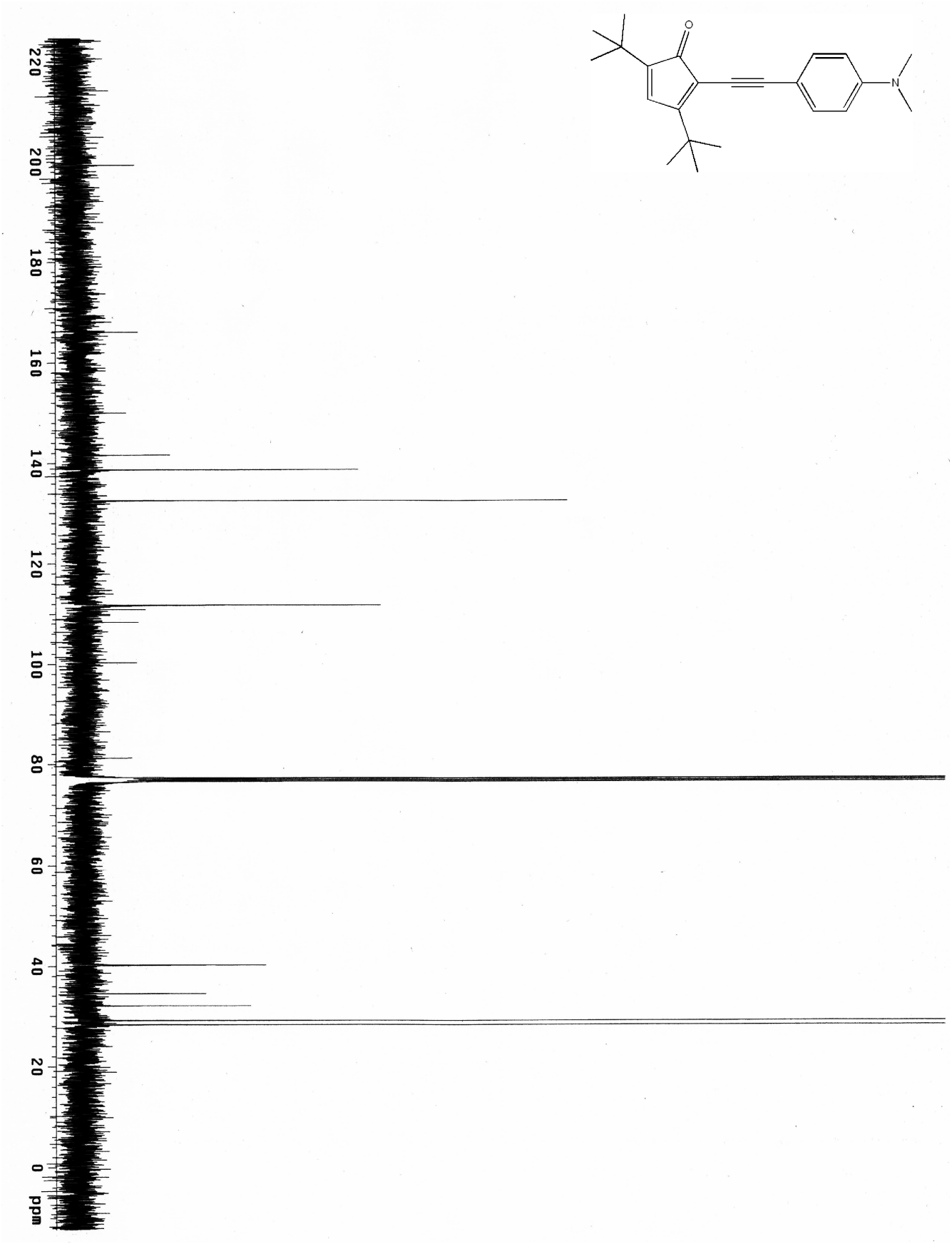
^{13}C NMR for compound **4i**



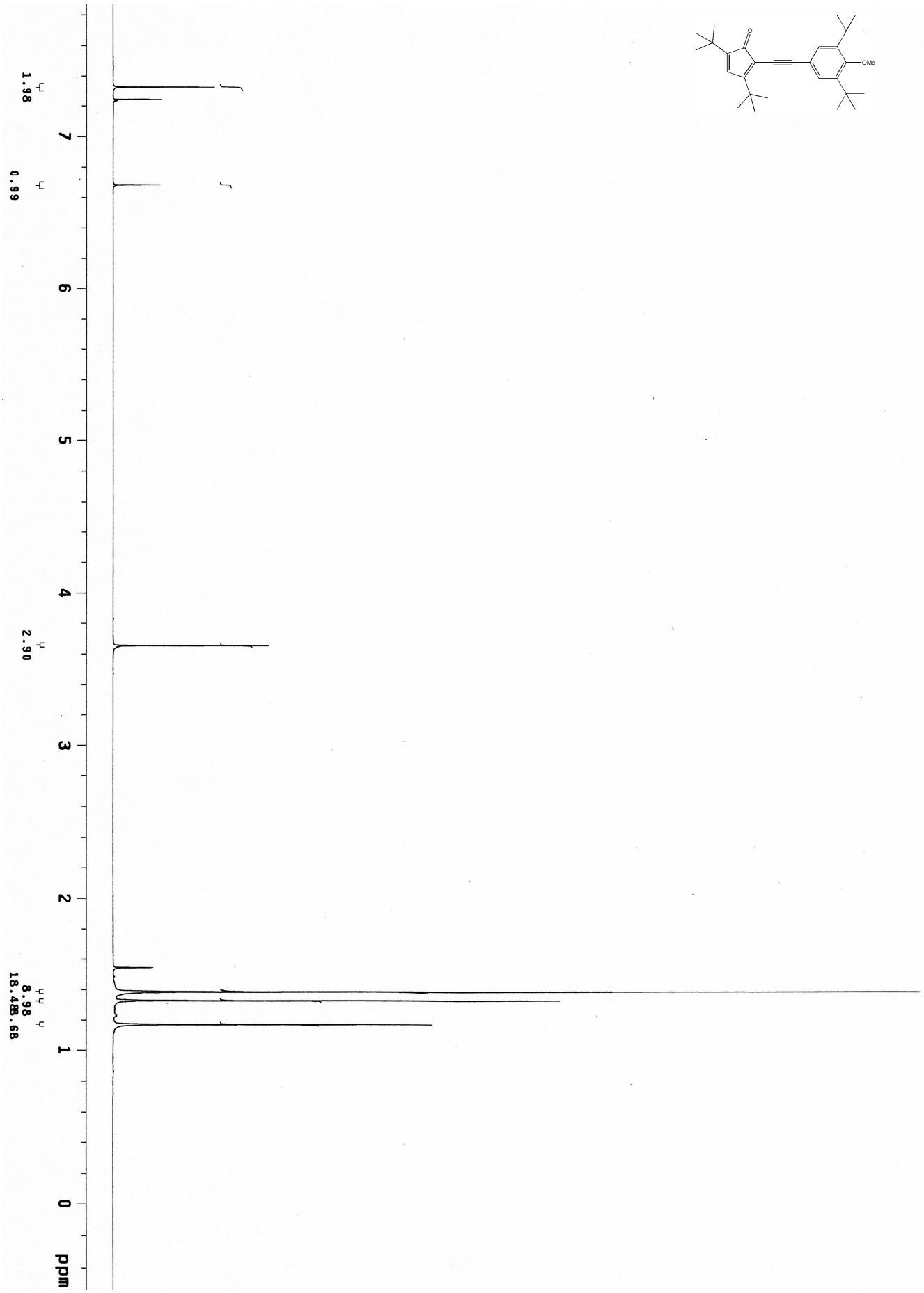
^{1}H NMR for compound **4j**



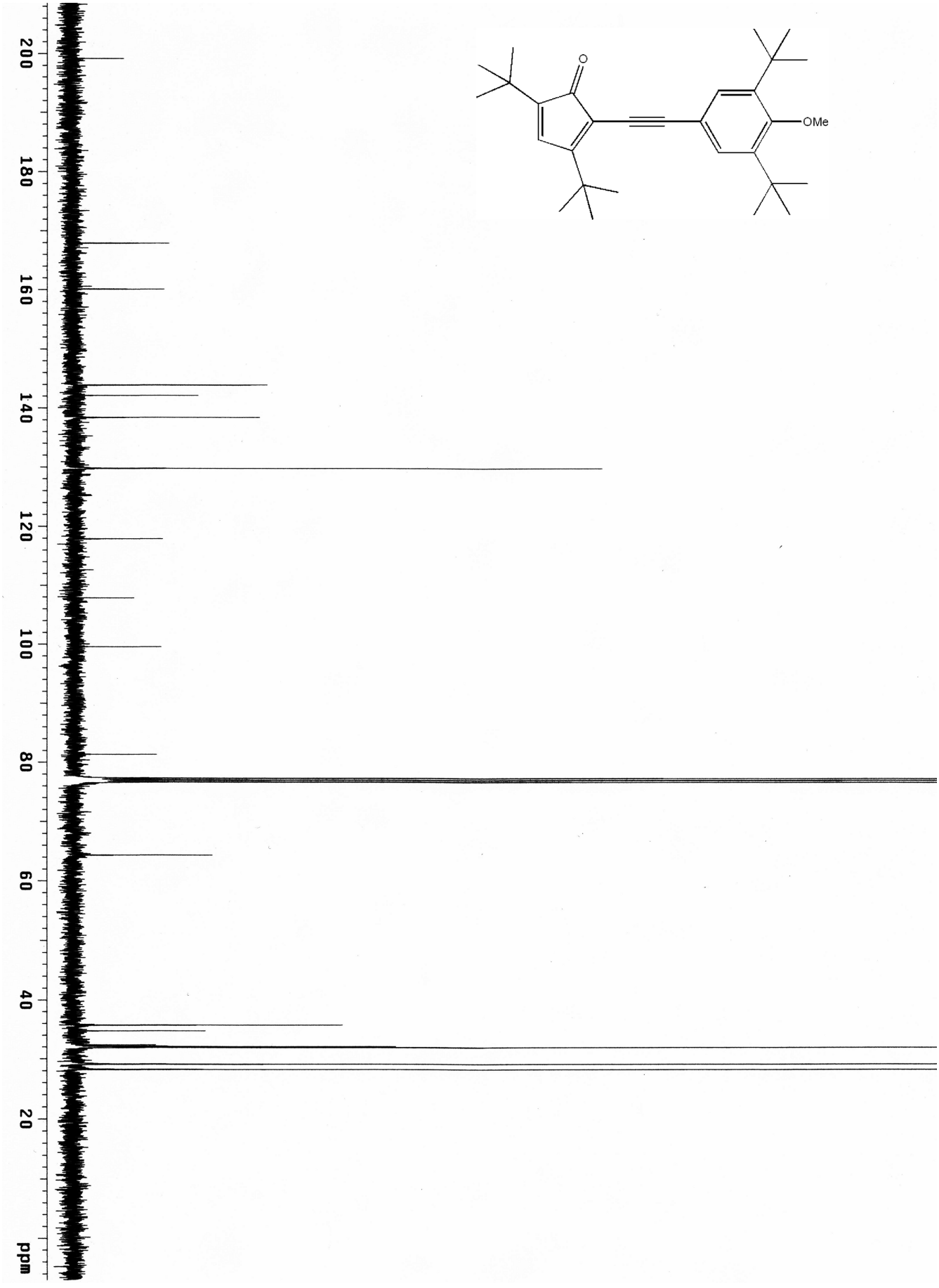
^{13}C NMR for compound **4j**



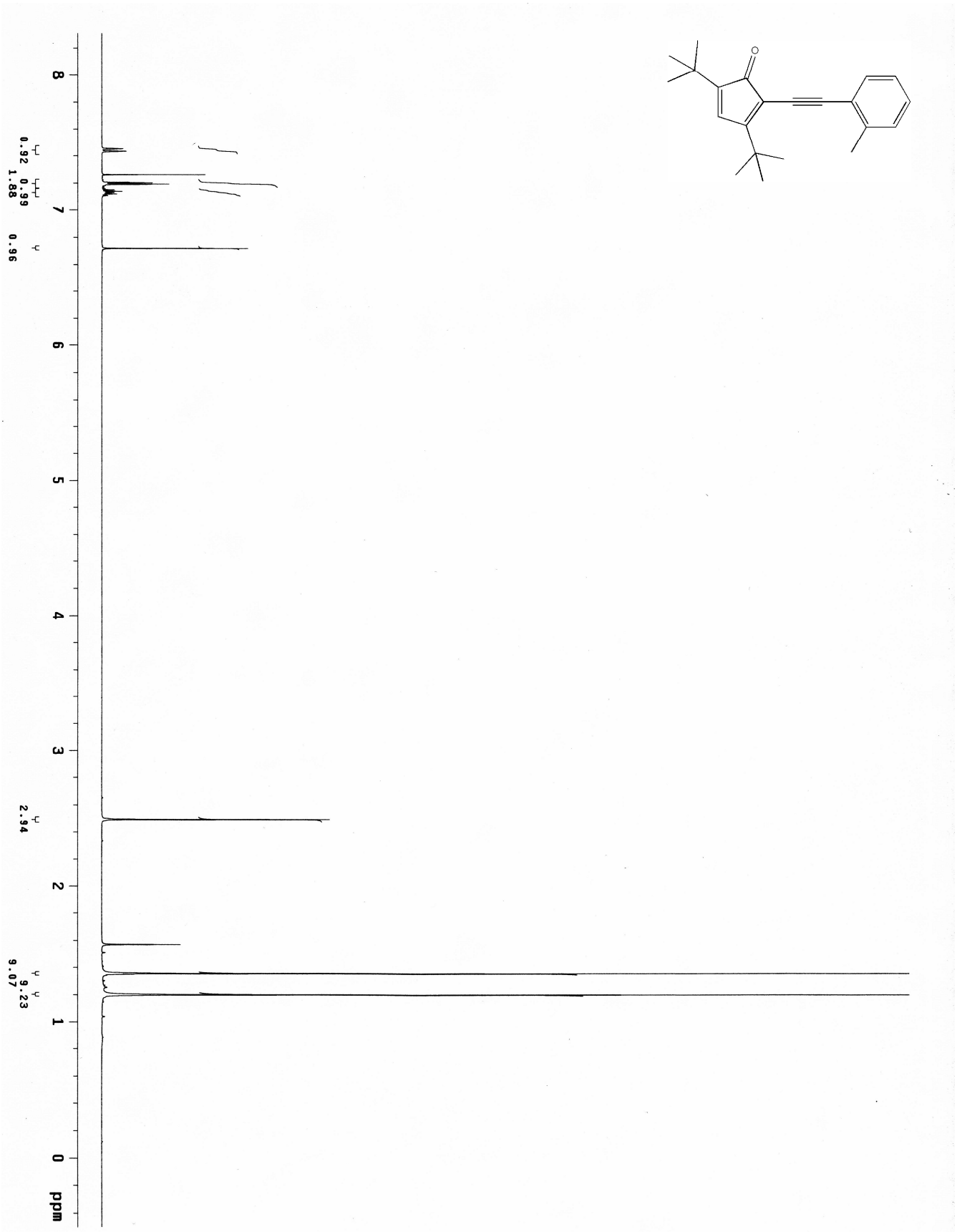
^{1}H NMR for compound **4k**



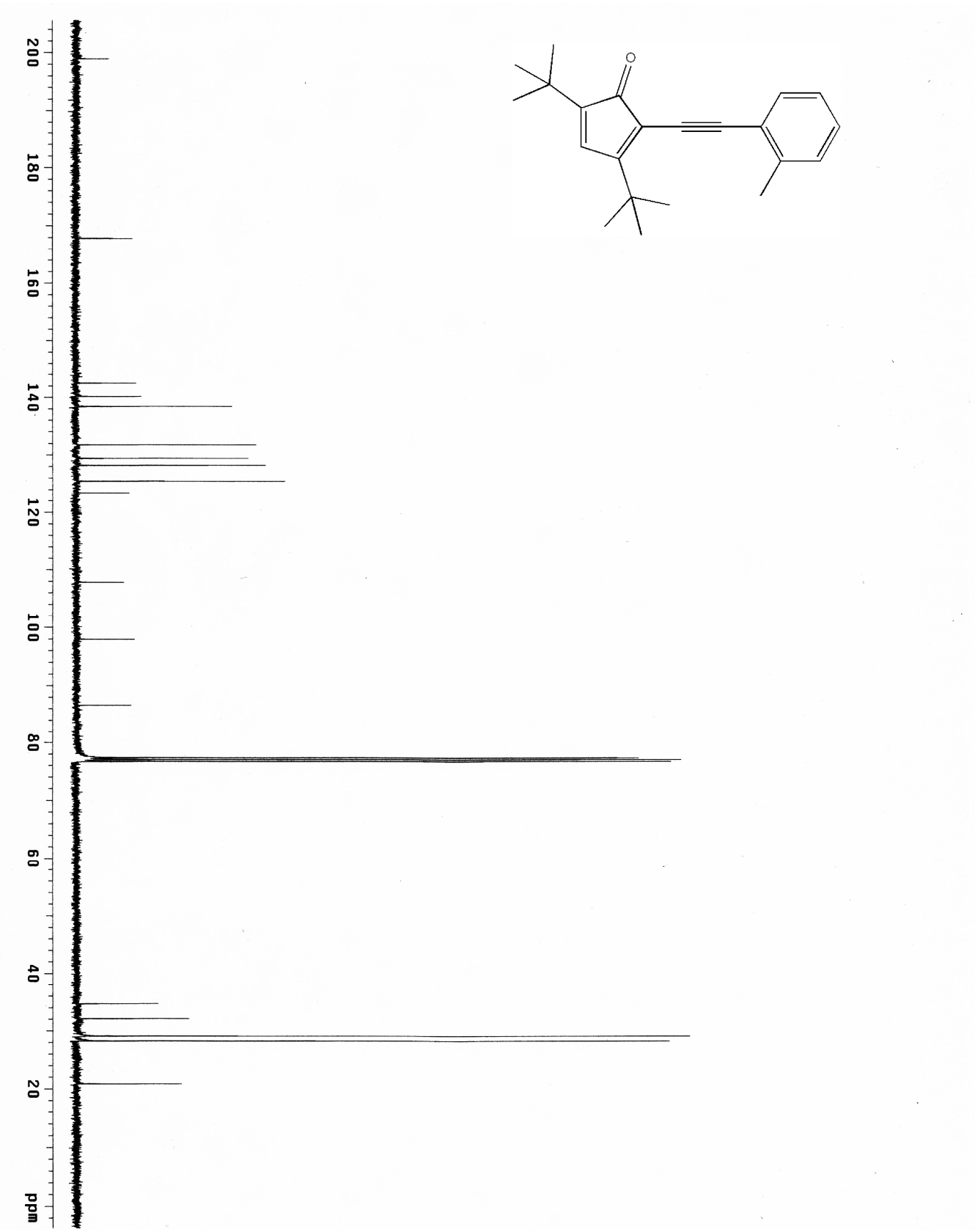
^{13}C NMR for compound **4k**



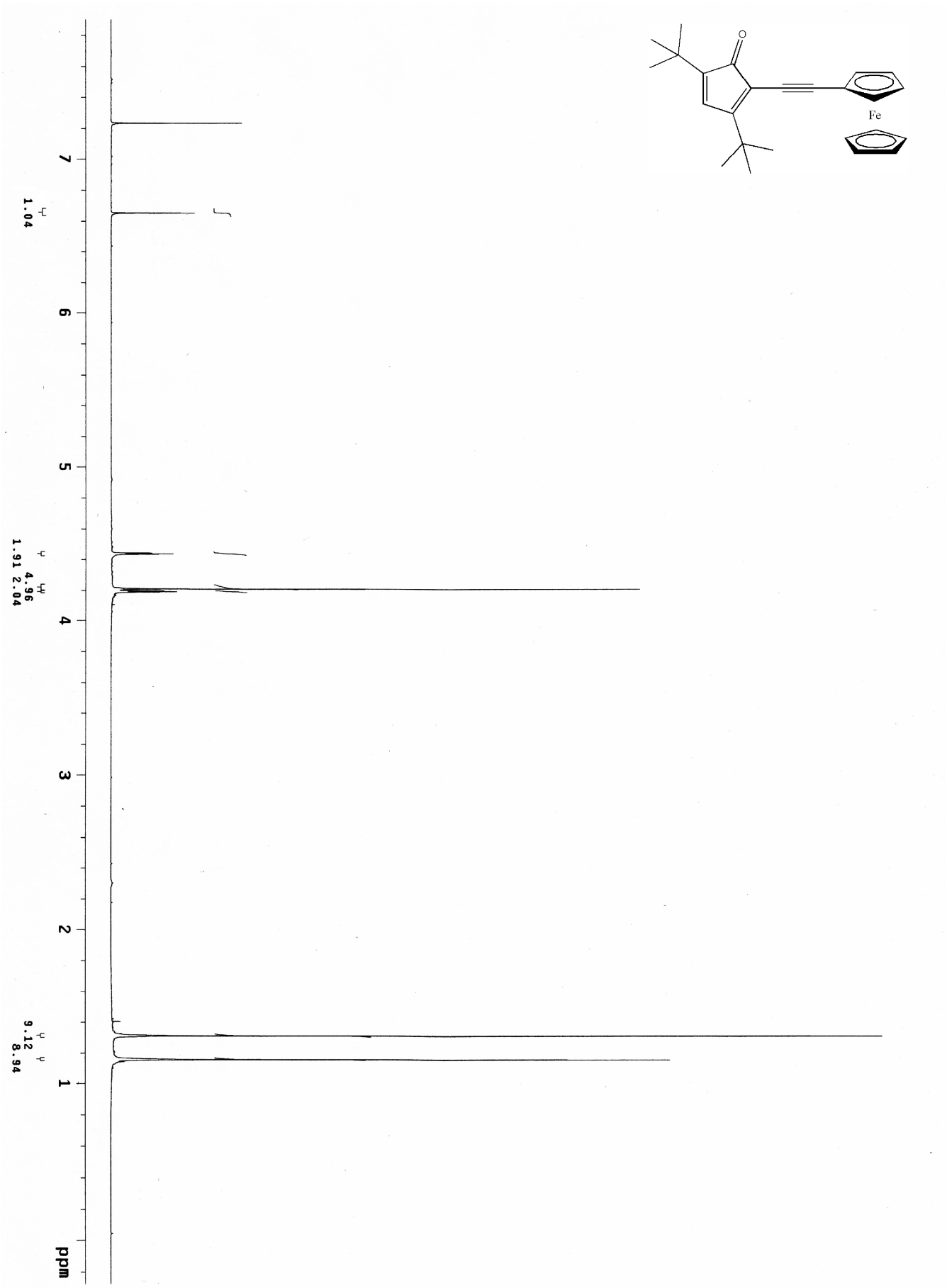
^{1}H NMR for compound **4l**



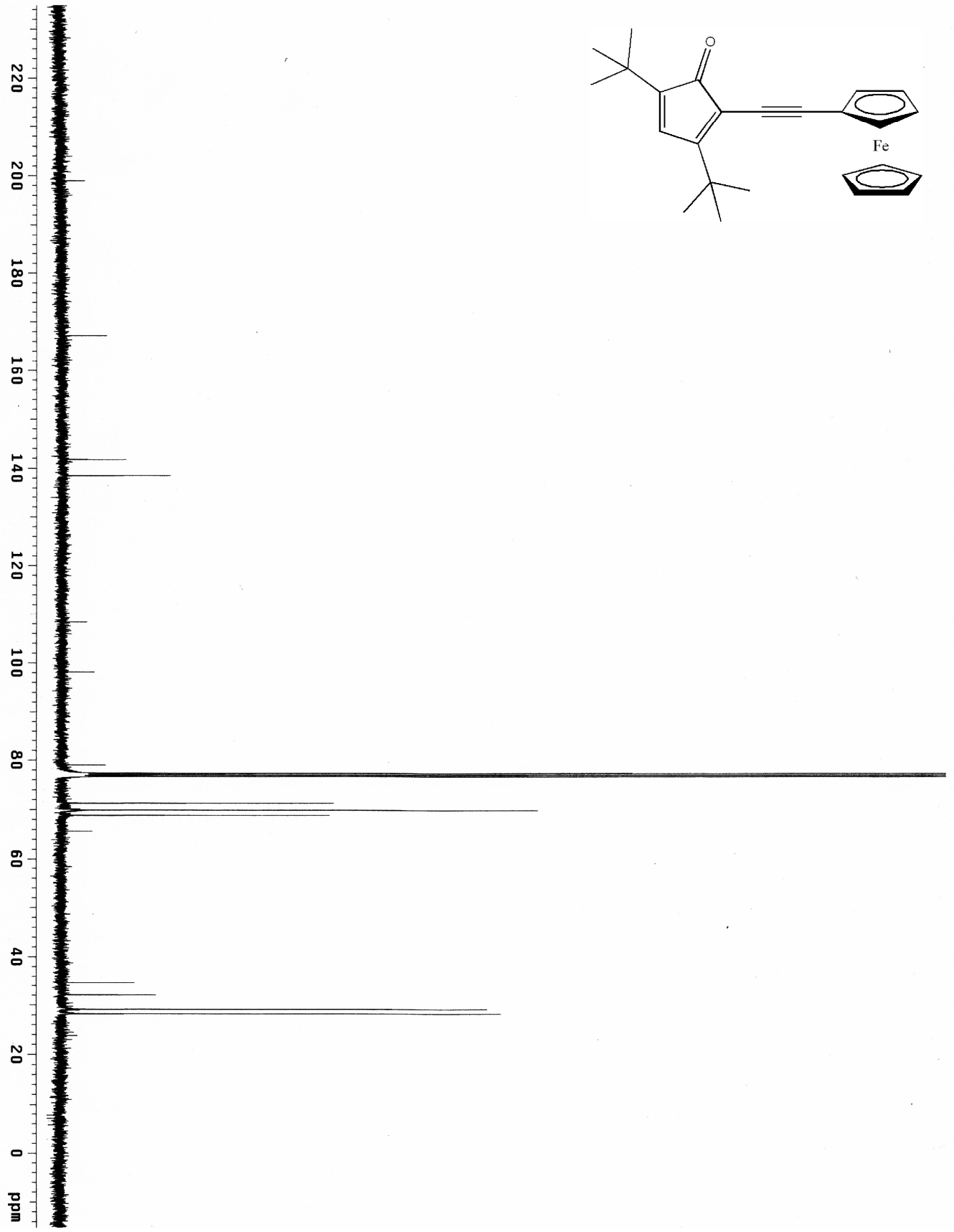
^{13}C NMR for compound **4l**



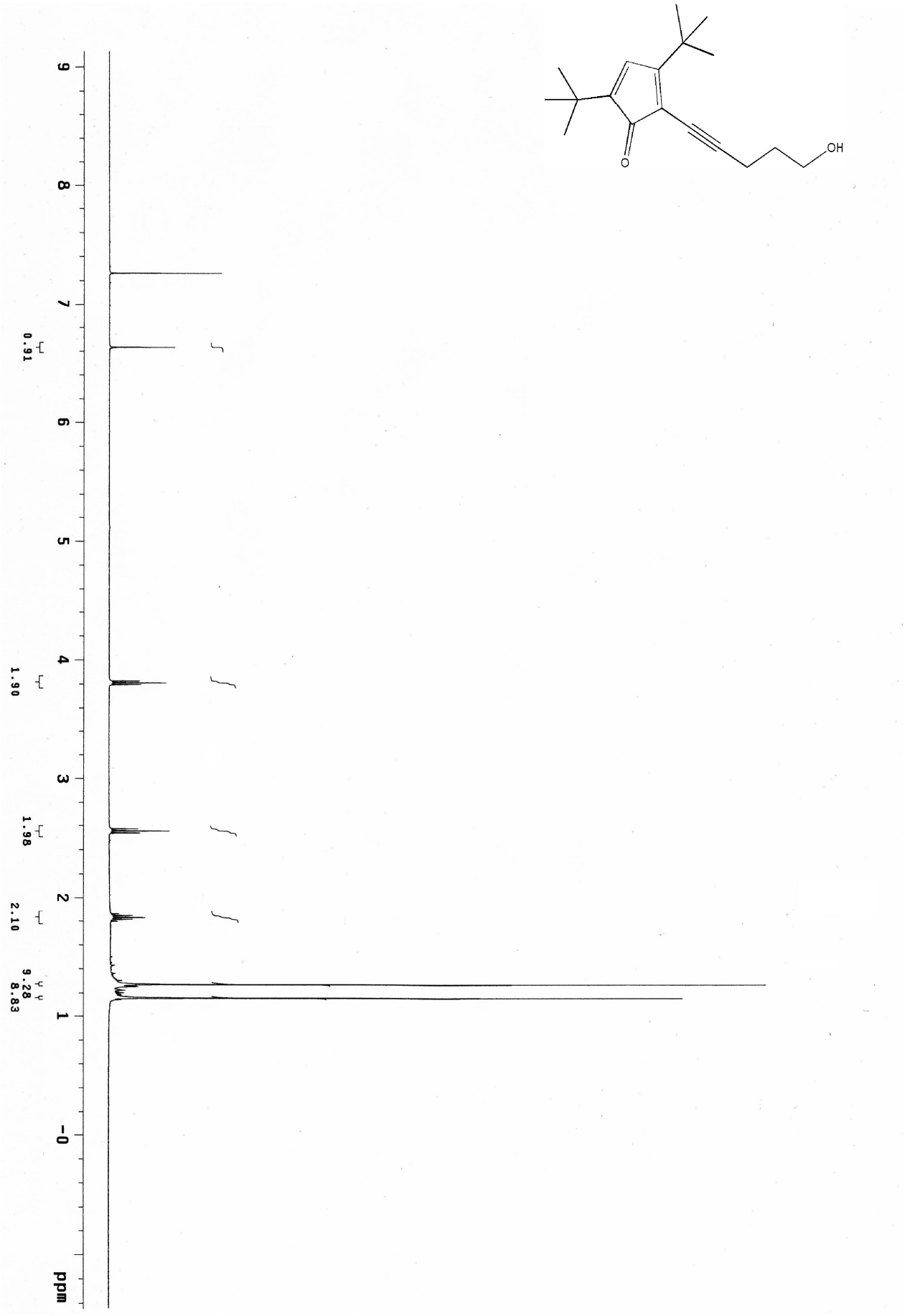
^{1}H NMR for compound **4m**



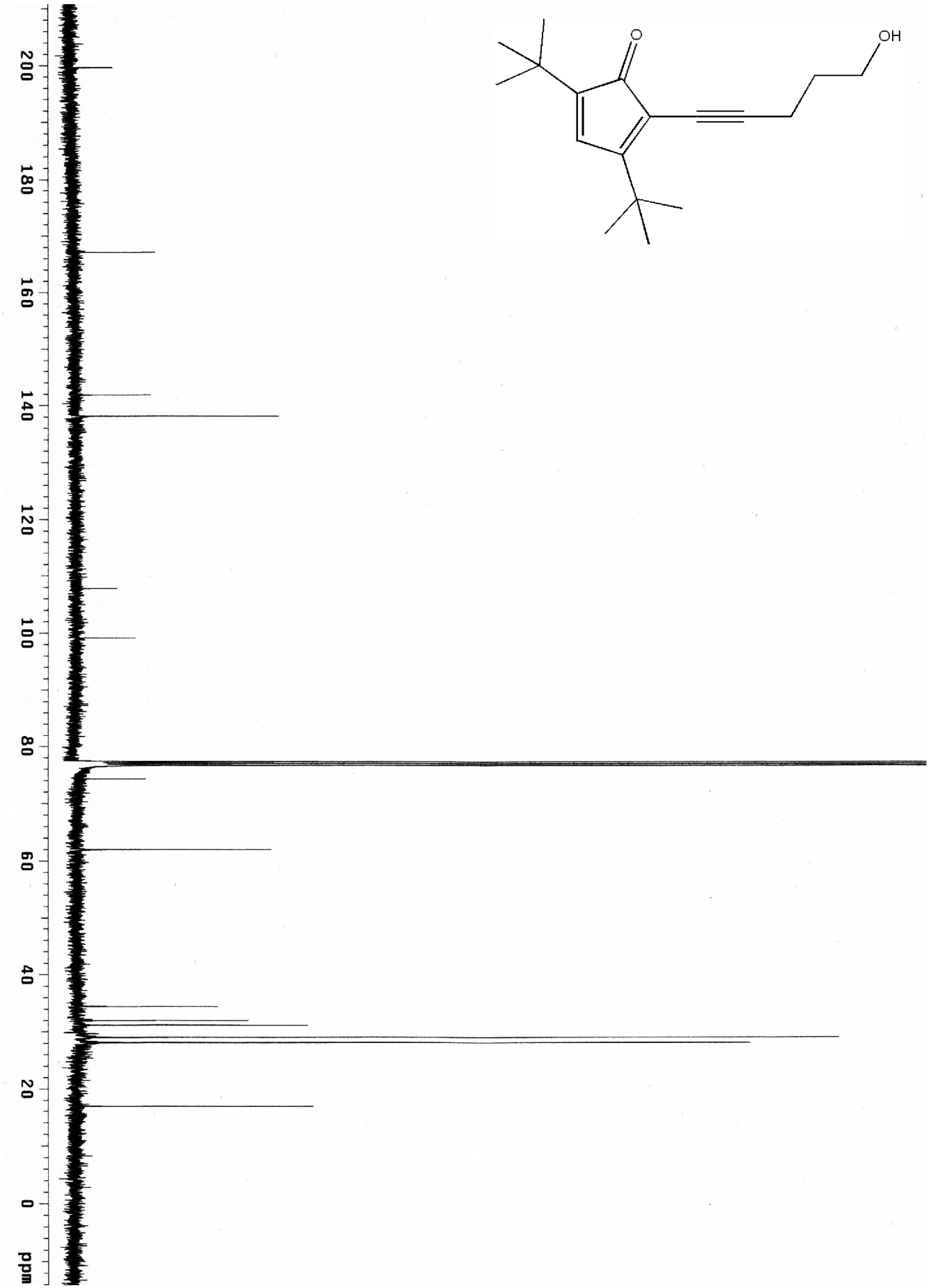
^{13}C NMR for compound **4m**



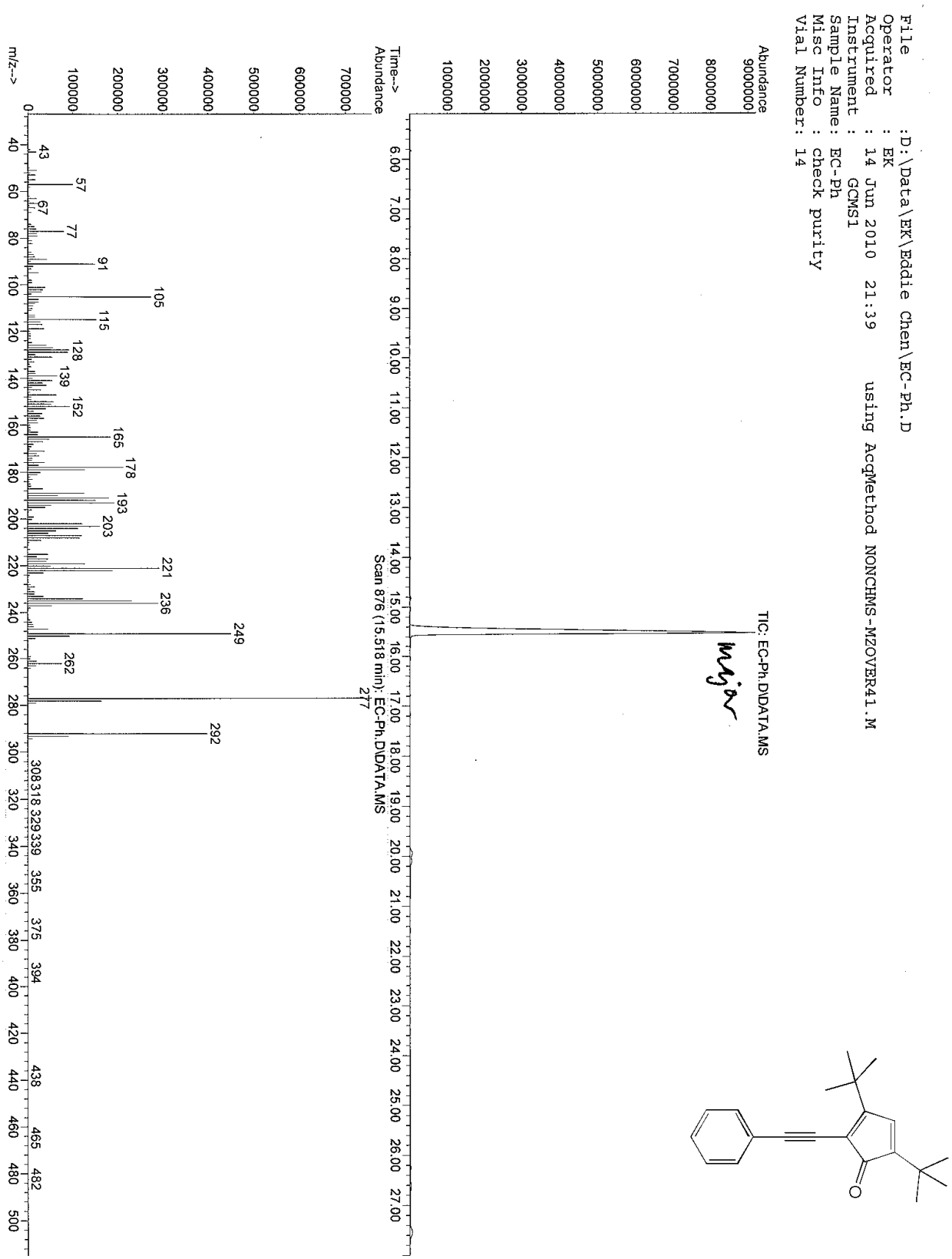
^{1}H NMR for compound **4s**



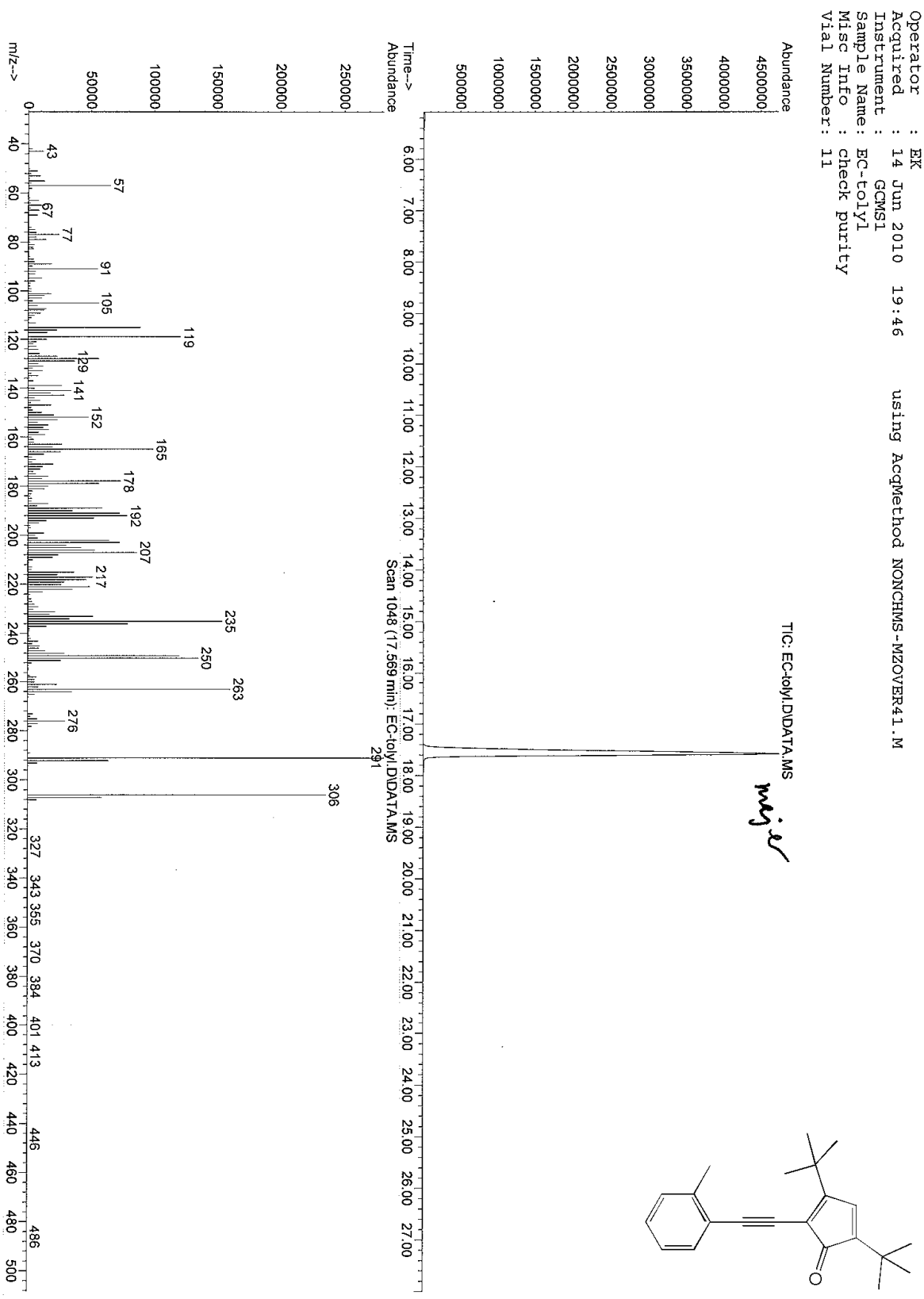
^{13}C NMR for compound **4s**



GC-MS for compound **4g**



GC-MS for compound **4l**



GC (purity check) for compound **4l**

Area Percent Report

Data Path : D:\Data\EK\Eddie Chen\
Data File : EC-tolyl.D
Acq On : 14 Jun 2010 19:46
Operator : EK
Sample : EC-tolyl
Misc : check purity
ALS Vial : 11 Sample Multiplier: 1

Integration Parameters: autoint1.e
Integrator: ChemStation

Method : D:\Data\Dylan\DW-10-4D.D\DWDICL.M
Title :

Signal : TIC: EC-tolyl.D\DATA.MS

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	7.897	234	237	260	PB 4	4359	164848	0.06%	0.059%
2	15.093	830	840	857	VV 4	5093	292157	0.11%	0.105%
3	17.580	1019	1049	1103	BV	4738914	278015335	100.00%	99.629%
4	21.487	1345	1377	1394	BV	5602	577106	0.21%	0.207%

major

Sum of corrected areas: 279049446

DWDICL.M Wed Jun 16 16:48:43 2010

The ^{13}C NMR spectrum (page 11) suggests that compound **3** contains 5 sp^2 carbons and two *tert*-butyl groups. Among the five sp^2 carbons, a typical ketone shift at low field (δ=196.32) is observed (Figure 1). In contrast to the literature value for non-iodine substituted cyclopentadienone derivatives,[13] the introduction of iodine substituent results in a ~30ppm upfield shift of the corresponding carbon to δ=80.1 ppm, whereas the introduction of *tert*-butyl groups results in a ~20 to 30ppm downfield shift of corresponding carbons to δ=167.3 ppm and 143.9 ppm. Thus these assignments are consistent with literature values.[13] The inferred cyclic structure is further confirmed by X-ray diffraction analysis which indicates that this product has a cyclopentadienone backbone with one iodine and two *tert*-butyl substituents.

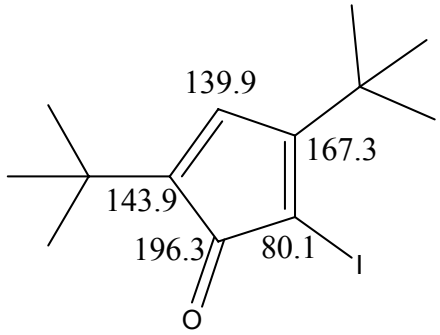
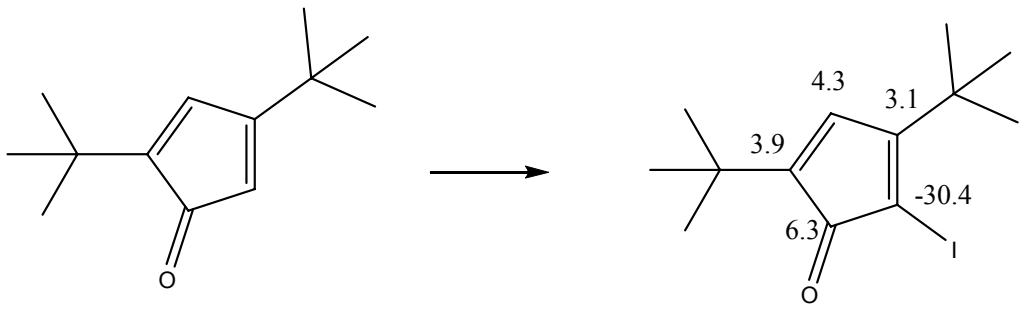


Figure 1. Chemical shifts of five membered ring carbons.

Consistent with literature values,[14] introduction of the iodine substituent onto compound **1**, does not significantly affect the shifts of the other 4 carbons on the ring (Figure 2), which suggests that there is only an inductive effect from iodine substitution and no clear resonance effect. This furthermore indicates that there is minimal conjugation on the five membered ring, although all five carbons are sp^2 carbons.



0 **3**

Figure 2. Chemical shift differences of the ring carbon atoms caused by the introduction of iodine to compound **0**.

[13] M. J. Loots, L. R. Weingarten, R. H. Levin, *J. Am. Chem. Soc.* **1976**, *98*, 4571

[14] H. O. Kalinowski, L. H. Franz, G. Maier, *Organic Magnetic Resonance* **1981**, *17*, 6.